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Fluid and Thermodynamics

Volume 3: Structured and Multiphase Fluids

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Preface

When in 2015, the first two volumes of our treatise on Fluid and Thermodynamics (FTD) were submitted to the publisher, it was not certain whether we would still be able to add a third volume. The aims were to add chapters on mixture and multiphase theories for the developments of which both of us had contributed, but not enough to fill a complete volume. However, in combination with the thermodynamic formulations of fluid materials exhibiting microstructure and/or anisotropy effects, a book on FTD of structured and mixture materials could be designed and we felt secure to be able to design a volume on advanced topics of FTD. This simultaneously brought the advantage to extend the class of BOLTZMANN continua to polar media, to naturally include two chapters on FTD of the kinematics and dynamics of Cosserat continua and concepts of thermodynamics of these.

General accounts on these subjects are treated in Chaps. 21–23. It opened the doors for a presentation of basic formulations of continuum theories of liquid crystals, one of the most important applications of continua exhibiting spin responses, introduced by ERICKSEN and LESLIE in the 1960s and 1970s by use of directors (vector quantities identifying orientation) attached to the material particles. Their elastic response was already mathematically described by Sir JAMES FRANK in 1958 and the restriction of the coefficients by thermodynamic ONSAGER relations is due to PARODI in the 1970s (Chap. 25). This ELP-director theory has been extended by introducing tensorial order parameters of second and higher rank in the 1980s and later. These theories resolve the subgrid structure of the material better but must necessarily also be in conformance with the angular momentum balance (Chap. 26).

Multiphase fluids are understood as mixtures of immiscible constituents. These often occupy disjoint regions of space with impermeable material surfaces and/or lines separating the different constituents; these are treated as flexible two- and one-dimensional material objects, interacting with the higher dimensional neighboring fluids of three or two dimensions. Derivation of an entropy principle for the bulk, interface surfaces and contact lines is the topic of Chaps. 27 and 28. This theoretical concept is presented for multiphase fluids within a BOLTZMANN-type formulation.

Whereas the chapters on multiphase media do not operate with additional equations modeling the substructure through three-dimensional space, but employ the concept of physical balance Laws on "singular regions" of lower dimensions, Chaps. 29–31 are devoted to situations, in which the fluid substructure is described by fields throughout the three-dimensional space. Granular materials as assemblages require the description of the temporal changes of the solid volume fraction (generally the space filled by the grains). The original description of the variation of this space is described by a scalar balance law, interpreted as a scalar momentum equation, called equilibrated force balance. Application of the concept to the entropy principle of MÜLLER–LIU and CLAUSIUS–DUHEM, respectively, generates distinct results and demonstrates that the ultimate form of the second law is still not found. Chapter 30 extends the concepts applied to a single constituent assemblage to a mixture of different grains; here, each grain constituent is modeled by postulating its own equilibrated force balance. The thermodynamic model is analogous to that of a single granular assemblage of distinct grains, but more complicated in detail.

Granular systems are often capable of performing slow and smooth—laminar—flows and rapid and fluctuating—turbulent—motions. When performing an ergodic (REYNOLDS) average of the basic equations, then equations for the mean motion emerge, that are complemented by turbulent correlation terms and additional balance laws for the classical and configurational turbulent kinetic energies and dissipation rates. These play analogous roles as the additional balance laws play in other theories where substructure processes are accounted for. So, the turbulent closure schemes can be interpreted as describing the microstructure effects of a hypothetical medium that performs the mean motion.

In the subsequent pages, the contents of the three volumes will be summarized.

Fluid and Thermodynamics—Volume 1: Basic Fluid Mechanics

This volume consists of 10 chapters and begins in an introductory **Chap. 1** with some historical facts, definition of the subject field and lists the most important properties of liquids.

This descriptive account is then followed in **Chap. 2** by the simple mathematical description of the fundamental hydrostatic equation and its use in analyses of equilibrium of fluid systems and stability of floating bodies, the derivation of the ARCHIMEDEan principle and determination of the pressure distribution in the atmosphere.

Chapter 3 deals with hydrodynamics of ideal incompressible (density preserving) fluids. Streamlines, trajectories, and streaklines are defined. A careful derivation of the balances of mass and linear momentum is given and it is shown how the BERNOULLI equation is derived from the balance law of momentum and how it is used in applications. In one-dimensional smooth flow problems, the momentum and BERNOULLI equations are equivalent. For discontinuous processes with jumps, this is not so. Nevertheless, the Bernoulli equation is a very useful equation in many engineering applications. This chapter ends with the balance law of moment of momentum and its application for Euler's turbine equation.

The conservation law of angular momentum, presented in **Chap. 4**, provides the occasion to define circulation and vorticity and the vorticity theorems, among them those of Helmholtz and Ertel. The goal of this chapter is to build a fundamental understanding of vorticity.

In **Chap. 5**, a collection of simple flow problems in ideal fluids is presented. It is shown how vector analytical methods are used to demonstrate the differential geometric properties of vortex free flow fields and to evaluate the motion-induced force on a body in a potential field. The concept of virtual mass is defined and two-dimensional fluid potential flow is outlined.

This almanac of flows of ideal fluids is complemented in **Chap. 6** by the presentation of the solution techniques of two-dimensional potential flows by complex-valued function theoretical methods using conformal mappings. Potential flows around two-dimensional air foils, laminar free jets, and the Schwarz–Chrystoffel transformations are employed to construct the mathematical descriptions of such flows through a slit or several slits, around air wings, free jets, and in ducts bounding an ideal fluid.

The mathematical physical study of viscous flows starts in **Chap. 7** with the derivation of the general stress–strain rate relation of viscous fluids, in particular Navier–Stokes fluids and more generally, non-Newtonian fluids. Application of these equations to viscometric flows, liquid films, Poiseuille flow, and the slide bearing theory due to Reynolds and Sommerfeld demonstrate their use in an engineering context. Creeping flow for a pseudo-plastic fluid with free surface then shows the application in the glaciological–geological context.

Chapter 8 continues with the study of two-dimensional and three-dimensional simple flows of the Navier–Stokes equations. Hagen–Poiseuille flow and the Ekman theory of the wall-near wall-parallel flow on a rotating frame (Earth) and its generalization are presented as solutions of the Navier–Stokes equations in the half-space above an oscillating wall and that of a stationary axisymmetric laminar jet. This then leads to the presentation of Prandtl's boundary layer theory with flows around wedges and the Blasius boundary layer and others.

In **Chap. 9**, two- and three-dimensional boundary layer flows in the vicinity of a stagnation point are studied as are flows around wedges and along wedge sidewalls. The flow, induced in the half plane above a rotating plane, is also determined. The technique of the boundary layer approach is commenced with the Blasius flow, but more importantly, the boundary layer solution technique for the Navier–Stokes equations is explained by use of the method of matched asymptotic expansions. Moreover, the global laws of the steady boundary layer theory are explained with the aid of the Holstein–Bohlen procedure. The chapter ends with a brief study of nonstationary boundary layers, in which, e. g., an impulsive start from rest, flows in the vicinity of a pulsating body, oscillation induced drift currents, and nonstationary plate boundary layers are studied.

In **Chap. 10**, pipe flow is studied for laminar (HAGEN–POISEUILLE) as well as for turbulent flows; this situation culminates via a dimensional analysis to the well-known MOODY diagram. The volume ends in this chapter with the plane boundary layer flow along a wall due to PRANDTL and VON KÁRMÁN with the famous logarithmic velocity profile. This last problem is later reanalyzed as the controversies between a power and logarithmic velocity profile near walls are still ongoing research today.

Fluid and Thermodynamics—Volume 2: Advanced Fluid Mechanics and Thermodynamic Fundamentals

This volume consists of 10 chapters and commences in **Chap. 11** with the determination of the creeping motion around spheres at rest in a NEWTONian fluid. This is a classical problem of singular perturbations in the form of matched asymptotic expansions. For creeping flows, the acceleration terms in NEWTON's law can be ignored to approximately calculate flows around the sphere by this so-called STOKES approximation. It turns out that far away from the sphere, the acceleration terms become larger than those in the STOKES solution, so that the latter solution violates the boundary conditions at infinity. This lowest order correction of the flow around the sphere is due to OSEEN (1910). In a systematic perturbation expansion, the outer —OSEEN—series and the inner—STOKES—series with the small REYNOLDS number as perturbation parameter must be matched together to determine all boundary and transition conditions of inner and outer expansions. This procedure is rather tricky, i.e., not easy to understand for beginners. This theory, originally due KAPLUN and to LAGERSTRÖM has been extended, and the drag coefficient for the sphere, which also can be measured is expressible in terms of a series expansion of powers of the REYNOLDS number. However, for REYNOLDS numbers larger than unity, convergence to measured values is poor. About 20–30 years ago, a new mathematical approach was designed—the so-called Homotopy Analysis Method; it is based on an entirely different expansion technique, and results for the drag coefficient lie much closer to the experimental values than values obtained with the "classical" matched asymptotic expansion, as shown, e.g., in Fig. 11.11. Incidentally, the laminar flow of a viscous fluid around a cylinder can analogously be treated, but is not contained in this treatise.

Chapter 12 is devoted to the approximate determination of the velocity field in a shallow layer of ice or granular soil, treated as a non-NEWTONian material flowing under the action of its own weight and assuming its velocity to be so small that STOKES flow can be assumed. Two limiting cases can be analyzed: (i) In the first, the flowing material on a steep slope (which is the case for creeping landslides or snow on mountain topographies with inclination angles that are large). (ii) In the second case, the inclination angles are small. Situation (ii) is apt to ice flow in large ice sheets such as Greenland and Antarctica, important in climate scenarios in a warming atmosphere. We derive perturbation schemes in terms of a shallowness parameter in the two situations and discuss applications under real-world conditions.

In shallow rapid gravity driven free surface flows, the acceleration terms in Newton's law are no longer negligible. **Chapter 13** is devoted to such granular flows in an attempt to introduce the reader to the challenging theory of the dynamical behavior of fluidized cohesionless granular materials in avalanches of snow, debris, mud, etc. The theoretical description of moving layers of granular assemblies begins with the one-dimensional depth integrated Mohr–Coulomb plastic layer flows down inclines—the so-called Savage–Hutter theory, but then continues with the general formulation of the model equations referred to topography following curvilinear coordinates with all its peculiarities in the theory and the use of shock-capturing numerical integration techniques.

Chapter 14 on uniqueness and stability provides a first flavor into the subject of laminar-turbulent transition. Two different theoretical concepts are in use and both assume that the laminar-turbulent transition is a question of loss of stability of the laminar motion. With the use of the energy method, one tries to find upper bound conditions for the laminar flow to be stable. More successful for pinpointing, the laminar-turbulent transition has been the method of linear instability analysis, in which a lowest bound is searched for, at which the onset of deviations from the laminar flow is taking place.

In **Chap. 15**, a detailed introduction to the modeling of turbulence is given. Filter operations are introduced to separate the physical balance laws into evolution equations for the averaged fields on the one hand, and into fluctuating or pulsating fields on the other hand. This procedure generates averages of products of fluctuating quantities, for which closure relations must be formulated. Depending upon the complexity of these closure relations, so-called zeroth, first and higher order turbulence models are obtained: simple algebraic gradient-type relations for the flux terms, one or two equation models, e.g., k-ε, k-ω, in which evolution equations for the averaged correlation products are formulated, etc. This is done for density preserving fluids as well as so-called Boussinesq fluids and convection fluids on a rotating frame (Earth), which are important models to describe atmospheric and oceanic flows.

Chapter 16 goes back one step by scrutinizing the early zeroth order closure relations as proposed by Prandtl, von Kármán and collaborators. The basis is Bossinesq's (1872) ansatz for the shear stress in plane parallel flow, τ_{12}, which is expressed to be proportional to the corresponding averaged shear rate $\partial \bar{v}_1 / \partial x_2$ with coefficient of proportionality $\rho\varepsilon$, where ρ is the density and ε a kinematic turbulent viscosity or turbulent diffusivity $[\mathrm{m}^2\mathrm{s}^{-1}]$. In turbulence theory, the flux terms of momentum, heat, and suspended mass are all parameterized as gradient-type relations with turbulent diffusivities treated as constants. Prandtl realized from data collected in his institute that ε was not a constant but depended on his mixing length squared and the magnitude of the shear rate (Prandtl 1925). This proposal was later improved (Prandtl 1942) to amend the unsatisfactory agreement at positions where shear rates disappeared. The 1942-law is still local, which means that the Reynolds stress tensor at a spatial point depends on spatial velocity derivatives at the *same* position. Prandtl in a second proposal of his 1942-paper suggested that the turbulent diffusivity should depend on the velocity *difference* at the points where the velocity of the turbulent path assumes maximum and minimum values. This proposal introduces some nonlocality, yielded better agreement with data, but Prandtl left the gradient-type dependence in order to stay in conformity with Boussinesq. It does neither become apparent or clear that Prandtl or the modelers at that time would have realized that nonlocal effects would be the cause for better agreement of the theoretical formulations with data. The proposal of complete nonlocal behavior of the Reynolds stress parameterization came in 1991 by P. Egolf and subsequent research articles during ~ 20 years, in which also the local strain rate (= local velocity gradient) is replaced by a difference quotient. We motivate and explain the proposed difference quotient turbulence model (DQTM) and demonstrate that for standard two-dimensional configurations analyzed in this chapter its performance is superior to other zeroth order models.

The next two chapters are devoted to thermodynamics; first, fundamentals are attacked and, second a field formulation is presented and explored.

Class experience has taught us that thermodynamic fundamentals (**Chap. 17**) are difficult to understand for novel readers. Utmost caution is therefore exercised to precisely introduce terminology such as “states”, “processes”, “extensive”, “intensive”, and “molar state variables” as well as concepts like “adiabatic”, and “diathermal walls”, “empirical” and “absolute temperature”, “equations of state”, and “reversible” and “irreversible processes”. The core of this chapter is, however, the presentation of the First and Second Laws of Thermodynamics. The *first law* balances the energies. It states that the time rate of change of the kinetic plus internal energies are balanced by the mechanical power of the stresses and the body forces plus the thermal analogies, which are the flux of heat through the boundary plus the specific radiation also referred to as energy supply. This conservation law then leads to the definitions of the caloric equations of state and the definitions of specific heats. The Second Law of thermodynamics is likely the most difficult to understand and it is introduced here as a balance law for the entropy and states that all physical processes are irreversible. We motivate this law by going from easy and simple systems to more complex systems by generalization and culminate in this tour with the Second Law as the statement that entropy production rate cannot be negative. Examples illustrate the implications in simple physical systems and show where the two variants of entropy principles may lead to different answers.

Chapter 18 extends and applies the above concepts to continuous material systems. The Second Law is written in global form as a balance law of entropy with flux, supply, and production quantities, which can be written in local form as a differential statement. The particular form of the Second Law then depends upon, which postulates the individual terms in the entropy balance are subjected to. When the entropy flux equals heat flux divided by absolute temperature and the entropy production rate density is requested to be nonnegative, the entropy balance law appears as the Clausius–Duhem inequality and its exploitation follows the axiomatic procedure of open systems thermodynamics as introduced by COLEMAN and NOLL. When the entropy flux is left arbitrary but is of the same function class as the other constitutive relations and the entropy supply rate density is identically zero, then the entropy inequality appears in the form of MÜLLER. In both cases, the Second Law is expressed by the requirement that the entropy production rate density must be nonnegative, but details of the exploitation of the Second Law in the two cases are subtly different from one another. For standard media such as elastic and/or viscous fluids the results are the same. However, for complex media they may well differ from one another. Examples will illustrate the procedures and results.

Chapter 19 on gas dynamics illustrates a technically important example of a fluid field theory, where the information deduced by the Second Law of Thermodynamics delivers important properties, expressed, e.g., by the thermal and caloric equations of state of, say, ideal and real gases. We briefly touch problems of acoustics, steady isentropic flow processes, and their stream filament theory. The description of the propagation of small perturbations in a gas serves in its one-dimensional form ideally as a model for the propagation of sound, e.g., in a flute or organ pipe, and it can be used to explain the DOPPLER shift occurring when the sound source is moving relative to the receiver. Moreover, with the stream filament theory the sub- and supersonic flows through a nozzle can be explained. In a final section the three-dimensional theory of shocks is derived as the set of jump conditions on surfaces for the balance laws of mass, momentum, energy and entropy. Their exploitation is illustrated for steady surfaces for simple fluids under adiabatic flow conditions. These problems are classics; gas dynamics, indeed forms an important advanced technical field that was developed in the 20th century as a subject of aerodynamics and astronautics and important specialties of mechanical engineering.

Chapter 20 is devoted to the subjects “Dimensional analysis, similitude and physical experimentation at laboratory scale”, topics often not systematically taught at higher technical education. However, no insider would deny their usefulness. Books treating these subjects separately and in sufficient detail have appeared since the mid 20th century. We give an account of Dimensional analysis, define dimensional homogeneity of functions of mathematical physics, the properties of which culminate in BUCKINGHAM’s theorem (which is proved in an appendix to the chapter); its use is illustrated by a diversity of problems from general fluid dynamics, gas dynamics and thermal sciences, e.g., propagation of a shock from a point source, rising gas bubbles, RAYLEIGH–BÉNARD instability, etc. The theory of physical models develops rules, how to down- or upscale physical processes from the size of a prototype to the size of the model. The theory shows that in general such scaling transformations are practically never exactly possible, so that scale effects enter in these cases, which distort the model results in comparison to those in the prototype. In hydraulic applications, this leads to the so-called FROUDE and REYNOLDS models, in which either the FROUDE or REYNOLDS number, respectively, remains a mapping invariant but not the other. Application on sediment transport in rivers, heat transfer in forced convection, etc. illustrate the difficulties. The chapter ends with the characterization of dimensional homogeneity of the equations describing physical processes by their governing differential equations. The NAVIER–STOKES-FOURIER–FICK fluid equations serve as illustration.

Fluid and Thermodynamics—Volume 3: Structured and Multiphase Fluids

In **Chap. 21**, the fundamental assumption of continuous systems in classical physics is the conjecture that the physical space is densely filled with matter. This hypothesis is applied to single and multiphase continua as well as mixtures consisting of a finite number of constituents. Three classes of mixtures are defined: In the most complex case, class III, balance laws of mass, momenta, energy are formulated for each constituent, which possess their own mass, momenta, energy (and, therefore temperature). In class II mixtures, all components possess the same temperature, but the constituents possess their individual momenta and masses. Finally, in class I mixtures, the constituents do have the same temperature and common velocity—there is no slip between them—but each component has its own mass.

The modern theories of continuous bodies differentiate between BOLTZMANN and *polar* continua. In the former, the balance of angular momentum is applied as moment of momentum. In such continua, the CAUCHY stress tensor of the mixture is symmetric. In the latter, angular momentum is expressed as moment of momentum plus spin with all its peculiar consequences. The balance laws of mass, momenta, and energy are formulated for the constituents for both cases in global and local forms in detail. The results for BOLTZMANN continua are well known. However, for polar media, different sub-theories emerge, depending upon how the specific spin is parameterized. In COSSERAT continua, the specific spin is motivated by rigid body dynamics as the "product of the tensor moment of inertia times angular velocity", see (21.32). If the micromotion is a pure rotation of the particles, i.e., the tensor of moments of inertia of the constituents do not change under motion, the mixture is called *micro-polar*, else *micro-morphic*.

The chapter is closed by formulating the physical balance laws of the mixture as a whole and stating the relations of the physical variables of the mixture in terms of those of the constituents.

The aim of **Chap. 22** is the presentation of the kinematics of classical (BOLTZMANN) and *polar* (COSSERAT) continuous mixtures. The motions of material points of constituent α are first mathematically introduced for a classical mixture as mappings from separate constituent points onto a single point in the present configuration, Fig. 22.3. This guarantees that material points in physical space are a merger of all constituents. This motion function then yields through spatial and temporal differentiations the well-known definitions of the classical deformation measures: deformation gradient, right and left CAUCHY–GREEN deformation tensors, EULER–LAGRANGE strains and associated strain rates. Of importance is the polar decomposition, which splits the deformation gradient into a sequence of pure strain and rotation or vice versa.

Whereas the classical stretch and stretching measures are obtained by inner products of the constituent vectorial line element with itself, deformation measures of COSSERAT kinematics are generated by inner products between vectorial material line increments and the directors. The mappings of the latter between the reference and present configurations are postulated to be pure rotations (Fig. 22.5). This then yields the various COSSERAT strain measures, which are analogous to, but not the same as those of the classical theory.

The kinematically independent rotation of the directors gives rise to the introduction of skew symmetric rank-3 and full rank-2 curvature tensors, quasi as measures of the spatial variation of the microrotation. Analogous to the additive decomposition of the velocity gradient into stretching and vorticity tensors in the classical formulation, two additional decompositions of the velocity gradient are introduced using the polar decomposition and leads to nonsymmetric strain rate and the so-called gyration tensors, and objective time derivatives of the COSSERAT version of the ALMANSI tensor and the curvature tensors. All these quantities are also written relative to the natural basis system.

The chapter ends with the presentation of the balance law of micro-inertia. It is based on the assumption that material points of micro-polar continua move like rigid bodies.

In **Chap.** 23, two versions of mixtures of BOLTZMANN-type continua are subject to thermodynamic analyses for viscous fluids. Of the two forms of the Second Law that were introduced—the CLAUSIUS–DUHEM inequality applied to open systems and the entropy principle of I. MÜLLER—the latter principle is employed in the process of deduction of the implications revealed by the particular Second Law. The goal in the two parts of the chapter is to derive the ultimate forms of the governing equations, which describe the thermomechanical response of the postulated constitutive behavior without violation of the Second Law of thermodynamics. The versions of mixtures which are analyzed are

- *Diffusion of tracers in a classical fluid*: The conceptual prerequisites of this type of processes are mixtures of class I, in which the major component is the bearer fluid within which a finite number of constituents with minute concentration are suspended or solved in the bearer fluid. The motion of these tracers is described by the difference of the constituent velocities relative to the barycentric velocity of the mixture as a whole. For the dissipative constitutive class applied to the entropy principle, the existence of the KELVIN temperature is proved, the form of the GIBBS relation could be determined as could the conditions of thermodynamic equilibrium and the constitutive behavior in its vicinity.
- *Thermodynamics of a saturated mixture of nonpolar solid–fluid constituents*: Conceptually, these systems are treated as classical mixtures of class II, in which the individual motions of the constituents are separately accounted for by their own balances of mass and momentum, but subject to a common temperature. The analysis of the dissipation inequality is performed subject to the assumption

> of constant true density of all constituents and the supposition of saturation of the mixture. The constitutive relations are postulated for a mixture of viscous heat conducting fluids. The explanation of the entropy principle is structurally analogous to that of the class I-diffusion theory, but is analytically much more complex. Unfortunately, intermediate ad hoc assumptions must be introduced to deduce concrete results that will lead to fully identifiable fluid dynamical equations, which are in conformity with the Second Law for the presented type of mixtures.

Chapter 24 demonstrates how complex it is to deduce a saturated binary solid–fluid COSSERAT mixture model that is in conformity with the second law of thermodynamics and sufficiently detailed to be ready for application in fluid dynamics. The second law is formulated for open systems using the CLAUSIUS–DUHEM inequality without mass and energy production under phase change for class II mixtures of elastic solids and viscoelastic fluids. It turns out that even with all these restrictions, the detailed exploitation of the entropy inequality is a rather involved endeavor. Inferences pertain to extensive functional restrictions of the fluid and solid free energies and allow determination of the constitutive quantities in terms of the latter in thermodynamic equilibrium and small deviations from it. The theory is presented for four models of compressible–incompressible fluid-solid constituents. Finally, explicit representations are given for the free energies and for the constitutive quantities that are obtained from them via differentiation processes.

Chapter 25 presents a continuum approach to liquid crystals. Liquid crystals (LCs) are likely the most typical example of a polar medium of classical physics, in which the balance of angular momentum is a generic property, not simply expressed as a symmetry requirement of the CAUCHY stress tensor. They were discovered in the second half of the nineteenth century. Liquid crystals are materials, which exhibit fluid properties, i.e., they possess high fluidity, but simultaneously exhibit crystalline anisotropy in various structural forms. We present an early phenomenological view of the behavior of these materials, which conquered a tremendous industrial significance in the second half of the twentieth century as liquid crystal devices (LCD) (Sect. 25.1). The theoretical foundation as a continuum of polar structure was laid in the late 1950s to 1990s by ERICKSEN, LESLIE, FRANK and PARODI, primarily for nematic LCs by postulating their general physical conservation laws, hydrostatics and hydrodynamics, thus, illustrating their connection with nontrivial balance laws of angular momentum (Sect. 25.2). This is all done by treating nematics as material continua equipped with continuous directors (long molecules), which by their orientation induce a natural anisotropy. The thermodynamic embedding (Sect. 25.3) is performed by employing an entropy balance law with nonclassical entropy flux and the requirement of EUCLIDIAN invariance of the constitutive quantities, which are assumed to be objective functions of the density, director, its gradient and velocity, as well as stretching, vorticity, temperature, and temperature gradient. This is specialized for an incompressible LC with directors of constant length (Sect. 25.4). Constitutive parameterizations with an explicit proposal of the free energy as a quadratic polynomial of the director and its gradient (according to Frank) are reduced to obey objectivity. Based on this, the objective form of the free energy is derived (Appendix 25.A), as are the linear dissipative Cauchy stress, director stress and heat flux vector for the cases that the Onsager relations are fulfilled. The chapter ends with the presentation of shear flow solutions in a two-dimensional half-space and in a two-dimensional channel.

Chapter 26 goes beyond the ELP-theory of LCs by modeling the microstructure of the liquid by a number of rank-i tensors ($i = 1,\ldots, n$) (generally just one) with vanishing trace. These tensors are called *alignment tensors* or *order parameters*. When formed as exterior products of the director vector and weighted with a scalar and restricted to just one rank-2 tensor the resulting mathematical model describes *uniaxial* LCs. The simplest extensions of the ELP-model are theories, for which the number of independent constitutive variables are complemented by a constant or variable order parameter S and its gradient grad S, paired with an evolution equation for it. We provide a review of the recent literature.

Two different approaches to deduce LC-models exist; they may be coined the balance equations models, outlined already in Chap. 25 for the ELP model, and the variational Lagrange potential models, which, following an idea by Lord Rayleigh, are extended by a dissipation potential. The two different approaches may lead to distinct anisotropic fluid descriptions. Moreover, it is not automatically guaranteed in either description that the balance law of angular momentum is identically satisfied. The answers to these questions cover an important part of the mathematical efforts in both model classes.

A significant conceptual difficulty in the two distinct theoretical concepts are the postulations of explicit forms of the elastic energy W and dissipation function R. Depending upon, how W and R are parameterized, different particular models emerge. Conditions are formulated especially for uniaxial models, which guarantee that the two model classes reduce to exactly corresponding mathematical models.

In **Chap. 27**, a general continuum description for thermodynamic immiscible multiphase flows is presented with intersecting dividing surfaces, and three-phase common contact line, taking the contribution of the excess surface and line thermodynamic quantities into account. Starting with the standard postulates of continuum mechanics and the general global balance statement for an arbitrary physical quantity in a physical domain of three bulk phases including singular material or nonmaterial phase interfaces and a three-phase contact line, the local conservation equations on the phase interfaces and at the contact line are derived, in addition to the classical local balance equations for each bulk phase. Then, these general additional interface and line balance laws are specified for excess surface and line physical quantities, e.g., excess mass, momentum, angular momentum, energy and entropy, respectively. Some simplified forms of these balance laws are also presented and discussed. In particular, for the massless phase interfaces and contact line, these balance laws reduce to the well-known jump conditions.

In **Chap. 28**, a thermodynamic analysis, based on the Müller–Liu thermodynamic approach of the second law of thermodynamics, is performed to derive the expressions of the constitutive variables in thermodynamic equilibrium. Nonequilibrium responses are proposed by use of a quasi-linear theory. A set of constitutive equations for the surface and line constitutive quantities is postulated. Some restrictions for the emerging material parameters are derived by means of the minimum conditions of the surface and line entropy productions in thermodynamic equilibrium. Hence, a complete continuum mechanical model to describe excess surface and line physical quantities is formulated.

Technically, in the exploitation of the entropy inequality, all field equations are incorporated with LAGRANGE parameters into the entropy inequality. In the process of its exploitation the LAGRANGE parameter of the energy balance is identified with the inverse of the absolute temperature in the bulk, the phase interface and in the three-phase contact line. Interesting results, among many others, are the GIBBS relations, which are formally the same in the bulk, on the interface and along the contact line, with the pressure in the compressible bulk replaced by the surface tension on the interface and by the line tension along the contact line, see (28.45 and 28.87).

Chapter 29 presents a continuum theory of a dry cohesionless granular material proposed by GOODMAN and COWIN (1972) in which the solid volume fraction v is treated as an independent kinematic field for which an additional balance law of equilibrated forces is postulated. They motivated this additional balance law as an equation describing the kinematics of the microstructure and employed a variational formulation for its derivation. By adopting the MÜLLER–LIU approach to the exploitation of the entropy inequality, we show that in a constitutive model containing $v, \dot{v}$ and $\operatorname{grad} v$ as independent variables, results agree with the classical COLEMAN–NOLL approach only, provided the HELMHOLTZ free energy does not depend on $\dot{v}$, for which the GOODMAN–COWIN equations are reproduced. This reduced theory is then applied to the analyses of steady fully developed horizontal shearing flows and gravity flows of granular materials down an inclined plane and between parallel plates. It is demonstrated that the equations and numerical results presented by PASSMAN et al. (1980) are false, and they are corrected. The results show that the dynamical behavior of these materials is quite different from that of a viscous fluid. In some cases, the dilatant shearing layers exist only in the narrow zones near the boundaries. They motivated this additional balance law as an equation describing the kinematics of the microstructure and employed a variational formulation for its derivation. In an appendix, we present a variational formulation, treating the translational velocity and solid volume fraction as generalized coordinates of a LAGRANGEan formulation.

In **Chap. 30**, a continuum theory of a granular mixture is formulated. In the basic balance laws, we introduce an additional balance of equilibrated forces to describe the microstructural response according to GOODMAN & COWIN and PASSMAN et al. for each constituent. Based on the MÜLLER–LIU form of the second law of thermodynamics, a set of constitutive equations for a viscous solid–fluid mixture with microstructure is derived. These relatively general equations are then reduced to a system of ordinary differential equations describing a steady flow of the solid–fluid mixture between two horizontal plates. The resulting boundary value problem is solved numerically and results are presented for various values of parameters and boundary conditions. It is shown that simple shearing generally does not occur.

Typically, for the solid phase, in the vicinity of a boundary, if the solid volume fraction is small, a layer of high shear rate occurs, whose thickness is nearly between 5 and 15 grain diameters, while if the solid volume fraction is high, an interlock phenomenon occurs. The fluid velocity depends largely on the drag force between the constituents. If the drag coefficient is sufficiently large, the fluid flow is nearly the same as that of the solid, while for a small drag coefficient, the fluid shearing flow largely decouples from that of the solid in the entire flow region. Apart from this, there is a tendency for solid particles to accumulate in regions of low shear rate.

Chapter 31 is devoted to a phenomenological theory of granular materials subjected to slow frictional as well as rapid flows with intense collisional interactions. The microstructure of the material is taken into account by considering the solid volume fraction as a basic field. This variable enters the formulation via the balance law of configurational momentum, including corresponding contributions to the energy balance, as originally proposed by GOODMAN and COWIN, but modified here by adequately introducing an internal length. The subgrid motion is interpreted as volume fraction variation in relatively moderate laminar variation *and* rapid fluctuations, which manifest themselves in correspondingly filtered equations in terms of correlation products as in turbulence theories. We apply an ergodic (REYNOLDS) filter to these equations as in classical turbulent RANS-modeling and deduce averaged balances of mass, linear and configurational momenta, energy, turbulent, and configurational kinetic energy. Moreover, we postulate balance laws for the dissipation rates of the turbulent kinetic energy. All these comprise 10 evolution equations for a larger number of field variables. Closure relations are formulated for the laminar constitutive quantities and the correlation terms, all postulated to obey the material objectivity rules. To apply the entropy principle, three coldness measures are introduced for capturing material, configurational and turbulent dissipative quantities, they simplify the analysis of MÜLLER's entropy principle. The thermodynamic analysis delivers equilibrium properties of the constitutive quantities and linear expressions for the nonequilibrium closure relations.

The intention of this treatise is, apart from presenting its addressed subjects, a clear, detailed, and somewhat rigorous mathematical presentation of FTD on the basis of limited knowledge as a prerequisite. Calculus or analysis of functions of a single or several variables, linear algebra and the basics of ordinary and partial differential equations are assumed to be known, as is Cartesian tensor calculus. The latter is not universally taught in engineering curricula of universities; we believe that readers not equipped with the theory of complex functions can easily familiarize themselves with its basics in a few weeks reading effort.

The books have been jointly drafted by us from notes that accumulated during years. As mentioned before, the Chaps. 1–3, 5, 7, 10, 17–20 are translated (and partly revised) from “Fluid- und Thermodynamik—eine Einführung”. Many of the other chapters in Vols. 1 & 2 were composed in handwriting and typed by K. H. and substantially revised and transformed to LaTeX by Y. W. Volume 3 contains chapters that were newly designed from our own papers or papers of other scientists in the recent literature. The authors share equal responsibility for the content and the errors that still remain. Figures, which are taken from others, are reproduced and mostly redrawn, but mentioned in the figure captions. Nevertheless, a substantial number of figures have been designed by us. However, we received help for their electronic production: Mr: Andreas Schlump, from the Laboratory of Hydraulics, Hydrology and Glaciology at ETH Zurich designed all these figures.

Volumes 1 and 2 of this treatise have been subjected to critical reviews by experts. This has also been done for this third volume. Such reviewing criticisms are in general hard to find, because of the extensive labor that is connected with such work. Nonetheless, this burden was taken up by two emeriti, Dr.-Ing. PETER HAUPT, Professor of Mechanics at the University Kassel, Germany and Dr. rer. nat. WOLFGANG MUSCHIK, Professor of Theoretical Physics at the Technical University Berlin, Germany. We thoroughly thank these colleagues for their extensive help. Their criticisms and recommendations have been taken into consideration and gratefully incorporated in the final manuscript wherever possible. We have, of course, amended detected misprints and errors, but are nearly certain that, despite our last and careful own reading, there will remain some undetected ones. We now finish—no abandon—this treatise and kindly invite the readers to inform us of such fallacies, whenever they find them.

K. H. wishes to express his sincere thanks to ETH Zurich and in particular Prof. Dr. R. BOES for the allowance to share a desk as an Emeritus Professor from Darmstadt at the Laboratory of Hydraulics, Hydrology and Glaciology at ETH Zurich and he equally thanks Prof. MARTIN FUNK of the Laboratory, for the support. Y. W. would like to express his thanks to Prof. Dr. MARTIN OBERLACK for the constructive collaboration in the fluid dynamic working unit at Technische Universität Darmstadt.

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Contents

Chapter 21
Balance Laws of Continuous System

Abstract The fundamental assumption of continuous systems in classical physics is the conjecture that the physical space is densely filled with matter. This hypothesis is applied to single and multiphase continua as well as mixtures consisting of a finite number of constituents. Three classes of mixtures are defined: In the most complex case, class III, balance laws of mass, momenta, energy are formulated for each constituent, which possess their own mass, momenta, energy (and, therefore temperature). In class II mixtures, all components possess the same temperature, but the constituents possess their individual momenta and masses. Finally, in class I mixtures, the constituents do have the same temperature and common velocity—there is no slip between them—but each component has its own mass. The modern theories of continuous bodies differentiate between BOLTZMANN and *polar* continua. In the former, the balance of angular momentum is applied as moment of momentum. In such continua, the CAUCHY stress tensor of the mixture is symmetric. In the latter, angular momentum is expressed as moment of momentum plus spin with all its peculiar consequences. The balance laws of mass, momenta, and energy are formulated for the constituents for both cases in global and local forms in detail. The results for BOLTZMANN continua are well known. However, for polar media, different sub-theories emerge, depending upon how the specific spin is parameterized. In COSSERAT continua, the specific spin is motivated by rigid body dynamics as the "product of the tensor moment of inertia times angular velocity", see (21.32). If the micromotion is a pure rotation of the particles, i.e., the tensors of moments of inertia of the constituents do not change under motion, the mixture is called *micro-polar*, else *micro-morphic*. The chapter is closed by formulating the physical balance laws of the mixture as a whole and stating the relations of the physical variables of the mixture in terms of those of the constituents.

Keywords Multiphase continua · Class I, II, III mixtures · BOLTZMANN, COSSERAT continua · Balance laws · Local balance laws

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List of Symbols

Roman Symbols

$\mathfrak{c}^\alpha$	Mass production of density of constituent α
$\boldsymbol{D}_C$	Angular momentum of a finite body with respect to C
$\mathrm{d}a$	Surface increment
$\mathrm{d}v$	Volume element
$\mathfrak{e}^\alpha$	Specific production of energy of constituent α per unit volume.
$\mathfrak{e}^\alpha_{\text{Euclid}}$	Euclidean-invariant energy production of constituent α
$\boldsymbol{F}$	Force
$\boldsymbol{f}$	Specific body force
$\mathfrak{k}^\alpha$	Specific spin production of constituent α
$\mathfrak{k}^\alpha_{\text{Euclid}}$	Euclidean-invariant spin production of constituent α (see Eq. (21.22))
$\boldsymbol{\ell}, \boldsymbol{\ell}^\alpha$	Specific body couple—of constituent α
$\boldsymbol{M}$	Moment, acting on a body
$\boldsymbol{m}, \boldsymbol{m}^\alpha$	Specific couple stress tensor—of constituent α
$\mathfrak{m}^\alpha$	Specific momentum production of constituent α, or interaction force of constituent α with the other constituents
$\mathfrak{m}^\alpha_{\text{Euclid}}$	Euclidean-invariant momentum production of constituent α
$\boldsymbol{n}, \boldsymbol{n}_{\mathfrak{s}}$	Unit normal vector (on singular surface $\mathfrak{s}$)
$\mathfrak{P}$	Surface production per unit area of a physical quantity
$\mathfrak{P}^{s^\alpha}$	Surface production of entropy s^α
$\boldsymbol{q}$	Energy (heat) flux vector of the mixture
$\mathfrak{r}^\alpha$	Energy supply (radiation) per unit mass of constituent α
s, s^α	Entropy density—of constituent α
$\boldsymbol{s}, \boldsymbol{s}^\alpha$	Self angular momentum or specific spin—of constituent α
$\mathfrak{S}^\alpha$	Micro-morphic spin production of constituent α
$\boldsymbol{t}, \boldsymbol{t}^\alpha$	CAUCHY stress tensor—of constituent α
$\boldsymbol{u}, \boldsymbol{u}_{\mathfrak{s}}$	Velocity of propagation of the surface $\mathfrak{s}$
$\boldsymbol{v}, \boldsymbol{v}^\alpha$	Barycentric velocity of a mixture particle—of constituent α
$\boldsymbol{W}$	Skew-symmetric rank-2 tensor
$\boldsymbol{u}^\alpha = \boldsymbol{v}^\alpha - \boldsymbol{v}$	Diffusion velocity of constituent α
$\boldsymbol{w} = \text{dual}\,\boldsymbol{W}$	Axial vector, isomorphic to $\boldsymbol{W}$. $w_i \mathrel{\hat{=}} (\text{dual}\,\boldsymbol{W})_i \mathrel{\hat{=}} \frac{1}{2}\epsilon_{ijk}W_{jk}$.
$\dot{\boldsymbol{x}}_{\mathcal{O}}$	Velocity of the point $\mathcal{O}$

Greek Symbols

α	Identifier for a constituent
γ^α	Unspecified physical quantity of constituent α
$\Delta\boldsymbol{\omega}^\alpha - \boldsymbol{\omega}$	Diffusive angular velocity of constituent α
ϵ^α	Specific production of energy of constituent α per unit area
ε^α	Specific internal energy of constituent α
ζ^α	Supply rate of γ for constituent α
η^{s^α}	Supply rate of entropy of constituent α

$\boldsymbol{\Theta}, \hat{\hat{\Theta}}_C$	Tensor of inertia of a finite body.
$\boldsymbol{\Theta}^\alpha$	Specific tensor of inertia of constituent α
$\boldsymbol{\Theta}$	Specific tensor of inertia of the mixture, $\boldsymbol{\Theta} = \sum_{\alpha=1}^{N} \xi^\alpha \boldsymbol{\Theta}^\alpha$
μ^α	Surface mass production of constituent α
$\xi^\alpha = \rho^\alpha / \rho$	Mass concentration of constituent α
π^α	Production rate of γ^α
ρ, ρ^α	Mass density of mixture and constituent α
$\boldsymbol{\sigma}^\alpha$	Specific surface production of constituent α
$\boldsymbol{\tau}^\alpha$	Specific surface momentum production of constituent α
$\boldsymbol{\phi}^\alpha$	Flux of γ^α of constituent α
$\boldsymbol{\phi}^{s^\alpha}$	Flux of s^α
ω	Material volume
$\boldsymbol{\omega}, \boldsymbol{\omega}^\alpha$	Angular velocity of the mixture—of constituent α

Miscellaneous Symbols

curl $\boldsymbol{v}$	Rotation of the differentiable field $\boldsymbol{v}$
div $\boldsymbol{v}$	Divergence of the differentiable field $\boldsymbol{v}$
grad $\boldsymbol{v}$	Gradient of the differentiable field $\boldsymbol{v}$
$\frac{\mathrm{d}}{\mathrm{d}t}$	Total time derivative holding the particle fixed
$\frac{\mathrm{d}^\alpha(\cdot)}{\mathrm{d}t} \equiv (\cdot)'^\alpha$	Material time derivative following the motion of constituent α
$[\![f]\!]$	Jump of f across a surface $\mathfrak{s}$ into the positive side of $\mathfrak{s}$, $[\![f]\!] = f^+ - f^-$
$\partial\omega$	Boundary of ω
ω	Material volume
$\frac{\mathrm{d}^\alpha \boldsymbol{\Theta}^\alpha}{\mathrm{d}t} = 0 \quad \longleftrightarrow$	micro-polar $\longleftrightarrow$ $\mathfrak{S}^\alpha = 0$
$\frac{\mathrm{d}^\alpha \boldsymbol{\Theta}^\alpha}{\mathrm{d}t} \neq 0 \quad \longleftrightarrow$	micro-morphic $\longleftrightarrow$ $\mathfrak{S}^\alpha \neq 0$.

21.1 Classification of Continuous Systems

The most common treatment of physical systems is probably their basis on the assumption of continuity, i.e., that matter is continuously distributed in domains of the existence of mass. Otherwise stated, it is assumed that in a body of certain extent *every spatial point is occupied by mass*.[1] This assumption is in conflict with the atomistic structure of matter as it has undoubtedly been proved to be the realistic view of matter. For many problems of classical physics as it was developed before the 20th century, quantum mechanics has disproved the continuity assumption on the atomic and molecular scale. For a large class of physical problems of classical physics at the super-atomic and super-molecular scale, the continuity assumption may be viewed in the spirit of spatial averaging of physical properties over so-called

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[1] This metaphysical principle was first spelled out by CLIFFORD AMBROSE TRUESDELL (1919–2000) [21] and forms the basis of all physical systems whose significant length scales are substantially larger than those of atomic and molecular systems.

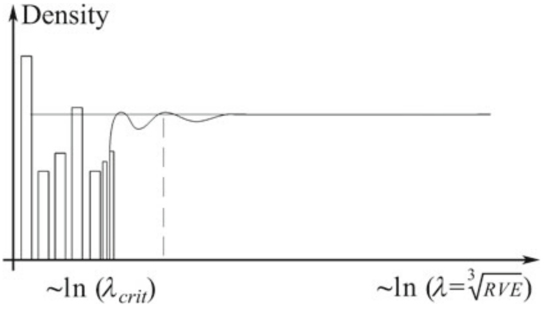

Fig. 21.1 Mass density of a specimen of a material body plotted against the logarithm of $\lambda = \sqrt[3]{RVE}$. *Below a critical length* $\lambda < \lambda_{\text{crit}}$ the continuity assumption breaks down

representative volume elements (RVE), whose size lengths are large in comparison to the corresponding length scales of the entities making up the body on the size of its RVE. This situation is pictured in **Fig. 21.1** for the mass density of a specimen of a body, which is plotted against a typical length scale $\lambda = \sqrt[3]{RVE}$. As this length scale decreases and becomes small, the smooth and (roughly) constant value of the density starts to vary, then to fluctuate until it eventually will become discontinuous. At such short typical values of λ, the continuity assumption will break down.

In ancient Greek philosophy, the word "atom" was used to describe the smallest bit of matter; this fundamental particle was used to characterize it as being "indivisible" or "indestructible". The atomistic concept as a basis of Natural Philosophy goes back to the Greek philosopher DEMOCRITUS (∼460 BC to ∼370 BC) from ABDERA and his teacher LEUCRIPTOS. The continuum assumption of nature with its arbitrary divisibility of matter was kept in Natural Philosophy until the beginning of the 20th century, when quantum mechanics was born. Despite this, for length scales much larger than atomic or molecular dimensions, it has proven to function as basis of the description of processes of matter for a wealth of circumstances. Only since the electronic computation has conquered the physical description of large assemblages of matter, the concept of indivisible elements has regained momentum, now much like "continuity" as a method of approximation concept. Indeed, since large electronic computations have become feasible, the continuous methods of the physical behavior of classical systems have become competitors in the discrete or distinct element method (DEM). This is in particular so, e.g., in granular and porous systems. Bulk behavior for such systems can be described by employing the classical physical laws to the individual grains or particles and analyzing the processes of encounter actions when particles interact in collisions. This particular view has become possible as modern computations can be conducted for systems consisting of many thousands of particles or element entities forming the material system in focus.

21.1.1 Balance Laws

It will be assumed in the ensuing developments that the artificial constructs of *continuous* bodies satisfy the basic principles of classical physics, i.e., the *conservation laws* of mass, linear and angular momentum, as well as energy and balance law of entropy. Here, a balance law is a statement for a quantity occupying a certain region in space; it says that the time rate of change of the quantity Ψ is balanced by its supply rate from the outside of the body, ω, Σ^Ψ, plus its flux rate into the body through its boundary $\mathcal{F}^\Psi$, $\partial\omega$, plus its production within the body, Π^Ψ. In short:

$$\left\{\begin{array}{l}\text{Time rate of change}\\ \text{of a quantity } \Psi \text{ in } \omega\end{array}\right\} = \left\{\begin{array}{l}\text{Flux (rate) of } \Psi,\ \mathcal{F}^\Psi \text{ through the boundary } \partial\omega \text{ of } \omega\\ +\text{Supply (rate) of } \Psi,\ \Sigma^\Psi \text{ within } \omega\\ +\text{Production (rate) of } \Psi,\ \Pi^\Psi \text{ within } \omega\end{array}\right\} \tag{21.1}$$

A balance law for Ψ reduces formally to a conservation law if its production rate vanishes for all time, $\Pi^\Psi = 0$.

Balance laws have already been discussed in Vol. 1 of this treatise and so, it may suffice to illustrate the principle by a simple example.

Example 21.1 Consider a herd of reindeers on a large Arctic island. The living animals may be identified by Ψ, the island by ω and the shoreline by $\partial\omega$. Reindeers swimming from the island to neighboring land or arriving on the island along its shore from the surrounding water form the flux $\mathcal{F}^\Psi$ along $\partial\omega$. Female reindeers giving birth to calves and reindeers being shot or naturally dying, form the production rate Π^Ψ within ω. A natural supply rate of reindeers does not exist, however, if reindeers should be brought to the island by helicopter, they would form Σ^Ψ within ω. •

21.1.2 Single Constituent Systems

Single-constituent material systems comprise bodies, which are assumed to be formed of one sort of matter or matter whose distinct physical or chemical elements need not be differentiated. Oxygen, O, and hydrogen, H_2, are single chemical elements, but water, H_2O is a molecule of O and H_2. The flow of water in our environment can be described by the physical laws without having to differentiate between the two gases H_2 and O. Similarly, many processes of the air in the atmosphere, in particular the mere physical motion of air as a compound of several chemical substances in meteorological flows can be treated as if air would be a single constituent medium. When cloud formations are in focus, then the water vapor, which is invisible, i.e., transparent, forms that constituent, which is part of the water saturated air. The clouds, on the other hand, are a suspended tracer within the saturated air, which consists of a large number of small water "particles"; their concentration grows or decreases according to whether the water in the cloud droplets evaporates to water vapor, or water vapor condensates at the droplets of the cloud, and eventually forms the rain. These examples show that the decision whether a body may be treated as a single constituent body or a kind of mingling of constituents depends also on the physical situation in focus.

21.1.3 Multiphase Continua and Mixtures

The denotations of multiphase continua and mixtures are not clearly differentiated in the literature. In large parts they mean the same, namely continua consisting of several distinguishable constituents, components, or phases, which all characterize the different entities, which make up the mixture. Occasionally, separable and unseparable mixtures or miscible and immiscible components are distinguished. Water saturated soil is a separable mixture of water and grains or soil particles. Ocean water is a miscible compound of pure water and salts; here the miscibility is due to the fact that the salt is in solution within the water.

As is the case for single-constituent bodies, the continuity idealization will also be introduced for mixtures: It reads here: Each spatial point is simultaneously occupied by material of all constituents. This postulate is a bit stronger than the analogous statement for single-constituent bodies, because it is assumed that every point in the body is occupied by all constituents. This, strictly, means that a body consisting of disjoint regions with different numbers of constituents must be subdivided into subbodies and a singular surface which separates the regions with different numbers of constituents.

It will be assumed as it was done for single-constituent bodies that the balance laws for mass, linear and angular momenta, energy and entropy also hold for the individual constituents, but for these, the production terms do not necessarily vanish. This generalization is natural, because the various components can in principle exchange mass, momenta and energy. So, these laws are not necessarily conservation laws.

Quite naturally, it will be assumed that the mixture as a whole, i.e., the response of the sum of all constituents together will behave as a single constituent material. This corresponds to the request that the sum of the production terms of mass, linear, and angular momenta and energy add up to zero.

In applications, full mixture theories, in which all the possible balance laws are employed, are very seldom used. For instance, if water percolates through the firn of a snow cover, it is necessary to differentiate between the temperatures of the water and the snow. This requires that two energy balance equations must be used. On the other hand, water flows in temperate ice at the common temperature. In this case, it suffices to formulate one energy conservation law for the mixture as a whole. Alternatively, for the description of the diffusive motion of a substance at very small concentration in a fluid, it may be sufficient to just describe the dynamic motion of the mixture (fluid + tracers) as a whole and the diffusive mass flow of the constituents relative to this. It is evident, such simplifications lead to a hierarchy of mixture theories. The most important models possess the following structure, [15, 16]:

- **Class I**: Here, the balance laws of mass of all constituents are used, however, only the momentum and energy balances of the mixture as a whole are employed. Often considerations of energy are left untouched, because only mechanical and no thermodynamic processes are in focus. These models are typical for the description of the *diffusive motion* of any particulate substance, which exists as a pollutant or tracer in another substance. The equations possess advective, diffuse, and possibly reactive structure. Examples are the salinity content in the water, the distribution of a nutrient (phosphate) or a chemical element (O_2, CO_2) in the water of a lake or in the ocean and many others.

A typical but complex example of class I mixture is the atmosphere with up to 40 reacting and interacting chemical tracers, one of which is ozone, O_3, in which the various reactions including radiation processes are combined to determine the spatial and temporal evolution of the ozone concentration around the Earth.

- **Class II**: These mixture theories are appropriate, if the interpenetrating constituents possess comparable concentrations of mass or specific momentum and move with different velocities. They are also known as *multiphase theories*. In this class, the balance laws of mass, momentum, and angular momentum are formulated for all constituents, but only one energy balance is used for the mixture as a whole. In other words, the individual constituents possess sufficiently distinct specific masses and momenta but the same temperature, so that to account for the thermodynamic effects the formulation of a single energy balance for the mixture as a whole suffices. These models go beyond the classical diffusion models which are only able to describe a dilution of a tracer substance, and no growth. The interaction forces that are active between the constituents are important and make it possible that the phase separation between the individual constituents can take place.

  Examples of theories of this class are practically all soil mechanics theories, which describe the interaction between the granular matrix and the water. For instance, DARCY's *law* is nothing else than a mathematical ansatz for the interaction force between the granulate and the pore water. Members of this class are also all mechanical models of multiphase suspension flows. In the geophysical context these are *powder snow avalanches*, of which the constituents are air and snow. In general, a diffusion model does not suffice to describe their dynamics, because, first, snow of the snow cover is entrained into the avalanche and, second, snow is deposited in the run-out zone. Both processes lead to an increase in the particle concentration. Other geophysical examples are *turbidity currents*, i.e., subaquatic slope motions similar to the *powder snow avalanches*, of which the constituents are soil and water, or *sturzstroms* and *mud flows*, mixtures of water and gravel or soil which move down a mountain slope, and finally *pyroclastic flows*, i.e., suspension flows of volcanic dust and air.
- **Class III**: The next level is occupied by the full thermodynamic mixture theories, in which the balance laws of mass, (linear and angular) momentum, and energy of all constituents must be formulated. *Plasmas* belong to this class; in the geophysical context there exist, however, equally a multitude of mixture concepts, which can be assigned to this class. For instance, the creeping deformation of cold firn in the uppermost layers of an ice sheet under the influence of the percolation flow of the melt water can be described by a mixture model of this complexity: Water and snow have distinct specific masses, velocities, and temperatures, and apart from these complexities, there may occur phase changes between the two constituents. Problems of geothermics also belong to this class of mixtures.

These classes may also occur in a mixed form. For instance, a saturated soil, which is contaminated by chemicals and/or oil, can well be regarded as a binary mixture of pure granules plus ground water with suspended chemicals. This would be a class II binary solid–fluid continuum, in which the fluid is itself also a class I mixture.

This classification should not be left without mentioning a somewhat peripheral case, which could also be categorized as a mixture. What is meant is rapid flow of cohesionless dense dry granular materials in air. Under such situations, the material body is a compound of a granular assemblage and interstitial air, which, dynamically, is negligible because its mass is very small. In this limiting and not completely realistic situation, the moving body consists of the granules and the interstitial empty space, of which the volume fraction is not constant, but varies in space and time. This body may structurally be categorized as a mixture but it is not of any one of the above classes, because the pore space has no mass; so, mass balance of the empty pore space is an empty statement. Nevertheless, this interstitial pore space certainly plays some dynamical role of the moving compound. It is the custom in the literature to account for its role by an "abstract" balance law, and the literature knows several variants of this balance law, [4, 9–14, 23]. Even though a connection of these models with mixture concepts seems natural, these granular systems are not viewed as limits of mixture theories.

21.1.4 Boltzmann and Polar Continua

We assume here that the reader is familiar with the classical statement derived in statics that the CAUCHY stress tensor is symmetric. This can be proved by applying the moment equilibrium condition on an infinitesimal cube. If one writes down the balance of moment of momentum over a body, then one may conclude that the CAUCHY stress tensor is also symmetric when the continuous body is in motion. LUDWIG BOLTZMANN[2] has in his lecture notes 'Über die Grundprinzipien und Grundgleichungen der Mechanik' [3] ("On the fundamental principles and fundamental equations of mechanics") emphasized the fact that the conjecture of the symmetry of the CAUCHY stress tensor possesses axiomatic character. Today, the symmetry of the CAUCHY stress tensor is unquestioned and adopted within the classical continuum theories, and indeed, the theory has proven its usefulness over and over again. To distinguish this classical formulation of continuum mechanics from more general formulations, e.g., polar continua, the symmetry requirement of the CAUCHY stress tensor is sometimes referred to as BOLTZMANN hypothesis, and the symmetry of the CAUCHY stress is then called the BOLTZMANN axiom.

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[2] For a biographical sketch of LUDWIG BOLTZMANN, see Vol. 2 of this treatise [18], Fig. 17.11 on p. 336.

Fig. 21.2 François Nicolas Cosserat (26. Oct. 1852–22. March 1914) (left), Eugène Cosserat (4. March 1866–31. May 1931) (right)

François Nicolas Cosserat was a French civil engineer who had studied at École Plolytecchnique (1870–1872), but finished his studies at École Nationale des Ponts et Chaussées with graduation in 1875. He subsequently worked as a railroad engineer being involved in the construction of railroad lines, bridges and tunnels in North and East France.

Besides his practical work as an engineer he worked intensely with his youngest brother Eugène, a trained mathematician and astronomer at the University of Toulouse, on elasticity. They together developed the Cosserat continuum in their now famous memoir of 1909 [6]. In 1893, François became a regular member of the Académie des Sciences and in 1913 president of the French Association of Mathematics. He also worked as an interpreter and as such translated Josiah Willard Gibbs 'Statistical Mechanics' into French.

Eugène Cosserat took at the age of 17 the competitive entrance examinations for École Polytechnique and École Normale Supérieure and was offered a place at both. He entered the latter school in 1883 and studied mathematics until 1886, when he was, after a brief intermission at Lucéé de Rennes, appointed as assistant astronomer to Édouard Benjamin Baillart (1848–1934). There, he performed a systematic study of 3112 binary stars and worked simultaneously on his doctorate '*Sur le cercle considéré comme élément générateur de l'espace*' with degree in 1889. Subsequently, he started to teach at the Faculty of Science at Toulouse and became professor of differential and integral calculus in 1896, replacing Thomas Stieltjes who had died on December 31, 1894. In 1908, he was appointed to the chair of Astronomy at Toulouse. Eugène became a full member of the Académie des Sciences in 1919 at Toulouse University, where he was a leading faculty member for 35 years.

The Cosserat brothers Eugène and François started to work together in 1896 with their joint publication "*Théorie de l'élasticité*", which was a study relating to the foundations of mechanics. They published more than 21 memories on the kinematics of continuous bodies and the foundation of mechanics, which culminated in 1909 in their book "*Théorie des corps deformables*" [6]. This innovative work ended with François Cosserat's death in 1914, after which time his brother Eugène Cosserat published nothing further on the topic.

The text is based on www.wikipedia.org

One way of motivating the generalization of BOLTZMANN continua[3] is to recall the balance laws of linear and angular momenta for rigid bodies. The resultant of all the forces and moments with respect to the center of mass $\mathcal{O}$ of the body is expressible in terms of an ordered pair at $\mathcal{O}$ of a force and a moment: $\{\boldsymbol{F}, \boldsymbol{M}\}$; this ordered pair of force and moment is sometimes called a motor [22]. The equations of motion of a rigid body relative to $\mathcal{O}$ can be expressed as a dynamical equation of the form

$$\{(m\dot{\boldsymbol{x}}_{\mathcal{O}})^{\cdot}, (\boldsymbol{\Theta}\boldsymbol{\omega})^{\cdot}\} = \{\boldsymbol{F}, \boldsymbol{M}\}, \tag{21.2}$$

in which $m\dot{\boldsymbol{x}}_{\mathcal{O}}$ is the body's momentum relative to $\mathcal{O}$, m being the mass of the body and $\dot{\boldsymbol{x}}_{\mathcal{O}}$ the translational velocity; analogously, $\boldsymbol{\Theta}\,\boldsymbol{\omega}$ is the body's *(self) angular momentum* or *specific spin*, $\boldsymbol{\Theta}$ being the tensor of inertia with respect to $\mathcal{O}$ and $\boldsymbol{\omega}$ the angular velocity of the body, which is independent of the translational velocity. Equation (21.2) summarizes NEWTON's second law and EULER's law of conservation of angular momentum.

If we now imagine the rigid body of the above equation to be replaced by an infinitesimal deformable cube, we replace (21.2) by

$$\{(\rho\dot{\boldsymbol{x}})^{\cdot}, (\rho\boldsymbol{s})^{\cdot}\} = \{\rho\boldsymbol{f}, \rho\boldsymbol{\ell}\}; \tag{21.3}$$

$\rho\dot{\boldsymbol{x}}$ and $\rho\boldsymbol{s}$ are the specific translational momentum and specific angular momentum, while $\rho\boldsymbol{f}$ and $\rho\boldsymbol{\ell}$ are the specific body force and specific body couple, respectively, all per unit volume. Equation (21.3) is short of an important additional term. Recall that the momentum equation of a classical continuum contains also a stress tensor term, $\operatorname{div}\boldsymbol{t}$. The analogue term in the balance of angular momentum must have the form $\operatorname{div}\boldsymbol{m}$, where $\boldsymbol{m}$ is called *couple stress*. So, for a continuous system the proper

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[3] The first attempt of generalizing BOLTZMANN continua to include a nontrivial angular momentum or spin balance was made by the brothers EUGÈNE and FRANÇOIS COSSERAT between the years 1896 and 1914 when the latter died, see **Fig. 21.2** on brief biographies. They published together *Théorie de l' élasticité* [5] and, apart from 21 brief scattered communications, the seminal work *Théorie des corps déformables* [6] appeared. Their model is now called "COSSERAT continuum" or "polar continuum", the first version of a theory of deformable continua *with microstructure* [8], which primarily were developed in the second half of the 20th century. An accurate historical account "about the COSSERATs' Book of 1909" is provided by G.A. MAUGIN in Chap. 8 in his book "Continuum Mechanics Through the 18–19th Century" [19], which contains 77 additional references.

There are several approaches to derive the governing equations of COSSERAT continua, which differ from the approaches of the COSSERAT brothers. Essentially two principal steps beyond a classical BOLTZMANN continuum have to be performed, a generalization of the *dynamical principles* and another one on *kinematic* principles; they are introduced in this book as in this chapter and Chap. 22, respectively. The method of generalization starts with rigid body dynamics, assumed to be known by first and second year undergraduate students. One of us (KH) still recalls how the concepts of "Kinemate" and "Dyname" (both German words with no English counterparts), defined as the left- and right-hand sides of Eq. (21.2) in the early 60'. The "projection" of this statement from a rigid finite body to an infinitesimal element of a deformable continuum essentially forms the step needed to obtain a polar continuum. This projection can be done on less than a page, is very imaginative and summarizes the essentials of the COSSERAT continuum in a nutshell.

equation replacing (21.3) is[4]

$$\{(\rho\dot{\boldsymbol{x}})^{\boldsymbol{\cdot}}, (\rho\boldsymbol{s})^{\boldsymbol{\cdot}}\} = \{\operatorname{div}\boldsymbol{t}, \operatorname{div}\boldsymbol{m}\} + \{\rho\boldsymbol{f}, \rho\boldsymbol{\ell}\}. \tag{21.4}$$

Spin $\boldsymbol{s}$, couple stress $\boldsymbol{m}$ and body couple $\boldsymbol{\ell}$ are all new elements, which characterize polar continua. In (21.3), the spin $\boldsymbol{s}$ is not specially parameterized. *Micro-polar* or COSSERAT *continua* assume $\boldsymbol{s} = \boldsymbol{\Theta}\,\boldsymbol{\omega}$ with a tensor of inertia, $\boldsymbol{\Theta}$ which can independently rotate but not deform. In a deformable body $\boldsymbol{\Theta}$ may, however, change with strain in time and space. Those theoretical formulations are called *micro-morphic*.

21.2 General Balance Laws for the Constituents

We present in this section the balance laws for the constituents of a polar mixture in the EULERian description. Constituents are identified by Greek indices from $\alpha = 1$ to $\alpha = N$. At first, a master balance law is presented for some physical quantity, its production, supply, and flux rates. It is assumed that all these quantities are additive. The mixture specific form of this general balance law is given by

$$\frac{\mathrm{d}^\alpha}{\mathrm{d}t}\int_\omega \gamma^\alpha(\boldsymbol{x},t)\mathrm{d}v = \int_\omega \left(\pi^\alpha(\boldsymbol{x},t) + \varsigma^\alpha(\boldsymbol{x},t)\right)\mathrm{d}v - \int_{\partial\omega} \boldsymbol{\phi}^\alpha(\boldsymbol{x},t)\cdot\boldsymbol{n}\,\mathrm{d}a, \tag{21.5}$$

with the following local counterparts

$$\frac{\partial\gamma^\alpha}{\partial t} + \operatorname{div}\left(\gamma^\alpha\boldsymbol{v}^\alpha\right) = -\operatorname{div}\,\boldsymbol{\phi}^\alpha + \pi^\alpha + \varsigma^\alpha, \tag{21.6}$$

$$\llbracket\gamma^\alpha((\boldsymbol{v}-\boldsymbol{u})\cdot\boldsymbol{n}_{\mathfrak{s}})\rrbracket - \llbracket\boldsymbol{\phi}^\alpha\cdot\boldsymbol{n}_{\mathfrak{s}}\rrbracket = \mathfrak{P}^\alpha. \tag{21.7}$$

In these equations, γ^α, π^α, ς^α, and $\boldsymbol{\phi}^\alpha$ denote an unspecified physical quantity of the constituent α, its production in, and its supply to ω as well as the flux across the boundary $\partial\omega$; d/dt is the material time derivative of the constituent α, i.e., the time derivative if one follows the motion of constituent α, and $\boldsymbol{v}^\alpha$ is the velocity vector of constituent α. If $\boldsymbol{\gamma}^\alpha$ is a vectorial field, then $\boldsymbol{\gamma}^\alpha\boldsymbol{v}^\alpha$ must be interpreted as a dyadic product: $\boldsymbol{\gamma}^\alpha \otimes \boldsymbol{v}^\alpha$. In the jump condition (21.7), $\boldsymbol{n}_{\mathfrak{s}}$ denotes the unit vector perpendicular to the singular surface, $\mathfrak{P}$ is the surface production of the constituent physical quantity γ^α, and $\boldsymbol{u}$ is the velocity with which the surface moves; it must not coincide with any of the constituents' particle velocity instantaneously sitting

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[4] The divergence terms on the right-hand side of (21.4) can be justified as follows: Note that in elementary statics, the {force, couple}-motor is the resultant motor in the center of mass $\mathcal{O}$ of the body of all forces, the volume, and surface forces. When applying this same principle to an infinitesimal cube, the forces and couples are separately introduced as body and surface forces and couples. It is a straightforward exercise to see that the surface stress traction and surface couple stress tractions contribute to (21.4) by the motor $\{\operatorname{div}\boldsymbol{t}, \operatorname{div}\boldsymbol{m}\}$.

upon the surface. Finally, $[\![f]\!] = f^+ - f^-$ is the difference of the values of f on the positive and negative sides of the singular surface. The derivation of the local statements (21.6) and (21.7) from the global law (21.5) is not entirely straightforward. The interested reader may consult the appendix to this chapter. A further extension of the jump condition (21.7), taking the contribution of the excess surface thermodynamic quantities into account, can be found in Chap. 27. In this case, the jump condition will be extended to the corresponding interfacial balance equation.

The various interpretations of the fields for the different physical balances are summarized in **Table 21.1**. In the **balance law of mass** for constituent α flux and supply vanish as they do for a single constituent material; however, there can arise a nontrivial production of mass for constituent α, $\mathfrak{c}^\alpha$; this is, e.g., the case if mass of constituent α is produced by chemical reactions or phase changes. Likewise, it is so that mass of a constituent can be generated on a singular surface, if phase change processes arise there. This is described as surface mass production μ^α.

In the **balance law of linear momentum**, the momentum density $\rho^\alpha \boldsymbol{v}^\alpha$ is balanced by the volume forces $\rho^\alpha \boldsymbol{f}^\alpha$ and the partial stress $\boldsymbol{t}^\alpha$; to these contributions, also arising in a one-component material, one must add a density of momentum production or interaction force $\boldsymbol{\mathfrak{m}}^\alpha$. This is the force that is exerted on constituent α by all other constituents $1, 2, \ldots, N$ (without α). In Table 21.1, we also list a surface momentum production $\boldsymbol{\tau}^\alpha$, which is for instance necessary when a singular surface separates two mixtures with different numbers of constituents.

The **balance of angular momentum** in Table 21.1 is formulated for a so-called *polar continuum*; more specifically, each entry in the line "Angular momentum" in Table 21.1 consists of two contributions for γ^α, an intrinsic angular momentum $\rho^\alpha \boldsymbol{s}^\alpha$, called *spin* and a *moment of momentum* $\boldsymbol{x} \times \rho^\alpha \boldsymbol{v}^\alpha$. Both are obviously axial vectors.[5] In much the same way, the supply of angular momentum consists of an external specific couple $\rho^\alpha \boldsymbol{\ell}^\alpha$ and the moment of the specific exterior volume force $\boldsymbol{x} \times \rho^\alpha \boldsymbol{f}^\alpha$; and the flux of angular momentum is obtained as the sum of the (negative) couple stresses $-\boldsymbol{m}^\alpha$ and the moment of the (negative) partial CAUCHY stresses $-\boldsymbol{x} \times \boldsymbol{t}^\alpha$. Likewise the angular momentum production is composed of two contributions, the production of the specific spin $\boldsymbol{\mathfrak{k}}^\alpha$ and the moment of the momentum production $\boldsymbol{x} \times \boldsymbol{\mathfrak{m}}^\alpha$. Finally, one may also compose the surface production of angular momentum in this way; however, we shall not do this here, because we see no advantages by doing so; we call $\boldsymbol{\sigma}^\alpha$ the surface production of angular momentum of constituent α.

The physical quantity in the **balance of energy**, the first law of thermodynamics, is the specific energy density, which is composed of the kinetic energy (of translation and rotation), $\frac{1}{2}\rho^\alpha(\boldsymbol{v}^\alpha \cdot \boldsymbol{v}^\alpha + \boldsymbol{s}^\alpha \cdot \boldsymbol{\omega}^\alpha)$ plus the internal energy, $\rho^\alpha \varepsilon^\alpha$. These are the kinetic and thermodynamic contributions; $\boldsymbol{v}^\alpha$ is the velocity of constituent α, and $\boldsymbol{\omega}^\alpha$ is its angular velocity; the latter is in no way related to the velocity $\boldsymbol{v}^\alpha$. Since $\boldsymbol{s}^\alpha$ and $\boldsymbol{\omega}^\alpha$ are both axial vectors, $\boldsymbol{s}^\alpha \cdot \boldsymbol{\omega}^\alpha$ is a scalar. Likewise, the energy supply and energy flux are composed of such contributions. For instance, the energy supply is given by the power of working of the specific volume forces $\boldsymbol{v}^\alpha \cdot \rho^\alpha \boldsymbol{f}^\alpha$ and specific volume couples $\rho^\alpha \boldsymbol{l}^\alpha \cdot \boldsymbol{\omega}^\alpha$ plus the specific radiation $\rho^\alpha \mathfrak{r}^\alpha$, all for constituent α. Similarly

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[5] A vector is called axial, if it changes its sign when the orientation of the basis changes.

the flux of the energy of constituent α is composed of the power of working of the negative partial stresses $-\boldsymbol{v}^\alpha \boldsymbol{t}^\alpha$, and the couple stresses $-\boldsymbol{\omega}^\alpha \boldsymbol{m}^\alpha$ plus the partial heat flux $\boldsymbol{q}^\alpha$ of constituent α. The production terms of energy are given by $\mathfrak{e}^\alpha$ and ϵ^α and denote specific quantities per unit volume and surface, respectively.

The individual quantities in the **entropy balance** are not specifically identified in Table 21.1 except that the quantities carry the superscript s^α.

With the identifications of Table 21.1 the local balance laws (21.6) and (21.7) take the following forms:

Mass:

$$\begin{aligned}
&\frac{\partial \rho^\alpha}{\partial t} + \operatorname{div}\,(\rho^\alpha \boldsymbol{v}^\alpha) = \mathfrak{c}^\alpha,\\
&\left\llbracket \rho^\alpha (\boldsymbol{v}^\alpha - \boldsymbol{u}) \cdot \boldsymbol{n}_{\mathfrak{s}}) \right\rrbracket = \mu^\alpha,
\end{aligned} \tag{21.8}$$

Momentum:

$$\begin{aligned}
&\frac{\partial}{\partial t}(\rho^\alpha \boldsymbol{v}^\alpha) + \operatorname{div}\,(\rho^\alpha \boldsymbol{v}^\alpha \otimes \boldsymbol{v}^\alpha - \boldsymbol{t}^\alpha) = \rho^\alpha \boldsymbol{f}^\alpha + \mathfrak{m}^\alpha,\\
&\left\llbracket \rho^\alpha \boldsymbol{v}^\alpha \otimes (\boldsymbol{v}^\alpha - \boldsymbol{u}) \cdot \boldsymbol{n}_{\mathfrak{s}} \right\rrbracket + \left\llbracket \boldsymbol{t}^\alpha \boldsymbol{n}_{\mathfrak{s}} \right\rrbracket = \boldsymbol{\tau}^\alpha,
\end{aligned} \tag{21.9}$$

Angular Momentum:

$$\begin{aligned}
&\frac{\partial}{\partial t}\,(\rho^\alpha \boldsymbol{s}^\alpha + \boldsymbol{x}^\alpha \times \rho^\alpha \boldsymbol{v}^\alpha) + \operatorname{div}\Big((\rho^\alpha \boldsymbol{s}^\alpha + \boldsymbol{x} \times \rho^\alpha \boldsymbol{v}^\alpha) \otimes \boldsymbol{v}^\alpha\\
&\qquad - \boldsymbol{m}^\alpha - \boldsymbol{x} \times \boldsymbol{t}^\alpha\Big) = \rho^\alpha \boldsymbol{\ell}^\alpha + \boldsymbol{x} \times \rho^\alpha \boldsymbol{f}^\alpha + \mathfrak{l}^\alpha + \boldsymbol{x} \times \mathfrak{m}^\alpha,\\
&\llbracket (\rho^\alpha \boldsymbol{s}^\alpha + \boldsymbol{x}^\alpha \times \rho^\alpha \boldsymbol{v}^\alpha)(\boldsymbol{v}^\alpha - \boldsymbol{u}) \cdot \boldsymbol{n}_{\mathfrak{s}} \rrbracket + \llbracket \boldsymbol{m}^\alpha + \boldsymbol{x} \times \boldsymbol{t}^\alpha \rrbracket \cdot \boldsymbol{n}_{\mathfrak{s}} = \boldsymbol{\sigma}^\alpha,
\end{aligned} \tag{21.10}$$

Energy:

$$\begin{aligned}
&\frac{\partial}{\partial t}\big(\tfrac{1}{2}\rho^\alpha \boldsymbol{v}^\alpha \cdot \boldsymbol{v}^\alpha + \tfrac{1}{2}\rho^\alpha \boldsymbol{s}^\alpha \cdot \boldsymbol{\omega}^\alpha + \rho^\alpha \varepsilon^\alpha\big) + \operatorname{div}\big((\tfrac{1}{2}\rho^\alpha \boldsymbol{v}^\alpha \cdot \boldsymbol{v}^\alpha\\
&+ \tfrac{1}{2}\rho^\alpha \boldsymbol{s}^\alpha \cdot \boldsymbol{\omega}^\alpha + \rho^\alpha \varepsilon^\alpha)\boldsymbol{v}^\alpha - \boldsymbol{v}^\alpha \boldsymbol{t}^\alpha - \boldsymbol{\omega}^\alpha \boldsymbol{m}^\alpha + \boldsymbol{q}^\alpha\big)\\
&= \mathfrak{e}^\alpha + \boldsymbol{v}^\alpha \cdot \rho^\alpha \boldsymbol{f}^\alpha + \boldsymbol{\omega}^\alpha \cdot \rho^\alpha \boldsymbol{\ell}^\alpha + \rho^\alpha \mathfrak{r}^\alpha,\\
&\left\llbracket (\tfrac{1}{2}\rho^\alpha \boldsymbol{v}^\alpha \cdot \boldsymbol{v}^\alpha + \tfrac{1}{2}\rho^\alpha \boldsymbol{s}^\alpha \cdot \boldsymbol{\omega}^\alpha + \rho^\alpha \varepsilon^\alpha)(\boldsymbol{v}^\alpha - \boldsymbol{u}) \cdot \boldsymbol{n}_{\mathfrak{s}} \right\rrbracket\\
&- \left\llbracket \boldsymbol{v}^\alpha \boldsymbol{t}^\alpha + \boldsymbol{\omega}^\alpha \boldsymbol{m}^\alpha - \boldsymbol{q}^\alpha \right\rrbracket \cdot \boldsymbol{n}_{\mathfrak{s}} = \epsilon^\alpha,
\end{aligned} \tag{21.11}$$

Entropy:

$$\begin{aligned}
&\frac{\partial}{\partial t}(\rho^\alpha s^\alpha) + \operatorname{div}\,\big(\rho^\alpha s^\alpha \boldsymbol{v}^\alpha + \boldsymbol{\phi}^{s^\alpha}\big) = \rho^\alpha \eta^{s^\alpha} + \rho^\alpha \pi^{s^\alpha},\\
&\left\llbracket \rho^\alpha s^\alpha (\boldsymbol{v}^\alpha - \boldsymbol{u}) \cdot \boldsymbol{n}_{\mathfrak{s}} \right\rrbracket - \left\llbracket \boldsymbol{\phi}^{s^\alpha} \right\rrbracket \cdot \boldsymbol{n}_{\mathfrak{s}} = \mathfrak{P}^{s^\alpha}.
\end{aligned} \tag{21.12}$$

Table 21.1 Field quantities which arise in the balance law (21.5) for mass, linear and angular momentum, energy and entropy for a physical quantity of constituent α. γ^α, $\boldsymbol{\phi}^\alpha$, ς^α, π^α and $\mathfrak{P}^\alpha$ denote the physical quantity, its flux, supply, volume production and surface production. Concerning the individual entries, see main text

Balance	γ^α	$\boldsymbol{\phi}^\alpha$	ς^α	π^α	$\mathfrak{P}^\alpha$
Mass	ρ^α	0	0	$\boldsymbol{\mathfrak{c}}^\alpha$	μ^α
Momentum	$\rho^\alpha\boldsymbol{v}^\alpha$	$-\boldsymbol{t}^\alpha$	$\rho^\alpha\boldsymbol{f}^\alpha$	$\boldsymbol{\mathfrak{m}}^\alpha$	$\boldsymbol{\tau}^\alpha$
Angular momentum	$\rho^\alpha\boldsymbol{s}^\alpha+\boldsymbol{x}\times\rho^\alpha\boldsymbol{v}^\alpha$	$-\boldsymbol{m}^\alpha-\boldsymbol{x}\times\boldsymbol{t}^\alpha$	$\rho^\alpha\boldsymbol{\ell}^\alpha+\boldsymbol{x}\times\rho^\alpha\boldsymbol{f}^\alpha$	$\boldsymbol{\mathfrak{t}}^\alpha+\boldsymbol{x}\times\boldsymbol{\mathfrak{m}}^\alpha$	$\boldsymbol{\sigma}^\alpha$
Energy	$\frac{1}{2}\rho^\alpha\boldsymbol{v}^\alpha\cdot\boldsymbol{v}^\alpha+\frac{1}{2}\rho^\alpha\boldsymbol{s}^\alpha\cdot\boldsymbol{\omega}^\alpha+\rho^\alpha\varepsilon^\alpha$	$-\boldsymbol{v}^\alpha\boldsymbol{t}^\alpha-\boldsymbol{\omega}^\alpha\boldsymbol{m}^\alpha+\boldsymbol{q}^\alpha$	$\boldsymbol{v}^\alpha\cdot\rho^\alpha\boldsymbol{f}^\alpha+\rho^\alpha\boldsymbol{\ell}^\alpha\cdot\boldsymbol{\omega}^\alpha+\rho^\alpha\boldsymbol{\mathfrak{r}}^\alpha$	$\boldsymbol{\mathfrak{e}}^\alpha$	ϵ^α
Entropy	$\rho^\alpha s^\alpha$	$\boldsymbol{\phi}^{s^\alpha}$	$\rho^\alpha\eta^{s^\alpha}$	$\rho^\alpha\pi^{s^\alpha}$	$\mathfrak{P}^{s^\alpha}$

These laws can be further simplified, however, they then no longer appear in the classical divergence form. To this end we use the material time derivative of constituent α

$$(\cdot)'^{\alpha} := \frac{\mathrm{d}^{\alpha}\,(\cdot)}{\mathrm{d}t} := \frac{\partial\,(\cdot)}{\partial t} + \big(\mathrm{grad}\ (\cdot)\,\big)\boldsymbol{v}^{\alpha}. \tag{21.13}$$

Example:
Mass:

$$\begin{aligned} &\frac{\partial \rho^{\alpha}}{\partial t} + \rho^{\alpha}\mathrm{div}\,\boldsymbol{v}^{\alpha} + \boldsymbol{v}^{\alpha}\cdot \mathrm{grad}\,\rho^{\alpha} = \mathfrak{c}^{\alpha},\\ \text{or}\ \ &\frac{\mathrm{d}^{\alpha}\rho^{\alpha}}{\mathrm{d}t} + \rho^{\alpha}\mathrm{div}\,\boldsymbol{v}^{\alpha} = \mathfrak{c}^{\alpha}. \end{aligned}$$

Introducing this in the above Eqs. (21.8)–(21.12) and sequentially using the results of the previous equations, it can be shown that the following alternative forms hold:

Momentum:

$$\begin{aligned} &\rho^{\alpha}\frac{\mathrm{d}^{\alpha}\boldsymbol{v}^{\alpha}}{\mathrm{d}t} = \mathrm{div}\,\boldsymbol{t}^{\alpha} + \rho^{\alpha}\boldsymbol{f}^{\alpha} + (\mathfrak{m}^{\alpha} - \mathfrak{c}^{\alpha}\boldsymbol{v}^{\alpha})\,,\\ &\llbracket \rho^{\alpha}\boldsymbol{v}^{\alpha}\otimes(\boldsymbol{v}^{\alpha}-\boldsymbol{u})\cdot\boldsymbol{n}_{\mathfrak{s}}\rrbracket + \llbracket \boldsymbol{t}^{\alpha}\boldsymbol{n}_{\mathfrak{s}}\rrbracket = \boldsymbol{\tau}^{\alpha}, \end{aligned} \tag{21.14}$$

Angular Momentum or Spin:

$$\begin{aligned} &\rho^{\alpha}\frac{\mathrm{d}^{\alpha}\boldsymbol{s}^{\alpha}}{\mathrm{d}t} = \mathrm{div}\,\boldsymbol{m}^{\alpha} + \rho^{\alpha}\boldsymbol{\ell}^{\alpha} - \mathrm{dual}\,\big(\boldsymbol{t}^{\alpha} - (\boldsymbol{t}^{\alpha})^{T}\big) + (\mathfrak{k}^{\alpha} - \mathfrak{c}^{\alpha}\boldsymbol{s}^{\alpha})\,,\\ &\llbracket \rho^{\alpha}\boldsymbol{s}^{\alpha}\left((\boldsymbol{v}^{\alpha}-\boldsymbol{u})\cdot\boldsymbol{n}_{\mathfrak{s}}\right)\rrbracket + \llbracket \boldsymbol{m}^{\alpha}\boldsymbol{n}_{\mathfrak{s}}\rrbracket = \boldsymbol{\sigma}^{\alpha}, \end{aligned} \tag{21.15}$$

Energy:

$$\begin{aligned} \rho^{\alpha}\frac{\mathrm{d}^{\alpha}\varepsilon^{\alpha}}{\mathrm{d}t} &= -\mathrm{div}\,\boldsymbol{q}^{\alpha} + \boldsymbol{\omega}^{\alpha}\cdot\big(\mathrm{dual}\,\big(\boldsymbol{t}^{\alpha} - (\boldsymbol{t}^{\alpha})^{T}\big)\big)\\ &\quad + \big(\mathrm{grad}\,\boldsymbol{v}^{\alpha}\cdot(\boldsymbol{t}^{\alpha})^{T}\big) + \big(\mathrm{grad}\,\boldsymbol{\omega}^{\alpha}\cdot(\boldsymbol{m}^{\alpha})^{T}\big)\\ &\quad + \tfrac{1}{2}\rho^{\alpha}\left(\boldsymbol{\omega}^{\alpha}\cdot\frac{\mathrm{d}^{\alpha}\boldsymbol{s}^{\alpha}}{\mathrm{d}t} - \boldsymbol{s}^{\alpha}\cdot\frac{\mathrm{d}^{\alpha}\boldsymbol{\omega}^{\alpha}}{\mathrm{d}t}\right) + \rho^{\alpha}\mathfrak{r}^{\alpha}\\ &\quad + \big(\mathfrak{e}^{\alpha} - \mathfrak{c}^{\alpha}\big(\varepsilon^{\alpha} + \tfrac{1}{2}\boldsymbol{v}^{\alpha}\cdot\boldsymbol{v}^{\alpha} + \tfrac{1}{2}\boldsymbol{s}^{\alpha}\cdot\boldsymbol{\omega}^{\alpha}\big)\\ &\qquad - (\mathfrak{m}^{\alpha} - \mathfrak{c}^{\alpha}\boldsymbol{v}^{\alpha})\cdot\boldsymbol{v}^{\alpha} - (\mathfrak{k}^{\alpha} - \mathfrak{c}^{\alpha}\boldsymbol{s}^{\alpha})\cdot\boldsymbol{\omega}^{\alpha}\big),\\ \llbracket (\tfrac{1}{2}\rho^{\alpha}\boldsymbol{v}^{\alpha}\cdot\boldsymbol{v}^{\alpha} &+ \tfrac{1}{2}\rho^{\alpha}\boldsymbol{s}^{\alpha}\cdot\boldsymbol{\omega}^{\alpha} + \rho^{\alpha}\varepsilon^{\alpha})(\boldsymbol{v}^{\alpha}-\boldsymbol{u})\cdot\boldsymbol{n}_{\mathfrak{s}}\rrbracket\\ &\quad - \llbracket \boldsymbol{v}^{\alpha}\boldsymbol{t}^{\alpha} + \boldsymbol{\omega}^{\alpha}\boldsymbol{m}^{\alpha} - \boldsymbol{q}^{\alpha}\rrbracket\cdot\boldsymbol{n}_{\mathfrak{s}} = \epsilon^{\alpha}\,. \end{aligned} \tag{21.16}$$

Entropy:

$$\begin{aligned} &\rho^\alpha \frac{\mathrm{d}^\alpha s^\alpha}{\mathrm{d}t} = -\operatorname{div} \boldsymbol{\phi}^{s^\alpha} + \rho^\alpha \eta^{s^\alpha} + \rho^\alpha \pi^{s^\alpha} \quad \text{with} \quad \pi^{s^\alpha} \geq 0, \\ &[\![\rho^\alpha s^\alpha (\boldsymbol{v}^\alpha - \boldsymbol{u}) \cdot \boldsymbol{n}_{\mathfrak{s}}]\!] - [\![\boldsymbol{\phi}^{s^\alpha}]\!] \cdot \boldsymbol{n}_{\mathfrak{s}} = \mathfrak{P}^{s^\alpha}. \end{aligned} \tag{21.17}$$

Let us demonstrate the above claim:

- For instance, employing product differentiation in (21.9) and collecting terms accordingly yields

$$\begin{aligned} &\underbrace{\left(\frac{\partial \rho^\alpha}{\partial t} + \operatorname{div} \, (\rho^\alpha \boldsymbol{v}^\alpha) \right)}_{=\mathfrak{c}^\alpha \text{ (mass balance (21.8)}_1\text{)}} \boldsymbol{v}^\alpha + \rho^\alpha \underbrace{\left(\frac{\partial \boldsymbol{v}^\alpha}{\partial t} + (\operatorname{grad} \boldsymbol{v}^\alpha) \, \boldsymbol{v}^\alpha \right)}_{\frac{\mathrm{d}^\alpha \boldsymbol{v}^\alpha}{\mathrm{d}t} \text{ (definition)}} - \operatorname{div} \boldsymbol{t}^\alpha \\ &= \rho^\alpha \boldsymbol{f}^\alpha + \mathfrak{m}^\alpha, \end{aligned} \tag{21.18}$$

  which agrees with (21.14).
- The left-hand side of the angular momentum equation $(21.10)_1$ can be written as

$$\begin{aligned} &\frac{\partial}{\partial t} (\rho^\alpha \boldsymbol{s}^\alpha) + \frac{\partial}{\partial t} (\boldsymbol{x} \times \rho^\alpha \boldsymbol{v}^\alpha) + \operatorname{div} \, (\rho^\alpha \boldsymbol{s}^\alpha \otimes \boldsymbol{v}^\alpha) + \operatorname{div} \, ((\boldsymbol{x} \times \rho^\alpha \boldsymbol{v}^\alpha) \otimes \boldsymbol{v}^\alpha) \\ &- \operatorname{div} \, (\boldsymbol{m}^\alpha) - \operatorname{div} \, (\boldsymbol{x} \times \boldsymbol{t}^\alpha) \\ = &\frac{\partial}{\partial t} (\rho^\alpha \boldsymbol{s}^\alpha) + \operatorname{div} \, (\rho^\alpha \boldsymbol{s}^\alpha \otimes \boldsymbol{v}^\alpha) - \operatorname{div} \, (\boldsymbol{m}^\alpha) \\ &+ \boldsymbol{x} \times \left\{ \frac{\partial}{\partial t} (\rho^\alpha \boldsymbol{v}^\alpha) + \operatorname{div} \, (\rho^\alpha \boldsymbol{v}^\alpha \otimes \boldsymbol{v}^\alpha) - \operatorname{div} \, (\boldsymbol{t}^\alpha) \right\} - \operatorname{dual} \left(\boldsymbol{t}^\alpha - (\boldsymbol{t}^\alpha)^T \right). \end{aligned}$$

  Combining this with the right-hand side of $(21.10)_1$ leads to the statement

$$\begin{aligned} &\boldsymbol{x} \times \left\{ \frac{\partial}{\partial t} (\rho^\alpha \boldsymbol{v}^\alpha) + \operatorname{div} \, (\rho^\alpha \boldsymbol{v}^\alpha \otimes \boldsymbol{v}^\alpha) - \operatorname{div} \, (\boldsymbol{t}^\alpha) - \rho^\alpha \boldsymbol{f}^\alpha - \mathfrak{m}^\alpha \right\} \\ &+ \frac{\partial}{\partial t} (\rho^\alpha \boldsymbol{s}^\alpha) + \operatorname{div} \, (\rho^\alpha \boldsymbol{s}^\alpha \otimes \boldsymbol{v}^\alpha) - \operatorname{div} \, (\boldsymbol{m}^\alpha) \\ &- \rho^\alpha \boldsymbol{\ell}^\alpha - \mathfrak{k}^\alpha + \operatorname{dual} \left(\boldsymbol{t}^\alpha - (\boldsymbol{t}^\alpha)^T \right) = 0. \end{aligned} \tag{21.19}$$

  The expression in the first line vanishes, as it is the cross product of $\boldsymbol{x}$ with the momentum balance, written as $\boldsymbol{\mathcal{M}} = \boldsymbol{0}$. Moreover, use was made of

$$
\begin{aligned}
\text{(i)}\quad & \operatorname{div}\,(\boldsymbol{x}\times\rho^\alpha\boldsymbol{v}^\alpha\otimes\boldsymbol{v}^\alpha) = \big(\epsilon_{ijk}x_j\rho^\alpha(v_k^\alpha v_l^\alpha)\big)_{,l} \\
& = \underbrace{\epsilon_{ijk}\rho^\alpha v_k^\alpha v_l^\alpha}_{=0} + \underbrace{\epsilon_{ijk}x_j\rho^\alpha v_{k,l}^\alpha v_l^\alpha + \epsilon_{ijk}x_j v_k^\alpha(\rho^\alpha v_l^\alpha)_{,l}}_{\epsilon_{ijk}x_j(v_k^\alpha\rho^\alpha v_l^\alpha)_{,l}} \\
& \mathrel{\hat{=}} \boldsymbol{x}\times\operatorname{div}\,(\rho^\alpha\boldsymbol{v}^\alpha\otimes\boldsymbol{v}^\alpha)\,, \\
\text{(ii)}\quad & \operatorname{div}\,(\boldsymbol{x}\times\boldsymbol{t}^\alpha)\mathrel{\hat{=}}\big(\epsilon_{ijk}x_j t_{kl}^\alpha\big)_{,l} = \epsilon_{ijk}\delta_{jl}t_{kl}^\alpha + \epsilon_{ijk}x_j t_{kl,l}^\alpha \\
& \mathrel{\hat{=}} \boldsymbol{x}\times\operatorname{div}\boldsymbol{t}^\alpha + \epsilon_{ijk}t_{kj}^\alpha \mathrel{\hat{=}} \boldsymbol{x}\times\operatorname{div}\boldsymbol{t}^\alpha - \operatorname{dual}\big(\boldsymbol{t}^\alpha - (\boldsymbol{t}^\alpha)^T\big)\,,
\end{aligned}
$$

in which dual $(\boldsymbol{W})$ is the dual vector of the skew-symmetric tensor $\boldsymbol{W}$. It follows from the above Eq. (21.19) that the local form of the angular momentum balance reduces to the spin balance

$$
\begin{aligned}
& \frac{\partial(\rho^\alpha\boldsymbol{s}^\alpha)}{\partial t} + \operatorname{div}\,(\rho^\alpha\boldsymbol{s}^\alpha\otimes\boldsymbol{v}^\alpha) \\
& = \operatorname{div}\,(\boldsymbol{m}^\alpha) - \rho^\alpha\boldsymbol{\ell}^\alpha - \boldsymbol{\mathfrak{k}}^\alpha + \operatorname{dual}\big(\boldsymbol{t}^\alpha - (\boldsymbol{t}^\alpha)^T\big)\,.
\end{aligned}
\tag{21.20}
$$

In this form, this balance occurs in mathematical conservative form. By applying product differentiation of the terms on the left-hand side, it can easily be reduced to the nonconservative form $(21.15)_1$.

- In a similar way, the energy equation can be handled, but the related computations are relatively complicated. However, if the nonconservative internal energy balance (21.16) is accepted, a conservative form of the internal energy balance can be deduced by combining the left-hand side of (21.16) with the mass balance as follows:

$$
\begin{aligned}
& \rho^\alpha\left(\frac{\partial\varepsilon^\alpha}{\partial t} + (\operatorname{grad}\varepsilon^\alpha)\,\boldsymbol{v}^\alpha\right) + \varepsilon^\alpha\underbrace{\left(\frac{\partial\rho^\alpha}{\partial t} + \operatorname{div}\,(\rho^\alpha\boldsymbol{v}^\alpha)\right)}_{\mathfrak{c}^\alpha} \\
& = \frac{\partial\,(\rho^\alpha\varepsilon^\alpha)}{\partial t} + \operatorname{div}\,(\rho^\alpha\varepsilon^\alpha\boldsymbol{v}^\alpha) = \rho^\alpha\frac{\mathrm{d}\varepsilon^\alpha}{\mathrm{d}t} + \varepsilon^\alpha\mathfrak{c}^\alpha.
\end{aligned}
\tag{21.21}
$$

Thus, replacing $\rho^\alpha\mathrm{d}\varepsilon^\alpha/\mathrm{d}t$ in (21.16) by the relation from (21.21) yields a conservative law for ε^α.

Remarks:

- The balance law of momentum is a vector equation. So $\boldsymbol{t}^\alpha$ is a second-order tensor, called Cauchy stress tensor of constituent α, but it is not necessarily symmetric. The vectors are *polar* vectors.
- The balance law of angular momentum orspin balance is also a vector equation in this form, but $\boldsymbol{s}^\alpha$, $\boldsymbol{\ell}^\alpha$, $\boldsymbol{\mathfrak{k}}^\alpha$ are *axial* vectors as is dual $\big(\boldsymbol{t}^\alpha - (\boldsymbol{t}^\alpha)^T\big)$. Dual vectors $\boldsymbol{w}$ are isomorphic to skew-symmetric tensors $\boldsymbol{W}$ as follows:

$$
w_i := \tfrac{1}{2}\epsilon_{ijk}W_{jk} \quad\longrightarrow\quad W_{ij} = \varepsilon_{ijk}w_k.
$$

So, angular momentum is often in the literature expressed as skew-symmetric tensor equations, e.g.,

$$\underbrace{\epsilon_{ijk} x_j \rho v_k}_{\text{axial vector}} \quad \longleftrightarrow \quad \underbrace{x_j \rho v_k - x_k \rho v_j}_{\text{skew sym. tensor}} .$$

- The above balance laws (21.14)–(21.17) or (21.8), (21.18), (21.20) with the substitution of (21.21) are not as convenient from a numerical point of view as (21.8)–(21.12) are not in *conservative form*. But they suggest new production quantities. These quantities are *non-convective* so-called intrinsic production densities of momentum, angular momentum and energy as follows:

$$\begin{aligned}
\mathfrak{m}^{\alpha}_{\text{Euclid}} &:= \mathfrak{m}^{\alpha} - \mathfrak{c}^{\alpha} \boldsymbol{v}^{\alpha}, \\
\mathfrak{k}^{\alpha}_{\text{Euclid}} &:= \mathfrak{k}^{\alpha} - \mathfrak{c}^{\alpha} \boldsymbol{s}^{\alpha}, \\
\mathfrak{e}^{\alpha}_{\text{Euclid}} &:= \mathfrak{e}^{\alpha} - \mathfrak{c}^{\alpha} \left(\varepsilon^{\alpha} + \tfrac{1}{2} \boldsymbol{v}^{\alpha} \cdot \boldsymbol{v}^{\alpha} + \tfrac{1}{2} \boldsymbol{s}^{\alpha} \cdot \boldsymbol{\omega}^{\alpha} \right) \\
&\qquad - (\mathfrak{m}^{\alpha} - \mathfrak{c}^{\alpha} \boldsymbol{v}^{\alpha}) \cdot \boldsymbol{v}^{\alpha} - (\mathfrak{k}^{\alpha} - \mathfrak{c}^{\alpha} \boldsymbol{s}^{\alpha}) \cdot \boldsymbol{\omega}^{\alpha}.
\end{aligned} \tag{21.22}$$

These are so defined that the combination of all production terms in (21.14)–(21.16) reduce to $\mathfrak{m}^{\alpha}_{\text{Euclid}}$ (momentum), $\mathfrak{k}^{\alpha}_{\text{Euclid}}$ (spin) and $\rho^{\alpha} \mathfrak{e}^{\alpha}_{\text{Euclid}}$ (energy). However, the choices (21.22) can also be physically motivated. Accordingly, the specific momentum production $\mathfrak{m}^{\alpha}$ is given by the intrinsic (i.e., non-convective) production $\mathfrak{m}^{\alpha}_{\text{Euclid}}$ plus the convective momentum of the specific mass production, $\mathfrak{c}^{\alpha} \boldsymbol{v}^{\alpha}$. Likewise, the spin production $\mathfrak{k}^{\alpha}$ is given as the sum of the intrinsic (non-convective) spin production $\mathfrak{k}^{\alpha}_{\text{Euclid}}$ plus the spin of the mass production. Both are quite natural definitions, and the same holds true for the energy production $\mathfrak{e}^{\alpha}$. This is additively composed of the intrinsic contribution, $\mathfrak{e}^{\alpha}_{\text{Euclid}}$, the production of internal energy due to the mass production, $\mathfrak{c}^{\alpha} \varepsilon^{\alpha}$, the kinetic energies of translation and rotation due to the mass production, $\frac{1}{2} \mathfrak{c}^{\alpha} \boldsymbol{v}^{\alpha} \cdot \boldsymbol{v}^{\alpha}$ and $\frac{1}{2} \mathfrak{c}^{\alpha} \boldsymbol{s}^{\alpha} \cdot \boldsymbol{\omega}^{\alpha}$, respectively, plus the powers of working of the intrinsic productions of momentum and spin, $(\mathfrak{m}^{\alpha}_{\text{Euclid}} \cdot \boldsymbol{v}^{\alpha})$ and $(\mathfrak{k}^{\alpha}_{\text{Euclid}} \cdot \boldsymbol{\omega}^{\alpha})$, respectively.
In addition, one can show that $\mathfrak{m}^{\alpha}_{\text{Euclid}}$, $\mathfrak{k}^{\alpha}_{\text{Euclid}}$ and $\mathfrak{e}^{\alpha}_{\text{Euclid}}$ are objective quantities under EUCLIDian transformations but $\mathfrak{m}^{\alpha}$, $\mathfrak{k}^{\alpha}$ and $\mathfrak{e}^{\alpha}$ are not. They transform, respectively, as a polar and axial vector and as a scalar, respectively. These remarks are important as constitutive equations must be formulated for these EUCLIDian objective quantities. For proofs of these facts, see [17].
- The above balance laws hold for polar continua with nontrivial spin balances. Such continua have independent degrees of freedom for translation and rotation; $\boldsymbol{v}^{\alpha}$, $\boldsymbol{\omega}^{\alpha}$ are kinematically independent fields. The independent rotations give rise to nontrivial fields $\boldsymbol{s}^{\alpha}$, $\boldsymbol{m}^{\alpha}$, $\boldsymbol{\ell}^{\alpha}$. If these vanish,

$$\boldsymbol{s}^{\alpha} = \boldsymbol{0}, \quad \boldsymbol{m}^{\alpha} = \boldsymbol{0}, \quad \boldsymbol{\ell}^{\alpha} = \boldsymbol{0}, \tag{21.23}$$

the CAUCHY stress must satisfy the relation

$$\operatorname{dual}\left(\boldsymbol{t}^{\alpha}-(\boldsymbol{t}^{\alpha})^{T}\right)=\boldsymbol{\mathfrak{k}}^{\alpha}_{\text{Euclid}}. \tag{21.24}$$

A continuum, for which (21.23) holds, is a classical continuum, also called a *non-polar* continuum. In such a continuum, the Cauchy stress $\boldsymbol{t}^{\alpha}$ of constituent α is only symmetric if the spin production rate density vanishes.

Remark: In a granular material with particle collisions $\boldsymbol{\mathfrak{k}}$ is not zero, since rotations of the particles change under collisions. So, such materials are actually polar continua. This may also hold for snow in flow and powder snow avalanches.

This result sheds some light on BOLTZMANN's statement that the symmetry of the CAUCHY stress tensor in a non-mixture body constitutes an axiom. Indeed, in such a solid continuum, the symmetry of the CAUCHY stress tensor requires that $\boldsymbol{\mathfrak{k}}^{\alpha}_{\text{Euclid}}=\mathbf{0}$, which cannot strictly be proved in a dynamic situation, but must be assumed.

- For a one-constituent medium, the polar continuum has been proposed by the COSSERAT brothers (1909) [6] in Paris. In that case, the index α is dropped in Eqs. (21.8)–(21.12) or (21.14)–(21.17) and production terms vanish. This then yields

$$\mathfrak{c}=0,\quad \boldsymbol{\mathfrak{m}}=\mathbf{0},\quad \boldsymbol{\mathfrak{k}}=\mathbf{0},\quad \mathfrak{e}=0, \tag{21.25}$$

$$\begin{aligned}
&\bullet\ \frac{\partial\rho}{\partial t}+\operatorname{div}(\rho\boldsymbol{v})=0,\\
&\bullet\ \frac{\partial}{\partial t}(\rho\boldsymbol{v})+\operatorname{div}\,(\rho\boldsymbol{v}\otimes\boldsymbol{v}-\boldsymbol{t})=\rho\boldsymbol{f},\\
&\bullet\ \frac{\partial}{\partial t}\,(\rho\boldsymbol{s}+\boldsymbol{x}\times\rho\boldsymbol{v})+\operatorname{div}\,((\rho\boldsymbol{s}+\boldsymbol{x}\times\rho\boldsymbol{v})\otimes\boldsymbol{v}-\boldsymbol{x}\times\boldsymbol{t}-\boldsymbol{m})\\
&\quad=\rho\boldsymbol{\ell}+\boldsymbol{x}\times\rho\boldsymbol{f}, \qquad\qquad (21.26)\\
&\bullet\ \frac{\partial}{\partial t}\left(\tfrac{1}{2}\rho\boldsymbol{v}\cdot\boldsymbol{v}+\tfrac{1}{2}\rho\boldsymbol{s}\cdot\boldsymbol{\omega}+\rho\varepsilon\right)\\
&\quad+\operatorname{div}\,\left(\left(\tfrac{1}{2}\rho\boldsymbol{v}\cdot\boldsymbol{v}+\tfrac{1}{2}\rho\boldsymbol{s}\cdot\boldsymbol{\omega}+\rho\varepsilon\right)\boldsymbol{v}-\boldsymbol{v}\boldsymbol{t}-\boldsymbol{\omega}\boldsymbol{m}+\boldsymbol{q}\right)\\
&\quad=\boldsymbol{v}\cdot\rho\boldsymbol{f}+\boldsymbol{\omega}\cdot\rho\boldsymbol{\ell}+\rho\mathfrak{r},\\
&\bullet\ \frac{\partial}{\partial t}(\rho s)+\operatorname{div}\,\left(\rho s\boldsymbol{v}+\boldsymbol{\phi}^{s}\right)=\rho\eta^{s}+\rho\pi^{s},
\end{aligned}$$

or

$$\begin{aligned}
&\bullet\ \frac{\partial \rho}{\partial t} + \operatorname{div}(\rho \boldsymbol{v}) = 0,\\
&\bullet\ \frac{\partial}{\partial t}(\rho \boldsymbol{v}) + \operatorname{div}\,(\rho \boldsymbol{v} \otimes \boldsymbol{v} - \boldsymbol{t}) = \rho \boldsymbol{f},\\
&\bullet\ \frac{\partial}{\partial t}(\rho \boldsymbol{s}) + \operatorname{div}\,(\rho \boldsymbol{s} \otimes \boldsymbol{v} - \boldsymbol{m}) = \rho \boldsymbol{\ell} + \operatorname{dual}\left(\boldsymbol{t} - \boldsymbol{t}^T\right),\\
&\bullet\ \frac{\partial}{\partial t}(\rho \varepsilon) + \operatorname{div}\,(\rho \varepsilon \boldsymbol{v}) = -\operatorname{div} \boldsymbol{q} + \boldsymbol{\omega} \cdot \left(\operatorname{dual}(\boldsymbol{t} - \boldsymbol{t}^T)\right)\\
&\quad + (\operatorname{grad} \boldsymbol{v} \cdot \boldsymbol{t}^T) + (\operatorname{grad} \boldsymbol{\omega} \cdot \boldsymbol{m}^T) + \tfrac{1}{2}\rho \left(\boldsymbol{\omega} \cdot \frac{\mathrm{d}\boldsymbol{s}}{\mathrm{d}t} - \boldsymbol{s} \cdot \frac{\mathrm{d}\boldsymbol{\omega}}{\mathrm{d}t}\right) + \rho \mathfrak{r},\\
&\bullet\ \frac{\partial}{\partial t}(\rho s) + \operatorname{div}\,\left(\rho s \boldsymbol{v} + \boldsymbol{\phi}^s\right) = \rho \eta^s + \rho \pi^s,
\end{aligned} \tag{21.27}$$

or

$$\begin{aligned}
&\bullet\ \frac{\mathrm{d}\rho}{\mathrm{d}t} + \rho \operatorname{div} \boldsymbol{v} = 0,\\
&\bullet\ \rho \frac{\mathrm{d}\boldsymbol{v}}{\mathrm{d}t} = \operatorname{div} \boldsymbol{t} + \rho \boldsymbol{f},\\
&\bullet\ \rho \frac{\mathrm{d}\boldsymbol{s}}{\mathrm{d}t} = \operatorname{div} \boldsymbol{m} + \rho \boldsymbol{\ell} + \operatorname{dual}\left(\boldsymbol{t} - \boldsymbol{t}^T\right),\\
&\bullet\ \rho \frac{\mathrm{d}\varepsilon}{\mathrm{d}t} = -\operatorname{div} \boldsymbol{q} + \boldsymbol{\omega} \cdot \left(\operatorname{dual}(\boldsymbol{t} - \boldsymbol{t}^T)\right)\\
&\quad + (\operatorname{grad} \boldsymbol{v} \cdot \boldsymbol{t}^T) + (\operatorname{grad} \boldsymbol{\omega} \cdot \boldsymbol{m}^T) + \tfrac{1}{2}\rho \left(\boldsymbol{\omega} \cdot \frac{\mathrm{d}\boldsymbol{s}}{\mathrm{d}t} - \boldsymbol{s} \cdot \frac{\mathrm{d}\boldsymbol{\omega}}{\mathrm{d}t}\right) + \rho \mathfrak{r},\\
&\bullet\ \rho \frac{\mathrm{d}s}{\mathrm{d}t} = -\operatorname{div} \boldsymbol{\phi}^s + \rho \eta^s + \rho \pi^s.
\end{aligned} \tag{21.28}$$

The jump conditions are not changed.

A component of a mixture or a continuum for which relations (21.23) are fulfilled is called a *nonpolar* or *a-polar* continuum. One concludes from (21.24) that in nonpolar mixtures the partial CAUCHY stress $\boldsymbol{t}^\alpha$ is only symmetric if the corresponding intrinsic spin production vanishes.

The local equation (21.15) for the spin is a balance equation that allows the following interpretations:

- Flux of spin $\equiv -\boldsymbol{m}^\alpha$ (negative couple stresses),
- Supply of spin $\equiv \rho^\alpha \boldsymbol{\ell}^\alpha$ (externally applied body couple),
- Production of spin $\equiv -\operatorname{dual}(\boldsymbol{t}^\alpha - (\boldsymbol{t}^\alpha)^T) + \boldsymbol{\mathfrak{t}}^\alpha_{\text{Euclid}}$.

Likewise, the equation for the internal energy of constituent α has the form of a balance law with the interpretations

- Flux of internal energy $\equiv \boldsymbol{q}^\alpha$ (heat flux),
- Supply of internal energy $\equiv \rho^\alpha \mathfrak{r}^\alpha$ (radiation),
- Production of internal energy

$$\equiv \left(\operatorname{grad} \boldsymbol{v}^\alpha \cdot (\boldsymbol{t}^\alpha)^T\right) + \boldsymbol{\omega}^\alpha \cdot \left(\operatorname{dual}(\boldsymbol{t}^\alpha - (\boldsymbol{t}^\alpha)^T)\right) + \left(\operatorname{grad} \boldsymbol{\omega}^\alpha \cdot (\boldsymbol{m}^\alpha)^T\right)$$
$$+\mathfrak{e}^\alpha_{\text{Euclid}} + \tfrac{1}{2}\rho^\alpha \left(\boldsymbol{\omega}^\alpha \cdot \frac{\mathrm{d}^\alpha \boldsymbol{s}^\alpha}{\mathrm{d}t} - \boldsymbol{s}^\alpha \cdot \frac{\mathrm{d}^\alpha \boldsymbol{\omega}^\alpha}{\mathrm{d}t}\right). \tag{21.29}$$

Apart from the well-known term for the power of working of nonpolar continua $(\operatorname{grad} \boldsymbol{v}^\alpha \cdot (\boldsymbol{t}^\alpha)^T)$, this formula contains an analogous term of the spin motion, namely $\boldsymbol{\omega}^\alpha \cdot (\operatorname{dual}(\boldsymbol{t}^\alpha - (\boldsymbol{t}^\alpha)^T)) + (\operatorname{grad} \boldsymbol{\omega}^\alpha \cdot (\boldsymbol{m}^\alpha)^T)$ plus a further term, new by its structure and given by

$$\mathfrak{S}^\alpha = \tfrac{1}{2}\rho^\alpha \left(\boldsymbol{\omega}^\alpha \cdot \frac{\mathrm{d}^\alpha \boldsymbol{s}^\alpha}{\mathrm{d}t} - \boldsymbol{s}^\alpha \cdot \frac{\mathrm{d}^\alpha \boldsymbol{\omega}^\alpha}{\mathrm{d}t}\right). \tag{21.30}$$

It may be called the *micro-morphic spin production of constituent* α. To fathom the significance of this term, let us be guided by rigid body dynamics of a solid body; its moment of momentum relative to its center of mass c is given by

$$\boldsymbol{D}_c = \hat{\boldsymbol{\Theta}}_c \boldsymbol{\omega}, \qquad \hat{\boldsymbol{\Theta}}_c = \hat{\boldsymbol{\Theta}}_c^T, \tag{21.31}$$

in which $\hat{\boldsymbol{\Theta}}_c$ denotes the *tensor of moment of inertia*, a symmetric second rank tensor. Being inspired by this, we now postulate the spin of constituent α to be given by

$$\boldsymbol{s}^\alpha = \boldsymbol{\Theta}^\alpha \boldsymbol{\omega}^\alpha, \qquad \boldsymbol{\Theta}^\alpha = (\boldsymbol{\Theta}^\alpha)^T, \tag{21.32}$$

where $\boldsymbol{\Theta}^\alpha$ is a symmetric second rank tensor, called the *tensor of specific inertia* of constituent α. It is a measure for the distribution of mass of constituent α in a region of influence of a particle at position $\boldsymbol{x}$. In general, this distribution changes with time for any material particle, so that $\mathrm{d}^\alpha \boldsymbol{\Theta}^\alpha / \mathrm{d}t \neq 0$. If the rotations are small for a particular deformation of the body, then the time rate of change of the distribution of mass of constituent α about the particle at position $\boldsymbol{x}$ may be ignored. One, therefore, distinguishes materials as follows:

- A constituent α is called *micro-polar* (hyphened here for emphasis) if the specific tensor of inertia is materially constant for that constituent,

$$\frac{\mathrm{d}^\alpha \boldsymbol{\Theta}^\alpha}{\mathrm{d}t} = \boldsymbol{0} \qquad \Longleftrightarrow \qquad \text{micro-polar.}$$

- A constituent α is called *micro-morphic* (hyphened here for emphasis) if the tensor of inertia may vary with time,

$$\frac{\mathrm{d}^\alpha \boldsymbol{\Theta}^\alpha}{\mathrm{d}t} \neq \boldsymbol{0} \qquad \Longleftrightarrow \qquad \text{micro-morphic.}$$

With these definitions and the representation (21.32) for the spin density, it follows that $\mathfrak{S}^\alpha$ vanishes for micro-polar continua, but may be different from zero for micro-morphic continua.

21.3 Balance Laws for the Mixture as a Whole

If the balance laws of mass, linear, and angular momenta and energy are summed over all constituents, one obtains the corresponding balance laws for the mixture as a whole. If one views the body as an entity it seems plausible to assume that an observer, who looks at the body as a whole and is not aware that it may be composed of a number of constituents, will recognize this body as a one-component material and impose the postulates of a one-component continuum. This suggests that *the balance laws of mass, momentum, angular momentum and energy for the mixture as a whole must be conservation laws*. If so, the sum of the production terms over all constituents of mass, momentum, angular momentum and energy must vanish, implying that

$$\sum_{\alpha=1}^{N} \mathfrak{c}^{\alpha} = 0, \quad \sum_{\alpha=1}^{N} \boldsymbol{\mathfrak{m}}^{\alpha} = \mathbf{0}, \quad \sum_{\alpha=1}^{N} \boldsymbol{\mathfrak{k}}^{\alpha} = \mathbf{0}, \quad \sum_{\alpha=1}^{N} \mathfrak{e}^{\alpha} = 0. \tag{21.33}$$

Notice that these statements are required for the production terms of the original balance laws and not their EUCLIDian invariant partners defined in (21.22).

If we request that the balance laws of the mixture as a whole are obtained as the sum of the partial balances, it is only natural if we also request that *these balance laws coincide with the balance laws of a one-constituent continuum*. In order to draw the inferences to this principle, which goes back to TRUESDELL and TOUPIN [21], it is necessary that variables for the mixture as a whole are related to the variables of the constituents. Summing (21.6) over all constituents yields

$$\sum_{\alpha=1}^{N} \frac{\partial \gamma^{\alpha}}{\partial t} + \sum_{\alpha=1}^{N} \operatorname{div}\left(\gamma^{\alpha} \boldsymbol{v}^{\alpha}\right) = -\sum_{\alpha=1}^{N} \operatorname{div} \boldsymbol{\phi}^{\alpha} + \sum_{\alpha=1}^{N} (\pi^{\alpha} + \varsigma^{\alpha}). \tag{21.34}$$

The second term on the left-hand side in this equation contains products of constituent quantities, $\gamma^{\alpha}\boldsymbol{v}^{\alpha}$. This is inconvenient; if we therefore introduce a mixture velocity $\boldsymbol{v}$—at the present state of the knowledge it is not clear how to specify it—by simply writing $\boldsymbol{v}^{\alpha} = \boldsymbol{v}^{\alpha} - \boldsymbol{v} + \boldsymbol{v}$, then we may write

$$\sum_{\alpha=1}^{N} \gamma^{\alpha} \boldsymbol{v}^{\alpha} = \sum_{\alpha=1}^{N} \gamma^{\alpha} \Big(\boldsymbol{v} + \underbrace{(\boldsymbol{v}^{\alpha} - \boldsymbol{v})}_{\boldsymbol{u}^{\alpha}} \Big) = \sum_{\alpha=1}^{N} \gamma^{\alpha} \boldsymbol{u}^{\alpha} + \left(\sum_{\alpha=1}^{N} \gamma^{\alpha} \right) \boldsymbol{v}. \tag{21.35}$$

The quantity $\boldsymbol{u}^{\alpha}$ is called *diffusion velocity* of constituent α relative to the mixture velocity. Introducing, moreover, the definitions

$$\gamma = \sum_{\alpha=1}^{N} \gamma^{\alpha}, \quad \pi = \sum_{\alpha=1}^{N} \pi^{\alpha}, \quad \varsigma = \sum_{\alpha=1}^{N} \varsigma^{\alpha}, \quad \boldsymbol{\phi} = \sum_{\alpha=1}^{N} \left(\boldsymbol{\phi}^{\alpha} + \gamma^{\alpha} \boldsymbol{u}^{\alpha} \right) \tag{21.36}$$

and, thus, defining the physical quantity γ of the mixture, its production π, supply ς and flux $\boldsymbol{\phi}$, respectively, one obtains from (21.34) the new balance law

$$\frac{\partial \gamma}{\partial t} + \operatorname{div}(\gamma \boldsymbol{v}) = -\operatorname{div} \boldsymbol{\phi} + \pi + \varsigma. \tag{21.37}$$

To guarantee that the balance law for the mixture takes the form of a balance law for a single constituent body, two things have necessarily to be satisfied. First, the physical quantity γ characterizing the mixture as a whole, its production π and its supply ς are given as the sum of the respective constituent quantities. Second, the flux $\boldsymbol{\phi}$ for the mixture is given as the sum of the constituent fluxes $\boldsymbol{\phi}^\alpha$ plus the diffusive fluxes $\gamma^\alpha \boldsymbol{u}^\alpha$.

Above, the mixture velocity $\boldsymbol{v}$ and the diffusion velocity of constituent α, $\boldsymbol{u}^\alpha = \boldsymbol{v}^\alpha - \boldsymbol{v}$ were introduced, but not defined. Their exact definition follows from the *balance law of mass*. With $\gamma^\alpha = \rho^\alpha$, $\gamma = \rho$, $\pi = 0$, $\varsigma = 0$ and $\boldsymbol{\phi}^\alpha_{\text{Mass}} = \boldsymbol{0}$ for all α, the mass flux of the mixture (21.36)$_4$ is given by

$$\boldsymbol{\phi}_{\text{Mass}} = \sum_{\alpha=1}^{N} \rho^\alpha \boldsymbol{u}^\alpha,$$

which ought to vanish, if the balance law of mass for the mixture as a whole should be formally the same as the balance law of mass for a single constituent material. One, therefore, must request

$$\sum_{\alpha=1}^{N} \rho^\alpha \boldsymbol{u}^\alpha = \boldsymbol{0} \qquad \Longleftrightarrow \qquad \rho \boldsymbol{v} = \sum_{\alpha=1}^{N} \rho^\alpha \boldsymbol{v}^\alpha. \tag{21.38}$$

This condition defines the mixture velocity, and only with this choice the mass balance for the mixture takes the form

$$\frac{\partial \rho}{\partial t} + \operatorname{div}(\rho \boldsymbol{v}) = 0. \tag{21.39}$$

The mixture velocity defined by (21.38) is called the *barycentric velocity* because it represents the averaged velocity, using the constituent densities as weights. Occasionally, it is also written as

$$\boldsymbol{v} = \sum_{\alpha=1}^{N} \xi^\alpha \boldsymbol{v}^\alpha, \qquad \xi^\alpha = \frac{\rho^\alpha}{\rho}, \tag{21.40}$$

where ξ^α is the mass concentration of constituent α.

For the *momentum balance*, one defines

$$\begin{aligned}
&\boldsymbol{\gamma} = \rho \boldsymbol{v} = \sum_{\alpha=1}^{N} \rho^\alpha \boldsymbol{v}^\alpha, \quad \boldsymbol{\varsigma} = \rho \boldsymbol{f} = \sum_{\alpha=1}^{N} \rho^\alpha \boldsymbol{f}^\alpha, \quad \boldsymbol{\pi} = \boldsymbol{0}, \\
&\boldsymbol{\phi} = -\boldsymbol{t} = -\sum_{\alpha=1}^{N} (\boldsymbol{t}^\alpha - \rho^\alpha \boldsymbol{v}^\alpha \otimes \boldsymbol{u}^\alpha) = -\sum_{\alpha=1}^{N} (\boldsymbol{t}^\alpha - \rho^\alpha \boldsymbol{u}^\alpha \otimes \boldsymbol{u}^\alpha)\,,
\end{aligned} \tag{21.41}$$

where $\sum_{\alpha=1}^{N} \rho^\alpha \boldsymbol{v} \otimes \boldsymbol{u}^\alpha = \boldsymbol{v} \otimes \underbrace{\left(\sum_{\alpha=1}^{N} \rho^\alpha \boldsymbol{u}^\alpha \right)}_{0} = 0$ has dropped out.

While the specific momentum and the specific body force of the mixture are given as the sums of the specific partial momenta and specific body forces of the constituents, the stress tensor for the mixture is composed of two contributions, the sum of the partial stress tensors over all constituents $\sum \boldsymbol{t}^\alpha$ minus the diffusive fluxes of the partial momenta $\sum (\rho^\alpha \boldsymbol{u}^\alpha) \otimes \boldsymbol{u}^\alpha$. With these identifications, the balance of momentum for the mixture as a whole takes the classical form

$$\frac{\partial(\rho \boldsymbol{v})}{\partial t} + \operatorname{div}(\rho \boldsymbol{v} \otimes \boldsymbol{v}) = \operatorname{div} \boldsymbol{t} + \rho \boldsymbol{f}. \tag{21.42}$$

Often, in mixture theory contexts, the mixture stress is given as the sum of the partial stresses without accounting for the diffusive contribution as stated in (21.41)$_4$. It is straightforward to show that this is only justified, if the convective contributions to the acceleration are negligible, viz.,

$$\frac{\mathrm{d}\boldsymbol{v}^\alpha}{\mathrm{d}t} \approx \frac{\partial \boldsymbol{v}^\alpha}{\partial t} \quad \forall \alpha \qquad \Longleftrightarrow \qquad \boldsymbol{t} \approx \sum_{\alpha=1}^{N} \boldsymbol{t}^\alpha. \tag{21.43}$$

Next, let us consider the *balance law of angular momentum*, and define

$$\begin{aligned}
&\boldsymbol{\gamma} = \sum_{\alpha=1}^{N} (\rho^\alpha \boldsymbol{s}^\alpha + \boldsymbol{x} \times \rho^\alpha \boldsymbol{v}^\alpha) = \underbrace{\sum_{\alpha=1}^{N} \rho^\alpha \boldsymbol{s}^\alpha}_{\rho \boldsymbol{s}} + \boldsymbol{x} \times \sum_{\alpha=1}^{N} \rho^\alpha \boldsymbol{v}^\alpha = \rho \boldsymbol{s} + \boldsymbol{x} \times \rho \boldsymbol{v}, \\
&\boldsymbol{\varsigma} = \sum_{\alpha=1}^{N} (\rho^\alpha \boldsymbol{\ell}^\alpha + \boldsymbol{x} \times \rho^\alpha \boldsymbol{f}^\alpha) = \underbrace{\sum_{\alpha=1}^{N} \rho^\alpha \boldsymbol{\ell}^\alpha}_{\rho \boldsymbol{\ell}} + \boldsymbol{x} \times \sum_{\alpha=1}^{N} \rho^\alpha \boldsymbol{f}^\alpha = \rho \boldsymbol{\ell} + \boldsymbol{x} \times \rho \boldsymbol{f}, \\
&\boldsymbol{\pi} = \boldsymbol{0}, \\
&\boldsymbol{\phi} = \sum_{\alpha=1}^{N} (-\boldsymbol{m}^\alpha - \boldsymbol{x} \times \boldsymbol{t}^\alpha + (\rho^\alpha \boldsymbol{s}^\alpha + \boldsymbol{x} \times \rho^\alpha \boldsymbol{v}^\alpha) \otimes \boldsymbol{u}^\alpha)
\end{aligned} \tag{21.44}$$

$$
\begin{aligned}
&= -\underbrace{\sum_{\alpha=1}^{N}(\boldsymbol{m}^\alpha - \rho^\alpha \boldsymbol{s}^\alpha \otimes \boldsymbol{u}^\alpha)}_{\boldsymbol{m}} - \boldsymbol{x} \times \underbrace{\sum_{\alpha=1}^{N}(\boldsymbol{t}^\alpha - \rho^\alpha \boldsymbol{u}^\alpha \otimes \boldsymbol{u}^\alpha)}_{\boldsymbol{t}} \\
&= -\boldsymbol{m} - \boldsymbol{x} \times \boldsymbol{t}.
\end{aligned}
$$

in which $\boldsymbol{x} \times \sum_{\alpha=1}^{N} \rho^\alpha \boldsymbol{v} \otimes \boldsymbol{u}^\alpha = \boldsymbol{x} \times \boldsymbol{v} \otimes \underbrace{\sum_{\alpha=1}^{N} \rho^\alpha \boldsymbol{u}^\alpha}_{0} = 0$ has again dropped out. Accordingly, the specific density of the angular momentum of the mixture is composed of the sum of the spin densities of the constituents and the moment of the linear momentum of the mixture; the supply of angular momentum is the sum of the specific body couples of the constituents and the moment of the body forces, and the flux of angular momentum of the mixture is given as the negative sum of the couple stresses of the constituents minus the sum of the diffusive spins of the constituents, minus the moment of the stress of the mixture. As was the case for the stress tensor of the mixture, the couple stress for the mixture is composed of the couple stresses of the constituents minus the diffusive fluxes of the specific spins of the constituents. With (21.44), therefore, the balance law of angular momentum for the mixture as a whole takes the form

$$
\begin{aligned}
&\frac{\partial}{\partial t}(\rho \boldsymbol{s} + \boldsymbol{x} \times \rho \boldsymbol{v}) + \operatorname{div}\,((\rho \boldsymbol{s} + \boldsymbol{x} \times \rho \boldsymbol{v}) \otimes \boldsymbol{v}) \\
&\qquad = \operatorname{div}\,(\boldsymbol{m} + \boldsymbol{x} \times \boldsymbol{t}) + \rho \boldsymbol{\ell} + \boldsymbol{x} \times \rho \boldsymbol{f}.
\end{aligned}
\tag{21.45}
$$

Straightforward calculation shows that this equation may alternatively also be written as

$$
\frac{\partial}{\partial t}(\rho \boldsymbol{s}) + \operatorname{div}\,(\rho \boldsymbol{s} \otimes \boldsymbol{v}) = \operatorname{div} \boldsymbol{m} + \operatorname{dual}(\boldsymbol{t} - \boldsymbol{t}^T) + \rho \boldsymbol{\ell}, \tag{21.46}
$$

which is the local spin balance. From this equation, it is directly evident that for $\boldsymbol{s} = \boldsymbol{0}$, $\boldsymbol{m} = \boldsymbol{0}$ and $\boldsymbol{l} = \boldsymbol{0}$ the CAUCHY stress tensor must be symmetric.

It is worth mentioning that in the above derivation of the balance of angular momentum for the mixture the kinematic variable associated with the spin does not arise; an angular velocity for the mixture was not defined and did not need to be defined. This can nevertheless be done by connecting the constituent spin density $\boldsymbol{s}^\alpha$ with the constituent angular velocity $\boldsymbol{\omega}^\alpha$, as done in (21.32) via $\boldsymbol{s}^\alpha = \boldsymbol{\Theta}^\alpha \boldsymbol{\omega}^\alpha$, where $\boldsymbol{\Theta}^\alpha$ is the tensor of constituent specific moment of inertia. If one writes now

$$
\boldsymbol{\omega}^\alpha = \boldsymbol{\omega} + \underbrace{(\boldsymbol{\omega}^\alpha - \boldsymbol{\omega})}_{\Delta \boldsymbol{\omega}^\alpha} = \boldsymbol{\omega} + \Delta \boldsymbol{\omega}^\alpha, \tag{21.47}
$$

where $\Delta\boldsymbol{\omega}^\alpha$ may be called *diffusive angular velocity of constituent* α, one obtains

$$\begin{aligned}\rho\boldsymbol{s} &= \sum_{\alpha=1}^{N}\rho^\alpha\boldsymbol{s}^\alpha = \sum_{\alpha=1}^{N}\rho^\alpha\boldsymbol{\Theta}^\alpha(\boldsymbol{\omega}+\Delta\boldsymbol{\omega}^\alpha)\\ &= \underbrace{\Big(\sum_{\alpha=1}^{N}\rho^\alpha\boldsymbol{\Theta}^\alpha\Big)}_{\rho\boldsymbol{\Theta}}\boldsymbol{\omega} + \sum_{\alpha=1}^{N}\underbrace{\rho^\alpha\boldsymbol{\Theta}^\alpha\Delta\boldsymbol{\omega}^\alpha}_{\Delta s^\alpha}.\end{aligned} \tag{21.48}$$

One may now define the *angular velocity of the mixture* by requiring

$$\sum_{\alpha=1}^{N}\Delta s^\alpha := \sum_{\alpha=1}^{N}\rho^\alpha\boldsymbol{\Theta}^\alpha\Delta\boldsymbol{\omega}^\alpha = \boldsymbol{0} \quad\Longleftrightarrow\quad \rho\boldsymbol{\Theta}\boldsymbol{\omega} = \sum_{\alpha=1}^{N}\rho^\alpha\boldsymbol{\Theta}^\alpha\boldsymbol{\omega}^\alpha, \tag{21.49}$$

in which

$$\rho\boldsymbol{\Theta} := \sum_{\alpha=1}^{N}\rho^\alpha\boldsymbol{\Theta}^\alpha \tag{21.50}$$

can be called the *barycentric specific moment of inertia*. With these specifications, the mixture density of spin takes the form

$$\rho\boldsymbol{s} = \rho\boldsymbol{\Theta}\boldsymbol{\omega}. \tag{21.51}$$

Of course, different definitions of the mixture angular velocity are thinkable, however, the above one seems to be particularly natural.

For the derivation of the *balance law of energy* for the mixture, we write

$$\begin{aligned}\gamma &= \sum_{\alpha=1}^{N}\Big(\tfrac{1}{2}\rho^\alpha\boldsymbol{v}^\alpha\cdot\boldsymbol{v}^\alpha + \tfrac{1}{2}\rho^\alpha\boldsymbol{s}^\alpha\cdot\boldsymbol{\omega}^\alpha + \rho^\alpha\varepsilon^\alpha\Big)\\ &= \sum_{\alpha=1}^{N}\tfrac{1}{2}\rho^\alpha\Big(\boldsymbol{v}\cdot\boldsymbol{v} + \boldsymbol{u}^\alpha\cdot\boldsymbol{v} + \boldsymbol{v}\cdot\boldsymbol{u}^\alpha + \boldsymbol{u}^\alpha\cdot\boldsymbol{u}^\alpha\Big)\\ &\quad+\sum_{\alpha=1}^{N}\tfrac{1}{2}\rho^\alpha\boldsymbol{\Theta}^\alpha(\boldsymbol{\omega}+\Delta\boldsymbol{\omega}^\alpha)\cdot(\boldsymbol{\omega}+\Delta\boldsymbol{\omega}^\alpha) + \sum_{\alpha=1}^{N}\rho^\alpha\varepsilon^\alpha\\ &= \tfrac{1}{2}\rho\boldsymbol{v}\cdot\boldsymbol{v} + \tfrac{1}{2}\rho\boldsymbol{s}\cdot\boldsymbol{\omega}\\ &\quad\underbrace{+\sum_{\alpha=1}^{N}\Big(\rho^\alpha\varepsilon^\alpha + \tfrac{1}{2}\rho^\alpha\boldsymbol{u}^\alpha\cdot\boldsymbol{u}^\alpha + \tfrac{1}{2}\rho^\alpha\boldsymbol{\Theta}^\alpha\Delta\boldsymbol{\omega}^\alpha\cdot\Delta\boldsymbol{\omega}^\alpha\Big)}_{\rho\varepsilon},\end{aligned} \tag{21.52}$$

$$\begin{aligned}
\varsigma &= \sum_{\alpha=1}^{N} \Big(\boldsymbol{v}^\alpha \cdot \rho^\alpha \boldsymbol{f}^\alpha + \boldsymbol{\omega}^\alpha \cdot \rho^\alpha \boldsymbol{\ell}^\alpha + \rho^\alpha \mathfrak{r}^\alpha \Big) \\
&= \sum_{\alpha=1}^{N} \Big((\boldsymbol{v} + \boldsymbol{u}^\alpha) \cdot \rho^\alpha \boldsymbol{f}^\alpha + (\boldsymbol{\omega} + \Delta\boldsymbol{\omega}^\alpha) \cdot \rho^\alpha \boldsymbol{\ell}^\alpha + \rho^\alpha \mathfrak{r}^\alpha \Big) \\
&= \boldsymbol{v} \cdot \rho \boldsymbol{f} + \boldsymbol{\omega} \cdot \rho \boldsymbol{\ell} \\
&\quad \underbrace{+ \sum_{\alpha=1}^{N} \Big(\rho^\alpha \mathfrak{r}^\alpha + \boldsymbol{u}^\alpha \cdot \rho^\alpha \boldsymbol{f}^\alpha + \Delta\boldsymbol{\omega}^\alpha \cdot \rho^\alpha \boldsymbol{\ell}^\alpha \Big)}_{\rho \mathfrak{r}} .
\end{aligned} \tag{21.53}$$

Thus, the specific energy of the mixture, $\rho\varepsilon$ is given as the sum of the partial internal plus translational and rotational kinetic energies formed with the diffusion velocities of the constituent motions, $\boldsymbol{u}^\alpha$ and $\Delta\boldsymbol{\omega}^\alpha$, respectively. Likewise, the energy supply of the mixture, $\rho\mathfrak{r}$ is the sum of the partial supplies, $\rho^\alpha \mathfrak{r}^\alpha$ plus the power of working of the volume forces and body couples on the diffuse motion of the constituents.

The mixture energy flux is given by

$$\begin{aligned}
\boldsymbol{\phi} = \sum_{\alpha=1}^{N} \Big[&-(\boldsymbol{v}^\alpha \boldsymbol{t}^\alpha + \boldsymbol{\omega}^\alpha \boldsymbol{m}^\alpha - \boldsymbol{q}^\alpha) \\
&+ (\tfrac{1}{2}\rho^\alpha \boldsymbol{v}^\alpha \cdot \boldsymbol{v}^\alpha + \tfrac{1}{2}\rho^\alpha \boldsymbol{s}^\alpha \cdot \boldsymbol{\omega}^\alpha + \rho^\alpha \varepsilon^\alpha)\boldsymbol{u}^\alpha \Big].
\end{aligned} \tag{21.54}$$

A simple but somewhat long calculation shows that it can be written as

$$\boldsymbol{\phi} = -\boldsymbol{v}\boldsymbol{t} - \boldsymbol{\omega}\boldsymbol{m} + \boldsymbol{q},$$

where

$$\begin{aligned}
\boldsymbol{q} := \sum_{\alpha=1}^{N} \Big[&\boldsymbol{q}^\alpha - \boldsymbol{u}^\alpha \boldsymbol{t}^\alpha - \Delta\boldsymbol{\omega}^\alpha \boldsymbol{m}^\alpha \\
&+ \Big(\rho^\alpha \varepsilon^\alpha + \tfrac{1}{2}\rho^\alpha \boldsymbol{u}^\alpha \cdot \boldsymbol{u}^\alpha + \tfrac{1}{2}\rho^\alpha \boldsymbol{s}^\alpha \cdot (\Delta\boldsymbol{\omega}^\alpha - \boldsymbol{\omega}) \Big) \boldsymbol{u}^\alpha \Big].
\end{aligned} \tag{21.55}$$

As this formula shows, the vector $\boldsymbol{q}$ cannot be interpreted as heat flux alone; energy flux is the better terminology. Evidently, the energy flux vector of the mixture is composed of the constituent heat flux vectors $\boldsymbol{q}^\alpha$, the powers of working of the stresses and couple stresses on the diffuse motion and the convective energy transport on the diffuse motion. Consequently, the balance law of energy for the mixture as a whole takes the form

$$\begin{aligned}&\frac{\partial}{\partial t}\left(\rho\varepsilon+\tfrac{1}{2}\rho\boldsymbol{v}\cdot\boldsymbol{v}+\tfrac{1}{2}\rho\boldsymbol{s}\cdot\boldsymbol{\omega}\right)+\operatorname{div}\left((\rho\varepsilon+\tfrac{1}{2}\rho\boldsymbol{v}\cdot\boldsymbol{v}+\tfrac{1}{2}\rho\boldsymbol{s}\cdot\boldsymbol{\omega})\boldsymbol{v}\right)\\&\quad=\operatorname{div}\left(\boldsymbol{v}\boldsymbol{t}+\boldsymbol{\omega}\boldsymbol{m}-\boldsymbol{q}\right)+\boldsymbol{v}\cdot\rho\boldsymbol{f}+\boldsymbol{\omega}\cdot\rho\boldsymbol{\ell}+\rho\mathfrak{r}\end{aligned}\tag{21.56}$$

and reduces for a nonpolar continuum with $\boldsymbol{s}=\mathbf{0}$, $\boldsymbol{\omega}=\mathbf{0}$, $\boldsymbol{\ell}=\mathbf{0}$ to the classical energy balance

$$\begin{aligned}&\frac{\partial}{\partial t}\left(\rho\left(\varepsilon+\tfrac{1}{2}\boldsymbol{v}\cdot\boldsymbol{v}\right)\right)+\operatorname{div}\left(\rho\left(\varepsilon+\tfrac{1}{2}\boldsymbol{v}\cdot\boldsymbol{v}\right)\boldsymbol{v}\right)\\&=\operatorname{div}\left(\boldsymbol{v}\boldsymbol{t}-\boldsymbol{q}\right)+\boldsymbol{v}\cdot\rho\boldsymbol{f}+\rho\mathfrak{r}.\end{aligned}\tag{21.57}$$

Incidentally, it is interesting to see that the energy flux $\boldsymbol{q}$ contains a term proportional to $\boldsymbol{\omega}$ which cannot be eliminated; indeed, $\boldsymbol{q}$ can be written in the form

$$\begin{aligned}\boldsymbol{q}=\sum_{\alpha=1}^{N}&\left\{\boldsymbol{q}^{\alpha}-\boldsymbol{u}^{\alpha}\boldsymbol{t}^{\alpha}-\Delta\boldsymbol{\omega}^{\alpha}\boldsymbol{m}^{\alpha}+\left(\rho^{\alpha}\varepsilon^{\alpha}+\frac{1}{2}\varepsilon^{\alpha}\boldsymbol{u}^{\alpha}\cdot\boldsymbol{u}^{\alpha}\right.\right.\\&\left.\left.+\frac{1}{2}\Delta\boldsymbol{s}^{\alpha}\cdot\Delta\boldsymbol{\omega}^{\alpha}\right)\boldsymbol{u}^{\alpha}\right\}+\boldsymbol{s}\sum_{\alpha=1}^{N}\frac{1}{2}\rho^{\alpha}\Delta\boldsymbol{\omega}^{\alpha}\otimes\boldsymbol{u}^{\alpha}-\boldsymbol{\omega}\sum_{\alpha=1}^{N}\frac{1}{2}\rho^{\alpha}\Delta\boldsymbol{s}^{\alpha}\otimes\boldsymbol{u}^{\alpha},\end{aligned}\tag{21.58}$$

in which the two terms that involve $\boldsymbol{s}$ and $\boldsymbol{\omega}$ do in general not cancel each other. The translational and rotational components of the motion have therefore a different effect on the mixture energy flux.

Finally, by summing the constituent *entropy balance laws* (21.12), one may deduce the relation

$$\frac{\partial}{\partial t}(\rho s)+\operatorname{div}\left(\rho s\boldsymbol{v}+\boldsymbol{\phi}^{\eta}\right)-\rho\eta^{s}=\rho\pi^{\eta}\geq 0,\tag{21.59}$$

in which

$$\begin{aligned}&\rho s=\sum_{\alpha}\rho^{\alpha}s^{\alpha},\quad\rho\eta^{s}=\sum_{\alpha}\rho^{\alpha}\eta^{s^{\alpha}},\quad\rho\pi^{s}=\sum_{\alpha}\rho\pi^{s^{\alpha}},\\&\boldsymbol{\phi}^{s}=\sum_{\alpha}\left(\boldsymbol{\phi}^{s^{\alpha}}+s^{\alpha}\boldsymbol{u}^{\alpha}\right),\end{aligned}\tag{21.60}$$

as anticipated already in (21.36).

21.4 Summary

The local balance laws of mass, momentum, angular momentum, energy and entropy for the mixture as a whole take the forms

$$
\begin{aligned}
&\frac{\partial \rho}{\partial t} + \operatorname{div}(\rho \boldsymbol{v}) = 0, \\
&\frac{\partial (\rho \boldsymbol{v})}{\partial t} + \operatorname{div}(\rho \boldsymbol{v} \otimes \boldsymbol{v}) = \operatorname{div} \boldsymbol{t} + \rho \boldsymbol{f}, \\
&\frac{\partial}{\partial t}(\rho \boldsymbol{s} + \boldsymbol{x} \times \rho \boldsymbol{v}) + \operatorname{div}\,((\rho \boldsymbol{s} + \boldsymbol{x} \times \rho \boldsymbol{v}) \otimes \boldsymbol{v}) \\
&\qquad = \operatorname{div}\,(\boldsymbol{m} + \boldsymbol{x} \times \boldsymbol{t}) + \rho \boldsymbol{\ell} + \boldsymbol{x} \times \rho \boldsymbol{f}, \\
&\frac{\partial}{\partial t}\big(\rho\varepsilon + \tfrac{1}{2}\rho \boldsymbol{v} \cdot \boldsymbol{v} + \tfrac{1}{2}\rho \boldsymbol{s} \cdot \boldsymbol{\omega}\big) + \operatorname{div}\,\big((\rho\varepsilon + \tfrac{1}{2}\rho \boldsymbol{v} \cdot \boldsymbol{v} + \tfrac{1}{2}\rho \boldsymbol{s} \cdot \boldsymbol{\omega}) \cdot \boldsymbol{v}\big) \\
&\qquad = \operatorname{div}(\boldsymbol{v}\boldsymbol{t} + \boldsymbol{\omega}\boldsymbol{m} - \boldsymbol{q}) + \boldsymbol{v} \cdot \rho \boldsymbol{f} + \boldsymbol{\omega} \cdot \rho \boldsymbol{\ell} + \rho \mathfrak{r}, \\
&\frac{\partial}{\partial t}(\rho s) + \operatorname{div}(\rho s \boldsymbol{v}) = -\operatorname{div} \boldsymbol{\phi}^{s} + \rho \eta^{s} + \rho \pi^{s},
\end{aligned}
\tag{21.61}
$$

in which the field quantities of the mixture (without index α) are related to those of the constituents (with index α) according to

$$
\begin{aligned}
\rho &= \sum_{\alpha=1}^{N} \rho^{\alpha}, & \rho \boldsymbol{v} &= \sum_{\alpha=1}^{N} \rho^{\alpha} \boldsymbol{v}^{\alpha}, \\
\rho \boldsymbol{\Theta} &= \sum_{\alpha=1}^{N} \rho^{\alpha} \boldsymbol{\Theta}^{\alpha}, & \rho \boldsymbol{\Theta} \boldsymbol{\omega} &= \sum_{\alpha=1}^{N} \rho^{\alpha} \boldsymbol{\Theta}^{\alpha} \boldsymbol{\omega}^{\alpha}, \\
\boldsymbol{u}^{\alpha} &= \boldsymbol{v}^{\alpha} - \boldsymbol{v}, & \Delta \boldsymbol{\omega}^{\alpha} &= (\boldsymbol{\omega}^{\alpha} - \boldsymbol{\omega}),
\end{aligned}
\tag{21.62}
$$

$$
\begin{aligned}
\boldsymbol{t} &= \sum_{\alpha=1}^{N} \big(\boldsymbol{t}^{\alpha} - \rho^{\alpha} \boldsymbol{u}^{\alpha} \otimes \boldsymbol{u}^{\alpha}\big), & \rho \boldsymbol{f} &= \sum_{\alpha=1}^{N} \rho^{\alpha} \boldsymbol{f}^{\alpha},
\end{aligned}
\tag{21.63}
$$

$$
\begin{aligned}
\rho \boldsymbol{s} &= \sum_{\alpha=1}^{N} \rho^{\alpha} \boldsymbol{s}^{\alpha}, & \rho \boldsymbol{\ell} &= \sum_{\alpha=1}^{N} \rho^{\alpha} \boldsymbol{\ell}^{\alpha}, \\
\boldsymbol{m} &= \sum_{\alpha=1}^{N} \big(\boldsymbol{m}^{\alpha} - \rho^{\alpha} \boldsymbol{s}^{\alpha} \otimes \boldsymbol{u}^{\alpha}\big),
\end{aligned}
\tag{21.64}
$$

$$
\begin{aligned}
\rho s &= \sum_{\alpha=1}^{N} \rho^{\alpha} s^{\alpha}, \qquad \rho \varsigma = \sum_{\alpha=1}^{N} \rho^{\alpha} \eta^{s^{\alpha}}, \qquad \rho \pi = \sum_{\alpha=1}^{N} \rho^{\alpha} \pi^{s^{\alpha}}, \\
\boldsymbol{\phi}^{s} &= \sum_{\alpha=1}^{N} \left(\phi^{s^{\alpha}} + s^{\alpha} \boldsymbol{u}^{\alpha}\right),
\end{aligned}
\tag{21.65}
$$

$$
\begin{aligned}
\rho\varepsilon &= \sum_{\alpha=1}^{N}\Big(\rho^\alpha\varepsilon^\alpha + \tfrac{1}{2}\rho^\alpha\boldsymbol{u}^\alpha\cdot\boldsymbol{u}^\alpha + \tfrac{1}{2}\rho^\alpha\boldsymbol{s}^\alpha\cdot\Delta\boldsymbol{\omega}^\alpha\Big),\\
\rho\mathfrak{r} &= \sum_{\alpha=1}^{N}\Big(\rho^\alpha\mathfrak{r}^\alpha + \boldsymbol{u}^\alpha\cdot\rho^\alpha\boldsymbol{f}^\alpha + \Delta\boldsymbol{\omega}^\alpha\cdot\rho^\alpha\boldsymbol{\ell}^\alpha\Big),\\
\boldsymbol{q} &= \sum_{\alpha=1}^{N}\Big[\boldsymbol{q}^\alpha - \boldsymbol{u}^\alpha\boldsymbol{t}^\alpha - \Delta\boldsymbol{\omega}^\alpha\boldsymbol{m}^\alpha\\
&\quad+\Big(\rho^\alpha\varepsilon^\alpha + \tfrac{1}{2}\rho^\alpha\boldsymbol{u}^\alpha\cdot\boldsymbol{u}^\alpha + \tfrac{1}{2}\rho^\alpha\boldsymbol{s}^\alpha(\Delta\boldsymbol{\omega}^\alpha - \omega)\Big)\boldsymbol{u}^\alpha\Big].
\end{aligned}
\tag{21.66}
$$

All these quantities were already previously defined and are repeated here for convenience. Simple computations, using product differentiation lead to the following alternative representations:

$$
\begin{aligned}
&\frac{\partial\rho}{\partial t} + \operatorname{div}\,(\rho\boldsymbol{v}) = 0,\\
&\frac{\partial}{\partial t}\,(\rho\boldsymbol{v}) + \operatorname{div}\,(\rho\boldsymbol{v}\otimes\boldsymbol{v}) = \operatorname{div}\boldsymbol{t} + \rho\boldsymbol{f},\\
&\frac{\partial}{\partial t}\,(\rho\boldsymbol{s}) + \operatorname{div}\,(\rho\boldsymbol{s}\otimes\boldsymbol{v}) = \operatorname{div}\boldsymbol{m} - \operatorname{dual}(\boldsymbol{t}-\boldsymbol{t}^T) + \rho\boldsymbol{\ell},\\
&\frac{\partial}{\partial t}\,(\rho\varepsilon) + \operatorname{div}\,(\rho\varepsilon\boldsymbol{v}) = -\operatorname{div}\boldsymbol{q} + \boldsymbol{\omega}\cdot\operatorname{dual}(\boldsymbol{t}-\boldsymbol{t}^T) + (\operatorname{grad}\boldsymbol{v})\cdot\boldsymbol{t}^T\\
&\qquad+(\operatorname{grad}\boldsymbol{\omega})\cdot\boldsymbol{m}^T + \rho\mathfrak{r},\\
&\frac{\partial}{\partial t}\,(\rho s) + \operatorname{div}\,(\rho s\boldsymbol{v}) = -\operatorname{div}\boldsymbol{\phi}^s + \rho\eta^s + \rho\pi^s.
\end{aligned}
\tag{21.67}
$$

or

$$
\begin{aligned}
&\frac{\mathrm{d}\rho}{\mathrm{d}t} + \rho\operatorname{div}\boldsymbol{v} = 0,\\
&\rho\frac{\mathrm{d}\boldsymbol{v}}{\mathrm{d}t} = \operatorname{div}\boldsymbol{t} + \rho\boldsymbol{f},\\
&\rho\frac{\mathrm{d}\boldsymbol{s}}{\mathrm{d}t} = \operatorname{div}\boldsymbol{m} - \operatorname{dual}(\boldsymbol{t}-\boldsymbol{t}^T) + \rho\boldsymbol{\ell},\\
&\rho\frac{\mathrm{d}\varepsilon}{\mathrm{d}t} = -\operatorname{div}\boldsymbol{q} + \boldsymbol{\omega}\cdot\operatorname{dual}(\boldsymbol{t}-\boldsymbol{t}^T) + (\operatorname{grad}\boldsymbol{v})\cdot\boldsymbol{t}^T + (\operatorname{grad}\boldsymbol{\omega})\cdot\boldsymbol{m}^T + \rho\mathfrak{r},\\
&\rho\frac{\mathrm{d}s}{\mathrm{d}t} = -\operatorname{div}\boldsymbol{\phi}^s + \rho\eta^s + \rho\pi^s.
\end{aligned}
\tag{21.68}
$$

In the above forms, these equations hold for *polar* continua. In exactly the same fashion as done for the constituent balance laws, a mixture is defined to be *nonpolar* if

$$
\boldsymbol{s} = \boldsymbol{0}, \qquad \boldsymbol{m} = \boldsymbol{0}, \qquad \boldsymbol{\ell} = \boldsymbol{0},
\tag{21.69}
$$

so that

$$\boldsymbol{t} = \boldsymbol{t}^T . \tag{21.70}$$

The Cauchy stress tensor of a nonpolar mixture is automatically symmetric. This conclusion also holds true if the partial Cauchy stress tensors should possess skew symmetric contributions, compare Eqs. (21.23) and (21.24).

The jump conditions, which hold across singular surfaces $\mathfrak{s}$ are

$$\begin{aligned}
&[\![\rho(\boldsymbol{w} - \boldsymbol{v}) \cdot \boldsymbol{n}_{\mathfrak{s}}]\!] = 0, \\
&[\![\rho\boldsymbol{v}(\boldsymbol{w} - \boldsymbol{v}) \cdot \boldsymbol{n}_{\mathfrak{s}}]\!] + [\![\boldsymbol{t}\boldsymbol{n}_{\mathfrak{s}}]\!] = 0, \\
&[\![\rho\boldsymbol{s}(\boldsymbol{w} - \boldsymbol{v}) \cdot \boldsymbol{n}_{\mathfrak{s}}]\!] + [\![\boldsymbol{m}\boldsymbol{n}_{\mathfrak{s}}]\!] = 0, \\
&\Big[\!\!\Big[\rho(\varepsilon + \tfrac{1}{2}\boldsymbol{v}^2 + \tfrac{1}{2}\boldsymbol{\omega} \cdot \boldsymbol{s})(\boldsymbol{w} - \boldsymbol{v}) \cdot \boldsymbol{n}_{\mathfrak{s}}\Big]\!\!\Big] + \Big[\!\!\Big[\boldsymbol{v}\boldsymbol{t} + \boldsymbol{\omega}\boldsymbol{m} - \boldsymbol{q}\Big]\!\!\Big] \cdot \boldsymbol{n}_{\mathfrak{s}} = 0, \\
&\Big[\!\!\Big[\rho s(\boldsymbol{w} - \boldsymbol{v}) - \boldsymbol{\phi}^s\Big]\!\!\Big] \cdot \boldsymbol{n}_{\mathfrak{s}} = -\mathfrak{P}^s_{\mathfrak{s}},
\end{aligned} \tag{21.71}$$

in which $\boldsymbol{w}$ is the velocity of the singular surface.

A further balance law of micro-inertia, formulated by Eringen in 1964 [8] is concerned with evolution equations for the tensor of inertia of the constituents, $\bar{\Theta}^\alpha$. These balance laws are better presented when the kinematics of Cosserat continua will have been introduced, see Chap. 22.

21.5 Discussion

The aim of this chapter has been the construction of the governing physical equations—balance laws of mass, linear momentum, angular momentum, energy and entropy—on the basic assumption that matter fills the physical space continuously. This was done for a mixture of a finite number of constituents or components and the tacit assumption that the principles of classical physics in continuous systems possess the structure of balance laws and field quantities are additive. The physical laws are expressible as local differential equations in interior body points where the field quantities are differentiable and as so-called jump conditions of fields between the two adjoining sides of singular surfaces.

The physical balance laws have been presented for polar, or so-called Cosserat, continua; their basic assumption is existence of a nontrivial spin balance. It entails kinematically separate descriptions, i.e., formal independence of the translational and rotational motion of the fluid particles. The governing dynamical equations have here been motivated by analogy to the equations of rigid body dynamics, Newton's second law and Euler's description of the angular momentum balance equation, which were condensed in a single statement of motor calculus. Its transformation to a continuous three-dimensional deformable body required definitions of specific spin density, $\rho\boldsymbol{s}$, couple stress tensor $\boldsymbol{m}$ and specific body couples, $\rho\boldsymbol{\ell}$, summarized in the motor-type Eq. (21.4). This equation and all its applications to the physical balance laws for the constituents α ($\alpha = 1, 2, \ldots, N$) and for the mixture as a whole form evolution equations for dynamical quantities, but also involve kinematic quantities, the velocity fields $\boldsymbol{v}^\alpha$ and the angular velocities $\boldsymbol{\omega}^\alpha$ of the constituents. The former couple the velocity fields with the specific momenta, $\rho\boldsymbol{v}^\alpha$; the latter are new and here specialized for a particular description of the micro-deformation, rotations accompanying the constituent moving fluid particles as stated in Eq. (21.32). Thus, the dynamical equations, derived in this chapter, are coupled with the principal kinematic fields $\boldsymbol{v}^\alpha$ and $\boldsymbol{\omega}^\alpha$ through the definitions of specific linear momentum, $\rho^\alpha\boldsymbol{v}^\alpha$ and specific spin $\rho^\alpha\boldsymbol{s}^\alpha$, both of constituent α, ($\alpha = 1, 2, \ldots, N$). The suggested parameterization (21.32) led to themicro-polar and micro-morphic continua, originally due to the COSSERAT brothers, but can be generalized if desired to describe more general substructural behavior.

Appendix 21.A Derivation of the Local Balance Law and Jump Condition

In this Appendix, the local statements (21.6) and (21.7) will be derived from (21.5) by assuming that all fields are additive quantities over their domains of definition. Notation will also be simplified by omitting the counting index α, because in the ensuing analysis only a single component is looked at.

Figure 21.3 shows the material body in its reference and present configurations, but split into two parts $\omega^\pm$. It is assumed that the fields γ, π, ζ, ϕ are continuous and differentiable in the two subregions $\omega^\pm$, but suffer a jump across an orientable nonmaterial surface, denoted as $\mathfrak{S}$ and $\mathfrak{s}$ in the reference and present configurations, respectively.

The two underlined terms in the balance law

$$\underline{\frac{\mathrm{d}}{\mathrm{d}t}\int_\omega \gamma(\boldsymbol{x}, t)\mathrm{d}v} = \int_\omega (\pi(\boldsymbol{x}, t) + \zeta(\boldsymbol{x}, t))\,\mathrm{d}v - \underline{\int_{\partial\omega} \boldsymbol{\phi}(\boldsymbol{x}, t)\cdot\boldsymbol{n}\mathrm{d}a} \tag{21.72}$$

are critical, because the classical REYNOLDS transport theorem and the Divergence theorem are not valid over ω and $\partial\omega$, respectively, if a singular surface is present.

For this reason, the body is divided in two parts as shown in Fig. 21.3. The left-hand side of (21.72) is thus written as

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_\omega \gamma\mathrm{d}v = \frac{\mathrm{d}}{\mathrm{d}t}\int_{\omega^+} \gamma\mathrm{d}v + \frac{\mathrm{d}}{\mathrm{d}t}\int_{\omega^-} \gamma\mathrm{d}v. \tag{21.73}$$

It is assumed that the singular surface moves with velocity $\boldsymbol{u}$ and REYNOLDS' transport theorem applied to the two parts. This yields

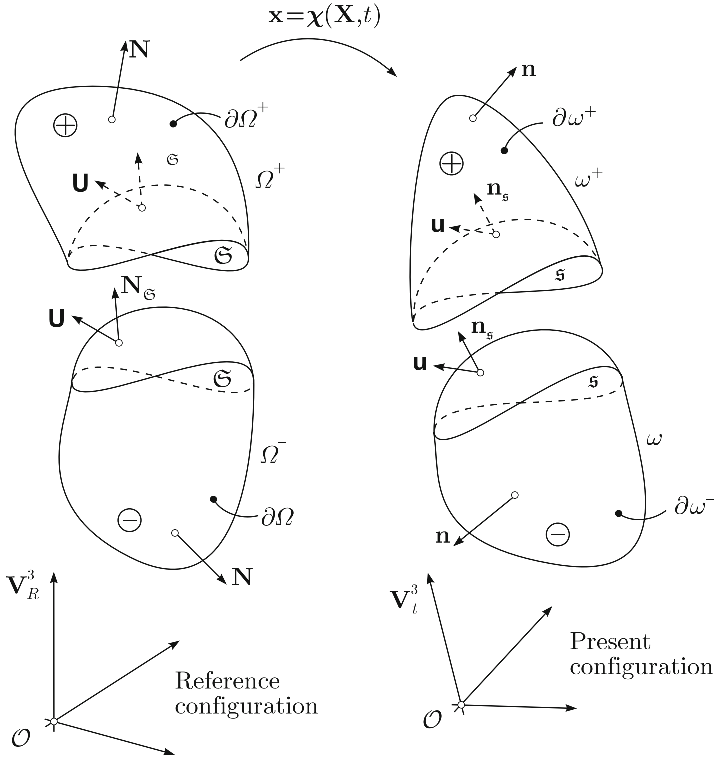

Fig. 21.3 Material body (actually here one component of a mixture) with interior singular surface in the present and reference configurations. *The body is separated in two parts by the singular surface which are indicated by + and −. The boundary surfaces* $\partial\Omega^{\pm}$, $\partial\omega^{\pm}$ *are the outer boundaries governed by the mantle surface plus the singular surfaces of the body in the two configurations.* $\mathfrak{S}$ *and* $\mathfrak{s}$ *indicate the singular surfaces,* $\boldsymbol{N}_{\mathfrak{S}}$ *and* $\boldsymbol{n}_{\mathfrak{s}}$ *represent the unit normal vectors and, finally* $\boldsymbol{U}^{\pm}$ it or $\boldsymbol{u}$ it the velocities of these surfaces in the two different configurations

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\int_{\omega^+}\gamma\mathrm{d}v &= \int_{\omega^+}\frac{\partial\gamma}{\partial t}\mathrm{d}v + \int_{\partial\omega^+\backslash\mathfrak{s}}\gamma\boldsymbol{v}\cdot\boldsymbol{n}\mathrm{d}a - \int_{\mathfrak{s}}\gamma^+\left(\boldsymbol{u}\cdot\boldsymbol{n}_{\mathfrak{s}}\right)\mathrm{d}a\\ \frac{\mathrm{d}}{\mathrm{d}t}\int_{\omega^-}\gamma\mathrm{d}v &= \int_{\omega^-}\frac{\partial\gamma}{\partial t}\mathrm{d}v + \int_{\partial\omega^-\backslash\mathfrak{s}}\gamma\boldsymbol{v}\cdot\boldsymbol{n}\mathrm{d}a + \int_{\mathfrak{s}}\gamma^-\left(\boldsymbol{u}\cdot\boldsymbol{n}_{\mathfrak{s}}\right)\mathrm{d}a,\end{aligned} \tag{21.74}$$

in which $\boldsymbol{u}$ is the velocity of the singular surface and $\boldsymbol{n}_{\mathfrak{s}}$ is pointing into the positive side of the partitioned body. At this state of the analysis, conditions of the applicability of the Divergence Theorem are not satisfied, but they can be artificially incorporated as follows:

$$
\begin{aligned}
\frac{\mathrm{d}}{\mathrm{d}t}\int_{\omega^+}\gamma \mathrm{d}v = \int_{\omega^+}\frac{\partial\gamma}{\partial t}\mathrm{d}v + \underbrace{\int_{\partial\omega^+\backslash\mathfrak{s}}\gamma\boldsymbol{v}\cdot\boldsymbol{n}\mathrm{d}a - \int_{\mathfrak{s}}\gamma\boldsymbol{v}^+\cdot\boldsymbol{n}_{\mathfrak{s}}\mathrm{d}a}_{\int_{\partial\omega^+}\operatorname{div}(\gamma\boldsymbol{v})\mathrm{d}v} \\
+\int_{\mathfrak{s}}\gamma\left(\boldsymbol{v}^+\cdot\boldsymbol{n}_{\mathfrak{s}}\right)\mathrm{d}a - \int_{\mathfrak{s}}\gamma^+\left(\boldsymbol{u}\cdot\boldsymbol{n}_{\mathfrak{s}}\right)\mathrm{d}a
\end{aligned}
\tag{21.75}
$$

$$
\begin{aligned}
\frac{\mathrm{d}}{\mathrm{d}t}\int_{\omega^-}\gamma \mathrm{d}v = \int_{\omega^-}\frac{\partial\gamma}{\partial t}\mathrm{d}v + \underbrace{\int_{\partial\omega^-\backslash\mathfrak{s}}\gamma\boldsymbol{v}\cdot\boldsymbol{n}\mathrm{d}a + \int_{\mathfrak{s}}\gamma\boldsymbol{v}^-\cdot\boldsymbol{n}_{\mathfrak{s}}\mathrm{d}a}_{\int_{\omega^-}\operatorname{div}(\gamma\boldsymbol{v})\mathrm{d}v} \\
-\int_{\mathfrak{s}}\gamma\boldsymbol{v}^-\cdot\boldsymbol{n}_{\mathfrak{s}}\mathrm{d}a + \int_{\mathfrak{s}}\gamma^-\left(\boldsymbol{u}\cdot\boldsymbol{n}_{\mathfrak{s}}\right)\mathrm{d}a.
\end{aligned}
\tag{21.76}
$$

Note that $\boldsymbol{n}_{\mathfrak{s}}$ is for ω^+ a surface vector pointing *into* ω^+. Combining (21.74)$_{1,2}$ leads to

$$
\begin{aligned}
\frac{\mathrm{d}}{\mathrm{d}t}\int_{\omega}\gamma \mathrm{d}v = \int_{\omega^+}\left(\frac{\partial\gamma}{\partial t}+\operatorname{div}(\gamma\boldsymbol{v})\right)\mathrm{d}v + \int_{\omega^-}\left(\frac{\partial\gamma}{\partial t}+\operatorname{div}(\gamma\boldsymbol{v})\right)\mathrm{d}v \\
-\int_{\mathfrak{s}}[\![\gamma(\boldsymbol{u}-\boldsymbol{v})\cdot\boldsymbol{n}_{\mathfrak{s}}]\!]\,\mathrm{d}a,
\end{aligned}
\tag{21.77}
$$

where the last two terms in (21.74) have been combined to the jump term in (21.77).

Next, adding Eq. (21.74) together and observing that $(\partial\omega^+\backslash\mathfrak{s})\cup(\partial\omega^-\backslash\mathfrak{s})=\partial\omega$, one obtains

$$
\frac{\mathrm{d}}{\mathrm{d}t}\int_{\omega}\gamma \mathrm{d}v = \int_{\omega}\frac{\partial\gamma}{\partial t}\mathrm{d}v + \int_{\partial\omega}\gamma\left(\boldsymbol{v}\cdot\boldsymbol{n}\right)\mathrm{d}a - \int_{\mathfrak{s}}[\![\gamma\left(\boldsymbol{u}\cdot\boldsymbol{n}_{\mathfrak{s}}\right)]\!]\,\mathrm{d}a. \tag{21.78}
$$

Comparing this result with (21.77) yields

$$
\int_{\partial\omega}\gamma\left(\boldsymbol{v}\cdot\boldsymbol{n}\right)\mathrm{d}a = \int_{\omega}\operatorname{div}\,(\gamma\boldsymbol{v})\,\mathrm{d}v + \int_{\mathfrak{s}}[\![\gamma\left(\boldsymbol{v}\cdot\boldsymbol{n}_{\mathfrak{s}}\right)]\!]\,\mathrm{d}a. \tag{21.79}
$$

The expressions (21.77) and (21.79) are the generalized REYNOLDS and Divergence Theorems for bodily regions with singular surface.

Substituting (21.77) and (21.79) for $[\gamma\boldsymbol{v}=\boldsymbol{\phi}]$ into the underlined terms in (21.72) yields

$$
\begin{aligned}
\int_{\omega}\left(\frac{\partial\gamma}{\partial t}+\operatorname{div}(\gamma\boldsymbol{v})\right)\mathrm{d}v - \int_{\mathfrak{s}}[\![\gamma(\boldsymbol{v}-\boldsymbol{u})\cdot\boldsymbol{n}_{\mathfrak{s}}]\!]\,\mathrm{d}a \\
= \int_{\omega}(\pi+\zeta)\,(\boldsymbol{x},t)\mathrm{d}v - \int_{\omega}\operatorname{div}(\boldsymbol{\phi})\mathrm{d}v - \int_{\mathfrak{s}}[\![\boldsymbol{\phi}\cdot\boldsymbol{n}_{\mathfrak{s}}]\!]\,\mathrm{d}a.
\end{aligned}
\tag{21.80}
$$

In the above analysis, it was consistently assumed that the singular surface was not equipped with substance; in (21.80) it only participates passively on the processes in the immediate neighborhood of the surface on parts ω^+ and ω^-. In the most general case it is, however, thinkable that the singular surface is equipped with physical surface quantities, for which a surface balance law may hold [1]. The most significant contribution is often the surface production term $\mathfrak{P}$; it represents a surface density of the production of the physical quantity. Here, this production term $\int_{\mathfrak{s}} \mathfrak{P} \mathrm{d}a$ is the only contribution that will be accounted for.[6] Therefore, (21.80) will now and henceforth be replaced by

$$\begin{aligned}
&\int_\omega \left(\frac{\partial \gamma}{\partial t} + \operatorname{div}(\gamma \boldsymbol{v}) \right) \mathrm{d}v - \int_{\mathfrak{s}} [\![\gamma (\boldsymbol{v} - \boldsymbol{u}) \cdot \boldsymbol{n}_{\mathfrak{s}}]\!] \, \mathrm{d}a \\
&= \int_\omega (\pi + \zeta)(\boldsymbol{x}, t) \mathrm{d}v - \int_\omega \operatorname{div}(\boldsymbol{\phi}) \mathrm{d}v - \int_{\mathfrak{s}} [\![\boldsymbol{\phi} \cdot \boldsymbol{n}_{\mathfrak{s}}]\!] \, \mathrm{d}a \\
&\quad - \int_{\mathfrak{s}} \mathfrak{P} \mathrm{d}a
\end{aligned} \tag{21.81}$$

If ω is a region not involving any singular surface, then (21.81) reduces to

$$\int_\omega \left\{ \left(\frac{\partial \gamma}{\partial t} + \operatorname{div}(\gamma \boldsymbol{v}) \right) + \operatorname{div}(\boldsymbol{\phi}) - (\pi + \zeta) \right\} (\boldsymbol{x}, t) \mathrm{d}v = 0,$$

for all such ω so that

$$\left\{ \frac{\partial \gamma}{\partial t} + \operatorname{div}(\gamma \boldsymbol{v}) + \operatorname{div}(\boldsymbol{\phi}) - (\pi + \zeta) \right\} (\boldsymbol{x}, t) = 0, \tag{21.82}$$

which agrees with (21.5).

Alternatively, taking for ω a small pillbox with height ε, of which the lid and bottom surfaces are very close and parallel to $\mathfrak{s}$ but on the $+$ and $-$ sides of it, respectively, and letting $\varepsilon \to 0$, relation (21.81) leads to

$$\int_{\mathfrak{s}} \left\{ [\![\gamma (\boldsymbol{v} - \boldsymbol{u}) \cdot \boldsymbol{n}_{\mathfrak{s}}]\!] - [\![\boldsymbol{\phi} \cdot \boldsymbol{n}_{\mathfrak{s}}]\!] - \mathfrak{P} \right\} (\boldsymbol{x}, t) \mathrm{d}a = 0,$$

from which, because of additivity,

$$[\![\gamma (\boldsymbol{v} - \boldsymbol{u}) \cdot \boldsymbol{n}_{\mathfrak{s}}]\!] - [\![\boldsymbol{\phi} \cdot \boldsymbol{n}_{\mathfrak{s}}]\!] = \mathfrak{P}, \tag{21.83}$$

which agrees with (21.7) in the main text.

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[6] Such production terms can, e. g., be the melting/freezing rate (a mass production or loss) between water and ice and the energy production/annihilation (surface energy release/consumption) associated with this phase change process.

References

1. Alts, T., Hutter, K.: Continuum description of the dynamics and thermodynamics of phase boundaries between ice and water. Part I: Surface balance laws and their interpretation in terms of three dimensional balance laws averaged over the phase change boundary layer. J. Non-Equilib. Thermodyn. **13**, 221–257 (1988)
2. Besdo, D.: Ein Beitrag zur nichtlinearen Theorie des Cosserat Kontinuums. Acta Mechanica **20**, 105–131 (1975)
3. Boltzmann, L.: Populäre Schriften. Verlag von Johann Ambrosius Berth, Leipzig (1905) reprint 1925, Kapitel 16: Über die Grundprinzipien und Grundgleichungen der Mechanik, pp. 253–307, Vorlesungen, gehalten an der Clark Universität im Jahre 1899
4. Chen, K-Ch., Lan, J.-Y.: Microcontinuum derivation of Goodman–Cowin theory for granular materials. Contin. Mech. Thermodyn. **20**, 345–931 (2008)
5. Cosserat, E., Cosserat, F.: Sur la Théorie de l' élasticité. Ann. Fac. Sci. **10**(3—-5), 1–116 (1896)
6. Cosserat, E., Cosserat, F.: Théorie des corps déformables. Herrmann & Fils, Paris (1909)
7. Diebels, S.: Mikropolare Zweiphasenmodelle: Formulierung auf der Basis der Theorie der porösen Medien Habilitationsschrift. Bericht Nr. II-4 aus dem Institut für Mechanik (Bauwesen). Lehrstuhl II, Universität Stuttgart, p. 188 (2000)
8. Eringen, C.A.: Simple microfluids. Int. J. Eng. Sci. **2**, 205–217 (1964)
9. Fang, C.: On the equilibrium response of different modeling approaches for the porosity variation in dry granular matter. Contin. Mech. Thermodyn. **22**, 121–136 (2010)
10. Fang, C.: Gravity driven slow flows down an inclined moving plane: a comparative study between two concepts of the evolution of porosity. Rheol. Acta (2016). https://doi.org/10.1007/s00397-009-0378-4
11. Fang, C., Wang, Y., Hutter, K.: A thermomechanical continuum theory with internal length for cohesionless granular materials. Part I. A class of constitutive models. Contin. Mech. Thermodyn. **17**, 545–576 (2006)
12. Fang, C., Wang, Y., Hutter, K.: A thermomechanical continuum theory with internal length for cohesionless granular materials. Part II. Nonequilibrium postulates and numerical simulation of simple shear, plane Poiseuille and gravity driven problems. Contin. Mech. Thermodyn. **17**, 577–607 (2006)
13. Fang, C., Wang, Y., Hutter, K.: A variational principle for the revised Goodman–Cowin theory with internal length. Arch. Appl. Mech. **76**, 119–131 (2006)
14. Goodman, M.A., Cowin, S.C.: A continuum theory for granular materials. Arch. Rational Mech. Anal. **44**, 249–266 (1972)
15. Hutter, K.: Continuum Mechanics in Environmental Sciences and Geophysics. CISM Courses and Lectures, vol. 337, p. 522. Springer, Vienna (1993)
16. Hutter, K.: Thermodynamically coupled ice sheet response. Cold, polythermal temperate. J. Glaciolo. **99**(131), 65–86 (1993)
17. Hutter, K.: Continuum Methods of Physical Modeling, p. 635. Springer, Berlin (2004)
18. Hutter, K., Wang, Y.: Fluid and Thermodynamics. Volume II: Advanced Fluid Mechanics and Thermodynamic Fundamentals, p. 633. Springer, Berlin (2016). ISBN: 978-3-319-33635-0
19. Maugin, G.A.: Continuum Mechanics Through the Eighteenth and Nineteenth Centuries. Solid Mechanics and its Applications, vol. 214. Springer, Switzerland (2014). https://doi.org/10.1007/978-3-319-05374-5-8
20. Schaefer, H.: Das Cosserat-Kontinuum. Zeitschr. für Angewandt Mathematik und Mechanik **47**(8), 485–498 (1967)
21. Truesdell, C.A., Toupin, R.A.: In: Flügge, S. (ed.) Principles of Classical Mechanics and field theory. Encyklopedia of Physics, Handbuch der Physik, vol. III,3, p. 632. Springer, Berlin (1960)
22. Von Mises, R.: Motorrechnung, ein neues Hilfsmittel der Mechanik. Zeitschrift für angewandte Mathematik und Mechanik **2**, 155–181 (1924)
23. Wilmanski, K.: Porous media at finite strains. The new model with the balance equation of porosity. Arch. Mech. **48**, 591–628 (1996)

Chapter 22
Kinematics of Classical and Cosserat Continua

Abstract The aim of this chapter is the presentation of the kinematics of classical (BOLTZMANN) and *polar* (COSSERAT) continuous mixtures. The motions of material points of constituent α are first mathematically introduced for a classical mixture as mappings from separate constituent points onto a single point in the present configuration, **Fig.** 22.3. This guarantees that material points in physical space are a merger of all constituents. This motion function then yields through spatial and temporal differentiations the well-known definitions of the classical deformation measures: deformation gradient, right and left CAUCHY–GREEN deformation tensors, EULER–LAGRANGE strains, and associated strain rates. Of importance is the polar decomposition, which splits the deformation gradient into a sequence of pure strain and rotation or vice versa. Whereas the classical stretch and stretching measures are obtained by inner products of the constituent vectorial line element with itself, deformation measures of COSSERAT kinematics are generated by inner products between vectorial material line increments and the directors. The mappings of the latter between the reference and present configurations are postulated to be pure rotations (**Fig.** 22.5). This then yields the various COSSERAT strain measures, which are analogous to, but not the same as those of the classical theory. The kinematically independent rotation of the directors gives rise to the introduction of skew-symmetric rank-3 and full rank-2 curvature tensors, quasi as measures of the spatial variation of the micro rotation. Analogous to the additive decomposition of the velocity gradient into stretching and vorticity tensors in the classical formulation, two additional decompositions of the velocity gradient are introduced using the polar decomposition and leads to non-symmetric strain rate and the so-called gyration tensors, and objective time derivatives of the COSSERAT version of the ALMANSI tensor and the curvature tensors. All these quantities are also written relative to the natural basis system. The chapter ends with the presentation of the balance law of micro-inertia. It is based on the assumption that material points of micro-polar continua move like rigid bodies.

Keywords Classical and extended deformation measures · Curvature tensor · Velocity gradient and gyration tensor · COSSERAT deformation tensor · Balance of micro-inertia · COSSERATS' book 100 app. years later

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List of Symbols

All quantities carrying a sub(super)script α are thought to be written for constituent α of a mixture. “Classical” theory means “Boltzmann” continuum

Roman Symbols

$\boldsymbol{A}^\alpha$	Euler–Almansi strain tensor of the classical theory, $\boldsymbol{A}^\alpha = \frac{1}{2}\left(\boldsymbol{I} - (\boldsymbol{B}^\alpha)^{-1}\right)$
$(\boldsymbol{A}^\alpha)^{\Delta^\alpha}$	Lie or Oldroyd derivative of $\boldsymbol{A}^\alpha$
$\bar{\boldsymbol{A}}^\alpha$	Cosserat Almansi strain tensor, $\bar{\boldsymbol{A}}^\alpha = \boldsymbol{I} - (\bar{\boldsymbol{V}}^\alpha)^{-1}$
$(\boldsymbol{a}^\alpha)_i$	Basis vectors in the present configuration, $i = 1, 2, 3$
$(\boldsymbol{a}^\alpha)^i$	Basis vector dual to $(\boldsymbol{a}^\alpha)_i$, $i = 1, 2, 3$
$\boldsymbol{B}^\alpha = \boldsymbol{V}^\alpha(\boldsymbol{V}^\alpha)^T$	Left Cauchy–Green deformation tensor expressed as classical stretch measure
$\boldsymbol{B}^\alpha = \bar{\boldsymbol{V}}^\alpha(\bar{\boldsymbol{V}}^\alpha)^T$	Left Cauchy–Green deformation tensor expressed as Cosserat stretch measure
$\boldsymbol{C}^\alpha = (\boldsymbol{U}^\alpha)^T\boldsymbol{U}^\alpha$	Right Cauchy–Green deformation tensor expressed as right classical stretch measure
$\boldsymbol{C}^\alpha = (\bar{\boldsymbol{U}}^\alpha)^T\bar{\boldsymbol{U}}^\alpha$	Right Cauchy–Green deformation tensor expressed as right Cosserat stretch measure
$\boldsymbol{D}^\alpha$	Stretching (strain rate) tensor, $\boldsymbol{D}^\alpha = \mathrm{sym}\boldsymbol{L}^\alpha$
$\boldsymbol{E}^\alpha$	Green–Lagrange strain tensor of classical theory, $\boldsymbol{E}^\alpha = \frac{1}{2}(\boldsymbol{C}^\alpha - \boldsymbol{I})$
$\bar{\boldsymbol{E}}^\alpha$	Cosserat–Green strain tensor, $\bar{\boldsymbol{E}}^\alpha = \bar{\boldsymbol{U}}^\alpha - \boldsymbol{I}$
$(\overset{3}{\boldsymbol{E}})_{ABC}$	Epsilon tensor, $(\overset{3}{\boldsymbol{E}})_{ABC} = \varepsilon_{ABC}$
$\boldsymbol{F}^\alpha$	Deformation gradient, $\boldsymbol{F}^\alpha = \mathrm{Grad}^\alpha\boldsymbol{x}$
$(\boldsymbol{F}^\alpha)^{-1}$	Inverse deformation gradient, $(\boldsymbol{F}^\alpha)^{-1} = \mathrm{grad}\,^\alpha\boldsymbol{X}^\alpha$
$(\boldsymbol{h}^\alpha)_i$	Basis vector in the reference configuration, $i = 1, 2, 3$
$(\boldsymbol{h}^\alpha)^i$	Basis vector dual to $(\boldsymbol{h}^\alpha)_i$, $i = 1, 2, 3$
$\boldsymbol{L}^\alpha$	Spatial velocity gradient, $\boldsymbol{L}^\alpha = \mathrm{grad}\,\boldsymbol{v}^\alpha$
$\boldsymbol{L}^\alpha = \boldsymbol{D}^\alpha + \boldsymbol{W}^\alpha$	Decomposition of $\boldsymbol{L}^\alpha$ into classical stretch and vorticity tensor
$\boldsymbol{L}^\alpha = \boldsymbol{\Delta}^\alpha + \boldsymbol{\Omega}^\alpha$	Decomposition of $\boldsymbol{L}^\alpha$ into strain $\boldsymbol{\Delta}^\alpha$ and gyration tensor $\boldsymbol{\Omega}^\alpha$
$\boldsymbol{R}^\alpha$	Rotation tensor of the classical theory
$\bar{\boldsymbol{R}}^\alpha$	rotation matrix for the map $\boldsymbol{\xi}^\alpha = \bar{\boldsymbol{R}}^\alpha\boldsymbol{\Xi}^\alpha$
$(\boldsymbol{R}^\alpha)^*,\ {}^*\boldsymbol{R}^\alpha$	Compositions of classical and Cosserat rotations, $(\boldsymbol{R}^\alpha)^* = \bar{\boldsymbol{R}}^T\boldsymbol{R}^\alpha$, ${}^*\boldsymbol{R}^\alpha = (\bar{\boldsymbol{R}}^\alpha)^T\boldsymbol{R}^\alpha$
$\bar{\boldsymbol{R}}$	Microrotation tensor in convected coordinates, $\bar{\boldsymbol{R}} = (\bar{R}^\alpha)^i_{\ j}(\boldsymbol{a}^\alpha)_i \otimes (\boldsymbol{h}^\alpha)^j$
$\boldsymbol{s}^\alpha$	Spin density of constituent α
$\boldsymbol{u}^\alpha$	Displacement vector, $\boldsymbol{u}^\alpha = \boldsymbol{x} - \boldsymbol{X}^\alpha$
$\boldsymbol{u}^\alpha$	Diffusion velocity of constituent α
$\boldsymbol{U}^\alpha$	Right stretch tensor of the classical theory (symmetric)

$\bar{\boldsymbol{U}}^{\alpha}$	Right COSSERAT stretch tensor, $\bar{\boldsymbol{U}}^{\alpha} = \bar{\boldsymbol{R}}^{T} \boldsymbol{F}^{\alpha} \neq (\bar{\boldsymbol{U}}^{\alpha})^{T}$
$\boldsymbol{v}$	mixture (barycentric) velocity
$\boldsymbol{v}^{\alpha}(\boldsymbol{x}, t)$	Velocity of constituent α at $\boldsymbol{x}$, referred to the present configuration
$(\boldsymbol{v}^{\alpha})'^{\alpha}\,(\boldsymbol{x}, t)$	Acceleration of constituent α at $\boldsymbol{x}$, referred to the present configuration
$\boldsymbol{V}^{\alpha}$	Left stretch tensor of the classical theory (symmetric)
$\bar{\boldsymbol{V}}^{\alpha}$	Left COSSERAT stretch tensor, $\bar{\boldsymbol{V}}^{\alpha} = \boldsymbol{F}^{\alpha} \bar{\boldsymbol{R}}^{\alpha} \neq (\bar{\boldsymbol{V}}^{\alpha})^{T}$
$\boldsymbol{W}^{\alpha}$	Vorticity tensor, $\boldsymbol{W}^{\alpha} = \operatorname{skw} \boldsymbol{L}^{\alpha}$
$\boldsymbol{x}$	Position of a material point in the present configuration
$\boldsymbol{X}^{\alpha}$	Placement of a material point of constituent α in the reference configuration
$\boldsymbol{x}'^{\alpha}$	Velocity of constituent particle α at time t
$\boldsymbol{x}''^{\alpha}$	Acceleration of constituent particle α at time t

Greek Symbols

α	Identifier of a non-specified constituent
$\boldsymbol{\Delta}^{\alpha}$	Non-symmetric rank-2 classical strain rate tensor, $\boldsymbol{\Delta}^{\alpha} = \boldsymbol{R}^{\alpha}(\boldsymbol{U}^{\alpha})'^{\alpha} (\boldsymbol{U}^{\alpha})^{-1}(\boldsymbol{R}^{\alpha})^{T}$
$\bar{\boldsymbol{\Delta}}^{\alpha}$	Non-symmetric rank-2 COSSERAT strain rate tensor in the present configuration, $\bar{\boldsymbol{\Delta}}^{\alpha} = \bar{\boldsymbol{R}}^{\alpha}(\bar{\boldsymbol{U}}^{\alpha})'^{\alpha}(\bar{\boldsymbol{U}}^{\alpha})^{-1}(\bar{\boldsymbol{R}}^{\alpha})^{T} = \boldsymbol{L}^{\alpha} - \bar{\boldsymbol{\Omega}}^{\alpha}$
Θ_{i}^{α}	Coordinate lines in a convected system, $i = 1, 2, 3$
$\bar{\boldsymbol{\Theta}}^{\alpha}$	Moment of inertia of constituent α
$\hat{\boldsymbol{\Theta}}^{m}$	Production of micro-inertia of a mixture, $\hat{\boldsymbol{\Theta}}^{m} = \sum^{\alpha} \left(\mathfrak{c}^{\alpha} \bar{\boldsymbol{\Theta}}^{\alpha} \boldsymbol{\Omega}^{\alpha} \right)$
$(\bar{\boldsymbol{\Theta}}^{\alpha})^{\blacklozenge}$	GREEN–NAGHDI derivative (see (22.99))
${}^{R}\overset{\underline{2}}{\boldsymbol{\mathcal{K}}}{}^{\alpha}$	Rank-2 COSSERAT curvature tensor, referred to the reference configuration, ${}^{R}\overset{\underline{2}}{\boldsymbol{\mathcal{K}}}{}^{\alpha} = -\frac{1}{2} \left(\overset{3}{\boldsymbol{E}}\, {}^{R}\overset{3}{\boldsymbol{\mathcal{K}}}{}^{\alpha} \right)^{\underline{2}}$
$\overset{\underline{2}}{\boldsymbol{\mathcal{K}}}{}^{\alpha}$	Rank-2 curvature tensor, referred to the present configuration, $\overset{\underline{2}}{\boldsymbol{\mathcal{K}}}{}^{\alpha} = -\frac{1}{2} \left(\overset{3}{\boldsymbol{E}} \overset{3}{\boldsymbol{\mathcal{K}}}{}^{\alpha} \right)^{\underline{2}}$
${}^{R}\overset{3}{\boldsymbol{\mathcal{K}}}{}^{\alpha}$	Rank-3 curvature tensor, a second COSSERAT deformation tensor referred to the reference configuration, ${}^{R}\overset{3}{\boldsymbol{\mathcal{K}}}{}^{\alpha} = \left((\bar{\boldsymbol{R}}^{\alpha})^{T} \operatorname{Grad} \bar{\boldsymbol{R}}^{\alpha} \right)^{\underline{3}}$
$\overset{3}{\boldsymbol{\mathcal{K}}}{}^{\alpha}$	Rank-3 curvature tensor, referred to the present configuration, $\overset{3}{\boldsymbol{\mathcal{K}}}{}^{\alpha} = \left[\left(\left(\operatorname{grad} \bar{\boldsymbol{R}}^{\alpha} \right)^{\overset{23}{T}} \bar{\boldsymbol{R}}^{\alpha} \right)^{\underline{3}} \right]^{\overset{23}{T}}$
$\boldsymbol{\Xi}^{\alpha}$	Director attached to a constituent particle α in its reference configuration

$\boldsymbol{\xi}^\alpha$	Director, attached to a constituent particle α in its present configuration, $\boldsymbol{\xi}^\alpha = \bar{\boldsymbol{R}}^\alpha \boldsymbol{\Xi}^\alpha$
$\boldsymbol{\phi}_{\boldsymbol{\Theta}}$	Flux of micro-inertia of a mixture, $\boldsymbol{\phi}_{\boldsymbol{\Theta}} = -\sum^\alpha \rho^\alpha \bar{\boldsymbol{\Theta}}^\alpha \otimes \boldsymbol{u}^\alpha$
$\boldsymbol{\chi}^\alpha$	Motion function of constituent α
$(\psi^\alpha)'^\beta(\boldsymbol{x}, t)$	Time rate of change of ψ^α following the motion of constituent β
$\boldsymbol{\Omega}^\alpha$	Gyration tensor, $\boldsymbol{\Omega}^\alpha = (\boldsymbol{R}^\alpha)'^\alpha\,(\boldsymbol{R}^\alpha)^T$
$\bar{\boldsymbol{\Omega}}^\alpha$	Micro-polar gyration tensor, $\bar{\boldsymbol{\Omega}}^\alpha = (\bar{\boldsymbol{R}}^\alpha)'^\alpha(\boldsymbol{R}^\alpha)^T$
$\boldsymbol{\omega}^\alpha$	Vorticity tensor, $\boldsymbol{\omega}^\alpha = \frac{1}{2}\text{curl}\,\boldsymbol{v}^\alpha$
$\boldsymbol{\omega}^\alpha$	Vector of angular velocity of the micromotion

Miscellaneous Symbols

curl $\boldsymbol{v}$	Rotation of the differentiable field $\boldsymbol{v}$
div $\boldsymbol{v}$	Divergence of the differentiable field $\boldsymbol{v}$
grad $\boldsymbol{v}$	Gradient of the differentiable field $\boldsymbol{v}$
$\frac{\mathrm{d}}{\mathrm{d}t}$	Total time derivative holding the particle fixed.

22.1 Preamble

In this chapter, we will present the continuum mechanical approach to kinematics of the classical continuum theory of BOLTZMANN continua and will then proceed to generalize the kinematic concepts to polar, i.e., COSSERAT continua. We shall do this in the context of mixture theory formulations. This does not complicate the mathematics, but it makes formulas a bit heavier, as variables now carry identifiers for the individual constituents. This approach has the advantage that specializations to single constituent media can be easily obtained by dropping the identifiers, but it freely delivers the formalism, when mixtures are considered, which is often the situation, as one encounters in geophysical and geotechnical applications.

Kinematics of classical continua is adequately treated in any book dealing with the subject in today's modern approach, since the appearance of the article "Nonlinear Field Theories of Mechanics" in the "Handbook of Physics" by TRUESDELL[1] and NOLL [30]. We generally refer to our own book, Hutter and Joehnk: "Continuum Methods of Physical Modeling" [16], which contains in chap. 7 an introduction into mixture theories.

On polar theories, a number of books do exist, notably those by ERINGEN [11]. We, however, base this chapter on DIEBELS' Habilitation Thesis, 'Mikropolare Zweiphasenmodelle: Formulierung auf der Basis der porösen Medien' [4] and literature, which is referenced there, but give the text our own flavor, when we find it appropriate. Additional references are inserted in the text as they are felt necessary.

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[1] For a brief biography of CLIFFORD AMBROSE TRUESDELL, see **Fig. 22.1**.

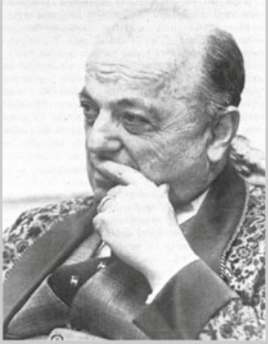

Fig. 22.1 CLIFFORD AMBROSE TRUESDELL III (18. Feb. 1919–14. Jan. 2000)

CLIFFORD AMBROSE TRUESDELL III was an American mathematician, natural philosopher, and historian of science. TRUESDELL was born in Los Angeles, California. After high school, he spent two years in Europe learning French, German, and Italian, and improving his Latin and Greek. His linguistic skills stood him in good stead in his later historical investigations. At Caltech, he was deeply influenced by the teaching of HARRY BATEMAN. In particular, a course in partial differential equations "taught me the difference between an ordinary good teacher and a great mathematician, and after that I never cared what grade I got in anything." He obtained a B.Sc. in mathematics and physics in 1941, and a MSc. in mathematics in 1942. In 1943, he completed a Ph.D. in mathematics at Princeton University. For the rest of the decade, the U.S. Navy employed him to do mechanics research.

TRUESDELL taught at Indiana University 1950–61, where his students included JAMES SERRIN, JERALD ERICKSEN, and WALTER NOLL. From 1961 until his retirement in 1989, TRUESDELL was Professor of Rational Mechanics at Johns Hopkins University. He and NOLL contributed to foundational rational mechanics, whose aim is to construct a mathematical model for treating (continuous) mechanical phenomena.

TRUESDELL was the founder and editor-in-chief of the journals *Archive for Rational Mechanics and Analysis* and*Archive for History of Exact Sciences*, which were unusual in several ways. Following TRUESDELL's criticisms of awkward style in scientific writing, the journal accepted papers in English, French, German, and Latin.

In addition to his original work in mechanics, TRUESDELL was a major historian of science and mathematics, editing or coediting six volumes of the collected works of Leonhard Euler. He received several awards for his achievements. Among these are: The EULER Medal of the USSR Academy of Sciences, 1958 and 1983; the BINGHAM Medal of the Society of Rheology, 1963; the BIRKHOFF Prize of the American Mathematical Society and Society for Industrial and Applied Mathematics, 1978; the THEODORE VON KÁRMÁN Medal, 1996. Some of his scientific treatizes are [23, 28–42].

The text is based on www.wikipedia.org

22.2 Classical Motion

Consider mixtures of constituents φ^α and associate with each component a separate reference configuration, which is mapped onto a single present configuration, **Fig. 22.2**.

The *motion* is defined as the smooth mapping

$$\boldsymbol{x} = \boldsymbol{\chi}^\alpha(\boldsymbol{X}^\alpha, t), \quad (\alpha = 1, 2, ..., \nu). \tag{22.1}$$

Note that $\boldsymbol{X}^\alpha = \boldsymbol{\chi}^\alpha(\boldsymbol{X}^\alpha, t_0)$, where t_0 is a fixed time. It is customary to select $t_0 = 0$. At time $t > t_0$, all material points $\boldsymbol{X}^\alpha$ occupy the same placement $\boldsymbol{x}$ in the present configuration. *Velocity* and *acceleration* of the particles are

$$\boldsymbol{x}'^\alpha = \frac{\partial \boldsymbol{\chi}^\alpha(\boldsymbol{X}^\alpha, t)}{\partial t}, \quad \boldsymbol{x}''^\alpha = \frac{\partial^2 \boldsymbol{\chi}^\alpha(\boldsymbol{X}^\alpha, t)}{\partial t^2}. \tag{22.2}$$

These are first and second time derivatives of the motion functions with the particle reference position held constant.

Because the motion of constituent α is assumed to be smooth, (22.1) can be inverted, at least in principle:

$$\boldsymbol{X}^\alpha = (\boldsymbol{\chi}^\alpha)^{-1}(\boldsymbol{x}, t). \tag{22.3}$$

With this function, velocity and acceleration can be referred to the present configuration,

$$\begin{aligned} \boldsymbol{v}^\alpha(\boldsymbol{x}, t) &= \boldsymbol{x}'^\alpha\left((\boldsymbol{\chi}^\alpha)^{-1}(\boldsymbol{x}, t), t\right), \\ (\boldsymbol{v}^\alpha)'^\alpha(\boldsymbol{x}, t) &= \boldsymbol{x}''^\alpha\left((\boldsymbol{\chi}^\alpha)^{-1}(\boldsymbol{x}, t), t\right). \end{aligned} \tag{22.4}$$

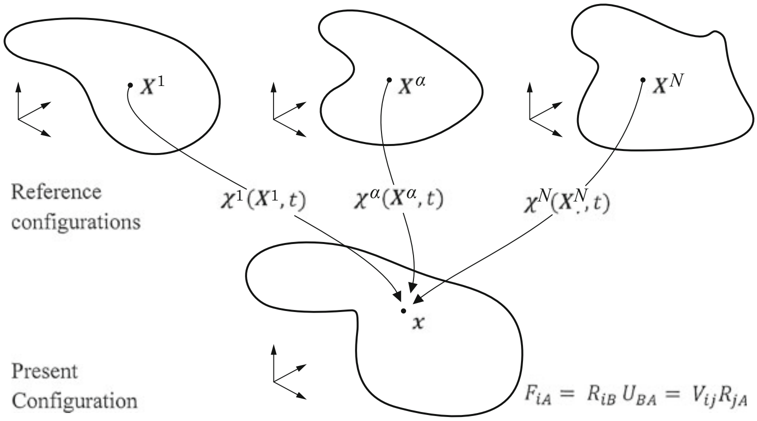

Fig. 22.2 Separate reference configurations of all constituents and common present configuration of all constituents

Here, the symbol $(\cdot)'^{\alpha}$ is the *material time derivative following constituent* α. It is obvious that the following chain rule of differentiation must hold:

$$\frac{\mathrm{d}^{\alpha}}{\mathrm{d}\,t}\Psi\,(\boldsymbol{x}(\boldsymbol{X}^{\alpha},t),t) = \Psi'^{\alpha}(\boldsymbol{x},t) = \frac{\partial\Psi}{\partial t} + (\operatorname{grad}\Psi)\cdot\boldsymbol{v}^{\alpha}. \tag{22.5}$$

Examples:

$$\begin{aligned}
\bullet(\boldsymbol{v}^{\alpha})'^{\alpha} &= \frac{\partial\boldsymbol{v}^{\alpha}}{\partial t} + (\operatorname{grad}\boldsymbol{v}^{\alpha})\boldsymbol{v}^{\alpha},\\
\bullet(\psi^{\alpha})'^{\beta} &= \frac{\partial\psi^{\alpha}}{\partial t} + (\operatorname{grad}\psi^{\alpha})\boldsymbol{v}^{\beta}.
\end{aligned} \tag{22.6}$$

Differentiation of the motion function with respect to $\boldsymbol{X}^{\alpha}$ yields the *deformation gradient*

$$\boldsymbol{F}^{\alpha} = \frac{\partial\chi^{\alpha}(\boldsymbol{X}^{\alpha},t)}{\partial\boldsymbol{X}^{\alpha}} = \operatorname{Grad}\chi^{\alpha} = \operatorname{Grad}^{\alpha}\boldsymbol{x}. \tag{22.7}$$

Similarly, the *inverse deformation gradient* $(\chi^{\alpha})^{-1}(\boldsymbol{x},t)$ [note, it exists since $\det\boldsymbol{F}^{\alpha} \neq 0$] yields

$$(\boldsymbol{F}^{\alpha})^{-1} = \frac{\partial(\chi^{\alpha})^{-1}(\boldsymbol{x},t)}{\partial\boldsymbol{x}} = \operatorname{grad}(\chi^{\alpha})^{-1} = \operatorname{grad}\boldsymbol{X}^{\alpha}. \tag{22.8}$$

Note the differences in the definitions of the operators Grad and grad.

In applications, the reference and present configurations are referred to the same basic frame in the initial configuration. Then, the *displacement vectors* $\boldsymbol{u}^{\alpha}$ may be defined as

$$\boldsymbol{u}^{\alpha} = \boldsymbol{x} - \boldsymbol{X}^{\alpha}, \tag{22.9}$$

from which we easily deduce

$$\begin{aligned}
\boldsymbol{F}^{\alpha} &= \operatorname{Grad}^{\alpha}(\boldsymbol{X}^{\alpha} + \boldsymbol{u}^{\alpha}) = \boldsymbol{I} + \operatorname{Grad}^{\alpha}\boldsymbol{u}^{\alpha},\\
(\boldsymbol{F}^{\alpha})^{-1} &= \operatorname{grad}(\boldsymbol{x} - \boldsymbol{u}^{\alpha}) = \boldsymbol{I} - \operatorname{grad}\boldsymbol{u}^{\alpha}.
\end{aligned} \tag{22.10}$$

The deformation gradient maps material vectorial line elements $\mathrm{d}\boldsymbol{X}$ onto line elements $\mathrm{d}\boldsymbol{x}$:

$$\mathrm{d}\boldsymbol{x} = \operatorname{Grad}^{\alpha}(\boldsymbol{x}(\boldsymbol{X}^{\alpha},t))\,\mathrm{d}\boldsymbol{X}^{\alpha} = \boldsymbol{F}^{\alpha}\mathrm{d}\boldsymbol{X}^{\alpha}. \tag{22.11}$$

Similarly, for the inverse mapping:

$$\mathrm{d}\boldsymbol{X}^{\alpha} = (\boldsymbol{F}^{\alpha})^{-1}\mathrm{d}\boldsymbol{x}. \tag{22.12}$$

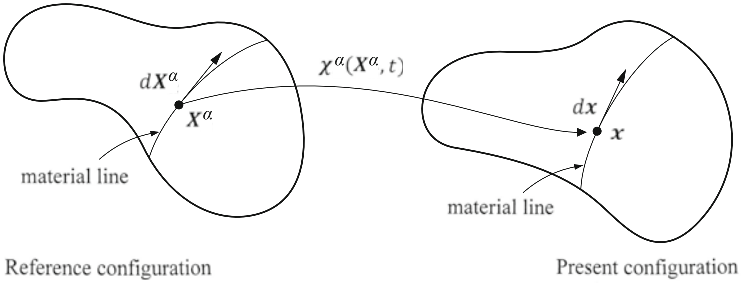

Fig. 22.3 Material line in the reference and present configurations and tangential increments in a material point on these lines

Figure 22.3 explains how the formulas can be interpreted. $\mathrm{d}\boldsymbol{X}^{\alpha}$ can be thought of being tangential to a material line at the location $\boldsymbol{X}^{\alpha}$ of the reference configuration. Then, $\mathrm{d}\boldsymbol{x}$ is tangential to the image of the material line at the placement $\boldsymbol{x}$ of the present configuration.

22.3 Classical Deformation Measures

We know from algebra or classical continuum mechanics, that any positive definite 3×3 matrix (rank-2 tensor over $\mathbb{R}^3$) possesses two *polar decompositions*, e.g., for the deformation tensor $\boldsymbol{F}^{\alpha}$,

$$\begin{aligned}
&\boldsymbol{F}^{\alpha} = \boldsymbol{R}^{\alpha}\boldsymbol{U}^{\alpha} = \boldsymbol{V}^{\alpha}\boldsymbol{R}^{\alpha}, && \boldsymbol{U}^{\alpha}(\boldsymbol{V}^{\alpha}) \text{ right (left) stretch tensors,}\\
&(\boldsymbol{R}^{\alpha})^T\boldsymbol{R}^{\alpha} = \boldsymbol{I}, && \boldsymbol{R}^{\alpha} \text{ rotation tensor,}\\
&\boldsymbol{U}^{\alpha} = (\boldsymbol{U}^{\alpha})^T,\, \boldsymbol{V}^{\alpha} = (\boldsymbol{V}^{\alpha})^T, && \text{positive definite,}\\
&\boldsymbol{U}^{\alpha} = \sqrt{\boldsymbol{C}^{\alpha}} = \sqrt{(\boldsymbol{F}^{\alpha})^T\boldsymbol{F}^{\alpha}}, && \\
& && \text{by spectral decomposition.}\\
&\boldsymbol{V}^{\alpha} = \sqrt{\boldsymbol{B}^{\alpha}} = \sqrt{\boldsymbol{F}^{\alpha}(\boldsymbol{F}^{\alpha})^T}, &&
\end{aligned} \tag{22.13}$$

Figure 22.4 explains the rotation and stretch operations geometrically. For the proof of all these statements, see, e.g., [16].

With $(22.13)_1$, we easily show

$$\boldsymbol{U}^{\alpha} = (\boldsymbol{R}^{\alpha})^T\boldsymbol{V}^{\alpha}\boldsymbol{R}^{\alpha}, \quad \boldsymbol{V}^{\alpha} = \boldsymbol{R}^{\alpha}\boldsymbol{U}^{\alpha}(\boldsymbol{R}^{\alpha})^T. \tag{22.14}$$

Remark

- $$\begin{aligned}
\mathrm{d}s^2 &= \mathrm{d}\boldsymbol{x}\cdot\mathrm{d}\boldsymbol{x} = \boldsymbol{F}^{\alpha}\mathrm{d}\boldsymbol{X}^{\alpha}\cdot\boldsymbol{F}^{\alpha}\mathrm{d}\boldsymbol{X}^{\alpha} = \mathrm{d}\boldsymbol{X}^{\alpha}\cdot(\boldsymbol{F}^{\alpha})^T\boldsymbol{F}^{\alpha}\mathrm{d}\boldsymbol{X}^{\alpha}\\
&= \mathrm{d}\boldsymbol{X}^{\alpha}\cdot\boldsymbol{C}^{\alpha}\mathrm{d}\boldsymbol{X}^{\alpha}, \qquad \boldsymbol{C}^{\alpha} = (\boldsymbol{F}^{\alpha})^T\boldsymbol{F}^{\alpha},\\
\boldsymbol{C}^{\alpha} &= right\ \text{CAUCHY–GREEN}\ deformation\ tensor.
\end{aligned} \tag{22.15}$$

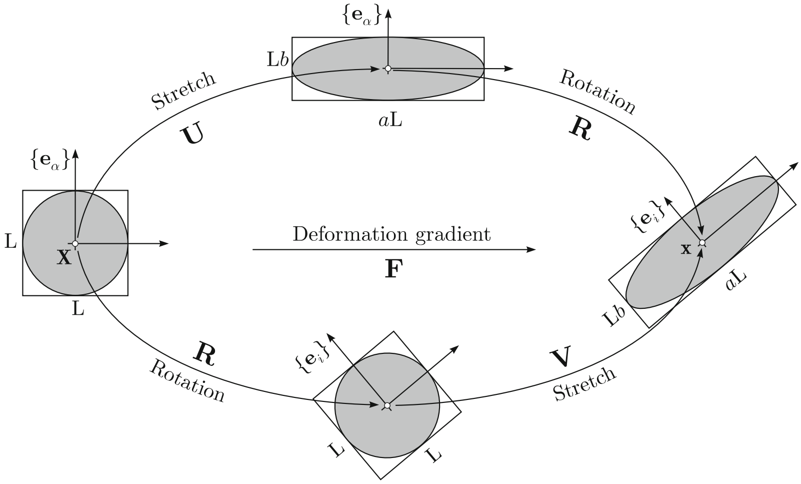

Fig. 22.4 Polar decomposition of the deformation gradient, interpreted as the composition process of stretch, followed by rotation or vice versa, from HUTTER–JÖHNK p. 28 [16]

- $$\begin{aligned} \mathrm{d}(S^\alpha)^2 &= \mathrm{d}\boldsymbol{X}^\alpha \cdot \mathrm{d}\boldsymbol{X}^\alpha = (\boldsymbol{F}^\alpha)^{-1}\mathrm{d}\boldsymbol{x} \cdot (\boldsymbol{F}^\alpha)^{-1}\mathrm{d}\boldsymbol{x} = \mathrm{d}\boldsymbol{x} \cdot (\boldsymbol{F}^\alpha)^{-T}(\boldsymbol{F}^\alpha)^{-1}\mathrm{d}\boldsymbol{x} \\ &= \mathrm{d}\boldsymbol{x} \cdot (\boldsymbol{B}^\alpha)^{-1}\mathrm{d}\boldsymbol{x}, \qquad \boldsymbol{B}^\alpha = \boldsymbol{F}^\alpha(\boldsymbol{F}^\alpha)^T, \\ \boldsymbol{B}^\alpha &= \textit{left}\ \text{CAUCHY–GREEN}\ \textit{deformation tensor}. \end{aligned} \tag{22.16}$$

- $$\begin{aligned} \boldsymbol{C}^\alpha &= (\boldsymbol{F}^\alpha)^T\boldsymbol{F}^\alpha = (\boldsymbol{R}^\alpha\boldsymbol{U}^\alpha)^T(\boldsymbol{R}^\alpha\boldsymbol{U}^\alpha) \\ &= (\boldsymbol{U}^\alpha)^T\left((\boldsymbol{R}^\alpha)^T\boldsymbol{R}^\alpha\right)\boldsymbol{U}^\alpha = (\boldsymbol{U}^\alpha)^T\boldsymbol{U}^\alpha = (\boldsymbol{U}^\alpha)^2, \\ \boldsymbol{B}^\alpha &= \boldsymbol{F}^\alpha(\boldsymbol{F}^\alpha)^T = \boldsymbol{V}^\alpha(\boldsymbol{R}^\alpha(\boldsymbol{R}^\alpha)^T)(\boldsymbol{V}^\alpha)^T = (\boldsymbol{V}^\alpha)^2. \end{aligned}$$

- $$\begin{aligned} \mathrm{d}s^2 - \mathrm{d}(S^\alpha)^2 &= \mathrm{d}\boldsymbol{x}\cdot\mathrm{d}\boldsymbol{x} - \mathrm{d}\boldsymbol{X}^\alpha\cdot\mathrm{d}\boldsymbol{X}^\alpha = \mathrm{d}\boldsymbol{X}^\alpha \cdot (\boldsymbol{C}^\alpha - \boldsymbol{I})\,\mathrm{d}\boldsymbol{X}^\alpha, \\ \boldsymbol{E}^\alpha &= \tfrac{1}{2}(\boldsymbol{C}^\alpha - \boldsymbol{I}), \\ \boldsymbol{E}^\alpha &= \text{GREEN or GREEN–LAGRANGE}\ \textit{strain tensor}. \end{aligned} \tag{22.17}$$

- $$\begin{aligned} \mathrm{d}s^2 - \mathrm{d}(S^\alpha)^2 &= \mathrm{d}\boldsymbol{x}\cdot\mathrm{d}\boldsymbol{x} - (\boldsymbol{F}^\alpha)^{-1}\mathrm{d}\boldsymbol{x}\cdot(\boldsymbol{F}^\alpha)^{-1}\mathrm{d}\boldsymbol{x} \\ &= \mathrm{d}\boldsymbol{x}\cdot\left(\boldsymbol{I} - (\boldsymbol{F}^\alpha)^{-T}(\boldsymbol{F}^\alpha)^{-1}\right)\mathrm{d}\boldsymbol{x} \\ &= \mathrm{d}\boldsymbol{x}\cdot\left(\boldsymbol{I} - (\boldsymbol{B}^\alpha)^{-1}\right)\mathrm{d}\boldsymbol{x} \\ &= \mathrm{d}\boldsymbol{x}\cdot 2\boldsymbol{A}^\alpha\mathrm{d}\boldsymbol{x}, \qquad \boldsymbol{A}^\alpha = \tfrac{1}{2}\left(\boldsymbol{I} - (\boldsymbol{B}^\alpha)^{-1}\right), \\ \boldsymbol{A}^\alpha &= \text{ALMANSI or EULER–ALMANSI}\ \textit{strain tensor}. \end{aligned} \tag{22.18}$$

In these– expressions, the notation $(\boldsymbol{F}^\alpha)^{-T} \equiv ((\boldsymbol{F}^\alpha)^{-1})^T = ((\boldsymbol{F}^\alpha)^T)^{-1}$ was employed as is customary in the continuum mechanics literature.

- It is easy to see that $\boldsymbol{E}^\alpha$ is a second-order tensor in the reference configuration and, thus, has the Cartesian tensor representation $(E^\alpha)_{AB}$. On the other hand,

$\boldsymbol{A}^\alpha$ is referred to the present configuration and has the Cartesian components $(A^\alpha)_{ij}$. Here, we have used upper (lower) case letters to indicate components in the reference (present) configuration. Somewhat colloquial we may say that "$\boldsymbol{E}^\alpha(\boldsymbol{A}^\alpha)$ has both legs in the reference (present) configuration".[2] It follows that these two strain measures are related to one another. Indeed,

$$\begin{aligned}
(\boldsymbol{F}^\alpha)^T\boldsymbol{A}^\alpha\boldsymbol{F}^\alpha &= \tfrac{1}{2}(\boldsymbol{F}^\alpha)^T\left(\boldsymbol{I}-(\boldsymbol{B}^\alpha)^{-1}\right)\boldsymbol{F}^\alpha \\
&= \tfrac{1}{2}\left((\boldsymbol{F}^\alpha)^T\boldsymbol{F}^\alpha-(\boldsymbol{F}^\alpha)^T((\boldsymbol{F}^\alpha)^{-T}(\boldsymbol{F}^\alpha)^{-1})\boldsymbol{F}^\alpha\right) \\
&= \tfrac{1}{2}\left(\boldsymbol{C}^\alpha-\boldsymbol{I}\right)\overset{def}{=}\boldsymbol{E}^\alpha, \quad \square \qquad (22.19) \\
(\boldsymbol{F}^\alpha)^{-T}\boldsymbol{E}^\alpha(\boldsymbol{F}^\alpha)^{-1} &= \tfrac{1}{2}(\boldsymbol{F}^\alpha)^{-T}\left((\boldsymbol{F}^\alpha)^T\boldsymbol{F}^\alpha-\boldsymbol{I}\right)(\boldsymbol{F}^\alpha)^{-1} \\
&= \tfrac{1}{2}\left(\boldsymbol{I}-(\boldsymbol{F}^\alpha)^{-T}(\boldsymbol{F}^\alpha)^{-1}\right) \\
&= \tfrac{1}{2}\left(\boldsymbol{I}-(\boldsymbol{B}^\alpha)^{-1}\right)\overset{def}{=}\boldsymbol{A}^\alpha, \quad \square \qquad (22.20)
\end{aligned}$$

- $$\boldsymbol{R}^\alpha=\boldsymbol{F}^\alpha(\boldsymbol{U}^\alpha)^{-1}=(\boldsymbol{V}^\alpha)^{-1}\boldsymbol{F}^\alpha. \qquad (22.21)$$

Result: The strain and rotation matrices are known, once the motion function $\boldsymbol{\chi}^\alpha(\boldsymbol{X}^\alpha,t)$ is determined. In fact, when $\boldsymbol{F}^\alpha$ is known, so are $\boldsymbol{U}^\alpha$, $\boldsymbol{V}^\alpha$ and $\boldsymbol{R}^\alpha$. This is not so for COSSERAT continua, as we shall see right now.

22.4 Micromotion

In the *micropolar* COSSERAT *theory*, the material points are treated as *rigid bodies*. In these, the additional rotational degrees of freedom are represented by vectors—so-called *directors*—which are attached to the material points and move with these, but perform independent rotations. In a micropolar theory, these directors perform rotations, which can be expressed by a *proper orthogonal rank-2 tensor* $\bar{\boldsymbol{R}}^\alpha$ (note the bar!), characteristic for the microrotation, which differs from the classical rotation tensor $\boldsymbol{R}^\alpha$ (without the bar!). We take the position that the COSSERAT tensor $\bar{\boldsymbol{R}}^\alpha$ rotates the directors $\boldsymbol{\Xi}^\alpha$ from their reference configuration into the present configuration as follows:

$$\boldsymbol{\xi}^\alpha=\bar{\boldsymbol{R}}^\alpha(\boldsymbol{X}^\alpha,t)\boldsymbol{\Xi}^\alpha. \qquad (22.22)$$

Obviously, the proper orthogonal tensor $\bar{\boldsymbol{R}}$ has the properties

$$(\bar{\boldsymbol{R}}^\alpha)^T\bar{\boldsymbol{R}}^\alpha=\boldsymbol{I}, \quad (\bar{\boldsymbol{R}}^\alpha)^{-1}=(\bar{\boldsymbol{R}}^\alpha)^T, \quad \det\bar{\boldsymbol{R}}=+1, \quad \boldsymbol{\Xi}^\alpha=(\bar{\boldsymbol{R}}^\alpha)^T\boldsymbol{\xi}^\alpha. \qquad (22.23)$$

---

[2] In this spirit, it is easily seen that $\boldsymbol{R}^\alpha$ is a two-point tensor with its first leg in the present configuration and the second leg in the reference configuration. We will henceforth use this somewhat colloquial way of identifying the spaces in which the tensors "live".

Note, the formal analogy between (22.22), (22.23) and (22.11), (22.12).

It should be remarked that micro deformations more general than (22.22) could be postulated. One possibility is to write

$$\boldsymbol{\xi}^\alpha = \bar{\bar{\boldsymbol{F}}}^\alpha (\boldsymbol{X}^\alpha, t)\boldsymbol{\Xi}^\alpha = \bar{\bar{\boldsymbol{R}}}^\alpha (\boldsymbol{X}^\alpha, t)\,\bar{\bar{\boldsymbol{U}}}^\alpha\, \boldsymbol{\Xi}^\alpha = \bar{\bar{\boldsymbol{V}}}^\alpha\, \bar{\bar{\boldsymbol{R}}}^\alpha (\boldsymbol{X}^\alpha, t)\boldsymbol{\Xi}^\alpha,$$

in which $\bar{\bar{\boldsymbol{F}}}^\alpha$ is a "micro-deformation gradient" and $\bar{\bar{\boldsymbol{U}}}^\alpha$ and $\bar{\bar{\boldsymbol{V}}}^\alpha$ are "micro-stretch" tensors. Double bars are used here to differentiate these from $\bar{\boldsymbol{F}}^\alpha$ and $\bar{\boldsymbol{U}}^\alpha$, $\bar{\boldsymbol{V}}^\alpha$, which would be associated with the micropolar formulation.

The concept of directors was originally introduced by the COSSERAT brothers, but the concept of extended deformation measures has largely been developed much later. An account on the COSSERATs approach to derive the governing equations for micropolar continua is given in Sect. 22.12 "COSSERATs book of 1909, its reception and influence on the 20th century and beyond". It may be advantageous to glance through Sect. 22.12 first.

22.5 Extended Deformation Measures

In COSSERAT continua, material particles are envisaged to constitute tiny particles, which, apart from their classical motion, are able to perform their independent (micro)-rotation. Figure 22.5 illustrates this graphically. The translational motion at a material point of constituent α is illustrated as in classical continua by a material vectorial increment $\mathrm{d}\boldsymbol{X}^\alpha$ (in the reference configuration). It is mapped by the motion function $\boldsymbol{x} = \chi^\alpha(\boldsymbol{X}^\alpha, t)$ to the corresponding placement in the reference configuration as the increment $\mathrm{d}\boldsymbol{x}$. Analogously, a vectorial element $\boldsymbol{\Xi}^\alpha$ in the reference configuration, participating in the deformation (here restricted to a rotation) of constituent α is independently mapped by a rotation $\bar{\boldsymbol{R}}^\alpha$ to $\boldsymbol{\xi}^\alpha$ in the present configuration: $\boldsymbol{\xi}^\alpha = \bar{\boldsymbol{R}}^\alpha \boldsymbol{\Xi}^\alpha$. Since the length of $\boldsymbol{\Xi}^\alpha$ is not relevant, but only its direction, these vectorial elements $\boldsymbol{\Xi}^\alpha(\boldsymbol{\xi}^\alpha)$ are called *directors* in the reference and present configurations, respectively. At this state of the development of the theory, this transformation satisfies orthogonality and continuity, i.e.,

$$\bar{\boldsymbol{R}}^\alpha(\bar{\boldsymbol{R}}^\alpha)^T = 1, \quad (\bar{\boldsymbol{R}}^\alpha)^{-1} = (\bar{\boldsymbol{R}}^\alpha)^T, \quad \det\bar{\boldsymbol{R}}^\alpha = +1,$$

but is not yet specified.

The deformation tensors of the standard continuum mechanical formulation are defined by combinations of squared line elements in the reference and present configurations. *By contrast, the deformation tensors in the* COSSERAT *continuum are based on scalar products of directors and line elements in the reference and present configurations, respectively.*

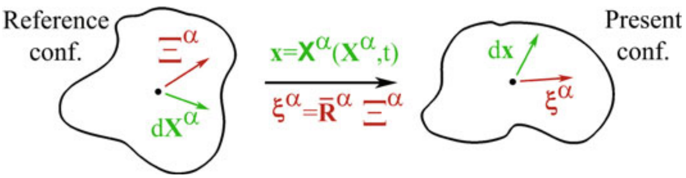

Fig. 22.5 Reference and present configurations of the component α of a mixture body isolating an initial and present placement of the particle α. dX^α is a material vectorial length increment of constituent α in the reference configuration that is mapped by the motion function $\boldsymbol{x} = \boldsymbol{\chi}(\boldsymbol{X}^\alpha, t)$ onto d$\boldsymbol{x}$ in the present configuration. Analogously, a director $\boldsymbol{\Xi}^\alpha$ in the reference configuration is mapped by $\bar{\boldsymbol{R}}^\alpha$ into the present configuration, $\boldsymbol{\xi}^\alpha$

Examples of Computations

Recall that the overbar will be used to identify quantities of the COSSERAT theory, which have their analogues in the classical theory (without overbar).

1.

$$\begin{aligned} \boldsymbol{\xi}^\alpha \cdot \mathrm{d}\boldsymbol{x} &= \bar{\boldsymbol{R}}^\alpha \boldsymbol{\Xi}^\alpha \cdot \boldsymbol{F}^\alpha \mathrm{d}\boldsymbol{X}^\alpha = \boldsymbol{\Xi}^\alpha \cdot (\bar{\boldsymbol{R}}^\alpha)^T \boldsymbol{F}^\alpha \mathrm{d}\boldsymbol{X}^\alpha \\ &= \quad \boldsymbol{\Xi}^\alpha \cdot \bar{\boldsymbol{U}}^\alpha \mathrm{d}\boldsymbol{X}^\alpha, \qquad \bar{\boldsymbol{U}}^\alpha = (\bar{\boldsymbol{R}}^\alpha)^T \boldsymbol{F}^\alpha. \end{aligned} \tag{22.24}$$

Note that the overbar indicates that this first COSSERAT *deformation tensor* is, in general, different from $\boldsymbol{U}^\alpha$ of the classical theory. Note, moreover, that $\bar{\boldsymbol{U}}^\alpha \neq (\bar{\boldsymbol{U}}^\alpha)^T$, in general; this follows immediately from (22.24).

2.

$$\begin{aligned} \boldsymbol{\Xi}^\alpha \cdot \mathrm{d}\boldsymbol{X}^\alpha &= (\bar{\boldsymbol{R}}^\alpha)^T \boldsymbol{\xi}^\alpha \cdot (\boldsymbol{F}^\alpha)^{-1} \mathrm{d}\boldsymbol{x} = \boldsymbol{\xi}^\alpha \cdot \underbrace{\left(\bar{\boldsymbol{R}}^\alpha (\boldsymbol{F}^\alpha)^{-1}\right)}_{(\bar{\boldsymbol{V}}^\alpha)^{-1}} \mathrm{d}\boldsymbol{x} \\ &= \boldsymbol{\xi}^\alpha \cdot (\bar{\boldsymbol{V}}^\alpha)^{-1} \mathrm{d}\boldsymbol{x}, \qquad \bar{\boldsymbol{V}}^\alpha = \boldsymbol{F}^\alpha (\bar{\boldsymbol{R}}^\alpha)^T. \end{aligned} \tag{22.25}$$

Note the similarities of the formulae $(22.24)_1$ and (22.25) with (22.13).

3. Solving $(22.24)_4$ and $(22.25)_4$ for $\boldsymbol{F}^\alpha$ gives

$$\boldsymbol{F}^\alpha = \bar{\boldsymbol{R}}^\alpha \bar{\boldsymbol{U}}^\alpha = \bar{\boldsymbol{V}}^\alpha \bar{\boldsymbol{R}}^\alpha. \tag{22.26}$$

Remark

- (22.26) is similar to the polar decompositions (22.13), but $\bar{\boldsymbol{R}}^\alpha$ is defined independently of the translational motion.
- $\bar{\boldsymbol{U}}^\alpha$ and $\bar{\boldsymbol{V}}^\alpha$ are not symmetric, they have in general both nontrivial symmetric and skew-symmetric components.
- $\bar{\boldsymbol{U}}^\alpha$ and $\bar{\boldsymbol{V}}^\alpha$ are called the *first* COSSERAT *stretch tensors*.

4. One can also derive formal analogues to (22.14)

$$\begin{aligned}\bar{\boldsymbol{U}}^{\alpha} &= (\bar{\boldsymbol{R}}^{\alpha})^{T}\boldsymbol{F}^{\alpha} = (\bar{\boldsymbol{R}}^{\alpha})^{T}\bar{\boldsymbol{V}}^{\alpha}\bar{\boldsymbol{R}}^{\alpha},\\ \bar{\boldsymbol{V}}^{\alpha} &= \boldsymbol{F}^{\alpha}(\bar{\boldsymbol{R}}^{\alpha})^{T} = \bar{\boldsymbol{R}}^{\alpha}\bar{\boldsymbol{U}}^{\alpha}(\bar{\boldsymbol{R}}^{\alpha})^{T}.\end{aligned} \tag{22.27}$$

5. From $\boldsymbol{F}^{\alpha} = \boldsymbol{R}^{\alpha}\boldsymbol{U}^{\alpha} = \boldsymbol{V}^{\alpha}, \boldsymbol{R}^{\alpha}$ we obtain

$$\begin{aligned}\bar{\boldsymbol{U}}^{\alpha} &= (\bar{\boldsymbol{R}}^{\alpha})^{T}\boldsymbol{F}^{\alpha} = \underbrace{\left((\bar{\boldsymbol{R}}^{\alpha})^{T}\boldsymbol{R}^{\alpha}\right)}_{(\boldsymbol{R}^{\alpha})^{*}}\boldsymbol{U}^{\alpha} = \left((\boldsymbol{R}^{\alpha})^{*}\right)\boldsymbol{U}^{\alpha},\\ \bar{\boldsymbol{V}}^{\alpha} &= \boldsymbol{F}^{\alpha}(\bar{\boldsymbol{R}}^{\alpha})^{T} = \boldsymbol{V}^{\alpha}\underbrace{\left(\boldsymbol{R}^{\alpha}(\bar{\boldsymbol{R}}^{\alpha})^{T}\right)}_{{}^{*}\boldsymbol{R}^{\alpha}} = \boldsymbol{V}^{\alpha}\left({}^{*}\boldsymbol{R}^{\alpha}\right).\end{aligned} \tag{22.28}$$

It is easy to derive from these relations the formulae

$$\left((\boldsymbol{R}^{\alpha})^{*}\right) = (\bar{\boldsymbol{R}}^{\alpha})^{T}\left({}^{*}\boldsymbol{R}^{\alpha}\right)\bar{\boldsymbol{R}}^{\alpha}, \quad \left({}^{*}\boldsymbol{R}^{\alpha}\right) = \bar{\boldsymbol{R}}^{\alpha}\left((\boldsymbol{R}^{\alpha})^{*}\right)(\bar{\boldsymbol{R}}^{\alpha})^{T}. \tag{22.29}$$

These formulae show that the COSSERAT stretch tensors $\bar{\boldsymbol{U}}^{\alpha}$ and $\bar{\boldsymbol{V}}^{\alpha}$ are compositions of classical stretch tensors with rotations, see (22.28), and the rotations ${}^{*}\boldsymbol{R}^{\alpha}$ and $(\boldsymbol{R}^{\alpha})^{*}$ themselves are compositions of $\boldsymbol{R}^{\alpha}$ and $\bar{\boldsymbol{R}}^{\alpha}$.

6. Now take $(22.28)_1$ and (22.26) and compute the right CAUCHY–GREEN deformation tensor as follows:

$$\begin{aligned}\boldsymbol{C}^{\alpha} &= (\boldsymbol{F}^{\alpha})^{T}\boldsymbol{F}^{\alpha} = \left(\bar{\boldsymbol{R}}^{\alpha}\bar{\boldsymbol{U}}^{\alpha}\right)^{T}\left(\bar{\boldsymbol{R}}^{\alpha}\bar{\boldsymbol{U}}^{\alpha}\right)\\ &= (\bar{\boldsymbol{U}}^{\alpha})^{T}\left((\bar{\boldsymbol{R}}^{\alpha})^{T}\bar{\boldsymbol{R}}^{\alpha}\right)\bar{\boldsymbol{U}}^{\alpha} = (\bar{\boldsymbol{U}}^{\alpha})^{T}\bar{\boldsymbol{U}}^{\alpha} = \bar{\boldsymbol{C}}^{\alpha}.\end{aligned} \tag{22.30}$$

Similarly for $\boldsymbol{B}^{\alpha}$:

$$\begin{aligned}\boldsymbol{B}^{\alpha} &= \boldsymbol{F}^{\alpha}(\boldsymbol{F}^{\alpha})^{T} = \bar{\boldsymbol{V}}^{\alpha}\left(\bar{\boldsymbol{R}}^{\alpha}(\bar{\boldsymbol{R}}^{\alpha})^{T}\right)(\bar{\boldsymbol{V}}^{\alpha})^{T},\\ &= \bar{\boldsymbol{V}}^{\alpha}(\bar{\boldsymbol{V}}^{\alpha})^{T} = \bar{\boldsymbol{B}}^{\alpha}.\end{aligned} \tag{22.31}$$

Note that the positions of the transposed tensors in (22.30) and (22.31) are important, because the tensors $\bar{\boldsymbol{U}}^{\alpha}$ and $\bar{\boldsymbol{V}}^{\alpha}$ are not symmetric. Furthermore, it is interesting that the classical CAUCHY–GREEN deformation tensors are expressible in the COSSERAT stretch tensors.

7.

$$
\begin{aligned}
\boldsymbol{\xi}^\alpha \cdot \mathrm{d}\boldsymbol{x} - \boldsymbol{\Xi}^\alpha \cdot d\boldsymbol{X}^\alpha &= \boldsymbol{\Xi}^\alpha \cdot \underbrace{(\bar{\boldsymbol{R}}^\alpha)^T \boldsymbol{F}^\alpha}_{\bar{U}^\alpha,(22.27)} \mathrm{d}\boldsymbol{X}^\alpha - \boldsymbol{\Xi}^\alpha \cdot \mathrm{d}\boldsymbol{X}^\alpha \\
&= \boldsymbol{\Xi}^\alpha \cdot \underbrace{\left(\bar{\boldsymbol{U}}^\alpha - \boldsymbol{I}\right)}_{\bar{\boldsymbol{E}}^\alpha} \mathrm{d}\boldsymbol{X}^\alpha, \qquad (22.32)\\
\bar{\boldsymbol{E}}^\alpha &= \left(\bar{\boldsymbol{U}}^\alpha - \boldsymbol{I}\right) \quad \text{compare with (22.17)}, \qquad (22.33)\\
\boldsymbol{\xi}^\alpha \cdot \mathrm{d}\boldsymbol{x} - \boldsymbol{\Xi}^\alpha \cdot d\boldsymbol{X}^\alpha &= \boldsymbol{\xi}^\alpha \cdot \mathrm{d}\boldsymbol{x} - (\bar{\boldsymbol{R}}^\alpha)^T \boldsymbol{\xi}^\alpha \cdot (\boldsymbol{F}^\alpha)^{-1} \mathrm{d}\boldsymbol{x} \\
&= \boldsymbol{\xi}^\alpha \cdot \left(\boldsymbol{I} - \underbrace{\bar{\boldsymbol{R}}^{-T} (\boldsymbol{F}^\alpha)^{-1}}_{(\bar{\boldsymbol{V}}^\alpha)^{-1}} \right) \mathrm{d}\boldsymbol{x} = \boldsymbol{\xi}^\alpha \cdot \bar{\boldsymbol{A}}^\alpha \mathrm{d}\boldsymbol{x}, \qquad (22.34)\\
\bar{\boldsymbol{A}}^\alpha &= \left(\boldsymbol{I} - (\bar{\boldsymbol{V}}^\alpha)^{-1}\right) \quad \text{compare with (22.18)}. \qquad (22.35)
\end{aligned}
$$

Remark

(i) $\bar{\boldsymbol{E}}^\alpha$ and $\bar{\boldsymbol{A}}^\alpha$ do not contain a factor $\frac{1}{2}$. This is so, because they are defined with $\bar{\boldsymbol{U}}^\alpha$ and $(\bar{\boldsymbol{V}}^\alpha)^{-1}$, not with $\bar{\boldsymbol{C}}^\alpha$ and $(\bar{\boldsymbol{B}}^\alpha)^{-1}$. These overbarred quantities are not even defined.

(ii) $\bar{\boldsymbol{E}}^\alpha$ is a strain measure of GREEN–LAGRANGE type; it has both "legs in the reference frame". Alternatively $\bar{\boldsymbol{A}}^\alpha$ is a rank-2 tensor of ALMANSI–EULER type with both "legs in the present configuration".

8. The following transformation formulae for $\bar{\boldsymbol{E}}^\alpha$ and $\bar{\boldsymbol{A}}^\alpha$ are easily verified with the formulae (22.32) and (22.34):

$$
\begin{aligned}
\bar{\boldsymbol{E}}^\alpha &= (\bar{\boldsymbol{R}}^\alpha)^T \bar{\boldsymbol{A}}^\alpha \boldsymbol{F}^\alpha, \qquad (22.36)\\
\bar{\boldsymbol{A}}^\alpha &= \bar{\boldsymbol{R}}^\alpha \bar{\boldsymbol{E}}^\alpha (\boldsymbol{F}^\alpha)^{-1}. \qquad (22.37)
\end{aligned}
$$

Indeed, consider (22.37)

$$
\begin{aligned}
\bar{\boldsymbol{A}}^\alpha \quad &\overset{?}{=} \quad \bar{\boldsymbol{R}}^\alpha \bar{\boldsymbol{E}}^\alpha (\boldsymbol{F}^\alpha)^{-1} \overset{(22.32)}{=} \bar{\boldsymbol{R}}^\alpha \left(\bar{\boldsymbol{U}}^\alpha - \boldsymbol{I}\right) (\boldsymbol{F}^\alpha)^{-1} \\
&\overset{(22.24)}{=} \quad \bar{\boldsymbol{R}}^\alpha \left((\bar{\boldsymbol{R}}^\alpha)^T \boldsymbol{F}^\alpha - \boldsymbol{I}\right) (\boldsymbol{F}^\alpha)^{-1} \\
&= \quad \boldsymbol{I} - \bar{\boldsymbol{R}}^\alpha (\boldsymbol{F}^\alpha)^{-1} \overset{(22.26)}{=} \boldsymbol{I} - \bar{\boldsymbol{R}}^\alpha (\bar{\boldsymbol{R}}^\alpha)^{-1} (\bar{\boldsymbol{V}}^\alpha)^{-1} \\
&= \quad \left(\boldsymbol{I} - (\bar{\boldsymbol{V}}^\alpha)^{-1}\right) \overset{(22.35)}{=} \bar{\boldsymbol{A}}^\alpha,
\end{aligned}
$$

which proves (22.37). With this result, Eq. (22.36) is now evident. Formulae (22.36), (22.37) are expressions of pullback and push-forward operations.[3]

---

[3] 'Pullback' and 'push-forward' operations mean mappings of a quantity from the present to the reference configuration and vice versa, e.g., $\mathrm{d}\boldsymbol{X}^\alpha = (\boldsymbol{F}^\alpha)^{-1}\mathrm{d}\boldsymbol{x}$ and $\mathrm{d}\boldsymbol{x} = \boldsymbol{F}^\alpha \mathrm{d}\boldsymbol{X}^\alpha$ (no sum over α).

22.6 Curvature Tensors

Apart from $\bar{\boldsymbol{U}}^{\alpha}$ and $\bar{\boldsymbol{V}}^{\alpha}$, another deformation measure is important in the description of the spatial change of the micromotion. The relevant quantity is the following third rank tensor:

$$ {}^{R}\overset{3}{\mathcal{K}}^{\alpha} = \left((\bar{\boldsymbol{R}}^{\alpha})^{T}\,\mathrm{Grad}\bar{\boldsymbol{R}}^{\alpha}\right)^{\underline{3}} \tag{22.38}$$

This tensor is called *curvature tensor* or *second* COSSERAT *deformation tensor*. The left upper R on the left-hand side is a reminder that ${}^{R}\overset{3}{\mathcal{K}}^{\alpha}$ has all legs in the reference configuration, and the superscripted '3' tells us that it is third order, as does the '$\underline{3}$' index on the right-hand side. So, we get the Cartesian index representation

$$\left({}^{R}\overset{3}{\mathcal{K}}^{\alpha}\right)_{ABC} = (\bar{R}^{\alpha})_{iA}(\bar{R}^{\alpha})_{iB,C}. \tag{22.39}$$

By using the identity

$$\mathrm{Grad}^{\alpha}\left((\bar{\boldsymbol{R}}^{\alpha})^{T}\bar{\boldsymbol{R}}^{\alpha}\right) = \overset{3}{\boldsymbol{0}}, \tag{22.40}$$

it can be shown that ${}^{R}\overset{3}{\mathcal{K}}^{\alpha}$ is skew-symmetric with respect to the first two indices of the basis system,

$${}^{R}\overset{3}{\mathcal{K}}^{\alpha} = -\left({}^{R}\overset{3}{\mathcal{K}}^{\alpha}\right)^{\overset{12}{T}}. \tag{22.41}$$

The symbol $(\cdot)^{\overset{12}{T}}$ indicates that of the Cartesian components, the first and second indices are interchanged. Because of the skew-symmetry of ${}^{R}\overset{3}{\mathcal{K}}^{\alpha}$ only 9 of its 27

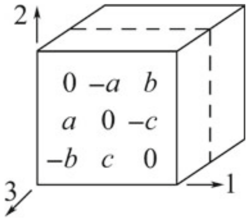

Fig. 22.6 The Cartesian components of a rank-3 tensor can be represented by the 27 elements of a 3 × 3 × 3 cube. If the tensor is skew-symmetric with respect to its 1−2 elements, it has in each of the three (1−2)-planes three independent elements, thus a total of nine independent elements, which can be arranged in a 3 × 3 rank-2 tensor

components are independent, as explained in **Fig. 22.6**. This suggests that a second-order curvature tensor can be constructed. Indeed, with the permutation tensor[4] $\overset{3}{\boldsymbol{E}}$, the following *rank-2 curvature tensor* may be defined,

$$
\begin{aligned}
{}^R\overset{2}{\mathcal{K}}{}^{\alpha} &= -\frac{1}{2}\left(\overset{3}{\boldsymbol{E}}\;{}^R\overset{3}{\mathcal{K}}{}^{\alpha}\right)^{\underline{2}},\\
\left({}^R\overset{2}{\mathcal{K}}{}^{\alpha}\right)_{AB} &= \frac{1}{2}\varepsilon_{AMN}\;{}^R\mathcal{K}_{MNB},
\end{aligned}
\tag{22.42}
$$

which shows its representation in symbolic and in Cartesian index notation. This tensor no longer exhibits symmetry properties, and it has ‘both legs in the reference basis’.

To prove (22.41), we start from

$$
\begin{aligned}
&\left((\bar{R}^{\alpha})_{iA}(\bar{R}^{\alpha})_{iB}\right)_{,C} = 0\\
\text{or}\qquad &\left((\bar{R}^{\alpha})_{iA}\right)_{,C}(\bar{R}^{\alpha})_{iB} + (\bar{R}^{\alpha})_{iA}\left(\bar{R}^{\alpha}\right)_{iB,C} = 0\\
\Longrightarrow\qquad &\underbrace{(\bar{R}^{\alpha})_{iA}(\bar{R}^{\alpha})_{iB,C}}_{\left({}^R\overset{3}{\mathcal{K}}{}^{\alpha}\right)_{AB,C}} = -(\bar{R}^{\alpha})_{iA,C}(\bar{R}^{\alpha})_{iB} = -\underbrace{(\bar{R}^{\alpha})_{iB})(\bar{R}^{\alpha})_{iA,C}}_{\left({}^R\overset{3}{\mathcal{K}}{}^{\alpha}\right)_{BA,C}}
\end{aligned}
$$

which proves the statement.

Another curvature tensor, which is referred to the present configuration, is

$$
\overset{3}{\mathcal{K}}{}^{\alpha} = \left[\left(\left(\operatorname{grad}\bar{\boldsymbol{R}}^{\alpha}\right)^{\overset{23}{T}}\bar{\boldsymbol{R}}^{\alpha}\right)^{\underline{3}}\right]^{\overset{23}{T}} \overset{(2)}{=} -\left(\bar{\boldsymbol{R}}^{\alpha}\operatorname{grad}\,(\bar{\boldsymbol{R}}^{\alpha})^{T}\right)^{\underline{3}}, \tag{22.43}
$$

in which the step $\overset{(2)}{=}$ follows by use of

$$
\operatorname{grad}\,\left(\bar{\boldsymbol{R}}^{\alpha}(\bar{\boldsymbol{R}}^{\alpha})^{T}\right) = \overset{3}{\boldsymbol{0}}.
$$

The tensor (22.43) is also skew-symmetric with only nine independent components. The associated rank-2 curvature tensor is constructible by

$$
\overset{2}{\mathcal{K}}{}^{\alpha} = -\frac{1}{2}\left(\overset{3}{\boldsymbol{E}}\overset{3}{\mathcal{K}}{}^{\alpha}\right)^{\underline{2}} \tag{22.44}
$$

---

[4] This is the same as the so-called ϵ-tensor or LEVI-CIVITÀ tensor with the Cartesian components given by

$$
\left(\overset{3}{\boldsymbol{E}}\right)_{ABC} = \varepsilon_{ABC} = \begin{cases} 1 & \text{for an even perturbation of } ABC,\\ 0 & \text{for no permutation of } ABC,\\ -1 & \text{for an odd permutation of } ABC. \end{cases}
$$

and “has both legs in the present configuration”. It is customary to omit the superscripts for the second-order curvature tensor:

$$
{}^{R}\overset{2}{\bar{\mathcal{K}}}{}^{\alpha} \equiv {}^{R}\bar{\mathcal{K}}^{\alpha}, \qquad \overset{2}{\bar{\mathcal{K}}}{}^{\alpha} \equiv \bar{\mathcal{K}}^{\alpha}.
$$

It can be shown, see later, that

$$
\bar{\mathcal{K}}^{\alpha} = \bar{\boldsymbol{R}}^{\alpha}\left({}^{R}\bar{\mathcal{K}}^{\alpha}\right)(\boldsymbol{F}^{\alpha})^{-1}, \quad {}^{R}\bar{\mathcal{K}}^{\alpha} = (\bar{\boldsymbol{R}}^{\alpha})^{T}\left(\bar{\mathcal{K}}^{\alpha}\right)\boldsymbol{F}^{\alpha} \tag{22.45}
$$

can be transformed into one another with the indicated push-forward and pullback operations. These curvature measures go back to ERINGEN and KAFADAR (1976) [9]. Other curvature measures have also been suggested; their “legs lie in intermediate configurations” and are needed in plasticity formulations (see STEINMANN [25] and VOLK [43]).

22.7 Velocity Gradient and Gyration Tensor

We commence with the presentation of the classical expressions of rate quantities.

The *spatial velocity gradient* grad $\boldsymbol{v}^{\alpha} = \boldsymbol{L}^{\alpha}$ can be related to $\boldsymbol{F}^{\alpha}$ as follows:

$$
\begin{aligned}
\mathrm{d}\boldsymbol{x}'^{\alpha} &= (\boldsymbol{F}^{\alpha})'^{\alpha}\mathrm{d}\boldsymbol{X}^{\alpha} = (\boldsymbol{F}^{\alpha})'^{\alpha}(\boldsymbol{F}^{\alpha})^{-1}\mathrm{d}\boldsymbol{x} = \boldsymbol{L}^{\alpha}\mathrm{d}\boldsymbol{x},\\
\boldsymbol{L}^{\alpha} &= (\boldsymbol{F}^{\alpha})'^{\alpha}(\boldsymbol{F}^{\alpha})^{-1}.
\end{aligned} \tag{22.46}
$$

Alternatively, the *material velocity gradient* is defined as

$$
(\boldsymbol{F}^{\alpha})'^{\alpha} = \mathrm{Grad}^{\alpha}\boldsymbol{x}'^{\alpha} \tag{22.47}
$$

and $\boldsymbol{L}^{\alpha}$ follows from this by a push-forward operation. Neither $\boldsymbol{L}^{\alpha}$ nor $(\boldsymbol{F}^{\alpha})'^{\alpha}$ has symmetry properties. For the spatial velocity gradient, we write

$$
\begin{aligned}
\boldsymbol{L}^{\alpha} &= \boldsymbol{D}^{\alpha} + \boldsymbol{W}^{\alpha},\\
\boldsymbol{D}^{\alpha} &= \tfrac{1}{2}\left(\boldsymbol{L}^{\alpha} + (\boldsymbol{L}^{\alpha})^{T}\right) = \mathrm{sym}\boldsymbol{L}^{\alpha},\\
\boldsymbol{W}^{\alpha} &= \tfrac{1}{2}\left(\boldsymbol{L}^{\alpha} - (\boldsymbol{L}^{\alpha})^{T}\right) = \mathrm{skw}\boldsymbol{L}^{\alpha}.
\end{aligned} \tag{22.48}
$$

$\boldsymbol{L}^{\alpha}$ is split into the symmetric *stretching tensor* (strain rate tensor) and the skew-symmetric *vorticity tensor*. Note,

$$
\boldsymbol{\omega}^{\alpha} = \tfrac{1}{2}\overset{3}{\boldsymbol{E}}(\boldsymbol{W}^{\alpha})^{T} = \tfrac{1}{2}\mathrm{curl}\boldsymbol{v}^{\alpha}. \tag{22.49}
$$

Properties

- $$(\mathrm{d}\boldsymbol{x}\cdot\mathrm{d}\boldsymbol{x})'^{\alpha} = \boldsymbol{L}^{\alpha}\mathrm{d}\boldsymbol{x}\cdot\mathrm{d}\boldsymbol{x} + \mathrm{d}\boldsymbol{x}\cdot\boldsymbol{L}^{\alpha}\mathrm{d}\boldsymbol{x} = \mathrm{d}\boldsymbol{x}\cdot 2\boldsymbol{D}^{\alpha}\mathrm{d}\boldsymbol{x}.$$
- Apart from the decomposition (22.48), the spatial velocity gradient possesses a second additive decomposition, namely

$$\begin{aligned}\boldsymbol{L}^{\alpha} &= \boldsymbol{\Delta}^{\alpha} + \boldsymbol{\Omega}^{\alpha},\\ \boldsymbol{\Delta}^{\alpha} &= \boldsymbol{R}^{\alpha}\,(\boldsymbol{U}^{\alpha})'^{\alpha}\,(\boldsymbol{U}^{\alpha})^{-1}(\boldsymbol{R}^{\alpha})^{T},\\ \boldsymbol{\Omega}^{\alpha} &= (\boldsymbol{R}^{\alpha})'^{\alpha}\,(\boldsymbol{R}^{\alpha})^{T}. \qquad \textit{Gyration tensor}\end{aligned} \tag{22.50}$$

Remark

1. $\boldsymbol{\Delta}^{\alpha}$ is not symmetric, it has symmetric and skew-symmetric components, but $\boldsymbol{\Omega}^{\alpha}$ is skew-symmetric. Note also that $\boldsymbol{\Delta}^{\alpha}$ and $\boldsymbol{\Omega}^{\alpha}$ are both expressed in terms of the classical deformation measures (no overbars!). Of course, similar quantities can also be defined with the COSSERAT variables $\bar{\boldsymbol{R}}^{\alpha}$ and $\bar{\boldsymbol{U}}^{\alpha}$ and are then written as $\bar{\boldsymbol{\Delta}}^{\alpha}$ and $\bar{\boldsymbol{\Omega}}^{\alpha}$.

$$\begin{aligned}\boldsymbol{L}^{\alpha} &= \bar{\boldsymbol{\Delta}}^{\alpha} + \bar{\boldsymbol{\Omega}}^{\alpha},\\ \bar{\boldsymbol{\Delta}}^{\alpha} &= \bar{\boldsymbol{R}}^{\alpha}\,\left(\bar{\boldsymbol{U}}^{\alpha}\right)'^{\alpha}\,(\bar{\boldsymbol{U}}^{\alpha})^{-1}(\bar{\boldsymbol{R}}^{\alpha})^{T},\\ \bar{\boldsymbol{\Omega}}^{\alpha} &= \left(\bar{\boldsymbol{R}}^{\alpha}\right)'^{\alpha}\,(\bar{\boldsymbol{R}}^{\alpha})^{T}.\end{aligned} \tag{22.51}$$

2. It can be shown that

$$\begin{aligned}\boldsymbol{D}^{\alpha} &= \mathrm{sym}\boldsymbol{\Delta}^{\alpha} = \tfrac{1}{2}\left(\boldsymbol{\Delta}^{\alpha} + (\boldsymbol{\Delta}^{\alpha})^{T}\right),\\ \boldsymbol{W}^{\alpha} &= \boldsymbol{\Omega}^{\alpha} + \tfrac{1}{2}\left(\boldsymbol{\Delta}^{\alpha} - (\boldsymbol{\Delta}^{\alpha})^{T}\right).\end{aligned} \tag{22.52}$$

   The advantage of this decomposition will become apparent in connection with the micropolar formulation of the material theory. The proof of (22.52) simply follows by taking sym$\boldsymbol{L}^{\alpha}$ and skw$\boldsymbol{L}^{\alpha}$ from $(22.50)_1$.

- The GREEN–LAGRANGE strain tensor $\boldsymbol{E}^{\alpha}$ allows definition of a *stretching tensor in the reference configuration*,

$$(\boldsymbol{E}^{\alpha})'^{\alpha} \qquad \text{LAGRANGEan } \textit{stretching tensor}. \tag{22.53}$$

  This is an objective rank-2 tensor, which transforms as nine scalars. It is easy to show that the push-forward operation into the present configuration generates

$$\boldsymbol{D}^{\alpha} = (\boldsymbol{F}^{\alpha})^{-T}\,(\boldsymbol{E}^{\alpha})'^{\alpha}\,(\boldsymbol{F}^{\alpha})^{-1} \tag{22.54}$$

  and thus defines the classical EULERian stretching tensor; indeed,

$$
\begin{aligned}
&(\boldsymbol{F}^{\alpha})^{-T}\left(\tfrac{1}{2}\left((\boldsymbol{F}^{\alpha})^{T}\boldsymbol{F}^{\alpha}-\boldsymbol{I}\right)^{\prime\alpha}\right)(\boldsymbol{F}^{\alpha})^{-1}\\
&=\frac{1}{2}\left\{(\boldsymbol{F}^{\alpha})^{-T}\left(\underbrace{\left((\boldsymbol{F}^{\alpha})^{T}\right)^{\prime\alpha}}_{(\boldsymbol{F}^{\alpha})^{T}(\boldsymbol{L}^{\alpha})^{T}}\boldsymbol{F}^{\alpha}+(\boldsymbol{F}^{\alpha})^{T}\underbrace{(\boldsymbol{F}^{\alpha})^{\prime\alpha}}_{\boldsymbol{L}^{\alpha}\boldsymbol{F}^{\alpha}}\right)(\boldsymbol{F}^{\alpha})^{-1}\right\}\\
&=\frac{1}{2}\left\{\underbrace{(\boldsymbol{F}^{\alpha})^{-T}(\boldsymbol{F}^{\alpha})^{T}}_{\boldsymbol{I}}(\boldsymbol{L}^{\alpha})^{T}\underbrace{\boldsymbol{F}^{\alpha}(\boldsymbol{F}^{\alpha})^{-1}}_{\boldsymbol{I}}+\underbrace{(\boldsymbol{F}^{\alpha})^{-T}(\boldsymbol{F}^{\alpha})^{T}}_{\boldsymbol{I}}\boldsymbol{L}^{\alpha}\underbrace{\boldsymbol{F}^{\alpha}(\boldsymbol{F}^{\alpha})^{-1}}_{\boldsymbol{I}}\right\}\\
&=\frac{1}{2}\left((\boldsymbol{L}^{\alpha})^{T}+\boldsymbol{L}^{\alpha}\right), \qquad\qquad \square
\end{aligned}
$$

- A different LAGRANGEan type representation of strain rate can be evaluated as follows:

$$
\begin{aligned}
\left(\bar{\boldsymbol{E}}^{\alpha}\right)^{\prime\alpha} \overset{(22.33)}{=} \left(\bar{\boldsymbol{U}}^{\alpha}\right)^{\prime\alpha} &\overset{(22.27)_1}{=} \left((\bar{\boldsymbol{R}}^{\alpha})^{T}\boldsymbol{F}^{\alpha}\right)^{\prime\alpha}\\
&= \underbrace{\left((\bar{\boldsymbol{R}}^{\alpha})^{T}\right)^{\prime\alpha}}_{(\bar{\boldsymbol{R}}^{\alpha})^{T}(\bar{\boldsymbol{\Omega}}^{\alpha})^{T},\ \text{see (22.50)}}\boldsymbol{F}^{\alpha}+\left((\bar{\boldsymbol{R}}^{\alpha})^{T}\right)\underbrace{(\boldsymbol{F}^{\alpha})^{\prime\alpha}}_{\boldsymbol{L}^{\alpha}\boldsymbol{F}^{\alpha}}\\
&= (\bar{\boldsymbol{R}}^{\alpha})^{T}\underbrace{\left(\boldsymbol{L}^{\alpha}-\bar{\boldsymbol{\Omega}}^{\alpha}\right)}_{\bar{\boldsymbol{\Delta}}^{\alpha}}\boldsymbol{F}^{\alpha} &&(22.55)\\
&= (\bar{\boldsymbol{R}}^{\alpha})^{T}\bar{\boldsymbol{\Delta}}^{\alpha}\boldsymbol{F}^{\alpha}. &&(22.56)
\end{aligned}
$$

$\bar{\boldsymbol{\Delta}}^{\alpha}$, formally defined in (22.57), is in the material theory of viscous micropolar materials an important quantity and replaces $\boldsymbol{D}^{\alpha}$ from the classical theory. However, $\bar{\boldsymbol{\Delta}}^{\alpha}$ is not symmetric as we have already seen.

- With the definition

$$
\bar{\boldsymbol{\Delta}}^{\alpha}=\boldsymbol{L}^{\alpha}-\bar{\boldsymbol{\Omega}}^{\alpha}, \tag{22.57}
$$

from (22.55), (22.56), we now have two additional additive decompositions of $\boldsymbol{L}^{\alpha}$:

$$
\boldsymbol{L}^{\alpha}=\underbrace{\boldsymbol{D}^{\alpha}+\boldsymbol{W}^{\alpha}}_{\text{standard}}=\underbrace{\boldsymbol{\Delta}^{\alpha}+\boldsymbol{\Omega}^{\alpha}}_{(1)}=\underbrace{\bar{\boldsymbol{\Delta}}^{\alpha}+\bar{\boldsymbol{\Omega}}^{\alpha}}_{(2)}. \tag{22.58}
$$

The standard decomposition is that of classical continuum mechanics; that of (1) is based on (22.50) and (2) is analogous to $(22.50)_1$, but with overbars, as shown in (22.57).

- $\boldsymbol{D}^{\alpha}$ can also be expressed by the objective LIE or OLDROYD derivative of the ALMANSI strain tensor. The relation is

$$
\boldsymbol{D}^{\alpha}=(\boldsymbol{A}^{\alpha})^{\triangle^{\alpha}}:=(\boldsymbol{A}^{\alpha})^{\prime\alpha}+(\boldsymbol{L}^{\alpha})^{T}\boldsymbol{A}^{\alpha}+\boldsymbol{A}^{\alpha}\boldsymbol{L}^{\alpha}. \tag{22.59}
$$

$(\cdot)^{\triangle^\alpha}$ is called LIE or OLDROYD derivative, here of the rank-2 tensor $\boldsymbol{A}^\alpha$.

Proof We start with

$$\begin{aligned}(\boldsymbol{A}^\alpha)'^\alpha &= \tfrac{1}{2}\left(\boldsymbol{I} - (\boldsymbol{B}^\alpha)^{-1}\right)'^\alpha = -\tfrac{1}{2}\left((\boldsymbol{B}^\alpha)^{-1}\right)'^\alpha = -\tfrac{1}{2}\left((\boldsymbol{F}^\alpha)^{-T}(\boldsymbol{F}^\alpha)^{-1}\right)'^\alpha \\ &= -\tfrac{1}{2}\Big\{\underbrace{\left((\boldsymbol{F}^\alpha)^{-T}\right)'^\alpha}_{(1)}(\boldsymbol{F}^\alpha)^{-1} + (\boldsymbol{F}^\alpha)^{-T}\underbrace{\left((\boldsymbol{F}^\alpha)^{-1}\right)'^\alpha}_{(2)}\Big\}. \end{aligned} \tag{22.60}$$

The underbraced quantities can be obtained as follows: Take

$$\begin{aligned}&\left(\boldsymbol{F}^\alpha(\boldsymbol{F}^\alpha)^{-1}\right)'^\alpha = (\boldsymbol{F}^\alpha)'^\alpha(\boldsymbol{F}^\alpha)^{-1} + \boldsymbol{F}^\alpha\left((\boldsymbol{F}^\alpha)^{-1}\right)'^\alpha = \boldsymbol{0}, \\ &\boldsymbol{F}^\alpha\left((\boldsymbol{F}^\alpha)^{-1}\right)'^\alpha = -(\boldsymbol{F}^\alpha)'^\alpha(\boldsymbol{F}^\alpha)^{-1}, \\ &\left((\boldsymbol{F}^\alpha)^{-1}\right)'^\alpha = -(\boldsymbol{F}^\alpha)^{-1}(\boldsymbol{F}^\alpha)'^\alpha(\boldsymbol{F}^\alpha)^{-1} \equiv (2).\end{aligned}$$

Taking the transpose expression of (2) yields

$$\left((\boldsymbol{F}^\alpha)^{-T}\right)'^\alpha = -(\boldsymbol{F}^\alpha)^{-T}\left((\boldsymbol{F}^\alpha)^T\right)'^\alpha(\boldsymbol{F}^\alpha)^{-T} \equiv (1).$$

Substituting the above expressions (1) and (2) into (22.60) yields

$$\begin{aligned}(\boldsymbol{A}^\alpha)'^\alpha = \tfrac{1}{2}\Big\{&\underbrace{(\boldsymbol{F}^\alpha)^{-T}\underbrace{\left((\boldsymbol{F}^\alpha)^T\right)'^\alpha}_{(\boldsymbol{F}^\alpha)^T(\boldsymbol{L}^\alpha)^T,\ \text{see (22.46)}}}_{(\boldsymbol{L}^\alpha)^T}(\boldsymbol{F}^\alpha)^{-T}(\boldsymbol{F}^\alpha)^{-1} \\ &+(\boldsymbol{F}^\alpha)^{-T}(\boldsymbol{F}^\alpha)^{-1}\underbrace{\underbrace{(\boldsymbol{F}^\alpha)'^\alpha}_{\boldsymbol{L}^\alpha\boldsymbol{F}^\alpha}(\boldsymbol{F}^\alpha)^{-1}}_{\boldsymbol{L}^\alpha}\Big\} \\ = \tfrac{1}{2}\Big\{&(\boldsymbol{L}^\alpha)^T\underbrace{\left((\boldsymbol{F}^\alpha)^{-T}(\boldsymbol{F}^\alpha)^{-1}\right)}_{(\boldsymbol{B}^\alpha)^{-1}} + \underbrace{\left((\boldsymbol{F}^\alpha)^{-T}(\boldsymbol{F}^\alpha)^{-1}\right)}_{(\boldsymbol{B}^\alpha)^{-1}}\boldsymbol{L}^\alpha\Big\} \\ = \tfrac{1}{2}&\left((\boldsymbol{L}^\alpha)^T(\boldsymbol{B}^\alpha)^{-1} + (\boldsymbol{B}^\alpha)^{-1}\boldsymbol{L}^\alpha\right), \quad \text{or since } (\boldsymbol{B}^\alpha)^{-1} = \boldsymbol{I} - 2\boldsymbol{A}^\alpha \\ = \tfrac{1}{2}&\left(-2(\boldsymbol{L}^\alpha)^T\boldsymbol{A}^\alpha + (\boldsymbol{L}^\alpha)^T + \boldsymbol{L}^\alpha - 2\boldsymbol{A}^\alpha\boldsymbol{L}^\alpha\right).\end{aligned}$$

Thus,

$$(\boldsymbol{A}^\alpha)'^\alpha = \boldsymbol{D}^\alpha - (\boldsymbol{L}^\alpha)^T\boldsymbol{A}^\alpha - \boldsymbol{A}^\alpha\boldsymbol{L}^\alpha, \tag{22.61}$$

which proves (22.59).

- The transformation (22.22) maps the directors $\boldsymbol{\Xi}^\alpha$ to the directors $\boldsymbol{\xi}^\alpha$ by the rotation matrix $\bar{\boldsymbol{R}}^\alpha$. Its time rate of change is given by

$$(\boldsymbol{\xi}^\alpha)'^\alpha = \big((\bar{\boldsymbol{R}}^\alpha)'^\alpha\big)\,\boldsymbol{\Xi}^\alpha =: \bar{\boldsymbol{\Omega}}^\alpha \bar{\boldsymbol{R}}^\alpha\,\boldsymbol{\Xi}^\alpha. \tag{22.62}$$

The rank-2 tensor $\bar{\boldsymbol{\Omega}}^\alpha$ is called the *micropolar gyration tensor*. Its skew-symmetry follows from the obvious identity

$$\begin{aligned}
& \big((\bar{\boldsymbol{R}}^\alpha)^T\bar{\boldsymbol{R}}^\alpha\big)'^\alpha = \boldsymbol{0},\\
\Longrightarrow\quad & \underbrace{\big((\bar{\boldsymbol{R}}^\alpha)^T\big)'^\alpha}_{(\bar{\boldsymbol{R}}^\alpha)^T(\bar{\boldsymbol{\Omega}}^\alpha)^T}\bar{\boldsymbol{R}}^\alpha + \big((\bar{\boldsymbol{R}}^\alpha)^T\big)\underbrace{(\bar{\boldsymbol{R}}^\alpha)'^\alpha}_{\bar{\boldsymbol{\Omega}}^\alpha\bar{\boldsymbol{R}}^\alpha} = 0,\\
\Longrightarrow\quad & (\bar{\boldsymbol{R}}^\alpha)^T(\bar{\boldsymbol{\Omega}}^\alpha)^T\bar{\boldsymbol{R}}^\alpha + (\bar{\boldsymbol{R}}^\alpha)^T\bar{\boldsymbol{\Omega}}^\alpha\bar{\boldsymbol{R}}^\alpha = 0,\\
\Longrightarrow\quad & (\bar{\boldsymbol{R}}^\alpha)^T\Big((\bar{\boldsymbol{\Omega}}^\alpha)^T + \bar{\boldsymbol{\Omega}}^\alpha\Big)\bar{\boldsymbol{R}}^\alpha = 0,\\
\Longrightarrow\quad & \bar{\boldsymbol{\Omega}}^\alpha = -(\bar{\boldsymbol{\Omega}}^\alpha)^T.
\end{aligned} \tag{22.63}$$

The dual axial vector to $\bar{\boldsymbol{\Omega}}^\alpha$ is given by

$$\bar{\boldsymbol{\omega}}^\alpha = \tfrac{1}{2}\overset{3}{\boldsymbol{E}}(\bar{\boldsymbol{\Omega}}^\alpha)^T \quad\Longrightarrow\quad (\bar{\omega}^\alpha)_m = \tfrac{1}{2}\varepsilon_{mpq}(\bar{\Omega}^\alpha)_{pq} \tag{22.64}$$

- In (22.56), the material time derivative of $\bar{\boldsymbol{E}}^\alpha$ corresponds to the pullback of $\bar{\boldsymbol{\Delta}}^\alpha$ into the reference configuration. If one demands in analogy to the classical continuum that a generalized Lie or Oldroyd derivative exists for the micropolar strain tensor $\bar{\boldsymbol{A}}^\alpha$ (in its present configuration), and that this agrees with the generalized deformation strain rate $\bar{\boldsymbol{\Delta}}^\alpha$, then one may write

$$\left(\bar{\boldsymbol{A}}^\alpha\right)^{\blacktriangle^\alpha} := \bar{\boldsymbol{R}}^\alpha\left(\bar{\boldsymbol{E}}^\alpha\right)'^\alpha(\boldsymbol{F}^\alpha)^{-1} = \bar{\boldsymbol{\Delta}}^\alpha. \tag{22.65}$$

Comparison of the material time derivative of $\bar{\boldsymbol{A}}^\alpha$ with (22.65) yields the rule of calculation for the generalized Lie derivative

$$\left(\bar{\boldsymbol{A}}^\alpha\right)^{\blacktriangle^\alpha} = \left(\bar{\boldsymbol{A}}^\alpha\right)'^\alpha + (\bar{\boldsymbol{\Omega}}^\alpha)^T\bar{\boldsymbol{A}}^\alpha + \bar{\boldsymbol{A}}^\alpha\boldsymbol{L}^\alpha. \tag{22.66}$$

Compare this with the classical Lie derivative (22.59); here, the micropolar gyration tensor $(\bar{\boldsymbol{\Omega}}^\alpha)^T$ arises in the middle term (instead of $(\boldsymbol{L}^\alpha)^T$). This difference is consistent with the different transport properties between the present and reference configurations, since in one of them the basic system is transported with $\boldsymbol{F}^\alpha$, whereas the other basic system is transported with $\bar{\boldsymbol{R}}^\alpha$. This justifies the different notations for $(\cdot)^{\triangle^\alpha}$ and $(\cdot)^{\blacktriangle^\alpha}$.

To prove (22.66), take

$$\begin{aligned}
\bar{\boldsymbol{A}}^\alpha \quad \overset{(22.35)}{=} \quad & \big(\boldsymbol{I} - (\bar{\boldsymbol{V}}^\alpha)^{-1}\big) \overset{(22.28)}{=} \big(\boldsymbol{I} - (\boldsymbol{F}^\alpha(\bar{\boldsymbol{R}}^\alpha)^T)^{-1}\big)\\
= \quad & \big(\boldsymbol{I} - (\bar{\boldsymbol{R}}^\alpha)^{-T}(\boldsymbol{F}^\alpha)^{-1}\big) = \big(\boldsymbol{I} - \bar{\boldsymbol{R}}^\alpha(\boldsymbol{F}^\alpha)^{-1}\big),
\end{aligned}$$

$$(\bar{\boldsymbol{A}}^{\alpha})'^{\alpha} \;=\; -\big(\bar{\boldsymbol{R}}^{\alpha}(\boldsymbol{F}^{\alpha})^{-1}\big)'^{\alpha} = -\underbrace{(\bar{\boldsymbol{R}}^{\alpha})'^{\alpha}}(\boldsymbol{F}^{\alpha})^{-1} - \bar{\boldsymbol{R}}^{\alpha}\,\underbrace{((\boldsymbol{F}^{\alpha})^{-1})'^{\alpha}}.$$

In this expression, the underbraced terms must be accordingly transformed. To this end, we employ $(\boldsymbol{F}^{\alpha}(\boldsymbol{F}^{\alpha})^{-1})'^{\alpha} = \boldsymbol{0}$ and deduce

$$\big((\boldsymbol{F}^{\alpha})^{-1}\big)'^{\alpha} = -(\boldsymbol{F}^{\alpha})^{-1}\boldsymbol{L}^{\alpha}.$$

Moreover, we know from (22.51)$_3$ that

$$\big(\bar{\boldsymbol{R}}^{\alpha}\big)'^{\alpha} = \bar{\boldsymbol{\Omega}}^{\alpha}\,\bar{\boldsymbol{R}}^{\alpha}.$$

Substituting these two results into the last equation, we obtain

$$\begin{aligned}
(\bar{\boldsymbol{A}}^{\alpha})'^{\alpha} &= -\big(\bar{\boldsymbol{R}}^{\alpha}\big)'^{\alpha}\,(\boldsymbol{F}^{\alpha})^{-1} + \underbrace{\bar{\boldsymbol{R}}^{\alpha}(\boldsymbol{F}^{\alpha})^{-1}}_{\boldsymbol{I}-\bar{\boldsymbol{A}}^{\alpha}}\boldsymbol{L}^{\alpha}\\
&= \underbrace{-\underbrace{\big(\bar{\boldsymbol{R}}^{\alpha}\big)'^{\alpha}}_{\bar{\boldsymbol{\Omega}}^{\alpha}\bar{\boldsymbol{R}}^{\alpha}}(\boldsymbol{F}^{\alpha})^{-1}}_{\bar{\boldsymbol{\Omega}}^{\alpha}(\boldsymbol{I}-\bar{\boldsymbol{A}}^{\alpha})} - \bar{\boldsymbol{A}}^{\alpha}\boldsymbol{L}^{\alpha} + \boldsymbol{L}^{\alpha}\\
&= -(\bar{\boldsymbol{\Omega}}^{\alpha})^{T}\,\bar{\boldsymbol{A}}^{\alpha} - \bar{\boldsymbol{A}}^{\alpha}\boldsymbol{L}^{\alpha} + \underbrace{\boldsymbol{L}^{\alpha} - \bar{\boldsymbol{\Omega}}^{\alpha}}_{\bar{\boldsymbol{\Delta}}^{\alpha}}.
\end{aligned}$$

The expression in the underbrace of the first line has been obtained with the aid of (22.35) and then (22.34). The remaining expressions follow immediately and from a combination of (22.51)$_1$ and (22.51)$_3$. Therefore,

$$\underbrace{(\bar{\boldsymbol{A}}^{\alpha})'^{\alpha} + (\bar{\boldsymbol{\Omega}}^{\alpha})^{T}\,\bar{\boldsymbol{A}}^{\alpha} + \bar{\boldsymbol{A}}^{\alpha}\boldsymbol{L}^{\alpha}}_{(\boldsymbol{A}^{\alpha})^{\blacktriangle\alpha}} = \bar{\boldsymbol{\Delta}}^{\alpha}, \qquad \square$$

- In the constitutive theory of viscoelastic COSSERAT continua, one also needs *time derivatives of the curvature tensors*. For the rank-3 curvature tensor in the reference configuration, DIEBELS [4] states, on using (22.43),

$$\left({}^{R}\overset{\underline{3}}{\boldsymbol{\mathcal{K}}}{}^{\alpha}\right)'^{\alpha} = \left\{\left[(\bar{\boldsymbol{R}}^{\alpha})^{T}\left(\left(\mathrm{Grad}\,\bar{\boldsymbol{\Omega}}^{\alpha}\right)^{\overset{23}{T}}\bar{\boldsymbol{R}}^{\alpha}\right)^{\underline{3}}\right]^{\overset{23}{T}}\right\}^{\underline{3}}, \tag{22.67}$$

in which $\bar{\boldsymbol{\Omega}}^{\alpha} = \big(\bar{\boldsymbol{R}}^{\alpha}\big)'^{\alpha}\,(\bar{\boldsymbol{R}}^{\alpha})^{T}$. Similarly, he states for the second rank curvature tensor

$$\left({}^{R}\overset{\underline{2}}{\boldsymbol{\mathcal{K}}}{}^{\alpha}\right)'^{\alpha} = (\bar{\boldsymbol{R}}^{\alpha})^{T}\,(\mathrm{grad}\,\bar{\boldsymbol{\omega}}^{\alpha})\,\boldsymbol{F}^{\alpha}. \tag{22.68}$$

The Cartesian index notations for (22.67) and (22.68) are

$$\left[\left({}^{R}\overset{3}{\mathcal{K}}{}^{\alpha}\right)^{\prime\alpha}\right]_{ABC} = (\bar{R}^{\alpha})_{iA}(\Omega^{\alpha})_{ij,C}(\bar{R}^{\alpha})_{jB},$$

$$\left[\left({}^{R}\overset{2}{\bar{\mathcal{K}}}{}^{\alpha}\right)^{\prime\alpha}\right]_{AB} = \left(\bar{R}^{\alpha}\right)_{iA}(\bar{\omega}^{\alpha})_{i,k}(F^{\alpha})_{kB},$$

in which

$$(\bar{\omega}^{\alpha})_i = \tfrac{1}{2}\varepsilon_{ijk}(\bar{\Omega}^{\alpha})_{kj}.$$

The corroboration of these expressions is left to the reader.

22.8 Natural Basis System

It is often[5] useful to introduce *convective coordinates*. These are body-fixed coordinates, which move like material lines with the body. The coordinate lines are given by three parameters Θ_i^{α}, $i = 1, 2, 3$, and each constituent can have its own parameterization. Generally, we have

$$\boldsymbol{X}^{\alpha} = \boldsymbol{X}^{\alpha}\left(\Theta_1^{\alpha}, \Theta_2^{\alpha}, \Theta_3^{\alpha}\right), \tag{22.69}$$

which is assumed to be one-to-one and onto (bijective), so that the inverse relations do also exist:

$$\Theta_i^{\alpha} = \Theta_i^{\alpha}(\boldsymbol{X}^{\alpha}), \quad i = 1, 2, 3. \tag{22.70}$$

Differential geometric properties

- **Basis Vectors**

  In the reference configuration:

$$(\boldsymbol{h}^{\alpha})_i = \frac{\partial \boldsymbol{X}^{\alpha}(\Theta_1^{\alpha}, \Theta_2^{\alpha}, \Theta_3^{\alpha})}{\partial \Theta_i^{\alpha}}; \tag{22.71}$$

  in the present configuration:

$$(\boldsymbol{a}^{\alpha})_i = \frac{\partial \boldsymbol{x}(\Theta_1^{\alpha}, \Theta_2^{\alpha}, \Theta_3^{\alpha})}{\partial \Theta_i^{\alpha}}. \tag{22.72}$$

---

[5] In Sect. 22.8, the general tensor calculus is used. So far, we have restricted analyses to Cartesian tensor notation. More general presentations are given, e.g., in BOWEN and WANG [2].

Obviously, by chain rule of differentiation,

$$(\boldsymbol{a}^\alpha)_i = \frac{\partial \boldsymbol{x}}{\partial \boldsymbol{X}^\alpha} \frac{\partial \boldsymbol{X}^\alpha}{\partial \Theta_i^\alpha} = \boldsymbol{F}^\alpha (\boldsymbol{h}^\alpha)_i. \tag{22.73}$$

The transformation (22.73) is analogous to $\mathrm{d}\boldsymbol{x} = \boldsymbol{F}^\alpha \mathrm{d}\boldsymbol{X}^\alpha$. $(\boldsymbol{h}^\alpha)_i$ and $(\boldsymbol{a}^\alpha)_i$, $i = 1, 2, 3$, are *tangential vectors to the coordinate lines* in their systems. They are covariant vectors, since $\mathrm{d}\Theta_i^\alpha$ are introduced as contravariant quantities.

- **Dual basis vectors**
  These are contravariant and are defined by the following scalar products:

$$\begin{aligned} (\boldsymbol{h}^\alpha)_j \cdot (\boldsymbol{h}^\alpha)^i &= \delta_j^i, \\ (\boldsymbol{a}^\alpha)_j \cdot (\boldsymbol{a}^\alpha)^i &= \delta_j^i, \end{aligned} \tag{22.74}$$

where δ_j^i is the KRONECKER Delta, $\delta_j^i = 1$ if $i = j$, else $\delta_j^i = 0$. It follows immediately from (22.71), (22.72), and (22.74)

$$\begin{aligned} (\boldsymbol{h}^\alpha)^i &= \frac{\partial \Theta_i^\alpha}{\partial \boldsymbol{X}^\alpha}, \\ (\boldsymbol{a}^\alpha)^i &= \frac{\partial \Theta_i^\alpha}{\partial \boldsymbol{x}}, \end{aligned} \tag{22.75}$$

- The metric tensors $(h^\alpha)_{ij}$, $(h^\alpha)^{ij}$, $(a^\alpha)_{ij}$, $(a^\alpha)^{ij}$ allow transformations from co- to contravariant tensor components and vice versa. They are defined as

$$\begin{aligned} (h^\alpha)_{ij} &= (\boldsymbol{h}^\alpha)_i \cdot (\boldsymbol{h}^\alpha)_j, \\ (h^\alpha)^{ij} &= (\boldsymbol{h}^\alpha)^i \cdot (\boldsymbol{h}^\alpha)^j, \\ (a^\alpha)_{ij} &= (\boldsymbol{a}^\alpha)_i \cdot (\boldsymbol{a}^\alpha)_j, \\ (a^\alpha)^{ij} &= (\boldsymbol{a}^\alpha)^i \cdot (\boldsymbol{a}^\alpha)^j, \end{aligned} \tag{22.76}$$

with the aid of which one obtains

$$\begin{aligned} (\boldsymbol{h}^\alpha)_i &= (h^\alpha)_{ij} (\boldsymbol{h}^\alpha)^j, \\ (\boldsymbol{h}^\alpha)^i &= (h^\alpha)^{ij} (\boldsymbol{h}^\alpha)_j, \\ (\boldsymbol{a}^\alpha)_i &= (a^\alpha)_{ij} (\boldsymbol{a}^\alpha)^j, \\ (\boldsymbol{a}^\alpha)^i &= (a^\alpha)^{ij} (\boldsymbol{a}^\alpha)_j. \end{aligned} \tag{22.77}$$

The downward and upward arrows in **Fig. 22.7** illustrate these mappings. The rank-2 unit tensor now becomes

$$\begin{aligned} \boldsymbol{I} &= \delta_i^j (\boldsymbol{h}^\alpha)^i \otimes (\boldsymbol{h}^\alpha)_j = \delta_j^i (\boldsymbol{h}^\alpha)_i \otimes (\boldsymbol{h}^\alpha)^j \\ &= (h^\alpha)_{ij} (\boldsymbol{h}^\alpha)^i \otimes (\boldsymbol{h}^\alpha)^j = (h^\alpha)^{ij} (\boldsymbol{h}^\alpha)_i \otimes (\boldsymbol{h}^\alpha)_j \end{aligned} \tag{22.78}$$

and similarly in the present configuration with the $(\boldsymbol{a}^\alpha)$'s,

$$\begin{aligned}\boldsymbol{I} &= \delta_i^j (\boldsymbol{a}^\alpha)^i \otimes (\boldsymbol{a}^\alpha)_j = \delta_j^i (\boldsymbol{a}^\alpha)_i \otimes (\boldsymbol{a}^\alpha)^j \\ &= (a^\alpha)_{ij} (\boldsymbol{a}^\alpha)^i \otimes (\boldsymbol{a}^\alpha)^j = (a^\alpha)^{ij} (\boldsymbol{a}^\alpha)_i \otimes (\boldsymbol{a}^\alpha)_j .\end{aligned} \tag{22.79}$$

22.9 Deformation Measures Referred to the Natural Basis

If the natural basis vectors $(\boldsymbol{h}^\alpha)_i$ and $(\boldsymbol{a}^\alpha)_i$ are interpreted as spatial line elements in the reference and present configurations, respectively, the deformation tensor can easily be expressed in terms of the basis vectors.

- For $\boldsymbol{F}^\alpha$:

$$\boldsymbol{F}^\alpha = \frac{\partial \boldsymbol{x}}{\partial \Theta_i^\alpha} \frac{\partial \Theta_i^\alpha}{\partial \boldsymbol{X}^\alpha} = (\boldsymbol{a}^\alpha)_i \otimes (\boldsymbol{h}^\alpha)^i , \tag{22.80}$$

- For $(\boldsymbol{F}^\alpha)^{-1}$:

$$(\boldsymbol{F}^\alpha)^{-1} = \frac{\partial \boldsymbol{X}^\alpha}{\partial (\Theta^\alpha)^i} \frac{\partial (\Theta^\alpha)^i}{\partial \boldsymbol{x}} = (\boldsymbol{h}^\alpha)_i \otimes (\boldsymbol{a}^\alpha)^i . \tag{22.81}$$

These representations show explicitly that $\boldsymbol{F}^\alpha$ and $(\boldsymbol{F}^\alpha)^{-1}$ have both "one leg in the present configuration and the other leg in the reference configuration", but the order is different. So, $\boldsymbol{F}^\alpha$ and $(\boldsymbol{F}^\alpha)^{-1}$ are *two-field tensors*. For example, (22.80) and (22.81) imply

$$\begin{aligned}
&\bullet\ \boldsymbol{F}^\alpha (\boldsymbol{h}^\alpha)_i = \Big((\boldsymbol{a}^\alpha)_j \otimes \underbrace{(\boldsymbol{h}^\alpha)^j \Big) (\boldsymbol{h}^\alpha)_i}_{\delta_i^j} = (\boldsymbol{a}^\alpha)_i , \\
&\bullet\ (\boldsymbol{F}^\alpha)^{-1} (\boldsymbol{a}^\alpha)_i = \Big((\boldsymbol{h}^\alpha)_j \otimes \underbrace{(\boldsymbol{a}^\alpha)^j \Big) (\boldsymbol{a}^\alpha)_i}_{\delta_i^j} = (\boldsymbol{h}^\alpha)_i , \\
&\bullet\ (\boldsymbol{F}^\alpha)^{-T} (\boldsymbol{h}^\alpha)^i = \Big((\boldsymbol{a}^\alpha)^j \otimes \underbrace{(\boldsymbol{h}^\alpha)_j \Big) (\boldsymbol{h}^\alpha)^i}_{\delta_j^i} = (\boldsymbol{a}^\alpha)^i , \\
&\bullet\ (\boldsymbol{F}^\alpha)^{T} (\boldsymbol{a}^\alpha)^i = \Big((\boldsymbol{h}^\alpha)^j \otimes \underbrace{(\boldsymbol{a}^\alpha)_j \Big) (\boldsymbol{a}^\alpha)^i}_{\delta_j^i} = (\boldsymbol{h}^\alpha)^i .
\end{aligned} \tag{22.82}$$

These mappings are illustrated in Fig. 22.7 by the horizontal arrows. With the use of (22.80), it is now also straightforward to write down expressions for the CAUCHY–GREEN deformation tensors as follows:

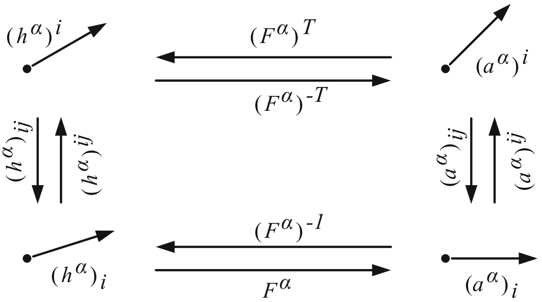

Fig. 22.7 Deformation gradient and its action in transformations of natural bases

- For $\boldsymbol{C}^\alpha$,

$$\boldsymbol{C}^\alpha = (\boldsymbol{F}^\alpha)^T \boldsymbol{F}^\alpha = \left((\boldsymbol{h}^\alpha)^j \otimes \underbrace{(\boldsymbol{a}^\alpha)_j (\boldsymbol{a}^\alpha)_k}_{(a^\alpha)_{jk}} \otimes (\boldsymbol{h}^\alpha)^k \right)$$
$$= (a^\alpha)_{jk} (\boldsymbol{h}^\alpha)^j \otimes (\boldsymbol{h}^\alpha)^k \qquad (22.83)$$

doubly contravariant in the reference configuration

- For $\boldsymbol{B}^\alpha$,

$$\boldsymbol{B}^\alpha = \boldsymbol{F}^\alpha (\boldsymbol{F}^\alpha)^T = \left((\boldsymbol{a}^\alpha)_j \otimes \underbrace{(\boldsymbol{h}^\alpha)^j (\boldsymbol{h}^\alpha)^k}_{(h^\alpha)^{jk}} \otimes (\boldsymbol{a}^\alpha)_k \right)$$
$$= (h^\alpha)^{jk} (\boldsymbol{a}^\alpha)_j \otimes (\boldsymbol{a}^\alpha)_k \qquad (22.84)$$

doubly covariant in the present configuration

- For $\boldsymbol{E}^\alpha$ and $\boldsymbol{A}^\alpha$, we obtain with the aid of (22.83) and (22.78) and (22.84) and (22.78) the following formulae:

$$\boldsymbol{E}^\alpha = \tfrac{1}{2} (\boldsymbol{C}^\alpha - \boldsymbol{I}) = \tfrac{1}{2} \left((a^\alpha)_{ij} - (h^\alpha)_{ij} \right) (\boldsymbol{h}^\alpha)^i \otimes (\boldsymbol{h}^\alpha)^j,$$
$$\boldsymbol{A}^\alpha = \tfrac{1}{2} \left(\boldsymbol{I} - (\boldsymbol{B}^\alpha)^{-1} \right) = \tfrac{1}{2} \left((a^\alpha)_{ij} - (h^\alpha)_{ij} \right) (\boldsymbol{a}^\alpha)^i \otimes (\boldsymbol{a}^\alpha)^j. \qquad (22.85)$$

Remark The numerical values of the components of $\boldsymbol{E}^\alpha$ and $\boldsymbol{A}^\alpha$ are the same, only the basis changes!

- The property just stated makes it very easy to verify the relations between $\boldsymbol{E}^\alpha$ and $\boldsymbol{A}^\alpha$. Indeed, with the help of the diagram in Fig. 22.7, one obtains

$$\boldsymbol{E}^\alpha = \tfrac{1}{2} \left((a^\alpha)_{ij} - (h^\alpha)_{ij} \right) (\boldsymbol{F}^\alpha)^T (\boldsymbol{a}^\alpha)^i \otimes (\boldsymbol{F}^\alpha)^T (\boldsymbol{a}^\alpha)^j$$

$$\begin{aligned} &= \tfrac{1}{2}\left((a^\alpha)_{ij} - (h^\alpha)_{ij}\right)\left[(\boldsymbol{F}^\alpha)^T(\boldsymbol{a}^\alpha)\right]^i \otimes \left[(\boldsymbol{a}^\alpha)\boldsymbol{F}^\alpha\right]^j \\ &= (\boldsymbol{F}^\alpha)^T \boldsymbol{A}^\alpha \boldsymbol{F}^\alpha, \qquad (22.86) \\ \boldsymbol{A}^\alpha &= \tfrac{1}{2}\left((a^\alpha)_{ij} - (h^\alpha)_{ij}\right)(\boldsymbol{F}^\alpha)^{-T}(\boldsymbol{h}^\alpha)^i \otimes (\boldsymbol{F}^\alpha)^{-T}(\boldsymbol{h}^\alpha)^j \\ &= \tfrac{1}{2}\left((a^\alpha)_{ij} - (h^\alpha)_{ij}\right)\left[(\boldsymbol{F}^\alpha)^{-T}(\boldsymbol{h}^\alpha)^i \otimes (\boldsymbol{h}^\alpha)^j(\boldsymbol{F}^\alpha)^{-1}\right] \\ &= (\boldsymbol{F}^\alpha)^{-T}\boldsymbol{E}^\alpha(\boldsymbol{F}^\alpha)^{-1}. \qquad (22.87) \end{aligned}$$

Compare these results with (22.36) and (22.37).

22.10 Cosserat Deformation Tensors and Natural Bases

The microrotation tensor $\bar{\boldsymbol{R}}^\alpha$ maps directors from the reference configuration onto the present configuration. It is therefore a two-field tensor; consequently, its representation in the bases $(\boldsymbol{a}^\alpha)_i$ and $(\boldsymbol{h}^\alpha)_j$ is of the form

$$\bar{\boldsymbol{R}}^\alpha = \left(\bar{R}^\alpha\right)^i_{\ j}(\boldsymbol{a}^\alpha)_i \otimes (\boldsymbol{h}^\alpha)^j. \qquad (22.88)$$

The coefficient matrix "$(\bar{R}^\alpha)^i_{\ j}$" can without restriction of the generality be collected with the basis in the reference configuration by summing over j. This leads to the new basis vectors $(\bar{\boldsymbol{h}}^\alpha)^i$, defined by

$$(\bar{\boldsymbol{h}}^\alpha)^i = (\bar{R}^\alpha)^i_{\ j}(\boldsymbol{h}^\alpha)^j, \qquad (22.89)$$

so that the microrotation (22.88) can also be written as

$$\bar{\boldsymbol{R}}^\alpha = (\boldsymbol{a}^\alpha)_i \otimes (\bar{\boldsymbol{h}}^\alpha)^i. \qquad (22.90)$$

This is the basis representation of $\bar{\boldsymbol{R}}^\alpha$.

An equivalent representation of (22.88) also exists, if one introduces the new basis in the present configuration by

$$(\bar{\boldsymbol{a}}^\alpha)_j = (\bar{R}^\alpha)^i_{\ j}(\boldsymbol{a}^\alpha)_i, \qquad (22.91)$$

so that

$$\bar{\boldsymbol{R}}^\alpha = (\bar{\boldsymbol{a}}^\alpha)_i \otimes (\boldsymbol{h}^\alpha)^i. \qquad (22.92)$$

The covariant basis vectors $(\bar{\boldsymbol{h}}^\alpha)_j$ and contravariant basis vectors $(\bar{\boldsymbol{a}}^\alpha)^j$ are obviously defined by

$$(\bar{\boldsymbol{h}}^\alpha)^i \cdot (\bar{\boldsymbol{h}}^\alpha)_j = \delta^i_j, \quad (\bar{\boldsymbol{a}}^\alpha)^i \cdot (\bar{\boldsymbol{a}}^\alpha)_j = \delta^i_j. \qquad (22.93)$$

We emphasize that the new basis vectors are not tangential to the parameter lines, defined by $\{(\Theta^\alpha)^i, i = 1, 2, 3\}$. This implies a loss of symmetry of the CHRISTOFFEL symbols.

Next, let us form $\bar{\boldsymbol{R}}^\alpha(\bar{\boldsymbol{h}}^\alpha)_i$ with (22.90) and $\bar{\boldsymbol{R}}^\alpha(\boldsymbol{h}^\alpha)_i$ with (22.92), respectively

$$\bar{\boldsymbol{R}}^\alpha(\bar{\boldsymbol{h}}^\alpha)_i \overset{(22.90)}{=} (\boldsymbol{a}^\alpha)_k \otimes \underbrace{(\bar{\boldsymbol{h}}^\alpha)^k(\bar{\boldsymbol{h}}^\alpha)_i}_{\delta_i^k} = (\boldsymbol{a}^\alpha)_i,$$

$$\bar{\boldsymbol{R}}^\alpha(\boldsymbol{h}^\alpha)_i \overset{(22.92)}{=} (\bar{\boldsymbol{a}}^\alpha)_k \otimes \underbrace{(\boldsymbol{h}^\alpha)^k(\boldsymbol{h}^\alpha)_i}_{\delta_i^k} = (\bar{\boldsymbol{a}}^\alpha)_i.$$

So, we have the two equivalent forms

$$(\boldsymbol{a}^\alpha)_i = \bar{\boldsymbol{R}}^\alpha(\bar{\boldsymbol{h}}^\alpha)_i, \quad (\bar{\boldsymbol{a}}^\alpha)_i = \bar{\boldsymbol{R}}^\alpha(\boldsymbol{h}^\alpha)_i. \tag{22.94}$$

Compare these representations with $\boldsymbol{\xi}^\alpha = \bar{\boldsymbol{R}}^\alpha \boldsymbol{\Xi}^\alpha$, (22.22). In $(22.94)_1$, $(\boldsymbol{a}^\alpha)_i$ may be compared with $\boldsymbol{\xi}^\alpha$ in (22.22). If this is done, $(\bar{\boldsymbol{h}}^\alpha)_i$ are then to be interpreted as reference directors. Because the microrotation $\bar{\boldsymbol{R}}^\alpha$ is a pure rotation and the basis vectors $(\boldsymbol{a}^\alpha)_i$ of the present configuration change their length, the reference directors $\boldsymbol{\Xi}^\alpha = (\bar{\boldsymbol{h}}^\alpha)_i$ also change their lengths. This must be accounted for in the computation of the gyration tensor $\bar{\boldsymbol{\Omega}}^\alpha$ in the present configuration. This complicates the computation of $\bar{\boldsymbol{\Omega}}^\alpha$.

The second choice identifies the directors of the reference configuration with $(\boldsymbol{h}^\alpha)_i$. In this case, the reference directors are temporarily constant. The directors in the present configuration $\boldsymbol{\xi}^\alpha$ are then to be identified with the basis vectors $(\bar{\boldsymbol{a}}^\alpha)_i$.

Obviously, apart from the reference and present configurations, two further configurations can be introduced on the basis that (22.89) and (22.91) are defined.

Choice (22.89) (see **Fig. 22.8**):

The reference directors are $\boldsymbol{\Xi}^\alpha = (\bar{\boldsymbol{h}}^\alpha)_i$. They are elements of the so-called *back-rotated* COSSERAT *configuration* and by $(22.94)_1$, they are mapped by $\bar{\boldsymbol{R}}^\alpha$ onto the present configuration. It is almost obvious and can be shown that the back-rotated COSSERAT configuration possesses the geometry of the present configuration. This is explicitly demonstrated by the fact that the two configurations have the same metric,

$$(a^\alpha)_{ij} = (\bar{h}^\alpha)_{ij} \tag{22.95}$$

For the directors, the back-rotated COSSERAT configuration must be interpreted as a reference configuration, so that $\bar{\boldsymbol{U}}^\alpha$ as a two-field tensor also possesses the property of a quantity in the reference configuration.

Choice $(22.91)_2$ (see Fig. 22.8):

The directors in the present configuration, $\boldsymbol{\xi}^\alpha$ are here to be identified with $(\bar{\boldsymbol{a}}^\alpha)_i$. Thus, $\boldsymbol{\xi}^\alpha = (\bar{\boldsymbol{a}}^\alpha)_i$; these are elements of the *pre-rotated* COSSERAT *configuration* and

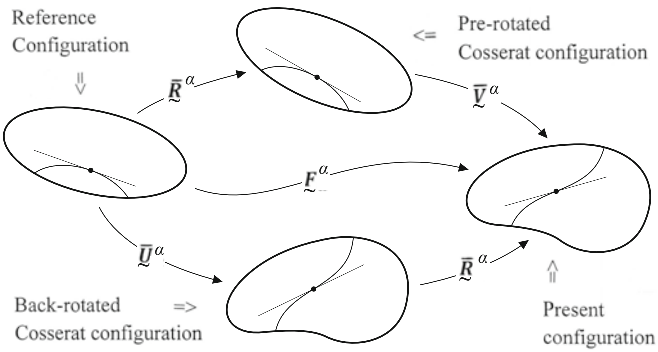

Fig. 22.8 COSSERAT configurations (for details see main text)

are obtained as mappings of the reference basis vectors with the aid of $(22.94)_2$. In this case, the geometry of the body in the reference configuration agrees with that of the pre-rotated COSSERAT configuration, so that the metrics agree,

$$(\bar{\boldsymbol{a}}^\alpha)_{ij} = (\boldsymbol{h}^\alpha)_{ij}. \tag{22.96}$$

For the directors, the pre-rotated COSSERAT configuration is identical to the present configuration.

Note also

$$\begin{aligned}\bar{\boldsymbol{U}}^\alpha &= (a^\alpha)_{ij}(\bar{\boldsymbol{h}}^\alpha)^i \otimes (\boldsymbol{h}^\alpha)^j = (\bar{\boldsymbol{h}}^\alpha)_i \otimes (\boldsymbol{h}^\alpha)^i,\\ \bar{\boldsymbol{V}}^\alpha &= (h^\alpha)^{ij}(\boldsymbol{a}^\alpha)_i \otimes (\bar{\boldsymbol{a}}^\alpha)_j = (\boldsymbol{a}^\alpha)_i \otimes (\bar{\boldsymbol{a}}^\alpha)^i.\end{aligned} \tag{22.97}$$

$\bar{\boldsymbol{U}}^\alpha$ maps the basis vectors $(\boldsymbol{h}^\alpha)_i$ of the reference configuration to the basis vectors $(\bar{\boldsymbol{h}}^\alpha)_i$ of the back-rotated COSSERAT configuration.

$\bar{\boldsymbol{V}}^\alpha$ maps the directors $(\bar{\boldsymbol{a}}^\alpha$ of the pre-rotated COSSERAT configuration onto the basis vectors $(\boldsymbol{a}^\alpha)_i$ of the present configuration.

22.11 Balance of Micro-Inertia

In this last section, the balance laws of micro inertia will be presented. They belong structurally into Chap. 21, but were postponed, as they do not form a physical law and make use of kinematic concepts, which were introduced in this chapter.

In polar continua, we expressed the specific spins $\boldsymbol{s}^\alpha$ of constituent α as

$$\boldsymbol{s}^\alpha = \bar{\boldsymbol{\Theta}}^\alpha \boldsymbol{\omega}^\alpha, \tag{22.98}$$

where $\boldsymbol{\omega}^\alpha$ is the *vector of angular velocity* of the microrotation and $\bar{\boldsymbol{\Theta}}^\alpha$ is the *tensor of volumetric inertia*, a symmetric positive definite tensor of rank-2. ERINGEN[6] in 1964 [12] formulated a balance law for this tensor, but this is not a physical axiom; the evolution equation is a consequence of the *tacit assumption that material points of micropolar continua behave like microscopic rigid bodies*, or more precisely, the moment of inertia at a material point experiences only rotations but no strains. This is the reason why an overbar is used. For micro-morphic media, the possible transformations of the tensor of inertia can be more general and even more complex micro-deformation fields are possible. It follows that for micropolar media the tensor $\bar{\boldsymbol{\Theta}}^\alpha$ changes its orientation with the motion, but does not change its principal values in the co-moving frame. Otherwise stated, the tensor of volume inertia remains constant in this frame. This fact can be expressed by the statement that the (objective) GREEN–NAGHDI derivative vanishes, viz.,

$$(\bar{\boldsymbol{\Theta}}^\alpha)^{\blacklozenge} \equiv \frac{\mathrm{d}^\alpha}{\mathrm{d}t}(\bar{\boldsymbol{\Theta}}^\alpha) - \bar{\boldsymbol{\Omega}}^\alpha \bar{\boldsymbol{\Theta}}^\alpha - \bar{\boldsymbol{\Theta}}^\alpha (\bar{\boldsymbol{\Omega}}^\alpha)^T \overset{!}{\equiv} \mathbf{0}, \tag{22.99}$$

in which $\bar{\boldsymbol{\Omega}}^\alpha$ is the dual tensor to the axial vector $\bar{\boldsymbol{\omega}}^\alpha$.

Pulling back the tensor $\bar{\boldsymbol{\Theta}}^\alpha$ to the reference frame, the statement is equivalent to the statement

$$\Big((\bar{\boldsymbol{R}}^\alpha)^T \bar{\boldsymbol{\Theta}}^\alpha \bar{\boldsymbol{R}}^\alpha\Big) = \text{const.} \quad \longrightarrow \quad \Big((\bar{\boldsymbol{R}}^\alpha)^T \bar{\boldsymbol{\Theta}}^\alpha \bar{\boldsymbol{R}}^\alpha\Big)^{\prime\alpha} = \mathbf{0}. \tag{22.100}$$

Here we have defined $(\cdot)^{\prime\alpha}$ as the total time derivative following the motion of constituent α. Product differentiation of the term on the right-hand side of the equation yields

$$\big((\bar{\boldsymbol{R}}^\alpha)^T\big)^{\prime\alpha} \bar{\boldsymbol{\Theta}}^\alpha \bar{\boldsymbol{R}}^\alpha + (\bar{\boldsymbol{R}}^\alpha)^T (\bar{\boldsymbol{\Theta}}^\alpha)^{\prime\alpha} \bar{\boldsymbol{R}}^\alpha + (\bar{\boldsymbol{R}}^\alpha)^T \bar{\boldsymbol{\Theta}}^\alpha (\bar{\boldsymbol{R}}^\alpha)^{\prime\alpha} = \mathbf{0}.$$

Multiplying this equation from the left by $\bar{\boldsymbol{R}}^\alpha(\cdot)$ and from the right by $(\bar{\boldsymbol{R}}^\alpha)^T$ yields the equation

$$\begin{aligned} &\bar{\boldsymbol{R}}^\alpha \big((\bar{\boldsymbol{R}}^\alpha)^T\big)^{\prime\alpha} \bar{\boldsymbol{\Theta}}^\alpha \underbrace{\bar{\boldsymbol{R}}^\alpha (\bar{\boldsymbol{R}}^\alpha)^T}_{\boldsymbol{I}} \\ &\quad + \underbrace{\bar{\boldsymbol{R}}^\alpha (\bar{\boldsymbol{R}}^\alpha)^T}_{\boldsymbol{I}} (\bar{\boldsymbol{\Theta}}^\alpha)^{\prime\alpha} \underbrace{\bar{\boldsymbol{R}}^\alpha (\bar{\boldsymbol{R}}^\alpha)^T}_{\boldsymbol{I}} \\ &\qquad + \underbrace{\bar{\boldsymbol{R}}^\alpha (\bar{\boldsymbol{R}}^\alpha)^T}_{\boldsymbol{I}} \bar{\boldsymbol{\Theta}}^\alpha (\bar{\boldsymbol{R}}^\alpha)^{\prime\alpha} (\bar{\boldsymbol{R}}^\alpha)^T = \mathbf{0}, \end{aligned}$$

---

[6] For a brief biography of AHMED CEMAL ERINGEN, see **Fig. 22.9**.

Fig. 22.9 AHMED CEMAL ERINGEN (15. Feb. 1921–7. Dec. 2009)

AHMED CEMAL ERINGEN was a Turkish-American engineering scientist. He was a Professor at Princeton University. The Eringen Medal is named in his honor. Eringen studied at the Technical University of Istanbul and graduated with a diploma degree in 1943 and then worked for the Turkish Aircraft Co. until 1944. In 1944/45, he was a trainee at the Glenn L. Martin Company and in 1945 was group leader at the Turkish Air League Company. He continued his studies at the Polytechnic Institute of Brooklyn in New York City where he received his doctorate in applied mechanics in 1948 under the supervision of NICHOLAS J. HOFF.

He became Assistant Professor at the Illinois Institute of Technology in 1948, Associate Professor in 1953, and Professor in 1955 at Purdue University. He was appointed as Professor of Aerospace and Mechanical Engineering at Princeton University in 1966. He became Professor of Continuum Mechanics in the Departments of *Civil and Geological Engineering* and *the program in applied and computational mathematics* at Princeton University. He is the founder of the *Int. J. Eng. Sci.* and the associated society. He retired in 1991 as the Dean of the School of Engineering and Applied Science at Princeton University and died in 2009. ERINGEN had been married since 1949 and had four children.

ERINGEN was a very influential educator, scientist and prolific scientific writer on general continuum mechanics, in particular micropolar and micromorphic and nonlocal field theories. Apart from his numerous papers with/without coauthors, his most significant books are

- Nonlocal Continuum Field Theories, Springer Verlag 2002
- Microcontinuum Field Theories, 2 volumes, Springer Verlag 1999
- with Gérard Maugin: Electrodynamics of Continua, 2 Volumes, Springer Verlag 1990
- with Erhan Kiral: Constitutive Equations of Nonlinear Electromagnetic-Elastic Crystals, Springer Verlag 1990
- (Editor): Continuum Physics, 4 volumes, Academic Press, 1974–1976
- with Erdogan S. Suhubi: Elastodynamics, Academic Press 1974
- Mechanics of Continua, Wiley 1967
- Nonlinear Theory of Continuous Media, McGraw Hill 1962

The text is based on www.wikipedia.org

or when solving for $(\bar{\boldsymbol{\Theta}}^\alpha)'^\alpha$,

$$
\begin{aligned}
(\bar{\boldsymbol{\Theta}}^\alpha)'^\alpha &= \underbrace{-\bar{\boldsymbol{R}}^\alpha((\bar{\boldsymbol{R}}^\alpha)^T)'^\alpha}_{\bar{\boldsymbol{\Omega}}^\alpha} \bar{\boldsymbol{\Theta}}^\alpha - \bar{\boldsymbol{\Theta}}^\alpha \underbrace{(\bar{\boldsymbol{R}}^\alpha)'^\alpha(\bar{\boldsymbol{R}}^\alpha)^T}_{\bar{\boldsymbol{\Omega}}^\alpha} \\
&= \bar{\boldsymbol{\Omega}}^\alpha \bar{\boldsymbol{\Theta}}^\alpha - \bar{\boldsymbol{\Theta}}^\alpha \bar{\boldsymbol{\Omega}}^\alpha = \bar{\boldsymbol{\Omega}}^\alpha \bar{\boldsymbol{\Theta}}^\alpha + \bar{\boldsymbol{\Theta}}^\alpha (\bar{\boldsymbol{\Omega}}^\alpha)^T \quad \text{skew-symmetry of } \bar{\boldsymbol{\Omega}}^\alpha \\
&= \bar{\boldsymbol{\Omega}}^\alpha \bar{\boldsymbol{\Theta}}^\alpha + (\bar{\boldsymbol{\Theta}}^\alpha)^T (\bar{\boldsymbol{\Omega}}^\alpha)^T = \bar{\boldsymbol{\Omega}}^\alpha \bar{\boldsymbol{\Theta}}^\alpha + (\bar{\boldsymbol{\Omega}}^\alpha \bar{\boldsymbol{\Theta}}^\alpha)^T \quad \text{symmetry of } \bar{\boldsymbol{\Theta}}^\alpha \\
&= 2\text{sym}(\bar{\boldsymbol{\Omega}}^\alpha \bar{\boldsymbol{\Theta}}^\alpha),
\end{aligned}
\tag{22.101}
$$

in which (22.51) has been used. With

$$
(\rho^\alpha \bar{\boldsymbol{\Theta}}^\alpha)'^\alpha = (\rho^\alpha)'^\alpha \bar{\boldsymbol{\Theta}}^\alpha + \rho^\alpha (\bar{\boldsymbol{\Theta}}^\alpha)'^\alpha \tag{22.102}
$$

and

$$
(\rho^\alpha)'^\alpha + \rho^\alpha \text{div}\,(\boldsymbol{x}'^\alpha) = \mathfrak{c}^\alpha, \tag{22.103}
$$

and substitution of (22.103) into (22.102) yields

$$
(\rho^\alpha \bar{\boldsymbol{\Theta}}^\alpha)'^\alpha + \rho^\alpha \bar{\boldsymbol{\Theta}}^\alpha \text{div}\,(\boldsymbol{x}'^\alpha) = 2\text{sym}(\rho^\alpha \bar{\boldsymbol{\Omega}}^\alpha \bar{\boldsymbol{\Theta}}^\alpha) + \mathfrak{c}^\alpha \bar{\boldsymbol{\Theta}}^\alpha. \tag{22.104}
$$

This law has the form of a balance law with vanishing flux term.

From Eq. (22.104) follows also the balance of micro-inertia for the mixture as a whole. We define

$$
\begin{aligned}
\rho\bar{\boldsymbol{\Theta}} &= \sum^\alpha \rho^\alpha \bar{\boldsymbol{\Theta}}^\alpha, && \text{(second rank tensor)}, \\
\boldsymbol{\Phi}_{\boldsymbol{\Theta}} &= -\sum^\alpha \rho^\alpha \bar{\boldsymbol{\Theta}}^\alpha \otimes \boldsymbol{u}^\alpha, && \text{(third rank tensor)}, \\
\boldsymbol{\sigma}_{\boldsymbol{\Theta}} &= \sum^\alpha 2\text{sym}(\rho^\alpha \bar{\boldsymbol{\Theta}}^\alpha \bar{\boldsymbol{\Omega}}^\alpha) && \text{(second rank tensor)}, \\
\hat{\boldsymbol{\Theta}}^m &= \sum^\alpha \mathfrak{c}^\alpha \bar{\boldsymbol{\Theta}}^\alpha, && \text{(second rank tensor)}.
\end{aligned}
\tag{22.105}
$$

in which

$$
\boldsymbol{u}^\alpha = \boldsymbol{v}^\alpha - \boldsymbol{v} \quad (\rho\boldsymbol{v} = \sum^\alpha \rho^\alpha \boldsymbol{v}^\alpha)
$$

is the diffusion velocity. The balance law of micro-inertia, thus, takes the form

$$
(\rho\bar{\boldsymbol{\Theta}})^{\cdot} + \rho\bar{\boldsymbol{\Theta}}\text{div}\,\dot{\boldsymbol{x}} = \text{div}\,\boldsymbol{\Phi}_{\boldsymbol{\Theta}} + \boldsymbol{\sigma}_{\boldsymbol{\Theta}} + \hat{\boldsymbol{\Theta}}^m, \tag{22.106}
$$

in which the terms on the right-hand side are given by (22.105) in terms of the corresponding quantities of the constituents. Note also that $\hat{\boldsymbol{\Theta}}^m = \mathbf{0}$, if all the particles have the same moment of micro-inertia, then $\hat{\boldsymbol{\Theta}}^m \equiv \mathbf{0}$, since $\sum_\alpha \mathfrak{c}^\alpha = 0$.

Note: In the literature $\boldsymbol{\sigma}_{\boldsymbol{\Theta}}$ is called a supply, but this is actually not appropriate, because (22.105) contains no external fields. So, $\boldsymbol{\sigma}_{\boldsymbol{\Theta}}$ is better called a contribution to the production of micro-inertia. Similarly, $\hat{\boldsymbol{\Theta}}$ is a production of micro-inertia due to mass production. Also, this production term does not need to vanish.

22.12 Cosserats Book of 1909, Its Reception and Influence on the 20th Century and Beyond

In Chap. 21 of this volume of fluid and thermodynamics, the field equations of a polar continuum were presented in a suggestive form, starting from the basic equations of rigid body dynamics: linear and angular momentum. In the formulation of motor calculus, NEWTON's second law and EULER's law of angular momentum were formally written as a motor equation, in which the *kinematic* motor with respect to a body point is balanced by a corresponding *dynamic* motor. This concept was then "transformed and extended" to a deformable continuous body and applied to a volume element of the body. Ingredients, new as compared to a BOLTZMANN continuum, are

- a specific spin density, expressed as $\boldsymbol{s} = \boldsymbol{\Theta}\boldsymbol{\omega}$, $\boldsymbol{\Theta} = \boldsymbol{\Theta}^T$,
- a spin flux—couple stress tensor, $\boldsymbol{m}$,
- a specific body couple $\rho\boldsymbol{\ell}$.

In this motivation, the dynamical spin density $\boldsymbol{s}$ was conjectured to be related to the finite body counterpart as "specific moment of inertia $\boldsymbol{\Theta}$ times angular velocity $\boldsymbol{\omega}$ of the body element", but nothing specific was expressed about the detailed properties of the spin parameterization $\boldsymbol{s} = \boldsymbol{\Theta}\boldsymbol{\omega}$, except its motivation by rigid body dynamics.

It is emphasized that this is *not* how the COSSERAT brothers formulated their mechanics of deformable bodies. According to G.A. MAUGIN [19]:

> The best analysis of the book remains the original review, written by WILSON [44] from M.I.T. [...], who had the right state of mind to capture the essential arguments of the Cosserats. First, he considers the book as a contribution to the analytical mechanics of continua, and this is spot on. In effect, the very object of the book is the deduction of what we now call 'field equations' of continua of one, two or three dimensions, from a LAGRANGEan–HAMILTONIAN principle of the general form
>
> $$\delta \int_T \int_V W \, \mathrm{d}v \mathrm{d}t = 0, \tag{22.107}$$
>
> where T is a time interval, V is a bounded volume in the considered physical space, and W is a known function of well chosen arguments. In standard variational mechanics W is made explicit in terms of an identified kinetic energy and a potential energy, so that W is the 'volume' [...] density, where the notion of mass (here density) is a basic one [...].

> [...] The COSSERATs' presentation is their initial remark that the *action* (energy multiplied by time) [...] is invariant under the group of EUCLIDian displacements. This requirement, systematically applied to (22.107) provides the notion of EUCLID*ian action* in the COSSERATs' formulation. From this should be deduced the basic local balance laws of linear momentum, angular momentum and energy, corresponding to the seven parameters (spatial translation, rotation, time translation) of the EUCLIDian group in $\overset{3}{E}$ [...]. What the COSSERATs do is to implement this approach in a well temperate manner with the successive examination of one, two and three-dimensional bodies, [...] with the possible extension to true dynamics [...]. As remarked by WILSON [44], p. 242, the COSSERATs' book may have proposed 'the most general and unifying theory of mechanics' so far (as of (1909)). Probably under the influence of DARBOUX, the COSSERATs considered that the *'fundamental geometric element in their system is not the point, but the point carrying a system of rectangular axes, that is, the tri-rectangular triedal angle'*. In this case the function W should be 'a function of the coordinates of the vertex but also a function of the nine direction cosines of the edges of the angle, and of the first derivatives of these coordinates and direction cosines with respect to time' (in the dynamical case) or the arc length in the case of the elastic filament. All these are WILSON's words [...].
>
> [...] The enforcement of the EUCLIDian group structure leads the COSSERATs to consider on an equal footing invariance under spatial translations *and* spatial rotations. That is how they are led to considering *non-symmetric stress tensors* and the presence of body couples and of a new internal force, called *couple stress tensor* in modern jargon.

So much for MAUGIN's text [19]. He states that it is not worth to "dwell in detail with the COSSERATs' treatment, which is somewhat repetitive and not very attractive in modern terms". He suggests looking into pp. 157–172 of [3], calling this unpleasant aspect to modern eyes, a "fantastic and frightening aspect of the individual component equations", which are now elegantly written in symbolic tensor notation as

$$\operatorname{div}\boldsymbol{t} + \rho\boldsymbol{f} = \rho\dot{\boldsymbol{v}}, \quad \operatorname{div}\boldsymbol{m} - \operatorname{dual}(\boldsymbol{t} - \boldsymbol{t}^T) + \rho\boldsymbol{\ell} = \rho\dot{\boldsymbol{s}}, \qquad (22.108)$$

written in this form in $(21.68)_{2,3}$ of Chap. 21. These equations remained essentially dormant through the first half of the twentieth century until they were "resurrected" in the 1950s–1970s. What, however, the COSSERAT brothers else achieved were a revival of a general viewpoint of mathematical physics in the use of *variational principles* and *group theoretical arguments* before EMMY NOETHER [22] had formulated her famous theorem. As quoted by MAUGIN [19] "WILSON [44] emphasized that an advantage of the COSSERAT approach is the association it provides with the transfer of any deductive-intuitional physical science to the corresponding formal deductive mathematical discipline".

As for applications, the COSSERAT brothers did, apart from very general formulae for the W function, not provide any specific information on possible constitutive equations. Apparently, they were not so much interested in problem solutions. In their memoir [3], only one- and two-dimensional models are close to engineering concepts, who model rods, plates, and shells as stated by ERICKSEN and TRUESDELL [7]. These are amply known to civil and mechanical engineers via the BERNOULLI–NAVIER, respectively TIMOSHENKO beam theories and KIRCHHOFF–LOVE, respectively REISSNER–MINDLIN plate bending theories in the eighteenth to twentieth centuries.

Apart from the singled-out review of WILSON [44] light to the "first half of the 20th COSSERAT-dark century" was—following MAUGIN [19]—brought by HEUN [15] and HELLINGER [14], and, in particular by the work of JOACHIM SUDRIA (1875–1950) [26, 27]. MAUGIN states, quoting [1], that TRUESDELL found SUDRIA's memoir of 1935 "while perusing work of the 1930s in continuum mechanics" and, thus uncovered the COSSERAT book of 1909, a study that led TRUESDELL to state that "the COSSERAT's Masterpiece stands as a tower in the field" [38].

The true rebirth of structured continua started in the second half of the twentieth century with pioneering work of the Germans GÜNTHER [13], NEUBER [21] and SCHÄFER [24], and in the United States by work of ERICKSEN and others [6, 7], where the use of "directors", the set of unit vectors attached to each material point in the line of DUHEM and the COSSERATs, reappeared first again since the COSSERATs time. Three mutually orthogonal directors which follow a material point and perform as a unit their independent rotational motion, to model the microrotation of the COSSERAT or micropolar continuum of this chapter. This concept was likely first generalized by ERINGEN and SHUHUBI [10]. "It is equivalent to a DUHEM kind of kinematic description with three deformable 'directors' and relative angle changes between these directors in the course of deformation: the microstructure itself is deformable and is in fact subjected to a homogeneous micro-deformation (represented by six additional internal degrees of freedom", [19]. Into this realm also belongs MINDLINs [20] paper on microstructure in elasticity.

The elegant derivation of micropolar strain measures from inner products of directors and displacement increments culminates in the works of ERINGEN and KAFADAR [9] and a bit earlier by KAFADAR [17, 18].

The last decades have not only brought uncountable contributions to solid mechanics: (i) theories of rods and shells, but equally also (ii) micro-continuum fluid field theories [11], (iii) "reduced" formulations, such as ERICKSENs liquid crystal theory, in which fluid particles are "only" equipped with a single director [5, 8], (iv) micropolar two-phase formulations on the basis of porous media by DIEBELS [4], and (v) formulations of localization behavior in plastic porous media by VOLK [43].

References

1. Ball, J.M., James, R.D.: The scientific life and influence of Clifford Ambrose Truesdell III. Arch. Rational Mech. Anal. **161**, 1–26 (2002)
2. Bowen, R.M., Wang, C.-C.: Introduction to Vectors and Tensors. Vol. 1: Linear and MultillinearAlgebra, Vol. 2: Vector and Tensor Analysis, p. 434. Plenum Press (1976)
3. Cosserat, E., Cosserat, F.: Théorie Des Corps Déformables. Herrmann & Fils, Paris (1909)
4. Diebels, S.: Mikropolare Zweiphasenmodelle. Formulierung auf der Basis der Theorie Poröser Medien. Bericht Nr II-4 aus dem Institut für Mechanik (Bauwesen) Lehrstuhl II. Universität Stuttgart, 188 Seiten (2000)
5. Ericksen, J.L., Kinderlehrer, D.: Theory and Applications of Liquid Crystals. The IMA Volumes in Mathematics and its Applications. Springer, Berlin (1987)
6. Ericksen, J.L., Rivlin, R.S.: Large deformations of homogeneous anisotropic materials. J. Rational Mech. Anal. **1**, 295–323 (1954)

7. Ericksen, J.L., Truesdell, C.A.: Exact theory of stress and strain in rods and shells. Arch. Rational Mech. Anal. **1**, 295–323 (1958)
8. Ericksen, J.L.: Conservation laws for liquid crystals. Trans. Soc. Rheol. **5**, 23–34 (1966)
9. Eringen, C.A., Kafadar, C.B.: Polar field theories. In: Eringen, C.A. (ed.) Continuum Physics, vol. IV, pp. 1–75. Academic Press, New York (1976)
10. Eringen, C.A., Shuhubi, E.S.: Nonlinear theory of simple microelastic solids. Int. J. Eng. Sci. **2**, 189–203 (1964)
11. Eringen, C.A.: Microcontinuum Field Theories, II Fluent Media, p. 341. Springer, New York (2001)
12. Eringen, C.A.: Simple microfluids. Int. J. Eng. Sci. **2**, 205–217 (1964)
13. Günther, W.: Zur Statik und Dynamik des Cosseratschen Kontinuums. Abh. Raunschweig. Wiss. Ges. **10**, 195 (1958)
14. Hellinger, E.: Die allgemeinen Ansätze der Mechanik der Kontinua. In: Klein, F., Wagner, K. (eds.) Encyklopaedia der mathematischen Wissenschaften, vol. 4, Part 4, pp. 602–694. Springer, Berlin (1914)
15. Heun, K.: Ansätze und allgemeine Methoden der Systemmechanik. In: Klein, F., Wagner, K. (eds.) Encyklopaedia der mathematischen Wissenschaften, vol. 4/2, Article 11, pp. 359–504. Springer, Berlin (1904)
16. Hutter, K., Jöhnk, K.: Continuum Methods of Physical Modeling, p. 635. Springer, Berlin (2004)
17. Kafadar, C.B., Eringen, C.A.: Micorpolar media I – the classical theory. Int. J. Eng. Sci. **9**, 291–308 (1971)
18. Kafadar, C.B.: On the nonlinear theory of rods. Int. J. Eng. Sci. **10**(4), 369–391 (1972)
19. Maugin, G.A.: Continuum Mechanics Through the Eighteenth and Nineteenth Centuries. Solid-Mechanics and its Application 214. Springer International Publishing, Switzerland (2014). https://doi.org/10.1007/978-3-319-05374-5-8
20. Mindlin, R.D.: Microstructure in linear elasticity. Arch. Rational Mech. Anal. **16**, 51–78 (1964)
21. Neuber, H.: On the general solution of linear elastic problems is isotropic and anisotropic Cosserat continua. In: Görtler, H. (ed) Proceedings of the 11th International Conference of Applied Mechanics (München 1964) pp. 153–158. Springer, Berlin (1964)
22. Noether, E.: Invariante Variationsprobleme. Kgl-Ges. Wiss, Gttingen, Math. Phys. Kl. **2**, 235–257 (1918). [Engl Translation by M. Tavel, Transp. Theory Stat. Phys. I, 186–207 (1971)]
23. Rational Fluid Mechanics, pp. 1687–1765. Orell Füssli, Switzerland (1954)
24. Schaefer, H.: Das Cosserat Continuum. Z. Angew. Math. Mech. **47**, 34 (1967)
25. Steinmann, P.: A micropolar theory of finite deformation and finite rotation multiplicative elastoplasticity. Int. J. Solids Struct. **31**, 1063–1084 (1994)
26. Sudria, J.: Contribution a thorie de l' action euclidiennne. Ann. Fac. Sci. Toulouse, 3i me s erie, **17**, 63–152 (1925)
27. Sudria, J.: L' action euclidiennne de deformationdes et de movement. Mémorial Sciences Mathématiques, vol. 29, p. 56. Gauthier-Villars, Paris (1935)
28. Truesdell, C.A., Bharatha, S., : In: Carnot, S., Reech, F. (eds.) The Concepts and Logic of Classical Thermodynamics as a Theory of Heat Engines. Rigorously Constructed Upon the Foundation Laid. Springer, New York (1977)
29. Truesdell, C.A., Muncaster, R.G.: Fundamentals of Maxwell's Kinetic Theory of a Simple Monatomic Gas. Treated as a Branch of Rational Mechanics. Academic Press, New York (1980)
30. Truesdell, C.A., Noll, W.: In: Flügge, S. (ed.) Non-Linear Field Theories of Mechanics. Handbuch Der Physik, vol. III/3, Springer, Berlin (1965)
31. Truesdell, C.A., Rajagopal, K.R.: An Introduction to the Mechanics of Fluids. Birkhäuser, Boston (1999)
32. Truesdell, C.A., Wang, C.C.: Introduction to Rational Elasticity. Leyden, Wolters-Noordhoff (1973)
33. Truesdell, C.A.: A First Course in Rational Continuum Mechanics. Academic Press, Boston (1977)

34. Truesdell, C.A.: An Essay Towards a Unified Theory of Special Functions. Princeton University Press, Princeton (1948)
35. Truesdell, C.A.: Essays in the History of Mechanics. Springer, Berlin (1968)
36. Truesdell, C.A.: Great Scientists of Old as Heretics in the Scientific Method. University of Virginia Press, Virginia (1987). ISBN 0-8139-1134-6
37. Truesdell, C.A.: Rational Thermodynamics. McGraw-Hill, New York (1969)
38. Truesdell, C.A.: The Elements of Continuum Mechanics. Springer, Berlin (1966)
39. Truesdell, C.A.: The Kinematics of Vorticity. Indiana University Press, Indiana (1954)
40. Truesdell, C.A.: The Tragicomical History of Thermodynamics, pp. 1822–1854. Springer, Berlin (1980). ISBN 0-387-90403-4
41. Truesdell, C.A.: Vorticity and the Thermodynamic State in a Gas Flow. Gauthier-Villars, Paris (1952)
42. Truesdell, C.A, Toupin, R.: In: Flügge, S. (ed.) Classical Field Theories of Mechanics. Handbuch Der Physik, vol. III/1. Springer, Berlin (1960)
43. Volk. W.: Untersuchung des Lokalisierungsverhaltens mikropolarer poröser Medien mit Hilfe der Cosserat Theorie. Bericht Nr II-2 aus dem Institut für Mechanik (Bauwesen) Lehrstuhl II. Universität Stuttgart, 188 Seiten (2000)
44. Wilson, E.B.: An advance in theoretical mechanics: Théorie des corps déformables by E. and F. Cosserat. Bull. Amer. Math. Soc. **19**(5), 242–246 (1913)

Chapter 23

Thermodynamics of Class I and Class II Classical Mixtures

Abstract In this chapter, two versions of mixtures of BOLTZMANN-type continua are subject to thermodynamic analyses for viscous fluids. Of the two forms of the Second Law that were introduced—the CLAUSIUS–DUHEM inequality applied to open systems and the entropy principle of MÜLLER—the latter principle is employed in the process of deduction of the implications revealed by the particular Second Law. The goal in the two parts of the chapter is to derive the ultimate forms of the governing equations, which describe the thermomechanical response of the postulated constitutive behavior without violation of the Second Law of thermodynamics. The versions of mixtures which are analyzed are

- *Diffusion of tracers in a classical fluid*: The conceptual prerequisites of this type of processes are mixtures of class I, in which the major component is the bearer fluid within which a finite number of constituents with minute concentration are suspended or solved in the bearer fluid. The motion of these tracers is described by the difference of the constituent velocities relative to the barycentric velocity of the mixture as a whole. For the dissipative constitutive class applied to the entropy principle, the existence of the KELVIN temperature is proved, the form of the GIBBS relation could be determined as could the conditions of thermodynamic equilibrium and the constitutive behavior in its vicinity.
- *Thermodynamics of a saturated mixture of nonpolar solid–fluid constituents*: Conceptually these systems are treated as classical mixtures of class II, in which the individual motions of the constituents are separately accounted for by their own balances of mass and momentum, but subject to a common temperature. The analysis of the dissipation inequality is performed subject to the assumption of constant true density of all constituents and the supposition of saturation of the mixture. The constitutive relations are postulated for a mixture of viscous heat conducting fluids. The explanation of the entropy principle is structurally analogous to that

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This chapter is a revised and somewhat extended version of Chap. 7 "Theory of Mixtures" of [20], which was fraught with a number of slips and computational errors. The text is also pruned in certain places and extended in others.

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of the class I-diffusion theory, but is analytically much more complex. Unfortunately, intermediate ad hoc assumptions must be introduced to deduce concrete results that will lead to fully identifiable fluid dynamical equations, which are in conformity with the Second Law for the presented type of mixtures.

Keywords Diffusion of classical fluid mixtures · MÜLLER-type thermodynamics · Thermodynamic equilibrium and nonequilibrium · Classical saturated solid–fluid mixtures

List of Symbols

All quantities carrying a sub(super)script α are thought to be written for constituent α of a mixture. "Classical" theory means "BOLTZMANN" continuum

Roman Symbols

$\boldsymbol{c}^*$	Translation vector in EUCLIDian transformations
$\mathfrak{c}^\alpha$	Specific mass production of constituent α
$C_{ij}^{\alpha\beta}$	Coefficients of a quadratic nonequilibrium representation of the dissipation potential, see (23.71)
$\boldsymbol{D}$	Strain rate or stretching tensor, $\boldsymbol{D} = \mathrm{sym}(\mathrm{grad}\,\boldsymbol{v})$
$\boldsymbol{D}^\alpha$	Constituent symmetrized relative deformation rate tensor, $\boldsymbol{D}^\alpha = \mathrm{sym}\boldsymbol{U}^\alpha = \mathrm{sym}(\mathrm{grad}\,\boldsymbol{v})^\alpha)$
D_T^α, $D_{\xi^\gamma}^\alpha$	Mass flux coefficients for $\boldsymbol{j}^\alpha$
$\mathrm{d}F$	Total differential of a function
$\boldsymbol{f}$	Vector of body force
$\boldsymbol{\mathcal{F}}_{x_i}$	Auxiliary variable, see $(23.100)_2$
g	Integrating denominator of a total differential $\mathrm{d}F$
$\boldsymbol{j}^\alpha$	Diffusive mass flux vector of consistent α
$\boldsymbol{k}$	Extra entropy flux vector, see $(23.61)_1$
$\boldsymbol{\mathfrak{k}}^\alpha$	Specific spin production of constituent α
$\boldsymbol{\ell}^\alpha$	Specific couple, spin supply of constituent α
$\boldsymbol{m}^\alpha$	Couple stress tensor of constituent α
$\boldsymbol{\mathfrak{m}}^\alpha$	Interaction force of constituent α
N	Number of constituents
$\mathfrak{n}^\alpha = \mathfrak{c}^\alpha/\hat{\rho}^\alpha$	Production rate of specific volume of constituent α
$\boldsymbol{O}^*$	Orthogonal 3×3 transformation matrix, $\boldsymbol{O}^*\boldsymbol{O}^{*T} = \boldsymbol{O}^{*T}\boldsymbol{O}^* = \boldsymbol{I}$
$p = -(\Lambda^\rho/\Lambda^\varepsilon)\rho$	Pressure, thermodynamic pressure
$\mathcal{P}_{x_i}$	Auxiliary variable, see $(23.100)_1$
$\boldsymbol{q}$	Heat flux vector of the mixture
$\boldsymbol{q}^\alpha$	Heat flux vector of constituent α
$\mathfrak{r}$	Specific energy supply rate density, radiation
s	Entropy density of the mixture
$\boldsymbol{s}^\alpha$	Specific spin density of constituent α

$\boldsymbol{t}$	Mixture Cauchy stress tensor ($\boldsymbol{t} = \boldsymbol{t}^T$)
$\boldsymbol{t}^\alpha$	Constituent Cauchy stress tensor
T	Absolute (Kelvin) temperature, $T = 1/(\Lambda^{\varepsilon}(\theta))$
$\boldsymbol{u}^\alpha$	Diffusion velocity of constituent α, $\boldsymbol{u}^\alpha := \boldsymbol{v}^\alpha - \boldsymbol{v}$
$\boldsymbol{U}^\alpha$	Relative (nonsymmetric) deformation, $\boldsymbol{U}^\alpha := \text{grad}\, \boldsymbol{v}^\alpha - \boldsymbol{W}$ rate tensor
$\boldsymbol{v}$	Barycentric velocity
$\boldsymbol{v}^\alpha$	Constituent velocity vector
$\boldsymbol{v}^*$	Obtained by a Euclidian transformation from $\boldsymbol{v}$
$\boldsymbol{W}$	Vorticity tensor of the barycentric velocity field, $\boldsymbol{W} = \text{skwgrad}\, \boldsymbol{v}$
$\boldsymbol{W}^\alpha$	Relative vorticity tensor of constituent α, $\boldsymbol{W}^\alpha = \text{skw}(\boldsymbol{U}^\alpha) = \text{skw}(\text{grad}\, \boldsymbol{v}^\alpha) - \boldsymbol{W}$
$\boldsymbol{X}$	Independent constitutive variables out of the thermodynamic equilibrium
x^*, y^*, z^*	Rotated and shifted coordinates of x, y, z.

Greek Symbols

α, β, γ	Counting indices of constituents ($= 1, \dots, N-1$)
$\boldsymbol{\alpha}(\boldsymbol{\Xi})$	Vector of Liu identities
$\boldsymbol{\beta}$	Vector of derivatives of the independent constitutive variables
$\Gamma(\boldsymbol{\Xi}) \geqslant 0$	Reduced entropy inequality
δ	Small positive real quantity
δ_{ij}	Kronecker delta ($\delta_{ij} = 1$ for $i = j$; $\delta_{ij} = 0$ for $i \neq j$)
ε	Internal energy of the mixture, small positive parameter
ε_I	Inner internal energy
ε_D	Diffusive internal energy
η^s	Specific entropy supply
θ	Empirical temperature
$\Theta(\theta)$	Absolute temperature as a function of θ
κ_T, κ_{ξ^α}	Thermal conductivity coefficients
Λ^ρ	Lagrange parameter of the mixture mass balance
Λ^{ξ^α}	Lagrange parameter of the specific mass balance of constituent α
$\boldsymbol{\Lambda}^{\boldsymbol{v}}$	Lagrange parameter of the mixture momentum balance
Λ^ε	Lagrange parameter of the mixture internal energy
λ	Integrating factor of a Pfaffian differential form
μ^{ξ^α}	Chemical potential of constituent α
ν^α	Volume fractions of constituent α
$\boldsymbol{\Xi}$	Symbol for independent constitutive variables
ξ^α	Constituent mass ratio or mass concentration
π^s	Specific entropy production
ρ	Density of the mixture
ρ^α	Constituent mass density
$\boldsymbol{\phi}, \boldsymbol{\phi}^s$	Entropy flux

ϕ	Entropy flux of the diffusive theory, see (23.61)$_2$, $\phi = \frac{1}{T}\left(\boldsymbol{q} - \mu^{\xi^\alpha}\boldsymbol{j}^\alpha\right)$, ($\alpha = 1, \dots, N$)
$\boldsymbol{\chi}(\boldsymbol{X}, t)$	Motion function of a fluid mixture particle from position $\boldsymbol{X}$ in the reference configuration.
Ψ	Symbol for the dependent constitutive variables
$\psi = \varepsilon - Ts$	Mixture HELMHOLTZ free energy
ψ_D	Dissipation potential
ψ_I	Internal HELMHOLTZ free energy of the mixture
ψ_D	Diffusive part of the HELMHOLTZ free energy, $\psi_D = \frac{1}{2}\sum_{\alpha=1}^{N}\rho^\alpha\boldsymbol{u}^\alpha\cdot\boldsymbol{u}^\alpha$

Miscellaneous Symbols

grad	Gradient operator with respect to the present coordinates
div	Divergence operator with respect to the present coordinates
curl	Curl operator with respect to the present coordinates
$\mathrm{grd}\mu^{\xi^\alpha}$	Gradient of μ^{ξ^α} reduced by its temperature gradient, $\mathrm{grd}\mu^{\xi^\alpha} = \left(\frac{\partial\hat{\hat{\mu}}^{\xi^\alpha}}{\partial\xi^\beta}\operatorname{grad}\xi^\beta - \frac{\partial\hat{\mu}^{\xi^\alpha}}{\partial T}\operatorname{grad}T\right)$.

23.1 General Introduction

The concept of diffusion is an ubiquitous phenomenon of processes occurring in physics, chemistry, biology, sociology, finance, etc. In each case, the object—atoms, molecules, aerosols, tracers, ideas—that is undergoing diffusion is "spreading out" from a source location at which there is higher concentration of the object under consideration, to locations of smaller concentration. Diffusion is generally introduced in two different ways: first, phenomenologically starting with FICK's law of diffusion, in which the flux of matter from the object is assumed proportional to the gradient from higher concentration to lower ones, or, second, by random walk of the objects. We shall here exclusively be concerned with the first phenomenological approach. Diffusion, interpreted as movement of heat from higher levels of molecular oscillations to lower ones, is expressed in FOURIER's heat law as heat flux from higher temperatures to lower ones. It is thus nearly obvious that for diffusion of matter or heat, the same thermodynamic concepts apply.

In modern science, the first experimental study of diffusion was performed by THOMAS GRAHAM (1805–1869). He studied diffusion in gases that he described between 1831–1833 as follows: "*…gases of different nature, when brought into contact, do not arrange themselves according to their density, the heaviest undermost, and the lighter uppermost, but they spontaneously diffuse, mutually and equally, through each other, and so remain in the intimate state of mixture for any length of time*".

Fig. 23.1 THOMAS GRAHAM (20 Dec. 1805–16 Sept. 1869)

THOMAS GRAHAM, born in GLASGOW, should, according to the desire of his father (a successful textile manufacturer), have become a priest at the church of Scotland, but studied chemistry at the University of Glasgow under the supervision of Professor THOMAS THOMSON and received his M.A. in 1824. Later, he studied medicine at the University of Edinburgh and, lacking further support from his father, occupied several positions as a chemist and professorial assignments in numerous colleges, including the University of Strathclyde in Glasgow, the Royal College of Science and Technology and the University of London. In 1828, at the age of only 23 years, he was elected an Honorary Fellow of the Royal Society of Edinburgh and won its Keith Medal for the period of 1831–1833. He founded the Chemical Society of London in 1841 and was, in 1866, elected a foreign member of the Royal Swedish Academy of Sciences. His final position was as Master of the Mint from 1855 to his death in 1869 (once occupied by ISAAC NEWTON). He is buried in the family grave at the Glasgow Cathedral.

THOMAS GRAHAM was elected a Fellow of the Edinburgh Royal Society in 1828 and of the Royal Society in 1836, from which he received the Royal Medal in 1837 and 1863 and the Copley Medal in 1862. He obtained an Honorary Doctorate from Oxford University in 1853 and the Prix Jecker of the Paris Academy of Sciences in 1862. A statue of GRAHAM, sculpted by WILLIAM BRODIE in *George Square* (see Fig. above) in Glasgow was erected in 1872, and the University of Strathclyde has named the building housing the Chemistry Department the *Thomas Graham Building*.

These signs of an outstanding science career of THOMAS GRAHAM are based on his studies of the behavior of gases, which resulted primarily in relations known as the two "GRAHAMs laws" regarding *gas diffusion* and *gas effusion*. For "diffusion", GRAHAM found by repeatedly measuring under the same conditions of pressure and temperature, that the rate of diffusive mixing of a gas is inversely proportional to the square root of its density (or alternatively its molar mass). A similar relation was also deduced by him for effusion. GRAHAM also made fundamental discoveries to *dialysis* and *colloids* that led to the ability of separating colloids and crystalloids using the "dialyser" technology, which he invented and for which he became famous. His book on colloid chemistry was a "best runner" for decades in the nineteenth century.

The text is based on www.wikipedia.org

The measurements of GRAHAM[1] contributed to JAMES CLERK MAXWELL (1831–1879) deriving, in 1867, the coefficient of diffusion of CO_2 in air. ADOLF FICK (1829–1901) proposed his law of diffusion in 1855 at the age of 26, moreover, FOURIERs (1768–1830) law of heat conduction was presented in 1822, and OHMs (1798–1854) law for the electric current was proposed in 1827. All these laws express a flux quantity with a concentration gradient of a "driving" quantity (see https://en.wikipedia.org/wiki/Diffusion).

The first two chapters in this volume are devoted to the derivation of the fundamental physical laws of mixtures of a finite number of constituents with micro-polar structure and the associated kinematic peculiarities of the description of their deformation. The dynamical laws of classical physics are in this case the balance laws of mass, linear and angular momenta, energy, and entropy. Such microstructural or COSSERAT continua are fraught with a nontrivial form of the angular momentum balance, i.e., a spin balance for each constituent. It was shown in these introductory chapters also that when spin density, couple stress tensor, and body couple of all constituents vanish—these are the conditions of constituents with BOLTZMANN structure, called here *classical mixtures*—the skew-symmetric parts of the constituent stress tensors are related to the EUCLIDian invariant constituent spin productions, see (21.24). If a particular such spin production vanishes, then the stress tensor of that constituent is symmetric. Often, it is assumed that all constituent stress tensors are symmetric; this is then tantamount to the statement that the EUCLIDian spin productions of all constituents vanish.

In the first two chapters of this volume, no attempt was made to formulate constitutive equations to characterize the material behavior of the mixture bodies in focus. This will be done in this and in ensuing chapters for particular types of mixtures, which may be deduced by simplifications from the general equations. In this chapter, classical mixtures of class I and II will be looked at. COSSERAT effects of polarity

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[1] For biographies of

- THOMAS GRAHAM, see **Fig. 23.1**;
- JAMES CLERK MAXWELL, see Fig. 17.10, Vol. 2 of this treatise, p. 334 [22];
- ADOLF EUGEN FICK, see Fig. 17.31, Vol. 2 of this treatise, p. 365 [22];
- JEAN BAPTISTE JOSEPH FOURIER, see Fig. 18.1, Vol. 2 of this treatise p. 439 [22].

will all be ignored. In particular, a mixture of nonpolar constituents will be looked at, for which

$$\boldsymbol{s}^{\alpha} = \boldsymbol{0}\,, \quad \boldsymbol{m}^{\alpha} = \boldsymbol{0}\,, \quad \boldsymbol{\ell}^{\alpha} = \boldsymbol{0}\,, \quad \boldsymbol{\mathfrak{t}}^{\alpha} = \boldsymbol{0}\,, \quad (\alpha = 1, 2, \ldots, N). \tag{23.1}$$

These assumptions will be maintained in this chapter and applied to diffusive tracers in a fluid (class I) mixture and a saturated (class II) mixture of solid and fluid constituents.

23.2 Diffusion of Tracers in a Classical Fluid

23.2.1 Basic Assumptions

It is assumed that this mixture consists of a fluid and $N - 1$ *substances* in suspension or solution, called *tracers*, which, in comparison to the main fluid, arise only in small concentrations. Examples of such fluid mixtures are all waters on Earth (rivers, lakes, the ocean), which contain minerals, salts and pollutants, but also nutrients (for instance phosphate and the plankton) in solved or particulate form. Another example is the atmosphere—primarily the troposphere and stratosphere[2] —of which the chemical composition varies spatially and temporally, and which is loaded by *aerosols*, i.e., suspended particles (dust and industrial waste).

If the masses of the tracers are small in comparison to the mass of the main fluid, it may be assumed that the tracer particles are carried by the main fluid and therefore possess the same or nearly the same velocity as the main fluid. Likewise, one may generally assume that the tracer particles have the same temperature as the fluid particle at the same location. Consequently, the prerequisites of a *mixture theory of class I* are here given, for which the differences of the momenta and internal energies of the individual components are dynamically and thermodynamically not important; it therefore suffices to model only the momentum and internal energy of the mixture as a whole, but to follow in detail the mass evolution of each constituent.[3]

It is customary to write down the balance laws of mass, momentum, and energy for the mixture as a whole and to complement these by the mass balance laws for the $N - 1$ tracers. Because of the simplifying prerequisites (23.1), one obtains

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} + \rho \operatorname{div} \boldsymbol{v} = 0, \tag{23.2}$$

$$\rho \frac{\mathrm{d}\xi^{\alpha}}{\mathrm{d}t} = \operatorname{div} \boldsymbol{j}^{\alpha} + \mathfrak{c}, \quad (\alpha = 1, 2, 3, \ldots, N - 1), \tag{23.3}$$

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[2] The troposphere is the lowest layer of the atmosphere, approximately 8–10 km thick. The stratosphere is the atmosphere layer immediately above the troposphere and extends about to 50 km above the Earth's surface.

[3] In counting the constituents, the index $\alpha = N$ will be reserved to the main fluid, so that $\alpha = 1, 2, 3, \ldots, N - 1$ will be used for the tracers. This convention will be retained in the sequel.

$$\rho \frac{\mathrm{d}\boldsymbol{v}}{\mathrm{d}t} = \operatorname{div} \boldsymbol{t} + \rho \boldsymbol{f}, \qquad (\boldsymbol{t} = \boldsymbol{t}^T), \tag{23.4}$$

$$\rho \frac{\mathrm{d}\varepsilon}{\mathrm{d}t} = -\operatorname{div} \boldsymbol{q} + (\operatorname{grad} \boldsymbol{v} \cdot \boldsymbol{t}^T) + \rho \mathfrak{r}, \tag{23.5}$$

in which $\boldsymbol{v}$ denotes the barycentric velocity and

$$\xi^\alpha := \frac{\rho^\alpha}{\rho}, \quad \boldsymbol{j}^\alpha := \rho \xi^\alpha (\boldsymbol{v}^\alpha - \boldsymbol{v}), \quad (\alpha = 1, 2, 3, \dots, N-1) \tag{23.6}$$

are the *mass ratio* or *concentration* and the so-called *diffusive fluxes* of the constituents α. The first variable, ξ^α, gives the ratio of the mass of constituent α to that of the mixture as a whole, the second describes the flux of mass of constituent α relative to the barycentric motion. Equations (23.2), (23.4) and (23.5) are derivable from (21.61).

To prove (23.3), let us start with the balance law of mass in the form

$$\frac{\partial \rho^\alpha}{\partial t} + \operatorname{div} (\rho^\alpha \boldsymbol{v}^\alpha) = \mathfrak{c}^\alpha \tag{23.7}$$

and use $\rho^\alpha = \xi^\alpha \rho$. Product differentiation then yields

$$\frac{\partial \rho}{\partial t} \xi^\alpha + \rho \frac{\partial \xi^\alpha}{\partial t} + \xi^\alpha \operatorname{div} (\rho \boldsymbol{v}^\alpha) + (\operatorname{grad} \xi^\alpha) \cdot \rho \boldsymbol{v}^\alpha = \mathfrak{c}^\alpha. \tag{23.8}$$

Adding and subtracting on the left-hand side the terms $\xi^\alpha \operatorname{div} (\rho \boldsymbol{v})$ and $(\operatorname{grad} \xi^\alpha) \cdot \rho \boldsymbol{v}$, one obtains, upon combining the respective terms

$$\begin{aligned} &\underbrace{\left(\frac{\partial \rho}{\partial t} + \operatorname{div} (\rho \boldsymbol{v}) \right)}_{=0} \xi^\alpha + \rho \underbrace{\left(\frac{\partial \xi^\alpha}{\partial t} + (\operatorname{grad} \xi^\alpha)\, \boldsymbol{v}^\alpha \right)}_{\mathrm{d}\xi^\alpha / \mathrm{d}t} \\ &+ \operatorname{div} \underbrace{(\rho\, \xi^\alpha\, (\boldsymbol{v}^\alpha - \boldsymbol{v}))}_{\boldsymbol{j}^\alpha} = \mathfrak{c}^\alpha, \end{aligned} \tag{23.9}$$

where $\boldsymbol{v} = \sum_\alpha \xi^\alpha \boldsymbol{v}^\alpha$ is the barycentric velocity. It follows that (23.9) implies

$$\rho \frac{\mathrm{d}\xi^\alpha}{\mathrm{d}\,t} = -\operatorname{div} \boldsymbol{j}^\alpha + \mathfrak{c}^\alpha, \quad (\alpha = 1, 2, \dots, N), \tag{23.10}$$

which is valid for all constituents and agrees with (23.3). Equations (23.2)–(23.5) constitute $[5 + (N-1)]$ partial differential equations for the $[15 + 5(N-1)]$ field variables

$$\{\rho, \xi^\alpha, \boldsymbol{v}, \boldsymbol{j}^\alpha, \mathfrak{c}^\alpha, \boldsymbol{t}, \varepsilon, \boldsymbol{q}, \theta\}, \quad (\alpha = 1, 2, \dots, N-1). \tag{23.11}$$

The exterior body force and the radiation $\rho\mathfrak{r}$ are regarded as prescribed field quantities. Finally, it is emphasized once more that ξ^N, $\boldsymbol{j}^N$, and $\mathfrak{c}^N$ do not constitute independent variables, since the relations

$$\sum_{\alpha=1}^{N} (\xi^\alpha, \boldsymbol{j}^\alpha, \mathfrak{c}^\alpha) = (1, \boldsymbol{0}, 0) \tag{23.12}$$

must be satisfied, so that ξ^N, $\boldsymbol{j}^N$, and $\mathfrak{c}^N$ are expressible as

$$\left(\xi^N, \boldsymbol{j}^N, \mathfrak{c}^N\right) = \left(1 - \sum_{\alpha=1}^{N-1} \xi^\alpha, -\sum_{\alpha=1}^{N-1} \boldsymbol{j}^\alpha, -\sum_{\alpha=1}^{N-1} \mathfrak{c}^\alpha\right) \tag{23.13}$$

and are thus given once these variables are prescribed for $\alpha = 1, 2, \dots, N-1$.

23.2.2 Material Theory for Diffusion Processes

Let us define the following variables as the $[5 + (N - 1)]$ independent fields:

$$\{\rho, \xi^\alpha, \boldsymbol{v}, \theta\}, \qquad (\alpha = 1, 2, \dots, N-1). \tag{23.14}$$

This implies that, consequently,

$$\Psi := \{\boldsymbol{j}^\alpha, \mathfrak{c}^\alpha, \boldsymbol{t}, \varepsilon, \boldsymbol{q}, \}, \qquad (\alpha = 1, 2, \dots, N-1) \tag{23.15}$$

are the $[10 + 4(N - 1)]$ field variables for which constitutive relations must be formulated in order to close the system (23.2)–(23.5) and (23.15). The intention is to consider the most simple form of a mixture theory that is capable of describing the dispersion of a number of tracers in a fluid; to this end, let us propose a *theory of diffusion* of a *heat conducting viscous fluid* with constitutive equations for the dependent field quantities (23.15) of the complexity

$$\Psi = \hat{\Psi}(\rho, \xi^\alpha, \boldsymbol{v}, \theta, \operatorname{grad}\boldsymbol{v}, \operatorname{grad}\xi^\alpha, \operatorname{grad}\theta), \tag{23.16}$$

in which $\alpha \in [1, \dots, N-1]$. The independent variables involve the fields (23.14) and the gradients of $\boldsymbol{v}$, ξ^α, and θ. The gradient of ρ need not be incorporated, since it is already accounted for by all $\operatorname{grad}\xi^\alpha$.

Because all variables listed in (23.15) are objective scalars, vectors, and tensors, and since it is requested that the constitutive relations (23.16) obey the rule of material frame indifference, it follows that $\hat{\Psi}(\cdot)$ in (23.16) cannot explicitly depend on $\boldsymbol{v}$; furthermore, $\hat{\Psi}(\cdot)$ can depend on grad $\boldsymbol{v}$ only via its symmetric part, sym(grad $\boldsymbol{v}$) $=:$ $\boldsymbol{D}$.[4] Therefore, for the considered constitutive class the material relations (23.16) reduce to

$$\Psi = \hat{\Psi}(\boldsymbol{\Xi}), \qquad \boldsymbol{\Xi} := (\rho, \xi^\alpha, \theta, \operatorname{grad} \xi^\alpha, \boldsymbol{D}, \operatorname{grad} \theta). \tag{23.20}$$

The material relations (23.20) must be in conformity with the second law of thermodynamics. The intention is to explore this requirement with the entropy principle of MÜLLER. Accordingly, there exists an additive quantity, the entropy of the mixture, which obeys the balance law

$$\rho \frac{\mathrm{d}s}{\mathrm{d}t} + \operatorname{div} \phi^s + \rho \eta^s = \rho \pi^s, \tag{23.21}$$

in which ϕ^s, η^s and π^s are the entropy flux, the entropy supply and entropy production of the mixture. According to the Second Law of Thermodynamics the entropy production must not be negative for any thermodynamic process; in other words, the inequality

$$\rho \pi^s \geqslant 0 \tag{23.22}$$

must hold for all thermodynamic processes, i.e., all solutions of (23.2)–(23.5) and all constitutive relations of the form (23.20) for the field variables (23.15). LIU has shown that instead of satisfying (23.22) for all fields which simultaneously also satisfy the field equations (23.2)–(23.5), (23.15), (23.20) one may also proceed as

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[4] To prove this, consider the EUCLIDian transformation

$$\boldsymbol{x}^* = \boldsymbol{O}^*(t)\boldsymbol{x} + \boldsymbol{c}^*(t), \qquad \boldsymbol{O}^*\boldsymbol{O}^{*T} = \boldsymbol{O}^{*T}\boldsymbol{O}^* = \boldsymbol{I}, \tag{23.17}$$

with the aid of which one obtains

$$\begin{aligned} \boldsymbol{v}^* &= \boldsymbol{O}^*\boldsymbol{v} + \dot{\boldsymbol{O}}^*\boldsymbol{x} + \dot{\boldsymbol{c}}^*, \\ \operatorname{grad}^*\boldsymbol{v}^* &= \boldsymbol{O}^*(\operatorname{grad} \boldsymbol{v})\boldsymbol{O}^{*T} + \dot{\boldsymbol{O}}^*\boldsymbol{O}^{*T}. \end{aligned} \tag{23.18}$$

It follows that neither $\boldsymbol{v}$ nor grad $\boldsymbol{v}$ are objective quantities under EUCLIDian transformations. However, since $\dot{\boldsymbol{O}}^*\boldsymbol{O}^{*T}$ is skew-symmetric, one obtains

$$\begin{aligned} \operatorname{sym} \operatorname{grad}^*\boldsymbol{v}^* &:= \boldsymbol{D}^* = \boldsymbol{O}^*\boldsymbol{D}\boldsymbol{O}^{*T}, \\ \operatorname{skw} \operatorname{grad} \boldsymbol{v}^* &:= \boldsymbol{W}^* = \boldsymbol{O}^*\boldsymbol{W}^*\boldsymbol{O}^{*T} + \dot{\boldsymbol{O}}^*\boldsymbol{O}^{*T}. \end{aligned} \tag{23.19}$$

.

follows: One subtracts (or adds, which only changes the signs of the LAGRANGE parameters) on the left-hand side of (23.22) the scalar products of the field equations with the appropriate LAGRANGE parameters, viz.,

$$\begin{aligned}
&\rho\frac{\mathrm{d}\hat{s}}{\mathrm{d}t}+\operatorname{div}\hat{\phi}^{s}-\rho\eta^{s}\\
&\quad-\Lambda^{\rho}\left(\frac{\mathrm{d}\rho}{\mathrm{d}t}+\rho\operatorname{div}\boldsymbol{v}\right)-\Lambda^{\xi^{\alpha}}\left(\rho\frac{\mathrm{d}\xi^{\alpha}}{\mathrm{d}t}+\operatorname{div}\hat{\boldsymbol{j}}^{\alpha}-\hat{\mathfrak{c}}^{\alpha}\right)\\
&\quad-\boldsymbol{\Lambda}^{\boldsymbol{v}}\cdot\left(\rho\frac{\mathrm{d}\boldsymbol{v}}{\mathrm{d}t}-\operatorname{div}\hat{\boldsymbol{t}}-\rho\boldsymbol{f}\right)-\Lambda^{\varepsilon}\left(\rho\frac{\mathrm{d}\hat{\varepsilon}}{\mathrm{d}t}+\operatorname{div}\hat{\boldsymbol{q}}-\boldsymbol{D}\cdot\hat{\boldsymbol{t}}-\rho\mathfrak{r}\right)\geqslant 0 \qquad (23.23)
\end{aligned}$$

and satisfies this extended inequality now for arbitrary, unconstrained fields. Λ^{ρ}, $\Lambda^{\xi^{\alpha}}$, $\boldsymbol{\Lambda}^{\boldsymbol{v}}$, and Λ^{ε} are LAGRANGE parameters, which must be determined along with the exploitation of the inequality (23.23). In this formula, summation must be understood over the doubly arising index $\alpha = 1, 2, 3, \dots, N-1$. The dot in the expression $\boldsymbol{\Lambda}^{\boldsymbol{v}} \cdot (\dots)$ is to be understood as the scalar product in $\mathbb{R}^3$, and all constitutive relations are thought to be substituted, a fact which we made visible by using the hat, $\hat{(\cdot)}$, in all dependent constitutive variables. The supplies or sources $\rho\eta^{s}$, $\rho\boldsymbol{f}$, and $\rho\mathfrak{r}$ are prescribable with any value we please.

If the constitutive relations for s, $\boldsymbol{j}^{\alpha}$, ξ^{α}, $\boldsymbol{t}$, ε, and $\boldsymbol{q}$ $\quad(\alpha = 1, 2, \dots, N-1)$ are substituted in (23.23) and the required differentiations are performed according to the chain rule of differentiation, one obtains after lengthy calculations an expression of the form

$$\boldsymbol{\alpha}(\boldsymbol{\Xi})\cdot\boldsymbol{\beta}+\Gamma(\boldsymbol{\Xi})-\left(\rho\eta^{s}-\boldsymbol{\Lambda}^{\boldsymbol{v}}\cdot\rho\boldsymbol{f}-\Lambda^{\varepsilon}\rho\mathfrak{r}\right)\geqslant 0. \qquad (23.24)$$

Here, $\boldsymbol{\Xi}$ is defined in (23.20), and $\boldsymbol{\alpha}$ as well as $\boldsymbol{\beta}$ are vectors with the same number of components (so that the scalar product is meaningful), and $\boldsymbol{\beta}$ is given by

$$\boldsymbol{\beta}=\left(\frac{\mathrm{d}v_i}{\mathrm{d}t};\,\dot{\rho};\,\dot{\xi}^{\alpha};\,\dot{\theta};\,(\xi^{\beta}_{,k})^{\cdot};\,\dot{D}_{kl};\,(\theta_{,k})^{\cdot};\,\xi^{\beta}_{,ij};\,D_{kl,j};\,\theta_{,kj};\,\rho_{,i}\right), \qquad (23.25)$$

in which Cartesian index notation has been used. The inequality (23.24) is linear in the vectorial variable $\boldsymbol{\beta}$; i.e., none of the variables that define $\boldsymbol{\beta}$ is contained in $\boldsymbol{\Xi}$. The inequality (23.24) contains in its third braced term also the sources, and it is equally linear in these source terms, if Λ^{ε} and $\boldsymbol{\Lambda}^{\boldsymbol{v}}$ are independent of these, a fact that we will provisionally assume but corroborate lateron.[5]

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[5] It is strongly recommended that the inexperienced reader tries to perform the computations leading to (23.24) (at least once) with β given by (23.25) and α and Γ given by (23.31)–(23.34). These computations are not difficult, but long and tedious.

It is plausible to request that the constitutive relations be independent of the sources, to which the material is subjected in a thermodynamic process. Since in (23.24), only the first two terms on the left-hand side are independent of the sources but not the third, the latter must identically vanish, so that

$$\eta^s = \Lambda^\varepsilon \mathfrak{r} + \boldsymbol{\Lambda}^{\boldsymbol{v}} \cdot \boldsymbol{f}. \tag{23.26}$$

The entropy supply is therefore known once the LAGRANGE parameters Λ^ε and $\boldsymbol{\Lambda}^{\boldsymbol{v}}$ are determined. It is a linear combination of the energy supply (radiation) and momentum supply (external body forces). With (23.26), inequality (23.24) reduces to

$$\boldsymbol{\alpha}(\boldsymbol{\Xi}) \cdot \boldsymbol{\beta} + \Gamma(\boldsymbol{\Xi}) \geqslant 0. \tag{23.27}$$

This inequality must hold for all values of $\boldsymbol{\Xi}$ and $\boldsymbol{\beta}$. Necessary and sufficient conditions for this are the requirements[6]

$$\boldsymbol{\alpha}(\boldsymbol{\Xi}) = \boldsymbol{0} \qquad \text{and} \qquad \Gamma(\boldsymbol{\Xi}) \geqslant 0. \tag{23.28}$$

To prove these, we see that sufficiency is obviously satisfied by (23.28). To prove necessity, note that $\boldsymbol{\alpha}$ and Γ are independent of $\boldsymbol{\beta}$ and $\boldsymbol{\beta}$ can assume arbitrary values. These conditions suffice to demonstrate that necessarily $\boldsymbol{\alpha} = \boldsymbol{0}$. To this end, assume that $\boldsymbol{\alpha} \neq 0$ with $\alpha_s \neq 0$ and all $\alpha_j = 0$ for $j \neq s$. Then, one may write $\boldsymbol{\alpha} = (\hat{\boldsymbol{\alpha}}, \alpha_s)$ and $\boldsymbol{\beta} = (\hat{\boldsymbol{\beta}}, \beta_s)$, in which $\hat{\boldsymbol{\alpha}}$ and $\hat{\boldsymbol{\beta}}$ do involve $\boldsymbol{\alpha}, \boldsymbol{\beta}$ without α_s and β_s. With this notation, inequality (23.27) may be written as

$$\hat{\boldsymbol{\alpha}} \cdot \hat{\boldsymbol{\beta}} + \alpha_s \beta_s + \Gamma \geqslant 0. \tag{23.29}$$

Now, since β_s can freely be selected, we choose

$$\beta_s = -\left[\Gamma + \hat{\boldsymbol{\alpha}} \cdot \hat{\boldsymbol{\beta}} + \varepsilon\right] / \alpha_s, \quad \varepsilon > 0, \tag{23.30}$$

which is admissible since $\alpha_s \neq 0$. Substituting (23.30) into (23.29) yields $-\varepsilon \geqslant 0$, a contradiction to the assignment that ε is positive. Thus, α_s must vanish. This argument can be repeated for all components of $\boldsymbol{\alpha}$, which proves (23.28) to be correct. □

Explicitly, the identities $(23.28)_1$ read

$$\boldsymbol{\Lambda}^{\boldsymbol{v}} \equiv \boldsymbol{0}, \tag{23.31}$$

and

---

[6] The equations $\boldsymbol{\alpha}(\boldsymbol{\Xi}) = \boldsymbol{0}$ are frequently called the LIU equations and $\Gamma(\boldsymbol{\Xi}) \geqslant 0$ is the residual entropy inequality.

$$\left.\begin{aligned}
&\frac{\partial\hat{s}}{\partial\rho} - \Lambda^{\varepsilon}\frac{\partial\hat{\varepsilon}}{\partial\rho} - \frac{\Lambda^{\rho}}{\rho} \equiv 0,\\
&\frac{\partial\hat{s}}{\partial\xi^{\alpha}} - \Lambda^{\varepsilon}\frac{\partial\hat{\varepsilon}}{\partial\xi^{\alpha}} - \Lambda^{\xi^{\alpha}} \equiv 0, \quad (\alpha = 1, 2, 3, \dots, N-1),\\
&\frac{\partial\hat{s}}{\partial\theta} - \Lambda^{\varepsilon}\frac{\partial\hat{\varepsilon}}{\partial\theta} \equiv 0,\\
&\frac{\partial\hat{s}}{\partial\xi^{\beta}_{,k}} - \Lambda^{\varepsilon}\frac{\partial\hat{\varepsilon}}{\partial\xi^{\beta}_{,k}} \equiv 0, \quad (\beta = 1, 2, \dots, N-1),\\
&\frac{\partial\hat{s}}{\partial D_{kl}} - \Lambda^{\varepsilon}\frac{\partial\hat{\varepsilon}}{\partial D_{kl}} \equiv 0,\\
&\frac{\partial\hat{s}}{\partial\theta_{,k}} - \Lambda^{\varepsilon}\frac{\partial\hat{\varepsilon}}{\partial\theta_{,k}} \equiv 0,
\end{aligned}\right\} \qquad (23.32)$$

$$\left.\begin{aligned}
&\frac{\partial\phi_{(i}}{\partial\xi^{\beta}_{,j)}} - \Lambda^{\varepsilon}\frac{\partial q_{(i}}{\partial\xi^{\beta}_{,j)}} - \Lambda^{\xi^{\alpha}}\frac{\partial j^{\alpha}_{(i}}{\partial\xi^{\beta}_{,j)}} \equiv 0, \quad (\beta = 1, 2, \dots, N-1),\\
&\frac{\partial\phi_{i}}{\partial D_{kl}} - \Lambda^{\varepsilon}\frac{\partial q_{i}}{\partial D_{kl}} - \Lambda^{\xi^{\alpha}}\frac{\partial j^{\alpha}_{i}}{\partial D_{kl}} \equiv 0,\\
&\frac{\partial\phi_{(k}}{\partial\theta_{,j)}} - \Lambda^{\varepsilon}\frac{\partial q_{(k}}{\partial\theta_{,j)}} - \Lambda^{\xi^{\alpha}}\frac{\partial j^{\alpha}_{(k}}{\partial\theta_{,j)}} \equiv 0,\\
&\frac{\partial\phi_{i}}{\partial\rho} - \Lambda^{\varepsilon}\frac{\partial q_{i}}{\partial\rho} - \Lambda^{\xi^{\alpha}}\frac{\partial j^{\alpha}_{i}}{\partial\rho} \equiv 0,
\end{aligned}\right\} \qquad (23.33)$$

as well as

$$\begin{aligned}
\Gamma \equiv {} & \left\{\frac{\partial\phi_i}{\partial\xi^{\beta}} - \Lambda^{\varepsilon}\frac{\partial q_i}{\partial\xi^{\beta}} - \Lambda^{\xi^{\alpha}}\frac{\partial j^{\alpha}_i}{\partial\xi^{\beta}}\right\}\xi^{\beta}_{,i} + \left\{\frac{\partial\phi_i}{\partial\theta} - \Lambda^{\varepsilon}\frac{\partial q_i}{\partial\theta} - \Lambda^{\xi^{\alpha}}\frac{\partial j^{\alpha}_i}{\partial\theta}\right\}\theta_{,i}\\
& + \Lambda^{\xi^{\alpha}}\mathfrak{c}^{\alpha} + \Lambda^{\varepsilon}\left\{t_{ij} - \frac{\Lambda^{\rho}}{\Lambda^{\varepsilon}}\rho\delta_{ij}\right\}D_{ij} \geqslant 0,
\end{aligned} \qquad (23.34)$$

in which indexed round brackets denote symmetrization and the summation is from $\alpha = 1$ to $\alpha = N - 1$; similarly for β. Our next goal is to draw all inferences from these identities.

Incidentally, it is easy to see that $\boldsymbol{\Lambda}^{\boldsymbol{v}}$ must vanish; this inference follows from (23.23) by recognizing that $\boldsymbol{\Lambda}^{\boldsymbol{v}} \cdot \rho(\mathrm{d}\boldsymbol{v}/\mathrm{d}t)$ is the only inner product of the entire imbalance involving the vector $\rho\mathrm{d}\boldsymbol{v}/\mathrm{d}t$. Since $(\mathrm{d}\boldsymbol{v}/\mathrm{d}t)$ may have any arbitrarily assigned value, there follows that $\boldsymbol{\Lambda}^{\boldsymbol{v}} \equiv \boldsymbol{0}$. This result means physically that NEWTON's second law does not affect the second law of thermodynamics and makes explicit computations mentioned in the last footnote somewhat simpler.

One may regard the identities (23.32)–(23.33) as equations for the determination of the LAGRANGE parameters Λ^{ε}, Λ^{ρ}, $\Lambda^{\xi^{\alpha}}$ and one concludes from this, that Λ^{ε}, Λ^{ρ},

Λ^{ξ^α} can only depend on the variables $\boldsymbol{\Xi}$. This is the a posteriori proof of the independence of the LAGRANGE parameters of the external source terms, that was assumed above. Indeed without such an assumption (23.31)–(23.34) would still follow and the independence of the Λ's of the sources would follow in exactly the same way. However, additional deductions are possible; with the identities (23.33) it is namely possible to demonstrate that Λ^ε is only a function of the empirical temperature,

$$\Lambda^\varepsilon = \Lambda^\varepsilon(\theta), \qquad \Theta = \frac{1}{\Lambda^\varepsilon(\theta)}. \tag{23.35}$$

This proof is long and rather involved.[7] Because of the above property, Λ^ε is called*coldness function* and its inverse is called the *absolute temperature* Θ; the latter agrees with the KELVIN temperature, a fact that we shall corroborate.

With the universality of the absolute temperature (23.35) and the earlier result that the LAGRANGE parameter $\boldsymbol{\Lambda}^{\boldsymbol{v}}$ vanishes (see (23.31)), conditions of the second law of thermodynamics in the form of the CLAUSIUS–DUHEM inequality are reached. It follows that the subsequent inferences are identical to analogous deductions from the simpler entropy inequality in the form of the CLAUSIUS–DUHEM inequality.

Therefore, if one starts from (23.35) as an assumption, one obtains from $(23.32)_{3,4}$ by cross differentiation

$$\frac{\partial^2 \hat{s}}{\partial \xi^\beta_{,k} \partial \theta} - \Lambda^\varepsilon \frac{\partial^2 \hat{\varepsilon}}{\partial \xi^\beta_{,k} \partial \theta} \equiv \frac{\partial^2 \hat{s}}{\partial \theta \partial \xi^\beta_{,k}} - \Lambda^\varepsilon \frac{\partial^2 \hat{\varepsilon}}{\partial \theta \partial \xi^\beta_{,k}} - \frac{\partial \Lambda^\varepsilon}{\partial \theta} \frac{\partial \hat{\varepsilon}}{\partial \xi^\beta_{,k}}, \tag{23.36}$$

from which one concludes, since $\partial \Lambda^\varepsilon / \partial \theta \neq 0$ that $\partial \hat{\varepsilon} / \partial \xi^\beta_{,k} = 0$ and, in view of $(23.32)_4$, also $\partial \hat{s} / \partial \xi^\beta_{,k} = 0$. Thus, internal energy and entropy cannot depend on $\xi^\beta_{,k}$. In much the same way, one may equally show by using $(23.32)_{3,5,6}$ that $\hat{\varepsilon}$ and $\hat{s}$ can neither depend on $\boldsymbol{D}$ nor on grad θ, so that the identities (23.32) lead to the reduced statements

$$\begin{aligned}
\varepsilon &= \hat{\varepsilon}(\rho, \xi^\beta, \theta), \\
s &= \hat{s}(\rho, \xi^\beta, \theta), \\
\Lambda^\rho &= \rho \left(\frac{\partial \hat{s}}{\partial \rho} - \Lambda^\varepsilon \frac{\partial \hat{\epsilon}}{\partial \rho} \right) = \Lambda^\rho(\rho, \xi^\beta, \theta), \\
\Lambda^{\xi^\alpha} &= \left(\frac{\partial \hat{s}}{\partial \xi^\alpha} - \Lambda^\varepsilon \frac{\partial \hat{\epsilon}}{\partial \xi^\alpha} \right) = \Lambda^{\xi^\alpha}(\rho, \xi^\beta, \theta).
\end{aligned} \tag{23.37}$$

The last two of these statements, together with $(23.32)_3$ may also be written as

---

[7] The interested reader is referred to the book by MÜLLER [24] for the explicit demonstration. One essential ingredient of the proof is that $\boldsymbol{\phi}$, $\boldsymbol{q}$, and $\boldsymbol{j}^\alpha$ are isotropic functions of their arguments. In this particular case, this is not a restriction because the chosen constitutive class (23.20) does not permit anisotropic behavior.

$$
\begin{aligned}
\frac{\partial \hat{s}}{\partial \theta} &= \Lambda^{\varepsilon} \frac{\partial \hat{\varepsilon}}{\partial \theta}, \\
\frac{\partial \hat{s}}{\partial \rho} &= \Lambda^{\varepsilon} \frac{\partial \hat{\varepsilon}}{\partial \rho} + \frac{1}{\rho} \Lambda^{\rho} = \Lambda^{\varepsilon} \left(\frac{\partial \hat{\varepsilon}}{\partial \rho} - \frac{\hat{p}}{\rho^2} \right), \qquad p := -\frac{\Lambda^{\rho}}{\Lambda^{\varepsilon}} \rho, \\
\frac{\partial \hat{s}}{\partial \xi^{\alpha}} &= \Lambda^{\varepsilon} \frac{\partial \hat{\varepsilon}}{\partial \xi^{\alpha}} + \Lambda^{\xi^{\alpha}} = \Lambda^{\varepsilon} \left(\frac{\partial \hat{\varepsilon}}{\partial \xi^{\alpha}} - \mu^{\xi^{\alpha}} \right), \qquad \mu^{\xi^{\alpha}} := -\frac{\Lambda^{\xi^{\alpha}}}{\Lambda^{\varepsilon}},
\end{aligned}
\tag{23.38}
$$

from which the total differential of the entropy is seen to be expressible as

$$
\begin{aligned}
\mathrm{d}s &= \Lambda^{\varepsilon} \left\{ \frac{\partial \hat{\varepsilon}}{\partial \theta} \mathrm{d}\theta + \left(\frac{\partial \hat{\varepsilon}}{\partial \rho} + \frac{\Lambda^{\rho}}{\Lambda^{\epsilon}} \frac{1}{\rho} \right) \mathrm{d}\rho + \left(\frac{\partial \hat{\varepsilon}}{\partial \xi^{\alpha}} + \frac{\Lambda^{\xi^{\alpha}}}{\Lambda^{\epsilon}} \right) \mathrm{d}\xi^{\alpha} \right\} \\
&= \Lambda^{\varepsilon} \left\{ \mathrm{d}\varepsilon + p \, \mathrm{d} \left(\frac{1}{\rho} \right) - \mu^{\xi^{\alpha}} \mathrm{d}\xi^{\alpha} \right\}.
\end{aligned}
\tag{23.39}
$$

This is the so-called GIBBS *relation*,[8] which connects the total differential of the entropy with the product of the inverse of the absolute temperature $\Theta^{-1} = \Lambda^{\varepsilon}(\theta)$ and the total differential of the internal energy plus the additional contributions

$$
\frac{\Lambda^{\rho}}{\rho \Lambda^{\epsilon}} \mathrm{d}\rho, \qquad \frac{\Lambda^{\xi^{\alpha}}}{\Lambda^{\epsilon}} \mathrm{d}\xi^{\alpha},
$$

which with the definitions for p and $\mu^{\xi^{\alpha}}$ become

$$
-\frac{p}{\rho^2} \mathrm{d}\rho = p \mathrm{d} \left(\frac{1}{\rho} \right) = \frac{\Lambda^{\rho}}{\rho \Lambda^{\epsilon}} \mathrm{d}\rho, \quad -\mu^{\xi^{\alpha}} \mathrm{d}\xi^{\alpha} = \frac{\Lambda^{\xi^{\alpha}}}{\Lambda^{\epsilon}} \mathrm{d}\xi^{\alpha}
\tag{23.40}
$$

so that

$$
\mathrm{d}s = \frac{1}{\Theta} \left\{ d\varepsilon + p \mathrm{d}(1/\rho) - \mu^{\xi^{\alpha}} \mathrm{d}\xi^{\alpha} \right\},
\tag{23.41}
$$

in which p is called the *thermodynamic pressure*, $\mu^{\xi^{\alpha}}$ is the *chemical potential of constituent* α.[9] The latter identification must, however, still be demonstrated.

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[8] For a brief biographical sketch of JOSIAH WILLARD GIBBS (1839–1903), see Fig. 17.12 in Vol. 2, p. 338 of this treatise on Fluid and Thermodynamics [22].

[9] If we would have written down the mass balance (23.3) for all constituents and if the mass fractions $\xi^{\alpha} (\alpha = 1, 2, \ldots, N)$ for all constituents would have been used as independent constitutive variables, then instead of (23.39) one would have obtained

$$
\begin{aligned}
\mathrm{d}s &= \frac{1}{\Theta} \left\{ \mathrm{d}\varepsilon + p \mathrm{d}(1/\rho) - \sum_{\alpha=1}^{N} \bar{\mu}^{\xi^{\alpha}} \mathrm{d}\xi^{\alpha} \right\} \\
&= \frac{1}{\Theta} \left\{ \mathrm{d}\varepsilon + p \mathrm{d}(1/\rho) - \sum_{\alpha=1}^{N-1} \left(\bar{\mu}^{\xi^{\alpha}} - \bar{\mu}^{\xi^{N}} \right) \mathrm{d}\xi^{\alpha} \right\}
\end{aligned}
\tag{23.42}
$$

The GIBBS equation must satisfy integrability conditions, which are deduced from (23.38) by performing the respective cross differentiations; for instance, from $(23.38)_{1,2}$ one obtains

$$\frac{\partial^2 \hat{s}}{\partial\rho\partial\theta} = \Lambda^{\varepsilon}\frac{\partial^2\hat{\varepsilon}}{\partial\rho\partial\theta}$$

and

$$\frac{\partial^2 \hat{s}}{\partial\theta\partial\rho} = \Lambda^{\varepsilon}\frac{\partial^2\hat{\varepsilon}}{\partial\theta\partial\rho} + \frac{\partial\Lambda^{\varepsilon}}{\partial\theta}\left(\frac{\partial\hat{\varepsilon}}{\partial\rho} - \frac{\hat{p}}{\rho^2}\right) - \Lambda^{\varepsilon}\frac{\partial\hat{p}}{\partial\theta}\frac{1}{\rho^2}.$$

Because the mixed derivatives $\partial^2 f/(\partial\rho\partial\theta) = \partial^2 f/(\partial\theta\partial\rho)$ must be equal if f is a unique function of its arguments, then the above two equations imply

$$\frac{1}{\Lambda^{\varepsilon}}\frac{\mathrm{d}\Lambda^{\varepsilon}}{\mathrm{d}\theta} = \frac{\partial\hat{p}/\partial\theta}{(\partial\hat{\varepsilon}/\partial\rho)\rho^2 - \hat{p}}. \tag{23.44}$$

Analogously, one can take $(23.38)_{1,3}$ to form

$$\begin{aligned}\frac{\partial^2 \hat{s}}{\partial\xi^{\alpha}\partial\rho} &= \Lambda^{\varepsilon}\frac{\partial^2\hat{\varepsilon}}{\partial\xi^{\alpha}\partial\rho} - \frac{\partial}{\partial\xi^{\alpha}}\left(\frac{\Lambda^{\varepsilon}p}{\rho^2}\right), \quad \text{and}\\ \frac{\partial^2 \hat{s}}{\partial\rho\partial\xi^{\alpha}} &= \Lambda^{\varepsilon}\frac{\partial^2\hat{\varepsilon}}{\partial\rho\partial\xi^{\alpha}} - \Lambda^{\varepsilon}\frac{\partial\mu^{\xi^{\alpha}}}{\partial\rho},\end{aligned}$$

which yields, upon combination,

$$\frac{\partial\mu^{\xi^{\alpha}}}{\partial\rho} = \frac{\partial}{\partial\xi^{\alpha}}\left(\frac{p}{\rho^2}\right), \quad \forall\,\alpha \in [1, 2, \ldots, N-1]. \tag{23.45}$$

Similarly, from $(23.38)_3$ one may deduce by cross differentiations $\partial^2/(\partial\xi^{\alpha}\partial\xi^{\beta}) = \partial^2/(\partial\xi^{\beta}\partial\xi^{\alpha})$,

$$\frac{\partial\mu^{\xi^{\alpha}}}{\partial\xi^{\beta}} = \frac{\partial\mu^{\xi^{\beta}}}{\partial\xi^{\alpha}}. \tag{23.46}$$

---

with new functions $\bar{\mu}^{\xi^{\alpha}}$; in the above expression $(23.42)_2$, the relation $\sum_{\alpha=1}^{N}\xi^{\alpha} = 1$ was used. Thus, one necessarily has

$$\mu^{\xi^{\alpha}} := \left(\bar{\mu}^{\xi^{\alpha}} - \bar{\mu}^{\xi^{N}}\right)\big|_{\xi^{N}=1-\sum_{\alpha=1}^{N-1}\xi^{\alpha}}, \tag{23.43}$$

where the subscript in (23.43) indicates that ξ^N is replaced by $(1-\sum_{\alpha=1}^{N-1}\xi^{\alpha})$. The variable $\mu^{\xi^{\alpha}}$ is therefore the difference of the chemical potentials $\left(\bar{\mu}^{\xi^{\alpha}} - \bar{\mu}^{\xi^{N}}\right)$, which, however, are functions of all ξ^{α} $(\alpha = 1, 2, \ldots, N)$.

Finally, from (23.38)$_{1,3}$ one may deduce

$$
\begin{aligned}
\frac{\partial^2 \hat{s}}{\partial \xi^\alpha \partial \theta} &= \Lambda^\varepsilon \frac{\partial^2 \hat{\varepsilon}}{\partial \xi^\alpha \partial \theta} \qquad \text{and} \\
\frac{\partial^2 \hat{s}}{\partial \theta \partial \xi^\alpha} &= \frac{\mathrm{d}\Lambda^\varepsilon}{\mathrm{d}\,\theta}\left(\frac{\partial \hat{\varepsilon}}{\partial \xi^\alpha} - \hat{\mu}^{\xi^\alpha}\right) + \Lambda^\varepsilon \left(\frac{\partial^2 \hat{\varepsilon}}{\partial \theta \partial \xi^\alpha} - \frac{\partial \hat{\mu}^{\xi^\alpha}}{\partial \theta}\right),
\end{aligned}
$$

from which

$$
\frac{1}{\Lambda^\varepsilon}\frac{\mathrm{d}\Lambda^\varepsilon}{\mathrm{d}\,\theta} = \frac{\partial \hat{\mu}^{\xi^\alpha}/\partial \theta}{\partial \hat{\varepsilon}/\partial \xi^\alpha - \hat{\mu}^{\xi^\alpha}}. \tag{23.47}
$$

The results (23.44)–(23.47) can be summarized as

$$
\begin{aligned}
\frac{d(\ln \Lambda^\varepsilon)}{d\theta} = \frac{1}{\Lambda^\varepsilon}\frac{d\Lambda^\varepsilon}{d\theta} &= \frac{\partial \hat{p}/\partial \theta}{(\partial \hat{\varepsilon}/\partial \rho)\rho^2 - \hat{p}} \\
&= \frac{\partial \hat{\mu}^{\xi^\alpha}/\partial \theta}{\partial \hat{\varepsilon}/\partial \xi^\alpha - \hat{\mu}^{\xi^\alpha}}, \quad (\alpha = 1, 2, \dots, N-1)
\end{aligned} \tag{23.48}
$$

as well as

$$
\frac{\partial \hat{\mu}^{\xi^\alpha}}{\partial \xi^\beta} = \frac{\partial \hat{\mu}^{\xi^\beta}}{\partial \xi^\alpha}, \quad \frac{\partial \hat{\mu}^{\xi^\alpha}}{\partial \rho} = \frac{\partial}{\partial \xi^\alpha}\left(\frac{\hat{p}}{\rho^2}\right), \quad (\alpha = 1, 2, \dots, N-1). \tag{23.49}
$$

The identities (23.48) state that the pressure, chemical potentials, and the internal energy must be constitutive equations of such a form that the $N-1$ different fractions (23.48) are the same function of the empirical temperature only. Equations (23.49), on the other hand, indicate that the pressure, chemical potentials (and entropy) are themselves derivable from a potential; this shall be ascertained shortly. Before, let us, however, integrate (23.48)$_1$ to obtain

$$
\ln \frac{\Lambda^\varepsilon}{\Lambda^\varepsilon_0} = -\ln \frac{\Theta}{\Theta_0} = \int_{\theta_0}^{\theta} \frac{\partial \hat{p}/\partial \theta}{\big((\partial \hat{\varepsilon}/\partial \rho)\rho^2 - \hat{p}\big)} d\bar{\theta},
$$

where $\Theta(\theta) = 1/\Lambda^\varepsilon$, or

$$
\frac{\Theta}{\Theta_0} = \exp\left\{-\int_{\theta_0}^{\theta} \frac{\partial \hat{p}/\partial \theta}{\big((\partial \hat{\varepsilon}/\partial \rho)\rho^2 - \hat{p}\big)} d\bar{\theta}\right\}. \tag{23.50}
$$

For an *ideal gas* with the thermal and caloric equations of state

$$
\hat{p} = R\Theta(\theta)\rho, \quad \hat{\varepsilon} = \hat{\varepsilon}(\theta), \tag{23.51}
$$

in which R is the ideal gas constant. Equation (23.50) leads to an identity $\Theta(\theta) \equiv \Theta(\theta)$. This can be taken as motivation to identify the empirical temperature θ with the temperature T of ideal gases (a special empirical temperature) and to request that

$$\Theta(\theta) =: T. \tag{23.52}$$

Because of the monotonicity of $\Theta(\theta)$ as a function of θ, one even may use T as a measure of temperature; from now on this will be our choice. So, the temperature is now uniquely defined, and therefore the identities (23.48) become constraint equations for the experimenter, which he must fulfill, if he determines p, μ^{ξ^α} and ε as functions of their variables by experiment. Thus, the chosen temperature is the *absolute* temperature or the KELVIN *temperature*.

The integrability conditions (23.48) and (23.49) can be satisfied identically, if the HELMHOLTZ free energy

$$\psi = \varepsilon - Ts = \hat{\psi}(\rho, \xi^\alpha, T) \tag{23.53}$$

is introduced. Computing with (23.53), the total differential of the internal energy

$$\mathrm{d}\varepsilon = \mathrm{d}\psi + T\mathrm{d}s + s\mathrm{d}T \tag{23.54}$$

and substituting this result into the GIBBS relation (23.41) yields

$$\left(\frac{\partial\hat{\psi}}{\partial\rho} - \frac{\hat{p}}{\rho^2}\right)\mathrm{d}\rho + \left(\frac{\partial\hat{\psi}}{\partial\xi^\alpha} - \hat{\mu}^{\xi^\alpha}\right)\mathrm{d}\xi^\alpha + \left(\frac{\partial\hat{\psi}}{\partial T} + \hat{s}\right)\mathrm{d}T \equiv 0, \tag{23.55}$$

which, as an identity, can only be satisfied, provided the following relations hold:

$$\frac{\hat{p}}{\rho^2} = \frac{\partial\hat{\psi}}{\partial\rho}, \quad \hat{\mu}^{\xi^\alpha} = \frac{\partial\hat{\psi}}{\partial\xi^\alpha}, \quad (\alpha = 1, 2, \ldots, N-1)\ , \quad \hat{s} = -\frac{\partial\hat{\psi}}{\partial T}. \tag{23.56}$$

Accordingly, the pressure, the chemical potentials, and the entropy are obtained from the HELMHOLTZ free energy by “taking the gradient” with respect to its independent variables. With the choice of $\hat{\psi}(\cdot)$ and the relations (23.56) the integrability conditions (23.48) and (23.49) are automatically satisfied. With these statements, all inferences deducible from (23.32) are duly explored.

Next, let us closely analyze the identities (23.33). They suggest the choice

$$\boldsymbol{\phi} = \Lambda^\varepsilon \boldsymbol{q} + \boldsymbol{k} = \frac{1}{T}\boldsymbol{q} + \boldsymbol{k}, \tag{23.57}$$

where (23.35) and (23.52) have been used. It is evident that the *extra entropy flux vector*, $\boldsymbol{k}$ describes that part of the entropy flux which may not be collinear to the heat flux. Incidentally, the choice (23.57) does not amount to a restriction. If we, furthermore, introduce

$$\mathfrak{F} = \boldsymbol{k} + \frac{\mu^{\xi^\alpha} \boldsymbol{j}^\alpha}{T} = \boldsymbol{k} - \Lambda^{\xi^\alpha} \boldsymbol{j}^\alpha \ , \tag{23.58}$$

then the identities (23.33) can equally be written as

$$\frac{\partial \mathfrak{F}_{(i}}{\partial \xi^\beta_{,j)}} = 0, \quad \frac{\partial \mathfrak{F}_i}{\partial D_{kl}} = 0, \quad \frac{\partial \mathfrak{F}_{(i}}{\partial T_{,j)}} = 0, \quad \frac{\partial \mathfrak{F}_i}{\partial \rho} = \frac{1}{T}\frac{\partial \hat{\mu}^{\xi^\alpha}}{\partial \rho} j^\alpha_i . \tag{23.59}$$

These equations can be satisfied by the trial solution

$$\mathfrak{F} = \mathbf{0}, \quad \hat{\psi} = \psi_1(\rho, T) + \psi_2(\xi^\alpha, T) \ , \tag{23.60}$$

which automatically satisfies $\partial \hat{\mu}^{\xi^\alpha}/\partial \rho = 0$, owing to (23.56). Equation (23.60) is not the most general solution of (23.59), however if one chooses it one obtains with (23.57) and (23.40)

$$\boldsymbol{k} = -\frac{\mu^{\xi^\alpha} \boldsymbol{j}^\alpha}{T} \quad \Rightarrow \quad \boldsymbol{\phi} = \frac{\boldsymbol{q} - \mu^{\xi^\alpha} \boldsymbol{j}^\alpha}{T} . \tag{23.61}$$

The entropy flux (multiplied with the absolute temperature) deviates from the heat flux via a vector, which is a linear combination of the diffusive fluxes; the weights of the individual diffusive fluxes are the chemical potentials of the corresponding constituents.

If the results (23.40), (23.52) and (23.61) are substituted into inequality (23.34), one obtains

$$\begin{aligned} \pi^s = & -\frac{\boldsymbol{q} - \mu^{\xi^\alpha} \boldsymbol{j}^\alpha}{T^2} \cdot \operatorname{grad} T - \frac{\boldsymbol{j}^\alpha \cdot \operatorname{grd}\mu^{\xi^\alpha}}{T} \\ & + \frac{(\boldsymbol{t} + p\mathbf{1}) \cdot \boldsymbol{D}}{T} - \frac{\mu^{\xi^\alpha} \mathfrak{c}^\alpha}{T} \geqslant 0 \ , \end{aligned} \tag{23.62}$$

in which $\operatorname{grd}\mu^{\xi^\alpha}$ denotes the reduced gradient of $\operatorname{grad} \mu^{\xi^\alpha}$, in which the density is regarded as constant (sometimes called a process with frozen density), i.e.,

$$\operatorname{grd}\mu^{\xi^\alpha} := \frac{\partial \hat{\mu}^{\xi^\alpha}}{\partial \xi^\beta} \operatorname{grad} \xi^\beta + \frac{\partial \hat{\mu}^{\xi^\alpha}}{\partial T} \operatorname{grad} T . \tag{23.63}$$

In evaluating (23.62), the fact was also used that the absolute temperature is a strictly positive function.[10] Inequality (23.62) suggests that entropy is produced by the inner product of the entropy flux with the temperature gradient, the diffusive fluxes with

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[10] Incidentally, the same result is also obtained, if the GIBBS equation

the reduced gradients of the chemical potentials, the extra stresses with the rates of deformation, and by the product of the mass productions with the chemical potentials.

The essential result that has been reached so far is the fact that the pressure, the chemical potentials, and the entropy density must be derived from the HELMHOLTZ free energy $\hat{\psi}$ according to the rules (23.56). It is this quantity that has to be postulated in a particular diffusion model that is in harmony with thermodynamics. However, there is more, namely the satisfaction of the imbalance (23.62), which will be attacked now.

Thermostatic equilibrium is defined as a process which does not produce any entropy. Inequality (23.62) shows then together with the definition of the reduced gradient of the chemical potentials, (23.63), that a thermostatic equilibrium process must fulfill the conditions

$$\begin{aligned} &\operatorname{grad} T = 0; \qquad \boldsymbol{D} = \boldsymbol{0}, \\ &\operatorname{grad} \xi^\beta = 0, \qquad \mathfrak{c}^\beta = 0, \quad (\beta = 1, 2, \ldots, N-1). \end{aligned} \tag{23.66}$$

Thus, the temperature and concentration fields must be homogeneous, the mass productions of all constituents must vanish—there are no chemical reactions and no phase change processes—and the barycentric velocity field is a rigid body field (or a rest field). Simultaneously, since the entropy production cannot take negative values, it assumes its minimum value, namely zero, in equilibrium. Of necessity then

$$\begin{aligned} &\left.\frac{\partial \pi^s}{\partial \mathfrak{X}}\right|_E = 0, \quad \mathfrak{X} := \left\{\operatorname{grad} \xi^\beta, \operatorname{grad} T, \boldsymbol{D}\right\}, \\ &\left|\frac{\partial \pi^s}{\partial \mathfrak{X} \partial \mathfrak{X}}\right|_E \quad \text{is positive semidefinite,} \end{aligned} \tag{23.67}$$

where the index $(\cdot)|_E$ is a reminder that the so indexed quantity must be evaluated in thermostatic equilibrium.

If the differentiations indicated in $(23.67)_1$ are performed, one obtains

$$\boldsymbol{t}|_E = -p\mathbf{1}, \quad \boldsymbol{q}|_E = \boldsymbol{0}, \quad \boldsymbol{j}^\alpha|_E = \boldsymbol{0}, \quad \text{and} \quad \mathfrak{c}^\alpha|_E = 0 \tag{23.68}$$

for $\alpha = 1, 2, \ldots, N-1$. Hence, the stress tensor in thermostatic equilibrium is given by the thermodynamic pressure, which itself is determined by the HELMHOLTZ free energy, see $(23.56)_1$. This relation now corroborates a posteriori the interpretation

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$$\dot{s} = \frac{1}{T}\left\{\dot{\varepsilon} - \frac{p}{\rho^2}\dot{\rho} - \mu^{\xi^\alpha}\dot{\xi^\alpha}\right\} \tag{23.64}$$

is used and the rates $\dot{\rho}$ and $\dot{\xi^\alpha}$ are eliminated with the aid of the balance equations (23.2), (23.3); one then obtains

$$\rho\dot{s} = -\operatorname{div}\left(\frac{\boldsymbol{q} - \mu^{\xi^\alpha}\boldsymbol{j}^\alpha}{T}\right) + \pi^s, \tag{23.65}$$

in which π^s is given in (23.62).

of the LAGRANGE parameter as the negative thermodynamic pressure according to (23.40)$_1$, $-\Lambda^\rho = \Lambda^\varepsilon p/\rho$. The heat flux and the diffusive fluxes of all tracers vanish in thermostatic equilibrium as one would expect. Finally, also all production rates of masses of the constituents must vanish.

Let us next scrutinize the second of relations (23.67). To exploit it, consider here the simplest possible forms for the constitutive relations for $\boldsymbol{j}^\alpha$, $\boldsymbol{q}$ and $\boldsymbol{t}^E = \boldsymbol{t} + p\mathbf{1}$; furthermore, ignore chemical reactions: $\mathfrak{c}^\beta = 0;\ \beta = 1, 2, \ldots, N-1$. To exploit the inequality (23.62), it shall also be assumed that the thermodynamic "fluxes"

$$\frac{1}{T}\left(\boldsymbol{q} - \mu^{\xi^\alpha}\boldsymbol{j}^\alpha\right) \quad \text{and} \quad \frac{\boldsymbol{j}^\alpha}{T} \tag{23.69}$$

are derivable from a dissipation potential Ψ_D which is expressible as a quadratic form of the corresponding thermodynamic "forces"

$$\frac{1}{T}\operatorname{grad} T, \quad \operatorname{grad} \mu^{\xi^\alpha} \tag{23.70}$$

according to

$$\begin{aligned}\Psi_D = {} & \frac{1}{2}C_{11}^{\alpha\beta}\left(\text{grd}\mu^{\xi^\alpha}\right)\cdot\left(\text{grd}\mu^{\xi^\beta}\right) + C_{12}^{\alpha}\left(\text{grd}\mu^{\xi^\alpha}\right)\cdot\frac{\operatorname{grad} T}{T} \\ & + \frac{1}{2}C_{22}\left(\frac{\operatorname{grad} T}{T}\right)\cdot\left(\frac{\operatorname{grad} T}{T}\right),\end{aligned} \tag{23.71}$$

in which $C_{11}^{\alpha\beta} = C_{11}^{\beta\alpha}$ is symmetric in the indices $\alpha\beta$ and where summation from 1 to $N-1$ is understood over doubly repeated Greek indices. If one requests that

$$\frac{\boldsymbol{j}^\alpha}{T} = -\frac{\partial\Psi_D}{\partial\text{grd}\mu^{\xi^\alpha}}, \quad \frac{1}{T}\left(\boldsymbol{q} - \mu^{\xi^\alpha}\boldsymbol{j}^\alpha\right) = -\frac{\partial\Psi_D}{\partial\left(\operatorname{grad} T/T\right)}, \tag{23.72}$$

(which gives Ψ_D the desired property of a potential), and if NEWTONian behavior[11]

$$\begin{aligned}& \boldsymbol{t} + p\mathbf{1} = \zeta(\text{tr}\,\boldsymbol{D})\mathbf{1} + 2\mu\boldsymbol{D}', \quad \boldsymbol{D}' = \boldsymbol{D} - \tfrac{1}{3}\left(\text{tr}\boldsymbol{D}\right)\boldsymbol{I}, \\ & \Rightarrow \Phi = (\boldsymbol{t} + p\mathbf{1})\cdot\boldsymbol{D} = \zeta(\text{tr}\,\boldsymbol{D})^2 + 2\mu\boldsymbol{D}'\cdot\boldsymbol{D}',\end{aligned} \tag{23.73}$$

is assumed, then for $\mathfrak{c}^\alpha = 0$ inequality (23.62) takes

$$\pi^s = 2\Psi_D + \frac{\Phi}{T} \geqslant 0, \tag{23.74}$$

a form of π^s, which is easily obtained by employing (23.71) and (23.72). In other words, Ψ_D and Φ are positive semidefinite quadratic forms. Therefore,

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[11] ζ and μ are the bulk and shear viscosities.

$$\begin{aligned} &\begin{pmatrix} C_{11}^{\alpha\beta} & C_{12}^{\alpha} \\ C_{12}^{\alpha T} & C_{22} \end{pmatrix} \quad \text{is a positive semidefinite} N \times N \text{ matrix,} \\ &\zeta \geqslant 0, \quad \mu \geqslant 0. \end{aligned} \tag{23.75}$$

The diffusive fluxes $\boldsymbol{j}^{\alpha}$ and the entropy flux $(\boldsymbol{q} - \mu^{\xi^{\alpha}} \boldsymbol{j}^{\alpha})$ are given by

$$\begin{pmatrix} \boldsymbol{j}^{\alpha} \\ \boldsymbol{q} - \mu^{\xi^{\alpha}} \boldsymbol{j}^{\alpha} \end{pmatrix} = - \begin{pmatrix} C_{11}^{\alpha\beta} T & C_{12}^{\alpha} \\ C_{12}^{\beta} T & C_{22} \end{pmatrix} \begin{pmatrix} \mathrm{grd} \mu^{\xi^{\beta}} \\ \mathrm{grad}\, T \end{pmatrix}, \tag{23.76}$$

which can easily be deduced from (23.71) and (23.72).

With the equation of state $\mu^{\xi^{\beta}} = \hat{\mu}^{\xi^{\beta}}(\rho, \xi^{\gamma}, T)$ for the chemical potentials and the aid of (23.63) as well as (23.76), one may deduce the formulae

$$\begin{aligned} \boldsymbol{q} &= -\kappa_T \mathrm{grad}\, T - \kappa_{\xi^{\gamma}} \mathrm{grad}\, \xi^{\gamma}, \\ \boldsymbol{j}^{\alpha} &= -D_T^{\alpha} \mathrm{grad}\, T - D_{\xi^{\gamma}}^{\alpha} \mathrm{grad}\, \xi^{\gamma}, \end{aligned} \tag{23.77}$$

in which

$$\begin{aligned} \kappa_T &:= \mu^{\xi^{\alpha}} \left(C_{11}^{\alpha\beta} T \frac{\partial \mu^{\xi^{\beta}}}{\partial T} + C_{12}^{\alpha} \right) + \left(C_{12}^{\beta} T \frac{\partial \mu^{\xi^{\beta}}}{\partial T} + C_{22} \right), \\ \kappa_{\xi^{\gamma}} &:= C_{11}^{\alpha\beta} T \mu^{\xi^{\alpha}} \frac{\partial \mu^{\xi^{\beta}}}{\partial \xi^{\gamma}} + C_{12}^{\beta} T \frac{\partial \mu^{\xi^{\beta}}}{\partial \xi^{\gamma}}, \\ D_{\xi^{\gamma}}^{\alpha} &:= C_{11}^{\alpha\beta} T \frac{\partial \mu^{\xi^{\beta}}}{\partial \xi^{\gamma}}, \\ D_T^{\alpha} &:= C_{11}^{\alpha\beta} T \frac{\partial \mu^{\xi^{\beta}}}{\partial T} + C_{12}^{\alpha}. \end{aligned} \tag{23.78}$$

κ_T is the coefficient of heat conduction, and $D_{\xi^{\gamma}}^{\alpha}$ represent the matrices of mass diffusivities; $\kappa_{\xi^{\gamma}}$ and D_T^{α} are coupling coefficients and their presence in (23.77) is known in a special case as LUDWIG–SORET effect.[12] It describes a particular tracer diffusive transport in a gas or liquid that is induced by a temperature difference, which leads to a partial demixing of the tracer substance. If such a temperature difference exists in a gas, the lighter components will accumulate in the hot region and the heavier ones in the cold region.[13]

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[12] For brief biographical sketches of CARL LUDWIG (1816–1895) and CHARLES SORET (1854–1904), see **Fig. 23.2**.

[13] The phenomenon is called *Thermophoresis* or *thermodiffusion* and describes the motion of suspended particles in a mixture against the temperature gradient. It can, for instance, be observed when the hot rod of an electric heater is surrounded by tobacco smoke: the smoke goes away from the immediate vicinity of the hot rod.

Fig. 23.2 Carl Ludwig (29 Dec.1816–23 April 1895) (left), the famous Physiologiocal Institute in Leipzig, founded by Ludwig in 1869 (middle), Charles Soret (23 Sept. 1854–04 April 1904 (right)

Carl Ludwig was a German physician and physiologist. He studied medicine in Marburg, starting in 1834, where he habilitated in 1842 on the mechanism of discharge of urine. On the recommendation of Franz–Ludwig Frick, the older brother of Adolf Fick, he received a position at the medical school in Marburg and, in 1846, the associate professorship of comparative anatomy. He was affected by the political turmoils in the 1848s and “escaped” in 1849 to the University of Zurich as a Full Professor of Physiology and Anatomy. In 1855, he was called as Full Professor of Physiology and Zoology at the Medical Chirurgical Military Academy in Vienna, where he and his many students were active in blood pressure, urinary excretion and anesthesia. In 1856, he discovered *thermodiffusion* [23], later denoted the Ludwig–Soret effect, after him and Charles Soret. In May 1865 Ludwig, became Full Professor of Physiology at the University of Leipzig, where he worked beyond the retirement age until his death in 1895. Here, he founded the (instantly famous) Physiological Institute in 1865, received the Copley Medal in 1884, and was elected a member of the Swedish Academy of Sciences in 1869.

Charles Soret was a Swiss mineralogist and physicist who lived in Geneva. In 1872, he graduated from an art college in Geneva and, 2 years later, he added a degree in mathematics and consulted additional courses in physics and the sciences. He also received an MS degree in mathematics from the Sorbonne in 1876. He felt that mathematics was the fundament for the sciences. So, he added an MS degree also in physics in 1878. Soon hereafter he was offered a position at the University of Geneva in the Department of Crystallography and Mineralogy, where he became lecturer in 1879 and Full Professor in 1881. In 1879, he published his significant paper on thermodiffusion [26] on the basis of experiments with solutions of $NaCl$ and KNO_3 in pipes with heated or cooled ends. He noticed higher concentration at the cooled end of the pipe. His experiments confirmed the results of Carl Ludwig (published 20 years earlier) of which SORET probably did not know. In 1898, he became rector of the University of Geneva. He died a few days after a successful operation.

The text is based on www.wikipedia.org

A significant simplification of the formulae (23.78) is achieved by further specialization. If, for instance, it is assumed that $C_{11}^{\alpha\beta}$ only contains nonvanishing entries in the diagonal, i.e., if $C_{11}^{\alpha\beta} = 0$ for $\alpha \neq \beta$ and if it is simultaneously assumed that also the interaction terms C_{12}^{α} vanish, then one obtains

$$\begin{aligned}\Psi_D = &\sum_{\alpha} \frac{1}{2} C_{11}^{\alpha\alpha} \left(\mathrm{grd}\mu^{\xi^\alpha}\right) \cdot \left(\mathrm{grd}\mu^{\xi^\alpha}\right)\\ &+ \frac{1}{2} C_{22} \left(\frac{\operatorname{grad} T}{T}\right) \cdot \left(\frac{\operatorname{grad} T}{T}\right). \end{aligned} \tag{23.79}$$

Assuming, furthermore, the HELMHOLTZ free energy (23.60) in the special form

$$\hat{\psi} = \psi_1(\rho, T) + \sum_{\alpha=1}^{N-1} \psi_2^{\alpha}(\xi^\alpha, T), \tag{23.80}$$

then one may show that $\boldsymbol{q}$ and $\boldsymbol{j}^\alpha$ take the forms

$$\begin{aligned} \boldsymbol{q} &= -\kappa_T \operatorname{grad} T - \sum_{\alpha=1}^{\gamma-1} \kappa_{\xi^\alpha} \operatorname{grad} \xi^\alpha, \\ \boldsymbol{j}^\alpha &= -D_T^\alpha \operatorname{grad} T - D_{\xi^\alpha}^{\alpha} \operatorname{grad} \xi^\alpha, \quad \text{(no summation over } \alpha) \end{aligned}$$

with the coefficients

$$\begin{aligned} \kappa_T &= C_{22} + \sum_{\alpha=1}^{N-1} \left(\frac{\partial \psi_2^\alpha}{\partial \xi^\alpha} C_{11}^{\alpha\alpha} T \frac{\partial^2 \psi_2^\alpha}{\partial \xi^\alpha \partial T} \right), \qquad & D_{\xi^\alpha}^{\alpha} &= C_{11}^{\alpha\alpha} T \frac{\partial^2 \psi_2^\alpha}{\partial {\xi^\alpha}^2}, \\ \kappa_{\xi^\alpha} &= \sum_{\alpha=1}^{N-1} C_{11}^{\alpha\alpha} T \frac{\partial \psi_2^\alpha}{\partial \xi^\alpha} \frac{\partial^2 \psi_2^\alpha}{\partial {\xi^\alpha}^2}, & D_T^\alpha &= C_{11}^{\alpha\alpha} T \frac{\partial^2 \psi_2^\alpha}{\partial \xi^\alpha \partial T}. \end{aligned} \tag{23.81}$$

These formulae permit significant qualitative inferences. As the temperature dependence of the chemical potentials is generally weak, one may ignore the coefficients involving the factor $\partial^2 \psi_2^\alpha / (\partial \xi^\alpha \partial T)$. Then (23.81) implies

$$\kappa_T \sim C_{22}, \qquad D_T^\alpha \sim 0,$$

while κ_{ξ^α} and $D_{\xi^\alpha}^{\alpha\alpha}$ are still given by (23.81). In this approximation the influence of the temperature gradient on the mass fluxes $\boldsymbol{j}^\alpha$ is ignored but that of the concentration gradients on the heat flux is maintained. This is the approximation usually referred to as the LUDWIG–Soret effect.

Remark In the theory derived above, the density of the mixture and the mass concentrations of the tracers $\xi^\alpha (\alpha = 1, 2, \ldots, N-1)$ were regarded as independent fields. Furthermore, the mass balance of the main fluid was not considered as a field equation and neither was the mass concentration of this fluid regarded as an independent constitutive variable. This was done so since $\xi^\alpha \ll 1, \quad \alpha = 1, 2, \ldots, N-1$, and $|\xi^N - 1| \ll 1$ were assumed; in other words the mass of the main fluid was assumed so much greater than the masses of the tracers that the dynamics of the mixture could be regarded as essentially indistinguishable from that of the main fluid. For many situations in environmental physics this is the case. However, for mixtures of gases, this need not be so. In such circumstances, it may be advantageous also to incorporate ξ^N as an independent variable in the constitutive relations; if this is done, however, one must account for the fact that $\xi^N = 1 - \sum_{\alpha=1}^{N-1} \xi^\alpha$. This identity may be taken care of by considering $\sum_{\alpha=1}^{N} \xi^\alpha = 1$ as a constraint equation in the exploitation of the entropy principle. In such a formulation, ξ^N is then treated as an independent field. It is clear that such a formulation of the model equations must yield a theory that is identical to that just derived; this is so but certain variables must be transformed to achieve this one-to-one correspondence. For details, see the footnote 9 on p. 89.

Summarizing this presentation of the general thermodynamic formulation of diffusive processes of reacting tracers in a viscous fluid shows that the ultimate form of the fluid mechanical equations depends chiefly on the proper exploitation of the second law of thermodynamics. This fact is explicit demonstration that these two scientific fields are interwoven with one another. In fact, the ultimate form of the governing fluid mechanical equations is dictated by proper exploitation of the entropy principle. This exploitation delivers results of two different physical qualities. They are stated in two sets of identities, namely (23.32), (23.33), and the residual inequality (23.34). The former, often called LIU identities, allow determination of the LAGRANGE parameters and the derivation of the GIBBS relation (23.39) or (23.41) and restrictions of assumed constitutive relations for pressure, chemical potentials, and entropy via the definition of the HELMHOLTZ free energy, see (23.56). Moreover, they yield an explicit expression for the entropy flux as stated in (23.61) and, above all in this case, allow to prove that Λ^ε is only a function of the empirical temperature,[14] so that $\Lambda^\varepsilon(\theta) \equiv 1/T$, where T is the absolute temperature. On the other hand, with all these intermediate results being given, the entropy production π^s for the constitutive class (23.20) is expressible in the form (23.62). The exploitation of this inequality has been proposed for *linear* deviations of the heat flux vector $\boldsymbol{q}$ and the mass flux vectors $\boldsymbol{j}^\alpha$ $(\alpha = 1, 2, \ldots, N-1)$ from a quadratic dissipation potential Ψ_D, defined in (23.71). It yields explicit constitutive forms for the heat flux vector, the mixture stress tensor, and the constituent mass flux vectors as stated in (23.73), (23.77), and (23.78).

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[14] This proof was not given here; it was only referred to [24], where this proof is given.

23.3 Saturated Mixture of Nonpolar Solid and Fluid Constituents

23.3.1 Motivation

There[15] exists a large number of *heterogeneous materials*, which constitute of both solid and fluid components. In *porous media*, the solid component consists of a connected coherent material or a number of such materials, and the so-called *pore space* is filled with the fluid constituents, usually fluids and/or gases. This pore space can by itself be connected, or it consists of isolated inclusions or may possess both isolated and connected pores. In *granular media*, the solid component consists of individual grains, which would fall apart, if they were not held together by an ambient pressure. Thus a granular heap can, in general, only assume special, distinct rest positions. Sand, soil, and snow belong to this class. If the pore space is partly or completely connected, then the pore fluid may move under the action of gravity or pressure differences. Displacements of fluid particles may then be several orders of magnitude larger than those of the solid constituents. This is the case e.g. in foams, that are used as acoustic insulators, or in the so-called "wind pumping" of the upper most snow layer in snow depositions, through which air percolates, under heavy storms sometimes with surprisingly large seepage velocities. It arises also in groundwater flows. However, if the groundwater current in the saturated soil is too strong, rapid earth movements may arise, which are known as *debris flows*, *sturzstroms* and *mudflows* in which the granular component also moves as a fluid. The transition from a groundwater flow in practically silent sand to the catastrophic flow of a sand water mixture is almost always very abrupt and is for this reason in geotechnique and geology called an instability; the phenomenon is, however, also called "*quick sand*".

If the differential lengths of the governing processes extend over several characteristic diameters of the grains, pores, and typical curvatures or twists of the composites, one may well apply a mixture concept with field variables that are thought to be homogenized over these differential lengths. In other words, within a volume of influence of a spatial point—this is called a *Representative Element Volume*, REV—all field variables are regarded as averaged quantities of true micro fields, and it is anticipated that these averaged quantities interact with each other such that balance laws of mixtures apply to them. Of course this is an assumption, which can be checked for correctness by more detailed averaging procedures; this we will, however, not do here. At last, the correctness of the procedure can be obtained by testing the complete theory against observations.

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[15] Whereas the text of this section has independently been drafted by K. Hutter, many of the detailed arguments have been influenced by the dissertation of G. Bauer [2]. We wish to acknowledge this source, as it has also streamlined and clarified the writings at other places of this book, even though its influence may only here directly be seen.

The applications in focus above are taken from the special fields of geotechnique, geology, geophysics, and environmental physics; industrial applications from chemical process engineering, chemistry, civil and mechanical engineering could equally be given. Our intention is the derivation of the governing equations of a solid–fluid–interaction theory from first thermodynamic principles by using the second law of thermodynamics and exploiting it. A thermodynamic view is also necessary for the derivation of the equations describing purely mechanical processes for which the evolution of the temperature as a variable is not pursued. This is so, because the particular formulation of the equilibrium conditions, especially with regard to the equilibrium pressure and the Darcy interaction force in saturated or unsaturated soil, directly depends on the postulated constitutive equations, i.e., the material complexity and the second law of thermodynamics.

As is transparent from this discussion, the physical circumstances in focus are here mixtures of (partly) *immiscible* constituents, which is quite contrary to the situation dealt with in Sect. 23.2, where the diffusion processes in a mixture of miscible constituents were studied. Furthermore, at least one of the constituents is here a solid. The prerequisites of the assumption that material of each constituent may occupy each point of the body is therefore less convincing than for miscible mixtures. Differential lengths are certainly larger and microstructural effects i.e., effects at the scale within an REV might have to be accounted for by formulating additional relations that describe the effects of the microstructure at the macro-level. Such equations may be additional balance laws for the volume fractions occupied by the individual constituents.

The concepts of mixture theory including Truesdell's metaphysical principles remain valid guidelines and so Truesdell [28–30] and Müller [24] are the pertinent references that should be mentioned. Early concepts of the dynamics of porous media are by Biot [3, 4] and, within the context of continuum mechanics, by Bowen [6, 7]. Additional balance laws for variables describing the effects of the porous or granular structure have, e.g., been introduced by Goodman and Cowin [13] and Passman, Nunziato, and others (see, e.g., the article "A theory of multiphase mixtures" by Passman et al. in Appendix 5C of Truesdell [30], or Drew and Passman [10] where a large number of references are stated).

In the abovementioned references, a postulational approach toward the formulation of the mixture balance laws is taken. Derivations of the balance relations by using an averaging procedure to arrive from physical statements at the micro-scale to relations of the macroscale have been given by Hassaniazadeh and Gray [17–19] and Gray [14] an approach that is also followed by Ehlers [11, 12] and Bluhm [5]. Further summaries of more general focus are by Schneider and Hutter [25] and Gray and Miller [15] as well as Wilmanski [31] and Albers and Wilmanski [1]. The history of the developments from the very early stages to present is given by De Boer [9].

We consider again a mixture of nonpolar constituents so that

$$\boldsymbol{s}^\alpha = \mathbf{0}, \quad \boldsymbol{m}^\alpha = \mathbf{0}, \quad \boldsymbol{l}^\alpha = \mathbf{0}, \quad \boldsymbol{\mathfrak{t}}^\alpha = \mathbf{0} \quad (\alpha = 1, 2, \dots, N). \tag{23.82}$$

Moreover, we shall assume that the individual constituents perform distinct motions, but that these motions are slow on the time scales of thermal relaxation, so that all constituents may be assumed to possess the same temperature. It follows that the prerequisites of a *mixture of class II* are fulfilled, for which the mass and momentum balance laws for all constituents must be formulated, but only the energy balance for the mixture as a whole is relevant. Consequently, the following balance laws define this mixture theory:

$$\begin{aligned}
&\frac{\partial \rho^\alpha}{\partial t} + \operatorname{div}(\rho^\alpha \boldsymbol{v}^\alpha) = \mathfrak{c}^\alpha, \quad (\alpha = 1, 2, \ldots, N)\ , \\
&\frac{\partial \rho^\alpha \boldsymbol{v}^\alpha}{\partial t} + \operatorname{div}(\rho^\alpha \boldsymbol{v}^\alpha \otimes \boldsymbol{v}^\alpha) = \operatorname{div} \boldsymbol{t}^\alpha + \rho^\alpha \boldsymbol{f}^\alpha + \mathfrak{m}^\alpha, \quad (\alpha = 1, 2, \ldots, N)\ , \\
&\frac{\partial \rho \varepsilon}{\partial t} + \operatorname{div}(\rho \varepsilon \boldsymbol{v}) = -\operatorname{div} \boldsymbol{q} + \operatorname{grad} \boldsymbol{v} \cdot \boldsymbol{t}^T + \rho \mathfrak{r}\ , \qquad (23.83) \\
&\frac{\partial \rho s}{\partial t} + \operatorname{div}(\rho s \boldsymbol{v} + \phi^{\rho s}) - \rho \eta^{\rho s} \geqslant 0.
\end{aligned}$$

These comprise the balance laws of mass and momentum for the constituents $(23.83)_{1,2}$, those of the internal energy of the mixture $(23.83)_3$ and of the entropy $(23.83)_4$. Because of the assumption (23.82), as follows from (21.24), the partial CAUCHY stress tensors $\boldsymbol{t}^\alpha$ are symmetric, $\boldsymbol{t}^\alpha = \boldsymbol{t}^{\alpha T}$; furthermore, the mixture variables are defined in (21.62)–(21.66) and could easily be written down in the simplified forms appropriate for the specification (23.82).

The goal in this section is not to derive a general theory of mixtures of class II, but rather to present an example of such a theory. For this reason, the following simplifying assumptions are introduced.

Assumption of Constant True Densities It shall be assumed that solid and fluid constituents are such that the density preserving property may be imposed. We shall thus assume that all constituents possess constant true densities.[16] The true independent variables are then not the mass densities ρ^α but the *constituent volume fractions* ν^α, which connect the partial densities ρ^α with the true densities $\hat{\rho}^\alpha$ according to

$$\rho^\alpha = \nu^\alpha \hat{\rho}^\alpha, \quad \hat{\rho}^\alpha = \text{constant}, \quad (\alpha = 1, 2, 3, \ldots, N). \qquad (23.84)$$

The assumption of constant $\hat{\rho}^\alpha$ means that the materials of which the individual constituents are made are density preserving.

If one substitutes (23.84) into the mass balance (23.83), then, after division by $\hat{\rho}^\alpha$, one obtains

$$\frac{\partial \nu^\alpha}{\partial t} + \operatorname{div}(\nu^\alpha \boldsymbol{v}^\alpha) = \frac{1}{\hat{\rho}^\alpha} \mathfrak{c}^\alpha =: \mathfrak{n}^\alpha, \quad (\alpha = 1, 2, \ldots, N)\ , \qquad (23.85)$$

which is an equation for the volume fractions ν^α; in other words, in this simple theory, the volume fractions replace the partial densities as independent variables.

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[16] The *true* density of constituent α is the mass of constituent α per unit volume of this constituent (and not that of the mixture). Sometimes this is also called the *apparent* density.

Assumption of Saturation of the Mixture We also wish to suppose that the considered mixture does not have any cavities or empty spaces; in other words, the sum of the volume fractions fills the entire space at all positions and at all times within the body, i.e.,

$$\sum_{\alpha=1}^{N} \nu^{\alpha} = 1. \tag{23.86}$$

This equation implies: of the N volume fraction variables only $(N-1)$ are independent. One particular ν^{α} can be replaced by $(1-\sum_{\beta\neq\alpha}\nu^{\beta})$; we shall do this in the sequel for the variable ν^{N}.

If a function $f = f(\nu^1, \dots, \nu^N)$ depends on all $\nu^1, \dots, \nu^N$, then, upon elimination of $\nu^N = (1-\sum_{\beta\neq N}\nu^{\beta})$ one may write

$$\tilde{f}(\nu^1, \dots, \nu^{N-1}) = f\left(\nu^1, \dots, \nu^{N-1}, 1-\sum_{\beta=1}^{N-1}\nu^{\beta}\right). \tag{23.87}$$

If one must differentiate this function with respect to time or space—this will be expressed by ∂—then one obtains

$$\partial f = \sum_{\alpha=1}^{N-1} \frac{\partial \tilde{f}}{\partial \nu^{\alpha}} \partial \nu^{\alpha} = \sum_{\alpha=1}^{N-1} \left(\frac{\partial f}{\partial \nu^{\alpha}} - \frac{\partial f}{\partial \nu^{N}}\right) \partial \nu^{\alpha}. \tag{23.88}$$

It follows that one must always be aware which independent variables one wants to use as field variables, either the first $N-1$ volume fractions as for $\tilde{f}$, or the N volume fractions as for f. It should also be observed that the balance law for the dependent volume fraction still constitutes an independent equation. In fact, the volume balance (23.85) can, for $\alpha = N$, be written as

$$-\left\{\sum_{\beta=1}^{N-1} \frac{\partial \nu^{\beta}}{\partial t}\right\} + \left\{\operatorname{div}\left[\left(1-\sum_{\beta=1}^{N-1}\nu^{\beta}\right)\boldsymbol{v}^{N}\right]\right\} = -\frac{1}{\hat{\rho}^{N}}\left(\sum_{\gamma=1}^{N-1}\mathfrak{c}^{\gamma}\right) =: \mathfrak{n}^{N}, \tag{23.89}$$

where the saturation condition (23.86) and $\sum_{\alpha=1}^{N}\mathfrak{c}^{\alpha} = 0$ have been used. This equation is independent of the other volume balances. The *saturation condition* must be interpreted as a constraint condition, which is the cause for the fact that in the resulting equations there will be an independent equation in excess to the number of independent variables. This will lead to the introduction of an additional constraint stress, the so-called *saturation pressure*.

23.3.2 Choice of the Material Class and Material Theory

The balance laws (23.83)$_{2,3}$ and the mass balance equations for the density preserving constituents in the form (23.85) constitute together $4N + 1$ equations for the $N - 1$ volume fractions ν^α, $3N$ velocity components of the constituents $\boldsymbol{v}^\alpha$, as well as the temperature θ, i.e., $4N$ variables. They must be complemented by phenomenological relations for the constitutive quantities

$$\Psi = \left\{\mathfrak{c}^\alpha, \boldsymbol{\mathfrak{m}}^\alpha, \boldsymbol{t}^\alpha, \varepsilon, s, \boldsymbol{q}^\alpha, \phi^{\rho s}\right\}, \tag{23.90}$$

which, according to the principle of equipresence, all are postulated to depend on the following set of constitutive variables:

$$\begin{aligned} \Xi = \big\{&\nu^1, \dots, \nu^{N-1}, \theta, \operatorname{grad}\nu^1, \dots, \operatorname{grad}\nu^{N-1}, \\ &\boldsymbol{v}^1, \dots, \boldsymbol{v}^N, \operatorname{grad}\boldsymbol{v}^1, \dots, \operatorname{grad}\boldsymbol{v}^N, \operatorname{grad}\theta\big\}. \end{aligned} \tag{23.91}$$

The chosen material class is therefore *a mixture of viscous, heat conducting constituents* which principally possess fluid character as will become apparent in due course with the developments. Elasticity effects are left out of consideration merely for reasons of mathematical simplicity. Such effects are important to be included for the solid constituent when rest positions are important for the physical processes under consideration. For such cases, one must add the deformation gradient $\boldsymbol{F}^s$ as an additional variable in (23.91), see, e.g., SVENDSEN and HUTTER [27] and, in particular, SCHNEIDER and HUTTER [25]. Thus, the postulate (23.91) is appropriate for modeling debris flows or mud flows where fluid and solid constituents are moving very much like fluids. Notice, moreover, that only $(N - 1)$ volume fractions are taken into account in (23.91), because the Nth volume fraction in a saturated mixture is determined by the other $(N - 1)$ constituent volume fractions. Furthermore, the grad ν^α-terms account for the fact that the momentum productions or interaction forces $\boldsymbol{\mathfrak{m}}^\alpha$ may also depend on the distribution of the constituents; such a theory is also known as a *gradient theory*, in any case it does have non-simple character.[17]

We also request that the constitutive relations $\Psi = \hat{\Psi}(\Xi)$ obey the rule of material objectivity, which requires that $\hat{\Psi}(\cdot)$ satisfies the equation

$$\begin{aligned} &\hat{\Psi}\left(\dots, \boldsymbol{v}^1, \dots, \boldsymbol{v}^N, \operatorname{grad}\boldsymbol{v}^1, \dots, \operatorname{grad}\boldsymbol{v}^N, \dots\right) \\ &= \hat{\Psi}\left(\dots, \boldsymbol{v}^1 + \boldsymbol{a}^1, \dots, \boldsymbol{v}^N + \boldsymbol{a}^N, \operatorname{grad}\boldsymbol{v}^1 + \boldsymbol{\Omega}^1, .., \operatorname{grad}\boldsymbol{v}^N + \boldsymbol{\Omega}^N, \dots\right) \end{aligned} \tag{23.92}$$

as an identity for any vector $\boldsymbol{a}^\alpha$ and any skew-symmetric tensor $\boldsymbol{\Omega}^\alpha$ $(\alpha = 1, 2, \dots, N)$. This requirement implies that $\hat{\Psi}$ cannot depend upon the constituent velocities

---

[17] In classical continuum mechanics, a non-simple material is defined as a medium in which higher gradients of the motion $\boldsymbol{\chi}(\boldsymbol{X}, t)$ may arise as independent constitutive variables. This is the case, if grad ρ is an independent constitutive variable, because $\rho = \rho_0 / \det \boldsymbol{F}$ and therefore $\operatorname{grad}\rho = \rho_0 \operatorname{grad} \det \boldsymbol{F}^{-1}$.

and velocity gradients themselves, but only upon the differences

$$\begin{aligned} \boldsymbol{u}^\alpha &:= \boldsymbol{v}^\alpha - \boldsymbol{v}, & \boldsymbol{v} &:= \sum_{\alpha=1}^{N} \xi^\alpha \boldsymbol{v}^\alpha, \\ \boldsymbol{U}^\alpha &:= \operatorname{grad} \boldsymbol{v}^\alpha - \boldsymbol{W}, & \boldsymbol{W} &:= \operatorname{skwgrad} \boldsymbol{v}, \end{aligned} \tag{23.93}$$

in which $\boldsymbol{u}^\alpha$ are the diffusion velocities relative to the barycentric velocity $\boldsymbol{v}$ and $\boldsymbol{U}^\alpha$ the relative deformation rate tensors. The quantities $\boldsymbol{u}^\alpha$ and $\boldsymbol{U}^\alpha$ are objective vectors and objective rank-2 tensors. The proof follows easily from the fact that $\boldsymbol{v}^\alpha$, $\boldsymbol{v}$, grad $\boldsymbol{v}$, and $\boldsymbol{W}$ apply at the same position $\boldsymbol{x}$ of constituent α, and the transformation rules (23.17)–(23.18) under EUCLIDian transformations.[18] With the above restrictions, the constitutive postulate (23.91) may also be written as

$$\begin{aligned} \Psi = \hat{\Psi}\Big(&\nu^1, \dots, \nu^{N-1}, \theta, \operatorname{grad} \nu^1, \dots, \operatorname{grad} \nu^{N-1}, \\ &\boldsymbol{u}^1, \dots, \boldsymbol{u}^N, \boldsymbol{U}^1, \dots, \boldsymbol{U}^N, \operatorname{grad} \theta\Big). \end{aligned} \tag{23.94}$$

In performing the explicit calculations, it has been seen, however, that it is more convenient to perform the calculations with the variables (23.91) rather than (23.94) and to incorporate the specialization (23.93) afterwards. This requires then that differentiations with respect to $\boldsymbol{u}^\alpha$ and $\boldsymbol{U}^\alpha$ must be executed with care. For instance, the following definitions and rules of differentiation apply. For their proofs, see Appendix 23.C in this chapter.

$$\begin{aligned} \operatorname{grad} \boldsymbol{v} &= \sum_{\gamma=1}^{N} \left[\xi^\gamma \operatorname{grad} \boldsymbol{v}^\gamma + \boldsymbol{v}^\gamma \otimes \operatorname{grad} \xi^\gamma\right], \\ \boldsymbol{D} &= \sum_{\gamma=1}^{N} \left[\xi^\gamma \boldsymbol{D}^\gamma + \operatorname{sym}(\boldsymbol{v}^\gamma \otimes \operatorname{grad} \xi^\gamma)\right], \\ \boldsymbol{W} &= \sum_{\gamma=1}^{N} \left[\xi^\gamma \boldsymbol{W}^\gamma + \operatorname{skw}(\boldsymbol{v}^\gamma \otimes \operatorname{grad} \xi^\gamma)\right], \\ \frac{\partial \boldsymbol{u}^\beta}{\partial \boldsymbol{v}^\alpha} &= \left(\delta_{\alpha\beta} - \xi^\alpha\right) \mathbf{1}, \\ \frac{\partial \boldsymbol{U}^\beta}{\partial \boldsymbol{W}^\alpha} &= \left(\delta_{\alpha\beta} - \xi^\alpha\right) \mathbf{1}_4, \end{aligned} \tag{23.95}$$

---

[18] $\boldsymbol{U}^\alpha$ contains symmetric and skew-symmetric contributions which can be separated into

$$\boldsymbol{D}^\alpha = \operatorname{sym}\boldsymbol{U}^\alpha = \operatorname{sym}(\operatorname{grad} \boldsymbol{v}^\alpha), \qquad \boldsymbol{W}^\alpha = \operatorname{skw} \boldsymbol{U}^\alpha = \operatorname{skw}(\operatorname{grad} \boldsymbol{v}^\alpha) - \boldsymbol{W}.$$

$\boldsymbol{D}^\alpha$ and $\boldsymbol{W}^\alpha$ are relative stretching and relative vorticity tensors.

$$\frac{\partial f}{\partial \boldsymbol{v}^\alpha} = \frac{\partial f}{\partial \boldsymbol{u}^\alpha} - \xi^\alpha \sum_{\gamma=1}^{N} \frac{\partial f}{\partial \boldsymbol{u}^\gamma}\,,$$

$$\frac{\partial f}{\partial \boldsymbol{W}^\alpha} = \frac{\partial f}{\partial \boldsymbol{U}^\alpha} - \xi^\alpha \sum_{\gamma=1}^{N} \frac{\partial f}{\partial \boldsymbol{U}^\gamma}\,,$$

$$\frac{\partial f}{\partial \mathrm{grad}\, \boldsymbol{v}^\alpha} = \frac{\partial f}{\partial \boldsymbol{D}^\alpha} + \frac{\partial f}{\partial \boldsymbol{U}^\alpha} - \xi^\alpha \sum_{\gamma=1}^{N} \frac{\partial f}{\partial \boldsymbol{U}^\gamma}\,,$$

in which $\mathbf{1}_4$ denotes the fourth-order unit tensor and $\delta_{\alpha\beta}$ the N-dimensional KRONECKER delta. Formula (23.95)$_6$ must, e.g., be applied if the internal energy of the mixture must be differentiated with respect to $\boldsymbol{v}^\alpha$:

$$\rho\varepsilon = \underbrace{\sum_{\alpha=1}^{N} \rho^\alpha \varepsilon^\alpha}_{\rho\varepsilon_I} + \underbrace{\sum_{\alpha=1}^{N} \frac{\rho^\alpha}{2} \boldsymbol{u}^\alpha \cdot \boldsymbol{u}^\alpha}_{\rho\varepsilon_D} = \rho\varepsilon_I + \rho\varepsilon_D,$$

$$\frac{\partial(\rho\varepsilon_D)}{\partial \boldsymbol{v}^\alpha} = \rho^\alpha \boldsymbol{u}^\alpha - \xi^\alpha \underbrace{\sum_{\gamma=1}^{N} \rho^\gamma \boldsymbol{u}^\gamma}_{0} = \rho^\alpha \boldsymbol{u}^\alpha, \tag{23.96}$$

$$\frac{\partial(\rho\varepsilon)}{\partial \boldsymbol{v}^\alpha} = \frac{\partial(\rho\varepsilon_I)}{\partial \boldsymbol{v}^\alpha} + \rho^\alpha \boldsymbol{u}^\alpha = \frac{\partial(\rho\varepsilon_I)}{\partial \boldsymbol{u}^\alpha} - \xi^\alpha \sum_{\gamma=1}^{N} \frac{\partial(\rho\varepsilon_I)}{\partial \boldsymbol{u}^\gamma} + \rho^\alpha \boldsymbol{u}^\alpha.$$

The quantities ε_I and ε_D are called *inner internal energy* and *diffusive internal energy*, respectively.

A *thermodynamic process* is in this section a set of field variables ν^α ($\alpha = 1, 2, \ldots, N-1$), $\boldsymbol{v}^1, \ldots, \boldsymbol{v}^N, \theta$ which obeys the balance laws of momenta and energy (23.83)$_{2,3}$, the volume balances (23.85) for $\alpha = 1, \ldots, N-1$, and (23.89) for $\alpha = N$ as well as the constitutive equations $\Psi = \Psi(\Xi)$ given in (23.91) or (23.94). If we now request, as usual, that the entropy inequality (23.83)$_4$ be satisfied for all thermodynamic processes, then the equations just mentioned play the role of constraint conditions for the entropy inequality. According to the procedure of LIU, this requirement can be fulfilled as follows: One subtracts the scalar products of these equations with the so-called LAGRANGE parameters (or adds them which only changes the signs of the LAGRANGE parameters) from the entropy inequality and satisfies this extended inequality for unrestricted fields. This extended inequality reads

$$
\begin{aligned}
&\frac{\partial(\rho\hat{s})}{\partial t} + \operatorname{div}\left(\hat{\phi}^{\rho s} + \rho\hat{s}\boldsymbol{v}\right) - \eta^{\rho s} - \sum_{\alpha=1}^{N-1} \Lambda^{\nu^\alpha}\left(\frac{\partial \nu^\alpha}{\partial t} + \operatorname{div}\left(\nu^\alpha \boldsymbol{v}^\alpha\right) - \hat{\mathfrak{n}}^\alpha\right)\\
&- \Lambda^{\nu^N}\left(-\Big\{\sum_{\alpha=1}^{N-1}\frac{\partial \nu^\beta}{\partial t}\Big\} + \Big\{1 - \sum_{\beta=1}^{N-1}\nu^\beta\Big\}\cdot \operatorname{div}\boldsymbol{v}^N - \Big\{\sum_{\beta=1}^{N-1}\operatorname{grad}\nu^\beta\Big\}\cdot\boldsymbol{v}^N - \hat{\mathfrak{n}}^N\right)\\
&- \sum_{\alpha=1}^{N}\boldsymbol{\Lambda}^{\boldsymbol{v}^\alpha}\cdot\left(\frac{\partial(\rho^\alpha\boldsymbol{v}^\alpha)}{\partial t} - \operatorname{div}\left(\hat{\boldsymbol{t}}^\alpha - \rho^\alpha\boldsymbol{v}^\alpha\otimes\boldsymbol{v}^\alpha\right) - \hat{\boldsymbol{\mathfrak{m}}}^\alpha - \rho^\alpha\boldsymbol{f}^\alpha\right)\\
&- \Lambda^\varepsilon\left(\frac{\partial(\rho\hat{\varepsilon})}{\partial t} + \operatorname{div}\left(\hat{\boldsymbol{q}} + \rho\hat{\varepsilon}\boldsymbol{v}\right) - \operatorname{tr}\left(\hat{\boldsymbol{t}}\boldsymbol{D}\right) - \rho\mathfrak{r}\right) \geqslant 0,
\end{aligned}
\tag{23.97}
$$

in which the materially dependent variables are thought to be substituted by their constitutive relations, a fact which we have made visible by writing a hat for such variables, $\hat{(\cdot)}$. In (23.97), the balance laws for the volume fractions appear multiplied with the LAGRANGE multiplier Λ^{ν^α}; the momentum balances are scalarly multiplied with $\boldsymbol{\Lambda}^{\boldsymbol{v}^\alpha}$ and the balance of internal energy appears multiplied with the factor Λ^ε. Apart from the supply terms of entropy $\eta^{\rho s}$, of momentum $\rho^\alpha\boldsymbol{f}^\alpha$ and of energy $\rho\mathfrak{r}$, inequality (23.97) depends explicitly (and implicitly via the constitutive quantities) upon the independent fields and or spatial and temporal derivatives of these. Hence, the LAGRANGE multipliers are in general also functionals of these quantities.[19]

A first step in the exploitation of inequality (23.97) consists in the requirement that the constitutive response of a body, since it describes the material behavior, does not depend upon the source terms that are applied to the body from its outside. The sum of the external supply terms in (23.97) must therefore add up to zero, so that

$$
\eta^{\rho s} = \Lambda^\varepsilon \rho\,\mathfrak{r} + \sum_{\alpha=1}^{N}\left(\boldsymbol{\Lambda}^{\boldsymbol{v}^\alpha}\cdot\rho^\alpha\boldsymbol{f}^\alpha\right)\ ; \tag{23.98}
$$

consequently, the entropy supply is a linear combination of the energy supply (radiation) and the momentum supplies (external forces) and is fixed once the LAGRANGE parameters Λ^ε and $\boldsymbol{\Lambda}^{\boldsymbol{v}^\alpha}$ are determined.

The further procedure in exploiting inequality (23.97), shortened by (23.98), consists now in the following steps: all differentiations are performed using the chain rule of differentiation where needed; the chain rule must, in particular, be used where a constitutive quantity is differentiated with respect to time or space. The inequality thus obtained is sorted and rearranged according to the independent constitutive variables (and their higher order derivatives). If this is done—a relatively lengthy procedure—one recognizes that the emerging inequality can be considerably con-

---

[19] It might be worth mentioning that most authors of papers dealing with thermodynamics of solid–fluid mixtures of porous or granular materials use the second law of thermodynamics in a form akin to the CLAUSIUS–DUHEM inequality with an exploitation following the COLEMAN–NOLL procedure of exploitation. In these approaches, the balance laws of peculiar momenta and energy are associated with arbitrary source terms.

densed, if the following one-forms[20] are defined:

$$\mathcal{P} := \mathrm{d}(\rho s) - \Lambda^{\varepsilon}\mathrm{d}(\rho\varepsilon), \quad \boldsymbol{\mathcal{F}} := \mathrm{d}\phi^{\rho s} - \Lambda^{\varepsilon}\mathrm{d}\boldsymbol{q} + \sum_{\alpha=1}^{N} \boldsymbol{\Lambda}^{\boldsymbol{v}^{\alpha}}(\mathrm{d}\boldsymbol{t}^{\alpha}), \tag{23.99}$$

with the coefficients

$$\mathcal{P}_{x_i} := \frac{\partial(\rho\hat{s})}{\partial x_i} - \Lambda^{\varepsilon}\frac{\partial(\rho\hat{\varepsilon})}{\partial x_i}, \quad \boldsymbol{\mathcal{F}}_{x_i} := \frac{\partial\hat{\phi}^{\rho s}}{\partial x_i} - \Lambda^{\varepsilon}\frac{\partial\hat{\boldsymbol{q}}}{\partial x_i} + \sum_{\alpha=1}^{N} \boldsymbol{\Lambda}^{\boldsymbol{v}^{\alpha}}\frac{\partial\hat{\boldsymbol{t}}^{\alpha}}{\partial x_i}, \tag{23.100}$$

so that[21]

$$\mathcal{P} = \mathcal{P}_{x_i}\mathrm{d}x_i \quad \text{and} \quad \mathcal{F} = \mathcal{F}_{x_i}\mathrm{d}x_i. \tag{23.101}$$

Furthermore, we use the abbreviation

$$\boldsymbol{\mathcal{O}}_{x_i} = \boldsymbol{v} \otimes \mathcal{P}_{x_i} + \mathcal{F}_{x_i}. \tag{23.102}$$

With these notations, the extended entropy inequality can be written in the following form[22]:

$$\begin{aligned}
&\mathcal{P}_{\theta}\frac{\partial\theta}{\partial t} + \mathcal{P}_{\operatorname{grad}\theta} \cdot \frac{\partial(\operatorname{grad}\theta)}{\partial t} \\
&+ \sum_{\alpha=1}^{N} \left\{ (\mathcal{P}_{\nu^{\alpha}} - \mathcal{P}_{\nu^{N}}) - (\Lambda^{\nu^{\alpha}} - \Lambda^{\nu^{N}}) - (\hat{\rho}^{\alpha}\boldsymbol{\Lambda}^{\boldsymbol{v}^{\alpha}} \cdot \boldsymbol{v}^{\alpha} - \hat{\rho}^{N}\boldsymbol{\Lambda}^{\boldsymbol{v}^{N}} \cdot \boldsymbol{v}^{N}) \right\} \frac{\partial\nu^{\alpha}}{\partial t} \\
&+ \sum_{\alpha=1}^{N-1} \left\{ \mathcal{P}_{\operatorname{grad}\nu^{\alpha}} - \mathcal{P}_{\operatorname{grad}\nu^{N}} \right\} \cdot \frac{\partial(\operatorname{grad}\nu^{\alpha})}{\partial t} \\
&+ \sum_{\alpha=1}^{N} \left(\mathcal{P}_{\boldsymbol{v}^{\alpha}} - \rho^{\alpha}\boldsymbol{\Lambda}^{\boldsymbol{v}^{\alpha}} \right) \cdot \frac{\partial\boldsymbol{v}^{\alpha}}{\partial t} + \sum_{\alpha=1}^{N} \mathcal{P}_{\operatorname{grad}\boldsymbol{v}^{\alpha}} \cdot \frac{\partial\operatorname{grad}\boldsymbol{v}^{\alpha}}{\partial t} \\
&+ \sum_{\alpha=1}^{N-1} \left\{ \boldsymbol{\mathcal{O}}_{\operatorname{grad}\nu^{\alpha}} - \boldsymbol{\mathcal{O}}_{\operatorname{grad}\nu^{N}} \right\} \cdot \operatorname{grad}(\operatorname{grad}\nu^{\alpha})
\end{aligned}$$

---

[20] *One-form* is a linear functional $\mathcal{F}$ (as a special case of multilinear functionals), in which $\mathcal{F} = \sum a_j \mathrm{d}x_j$ is a sum of finite coefficients a_j multiplied with differentials $\mathrm{d}x_j$.

[21] Notice that $\mathcal{P}_{x_i}$ and $\mathcal{F}_{x_i}$ do not represent derivatives of $\mathcal{P}$ and $\mathcal{F}$, since Λ^{ε} in (23.100) cannot be pulled into the differential of $\rho\varepsilon$. So, neither $\mathcal{P}$ nor $\mathcal{F}$ are complete differentials.

[22] The derivation of this formidably looking inequality is not difficult, however it is lengthy and time consuming, and its derivation is susceptible to error. For this text, it was derived several times and has multiply been checked.

$$
\begin{aligned}
&+\sum_{\alpha=1}^{N}(\boldsymbol{\mathcal{O}}_{\mathrm{grad}\,\boldsymbol{v}^\alpha})\cdot\mathrm{grad}\,(\mathrm{grad}\,\boldsymbol{v}^\alpha)+(\boldsymbol{\mathcal{O}}_{\mathrm{grad}\,\theta})\cdot(\mathrm{grad}\,(\mathrm{grad}\,\theta))\\
&+\boldsymbol{\mathcal{O}}_\theta\cdot\mathrm{grad}\,\theta\\
&+\sum_{\alpha=1}^{N-1}\Big\{\boldsymbol{\mathcal{O}}_{\nu^\alpha}-\boldsymbol{\mathcal{O}}_{\nu^N}-(\Lambda^{\nu^\alpha}\boldsymbol{v}^\alpha-\Lambda^{\nu^\alpha}\boldsymbol{v}^N)+\Lambda^\varepsilon\frac{\boldsymbol{t}}{\rho}(\hat{\rho}^\alpha\boldsymbol{u}^\alpha-\hat{\rho}^N\boldsymbol{u}^N)\\
&-(\hat{\rho}^\alpha\boldsymbol{\Lambda}^{\boldsymbol{v}^\alpha}\cdot\boldsymbol{v}^\alpha\otimes\boldsymbol{v}^\alpha-\hat{\rho}^N\boldsymbol{\Lambda}^{\boldsymbol{v}}\cdot\boldsymbol{v}^N\otimes\boldsymbol{v}^N)\\
&+(s-\Lambda^\varepsilon\varepsilon)(\hat{\rho}^\alpha\boldsymbol{u}^\alpha-\hat{\rho}^N\boldsymbol{u}^N)\Big\}\cdot\mathrm{grad}\,\nu^\alpha\\
&+\sum_{\alpha=1}^{N}\Big\{\boldsymbol{\mathcal{O}}_{\boldsymbol{v}^\alpha}+\rho^\alpha(s-\Lambda^\varepsilon\varepsilon)\mathbf{1}+\Lambda^\varepsilon\frac{\rho^\alpha}{\rho}\boldsymbol{t}-(\Lambda^{\nu^\alpha}\nu^\alpha+\rho^\alpha\boldsymbol{\Lambda}^{\boldsymbol{v}^\alpha}\cdot\boldsymbol{v}^\alpha)\mathbf{1}\\
&-\rho^\alpha(\boldsymbol{\Lambda}^{\boldsymbol{v}^\alpha}\otimes\boldsymbol{v}^\alpha)\Big\}\cdot\mathrm{grad}\,\boldsymbol{v}^\alpha+\sum_{\alpha=1}^{N}\left\{\Lambda^{\nu^\alpha}\mathfrak{n}^\alpha+\boldsymbol{\Lambda}^{\boldsymbol{v}^\alpha}\cdot\boldsymbol{\mathfrak{m}}^\alpha\right\}\geqslant 0.
\end{aligned}
\tag{23.103}
$$

This still rather formidably looking inequality is written in two blocks which are separated from one another by an empty line. The block above this empty line consists of a sum of products of two factors $\boldsymbol{\alpha}\cdot\boldsymbol{\beta}$ where

$$
\boldsymbol{\beta}=\left\{\mathrm{grad}\,(\mathrm{grad}\,\zeta),\ \frac{\partial\mathrm{grad}\,\zeta}{\partial t},\ \frac{\partial\zeta}{\partial t}\right\},\qquad \zeta=(\theta,\nu^\alpha,\boldsymbol{v}^\alpha)
\tag{23.104}
$$

and the prefactors of $\boldsymbol{\beta}$ are collected in the second vector $\boldsymbol{\alpha}$ with the same dimension; $\boldsymbol{\alpha}$ only depends upon the independent constitutive variables and upon $\boldsymbol{v}^\alpha$. The upper block of inequality (23.103) is therefore linear in $\boldsymbol{\beta}$. The lower block in (23.103) does not contain variables from $\boldsymbol{\beta}$ and only depends upon the independent constitutive variables and $\boldsymbol{v}^\alpha$ $(\alpha=1,2,\ldots,N)$ and $\boldsymbol{v}$; let it be collected in the scalar $\varGamma$. In summary, inequality (23.103) has the form

$$
\boldsymbol{\alpha}\cdot\boldsymbol{\beta}+\varGamma\geqslant 0
\tag{23.105}
$$

and is linear in $\boldsymbol{\beta}$.

It is relatively easy to become convinced that to any chosen $\boldsymbol{\beta}$ in a neighborhood of a material point, there exists (at least) one admissible thermodynamic process (which satisfies the balance equations and constitutive relations). A fortiori, since the balance laws are accounted for in inequality (23.103) via the terms involving the LAGRANGE parameters, $\boldsymbol{\beta}$ may assume any value we please; of necessity then, (23.105) is satisfied if and only if

$$
\boldsymbol{\alpha}=\mathbf{0}\quad\text{and}\quad\varGamma\geqslant 0.
\tag{23.106}
$$

The proof of (23.106) is outlined in this chapter after the analogous statements (23.28). The first equations comprise the LIU equations, the latter is the residual entropy inequality. The statement $\boldsymbol{\alpha} = \mathbf{0}$ corresponds in (23.103) to the following conditions, which must be satisfied as identities:[23]

$$
\begin{aligned}
&\mathcal{P}_{\theta} = 0,\\
&\mathcal{P}_{\operatorname{grad}\theta} = \mathbf{0}\,,\\
&(\mathcal{P}_{\nu^\alpha} - \mathcal{P}_{\nu^N}) - (\Lambda^{\nu^\alpha} - \Lambda^{\nu^N}) - (\hat{\rho}^\alpha \boldsymbol{\Lambda}^{\boldsymbol{v}^\alpha} \cdot \boldsymbol{v}^\alpha - \hat{\rho}^N \boldsymbol{\Lambda}^{\boldsymbol{v}^N} \cdot \boldsymbol{v}^N) = \mathbf{0},\\
&\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (\alpha = 1, 2, \dots, N-1),\\
&(\mathcal{P}_{\operatorname{grad}\nu^\alpha} - \mathcal{P}_{\operatorname{grad}\nu^N}) = \mathbf{0}, \qquad\qquad\qquad (\alpha = 1, 2, \dots, N-1),\\
&(\mathcal{P}_{\boldsymbol{v}^\alpha} - \rho^\alpha \boldsymbol{\Lambda}^{\boldsymbol{v}^\alpha}) = \mathbf{0}, \qquad\qquad\qquad\qquad (\alpha = 1, 2, \dots, N),\\
&\mathcal{P}_{\operatorname{grad}\boldsymbol{v}^\alpha} = \mathbf{0}, \qquad\qquad\qquad\qquad\qquad\qquad (\alpha = 1, 2, \dots, N),\\
&(\boldsymbol{\mathcal{F}}_{\operatorname{grad}\nu^\alpha} - \boldsymbol{\mathcal{F}}_{\operatorname{grad}\nu^N})_{\text{sym}} = \mathbf{0}, \qquad\quad (\alpha = 1, 2, \dots, N-1),\\
&(\boldsymbol{\mathcal{F}}_{\operatorname{grad}\boldsymbol{v}^\alpha})_{\text{sym}} = \mathbf{0},\ (\alpha = 1, 2, \dots, N)\\
&(\boldsymbol{\mathcal{F}}_{\operatorname{grad}\theta})_{\text{sym}} = \mathbf{0}\ .
\end{aligned}
\tag{23.107}
$$

The first six statements of (23.107) follow directly from the first four lines of (23.103), since

$$
\frac{\partial}{\partial t}\{\theta;\ \operatorname{grad}\theta;\ (\nu^\alpha, \operatorname{grad}\nu^\alpha),\ \alpha = 1, \dots, N-1;\ (\boldsymbol{v}^\alpha, \operatorname{grad}\boldsymbol{v}^\alpha),\ \alpha = 1, \dots, N\}
$$

can all freely assume any value. In the three last identities, the results $(23.107)_{2,4,6}$ were used. The residual inequality now only consists of the last block in (23.103).

The identities (23.107) allow a number of inferences, of which the most simple ones are presented now. First, it follows from the first six identities (23.107) plus the definitions (23.99) that the *generalized* Gibbs[24] *relation*

$$
\begin{aligned}
\mathrm{d}(\rho\hat{s}) = {} & \Lambda^{\varepsilon}\mathrm{d}(\rho\hat{\varepsilon})\\
& + \sum_{\alpha=1}^{N-1}\Big\{(\Lambda^{\nu^\alpha} - \Lambda^{\nu^N}) + (\hat{\rho}^\alpha \boldsymbol{\Lambda}^{\boldsymbol{v}^\alpha} \cdot \boldsymbol{v}^\alpha - \hat{\rho}^N \boldsymbol{\Lambda}^{\boldsymbol{v}^N} \cdot \boldsymbol{v}^N)\Big\}\,\mathrm{d}\nu^\alpha\\
& + \sum_{\alpha=1}^{N} \rho^\alpha \boldsymbol{\Lambda}^{\boldsymbol{v}^\alpha} \cdot \mathrm{d}\boldsymbol{v}^\alpha
\end{aligned}
\tag{23.108}
$$

must hold. It can equally be written as

---

[23] With regard to the terms $\mathcal{P}_{\nu^\alpha}$, $\mathcal{P}_{\operatorname{grad}\nu^\alpha}$, and $\mathcal{F}_{\nu^\alpha}$, the identities $(23.107)_{3,4,7}$ are to be understood in the sense of Eq. (23.88). If $\mathrm{d}\nu^N$ should not be replaced by $-\sum_{\alpha=1}^{N-1}\mathrm{d}\nu^\alpha$ as in (23.103), then the following substitutions should be made:

$$
\begin{aligned}
\mathcal{P}_{\nu^\alpha} - \mathcal{P}_{\nu^N} &\longrightarrow \mathcal{P}_{\nu^\alpha},\\
\mathcal{P}_{\operatorname{grad}\nu^\alpha} - \mathcal{P}_{\operatorname{grad}\nu^N} &\longrightarrow \mathcal{P}_{\operatorname{grad}\nu^\alpha},\\
\mathcal{F}_{\operatorname{grad}\nu^\alpha} - \mathcal{F}_{\operatorname{grad}\nu^N} &\longrightarrow \mathcal{F}_{\operatorname{grad}\nu^\alpha},
\end{aligned}
$$

(later in (23.122)–(23.128) this is done so).

[24] For a brief biographical sketch of Johann Friedrich Pfaff (1765–1825), see Fig. 17.46 in Vol. 2, p. 401 of this treatise on Fluid and Thermodynamics [22].

$$
\begin{aligned}
\mathrm{d}(\rho\hat{s}) = \Lambda^{\varepsilon}\Bigg\{ & \mathrm{d}(\rho\hat{\varepsilon}) \\
& + \sum_{\alpha=1}^{N-1}\left\{(\tilde{\Lambda}^{\nu^\alpha} - \tilde{\Lambda}^{\nu^N}) + (\hat{\rho}^\alpha \tilde{\boldsymbol{\Lambda}}^{\boldsymbol{v}^\alpha}\cdot\boldsymbol{v}^\alpha - \hat{\rho}^N\tilde{\boldsymbol{\Lambda}}^{\boldsymbol{v}^\alpha}\cdot\boldsymbol{v}^N)\right\}\mathrm{d}\nu^\alpha \\
& + \sum_{\alpha=1}^{N}\rho^\alpha\tilde{\boldsymbol{\Lambda}}^{\boldsymbol{v}^\alpha}\cdot\mathrm{d}\boldsymbol{v}^\alpha\Bigg\},
\end{aligned}
\tag{23.109}
$$

in which

$$
\tilde{\Lambda}^{\nu^\alpha} = \frac{\Lambda^{\nu^\alpha}}{\Lambda^{\varepsilon}}, \quad \tilde{\boldsymbol{\Lambda}}^{\boldsymbol{v}^\alpha} = \frac{\boldsymbol{\Lambda}^{\boldsymbol{v}^\alpha}}{\Lambda^{\varepsilon}} \quad (\alpha = 1, 2, \dots, N).
\tag{23.110}
$$

The total differential of the entropy is thus given by the total differential of the internal energy plus additional incremental "corrections" multiplied with Λ^{ε}. These additional terms are necessary to allow the differential $\mathrm{d}(\rho\hat{s})$ to become total. If one uses also the representation

$$
\begin{aligned}
\mathrm{d}(\rho\hat{\varepsilon}) &= \mathrm{d}(\rho\hat{\varepsilon}_I) + \mathrm{d}\left(\sum_{\alpha=1}^{N}\frac{\rho^\alpha}{2}\boldsymbol{u}^\alpha\cdot\boldsymbol{u}^\alpha\right) \\
&= \mathrm{d}(\rho\hat{\varepsilon}_I) + \sum_{\alpha=1}^{N}\left(\rho^\alpha\boldsymbol{u}^\alpha\cdot\mathrm{d}\boldsymbol{u}^\alpha + \tfrac{1}{2}\boldsymbol{u}^\alpha\cdot\boldsymbol{u}^\alpha\mathrm{d}\rho^\alpha\right) \\
&= \mathrm{d}(\rho\hat{\varepsilon}_I) + \sum_{\alpha=1}^{N}\rho^\alpha\boldsymbol{u}^\alpha\cdot\mathrm{d}\boldsymbol{v}^\alpha + \tfrac{1}{2}\sum_{\alpha=1}^{N}\hat{\rho}^\alpha\boldsymbol{u}^\alpha\cdot\boldsymbol{u}^\alpha\mathrm{d}\nu^\alpha,
\end{aligned}
\tag{23.111}
$$

then one may write (23.109) also in the form

$$
\begin{aligned}
\mathrm{d}(\rho\hat{s}) = \Lambda^{\varepsilon}\Bigg\{ & \mathrm{d}(\rho\hat{\varepsilon}_I) + \sum_{\alpha=1}^{N-1}\bigg\{(\tilde{\Lambda}^{\nu^\alpha} - \tilde{\Lambda}^{\nu^N}) + \hat{\rho}^\alpha\left(\tilde{\boldsymbol{\Lambda}}^{\boldsymbol{v}^\alpha}\cdot\boldsymbol{v}^\alpha + \tfrac{1}{2}\boldsymbol{u}^\alpha\cdot\boldsymbol{u}^\alpha\right) \\
& -\hat{\rho}^N(\tilde{\Lambda}^{\boldsymbol{v}^\alpha}\cdot\boldsymbol{v}^N)\bigg\}\mathrm{d}\nu^\alpha + \tfrac{1}{2}\boldsymbol{u}^N\cdot\boldsymbol{u}^N\mathrm{d}\nu^N \\
& + \sum_{\alpha=1}^{N}\rho^\alpha(\tilde{\boldsymbol{\Lambda}}^{\boldsymbol{v}^\alpha} + \boldsymbol{u}^\alpha)\cdot\mathrm{d}\boldsymbol{u}^\alpha\Bigg\}.
\end{aligned}
\tag{23.112}
$$

This form of the generalized Gibbs relation suggests that for reasons of simplicity one should take $\tilde{\boldsymbol{\Lambda}}^{\boldsymbol{v}^\alpha} = -\boldsymbol{u}^\alpha$, a choice which we shall make lateron. This choice is also supported by the identity (23.107)$_5$ which after summation over all constituents leads to the equation

$$\begin{aligned}\sum_{\alpha=1}^{N}\rho^\alpha \boldsymbol{\Lambda}^{\boldsymbol{v}^\alpha} &= \sum_{\alpha=1}^{N}\mathcal{P}_{\boldsymbol{v}^\alpha} = \sum_{\alpha=1}^{N}\left\{\frac{\partial(\rho\hat{s})}{\partial \boldsymbol{v}^\alpha} - \Lambda^\varepsilon\frac{\partial(\rho\hat{\varepsilon})}{\partial \boldsymbol{v}^\alpha}\right\}\\ &\overset{(23.95)_6}{=} \sum_{\alpha=1}^{N}\left(\frac{\partial(\rho\hat{s})}{\partial \boldsymbol{u}^\alpha} - \Lambda^\varepsilon\frac{\partial(\rho\hat{\varepsilon})}{\partial \boldsymbol{u}^\alpha}\right)\\ &\qquad - \underbrace{\left(\sum_{\alpha=1}^{N}\xi^\alpha\right)}_{=1}\sum_{\gamma=1}^{N}\left(\frac{\partial(\rho\hat{s})}{\partial \boldsymbol{u}^\gamma} - \Lambda^\varepsilon\frac{\partial(\rho\hat{\varepsilon})}{\partial \boldsymbol{u}^\gamma}\right) = \boldsymbol{0}\,, \end{aligned} \qquad (23.113)$$

which is automatically and identically satisfied if $\boldsymbol{\Lambda}^{\boldsymbol{v}^\alpha} = -\Lambda^\varepsilon \boldsymbol{u}^\alpha$ is chosen.

23.3.3 Some Properties of Differential (Pfaffian) Forms

The generalized GIBBS equation (23.108), (23.109) or (23.112) is mathematically of the form of a PFAFFIAN *differential equation*[25]

$$\mathrm{d}F = \sum_{i=1}^{N} X_i(x_j)\mathrm{d}x_i = \boldsymbol{X}(\boldsymbol{x})\cdot \mathrm{d}\boldsymbol{x}, \qquad (23.114)$$

in which the coefficient functions X_i depend continuously and differentiably upon the arguments x_j of the so-called phase space. If one writes Eq. (23.114) in its homogeneous form $\mathrm{d}F = 0$, then it is evident that the functions X_i define a normal field that stays perpendicularly on the hypersurface,[26] on which the value of F does not change. Solutions of the equation $\mathrm{d}F = 0$ are hypersurfaces on which the value of F equals a constant.

Locally, such a surface can always be determined; however, it may perhaps not possess the maximum possible dimension $(N-1)$; if it does, one says that the equation is *completely integrable*. Beginning at a particular point in phase space, it is in this case possible to construct a surface (this is the $(N-1)$ dimensional hypersurface) within which every arbitrary integration of the right-hand side of (23.114) furnishes the zero value. In this way, one succeeds to cover the entire phase space with "shells" on which $\mathrm{d}F = 0$, and which do not mutually intersect nor touch each other. It is now possible to assign to each "shell" a value—the so-called potential value—furthermore, one can see to it that an integration of the differential between the different shells always delivers the difference of these potential values, independent upon, where between these shells this integration is performed. This procedure

---

[25] For a brief biographical sketch of JOSIAH WILLARD GIBBS (1839–1903), see Fig. 17.12 in Vol. 2, p. 338 of this treatise on Fluid and Thermodynamics [22].

[26] In an n-dimensional space, manifolds with the dimension $n-1$ or smaller are called hypersurfaces.

accounts for the fact that the “distance” of two neighboring shells depends on the location within the phase space. However, once the shells are constructed and once adequate potential values are assigned to the shells, then these define uniquely a function, the *integrating factor*, with which the right-hand side of (23.114) must be multiplied to achieve the correct “distance” between the equipotential surfaces and to construct the desired connection between the differential $\mathrm{d}F$ and the potential, provided it is not already a priori given.

This construction indicates that there exists a certain arbitrariness in assigning potential values to the shells. However, except for this freedom, it is nevertheless possible in this way, to construct for each vector field $\boldsymbol{X}(\boldsymbol{x})$, that allows at every point in phase space to locally find an equipotential surface, an integrating function with the aid of which the vector field can be globally derived from a potential. The differential $\mathrm{d}F = \boldsymbol{X} \cdot \mathrm{d}\boldsymbol{x}$ becomes total or complete and, consequently, integrals between two fixed points in phase space assume a unique single value irrespective of the chosen path along which the integration is performed. In this sense, the PFAFFIAN form is then called *completely integrable*. The question, how a differential expression of the form (23.114) must look like that, one can decide whether it is completely integrable or may be put into completely integrable form by multiplying it with a factor, is the subject of the theory of differential forms and is answered by the *Theorem of* POINCARÉ and the *Condition of* FROBENIUS. In the language of analysis, these two statements read (see, e.g., BOWEN and WANG [8]):

Theorem of POINCARÉ[27] A PFAFFIAN form $\mathrm{d}F = \sum_{i=1}^{n} X_i(x_j)\mathrm{d}x_i$ *is total and can be derived from a potential if and only if the coefficient functions* X_i, *after a further differentiation, are crosswise equal, viz.,*

$$\frac{\partial X_i}{\partial x_j} = \frac{\partial X_j}{\partial x_i}, \quad (i, j = 1, 2, \dots, n). \tag{23.115}$$

■

The reader may recall from analysis of functions of several variables that for a differentiable function $F(x_i)$ the order of differentiation is irrelevant,

$$\frac{\partial^2 F}{\partial x_i \partial x_j} = \frac{\partial^2 F}{\partial x_j \partial x_i} \qquad (i, j = 1, 2, \dots, n). \tag{23.116}$$

Conversely, if a twice differentiable function is constructed from its first derivatives $\partial F/\partial x_i = X_i(x_i)$, it is only uniquely determined, if (23.116) is fulfilled i.e., if (23.115) holds.

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[27] For a brief biographical sketch of JULES HERI POINCARÉ (1854–1912), see **Fig. 23.3**.

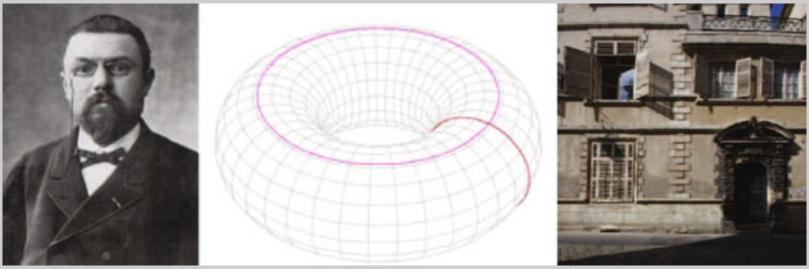


Fig. 23.3 Herni Poincaré (29 April 1854–17 July 1912) (left), Torus shown to explain the Poincaré conjecture: The two colored loops cannot be reduced to a single point (middle), House of birth, Hôtel de Martigny ©CCBY-SA30 (right)

Jules Henri Poincaré (April 29, 1854–July 17, 1912) was a French mathematician, theoretical physicist, engineer, and philosopher of science. He is often described as a polymath, and in mathematics as The Last Universalist since he excelled in all fields of the discipline as it existed during his lifetime.

In 1862, Henri entered the Lycée in Nancy (now renamed the Lycée Henri Poincaré in his honor, along with the University of Nancy. During this time, he proved to be one of the top students in every topic he studied. He won first prizes in the concours général, a competition between the top pupils from all the Lycées across France. He graduated from the Lycée in 1871 with a bachelor's degree in letters and sciences. Poincaré entered the École Polytechnique in 1873 and graduated in 1875. There, he studied mathematics as a student of Charles Hermite. From November 1875 to June 1878 he studied at the École des Mines, while continuing the study of mathematics in addition to the mining engineering syllabus, and received the degree of ordinary mining engineer in March 1879. At the same time, Poincaré was preparing for his Doctorate in Science in mathematics under the supervision of Charles Hermite. His doctoral thesis was in the field of differential equations. He graduated from the University of Paris in 1879.

As a mathematician and physicist, he made many original fundamental contributions to pure and applied mathematics, mathematical physics, and celestial mechanics. He was responsible for formulating the Poincaré conjecture, which was solved during 2002–2003 by Grigori Perelman. In his research on the three-body problem, Poincaré became the first person to discover a chaotic deterministic system which laid the foundations of modern chaos theory. He is also considered to be one of the founders of the field of topology.

Poincaré made clear the importance of paying attention to the invariance of laws of physics under different transformations, and was the first to present the Lorentz transformations in their modern symmetrical form. Poincaré discovered the remaining relativistic velocity transformations and recorded them in a letter to Dutch physicist Hendrik Lorentz (1853–1928) in 1905. Thus, he obtained perfect invariance of all of Maxwell's equations, an important step in the formulation of the theory of special relativity. In 1905, Poincaré first proposed gravitational waves emanating from a body and propagating at the speed of light as being required by the Lorentz transformations.

The text is based on `wikipedia`, where detailed descriptions on Poincaré's achievements can be found in English, French, German, and other languages.

If the prerequisites of the Theorem of POINCARÉ are not fulfilled for a differential form $\mathrm{d}F = X_i \mathrm{d}x_i$, one may ask whether such a form can be reached by multiplying this form by an integrating factor. The answer to this question may FROBENIUS be given by the

Condition of FROBENIUS[28] *Let* $\mathrm{d}F = X_i(x_j)\mathrm{d}x_i$ *be a differential form which does not satisfy the conditions* (23.115) *of the Theorem of* POINCARÉ. *Then this differential can be made a total or complete differential by multiplying it with an integrating factor, if and only if*

$$\sum_{i,j,k} \epsilon_{ijk} \left(\frac{\partial X_i}{\partial x_j} \right) X_k = 0, \tag{23.117}$$

holds, in which the sum is taken over all possible combinations of the indices i, j, k *and where* ϵ_{ijk} *denotes the completely antisymmetric tensor of rank three.* ■

Notice that in (23.117) the order of the indices (i, j, k) is irrelevant. Some details on the POINCARÉ theorem and the condition of FROBENIUS are given in Appendix 23.A to this chapter. In particular, with respect to the complexity of the results, the dimensionality of the phase space is significant: In two dimensions, a differential can always be made total, in higher dimensions this may or may not be possible.

23.3.4 The Differential of the Entropy

The ultimate goal in dealing with differential forms in the last section was to identify properties of the differential of the entropy as presented for instance in (23.108), (23.109) and (23.112). If one accounts in (23.108) for the fact that, because of the saturation condition, one has $\mathrm{d}\nu^N = -\sum_{\alpha=1}^{N-1} \mathrm{d}\nu^\alpha$, then (23.108) may equally be written as

$$\mathrm{d}(\rho s) = \Lambda^\varepsilon \mathrm{d}(\rho\varepsilon) + \sum_{\alpha=1}^{N} (\Lambda^{\nu^\alpha} \mathrm{d}\nu^\alpha + \boldsymbol{\Lambda}^{\boldsymbol{v}^\alpha} \cdot \mathrm{d}(\rho^\alpha \boldsymbol{v}^\alpha)), \tag{23.118}$$

where now $\nu^1, \ldots, \nu^N$ must be regarded as the independent variables and not $\nu^1, \ldots, \nu^{N-1}$. The differential for the entropy, (23.118) is very simple; it identifies on the right-hand side in a particularly transparent way the variables upon which the entropy depends. These are the specific energy $\rho\varepsilon$, the specific volume fractions ν^α (or the specific mass fractions $(\hat{\rho}^\alpha \nu^\alpha)$ which would only change the LAGRANGE multiplier $\Lambda^{\nu^\alpha} \to \Lambda^{\nu^\alpha}/\hat{\rho}^\alpha$), and the specific partial momenta, according to the balance laws of energy, masses and momenta. A dependence on the chosen constitutive

---

[28] For a brief biographical sketch of FERDINAND GEORG FROBENIUS (1849–1917), see Fig. 7.31 in Vol. 1, p. 417 of this treatise on Fluid and Thermodynamics [21].

variables only arises if the free energy is assumed as a function of such variables. One could for instance easily dispense with the dependence of the internal energy upon the empirical temperature and introduce the internal energy as a measure of the coldness of the body as it is essentially customary in the kinetic theory. On the other hand, the constitutive variables (e.g., (23.91)) enter the differential for the internal energy only implicitly. Consequently, the entropy depends in fact only upon the variables which are contained in the quantities ν^α, $(\rho^\alpha \boldsymbol{v}^\alpha)$ and $(\rho\varepsilon)$.

With regard to the LAGRANGE multipliers Λ^ε, $\boldsymbol{\Lambda}^{\boldsymbol{v}^\alpha}$ and Λ^{ν^α}, we may state that they cannot be constrained any further by only using the GIBBS relation, since according to it, they are anyhow only determined to within an unspecified function of the entropy. Proof of this is given in Appendix 23.B at the end of this chapter. A set of LAGRANGE multipliers, which makes the differential for the entropy complete, can always be multiplied with a suitable, but arbitrary differentiable function of the entropy without loosing the property of a complete differential. Thus, there follows the important conclusion: *With the tools of the integrability conditions it is not possible to reduce the constitutive dependence of the* LAGRANGE *multipliers without a simultaneous reduction of the constitutive dependence of the entropy and the internal energy* [2].

With the above considerations, it was not possible to decide whether the differential (23.118) is complete or not. Only when we succeed in demonstrating this property, the entropy will serve as a thermodynamic potential. And even, if this should be successful, a unique definition of the entropy is mathematically not possible, since there exists an arbitrary number of factors with which (23.118) may be multiplied, so that the resulting differential is complete. If one requires that the right-hand side of (23.118) with the given Λ^ε, Λ^{ν^α}, and $\boldsymbol{\Lambda}^{\boldsymbol{v}^\alpha}$ satisfies the FROBENIUS condition, then one guarantees thereby that the differential can be made complete at least after multiplication with another multiplier Λ^T. This last multiplication corresponds to the replacement $\Lambda^\varepsilon \leftrightarrow \Lambda^T\Lambda^\varepsilon$, $\Lambda^{\nu^\alpha} \leftrightarrow \Lambda^T\Lambda^{\nu^\alpha}$ and $\boldsymbol{\Lambda}^{\boldsymbol{v}^\alpha} \leftrightarrow \Lambda^T\boldsymbol{\Lambda}^{\boldsymbol{v}^\alpha}$, so that one now has

$$\mathrm{d}(\rho s) = \Lambda^T \left\{ \Lambda^\varepsilon \mathrm{d}(\rho\varepsilon) + \sum_{\alpha=1}^{N} \left(\Lambda^{\nu^\alpha}\mathrm{d}\nu^\alpha + \boldsymbol{\Lambda}^{\boldsymbol{v}^\alpha}\mathrm{d}(\rho\boldsymbol{v}^\alpha)\right) \right\}, \tag{23.119}$$

in other words, Λ^T could simply be absorbed into the other LAGRANGE multipliers. The FROBENIUS condition (23.117) now requires for instance that the $\Lambda' s$ must satisfy the identities

$$\begin{aligned} &\left(\frac{\partial\Lambda^\varepsilon}{\partial\nu^\alpha} - \frac{\partial\Lambda^{\nu^\alpha}}{\partial(\rho\varepsilon)}\right)(\boldsymbol{\Lambda}^{\boldsymbol{v}^\beta})_i + \left(\frac{\partial\Lambda^{\nu^\alpha}}{\partial(\rho\nu^\beta)_i} - \frac{\partial(\boldsymbol{\Lambda}^{\boldsymbol{v}^\beta})_i}{\partial\nu^\alpha}\right)\Lambda^\varepsilon \\ &+ \left(\frac{\partial(\boldsymbol{\Lambda}^{\boldsymbol{v}^\beta})_i}{\partial(\rho\varepsilon)} - \frac{\partial\Lambda^\varepsilon}{\partial(\rho\nu^\beta)_i}\right)\Lambda^{\nu^\alpha} = 0. \end{aligned} \tag{23.120}$$

This is only one of many such relations, which can be obtained by varying α, $\beta(= 1, 2, \ldots, N)$ and $i(= 1, 2, 3)$. Once all equations of the form (23.120) are satisfied, the POINCARÉ theorem must still be fulfilled; this yields equations of the form

$$\frac{\partial(\Lambda^T \Lambda^\varepsilon)}{\partial \nu^\alpha} = \frac{\partial(\Lambda^T \Lambda^{\nu^\alpha})}{\partial(\rho\varepsilon)} \tag{23.121}$$

or

$$\Lambda^T \left(\frac{\partial \Lambda^\varepsilon}{\partial \nu^\alpha} - \frac{\partial(\Lambda^{\nu^\alpha})}{\partial(\rho\varepsilon)} \right) = \Lambda^{\nu^\alpha} \frac{\partial \Lambda^T}{\partial(\rho\varepsilon)} - \Lambda^\varepsilon \frac{\partial \Lambda^T}{\partial \nu^\alpha}, \quad \text{etc.}$$

All these equations can easily be satisfied, namely by choosing constant Λ's. Despite its triviality, this result is helpful, because it demonstrates the existence of *one* single potential (and therefore many others); else, it does not have any physical significance.

The above analysis shows that *pure mathematical considerations have not led to any constraints for the* LAGRANGE *parameters. To determine or to constrain their dependence one must rely upon assumptions and physical principles*. Such rules may be material objectivity, considerations of symmetry and other postulates as, e.g., the expression of extremity of the entropy production.

In the above analysis, it should have become apparent that the functional dependence of the LAGRANGE multipliers is dictated by that of the internal energy, so that functional restrictions of the Λ's can be obtained by restricting the functional dependence of the internal energy and vice versa. If one starts with the independent constitutive variables (23.91) and writes $\rho\varepsilon = \rho\hat{\varepsilon}(\boldsymbol{\Xi})$, then the necessary requirements are obtained by satisfying the Theorem of POINCARÉ; the identities which follow from (23.107)$_{1-6}$ after simple but somewhat lengthy manipulations are

$$\frac{\partial \mathcal{P}_\theta}{\partial \nu^\alpha} \equiv \frac{\partial \mathcal{P}_{\nu^\alpha}}{\partial \theta} - \frac{\partial}{\partial \theta} \left\{ (\Lambda^{\nu^\alpha} - \Lambda^{\nu^N}) + (\hat{\rho}^\alpha \boldsymbol{\Lambda}^{\boldsymbol{v}^\alpha} \cdot \boldsymbol{v}^\alpha - \hat{\rho}^N \boldsymbol{\Lambda}^{\boldsymbol{v}^N} \cdot \boldsymbol{v}^N) \right\}, \tag{23.122}$$

$$\frac{\partial \mathcal{P}_\theta}{\partial x_i} \equiv \frac{\partial \mathcal{P}_{x_i}}{\partial \theta}, \qquad \frac{\partial \mathcal{P}_{x_i}}{\partial x_j} \equiv \frac{\partial \mathcal{P}_{x_j}}{\partial x_i}, \tag{23.123}$$

$$\frac{\partial \mathcal{P}_{x_i}}{\partial \boldsymbol{v}^\beta} \equiv \frac{\partial \mathcal{P}_{\boldsymbol{v}^\beta}}{\partial x_i} - \frac{\partial}{\partial x_i} (\rho^\beta \boldsymbol{\Lambda}^{\boldsymbol{v}^\beta}), \tag{23.124}$$

$$\begin{aligned} &\frac{\partial \mathcal{P}_{\nu^\alpha}}{\partial x_i} - \frac{\partial}{\partial x_i} \left\{ \left(\Lambda^{\nu^\alpha} - \Lambda^{\nu^N} \right) + \left(\hat{\rho}^\alpha \boldsymbol{\Lambda}^{\boldsymbol{v}^\alpha} \cdot \boldsymbol{v}^\alpha - \Lambda^{\nu^N} \boldsymbol{\Lambda}^{\boldsymbol{v}^N} \cdot \boldsymbol{v}^N \right) \right\} \\ &\quad \equiv \frac{\partial \mathcal{P}_{x_i}}{\partial \nu^\alpha}, \end{aligned} \tag{23.125}$$

$$\frac{\partial \mathcal{P}_\theta}{\partial \boldsymbol{v}^\beta} \equiv \frac{\partial \mathcal{P}_{\boldsymbol{v}^\beta}}{\partial \theta} - \rho^\beta \frac{\partial \boldsymbol{\Lambda}^{\boldsymbol{v}^\beta}}{\partial \theta} \tag{23.126}$$

$$\begin{aligned} &\frac{\partial \mathcal{P}_{\nu^\alpha}}{\partial \boldsymbol{v}^\beta} - \frac{\partial}{\partial \boldsymbol{v}^\beta} \Big((\Lambda^{\nu^\alpha} - \Lambda^{\nu^N}) + (\hat{\rho}^\alpha \boldsymbol{\Lambda}^{\boldsymbol{v}^\alpha} \cdot \boldsymbol{v}^\alpha - \hat{\rho}^N \boldsymbol{\Lambda}^{\boldsymbol{v}^N} \cdot \boldsymbol{u}^N) \Big) \\ &\quad \equiv \frac{\partial \mathcal{P}_{\boldsymbol{v}^\beta}}{\partial \nu^\beta} - \frac{\partial}{\partial \nu^\alpha} (\rho^\beta \boldsymbol{\Lambda}^{\boldsymbol{v}^\beta}) \end{aligned} \tag{23.127}$$

$$
\begin{aligned}
&\frac{\partial \mathcal{P}_{\nu^\alpha}}{\partial \nu^\gamma} - \frac{\partial}{\partial \nu^\gamma}\Big((\Lambda^{\nu^\alpha} - \Lambda^{\nu^N}) + (\hat{\rho}^\alpha \boldsymbol{\Lambda}^{\boldsymbol{v}^\alpha} \cdot \boldsymbol{v}^\alpha - \hat{\rho}^N \boldsymbol{\Lambda}^{\boldsymbol{v}^N} \cdot \boldsymbol{v}^N) \Big) \\
&\quad \equiv \frac{\partial \mathcal{P}_{\nu^\gamma}}{\partial \nu^\alpha} - \frac{\partial}{\partial \nu^\alpha}\Big((\Lambda^{\nu^\gamma} - \Lambda^{\nu^N}) + (\hat{\rho}^\gamma \boldsymbol{\Lambda}^{\boldsymbol{v}^\gamma} \cdot \boldsymbol{v}^\gamma - \hat{\rho}^N \boldsymbol{\Lambda}^{\boldsymbol{v}^N} \cdot \boldsymbol{v}^N) \Big),
\end{aligned}
\tag{23.128}
$$

$$
\frac{\partial \mathcal{P}_{\boldsymbol{v}^\beta}}{\partial \boldsymbol{v}^\delta} - \frac{\partial}{\partial \boldsymbol{v}^\delta}\Big(\rho^\beta \boldsymbol{\Lambda}^{\boldsymbol{v}^\beta} \Big) \equiv \frac{\partial \mathcal{P}_{\boldsymbol{v}^\delta}}{\partial \boldsymbol{v}^\beta} - \frac{\partial}{\partial \boldsymbol{v}^\beta}\Big(\rho^\delta \boldsymbol{\Lambda}^{\boldsymbol{v}}_\delta \Big),
\tag{23.129}
$$

in which $(x_i, x_j) \in \left\{ \operatorname{grad}\theta, \operatorname{grad}\nu^\alpha, \operatorname{grad}\boldsymbol{v}^\beta \right\}$ and $(\alpha, \gamma) = 1, 2, \dots, N-1$ and $(\beta, \delta) = 1, 2, \dots, N$. These identities pose a considerable number of conditions which constrain the functional dependence of the free energy and the LAGRANGE multipliers. The following propositions are helpful.

Proposition 23.1 *Assume—in explicit violation of the rule of equipresence—that the internal energy does not depend on the variables* $\operatorname{grad}\theta$, $\operatorname{grad}\nu^\alpha$ *and* $\operatorname{grad}\boldsymbol{v}^\beta$, *viz.,*

$$
\rho\varepsilon = \rho\hat{\varepsilon}(\theta, \nu^\alpha, \boldsymbol{v}^\beta) \ ;
\tag{23.130}
$$

then the LAGRANGE *multipliers take the form*

$$
\begin{aligned}
\Lambda^\varepsilon &= \hat{\Lambda}^\varepsilon(\theta, \nu^\alpha, \boldsymbol{v}^\beta), \\
\lambda^{\nu^\alpha} &:= (\Lambda^{\nu^\alpha} - \Lambda^{\nu^N}) = \hat{\lambda}^{\nu^\alpha}(\theta, \nu^\alpha, \boldsymbol{v}^\beta), \\
\boldsymbol{\Lambda}^{\boldsymbol{v}^\beta} &= \hat{\boldsymbol{\Lambda}}^{\boldsymbol{v}^\beta}(\theta, \nu^\alpha, \boldsymbol{v}^\beta).
\end{aligned}
\tag{23.131}
$$

In other words, if the internal energy does not depend on $\operatorname{grad}\theta$, $\operatorname{grad}\nu^\alpha$ *and* $\operatorname{grad}\boldsymbol{v}^\beta$ *then the* LAGRANGE *multipliers can neither be functions of these variables.* ■

Proposition 23.2 *Conversely, if* Λ^ε *does not depend on* $\operatorname{grad}\theta$, $\operatorname{grad}\nu^\alpha$ *and* $\operatorname{grad}\boldsymbol{v}^\beta$ *then* $\rho\varepsilon$, $\boldsymbol{\Lambda}^{\boldsymbol{v}^\beta}$ *and* λ^{ν^α} *can neither depend on them.*[29] ■

Proposition 23.3 *If the internal energy depends on* $\operatorname{grad}\theta$, $\operatorname{grad}\nu^\alpha$ *and* $\operatorname{grad}\boldsymbol{v}^\beta$, *then also* Λ^ε *must depend on these variables and vice versa.* ■

Proof We shall only present a sketch of a proof, which reads as follows: With the definitions $(23.100)_1$ of $\mathcal{P}_{x_i}$ one may deduce from $(23.123)_1$, that

$$
\frac{\partial \hat{\Lambda}^\varepsilon}{\partial \theta}\frac{\partial(\rho\hat{\varepsilon})}{\partial x_i} - \frac{\partial \hat{\Lambda}^\varepsilon}{\partial x_i}\frac{\partial(\rho\hat{\varepsilon})}{\partial \theta} \equiv 0.
\tag{23.132}
$$

---

[29] Of the LAGRANGE multipliers Λ^{ν^α}, only the difference $\lambda^{\nu^\alpha} := \Lambda^{\nu^\alpha} - \lambda^{\nu^N}$ can be determined. λ^{ν^N} remains undetermined and forms an independent variable of the theory.

Provided $\hat{\Lambda}^\varepsilon$ and $\rho\hat{\varepsilon}$ are nontrivial functions[30] of θ, this necessarily leads to the statement

$$\frac{\partial(\rho\hat{\varepsilon})}{\partial x_i} = 0 \qquad \Leftrightarrow \qquad \frac{\partial \hat{\Lambda}^\varepsilon}{\partial x_i} = 0. \tag{23.133}$$

Therefore, the assumption that $\rho\hat{\varepsilon}$ is not a function of x_i necessarily leads to the result that $\hat{\Lambda}^\varepsilon$ can neither depend on x_i and vice versa. With (23.132) and (23.133) the identities (23.123)$_2$ are now trivially satisfied, and (23.124) takes the form

$$\frac{\partial}{\partial x_i}\left(\rho^\beta \hat{\boldsymbol{\Lambda}}^{\boldsymbol{v}^\beta}\right) = \mathbf{0}. \tag{23.134}$$

Hence, neither $\hat{\boldsymbol{\Lambda}}^{\boldsymbol{v}^\beta}$ can be functions of x_i. Substitution of the results (23.132) and (23.133) in (23.125) then yields

$$\frac{\partial}{\partial x_i}\left(\hat{\lambda}^{\nu^\alpha}\right) = 0, \tag{23.135}$$

which completes the proof of Proposition 23.1.

To prove Proposition 23.2, one starts from (23.132) and assumes that $\hat{\Lambda}^\varepsilon$ is independent of x_i and then deduces from (23.132) that $\rho\hat{\varepsilon}$ can neither depend on x_i, which then leads to statement (23.134). Finally, Proposition 23.3 is clear, since no simplification emerges from (23.132) if either a dependence on x_i is assumed for the internal energy or the LAGRANGE multiplier Λ^ε. ■

It is clear that one would wish $\hat{\Lambda}^\varepsilon$ to be a function of the empirical temperature alone whose inverse may be identifiable with the absolute temperature. This interpretation is supported if the HELMHOLTZ free energy

$$\psi := \varepsilon - \frac{s}{\Lambda^\varepsilon} \tag{23.136}$$

is introduced, and this energy is split according to

$$\rho\psi = \rho\psi_I + \frac{1}{2}\sum_{\alpha=1}^{N} \rho^\alpha \boldsymbol{u}^\alpha \cdot \boldsymbol{u}^\alpha \tag{23.137}$$

into an inner contribution ψ_I, the *inner* HELMHOLTZ *free energy*, and a diffusive part. With (23.136) and (23.137), the identities (23.107)$_{3,5}$ become

---

[30] This is a very natural assumption, because earlier experience has shown us that $1/\Lambda^\varepsilon$ has the meaning of absolute temperature.

$$-\frac{\partial\rho\psi_I}{\partial\boldsymbol{v}^\alpha} - \frac{1}{(\Lambda^\varepsilon)^2}\frac{\partial\Lambda^\varepsilon}{\partial\boldsymbol{v}^\alpha}\rho s = -\rho^\alpha\left(\frac{\boldsymbol{\Lambda}^{\boldsymbol{v}^\alpha}}{\Lambda^\varepsilon} + \boldsymbol{u}^\alpha\right), \tag{23.138}$$

$$\begin{aligned}
&-\frac{\partial\rho\psi_I}{\partial\nu^\alpha} + \frac{\partial\rho\psi_I}{\partial\nu^N} + \frac{1}{(\Lambda^\varepsilon)^2}\left(\frac{\partial\Lambda^\varepsilon}{\partial\nu^\alpha} - \frac{\partial\Lambda^\varepsilon}{\partial\nu^N}\right)\rho s \\
&\qquad = \frac{1}{\Lambda^\varepsilon}\left\{\lambda^{\nu^\alpha} + \left(\hat\rho^\alpha\boldsymbol{\Lambda}^{\boldsymbol{v}^\alpha}\cdot\boldsymbol{v}^\alpha - \hat\rho^N\boldsymbol{\Lambda}^{\boldsymbol{v}^N}\cdot\boldsymbol{v}^N\right)\right\},
\end{aligned} \tag{23.139}$$

in the derivation of which also (23.95)$_6$ was used. These formulas are massively simplified, if one requests that Λ^ε is merely a function of the temperature,

$$\Lambda^\varepsilon = \Lambda^\varepsilon(\theta). \tag{23.140}$$

If, furthermore, it is also requested that

$$\boldsymbol{\Lambda}^{\boldsymbol{v}^\alpha} = -\Lambda^\varepsilon(\theta)\boldsymbol{u}^\alpha, \tag{23.141}$$

one recognizes that the inner part ψ_I of the HELMHOLTZ free energy cannot be a function of $\boldsymbol{v}^\alpha$ ($\alpha = 1, 2, \dots, N$) as deduced from (23.138). Finally, it follows with (23.140) and (23.141) from (23.139), that the LAGRANGE multipliers λ^{ν^α} are given by

$$\begin{aligned}
\lambda^{\nu^\alpha} \overset{(23.131)}{:=} \Lambda^{\nu^\alpha} - \Lambda^{\nu^N} = -\Lambda^\varepsilon(\theta)\Big\{&\left(\frac{\partial\rho\psi_I}{\partial\nu^\alpha} - \frac{\partial\rho\psi_I}{\partial\nu^N}\right) \\
&+ \left(\hat\rho^\alpha\boldsymbol{u}^\alpha\cdot\boldsymbol{v}^\alpha - \hat\rho^N\boldsymbol{u}^N\cdot\boldsymbol{v}^N\right)\Big\} \quad (\alpha = 1, 2, \dots, N-1).
\end{aligned} \tag{23.142}$$

With this result and with $\Lambda^\varepsilon = \hat\Lambda^\varepsilon(\theta)$, all LAGRANGE multipliers are determined except λ^{ν^N}. Conversely, with the postulated or established results (23.140)–(23.142), it is straightforward to demonstrate that the remaining integrability conditions (23.122)–(23.129) are identically satisfied.

As last assumption we will now relate $\Lambda^\varepsilon(\theta)$ to the absolute temperature and identify it with the KELVIN temperature

$$\Lambda^\varepsilon(\theta) = \frac{1}{T}. \tag{23.143}$$

With this choice, one obtains from (23.107)$_1$ and (23.136)

$$s = -\frac{\partial\psi_I}{\partial T}, \quad \rightarrow \quad s = \hat s(T, \nu^\alpha), \tag{23.144}$$

whence the classical relation, which one would have expected.

The above analysis shows that all restrictions on the constitutive relations of ε, s, and ψ are at last tied to two basic assumptions, *first the hypothesis that the* LAGRANGE *multiplier for the internal energy, Λ^ε, is only a function of the empirical temperature* *and second, that the inner part of the* HELMHOLTZ *free energy* ψ_I *is not a function of the velocities*. With these two assumptions, all LAGRANGEan multipliers could be determined with the exception of Λ^{ν^N}, which will play the role of an independent variable and which represents the constraint variable for the saturation condition. Since, moreover, we succeeded with the help of (23.140)–(23.142) to satisfy all conditions of the POINCARÉ theorem, the differential of the entropy, as given by the GIBBS relation is complete and the entropy therefore a thermodynamic potential. Alternatively, one also knows (see Appendix 23.B) that one may multiply the right-hand side of the GIBBS relation with arbitrary differentiable function $\Lambda^T(\rho s)$ and that this new differential may also represent a possible entropy function. *We now* wish to *declare that only those functions be used as thermodynamic entropy function which depend merely upon the empirical temperature*. This corresponds to the selection of the LAGRANGE multiplier $\Lambda^\varepsilon(\theta)$, its identification with the coldness function and its inverse with the absolute temperature according to (23.143).

Of the identities (23.107) there still remain the identities $(23.107)_{7-9}$, which concern the entropy flux. If one introduces the extra entropy flux vector according to

$$\boldsymbol{k} := \Lambda^\varepsilon \boldsymbol{q} - \sum_{\alpha=1}^{N} \boldsymbol{\Lambda}^{\boldsymbol{v}^\alpha} \boldsymbol{t}^\alpha - \phi^{\rho s}, \tag{23.145}$$

then the identities $(23.107)_{7-9}$ take the forms

$$\begin{aligned} &\left(\frac{\partial \boldsymbol{k}}{\partial \mathrm{grad}\, T}\right)_{\mathrm{sym}} = \boldsymbol{0}, \\ &\left(\frac{\partial \boldsymbol{k}}{\partial \mathrm{grad}\, \nu^\alpha} - \frac{\partial \boldsymbol{k}}{\partial \mathrm{grad}\, \nu^N}\right)_{\mathrm{sym}} = \boldsymbol{0}, \\ &\left(\frac{\partial \boldsymbol{k}}{\partial \mathrm{grad}\, \boldsymbol{v}^\beta}\right)_{\mathrm{sym}(1,3)} = \boldsymbol{0}, \end{aligned} \tag{23.146}$$

in which use has been made of (23.140). In simpler theories, one can start from isotropic representations for $\boldsymbol{q}$ and $\phi^{\rho s}$ and *prove* with such representations from $(23.107)_{7-9}$ that Λ^ε can only be a function of θ. The identities $(23.107)_{7-9}$ therefore provide for such materials restrictions to the LAGRANGE multiplier Λ^ε, which were introduced above as an assumption. For the present constitutive class, the corresponding analysis is so complex that we were unable to deduce the result $\Lambda^\varepsilon = \hat{\Lambda}^\varepsilon(\theta)$. If this is introduced now as an assumption, there still remain the identities (23.146) to be fulfilled, which could identically be satisfied by $\boldsymbol{k} = \boldsymbol{0}$ which, however, we do not wish to select for reasons that will become apparent below.

Of inequality (23.103) the upper block is now identically zero, when all conditions derived above are fulfilled. There still remains the lower block, which comprises what commonly is called the *residual entropy inequality*. If the definitions (23.100), (23.102), (23.145) and the results (23.107) are substituted and if $\boldsymbol{v}^\alpha$ is replaced by $\boldsymbol{v} + \boldsymbol{u}^\alpha$ wherever possible and Λ^ε is replaced by $1/T$, then this residual entropy inequality takes the following form:

$$
\begin{aligned}
\pi^s = & -\left\{\frac{\partial \boldsymbol{k}}{\partial T}+\frac{1}{T^2}\left(\boldsymbol{q}+\sum_{\alpha=1}^{N}\boldsymbol{u}^\alpha\cdot\boldsymbol{t}^\alpha\right)\right\}\cdot\operatorname{grad}T \\
& +\sum_{\alpha=1}^{N-1}\Bigg\{\left(\Lambda^{\nu^N}\boldsymbol{u}^N-\Lambda^{\nu^\alpha}\boldsymbol{u}^\alpha\right)+\frac{1}{T}\Big(\hat{\rho}^\alpha\left(\boldsymbol{u}^\alpha\cdot\boldsymbol{v}^\alpha\right)\boldsymbol{u}^\alpha \\
& -\hat{\rho}_N\left(\boldsymbol{u}^N\cdot\boldsymbol{v}^N\right)\boldsymbol{u}^N\Big)-\left(\frac{\partial \boldsymbol{k}}{\partial \nu^\alpha}-\frac{\partial \boldsymbol{k}}{\partial \nu^N}\right) \\
& +\frac{1}{\rho T}\left(\hat{\rho}^N\boldsymbol{u}^N-\hat{\rho}^\alpha\boldsymbol{u}^\alpha\right)\left(\sum_{\beta=1}^{N}\rho^\beta\left(\boldsymbol{u}^\beta\otimes\boldsymbol{u}^\beta\right)+\rho\psi\mathbf{1}\right)\Bigg\}\cdot\operatorname{grad}\nu^\alpha \\
& +\sum_{\alpha=1}^{N}\Bigg\{-\frac{\partial \boldsymbol{k}}{\partial \boldsymbol{v}^\alpha}+\frac{1}{T}\boldsymbol{t}^\alpha+\frac{\rho^\alpha}{T}\left(\boldsymbol{u}^\alpha\otimes\boldsymbol{v}^\alpha-\boldsymbol{v}\otimes\boldsymbol{u}^\alpha\right) \\
& -\left(\frac{\rho^\alpha}{T}\psi+\Lambda^{\nu^\alpha}\nu^\alpha-\frac{\rho^\alpha}{T}\left(\boldsymbol{u}^\alpha\cdot\boldsymbol{v}^\alpha\right)\right)\mathbf{1} \\
& -\frac{\rho^\alpha}{T}\sum_{\beta=1}^{N}\rho^\beta\left(\boldsymbol{u}^\beta\otimes\boldsymbol{u}^\beta\right)\Bigg\}\cdot\operatorname{grad}\boldsymbol{v}^\alpha \\
& +\sum_{\alpha=1}^{N}\left\{\Lambda^{\nu^\alpha}\mathfrak{n}^\alpha-\frac{1}{T}\boldsymbol{u}^\alpha\cdot\mathfrak{m}^\alpha\right\}\geqslant 0.
\end{aligned}
\tag{23.147}
$$

This formidably looking inequality must be identically satisfied for all constitutive equations for $\boldsymbol{k}$, $\boldsymbol{q}$, $\mathfrak{m}^\alpha$, $\boldsymbol{t}^\alpha$, and ψ, and thus constrains them, but because of its complexity this must be done for a restricted class of processes only, namely those describing *thermodynamic equilibrium* and processes in its neighborhood. This will be our next task.

23.3.5 Thermodynamic Equilibrium

Thermodynamic equilibrium is a process for which the entropy production is a minimum, namely zero. According to (23.147) this is the case, if the constituent velocities $\boldsymbol{v}^\alpha$ (or, equivalently, $\boldsymbol{v}$ and all $\boldsymbol{u}^\alpha$), their gradients, grad $\boldsymbol{v}^\alpha$, the temperature gradient grad T, and the volume exchange terms $\mathfrak{n}^\alpha$ vanish identically for all $\alpha = 1, \ldots, N$. Under such conditions, of all the terms in the inequality (23.147) only the derivatives of $\boldsymbol{k}$ with respect to ν^α remain, $(\partial\boldsymbol{k}/\partial\nu^\alpha - \partial\boldsymbol{k}/\partial\nu^N)$. To assure that these terms also vanish in equilibrium, the functional form of $\boldsymbol{k}$ must be determined. It can be shown that close to equilibrium,

$$\boldsymbol{k} = \sum_{\alpha=1}^{N} \left(\frac{\partial \boldsymbol{k}}{\partial \boldsymbol{v}^\alpha}\right)^{\text{equil}} \boldsymbol{v}^\alpha = \sum_{\alpha=1}^{N} \left(\frac{\partial \boldsymbol{k}}{\partial \boldsymbol{u}^\alpha}\right)^{\text{equil}} \boldsymbol{u}^\alpha, \tag{23.148}$$

which indeed vanishes in equilibrium. The proof of (23.148) is nontrivial and relatively lengthy and makes use of the identities (23.146). It may also be mentioned that the first of (23.148) is the result of this proof when the rule of material objectivity is not enforced; the second is its objective counterpart. This proof follows an argument by GURTIN [16] as presented by BAUER [2] and is also given in [20]. It guaranties that $(\partial \boldsymbol{k}/\partial \nu^\alpha)^{\text{equil}} = \mathbf{0}$ for all $\alpha = 1, \ldots, N$.[31]

The left-hand side of (23.147) represents the entropy production π^s, and we just explained above that π^s as a function of the nonequilibrium variables grad T, $\boldsymbol{v}^\alpha$ and grad $\boldsymbol{v}^\alpha$ assumes its minimum in equilibrium, $(\pi^s)^{\text{equil}} = 0$. Since π^s is a continuously differentiable function of these variables, of necessity then

$$\begin{aligned} &\left(\frac{\partial \pi^s}{\partial \mathfrak{X}}\right)^{\text{equil}} = \mathbf{0}, \quad \mathfrak{X} = \{\operatorname{grad} T, \boldsymbol{v}^\alpha, \operatorname{grad} \boldsymbol{v}^\alpha\}, \\ &\left(\frac{\partial^2 \pi^s}{\partial \mathfrak{X}\, \partial \mathfrak{X}}\right)^{\text{equil}}, \quad \text{is positive semidefinite.} \end{aligned} \tag{23.149}$$

We shall first draw the inferences implied by the first of (23.149).

If one evaluates $\partial \pi^s / \partial \operatorname{grad} T$ in thermodynamic equilibrium and sets the result equal to zero one obtains

$$\left\{\frac{\partial \boldsymbol{k}}{\partial T} + \frac{1}{T^2}\left(\boldsymbol{q} + \sum_{\alpha=1}^{N} \underbrace{\boldsymbol{u}^\alpha \cdot \boldsymbol{t}^\alpha}_{=0}\right)\right\}^{\text{equil}} - \frac{\partial}{\partial \operatorname{grad} T}\left(\sum_{\alpha=1}^{N} \varLambda^{\nu^\alpha} \mathfrak{n}^\alpha\right)^{\text{equil}} = \mathbf{0}. \tag{23.150}$$

Now, in view of (23.148),

$$\left(\frac{\partial \boldsymbol{k}}{\partial T}\right)^{\text{equil}} = \left(\sum_{\alpha=1}^{N} \frac{\partial^2 \boldsymbol{k}}{\partial T\, \partial \boldsymbol{u}^\alpha} \boldsymbol{u}^\alpha\right)^{\text{equil}} = \mathbf{0}.$$

Moreover, since, according to (23.131), $\varLambda^{\nu^\alpha}$ is not a function of grad T, $\varLambda^{\nu^\alpha}$ can be pulled out of the differentiation sign in (23.150), which, thus, reduces to

$$\boldsymbol{q}^{\text{equil}} = T^2 \sum_{\alpha=1}^{N} \varLambda^{\nu^\alpha} \underline{\left(\frac{\partial \mathfrak{n}^\alpha}{\partial \operatorname{grad} T}\right)^{\text{equil}}} = \mathbf{0}. \tag{23.151}$$

---

[31] The reader may recall (23.88), which explains the peculiarities when differentiating functions (here $\boldsymbol{k}$) of $\nu^1, \ldots, \nu^{N-1}$, and $\nu^1, \ldots, \nu^N$, respectively.

To prove this, consider the volume exchange terms more closely. It will be assumed that the thermodynamic equilibrium under consideration is distant from any phase (change) equilibrium of the constituents. A small deviation of the temperature from this equilibrium will then not cause melting or evaporation processes of any constituent.[32] If such a situation prevails all derivatives of $\mathfrak{n}^\alpha$ as well as $\mathfrak{n}^\alpha$ itself must vanish throughout the entire domain where the thermodynamic equilibrium exists. This is obvious, since $\mathfrak{n}^\alpha$ must vanish according to (23.85) everywhere in the domain; so it is the zero function over a region with nonvanishing measure, implying that also its derivatives are zero. Thus we have in particular

$$\left(\frac{\partial \mathfrak{n}^\alpha}{\partial \text{grad}\, T}\right)^{\text{equil}} = \mathbf{0} \qquad \text{for } \alpha = 1, \dots, N. \tag{23.152}$$

The mixture heat flux thus vanishes in thermodynamic equilibrium. BAUER [2] proves this to hold true also in the case when phase changes do occur.

Next we evaluate the inferences that are implied by $\partial \pi^s / \partial \boldsymbol{v}^\alpha = \mathbf{0}$. The reader may deduce the validity of the following $N-1$ relations for the equilibrium interaction forces:

$$\begin{aligned} (\mathfrak{m}^\alpha)^{\text{equil}} = \sum_{\beta=1}^{N-1} \Bigg\{ & T\Lambda^{\nu^N}\left(\delta_{N\alpha} - \xi^\alpha\right) - T\Lambda^{\nu^\beta}\left(\delta_{\alpha\beta} - \xi^\alpha\right) \\ & - T\left(\frac{\partial}{\partial \nu^\beta} - \frac{\partial}{\partial \nu^N}\right)\left(\frac{\partial \boldsymbol{k}}{\partial \boldsymbol{v}^\alpha}\right)^{\text{equil}} \\ & - \psi \mathbf{1}\left[\hat{\rho}^\beta\left(\delta_{\beta\alpha} - \xi^\alpha\right) - \hat{\rho}_N\left(\delta_{N\alpha} - \xi^\alpha\right)\right] \Bigg\} \text{grad}\, \nu^\beta \\ & + T\sum_{\beta=1}^{N} \Lambda^{\nu^\beta} \underbrace{\left(\frac{\partial \mathfrak{n}^\beta}{\partial \boldsymbol{v}^\alpha}\right)^{\text{equil}}}_{\mathbf{0}}, \end{aligned} \tag{23.153}$$

in the derivation of which $\delta_{\alpha\beta}$, $\delta_{N\alpha}$ are delta functions; moreover, excessive use of $(23.95)_4$ was made, and where $(\partial \mathfrak{n}^\beta / \partial \boldsymbol{v}^\alpha)^{\text{equil}}$ vanishes for the same reason as (23.152) was found to be true. The relations (23.153) hold for the $N-1$ first interaction forces $\mathfrak{m}^\alpha$; $\mathfrak{m}^N$ is obtained via the condition $\sum_{\alpha=1}^{N} \mathfrak{m}^\alpha = \mathbf{0}$.

It is worth pointing out that the above expressions involve a term that depends on the extra entropy flux $\boldsymbol{k}$. It will be interesting to see how this term combines with the divergence of the stress term div $\boldsymbol{t}^\alpha$.

If the term $(\partial \pi^s / \partial \text{grad}\, \boldsymbol{v}^\alpha)^{\text{equil}} = \mathbf{0}$ is evaluated the partial equilibrium stress is obtained,

---

[32] This, for instance, excludes the situation of simultaneous existence of ice and water and mass exchanges between these two constituents as it occurs, e.g., in temperate ice. Solidification of rock or the mushy behavior of the interior core of the Earth would also be examples where such phase changes occur. This more general case is treated by BAUER [2].

$$
\begin{aligned}
(\boldsymbol{t}^{\alpha})^{\text{equil}} &= \left(\rho^{\alpha}\psi + T\Lambda^{\nu^{\alpha}}\nu^{\alpha}\right)\mathbf{1} \\
&\quad + \sum_{\beta=1}^{N-1}\left\{T\left(\frac{\partial}{\partial\nu^{\beta}} - \frac{\partial}{\partial\nu^{N}}\right)\left(\frac{\partial\boldsymbol{k}}{\partial\operatorname{grad}\boldsymbol{v}^{\alpha}}\right)^{\text{equil}}\right\}\operatorname{grad}\nu^{\beta} \\
&\quad + T\left(\frac{\partial\boldsymbol{k}}{\partial\boldsymbol{v}^{\alpha}}\right)^{\text{equil}} - T\sum_{\beta=1}^{N}\Lambda^{\nu^{\beta}}\underbrace{\left(\frac{\partial\mathfrak{n}^{\beta}}{\partial\operatorname{grad}\boldsymbol{v}^{\alpha}}\right)^{\text{equil}}}_{\mathbf{0}},
\end{aligned}
\qquad (23.154)
$$

where we have not yet accounted for the fact that the partial stress $\boldsymbol{t}^{\alpha}$ is symmetric. Neither are the requirements of objectivity yet inserted. Furthermore, the last term in (23.154) vanishes for the same reason as (23.152) does; and the term that is multiplied with grad ν^{β} vanishes since in view of (23.148) close to equilibrium

$$
\frac{\partial}{\partial\nu^{\beta}}\left(\frac{\partial\boldsymbol{k}}{\partial\operatorname{grad}\boldsymbol{v}^{\alpha}}\right)\bigg|_{\text{equil}} = \frac{\partial^{2}}{\partial\nu^{\beta}\,\partial\operatorname{grad}\boldsymbol{v}^{\alpha}}\left(\sum_{\gamma=1}^{N}\left(\frac{\partial\boldsymbol{k}}{\partial\boldsymbol{v}^{\gamma}}\right)^{\text{equil}}\boldsymbol{v}^{\gamma}\right)\Bigg|_{\text{equil}} = \mathbf{0},
$$

in which use was also made of (23.88). Therefore,

$$
(\boldsymbol{t}^{\alpha})^{\text{equil}} = \left(\rho^{\alpha}\psi + T\Lambda^{\nu^{\alpha}}\nu^{\alpha}\right)\mathbf{1} + T\left(\frac{\partial\boldsymbol{k}}{\partial\boldsymbol{v}^{\alpha}}\right)^{\text{equil}}. \qquad (23.155)
$$

The constituent stress tensor $\boldsymbol{t}^{\alpha}$ in thermodynamic equilibrium contains a term that depends on the extra entropy flux $\boldsymbol{k}$. In the local balance law of momentum for the constituent α, the stress and the interaction force contribute with the combination div $\boldsymbol{t}^{\alpha} + \mathfrak{m}^{\alpha}$. It is easy to show by means of (23.153), (23.155) that

$$
\boldsymbol{k}\text{−dependent term}\,\{\operatorname{div}\boldsymbol{t}^{\alpha} + \mathfrak{m}^{\alpha}\} = \mathbf{0}\ ;
$$

so, *the entropy-flux-dependent terms in the local balance of the linear momentum of the constituents in thermodynamic equilibrium cancel out. They can enter the momentum balance at most through the stress boundary conditions.*

The above four Eqs. (23.151)–(23.153) and (23.155) exhaust the thermodynamic equilibrium conditions as far as the first derivatives $(23.149)_1$ are concerned. Since $\pi^{s} = \pi^{s}(\boldsymbol{X}_E, \boldsymbol{X}_{NE})$, where $\boldsymbol{X}_E = \{T, \nu^{\alpha}, \operatorname{grad}\nu^{\alpha}\}$, $\boldsymbol{X}_{NE} = \{\operatorname{grad} T, \boldsymbol{v}^{\alpha}, \operatorname{grad}\boldsymbol{v}^{\alpha}\}$ and

$$
\pi^{s}(\boldsymbol{X}_E, \boldsymbol{X}_{NE} = \mathbf{0}) = 0, \quad \text{for all } \boldsymbol{X}_E,
$$

one necessarily also has

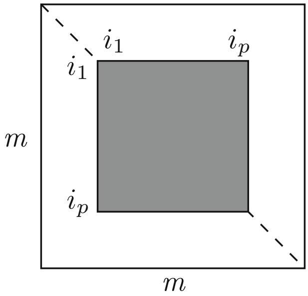
$$
\left(\frac{\partial\pi^{s}}{\partial\boldsymbol{X}_E}\right)^{\text{equil}} = \mathbf{0}, \quad \left(\frac{\partial^{2}\pi^{s}}{\partial\boldsymbol{X}_E\,\partial\boldsymbol{X}_E}\right)^{\text{equil}} = \mathbf{0}, \quad \text{etc.} \qquad (23.156)
$$

or, according to (23.147),

$$\begin{aligned}
&\left\{\sum_{\alpha=1}^{N} \Lambda^{\nu^\alpha} \frac{\partial \mathfrak{n}^\alpha}{\partial T}\right\}^{\text{equil}} = 0, \\
&\left\{\sum_{\beta=1}^{N} \Lambda^{\nu^\beta} \frac{\partial \mathfrak{n}^\beta}{\partial \nu^\alpha}\right\}^{\text{equil}} = 0, \qquad \alpha = 1, \dots, N-1, \\
&\left\{\sum_{\beta=1}^{N} \Lambda^{\nu^\beta} \frac{\partial \mathfrak{n}^\beta}{\partial \operatorname{grad} \nu^\alpha}\right\}^{\text{equil}} = \mathbf{0}, \quad \alpha = 1, \dots, N-1.
\end{aligned} \tag{23.157}$$

Similar expressions also hold for all higher derivative expressions. They do not express any particularly interesting fact other than if a function is identically zero, so are all its derivatives.

In a theory as complicated as this one, it is generally very difficult to exploit the conditions (23.149)$_2$, saying that the Hessian matrix of the second derivatives of π^s is positive semidefinite. A quadratic form for the symmetric matrix $\boldsymbol{A} = \boldsymbol{A}^t$ of dimension $m \times m$ is positive semidefinite, $\boldsymbol{x} \cdot \boldsymbol{A}\boldsymbol{x} \geqslant 0$ for all $\boldsymbol{x}$, if and only if all its principal minors are nonnegative. These principal minors are all determinants of submatrices, two corners of which are positioned on the principal diagonal as shown here:



(23.158)

The diagonal elements are also principal minors, and they correspond in our case to the non-mixed second derivatives of π^s. We shall not derive these relations here, but refer for some detailed results to Bauer [2]. One diagonal element of the matrix (23.158) is

$$\left(\frac{\partial^2 \pi^s}{\partial (\operatorname{grad} T)^2}\right)^{\text{equil}} \geqslant 0 \quad \Longrightarrow \quad -\frac{2}{T^2}\left(\frac{\partial \boldsymbol{q}}{\partial \operatorname{grad} T}\right)^{\text{equil}} \geqslant 0, \tag{23.159}$$

which allows the easy interpretation, namely,

$$\left(\frac{\partial \boldsymbol{q}}{\partial \operatorname{grad} T}\right)^{\text{equil}} \leq 0. \tag{23.160}$$

If one assumes close to thermodynamic equilibrium a linear relation between the heat flux of the mixture, $\boldsymbol{q}$, and the temperature gradient, grad T, then $\boldsymbol{q} = -\boldsymbol{\kappa} \operatorname{grad} T$, and $\boldsymbol{\kappa}$ must be a positive semidefinite matrix. The heat flux is in this case directed toward falling temperature.

It is advisable in most cases to await satisfaction of the positive semidefiniteness of the principal minors of $(23.149)_2$ until explicit constitutive relations are formulated for a concrete case. These are usually much simpler so that thermodynamic compatibility with $(23.149)_2$ becomes equally somewhat easier.

23.3.6 Extension to Nonequilibrium States

The ultimate goal is the determination of nonequilibrium states. We shall subsequently propose a first possibility to extend the constitutive relations valid in thermodynamic equilibrium to nonequilibrium. Such an extension cannot be justified in all details but must be regarded as an approximation. Furthermore, explicit expressions of nonequilibrium constitutive relations are always proposed with a certain application of the emerging theory in mind. Of course, this application is already anticipated in (23.91) which shows that the present model gives rise to heat conduction and viscous effects but no elasticity and may therefore be approximate in describing the viscous motion under isothermal or non-isothermal conditions. Such conditions prevail for instance in debris and mud flows of a gravel water mixture. In what follows, only the most simple extensions of the equilibrium expressions to nonequilibrium are presented.

For the *heat flux* $\boldsymbol{q}^\alpha$ of constituent α, a Fourier *type* relation

$$\boldsymbol{q}^\alpha = -c_q^\alpha \operatorname{grad} T \tag{23.161}$$

is suggested for which (21.55) yields

$$\boldsymbol{q} = -\sum_{\alpha=1}^{N} \left\{ c_q^\alpha \operatorname{grad} T + \boldsymbol{u}^\alpha \boldsymbol{t}^\alpha - \rho^\alpha \left(\varepsilon + \frac{1}{2} \boldsymbol{u}^\alpha \cdot \boldsymbol{u}^\alpha \right) \boldsymbol{u}^\alpha \right\}. \tag{23.162}$$

The *interaction forces* $\mathfrak{m}^\alpha$ are extended by terms which depend upon the difference velocities to the other constituents of the mixture. In so doing, it must be remembered that $\mathfrak{m}^\alpha$ in nonequilibrium is not a Euclidian objective vector valued variable; such a variable is, however, $\mathfrak{m}^\alpha_{\text{Euclid}}$ defined by $(21.24)_1$. Thus, we may set

$$\begin{aligned} \mathfrak{m}^{\alpha}_{\text{Euclid}} &= \mathfrak{m}^{\alpha} - \rho^{\alpha}\mathfrak{n}^{\alpha}\boldsymbol{v}^{\alpha} = (\mathfrak{m}^{\alpha})^{\text{equil}} + \sum_{\beta\neq\alpha}^{N} c_{\boldsymbol{v}}^{\alpha\beta}(\boldsymbol{v}^{\beta} - \boldsymbol{v}^{\alpha}), \\ c_{\boldsymbol{v}}^{\alpha\beta} &= c_{\boldsymbol{v}}^{\beta\alpha}. \end{aligned} \tag{23.163}$$

The last term in this expression is linear in the difference velocities, if $c_{\boldsymbol{v}}^{\alpha\beta}$ are independent of $|\boldsymbol{v}^{\beta} \cdot \boldsymbol{v}^{\alpha}|$. In that form, this summation term is then reminiscent of DARCY's *law*[33] and $c_{\boldsymbol{v}}^{\alpha\beta}$ are permeabilities, but obviously, this analogy is complete only for a binary mixture. It is also natural to assume that $c_{\boldsymbol{v}}^{\alpha\beta} = c_{\boldsymbol{v}}^{\beta\alpha}$, for in that case the "DARCY term" satisfies the condition

$$\sum_{\alpha=1}^{N}\sum_{\beta\neq\alpha}^{N} c_{\boldsymbol{v}}^{\alpha\beta}(\boldsymbol{v}^{\beta} - \boldsymbol{v}^{\alpha}) = \mathbf{0},$$

which must necessarily hold, if $\sum_{\alpha=1}^{N} \mathfrak{m}^{\alpha} = \mathbf{0}$. Furthermore the "DARCY term" is not restricted to a linear dependence in the difference velocities. The coefficients $c_{\boldsymbol{v}}^{\alpha\beta}$ may well depend upon scalar variables such as $|\boldsymbol{v}^{\beta} - \boldsymbol{v}^{\alpha}|$. In groundwater flow a quadratic dependence of the "DARCY term" is known as FORCHHEIMER *law*; it is known to better approximate the viscous effects of the flow of water through the pore space of soil if this flow is turbulent, and it is believed that this quadratic dependence also models somewhat the tortuosity effects of the pore space. This is plausible as the *tortuosity* enhances the onset of turbulence in the flow of the interstitial fluid.

For a mixture of viscous constituents, objective tensor variables with the notion of viscous behavior and deducible from (23.91) are

$$\boldsymbol{D}^{\alpha} = \text{sym grad}\, \boldsymbol{v}^{\alpha}, \quad \boldsymbol{W}^{\alpha} = \text{skw grad}\, \boldsymbol{v}^{\alpha} - \boldsymbol{W}, \quad \boldsymbol{V}^{\alpha\beta} = \boldsymbol{u}^{\alpha} \otimes \boldsymbol{u}^{\beta}, \tag{23.164}$$

where $\boldsymbol{W} = \text{skw grad}\, \boldsymbol{v}$. So, the nonequilibrium stress $\boldsymbol{t}^{\alpha}$ may be assumed in the form

$$\boldsymbol{t}^{\alpha} - (\boldsymbol{t}^{\alpha})^{\text{equil}} = \boldsymbol{t}^{\alpha}_{NE}(\cdot, \boldsymbol{D}^{\alpha}, \boldsymbol{W}^{\alpha}, \boldsymbol{V}^{\alpha\beta}). \tag{23.165}$$

The dot in the argument of $\boldsymbol{t}^{\alpha}_{NE}$ indicates additional dependences of (23.91) not explicitly stated in (23.165). It is thought that the dominant dependence of $\boldsymbol{t}^{\alpha}$ on the variables (23.164) is through $\boldsymbol{D}^{\alpha}$, and so a first "guess" may have the form

$$\boldsymbol{t}^{\alpha}_{NE} = a\mathbf{1} + b\boldsymbol{D}^{\alpha} + c(\boldsymbol{D}^{\alpha})^2, \tag{23.166}$$

in which a, b, c may depend on the invariants of $\boldsymbol{D}^{\alpha}$ (and other scalar variables if needed). Nevertheless, the ansatz (23.166) is usually thought to be too complicated. A popular relation is a reduced version of the form

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[33] For a brief biographical sketch of HENRY PHILIBERT GASPARD DARCY (1803–1858), see Fig. 10.9 in Vol. 1, p. 594 of this treatise on Fluid and Thermodynamics [21].

$$\boldsymbol{t}^{\alpha}_{NE} = c^{\alpha}_{\boldsymbol{t}}\left(II_{\boldsymbol{D}^{\alpha}}\right)\boldsymbol{D}^{\alpha}, \qquad II_{\boldsymbol{D}^{\alpha}} = \tfrac{1}{2}\mathrm{tr}\,\left((\boldsymbol{D}^{\alpha})^2\right). \tag{23.167}$$

If

$$c^{\alpha}_{\boldsymbol{t}} = \left(II_{\boldsymbol{D}^{\alpha}}\right)^m, \;\; 0 < m < 1, \tag{23.168}$$

then (23.167) is called a power law and the constituent body a power law material. Other denotations are GLEN's flow law (glaciology), NORTON's law (metallurgy), or OSWALD- DE WAELE flow law (rheology). In a binary mixture of soil and water $c^{\boldsymbol{t}}_s$ for the solid is nonzero while $c^{\boldsymbol{t}}_w$ for the water is often set to zero.

Apart from the above representations, a complete postulation of the constitutive relations also requires the postulation of an expression of the internal energy ε^{α} (it is needed in the parameterization of the heat flux vector). The most common assumption is

$$\varepsilon^{\alpha} = \varepsilon^{\alpha}_0 + \int_{T_0}^{T} c^{\alpha}_{\varepsilon}(\theta)\mathrm{d}\theta = \varepsilon^{\alpha}_0 + c^{\alpha}_{\varepsilon}(T - T_0), \tag{23.169}$$

where the second formula applies if c^{α}_{ε} may be considered to be constant. Finally, an expression for the inner free energy ψ_I is needed. Since $\psi_I = \hat{\psi}_I(T, \nu^{\alpha})$ —a dependence on $\boldsymbol{v}^{\alpha}$ has been excluded—we may choose as the simplest possibility for the internal HELMHOLTZ free energy

$$\psi_I = \psi_0(\nu^{\alpha}) + c^1_{\psi}(T - T_0) + \tfrac{1}{2}c^2_{\psi}(T - T_0)^2, \tag{23.170}$$

implying that

$$\begin{aligned} s &= -\frac{\partial \psi_I}{\partial T} = c^1_{\psi} + c^2_{\psi}(T - T_0), \\ \rho\varepsilon_I &= \sum_{\alpha=1}^{N} \rho^{\alpha}\varepsilon^{\alpha}_0 + \sum_{\alpha=1}^{N} \rho^{\alpha} c^{\alpha}_{\varepsilon}(T - T_0) = \rho(\psi_I - sT), \end{aligned} \tag{23.171}$$

the second of which imposes restrictions on the coefficients c^{α}_{ε}, $c^{1,2}_{\psi}$.

This completes the formulation of the model equations in one case, namely when the constitutive relations are chosen as suggested above. The next step would now be the numerical determination of all the parameters. This step is called *parameter identification* and involves performing experiments for typical deformation fields and their optimal imitation with the corresponding boundary value problem of this theory. This is generally a similarly difficult problem as the derivation of the thermodynamic model equations itself.

One particular problem in this process is the selection of the extra entropy flux vector $\boldsymbol{k}$, which we know vanishes in equilibrium with many of its derivatives. In fact its form close to thermodynamic equilibrium is given by (23.148). In the local balance laws of the constituent momenta in equilibrium, it has been shown that its contribution equally vanishes, and so does it in nonequilibrium with the choices of the nonequilibrium stresses $\boldsymbol{t}^{\alpha}_{NE}$ and the interaction forces $\mathfrak{m}^{\alpha}$ as selected in (23.163), (23.166) or (23.167). Thus, as far as purely mechanical equations are concerned, a nontrivial $\boldsymbol{k}$ manifests itself only in the boundary conditions, and if so, in dynamical processes. All these reasons may serve as motivation to select

$$\boldsymbol{k} = \boldsymbol{0}. \tag{23.172}$$

This then yields, on using (23.145),

$$\phi^{\rho s} = \frac{1}{T}\left(\boldsymbol{q} + \sum_{\alpha=1}^{N} \boldsymbol{u}^{\alpha}\boldsymbol{t}^{\alpha}\right), \tag{23.173}$$

the classical expression in mixture theory. Compare this expression with the entropy flux of the diffusion theory, (23.61).

23.4 Discussion

Summarizing the essential findings of the thermodynamic theory of a saturated mixture of nonpolar constituents as a second class classical mixture, the reader is reminded that the inferences were drawn for the entropy principle as proposed by MÜLLER under the specializations that

- all constituents have constant true densities, so that the constituent volume fractions are the pertinent descriptions of their concentration,
- the mixture is saturated, i.e., all constituents fill together the entire space of the body. Stated differently, this is tantamount to the nonexistence of empty pores within the body.

Thermodynamic theories of porous media, in which these two assumptions do not hold, are more complicated.

The choice of the material class has been so selected that elasticity effects have been ignored. For a fluid mixture of density preserving components, ignoring elasticity effects is compelling, because their inclusion would include the compressibility of the constituent materials. Thus, the independent constitutive variables, stated in (23.91), are the empirical temperature, the constituent volume fractions, the constituent velocities and their gradients. Requiring material objectivity of the constitutive relations then demands the introduction of the diffusion and barycentric velocities for these variables as well as the relative deformation rates as stated in (23.93). This process then yields the EUCLIDian objective form of the constitutive relations (23.94) for the materially dependent variables (23.90).

Satisfaction of the entropy inequality subject to all relevant field equations and constraint conditions in the spirit of I. MÜLLER can be achieved by subtracting from this inequality

- $N-1$ mass balances weighted with the LAGRANGEan scalars Λ^{ν^α},
- the saturation condition weighted with the LAGRANGE parameter Λ_N^ν,
- the N momentum balances weighted with with the vectorial LAGRANGE parameter $\boldsymbol{\Lambda}^{\boldsymbol{v}^\alpha}$,
- the energy balance weighted with the scalar LAGRANGE parameter Λ^ε

as explicitly indicated by (23.97).

Exploitation of this extended entropy inequality has been quite an analytically challenging set of transformations until its ultimate form (23.105) was reached, from which the two statements (23.106), which comprise the LIU identities $\boldsymbol{\alpha} = \mathbf{0}$ and the residual inequality $\Gamma \geqslant 0$, stated explicitly as (23.107) and (23.147). The LIU identities allow derivation of the explicit form of the GIBBS relation, but not of all the LAGRANGE parameters , which are involved. The differential of the specific entropy, $\mathrm{d}(\rho s)$, could in this process be written as a total differential of a number of terms, which are pre-multiplied by the LAGRANGE parameter of the energy, Λ^ε. This parameter can be proved to be equal to the inverse absolute temperature, $\Lambda^\varepsilon = 1/T$, but this proof was not demonstrated, see, however, [24]. With it, the remaining LAGRANGE parameters are given by (23.141) and (23.142), in which Λ_N^ν remains undetermined as an independent variable for the saturation condition, thus forming the saturation pressure.

The reduced entropy inequality (23.147) is primarily employed to deduce inferences at thermodynamic equilibrium and in its immediate vicinity via the statements (23.149). Exploitation of the former allows determination of the equilibrium expressions for the interaction forces (23.153) and the partial pressures (23.155). Their analytic forms are such that the extra entropy flux, $\boldsymbol{k}$, defined in (23.145) does not enter the momentum equation and, therefore, will only be "visible" through the boundary conditions. The chapter ends with a few presentations of the forms of the heat flux (23.162), interaction forces (23.163), partial stress tensors (23.167), and entropy and internal energy (23.169)–(23.171).

Appendix 23.A Some Details on the Poincaré Theorem and the Condition of Frobenius

In this appendix, we shall prove the correctness of the following statements:

Proposition 23.4 *(i) In the one-dimensional case ($n = 1$) every total differential is complete.*

(ii) In two dimensions ($n = 2$), every differential can be transformed into a total differential by multiplying it with an integrating factor.

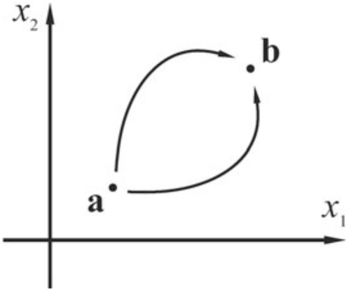

Fig. 23.4 Explaining the path independence of the integration of a differential in two dimensions

(iii) *In three-dimensional space ($n = 3$), the condition that an arbitrary differential $\mathrm{d}F = X_i \mathrm{d}x_i$ can be made complete is the requirement that the vector field* $\boldsymbol{X}$ *stays perpendicular to its vorticity,* curl $\boldsymbol{X}$. ■

Proof (i) In the one-dimensional case, there is no possibility to select between different paths of integration between two points to reach point b from point a. Every RIEMANN integral from a to a certainly vanishes.

(ii) In two dimensions, one has $\mathrm{d}F = X_1\mathrm{d}x_1 + X_2\mathrm{d}x_2$. If POINCARÉ's theorem holds, then

$$\frac{\partial X_1}{\partial x_2} = \frac{\partial X_2}{\partial x_1} \tag{23.174}$$

and F is a potential such that

$$X_1 = \frac{\partial F}{\partial x_1}, \quad X_2 = \frac{\partial F}{\partial x_2} \quad \overset{(23.147)}{\Longrightarrow} \quad \frac{\partial^2 F}{\partial x_2 \partial x_1} = \frac{\partial^2 F}{\partial x_1 \partial x_2}. \tag{23.175}$$

The value $F(\boldsymbol{x})$ can be determined by integrating from $\boldsymbol{x}_0$ to $\boldsymbol{x}$ along any continuous curve,

$$F(\boldsymbol{x}) = \int_{\boldsymbol{x}_0}^{\boldsymbol{x}} \left(X_1(x_1, x_2)\mathrm{d}x_1 + X_2(x_1, x_2)\mathrm{d}x_2\right). \tag{23.176}$$

It follows that the integral along any curve from $\boldsymbol{a}$ to $\boldsymbol{b}$ yields

$$\int_{\boldsymbol{a}}^{\boldsymbol{b}} \left(X_1(x_1, x_2)\mathrm{d}x_1 + X_2(x_1, x_2)\mathrm{d}x_2\right) = \int_{\boldsymbol{a}}^{\boldsymbol{b}} \mathrm{d}F = F(\boldsymbol{b}) - F(\boldsymbol{a}) \tag{23.177}$$

and is independent of the path chosen between $\boldsymbol{a}$ and $\boldsymbol{b}$, see **Fig. 23.4**.

If the POINCARÉ theorem is not fulfilled, one may try its satisfaction by an integrating factor. In that case, one writes

$$\mathrm{d}F_\lambda = \lambda X_1 \mathrm{d}x_1 + \lambda X_2 \mathrm{d}x_2. \tag{23.178}$$

Satisfaction of the POINCARÉ theorem for this differential requires

$$\frac{\partial(\lambda X_1)}{\partial x_2} = \frac{\partial(\lambda X_2)}{\partial x_1}, \qquad \text{or} \tag{23.179}$$

$$\lambda \underbrace{\left(\frac{\partial X_1}{\partial x_2} - \frac{\partial X_2}{\partial x_1}\right)}_{\neq 0} = \frac{\partial \lambda}{\partial x_1} X_2 - \frac{\partial \lambda}{\partial x_2} X_1, \tag{23.180}$$

in which the underbraced term differs from zero since the starting equation does not satisfy the POINCARÉ condition. Evidently, $\lambda = \text{const.}$ is not a possible integrating factor. However, the determination of a nonconstant integrating factor is not unique.

- If $X_2 \neq 0$, one may, for instance, select $\lambda = \lambda_1(x_1)$; then it follows from (23.180) that

  $$\frac{\mathrm{d}\lambda_1}{\mathrm{d}x_1} - \frac{1}{X_2}\left(\frac{\partial X_1}{\partial x_2} - \frac{\partial X_2}{\partial x_1}\right)\lambda_1 = 0, \quad \text{with the solution}$$

  $$\Longrightarrow \lambda_1 = \exp\left\{\int_0^{x_1}\left(\frac{1}{X_2}\left(\frac{\partial X_1}{\partial x_2} - \frac{\partial X_2}{\partial \bar{x}_1}\right)\right)(\bar{x}_1, x_2)\mathrm{d}\bar{x}_1\right\}. \tag{23.181}$$

  This formula shows that λ_1 is a function of x_1 alone only, if the integrand function is independent of x_2
- If $X_1 \neq 0$ and $\lambda = \lambda_2(x_2)$ is assumed, the analogous procedure leads to

  $$\Longrightarrow \lambda_2 = \exp\left\{\int_0^{x_2}\left(-\frac{1}{X_2}\left(\frac{\partial X_1}{\partial \bar{x}_2} - \frac{\partial X_2}{\partial x_1}\right)\right)(x_1, \bar{x}_2)\mathrm{d}\bar{x}_2\right\}, \tag{23.182}$$

  which shows that $\lambda = \lambda_2(x_2)$ is only a function of x_2, if the integrand function does not depend on x_1.
- In all other cases, λ must be determined by solving the partial differential equation (23.180).

(iii) In the three-dimensional case, it is known that a vector field $\boldsymbol{X}$ can be written as the gradient of a scalar potential field only, if curl $\boldsymbol{X} = \mathbf{0}$. In Cartesian component form, this then yields the POINCARÉ condition

$$\frac{\partial X_i}{\partial x_j} - \frac{\partial X_j}{\partial x_i} = 0, \quad (i, j = 1, 2, 3).$$

If curl $\boldsymbol{X} \neq \mathbf{0}$, one may try to construct a total differential

$$\mathrm{d}F_\lambda = \lambda X_1 \mathrm{d}x_1 + \lambda X_2 \mathrm{d}x_2 + \lambda X_3 \mathrm{d}x_3, \tag{23.183}$$

by multiplying $\mathrm{d}F$ with an integrating factor. The condition for this to be successful is

$$\mathbf{0} \overset{!}{=} \operatorname{curl}(\lambda \boldsymbol{X}) = \lambda(\operatorname{curl} \boldsymbol{X}) + (\operatorname{grad} \lambda) \times \boldsymbol{X}. \tag{23.184}$$

Multiplying this equation scalarly with $\boldsymbol{X}$ yields

$$\operatorname{curl} \boldsymbol{X} \cdot \boldsymbol{X} = 0, \quad \text{if } \lambda \neq 0. \tag{23.185}$$

Thus, $\boldsymbol{X}$ and curl $\boldsymbol{X}$ are perpendicular to one another; in Cartesian components, this reads

$$\varepsilon_{ijk} X_{k,j} X_i = 0, \tag{23.186}$$

which is nothing else than the FROBENIUS condition.

For a plane vector field, condition (23.185) is always satisfied; a fact that corroborates the statement that in two dimensions an integrating factor always exists.

Appendix 23.B Proof of a Statement About a Complete Differential

In this Appendix, the following statement is proved:
Let $\mathrm{d}f$ *be an incomplete differential of the variables* x_i $(i = 1, \ldots, n)$. *Let, moreover,* $g \neq 0$ *be an integrating denominator, which makes*

$$\mathrm{d}F := \frac{\mathrm{d}f}{g} \tag{23.187}$$

a total (complete) differential. Then,

$$\mathrm{d}H = G(F)\frac{\mathrm{d}f}{g} \tag{23.188}$$

is equally complete.

Proof In long-hand notation, $\mathrm{d}H$ is written as

$$\mathrm{d}H = \frac{G(F)}{g}\left\{\cdots + \frac{\partial f}{\partial x_i}\mathrm{d}x_i + \cdots + \frac{\partial f}{\partial x_j}\mathrm{d}x_j + \cdots\right\}. \tag{23.189}$$

Hence,

$$\frac{\partial H}{\partial x_i} = \frac{G(F)}{g}\frac{\partial f}{\partial x_i}, \quad \frac{\partial H}{\partial x_j} = \frac{G(F)}{g}\frac{\partial f}{\partial x_j}. \tag{23.190}$$

Testing POINCARÉ's theorem, one deduces,

$$\begin{aligned}\frac{\partial^2 H}{\partial x_j \partial x_i} &= \left\{\frac{\partial G}{\partial F}\frac{\partial F}{\partial x_j}\frac{1}{g}\frac{\partial f}{\partial x_i} + G(F)\frac{\partial}{\partial x_j}\left(\frac{1}{g}\frac{\partial f}{\partial x_i}\right)\right\},\\ \frac{\partial^2 H}{\partial x_i \partial x_j} &= \left\{\frac{\partial G}{\partial F}\frac{\partial F}{\partial x_i}\frac{1}{g}\frac{\partial f}{\partial x_j} + G(F)\frac{\partial}{\partial x_i}\left(\frac{1}{g}\frac{\partial f}{\partial x_j}\right)\right\}.\end{aligned} \tag{23.191}$$

In these expressions, the second terms are equal, because, by prerequisite, $\mathrm{d}f/g$ is a complete differential (POINCARÉ theorem). This is also true for the first term, since according to (23.187)

$$\frac{\partial G}{\partial F}\frac{\partial F}{\partial x_j}\frac{\partial F}{\partial x_i} = \frac{\partial G}{\partial F}\frac{\partial F}{\partial x_i}\frac{\partial F}{\partial x_j}. \tag{23.192}$$

It has, therefore, been proved that the two mixed derivatives (23.191) have the same value. It follows that $\mathrm{d}H$ is necessarily a complete differential, if $\mathrm{d}F$ is one.

Appendix 23.C Proof of Some Rules of Differentiation

(i) The formulae $(23.95)_{1,2,3}$ follow from the definition of the barycentric velocity, $\boldsymbol{v} = \sum_{\gamma=1}^{N} \xi^\gamma \boldsymbol{v}^\gamma$ by applying the product rule of differentiation. For instance,

$$\operatorname{grad} \boldsymbol{v} = \sum_{\gamma=1}^{N} \{\xi^\gamma \operatorname{grad} \boldsymbol{v}^\gamma + \boldsymbol{v}^\gamma \otimes \operatorname{grad} \xi^\gamma\}, \tag{23.193}$$

from which expressions for $\boldsymbol{D}$ and $\boldsymbol{W}$ may be derived by applying the operators "sym" and "skw",

$$\begin{aligned}\boldsymbol{D} &= \sum_{\gamma=1}^{N} \{\xi^\gamma \boldsymbol{D}^\gamma + \operatorname{sym}(\boldsymbol{v}^\gamma \otimes \operatorname{grad} \xi^\gamma)\},\\ \boldsymbol{W} &= \sum_{\gamma=1}^{N} \{\xi^\gamma \boldsymbol{W}^\gamma + \operatorname{skw}(\boldsymbol{v}^\gamma \otimes \operatorname{grad} \xi^\gamma)\}.\end{aligned} \tag{23.194}$$

(ii) From the definition of the diffusion velocity, there follows

$$\frac{\partial \boldsymbol{u}^\beta}{\partial \boldsymbol{v}^\alpha} = \frac{\partial}{\partial \boldsymbol{v}^\alpha}\left(\boldsymbol{v}^\beta - \sum_{\gamma=1}^{N} \xi^\gamma \boldsymbol{v}^\gamma\right) = \delta_{\alpha\beta}\boldsymbol{I} - \xi^\alpha \boldsymbol{I} = \left(\delta_{\alpha\beta} - \xi^\alpha\right)\boldsymbol{I}, \tag{23.195}$$

in which $\boldsymbol{I}$ is the 3×3 unit rank-2 tensor.

Similarly,

$$
\begin{aligned}
\frac{\partial \boldsymbol{U}^\beta}{\partial \boldsymbol{W}^\alpha} &= \frac{\partial}{\partial \boldsymbol{W}^\alpha}\left\{ \operatorname{grad} \boldsymbol{v}^\beta - \sum_{\gamma=1}^{N} \left(\xi^\gamma \boldsymbol{W}^\gamma + \operatorname{skw}\left(\boldsymbol{v}^\gamma \otimes \operatorname{grad} \xi^\gamma\right)\right)\right\} \\
&= \delta_{\alpha\beta}\boldsymbol{I}_4 - \xi^\alpha \boldsymbol{I}_4 = \left(\delta_{\alpha\beta} - \xi^\alpha\right)\boldsymbol{I}_4,
\end{aligned} \tag{23.196}
$$

in which $\boldsymbol{I}_4$ is the unit rank-4 tensor with $(\boldsymbol{I}_4)_{ijkl} = \delta_{ij}\delta_{kl}$.

(iii) With the results (23.195) and (23.196), we may now deduce

$$
\begin{aligned}
\frac{\partial f}{\partial \boldsymbol{v}^\alpha} &= \sum_\beta \frac{\partial f}{\partial \boldsymbol{u}^\beta}\frac{\partial \boldsymbol{u}^\beta}{\partial \boldsymbol{v}^\alpha} = \sum_\beta \frac{\partial f}{\partial \boldsymbol{u}^\beta}\left(\delta_{\alpha\beta} - \xi^\alpha\right)\boldsymbol{I} \\
&= \frac{\partial f}{\partial \boldsymbol{u}^\alpha} - \xi^\alpha \sum_\beta \frac{\partial f}{\partial \boldsymbol{u}^\beta},
\end{aligned} \tag{23.197}
$$

$$
\begin{aligned}
\frac{\partial f}{\partial \boldsymbol{W}^\alpha} &= \sum_\beta \frac{\partial f}{\partial \boldsymbol{U}^\beta}\frac{\partial \boldsymbol{U}^\beta}{\partial \boldsymbol{W}^\alpha} = \sum_\beta \frac{\partial f}{\partial \boldsymbol{U}^\beta}\left(\delta_{\alpha\beta} - \xi^\alpha\right)\boldsymbol{I}_4 \\
&= \frac{\partial f}{\partial \boldsymbol{U}^\alpha} - \xi^\alpha \sum_\beta \frac{\partial f}{\partial \boldsymbol{U}^\beta}.
\end{aligned} \tag{23.198}
$$

This result can now be used in the evolution of $\partial f / \partial \operatorname{grad} \boldsymbol{v}^\alpha$

$$
\begin{aligned}
\frac{\partial f}{\partial \operatorname{grad} \boldsymbol{v}^\alpha} &= \frac{\partial f}{\partial \boldsymbol{D}^\alpha} + \frac{\partial f}{\partial \boldsymbol{W}^\alpha} \\
&\overset{(23.198)}{=} \frac{\partial f}{\partial \boldsymbol{D}^\alpha} + \frac{\partial f}{\partial \boldsymbol{U}^\alpha} - \xi^\alpha \sum_\beta \frac{\partial f}{\partial \boldsymbol{U}^\beta},
\end{aligned} \tag{23.199}
$$

where $\operatorname{grad} \boldsymbol{v}^\alpha = \boldsymbol{D}^\alpha + \boldsymbol{W}^\alpha$ has been used.

References

1. Albers, B., Wilmanski, K.: Continuum Thermodynamics, Part II: Applications and Examples, p. 464. World Scientific, New Jersey (2015). ISBN 978-981-4412-37-7
2. Bauer, G.: Thermodynamische Betrachtung einer gesättigten Mischung. Doctoral dissertation, Department of Mechanics, Darmstadt University of Technology, 126p. (1997)
3. Biot, M.A.: General theory of three dimensional consolidation. J. Appl. Phys. **12**, 155–164 (1941)
4. Biot, M.A.: Theory of deformation of a porous viscoelastic anisotropic solid. J. Appl. Phys. **27**, 459–467 (1956)
5. Bluhm, J.: A Consistent Model for Saturated and Empty Porous Media. Forschungsberichte aus dem Fachbereich Bauwesen, vol. 74, p. 133p. Universität GH Essen, Essen (1997)

6. Bowen, R.M.: Incompressible porous media models by use of the theory of mixtures. Int. J. Eng. Sci. **18**, 1129–1148 (1980)
7. Bowen, R.M.: Compressible porous media models by use of the theory of mixtures. Int. J. Eng. Sci. **20**, 697–763 (1982)
8. Bowen, R.M., Wang, C.-C.: Introduction to Vectors and Tensors. Vol. 1: Linear and Multillinear Algebra, pp. 1–296; Vol. 2: Vector and Tensor Analysis, pp. 297–520. Plenum Press (1976)
9. de Boer, R.: Theory of Porous Media. Highlights in the Historical Development and Current State, 618p. Springer, Berlin (2000)
10. Drew, D.A., Passman, S.L.: Theory of Multicomponent Fluids. Applied Mathematical Sciences, vol. 135l, 308p. Springer, New York (1998)
11. Ehlers, W.: Poröse Medien – Ein kontinuumsmechanisches Model auf der Basis der Mischungstheorie. Forschungsberichte aus dem Fachbereich Bauwesen, vol. 47, 322p. Universität GH Essen, Essen (1989)
12. Ehlers, W.: Constitutive equations for granular materials in geomechanical context. In: Hutter, K. (ed.) Continuum Mechanics in Environmental Sciences and Geophysics. CISM Courses and Lectures, vol. 337, pp. 313–402. Springer, Vienna (1993)
13. Goodman, M.A., Cowin, S.C.: A continuum theory of granular materials. Arch. Ration. Mech. Anal. **44**, 249–266 (1972)
14. Gray, W.G.: Elements of a systematic procedure for the derivation of macroscale conservation equations for multiphase flows in porous media. In: Hutter, K. (ed.) Kinematic and Continuum Theories of Granular and Porous Media. CISM Courses and Lectures, vol. 400, pp. 67–129. Springer, Berlin (1999)
15. Gray, W.G., Miller, C.T.: Introduction to the thermodynamically constrained averaging theory for porous media systems. In: Hutter, K. (ed.) Advances in Geophysical and Environmental Mechanics and Mathematics (AGEM^2). Springer, Cham (2014)
16. Gurtin, M.E.: On the thermodynamics of chemically reacting fluid mixtures. Arch. Ration. Mech. Anal. **43**, 198–212 (1971)
17. Hassaniazadeh, S.M., Gray, W.G.: General conservation equations for multiphase systems: 1. Averaging procedure. Adv. Water Res. **2**, 25–40 (1979)
18. Hassaniazadeh, S.M., Gray, W.G.: General conservation equations for multiphase systems: 1. Averaging procedure. Adv. Water Res. **2**, 131–144 (1979)
19. Hassaniazadeh, S.M., Gray, W.G.: General conservation equations for multiphase systems: 2. Mass, momenta, energy and entropy equations. Adv. Water Res. **2**, 191–208 (1979)
20. Hutter, K., Jöhnk, K.: Continuum Methods of Physical Modeling, p. 635. Springer, Berlin (2004)
21. Hutter, K., Wang, Y.: Fluid and Thermodynamics. Volume 1: Basic Fluid Mechanics, 639p. Springer, Berlin (2016). ISBN: 978-3319336329
22. Hutter, K., Wang, Y.: Fluid and Thermodynamics. Volume II: Advanced Fluid Mechanics and Thermodynamic Fundamentals. Springer, Berlin, 633p. (2016). ISBN: 978-3-319-33635-0
23. Ludwig, C.: Diffusion zwischen ungleich erwärmten Orten gleich zusammengesetzter Lösungen. Sitzungsbericbht Kaiser. Akad. Wiss. (Mathem-Naturwiss. Cl.) Wien, **65**, 539 (1856)
24. Müller, I.: Thermodynamics. Pitman, 521p. (1985)
25. Schneidere, L., Hutter, K.: Solid-fluid mixtures of frictional materials in geophysical and geotechnical context. In: Hutter, K. (ed.) Advances in Geophysical and Environmental Mechanics and Mathematics (AGEM^2), p. 247. Springer, Berlin (2009)
26. Soret, C.: Sur l'état d' équilibre que prend, du point de vue de sa concentration, une dissolution saline primitivement homogéne, dont deux parties sont portées à des tempéeratures difféerantes. Archives de Genève, 3e période, tome II, 48 (1879)
27. Svendsen, B., Hutter, K.: On the thermodynamics of a mixture of isotropic viscous materials with kinematic constraints. Int. J. Eng. Sci. **33**, 2021–2054 (1995)
28. Truesdell, C.A., Toupin, R.A.: The classical field theories. In: Flügge, S. (ed.) Encyclopedia of Physics, vol. III/1, pp. 226–793. Springer, Berlin (1957)
29. Truesdell, C.A.: Essays in the History of Mechanics, 383p. Springer, Berlin (1968)
30. Truesdell, C.A.: Rational Thermodynamics, 2nd edn, 578p. Springer, Berlin (1984)
31. Wilmanski, K.: Continuum Thermodynamics, Part I: Foundations, p. 402. Wold Scientific, Singapore (2008). ISBN 978-981-283-556-7

Chapter 24
Thermodynamics of Binary Solid–Fluid Cosserat Mixtures

Abstract It is demonstrated in this chapter, how complex it is to deduce a saturated binary solid–fluid COSSERAT mixture model that is in conformity with the second law of thermodynamics and sufficiently detailed to be ready for application in fluid dynamics. The second law is formulated for open systems using the CLAUSIUS–DUHEM inequality without mass and energy production under phase change for class II mixtures of elastic solids and viscoelastic fluids. It turns out that even with all these restrictions the detailed exploitation of the entropy inequality is a rather involved endeavor. Inferences pertain to extensive functional restrictions of the fluid- and solid- free energies and allow determination of the constitutive quantities in terms of the latter in thermodynamic equilibrium and small deviations from it. The theory is presented for four models of compressible–incompressible fluid–solid constituents. Finally, explicit representations are given for the free energies and for the constitutive quantities that are obtained from them via differentiation processes

Keywords Open systems thermodynamics · CLAUSIUS–DUHEM exploitation of the entropy principle · Elastic solids + viscoelastic fluids · Volume fraction parameterization · Alternative viscoelastic compressible/incompressible models

List of Symbols

Roman Symbols

$\boldsymbol{A}$	Rank-2 tensor
$\overset{2\times2}{\mathcal{A}}_{ij}$, $\overset{4\times4}{\mathcal{A}}_{ijkl}$	Rank-2, rank-4 general material tensors (conductivities, viscosities, etc.)
$\boldsymbol{a}(\boldsymbol{\mathcal{Y}})$	Vector-valued quantity formed with constitutive quantities $\boldsymbol{\mathcal{Y}}$, see (24.46)

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$(a)_0$	Initial value of the quantity a, its value in the reference configuration
(a^*)	Constant scaling value of $\boldsymbol{a}$ in a particular 3D spatial direction, see (24.75), $\boldsymbol{a} = \iota(\boldsymbol{a}^*)$
$\boldsymbol{B}$ $(\boldsymbol{C})$	Left (right) Cauchy–Green deformation tensor.
$\overset{4\times4}{\mathcal{C}}$	Rank-4 'viscosity tensor' of the fluid constituent, $\overset{4\times4}{\mathcal{C}} = (\partial \boldsymbol{t}^F / \partial \bar{\boldsymbol{\Delta}}^F)_0$
$\mathfrak{c}^\alpha$	Specific mass production rate of constituent α
$\{\{\boldsymbol{C}_\mathsf{T}\}\}$	Linear positive operator on C, see (24.85)
$\boldsymbol{d}^\alpha$	Diffusion velocity of the velocity of constituent α minus the barycentric velocity, $\boldsymbol{d}^\alpha = \boldsymbol{v}^\alpha - \boldsymbol{v} = \boldsymbol{v}^\alpha - \left(\sum_\beta (\rho^\beta/\rho)\boldsymbol{v}^\beta\right)$
$\boldsymbol{d}^S$	Barycentric diffusion velocity of the solid constituent, $\boldsymbol{d}^S = -(\rho^F/\rho)\boldsymbol{w}^F$
$\boldsymbol{d}^F$	Barycentric diffusion velocity of the fluid constituent, $\boldsymbol{d}^F = \left(\rho^S/\rho\right)\boldsymbol{w}^F$
$\mathcal{D}$ $(\geqslant 0)$	Residual entropy inequality
$E^F_{\mathcal{C}}$	'Young's' modulus for the fluid quantity $\mathcal{C}$, see (24.114)
$\mathfrak{E}^\alpha$	Internal energy production rate density of constituent α, see (24.10)
$\mathfrak{e}^\alpha$	Specific production rate density of the energy of constituent α due to phase change
$\boldsymbol{F}^\alpha$	Deformation gradient of constituent α
$\boldsymbol{f}^\alpha$	Specific body force of constituent α
$f(\vartheta)$	Temperature-dependent function describing the dependence of ψ^S_2 on $\hat{\rho}^F$, see (24.129)
$g_{ij}(\vartheta), i, j = 1, 2$	Temperature-dependent functions describing the dependences of ψ^F_2 on $\bar{\boldsymbol{U}}^S$ and ${}^R\bar{\boldsymbol{\mathcal{K}}}^S$
$g(\vartheta)\delta_{ij}$	Isotropic reduction of $g_{ij}(\vartheta)$
$\boldsymbol{I}$	Three-dimensional unit tensor
$I_{\boldsymbol{A}}, II_{\boldsymbol{A}}, III_{\boldsymbol{A}}$	Classical invariants of the symmetric rank-2 tensor $\boldsymbol{A}$
$I_{\hat{\boldsymbol{B}}}, II_{\hat{\boldsymbol{B}}}, III_{\hat{\boldsymbol{B}}}$	Alternative invariants of the rank-2 left Cauchy–Green deformation tensor $\boldsymbol{B}$, see (24.181)
$J = (III_{\boldsymbol{B}})^{1/2}$	Volumetric strain of $\boldsymbol{B}$ or $\boldsymbol{F}$
K	Coefficient in the parameterizations of U_ℓ, $\ell = 3, 4, 5, 6, 7, 8$, see **Table 24.4**
$k^F_{\mathcal{C}}$	Bulk coefficient of the fluid quantity $\mathcal{C}$
${}^R\bar{\boldsymbol{\mathcal{K}}}^S$	Lagrange curvature tensor of the solid constituent
$k^F_{\mathcal{C}}$	Bulk coefficient of the fluid quantity $\mathcal{C}$

$\boldsymbol{\mathfrak{k}}^\alpha$, $\boldsymbol{\mathfrak{k}}^F$	Specific interaction couple of the constituent α or the fluid phase
$[\boldsymbol{\mathcal{K}}^{S,F}\vert_E]$	Symmetric 9×9 or 3×3 matrix for the nonlinear equilibrium free energies of the solid and fluid, see (24.71), (24.72)
$\boldsymbol{L}^\alpha = \operatorname{grad} \boldsymbol{v}^\alpha$	Velocity gradient tensor of constituent α
$\boldsymbol{\ell}^\alpha$	Specific body couple of constituent α
$\overset{2\times 2}{\mathcal{M}}$	Viscosity of the COSSERAT fluid interaction couple, $\overset{2\times 2}{\mathcal{M}} = \big((\partial \boldsymbol{\mathfrak{k}}^F)/(\partial \bar{\nu}^F)\big)_0$
$\overset{4\times 4}{\mathcal{M}}$	Rank-4 fluid rotational viscosity tensor, $\overset{4\times 4}{\mathcal{M}} = \big((\partial \boldsymbol{m}^F)/(\partial \operatorname{grad} \bar{\boldsymbol{\omega}}^F)\big)_0$
$\boldsymbol{m}^\alpha$	(CAUCHY) couple stress tensor of constituent α
$\boldsymbol{\mathfrak{m}}^{\alpha,F}$	Specific interaction force of constituent α or fluid constituent
P	Pressure-type LAGRANGE parameter for the HMI and IM models
p_c	Configuration pressure
p^F_{th}	Thermodynamic pressure of the fluid constituent
p^F_R	Pore-fluid pressure
$\overset{2\times 2}{\mathcal{P}}$	Viscosity of the COSSERAT interaction couple, $\overset{2\times 2}{\mathcal{P}} = \big((\partial \boldsymbol{\mathfrak{m}}^F)/(\partial \boldsymbol{w}^F)\big)_0$
$\mathfrak{P}^{s^\alpha}$	Surface production rate density of the entropy of constituent α
$\boldsymbol{q}^\alpha$	Heat flux vector of constituent α
$\boldsymbol{q}^I = \boldsymbol{q}^S + \boldsymbol{q}^F$	Inner heat flux vector
$\overset{2\times 2}{\boldsymbol{Q}}$	Heat conductivity tensor, $\overset{2\times 2}{\boldsymbol{Q}} = \big((\partial \boldsymbol{q}^I)/(\partial \operatorname{grad} \vartheta)\big)_0$
$\boldsymbol{R}^\alpha$	Rotation tensor of constituent α, $\boldsymbol{R}^\alpha = \boldsymbol{F}^\alpha \big(\bar{\boldsymbol{U}}^\alpha\big)^{-1}$
$\bar{\boldsymbol{R}}^S$	COSSERAT rotation tensor of the solid constituent
$\mathcal{R}$	Set of constitutive response functions
$\mathfrak{r}^\alpha$	Specific radiation of constituent α
$\mathcal{S}$	Phase space
s^α	Specific entropy of constituent α
$\mathfrak{S}^\alpha$	Microscopic spin production density of constituent α, see (21.30)
$\{\mathsf{T}\}$	$\{\mathsf{T}\} = \{\boldsymbol{t}^F, \boldsymbol{m}^F, \boldsymbol{\mathfrak{m}}^F, \boldsymbol{\mathfrak{k}}^F, \boldsymbol{q}^I\}$
$\boldsymbol{t}^\alpha$	CAUCHY stress tensor of constituent α, $\boldsymbol{t}^F$, $\boldsymbol{t}^S$ for $\alpha = F, S$
$\boldsymbol{t}_{\text{elast}} = J \boldsymbol{\sigma}_{\text{elast}}$	J-weighted CAUCHY stress tensor
$\boldsymbol{U}^\alpha$	Right stretch (deformation) tensor of constituent α
$\bar{\boldsymbol{U}}^\alpha = (\boldsymbol{R}^\alpha)^T \boldsymbol{F}^\alpha$	Right COSSERAT stretch (deformation) tensor of constituent α
$\boldsymbol{V}$	Left stretch (deformation) tensor of constituent α
$\bar{\boldsymbol{V}}^\alpha = \boldsymbol{F}^\alpha (\bar{\boldsymbol{R}}^\alpha)^T$	Left COSSERAT stretch (deformation) tensor of constituent α
$\boldsymbol{v}^\alpha$	Velocity vector of constituent α
$\boldsymbol{v}$	Barycentric velocity of the mixture, $\boldsymbol{v} = \sum(\rho^\alpha \boldsymbol{v}^\alpha)/(\sum \rho^\alpha)$
$\{\mathsf{v}\}$	$\{\mathsf{v}\} = \{\bar{\boldsymbol{A}}^F, \operatorname{grad} \bar{\boldsymbol{\omega}}^F, \boldsymbol{w}^F, \nu^F, \operatorname{grad} \vartheta\}$
$W, \bar{W}, \tilde{W}, \hat{W}$	Free energy functions
$\hat{W} = W_{\text{isochor}}$	Free energy function describing isochoric deformations
$\boldsymbol{w}^F = \boldsymbol{v}^F - \boldsymbol{v}^S$	Difference velocity of the fluid minus solid constituents

$\boldsymbol{\mathcal{X}}$	Vector-valued quantity of the differentiated variables in the long entropy inequality (24.46)
$\boldsymbol{\mathcal{Y}}$	State variables
z^S	Constitutive variable accounting for the dynamics of the pore space.

Greek Symbols

α, β, γ	Constituent identifiers
$\bar{\boldsymbol{\Delta}}^\alpha, \bar{\boldsymbol{\Delta}}^F$	Nonsymmetric COSSERAT stretching tensor of constituent α, see (22.51)
$\boldsymbol{\Delta}^\alpha, \boldsymbol{\Delta}^F$	Nonsymmetric stretching tensor of constituent α, – of the fluid
$\bar{\boldsymbol{\delta}}^\alpha$	Angular (COSSERAT) diffusion velocity of constituent α, $\bar{\boldsymbol{\delta}}^\alpha = \bar{\boldsymbol{\omega}}^\alpha - \bar{\boldsymbol{\omega}}$
$\bar{\boldsymbol{\delta}}^F$	Angular diffusion velocity of the fluid constituent, $\bar{\boldsymbol{\delta}}^F = \big((\rho^S)/\rho\big)\,\bar{\nu}^F$
$\bar{\boldsymbol{\delta}}^S = -(\rho^S/\rho)\bar{\nu}^F$	Angular diffusion velocity of the solid constituent
ε^α	Specific internal energy of constituent α
$\boldsymbol{\Theta}^\alpha$	Specific tensor of inertia of a body element of constituent α
ϑ^α	Absolute temperature of constituent α
ι	Intensity parameter
$\lambda_1, \lambda_2, \lambda_3$	Eigenvalues of the left (or right) CAUCHY–GREEN deformation tensor
$\lambda_{\mathcal{C}}^F, \mu_{\mathcal{C}}^F$	'LAMÉ' constants of the fluid rank-2 tensor quantity $\mathcal{C}$
$\nu^{F,S}, \bar{\nu}^{F,S}$	(COSSERAT) volume fractions of the fluid and solid constituents
$(\nu^S)'^\alpha$	Total derivative of ν^S following the motion of constituent α
$\bar{\boldsymbol{\nu}}$	COSSERAT difference of the angular velocities of the fluid and solid constituents, $\bar{\boldsymbol{\nu}} = \bar{\boldsymbol{\omega}}^F - \bar{\boldsymbol{\omega}}^S$
π^{s^α}	Production rate density of the entropy of constituent α
π^s	Production rate density of the entropy of the mixture
ρ^α	Partial density of constituent α
$\hat{\rho}^{S,F}$	True (effective) mass density of the solid and fluid constituents, respectively
$\hat{\rho}_0^F$	True fluid density in the reference configuration
$\boldsymbol{\sigma}_{\text{elast}}$	Elastic CAUCHY stress tensor
$\boldsymbol{\phi}_s$	Entropy flux vector of the mixture
$\varphi_0, \varphi_1, \varphi_2$	Coefficients of the general representation of $\boldsymbol{t}_{\text{elast}}$ in terms of $\boldsymbol{B}$, see (24.186)

$\bar{\varphi}_0, \bar{\varphi}_1, \bar{\varphi}_2$	Coefficients of the general representation of $\boldsymbol{t}_{\text{elast}}$ in terms of $\hat{\boldsymbol{B}}$, see (24.187)
ψ^α	HELMHOLTZ free energy density of constituent α, $\psi^\alpha = \varepsilon^\alpha - s^\alpha \vartheta^\alpha$
$\psi^{S,F}$	HELMHOLTZ free energy density of the solid and fluid constituents
$\boldsymbol{\Omega}^\alpha$	Gyration tensor of constituent α, $\boldsymbol{\Omega}^\alpha = (\boldsymbol{R}^\alpha)'^\alpha (\boldsymbol{R}^\alpha)^T$
$\bar{\boldsymbol{\Omega}}^\alpha$	COSSERAT gyration tensor of constituent α
$\boldsymbol{\omega}$	Angular velocity of the mixture
$\bar{\boldsymbol{\omega}}^\alpha$	COSSERAT angular velocity of the director of constituent α

Miscellaneous Symbols

$(\cdot)'^\alpha$	Material derivative of $(\cdot)$ following constituent α
∇	Nabla operator
$\boldsymbol{A}^T$	Transpose of $\boldsymbol{A}$
$\boldsymbol{A}^{-T} = (\boldsymbol{A}^T)^{-1} =$	$(\boldsymbol{A}^{-1})^T$
$\|\boldsymbol{b}\|$	Norm of $\boldsymbol{b}$
CM	Compressible Model for solid and fluid
HMI	Hybrid Model I
HMII	Hybrid Model II

24.1 Introductory Remarks

Chapter 21 in this third volume of Fluid and Thermodynamics (FTD) was devoted to the dynamical equations of classical (BOLTZMANN) and polar (COSSERAT) continuous mixtures of an arbitrary but finite number of constituents. The focus was laid upon the structure of the balances of mass, linear and angular momenta, energy, and entropy and less upon the kinematic description of the processes. This was done in Chap. 22 of this volume, in which the kinematic fields of the constituent material particles are independent translations and rotations. No specific constitutive properties were introduced to combine the dynamic and kinematic statements to a set of governing equations for general processes under applied external fields.

This step is done with the aid of the Second Law of Thermodynamics—here the entropy principle. In Chaps. 17 and 18 of Vol. 2 of this treatise on FTD [42] the Second Law is introduced and formulated as an entropy balance, for which the production rate needs for all thermodynamic processes to be nonnegative, if such processes are to be physically realizable. The analytical exploitation of this requirement is for simple systems straightforward, but for mixtures of solid–fluid constituents, it is complex and often mathematically cumbersome. The reader can easily recognize this when recalling Chap. 23 of this volume, where heavy algebraic computations were needed for the exploitation of the entropy principle.

Recall that in Chaps. 17 and 18 of Vol. 2 of FTD two different forms of the exploitation of the entropy principle were presented.

1. the CLAUSIUS–DUHEM inequality with the treatment of COLEMAN–NOLL to handle open systems thermodynamics and
2. the general entropy inequality due to MÜLLER with arbitrary (i.e., unspecified) entropy flux for closed systems thermodynamics and the LAGRANGE parameter method of its exploitation by LIU.

The concepts of balance laws of mass, linear and angular momenta, energy, entropy, and micro-inertia of ν-component mixtures of polar constituents and kinematics of COSSERAT continua are assumed to be known. We shall base our thermodynamic analysis on the CLAUSIUS–DUHEM postulate. We are guided to do so by the experience gained in the last chapter, in which of the two forms of the entropy principle, exploitation of the analytically more complex one due to MÜLLER, applied to a classical mixture, led, apart from a wealth of inferences to rather complex and cumbersome computations. For a polar mixture of $n \geqslant 2$ constituents with a larger number of physical conservation laws than for a classical fluid and with independent translational and rotational kinematic variables that also imply a larger number of constitutive quantities, the corresponding computations of the exploitation are substantially more complex, implying, perhaps, unsurmountable difficulties. We shall, therefore, base the thermodynamic analysis on the CLAUSIUS–DUHEM postulate and will apply the exploitation of the entropy inequality, formulated for a *binary mixture model of an elastic solid and viscoelastic fluid*. In so doing, we shall treat the linear and angular momentum and energy equations as open equations, in which the supply terms can assume arbitrarily assigned values, as first systematically introduced by COLEMAN[1] and NOLL[2] in 1964 [10].[3] We will demonstrate that the resulting constitutive theory will be substantially simplified as compared to a completely closed system of equations (with no supply terms). Finally, as customary with the CLAUSIUS–DUHEM inequality, the entropy flux and entropy supply terms of the constituents are postulated with the DUHEM (1886) [17] and TRUESDELL (1957) [77] proposals stated in the relations (24.1) below.

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[1] For a brief biographical sketch of BERNARD D. COLEMAN (1930–2018), see **Fig. 24.1**.

[2] For a brief biographical sketch of WALTER NOLL (1925–2017), see **Fig. 24.2**.

[3] For brief biographies of

- RUDOLF JULIUS EMANUEL CLAUSIUS, see Fig. 17.8, Vol. 2 of this treatise, p. 330 [42];
- PIERRE MAURICE MARIE DUHEM, see Fig. 17.16, Vol. 2 of this treatise, p. 343 [42];
- WALTER NOLL, see [43];
- CLIFFORD AMBROSE TRUESDELL, see Fig. 22.1, this volume, p. 40.

Fig. 24.1 BERNARD D. COLEMAN (5 July 1930–2018)

BERNARD COLEMAN received his B.S. from Indiana University in 1951 and the M.S. and Ph.D. at Yale University in 1952 and 1954, respectively. He worked as a research chemist at the Carothers Research Laboratory of the du Pont Company, 1954–1957 and as Senior Fellow of the Mellon Institute, Pittsburgh 1957–1988. He was Professor of Mathematics 1967–1988, of Biology 1974–1988, and Chemistry 1984–1988, all at the Carnegie Mellon University in Pittsburgh. He is the J. WILLARD GIBBS Professor of Thermomechanics at Rutgers University since 1988.

Professor COLEMAN had many visiting and short-term research and teaching appointments, is recipient of the BINGHAM Medal of the Society of Rheology, 1984, holds an honorary doctorate of the University of Roma (II) (1993), and was elected to the College of Fellows of the American Institute of Medical and Biological Engineering, among others. COLEMAN has been a member of the Editorial Board of the Archives for Rational Mechanics and Analysis, 1962–2000. He was Editor-in-Chief of the Springer Tracts in Natural Philosophy and served in many positions of professional scientific organizations.

His research interests are/were in the mathematical sciences with emphasis on functional analysis in continuum mechanics and thermodynamics, material sciences, biophysics as DNA topology and DNA–protein interactions. In the fields of Continuum Mechanics and Thermodynamics, he wrote $\sim$20 papers with WALTER NOLL (and many more alone and with others including 190 works and two books, not including the many invited lecture and course notes) on the use of the Second Law of Thermodynamics and the (now) COLEMAN–NOLL procedure to exploit the CLAUSIUS–DUHEM inequality as an open physical system. These papers had a dominant effect on twentieth century's thermodynamics.

This text is based on a tabular vita of B.D. COLEMAN himself from the Internet. Additional information see [74]

Fig. 24.2 WALTER NOLL (January 7, 1925 in Berlin–June 6, 2017)

Professor WALTER NOLL was a German-American mathematician who, in particular, devoted his scientific activities to the foundations of continuum mechanics and thermodynamics. He started his studies of mathematics in 1946 at the Tech. University Berlin, but also visited courses at the Free University and the Humboldt University, both equally at Berlin, and at the University in Paris. In 1951, he received his Diploma degree in mathematics at TU Berlin and assumed there the position as Assistant working with the Profs. HAMEL and SZABO. In 1953, he entered the graduate school at Indiana University, was associated with Prof. TRUESDELL (see Fig. 22.1, this volume), where he earned, in 1954, his Ph.D. degree in applied mathematics. Thereafter, he returned to Berlin, but moved in1955 again to the USA to the University of Southern California and, starting in 1956 as Associate Professor at the Carnegie Institute of Technology, later the Carnegie Mellon University, where he assumed emeritus status in 1993. Professor NOLL had visiting positions at the Johns Hopkins University, the Karlsruhe University, the Israel University of Technology, École Polytéchnique in Nancy, the Universities at Pisa, Pavia, and Oxford. He was a fellow of the American Mathematical Society.

Starting in the mid-1950s, he began his collaboration with CLIFFORD TRUESDELL on the *Nonlinear Field Theories of Mechanics* [78], which became in 1965 part of the HANDBUCH DER PHYSIK. Apart from this, WALTER NOLL was single author of fundamental work in the mathematical formulation of mechanical principles [55], created in several papers primarily with Professor BERNARD COLEMAN and others the now standard method of the exploitation of the second law of thermodynamics in the form of the CLAUSIUS–DUHEM inequality [10] and was also well known for his creative mathematical writings. His work up to 1974 is reprinted in [55], see also [56].

A large professional and personal biography is given by IGNATIEFF [43]

One particular point on the Second Law of Thermodynamics applied to mixtures should be emphasized. This point concerns the application of the entropy principle. Even though we presented in Chap. 21 of this volume entropy balance laws for each constituent of the mixture, the imbalance statement that the entropy production must be positive is not required for each constituent individually, but for the sum of all constituent entropy productions together. This statement is weaker than if it would be applied to each constituent entropy production and gives the constitutive relations more flexibility, when reducing them to a physically realizable form.

Our text follows closely DIEBELS [13], pp. 73–135.

24.2 Thermodynamics of an Elastic Solid Plus a Viscoelastic Fluid

In the CLAUSIUS–DUHEM–COLEMAN–NOLL procedure to the entropy balance laws of constituent α one employs the following postulates:

$$\begin{aligned} (i)\ \ &\text{Entropy flux of constituent}\ \alpha = \frac{\boldsymbol{q}^{\alpha}}{\vartheta^{\alpha}},\\ (ii)\ \ &\text{Entropy supply of constituent}\ \alpha = \frac{\rho^{\alpha}\mathfrak{r}^{\alpha}}{\vartheta^{\alpha}}. \end{aligned} \tag{24.1}$$

In the above expressions, $\boldsymbol{q}^{\alpha}$ is the heat flux vector, $\mathfrak{r}^{\alpha}$ the heat supply, ϑ^{α} the absolute temperature, all of constituent α. With these expressions, the entropy balance of constituent α takes the form

$$\rho^{\alpha}(s^{\alpha})'^{\alpha} = -\text{div}\left(\frac{\boldsymbol{q}^{\alpha}}{\vartheta^{\alpha}}\right) + \frac{\rho^{\alpha}\mathfrak{r}^{\alpha}}{\vartheta^{\alpha}} + \pi^{s^{\alpha}} - \mathfrak{c}^{\alpha}s^{\alpha}. \tag{24.2}$$

In this equation, s^{α} is the entropy density of constituent α, $\pi^{s^{\alpha}}$ the entropy production density, and $\mathfrak{c}^{\alpha}$ the mass production density, both of constituent α.

It is convenient to introduce the HELMHOLTZ *free energy* of constituent α, $\psi^{\alpha} := \varepsilon^{\alpha} - s^{\alpha}\vartheta^{\alpha}$. From this expression, we deduce

$$\begin{aligned} (\psi^{\alpha})'^{\alpha} &= (\varepsilon^{\alpha})'^{\alpha} - (s^{\alpha})'^{\alpha}\vartheta^{\alpha} - s^{\alpha}(\vartheta^{\alpha})'^{\alpha},\\ s^{\alpha} &= \frac{(\varepsilon^{\alpha} - \psi^{\alpha})}{\vartheta^{\alpha}},\\ (s^{\alpha})'^{\alpha} &= \frac{1}{\vartheta^{\alpha}}\left((\varepsilon^{\alpha})'^{\alpha} - (\psi^{\alpha})'^{\alpha}\right) - \frac{s^{\alpha}}{\vartheta^{\alpha}}(\vartheta^{\alpha})'^{\alpha}. \end{aligned} \tag{24.3}$$

With (24.3), Eq. (24.2) becomes

$$\begin{aligned}
&\frac{1}{\vartheta^\alpha}\rho^\alpha\left((\varepsilon^\alpha)'^\alpha - (\psi^\alpha)'^\alpha\right) - \frac{\rho^\alpha s^\alpha}{\vartheta^\alpha}(\vartheta^\alpha)'^\alpha \\
&= -\mathrm{div}\left(\frac{\boldsymbol{q}^\alpha}{\vartheta^\alpha}\right) + \frac{\rho^\alpha \mathfrak{r}^\alpha}{\vartheta^\alpha} + \pi^{s^\alpha} - \mathfrak{c}^\alpha s^\alpha.
\end{aligned} \tag{24.4}$$

To eliminate from this entropy balance the time rate of change of the internal energy, $(\varepsilon^\alpha)'^\alpha$, we start from the constituent energy balance of Chap. 21, which we write in the form

$$\begin{aligned}
&\frac{\partial}{\partial t}\left\{\rho^\alpha\varepsilon^\alpha + \tfrac{1}{2}\rho^\alpha\boldsymbol{v}^\alpha\cdot\boldsymbol{v}^\alpha + \tfrac{1}{2}\rho^\alpha\boldsymbol{\Theta}^\alpha\bar{\boldsymbol{\omega}}^\alpha\cdot\bar{\boldsymbol{\omega}}^\alpha\right\} \\
&+\mathrm{div}\left\{\left[\rho^\alpha\varepsilon^\alpha + \tfrac{1}{2}\rho^\alpha\boldsymbol{v}^\alpha\cdot\boldsymbol{v}^\alpha + \tfrac{1}{2}\rho^\alpha\boldsymbol{\Theta}^\alpha\bar{\boldsymbol{\omega}}^\alpha\cdot\bar{\boldsymbol{\omega}}^\alpha\right]\boldsymbol{v}^\alpha\right\} \\
=\ &\mathrm{div}\left((\boldsymbol{t}^\alpha)^T\boldsymbol{v}^\alpha + (\boldsymbol{m}^\alpha)^T\bar{\boldsymbol{\omega}}^\alpha - \boldsymbol{q}^\alpha\right) + \rho^\alpha\boldsymbol{f}^\alpha\cdot\boldsymbol{v}^\alpha + \rho^\alpha\boldsymbol{\ell}^\alpha\cdot\bar{\boldsymbol{\omega}}^\alpha \\
&+\rho^\alpha\mathfrak{r}^\alpha + \mathfrak{e}^\alpha.
\end{aligned} \tag{24.5}$$

For notation, see Chap. 21. This equation is now transformed to a balance law of internal energy. This was already done in Chap. 21, but here we now wish to write this balance equation in terms of the COSSERAT kinematic quantities introduced in Chap. 22. The procedure is to employ in (24.5) the product rule of differentiation and then to use the information from the balances of mass, momenta and the kinematic statements of the COSSERAT formulation.

Consider first the left-hand side of (24.5): Employing the product rule of differentiation, we may easily demonstrate that

$$\begin{aligned}
&\frac{\partial}{\partial t}(\rho^\alpha\varepsilon^\alpha) + \mathrm{div}\,(\rho^\alpha\varepsilon^\alpha\boldsymbol{v}^\alpha) = \rho^\alpha(\varepsilon^\alpha)'^\alpha + \mathfrak{c}^\alpha\varepsilon^\alpha, \\
&\frac{\partial}{\partial t}\left(\tfrac{1}{2}\rho^\alpha\boldsymbol{v}^\alpha\cdot\boldsymbol{v}^\alpha\right) + \mathrm{div}\,\left(\left(\tfrac{1}{2}\rho^\alpha\boldsymbol{v}^\alpha\cdot\boldsymbol{v}^\alpha\right)\boldsymbol{v}^\alpha\right) \\
&\quad= \mathfrak{c}^\alpha\tfrac{1}{2}\left(\boldsymbol{v}^\alpha\cdot\boldsymbol{v}^\alpha\right) + \left(\rho^\alpha(\boldsymbol{v}^\alpha)'^\alpha\right)\cdot\boldsymbol{v}^\alpha, \\
&\frac{\partial}{\partial t}\left(\tfrac{1}{2}\rho^\alpha\boldsymbol{\Theta}^\alpha\bar{\boldsymbol{\omega}}^\alpha\cdot\bar{\boldsymbol{\omega}}^\alpha\right) + \mathrm{div}\,\left(\left(\tfrac{1}{2}\rho^\alpha\boldsymbol{\Theta}^\alpha\bar{\boldsymbol{\omega}}^\alpha\cdot\bar{\boldsymbol{\omega}}^\alpha\right)\cdot\boldsymbol{v}^\alpha\right) \\
&\quad= \tfrac{1}{2}\mathfrak{c}^\alpha\boldsymbol{\Theta}^\alpha\bar{\boldsymbol{\omega}}^\alpha\cdot\bar{\boldsymbol{\omega}}^\alpha + \left(\rho^\alpha\boldsymbol{\Theta}^\alpha(\bar{\boldsymbol{\omega}}^\alpha)'^\alpha\right)\cdot\bar{\boldsymbol{\omega}}^\alpha + \tfrac{1}{2}\rho^\alpha\bar{\boldsymbol{\omega}}^\alpha\cdot(\boldsymbol{\Theta}^\alpha)'^\alpha\bar{\boldsymbol{\omega}}^\alpha \\
&\quad= \tfrac{1}{2}\mathfrak{c}^\alpha\boldsymbol{\Theta}^\alpha\bar{\boldsymbol{\omega}}^\alpha\cdot\bar{\boldsymbol{\omega}}^\alpha + \left(\rho^\alpha\boldsymbol{\Theta}^\alpha(\bar{\boldsymbol{\omega}}^\alpha)'^\alpha\right)\cdot\bar{\boldsymbol{\omega}}^\alpha + \bar{\boldsymbol{\omega}}^\alpha\cdot\left[\mathrm{sym}\left(\rho^\alpha\bar{\boldsymbol{\Omega}}^\alpha\boldsymbol{\Theta}^\alpha\right)\bar{\boldsymbol{\omega}}^\alpha\right].
\end{aligned} \tag{24.6}$$

In the derivation of $(24.6)_3$ use was made of the symmetry of the micro-inertia tensor, $\boldsymbol{\Theta}^\alpha = (\boldsymbol{\Theta}^\alpha)^T$ and the fact that for COSSERAT continua (22.101) holds true. Moreover, in the above, the momentum and spin balances are

$$\begin{aligned}
\rho^\alpha(\boldsymbol{v}^\alpha)'^\alpha &= \mathrm{div}\,\boldsymbol{t}^\alpha + \rho^\alpha\boldsymbol{f}^\alpha + \mathfrak{m}^\alpha, \\
\rho^\alpha\boldsymbol{\Theta}^\alpha\bar{\boldsymbol{\omega}}'^\alpha &= \mathrm{div}\,\boldsymbol{m}^\alpha + \rho^\alpha\boldsymbol{\ell}^\alpha + \mathfrak{k}^\alpha.
\end{aligned} \tag{24.7}$$

Here, $\mathfrak{m}^\alpha$, $\mathfrak{k}^\alpha$ are the corresponding specific constituent momentum and spin production rates, respectively, which are substituted in the expression $(24.6)_{2,3}$.

The expression on the right-hand side (RHS) of (24.5) can be written as

$$
\begin{aligned}
\text{RHS (24.5)} = {} & \boldsymbol{v}^\alpha \cdot \operatorname{div} \boldsymbol{t}^\alpha + \boldsymbol{t}^{\alpha T} \cdot \boldsymbol{L}^\alpha + \bar{\boldsymbol{\omega}}^\alpha \cdot \operatorname{div} \boldsymbol{m}^\alpha + (\boldsymbol{m}^\alpha)^T \cdot \operatorname{grad} \bar{\boldsymbol{\omega}}^\alpha \\
& - \operatorname{div} \boldsymbol{q}^\alpha + \boldsymbol{v}^\alpha \cdot \rho^\alpha \boldsymbol{f}^\alpha + \bar{\boldsymbol{\omega}}^\alpha \cdot \rho^\alpha \boldsymbol{\ell}^\alpha + \rho^\alpha \mathfrak{r}^\alpha + \mathfrak{e}^\alpha . \qquad (24.8)
\end{aligned}
$$

If (24.6)–(24.8) are substituted into (24.5) a great number of terms drop out, and the balance law for ε^α takes the form

$$
\begin{aligned}
\rho^\alpha (\varepsilon^\alpha)'^\alpha = {} & \boldsymbol{t}^\alpha \cdot \bar{\boldsymbol{\Delta}}^\alpha + \boldsymbol{m}^\alpha \cdot \operatorname{grad} \bar{\boldsymbol{\omega}}^\alpha - \operatorname{div} \boldsymbol{q}^\alpha + \rho^\alpha \mathfrak{r}^\alpha + \mathfrak{E}^\alpha \\
& + \bar{\boldsymbol{\omega}}^\alpha \cdot \left[\operatorname{sym}(\rho^\alpha \bar{\boldsymbol{\Omega}}^\alpha \boldsymbol{\Theta}^\alpha) \bar{\boldsymbol{\omega}}^\alpha \right], \qquad (24.9)
\end{aligned}
$$

with

$$
\mathfrak{E}^\alpha = \mathfrak{e}^\alpha - \mathfrak{c}^\alpha \varepsilon^\alpha - \tfrac{1}{2} \mathfrak{c}^\alpha \boldsymbol{v}^\alpha \cdot \boldsymbol{v}^\alpha - \tfrac{1}{2} \mathfrak{c}^\alpha \boldsymbol{\Theta}^\alpha \bar{\boldsymbol{\omega}}^\alpha \cdot \bar{\boldsymbol{\omega}}^\alpha - \mathfrak{m}^\alpha \cdot \boldsymbol{v}^\alpha - \mathfrak{k}^\alpha \cdot \bar{\boldsymbol{\omega}}^\alpha . \qquad (24.10)
$$

In this equation, $\mathfrak{c}^\alpha$, $\mathfrak{m}^\alpha$, $\mathfrak{k}^\alpha$, and $\mathfrak{e}^\alpha$ are specific production rate densities of mass, momentum, angular momentum, and energy. Substitution into (24.4) gives, after some routine calculation,

$$
\begin{aligned}
& -\frac{\rho^\alpha}{\vartheta^\alpha} (\psi^\alpha)'^\alpha - \frac{\rho^\alpha s^\alpha}{\vartheta^\alpha} (\vartheta^\alpha)'^\alpha \\
& = -\frac{1}{\vartheta^\alpha} \left\{ \boldsymbol{t}^\alpha \cdot \bar{\boldsymbol{\Delta}}^\alpha + \boldsymbol{m}^\alpha \cdot \operatorname{grad} \bar{\boldsymbol{\omega}}^\alpha \right\} + \frac{\operatorname{grad} \vartheta^\alpha \cdot \boldsymbol{q}^\alpha}{(\vartheta^\alpha)^2} + \pi^{s^\alpha} \\
& \quad - \frac{1}{\vartheta^\alpha} \left\{ \mathfrak{E}^\alpha - \mathfrak{c}^\alpha \vartheta^\alpha s^\alpha + \bar{\boldsymbol{\omega}}^\alpha \cdot \left[\operatorname{sym}(\rho^\alpha \bar{\boldsymbol{\Omega}}^\alpha \boldsymbol{\Theta}^\alpha) \bar{\boldsymbol{\omega}}^\alpha \right] \right\} . \qquad (24.11)
\end{aligned}
$$

Note, in this expression the very last term vanishes if $\boldsymbol{\Theta}^\alpha = \Theta^\alpha \boldsymbol{I}$, since $\bar{\boldsymbol{\Omega}}^\alpha$ is skew-symmetric.

Let us now specialize for a binary mixture as follows:

- $\boldsymbol{\Theta}^\alpha = \Theta^\alpha \boldsymbol{I}$ isotropic moment of inertia.
- $\mathfrak{c}^\alpha = 0$ no phase change, no mass production of the constituents.
- $\mathfrak{e}^\alpha = 0$ no energy production due to phase change.
- $\vartheta^\alpha = \vartheta$ common (KELVIN) temperature for the constituents.

The assumption of an isotropic moment of inertia supposes the microstructure to possess isotropic spin orientation; on the other hand, to assume a common temperature means that energy exchanges between the constituents are ideally instantaneous.

With these assumptions (24.11) can be put into the following form:

$$
\begin{aligned}
-\rho^\alpha (\psi^\alpha)'^\alpha - \rho^\alpha s^\alpha \vartheta'^\alpha = {} & -\left(\boldsymbol{t}^\alpha \cdot \bar{\boldsymbol{\Delta}}^\alpha + \boldsymbol{m}^\alpha \cdot \operatorname{grad} \bar{\boldsymbol{\omega}}^\alpha \right) + \frac{\operatorname{grad} \vartheta \cdot \boldsymbol{q}^\alpha}{\vartheta} \\
& + \vartheta \pi^{s^\alpha} - (\mathfrak{m}^\alpha \cdot \boldsymbol{v}^\alpha + \mathfrak{k}^\alpha \cdot \bar{\boldsymbol{\omega}}^\alpha) . \qquad (24.12)
\end{aligned}
$$

For the derivation of this expression, all quantities in (24.11) involving $\mathfrak{e}^\alpha$ and $\mathfrak{c}^\alpha$ dropped out as did the term involving $\operatorname{sym}(\rho^\alpha \bar{\boldsymbol{\Omega}}^\alpha \boldsymbol{\Theta}^\alpha)$. The entropy inequality is now obtained by summing the expressions (24.12) over the solid and fluid constituents:

$$
\begin{aligned}
&-\sum_\alpha \rho^\alpha (\psi^\alpha)'^\alpha + \sum_\alpha \Big(\boldsymbol{t}^\alpha \cdot \bar{\boldsymbol{\varDelta}}^\alpha + \boldsymbol{m}^\alpha \cdot \operatorname{grad} \bar{\boldsymbol{\omega}}^\alpha \Big) - \sum_\alpha \rho^\alpha s^\alpha \vartheta'^\alpha \\
&-\frac{\operatorname{grad}\vartheta \cdot \sum_\alpha \boldsymbol{q}^\alpha}{\vartheta} + \sum_\alpha \boldsymbol{\mathfrak{m}}^\alpha \cdot \boldsymbol{v}^\alpha + \sum_\alpha \boldsymbol{\mathfrak{k}}^\alpha \cdot \bar{\boldsymbol{\omega}}^\alpha \\
= {}& \vartheta \sum_\alpha \pi^{s^\alpha} = \vartheta \pi^s \overset{!}{>} 0. \qquad (24.13)
\end{aligned}
$$

At this stage, four transformations need to be implemented in this expression. These are as follows:

$$
\begin{aligned}
\bullet \sum_\alpha \rho^\alpha s^\alpha \vartheta'^\alpha &= \sum_\alpha \rho^\alpha s^\alpha \left\{ \frac{\partial \vartheta}{\partial t} + \operatorname{grad}\vartheta \cdot (\boldsymbol{v}^\alpha + \boldsymbol{v} - \boldsymbol{v}) \right\} \\
&= \underbrace{\sum_\alpha \rho^\alpha s^\alpha}_{\rho s} \left\{ \frac{\partial \vartheta}{\partial t} + (\operatorname{grad}\vartheta) \cdot \boldsymbol{v} \right\} + \sum_\alpha \rho^\alpha s^\alpha \operatorname{grad}\vartheta \cdot \underbrace{(\boldsymbol{v}^\alpha - \boldsymbol{v})}_{\boldsymbol{d}^\alpha} \\
&= \rho s \frac{\mathrm{d}\vartheta}{\mathrm{d}\,t} + \sum_\alpha \rho^\alpha s^\alpha \boldsymbol{d}^\alpha \cdot \operatorname{grad}\vartheta,
\end{aligned}
$$

$$
\bullet -\frac{\operatorname{grad}\vartheta \cdot \sum_\alpha \boldsymbol{q}^\alpha}{\vartheta} - \sum_\alpha \rho^\alpha s^\alpha \boldsymbol{d}^\alpha \cdot \operatorname{grad}\vartheta = -\underbrace{\sum_\alpha \left(\frac{\boldsymbol{q}^\alpha}{\vartheta} + \rho^\alpha s^\alpha \boldsymbol{d}^\alpha \right)}_{\boldsymbol{\varphi}_s} \cdot \operatorname{grad}\vartheta,
$$

$$
\bullet \sum_\alpha \boldsymbol{\mathfrak{m}}^\alpha \cdot \boldsymbol{v}^\alpha = \boldsymbol{\mathfrak{m}}^F \cdot \boldsymbol{v}^F - \boldsymbol{\mathfrak{m}}^F \cdot \boldsymbol{v}^S = \boldsymbol{\mathfrak{m}}^F \cdot (\boldsymbol{v}^F - \boldsymbol{v}^S) = \boldsymbol{\mathfrak{m}}^F \cdot \boldsymbol{w}^F,
$$

$$
\bullet \sum_\alpha \boldsymbol{\mathfrak{k}}^\alpha \cdot \bar{\boldsymbol{\omega}}^\alpha = \boldsymbol{\mathfrak{k}}^F \cdot \bar{\boldsymbol{\omega}}^F - \boldsymbol{\mathfrak{k}}^F \cdot \bar{\boldsymbol{\omega}}^S = \boldsymbol{\mathfrak{k}}^F \cdot \underbrace{(\bar{\boldsymbol{\omega}}^F - \bar{\boldsymbol{\omega}}^S)}_{\bar{\boldsymbol{\nu}}^F} = \boldsymbol{\mathfrak{k}}^F \cdot \bar{\boldsymbol{\nu}}^F.
$$

Substituting these expressions into (24.13) yields

$$
\begin{aligned}
&-\sum_\alpha \rho^\alpha (\psi^\alpha)'^\alpha + \sum_\alpha \Big(\boldsymbol{t}^\alpha \cdot \bar{\boldsymbol{\varDelta}}^\alpha + \boldsymbol{m}^\alpha \cdot \operatorname{grad} \bar{\boldsymbol{\omega}}^\alpha \Big) - \rho s \dot{\vartheta} \\
&-\boldsymbol{\varphi}_s \cdot \operatorname{grad}\vartheta + \boldsymbol{\mathfrak{m}}^F \cdot \boldsymbol{w}^F + \boldsymbol{\mathfrak{k}}^F \cdot \hat{\boldsymbol{\nu}}^F \geqslant 0. \qquad (24.14)
\end{aligned}
$$

In the above analysis, we introduced two new quantities,

$$
\boldsymbol{d}^\alpha \equiv \boldsymbol{v}^\alpha - \boldsymbol{v}, \quad \text{and} \quad \bar{\boldsymbol{\delta}}^\alpha \equiv \bar{\boldsymbol{\omega}}^\alpha - \bar{\boldsymbol{\omega}},
$$

the barycentric diffusion velocity $\boldsymbol{d}^\alpha$ and the barycentric micro-rotation diffusion angular velocity $\bar{\boldsymbol{\delta}}^\alpha$. They are also given by

$$\boldsymbol{d}^\alpha = \boldsymbol{v}^\alpha - \sum_\beta \frac{\rho^\beta}{\rho}\boldsymbol{v}^\beta, \quad \bar{\boldsymbol{\delta}}^\alpha = \bar{\boldsymbol{\omega}}^\alpha - \sum_\beta \frac{\rho^\beta}{\rho}\bar{\boldsymbol{\omega}}^\beta, \quad \rho = \sum_\beta \rho^\beta.$$

For a binary solid–fluid mixture, they are obtained as

$$\begin{aligned} \boldsymbol{d}^S &= \frac{\rho^F}{\rho}\left(\boldsymbol{v}^S - \boldsymbol{v}^F\right) = -\frac{\rho^F}{\rho}\boldsymbol{w}^F, \quad \boldsymbol{d}^F = \frac{\rho^S}{\rho}\boldsymbol{w}^F, \quad \boldsymbol{w}^F = \boldsymbol{v}^F - \boldsymbol{v}^S, \\ \bar{\boldsymbol{\delta}}^S &= \frac{\rho^F}{\rho}\left(\bar{\boldsymbol{\omega}}^S - \bar{\boldsymbol{\omega}}^F\right) = -\frac{\rho^F}{\rho}\bar{\boldsymbol{\nu}}^F, \quad \bar{\boldsymbol{\delta}}^F = \frac{\rho^S}{\rho}\bar{\boldsymbol{\nu}}^F, \quad \bar{\boldsymbol{\nu}}^F = \bar{\boldsymbol{\omega}}^F - \bar{\boldsymbol{\omega}}^S. \end{aligned}$$

Remark: The diffusion velocities $\boldsymbol{d}^\alpha$ and $\bar{\boldsymbol{\delta}}^\alpha$ only occur in the subsequent analysis in a peripheral manner. Because the solid skeleton imprints the structure to the porous body, the solid constituent motion is regarded as the reference motion, so that the replacement of $\boldsymbol{d}^\alpha$ and $\bar{\boldsymbol{\delta}}^\alpha$ by $\boldsymbol{w}^\alpha$ and $\bar{\boldsymbol{\nu}}^\alpha$ is a natural consequence.

24.3 Evolution Equations for the Volume Fractions

We do not follow here GOODMAN and COWIN [36], or WILMANSKI [81] or FANG et al. [31], who all formulate different balance laws for the volume fractions.[4] We rather follow DIEBELS [13] who starts with the production-free solid mass balance equation

$$(\rho^S)'^S + \rho^S \operatorname{div} \boldsymbol{v}^S = 0. \tag{24.15}$$

With $\rho^S = \nu^S \hat{\rho}^S$, [$\nu^S$ = solid volume fraction; $\hat{\rho}^S$ = effective density, true density], relation (24.15) can also be written as

$$\begin{aligned} &\hat{\rho}^S\left[(\nu^S)'^S + z^S\nu^S \operatorname{div} \boldsymbol{v}^S\right] \\ &+ \nu^S\left[(\hat{\rho}^S)'^S + (1-z^S)\hat{\rho}^S \operatorname{div} \boldsymbol{v}^S\right] = 0, \end{aligned} \tag{24.16}$$

where $z^S \in [0, 1]$ is a new internal variable for which, however, no evolution equation is written down; rather, its introduction allows us to treat ν^S and $\hat{\rho}^S$ as independent process variables, so that (24.16) can be split into two equations

$$\begin{aligned} &(\nu^S)'^S + z^S\nu^S \operatorname{div} \boldsymbol{v}^S = 0, \\ &(\hat{\rho}^S)'^S + (1-z^S)\hat{\rho}^S \operatorname{div} \boldsymbol{v}^S = 0. \end{aligned} \tag{24.17}$$

The evolution equation for ν^F follows from the differentiated saturation condition $\nu^S + \nu^F = 1$, namely

---

[4] A separate thermodynamic formulation on granular-fluid continua will be given in Chap. 30.

$$
\begin{aligned}
&(\nu^F)'^F + (\nu^S)'^F = 0,\\
&(\nu^F)'^F + \left\{ \frac{\partial \nu^S}{\partial t} + (\operatorname{grad} \nu^S) \cdot \left(\underbrace{\boldsymbol{v}^F - \boldsymbol{v}^S}_{\boldsymbol{w}^F} + \boldsymbol{v}^S \right) \right\} = 0,\\
&(\nu^F)'^F + (\nu^S)'^S + (\operatorname{grad} \nu^S) \cdot \boldsymbol{w}^F = 0,
\end{aligned}
$$

or with (24.17)

$$
(\nu^F)'^F = z^S\, \nu^S \operatorname{div} \boldsymbol{v}^S - (\operatorname{grad} \nu^S) \cdot \boldsymbol{w}^F = 0. \tag{24.18}
$$

This procedure shows that the porosity, i.e., the volume fraction of the fluid is primarily governed by the solid constituent motion.

In the above, z^S is a new variable, which likely serves as a constitutive quantity. We will see that its selection as such may, however, be very special. For instance, as seen in $(24.17)_2$ a density-preserving solid requires $z^S \equiv 1$. This property makes DIEBELS' proposal of an additional variable z^S a bit suspicious as it primarily operates as a 'deus ex machina' that simplifies the implications in the exploitation process of the entropy inequality and rather not as a physical variable accounting for the granular structure of the solid–fluid mixture.

24.4 Process Variables and Constitutive Functions

In our search for a viscoelastic COSSERAT solid–fluid binary mixture, we have not found a thermodynamic model, in which both solid and fluid constituents would be treated as elastic and viscous. Modelers seem to be primarily interested in elastic or elastoplastic solids and ideal, perhaps viscous fluids.

- NEFF [53] presents a one-constituent constitutive model, in which only COSSERAT rotations exhibit a viscoelastic response, whilst the translational degrees of freedom are elastoplastic.
- VOLK [80] models a granular or porous material as an elastoplastic continuum, in which the translational and rotational motions exhibit elastoplastic behavior.
- DIEBELS [13] formulates a thermodynamic theory for a binary solid–fluid model, in which the solid constituent is treated elastically, while the fluid is viscoelastic.

In what follows, our ultimate aim is to design a constitutive model for a binary mixture, in which both constituents are viscoelastic as is the rotary motion. Such a generality is needed for instance for a solid–fluid mixture under rapid avalanching motion. Before presenting DIEBELS' model and perhaps an extension of it, we mention that in the formulation of any constitutive model, we employ the *rule of equipresence*; it states that all dependent constitutive variables should in a given constitutive class depend on the same numbers of independent constitutive variables. Reduction of certain independent constitutive variables in some dependent constitutive equation should be proven, not assumed. In mixture theories, maintenance of the rule of aequipresence is very often not kept, but replaced by the so-called *rule of phase separation*, which states that with the exception of production rate terms (these are constituent interaction terms), constitutive variables of constituent α should not depend on variables of constituent $\beta \neq \alpha$, see BOWEN [6, 8], PASSMAN et al. [60]. This postulate simplifies the mathematical analysis considerably, but also eliminates certain physical process behaviors. Most early mixture models were based on the rule of phase separation, rather than aequipresence.

The independent constitutive variables are called *process variables*, and the space spanned by these variables is called the *phase space* S. A 'wordy' version of S as chosen by DIEBELS may be expressed as

$$S = \left\{ \begin{array}{l} \text{[elastic solid], [elastic fluid], [viscous fluid],} \\ \text{[interaction terms], [porosity], [temperature]} \end{array} \right\}. \tag{24.19}$$

This equation wants to say that the properties contained in brackets must be expressed in terms of variables, which are representative for responses [elastic solids], [elastic fluids], etc. In terms of the kinematic and dynamic quantities of a COSSERAT binary mixture the bracketed properties of S above take the forms

$$\left.\begin{array}{ll} \text{[elastic solid]} & = [\bar{\boldsymbol{U}}^S, \nabla\bar{\boldsymbol{U}}^S, {}^R\boldsymbol{\mathcal{K}}^S, \nabla{}^R\boldsymbol{\mathcal{K}}^S], \\ \text{[elastic fluid]} & = [\hat{\rho}^F, \nabla\hat{\rho}^F], \\ \text{[viscous fluid]} & = [\bar{\boldsymbol{\Delta}}^F, \operatorname{grad}\bar{\boldsymbol{\omega}}^F], \\ \text{[constituent interaction]} & = [\boldsymbol{w}^F, \bar{\boldsymbol{\nu}}^F], \\ \text{[influence of porosity]} & = [\nu^S, \operatorname{grad}\nu^S], \\ \text{[temperature effect]} & = [\vartheta, \operatorname{grad}\vartheta], \end{array}\right\} \tag{24.20}$$

in which the notation $\nabla(\ldots) = \text{Grad}(\ldots)$ has been employed. In (24.20) the elastic behavior of the solid is expressed by the COSSERAT deformation tensor $\bar{\boldsymbol{U}}^S$, and the curvature tensor ${}^R\boldsymbol{\mathcal{K}}^S$ and their gradients $\nabla\bar{\boldsymbol{U}}^S$, $\nabla\,{}^R\boldsymbol{\mathcal{K}}^S$; these gradients are present in $(24.20)_1$ because in mixtures (which are not simple) such dependences are known to be needed for consistency (see BOWEN 1969 [4], 1976 [5]; MÜLLER 1968 [52]).

The list (24.20) is incomplete with regard to viscous behavior of the solid constituent. Such solid viscous behavior should not be ignored in slow and rapid flows of landslides and snow avalanches and any other rapid flows of granular assemblies. This viscous solid behavior would be described by

$$\text{[viscous solid]} = [\bar{\boldsymbol{\Delta}}^S, \operatorname{grad}\bar{\boldsymbol{\omega}}^S]. \tag{24.21}$$

Consideration of these terms, however, can likely be omitted in consolidation and groundwater hydraulic contexts, where the dominant contribution of dissipation is caused by the water motion in the pore space, expressed by $(24.20)_{3,4}$ and quantified by the COSSERAT translational stretching $\bar{\boldsymbol{\Delta}}^F$, diffusion of angular velocity $\operatorname{grad}\bar{\boldsymbol{\omega}}^F$

and DARCY-type translational and rotational difference velocities $\boldsymbol{w}^F$ and angular velocities $\bar{\boldsymbol{\nu}}^F$ in (24.20)$_{3,4}$. The influence of the porosity in (24.20)$_5$ is analogous to that of the fluid partial density in (24.20)$_2$. It is known in mixture theories that the latter gives rise to the partial (pore-fluid) pressure; so the former, due to the porosity dependence in (24.20)$_5$, will lead to the so-called configurational pressure. At last, (24.20)$_6$ describes the usual heat-conducting property of the mixture.

The variables listed in (24.20) are the independent variables for the following constitutive response functions

$$\mathcal{R}(S) = \left\{ s^\alpha, \varphi_s, \psi^\alpha, \boldsymbol{t}^\alpha, \boldsymbol{m}^\alpha, \mathfrak{m}^F, \mathfrak{k}^F, (\nu^S)'^\alpha \right\}. \tag{24.22}$$

Note, there is no need to include $\mathfrak{m}^S$, $\mathfrak{k}^S$, as these quantities are given by the fact that $\sum_\alpha \mathfrak{m}^\alpha = \mathbf{0}$, $\sum_\alpha \mathfrak{k}^\alpha = \mathbf{0}$. We, however, request a constitutive relation for $(\nu^S)'^S$, because this will fix z^S. [We could alternatively, also request an equation for z^S, instead.]

24.5 Handling of the Entropy Inequality

The entropy inequality (24.14) will be exploited in the sense of COLEMAN–NOLL, i.e., as an open system. This means:

- The balance laws of linear and angular momenta and the energy equation are assumed to have external source terms, which can be assigned arbitrarily. So, they do not form constraint conditions for the entropy inequality.
- When the differentiations are performed in the exploitation of the entropy inequality, derivatives in the solid quantities are expressed in terms of the solid motion, those of the fluid in terms of the fluid motion; derivatives of the temperature are, however, expressed in terms of the barycentric velocity.
- In the exploitation process of the entropy inequality, the question arises, whether the saturation condition must enter the entropy inequality (24.14) as a constraint condition. This would be done by extending the entropy inequality with the LAGRANGE parameter multiplied with the saturation equation. This need not be done here, as explained by DIEBELS [13], because in the present constitutive approach, the saturation condition is automatically satisfied by the evolution equations chosen for the volume fractions ν^S and ν^F, (24.17)$_1$ and (24.18) paired with a selection of a constitutive quantity for $(\nu^S)'^S$ or z^S.
- The reader may also ask why the balance of mass is not treated as a constraint condition in the exploitation of the entropy inequality, a procedure, required in fluid dynamics. The reason is that with the evolutions of the volume fractions according to (24.17)$_1$ and (24.18) the mixture density $\rho = \nu^S \hat{\rho}^S + \nu^F \hat{\rho}^F$ can automatically be updated, once ν^S, ν^F, $\hat{\rho}^S$, $\hat{\rho}^F$ are known.

The imbalance (24.14) must be executed subject to the conditions that the balance laws of linear and angular momenta and energy, as well as the equations of solid and fluid volume fractions. and the balance of mixture mass are simultaneously satisfied. The major advantage of the CLAUSIUS–DUHEM approach for an open system introduced above is the fact that none of these equations need to be incorporated in this evaluation process, because

(i) the balance laws of linear and angular momenta and energy are equipped with freely assignable supply terms,
(ii) the evolution equations for the volume fractions are so chosen that the saturation condition is automatically satisfied, and
(iii) the conservation of mixture mass is automatically fulfilled by updating the volume fraction expressions $(24.17)_1$ and (24.18).

This is the computational advantage of the CLAUSIUS–DUHEM inequality, coupled with the COLEMAN–NOLL approach of its exploitation and the introduction of variable z^S. In this case, this procedure implies that no side conditions need to be incorporated in the analysis when exploiting imbalance (24.14). For a phase space involving the variables (24.20), computations are nevertheless a respectful endeavor by executing the differentiations involving the chain rule of differentiation. These long computations yield the following extended inequality

$$
\begin{aligned}
\bar{\boldsymbol{\Delta}}^S \quad & \cdot \Bigg[\boldsymbol{t}^S - \bar{\boldsymbol{R}}^S \left(\rho^S \frac{\partial \psi^S}{\partial \bar{\boldsymbol{U}}^S} + \rho^F \frac{\partial \psi^F}{\partial \bar{\boldsymbol{U}}^S} \right) (\boldsymbol{F}^S)^T \\
& \quad + z^S \nu^S \left(\rho^S \frac{\partial \psi^S}{\partial \nu^S} + \rho^F \frac{\partial \psi^F}{\partial \nu^S} \right) \boldsymbol{I} \qquad\qquad (24.23)\\
& \quad + z^S \nu^S \left(\frac{\rho^S \hat{\rho}^F}{\nu^F} \frac{\partial \psi^S}{\partial \hat{\rho}^F} + \frac{\rho^F \hat{\rho}^F}{\nu^F} \frac{\partial \psi^F}{\partial \hat{\rho}^F} \right) \boldsymbol{I} \Bigg] +
\end{aligned}
$$

$$
(\nabla \bar{\boldsymbol{U}}^S)'^S \quad \cdot \left[-\rho^S \frac{\partial \psi^S}{\partial \nabla \bar{\boldsymbol{U}}^S} - \rho^F \frac{\partial \psi^F}{\partial \nabla \bar{\boldsymbol{U}}^S} \right] + \tag{24.24}
$$

$$
\nabla \nabla \bar{\boldsymbol{U}}^S \quad \cdot \left[-\rho^F \frac{\partial \psi^F}{\partial \nabla \bar{\boldsymbol{U}}^S} \otimes (\boldsymbol{F}^S)^{-1} \boldsymbol{w}^F \right] + \tag{24.25}
$$

$$
\operatorname{grad} \bar{\boldsymbol{\omega}}^S \quad \cdot \left[\boldsymbol{m}^S - \bar{\boldsymbol{R}}^S \left(\rho^S \frac{\partial \psi^S}{\partial {}^R \bar{\boldsymbol{\mathcal{K}}}^S} + \rho^F \frac{\partial \psi^F}{\partial {}^R \bar{\boldsymbol{\mathcal{K}}}^S} \right) (\boldsymbol{F}^S)^T \right] + \tag{24.26}
$$

$$
\left(\nabla^R \bar{\boldsymbol{\mathcal{K}}}^S \right)'^S \quad \cdot \left[-\rho^S \frac{\partial \psi^S}{\partial \nabla^R \bar{\boldsymbol{\mathcal{K}}}^S} - \rho^F \frac{\partial \psi^F}{\partial \nabla^R \bar{\boldsymbol{\mathcal{K}}}^S} \right] + \tag{24.27}
$$

$$
\nabla \nabla^R \bar{\boldsymbol{\mathcal{K}}}^S \quad \cdot \left[-\rho^F \frac{\partial \psi^F}{\partial \nabla^R \bar{\boldsymbol{\mathcal{K}}}^S} \otimes (\boldsymbol{F}^S)^{-1} \boldsymbol{w}^F \right] + \tag{24.28}
$$

$$
\left(\operatorname{grad} \hat{\rho}^F \right)'^F \quad \cdot \left[-\rho^S \frac{\partial \psi^S}{\partial \operatorname{grad} \hat{\rho}^F} - \rho^F \frac{\partial \psi^F}{\partial \operatorname{grad} \hat{\rho}^F} \right] + \tag{24.29}
$$

$$
\operatorname{grad} \operatorname{grad} \hat{\rho}^F \quad \cdot \left[\rho^S \frac{\partial \psi^S}{\partial \operatorname{grad} \hat{\rho}^F} \otimes \boldsymbol{w}^F \right] + \tag{24.30}
$$

$$
\left(\bar{\boldsymbol{\Delta}}^F \right)'^F \quad \cdot \left[-\rho^S \frac{\partial \psi^S}{\partial \bar{\boldsymbol{\Delta}}^F} - \rho^F \frac{\partial \psi^F}{\partial \bar{\boldsymbol{\Delta}}^F} \right] + \tag{24.31}
$$

$$\operatorname{grad}\bar{\boldsymbol{\Delta}}^F \cdot \left[\rho^S \frac{\partial \psi^S}{\partial \bar{\boldsymbol{\Delta}}^F} \otimes \boldsymbol{w}^F\right] + \tag{24.32}$$

$$\big(\operatorname{grad}\bar{\boldsymbol{\omega}}^F\big)'^F \cdot \left[-\rho^S \frac{\partial \psi^S}{\partial \operatorname{grad}\bar{\boldsymbol{\omega}}^F} - \rho^F \frac{\partial \psi^F}{\partial \operatorname{grad}\bar{\boldsymbol{\omega}}^F}\right] + \tag{24.33}$$

$$\operatorname{grad}\operatorname{grad}\bar{\boldsymbol{\omega}}^F \cdot \left[\rho^S \frac{\partial \psi^S}{\partial \operatorname{grad}\bar{\boldsymbol{\omega}}^F} \otimes \boldsymbol{w}^F\right] + \tag{24.34}$$

$$\big((\boldsymbol{x}^F)'' - (\boldsymbol{x}^S)''\big) \cdot \left[-\rho^S \frac{\partial \psi^S}{\partial \boldsymbol{w}^F} - \rho^F \frac{\partial \psi^F}{\partial \boldsymbol{w}^F}\right] \tag{24.35}$$

$$\operatorname{grad}\boldsymbol{x}'^F \cdot \rho^S \frac{\partial \psi^S}{\partial \boldsymbol{w}^F} \otimes \boldsymbol{w}^F + \operatorname{grad}\boldsymbol{x}'^S \cdot \rho^F \frac{\partial \psi^F}{\partial \boldsymbol{w}^F} \otimes \boldsymbol{w}^F + \tag{24.36}$$

$$((\bar{\boldsymbol{\omega}}^F)'^F - (\bar{\boldsymbol{\omega}}^S)'^S) \cdot \left[-\rho^S \frac{\partial \psi^S}{\partial \bar{\boldsymbol{\nu}}^F} - \rho^F \frac{\partial \psi^F}{\partial \bar{\boldsymbol{\nu}}^F}\right] + \tag{24.37}$$

$$\operatorname{grad}\bar{\boldsymbol{\omega}}^F \cdot \rho^S \frac{\partial \psi^S}{\partial \bar{\boldsymbol{\nu}}^F} \otimes \boldsymbol{w}^F + \operatorname{grad}\boldsymbol{\omega}^S \cdot \rho^F \frac{\partial \psi^F}{\partial \bar{\boldsymbol{\nu}}^F} \otimes \boldsymbol{w}^F + \tag{24.38}$$

$$\big(\operatorname{grad}\nu^S\big)'^S \cdot \left[-\rho^S \frac{\partial \psi^S}{\partial \operatorname{grad}\nu^S} - \rho^F \frac{\partial \psi^F}{\partial \operatorname{grad}\nu^S}\right] + \tag{24.39}$$

$$\operatorname{grad}\operatorname{grad}\nu^S \cdot \left[-\rho^F \frac{\partial \psi^F}{\partial \operatorname{grad}\nu^S} \otimes \boldsymbol{w}^F\right] + \tag{24.40}$$

$$\dot{\vartheta} \cdot \left[-\rho s - \rho^S \frac{\partial \psi^S}{\partial \vartheta} - \rho^F \frac{\partial \psi^F}{\partial \vartheta}\right] + \tag{24.41}$$

$$(\operatorname{grad}\vartheta)^{\dot{}} \cdot \left[-\rho^S \frac{\partial \psi^S}{\partial \operatorname{grad}\vartheta} - \rho^F \frac{\partial \psi^F}{\partial \operatorname{grad}\vartheta}\right] + \tag{24.42}$$

$$\operatorname{grad}\operatorname{grad}\vartheta \cdot \left[-\rho^S \frac{\partial \psi^S}{\partial \operatorname{grad}\vartheta} \otimes \boldsymbol{d}^S - \rho^F \frac{\partial \psi^F}{\partial \operatorname{grad}\vartheta} \otimes \boldsymbol{d}^F\right] + \tag{24.43}$$

$$\mathcal{D} \geqslant 0. \tag{24.44}$$

It will be shown below that (24.23)–(24.43) will identically vanish. Then, it follows that $\mathcal{D}$ by itself must be nonnegative; $\mathcal{D}$ is the so-called *residual entropy inequality*, given by

$$\begin{aligned}
\mathcal{D} = {} & \bar{\boldsymbol{\Delta}}^F \cdot \left[\boldsymbol{t}^F + \rho^S\,\hat{\rho}^F \frac{\partial \psi^S}{\partial \hat{\rho}^F}\boldsymbol{I} + \rho^F\,\hat{\rho}^F \frac{\partial \psi^F}{\partial \hat{\rho}^F}\boldsymbol{I} + \rho^S \frac{\partial \psi^S}{\partial \boldsymbol{w}^F} \otimes \boldsymbol{w}^F\right] + \\
& \operatorname{grad}\bar{\boldsymbol{\omega}}^F \cdot \left[\boldsymbol{m}^F + \rho^S \frac{\partial \psi^S}{\partial \bar{\boldsymbol{\nu}}^F} \otimes \boldsymbol{w}^F\right] - \boldsymbol{\mathfrak{m}}^F \cdot \boldsymbol{w}^F - \boldsymbol{\mathfrak{k}}^F \cdot \bar{\boldsymbol{\nu}}^F - \\
& \operatorname{grad}\vartheta \cdot \left[\boldsymbol{\varphi}_s + \rho^S \frac{\partial \psi^S}{\partial \vartheta}\boldsymbol{d}^S + \rho^F \frac{\partial \psi^F}{\partial \vartheta}\boldsymbol{d}^F\right] - \\
& \boldsymbol{w}^F \cdot \left[\frac{\rho^S\,\hat{\rho}^F}{\nu^F} \frac{\partial \psi^S}{\partial \hat{\rho}^F} + \frac{\rho^F\,\hat{\rho}^F}{\nu^F} \frac{\partial \psi^F}{\partial \hat{\rho}^F} + \rho^F \frac{\partial \psi^F}{\partial \nu^S}\right] \operatorname{grad}\nu^S -
\end{aligned}$$

$$\rho^F \frac{\partial \psi^F}{\partial \bar{\boldsymbol{U}}^S} \cdot \nabla \bar{\boldsymbol{U}}^S (\boldsymbol{F}^S)^{-1} \boldsymbol{w}^F - \rho^F \frac{\partial \psi^F}{\partial^R \bar{\boldsymbol{\mathcal{K}}}^S} \cdot \nabla^R \bar{\boldsymbol{\mathcal{K}}}^S (\boldsymbol{F}^S)^{-1} \boldsymbol{w}^F +$$

$$\boldsymbol{w}^F \cdot \rho^S \frac{\partial \psi^S}{\partial \hat{\rho}^F} \operatorname{grad} \hat{\rho}^F \geqslant 0. \tag{24.45}$$

Note that every line in the above extended entropy inequality bears its own number of identification. These results agree with those of DIEBELS as obtained by him in 2000 [13].

We shall prove below that (24.23)–(24.43) together all vanish as a global statement, so that at last only the imbalance $\mathcal{D} \geqslant 0$ must be fulfilled. This vanishing of (24.23)–(24.43) will imply a large number of inferences, which, in particular, will reduce the number of independent variables in the constituent HELMHOLTZ free energies.

Note that the expressions (24.23)–(24.43) in the long version of the entropy inequality are linear in the time and space derivatives of the process variables. On the contrary, the residual inequality (24.45) contains only process variables, and the expression in (24.45) is nonlinear in these variables. Because the entropy inequality must hold for all thermodynamic processes for which the derivatives of the process variables may have any assigned value, it follows that (24.23)–(24.43) must vanish. [The proof of this fact has been given at several places in Chap. 23 of this volume for a diffusive mixture. It is easily seen that this proof can readily be extended to the present situation]. We conclude that the residual inequality must be the imbalance $\mathcal{D} \geqslant 0$.

24.6 Detailed Exploitation of (24.23)–(24.43)

A short way of writing the long entropy inequality is as follows:

$$\boldsymbol{\mathcal{X}} \cdot \boldsymbol{a}(\boldsymbol{\mathcal{Y}}) + \mathcal{D}(\boldsymbol{\mathcal{Y}}) \geqslant 0, \tag{24.46}$$

in which $\boldsymbol{\mathcal{X}}$ are the terms in (24.23)–(24.43), which are expressed as some space and time derivatives of the state variables $\boldsymbol{\mathcal{Y}}$ or other variables arising in the field equations; $\boldsymbol{a}$ is the shorthand notation for the collection of the expressions in braces in (24.23)–(24.43), and the dot, $)\cdot($, is the symbol of the inner products between the components of $\boldsymbol{\mathcal{X}}$ and $\boldsymbol{a}$. The main theorem of the exploitation of the entropy inequality states that $\sum_\nu \mathcal{X}_\nu \cdot a_\nu = 0$ for ν corresponding to each line in (24.23)–(24.43). The statements following from this requirement are sometimes called the LIU-identities: In this case the following inferences can be drawn.

- Equation (24.23): Because $\bar{\boldsymbol{\Delta}}^S$ is a full rank-2 tensor, we have $[\cdot]_{(24.23)} = 0$, or

$$\begin{aligned}\boldsymbol{t}^S = \bar{\boldsymbol{R}}^S &\left[\rho^S \frac{\partial\psi^S}{\partial\bar{\boldsymbol{U}}^S} + \rho^F \frac{\partial\psi^F}{\partial\bar{\boldsymbol{U}}^S}\right](\boldsymbol{F}^S)^T \\ &- z^S\nu^S\left[\frac{\rho^S\,\hat{\rho}^F}{\nu^F}\,\frac{\partial\psi^S}{\partial\hat{\rho}^F} + \frac{\rho^F\,\hat{\rho}^F}{\nu^F}\,\frac{\partial\psi^F}{\partial\hat{\rho}^F} + \rho^S\,\frac{\partial\psi^S}{\partial\nu^S} + \rho^F\,\frac{\partial\psi^F}{\partial\nu^S}\right]\boldsymbol{I}. \qquad (24.47)\end{aligned}$$

The solid partial stress tensor $\boldsymbol{t}^S$ is fully determined, if the free energies ψ^S, ψ^F and ρ^S, ρ^F, ν^S, ν^F, and z^S are known. It consists of a contribution, directly related to the COSSERAT strains

$$\bar{\boldsymbol{R}}^S\left[\rho^S \frac{\partial\psi^S}{\partial\bar{\boldsymbol{U}}^S} + \rho^F \frac{\partial\psi^F}{\partial\bar{\boldsymbol{U}}^S}\right](\boldsymbol{F}^S)^T$$

(first line in (24.47)), which is nonsymmetric, and a pressure term (second line in (24.47)), which may be split into

$$\begin{aligned} p_c &= z^S\nu^S\left[\rho^S\,\frac{\partial\psi^S}{\partial\nu^S} + \rho^F\,\frac{\partial\psi^F}{\partial\nu^S}\right] && \text{configurational pressure,} \\ p_{\text{th}} &= z^S\nu^S\left[\frac{\rho^S\,\hat{\rho}^F}{\nu^F}\,\frac{\partial\psi^S}{\partial\hat{\rho}^F} + \frac{\rho^F\,\hat{\rho}^F}{\nu^F}\,\frac{\partial\psi^F}{\partial\hat{\rho}^F}\right] && \text{thermodynamic pressure.}\end{aligned} \qquad (24.48)$$

- Equation (24.26): Here, grad $\bar{\boldsymbol{\omega}}^S$ is a full rank-2 tensor, so that $[\cdot]_{(24.46)} = 0$, implying

$$\boldsymbol{m}^S = \bar{\boldsymbol{R}}^S\left[\rho^S \frac{\partial\psi^S}{\partial^R\bar{\boldsymbol{\mathcal{K}}}^S} + \rho^F \frac{\partial\psi^F}{\partial^R\bar{\boldsymbol{\mathcal{K}}}^S}\right](\boldsymbol{F}^S)^T \qquad (24.49)$$

for the nonsymmetric couple stress tensor, in which quantities in braces in (24.47) and (24.49) are referred to the reference configuration and back rotated COSSERAT configuration, respectively, which are pushed forward by the forward transport into the present configuration.

- Equation (24.41): Since $\dot{\vartheta}$ is a scalar, $[\cdot]_{(24.41)} = 0$ implies

$$\rho s = -\rho^S\frac{\partial\psi^S}{\partial\vartheta} - \rho^F\frac{\partial\psi^F}{\partial\vartheta}. \qquad (24.50)$$

So, the mixture entropy is given by $-\sum_\alpha \rho^\alpha(\partial\psi^\alpha/\partial\vartheta)$, as one would expect. The results (24.47), (24.49), and (24.50) reflect the expected properties that are revealed by the LEGENDRE transformation on ψ^S and ψ^F.

- Equations (24.24), (24.25): As $\nabla\,\nabla\bar{\boldsymbol{U}}^S$ is a full rank-4 tensor, $[\cdot]_{(24.25)} = 0$ implies that

$$\rho^F\,\frac{\partial\psi^F}{\partial\nabla\bar{\boldsymbol{U}}^S}\otimes(\boldsymbol{F}^S)^{-1}\boldsymbol{w}^F = 0,\ \forall(\boldsymbol{F}^S)^{-1}\boldsymbol{w}^F \implies \frac{\partial\psi^F}{\partial\nabla\bar{\boldsymbol{U}}^S} = 0,\ \forall\nabla\bar{\boldsymbol{U}}^S.$$

Using this result in the expression $[\cdot]_{(24.24)} = 0$ then yields also $\partial\psi^S/\partial\nabla\,\bar{\boldsymbol{U}}^S = 0$. Thus,

$$\frac{\partial\psi^S}{\partial\nabla\,\bar{\boldsymbol{U}}^S} = \frac{\partial\psi^F}{\partial\nabla\,\bar{\boldsymbol{U}}^S} = \mathbf{0}. \tag{24.51}$$

The free energies ψ^S and ψ^F cannot depend on $\nabla\bar{\boldsymbol{U}}^S$.

- Equations (24.27), (24.28): The inferences here are analogous to the above ones; so,

$$\frac{\partial\psi^S}{\partial\nabla\,^R\bar{\boldsymbol{\mathcal{K}}}^S} = \frac{\partial\psi^F}{\partial\nabla\,^R\bar{\boldsymbol{\mathcal{K}}}^S} = \mathbf{0}. \tag{24.52}$$

Hence, the free energies ψ^S and ψ^F can neither depend on $\nabla^R\bar{\boldsymbol{\mathcal{K}}}^S$.
The inferences (24.51) and (24.52) have been obtained with the tacit assumption that these relations, (24.51) and (24.52), also hold when $\boldsymbol{w}^F$ goes through a zero value. This result is based upon the natural 'principle of continuity', namely that a continuous transition of $\boldsymbol{w}^F$ through zero will not reveal a discontinuity of the quantities (24.51) and (24.52).

- Equations (24.31), (24.32): Here, the situation is analogous to (24.51) and (24.52). More specifically, (24.32) implies, since $\boldsymbol{w}^F$ may have any value, that $\partial\psi^S/\partial\bar{\boldsymbol{\Delta}}^F = \mathbf{0}$. Thus,

$$\frac{\partial\psi^S}{\partial\bar{\boldsymbol{\Delta}}^F} = \frac{\partial\psi^F}{\partial\bar{\boldsymbol{\Delta}}^F} = \mathbf{0}. \tag{24.53}$$

The free energies ψ^S and ψ^F cannot depend on $\bar{\boldsymbol{\Delta}}^S$.

- Equations (24.33), (24.34): analogous arguments imply here

$$\frac{\partial\psi^S}{\partial\mathrm{grad}\,\bar{\boldsymbol{\omega}}^F} = \frac{\partial\psi^F}{\partial\mathrm{grad}\,\bar{\boldsymbol{\omega}}^F} = \mathbf{0}. \tag{24.54}$$

So, ψ^S and ψ^F cannot depend on $\mathrm{grad}\,\bar{\boldsymbol{\omega}}^F$ either.

- Equations (24.35), (24.36): These two lines are a bit more difficult to analyze. Line (24.36) can also be written as

$$\begin{aligned}&\underbrace{\mathrm{grad}\,\left(\boldsymbol{x}'^F - \boldsymbol{x}'^S\right)}_{\mathrm{grad}\,\boldsymbol{w}^F}\left[\rho^S\frac{\partial\psi^S}{\partial\boldsymbol{w}^F}\otimes\boldsymbol{w}^F\right]\\ &+\mathrm{grad}\,\boldsymbol{v}^S\cdot\left\{\rho^S\frac{\partial\psi^S}{\partial\boldsymbol{w}^F}\otimes\boldsymbol{w}^F + \rho^F\frac{\partial\psi^F}{\partial\boldsymbol{w}^F}\otimes\boldsymbol{w}^F\right\} = 0.\end{aligned} \tag{24.55}$$

Because $\mathrm{grad}\,\boldsymbol{w}^F$ is not a process variable, the first line of this expression is linear in $\mathrm{grad}\,\boldsymbol{w}^F$, so that $\partial\psi^S/\partial\boldsymbol{w}^F = \mathbf{0}$. With this inference, $[\cdot]_{(24.35)}$ vanishes identically.

Therefore,

$$\frac{\partial \psi^S}{\partial \boldsymbol{w}^F} = \frac{\partial \psi^F}{\partial \boldsymbol{w}^F} = \boldsymbol{0}. \tag{24.56}$$

- Equations (24.37), (24.38): These two lines are analogous to (24.35) and (24.36). By the same method as above, we may show that

  $$\frac{\partial \psi^S}{\partial \bar{\boldsymbol{\nu}}^F} = \frac{\partial \psi^F}{\partial \bar{\boldsymbol{\nu}}^F} = \boldsymbol{0}. \tag{24.57}$$

  The free energies are also independent of $\bar{\boldsymbol{\nu}}^F$.
- Equations (24.29), (24.39), (24.42): The expressions on these lines are linear functionals of

  $$[\mathrm{grad}\,(\hat{\rho}^F)]', \quad [\mathrm{grad}\,(\nu^S)]'^S, \quad [\mathrm{grad}\,(\vartheta)]^{\cdot} \tag{24.58}$$

  so that the corresponding brackets $[\cdot]$ must vanish. This yields

  $$\begin{aligned} \rho^S \frac{\partial \psi^S}{\partial \mathrm{grad}\,\hat{\rho}^F} + \rho^F \frac{\partial \psi^F}{\partial \mathrm{grad}\,\hat{\rho}^F} &= \boldsymbol{0}, \\ \rho^S \frac{\partial \psi^S}{\partial \mathrm{grad}\,\nu^S} + \rho^F \frac{\partial \psi^F}{\partial \mathrm{grad}\,\nu^S} &= \boldsymbol{0}, \\ \rho^S \frac{\partial \psi^S}{\partial \mathrm{grad}\,\vartheta} + \rho^F \frac{\partial \psi^F}{\partial \mathrm{grad}\,\vartheta} &= \boldsymbol{0}. \end{aligned} \tag{24.59}$$

- Equations (24.30), (24.40), (24.43): Because in these statements the prefactors of the braces $[\cdot]$ are the grad grad -operators, their inner products with $[\cdot]$ implies that $[\cdot]$ need to be skew-symmetric, so that

  $$\begin{aligned} \rho^S \frac{\partial \psi^S}{\partial \mathrm{grad}\,\hat{\rho}^F} \otimes \boldsymbol{w}^F &= -\boldsymbol{w}^F \otimes \rho^S \frac{\partial \psi^S}{\partial \mathrm{grad}\,\hat{\rho}^F} \\ \rho^F \frac{\partial \psi^F}{\partial \mathrm{grad}\,\nu^S} \otimes \boldsymbol{w}^F &= -\boldsymbol{w}^F \otimes \rho^S \frac{\partial \psi^S}{\partial \mathrm{grad}\,\nu^S}, \\ \rho^S \frac{\partial \psi^S}{\partial \mathrm{grad}\,\vartheta} \otimes \boldsymbol{w}^F &= -\boldsymbol{w}^F \otimes \rho^S \frac{\partial \psi^S}{\partial \mathrm{grad}\,\vartheta}. \end{aligned} \tag{24.60}$$

The statements (24.47)–(24.60) summarize all the inferences that could be drawn from the (long) entropy inequality. They imply that the state variables can be grouped into two disjoint sets

$$\begin{aligned} &\left\{\bar{\boldsymbol{U}}^S,\, {}^R\boldsymbol{\mathcal{K}}^S,\, \hat{\rho}^F,\, \operatorname{grad}\hat{\rho}^F,\, \nu^S,\, \operatorname{grad}\nu^S,\, \vartheta,\, \operatorname{grad}\vartheta\right\} \quad \text{(set I)},\\ &\left\{\nabla\bar{\boldsymbol{U}}^S,\, \nabla{}^R\boldsymbol{\mathcal{K}}^S,\, \bar{\boldsymbol{\Delta}}^F,\, \operatorname{grad}\bar{\boldsymbol{\omega}},\, \boldsymbol{w}^F,\, \bar{\boldsymbol{\nu}}^F\right\} \quad \text{(set II)}. \end{aligned} \tag{24.61}$$

We demonstrated that the free energies ψ^S and ψ^F can only depend on the variables of the first set but not on those of the second set, viz.,

$$\psi^\alpha = \psi^\alpha\left\{\bar{\boldsymbol{U}}^S,\, {}^R\boldsymbol{\mathcal{K}}^S,\, \hat{\rho}^F,\, \operatorname{grad}\hat{\rho}^F,\, \nu^S,\, \operatorname{grad}\nu^S,\, \vartheta,\, \operatorname{grad}\vartheta\right\},\ \ \alpha = S, F. \tag{24.62}$$

We proved that the solid stress, $\boldsymbol{t}^S$, solid couple stress, $\boldsymbol{m}^S$, and the entropy, s, only depend on certain derivatives of the HELMHOLTZ free energies ψ^S and ψ^F, as demonstrated in (24.47), (24.49), and (24.50). Moreover, $(24.3)_1$, together with the definition $s^\alpha = -\partial\psi^\alpha/\partial\vartheta$ implies

$$\varepsilon^\alpha = \psi^\alpha + s^\alpha\vartheta = \psi^\alpha - \vartheta\frac{\partial\psi^\alpha}{\partial\vartheta} = -\vartheta^2\frac{\partial}{\partial\vartheta}\left(\frac{\psi^\alpha}{\vartheta}\right),$$

so that the HELMHOLTZ free energy of constituent α also determines the internal energy of constituent α. Within the function class (24.62) the functions ψ^α are, however, not completely free; they must satisfy the constraints (24.59) and (24.60).

24.7 Behavior at and Near Thermodynamic Equilibrium

Our next task is to draw further inferences from the residual inequality (24.45) close to thermodynamic equilibrium. The latter is defined by the request that in such an equilibrium process no entropy is produced. Thus, $\mathcal{D} \geqslant 0$ reduces in equilibrium to $\mathcal{D}|_E = 0$, in which the subscript $(\cdot)|_E$ identifies this equilibrium. It follows that $\mathcal{D}$ assumes its minimum in equilibrium. Introducing the *inner heat flux vector*

$$\boldsymbol{q}^I := \sum_\alpha \boldsymbol{q}^\alpha = \boldsymbol{q}^S + \boldsymbol{q}^F \tag{24.63}$$

and

$$\begin{aligned} \boldsymbol{\varphi}_s &= \sum_\alpha\left(\frac{\boldsymbol{q}^\alpha}{\vartheta} + \rho^\alpha s^\alpha \boldsymbol{d}^\alpha\right) = \sum_\alpha\left(\frac{\boldsymbol{q}^\alpha}{\vartheta} - \rho^\alpha\frac{\partial\psi^\alpha}{\partial\vartheta}\boldsymbol{d}^\alpha\right),\\ \boldsymbol{\varphi}_s &+ \sum_\alpha \rho^\alpha\frac{\partial\psi^\alpha}{\partial\vartheta}\boldsymbol{d}^\alpha = \sum_\alpha\frac{\boldsymbol{q}^\alpha}{\vartheta}, \end{aligned} \tag{24.64}$$

the residual inequality takes the form

$$
\begin{aligned}
\mathcal{D} = \bar{\boldsymbol{\Delta}}^F \cdot \left[\boldsymbol{t}^F + \rho^S\, \hat{\rho}^F \frac{\partial \psi^S}{\partial \hat{\rho}^F} \boldsymbol{I} + \rho^F\, \hat{\rho}^F \frac{\partial \psi^F}{\partial \hat{\rho}^F} \boldsymbol{I} \right] + \\
\boldsymbol{m}^F \cdot \operatorname{grad} \bar{\boldsymbol{\omega}}^F - \mathfrak{m}^F \cdot \boldsymbol{w}^F - \mathfrak{k}^F \cdot \bar{\boldsymbol{\nu}}^F - \frac{1}{\vartheta} \operatorname{grad} \vartheta \cdot \boldsymbol{q}_I - \\
\boldsymbol{w}^F \cdot \left[\frac{\rho^S\, \hat{\rho}^F}{\nu^F} \frac{\partial \psi^S}{\partial \hat{\rho}^F} + \frac{\rho^F\, \hat{\rho}^F}{\nu^F} \frac{\partial \psi^F}{\partial \hat{\rho}^F} + \rho^F \frac{\partial \psi^F}{\partial \nu^S} \right] \operatorname{grad} \nu^S - \\
\rho^F \frac{\partial \psi^F}{\partial \bar{\boldsymbol{U}}^S} \cdot \nabla \bar{\boldsymbol{U}}^S (\boldsymbol{F}^S)^{-1} \boldsymbol{w}^F - \rho^F \frac{\partial \psi^F}{\partial^R \bar{\boldsymbol{\mathcal{K}}}^S} \cdot \nabla^R \bar{\boldsymbol{\mathcal{K}}}^S (\boldsymbol{F}^S)^{-1} \boldsymbol{w}^F + \\
\rho^S \frac{\partial \psi^S}{\partial \hat{\rho}^F} \operatorname{grad} \hat{\rho}^F \cdot \boldsymbol{w}^F \geqslant 0.
\end{aligned}
\tag{24.65}
$$

$\mathcal{D}$ vanishes, and, thus assumes its minimum, when the non-equilibrium variables $\bar{\boldsymbol{\Delta}}^F$, $\operatorname{grad} \bar{\boldsymbol{\omega}}^F$, $\boldsymbol{w}^F$, $\bar{\boldsymbol{\nu}}^F$, and $\operatorname{grad} \vartheta$ vanish:

$$
\left.
\begin{aligned}
\bar{\boldsymbol{\Delta}}^F &= \boldsymbol{0} \\
\operatorname{grad} \bar{\boldsymbol{\omega}}^F &= \boldsymbol{0} \\
\boldsymbol{w}^F &= \boldsymbol{0} \\
\bar{\boldsymbol{\nu}}^F &= \boldsymbol{0} \\
\operatorname{grad} \vartheta &= \boldsymbol{0}
\end{aligned}
\right\} \text{ at thermodynamic equilibrium.}
\tag{24.66}
$$

24.7.1 Equilibrium Helmholtz Free Energies

Before drawing the inferences implied by relations (24.66), let us return to the identities (24.59) and (24.60), which must be fulfilled by the free energies $\psi^{S,F}$. When evaluating (24.60) at equilibrium, one merely deduces three times the trivial statements $\boldsymbol{0} = \boldsymbol{0}$. Following an idea by EHLERS (1989) [18], one may differentiate (24.60) with respect to $\boldsymbol{w}^F$ and then take the equilibrium limit of the resulting relations. For $(24.60)_3$ this step yields

$$
\begin{aligned}
& \rho^S \frac{\partial^2 \psi^S}{\partial \operatorname{grad} \vartheta \otimes \partial \boldsymbol{w}^F} \otimes \boldsymbol{w}^F + \rho^S \frac{\partial \psi^S}{\partial \operatorname{grad} \vartheta} \otimes \boldsymbol{I} \\
&= -\boldsymbol{I} \otimes \rho^S \frac{\partial \psi^S}{\partial \operatorname{grad} \vartheta} - \boldsymbol{w}^F \otimes \rho^S \frac{\partial^2 \psi^S}{\partial \operatorname{grad} \vartheta \otimes \partial \boldsymbol{w}^F},
\end{aligned}
\tag{24.67}
$$

and for $\boldsymbol{w}^F = \boldsymbol{0}$ in equilibrium

$$
\left. \frac{\partial \psi^S}{\partial \operatorname{grad} \vartheta} \right|_E = \boldsymbol{0} \quad \overset{(24.59)_3}{\Longrightarrow} \quad \left. \frac{\partial \psi^F}{\partial \operatorname{grad} \vartheta} \right|_E = \boldsymbol{0}.
\tag{24.68}
$$

Analogous results can be derived for $(24.60)_{1,2}$ and $(24.59)_{1,2}$ (the method of derivation is the same). In summary, these considerations yield

$$
\begin{aligned}
\left.\frac{\partial \psi^S}{\partial \operatorname{grad} \vartheta}\right|_E &= \left.\frac{\partial \psi^F}{\partial \operatorname{grad} \vartheta}\right|_E = \mathbf{0}, \\
\left.\frac{\partial \psi^S}{\partial \operatorname{grad} \nu^S}\right|_E &= \left.\frac{\partial \psi^F}{\partial \operatorname{grad} \nu^S}\right|_E = \mathbf{0}, \\
\left.\frac{\partial \psi^S}{\partial \operatorname{grad} \hat{\rho}^F}\right|_E &= \left.\frac{\partial \psi^F}{\partial \operatorname{grad} \hat{\rho}^F}\right|_E = \mathbf{0}.
\end{aligned}
$$

in thermodynamic equilibrium. It follows that the HELMHOLTZ free energies have the functional form

$$
\psi^{S,F}|_E = \psi^{S,F}|_E\left(\bar{\boldsymbol{U}}^S, {}^R\bar{\boldsymbol{\mathcal{K}}}^S, \hat{\rho}^F, \nu^S, \vartheta\right). \tag{24.69}
$$

This function class is a considerably simplified class implied by the LIU-relations, see (24.62). The extension of the free energies $\psi^{S,F}$ to nonequilibrium must be at least quadratic in the variables grad θ, grad ν^S, grad $\hat{\rho}^F$ and can be written as

$$
\begin{aligned}
\psi^{S,F} &= (\psi^{S,F})|_E\left(\bar{\boldsymbol{U}}^S, {}^R\bar{\boldsymbol{\mathcal{K}}}^S, \hat{\rho}^F, \nu^S, \vartheta\right) \\
&\quad + \tfrac{1}{2}\,\mathfrak{x} \cdot \left[\boldsymbol{\mathcal{K}}^{S,F}|_E\left(\bar{\boldsymbol{U}}^S, {}^R\bar{\boldsymbol{\mathcal{K}}}^S, \hat{\rho}^F, \nu^S, \vartheta\right)\right]\mathfrak{x}, \qquad (24.70)\\
\mathfrak{x} &= \left(\operatorname{grad}\vartheta, \operatorname{grad}\nu^S, \operatorname{grad}\hat{\rho}^F\right), \qquad (24.71)\\
\left[\boldsymbol{\mathcal{K}}^{S,F}|_E\right] &= \begin{pmatrix}
\boldsymbol{\mathcal{K}}^{S,F}_{\vartheta\vartheta} & \boldsymbol{\mathcal{K}}^{S,F}_{\vartheta\nu^S} & \boldsymbol{\mathcal{K}}^{S,F}_{\vartheta\hat{\rho}^F} \\
\boldsymbol{\mathcal{K}}^{S,F}_{\nu^S\vartheta} & \boldsymbol{\mathcal{K}}^{F,S}_{\nu^S\nu^S} & \boldsymbol{\mathcal{K}}^{S,F}_{\nu^S\hat{\rho}^F} \\
\boldsymbol{\mathcal{K}}^{F,S}_{\hat{\rho}^F\vartheta} & \boldsymbol{\mathcal{K}}^{S,F}_{\hat{\rho}^F\nu^S} & \boldsymbol{\mathcal{K}}^{S,F}_{\hat{\rho}^F\hat{\rho}^F}
\end{pmatrix}. \qquad (24.72)
\end{aligned}
$$

$\left[\boldsymbol{\mathcal{K}}^{S,F}|_E\right]$ is a symmetric 9 × 9 matrix and each of the 3 × 3 submatrices is equally symmetric. Moreover, each may be a function of the equilibrium variables. In total, they comprise 54 coefficients, which are unlikely to be completely identifiable by experiments. Simplifications are called for, of which a drastic one is

$$
\begin{aligned}
\left[\boldsymbol{\mathcal{K}}^{S,F}_{\vartheta\,\vartheta}\right] &= \tfrac{1}{2}\mathcal{K}^{S,F}_{\vartheta\vartheta}\boldsymbol{I}, \\
\left[\boldsymbol{\mathcal{K}}^{S,F}_{\nu^S\nu^S}\right] &= \tfrac{1}{2}\mathcal{K}^{S,F}_{\nu^S\nu^S}\boldsymbol{I}, \\
\left[\boldsymbol{\mathcal{K}}^{S,F}_{\hat{\rho}^F\hat{\rho}^F}\right] &= \tfrac{1}{2}\mathcal{K}^{S,F}_{\hat{\rho}^F\hat{\rho}^F}\boldsymbol{I}
\end{aligned} \tag{24.73}
$$

with all off-diagonal elements in (24.72) equal to zero. In this restricted case, the free energies $\psi^{S,F}$ can also be written as

$$
\begin{aligned}
\psi^{S,F} &= (\psi^{S,F})|_E\left(\bar{\boldsymbol{U}}^S, {}^R\bar{\boldsymbol{\mathcal{K}}}^S, \hat{\rho}^F, \nu^S, \vartheta\right) + \tfrac{1}{2}\mathcal{K}^{S,F}_{\vartheta\vartheta}|_E\|\operatorname{grad}\vartheta\|^2 \\
&\quad + \tfrac{1}{2}\mathcal{K}^{S,F}_{\nu^S\nu^S}|_E\|\operatorname{grad}\nu^S\|^2 + \tfrac{1}{2}\mathcal{K}^{S,F}_{\hat{\rho}^F\hat{\rho}^F}|_E\|\operatorname{grad}\hat{\rho}^F\|^2,
\end{aligned} \tag{24.74}
$$

which has at most 6 different coefficients. It is customary in the current literature to set all nonequilibrium terms in $\psi^{S,F}$ equal to zero. The free energy in nonequilibrium is then equal to the equilibrium energy 'frozen' to the nonequilibrium process.

24.7.2 Equilibrium Implications

Let us now return to (24.65) and exploit it in the neighborhood of thermodynamic equilibrium. To this end, we write the nonequilibrium variables as

$$
\begin{aligned}
\bar{\boldsymbol{\varDelta}}^F &= \iota(\bar{\boldsymbol{\varDelta}}^F)^*,\\
\operatorname{grad}\bar{\boldsymbol{\omega}}^F &= \iota\operatorname{grad}(\bar{\boldsymbol{\omega}}^F)^*,\\
\boldsymbol{w}^F &= \iota(\boldsymbol{w}^F)^*,\\
\bar{\boldsymbol{\nu}}^F &= \iota(\bar{\boldsymbol{\nu}}^F)^*,\\
\operatorname{grad}\vartheta &= \iota\operatorname{grad}\vartheta^*.
\end{aligned}
\tag{24.75}
$$

The quantities with asterisks are constants, which determine the *direction* of the process and ι measures their *intensities*. In the limit as $\iota \to 0$, the equilibrium, $\mathcal{D}|_E = 0$, is reached. Because in this equilibrium $\mathcal{D}$ assumes its minimum, one necessarily has for smooth processes

$$
\left.\frac{\partial\mathcal{D}}{\partial\iota}\right|_{\iota=0} = 0, \quad \left.\frac{\partial^2\mathcal{D}}{\partial\iota^2}\right|_{\iota=0} > 0,
\tag{24.76}
$$

If we substitute (24.75) into (24.65) and then perform the differentiations $(24.76)_1$, we obtain

$$
\begin{array}{rl}
(\bar{\boldsymbol{\varDelta}}^F)^* & \cdot\left[(\boldsymbol{t}^F)_0 + \rho^S\,\hat{\rho}^F\dfrac{\partial\psi^S}{\partial\hat{\rho}^F}\boldsymbol{I} + \rho^F\,\hat{\rho}^F\dfrac{\partial\psi^F}{\partial\hat{\rho}^F}\boldsymbol{I}\right] +\\
\operatorname{grad}(\bar{\boldsymbol{\omega}}^F)^* & \cdot(\boldsymbol{m}^F)_0 +\\
(\boldsymbol{w}^F)^* & \cdot\left[-\left(\dfrac{\rho^S\,\hat{\rho}^F}{\nu^F}\dfrac{\partial\psi^S}{\partial\hat{\rho}^F} + \dfrac{\rho^F\,\hat{\rho}^F}{\nu^F}\dfrac{\partial\psi^F}{\partial\hat{\rho}^F} + \rho^F\dfrac{\partial\psi^F}{\partial\nu^S}\right)\operatorname{grad}\nu^S\right.\\
& -\rho^F(\boldsymbol{F}^S)^{-T}\left(\dfrac{\partial\psi^F}{\partial\bar{\boldsymbol{U}}^S}\nabla\bar{\boldsymbol{U}}^S\right)^{\underline{1}} - \rho^F(\boldsymbol{F}^S)^{-T}\left(\dfrac{\partial\psi^F}{\partial^R\bar{\boldsymbol{\mathcal{K}}}^S}\nabla^R\bar{\boldsymbol{\mathcal{K}}}^S\right)^{\underline{1}}\\
& \left.-(\boldsymbol{\mathfrak{m}}^F)_0 + \rho^S\dfrac{\partial\psi^S}{\partial\hat{\rho}^F}\operatorname{grad}\hat{\rho}^F\right] +\\
(\bar{\boldsymbol{\nu}}^F)^* & \cdot\left(-\boldsymbol{\mathfrak{t}}^F\right) +\\
\operatorname{grad}\vartheta^* & \cdot\left(-\dfrac{1}{\vartheta}\cdot(\boldsymbol{q}_I)_0\right) = \left.\dfrac{\partial\mathcal{D}}{\partial\iota}\right|_{\iota=0} = 0,\\
& \forall\,(\cdot)^*\text{-variables in (24.75)},
\end{array}
\tag{24.77}
$$

in which the quantities indexed by $(\cdot)_0$ are equilibrium quantities. Equation (24.77) as an identity must be valid for any values of the $(\cdot)^*$-indexed quantities, which may have arbitrarily assigned values. Therefore, all terms to the right of the scalar multiplication signs must vanish, implying

$$(\boldsymbol{t}^F)_0 = -\rho^S\,\hat{\rho}^F\,\frac{\partial\psi^S}{\partial\hat{\rho}^F}\boldsymbol{I} - \rho^F\,\hat{\rho}^F\,\frac{\partial\psi^F}{\partial\hat{\rho}^F}\boldsymbol{I} =: -\nu^F\,p_R^F\boldsymbol{I}, \tag{24.78}$$

$$p_R^F = (\hat{\rho}^F)^2\frac{\partial\psi^F}{\partial\hat{\rho}^F} + \frac{\rho^S\,\hat{\rho}^F}{\nu^F}\,\frac{\partial\psi^S}{\partial\hat{\rho}^F}, \tag{24.79}$$

$$\begin{aligned}(\boldsymbol{\mathfrak{m}}^F)_0 = &-\left(p_R^F + \rho^F\,\frac{\partial\psi^F}{\partial\nu^S}\right)\operatorname{grad}\nu^S + \rho^S\frac{\partial\psi^S}{\partial\hat{\rho}^F}\operatorname{grad}\hat{\rho}^F\\ &-\rho^F\,(\boldsymbol{F}^S)^{-T}\left(\frac{\partial\psi^F}{\partial\bar{\boldsymbol{U}}^S}\nabla\bar{\boldsymbol{U}}^S\right)^{\underline{1}}\\ &-\rho^F\,(\boldsymbol{F}^S)^{-T}\left(\frac{\partial\psi^F}{\partial^R\bar{\mathcal{K}}^S}\nabla^R\bar{\mathcal{K}}^S\right)^{\underline{1}},\end{aligned} \tag{24.80}$$

$$(\boldsymbol{m}^F)_0 = \boldsymbol{0}, \tag{24.81}$$

$$(\boldsymbol{\mathfrak{k}}^F)_0 = \boldsymbol{0}, \tag{24.82}$$

$$\boldsymbol{q}_0^I = \boldsymbol{0}. \tag{24.83}$$

The equilibrium fluid stress is a pressure. It is determined by the free energies $\psi_{F,S}$. This typically characterizes the compressibility of the fluid *and* the solid. The fluid equilibrium interaction force (fluid momentum production), $(\boldsymbol{\mathfrak{m}}^F)_0$, the equilibrium fluid couple stresses, $(\boldsymbol{m}^F)_0$, fluid equilibrium interaction couple, $(\boldsymbol{\mathfrak{k}}^F)_0$, and the equilibrium inner heat flux vector, $\boldsymbol{q}_0^I$, are all given by (24.78) to (24.83). They are determined once functional expressions for the free energies are chosen. These formulae are important, because they could not be guessed without the exploitation of the entropy inequality. This remains so even in isothermal processes, which seemingly do not reflect thermodynamic considerations.

24.7.3 Exploitation of the Entropy Inequality in the Neighborhood of the Equilibrium

In the above, the equilibrium conditions $(24.76)_1$ were exploited, which led to the expressions (24.78)–(24.83). We now introduce the shorthand notations

$$\begin{aligned}\{\mathsf{T}\} &= \left\{\boldsymbol{t}^F, \boldsymbol{m}^F, \boldsymbol{\mathfrak{m}}^F, \boldsymbol{\mathfrak{k}}^F, \boldsymbol{q}^I\right\},\\ \{\mathsf{v}\} &= \left\{\bar{\boldsymbol{\Delta}}^F, \operatorname{grad}\bar{\boldsymbol{\omega}}^F, \boldsymbol{w}^F, \bar{\boldsymbol{\nu}}^F, \operatorname{grad}\vartheta\right\}\end{aligned} \tag{24.84}$$

and wish to express the near equilibrium response by the linear relation

$$\{\mathsf{T}\} := \{\mathsf{T}_0\} + \{\{\mathsf{C}_\mathsf{T}\}\}\,\{\mathsf{v}\}\,. \tag{24.85}$$

$\{\mathsf{T}_0\}$ collects the equilibrium values of $\{\mathsf{T}\}$. Moreover, the term $\{\{\mathsf{C}_\mathsf{T}\}\}$ is a linear and positive definite operator on $\{\mathsf{v}\}$ and can readily be evaluated by the following expansions:

$$\begin{aligned}
\boldsymbol{t}^F &= (\boldsymbol{t}^F)_0 + \left(\frac{\partial \boldsymbol{t}^F}{\partial \bar{\boldsymbol{\Delta}}^F}\right)_0 \bar{\boldsymbol{\Delta}}^F + \left(\frac{\partial \boldsymbol{t}^F}{\partial \operatorname{grad} \bar{\boldsymbol{\omega}}^F}\right)_0 \operatorname{grad} \bar{\boldsymbol{\omega}}^F \\
&\quad + \left(\frac{\partial \boldsymbol{t}^F}{\partial \boldsymbol{w}^F}\right)_0 \boldsymbol{w}^F + \left(\frac{\partial \boldsymbol{t}^F}{\partial \bar{\boldsymbol{\nu}}^F}\right)_0 \bar{\boldsymbol{\nu}}^F + \left(\frac{\partial \boldsymbol{t}^F}{\partial \operatorname{grad} \vartheta}\right)_0 \operatorname{grad} \vartheta, && (24.86)\\
\boldsymbol{m}^F &= \left(\frac{\partial \boldsymbol{m}^F}{\partial \bar{\boldsymbol{\Delta}}^F}\right)_0 \bar{\boldsymbol{\Delta}}^F + \left(\frac{\partial \boldsymbol{m}^F}{\partial \operatorname{grad} \bar{\boldsymbol{\omega}}^F}\right)_0 \operatorname{grad} \bar{\boldsymbol{\omega}}^F \\
&\quad + \left(\frac{\partial \boldsymbol{m}^F}{\partial \boldsymbol{w}^F}\right)_0 \boldsymbol{w}^F + \left(\frac{\partial \boldsymbol{m}^F}{\partial \bar{\boldsymbol{\nu}}^F}\right)_0 \bar{\boldsymbol{\nu}}^F + \left(\frac{\partial \boldsymbol{m}^F}{\partial \operatorname{grad} \vartheta}\right)_0 \operatorname{grad} \vartheta, && (24.87)\\
\mathfrak{m}^F &= (\mathfrak{m}^F)_0 + \left(\frac{\partial \mathfrak{m}^F}{\partial \bar{\boldsymbol{\Delta}}^F}\right)_0 \bar{\boldsymbol{\Delta}}^F + \left(\frac{\partial \mathfrak{m}^F}{\partial \operatorname{grad} \bar{\boldsymbol{\omega}}^F}\right)_0 \operatorname{grad} \bar{\boldsymbol{\omega}}^F \\
&\quad + \left(\frac{\partial \mathfrak{m}^F}{\partial \boldsymbol{w}^F}\right)_0 \boldsymbol{w}^F + \left(\frac{\partial \mathfrak{m}^F}{\partial \bar{\boldsymbol{\nu}}^F}\right)_0 \bar{\boldsymbol{\nu}}^F + \left(\frac{\partial \mathfrak{m}^F}{\partial \operatorname{grad} \vartheta}\right)_0 \operatorname{grad} \vartheta, && (24.88)\\
\mathfrak{k}^F &= \left(\frac{\partial \mathfrak{k}^F}{\partial \bar{\boldsymbol{\Delta}}^F}\right)_0 \bar{\boldsymbol{\Delta}}^F + \left(\frac{\partial \mathfrak{k}^F}{\partial \operatorname{grad} \bar{\boldsymbol{\omega}}^F}\right)_0 \operatorname{grad} \bar{\boldsymbol{\omega}}^F \\
&\quad + \left(\frac{\partial \mathfrak{k}^F}{\partial \boldsymbol{w}^F}\right)_0 \boldsymbol{w}^F + \left(\frac{\partial \mathfrak{k}^F}{\partial \bar{\boldsymbol{\nu}}^F}\right)_0 \bar{\boldsymbol{\nu}}^F + \left(\frac{\partial \mathfrak{k}^F}{\partial \operatorname{grad} \vartheta}\right)_0 \operatorname{grad} \vartheta, && (24.89)\\
\boldsymbol{q}^I &= \left(\frac{\partial \boldsymbol{q}^I}{\partial \bar{\boldsymbol{\Delta}}^F}\right)_0 \bar{\boldsymbol{\Delta}}^F + \left(\frac{\partial \boldsymbol{q}^I}{\partial \operatorname{grad} \bar{\boldsymbol{\omega}}^F}\right)_0 \operatorname{grad} \bar{\boldsymbol{\omega}}^F \\
&\quad + \left(\frac{\partial \boldsymbol{q}^I}{\partial \boldsymbol{w}^F}\right)_0 \boldsymbol{w}^F + \left(\frac{\partial \boldsymbol{q}^I}{\partial \bar{\boldsymbol{\nu}}^F}\right)_0 \bar{\boldsymbol{\nu}}^F + \left(\frac{\partial \boldsymbol{q}^I}{\partial \operatorname{grad} \vartheta}\right)_0 \operatorname{grad} \vartheta, && (24.90)
\end{aligned}$$

in which the index $(\cdot)_0$ indicates evaluation of $(\cdot)$ in thermodynamic equilibrium. Substitution of (24.86)–(24.90) into the residual inequality (24.65) yields

$$\begin{aligned}
\bar{\boldsymbol{\Delta}}^F \quad &\cdot \Bigg[\left(\frac{\partial \boldsymbol{t}^F}{\partial \bar{\boldsymbol{\Delta}}^F}\right)_0 \bar{\boldsymbol{\Delta}}^F + \left(\frac{\partial \boldsymbol{t}^F}{\partial \operatorname{grad} \bar{\boldsymbol{\omega}}^F}\right)_0 \operatorname{grad} \bar{\boldsymbol{\omega}}^F \\
&\quad + \left(\frac{\partial \boldsymbol{t}^F}{\partial \boldsymbol{w}^F}\right)_0 \boldsymbol{w}^F + \left(\frac{\partial \boldsymbol{t}^F}{\partial \bar{\boldsymbol{\nu}}^F}\right)_0 \bar{\boldsymbol{\nu}}^F + \left(\frac{\partial \boldsymbol{t}^F}{\partial \operatorname{grad} \vartheta}\right)_0 \operatorname{grad} \vartheta\Bigg] + \\
\operatorname{grad} \bar{\boldsymbol{\omega}}^F \quad &\cdot \Bigg[\left(\frac{\partial \boldsymbol{m}^F}{\partial \bar{\boldsymbol{\Delta}}^F}\right)_0 \bar{\boldsymbol{\Delta}}^F + \left(\frac{\partial \boldsymbol{m}^F}{\partial \operatorname{grad} \bar{\boldsymbol{\omega}}^F}\right)_0 \operatorname{grad} \bar{\boldsymbol{\omega}}^F
\end{aligned}$$

$$
\begin{aligned}
& && +\left(\frac{\partial \boldsymbol{m}^F}{\partial \boldsymbol{w}^F}\right)_0 \boldsymbol{w}^F + \left(\frac{\partial \boldsymbol{m}^F}{\partial \bar{\boldsymbol{\nu}}^F}\right)_0 \bar{\boldsymbol{\nu}}^F + \left(\frac{\partial \boldsymbol{m}^F}{\partial \operatorname{grad} \vartheta}\right)_0 \operatorname{grad} \vartheta \Bigg] - \\
& \boldsymbol{w}^F && \cdot \Bigg[\left(\frac{\partial \mathfrak{m}^F}{\partial \bar{\boldsymbol{\Delta}}^F}\right)_0 \bar{\boldsymbol{\Delta}}^F + \left(\frac{\partial \mathfrak{m}^F}{\partial \operatorname{grad} \bar{\boldsymbol{\omega}}^F}\right)_0 \operatorname{grad} \bar{\boldsymbol{\omega}}^F \\
& && +\left(\frac{\partial \mathfrak{m}^F}{\partial \boldsymbol{w}^F}\right)_0 \boldsymbol{w}^F + \left(\frac{\partial \mathfrak{m}^F}{\partial \bar{\boldsymbol{\nu}}^F}\right)_0 \bar{\boldsymbol{\nu}}^F + \left(\frac{\partial \mathfrak{m}^F}{\partial \operatorname{grad} \vartheta}\right)_0 \operatorname{grad} \vartheta \Bigg] - \\
& \bar{\boldsymbol{\nu}}^F && \cdot \Bigg[\left(\frac{\partial \mathfrak{k}^F}{\partial \bar{\boldsymbol{\Delta}}^F}\right)_0 \bar{\boldsymbol{\Delta}}^F + \left(\frac{\partial \mathfrak{k}^F}{\partial \operatorname{grad} \bar{\boldsymbol{\omega}}^F}\right)_0 \operatorname{grad} \bar{\boldsymbol{\omega}}^F \\
& && +\left(\frac{\partial \mathfrak{k}^F}{\partial \boldsymbol{w}^F}\right)_0 \boldsymbol{w}^F + \left(\frac{\partial \mathfrak{k}^F}{\partial \bar{\boldsymbol{\nu}}^F}\right)_0 \bar{\boldsymbol{\nu}}^F + \left(\frac{\partial \mathfrak{k}^F}{\partial \operatorname{grad} \vartheta}\right)_0 \operatorname{grad} \vartheta \Bigg] - \\
& \operatorname{grad} \vartheta && \cdot \Bigg[\left(\frac{\partial \boldsymbol{q}^I}{\partial \bar{\boldsymbol{\Delta}}^F}\right)_0 \bar{\boldsymbol{\Delta}}^F + \left(\frac{\partial \boldsymbol{q}^I}{\partial \operatorname{grad} \bar{\boldsymbol{\omega}}^F}\right)_0 \operatorname{grad} \bar{\boldsymbol{\omega}}^F \\
& && +\left(\frac{\partial \boldsymbol{q}^I}{\partial \boldsymbol{w}^F}\right)_0 \boldsymbol{w}^F + \left(\frac{\partial \boldsymbol{q}^I}{\partial \bar{\boldsymbol{\nu}}^F}\right)_0 \bar{\boldsymbol{\nu}}^F + \left(\frac{\partial \boldsymbol{q}^I}{\partial \operatorname{grad} \vartheta}\right)_0 \operatorname{grad} \vartheta \Bigg] \\
& \geqslant 0. && \qquad (24.91)
\end{aligned}
$$

This inequality is a quadratic form of the nonequilibrium phase space variables. Because the nonequilibrium variables may independently assume arbitrary values, this positivity is fulfilled provided the following rank-2 and rank-4 tensors, evaluated in thermodynamic equilibrium, are positive definite:

$$
\underbrace{\frac{\partial \boldsymbol{t}^F}{\partial \bar{\boldsymbol{\Delta}}^F}, \quad \frac{\partial \boldsymbol{m}^F}{\partial \operatorname{grad} \bar{\boldsymbol{\omega}}^F},}_{\text{rank}-4} \qquad \underbrace{-\frac{\partial \mathfrak{m}^F}{\partial \boldsymbol{w}^F}, \quad -\frac{\partial \mathfrak{k}^F}{\partial \bar{\boldsymbol{\nu}}^F}, \quad -\frac{\partial \boldsymbol{q}^I}{\partial \operatorname{grad} \vartheta}}_{\text{rank}-2}. \tag{24.92}
$$

Besides (24.92) further criteria must be fulfilled to guarantee positive semidefiniteness of (24.91). To this end, sufficiency can be achieved by requiring that the remaining mixed terms of (24.91) vanish. For instance, two such terms are

$$
\bar{\boldsymbol{\Delta}}^F \cdot \left[\cdots \left(\frac{\partial \boldsymbol{t}^F}{\partial \operatorname{grad} \bar{\boldsymbol{\omega}}^F}\right)_0 \operatorname{grad} \boldsymbol{\omega}^F \right] + \cdots \operatorname{grad} \bar{\boldsymbol{\omega}}^F \cdot \left[\left(\frac{\partial \boldsymbol{m}^F}{\partial \bar{\boldsymbol{\Delta}}^F}\right)_0 \cdots \right] \bar{\boldsymbol{\Delta}}^F,
$$

or in Cartesian component notation

$$
\begin{aligned}
& (\bar{\Delta}^F)_{ij} \frac{\partial (\boldsymbol{t}^F)_{ij}}{\partial (\bar{\omega}^F)_{k,\ell}} \bar{\omega}^F_{k,\ell} + \cdots + \bar{\omega}^F_{i,j} \frac{\partial (m^F)_{ij}}{\partial \bar{\Delta}^F_{k,\ell}} \bar{\Delta}_{k\ell} + \cdots \\
= {} & (\bar{\Delta}^F)_{ij} \frac{\partial (\boldsymbol{t}^F)_{ij}}{\partial (\bar{\omega}^F)_{k,\ell}} \bar{\omega}^F_{k,\ell} + \cdots + \bar{\Delta}_{ij} \frac{\partial m^F_{k\ell}}{\partial (\bar{\Delta}^F)_{ij}} \bar{\omega}^F_{k,\ell} + \cdots
\end{aligned}
$$

$$
\begin{aligned}
&= (\bar{\Delta}^F)_{ij} \left\{ \frac{\partial (\boldsymbol{t}^F)_{ij}}{\partial(\bar{\omega}^F)_{k,\ell}} + \frac{\partial m^F_{k\ell}}{\partial(\bar{\Delta}^F)_{ij}} \right\} \bar{\omega}^F_{k,\ell} \overset{!}{=} 0,\\
\Longrightarrow \quad & \frac{\partial (\boldsymbol{t}^F)_{ij}}{\partial(\bar{\omega}^F)_{k,\ell}} = -\frac{\partial m^F_{k\ell}}{\partial(\bar{\Delta}^F)_{ij}}
\end{aligned}
$$

and again written in symbolic notation

$$
\left(\frac{\partial \boldsymbol{t}^F}{\partial \mathrm{grad}\,\boldsymbol{\omega}^F}\right)_0 = -\left(\frac{\partial \boldsymbol{m}^F}{\partial \bar{\boldsymbol{\Delta}}^F}\right)_0^T, \tag{24.93}
$$

In an analogous manner, we may select

$$
\bar{\boldsymbol{\Delta}}^F \cdot \left[\cdots \left(\frac{\partial \boldsymbol{t}^F}{\partial \bar{\boldsymbol{w}}^F}\right)_0\right] \boldsymbol{w}^F + \cdots - \boldsymbol{w}^F \cdot \left[\left(\frac{\partial \mathbf{m}^F}{\partial \bar{\boldsymbol{\Delta}}^F}\right)_0\right] \bar{\boldsymbol{\Delta}}^F,
$$

or in Cartesian notation

$$
\begin{aligned}
&\bar{\Delta}_{ij} \left(\frac{\partial t^F_{ij}}{\partial w^F_m}\right)_0 w^F_m + \cdots - w^F_i \left(\frac{\partial \mathbf{m}^F_i}{\partial \bar{\Delta}^F_{k\ell}}\right)_0 \bar{\Delta}^F_{k\ell}\\
&= \bar{\Delta}^F_{ij} \left\{ \left(\frac{\partial t^F_{ij}}{\partial w^F_m}\right)_0 - \left(\frac{\partial \mathbf{m}^F_m}{\partial \bar{\Delta}^F_{ij}}\right)_0 \right\} w^F_m\\
&= \bar{\Delta}^F_{ij} \left\{ \frac{\partial t^F_{ij}}{\partial w^F_m} - \left[\left(\frac{\partial \mathbf{m}^F_j}{\partial \bar{\Delta}^F_{im}}\right)^{\overset{13}{T}}\right] \right\} w^F_m\\
&= \bar{\Delta}^F_{ij} \left\{ \frac{\partial t^F_{ij}}{\partial w^F_m} - \left[\left(\frac{\partial \mathbf{m}^F_i}{\partial \bar{\Delta}^F_{jm}}\right)^{\overset{13}{T}}\right]^{\overset{12}{T}} \right\} w^F_m = 0.
\end{aligned}
$$

Because $\bar{\Delta}^F_{ij}$ and w^F_m may have any value the expression in braces must vanish. In symbolic notation, we therefore have

$$
\left(\frac{\partial \boldsymbol{t}^F}{\partial \boldsymbol{w}^F}\right)_0 = \left(\left(\frac{\partial \mathbf{m}^F}{\partial \bar{\Delta}^F}\right)^{\overset{13}{T}}\right)^{\overset{12}{T}}. \tag{24.94}
$$

All mixed terms in (24.91) are of the structure (24.93) and (24.94). The reader may easily check that the following symmetry conditions are obtained:

$$\left(\frac{\partial \boldsymbol{t}^F}{\partial \operatorname{grad} \bar{\boldsymbol{\omega}}^F}\right)_0 = -\left(\frac{\partial \boldsymbol{m}^F}{\partial \bar{\boldsymbol{\Delta}}^F}\right)_0^T, \tag{24.95}$$

$$\left(\frac{\partial \boldsymbol{t}^F}{\partial \boldsymbol{w}^F}\right)_0 = \left(\left(\frac{\partial \boldsymbol{\mathfrak{m}}^F}{\partial \bar{\boldsymbol{\Delta}}^F}\right)_0^{\overset{13}{T}}\right)^{\overset{12}{T}}, \tag{24.96}$$

$$\left(\frac{\partial \boldsymbol{t}^F}{\partial \bar{\boldsymbol{\nu}}^F}\right)_0 = \left(\left(\frac{\partial \boldsymbol{\mathfrak{k}}^F}{\partial \bar{\boldsymbol{\Delta}}^F}\right)_0^{\overset{13}{T}}\right)^{\overset{12}{T}}, \tag{24.97}$$

$$\left(\frac{\partial \boldsymbol{t}^F}{\partial \operatorname{grad} \vartheta}\right)_0 = \left(\left(\frac{\partial \boldsymbol{q}^I}{\partial \bar{\boldsymbol{\Delta}}^F}\right)_0^{\overset{13}{T}}\right)^{\overset{12}{T}}, \tag{24.98}$$

$$\left(\frac{\partial \boldsymbol{m}^F}{\partial \boldsymbol{w}^F}\right)_0 = \left(\left(\frac{\partial \boldsymbol{\mathfrak{m}}^F}{\partial \operatorname{grad} \bar{\boldsymbol{\omega}}^F}\right)_0^{\overset{13}{T}}\right)^{\overset{12}{T}}, \tag{24.99}$$

$$\left(\frac{\partial \boldsymbol{m}^F}{\partial \bar{\boldsymbol{\nu}}^F}\right)_0 = \left(\left(\frac{\partial \boldsymbol{\mathfrak{k}}^F}{\partial \operatorname{grad} \bar{\boldsymbol{\omega}}^F}\right)_0^{\overset{13}{T}}\right)^{\overset{12}{T}}, \tag{24.100}$$

$$\left(\frac{\partial \boldsymbol{m}^F}{\partial \operatorname{grad} \vartheta}\right)_0 = \left(\left(\frac{\partial \hat{\boldsymbol{q}}^I}{\partial \operatorname{grad} \bar{\boldsymbol{\omega}}^F}\right)_0^{\overset{13}{T}}\right)^{\overset{12}{T}}, \tag{24.101}$$

$$\left(\frac{\partial \boldsymbol{\mathfrak{m}}^F}{\partial \bar{\boldsymbol{\nu}}^F}\right)_0 = -\left(\frac{\partial \boldsymbol{\mathfrak{k}}^F}{\partial \boldsymbol{w}^F}\right)_0^T, \tag{24.102}$$

$$\left(\frac{\partial \boldsymbol{\mathfrak{m}}^F}{\partial \operatorname{grad} \vartheta}\right)_0 = -\left(\frac{\partial \boldsymbol{q}^I}{\partial \boldsymbol{w}^F}\right)_0^T, \tag{24.103}$$

$$\left(\frac{\partial \boldsymbol{\mathfrak{k}}^F}{\partial \operatorname{grad} \vartheta}\right)_0 = -\left(\frac{\partial \boldsymbol{q}^I}{\partial \bar{\boldsymbol{\nu}}^F}\right)_0^T. \tag{24.104}$$

With the assumptions (24.95)–(24.104) the imbalance (24.91) reduces to

$$\begin{aligned}&\bar{\boldsymbol{\Delta}}^F \cdot \left(\frac{\partial \boldsymbol{t}^F}{\partial \bar{\boldsymbol{\Delta}}^F}\right)_0 \bar{\boldsymbol{\Delta}}^F + \operatorname{grad}\bar{\boldsymbol{\omega}}^F \cdot \left(\frac{\partial \boldsymbol{m}^F}{\partial \operatorname{grad}\bar{\boldsymbol{\omega}}^F}\right)_0 \operatorname{grad}\bar{\boldsymbol{\omega}}^F\\ &+ \boldsymbol{w}^F\left(\frac{\partial \mathfrak{m}^F}{\partial \boldsymbol{w}^F}\right)_0 \boldsymbol{w}^F + \bar{\boldsymbol{\nu}}^F \left(\frac{\partial \mathfrak{k}^F}{\partial \bar{\boldsymbol{\nu}}^F}\right)_0 \bar{\boldsymbol{\nu}}^F\\ &+ \operatorname{grad}\vartheta \cdot \left(\frac{\partial \boldsymbol{q}^I}{\partial \operatorname{grad}\vartheta}\right)_0 \operatorname{grad}\vartheta \geqslant 0. \qquad (24.105)\end{aligned}$$

This imbalance shows very clearly that, since the nonequilibrium variables may independently assume arbitrary values, the expression (24.105) is nonnegative, if and only if the tensors (24.92), evaluated in equilibrium, are positive semidefinite. Together with (24.78)–(24.83) and the expressions (24.86)–(24.90) [reduced according to (24.105)], the following *near equilibrium expressions* can be deduced:

Fluid and solid stresses:

- $$\left.\begin{aligned}&\boldsymbol{t}^F \overset{(24.78)}{=} -\nu^F\, p_R^F \boldsymbol{I} + \overset{4\times4}{\mathcal{C}}\ \bar{\boldsymbol{\Delta}}^F,\\ &\qquad p_R^F, \quad \text{effective fluid pressure given in (24.79)},\\ &\qquad \overset{4\times4}{\mathcal{C}} \equiv \left(\frac{\partial \boldsymbol{t}^F}{\partial \bar{\boldsymbol{\Delta}}^F}\right)_0 \quad \text{positive definite ‘viscosity’ tensor.}\end{aligned}\right\} \qquad (24.106)$$

- $$\left.\begin{aligned}\boldsymbol{t}^S &\overset{(24.47)}{=} \bar{\boldsymbol{R}}^S \left\{\rho^S \frac{\partial \psi^S}{\partial \bar{\boldsymbol{U}}^S} + \rho^F \frac{\partial \psi^F}{\partial \bar{\boldsymbol{U}}^S}\right\} \left(\boldsymbol{F}^S\right)^T - (p_c + p_{\text{th}})\,\boldsymbol{I},\\ p_c &= z^S \nu^S \left\{\rho^S \frac{\partial \psi^S}{\partial \nu^S} + \rho^F \frac{\partial \psi^F}{\partial \nu^S}\right\}\\ &\qquad\qquad \text{configurational pressure}\\ p_{\text{th}} &= z^S \nu^S \left\{\frac{\rho^S \hat{\rho}^F}{\nu^F} \frac{\partial \psi^S}{\partial \hat{\rho}^F} + \frac{\rho^F \hat{\rho}^F}{\nu^F} \frac{\partial \psi^F}{\partial \hat{\rho}^F}\right\}\\ &\qquad\qquad \text{thermodynamic pressure}\end{aligned}\right\} \qquad (24.107)$$

Fluid and solid couple stresses:

$$\left.\begin{aligned}&\bullet\ \boldsymbol{m}^F = \overset{4\times4}{\mathcal{M}} \operatorname{grad}\bar{\boldsymbol{\omega}}^F, \quad \overset{4\times4}{\mathcal{M}} = \left(\frac{\partial \boldsymbol{m}^F}{\partial \operatorname{grad}\bar{\boldsymbol{\omega}}^F}\right)_0, \ \text{positive semidefinite}\\ &\bullet\ \boldsymbol{m}^S \overset{(24.49)}{=} \bar{\boldsymbol{R}}^S \left\{\rho^S \frac{\partial \psi^S}{\partial\, {}^R\bar{\boldsymbol{\mathcal{K}}}^S} + \rho^F \frac{\partial \psi^F}{\partial\, {}^R\bar{\boldsymbol{\mathcal{K}}}^S}\right\} \left(\boldsymbol{F}^S\right)^T,\end{aligned}\right\} \qquad (24.108)$$

Interaction force and interaction couple:

$$
\left.\begin{array}{l}
\bullet\ \boldsymbol{\mathfrak{m}}^F \overset{(24.80)}{=} -\left(p_R^F + \rho^F \dfrac{\partial \psi^F}{\partial \nu^S}\right) \operatorname{grad} \nu^S + \rho^S \dfrac{\partial \psi^S}{\partial \hat{\rho}^F} \operatorname{grad} \hat{\rho}^F \\
\qquad -\rho^F \left(\boldsymbol{F}^S\right)^{-T} \left(\dfrac{\partial \psi^F}{\partial \bar{\boldsymbol{U}}^S} \nabla \bar{\boldsymbol{U}}^S\right)^{\underline{1}} \\
\qquad -\rho^F \left(\boldsymbol{F}^S\right)^{-T} \left(\dfrac{\partial \psi^F}{\partial {}^R\bar{\boldsymbol{\mathcal{K}}}^S} \nabla\, {}^R\bar{\boldsymbol{\mathcal{K}}}^S\right)^{\underline{1}} + \overset{2\times 2}{\mathcal{P}}\ \boldsymbol{w}^F, \\
\qquad -\overset{2\times 2}{\mathcal{P}} = -\left(\dfrac{\partial \boldsymbol{\mathfrak{m}}^F}{\partial \boldsymbol{w}^F}\right) \quad \text{positive semidefinite} \\
\bullet\ \boldsymbol{\mathfrak{k}}^F = \overset{2\times 2}{\mathcal{M}}\ \bar{\boldsymbol{\nu}}^F, \quad -\overset{2\times 2}{\mathcal{M}} = -\left(\dfrac{\partial \boldsymbol{\mathfrak{k}}^F}{\partial \bar{\boldsymbol{\nu}}^F}\right)_0, \\
\qquad\qquad\qquad\qquad \text{positive semidefinite}
\end{array}\right\} \tag{24.109}
$$

Entropy and inner heat flux:

$$
\left.\begin{array}{l}
\bullet\ \rho\, s \overset{(24.50)}{=} -\rho^F \dfrac{\partial \psi^S}{\partial \vartheta} - \rho^F \dfrac{\partial \psi^F}{\partial \vartheta}, \quad \text{mixture entropy}, \\
\bullet\ \boldsymbol{q}^I = \overset{2\times 2}{\mathcal{Q}} \operatorname{grad} \vartheta, \quad -\overset{2\times 2}{\mathcal{Q}} = -\left(\dfrac{\partial \boldsymbol{q}^I}{\partial \operatorname{grad} \vartheta}\right)_0, \\
\qquad\qquad\qquad \text{positive semidefinite.}
\end{array}\right\} \tag{24.110}
$$

The above expressions for the fluid and solid stresses, couple stresses, interaction forces, interaction couples, and entropy are known once the free energies $\psi^{S,F}$ are known as functions of their variables (24.62) and the coefficient functions

$$
\overset{4\times 4}{\mathcal{C}}, \quad \overset{4\times 4}{\mathcal{M}}, \quad \overset{2\times 2}{\mathcal{P}}, \quad \overset{2\times 2}{\mathcal{M}}, \quad \text{and} \quad \overset{2\times 2}{\mathcal{Q}} \tag{24.111}
$$

are prescribed. The statements, compiled in Eqs. (24.106)–(24.110) as inferences of the entropy inequality in the form of CLAUSIUS–DUHEM, summarize the explicit forms for the field variables $\boldsymbol{t}^{S,F}$, $\boldsymbol{m}^{S,F}$, $\boldsymbol{\mathfrak{m}}^F$, $\boldsymbol{\mathfrak{k}}$ and s in terms of the kinematic and thermal variables, stated in Eq. (24.61). The allowable processes are restricted to near thermodynamic equilibria, i.e., field formulations, in which the variables of set II in (24.61) only arise in the governing field equations in linear form. The formulae (24.106)–(24.110) merely state possible forms of the satisfaction of the Second Law; for applications of these in solid–fluid flow problems, they must be made concrete. To this end, it is advantageous to introduce further simplifications. This will be done in the next subsection. Here we focus on isotropic variants of the coefficients (24.111).

For isotropic response, the second and fourth order material tensors (24.111) have the form

$$
\overset{2\times 2}{\mathcal{A}}_{ij} = -k_{\mathcal{A}} \delta_{ij}, \qquad \overset{4\times 4}{\mathcal{A}}_{ijkl} = \lambda_{\mathcal{A}} \delta_{ij} \delta_{kl} + \mu_{\mathcal{A}} \left(\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}\right). \tag{24.112}
$$

It is shown in the material theory—suggested by the linear theory of elasticity – that the coefficients $\lambda_{\mathcal{C}}$ and $\mu_{\mathcal{C}}$ can, alternatively, be replaced by

$$E_{\mathcal{C}}^{F} := \frac{\mu_{\mathcal{C}}^{F}\left(3\lambda_{\mathcal{C}}^{F} + 2\mu_{\mathcal{C}}^{F}\right)}{\lambda_{\mathcal{C}}^{F} + \mu_{\mathcal{C}}^{F}}, \quad k_{\mathcal{C}}^{F} := \lambda_{\mathcal{C}}^{F} + \frac{2}{3}\mu_{\mathcal{C}}^{F}, \tag{24.113}$$

see [40]. The coefficients $\lambda_{\mathcal{C}}^{F}$, $\mu_{\mathcal{C}}^{F}$, $E_{\mathcal{C}}^{F}$, $k_{\mathcal{C}}^{F}$ are, in elasticity theory called the LAMÉ constants, YOUNG's modulus, and the bulk modulus. Here, they have the meaning of COSSERAT viscosities: $\mu_{\mathcal{C}}^{F}$, is the COSSERAT shear viscosity of the fluid constituent and $k_{\mathcal{C}}^{F}$ is the Cosserat bulk viscosity. Analogously, $\lambda_{\mathcal{M}}^{F}$, $\mu_{\mathcal{M}}^{F}$, $E_{\mathcal{M}}^{F}$, $k_{\mathcal{M}}^{F}$ are corresponding couple stress viscosities. The second order isotropic tensors $\overset{2\times 2}{\mathcal{P}}$ and $\overset{2\times 2}{\mathcal{M}}$ are expressible in the form (24.112)$_1$. All these coefficients are positive and meant here to apply for the fluid constitutive parameterizations. Thus,

$$E_{\mathcal{A}}^{F} > 0, \quad k_{\mathcal{A}}^{F} > 0 \qquad \text{for } \mathcal{A} \in [\mathcal{C}, \mathcal{M}]. \tag{24.114}$$

By contrast, the solid stress consists only of equilibrium contributions; this is in conformity with our expectation, as the strain rate tensor was not assumed to act as an independent constitutive variable. Its elastic response has a pure pressure-dependent part due to the configurational and thermodynamic pressures; the former is a response of the mixture to the solid volume fraction [or its complement, the pore volume], the latter is due to the compressibility of the grains. The first term in (24.107) expresses the fact that the solid elastic response for the solid stress $\boldsymbol{t}^S$ may sustain bulk and shear deformations with bulk and shear moduli. The form of this term is interesting as ψ^F depends on $\bar{\boldsymbol{U}}^S$ and generates only an elastic solid stress contribution, if ψ^F indeed has a $\bar{\boldsymbol{U}}^S$-dependence. When the rule of phase separation is applied, according to which constitutive quantities of phase α cannot depend on variables of phase β ($\alpha \neq \beta$) this term is absent, except for interaction terms (BOWEN 1980, 1982 [6, 8]). For swelling of clay or deformation of hydrophilic polymers[5] maintaining the rule of aequipresence is significant (DIEBELS [13]).

The fluid couple stress possesses in this formulation only a nonvanishing nonequilibrium response linear in grad $\boldsymbol{\omega}^F$, see (24.108). This contribution may be called a rotational viscous response with a rank-4 rotational viscosity tensor. In thermodynamic equilibrium, the fluid couple stress vanishes. By contrast, the solid couple stress possesses only an equilibrium contribution that is 'frozen' to the particle in question and is only nontrivial if the free energies depend on the solid curvature tensor in the reference system. This term is analogous to the corresponding term of $\boldsymbol{t}^S$.

We summarize the remaining constitutive quantities at one single place as follows:

- *Stresses*:

$$(\boldsymbol{t}^F)_0 \overset{(24.78),(24.79)}{=} -\nu^F p_R^F \boldsymbol{I}, \tag{24.115}$$

$$p_R^F = (\hat{\rho}^F)^2 \frac{\partial \psi^F}{\partial \hat{\rho}^F} + \frac{\rho^S \hat{\rho}^F}{\nu^F} \frac{\partial \psi^S}{\partial \hat{\rho}^F},$$

---

[5] Hydrophilic polymers swell under water (vapor) adsorption.

$$
\begin{aligned}
\boldsymbol{t}^S &\overset{(24.47),(24.48)}{=} \bar{\boldsymbol{R}}^S \left\{ \rho^S \frac{\partial \psi^S}{\partial \bar{\boldsymbol{U}}^S} + \rho^F \frac{\partial \psi^F}{\partial \bar{\boldsymbol{U}}^S} \right\} (\boldsymbol{F}^S)^T - (p_c + p_{th}) \boldsymbol{I}, \qquad (24.116)\\
& p_c = z^S \nu^S \left\{ \rho^S \frac{\partial \psi^S}{\partial \nu^S} + \rho^F \frac{\partial \psi^F}{\partial \nu^S} \right\},\\
& p_{\mathrm{th}} = z^S \nu^S \left\{ \frac{\rho^S \hat{\rho}^F}{\nu^F} \frac{\partial \psi^S}{\partial \hat{\rho}^F} + \underbrace{\frac{\rho^F \hat{\rho}^F}{\nu^F}}_{(\hat{\rho}^F)^2} \frac{\partial \psi^F}{\partial \hat{\rho}^F} \right\}.
\end{aligned}
$$

- *Couple stresses*:

$$
\begin{aligned}
(\boldsymbol{m}^F)_0 &= \boldsymbol{0},\\
\boldsymbol{m}^S &\overset{(24.49)}{=} \bar{\boldsymbol{R}}^S \left\{ \rho^S \frac{\partial \psi^S}{\partial^R \bar{\boldsymbol{\mathcal{K}}}^S} + \rho^F \frac{\partial \psi^F}{\partial^R \bar{\boldsymbol{\mathcal{K}}}^S} \right\} \left(\boldsymbol{F}^S\right)^T .
\end{aligned}
\qquad (24.117)
$$

- *Interaction force and interaction couple*:

$$
\begin{aligned}
(\mathfrak{m}^F)_0 \overset{(24.80)}{=} & - \left(p_R^F + \rho^F \frac{\partial \psi^F}{\partial \nu^S} \right) \operatorname{grad} \nu^S + \rho^S \frac{\partial \psi^S}{\partial \hat{\rho}^F} \operatorname{grad} \hat{\rho}^F\\
& - \rho^F \left(\boldsymbol{F}^S\right)^{-T} \left(\left(\frac{\partial \psi^F}{\partial \bar{\boldsymbol{U}}^S} \nabla \bar{\boldsymbol{U}}^S \right)^{\underline{1}} \right.\\
& \left. + \left(\frac{\partial \psi^F}{\partial^R \bar{\boldsymbol{\mathcal{K}}}^S} \nabla^R \bar{\boldsymbol{\mathcal{K}}}^S \right)^{\underline{1}} \right),\\
(\mathfrak{k}^F)_0 = & \ \boldsymbol{0}.
\end{aligned}
\qquad (24.118)
$$

- *Heat flux vector*:

$$
\boldsymbol{q}^I = -\mathcal{Q} \operatorname{grad} \theta, \quad \mathcal{Q} > 0. \qquad (24.119)
$$

Quantities $(\cdot)_0$ are values of $(\cdot)$ at thermodynamic equilibrium, which are in nonequilibrium complemented by linear dissipative terms; quantities $(\cdot)$ without a subscript apply in equilibrium as well as in non-equilibrium. In this spirit, the expressions (24.115)–(24.119) complete the exploitation of the Second Law of Thermodynamics for this model of a binary solid–fluid COSSERAT mixture. However, the work is not yet completed. Indeed, fluid mechanicians can still not even formulate a mathematical fluid flow problem as long as explicit expressions for the free energies are not proposed. In the generality expressed by (24.115)–(24.119) such explicit expressions are very difficult to guess. Simplifications are called for. DIEBELS [13], e.g., supposes that

1. ψ^F does not depend upon $\bar{\boldsymbol{U}}^S$ and ${}^R\bar{\boldsymbol{\mathcal{K}}}^S \to \psi^F = \psi_1^F \left(\hat{\rho}^F, \nu^F, \vartheta, \right)$,

2. ψ^S does not depend upon $\hat{\rho}^F \rightarrow \psi^S = \psi_1^S\left(\bar{\boldsymbol{U}}^S, {}^R\bar{\boldsymbol{\mathcal{K}}}^S, \nu^S, \vartheta\right)$, but
3. $\psi^{S,F}$ depend both upon ν^S which is consequential in view of the saturation condition $\nu^F + \nu^S = 1$.

It is straightforward to show with the aid of (24.115)–(24.118) that in this reduced case the following results are obtained[6]:

- *Stresses*:

$$(\boldsymbol{t}^F)_{01} = -\nu^F p_R^F \boldsymbol{I} = -\nu^F (\hat{\rho}^F)^2 \frac{\partial \psi_1^F}{\partial \hat{\rho}^F} \boldsymbol{I}, \tag{24.120}$$

$$(\boldsymbol{t}^S)_1 = \bar{\boldsymbol{R}}^S \left\{\rho^S \frac{\partial \psi_1^S}{\partial \bar{\boldsymbol{U}}^S}\right\} \left(\boldsymbol{F}^S\right)^T - (p_{\mathrm{c}} + p_{\mathrm{th}})\boldsymbol{I}, \tag{24.121}$$

$$p_{\mathrm{c}} = z^S \nu^S \left\{\rho^S \frac{\partial \psi_1^S}{\partial \nu^S} + \rho^F \frac{\partial \psi_1^F}{\partial \nu^S}\right\},$$

$$p_{\mathrm{th}} = z^S \nu^S \left\{\left(\hat{\rho}^F\right)^2 \frac{\partial \psi_1^F}{\partial \hat{\rho}^F}\right\}.$$

- *Couple stresses*:

$$\begin{aligned} (\boldsymbol{m}^F)_{01} &= \boldsymbol{0}, \\ (\boldsymbol{m}^S)_1 &= \bar{\boldsymbol{R}}^S \left\{\rho^S \frac{\partial \psi_1^S}{\partial {}^R\bar{\boldsymbol{\mathcal{K}}}^S}\right\} \left(\boldsymbol{F}^S\right)^T. \end{aligned} \tag{24.122}$$

- *Interaction force and interaction couple*:

$$\begin{aligned} (\mathfrak{m}^F)_1 &= -\left(p_R^F + \rho^F \frac{\partial \psi_1^F}{\partial \nu^S}\right) \operatorname{grad} \nu^S, \\ (\mathfrak{m}^S)_1 &= -(\mathfrak{m}^F)_1. \end{aligned} \tag{24.123}$$

The two specifications for $\psi^{F,S}$ above abandon the rule of aequipresence in favor of the rule of phase separation. As already indicated earlier, this latter assumption may be too restrictive. To rescue the results (24.120)–(24.123) in the spirit of the enumeration above, we additively compose the free energies $\psi^{F,S}$ as follows:

$$\begin{aligned} \psi^S &= \psi_1^S\left(\bar{\boldsymbol{U}}^S, {}^R\bar{\boldsymbol{\mathcal{K}}}^S, \nu^S, \vartheta\right) + \psi_2^S\left(\hat{\rho}^F, \vartheta\right), \\ \psi^F &= \psi_1^F\left(\hat{\rho}^F, \nu^S, \vartheta\right) + \psi_2^F\left(\bar{\boldsymbol{U}}^S, {}^R\bar{\boldsymbol{\mathcal{K}}}^S, \vartheta\right). \end{aligned} \tag{24.124}$$

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[6] In the formulae (24.120)–(24.123), a subscript $(\cdot)_1$ has been introduced to identify that the so subscripted quantities are based on the rule of phase separation rather than the rule of aequipresence.

Here, the functions $\psi^{F,S}$, which led to (24.120)–(24.123) are to be interpreted as the functions $(\cdot)_1$. Alternatively, the functions ψ_2, deliver, with the aid of (24.115)–(24.118), the following results:

- *Additional stresses*:

$$\begin{aligned} (\boldsymbol{t}^F)_{02} &= -\rho^S \hat{\rho}^F \frac{\partial \psi_2^S}{\partial \hat{\rho}^F} \boldsymbol{I}, \\ (\boldsymbol{t}^S)_2 &= -(p_{\text{th}})_2 = -z^S \nu^S \left\{ \frac{\rho^S \hat{\rho}^F}{\nu^F} \frac{\partial \psi_2^S}{\partial \hat{\rho}^F} \right\} \boldsymbol{I}. \end{aligned} \tag{24.125}$$

- *Additional couple stresses*:

$$\begin{aligned} (\boldsymbol{m}^F)_{02} &= \boldsymbol{0}, \\ (\boldsymbol{m}^S)_2 &= \bar{\boldsymbol{R}}^S \left\{ \rho^F \frac{\partial \psi_2^F}{\partial {}^R\bar{\boldsymbol{\mathcal{K}}}^S} \right\} (\boldsymbol{F}^S)^T. \end{aligned} \tag{24.126}$$

- *Additional interaction force & interaction couple*:

$$\begin{aligned} (\boldsymbol{\mathfrak{m}}^F)_2 &= \rho^S \frac{\partial \psi_2^S}{\partial \hat{\rho}^F} \operatorname{grad} \hat{\rho}^F \\ &\quad - \left(\rho^F (\boldsymbol{F}^S)^{-T} \left(\frac{\partial \psi_2^F}{\partial \bar{\boldsymbol{U}}^S} \nabla \bar{\boldsymbol{U}}^S + \frac{\partial \psi_2^F}{\partial {}^R\bar{\boldsymbol{\mathcal{K}}}^S} \nabla \, {}^R\bar{\boldsymbol{\mathcal{K}}}^S \right) \right), \\ (\boldsymbol{\mathfrak{m}}^S)_2 &= \boldsymbol{0}. \end{aligned} \tag{24.127}$$

With these results, we obtain

$$\begin{aligned} &\mathcal{Y} = \mathcal{Y}_1 + \mathcal{Y}_2, \quad \text{where} \\ &\mathcal{Y}_1 + \mathcal{Y}_2 = \left\{ \boldsymbol{t}_{01}^F + \boldsymbol{t}_{02}^F, \boldsymbol{t}_1^S + \boldsymbol{t}_2^S, \boldsymbol{m}_{01}^F + \boldsymbol{m}_{02}^F, \boldsymbol{m}_1^S + \boldsymbol{m}_2^S, \boldsymbol{\mathfrak{m}}_1^F + \boldsymbol{\mathfrak{m}}_2^F \right\}. \end{aligned} \tag{24.128}$$

The functions $\psi_2^{F,S}$ are selected as follows:

$$\begin{aligned} \psi_2^S &= \tfrac{1}{2} f(\vartheta) \left(\hat{\rho}^F - \hat{\rho}_0^F \right)^2, \\ \psi_2^F &= \left(\bar{\boldsymbol{U}}^S, {}^R\bar{\boldsymbol{\mathcal{K}}}^S \right) \frac{1}{2} \begin{pmatrix} g_{11}(\vartheta) & g_{12}(\vartheta) \\ g_{21}(\vartheta) & g_{22}(\vartheta) \end{pmatrix} \begin{pmatrix} \bar{\boldsymbol{U}}^S \\ {}^R\bar{\boldsymbol{\mathcal{K}}}^S \end{pmatrix} \\ &= \tfrac{1}{2} g_{11}(\vartheta) \bar{\boldsymbol{U}}^S \cdot \bar{\boldsymbol{U}}^S + \tfrac{1}{2} \left(g_{12}(\vartheta) \bar{\boldsymbol{U}}^S \cdot {}^R\bar{\boldsymbol{\mathcal{K}}}^S + g_{21}(\vartheta) {}^R\bar{\boldsymbol{\mathcal{K}}}^S \cdot \bar{\boldsymbol{U}}^S \right) \\ &\quad + \tfrac{1}{2} g_{22}(\vartheta) {}^R\bar{\boldsymbol{\mathcal{K}}}^S \cdot {}^R\bar{\boldsymbol{\mathcal{K}}}^S. \end{aligned} \tag{24.129}$$

Here, $f(\vartheta)$ and $g_{\alpha\beta},\ \alpha, \beta = 1, 2$ are scalar coefficients,[7] possibly dependent on the temperature, which, in a first attempt may be taken as constants; $\hat{\rho}_0^F$ is the fluid density in the reference configuration (usually a constant for a liquid). With the parameterizations (24.129) one obtains from (24.125)–(24.127):

- *Particular additional stresses*:

$$\begin{aligned} (\boldsymbol{t}^F)_{02} &= -\rho^S \hat{\rho}^F f(\vartheta) \left(\hat{\rho}^F - \hat{\rho}_0^F\right) \boldsymbol{I}, \\ (\boldsymbol{t}^S)_2 &= -z^S \nu^S \left\{ \frac{\rho^S \hat{\rho}^F}{\nu^F} f(\vartheta) \left(\hat{\rho}^F - \hat{\rho}_0^F\right) \right\} \boldsymbol{I}. \end{aligned} \tag{24.130}$$

- *Particular additional couple stresses*:

$$\begin{aligned} (\boldsymbol{m}^F)_{02} &= \boldsymbol{0}, \\ (\boldsymbol{m}^S)_2 &= \rho^F \bar{\boldsymbol{R}}^S \left\{ \tfrac{1}{2} \left(g_{12}(\vartheta) + g_{21}(\vartheta)\right) \bar{\boldsymbol{U}}^S + g_{22}(\vartheta)\, {}^R\bar{\boldsymbol{\mathcal{K}}}^S \right\} \left(\boldsymbol{F}^S\right)^T. \end{aligned} \tag{24.131}$$

- *Particular additional interaction forces*:

$$\begin{aligned} \left(\mathfrak{m}^F\right)_2 &= \rho^S f(\vartheta) \left(\hat{\rho}^F - \hat{\rho}_0^F\right) \operatorname{grad} \hat{\rho}^F \\ &- \rho^F \left(\boldsymbol{F}^S\right)^{-T} \left\{ g_{11}(\vartheta) \bar{\boldsymbol{U}}^S + \tfrac{1}{2} \left(g_{12}(\vartheta) + g_{21}(\vartheta)\right)\, {}^R\bar{\boldsymbol{\mathcal{K}}}^S \right\} \nabla \bar{\boldsymbol{U}}^S \\ &- \rho^F \left(\boldsymbol{F}^S\right)^{-T} \left\{ \tfrac{1}{2} \left(g_{12}(\vartheta) + g_{21}(\vartheta)\right) \bar{\boldsymbol{U}}^S + g_{22}(\vartheta)\, {}^R\bar{\boldsymbol{\mathcal{K}}}^S \right\} \nabla\, {}^R\bar{\boldsymbol{\mathcal{K}}}^S, \\ \left(\mathfrak{m}^S\right)_2 &= \boldsymbol{0}, \end{aligned} \tag{24.132}$$

  or in Cartesian tensor notation

$$\begin{aligned} \left(\left(\mathfrak{m}^F\right)_2\right)_i &= \rho^S f(\vartheta) \left(\hat{\rho}^F - \hat{\rho}_0^F\right) \hat{\rho}^F_{,i} \\ &- \rho^F \left(F^S\right)^{-1}_{Di} \left\{ g_{11}(\vartheta) \bar{U}^S_{DC} + \tfrac{1}{2} \left(g_{12}(\vartheta) + g_{21}(\vartheta)\right)^R \bar{\mathcal{K}}^S_{DC} \right\} \bar{U}^S_{CM,M} \\ &- \rho^F \left(F^S\right)^{-1}_{Di} \left\{ \tfrac{1}{2} \left(g_{12}(\vartheta) + g_{21}(\vartheta)\right) \bar{U}^S_{DC} + g_{22}(\vartheta)\, {}^R\bar{\mathcal{K}}^S_{DC} \right\} {}^R\bar{\mathcal{K}}^S_{CM,M}. \end{aligned} \tag{24.133}$$

Here, lower (upper) case indices denote components with respect to the present (reference) coordinates.

The parameterization (24.129) with the five coefficient functions f, $g_{\alpha\beta}$ $(\alpha, \beta = 1, 2)$ can be simplified, if $g_{\alpha\beta} = g\delta_{\alpha\beta}$ is chosen. Then, one obtains,

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[7] In the most general case of (24.129) the g-functions are fourth-order tensors over $\mathbb{R}^3$. Here, by assuming the simplest representation of isotropy, they are merely scalars.

$$
\begin{aligned}
\left(\boldsymbol{m}^S\right)_2^{\text{reduced}} &= \rho^F g(\vartheta)\bar{\boldsymbol{R}}^S \left(\bar{\boldsymbol{U}}^S + {}^R\bar{\boldsymbol{\mathcal{K}}}^S\right)\left(\boldsymbol{F}^S\right)^T ,\\
\left(\mathfrak{m}^F\right)_2^{\text{reduced}} &= \rho^S f(\vartheta)\left(\hat{\rho}^F - \hat{\rho}_0^F\right)\operatorname{grad}\hat{\rho}^F \\
&\quad -\rho^F \left(\boldsymbol{F}^S\right)^{-T} g(\vartheta)\bar{\boldsymbol{U}}^S\nabla\bar{\boldsymbol{U}}^S - \rho^F \left(\boldsymbol{F}^S\right)^{-T} g(\vartheta){}^R\bar{\boldsymbol{\mathcal{K}}}\nabla{}^R\bar{\boldsymbol{\mathcal{K}}}^S .
\end{aligned}
\tag{24.134}
$$

The complete constitutive functions (24.128) are now obtained by adding $\mathcal{Y}_1$ and $\mathcal{Y}_2$, given in (24.120)–(24.123) and (24.130)–(24.132) [or their reduced versions (24.134)].

24.8 On Classes of Alternative Models

The inferences drawn from the entropy principle in the CLAUSIUS–DUHEM inequality deduced in the preceding analysis were obtained under the bold assumptions that

1. the solid and fluid constituents of the binary mixture are *both elastic* (and in particular compressible),
2. *the fluid is dissipative*, but *the solid is not* [see (24.20)],
3. the *rule of aequipresence* is applied, i. e., the constitutive variables of any constituent phase may depend on the independent constitutive variables *of all phases*. This generality is in harmony with DIEBELS [13]. The rule of aequipresence is more general than the rule of phase separation, which is used by most authors of mixture models (of BOLTZMANN structure), e.g., BOWEN (1980/1982) [7, 8], Ehlers (1989/1993) [18–20], and PASSMAN et al. (1984) [60].
4. Owing to the maintenance of the existence of the *saturation condition*, i.e., $\nu^F + \nu^S = 1$, the sum of the volume fractions of the solid and fluid add up to unity, or the fluid and solid fill up the whole space (no empty holes).

The prerequisites of the existence of general elastic deformations of the solid and fluid constituents, and the saturation condition give rise through the exploitation of the entropy principle to three different types of pressures:

(i) the *thermodynamic* pressure of the fluid p_{th}^F, (24.120),
(ii) the *thermodynamic* pressure of the solid p_{th}^S, $(24.121)_3$,
(iii) the *configurational* pressure p_c, $(24.121)_2$.

Within the class of saturated binary mixtures, these prerequisites, (i)–(iii), comprise most general constituting material properties. Limiting situations are, where either the solid or the fluid or both are compressible/incompressible as shown in **Table 24.1**. DIEBELS [13] presents the compressible model in all details as we have done in the previous pages of this chapter. In what follows, we shall comment on results obtained for the hybrid models and the incompressible model.

Table 24.1 Classes of binary solid–fluid COSSERAT models treated in this chapter

Fluid	Solid	References for BOLTZMANN models	Denotation, acronym remarks
Compressible	Compressible	[1–3]	Compressible model (CM)
Incompressible	Compressible	[19, 20]	Hybrid model I (HMI)
Compressible	Incompressible	[1–3]	Hybrid model II (HMII)
Incompressible	Incompressible	[7, 12, 14, 15, 18, 21, 23]	Incompressible model (IM) (see also add. references in [13])

24.8.1 The Hybrid Model I (HMI)

If the true or effective density of the fluid, $\hat{\rho}^F$, is constant, then the 'pore'-fluid is called microscopically incompressible or microscopically density preserving, for which

$$\frac{\partial \psi^\alpha}{\partial \hat{\rho}^F} = 0, \quad \alpha = F, S \quad (\hat{\rho}^F = \text{const.}) \tag{24.135}$$

in all previous formulae. In view of the relation $\rho^F = \nu^F \hat{\rho}^F$, the balance law for the fluid constituent takes the form

$$(\nu^F)'^F + \nu^F \text{div}\,(\boldsymbol{v}^F) = 0, \tag{24.136}$$

which is in conformity with the saturation condition, provided that [see (24.18)]

$$(\nu^F)'^F - z^S \nu^S \text{div}\,(\boldsymbol{v}^S) + (\text{grad}\,\nu^S) \cdot \boldsymbol{w}^F = 0. \tag{24.137}$$

With the fluid mass balance

$$(\nu^F)'^F + \nu^F \text{div}\,(\boldsymbol{v}^F) = 0$$

and $\text{div}\,(\boldsymbol{v}^{F,S}) = \bar{\boldsymbol{\Delta}}^{F,S} \cdot \boldsymbol{I}$ [see Chap. 22. Eqs. (22.57), (22.63)], Eq. (24.137) may also be written as

$$-\,\nu^F \bar{\boldsymbol{\Delta}}^F \cdot \boldsymbol{I} - z^S \nu^S \bar{\boldsymbol{\Delta}}^S \cdot \boldsymbol{I} + (\text{grad}\,\nu^S) \cdot \boldsymbol{w}^F = 0. \tag{24.138}$$

This condition was automatically satisfied by the compressible model CM, but must here be incorporated in the entropy inequality, multiplied with a LAGRANGE parameter P. It follows that to the long entropy inequality, stated as (24.23)–(24.45), the following terms must be added:

$$\begin{array}{lll}\bullet & +P\,\nu^F\bar{\boldsymbol{\Delta}}\cdot\boldsymbol{I} & \text{in line 1 of (4.45)},\\ \bullet & +P\,z^S\nu^S\bar{\boldsymbol{\Delta}}^S\cdot\boldsymbol{I} & \text{in line 1 of (4.23)},\\ \bullet & -P\,\mathrm{grad}\,\nu^S & \text{in line 4 of (4.45)}.\end{array}\tag{24.139}$$

If, moreover, in the long inequality extended by these terms all variables differentiated with respect to $\hat{\rho}^F$ and some of its derivatives are dropped (because these expressions vanish owing to the constancy of $\hat{\rho}^F$) and the analogous inferences are drawn as in Sects. 24.6 and 24.7, then the following results are obtained:

- $$\begin{aligned}\boldsymbol{t}^S = \bar{\boldsymbol{R}}^S&\left\{\rho^S\frac{\partial\psi^S}{\partial\bar{\boldsymbol{U}}^S}+\rho^F\frac{\partial\psi^F}{\partial\bar{\boldsymbol{U}}^S}\right\}(\boldsymbol{F}^S)^T\\ &-z^S\nu^S\left\{P+\rho^S\frac{\partial\psi^S}{\partial\nu^S}+\rho^F\frac{\partial\psi^F}{\partial\nu^S}\right\}\boldsymbol{I}.\end{aligned}\tag{24.140}$$

  Compare this result with (24.47) and note that P takes now the role of the thermodynamic pressure (24.48).

- $$(\boldsymbol{t}^F)_0 = -P\,\nu^F\boldsymbol{I},\tag{24.141}$$

  which corresponds to (24.106) or (24.78) of the CM. The constraint pressure corresponds here also to the fluid part of the thermodynamic pressure.
- The couple stresses in thermodynamic nonequilibrium, (24.48) and in equilibrium remain the same as for the CM,

  $$\begin{aligned}\boldsymbol{m}^S &= \bar{\boldsymbol{R}}^S\left\{\rho^S\frac{\partial\psi^S}{\partial\,{}^R\bar{\boldsymbol{\mathcal{K}}}^S}+\rho^F\frac{\partial\psi^F}{\partial\,{}^R\bar{\boldsymbol{\mathcal{K}}}^S}\right\}(\boldsymbol{F}^S)^T,\\ (\boldsymbol{m}^F)_0 &= \boldsymbol{0}.\end{aligned}\tag{24.142}$$

- The interaction forces and couples in thermodynamic equilibrium take the forms

  $$\begin{aligned}(\mathfrak{m}^F)_0 = -P\,\mathrm{grad}\,\nu^S &- \rho^F(\boldsymbol{F}^S)^{-T}\left(\frac{\partial\psi^F}{\partial\bar{\boldsymbol{U}}^S}\nabla\bar{\boldsymbol{U}}^S\right)^{\underline{1}}\\ &-\rho^F(\boldsymbol{F}^S)^{-T}\left(\frac{\partial\psi^F}{\partial\,{}^R\bar{\boldsymbol{\mathcal{K}}}^S}\nabla\,{}^R\bar{\boldsymbol{\mathcal{K}}}^S\right)^{\underline{1}},\\ (\mathfrak{t}^F)_0 = \boldsymbol{0}.&\end{aligned}\tag{24.143}$$

  These relations correspond in the CM to (24.81) and (24.82) and can be deduced from (24.76), if the terms involving $\partial(\cdot)/\partial\hat{\rho}^F$ are dropped and $(\boldsymbol{w}^F)^*\cdot(-P)\mathrm{grad}\,\nu^S$ is added to (24.77). As before, the constraint pressure term $-P\mathrm{grad}\,\nu^S$ in $(24.127)_1$ is replacing the thermodynamic fluid pressure.
- The internal heat flux in the equilibrium vanishes,

  $$(\boldsymbol{q}^{\mathrm{I}})_0 = \boldsymbol{0}.\tag{24.144}$$

The constraint pressure P, which agrees with the LAGRANGE parameter of equation (24.138) is for HMI an independent field variable that is only determined by solving a concrete boundary value problem. In this regard, P corresponds to the pressure in an incompressible fluid. Further reaching analyses of the model have, e.g., been presented by BLUHM [1–3].

The HMI assumes to consist of a compressible solid component, but an incompressible fluid component and is for this reason severely restricted. It is certainly inappropriate as a model for a grain–air mixture, such as for a dry soil or the upper firn-ice layer of glaciers and ice sheets. However, it may be adequate for water-saturated soft foodstuff.

24.8.2 The Hybrid Model II (HMII)

According to Table 24.1, this model consists of an incompressible solid constituent that is saturated by a compressible fluid. The true density of the solid component is set to a constant,

$$\hat{\rho}^S = \text{const}, \tag{24.145}$$

which implies that the mass balance equation for the solid volume fraction takes the form

$$\frac{\partial \nu^S}{\partial t} + \nu^S \text{div}\,(\boldsymbol{v}^S) = 0, \tag{24.146}$$

which is only consistent with (24.17)$_2$, provided that

$$z^S = 1. \tag{24.147}$$

The volume balance (24.146) can straightaway be integrated. With the initial solid volume fraction ν_0^S in the reference configuration, one obtains[8]

$$\nu^S = \nu_0^S \det\left((\boldsymbol{F}^S)^{-1}\right) = \nu_0^S \det(\bar{\boldsymbol{U}})^{-1}, \tag{24.148}$$

owing to $\boldsymbol{F}^S = \bar{\boldsymbol{R}}^S \bar{\boldsymbol{U}}^S$ [see this volume, Chap. 22, Eq. (22.26)] and the orthogonality of $\bar{\boldsymbol{R}}^S$. The solid volume fraction in the present configuration can, thus directly be evaluated from the determinant of the COSSERAT stretch tensor of the solid constituent by successive updating. Consequently, ν^S is no longer an independent constitutive variable (provided $\bar{\boldsymbol{U}}^S$ is such a variable) and ψ^α, $\alpha = F, S$, can be assumed as functions of the form

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[8] See e.g., [40], Chap. 1, homework 8, p. 43.

$$\psi^\alpha = \psi^\alpha\left(\bar{\boldsymbol{U}}^S, {}^R\bar{\boldsymbol{\mathcal{K}}}^S, \hat{\rho}^F, \vartheta\right), \quad \alpha = F, S. \tag{24.149}$$

It transpires that in the HMII, no additional constraint condition enters the exploitation of the entropy principle. The constitutive quantities can be obtained from those of the CM simply by omitting all terms of the form $\partial(\cdot)/\partial\hat{\rho}^S$ and $\partial(\cdot)/\partial\nu^S$, (since ν^S is no longer an independent constitutive variable).

- The solid stress in equilibrium and the fluid stress in thermodynamic equilibrium, stated in (24.47) and (24.77), respectively, take the forms

$$\begin{aligned}
\boldsymbol{t}^S = {} & \bar{\boldsymbol{R}}^S\left\{\rho^S\frac{\partial\psi^S}{\partial\bar{\boldsymbol{U}}^S} + \rho^F\frac{\partial\psi^F}{\partial\bar{\boldsymbol{U}}^S}\right\}(\boldsymbol{F}^S)^T \\
& -\nu^S\left\{\frac{\rho^S\hat{\rho}^F}{\nu^F}\frac{\partial\psi^S}{\partial\hat{\rho}^F} + \left(\hat{\rho}^F\right)^2\frac{\partial\psi^F}{\partial\hat{\rho}^F}\right\}, \\
\left(\boldsymbol{t}^F\right)_0 = {} & -\left\{\rho^S\hat{\rho}^F\frac{\partial\psi^S}{\partial\hat{\rho}^F} + \left(\hat{\rho}^F\right)^2\nu^F\frac{\partial\psi^F}{\partial\hat{\rho}^F}\right\}\boldsymbol{I} = -\nu^F p_R^F\boldsymbol{I}, \\
p_R^F := {} & \frac{\rho^S\hat{\rho}^F}{\nu^F}\frac{\partial\psi^S}{\partial\hat{\rho}^F} + \left(\hat{\rho}^F\right)^2\frac{\partial\psi^F}{\partial\hat{\rho}^F}.
\end{aligned} \tag{24.150}$$

  These expressions agree with those of the CM.
- The couple stresses of the solid and fluid assume for this HMII the form [compare (24.49) and (24.81)]:

$$\begin{aligned}
\boldsymbol{m}^S &= \bar{\boldsymbol{R}}^S\left\{\rho^S\frac{\partial\psi^S}{\partial{}^R\bar{\boldsymbol{\mathcal{K}}}^S} + \rho^F\frac{\partial\psi^F}{\partial{}^R\bar{\boldsymbol{\mathcal{K}}}^S}\right\}(\boldsymbol{F}^S)^T, \\
(\boldsymbol{m}^F) &= \boldsymbol{0}.
\end{aligned} \tag{24.151}$$

  These expressions equally agree with those of the CM.
- For the interaction force $(\mathfrak{m}^F)_0$ and the interaction couple $(\mathfrak{k})_0$ in thermodynamic equilibrium, given for the CM by (24.80) and (24.82), we obtain with $\partial(\cdot)/\partial\nu^S = 0$ [since ν^S is not an independent constitutive variable]

$$\begin{aligned}
\left(\mathfrak{m}^F\right)_0 = {} & -\left\{\frac{\rho^S\hat{\rho}^F}{\nu^F}\frac{\partial\psi^S}{\partial\hat{\rho}^F} + \left(\hat{\rho}^F\right)^2\frac{\partial\psi^F}{\partial\hat{\rho}^F}\right\}\operatorname{grad}\nu^S + \rho^S\frac{\partial\psi^S}{\partial\hat{\rho}^F}\operatorname{grad}\hat{\rho}^F \\
& -\rho^F\left(\boldsymbol{F}^S\right)^{-T}\left(\frac{\partial\psi^F}{\partial\bar{\boldsymbol{U}}^S}\nabla\bar{\boldsymbol{U}}^S\right)^{\underline{1}} \\
& -\rho^F\left(\boldsymbol{F}^S\right)^{-T}\left(\frac{\partial\psi^F}{\partial{}^R\bar{\boldsymbol{\mathcal{K}}}^S}\nabla{}^R\bar{\boldsymbol{\mathcal{K}}}^S\right)^{\underline{1}}, \\
(\mathfrak{k})_0 = {} & \boldsymbol{0}.
\end{aligned} \tag{24.152}$$

- Finally, the equilibrium inner heat flux vector in thermodynamic equilibrium vanishes:

$$\left(\boldsymbol{q}^{\mathrm{I}}\right)_0 = \mathbf{0}. \tag{24.153}$$

24.8.3 The Incompressible Model (IM)

For Boltzmann continua, the incompressible model for binary mixtures has often been presented in the literature, see e.g., Bowen (1980) [7], De Boer and Ehlers (1986) [12] and Ehlers (1989) [18]. It is also popular in multiphase fluids and in consolidation theories.

Because the true densities are constant,

$$\hat{\rho}^{\alpha} = \text{const.}, \quad \alpha = 1, 2, \tag{24.154}$$

the mass balances for the solid and fluid can be written as balances for the volume fractions,

$$(\nu^{\alpha})'^{\alpha} + \nu^{\alpha} \mathrm{div}\,(\boldsymbol{v}^{\alpha}) = 0. \tag{24.155}$$

For the solid, conformity of (24.155) with (24.17) requires $z^S = 1$; for the fluid, the saturation condition implies the balance (24.137) (as for the HMI, which serves also for this IM as a constraint condition). With the Lagrange parameter P, the terms (24.139) must also here be added to the long entropy inequality (24.23)–(24.45). The inferences due to the exploitation of this extended inequality must then be the same as for the HMI, but the terms $\partial(\cdot)/\partial\hat{\rho}^S$ must be dropped. Thus, one obtains from (24.140)–(24.143)

$$\bullet \quad \boldsymbol{t}^S = \bar{\boldsymbol{R}}^S \left\{ \rho^S \frac{\partial \psi^S}{\partial \bar{\boldsymbol{U}}^S} + \rho^F \frac{\partial \psi^F}{\partial \bar{\boldsymbol{U}}^S} \right\} (\boldsymbol{F}^S)^T - P \nu^S \boldsymbol{I}, \tag{24.156}$$

$$\bullet \quad \left(\boldsymbol{t}^F\right)_0 = -P \nu^F \boldsymbol{I}, \tag{24.157}$$

$$\begin{aligned} \bullet \quad \boldsymbol{m}^S &= \bar{\boldsymbol{R}}^S \left\{ \rho^S \frac{\partial \psi^S}{\partial\, {}^R\bar{\boldsymbol{\mathcal{K}}}^S} + \rho^F \frac{\partial \psi^F}{\partial\, {}^R\bar{\boldsymbol{\mathcal{K}}}^S} \right\} (\boldsymbol{F}^S)^T, \\ (\boldsymbol{m}^F)_0 &= \mathbf{0}, \end{aligned} \tag{24.158}$$

$$\begin{aligned} \bullet \quad \left(\boldsymbol{\mathfrak{m}}^F\right)_0 = {} & -P \,\mathrm{grad}\, \nu^S - \rho^F (\boldsymbol{F}^S)^{-T} \left(\frac{\partial \psi^F}{\partial \bar{\boldsymbol{U}}^S} \nabla \bar{\boldsymbol{U}}^S \right)^{\underline{1}} \\ & -\rho^F (\boldsymbol{F}^S)^{-T} \left(\frac{\partial \psi^F}{\partial\, {}^R\bar{\boldsymbol{\mathcal{K}}}^S} \nabla\, {}^R\bar{\boldsymbol{\mathcal{K}}}^S \right)^{\underline{1}}, \\ \left(\boldsymbol{\mathfrak{k}}^F\right)_0 = {} & \mathbf{0}. \end{aligned} \tag{24.159}$$

Evidently, only the stresses (24.156), (24.157), and the interaction force $(24.159)_1$ are directly influenced by the constraint parameter P.

24.9 Specification of the Material Behavior

24.9.1 Rules of Aequipresence and Phase Separation and Their Approximate use for a Binary Mixture

In Sect. 24.7.1 formula (24.69) was proved to be the permissible thermodynamic functional relation of the HELMHOLTZ free energies of the solid and fluid constituents for a binary saturated mixture of the class (24.20), if the rule of aequipresence was observed as a principal basis. In Sect. 24.7.3, following DIEBELS (2000) [13], this constitutive postulate was then simplified by replacing the rule of aequipresence by the rule of phase separation, which led to

$$\psi^S = \psi^S\left(\bar{\boldsymbol{U}}^S, {}^R\bar{\boldsymbol{\mathcal{K}}}^S, \nu^S, \vartheta\right), \qquad \psi^F = \psi^F\left(\hat{\rho}^F, \vartheta\right),$$

and the consequential stress, couple stress, and interaction force and couple formulae (24.120)–(24.123). Limitation to the rule of phase separation means that the derived quantities for the stresses, couple stresses are functionally the same as for a single- constituent solid or single-constituent fluid without a solid–fluid interaction. The influence of the rule of aequipresence can then at least approximately be recovered by the additive decomposition of the functions $\psi_2^{S,F}$ given in (24.124). The stress, couple stress, and interaction force and couple are then equally given by the respective additions of the expressions (24.120)–(24.123) and (24.125)–(24.127), respectively. An example for a weak (linear) contribution of the 'aequipresence' term is suggested in (24.129) with consequential additions for the stresses, couple stresses and interaction force and couple in (24.130)–(24.134).

In the following subsections, the intention is to present explicit forms of the solid and fluid HELMHOLTZ free energies that may serve as master functions when attempting the formulation and solution of initial boundary value problems for the type of binary solid–fluid mixtures of the constituents dealt with in this chapter. Explicit forms of the free energies are known for BOLTZMANN continua of single-constituent media; they provide a guidance in our attempt to invent explicit functional forms for $\psi^{S,F}$ of the solid and fluid, respectively. For this reason, it is certainly helpful, if proposals for single-constituent models are presented, before proposals for binary solid–fluid mixtures are suggested. This is all the more justified in view of the fact that with the assumption of phase separation the free energies $\psi^{S,F}$

[see in (24.124) the functions $\psi_1^{S,F}$] are formally such as if they were formulated for a single- constituent body.

24.9.2 *A Linear Model of Thermoelasticity of a Cosserat Single-Constituent Body*

Early elasticity models for Cosserat solids were developed by Eringen and Suhubi [30, 73], Nowacki [57, 58].[9] They concern linear and nonlinear constitutive modeling, consistent with the Second Law. Below, the linear thermoelastic model due to Nowacki [58] is presented that is based on consequential linearization using the Clausius–Duhem–Coleman–Noll procedure. Nowacki presents his model in the Euler description, using Cartesian tensor notation. Central kinematic quantities are, therefore, the *asymmetric strain* tensor, γ_{ij} and the *torsion* tensor, κ_{ij}, defined by

$$\gamma_{ij} = u_{i,j} + \varepsilon_{ijk}\phi_k, \quad \kappa_{ij} = \phi_{j,i}. \tag{24.160}$$

Balances of internal energy, ε, and entropy, s, are given by

$$\begin{aligned} \rho\dot{\varepsilon} &= \sigma_{ij}\dot{\gamma}_{ij} + m_{ij}\dot{\kappa}_{ij} - q_{i,i} + \rho\mathfrak{r}, \\ \rho\dot{s} &= -\frac{q_{i,i}}{T} + \frac{q_k T_{,k}}{T^2} + \frac{\rho\mathfrak{r}}{T} + \rho\eta^s, \end{aligned} \tag{24.161}$$

in which σ_{ij} and m_{ij} are the Cauchy stress and couple stress tensors; q_i, $\mathfrak{r}$ and η^s are the heat flux vector, the specific energy supply, and the specific entropy production rate, while $T > 0$ is the absolute temperature. Eliminating between $(24.161)_{1,2}$ the energy supply rate density, $\mathfrak{r}$, and introducing the Helmholtz free energy $\psi = \varepsilon - Ts$, leads to

$$\dot{\psi} = \sigma_{ij}\dot{\gamma}_{ij} + m_{ij}\dot{\kappa}_{ij} - s\dot{T} - T\left(\rho\eta^s + \frac{q_k T_{,k}}{T}\right). \tag{24.162}$$

At this point, constitutive relations of the form

$$\mathcal{C} = \mathcal{C}\left(\gamma_{ij}, \kappa_{ij}, T, T_{,k}\right), \quad \mathcal{C} = \{\psi, q_k\} \tag{24.163}$$

are assumed; materials of this class are called *thermoelastic* Cosserat solids. With these, and the use of the chain rule of differentiation, (24.162) takes the form

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[9] Pertinent early memoirs are as well by Eringen [28, 29], Grioli [38, 39], Mindlin and Tiersten [50], Neuber [54], Schäfer [63, 64], [65], Smith [69, 70], Soos [71, 72], Toupin [76], Wozniak [82], Wyrwinski [83], and many others, see e.g., [58].

$$-\left(\frac{\partial\psi}{\partial\gamma_{ij}}-\sigma_{ij}\right)\dot{\gamma}_{ij}-\left(\frac{\partial\psi}{\partial\kappa_{ij}}-m_{ij}\right)\dot{\kappa}_{ij}-\left(\frac{\partial\psi}{\partial T}+s\right)\dot{T}-\frac{\partial\psi}{\partial T_{,k}}\dot{T}_{,k}$$
$$-\frac{q_k T_{,k}}{T}=T\rho\eta^s\overset{!}{\geqslant}0, \tag{24.164}$$

in which the Second Law implies that $\eta^s \geqslant 0$. Because the above inequality is linear in the quantities $\{\dot{\gamma}_{ij}, \dot{\kappa}_{ij}, \dot{T}, \dot{T}_{,k}\}$ and must hold for arbitrary values of $\{\dot{\gamma}_{ij}, \dot{\kappa}_{ij}, \dot{T}, \dot{T}_{,k}\}$, we necessarily have[10]

$$\sigma_{ij}=\frac{\partial\psi}{\partial\gamma_{ij}},\quad m_{ij}=\frac{\partial\psi}{\partial\kappa_{ij}},\quad s=-\frac{\partial\psi}{\partial T},\quad \psi\neq\psi(\cdot,T_{,k}), \tag{24.165}$$

as well as

$$-q_k T_{,k}=T\rho\eta^s\geqslant 0\quad\xrightarrow{T\rho>0}\quad q_k T_{,k}\leqslant 0. \tag{24.166}$$

With the FOURIER law of heat conduction, $q_k=-KT_{,k}$, this implies $K\geqslant 0$. The heat conductivity is nonnegative.

In an isotropic, homogeneous and centrosymmetric[11] body and in a formally linear thermoelastic body, the free energy $\rho\psi$ has the following quadratic expansion [58],

$$\rho\psi=\frac{\mu+\alpha}{2}\gamma_{ij}\gamma_{ij}+\frac{\mu-\alpha}{2}\gamma_{ij}\gamma_{ji}+\frac{\lambda}{2}\gamma_{kk}\gamma_{nn}+\frac{\xi+\varepsilon}{2}\kappa_{ij}\kappa_{ij}$$
$$+\frac{\xi-\varepsilon}{2}\kappa_{ij}\kappa_{ji}+\frac{\beta}{2}\kappa_{kk}\kappa_{nn}-\nu\gamma_{kk}\theta-\chi\kappa_{kk}\theta+G(\theta). \tag{24.167}$$

Here, $\mu, \alpha, \lambda, \xi, \varepsilon, \beta, \nu$ and χ are constants, while $\theta = T - T_0$, where T_0 is a constant reference temperature at zero deformation. Thus, θ is the small temperature difference above a constant base temperature and $G(\theta)$ is a smooth integrable function of $\theta = T - T_0$. The quadratic representation (24.167) does not involve mixed terms $\gamma_{ij}\kappa_{ij}, \gamma_{ij}\kappa_{ji}$, the reason being that, according to (24.160), the terms $\gamma_{ij}\kappa_{ij}, \gamma_{ij}\kappa_{ji}$ are not invariant under rotations reflecting central symmetry; [take e.g., a rotation by 180°, which changes the sign of $\gamma_{ij}\kappa ij$]. As noted also by DIEBELS [13], this makes some models violating centro symmetry, [47, 48], which is regarded as unphysical.

In general, ψ as a scalar quantity is an *isotropic tensor function* of the invariants γ_{ij} and κ_{ij}, namely,

$$\gamma_{ij}\gamma_{ij},\ \gamma_{ij}\gamma_{ji},\ \gamma_{kk}\gamma_{nn};\qquad \kappa_{ij}\kappa_{ij},\ \kappa_{ij}\kappa_{ji},\ \kappa_{kk}\kappa_{nn}, \tag{24.168}$$

among others (of higher than quadratic dependences). With the restrictions (24.168)

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[10] A detailed explanation of these arguments is given in Vol. 2 Chap. 18 'Thermodynamics – Field Formulation' of this treatise [42].

[11] This means, constitutive equations are invariant with respect to arbitrary rotations.

the coefficients $\{\mu, \alpha, \lambda, \xi, \varepsilon, \beta, \nu, \chi\}$ must be treated as constants. Relations (24.165) then yield

$$\begin{aligned}
\sigma_{ij} &= (\mu+\alpha)\gamma_{ij} + (\mu-\alpha)\gamma_{ji} + (\lambda\gamma_{kk} - \nu\theta)\delta_{ij},\\
m_{ij} &= (\xi+\varepsilon)\kappa_{ij} + (\xi-\varepsilon)\kappa_{ji} + (\beta\kappa_{kk} + \nu\theta)\delta_{ij},\\
s &= \nu\gamma_{kk} + \chi\kappa_{kk}\theta - \frac{\partial G(\theta)}{\partial T}.
\end{aligned} \tag{24.169}$$

These can also be written as

$$\begin{aligned}
\sigma_{ij} &= 2\mu\gamma_{(ij)} + 2\alpha\gamma_{[ij]} + (\lambda\gamma_{kk} - \nu\theta)\delta_{ij},\\
m_{ij} &= 2\xi\kappa_{(ij)} + 2\varepsilon\kappa_{[ij]} + (\lambda\kappa_{kk} + \nu\theta)\delta_{ij},\\
s &= \nu\gamma_{kk} + \chi\kappa_{kk}\theta - \frac{\partial G(\theta)}{\partial T}.
\end{aligned} \tag{24.170}$$

The coefficients μ and λ are LAMÉ constants, while $\alpha, \beta, \xi, \varepsilon$ are new COSSERAT elasticity constants. These are the constants of isothermal elasticity, whereas ν and χ depend on both, the mechanical and thermal processes of the body. NOWACKI [58] derived the inverse relations to (24.169) as follows:

$$\begin{aligned}
\gamma_{ij} &= \alpha_t\theta\delta_{ij} + 2\mu'\sigma_{(ij)} + 2\alpha'\sigma_{[ij]} + \lambda'\sigma_{kk}\delta_{ij},\\
\kappa_{ij} &= \beta_t\theta\delta_{ij} + 2\xi' m_{(ij)} + 2\varepsilon' m_{[ij]} + \beta' m_{kk}\delta_{ij},
\end{aligned} \tag{24.171}$$

with new constant parameters $\alpha_t, \beta_t, \mu', \xi', \alpha', \varepsilon', \beta'$. By substituting (24.171) into (24.170) and requesting the emerging equations to be identities, the following correspondences are obtained:

$$\begin{gathered}
2\mu' = \frac{1}{2\mu}, \quad 2\alpha' = \frac{1}{2\alpha}, \quad \lambda' = \frac{\lambda}{6\mu K}, \quad \alpha_t = \frac{\nu}{3K},\\
2\xi' = \frac{1}{2\xi}, \quad 2\varepsilon' = \frac{1}{2\varepsilon}, \quad \beta' = \frac{\beta}{6\xi\Omega} \quad \beta_t = \frac{\chi}{3\Omega},\\
\text{with} \quad K = \lambda + \frac{2}{3}\mu, \quad \Omega = \beta + \frac{2}{3}\xi.
\end{gathered} \tag{24.172}$$

Next, let us consider Eq. (24.171) for stress and couple stress free conditions. Then,

$$\gamma_{ij} = \alpha_t\theta\delta_{ij} \quad \text{and} \quad \kappa_{ij} = \beta_t\theta\delta_{ij}. \tag{24.173}$$

Because an isotropic solid cannot generate a rotation dependent deformation, as noted by NOWACKI [57], (24.173)$_2$ requires that

$$\beta_t \equiv 0 \quad \overset{(24.172)}{\Longrightarrow} \quad \chi = 0, \tag{24.174}$$

so that, finally,

$$\begin{aligned} \sigma_{ij} &= 2\mu\gamma_{(ij)} + 2\alpha\gamma_{[ij]} + (\lambda\gamma_{kk} - \nu\theta)\delta_{ij}, \\ m_{ij} &= 2\xi\kappa_{(ij)} + 2\varepsilon\kappa_{[ij]} + \beta\kappa_{kk}\delta_{ij}, \\ s &= \nu\gamma_{kk} - \frac{\partial G(\theta)}{\partial T} \end{aligned} \tag{24.175}$$

is obtained. [In plane deformation, the terms involving ξ and β in (24.175)$_2$ drop out.] More generally, in three dimensions (24.175)$_3$ implies

$$\mathrm{d}s = \nu \mathrm{d}\gamma_{kk} - \frac{\partial^2 G(\theta)}{\partial T^2}\mathrm{d}T. \tag{24.176}$$

With the specific heat c_ε at constant deformation, we have

$$c_\varepsilon = T\left(\frac{\partial s}{\partial T}\right)_{\gamma,\kappa} = -\frac{\partial^2 G}{\partial T^2}T.$$

Integration yields

$$\begin{aligned} & G(\theta) = -\int_{T_0}^{T} \mathrm{d}T' \int_{T_0}^{T'} \frac{c_\varepsilon \mathrm{d}T''}{T''} = -\int_{T_0}^{T} c_\varepsilon \ln\left(\frac{T'}{T_0}\right)\mathrm{d}T' \\ \longrightarrow \quad & -\frac{\partial G(\theta)}{\partial T} = c_\varepsilon \ln\left(\frac{T}{T_0}\right) \\ \Longrightarrow \quad & s = \nu\gamma_{kk} + c_\varepsilon \ln\left(1 + \frac{\theta}{T_0}\right) = \nu\gamma_{kk} + c_\varepsilon\frac{\theta}{T_0}. \end{aligned} \tag{24.177}$$

This thermodynamic linearized thermoelastic model is due to NOVACHKI [58]. The model has subsequently been re-derived and/or used by LAKES [45] and for two dimensional problems by DE BORST [11], and EHLERS and VOLK [24–26], as stated by DIEBELS [13].

The results presented above have been derived for a single-constituent body, for which the volume fraction has neither entered the balance relations nor the constitutive modeling. For linearized thermoelasticity such an assumption is permissible on the basis that the material compressibility is accounted for by the LAMÉ constants. When large volumetric changes within a nonlinear theory are in focus and the configurational porosity is large, such a simplification is no longer justified.

As a preliminary step toward such an extended formulation, let us in the next subsection provide a glimpse onto the nonlinear elasticity theory of isotropic solids, first again for a single-constituent body of BOLTZMANN structure and by omitting the porosity.

24.9.3 Elastic Energies for Isotropic Solid Boltzmann Bodies

As is well known, see PENN (1970) [61], GREEN and ZERNA (1954) [37], HUTTER and JÖHNK (2004) [40] for any elastic material, it is customary to write the general strain energy (HELMHOLTZ free energy) function W as

$$W = W(I_{\boldsymbol{B}}, II_{\boldsymbol{B}}, III_{\boldsymbol{B}}), \tag{24.178}$$

where $\boldsymbol{B} = \boldsymbol{F}\boldsymbol{F}^T$ is the left CAUCHY–GREEN deformation tensor and $I_{\boldsymbol{B}}$, $II_{\boldsymbol{B}}$, $III_{\boldsymbol{B}}$ are the invariants

$$\begin{aligned} I_{\boldsymbol{B}} &= \lambda_1^2 + \lambda_2^2 + \lambda_3^2, \\ II_{\boldsymbol{B}} &= \lambda_1^2\lambda_2^2 + \lambda_2^2\lambda_3^2 + \lambda_3^2\lambda_1^2, \\ III_{\boldsymbol{B}} &= \lambda_1^2\lambda_2^2\lambda_3^2 \qquad (= \det \boldsymbol{B}), \end{aligned} \tag{24.179}$$

and λ_1, λ_2, λ_3 are the principal stretches (the eigenvalues of $\sqrt{\boldsymbol{B}}$).[12]

For compressible materials it is customary to separate the influence of the *isochoric* and *dilatational* deformations additively in the form

$$W = \hat{W} + U, \quad \text{where} \quad \hat{W} = W_{\text{isochor}}, \quad U = W_{\text{dilat}}. \tag{24.180}$$

To this end, combinations of the invariants $I_{\boldsymbol{B}}$, $II_{\boldsymbol{B}}$, $III_{\boldsymbol{B}}$ are introduced as follows [61]

$$I_{\hat{\boldsymbol{B}}} = \frac{I_{\boldsymbol{B}}}{III_{\boldsymbol{B}}^{1/3}}, \quad II_{\hat{\boldsymbol{B}}} = \frac{II_{\boldsymbol{B}}}{III_{\boldsymbol{B}}^{2/3}}, \quad III_{\hat{\boldsymbol{B}}} = III_{\boldsymbol{B}} =: J^2. \tag{24.181}$$

For isotropic elastic bodies the function W in (24.178) must be an isotropic function that is invariant under orthogonal transformations. For pure dilatation $\lambda_1 = \lambda_2 = \lambda_3 = \lambda$, it is easy to show that

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[12] Alternatively, (24.178) and (24.179) can also be formulated for the right CAUCHY–GREEN deformation tensor $\boldsymbol{C} = \boldsymbol{F}^T\boldsymbol{F}$; the eigenvalues λ_i $(i = 1, 2, 3)$ are the same for $\sqrt{\boldsymbol{C}}$ as for $\sqrt{\boldsymbol{B}}$, see e.g., [40].

$$I_{\hat{\boldsymbol{B}}} = \frac{3\,\lambda^2}{\lambda^2} = 3, \quad II_{\hat{\boldsymbol{B}}} = \frac{3\,\lambda^4}{\lambda^4} = 3, \quad III_{\hat{\boldsymbol{B}}} = \lambda^2 =: J^2. \tag{24.182}$$

The free energy W, given as a function of the principal invariants in (24.178) can, also be formulated as a function of the alternative invariants (24.181) as

$$W = \tilde{W}(I_{\hat{\boldsymbol{B}}}, II_{\hat{\boldsymbol{B}}}, III_{\hat{\boldsymbol{B}}}) \quad \text{or} \quad W = \bar{W}(I_{\hat{\boldsymbol{B}}}, II_{\hat{\boldsymbol{B}}}, J), \tag{24.183}$$

which straightaway suggests the decomposition

$$W = \hat{W}(I_{\hat{\boldsymbol{B}}}, II_{\hat{\boldsymbol{B}}}) + U(III_{\hat{\boldsymbol{B}}}), = \hat{W}(I_{\hat{\boldsymbol{B}}}, II_{\hat{\boldsymbol{B}}}) + U(J), \tag{24.184}$$

that separates the free energy into a purely *isochoric* part $\hat{W}$ [since $I_{\hat{\boldsymbol{B}}} = II_{\hat{\boldsymbol{B}}} = 3$ for a pure dilatation, $\hat{W}$ is a constant for this motion (with value zero)] and a *dilatational* part U accounting for the compressibility of the material.

It follows from the theory of hyperelastic continua that the KIRCHHOFF stress tensor, the J-weighted CAUCHY stress tensor, $\boldsymbol{t}_{\text{elast}} = J\boldsymbol{\sigma}_{\text{elast}}$, is derivable from W as follows:

$$\boldsymbol{t}_{\text{elast}} = 2\left(\frac{\partial W}{\partial \boldsymbol{B}}\right)\boldsymbol{B} \qquad \left[= 2\boldsymbol{F}\left(\frac{\partial W}{\partial \boldsymbol{C}}\right)\boldsymbol{F}^T\right]. \tag{24.185}$$

These two formulae can be obtained if the Second Law is exploited for an isotropic elastic solid body. It is also straightforward to show that[13]

$$\begin{aligned} \boldsymbol{t}_{\text{elast}} &= 2\varphi_0\boldsymbol{I} + 2\varphi_1\boldsymbol{B} + 2\varphi_2\boldsymbol{B}\boldsymbol{B}, \\ \varphi_0 &:= \frac{1}{2}J\frac{\partial W}{\partial J}, \\ \varphi_1 &:= \left(\frac{\partial W}{\partial I_{\boldsymbol{B}}} + I_{\boldsymbol{B}}\frac{\partial W}{\partial II_{\boldsymbol{B}}}\right), \\ \varphi_2 &:= -\frac{\partial W}{\partial II_{\boldsymbol{B}}}, \end{aligned} \tag{24.186}$$

or in terms of $W = \bar{W}(I_{\hat{\boldsymbol{B}}}, II_{\hat{\boldsymbol{B}}}, J)$,

$$\begin{aligned} \boldsymbol{t}_{\text{elast}} &= 2\bar{\varphi}_0\boldsymbol{I} + 2\bar{\varphi}_1\hat{\boldsymbol{B}}^D + 2\bar{\varphi}_2(\hat{\boldsymbol{B}}\hat{\boldsymbol{B}})^D, \\ \bar{\varphi}_0 &:= \frac{1}{2}J\frac{\partial \bar{W}}{\partial J}, \\ \bar{\varphi}_1 &:= \frac{\partial \bar{W}}{\partial I_{\hat{\boldsymbol{B}}}} + I_{\hat{\boldsymbol{B}}}\frac{\partial \bar{W}}{\partial II_{\hat{\boldsymbol{B}}}}, \end{aligned} \tag{24.187}$$

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[13] The representation (24.186), (24.187) as quadratic polynomial tensor relations of $\boldsymbol{I}$, $\boldsymbol{B}$, $\boldsymbol{B}\boldsymbol{B}$ is a consequence of the CAYLEY–HAMILTON theorem for any smooth function.

Table 24.2 Free energies for nonlinear elastic solids

$W = \frac{1}{2}\mu\,(I_{\boldsymbol{B}} - 3) - \mu \ln J + U(J)$	NEO-HOOKE [51, 62]
$W = \frac{1}{2}\mu\,(I_{\boldsymbol{B}} - 3) - \mu \ln J + \frac{1}{2}\Lambda\,(\ln J)^2$	SIMO–PISTER [66]
$W = \left(\frac{\mu}{2} - C_1\right)\left(J^{-4/3} II_{\boldsymbol{B}} - 3\right)$ $-C_1\left(J^{-2/3} I_{\boldsymbol{B}} - 3\right) + \frac{k}{2}(J-1)^2$	MOONEY–RIVLIN[a] [51, 62]
$\bar{W} = \frac{1}{2}\mu\left(I_{\hat{\boldsymbol{B}}} - 3\right) + \frac{1}{2}k\,(\ln J)^2$	FLORY[a] [33]

[μ is a shear modulus and Λ or k are bulk moduli. C_1 is a constant]

[a] For short biographies of JOHN PAUL FLORY and RONALD SAMUEL RIVLIN, see **Fig.** 24.3

Table 24.3 KIRCHHOFF stress tensors $\boldsymbol{t}_{\text{elast}}$ evaluated from the free energies stated in Table 24.2 with the aid of the rules (24.186) and (24.187).

$\boldsymbol{t}_{\text{elast}} = \mu(\boldsymbol{B} - \boldsymbol{I}) + J\dfrac{\partial U}{\partial J}\boldsymbol{I}$	NEO-HOOKE [51, 62]
$\boldsymbol{t}_{\text{elast}} = \mu(\boldsymbol{B} - \boldsymbol{I}) + (\Lambda \ln J)\,\boldsymbol{I}$	SIMO-PISTER [22, 66]
$\boldsymbol{t}_{\text{elast}} = \left\{-\left(\dfrac{\mu}{2} - C_1\right)\dfrac{4}{3}J^{-4/3} + \dfrac{2}{3}C_1 J^{-2/3} I_{\boldsymbol{B}} + kJ(J-1)\right\}\boldsymbol{I}$ $+2\left\{\left(\dfrac{\mu}{2} - C_1\right)J^{-4/3} I_{\boldsymbol{B}} - C_1 J^{-2/3}\right\}\boldsymbol{B}$ $-2\left\{\left(\dfrac{\mu}{2} - C_1\right)J^{-4/3}\right\}\boldsymbol{B}\boldsymbol{B}.$	MOONEY–RIVLIN [22, 51, 62]
$\boldsymbol{t}_{\text{elast}} = \mu\boldsymbol{B}^D + (k \ln J)\,\boldsymbol{I}$	FLORY [22, 34]

[$\boldsymbol{B}^D$ is the deviatoric part of $\boldsymbol{B}$]

$$\bar{\varphi}_2 := -\frac{\partial \bar{W}}{\partial II_{\hat{\boldsymbol{B}}}},$$

in which $\boldsymbol{B} = \hat{\boldsymbol{B}}\left(J^{2/3}\right)$, and the superscript D indicates that the superscripted quantity is a deviator. For the relatively easy proofs of (24.186) and (24.187), see EHLERS and EIPPER (1998) [22].

Examples of popular nonlinear free energy functions are collected in **Table 24.2** and corresponding KIRCHHOFF stress formulae, evaluated with the rules (24.186) and (24.187), are given in **Table 24.3**.

Fig. 24.3 JOHN PAUL FLORY (June 19, 1910–September 9, 1985) and RONALD SAMUEL RIVLIN (May 6, 1915–October 4, 2005)

JOHN PAUL FLORY (1910–1985) was an American chemist and Nobel laureate (1974), known through his work on polymers and macromolecules. He was Professor of Chemistry at Cornell (1948–1961), then Stanford universities. His best known works are summarized in

- *Principles of Polymere Chemistry* (1953) [32],
- *Statistical Mechanics of Macromolecules* (1969), [34], and
- his Selected Works [35].

RONALD SAMUEL RIVLIN (1915–2005) was a British-American physicist, applied mathematician, rheologist, and noted specialist on rubber. He earned his Ph.D. at Cambridge University in Mathematics. After a number of assignments in the British rubber industry, he took posts at Brown University (1953–1967) and Lehigh University (1967–1980), where he became Director of the Center of the Application of Mathematics. Professionally, he was known for his pioneering work on large elastic deformations and neo-HOOKE and MOONEY–RIVLIN solids and nonNEWTONian Fluids, where the RIVLIN–ERICKSEN tensors play an important role. See also the biographical note on REINER–RIWLIN fluids in Vol. 1 of this treatise on fluid and thermodynamics on p. 355 [41].

The text is based on www.wikipedia.org

The CAUCHY stress tensor, expressed in terms of the function $\bar{W}$ in (24.183) and (24.184) is given in [61] as

$$\boldsymbol{\sigma}_{\text{elast}} = \frac{2}{III_{\hat{\boldsymbol{B}}}^{1/2}} \left\{ \left[\frac{II_{\hat{\boldsymbol{B}}}}{3} \frac{\partial \tilde{W}}{\partial II_{\hat{\boldsymbol{B}}}} - \frac{I_{\hat{\boldsymbol{B}}}}{3} \frac{\partial \tilde{W}}{\partial I_{\hat{\boldsymbol{B}}}} + III_{\hat{\boldsymbol{B}}} \frac{\partial \tilde{W}}{\partial III_{\hat{\boldsymbol{B}}}} \right] \boldsymbol{I} \right.$$

$$
\begin{aligned}
&\qquad + \frac{1}{III_{\hat{\boldsymbol{B}}}^{1/3}}\frac{\partial\tilde{W}}{\partial I_{\hat{\boldsymbol{B}}}}\boldsymbol{B} - III_{\hat{\boldsymbol{B}}}^{1/3}\frac{\partial\tilde{W}}{\partial II_{\hat{\boldsymbol{B}}}}\boldsymbol{B}^{-1}\Bigg\} \\
\overset{(24.184)}{=} \quad & \frac{2}{III_{\hat{\boldsymbol{B}}}^{1/2}}\Bigg\{\left[\frac{II_{\hat{\boldsymbol{B}}}}{3}\frac{\partial\hat{W}}{\partial II_{\hat{\boldsymbol{B}}}} - \frac{I_{\hat{\boldsymbol{B}}}}{3}\frac{\partial\hat{W}}{\partial I_{\hat{\boldsymbol{B}}}}\right]\boldsymbol{I} + \frac{1}{III_{\hat{\boldsymbol{B}}}^{1/3}}\frac{\partial\hat{W}}{\partial I_{\hat{\boldsymbol{B}}}}\boldsymbol{B} \\
& - III_{\hat{\boldsymbol{B}}}^{1/3}\frac{\partial\hat{W}}{\partial II_{\hat{\boldsymbol{B}}}}\boldsymbol{B}^{-1}\Bigg\} + \frac{2}{III_{\hat{\boldsymbol{B}}}^{1/2}}\left\{III_{\hat{\boldsymbol{B}}}\frac{\partial U}{\partial III_{\hat{\boldsymbol{B}}}}\right\}\boldsymbol{I}. \qquad (24.188)
\end{aligned}
$$

In expression (24.188), the trace of the first curly bracket vanishes[14]; therefore, the mean elastic pressure is

$$
\begin{aligned}
p_{\text{elast}}^{\text{mean}} \quad = \quad & -\frac{1}{3}\operatorname{tr}(\boldsymbol{\sigma}_{\text{elast}}) = -2III_{\hat{\boldsymbol{B}}}^{1/2}\frac{\partial U(III_{\hat{\boldsymbol{B}}})}{\partial III_{\hat{\boldsymbol{B}}}} \\
\overset{(24.182)_3}{=} \quad & -2\,J\frac{\partial U(J)}{\partial J}\underbrace{\frac{\partial J}{\partial III_{\hat{\boldsymbol{B}}}}}_{1/(2J)} = -\frac{\partial U(J)}{\partial J}. \qquad (24.189)
\end{aligned}
$$

For a stress-free reference configuration, it follows from (24.189) that $(\partial U/\partial J)|_{J=1} = 0$.

According to Penn (1970) [61] the decomposition (24.184) is not fully supported by experiments (on a rubber specimen), and Diebels (2000) [13]—quoting Ehlers

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[14] To prove this, take the trace of the term $\{\cdot\}$ in the first curly brackets of (24.188). This yields

$$
II_{\hat{\boldsymbol{B}}}\frac{\partial\hat{W}}{\partial II_{\hat{\boldsymbol{B}}}} - I_{\hat{\boldsymbol{B}}}\frac{\partial\hat{W}}{\partial I_{\hat{\boldsymbol{B}}}} + \frac{1}{III_{\hat{\boldsymbol{B}}}^{1/3}}\frac{\partial\hat{W}}{\partial I_{\hat{\boldsymbol{B}}}}I_{\boldsymbol{B}} - III_{\hat{\boldsymbol{B}}}^{1/3}\frac{\partial\hat{W}}{\partial II_{\hat{\boldsymbol{B}}}}I_{\boldsymbol{B}^{-1}} \overset{\text{def.}}{=} \mathfrak{Q}.
$$

Owing to $(24.181)_1$, the second and third term of this expression cancel each other. To conclude the same for the remaining terms, $I_{\boldsymbol{B}^{-1}}$ must be expressed in terms of the invariants of $\boldsymbol{B}$. This follows from the Cayley–Hamilton theorem

$$
\boldsymbol{B}^3 - I_{\boldsymbol{B}}\boldsymbol{B}^2 + II_{\boldsymbol{B}}\boldsymbol{B} - III_{\boldsymbol{B}}\boldsymbol{I} \equiv 0,
$$

from which one easily deduces

$$
\begin{aligned}
& \boldsymbol{B}^2 - I_{\boldsymbol{B}}\boldsymbol{B} + II_{\boldsymbol{B}}\boldsymbol{I} - III_{\boldsymbol{B}}\boldsymbol{B}^{-1} = 0, \\
\Longrightarrow \quad & \boldsymbol{B}^{-1} = \frac{1}{III_{\boldsymbol{B}}}\boldsymbol{B}^2 - \frac{I_{\boldsymbol{B}}}{III_{\boldsymbol{B}}}\boldsymbol{B} + \frac{II_{\boldsymbol{B}}}{III_{\boldsymbol{B}}}\boldsymbol{I}.
\end{aligned}
$$

Forming the trace of this equation yields

$$
\operatorname{tr}\boldsymbol{B}^{-1} \equiv I_{\boldsymbol{B}^{-1}} = \frac{1}{III_{\boldsymbol{B}}}\Bigg\{\underbrace{I_{\boldsymbol{B}^2} - (I_{\boldsymbol{B}})^2}_{-2II_{\boldsymbol{B}}} + 3II_{\boldsymbol{B}}\Bigg\} = \frac{II_{\boldsymbol{B}}}{III_{\boldsymbol{B}}} \overset{(24.181)_2}{=} II_{\hat{\boldsymbol{B}}}III_{\boldsymbol{B}}^{-1/3},
$$

which proves now that $\mathfrak{Q} = 0$.

and EIPPER (1998) [22]—states ‘that a full decoupling in the domain of large deformations leads to questionable results’. Nevertheless, the decomposition is kept in many articles; we shall do so here as well as a first step toward a quantification of W as a realistic functional solution of it.

The free energy function W must satisfy the following relations, which are primarily motivated by requirements of physics [16]:

1. In a strainless initial state, the value of W should be zero,
$$\hat{W}(3,3) = 0, \quad U(J=1) = 0. \tag{24.190}$$
2. It is assumed that the strainless state is stress free (no prestress!). Since $I_{\hat{\boldsymbol{B}}}$ and $II_{\hat{\boldsymbol{B}}}$ are constant in this state, $\hat{W}$ does not contribute to the CAUCHY stress so that (24.186) implies for a stress-free reference state
$$\left.\frac{\partial U}{\partial III_{\hat{\boldsymbol{B}}}}\right|_{III_{\hat{\boldsymbol{B}}}=1} = 0 \quad \longrightarrow \quad \left.\frac{\partial U}{\partial J}\right|_{J=1} = 0. \tag{24.191}$$
3. The free energy function must be positive semidefinite, i.e., for any strained state
$$\left\{\hat{W}(I_{\hat{\boldsymbol{B}}}, II_{\hat{\boldsymbol{B}}}) \geqslant 0\right\} \cup \left\{\hat{W}(3,0) = 0\right\}, \quad U(J)|_{J\neq 1} \geqslant 0. \tag{24.192}$$
4. For infinitesimal strains the free energy function must coincide with the SAINT VENANT–KIRCHHOFF strain energy, i.e.,
$$\left.\frac{\partial^2 U}{\partial J^2}\right|_{J=1} > 0 \quad \rightarrow \quad K > 0, \tag{24.193}$$
where K is the bulk modulus.[15]
5. When a continuum element is compressed to a single point, the value of the free energy must approach ∞, and the volumetric stress (i.e., the elastic negative pressure) must approach the value $-\infty$:
$$U(J \rightarrow +0) \rightarrow +\infty, \quad \left.\frac{\partial U}{\partial J}\right|_{J\rightarrow +0} \rightarrow -\infty. \tag{24.194}$$
Physically, this requirement states that an infinitely large energy and equally an infinitely large pressure are required to compress a material element to zero volume.
6. Quite similarly, for an infinitely stretched continuum, the free energy, as well as the associated stress should be infinitely large,

---

[15] In [16] also a condition on $\hat{W}$ is stated from which the shear modulus follows, but that condition does not affect U.

$$U(J \to \infty) \to +\infty, \quad \left.\frac{\partial U}{\partial J}\right|_{J\to\infty} \to +\infty. \tag{24.195}$$

7. To satisfy the requirement of polyconvexity, the volumetric part U of W must satisfy the convexity condition

$$\frac{\partial^2 U}{\partial J^2} \geqslant 0, \tag{24.196}$$

which is important in conjunction with existence proofs of solutions (see, e.g., Ciarlet (1988) [9]).

For the popular choice [66]

$$\begin{aligned} & U(J) = \frac{1}{4}\left[(J-1)^2 + (\ln J)^2\right], \\ \longrightarrow \quad & \frac{\partial U}{\partial J} = \frac{1}{4}\left[2(J-1) + \frac{2\ln J}{J}\right], \\ \longrightarrow \quad & \frac{\partial^2 U}{\partial J^2} = \frac{1}{4}\left[2 + \frac{2}{J^2} - \frac{2}{J^2}\ln J\right] \quad > 0, \quad \forall J > 0, \end{aligned} \tag{24.197}$$

one easily deduces

$$\begin{aligned} & U|_{J=1} = 0, && \left.\frac{\partial U}{\partial J}\right|_{J=1} = 0, && \left.\frac{\partial^2 U}{\partial J^2}\right|_{J=1} = 1, \\ & U|_{J\to 0^+} \to +\infty, && \left.\frac{\partial U}{\partial J}\right|_{J\to 0^+} \to -\infty, && \left.\frac{\partial^2 U}{\partial J^2}\right|_{J\to 0^+} \to +\infty, \\ & U|_{J\to\infty} \to +\infty, && \left.\frac{\partial U}{\partial J}\right|_{J\to\infty} \to +\infty, && \left.\frac{\partial^2 U}{\partial J^2}\right|_{J\to\infty} \to \frac{1}{2}, \end{aligned} \tag{24.198}$$

in agreement with (24.190)–(24.196). The function U above arises in Table 24.4 as U_3, scaled with $K = 1$.

Doll and Schweizerhof [16] discuss a number of volumetric strain energy functions. Those, which fulfill all of the conditions (24.190)–(24.196) are stated in Table 24.4 (with the numbering of these authors). The functions U_3 and U_4 are very popular in the finite element literature of elastic bodies subject to large deformations. The functions U_6, U_7, U_8 are proposals by Doll and Schweizerhof (1999) [16]. U_6 allows via the parameters α and β to influence the shape of the function $U_6(J)$ and offers more flexible adjustment to experimental results than the others. All functions U_α ($\alpha = 3, \ldots, 8$) have a common scaling factor, K, which can be interpreted as a penalty parameter that enforces incompressibility (in numerical computations) if large values are chosen; for details, see [16].

Table 24.4 Volumetric strain energy functions, which fulfill the requirements (24.190)–(24.196)

$U_3(J) = \dfrac{K}{4}\left[(J-1)^2 + (\ln J)^2\right]$	[13, 46, 66, 67, 79]
$U_4(J) = \dfrac{K}{\theta^2}\left[\theta \ln J + J^{-\theta} - 1\right]$, for $\theta < -1$	[13, 44, 49, 59, 68]
$U_6(J) = K\left\{\left[\dfrac{J^{(\alpha+1)}}{\alpha+1} + \dfrac{J^{-(\beta-1)}}{\beta-1}\right]\dfrac{1}{\alpha+\beta} - \dfrac{1}{(\alpha+\beta)(\beta-1)}\right\}$ $\alpha > 0, \beta > 1$	[16]
$U_7(J) = \dfrac{K}{2}\left[\exp(J-1) - \ln J - 1\right]$	[16]
$U_8(J) = \dfrac{K}{2}\left[(J-1)\ln J\right]$	[16]

[For large values of K this parameter serves as a penalty for incompressibility. Its standard value is $K = 1$ or the bulk elasticity on the unloaded material]

The above choices of the bulk part of the free energy, U, shows a dependence on the volumetric invariant J only. For materials with moderately large pore space a functional dependence on the solid volume fraction ν^S must be included: $U = U(J, \nu^S)$. According to DIEBELS [13] the proposed free energies in Table 24.4 fail in particular for materially incompressible solid constituents. In such cases a *point of compression* exists, when all pores are closed. For such conditions the solid material must behave macroscopically as incompressible. To this end, EHLERS and EIPPER [21, 22, 27] proposed the following alternative free energy

$$\begin{aligned}
\frac{1}{K}U^S\left(J^S, \nu_0^S\right) &= \left(1-\nu_0^S\right)^2\left\{\frac{J^S-1}{1-\nu_0^S} - \ln\left(\frac{J^S-\nu_0^S}{1-\nu_0^S}\right)\right\} \\
&= \left(1-\nu_0^S\right)^2\left\{\frac{J^S-1}{1-\nu_0^S} - \ln\left(J^S-\nu_0^S\right) + \ln\left(1-\nu_0^S\right)\right\},
\end{aligned} \tag{24.199}$$

$$\longrightarrow \quad \frac{1}{K}\frac{\partial U^S}{\partial J^S} = \left(1-\nu_0^S\right)^2\left\{\frac{1}{1-\nu_0^S} - \frac{1}{J^S-\nu_0^S}\right\}, \tag{24.200}$$

$$\longrightarrow \quad \frac{1}{K}\frac{\partial^2 U^S}{\partial (J^S)^2} = \left(1-\nu_0^S\right)^2\left\{\frac{1}{\left(J^S-\nu_0^S\right)^2}\right\} \quad \geqslant 0, \quad \forall J^S \in [0, \infty), \tag{24.201}$$

in which ν_0^S is the solid volume fraction at the point of compression. From (24.198)–(24.201) one may deduce

$$
\begin{aligned}
&\frac{1}{K}U^S|_{J^S=1}=0, && \frac{1}{K}\frac{\partial U^S}{\partial J^S}\Big|_{J^S}=0, && \frac{1}{K}\frac{\partial^2 U^S}{\partial (J^S)^2}\Big|_{J^S=1}=1,\\
&\frac{1}{K}U^S|_{J^S=\nu_0^S}\to+\infty, && \frac{1}{K}\frac{\partial U^S}{\partial J^S}\Big|_{J^S=\nu_0^S}\to-\infty, && \frac{1}{K}\frac{\partial^2 U S}{\partial (J^S)^2}\Big|_{J^S=\nu_0^S}\to+\infty,\\
&\frac{1}{K}U^S|_{J^S\to+\infty}\to+\infty, && \frac{1}{K}\frac{\partial U^S}{\partial J^S}\Big|_{J^S\to+\infty}\to\left(1-\nu_0^S\right), && \frac{1}{K}\frac{\partial^2 U^S}{\partial (J^S)^2}\Big|_{J^S\to+\infty}=0.
\end{aligned}
\tag{24.202}
$$

According to these results, the KIRCHHOFF stresses remain finite for $J^S\to\infty$; moreover, neither the polyconvexity is satisfied in this limit.

A better proposal for U^S than (24.199) is obtained as a rather obvious extension of the SIMO–PISTER [66] free energy as follows:

$$
\begin{aligned}
\frac{1}{K}U^S\left(J^S,\nu_0^S\right) &= (1-\nu_0^S)^2\left\{\frac{(J^S-1)^2}{(1-\nu_0^S)^2}-\left(\ln\frac{J^S-\nu_0^S}{1-\nu_0^S}\right)^2\right\}\\
&= (1-\nu_0^S)^2\left\{\frac{(J^2-1)^2}{(1-\nu_0^S)^2}-\left(\ln\left(J^S-\nu_0^S\right)\right)^2\right.\\
&\qquad \left.+2\ln(1-\nu_0^S)\ln\left(J^S-\nu_0^S\right)-\left(\ln(1-\nu_0^S)\right)^2\right\},
\end{aligned}
\tag{24.203}
$$

$$
\begin{aligned}
\longrightarrow \frac{1}{K}\frac{\partial U^S}{\partial J^S} &= \left(1-\nu_0^2\right)\left\{\frac{2(J^S-1)}{(1-\nu_0^S)^2}-\frac{2\ln(J^S-\nu_0^S)}{J^S-\nu_0^S}\right.\\
&\qquad \left.+\frac{2\ln(1-\nu_0^S)}{J^S-\nu_0^S}\right\},
\end{aligned}
\tag{24.204}
$$

$$
\begin{aligned}
\longrightarrow \frac{1}{K}\frac{\partial^2 U^S}{\partial (J^S)^2} &= \left(1-\nu_0^2\right)\left\{\frac{2}{(1-\nu_0^S)^2}-\frac{2}{(J^S-\nu_0^S)^2}\right.\\
&\qquad \left.+\frac{2\ln(J^S-\nu_0^S)}{(J^S-\nu_0)^2}-\frac{2\ln(1-\nu_0^S)}{(J^S-\nu_0^S)^2}\right\},
\end{aligned}
\tag{24.205}
$$

which imply

$$
\begin{aligned}
&\frac{1}{K}U^S|_{J^S=1}=0, && \frac{1}{K}\frac{\partial U^S}{\partial J^S}\Big|_{J^S=1}=0, && \frac{1}{K}\frac{\partial^2 U^S}{\partial (J^S)^2}\Big|_{J^S=1}=0,\\
&\frac{1}{K}U^S|_{J^S=(\nu_0^S)^+}\to+\infty, && \frac{1}{K}\frac{\partial U^S}{\partial J^S}\Big|_{J^S=(\nu_0^S)^+}\to-\infty, && \frac{1}{K}\frac{\partial^2 U S}{\partial (J^S)^2}\Big|_{J^S=(\nu_0^S)^+}\to+\infty,\\
&\frac{1}{K}U^S|_{J^S\to+\infty}\to+\infty, && \frac{1}{K}\frac{\partial U^S}{\partial J^S}\Big|_{J^S\to+\infty}\to+\infty, && \frac{1}{K}\frac{\partial^2 U^S}{\partial (J^S)^2}\Big|_{J^S\to+\infty}=2,
\end{aligned}
\tag{24.206}
$$

and it is easy to show by computation that the free energy (24.203) is positive definite and that the condition of polyconvexity is satisfied for all values of $J^S \in (\nu_0^S, \infty)$. Moreover the reference configuration is stress free and compression to the point of compression requires an infinitely large pressure. Similarly, for an infinitely stretched specimen the stress to achieve this configuration must be infinitely large.[16]

The above detailed analysis of the selection of an adequate HELMHOLTZ free energy function is only preliminary, as it applies to BOLTZMANN continua. It has primarily been presented in such detail for educational purposes to learn how difficult it is to adequately 'guess' proper free energy functions. How more difficult must it be for COSSERAT solids!

Let us summarize what has been achieved by the exploitation of the entropy inequality.

1. The principal thermodynamic postulate that served as basis of the Second Law of Thermodynamics was the assumption that in any process to which a material is subjected, the production of the mixture entropy in any process is nonnegative.
2. This requirement was put into practice by transforming the individual constituent entropy balances of the form (24.11). In this transformation process, the CLAUSIUS–DUHEM expressions for the constituent entropy fluxes and entropy supply terms were employed and the constituent entropy balances were added to form the entropy balance of the mixture as stated in (24.14).
3. This final entropy inequality was in further steps exploited by using the COLEMAN–NOLL approach. Explicitly, this means that all the balance laws of linear and angular momenta as well as the mixture energy balance law are subjected to arbitrary external supply terms and, consequently, do not serve as constraint equations in the exploitation process of the entropy inequality.
4. The inferences which follow from the application of the above 'metaphysical' principles were applied to a binary mixture of solid and fluid COSSERAT constituents, in which the micro-inertia tensor is isotropic, no phase change processes occur ($\hat{\rho} = 0$) and all constituents have the same temperature $\vartheta^\alpha = \vartheta$.
5. The evolution equations for the solid and fluid volume fractions are closed in such a way that the saturation condition is automatically satisfied and the balance law of mass of the mixture can be identically satisfied by forward integration steps.
6. In this process of exploitation the entropy inequality was transformed by applying the chain rule of differentiation to the functionals of the constitutive relations and divergence and time-differenced terms into

$$\boldsymbol{\mathcal{X}} \cdot \boldsymbol{a}(\boldsymbol{\mathcal{Y}}) + \mathcal{D}(\boldsymbol{\mathcal{Y}}) \geqslant 0, \quad \forall \boldsymbol{\mathcal{X}}, \tag{24.207}$$

   as shown in (24.46); this is an inequality, which is linear in $\boldsymbol{\mathcal{X}}$, implying that its satisfaction requests

$$\boldsymbol{\mathcal{X}} \cdot \boldsymbol{a} \equiv \mathbf{0} \quad \text{and} \quad \mathcal{D}(\boldsymbol{\mathcal{Y}}) \geqslant 0, \tag{24.208}$$

---

[16] This latter condition is not satisfied by the free energy function (24.199).

statements, expressed in (24.23)–(24.43) and (24.44). The first identity, $(24.208)_1$, known as LIU identity, delivers a large number of restrictions to the postulated constitutive relations:

- The solid stress tensor, solid couple stress tensor, and mixture entropy are computable as certain differentiated expressions of the HELMHOLTZ free energies, $\psi^{S,F}$, see (24.47)–(24.50).
- The free energies $\psi^{S,F}$ cannot depend on all variables stated in (24.20); they are reduced in general to $(24.61)_1$ and in thermodynamic equilibrium to (24.69).

7. Thermodynamic equilibrium is defined by all those processes for which $\mathcal{D} \equiv 0$. Thus, $\mathcal{D}$ assumes its minimum in thermodynamic equilibrium. If $\{\mathsf{v}\}$ denote the nonequilibrium state variables, then

$$\left.\frac{\partial \mathcal{D}}{\partial \mathsf{v}}\right|_E = \mathsf{0}, \quad \text{and} \quad \left.\frac{\partial^2 \mathcal{D}}{\partial \mathsf{v}^2}\right|_E \geqslant 0. \tag{24.209}$$

must hold in this equilibrium. Exploitation of the requirement (24.209) implies the equilibrium expressions (24.78)–(24.83) for the constitutive quantities $(\boldsymbol{t}^F)_0$, $(\mathfrak{m}^F)_0$, $(\boldsymbol{m}^F)_0$, $(\boldsymbol{q}^F)_0$ and explicit expressions of the nonequilibrium expressions for these constitutive quantities, which are linear in the nonequilibrium constitutive variables. Moreover, the signs of the phenomenological tensors, expressing the dissipative nature of such nonequilibrium processes are constrained by $(24.209)_2$.

In conclusion, these inferences are formidable.

References

1. Bluhm, J.: A model for liquid saturated compressible porous solids. In: Walther, W. (ed.) Beiträge zur Mechanik (Festschrift zum 60. Geburtstag von Prof. Dr.-Ing. Reint de Boer). Forschunsbericht aus dem Fachbereich Bauwesen, vol. 66, pp. 41–50. Unitversität-GH-Essen (1995)
2. Bluhm, J.: A consistent model for saturated and empty porous media. Forschunsberichte aus dem Fachbereich Bauwesen, vol. 74. Universität-GH-Essen (1997)
3. Bluhm, J.: Zur Berücksichtigung der Kompressibilität des Festkörpers bei porösen Materialien. Zeitschrift Angew. Math. Mech (ZAMM) **77**, 39–40 (1997)
4. Bowen, R.: The thermochemistry of a reacting mixture of elastic materials with diffusion. Arch. Rational Mech. Anal. **34**, 97–127 (1969)
5. Bowen, R.: Theory of mixtures. In: Eringen, C.A. (ed.) Continuum Physics, vol. III, pp. 1–127. Academic Press, New York (1976)
6. Bowen, R.M.: Incompressible porous media models by use of the theory of mixtures. Int. J. Eng. Sci. **18**, 1129–1148 (1980)
7. Bowen, R.M.: Theory of mixtures. In: Eringen, A.C. (ed.) Continuum Physics. Vol III – Mixtures and EM-Field Theories, pp. 1–127. Academic Press, New York (1980)
8. Bowen, R.M.: Compressible porous media models by use of the theory of mixtures. Int. J. Eng. Sci. **20**, 697–735 (1982)

9. Ciarlet, P.G.: Mathematical Elasticity. Vol. 1 Three Dimensional Elasticity. North Holland, Amsterdam (1988)
10. Coleman, B.D., Noll, W.: The thermodynamics of materials with memory. Arch Rational Mech. Anal. **17**, 1–46 (1964)
11. de Borst, R.: Numerical modelling of bifurcation and localization in cohesive-frictional materials. Pageoph **137**, 368–390 (1991)
12. de Boer, R., Ehlers, W.: Theorie der Mehrkomponenten Kontinua mit Anwendung auf bodenmechanische Probleme, Teil 1. Forschungsbericht aus dem Fachbereich Bauwesen, vol. 40. Universität-GH-Essen (1986)
13. Diebels, S.: Mikropolare Zweiphasenmodelle: Formulierung auf der Basis der Theorie Poröser Medien. Bericht Nr. II-4 aus dem Institut für Mechanik (Bauwesen) Lehrstuhl II, p. 188. Universität Stuttgart (2000)
14. Diebels, S., Ehlers, W.: Dynamic analysis of a fully saturated porous medium accounting for geometrical and material nonlinearities. Int. J. Numer. Methods Eng. **39**, 81–97 (1996)
15. Diebels, S., Ehlers, W.: On basic equations of multiphase micropolar materials. Technische Mechanik **16**, 77–88 (1996)
16. Doll, S., Schweizerhof, K.: On the development of volumetric strain energy functions. Report: Institut für Mechanik, Universität Karlsruhe, Deutschland (1999). ifm@uni-jkarlsruhe.de
17. Duhem, P.: Le Potentiel Thermodynamique et ses Applications. A. Hermann, Librairie Scientifique, Paris (1886)
18. Ehlers, W.: Poröse Medien – Ein kontinuumsmechanisches Modell auf der Basis der Mischungstheorie. Habilitationsschrift, Forschungsbericht aus dem Fachbereich Bauwesen, vol. 45, p. 332. Universität-GH-Essen (1989)
19. Ehlers, W.: Compressible, incompressible and hybrid two-phase models in porous media theories. In: Angel, Y.C. (ed.) Anisotropy and Inhomogeneity in Elasticity and Plasticity, ADM-Vol. 158, pp. 25–38. ASME, New York (1993)
20. Ehlers, W.: Constitutive equations for granular materials in geomechanical context. In: Hutter, K. (ed.) Continuum Mechanics in Environmental Sciences and Geophysics. CISM Courses and Lectures, vol. 337, pp. 313–402. Springer, Wien (1993)
21. Ehlers, W., Eipper, G.: Finite Elastizität bei fluidgesättigten hoch porösen Festkörpern. J. Appl. Math. Mech. (ZAMM) **77**, 79–80 (1997)
22. Ehlers, W., Eipper, G.: The simple tension problem at large volumetric strains computed from finite hyperelastic material laws. Acta Mech. **130**, 17–17 (1998)
23. Ehlers, W., Eipper, G.: Finite elastic deformations in liquid-saturated and empty porous solids. Transp. Porous Media **34**, 179–191 (1999)
24. Ehlers, W., Volk, W.: On the shear band localization phenomena induced by elasto-plastic consolidation of fluid-saturated soils. In: Oden, D.J.R., Oñate, E., Hilton, E. (eds.) Computational Plasticity – Fundamentals and Applications, vol. 2, pp. 1657–1664. CIMNE, Barcelona (1997)
25. Ehlers, W., Volk, W.: On shear-band localization phenomena of liquid-saturated granular elasto-plastic solid materials accounting for fluid viscosity and micropolar solid rotations. Mech. Cohesive-Frict. Mater. **2**, 301–320 (1997)
26. Ehlers, W., Volk, W.: On theoretical and numerical methods of the theory of porous media based on polar and non-polar materials. Int. J. Solids Struct. **35**, 4597–4617 (1998)
27. Eipper, G.: Theorie und Numerik finiter elastischer Deformationen in fluid-gesättigten porösen-Festkörpern. Ph.D. thesis, Bericht Nr. II-1, Institut für Mechanik (Bauwesen), Lehrstuhl 2. Universität Stuttgart (1998)
28. Eringen, A.C.: Linear theory of micropolar elasticity. J. Math. Mech. **15**, 909 (1966)
29. Eringen, A.C.: Theory of Micropolar Elasticity. Fracture, vol. II. Academic Press, New York (1968)
30. Eringen, C.A., Suhubi, D.G.B.: Nonlinear theory of simple microelastic solids. Int. J. Eng. Sci. **2**, 189–203 (1964)
31. Fang, C., Wang, Y., Hutter, K.: A thermomechanical continuum theory with internal length for cohesionless granular materials. Part I & Part II. Contin. Mech. Thermodyn. **17**, 545–576 and 577–607 (2006)

32. Flory, J.P.: Principles of Polymer Chemistry. Cornell University Press (1953). ISBN 0-8014-0134-8
33. Flory, J.P.: Thermodynamic relations for high elastic materials. Trans. Faraday Soc. **57**, 829–838 (1961)
34. Flory, J.P.: Statistical Mechanics of Chain Molecules. Interscience. ISBN 0-470-26495-0 (1969), ISBN 1-56990-019-1 Reissued (1989)
35. Flory, J.P.: Selected Works of Paul J. Flory. Stanford University Press (1985). ISBN 0-8047-1277-8
36. Goodman, M.A., Cowin, S.C.: A continuum theory for granular materials. Arch. Rational Mech. Anal. **44**, 249–266 (1972)
37. Green, A.E., Zerna, W.: Theoretical Elasticity. Clarendon Press, London (1954)
38. Grioli, G.: Elasticità asimmetrica. Annali di Mat Pura e Applicata **4**(4), 389 (1960)
39. Grioli, G.: On the thermodynamic potential for continuum with reversible transformations – some possible types. Meccanica **1**(1, 2), 15 (1966)
40. Hutter, K., Jöhnk, K.: Continuum Methods of Physical Modeling, p. 635. Springer, Berlin (2004)
41. Hutter, K., Wang, Y.: Fluid and Thermodynamics. Volume 1: Basic Fluid Mechanics. Springer, Berlin (2016). ISBN: 978-3319336329, 639 p
42. Hutter, K., Wang, Y.: Fluid and Thermodynamics. Volume II: Advanced Fluid Mechanics and Thermodynamic Fundamentals. Springer, Berlin (2016). ISBN: 978-3-319-33635-0, 633 p
43. Ignatieff, Y.A.: The Mathematical World of Walter Noll, A Scientific Biography. Springer, Berlin (1996). https://doi.org/10.1007/978-3-642-79833-7
44. Kaliske, M., Rothert, H.: On the finite element implication of rubber-like materials at finite strains. Eng. Comput. **14**, 216–232 (1997)
45. Lakes, R.S.: Experimental microelasticity of two porous solids. Int. J. Solids Struct. **22**, 55–63 (1986)
46. Liu, C.H., Mang, H.A.: A critical assessment of volumetric strain energy functions for hyper-elasticity at large strains. J. Appl. Math. Mech. (ZAMM) **76**(S5), 305–306 (1996)
47. Martin, M.: Asymptotic equipartition of energies in thermoelasticity of dipolar bodies. In: Brillard, A., Ganghoffer, J.F. (eds.) Proceedings of the EUROMECH Colloquium 378: Nonlocal Aspects in Solid Mechanics, pp. 77–82. University of Mulhouse, Mulhouse, France (1998)
48. Martinez, F., Quintanilla, R.: Existence and uniqueness of solutions in micropolar viscoelastic bodies. In: Brillard, A., Ganghoffer, J.F. (eds.) Proceedings of the EUROMECH Colloquium 378: Nonlocal Aspects in Solid Mechanics, pp. 83–87. University of Mulhouse, Mulhouse, France (1998)
49. Miehe, C.: Aspects of the formulation and implementation of large strain isotropic elasticity. Int. J. Numer. Methods Eng. **37**, 1998–2004 (1994)
50. Mindlin, R.D., Tiersten, H.F.: Effects of couple stresses in linear elasticity. Arch. Rational Mech. Anal. **11**(5), 415 (1962)
51. Mooney, M.: A theory of large elastic deformation. J. Appl. Phys. **11**, 582–592 (1940)
52. Müller, I.: A thermodynamic theory of mixtures of fluids. Arch. Rational Mech. Anal. **28**, 1–39 (1968)
53. Neff, P.: A finite-strain elastic-plastic Cosserat theory for polycrystals with grain rotations. Int. J. Eng. Sci. **44**, 574–595 (2006)
54. Neuber, H.: On the general solution of linear elastic problem in anisotropic and isotropic Cosserat continua. In: Proceedings of the XI International Congress of Applied Mechanics, München, vol. 1964, p. 153 (1966)
55. Noll, W.: Foundations of Mechanics and Thermodynamics, Selected Papers. Springer, New York (1974). ISBN 0-387-06646-2
56. Noll, W.: Five contributions to natural philosophy. Published on Professor Noll's website (2004). http://repository.cmu.edu/cgi/viewcontent.cgi?article=1008&context=math
57. Nowacki, W.: Couple-stresses in the theory of thermoelaticity. I. Bull. Acad. Polon. Sci. Sér. Sci. Tech. I, **14**, 97; II, **14**, 293; III, **14** (1966)

58. Nowacki, W.: Theory of Micropolar Elasticity. International Centre of Mechanical Sciences, Course Nr 25, Udine. Springer, Wien, p. 283 (1970)
59. Ogden, R.W.: Large deformation isotropic elasticity: on the correlation of theory and experiment for compressible rubberlike solid solids. Proc. R. Soc. Lond. **A328**, 567–583 (1972)
60. Passman, S.L., Nunziato, J.W., Walsh, E.K.: A theory of multiphase mixtures. In: Truesdell, C. (ed.) Rational Thermodynamics, 2nd edn, pp. 286–325. Springer, Berlin (1984)
61. Penn, R.W.: Volume changes accompanying the extension of rubber. Trans. Soc. Rheol. **14**(4), 509–517 (1970)
62. Rivlin, R.S.: Large elastic deformations of isotropic materials: I fundamental concepts. Proc. R. Soc. Lond. **A240**, 459–490 (1948)
63. Schäfer, H.: Die Spannungsfunktionen des dreidimensionalen Kontinuums und des elastischen Körpers. ZAMM **33**, 356 (1953)
64. Schäfer, H.: Die Spannungsfunktionen des dreidimensionalen Kontinuums; statische Deutung und Randwerte. Ing. Arch. **18**, 291 (1959)
65. Schäfer, H.: Versuch einer Elastizitätstheorie des zweidimensionalen ebenen Cosserat-Kontinuums. Misszellanien der angew. Mechanik, Festschrift W. Tollmien, p. 277 (1962)
66. Simo, J.C., Pister, K.S.: Remarks on rate constitutive equations for finite deformation. Comput. Methods Appl. Mech. Eng. **46**, 201–215 (1984)
67. Simo, J.C., Taylor, R.L.: Penalty function formulations for incompressible nonlinear elastostatics. Comput. Methods Appl. Mech. Eng. **35**, 107–118 (1982)
68. Simo, J.C., Taylor, R.L.: Quasi-incompressible finite elasticity in principal stretches. Continuum basis and numerical algorithms. Comput. Methods Appl. Mech. Eng. **85**, 273–310 (1991)
69. Smith, A.C.: Deformations of micropolar elastic solids. Int. J. Eng. Sci. **5**(8), 637 (1967)
70. Smith, A.C.: Waves in micropolar elastics. Int. J. Eng. Sci. **5**(10), 741 (1967)
71. Soos, E.: Some applications of the theorem on reciprocity for an elastic and thermoelastic material with microstructure. Bull. Acad. Polon. Sci. Sér. Sci. Tech. **16**(11/12), 541 (1968)
72. Soos, E.: Uniqueness theorem for homogeneous, isotropic simple elastic and thermoelastic material having a microstructure. Int. J. Eng. Sci. **7**(3), 257 (1969)
73. Suhubi, E.S., Eringen, A.C.: Non-linear theory of simple microelastic solids II. Int. J. Eng. Sci. **2**, 389–404 (1964)
74. Tanner, R.I., Walters, K.: Rheology. An Historical Perspective, vol. 7, p. 254. Elsevier Science, Amsterdam (1998). ISBN 9780444829467
75. Toupin, R.A.: Elastic materials with couple-stresses. Arch. Rational Mech. Anal. **11**(5), 385 (1962)
76. Toupin, R.A.: Theories of elasticity with couple stresses. Arch. Rational Mech. Anal. **17**(2), 85 (1964)
77. Truesdell, C.A.: Sulle basi della termomeccanica. Rend. Lincei. **22**(8), 33–38, 156–166 (1957)
78. Truesdell, C.A., Noll, W.: The nonlinear field theories of mechanics. Encyclopedia of Physics, vol. III/3. Springer, Berlin (1965). ISBN 3-540-02779-3, amended and actualized third edition by S. Antman (2004)
79. van den Bogert, P.A.J., de Borst, R.: Constitutive aspects and finite element analysis of 3-d rubber specimens in compression and shear. In: Panda, G.N., Middleton, J. (eds.) NUMETA 90: Numerical Methods in Engineering: Theory and Applications, pp. 870–877. Elsevier Applied Science, Swansea (1990)
80. Volk, W.: Untersuchung des Lokalisierungsverhaltens mikropolarer poröser - Medien mit Hilfe der Cosserat Theorie. Bericht Nr. II-2 aus dem Institut für Mechanik (Bauwesen) Lehrstuhl II, Universität Stuttgart, p. 141 (1999)
81. Wilmanski, K.: Thermomechanics of Contonua. Springer, Berlin (1998), 273 p
82. Wozniak, C.: Thermoelasticity of non-simple continuous media with internal degrees of freedom. Int. J. Eng. Sci. **5**(8), 605 (1967)
83. Wyrwinski, J.: Green functions for a thermoelastic Cosserat medium. Bull. De l' acad. Pol. Sci. Sér. Sci. Tech. **14**, 145 (1966)

Chapter 25

A Continuum Approach to Liquid Crystals—The Ericksen–Leslie–Parody Formulation

Abstract Liquid crystals (LCs) are likely the most typical example of a polar medium of classical physics, in which the balance of angular momentum is a generic property, not simply expressed as a symmetry requirement of the CAUCHY stress tensor. They were discovered in the second half of the nineteenth century. Liquid crystals are materials, which exhibit fluid properties, i.e., they possess high fluidity, but simultaneously exhibit crystalline anisotropy in various structural forms. We present an early phenomenological view of the behavior of these materials, which conquered a tremendous industrial significance in the second half of the twentieth century as liquid crystal devices (LCD) (Sect. 25.1). The theoretical foundation as a continuum of polar structure was laid in the late 1950s to 1990s by ERICKSEN, LESLIE, FRANK, and PARODI, primarily for nematic LCs by postulating their general physical conservation laws, hydrostatics, and hydrodynamics, thus, illustrating their connection with nontrivial balance laws of angular momentum (Sect. 25.2). This is all done by treating nematics as material continua equipped with continuous directors (long molecules), which by their orientation induce a natural anisotropy. The thermodynamic embedding (Sect. 25.3) is performed by employing an entropy balance law with nonclassical entropy flux and the requirement of EUCLIDian invariance of the constitutive quantities, which are assumed to be objective functions of the density, director, its gradient, and velocity, as well as stretching, vorticity, temperature, and temperature gradient. This is specialized for an incompressible LC with directors of constant length (Sect. 25.4). Constitutive parameterizations with an explicit proposal of the free energy as a quadratic polynomial of the director and its gradient (according to FRANK) are reduced to obey objectivity. Based on this, the objective form of the free energy is derived (Appendix 25.A), as are the linear dissipative CAUCHY stress, director stress, and heat flux vector for the cases that the ONSAGER relations are fulfilled. The chapter ends with the presentation of shear flow solutions in a two-dimensional half-space and in a two-dimensional channel.

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List of Symbols

Roman Symbols

$\underline{\boldsymbol{A}}$	Rank-2 tensor
$\overset{=}{\boldsymbol{A}}$	Dual tensor to the axial vector $\boldsymbol{A}$
$A_{ij}(= D_{ij})$	Strain rate tensor, often used instead of D_{ij}
a, c	Constants of integration in isotropic nematic shear flows of an incompressible liquid
$a_1, \dots, a_6$	Parameters characterizing the curvature of directors
$a'_1, \dots, a'_6$	Parameters characterizing the curvature of directors in rotated coordinates
$a_{ij} = -a_{ji}$	Instantaneous skew-symmetric tensor arising in an EUCLIDian transformation
$\mathfrak{a}_i, \mathfrak{b}_i, c_i, d_i$	Quantities arising in the principle of virtual work
b_1, b_2	Parameters characterizing the "bend" contribution to the curvature of $\boldsymbol{\mathcal{L}}$
$\mathcal{B}$	Open set of body particles
c_i, c_i^*	Translation vectors arising in EUCLIDian transformations
D_{ij}	Strain rate tensor, also called stretching or rate of strain tensor, $D_{ij} = \frac{1}{2}(v_{i,j} + v_{j,i})$
D_{ii}	Trace of D_{ij}, $D_{ii} = \mathrm{tr}\boldsymbol{D} = v_{i,i}$
D'_{ij}	Deviator of strain rate tensor D_{ij}, $D'_{ij} = D_{ij} - \frac{1}{3}D_{kk}\delta_{ij}$
$\bar{d}_i, d_i$	External director force per unit volume/per unit mass
$\mathrm{d}V$	Volume increment
$\mathrm{d}a_i$	Vectorial surface element
e	Specific energy density (kinetic and internal), $e = \frac{1}{2}\rho(\dot{x}_i\dot{x}_i + \dot{n}_i\dot{n}_i) + \rho\varepsilon$
$\bar{\mathfrak{e}}, \mathfrak{e}$	Specific energy source density per unit volume/per unit mass
$f(\theta), g(\theta)$	Functions arising in the simple shear solution for a nematic LC
$\bar{f}_i, f_i$	External body force per unit volume/per unit mass
$F_{\theta_2}(\theta)$	Auxiliary function in simple shear between parallel plates
G_i	External specific director force per unit ρ_1
$\boldsymbol{\mathfrak{G}}$	Torque exerted by the director on the fluid $(= \mathrm{skw}(\boldsymbol{t}^E)')$
$\overset{=}{\boldsymbol{\mathfrak{G}}}$	Dual rank-2 tensor to $\boldsymbol{\mathfrak{G}}$
$g(\theta)$	See $f(\theta)$
g_i	Intrinsic specific director force, specific gravity force per unit mass

g_i^0	Equilibrium value to g_i, not producing entropy
$\hat{g}_i$	Extra intrinsic director force
g_i'	Extra dissipative intrinsic director force
h	Surface heat flow out of the volume
h_i	Flux density of the specific energy
$h_{\theta_2}(\theta)$	Auxiliary function in simple shear between parallel plates
$\bar{\bar{J}}^i$ (or J^i)	Thermodynamic force, see Eq. (25.178)
$k_i = \pi_{ij} n_j^+$	Director surface traction
$\bar{k}_{ij}, k_{ij}$	Tensorial spin source density per unit volume/per unit mass
k_i, k_{ij}	Parameter measures of the influence of the director curvatures on the free energy (25.145)–(25.148) direction curvatures
$\boldsymbol{\mathcal{L}}$	Unit vector (later identified with the director of constant length)
$\mathcal{L}_x, \mathcal{L}_y, \mathcal{L}_z$	Cartesian components of $\boldsymbol{\mathcal{L}}$
$\ell_i, \boldsymbol{\ell}$	Specific external + internal director force
$L^{ij}_{pq.rs} = L^{ji}_{pq.rs}$	Onsager relations (25.179) for thermodynamic flux–force relations
M, M_1, M_2	Masses of the LC and the fluid
m_{ijk}	Flux of the tensorial spin density
n_i	Director, as a vector
$\dot{n}_i$	Director velocity
$\ddot{n}_i$	Director acceleration
$n_{i,j}$	Director gradient
$N_i = \dot{n}_i - \omega_{ij} n_j$	Objective director velocity, see (25.60)
N_{ij}	Objective director, velocity gradient, see (25.60), $N_{ij} = [(\dot{n}_i)_{,j} - \omega_{ik} n_{k,j}]$
n_i^*	Component of $\boldsymbol{n}$ in the rotated Cartesian system
n_i^+	Unit vector perpendicular to a surface
$\mathcal{N}_i$	See (25.112). Objective form of the director gradient see (25.107), $\mathcal{N}_i = [n_i n_{j,j} - n_j n_{i,j}]$
$\mathcal{O}, o$	Order symbols
p_0	Constant pressure in a shear flow of an incompressible fluid
p_i	Momentum density, specific entropy flux density
$p_i = \rho \dot{x}_i$	Momentum density of the fluid
Q_{ij}	Orthogonal transformation, rotation matrix
$\dot{Q}_{ij}$	Time rate of change of Q_{ij}
q_i	Heat flux vector, general vector valued variable
R_{ij}	Rotation matrix of a proper EUCLIDian transformation ($R_{ik} R_{jk} = \delta_{ij}$, det $R_{ij} = +1$)
r or q	Energy supply rate density per unit mass
s	Entropy density per unit mass, scalar variable, see (25.81)
s_1, s_2	"Splay" contributions of the curvature tensor $\boldsymbol{\mathcal{L}}$, see (25.144)
s_{ij}	Tensorial spin density, $s_{ij} = -\varepsilon_{ijk} s_k$
s_i	Vectorial spin density, $s_i = -\frac{1}{2} \varepsilon_{ijk} s_{jk}$
s_{ij}	$s_{ij} = \rho \left(x_{[i} \dot{x}_{j]} \right) + \rho_1 \left(n_{[i} \dot{n}_{j]} \right)$ [for compressible liquid $\rho_1 = \rho$]

s_0, t_0	Splays and twists making $\tilde{\psi} = 0$ at the optimum, $s_0 = -k_1/k_{11}$, $t_0 = -k_2/k_{22}$
T	Absolute temperature
t_1, t_2	Twist variables, see (25.144)
t_{ij}	Cauchy stress tensor
$\tilde{t}_{ij} = \tilde{t}_{ji}$	Stress tensor defined in (25.75) (symmetric combination of $\boldsymbol{t}$, $\boldsymbol{\pi}$, and $\boldsymbol{g}$, see (25.124))
t^E_{ij}	Extra stress tensor (deviator)
t^0_{ij}	Equilibrium value of t_{ij}
$(t_{ij})'$	Extra dissipative Cauchy stress
V	Boundary velocity in simple shear flows between parallel plates
$v_{i,j}$	Material velocity gradient
$x_1, x_2, x_3; x, y, z$	Cartesian coordinates in three dimensional space
$x^*, y^* z^*$	Cartesian coordinates, rotated relative to x, y, z
$\dot{x}_i = v_i$	Velocity vector
$\ddot{x}_i = \dot{v}_i$	Acceleration vector $\ddot{x}, \ddot{y}, \ddot{z}$
$\bar{\bar{X}}^i, X^i$	Thermodynamic forces, see Parodi relations (25.178)

Greek Symbols

α	Rotation angle between two Cartesian coordinates
α	Scalar coefficient in the isotropic representation of φ_i, see (25.107), $\alpha = \alpha(T, n_i n_i, n_i N_i)$
α_i, α_{ij}	Coefficients in the hemotropic representation of φ, the extra entropy flux vector, see (25.106); quantities defined in (25.29)
$\beta = \mu_3 + \mu_6$	Parodi parameters
β_{ik}, β_{ijk}	Coefficients in the hemotropic representation of φ_i
γ	Director tension, see (25.132)
γ_i	Shorthand notation for quantities defined in (25.31)
$\gamma_{ijk}, \gamma_{ijkp}$	Coefficients in the hemotropic representation of φ_i, see (25.106)
δ	Variational symbol
$\delta(\rho, \phi, \psi)$	Variation of ρ, ϕ and ψ
δ_{ij}	Dirac tensor, $= 1$, if $i = j$ and $= 0$ if $i \neq j$
δn_i	Variation of n_i
δx_i	Variation of x_i
$\Delta_j = \delta n_j + n_{j,i} \delta x_i$	
ε	Density of internal energy
ε_{ijk}	Levi- Cività tensor
η_{apparent}	Apparent viscosity
θ	Inclination angle of the director relative to the orientation of the parallel liquid flow
$\kappa, \kappa_1, \kappa_2$	Heat conductivities, see (25.140), (25.163)
λ, λ'	Parameters measuring the length regime of a director, usually $\lambda \in [0, 1]$; Lagrange parameter of the incompressibility condition (=pressure)

λ_1, λ_2	Dissipation parameters for g_i', see (25.162), $\lambda_1 = \mu_2 - \mu_3$, $\lambda_2 = \mu_6 - \mu_5$
μ	Mass per unit length of a nematic LC ; dynamic viscosity
$\mu_1, \ldots, \mu_6$	Viscosity coefficients for nematic LCs in an anisotropic formulation
$\mu_2 + \mu_3 = \mu_6 - \mu_5$	PARODI relation if ONSAGER relations are valid in an isotropic nematic LC, see (25.167)
$\mu_1, \mu_4, \lambda_1, \lambda_2, \beta$	PARODI viscosity parameters
$\boldsymbol{\nu}$	Unit vector, representative for a single director
$\mathit{\Pi}$	Specific entropy production
π_{ij}	Director stress tensor; flux density of the director momentum density ρn_i
$\hat{\pi}_{ij}$	Extra director stress
ρ	Mass density of the LC fluid, [M/L^3]
ρ_1	Mass density for the directors, [M/L]
$\phi = \phi_i n_i^+$	Entropy flow out of the surface ∂V
φ also ψ	HELMHOLTZ free energy per unit mass
$\varphi_i = q_i - T\phi_i$	Extra entropy flux vector, see (25.85)
χ	Scalar potential for the fluid body forces; director force viscosity
ψ; (also φ)	HELMHOLTZ free energy per unit mass
$\tilde{\psi}$	Scaled free energy, see (25.156)
$\mathit{\Omega}_{ij}$	Small rotation tensor, see (25.45); dual tensor of the angular velocity of a rigid body rotation, $\mathit{\Omega}_{ij} = -\mathit{\Omega}_{ji} = Q_{jk}\dot{Q}_{ik} = -\mathit{\Omega}_{ji}$
ω_{ij}	Skew-symmetric angular velocity tensor, vorticity tensor
$\bar{\bar{\boldsymbol{\Omega}}}$	Dual tensor to the axial rotation rate vector $\boldsymbol{\Omega}$
$\bar{\bar{\boldsymbol{\omega}}}$	Dual rank-2 tensor to the axial vorticity vector $\bar{\bar{\omega}}_{ij} = \frac{1}{2}(v_{i,j} - v_{j,i})$

Miscellaneous Symbols

$\mathrm{d}/\mathrm{d}t$	Total time derivative (following an LC particle)
∂V	Boundary of volume V
LC	Liquid crystal
$\boldsymbol{A}^T$	Transpose of $\boldsymbol{A}$
$\boldsymbol{A}^{-T} = (\boldsymbol{A}^T)^{-1} =$	$(\boldsymbol{A}^{-1})^T$
$\lVert \boldsymbol{b} \rVert$	Norm of $\boldsymbol{b}$

25.1 A Phenomenological View of Liquid Crystals

"Liquid crystals[1] (LCs) are a state of matter intermediate between that of a crystalline solid and an isotropic liquid. They exhibit many of the mechanical properties of a liquid, e.g., possess high fluidity, do not support shear at rest, and may form droplets. Simultaneously, they exhibit crystalline anisotropic structure, primarily in their optical, electrical and magnetic properties" [72]. These properties were first observed by the Austrian botanist FRIEDRICH REINITZER[2] (1857–1927) in 1888 [62]. He found that cholesteryl benzonite does not melt in the same manner as other compounds, but has two phase change points. At 145.5 °C, it melts into a cloudy liquid, and at 178.5 °C it melts again and the cloudy liquid becomes clear. The phenomenon is reversible. Seeking help from a physicist on March 14, 1888, he wrote to OTTO LEHMANN[3] (1855–1922) in Aachen "…. LEHMANN examined the intermediate cloudy fluid, and reported seeing crystallites. REINITZER's Viennese colleague VON ZEPHAROWICH also indicated that the intermediate "fluid" was crystalline. The exchange of letters with LEHMANN ended on April 24, 1988, with many questions unanswered. Reinitzer presented his results with credits to LEHMANN and VON ZEPHAROWICH, at a meeting of the Viennese Chemical Society on May 3, 1888" (after [40]). REINITZER did not pursue studying LCs any further. The research was continued by LEHMANN, however, but further study convinced him that with the "cloudy" fluid, he was actually dealing with a solid. REINITZER and LEHMANN had discovered and described three important features of (cholesteric) liquid crystals (the name was coined by OTTO LEHMANN in 1904), [45]: (1) the existence of two melting points, (2) the reflection of circularly polarized light, and (3) the ability to rotate the polarization direction of light. They had acquired these results and LEHMANN reported them at the end of August 1889 in the *Zeitschrift für Physikalische Chemie* [44].

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[1] General texts dealing with liquid crystals are ubiquitous and can easily be found via google or wikipedia. Here we list the following works that were consulted by us:

- *Phenomenology* as presented in this section, can e.g., also be found from CASTELLANO [5], GRAY [33],
- *Mechanics* or *Thermomechanics* with internal microstructure is treated by BERIS and EDWARDS [2], CAPRIZ [4],
- *General physics, chemistry* and *mineralogy* of liquid crystals is also given by BUSCH and BUSCH [3], CHANDRASEKHAR [6], COLLINGS and HIRD [8], DE GENNES [10, 11], DE GENNES and PROST [12], DIERKING [16], DOI [17], DUNMUR and SLUKIN [19],
- *Continuum mechanics of multipolar media* is treated by GREEN and RIVLIN [34], GREEN, NAGHDI and RIVLIN [35],
- *Hydrodynamics of Liquid Crystals* is dealt with by VERTOGEN and JEU [76], MÜLLER [54].

[2] For a brief biography of FRIEDRICH REINITZER, see **Fig. 25.1**.

[3] For a brief biography of OTTO LEHMAN see **Fig. 25.2**.

Fig. 25.1 FRIEDRICH REINITZER (25. Feb. 1857, Prague–16 Feb. 1927, Graz)
FRIEDRICH REINITZER was an Austrian botanist and chemist, who discovered phase change properties of cholesteryl benzoate, which led to the discovery of what later was named a "liquid crystal". He studied chemistry at the German technical university in Prague; in 1883, he was habilitated there as a private docent. During 1888–1910, he was Professor at the Karl Ferdinand University and subsequently Professor at TH Graz. While at the university in Prague in 1888, he observed a strange behavior of cholesteryl benzoate and asked VIKTOR LEOPOLD ZEPHAROVIC in Prague and Otto Lehmann in Aachen for help. The latter recognized that the intermediate "cloudy fluid" between the fluid and solid phases was equally a separate phase, which shows double reflection. For this phase, LEHMANN coined in 1904 the name liquid crystal.
The text is based on www.wikipedia.org

Liquid crystals, which are obtained by melting a crystalline solid, are called *thermotropic*. "Liquid crystalline behavior is also formed in certain colloidal solutions and certain polymers .... This type of LCs is called *lyotropic*. For this class of LCs concentration (and secondarily temperature) is the controllable parameter, rather than temperature (and secondarily pressure) as in the thermotropic case, [72]. Research on LCs was generally kept at low key for approximately 80 years after OTTO LEHMANN's significant contributions. In Germany DANIEL VORLÄNDER (1867–1941) kept it active from the 1920s until his retirement in 1935, see [65]. After World War II, GEORGE WILLIAM GRAY[4] (1926–2013) and his group members researched on the topic from the late 1940s for approximately 30 years, which is documented in [33]. In the 1960s to 1980s interest in LCs acquired considerable momentum, in particular because of the significance of the development of electronic Liquid Crystal Devices (LCD), which conquered the present electronic hardware industry [5]" [72].

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[4] For a brief biography of GEORGE WILLIAM GRAY, see **Fig. 25.3**.

Fig. 25.2 Otto Lehmann (January 13, 1855, Konstanz–June 13, 1922, Karlsruhe)

Otto Lehmann studied Natural Sciences from 1872 to 1877 at the University of Strassburg and obtained his Ph.D. under crystallographer Paul Groth, the founder of *Zeitschrift für Mineralogie und Kristallographie*. He started his professional career as a "gymnasium teacher" of physics, mathematics, and chemistry in Mülhausen (Alsace-Lorraine), but moved up as a university teacher at what is now the RWTH Aachen, went to the Royal Saxon Polytechnical School in Dresden, but soon thereafter became successor of Heinrich at the TH Karlsruhe. He was an unsuccessful nominee for the Nobel Prize from 1913 to 1922.

Lehmann successfully used polarisers in a microscope to watch birefringence in the process of crystallization. In 1888, Reinitzer had approached him for help in the interpretation of the double-melting liquid mentioned in the main text. As Dunmur and Slukin say [19]:

> It was Lehmann's jealously guarded and increasingly prestigious microscope, not yet available off the shelf, which had attracted Reinitzer's attention. With Reinitzer's peculiar double-melting liquid, a problem in search of a scientist had met a scientist in search of a problem.

The text is based on www.wikipedia.org

According to Stephen and Straley, [72], "the quintessential property of a liquid crystal is its anisotropy …. Essentially no other assumptions about the nature of a liquid crystal are necessary".

"Liquid crystals are found among organic materials. Their molecules may be of a variety of chemical types …. Certain structural features are often found in the molecules forming LC phases, and they may be summarized as follows:

Fig. 25.3 George William Gray (September 4, 1926–May 12, 2013)

George William Gray was Professor of Organic Chemistry at the University of Hull, who was instrumental in developing the materials making the LCDs possible. He was educated at the University of Glasgow and obtained his Ph.D. in 1953 at the University of Hull (then part of the University of London). Continuing at this university his career, he was there Senior Lecturer in 1960, Professor of Organic Chemistry in 1974 and Grant Professor of Chemistry in 1984 and, finally an Emeritus of the University of Hull. In 1990, he joined the chemical company Merck, and in 1996 he was an independent consultant. He is known for the demonstration that $4'$ pentylbiphenyl possesses a stable nematic phase at room temperature and for writing the first book on liquid crystals [33].

The text is based on www.wikipedia.org

(a) The molecules are elongated. Liquid crystallinity is more likely to occur if the molecules have flat segments, e.g., benzene rings.
(b) The fairly rigid backbone containing double bonds defines the long axis of the molecule.
(c) The existence of strong dipoles and easily polarizable groups in the molecule seems important.
(d) The groups attached to the extremities of the molecules are generally of lesser importance.” [72]

It is customary to classify the different types of LCs as nematic LCs, cholesteric LCs, and smectic LCs, see G. Friedel (1865–1933), [32].

(1) Nematic LCs: This is the most common LC phase. The word *nematic* derives from ancient Greek, $\nu\acute{\eta}\mu\alpha$, which means “thread” and has been so coined because of the elongated rod-like appearance, see **Fig. 25.4**a.Thread-like topological defects, similar to dislocations in the theory of elasticity, are formally called *disclinations*,

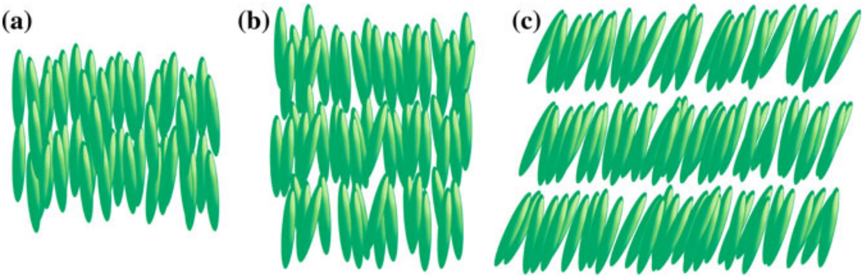

Fig. 25.4 Arrangements of liquid crystals formed from rod-like molecules: **a** nematic LCs, arranged close to a distinguished direction; **b** when the "elements" are stacked in layers; this arrangement is called the *smectic-A phase*, in which the molecular rods are perpendicular to the layers; **c** in the *smectic-C phase*, the molecules are tilted ($0 < \alpha < 90°$) relative to the orientation of their layers, after [40]

as suggested by FRANK [30, 31]. The nematic phase of LCs is characterized by long-range oriental order, i. e., the long axes of the molecules tend to align along a preferred direction. Most nematics are *uniaxial*, i.e., they have one axis that is longer and preferred, with the other two being equivalent. They may, thus, be represented as rods or elongated ellipses. However, there exist also *biaxial* nematics: they orient primarily along the long axis and secondarily along an axis perpendicular to the preferred long axis [50]. "The interesting phenomenology of nematic LCs involves the geometry and dynamics of the preferred axis, and so it is useful to define a vector field $\boldsymbol{n}(\boldsymbol{r})$ giving its local orientation. This vector is called the **director**. Since its magnitude has no significance, its length is taken to be unity. The director field is easily distorted and can be aligned by magnetic and electric fields and surfaces, which have been properly prepared" [72]. When nematic LCs are arranged in layers, they are called *smectic*, see below and item **(3)** [72].

The positions of the centers of mass of the molecules of nematic LCs are not ordered among the molecules. This is expressed as the absence of *long-range ordering*. The molecules, however, appear to be able to rotate about their long axes, and they seem to have no preferential arrangement of the two ends of the molecules. Thus, the sign of the director is of no physical significance [72].

(2) Cholesteric LCs: This phase was so called because it was first observed for cholesterol derivatives. Phenomenologically, it might also be called *chiral* phase because chirality (∼handedness) is the new distinctive feature of this phase. "Only chiral molecules (i.e., those that have no internal plane of symmetry) can give rise to such a phase" [40]. This phase differs from the nematic phase in that the director varies in the direction throughout the medium in a regular way. **Figure 25.5**a, b illustrates the situation: It shows the vertical twist axis and right and left screws, which indicate the position of a nematic as one moves upward. The front arrow is seen in the two arrangements to rotate clockwise (counterclockwise) for the left (right) handedness of the arrangements of the figure. Since there is no physical preference of the front

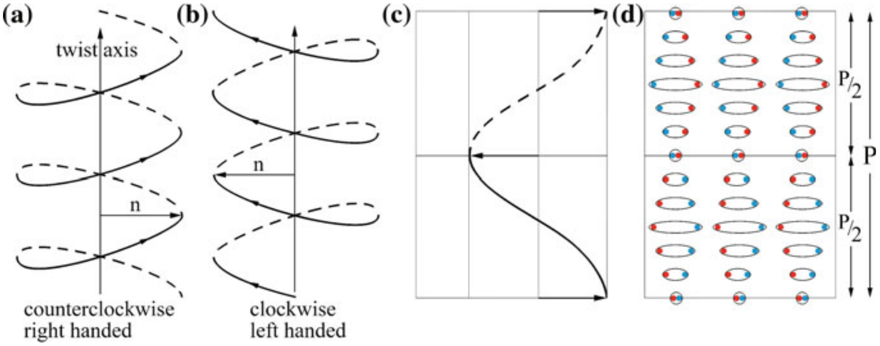

Fig. 25.5 The panels show a right- and left-handed helix, winding up a vertical twist axis. A nematic director ***n*** (displayed in **a** and **b** at two initial positions) will rotate up the helix as it moves upward (always remaining horizontal). In panel **a** [panel **b**], the rotation is counterclockwise [clockwise]. Panel **c** shows the helix within a *pitch* P where the rod performs a full rotation. Panel **d** indicates how the series of projections of the rod is qualitatively seen in a vertical plane through the twist axis. Since there is no difference between the front (red) and the rear (blue) ends of the elliptical rods, the period of a cholesteric crystal is $P/2$

and rear ends of the molecule of a nematic LC, the chirality of the final arrangement of the molecules is neutralized.

From the side, projected to a vertical plane through the twist axis, the arrangement shows the rods as ellipses and their tips as red and blue bullets, Fig. 25.5d. This secondary structure of the cholesteric LC is characterized by the distance measured along the twist axis, over which the director rotates through a full circle. This distance is called the pitch, P, of the cholesteric LC. Its periodicity length is actually only half this distance, since $\boldsymbol{n}$ and $-\boldsymbol{n}$ are indistinguishable, [72], Fig. 25.5d. “A nematic LC is just a cholesteric LC of infinite pitch, and is not really an independent case; in particular:

- There is no phase transition between nematic and cholesteric phases in a given material.
- Nematic LCs doped with enantiomorphic (not mirror symmetric) materials become cholesteric LCs of long (but finite pitch).
- The molecules forming this phase are optically active, i.e., they have distinct right- and left-handed forms and are distinct as shown in Fig. 25.5b.
- The pitch of the common cholesteric is of the order of several thousand angström (1 Å $= 10^{-7}$ mm) and, thus, comparable with the wavelength of visible light. This fact is responsible for the characteristic colors of cholesteric LCs in reflection” [72].
- For a theory of flow alignment in nematics, see [29].

(3) Smectic LCs: The smectic phases are found at lower temperatures than the nematic phases; they form well-defined layers that can slide over one another in a manner similar to that of soap, Fig. 25.4b, c. This layering can also be interpreted

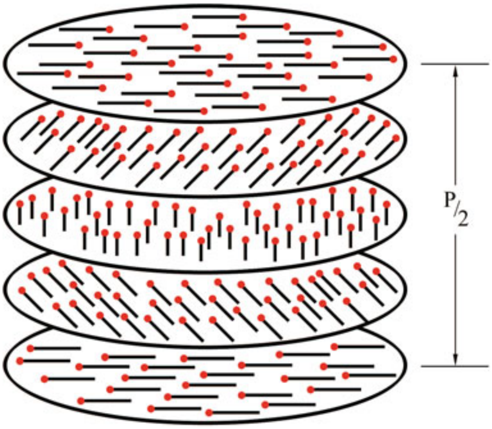

Fig. 25.6 Chiral nematic phase. *P* refers to the chiral pitch, after [40]

as stratification. The word "smectic" originates from the Latin word "smecticus", meaning cleaning, or having soap-like properties. The molecules in this phase are arranged in layers and exhibit some correlations in their positions in addition to the orientational ordering. A number of classes of smectics have been recognized; they are distinguished by capitals of the Roman alphabet, smectic-A, smectic-B, smectic-C, D, E . . . [49]. In the smectic-A phase, the molecules are aligned perpendicular to the layers with no crystalline order within the layers, Fig. 25.4b. In the smectic-C phase, the preferred molecule axis is inclined with respect to the layer with inclination angle $\alpha \in (0, \pi/2)$, Fig. 25.4c; this phase, thus, has biaxial symmetry [7, 15]. A model for it has been given by DE GENNES and SARMA in 1972 [13]. In this model, the layers can slip one over the other but cannot rotate on each other. There are also smectic-D and smectic-E phases. STEPHEN and STRALEY [72] state a number of references prior to 1974.

There are yet other LC phases. "*Blue phases* are LC phases that appear in the temperature range between a chiral nematic phase and an isotropic liquid phase. They have a regular three-dimensional cubic structure of defects with lattice periods of several hundred nanometers …. It was theoretically predicted in 1981 that these phases can possess icosahedral symmetry (a polyhedron with 20 faces) similar to quasi-crystals [43, 64]. Disk shaped LC molecules can orient themselves in layer-like fashion, known as *discotic nematic* phase. If the disks pack into stacks, the phase is called *discotic columnar*. Chiral discotic phases, similar to the chiral nematic phase are also known" [40], see **Fig. 25.6**.

The above description of LCs suggests that nematics and cholesterics can be modeled with the aid of directors, represented by the unit vector field $\boldsymbol{n}$. If there is no physical polarity along the director axis, $\boldsymbol{n}$ and $-\boldsymbol{n}$ are equivalent. Most LCs are nonpolar. It follows that theoretical formulations must be invariant under replacement of $\boldsymbol{n}$ by $-\boldsymbol{n}$.

A further significant property of LCs is the fact that ensembles of nematics and cholesterics are, in general, not exactly parallel-oriented and show some orientation

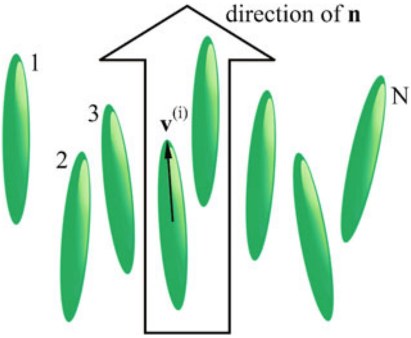

Fig. 25.7 Nematic crystals with unit vectors $\boldsymbol{v}^{(i)}$, $(i = 1, 2, \ldots, N)$ (directors). The local nematic director is given by the spatial and temporal average of the long molecular axes

deviations from a mean direction, see **Fig. 25.7**, in which the local nematic direction, which is also the optical axis, is given by the spatial and temporal average of the long molecular axes [40].

We can introduce the unit vector $\boldsymbol{\nu}^{(\alpha)}$ of the ith molecule, which describes its orientation. Because LCs possess a center of symmetry, the average of $\boldsymbol{\nu}^{(\alpha)}$ over all $i \in [1, N]$ vanishes. It is, thus, not possible to introduce a vector order parameter (as the average over all molecules), since the molecules have no polarization [$\boldsymbol{\nu}^{(\alpha)}$ and $(-\boldsymbol{\nu}^{(\alpha)})$ are equivalent] [72]. Higher order tensors formed with the unit vectors $\boldsymbol{\nu}^{(\alpha)}$ must be introduced to measure the degree of disorder of the LCs on the mesoscale of the continuum. A neutral order parameter to describe the degree of ordering in a nematic or cholesteric LC is the second rank tensor

$$S_{ij}(\boldsymbol{x}) = \frac{1}{N} \sum_{\alpha=1}^{N} \left(\nu_i^{(\alpha)} \nu_j^{(\alpha)} - \tfrac{1}{3}\delta_{ij} \right), \tag{25.1}$$

in which the summation is over all N $(\alpha = 1, 2, \ldots, N)$ molecules in a small but macroscopic volume element [a representative volume element (RVE)] at position $\boldsymbol{x}$. The indices $i, j = 1, 2, 3$ define the Cartesian components in a laboratory fixed coordinate system and δ_{ij} is the KRONECKER delta. Higher rank tensors may also be defined [21]. The order parameter (25.1) is a symmetric second rank deviator, $S_{ij} = S_{ji}$, $S_{ii} = 0$, in which summation is understood over doubly repeated indices. S_{ij}, thus, has five independent components. In an isotropic state, in which molecules have random orientation, S_{ij} vanishes.

There are also other definitions of order parameters. SAUPE (1965) [63] defines

$$S_{i'j'}(\boldsymbol{x}) = \left\langle \cos\theta_{i'} \cos\theta_{j'} - \tfrac{1}{3}\delta_{i'j'} \right\rangle, \tag{25.2}$$

in which primes in $x_{i'}$ denote Cartesian coordinates fixed in the molecule, and $\theta_{i'}$ is the angle between the i' axis and the long molecular director axis; moreover, the angular brackets, $\langle \cdot \rangle$, indicate an average over the molecules [72].

"In real LCs the molecules will be flexible. Different parts of the molecules would then have to be described by different $S_{i'j'}$ tensors. It is then preferable, as suggested by DE GENNES [10], to define the amount of order in terms of a macroscopic property, which is independent of assumptions about the rigidity of the molecules. Such a definition of the order parameter is also preferable from a thermodynamic point of view. The macroscopic property chosen by DE GENNES to represent the amount of order is the anisotropy in the diamagnetic susceptibility" [72]. Thus,

$$Q_{ij} = \chi_{ij} - \tfrac{1}{3}\chi_{kk}\delta_{ij}, \tag{25.3}$$

where χ_{ij} is the magnetic susceptibility tensor per unit volume. Q_{ij} is again a symmetric traceless tensor of rank two, which has again five independent components [72].

Order parameters are primarily important in the development of molecular field theories of LCs. In continuum formulations of LCs at the meso- or macroscale, the effects of a small oriental deviation of the nematics from the spatial–temporal average over a representative volume element may be small, so that order parameters may, in a first approximation of a thermodynamic formulation, be omitted. Such a simplified formulation is the ERICKSEN–LESLIE (EL) or the ERICKSEN–LESLIE–PARODI (ELP) theory [27]. General formulations of continuum theories for nematic liquid crystals with tensorial order have been presented from the 70s of the twentieth century onward, perhaps culminating with a paper on the continuum theory for nematic LCs with tensorial order of rank-2, by SONNET et al. [69] with an intermediate attempt by ERICKSEN [27]. This work and references to the significant literature will be detailed in Chap. 26.

25.2 A Continuum Formulation of Nematic Liquid Crystals

In this[5] section, a theory of nematic LCs will be given, in which all molecules in the LC domain are strictly parallel-oriented. So, order parameters will not play any role in this section and will be absent from the theory. First, balance laws for nematics will be presented, followed by a continuum mechanical approach, using an entropy principle based on an analogue of the CLAUSIUS–DUHEM inequality. We try to frame the developments in a concrete, physically based rigid rod model. This type of formulation has been introduced in the 60s of the twentieth century by ERICKSEN[6] (*1924) in 1961 [23] and LESLIE[7] (1935–2000) in 1968 [47] complemented by follow-up papers.

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[5] We follow closely [23]. This paper contains a number of misprints which one only catches by careful reading. We hope to have captured all.

[6] For a brief biography of JERALD LAVERNE ERICKSEN, see **Fig. 25.8**.

[7] For a brief biography of FRANK MATHEWS LESLIE, see **Fig. 25.9**.

Fig. 25.8 JERALD LAVERNE ERICKSEN (December 20, 1924)
JERALD LAVERNE ERICKSEN, an American mathematician specialized in continuum mechanics, was born in Portland, Oregon. His father worked at a Portland creamery and soon acquired a small creamery in Vancouver, Washington, where the family moved; JERALD helped out in the creamery. Quite possible that this determined his professional love of rheology! In the fall of 1942, he entered Oregon State College in Corvallis. At the age of 18, he entered the U.S. Navy and received his training at the University of Idaho, Pascatello, USA and then was transferred to ROTC at the University of Washington, Seattle. On active duty, he also served in the Philippines. During his 85.5 weeks of duties, he also met his wife MARION POOK, whom he married in 1946 and resigned from the service that summer.
ERICKSEN obtained his bachelor's degree from the University of Washington; he was a mathematics major and had a minor in Naval Science. His graduate schools were Oregon State and then Indiana Universities. It was there where he met DAVID GILBARG, VACLAV HLAVATY, EBERHARD HOPF, MAX ZORN, and above all CLIFFORD TRUESDELL, who was at that time working on his critical reformulation of continuum mechanics. ERICKSEN obtained his Ph.D in 1951. Subsequently, he spent a few years at the U.S. Naval Research Laboratory, where he worked on continuum mechanics with TRUESDELL, SAENZ, TOUPIN, and RIVLIN. He also worked at the National Bureau of Standards. In 1957, ERICKSEN joined JOHNS HOPKINS University in Baltimore in the Department of Mechanical Engineering; he and TRUESDELL formed the continuum mechanics group. They conducted weekly seminars on "properly invariant material theories" and attracted many top students and researchers, such as BERNARD COLEMAN, MORTON GURTIN, C.C WANG, CONSTANTINE DAFERMOS, FRANK LESLIE, RICHARD JAMES, ROMESH BATRA, INGO MÜLLER, and others. In 1982, ERICKSEN moved to the University of Minnesota, Minneapolis, receiving a joint appointment in the School of Mathematics and the Aerospace and Mechanics Department. In this period, he wrote his textbook on *Introduction to the Thermodynamics of Solids* [28]. He received in 1988 the Dr.h.c. from Heriot Watt University, Edinburgh. In 1968, he was already awarded the BINGHAM Medal of the Society of Rheology, and in 1979 he received the TIMOSHENKO Medal from ASME. He retired at the age of 65 and moved with his wife to Florence, Oregon. Adapted from https://en.wikipedia.org/wiki/Jerald_Ericksen. See also the Laudatio of ROGER FOSDICK, J. Elasticity **14**, 337–3412 (1984)

Fig. 25.9 FRANK MATHEWS LESLIE (March 8, 1935–June 15, 2000)

FRANK MATHEWS LESLIE was educated at the Harris Academy and Queen's College, Dundee, Scotland where he gained a First Class Honors in Mathematics in 1957. He earned his Ph.D. in 1961 at the University of Manchester, England. From 1961 until 1962, he spent a year at MIT, Cambridge, USA as a Research Associate. It was there that he came across the work of JERALD ERICKSEN on anisotropic liquids; this shaped his subsequent research career. He was a lecturer of mathematics at the University of Newcastle, England from 1962 until 1968, spent a sabbatical 1966–1967 at JOHNS HOPKINS University Baltimore. It was there, where he first met JERALD ERICKSEN and started research on liquid crystals. He accepted the position of Senior Lecturer at the University of Strathclyde, Glasgow, Scotland in 1968, becoming a Reader in 1971 and a Professor in 1979. He held visiting positions at the Universities of Tulane, Paderborn, Hokkaido, and Pisa, visited the main crystal research groups throughout the world and influenced the LCD industry considerably. The development of all LCD devices owes a great deal to him.

FRANK LESLIE gained many honors for his research. He was elected a Fellow of the Royal Society of Edinburgh in 1980. He received the Annual Award of the British Society of Rheology in 1982. In 1995, he was elected a Fellow of the Royal Society of London, in 1996 he was awarded the Sykes Gold Medal by the University of St Andrews for his DSc. Degree, and in 1997 he was the proud recipient of the GEORGE GRAY Medal of the British Liquid Crystal Society. As Professor DAVID SLOAN says, "it is impossible to estimate the profound impact that FRANK LESLIE's ideas have had on the worldwide activities in nematics and smectic liquid crystals."

Based on the memorial statement of Prof. DAVID SLOAN at Strathclide University, and www.wikipedia.org

25.2.1 General Physical Conservation Laws

Let us start with the general global balance laws of a COSSERAT continuum in the EULERian description. Cartesian tensor notation will be used. These laws are

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_V \rho\,\mathrm{d}V = 0, \tag{25.4}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_V p_i\mathrm{d}V = \int_{\partial V} t_{ij}\mathrm{d}a_j + \int_V \bar{f}_i\mathrm{d}V, \tag{25.5}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_V s_{ij}\mathrm{d}V = \int_{\partial V} m_{ijk}\mathrm{d}a_k + \int_V \bar{k}_{ij}\mathrm{d}V, \tag{25.6}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_V e\,\mathrm{d}V = \int_{\partial V} h_i\mathrm{d}a_i + \int_V \bar{\mathfrak{e}}\,\mathrm{d}V. \tag{25.7}$$

Here, V denotes a material volume with boundary ∂V and $\mathrm{d}a_i$ is a vectorial surface element directed outward of V. Moreover,[8]

- ρ, p_i, s_{ij}, e are the densities of mass, momentum, angular momentum, and the specific total energy (kinetic plus internal) per unit volume,
- t_{ij}, m_{ijk}, h_i denote the CAUCHY stress tensor, the dual third rank tensor of the specific couple stress tensor, and the specific energy flux vector,
- $\bar{f}_i$, $\bar{k}_{ij}$, $\bar{\mathfrak{e}}$ are the specific body force, the dual of the specific body couple, and the specific energy supply, per unit volume.[9]

As noted by ERICKSEN [23], Eq. (25.5) only partially describes conservation of linear momentum, as will be seen below.

The molecules arranged in a packet are idealized as rigid rods that are strictly parallel-aligned, but the orientation may smoothly change from packet to packet; they may have mass M which, per unit length, may not be uniform. A packet is then represented by equations of the form

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[8] In the above the balance law of angular momentum is written for an antisymmetric second rank tensor s_{ij} rather than an axial vector s_i. The two are isomorphic to one another and the correspondence relations are

$$s_{ij} = -\varepsilon_{ijk}s_k, \quad s_i = -\tfrac{1}{2}\varepsilon_{ijk}s_{jk},$$

where ε_{ijk} is the LEVI-CIVITÀ or epsilon tensor, whose value is $+1$ if the indices form an even permutation, -1 if they form an odd permutation and 0, if they form no permutation, see [41]. Thus we have

$$\begin{aligned} s_i &= -\tfrac{1}{2}\varepsilon_{ijk}s_{jk}, \\ \pi_{ij} &= \tfrac{1}{2}\varepsilon_{ijk}m_{lkj}, \\ k_i &= -\tfrac{1}{2}\varepsilon_{ijk}k_{jk}. \end{aligned}$$

[9] Later, all these quantities (then without the overbar) are defined per unit mass.

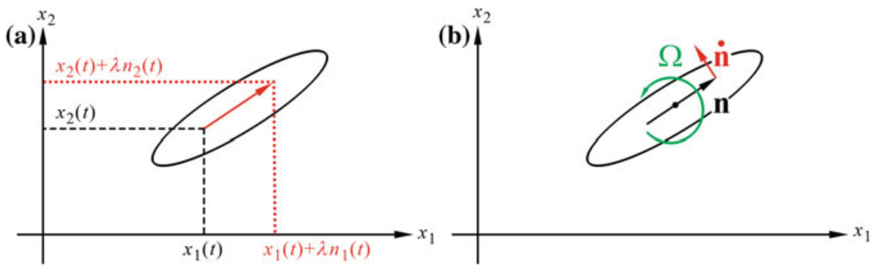

Fig. 25.10 **a** A director, drawn as an ellipse with its mathematical representation as an arrow. Any point along this arrow can be described by Eq. (25.8), in which λ varies in a finite interval to embrace the entire ellipse length. **b** If the director performs a pure rotation with angular velocity $\boldsymbol{\Omega}$ about its center, then obviously, $\dot{\boldsymbol{n}} = \boldsymbol{\Omega} \times \boldsymbol{n}$

$$y_i = y_i(\lambda, t) = x_i(t) + \lambda n_i(t) \tag{25.8}$$

in which y_i denotes any point on the rod at time t. n_i is a unit vector in the long direction of the molecule and λ is a real parameter with values in a finite interval I, see **Fig. 25.10**. If $\mu(\lambda)$ denotes the mass density per unit length of the rod, then

$$M = \int_I \mu(\lambda)\mathrm{d}\lambda \tag{25.9}$$

is its total mass. With no loss of generality, we may also assume

$$\int_I \lambda\mu(\lambda)\mathrm{d}\lambda = 0 \quad \text{and} \quad \int_I \lambda^2\mu(\lambda)\mathrm{d}\lambda = M. \tag{25.10}$$

If these are not satisfied for one choice of $\lambda \in I$, then they are satisfied for

$$\lambda' = a\lambda + b \quad \Longrightarrow \quad \lambda = \frac{1}{a}\left(\lambda' - b\right) \longrightarrow \mathrm{d}\lambda = \frac{1}{a}\mathrm{d}\lambda'$$

for adequately selected a and b. Indeed, let

$$\int_I \lambda\mu(\lambda)\mathrm{d}\lambda = M_1, \quad \int_I \lambda^2\mu(\lambda)\mathrm{d}\lambda = M_2 \tag{25.11}$$

with $M_1 \neq 0$, $M_2 \neq 0$. Then,

$$M_1 = \frac{1}{a^2}\underbrace{\int_{I'} \lambda'\mu(\lambda')\mathrm{d}\lambda'}_{=0} - \frac{b}{a^2}\underbrace{\int_{I'} \mu(\lambda')\mathrm{d}\lambda'}_{=M}, \tag{25.12}$$

$$M_2 = \frac{1}{a^3}\left\{\underbrace{\int_{I'} (\lambda')^2\mu(\lambda')\mathrm{d}\lambda'}_{=M} - 2b\underbrace{\int_{I'} \lambda'\mu(\lambda')\mathrm{d}\lambda'}_{=0} + b^2\underbrace{\int_{I'} \mu(\lambda')\mathrm{d}\lambda'}_{=M}\right\},$$

in which the underbraced quantities are so selected to enforce the identities analogous to (25.10), now for λ':

$$\int_{I'} \lambda' \mu(\lambda')\mathrm{d}\lambda' = 0 \quad \text{and} \quad \int_{I'} (\lambda')^2 \mu(\lambda')\mathrm{d}\lambda' = M. \tag{25.13}$$

With these choices, (25.12) implies

$$\frac{M_1}{M} = -\frac{b}{a^2}, \quad \frac{M_2}{M} = \frac{1+b^2}{a^3} = \frac{1}{a^3} + a\frac{M_1^2}{M^2},$$

which are two nonlinear equations for a and b.

We now may return to (25.9) and (25.10). When these equations hold, we have

$$\begin{aligned} \int_I \mu(\lambda) y_i(\lambda,t)\mathrm{d}\lambda &= \int_I \mu(\lambda)\left[x_i(t) + \lambda n_i(t)\right]\mathrm{d}\lambda \\ &= x_i(t) \underbrace{\int_I \mu(\lambda)\mathrm{d}\lambda}_{=M} + n_i(t) \underbrace{\int_I \lambda\mu(\lambda)\mathrm{d}\lambda}_{=0} = M\, x_i(t), \end{aligned} \tag{25.14}$$

$$\begin{aligned} \int_I \lambda\mu(\lambda) y_i(\lambda,t)\mathrm{d}\lambda &= \int_I \lambda\mu(\lambda)\left[x_i(t) + \lambda n_i(t)\right]\mathrm{d}\breve{} \\ &= x_i(t) \underbrace{\int_I \lambda\mu(\lambda)\mathrm{d}\lambda}_{=0} + n_i(t) \underbrace{\int_I \lambda^2\mu(\lambda)\mathrm{d}\lambda}_{=M} = M\, n_i(t). \end{aligned} \tag{25.15}$$

Similarly,

$$\int_I \mu(\lambda)\frac{\partial y_i}{\partial t}\mathrm{d}\lambda = \int_I \mu(\lambda)\left[\dot{x}_i(t) + \lambda\dot{n}_i(t)\right]\mathrm{d}\lambda = M\dot{x}(t), \tag{25.16}$$

$$\begin{aligned} \frac{1}{2}\int_I \mu(\lambda)\frac{\partial y_i}{\partial t}\frac{\partial y_i}{\partial t}\mathrm{d}\lambda &= \frac{1}{2}\left\{\int_I \mu(\lambda)\left[\dot{x}_i\dot{x}_i + \dot{n}_i\dot{n}_i\right]\mathrm{d}\lambda\right\} \\ &= \frac{1}{2}M\left(\dot{x}_i\dot{x}_i + \dot{n}_i\dot{n}_i\right), \end{aligned} \tag{25.17}$$

$$\begin{aligned} \int_I \mu(\lambda) y_{[i}\frac{\partial y_{j]}}{\partial t}\mathrm{d}\lambda &= \int_I \mu(\lambda)\left(x_{[i}\dot{x}_{j]} + n_{[i}\dot{n}_{j]}\right)\mathrm{d}\lambda \\ &= M\left(x_{[i}\dot{x}_{j]} + n_{[i}\dot{n}_{j]}\right), \end{aligned} \tag{25.18}$$

in which $(\cdot)_{[ij]} = (\cdot)_{ij} - (\cdot)_{ji}$ and dots represent total time derivatives. These results allow the following interpretations: Equation (25.14) states that $x_i(t)$ is the center of mass of the packet. Equation (25.16) yields its total momentum, (25.17) its total kinetic energy, and (25.18) its total dual of the angular momentum.

An interpretation of (25.15) is not obvious. It will later give rise to the introduction of the director momentum.

It is now tempting to assign the following identifications:

$$\begin{aligned} p_i &= \rho \dot{x}_i, \\ s_{ij} &= \rho \left(x_{[i}\dot{x}_{j]} + n_{[i}\dot{n}_{j]} \right), \\ e &= \tfrac{1}{2}\rho \left(\dot{x}_i \dot{x}_i + \dot{n}_i \dot{n}_i \right) + \rho\varepsilon \end{aligned} \tag{25.19}$$

with the specific momentum, dual of the angular momentum, and energy. The first of these is the "classical" momentum, but the second contains in addition a contribution due to the directors; it may be interpreted as the spin density of the directors. Similarly, the density of the kinetic energy comprises the classical translational kinetic energy and the rotational kinetic energy of the directors. These were already introduced by ERICKSEN [22]. In that paper, he had postulated a *director momentum* equation of the form

$$\frac{\mathrm{d}}{\mathrm{d}t} \int_V \rho \dot{n}_i \mathrm{d}V = \int_V \bar{\ell}_i \mathrm{d}V$$

to supplement equations (25.4)–(25.7), with an external *director force* $\bar{\ell}_i$, but this equation is short of a flux term. So, in [23] ERICKSEN adopted the generalization

$$\frac{\mathrm{d}}{\mathrm{d}t} \int_V \rho \dot{n}_i \mathrm{d}V = \int_{\partial V} \pi_{ij} \mathrm{d}a_j + \int_V \bar{\ell}_i \mathrm{d}V, \tag{25.20}$$

in which π_{ij} may be called the *director stress* or *director flux* and $\mathrm{d}a_j$ is the vectorial surface element pointing out of V. Moreover, $\bar{\ell}_i$ is the internal + external director force per unit volume (later we shall use ℓ_i defined by $\bar{\ell}_i = \rho\ell_i$). An equation similar to this was already employed by OSEEN [58] as early as 1933 [see Fig. 11.8 in Vol. 2 of this treatise [42], p. 23 for his biography].

To find an estimate for the director force, ERICKSEN tested the gravitational field. With the assumption that the gravitational field per unit mass is a constant, say $\boldsymbol{g}$, and ignoring all other forces, then we have

$$\mu \frac{\partial^2 y_i}{\partial t^2} = \mu\, g_i .$$

With (25.14)–(25.17) one obtains

$$\begin{aligned} M\ddot{x}_i &= \int_I \mu \frac{\partial^2 y_i}{\partial t^2} \mathrm{d}\lambda = g_i \int_I \mu \mathrm{d}\lambda = M\, g_i, \\ M\ddot{n}_i &= \int_I \lambda\mu \frac{\partial^2 y_i}{\partial t^2} \mathrm{d}\lambda = g_i \int_I \lambda\mu \mathrm{d}\lambda = 0, \end{aligned} \tag{25.21}$$

suggesting that this force contributes the usual term $M g_i$ to f_i but nothing to the vector $\bar{\ell}_i$ in Eq. (25.20). This might be different for polarizable and magnetizable materials.[10]

It is now evident that the global physical balance laws for liquid crystals are given by (25.4)–(25.7) and (25.20).

25.2.2 Hydrostatics of Nematic Liquid Crystals

ERICKSEN based his *hydrostatic theory* on the assumption that the free energy per unit volume, ψ, is a function of the unit vector n_i and its gradient $n_{i,j}$ (being a quadratic function of the gradient). Its variation is then

$$\delta \int_V \psi \mathrm{d}V, \tag{25.22}$$

where n_i is varied, subject to the condition that its length be restricted to unity and $\delta n_i = 0$ on the boundary. The free energy per unit mass, $\varphi = \psi/\rho$, is assumed a function of the form

$$\varphi = \frac{\psi}{\rho} = \varphi(\rho, n_i, n_{j,k}, T). \tag{25.23}$$

The variational (25.22) then takes the form

$$\delta \int_V \rho\varphi \mathrm{d}V \tag{25.24}$$

and will be conducted by varying ρ, x_i and n_i, subject to the constraint that local mass is balanced

$$\delta\rho + (\rho\delta x_j)_{,j} = 0 \quad \Longleftrightarrow \quad \delta\rho + \rho_{,j}\delta x_j + \rho\delta x_{j,j} = 0 \tag{25.25}$$

is identically satisfied. We note, moreover, that

$$\delta n_{j,k} + n_{j,k}\delta x_i = \Big(\underbrace{\delta n_j + n_{j,i}\delta x_i}_{\overset{\text{Def}}{=}\Delta_j}\Big)_{,k} - n_{j,i}\delta x_{i,k} = \Delta_{j,k} - n_{j,i}\delta x_{i,k}. \tag{25.26}$$

Next, we write

---

[10] This is so, because polarization gradients and magnetization gradients contribute to torques.

$$
\begin{aligned}
\delta \int_V \rho\varphi \mathrm{d}V &= \int_V \delta(\rho\varphi)\mathrm{d}V + \int_{\partial V} \rho\varphi \underbrace{\delta(\mathrm{d}V)}_{\delta x_i \mathrm{d}a_i} \\
&\overset{*}{=} \int_V \left[\delta(\rho\varphi) + (\rho\varphi\delta x_j)_{,j}\right] \mathrm{d}V \\
&= \int_V \left[\delta(\rho\varphi) + (\rho\varphi)_{,j}\mathrm{d}x_j + \rho\varphi\delta x_{j,j}\right] \mathrm{d}V \\
&= \int_V \left[\rho\delta\varphi + \varphi\delta\rho + \rho\varphi_{,j}\delta x_j + \rho_{,j}\varphi\delta x_j + \rho\varphi\delta x_{j,j}\right] \mathrm{d}V \\
&= \int_V \Big[\varphi \underbrace{\left(\delta\rho + \rho_{,j}\delta x_j\right)}_{=-\underline{\rho\delta x_{j,j}}} + \rho\delta\varphi + \rho\varphi_{,j}\delta x_j + \underline{\rho\varphi\delta x_{j,j}}\Big]\mathrm{d}V \\
&= \int_V \left[\rho(\delta\varphi + \varphi_{,j}\delta x_j)\right] \mathrm{d}V. \qquad (25.27)
\end{aligned}
$$

In this chain of expressions, at step ($\overset{*}{=}$) the divergence theorem was applied and the underbraced term follows from (25.25). Furthermore, since φ is a function of class (25.23), one obtains for isothermal processes, for which $\delta T = 0$,

$$
\begin{aligned}
&\rho\left(\delta\varphi + \varphi_{,j}\delta x_j\right) \\
&= \rho\Bigg[\frac{\partial\varphi}{\partial\rho}\underbrace{\left(\delta\rho + \rho_{,j}\delta x_j\right)}_{\overset{(25.25)}{=}-\rho\delta x_{j,j}} + \frac{\partial\varphi}{\partial n_i}\left(\delta n_i + n_{i,j}\delta x_j\right) + \frac{\partial\varphi}{\partial n_{j,k}}\left(\delta n_{j,k} + n_{j,ki}\delta x_i\right)\Bigg] \\
&= \rho\Bigg[-\rho\frac{\partial\varphi}{\partial\rho}\delta x_{j,j} + \underbrace{\frac{\partial\varphi}{\partial n_i}}_{\overset{\mathrm{Def}}{=}\gamma_i/\rho}\underbrace{\left(\delta n_i + n_{i,j}\delta x_j\right)}_{=\Delta n_i} + \frac{\partial\varphi}{\partial n_{j,k}}\underbrace{\left(\delta n_{j,k} + n_{j,ki}\delta x_i\right)}_{=\Delta n_{j,k} - n_{j,i}\delta x_{i,k}}\Bigg] \\
&\overset{*}{=} \rho\Bigg[-\rho\frac{\partial\varphi}{\partial\rho}\delta x_{j,j} - \frac{\gamma_i}{\rho}\Delta n_i + \frac{\partial\varphi}{\partial n_{j,k}}\left(\Delta n_{j,k} - n_{j,i}\delta x_{i,k}\right)\Bigg] \\
&= \alpha_{i,k}\delta x_{i,k} + \beta_{jk}\Delta n_{j,k} - \gamma_j\Delta n_j \\
&= \left(\alpha_{ik}\delta x_i + \beta_{jk}\Delta n_j\right)_{,k} - \alpha_{ik,k}\delta x_i - \left(\beta_{jk,k} - \gamma_j\right)\Delta n_j. \qquad (25.28)
\end{aligned}
$$

Here, at step ($\overset{*}{=}$), the definitions [23]

$$\alpha_{ik} := -\rho^2\frac{\partial\varphi}{\partial\rho}\delta_{ik} - \rho\frac{\partial\varphi}{\partial n_{\ell,k}}n_{\ell,i}, \qquad (25.29)$$

$$\beta_{jk} := \rho\frac{\partial\varphi}{\partial n_{j,k}}, \qquad (25.30)$$

$$\gamma_i := -\rho\frac{\partial\varphi}{\partial n_i} \qquad (25.31)$$

were introduced. Back substituting the expression (25.28) into (25.27) yields

$$\delta \int_V \rho\varphi \mathrm{d}V = \int_{\partial V} \left\{ \alpha_{ij}\delta x_i + \beta_{ij}\Delta n_i \right\} \mathrm{d}a_j \\ - \int_V \left\{ \alpha_{ij,j}\delta x_i + \left(\beta_{ij,j} + \gamma_i\right)\Delta n_i \right\} \mathrm{d}V. \qquad (25.32)$$

It is tempting to interpret the expressions (25.29)–(25.31), α_{ij}, β_{jk}, and γ_i as quantities determined by the free energy φ (25.23) as CAUCHY stress, director stress, and intrinsic director force. In the spirit of the classical principle of virtual work, the variation expression (25.24) is equal to the virtual work of the volume and surface forces. Based on the form of (25.32) it is natural, as ERICKSEN [23] says, to assume a principle of virtual work of the form

$$\delta \int_V \rho\varphi \mathrm{d}V = \int_{\partial V} \{\mathfrak{a}_i\delta x_i + \mathfrak{b}_i\Delta n_i\} \mathrm{d}a + \int_V \{c_i\delta x_i + d_i\Delta n_i\} \mathrm{d}V, \qquad (25.33)$$

in which $\mathfrak{a}_i, \mathfrak{b}_i, c_i, d_i$ represent generalized surface and volume forces of the fluid. Comparison of (25.32) and (25.33) leads to

$$\alpha_{ij,j} + c_i = 0, \quad \text{and} \quad \beta_{ij,j} + \gamma_i + d_i = 0, \quad \boldsymbol{x} \in V \qquad (25.34)$$

as well as

$$\alpha_{ij}\mathrm{d}a_j = \mathfrak{a}_i\mathrm{d}a, \quad \text{and} \quad \beta_{ij}\mathrm{d}a_j = \mathfrak{b}_i\mathrm{d}a, \quad \boldsymbol{x} \in \partial V. \qquad (25.35)$$

In a classical fluid, for which $n_i = 0$, these reduce to $\alpha_{ij,j} + c_i = 0 \in V$ and $\alpha_{ij}n_j^+ = a_i \in \partial V$, where n_j^+ is the unit normal vector pointing out of V. Hence, in line with (25.4), (25.5), (25.20), we make the identifications

$$\begin{aligned} t_{ij} &= \alpha_{ij}, & \rho f_i &= c_i, \\ \pi_{ij} &= \beta_{ij}, & \rho k_i &= \rho(\gamma_i + d_i), \end{aligned} \qquad (25.36)$$

for liquid crystals in equilibrium.

25.2.3 Hydrodynamics of Nematic Liquid Crystals

The dynamical field equations for LCs must account for (25.16)–(25.18), (25.20), and the identifications $(25.19)_1$.

- *Linear momentum*
  Conservation of linear momentum is best postulated by the classical relation (25.5), with p_i given by $(25.19)_1$, [26]:

$$\frac{\mathrm{d}}{\mathrm{d}t} \int_V \rho\dot{x}_i \mathrm{d}V = \int_{\partial V} t_{ij}\mathrm{d}a_j + \int_V \rho f_i \mathrm{d}V, \qquad (25.37)$$

or locally, for smooth processes, as

$$\rho \ddot{x}_i = t_{ij,j} + \rho f_i. \tag{25.38}$$

However, these must be complemented by the director momentum equation (25.20), which is adopted as a further balance law with smooth local form

$$\rho \ddot{n}_i = \pi_{ij,j} + \rho \ell_i, \tag{25.39}$$

$$\ell_i = g_i + G_i, \tag{25.40}$$

where g_i represents an intrinsic part, reminiscent of a production, with values $g_i = \gamma_i$ in equilibrium, and G_i represents an external supply term, which we ignore.

- *Balance of energy*
The global conservation law of energy of a BOLTZMANN continuum is given by the black-printed terms in

$$\begin{aligned} &\frac{\mathrm{d}}{\mathrm{d}t}\int_V e\,\mathrm{d}V \\ &= \frac{\mathrm{d}}{\mathrm{d}t}\int_V \left[\rho\varepsilon + \left(\tfrac{1}{2}\rho\dot{x}_i\dot{x}_i + \tfrac{1}{2}\rho\dot{n}_i\dot{n}_i\right)\right]\mathrm{d}V \\ &= \int_{\partial V} \underbrace{\left[t_{ij}\dot{x}_j + \pi_{ij}\dot{n}_j - q_i\right]}_{h_i}\mathrm{d}a_i + \int_V \rho\,\underbrace{\left(f_i\dot{x}_i + g_i\dot{n}_i + q\right)}_{\mathfrak{e}}\mathrm{d}V, \end{aligned} \tag{25.41}$$

in which h_i is composed of the power of working of the stresses $(t_{ij}\dot{x}_j)$ plus the heat flux $(-q_i)$ into the body. Analogously, the energy supply is given by the power of working of the body forces $(f_i\dot{x}_i)$ and the heat supply q. This law appears in (25.41) in black writing. For LCs, further terms are added as natural extrapolations. These are given in (25.41) in red printing. The kinetic energy of the directors has been motivated by Eq. (25.17). The power of working of the director stress may then be suggested as $(\pi_{ij}\dot{n}_i)$ in analogy to the power of working of the CAUCHY stress. Moreover, the power of working of the intrinsic nonequilibrium director force is given by $(g_i\dot{n}_i)$. All these extensions seem to naturally suggest themselves. The local form of (25.41) reads

$$\rho\dot{\varepsilon} = t_{ij}\dot{x}_{ij} + \pi_{ij}\dot{n}_{i,j} - q_{j,j} - \rho g_i\dot{n}_i - \rho q. \tag{25.42}$$

For its derivation, the balance of mass, linear momentum, and director momentum were used. ERICKSEN, in his formulation of anisotropic fluids used (25.42) with $\pi_{ij} = 0$, but $g_i \neq 0$ [22].

- *Balance of angular momentum*
ERICKSEN starts his analysis of the angular momentum conservation by requesting that the free energy function must be invariant under EUCLIDian transformations;

it is sufficient to draw the respective inferences by applying infinitesimal rotations. Thus,

$$D\,\varphi = \varphi\left(\rho, n_i', n_{j,k}', T\right) - \varphi(\rho, n_i, n_{j,k}, T) = 0, \tag{25.43}$$

$$n_i' = R_{ij} n_j, \qquad n_{i,j}' = R_{ik} R_{j\ell} n_{k,\ell}, \tag{25.44}$$

where R_{ij} is an orthogonal transformation such that $R_{ij} R_{ik} = \delta_{jk}$ and $\det(R_{ij}) = +1$. For an infinitesimal rotation, we have

$$R_{ij} = \delta_{ij} + \Omega_{ij}, \quad \Omega_{ij} = -\Omega_{ji}. \tag{25.45}$$

For infinitesimal rotations, we shall neglect higher order products such as $\Omega_{ij}\Omega_{kl}$. It follows from (25.43) and (25.44) that

$$\begin{aligned} n_i' - n_i &= \Omega_{ij} n_j, \\ n_{i,j}' - n_{i,j} &= (\delta_{ik} + \Omega_{ik})(\delta_{j\ell} + \Omega_{j\ell}) n_{k\ell} - n_{i,j} \\ &= \Omega_{ik} n_{k,j} + \Omega_{jk} n_{i,k} + \mathcal{O}(|\boldsymbol{\Omega}|^2). \end{aligned} \tag{25.46}$$

It then follows from (25.43) that

$$\begin{aligned} D\varphi = \varphi\left(\rho, (\delta_{ij} + \Omega_{ij}) n_j, (n_{i,j} + \Omega_{ik}) n_{k,j} + \Omega_{jk} n_{i,k}, T\right) \\ -\varphi(\rho, n_i, n_{i,j}, T) \end{aligned} \tag{25.47}$$

$$\overset{*}{=} \left\{ \frac{\partial \varphi}{\partial n_i} n_j + \frac{\partial \varphi}{\partial n_{i,k}} n_{j,k} + \frac{\partial \varphi}{\partial n_{k,i}} n_{k,j} \right\} \Omega_{ij} + \mathcal{O}(\|\boldsymbol{\Omega}\|^2) = 0. \tag{25.48}$$

At the step ($\overset{*}{=}$), the first function on the right-hand side of (25.47) has been expanded in a TAYLOR series of n_i' and $n_{k,j}'$, thereby dropping terms of higher order, which we simply write as $\mathcal{O}(\|\boldsymbol{\Omega}\|^2)$. Because Ω_{ij} is skew-symmetric, the tensor between braces in (25.48) must be symmetric; so, its skew-symmetric part must vanish. Introducing then (25.29)–(25.31) for notational reasons, this requirement implies

$$\gamma_j n_i - \gamma_i n_j + \beta_{ik} n_{j,k} - \beta_{jk} n_{i,k} + \alpha_{ij} - \alpha_{ji} = 0.$$

Because this relation must also hold in equilibrium, we have

$$g_j n_i - g_i n_j + t_{ij} - t_{ji} + \pi_{ik} n_{j,k} - \pi_{jk} n_{i,k} = 0, \tag{25.49}$$

in which (25.36) and (25.40) have been used. When $\pi_{ij} = 0$ and $g_i = 0$, this equation reduces to $t_{ij} = t_{ji}$, the conventional statement that in a BOLTZMANN continuum the CAUCHY stress tensor is symmetric.

From Eqs. (25.6) and (25.19)$_2$, the local form of the angular momentum equation can be written as

$$\rho\left(x_{[i}\ddot{x}_{j]}+n_{[i}\ddot{n}_{j]}\right)=m_{ijk,k}+\rho k_{ij}. \tag{25.50}$$

With the use of the local momentum equations (25.38) and (25.39) to eliminate $\ddot{x}_i$ and $\ddot{n}_i$, we obtain from (25.50)

$$\rho x_{[i}f_{j]}+x_{[i}t_{j]k,k}+\rho n_{[i}g_{j]}+n_{[i}\pi_{j]k,k}=m_{ijk,k}+\rho k_{ij}. \tag{25.51}$$

This equation can be put into a better interpretable form by employing the relations

$$\begin{aligned} x_{[i}t_{j]k,k} &= \tfrac{1}{2}\left(x_i t_{jk,k}-x_j t_{ik,k}\right)=\tfrac{1}{2}\left(x_i t_{jk}-x_j t_{ik}\right)_{,k}+\tfrac{1}{2}\left(t_{ij}-t_{ji}\right), \\ n_{[i}\pi_{j]k,k} &= \tfrac{1}{2}\left(n_i\pi_{jk}-n_j\pi_{ik}\right)_{,k}+\tfrac{1}{2}\left(n_{j,k}\pi_{ik}-n_{i,k}\pi_{jk}\right). \end{aligned} \tag{25.52}$$

Substituting these into (25.51) and using (25.40) and (25.49) yields

$$\underline{\left(x_{[i}t_{j]k,k}+n_{[i}\pi_{j]k}\right)_{,k}}+\rho x_{[i}f_{j]}+\rho n_{[i}g_{j]}=\underline{m_{ijk,k}}+\rho k_{ij}, \tag{25.53}$$

suggesting that

$$\begin{aligned} m_{ijk} &= x_{[i}t_{j]k}+n_{[i}\pi_{j]k}, \\ h_{ij} &= x_{[i}\rho f_{j]}+n_{[i}\rho g_{j]}. \end{aligned} \tag{25.54}$$

These expressions have obvious interpretations. Indeed, v_{ijk} can be interpreted as the dual of the torque density due to the CAUCHY stresses plus the director stresses, while h_{ij} is the torque due to the body force and the director force. The global angular momentum balance (25.6) is therefore

$$\begin{aligned} &\frac{\mathrm{d}}{\mathrm{d}t}\int_V \rho\left(x_{[i}\dot{x}_{j]}+n_{[i}\dot{n}_{j]}\right)\mathrm{d}V \\ &=\int_{\partial V}\left(x_{[i}t_{j]k}+n_{[i}\pi_{j]k}\right)\mathrm{d}a_k+\int_V \rho\left(x_{[i}f_{j]}+n_{[i}g_{j]}\right)\mathrm{d}V. \end{aligned} \tag{25.55}$$

For convenience, we state in **Table 25.1** the equations, where the final forms of the physical conservation laws for liquid crystals can be found.

An alternative article to the hydrodynamics of nematics is also given by Vertogen [75].

Table 25.1 Balance laws for liquid crystals

Law	Global	Local
Mass	(25.4)	
Classical momentum	(25.37)	(25.38)
Director momentum	(25.20)	(25.39)
Energy	(25.41)	(25.42)
Angular momentum	(25.55)	(25.50)

25.3 A Thermodynamic Theory for Nematic Liquid Crystals

Since their discovery at the end of the nineteenth century, the materials best known as liquid crystal displays (LCD) have conquered an incredible position in the industrialized world. There are virtually no electrical–electronic gadgets without them being parts of these. However, their victorious success is based on a rather complex theoretical physical fundament.

While DUHEM in 1893 [18], OSEEN in 1933 [58][11] formulated static models for LCs, it was ERICKSEN [22, 23] who presented the first robust set of balance laws for LCs. LESLIE [46] formulated constitutive equations similar to those discussed earlier by ERICKSEN [22] and essentially recovered ERICKSEN's theory of anisotropic fluids. Following the COLEMANN–NOLL procedure, he discussed the restrictions placed upon these constitutive equations by the CLAUSIUS–DUHEM inequality. In his 1968 paper [47], he made broader constitutive assumptions and obtained a formulation, which, apart from minor differences, reduces statically to the theory discussed by ERICKSEN [23]. One essential step toward this new formulation consisted in the adoption of a generalization of the entropy inequality due to MÜLLER[12] [53], in which the entropy flux is not assumed to be equal to heat flux divided by absolute temperature, but is of constitutive nature of the same class as the remaining constitutive equations of the theory. In principle, LESLIE found that the entropy flux differs in general from "heat flux divided by absolute temperature."

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[11] For biographical sketches of PIERRE MAURICE MARIE DUHEM see Fig. 17.16 in Vol. 2 of this treatise [42] p 343, and for those of Carl Wilhelm Oseen see Fig. 11.8 in Vol. 2 of this treatise [42], p 23.

[12] This generalization of the entropy principle is different from MÜLLER's generalization treated in volume 2 of this treatise [42]. Its exploitation follows the COLEMAN–NOLL procedure of open systems thermodynamics.

In the ensuing developments, we follow LESLIE's 1968 paper [47] that is based on ERICKSEN's balance laws of LCs [23] and is now called the EL theory.

25.3.1 Kinematics

In what follows, we employ the EULERian formulation and refer any field quantity f to the coordinates x_i in the laboratory frame and the present time t: $f = f(x_i, t)$. The velocity v_i will denote the total or substantive time derivative holding the fluid particle fixed, $v_i = \dot{x}_i$,

$$v_i = v_i(x_j, t) \tag{25.56}$$

for $x_i \in V \cup \partial V$. The tensors

$$D_{ij} = \tfrac{1}{2}(v_{i,j} + v_{j,i}), \quad \omega_{ij} = \tfrac{1}{2}(v_{i,j} - v_{j,i}) \tag{25.57}$$

will denote the *stretching* or *strain rate* or *rate of strain* tensor and the *vorticity* tensor, respectively. Moreover, directors will be denoted by

$$n_i = n_i(x_j, t) \tag{25.58}$$

as before and their material or total time derivatives[13] are

$$\dot{n}_i = \frac{\partial n_i}{\partial x_j} v_j + \frac{\partial n_i}{\partial t}. \tag{25.59}$$

It is, however, convenient to introduce the EUCLIDian objective quantities

$$\begin{aligned} N_i &= \dot{n}_i - \omega_{ij} n_j, \\ N_{ij} &= \dot{n}_{i,j} - \omega_{ik} n_{k,j}. \end{aligned} \tag{25.60}$$

Consider the EUCLIDian change of frame

$$\begin{aligned} x_i^* &= c_i^* + Q_{ij}(x_j - c_j), \\ n_i^* &= Q_{ij} n_j, \end{aligned} \tag{25.61}$$

in which c_i^*, c_i are time-dependent vectors and Q_{ij} is a time-dependent orthogonal transformation $[Q_{ik} Q_{jk} = \delta_{ij}]$. It is a straightforward exercise to prove that

$$\begin{aligned} D_{ij}^* &= Q_{ip} Q_{jq} D_{pq}, & \omega_{ij}^* &= Q_{ip} Q_{jq} \omega_{pq} + \Omega_{ij}, \\ N_i^* &= Q_{ip} N_p, & N_{ij}^* &= Q_{ip} Q_{jq} N_{pq}, \end{aligned} \tag{25.62}$$

---

[13] We shall not use a separate symbol, say w_i, for $\dot{n}_i$, as done by LESLIE in [47].

in which

$$\Omega_{ij} = -\Omega_{ji} = Q_{jk}\dot{Q}_{ik}. \tag{25.63}$$

Indeed, with the definition of the orthogonality of Q_{ij} the expressions for D^*_{ij} and ω^*_{ij} are almost obvious. For N^*_i we then can write

$$\begin{aligned} N^*_i &= \dot{n}^*_i - \omega^*_{ik} n^*_k = Q_{ij}\dot{n}_j + \dot{Q}_{ij} n_j - \left[\left(Q_{ip} Q_{kq} \omega_{pq} + \Omega_{ik}\right)\left(Q_{k\ell} n_\ell\right)\right] \\ &= Q_{ij}\dot{n}_j + \dot{Q}_{ij} n_j - \Big[Q_{ip}\delta_{q\ell}\omega_{pq} n_\ell + \underbrace{\Omega_{ik} Q_{k\ell} n_\ell}_{Q_{km}\dot{Q}_{im} Q_{k\ell} n_\ell}\Big] \\ &= Q_{ij}\dot{n}_j + \dot{Q}_{ij} n_j - \Big[\underbrace{Q_{ip}\omega_{pq} n_q}_{Q_{ip}\omega_{pj} n_j} + \dot{Q}_{im} n_m\Big] \\ &= Q_{ij}\dot{n}_j + \underline{\dot{Q}_{ij} n_j} - Q_{ip}\omega_{pj} n_j - \underline{\dot{Q}_{im} n_m} \\ &= Q_{ip}\left(\dot{n}_p - \omega_{pj} n_j\right) = Q_{ip} N_p. \end{aligned}$$

□

It is now straightforward also to verify (25.62)$_4$; this is left as an exercise to the reader.

25.3.2 Conservation Laws and Entropy Inequality

It would now be straightforward to copy the conservation laws of mass, momenta, and energy from Sect. 25.2, see Table 25.1. In the 1960s it has, on the other hand, been fashionable to discuss these laws in a more general context, namely the invariance of the total energy balance and of the director momentum equation under Euclidian transformations or superposition of rigid body motions (25.61). This was done by Green, Naghdi and Rivlin [35], Beatty [1], Truesdell [73], and Truesdell and Noll [74] in a general context. The procedure will now also be explained here, mainly for educational reasons.

For a material volume V, the energy balance and the director momentum equations are given as

$$\begin{aligned} &\frac{\mathrm{d}}{\mathrm{d}t}\int_V \rho\left\{\tfrac{1}{2}\left(v_i v_i + \dot{n}_i \dot{n}_i\right) + \varepsilon\right\}\mathrm{d}V \\ &\qquad = \int_V \rho\left\{r + f_i v_i + \ell_i \dot{n}_i\right\}\mathrm{d}V + \int_{\partial V}\left\{t_i v_i + m_i \dot{n}_i - h\right\}\mathrm{d}a, \end{aligned} \tag{25.64}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_V \rho\dot{n}_i \mathrm{d}V = \int_V \rho\left(\ell_i + g_i\right)\mathrm{d}V + \int_{\partial V}\rho k_i \mathrm{d}a. \tag{25.65}$$

Here, ρ is the mass density and all remaining volume quantities are defined per unit mass and unit volume element. ε is the specific internal energy. $\{r, f_i, \ell_i, g_i\}$ are the energy supply, the external body force, the external director body force, the intrinsic director body force, all per unit mass. $\{t_i, m_i, h\}$ are the surface traction, the director surface traction and the energy flow out of the volume, and k_i is the director surface traction, all per unit area.

Note, it will now be postulated that the balance equations (25.64), (25.65) are invariant under EUCLIDian transformations, but to set this requirement into practice, it must be known, or postulated how the various field quantities transform under EUCLIDian transformations. We will assume that

$$\begin{aligned}
&\rho^* = \rho, \quad \varepsilon^* = \varepsilon, \quad h^* = h, \quad r^* = r, \\
&t_i^* = Q_{ij} t_j, \quad m_i^* = Q_{ij} m_j, \quad g_i^* = Q_{ij} g_j, \\
&f_i^* - (v_i^*)^{\cdot} = Q_{ij}\left(f_i - \dot{v}_i\right), \quad \ell_i^* - (\dot{n}_i)^* = Q_{ij}\left(\ell_i - \dot{n}_i\right).
\end{aligned} \tag{25.66}$$

In these expressions, it is assumed that $\{\rho, \varepsilon, h, r\}$ transform under EUCLIDian changes of frames as objective scalars and the surface flux quantities $\{t_i, m_i, g_i\}$ as objective vectors. By contrast, the external supply terms are postulated to behave differently: Here, $\{(f_i - \dot{v}_i), (\ell - \dot{n}_i)\}$ are assumed to behave objectively. This follows the classical inertial behavior of the EUCLIDian invariance of $(f_i - \dot{v}_i)$ and carries this over to the analogous terms of the director momentum behavior as evidenced by $(\ell_i - \dot{n}_i)$.

We now select two special transformations (25.61):
Choice 1: Simple temporal shift with the velocity $a_i \tau$:

$$c_i^* = a_i \tau, \quad c_i = 0, \quad Q_{ij} = \delta_{ij}, \tag{25.67}$$

where a_i is an arbitrary, constant vector. From Eq. (25.61) we, thus, deduce $v_i^* = v_i + a_i$ and so (25.64) takes the form

$$\begin{aligned}
&\frac{\mathrm{d}}{\mathrm{d}t}\int_V \rho\left\{\tfrac{1}{2}\left(v_i + a_i\right)\left(v_i + a_i\right) + \tfrac{1}{2}\dot{n}_i\dot{n}_i + \varepsilon\right\}\mathrm{d}V \\
&= \int_V \rho\left\{r + f_i(v_i + a_i) + \ell_i\dot{n}_i\right\}\mathrm{d}V \\
&\quad + \int_{\partial V}\left\{t_i\left(v_i + a_i\right) + m_i\dot{n}_i - h\right\}\mathrm{d}a.
\end{aligned} \tag{25.68}$$

This equation must hold for arbitrary values of a_i. Subtracting, therefore from (25.68) the same equation with $a_i = 0$, one finds

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_V \rho\left\{v_i a_i + \tfrac{1}{2}a_i a_i\right\}\mathrm{d}V = \int_V \rho f_i a_i \mathrm{d}V + \int_{\partial V} t_i a_i \mathrm{d}a, \tag{25.69}$$

from which one deduces, since a_i is arbitrary,

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_V \rho \mathrm{d}V = 0, \quad \frac{\mathrm{d}}{\mathrm{d}t}\int_V \rho v_i \mathrm{d}V = \int_V \rho f_i \mathrm{d}V + \int_{\partial V} t_i \mathrm{d}a. \tag{25.70}$$

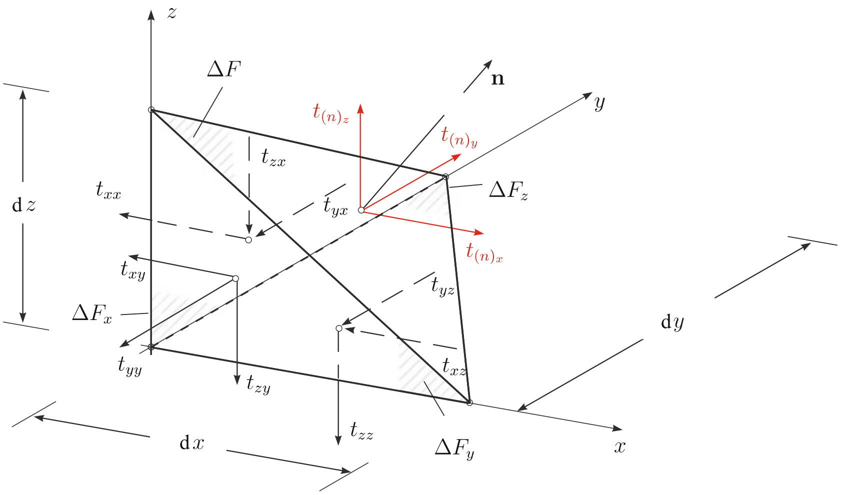

Fig. 25.11 CAUCHY stress tensor *To find the interpretation of the* CAUCHY *stress tensor we consider an infinitesimal material tetrahedron with three triangular boundary surfaces perpendicular to the coordinate lines and an inclined element with exterior unit normal vector* $\boldsymbol{n}$. *On each surface element, we have normal and shear stresses*

These are the familiar global balance laws of mass and linear momentum. Sufficient smoothness of the fields assumed, their local forms are

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} + \rho v_{i,i} = 0, \quad \rho\frac{\mathrm{d}v_i}{\mathrm{d}t} = \rho f_i + t_{ij,j}, \quad t_i = t_{ij}n_j^+, \tag{25.71}$$

in which t_{ij} is the CAUCHY stress tensor and n_j^+ a unit vector on a plane forming the tetrahedron shown in **Fig. 25.11**.

Similarly, employing CAUCHY's lemma for the surface traction, $k_i = \pi_{ij}n_j^+$, the global director momentum equation (25.65) takes the form

$$\rho\frac{\mathrm{d}}{\mathrm{d}t}\left(\dot{n}_i\right) = \rho\ell_i + \rho g_i + \pi_{ij,j}, \quad k_i = \pi_{ij}n_j^+, \tag{25.72}$$

in which π_{ij} are the components of the director surface force across the x_i-planes. If we also introduce the energy flux vector via

$$h = q_i n_i^+, \tag{25.73}$$

we can write the energy equation (25.64) in the form

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_V \rho\left\{\tfrac{1}{2}\left(v_i v_i + \dot{n}_i\dot{n}_i\right) + \varepsilon\right\}\mathrm{d}V$$

$$
\begin{aligned}
&-\int_V \left\{\rho\left[r + f_i v_i + \ell_i \dot{n}_i\right] + (t_{ij} v_i)_{,j} + (\pi_{ij}\dot{n}_i)_{,j} - q_{j,j}\right\} \mathrm{d}V = 0 \\
\overset{*}{=} &\int_V \Big\langle \dot{\rho}\left\{\tfrac{1}{2}\left(v_i v_i + \dot{n}_i\dot{n}_i\right) + \varepsilon\right\} + \rho\left\{v_i\dot{v}_i + \dot{n}_i\,(\dot{n}_i)^{\cdot} + \dot{\varepsilon}\right\} \\
&+ \rho\left\{\tfrac{1}{2}\left(v_i v_i + \dot{n}_i\dot{n}_i\right) + \varepsilon\right\} v_{k,k} - \rho\left[r + f_i v_i + \ell_i\dot{n}_i\right] \\
&- \left(t_{ij} v_i\right)_{,j} - \left(\pi_{ij}\dot{n}_i\right)_{,j} + q_{j,j}\Big\rangle \mathrm{d}V = 0 \\
\overset{**}{=} &\int_V \Big\langle \big(\underbrace{\dot{\rho} + \rho v_{k,k}}_{=0}\big)\left\{\tfrac{1}{2}\left(v_i v_i + \dot{n}_i\dot{n}_i\right) + \varepsilon\right\} \\
&+ v_i\big\{\underbrace{\rho\dot{v}_i - \rho f_i - t_{ij,j}}_{=0}\big\} - t_{ij} v_{i,j} \\
&+ \dot{n}_i\big\{\underbrace{\rho(\dot{n}_i)^{\cdot} - \rho\ell_i - \pi_{ij,j}}_{=g_i}\big\} - \pi_{ij}(\dot{n}_i)_{,j} \\
&+ \rho\dot{\varepsilon} - \rho r + q_{i,i} - t_{ij} v_{i,j} - \pi_{ij}\,(\dot{n}_i)_{,j} + \dot{n}_i g_i\Big\rangle \mathrm{d}V = 0 \\
\overset{***}{=} &\int_V \Big\langle \rho\dot{\varepsilon} - \rho r + q_{i,i} - t_{ij}\left(D_{ij} + \omega_{ij}\right) \\
&- \pi_{ij}\left(N_{ij} + \omega_{ik} n_{k,j}\right) + g_i\left(N_i + \omega_{ij} n_j\right)\Big\rangle \mathrm{d}V = 0 \\
= &\int_V \Big\langle \rho\dot{\varepsilon} - \rho r + q_{i,i} - t_{ij} D_{ij} - \pi_{ij} N_{ij} + g_i N_i - \tilde{t}_{ij}\omega ij\Big\rangle \mathrm{d}V = 0,
\end{aligned}
\tag{25.74}
$$

where

$$
\tilde{t}_{ij} := t_{ij} + \pi_{ik} n_{j,k} - g_i n_j. \tag{25.75}
$$

In the second line of (25.74), the GAUSS law has been employed. Furthermore, at step ($\overset{*}{=}$) we employed the property

$$
\begin{aligned}
\frac{\mathrm{d}}{\mathrm{d}t}\int_V \rho f \mathrm{d}V &= \int_V \left(\dot{\rho} f + \rho\dot{f} + \rho f v_{k,k}\right) \mathrm{d}V \\
&= \int_V \big\{\underbrace{\left(\dot{\rho} + \rho v_{k,k}\right)}_{=0} f + \rho\dot{f}\big\} \mathrm{d}V = \int_V \rho\dot{f} \mathrm{d}V
\end{aligned}
$$

and at step ($\overset{**}{=}$) the balance laws of mass and classical and director momenta have been used, while at step ($\overset{***}{=}$) the objective vector N_i and second rank tensor N_{ij}, defined in (25.60), have been substituted. This, finally, led to the introduction of the tensor $\tilde{t}_{ij}$ in (25.75). The energy balance law, thus, reduces to the statement

$$
\left\langle \rho\dot{\varepsilon} - \rho r + q_{i,i} - t_{ij} D_{ij} - \pi_{ij} N_{ij} + g_i N_i - \tilde{t}_{ij}\omega_{ij}\right\rangle = 0. \tag{25.76}
$$

Choice 2: Following LESLIE [48], we select as special transformation (25.61)

$$c_i^* = c_i = 0 \quad Q_{ij} = \delta_{ij}, \quad \text{and} \quad \dot{Q}_{ij} = a_{ij}, \tag{25.77}$$

where $a_{ij} = -a_{ji}$ is skew-symmetric. This transforms ω_{ij} to $\omega_{ij} + a_{ij}$ [see (25.61)] and leaves the energy equation unchanged except for the last term on the left-hand side, which reads $\tilde{t}_{ij}(\omega_{ij} + a_{ij})$. Because a_{ij} is arbitrary among all rank-2 skew-symmetric tensors, we have

$$\tilde{t}_{ij} a_{ij} = 0. \tag{25.78}$$

It follows that $\tilde{t}_{ij}$ is necessarily symmetric,

$$\tilde{t}_{ij} = \tilde{t}_{ji}. \tag{25.79}$$

Thus, the energy equation takes the form

$$\rho\dot{\varepsilon} = -q_{i,i} + t_{ij} D_{ij} + \pi_{ij} N_{ij} - g_i N_i + \rho r. \tag{25.80}$$

The governing physical balance laws are now given by the balances of mass and linear momentum $(25.71)_{1,2}$, the director momentum balance law (25.72), the energy equation (25.76), and the symmetry relations for the tensor $\tilde{t}_{ij}$ (25.79).

We now complement these conservation laws by the entropy inequality, which we take in the form

$$\frac{\mathrm{d}}{\mathrm{d}t} \int_V \rho s \mathrm{d}V + \int_{\partial V} \phi \mathrm{d}a - \int_V \frac{\rho r}{T} \mathrm{d}V \geqslant 0. \tag{25.81}$$

Here, s denotes the entropy density per unit mass, ϕ is the entropy flow through the boundary ∂V of V, and r/T is the entropy supply per unit mass. It has been chosen above as the energy supply divided by the absolute temperature. Introducing the entropy flux vector ϕ_i and noting CAUCHY's lemma, we write

$$\phi = \phi_i n_i^+. \tag{25.82}$$

Substituting this into (25.81) and employing the divergence theorem then yields

$$\int_V \left(\rho\dot{s} + \phi_{i,i} - \frac{\rho r}{T} \right) \mathrm{d}V \geqslant 0, \tag{25.83}$$

or, when localized

$$\rho\dot{s} + \phi_{i,i} - \frac{\rho r}{T} \geqslant 0. \tag{25.84}$$

The CLAUSIUS–DUHEM inequality has been generalized by selecting the entropy flux vector as a vector of the constitutive class to be selected below. This follows MÜLLER's paper [53]. The HELMHOLTZ free energy and the extra entropy flux vector

ϕ_i are defined by

$$\psi = \varepsilon - Ts, \quad \varphi_i = q_i - T\phi_i. \tag{25.85}$$

Substituting these into (25.84) and eliminating $\rho r/T$ with the help of (25.76) yields the entropy inequality, (in this form often called dissipation inequality) as

$$-\rho\left(\dot{\psi} + s\dot{T}\right) + t_{ij}D_{ij} + \pi_{ij}N_{ij} - g_i N_i - \phi_i T_{,i} - \varphi_{i,i} \geqslant 0. \tag{25.86}$$

Note that, if $\varphi_i = 0$, then $\phi_i = q_i/T$ and (25.86) reduces to the Clausius–Duhem inequality as used by Ericksen [22].

25.3.3 Constitutive Relations and Exploitation of the Entropy Principle

The balance laws of mass, linear momentum, director momentum, and energy comprise eight differential relations for ρ, v_i, n_i, and T. They involve

$$\{\varepsilon, s, q_i, \varphi_i, t_{ij}, \pi_{ij}, g_i\} \tag{25.87}$$

as field quantities, which must uniquely be expressed as constitutive relations in terms of the independent constitutive variables. Our intention is to express these as functions of[14]

$$\left\{\rho, n_i, n_{i,j}, \dot{n}_i, v_{i,j}, T, T_{,i}\right\}. \tag{25.88}$$

They comprise, via $\{\rho, n_i, n_{i,j}\}$, elasticity effects, via $v_{i,j}$ viscous effects and via $\{T, T_{,i}\}$ heat conducting effects. Owing to (25.60), an alternative set of independent variables can also be

$$\left\{\rho, n_i, n_{i,j}, N_i, D_{ij}, \omega_{ij}, T, T_{,i}\right\}. \tag{25.89}$$

It has already been made clear that all variables in (25.89) are objective under Euclidian transformations, except ω_{ij}, which transforms as

$$\omega^*_{ij} = Q_{ip}Q_{jq}\omega_{pq} + \Omega_{ij}, \tag{25.90}$$

as already stated in (25.62); Ω_{ij} is defined in (25.63). The occurrence of Ω_{ij} in (25.90) makes ω^*_{ij} non-objective under Euclidian transformations. If constitutive relations are requested to be objective under such transformations ω_{ij} is only allowed to arise

---

[14] A dependence on $(\dot{n}_i)_{,j}$ is in principle also possible, however, when it is thought that elongations of directors are small, this stretching may be small as well.

in combination with other independent constitutive variables, which are EUCLIDian objective, such as N_i or N_{ij}; so, (25.89) reduces to

$$\left\{\rho, n_i, N_i, D_{ij}, T, T_{,i}\right\}. \tag{25.91}$$

Apart from the reduction of the independent constitutive relations to the class (25.91), the exploitation of the entropy principle will be conducted, subject to the following conditions:

- We restrict considerations to nematic LCs, so that constitutive relations are invariant under reflections through planes containing the directors; this requirement implies that constitutive equations are isotropic functions, so that the constitutive variables are invariant under proper *and* improper orthogonal transformations Q_{ij}, viz.,

$$\begin{array}{lll} \text{for scalars :} & s^* = s, & \{\varepsilon, \rho, T, s\}, \\ \text{for vectors :} & q_i^* = Q_{ip} q_p, & \{q_i, \phi_i, g_i, n_i, T_i\}, \\ \text{for rank-2 tensors :} & t_{ij}^* = Q_{ip} Q_{jq} t_{pq}, & \{t_{ij}, \pi_{ij}, n_{i,j}, D_{ij}, \ldots\}, \end{array} \tag{25.92}$$

  where the second column in this table shows the transformation rule for arbitrary $\pm Q_{ij}$ and the third column lists the possible variables to which the transformation in the second column applies.
- The assumption that n_i and $-n_i$ are to be physically indistinguishable in the theory requires that the change $n_i \to -n_i$ must imply the changes

$$\begin{aligned} &\varepsilon \to \varepsilon, \quad s \to s, \quad q_i \to q_i, \quad \phi_i \to \phi_i, \\ &t_{ij} \to t_{ij}, \quad \pi_{ij} \to -\pi_{ij}, \quad g_i \to -g_i, \end{aligned} \tag{25.93}$$

  provided that

$$n_{i,j} \to -n_{i,j}, \quad \dot{n}_i \to -\dot{n}_i, \quad N_i \to -N_i. \tag{25.94}$$

  In these expressions, the invariance rules for π_{ij} and g_i follow from the invariance of the director momentum equation (25.20) with (25.40); moreover, those for $\dot{n}_i$ and N_i are a consequence of (25.60).
- Of particular significance is the fact that the balance laws of mass (1), momenta (6), and energy (1) form a set of eight equations. To arrive at an integrable system of equations, constitutive relations are formulated for the quantities (25.87), but these may not automatically satisfy the symmetry of the stress $\tilde{t}_{ij}$, given in (25.75) and (25.79). It must separately be guaranteed that this symmetry is automatically satisfied.
- The dissipation inequality (25.86) will be exploited here in the spirit of COLEMAN–NOLL, see [42], Chap. 18, i.e., it is assumed that the balance laws of classical and director momenta have external body and director forces f_i and ℓ_i, respectively, which may have any assigned values. This means that—whatever

values the remaining fields or their time or space derivatives may have—there exist forces f_i and ℓ_i, which make the linear and director momentum equations identically be satisfied. Similarly, the conservation law of energy (25.76) equally contains an external source, r, which may have any arbitrary value. So, whatever values the other variables arising in (25.76) may have, they can be thought to be generated by a source ρr, which satisfies (25.76) identically. Therefore, the balance laws of momenta and energy do formally not serve as constraint conditions when exploiting (25.86).

It is clear that the condition of arbitrarily assigned fields f_i, ℓ_i, and r delivers mathematically a considerable simplification of the entropy analysis, but whether such an assumption is equally physically justified is a different matter. More on this will be said below.

With the above-itemized provisos in mind, the entropy inequality (25.86) can now be exploited. To this end, the following auxiliary computations are needed:

$$\begin{aligned}\varphi_{i,i} = {} & \frac{\partial\varphi_i}{\partial\rho}\rho_{,i} + \frac{\partial\varphi_i}{\partial n_j}n_{j,i} + \frac{\partial\varphi_i}{\partial n_{j,k}}n_{j,ki} + \frac{\partial\varphi_i}{\partial N_j}N_{j,i} \\ & + \frac{\partial\varphi_i}{\partial D_{jk}}D_{jk,i} + \frac{\partial\varphi_i}{\partial T}T_{,i} + \frac{\partial\varphi_i}{\partial T_{,j}}T_{,ij},\end{aligned} \tag{25.95}$$

in which (25.60) and the definition of ω_{ik} in (25.57) can be used to substitute

$$N_{i,j} = N_{ij} + \omega_{ik,j}n_k = N_{ij} + D_{ik,j}n_k - D_{kj,i}n_k, \tag{25.96}$$

so that (25.95) takes the form

$$\begin{aligned}\varphi_{i,i} = {} & \frac{\partial\varphi_i}{\partial\rho}\rho_{,i} + \frac{\partial\varphi_i}{\partial T}T_{,i} + \frac{\partial\varphi_i}{\partial T_{,j}}T_{,ij} + \frac{\partial\varphi_i}{\partial n_{j,k}}n_{j,ik} + \frac{\partial\varphi_i}{\partial N_j}N_{ij} \\ & + \left(\frac{\partial\varphi_i}{\partial D_{jk}} - \frac{\partial\varphi_i}{\partial N_j}n_k + \frac{\partial\varphi_j}{\partial N_i}n_k\right)D_{jk,i}.\end{aligned} \tag{25.97}$$

Similarly,

$$\begin{aligned}\dot{\psi} = {} & \frac{\partial\psi}{\partial\rho}\dot{\rho} + \frac{\partial\psi}{\partial n_i}\dot{n}_i + \frac{\partial\psi}{\partial n_{i,k}}(n_{i,k})^{\cdot} + \frac{\partial\psi}{\partial N_i}\dot{N}_i \\ & + \frac{\partial\psi}{\partial D_{ij}}(D_{ij})^{\cdot} + \frac{\partial\psi}{\partial T}\dot{T} + \frac{\partial\psi}{\partial T_{,i}}(T_{,i})^{\cdot}\end{aligned}$$

and with

$$\begin{aligned}& \dot{\rho} = -\rho D_{ij}\delta_{ij}, \qquad (n_i)^{\cdot} \overset{(25.60)}{=} \left(N_i - \omega_{ij}n_j\right), \\ & (n_{i,k})^{\cdot} = (\dot{n}_i)_{,k} - v_{j,k}n_{i,j} \overset{(25.60)}{=} N_{ik} - \omega_{i\ell}n_{\ell,k} - D_{jk}n_{ij} - \omega_{jk}n_{i,j},\end{aligned}$$

this yields

$$
\begin{aligned}
\dot{\psi} = {} & -\rho\frac{\partial\psi}{\partial\rho}D_{ij}\delta_{ij} + \frac{\partial\psi}{\partial n_i}N_i - \frac{\partial\psi}{\partial n_i}\omega_{ij}n_j + \frac{\partial\psi}{\partial N_i}\dot{N}_i \\
& + \frac{\partial\psi}{\partial D_{ij}}(D_{ij})^{\cdot} + \frac{\partial\psi}{\partial T}\dot{T} + \frac{\partial\psi}{\partial T_{,i}}(T_{,i})^{\cdot} \\
& + \frac{\partial\psi}{\partial n_{i,k}}\Big(\underbrace{(\dot{n}_i)_{,k}}_{\overset{(25.60)}{=}N_{ik}-\omega_{i\ell}n_{\ell,k}} - \underbrace{v_{j,k}}_{(D_{jk}+\omega_{jk})}n_{i,j}\Big).
\end{aligned}
\tag{25.98}
$$

Substituting (25.97) and (25.98) into the entropy imbalance (25.86), rearranging terms (and adjusting indices) leads to the following long inequality:

$$
\begin{aligned}
& \left(t_{ij} + \rho^2\frac{\partial\psi}{\partial\rho}\delta_{ij} + \rho\frac{\partial\psi}{\partial n_{k,j}}n_{k,i}\right)D_{ij} + \left(\pi_{ij} - \rho\frac{\partial\psi}{\partial n_{i,j}} - \frac{\partial\varphi_j}{\partial N_i}\right)N_{ij} \\
& - \left(g_i + \rho\frac{\partial\psi}{\partial n_i}\right)N_i - \left(p_i + \frac{\partial\varphi_i}{\partial T}\right)T_{,i} - \frac{\partial\varphi_i}{\partial n_j}n_{j,i} \\
& + \rho\left(n_j\frac{\partial\psi}{\partial n_i} + n_{j,k}\frac{\partial\psi}{\partial n_{i,k}} + n_{k,j}\frac{\partial\psi}{\partial n_{k,i}}\right)\omega_{ji} - \frac{\partial\varphi_i}{\partial\rho}\rho_{,i} - \frac{\partial\varphi_i}{\partial n_{k,j}}n_{k,ij} \\
& - \frac{\partial\varphi_i}{\partial T_{,j}}T_{,ij} - \left(\frac{\partial\varphi_i}{\partial D_{jk}} + n_k\frac{\partial\varphi_j}{\partial N_i} - n_i\frac{\partial\varphi_k}{\partial N_j}\right)D_{jk,i} \\
& - \rho\left(\frac{\partial\psi}{\partial T} + s\right)\dot{T} - \rho\frac{\partial\psi}{\partial N_i}\dot{N}_i - \rho\frac{\partial\psi}{\partial D_{ij}}\dot{D}_{ij} - \rho\frac{\partial\psi}{\partial T_{,i}}(T_{,i})^{\cdot} \geqslant 0.
\end{aligned}
\tag{25.99}
$$

This inequality must be identically satisfied for arbitrarily smooth fields. It is linear in the colored quantities, which can be freely assigned. This is so, because we assume that the linear and director momentum equations as well as the energy equation are equipped with external source terms, which may be selected such that for any selected values of the colored quantities in (25.99) the momentum and energy equations are identically satisfied. Taking the terms in the last line of (25.99), we therefore conclude that

$$
\frac{\partial\psi}{\partial T_{,i}} \equiv 0, \quad \frac{\partial\psi}{\partial N_i} \equiv 0, \quad \frac{\partial\psi}{\partial D_{ij}} + \frac{\partial\psi}{\partial D_{ji}} \equiv 0, \tag{25.100}
$$

while

$$
s = -\frac{\partial\psi}{\partial T}. \tag{25.101}
$$

Hence, ψ can neither depend upon $T_{,i}$ nor N_i, implying that

$$
\psi = \psi(\rho, T, n_i, n_{i,j}). \tag{25.102}
$$

The result (25.101) agrees with the classical relation between entropy and the free energy. Moreover, since the imbalance (25.99) is also linear in the vorticity tensor, its prefactor in (25.99) must be a symmetric rank-2 tensor; this condition reads

$$n_i \frac{\partial \psi}{\partial n_j} + n_{i,k} \frac{\partial \psi}{\partial n_{j,k}} + n_{k,i} \frac{\partial \psi}{\partial n_{k,j}} \equiv n_j \frac{\partial \psi}{\partial n_i} + n_{j,k} \frac{\partial \psi}{\partial n_{i,k}} + n_{k,j} \frac{\partial \psi}{\partial n_{k,i}}. \quad (25.103)$$

If the free energy function is an isotropic function of n_i and $n_{i,j}$, which we will assume, this equation is identically satisfied. This proof has been given in the text following Eq. (25.48) [where the free energy function is denoted by φ and not ψ]; it is due to ERICKSEN [23].

There remain the terms involving the blue colored quantities in (25.99), which can be assigned arbitrary values, implying

$$\frac{\partial \varphi_i}{\partial \rho} \equiv 0, \qquad \frac{\partial \varphi_i}{\partial n_{k,j}} + \frac{\partial \varphi_j}{\partial n_{k,i}} \equiv 0, \qquad \frac{\partial \varphi_i}{\partial T_{,j}} + \frac{\partial \varphi_j}{\partial T_{,i}} \equiv 0, \quad (25.104)$$

$$\frac{\partial \varphi_i}{\partial D_{jk}} + \frac{\partial \varphi_i}{\partial D_{kj}} + n_k \frac{\partial \varphi_j}{\partial N_i} + n_j \frac{\partial \varphi_k}{\partial N_i} - n_i \frac{\partial \varphi_k}{\partial N_j} - n_i \frac{\partial \varphi_{ij}}{\partial N_k} \equiv 0. \quad (25.105)$$

Equation $(25.104)_1$ says that φ_i cannot depend upon ρ. LESLIE [47] then mentions

- that it is relatively easy to show with the use of $(25.104)_3$ that φ_i can only linearly depend upon the temperature gradient,
- that from Eq. (25.105) one can show that, apart from an arbitrary dependence upon the scalar product $n_i N_i$, φ_i is linear in the vector N_i and the rate of strain tensor D_{ij}. Hence, φ_i is of the form

$$\varphi_i = \alpha_i + \alpha_{ij} T_{,j} + \beta_{ij} N_j + \beta_{ijk} D_{jk} + \gamma_{ijk} T_{,j} N_k + \gamma_{ijkp} T_{,j} D_{kp}, \quad (25.106)$$

  where the coefficients may depend upon T, n_i, $n_{i,j}$, and $n_i N_i$; moreover, β_{ijk} and γ_{ijkp} are obviously symmetric in the last two indices.
- that one can show by employing Eq. $(25.104)_2$ that
  - (i) α_i is at most quadratic in $n_{i,j}$,
  - (ii) α_{ij}, β_{ij} and β_{ijk} are at most linear in $n_{i,j}$,
  - (iii) γ_{ijk} are independent of the director gradients.[15]
- that, as a result of the work of SMITH [66] on isotropic integrity bases, and by recalling (25.92), (25.93), it is a straightforward matter to show that

$$\varphi_i = \alpha\,(T, n_i n_i, n_i N_i) \left\{ n_i n_{j,j} - n_j n_{i,j} \right\}. \quad (25.107)$$

---

[15] Up to this point, these results are independent of whether the constitutive functions are isotropic or hemotropic.

The reader may partially satisfy himself/herself, by taking the above-itemized statements as facts, and verify that with them, Eqs. (25.104) and (25.105) are identically satisfied.[16]

Finally, inequality (25.99) is also linear in N_{ij} [see (25.60)], so that the director stress π_{ij} is given by

$$\pi_{ij} = \rho \frac{\partial \psi}{\partial n_{i,j}} - \frac{\partial \varphi_j}{\partial N_i}. \tag{25.108}$$

It depends not only on the free energy, ψ, but equally also upon φ_j, the extra entropy flux.

The scalar coefficient α in (25.107) depends only upon the temperature, the magnitude of n_i, and the scalar product $n_i N_i$. The proof of (25.107) is relatively lengthy and involves the theory of isotropic functions [66, 71, 77, 78].

With these results, the inequality (25.99) reduces to

$$\begin{aligned}&\left(t_{ij} + \rho^2 \frac{\partial \psi}{\partial \rho}\delta_{ij} + \rho \frac{\partial \psi}{\partial n_{k,j}} n_{k,i}\right) D_{ij}\\ &-\left(g_i + \rho \frac{\partial \psi}{\partial n_i}\right) N_i - \left(p_i + \frac{\partial \varphi_i}{\partial T}\right) T_{,i} - \frac{\partial \varphi_i}{\partial n_j} n_{j,i} \geqslant 0.\end{aligned} \tag{25.109}$$

This residual entropy inequality will now be used to draw inferences for thermodynamic equilibrium. To this end, consider a static (time independent) isothermal process, in which the magnitude of the director does not vary. For such a process $D_{ij} = N_{ij} = N_i = T_{,i} = 0$ [see (25.60)], so that

$$-\frac{\partial \varphi_i}{\partial n_j} n_{j,i} \equiv 0. \tag{25.110}$$

The equality sign applies here instead of "($\geqslant 0$)" because this static process is a thermodynamic equilibrium for which no entropy is produced. Substituting $n_i n_i =$ const. and $n_i N_i = 0$ into (25.107) yields

$$\alpha(T, \text{const.}, 0)\{\underbrace{\delta_{ij} n_{k,k} - n_{i,j}}_{\neq 0}\} = 0 \quad \Longrightarrow \quad \alpha(T, \text{const.}, 0) = 0. \tag{25.111}$$

Thus, we may write

$$\begin{aligned}&\mathcal{N}_i := n_i n_{j,j} - n_j n_{i,j}, &(25.112)\\ &\varphi_i = \left[\alpha_0(T, n_k n_k) n_j N_j + \alpha_1\left(T, n_k n_k, n_j N_j\right)\right]\mathcal{N}_i, &(25.113)\\ &\text{in which} \quad \alpha_1 = o(n_i N_i) \quad \text{as } n_i N_i \to 0.\end{aligned}$$

---

[16] The authors neither fully verified these statements.

With this selection of φ_i, it is now evident that for $D_{ij} = 0$, $N_i = 0$, $T_{,i} = 0$, and $n_i N_i \to 0$, no entropy is produced. Thus, we may compose the stress t_{ij}, the intrinsic body force g_i, and the entropy flux p_i as

$$t_{ij} = t_{ij}^0 + t'_{ij}, \quad g_i = g_i^0 + g'_i \quad p_i = p_i^0 + p'_i. \tag{25.114}$$

Substituting these expressions into the imbalance (25.109) and requesting that the $(\cdot)^0$-quantities produce no entropy, we obtain the equilibrium values

$$\begin{aligned} t_{ij}^0 &= -\rho^2 \frac{\partial \psi}{\partial \rho}\delta_{ij} - \rho \frac{\partial \psi}{\partial n_{k,j}} n_{k,i}, \\ g_i^0 &= -\rho \frac{\partial \psi}{\partial n_i} - \frac{\partial}{\partial n_k}\left(\alpha_0 \mathcal{N}_j n_i\right) n_{k,j}, \\ p_i^0 &= 0, \end{aligned} \tag{25.115}$$

as well as the residual inequality in the form

$$t'_{ij} D_{ij} - g'_i N_i - \frac{\partial}{\partial n_i}\left(\alpha_1 \mathcal{N}_i\right) n_{j,i} - \left(p'_i + \frac{\partial \varphi_i}{\partial T}\right) T_{,i} \geqslant 0. \tag{25.116}$$

Expressions for t'_{ij}, g'_i, and p'_i could now be obtained for the nonequilibrium parts t'_{ij}, g'_i, and p'_i from isotropic function representations of these quantities; however, on account of their complexity, this was not done by Leslie [47]. He restricted considerations to static isothermal deformations. For these, the stresses and the intrinsic body force are given by (25.115), (25.108) and are below written without the $(\cdot)^0$-index:

$$\begin{aligned} t_{ij} &= -\rho^2 \frac{\partial \psi}{\partial \rho}\delta_{ij} - \rho \frac{\partial \psi}{\partial n_{k,j}} n_{k,i}, \\ \pi_{ij} &= \rho \frac{\partial \psi}{\partial n_{i,j}} + \alpha_0 \mathcal{N}_j n_i, \\ g_i &= -\rho \frac{\partial \psi}{\partial n_i} - \left(\alpha_0 \mathcal{N}_j n_i\right)_{,j}. \end{aligned} \tag{25.117}$$

In these static processes, the heat and entropy flux vectors are zero. Leslie [47] states that apart from the terms involving α_0, the above expressions were already given by Ericksen [23]. However, these extra terms do not appear in the equilibrium equations and are therefore significant only, if the director stress is specified as a boundary condition. Indeed, the static equilibrium equation of the director momentum balance is, according to (25.72) given by $\pi_{ij,j} + g_i - \rho \ell_i = 0$. Equation (25.72) show that the α_0-contributions to $(\pi_{ij,j} + g_i)$ drop out. These terms are therefore significant only, if the director stress is specified as a boundary condition.

Remark: Technically, boundary conditions exert a significant effect on optical properties of LCs. This is reason for the success of LC devices. (LCDs). The fundamental

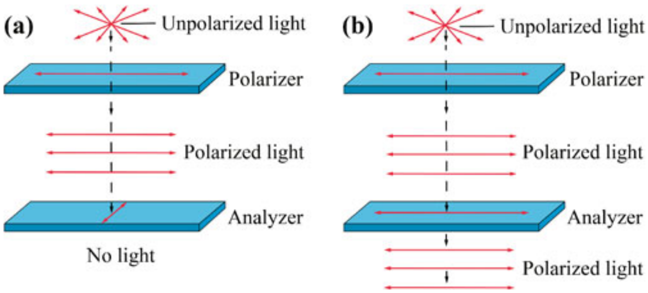

Fig. 25.12 Two polarizers (polarizer/analyser) with a neutral medium in between transmit unpolarized light by orienting the transmitted light in only one plane of oscillation. If the directions of the two polarizers are oriented in parallel, then all the light passing the first polarizer also passes the second polarizer [panel **b**], if they are oriented perpendicularly, no light passes the second polarizer [panel **a**] [54]

principle is realized in TN (twisted nematic) devices first discussed by M. SCHARDT and W. HELFRICH and independently also by JAMES FERGASON (1934–2008).[17] The principle consists of a twisted fluid cell, which rotates the polarization of light differently, according to whether the electric field is either switched on or off. **Figure 25.12** and the caption to it explain the optical effect of polarizers, when an ordinary gas or fluid is exposed to a pair of such polarizers. When the light is switched on, it passes the two polarizing filters bounding the device undisturbed; however, for unpolarized (natural) light, only light of a certain polarization can pass the filter.

A TN device consists of an approximately $5-\mu$-thick nematic fluid film between two glass plates onto each of which an electrically conductive transparent layer of *indium tin oxide* is evaporated. Between these films and the fluid-crystalline layer, a likewise transparent orienting film is positioned (which is usually a plastic). It serves to orient the long axes of the neighboring liquid crystalline molecules into a preferred direction.

In the TN device (see **Fig. 25.13**), then different orienting layers are so mounted that the long axes of the molecules, which are in contact with the upper and lower glass platelets, are rotated relative to one another by 90°. Owing to the tendency of the molecules in the fluid-crystalline layer to be parallel-oriented, their preferred orientation between the two glass surfaces changes gradually from that of the upper to that of the lower glass platelet, and the molecules arrange themselves as in a twisted strap.

The polarization filters are equally so arranged that the orientation of the light transfer agrees optimally with the preferred orientation of the molecular axes of the two bounding surfaces. The transmitted polarized light then is guided by the molecules of the LC and follows the twisted structure, so that its oscillation plane

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[17] A read-worthy professional biography of JAMES FERGASON is given by AMELIA CAROLINA SPARAVIGNA [70].

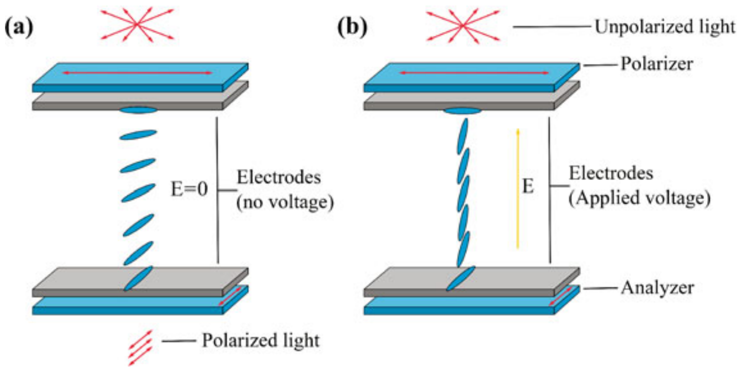

Fig. 25.13 Structure of a TN cell. The polarizer and analyser (whose arrangement is detailed in the main text) and bounding a nematic LC in the layer in between, are crosswise arranged. The main axis of the LC molecules at the glass platelets is parallel to the respective directions of the polarizers. Without the application of an electric field, the orientation of the directors changes smoothly from the polarizer to the analyser [panel **a**], when the electric field is switched on, the directors in the core region have a strong tendency to be parallel to the electric field [panel **b**]

after the passage of the layer at the other bounding surface of the display has equally been rotated by 90°. Because the light plane is, thus, parallel-oriented to the second polarization filter, the light can leave the display without any disturbance.

25.4 Thermodynamics of an Incompressible Liquid with Director of Constant Magnitude

It is known from classical thermodynamics that kinematic constraint conditions affect the exploitation of the entropy inequality by the fact that each kinematic constriction generates “constraint forces” (pressures, stress tensors), which guarantee the maintenance of the kinematic constraints. When the director is constrained to be of fixed length, it is convenient to absorb its magnitude into other fluid properties and to consider the vector n_i as a unit vector. Hence, redefining the director body forces and stress, we postulate [47]

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\int_V & \left[\rho\left(\tfrac{1}{2}v_i v_i + \varepsilon\right) + \tfrac{1}{2}\rho_1 \dot{n}_i \dot{n}_i\right]\mathrm{d}V \\ &= \int_V \left[\rho(r + f_i v_i) + \rho_1 G_i \dot{n}_i\right]\mathrm{d}V \\ &\quad + \int_{\partial V}\left(t_{ij}v_i + \pi_{ij}\dot{n}_i - q_i\right)\mathrm{d}a_i, \end{aligned} \tag{25.118}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_V \rho_1 \dot{n}_i \mathrm{d}V = \int_V \rho_1\left(G_i + g_i\right)\mathrm{d}V + \int_{\partial V}\pi_{ij} n_i^{+}\mathrm{d}a. \tag{25.119}$$

In the above energy and director momentum balance laws, ρ and ρ_1 are constant densities per unit volume and unit director length, respectively. Correspondingly, if $[M]$, $[L]$, $[T]$ are the dimensions for mass, length, and time, then we have

$$[\rho] = [ML^{-3}], \qquad [\rho_1] = [ML^{-1}],$$
$$[G_i] = [g_i] = [ML^{-1}T^{-2}], \qquad [\ell_i] = [MT^{-2}]$$

for the dimensions of ρ, ρ_1, G_i, and ℓ_i. Moreover, we have used (25.71)$_3$, (25.72)$_1$, and (25.73). If we then subject in (25.118), (25.119) the motion to a EUCLIDian transformation as done with (25.68), (25.69), we again obtain the balance laws of mass and linear momentum in global form as stated in (25.70), which, owing to the constancy of ρ, take the forms

$$v_{i,i} = 0, \qquad \rho \frac{\mathrm{d}v_i}{\mathrm{d}t} = \rho f_i + t_{ij,j}. \tag{25.120}$$

Similarly, the local form of the director momentum equation (25.119) is given by

$$\rho_1 \, (\dot{n}_i)^{\cdot} = \rho_1 (G_i + g_i) + \pi_{ij,j} \tag{25.121}$$

and only differs from (25.72) by the fact that ρ is replaced by ρ_1.

Omitting the densities ρ and ρ_1 as phase space variables (because they are constant), the phase space is now reduced from (25.91) to

$$\{n_i, n_{i,j}, D_{ij}, T, T_i\}. \tag{25.122}$$

Performing with (25.118) transformations analogous to those which led to (25.74) shows that the energy balance is expressible as

$$\rho \dot{\varepsilon} = -q_{i,i} + t_{ij} D_{ij} + \pi_{ij} N_{ij} - g_i N_i + \rho r, \tag{25.123}$$

as in (25.80), and that $\tilde{t}_{ij}$ is defined as in (25.75), viz.,

$$\tilde{t}_{ij} = t_{ij} + \pi_{ik} n_{j,k} - g_i n_j \tag{25.124}$$

and is symmetric, $\tilde{t}_{ij} = \tilde{t}_{ji}$.

The entropy inequality in the form (25.84) is combined now with the energy Eq. (25.123). Elimination of the specific external energy supply r again yields the imbalance (25.86). On account of the constraints, it is, however, no longer possible to choose the kinematic quantities completely arbitrarily. One constraint is the continuity equation, $v_{k,k} = 0$. It will be incorporated into the entropy inequality by the LAGRANGEan term $-\lambda D_{ij} \delta_{ij}$. Introducing the free pressure p and the extra stress deviator t^E_{ij} by[18]

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[18] A possible isotropic part may be absorbed into the free pressure p, so t_{ij} is a deviator.

$$t_{ij} = -p\delta_{ij} + t^E_{ij}, \qquad (t^E_{ii} = 0), \tag{25.125}$$

the entropy inequality takes the form

$$\begin{aligned}
&\left(t^E_{ij} + \rho\frac{\partial\psi}{\partial n_{k,j}}n_{k,i}\right)D'_{ij} - (p-\lambda)D_{ii} + \left(\pi_{ij} - \rho\frac{\partial\psi}{\partial n_{i,j}} - \frac{\partial\varphi_j}{\partial N_i}\right)N_{ij}\\
&-\left(g_i + \rho\frac{\partial\psi}{\partial n_i}\right)N_i - \left(p_i + \frac{\partial\varphi_i}{\partial T}\right)T_{,i} - \frac{\partial\varphi_i}{\partial n_j}n_{j,i}\\
&+\rho\left(n_j\frac{\partial\psi}{\partial n_i} + n_{j,k}\frac{\partial\psi}{\partial n_{i,k}} + n_{k,j}\frac{\partial\psi}{\partial n_{k,i}}\right)\omega_{ji} - \frac{\partial\varphi_i}{\partial n_{k,j}}n_{k,ij}\\
&-\frac{\partial\varphi_i}{\partial T_i}T_{,ij} - \left(\frac{\partial\varphi_i}{\partial D_{jk}} + n_k\frac{\partial\varphi_j}{\partial N_i} - n_i\frac{\partial\varphi_k}{\partial N_j}\right)D_{jk,i}\\
&-\rho\left(\frac{\partial\psi}{\partial T} + s\right)\dot{T} - \rho\frac{\partial\psi}{\partial N_i}\dot{N}_i - \rho\frac{\partial\psi}{\partial D_{ij}}\dot{D}_{ij} - \rho\frac{\partial\psi}{T_{,i}}\left(T_{,i}\right)^{\cdot} \geqslant 0,
\end{aligned} \tag{25.126}$$

where $D'_{ij} = D_{ij} - D_{kk}\delta_{ij}$ is the deviator of D_{ij}. Because the continuity equation is embedded in this inequality, D_{ij} may form a full symmetric rank-2 tensor; in particular, D_{ii} does not need to vanish under these conditions. In (25.126), all terms having a red factor are linear in these factors. This implies as before that the conditions (25.100), (25.101), and (25.103) must hold also for liquid crystals with $\rho =$ const. and $\rho_1 =$ const. More importantly, since D_{ii} may differ from zero in (25.126), one concludes that

$$p = \lambda. \tag{25.127}$$

The LAGRANGE parameter of the continuity equation equals the free pressure.

Scrutiny of the terms of (25.126) involving the factors printed in blue color then leads to the statements (25.104), (25.105). For the exploitation of these, LESLIE states in [47] that it can be shown that the extra entropy flux is given by

$$\varphi_i = \alpha(T)\left\{n_i n_{j,j} - n_j n_{i,j}\right\}, \tag{25.128}$$

where α is a function of the temperature only. Conversely, accepting the representation (25.128), it follows that φ_i does not depend on $T_{,i}$, N_i and neither on D_{ij}. The residual entropy inequality thus takes the form

$$\begin{aligned}
&\left(t^E_{ij} + \rho\frac{\partial\psi}{\partial n_{k,j}}n_{k,i}\right)D_{ij} + \underline{\left(\pi_{ij} - \rho\frac{\partial\psi}{\partial n_{i,j}}\right)}N_{ij}\\
&-\left(g_i + \rho\frac{\partial\psi}{\partial n_i}\right)N_i - \frac{q_i T_{,i}}{T} \geqslant 0.
\end{aligned} \tag{25.129}$$

The reduction of the extra entropy flux to (25.128) can be made using isotropic function relations by ignoring the fact that the term in (25.126) is linear in N_{ij}, which can take arbitrary values.

The claim

$$\pi_{ij} = \rho \frac{\partial \psi}{\partial n_{i,j}} \tag{25.130}$$

would, however, be premature, because the director length is postulated to be unity, a condition, which imposes constraints on N_i and N_{ij}. The following elegant incorporation of this constraint is due to LESLIE [47].

Consider the combination

$$\pi_{ij} N_{ij} - g_i N_i, \tag{25.131}$$

that arises in (25.129), and select the director stress π_{ij} and intrinsic director force g_i as

$$\pi_{ij} = \beta_j n_i, \qquad g_i = \gamma n_i - \beta_k n_{i,k}, \tag{25.132}$$

in which γ and β_i are an arbitrary scalar and vector, respectively. Substituting (25.132) into (25.131) yields

$$\beta_k \{ \underbrace{n_{i,k} N_i + n_i N_{ik}}_{=0} \} - \gamma \{ \underbrace{n_i N_i}_{=0} \} = 0. \tag{25.133}$$

With the definition (25.60) of N_i and N_{ij} and the property that n_i is a unit vector, it can be shown that the two underbraced terms in (25.133) vanish. Indeed, on account that ω_{ki} is skew-symmetric, we have

(i)

$$n_i N_i = n_i \{ \dot{n}_i + \omega_{ki} n_k \} = \underbrace{n_i \dot{n}_i}_{\frac{1}{2}(n_i n_i)^{\cdot} = 0} + \underbrace{\omega_{ki} n_i n_k}_{=0} = 0, \qquad \square$$

(ii)

$$\begin{aligned} n_i N_{ij} + n_{i,j} N_i &= n_i \left\{ (\dot{n}_i)_{,j} + \omega_{ki} n_{k,j} \right\} + n_{i,j} \{ \dot{n}_i + \omega_{ki} n_k \} \\ &= \underbrace{n_i\, (\dot{n}_i)_{,j} + n_{i,j} \dot{n}_i}_{(n_i \dot{n}_i)_{,j} = \frac{1}{2}\left[(n_i n_i)^{\cdot} \right]_{,j} = 0} + \omega_{ki} \big(\underbrace{n_i n_{k,j} + n_{i,j} n_k}_{(n_i n_k)_{,j}} \big) \\ &= \underbrace{(\omega_{ki} n_i n_k)}_{=0}{}_{,j} - \underbrace{\omega_{ki,j} n_i n_k}_{=0}, \qquad \square \end{aligned}$$

It follows that the combination (25.131) plays no role in the inequality (25.129), or in the energy Eq. (25.76). Moreover, Eq. (25.79) [with the definition (25.75)] is identically satisfied with the choices (25.132); and the contribution

$$\pi_{ij,j} + g_i \overset{(25.132)}{=} (\beta_{j,j} + \gamma) n_i \tag{25.134}$$

to the balance law of director momentum (25.39) is thus simply a multiple of n_i. This scalar may be determined from the solution of (25.39) in an initial-boundary-value problem.

The nontrivial result (25.134) is the reason for keeping the underlined term in (25.129). The combination (25.131) does not contribute to the entropy production and neither to the energy equation. It does not enter the mass and linear momentum balances and fulfills the symmetry requirements of $\tilde{t}_{ij}$ identically. However, it enters the director momentum balance, which may be used to determine the factor $(\beta_{j,j} + \gamma)$ in (25.134). On account of these facts, we now set

$$\pi_{ij} = \beta_i n_j + \hat{\pi}_{ij}, \quad g_i = \gamma n_i - \beta_j n_{i,j} + \hat{g}_i \tag{25.135}$$

and call $\hat{\pi}_{ij}$ *the extra director stress*, $\hat{g}_i$, the *extra intrinsic director force*, and γ the *director tension*. The terms involving β_i contribute nothing new to the equations of motion, but they could be significant if the director stress is specified at the boundary.

Substituting (25.135) into (25.129) now allows to conclude that

$$\hat{\pi}_{ij} = \rho \frac{\partial \psi}{\partial n_{i,j}}, \tag{25.136}$$

which evidently differs from (25.130). It states that $\hat{\pi}_{ij}$ does have a form, as if it were an equilibrium quantity.

It is evident that the entropy production (25.129) vanishes, if $D_{ij} = N_{ij} = N_i = T_{,i} = 0$. Equilibrium values of t^E_{ij}, π_{ij}, g_i, and q_i are then obtained from (25.129) as

$$\begin{aligned} t^E_{ij}|_E &= -\rho \frac{\partial \psi}{\partial n_{k,i}} n_{k,j}, \qquad g_i|_E = -\rho \frac{\partial \psi}{\partial n_i}, \\ \hat{\pi}_{ij} &= \hat{\pi}_{ij}|_E = \rho \frac{\partial \psi}{\partial n_{i,j}}, \qquad q_i|_E = 0, \end{aligned} \tag{25.137}$$

which determine the extra stress, the extra director stress, the extra intrinsic body force, and equilibrium heat flux once the functional relation for the free energy $\psi(n_i, n_{j,k}, T)$ is prescribed. Writing then

$$\begin{aligned} t^E_{ij} &= t^E_{ij}|_E + \left(t^E_{ij}\right)' = -\rho \frac{\partial \psi}{\partial n_{k,i}} n_{k,j} + \left(t^E_{ij}\right)', \\ \pi_{ij} &= \beta_i n_j + \hat{\pi}_{ij} = \beta_i n_j + \rho \frac{\partial \psi}{\partial n_{i,j}}, \\ g_i &= g_i|_E + g'_i = -\rho \frac{\partial \psi}{\partial n_i} + g'_i, \\ q_i &= q_i|_E + q'_i, \end{aligned} \tag{25.138}$$

where the primed nonequilibrium parts must satisfy the inequality

$$(t_{ij}^E)' D'_{ij} - g'_i N_i - \frac{q'_i T_{,i}}{T} \geqslant 0. \tag{25.139}$$

The general forms of isotropic functions for t'_{ij}, g'_i and q'_i are difficult to postulate. Simple linear representations can, however, easily be obtained. Linear isotropic behavior upon D_{ij}, N_i and $T_{,i}$ and no dependence upon the director or its gradient is given by

$$\begin{aligned} &t'_{ij} = \mu D_{ij}, \quad g'_i = -\chi N_i, \quad q'_i = -\kappa T_{,i} \\ &\text{with} \quad \mu > 0, \quad \chi > 0, \quad \kappa > 0. \end{aligned} \tag{25.140}$$

However, this is too simple, as dependences upon the director or its gradient cannot be ignored. We shall give an account of constitutive quantities for ψ, t_{ij}^E, g_i, and q_i below.

Leslie also states the equations for isotropic static deformations. From (25.125), (25.137), we obtain

$$\begin{aligned} t_{ij} &= -p\delta_{ij} - \rho \frac{\partial \psi}{\partial n_{k,i}} n_{k,j}, \\ \pi_{ij} &= \beta_j n_i + \rho \frac{\partial \psi}{\partial n_{i,j}}, \\ g_i &= \gamma n_i - \beta_k n_{i,k} - \rho \frac{\partial \psi}{\partial n_i} \end{aligned} \tag{25.141}$$

and the heat and entropy fluxes vanish. Leslie [47] states that "apart from the terms involving β_i, these are the expressions obtained by Ericksen [24]. However, Ericksen seems to have overlooked the possibility of such an additional indeterminacy."

25.5 Explicit Constitutive Parameterizations

Before specific flow parameterizations can be analyzed for fluid mechanical aspects, the free energy and the nonequilibrium parts of the extra stress and extrinsic director force must be prescribed. A first rather elementary suggestion, given by (25.140), has been stated to be oversimplified, mainly because dependencies on n_i and $n_{i,j}$ have been ignored. In what follows we shall look at a model of an incompressible LC with directors of constant magnitude. For the parameterization of the free energy, we retain only terms of lowest degree of director gradients, i.e., quadratic terms $n_{i,k} n_{k,\ell}$, as already introduced by Frank [31] and further elaborated on by Ericksen [22] and Leslie [47].

25.5.1 Frank's Parameterization of the Free Energy

"The first paper in the 1933 Discussions [of the FARADAY Society] was one by OSEEN [58], offering a general structural theory of the classical LCs, i.e., the three types: smectic, nematic and cholesteric, recognized by FRIEDEL [32] in 1922. [In FRANK's paper] OSEEN's theory (with slight modification) is re-founded on a securer basis. As with OSEEN, this is a theory for the molecular uniaxial liquid crystals, that is to say those in which the long-range order governs the orientation of only one molecular axis" [31].

FRANK states that "in a thin film, say, of a nematic substance particular orientations are imposed at the surfaces, depending on the nature or prior treatment of the materials at these surfaces; if the imposed orientations are not parallel, some curved transition from one orientation to the other is required. Curvature may also be introduced when, say, the orientating effect of a magnetic field conflicts with orientations imposed by surface contacts. Something analogous to elasticity theory is required to define the equilibrium form of such curvatures, [however, essentially different from the elasticity theory of a solid …]. In a liquid, these are not determined by restoring forces but rather restoring torques which directly oppose the curvature." FRANK states, "we may refer to these as torque stresses, and assume an equivalent of HOOKE's law, making them proportional to the curvature strains […]. It is an equivalent procedure to assume that the free energy, in which the analogues of elastic moduli appear as coefficients." This is the procedure, which FRANK adopted.

The properties of LCs are primarily determined by the elastic response of their directors. One differentiates basically between three types of deformations of the director field as sketched in **Fig. 25.14**, each associated with its characteristic coefficient. Possible deformations are "splays", "bends", and "twists".

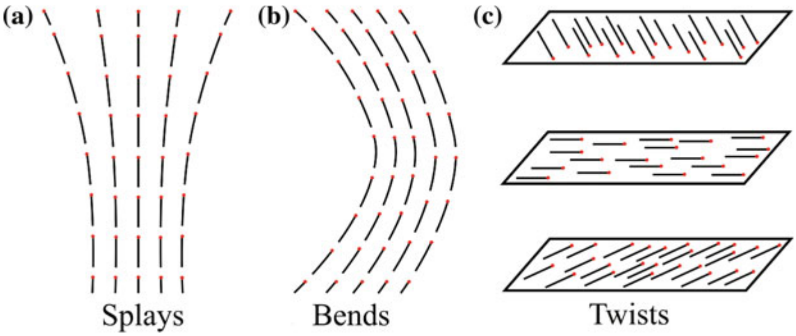

Fig. 25.14 Sketch illustrating deformations characterizing "splays", "bends", and "twists"

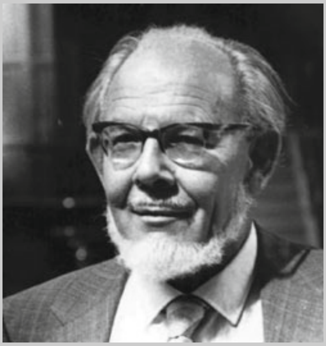

Fig. 25.15 (FREDERICK) CHARLES FRANK (March 6, 1911–April 12, 1998)

Sir (FREDERICK) CHARLES FRANK, known as Sir CHARLES FRANK, was a British theoretical physicist and best known for his work on crystal dislocations. He also made many additional contributions in solid-state physics, geophysics, and the theory of liquid crystals. One can illustrate the breadth of his scientific activities by his incisive papers on (i) asymmetry in nature in 1953 [30], in which he anticipated population dynamics studies, (ii) on liquid crystals in 1958 [31], and (iii) on island arcs in 1958 [31] and many others. He was born in Durban, South Africa, although his parents returned to England soon afterward. He was educated at Thetford Grammar School and Ipswich School and went on to study chemistry at Lincoln College, Oxford, gaining a doctorate at the university's Engineering Laboratory.

Prior to World War 2, FRANK worked as a Physicist in Berlin and as a Colloid Chemist in Cambridge. During World War II, he joined the Chemical Defense Experimental Station at Porton Down, Wiltshire, but in 1940 he was transferred to the Air Ministry's Assistant Directorate of Intelligence (Science) and spent the rest of the war with the Air Ministry. Due to his work, he was made Officer of the Most Excellent Order of the British Empire in 1946.

After the war, he moved to the University of Bristol Physics Department to do research in solid-state physics, but switched to research on crystal dislocation. His work was to demonstrate the role dislocations played in the growth of crystals. Apart from crystal defects, his wide-ranging research interests at Bristol included the mechanical properties of polymers, the theory of liquid crystals and the mechanics of the interior of the Earth. He was appointed Reader in 1951, Melville Wills Professor in 1954, Henry Overton Wills Professor, and Director of the H.H. Wills Physics Laboratory in 1969. He retired in 1976 but remained active in attending conferences, writing papers and corresponding with colleagues well into the 1990s. He edited the Farm Hall Transcripts from Operation Epsilon well into his eighties.

Frank was elected Fellow of the Royal Society in 1954, delivering the Bakerian Lecture in 1973. He was knighted in 1977. He was also awarded honorary degrees by seven universities. In 1967, he was awarded the A. A. Griffith Medal and Prize and in 1994 the Royal Society's Copley Medal, its highest honor, "in recognition of his fundamental contribution to the theory of crystal morphology."
FRANK married MAITA ASCHÉ (1918–2009) in 1940 from St. Petersburg. She was from Finnland but because of the turmoil of the war grew up in Czechoslovakia.
The Text is based on

- https://en.wikipedia.org/wiki/Frederick_Charles_Frank,
- "SIR CHARLES FRANK" National Academy of Engineering, *Memorial Tributes*, Vol. 17, The National academic Press, 2013 doi: 10.17226/18477.
- Obituaries in the *Guardian* (April 10, 1998), *Independent* (April 15, 1998), *Telegraph* April 24, 1998, *Times* (April 27, 1998)

See also [3, 52]

"OSEEN likewise proceeded by setting up an expression for the energy density, in terms of chosen measures of curvature. However, he based his argument on the postulate that the energy is expressible as a sum of energies between molecules taken in pairs. This is analogous to the way in which CAUCHY set up the theory of elasticity for solids, and in his case it is known that the theory predicted fewer independent elasticity constants than actually exist, and we may anticipate a similar consequence with OSEEN's theory" [31].

Frank's Model[19] Let $\boldsymbol{\mathcal{L}}$ be a unit vector, representing the direction of the preferred orientation in the neighborhood of any spatial point occupied by the LC. The basis of the ensuing analysis is [31].

We shall assume that the sign of $\boldsymbol{\mathcal{L}}$ is essential but will eventually be without physical significance and we suppose that its orientation changes slowly as one moves away from the point in question. Introducing Cartesian coordinates with origin at the point in question and its z-axis parallel to $\boldsymbol{\mathcal{L}}$ at the origin, the x- and y-axes are then within the plane perpendicular to the z-axis and are chosen such that (x, y, z) form a right-handed system.

Referred to these axes, the six components of the curvature at this point are (see **Fig. 25.16**)

$$\begin{aligned} &\text{“Splay”}: \quad s_1 = \frac{\partial \mathcal{L}_x}{\partial x}, \qquad s_2 = \frac{\partial \mathcal{L}_y}{\partial y}, \\ &\text{“Twist”}: \quad t_1 = -\frac{\partial \mathcal{L}_y}{\partial x}, \quad t_2 = \frac{\partial \mathcal{L}_x}{\partial y}, \\ &\text{“Bend”}: \quad b_1 = \frac{\partial \mathcal{L}_x}{\partial z}, \qquad b_2 = \frac{\partial \mathcal{L}_y}{\partial z}. \end{aligned} \tag{25.142}$$

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[19] For a biographical sketch of F.C. FRANK see **Fig. 25.15**.

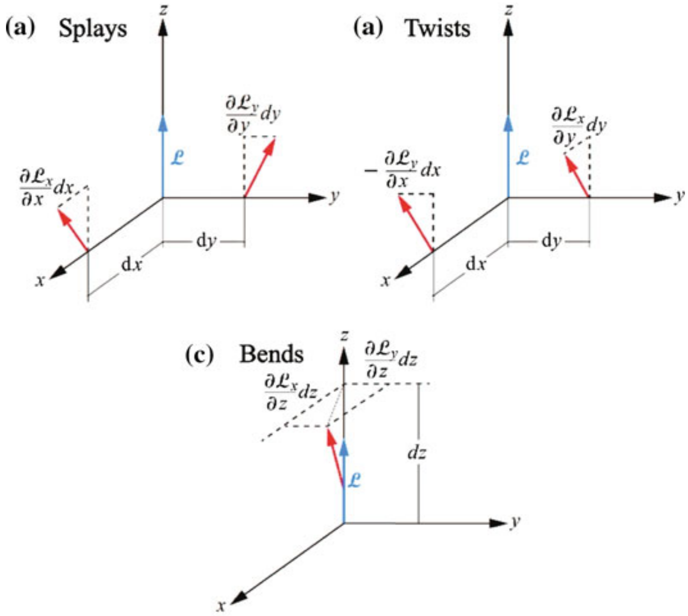

Fig. 25.16 Explaining pairs of the components of the slow changes of a vector $\boldsymbol{\mathcal{L}}$ with nearly constant magnitude. **a** *"Splays" describe a spreading in the* (xy)*-plane*. **b** *"twists" give an infinitesimal rotation round the* $\boldsymbol{\mathcal{L}}$*-axis*. **c** *"Bends" describe a bending in the* z*-direction*, after [31]

Frank assumes approximately a linear change of $\mathcal{L}_x$, $\mathcal{L}_y$, $\mathcal{L}_z$ according to

$$\begin{aligned} \mathcal{L}_x &= a_1 x + a_2 y + a_3 z + \mathcal{O}(\ell^2), \\ \mathcal{L}_y &= a_4 x + a_5 y + a_6 z + \mathcal{O}(\ell^2), \\ \mathcal{L}_z &= 1 + \mathcal{O}(\ell^2), \end{aligned} \tag{25.143}$$

where $\ell^2 = x^2 + y^2 + z^2$ and then obtains

$$\begin{aligned} s_1 &= a_1, \quad t_1 = -a_4, \quad b_1 = a_3, \\ s_2 &= a_5, \quad\ \ t_2 = a_2, \quad b_2 = a_6. \end{aligned} \tag{25.144}$$

He then postulates that the free energy density $\rho\psi$ is a quadratic function of the six differential coefficients, which measure the curvature[20]: In that theory, the six

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[20] It is at this point, where Frank's analogy with linear elasticity is visible.

deformation measures are the six independent components of the strain tensor, and the free energy is a quadratic function of these strain components:

$$\begin{aligned} \Psi &= \int_V \rho\psi \mathrm{d}V, \\ \rho\psi &= \sum_{i=1}^{6} k_i a_i + \tfrac{1}{2} \sum_{i,j=1}^{6} k_{ij} a_i a_j, \quad (k_{ij} = k_{ji}). \end{aligned} \tag{25.145}$$

When the local coordinate frame is arbitrarily rotated to a Cartesian system (x', y', z'), then the curvatures will change to a_i' $(i = 1, \ldots, 6)$; however, for hemotropic or isotropic behavior of the material it is postulated that $\rho\psi$ is the same function of the primed quantities a_i' $(i = 1, \ldots, 6)$,

$$\rho\psi = \sum_{i=1}^{6} k_i a_i' + \tfrac{1}{2} \sum_{i,j=1}^{6} k_{ij} a_i' a_j', \quad (k_{ij} = k_{ji}) \tag{25.146}$$

with the same value for $\rho\psi$ as in $(25.145)_2$. This requirement imposes restrictions on the moduli k_i, k_{ij}. It is shown in Appendix 25.A to this chapter that, for invariance of the free energy under arbitrary such rotations, k_i and k_{ij} are restricted to the forms

$$k_i = (k_1, k_2, 0, -k_2, k_1, 0)^T \tag{25.147}$$

and

$$k_{ij} = \begin{pmatrix} k_{11} & k_{12} & 0 & -k_{12} & (k_{11} - k_{22} - k_{24}) & 0 \\ k_{12} & k_{22} & 0 & k_{24} & k_{12} & 0 \\ 0 & 0 & k_{33} & 0 & 0 & 0 \\ -k_{12} & k_{24} & 0 & k_{22} & -k_{12} & 0 \\ (k_{11} - k_{22} - k_{24}) & k_{12} & 0 & -k_{12} & k_{11} & 0 \\ 0 & 0 & 0 & 0 & 0 & k_{33} \end{pmatrix}. \tag{25.148}$$

In reducing the vector k_i and the symmetric rank-2 tensor k_{ij} $(i, j = 1, \ldots, 6)$ to the forms (25.147) and (25.148) use was not yet made of our hypothesis that for most nematic LCs $\boldsymbol{\mathcal{L}}$ and $-\boldsymbol{\mathcal{L}}$ are equivalent. If the molecules are nonpolar with respect to the preferentially oriented axis, or if they are distributed with equal likelihood in both directions, the sign of $\boldsymbol{\mathcal{L}}$ is arbitrary. “It is a significant convention in our definition of curvature components that z is positive in the positive direction of $\boldsymbol{\mathcal{L}}$: and if z changes sign, one of x and y should change sign also to retain right-handed coordinates. Hence, a permissible transformation *in the absence of physical polarity* is $\boldsymbol{\mathcal{L}} = -\boldsymbol{\mathcal{L}}$, $x = x'$, $y = -y'$, $z = -z'$” [31]. Therefore,

$$\begin{aligned}
\frac{\partial \mathcal{L}'_{x'}}{\partial x'} &= -\frac{\partial \mathcal{L}_x}{\partial x} = -a_1 x - a_2 y - a_3 z + \mathcal{O}(\ell^2) \\
&= -a_1 x' + a_2 y' + a_3 z' + \mathcal{O}(\ell^2), \\
\frac{\partial \mathcal{L}'_{y'}}{\partial y'} &= \frac{\partial \mathcal{L}_y}{\partial y} = a_4 x + a_5 y + a_6 z + \mathcal{O}(\ell^2) \\
&= a_4 x' - a_5 y' - a_6 z' + \mathcal{O}(\ell^2).
\end{aligned} \tag{25.149}$$

Because in these two representations in primed coordinates the coefficients with indices 1, 5, and 6 have changed sign compared with (25.143), the invariance of (25.146) leads to further restrictions, namely

$$k_1 = 0, \quad k_5 = 0, \quad k_6 = 0, \tag{25.150}$$

as well as

$$k_{12} = k_{13} = k_{14} = k_{25} = k_{26} = k_{35} = k_{36} = k_{45} = k_{46} = 0. \tag{25.151}$$

So, k_1 and k_{12} vanish (beyond those coefficients which have already been shown to vanish), so that

$$\begin{aligned}
&k_i = (0, k_2, 0, -k_2, 0, 0)^T \\
&\begin{pmatrix}
k_{11} & 0 & 0 & 0 & (k_{11} - k_{22} - k_{24}) & 0 \\
0 & k_{22} & 0 & k_{24} & 0 & 0 \\
0 & 0 & k_{33} & 0 & 0 & 0 \\
0 & k_{24} & 0 & k_{22} & 0 & 0 \\
(k_{11} - k_{22} - k_{24}) & 0 & 0 & 0 & k_{11} & 0 \\
0 & 0 & 0 & 0 & 0 & k_{33}
\end{pmatrix}.
\end{aligned} \tag{25.152}$$

Thus, for nonpolar directors only 2 elements of k_i and only 10 elements of k_{ij} differ from zero, but of these nontrivial elements only one (for k_i) and 4 (for k_{ij}) must experimentally independently be determined.

There exist further possible restrictions for k_i and k_{ij}, which occur, if the molecules are enantiomorphic or enantiomorphically arranged.[21]

Most LCs are not enantiomorphic. In the absence of enantiomorphism of the directors, the value of $\rho\psi$ should be invariant under right- and left-handed changes of coordinates. Thus, we may choose

$$(x', y', z') = (x, -y, z)$$

for such an invariance and then have

---

[21] Such crystals or molecules have the same dimension and the same degree of symmetry, but can only be brought to congruence with their mirror picture. **Figure 25.17** illustrates enantiomorphic (or equivalently chiral) objects.

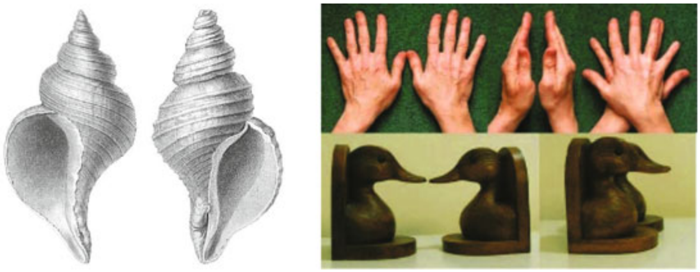

Fig. 25.17 Hands are enantiomorphic or chiral objects. Such objects often occur in Nature, see the shells of snails. © Institute of Chemical Biology, Van der Built University

$$\begin{aligned}\frac{\partial \mathcal{L}'_{x'}}{\partial x'} &= \frac{\partial \mathcal{L}_x}{\partial x} = a_1 x' - a_2 y' + a_3 z' + \mathcal{O}(\ell^2),\\ \frac{\partial \mathcal{L}'_{y'}}{\partial y'} &= -\frac{\partial \mathcal{L}_y}{\partial y} = -a_4 x' + a_5 y' - a_6 z' + \mathcal{O}(\ell^2).\end{aligned} \tag{25.153}$$

Comparing these expressions with (25.143), it is seen that the indices 2, 4, and 6 have changed signs and so, based on the procedure explained in Appendix 25.A, we have

$$\begin{aligned}&k_2 = 0,\\ &k_{12} = k_{14} = k_{16} = k_{23} = k_{25} = k_{26} = k_{34} = k_{36} = k_{45} = k_{56} = 0,\end{aligned}$$

in which only

$$k_2 = 0, \qquad k_{12} = 0 \tag{25.154}$$

go beyond the inferences stated in (25.151), (25.152). In conclusion, “while (25.150), (25.151) express the most general dependence of the free energy density on the curvature in molecularly uniaxial LCs, k_1 vanishes in the absence of an enantiomorphism, and k_{12} vanishes, unless both polarity and chirality occur together” [31]. It might be emphasized that for nonpolar LCs (the usual case for nematics) the vector k_i vanishes identically.

Given the representations (25.147), (25.148), the free energy (25.145) can be written down in terms of the a_i ($i = 1, \ldots, 6$) and then expressed in the quantities $s_1, s_2, t_1, t_2, b_1, b_2$ defined in (25.144). The explicit computation yields

$$\begin{aligned}\rho\psi = {} & \underline{k_1(s_1 + s_2)} + k_2(t_1 + t_2)\\ & + \tfrac{1}{2}k_{11}(s_1 + s_2)^2 + \tfrac{1}{2}k_{22}(t_1 + t_2)^2 + \tfrac{1}{2}k_{33}(b_1^2 + b_2^2)\\ & + k_{12}(s_1 + s_2)(t_1 + t_2) - \underline{(k_{22} + k_{24})(s_1 s_2 + t_1 t_2)}.\end{aligned} \tag{25.155}$$

This is FRANK's expression for the free energy and it differs from the corresponding expression, obtained by OSEEN [58] 25 years earlier, by the underlined terms, which are missing in [58]. The first, $k_1(s_1 + s_2)$ vanishes for nonpolar LCs ($k_1 = 0$); the second is more relevant, see FRANK [31].

FRANK next rescaled the expression (25.155) by selecting

$$\begin{aligned} s_0 &= -\frac{k_1}{k_{11}}, \qquad t_0 = -\frac{k_2}{k_{22}}, \\ \rho\tilde{\psi} &= \rho\psi + \tfrac{1}{2}k_{11}s_0^2 + \tfrac{1}{2}k_{22}t_0^2. \end{aligned} \tag{25.156}$$

This is tantamount to scaling ψ such that $\tilde{\psi}$ reaches the minimum value, $\tilde{\psi} = 0$, with the optimum degree of splay and twist. With $(25.156)_{1,2}$ one obtains from (25.155) that

$$\begin{aligned} \rho\tilde{\psi} = {} & \tfrac{1}{2}k_{11}(s_1 + s_2 - s_0)^2 + \tfrac{1}{2}k_{22}(t_1 + t_2 - t_0)^2 + \tfrac{1}{2}k_{33}(b_1^2 + b_2^2) \\ & + k_{12}(s_1 + s_2)(t_1 + t_2) - (k_{22} + k_{24})(s_1 s_2 + t_1 t_2). \end{aligned} \tag{25.157}$$

Note that for a nonpolar director $k_1 = 0$, (see (25.150)), so, also $s_0 = 0$ provided $k_{11} \neq 0$; similarly, for non-enantiomorphic conditions (vanishing chirality) one also has $k_2 = 0$, which implies $t_0 = 0$, provided $k_{22} \neq 0$, as well as $k_{12} = 0$, see (25.154). This is the case for most LCs.

Finally, it will be advantageous to write $\rho\tilde{\psi}$ in coordinate invariant form. To this end, note that with $\boldsymbol{\mathcal{L}} = (0, 0, 1)$ and $\partial\mathcal{L}_z/\partial z \approx 0$ we have

$$\begin{aligned} \nabla\boldsymbol{\mathcal{L}} \quad &= \left(\frac{\partial\mathcal{L}_x}{\partial x}, \frac{\partial\mathcal{L}_y}{\partial y}, \frac{\partial\mathcal{L}_z}{\partial z}\right), \\ \nabla \times \boldsymbol{\mathcal{L}} \quad &= \left(\frac{\partial\mathcal{L}_z}{\partial y} - \frac{\partial\mathcal{L}_y}{\partial z}, \frac{\partial\mathcal{L}_x}{\partial z} - \frac{\partial\mathcal{L}_z}{\partial y}, \frac{\partial\mathcal{L}_y}{\partial x} - \frac{\partial\mathcal{L}_x}{\partial y}\right), \\ \boldsymbol{\mathcal{L}} \cdot \nabla \quad &= (0, 0, 1) \cdot \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right) = \frac{\partial}{\partial z}, \\ (\boldsymbol{\mathcal{L}} \cdot \nabla)\,\boldsymbol{\mathcal{L}} &= \frac{\partial\boldsymbol{\mathcal{L}}}{\partial z} = \left(\frac{\mathcal{L}_x}{\partial z}, \frac{\mathcal{L}_y}{\partial z}, 0\right), \end{aligned}$$

from which we deduce

$$\begin{aligned} \nabla \cdot \boldsymbol{\mathcal{L}} &= \frac{\partial\mathcal{L}_x}{\partial x} + \frac{\partial\mathcal{L}_y}{\partial y} + 0 \overset{(25.142)}{=} (s_1 + s_2), \\ \boldsymbol{\mathcal{L}} \cdot \nabla \times \boldsymbol{\mathcal{L}} &= \frac{\partial\mathcal{L}_y}{\partial x} - \frac{\partial\mathcal{L}_x}{\partial y} \overset{(25.142)}{=} -(t_1 + t_2), \\ [(\boldsymbol{\mathcal{L}} \cdot \nabla)\,\boldsymbol{\mathcal{L}}]^2 &= \left(\frac{\partial\mathcal{L}_x}{\partial z}\right)^2 + \left(\frac{\partial\mathcal{L}_y}{\partial z}\right)^2 = b_1^2 + b_2^2, \\ \nabla\boldsymbol{\mathcal{L}} : \nabla\boldsymbol{\mathcal{L}} &= \left[\left(\frac{\partial\mathcal{L}_x}{\partial x}\right)^2 + \left(\frac{\partial\mathcal{L}_y}{\partial y}\right)^2 + \left(\frac{\partial\mathcal{L}_z}{\partial z}\right)^2\right] \end{aligned}$$

$$
\begin{aligned}
&+\left[\left(\frac{\partial \mathcal{L}_y}{\partial x}\right)^2+\left(\frac{\partial \mathcal{L}_y}{\partial y}\right)^2+\left(\frac{\partial \mathcal{L}_y}{\partial z}\right)^2\right]\\
&+\left[\left(\frac{\partial \mathcal{L}_z}{\partial x}\right)^2+\left(\frac{\partial \mathcal{L}_z}{\partial y}\right)^2+\left(\frac{\partial \mathcal{L}_z}{\partial z}\right)^2\right],
\end{aligned}
$$

$$
\begin{aligned}
&(\nabla\cdot\boldsymbol{\mathcal{L}})^2+(\nabla\times\boldsymbol{\mathcal{L}})^2-(\nabla\boldsymbol{\mathcal{L}}:\nabla\boldsymbol{\mathcal{L}})\\
&\quad=2\left\{\frac{\partial \mathcal{L}_x}{\partial x}\frac{\partial \mathcal{L}_y}{\partial y}+\frac{\partial \mathcal{L}_y}{\partial y}\frac{\partial \mathcal{L}_z}{\partial z}+\frac{\partial \mathcal{L}_z}{\partial z}\frac{\partial \mathcal{L}_x}{\partial x}\right.\\
&\qquad\left.-\frac{\partial \mathcal{L}_y}{\partial x}\frac{\partial \mathcal{L}_x}{\partial y}-\frac{\partial \mathcal{L}_z}{\partial y}\frac{\partial \mathcal{L}_y}{\partial z}-\frac{\partial \mathcal{L}_x}{\partial z}\frac{\partial \mathcal{L}_z}{\partial x}\right\}\\
&\quad\approx s_1s_2+t_1t_2.
\end{aligned}
$$

Employing these operators in the representation (25.157) yields

$$
\begin{aligned}
\rho\tilde{\psi}=&\tfrac{1}{2}k_{11}\left(\nabla\cdot\boldsymbol{\mathcal{L}}-s_0\right)^2+\tfrac{1}{2}k_{22}\left(\boldsymbol{\mathcal{L}}\cdot\nabla\times\boldsymbol{\mathcal{L}}+t_0\right)^2\\
&+\tfrac{1}{2}k_{33}\left[(\boldsymbol{\mathcal{L}}\cdot\nabla)\boldsymbol{\mathcal{L}}\right]^2-k_{12}\left(\nabla\cdot\boldsymbol{\mathcal{L}}\right)\left(\boldsymbol{\mathcal{L}}\cdot\nabla\times\boldsymbol{\mathcal{L}}\right)\\
&-\tfrac{1}{2}\left(k_{22}+k_{24}\right)\left\{(\nabla\cdot\boldsymbol{\mathcal{L}})^2+(\nabla\times\boldsymbol{\mathcal{L}})^2-\nabla\boldsymbol{\mathcal{L}}:\nabla\boldsymbol{\mathcal{L}}\right\},
\end{aligned}
\tag{25.158}
$$

applicable in every arbitrary system of coordinates.

For nonpolar and non-enantiomorphic nematics, $k_i=0$ $(i=1,\dots,6)$ and $k_{12}=0$, as shown in (25.150) and (25.154), as well as $s_0=t_0=0$ as defined in (25.154). In this case, we have

$$
\begin{aligned}
\rho\tilde{\psi}=&\tfrac{1}{2}k_{22}\underbrace{(\boldsymbol{\mathcal{L}}\cdot\nabla\times\boldsymbol{\mathcal{L}})^2}_{=n_{i,j}n_{j,i}}+\tfrac{1}{2}\left(k_{11}-k_{22}-k_{44}\right)\underbrace{(\nabla\cdot\boldsymbol{\mathcal{L}})^2}_{n_{i,i}n_{j,j}}\\
&+\tfrac{1}{2}(k_{33}-k_{22})\underbrace{[(\boldsymbol{\mathcal{L}}\cdot\nabla)\boldsymbol{\mathcal{L}}]^2}_{=n_in_jn_{k,i}n_{k,j}}\\
&-\tfrac{1}{2}(k_{22}+k_{24})\Big(\underbrace{(\boldsymbol{\mathcal{L}}\cdot\nabla\times\boldsymbol{\mathcal{L}})^2+(\nabla\times\boldsymbol{\mathcal{L}})^2-\nabla\boldsymbol{\mathcal{L}}:\nabla\boldsymbol{\mathcal{L}}}_{\approx 0}\Big)\\
&+\tfrac{1}{2}(k_{24})\underbrace{(\boldsymbol{\mathcal{L}}\cdot\nabla\times\boldsymbol{\mathcal{L}})^2}_{=n_{i,j}n_{j,i}}.
\end{aligned}
\tag{25.159}
$$

In this expression, we have changed notation in the underbraced terms from symbolic to Cartesian tensor notation. Moreover, we have also replaced $\boldsymbol{\mathcal{L}}$ by the vector n_i to obtain agreement with the earlier notation in this chapter. In this new notation, the free energy takes the form

$$
\begin{aligned}
2\rho\tilde{\psi}=&k_{22}n_{i,j}n_{i,j}+(k_{11}-k_{22}-k_{24})n_{i,i}n_{j,j}\\
&+(k_{33}-k_{22})n_in_jn_{k,i}n_{k,j}+k_{24}n_{i,j}n_{j,i}.
\end{aligned}
\tag{25.160}
$$

This is LESLIE's expression stated in [47].

25.5.2 *Parameterization of the Nonequilibrium Stress, Intrinsic Director Body Force, and Heat Flux Vector*

For the nonequilibrium parts of $(t_{ij}^E)'$, g_i' and $q_i = q_i'$, we assume linear dependences upon N_i, D_{ij} and $T_{,i}$, and omit terms involving director gradients. This can easily be shown to lead to the expressions

$$\begin{aligned}(t_{ij}^E)' &= \mu_1(n_k n_p D_{kp} n_i n_j) + \mu_2 n_j N_i + \mu_3 n_i N_j \\ &\quad + \mu_4 D_{ij} + \mu_5 n_j n_k D_{ki} + \mu_6 n_i n_k D_{kj}, \qquad (25.161)\\ g_i' &= \lambda_1 N_i + \lambda_2 n_j D_{ji} + \underbrace{\lambda_3 n_i D_{j,j}}_{=0} \qquad (25.162)\\ q_i &= q_i' = -\kappa_1 T_{,i} - \kappa_2 n_i T_{,j} n_j. \qquad (25.163)\end{aligned}$$

Here, the coefficients μ_i, λ_i, and κ_i are at most functions of the temperature or are treated as constants. In order to satisfy the identity (25.79) for the nonequilibrium stresses (t_{ij}^E) [the terms involving the free energy satisfy this equation identically], a straightforward computation yields

$$\lambda_1 = \mu_2 - \mu_3, \qquad \lambda_2 = \mu_6 - \mu_5. \qquad (25.164)$$

The inequality (25.139) imposes further restrictions upon the coefficients arising in the parameterizations (25.161)–(25.163). Substituting these into (25.139) leads to the polynomial inequality

$$\begin{aligned}&\mu_1(n_i n_j D_{ij})^2 + (\mu_2 + \mu_3 + \lambda_2) n_i N_j D_{ij} + \mu_4 D_{ik} D_{ki} \\ &+ (\mu_5 + \mu_6) n_i n_k D_{kj} D_{ij} + \lambda_1 N_i N_i + \frac{\kappa_2}{T}(n_i T_{,i})^2 + \frac{\kappa_1}{T}(T_{,i} T_{,i}) \geqslant 0. \qquad (25.165)\end{aligned}$$

LESLIE [46] determined the conditions on the coefficients of the quadratic form (25.165) to be positive definite but mentioned no details. These conditions are[22]

$$\begin{aligned}&\mu_4 \geqslant 0, \quad 2\mu_1 + 3\mu_4 + 2\mu_5 + 2\mu_6 \geqslant 0, \quad \mu_3 - \mu_2 \geqslant 0, \\ &2\mu_4 + \mu_5 + \mu_6 \geqslant 0, \quad 4\lambda_1(2\mu_4 + \mu_5 + \mu_6) \geqslant (\mu_2 + \mu_3 + \lambda_2)^2, \qquad (25.166)\\ &\kappa_1 \geqslant 0, \quad \kappa_1 + \kappa_2 \geqslant 0.\end{aligned}$$

---

[22] One way of demonstrating this is to introduce the 15-dimensional vector

$$\mathbb{X} = (n_i, N_i, D_{ij}, T_{,i}), \qquad i = 1, 2, 3, \ j \geqslant i$$

and to write (25.165) as the quadratic form $\mathbb{X} \cdot \mathbb{A}\mathbb{X}$, where $\mathbb{A}$ is a 15×15-matrix. To this matrix, the ROUTH–HURWITZ criterion is applied. This yields six conditions. For a simpler model of anisotropic fluids, ERICKSEN [25] has given a simple procedure to obtain inequalities analogous to (25.166). We shall also employ a different procedure below.

Of the above inequalities $\mu_4 \geqslant 0$ and $\kappa_1 \geqslant 0$ are well-known results of the simple viscous heat conducting fluids, stating that the classical viscosity and the classical coefficient of heat conduction must be nonnegative.

25.5.3 *Parodi Relation for a Nematic Liquid Crystal*

The dissipative parts of the constitutive relations for $(t^E_{ij})'$, g'_i and q_i given in (25.161)–(25.163), contain a total of eight independent parameters $\mu_1, \ldots, \mu_6, \kappa_1, \kappa_2$, which are at most functions of the absolute temperature. PARODI [59] showed that the ONSAGER [57][23] reciprocal relations lead to the additional dependence

$$\mu_2 + \mu_3 = \mu_6 - \mu_5. \tag{25.167}$$

It follows that, if one adopts the ONSAGER relations, the dissipative stress parameterization (25.161) has "only" seven (five if κ_1 and κ_2 are not counted) independent parameters.

In order to apply the ONSAGER reciprocal relations, let us start with the entropy production expressed as

$$\Pi := (t^E_{ij})'_{\text{sym}} D_{ij} - g'_i N_i - \frac{q_i T_{,i}}{T}, \qquad (\geqslant 0). \tag{25.168}$$

Here, the contribution of $(t^E_{ij})'_{\text{skw}}$ in the first term on the right-hand side vanishes.[24]

Note that

$$\boldsymbol{N} = (\boldsymbol{\Omega} - \boldsymbol{\omega}) \times \boldsymbol{n} = \boldsymbol{n} \cdot \left(\bar{\bar{\boldsymbol{\Omega}}} - \bar{\bar{\boldsymbol{\omega}}}\right) = -\left(\bar{\bar{\boldsymbol{\Omega}}} - \bar{\bar{\boldsymbol{\omega}}}\right) \cdot \boldsymbol{n} \tag{25.169}$$

is the angular velocity of the director relative to the fluid (vorticity). From this, we also obtain

$$\boldsymbol{n} \otimes \boldsymbol{N} + \boldsymbol{N} \otimes \boldsymbol{n} = (\boldsymbol{n} \otimes \boldsymbol{n}) \cdot \left(\bar{\bar{\boldsymbol{\Omega}}} - \bar{\bar{\boldsymbol{\omega}}}\right) - \left(\bar{\bar{\boldsymbol{\Omega}}} - \bar{\bar{\boldsymbol{\omega}}}\right) \cdot (\boldsymbol{n} \otimes \boldsymbol{n}), \tag{25.170}$$

to be used later on. Moreover, in view of (25.162), the axial vector

$$\boldsymbol{\mathfrak{G}} = \boldsymbol{n} \times (\lambda_1 \boldsymbol{N} + \lambda_2 \boldsymbol{D} \cdot \boldsymbol{n}) \tag{25.171}$$

is the torque exerted by the director on the fluid. Associated with $\boldsymbol{\mathfrak{G}}$ is the skew-symmetric rank-2 tensor

---

[23] For an exposition on these, see DE GROOT and MAZUR [14].

[24] In the ensuing analysis, the dual tensor to the axial vector $\boldsymbol{A}$ will be denoted by $\bar{\bar{\boldsymbol{A}}}$.

$$\bar{\bar{\boldsymbol{\mathfrak{G}}}} = \frac{\lambda_1}{2}\left(\boldsymbol{n} \otimes \boldsymbol{N} - \boldsymbol{N} \otimes \boldsymbol{n}\right) + \frac{\lambda_2}{2}\left(\boldsymbol{n} \otimes \boldsymbol{n} \cdot \boldsymbol{D} - \boldsymbol{D} \cdot \boldsymbol{n} \otimes \boldsymbol{n}\right). \tag{25.172}$$

Employing Eq. (25.161) for $(\boldsymbol{t}^E)'$ and (25.171) for $\boldsymbol{\mathfrak{G}}$, it can be demonstrated that the antisymmetric part of $(\boldsymbol{t}^E)'$ is given by $-\bar{\bar{\boldsymbol{\mathfrak{G}}}}$ and that

$$(\bar{\bar{\boldsymbol{\mathfrak{G}}}})_{ij} = -(\bar{\bar{\boldsymbol{\mathfrak{G}}}})_{ji}. \tag{25.173}$$

With the expression (25.161) the symmetric part of $(\boldsymbol{t}^E)'$, $(\boldsymbol{t}^E)'_{\text{sym}}$, takes the form

$$\begin{aligned}
(t^E_{ij})'_{\text{sym}} &= \mu_1 (n_k n_p D_{kp} n_i n_j) \\
&\quad + \frac{\mu_2 + \mu_3}{2}\left(n_i n_k \left(\bar{\bar{\boldsymbol{\Omega}}} - \bar{\bar{\boldsymbol{\omega}}}\right)_{kj} - \left(\bar{\bar{\boldsymbol{\Omega}}} - \bar{\bar{\boldsymbol{\omega}}}\right)_{jk} n_k n_i\right) \\
&\quad + \mu_4 D_{ij} + \frac{\mu_5 + \mu_6}{2}\left(n_i n_k D_{kj} + n_j n_k D_{ki}\right).
\end{aligned} \tag{25.174}$$

Analogously, with (25.170) and (25.172)) we have

$$\begin{aligned}
-g'_i N_i &= \frac{\lambda_1}{2}\left(n_i n_k \left(\bar{\bar{\boldsymbol{\Omega}}} - \bar{\bar{\boldsymbol{\omega}}}\right)_{kj} + \left(\bar{\bar{\boldsymbol{\Omega}}} - \bar{\bar{\boldsymbol{\omega}}}\right)_{ik} n_j n_k\right) \\
&\quad + \frac{\lambda_2}{2}\left(n_i n_k D_{kj} + D_{ki} n_j n_k\right)
\end{aligned} \tag{25.175}$$

and

$$-\frac{q_i}{T} = \frac{\kappa_1}{T} T_{,i} + \frac{\kappa_2}{T} n_i n_j T_{,j}. \tag{25.176}$$

With these notations, inequality (25.168) can symbolically be written as[25]

$$(\boldsymbol{t}^E)'_{\text{sym}} : \boldsymbol{D} + \bar{\bar{\boldsymbol{\mathfrak{G}}}} : \left(\bar{\bar{\boldsymbol{\Omega}}} - \bar{\bar{\boldsymbol{\omega}}}\right) - \boldsymbol{q} \cdot \frac{\text{grad}\, T}{T} \geqslant 0. \tag{25.177}$$

Here, the colored tensor and vector quantities are in ONSAGERism [14, 57] called thermodynamic fluxes, while $\boldsymbol{D}$, $\left(\bar{\bar{\boldsymbol{\Omega}}} - \bar{\bar{\boldsymbol{\omega}}}\right)$ and $(\text{grad}\, T)/T$ are the thermodynamic forces. Moreover, (:) and $(\cdot)$ are linear operators connecting the forces with the fluxes. In ONSAGERism, these fluxes $\bar{\bar{J}}^i$ and forces $\bar{\bar{X}}^i$ are assumed to be linearly connected. The superscripts enumerate the number of these objects (three in (25.176)). So, following PARODI [59] we may set

---

[25] Note that in (25.177) the fluxes $(\bar{\bar{\boldsymbol{\Omega}}} - \bar{\bar{\omega}})$ are used not $(\boldsymbol{\Omega} - \boldsymbol{\omega})$. However, $\boldsymbol{D}$ and grad T/T do not have dual counterparts. So, it is not clear whether we should write J^i_{pq} not $\bar{\bar{J}}^i_{pq}$. Nevertheless, it should be obvious what is meant by (25.178).

$$J^i_{pq} = \sum_{rsij} L^{ij}_{pq.rs} X^j_{rs}, \tag{25.178}$$

in which the operators $L^{ij}_{pq.rs}$ are taken as independent of the forces X^j_{rs}. The ONSAGER reciprocal relations state now that

$$L^{ij}_{pq.rs} = L^{ji}_{pq.rs}. \tag{25.179}$$

The matrices $\boldsymbol{L}^{12}$ and $\boldsymbol{L}^{21}$ can be identified from (25.174) and (25.175) as

$$\begin{aligned} L^{12}_{pq.rs} &= \frac{\mu_2 + \mu_3}{2} \left(n_p n_r \delta_{qs} - \delta_{pr} n_q n_s\right) \\ L^{21}_{pq.rs} &= \frac{\lambda_2}{2} \left(n_p n_r \delta_{qs} - \delta_{pr} n_q n_s\right). \end{aligned} \tag{25.180}$$

The symmetry statement (25.179) now implies that

$$\mu_2 + \mu_3 = \lambda_2 \overset{(25.167)}{=} \mu_6 - \mu_5. \tag{25.181}$$

There are now five independent viscosity coefficients μ_1, μ_4, λ_1, λ_2 and

$$\beta = \mu_5 + \mu_6. \tag{25.182}$$

The symmetric part of the stress tensor is

$$\begin{aligned} (t^E_{ij})'_{\text{sym}} &= \mu_1 (n_k D_{kp} n_p) n_i n_j + \mu_4 D_{ij} \\ &\quad + \frac{\beta}{2}(n_i n_k D_{kj} + D_{ik} n_k n_j) + \frac{\lambda_2}{2}(n_i N_j + N_i n_j), \end{aligned} \tag{25.183}$$

and the antisymmetric part (25.172) can be expressed as displayed in (25.172). With these results, the full dissipative stress takes the form

$$\begin{aligned} (t^E_{ij})' &= \mu_1 (n_k D_{kp} n_p) n_i n_j + \frac{\lambda_2 - \lambda_1}{2} \left(n_i N_j\right) + \frac{\lambda_2 + \lambda_1}{2} \left(N_j n_i\right) \\ &\quad + \mu_4 D_{ij} + \frac{\beta - \lambda_2}{2} n_i n_k D_{kj} + \frac{\beta + \lambda_2}{2} D_{ik} n_k n_j, \end{aligned} \tag{25.184}$$

in which μ_1, μ_4, λ_1, λ_2, and β now serve as the five independent viscosity parameters.

Finally, the entropy production (25.165) may be written as

$$\begin{aligned} \Pi &= \mu_4 D_{ik} D_{ik} + \beta (n_i D_{ik})(n_j D_{jk}) + \mu_1 (n_i D_{ik} n_k)(n_j D_{j\ell} n_\ell) \\ &\quad + 2\lambda_2 n_i D_{ik} N_k + \lambda_1 N_i N_i + \frac{\kappa_1}{T}(T_{,i} n_i)(T_{,j} n_j) \\ &\quad + \frac{\kappa_2}{T} T_{,i} T_{,i} \geqslant 0. \end{aligned} \tag{25.185}$$

Parodi [59] takes $\boldsymbol{n}$ in the z-axis for which choice this inequality takes the form[26]

$$
\begin{aligned}
\Pi &= \mu_4 D_{\gamma\delta} D_{\delta\gamma} + \mu_4 D_{z\gamma} D_{\gamma z} + \mu_4 D_{zz}^2 + \beta D_{z\gamma} D_{z\gamma} \\
&\quad + \beta D_{zz}^2 + \mu_1 D_{zz}^2 + 2\lambda_2 (D_{z\gamma} N_\gamma) \\
&\quad + \lambda_1 N_\gamma N_\gamma + \frac{\kappa_1}{T} T_{,\gamma} T_{,\gamma} + \frac{\kappa_1}{T} (T_{,z})^2 + \frac{\kappa_2}{T} (T_{,z})^2 \\
&= \mu_4 D_{\gamma\delta} D_{\gamma\delta} + \left\{ \underline{(2\mu_4 + \beta) D_{z\gamma} D_{z\gamma} + 2\lambda_2 D_{z\gamma} N_\gamma + \lambda_1 N_\gamma N_\gamma} \right\} \\
&\quad + (\mu_1 + \mu_4 + \beta) D_{zz}^2 + \frac{\kappa_1}{T} T_{,\gamma} T_{,\gamma} + \frac{\kappa_1 + \kappa_2}{T} (T_{,z})^2 \geqslant 0. \qquad (25.186)
\end{aligned}
$$

In this inequality, all terms appear as pure quadratics except the underlined term. However, this term must also be a positive quadratic form if Π should be strictly nonnegative. It is indeed a pure quadratic, written as $(\mathbb{A} D_{z\gamma} + \mathbb{B} N_\gamma)^2$ with $\mathbb{A}^2 = 2\mu_4 + \beta$, $\mathbb{B}^2 = \lambda_1$ if

$$2\mathbb{A}\mathbb{B} = 2\sqrt{2\mu_4 + \beta}\sqrt{\lambda_1}.$$

Therefore, to make the underlined term in (25.186) nonnegative, $2\mathbb{A}\mathbb{B}$ must be larger than $2\lambda_2$ or

$$\lambda_1 (2\mu_4 + \beta) - \lambda_2^2 \geqslant 0. \qquad (25.187)$$

With this restriction, the underlined term in (25.186) is positive. It follows that all terms on the right-hand side of (25.186) are positive if

$$
\begin{aligned}
&\mu_4 > 0, \quad \lambda_1 > 0, \quad 2\mu_4 + \beta > 0 \quad \mu_1 + \mu_4 + \beta > 0, \\
&\kappa_1 > 0, \quad \kappa_1 + \kappa_2 > 0, \quad \lambda_1 (2\mu_4 + \beta) - \lambda_2^2 > 0.
\end{aligned} \qquad (25.188)
$$

These restrictions of the coefficients of the dissipative stress, intrinsic force, and heat flux vector defined in (25.161)–(25.163) replace the constraint conditions (25.166), if the Onsager relations are adopted in the Ericksen–Leslie (EL) model for nematic LCs. The popular acronym for this model is ELP model.

Let us close this analysis by a few remarks about the incorporation of the Parodi relation into the dissipation inequality. According to the Ericksen–Leslie theory, the six viscosity coefficients satisfy the inequalities (25.166) [with $\lambda_{1,2}$ given by (25.164)]. Moreover, the Parodi relation (25.181) contains these by a further relation and, thus, reduces the number of viscosities from six to five. Currie [9] reports that the Parodi relation has been adopted by the Orsay Liquid Crystal Group [20] when analyzing their experiments on wave propagation in nematic LCs. Thus, the values for the viscosity coefficients derived from these experiments depend on the

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[26] Greek indices have values 1 and 2 and double occurrence of these indices indicates summation over 1 and 2, and $(\cdot)_z$ means that this index is the direction of $\boldsymbol{n}$. According to the definition of $\boldsymbol{N}$ and assuming $|\boldsymbol{n}|$ to be constant then implies $N_z = 0$.

assumption that (25.164) is valid. On the other hand, Truesdell [73] has severely criticized the Onsager relations, but, in his own words, suggests that "for particular materials, counterparts of Onsager relations can be found and given a specific meaning, …and that meaning will express on the phenomenological scale a *special symmetry or stability*" [9]. Currie then reports that his linear stability analysis of in-plane wave motion has shown that the *uniformly oriented state is unstable unless the* Parodi *relation holds* and

$$\mu_2 \neq \mu_3 \quad \text{plus} \quad \{\mu_2 < 0 < \mu_3 \;\; \text{or} \;\; \mu_2 - \mu_3 < \mu_5 - \mu_6 < \mu_3 < \mu_2\}\,. \tag{25.189}$$

A thorough mathematical analysis of the general Ericksen–Leslie–Parodi system focussing on well-posedness and stability is given by Wu et al. [79]. They state "that the Parodi relation can be viewed as a sufficient condition for the non-linear stability of the Ericksen–Leslie system …. [However], it is still an open problem whether a similar result holds for the original Ericksen–Leslie system." Regarding linear stability, they found that—subject to a number of side conditions regarding the viscosities μ_i $(i = 1, 2, \ldots, 6)$, not satisfying the Parodi relation—the EL system admits unstable plane wave solutions.

25.6 Solutions for Simple Flow Problems

The purpose of this section is to investigate simple solutions for flows of an incompressible liquid with a director of constant magnitude. Regarding the theoretical basis, we rely on the developments and resulting equations obtained in the previous sections and, thus, rely on Frank's expression of the free energy. Moreover, for the nonequilibrium parts of the extra stress and extra intrinsic body force, we assume a linear dependence on N_i, D_{ij} and $T_{,i}$ and omit terms involving director gradients. In a first attempt of finding solutions, we assume that thermodynamic effects are unimportant. So, all phenomenological parameters, μ_i and λ_i, etc., will be assumed to be constants. The energy equation will therefore play no active role in the analysis and will henceforth be omitted. As dynamic equations we employ [see (25.38)–(25.39)]

$$\begin{aligned} v_{i,i} &= 0, \\ \rho \dot{v}_i &= \rho F_i + t_{ij,j}, \\ \rho \dot{n}_i &= \rho_1 G_i + g_i + \pi_{ij,j}, \end{aligned} \tag{25.190}$$

in which, from equations (25.141), (25.160), (25.161), (25.162),

$$\begin{aligned} t_{ij} &= -p\delta_{ij} - \rho \frac{\partial \psi}{\partial n_{k,i}} n_{k,j} + (t^E_{ij})', \\ \pi_{ij} &= = \beta_j n_i + \rho \frac{\partial \psi}{\partial n_{i,j}}, \end{aligned} \tag{25.191}$$

$$g_i = \gamma n_i - \beta_j n_{i,j} - \rho \frac{\partial \psi}{\partial n_i} + (g_i^E)'$$

with

$$\begin{aligned} 2\rho\psi &= k_{22} n_{i,j} n_{i,j} + (k_{11} - k_{22} - k_{24}) n_{i,i} n_{j,j} \\ &\quad + (k_{33} - k_{22}) n_i n_j n_{k,i} n_{k,j} + k_{24} n_{i,j} n_{j,i}, \\ (t_{ij}^E)' &= \mu_1 n_k n_p D_{kp} n_i n_j + \mu_2 n_j N_i + \mu_3 n_i N_j + \mu_4 D_{ij} \\ &\quad + \mu_5 n_j n_k D_{ki} + \mu_6 n_i n_k D_{kj}, \\ (g_i^E)' &= \lambda_1 N_i + \lambda_2 n_j D_{ij}, \end{aligned} \tag{25.192}$$

in which β, λ_1, and λ_2 satisfy the relations[27]

$$\beta = \mu_3 + \mu_6, \quad \lambda_1 = \mu_2 - \mu_3, \quad \lambda_2 = \mu_5 - \mu_6. \tag{25.193}$$

In the ensuing calculations, we shall also explicitly use (25.166)$_3$ which, according to (25.164)$_1$, implies

$$\lambda_1 \leqslant 0. \tag{25.194}$$

Furthermore, it will also be necessary to require

$$\|\lambda_1\| \leqslant \|\lambda_2\| \neq 0. \tag{25.195}$$

Equation (25.190), with the substitutions of the constitutive relations (25.191)–(25.193), become seven equations for the seven unknowns: velocity v_i (3), pressure p (1), unit vector n_i (2), and director tension γ (1).

25.6.1 Shear Flows

Leslie [47] considers situations, for which the body forces are conservative and the external director forces are absent ($G_i = 0$). Thus,

$$\rho F_i = -\chi_{,i}, \tag{25.196}$$

where χ is a scalar potential. We also restrict motions to in-plane deformations for both the liquid and the director. For steady shear flows, we then may write

$$\begin{aligned} v_x &= u(y), & v_y &= v_z = 0, \\ n_x &= \cos(\theta(y)), & n_y &= \sin(\theta(y)), \quad n_z = 0, \end{aligned} \tag{25.197}$$

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[27] This restriction for β holds if the Parodi relation applies.

in which θ is the slope angle between the x-axis and the director axis. The mass balance equation $(25.190)_1$ is identically satisfied with $(25.197)_{1,2}$; the remaining relations lead to the equations

$$\frac{\partial t_{xy}}{\partial y} - \frac{\partial (p+\chi)}{\partial x} = 0, \quad \frac{\partial ((t^E_{yy})' - p - \chi)}{\partial y} = 0, \quad \frac{\partial (p+\chi)}{\partial z} = 0, \tag{25.198}$$

$$\frac{\partial \pi_{xy}}{\partial y} + g_x = 0, \quad \frac{\partial \pi_{yy}}{\partial y} + g_y = 0. \tag{25.199}$$

It can easily be verified that Eq. (25.198) are solved by

$$t_{xy} = ay + c, \quad p + \chi = p_0 + ax + (t^E_{yy})', \tag{25.200}$$

in which a, c, and p_0 are constants. This solution is readily constructed by recognizing that in simple shearing $\partial t_{xy}/\partial y$ is a constant. Evaluating $(t^E_{xy})'$ with the aid of $(25.192)_2$ yields

$$\begin{aligned}(t^E_{xy})' = {} & 2\mu_1 n_x^2 n_y^2 \tfrac{1}{2}\frac{\mathrm{d}u}{\mathrm{d}y} + \mu_2 n_y N_x + \mu_3 n_x N_y + \mu_4 \tfrac{1}{2}\frac{\mathrm{d}u}{\mathrm{d}y} \\ & + \mu_5 n_y^2 \tfrac{1}{2}\frac{\mathrm{d}u}{\mathrm{d}y} + \mu_6 n_x^2 \tfrac{1}{2}\frac{\mathrm{d}u}{\mathrm{d}y}.\end{aligned} \tag{25.201}$$

In this expression, we employ

$$(N_i)_{\text{steady}} \overset{(25.60)}{=} -\omega_{ij} n_j \overset{(25.57)}{=} -\tfrac{1}{2}(v_{i,j} - v_{j,i}) n_j$$

or

$$(N_x)_{\text{steady}} = -\omega_{xy} n_y = -\tfrac{1}{2} n_y \frac{\mathrm{d}u}{\mathrm{d}y}, \quad (N_y)_{\text{steady}} = -\omega_{yx} n_x = \tfrac{1}{2} n_x \frac{\mathrm{d}u}{\mathrm{d}y}, \tag{25.202}$$

so that with $n_x = \cos\theta$, $n_y = \sin\theta$, (25.201) assumes the form

$$\begin{aligned}(t^E_{xy})' &= g(\theta)\frac{\mathrm{d}u}{\mathrm{d}y} = ay + c, \\ 2g(\theta) &= 2\mu_1 \sin^2\theta \cos^2\theta + (\mu_5 - \mu_2)\sin^2\theta + (\mu_6 + \mu_3)\cos^2\theta + \mu_4.\end{aligned} \tag{25.203}$$

Equation (25.199) can be treated in an analogous fashion and what obtains reads[28]

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[28] This equation is stated in [47] with no indication how it was obtained in detail. We tried to reproduce the result for several days, but gave up in vainness.

$$2f(\theta)\frac{\mathrm{d}^2\theta}{\mathrm{d}y^2}+\frac{\mathrm{d}f(\theta)}{\mathrm{d}\theta}\left(\frac{\mathrm{d}\theta}{\mathrm{d}y}\right)^2+\frac{\mathrm{d}u}{\mathrm{d}y}\left(\lambda_1+\lambda_2\cos 2\theta\right)=0, \tag{25.204}$$
$$f(\theta)=k_{11}\cos^2\theta+k_{33}\sin^2\theta.$$

It follows from ERICKSEN's analysis (see [25], his inequalities (18)) that $f(\theta)$ is positive. Moreover, for shear flows in the (x, y)-plane as given in (25.197), we have

$$(t^E_{ij})'D_{ij}=(t^E_{xy})'D_{xy}=\frac{1}{2}g(\theta)\left(\frac{\mathrm{d}u}{\mathrm{d}y}\right)^2, \tag{25.205}$$

owing to (25.203) and $D_{xy}=D_{yx}=\frac{1}{2}\frac{\mathrm{d}u}{\mathrm{d}y}$. Similarly,

$$\begin{aligned}(g^E_i)'N_i &= g'_xN_x+g'_yN_y\\ &\overset{(25.202)}{=}\frac{1}{2}\left(-g'_xn_y\frac{\mathrm{d}u}{\mathrm{d}y}+g'_yn_x\frac{\mathrm{d}u}{\mathrm{d}y}\right)\\ &\overset{(25.192)}{=}\frac{1}{2}\left\{\left(\lambda_1n_y^2\left(\frac{\mathrm{d}u}{\mathrm{d}y}\right)^2+\frac{1}{2}\lambda_2n_x^2\left(\frac{\mathrm{d}u}{\mathrm{d}y}\right)^2\right)\right.\\ &\qquad\left.-\left(\lambda_1n_y^2\left(\frac{\mathrm{d}u}{\mathrm{d}y}\right)^2+\frac{1}{2}\lambda_2n_x^2\left(\frac{\mathrm{d}u}{\mathrm{d}y}\right)^2\right)\right\}\\ &\overset{!}{=}0,\end{aligned} \tag{25.206}$$

and owing to isothermicity of the processes,

$$\frac{q_iT_{,i}}{T}\equiv 0. \tag{25.207}$$

Substituting the last three expressions into the residual entropy inequality (25.168) yields

$$g(\theta)\left(\frac{\mathrm{d}u}{\mathrm{d}y}\right)^2\geqslant 0, \tag{25.208}$$

requiring that $g(\theta)$ is nonnegative (which shall be interpreted as strictly positive). LESLIE also restricted the analysis to cases for which $a=0$, see (25.200). In this case, elimination of the velocity gradient $\mathrm{d}u/\mathrm{d}y$ from Eqs. (25.203) and (25.204) leads to the single ordinary differential equation

$$2f(\theta)\frac{\mathrm{d}^2\theta}{\mathrm{d}y^2}+\frac{\mathrm{d}f(\theta)}{\mathrm{d}\theta}\left(\frac{\mathrm{d}\theta}{\mathrm{d}y}\right)^2+c\frac{(\lambda_1+\lambda_2\cos(2\theta))}{g(\theta)}=0. \tag{25.209}$$

It is easy to show that

$$\frac{\mathrm{d}\theta}{\mathrm{d}y}\left\{2f(\theta(y))\frac{\mathrm{d}^2\theta}{\mathrm{d}y^2}+\frac{\mathrm{d}f(\theta)}{\mathrm{d}y}\left(\frac{\mathrm{d}\theta}{\mathrm{d}y}\right)^2\right\}\equiv\frac{\mathrm{d}}{\mathrm{d}y}\left(f(\theta(y))\left(\frac{\mathrm{d}\theta}{\mathrm{d}y}\right)^2\right).$$

So, Eq. (25.209) can also be written as

$$\frac{\mathrm{d}}{\mathrm{d}y}\left(f(\theta(y))\left(\frac{\mathrm{d}\theta}{\mathrm{d}y}\right)^2\right)+c\frac{\lambda_1+\lambda_2\cos(2\theta(y))}{g(\theta(y))}\frac{\mathrm{d}\theta}{\mathrm{d}y}=0. \qquad (25.210)$$

Leslie [47] searches for solutions of boundary value problems for this equation.

(a) Flows Near a Boundary Consider the half-plane $y \geqslant 0$ with a flow satisfying the boundary conditions

$$\begin{aligned} u(0)&=0, & \theta(0)&=\theta_1, \\ \theta(y)&\to\theta_0 & \text{as } y&\to\infty, \end{aligned} \qquad (25.211)$$

where θ_0 and θ_1 are constants in the range $0 < \theta_0, \theta_1 < 2\pi$. This corresponds to a boundary layer flow, in which the director adjusts its orientation from $\theta = \theta_1$ at the wall to $\theta = \theta_0$ as $y \to \infty$. Since $\boldsymbol{n}$ and $-\boldsymbol{n}$ are indistinguishable for LCs, the values θ and $\theta \pm \pi$ are equivalent, requesting invariance of (25.209) under changes $\theta \to \theta \pm \pi$ as $y \to \infty$, for which we must have $\mathrm{d}\theta/\mathrm{d}y = 0$ and $\mathrm{d}^2\theta/\mathrm{d}y^2 = 0$, implying in view of (25.209) that

$$\cos(2\theta_0) = -\frac{\lambda_1}{\lambda_2}. \qquad (25.212)$$

Moreover, recalling the conditions (25.195), this gives two possible values for θ_0. The trivial cases $\theta_1 = \theta_0$ and $\theta_1 = \theta_0 \pm \pi$ are excluded [47].

Combining (25.210) with (25.212) and integrating the emerging equation yields

$$\begin{aligned} f(\theta)\left(\frac{\mathrm{d}\theta}{\mathrm{d}y}\right)^2 &= -c\lambda_2\int_{y(\theta_0)\to\infty}^{y(\theta)}\frac{[\cos(2\varphi(y))-\cos(2\theta_0)]}{g(\varphi(y))}\underbrace{\frac{\mathrm{d}\varphi(y)}{\mathrm{d}y}\mathrm{d}y}_{\mathrm{d}\varphi} \\ &= -c\lambda_2\int_{\theta_0}^{\theta}\frac{[\cos(2\varphi)-\cos(2\theta_0)]}{g(\varphi)}\mathrm{d}\varphi. \end{aligned} \qquad (25.213)$$

In the first line of this expression, integration is over the variable y and the integration is from $y \to \infty$ to an arbitrary value of y. In the second line, the variable of integration is changed to the (dummy) variable φ from $\varphi = \theta_0$ to $\varphi = \theta$.

Since the left-hand side of this equation is strictly positive, so must be its right-hand side. This condition determines the value of θ_0 which one obtains. In view of $\lambda_1 \leqslant 0$ and (25.212), Leslie [47] found that

$$\left.\begin{array}{llll} (i) & 0 \leqslant \theta_0 \leqslant \frac{1}{4}\pi, & \text{when } c > 0, & \lambda_2 > 0, \\ (ii) & \frac{1}{4}\pi \leqslant \theta_0 \leqslant \frac{1}{2}\pi, & \text{when } c < 0, & \lambda_2 < 0, \\ (iii) & \frac{1}{2}\pi \leqslant \theta_0 \leqslant \frac{3}{4}\pi, & \text{when } c > 0, & \lambda_2 < 0, \\ (iv) & \frac{3}{4}\pi \leqslant \theta_0 \leqslant \pi, & \text{when } c < 0, & \lambda_2 > 0. \end{array}\right\} \tag{25.214}$$

These may easily be verified by the reader. We may now write

$$\left(\frac{\mathrm{d}y}{\mathrm{d}\theta}\right)^2 = \frac{f(\theta)}{c\,h(\theta)}, \quad h(\theta) := \lambda_2 \int_\theta^{\theta_0} \frac{\cos(2\phi) - \cos(2\theta_0)}{g(\phi)}\mathrm{d}\phi, \tag{25.215}$$

from which now follows by integration

$$y = \pm \int_{\theta_1}^{\theta} \left\{\frac{f(\xi)}{c\,h(\xi)}\right\}^{1/2} \mathrm{d}\xi. \tag{25.216}$$

This relation determines the function $y = y(\theta)$ or $\theta = \theta(y)$, which, in view of (25.216), is monotone and, alternatively, also delivers $g(\theta) = g(\theta(y)) = g(y)$ in $(25.203)_1$. Consequently, from $(25.203)_1$ with $a = 0$,

$$\frac{\mathrm{d}u}{\mathrm{d}y} = \frac{c}{g(y)}, \quad u(y) = c\int_0^y \frac{1}{g(\bar{y})}\mathrm{d}\bar{y}, \tag{25.217}$$

which delivers the velocity profile corresponding to the above director profile.

Note that $\lim_{\theta\to\theta_0} g(\theta)$ is bounded away from zero and $\lim_{\theta\to\theta_0} f(\theta)$ is equally bounded away from zero if $\theta_0 \neq 0$. Thus, the integral (25.216) has an integrable square root singularity at $\theta = \theta_0$. Consequently, the director orientation approaches θ_0 asymptotically as $y \to \infty$. LESLIE [47] also mentions that one may show with the use of $(25.204)_2$ and (25.216) that

$$\lim_{\zeta\to 0} y = 0, \quad \zeta :=, \frac{\|k_{11}\| + \|k_{33}\|}{\|c\|}, \quad \text{provided } \theta \neq \theta_0.$$

This indicates boundary layer behavior when the length $\sqrt{\zeta}$ is sufficiently small.

Moreover, it is of interest to compare the above results with those of the simpler theories of anisotropic liquids discussed by ERICKSEN [22] and LESLIE [46]. In contrast with these theories, one obtains only one solution of the type considered. However, the asymptotic values given by (25.216) correspond to ERICKSEN's stable solutions, which, according to [47], "is rather a satisfactory state of affairs."

(b) Flow Between Parallel Plates This flow configuration corresponds to a possible generalization of shear flows of simple fluids to shear flows of nematic LCs. We take the flow as before between two parallel plates at $y = -h$ and $y = h$, subject to the boundary conditions

$$u(-h) = 0, \quad u(h) = V, \qquad \theta(-h) = \theta(h) = 0. \tag{25.218}$$

The liquid moves in a gap of width $2h$ with vanishing velocity at the bottom $y = -h$ and with velocity V at $y = h$. At the walls, the directors are parallel to the walls. We also consider λ_2 to be positive. Solutions for negative λ_2 and different director angles at the boundaries can also be constructed. With the above boundary conditions on θ, it is tempting to assume the solution to exhibit the symmetry

$$\theta(-y) = \theta(y) \quad \text{and} \quad \frac{\mathrm{d}\theta(0)}{\mathrm{d}y} = 0, \quad \frac{\mathrm{d}^2\theta(0)}{\mathrm{d}y^2} = 0 \tag{25.219}$$

and to assume the constants in (25.200) to be $a = 0$ and $c > 0$. In view of the symmetry assumption on θ in (25.219), integration of Eq. (25.209) can be performed again subject to condition (25.212).[29] The angle θ_0 lies for this case in the interval $0 < \theta_0 < \pi/4$, so that

$$f(\theta)\left(\frac{\mathrm{d}\theta}{\mathrm{d}y}\right)^2 = c\,\lambda_2 \int_\theta^{\theta_2} \frac{\cos(2\phi) - \cos(2\theta_0)}{g(\phi)}\mathrm{d}\phi, \quad 0 \leqslant \theta \leqslant \theta_2. \tag{25.220}$$

θ_2 is the orientation of the director at $y = 0$. Its solution is

$$F_{\theta_2}(\theta) = \int_0^\theta \left\{\frac{f(\xi)}{h_{\theta_2}(\xi)}\right\}^{1/2} \mathrm{d}\xi, \tag{25.221}$$

where

$$h_{\theta_2}(\theta) = \lambda_2 \int_\theta^{\theta_2} \frac{\cos(2\xi) - \cos(2\theta_0)}{g(\xi)}\mathrm{d}\xi. \tag{25.222}$$

In this solution, θ_2 and c are still not yet determined. This is done by the choice

$$\sqrt{c}\,h = F_{\theta_2}(\theta_2), \tag{25.223}$$

in which h is the half-width of the gap. Once θ_2 and c are determined from (25.220)–(25.223), the required solution is given by

$$\begin{aligned} \sqrt{c}(h - y) &= F_{\theta_2}(\theta), & y &\geqslant 0, \\ \sqrt{c}(h + y) &= F_{\theta_2}(\theta), & y &< 0, \\ \text{or} \quad y &= \pm\left\{h - \frac{F_{\theta_2}(\theta)}{\sqrt{c}}\right\}, & &\begin{matrix} y \geqslant 0, \\ y < 0. \end{matrix} \end{aligned} \tag{25.224}$$

It follows from (25.221) and $(25.224)_{1,2}$ that θ is a monotone function of y in either half of the gap.

At last, the velocity profile can be determined with Eq. $(25.217)_2$ as

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[29] With the conditions (25.219) Eq. (25.209) implies at $y = 0$ condition (25.212).

$$u = c \int_{-h}^{y} \frac{\mathrm{d}\bar{y}}{g(\theta(\bar{y}))}. \tag{25.225}$$

This solution can now be used to construct a formula for the apparent viscosity. To this end, we evaluate the velocity at the upper plate, which equals V, thereby using the skew-symmetry of $\theta(y)$ about the position $y = h$. Then, we find

$$V = 2c \int_{0}^{h} \frac{\mathrm{d}\bar{y}}{g[\theta(\bar{y})]} = 2\sqrt{c} \int_{0}^{\sqrt{c}\,h} \frac{\mathrm{d}\xi}{g[F_{\theta_2}^{-1}(\xi)]}, \tag{25.226}$$

in which (25.223) was employed. Moreover, using again (25.223),

$$V\,h = 2\,F_{\theta_2}(\theta_2) \int_{0}^{F_{\theta_2}(\theta_2)} \frac{\mathrm{d}\xi}{g[F_{\theta_2}^{-1}(\xi)]}. \tag{25.227}$$

With this, we now calculate the apparent viscosity as

$$\eta_{\text{apparent}} := \frac{(t_{xy}^{E})'(y=h)}{V/(2h)} \overset{(25.203)_1}{=} \frac{2c\,h}{V} \overset{(25.227)}{=} \frac{F_{\theta_2}(\theta_2)}{\int_0^{F_{\theta_2}(\theta_2)} \frac{\mathrm{d}\xi}{g[F_{\theta_2}^{-1}(\xi)]}}. \tag{25.228}$$

This result indicates that η_{apparent} is a function of θ_2 or, owing to (25.227), of the product of Vh.

This computation of LESLIE [47] is completed by pointing out that a boundary layer phenomenon can be demonstrated for this solution. It is easy to see, on the basis of (25.220), (25.221), that the function $F_{\theta_2}(\theta_2)$ becomes infinite as θ_2 approaches the value θ_0. LESLIE then shows that the director orientation will everywhere have a value close to θ_0, except for boundary layers at either boundary.

For other shear flow problems of nematics, see also OLMSTED and GOLDBART [55, 56].

25.7 Discussion

The foregoing analysis restricted its focus upon the ERICKSEN–LESLIE–PARODI formulation of nematic LCs, in which one-dimensional directors that are equipped along their axis with a mass density, can sufficiently accurately describe the polar nature of the substructure of the fluid. The theoretical concepts are the classical balance laws of mass, momenta, and energy. These are special when compared with the physical balance laws by the fact that the equation of fluid momentum is complemented by a balance law of director momentum, comprising director momentum, director stress, and director force. These must satisfy constraint conditions (i) that the balance law of angular momentum is identically satisfied and (ii) the balance law of internal energy accounts, beyond the terms known from the corresponding laws of the Boltzmann continuum, also for the additional stress power of the directors and the work of the internal director force are accounted for.

All this has been demonstrated to be in harmony with the basic principles in the pioneering articles of Ericksen [23] and Leslie [47]. The contributions to thermodynamics are by Leslie [47], Frank [31], and Parodi [59]. Leslie postulated an entropy flux going beyond "heat flux divided by absolute temperature" but kept the Coleman–Noll postulate ([42], Chap. 18) of open systems thermodynamics with (among others) arbitrarily applied external director forces. Some of us may question this assumption. Frank's contribution [31] was to postulate a Helmholtz free energy, being a quadratic form of the director gradient and other variables. He, for the first time, stated explicitly the number of independent coefficients arising in this function to hemotropic and isotropic materials. Parodi then adopted the Onsager reciprocity relations and demonstrated the reduction of the number of the Frank coefficients by an additional one. It was illustrated by a simple shear flow problem that derivation of analytical solutions to the emerging boundary value problems is nontrivial.

It is clear that a simple director is the most primitive representation that characterizes longish molecules; in particular, such a model ignores the variation of the mass distribution along the molecule axis. A more detailed description of this transverse variation can be introduced by tensorial order parameters of order higher than 1. Models of this complexity were started in the 1980s and 1990s, see e.g., Hess [38], and Ericksen [27], and later by Maffettone, Sonnet, and Virga [51, 67–69]. Concepts of such structures will be dealt with in Chap. 26. For further literature on thermomechanical behavior of LCs, see [36–39, 60, 61].

Appendix 25.A Evaluation of the Curvature Vector $\boldsymbol{k_i}$ and Tensor $\boldsymbol{k_{ij}}$

The reduction of the free energy (25.145) to a form suitable of an isotropic response is conducted in several steps by subjecting (25.145) to a selection of rotated coordinates. The choice of the coordinate system in the main text has been to let the z-coordinate coincide with the axis of the director; the coordinates (x, y) were chosen in the plane perpendicular to the z-axis, being mutually orthogonal, but otherwise free. We take now in a first step new Cartesian coordinate systems as shown in **Fig. 25.18**a, rotated around the z-axis by the angle $\pi/2$. Clearly, $x' = y$, $y' = -x$, $z' = z$. With the help of Fig. 25.16, we may identify the following relations:

$$\begin{aligned} \frac{\partial \mathcal{L}_{x'}}{\partial x'} &= \tfrac{\partial \mathcal{L}_y}{\partial y}, \qquad \tfrac{\partial \mathcal{L}_{y'}}{\partial y'} = \frac{\partial \mathcal{L}_x}{\partial x}, \\ \frac{\partial \mathcal{L}_{y'}}{\partial x'} &= -\tfrac{\partial \mathcal{L}_x}{\partial y}, \quad \tfrac{\partial \mathcal{L}_{x'}}{\partial y'} = -\frac{\partial \mathcal{L}_y}{\partial x}, \end{aligned} \tag{25.229}$$

$$\frac{\partial \mathcal{L}_{x'}}{\partial z'} = \frac{\partial \mathcal{L}_y}{\partial z}, \qquad \frac{\partial \mathcal{L}_{y'}}{\partial z'} = -\frac{\partial \mathcal{L}_x}{\partial z}.$$

These relations, together with the linear representations (25.143) for the primed and unprimed quantities, imply

$$\begin{aligned} a'_1 &= a_5, & a'_2 &= -a_4, & a'_3 &= a_6, \\ a'_4 &= -a_2, & a'_5 &= a_1, & a'_6 &= -a_3. \end{aligned} \tag{25.230}$$

Next, we write the free energy density $(\rho\psi)'$ in the primed Cartesian system in long form as follows:

$$\begin{aligned} (\rho\psi)' = {} & k_1 a'_1 + k_2 a'_2 + k_3 a'_3 + k_4 a'_4 + k_5 a'_5 + k_6 a'_6 \\ & + \tfrac{1}{2} k_{11} a'_1 a'_1 + k_{12} a'_1 a'_2 + k_{13} a'_1 a'_3 + k_{14} a'_1 a'_4 + k_{15} a'_1 a'_5 + k_{16} a'_1 a'_6 \\ & + \tfrac{1}{2} k_{22} a'_2 a'_2 + k_{23} a'_2 a'_3 + k_{24} a'_2 a'_4 + k_{25} a'_2 a'_5 + k_{26} a'_2 a'_6 \\ & + \tfrac{1}{2} k_{33} a'_3 a'_3 + k_{34} a'_3 a'_4 + k_{35} a'_3 a'_5 + k_{36} a'_3 a'_6 \\ & + \tfrac{1}{2} k_{44} a'_4 a'_4 + k_{45} a'_4 a'_5 + k_{46} a'_4 a'_6 \\ & + \tfrac{1}{2} k_{55} a'_5 a'_5 + k_{56} a'_5 a'_6 \\ & + \tfrac{1}{2} k_{66} a'_6 a'_6 \\ \overset{(25.230)}{=} {} & k_1 a_5 - k_2 a_4 + k_3 a_6 - k_4 a_2 + k_5 a_1 + k_6 a_3 \\ & + \tfrac{1}{2} k_{11} a_5 a_5 - k_{12} a_4 a_5 + k_{13} a_5 a_6 - k_{14} a_2 a_5 + k_{15} a_5 a_1 - k_{16} a_3 a_5 \\ & + \tfrac{1}{2} k_{22} a_4 a_4 - k_{23} a_4 a_6 + k_{24} a_4 a_2 - k_{25} a_4 a_1 - k_{26} a_4 a_3 \\ & + \tfrac{1}{2} k_{33} a_6 a_6 - k_{34} a_6 a_2 - k_{35} a_6 a_1 + k_{36} a_6 a_3 \\ & + \tfrac{1}{2} k_{44} a_2 a_2 - k_{45} a_2 a_1 - k_{46} a_2 a_3 \\ & + \tfrac{1}{2} k_{55} a_1 a_1 - k_{56} a_3 a_1 \\ & + \tfrac{1}{2} k_{66} a_3 a_3 . \end{aligned} \tag{25.231}$$

In this expression, relations (25.230) have been substituted. On the other hand, $(\rho\psi)$ in the unprimed system is given by

$$\begin{aligned} (\rho\psi) = {} & k_1 a_1 + k_2 a_2 + k_3 a_3 + k_4 a_4 + k_5 a_5 + k_6 a_6 \\ & + \tfrac{1}{2} k_{11} a_1 a_1 + k_{12} a_1 a_2 + k_{13} a_1 a_3 + k_{14} a_1 a_4 + k_{15} a_1 a_5 + k_{16} a_1 a_6 \\ & + \tfrac{1}{2} k_{22} a_2 a_2 + k_{23} a_2 a_3 + k_{24} a_2 a_4 + k_{25} a_2 a_5 + k_{26} a_2 a_6 \\ & + \tfrac{1}{2} k_{33} a_3 a_3 + k_{34} a_3 a_4 + k_{35} a_3 a_5 + k_{36} a_3 a_6 \\ & + \tfrac{1}{2} k_{44} a_4 a_4 + k_{45} a_4 a_5 + k_{46} a_4 a_6 \\ & + \tfrac{1}{2} k_{55} a_5 a_5 + k_{56} a_5 a_6 \\ & + \tfrac{1}{2} k_{66} a_6 a_6 . \end{aligned} \tag{25.232}$$

The values of $(\rho\psi)'$ and $(\rho\psi)$ must be equal, if the free energy is insensitive to this coordinate change; so, (25.231) = (25.232) allows the inferences:

- Compare the linear terms involving a_3 and a_6:

$$\begin{aligned} & k_3 a_6 - k_6 a_3 = -k_3 a_3 + k_6 a_6, \\ \longrightarrow \quad & (k_3 - k_6) a_6 = -(k_3 - k_6) a_3 . \end{aligned} \tag{25.233}$$

This implies $k_3 = k_6$. The inference $k_3 = k_6 = 0$ follows by applying an infinitesimal rotation for which the coefficients a_i and a'_j are related by (25.230). Substituting these expressions in (25.231) and (25.232) then yields for $k_3 a'_3 + k_6 a'_6 = k_3 a_3 + k_6 a_6$ the result $k_3 a_6 - k_6 a_3 = 0$ or, since a_3 and a_6 are arbitrary, $k_3 = 0$, $k_6 = 0$.

- Compare the linear terms involving a_2:

$$k_2 a_2 = -k_4 a_2, \quad \longrightarrow \quad \underline{k_2 = -k_4}. \tag{25.234}$$

- Compare the linear terms involving a_5:

$$k_1 a_5 = k_5 a_5, \quad \longrightarrow \quad \underline{k_1 = k_5}. \tag{25.235}$$

Thus, the vector k_i is given by $(k_1, k_2, 0, -k_2, k_1, 0)^T$. Of the six components, two are zero and of the remaining four, only two are independent. Next, compare the quadratic terms.

- Compare the terms involving $a_5 a_5$:

$$\tfrac{1}{2} k_{11} a_5 a_5 = \tfrac{1}{2} k_{55} a_5 a_5, \quad \longrightarrow \quad \underline{k_{11} = k_{55}}. \tag{25.236}$$

- Compare the terms involving $a_1 a_3$, $a_1 a_6$, $a_2 a_3$, $a_2 a_6$, $a_3 a_4$, $a_3 a_5$, $a_3 a_6$, $a_4 a_6$, $a_5 a_6$: Therefore, according to these results and that in the footnote,[30] we have

$$\underline{k_{13} = k_{16} = k_{23} = k_{26} = k_{34} = k_{35} = k_{36} = k_{46} = k_{56} \equiv 0}. \tag{25.237}$$

- Compare the terms involving $a_2 a_2$:

$$\tfrac{1}{2} k_{22} a_2 a_2 = \tfrac{1}{2} k_{44} a_2 a_2, \quad \longrightarrow \quad \underline{k_{22} = k_{44}}. \tag{25.238}$$

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[30] This comparison yields the following nine statements:

$$\begin{array}{lll} k_{13} = -k_{56}, & k_{16} = -k_{35}, & k_{46} = k_{23}, \\ \underline{k_{26} = -k_{34}}, & \underline{k_{26} = k_{34}}, & \underline{k_{36} = -k_{36}}, \\ k_{23} = k_{56}, & k_{23} = -k_{46}, & \underline{k_{46} = -k_{46}}. \end{array}$$

The underlined identities only allow the solutions $k_{26} = k_{34} = k_{36} = k_{46} = 0$; these then imply straightforwardly $k_{23} = 0$, $k_{56} = 0$, and $k_{13} = 0$. Only $k_{16} = -k_{35}$ remain undetermined. To prove that these coefficients vanish as well, a rotation of the coordinate system by the angle π around the z-axis is performed. An analogous computation as above then leads to the additional conclusion

$$k_{13} = k_{56},$$

which, combined with the first of the above nine statements, then yields the desired result

$$k_{13} = k_{56} = 0.$$

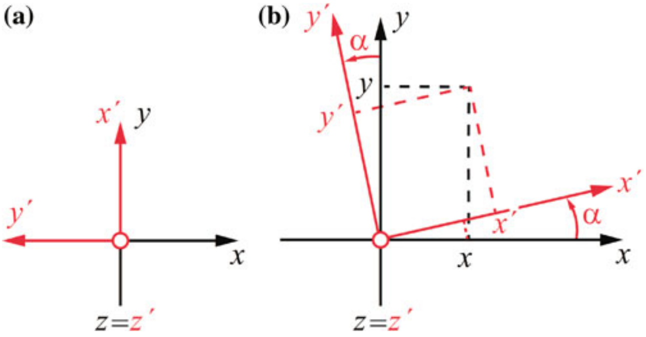

Fig. 25.18 Cartesian coordinates in the plane (x, y). The director points into the $z = z'$-axis. In **a** the (x, y)-coordinates are rotated counterclockwise by the angle $\alpha = \pi/2$; in **b** α is arbitrary

- Compare the terms involving $a_3 a_3$:

$$\tfrac{1}{2} k_{33} a_3 a_3 = \tfrac{1}{2} k_{66} a_3 a_3, \quad \longrightarrow \quad \underline{k_{33} = k_{66}}. \tag{25.239}$$

- Compare the terms involving $a_2 a_5$:

$$- k_{14} a_2 a_5 = k_{25} a_4 a_5, \quad \longrightarrow \quad \underline{k_{14} = -k_{25}}. \tag{25.240}$$

- Compare the terms involving $a_4 a_5$:

$$k_{12} a_4 a_5 = -k_{45} a_4 a_5, \quad \longrightarrow \quad \underline{k_{12} = -k_{45}}. \tag{25.241}$$

Thus, the vector k_i and the matrix $k_{ij} (i, j = 1, \dots, 6)$ reduce with these results to

$$k_1 = (k_1, k_2, 0, -k_2, k_1, 0)^T = 0, \tag{25.242}$$

$$k_{ij} = \begin{pmatrix} k_{11} & k_{12} & 0 & k_{14} & k_{15} & 0 \\ & k_{22} & 0 & k_{24} & -k_{14} & 0 \\ & & k_{33} & 0 & 0 & 0 \\ & & & k_{22} & -k_{12} & 0 \\ & \text{sym} & & & k_{11} & 0 \\ & & & & & k_{33} \end{pmatrix}. \tag{25.243}$$

Of the six coefficients k_i, four are nonzero, but only two are possibly distinct. Similarly, of the 36 coefficients of the symmetric matrix k_{ij}, 12 of the upper diagonal 21 coefficients are different from zero but only seven are possibly distinct from one another.

We next consider a rotation of the Cartesian coordinates by an arbitrary angle α. In view of **Fig.** 25.18b, we then obtain

$$\begin{array}{ll} x = \cos(\alpha)x' - \sin(\alpha)y', & \mathcal{L}'_x = \cos(\alpha)\mathcal{L}_x + \sin(\alpha)\mathcal{L}_y, \\ y = \sin(\alpha)x' + \cos(\alpha)y', & \mathcal{L}'_y = -\sin(\alpha)\mathcal{L}_x + \cos(\alpha)\mathcal{L}_y, \\ z = z', & \mathcal{L}'_z = \mathcal{L}_z. \end{array} \tag{25.244}$$

With these expressions, it is straightforward to compute the components of the curvature tensor $\partial\mathcal{L}'_i/\partial x'_j$ as follows:

$$\begin{aligned} \frac{\partial\mathcal{L}'_x}{\partial x'} &= \cos^2(\alpha)\frac{\partial\mathcal{L}_x}{\partial x} + \sin(\alpha)\cos(\alpha)\left(\frac{\partial\mathcal{L}_x}{\partial y} + \frac{\partial\mathcal{L}_y}{\partial x}\right) + \sin^2(\alpha)\frac{\partial\mathcal{L}_y}{\partial y}, \\ \frac{\partial\mathcal{L}'_y}{\partial y'} &= \cos^2(\alpha)\frac{\partial\mathcal{L}_y}{\partial y} - \sin(\alpha)\cos(\alpha)\left(\frac{\partial\mathcal{L}_x}{\partial y} + \frac{\partial\mathcal{L}_y}{\partial x}\right) + \sin^2(\alpha)\frac{\partial\mathcal{L}_x}{\partial x}, \\ \frac{\partial\mathcal{L}'_y}{\partial x'} &= \cos^2(\alpha)\frac{\partial\mathcal{L}_y}{\partial x} - \sin(\alpha)\cos(\alpha)\left(\frac{\partial\mathcal{L}_x}{\partial x} - \frac{\partial\mathcal{L}_y}{\partial y}\right) - \sin^2(\alpha)\frac{\partial\mathcal{L}_x}{\partial y}, \\ \frac{\partial\mathcal{L}'_x}{\partial y'} &= \cos^2(\alpha)\frac{\partial\mathcal{L}_x}{\partial y} - \sin(\alpha)\cos(\alpha)\left(\frac{\partial\mathcal{L}_x}{\partial x} - \frac{\partial\mathcal{L}_y}{\partial y}\right) - \sin^2(\alpha)\frac{\partial\mathcal{L}_y}{\partial x}, \\ \frac{\partial\mathcal{L}'_x}{\partial z'} &= \cos(\alpha)\frac{\partial\mathcal{L}_x}{\partial z} + \sin(\alpha)\frac{\partial\mathcal{L}_y}{\partial z}, \\ \frac{\partial\mathcal{L}'_y}{\partial z'} &= \cos(\alpha)\frac{\partial\mathcal{L}_y}{\partial z} - \sin(\alpha)\frac{\partial\mathcal{L}_x}{\partial z}, \\ \frac{\partial\mathcal{L}'_z}{\partial x'} &= \cos(\alpha)\frac{\partial\mathcal{L}_z}{\partial x} + \sin(\alpha)\frac{\partial\mathcal{L}_z}{\partial y}, \\ \frac{\partial\mathcal{L}'_z}{\partial y'} &= \cos(\alpha)\frac{\partial\mathcal{L}_z}{\partial y} - \sin(\alpha)\frac{\partial\mathcal{L}_z}{\partial x}, \\ \frac{\partial\mathcal{L}'_z}{\partial z'} &= \frac{\partial\mathcal{L}_z}{\partial z}. \end{aligned} \tag{25.245}$$

If we select $\alpha = \frac{\pi}{2}$, the formulae (25.245) verify (25.229). On the other hand, for $\alpha = \pi/4$, $\sin(\alpha) = \cos(\alpha) = \frac{1}{\sqrt{2}}$ and $\sin^2(\alpha) = \cos^2(\alpha) = \sin(\alpha)\cos(\alpha) = \frac{1}{2}$. Consequently, in view of (25.243), written for the primed and unprimed coordinates, we have

$$\begin{aligned} a'_1 &= \frac{\partial\mathcal{L}'_x}{\partial x'} = \frac{1}{2}\left(\frac{\partial\mathcal{L}_x}{\partial x} + \frac{\partial\mathcal{L}_x}{\partial y} + \frac{\partial\mathcal{L}_y}{\partial x} + \frac{\partial\mathcal{L}_y}{\partial y}\right) = \frac{1}{2}\left(a_1 + a_2 + a_4 + a_5\right), \\ a'_2 &= \frac{\partial\mathcal{L}'_x}{\partial y'} = \frac{1}{2}\left(-\frac{\partial\mathcal{L}_x}{\partial x} + \frac{\partial\mathcal{L}_y}{\partial y} + \frac{\partial\mathcal{L}_y}{\partial y} - \frac{\partial\mathcal{L}_y}{\partial x}\right) = \frac{1}{2}\left(-a_1 + a_2 - a_4 + a_5\right), \\ a'_3 &= \frac{\partial\mathcal{L}'_x}{\partial z'} = \frac{1}{\sqrt{2}}(a_3 + a_6), \\ a'_4 &= \frac{\partial\mathcal{L}'_y}{\partial x'} = \frac{1}{2}\left(\frac{\partial\mathcal{L}_y}{\partial x} - \frac{\partial\mathcal{L}_x}{\partial x} + \frac{\partial\mathcal{L}_y}{\partial y} - \frac{\partial\mathcal{L}_x}{\partial y}\right) = \frac{1}{2}\left(-a_1 - a_2 + a_4 + a_5\right), \\ a'_5 &= \frac{\partial\mathcal{L}'_y}{\partial y'} = \frac{1}{2}\left(\frac{\partial\mathcal{L}_x}{\partial x} - \frac{\partial\mathcal{L}_x}{\partial y} - \frac{\partial\mathcal{L}_y}{\partial x} + \frac{\partial\mathcal{L}_y}{\partial y}\right) = \frac{1}{2}\left(a_1 - a_2 - a_4 + a_5\right), \end{aligned} \tag{25.246}$$

$$a_6' = \frac{\partial \mathcal{L}_y'}{\partial z'} = \frac{1}{\sqrt{2}}(-a_3 + a_6).$$

It follows that

$$\begin{aligned}
2a_1' &= a_1 + a_2 + a_4 + a_5,\\
2a_2' &= -a_1 + a_2 - a_4 + a_5,\\
\sqrt{2}a_3' &= a_3 + a_6,\\
2a_4' &= -a_1 - a_2 + a_4 + a_5,\\
2a_5' &= a_1 - a_2 - a_4 + a_5,\\
\sqrt{2}a_6' &= -a_3 + a_6.
\end{aligned} \tag{25.247}$$

If we now consider the representations (25.145) and (25.146) for the free energy in the primed and unprimed coordinates, the linear contributions yield, with the k-values as given by (25.147),

$$\begin{aligned}
(\rho\psi)_{\text{lin}}' &= k_1\left(a_1' + a_5'\right) + k_2\left(a_2' - a_4'\right)\\
&\overset{(25.247)}{=} k_1(a_1 + a_5) + k_2(a_2 - a_4),\\
(\rho\psi)_{\text{lin}} &= k_1(a_1 + a_5) + k_2(a_2 - a_4).
\end{aligned} \tag{25.248}$$

Therefore, the requirement $(\rho\psi)' = (\rho\psi)$ implies an identity and no reduction of the number of coefficients k_1 and k_2. The same result is also obtained for the linear terms of representation (25.146) for ψ with an arbitrary such rotation. Indeed, with (25.245) and (25.143), we may easily compute

$$\begin{aligned}
(\rho\psi)_{\text{lin}}' &= k_1\left(a_1' + a_5'\right) + k_2\left(a_2' - a_4'\right),\\
(\rho\psi)_{\text{lin}} &= k_1\left(a_1 + a_5\right) + k_2\left(a_2 - a_4\right).
\end{aligned}$$

This shows that the requirement $(\rho\psi)_{\text{lin}}' = (\rho\psi)_{\text{lin}}$ implies

$$(a_1' + a_5') = (a_1 + a_5) \quad \text{and} \quad (a_2' - a_5') = (a_2 - a_4), \tag{25.249}$$

identically, for any values of α. We emphasize that this result holds for *proper* rotations.

The analogous computations for the quadratic terms of the free energy $(\rho\psi)_{\text{quad}} = \sum_{i,j=1}^{6} a_i' a_j'$, $k_{ij} = k_{ji}$, are much more involved, even though they are not difficult. With the results (25.243) we may write

$$\begin{aligned}
(\rho\psi)'_{\text{quad}} &= k_{11}\left(a'_1 a'_1 + a'_5 a'_5\right) + 2k_{12}\left(a'_1 a'_2 - a'_4 a'_5\right)\\
&\quad + 2k_{14}\left(a'_1 a'_4 - a'_2 a'_5\right) + 2k_{15}\left(a'_1 a'_5\right)\\
&\quad + k_{22}\left(a'_2 a'_2 + a'_4 a'_4\right) + 2k_{24}\left(a'_2 a'_4\right) + k_{33}\left(a'_3 a'_3 + a'_6 a'_6\right)
\end{aligned} \tag{25.250}$$

$$\begin{aligned}
\equiv (\rho\psi)_{\text{quad}} &= k_{11}\left(a_1 a_1 + a_5 a_5\right) + 2k_{12}\left(a_1 a_2 - a_4 a_5\right)\\
&\quad + 2k_{14}\left(a_1 a_4 - a_2 a_5\right) + 2k_{15}\left(a_1 a_5\right)\\
&\quad + k_{22}\left(a_2 a_2 + a_4 a_4\right) + 2k_{24}\left(a_2 a_4\right) + k_{33}\left(a_3 a_3 + a_6 a_6\right).
\end{aligned}$$

This statement must hold under conditions of material isotropy for any value of the rotation angle α. Its identical satisfaction for $\alpha = \pi/2$ is already incorporated. For $\alpha = \pi/4$ relations (25.247) apply; they allow computation of $a'_i a'_j$ as functions of $a_k a_\ell (i, j, k, \ell = 1, \ldots, 6)$, of which the results can be substituted into (25.250). The outcome of this long and rather dull computation yields the following identity:

$$\begin{aligned}
&(k_{11} - k_{15} - k_{22} - k_{24})\left\{-\tfrac{1}{2}a_1 a_1 + \tfrac{1}{2}a_2 a_2 + \tfrac{1}{2}a_4 a_4 + \tfrac{1}{2}a_5 a_5 + a_2 a_4\right\}\\
&+\Big\{k_{11} a_1 a_5 + k_{12}\left(-2a_1 a_4 + 2a_2 a_5 - a_1 a_2 - a_4 a_5\right)\\
&+k_{14}\left(2a_4 a_5 - 2a_1 a_2 - a_1 a_4 - a_2 a_5\right) - k_{22}\left(a_1 a_5 + a_5 a_5\right)\\
&-k_{24}\left(a_1 a_5 + a_4 a_5\right)\Big\} \equiv 0.
\end{aligned} \tag{25.251}$$

This identity must be valid for any values of a_i $(i = 1, \ldots, 6)$. It, thus, follows that the terms in the first line and then in the subsequent line(s) of (25.251) must independently vanish. This conclusion follows, e.g., simply from the fact that the products $a_1 a_5$ and $a_2 a_5$ do not arise in the first line, but in all remaining terms of (25.251). Thus, we conclude that

$$k_{15} = k_{11} - k_{22} - k_{24}, \tag{25.252}$$

a result stated by Sir CHARLES FRANK [31], but not explicitly demonstrated by him.

A further relation is obtained by performing an infinitesimal rotation with the transformation employing (25.245) in the limit $\alpha \ll 1$, so that $\cos(\alpha) = 1$, $\sin(\alpha) \approx \alpha$ and ignoring terms quadratic in α. These computations yield

$$\begin{aligned}
&\frac{\partial \mathcal{L}'_x}{\partial x'} = \frac{\partial \mathcal{L}_x}{\partial x} + \alpha\left(\frac{\partial \mathcal{L}_x}{\partial y} + \frac{\partial \mathcal{L}_y}{\partial x}\right), && \frac{\partial \mathcal{L}'_y}{\partial x'} = \frac{\partial \mathcal{L}_y}{\partial x} - \alpha\left(\frac{\partial \mathcal{L}_x}{\partial x} - \frac{\partial \mathcal{L}_y}{\partial y}\right),\\
&\frac{\partial \mathcal{L}'_y}{\partial y'} = \frac{\partial \mathcal{L}_y}{\partial y} - \alpha\left(\frac{\partial \mathcal{L}_x}{\partial y} + \frac{\partial \mathcal{L}_y}{\partial x}\right), && \frac{\partial \mathcal{L}'_x}{\partial y'} = \frac{\partial \mathcal{L}_x}{\partial y} - \alpha\left(\frac{\partial \mathcal{L}_x}{\partial x} - \frac{\partial \mathcal{L}_y}{\partial y}\right),\\
&\frac{\partial \mathcal{L}'_x}{\partial z'} = \frac{\partial \mathcal{L}_x}{\partial z} + \alpha\left(\frac{\partial \mathcal{L}_y}{\partial z}\right), && \frac{\partial \mathcal{L}'_y}{\partial z'} = \frac{\partial \mathcal{L}_y}{\partial z} - \alpha\left(\frac{\partial \mathcal{L}_x}{\partial z}\right),\\
&\frac{\partial \mathcal{L}'_z}{\partial x'} = \frac{\partial \mathcal{L}_z}{\partial x} + \alpha\left(\frac{\partial \mathcal{L}_z}{\partial y}\right), && \frac{\partial \mathcal{L}'_z}{\partial y'} = \frac{\partial \mathcal{L}_z}{\partial y} - \alpha\left(\frac{\partial \mathcal{L}_z}{\partial x}\right)\\
&\frac{\partial \mathcal{L}'_z}{\partial z'} = \frac{\partial \mathcal{L}_z}{\partial z}.
\end{aligned} \tag{25.253}$$

Substituting the expansions for $\mathcal{L}$ in terms of the parameters a_i $(i = 1, \ldots, 6)$ expressed in terms of a_i and a'_k $(i, k = 1, \ldots, 6)$, respectively, the above expressions yield

$$\begin{aligned} a'_1 &= a_1 + \alpha(a_2 + a_4), & a'_4 &= a_4 - \alpha(a_1 - a_5), \\ a'_5 &= a_5 - \alpha(a_2 + a_4), & a'_2 &= a_2 - \alpha(a_1 - a_5), \\ a'_3 &= a_3 + \alpha a_6, & a'_6 &= a_6 - \alpha a_3, \\ a'_7 &= a_7 + \alpha a_8, & a'_8 &= a_8 - \alpha a_7. \end{aligned} \tag{25.254}$$

With these expressions and with relation (25.252) for k_{15}, the free energy condition for isotropic behavior is

$$\begin{aligned} (\rho\psi)'_{\text{quad}} &= k_{11}\left(a'_1a'_1 + 2a'_1a'_5 + a'_5a'_5\right) + 2k_{12}\left(a'_1a'_2 - a'_4a'_5\right) \\ &\quad + k_{14}\left(a'_1a'_4 - a'_2a'_5\right) + k_{22}\left(a'_2a'_2 - 2a'_1a'_5 + a'_4a'_4\right) \\ &\quad + 2k_{24}\left(a'_2a'_4 - a'_1a'_5\right) + k_{33}\left(a'_3a'_3 + a'_6a'_6\right), \\ \equiv (\rho\psi)_{\text{quad}} &= k_{11}\left(a_1a_1 + 2a_1a_5 + a_5a_5\right) + 2k_{12}\left(a_1a_2 - a_4a_5\right) \\ &\quad + k_{14}\left(a_1a_4 - a_2a_5\right) + k_{22}\left(a_2a_2 - 2a_1a_5 + a_4a_4\right) \\ &\quad + 2k_{24}\left(a_2a_4 - a_1a_5\right) + k_{33}\left(a_3a_3 + a_6a_6\right). \end{aligned} \tag{25.255}$$

If in this identity the parameters a'_k $(k = 1, \ldots, 6)$ are expressed in terms of the parameters a_i $(i = 1, \ldots, 6)$, it turns out that only those parts of the equation survive, which contain the linear factor α; this expression reduces to

$$(k_{12} + k_{14})\left[-a_1a_1 + a_2a_2 - a_5a_5 + 2a_1a_5 + a_2a_4 - a_2a_6\right] \equiv 0,$$

which must identically vanish for arbitrary values of $a_j(j = 1, \ldots, 6))$. Therefore,

$$k_{12} = -k_{14}. \tag{25.256}$$

This result agrees as well with that stated by Sir Charles Frank [31]. Further reductions of the parameter set are not possible.

The results of this appendix are stated in the main text as (25.147) and (25.148).

References

1. Beatty, M.F.: On the foundation principles of general classical mechanics. Arch. Rational Mech. Anal. **24**, 264–273 (1967)
2. Beris, A.N., Edwards, B.J.: Thermodynamics of Flowing Systems with Internal Microstructure. Oxford Engineering Science Series, vol. 36. Oxford University Press, Oxford (1994)
3. Busch, K.W., Busch, M.A.: Chiral Analysis. Elsevier, Amsterdam (2006)
4. Capriz, G.: Continua with Microstructure. Springer, New York (1989)
5. Castellano, J.A.: Liquid Gold: The Story of Liquid Crystal Displays and the Creation of an Industry. World Scientific Publishing (2005). ISBN 978-238-956-8

6. Chandrasekhar, S.: Liquid Crystals. Cambridge University Press, Cambridge (1977)
7. Chistyakov, I.G., Schabischev, L.S., Jarenov, R.I., Gusakova, L.A.: The polymorphism of the smectic liquid crystal. Mol. Cryst. Liq. Cryst. **7**, 279 (1969) and Liq. Cryst. **2**, Part II, Proceedings of the Second International Conference, G.H. Brown (ed.) Gorden and Breach, New York, p. 813 (1969)
8. Collings, P.J., Hird, M.: Introduction to Liquid Crystals. Taylor and Francis, Bristol (1997). ISBN 0-7484-0643-3
9. Currie, P.K.: Parodi's relation as a stability condition for nematics. Mol. Cryst. Liq. Cryst. **28**, 335–338 (1974)
10. de Gennes, P.G.: Short range order effects in the isotropic phase of nematics and cholesterics. Mol. Cryst. Liq. Cryst. **12**, 193–214 (1971)
11. de Gennes, P.G.: The Physics of Liquid Crystals. Oxford University Press (Clarendon), London (1974)
12. de Gennes, P.G., Prost, J.: The Physics of Liquid Crystals. Clarendon Press, Oxford (1993). ISNB 0-19-852024-7
13. de Gennes, P.G., Sarma, G.: Tentative model for the smectic B phase. Phys. Lett. **A38**, 219–220 (1972)
14. De Groot, S.R., Mazur, P.: Non-equilibrium Thermodynamics. Dover Publications Inc.; Dover Ed, New York (1985). ISBN-10: 0486647412, ISBN-13: 978-0486647418
15. de Vries, A.: Evidence for the existence of more than one type of nematic phase. Mol. Cryst. Liq. Cryst. **10**, 31–37 (1970)
16. Dierking, I.: Textures of Liquid Crystals. Wiley-VCH, Weinheim (1993). ISBN 3-527-30725-7 (1993)
17. Doi, M.: Molecular dynamics and rheological properties of concentrated solutions of rodlike polymers in isotropic and liquid crystalline phases. J. Polym. Sci. Polym. Phys. **19**(2), 229–243 (1981)
18. Duhem, P.M.: Introduction a la Mecanique Chimique. Kessinger Publishing, Whitefish (1893). ISBN-13: 978-1168396204
19. Dunmur, D., Sluckin, T.: Soap, Science, and Flat-Screen TVs: A History of Liquid Crystals. Oxford University Press, Oxford (2011). ISBN 978-0-19-954940-5
20. Durand, G., Leger, L., Rondelez, F., Veyssie, M.: (Orsay Liquid Crystal Group) Quasielastic Rayleigh scattering in nematic liquid crystals. Phys. Rev. Lett. **22**, 1361 (1969); Erratum Phys. Rev. Lett. **23**, 208 (1969)
21. Ehrentraut, H.: A unified mesoscopic continuum theory of uniaxial and biaxial liquid crystals. Ph.D. thesis, TU Berlin, Department of Physics (1996)
22. Ericksen, J.L.: Anisotropic fluids. Arch. Rational Mech. Anal. **4**, 231 (1960)
23. Ericksen, J.L.: Conservation laws for liquid crystals. Trans. Soc. Rheol. **5**, 23–34 (1961)
24. Ericksen, J.L.: Hydrostatic theory of liquid crystals. Arch. Rational Mech. Anal. **21**, 371–378 (1962)
25. Ericksen, J.L.: Inequalities in liquid crystal theory. Phys. Fluids **9**(9), 1205–1207 (1966)
26. Ericksen, J.L.: On equations of motion for liquid crystals. Q. J. Mech. Appl. Math. **29**, 203–208 (1976)
27. Ericksen, J.L.: Liquid crystals with variable degree of orientation. Arch. Rational Mech. Anal. **113**, 97–120 (1991)
28. Ericksen, J.L.: Introduction to the Thermodynamics of Solids. Applied Mathematical Sciences, vol. 131. Springer, Berlin (1998)
29. Forster, D.: Microscopic theory of flow alignment in nematic liquid crystals. Phys. Rev. Lett. **32**, 1161 (1974)
30. Frank, F.C.: On spontaneous asymmetric synthesis. Biochem. Biophys. Acta **11**, 459 (1953)
31. Frank, F.C.: I. Liquid crystals. On the theory of liquid crystals. Discuss. Faraday Soc. **25**, 19–28 (1958)
32. Friedel, G.: Mesomorphic states of matter. Ann. Phys. (Paris) **19**, 273 (1922)
33. Gray, G.W.: Molecular Structure and the Properties of Liquid Crystals. Academic Press, New York (1962)

34. Green, A.E., Rivlin, R.S.: Simple force and stress multipoles. Arch. Rational Mech. Anal. **16**, 325–354 (1964)
35. Green, A.E., Naghdi, P.M., Rivlin, R.S.: Directors and multipolar displacements in continuum mechanics. Int. J. Eng. Sci. **2**, 611–620 (1965)
36. Hess, S.: Irreversible thermodynamics of non-equilibrium alignment phenomena in molecular liquids and in liquid crystals. Z. Naturforsch. **30a**, 728 (1975)
37. Hess, S.: Pre- and post-transitional behavior of the flow alignment and flow-induced phase transition in liquid crystals. Z. Naturforsch. **31a**, 1507–1513 (1976)
38. Hess, S.: Transport phenomena in anisotropic fluids and liquid crystals. J. Non-Equilib. Thermodyn. **11**, 175–193 (1986)
39. Hess, S., Pardowitz, Z.: On the unified theory for non-equilibrium phenomena in the isotropic and nematic phases of a liquid crystal – spatially homogeneous alignment. Z. Naturforsch. **36a**, 554–558 (1981)
40. https://en.wikipedia.org/wiki/Liquid_crystal
41. Hutter, K., Jöhnk, K.: Continuum Methods of Physical Modeling. Springer, Berlin (2004), 635 pp
42. Hutter, K., Wang, Y.: Fluid and Thermodynamics. Advanced Fluid Mechanics and Thermodynamic Fundamentals, vol. 2, p. 633. Springer, Berlin (2016). https://doi.org/10.1007/978-3-319.33636-7
43. Kleinert, H., Maki, K.: Lattice textures in cholesteric liquid crystals. Fortschritte der Physik **29**(5), 219–259 (1981)
44. Lehmann, O.: Über fließende Kristalle. Zeitschrift für Physikalische Chemie **4**, 462–472 (1889)
45. Lehmann, O.: Flssige Kristalle: sowie Plastizität von Kristallen im allgemeinen, molekulare Umlagerungen und Aggregatzustandsänderungen. Wilhelm Engelmann, Leipzig (1904)
46. Leslie, F.M.: Some constitutive equations for anisotropic fluids. Q. J. Mech. Appl. Math. **19**, 357–370 (1966)
47. Leslie, F.M.: Some constitutive equations for liquid crystals. Arch. Rational Mech. Anal. **28**, 265–283 (1968)
48. Leslie, F.M.: Continuum theory for nematic liquid crystals. Contin. Mech. Thermodyn. **4**, 167–175 (1992)
49. Levelut, A.M., Lambert, M.: Structure des cristaux liquides smectic B. C. R. Acad. Sci. **B 272**, 1018–1021 (1971)
50. Madsden, L.A., Dingemans, T.J., Nakata, M., Samuelski, E.T.: Thermotropic nematic liquid crystals. Phys. Rev. Lett. **92**(14), 145505 (2004). https://doi.org/10.1103/PhysRevLett.92.145505
51. Maffettone, P.L., Sonnet, A.M., Virga, E.G.: Shear-induced biaxiality in nematic polymers. J. Non-Newton. Fluid Mech. **90**, 283–297 (2000)
52. Mainzer, K.: Symmetries of Nature - A Handbook for Philosophy of Nature and Science. Walter de Gruyter, Berlin (1996)
53. Müller, I.: On the entropy inequality. Arch. Rational Mech. Anal. **26**, 118–141 (1967)
54. Müller, M.: Twisted nematic Flüssigkeiten (2006). http://www.tu.berlin.de/~insi/agppke/clkark/tnicd.htlm
55. Olmsted, P.D., Goldbart, P.: Theory of the nonequilibrium phase transition for nematic liquid crystals under shear flow. Phys. Rev. **A41**, 4578–4581 (1990)
56. Olmsted, P.D., Goldbart, P.: Isotropic-nematic transition in shear flow: state selection, coexistence, phase transitions, and critical behavior. Phys. Rev. **A46**, 4966–4993 (1992)
57. Onsager, L.: Reciprocal relations in irreversible processes I. Phys. Rev. **37**, 405 (1931); II, Phys. Rev. **38**, 2265 (1931)
58. Oseen, C.W.: The theory of liquid crystals. Trans. Faraday Soc. **29**(140), 883–885 (1933)
59. Parodi, O.: Stress tensor for a nematic liquid crystal. Le journal de Physque **31**, 581–584 (1970)
60. Pereira-Borgmeyer, C., Hess, S.: Unified description of the flow alignment and viscosity in the isotropic and nematic phases of liquid crystals. J. Non-Equilib. Thermodyn. **20**, 359–384 (1995)

61. Qian, T., Sheng, P.: Generalized hydrodynamic equations for nematic liquid crystals. Phys. Rev. E **58**, 7475 (1998)
62. Reinitzer, F.: Beiträge zur Kenntniss des Cholesterins. Monatshefte für Chemie (Wien) **9**, 421–441 (1888)
63. Saupe, A.: Das Protonenresonanzspektrum von orientiertem Benzol in nematisch-kristallinflüssiger Lösung. Z. Naturforschung **20a**, 572–580 (1965)
64. Seideman, T.: The liquid-crystalline blue phases. Rep. Prog. Phys. **53**(6), 659–705 (1990). https://doi.org/10.1088/0034-4885/53/6/001
65. Slukin, T.J., Dunmur, D.A., Stegmeyer, H.: Crystals that Flow - Classic Papers from the History of Liquid Crystals. Taylor and Francis, London (2004)
66. Smith, G.E.: On isotropic integrity bases. Arch. Rational Mech. Anal. **18**, 282–292 (1965)
67. Sonnet, A.M., Virga, E.G.: Dynamics of dissipative ordered fluids. Phys. Rev. E **64**(3), 031705-1-10 (2001)
68. Sonnet, A.M., Virga, E.G.: Dissipative Ordered Fluid: Theories for Liquid Crystals. Springer Science & Business Media LLC, New York (2012)
69. Sonnet, A.M., Maffettone, P.L., Virga, E.G.: Continuum theory for nematic liquid crystals with tensorial order. J. Non-Newton. Fluid Mech. **119**, 51–59 (2004)
70. Sparavigna, A.C.: James Fergason, a pioneer in advancing of liquid crystal technology (2006). https://arxiv.org/ftp/arxiv/papers/1310/1310.7569.pdf
71. Spencer, A.J.M.: Theory of invariants. In: Eringen, A.C. (ed.) Continuum Physics. Mathematics, vol. 1, pp. 239–353. Academic Press, New York (1971)
72. Stephen, M.J., Straley, J.P.: Physics of liquid crystals. Rev. Mod. Phys. **46**(4), 617–703 (1974). https://doi.org/10.1007/BF01516710
73. Truesdell, C.A.: Rational Thermodynamics, 2nd edn. Springer, New York (1984). https://doi.org/10.1007/978-1-4612-5206-1
74. Truesdell, C.A., Noll, W.: Non-linear field theories of mechanics, vol. III/3. Handbuch der Physik edited by Siegfried Flügge (1965)
75. Vertogen, G.: The equations of motion for nematics. Z. Naturforsch. **38a**, 1273 (1983)
76. Vertogen, G., de Jeu, W.H.: Thermotropic Liquid Crystals, Fundamentals. Springer Series in Chemical Physics, vol. 45. Springer, Berlin (1988)
77. Wang, C.C.: A new representation for isotropic functions. Parts I and II. Arch. Rational Mech. Anal. **36**, 166–197, 198–223 (1970)
78. Wang, C.C.: Corrigendum to my recent paper on ‘Representations for isotropic functions’. Arch. Rational Mech. Anal. **43**, 392–395 (1971)
79. Wu, H., Xu, X., Liu, C.: On the general Ericksen-Leslie system: Parodi’s relatation, well posedness and stability (2012). arXiv:1105.2180v6 [math.AP]

Chapter 26
Nematic Liquid Crystals with Tensorial Order Parameters

Abstract This chapter goes beyond the ELP theory of LCs by modeling the microstructure of the liquid by a number of rank-i tensors ($i = 1, \dots, n$) (generally just one) with vanishing trace. These tensors are called *alignment tensors* or *order parameters*. When formed as exterior products of the director vector and weighted with a scalar and restricted to just one rank-2 tensor, the resulting mathematical model describes *uniaxial* LCs. The simplest extensions of the ELP model are theories, for which the number of independent constitutive variables are complemented by a constant or variable order parameter S and its gradient grad S paired with an evolution equation for it. We provide a review of the recent literature. Two different approaches to deduce LC models exist; they may be coined the balance equations models, outlined already in Chap. 25 for the ELP model, and the variational LAGRANGE potential models, which, following an idea by Lord RAYLEIGH (Strutt, Proc Lond Math Soc 4:357–368, 1873, [50]), are extended by a dissipation potential. The two different approaches may lead to distinct anisotropic fluid descriptions. Moreover, it is not automatically guaranteed in either description that the balance law of angular momentum is identically satisfied. The answers to these questions cover an important part of the mathematical efforts in both model classes. Significant conceptual difficulties in the two distinct theoretical concepts are the postulations of explicit forms of the elastic energy W and dissipation function R. Depending upon, how W and R are parametrized, different particular models emerge. Conditions are formulated especially for uniaxial models, which guarantee that the two model classes reduce to exactly corresponding mathematical models.

Keywords Liquid crystals of tensorial microstructure · Balance law approach
Variational formulation · Alignment tensor model · Uniaxial LC theory

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List of Symbols

Roman Symbols

$\boldsymbol{\mathbb{A}}$, $\mathbb{A}_I$	Rank-i $(i = 1, \ldots, N)$ tensor
a	Symbol for area
$\boldsymbol{a}$	Uniaxial rank-2 tensorial order parameter
a_k	Scalar coefficient in the definition of $\hat{\boldsymbol{\mathbb{O}}}$ or $\breve{\mathbb{O}}_I$ see (26.53)
$\boldsymbol{\mathbb{B}}$, $\mathbb{B}_I$	Rank-i $(i = 1, \ldots, N)$ tensor
$\boldsymbol{b}^*$	Translation of the origin of a Cartesian coordinate system, $\boldsymbol{b}^* = (b_1^*, b_2^*, b_3^*)$
$\boldsymbol{D}$	Stretching tensor, strain rate tensor, rate of strain tensor, $\boldsymbol{D} =$ sym grad $\boldsymbol{v}$
$Diss$	Dissipation rate in $\mathcal{B}$ per unit volume
da	Surface element
dV	Volume element
E	Electric field density
$\mathcal{E}$	Elastic modulus for the microstructure, see (26.173)
F	Symbol for a function
F	Total mechanical energy of a material unit volume
$\boldsymbol{F}_i$ $(i = 1, \ldots, n)$	External and internal force acting on a mechanical system
$\boldsymbol{F}_i^{(a)}$, $\boldsymbol{F}_i^{(c)}$	Applied and constraint forces
$\boldsymbol{\mathcal{F}} = \boldsymbol{\mathcal{T}} + \boldsymbol{\mathcal{V}}$	Total mechanical energy of a material unit volume
f	Degrees of freedom for a mechanical system
$\boldsymbol{f}$	Specific body force per unit mass
$\boldsymbol{H}$	Magnetic field density
$i, j, \ldots$	Indices for vector and tensor components
L, $\mathcal{L}$	Lagrange function of a holonomic system, length of a system
$\mathcal{L} = \mathcal{T} - \mathcal{V}$	Lagrange function
$\boldsymbol{\ell}$, ℓ_{ij}	Tensorial body couple per unit mass
$\boldsymbol{\mathbb{M}}$, $\boldsymbol{M}$	Lagrangean operator on $\kappa(\boldsymbol{\mathcal{O}}, \dot{\boldsymbol{\mathbb{O}}})$ and $\kappa(\boldsymbol{Q},\ \dot{\boldsymbol{Q}})$, respectively, see (26.182), (26.20)
m	Upper limit of a counting number
$\boldsymbol{m}$, m_{ij}	Couple stress tensor, angular momentum flux
$\tilde{\boldsymbol{m}}$, $\tilde{m}_{ij}$	Dynamic viscous couple stress tensor
N	Upper limit of a counting number
$\boldsymbol{n}$, n_i	Director vector of unit length, unit vector perpendicular to the body surface $\partial\mathcal{B}$
$\boldsymbol{n}^+$	Unit vector perpendicular to the body surface $\partial\mathcal{B}$
$\boldsymbol{n}_{\parallel}$	Surface vector parallel to the surface
$\boldsymbol{n}_{\perp}$	Surface vector perpendicular to the surface
$\boldsymbol{\mathbb{O}}$, $\mathbb{O}_{ij\ldots N}$	Tensor valued order parameters
$\dot{\mathbb{O}}_I$	Time rate of change of $\mathbb{O}_I$, $\dot{\mathbb{O}}_I = \partial \mathbb{O}_I / \partial t + \operatorname{grad} \mathbb{O}_I \boldsymbol{v}$
$\overset{\circ}{\mathbb{O}}_I$	Corotational time derivative of $\mathbb{O}_I$, $\overset{\circ}{\mathbb{O}}_I = \dot{\mathbb{O}}_I - \sum_{k=1}^{n} W_{I_k^j} \mathbb{O}_{I_k^j}$

$\hat{\mathbb{O}}$	Co-deformational time derivative of $\mathbb{O}_I$, $\hat{\mathbb{O}} = \overset{\circ}{\mathbb{O}}_I + \sum_{k=1}^{n} a_k D_{I_k^j} \mathbb{O}_{I_k^j}$
P_2	Second-order Legendre polynomial
$\mathcal{P}_{\mathcal{B}}$	Power of working of the forces within the body $\mathcal{B}$
$\boldsymbol{p}$, p_i $(i = 1, \dots, n)$	Momentum of a mechanical system
$\boldsymbol{Q}$	Rank-2 tensorial order parameter, orthogonal transformation in $\mathbb{R}^3$
Q_j $(j = 1, \dots, f)$	Generalized jth force
$\boldsymbol{q}, q_1, q_2, \dots, q_m$	Generalized coordinates
$\dot{q}_1, \dots, \dot{q}_m$	Generalized velocities
RVE	Representative volume element
R_{PH}	Rayleigh dissipation function as parameterized in (26.167)
$\mathbb{R}^n$	Real Euclidian n-dimensional space
$R(\mathbb{O}, \hat{\mathbb{O}}, \boldsymbol{D})$	Specific Rayleigh dissipation potential (per unit volume)
$\boldsymbol{R}$, R_{ij}	Rank-2 orthogonal transformation
$\mathcal{R}(\boldsymbol{q}, \dot{\boldsymbol{q}})$	Rayleigh dissipative potential, a quadratic form of $\boldsymbol{q}$ and $\dot{\boldsymbol{q}}$
S, $\boldsymbol{S}$, S_{ij}	Scalar and rank-2 tensor valued order parameter
T, $\mathcal{T}(\boldsymbol{q}, \dot{\boldsymbol{q}})$	Kinetic energy of a rigid body—as a function of the generalized coordinates and velocities
$\boldsymbol{t}$, t_{ij}	Cauchy stress tensor
$\boldsymbol{t}^e$	Elastic stress contribution
$\boldsymbol{t}^v$, $\tilde{\boldsymbol{t}}$	Viscous stress, nonequilibrium stress
$\boldsymbol{t}^*$	Skew-symmetric part of the Cauchy stress, $\boldsymbol{t}^* = \boldsymbol{n} \times \partial R / \partial \overset{\circ}{\boldsymbol{n}}$
V	Volume
$\boldsymbol{v}$, v_i	Velocity vector
$\mathcal{V}(\boldsymbol{q})$	Potential energy of a body
W	Elastic energy, connected with the microstructure, $W(\mathbb{O}, \text{grad}\ \mathbb{O})$
$\mathcal{W}$	Working, power of working
W^s	Power of working of the surface forces per unit surface area, postulated as a potential, see (26.25)
$\mathcal{W}^s$	Total power of working of the surface forces
$\boldsymbol{W}^*$	Vorticity tensor $\boldsymbol{W}^* = \text{skw grad}\ \boldsymbol{v} = \frac{1}{2}(\text{grad}\ \boldsymbol{v} - \text{grad}^T \boldsymbol{v})$
$\boldsymbol{x} = (x_1, x_2, x_3)$	Cartesian coordinates in $\mathbb{R}^3$
$\boldsymbol{x}^*$	Rotated and shifted Cartesian coordinates in $\mathbb{R}^3$
$\boldsymbol{X}$, $\mathbb{X}$, X_i, $\mathbb{X}_i$	Generalized forces
$\boldsymbol{X}^b$, $\mathbb{X}^b$	Generalized intrinsic forces acting on a boundary $\partial\mathcal{B}$ of $\mathcal{B}$
$\boldsymbol{X}^s$, $\mathbb{X}^s$	Generalized intrinsic forces at a moving boundary
$\boldsymbol{Y}$, Y_i	Generalized frictional forces

Greek Symbols

α	Counting index for constituents
α_i $(i = 1, \dots, 6)$	Constant parameters in the viscous stress representation (26.91), expressible in terms of γ_j $(j = 1, \dots, 5)$ according to (26.92), (26.86)

α_i $(i = 1, \ldots, 7)$	Constant parameters in Leslie's viscous stress of his 1992 theory, see (26.119)
β, β_1, β_2	Two of total seven parameters in the Rayleigh dissipation function $R(\boldsymbol{n}, \overset{\circ}{\boldsymbol{n}}, \dot{S}, \boldsymbol{D})$ see (26.132)
$\gamma_i (i = 1, \ldots, 5)$	Constant parameters for an isotropic invariant $R(\boldsymbol{n}, \overset{\circ}{\boldsymbol{n}}, \boldsymbol{D})$ representation, see (26.132)
δ_{ij}	Kronecker delta, $\delta_{ij} = 1$ if $i = j$; $\delta_{ij} = 0$ if $i \neq j$
δ	Dirac function, variational symbol
ε_{ijk}	Levi-Cività tensor, epsilon tensor $= 1$ for cyclic permutation of the indices; $= -1$ for anti-cyclic permutation of the indices; $= 0$ for no permutation of the indices.
$\boldsymbol{\epsilon}$	Electric permittivity (magnetic susceptibility) anisotropy tensor
$\epsilon_{\parallel}, \epsilon_{\perp}$	Parallel and perpendicular to the molecular symmetry axis
θ	Angle between the LC axis and the local director
κ	Bulk viscosity of a Newtonian fluid
$\kappa(\mathbb{O}, \dot{\mathbb{O}})$	Kinetic energy per unit mass due to the microstructure
λ	Lagrange parameter
μ	Shear viscosity of a Newtonian fluid
$\boldsymbol{\varpi}$	Objective form of an angular velocity at a material element
ρ	Mass density of the LC fluid, $[\mathrm{M/L}^3]$
ϕ	Potential energy of the body force per unit mass
$\chi(\mathbb{O})$	Potential energy of the external actions exerted on $\mathbb{O}$
σ	Constant arising in the definition of $\overset{\diamond}{\mathbb{O}}$
$\sigma(\rho)$	Potential energy per unit mass due to the compressibility of the fluid material
$\boldsymbol{\tau}, \tau_i = \epsilon_{ijk} t_{kj}$	Axial vector of the skew-symmetric part of the Cauchy stress tensor
$\zeta_{[i]}$ $(i = 1, 2, 3)$	Constant coefficients in the parameterization of $R(\boldsymbol{Q}, \overset{\circ}{\boldsymbol{Q}}, \boldsymbol{D})$ see (26.163)
$\zeta_{[ij]}$	Constant coefficients in the parameterization of $\boldsymbol{R}(\boldsymbol{Q}, \overset{\circ}{\boldsymbol{Q}}, \boldsymbol{D})$ $(ij = 21, 31, 32, 33, 34)$ see (26.163)

Miscellaneous Symbols

$\mathrm{d}/\mathrm{d}t$	Total time derivative (following an LC particle)
$\partial \mathcal{B}$	Boundary of volume V
LC	Liquid crystal
$\boldsymbol{A}^T$	Transpose of $\boldsymbol{A}$
$\boldsymbol{A}^{-T}$	$= (\boldsymbol{A}^T)^{-1} = (\boldsymbol{A}^{-1})^T$
$\lVert \boldsymbol{b} \rVert$	Norm of $\boldsymbol{b}$
$\boldsymbol{I}$	Multi-index $= (I_1, I_1, \ldots, I_n)$

I_{k^j}	$= I_1, \dots, I_{k-1}, j, I_{k+1}, \dots, I_n$
$f_{[ij]}$	Skew-symmetric part of f_{ij} $f_{[ij]} = \frac{1}{2}(f_{ij} - f_{ji})$
$f_{(ij)}$	Symmetric part of f_{ij} $f_{(ij)} = \frac{1}{2}(f_{ij} + f_{ji})$
$\circ$	Symbol for composition operator
$\odot$	Let $\mathbb{A}, \mathbb{B}$ two I-rank tensors. Then, $(\text{grad}\,\mathbb{A} \odot \text{grad}\,\mathbb{B})_{k\ell} = \mathbb{A}_{I,k}\mathbb{B}_{I,\ell}$
$\overset{\sqcap}{\boldsymbol{A}}$	Deviator of the rank-2 tensor $\boldsymbol{A}$
$\langle\, (\cdot) \,\rangle$	Spatial and temporal average of $(\cdot)$

26.1 Nematic Liquid Crystals with Tensorial Order Variables

26.1.1 Motivation and Literature Review

Up to now, the theory of LCs has been based on the ERICKSEN–LESLIE–PARODI formulation, in which the polar nature of this model is based on the assumption that the long molecules can sufficiently accurately be described by one-dimensional directors, which are equipped with a one-dimensional mass density along their axis. It was, however, already explained in Sect. 25.1 to Chap. 25 that in a liquid crystal continuum consisting of individual directors of nearly parallel orientation the directors of a representative volume element (RVE) can be summarized by the exterior product of their vectors with unit length, e.g.,

$$S_{ij} = \frac{1}{N} \sum_{\alpha=1} N \left(\nu_i^{(\alpha)} \nu_j^{(\alpha)} - \frac{1}{3}\delta_{ij} \right),$$

in which ν_i^α is a unit vector of the director α and N is the number of individual directors within the RVE. The above tensor is called an *order parameter*, here as a rank-2 deviator, whose trace vanishes ($S_{ii} = 0$) in an isotropic state in which molecules have uniformly random orientation. Order parameters based on other variables have equally been defined, see Eqs. (25.1)–(25.3), [5, 41]; moreover, tensors $\mathbb{O}$ of rank larger than 2 can also be defined, [11, 44]. All these tensors will here be denoted as $\mathbb{O}$ irrespective of their rank.

The introduction of tensorial order parameters for the description of nematic LCs is obviously also needed, if the directors are interpreted as long, three-dimensional bodies, e.g., ellipsoids or shafts. This has led to the theoretical formulations of rank-2 alignment tensors. SONNET et al. (2004) [46] write, “A general continuum theory for an LC described by a second rank alignment tensor [...] is still missing. The case where the alignment tensor is uniaxial with a variable degree of orientation has been treated by ERICKSEN in a comprehensive way [15]. For the full alignment tensor nonequilibrium thermodynamic methods have been used by HESS [21, 22] and later also by Olmsted and Goldbart [36] to obtain first constitutive theories for homogeneous alignments which have been generalized by Hess and Pardowitz [24] to include also spatial variation. All these attempts have been impaired by not yielding the full anisotropy of viscosities predicted by ELP theory and confirmed experimentally. The extension to a co-deformational model was also proposed [23], which recovered the complete anisotropy of viscosities, but failed to be otherwise fully consistent with the phenomenological ELP theory [38].”

Sonnet et al. [46] review further recent literature [2, 17, 39, 49], in which analytical dynamic methods (Poisson bracket method, introducing a dissipation invariant) are employed using the statistical averaging methods to deduce the coarse-grained averages from the corresponding microscopic counterparts. In a similar vein are also papers in which closure approximations were used to obtain equations from the Fokker–Planck equation for the rank-2 alignment tensor [10, 22, 30].

Sonnet et al. [46] mention that “one major problem in extending the reasoning behind the ELP theory to the alignment tensor description is that the balance of angular momentum can only govern a rigid rotation of the material element, that is the eigenframe of the alignment tensor, while changes in the type of alignment reflected by the eigenvalues, would remain undetermined. The key [...] is the derivation of both the stress tensor and the equation describing the alignment evolution from a single variational principle. There is no need to resort to the balance of angular momentum, though it remains necessarily valid, and even the balance of linear momentum is only invoked to identify the stress tensor. Essentially the same idea has been used by Vertogen [51] for a uniaxial alignment tensor with constant modulus. He started from an analogy to classical Lagrange mechanics with a Rayleigh dissipation function.” According to [46], this method misses proper derivation of the elastic stress and proper boundary conditions. Moreover, Sonnet and Virga [44] mention that the role played by the dissipation function within the classical director theory of LCs was first realized by Ericksen [14].

In the ensuing analysis, we follow Sonnet et al. [46] on the basis of work presented by them in [44], which itself is based on work by Vertogen [51] and Leslie [28].

26.1.2 Variational Principle

Sonnet and Virga [44] present their variational principle, applicable to nematic LCs as an extension of Lord Rayleigh’s [50] dissipation principle, who put it forward for discrete dissipative systems. Prerequisites for its ensuing development are two assumptions,

- that the total mechanical power of working—excluding dissipation—can be written as a sum of products of generalized forces with their generalized velocities and
- that these forces are balanced by frictional forces which possess a quadratic velocity potential.

Fundamental for the theoretical model describing LCs are the LAGRANGE equations. They hold for a holonomic dynamical system consisting of m generalized coordinates $(q_1, \dots, q_m)$ which can be written in vector form as $\boldsymbol{q}$. The generalized velocities $\dot{\boldsymbol{q}} = (\dot{q}_1 \dots, \dot{q}_m)$ and $\boldsymbol{q}$ are vectors in $\mathbb{R}^m$. Provided that all external forces are conservative, the total mechanical power of working can be written as the rate of change of the total mechanical energy $\mathcal{F}$. We let $\mathcal{V}(\boldsymbol{q})$ be the potential energy of the system and $\mathcal{T}(\boldsymbol{q}, \dot{\boldsymbol{q}})$ its kinetic energy, which is supposed to be a positive-definite quadratic form in the velocities $\dot{q}_i$ $(i = 1, \dots, m)$. It is known from analytical mechanics that

$$\dot{\mathcal{F}} = \dot{\mathcal{T}} + \dot{\mathcal{V}} = \sum_{i=1}^{m} \left(\frac{\mathrm{d}}{\mathrm{d}t} \left(\frac{\partial \mathcal{L}}{\partial \dot{q}_i} \right) - \frac{\partial \mathcal{L}}{\partial q_i} \right) \dot{q}_i, \quad \mathcal{L} = \mathcal{T} - \mathcal{V}, \tag{26.1}$$

in which $\mathcal{L}$ is called the LAGRANGE function.[1]

The generalized forces X_i conjugate to the velocities $\dot{q}_i$ are defined by

$$\dot{\mathcal{F}} = \sum_{i=1}^{m} X_i \dot{q}_i = \boldsymbol{X} \cdot \dot{\boldsymbol{q}}, \qquad X_i : = \frac{\mathrm{d}}{\mathrm{d}t} \left(\frac{\partial \mathcal{L}}{\partial \dot{q}_i} \right) - \frac{\partial \mathcal{L}}{\partial q_i}. \tag{26.2}$$

Thus, in a dissipation-free system, $\dot{\mathcal{F}}$ can be identified with the power of working $\mathcal{W}$ of the generalized forces $\boldsymbol{X}$. So, (26.1) can simply be written as

$$\mathcal{W} = \dot{\mathcal{F}} = \sum_{i=1}^{m} X_i \dot{q}_i = \boldsymbol{X} \cdot \dot{\boldsymbol{q}}. \tag{26.3}$$

When in addition to these forces the system is also subject to dissipation, i.e., if frictional generalized forces, Y_i $(i = 1, \dots, m)$ are also at work, these forces satisfy the balance equation

$$(X_i + Y_i) = 0 \quad (i = 1, \dots, m) \quad \longrightarrow \quad \boldsymbol{X} + \boldsymbol{Y} = \boldsymbol{0}. \tag{26.4}$$

If we now introduce the so-called RAYLEIGH dissipation potential, a positive-definite quadratic form $\mathcal{R}$ of q_i and $\dot{q}_i$ and require[2]

$$Y_i = \frac{\partial \mathcal{R}}{\partial \dot{q}_i}, \quad \text{or} \quad \boldsymbol{Y} = \frac{\partial \mathcal{R}}{\partial \dot{\boldsymbol{q}}} \tag{26.5}$$

as a "constitutive assignment", combination of the equations (26.2)–(26.5) yields

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[1] The derivation of (26.1) is presented in almost every book treating the "dynamics of mechanical systems," see e.g., [54] or any other book dealing with "dynamics of rigid bodies." For ease to the reader, we give its derivation in Appendix 26.A.

[2] It turns out that the requirement of the existence of the RAYLEIGH dissipation potential corresponds to the assumption of the ONSAGER relations.

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial \mathcal{L}}{\partial \dot{q}_i}\right) - \frac{\partial \mathcal{L}}{\partial q_i} + \frac{\partial \mathcal{R}}{\partial \dot{q}_i} = 0 \quad (i = 1, \ldots, m). \tag{26.6}$$

This equation is the standard form of the LAGRANGE equations of a dissipative system ([54], p. 231). Multiplying (26.6) scalarly with $\dot{q}_i$ and summing over the index i yields, since $\mathcal{R}$ is a homogeneous function of degree two,

$$\sum_{i=1}^{m} \frac{\partial \mathcal{R}}{\partial \dot{q}_i}\dot{q}_i = 2\mathcal{R}, \tag{26.7}$$

and the balance of energy in the form

$$\sum_{i=1}^{m} \underbrace{\left[\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial \mathcal{L}}{\partial \dot{q}_i}\right) - \frac{\partial \mathcal{L}}{\partial q_i}\right]}_{X_i} \dot{q}_i + 2\mathcal{R} \overset{(26.2)}{=} \underline{\dot{\mathcal{F}} + 2\mathcal{R} = 0}. \tag{26.8}$$

For the variational formulation to a continuous dissipative system, the RAYLEIGH dissipation function $\mathcal{R}$ must be minimized for variations $\delta\dot{\boldsymbol{q}}$ of the vector $\dot{\boldsymbol{q}} \in \mathbb{R}^m$ constrained such that the generalized forces $\boldsymbol{X}$ and their power of working $\dot{\mathcal{F}}$ remain unchanged, see SONNET and VIRGA [44, 45]. Using a LAGRANGE parameter λ, this implies

$$\delta\mathcal{R} + \lambda\,\delta\mathcal{W} = \left(\frac{\partial \mathcal{R}}{\partial \dot{\boldsymbol{q}}} + \lambda \boldsymbol{X}\right) \cdot \delta\dot{\boldsymbol{q}} = 0. \tag{26.9}$$

Since $\delta\dot{\boldsymbol{q}}$ is arbitrary, this equation implies

$$\lambda \boldsymbol{X} + \frac{\partial \mathcal{R}}{\partial \dot{\boldsymbol{q}}} = \boldsymbol{0}. \tag{26.10}$$

The LAGRANGE parameter λ which is still unknown is determined by multiplying Eq. (26.10) with $\dot{\boldsymbol{q}}$ and requiring the energy balance (26.8) to hold. Therefore,

$$\lambda \boldsymbol{X} \cdot \dot{\boldsymbol{q}} + \underbrace{\frac{\partial \mathcal{R}}{\partial \dot{\boldsymbol{q}}} \cdot \dot{\boldsymbol{q}}}_{2\mathcal{R}} = \lambda \underbrace{\boldsymbol{X} \cdot \dot{\boldsymbol{q}}}_{\overset{(26.3)}{=} \dot{\mathcal{F}}} + 2\mathcal{R} \quad \overset{(26.8)}{\Longrightarrow} \quad \lambda = 1. \tag{26.11}$$

With this value of λ $(= 1)$ Eq. (26.10) becomes the equation of motion.

26.1.3 Liquid Crystals with Tensorial Order Parameters and Dissipative Microstructure

It is our intention in this section to apply the variational principle stated in the preceding section. Following [44], we consider a bodily region $\mathcal{B}$ with smooth boundary $\partial\mathcal{B}$. The microstructure will be described by a finite number of rank-i tensors $(i = 2, \ldots, n)$, which will be denoted by $\mathbb{O}$ (irrespective of the value of the index

i). Thus, we consider a material of order parameter space equal to the linear space of all rank-i tensors with $i = (2, \dots, n)$. The generalized velocities of the material space are the mass velocity $\boldsymbol{v}$ and the material derivative of $\mathbb{O}$

$$\dot{\mathbb{O}} = \frac{\partial \mathbb{O}}{\partial t} + (\operatorname{grad} \mathbb{O}) \cdot \boldsymbol{v} \tag{26.12}$$

or in Cartesian components

$$\dot{\mathbb{O}}_I = \frac{\partial \mathbb{O}_I}{\partial t} + \mathbb{O}_{I,j} v_j . \tag{26.13}$$

Here, a comma denotes differentiation with respect to a space variable (here x_j), and I is the multi-index $I = (I_1, \dots, I_n)$. Below, we will also use the notation I_{k^j} defined by

$$I_{k^j} := (I_1, \dots, I_{k-1}, j, I_{k+1}, \dots, I_n); \tag{26.14}$$

this means that the index at the kth position is replaced by the index j. The dissipation function $\mathcal{R}$ and the free energy W must be materially objective functions of their variables. We shall confine attention to dependences on grad $\boldsymbol{v}$, $\mathbb{O}$ and $\dot{\mathbb{O}}$. Invariance under Euclidian transformations,

$$\boldsymbol{x}^* = \boldsymbol{Q}(t)\boldsymbol{x} + \boldsymbol{b}^*(t), \quad \boldsymbol{x} = \boldsymbol{Q}^T(\boldsymbol{x}^* - \boldsymbol{b}^*), \tag{26.15}$$

shows that of the stretching, $\boldsymbol{D}$ and vorticity, $\boldsymbol{W}$ tensors defined by

$$\boldsymbol{D} = \tfrac{1}{2}(\operatorname{grad} \boldsymbol{v} + \operatorname{grad}^T \boldsymbol{v}) \quad \text{and} \quad \boldsymbol{W} = \tfrac{1}{2}(\operatorname{grad} \boldsymbol{v} - \operatorname{grad}^T \boldsymbol{v}).$$

$\boldsymbol{D}$ is objective, but $\boldsymbol{W}$ is not objective, viz.,

$$\boldsymbol{D}^* = \boldsymbol{Q}\boldsymbol{D}\boldsymbol{Q}^T, \quad \boldsymbol{W}^* = \boldsymbol{Q}\boldsymbol{W}\boldsymbol{Q}^T + \dot{\boldsymbol{Q}}\boldsymbol{Q}^T, \tag{26.16}$$

as can easily be demonstrated.[3] It is known that $\dot{\mathbb{O}}$ is not frame indifferent. A *frame indifferent time derivative* of $\mathbb{O}$ is the *corotational time derivative*, defined by

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[3] With the aid of (26.15) we find in Cartesian coordinates x_i $(i = 1, 2, 3)$ and $x^*_{i^*}$ $(i^* = 1, 2, 3)$

$$\begin{aligned}
\frac{\partial v^*_{i^*}}{\partial x^*_{j^*}} &= \frac{\partial}{\partial x^*_{j^*}} \left(Q_{i^*j} v_j + \dot{Q}_{i^*j} x_j + \dot{b}_{i^*} \right) = \frac{\partial}{\partial x_k} \left(Q_{i^*j} v_j + \dot{Q}_{i^*j} x_j + \dot{b}_{i^*} \right) \underbrace{\frac{\partial x_k}{\partial x^*_{j^*}}}_{Q_{j^*k}} \\
&= \left(Q_{i^*j} \frac{\partial v_j}{\partial x_k} + \dot{Q}_{i^*k} \right) Q_{j^*k} = \underline{Q_{i^*j} \frac{\partial v_j}{\partial x_k} Q_{j^*k} + \dot{Q}_{i^*k} Q_{j^*k}} \, , \\
\frac{\partial v^*_j}{\partial x_{i^*}} &= Q_{j^*j} \frac{\partial v_j}{\partial x_k} Q_{i^*k} + \dot{Q}_{j^*k} Q_{i^*k} \overset{j \leftrightarrow k}{=} Q_{j^*k} \frac{\partial v_k}{\partial x_j} Q_{i^*j} + \underbrace{\dot{Q}_{j^*k} Q_{i^*k}}_{-Q_{j^*k} \dot{Q}_{i^*k}}
\end{aligned}$$

$$\overset{\circ}{\mathbb{O}}_I = \dot{\mathbb{O}}_I - \sum_{k=1}^{n} W_{I_{kj}} \mathbb{O}_{I_{kj}} \,. \tag{26.17}$$

Another one is the *co-deformational time derivative*

$$\hat{\mathbb{O}}_I = \overset{\circ}{\mathbb{O}}_I + \sum_{k=1}^{n} a_k D_{I_{kj}} \mathbb{O}_{I_{kj}} \,, \tag{26.18}$$

in which a_k are scalar coefficients, which are of constitutive nature and may depend on objective scalar quantities. The additional summation term in (26.18) is a measure to what extent the deformation of the fluid affects the microstructure.

The proof of the material frame indifference of the corotational derivative (26.17), $\overset{\circ}{\mathbb{O}}_I$, follows the procedure outlined in the footnote 3 of this chapter, but it is a bit cumbersome in view of the occurrence of the multi-indices; that of the co-deformational time derivative (26.18) is trivial, because the contraction of the objective tensors $\boldsymbol{D}$ and $\mathbb{O}$ is automatically objective. So $\hat{\mathbb{O}}_I$ is objective once the objectivity of $\overset{\circ}{\mathbb{O}}$ has been proved.

To apply the principle of virtual work (power), it is convenient to write for the total energy in $\mathcal{B}$

$$\begin{aligned} \mathcal{F} &= \int_{\mathcal{B}} F \mathrm{d}V, \quad \text{with} \\ F &= \rho\Big(\boldsymbol{v}\cdot\boldsymbol{v} + \phi + \sigma(\rho) + \kappa(\mathbb{O}, \dot{\mathbb{O}}) + \chi(\mathbb{O}) + W(\mathbb{O}, \operatorname{grad}\mathbb{O})\Big), \end{aligned} \tag{26.19}$$

in which

- ρ is the mass density,
- $\frac{1}{2}\boldsymbol{v}\cdot\boldsymbol{v}$ the translational kinetic energy of the fluid,
- ϕ the potential energy of the body force, $\boldsymbol{f} = -\operatorname{grad}\phi$,
- σ the potential energy due to the compressibility of the material,
- κ the kinetic energy connected with the microstructure,
- χ the potential energy of the external actions exerted on $\mathbb{O}$,
- W the elastic energy connected with the microstructure.

Among these variables, σ as a function of the mass density ρ is automatically a frame indifferent energy. W will be required to be frame indifferent; in principle, it could also depend on higher order forces and moments (couple stresses, double forces, etc.) necessary within $\mathcal{B}$ and corresponding flux terms on the bounding surfaces $\partial\mathcal{B}$ of $\mathcal{B}$. More on this is contained in [18, 19].

$$= Q_{i^*j}\frac{\partial v_k}{\partial x_j}Q_{j^*k} - \dot{Q}_{i^*k}Q_{j^*k} = \underline{Q_{i^*j}\frac{\partial v_k}{\partial x_j}Q_{j^*k} + \dot{Q}_{j^*k}Q_{i^*k}} \,.$$

The underbraced term follows from $Q_{i^*k}Q_{j^*k} = \delta_{i^*j^*}$ and relations (26.16) are immediate consequences of the underlined terms.

Next, we evaluate the total derivative of $\mathcal{F}$. The individual terms give the following contributions:

- $\dfrac{\mathrm{d}}{\mathrm{d}t}\displaystyle\int_{\mathcal{B}} \tfrac{1}{2}\rho\,(\boldsymbol{v}\cdot\boldsymbol{v})\,\mathrm{d}V \overset{*}{=} \int_{\mathcal{B}} \tfrac{1}{2}\rho\,(\boldsymbol{v}\cdot\boldsymbol{v})^{\cdot}\,\mathrm{d}V = \int_{\mathcal{B}} \rho\dot{\boldsymbol{v}}\cdot\boldsymbol{v}\,\mathrm{d}V,$
- $\dfrac{\mathrm{d}}{\mathrm{d}t}\displaystyle\int_{\mathcal{B}} \rho\phi\,\mathrm{d}V \overset{*}{=} \int_{\mathcal{B}} \rho\dot{\phi}\,\mathrm{d}V = \int_{\mathcal{B}} \rho\left(\frac{\partial\phi}{\partial t} + \mathrm{grad}\,\phi\cdot\boldsymbol{v}\right)\mathrm{d}V = -\int_{\mathcal{B}} \rho\boldsymbol{f}\cdot\boldsymbol{v}\,\mathrm{d}V,$
- $\dfrac{\mathrm{d}}{\mathrm{d}t}\displaystyle\int_{\mathcal{B}} \rho\sigma(\rho)\,\mathrm{d}V \overset{*}{=} \int_{\mathcal{B}} \rho\dot{\sigma}(\rho)\,\mathrm{d}V = \int_{\mathcal{B}} \rho\,\underbrace{\frac{\mathrm{d}\sigma}{\mathrm{d}\rho}}_{\sigma'}\,\dot{\rho}\,\mathrm{d}V = -\int_{\mathcal{B}} \rho^2\sigma'(\rho)\mathrm{div}\,\boldsymbol{v}\,\mathrm{d}V,$
- $\dfrac{\mathrm{d}}{\mathrm{d}t}\displaystyle\int_{\mathcal{B}} \rho\chi(\mathbb{O})\,\mathrm{d}V \overset{*}{=} \int_{\mathcal{B}} \rho\dot{\chi}(\mathbb{O})\,\mathrm{d}V = \int_{\mathcal{B}} \rho\frac{\mathrm{d}\chi}{\mathrm{d}\mathbb{O}}\dot{\mathbb{O}}\,\mathrm{d}V,$
- $\dfrac{\mathrm{d}}{\mathrm{d}t}\displaystyle\int_{\mathcal{B}} W\,\mathrm{d}V \overset{*}{=} \int_{\mathcal{B}} \left(\frac{\partial W}{\partial\mathbb{O}}\dot{\mathbb{O}} + \frac{\partial W}{\partial\mathrm{grad}\,\mathbb{O}}\,(\mathrm{grad}\,\mathbb{O})^{\cdot} + W\mathrm{div}\,\boldsymbol{v}\right)\mathrm{d}V,$
- $\dfrac{\mathrm{d}}{\mathrm{d}t}\displaystyle\int_{\mathcal{B}} \rho\kappa\left(\mathbb{O},\dot{\mathbb{O}}\right)\mathrm{d}V \overset{*}{=} \int_{\mathcal{B}} \rho\left(\kappa(\mathbb{O},\dot{\mathbb{O}})\right)^{\cdot}\,\mathrm{d}V$

$$= \int_{\mathcal{B}} \rho\underbrace{\left\{\left(\frac{\partial\kappa}{\partial\dot{\mathbb{O}}}\right)^{\cdot} - \frac{\partial\kappa}{\partial\mathbb{O}}\right\}}_{\mathbb{M}}\cdot\dot{\mathbb{O}}\,\mathrm{d}V = \int_{\mathcal{B}} \rho\mathbb{M}\cdot\dot{\mathbb{O}}\,\mathrm{d}V. \tag{26.20}$$

In these equations, we have used at the step ($\overset{*}{=}$) that

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathcal{B}} \rho f\mathrm{d}V = \int_{\mathcal{B}} \rho\dot{f}\mathrm{d}V,$$

for differentiable ρ and f. Moreover, the mass balance $\dot{\rho} = -\rho\mathrm{div}\,\boldsymbol{v}$ has also been used, and it was assumed that $\partial\phi/\partial t \equiv 0$, i.e., the force potential does not explicitly depend on time. The last of the above itemized statements requires some deeper justification. The basis of it is that $\mathbb{O}$ and $\dot{\mathbb{O}}$ are interpreted as generalized coordinates and generalized velocities in a LAGRANGE an formulation, see (26.206),

$$\left(\frac{\partial T}{\partial\dot{\mathbb{O}}}\right)^{\cdot} - \frac{\partial T}{\partial\mathbb{O}} = \mathbb{Q}, \tag{26.21}$$

in which T is now identified with the specific energy of the micromotion, κ and $\mathbb{Q} = \rho\mathbb{M}$ is the associated generalized microforce [More on this in a fundamental manner can be looked up in [4, 22], pp. 16–20.].

Putting all the above energy rates together yields

$$\begin{aligned}\dot{\mathcal{F}} = \int_{\mathcal{B}} \Bigg\{&\rho\,(\dot{\boldsymbol{v}} - \boldsymbol{f})\cdot\boldsymbol{v} + \rho\mathbb{M}\cdot\dot{\mathbb{O}} + \left(\rho\frac{\partial\chi}{\partial\mathbb{O}} + \frac{\partial W}{\partial\mathbb{O}}\right)\cdot\dot{\mathbb{O}}.\\ &+\frac{\partial W}{\partial\mathrm{grad}\,\mathbb{O}}\cdot(\mathrm{grad}\,\mathbb{O})^{\cdot} + \left(W - \rho^2\sigma'\right)\mathrm{div}\,\boldsymbol{v}\Bigg\}\,\mathrm{d}V.\end{aligned} \tag{26.22}$$

In the classical principle of virtual power, $\dot{\mathcal{F}}$ is balanced by the power of working of the forces within $\mathcal{B}$ which is given here by

$$\mathcal{P}_{\mathcal{B}} = \int_{\mathcal{B}} \left\{ \boldsymbol{X} \cdot \boldsymbol{v} + \mathbb{X} \cdot \dot{\mathbb{O}} \right\} \mathrm{d}V. \tag{26.23}$$

However, as SONNET and VIRGA [44] emphasize, $\dot{\mathcal{F}}$ "fails to be the total power input for the system [here]; it must be supplemented with the *surface power* $\mathcal{W}^s$ which for a movable boundary $\partial\mathcal{B}$ takes the general form

$$\mathcal{W}^s = \int_{\partial\mathcal{B}} \left\{ \boldsymbol{X}^s \cdot \boldsymbol{v} + \mathbb{X}^s \cdot \dot{\mathbb{O}} \right\} \mathrm{d}a, \tag{26.24}$$

where $\boldsymbol{X}^s$ $\mathbb{X}^s$ are generalized external forces associated with the velocities $\boldsymbol{v}$ and $\dot{\mathbb{O}}$, respectively. While $\boldsymbol{X}^s$ is a vector in the ordinary space, $\mathbb{X}^s$ is an ith ($i = 2, \dots, n$) rank tensor".

If the surface power can be derived from a surface potential, i.e., if

$$\mathcal{W}^s = \frac{\mathrm{d}}{\mathrm{d}t} \int_{\partial\mathcal{B}} W^s(\boldsymbol{x}, \mathbb{O}) \mathrm{d}a, \tag{26.25}$$

in which W^s is a scalar function of the position $\boldsymbol{x}$ in space and the tensorial order parameter $\mathbb{O}$ then the relations

$$\boldsymbol{X}^s = \frac{\partial W^s}{\partial \boldsymbol{x}} \quad \text{and} \quad \mathbb{X}^s = \frac{\partial W^s}{\partial \mathbb{O}} \tag{26.26}$$

ensue. Thus, the rate of energy in the bulk $\dot{\mathcal{F}}$ and the power of working on the surface $\mathcal{W}^s$ are given by

$$\begin{aligned} \dot{\mathcal{F}} + \mathcal{W}^s = \int_{\mathcal{B}} \Bigg\{ & \rho(\dot{\boldsymbol{v}} - \boldsymbol{f}) \cdot \boldsymbol{v} + \rho \mathbb{M} \cdot \dot{\mathbb{O}} + \left(\rho \frac{\partial \chi}{\partial \mathbb{O}} + \frac{\partial W}{\partial \mathbb{O}} \right) \cdot \dot{\mathbb{O}} \\ & + \frac{\partial W}{\partial \operatorname{grad} \mathbb{O}} \underbrace{\Big(\operatorname{grad} \dot{\mathbb{O}} - (\operatorname{grad} \mathbb{O}) \cdot (\operatorname{grad} \boldsymbol{v}) \Big)}_{(\operatorname{grad} \mathbb{O})^{\cdot}} + (W - \rho^2 \sigma') \operatorname{div} \boldsymbol{v} \Bigg\} \mathrm{d}V \\ & + \int_{\partial\mathcal{B}} \left(\boldsymbol{X}^s \cdot \boldsymbol{v} + \mathbb{X}^s \cdot \dot{\mathbb{O}} \right) \mathrm{d}a. \end{aligned} \tag{26.27}$$

In this expression, several integrations by parts need to be performed; these are as follows (we employ now Cartesian tensor notation):

- $$\begin{aligned}&\int_{\mathcal{B}} \left(W-\rho^2\sigma'\right) v_{i,i}\mathrm{d}V\\ &=\int_{\mathcal{B}} \left(\left(W-\rho^2\sigma'\right) v_i\right)_{,i} - \left(W-\rho^2\sigma'\right)_{,i} v_i\mathrm{d}V\\ &\overset{\text{Gauss}}{=} -\int_{\mathcal{B}} \left(W-\rho^2\sigma'\right)_{,i} v_i\mathrm{d}V + \int_{\partial\mathcal{B}} \left(W-\rho^2\sigma'\right) v_i n_i\mathrm{d}a\\ &= -\int_{\mathcal{B}} \operatorname{grad}\left(W-\rho^2\sigma'\right)\cdot \boldsymbol{v}\,\mathrm{d}V + \int_{\partial\mathcal{B}} \left(W-\rho^2\sigma'\right) \boldsymbol{v}\cdot\boldsymbol{n}\,\mathrm{d}a,\end{aligned}$$

- $$\int_{\mathcal{B}} \frac{\partial W}{\partial \mathbb{O}_{I,\ell}}\left(\dot{\mathbb{O}}_{I,\ell}-\mathbb{O}_{I,k}v_{k,\ell}\right) = \underbrace{\int_{\mathcal{B}} \frac{\partial W}{\partial \mathbb{O}_{I,\ell}}\dot{\mathbb{O}}_{I,\ell}\mathrm{d}V}_{(1)} - \underbrace{\int_{\mathcal{B}} \frac{\partial W}{\partial \mathbb{O}_{I,\ell}}\mathbb{O}_{I,k}v_{k,\ell}\,\mathrm{d}V}_{(2)},$$

$$\begin{aligned}(1) &= \int_{\mathcal{B}} \left\{\left(\frac{\partial W}{\partial \mathbb{O}_{I,\ell}}\dot{\mathbb{O}}_I\right)_{,\ell} - \left(\frac{\partial W}{\partial \mathbb{O}_{I,\ell}}\right)_{,\ell}\dot{\mathbb{O}}_I\right\}\mathrm{d}V\\ &\overset{\text{Gauss}}{=} \int_{\partial\mathcal{B}} \left\{\frac{\partial W}{\partial \mathbb{O}_{I,\ell}}\dot{\mathbb{O}}_I n_\ell\right\}\mathrm{d}a - \int_{\mathcal{B}} \left(\frac{\partial W}{\partial \mathbb{O}_{I,\ell}}\right)_{,\ell}\dot{\mathbb{O}}_I\,\mathrm{d}V\\ &= \int_{\partial\mathcal{B}} \underbrace{\left(\frac{\partial W}{\partial \operatorname{grad}\boldsymbol{\mathbb{O}}}\boldsymbol{n}\right)}_{\boldsymbol{\mathbb{X}}^b}\cdot\dot{\boldsymbol{\mathbb{O}}}\,\mathrm{d}a - \int_{\mathcal{B}} \operatorname{div}\left(\frac{\partial W}{\partial \operatorname{grad}\boldsymbol{\mathbb{O}}}\right)\cdot\dot{\boldsymbol{\mathbb{O}}}\,\mathrm{d}V,\\ (2) &= \int_{\mathcal{B}} \frac{\partial W}{\partial \mathbb{O}_{I,\ell}}\mathbb{O}_{I,k}v_{k,\ell}\,\mathrm{d}V\\ &= \int_{\mathcal{B}} \left\{\left(\frac{\partial W}{\partial \mathbb{O}_{I,\ell}}\mathbb{O}_{I,k}v_k\right)_{,\ell} - \left(\left(\frac{\partial W}{\partial \mathbb{O}_{I,\ell}}\right)\mathbb{O}_{I,k}\right)_{,\ell}v_k\right\}\mathrm{d}V\\ &\overset{\text{Gauss}}{=} \int_{\partial\mathcal{B}} \left(\frac{\partial W}{\partial \mathbb{O}_{I,\ell}}\mathbb{O}_{I,k}v_k n_\ell\right)\mathrm{d}a - \int_{\mathcal{B}} \left(\frac{\partial W}{\partial \mathbb{O}_{I,\ell}}\mathbb{O}_{I,k}\right)_{,\ell}v_k\,\mathrm{d}V.\end{aligned}$$

Introducing the notation

$$\mathbb{O}_{I,k}\frac{\partial W}{\partial \mathbb{O}_{I,\ell}} = \left(\operatorname{grad}\boldsymbol{\mathbb{O}}\odot\frac{\partial W}{\partial \operatorname{grad}\boldsymbol{\mathbb{O}}}\right)_{k\ell}, \tag{26.28}$$

one gets

$$(2) = \int_{\partial\mathcal{B}} \left(\operatorname{grad}\boldsymbol{\mathbb{O}}\odot\frac{\partial W}{\partial \operatorname{grad}\boldsymbol{\mathbb{O}}}\right)\boldsymbol{n}\cdot\boldsymbol{v}\,\mathrm{d}a - \int_{\mathcal{B}} \operatorname{div}\left\{\operatorname{grad}\boldsymbol{\mathbb{O}}\odot\frac{\partial W}{\partial \operatorname{grad}\boldsymbol{\mathbb{O}}}\right\}\cdot\boldsymbol{v}\,\mathrm{d}V.$$

Substituting the above expressions into (26.27), one obtains

$$\begin{aligned}\dot{\mathcal{F}} + \mathcal{W}^s = &\int_{\mathcal{B}} \left\{ \boldsymbol{X}\cdot\boldsymbol{v} + \mathbb{X}\cdot\dot{\mathbb{O}}\right\} \mathrm{d}V \\ &+ \int_{\partial\mathcal{B}} \left\{(\boldsymbol{X}^b+\boldsymbol{X}^s)\cdot\boldsymbol{v} + (\mathbb{X}^b+\mathbb{X}^s)\cdot\dot{\mathbb{O}}\right\}\mathrm{d}a,\end{aligned} \tag{26.29}$$

in which

$$\begin{aligned}\boldsymbol{X} &= \rho(\dot{\boldsymbol{v}} - \boldsymbol{f}) - \operatorname{grad}\left(W - \rho^2\sigma'\right) + \operatorname{div}\left(\operatorname{grad}\mathbb{O} \odot \frac{\partial W}{\partial \operatorname{grad}\mathbb{O}}\right), \\ \mathbb{X} &= \rho\left(\mathbb{M} + \frac{\partial\chi}{\partial\mathbb{O}}\right) + \frac{\partial W}{\partial\mathbb{O}} - \operatorname{div}\left(\frac{\partial W}{\partial\operatorname{grad}\mathbb{O}}\right), \\ \boldsymbol{X}^b &= \left(W - \rho^2\sigma'\right)\boldsymbol{n} - \left(\operatorname{grad}\mathbb{O}\odot\frac{\partial W}{\partial\operatorname{grad}\mathbb{O}}\right)\boldsymbol{n}, \\ \mathbb{X}^b &= \frac{\partial W}{\partial\operatorname{grad}\mathbb{O}}\boldsymbol{n}.\end{aligned} \tag{26.30}$$

In all these expressions, $\boldsymbol{n}$ is the unit normal vector perpendicular to $\partial\mathcal{B}$ pointing to the exterior of $\mathcal{B}$. $\boldsymbol{X}$ $\mathbb{X}$ and $\boldsymbol{X}^b$ $\mathbb{X}^b$ are the generalized intrinsic forces in the body and on its boundary, respectively; $\mathbb{X}$ and $\mathbb{X}^b$ are rank-i tensors ($i = 1, \dots, n$) and $\boldsymbol{X}$ $\boldsymbol{X}^b$ are vectors.

It is physically significant to note that the surface integral in (26.29) provides the rational argument, why the surface potential (26.25) with the generalized surface forces (26.26) was introduced. In the absense of dissipative terms, it will be shown that the principle of virtual power will require that $\boldsymbol{X}^b + \boldsymbol{X}^s = \boldsymbol{0}$ and $\mathbb{X}^b + \mathbb{X}^s = \boldsymbol{0}$. With $\mathcal{W}^s \equiv 0$ also $\boldsymbol{X}^b$ and $\mathbb{X}^b$ would have to separately vanish. This would severely constrain the model.

In the next step, we introduce the dissipation potential of SONNET and VIRGA [44], originally introduced in a simpler context by RAYLEIGH, see (26.3)–(26.11). In the present situation, this potential will be postulated as a frame indifferent functional of the stretching tensor $\boldsymbol{D}$ the order parameter(s) $\mathbb{O}$ and their rates $\hat{\mathbb{O}}$, viz.,

$$\mathcal{R} = \int_{\mathcal{B}} R\,\mathrm{d}V, \quad R = R(\mathbb{O}, \hat{\mathbb{O}}, \boldsymbol{D}), \tag{26.31}$$

where $\hat{\mathbb{O}}$ is defined in (26.18), [it could also be replaced by $\mathring{\mathbb{O}}$ (26.17)] and is assumed to be *bilinear* in $\hat{\mathbb{O}}$ and $\boldsymbol{D}$. The variation of the dissipation functional $\mathcal{R}$ is given by

$$\begin{aligned}\delta\mathcal{R} &= \int_{\mathcal{B}}\left\{\frac{\partial R}{\partial\dot{\mathbb{O}}}\cdot\delta\dot{\mathbb{O}} + \frac{\partial R}{\partial\operatorname{grad}\boldsymbol{v}}\cdot\underbrace{\delta(\operatorname{grad}\boldsymbol{v})}_{\operatorname{grad}(\delta\boldsymbol{v})}\right\}\mathrm{d}V \qquad (*) \\ &= \int_{\mathcal{B}}\left\{\frac{\partial R}{\partial\dot{\mathbb{O}}}\cdot\delta\dot{\mathbb{O}} - \operatorname{div}\left(\frac{\partial R}{\partial\operatorname{grad}\boldsymbol{v}}\right)\cdot\delta\boldsymbol{v}\right\}\mathrm{d}V \\ &\quad + \int_{\partial\mathcal{B}}\left(\frac{\partial R}{\partial\operatorname{grad}\boldsymbol{v}}\boldsymbol{n}\right)\cdot\delta\boldsymbol{v}\,\mathrm{d}a,\end{aligned} \tag{26.32}$$

in which $\boldsymbol{n}$ is the outward unit normal vector on $\partial\mathcal{B}$ and the second term in the line indicated by $(*)$ has been transformed by integration by parts and use of the GAUSS' theorem. Further transformations can be made using the chain rule of differentiation in the following terms.

- $$\frac{\partial R}{\partial \dot{\mathbb{O}}} = \frac{\partial R}{\partial \hat{\mathbb{O}}} \circ \frac{\partial \hat{\mathbb{O}}}{\partial \dot{\mathbb{O}}} + \frac{\partial R}{\partial \boldsymbol{D}} \circ \underbrace{\frac{\partial \boldsymbol{D}}{\partial \dot{\mathbb{O}}}}_{0} = \frac{\partial R}{\partial \hat{\mathbb{O}}}\,. \tag{26.33}$$

  Here, the symbol $\circ$ denotes composition. Moreover, (26.17) and (26.18) have been used to conclude that $\partial\hat{\mathbb{O}}/\partial\dot{\mathbb{O}}$ is the unity operator.
- $$\begin{aligned} \frac{\partial R}{\partial \mathrm{grad}\,\boldsymbol{v}} &= \frac{\partial R}{\partial \hat{\mathbb{O}}} \circ \frac{\partial \hat{\mathbb{O}}}{\partial \mathrm{grad}\,\boldsymbol{v}} + \frac{\partial R}{\partial \boldsymbol{D}} \circ \underbrace{\frac{\partial \boldsymbol{D}}{\partial \mathrm{grad}\,\boldsymbol{v}}}_{\boldsymbol{I}} \\ &= \frac{\partial R}{\partial \hat{\mathbb{O}}} \circ \frac{\partial \hat{\mathbb{O}}}{\partial \mathrm{grad}\,\boldsymbol{v}} + \frac{\partial R}{\partial\, \boldsymbol{D}}. \end{aligned} \tag{26.34}$$

Using (26.29) and taking its variation gives

$$\begin{aligned} \delta(\dot{\mathcal{F}} + \mathcal{W}^s) = {} & \int_{\mathcal{B}} \Big(\boldsymbol{X}\cdot\delta\boldsymbol{v} + \mathbb{X}\cdot\delta\dot{\mathbb{O}}\Big)\,\mathrm{d}V \\ & + \int_{\partial\mathcal{B}} \Big(\big(\boldsymbol{X}^b + \boldsymbol{X}^s\big)\cdot\delta\boldsymbol{v} + \big(\mathbb{X}^b + \mathbb{X}^s\big)\cdot\delta\dot{\mathbb{O}}\Big)\,\mathrm{d}a, \end{aligned}$$

and substituting (26.33), (26.34) into (26.32) yields

$$\begin{aligned} \delta\mathcal{R} = {} & \int_{\mathcal{B}} \left\{ \frac{\partial R}{\partial \hat{\mathbb{O}}}\cdot\delta\dot{\mathbb{O}} - \mathrm{div}\left(\frac{\partial R}{\partial \hat{\mathbb{O}}} \circ \frac{\partial \hat{\mathbb{O}}}{\partial \mathrm{grad}\,\boldsymbol{v}} + \frac{\partial R}{\partial \boldsymbol{D}} \right)\cdot\delta\boldsymbol{v} \right\}\mathrm{d}V \\ & + \int_{\partial\mathcal{B}} \left(\frac{\partial R}{\partial \hat{\mathbb{O}}} \circ \frac{\partial \hat{\mathbb{O}}}{\partial \mathrm{grad}\,\boldsymbol{v}} + \frac{\partial R}{\partial \boldsymbol{D}} \right)\cdot\boldsymbol{n}\,\mathrm{d}a. \end{aligned} \tag{26.35}$$

The principle of virtual power now requires

$$\delta\left(\dot{\mathcal{F}} + \mathcal{W}^s\right) + \delta\mathcal{R} = 0, \qquad \text{for all } \{\delta\boldsymbol{v}, \delta\dot{\mathbb{O}}\} \tag{26.36}$$

with the understanding that the generalized forces and their power of working remain constant during variation, see (26.8)–(26.11). Under such conditions, Eq. (26.36) yields

$$\left.\begin{aligned} & \boldsymbol{X} - \mathrm{div}\left(\frac{\partial R}{\partial \hat{\mathbb{O}}} \circ \frac{\partial \hat{\mathbb{O}}}{\partial \mathrm{grad}\,\boldsymbol{v}} + \frac{\partial R}{\partial \boldsymbol{D}} \right) = \boldsymbol{0}\,, \\ & \mathbb{X} + \frac{\partial R}{\partial \hat{\mathbb{O}}} = \boldsymbol{0} \end{aligned}\right\} \text{ in } \mathcal{B}\,, \tag{26.37}$$

and

$$\left.\begin{aligned} &\boldsymbol{X}^b + \boldsymbol{X}^s + \left(\frac{\partial R}{\partial \hat{\mathbb{O}}} \circ \frac{\partial \hat{\mathbb{O}}}{\partial \operatorname{grad} \boldsymbol{v}} + \frac{\partial R}{\partial \boldsymbol{D}}\right) \cdot \boldsymbol{n} = \boldsymbol{0}, \\ &\mathbb{X}^b + \mathbb{X}^s = \boldsymbol{0} \end{aligned}\right\} \text{ on } \partial\mathcal{B}\,. \tag{26.38}$$

These are the equations of motion in $\mathcal{B}$ and boundary conditions on $\partial\mathcal{B}$. SONNET and VIRGA [44] mention that the boundary conditions (26.38), as derived here, are valid for freely moving boundaries. If the boundary is not free to change position, e.g., partly or fully constrained, then, when $\delta\boldsymbol{v} = \boldsymbol{0}$ on $\partial\mathcal{B}$ one may still regard $(26.38)_1$ to hold, and $\boldsymbol{X}^s$ will in this case be interpreted as a reactive generalized force exerted by the boundary. Similarly, if $\dot{\mathbb{O}}$ on $\mathcal{B}$ would be prescribed, then the generalized force $\mathbb{X}^s$ is the reaction, when $\dot{\mathbb{O}}$ is prescribed on $\partial\mathcal{B}$.

Equations (26.37) and (26.38) together with Eq. $(26.30)_{1,2}$ are the basic governing equations of this theory, and initial-boundary-value problems can be solved for a given body $\mathcal{B}$ once the free energies W $\mathcal{W}^s$ and the external forces $\boldsymbol{X}^s$ and $\mathbb{X}^s$ are prescribed. These computations detail the presentation provided in [44].

It is certainly compulsory that the governing equations do not violate the balance laws of linear and angular momenta, given in local form as

$$\begin{aligned} \rho\dot{\boldsymbol{v}} &= \operatorname{div} \boldsymbol{t} + \rho\boldsymbol{f}, \\ \rho\dot{\boldsymbol{s}} &= \operatorname{div} \boldsymbol{m} + \rho\boldsymbol{\ell} + \boldsymbol{\tau}, \end{aligned} \tag{26.39}$$

in which $\boldsymbol{v} = \dot{\boldsymbol{x}}$ is the material velocity, $\boldsymbol{f}$ the specific body force per unit mass, and $\boldsymbol{t}$ the CAUCHY stress tensor. Similarly, $\boldsymbol{s}$ is the spin density per unit mass, $\boldsymbol{m}$ the couple stress tensor, and $\boldsymbol{\ell}$ the body couple per unit mass. It is known that $\boldsymbol{\tau}$ is related to the skew-symmetric part of the CAUCHY stress tensor (see e.g., [25], pp. 260–261)

$$\boldsymbol{\tau} = \operatorname{dual}(\boldsymbol{t} - \boldsymbol{t}^T), \quad \tau_i = \varepsilon_{ijk} t_{kj}. \tag{26.40}$$

Evidently, if $\boldsymbol{s} \equiv \boldsymbol{0}$, $\boldsymbol{m} \equiv \boldsymbol{0}$ and $\boldsymbol{\ell} \equiv \boldsymbol{0}$ then $\boldsymbol{\tau} \equiv \boldsymbol{0}$; in this case, the CAUCHY stress tensor is symmetric.

If we next substitute the generalized intrinsic force $\mathbb{X}$ given in (26.30), into the evolution Eq. (26.37), we obtain

$$\begin{aligned} \rho\dot{\boldsymbol{v}} = \rho\boldsymbol{f} + \underbrace{\operatorname{grad}\left(W - \rho^2\sigma'\right)}_{\operatorname{div}\left((W-\rho^2\sigma')\boldsymbol{I}\right)} &- \operatorname{div}\left(\operatorname{grad}\mathbb{O} \odot \frac{\partial W}{\partial \operatorname{grad}\mathbb{O}}\right) \\ &+ \operatorname{div}\left(\frac{\partial R}{\partial \hat{\mathbb{O}}} \odot \frac{\partial \mathbb{O}}{\partial \operatorname{grad} \boldsymbol{v}} + \frac{\partial R}{\partial \boldsymbol{D}}\right). \end{aligned} \tag{26.41}$$

If this is compared with $(26.40)_1$, the CAUCHY stress can be identified as

$$\boldsymbol{t} = (W - \rho^2\sigma')\boldsymbol{I} - \underline{\operatorname{grad}\mathbb{O} \odot \frac{\partial W}{\partial \operatorname{grad}\mathbb{O}} + \frac{\partial R}{\partial \hat{\mathbb{O}}} \odot \frac{\partial \hat{\mathbb{O}}}{\partial \operatorname{grad}\boldsymbol{v}}} + \frac{\partial R}{\partial \boldsymbol{D}}. \tag{26.42}$$

Notice that in the absence of microrotation the underlined middle term in (26.42) drops out. In this case, $\boldsymbol{t}$ is symmetric and consists of a pressure $p = -(W - \rho^2\sigma')$ due to the compressibility and the linear viscous stress

$$\frac{\partial R}{\partial \boldsymbol{D}} = \kappa(\operatorname{div}\boldsymbol{v})\boldsymbol{I} + 2\mu\left(\boldsymbol{D} - \tfrac{1}{3}(\operatorname{div}\boldsymbol{v})\boldsymbol{I}\right), \tag{26.43}$$

in which $\kappa > 0$ is the fluid bulk viscosity and $\mu > 0$ the shear viscosity. In the more general case of nematic liquid crystals, R (and W) can also depend on $\hat{\mathbb{O}}$ as evidenced by the underlined terms in (26.42).

For the analogous computations—in order to corroborate the satisfaction of the balance law of angular momentum—it is advantageous to search for the implication of the objectivity requirement of the energy function, i.e.,

$$W\left(\mathbb{O}_I, \mathbb{O}_{I,j}\right) = W\left(\left(\mathbb{O}_I \prod_{m=1}^{n} R_{I_m^* J_m}\right); \left(\mathbb{O}_{J,k} R_{j^*k} \prod_{p=1}^{m} R_{I_p^* J_p}\right)\right), \tag{26.44}$$

in which $\boldsymbol{R}$ is an arbitrary rotation matrix $[R_{i^*k}R_{j^*\ell} = \delta_{k\ell}]$. Such proofs go back to Green, Naghdi and Rivlin [18, 19] within the context of multipolar theories and were explicitly demonstrated in the context of a director theory by Ericksen [12] and noted but not proven in detail by Leslie [26, 27], Sonnet and Virga [44], and Sonnet, Moffettone and Virga [46]. The inferences of the frame indifference requirement (26.44) for the free energy W have been demonstrated by Ericksen in [12] for an LC modeled by a director $\boldsymbol{n}$. This proof is given in Chap. 25 and culminates in the statement (25.48) [in which the free energy is denoted by φ]. When this is written as W, the decisive equation reads

$$DW = \left\{\frac{\partial W}{\partial n_i} n_j + \frac{\partial W}{\partial n_{i,k}} n_{j,k} + \frac{\partial W}{\partial n_{k,i}} n_{k,j}\right\} \varOmega_{ij} \equiv 0, \tag{26.45}$$

where $\boldsymbol{\varOmega}$ is skew-symmetric. It follows that the term in curly brackets $\{\cdot\}$ must be a symmetric rank-2 tensor, which can also be stated as

$$\varepsilon_{ijk}\left\{\frac{\partial W}{\partial n_j} n_k + \frac{\partial W}{\partial n_{j,\ell}} n_{k,\ell} + \frac{\partial W}{\partial n_{\ell,j}} n_{\ell,k}\right\} = 0. \tag{26.46}$$

If W is assumed to be a function of a rank-2 tensor, $\mathbb{O}$, and its gradient $\operatorname{grad}\mathbb{O}$, the corresponding computations are explicitly performed in Appendix 26.B. The results, analogous to (26.46), are then given as Eqs. (26.220) and (26.221). These equations then suggest how one has to proceed if W depends on a set of tensorial order parameters $\mathbb{O}$ of rank i $(i = 1, 2, \ldots, n)$ and their gradients, $\operatorname{grad}\mathbb{O}$. This representation is given as Eq. (26.222) and is repeated here as Eq. (26.47),

$$\varepsilon_{pk^*k}\left\{\sum_{i^*=1}^{n}\left(\frac{\partial W}{\partial \mathbb{O}_{I^*{}_{i^*}{}^{k^*}}}\mathbb{O}_{I^*{}_{i^*}{}^{k}}+\frac{\partial W}{\partial \mathbb{O}_{I^*{}_{i^*}{}^{k^*},\ell^*}}\mathbb{O}_{I^*{}_{i^*}{}^{k},\ell^*}\right)\right.$$
$$\left.+\frac{\partial W}{\partial \mathbb{O}_{I^*,k^*}}\mathbb{O}_{I^*,k}\right\}=0. \tag{26.47}$$

Sonnet and Virga [44] introduce a symbolic notation of this that is given in index notation. To this end, they define the generalized vector valued product of two tensors of the same rank by

$$(\boldsymbol{\mathbb{A}}\times\boldsymbol{\mathbb{B}})_p=\varepsilon_{pk^*k}\sum_{i^*=1}^{n}\mathbb{A}_{I^*{}_{i^*}{}^{k^*}}\mathbb{B}_{I^*{}_{i^*}{}^{k}}. \tag{26.48}$$

Equation (26.47) can then be written in symbolic form as

$$\boldsymbol{\mathbb{O}}\times\frac{\partial W}{\partial\boldsymbol{\mathbb{O}}}+\operatorname{grad}\boldsymbol{\mathbb{O}}\times\frac{\partial W}{\partial\operatorname{grad}\boldsymbol{\mathbb{O}}}=\mathbf{0}. \tag{26.49}$$

Requiring, similarly, the kinetic energy of the micromotion, $\kappa(\boldsymbol{\mathbb{O}},\dot{\boldsymbol{\mathbb{O}}})$ to be a frame indifferent function of its variables, computations analogous to that leading to (26.49) for W yields

$$\boldsymbol{\mathbb{O}}\times\frac{\partial\kappa}{\partial\boldsymbol{\mathbb{O}}}+\dot{\boldsymbol{\mathbb{O}}}\times\frac{\partial\kappa}{\partial\dot{\boldsymbol{\mathbb{O}}}}=\mathbf{0}. \tag{26.50}$$

Returning to the representation (26.42) of the Cauchy stress tensor $\boldsymbol{t}$ it is obvious that only the underlined terms possess skew-symmetric contributions so that the vector $\boldsymbol{\tau}$ is given by

$$\begin{aligned}\tau_i&=\varepsilon_{ijk}\Bigg(\underbrace{\frac{\partial R}{\partial\hat{\mathbb{O}}_I}\frac{\partial\hat{\mathbb{O}}_I}{\partial v_{j,k}}}_{\Delta_{ij}}-\mathbb{O}_{I,j}\frac{\partial W}{\partial\mathbb{O}_{I,k}}\Bigg)\\&=\varepsilon_{ijk}\Bigg(\underbrace{\frac{\partial R}{\partial\hat{\mathbb{O}}_I}\frac{\partial\hat{\mathbb{O}}_I}{\partial v_{j,k}}}_{\Delta_{ij}}+\frac{\partial W}{\partial\mathbb{O}_{I,j}}\mathbb{O}_{I,k}\Bigg).\end{aligned} \tag{26.51}$$

Owing to $(26.37)_2$ we may replace $\partial R/\partial\hat{\mathbb{O}}_I$ by $(-\mathbb{X}_I)$. Similarly, we may employ (26.18) to evaluate $\partial\hat{\mathbb{O}}/\partial v_{j,k}$. To this end let

$$\hat{\mathbb{O}}_I=\mathring{\mathbb{O}}_I+\breve{\mathbb{O}}_I \tag{26.52}$$

with

$$\begin{aligned}
\mathring{\mathbb{O}}_I &= \underbrace{\frac{\partial \mathbb{O}_I}{\partial t} + \mathbb{O}_{I,p} v_p}_{\text{not a function of } v_{p,q}} = \dot{\mathbb{O}}_I - \sum_{p=1}^{n} W_{I_p^j} \mathbb{O}_{I_p^j}, \\
\breve{\mathbb{O}}_I &= \sum_{p=1}^{n} a_p D_{I_p^q} \mathbb{O}_{I_p^q},
\end{aligned} \tag{26.53}$$

so that

$$\begin{aligned}
\frac{\partial \mathring{\mathbb{O}}_I}{\partial v_{j,k}} &= -\frac{\partial}{\partial v_{j,k}} \sum_{p=1}^{n} W_{I_p^q} \mathbb{O}_{I_p^q} \\
&= -\frac{\partial}{\partial v_{j,k}} \left(\sum_{p=1}^{n} \frac{1}{2} \left(v_{p,q} - v_{q,p} \right) \mathbb{O}_{I_p^q} \right) \\
&= -\frac{1}{2} \left(\sum_{p=1}^{n} \delta_{jI_p} \delta_{kq} \mathbb{O}_{I_p^q} - \sum_{p=1}^{n} \delta_{jq} \delta_{kI_p} \mathbb{O}_{I_p^q} \right),
\end{aligned} \tag{26.54}$$

from which we find that

$$\begin{aligned}
\varepsilon_{ijk} \left(\frac{\partial R}{\partial \hat{\mathbb{O}}_I} \frac{\partial \mathring{\mathbb{O}}}{\partial v_{j,k}} \right) &= -\varepsilon_{ijk} \mathbb{X}_I \frac{\partial \mathring{\mathbb{O}}}{\partial v_{j,k}} \\
&= \varepsilon_{ijk} \mathbb{X}_I \sum_{p=1}^{n} \frac{1}{2} \left(\delta_{jI_p} \mathbb{O}_{I_p^k} - \delta_{kI_p} \mathbb{O}_{I_p^j} \right) \\
&= \varepsilon_{ijk} \left(\frac{1}{2} \sum_{p=1}^{n} \left(\mathbb{X}_{I_p^j} \mathbb{O}_{I_p^k} - \mathbb{X}_{I_p^k} \mathbb{O}_{I_p^j} \right) \right) \\
&= \varepsilon_{ijk} \sum_{p=1}^{n} \left(\mathbb{X}_{I_p^j} \mathbb{O}_{I_p^k} \right).
\end{aligned} \tag{26.55}$$

Similarly,

$$\begin{aligned}
\frac{\partial \breve{\mathbb{O}}}{\partial v_{j,k}} &= \frac{\partial}{\partial v_{j,k}} \left(\sum_{p=1}^{n} \frac{1}{2} a_p \left(v_{I_p,q} + v_{I_q,p} \right) \mathbb{O}_{I_p^q} \right) \\
&= \frac{1}{2} \sum_{p=1}^{n} \left(a_p \delta_{jp} \delta_{kq} \mathbb{O}_{I_p^q} + a_p \delta_{jq} \delta_{kp} \mathbb{O}_{I_p^q} \right) \\
&= \frac{1}{2} \sum_{p=1}^{n} \left(a_p \delta_{jI_p} \mathbb{O}_{I_p^q} + a_p \delta_{kI_p} \mathbb{O}_{I_p^j} \right),
\end{aligned} \tag{26.56}$$

and, consequently,

$$
\begin{aligned}
\varepsilon_{ijk}\left(\frac{\partial R}{\partial \hat{\mathbb{O}}_I}\,\frac{\partial \breve{\mathbb{O}}_I}{\partial v_{j,k}}\right) &= -\frac{1}{2}\varepsilon_{ijk}\mathbb{X}_I\sum_{p=1}^{n}\left\{a_p\delta_{jI_p}\mathbb{O}_{I_p^k} + a_p\delta_{kI_p}\mathbb{O}_{I_p^j}\right\} \\
&= -\frac{1}{2}\varepsilon_{ijk}\sum_{p=1}^{n}a_p\left\{\mathbb{X}_{I_p^j}\mathbb{O}_{I_p^k} + \mathbb{X}_{I_p^k}\mathbb{O}_{I_p^j}\right\} \equiv 0. \qquad (26.57)
\end{aligned}
$$

It follows that $\breve{\tau}$ vanishes for any (finite) value of a_p because the $\{\cdot\}$-term in (26.57) is symmetric in the indices jk whilst ε_{ijk} is skew-symmetric. So,

$$
\begin{aligned}
\tau_i = \mathring{\tau}_i &= \varepsilon_{ijk}\left\{\frac{\partial R}{\partial \hat{\mathbb{O}}_I}\,\frac{\partial \mathring{\mathbb{O}}_I}{\partial v_{j,k}} + \frac{\partial W}{\partial \mathbb{O}_{I,j}}\mathbb{O}_{I,k}\right\} \\
&\overset{(26.55)}{=} \varepsilon_{ijk}\left\{\sum_{p=1}^{n}\left(\mathbb{X}_{I_p^j}\mathbb{O}_{I_p^k}\right) + \frac{\partial W}{\partial \mathbb{O}_{I,j}}\mathbb{O}_{I,k}\right\}.
\end{aligned}
$$

Inserting in these relations the expression $(26.30)_2$ for $\mathbb{X}_I$ implies

$$
\begin{aligned}
\tau_i = \varepsilon_{ijk}\Bigg\{&\rho\sum_{p=1}^{n}\left(\mathbb{M}_{I_p^j} + \frac{\partial \chi}{\partial \mathbb{O}_{I_p^j}}\right)\mathbb{O}_{I_p^k} \\
&+\sum_{p=1}^{n}\left[\frac{\partial W}{\partial \mathbb{O}_{I_p^j}} - \left(\frac{\partial W}{\partial \mathbb{O}_{I_p^k,m}}\right)_{,m}\right]\mathbb{O}_{I_p^k} + \frac{\partial W}{\partial \mathbb{O}_{I,j}}\mathbb{O}_{I,k}\Bigg\} \qquad (26.58) \\
\overset{*}{=} \varepsilon_{ijk}&\rho\sum_{p=1}^{n}\left\{\left(\mathbb{M}_{I_p^j} + \frac{\partial \chi}{\partial \mathbb{O}_{I_p^j}}\right)\mathbb{O}_{I_p^k} - \left(\frac{\partial W}{\partial \mathbb{O}_{I_p^j,m}}\mathbb{O}_{I_pk}\right)_{,m}\right\}, \qquad (26.59)
\end{aligned}
$$

where at $\overset{*}{=}$ expression (26.47) was employed to alter the second line of (26.58). To this end, by reshuffling indices, (26.47) is written in the form

$$
\varepsilon_{ijk}\frac{\partial W}{\partial \mathbb{O}_{I,j}}\mathbb{O}_{I,k} = -\varepsilon_{ijk}\sum_{p=1}^{n}\left(\frac{\partial W}{\partial \mathbb{O}_{I_p^j}} + \frac{\partial W}{\partial \mathbb{O}_{I_p^j,m}}\mathbb{O}_{I_p^k,m}\right). \qquad (26.60)
$$

The explicit form of Eq. (26.59) suggests that we may try to identify the individual terms of the spin balance $(26.39)_2$. Indeed, by writing $(26.39)_2$ as

$$
\tau_p = \rho\dot{s}_p - m_{pk,k} - \rho\ell_p, \qquad (26.61)
$$

and comparison of this equation with (26.59), we obtain

$$\dot{s}_p = \varepsilon_{pk^*k} \sum_{i^*=1}^{n^*} \mathbb{M}_{{I^*}_{i^*}{}^{k^*}} \mathbb{O}_{I^*_{i^*}}, \qquad \dot{\boldsymbol{s}} = \boldsymbol{\mathbb{M}} \times \boldsymbol{\mathbb{O}}, \tag{26.62}$$

$$\ell_p = -\varepsilon_{pk^*k} \sum_{i^*=1}^{n^*} \frac{\partial \chi}{\partial \mathbb{O}_{{I^*}_{i^*}{}^{k^*}}} \mathbb{O}_{{I^*}_{i^*}{}^{k}}, \qquad \boldsymbol{\ell} = -\frac{\partial \chi}{\partial \boldsymbol{\mathbb{O}}} \times \boldsymbol{\mathbb{O}}, \tag{26.63}$$

$$m_{pk} = \varepsilon_{pk^*k} \sum_{i^*=1}^{n^*} \frac{\partial W}{\partial \mathbb{O}_{{I^*}_{i^*}{}^{k^*}}} \mathbb{O}_{{I^*}_{i^*}{}^{k}}, \qquad \boldsymbol{m} = \frac{\partial W}{\partial \operatorname{grad} \boldsymbol{\mathbb{O}}} \times \boldsymbol{\mathbb{O}}. \tag{26.64}$$

26.2 Uniaxial Nematic Crystals

26.2.1 Introductory Note

In this section, we shall specialize the general theoretical model developed in Sect. 26.1 for nematic LCs with tensorial order variables to uniaxial nematics. Two different classes of models describing such LCs exist, and they differ from one another by accounting for a scalar order parameter S. This parameter is a measure of the deviations of the individual molecules in a representative volume element (RVE) from that of the mathematical director $\boldsymbol{n}$ see Fig. 25.7 in Chap. 25. When S is assumed to be a constant, this means physically that the deviations of the orientations of the molecules from one another is negligibly small. Ideally, this means that the orientation of the molecules is perfect. Formally, this is tantamount to a constant order, $S =$ constant.

The mathematical model for this somewhat ideal situation is the ELP theory, in which the variable S does not even arise. The model equations in this case are obtained from the balance laws of linear and angular momenta (and those of mass and energy).

The more general case is the situation when the values of S in the RVE of material points differ from point to point. The dynamics of nematic LCs with variable scalar order parameter was treated in the 90s of the twentieth century by ERICKSEN [15] and LESLIE [28]. Their approaches led to an additional evolution equation for the scalar order parameter.

Our approach in dealing with nematic LCs has been the adoption of the LAGRANGE a method to dissipative systems as suggested by Lord RAYLEIGH [50] and perfected by SONNET and VIRGA [44] for LCs with arbitrary tensorial order. The mathematical structure of the two approaches is quite distinct. It is, therefore, important to investigate whether this LAGRANGE–RAYLEIGH method leads to the same nematic field descriptions as does the balance equation approach by ERICKSEN [15] and LESLIE [28]. SONNET and VIRGA [44] prove that the LAGRANGE–RAYLEIGH method, as outlined in Sect. 26.1, yields the same governing field equations as does the balance equation approach.[4] This is important as it assigns to these models a high degree of credibility. SONNET and VIRGA give in the introduction to their paper a review of the literature of the past approximately 40 years, which indicates that such a perfect agreement is not obtained with a wealth of models in papers on LCs during this period.[5]

26.2.2 Uniaxial Nematics with Constant Order Parameter

The description of LCs involves an analysis of order.[6] To describe it, it is customary for nematics to use a rank-2 symmetric traceless tensor, although a scalar order parameter is usually sufficient to describe uniaxial nematic LCs. This order can be measured by the MAIER–SAUPE [31] order parameter

$$S = \langle P_2(\cos\theta)\rangle = \langle \tfrac{1}{2}(3\cos^2\theta - 1)\rangle,$$

where θ is the angle between the LCs molecular axis and the local director, see Fig. 25.7 in Chap. 25. P_2 denotes the second rank LEGENDRE polynomial and the brackets $\langle(\cdot)\rangle$ denote both a temporal and spatial average. The value for S lies in the interval $S \in [0, 1]$ $S = 1$ being representative for $\theta = (0, \pi)$ and $S = 0$ for a completely random, isotropic sample. For a typical LC sample $S \in [0.3, 0.8]$ generally decreasing in value as the temperature increases. To describe the average orientation along with the scalar order, it is convenient to use the uniaxial rank-2 alignment tensor.

$$\boldsymbol{a} = S\left(\boldsymbol{n} \otimes \boldsymbol{n} - \tfrac{1}{3}\boldsymbol{I}\right),$$

which also reflects the nematic invariance changes from $\boldsymbol{n} \rightarrow -\boldsymbol{n}$. With the use of the above relation, a theory of uniaxial nematics with variable order is obtained as a special case of a theory for the full rank-2 alignment tensor, treated in Sect. 26.1. Here, we address a formulation using first a constant scalar order parameter, i.e., at this approximation this parameter does not even appear in the formulation, later we will work with a variable scalar order parameter that enters via S and grad S into a uniaxial constitutive assumption. The more general case will be reserved to a separate treatment.

Chapter 25 was devoted to the ELP model [13, 15, 27, 37] of nematic LCs "consisting of effectively uniaxial molecules that exhibit the tendency to align their long axis in a common direction. It is generally described by a unit vector field $\boldsymbol{n}$ the nematic director, which indicates the local average orientation" [44].

---

[4] This statement is restricted to those models satisfying the ONSAGER relations; this is so, because the existence of a dissipation potential as in the LAGRANGE–RAYLEIGH formulation exactly corresponds to the application of the ONSAGER relations.

[5] This fact is informative and the introductory text in [44] is worth reading. However, in this electronic time, we refrain from copying it.

[6] See: https://en.wikipedia.org/wiki/Liquid_crystal.

Because the processes describing the variability of the orientation of the director are slow [when compared with the velocity of sound], the fluid can be assumed to be density preserving. Under such conditions, $\rho =$ constant, and the velocity field is solenoidal, $\operatorname{div} \boldsymbol{v} = 0$.

Consider $\dot{\mathcal{F}}$ as stated in (26.22) and write it for the $\boldsymbol{n}$'s rather than the $\mathbb{O}$'s. In this section, we shall assume that

(1) external forces are not present, $\boldsymbol{f} = \boldsymbol{0}$
(2) the fluid is density preserving, $\sigma' = 0$
(3) the potential of the external actions vanishes, $\chi = 0$
(4) the director has unit length, $|\boldsymbol{n}| = 1$
(5) the kinetic energy connected with the microstructure is ignored, $\kappa = 0 \rightarrow \mathbb{M} = \boldsymbol{0}$.

With these restrictions, (26.22) simplifies to

$$\dot{\mathcal{F}} = \int_{\mathcal{B}} \left\{ \rho \dot{\boldsymbol{v}} \cdot \boldsymbol{v} + \frac{\partial W}{\partial \boldsymbol{n}} \cdot \dot{\boldsymbol{n}} + \underbrace{\frac{\partial W}{\partial \operatorname{grad} \boldsymbol{n}} \underbrace{(\operatorname{grad} \boldsymbol{n})^{\cdot}}_{\operatorname{grad} \dot{\boldsymbol{n}} - \operatorname{grad} \boldsymbol{n} \operatorname{grad} \boldsymbol{v}}}_{[1]} + W \underbrace{\operatorname{div} \boldsymbol{v}}_{0} \right\} \mathrm{d}V. \tag{26.65}$$

The underbraced term [1] now written in Cartesian tensor notation can be transformed by integration by parts and use of the divergence theorem due to Gauss as follows:

$$\begin{aligned}
[1] &= \int_{\mathcal{B}} \left\{ \frac{\partial W}{\partial n_{i,j}} \left(\dot{n}_{i,j} - n_{i,k} v_{k,j} \right) \right\} \mathrm{d}V \\
&= \int_{\mathcal{B}} \left\{ \left(\frac{\partial W}{\partial n_{i,j}} \dot{n}_i \right)_{,j} - \left(\frac{\partial W}{\partial n_{i,j}} \right)_{,j} \dot{n}_i - \frac{\partial W}{\partial n_{i,j}} n_{i,k} v_{k,j} \right\} \mathrm{d}V \\
&= - \int_{\mathcal{B}} \left\{ \left(\frac{\partial W}{\partial n_{i,j}} \right)_{,j} \dot{n}_i + \frac{\partial W}{\partial n_{i,j}} n_{i,k} v_{k,j} \right\} \mathrm{d}V + \int_{\partial \mathcal{B}} \frac{\partial W}{\partial n_{i,j}} \dot{n}_j n_i^{+} \mathrm{d}a \\
&= - \int_{\mathcal{B}} \left\{ \operatorname{div} \frac{\partial W}{\partial \operatorname{grad} \boldsymbol{n}} \cdot \dot{\boldsymbol{n}} + \left((\operatorname{grad} \boldsymbol{n})^T \frac{\partial W}{\partial \operatorname{grad} \boldsymbol{n}} \right) \cdot \operatorname{grad} \boldsymbol{v} \right\} \mathrm{d}V \\
&\quad + \int_{\partial \mathcal{B}} \left(\frac{\partial W}{\partial \operatorname{grad} \boldsymbol{n}} \boldsymbol{n}^{+} \right) \cdot \dot{\boldsymbol{n}} \, \mathrm{d}a.
\end{aligned} \tag{26.66}$$

So, we can write (26.22) in the form

$$\begin{aligned}
\dot{\mathcal{F}} = \int_{\mathcal{B}} \Bigg\{ & \rho \dot{\boldsymbol{v}} \cdot \boldsymbol{v} + \left(\frac{\partial W}{\partial \boldsymbol{n}} - \operatorname{div} \frac{\partial W}{\partial \operatorname{grad} \boldsymbol{n}} \right) \cdot \dot{\boldsymbol{n}} \\
& - \left((\operatorname{grad} \boldsymbol{n})^T \frac{\partial W}{\partial \operatorname{grad} \boldsymbol{n}} \right) \cdot \operatorname{grad} \boldsymbol{v} \Bigg\} \mathrm{d}V \\
& + \int_{\partial \mathcal{B}} \left(\frac{\partial W}{\partial \operatorname{grad} \boldsymbol{n}} \boldsymbol{n}^{+} \right) \cdot \dot{\boldsymbol{n}} \, \mathrm{d}a,
\end{aligned} \tag{26.67}$$

in which $\boldsymbol{n}^+$ is the unit normal vector on $\partial\mathcal{B}$ pointing to the exterior of the body. $\dot{\mathcal{F}}$ is physically the power of working exhibited in the body $\mathcal{B}$ and on its boundary $\partial\mathcal{B}$. Therefore, we can arbitrarily add or subtract the following terms to $\dot{\mathcal{F}}$:

- $\int_{\mathcal{B}} \mu(\boldsymbol{n} \cdot \dot{\boldsymbol{n}})\mathrm{d}V$ $(= 0$ since $|\boldsymbol{n}| = 1$ or $\dot{\boldsymbol{n}} \perp \boldsymbol{n})$. The coefficient μ is an arbitrary scalar.
- On the boundary $\partial\mathcal{B}$ a similar scalar quantity μ_b can be active, for which

$$\int_{\partial\mathcal{B}} \mu_b(\boldsymbol{n} \cdot \dot{\boldsymbol{n}})\mathrm{d}a \quad (= 0,\ \text{since } \dot{\boldsymbol{n}} \perp \boldsymbol{n} \text{ on } \partial\mathcal{B}).$$

- In $\mathcal{B}$ the term

$$\int_{\mathcal{B}} p \operatorname{div} \boldsymbol{v} \, \mathrm{d}\boldsymbol{v} \quad (= 0)$$

may be added, since in a density-preserving medium the velocity field is solenoidal.

So, without any effect to the value of $\dot{\mathcal{F}}$, we may write

$$\begin{aligned}
\dot{\mathcal{F}} = \int_{\mathcal{B}} \bigg\{ & \rho\dot{\boldsymbol{v}} \cdot \boldsymbol{v} + \left(\frac{\partial W}{\partial \boldsymbol{n}} - \operatorname{div} \frac{\partial W}{\partial \operatorname{grad} \boldsymbol{n}} + \mu\boldsymbol{n} \right) \cdot \dot{\boldsymbol{n}} \\
& - \left((\operatorname{grad} \boldsymbol{n})^T \frac{\partial W}{\partial \operatorname{grad} \boldsymbol{n}} + p\boldsymbol{I} \right) \cdot \operatorname{grad} \boldsymbol{v} \bigg\} \mathrm{d}V \\
& + \int_{\partial\mathcal{B}} \left(\frac{\partial W}{\partial \operatorname{grad} \boldsymbol{n}} \boldsymbol{n}^+ + \mu_b \boldsymbol{n} \right) \cdot \dot{\boldsymbol{n}} \mathrm{d}a, \qquad (26.68)
\end{aligned}$$

in which μ, p, and μ_b are arbitrary scalar fields. Obviously, their meaning is "constraint forces" guaranteeing density preserving (p), and orthogonality of $\boldsymbol{n}$ and $\dot{\boldsymbol{n}}(\mu, \mu_b)$. The generalized forces, analogous to (26.30) are now

$$\begin{aligned}
\boldsymbol{X} &= \frac{\partial W}{\partial \boldsymbol{n}} - \operatorname{div} \frac{\partial W}{\partial \operatorname{grad} \boldsymbol{n}} + \mu\boldsymbol{n}, \\
\mathbb{X} &= \rho\dot{\boldsymbol{v}} + \operatorname{div} \left((\operatorname{grad} \boldsymbol{n})^T \frac{\partial W}{\partial \operatorname{grad} \boldsymbol{n}} + p\boldsymbol{I} \right), \\
\boldsymbol{X}^b &= \frac{\partial W}{\partial \operatorname{grad} \boldsymbol{n}} \boldsymbol{n}^+ + \mu_b \boldsymbol{n}, \\
\mathbb{X}^b &= \left((\operatorname{grad} \boldsymbol{n})^T \frac{\partial W}{\partial \operatorname{grad} \boldsymbol{n}} + p\boldsymbol{I} \right) \boldsymbol{n}^+, \qquad (26.69)
\end{aligned}$$

in which μ, μ_b and p p_b appear as LAGRANGE multipliers corresponding to the constraints that $\boldsymbol{n}$ has unit length in $\mathcal{B}$ and on $\partial\mathcal{B}$ and that the velocity field is solenoidal.

Next, we need to incorporate the dissipative effects. These require the postulation of the RAYLEIGH dissipation function R. We select the dependence $R = R(\boldsymbol{n}, \overset{\circ}{\boldsymbol{n}}, \boldsymbol{D})$

and assume it to be a bilinear homogeneous function of $\boldsymbol{D} :=$ sym grad$\boldsymbol{v}$ and $\overset{\circ}{\boldsymbol{n}}$ where

$$\overset{\circ}{\boldsymbol{n}} = \dot{\boldsymbol{n}} - \boldsymbol{W}\boldsymbol{n} = \dot{\boldsymbol{n}} - \boldsymbol{\omega} \times \boldsymbol{n}, \tag{26.70}$$

in which $\boldsymbol{W} =$ skw grad$\boldsymbol{v}$ is the skew-symmetric vorticity tensor and $\boldsymbol{\omega} = \frac{1}{2}$curl$\boldsymbol{v}$ its dual axial vector, see its analogue (26.17).

From EULER'S theorem on homogeneous functions[7] of order 2, we have

$$\frac{\partial R}{\partial \overset{\circ}{\boldsymbol{n}}} \cdot \overset{\circ}{\boldsymbol{n}} + \frac{\partial R}{\partial \boldsymbol{D}} \cdot \boldsymbol{D} = 2R. \tag{26.73}$$

Moreover,

$$\frac{\partial R}{\partial \dot{\boldsymbol{n}}} = \frac{\partial R}{\partial \overset{\circ}{\boldsymbol{n}}} \circ \underbrace{\frac{\partial \overset{\circ}{\boldsymbol{n}}}{\partial \dot{\boldsymbol{n}}}}_{=1} = \frac{\partial R}{\partial \overset{\circ}{\boldsymbol{n}}}, \tag{26.74}$$

according to (26.70). On the other hand,

$$\frac{\partial R}{\partial v_{k,\ell}} = \underbrace{\frac{\partial R}{\partial \overset{\circ}{n}_i} \underbrace{\frac{\partial \overset{\circ}{n}_i}{\partial v_{k,\ell}}}_{(1)}}_{[1]_{kl}} + \underbrace{\frac{\partial R}{\partial D_{ij}} \underbrace{\frac{\partial D_{ij}}{\partial v_{k,\ell}}}_{(2)}}_{[2]_{kl}}. \tag{26.75}$$

With $\overset{\circ}{n}_i = \dot{n}_i - \frac{1}{2}(v_{i,j} - v_{j,i})n_j$, we obtain

$$\begin{aligned}
(1) &= \frac{1}{2}\left(-\delta_{ik}\delta_{j\ell}n_j + \delta_{jk}\delta_{i\ell}n_j\right), \\
(2) &= \frac{\partial}{\partial v_{k,\ell}}\left(\frac{1}{2}(v_{i,j} + v_{j,i})\right) = \frac{1}{2}\left(\delta_{ik}\delta_{j\ell} + \delta_{jk}\delta_{i\ell}\right), \\
[1]_{kl} &= \frac{1}{2}\frac{\partial R}{\partial \overset{\circ}{n}_i}\left(-\delta_{ik}\delta_{j\ell}n_j + \delta_{jk}\delta_{i\ell}n_j\right)
\end{aligned}$$

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[7] Let $f(xy)$ be a homogeneous function of order $\boldsymbol{n}$ so that

$$f(tx, ty) = t^n f(x, y). \tag{26.71}$$

Then, it is easy to show that

$$nt^{n-1} f(x, y) = x\frac{\partial f}{\partial(xt)} + y\frac{\partial f}{\partial(yt)} \xrightarrow{t=1} nf(x, y) = x\frac{\partial f}{\partial x} + y\frac{\partial f}{\partial y} \tag{26.72}$$

for a homogeneous function of order n. For a bilinear homogeneous function $n = 2$.

$$= -\frac{1}{2}\left(\frac{\partial R}{\partial \overset{\circ}{n}_k} n_\ell - \frac{\partial R}{\partial \overset{\circ}{n}_\ell} n_k\right), \tag{26.76}$$

$$\begin{aligned}
[2]_{kl} &= \frac{\partial R}{\partial D_{ij}} \frac{\partial D_{ij}}{\partial v_{k\ell}} = \frac{1}{2} \frac{\partial R}{\partial D_{ij}} \left(\delta_{ik}\delta_{j\ell} + \delta_{jk}\delta_{i\ell}\right) \\
&= \frac{1}{2}\left(\frac{\partial R}{\partial D_{k\ell}} + \frac{\partial R}{\partial D_{\ell k}}\right) = \frac{\partial R}{\partial D_{k\ell}}.
\end{aligned} \tag{26.77}$$

Therefore, and now reverting to symbolic notation, Eq. (26.67) reads

$$\frac{\partial R}{\partial \operatorname{grad} \boldsymbol{v}} = \frac{1}{2}\left(\boldsymbol{n} \otimes \frac{\partial R}{\partial \overset{\circ}{\boldsymbol{n}}} - \frac{\partial R}{\partial \overset{\circ}{\boldsymbol{n}}} \otimes \boldsymbol{n}\right) + \frac{\partial R}{\partial \boldsymbol{D}}. \tag{26.78}$$

This agrees with formula (59) in [44]. Next, with $\mathbb{X}$ given by $(26.69)_2$ and the analogue of the last term on the right-hand side of (26.41), which here reads [$\mathbb{O}$ is replaced by $\overset{\circ}{\boldsymbol{n}}$]

$$\operatorname{div}\left(\frac{\partial R}{\partial \operatorname{grad} \boldsymbol{v}}\right),$$

the CAUCHY stress can be identified as the expression

$$\boldsymbol{t} = -p\boldsymbol{I} - (\operatorname{grad} \boldsymbol{n})^T \frac{\partial W}{\partial \operatorname{grad} \boldsymbol{n}} + \underline{\frac{1}{2}\left(\boldsymbol{n} \otimes \frac{\partial R}{\partial \overset{\circ}{\boldsymbol{n}}} - \frac{\partial R}{\partial \overset{\circ}{\boldsymbol{n}}} \otimes \boldsymbol{n}\right)} + \frac{\partial R}{\partial \boldsymbol{D}}. \tag{26.79}$$

Thus, we obtain the field equations

$$\left.\begin{aligned}
&\rho\dot{\boldsymbol{v}} - \operatorname{div} \boldsymbol{t} = \boldsymbol{0}, \\
&\frac{\partial W}{\partial \boldsymbol{n}} - \operatorname{div}\left(\frac{\partial W}{\partial \operatorname{grad} \boldsymbol{n}}\right) + \frac{\partial R}{\partial \overset{\circ}{\boldsymbol{n}}} + \mu\boldsymbol{n} = \boldsymbol{0}
\end{aligned}\right\} \quad \text{in } \mathcal{B} \tag{26.80}$$

and boundary conditions

$$\left.\begin{aligned}
&\boldsymbol{t}\boldsymbol{n}^+ + \boldsymbol{X}^b = \boldsymbol{0}, \\
&\frac{\partial W}{\partial \operatorname{grad} \boldsymbol{n}}\boldsymbol{n}^+ + \mu_b\boldsymbol{n} + \mathbb{X}^s = \boldsymbol{0}
\end{aligned}\right\} \quad \text{on } \partial\mathcal{B}. \tag{26.81}$$

Obviously, according to (26.79), $-p\boldsymbol{I}$ is the constraint pressure due to the density preserving of the fluid, while

$$\begin{aligned}
\boldsymbol{t}^e &:= -(\operatorname{grad} \boldsymbol{n})^T \frac{\partial W}{\partial \operatorname{grad} \boldsymbol{n}}, \\
\boldsymbol{t}^v &:= \frac{1}{2}\left(\boldsymbol{n} \otimes \frac{\partial R}{\partial \overset{\circ}{\boldsymbol{n}}} - \frac{\partial R}{\partial \overset{\circ}{\boldsymbol{n}}} \otimes \boldsymbol{n}\right) + \frac{\partial R}{\partial \boldsymbol{D}}
\end{aligned} \tag{26.82}$$

are the elastic stress due to variations of the orientation of the director $\boldsymbol{n}$ in space and the viscous stress due to variations of $\boldsymbol{n}$ in time [as expressed by $\overset{\circ}{\boldsymbol{n}}$] and fluid viscous effects. Furthermore, $(26.80)_2$ serves as a field equation for the LAGRANGE parameter μ as scalar response to the rigidity of the director length. A similar role is also played by μ_b whose determination by $(26.81)_2$ guarantees the orthogonality of $\boldsymbol{n}$ and $\overset{\circ}{\boldsymbol{n}}$ at the boundary $\partial\mathcal{B}$.

The skew-symmetric part of the stress tensor (26.79) is given by the underlined term. Its dual (axial) vector is given by

$$t_i^* = \varepsilon_{ijk}\left(n_j\frac{\partial R}{\partial \overset{\circ}{n}_k} - \frac{\partial R}{\partial \overset{\circ}{n}_j}n_k\right) \quad \longleftrightarrow \quad \boldsymbol{t}^* = \boldsymbol{n}\times\left(\frac{\partial R}{\partial \overset{\circ}{\boldsymbol{n}}}\right). \tag{26.83}$$

Solving $(26.80)_2$ for $(\partial R/\partial \overset{\circ}{\boldsymbol{n}})$ substituting the emerging expression into $(26.82)_2$ and recognizing that $\boldsymbol{n}\times\boldsymbol{n} = \boldsymbol{0}$ yields the identity

$$\boldsymbol{n}\times\left(\operatorname{div}\frac{\partial W}{\partial \operatorname{grad}\boldsymbol{n}} - \frac{\partial W}{\partial \boldsymbol{n}} - \frac{\partial R}{\partial \overset{\circ}{\boldsymbol{n}}}\right) \equiv \boldsymbol{0}. \tag{26.84}$$

SONNET and VIRGA [44] interpret this equation as a balance of torques, viz.,

$$\underbrace{\boldsymbol{n}\times\left(\operatorname{div}\frac{\partial W}{\partial \operatorname{grad}\boldsymbol{n}} - \frac{\partial W}{\partial \boldsymbol{n}}\right)}_{\text{torque due to the elastic deformation of the directors}} = \underbrace{\boldsymbol{n}\times\frac{\partial R}{\partial \overset{\circ}{\boldsymbol{n}}}}_{\text{torque due to the viscous deformation of the directors}}. \tag{26.85}$$

Similarly, when taking the cross product of $(26.69)_2$ with $\boldsymbol{n}$, viz.,

$$\underbrace{\boldsymbol{n}\times\mathbb{X}^s}_{\text{torque at the bound. due to the microforce}} = \underbrace{-\boldsymbol{n}\times\left[\left(\frac{\partial W}{\partial \operatorname{grad}\boldsymbol{n}}\right)\boldsymbol{n}^+\right]}_{\text{torque at the boundary due to elastic deformations of the directors}}. \tag{26.86}$$

We recognize a balance of torques due to the microforce $\mathbb{X}^s$ with an elastic surface torque, both at the boundary $\partial\mathcal{B}$. Moreover, according to (26.64) the couple stress tensor takes the form

$$m_{pk} = \varepsilon_{pk^*\ell}n_k^*\frac{\partial W}{\partial n_{\ell,k}}. \tag{26.87}$$

There remains the postulation of the dissipation function as a function of $\overset{\circ}{\boldsymbol{n}}$ and $\boldsymbol{D}$ that can be constructed from the scalar invariants built with these variables and with $\boldsymbol{n}$. There are five such invariants, see [43, 47, 52, 53], and their linear combination yields for R the representation

$$\begin{aligned} R = {} & \tfrac{1}{2}\gamma_1 \overset{\circ}{\boldsymbol{n}}{}^2 + \gamma_2 \overset{\circ}{\boldsymbol{n}} \cdot \boldsymbol{D}\boldsymbol{n} + \tfrac{1}{2}\gamma_3 (\boldsymbol{D}\boldsymbol{n})^2 \\ & + \tfrac{1}{2}\gamma_4 \mathrm{tr}(\boldsymbol{D}^2) + \tfrac{1}{2}\gamma_5 (\boldsymbol{n} \cdot \boldsymbol{D}\boldsymbol{n})^2, \end{aligned} \tag{26.88}$$

where γ_i $(i = 1, \dots, 5)$ are constants. It follows from (26.88) that

$$\frac{\partial R}{\partial \overset{\circ}{\boldsymbol{n}}} = \gamma_1 \overset{\circ}{\boldsymbol{n}} + \gamma_2 \boldsymbol{D}\boldsymbol{n}, \tag{26.89}$$

$$\begin{aligned} \frac{\partial R}{\partial \boldsymbol{D}} = {} & \tfrac{1}{2}\gamma_2 \left(\overset{\circ}{\boldsymbol{n}} \otimes \boldsymbol{n} + \boldsymbol{n} \otimes \overset{\circ}{\boldsymbol{n}} \right) + \tfrac{1}{2}\gamma_3 \left(\boldsymbol{D}\boldsymbol{n} \otimes \boldsymbol{n} + \boldsymbol{n} \otimes \boldsymbol{D}\boldsymbol{n} \right) \\ & + \gamma_4 \boldsymbol{D} + \gamma_5 \left(\boldsymbol{n} \cdot \boldsymbol{D}\boldsymbol{n} \right) \boldsymbol{n} \otimes \boldsymbol{n}. \end{aligned} \tag{26.90}$$

Substituting these R-derivatives into the viscous stress formula (26.82) yields

$$\begin{aligned} \boldsymbol{t}^v = {} & \alpha_1 \left(\boldsymbol{n} \cdot \boldsymbol{D}\boldsymbol{n} \right) \boldsymbol{n} \otimes \boldsymbol{n} + \alpha_2 \left(\overset{\circ}{\boldsymbol{n}} \otimes \boldsymbol{n} \right) + \alpha_3 \boldsymbol{n} \otimes \overset{\circ}{\boldsymbol{n}} \\ & + \alpha_4 \boldsymbol{D} + \alpha_5 \left(\boldsymbol{D}\boldsymbol{n} \otimes \boldsymbol{n} \right) + \alpha_6 \boldsymbol{n} \otimes \boldsymbol{D}\boldsymbol{n}, \end{aligned} \tag{26.91}$$

where the coefficients α_i $(i = 1, \dots, 6)$ are given by coefficients γ_j $(j = 1, \dots, 5)$ through the relations

$$\begin{aligned} & \alpha_1 = \gamma_5, \quad \alpha_2 = \tfrac{1}{2}(\gamma_2 - \gamma_1), \quad \alpha_3 = \tfrac{1}{2}(\gamma_1 + \gamma_2), \\ & \alpha_4 = \gamma_4, \quad \alpha_5 = \tfrac{1}{2}(\gamma_3 - \gamma_2), \quad \alpha_6 = \tfrac{1}{2}(\gamma_2 + \gamma_3), \end{aligned} \tag{26.92}$$

where between the α-coefficients the equation

$$\alpha_6 - \alpha_5 = \alpha_2 + \alpha_3 \tag{26.93}$$

must exist (because six α's are expressed in terms of five γ's.) Equation (26.93) is known as Onsager–Parodi relation [44]. Sonnet and Virga also mention that "this relation is automatically satisfied, because the generalized viscous forces derive from a potential R. Here indeed Onsager's principle reduces to the symmetry in the mixed second derivatives of R".

26.2.3 Leslie's Alternative Formulation for Uniaxial Nematics

It is worth noting that the viscous stress representation (26.91), derived by Sonnet and Virga [44], agrees in substance with the alternative dynamical theory of LCs by Leslie [28]. He derived his model based on the balance laws for linear and angular momenta and energy. These laws form the natural foundation for the expressions of stress and couple stress in such transversely isotropic liquids. Leslie in 1992 [28] restricts attention to processes for which thermal effects can be ignored; moreover, the liquid is viewed as density preserving and the director $\boldsymbol{n}$ is restricted to unit length. The significant balance laws are then given by

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathcal{B}} \rho v_i \mathrm{d}V = \int_{\mathcal{B}} \rho f_i \mathrm{d}V + \int_{\partial\mathcal{B}} t_i \mathrm{d}a \tag{26.94}$$

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathcal{B}} \rho\varepsilon_{ijk} x_j v_k \mathrm{d}V &= \int_{\mathcal{B}} \rho\left(\varepsilon_{ijk} x_j f_k + \ell_i\right)\mathrm{d}V \\ &\quad + \int_{\partial\mathcal{B}}\left(\varepsilon_{ijk} x_j t_k + m_i\right)\mathrm{d}a,\end{aligned} \tag{26.95}$$

where we have employed Cartesian tensor notation and also ignored the spin density, which is generally small. In the above, apart from the common and well-known terms ρ, v_i the fluxes t_i and m_i represent the surface tractions and couples per unit volume, whereas f_i and ℓ_i are the external body force and body couple per unit mass, respectively.

If $\boldsymbol{n}^+$ is the unit vector at surface points normal to $\partial\mathcal{B}$ and pointing to the exterior region of $\mathcal{B}$ the usual tetrahedronal argument leads to the expressions

$$t_i = t_{ij} n_j^+, \qquad m_i = m_{ij} n_j^+. \tag{26.96}$$

With these, the local balance laws take the forms

$$\rho\dot{v}_i = \rho f_i + t_{ij,j}, \quad 0 = m_{ij,j} + \varepsilon_{ijk} t_{kj} + \rho\ell_i, \tag{26.97}$$

the superimposed dot representing the total (material) time derivative.

The stored energy density W as a function of the unit director field $\boldsymbol{n}$ is, for static processes, given by

$$W = W(n_i, n_{i,j}). \tag{26.98}$$

ERICKSEN [12, 13] shows that invariance of $W(n_i, n_{i,j})$ under EUCLIDian transformations requires W to satisfy the identity

$$\varepsilon_{ipq}\left\{ n_q \frac{\partial W}{\partial n_p} + n_{p,k}\frac{\partial W}{\partial n_{q,k}} + n_{k,p}\frac{\partial W}{\partial n_{k,q}}\right\} \equiv 0. \tag{26.99}$$

The proof of this is reproduced in Chap. 25 [see Eq. (25.48)].

Detailed information on the stresses and couple stresses can be obtained from the energy balance [28],

$$\begin{aligned}&\frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathcal{B}}\left(\tfrac{1}{2}\rho v_i v_i + W\right)\mathrm{d}V + \int_{\mathcal{B}} Diss\,\mathrm{d}V \\ &= \int_{\mathcal{B}} \rho\left(f_i v_i + \ell_i\omega_i\right)\mathrm{d}V + \int_{\partial\mathcal{B}}\left(t_i v_i + m_i\omega_i\right)\mathrm{d}a.\end{aligned} \tag{26.100}$$

In this expression, the two terms on the left-hand side represent the time rate of change of the kinetic and internal energy plus the dissipation rate $Diss$ in $\mathcal{B}$. Those on the right-hand side are the power of working of the body and surface forces and couples, respectively, v_i and ω_i being the local velocity and angular velocity of the material element. The local form of (26.100) reads

$$t_{ij} v_{i,j} + m_{ij} \omega_{i,j} - \varepsilon_{ijk} t_{jk} \omega_i = \dot{W} + Diss. \tag{26.101}$$

Since the vector ω_i is the angular velocity of the material element, we have

$$\dot{n}_i = \varepsilon_{ipq} \omega_p n_q, \quad (n_{i,j})^{\cdot} = (\dot{n}_i)_{,j} - n_{i,k} v_{k,j}. \tag{26.102}$$

It is straightforward to show that

$$\begin{aligned} \dot{W} &= \frac{\partial W}{\partial n_p} \dot{n}_p + \frac{\partial W}{\partial n_{p,q}} (n_{p,q})^{\cdot} \\ &= \varepsilon_{ipq} \left(n_p \frac{\partial W}{\partial n_{q,j}} \omega_{i,j} - n_{k,p} \frac{\partial W}{\partial n_{k,q}} \omega_i \right) - \frac{\partial W}{\partial n_{p,j}} n_{p,i} v_{i,j}. \end{aligned} \tag{26.103}$$

In this derivation, (26.102) and (26.99) have been employed. Combining (26.103) with (26.101), finally, yields, after some rearrangements,

$$\begin{aligned} &\left(t_{ij} + p\delta_{ij} + \frac{\partial W}{\partial n_{p,j}} \right) v_{i,j} + \left(m_{ij} - \varepsilon_{ipq} n_p \frac{\partial W}{\partial n_{q,j}} \right) \omega_{i,j} \\ &\quad - \omega_i \varepsilon_{ipq} \left(t_{qp} - \frac{\partial W}{\partial n_{k,q}} n_{k,p} \right) = Diss, \end{aligned} \tag{26.104}$$

the pressure term (in red color) has been added because its contribution vanishes, owing to $v_{i,i} = 0$ due to density preserving of the liquid. At this stage, LESLIE [28] imposes the thermodynamic requirement $Diss \geqslant 0$ whereby $Diss = 0$ holds in equilibrium. For equilibrium, the first line of (26.104) is linear in $v_{i,j}$ and $\omega_{i,j}$ which may have arbitrary values, implying

$$\begin{aligned} t_{ij}^{\text{eq}} &= -p\delta_{ij} - \frac{\partial W}{\partial n_{p,j}} n_{p,i}, \\ m_{ij}^{\text{eq}} &= \varepsilon_{ipq} n_p \frac{\partial W}{\partial n_{q,j}}. \end{aligned} \tag{26.105}$$

This suggests for the dynamic case the decomposition

$$\begin{aligned} t_{ij} &= -p\delta_{ij} - \frac{\partial W}{\partial n_{p,j}} n_{p,i} + \tilde{t}_{ij}, \\ m_{ij} &= \varepsilon_{ipq} n_p \frac{\partial W}{\partial n_{q,j}} + \tilde{m}_{ij}. \end{aligned} \tag{26.106}$$

Here, $\tilde{t}_{ij}$ and $\tilde{m}_{ij}$ denote the dynamic contributions. Substituting these expressions into (26.104) leads to

$$\tilde{t}_{ij} v_{i,j} + \tilde{m}_{ij} \omega_{i,j} - \omega_i \varepsilon_{ijk} \tilde{t}_{kj} \geqslant 0, \tag{26.107}$$

which is the dissipation inequality. LESLIE [28] requires $\tilde{t}_{ij}$ and $\tilde{m}_{ij}$ to be functions of $n_k, n_{p,q}, \omega_\ell$ (but not $\omega_{\ell,m}$). This implies that (26.107) is linear in the gradient of the angular velocity; so, one immediately concludes

$$\tilde{m}_{ij} \equiv 0. \tag{26.108}$$

Recalling (26.106) and using (26.108), the balance law of angular momentum, (26.97), becomes

$$\varepsilon_{ipq} \left(n_p \frac{\partial W}{\partial n_{q,j}} \right)_{,j} + \rho \ell_i + \varepsilon_{ipq} \tilde{t}_{pq} - \varepsilon_{ipq} \frac{\partial W}{\partial n_{k,p}} n_{k,p} = 0. \tag{26.109}$$

This equation can be simplified by writing

$$\varepsilon_{ijk} \tilde{t}_{kj} = \varepsilon_{ijk} n_j \tilde{g}_k + \tilde{g} n_i. \tag{26.110}$$

This decomposition splits the axial vector of $\tilde{t}_{kj}$ into a component parallel to n_i and a second component perpendicular to n_i. Employing this in (26.109) and using (26.45), viz.,

$$\varepsilon_{ipq} \frac{\partial W}{\partial n_{k,p}} n_{k,q} = \varepsilon_{ipq} n_p \frac{\partial W}{\partial n_q} + \varepsilon_{ipq} n_{p,k} \frac{\partial W}{\partial n_{q,k}},$$

yields for (26.109)

$$\varepsilon_{ipq} n_p \left[\left(\frac{\partial W}{\partial n_{q,j}} \right)_{,j} - \frac{\partial W}{\partial n_q} + \tilde{g}_q \right] + \tilde{g} n_i + \rho \ell_i = 0. \tag{26.111}$$

The body couple $\rho \ell_i$ generally vanishes in a purely mechanical formulation. However, for a nematics LC the body moment due to an external magnetic field or an electric field is generally assumed to have the form [13]

$$\rho \ell_i = \varepsilon_{ipq} n_p G_q, \tag{26.112}$$

where for a magnetic field $\boldsymbol{H}$ or an electric field $\boldsymbol{E}$

$$G_i^m = \Delta \chi^m n_p H_p H_i, \quad G_i^e = \Delta \varepsilon^e n_p E_p E_i, \tag{26.113}$$

in which $\varDelta\chi^m$ is the diamagnetic susceptibility anisotropy and $\varDelta\varepsilon^e$ the dielectric permittivity anisotropy, [28]. Employing (26.112) in (26.111) reduces the latter equation to

$$\underbrace{\varepsilon_{ipq} n_p \left[\left(\frac{\partial W}{\partial n_{q,j}} \right)_{,j} - \frac{\partial W}{\partial n_q} + \tilde{g}_q + G_q \right]}_{\perp n_i} + \tilde{g} n_i = 0, \tag{26.114}$$

from which one immediately concludes that

$$\tilde{g} = 0 \quad \text{and} \quad \left[\left(\frac{\partial W}{\partial n_{i,j}} \right)_{,j} - \frac{\partial W}{\partial n_i} + \tilde{g}_i + G_i \right] = \gamma n_i, \tag{26.115}$$

γ being an arbitrary scalar.

Concerning constitutive relations LESLIE [28] assumes $\tilde{t}_{ij}$ to be an isotropic function of n_i, $v_{i,j}$ and ω_i objective under EUCLIDian transformations, linear in the velocity gradients and the angular velocity. In terms of the objective variables

$$D_{ij} = \tfrac{1}{2}(v_{i,j} + v_{j,i}) \quad \text{and} \quad \varpi_i = \omega_i - \tfrac{1}{2}\varepsilon_{ijk} v_{k,j}, \tag{26.116}$$

and the definitions

$$N_i := \varepsilon_{ipq} \omega_p n_q, \quad \varpi := \omega_p n_p, \tag{26.117}$$

which, alternatively, imply

$$\omega_i = \varepsilon_{ijk} n_j N_k + \varpi n_i, \tag{26.118}$$

LESLIE asserts the viscous stress $\tilde{t}_{ij}$ which is bilinear in n_p and ω_q to be given by

$$\begin{aligned} \tilde{t}_{ij} &= \alpha_1 n_p n_k D_{pk} n_i n_j + \alpha_2 N_i n_j + \alpha_3 N_j n_i + \alpha_4 D_{ij} \\ &\quad + \alpha_5 D_{ip} n_p n_j + \alpha_6 D_{jp} n_i n_p + \alpha_7 \varepsilon_{ijp} n_p \varpi, \end{aligned} \tag{26.119}$$

where the α_i's are constants. Each term in this expression is linear in D_{pq} and ω_p and even in the director $\boldsymbol{n}$ and, thus, invariant against changes $\boldsymbol{n} \to -\boldsymbol{n}$; moreover, since ϖ and ω_p are an axial scalar and axial vector, all seven terms of $\tilde{t}_{ij}$ are objective rank-2 tensors under the full orthogonal group. Next, constructing the axial vector from (26.119), and employing the decomposition (26.110), allows explicit identification of $\tilde{g}_k$ and $\tilde{g}$ as follows:

$$\tilde{g}_i = -\gamma_1 N_i - \gamma_2 D_{ip} n_p, \quad \tilde{g} = -\gamma_3 \varpi, \tag{26.120}$$

where

$$\gamma_1 = \alpha_3 - \alpha_2, \quad \gamma_2 = \alpha_6 - \alpha_5, \quad \gamma_3 = 2\alpha_7.$$

The coefficients γ_1 and γ_2 agree with the corresponding coefficients obtained in (26.92) of the earlier SONNET-VIRGA model. However, the coefficient γ_3 from (26.92) is obtained from the sum $\alpha_5 + \alpha_6$ and is not separately given as $2\alpha_7$. The reason is the adoption of the ONSAGER–PARODI relation in the former parameterization of $\tilde{t}_{ij}$ but not in the latter. With (26.108) and (26.116), the inequality (26.107) takes the form

$$\tilde{t}_{ij} D_{ij} - \omega_i \varepsilon_{ijk} \tilde{t}_{kj} \geqslant 0, \tag{26.121}$$

or when expressed in terms of (26.116)

$$\tilde{t}_{ij} D_{ij} - \tilde{g}_i N_i - \tilde{g} n_i \geqslant 0. \tag{26.122}$$

According to LESLIE [28], this “differs from his earlier theory [27] through the final term.” The imbalance (26.122) is used to constrain the coefficients of the constitutive quantities $\tilde{t}_{ij}$, $\tilde{g}_i$, and $\tilde{g}$.

SONNET and VIRGA [44] emphasize that

(1) the field equations of their uniaxial nematic LC formulation, expressed by (26.79), (26.80) correspond to the balance laws of linear and angular momenta (26.97) of LESLIE [28].
(2) their expressions for the viscous stress $(26.82)_2$ or (26.91) correspond to LESLIE’s expression (26.119) [except for the term involving α_7].
(3) the couple stress tensor is given in both formulations by

$$m_{ij} = \varepsilon_{ik\ell} n_k \frac{\partial W}{\partial n_{k,\ell}}, \quad \text{in } \mathcal{B} \cup \partial\mathcal{B}, \tag{26.123}$$

having only elastic but no viscous contributions. This is a consequence of the fact that grad $\dot{\boldsymbol{n}}$ is not an independent constitutive quantity.

Finally, combining the result in $(26.115)_1$ $\tilde{g} = 0$ with the definition of $\tilde{g}$ in (26.120) implies

$$\varpi = 0 \quad \xrightarrow{(26.116)} \quad \omega_p n_p = \tfrac{1}{2} n_p \varepsilon_{pjk} v_{k,j}. \tag{26.124}$$

This equation states that “the local spin about the director must always be equal to the local component of vorticity in that direction” [28].

Fig. 26.1 PIERRE- GILLES DE GENNES (October 24, 1932–May 18, 2007)

PIERRE-GILLES DE GENNES was a French physicist and NOBEL Prize Laureate of physics in 1991.

Born in Paris, DE GENNES was homeschooled to the age of 12 and early matured. He graduated in 1955 from École Normale Superieur and subsequently became a Research Engineer at the Saclac Center of Atomic Energy, where he was engaged in neutron scattering and magnetism. In 1957, he earned his doctorate and left the centre in 1959 to the University of California in Berkeley to work with CHARLES KITTEL on solid-state physics.

After a 27-month service in the French Marine, he became in 1961 Assistant Professor in Orsay, where he first devoted his research activities to superconductors, but switched in 1968 to the physics of liquid crystals. In 1971, he was appointed as Professor of Physics at the Collége de France. He was honored by the Prix AMPÉRE (1977), the GAY-LUSSAC-HUMBOLDT-Prize (1983), the ACS Award in polymer chemistry (1988), the LORENTZ Medaille (1990), and the NOBEL Prize in Physics (1991) for his discovery that methods, developed for studying order phenomena in simple systems can be generalized to more complex forms of matter, in particular to liquid crystals and to polymers. See [1, 6–8].

The text is based on www.wikipedia.org

26.2.4 Uniaxial Nematics with Variable Scalar Order Parameter

As explained in Sect. 26.2.1, we shall now apply an expression for the LC internal energy as a function of $\boldsymbol{n}$ grad $\boldsymbol{n}$ S and grad S, viz.,

$$W = W(S, \operatorname{grad} S, \boldsymbol{n}, \operatorname{grad} \boldsymbol{n}), \tag{26.125}$$

which, in general will describe elastic terms as well as terms due to the LANDAU–DE GENNES[8] potential through a single dependence on S. The time rate of change of the kinetic and internal energy, $\dot{\mathcal{F}}$ as given in (26.65), is now of the form[9]

$$\begin{aligned}
\dot{\mathcal{F}} &= RHS(6.65) + \int_{\mathcal{B}} \left\{ \left(\frac{\partial W}{\partial S}\right)\dot{S} + \left(\frac{\partial W}{\partial \operatorname{grad} S}\right) \cdot \underbrace{(\operatorname{grad} S)^{\cdot}}_{\operatorname{grad}\dot{S} - (\operatorname{grad} S)\cdot \operatorname{grad} \boldsymbol{v}} \right\} \mathrm{d}V \\
&= RHS(6.67) - \int_{\mathcal{B}} \left\{ \operatorname{div}\left(\frac{\partial W}{\partial \operatorname{grad} S}\right) \cdot \dot{S} \right. \\
&\qquad \left. + \left(\operatorname{grad} S \otimes \frac{\partial W}{\partial \operatorname{grad} S}\right)^T \cdot \operatorname{grad} \boldsymbol{v} \right\} \mathrm{d}V \\
&\qquad + \int_{\partial\mathcal{B}} \left(\frac{\partial W}{\partial \operatorname{grad} S}\right) \dot{S} \cdot \boldsymbol{n}^+ \mathrm{d}a.
\end{aligned} \tag{26.126}$$

It follows that $\dot{\mathcal{F}}$ now takes the form

$$\begin{aligned}
\dot{\mathcal{F}} = RHS(6.68) &- \int_{\mathcal{B}} \left\{ \operatorname{div}\left(\frac{\partial W}{\partial \operatorname{grad} S}\right) \cdot \dot{S} \right. \\
&\left. + \left(\operatorname{grad} S \otimes \left(\frac{\partial W}{\partial \operatorname{grad} S}\right)\right)^T \cdot \operatorname{grad} \boldsymbol{v} \right\} \mathrm{d}V \\
&+ \int_{\partial\mathcal{B}} \left(\frac{\partial W}{\partial \operatorname{grad} S}\right) \dot{S} \cdot \boldsymbol{n}^+ \mathrm{d}a.
\end{aligned} \tag{26.127}$$

The generalized force, analogous to $(26.30)_1$, becomes

$$\begin{aligned}
\boldsymbol{X} = \rho\dot{\boldsymbol{v}} + \operatorname{div} &\left((\operatorname{grad} \boldsymbol{n})^T \left(\frac{\partial W}{\partial \operatorname{grad} \boldsymbol{n}}\right) \right. \\
&\left. + \operatorname{grad} S \otimes \left(\frac{\partial W}{\partial \operatorname{grad} S}\right)\right)^T + p\boldsymbol{I}.
\end{aligned} \tag{26.128}$$

---

[8] For a brief biographical sketch of PIERRE-GILLES DE GENNES (1932–2007), see **Fig. 26.1**.

[9] $RHS(\cdot)$ and $LHS(\cdot)$ denote the right- and left-hand sides of the equation $(\cdot)$.

Equation (26.30)$_2$ as a generalized force conjugate to $\dot{\boldsymbol{n}}$ remains unchanged. However, a generalized force conjugate to $\dot{S}$ and analogous to (26.30)$_2$ is given by

$$\mathbb{X}^S = \frac{\partial W}{\partial S} - \operatorname{div}\left(\frac{\partial W}{\partial \operatorname{grad} S}\right), \tag{26.129}$$

which enters the balance Eq. (26.37)$_2$ [in which $\hat{\mathbb{O}}$ is replaced by S], given by

$$\mathbb{X}^S + \frac{\partial R}{\partial \dot{S}} = 0. \tag{26.130}$$

In order to complete the model, the dissipation function needs to be specified. This is done by requesting R to be of the form

$$R = R(\boldsymbol{n}, \overset{\circ}{\boldsymbol{n}}\ S, \operatorname{grad} S, \boldsymbol{D}), \tag{26.131}$$

objective under EUCLIDian transformations and quadratic in the rate variables $\overset{\circ}{\boldsymbol{n}}$, $\dot{S}$, and $\boldsymbol{D}$. Equation (26.88) lists the most general form of such an R when $R = R(\boldsymbol{n}, \overset{\circ}{\boldsymbol{n}}$, $\boldsymbol{D})$. This expression must be complemented by two additional terms, which are of the form $\dot{S}\boldsymbol{n} \cdot \boldsymbol{D}\boldsymbol{n}$ and $\dot{S}^2$. It follows that

$$\begin{aligned} R = {} & \beta_1 \dot{S}\boldsymbol{n} \cdot \boldsymbol{D}\boldsymbol{n} + \tfrac{1}{2}\beta_2 \dot{S}^2 + \tfrac{1}{2}\gamma_1 \overset{\circ}{\boldsymbol{n}}{}^2 + \gamma_2 \overset{\circ}{\boldsymbol{n}} \cdot \boldsymbol{D}\boldsymbol{n} \\ & + \tfrac{1}{2}\gamma_3 \tfrac{1}{2} (\boldsymbol{D}\boldsymbol{n})^2 + \tfrac{1}{2}\gamma_4 \operatorname{tr} \boldsymbol{D}^2 + \tfrac{1}{2}\gamma_5 (\boldsymbol{n} \cdot \boldsymbol{D}\boldsymbol{n})^2, \end{aligned} \tag{26.132}$$

in which the coefficients β and γ are now functions of S. With

$$\frac{\partial R}{\partial \dot{S}} = \beta_1 \boldsymbol{n} \cdot \boldsymbol{D}\boldsymbol{n} + \beta_2 \dot{S}, \tag{26.133}$$

the additional evolution Eq. (26.130) becomes

$$\frac{\partial W}{\partial S} - \operatorname{div}\left(\frac{\partial W}{\partial \operatorname{grad} S}\right) + \beta_1 \boldsymbol{n} \cdot \boldsymbol{D}\boldsymbol{n} + \beta_2 \dot{S} = 0, \tag{26.134}$$

where (26.129) has also been used.

There remains the complementation of the stress tensor (26.79) by the contribution due to a dependence of W and R on S and $\dot{S}$. That of W must be of the form

$$\boldsymbol{t}^{S_1} = -\operatorname{grad} S \left(\frac{\partial W}{\partial \operatorname{grad} S}\right), \tag{26.135}$$

while that owing to R is manifest by the contribution of $\partial R/\partial \boldsymbol{D}$ or

$$\boldsymbol{t}^{S_2} = \beta_1 \dot{S}\boldsymbol{n} \otimes \boldsymbol{n}. \tag{26.136}$$

Apart from the effects of microrotation, which have been neglected here, the evolution equations derived in this and the previous sections are the same as those obtained by Ericksen in [15].

26.3 Nematic Liquid Crystals Based on a Rank-2 Alignment Tensor

26.3.1 Motivation

This section presents a straightforward generalization of the formulation of the LC theory, based on a variable scalar order parameter S. Here, our aim is the derivation of a model that is based on a rank-2 alignment tensor. Such models have been formulated by Hess [21, 22] and later by Olmsted and Goldbart [35, 36] for homogeneous alignment and by Hess and Pardowitz [24]. As stated by Sonnet et al. [46] “all these attempts have been impaired by not yielding the full anisotropy of viscosities predicted by the ELP theory and confirmed experimentally. The extension to a co-deformational model was proposed by Hess [23] who recovered the complete anisotropies, but failed otherwise to be in full agreement with the ELP theory as shown in [38].”

Sonnet et al. [46] provide a detailed review of attempts of employing rank-2 alignment tensors [10, 16, 20, 22, 34, 40, 42], starting from a Fokker–Planck statistical approach, ultimately also including spatial variations of the orientation of the alignment tensor. They also emphasize that the variational Lagrange–Rayleigh approach, as demonstrated in Sect. 26.1 is advantageous; specifically, “there is no need to resort to the balance of angular momentum, though it remains valid, and even the balance of linear momentum is only invoked to identify the stress tensor” [44].

In the ensuing analysis, we shall employ the variational principle outlined in Sect. 26.1.2 to nematic LCs with rank-2 alignment tensors. To this end, the reader may with advantage rehearse the key steps of the developments of this section. We shall simply refer to the relevant equations without deeper explanation at this place.

26.3.2 Lagrange–Rayleigh Theory of the Alignment Tensor

As already pointed out earlier, a second rank alignment tensor $\boldsymbol{Q}$ is defined as the deviator constructed with the dyadic product of a unit vector $\boldsymbol{\nu}$

$$\boldsymbol{Q} = \langle \boldsymbol{\nu} \otimes \boldsymbol{\nu} - \tfrac{1}{3}\boldsymbol{I} \rangle =: \langle \overbracket{\boldsymbol{\nu} \otimes \boldsymbol{\nu}} \rangle, \tag{26.137}$$

where $\boldsymbol{I}$ is the identity tensor and $\langle \cdot \rangle$ denotes temporal plus spatial averaging.

For a specific LC, the alignment tensor must be defined on the basis of material properties, e.g., $\boldsymbol{Q}$ is proportional to the anisotropic traceless part of the electric permittivity tensor or of the magnetic susceptibility tensor. If the permittivity (susceptibility) tensor is $\boldsymbol{\epsilon}$ and $\epsilon_{\|}$ and $\epsilon_{\perp}$ are the permittivities (susceptibilities) parallel and perpendicular to the molecular symmetry axis for a perfectly oriented sample, then [48]

$$\boldsymbol{\epsilon} = \tfrac{1}{3}(\epsilon_{\|} + 2\epsilon_{\perp})\boldsymbol{I} + (\epsilon_{\|} - \epsilon_{\perp})\,\boldsymbol{Q}$$

defines the alignment tensor $\boldsymbol{Q}$.

(a) Free Energy. Following the scheme outlined in Sect. 26.1, we write the total energy as in (26.19), viz.,

$$\mathcal{F} = \int_{\mathcal{B}} \left\{\tfrac{1}{2}\rho\boldsymbol{v}\cdot\boldsymbol{v} + \chi(\boldsymbol{Q}) + W(\boldsymbol{Q}, \text{grad}\,\boldsymbol{Q})\right\}\mathrm{d}V, \tag{26.138}$$

and have omitted here the contributions

(1) ϕ the potential energy due to the body force ($\boldsymbol{f} = \boldsymbol{0}$),
(2) σ the potential energy due to the compressibility of the fluid, since considerations are restricted to density preserving liquids,
(3) the kinetic energy due to the microstructure as we ignore rotational inertia.

Evaluation of the time rate of change of $\mathcal{F}$ then follows exactly the procedure as outlined between the formulae (26.19) and (26.28). Following these lines yields

$$\begin{aligned}
\dot{\mathcal{F}} &= \int_{\mathcal{B}} \left\{\rho\dot{\boldsymbol{v}}\cdot\boldsymbol{v} + \left(\frac{\partial\chi}{\partial\boldsymbol{Q}} + \frac{\partial W}{\partial\boldsymbol{Q}}\right)\cdot\dot{\boldsymbol{Q}} + \frac{\partial W}{\partial\text{grad}\,\boldsymbol{Q}}\cdot(\text{grad}\,\boldsymbol{Q})^{\cdot}\right\}\mathrm{d}V \\
&\;\vdots \\
&= \int_{\mathcal{B}} \left\{\left[\rho\dot{\boldsymbol{v}} + \text{div}\left(p\boldsymbol{I} + \text{grad}\,\boldsymbol{Q}\odot\frac{\partial W}{\partial\text{grad}\,\boldsymbol{Q}}\right)\right]\cdot\boldsymbol{v}\right. \\
&\qquad\left. + \left[\frac{\partial\chi}{\partial\boldsymbol{Q}} + \frac{\partial W}{\partial\boldsymbol{Q}} - \text{div}\,\frac{\partial W}{\partial\text{grad}\,\boldsymbol{Q}}\right]\cdot\dot{\boldsymbol{Q}}\right\}\mathrm{d}V \\
&\quad + \int_{\partial\mathcal{B}} \left\{\left[\left(p\boldsymbol{I} + \text{grad}\,\boldsymbol{Q}\odot\frac{\partial W}{\partial\text{grad}\,\boldsymbol{Q}}\right)\boldsymbol{n}^{+}\right]\cdot\boldsymbol{v}\right. \\
&\qquad\left. + \left(\frac{\partial W}{\partial\text{grad}\,\boldsymbol{Q}}\boldsymbol{n}^{+}\right)\cdot\dot{\boldsymbol{Q}}\right\}\mathrm{d}a,
\end{aligned} \tag{26.139}$$

in which the operator $\odot$ is defined by

$$\left(\text{grad}\,\boldsymbol{Q}\odot\frac{\partial W}{\partial\text{grad}\,\boldsymbol{Q}}\right)_{ij} = Q_{k\ell,i}\frac{\partial W}{\partial Q_{k\ell,j}}, \tag{26.140}$$

as already shown in (26.28). $p\boldsymbol{I}$ is the contribution of the constraint pressure due to the density preserving of the fluid. This term also arose in the expression (26.68) for $\dot{\mathcal{F}}$ of a uniaxial nematics LC. However, corresponding constraint terms like $\mu\boldsymbol{n}$ and $\mu_b\boldsymbol{n}$ do not arise here, because at this point no constraints on $\boldsymbol{Q}$ are imposed.

(b) Variation of the Dissipation Function $\boldsymbol{R}$. In line with the assumption of constraint-free deformation of $\boldsymbol{Q}$, we introduce as EUCLIDian objective time derivative the corotational derivative already introduced in (26.18). For the present purposes, it is written as

$$\overset{\diamond}{\boldsymbol{Q}} := \dot{\boldsymbol{Q}} - 2\,\overbracket{\boldsymbol{W}\boldsymbol{Q}} - 2\sigma\,\overbracket{\boldsymbol{D}\boldsymbol{Q}}, \tag{26.141}$$

where σ is a scalar constitutive parameter or a constant [38]. We prove frame indifference of (26.141) in Appendix 26.C. According to SONNET et al. [46] "ERICKSEN [15] remarked that choosing $\sigma \neq 0$ in general just amounts to reordering the same terms. If $\sigma = 0$ (26.141) delivers the corotational derivative $\overset{\circ}{\boldsymbol{Q}} = \dot{\boldsymbol{Q}} - 2\,\overbracket{\boldsymbol{W}\boldsymbol{Q}}$ that describes how $\boldsymbol{Q}$ changes in a frame that rotates with the fluid element." It follows that it suffices, in principle, to choose $R = R(\boldsymbol{Q}, \overset{\circ}{\boldsymbol{Q}}, \boldsymbol{D})$ in lieu of $R(\boldsymbol{Q}, \overset{\diamond}{\boldsymbol{Q}}, \boldsymbol{D})$. This is all the more justified as both $\overset{\diamond}{\boldsymbol{Q}}$ and $\overset{\circ}{\boldsymbol{Q}}$ are linear in $\boldsymbol{D}$ or grad $\boldsymbol{v}$. Following [46], we shall choose R to be bilinear in $\dot{\boldsymbol{Q}}$ and grad $\boldsymbol{v}$. Based on this device, the variational principle $\delta\dot{\mathcal{F}} + \delta R = 0$ requires evaluation of the following derivatives of R:

$$\frac{\partial R}{\partial \overset{\circ}{\boldsymbol{Q}}} = \frac{\partial R}{\partial \dot{Q}} \circ \frac{\partial \dot{\boldsymbol{Q}}}{\partial \overset{\circ}{\boldsymbol{Q}}} = \frac{\partial R}{\partial \dot{\boldsymbol{Q}}}, \tag{26.142}$$

$$\begin{aligned}\frac{\partial R}{\partial \mathrm{grad}\,\boldsymbol{v}} &= \frac{\partial R}{\partial \boldsymbol{D}} \circ \frac{\partial \boldsymbol{D}}{\partial \mathrm{grad}\,\boldsymbol{v}} + \frac{\partial R}{\partial \overset{\circ}{\boldsymbol{Q}}} \circ \frac{\partial \overset{\circ}{\boldsymbol{Q}}}{\partial \mathrm{grad}\,\boldsymbol{v}} \\ &= \frac{\partial R}{\partial \boldsymbol{D}} + \boldsymbol{Q}\frac{\partial R}{\partial \overset{\circ}{\boldsymbol{Q}}} - \frac{\partial R}{\partial \overset{\circ}{\boldsymbol{Q}}}\boldsymbol{Q},\end{aligned} \tag{26.143}$$

which both can best be verified by using the chain rule of differentiation, the definition of $\overset{\circ}{\boldsymbol{Q}} = \dot{\boldsymbol{Q}} - 2(\overbracket{\boldsymbol{W}\boldsymbol{Q}})$ and employing Cartesian tensor notation. With the above expressions, the variation of the dissipation function R takes the form

$$\delta R = \int_{\mathcal{B}} \left\{ \frac{\partial R}{\partial \dot{\boldsymbol{Q}}} \delta \dot{\boldsymbol{Q}} + \frac{\partial R}{\partial \mathrm{grad}\,\boldsymbol{v}} \cdot \mathrm{grad}\,(\delta \boldsymbol{v}) \right\} \mathrm{d}V. \tag{26.144}$$

With $(26.142)_2$ we may write

$$\begin{aligned}\int_{\mathcal{B}} \frac{\partial R}{\partial \boldsymbol{D}} \cdot (\delta \operatorname{grad} \boldsymbol{v}) \mathrm{d}V = &- \int_{\mathcal{B}} \operatorname{div} \left(\frac{\partial R}{\partial \boldsymbol{D}} \right) \cdot \delta \boldsymbol{v} \mathrm{d}V \\ &+ \int_{\partial \mathcal{B}} \left(\frac{\partial R}{\partial \boldsymbol{D}} \boldsymbol{n}^{+} \right) \cdot \delta \boldsymbol{v} \mathrm{d}a, \end{aligned} \tag{26.145}$$

and

$$\begin{aligned} &\int_{\mathcal{B}} \left\{ \left[\boldsymbol{Q} \frac{\partial R}{\partial \overset{\circ}{\boldsymbol{Q}}} - \frac{\partial R}{\partial \overset{\circ}{\boldsymbol{Q}}} \boldsymbol{Q} \right] \right\}_{ij} \delta v_{i,j} \mathrm{d}V \\ &= \int_{\mathcal{B}} \left\{ \left[\boldsymbol{Q} \frac{\partial R}{\partial \overset{\circ}{\boldsymbol{Q}}} - \frac{\partial R}{\partial \overset{\circ}{\boldsymbol{Q}}} \boldsymbol{Q} \right]_{ij} \delta v_i \right\}_{,j} \mathrm{d}V \\ &\quad - \int_{\mathcal{B}} \left\{ \left[\boldsymbol{Q} \frac{\partial R}{\partial \overset{\circ}{\boldsymbol{Q}}} - \frac{\partial R}{\partial \overset{\circ}{\boldsymbol{Q}}} \boldsymbol{Q} \right]_{ij,j} \delta v_i \right\} \mathrm{d}V \\ &= - \int_{\mathcal{B}} \left\{ \operatorname{div} \left[\boldsymbol{Q} \frac{\partial R}{\partial \overset{\circ}{\boldsymbol{Q}}} - \frac{\partial R}{\partial \overset{\circ}{\boldsymbol{Q}}} \right] \cdot \delta \boldsymbol{v} \right\} \mathrm{d}V \\ &\quad + \int_{\partial \mathcal{B}} \left[\boldsymbol{Q} \frac{\partial R}{\partial \overset{\circ}{\boldsymbol{Q}}} - \frac{\partial R}{\partial \overset{\circ}{\boldsymbol{Q}}} \boldsymbol{Q} \right] \boldsymbol{n}^{+} \cdot \delta \boldsymbol{v} \, \mathrm{d}a, \end{aligned} \tag{26.146}$$

upon integration by parts and use of the divergence (GAUSS) theorem. These results agree with those of SONNET et al. [46]. Putting all together, we obtain

$$\begin{aligned} \delta R = \int_{\mathcal{B}} &\left\{ \frac{\partial R}{\partial \overset{\circ}{\boldsymbol{Q}}} \cdot \delta \overset{\circ}{\boldsymbol{Q}} \right. \\ &\left. - \operatorname{div} \left(\frac{\partial R}{\partial \boldsymbol{D}} + \boldsymbol{Q} \frac{\partial R}{\partial \overset{\circ}{\boldsymbol{Q}}} - \frac{\partial R}{\partial \overset{\circ}{\boldsymbol{Q}}} \boldsymbol{Q} \right) \cdot \delta \boldsymbol{v} \right\} \mathrm{d}V \\ &+ \int_{\partial \mathcal{B}} \left\{ \left(\frac{\partial R}{\partial \boldsymbol{D}} + \boldsymbol{Q} \frac{\partial R}{\partial \overset{\circ}{\boldsymbol{Q}}} - \frac{\partial R}{\partial \overset{\circ}{\boldsymbol{Q}}} \boldsymbol{Q} \right) \boldsymbol{n}^{+} \right\} \cdot \delta \boldsymbol{v} \, \mathrm{d}a. \end{aligned} \tag{26.147}$$

(c) Equations of Motion. These equations are obtained from the variational theorem

$$\delta(\dot{\mathcal{F}} + \lambda R) = 0, \quad \forall \delta \dot{\boldsymbol{Q}} \text{ and } \delta \boldsymbol{v}, \tag{26.148}$$

where $\dot{\mathcal{F}}$ is given in (26.139) and δR in (26.147), and $\lambda = 1$. From the expression in the bulk and for independent variations of $\delta \dot{\boldsymbol{Q}}$ and $\delta \boldsymbol{v}$, we obtain

$$\left.\begin{aligned}&\frac{\partial R}{\partial \overset{\circ}{\boldsymbol{Q}}}+\frac{\partial \chi}{\partial \boldsymbol{Q}}+\frac{\partial W}{\partial \boldsymbol{Q}}-\operatorname{div}\left(\frac{\partial W}{\partial \operatorname{grad} \boldsymbol{Q}}\right)=0,\\ &\rho \dot{\boldsymbol{v}}=\operatorname{div} \boldsymbol{t}\end{aligned}\right\}\quad \text{in } \mathcal{B}, \tag{26.149}$$

in which

$$\boldsymbol{t}=-p\boldsymbol{I}-\underline{\operatorname{grad}\boldsymbol{Q}\odot\frac{\partial W}{\partial \operatorname{grad}\boldsymbol{Q}}}+\frac{\partial R}{\partial \boldsymbol{D}}+\underline{\boldsymbol{Q}\frac{\partial R}{\partial \overset{\circ}{\boldsymbol{Q}}}-\frac{\partial R}{\partial \overset{\circ}{\boldsymbol{Q}}}\boldsymbol{Q}}. \tag{26.150}$$

It is straightforward to show that only the underlined terms contribute to the skew-symmetric part of $\boldsymbol{t}$.[10] On a free boundary $\partial\mathcal{B}$, the variations of $\dot{\boldsymbol{Q}}$ and $\boldsymbol{v}$ are independent and arbitrary. It then follows easily from (26.139) and (26.147) that

$$\frac{\partial W}{\partial \operatorname{grad}\boldsymbol{Q}}\boldsymbol{n}^{+}=\boldsymbol{0}\quad\text{and}\quad \boldsymbol{t}\boldsymbol{n}^{+}=\boldsymbol{0},\quad \text{on } \partial\mathcal{B}. \tag{26.151}$$

These equations state that the micro- and macroforces vanish on a free surface.

(d) Balances of Linear and Angular Momenta. Equation (26.149) evidences for this LC model the satisfaction of the local form of the linear momentum balance equation, if body forces are absent. Moreover, it provides a formula for the CAUCHY stress tensor, if the internal energy W and the dissipation function R are prescribed. Alternatively, it is not directly evident from the field Eq. $(26.149)_1$ and given constitutive relations, whether the balance law of angular momentum

$$\rho\boldsymbol{\ell}+\operatorname{div}\boldsymbol{m}-\boldsymbol{\tau}=\boldsymbol{0}, \tag{26.152}$$

in which $\boldsymbol{\ell}$ is the body couple per unit mass, $\boldsymbol{m}$ is the couple stress, and $\boldsymbol{\tau}$ is the dual axial vector of the skew-symmetric part of the stress tensor ($\tau_i=\varepsilon_{ijk}t_{kj}$) is identically satisfied. This is indeed so and will now be demonstrated.

The crucial idea to this end is to search for the implications of W to be invariant under EUCLIDian transformations,

$$W(Q_{ij},Q_{ij,k})=W(R_{ip}R_{jq}Q_{pq},R_{ip}R_{jq}R_{kr}Q_{pq,r}), \tag{26.153}$$

in which R_{ip} is a proper orthogonal transformation ($R_{ip}R_{jp}=\delta_{ij}$). We leave it as an exercise to the reader, to follow the guidelines, leading to Eq. (25.48) in Chap. 25 that satisfaction of (26.153) is equivalent to the statement

$$\varepsilon_{ijk}\left(2Q_{jp}\frac{\partial W}{\partial Q_{pk}}+2Q_{jp,q}\frac{\partial W}{\partial Q_{pk,q}}+\underline{Q_{pq,j}\frac{\partial W}{\partial Q_{pq,k}}}\right)=0. \tag{26.154}$$

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[10] We will show that for the choice of the function W the first of the underlined terms will be symmetric.

Guided by the process leading to the axial vector τ of the CAUCHY stress (26.150), we find, owing to the definition (26.150),

$$\tau_i = \varepsilon_{ijk}\left(2Q_{j\ell}\frac{\partial R}{\partial \overset{\circ}{Q}_{kl}} - \underline{Q_{\ell m,j}\frac{\partial W}{\partial Q_{\ell m,k}}}\right). \tag{26.155}$$

Replacing the underlined term in this equation by the corresponding term in (26.154) yields

$$\tau_i = 2\varepsilon_{ijk}\left(Q_{j\ell}\frac{\partial R}{\partial \overset{\circ}{Q}_{\ell k}} + Q_{j\ell}\frac{\partial W}{\partial Q_{\ell k}} + Q_{j\ell,m}\frac{\partial W}{\partial Q_{\ell k,m}}\right). \tag{26.156}$$

A last change can be made by eliminating the dissipation function by the expression

$$\frac{\partial R}{\partial \overset{\circ}{Q}_{\ell k}} = -\frac{\partial \chi}{\partial Q_{\ell k}} - \frac{\partial W}{\partial Q_{\ell k}} + \left(\frac{\partial W}{\partial Q_{\ell k,m}}\right)_{,m},$$

as follows from the field Eq. (26.149) for the alignment tensor,

$$\begin{aligned}\tau_i &= 2\varepsilon_{ijk}\left\{-Q_{j\ell}\frac{\partial \chi}{\partial Q_{\ell k}} - Q_{j\ell}\frac{\partial W}{\partial Q_{\ell k}} + Q_{j\ell}\left(\frac{\partial W}{\partial Q_{\ell k,m}}\right)_{,m}\right.\\ &\qquad \left. + Q_{j\ell}\frac{\partial W}{\partial Q_{\ell k}} + Q_{j\ell,m}\frac{\partial W}{\partial Q_{\ell k,m}}\right\}\\ &= 2\varepsilon_{ijk}\left\{\left(Q_{j\ell}\frac{\partial W}{\partial Q_{\ell k,m}}\right)_{,m} - Q_{j\ell}\frac{\partial \chi}{\partial Q_{\ell k}}\right\}.\end{aligned} \tag{26.157}$$

From the balance of angular momentum (26.152) as an axial vector statement, we obtain

$$\tau_i = \rho\ell_i + \varepsilon_{ijk}(m_{jk,n})_{,n} \quad \text{where } \ell_i := \varepsilon_{ijk}\ell_{jk}. \tag{26.158}$$

Comparison of (26.156) and (26.157) now yields

$$\rho\ell_i = -2\varepsilon_{ijk}Q_{j\ell}\frac{\partial \chi}{\partial Q_{\ell k}}, \quad m_{jk} = Q_{j\ell}\frac{\partial W}{\partial Q_{\ell k}}, \tag{26.159}$$

as conditions for the satisfaction of the angular momentum balance. The second of Eq. (26.159) indicates that the couple stress tensor only depends upon the elastic energy W. The absence of viscous contributions to m_{jk} is due to the omission of (grad $\overset{\circ}{\boldsymbol{Q}}$) as independent constitutive quantity as already alerted to in the director LC theory in Chap. 25.

On the other hand, a possible body couple is induced by a nontrivial potential χ which could, e.g., be formulated when an electric or magnetic field would be present. For an electric field $\boldsymbol{E}$ [46]

$$\begin{aligned} \chi(\boldsymbol{Q}) &= -\tfrac{1}{2}\epsilon \boldsymbol{E}\cdot\boldsymbol{Q}\boldsymbol{E}, \quad \epsilon = \epsilon_0(\epsilon_{\parallel} - \epsilon_{\perp}), \\ \frac{\partial\chi}{\partial\boldsymbol{Q}} &= \tfrac{1}{2}\epsilon\,\overbracket{\boldsymbol{E}\otimes\boldsymbol{E}}, \quad \rho\boldsymbol{\ell} = \epsilon\boldsymbol{E}\times\boldsymbol{Q}\boldsymbol{E}. \end{aligned} \tag{26.160}$$

So, if $\boldsymbol{Q}\boldsymbol{E}$ is proportional to $\boldsymbol{E}$ then $\rho\boldsymbol{\ell} = \boldsymbol{0}$; no intrinsic couple is generated.

(e) Parameterization of the Dissipation Function. As a function of $\boldsymbol{Q}$, $\overset{\circ}{\boldsymbol{Q}}$, and $\boldsymbol{D}$, the most general form for R is obtained by writing it as a function of all invariants that can be formed with these three rank-2 tensors. We had already earlier restricted R to be bilinear in $\overset{\circ}{\boldsymbol{Q}}$ and $\boldsymbol{D}$ and quadratic in $\boldsymbol{Q}$. ERICKSEN [15] showed that in this case there are 15 invariants. SONNET et al. [46] chose the minimal basis for invariant polynomial functions given by SMITH [43] as stated in **Table 26.1**. When the order is restricted to be uniaxial, the alignment tensor, written in terms of the director is

$$\boldsymbol{Q} = S\,\overbracket{\boldsymbol{n}\otimes\boldsymbol{n}}, \tag{26.161}$$

where S is the MAIER–SAUPE order parameter and

$$\overset{\circ}{\boldsymbol{n}} = \dot{\boldsymbol{n}} - \boldsymbol{W}\boldsymbol{n}, \quad \overset{\circ}{\boldsymbol{Q}} = \dot{\boldsymbol{Q}} - 2\,\overbracket{\boldsymbol{W}\boldsymbol{Q}} \tag{26.162}$$

are the corotational derivatives of $\boldsymbol{n}$ and $\boldsymbol{Q}$.

Based on these definitions, and the assumption of a constant order parameter S detailed, but in principle not difficult, computations lead to **Table 26.2**.[11] Because S is generally smaller than unity, it is customary to restrict the number of invariants in Table 26.1 to those elements, which are in Table 26.2 independent of S and/or at most quadratic in S. This then restricts the number of invariants in Table 26.1 to 10 elements that are accounted for.

---

[11] In these tables, the first line shows those combinations of $\overset{\circ}{\boldsymbol{Q}}$ and $\boldsymbol{D}$ which do not involve $\boldsymbol{Q}$. The remaining four lines then show those scalar invariants, which are combinations with linear or quadratic $\boldsymbol{Q}$-dependences. We shall identify the 15 elements of these tables by the indices

[1]	[2]	[3]
[11]	[21]	[31]
[12]	[22]	[32]
[13]	[23]	[33]
[14]	[24]	[34]

Table 26.1 Building blocks for the dissipation function

$\overset{\circ}{\boldsymbol{Q}} \cdot \overset{\circ}{\boldsymbol{Q}}$	$\boldsymbol{D} \cdot \overset{\circ}{\boldsymbol{Q}}$	$\boldsymbol{D} \cdot \boldsymbol{D}$
$\overset{\circ}{\boldsymbol{Q}} \cdot (\overset{\circ}{\boldsymbol{Q}}\, \boldsymbol{Q})$	$\overset{\circ}{\boldsymbol{Q}} \cdot (\boldsymbol{D}\boldsymbol{Q})$	$\boldsymbol{D} \cdot (\boldsymbol{D}\boldsymbol{Q})$
$(\overset{\circ}{\boldsymbol{Q}} \cdot \boldsymbol{Q})^2$	$(\boldsymbol{D} \cdot \boldsymbol{Q})(\overset{\circ}{\boldsymbol{Q}} \cdot \boldsymbol{Q})$	$(\boldsymbol{D} \cdot \boldsymbol{Q})^2$
$(\overset{\circ}{\boldsymbol{Q}}\, \boldsymbol{Q}) \cdot (\overset{\circ}{\boldsymbol{Q}}\, \boldsymbol{Q})$	$(\boldsymbol{D}\boldsymbol{Q}) \cdot (\overset{\circ}{\boldsymbol{Q}}\, \boldsymbol{Q})$	$(\boldsymbol{D}\boldsymbol{Q}) \cdot (\boldsymbol{D}\boldsymbol{Q})$
$(\boldsymbol{Q} \cdot \boldsymbol{Q})(\overset{\circ}{\boldsymbol{Q}} \cdot \overset{\circ}{\boldsymbol{Q}})$	$(\boldsymbol{Q} \cdot \boldsymbol{Q})(\boldsymbol{D} \cdot \overset{\circ}{\boldsymbol{Q}})$	$(\boldsymbol{Q} \cdot \boldsymbol{Q})(\boldsymbol{D} \cdot \boldsymbol{D})$

Table 26.2 Same as Table 26.1 for uniaxial alignment with constant scalar parameter S

$2S^2 \overset{\circ}{\boldsymbol{n}}{}^2$	$2S\, \overset{\circ}{\boldsymbol{n}} \cdot \boldsymbol{D}\boldsymbol{n}$	$\boldsymbol{D} \cdot \boldsymbol{D}$
$\frac{1}{3} S^3\, \overset{\circ}{\boldsymbol{n}}{}^2$	$\frac{1}{3} S^2\, \overset{\circ}{\boldsymbol{n}} \cdot \boldsymbol{D}\boldsymbol{n}$	$S(\lVert \boldsymbol{D}\boldsymbol{n} \rVert^2 - \frac{1}{3} \boldsymbol{D} \cdot \boldsymbol{D})$
0	0	$S^2 (\boldsymbol{n} \cdot \boldsymbol{D}\boldsymbol{n})^2$
$\frac{5}{9} S^4\, \overset{\circ}{\boldsymbol{n}}{}^2$	$\frac{5}{9} S^3\, \overset{\circ}{\boldsymbol{n}} \cdot \boldsymbol{D}\boldsymbol{n}$	$S^2 \left(\frac{1}{9} \boldsymbol{D} \cdot \boldsymbol{D} + \frac{1}{3} \lVert \boldsymbol{D}\boldsymbol{n} \rVert^2\right)$
$\frac{4}{3} S^4\, \overset{\circ}{\boldsymbol{n}}{}^2$	$\frac{4}{3} S^3\, \overset{\circ}{\boldsymbol{n}} \cdot \boldsymbol{D}\boldsymbol{n}$	$\frac{2}{3} S^2 \boldsymbol{D} \cdot \boldsymbol{D}$

It is evident from these two tables that the number of independent invariants is 15 in general, but when formulated with uniaxial rank-2 alignment tensors this number reduced to 13. This latter proof has first been given by ERICKSEN [15]. Let us evaluate a few elements of Table 26.2 on the basis of Table 26.1 and the definitions (26.161) and (26.162)

- For element [34] one needs

$$
\begin{aligned}
Q_{ik} Q_{ki} &= S^2 \left(n_i n_k - \tfrac{1}{3}(n_m n_m)\delta_{ik}\right) \left(n_k n_i - \tfrac{1}{3} n_m n_m \delta_{ki}\right) \\
&= S^2 \Big(n_k n_k\, n_i n_i - \tfrac{1}{3}(n_\ell n_\ell\, n_k n_k) \\
&\qquad - \tfrac{1}{3}(n_i n_i\, n_m n_m) + \tfrac{1}{9}(n_\ell n_\ell\, n_m n_m)\delta_{ii}\Big) \\
&= S^2 \left(1 - \tfrac{1}{3} - \tfrac{1}{3} + \tfrac{1}{3}\right) = \tfrac{2}{3} S^2 .
\end{aligned}
$$

  Thus,

$$
[34] = \tfrac{2}{3} S^2 (\boldsymbol{D} \cdot \boldsymbol{D}).
$$

- For element [32] one must compute

$$
D_{ik} Q_{ki} = S D_{ik} \left(n_i n_k - \tfrac{1}{3} n_\ell n_\ell \delta_{ik}\right) = S \left(n_i D_{ik} n_k - \tfrac{1}{3} D_{ii}\right).
$$

  It follows that

$$
[32] = S^2 \left(\boldsymbol{n} \cdot \boldsymbol{D}\boldsymbol{n}\right)^2 .
$$

- For element [31], we must compute

$$\begin{aligned}[31] = D_{ik}D_{k\ell}Q_{\ell i} &= D_{ik}D_{k\ell}S\left(n_\ell n_i - \tfrac{1}{3}n_p n_p \delta_{\ell i}\right)\\ &= S\left(D_{ki}n_i D_{k\ell}n_\ell - \tfrac{1}{3}D_{ik}D_{ki}\right)\\ &= S\left(\|\boldsymbol{D}\boldsymbol{n}\|^2 - \tfrac{1}{3}\boldsymbol{D}\cdot\boldsymbol{D}\right).\end{aligned}$$

- For element [33], we must compute

$$D_{ij}Q_{jk} = D_{ij}S\left(n_j n_k - \tfrac{1}{3}n_\ell n_\ell \delta_{jk}\right) = S\left(D_{ij}n_j n_k - \tfrac{1}{3}D_{ik}\right).$$

  Therefore, we obtain

$$\begin{aligned}[33] = (\boldsymbol{D}\boldsymbol{Q})\cdot(\boldsymbol{D}\boldsymbol{Q}) &= S^2\left(D_{ij}n_j n_k - \tfrac{1}{3}D_{ik}\right)\left(D_{km}n_m n_i - \tfrac{1}{3}n_p n_p D_{ki}\right)\\ &= S^2\left(\tfrac{1}{9}\boldsymbol{D}\cdot\boldsymbol{D} + \tfrac{1}{3}\|\boldsymbol{D}\boldsymbol{n}\|^2\right).\end{aligned}$$

The remaining elements involve $\overset{\circ}{\boldsymbol{n}}$; their verification is left to the reader. It is obvious that according to Tables 6.1 and 6.2, the number of invariants is excessively large (15 and 13, respectively). We shall ignore those elements, which in Table 26.2 are of order S^n, $n > 2$ and shall also ignore the elements in Table 26.1 which are of order larger or equal to 2 in $\overset{\circ}{\boldsymbol{Q}}$. This leaves us with eight scalar invariants, of which a linear combination gives R of the form

$$\begin{aligned}R = {}&\tfrac{1}{2}\zeta_{[1]}\overset{\circ}{\boldsymbol{Q}}\cdot\overset{\circ}{\boldsymbol{Q}} + \zeta_{[2]}\boldsymbol{D}\cdot\overset{\circ}{\boldsymbol{Q}} + \zeta_{[3]}\boldsymbol{D}\cdot\boldsymbol{D}\\ &+\zeta_{[21]}\overset{\circ}{\boldsymbol{Q}}\cdot(\boldsymbol{D}\boldsymbol{Q}) + \tfrac{1}{2}\zeta_{[31]}\boldsymbol{D}\cdot(\boldsymbol{D}\boldsymbol{Q}) + \tfrac{1}{2}\zeta_{[32]}(\boldsymbol{D}\cdot\boldsymbol{Q})^2\\ &+\tfrac{1}{2}\zeta_{[33]}(\boldsymbol{D}\boldsymbol{Q})\cdot(\boldsymbol{D}\boldsymbol{Q}) + \tfrac{1}{2}\zeta_{[34]}(\boldsymbol{Q}\cdot\boldsymbol{Q})(\boldsymbol{D}\cdot\boldsymbol{D}),\end{aligned} \tag{26.163}$$

in which the $\zeta_{[ij]}$'s are viscosity constants.

Sonnet et al. [46] write the corresponding dissipation function for uniaxial LCs of the ELP theory and refer to [15, 44]. This function possesses the form

$$\begin{aligned}R = {}&\tfrac{1}{2}\gamma_1\overset{\circ}{\boldsymbol{n}}^{2} + \gamma_2\overset{\circ}{\boldsymbol{n}}\cdot\boldsymbol{D}\boldsymbol{n} + \tfrac{1}{2}\gamma_3(\boldsymbol{D}\boldsymbol{n})^2\\ &+\tfrac{1}{2}\alpha_1(\boldsymbol{n}\cdot\boldsymbol{D}\boldsymbol{n})^2 + \tfrac{1}{2}\alpha_4\boldsymbol{D}\cdot\boldsymbol{D},\end{aligned} \tag{26.164}$$

where

$$\gamma_1 = \alpha_3 - \alpha_2, \quad \gamma_2 = \alpha_5 - \alpha_6, \quad \gamma_3 = \alpha_5 + \alpha_6 \tag{26.165}$$

and the α's are the Leslie coefficients, see (26.92). If we next identify the individual elements of (26.164) with those in Table 26.2, the following correspondences can be identified

$$\begin{aligned}&\gamma_1 = 2S^2\zeta_{[1]}, \quad \gamma_2 = 2S^2\zeta_{[2]} + \tfrac{1}{3}S^2\zeta_{[21]}, \quad \gamma_3 = S\zeta_{[31]} + \tfrac{1}{3}S^2\zeta_{[33]},\\ &\alpha_1 = S^2\zeta_{[32]}, \quad \alpha_4 = \zeta_{[3]} - \tfrac{1}{3}S\zeta_{[31]} + \tfrac{1}{9}S^2\zeta_{[33]}\tfrac{2}{3}S^2\zeta_{[34]}.\end{aligned} \tag{26.166}$$

There are five coefficients γ and α but eight coefficients ζ and one parameter S. Sonnet et al. [46] attribute the assignments (26.166) to Diogo and Martins [9].

26.4 Discussion and Conclusions

With the variational procedure, extended by a dissipative function, applied to LCs of tensorial order, a great number of special dynamic LC models can be generated by choosing the elastic energy W and the dissipation potential R accordingly. We presented essentially two theories, one with 15 viscosities and the second one with only eight such parameters. Sonnet et al. [46] show that the variational formulation demonstrates how the theory, put forward by Pereira Borgmeyer and Hess in a different way, and applicable to homogeneous alignments, can be deduced by the variational procedure. This theory works with only three viscosities and can be obtained by suitably choosing W and R. Moreover, the Pereira Borgmeyer–Hess model can be generalized by adding the elasticity of the alignment and/or the kinetic energy associated with the alignment.

26.4.1 Pereira Borgmeyer–Hess Theory

The model presented in [38] can be obtained by the dissipation function

$$R_{PH} = \tfrac{1}{2}\zeta_{[1]}\overset{\diamond}{\boldsymbol{Q}}\cdot\overset{\diamond}{\boldsymbol{Q}} + \zeta_{[2]}\boldsymbol{D}\cdot\overset{\diamond}{\boldsymbol{Q}} + \tfrac{1}{2}\zeta_{[3]}\boldsymbol{D}\cdot\boldsymbol{D}, \tag{26.167}$$

in which $\zeta_{[1]}, \zeta_{[2]}, \zeta_{[3]}$ are the three viscosity coefficients and

$$\overset{\diamond}{\boldsymbol{Q}} = \overset{\circ}{\boldsymbol{Q}} - 2\sigma\,\overbracket{\boldsymbol{D}\boldsymbol{Q}} \tag{26.168}$$

denotes the co-deformational time derivative. When $\sigma = 0$, i.e., $\overset{\diamond}{\boldsymbol{Q}} = \overset{\circ}{\boldsymbol{Q}}$ this theory is not able to reproduce the full ELP model. Sonnet et al. [46] then state that, since the alignment is assumed to be homogeneous, the free energy is only given by the Landau-de Gennes potential ϕ so that $(26.149)_1$ reduces to

$$\frac{\partial R}{\partial \overset{\circ}{\boldsymbol{Q}}} = -\frac{\partial W}{\partial \boldsymbol{Q}}, \quad \text{which here yields } \zeta_{[1]}\overset{\diamond}{\boldsymbol{Q}} = -\boldsymbol{\Phi} - \zeta_{[2]}\boldsymbol{D}, \tag{26.169}$$

where $\boldsymbol{\Phi} = \partial\phi/\partial\boldsymbol{Q}$. As a consequence, the skew-symmetric part of the viscous stress takes the form

$$\boldsymbol{t}^{(v)}_{\text{skw}} = \boldsymbol{Q}\frac{\partial R}{\partial \overset{\circ}{\boldsymbol{Q}}} - \frac{\partial R}{\partial \overset{\circ}{\boldsymbol{Q}}}\boldsymbol{Q} \overset{(26.168)}{=} \boldsymbol{\Phi}\boldsymbol{Q} - \boldsymbol{Q}\boldsymbol{\Phi}, \tag{26.170}$$

an expression also given in [38]. SONNET et al. [46] emphasize that this result is exact, while it was obtained in [38] by imposing approximations. The reader may also easily show that $\boldsymbol{t}^{(v)}_{\text{skw}} = \boldsymbol{0}$ when ϕ is a polynomial function of $\boldsymbol{Q}$.

SONNET et al. also list the symmetric traceless part of the stress tensor. This stress contribution is obtained from (26.150) by recognizing that the pressure and the term involving W will not arise. So only

$$\text{sym dev}\,\boldsymbol{t}^{(v)} = \frac{\partial R_{PH}}{\partial \boldsymbol{D}} + \text{sym dev}\left(\boldsymbol{Q}\frac{\partial R_{PH}}{\partial \overset{\circ}{\boldsymbol{Q}}} - \frac{\partial R_{PH}}{\partial \overset{\circ}{\boldsymbol{Q}}}\boldsymbol{Q}\right) \tag{26.171}$$

will contribute. Substituting (26.167) and (26.168) and recognizing that sym dev $(\partial R_{PH}/\partial\boldsymbol{D}) = \text{dev}(\zeta_{[3]}\boldsymbol{D}) = \boldsymbol{0}$ the computations yield

$$\text{sym}\left(\overbracket{\boldsymbol{t}}\right) = \zeta_{[2]}\,\overset{\circ}{\boldsymbol{Q}} + \zeta_{[3]}\boldsymbol{D} - 2\sigma\zeta_{[1]}\,\overbracket{\overset{\circ}{\boldsymbol{Q}}\,\boldsymbol{Q}} - 4\sigma\zeta_{[2]}\,\overbracket{\boldsymbol{D}\boldsymbol{Q}} + 4\sigma^2\,\overbracket{\boldsymbol{Q}\,\overbracket{\boldsymbol{D}\boldsymbol{Q}}} \tag{26.172}$$

Further properties can be found in [38].

26.4.2 Elastic and Viscous Contributions

SONNET et al. [46] present also a formulation of their model, which, in the uniaxial limit, is closest to the EPL model. They treat nonuniform alignments and postulate a free elastic energy as

$$W = \phi + \tfrac{1}{2}\mathcal{E}|\text{grad}\,\boldsymbol{Q}|^2, \tag{26.173}$$

where ϕ is the LANDAU- DE GENNES potential and $\mathcal{E}$ is a scalar elastic modulus. To reproduce the ELP model in the uniaxial specialization at least five viscosities need to be taken into account, see (26.166), and they suggest to consider in Table 26.2 the entries [1], [2], [3], [31], [32] and to ignore all the other elements. When compared with Table 26.2, this says that all elements of order S^0 and S^1 but not all elements of order S^2 are accounted for, while all higher order elements are dropped. In terms of Table 26.1, this means that

$$\begin{aligned} R = {} & \tfrac{1}{2}\zeta_{[1]}\overset{\circ}{\boldsymbol{Q}}\cdot\overset{\circ}{\boldsymbol{Q}} + \zeta_{[2]}\boldsymbol{D}\cdot\overset{\circ}{\boldsymbol{Q}} + \tfrac{1}{2}\zeta_{[3]}\boldsymbol{D}\cdot\boldsymbol{D} \\ & + \tfrac{1}{2}\zeta_{[31]}\boldsymbol{D}\cdot(\boldsymbol{D}\boldsymbol{Q}) + \tfrac{1}{2}\zeta_{[32]}(\boldsymbol{D}\cdot\boldsymbol{Q})^2. \end{aligned} \tag{26.174}$$

The evolution equation for the alignment tensor can be derived from (26.149). Accordingly, we need

$$\begin{aligned} & \frac{\partial R}{\partial\overset{\circ}{\boldsymbol{Q}}} = \zeta_{[1]}\overset{\circ}{\boldsymbol{Q}} + \zeta_{[2]}\boldsymbol{D}, \\ & \frac{\partial W}{\partial\boldsymbol{Q}} = \frac{\partial\phi}{\partial\boldsymbol{Q}}, \quad \operatorname{div}\left(\frac{\partial W}{\operatorname{grad}\boldsymbol{Q}}\right) = \mathcal{E}\Delta\boldsymbol{Q}. \end{aligned} \tag{26.175}$$

Based on these results, (26.149) assumes the form

$$\begin{aligned} & \zeta_{[1]}\overset{\circ}{\boldsymbol{Q}} = -\boldsymbol{\Phi} - \zeta_{[2]}\boldsymbol{D} + \mathcal{E}\Delta\boldsymbol{Q} \quad \text{or} \\ & \zeta_{[1]}\overset{\circ}{\boldsymbol{Q}} + \zeta_{[2]}\boldsymbol{D} = -\boldsymbol{\Phi} + \mathcal{E}\Delta\boldsymbol{Q}. \end{aligned} \tag{26.176}$$

On the other hand, the skew-symmetric part of the stress tensor can be computed from the second underlined term in (26.150):

$$\begin{aligned} \boldsymbol{t}^{(v)}_{\text{skw}} & = \boldsymbol{Q}\frac{\partial R}{\partial\overset{\circ}{\boldsymbol{Q}}} - \frac{\partial R}{\partial\overset{\circ}{\boldsymbol{Q}}}\boldsymbol{Q} \\ & = \zeta_{[1]}(\boldsymbol{Q}\overset{\circ}{\boldsymbol{Q}} - \overset{\circ}{\boldsymbol{Q}}\boldsymbol{Q}) + \zeta_{[2]}(\boldsymbol{Q}\boldsymbol{D} - \boldsymbol{D}\boldsymbol{Q}) \\ & = \boldsymbol{Q}(\zeta_{[1]}\overset{\circ}{\boldsymbol{Q}} + \zeta_{[2]}\boldsymbol{D}) - \left(\zeta_{[1]}\overset{\circ}{\boldsymbol{Q}} + \zeta_{[2]}\boldsymbol{D}\right)\boldsymbol{Q} \\ & \overset{(26.176)}{=} (\boldsymbol{\Phi}\boldsymbol{Q} - \boldsymbol{Q}\boldsymbol{\Phi}) + \mathcal{E}\left(\boldsymbol{Q}(\Delta\boldsymbol{Q}) - (\Delta\boldsymbol{Q})\boldsymbol{Q}\right). \end{aligned} \tag{26.177}$$

SONNET et al. [46] also list the symmetric part of the traceless viscous stress. To corroborate their result, we start from the representation (26.163) and assume, in order to reduce the number of coefficients to five, that $\zeta_{[21]}, \zeta_{[33]}, \zeta_{[34]}$ are zero. Then,

$$\begin{aligned} R = {} & \underbrace{\zeta_{[1]}\overset{\circ}{\boldsymbol{Q}}\cdot\overset{\circ}{\boldsymbol{Q}}}_{①} + \underbrace{\zeta_{[2]}\boldsymbol{D}\cdot\overset{\circ}{\boldsymbol{Q}}}_{②} + \underbrace{\zeta_{[3]}\boldsymbol{D}\cdot\boldsymbol{D}}_{③} \\ & + \underbrace{\tfrac{1}{2}\zeta_{[31]}\boldsymbol{D}\cdot(\boldsymbol{D}\boldsymbol{Q})}_{④} + \underbrace{\tfrac{1}{2}\zeta_{[32]}(\boldsymbol{D}\cdot\boldsymbol{Q})^2}_{⑤}, \end{aligned} \tag{26.178}$$

and the symmetric part of the viscous stress is given by $\partial R/\partial\boldsymbol{D}$. This implies

$$
\begin{aligned}
\text{①}_{pq} &= \frac{\partial \zeta_{[1]}\,\overset{\circ}{\boldsymbol{Q}}\cdot\overset{\circ}{\boldsymbol{Q}}}{\partial D_{pq}} = 0,\\
\text{②}_{pq} &= \frac{\partial\left(\zeta_{[2]} D_{ij}\,\overset{\circ}{Q}_{ij}\right)}{\partial D_{pq}} = \zeta_{[2]}\delta_{ip}\delta_{jq}\,\overset{\circ}{Q}_{ij} = \zeta_{[2]}\,\overset{\circ}{Q}_{pq},\\
\text{③}_{pq} &= \frac{\partial\left(\zeta_{[3]} D_{ij} D_{ij}\right)}{2\partial D_{pq}} = \zeta_{[3]}\delta_{ip}\delta_{jq} D_{ij} = \zeta_{[3]} D_{pq},\\
\text{④}_{pq} &= \frac{\partial(\zeta_{[31]} D_{ij} D_{j\ell} Q_{\ell i})}{2\partial D_{pq}} = \frac{\zeta_{[31]}}{2}\left(\delta_{ip}\delta_{jq} D_{j\ell} Q_{\ell i} + \delta_{jp}\delta_{\ell q} D_{ij} Q_{\ell i}\right)\\
&= \frac{\zeta_{[31]}}{2}\left(D_{q\ell} Q_{\ell p} + D_{\ell p} Q_{q\ell}\right) = \zeta_{[31]} D_{p\ell} Q_{q\ell},
\end{aligned}
$$

since $\boldsymbol{D}$, $\boldsymbol{Q}$ are symmetric, but this is not a deviator. So,

$$
\begin{aligned}
\overbracket{\text{④}}_{pq} &= \zeta_{[31]}\left(D_{p\ell} Q_{p\ell} - \tfrac{1}{3} D_{mn} Q_{mn}\delta_{pq}\right)\\
&= \zeta_{[31]}\left(D_{\ell p} Q_{\ell q} - \tfrac{1}{3} D_{mn} Q_{mn}\delta_{pq}\right),\\
\operatorname{tr}\left(\overbracket{\text{④}}_{pq}\right) &= \zeta_{[31]}\left(D_{p\ell} Q_{p\ell} - D_{mn} Q_{mn}\right) \equiv 0,\\
\overbracket{\text{⑤}}_{pq} &= \frac{\zeta_{[32]}}{2}\frac{\partial(D_{mn} Q_{mn})^2}{\partial D_{pq}} = \zeta_{32}(D_{mn} Q_{mn})\delta_{mp}\delta_{nq} Q_{mn}\\
&= \zeta_{[32]}(\boldsymbol{D}\cdot\boldsymbol{Q}) Q_{pq}.
\end{aligned}
$$

Therefore, collecting the contributions ① to ⑤ generates

$$
\overbracket{\boldsymbol{t}^{(v)}}_{\text{sym}} = \zeta_{[2]}\,\overset{\circ}{\boldsymbol{Q}} + \zeta_{[3]}\boldsymbol{D} + \zeta_{[31]}\,\overbracket{\boldsymbol{D}\boldsymbol{Q}} + \zeta_{[32]}(\boldsymbol{D}\cdot\boldsymbol{Q})\,\boldsymbol{Q}, \tag{26.179}
$$

which reproduces the result obtained by Sonnet et al. [46]. Moreover, the elastic stress contribution is given in (26.150) by the term

$$
\begin{aligned}
\boldsymbol{t}^{e} &= -\text{grad}\,\boldsymbol{Q}\odot\frac{\partial W}{\partial\text{grad}\,\boldsymbol{Q}} \overset{(26.173)}{=} -\mathcal{E}\text{grad}\,\boldsymbol{Q}\odot\underbrace{\frac{\partial}{\partial\text{grad}\,\boldsymbol{Q}}\left(|\text{grad}\,\boldsymbol{Q}|^2\right)}_{2\text{grad}\,\boldsymbol{Q}}\\
&= -2\mathcal{E}\text{grad}\,\boldsymbol{Q}\odot\text{grad}\,\boldsymbol{Q},
\end{aligned} \tag{26.180}
$$

which confirms a posteriori that $\boldsymbol{t}^{(e)}$ is symmetric. According to Sonnet et al., this expression is originally due to Qian and Sheng [39].

The above biaxial alignment description of LCs is based upon a dissipation function R having five viscosity coefficients as shown in (26.178) that is reduced from the expression having eight coefficients out of 15 that would in principle be needed. The criteria for the reduction of its number were semi-rational only. An alternative way of an independent development is thus desirable to put the model equations on more secure ground. According to Sonnet et al. [46] "such a perspective is offered by the microscopic theory for the constitutive equation of polymeric LCs proposed by Doi [10].” They state that “the ELP theory can be derived from Doi’s [theory] in the limit of weak velocity gradients and for small perturbations of the equilibrium state,” and they briefly discuss situations close to the ELP theory as given in [3, 29, 32, 33] and others.

“It would be desirable to address systematically the circumstances that could justify on a microscopic basis the choices of simplified dissipation functions proposed here only under the guidance of phenomenological arguments.”

26.4.3 The Role of the Inertia of the Microrotation

The foregoing analysis was conducted under the assumption that the inertia of the microrotation was negligible. Conceptually, it is given by the kinetic energy of the microrotation $\kappa(\boldsymbol{Q}, \dot{\boldsymbol{Q}})$ in Eq. (26.19), where we also have changed notation from $\mathbb{O}$ to $\boldsymbol{Q}$ because considerations are restricted to uniaxial LCs, where $\boldsymbol{Q} = S\langle \boldsymbol{n} \otimes \boldsymbol{n} - \frac{1}{3}(\boldsymbol{n} \cdot \boldsymbol{n})\boldsymbol{I}\rangle$. We derived in Eq. (26.19)

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathcal{B}} \rho\kappa(\boldsymbol{Q}, \dot{\boldsymbol{Q}})\mathrm{d}V &= \int_{\mathcal{B}} \rho\left(\kappa(\boldsymbol{Q}, \dot{\boldsymbol{Q}})\right)^{\cdot}\,\mathrm{d}V \\ &\overset{*}{=} \int_{\mathcal{B}} \rho \underbrace{\left\{\left(\frac{\partial\kappa}{\partial\dot{\boldsymbol{Q}}}\right)^{\cdot} - \frac{\partial\kappa}{\partial\boldsymbol{Q}}\right\}}_{\boldsymbol{M}} \cdot \dot{\boldsymbol{Q}}\,\mathrm{d}V \\ &= \int_{\mathcal{B}} \rho\boldsymbol{M} \cdot \dot{\boldsymbol{Q}}\,\mathrm{d}V,\end{aligned} \tag{26.181}$$

where

$$\boldsymbol{M} := \left(\frac{\partial\kappa}{\partial\dot{\boldsymbol{Q}}}\right)^{\cdot} - \frac{\partial\kappa}{\partial\boldsymbol{Q}}. \tag{26.182}$$

The step $\overset{*}{=}$ is detailed in Appendix 26.A. Because no operator $\int_{\mathcal{B}}(\cdot)\cdot\dot{\boldsymbol{v}}\mathrm{d}V$ arises in the above expression, we may conclude that microinertia does not contribute to the stress tensor.

We also derived early in this chapter [see (26.30)] the expression

$$\mathbb{X} = \rho\left(\boldsymbol{M} + \frac{\partial\chi}{\partial\boldsymbol{Q}}\right) + \frac{\partial W}{\partial\boldsymbol{Q}} - \operatorname{div}\left(\frac{\partial W}{\partial \operatorname{grad}\boldsymbol{Q}}\right). \tag{26.183}$$

The variational principle (26.9) with Lagrange parameter $\lambda = 1$ transfers here to

$$\begin{aligned}
&\frac{\partial R}{\partial \overset{\circ}{\boldsymbol{Q}}} + \mathbb{X} = \mathbf{0} \text{ or} \\
&\frac{\partial R}{\partial \overset{\circ}{\boldsymbol{Q}}} + \rho \boldsymbol{M} + \frac{\partial(\rho\chi)}{\partial \boldsymbol{Q}} + \frac{\partial W}{\partial \boldsymbol{Q}} - \operatorname{div}\left(\frac{\partial W}{\partial \operatorname{grad} \boldsymbol{Q}}\right) = \mathbf{0},
\end{aligned} \tag{26.184}$$

in which $\mathbb{X}$ has already been given in (26.30) [replacing there $\mathbb{O}$ by $\boldsymbol{Q}$]. Equation (26.184)$_2$ differs formally slightly from the corresponding equation by SONNET et al.; they define χ per unit volume, while we have done it here per unit mass.

We require EUCLIDian invariance of the energy function W, i.e., and request that

$$W(Q_{ij}, Q_{ij,k}) = W(R_{ip}R_{jq}Q_{pq}, R_{ip}R_{jq}R_{kr}Q_{pq,r}), \tag{26.185}$$

in which R_{ip} is a proper orthogonal transformation. ERICKSEN [15] has shown (for a similar case) that (26.185) necessarily implies[12]

$$\varepsilon_{ijk}\left(2Q_{jp}\frac{\partial W}{\partial Q_{pk}} + 2Q_{jp,q}\frac{\partial W}{\partial Q_{pk,q}} + Q_{pq,j}\frac{\partial W}{\partial Q_{pq,k}}\right) \equiv 0. \tag{26.186}$$

A similar objectivity requirement must also hold for the kinetic energy of the microrotation function $\kappa(\boldsymbol{Q}, \dot{\boldsymbol{Q}})$; it is expressible as

$$\varepsilon_{ijk}\left(Q_{jp}\frac{\partial \kappa}{\partial Q_{pk}} + \dot{Q}_{jp}\frac{\partial \kappa}{\partial \dot{Q}_{pk}}\right) \equiv 0. \tag{26.187}$$

The above identity (26.187) is needed for the skew-symmetric part of the stress tensor. This skew-symmetric part, written in Cartesian tensor notation, is given by

$$\begin{aligned}
t_{[ij]} &= -Q_{pq,[i}\frac{\partial W}{\partial Q_{pq,j]}} + Q_{[i\ell}\frac{\partial R}{\partial \overset{\circ}{Q}_{\ell j]}} \underbrace{- \frac{\partial R}{\partial \overset{\circ}{Q}_{[i\ell}} Q_{\ell j]}}_{-Q_{\ell[j}\frac{\partial R}{\partial \overset{\circ}{Q}_{\ell i]}}} \\
&= -Q_{pq,[i}\frac{\partial W}{\partial Q_{pq,j]}} + 2Q_{[i\ell}\frac{\partial R}{\partial \overset{\circ}{Q}_{\ell j]}},
\end{aligned}$$

of which the dual axial vector is given by

---

[12] We remark that an analogous identity has been given by us in this chapter between the formulae (26.44)–(26.46) for a director theory.

$$
\begin{aligned}
\tau_i = \varepsilon_{ijk} t_{jk} &= \varepsilon_{ijk}\Bigg\{ 2Q_{j\ell}\frac{\partial R}{\partial \dot{Q}_{\ell k}} \quad \underbrace{-Q_{pq,j}\frac{\partial W}{\partial Q_{pq,k}}}_{2Q_{jp}\frac{\partial W}{\partial Q_{pk}}+2Q_{jp,q}\frac{\partial W}{\partial Q_{pk,q}}} \quad \Bigg\} \\
&= 2\varepsilon_{ijk}\Bigg\{ Q_{jp}\frac{\partial W}{\partial q_{pk}} + Q_{jp,q}\frac{\partial W}{\partial Q_{pk,q}} + Q_{j\ell}\frac{\partial R}{\partial \overset{\circ}{Q}_{\ell k}} \Bigg\},
\end{aligned}
$$

in which (26.186) has been used to obtain the sub-braced term. At last, we employ (26.184)$_2$ to replace $\partial R/\partial \overset{\circ}{Q}_{\ell k}$. Straightforward substitution then yields

$$
\tau_i = 2\varepsilon_{ijk}\left\{ \left(Q_{j\ell}\frac{\partial W}{\partial Q_{k\ell,r}} \right)_{,r} - Q_{j\ell}\frac{\partial(\rho\chi)}{\partial Q_{\ell k}} - \rho Q_{j\ell} M_{\ell k} \right\}. \tag{26.188}
$$

In view of the angular momentum balance (26.39)$_2$ τ_i can be expressed as

$$
\tau_i = m_{ij,j} + \rho\ell_i - \rho\dot{s}_i .
$$

It is clear that (26.187) enforces the identifications

$$
\begin{aligned}
m_{ir} &= 2\varepsilon_{ijk} Q_{j\ell}\frac{\partial W}{\partial Q_{k\ell,r}}, \\
\rho\ell_i &= -2Q_{j\ell}\frac{\partial \rho\chi}{\partial Q_{\ell k}}, \\
\rho\dot{s}_i &= 2\varepsilon_{ijk} Q_{j\ell} M_{\ell k}.
\end{aligned} \tag{26.189}
$$

In these expressions, the quantity $\rho\dot{s}_i$ is for constant ρ a total time derivative; so must be also the right-hand side of (26.189). To prove this, we propose the constitutive postulate

$$
\rho s_i := 2\varepsilon_{ijk} Q_{j\ell}\frac{\partial \kappa}{\partial \dot{Q}_{k\ell}}. \tag{26.190}
$$

Thus,

$$
\begin{aligned}
\rho\dot{s}_i &= 2\varepsilon_{ijk}\left\{ \dot{Q}_{j\ell}\frac{\partial \kappa}{\partial \dot{Q}_{\ell k}} + Q_{j\ell}\left(\frac{\partial \kappa}{\partial \dot{Q}_{\ell k}} \right)^{\boldsymbol{\cdot}} \right\} \\
&\overset{(26.182),(26.187)}{=} 2\varepsilon_{ijk}\left\{ -Q_{j\ell}\frac{\partial \kappa}{\partial Q_{\ell k}} + Q_{j\ell}\left(M_{\ell k} + \frac{\partial \kappa}{\partial Q_{\ell k}} \right) \right\} \\
&= 2\varepsilon_{ijk} Q_{j\ell} M_{\ell k},
\end{aligned} \tag{26.191}
$$

which agrees with (26.189)$_2$.

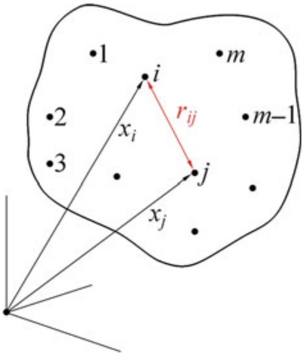

Fig. 26.2 System of n mass points in $\mathbb{R}^3$ with positions $\boldsymbol{x}_i$ $i = 1, 2, \ldots, n$ and distances r_{ij}

Appendix 26.A Lagrange Equations

26.A.1 Constraints of Coordinates

Consider a mechanical system (e.g., of mass points $\mathcal{P}_i$ $i = 1, 2, \ldots, n$) whose motion can be determined by prescribing their coordinates $\{\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_n\}$ see **Fig. 26.2**. The *degree of freedom* of a mechanical system is the number of independent coordinates needed to describe the motion of the system. *Constraints* or *constraint conditions* are equations between coordinates, which restrain the motion of the system. Rigid point systems with constants of the form

$$\forall i, j \quad \boldsymbol{x}_i - \boldsymbol{x}_j = \boldsymbol{r}_{ij} = \text{const.} \Longleftrightarrow \boldsymbol{x}_i - \boldsymbol{x}_j - \boldsymbol{r}_{ij} = 0, \quad \text{where } |\boldsymbol{r}_{ij}| = \text{const.}$$

express rigid body motions. They have six degrees of freedom, three for translation and three for rotation. In analytical dynamics, one differentiates between two kinds of constraint conditions.

(i) Constraint conditions, which are expressible as equations between coordinates, are called *holonomic*.[13]

(ii) If constraints are not expressible in holonomic form, they are called *anholonomic* or *skleronomic*. If such a constraint condition is not explicitly expressible as a function also of time it is called skleronomic, else *rheonomic*.

26.A.2 Generalized Coordinates

When holonomic constraints exist between the coordinates $\{\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_n\}$, these constraint conditions will reduce the degree of freedom. If these Λ equations are

---

[13] The term “holonomic” was introduced by HEINRICH HERTZ in 1894 from the Greek “ὅλος” (whole, entire) and “νόμος” (law).

independent of one another, the degree of freedom f will be $f = 3n - \Lambda$. In this case, the mechanical system can be described by the so-called generalized coordinates

$$q_1, q_2, \ldots, q_f. \tag{26.192}$$

In other words, these coordinates determine the values of $\{\boldsymbol{x}_1, \ldots, \boldsymbol{x}_n\}$ uniquely as functions of time as follows:

$$\begin{aligned} \boldsymbol{x}_1 &= \boldsymbol{x}_1\left(q_1, q_2, \ldots, q_f, t\right), \\ \boldsymbol{x}_2 &= \boldsymbol{x}_2\left(q_1, q_2, \ldots, q_f, t\right), \\ \vdots \quad & \vdots \quad \vdots \\ \boldsymbol{x}_n &= \boldsymbol{x}_n\left(q_1, q_2, \ldots, q_f, t\right). \end{aligned} \tag{26.193}$$

These are $3n$ transformation equations between the dependent coordinates $\{x_i, y_i, z_i\}$ $i = 1, 2, \ldots, n$ and the independent generalized coordinates $\{q_1, \ldots, q_f\}$. Their total time derivatives $\{\dot{q}_1, \ldots, \dot{q}_f\}$ are called generalized velocities.

26.A.3 d'Alembert's Principle, Principle of Virtual Work

A *virtual displacement* of $\{\boldsymbol{x}_i \; i = 1, \ldots, n\}$ of a mechanical system is a set $\{\delta\boldsymbol{x}_i \; i = 1, \ldots, n\}$ of instantaneous infinitesimal changes of the positions $\{\boldsymbol{x}_i \; i = 1, \ldots, n\}$ which are consistent with the existing forces and constraints. Here, the qualification "instantaneous" wants to emphasize that the displacement is performed, while the time is held fixed; this displacement is called "consistent with the applied forces and with the constraints," because these displacements are kinematically force-freely admissible. Often, one also speaks of virtual velocities. This then leads to the *Principle of Virtual Power*. To derive it, let us start with the momentum equation in the form

$$\boldsymbol{F}_i = \dot{\boldsymbol{p}}_i, \quad (i = 1, \ldots, n), \tag{26.194}$$

in which $\boldsymbol{F}_i$ are the external and internal forces and p_i is the momentum corresponding to $\boldsymbol{F}_i$. Multiplying both sides of (26.194) scalarly with $\delta\boldsymbol{x}_i$ and summation over all indices $1, \ldots, n$ yields

$$\sum_{i=1}^{n} \left(\boldsymbol{F}_i - \dot{\boldsymbol{p}}_i\right) \cdot \delta\boldsymbol{x}_i = 0. \tag{26.195}$$

In general, $\boldsymbol{F}_i$ is the sum of the applied force $\boldsymbol{F}_i^{(a)}$ and the constraint force $\boldsymbol{F}_i^{(c)}$

$$\boldsymbol{F}_i = \boldsymbol{F}_i^{(a)} + \boldsymbol{F}_i^{(c)}. \tag{26.196}$$

The decisive additional assumption for the elimination of the constraint forces from the problem is the postulate that the virtual work of the constraint forces is null,

$$\sum_{i=1}^{n} \boldsymbol{F}_i^{(c)} \delta \boldsymbol{x}_i = 0. \tag{26.197}$$

This equation is the expression of the *Principle of Virtual Work*, or when expressed in virtual velocities the *Principle of Virtual Power*.

Combining (26.195) with (26.196), (26.197) yields

$$\sum_{i=1}^{n} \left(\boldsymbol{F}_i^{(a)} - \dot{\boldsymbol{p}}_i \right) \cdot \delta \boldsymbol{x}_i = 0. \tag{26.198}$$

This is known as *d'Alembert's Principle*.

26.A.4 Derivation of the Lagrange Equations

Consider now virtual displacements of the generalized coordinates $\delta \boldsymbol{q}_i$ $(i = 1, \ldots, f)$. If the functions (26.193) are differentiable, which we will assume, we may write

$$\delta \boldsymbol{x}_i = \sum_{i=1}^{f} \frac{\partial \boldsymbol{x}_i}{\partial q_j} \delta q_j. \tag{26.199}$$

A differentiation with respect to time is missing in this expression because the virtual displacements are instantaneously performed. Substitution of (26.199) into D'ALEMBERT's Principle yields with $\dot{\boldsymbol{p}}_i = m_i \ddot{\boldsymbol{x}}_i$

$$\sum_{i,j} \boldsymbol{F}_i \cdot \frac{\partial \boldsymbol{x}_i}{\partial q_j} \delta q_j - \sum_{i,j} m_i \ddot{\boldsymbol{x}}_i \cdot \frac{\partial \boldsymbol{x}_i}{\partial q_j} \delta q_j = 0. \tag{26.200}$$

Remarks:

- The quantity

$$Q_j := \sum_{i=1}^{n} \boldsymbol{F}_i \cdot \frac{\partial \boldsymbol{x}_i}{\partial q_j} \quad (j = 1, \ldots, f) \tag{26.201}$$

  is known as jth *generalized force*.
- The reader can easily verify the following formulae:

(1)

$$\boldsymbol{v}_i = \dot{\boldsymbol{x}}_i = \sum_{j=1}^{f} \frac{\partial \boldsymbol{x}_i}{\partial q_j}\dot{q}_j + \frac{\partial \boldsymbol{x}_i}{\partial t} \quad \Longrightarrow \quad \frac{\partial \boldsymbol{v}_i}{\partial \dot{q}_j} = \frac{\partial \boldsymbol{x}_i}{\partial q_j}, \tag{26.202}$$

(2)

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial \boldsymbol{x}_i}{\partial q_j}\right) &= \sum_k \frac{\partial^2 \boldsymbol{x}_i}{\partial q_j \partial q_k}\dot{q}_k + \frac{\partial^2 \boldsymbol{x}_i}{\partial q_j \partial t}\\ &= \frac{\partial}{\partial q_j}\left(\sum_k \frac{\partial \boldsymbol{x}_i}{\partial q_k}\dot{q}_k + \frac{\partial \boldsymbol{x}_i}{\partial t}\right) = \frac{\partial \boldsymbol{v}_i}{\partial q_j},\end{aligned} \tag{26.203}$$

(3)

$$\begin{aligned}&\sum_{ij} m\ddot{\boldsymbol{x}}_i \cdot \frac{\partial \boldsymbol{x}_i}{\partial q_j}\delta q_j\\ &= \sum_{i,j}\left\{\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial}{\partial \dot{q}_j}\frac{m_i \boldsymbol{v}_i \cdot \boldsymbol{v}_i}{2}\right) - \frac{\partial}{\partial q_j}\left(\frac{m_i \boldsymbol{v}_i \cdot \boldsymbol{v}_i}{2}\right)\right\}\delta q_j\\ &= \sum_j \left\{\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial}{\partial \dot{q}_j}\frac{\sum_i m_i \boldsymbol{v}_i \cdot \boldsymbol{v}_i}{2}\right) - \frac{\partial}{\partial q_j}\left(\frac{\sum_i m_i \boldsymbol{v}_i \cdot \boldsymbol{v}_i}{2}\right)\right\}\delta q_j\\ &= \sum_j \left\{\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial T}{\partial \dot{q}_j}\right) - \frac{\partial T}{\partial q_j}\right\}\delta q_j,\end{aligned} \tag{26.204}$$

where T is the kinetic energy.

Substituting (26.201)–(26.204) into (26.200) D'ALEMBERT's Principle leads to

$$\sum_j \left\{\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial T}{\partial \dot{q}_j}\right) - \frac{\partial T}{\partial q_j} - Q_j\right\}\delta q_j = 0, \quad \forall \delta q_j. \tag{26.205}$$

Consequently,

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial T}{\partial \dot{q}_j}\right) - \frac{\partial T}{\partial q_j} = Q_j \quad (j = 1, \ldots, f). \tag{26.206}$$

These equations are sometimes called the LAGRANGE equations. Regularly, this denotation is, however, only used, if the forces $\boldsymbol{F}_i$ are derivable from a potential $V(q_1, \ldots, q_f, t) = V(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_n)$ according to

$$\boldsymbol{F}_i = -\mathrm{grad}_i(V). \tag{26.207}$$

The generalized forces can then be written as

$$Q_j = -\sum_i (\mathrm{grad}_i V) \cdot \frac{\partial \boldsymbol{x}_i}{\partial q_j} = -\frac{\partial V}{\partial \boldsymbol{x}_i} \cdot \frac{\partial \boldsymbol{x}_i}{\partial q_j} = -\frac{\partial V}{\partial q_j}. \tag{26.208}$$

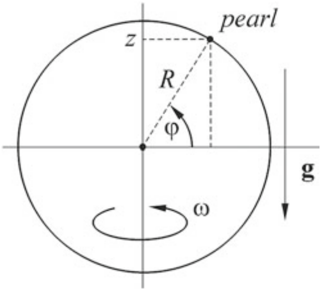

Fig. 26.3 Pearl moving on a permanently rotating circular wire

Introducing the LAGRANGE function

$$L = T - V \tag{26.209}$$

and using (26.208) and the fact that V does not depend upon $\dot{q}_i$ we deduce from (26.205)

$$\left(\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial L}{\partial \dot{q}_j}\right) - \frac{\partial L}{\partial q_j}\right)\delta q_j = 0, \quad \forall \delta q_j,$$

or

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial L}{\partial \dot{q}_j}\right) - \frac{\partial L}{\partial q_j} = 0, \quad (j = 1, \ldots, f), \tag{26.210}$$

which is equivalent to (26.206).

Example: Consider a pearl with mass m tied to a vertical circular wire, which rotates with constant angular velocity ω around a vertical axis, see **Fig. 26.3**. The pearl can freely move along the wire. Let the radius of the circle of the wire be R and let the gravity vector in the vertical plane be g positive downward. The motion of the pearl can be described by the angle φ. So, this angle serves as the only generalized coordinate. For the pearl, treated as a mass point, we have

$$\begin{aligned}
\boldsymbol{v} &= R\dot{\varphi}\boldsymbol{e}_\varphi + r\omega\boldsymbol{e}_\perp = R\dot{\varphi}\boldsymbol{e}_\varphi + R\omega\cos_\varphi \boldsymbol{e}_\perp,\\
T &= \frac{m}{2}R^2\dot{\varphi}^2 + \frac{m}{2}R^2\omega^2\cos^2\varphi,\\
V &= mgz = mgR\sin\varphi,\\
\mathcal{L} &= T - V = \frac{m}{2}R^2\left(\dot{\varphi}^2 + \omega^2\cos^2\varphi\right) - mgR\sin\varphi.
\end{aligned}$$

Because the system has only one degree of freedom, we have only a single LAGRANGE equation:

$$\begin{aligned}
\frac{\partial \mathcal{L}}{\partial \dot{\varphi}} &= mR^2 \dot{\varphi}, \quad \frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial \mathcal{L}}{\partial \dot{\varphi}}\right) = mR^2 \ddot{\varphi}, \\
\frac{\partial \mathcal{L}}{\partial \varphi} &= -mR^2\omega^2 \sin\varphi \cos\varphi - mgR\cos\varphi \\
&= -\frac{m}{2} R^2\omega^2 \sin(2\varphi) - mgR\cos\varphi.
\end{aligned}$$

Substituting these expressions into the LAGRANGE Equation (26.210) yields

$$\begin{aligned}
& mR^2\ddot{\varphi} + \frac{m}{2}R^2\omega^2\sin(2\varphi) + mgR\cos\varphi = 0, \\
\Longrightarrow\quad & \ddot{\varphi} + \frac{\omega^2}{2}\sin(2\varphi) + \frac{g}{R}\cos\varphi = 0, \\
\Longrightarrow\quad & \underbrace{\ddot{\varphi}\dot{\varphi}}_{(\dot{\varphi}^2/2)^{\cdot}} + \frac{\omega^2}{2}\underbrace{\sin(2\varphi)\dot{\varphi}}_{-\frac{1}{2}[\cos(2\varphi)]^{\cdot}} + \frac{g}{R}\underbrace{\cos(\varphi)\dot{\varphi}}_{(\sin\varphi)^{\cdot}} = 0 \\
\Longrightarrow\quad & \left\{\frac{\dot{\varphi}^2}{2} - \frac{\omega^2}{4}\cos(2\varphi) + \frac{g}{R}\sin\varphi\right\}^{\cdot} = 0, \\
& \frac{\dot{\varphi}^2}{2} - \frac{\omega^2}{4}\cos(2\varphi) + \frac{g}{R}\sin\phi = \text{const.} = c, \\
\Longrightarrow\quad & t - t_0 = \int_{\varphi_0}^{\varphi} \frac{\mathrm{d}\bar{\varphi}}{\left[c + \frac{\omega^2}{2}\cos(2\bar{\varphi}) - \frac{g}{R}\sin\bar{\varphi}\right]^{1/2}},
\end{aligned}$$

which is the solution of the equation of motion.

Appendix 26.B Implications of the Frame Indifference Requirement of the Free Energy as a Function of Tensorial Order Parameters

Let W be the free energy. In the main text, it is assumed to be a function of the director $\boldsymbol{n}$ and its gradient, grad $\boldsymbol{n}$. Satisfaction of the frame indifference requirement has been expressed as the statement (26.45) or (26.46). If W depends on a set of rank-i tensors ($i = 2, \ldots, n$) its frame indifference is expressed as Eq. (26.44). Here, we begin with a W-function that depends only on a rank-2 tensor and its gradient: $W = W(\mathbb{O}, \operatorname{grad}\mathbb{O})$. Invariance of W under EUCLIDian transformations (rigid body motions) then implies

$$DW = W\left(\mathbb{O}_{i^*j^*}, \mathbb{O}_{i^*j^*,k^*}\right) - W\left(\mathbb{O}_{ij}, \mathbb{O}_{ij,k}\right) \overset{!}{=} 0, \tag{26.211}$$

in which

$$\boldsymbol{x}^* = \boldsymbol{R}\boldsymbol{x} + \boldsymbol{b}^*, \quad x^*_{k^*} = R_{k^*k}x_k + b^*_{k^*}, \quad x_k = (x^*_{k^*} - b^*_{k^*})R_{k^*k}. \tag{26.212}$$

$\boldsymbol{R}$ is an orthogonal transformation $[\boldsymbol{R}\boldsymbol{R}^T = \boldsymbol{I}]$. Cartesian tensor notation is used with indices $i, j, k, \ldots$ and $i^*, j^*, k^*, \ldots$ in the original and in the rotated coordinates, respectively. $\boldsymbol{x}^*$ is the position of the point $\boldsymbol{x}$ measured in the rotated coordinates given by $\boldsymbol{R}$ and translation by $\boldsymbol{b}^*$. Below we shall restrict attention to infinitesimal rotations,

$$R_{i^*m} = \delta_{i^*m} + \Omega_{i^*m}, \quad \|\Omega_{i^*m}\Omega_{j^*m}\| \ll 1, \tag{26.213}$$

for which only linear terms in $\boldsymbol{\Omega}$ are accounted for. It is then easily shown that

$$\begin{aligned} \delta_{i^*j^*} &\equiv R_{i^*m}R_{j^*m} = (\delta_{i^*m} + \Omega_{i^*m})(\delta_{j^*m} + \Omega_{j^*m}) \qquad (26.214) \\ &\approx \delta_{i^*j^*} + \Omega_{i^*j^*} + \Omega_{j^*i^*} \\ \Longrightarrow &\quad \Omega_{i^*j^*} = -\Omega_{j^*i^*}. \qquad (26.215) \end{aligned}$$

Our next step is evaluation of $\mathbb{O}$ and grad $\mathbb{O}$ in the rotated coordinates:

- $$\begin{aligned} \mathbb{O}_{i^*j^*} &= R_{i^*m}R_{j^*m}\mathbb{O}_{mn} = (\delta_{i^*m} + \Omega_{i^*m})(\delta_{j^*m} + \Omega_{j^*m})\mathbb{O}_{mn} \\ &= \left(\delta_{i^*m}\delta_{j^*m} + \delta_{i^*m}\Omega_{j^*n} + \delta_{j^*n}\Omega_{i^*m}\right)\mathbb{O}_{mn} \\ &= \mathbb{O}_{i^*j^*} + \mathbb{O}_{i^*n}\Omega_{j^*n} + \mathbb{O}_{mj^*}\Omega_{i^*m}, \end{aligned} \tag{26.216}$$

- $$\begin{aligned} \mathbb{O}_{i^*j^*,k^*} &= R_{i^*m}R_{j^*n}\mathbb{O}_{mn,k}\frac{\partial x_k}{\partial x^*_{k^*}} \overset{(6.B2)}{=} R_{i^*m}R_{j^*n}R_{k^*k}\mathbb{O}_{mn,k} \\ &= \left(\delta_{i^*m}\delta_{j^*m} + \delta_{i^*m}\Omega_{j^*n} + \delta_{j^*n}\Omega_{i^*m}\right)(\delta_{k^*k} + \Omega_{k^*k})\,\mathbb{O}_{mn,k} \\ &= \big(\delta_{i^*m}\delta_{j^*n}\delta_{k^*k} + \delta_{i^*m}\delta_{k^*k}\Omega_{j^*n} \\ &\quad + \delta_{j^*n}\delta_{k^*k}\Omega_{i^*m}\Omega_{i^*m} + \delta_{i^*m}\delta_{j^*n}\Omega_{k^*k}\big)\,\mathbb{O}_{mn,k} \\ &= \mathbb{O}_{i^*j^*,k^*} + \mathbb{O}_{i^*n,k^*}\Omega_{j^*n} + \mathbb{O}_{mj^*,k^*}\Omega_{i^*m} \\ &\quad + \mathbb{O}_{i^*j^*,k^*}\Omega_{k^*k}. \end{aligned} \tag{26.217}$$

With the normalization $W(\mathbb{O}_{ij} = 0\ \mathbb{O}_{ij,k} = 0) = 0$ and employing first-order Taylor series expansion one may write

$$\begin{aligned} DW \approx \Bigg\{ &\frac{\partial W}{\partial \mathbb{O}_{i^*j^*}}\left(\mathbb{O}_{i^*j^*} + \mathbb{O}_{i^*n}\Omega_{j^*n} + \mathbb{O}_{mj^*}\Omega_{i^*m} - \mathbb{O}_{i^*j^*}\right) \\ &+ \frac{\partial W}{\partial \mathbb{O}_{i^*j^*,k^*}}\big(\mathbb{O}_{i^*j^*,k^*} + \mathbb{O}_{i^*n,k^*}\Omega_{j^*n} \\ &+ \mathbb{O}_{mj^*,k^*}\Omega_{i^*m} + \mathbb{O}_{i^*j^*,k}\Omega_{k^*k} - \mathbb{O}_{i^*j^*,k^*}\big)\Bigg\} \\ &= \frac{\partial W}{\partial \mathbb{O}_{i^*j^*}}\left(\mathbb{O}_{i^*n}\Omega_{j^*n} + \mathbb{O}_{mj^*}\Omega_{i^*m}\right) \end{aligned}$$

$$
\begin{aligned}
&+\frac{\partial W}{\partial \mathbb{O}_{i^*j^*,k^*}}\left(\mathbb{O}_{i^*n,k^*}\mathit{\Omega}_{j^*n}+\mathbb{O}_{mj^*,k^*}\mathit{\Omega}_{i^*m}+\mathbb{O}_{i^*j^*,k}\mathit{\Omega}_{k^*k}\right)\\
&\overset{!}{\equiv} 0. \qquad (26.218)
\end{aligned}
$$

This expression is linear in the skew-symmetric rank-2 tensor $\boldsymbol{\Omega}$ and can be written in the following new form by reshuffling indices.[14] Such a reshuffling yields

$$
\begin{aligned}
DW = \Bigg\{&\frac{\partial W}{\partial \mathbb{O}_{i^*k*}}\mathbb{O}_{i^*k}+\frac{\partial W}{\partial \mathbb{O}_{k^*i*}}\mathbb{O}_{ki^*}+\frac{\partial W}{\partial \mathbb{O}_{i^*k^*,\ell^*}}\mathbb{O}_{i^*k,\ell^*}\\
&+\frac{\partial W}{\partial \mathbb{O}_{k^*i^*,\ell^*}}\mathbb{O}_{i^*k,\ell^*}+\frac{\partial W}{\partial \mathbb{O}_{i^*j^*,k}}\mathbb{O}_{i^*j^*,k^*}\Bigg\}\mathit{\Omega}_{k^*k}\equiv 0. \qquad (26.219)
\end{aligned}
$$

Because the tensor $\mathit{\Omega}_{k^*k}$ is skew-symmetric, the rank-2 tensor F_{k^*k} in the curly bracket of this expression must be symmetric, or its skew-symmetric part must vanish. This can be expressed as $\varepsilon_{pk^*k}F_{k^*k}=0$ or

$$
\begin{aligned}
\varepsilon_{pk^*k}\Bigg\{\Bigg(&\frac{\partial W}{\partial O_{i^*k^*}}\mathbb{O}_{i^*k}+\frac{\partial W}{\partial \mathbb{O}_{k^*i^*}}\mathbb{O}_{ki^*}\\
&+\frac{\partial W}{\partial \mathbb{O}_{i^*k^*,\ell^*}}\mathbb{O}_{i^*k,\ell^*}+\frac{\partial W}{\partial \mathbb{O}_{i^*j^*,k}}\mathbb{O}_{i^*k,k^*}\Bigg)\\
&+\frac{\partial W}{\partial \mathbb{O}_{i^*k,\ell^*}}\mathbb{O}_{i^*k,\ell^*}\Bigg\}\equiv 0. \qquad (26.220)
\end{aligned}
$$

Introducing the multi-indices I and I_{kj} as defined in (26.14), this expression can alternatively be written as

$$
\begin{aligned}
\varepsilon_{pk^*k}\Bigg\{&\sum_{i^*=1}^{2}\left(\frac{\partial W}{\partial \mathbb{O}_{{I^*}_{i^*}{}^{k^*}}}\mathbb{O}_{{I^*}_{i^*}{}^{k^*}}+\frac{\partial W}{\partial \mathbb{O}_{{I^*}_{i^*}{}^{k^*},\ell^*}}\mathbb{O}_{{I^*}_{i^*}{}^{k},\ell^*}\right)\\
&+\frac{\partial W}{\partial \mathbb{O}_{I^*,\ell^*}}\mathbb{O}_{I^k_{i^*},\ell^*}\Bigg\}\equiv 0. \qquad (26.221)
\end{aligned}
$$

Sonnet and Virga [44] must have performed the analogous computation for a free energy function W which is a function of a finite number of rank-i tensors $\mathbb{O}$ ($i=1,2,\ldots,n$). The frame indifference postulate is then Eq. (26.44). Invariance of W under an infinitesimal rigid body rotation is then expressible as a statement analogous to (26.219), explicitly as

---

[14] Reshuffling indices means that the name of a doubly repeated index may be changed at liberty to possibly reach a formula that might formally agree with some other formula.

$$\varepsilon_{pk^*k}\left\{\sum_{i^*=1}^{n}\left(\frac{\partial W}{\partial \mathbb{O}_{I^*{}_{i^*}{}^{k^*}}}\mathbb{O}_{I^*{}_{i^*}{}^{k}}+\frac{\partial W}{\partial \mathbb{O}_{I^*{}_{i^*}{}^{k^*},\ell^*}}\mathbb{O}_{I^*{}_{i^*}{}^{k},\ell^*}\right)\right.$$
$$\left.+\frac{\partial W}{\partial \mathbb{O}_{I^*,k^*}}\mathbb{O}_{I^*,k^*}\right\}=0. \tag{26.222}$$

With the above proof of the frame indifference as a function of the rank-2 order parameters $\mathbb{O}$, it is quite natural, how (26.221) can be proven, e.g., by the reader.

Appendix 26.C Euclidian Invariance of $\overset{\diamond}{\boldsymbol{Q}}$

We prove here the frame indifference of the co-deformational derivative of the rank-2 order parameter

$$\overset{\diamond}{\boldsymbol{Q}} := \left(\dot{\boldsymbol{Q}} - 2\overbracket{\boldsymbol{W}\boldsymbol{Q}}\right) - 2\sigma\overbracket{\boldsymbol{D}\boldsymbol{Q}}, \tag{26.223}$$

where σ is a scalar constitutive parameter or a constant. Let $\boldsymbol{R}$ be an orthogonal second rank tensor, so that $\boldsymbol{R}\boldsymbol{R}^T = \boldsymbol{I}$. Note, moreover, that $\boldsymbol{Q}$ is a deviator by definition. Then

$$\begin{aligned}
&(\boldsymbol{R}\boldsymbol{Q}\boldsymbol{R}^T)^{\cdot} - 2\overbracket{(\boldsymbol{R}\boldsymbol{W}\boldsymbol{R}^T + \dot{\boldsymbol{R}}\boldsymbol{R}^T)(\boldsymbol{R}\boldsymbol{Q}\boldsymbol{R}^T)}\\
&= \dot{\boldsymbol{R}}\boldsymbol{Q}\boldsymbol{R}^T + \boldsymbol{R}\dot{\boldsymbol{Q}}\boldsymbol{R}^T + \boldsymbol{R}\boldsymbol{Q}\dot{\boldsymbol{R}}^T - 2\overbracket{(\boldsymbol{R}\boldsymbol{W}\boldsymbol{R}^T\boldsymbol{R}\boldsymbol{Q}\boldsymbol{R}^T + \dot{\boldsymbol{R}}\boldsymbol{R}^T\boldsymbol{R}\boldsymbol{Q}\boldsymbol{R}^T)}\\
&= \boldsymbol{R}\left\{\dot{\boldsymbol{Q}} - 2\overbracket{\boldsymbol{W}\boldsymbol{Q}}\right\}\boldsymbol{R}^T + \dot{\boldsymbol{R}}\boldsymbol{Q}\boldsymbol{R}^T + \boldsymbol{R}\boldsymbol{Q}\dot{\boldsymbol{R}}^T - 2\overbracket{\dot{\boldsymbol{R}}\boldsymbol{Q}\boldsymbol{R}^T}\\
&= \boldsymbol{R}\left\{\dot{\boldsymbol{Q}} - 2\overbracket{\boldsymbol{W}\boldsymbol{Q}}\right\}\boldsymbol{R}^T,
\end{aligned} \tag{26.224}$$

which demonstrates objectivity of the quantity $(\cdot)$ in (26.223). Next,

$$\overbracket{(\boldsymbol{R}\boldsymbol{D}\boldsymbol{R}^T)(\boldsymbol{R}\boldsymbol{Q}\boldsymbol{R}^T)} = \overbracket{\boldsymbol{R}\boldsymbol{D}\boldsymbol{Q}\boldsymbol{R}^T}, \tag{26.225}$$

demonstrating Euclidian invariance of the last term on the right-hand side of (26.223). It follows that the co-deformational derivative of $\boldsymbol{Q}$ is an objective rank-2 tensor.

References

1. Ajdari, A.: Pierre-Gilles de Gennes (1932–2007). Science **317**(5837), 466 (2007). https://doi.org/10.1126/science.1146688
2. Beris, A.N., Edwards, B.J.: Thermodynamics of Flowing Systems with Internal Microstructure. Oxford Engineering Science Series, vol. 36. Oxford University Press, New York (1994)

3. Carlsson, T., Leslie, F.M., Laverty, J.S.: Flow properties of biaxial nematioc liquid crystals. Mol. Cryst. Liq. Cryst. **210**, 95–127 (1992)
4. Capriz, G.: Continua with Microstructure. Springer, New York (1989)
5. de Gennes, P.G.: Short range order effects in the isotropic phase of nematics and cholesterics. Mol. Cryst. Liq. Cryst. **12**, 193–214 (1971)
6. de Gennes, P.G.: Scaling Concepts in Polymer Physics. Cornell University Press, Ithaca (1979). ISBN 0-8014-1203-X
7. de Gennes, P.G., Prost, J.: The Physics of Liquid Crystals. Clarendon Press, Oxford (1993). ISBN 0-19-852024-7
8. de Gennes, P.G., Brochard-Wyart, F., Quéré, D.: Capillarity and Wetting Phenomena: Drops, Bubbles, Pearls, Waves. Springer, Berlin (2003). ISBN 0-387-00592-7
9. Diogo, A.C., Martins, A.F.: Order parameter and temperature dependence of the hydrodynamic viscosities of nematics liquid crystals. Journal de Physique **43**, 779–782 (1972)
10. Doi, M.: Molecular dynamics and rheological properties of concentrated solutions of rodlike polymers in isotropic and liquid crystalline phases. J. Polym. Sci. Polym. Phys. **19**(2), 229–243 (1981)
11. Ehrentraut, H.: A unified mesoscopic continuum theory of uniaxial and biaxial liquid crystals. Ph.D. thesis, TU Berlin, Department of Physics (1996)
12. Ericksen, J.L.: Conservation laws for liquid crystals. Trans. Soc. Rheol. **5**, 23–34 (1961)
13. Ericksen, J.L.: Hydrostatic theory of liquid crystals. Arch. Ration. Mech. Anal. **21**, 371–378 (1962)
14. Ericksen, J.L.: On equations of motion for liquid crystals. Quart. J. Mech. Appl. Math. **29**, 203–208 (1976)
15. Ericksen, J.L.: Liquid crystals with variable degree of orientation. Arch. Ration. Mech. Anal. **113**, 97–120 (1991)
16. Faraoni, V., Grosso, M., Crescitelli, S., Maffettone, P.L.: The rigid rod model for neematic polymers: an analysis of the shear problem. J. Rheol. **43**, 829–843 (1999)
17. Forster, D.: Microscopic theory of flow alignment in nematic liquid crystals. Phys. Rev. Lett. **32**, 1161 (1974)
18. Green, A.E., Rivlin, R.S.: Simple force and stress multipoles. Arch. Ration. Mech. Anal. **16**, 325–354 (1964)
19. Green, A.E., Naghdi, P.M., Rivlin, R.S.: Directors and multipolar displacements in continuum mechanics. Int. J. Eng. Sci. **2**, 611–620 (1965)
20. Grosso, M., Maffettone, P.L., Dupret, F.: A closure approximation for nematic liquid crystals based on the canonical distribution subspace theory. Rheol. Acta **39**, 301–310 (2000)
21. Hess, S.: Irreversible thermodynamics of non-equilibrium alignment phenomena in molecular liquids and in liquid crystals. Z. Naturforsch. **30a**, 728 (1975)
22. Hess, S.: Pre- and post-transitional behavior of the flow alignment and flow-induced phase transition in liquid crystals. Z. Naturforsch. **31a**, 1507–1513 (1976)
23. Hess, S.: Transport phenomena in anisotropic fluids and liquid crystals. J. Non-Equilib. Thermodyn. **11**, 175–193 (1986)
24. Hess, S., Pardowitz, Z.: On the unified theory for non-equilibrium phenomena in the isotropic and nematic phases of a liquid crystal – spatially homogeneous alignment. Z. Naturforsch. **36a**, 554–558 (1981)
25. Hutter, K., Jöhnk, K.: Continuum Methods of Physical Modeling, 635 pp. Springer, Berlin (2004)
26. Leslie, F.M.: Some constitutive equations for anisotropic fluids. Quart. J. Mech. Appl. Math. **19**, 357–370 (1966)
27. Leslie, F.M.: Some constitutive equations for liquid crystals. Arch. Ration. Mech. Anal. **28**, 265–283 (1968)
28. Leslie, F.M.: Continuum theory for nematic liquid crystals. Contin. Mech. Thermodyn. **4**, 167–175 (1992)
29. Leslie, F.M., Laverty, J.S., Carlsson, T.: Continuum theory of biaxial nematic liquid crystals. Quart. J. Mech. Appl. Math. **45**, 595–606 (1992)

30. Maffettone, P.L., Sonnet, A.M., Virga, E.G.: Shear-induced biaxiality in nematic polymers. J. Non-Newton. Fluid Mech. **90**, 283–297 (2000)
31. Maier, W., Saupe, A.: Eine einfache molecular-statistische Theorie der nematischen kristallflüssigen Phase. Zeitschrift für Naturforschung A **14**(10), 882–889 (1959). https://doi.org/10.1515/zna-1959-10005
32. Marrucci, G.: Prediction of Leslie coefficients fior rodlike polymer nematics. Mol. Cryst. Liq. Cryst. (Lett.) **72**, 153–161 (1982)
33. Marrucci, G.: The Doi-Edwards model in slow flow. Predictions on the Weissenberg effect. J. Non-Newton. Fluid Mech. **21**(3), 319–328 (1986)
34. Moffettone, P.L., Sonnet, A.M., Virga, E.G.: Shear-induced bi-axiality in nematics polymers. J. Non-Newton. Fluid Mech. **90**, 283–297 (2000)
35. Olmsted, P.D., Goldbart, P.: Theory of the nonequilibrium phase transition for nematic liquid crystals under shear flow. Phys. Rev. A **41**, 4578–4581 (1990)
36. Olmsted, P.D., Goldbart, P.: Isotropic-nematic transition in shear flow: state selection, coexistence, phase transitions, and critical behavior. Phys. Rev. A **46**, 4966–4993 (1992)
37. Parodi, O.: Stress tensor for a nematic liquid crystal. Le journal de Physque **31**, 581–584 (1970)
38. Pereira-Borgmeyer, C., Hess, S.: Unified description of the flow alignment and viscosity in the isotropic and nematic phases of liquid crystals. J. Non-Equilib. Thermodyn. **20**, 359–384 (1995)
39. Qian, T., Sheng, P.: Generalized hydrodynamic equations for nematic liquid crystals. Phys. Rev. E **58**, 7475 (1998)
40. Rienaecker, G., Hess, S.: Oriental dynamics of nematics liquid crystals under a shear flow. Phys. A **267**, 294–321 (1999)
41. Saupe, A.: Das Protonenresonanzspektrum von orientiertem Benzol in nematisch-kristallinflüssiger Lösung. Z. Naturforsch. **20a**, 572–580 (1965)
42. Singh, A.P., Rey, A.D.: Theory and simuation of extensional flow-induced biaxiality in duiscotic mesophases. Journal de Physique **II**(5), 1321–1348 (1995)
43. Smith, G.E.: On isotropic integrity bases. Arch. Ration. Mech. Anal. **18**, 282–292 (1965)
44. Sonnet, A.M., Virga, E.G.: Dynamics of dissipative ordered fluids. Phys. Rev. E **64**(3), 031705-1-10 (2001)
45. Sonnet, A.M., Maffettone, P.L., Virga, E.G.: Dissipative Ordered Fluid: Theories for Liquid Crystals. Springer Science & Business Media LLC, New York (2012)
46. Sonnet, A.M., Maffettone, P.L., Virga, E.G.: Continuum theory for nematic liquid crystals with tensorial order. J. Non-Newton. Fluid Mech. **119**, 51–59 (2004)
47. Spencer, A.J.M.: Theory of invariants. In: Eringen, A.C. (ed.) Continuum Physics: Volume 1–Mathematics, pp. 239–353. Academic Press, New York (1971)
48. Stephen, M.J., Straley, J.P.: Physics of liquid crystals. Rev. Mod. Phys. **46**(4), 617–703 (1974). https://doi.org/10.1007/BF01516710
49. Stark, H., Lubensky, T.C.: Poisson-bracket approach to the dynamics of nematic liquid crystals - The role of spin angular momentum. Phys. Rev. E **72**, 051714 (2005)
50. Strutt, J.W.: (Lord Rayleigh): some general theorems relating to vibrations. Proc. Lond. Math. Soc. **4**, 357–368 (1873)
51. Vertogen, G.: The equations of motion for nematics. Z. Naturforsch. **38a**, 1273 (1983)
52. Wang, C.C.: A new representation for isotropic functions. Parts I and II. Arch. Ration. Mech. Anal. **36**(166–197), 198–223 (1970)
53. Wang, C.C.: Corrigendum to my recent paper on 'Representations for isotropic functions'. Arch Ration. Mech. Anal. **43**, 392–395 (1971)
54. Whittaker, E.T.: A Treatize on the Analytical Dynamics of Particles and Rigid Bodies, 4th edn. Cambridge University Press, Cambridge (1937)

Chapter 27
Multiphase Flows with Moving Interfaces and Contact Line—Balance Laws

Abstract A general continuum description for thermodynamic immiscible multiphase flows is presented with intersecting dividing surfaces, and three-phase common contact line, taking the contribution of the excess surface and line thermodynamic quantities into account. Starting with the standard postulates of continuum mechanics and the general global balance statement for an arbitrary physical quantity in a physical domain of three bulk phases including singular material or nonmaterial phase interfaces and a three-phase contact line, the local conservation equations on the phase interfaces and at the contact line are derived, in addition to the classical local balance equations for each bulk phase. Then, these general additional interface and line balance laws are specified for excess surface and line physical quantities, e.g., excess mass, momentum, angular momentum, energy, and entropy, respectively. Some simplified forms of these balance laws are also presented and discussed. In particular, for the massless phase interfaces and contact line, these balance laws reduce to the well-known jump conditions.

Keywords Multiphase flows · Three-phase contact line · Surface balance equations · Line balance equations · Phase interface · Three-phase contact line · Jump condition

List of Symbols

Roman Symbols

$c^{(i)}$, $c^{(\mathfrak{s}_i)}$, $c^{(\mathfrak{c})}$	Bulk, surface, and line concentrations of the solute
$c_s^{(i)}$	Bulk concentration of surfactant immediately adjacent to the interface $\mathfrak{S}^{(i)}$
$c_\infty^{(\mathfrak{s}_i)}$	Upper bound to the surface concentration that can be accommodated in the interface $\mathfrak{S}^{(i)}$
$\boldsymbol{g}$	Gravitational force per unit mass

This chapter heavily draws from WANG and OBERLACK (2011) [56].

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$H^{(\mathfrak{s})}$	Total (i.e., twice the mean) surface curvature of surface $\mathfrak{S}$, $H^{(\mathfrak{s})} = \nabla^{(\mathfrak{s})} \cdot \boldsymbol{n}^{(\mathfrak{s})}$
$H^{(\mathfrak{s}_i)}$	Total (i.e., twice the mean) surface curvature of surface $\mathfrak{S}^{(i)}$
$\boldsymbol{I}^{(\mathfrak{c})}$	Line projection tensor, $\boldsymbol{I}^{(\mathfrak{c})} = \boldsymbol{\lambda}^{(\mathfrak{c})} \otimes \boldsymbol{\lambda}^{(\mathfrak{c})}$
$\boldsymbol{I}^{(\mathfrak{s})}$	Surface projection tensor on the interface $\mathfrak{S}$, $\boldsymbol{I}^{(\mathfrak{s})} \equiv \boldsymbol{I} - \boldsymbol{n}^{(\mathfrak{s})} \otimes \boldsymbol{n}^{(\mathfrak{s})}$
$\boldsymbol{I}^{(\mathfrak{s}_i)}$	Surface projection tensor on the interface $\mathfrak{S}^{(i)}$
$\boldsymbol{j}^{(i)}$, $\boldsymbol{j}^{(\mathfrak{s}_i)}$, $\boldsymbol{j}^{(\mathfrak{c})}$	Bulk, surface, and line solute flux vectors
k_{ad}, k_{de}	Adsorption and desorption coefficients of surfactant, see (27.92)
$\boldsymbol{n}$	Unit outward normal vector to the surface $\partial\mathfrak{B}$ of the domain $\mathfrak{B}$
$\boldsymbol{n}^{(\mathfrak{c})}$	Unit principal normal at a point on the contact line $\mathfrak{C}$, defined by (27.51)
$\boldsymbol{n}^{(i)}$	Unit outward normal vector to the surface $\partial\mathfrak{B}^{(i)}$ of the subdomain $\mathfrak{B}^{(i)}$
$\boldsymbol{n}^{(\mathfrak{s}_i)}$	Unit normal vector of the interface $\mathfrak{S}^{(i)}$, pointing into the domain $\mathfrak{B}^{(i)}$
$p^{(i)}$	Hydrostatic pressure in the phase $\mathfrak{B}^{(i)}$
$\boldsymbol{q}^{(i)}$, $\boldsymbol{q}^{(\mathfrak{s}_i)}$, $\boldsymbol{q}^{(\mathfrak{c})}$	Bulk, surface, and line heat flux vectors
$\mathcal{R}$	Ideal gas constant
$r^{(i)}$, $r^{(\mathfrak{s}_i)}$, $r^{(\mathfrak{c})}$	Specific bulk, surface, and line heat supplies
$\boldsymbol{s}^{(i)}$	Unit vector normal to the boundary curves $\mathfrak{C}^{(i)}$ but tangent to the interface $\mathfrak{S}^{(i)}$ outward from the system
$t^{(\mathfrak{c})}$	Torsion of the curve $\mathfrak{C}$.
$\boldsymbol{T}^{(i)}$, $\boldsymbol{T}^{(\mathfrak{s}_i)}$, $\boldsymbol{T}^{(\mathfrak{c})}$	Cauchy, surface, and line stress tensors
$\boldsymbol{T}_{\parallel}^{(\mathfrak{s}_i)}$	Tangential surface stress, $\boldsymbol{T}_{\parallel}^{(\mathfrak{s}_i)} \in \mathbb{R}^{2\times 2}$, see (27.124)
$\boldsymbol{T}_{\perp}^{(\mathfrak{s}_i)}$	Normal surface stress, $\boldsymbol{T}_{\perp}^{(\mathfrak{s}_i)} \in \mathbb{R}^{2}$, see (27.124)
$u^{(i)}$, $u^{(\mathfrak{s}_i)}$, $u^{(\mathfrak{c})}$	Specific bulk, surface, and line internal energy densities
$\boldsymbol{v}^{(\mathfrak{c})}$	Material velocities of fluid particles that lie on the line $\mathfrak{C}$ at the instant of time
$\boldsymbol{v}^{(i)}$	Material velocity in the subdomain $\mathfrak{B}^{(i)}$
$\boldsymbol{v}^{(\mathfrak{s}_i)}$	Velocity of material points which lie on the surface $\mathfrak{S}^{(i)}(t)$ at time t
$\boldsymbol{v}_t^{(\mathfrak{c})}$	Projection of the velocity $\boldsymbol{v}^{(\mathfrak{c})}$ in the direction $\boldsymbol{\lambda}^{(\mathfrak{c})}$
$\boldsymbol{v}_t^{(\mathfrak{s}_i)}$	Projection of the vector $\boldsymbol{v}^{(\mathfrak{s}_i)}$ in the plane tangent to the interface $\mathfrak{S}^{(i)}$
$\boldsymbol{w}^{(\mathfrak{c})}$	Velocity of the three-phase contact line $\mathfrak{C}$
$\boldsymbol{w}_t^{(\mathfrak{c})}$	Velocity component of the curve, tangent to the curve $\mathfrak{C}$
$\boldsymbol{w}^{(\mathfrak{s})}$	Velocity of the surface $\mathfrak{S}$
$\boldsymbol{w}_t^{(\mathfrak{s})}$	Velocity component of the surface, tangent to the surface $\mathfrak{S}$
$\boldsymbol{w}^{(\mathfrak{s}_i)}$	Velocity of the interface $\mathfrak{S}^{(i)}$
$\boldsymbol{w}_t^{(\mathfrak{s}_i)}$	Velocity component of the surface, tangent to the surface $\mathfrak{S}^{(i)}$
$\boldsymbol{x}^{\mathfrak{c}^{(i)}}$	Coordinate of $\mathfrak{C}^{(i)}$
$\boldsymbol{x}^{(\mathfrak{s})}$	Coordinate of an evolving surface $\mathfrak{S}(t)$

Greek Symbols

$\eta^{(i)}$, $\eta^{(\mathfrak{s}_i)}$, $\eta^{(\mathfrak{c})}$	Specific bulk, surface, and line entropy densities
γ	Bulk densities of the investigated physical quantity Γ in the domains $\mathfrak{B}$
$\gamma^{(\mathfrak{c})}$	Line density of Γ along the three-phase contact line $\mathfrak{C}$
$\gamma^{(i)}$	Bulk densities of the investigated physical quantity Γ in the phase domains $\mathfrak{B}^{(i)}$ ($i = 1, 2, 3$), respectively,
$\gamma^{(\mathfrak{s}_i)}$	Surface densities of Γ on the phase interfaces $\mathfrak{S}^{(i)}$
Γ	Physical quantity in the domains $\mathfrak{B}$
$\kappa^{(\mathfrak{c})}$	Normal curvature of the contact line $\mathfrak{C}$
$\boldsymbol{\lambda}^{(\mathfrak{c})}$	Unit vector tangent to the contact line $\mathfrak{C}$ directed toward the end II from the end I
$\boldsymbol{\lambda}^{(i)}$	Unit vector $\boldsymbol{\lambda}^{(i)}$ tangent to the curve $\mathfrak{C}^{(i)}$, $\boldsymbol{s}^{(i)} = \boldsymbol{\lambda}^{(i)} \times \boldsymbol{n}^{(i)}$
$\boldsymbol{\phi}$	Non-convective bulk flux densities of Γ (per unit surface area) through the material outer surfaces $\partial\mathfrak{B}$
$\boldsymbol{\phi}^{(i)}$	Non-convective bulk flux densities of Γ (per unit surface area) through the material outer surfaces $\partial\mathfrak{B}^{(i)}$ of the bulk phase $\mathfrak{B}^{(i)}$
$\boldsymbol{\phi}^{(\mathfrak{s}_i)}$	Non-convective surface flux densities of Γ (per unit line length) through the outer boundary curves $\mathfrak{C}^{(i)}$ of the phase interfaces $\mathfrak{S}^{(i)}$
$\boldsymbol{\phi}^{(\mathfrak{c})}$	Non-convective line flux density of Γ (per point along the line) through the three-phase contact line $\mathfrak{C}$
$\boldsymbol{\phi}_C^{(\mathfrak{s}_i)}$	Surface flux vector (or scalar for the scalar quantity Γ) per unit length at the curve $\mathfrak{C}^{(i)}$
$\boldsymbol{\phi}_\eta^{(i)}$, $\boldsymbol{\phi}_\eta^{(\mathfrak{s}_i)}$, $\boldsymbol{\phi}_\eta^{(\mathfrak{c})}$	Bulk, surface, and line entropy flux vectors
$\varphi^{(\mathfrak{s}_i)}(\boldsymbol{x}, t)$	A scalar function whose zero level set $\{\boldsymbol{x}^{(\mathfrak{s}_i)} : \varphi^{(\mathfrak{s}_i)}\left(\boldsymbol{x}^{(\mathfrak{s}_i)}, t\right) = 0\}$ represents the phase interface $\mathfrak{S}^{(i)}$
π	Bulk production rate density of the investigated physical variable Γ in the physical domain $\mathfrak{B}$
$\pi^{(i)}$	Bulk production rate density of the investigated physical variable Γ in the phase subdomain $\mathfrak{B}^{(i)}$
$\pi^{(\mathfrak{s}_i)}$	Surface production rate density of the investigated physical variable Γ on the phase interface $\mathfrak{S}^{(i)}$
$\pi^{(\mathfrak{c})}$	Line production rate density of the investigated physical variable Γ at the three-phase contact line $\mathfrak{C}$
$\pi_\eta^{(i)}$, $\pi_\eta^{(\mathfrak{s}_i)}$, $\pi_\eta^{(\mathfrak{c})}$	Specific bulk, surface, and line entropy production densities
$\rho^{(i)}$, $\rho^{(\mathfrak{s}_i)}$, $\rho^{(\mathfrak{c})}$	Bulk, surface, and line mass densities
$\sigma^{(\mathfrak{s}_i)}$	Surface tension on the interface $\mathfrak{S}^{(i)}$
$\sigma_0^{(\mathfrak{s}_i)}$	Surface tension of clean interface $\mathfrak{S}^{(i)}$
σ^{lv}, σ^{sv}, σ^{sl}	Liquid–vapor, solid–vapor, and solid–liquid interfacial tensions
$\tau^{(\mathfrak{c})}$	Line tension at the three-phase contact line $\mathfrak{C}$
$\Theta^{(\mathfrak{s}_i)}$	Absolute surface temperature of the interface $\mathfrak{S}^{(i)}$
θ	Contact angle, see (27.113)

ζ	Bulk supply rate density of the investigated physical variable $\varGamma$ in the physical domain $\mathfrak{B}$
$\zeta^{(i)}$	Bulk supply rate density of the investigated physical variable $\varGamma$ in the phase subdomain $\mathfrak{B}^{(i)}$
$\zeta^{(\mathfrak{s}_i)}$	Surface supply rate density of the investigated physical variable $\varGamma$ on the phase interface $\mathfrak{S}^{(i)}$
$\zeta^{(\mathfrak{c})}$	Line supply rate density of the investigated physical variable $\varGamma$ at the three-phase contact line $\mathfrak{C}$
$\boldsymbol{\xi}^{(\mathfrak{s})} = \{\xi_1^{(\mathfrak{s})}, \xi_2^{(\mathfrak{s})}\}$	Two-dimensional parameter space of the surface $\mathfrak{S}$
$\zeta_\eta^{(i)}$, $\zeta_\eta^{(\mathfrak{s}_i)}$, $\zeta_\eta^{(\mathfrak{c})}$	Specific bulk, surface, and line entropy supplies

Miscellaneous Symbols

$\mathfrak{B}$	Material domain of a body
$\mathfrak{B}^{(i)}$	Subdomain of phase i
$\partial\mathfrak{B}$	Bounding surface of the material domain $\mathfrak{B}$
$\partial\mathfrak{B}^{(i)}$	Bounding surface of the subdomain $\mathfrak{B}^{(i)}$
$\mathfrak{C}$	Three-phase contact line
$\mathfrak{C}^{(i)}$	Outer boundary curve of the phase interface $\mathfrak{S}^{(i)}$
$\mathrm{d}/\mathrm{d}t$	Material time derivative
$\mathrm{d}^{(\mathfrak{c})}\gamma^{(\mathfrak{c})}/\mathrm{d}t$	Time derivatives of a line field $\gamma^{(\mathfrak{c})}$ following the evolution of the curve $\mathfrak{C}$ defined by means of the parameterization $\boldsymbol{x}^{(\mathfrak{c})} = \hat{\boldsymbol{x}}^{(\mathfrak{c})}\left(\xi^{(\mathfrak{c})}, t\right)$
$\mathrm{d}^{(\mathfrak{s})}\gamma^{(\mathfrak{s})}/\mathrm{d}t$	Time derivative of a surface scalar field $\gamma^{(\mathfrak{s})}$ following the evolution of the surface $\mathfrak{S}(t)$ by using the parameterization $\boldsymbol{x}^{(\mathfrak{s})} = \hat{\boldsymbol{x}}^{(\mathfrak{s})}\left(\xi_1^{(\mathfrak{s})}, \xi_2^{(\mathfrak{s})}, t\right)$
$\delta^{(\mathfrak{c})}\gamma^{(\mathfrak{c})}/\delta t$	Normal time derivative of a line field $\gamma^{(\mathfrak{c})}$, following $\mathfrak{C}(t)$, denoting the time derivative following the normal trajectory of the moving curve
$\delta^{(\mathfrak{s})}\gamma^{(\mathfrak{s})}/\delta t$	Normal time derivative of a surface scalar field $\gamma^{(\mathfrak{s})}$, denoting the time derivative for a given point on the surface $\mathfrak{S}$ following the normal trajectory of the surface
$\partial/\partial t$	Partial (local) time derivative
$\mathcal{H}$	Heaviside function, defined by (27.150)
$\mathrm{sgn}(\chi)$	Sign function of χ defined in (27.145)
∇	Gradient operator
$\nabla^{(\mathfrak{c})}$	Line gradient operator, defined by (27.49)
$\nabla^{(\mathfrak{s})}$	Surface gradient operator, see (27.32)
$\nabla^{(\mathfrak{s}_i)}$	Surface gradient operator on the interface $\mathfrak{S}^{(i)}$
$\mathfrak{S}^{(i)}$	Phase interface between phases $i-1$ and i
$[\![\mathcal{G}]\!]^{(i)}$	Jump of the quantity $\mathcal{G}$ over the interface $\mathfrak{S}^{(i)}$, $[\![\mathcal{G}]\!]^{(i)} = \mathcal{G}^{(i)} - \mathcal{G}^{(i-1)}$ (if $i-1=0$, it is set $i-1=3$)

27.1 Introduction

A particular feature of multiphase immiscible flows is the presence of interfaces separating two phases. Such a phase interface is often considered as a two-dimensional singular surface embedded in the three-dimensional Euclidian space. In this approach, the bulk properties are extrapolated up to the interface. Further, for multiphase flows with more than two phases, a three-phase common zone may occur. For this case, like the interfacial regions, we can extrapolate the dividing surfaces into the three-phase common zones to their intersecting space curve, the so-called three-phase contact line.

In the classical approach of the multiphase models, the conservation laws of mass, momentum, and energy, even moment of momentum and entropy, are established for each phase. Nevertheless, each phase does not evolve independently since they are strongly coupled through the mass, momentum, and energy exchanges between them. These transfers of physical quantities can be described by a set of jump conditions on the singular phase interfaces and at the singular contact lines.

However, in many cases, such simplifications may be insufficient to investigate the details of phase transformations. Our view is that a phase boundary is not a surface of sudden change of density, momentum, energy, and entropy; it rather constitutes a thin layer across which density, momentum, energy, etc., change smoothly but rapidly between the ones of the adjacent bulk materials. The reason for this is the necessity of molecular adjustment between different molecular arrays of the adjacent bulk phases. Such boundary layers possess a thickness of only a few molecular distances. Compared to the dimensions of the adjacent bulk materials, they are almost infinitely thin and can, therefore, be described as two-dimensional continua, representing mathematically singular surfaces with their own thermomechanical properties. Moreover, due to its different molecular orderings, the boundary layers have constitutive properties which differ from those of the adjacent bulk materials. One manifestation of this is the appearance of surface tension. The cumulative effects on the phase interface need to be described by associating excess thermodynamic quantities like surface mass density, surface velocity, surface temperature, etc. Similar to the surface excess quantities, for a three-phase contact line, corresponding line excess quantities can also be introduced to describe the cumulative effect in the three-phase common zone. To investigate these excess surface and line quantities, additional balance equations for the phase interfaces and three-phase contact line are necessary.

Analogous to the classical bulk balance equations in continuum mechanics, the balance equations for the interfaces and the contact line may be essential in the study of phase boundary evolution, contact line motion, thin films undergoing large deformations, epitaxial growth[1], etc. It is also important in the modeling of a singular surface which carries a certain structure of its own as it migrates through and interacts with a material body. A further example where surface equations can be of importance is the one of reacting single-phase flows. In certain gas combustion problems, the

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[1] The term *epitaxy* refers to the growth of a crystalline layer above (epi) the surface of a crystalline substrate, whose crystallographic orientation imposes a crystalline order (taxis) onto the thin film.

flame is quite similar to a surface separating fresh gases and burnt products. For this case, one can define a flame surface density. Likewise, if one is interested in the details of three-phase contact line or contact angle, corresponding line balance equations may be necessary.

In formulating the balance equations of excess surface and line momenta, two important quantities emerge: surface tension (for example, see **Fig. 27.1**) and line tension. Surface tension is a material property of a fluid–liquid or fluid–solid or fluid–gas interface whose origins lie in the different attractive intermolecular forces that act in the two adjacent phases. Fluids between which no interfacial tension arises are said to be miscible. Surface tension is visible in everyday life, e.g., beading of rainwater on the surface of a waxed automobile, formation of drops occurs when a mass of liquid is stretched, and separation of oil and water is caused by a tension in the surface between dissimilar liquids. The importance of surface tension is well known. If no surface tension exists, the surface of a motionless fluid must remain flat. Surface tension may be a function of temperature and mass distribution of surfactants on the surface. The presence of a gradient in surface tension (e.g., in turn caused by a concentration gradient or by a temperature gradient along the surface) will naturally cause the liquid to flow away from regions of low surface tension (the MARANGONI effect).

The line tension is also of considerable importance in many technological problems, although it is not so well known and obvious as surface tension. It has been suggested [16, 18] that the efficiency of dropwise condensation heat transfer is connected with properties of the condenser surface, or more specifically, with contact angle phenomena. A positive line tension operating on a small sessile drop resting on the condenser surface tends to reduce the length of three-phase line and hence to increase the contact angle. This may lead to the droplet being pinched off from the condenser surface. In such a situation, drop departure from the condenser surface is facilitated, and since most of the heat transfer occurs during the early stages of the formation and growth of a droplet, the heat transfer efficiency will be increased. Another example is the role that line tension can play in froth flotation. The modification of the contact angle by line tension may promote or hinder particle wetting and displacement into the aqueous phase. It has been found that particles of irregular shape, especially with sharp edges, will resist the immersion into the liquid phase because of line tension effects [34].

In the last few years, researchers have paid a fair amount of attention to the surface balance equations. It is not argued about the necessity of surface balance equations in many applications, especially in the research of surfactant transport [11, 13, 27, 36]. However, in many works, the balance equations were derived by using different approaches and assumptions, which may be suitable only for special cases [8, 14, 22, 31, 43–45]. They are either formulated only for describing the motion of a surfactant on a surface or valid only for material interfaces, for which mass transfer across phase interfaces is excluded. Some authors claim their conservation laws to be suitable for nonmaterial interfaces on the one hand, but on the other hand do not distinguish the difference of the surface velocity from the material velocity [1]. To the best of

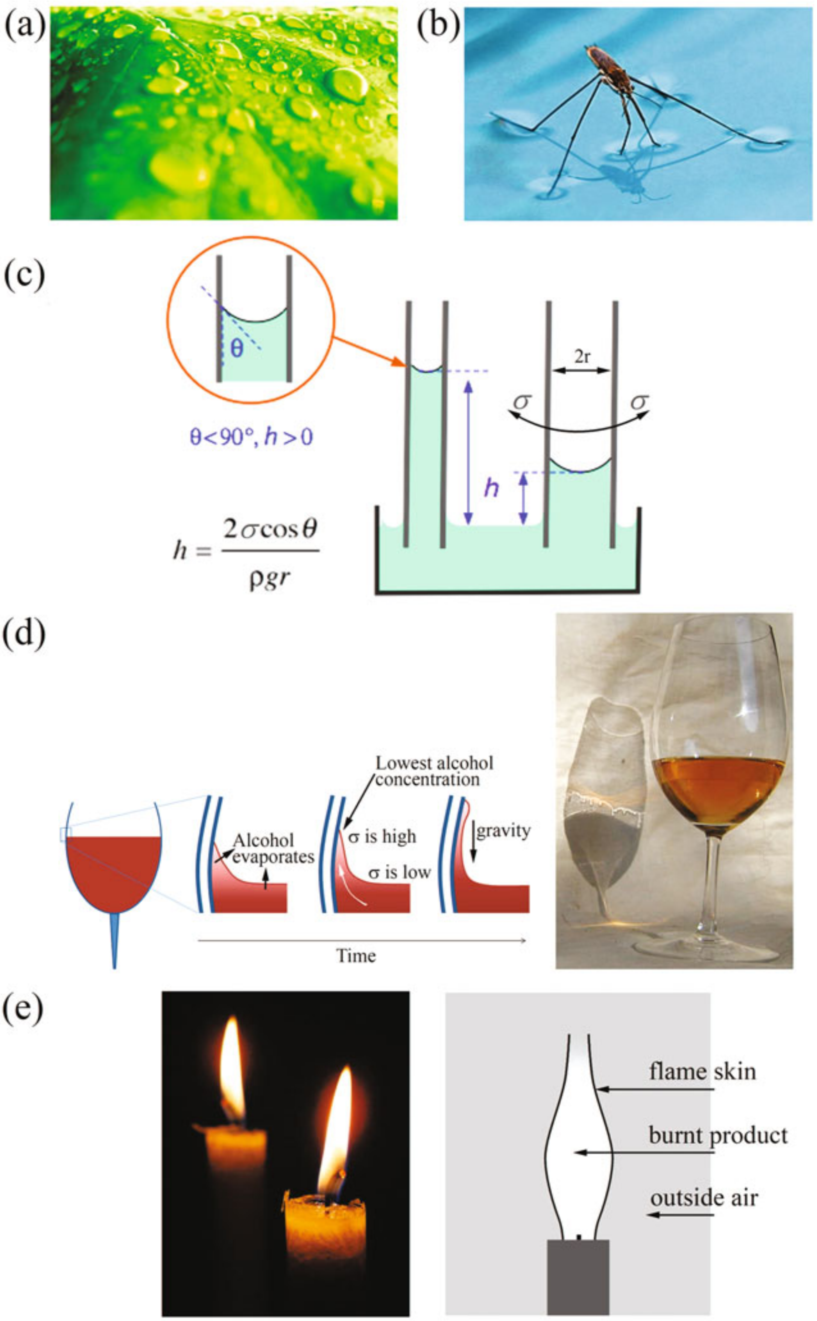

Fig. 27.1 (Continued)

◀ **Fig. 27.1** Surface tension is manifest in many everyday phenomena. **a** Raindrops on leaves of plants form, because of the existence of surface stress. We have never seen a drop of gas. Or **b** insects can only rest on the water surface of still water, because of surface tension and **c** Water rises in a pipette because of surface tension σ acting between the fluid and the pipette wall. Thereby, the height of rise is obtained from a balance between the weight of the liquid in the pipette above the liquid free surface in the basin, $r^2\pi\rho\boldsymbol{g}h$ and the wall-parallel component of surface tension around the pipette, $2\pi r\sigma\cos\theta$. Note, for $\frac{1}{2} < \theta < \frac{3\pi}{2}h$ is not a rise but a drop. **d** In a glass of wine (a mixture of water and alcohol), the wine close to the glass boundary contains less alcohol than farther away from it (owing to enhanced evaporation). This causes a gradient in the surface tension and, consequently a flow of liquid away from regions of low surface tension. **e** In a flame of a candle, the flame surface separates cold and fresh air from the brunt product

our knowledge, there exists no complete set of conservation laws for excess surface quantities on nonmaterial phase interfaces.

Very little work has been done to extend existing theories to include the effects of line excess quantities [6, 42, 45], since there is very little experimental evidence that these excess quantities have a significant influence on the system as a whole. Line tension may be the only exception. Theoretically, the line tension may be considered as a cumulative effect of the deviation of the surface tensions as compared with their values far from the common line for all surfaces meeting at the line [4, 41]. It is implied that line tension is a manifestation of the imbalance of intermolecular forces experienced by molecules located in and around the three-phase confluence zone [15, 26, 46]. Many experimental results demonstrate the existence of line tension [2, 3, 7, 10, 20, 38, 40, 53, 55]. Further, line tension may even be estimated theoretically [5, 11, 26, 29, 39, 49, 54].

In this chapter, we will present a general derivation of balance equations for multiphase immiscible flows and attempt to derive these additional interface and line balance equations for surface and line excess physical quantities as general as possible. In Sect. 27.2, we start to formulate a general global balance equation with respect to multiphase flows for a physical domain of three phases including singular phase interfaces and three-phase contact line from a viewpoint of continuum mechanics and then derive the general local forms of balance equations for the bulk, surface, and line quantities, respectively. In Sect. 27.3, the special forms of local conservation laws for mass, momentum, energy, and entropy in the bulk phase subdomains, on the phase interfaces and at the three-phase contact line are presented, and some of their simplified forms are discussed. In particular, for the case of negligible surface and line mass densities, these conservation laws reduce to jump conditions, some of which, e.g., jump conditions for mass, momentum on the interface and the YOUNG equation at the three-phase contact line are well known. An implicit presentation of the phase interfaces and the three-phase contact line is briefly presented by means of the level set method in Sect. 27.4, which can be employed to trace the motion and deformation of the phase interfaces and the contact line in numerical simulation. For the case of negligible surface and line mass densities, for which the conservation laws on the interfaces and the contact line are reduced to jump conditions, a set of one-fluid conservation equations are given in Sect. 27.5, which are valid for the whole multiphase flow domain. In these formulations, the surface and line tensions can be implemented to the balance equations as local body forces.

To the best of our knowledge, it may be the first attempt to apply a general continuum approach to a physical domain including three bulk phases and a three-phase contact line and systematically derive the conservation laws for phase interfaces and three-phase contact line, in addition to those for bulk phases, simultaneously. The derived results are generally also applicable to nonmaterial phase interfaces and contact lines. This is an important extension of the existing theories.

The following chapter will be devoted to the derivation of the constitutive relations of the emerging surface and line material-dependent quantities from thermodynamic considerations of the first and second law.

27.2 General Balance Equations for Physical Bulk, Surface, and Line Quantities

In this section, we will derive the general local balance equations for physical quantities associated with bulk phases, phase interfaces and three-phase contact line from the approach of continuum mechanics. We start from an integral form of the general balance statement for a physical domain of a material body including three bulk phases, phase interfaces, and a three-phase contact line.

27.2.1 Integral Form of the General Balance Statement

Let Γ be a physical variable which characterizes a partial aspect of the state of a body at time t, and γ denote the corresponding density in the EULER representation. Further, we choose a certain material domain $\mathfrak{B}(t)$ of the body under consideration with its bounding surface $\partial\mathfrak{B}(t)$ in the LANGRANGE representation with respect to which the physical variable is evaluated.

The time rate of change of the variable Γ of the body per unit time may be written as

$$\frac{\mathrm{d}\Gamma}{\mathrm{d}t} = \mathcal{F} + \mathcal{P} + \mathcal{S}, \tag{27.1}$$

where $\mathcal{F}$ is the flux of the variable Γ flowing from the outside into the body through the surface $\partial\mathfrak{B}$, $\mathcal{P}$ is the corresponding production within the domain $\mathfrak{B}$, and $\mathcal{S}$ is the supply or source by action at a distance from outside of the body. $\mathrm{d}/\mathrm{d}t$ denotes the total time derivative. The quantities arising in this equation express the corresponding entities for the whole domain; they are equivalent to a sum of individual contributions for all particles contained in the domain $\mathfrak{B}$ (or on the boundary $\partial\mathfrak{B}$). The quantity Γ for the whole domain $\mathfrak{B}$ is thus equal to the sum of all parts of it for the individual material points with position $\boldsymbol{x}$ at time t, i.e., the integration over the volume. If the investigated physical quantity $\varGamma$ is continuous in the domain $\mathfrak{B}$, we have

$$\begin{aligned} \varGamma &= \int_{\mathfrak{B}} \gamma(\boldsymbol{x}, t)\,\mathrm{d}v, & \mathcal{F} &= \oint\limits_{\partial\mathfrak{B}} \tilde{\phi}(\boldsymbol{x}, t, \boldsymbol{n})\,\mathrm{d}a, \\ \mathcal{P} &= \int_{\mathfrak{B}} \pi(\boldsymbol{x}, t)\,\mathrm{d}v, & \mathcal{S} &= \int_{\mathfrak{B}} \zeta(\boldsymbol{x}, t)\,\mathrm{d}v, \end{aligned} \tag{27.2}$$

where γ is the bulk density of the investigated physical quantity $\varGamma$, π and ζ denote the bulk production and supply rate densities of $\varGamma$ in the domain $\mathfrak{B}$, and $\tilde{\phi}$ the non-convective flux density through the boundary $\partial\mathfrak{B}$ into the domain $\mathfrak{B}$. With (27.2) the global balance statement (27.1) can now be written as

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathfrak{B}} \gamma(\boldsymbol{x}, t)\,\mathrm{d}v = \oint\limits_{\partial\mathfrak{B}} \tilde{\phi}(\boldsymbol{x}, t, \boldsymbol{n})\,\mathrm{d}a + \int_{\mathfrak{B}} \pi(\boldsymbol{x}, t)\,\mathrm{d}v + \int_{\mathfrak{B}} \zeta(\boldsymbol{x}, t)\,\mathrm{d}v. \tag{27.3}$$

We have assumed that the bulk flux density (flux per unit surface) $\tilde{\phi}$ depends not only on position $\boldsymbol{x}$ and time t but also on the orientation of the surface or on the normal vector on the surface with respect to which the flux is taken. In order to clarify this statement, $\boldsymbol{n}$ is considered as additional argument of the flux $\tilde{\phi}$, whose dependence on position and time is thus complemented by a direction. Because of this dependence on surface properties, namely, $\boldsymbol{n}$, the quantity $\tilde{\phi}$ is not just a simple field whose value would be determined if $\boldsymbol{x}$ and t are known.[2] This concept leads to an important consequence which shall be described in the following lemma.

Theorem 27.1 (Cauchy Lemma) *If the flux density (flux per unit surface) $\tilde{\phi}$ depends on the normal **n** at the surface, this dependency is linear:*

$$\tilde{\phi}(\boldsymbol{x}, t, \boldsymbol{n}) = -\boldsymbol{\phi}(\boldsymbol{x}, t) \cdot \boldsymbol{n}. \tag{27.4}$$

The multiplication on the right-hand side is a contraction. ■

Proof The proof of this lemma results from the balance law (27.3) applied to an infinitesimal tetrahedron (see **Fig. 27.2**), whose corners are located along lines parallel to the coordinate axes, with volume $\Delta V = \mathcal{O}\left(h^3\right)$, side areas ΔA_1, ΔA_2, ΔA_3, $\Delta A = \mathcal{O}(h^2)$ and side lengths $h_1, h_2, h_3 = \mathcal{O}(h)$. Here, the notation $f = \mathcal{O}(a)$ means that in the limit as $a \rightarrow 0$, f is proportional to a with a proportionality different from 0 and ∞. The position vector of the origin of the local coordinate system is $\boldsymbol{x}$. Furthermore, we assume that all densities appearing in (27.3) are finite, continuous, and therefore integrable. According to the mean value theorem of integral calculus, there exist points $\boldsymbol{x}^{(a)}$, $\boldsymbol{x}^{(b)}$, $\boldsymbol{x}^{(c)}$ in the tetrahedron and $\boldsymbol{x}^{(1)}$, $\boldsymbol{x}^{(2)}$, $\boldsymbol{x}^{(3)}$, $\boldsymbol{x}^{(4)}$

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[2] It is tacitly assumed that the flux depends only on the outer normal vector at the surface points and not on differential geometric properties of the surface such as mean or Gaussian curvature. This assumption has first been spelled out by Cauchy and is referred to as the Cauchy assumption.

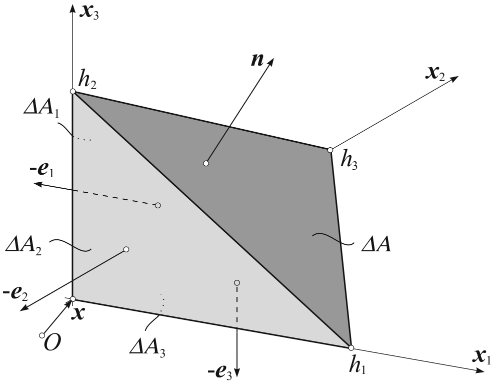

Fig. 27.2 Infinitesimal tetrahedron with normal vectors $\boldsymbol{n}$ on the abutting face and $-\boldsymbol{e}_i,\ i = 1, 2, 3$ on the side faces. The characteristic edge length of the tetrahedron is h, its surfaces are ΔA and ΔA_i for $i = 1, 2, 3$

on its side surfaces, respectively, so that for the tetrahedron the global balance law (27.3) takes the form

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\gamma\left(\boldsymbol{x}^{(a)}, t\right)\ \Delta V\right) = \sum_{k=1}^{3} \tilde{\phi}\left(\boldsymbol{x}^{(k)}, t, -\boldsymbol{e}_k\right)\ \Delta A_k + \tilde{\phi}\left(\boldsymbol{x}^{(4)}, t, \boldsymbol{n}\right)\ \Delta A$$
$$+ \pi\left(\boldsymbol{x}^{(b)}, t\right)\ \Delta V + \zeta\left(\boldsymbol{x}^{(c)}, t\right)\ \Delta V, \tag{27.5}$$

where the surface integral emerging in (27.3) has been divided into four parts corresponding to the four triangular segments of the tetrahedron. Dividing (27.5) by ΔA yields

$$\sum_{k=1}^{3} \tilde{\phi}\left(\boldsymbol{x}^{(k)}, t, -\boldsymbol{e}_k\right)\ \frac{\Delta A_k}{\Delta A} + \tilde{\phi}\left(\boldsymbol{x}^{(4)}, t, \boldsymbol{n}\right) = \mathcal{O}(h). \tag{27.6}$$

Since the side surfaces ΔA_k correspond to the projections of ΔA along the coordinate axes, one can write, geometrically,

$$\Delta A_k = (\boldsymbol{e}_k \cdot \boldsymbol{n})\ \Delta A, \tag{27.7}$$

so that

$$\tilde{\phi}\left(\boldsymbol{x}^{(4)}, t, \boldsymbol{n}\right) = -\sum_{k=1}^{3} \tilde{\phi}\left(\boldsymbol{x}^{(k)}, t, -\boldsymbol{e}_k\right)\ (\boldsymbol{e}_k \cdot \boldsymbol{n}) + \mathcal{O}(h). \tag{27.8}$$

In the limiting case as $h \to 0$, the expression (27.8) reduces to

$$\tilde{\phi}\,(\boldsymbol{x}, t, \boldsymbol{n}) = -\sum_{k=1}^{3} \tilde{\phi}\,(\boldsymbol{x}, t, -\boldsymbol{e}_k)\;(\boldsymbol{e}_k \cdot \boldsymbol{n})\,. \tag{27.9}$$

If one now introduces the relation

$$\boldsymbol{\phi}(\boldsymbol{x}, t) := \sum_{k=1}^{3} \tilde{\phi}\,(\boldsymbol{x}, t, -\boldsymbol{e}_k)\;\boldsymbol{e}_k, \tag{27.10}$$

which is independent of $\boldsymbol{n}$, one obtains

$$\tilde{\phi}(\boldsymbol{x}, t, \boldsymbol{n}, t) = -\boldsymbol{\phi}(\boldsymbol{x}, t) \cdot \boldsymbol{n}. \tag{27.11}$$

The choice of the sign is such that the flow from outside into the body is taken positive. With these relations, the proof of (27.4) is achieved.[3] ■

By means of Theorem 27.1, the global integral balance law (27.3) takes the form

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathfrak{B}} \gamma(\boldsymbol{x}, t)\,\mathrm{d}v = -\oint_{\partial\mathfrak{B}} \boldsymbol{\phi}(\boldsymbol{x}, t) \cdot \boldsymbol{n}\,\mathrm{d}a + \int_{\mathfrak{B}} \pi(\boldsymbol{x}, t)\,\mathrm{d}v + \int_{\mathfrak{B}} \zeta(\boldsymbol{x}, t)\,\mathrm{d}v. \tag{27.12}$$

To deduce the physical balance relations for phase interfaces and three-phase contact line, we now consider a material domain $\mathfrak{B}$ which is composed of three subdomains occupied by three phases $\mathfrak{B}^{(i)}$ $(i = 1, 2, 3)$ $(\mathfrak{B} = \cup_{i=1}^{3}\mathfrak{B}^{(i)})$, separated from one another by three discontinuities generally curved surfaces $\mathfrak{S}^{(i)}$ $(i = 1, 2, 3)$, called phase interfaces, respectively, i.e., $\mathfrak{S}^{(1)}$ is the interface between the phase 3 and phase 1, $\mathfrak{S}^{(2)}$ the interface between the phase 1 and phase 2, and $\mathfrak{S}^{(3)}$ is the interface between the phase 2 and phase 3, see **Fig. 27.3**. These phase interfaces are represented by moving, singular orientable surfaces. The meaning of a singular surface at this point solely refers to the fact that a vanishing interface thickness is considered, across which the physical quantities may be discontinuous. Generally, the phase interfaces are nonmaterial. It is the case, e.g., when mass transfer occurs between the interface and the two adjoining phases. The common line $\mathfrak{C}$ between the three phases is called the three-phase contact line. The outer boundaries of $\mathfrak{B}^{(i)}$,

---

[3] The derivation of the result (27.11) requires a number of clarifying remarks to put it into the proper perspectives. The result was obtained by applying the balance law for a physical quantity to a material tetrahedronal volume with sharp edges and points for which unit normal vectors cannot uniquely be defined. Thus, to make the above argument mathematically "clean" the tetrahedron must be smoothed out such that the edges and vertices become "diffuse" with uniquely defined normal vectors. This smoothing can formally be done and the limit to a tetrahedron with sharp edges and vertices can be performed such that in the limit (27.11) is obtained. The assumption that is needed is that the flux $\boldsymbol{\phi}$ is nontrivially defined with respect to surface measure, but that there is no specific flux quantity defined along the edges or at the vertices.
A historical account on CAUCHY's Lemma is given by TRUESDELL and TOUPIN [52], Sect. 203, more general treatments, in which nontrivial edge fluxes and vertex fluxes are allowed for, are given by NOLL [32], NOLL and VIRGA [33] and DELL'ISOLA and SEPPECHER [9].

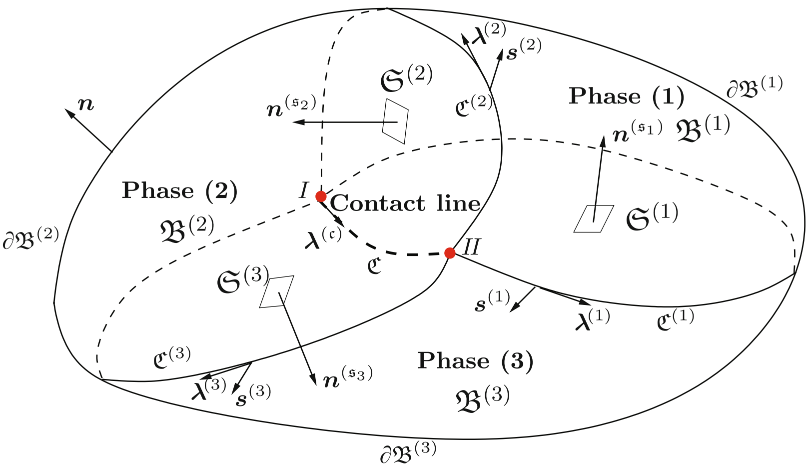

Fig. 27.3 The investigated material domain $\mathfrak{B}$ with its outer boundary $\partial\mathfrak{B}$ consisting of three-phase subdomains $\mathfrak{B}^{(i)}$ $(i = 1, 2, 3)$ surrounded by their outer boundaries $\partial\mathfrak{B}^{(i)}$ and phase interfaces $\mathfrak{S}^{(i)}$. Note especially, the contact points I and II (red), from WANG and OBERLACK [56]

denoted by $\partial\mathfrak{B}^{(i)}$ $(\partial\mathfrak{B} = \bigcup_{i=1}^{3}\partial\mathfrak{B}^{(i)})$, join at the common curves $\mathfrak{C}^{(i)}$ which are the intersections of the singular surface $\mathfrak{S}^{(i)}$ with the surface $\partial\mathfrak{B}$ of $\mathfrak{B}$, respectively.

The interface or phase boundary may not be a surface of sudden change of mass, momentum, energy, and entropy; it rather constitutes a thin layer across which mass, momentum, energy, etc., change smoothly but rapidly between the densities of the adjacent phase materials. The reason for this is the necessity of molecular arrays of the adjacent bulk phases. Such an interface layer possesses a thickness of only a few molecular diameters or molecular mean free paths. Compared to the dimensions of the adjacent bulk materials, the interface is almost infinitely thin and can therefore be described as a two-dimensional continuum, representing mathematically a singular surface with its own thermomechanical properties. The interface can carry mass, momentum, energy, and entropy. The interface is considered to be material in the following sense: if we assume that its tangential velocity is the tangential material velocity of fluid particles that lie on the interface at some instant of time, which is almost always so assumed in this chapter. The singular surface as a whole, however, may be nonmaterial, because matter may cross it when it represents a phase boundary. A thermodynamic theory of phase boundaries can thus be founded on the postulation of conservation laws for surface mass, momentum, and energy and a balance law for surface entropy together with constitutive assumptions for surface-dependent fields and jump relations of the bulk fields at the phase boundary. The situation is analogous for the three-phase contact line, which represents a three-phase-interaction region and hence may also possess mass, momentum, energy, and entropy, for which corresponding conservation laws can also be postulated.

For the material domain $\mathfrak{B}$, the quantities arising in Eq. (27.1) express the corresponding entities for the whole domain; they are equivalent to a sum of individual contributions for all particles contained in the domain $\mathfrak{B}$ or on the boundary $\partial\mathfrak{B}$. Thus, for the three-phase material domain $\mathfrak{B}$ displayed in Fig. 27.3 including non-negligible surface densities on the phase interfaces and line densities at the three-phase contact line for corresponding physical quantities, relations (27.2) can be extended to

$$
\begin{aligned}
\Gamma &= \int_{\mathfrak{B}} \gamma \, \mathrm{d}v = \sum_{i=1}^{3} \int_{\mathfrak{B}^{(i)}} \gamma^{(i)} \, \mathrm{d}v + \sum_{i=1}^{3} \int_{\mathfrak{S}^{(i)}} \gamma^{(\mathfrak{s}_i)} \, \mathrm{d}a + \int_{\mathfrak{C}} \gamma^{(\mathfrak{c})} \, \mathrm{d}\ell, \\
\mathcal{F} &= -\oint_{\partial\mathfrak{B}} \boldsymbol{\phi} \cdot \boldsymbol{n} \, \mathrm{d}a = -\sum_{i=1}^{3} \int_{\partial\mathfrak{B}^{(i)}} \boldsymbol{\phi}^{(i)} \cdot \boldsymbol{n} \, \mathrm{d}a - \sum_{i=1}^{3} \int_{\mathfrak{C}^{(i)}} \boldsymbol{\phi}^{(\mathfrak{s}_i)} \cdot \boldsymbol{s}^{(i)} \, \mathrm{d}\ell \\
&\qquad - \left[\left(\boldsymbol{\phi}^{(\mathfrak{c})} \cdot \boldsymbol{\lambda}^{(\mathfrak{c})} \right)^{II} - \left(\boldsymbol{\phi}^{(\mathfrak{c})} \cdot \boldsymbol{\lambda}^{(\mathfrak{c})} \right)^{I} \right], \qquad (27.13) \\
\mathcal{P} &= \int_{\mathfrak{B}} \pi \, \mathrm{d}v = \sum_{i=1}^{3} \int_{\mathfrak{B}^{(i)}} \pi^{(i)} \, \mathrm{d}v + \sum_{i=1}^{3} \int_{\mathfrak{S}^{(i)}} \pi^{(\mathfrak{s}_i)} \, \mathrm{d}a + \int_{\mathfrak{C}} \pi^{(\mathfrak{c})} \, \mathrm{d}\ell, \\
\mathcal{S} &= \int_{\mathfrak{B}} \zeta \, \mathrm{d}v = \sum_{i=1}^{3} \int_{\mathfrak{B}^{(i)}} \zeta^{(i)} \, \mathrm{d}v + \sum_{i=1}^{3} \int_{\mathfrak{S}^{(i)}} \zeta^{(\mathfrak{s}_i)} \, \mathrm{d}a + \int_{\mathfrak{C}} \zeta^{(\mathfrak{c})} \, \mathrm{d}\ell.
\end{aligned}
$$

The field quantities included in (27.13) have the following meanings:

$\gamma^{(i)}$	bulk densities of the investigated physical quantity Γ in the phase domains $\mathfrak{B}^{(i)}$ ($i = 1, 2, 3$), respectively;
$\gamma^{(\mathfrak{s}_i)}$	surface densities of Γ on the phase interfaces $\mathfrak{S}^{(i)}$;
$\gamma^{(\mathfrak{c})}$	line density of Γ along the three-phase contact line $\mathfrak{C}$;
$\boldsymbol{\phi}^{(i)}$	non-convective bulk flux densities of Γ (per unit surface area) through the material outer surfaces $\partial\mathfrak{B}^{(i)}$ of the bulk phase $\mathfrak{B}^{(i)}$;
$\boldsymbol{\phi}^{(\mathfrak{s}_i)}$	non-convective surface flux densities of Γ (per unit line length) through the outer boundary curves $\mathfrak{C}^{(i)}$ of the phase interfaces $\mathfrak{S}^{(i)}$;
$\boldsymbol{\phi}^{(\mathfrak{c})}$	non-convective line flux density of Γ (per point along the line) at the three-phase contact line $\mathfrak{C}$; $\left(\boldsymbol{\phi}^{(\mathfrak{c})} \cdot \boldsymbol{\lambda}^{(\mathfrak{c})}\right)^{I}$ and $\left(\boldsymbol{\phi}^{(\mathfrak{c})} \cdot \boldsymbol{\lambda}^{(\mathfrak{c})}\right)^{II}$ are the fluxes through both boundary points I and II;
$\boldsymbol{\lambda}^{(\mathfrak{c})}$	unit vector tangent to the contact line $\mathfrak{C}$ directed toward the end II from the end I;
$\pi^{(i)}$, $\zeta^{(i)}$	bulk production and supply rate densities of Γ in the phase domain $\mathfrak{B}^{(i)}$;

$\pi^{(\mathfrak{s}_i)}$, $\zeta^{(\mathfrak{s}_i)}$	surface production and supply rate densities of Γ on the interface $\mathfrak{S}^{(i)}$;
$\pi^{(\mathfrak{c})}$, $\zeta^{(\mathfrak{c})}$	line production and supply rate densities of Γ at the contact line $\mathfrak{C}$;
$\boldsymbol{n}$	unit outward normal vector to the surface $\partial\mathfrak{B}$ of the domain $\mathfrak{B}$;
$\boldsymbol{s}^{(i)}$	unit vector normal to the boundary curves $\mathfrak{C}^{(i)}$ but tangent to the interface $\mathfrak{S}^{(i)}$, outward from the system.

Note we do not assume the contact points I and II to be equipped with mass.

As shown above, throughout this chapter, the physical quantities for the bulk phase $\mathfrak{B}^{(i)}$ are indicated by the superscript (i), the interfacial quantities for the phase interface $\mathfrak{S}^{(i)}$ are denoted by the superscript $(\mathfrak{s}_i)$, and the superscript $(\mathfrak{c})$ characterizes the line quantities at the three-phase contact line $\mathfrak{C}$.

The integral of the traction $\boldsymbol{\phi}^{(\mathfrak{s}_i)} \cdot \boldsymbol{s}^{(i)}$ over the curve $\mathfrak{C}^{(i)}$ (the second term of the right-hand side in (27.13)$_2$) represents the flux exerted on $\mathfrak{B}$ by the portion of the curve $\mathfrak{S}^{(i)}$ exterior to the domain $\mathfrak{B}$. In deriving this flux, it has been assumed that the surface flux $\tilde{\phi}^{(\mathfrak{s}_i)}$ (or vector for the vector quantity Γ), i.e., flux per unit length at the curve $\mathfrak{C}^{(i)}$, depends on the coordinate of $\mathfrak{C}^{(i)}$, $\boldsymbol{x}^{\mathfrak{c}^{(i)}}$, the time t and the line normal $\boldsymbol{s}^{(i)}$ by

$$\tilde{\phi}^{(\mathfrak{s}_i)} = \tilde{\phi}^{(\mathfrak{s}_i)}\left(\boldsymbol{x}^{\mathfrak{c}^{(i)}}, t, \boldsymbol{s}^{(i)}\right)$$

and the CAUCHY lemma for the flux per unit line length has been employed.

Theorem 27.2 (CAUCHY Lemma for the surface flux density) *If the surface flux density, i.e., flux per unit line length, $\tilde{\phi}^{(\mathfrak{s}_i)}$ depends on the normal $\boldsymbol{s}^{(i)}$ at the line, this dependency is linear:*

$$\tilde{\phi}^{(\mathfrak{s}_i)}\left(\boldsymbol{x}^{\mathfrak{c}^{(i)}}, t, \boldsymbol{s}^{(i)}\right) = -\boldsymbol{\phi}^{(\mathfrak{s}_i)}\left(\boldsymbol{x}^{\mathfrak{c}^{(i)}}, t\right) \cdot \boldsymbol{s}^{(i)}. \tag{27.14}$$

$\boldsymbol{\phi}^{(\mathfrak{s}_i)}$ denotes the corresponding flux vector (or tensor for the vector quantity Γ). ■

This relation is fairly similar to the well-known CAUCHY lemma for the bulk flux density (i.e., flux per unit surface), see Theorem 27.1, as used in the first term of the right-hand side in (27.13)$_2$. A proof of relation (27.14) can be found, e.g., in TRUESDELL [51].

In the last term of the right-hand side in (27.13)$_2$, a similar lemma has also been employed for the flux through the boundary points I and II along the three-phase contact line $\mathfrak{C}$ into the domain $\mathfrak{B}$, $\left[\left(\boldsymbol{\phi}^{(\mathfrak{c})} \cdot \boldsymbol{\lambda}^{(\mathfrak{c})}\right)^{II} - \left(\boldsymbol{\phi}^{(\mathfrak{c})} \cdot \boldsymbol{\lambda}^{(\mathfrak{c})}\right)^{I}\right]$, in which the line flux density (per point along the line), $\boldsymbol{\phi}^{(\mathfrak{c})}$, is introduced.

Substituting (27.13) into (27.1), we obtain

$$
\begin{aligned}
&\sum_{i=1}^{3}\frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathfrak{B}^{(i)}}\gamma^{(i)}\,\mathrm{d}v+\sum_{i=1}^{3}\frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathfrak{S}^{(i)}}\gamma^{(\mathfrak{s}_i)}\,\mathrm{d}a+\frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathfrak{C}}\gamma^{(\mathfrak{c})}\,\mathrm{d}\ell\\
&=-\sum_{i=1}^{3}\int_{\partial\mathfrak{B}^{(i)}}\boldsymbol{\phi}^{(i)}\cdot\boldsymbol{n}\,\mathrm{d}a-\sum_{i=1}^{3}\int_{\mathfrak{C}^{(i)}}\boldsymbol{\phi}^{(\mathfrak{s}_i)}\cdot\boldsymbol{s}^{(i)}\mathrm{d}\ell\\
&\quad-\Big[\big(\boldsymbol{\phi}^{(\mathfrak{c})}\cdot\boldsymbol{\lambda}^{(\mathfrak{c})}\big)^{II}-\big(\boldsymbol{\phi}^{(\mathfrak{c})}\cdot\boldsymbol{\lambda}^{(\mathfrak{c})}\big)^{I}\Big]\\
&\quad+\sum_{i=1}^{3}\int_{\mathfrak{B}^{(i)}}\big(\pi^{(i)}+\zeta^{(i)}\big)\,\mathrm{d}v+\sum_{i=1}^{3}\int_{\mathfrak{S}^{(i)}}\big(\pi^{(\mathfrak{s}_i)}+\zeta^{(\mathfrak{s}_i)}\big)\,\mathrm{d}a\\
&\quad+\int_{\mathfrak{C}}\big(\pi^{(\mathfrak{c})}+\zeta^{(\mathfrak{c})}\big)\,\mathrm{d}\ell. \qquad (27.15)
\end{aligned}
$$

In order to describe the motions of the material points and the temporal and spatial changes of investigated local physical quantities in a bulk phase, on a phase interface or at the three-phase contact line, the above derived global balance expression in an integral form may not be convenient. Our aim is to achieve its local forms for the bulk phases, interfaces, and three-phase common line, when sufficient differentiability assumptions in the bulk phases, on the phase interfaces and along the contact line, respectively, are satisfied. For this purpose, the transport theorems and kinematic description of the moving interfaces and contact line are needed.

27.2.2 Transport Theorems, Divergence Theorems, and Kinematics

Theorem 27.3 (Reynolds[4] Transport Theorem) *The time derivative of the integral of the physical quantity* $\gamma(\boldsymbol{x},t)$ *over the continuous material domain* $\mathfrak{B}(t)$ *with boundary* $\partial\mathfrak{B}(t)$ *takes the form*

$$
\frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathfrak{B}}\gamma\mathrm{d}v=\int_{\mathfrak{B}}\frac{\partial\gamma}{\partial t}\mathrm{d}v+\int_{\partial\mathfrak{B}}\gamma\,(\boldsymbol{v}\cdot\boldsymbol{n})\,\mathrm{d}a, \qquad (27.16)
$$

in which $\boldsymbol{n}(\boldsymbol{x},t)$ *is the outward-pointing unit normal vector,* $\boldsymbol{x}$ *is a point in the region,* $\mathrm{d}v$ *and* $\mathrm{d}a$ *are the variables of integration, and* $\boldsymbol{v}(\boldsymbol{x},t)$ *is the material velocity of the flow. The function* γ *may be tensor, vector, or scalar valued.* ■

Proof We employ the relation for the time derivative of an infinitesimal material volume element $\mathrm{d}v$,

$$
(\mathrm{d}v)^{\cdot}=\nabla\cdot\boldsymbol{v}\,\mathrm{d}v, \qquad (27.17)
$$

---

[4] For a brief biography of OSBORNE REYNOLDS (1842–1912), see Vol. 2 of this treatise [25], Fig. 15.2 on p. 230.

in which $(\,)^{\cdot}$ denotes the material time derivative. The proof of relation (27.17) can be found in almost all textbooks of Continuum Mechanics, see, e.g., [23, 24]. To prove the relation (27.17), we consider three material line elements $\mathrm{d}\boldsymbol{x}_1, \mathrm{d}\boldsymbol{x}_2, \mathrm{d}\boldsymbol{x}_3$ and $\mathrm{d}\boldsymbol{X}_1$, $\mathrm{d}\boldsymbol{X}_2$, $\mathrm{d}\boldsymbol{X}_3$ in the present and reference configuration (see Sect. 22.2), respectively. The scalars

$$\mathrm{d}v = (\mathrm{d}\boldsymbol{x}_1 \times \mathrm{d}\boldsymbol{x}_2) \cdot \mathrm{d}\boldsymbol{x}_3 \quad \text{and} \quad \mathrm{d}V = (\mathrm{d}\boldsymbol{X}_1 \times \mathrm{d}\boldsymbol{X}_2) \cdot \mathrm{d}\boldsymbol{X}_3 \tag{27.18}$$

form a material volume element in the present and the reference configuration. The deformation gradient of any given motion, defined in (22.7), i.e.,

$$\boldsymbol{F} = \frac{\partial \boldsymbol{x}}{\partial \boldsymbol{X}} = \frac{\partial \boldsymbol{\chi}(\boldsymbol{X}, t)}{\partial \boldsymbol{X}} = \mathrm{Grad}\boldsymbol{x}, \tag{27.19}$$

maps material vectorial line elements $(\mathrm{d}\boldsymbol{X}_1, \mathrm{d}\boldsymbol{X}_2, \mathrm{d}\boldsymbol{X}_3)$ in the reference configuration onto line elements $(\mathrm{d}\boldsymbol{x}_1, \mathrm{d}\boldsymbol{x}_2, \mathrm{d}\boldsymbol{x}_3)$ in the present configuration by (see (22.11))

$$\mathrm{d}\boldsymbol{x}_1 = \boldsymbol{F}\mathrm{d}\boldsymbol{X}_1, \quad \mathrm{d}\boldsymbol{x}_2 = \boldsymbol{F}\mathrm{d}\boldsymbol{X}_2, \quad \mathrm{d}\boldsymbol{x}_3 = \boldsymbol{F}\mathrm{d}\boldsymbol{X}_3. \tag{27.20}$$

By means of the algebraic identity

$$(\boldsymbol{A}\boldsymbol{a} \times \boldsymbol{A}\boldsymbol{b}) \cdot \boldsymbol{A}\boldsymbol{c} = (\det \boldsymbol{A})\,[(\boldsymbol{a} \times \boldsymbol{b}) \cdot \boldsymbol{c}]\,, \tag{27.21}$$

valid for any second-order tensor $\boldsymbol{A} \in \mathbb{R}^{3\times3}$ and vectors $\boldsymbol{a}, \boldsymbol{b}, \boldsymbol{c} \in \mathbb{R}^3$, one obtains from (27.18)

$$\mathrm{d}v = (\det \boldsymbol{F})\mathrm{d}V. \tag{27.22}$$

In terms of (27.22), the time derivative of the volume element, $\mathrm{d}v$, is transferred to the time derivative of the determinant of the deformation gradient, $\det \boldsymbol{F}$; this is calculated by using the chain rule

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\left(\det \boldsymbol{F}(\boldsymbol{X}, t)\right) &= \left(\frac{\mathrm{d}}{\mathrm{d}\boldsymbol{F}}\det \boldsymbol{F}\right) \cdot \dot{\boldsymbol{F}}(\boldsymbol{X}, t) \overset{\star}{=} (\det \boldsymbol{F})\,\boldsymbol{F}^{-T} \cdot \dot{\boldsymbol{F}} \\ &= (\det \boldsymbol{F})\,\mathrm{tr}(\dot{\boldsymbol{F}}\boldsymbol{F}^{-1}).\end{aligned} \tag{27.23}$$

At the step, "$\overset{\star}{=}$" the identity

$$\frac{\mathrm{d}}{\mathrm{d}\boldsymbol{F}}\det \boldsymbol{F} = (\det \boldsymbol{F})\,\boldsymbol{F}^{-1},$$

valid for all invertible tensors $\boldsymbol{F}$, has been used. Furthermore, the time derivative of the deformation gradient (27.19) yields

$$\dot{\boldsymbol{F}} = \frac{\partial \dot{\boldsymbol{x}}}{\partial \boldsymbol{X}} = \frac{\partial \boldsymbol{v}}{\partial \boldsymbol{X}} = \text{Grad}\boldsymbol{v} = \frac{\partial \boldsymbol{v}}{\partial \boldsymbol{x}}\frac{\partial \boldsymbol{x}}{\partial \boldsymbol{X}} = \boldsymbol{L}\boldsymbol{F}, \quad \text{or} \quad \boldsymbol{L} = \dot{\boldsymbol{F}}\boldsymbol{F}^{-1}.$$

Employing this relation to (27.23) results in

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\det \boldsymbol{F}(\boldsymbol{X},t)\right) = (\det \boldsymbol{F})\,\text{tr}\boldsymbol{L} = \nabla \cdot \boldsymbol{v}\,(\det \boldsymbol{F}). \tag{27.24}$$

Following this, one obtains by taking the time derivative in (27.22)

$$(\mathrm{d}v)^{\cdot} = \frac{\mathrm{d}}{\mathrm{d}t}\left(\det \boldsymbol{F}(\boldsymbol{X},t)\right)\mathrm{d}V = \nabla \cdot \boldsymbol{v}\,(\det \boldsymbol{F})\mathrm{d}V = \nabla \cdot \boldsymbol{v}\,\mathrm{d}v,$$

the relation (27.17) is proved.

Now, we rewrite the time derivative of the volume integral on the right-hand side of (27.16) as

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathfrak{B}}\gamma\mathrm{d}v &= \int_{\mathfrak{B}}\left(\frac{\mathrm{d}\gamma}{\mathrm{d}t}\mathrm{d}v + \gamma\,(\mathrm{d}v)^{\cdot}\right) \overset{(7.17)}{=} \int_{\mathfrak{B}}\left(\frac{\mathrm{d}\gamma}{\mathrm{d}t} + \gamma\nabla\cdot\boldsymbol{v}\right)\mathrm{d}v \\ &= \int_{\mathfrak{B}}\frac{\partial\gamma}{\partial t}\mathrm{d}v + \int_{\partial\mathfrak{B}}\gamma\,(\boldsymbol{v}\cdot\boldsymbol{n})\,\mathrm{d}a.\end{aligned} \tag{27.25}$$

In the last step, the GAUSS divergence theorem has been employed. Hence, (27.16) is proved. ■

More generally, the REYNOLDS transport theorem can be extended to a nonmaterial domain $\mathfrak{B}(t)$ and remains valid for any motion of its boundary.

Theorem 27.4 (Extended Reynolds Transport Theorem) *Let* $\mathfrak{B}(t)$ *be a volume bounded by a closed surface* $\partial\mathfrak{B}(t)$ *moving with the velocity* $\boldsymbol{w}(\boldsymbol{x},t)$*. The time derivative of the integral of the physical quantity* $\gamma(\boldsymbol{x},t)$ *over the continuous domain* $\mathfrak{B}(t)$ *takes the form*

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathfrak{B}}\gamma\mathrm{d}v = \int_{\mathfrak{B}}\frac{\partial\gamma}{\partial t}\mathrm{d}v + \int_{\partial\mathfrak{B}}\gamma\,(\boldsymbol{w}\cdot\boldsymbol{n})\,\mathrm{d}a. \tag{27.26}$$

■

This result follows LEIBNIZ's theorem that the total time derivative of an integral with time-dependent limits equals the integral of the partial time derivative of the integrand plus a term that accounts for the motion of the integration boundary.

For the material domain $\mathfrak{B}$ considered presently, which is composed of three phases $\mathfrak{B}^{(i)}$ $(i = 1, 2, 3)$ $(\mathfrak{B} = \cup_{i=1}^{3}\mathfrak{B}^{(i)})$, separated from one another by three-phase interfaces $\mathfrak{S}^{(i)}$ $(i = 1, 2, 3)$, the physical quantities are continuous only within the subdomains $\mathfrak{B}^{(i)}$ $(i = 1, 2, 3)$, respectively, and the interfaces may be nonmaterial due to possible mass transfers between the phases. For this case, we can interchange the time derivatives and the volume integrations emerging in the first term on the left-hand side of (27.15) with the aid of the extended REYNOLDS transport theorem (Theorem 27.4), i.e.,

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathfrak{B}^{(i)}}\gamma^{(i)}\mathrm{d}v &= \int_{\mathfrak{B}^{(i)}}\frac{\partial\gamma^{(i)}}{\partial t}\mathrm{d}v + \int_{\partial\mathfrak{B}^{(i)}}\gamma^{(i)}\left(\boldsymbol{v}^{(i)}\cdot\boldsymbol{n}\right)\mathrm{d}a \\ &\quad -\int_{\mathfrak{S}^{(i)}}\gamma^{(i)}\left(\boldsymbol{w}^{(\mathfrak{s}_i)}\cdot\boldsymbol{n}^{(\mathfrak{s}_i)}\right)\mathrm{d}a \\ &\quad +\int_{\mathfrak{S}^{(i+1)}}\gamma^{(i)}\left(\boldsymbol{w}^{(\mathfrak{s}_{i+1})}\cdot\boldsymbol{n}^{(\mathfrak{s}_{i+1})}\right)\mathrm{d}a \\ &= \int_{\mathfrak{B}^{(i)}}\frac{\partial\gamma^{(i)}}{\partial t}\,\mathrm{d}v + \oint_{\partial\mathfrak{B}^{(i)}\cup\mathfrak{S}^{(i)}\cup\mathfrak{S}^{(i+1)}}\gamma^{(i)}\left(\boldsymbol{v}^{(i)}\cdot\boldsymbol{n}\right)\mathrm{d}a \\ &\quad -\int_{\mathfrak{S}^{(i)}}\gamma^{(i)}\left(\boldsymbol{w}^{(\mathfrak{s}_i)}-\boldsymbol{v}^{(i)}\right)\cdot\boldsymbol{n}^{(\mathfrak{s}_i)}\mathrm{d}a \\ &\quad +\int_{\mathfrak{S}^{(i+1)}}\gamma^{(i)}\left(\boldsymbol{w}^{(\mathfrak{s}_{i+1})}-\boldsymbol{v}^{(i)}\right)\cdot\boldsymbol{n}^{(\mathfrak{s}_{i+1})}\,\mathrm{d}a,\end{aligned}\tag{27.27}$$

where $\boldsymbol{w}^{(\mathfrak{s}_i)}$ denotes the speed of the interface $\mathfrak{S}^{(i)}$, $\boldsymbol{v}^{(i)}$ is the material velocity in the subdomain $\mathfrak{B}^{(i)}$, $\boldsymbol{n}^{(\mathfrak{s}_i)}$ is the unit normal vector of the interface $\mathfrak{S}^{(i)}$, which is chosen to point into the domain $\mathfrak{B}^{(i)}$, respectively. Together with the unit vector $\boldsymbol{\lambda}^{(i)}$ tangent to the curve $\mathfrak{C}^{(i)}$, $(\boldsymbol{\lambda}^{(i)}, \boldsymbol{n}^{(i)}, \boldsymbol{s}^{(i)})$ form an orthonormal basis of a local right-handed coordinate system along the space curve $\mathfrak{C}^{(i)}$. Note that the local coordinate frame on $\mathfrak{C}^{(i)}$, $(\boldsymbol{\lambda}^{(i)}, \boldsymbol{n}^{(i)}, \boldsymbol{s}^{(i)})$, does not define a classical FRENET–SERRET frame. In fact, we need to extend the definition of $\boldsymbol{n}^{(i)}$ as a continuation of the inner part of $\mathfrak{C}^{(i)}$, while $\boldsymbol{s}^{(i)}$ is given by the relation $\boldsymbol{s}^{(i)} = \boldsymbol{\lambda}^{(i)} \times \boldsymbol{n}^{(i)}$. In (27.27) and the following text, if the superscript $(i + 1)$ takes the value of 4, it will be automatically set as $(i + 1) = 1$. Alternatively, the superscript $(i + 1)$ may be replaced by $(\mathrm{mod}(i, 3) + 1)$.

Since $\mathfrak{S}^{(i)}$ is generally nonmaterial, the velocity of $\mathfrak{S}^{(i)}$, $\boldsymbol{w}^{(\mathfrak{s}_i)}$, may not coincide with the velocities of fluid particles that lie on $\mathfrak{S}^{(i)}$ at some instant of time. Such a situation prevails, e.g., when the mass transfer occurs across the interface. This is an important difference of the present investigation from all existing theories, in which the last two terms in (27.27) vanish.

An evolving surface $\mathfrak{S}(t)$ oriented by the unit normal field $\boldsymbol{n}^{(\mathfrak{s})}$ may be parametrized locally by a mapping

$$\boldsymbol{x}^{(\mathfrak{s})} = \hat{\boldsymbol{x}}^{(\mathfrak{s})}(\boldsymbol{\xi}, t), \quad \text{or} \quad x_i^{(\mathfrak{s})} = \hat{x}_i^{(\mathfrak{s})}(\xi_\alpha^{(\mathfrak{s})}, t), \quad i \in \{1, 2, 3\}, \ \alpha \in \{1, 2\}, \tag{27.28}$$

where $\boldsymbol{\xi}^{(\mathfrak{s})} = \{\xi_1^{(\mathfrak{s})}, \xi_2^{(\mathfrak{s})}\}$ establishes a two-dimensional parameter space. It is assumed that the mapping is sufficiently smooth. The tangent vectors of the surface can be computed by $\partial x_i^{(\mathfrak{s})}/\partial\xi_\alpha^{(\mathfrak{s})} \equiv x_{i,\alpha}^{(\mathfrak{s})}$. The partial time derivative

$$\boldsymbol{w}^{(\mathfrak{s})}(\boldsymbol{x}, t) = \left.\frac{\partial\hat{\boldsymbol{x}}^{(\mathfrak{s})}}{\partial t}\right|_{(\xi_1^{(\mathfrak{s})}, \xi_2^{(\mathfrak{s})})} \tag{27.29}$$

represents a local velocity field of the surface $\mathfrak{S}(t)$. Obviously, this velocity field depends on the choice of parameterization. Specifically, the normal component of $\boldsymbol{w}^{(\mathfrak{s})}$, i.e., $(\boldsymbol{w}^{(\mathfrak{s})} \cdot \boldsymbol{n}^{(\mathfrak{s})})\boldsymbol{n}^{(\mathfrak{s})}$, is independent of the parameterization, but the tangential velocity $\boldsymbol{w}_t^{(\mathfrak{s})} = \boldsymbol{w}^{(\mathfrak{s})} - (\boldsymbol{w}^{(\mathfrak{s})} \cdot \boldsymbol{n}^{(\mathfrak{s})})\boldsymbol{n}^{(\mathfrak{s})}$, is not. Hence, if a surface is nonmaterial, its tangential velocity defined by (27.29) is not intrinsic and not well defined, but dependent of the parameterization. The tangential velocity of the nonmaterial surface may be arbitrarily chosen by different parameterizations. Actually, the so-defined tangential component of the surface velocity is meaningless, because it represents neither the interface deformation, which depends only on the normal component of the surface velocity, nor the component of the material velocity. *It may be convenient to choose the tangential velocity of the material point, lying on the surface in an instant of time, as the tangential velocity of the surface.*

In comparison with the REYNOLDS transport theorem (27.27) for a bulk quantity, a difficulty in deriving the transport relation for the surface integrals occurring in (27.15) is associated with determining appropriate superficial analogues of the time derivatives. For a surface field $\gamma^{(\mathfrak{s})}$, if the surface is nonmaterial, then neither the material derivative $\mathrm{d}\gamma^{(\mathfrak{s})}/\mathrm{d}t$ nor the partial derivative $\partial\gamma^{(\mathfrak{s})}/\partial t$ is well defined. Since material points flow across the interface, it is not generally possible to compute a time derivative holding material points fixed. Further, the conventional partial derivative $\partial\gamma^{(\mathfrak{s})}/\partial t$ without further explanation is also meaningless, because there is no assurance that the position $\boldsymbol{x}$ lies on the surface $\mathfrak{S}(t + \Delta t)$ at time $t + \Delta t$ when $\boldsymbol{x}$ lies on $\mathfrak{S}(t)$ at time t, even for sufficiently small Δt.

The simplest time derivative of a surface scalar field $\gamma^{(\mathfrak{s})}$ following the evolution of the surface $\mathfrak{S}(t)$ can be defined by using the parameterization $\boldsymbol{x}^{(\mathfrak{s})} = \hat{\boldsymbol{x}}^{(\mathfrak{s})}\left(\xi_1^{(\mathfrak{s})}, \xi_2^{(\mathfrak{s})}, t\right)$ as follows:

$$\frac{\mathrm{d}^{(\mathfrak{s})}\gamma^{(\mathfrak{s})}}{\mathrm{d}t} = \left.\frac{\mathrm{d}\gamma^{(\mathfrak{s})}\left(\hat{\boldsymbol{x}}^{(\mathfrak{s})}\left(\xi_1^{(\mathfrak{s})}, \xi_2^{(\mathfrak{s})}, t\right), t\right)}{\mathrm{d}t}\right|_{(\xi_1^{(\mathfrak{s})}, \xi_2^{(\mathfrak{s})})}, \tag{27.30}$$

which depends on the choice of parameterization $(\xi_1^{(\mathfrak{s})}, \xi_2^{(\mathfrak{s})})$. A time derivative that is independent of the choice of parameterization is the normal time derivative $\delta^{(\mathfrak{s})}\gamma^{(\mathfrak{s})}/\delta t$ of $\gamma^{(\mathfrak{s})}$ following $\mathfrak{S}(t)$ [50], denoting the time derivative for a given point on the surface following the normal trajectory of the surface. It can be demonstrated that the normal time derivative is the conventional partial time derivative of $\gamma^{(\mathfrak{s})}$ when $\gamma^{(\mathfrak{s})}$ is extended to be constant along the normal lines of the surface. A simple relation between the two time derivatives is given in CERMELLI, Fried and GURTIN [8]

$$\frac{\mathrm{d}^{(\mathfrak{s})}\gamma^{(\mathfrak{s})}}{\mathrm{d}t} = \frac{\delta^{(\mathfrak{s})}\gamma^{(\mathfrak{s})}}{\delta t} + \boldsymbol{w}_t^{(\mathfrak{s})} \cdot \nabla^{(\mathfrak{s})}\gamma^{(\mathfrak{s})} = \frac{\delta^{(\mathfrak{s})}\gamma^{(\mathfrak{s})}}{\delta t} + \boldsymbol{w}^{(\mathfrak{s})} \cdot \nabla^{(\mathfrak{s})}\gamma^{(\mathfrak{s})}, \tag{27.31}$$

where $\boldsymbol{w}_t^{(\mathfrak{s})}$ is the velocity component of the surface, tangent to the surface.

The *surface gradient operator* $\nabla^{(\mathfrak{s})}$ appears in (27.31) because $\gamma^{(\mathfrak{s})}$ is defined only on the surface. For a bulk field that is well defined and smooth up to the surface from one or both sides, the surface gradient is simply the tangential component of the standard gradient, defined by

$$\nabla^{(\mathfrak{s})} = \left[\boldsymbol{I} - \boldsymbol{n}^{(\mathfrak{s})} \otimes \boldsymbol{n}^{(\mathfrak{s})}\right] \cdot \nabla \equiv \boldsymbol{I}^{(\mathfrak{s})} \cdot \nabla, \tag{27.32}$$

where $\boldsymbol{I}^{(\mathfrak{s})} \equiv \boldsymbol{I} - \boldsymbol{n}^{(\mathfrak{s})} \otimes \boldsymbol{n}^{(\mathfrak{s})}$ is the surface projection tensor, e.g., for a bulk field $\varPhi$,

$$\nabla^{(\mathfrak{s})}\varPhi = \nabla\varPhi - \left(\boldsymbol{n}^{(\mathfrak{s})} \cdot \nabla\varPhi\right)\boldsymbol{n}^{(\mathfrak{s})}.$$

Further, it can be demonstrated that, if the surface is material, i.e., the velocity of the surface $\boldsymbol{w}^{(\mathfrak{s})}$ coincides with the material velocity $\boldsymbol{v}^{(\mathfrak{s})}$, the material time derivative of $\gamma^{(\mathfrak{s})}$ is given by

$$\dot{\gamma}^{(\mathfrak{s})} = \frac{\mathrm{d}\gamma^{(\mathfrak{s})}}{\mathrm{d}t} = \frac{\delta^{(\mathfrak{s})}\gamma^{(\mathfrak{s})}}{\delta t} + \boldsymbol{v}_t^{(\mathfrak{s})} \cdot \nabla^{(\mathfrak{s})}\gamma^{(\mathfrak{s})} = \frac{\partial\gamma^{(\mathfrak{s})}}{\partial t} + \boldsymbol{v}^{(\mathfrak{s})} \cdot \nabla^{(\mathfrak{s})}\gamma^{(\mathfrak{s})}, \tag{27.33}$$

where the tangential component of the material velocity on the surface $\mathfrak{S}(t)$ can be given by $\boldsymbol{v}_t^{(\mathfrak{s})} = \boldsymbol{I}^{(\mathfrak{s})} \cdot \boldsymbol{v}^{(\mathfrak{s})}$.

Theorem 27.5 (Transport Theorem for a surface integral) *The transport theorem for the surface integral of a surface variable* $\gamma^{(\mathfrak{s})}$ *over a material surface* $\mathfrak{S}$ *(the normal unit vector* $\boldsymbol{n}^{(\mathfrak{s})}$*), moving with the material velocity* $\boldsymbol{v}^{(\mathfrak{s})}$*, closed by the curve* $\mathfrak{C}$ *(with unit vector* $\boldsymbol{s}$*, normal to* $\mathfrak{C}$ *and tangent to* $\mathfrak{S}$*) reads*

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathfrak{S}} \gamma^{(\mathfrak{s})}\,\mathrm{d}a = {} & \int_{\mathfrak{S}} \left(\frac{\delta^{(\mathfrak{s})}\gamma^{(\mathfrak{s})}}{\delta t} + \gamma^{(\mathfrak{s})}\left(\boldsymbol{v}^{(\mathfrak{s})} \cdot \boldsymbol{n}^{(\mathfrak{s})}\right)H^{(\mathfrak{s})}\right)\mathrm{d}a \\ & + \int_{\mathfrak{C}} \gamma^{(\mathfrak{s})}\left(\boldsymbol{v}^{(\mathfrak{s})} \cdot \boldsymbol{s}\right)\mathrm{d}\ell,\end{aligned} \tag{27.34}$$

in which

$$H^{(\mathfrak{s})} = \nabla^{(\mathfrak{s})} \cdot \boldsymbol{n}^{(\mathfrak{s})} \tag{27.35}$$

is the total (i.e., twice the mean) surface curvature. ■

This transport theorem was established first by PETRYK and MROZ [37] and GURTIN et al. [21]. Here, we demonstrate a proof from the viewpoint of continuum mechanics without the prerequisite of inclusion of the relevant background knowledge.

Proof We first prove the relation for the time derivative of an infinitesimal material surface element da,

$$(\mathrm{d}a)^{\cdot} = \boldsymbol{n}^{(\mathfrak{s})} \cdot \left([(\operatorname{tr}\boldsymbol{L}^{(\mathfrak{s})})\,\boldsymbol{I} - (\boldsymbol{L}^{(\mathfrak{s})})^{\mathrm{T}}] \cdot \boldsymbol{n}^{(\mathfrak{s})}\right)\mathrm{d}a, \tag{27.36}$$

with $\boldsymbol{L}^{(\mathfrak{s})} = \operatorname{grad} \boldsymbol{v}^{(\mathfrak{s})}$, or with the index notation in the form

$$(\mathrm{d}a)^{\cdot} = \left(v_{i,j}^{(\mathfrak{s})}\delta_{ij} - v_{i,j}^{(\mathfrak{s})} n_i^{(\mathfrak{s})} n_j^{(\mathfrak{s})}\right) \mathrm{d}a = \left(\delta_{ij} - n_i^{(\mathfrak{s})} n_j^{(\mathfrak{s})}\right) v_{i,j}^{(\mathfrak{s})} \mathrm{d}a. \tag{27.37}$$

For this purpose, we assume that $\mathrm{d}\boldsymbol{x}_1$, $\mathrm{d}\boldsymbol{x}_2$ and $\mathrm{d}\boldsymbol{X}_1$, $\mathrm{d}\boldsymbol{X}_2$ are two material line elements on the material surface $\mathfrak{S}$, respectively, in the present and reference configuration. Hence, the two vectors

$$\mathrm{d}\boldsymbol{a} = \mathrm{d}\boldsymbol{x}_1 \times \mathrm{d}\boldsymbol{x}_2 \quad \text{and} \quad \mathrm{d}\boldsymbol{A} = \mathrm{d}\boldsymbol{X}_1 \times \mathrm{d}\boldsymbol{X}_2$$

form an (oriented) *material surface element* in the present and reference configuration, respectively. The mapping of material line elements obeys the relation, as given in (27.20),

$$\mathrm{d}\boldsymbol{x}_1 = \boldsymbol{F}\mathrm{d}\boldsymbol{X}_1 \quad \text{and} \quad \mathrm{d}\boldsymbol{x}_2 = \boldsymbol{F}\mathrm{d}\boldsymbol{X}_2.$$

Based on the identity

$$\boldsymbol{A}^T(\boldsymbol{A}\boldsymbol{a} \times \boldsymbol{A}\boldsymbol{b}) = (\det \boldsymbol{A})(\boldsymbol{a} \times \boldsymbol{b}),$$

which can be obtained by requiring (27.21) for any two fixed vectors $\boldsymbol{a}$, $\boldsymbol{b}$ and all $\boldsymbol{c} \in \mathbb{R}^3$, the following relation for the material surface element applies

$$\begin{aligned}\mathrm{d}\boldsymbol{a} &= \mathrm{d}\boldsymbol{x}_1 \times \mathrm{d}\boldsymbol{x}_2 = (\boldsymbol{F}\mathrm{d}\boldsymbol{X}_1) \times (\boldsymbol{F}\mathrm{d}\boldsymbol{X}_2) \\ &= (\det \boldsymbol{F})\boldsymbol{F}^{-T}(\mathrm{d}\boldsymbol{X}_1 \times \mathrm{d}\boldsymbol{X}_2) = (\det \boldsymbol{F})\boldsymbol{F}^{-T}\mathrm{d}\boldsymbol{A}.\end{aligned} \tag{27.38}$$

Employing relation (27.24), i.e., $(\det \boldsymbol{F})^{\cdot} = \nabla \cdot \boldsymbol{v}^{(\mathfrak{s})}\,(\det \boldsymbol{F})$, and the identity

$$\left(\boldsymbol{F}^{-T}\right)^{\cdot} = -\boldsymbol{F}^{-T}\dot{\boldsymbol{F}}\boldsymbol{F}^{-T},$$

which results from the differentiation of $\boldsymbol{F}^{-T}\boldsymbol{F}^{T} = \boldsymbol{1}$, we calculate the time derivative of (27.38)

$$\begin{aligned}(\mathrm{d}\boldsymbol{a})^{\cdot} &= \left[(\det \boldsymbol{F})^{\cdot}\boldsymbol{F}^{-T} + (\det \boldsymbol{F})(\boldsymbol{F}^{-T})^{\cdot}\right]\mathrm{d}\boldsymbol{A} \\ &= \left[(\det \boldsymbol{F})(\nabla \cdot \boldsymbol{v}^{(\mathfrak{s})})\boldsymbol{F}^{-T} - (\det \boldsymbol{F})\boldsymbol{F}^{-T}\dot{\boldsymbol{F}}^{T}\boldsymbol{F}^{-T}\right]\mathrm{d}\boldsymbol{A} \\ &= \left[\nabla \cdot \boldsymbol{v}^{(\mathfrak{s})} - (\dot{\boldsymbol{F}}\boldsymbol{F}^{-1})^{T}\right](\det\ \boldsymbol{F})\boldsymbol{F}^{-T}\mathrm{d}\boldsymbol{A} \\ &= \left[(\operatorname{tr} \boldsymbol{L}^{(\mathfrak{s})})\,\boldsymbol{I} - (\boldsymbol{L}^{(\mathfrak{s})})^{\mathrm{T}}\right]\mathrm{d}\boldsymbol{a}.\end{aligned} \tag{27.39}$$

In the last step, relations (27.24) and (27.38) have been used. (27.39) is the vectorial form of (27.36). Its component in the direction $\boldsymbol{n}^{(\mathfrak{s})}$, perpendicularly to the surface element, yields the expression (27.36). Hence, relation (27.36) is proven. This proof can also be found in textbooks of Continuum Mechanics, e.g., [19, 23].

By means of the surface projection tensor, defined in (27.32), it further follows a really simple form,

$$(\mathrm{d}a)^{\cdot} = \boldsymbol{I}^{(\mathfrak{s})} \cdot \nabla \boldsymbol{v}^{(\mathfrak{s})}\, \mathrm{d}a = \nabla^{(\mathfrak{s})} \cdot \boldsymbol{v}^{(\mathfrak{s})}\, \mathrm{d}a. \tag{27.40}$$

This relation is fairly similar to the time derivative of a material volume element $(\mathrm{d}v)^{\cdot} = \nabla \cdot \boldsymbol{v}\, \mathrm{d}v$, see (27.17), which has been employed to prove Theorem 27.3. By means of relation (27.40), the time derivative of the surface integral can be written as

$$\begin{aligned}
&\frac{\mathrm{d}}{\mathrm{d}t} \int_{\mathfrak{s}} \gamma^{(\mathfrak{s})}\, \mathrm{d}a \\
&= \int_{\mathfrak{s}} \left(\frac{\mathrm{d}\gamma^{(\mathfrak{s})}}{\mathrm{d}t}\, \mathrm{d}a + \gamma^{(\mathfrak{s})}\, (\mathrm{d}a)^{\cdot} \right) \overset{(7.40)}{=} \int_{\mathfrak{s}} \left(\frac{\mathrm{d}\gamma^{(\mathfrak{s})}}{\mathrm{d}t} + \gamma^{(\mathfrak{s})} \nabla^{(\mathfrak{s})} \cdot \boldsymbol{v}^{(\mathfrak{s})} \right) \mathrm{d}a \\
&\overset{(7.33)}{=} \int_{\mathfrak{s}} \left(\frac{\delta^{(\mathfrak{s})}\gamma^{(\mathfrak{s})}}{\delta^{(\mathfrak{s})}t} + \boldsymbol{v}_t^{(\mathfrak{s})} \cdot \nabla^{(\mathfrak{s})}\gamma^{(\mathfrak{s})} + \gamma^{(\mathfrak{s})}\nabla^{(\mathfrak{s})} \cdot \left(\boldsymbol{v}_t^{(\mathfrak{s})} + \left(\boldsymbol{v}^{(\mathfrak{s})} \cdot \boldsymbol{n}^{(\mathfrak{s})} \right) \boldsymbol{n}^{(\mathfrak{s})} \right) \right) \mathrm{d}a \\
&= \int_{\mathfrak{s}} \left(\frac{\delta^{(\mathfrak{s})}\gamma^{(\mathfrak{s})}}{\delta^{(\mathfrak{s})}t} + \nabla^{(\mathfrak{s})} \cdot \left(\gamma^{(\mathfrak{s})} \boldsymbol{v}_t^{(\mathfrak{s})} \right) + \gamma^{(\mathfrak{s})} \left(\boldsymbol{v}^{(\mathfrak{s})} \cdot \boldsymbol{n}^{(\mathfrak{s})} \right) \nabla^{(\mathfrak{s})} \cdot \boldsymbol{n}^{(\mathfrak{s})} \right) \mathrm{d}a \\
&= \int_{\mathfrak{s}} \left(\frac{\delta^{(\mathfrak{s})}\gamma^{(\mathfrak{s})}}{\delta^{(\mathfrak{s})}t} + \gamma^{(\mathfrak{s})} \left(\boldsymbol{v}^{(\mathfrak{s})} \cdot \boldsymbol{n}^{(\mathfrak{s})} \right) H^{(\mathfrak{s})} + \nabla^{(\mathfrak{s})} \cdot \left(\gamma^{(\mathfrak{s})} \boldsymbol{v}_t^{(\mathfrak{s})} \right) \right) \mathrm{d}a \\
&= \int_{\mathfrak{s}} \left(\frac{\delta^{(\mathfrak{s})}\gamma^{(\mathfrak{s})}}{\delta^{(\mathfrak{s})}t} + \gamma^{(\mathfrak{s})} \left(\boldsymbol{v}^{(\mathfrak{s})} \cdot \boldsymbol{n}^{(\mathfrak{s})} \right) H^{(\mathfrak{s})} \right) \mathrm{d}a + \int_{\mathfrak{c}} \gamma^{(\mathfrak{s})} \left(\boldsymbol{v}^{(\mathfrak{s})} \cdot \boldsymbol{n}^{\mathfrak{c}} \right) \mathrm{d}\ell.
\end{aligned} \tag{27.41}$$

In the last step, the GREEN theorem has been employed. Hence, (27.34) is proved. ■

For a nonmaterial surface $\mathfrak{S}$ with the surface velocity $\boldsymbol{w}^{(\mathfrak{s})}$, the transport theorem of a surface integral can be extended to the form (without proof)

$$\begin{aligned}
\frac{\mathrm{d}}{\mathrm{d}t} \int_{\mathfrak{S}} \gamma^{(\mathfrak{s})}\, \mathrm{d}a = \int_{\mathfrak{S}} &\left(\frac{\delta^{(\mathfrak{s})}\gamma^{(\mathfrak{s})}}{\delta t} + \gamma^{(\mathfrak{s})} \left(\boldsymbol{w}^{(\mathfrak{s})} \cdot \boldsymbol{n}^{(\mathfrak{s})} \right) H^{(\mathfrak{s})} \right) \mathrm{d}a \\
&+ \int_{\mathfrak{C}} \gamma^{(\mathfrak{s})} \left(\boldsymbol{w}^{(\mathfrak{s})} \cdot \boldsymbol{s} \right) \mathrm{d}\ell,
\end{aligned} \tag{27.42}$$

similar to the extension of the REYNOLDS transport theorem (27.16) to the form (27.26).

By means of relation (27.42), the time derivative of the surface integration arising in (27.15) can be written as

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathfrak{S}^{(i)}}\gamma^{(\mathfrak{s}_i)}\,\mathrm{d}a &= \int_{\mathfrak{S}^{(i)}}\left(\frac{\delta^{(\mathfrak{s}_i)}\gamma^{(\mathfrak{s}_i)}}{\delta t}+\gamma^{(\mathfrak{s}_i)}H^{(\mathfrak{s}_i)}\left(\boldsymbol{w}^{(\mathfrak{s}_i)}\cdot\boldsymbol{n}^{(\mathfrak{s}_i)}\right)\right)\mathrm{d}a\\&\quad+\int_{\mathfrak{C}^{(i)}}\gamma^{(\mathfrak{s}_i)}\left(\boldsymbol{w}^{(\mathfrak{s}_i)}\cdot\boldsymbol{s}^{(i)}\right)\mathrm{d}\ell+\int_{\mathfrak{C}}\gamma^{(\mathfrak{s}_i)}\left(\boldsymbol{w}^{(\mathfrak{c})}\cdot\boldsymbol{s}^{(i)}\right)\mathrm{d}\ell\\&=\int_{\mathfrak{S}^{(i)}}\left(\frac{\delta^{(\mathfrak{s}_i)}\gamma^{(\mathfrak{s}_i)}}{\delta t}+\gamma^{(\mathfrak{s}_i)}H^{(\mathfrak{s}_i)}\left(\boldsymbol{w}^{(\mathfrak{s}_i)}\cdot\boldsymbol{n}^{(\mathfrak{s}_i)}\right)\right)\mathrm{d}a\\&\quad+\oint\limits_{\mathfrak{C}^{(i)}\cup\mathfrak{C}}\gamma^{(\mathfrak{s}_i)}\left(\boldsymbol{w}^{(\mathfrak{s}_i)}\cdot\boldsymbol{s}^{(i)}\right)\mathrm{d}\ell\\&\quad+\int_{\mathfrak{C}}\gamma^{(\mathfrak{s}_i)}\left(\left(\boldsymbol{w}^{(\mathfrak{c})}-\boldsymbol{w}^{(\mathfrak{s}_i)}\right)\cdot\boldsymbol{s}^{(i)}\right)\mathrm{d}\ell,\end{aligned}\tag{27.43}$$

where $\boldsymbol{w}^{(\mathfrak{c})}$ denotes the velocity of the three-phase contact line and where $\oint$ is the line integral along the closed loop $\mathfrak{C}^{(i)}\cup\mathfrak{C}$.

Now, it should be emphasized that the investigated volume $\mathfrak{B}(t)$ is a material subdomain of the body, whose surrounding surface $\partial\mathfrak{B}(t)$ is also a material surface. Hence, the velocity component of the outer surrounding curve $\mathfrak{C}^{(i)}$, tangent to the surface $\mathfrak{S}^{(i)}$, is coincided with the material velocity component of the material point lying on the surface at an instant of time. As we have also seen, the tangential component of the surface velocity according to definition (27.29) depends on the parameterization and hence is physically meaningless. Physically, it may be reasonable to employ the material velocity component tangent to the surface as the tangential surface velocity, $\boldsymbol{w}_t^{(\mathfrak{s}_i)}=(\boldsymbol{w}^{(\mathfrak{s}_i)}\cdot\boldsymbol{s}^{(i)})\boldsymbol{s}^{(i)}=(\boldsymbol{v}^{(\mathfrak{s}_i)}\cdot\boldsymbol{s}^{(i)})\boldsymbol{s}^{(i)}$, where $\boldsymbol{v}^{(\mathfrak{s}_i)}$ is the velocity of material points which lie on the surface $\mathfrak{S}^{(i)}(t)$ at time t. In this case, (27.43) can be rewritten as

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathfrak{S}^{(i)}}\gamma^{(\mathfrak{s}_i)}\,\mathrm{d}a &= \int_{\mathfrak{S}^{(i)}}\left(\frac{\delta^{(\mathfrak{s}_i)}\gamma^{(\mathfrak{s}_i)}}{\delta t}+\gamma^{(\mathfrak{s}_i)}H^{(\mathfrak{s}_i)}\left(\boldsymbol{w}^{(\mathfrak{s}_i)}\cdot\boldsymbol{n}^{(\mathfrak{s}_i)}\right)\right)\mathrm{d}a\\&\quad+\oint\limits_{\mathfrak{C}^{(i)}\cup\mathfrak{C}}\gamma^{(\mathfrak{s}_i)}\left(\boldsymbol{v}^{(\mathfrak{s}_i)}\cdot\boldsymbol{s}^{(i)}\right)\mathrm{d}\ell\\&\quad+\int_{\mathfrak{C}}\gamma^{(\mathfrak{s}_i)}\left(\left(\boldsymbol{w}^{(\mathfrak{c})}-\boldsymbol{v}^{(\mathfrak{s}_i)}\right)\cdot\boldsymbol{s}^{(i)}\right)\mathrm{d}\ell.\end{aligned}\tag{27.44}$$

If the contact line is material, the last term in (27.44) vanishes.

Further, the motion of the curve $\mathfrak{C}$ can be defined by a one-parameter configuration

$$\boldsymbol{x}^{(\mathfrak{c})}=\hat{\boldsymbol{x}}^{(\mathfrak{c})}\left(\xi^{(\mathfrak{c})},t\right),\quad\text{or}\quad x_i^{(\mathfrak{c})}=\hat{x}_i^{(\mathfrak{c})}(\xi^{(\mathfrak{c})},t).\tag{27.45}$$

The tangent vector of the curve $\mathfrak{C}$ is $\partial x_i^{(\mathfrak{c})}/\partial\xi^{(\mathfrak{c})}$. The local velocity field $\boldsymbol{w}^{(\mathfrak{c})}$ of the curve can be represented by the time rate of change of position $\boldsymbol{x}^{(\mathfrak{c})}$ for the fixed parameter $\xi^{(\mathfrak{c})}$,

$$\boldsymbol{w}^{(\mathrm{c})}(\boldsymbol{x},t) = \left.\frac{\partial \hat{\boldsymbol{x}}^{(\mathrm{c})}}{\partial t}\right|_{\xi^{(\mathrm{c})}}. \tag{27.46}$$

Only the component of $\boldsymbol{w}^{(\mathrm{c})}$ normal to $\mathfrak{C}$, i.e., $\boldsymbol{w}^{(\mathrm{c})} - (\boldsymbol{w}^{(\mathrm{c})} \cdot \boldsymbol{\lambda}^{(\mathrm{c})})\boldsymbol{\lambda}^{(\mathrm{c})}$, is independent of the parameterization of $\mathfrak{C}$ and, hence, intrinsic to the motion. Its tangential component along the curve, $(\boldsymbol{w}^{(\mathrm{c})} \cdot \boldsymbol{\lambda}^{(\mathrm{c})})\boldsymbol{\lambda}^{(\mathrm{c})}$, depends on the parameterization.

For a line field $\gamma^{(\mathrm{c})}$ following the evolution of the curve $\mathfrak{C}$, if the curve $\mathfrak{C}$ is non-material, its (local or material) time derivative is equally not well defined. One of its time derivatives can be defined by means of the parameterization $\boldsymbol{x}^{(\mathrm{c})} = \hat{\boldsymbol{x}}^{(\mathrm{c})}\left(\xi^{(\mathrm{c})}, t\right)$ as follows:

$$\frac{\mathrm{d}^{(\mathrm{c})}\gamma^{(\mathrm{c})}}{\mathrm{d}t} = \left.\frac{\mathrm{d}\gamma^{(\mathrm{c})}\left(\hat{\boldsymbol{x}}^{(\mathrm{c})}(\xi^{(\mathrm{c})},t),t\right)}{\mathrm{d}t}\right|_{\xi^{(\mathrm{c})}}, \tag{27.47}$$

which depends on the choice of parameterization. A time derivative that is independent of the choice of parameterization is the normal time derivative $\delta^{(\mathrm{c})}\gamma^{(\mathrm{c})}/\delta t$ of $\gamma^{(\mathrm{c})}$ following $\mathfrak{C}(t)$, equivalent to the time derivative following the normal trajectory of the moving curve. It can also be shown that this normal time derivative coincides with the conventional partial time derivative of $\gamma^{(\mathrm{c})}$ when $\gamma^{(\mathrm{c})}$ is extended as a constant in the directions perpendicular to the curve. Both time derivatives can be related by

$$\begin{aligned}\frac{\mathrm{d}^{(\mathrm{c})}\gamma^{(\mathrm{c})}}{\mathrm{d}t} &= \frac{\delta^{(\mathrm{c})}\gamma^{(\mathrm{c})}}{\delta t} + \boldsymbol{w}_t^{(\mathrm{c})} \cdot \nabla^{(\mathrm{c})}\gamma^{(\mathrm{c})} \\ &= \frac{\delta^{(\mathrm{c})}\gamma^{(\mathrm{c})}}{\delta t} + \boldsymbol{w}^{(\mathrm{c})} \cdot \nabla^{(\mathrm{c})}\gamma^{(\mathrm{c})},\end{aligned} \tag{27.48}$$

where $\boldsymbol{w}_t^{(\mathrm{c})}$ is the velocity component of the curve, tangential to the curve, and $\nabla^{(\mathrm{c})}$ is the *line gradient operator*, which is the component of the standard gradient tangent to the contact line, defined by

$$\nabla^{(\mathrm{c})} = (\boldsymbol{\lambda}^{(\mathrm{c})} \otimes \boldsymbol{\lambda}^{(\mathrm{c})}) \cdot \nabla \equiv \boldsymbol{I}^{(\mathrm{c})} \cdot \nabla, \tag{27.49}$$

where $\boldsymbol{I}^{(\mathrm{c})} = \boldsymbol{\lambda}^{(\mathrm{c})} \otimes \boldsymbol{\lambda}^{(\mathrm{c})}$ is the line projection tensor.

If the curve $\mathfrak{C}$ is material, the material time derivative of $\gamma^{(\mathrm{c})}$ and the normal time derivative $\delta^{(\mathrm{c})}\gamma^{(\mathrm{c})}/\delta t$ are related to one another by

$$\begin{aligned}\dot{\gamma}^{(\mathrm{c})} = \frac{\mathrm{d}\gamma^{(\mathrm{c})}}{\mathrm{d}t} &= \frac{\delta^{(\mathrm{c})}\gamma^{(\mathrm{c})}}{\delta t} + (\boldsymbol{v}^{(\mathrm{c})} \cdot \boldsymbol{\lambda}^{(\mathrm{c})})\frac{\partial \gamma^{(\mathrm{c})}}{\partial \ell} \\ &= \frac{\delta^{(\mathrm{c})}\gamma^{(\mathrm{c})}}{\delta t} + \boldsymbol{v}^{(\mathrm{c})} \cdot \nabla^{(\mathrm{c})}\gamma^{(\mathrm{c})}.\end{aligned} \tag{27.50}$$

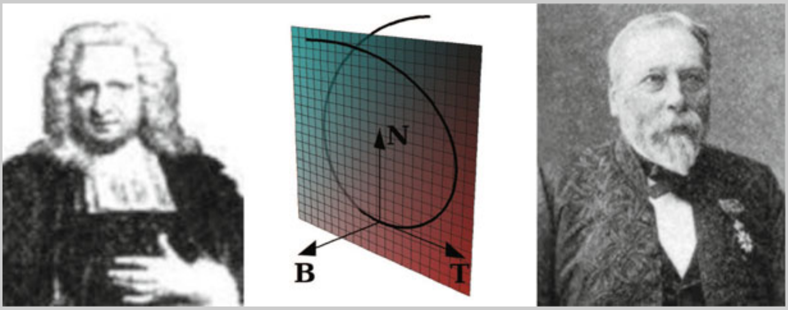

Fig. 27.4 JEAN FRÉDÉRIC FRENET (February 7, 1816–June 12, 1900) (right) and JOSEPH ALFRED SERRET (August 30, 1819–March 2, 1885) (left)

JEAN FRÉDÉRIC FRENET was a French mathematician, astronomer, and meteorologist. He was born and died in Périgueux, France.

He is best known for being an (independent) codiscoverer of the Frenet–Serret formulas. He wrote six out of the nine formulas, which at that time were not expressed in vector notation, nor using linear algebra. These formulas are important in the theory of space curves (differential geometry), and they were presented in his doctoral thesis at Toulouse in 1847. That year he became a Professor at Toulouse, and one year later, 1848, he became Professor of Mathematics at Lyon. He also was director of an astronomical observatory at Lyon. Four years later, in 1852, he published the FRENET formulas in the Journal de Mathématiques Pures et Appliquées. In 1856, his calculus primer was first published, which ran through seven editions, the last one published posthumously in 1917.

JOSEPH ALFRED SERRET was a French mathematician. He studied at the École Polytechnique in Paris, where he graduated in 1840. In 1848, he was occupied there as examiner of the admissions exams. In 1861, he became Professor of Celestial Mechanics at the Collège de France and in 1863 Professor of Analysis at the Sorbonne. In 1871, he went on retirement, but was in 1873 at the Bureau des Longitudes.

SERRET is still known today for his work on differential geometry, in particular the FRENET–SERRET formulas of curves in $\mathbb{R}^3$. He researched also in number theory, analysis, and mechanics. He was the editor of the works of JOSEPH LOUIS LAGRANGE.

The FRENET–SERRET formulas

$$\begin{pmatrix} \dfrac{\mathrm{d}\boldsymbol{T}}{\mathrm{d}\ell} \\ \dfrac{\mathrm{d}\boldsymbol{N}}{\mathrm{d}\ell} \\ \dfrac{\mathrm{d}\boldsymbol{B}}{\mathrm{d}\ell} \end{pmatrix} = \begin{pmatrix} 0 & \kappa & 0 \\ -\kappa & 0 & \tau \\ 0 & -\tau & 0 \end{pmatrix} \begin{pmatrix} \boldsymbol{T} \\ \boldsymbol{N} \\ \boldsymbol{B} \end{pmatrix}$$

were independently discovered by FRENET in his dissertation in 1847 and by SERRET in 1851. In the above formulas, $\boldsymbol{T}$, $\boldsymbol{N}$, $\boldsymbol{B}$, κ, τ are three unit vectors into the tangential, normal, and binormal directions of a curve; κ is the curvature and τ the torsion of the curve. The curvature measures the failure of a curve to be a straight line, while the torsion measures the failure of a curve to be planar.

The text is based on www.wikipedia.org

Note that along the contact line $\mathfrak{C}$, the tangent, principal normal, and binormal unit vectors, $\boldsymbol{\lambda}^{(c)}$, $\boldsymbol{n}^{(c)}$ and $\boldsymbol{b}^{(c)} = \boldsymbol{\lambda}^{(c)} \times \boldsymbol{n}^{(c)}$, define the basis vectors of a FRENET–SERRET[5] frame. The relations of its unit vectors are given by the FRENET–SERRET formulae

$$\begin{aligned} \frac{\mathrm{d}\boldsymbol{\lambda}^{(c)}}{\mathrm{d}\ell} &= \kappa^{(c)}\boldsymbol{n}^{(c)} \\ \frac{\mathrm{d}\boldsymbol{n}^{(c)}}{\mathrm{d}\ell} &= -\kappa^{(c)}\boldsymbol{\lambda}^{(c)} + \tau^{(c)}\boldsymbol{b}^{(c)}, \\ \frac{\mathrm{d}\boldsymbol{b}^{(c)}}{\mathrm{d}\ell} &= -\tau^{(c)}\boldsymbol{n}^{(c)}, \end{aligned} \tag{27.51}$$

where $\tau^{(c)}$ is the torsion of the curve $\mathfrak{C}$ and

$$\kappa^{(c)} = -\nabla^{(c)} \cdot \boldsymbol{n}^{(c)} \tag{27.52}$$

is referred to as the normal curvature at the point on the contact line with arc length ℓ. The FRENET–SERRET formulae, (27.51), are usually written as

$$\frac{\mathrm{d}}{\mathrm{d}\ell}\begin{pmatrix} \boldsymbol{\lambda} \\ \boldsymbol{n} \\ \boldsymbol{b} \end{pmatrix}^{(c)} = \begin{pmatrix} 0 & \kappa & 0 \\ -\kappa & 0 & \tau \\ 0 & -\tau & 0 \end{pmatrix}^{(c)} \begin{pmatrix} \boldsymbol{\lambda} \\ \boldsymbol{n} \\ \boldsymbol{b} \end{pmatrix}^{(c)}. \tag{27.53}$$

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[5] For brief biographical sketches of JEAN FRÉDÉRIC FRENET (1816–1900) and JOSEPH ALFRED SERRET (1819–1885), see **Fig. 27.4**.

Similarly to the transport theorem for the surface integral (27.42), the transport relation for the time derivative of the line integration emerging in (27.15) can also be derived.

Theorem 27.6 (Transport Theorem for a line integral) *Consider a line integral of a line variable $\gamma^{(c)}$ with respect to the arc length ℓ, $\mathfrak{I}^{(c)} = \int_{\mathfrak{C}} \gamma^{(c)}\, \mathrm{d}\ell$, taken along a smooth curve $\mathfrak{C}$ (the unit principal normal $\boldsymbol{n}^{(c)}$ and the tangential unit vector $\boldsymbol{\lambda}^{(c)}$) with two ends I and II, moving in space with a spatially and temporally varying velocity $\boldsymbol{w}^{(c)}$. Its time derivative can be expressed by*

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathfrak{C}} \gamma^{(c)}\, \mathrm{d}\ell = \int_{\mathfrak{C}} \left(\frac{\delta^{(c)}\gamma^{(c)}}{\delta t} + \gamma^{(c)} \left(\boldsymbol{w}^{(c)} \cdot \boldsymbol{n}^{(c)}\right) \left(\nabla^{(c)} \cdot \boldsymbol{n}^{(c)}\right)\right) \mathrm{d}\ell \\ + \left[\left(\gamma^{(c)}\boldsymbol{w}^{(c)} \cdot \boldsymbol{\lambda}^{(c)}\right)^{II} - \left(\gamma^{(c)}\boldsymbol{w}^{(c)} \cdot \boldsymbol{\lambda}^{(c)}\right)^{I} \right]. \qquad (27.54)\end{aligned}$$

■

This transport theorem was derived first by PETRYK and MROZ [37]. Here, we follow their derivation.

Proof As shown in (27.45), the curve $\mathfrak{C}$ can be parametrized by a scalar variable $\xi^{(c)}$ such that a point along the curve has the space coordinate $\hat{\boldsymbol{\eta}}^{(c)}$ at $t = 0$ and space coordinate at an instant t

$$\begin{aligned} \boldsymbol{x}^{(c)} &= \hat{\boldsymbol{x}}^{(c)}\left(\xi^{(c)}, t\right) = \hat{\boldsymbol{\eta}}^{(c)}(\xi^{(c)}) + \boldsymbol{\zeta}^{(c)}(\hat{\boldsymbol{\eta}}^{(c)}(\xi^{(c)}), t), \\ \text{or} \quad x_i^{(c)} &= \hat{x}_i^{(c)}(\xi^{(c)}, t) = \hat{\eta}_i^{(c)}(\xi^{(c)}) + \zeta_i^{(c)}(\hat{\eta}_j^{(c)}(\xi^{(c)}), t). \end{aligned}$$

The line integral $\mathfrak{I}^{(c)}$ can be equivalently written as an integral over the fixed interval $\xi^{(c)} \in [\xi_I^{(c)}, \xi_{II}^{(c)}]$,

$$\mathfrak{I}^{(c)} = \int_{\mathfrak{C}} \gamma^{(c)}(\boldsymbol{x}^{(c)}, t)\, \mathrm{d}\ell = \int_{\xi_I^{(c)}}^{\xi_{II}^{(c)}} \gamma^{(c)} \left(\hat{\boldsymbol{x}}^{(c)}(\xi^{(c)}, t), t\right) \mathsf{s}^{(c)}(\xi^{(c)}, t)\mathrm{d}\xi^{(c)}, \quad (27.55)$$

where $\xi_I^{(c)}$ and $\xi_{II}^{(c)}$ are the fixed values of $\xi^{(c)}$ at the ends, I and II, of the curve $\mathfrak{C}$, and

$$\mathsf{s}^{(c)} = \sqrt{\frac{\partial \hat{x}_i^{(c)}}{\partial \xi^{(c)}} \frac{\partial \hat{x}_i^{(c)}}{\partial \xi^{(c)}}} \neq 0, \qquad \mathrm{d}\ell = \mathsf{s}^{(c)}\mathrm{d}\xi^{(c)}.$$

The unit vector tangent to the curve $\mathfrak{C}$, $\boldsymbol{\lambda}^{(c)}$, can be written as

$$\boldsymbol{\lambda}^{(c)} = \frac{1}{\mathsf{s}^{(c)}} \frac{\partial \hat{\boldsymbol{x}}^{(c)}}{\partial \xi^{(c)}}, \quad \text{or} \quad \lambda_i^{(c)} = \frac{1}{\mathsf{s}^{(c)}} \frac{\partial x_i^{(c)}}{\partial \xi^{(c)}}.$$

It can easily be shown that

$$\frac{\mathrm{d}^{(\mathfrak{c})}\mathsf{s}^{(\mathfrak{c})}}{\mathrm{d}t} \equiv \left.\frac{\partial \mathsf{s}^{(\mathfrak{c})}(\xi^{(\mathfrak{c})}, t)}{\partial t}\right|_{\xi^{(\mathfrak{c})}=\text{const}} = \mathsf{s}^{(\mathfrak{c})} w_{i,j}^{(\mathfrak{c})} \lambda_i^{(\mathfrak{c})} \lambda_j^{(\mathfrak{c})}, \tag{27.56}$$

where $w_i^{(\mathfrak{c})} = \partial \hat{x}_i^{(\mathfrak{c})}/\partial t|_{\xi^{(\mathfrak{c})}}$ denotes the local velocity field of the curve, defined in (27.46). By differentiating the line integral (27.55) with respect to t, using (27.56) and returning to the arc length variable, we obtain

$$\begin{aligned}\frac{\mathrm{d}\mathfrak{I}^{(\mathfrak{c})}}{\mathrm{d}t} &= \int_{\mathfrak{C}} \left(\frac{\mathrm{d}^{(\mathfrak{c})}\gamma^{(\mathfrak{c})}}{\mathrm{d}t} + \gamma^{(\mathfrak{c})} w_{i,j}^{(\mathfrak{c})} \lambda_i^{(\mathfrak{c})} \lambda_j^{(\mathfrak{c})} \right) \mathrm{d}\ell \\ &= \int_{\mathfrak{C}} \left(\frac{\mathrm{d}^{(\mathfrak{c})}\gamma^{(\mathfrak{c})}}{\mathrm{d}t} + \gamma^{(\mathfrak{c})} (\boldsymbol{\lambda}^{(\mathfrak{c})} \cdot \nabla \boldsymbol{w}^{(\mathfrak{c})}) \cdot \boldsymbol{\lambda}^{(\mathfrak{c})} \right) \mathrm{d}\ell.\end{aligned} \tag{27.57}$$

By employing $(27.51)_1$, i.e.,

$$\frac{\mathrm{d}\boldsymbol{\lambda}^{(\mathfrak{c})}}{\mathrm{d}\ell} = \boldsymbol{\lambda}^{(\mathfrak{c})} \cdot \nabla^{(\mathfrak{c})} \boldsymbol{\lambda}^{(\mathfrak{c})} = \kappa^{(\mathfrak{c})} \boldsymbol{n}^{(\mathfrak{c})}, \tag{27.58}$$

the expression (27.57) can be rearranged as follows:

$$\begin{aligned}\frac{\mathrm{d}\mathfrak{I}^{(\mathfrak{c})}}{\mathrm{d}t} = \int_{\mathfrak{C}} \Bigg(&\frac{\mathrm{d}^{(\mathfrak{c})}\gamma^{(\mathfrak{c})}}{\mathrm{d}t} - \boldsymbol{w}^{(\mathfrak{c})} \cdot \nabla^{(\mathfrak{c})} \gamma^{(\mathfrak{c})} - \gamma^{(\mathfrak{c})} \kappa^{(\mathfrak{c})} \left(\boldsymbol{w}^{(\mathfrak{c})} \cdot \boldsymbol{n}^{(\mathfrak{c})} \right) \\ &+ \boldsymbol{\lambda}^{(\mathfrak{c})} \cdot \nabla^{(\mathfrak{c})} \left(\gamma^{(\mathfrak{c})} \boldsymbol{w}^{(\mathfrak{c})} \cdot \boldsymbol{\lambda}^{(\mathfrak{c})} \right) \Bigg) \mathrm{d}\ell.\end{aligned} \tag{27.59}$$

Here, the line gradient operator $\nabla^{(\mathfrak{c})}$, defined in (27.49), can also be expressed as

$$\nabla^{(\mathfrak{c})} = \frac{\partial}{\partial \boldsymbol{\ell}} = \boldsymbol{\lambda}^{(\mathfrak{c})} \frac{\partial}{\partial \ell}.$$

Using the relation of the total and normal time derivatives, $\mathrm{d}^{(\mathfrak{c})}\gamma^{(\mathfrak{c})}/\mathrm{d}t$ and $\delta^{(\mathfrak{c})}\gamma^{(\mathfrak{c})}/\delta t$, given in (27.48), and integrating the last term of the integrand in (27.59), we finally obtain

$$\begin{aligned}\frac{\mathrm{d}\mathfrak{I}^{(\mathfrak{c})}}{\mathrm{d}t} = &\int_{\mathfrak{C}} \left(\frac{\delta^{(\mathfrak{c})}\gamma^{(\mathfrak{c})}}{\delta t} + \gamma^{(\mathfrak{c})} \left(\nabla^{(\mathfrak{c})} \cdot \boldsymbol{n}^{(\mathfrak{c})} \right) \left(\boldsymbol{w}^{(\mathfrak{c})} \cdot \boldsymbol{n}^{(\mathfrak{c})} \right) \right) \mathrm{d}\ell \\ &+ \left(\gamma^{(\mathfrak{c})} \boldsymbol{w}^{(\mathfrak{c})} \cdot \boldsymbol{\lambda}^{(\mathfrak{c})} \right) \Big|_I^{II}.\end{aligned} \tag{27.60}$$

Hence, the transport theorem for a line integral, (27.54), is proved. ■

In order to be in consistent with the definition of the total surface curvature $H^{(\mathfrak{s})} = \nabla^{(\mathfrak{s})} \cdot \boldsymbol{n}^{(\mathfrak{s})}$ given in (27.35), from here on, we definite the line curvature by

$$\kappa^{(\mathfrak{c})} = \nabla^{(\mathfrak{c})} \cdot \boldsymbol{n}^{(\mathfrak{c})}, \tag{27.61}$$

which is different from the previous definition, (27.52), employed in the FRENET–SERRET formulae (27.51). Hence, the transport theorem for a line integral, (27.54), can be rewritten as

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathfrak{C}}\gamma^{(\mathrm{c})}\,\mathrm{d}\ell = \int_{\mathfrak{C}}\left(\frac{\delta^{(\mathrm{c})}\gamma^{(\mathrm{c})}}{\delta t}+\gamma^{(\mathrm{c})}\kappa^{(\mathrm{c})}\left(\boldsymbol{w}^{(\mathrm{c})}\cdot\boldsymbol{n}^{(\mathrm{c})}\right)\right)\mathrm{d}\ell \\ +\left[\left(\gamma^{(\mathrm{c})}\boldsymbol{w}^{(\mathrm{c})}\cdot\boldsymbol{\lambda}^{(\mathrm{c})}\right)^{II}-\left(\gamma^{(\mathrm{c})}\boldsymbol{w}^{(\mathrm{c})}\cdot\boldsymbol{\lambda}^{(\mathrm{c})}\right)^{I}\right].\end{aligned} \tag{27.62}$$

Considering that the investigated domain $\mathfrak{B}(t)$ is a material volume, the convective fluxes through its outer surface $\partial\mathfrak{B}$ in the present configuration are induced by the material velocity on the surface. This is also the case for the convective flux along the contact line through $\partial\mathfrak{B}$. Therefore, in the fluxes at the intersecting points I and II of $\mathfrak{C}$ and $\partial\mathfrak{B}$ arising in (27.62), the tangential line velocity $\boldsymbol{w}^{(\mathrm{c})}\cdot\boldsymbol{\lambda}^{(\mathrm{c})}$ should be replaced by its material counterpart $\boldsymbol{v}^{(\mathrm{c})}\cdot\boldsymbol{\lambda}^{(\mathrm{c})}$, where $\boldsymbol{v}^{(\mathrm{c})}$ is the material velocity at the line $\mathfrak{C}$, i.e.,

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathfrak{C}}\gamma^{(\mathrm{c})}\,\mathrm{d}\ell = \int_{\mathfrak{C}}\Bigg(\frac{\delta^{(\mathrm{c})}\gamma^{(\mathrm{c})}}{\delta t}+\gamma^{(\mathrm{c})}\kappa^{(\mathrm{c})}\left(\boldsymbol{w}^{(\mathrm{c})}\cdot\boldsymbol{n}^{(\mathrm{c})}\right) \\ +\nabla^{(\mathrm{c})}\cdot\left(\gamma^{(\mathrm{c})}\boldsymbol{v}_t^{(\mathrm{c})}\right)\Bigg)\mathrm{d}\ell.\end{aligned} \tag{27.63}$$

Here $\boldsymbol{v}_t^{(\mathrm{c})}$ is the projection of the velocity $\boldsymbol{v}^{(\mathrm{c})}$ in the direction $\boldsymbol{\lambda}^{(\mathrm{c})}$, and $\boldsymbol{v}_t^{(\mathrm{c})} = (\boldsymbol{v}^{(\mathrm{c})}\cdot\boldsymbol{\lambda}^{(\mathrm{c})})\boldsymbol{\lambda}^{(\mathrm{c})} = \boldsymbol{I}^{(\mathrm{c})}\cdot\boldsymbol{v}^{(\mathrm{c})}$.

Theorem 27.7 (Gauss Divergence Theorem) *If $\mathfrak{B}$ is a volume bounded by a surface $\partial\mathfrak{B}$ with outward unit normal $\boldsymbol{n}$ and $\boldsymbol{f}$ is a continuously differential vector field in $\mathfrak{B}$, then*

$$\int_{\partial\mathfrak{B}}\boldsymbol{f}\cdot\boldsymbol{n}\mathrm{d}a = \int_{\mathfrak{B}}\nabla\cdot\boldsymbol{f}\mathrm{d}v. \tag{27.64}$$

■

By means of the GAUSS divergence theorem, the surface integrations on the right-hand side of (27.15) can be transformed to volume integration, see Fig. 27.3,

$$\begin{aligned}&\int_{\partial\mathfrak{B}^{(i)}}\left(\boldsymbol{\phi}^{(i)}\cdot\boldsymbol{n}\right)\mathrm{d}a \\ &= \oint\limits_{\partial\mathfrak{B}^{(i)}\cup\mathfrak{S}^{(i)}\cup\mathfrak{S}^{(i+1)}}\left(\boldsymbol{\phi}^{(i)}\cdot\boldsymbol{n}\right)\mathrm{d}a+\int_{\mathfrak{S}^{(i)}}\boldsymbol{\phi}^{(i)}\cdot\boldsymbol{n}^{(\mathfrak{s}_i)}\,\mathrm{d}a \\ &\quad -\int_{\mathfrak{S}^{(i+1)}}\boldsymbol{\phi}^{(i)}\cdot\boldsymbol{n}^{(\mathfrak{s}_{i+1})}\,\mathrm{d}a \\ &= \int_{\mathfrak{B}^{(i)}}\nabla\cdot\boldsymbol{\phi}^{(i)}\,\mathrm{d}v+\int_{\mathfrak{S}^{(i)}}\boldsymbol{\phi}^{(i)}\cdot\boldsymbol{n}^{(\mathfrak{s}_i)}\,\mathrm{d}a\end{aligned}$$

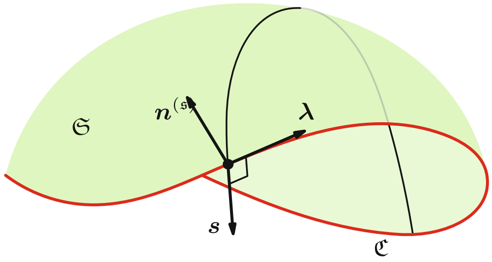

Fig. 27.5 An open surface $\mathfrak{S}$ spanned over a simple double-point free closed loop $\mathfrak{C}$. Note: $\boldsymbol{s} = \boldsymbol{\lambda} \times \boldsymbol{n}^{(\mathfrak{s})}$

$$-\int_{\mathfrak{S}^{(i+1)}} \phi^{(i)} \cdot \boldsymbol{n}^{(\mathfrak{s}_{i+1})}\, \mathrm{d}a, \tag{27.65}$$

and similarly for the red term in (27.27)

$$\oint_{\partial\mathfrak{B}^{(i)} \cup \mathfrak{S}^{(i)} \cup \mathfrak{S}^{(i+1)}} \gamma^{(i)} \left(\boldsymbol{v}^{(i)} \cdot \boldsymbol{n}\right) \mathrm{d}a = \int_{\mathfrak{B}^{(i)}} \nabla \cdot \left(\gamma^{(i)} \boldsymbol{v}^{(i)}\right) \mathrm{d}v. \tag{27.66}$$

Moreover, in order to transform the contour integrals in (27.15) and (27.44) into surface integrals, we apply the classical KELVIN–STOKES theorem.

Theorem 27.8 (Kelvin–Stokes Theorem or simply Stokes Theorem) *This theorem relates the surface integral of the curl of an arbitrary vector field* $\boldsymbol{F}$ *over an open surface* $\mathfrak{S}$ *in Euclidean three-dimensional space to the line integral of the vector field over its simple closed boundary curve* $\mathfrak{C}$ *by*

$$\oint_{\mathfrak{C}} \boldsymbol{F} \cdot \mathrm{d}\boldsymbol{\ell} = \int_{\mathfrak{S}} \left(\nabla^{(\mathfrak{s})} \times \boldsymbol{F}\right) \cdot \boldsymbol{n}^{(\mathfrak{s})} \mathrm{d}a. \tag{27.67}$$

The line element vector $\mathrm{d}\boldsymbol{\ell}$ *is tangent to* $\mathfrak{C}$*, while* $\boldsymbol{n}^{(\mathfrak{s})}$ *is a unit vector normal to* $\mathfrak{S}$. ■

The length element vector $\mathrm{d}\boldsymbol{\ell}$ takes the form $\mathrm{d}\boldsymbol{\ell} = \boldsymbol{\lambda}\mathrm{d}\ell$ with the unit vector $\boldsymbol{\lambda}$ tangential to $\mathfrak{C}$ and traces $\mathfrak{C}$ counterclockwise when the surface normal $\boldsymbol{n}^{(\mathfrak{s})}$ points toward the viewer. $(\boldsymbol{\lambda}, \boldsymbol{n}^{(\mathfrak{s})}, \boldsymbol{s})$ forms a local right-handed coordinate system with $\boldsymbol{s} = \boldsymbol{\lambda} \times \boldsymbol{n}^{(\mathfrak{s})}$, as shown in **Fig. 27.5**.

Proof Let $\boldsymbol{x}^{(\mathfrak{s})} = \hat{\boldsymbol{x}}^{(\mathfrak{s})}(\boldsymbol{\xi}, t)$, or $x_i^{(\mathfrak{s})} = \hat{x}_i^{(\mathfrak{s})}(\xi_\alpha^{(\mathfrak{s})}, t)$, $i \in \{1, 2, 3\}$, $\alpha \in \{1, 2\}$, given in (27.29), be a smooth parametrization of the surface $\mathfrak{S}$ including its boundary $\mathfrak{C}$. First, the left-hand side of (27.67) can be converted into a line integral

$$\oint_{\mathfrak{C}} \boldsymbol{F} \cdot \mathrm{d}\boldsymbol{\ell} = \oint_{\mathfrak{C}} \left(\boldsymbol{F} \cdot \frac{\partial \hat{\boldsymbol{x}}^{(\mathfrak{s})}}{\partial \xi_1^{(\mathfrak{s})}} \mathrm{d}\xi_1^{(\mathfrak{s})} + \boldsymbol{F} \cdot \frac{\partial \hat{\boldsymbol{x}}^{(\mathfrak{s})}}{\partial \xi_2^{(\mathfrak{s})}} \mathrm{d}\xi_2^{(\mathfrak{s})} \right),$$

so that, if one defines

$$\boldsymbol{G} = (G_1, G_2) = \left(\boldsymbol{F} \cdot \frac{\partial \hat{\boldsymbol{x}}^{(\mathfrak{s})}}{\partial \xi_1^{(\mathfrak{s})}}, \boldsymbol{F} \cdot \frac{\partial \hat{\boldsymbol{x}}^{(\mathfrak{s})}}{\partial \xi_2^{(\mathfrak{s})}} \right),$$

then

$$\oint_{\mathfrak{C}} \boldsymbol{F} \cdot \mathrm{d}\boldsymbol{\ell} = \oint_{\mathfrak{C}} \boldsymbol{G} \cdot \mathrm{d}\boldsymbol{\xi}^{(\mathfrak{s})},$$

where $\boldsymbol{\xi}^{(\mathfrak{s})}$ is the position vector in the $(\xi_1^{(\mathfrak{s})}, \xi_2^{(\mathfrak{s})})$-plane.

We turn now to the right-hand expression in (27.67) and write it in terms of the parameterization $\xi_1^{(\mathfrak{s})}$ and $\xi_2^{(\mathfrak{s})}$

$$\begin{aligned}
\int_{\mathfrak{S}} \left(\nabla^{(\mathfrak{s})} \times \boldsymbol{F}\right) \cdot \boldsymbol{n}^{(\mathfrak{s})} \mathrm{d}a &= \int_{\mathfrak{S}} \left(\nabla^{(\mathfrak{s})} \times \boldsymbol{F}\right) \cdot \left(\frac{\partial \hat{\boldsymbol{x}}^{(\mathfrak{s})}}{\partial \xi_1^{(\mathfrak{s})}} \times \frac{\partial \hat{\boldsymbol{x}}^{(\mathfrak{s})}}{\partial \xi_2^{(\mathfrak{s})}} \right) \mathrm{d}\xi_1^{(\mathfrak{s})} \mathrm{d}\xi_2^{(\mathfrak{s})} \\
&= \int_{\mathfrak{S}} \left(\frac{\partial G_2}{\partial \xi_1^{(\mathfrak{s})}} - \frac{\partial G_1}{\partial \xi_2^{(\mathfrak{s})}} \right) \mathrm{d}\xi_1^{(\mathfrak{s})} \mathrm{d}\xi_2^{(\mathfrak{s})} \\
&= \oint_{\mathfrak{C}} \boldsymbol{G} \cdot \mathrm{d}\boldsymbol{\xi}^{(\mathfrak{s})}.
\end{aligned}$$

In the last step, GREEN's Theorem has been used. Hence, it is proved that both sides of (27.67) are equal. ■

To apply the KELVIN–STOKES theorem to the contour integrals in (27.15) and (27.44), we employ an extended form of the KELVIN–STOKES theorem.

Theorem 27.9 (Surface Divergence Theorem) *For any vector $\boldsymbol{G}^{(\mathfrak{s})}$ defined on the surface $\mathfrak{S}$ and its boundary $\mathfrak{C}$ (see Fig. 27.5), one has*

$$\int_{\mathfrak{C}} \boldsymbol{G}^{(\mathfrak{s})} \cdot \boldsymbol{s}\, \mathrm{d}\ell = \int_{\mathfrak{S}} \left(\nabla^{(\mathfrak{s})} \cdot \boldsymbol{G}^{(\mathfrak{s})} - H^{(\mathfrak{s})} \left(\boldsymbol{G}^{(\mathfrak{s})} \cdot \boldsymbol{n}^{(\mathfrak{s})} \right) \right) \mathrm{d}a, \tag{27.68}$$

where $H^{(\mathfrak{s})} = \nabla^{(\mathfrak{s})} \cdot \boldsymbol{n}^{(\mathfrak{s})}$ denotes the total surface curvature of the surface $\mathfrak{S}$. ■

Proof We employ the identities

$$\boldsymbol{a} \cdot (\boldsymbol{b} \times \boldsymbol{c}) = (\boldsymbol{a} \times \boldsymbol{b}) \cdot \boldsymbol{c}, \tag{27.69}$$

$$\nabla \times (\boldsymbol{a} \times \boldsymbol{b}) = \boldsymbol{a}(\nabla \cdot \boldsymbol{b}) - \boldsymbol{b}(\nabla \cdot \boldsymbol{a}) + (\boldsymbol{b} \cdot \nabla)\boldsymbol{a} - (\boldsymbol{a} \cdot \nabla)\boldsymbol{b} \tag{27.70}$$

for any differentiable vectors $\boldsymbol{a}$, $\boldsymbol{b}$, $\boldsymbol{c}$, and then obtain for any vector $\boldsymbol{G}^{(\mathfrak{s})}$ defined on the surface $\mathfrak{S}$ and its boundary $\mathfrak{C}$,

$$\oint_{\mathfrak{C}} \boldsymbol{G}^{(\mathfrak{s})} \cdot \boldsymbol{s}\, \mathrm{d}\ell = -\oint_{\mathfrak{C}} \boldsymbol{G}^{(\mathfrak{s})} \cdot \left(\boldsymbol{n}^{(\mathfrak{s})} \times \boldsymbol{\lambda} \right) \mathrm{d}\ell$$

$$
\begin{aligned}
&\overset{(27.69)_1}{=} -\oint\limits_{\mathfrak{C}} \left(\boldsymbol{G}^{(\mathfrak{s})} \times \boldsymbol{n}^{(\mathfrak{s})}\right) \cdot \boldsymbol{\lambda} \, \mathrm{d}\ell \\
&= \oint\limits_{\mathfrak{C}} \left(\boldsymbol{n}^{(\mathfrak{s})} \times \boldsymbol{G}^{(\mathfrak{s})}\right) \cdot \mathrm{d}\boldsymbol{\ell} \\
&\overset{(27.67)}{=} \int_{\mathfrak{S}} \left(\nabla^{(\mathfrak{s})} \times \left(\boldsymbol{n}^{(\mathfrak{s})} \times \boldsymbol{G}^{(\mathfrak{s})}\right)\right) \cdot \boldsymbol{n}^{(\mathfrak{s})} \mathrm{d}\boldsymbol{a} \\
&\overset{(27.70)}{=} \int_{\mathfrak{S}} \left[\boldsymbol{n}^{(\mathfrak{s})} \left(\nabla^{(\mathfrak{s})} \cdot \boldsymbol{G}^{(\mathfrak{s})}\right) - \boldsymbol{G}^{(\mathfrak{s})} \left(\nabla^{(\mathfrak{s})} \cdot \boldsymbol{n}^{(\mathfrak{s})}\right)\right. \\
&\left. + \boldsymbol{G}^{(\mathfrak{s})} \cdot \left(\nabla^{(\mathfrak{s})} \boldsymbol{n}^{(\mathfrak{s})}\right) - \boldsymbol{n}^{(\mathfrak{s})} \cdot \left(\nabla^{(\mathfrak{s})} \boldsymbol{G}^{(\mathfrak{s})}\right)\right] \cdot \boldsymbol{n}^{(\mathfrak{s})} \mathrm{d}\boldsymbol{a} \\
&\overset{*}{=} \int_{\mathfrak{S}} \left(\nabla^{(\mathfrak{s})} \cdot \boldsymbol{G}^{(\mathfrak{s})} - H^{(\mathfrak{s})} \left(\boldsymbol{G}^{(\mathfrak{s})} \cdot \boldsymbol{n}^{(\mathfrak{s})}\right)\right) \mathrm{d}a. \qquad (27.71)
\end{aligned}
$$

In the last step, ($\overset{*}{=}$) the identities

$$
\begin{aligned}
&\boldsymbol{n}^{(\mathfrak{s})} \cdot \nabla^{(\mathfrak{s})}(\cdots) = 0, \\
&\left(\nabla^{(\mathfrak{s})} \boldsymbol{n}^{(\mathfrak{s})}\right) \cdot \boldsymbol{n}^{(\mathfrak{s})} = \tfrac{1}{2} \nabla^{(\mathfrak{s})} \left(\boldsymbol{n}^{(\mathfrak{s})} \cdot \boldsymbol{n}^{(\mathfrak{s})}\right) = \tfrac{1}{2} \nabla^{(\mathfrak{s})}(1) = \boldsymbol{0}
\end{aligned}
$$

and $H^{(\mathfrak{s})} = \nabla^{(\mathfrak{s})} \cdot \boldsymbol{n}^{(\mathfrak{s})}$ have been used. ■

Using relation (27.68), we can rewrite the contour integrals in (27.15) and (27.44) in the forms

$$
\begin{aligned}
\int_{\mathfrak{C}^{(i)}} \boldsymbol{\phi}^{(\mathfrak{s}_i)} \cdot \boldsymbol{s}^{(i)} \, \mathrm{d}\ell &= \oint\limits_{\mathfrak{C}^{(i)} \cup \mathfrak{C}} \boldsymbol{\phi}^{(\mathfrak{s}_i)} \cdot \boldsymbol{s}^{(i)} \, \mathrm{d}\ell - \int_{\mathfrak{C}} \boldsymbol{\phi}^{(\mathfrak{s}_i)} \cdot \boldsymbol{s}^{(i)} \, \mathrm{d}\ell \\
&= \int_{\mathfrak{S}^{(i)}} \left(\nabla^{(\mathfrak{s}_i)} \cdot \boldsymbol{\phi}^{(\mathfrak{s}_i)} - H^{(\mathfrak{s}_i)} \left(\boldsymbol{\phi}^{(\mathfrak{s}_i)} \cdot \boldsymbol{n}^{(\mathfrak{s}_i)}\right)\right) \mathrm{d}a \\
&\quad - \int_{\mathfrak{C}} \boldsymbol{\phi}^{(\mathfrak{s}_i)} \cdot \boldsymbol{s}^{(i)} \, \mathrm{d}\ell, \qquad (27.72)
\end{aligned}
$$

$$
\begin{aligned}
\oint\limits_{\mathfrak{C}^{(i)} \cup \mathfrak{C}} \gamma^{(\mathfrak{s}_i)} \left(\boldsymbol{v}^{(\mathfrak{s}_i)} \cdot \boldsymbol{s}^{(i)}\right) \mathrm{d}\ell &= \int_{\mathfrak{S}^{(i)}} \Big(\nabla^{(\mathfrak{s}_i)} \cdot \left(\gamma^{(\mathfrak{s}_i)} \boldsymbol{v}^{(\mathfrak{s}_i)}\right) \\
&\quad - \gamma^{(\mathfrak{s}_i)} H^{(\mathfrak{s}_i)} \left(\boldsymbol{v}^{(\mathfrak{s}_i)} \cdot \boldsymbol{n}^{(\mathfrak{s}_i)}\right)\Big) \mathrm{d}a. \qquad (27.73)
\end{aligned}
$$

In lieu of (27.73), another form is often employed

$$
\begin{aligned}
\oint\limits_{\mathfrak{C}^{(i)}\cup\mathfrak{C}} \gamma^{(\mathfrak{s}_i)}\left(\boldsymbol{v}^{(\mathfrak{s}_i)}\cdot\boldsymbol{s}^{(i)}\right)\mathrm{d}\ell &= \oint\limits_{\mathfrak{C}^{(i)}\cup\mathfrak{C}} \gamma^{(\mathfrak{s}_i)}\left(\boldsymbol{v}_t^{(\mathfrak{s}_i)}\cdot\boldsymbol{s}^{(i)}\right)\mathrm{d}\ell \\
&= \int_{\mathfrak{S}^{(i)}} \nabla^{(\mathfrak{s}_i)}\cdot\left(\gamma^{(\mathfrak{s}_i)}\boldsymbol{v}_t^{(\mathfrak{s}_i)}\right)\mathrm{d}a,
\end{aligned}
\tag{27.74}
$$

where $\boldsymbol{v}_t^{(\mathfrak{s}_i)}$ is the projection of the vector $\boldsymbol{v}^{(\mathfrak{s}_i)}$ in the plane tangent to the interface with the relation $\boldsymbol{v}_t^{(\mathfrak{s}_i)} = [\boldsymbol{I} - \boldsymbol{n}^{(\mathfrak{s}_i)}\otimes\boldsymbol{n}^{(\mathfrak{s}_i)}]\cdot\boldsymbol{v}^{(\mathfrak{s}_i)}$.

Likewise, the flux through the two end points intersecting with $\partial\mathfrak{B}$ into $\mathfrak{B}$, arising in (27.15), can be written in the form of a line integral

$$
\begin{aligned}
&\left[\left(\boldsymbol{\phi}^{(\mathfrak{c})}\cdot\boldsymbol{\lambda}^{(\mathfrak{c})}\right)^{II} - \left(\boldsymbol{\phi}^{(\mathfrak{c})}\cdot\boldsymbol{\lambda}^{(\mathfrak{c})}\right)^{I}\right] \\
&= \int_{\mathfrak{C}}\left(\nabla^{(\mathfrak{c})}\cdot\boldsymbol{\phi}^{(\mathfrak{c})} - \kappa^{(\mathfrak{c})}\left(\boldsymbol{\phi}^{(\mathfrak{c})}\cdot\boldsymbol{n}^{(\mathfrak{c})}\right)\right)\mathrm{d}\ell.
\end{aligned}
\tag{27.75}
$$

With the above vector-analytic breakdown of volume integrals into other volume plus surface integrals and possibly line integrals, using the GREEN, STOKES and GAUSS laws, we are now in a position to deduce the local forms of the general balance equations. By means of the relations derived above, we can obtain the local forms of the general balance equations.

27.2.3 *Local Forms of the General Balance Statement*

Substituting relations (27.27), (27.44), (27.63), (27.65), (27.66), (27.72), (27.74), and (27.75) into the balance equation (27.15) yields

$$
\begin{aligned}
&\sum_{i=1}^{3}\int_{\mathfrak{B}^{(i)}}\left\{\frac{\partial\gamma^{(i)}}{\partial t} + \nabla\cdot\left(\gamma^{(i)}\boldsymbol{v}^{(i)}\right) + \nabla\cdot\boldsymbol{\phi}^{(i)} - \pi^{(i)} - \zeta^{(i)}\right\}\mathrm{d}v \\
&+\sum_{i=1}^{3}\int_{\mathfrak{S}^{(i)}}\left\{\frac{\delta^{(\mathfrak{s}_i)}\gamma^{(\mathfrak{s}_i)}}{\delta t} + \nabla^{(\mathfrak{s}_i)}\cdot\left(\gamma^{(\mathfrak{s}_i)}\boldsymbol{v}_t^{(\mathfrak{s}_i)}\right) + \gamma^{(\mathfrak{s}_i)}H^{(\mathfrak{s}_i)}\left(\boldsymbol{w}^{(\mathfrak{s}_i)}\cdot\boldsymbol{n}^{(\mathfrak{s}_i)}\right)\right. \\
&\qquad +\nabla^{(\mathfrak{s}_i)}\cdot\boldsymbol{\phi}^{(\mathfrak{s}_i)} - H^{(\mathfrak{s}_i)}\left(\boldsymbol{\phi}^{(\mathfrak{s}_i)}\cdot\boldsymbol{n}^{(\mathfrak{s}_i)}\right) - \left(\pi^{(\mathfrak{s}_i)} + \zeta^{(\mathfrak{s}_i)}\right) \\
&\qquad \left. - [\![\gamma\left(\boldsymbol{w}^{(\mathfrak{s})} - \boldsymbol{v}\right)\cdot\boldsymbol{n}^{(\mathfrak{s})} - \boldsymbol{\phi}\cdot\boldsymbol{n}^{(\mathfrak{s})}]\!]^{(i)}\right\}\mathrm{d}a \\
&+\int_{\mathfrak{C}}\left\{\frac{\delta^{(\mathfrak{c})}\gamma^{(\mathfrak{c})}}{\delta t} + \nabla^{(\mathfrak{c})}\cdot\left(\gamma^{(\mathfrak{c})}\boldsymbol{v}_t^{(\mathfrak{c})}\right) + \gamma^{(\mathfrak{c})}\kappa^{(\mathfrak{c})}\left(\boldsymbol{w}^{(\mathfrak{c})}\cdot\boldsymbol{n}^{(\mathfrak{c})}\right)\right. \\
&\qquad +\nabla^{(\mathfrak{c})}\cdot\boldsymbol{\phi}^{(\mathfrak{c})} - \kappa^{(\mathfrak{c})}\left(\boldsymbol{\phi}^{(\mathfrak{c})}\cdot\boldsymbol{n}^{(\mathfrak{c})}\right) - \left(\pi^{(\mathfrak{c})} + \zeta^{(\mathfrak{c})}\right) \\
&\qquad \left. +\sum_{i=1}^{3}\left(\gamma^{(\mathfrak{s}_i)}\left(\boldsymbol{w}^{(\mathfrak{c})} - \boldsymbol{v}^{(\mathfrak{s}_i)}\right)\cdot\boldsymbol{s}^{(i)} - \boldsymbol{\phi}^{(\mathfrak{s}_i)}\cdot\boldsymbol{s}^{(i)}\right)\right\}\mathrm{d}\ell = 0,
\end{aligned}
\tag{27.76}
$$

where $[\![\mathcal{G}]\!]^{(i)} = \mathcal{G}^{(i)} - \mathcal{G}^{(i-1)}$ denotes the jump of the quantity $\mathcal{G}$ over the interface $\mathfrak{S}^{(i)}$ (if $i - 1 = 0$, it is set $i - 1 = 3$).

In the above equation, the integration domains $\mathfrak{B}^{(i)}$ are arbitrary, as are consequently also $\mathfrak{S}^{(i)}$ and $\mathfrak{C}$; thus, the integrands of the volume integrals must vanish identically. This yields the so-called *local* balance equations for each phase $\mathfrak{B}^{(i)}$,

$$\boxed{\frac{\partial \gamma^{(i)}}{\partial t} + \nabla \cdot \left(\gamma^{(i)} \boldsymbol{v}^{(i)}\right) + \nabla \cdot \boldsymbol{\phi}^{(i)} - \pi^{(i)} - \zeta^{(i)} = 0,} \tag{27.77}$$

which hold true at all points of the body except on the singular surfaces $\mathfrak{S}^{(i)}$ and the contact line $\mathfrak{C}$.

Likewise, the surface integrals must vanish for an arbitrary area of the singular surface; as a result, the corresponding integrand must also vanish identically, i.e.,

$$\boxed{\begin{aligned} &\frac{\delta^{(\mathfrak{s}_i)} \gamma^{(\mathfrak{s}_i)}}{\delta t} + \nabla^{(\mathfrak{s}_i)} \cdot \left(\gamma^{(\mathfrak{s}_i)} \boldsymbol{v}_t^{(\mathfrak{s}_i)}\right) + \gamma^{(\mathfrak{s}_i)} H^{(\mathfrak{s}_i)} \left(\boldsymbol{w}^{(\mathfrak{s}_i)} \cdot \boldsymbol{n}^{(\mathfrak{s}_i)}\right) \\ &+ \nabla^{(\mathfrak{s}_i)} \cdot \boldsymbol{\phi}^{(\mathfrak{s}_i)} - H^{(\mathfrak{s}_i)} \left(\boldsymbol{\phi}^{(\mathfrak{s}_i)} \cdot \boldsymbol{n}^{(\mathfrak{s}_i)}\right) - \left(\pi^{(\mathfrak{s}_i)} + \zeta^{(\mathfrak{s}_i)}\right) \\ &- [\![\gamma \left(\boldsymbol{w}^{(\mathfrak{s})} - \boldsymbol{v}\right) \cdot \boldsymbol{n}^{(\mathfrak{s})} - \boldsymbol{\phi} \cdot \boldsymbol{n}^{(\mathfrak{s})}]\!]^{(i)} = 0, \end{aligned}} \tag{27.78}$$

which is valid on the interface $\mathfrak{S}^{(i)}$ ($i = 1, 2, 3$), except at the contact line $\mathfrak{C}$.

Substituting (27.77) and (27.78) into (27.76), the line integral in (27.76) must also vanish for an arbitrary length element of the contact line $\mathfrak{C}$, explicitly,

$$\boxed{\begin{aligned} &\frac{\delta^{(\mathfrak{c})} \gamma^{(\mathfrak{c})}}{\delta t} + \nabla^{(\mathfrak{c})} \cdot \left(\gamma^{(\mathfrak{c})} \boldsymbol{v}_t^{(\mathfrak{c})}\right) + \gamma^{(\mathfrak{c})} \kappa^{(\mathfrak{c})} \left(\boldsymbol{w}^{(\mathfrak{c})} \cdot \boldsymbol{n}^{(\mathfrak{c})}\right) \\ &+ \nabla^{(\mathfrak{c})} \cdot \boldsymbol{\phi}^{(\mathfrak{c})} - \kappa^{(\mathfrak{c})} \left(\boldsymbol{\phi}^{(\mathfrak{c})} \cdot \boldsymbol{n}^{(\mathfrak{c})}\right) - \left(\pi^{(\mathfrak{c})} + \zeta^{(\mathfrak{c})}\right) \\ &+ \sum_{i=1}^{3} \left(\gamma^{(\mathfrak{s}_i)} \left(\boldsymbol{w}^{(\mathfrak{c})} - \boldsymbol{v}^{(\mathfrak{s}_i)}\right) \cdot \boldsymbol{s}^{(i)} - \boldsymbol{\phi}^{(\mathfrak{s}_i)} \cdot \boldsymbol{s}^{(i)}\right) = 0, \end{aligned}} \tag{27.79}$$

which hold true at all points of the three-phase contact line $\mathfrak{C}$.

These general local balance equations will now be specified for mass, momentum, angular momentum, energy, and entropy.

It is worth noting that in the above derivation of the local balance laws for bulk, areal, and line subregions of a body, it would strictly also be possible to interpret the endpoints I and II (see Fig. 27.3) as limiting (dimensionless) material points for which balance laws could be formulated. To our knowledge, this has so far not been done and will not be done here either.

Table 27.1 Thermodynamic fields for balance equations

Quantity	Mass	Solute	Momentum	Angular momentum	Energy	Entropy
			Bulk field quantities in the phase subdomain $\mathfrak{B}^{(i)}$			
$\gamma^{(i)}$	$\rho^{(i)}$	$c^{(i)}$	$\rho^{(i)}\boldsymbol{v}^{(i)}$	$\boldsymbol{x} \times \rho^{(i)}\boldsymbol{v}^{(i)}$	$\rho^{(i)}\left(u^{(i)} + \frac{1}{2}\boldsymbol{v}^{(i)} \cdot \boldsymbol{v}^{(i)}\right)$	$\rho^{(i)}\eta^{(i)}$
$\boldsymbol{\phi}^{(i)}$	0	$\boldsymbol{j}^{(i)}$	$-\boldsymbol{T}^{(i)}$	$-\boldsymbol{x} \times \boldsymbol{T}^{(i)}$	$\boldsymbol{q}^{(i)} - {\boldsymbol{T}^{(i)}}^T\boldsymbol{v}^{(i)}$	$\boldsymbol{\phi}_\eta^{(i)}$
$\pi^{(i)}$	0	0	0	0	0	$\rho^{(i)}\pi_\eta^{(i)}$
$\zeta^{(i)}$	0	0	$\rho^{(i)}\boldsymbol{g}$	$\boldsymbol{x} \times \rho^{(i)}\boldsymbol{g}$	$\rho^{(i)}\left(\boldsymbol{v}^{(i)} \cdot \boldsymbol{g}\right) + \rho^{(i)}r^{(i)}$	$\rho^{(i)}\zeta_\eta^{(i)}$
			Surface field quantities on the phase interfaces $\mathfrak{S}^{(i)}$			
$\gamma^{(\mathfrak{s}_i)}$	$\rho^{(\mathfrak{s}_i)}$	$c^{(\mathfrak{s}_i)}$	$\rho^{(\mathfrak{s}_i)}\boldsymbol{v}^{(\mathfrak{s}_i)}$	$\boldsymbol{x}^{(\mathfrak{s}_i)} \times \rho^{(\mathfrak{s}_i)}\boldsymbol{v}^{(\mathfrak{s}_i)}$	$\rho^{(\mathfrak{s}_i)}\left(u^{(\mathfrak{s}_i)} + \frac{1}{2}\boldsymbol{v}^{(\mathfrak{s}_i)} \cdot \boldsymbol{v}^{(\mathfrak{s}_i)}\right)$	$\rho^{(\mathfrak{s}_i)}\eta^{(\mathfrak{s}_i)}$
$\boldsymbol{\phi}^{(\mathfrak{s}_i)}$	0	$\boldsymbol{j}^{(\mathfrak{s}_i)}$	$-\boldsymbol{T}^{(\mathfrak{s}_i)}$	$-\boldsymbol{x}^{(\mathfrak{s}_i)} \times \boldsymbol{T}^{(\mathfrak{s}_i)}$	$\boldsymbol{q}^{(\mathfrak{s}_i)} - {\boldsymbol{T}^{(\mathfrak{s}_i)}}^T\boldsymbol{v}^{(\mathfrak{s}_i)}$	$\boldsymbol{\phi}_\eta^{(\mathfrak{s}_i)}$
$\pi^{(\mathfrak{s}_i)}$	0	0	0	0	0	$\rho^{(\mathfrak{s}_i)}\pi_\eta^{(\mathfrak{s}_i)}$
$\zeta^{(\mathfrak{s}_i)}$	0	0	$\rho^{(\mathfrak{s}_i)}\boldsymbol{g}$	$\boldsymbol{x}^{(\mathfrak{s}_i)} \times \rho^{(\mathfrak{s}_i)}\boldsymbol{g}$	$\rho^{(\mathfrak{s}_i)}\left(\boldsymbol{v}^{(\mathfrak{s}_i)} \cdot \boldsymbol{g}\right) + \rho^{(\mathfrak{s}_i)}r^{(\mathfrak{s}_i)}$	$\rho^{(\mathfrak{s}_i)}\zeta_\eta^{(\mathfrak{s}_i)}$
			Line field quantities at the three-phase contact line $\mathfrak{C}$			
$\gamma^{(\mathfrak{c})}$	$\rho^{(\mathfrak{c})}$	$c^{(\mathfrak{c})}$	$\rho^{(\mathfrak{c})}\boldsymbol{v}^{(\mathfrak{c})}$	$\boldsymbol{x}^{(\mathfrak{c})} \times \rho^{(\mathfrak{c})}\boldsymbol{v}^{(\mathfrak{c})}$	$\rho^{(\mathfrak{c})}\left(u^{(\mathfrak{c})} + \frac{1}{2}\boldsymbol{v}^{(\mathfrak{c})} \cdot \boldsymbol{v}^{(\mathfrak{c})}\right)$	$\rho^{(\mathfrak{c})}\eta^{(\mathfrak{c})}$
$\boldsymbol{\phi}^{(\mathfrak{c})}$	0	$\boldsymbol{j}^{(\mathfrak{c})}$	$-\boldsymbol{T}^{(\mathfrak{c})}$	$-\boldsymbol{x}^{(\mathfrak{c})} \times \boldsymbol{T}^{(\mathfrak{c})}$	$\boldsymbol{q}^{(\mathfrak{c})} - {\boldsymbol{T}^{(\mathfrak{c})}}^T\boldsymbol{v}^{(\mathfrak{c})}$	$\boldsymbol{\phi}_\eta^{(\mathfrak{c})}$
$\pi^{(\mathfrak{c})}$	0	0	0	0	0	$\rho^{(\mathfrak{c})}\pi_\eta^{(\mathfrak{c})}$
$\zeta^{(\mathfrak{c})}$	0	0	$\rho^{(\mathfrak{c})}\boldsymbol{g}$	$\boldsymbol{x}^{(\mathfrak{c})} \times \rho^{(\mathfrak{c})}\boldsymbol{g}$	$\rho^{(\mathfrak{c})}\left(\boldsymbol{v}^{(\mathfrak{c})} \cdot \boldsymbol{g}\right) + \rho^{(\mathfrak{c})}r^{(\mathfrak{c})}$	$\rho^{(\mathfrak{c})}\zeta_\eta^{(\mathfrak{c})}$

27.3 Specified Balance Equations

The identifications of the variables in the general balance equations (27.77)–(27.79) are given in **Table 27.1** for the specified physical balance equations. Here, $\boldsymbol{T}^{(i)}$, $\boldsymbol{T}^{(\mathfrak{s}_i)}$, $\boldsymbol{T}^{(\mathfrak{c})}$ are the Cauchy, surface, and line stress tensors, respectively; $\boldsymbol{q}^{(i)}$, $\boldsymbol{q}^{(\mathfrak{s}_i)}$, $\boldsymbol{q}^{(\mathfrak{c})}$, denote the bulk, surface, and line heat flux vectors; $\boldsymbol{j}^{(i)}$, $\boldsymbol{j}^{(\mathfrak{s}_i)}$, $\boldsymbol{j}^{(\mathfrak{c})}$ the bulk, surface, and line solute flux vectors; moreover, $\boldsymbol{\phi}_\eta^{(i)}$, $\boldsymbol{\phi}_\eta^{(\mathfrak{s}_i)}$, $\boldsymbol{\phi}_\eta^{(\mathfrak{c})}$ are the bulk, surface, and line entropy flux vectors; $u^{(i)}$, $u^{(\mathfrak{s}_i)}$, $u^{(\mathfrak{c})}$ indicate the specific internal energy densities; $r^{(i)}$, $r^{(\mathfrak{s}_i)}$, $r^{(\mathfrak{c})}$ denote the specific heat supplies; $\pi_\eta^{(i)}$, $\pi_\eta^{(\mathfrak{s}_i)}$, $\pi_\eta^{(\mathfrak{c})}$ are the specific entropy productions; $\zeta_\eta^{(i)}$, $\zeta_\eta^{(\mathfrak{s}_i)}$, $\zeta_\eta^{(\mathfrak{c})}$ the specific entropy supplies; $\rho^{(i)}$, $\rho^{(\mathfrak{s}_i)}$, $\rho^{(\mathfrak{c})}$ the mass densities; $c^{(i)}$, $c^{(\mathfrak{s}_i)}$, $c^{(\mathfrak{c})}$ the concentrations of the solute; $\eta^{(i)}$, $\eta^{(\mathfrak{s}_i)}$, $\eta^{(\mathfrak{c})}$ the specific entropy densities. Moreover, $\boldsymbol{g}$ is the gravitational force per unit mass, and $\boldsymbol{v}^{(\mathfrak{s}_i)}$, $\boldsymbol{v}^{(\mathfrak{c})}$ are the material velocities of the fluid particles that lie on the surface $\mathfrak{S}^{(i)}$ and the line $\mathfrak{C}$ at the instant of time, respectively.

It should be pointed out that in Table 27.1 the expressions of the physical quantities are specified only for classical multiphase flows. For some special flow problems, additional terms may be necessary. It has been assumed that the material is a BOLTZMANN or nonpolar continuum. For example, for a polar continuum, intrinsic angular momentum (spin), couple stress tensor, and body couple will arise in the balance equation of angular momentum, while their corresponding workings will be included in the conservation equation of energy, as in Chap. 1, Table 21.1. For flows of electrically conducting fluids in the presence of an electromagnetic field, the electric and magnetic forces need also to be accounted for as additional body forces to the gravitational force. If material features of the fluids are homogeneous for each phase, the electric force appears usually only as a surface force on the interface. Furthermore, if chemical reactions are considered, production terms must be added to the mass balances.

Substituting these specified variables listed in Table 27.1 in the general balance equations derived above, the special balance equations for mass, solute, momentum, angular momentum, energy, and entropy can be furnished with little more labor.

27.3.1 Conservations of Mass

Substituting the corresponding variables of Table 27.1 for the mass balance in (27.77)–(27.79), respectively, the conservation laws of mass can be obtained:

in the phase subdomain $\mathfrak{B}^{(i)}$:

$$\frac{\partial \rho^{(i)}}{\partial t} + \nabla \cdot \left(\rho^{(i)} \boldsymbol{v}^{(i)}\right) = 0, \tag{27.80}$$

on the phase interface $\mathfrak{S}^{(i)}$:

$$\begin{aligned} &\frac{\delta^{(\mathfrak{s}_i)} \rho^{(\mathfrak{s}_i)}}{\delta t} + \nabla^{(\mathfrak{s}_i)} \cdot \left(\rho^{(\mathfrak{s}_i)} \boldsymbol{v}_t^{(\mathfrak{s}_i)}\right) + \rho^{(\mathfrak{s}_i)} H^{(\mathfrak{s}_i)} \left(\boldsymbol{w}^{(\mathfrak{s}_i)} \cdot \boldsymbol{n}^{(\mathfrak{s}_i)}\right) \\ &= \left[\!\left[\rho \left(\boldsymbol{w}^{(\mathfrak{s})} - \boldsymbol{v}\right) \cdot \boldsymbol{n}^{(\mathfrak{s})} \right]\!\right]^{(i)}, \end{aligned} \tag{27.81}$$

along the three-phase contact line $\mathfrak{C}$:

$$\begin{aligned} &\frac{\delta^{(\mathfrak{c})} \rho^{(\mathfrak{c})}}{\delta t} + \nabla^{(\mathfrak{c})} \cdot \left(\rho^{(\mathfrak{c})} \boldsymbol{v}_t^{(\mathfrak{c})}\right) + \rho^{(\mathfrak{c})} \kappa^{(\mathfrak{c})} \left(\boldsymbol{w}^{(\mathfrak{c})} \cdot \boldsymbol{n}^{(\mathfrak{c})}\right) \\ &= -\sum_{i=1}^{3} \left(\rho^{(\mathfrak{s}_i)} \left(\boldsymbol{w}^{(\mathfrak{c})} - \boldsymbol{v}^{(\mathfrak{s}_i)}\right) \cdot \boldsymbol{s}^{(i)}\right). \end{aligned} \tag{27.82}$$

The conservations of mass on the surface $\mathfrak{S}^{(i)}$, (27.81), and for the three-phase contact line $\mathfrak{C}$, (27.82), can also be written in the forms

on the phase interface $\mathfrak{S}^{(i)}$:

$$\begin{aligned} &\frac{\delta^{(\mathfrak{s}_i)} \rho^{(\mathfrak{s}_i)}}{\delta t} + \nabla^{(\mathfrak{s}_i)} \cdot \left(\rho^{(\mathfrak{s}_i)} \boldsymbol{v}^{(\mathfrak{s}_i)}\right) + \rho^{(\mathfrak{s}_i)} H^{(\mathfrak{s}_i)} \left(\left(\boldsymbol{w}^{(\mathfrak{s}_i)} - \boldsymbol{v}^{(\mathfrak{s}_i)}\right) \cdot \boldsymbol{n}^{(\mathfrak{s}_i)}\right) \\ &= \left[\!\left[\rho \left(\boldsymbol{w}^{(\mathfrak{s})} - \boldsymbol{v}\right) \cdot \boldsymbol{n}^{(\mathfrak{s})} \right]\!\right]^{(i)}; \end{aligned} \tag{27.83}$$

along the three-phase contact line $\mathfrak{C}$:

$$
\begin{aligned}
&\frac{\delta^{(\mathfrak{c})}\rho^{(\mathfrak{c})}}{\delta t} + \nabla^{(\mathfrak{c})}\cdot\left(\rho^{(\mathfrak{c})}\boldsymbol{v}^{(\mathfrak{c})}\right) + \rho^{(\mathfrak{c})}\kappa^{(\mathfrak{c})}\left(\left(\boldsymbol{w}^{(\mathfrak{c})}-\boldsymbol{v}^{(\mathfrak{c})}\right)\cdot\boldsymbol{n}^{(\mathfrak{c})}\right)\\
&= -\sum_{i=1}^{3}\left(\rho^{(\mathfrak{s}_i)}\left(\boldsymbol{w}^{(\mathfrak{c})}-\boldsymbol{v}^{(\mathfrak{s}_i)}\right)\cdot\boldsymbol{s}^{(i)}\right). \qquad (27.84)
\end{aligned}
$$

If we neglect the mass density on the phase interface, the mass balance equation on the phase interface $\mathfrak{S}^{(i)}$, (27.81), is simplified to the classical mass jump condition

$$
[\![\rho\left(\boldsymbol{w}^{(\mathfrak{s})}-\boldsymbol{v}\right)]\!]^{(i)}\cdot\boldsymbol{n}^{(\mathfrak{s}_i)} = 0, \qquad (27.85)
$$

i.e., the mass flux from one side onto the interface must be equal to the same mass flux into the other side.

If the line mass density along the contact line is neglected, the mass balance equation along the contact line $\mathfrak{C}$, (27.82), is reduced to

$$
\sum_{i=1}^{3}\left(\rho^{(\mathfrak{s}_i)}\left(\boldsymbol{w}^{(\mathfrak{c})}-\boldsymbol{v}^{(\mathfrak{s}_i)}\right)\cdot\boldsymbol{s}^{(i)}\right) = 0, \qquad (27.86)
$$

which indicates that the total mass transfer through the common line vanishes.

27.3.2 Solute Transport

In many applications, one is interested in the transport process of a solute whose concentration is small, and its influence on the flow field is negligible. Such a solute is considered as a passive constituent which is converted by the fluid flow and whose relative motion to the fluid flow is modeled by a diffusive flux. The mass balance equation of the solute can also be established by the general balance equations (27.77)–(27.79) by means of the following identifications listed in Table 27.1 for the solute investigated. Here, $c^{(i)}$ and $\boldsymbol{j}^{(i)}$ denote the bulk concentration and flux of the solute in the domain $\mathfrak{B}^{(i)}$, $c^{(\mathfrak{s}_i)}$ and $\boldsymbol{j}^{(\mathfrak{s}_i)}$ the surface concentration and flux of the solute on the interface $\mathfrak{S}^{(i)}$, as well as $c^{(\mathfrak{c})}$ and $\boldsymbol{j}^{(\mathfrak{c})}$ are the line concentration and flux of the solute along the three-phase contact line $\mathfrak{C}$.

Substituting the corresponding variables of Table 27.1 for the solute mass balance in (27.77)–(27.79), respectively, the conservation laws of mass can be obtained:

in the phase subdomain $\mathfrak{B}^{(i)}$:

$$
\frac{\partial c^{(i)}}{\partial t} + \nabla\cdot\left(c^{(i)}\boldsymbol{v}^{(i)}\right) = -\nabla\cdot\boldsymbol{j}^{(i)}, \qquad (27.87)
$$

on the phase interface $\mathfrak{S}^{(i)}$:

$$\begin{aligned} &\frac{\delta^{(\mathfrak{s}_i)} c^{(\mathfrak{s}_i)}}{\delta t} + \nabla^{(\mathfrak{s}_i)} \cdot \left(c^{(\mathfrak{s}_i)} \boldsymbol{v}_t^{(\mathfrak{s}_i)} \right) + c^{(\mathfrak{s}_i)} H^{(\mathfrak{s}_i)} \left(\boldsymbol{w}^{(\mathfrak{s}_i)} \cdot \boldsymbol{n}^{(\mathfrak{s}_i)} \right) \\ &+\nabla^{(\mathfrak{s}_i)} \cdot \boldsymbol{j}^{(\mathfrak{s}_i)} - H^{(\mathfrak{s}_i)} \left(\boldsymbol{j}^{(\mathfrak{s}_i)} \cdot \boldsymbol{n}^{(\mathfrak{s}_i)} \right) \\ = &\left[\!\left[c \left(\boldsymbol{w}^{(\mathfrak{s})} - \boldsymbol{v} \right) \cdot \boldsymbol{n}^{(\mathfrak{s})} - \boldsymbol{j} \cdot \boldsymbol{n}^{(\mathfrak{s})} \right]\!\right]^{(i)}, \end{aligned} \tag{27.88}$$

along the three-phase contact line $\mathfrak{C}$:

$$\begin{aligned} &\frac{\delta^{(\mathfrak{c})} c^{(\mathfrak{c})}}{\delta t} + \nabla^{(\mathfrak{c})} \cdot \left(c^{(\mathfrak{c})} \boldsymbol{v}_t^{(\mathfrak{c})} \right) + c^{(\mathfrak{c})} \kappa^{(\mathfrak{c})} \left(\boldsymbol{w}^{(\mathfrak{c})} \cdot \boldsymbol{n}^{(\mathfrak{c})} \right) \\ &+\nabla^{(\mathfrak{c})} \cdot \boldsymbol{j}^{(\mathfrak{c})} - \kappa^{(\mathfrak{c})} \left(\boldsymbol{j}^{(\mathfrak{c})} \cdot \boldsymbol{n}^{(\mathfrak{c})} \right) \\ = &-\sum_{i=1}^{3} \left(c^{(\mathfrak{s}_i)} \left(\boldsymbol{w}^{(\mathfrak{c})} - \boldsymbol{v}^{(\mathfrak{s}_i)} \right) \cdot \boldsymbol{s}^{(i)} - \boldsymbol{j}^{(\mathfrak{s}_i)} \cdot \boldsymbol{s}^{(i)} \right). \end{aligned} \tag{27.89}$$

In most cases, FICK's first law is employed to relate the diffusive fluxes to the concentration fields

$$\boldsymbol{j}^{(i)} = -D \nabla c^{(i)}, \quad \boldsymbol{j}^{(\mathfrak{s}_i)} = -D^{(\mathfrak{s})} \nabla^{(\mathfrak{s}_i)} c^{(\mathfrak{s}_i)}, \quad \boldsymbol{j}^{(\mathfrak{c})} = -D^l \nabla^{(\mathfrak{c})} c^{(\mathfrak{c})}, \tag{27.90}$$

where D, $D^{(\mathfrak{s})}$, and D^l denote the bulk, surface, and line diffusion coefficients or diffusivities, respectively. Relations (27.90) are reasonable if interactions between solute molecules are negligible. Furthermore, if there exist chemical reactions the solute may also be created as a result of chemical reactions, corresponding source terms need to be included in (27.87)–(27.89).

By assuming that the phase interface $(\mathfrak{s}_i)$ is material and adsorbs or desorbs solute from the adjacent phases $(i-1)$ and (i), and employing relations (27.90), the well-known conservation law of surfactant mass is obtained

$$\begin{aligned} &\frac{\mathrm{d}c^{(\mathfrak{s}_i)}}{\mathrm{d}t} + c^{(\mathfrak{s}_i)} \nabla^{(\mathfrak{s}_i)} \cdot \boldsymbol{v}_t^{(\mathfrak{s}_i)} + c^{(\mathfrak{s}_i)} H^{(\mathfrak{s}_i)} V^{(\mathfrak{s}_i)} \\ = &D^{(\mathfrak{s})} \Delta^{(\mathfrak{s}_i)} c^{(\mathfrak{s}_i)} + \left(D \Delta c^{(i)} \right)|_{(\mathfrak{s}_i)} - \left(D \Delta c^{(i-1)} \right)|_{(\mathfrak{s}_i)}, \end{aligned} \tag{27.91}$$

where $\mathrm{d}/\mathrm{d}t$ is the material time derivative, $V^{(\mathfrak{s}_i)} = \boldsymbol{w}^{(\mathfrak{s}_i)} \cdot \boldsymbol{n}^{(\mathfrak{s}_i)}$ is the normal (material) velocity of the interface $(\mathfrak{s}_i)$, and $(D\Delta c^{(i)})|_{(\mathfrak{s}_i)}$ denotes the diffusion flux in the phase (i) immediately adjacent to the interface $(\mathfrak{s}_i)$.

Further, the mass flux from the bulk (i) to the interface (s^i) is controlled, in general, by both diffusion and adsorption–desorption fluxes [12]

$$-\left(D \Delta c^{(i)} \right)|_{(\mathfrak{s}_i)} = k_{\mathrm{ad}} c_s^{(i)} \left(c_\infty^{(\mathfrak{s}_i)} - c^{(\mathfrak{s}_i)} \right) - k_{\mathrm{de}} c^{(\mathfrak{s}_i)}, \tag{27.92}$$

where k_{ad} and k_{de} are adsorption and desorption coefficients, respectively, $c_s^{(i)}$ is the bulk concentration of surfactant immediately adjacent to the interface, and $c_\infty^{(\mathfrak{s}_i)}$ is the upper bound to the surface concentration that can be accommodated in the interface.

27.3.3 Balance of Linear Momentum

Substituting the corresponding variables of Table 27.1 for the momentum balance in (27.77)–(27.79), respectively, the conservation laws of momentum can be obtained:

in the phase subdomain $\mathfrak{B}^{(i)}$:

$$\frac{\partial\left(\rho^{(i)}\boldsymbol{v}^{(i)}\right)}{\partial t}+\nabla\cdot\left(\rho^{(i)}\boldsymbol{v}^{(i)}\otimes\boldsymbol{v}^{(i)}\right)=\nabla\cdot\boldsymbol{T}^{(i)}+\rho^{(i)}\boldsymbol{g}, \tag{27.93}$$

on the phase interface $\mathfrak{S}^{(i)}$:

$$\begin{aligned}
&\frac{\delta^{(\mathfrak{s}_i)}\left(\rho^{(\mathfrak{s}_i)}\boldsymbol{v}^{(\mathfrak{s}_i)}\right)}{\delta t}+\nabla^{(\mathfrak{s}_i)}\cdot\left(\rho^{(\mathfrak{s}_i)}\boldsymbol{v}^{(\mathfrak{s}_i)}\otimes\boldsymbol{v}_t^{(\mathfrak{s}_i)}\right)\\
&+\rho^{(\mathfrak{s}_i)}\boldsymbol{v}^{(\mathfrak{s}_i)}H^{(\mathfrak{s}_i)}\left(\boldsymbol{w}^{(\mathfrak{s}_i)}\cdot\boldsymbol{n}^{(\mathfrak{s}_i)}\right)\\
=\;&\nabla^{(\mathfrak{s}_i)}\cdot\boldsymbol{T}^{(\mathfrak{s}_i)}-H^{(\mathfrak{s}_i)}\left(\boldsymbol{T}^{(\mathfrak{s}_i)}\cdot\boldsymbol{n}^{(\mathfrak{s}_i)}\right)+\rho^{(\mathfrak{s}_i)}\boldsymbol{g}\\
&+\left[\!\left[\rho\boldsymbol{v}\left(\boldsymbol{w}^{(\mathfrak{s})}-\boldsymbol{v}\right)\cdot\boldsymbol{n}^{(\mathfrak{s})}+\boldsymbol{T}\cdot\boldsymbol{n}^{(\mathfrak{s})}\right]\!\right]^{(i)},
\end{aligned} \tag{27.94}$$

along the three-phase contact line $\mathfrak{C}$:

$$\begin{aligned}
&\frac{\delta^{(\mathfrak{c})}\left(\rho^{(\mathfrak{c})}\boldsymbol{v}^{(\mathfrak{c})}\right)}{\delta t}+\nabla^{(\mathfrak{c})}\cdot\left(\rho^{(\mathfrak{c})}\boldsymbol{v}^{(\mathfrak{c})}\otimes\boldsymbol{v}_t^{(\mathfrak{c})}\right)+\rho^{(\mathfrak{c})}\boldsymbol{v}^{(\mathfrak{c})}\kappa^{(\mathfrak{c})}\left(\boldsymbol{w}^{(\mathfrak{c})}\cdot\boldsymbol{n}^{(\mathfrak{c})}\right)\\
=\;&\nabla^{(\mathfrak{c})}\cdot\boldsymbol{T}^{(\mathfrak{c})}-\kappa^{(\mathfrak{c})}\left(\boldsymbol{T}^{(\mathfrak{c})}\cdot\boldsymbol{n}^{(\mathfrak{c})}\right)+\rho^{(\mathfrak{c})}\boldsymbol{g}\\
&-\sum_{i=1}^{3}\left(\rho^{(\mathfrak{s}_i)}\boldsymbol{v}^{(\mathfrak{s}_i)}\left(\boldsymbol{w}^{(\mathfrak{c})}-\boldsymbol{v}^{(\mathfrak{s}_i)}\right)\cdot\boldsymbol{s}^{(i)}+\boldsymbol{T}^{(\mathfrak{s}_i)}\cdot\boldsymbol{s}^{(i)}\right).
\end{aligned} \tag{27.95}$$

Considering the conservation relations of mass, (27.80)–(27.82), we can rewrite the balance laws of momentum in the forms:

in the phase subdomain $\mathfrak{B}^{(i)}$:

$$\rho^{(i)}\frac{\partial\boldsymbol{v}^{(i)}}{\partial t}+\rho^{(i)}\boldsymbol{v}^{(i)}\cdot\nabla\boldsymbol{v}^{(i)}=\nabla\cdot\boldsymbol{T}^{(i)}+\rho^{(i)}\boldsymbol{g}, \tag{27.96}$$

on the phase interface $\mathfrak{S}^{(i)}$:

$$\begin{aligned}
&\rho^{(\mathfrak{s}_i)}\frac{\delta^{(\mathfrak{s}_i)}\boldsymbol{v}^{(\mathfrak{s}_i)}}{\delta t}+\rho^{(\mathfrak{s}_i)}\boldsymbol{v}^{(\mathfrak{s}_i)}\cdot\nabla^{(\mathfrak{s}_i)}\boldsymbol{v}^{(\mathfrak{s}_i)}\\
&=\nabla^{(\mathfrak{s}_i)}\cdot\boldsymbol{T}^{(\mathfrak{s}_i)}-H^{(\mathfrak{s}_i)}\left(\boldsymbol{T}^{(\mathfrak{s}_i)}\cdot\boldsymbol{n}^{(\mathfrak{s}_i)}\right)+\rho^{(\mathfrak{s}_i)}\boldsymbol{g}\\
&\quad+\left[\!\left[\rho\left(\boldsymbol{v}-\boldsymbol{v}^{(\mathfrak{s})}\right)\left(\boldsymbol{w}^{(\mathfrak{s})}-\boldsymbol{v}\right)\cdot\boldsymbol{n}^{(\mathfrak{s})}+\boldsymbol{T}\cdot\boldsymbol{n}^{(\mathfrak{s})}\right]\!\right]^{(i)},
\end{aligned}\tag{27.97}$$

along the three-phase contact line $\mathfrak{C}$:

$$\begin{aligned}
&\rho^{(\mathfrak{c})}\frac{\delta^{(\mathfrak{c})}\boldsymbol{v}^{(\mathfrak{c})}}{\delta t}+\rho^{(\mathfrak{c})}\boldsymbol{v}^{(\mathfrak{c})}\cdot\nabla^{(\mathfrak{c})}\boldsymbol{v}^{(\mathfrak{c})}\\
&=\nabla^{(\mathfrak{c})}\cdot\boldsymbol{T}^{(\mathfrak{c})}-\kappa^{(\mathfrak{c})}\left(\boldsymbol{T}^{(\mathfrak{c})}\cdot\boldsymbol{n}^{(\mathfrak{c})}\right)+\rho^{(\mathfrak{c})}\boldsymbol{g}\\
&\quad-\sum_{i=1}^{3}\left(\rho^{(\mathfrak{s}_i)}\left(\boldsymbol{v}^{(\mathfrak{s}_i)}-\boldsymbol{v}^{(\mathfrak{c})}\right)\left(\boldsymbol{w}^{(\mathfrak{c})}-\boldsymbol{v}^{(\mathfrak{s}_i)}\right)\cdot\boldsymbol{s}^{(i)}+\boldsymbol{T}^{(\mathfrak{s}_i)}\cdot\boldsymbol{s}^{(i)}\right).
\end{aligned}\tag{27.98}$$

Usually, the stress tensors can be decomposed into isotropic parts and dynamic parts in the forms

$$\boldsymbol{T}^{(i)}=-p^{(i)}\boldsymbol{I}+\left(\boldsymbol{T}^{(i)}\right)^{D},\tag{27.99}$$

$$\boldsymbol{T}^{(\mathfrak{s}_i)}=\sigma^{(\mathfrak{s}_i)}\boldsymbol{I}^{(\mathfrak{s}_i)}+\left(\boldsymbol{T}^{(\mathfrak{s}_i)}\right)^{D},\tag{27.100}$$

$$\boldsymbol{T}^{(\mathfrak{c})}=\tau^{(\mathfrak{c})}\boldsymbol{I}^{(\mathfrak{c})}+\left(\boldsymbol{T}^{(\mathfrak{c})}\right)^{D},\tag{27.101}$$

where $p^{(i)}$ denotes the hydrostatic pressure in phase $\mathfrak{B}^{(i)}$, $\sigma^{(\mathfrak{s}_i)}$ the surface tension on interface $\mathfrak{S}^{(i)}$, $\tau^{(\mathfrak{c})}$ is the line tension along the contact line, and $\boldsymbol{I}^{(\mathfrak{s}_i)}$ and $\boldsymbol{I}^{(\mathfrak{c})}$ are the surface and line projection tensor, defined in (27.32) and (27.49), respectively. Moreover, the superscript D indicates "dynamic" contributions.

If we employ the expressions of the stress tensors (27.99)–(27.101), the momentum balances (27.96)–(27.98) can be rewritten, respectively, as

in the phase subdomain $\mathfrak{B}^{(i)}$:

$$\rho^{(i)}\frac{\partial\boldsymbol{v}^{(i)}}{\partial t}+\rho^{(i)}\boldsymbol{v}^{(i)}\cdot\nabla\boldsymbol{v}^{(i)}=-\nabla p^{(i)}+\nabla\cdot\left(\boldsymbol{T}^{(i)}\right)^{D}+\rho^{(i)}\boldsymbol{g},\tag{27.102}$$

on the phase interface $\mathfrak{S}^{(i)}$:

$$\begin{aligned}
&\rho^{(\mathfrak{s}_i)}\frac{\delta^{(\mathfrak{s}_i)}\boldsymbol{v}^{(\mathfrak{s}_i)}}{\delta t}+\rho^{(\mathfrak{s}_i)}\boldsymbol{v}^{(\mathfrak{s}_i)}\cdot\nabla^{(\mathfrak{s}_i)}\boldsymbol{v}^{(\mathfrak{s}_i)}\\
&=\nabla^{(\mathfrak{s}_i)}\sigma^{(\mathfrak{s}_i)}-\sigma^{(\mathfrak{s}_i)}H^{(\mathfrak{s}_i)}\boldsymbol{n}^{(\mathfrak{s}_i)}+\nabla^{(\mathfrak{s}_i)}\cdot\left(\boldsymbol{T}^{(\mathfrak{s}_i)}\right)^{D}\\
&\quad-H^{(\mathfrak{s}_i)}\left(\left(\boldsymbol{T}^{(\mathfrak{s}_i)}\right)^{D}\cdot\boldsymbol{n}^{(\mathfrak{s}_i)}\right)+\rho^{(\mathfrak{s}_i)}\boldsymbol{g}\\
&\quad+\left[\!\left[\rho\left(\boldsymbol{v}-\boldsymbol{v}^{(\mathfrak{s})}\right)\left(\boldsymbol{w}^{(\mathfrak{s})}-\boldsymbol{v}\right)\cdot\boldsymbol{n}^{(\mathfrak{s})}-p\boldsymbol{n}^{(\mathfrak{s})}+(\boldsymbol{T})^{D}\cdot\boldsymbol{n}^{(\mathfrak{s})}\right]\!\right]^{(i)},
\end{aligned}\tag{27.103}$$

along the three-phase contact line $\mathfrak{C}$:

$$\begin{aligned}
&\rho^{(\mathfrak{c})}\frac{\delta^{(\mathfrak{c})}\boldsymbol{v}^{(\mathfrak{c})}}{\delta t}+\rho^{(\mathfrak{c})}\boldsymbol{v}^{(\mathfrak{c})}\cdot\nabla^{(\mathfrak{c})}\boldsymbol{v}^{(\mathfrak{c})}\\
&=\nabla^{(\mathfrak{c})}\tau^{(\mathfrak{c})}-\tau^{(\mathfrak{c})}\kappa^{(\mathfrak{c})}\boldsymbol{n}^{(\mathfrak{c})}+\nabla^{(\mathfrak{c})}\cdot\left(\boldsymbol{T}^{(\mathfrak{c})}\right)^{D}-\kappa^{(\mathfrak{c})}\left(\left(\boldsymbol{T}^{(\mathfrak{c})}\right)^{D}\cdot\boldsymbol{n}^{(\mathfrak{c})}\right)+\rho^{(\mathfrak{c})}\boldsymbol{g}\\
&\quad-\sum_{i=1}^{3}\Big(\rho^{(\mathfrak{s}_i)}\left(\boldsymbol{v}^{(\mathfrak{s}_i)}-\boldsymbol{v}^{(\mathfrak{c})}\right)\left(\boldsymbol{w}^{(\mathfrak{c})}-\boldsymbol{v}^{(\mathfrak{s}_i)}\right)\cdot\boldsymbol{s}^{(i)}+\sigma^{(\mathfrak{s}_i)}\boldsymbol{s}^{(i)}\\
&\qquad+\left(\boldsymbol{T}^{(\mathfrak{s}_i)}\right)^{D}\cdot\boldsymbol{s}^{(i)}\Big),
\end{aligned}\tag{27.104}$$

where on the basis of (27.49), the following relation has been used:

$$\nabla^{(\mathfrak{c})}\cdot\left(\tau^{(\mathfrak{c})}\boldsymbol{I}^{(\mathfrak{c})}\right)=\nabla^{(\mathfrak{c})}\tau^{(\mathfrak{c})}+\tau^{(\mathfrak{c})}\boldsymbol{\lambda}^{(\mathfrak{c})}\cdot\nabla^{(\mathfrak{c})}\boldsymbol{\lambda}^{(\mathfrak{c})}=\nabla^{(\mathfrak{c})}\tau^{(\mathfrak{c})}-\tau^{(\mathfrak{c})}\kappa^{(\mathfrak{c})}\boldsymbol{n}^{(\mathfrak{c})}.$$

Neglecting the surface mass density and the surface dynamic stress on the phase interface, the surface momentum balance equation on the interface $\mathfrak{S}^{(i)}$, (27.103), is reduced to the momentum jump condition

$$\begin{aligned}
&[\![\rho\left(\boldsymbol{v}-\boldsymbol{v}^{(\mathfrak{s})}\right)\left(\boldsymbol{w}^{(\mathfrak{s})}-\boldsymbol{v}\right)-p\boldsymbol{I}+(\boldsymbol{T})^{D}]\!]^{(i)}\cdot\boldsymbol{n}^{(\mathfrak{s}_i)}\\
&=-\nabla^{(\mathfrak{s}_i)}\sigma^{(\mathfrak{s}_i)}+\sigma^{(\mathfrak{s}_i)}H^{(\mathfrak{s}_i)}\boldsymbol{n}^{(\mathfrak{s}_i)}.
\end{aligned}\tag{27.105}$$

By means of the jump condition of mass, (27.85), the condition (27.105) can be further reduced to

$$\begin{aligned}
&[\![\rho\boldsymbol{v}\left(\boldsymbol{w}^{(\mathfrak{s})}-\boldsymbol{v}\right)-p\boldsymbol{I}+(\boldsymbol{T})^{D}]\!]^{(i)}\cdot\boldsymbol{n}^{(\mathfrak{s}_i)}\\
&=-\nabla^{(\mathfrak{s}_i)}\sigma^{(\mathfrak{s}_i)}+\sigma^{(\mathfrak{s}_i)}H^{(\mathfrak{s}_i)}\boldsymbol{n}^{(\mathfrak{s}_i)}.
\end{aligned}\tag{27.106}$$

Furthermore, for the static case, this jump condition is simplified to

$$[\![p]\!]^{(i)}=-\sigma^{(\mathfrak{s}_i)}H^{(\mathfrak{s}_i)},\qquad\sigma^{(\mathfrak{s}_i)}=\text{const.}\tag{27.107}$$

The above second condition in (27.107) indicates that a nonuniformly distributed surface tension will always induce motion (the Marangoni[6] effect).

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[6] For a brief biographical sketch of Carlo Giuseppe Matteo Marangoni (1840–1925), see **Fig. 27.6**.

Fig. 27.6 CARLO GIUSEPPE MATTEO MARANGONI (April 29, 1840–April 14, 1925)

CARLO GIUSEPPE MATTEO MARANGONI was an Italian physicist.

He graduated in 1865 from the University of Pavia under the supervision of Giovanni Cantoni with a dissertation entitled "Sull' espansione delle gocce liquide" ("On the spreading of liquid droplets"). He then moved to Florence where he first worked at the "Museo di Fisica" (1866) and later at the Liceo Dante (1870), where he held the position of High School Physics Teacher for 45 years until retirement in 1916. He primarily studied surface phenomena in liquids, and the Marangoni effect and the Marangoni number are named after him. He also contributed to meteorology and invented a Nefoscopio to observe clouds.

The text is based on www.wikipedia.org

Generally, the interfacial surface tension $\sigma^{(\mathfrak{s}_i)}$ is a function of the surface concentration of the solute (surfactant concentration), $c^{(\mathfrak{s}_i)}$ and surface temperature, according to an equation of state. That due to LANGMUIR[7] equation of state [28] has the form

$$\sigma^{(\mathfrak{s}_i)} = \sigma_0^{(\mathfrak{s}_i)} + \mathcal{R}\Theta^{(\mathfrak{s}_i)} c_\infty^{(\mathfrak{s}_i)} \ln\left(1 - \frac{c^{(\mathfrak{s}_i)}}{c_\infty^{(\mathfrak{s}_i)}}\right), \qquad (27.108)$$

where $\mathcal{R}$ is the ideal gas constant, $\Theta^{(\mathfrak{s}_i)}$ the absolute surface temperature, $\sigma_0^{(\mathfrak{s}_i)}$ the surface tension of a clean interface and $c_\infty^{(\mathfrak{s}_i)}$ is the maximum packing concentration. This relation provides a good model for low interfacial surfactant concentrations. Nonuniform surfactant concentration leads to nonuniform normal (capillary) and tangential (MARANGONI) stresses on the phase interfaces which can significantly affect the motion and deformation of interfaces of multiphase flows.

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[7] For a brief biographical sketch of IRVING LANGMUIR (1881–1957), see **Fig. 27.7**.

Fig. 27.7 IRVING LANGMUIR (January 31, 1881–August 16, 1957)

IRVING LANGMUIR, the son of wealthy parents, studied at the Chestnut Hill Academy in Philadelphia, the Pratt Institute in Brooklyn and at the School of Mines at the Columbia University in New York. A three-year study period in Europe thereafter brought him also to W. Nernst, who initiated his interest in physical chemistry at Göttingen. Under his supervision, he obtained in 1906 the doctorate. Between 1906 and 1909, he was a teacher for chemistry at the Stevens Institute of Technology in Hoboken. In 1909, he joined the Research Laboratory of the General Electric Company in Schenectady (N.Y.), where he assumed the CEO position in 1950. It is here where most of his fundamental scientific and industrially significant research results were established.

LANGMUIR researched in the fields of colloid chemistry, phase boundary chemistry, absorption and adsorption techniques, reaction kinetics, heterogeneous catalysis, etc., and contributed fundamentally to the development of physical chemistry of the twentieth century, as well as its technological application. This brought him honorary membership in many national and international scientific and industrial societies. In 1932, LANGMUIR was awarded the Nobel prize in chemistry as the first American chemist from industry; 13 universities also awarded him honorary doctorates.

LANGMUIR contributed fundamentally to the theory of valence, as well as the chemical adsorption of monocular layers. He contributed to reaction kinetics of catalytic processes and studied in particular reactions at interface surfaces of heterogeneous systems, of which (27.108) is a special example.

The text is based on

- *Fachlexikon: Forscher und Erfinder*, Nikol Verlagsgesellschaft mbH and Co.KG, Hamburg 2005, 3. Auflage ©1992 Verlag Arry Deutsch, Thun, Frankfurt am Main, Pages 346.
- *The collected works of Irving Langmuir*, 12 Volumes (Eds: C.G Suits and H.E. Way), New York, London (1960–1962)

If we neglect the line mass density and the dynamic line stress along the contact line, the momentum balance equation along the contact line $\mathfrak{C}$, (27.104), is reduced to

$$\begin{aligned}&\sum_{i=1}^{3}\Big(\rho^{(\mathfrak{s}_i)}\big(\boldsymbol{v}^{(\mathfrak{s}_i)}-\boldsymbol{v}^{(\mathfrak{c})}\big)\big(\boldsymbol{w}^{(\mathfrak{c})}-\boldsymbol{v}^{(\mathfrak{s}_i)}\big)\cdot\boldsymbol{s}^{(i)}+\sigma^{(\mathfrak{s}_i)}\boldsymbol{s}^{(i)}+\big(\boldsymbol{T}^{(\mathfrak{s}_i)}\big)^{D}\cdot\boldsymbol{s}^{(i)}\Big)\\&-\nabla^{(\mathfrak{c})}\tau^{(\mathfrak{c})}+\tau^{(\mathfrak{c})}\kappa^{(\mathfrak{c})}\boldsymbol{n}^{(\mathfrak{c})}=\boldsymbol{0},\end{aligned}\tag{27.109}$$

which is a balance between the momentum transfer, the contact line force, and the surface tensions of all three phases at every point of the three-phase contact line. By employing the relation of the mass balance along the contact line, (27.86), the momentum balance (27.109) can be reduced to

$$\begin{aligned}&\sum_{i=1}^{3}\Big(\rho^{(\mathfrak{s}_i)}\boldsymbol{v}^{(\mathfrak{s}_i)}\big(\boldsymbol{w}^{(\mathfrak{c})}-\boldsymbol{v}^{(\mathfrak{s}_i)}\big)\cdot\boldsymbol{s}^{(i)}+\sigma^{(\mathfrak{s}_i)}\boldsymbol{s}^{(i)}+\big(\boldsymbol{T}^{(\mathfrak{s}_i)}\big)^{D}\cdot\boldsymbol{s}^{(i)}\Big)\\&-\nabla^{(\mathfrak{c})}\tau^{(\mathfrak{c})}+\tau^{(\mathfrak{c})}\kappa^{(\mathfrak{c})}\boldsymbol{n}^{(\mathfrak{c})}=\boldsymbol{0},\end{aligned}\tag{27.110}$$

in which the material velocity of the contact line, $\boldsymbol{v}^{(\mathfrak{c})}$, does not occur as one may expect.

For static cases, this balance relation is further reduced to

$$\sigma^{(1)}\boldsymbol{s}^{(1)}+\sigma^{(2)}\boldsymbol{s}^{(2)}+\sigma^{(3)}\boldsymbol{s}^{(3)}+\tau^{(\mathfrak{c})}\kappa^{(\mathfrak{c})}\boldsymbol{n}^{(\mathfrak{c})}=\boldsymbol{0},\quad \tau^{(\mathfrak{c})}=\text{const.}\tag{27.111}$$

The above second relation indicates that a nonconstant line tension will always induce material motion near the contact line like the MARANGONI effect due to a nonuniform surface tension.

Neglecting the line tension along the contact line, this relation takes the simple form

$$\sigma^{(1)}\boldsymbol{s}^{(1)}+\sigma^{(2)}\boldsymbol{s}^{(2)}+\sigma^{(3)}\boldsymbol{s}^{(3)}=\boldsymbol{0},\tag{27.112}$$

which is the generalized YOUNG[8] equation.

Upon simplifications for a sessile drop on an ideal (rigid, homogeneous, horizontal, and smooth) surface, the horizontal component of the force balance $(27.111)_1$ at the contact line can be written as

$$\sigma^{lv}\cos\theta=\sigma^{sv}-\sigma^{sl}-\frac{\tau^{(\mathfrak{c})}}{R},\tag{27.113}$$

where R is the radius of the three-phase contact circle; σ^{lv}, σ^{sv}, and σ^{sl} are liquid–vapor, solid–vapor, and solid–liquid interfacial tensions; θ is the contact angle corresponding to a finite contact radius (R); and $\tau^{(\mathfrak{c})}$ is the line tension. This relation is often employed to determine line tension for solid–liquid–vapor systems by investigating the drop size dependence of the contact angle for sessile drops on a solid surface [2, 3, 10, 20, 40, 55].

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[8] For a brief biographical sketch of THOMAS YOUNG (1773–1829), see **Fig. 27.8**.

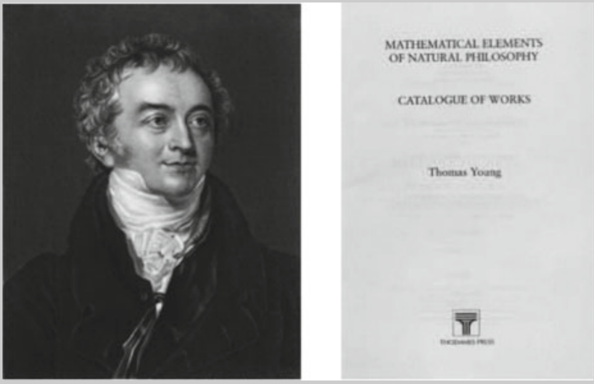

Fig. 27.8 Thomas Young (June 13, 1773–May 10, 1829)

Thomas Young was an English mathematician, physicist, and physician. He made notable contributions to the fields of vision, light, solid mechanics, energy, physiology, language, musical harmony, and Egyptology. At the age of 14, he had learned Greek and Latin and was acquainted with French, Italian, Hebrew, German, Aramaic, Syriac, Samaritan, Arabic, Persian, Turkish, and Amharic. He contributed significantly to the decipherment of Egyptian hieroglyphs (in particular the Rosetta Stone) and was highly recognized in physics by Herschel, Helmholtz, Maxwell, and Einstein. He has been described as “The last man who knew everything”.

Young began to study medicine in London in 1792, moved to the University of Edinburgh Medical School in 1794 and a year later to Göttingen, Germany, where he obtained the doctorate in medicine in 1796. In 1797, he entered Emmanuel College Cambridge and in 1799 established himself as a physician. In 1801, Young was appointed Professor of Natural Philosophy at the Royal Institution and in 1802 foreign secretary of the Royal Society, of which he had become a fellow in 1794. He resigned his professorship in 1803. His university lectures were published in 1807 as *Course of Lectures on Natural Philosophy*. In 1811, he became physician to the St. George’s Hospital and in 1818 secretary of the Board of Longitude. Young was elected a foreign Honorary Member of the American Academy of Arts and Sciences in 1822.

Young’s most important achievement was to establish the wave theory of light. To this end, he had to overcome the century-old view that light is a particle, expressed in the century-old view that light is a particle, expressed in Newton’s *Opticks*. Nevertheless, with his interference experiments in the context of water waves and his double slit experiment, he demonstrated interference in the context of light as a wave. His research on diffraction and Newton’s rings is summarized in *Course of Lectures on Natural Philosophy and the Mechanical Arts* (1807), in which he also gives Grimaldi credit for first observing the fringes in the shadow of a light beam.

YOUNG is credited (primarily in the Anglo-Saxon science literature) for the characterization of elasticity of a material body, known as YOUNG's modulus, denoted as E (1807). It must, however, be acknowledged that GIORDANO RICCATI in 1782 and LEONHARD EULER in (1727) had preceded this concept earlier. Special in this concept was that "(stress) $=E\times$ (strain)" expressed a pure material property that did not include the geometry of the specimen of which the "(Force) $=k$(displacement)" relation depends. In his own words, YOUNG introduced his modulus as follows: "*The modulus of elasticity of any substance is a column of the same substance, capable of producing a pressure on its base which is to the weight causing a certain degree of compression as the length of the substance is to the diminution of its length*". His commissioner – the British Admiralty – responded immediately: "*Though science is much respected by their Lordship and your paper is much esteemed, it is too learned ... in short, it is not understood*" (after [17]).

THOMAS YOUNG also developed the theory of capillary phenomena on the principle of surface tension (1804). One year later, PIERRE- SIMON LAPLACE discovered the significance of meniscus radii in capillary action. Their work was combined in 1830 by CARL FRIEDRICH GAUSS in the YOUNG–LAPLACE equation that describes the capillary pressure difference sustained across the interphase between two static fluids.
The text is based on www.wikipedia.org and [17]

27.3.4 Balance of Angular Momentum

As with the balance of linear momentum, the balance law of angular momentum is also one of the basic axioms of Galilean physics. In general, angular momentum is "moment of momentum plus self-angular momentum" (also called spin). The form chosen by us in Table 27.1 indicates that the spin is not taken into account there. These are also called nonpolar continua. Substituting the angular momentum density, the flux, the production, and the supply of angular momentum as listed in Table 27.1 in the general conservation equations (27.77)–(27.79), respectively, the balance laws of angular momentum can be written as follows:

in the phase subdomain $\mathfrak{B}^{(i)}$:

$$\begin{aligned}&\frac{\partial\left(\boldsymbol{x}\times\rho^{(i)}\boldsymbol{v}^{(i)}\right)}{\partial t}+\nabla\cdot\left(\boldsymbol{x}\times\rho^{(i)}\boldsymbol{v}^{(i)}\otimes\boldsymbol{v}^{(i)}\right)\\&=\nabla\cdot\left(\boldsymbol{x}\times\boldsymbol{T}^{(i)}\right)+\boldsymbol{x}\times\rho^{(i)}\boldsymbol{g},\end{aligned}\tag{27.114}$$

on the phase interface $\mathfrak{S}^{(i)}$:

$$\begin{aligned}
&\frac{\delta^{(\mathfrak{s}_i)}\left(\boldsymbol{x}^{(\mathfrak{s}_i)}\times\rho^{(\mathfrak{s}_i)}\boldsymbol{v}^{(\mathfrak{s}_i)}\right)}{\delta t}+\nabla^{(\mathfrak{s}_i)}\cdot\left(\boldsymbol{x}^{(\mathfrak{s}_i)}\times\rho^{(\mathfrak{s}_i)}\boldsymbol{v}^{(\mathfrak{s}_i)}\otimes\boldsymbol{v}_t^{(\mathfrak{s}_i)}\right)\\
&+\left(\boldsymbol{x}^{(\mathfrak{s}_i)}\times\rho^{(\mathfrak{s}_i)}\boldsymbol{v}^{(\mathfrak{s}_i)}\right)H^{(\mathfrak{s}_i)}\left(\boldsymbol{w}^{(\mathfrak{s}_i)}\cdot\boldsymbol{n}^{(\mathfrak{s}_i)}\right)\\
=\ &\nabla^{(\mathfrak{s}_i)}\cdot\left(\boldsymbol{x}^{(\mathfrak{s}_i)}\times\boldsymbol{T}^{(\mathfrak{s}_i)}\right)-H^{(\mathfrak{s}_i)}\left(\left(\boldsymbol{x}^{(\mathfrak{s}_i)}\times\boldsymbol{T}^{(\mathfrak{s}_i)}\right)\cdot\boldsymbol{n}^{(\mathfrak{s}_i)}\right)+\boldsymbol{x}^{(\mathfrak{s}_i)}\times\rho^{(\mathfrak{s}_i)}\boldsymbol{g}\\
&+[\![(\boldsymbol{x}\times\rho\boldsymbol{v})\left(\boldsymbol{w}^{(\mathfrak{s})}-\boldsymbol{v}\right)\cdot\boldsymbol{n}^{(\mathfrak{s})}+(\boldsymbol{x}\times\boldsymbol{T})\cdot\boldsymbol{n}^{(\mathfrak{s})}]\!]^{(i)}\,,
\end{aligned}\qquad(27.115)$$

along the three-phase contact line $\mathfrak{C}$:

$$\begin{aligned}
&\frac{\delta^{(\mathfrak{c})}\left(\boldsymbol{x}^{(\mathfrak{c})}\times\rho^{(\mathfrak{c})}\boldsymbol{v}^{(\mathfrak{c})}\right)}{\delta t}+\nabla^{(\mathfrak{c})}\cdot\left(\boldsymbol{x}^{(\mathfrak{c})}\times\rho^{(\mathfrak{c})}\boldsymbol{v}^{(\mathfrak{c})}\otimes\boldsymbol{v}_t^{(\mathfrak{c})}\right)\\
&+\left(\boldsymbol{x}^{(\mathfrak{c})}\times\rho^{(\mathfrak{c})}\boldsymbol{v}^{(\mathfrak{c})}\right)\kappa^{(\mathfrak{c})}\left(\boldsymbol{w}^{(\mathfrak{c})}\cdot\boldsymbol{n}^{(\mathfrak{c})}\right)\\
=\ &\nabla^{(\mathfrak{c})}\cdot\left(\boldsymbol{x}^{(\mathfrak{c})}\times\boldsymbol{T}^{(\mathfrak{c})}\right)-\kappa^{(\mathfrak{c})}\left(\left(\boldsymbol{x}^{(\mathfrak{c})}\times\boldsymbol{T}^{(\mathfrak{c})}\right)\cdot\boldsymbol{n}^{(\mathfrak{c})}\right)+\boldsymbol{x}^{(\mathfrak{c})}\times\rho^{(\mathfrak{c})}\boldsymbol{g}\\
&-\sum_{i=1}^{3}\left(\left(\boldsymbol{x}^{(\mathfrak{s}_i)}\times\rho^{(\mathfrak{s}_i)}\boldsymbol{v}^{(\mathfrak{s}_i)}\right)\left(\boldsymbol{w}^{(\mathfrak{c})}-\boldsymbol{v}^{(\mathfrak{s}_i)}\right)\cdot\boldsymbol{s}^{(i)}+\left(\boldsymbol{x}^{(\mathfrak{s}_i)}\times\boldsymbol{T}^{(\mathfrak{s}_i)}\right)\cdot\boldsymbol{s}^{(i)}\right).
\end{aligned}\qquad(27.116)$$

The balance of bulk angular momentum (27.114), together with the balance of bulk linear momentum (27.93), yields the well-known result, $\boldsymbol{T}^{(i)}=\left(\boldsymbol{T}^{(i)}\right)^T$, i.e., the CAUCHY stress tensor must be symmetric for nonpolar continua.

To evaluate the balance of surface angular momentum (27.115), after subtracting $\boldsymbol{x}^{(\mathfrak{s}_i)}\times$ (7.94), (27.115) is reduced to

$$\begin{aligned}
&\frac{\delta^{(\mathfrak{s}_i)}\boldsymbol{x}^{(\mathfrak{s}_i)}}{\delta t}\times\left(\rho^{(\mathfrak{s}_i)}\boldsymbol{v}^{(\mathfrak{s}_i)}\right)\\
&+\nabla^{(\mathfrak{s}_i)}\cdot\left(\boldsymbol{x}^{(\mathfrak{s}_i)}\times\rho^{(\mathfrak{s}_i)}\boldsymbol{v}^{(\mathfrak{s}_i)}\otimes\boldsymbol{v}_t^{(\mathfrak{s}_i)}\right)-\boldsymbol{x}^{(\mathfrak{s}_i)}\times\left(\nabla^{(\mathfrak{s}_i)}\cdot\left(\rho^{(\mathfrak{s}_i)}\boldsymbol{v}^{(\mathfrak{s}_i)}\otimes\boldsymbol{v}_t^{(\mathfrak{s}_i)}\right)\right)\\
&=\nabla^{(\mathfrak{s}_i)}\cdot\left(\boldsymbol{x}^{(\mathfrak{s}_i)}\times\boldsymbol{T}^{(\mathfrak{s}_i)}\right)-\boldsymbol{x}^{(\mathfrak{s}_i)}\times\left(\nabla^{(\mathfrak{s}_i)}\cdot\boldsymbol{T}^{(\mathfrak{s}_i)}\right).
\end{aligned}\qquad(27.117)$$

To further simplify (27.117), we employ the following identity:

$$\begin{aligned}
&\nabla^{(\mathfrak{s}_i)}\cdot\left(\boldsymbol{x}^{(\mathfrak{s}_i)}\times\boldsymbol{P}^{(\mathfrak{s}_i)}\right)\\
&=\boldsymbol{x}^{(\mathfrak{s}_i)}\times\left(\nabla^{(\mathfrak{s}_i)}\cdot\boldsymbol{P}^{(\mathfrak{s}_i)}\right)+\boldsymbol{\varepsilon}:\left(\boldsymbol{P}^{(\mathfrak{s}_i)}\cdot\frac{\partial\boldsymbol{x}^{(\mathfrak{s}_i)}}{\partial\boldsymbol{\xi}^{(\mathfrak{s}_i)}}\right),
\end{aligned}\qquad(27.118)$$

where $\boldsymbol{P}^{(\mathfrak{s}_i)}\in\mathbb{R}^{3\times2}$ is a second-rank tensor defined on the surface $\mathfrak{S}^{(i)}$, $\boldsymbol{x}^{(\mathfrak{s}_i)}=\boldsymbol{x}^{(\mathfrak{s}_i)}\left(\boldsymbol{\xi}^{(\mathfrak{s}_i)},t\right)$ is the surface parameterization $\boldsymbol{\xi}^{(\mathfrak{s}_i)}$ as indicated in (27.28) and $\boldsymbol{\varepsilon}=\{\varepsilon_{ijk}\}$ is third-rank epsilon tensor (or fully antisymmetric tensor). The component form of (27.118) is

$$\frac{\partial}{\partial \xi_\alpha^{(\mathfrak{s}_i)}}\left(\varepsilon_{ijk} x_j^{(\mathfrak{s}_i)} P_{k\alpha}^{(\mathfrak{s}_i)}\right) = \varepsilon_{ijk} x_j^{(\mathfrak{s}_i)} \frac{\partial P_{k\alpha}^{(\mathfrak{s}_i)}}{\partial \xi_\alpha^{(\mathfrak{s}_i)}} + \varepsilon_{ijk} P_{k\alpha}^{(\mathfrak{s}_i)} \frac{\partial x_j^{(\mathfrak{s}_i)}}{\partial \xi_\alpha^{(\mathfrak{s}_i)}}, \quad i \in \{1,2,3\},\ \alpha \in \{1,2\}. \tag{27.119}$$

By means of identify (27.118), (27.117) is reducible to

$$\begin{aligned}&\frac{\delta^{(\mathfrak{s}_i)} \boldsymbol{x}^{(\mathfrak{s}_i)}}{\delta t} \times \left(\rho^{(\mathfrak{s}_i)} \boldsymbol{v}^{(\mathfrak{s}_i)}\right) + \boldsymbol{\varepsilon} : \left(\left(\rho^{(\mathfrak{s}_i)} \boldsymbol{v}^{(\mathfrak{s}_i)} \otimes \boldsymbol{v}_t^{(\mathfrak{s}_i)}\right) \cdot \frac{\partial \boldsymbol{x}^{(\mathfrak{s}_i)}}{\partial \boldsymbol{\xi}^{(\mathfrak{s}_i)}}\right)\\ &- \boldsymbol{\varepsilon} : \left(\boldsymbol{T}^{(\mathfrak{s}_i)} \cdot \frac{\partial \boldsymbol{x}^{(\mathfrak{s}_i)}}{\partial \boldsymbol{\xi}^{(\mathfrak{s}_i)}}\right) = 0.\end{aligned} \tag{27.120}$$

By simplifying the second term on the left-hand side of (27.120) into

$$\begin{aligned}\boldsymbol{\varepsilon} : \left(\left(\rho^{(\mathfrak{s}_i)} \boldsymbol{v}^{(\mathfrak{s}_i)} \otimes \boldsymbol{v}_t^{(\mathfrak{s}_i)}\right) \cdot \frac{\partial \boldsymbol{x}^{(\mathfrak{s}_i)}}{\partial \boldsymbol{\xi}^{(\mathfrak{s}_i)}}\right) &= \boldsymbol{\varepsilon} : \left(\rho^{(\mathfrak{s}_i)} \boldsymbol{v}^{(\mathfrak{s}_i)} \otimes \boldsymbol{v}_t^{(\mathfrak{s}_i)}\right)\\ &= \boldsymbol{v}_t^{(\mathfrak{s}_i)} \times \left(\rho^{(\mathfrak{s}_i)} \boldsymbol{v}^{(\mathfrak{s}_i)}\right),\end{aligned} \tag{27.121}$$

and then combining it with the first term on the left-hand side of (27.120), the whole left-hand side results in $\boldsymbol{w}^{(\mathfrak{s}_i)} \times \left(\rho^{(\mathfrak{s}_i)} \boldsymbol{v}^{(\mathfrak{s}_i)}\right)$. Hence, (27.120) is reduced to

$$\boldsymbol{w}^{(\mathfrak{s}_i)} \times \left(\rho^{(\mathfrak{s}_i)} \boldsymbol{v}^{(\mathfrak{s}_i)}\right) + \boldsymbol{\varepsilon} : \left(\boldsymbol{T}^{(\mathfrak{s}_i)} \cdot \frac{\partial \boldsymbol{x}^{(\mathfrak{s}_i)}}{\partial \boldsymbol{\xi}^{(\mathfrak{s}_i)}}\right) = 0. \tag{27.122}$$

Further, if the interface $\mathfrak{S}^{(i)}$ is a material surface, $\boldsymbol{w}^{(\mathfrak{s}_i)} = \boldsymbol{v}^{(\mathfrak{s}_i)}$, (27.122) yields

$$\boldsymbol{\varepsilon} : \left(\boldsymbol{T}^{(\mathfrak{s}_i)} \cdot \frac{\partial \boldsymbol{x}^{(\mathfrak{s}_i)}}{\partial \boldsymbol{\xi}^{(\mathfrak{s}_i)}}\right) = 0 \quad \text{or} \quad \varepsilon_{ijk} T_{k\alpha}^{(\mathfrak{s}_i)} \frac{\partial x_j^{(\mathfrak{s}_i)}}{\partial \xi_\alpha^{(\mathfrak{s}_i)}} = 0. \tag{27.123}$$

The (full) surface stress $\boldsymbol{T}^{(\mathfrak{s}_i)}$ can be decomposed into two parts

$$\begin{aligned}\boldsymbol{T}^{(\mathfrak{s}_i)} &= \boldsymbol{T}_\parallel^{(\mathfrak{s}_i)} \cdot \frac{\partial \boldsymbol{x}^{(\mathfrak{s}_i)}}{\partial \boldsymbol{\xi}^{(\mathfrak{s}_i)}} + \boldsymbol{T}_\perp^{(\mathfrak{s}_i)} \otimes \boldsymbol{n}^{(\mathfrak{s}_i)},\\ \text{or} \quad T_{k\alpha}^{(\mathfrak{s}_i)} &= \left(T_\parallel^{(\mathfrak{s}_i)}\right)_{\alpha\beta} \frac{\partial x_k^{(\mathfrak{s}_i)}}{\partial \xi_\beta^{(\mathfrak{s}_k)}} + \left(T_\perp^{(\mathfrak{s}_i)}\right)_\alpha n_k^{(\mathfrak{s}_i)},\\ &\qquad i \in \{1,2,3\},\ \alpha, \beta \in \{1,2\},\end{aligned} \tag{27.124}$$

where $\boldsymbol{T}_\parallel^{(\mathfrak{s}_i)} \in \mathbb{R}^{2\times 2}$ is the tangential surface stress and $\boldsymbol{T}_\perp^{(\mathfrak{s}_i)} \in \mathbb{R}^2$ the normal surface stress. **Figure 27.9** shows their distribution on the edges of a surface element $\delta\mathfrak{S}^{(i)}$. Substituting (27.124) into (27.123) yields

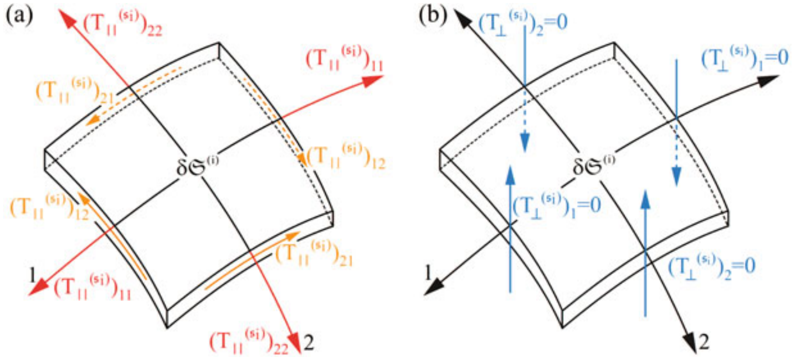

Fig. 27.9 **a** Surface element $\delta\mathfrak{S}^{(i)}$ drawn with small finite thickness and side faces parallel to the curved coordinates 1 and 2. In red color, the normal membrane stress components in the directions 1 and 2 are shown, and in orange color, the shear membrane stresses are displayed. **b** Analogous plot for the surface normal shear stress components are shown but according to (27.126) these stress components are zero

$$\varepsilon_{ijk}\left(T_{\parallel}^{(\mathfrak{s}_i)}\right)_{\alpha\beta}\frac{\partial x_k^{(\mathfrak{s}_i)}}{\partial \xi_\beta^{(\mathfrak{s}_k)}}\frac{\partial x_j^{(\mathfrak{s}_i)}}{\partial \xi_\alpha^{(\mathfrak{s}_i)}}+\varepsilon_{ijk}\left(T_{\perp}^{(\mathfrak{s}_i)}\right)_{\alpha} n_k^{(\mathfrak{s}_i)}\frac{\partial x_j^{(\mathfrak{s}_i)}}{\partial \xi_\alpha^{(\mathfrak{s}_i)}}=0,$$

$$\text{or}\quad \left(T_{\parallel}^{(\mathfrak{s}_i)}\right)_{\alpha\beta}\boldsymbol{t}_\alpha^{(\mathfrak{s}_i)}\times\boldsymbol{t}_\beta^{(\mathfrak{s}_i)}+\left(T_{\perp}^{(\mathfrak{s}_i)}\right)_{\alpha}\boldsymbol{t}_\alpha^{(\mathfrak{s}_i)}\times\boldsymbol{n}^{(\mathfrak{s}_i)}=0, \tag{27.125}$$

where $\boldsymbol{t}_\alpha^{(\mathfrak{s}_i)}=\partial\boldsymbol{x}^{(\mathfrak{s}_i)}/\partial\xi_\alpha^{(\mathfrak{s}_i)}$ is the surface tangent vector. (27.123) is equivalent to

$$\boldsymbol{T}_{\parallel}^{(\mathfrak{s}_i)}=\left(\boldsymbol{T}_{\parallel}^{(\mathfrak{s}_i)}\right)^{\top},\qquad \boldsymbol{T}_{\perp}^{(\mathfrak{s}_i)}=0, \tag{27.126}$$

i.e., $\boldsymbol{T}^{(\mathfrak{s}_i)}$ is a surface stress tensor and must be symmetric. This result was obtained also by MOECKEL [30].

A similar evaluation for the balance of angular momentum along the three-phase contact line $\mathfrak{C}$ (without consideration of additional torques) can be performed. Repeating the steps from (27.118) to (27.122), but here for the contact line $\mathfrak{C}$, and forming "(27.116) $-\,\boldsymbol{x}^{(\mathfrak{c})}\times$ (27.95)" yield

$$\boldsymbol{w}^{(\mathfrak{c})}\times\left(\rho^{(\mathfrak{c})}\boldsymbol{v}^{(\mathfrak{c})}\right)+\boldsymbol{\varepsilon}:\left(\boldsymbol{T}^{(\mathfrak{c})}\cdot\nabla^{(\mathfrak{c})}\boldsymbol{x}^{(\mathfrak{c})}\right)=0, \tag{27.127}$$

which is fully similar to relation (27.122) obtained for the interface $\mathfrak{S}^{(i)}$. For a material contact line, for which $\boldsymbol{w}^{(\mathfrak{c})}=\boldsymbol{v}^{(\mathfrak{c})}$, (27.127) is reduced to

$$\boldsymbol{\varepsilon}:\left(\boldsymbol{T}^{(\mathfrak{c})}\cdot\nabla^{(\mathfrak{c})}\boldsymbol{x}^{(\mathfrak{c})}\right)=0. \tag{27.128}$$

By means of a one-parameter configuration of the contact line $\boldsymbol{x}^{(\mathfrak{c})}=\hat{\boldsymbol{x}}^{(\mathfrak{c})}\left(\xi^{(\mathfrak{c})},t\right)$, as indicated in (27.45), (27.128) can be rewritten as

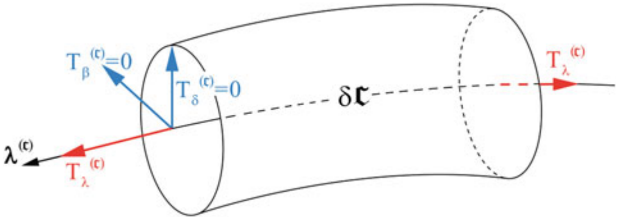

Fig. 27.10 Line element $\delta\mathfrak{C}$, drawn with small cross section. The normal stress component $T_\lambda^{(c)} = \left(\boldsymbol{T}^{(c)} \cdot \boldsymbol{\lambda}^{(c)}\right) \cdot \boldsymbol{\lambda}^{(c)} = \boldsymbol{t}^{(c)} \cdot \boldsymbol{\lambda}^{(c)}$ (in red color) is tangential to the line. The shear forces (in blue color) are within the cross section, arranged according to the SERRET–FRENET, but vanish in view of (27.129)

$$\boldsymbol{\varepsilon} : \left(\boldsymbol{T}^{(c)} \cdot \boldsymbol{\lambda}^{(c)} \frac{\partial \boldsymbol{x}^{(c)}}{\partial \xi^{(c)}}\right) = 0 \Longrightarrow \left(\boldsymbol{T}^{(c)} \cdot \boldsymbol{\lambda}^{(c)}\right) \times \boldsymbol{\lambda}^{(c)} = 0. \qquad (27.129)$$

Since the line stress tensor is a tensor with $\boldsymbol{T}^{(c)} \in \mathbb{R}^{3\times 1}$ in the one-parameter configuration, it can be expressed as $\boldsymbol{T}^{(c)} = \boldsymbol{t}^{(c)} \otimes \boldsymbol{\lambda}^{(c)}$ with $\boldsymbol{t}^{(c)} \in \mathbb{R}^3$. It is concluded from (27.129) that $\boldsymbol{t}^{(c)}$ is parallel to the contact line, see **Fig. 27.10**.

As indicated above, if there is an additional spin on the singular surface and along the contact line or the surface and the contact line are nonmaterial, one needs the conditions for a full angular momentum, accounting for a spin balance.

27.3.5 Conservation of Energy

Substituting the specifications of the corresponding variables for the energy balance (listed in Table 27.1) in (27.77)–(27.79) and employing the conservation relations of mass (27.80)–(27.82), respectively, the conservation laws of energy can be obtained[9]:

in the phase subdomain $\mathfrak{B}^{(i)}$:

$$\begin{aligned} &\rho^{(i)} \frac{\partial}{\partial t}\left(u^{(i)} + \tfrac{1}{2}\boldsymbol{v}^{(i)} \cdot \boldsymbol{v}^{(i)}\right) + \rho^{(i)}\boldsymbol{v}^{(i)} \cdot \nabla\left(u^{(i)} + \tfrac{1}{2}\boldsymbol{v}^{(i)} \cdot \boldsymbol{v}^{(i)}\right) \\ &= -\nabla \cdot \left(\boldsymbol{q}^{(i)} - \boldsymbol{T}^{(i)}\boldsymbol{v}^{(i)}\right) + \rho^{(i)}\left(\boldsymbol{v}^{(i)} \cdot \boldsymbol{g}\right) + \rho^{(i)} r^{(i)}, \end{aligned} \qquad (27.130)$$

---

[9] The derivation of these expressions is not difficult as it follows the procedure already used in simpler situations, but it is a bit long and tedious.

on the phase interface $\mathfrak{S}^{(i)}$:

$$\begin{aligned}
&\rho^{(\mathfrak{s}_i)}\frac{\delta^{(\mathfrak{s}_i)}}{\delta t}\left(u^{(\mathfrak{s}_i)}+\tfrac{1}{2}\boldsymbol{v}^{(\mathfrak{s}_i)}\cdot\boldsymbol{v}^{(\mathfrak{s}_i)}\right)+\rho^{(\mathfrak{s}_i)}\boldsymbol{v}^{(\mathfrak{s}_i)}\cdot\nabla^{(\mathfrak{s}_i)}\left(u^{(\mathfrak{s}_i)}+\tfrac{1}{2}\boldsymbol{v}^{(\mathfrak{s}_i)}\cdot\boldsymbol{v}^{(\mathfrak{s}_i)}\right)\\
&=-\nabla^{(\mathfrak{s}_i)}\cdot\left(\boldsymbol{q}^{(\mathfrak{s}_i)}-\boldsymbol{T}^{(\mathfrak{s}_i)}\boldsymbol{v}^{(\mathfrak{s}_i)}\right)+H^{(\mathfrak{s}_i)}\left(\left(\boldsymbol{q}^{(\mathfrak{s}_i)}-\boldsymbol{T}^{(\mathfrak{s}_i)}\boldsymbol{v}^{(\mathfrak{s}_i)}\right)\cdot\boldsymbol{n}^{(\mathfrak{s}_i)}\right)\\
&\quad+\llbracket\rho\left(\left(u+\tfrac{1}{2}\boldsymbol{v}\cdot\boldsymbol{v}\right)-\left(u^{(\mathfrak{s})}+\tfrac{1}{2}\boldsymbol{v}^{(\mathfrak{s})}\cdot\boldsymbol{v}^{(\mathfrak{s})}\right)\right)\left(\left(\boldsymbol{w}^{(\mathfrak{s})}-\boldsymbol{v}\right)\cdot\boldsymbol{n}^{(\mathfrak{s})}\right)\\
&\quad-\ (\boldsymbol{q}-\boldsymbol{T}\boldsymbol{v})\cdot\boldsymbol{n}^{(\mathfrak{s})}\rrbracket^{(i)}+\rho^{(\mathfrak{s}_i)}\left(\boldsymbol{v}^{(\mathfrak{s}_i)}\cdot\boldsymbol{g}\right)+\rho^{(\mathfrak{s}_i)}r^{(\mathfrak{s}_i)},
\end{aligned}\tag{27.131}$$

along the three-phase contact line $\mathfrak{C}$:

$$\begin{aligned}
&\rho^{(\mathfrak{c})}\frac{\delta^{(\mathfrak{c})}}{\delta t}\left(u^{(\mathfrak{c})}+\tfrac{1}{2}\boldsymbol{v}^{(\mathfrak{c})}\cdot\boldsymbol{v}^{(\mathfrak{c})}\right)+\rho^{(\mathfrak{c})}\boldsymbol{v}^{(\mathfrak{c})}\cdot\nabla^{(\mathfrak{c})}\left(u^{(\mathfrak{c})}+\tfrac{1}{2}\boldsymbol{v}^{(\mathfrak{c})}\cdot\boldsymbol{v}^{(\mathfrak{c})}\right)\\
&=-\nabla^{(\mathfrak{c})}\cdot\left(\boldsymbol{q}^{(\mathfrak{c})}-\boldsymbol{T}^{(\mathfrak{c})}\boldsymbol{v}^{(\mathfrak{c})}\right)+\kappa^{(\mathfrak{c})}\left(\boldsymbol{q}^{(\mathfrak{c})}-\boldsymbol{T}^{(\mathfrak{c})}\boldsymbol{v}^{(\mathfrak{c})}\right)\cdot\boldsymbol{n}^{(\mathfrak{c})}\\
&\quad+\rho^{(\mathfrak{c})}\left(\boldsymbol{v}^{(\mathfrak{c})}\cdot\boldsymbol{g}\right)+\rho^{(\mathfrak{c})}r^{(\mathfrak{c})}\\
&\quad-\sum_{i=1}^{3}\left(\rho^{(\mathfrak{s}_i)}\left(\left(u^{(\mathfrak{s}_i)}+\tfrac{1}{2}\boldsymbol{v}^{(\mathfrak{s}_i)}\cdot\boldsymbol{v}^{(\mathfrak{s}_i)}\right)-\left(u^{(\mathfrak{c})}+\tfrac{1}{2}\boldsymbol{v}^{(\mathfrak{c})}\cdot\boldsymbol{v}^{(\mathfrak{c})}\right)\right)\right.\\
&\qquad\qquad\left.\cdot\left(\boldsymbol{w}^{(\mathfrak{c})}-\boldsymbol{v}^{(\mathfrak{s}_i)}\right)\cdot\boldsymbol{s}^{(i)}-\left(\boldsymbol{q}^{(\mathfrak{s}_i)}-\boldsymbol{T}^{(\mathfrak{s}_i)}\boldsymbol{v}^{(\mathfrak{s}_i)}\right)\cdot\boldsymbol{s}^{(i)}\right).
\end{aligned}\tag{27.132}$$

We rewrite the balance relations of the total energy (27.130)–(27.132) in the form of the balance equations for the internal energy. For this purpose, we first take the scalar product of the bulk velocity $\boldsymbol{v}^{(i)}$ with the bulk momentum balance (27.102), the surface velocity $\boldsymbol{v}^{(\mathfrak{s}_i)}$ with the surface momentum balance (27.103), and the line velocity $\boldsymbol{v}^{(\mathfrak{c})}$ with the line momentum balance (27.104), respectively, then subtract these resulting equations from (27.130)–(27.132), respectively. By performing these indicated computations, the following reduced balances for the bulk, surface, and line internal energies are obtained:

in the phase subdomain $\mathfrak{B}^{(i)}$:

$$\rho^{(i)}\frac{\partial u^{(i)}}{\partial t}+\rho^{(i)}\boldsymbol{v}^{(i)}\cdot\nabla u^{(i)}=-\nabla\cdot\boldsymbol{q}^{(i)}+\operatorname{tr}\left(\boldsymbol{T}^{(i)}\left(\nabla\boldsymbol{v}^{(i)}\right)\right)+\rho^{(i)}r^{(i)},\tag{27.133}$$

on the phase interface $\mathfrak{S}^{(i)}$:

$$\begin{aligned}
&\rho^{(\mathfrak{s}_i)}\frac{\delta^{(\mathfrak{s}_i)}u^{(\mathfrak{s}_i)}}{\delta t}+\rho^{(\mathfrak{s}_i)}\boldsymbol{v}^{(\mathfrak{s}_i)}\cdot\nabla^{(\mathfrak{s}_i)}u^{(\mathfrak{s}_i)}\\
&=-\nabla^{(\mathfrak{s}_i)}\cdot\boldsymbol{q}^{(\mathfrak{s}_i)}+\operatorname{tr}\left(\boldsymbol{T}^{(\mathfrak{s}_i)}\left(\nabla^{(\mathfrak{s}_i)}\boldsymbol{v}^{(\mathfrak{s}_i)}\right)\right)+H^{(\mathfrak{s}_i)}\left(\boldsymbol{q}^{(\mathfrak{s}_i)}\cdot\boldsymbol{n}^{(\mathfrak{s}_i)}\right)+\rho^{(\mathfrak{s}_i)}r^{(\mathfrak{s}_i)}\\
&\quad+\llbracket\rho\left(\left(u-u^{(\mathfrak{s})}\right)+\tfrac{1}{2}\left(\boldsymbol{v}-\boldsymbol{v}^{(\mathfrak{s})}\right)\cdot\left(\boldsymbol{v}-\boldsymbol{v}^{(\mathfrak{s})}\right)\right)\left(\left(\boldsymbol{w}^{(\mathfrak{s})}-\boldsymbol{v}\right)\cdot\boldsymbol{n}^{(\mathfrak{s})}\right)\\
&\quad-\boldsymbol{q}\cdot\boldsymbol{n}^{(\mathfrak{s})}+\left(\boldsymbol{T}\left(\boldsymbol{v}-\boldsymbol{v}^{(\mathfrak{s})}\right)\right)\cdot\boldsymbol{n}^{(\mathfrak{s})}\rrbracket^{(i)},
\end{aligned}\tag{27.134}$$

along the three-phase contact line $\mathfrak{C}$:

$$\begin{aligned}
&\rho^{(\mathfrak{c})}\frac{\delta^{(\mathfrak{c})}u^{(\mathfrak{c})}}{\delta t}+\rho^{(\mathfrak{c})}\boldsymbol{v}^{(\mathfrak{c})}\cdot\nabla^{(\mathfrak{c})}u^{(\mathfrak{c})}\\
&=-\nabla^{(\mathfrak{c})}\cdot\boldsymbol{q}^{(\mathfrak{c})}+\operatorname{tr}\left(\boldsymbol{T}^{(\mathfrak{c})}\left(\nabla^{(\mathfrak{c})}\boldsymbol{v}^{(\mathfrak{c})}\right)\right)+\kappa^{(\mathfrak{c})}\left(\boldsymbol{q}^{(\mathfrak{c})}\cdot\boldsymbol{n}^{(\mathfrak{c})}\right)+\rho^{(\mathfrak{c})}r^{(\mathfrak{c})}\\
&\quad-\sum_{i=1}^{3}\Bigg(\rho^{(\mathfrak{s}_i)}\left(\left(u^{(\mathfrak{s}_i)}-u^{(\mathfrak{c})}\right)+\tfrac{1}{2}\left(\boldsymbol{v}^{(\mathfrak{s}_i)}-\boldsymbol{v}^{(\mathfrak{c})}\right)\cdot\left(\boldsymbol{v}^{(\mathfrak{s}_i)}-\boldsymbol{v}^{(\mathfrak{c})}\right)\right)\\
&\qquad\cdot\left(\left(\boldsymbol{w}^{(\mathfrak{c})}-\boldsymbol{v}^{(\mathfrak{s}_i)}\right)\cdot\boldsymbol{s}^{(i)}\right)\\
&\qquad-\boldsymbol{q}^{(\mathfrak{s}_i)}\cdot\boldsymbol{s}^{(i)}+\left(\boldsymbol{T}^{(\mathfrak{s}_i)}\left(\boldsymbol{v}^{(\mathfrak{s}_i)}-\boldsymbol{v}^{(\mathfrak{c})}\right)\right)\cdot\boldsymbol{s}^{(i)}\Bigg).
\end{aligned}\tag{27.135}$$

If we neglect the surface mass density (and thus also neglect the surface dynamic stress and surface heat flux), or strictly speaking, if our concern is primarily with the energy transfer through the interface rather than with the energy associated with the interface, we can rewrite the energy conservation equation (27.134) on the phase interface $\mathfrak{S}^{(i)}$ as a balance between the jump quantity and the surface tension as

$$\begin{aligned}
&\Big[\!\!\Big[\rho\left(\left(u-u^{(\mathfrak{s})}\right)+\tfrac{1}{2}\left(\boldsymbol{v}-\boldsymbol{v}^{(\mathfrak{s})}\right)\cdot\left(\boldsymbol{v}-\boldsymbol{v}^{(\mathfrak{s})}\right)\right)\left(\left(\boldsymbol{w}^{(\mathfrak{s})}-\boldsymbol{v}\right)\cdot\boldsymbol{n}^{(\mathfrak{s})}\right)\\
&-\boldsymbol{q}\cdot\boldsymbol{n}^{(\mathfrak{s})}+\left(\boldsymbol{T}\left(\boldsymbol{v}-\boldsymbol{v}^{(\mathfrak{s})}\right)\right)\cdot\boldsymbol{n}^{(\mathfrak{s})}\Big]\!\!\Big]^{(i)}+\sigma^{(\mathfrak{s}_i)}\left(\nabla^{(\mathfrak{s}_i)}\cdot\boldsymbol{v}^{(\mathfrak{s}_i)}\right)=0,
\end{aligned}\tag{27.136}$$

where relation (27.100) has been used. By means of the jump conditions for mass, (27.85), and for momentum, (27.106), the above jump condition for energy, (27.136), can be reduced to

$$\begin{aligned}
&\Big[\!\!\Big[\rho\left(u+\tfrac{1}{2}(\boldsymbol{v}\cdot\boldsymbol{v})-\boldsymbol{v}^{(\mathfrak{s})}\cdot\boldsymbol{v}\right)\left(\left(\boldsymbol{w}^{(\mathfrak{s})}-\boldsymbol{v}\right)\cdot\boldsymbol{n}^{(\mathfrak{s})}\right)-\left(\boldsymbol{q}-\boldsymbol{T}\boldsymbol{v}\right)\cdot\boldsymbol{n}^{(\mathfrak{s})}\Big]\!\!\Big]^{(i)}\\
&=-\nabla^{(\mathfrak{s}_i)}\cdot\left(\sigma^{(\mathfrak{s}_i)}\boldsymbol{v}^{(\mathfrak{s}_i)}\right)+\sigma^{(\mathfrak{s}_i)}H^{(\mathfrak{s}_i)}\left(\boldsymbol{v}^{(\mathfrak{s}_i)}\cdot\boldsymbol{n}^{(\mathfrak{s}_i)}\right).
\end{aligned}\tag{27.137}$$

Similarly, if the line mass density, line dynamic stress, and line heat flux are negligible, the conservation equation of energy along the contact line, (27.135), can be reduced to the jump condition

$$\begin{aligned}
&\sum_{i=1}^{3}\Bigg(\rho^{(\mathfrak{s}_i)}\left(\left(u^{(\mathfrak{s}_i)}-u^{(\mathfrak{c})}\right)+\tfrac{1}{2}\left(\boldsymbol{v}^{(\mathfrak{s}_i)}-\boldsymbol{v}^{(\mathfrak{c})}\right)\cdot\left(\boldsymbol{v}^{(\mathfrak{s}_i)}-\boldsymbol{v}^{(\mathfrak{c})}\right)\right)\\
&\qquad\cdot\left(\left(\boldsymbol{w}^{(\mathfrak{c})}-\boldsymbol{v}^{(\mathfrak{s}_i)}\right)\cdot\boldsymbol{s}^{(i)}\right)\\
&\qquad-\boldsymbol{q}^{(\mathfrak{s}_i)}\cdot\boldsymbol{s}^{(i)}+\left(\boldsymbol{T}^{(\mathfrak{s}_i)}\left(\boldsymbol{v}^{(\mathfrak{s}_i)}-\boldsymbol{v}^{(\mathfrak{c})}\right)\right)\cdot\boldsymbol{s}^{(i)}\Bigg)\\
&\qquad-\tau^{(\mathfrak{c})}\left(\nabla^{(\mathfrak{c})}\cdot\boldsymbol{v}^{(\mathfrak{c})}\right)=0.
\end{aligned}\tag{27.138}$$

Further, if the surface mass densities (and the surface dynamic stresses and heat fluxes) on the interfaces are also neglected (see (27.100) and (27.101), where the dynamic stresses are ignored), this relation can be simplified to

$$\sum_{i=1}^{3}\left(\left(\sigma^{(\mathfrak{s}_i)}\boldsymbol{I}^{(\mathfrak{s}_i)}\left(\boldsymbol{v}^{(\mathfrak{s}_i)}-\boldsymbol{v}^{(\mathfrak{c})}\right)\right)\cdot\boldsymbol{s}^{(i)}\right)-\tau^{(\mathfrak{c})}\left(\nabla^{(\mathfrak{c})}\cdot\boldsymbol{v}^{(\mathfrak{c})}\right)=0. \tag{27.139}$$

This relation represents a conservation of the works at the contact line performed by both the surface tension due to the difference of the interface and contact line material velocities, and the line tension on account of the stretching of the contact line.

27.3.6 Entropy Inequality

Substituting the corresponding variables of Table 27.1 for the conservation of entropy in (27.77)–(27.79) and employing the conservation relations of mass (27.80)–(27.82), respectively, the conservation laws of entropy can be obtained:

in the phase subdomain $\mathfrak{B}^{(i)}$:

$$\rho^{(i)}\frac{\partial\eta^{(i)}}{\partial t}+\rho^{(i)}\boldsymbol{v}^{(i)}\cdot\nabla\eta^{(i)}=-\nabla\cdot\boldsymbol{\phi}_\eta^{(i)}+\rho^{(i)}\pi_\eta^{(i)}+\rho^{(i)}\zeta_\eta^{(i)}, \tag{27.140}$$

on the phase interface $\mathfrak{S}^{(i)}$:

$$\begin{aligned}&\rho^{(\mathfrak{s}_i)}\frac{\delta^{(\mathfrak{s}_i)}\eta^{(\mathfrak{s}_i)}}{\delta t}+\rho^{(\mathfrak{s}_i)}\boldsymbol{v}^{(\mathfrak{s}_i)}\cdot\nabla^{(\mathfrak{s}_i)}\eta^{(\mathfrak{s}_i)}\\
&=-\nabla^{(\mathfrak{s}_i)}\cdot\boldsymbol{\phi}_\eta^{(\mathfrak{s}_i)}+H^{(\mathfrak{s}_i)}\left(\boldsymbol{\phi}_\eta^{(\mathfrak{s}_i)}\cdot\boldsymbol{n}^{(\mathfrak{s}_i)}\right)+\rho^{(\mathfrak{s}_i)}\pi_\eta^{(\mathfrak{s}_i)}+\rho^{(\mathfrak{s}_i)}\zeta_\eta^{(\mathfrak{s}_i)}\\
&\quad+\left[\!\left[\rho\left(\eta-\eta^{(\mathfrak{s})}\right)\left(\boldsymbol{w}^{(\mathfrak{s})}-\boldsymbol{v}\right)\cdot\boldsymbol{n}^{(\mathfrak{s})}-\boldsymbol{\phi}_\eta\cdot\boldsymbol{n}^{(\mathfrak{s})}\right]\!\right]^{(i)},\end{aligned} \tag{27.141}$$

along the three-phase contact line $\mathfrak{C}$:

$$\begin{aligned}&\rho^{(\mathfrak{c})}\frac{\delta^{(\mathfrak{c})}\eta^{(\mathfrak{c})}}{\delta t}+\rho^{(\mathfrak{c})}\boldsymbol{v}^{(\mathfrak{c})}\cdot\nabla^{(\mathfrak{c})}\eta^{(\mathfrak{c})}\\
&=-\nabla^{(\mathfrak{c})}\cdot\boldsymbol{\phi}_\eta^{(\mathfrak{c})}+\kappa^{(\mathfrak{c})}\left(\boldsymbol{\phi}_\eta^{(\mathfrak{c})}\cdot\boldsymbol{n}^{(\mathfrak{c})}\right)+\rho^{(\mathfrak{c})}\pi_\eta^{(\mathfrak{c})}+\rho^{(\mathfrak{c})}\zeta_\eta^{(\mathfrak{c})}\\
&\quad-\sum_{i=1}^{3}\left(\rho^{(\mathfrak{s}_i)}\left(\eta^{(\mathfrak{s}_i)}-\eta^{(\mathfrak{c})}\right)\left(\boldsymbol{w}^{(\mathfrak{c})}-\boldsymbol{v}^{(\mathfrak{s}_i)}\right)\cdot\boldsymbol{s}^{(i)}-\boldsymbol{\phi}_\eta^{(\mathfrak{s}_i)}\cdot\boldsymbol{s}^{(i)}\right).\end{aligned} \tag{27.142}$$

The entropy principle states that the entropy production is nonnegative in all thermodynamic processes, i.e.,

$$\pi_\eta^{(i)}\geq 0,\qquad \pi_\eta^{(\mathfrak{s}_i)}\geq 0,\qquad \pi_\eta^{(\mathfrak{c})}\geq 0.$$

With these conditions, the conservation laws of entropy (27.140)–(27.142) yield the entropy inequalities for the bulk phases, phase interfaces, and the contact line, respectively. The exploitation of these entropy inequalities will be given in Chap. 28.

27.4 Implicit Representation of Phase Interfaces and Contact Line

In the last section, the balance equations for phase interfaces and the three-phase contact line have been derived. To apply these equations, the motion of the phase interfaces, and the contact line and their shapes must be represented and (numerically) tracked. For this purpose, the level set method may be a suitable technique. The level set method was introduced by Osher and Sethian [35] and has become an increasingly popular method for simulating multiphase flows. The advantage of the level set method is that one can perform numerical computations involving curves and surfaces on a fixed grid without having to parameterize these objects. Also, the level set method makes it very easy to follow shapes that change topology, for example, when a shape splits into two, develops holes, or when the reverse of these operations occurs.

Let $\varphi^{(\mathfrak{s}_i)}(\boldsymbol{x}, t)$ be a scalar function whose zero level set $\{\boldsymbol{x}^{(\mathfrak{s}_i)} : \varphi^{(\mathfrak{s}_i)}\left(\boldsymbol{x}^{(\mathfrak{s}_i)}, t\right) = 0\}$ represents the phase interface $\mathfrak{S}^{(i)}$. For example, we may set $\varphi^{(\mathfrak{s}_i)}(\boldsymbol{x}, t)$ to be the signed distance from the point $\boldsymbol{x}$ to $\mathfrak{S}^{(i)}$ at time t. Since the interface moves with the velocity $\boldsymbol{w}^{(\mathfrak{s}_i)}$, [which may depend on position, time, the geometry of the interface (e.g., its normal or its mean curvature) and the external physics, or be given externally, for instance, as the material velocity in a fluid flow simulation] the evolution equation for the level set function $\varphi^{(\mathfrak{s}_i)}$ is given by

$$\frac{\partial \varphi^{(\mathfrak{s}_i)}}{\partial t} + \boldsymbol{w}^{(\mathfrak{s}_i)} \cdot \nabla \varphi^{(\mathfrak{s}_i)} = 0. \tag{27.143}$$

Here $\boldsymbol{w}^{(\mathfrak{s}_i)}$ is the surface velocity on the interface that is arbitrary elsewhere. If the interface $\mathfrak{S}^{(i)}$ is a material surface, $\boldsymbol{w}^{(\mathfrak{s}_i)}$ can be replaced by the fluid velocity. It is convenient to make $\varphi^{(\mathfrak{s}_i)}$ equal to the signed distance to the interface so that $|\nabla \varphi^{(\mathfrak{s}_i)}| = 1$. This ensures that the level set is a smoothly varying function, well suited for high-order accurate numerical methods. Unfortunately, as noted in Sussman, Smereka and Osher [48] the level set function can quickly cease to be a signed distance function especially for flows undergoing extreme topological changes. To avoid this, the level set function is re-initialized after each time step to be a signed distance function at least locally near the interface [47, 48]. This is performed by solving the following Hamilton–Jacobi equation to steady state (as fictitious time $\tau \to \infty$)

$$\frac{\partial \varphi^{(\mathfrak{s}_i)}}{\partial \tau} + \operatorname{sgn}\left(\varphi_0^{(\mathfrak{s}_i)}\right)\left(|\nabla \varphi^{(\mathfrak{s}_i)}| - 1\right) = 0, \quad \varphi^{(\mathfrak{s}_i)}(\boldsymbol{x}, 0) = \varphi_0^{(\mathfrak{s}_i)}(\boldsymbol{x}), \tag{27.144}$$

where $\varphi_0^{(\mathfrak{s}_i)}$ is the level set function before the re-initialization, and τ is the pseudo-time and $\mathrm{sgn}(\chi)$ the sign function of χ defined as

$$\mathrm{sgn}(\chi) = \begin{cases} -1, & \text{if} \quad \chi < 0, \\ 0, & \text{if} \quad \chi = 0, \\ 1, & \text{if} \quad \chi > 0. \end{cases} \tag{27.145}$$

One of the advantages of the level set method is that geometrical quantities can be easily computed from the level set function. Assume that the set of $\boldsymbol{x}$ such that $\varphi^{(\mathfrak{s}_i)}(\boldsymbol{x}, t) > 0$ is contained in $\mathfrak{B}^{(i)}$, then the normal, curvature, and surface delta function of the interface $\mathfrak{S}^{(i)}$ are

$$\begin{aligned} \boldsymbol{n}^{(\mathfrak{s}_i)} &= \frac{\nabla \varphi^{(\mathfrak{s}_i)}}{|\nabla \varphi^{(\mathfrak{s}_i)}|}, \\ H^{(\mathfrak{s}_i)} &= \nabla \cdot \left(\frac{\nabla \varphi^{(\mathfrak{s}_i)}}{|\nabla \varphi^{(\mathfrak{s}_i)}|} \right), \\ \delta^{(\mathfrak{s}_i)} &= \delta(\varphi^{(\mathfrak{s}_i)}) |\nabla \varphi^{(\mathfrak{s}_i)}|, \end{aligned} \tag{27.146}$$

where $\delta(\chi) = \mathrm{d}\left(\mathrm{sgn}(\chi)\right)/\mathrm{d}\chi$ is the usual one-dimensional delta function.

With the specified velocities of the three-phase interfaces, $\boldsymbol{w}^{(\mathfrak{s}_i)}$ $(i = 1, 2, 3)$, the motion and deformation of the interfaces can be represented and numerically tracked by means of the level set method. However, it is necessary to point out that the three surface velocities $\boldsymbol{w}^{(\mathfrak{s}_i)}$ are not independent of each other. They must fulfill some condition (at least near the moving contact line) so that the following compatibility conditions are met:

$$\left\{\varphi^{(\mathfrak{s}_1)} \cap \varphi^{(\mathfrak{s}_2)}\right\} = \left\{\varphi^{(\mathfrak{s}_2)} \cap \varphi^{(\mathfrak{s}_3)}\right\} = \left\{\varphi^{(\mathfrak{s}_3)} \cap \varphi^{(\mathfrak{s}_1)}\right\}. \tag{27.147}$$

This common domain constructs the three-phase contact line.

Furthermore, the motion of the three-phase contact line is determined only by the motions of the three-phase interfaces. The velocity of the moving three-phase contact line can be easily obtained by the velocities of any two of the three intersecting phase interfaces due to the fact that its projection to the normal direction of any interface is consistent with the normal velocity of that interface. Hence, the velocity of the three-phase contact line can be given by

$$\begin{aligned} \boldsymbol{w}^{(\mathrm{c})} = \Bigg\{ & \frac{\boldsymbol{w}^{(\mathfrak{s}_{\mathrm{l}})} \cdot \boldsymbol{n}^{(\mathfrak{s}_{\mathrm{l}})}}{1 - \left(\boldsymbol{n}^{(\mathfrak{s}_{\mathrm{l}})} \cdot \boldsymbol{n}^{(\mathfrak{s}_{\mathrm{m}})}\right)^2} \left(\boldsymbol{n}^{(\mathfrak{s}_{\mathrm{l}})} - \left(\boldsymbol{n}^{(\mathfrak{s}_{\mathrm{l}})} \cdot \boldsymbol{n}^{(\mathfrak{s}_{\mathrm{m}})}\right) \boldsymbol{n}^{(\mathfrak{s}_{\mathrm{m}})}\right) \\ & + \frac{\boldsymbol{w}^{(\mathfrak{s}_{\mathrm{m}})} \cdot \boldsymbol{n}^{(\mathfrak{s}_{\mathrm{m}})}}{1 - \left(\boldsymbol{n}^{(\mathfrak{s}_{\mathrm{l}})} \cdot \boldsymbol{n}^{(\mathfrak{s}_{\mathrm{m}})}\right)^2} \left(\boldsymbol{n}^{(\mathfrak{s}_{\mathrm{m}})} - \left(\boldsymbol{n}^{(\mathfrak{s}_{\mathrm{l}})} \cdot \boldsymbol{n}^{(\mathfrak{s}_{\mathrm{m}})}\right) \boldsymbol{n}^{(\mathfrak{s}_{\mathrm{l}})}\right) \Bigg\} \Bigg|_{\mathfrak{C}}, \end{aligned} \tag{27.148}$$

and its tangential direction can be specified simply by

$$\boldsymbol{\lambda}^{(\mathfrak{c})} = \left.\frac{\boldsymbol{n}^{(\mathfrak{s}_\mathfrak{l})} \times \boldsymbol{n}^{(\mathfrak{s}_\mathfrak{m})}}{\left|\boldsymbol{n}^{(\mathfrak{s}_\mathfrak{l})} \times \boldsymbol{n}^{(\mathfrak{s}_\mathfrak{m})}\right|}\right|_{\mathfrak{C}}, \tag{27.149}$$

where $\{\mathfrak{l}, \mathfrak{m}\} \subset \{1, 2, 3\}$ with $\mathfrak{l} \neq \mathfrak{m}$, i.e., $(\mathfrak{l}, \mathfrak{m}) \in \{(1, 2), (2, 3), (3, 1)\}$, and the subscript $|_{\mathfrak{C}}$ denotes the quantities evaluated near the contact line. Obviously, the velocity of the three-phase contact line depends on the normal velocity components of any two of the three-phase interfaces composing the three-phase contact line and their orientations immediately adjacent to the contact line. In general, in (27.148) and (27.149), the two-phase interfaces $\mathfrak{S}_\mathfrak{l}$ and $\mathfrak{S}_\mathfrak{m}$ can be chosen arbitrarily unless their orientations immediately adjacent to the contact line are identical. For that case, $\left(\boldsymbol{n}^{(\mathfrak{s}_\mathfrak{l})} \cdot \boldsymbol{n}^{(\mathfrak{s}_\mathfrak{m})}\right)|_{\mathfrak{C}} = 1$, the other two possible combinations of $(\mathfrak{l}, \mathfrak{m})$ should be chosen.

27.5 One-Fluid Conservation Equations

If the surface and line densities on the phase interfaces and along the contact line are small and negligible, three-phase flows with interfaces and the three-phase contact line can be treated by a single set of conservation laws for the whole flow field. For this purpose, it is necessary to account for the differences in the material properties of the different phases such as density, viscosity, and molecular diffusion coefficient and to add appropriate interface terms for interfacial and line phenomena, such as surface and line tensions. Since these terms are concentrated at the phase interfaces and the contact line between the different phases, they are represented by delta (δ) functions.

By means of the level set functions, $\varphi^{(\mathfrak{s}_1)}$, $\varphi^{(\mathfrak{s}_2)}$, and $\varphi^{(\mathfrak{s}_3)}$, introduced in the last section, the three-phase domains can be identified uniquely by the signs of the level set functions (see **Fig. 27.11**)

$$\begin{aligned}
\text{Phase}(1) &: \left\{\varphi^{(\mathfrak{s}_1)} > 0\right\} \cap \left\{\varphi^{(\mathfrak{s}_2)} < 0\right\}, \\
\text{Phase}(2) &: \left\{\varphi^{(\mathfrak{s}_2)} > 0\right\} \cap \left\{\varphi^{(\mathfrak{s}_3)} < 0\right\}, \\
\text{Phase}(3) &: \left\{\varphi^{(\mathfrak{s}_3)} > 0\right\} \cap \left\{\varphi^{(\mathfrak{s}_1)} < 0\right\}.
\end{aligned}$$

By introducing the Heaviside function

$$\mathcal{H}(x) = \begin{cases} 0, & \text{if} \quad x < 0, \\ 1, & \text{if} \quad x \geq 0, \end{cases} \tag{27.150}$$

any fluid property ψ is expressible as

$$\begin{aligned}
\psi = {} & \psi^{(1)}\mathcal{H}\left(\varphi^{(\mathfrak{s}_1)}\right)\mathcal{H}\left(-\varphi^{(\mathfrak{s}_2)}\right) + \psi^{(2)}\mathcal{H}\left(\varphi^{(\mathfrak{s}_2)}\right)\mathcal{H}\left(-\varphi^{(\mathfrak{s}_3)}\right) \\
& + \psi^{(3)}\mathcal{H}\left(\varphi^{(\mathfrak{s}_3)}\right)\mathcal{H}\left(-\varphi^{(\mathfrak{s}_1)}\right),
\end{aligned} \tag{27.151}$$

where ψ stands for density ρ, viscosity μ, or diffusivity D, i.e., $\psi \in \{\rho, \mu, D\}$.

Then, the one-fluid conservation equations, here, for example, only for mass and momentum, can be written as

- Conservations of mass

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \boldsymbol{v}) = 0; \tag{27.152}$$

- Balance of linear momentum

$$\begin{aligned} &\frac{\partial (\rho \boldsymbol{v})}{\partial t} + \nabla \cdot (\rho \boldsymbol{v} \otimes \boldsymbol{v}) \\ = &-\nabla p + \nabla \cdot \left(\mu \left(\nabla \boldsymbol{v} + (\nabla \boldsymbol{v})^T\right)\right) + \rho \boldsymbol{g} \\ &+ \sum_{i=1}^{3} \left(\nabla^{(\mathfrak{s}_i)} \sigma^{(\mathfrak{s}_i)} - \sigma^{(\mathfrak{s}_i)} H^{(\mathfrak{s}_i)} \boldsymbol{n}^{(\mathfrak{s}_i)}\right) \delta\left(\varphi^{(\mathfrak{s}_i)}\right) \\ &+ \left(\nabla^{(\mathfrak{c})} \tau^{(\mathfrak{c})} - \tau^{(\mathfrak{c})} \kappa^{(\mathfrak{c})} \boldsymbol{n}^{(\mathfrak{c})}\right) \delta\left(\varphi^{(\mathfrak{s}_\mathfrak{l})}\right) \delta\left(\varphi^{(\mathfrak{s}_\mathfrak{m})}\right), \end{aligned} \tag{27.153}$$

where $\mathfrak{s}_\mathfrak{l}$ and $\mathfrak{s}_\mathfrak{m}$ are two arbitrarily chosen phase interfaces whose orientations immediately adjacent to the contact line are different. This equivalence can be traced back to the compatibility condition (27.147). In writing the balance equation (27.153) a NEWTONian fluid with viscosity μ has been assumed. The expressions of the last two terms in (27.153) are based on the identities

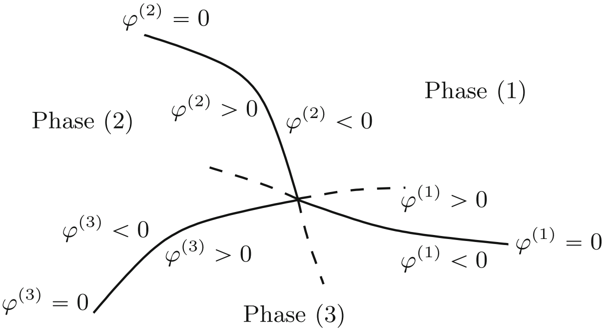

Fig. 27.11 Three-phase subdomains defined by level set functions in a two-dimensional description

$$
\begin{aligned}
&\int_{\mathfrak{B}} \left(\nabla^{(\mathfrak{s}_i)}\sigma^{(\mathfrak{s}_i)} - \sigma^{(\mathfrak{s}_i)} H^{(\mathfrak{s}_i)} \boldsymbol{n}^{(\mathfrak{s}_i)}\right) \delta\left(\varphi^{(\mathfrak{s}_i)}\right) \mathrm{d}v \\
&= \int_{\mathfrak{S}^{(i)}} \left(\nabla^{(\mathfrak{s}_i)}\sigma^{(\mathfrak{s}_i)} - \sigma^{(\mathfrak{s}_i)} H^{(\mathfrak{s}_i)} \boldsymbol{n}^{(\mathfrak{s}_i)}\right) \mathrm{d}a, \\
&\int_{\mathfrak{B}} \left(\nabla^{(\mathfrak{c})}\tau^{(\mathfrak{c})} - \tau^{(\mathfrak{c})} \kappa^{(\mathfrak{c})} \boldsymbol{n}^{(\mathfrak{c})}\right) \delta\left(\varphi^{(\mathfrak{s}_\mathfrak{l})}\right) \delta\left(\varphi^{(\mathfrak{s}_\mathfrak{m})}\right) \mathrm{d}v \\
&= \int_{\mathfrak{C}} \left(\nabla^{(\mathfrak{c})}\tau^{(\mathfrak{c})} - \tau^{(\mathfrak{c})} \kappa^{(\mathfrak{c})} \boldsymbol{n}^{(\mathfrak{c})}\right) \mathrm{d}\ell.
\end{aligned}
\tag{27.154}
$$

In numerical simulations, it may be advantageous to implement such one-fluid conservation equations (27.152) and (27.153) in the whole flow domain $\mathfrak{B}$.

27.6 Concluding Remarks

In this chapter, the local forms of the conservation laws of mass, momentum, angular momentum, (internal) energy, and entropy for the bulk, surface, and line quantities have been derived, starting from a general global balance equation for a multiphase flow domain including phase interfaces and three-phase contact line. The derived local balance laws for mass, (27.80)–(27.82), for momentum, (27.102)–(27.104), and for energy, (27.130)–(27.132), do not determine the field variables defined and interrelated by them uniquely. To that end, some fields (here $\boldsymbol{T}^{(i)}$, $\boldsymbol{T}^{(\mathfrak{s}_i)}$, $\boldsymbol{T}^{(\mathfrak{c})}$, $\boldsymbol{q}^{(i)}$, $\boldsymbol{q}^{(\mathfrak{s}_i)}$, $\boldsymbol{q}^{(\mathfrak{c})}$) must be expressed as functionals of the others, such that the emerging equations have the potential of generating well-defined functional equations. The forms of these constitutive relations must obey the known universal physical principles which have been abstracted from experience, and are reduced or constrained by them. The most important of these principles is the second law of thermodynamics, which is formulated as an entropy principle. This issue will be discussed in the following chapter.

References

1. Alts, T., Hutter, K.: Continuum description of the dynamics and thermodynamics of phase boundaries between ice and water, part I: surface balance laws and their interpretation in terms of three-dimensional balance laws averaged over the phase change boundary layer. J. Non-Equil. Thermo. **13**, 221–257 (1988)
2. Amirfazli, A., Kwok, D.Y., Gaydos, J., Neumann, A.W.: Line tension measurements through drop size dependence of contact angle. J. Colloid Interface Sci. **205**, 1–11 (1998)
3. Amirfazli, A., Keshavarz, A., Zhang, L., Neumann, A.W.: Determination of line tension for systems near wetting. J. Colloid Interface Sci. **265**, 152–160 (2003)
4. Amirfazli, A., Neumann, A.W.: Status of the three-phase line tension: a review. Adv. Colloid Interface Sci. **110**, 121–141 (2004)
5. Babak, V.G.: Generalised line tension theory revisited. Colloids Surf., A **156**, 423–448 (1999)
6. Bedeaux, D.: Nonequilibrium thermodynamic description of the three-phase contact line. J. Chem. Phys. **120**, 3744–3748 (2004)
7. Bier, M., Chen, W., Gowrishankar, T.R., Astumian, R.D., Lee, R.C.: Resealing dynamics of a cell membrane after electroporation. Phys. Rev. E **66**(6), 062905 (2002)

8. Cermelli, P., Fried, E., Gurtin, M.: Transport relation for surface integrals arising in the formulation of balance laws for evolving fluid interfaces. J. Fluid Mech. **544**, 339–351 (2005)
9. dell'Isola, F., Seppecher, P.: Edge contact forces and quasi-balanced power. Mechanica **32**, 33–52 (1997)
10. Dussaud, A., Vignes-Adler, M.: Wetting transition of n-alkanes on concentrated aqueous salt solutions. Line tension effect. Langmuir **13**, 581–589 (1997)
11. Edwards, D.A., Brenner, H., Wasan, D.T.: Interfacial Transport Processes and Rheology. Butterworth-Heinemann, Boston (1991)
12. Eggleton, C.D., Stebe, K.J.: An adsorption-desorption controlled surfactant on a deforming droplet. J. Coll. Int. Sci. **208**, 68–80 (1998)
13. Eggleton, C.D., Tsai, T.M., Stebe, K.J.: Tip streaming from a drop in the presence of surfactants. Phys. Rev. Lett. **87**, 048302 (2001)
14. Gatignol, R., Prud'homme, R.: Mechanical and Thermodynamical Modeling of Fluid Interfaces. World Scientific, Singapore (2001)
15. Getta, T., Dietrich, S.: Line tension between fluid phases and a substrate. Phys. Rev. E **57**, 655–671 (1998)
16. Gokhale, S.J., Plawsky, J.L., Wayner Jr., P.C.: Effect of interfacial phenomena on dewetting in dropwise condensation. Adv. Colloid Interface Sci. **104**, 175–190 (2003)
17. Gordon, J.E.: Structures or Why Things Don't Fall Down. Penguin Books, London (1978)
18. Graham, C., Griffith, P.: Drop size distributions and heat transfer in dropwise condensation. Int. J. Heat Mass Transfer. **16**, 337–346 (1973)
19. Greve, R.: Kontinuumsmechanik – Ein Grundkurs, p. 302. Springer, Berlin (2003)
20. Gu, Y.: Drop size dependence of contact angles of oil drops on a solid surface in water. J. Colloids Surf. A **181**, 215–224 (2001)
21. Gurtin, M.E., Struthers, A., Williams, W.O.: A transport theorem for moving interfaces. Q. Appl. Maths **47**, 773–777 (1989)
22. Gurtin, M.E.: On thermomechanical laws for the motion of a phase interface. J. App. Math. Phys. **42**, 370–388 (1991)
23. Haupt, P.: Continuum Mechanics and Theory of Materials, p. 643. Springer, Berlin (2002)
24. Hutter, K., Jöhnk, K.: Continuum Methods of Physical Modeling, p. 635. Springer, Berlin (2004)
25. Hutter, K., Wang, Y.: Fluid and Thermodynamics. Volume II: Advanced Fluid Mechanics and Thermodynamic Fundamentals, p. 633. Springer, Berlin (2016). ISBN: 978-3-319-33635-0
26. Indekeu, J.O.: Line tension at wetting. J. Mod. Phys., B **8**, 309–345 (1994)
27. Jin, F., Gupta, N.R., Stebe, K.J.: The detachment of a viscous drop in a viscous solution in the presence of a soluble surfactant. Phys. Fluids **18**, 022103 (2006)
28. Levich, V.G.: Physicochemical Hydrodynamics. Prentice Hall, Upper Saddle River (1962)
29. Marmur, A.: Line tension and the intrinsic contact angle in solid-liquid-fluid systems. J. Colloid Interface Sci. **186**, 462–466 (1997)
30. Moeckel, G.P.: Thermodynamics of an interface. Arch. Ration. Mech. Anal. **57**, 255–280 (1975)
31. Morel, C.: On the surface equations in two-phase flows and reacting single-phase flows. Int. J. Multiphase Flow **33**, 1045–1073 (2007)
32. Noll, W.: The foundation of classical mechanics in the light of recent advances in continuum mechanics. In: Proceedings of the Berkeley Symposium on Aximatic Methods, pp. 226–228. Amsterdam (1959)
33. Noll, W., Virga, E.G.: On edge interactions and surface tension. Arch. Ration. Mech. Anal. **111**(1), 1–31 (1990)
34. Oliver, J.F., Huh, C., Mason, S.G.: Resistance to spreading of liquids by sharp edges. J. Colloid Interface Sci. **59**, 568–581 (1977)
35. Osher, S., Sethian, J.A.: Fronts propagating with curvature dependent speed: algorithms based on Hamilton-Jacobi formulations. J. Comput. Phys. **79**, 12–49 (1988)
36. Otis Jr., D.R., Ingenito, E.P., Kamm, R.D., Johnson, M.: Dynamic surface tension of surfactant TA: experiments and theory. J. Appl. Physiol. **77**, 2681–2688 (1994)

37. Petryk, H., Mroz, Z.: Time derivatives of integrals and functionals defined on varying volume and surface domains. Arch. Mech. **38**, 697–724 (1986)
38. Pompe, T.: Line tension behavior of a first-order wetting system. Phys Rev. Lett. **89**(7) Art.No. 076102 (2002)
39. Qu, W., Li, D.: Line tension of simple liquid-liquid-fluid systems. Colloids Surf, A **156**, 123–135 (1999)
40. Rodrigues, J.F., Saramago, B., Fortes, M.A.: Apparent contact angle and triple-line tension of a soap bubble on a substrate. J. Colloid Interface Sci. **239**, 577–580 (2001)
41. Rusanov, A.I.: Surface thermodynamics revisited. Surf. Sci. Rep. **58**, 111–239 (2005)
42. Sagis, L.M., Slattery, J.C.: Incorporation of line quantities in the continuum description for multiphase, multicomponent bodies with intersecting dividing surfaces. I. Kinematics and conservation principles. J. Colloid Interface Sci. **176**, 150–164 (1995)
43. Shikhmurzaev, Y.D.: The moving contact line on a smooth solid surface. Int. J. Multiphase Flow **19**, 589–610 (1993)
44. Shikhmurzaev, Y.D.: Capillary Flows with Forming Interfaces. Chapman & Hall/CRC, London (2008)
45. Slattery, J.C., Sagis, L., Oh, E.-S.: Interfacial Transport Phenomena. Springer, New York (2007)
46. Solomentsev, Y., White, L.R.: Microscopic drop profiles and the origins of line tension. J. Colloid Interface Sci. **218**, 122–136 (1999)
47. Sussman, M., Fatemi, E., Smereka, P., Osher, S.: An improved level set method for incompressible two-phase flows. Comput. Fluids **277**, 663–680 (1998)
48. Sussman, M., Smereka, P., Osher, S.: A level set approach for computing solutions to incompressible two-phase flow. J. Comput. Phys. **114**, 146–159 (1994)
49. Szleifer, I., Widom, B.: Surface tension, line tension, and wetting. Mol. Phys. **75**, 925–943 (1992)
50. Thomas, T.Y.: Extended compatibility conditions for the study of surfaces of discontinuity in continuum mechanics. J. Maths Mech. **6**, 311–322 (1957)
51. Truesdell, C.: A First Course in Rational Continuum Mechanics. Academic Press, New York (1977)
52. Truesdell, C.A., Toupin, R.A.: The classical field theories. In: Flügge, S (ed.) Encyclopedia of Physics, vol. III/1, pp. 226–793. Springer, Berlin (1957)
53. Vera-Graziano, R., Muhl, S., Rivera-Torres, F.: The effect of illumination on contact angles of pure water on crystalline silicon. J. Colloid Interface Sci. **170**, 591–597 (1995)
54. Vignes-Adler, M., Brenner, H.: A micromechanical derivation of the dierential equations of interfacial statics. III. Line tension. J. Colloid Interface Sci. **103**, 11–44 (1985)
55. Wallace, J.A., Schürch, S.: Line tension of sessile drops placed on a phospholipid monolayer at the water-fluorocarbon interface. Colloids Surf. **43**, 207–221 (1990)
56. Wang, Y., Oberlack, M.: A thermodynamic model of multiphase flows with moving interfaces and contact line. Continuum Mech. Thermodyn. **23**, 409–433 (2011)

Chapter 28

Multiphase Flows with Moving Interfaces and Contact Line—Constitutive Modeling

Abstract A thermodynamic analysis, based on the MÜLLER–LIU thermodynamic approach of the second law of thermodynamics, is performed to derive the expressions of the constitutive variables in thermodynamic equilibrium. Non-equilibrium responses are proposed by use of a quasi-linear theory. A set of constitutive equations for the surface and line constitutive quantities is postulated. Some restrictions for the emerging material parameters are derived by means of the minimum conditions of the surface and line entropy productions in thermodynamic equilibrium. Hence, a complete continuum mechanical model to describe excess surface and line physical quantities is formulated. Technically, in the exploitation of the entropy inequality, all field equations are incorporated with LAGRANGE parameters into the entropy inequality. In the process of its exploitation, the LAGRANGE parameter of the energy balance is identified with the inverse of the absolute temperature in the bulk, the phase interface, and in the three-phase contact line. Interesting results, among many others, are the GIBBS relations, which are formally the same in the bulk, on the interface and along the contact line, with the pressure in the compressible bulk replaced by the surface tension on the interface and by the line tension along the contact line, see (28.45), (28.87).

Keywords Multiphase flows · Entropy principle · Constitutive equations · Phase interface · Three-phase contact line

List of Symbols

Roman Symbols

$\boldsymbol{D}^{(\mathfrak{c})}$	Contact line stretching tensor, $\boldsymbol{D}^{(\mathfrak{c})} = \frac{1}{2}\left(\nabla^{(\mathfrak{c})}\boldsymbol{v}^{(\mathfrak{c})} + (\nabla^{(\mathfrak{c})}\boldsymbol{v}^{(\mathfrak{c})})^T\right)$
$\boldsymbol{D}^{(\mathfrak{s}_i)}$	Surface stretching tensor, $\boldsymbol{D}^{(\mathfrak{s}_i)} = \frac{1}{2}\left(\nabla^{(\mathfrak{s}_i)}\boldsymbol{v}^{(\mathfrak{s}_i)} + (\nabla^{(\mathfrak{s}_i)}\boldsymbol{v}^{(\mathfrak{s}_i)})^T\right)$

This chapter heavily draws from WANG, OBERLACK and ZIELENIEWICZ (2013) [40].

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$\boldsymbol{g}$	Gravitational force per unit mass
$H^{(\mathfrak{s}_i)}$	Total (i.e., twice the mean) surface curvature of surface $\mathfrak{S}^{(i)}$, $H^{(\mathfrak{s}_i)} = \nabla^{(\mathfrak{s}_i)} \cdot \boldsymbol{n}^{(\mathfrak{s}_i)}$
$\boldsymbol{I}^{(\mathfrak{c})}$	Line projection tensor, $\boldsymbol{I}^{(\mathfrak{c})} = \boldsymbol{\lambda}^{(\mathfrak{c})} \otimes \boldsymbol{\lambda}^{(\mathfrak{c})}$
$\boldsymbol{I}^{(\mathfrak{s}_i)}$	Surface projection tensor on the interface $\mathfrak{S}^{(i)}$, $\boldsymbol{I}^{(\mathfrak{s}_i)} \equiv \boldsymbol{I} - \boldsymbol{n}^{(\mathfrak{s}_i)} \otimes \boldsymbol{n}^{(\mathfrak{s}_i)}$
$\boldsymbol{n}^{(\mathfrak{c})}$	Unit principal normal to the contact line $\mathfrak{C}$
$\boldsymbol{n}^{(\mathfrak{s}_i)}$	Unit normal vector of the interface $\mathfrak{S}^{(i)}$, pointing into the phase domain $\mathfrak{B}^{(i)}$
$p^{(i)}$	Hydrostatic pressure in the phase domain $\mathfrak{B}^{(i)}$
$\boldsymbol{q}^{(i)}, \boldsymbol{q}^{(\mathfrak{s}_i)}, \boldsymbol{q}^{(\mathfrak{c})}$	Bulk, surface, and line heat flux vectors
$r^{(i)}, r^{(\mathfrak{s}_i)}, r^{(\mathfrak{c})}$	Specific bulk, surface, and line heat supplies
$\boldsymbol{s}^{(i)}$	Unit vector normal to the boundary curves $\mathfrak{C}^{(i)}$ but tangent to the interface $\mathfrak{S}^{(i)}$ pointing to the exterior of the system
$\boldsymbol{T}^{(i)}, \boldsymbol{T}^{(\mathfrak{s}_i)}, \boldsymbol{T}^{(\mathfrak{c})}$	Cauchy, surface, and line stress tensors
$u^{(i)}, u^{(\mathfrak{s}_i)}, u^{(\mathfrak{c})}$	Specific bulk, surface, and line internal energy densities
$\boldsymbol{v}^{(\mathfrak{c})}$	Material velocities of fluid particles that lie on the line $\mathfrak{C}$ at the instant of time
$\boldsymbol{v}^{(i)}$	Material velocity in the subdomain $\mathfrak{B}^{(i)}$
$\boldsymbol{v}^{(\mathfrak{s}_i)}$	Velocity of material points which lie on the surface $\mathfrak{S}^{(i)}(t)$ at time t
$\boldsymbol{w}^{(\mathfrak{c})}$	Velocity of the three-phase contact line $\mathfrak{C}$
$\boldsymbol{w}^{(\mathfrak{s}_i)}$	Velocity of the interface $\mathfrak{S}^{(i)}$
$\boldsymbol{W}_\mathfrak{c}, \boldsymbol{W}_\mathfrak{c}^i$	$\boldsymbol{W}_\mathfrak{c} = \boldsymbol{w}^{(\mathfrak{c})} - \boldsymbol{v}^{(\mathfrak{c})}$, and $\boldsymbol{W}_\mathfrak{c}^i = \boldsymbol{w}^{(\mathfrak{c})} - \boldsymbol{v}^{(\mathfrak{s}_i)}$ $(i \in \{1, 2, 3\})$
$\boldsymbol{W}_\mathfrak{s}^+, \boldsymbol{W}_\mathfrak{s}^-, \boldsymbol{W}_\mathfrak{s}$	$\boldsymbol{W}_\mathfrak{s}^+ = \boldsymbol{w}^{(\mathfrak{s}_i)} - \boldsymbol{v}^{(i)}$, $\boldsymbol{W}_\mathfrak{s}^- = \boldsymbol{w}^{(\mathfrak{s}_i)} - \boldsymbol{v}^{(i-1)}$, and $\boldsymbol{W}_\mathfrak{s} = \boldsymbol{w}^{(\mathfrak{s}_i)} - \boldsymbol{v}^{(\mathfrak{s}_i)}$

Greek Symbols

$\eta^{(i)}, \eta^{(\mathfrak{s}_i)}, \eta^{(\mathfrak{c})}$	Specific bulk, surface, and line entropy densities
$\kappa^{(\mathfrak{c})}$	Normal curvature of the contact line $\mathfrak{C}$
$\boldsymbol{\lambda}^{(\mathfrak{c})}$	Unit vector tangent to the contact line $\mathfrak{C}$ directed toward to the end II from the end I
$\varLambda_\rho^{(i)}, \boldsymbol{\varLambda}_v^{(i)}, \varLambda_\varepsilon^{(i)}$	LAGRANGE multipliers associated with the constraints placed on the bulk entropy inequality by the other balance relations in phase (i), see (28.16)
$\varLambda_\rho^{(\mathfrak{s}_i)}, \boldsymbol{\varLambda}_v^{(\mathfrak{s}_i)}, \varLambda_\varepsilon^{(\mathfrak{s}_i)}$	LAGRANGE multipliers associated with the constraints placed on the surface entropy inequality by the other balance relations on the phase interface, see (28.17)
$\varLambda_\rho^{(\mathfrak{c})}, \boldsymbol{\varLambda}_v^{(\mathfrak{c})}, \varLambda_\varepsilon^{(\mathfrak{c})}$	LAGRANGE multipliers associated with the constraints placed on the line entropy inequality by the other balance relations at the contact line, see (28.18)
$\boldsymbol{\phi}_\eta^{(i)}, \boldsymbol{\phi}_\eta^{(\mathfrak{s}_i)}, \boldsymbol{\phi}_\eta^{(\mathfrak{c})}$	Bulk, surface, and line entropy flux vectors

$\varPi^{(i)}$, $\varPi^{(\mathfrak{s}_i)}$, $\varPi^{(\mathfrak{c})}$	entropy productions per unit volume in the phase $\mathfrak{B}^{(i)}$, per unit area on the phase interface $\mathfrak{S}^{(i)}$, and per unit length along the three-phase contact line $\mathfrak{C}$, respectively
$\psi^{(i)}$, $\psi^{(\mathfrak{s}_i)}$, $\psi^{(\mathfrak{c})}$	Helmholtz free energies for bulk phases $\mathfrak{B}^{(i)}$, interfaces $\mathfrak{S}^{(i)}$, and the contact line $\mathfrak{C}$
$\rho^{(i)}$, $\rho^{(\mathfrak{s}_i)}$, $\rho^{(\mathfrak{c})}$	Bulk, surface, and line mass densities
$\sigma^{(\mathfrak{s}_i)}$	Surface tension on the interface $\mathfrak{S}^{(i)}$
$\tau^{(\mathfrak{c})}$	Line tension at the three-phase contact line $\mathfrak{C}$
$\varTheta^{(i)}$, $\varTheta^{(\mathfrak{s}_i)}$, $\varTheta^{(\mathfrak{c})}$	Absolute temperatures in the phase $\mathfrak{B}^{(i)}$, on the interface $\mathfrak{S}^{(i)}$, and at the three-phase contact line $\mathfrak{C}$, respectively
$\zeta_\eta^{(i)}$, $\zeta_\eta^{(\mathfrak{s}_i)}$, $\zeta_\eta^{(\mathfrak{c})}$	Specific bulk, surface, and line entropy supplies

Miscellaneous Symbols

$\mathfrak{B}^{(i)}$	Subdomain of phase i
$\mathfrak{C}$	Three-phase contact line
$\mathrm{d}/\mathrm{d}t$	Material time derivative
$\mathrm{d}^{(\mathfrak{s})}\gamma^{(\mathfrak{s})}/\mathrm{d}t$	Time derivative of a surface scalar field $\gamma^{(\mathfrak{s})}$ following the evolution of the surface $\mathfrak{S}(t)$ by using the parameterization $\boldsymbol{x}^{(\mathfrak{s})} = \hat{\boldsymbol{x}}^{(\mathfrak{s})}\left(\xi_1^{(\mathfrak{s})}, \xi_2^{(\mathfrak{s})}, t\right)$
$\mathrm{d}^{(\mathfrak{c})}\gamma^{(\mathfrak{c})}/\mathrm{d}t$	Time derivatives of a line field $\gamma^{(\mathfrak{c})}$ following the evolution of the curve $\mathfrak{C}$ defined by means of the parameterization $\boldsymbol{x}^{(\mathfrak{c})} = \hat{\boldsymbol{x}}^{(\mathfrak{c})}\left(\xi^{(\mathfrak{c})}, t\right)$
$\delta^{(\mathfrak{s}_i)}\gamma^{(\mathfrak{s}_i)}/\delta t$	Normal time derivative of a surface scalar field $\gamma^{(\mathfrak{s}_i)}$, denoting the time derivative for a given point on the surface $\mathfrak{S}^{(i)}$ following the normal trajectory of the surface
$\delta^{(\mathfrak{c})}\gamma^{(\mathfrak{c})}/\delta t$	Normal time derivative of a line field $\gamma^{(\mathfrak{c})}$, following $\mathfrak{C}(t)$, denoting the time derivative following the normal trajectory of the moving curve
$\partial/\partial t$	Partial (local) time derivative
∇	Gradient operator
$\nabla^{(\mathfrak{c})}$	Line gradient operator, defined by $\nabla^{(\mathfrak{c})} = (\boldsymbol{\lambda}^{(\mathfrak{c})} \otimes \boldsymbol{\lambda}^{(\mathfrak{c})}) \cdot \nabla \equiv \boldsymbol{I}^{(\mathfrak{c})} \cdot \nabla$
$\nabla^{(\mathfrak{s}_i)}$	Surface gradient operator on the interface $\mathfrak{S}^{(i)}$
$\mathfrak{S}^{(i)}$	Phase interface between phases $i-1$ and i
$[\![\mathcal{G}]\!]^{(i)}$	Jump of the quantity $\mathcal{G}$ over the interface $\mathfrak{S}^{(i)}$, $[\![\mathcal{G}]\!]^{(i)} = \mathcal{G}^{(i)} - \mathcal{G}^{(i-1)}$ (if $i-1=0$, it is set $i-1=3$)
$\mathcal{E}^{(i)} = 0$	Conservation equation of energy in the phase subdomain $\mathfrak{B}^{(i)}$
$\mathcal{E}^{(\mathfrak{s}_i)} = 0$	Conservation equation of energy on the phase interface $\mathfrak{S}^{(i)}$
$\mathcal{E}^{(\mathfrak{c})} = 0$	Conservation equation of energy along the three-phase contact line $\mathfrak{C}$
$\mathcal{M}^{(i)} = 0$	Balance equation of momentum in the phase subdomain $\mathfrak{B}^{(i)}$
$\mathcal{M}^{(\mathfrak{s}_i)} = 0$	Balance equation of momentum on the phase interface $\mathfrak{S}^{(i)}$

$\mathcal{M}^{(\mathfrak{c})} = 0$	Balance equation of momentum along the three-phase contact line $\mathfrak{C}$
$\mathcal{R}^{(i)} = 0$	Conservation equation of mass in the phase subdomain $\mathfrak{B}^{(i)}$
$\mathcal{R}^{(\mathfrak{s}_i)} = 0$	Conservation equation of mass on the phase interface $\mathfrak{S}^{(i)}$
$\mathcal{R}^{(\mathfrak{c})} = 0$	Conservation equation of mass along the three-phase contact line $\mathfrak{C}$
$\Pi^{(i)} \geq 0$	Entropy inequality in the phase subdomain $\mathfrak{B}^{(i)}$
$\Pi^{(\mathfrak{s}_i)} \geq 0$	Entropy inequality on the phase interface $\mathfrak{S}^{(i)}$
$\Pi^{(\mathfrak{c})} \geq 0$	Entropy inequality along the three-phase contact line $\mathfrak{C}$

28.1 Introduction

It[1] is widely known today that, to better investigate the behaviors of multiphase flows including singular phase interfaces and three-phase contact line, it may be necessary for some cases to introduce excess surface quantities associated with the phase interfaces and excess line quantities at the contact line. For these excess physical quantities (e.g., surface mass density, surface momentum density, and surface internal energy, as well as line mass density, line momentum density and line internal energy, etc.), the conservation laws have been presented in Chap. 27. In these conservation equations, some new constitutive quantities, e.g., the surface and line stress tensors, heat flux vectors, internal energies, must be postulated by suitable constitutive relations, which must obey the known universal physical principles.

To some extent, modern continuum thermodynamics amounts to a collection of thermodynamical theories sharing common premises and common methodology. There are theories of elastic materials, of viscous materials, of materials with memory, of mixtures, and so on. It is generally the case that, in the context of each theory, one considers all processes (compatible with classical conservation laws) that bodies composed of the prescribed material might admit. Moreover, there exist for the theory some universal physical principles that have been abstracted from experience. Therefore, one can reduce the generality of the constitutive relations of dependent material variables by relying upon these principles. The most important of these principles is the second law of thermodynamics.

In WANG and HUTTER (1999) [35], an attempt was made to explain how the basic postulates of two forms of the entropy principle, (i) the generalized CLAUSIUS–DUHEM inequality with the COLEMAN–NOLL approach and (ii) the MÜLLER–LIU entropy principle, differ from one another and then demonstrate that they may yield different results in many cases, especially for some complicated materials, e.g., for granular materials [36, 37]. In Chap. 18 in Vol. 2 of this treatise, both forms of the entropy principle have been introduced and extensively discussed.

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[1] Additional symbols are the same as in Chap. 27.

Most of the modern work on rational thermodynamics is based upon the CLAUSIUS–DUHEM inequality after COLEMAN and NOLL [5] had suggested a method for its exploitation, in which the entropy flux was assumed to be equal to the heat flux divided by the absolute temperature, just as in linear irreversible thermodynamics, and the entropy supply has been assumed to be equal to the specific energy supply divided by the absolute temperature. These assumptions may only be adopted in linear irreversible thermodynamics with the principle of local equilibrium. Another key to the exploitation of the CLAUSIUS–DUHEM inequality is the statement that this inequality holds only for thermodynamic processes, i.e., solutions of the field equations rather than for arbitrary fields. In the COLEMAN–NOLL approach of thermodynamics, it is considered that the linear momentum equation and the energy balance have all arbitrarily assignable external source terms, so that these balance laws would not affect the exploitation of the entropy inequality, because whatever the fields are, the conservation equations of momentum and energy would be satisfied by a suitable body force and radiation supply. Such a procedure may not be physically justified and has been criticized [42]. The formulation of the CLAUSIUS–DUHEM inequality has provided a step away from thermostatics in the direction of a properly formulated thermodynamic theory, because it allows the entropy to depend on non-equilibrium variables. Such an extension is proper and in fact is dictated by the kinetic theory of gases that shows the entropy in non-equilibrium to deviate from the equilibrium entropy [11, 27]. However, once this step is made, it would seem inconsistent to rely upon thermostatics to suggest the expression for the entropy flux. It is shown that in general, the entropy flux is different from the heat flux divided by the temperature [11, 27].

MÜLLER [24] proposed an entropy principle which is free of these special assumptions. Rather, the entropy flux is given by a constitutive equation. Just like in the exploitation of the CLAUSIUS–DUHEM inequality, the entropy inequality must hold for all thermodynamic processes, i.e., solutions of the field equations. Thus, the field equations can be considered as constraints, i.e., the fields that satisfy the entropy inequality are constrained by the requirement that they must be solutions of all field equations, regardless of whether external sources are included or not. LIU [21] has shown that one may take account of such constraints to MÜLLER's entropy inequality explicitly by use of LAGRANGE multipliers. Thus, the entropy principle with the MÜLLER–LIU approach is more general than that of the COLEMAN–NOLL approach.

Mathematicians interested in continuum thermodynamics are generally not aware of the differences in the various postulations of the second law of thermodynamics. Virtually, the same is true for many continuum mechanicians. It appears that they have learned how COLEMAN–NOLL apply the CLAUSIUS–DUHEM inequality and use it as a "machine" to generate inferences with little contemplation whether the deduced results make physical sense. It was demonstrated in HUTTER, JÖHNK and SVENDSEN [14] that the emerging solutions of a constitutive mixture theory, if it is obtained by the COLEMAN–NOLL exploitation of the CLAUSIUS–DUHEM inequality [6], are extremely restricted. There exists no solution for a simple gravity-driven shearing flow of viscous constituents. However, in this case, if the mixture theory is derived from the MÜLLER–LIU approach of the entropy principle [30], this nonexistence of the solution can be avoided. This is tempting to favor the MÜLLER–LIU approach of the entropy principle over the COLEMAN–NOLL exploitation of the CLAUSIUS–DUHEM inequality on another account. The MÜLLER–LIU approach of the entropy principle has been widely employed to deduce restrictions on constitutive equations and postulate thermodynamically consistent constitutive laws in many research fields. Some examples can be found, e.g., in references [4, 7–10, 15, 16, 19, 20, 23, 28, 30–32, 35–38, 41].

In the present work, we intend to derive the constitutive equations of the excess material-dependent quantities in conservation laws of multiphase flows, associated with phase interfaces and three-phase contact line, by means of the entropy principle using the MÜLLER–LIU approach. Because in this approach all balance laws are considered as constraint conditions to the entropy inequality, its exploitation is much more complicated than, e.g., with the CLAUSIUS–DUHEM inequality. In the evaluation of the entropy principle, we assume that the LAGRANGE multiplier for the energy equation is inversely proportional to the temperature, and the material behavior is independent of the external supplies. Furthermore, when the phase interface is in thermodynamic equilibrium, the net heat flux and the net entropy flux from the neighboring bulk phases into the interface are assumed to vanish, and the temperatures of the neighboring bulk phases at the interface are the same. These assumptions are physically plausible and will be further argued when they occur later.

In Sect. 28.2, the conservation laws of multiphase flows for bulk, surface, and line quantities, which were derived in Chap. 27, are briefly presented. Further, the bulk, surface, and line entropy inequalities are formulated and the postulations of the MÜLLER–LIU exploitation are introduced. Section 28.3 is devoted to the derivation of the constitutive equations of the material-dependent quantities associated with phase interfaces from thermodynamic consideration of the second law together with the surface conservation laws of mass, momentum, and energy. The forms of the constitutive quantities, e.g., the interfacial stress tensor, the heat flux vector in the context of thermodynamic equilibrium are derived. The interfacial GIBBS equation and some extended relations for thermodynamic equilibrium are obtained. By the postulation of the nonequilibrium parts for the constitutive quantities, some restrictions for the emerging material parameters are also determined. In Sect. 28.4, the constitutive relations of the material-dependent quantities associated with the three-phase contact line are derived by obeying the line entropy inequality and simultaneously satisfying all line balance laws. In Sect. 28.6, this chapter is summarized.

28.2 Thermodynamic Processes in a Boltzmann-Type Mixture

28.2.1 Balance Relations

Starting with the standard postulates of continuum mechanics and the general global balance statement for an arbitrary physical quantity in a physical domain of three bulk phases $\mathfrak{B}^{(i)}$ $(i = 1, 2, 3)$ including singular material or nonmaterial phase interfaces $\mathfrak{S}^{(i)}$ $(i = 1, 2, 3)$ and a three-phase contact line $\mathfrak{C}$, see **Fig. 28.1**, In Chap. 27 (see also WANG and OBERLACK (2011) [39]), the local balance laws for physical quantities associated with the bulk phases, the phase interfaces, and the common three-phase contact line are presented. The obtained conservation equations of mass, momentum, and energy for bulk quantities in the phase subdomain $\mathfrak{B}^{(i)}$, (27.80), (27.96), and (27.133), surface quantities on the phase interfaces $\mathfrak{S}^{(i)}$, (27.83), (27.97), and (27.134), and line quantities at the three-phase contact line $\mathfrak{C}$, (27.84), (27.98), and (27.135), respectively, are listed with some slight reformulation as follows:
In the phase subdomain $\mathfrak{B}^{(i)}$:

$$\mathcal{R}^{(i)} := \frac{\mathrm{d}\rho^{(i)}}{\mathrm{d}t} + \rho^{(i)}\nabla\cdot\boldsymbol{v}^{(i)} = 0, \tag{28.1}$$

$$\boldsymbol{\mathcal{M}}^{(i)} := \rho^{(i)}\frac{\mathrm{d}\boldsymbol{v}^{(i)}}{\mathrm{d}t} - \nabla\cdot\boldsymbol{T}^{(i)} - \rho^{(i)}\boldsymbol{g} = 0, \tag{28.2}$$

$$\mathcal{E}^{(i)} := \rho^{(i)}\frac{\mathrm{d}u^{(i)}}{\mathrm{d}t} + \nabla\cdot\boldsymbol{q}^{(i)} - \mathrm{tr}\left(\boldsymbol{T}^{(i)}\left(\nabla\boldsymbol{v}^{(i)}\right)\right) - \rho^{(i)}r^{(i)} = 0, \tag{28.3}$$

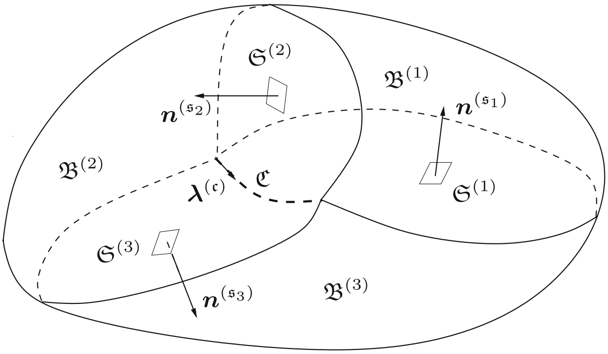

Fig. 28.1 Physical domain $\mathfrak{B}$ consisting of three-phase subdomains $\mathfrak{B}^{(i)}$ $(i = 1, 2, 3)$ with three-phase interfaces $\mathfrak{S}^{(i)}$ $(i = 1, 2, 3)$ and a three-phase contact line $\mathfrak{C}$, from WANG et al. [40]

on the phase interface $\mathfrak{S}^{(i)}$:

$$\begin{aligned}
\mathcal{R}^{(\mathfrak{s}_i)} :=& \frac{\mathrm{d}^{(\mathfrak{s}_i)}\rho^{(\mathfrak{s}_i)}}{\mathrm{d}t} + \rho^{(\mathfrak{s}_i)}\nabla^{(\mathfrak{s}_i)}\cdot\boldsymbol{v}^{(\mathfrak{s}_i)} + \rho^{(\mathfrak{s}_i)}H^{(\mathfrak{s}_i)}\left(\left(\boldsymbol{w}^{(\mathfrak{s}_i)}-\boldsymbol{v}^{(\mathfrak{s}_i)}\right)\cdot\boldsymbol{n}^{(\mathfrak{s}_i)}\right)\\
&-\llbracket\rho\left(\boldsymbol{w}^{(\mathfrak{s})}-\boldsymbol{v}\right)\cdot\boldsymbol{n}^{(\mathfrak{s})}\rrbracket^{(i)}=0, && (28.4)\\
\boldsymbol{\mathcal{M}}^{(\mathfrak{s}_i)} :=& \rho^{(\mathfrak{s}_i)}\frac{\mathrm{d}^{(\mathfrak{s}_i)}\boldsymbol{v}^{(\mathfrak{s}_i)}}{\mathrm{d}t} - \nabla^{(\mathfrak{s}_i)}\cdot\boldsymbol{T}^{(\mathfrak{s}_i)} + H^{(\mathfrak{s}_i)}\left(\boldsymbol{T}^{(\mathfrak{s}_i)}\cdot\boldsymbol{n}^{(\mathfrak{s}_i)}\right) - \rho^{(\mathfrak{s}_i)}\boldsymbol{g}\\
&-\llbracket\rho\left(\boldsymbol{v}-\boldsymbol{v}^{(\mathfrak{s})}\right)\left(\boldsymbol{w}^{(\mathfrak{s})}-\boldsymbol{v}\right)\cdot\boldsymbol{n}^{(\mathfrak{s})}+\boldsymbol{T}\cdot\boldsymbol{n}^{(\mathfrak{s})}\rrbracket^{(i)}=0, && (28.5)\\
\mathcal{E}^{(\mathfrak{s}_i)} :=& \rho^{(\mathfrak{s}_i)}\frac{\mathrm{d}^{(\mathfrak{s}_i)}u^{(\mathfrak{s}_i)}}{\mathrm{d}t} + \nabla^{(\mathfrak{s}_i)}\cdot\boldsymbol{q}^{(\mathfrak{s}_i)} - \operatorname{tr}\left(\boldsymbol{T}^{(\mathfrak{s}_i)}\left(\nabla^{(\mathfrak{s}_i)}\boldsymbol{v}^{(\mathfrak{s}_i)}\right)\right)\\
&- H^{(\mathfrak{s}_i)}(\boldsymbol{q}^{(\mathfrak{s}_i)}\cdot\boldsymbol{n}^{(\mathfrak{s}_i)}) - \rho^{(\mathfrak{s}_i)}r^{(\mathfrak{s}_i)}\\
&-\llbracket\rho\left(\left(u-u^{(\mathfrak{s})}\right)+\tfrac{1}{2}\left(\boldsymbol{v}-\boldsymbol{v}^{(\mathfrak{s})}\right)\cdot\left(\boldsymbol{v}-\boldsymbol{v}^{(\mathfrak{s})}\right)\right)\,\left(\left(\boldsymbol{w}^{(\mathfrak{s})}-\boldsymbol{v}\right)\cdot\boldsymbol{n}^{(\mathfrak{s})}\right)\\
&-\boldsymbol{q}\cdot\boldsymbol{n}^{(\mathfrak{s})}+\left(\boldsymbol{T}\left(\boldsymbol{v}-\boldsymbol{v}^{(\mathfrak{s})}\right)\right)\cdot\boldsymbol{n}^{(\mathfrak{s})}\rrbracket^{(i)}=0, && (28.6)
\end{aligned}$$

along the three-phase contact line $\mathfrak{C}$:

$$\begin{aligned}
\mathcal{R}^{(\mathfrak{c})} :=& \frac{\mathrm{d}^{(\mathfrak{c})}\rho^{(\mathfrak{c})}}{\mathrm{d}t} + \rho^{(\mathfrak{c})}\nabla^{(\mathfrak{c})}\cdot\boldsymbol{v}^{(\mathfrak{c})} + \rho^{(\mathfrak{c})}\kappa^{(\mathfrak{c})}\left(\left(\boldsymbol{w}^{(\mathfrak{c})}-\boldsymbol{v}^{(\mathfrak{c})}\right)\cdot\boldsymbol{n}^{(\mathfrak{c})}\right)\\
&+\sum_{i=1}^{3}\left(\rho^{(\mathfrak{s}_i)}\left(\boldsymbol{w}^{(\mathfrak{c})}-\boldsymbol{v}^{(\mathfrak{s}_i)}\right)\cdot\boldsymbol{s}^{(i)}\right)=0, && (28.7)\\
\boldsymbol{\mathcal{M}}^{(\mathfrak{c})} :=& \rho^{(\mathfrak{c})}\frac{\mathrm{d}^{(\mathfrak{c})}\boldsymbol{v}^{(\mathfrak{c})}}{\mathrm{d}t} - \nabla^{(\mathfrak{c})}\cdot\boldsymbol{T}^{(\mathfrak{c})} + \kappa^{(\mathfrak{c})}\left(\boldsymbol{T}^{(\mathfrak{c})}\cdot\boldsymbol{n}^{(\mathfrak{c})}\right) - \rho^{(\mathfrak{c})}\boldsymbol{g}\\
&+\sum_{i=1}^{3}\left(\rho^{(\mathfrak{s}_i)}\left(\boldsymbol{v}^{(\mathfrak{s}_i)}-\boldsymbol{v}^{(\mathfrak{c})}\right)\left(\boldsymbol{w}^{(\mathfrak{c})}-\boldsymbol{v}^{(\mathfrak{s}_i)}\right)\cdot\boldsymbol{s}^{(i)}+\boldsymbol{T}^{(\mathfrak{s}_i)}\cdot\boldsymbol{s}^{(i)}\right)\\
=&\, 0, && (28.8)\\
\mathcal{E}^{(\mathfrak{c})} :=& \rho^{(\mathfrak{c})}\frac{\mathrm{d}^{(\mathfrak{c})}u^{(\mathfrak{c})}}{\mathrm{d}t} + \nabla^{(\mathfrak{c})}\cdot\boldsymbol{q}^{(\mathfrak{c})} - \operatorname{tr}\left(\boldsymbol{T}^{(\mathfrak{c})}\left(\nabla^{(\mathfrak{c})}\boldsymbol{v}^{(\mathfrak{c})}\right)\right) - \kappa^{(\mathfrak{c})}\left(\boldsymbol{q}^{(\mathfrak{c})}\cdot\boldsymbol{n}^{(\mathfrak{c})}\right)\\
&+\sum_{i=1}^{3}\left(\rho^{(\mathfrak{s}_i)}\left(\left(u^{(\mathfrak{s}_i)}-u^{(\mathfrak{c})}\right)+\tfrac{1}{2}\left(\boldsymbol{v}^{(\mathfrak{s}_i)}-\boldsymbol{v}^{(\mathfrak{c})}\right)\cdot\left(\boldsymbol{v}^{(\mathfrak{s}_i)}-\boldsymbol{v}^{(\mathfrak{c})}\right)\right)\right.\\
&\left.\cdot\left(\left(\boldsymbol{w}^{(\mathfrak{c})}-\boldsymbol{v}^{(\mathfrak{s}_i)}\right)\cdot\boldsymbol{s}^{(i)}\right)-\boldsymbol{q}^{(\mathfrak{s}_i)}\cdot\boldsymbol{s}^{(i)}+\left(\boldsymbol{T}^{(\mathfrak{s}_i)}\left(\boldsymbol{v}^{(\mathfrak{s}_i)}-\boldsymbol{v}^{(\mathfrak{c})}\right)\right)\cdot\boldsymbol{s}^{(i)}\right)\\
&-\rho^{(\mathfrak{c})}r^{(\mathfrak{c})}=0. && (28.9)
\end{aligned}$$

In the conservation laws (28.1)–(28.9), the superscript (i) indicates the bulk quantities in the phase subdomain $\mathfrak{B}^{(i)}$, the superscript $(\mathfrak{s}_i)$ denotes the surface quantities on the phase interface $\mathfrak{S}^{(i)}$ separating the phase subdomains $\mathfrak{B}^{(i-1)}$ and $\mathfrak{B}^{(i)}$, and the superscript $(\mathfrak{c})$ stands for the line quantities in the three-phase contact line $\mathfrak{C}$. The emerging physical quantities have the following meanings: ρ is the (bulk, surface, line) mass density, $\boldsymbol{v}$ the material velocity, $\boldsymbol{T}$ the stress tensor, u the internal energy, $\boldsymbol{q}$ the heat flux vector, $\boldsymbol{g}$ the body force per unit mass, r the energy supply/source per unit mass, $\boldsymbol{w}^{(\mathfrak{s}_i)}$ and $\boldsymbol{w}^{(\mathfrak{c})}$ indicate the velocities of the interface $\mathfrak{S}^{(i)}$ and the contact line $\mathfrak{C}$, respectively, $\boldsymbol{n}^{(\mathfrak{s}_i)}$ the unit normal vector of the interface $\mathfrak{S}^{(i)}$ pointing into the domain $\mathfrak{B}^{(i)}$, $\boldsymbol{n}^{(\mathfrak{c})}$ the unit principal normal to the contact line, $\boldsymbol{s}^{(i)}$ the unit vector tangent to the surface $\mathfrak{S}^{(i)}$, normal and pointing to the contact line $\mathfrak{C}$. $H^{(\mathfrak{s}_i)}$ is the total surface curvature of the interface $\mathfrak{S}^{(i)}$ ($H^{(\mathfrak{s}_i)} = \nabla^{(\mathfrak{s}_i)} \cdot \boldsymbol{n}^{(\mathfrak{s}_i)}$), and $\kappa^{(\mathfrak{c})}$ denotes the normal curvature of the contact line ($\kappa^{(\mathfrak{c})} = \nabla^{(\mathfrak{c})} \cdot \boldsymbol{n}^{(\mathfrak{c})}$). $[\![\mathcal{G}]\!]^{(i)} = \mathcal{G}^{(i)} - \mathcal{G}^{(i-1)}$ denotes the jump of the quantity $\mathcal{G}$ across the interface $\mathfrak{S}^{(i)}$ (if $i - 1 = 0$, it is set $i - 1 \equiv 3$).

The surface and line gradient operators, $\nabla^{(\mathfrak{s}_i)}$ and $\nabla^{(\mathfrak{c})}$ are defined, respectively, by

$$\begin{aligned}\nabla^{(\mathfrak{s}_i)} &= [\boldsymbol{I} - \boldsymbol{n}^{(\mathfrak{s}_i)} \otimes \boldsymbol{n}^{(\mathfrak{s}_i)}] \cdot \nabla \equiv \boldsymbol{I}^{(\mathfrak{s}_i)} \cdot \nabla,\\ \nabla^{(\mathfrak{c})} &= (\boldsymbol{\lambda}^{(\mathfrak{c})} \otimes \boldsymbol{\lambda}^{(\mathfrak{c})}) \cdot \nabla \equiv \boldsymbol{I}^{(\mathfrak{c})} \cdot \nabla,\end{aligned} \tag{28.10}$$

where $\boldsymbol{\lambda}^{(\mathfrak{c})}$ is the unit vector tangent to the contact line, while $\boldsymbol{I}^{(\mathfrak{s}_i)} \equiv \boldsymbol{I} - \boldsymbol{n}^{(\mathfrak{s}_i)} \otimes \boldsymbol{n}^{(\mathfrak{s}_i)}$ and $\boldsymbol{I}^{(\mathfrak{c})} \equiv \boldsymbol{\lambda}^{(\mathfrak{c})} \otimes \boldsymbol{\lambda}^{(\mathfrak{c})}$ are the surface and line projection tensors, respectively.

The bulk, surface, and line time derivatives are defined by

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t} &= \frac{\partial}{\partial t} + \boldsymbol{v}^{(i)} \cdot \nabla,\\ \frac{\mathrm{d}^{(\mathfrak{s}_i)}}{\mathrm{d}t} &= \frac{\delta^{(\mathfrak{s}_i)}}{\delta t} + \boldsymbol{v}^{(\mathfrak{s}_i)} \cdot \nabla^{(\mathfrak{s}_i)},\\ \frac{\mathrm{d}^{(\mathfrak{c})}}{\mathrm{d}t} &= \frac{\delta^{(\mathfrak{c})}}{\delta t} + \boldsymbol{v}^{(\mathfrak{c})} \cdot \nabla^{(\mathfrak{c})},\end{aligned} \tag{28.11}$$

where the normal surface time derivative $\delta^{(\mathfrak{s}_i)}/\delta t$ indicates the time derivative for a given point on the surface following the normal trajectory of the surface, while the normal line time derivative $\delta^{(\mathfrak{c})}/\delta t$ denotes the time derivative following the normal trajectory of the moving curve. It can be easily shown that if the interface $\mathfrak{S}^{(i)}$ and the contact line $\mathfrak{C}$ are material, the surface and line time derivatives, $\mathrm{d}^{(\mathfrak{s}_i)}/\mathrm{d}t$ and $\mathrm{d}^{(\mathfrak{c})}/\mathrm{d}t$, coincide with the corresponding material time derivative $\mathrm{d}/\mathrm{d}t$. All these quantities have already been introduced and explained in Chap. 27.

In the balance laws presented above, the dependent field quantities are the bulk, surface, and line stress tensors, $\boldsymbol{T}^{(i)}$, $\boldsymbol{T}^{(\mathfrak{s}_i)}$, and $\boldsymbol{T}^{(\mathfrak{c})}$, the bulk, surface, and line heat flux vectors, $\boldsymbol{q}^{(i)}$, $\boldsymbol{q}^{(\mathfrak{s}_i)}$ and $\boldsymbol{q}^{(\mathfrak{c})}$, as well as the bulk, surface, and line internal energy densities, $u^{(i)}$, $u^{(\mathfrak{s}_i)}$ and $u^{(\mathfrak{c})}$. They must be expressed as functional relations of the independent field variables, such as mass densities, velocities, temperature, etc. These functional relations are called constitutive relations or constitutive equations.

In most continuum thermodynamic theories, it is stipulated that the union of the balance laws and constitutive relations forms so-called field equations, which are conjectured to define a well-posed problem; in other words, with appropriate initial and boundary conditions these equations are supposed to yield unique functions of space and time for the field variables, at least for some finite nonzero interval of time. Any set of the independent fields that satisfies the equations is called a thermodynamic process. In reality, the constitutive relations are not arbitrary, they should obey universal physical principles, i.e., one can reduce the generality of these functions by relying upon these physical principles. The most important of these principles is the second law of thermodynamics, which we now introduce in the form of the entropy principle.

28.2.2 Entropy Principle

It is assumed that there exist an entropy density η, entropy flux $\boldsymbol{\phi}_\eta$, entropy production density π_η, and entropy supply density ζ_η, which obey a balance law. The second law of thermodynamics requires that the entropy production π_η should be nonnegative during a physical process; thus, the following inequality must be satisfied:

$$\pi_\eta := \mathcal{H}\left(\eta, \boldsymbol{\phi}_\eta\right) - \zeta_\eta \geq 0. \tag{28.12}$$

In this imbalance relation, $\mathcal{H}(\eta, \boldsymbol{\phi}_\eta)$ is a function of the entropy density η and the local flux of the entropy $\boldsymbol{\phi}_\eta$ and ζ_η is the entropy supply density. Moreover, unlike in previous chapters, we now denote the entropy density by η, since the various s's are here surface identities. Now, any process which satisfies (28.12) (via the constitutive relations) represents a so-called physically admissible process. The entropy inequality, however, need not hold for arbitrary fields, but only for thermodynamic processes, i.e., any acceptable solutions of the field equations via the constitutive assumptions. The working principle is therefore that all thermodynamic processes must satisfy (28.12) or all fields which satisfy field equations must in addition satisfy (28.12). We must point out that as long as η, $\boldsymbol{\phi}_\eta$, ζ_η are not related to any of the field quantities, the second law is an empty statement. Various second laws differ by the method how this link is made.

In the generalized CLAUSIUS–DUHEM inequality with the COLEMAN–NOLL approach, the flux and the supply of entropy are related *a priori* to the flux and supply of heat. And free sources are assumed for all balance equations except perhaps the balance of mass. In order to relax these assumptions, MÜLLER [24, 25] proposed an entropy principle in which the entropy and its flux are both *a priori* unrestricted constitutive quantities. LIU [21] introduced LAGRANGE multipliers to consider the influences of all balance laws on the entropy inequality, by which the exploitation of the general entropy inequality is much facilitated.

In the investigation of multiphase flows, for the bulk phase, the phase interface, and the three-phase contact line, the entropy inequality (28.12) can be written, respectively, as (see also (27.140), (27.141), and (27.142))

In the phase subdomain $\mathfrak{B}^{(i)}$:

$$\varPi^{(i)} = \rho^{(i)} \frac{\mathrm{d}\eta^{(i)}}{\mathrm{d}t} + \nabla \cdot \boldsymbol{\phi}_\eta^{(i)} - \rho^{(i)} \zeta_\eta^{(i)} \geq 0, \tag{28.13}$$

on the phase interface $\mathfrak{S}^{(i)}$:

$$\begin{aligned} \varPi^{(\mathfrak{s}_i)} = \rho^{(\mathfrak{s}_i)} & \frac{\mathrm{d}^{(\mathfrak{s}_i)}\eta^{(\mathfrak{s}_i)}}{\mathrm{d}t} + \nabla^{(\mathfrak{s}_i)} \cdot \boldsymbol{\phi}_\eta^{(\mathfrak{s}_i)} - H^{(\mathfrak{s}_i)} \left(\boldsymbol{\phi}_\eta^{(\mathfrak{s}_i)} \cdot \boldsymbol{n}^{(\mathfrak{s}_i)}\right) \\ & - \llbracket \rho(\eta - \eta^{(\mathfrak{s})})(\boldsymbol{w}^{(\mathfrak{s})} - \boldsymbol{v}) \cdot \boldsymbol{n}^{(\mathfrak{s})} - \boldsymbol{\phi}_\eta \cdot \boldsymbol{n}^{(\mathfrak{s})} \rrbracket^{(i)} \\ & - \rho^{(\mathfrak{s}_i)} \zeta_\eta^{(\mathfrak{s}_i)} \geq 0, \end{aligned} \tag{28.14}$$

along the three-phase contact line $\mathfrak{C}$:

$$\begin{aligned} \varPi^{(\mathfrak{c})} = \rho^{(\mathfrak{c})} & \frac{\mathrm{d}^{(\mathfrak{c})}\eta^{(\mathfrak{c})}}{\mathrm{d}t} + \nabla^{(\mathfrak{c})} \cdot \boldsymbol{\phi}_\eta^{(\mathfrak{c})} - \kappa^{(\mathfrak{c})} \left(\boldsymbol{\phi}_\eta^{(\mathfrak{c})} \cdot \boldsymbol{n}^{(\mathfrak{c})}\right) \\ & + \sum_{i=1}^{3} \left(\rho^{(\mathfrak{s}_i)} \left(\eta^{(\mathfrak{s}_i)} - \eta^{(\mathfrak{c})}\right) \left(\boldsymbol{w}^{(\mathfrak{c})} - \boldsymbol{v}^{(\mathfrak{s}_i)}\right) \cdot \boldsymbol{s}^{(i)} - \boldsymbol{\phi}_\eta^{(\mathfrak{s}_i)} \cdot \boldsymbol{s}^{(i)}\right) \\ & - \rho^{(\mathfrak{c})} \zeta_\eta^{(\mathfrak{c})} \geq 0. \end{aligned} \tag{28.15}$$

Here, $\eta^{(i)}$, $\eta^{(\mathfrak{s}_i)}$, $\eta^{(\mathfrak{c})}$ are the bulk, surface, and line entropy densities per unit mass, $\boldsymbol{\phi}_\eta^{(i)}$, $\boldsymbol{\phi}_\eta^{(\mathfrak{s}_i)}$, $\boldsymbol{\phi}_\eta^{(\mathfrak{c})}$ the bulk, surface, and line entropy fluxes, and $\zeta_\eta^{(i)}$, $\zeta_\eta^{(\mathfrak{s}_i)}$, $\zeta_\eta^{(\mathfrak{c})}$ are the bulk, surface, and line entropy supply densities per unit mass, respectively. $\varPi^{(i)}$, $\varPi^{(\mathfrak{s}_i)}$ and $\varPi^{(\mathfrak{c})}$ are entropy productions per unit volume in the phase $\mathfrak{B}^{(i)}$, per unit area on the phase interface $\mathfrak{S}^{(i)}$, and per unit length along the three-phase contact line $\mathfrak{C}$, respectively.

For a physically realizable process, the entropy inequality for the bulk phase $\mathfrak{B}^{(i)}$, (28.13), must be satisfied subject to the simultaneous satisfaction of the balance laws (28.1)–(28.3), while for the phase interface $\mathfrak{S}^{(i)}$, the entropy inequality (28.14) must hold subject to the simultaneous satisfaction of the balance laws (28.4)–(28.6), as well as for the three-phase contact line $\mathfrak{C}$ the entropy inequality (28.15) subject to the simultaneous satisfaction of the balance laws (28.7)–(28.9), respectively. The moment of momentum, which yields the symmetry of the peculiar stress tensors, is satisfied by postulating the constitutive relation accordingly, thus it is not considered as a constraint condition for the exploitation of the entropy inequality.

LIU [21] has shown that instead of fulfilling the entropy inequality for independent fields that are constrained by the balance laws one may extend the entropy inequality by subtracting from it the products of each constraining equation with a LAGRANGE multiplier and satisfying this extended inequality for unrestricted independent fields. For the investigated multiphase flows these extended entropy inequalities are

In the phase subdomain $\mathfrak{B}^{(i)}$:

$$\Pi^{(i)} - (1/\Theta^{(i)})\Lambda_\rho^{(i)}\mathcal{R}^{(i)} - (1/\Theta^{(i)})\boldsymbol{\Lambda}_v^{(i)} \cdot \boldsymbol{\mathcal{M}}^{(i)} - \Lambda_\varepsilon^{(i)}\mathcal{E}^{(i)} \geq 0, \tag{28.16}$$

on the phase interface $\mathfrak{S}^{(i)}$:

$$\Pi^{(\mathfrak{s}_i)} - (1/\Theta^{(\mathfrak{s}_i)})\Lambda_\rho^{(\mathfrak{s}_i)}\mathcal{R}^{(\mathfrak{s}_i)} - (1/\Theta^{(\mathfrak{s}_i)})\boldsymbol{\Lambda}_v^{(\mathfrak{s}_i)} \cdot \boldsymbol{\mathcal{M}}^{(\mathfrak{s}_i)} - \Lambda_\varepsilon^{(\mathfrak{s}_i)}\mathcal{E}^{(\mathfrak{s}_i)} \geq 0, \tag{28.17}$$

at the three-phase contact line $\mathfrak{C}$:

$$\Pi^{(\mathrm{c})} - (1/\Theta^{(\mathrm{c})})\Lambda_\rho^{(\mathrm{c})}\mathcal{R}^{(\mathrm{c})} - (1/\Theta^{(\mathrm{c})})\boldsymbol{\Lambda}_v^{(\mathrm{c})} \cdot \boldsymbol{\mathcal{M}}^{(\mathrm{c})} - \Lambda_\varepsilon^{(\mathrm{c})}\mathcal{E}^{(\mathrm{c})} \geq 0, \tag{28.18}$$

where the quantities $\Lambda_\rho^{(i)}$, $\boldsymbol{\Lambda}_v^{(i)}$, $\Lambda_\varepsilon^{(i)}$, and $\Lambda_\rho^{(\mathfrak{s}_i)}$, $\boldsymbol{\Lambda}_v^{(\mathfrak{s}_i)}$, $\Lambda_\varepsilon^{(\mathfrak{s}_i)}$, as well as $\Lambda_\rho^{(\mathrm{c})}$, $\boldsymbol{\Lambda}_v^{(\mathrm{c})}$, $\Lambda_\varepsilon^{(\mathrm{c})}$ represent the LAGRANGE multipliers associated with the constraints placed on the entropy balances by the other balance relations. For convenience the factors $1/\Theta^{(i)}$, $1/\Theta^{(\mathfrak{s}_i)}$ and $1/\Theta^{(\mathrm{c})}$ (Θ is interpreted as absolute temperature) have been extracted above from the LAGRANGE multipliers referring to the mass and momentum balance relations, respectively. These LAGRANGE multipliers may be constitutive quantities and given by some constitutive relations, see, however, LIU [21] or HUTTER [12], for the more general situation.

In the above point, the inequalities (28.16)–(28.18) hold for arbitrary bulk, surface, and line fields.

To further exploit the entropy inequalities (28.16)–(28.18), the following plausible assumptions are taken into consideration:

- The LAGRANGE multiplier for the energy equation is inversely proportional to the temperature

$$\Lambda_\varepsilon^{(i)} = \frac{1}{\Theta^{(i)}}, \quad \Lambda_\varepsilon^{(\mathfrak{s}_i)} = \frac{1}{\Theta^{(\mathfrak{s}_i)}}, \quad \Lambda_\varepsilon^{(\mathrm{c})} = \frac{1}{\Theta^{(\mathrm{c})}}. \tag{28.19}$$

- The material behavior is independent of the supplies, i.e., that all external source terms balance, viz.,

$$\begin{aligned} &\Theta^{(i)}\rho^{(i)}\zeta_\eta^{(i)} - \boldsymbol{\Lambda}_v^{(i)} \cdot \rho^{(i)}\boldsymbol{g} - \rho^{(i)}r^{(i)} = 0, \\ &\Theta^{(\mathfrak{s}_i)}\rho^{(\mathfrak{s}_i)}\zeta_\eta^{(\mathfrak{s}_i)} - \boldsymbol{\Lambda}_v^{(\mathfrak{s}_i)} \cdot \rho^{(\mathfrak{s}_i)}\boldsymbol{g} - \rho^{(\mathfrak{s}_i)}r^{(\mathfrak{s}_i)} = 0, \\ &\Theta^{(\mathrm{c})}\rho^{(\mathrm{c})}\zeta_\eta^{(\mathrm{c})} - \boldsymbol{\Lambda}_v^{(\mathrm{c})} \cdot \rho^{(\mathrm{c})}\boldsymbol{g} - \rho^{(\mathrm{c})}r^{(\mathrm{c})} = 0, \end{aligned} \tag{28.20}$$

  which serve as identities for the entropy supplies.

The assumption of the LAGRANGE multiplier $\Lambda_\varepsilon^{(i)}$ for the bulk phase $\mathfrak{B}^{(i)}$, $(28.19)_1$, is not reasonable in cases when the time derivative of the temperature $(\mathrm{d}\Theta^{(i)}/\mathrm{d}t)$ should also be an independent variable in the constitutive functions. As we will not include such a dependence the a priori assignment is justifiable on the basis that LIU and MÜLLER have proved it in [22]. It was based on the empirical assumption that there exists an impermeable ideal wall where the entropy production vanishes so that the entropy flux into the wall on one side exits on the other side as a flux out of the wall. On ideal walls the temperature is also assumed continuous. Hence, condition $(28.19)_1$ can be derived (see, e.g., LIU [22], MÜLLER [27]).

To postulate the LAGRANGE multiplier $\Lambda_\varepsilon^{(\mathfrak{s}_i)}$ for the phase interface $\mathfrak{S}^{(i)}$, $(28.19)_2$, one can extend MÜLLER's postulation of the existence of an ideal wall for the bulk phase [26] to the interface, by assuming that there exists an ideal heat conducting singular quasi-material line separating two different surface materials across which the normal jump of the entropy flux vanishes when the temperature and the normal component of the heat flux are continuous. With this assumption one can obtain from the evaluation of the entropy inequality that the multiplier $\Lambda_\varepsilon^{(\mathfrak{s}_i)}$ must be independent of the particular phase interface material and be a universal function of the surface temperature in the expression of $(28.19)_2$ if the time derivative of temperature is not included in the constitutive variables [1, 2, 13].

For the LAGRANGE multiplier $\Lambda_\varepsilon^{(\mathfrak{c})}$ associated with the line energy equation we directly employ the postulation $(28.19)_3$ without any further explanation although it may be obtained if one extends MÜLLER's assumption also to the line quantities.

Concerning assumption (28.20), when MÜLLER [24] proposed the general entropy principle in which the entropy and its flux were both constitutive quantities, *a priori* unrestricted, he argued that, since constitutive properties of a material should not depend on external supplies in exploiting constitutive restrictions, it suffices to consider only supply free bodies. Relation (28.20) may be considered as an extension of MÜLLER's entropy principle when LIU [21] introduced LAGRANGE multipliers by which the exploitation of the general entropy inequality was much improved. Both assumptions, namely, supply free bodies expressed in equations (28.20), are a result of the fact that the material behavior is independent of the supplies.

Further, we will introduce the HELMHOLTZ free energies for bulk phases, interfaces and the contact line

$$\begin{aligned}
\psi^{(i)} &= u^{(i)} - \Theta^{(i)}\eta^{(i)}, \\
\psi^{(\mathfrak{s}_i)} &= u^{(\mathfrak{s}_i)} - \Theta^{(\mathfrak{s}_i)}\eta^{(\mathfrak{s}_i)}, \\
\psi^{(\mathfrak{c})} &= u^{(\mathfrak{c})} - \Theta^{(\mathfrak{c})}\eta^{(\mathfrak{c})}.
\end{aligned} \tag{28.21}$$

In this chapter, we will not intend to discuss the exploitation of the entropy inequality for the bulk phase $\mathfrak{B}^{(i)}$, (28.16), which has been excessively investigated for various materials. Some examples have been given in Chap. 18 in Vol. 2 of this treatise. For instance, for an isotropic, viscous, heat conducting fluid, the constitutive functions for the stress $\boldsymbol{T}^{(i)}$, the heat flux $\boldsymbol{q}^{(i)}$, the internal energy $u^{(i)}$ and the entropy flux $\boldsymbol{\phi}_\eta^{(i)}$ obeying the entropy principle take the forms (see, e.g., HUTTER and JÖHNK [15])

$$\begin{aligned}
\boldsymbol{T}^{(i)} &= -\, p^{(i)}\boldsymbol{I} + \alpha_0^{(i)}\boldsymbol{I} + \alpha_1^{(i)}\boldsymbol{D}^{(i)} + \alpha_2^{(i)}\left(\boldsymbol{D}^{(i)}\right)^2, \\
\boldsymbol{q}^{(i)} &= -\, \kappa^{(i)}\operatorname{grad}\Theta^{(i)}, \\
u^{(i)} &= \hat{u}^{(i)}\left(\Theta^{(i)}\right), \\
\boldsymbol{\phi}_\eta^{(i)} &= \boldsymbol{q}^{(i)}/\Theta^{(i)},
\end{aligned} \tag{28.22}$$

where

$$\begin{aligned}\alpha_j^{(i)} &= \hat{\alpha}_j^{(i)}(\rho^{(i)}, \Theta^{(i)}, I_{\boldsymbol{D}^{(i)}}, II_{\boldsymbol{D}^{(i)}}, III_{\boldsymbol{D}^{(i)}}), \quad (j = 0, 1, 2),\\ &\hat{\alpha}_j^{(i)}(\rho^{(i)}, \Theta^{(i)}, 0, 0, 0) = 0,\\ \kappa^{(i)} &= \hat{\kappa}^{(i)}\left(\rho^{(i)}, \Theta^{(i)}, |\mathrm{grad}\,\Theta^{(i)}|\right),\end{aligned}$$

and $I_{\boldsymbol{D}^{(i)}}$, $II_{\boldsymbol{D}^{(i)}}$ and $III_{\boldsymbol{D}^{(i)}}$ denote the first, second, and third invariants of the symmetric part of the velocity gradient ($\boldsymbol{D}^{(i)} = \mathrm{sym}\left(\mathrm{grad}\,\boldsymbol{v}^{(i)}\right)$), respectively. For an incompressible fluid, the pressure $p^{(i)}$ is an independent field quantity determined by the conservation laws. In case of a compressible fluid, $p^{(i)}$ is given by an equation of state $p^{(i)} = \hat{p}^{(i)}\left(\rho^{(i)}, \Theta^{(i)}\right)$. Moreover, the GIBBS relation takes the form (see (18.70) in Chap. 18 in Vol. 2 of this treatise [18], adjusted to the notation in this chapter),

$$\mathrm{d}\eta^{(i)} = \frac{1}{\Theta^{(i)}}\left(\mathrm{d}u^{(i)} + p^{(i)}\mathrm{d}\left(\frac{1}{\rho^{(i)}}\right)\right). \tag{28.23}$$

The linear forms of (28.22) for the stress $\boldsymbol{T}^{(i)}$ and the heat flux $\boldsymbol{q}^{(i)}$ correspond to the constitutive equations for NEWTONian fluids in the form

$$\begin{aligned}\boldsymbol{T}^{(i)} &= (-p^{(i)} + \lambda^{(i)})\boldsymbol{I} + 2\mu^{(i)}\boldsymbol{D}^{(i)},\\ \boldsymbol{q}^{(i)} &= -\kappa^{(i)}\mathrm{grad}\,\Theta^{(i)},\end{aligned} \tag{28.24}$$

where $\lambda^{(i)}$, $\mu^{(i)}$, and $\kappa^{(i)}$ are functions only of $\rho^{(i)}$ and $\Theta^{(i)}$. According to the minimum condition of the entropy production in thermodynamic equilibrium, the following restrictions on these material parameters must hold (see, e.g., HUTTER and JÖHNK [15], SPURK [29], HUTTER and WANG, Chap. 7 of Vol. 1 of this treatise [17])

$$\lambda^{(i)} + \tfrac{2}{3}\mu^{(i)} \geq 0, \quad \mu^{(i)} \geq 0, \quad \kappa^{(i)} \geq 0. \tag{28.25}$$

The entropy inequalities, (28.17) on the phase interface and (28.18) at the three-phase contact line, respectively, will be used to investigate the postulates for the constitutive quantities emerging in the conservation laws on the interface $\mathfrak{S}^{(i)}$ and at the contact line $\mathfrak{C}$ in the following sections.

28.3 Constitutive Relations for the Phase Interface

The basic objective of thermodynamics on singular phase interfaces is the determination of the basic fields of surface density, motion, and surface temperature. These can be determined from the balance equations (28.4)–(28.6), provided the surface-dependent fields $\boldsymbol{T}^{(\mathfrak{s}_i)}$, $\boldsymbol{q}^{(\mathfrak{s}_i)}$ and $u^{(\mathfrak{s}_i)}$ are related in a "materially dependent manner" to the basic fields. Such relations are called constitutive equations for phase interfaces. They must reflect the peculiarities of the phase-change interface in nonequilibrium. We recall that the purpose of the entropy principle is to derive restrictions upon the constitutive relations. The entropy and its flux as well as the LAGRANGE multipliers must be considered as auxiliary quantities. In this section, we evaluate the entropy inequality (28.17) on the interface $\mathfrak{S}^{(i)}$ for a given constitutive class, which may be suitable for a liquid–fluid interface.

28.3.1 Constitutive Assumptions and Restrictions

To investigate the material behaviors of an interface, we must first postulate its constitutive class, in which a dependent variable is expressed as a function of its independent variables (and not a functional). The constitutive class fathomed by this assumption may be very large and should be restricted by thermodynamic principles. In some complicated cases, a constitutive relation may be expressed as a differential equation among some variables [7, 10]. Such a setting will not be discussed in this chapter.

We consider the phase interface $\mathfrak{S}^{(i)}$ consisting of heat conducting viscous materials whose response is characterized by constitutive functions of the form

$$\begin{aligned}\mathcal{S} = \hat{\mathcal{S}}\big(&\rho^{(\mathfrak{s}_i)}, \nabla^{(\mathfrak{s}_i)}\rho^{(\mathfrak{s}_i)}, \Theta^{(\mathfrak{s}_i)}, \nabla^{(\mathfrak{s}_i)}\Theta^{(\mathfrak{s}_i)},\\ &\nabla^{(\mathfrak{s}_i)}\boldsymbol{v}^{(\mathfrak{s}_i)}, H^{(\mathfrak{s}_i)}, \boldsymbol{v}^{(\mathfrak{s}_i)}, \boldsymbol{v}^{(i)}, \boldsymbol{v}^{(i-1)}, \boldsymbol{w}^{(\mathfrak{s}_i)}\big),\end{aligned}\tag{28.26}$$

for the material variables

$$\mathcal{S} \in \left\{\boldsymbol{T}^{(\mathfrak{s}_i)}, \boldsymbol{q}^{(\mathfrak{s}_i)}, \phi_\eta^{(\mathfrak{s}_i)}, \psi^{(\mathfrak{s}_i)}, \eta^{(\mathfrak{s}_i)}\right\}.\tag{28.27}$$

Invoking the principle of material objectivity, which requires that the material response is independent of the velocity and skew-symmetric part of the velocity gradient, equation (28.26) reduces to

$$\begin{aligned}\mathcal{S} = \hat{\mathcal{S}}\ \big(&\rho^{(\mathfrak{s}_i)}, \nabla^{(\mathfrak{s}_i)}\rho^{(\mathfrak{s}_i)}, \Theta^{(\mathfrak{s}_i)}, \nabla^{(\mathfrak{s}_i)}\Theta^{(\mathfrak{s}_i)},\\ &\boldsymbol{D}^{(\mathfrak{s}_i)}, H^{(\mathfrak{s}_i)}, \boldsymbol{W}_{\mathfrak{s}}, \boldsymbol{W}_{\mathfrak{s}}^{+}, \boldsymbol{W}_{\mathfrak{s}}^{-}\big),\end{aligned}\tag{28.28}$$

where $\boldsymbol{D}^{(\mathfrak{s}_i)} = \frac{1}{2}\left(\nabla^{(\mathfrak{s}_i)}\boldsymbol{v}^{(\mathfrak{s}_i)} + (\nabla^{(\mathfrak{s}_i)}\boldsymbol{v}^{(\mathfrak{s}_i)})^T\right)$ is the surface stretching tensor and $\boldsymbol{W}_{\mathfrak{s}}^{+} = \boldsymbol{w}^{(\mathfrak{s}_i)} - \boldsymbol{v}^{(i)}$, $\boldsymbol{W}_{\mathfrak{s}}^{-} = \boldsymbol{w}^{(\mathfrak{s}_i)} - \boldsymbol{v}^{(i-1)}$, and $\boldsymbol{W}_{\mathfrak{s}} = \boldsymbol{w}^{(\mathfrak{s}_i)} - \boldsymbol{v}^{(\mathfrak{s}_i)}$.

These constitutive equations must satisfy the entropy inequality (28.17), which can be rewritten, by inserting the conservation equations (28.4)–(28.6) and employing the relations in $(28.19)_2$, $(28.20)_2$, and $(28.21)_2$, as

$$
\begin{aligned}
&\Theta^{(\mathfrak{s}_i)}\Pi^{(\mathfrak{s}_i)}\\
=&-\rho^{(\mathfrak{s}_i)}\frac{\mathrm{d}^{(\mathfrak{s}_i)}\psi^{(\mathfrak{s}_i)}}{\mathrm{d}t}-\rho^{(\mathfrak{s}_i)}\eta^{(\mathfrak{s}_i)}\frac{\mathrm{d}^{(\mathfrak{s}_i)}\Theta^{(\mathfrak{s}_i)}}{\mathrm{d}t}+\Theta^{(\mathfrak{s}_i)}\nabla^{(\mathfrak{s}_i)}\cdot\boldsymbol{\phi}_\eta^{(\mathfrak{s}_i)}\\
&-\Theta^{(\mathfrak{s}_i)}H^{(\mathfrak{s}_i)}\left(\boldsymbol{\phi}_\eta^{(\mathfrak{s}_i)}\cdot\boldsymbol{n}^{(\mathfrak{s}_i)}\right)-\Lambda_\rho^{(\mathfrak{s}_i)}\frac{\mathrm{d}\rho^{(\mathfrak{s}_i)}}{\mathrm{d}t}-\Lambda_\rho^{(\mathfrak{s}_i)}\rho^{(\mathfrak{s}_i)}\nabla^{(\mathfrak{s}_i)}\cdot\boldsymbol{v}^{(\mathfrak{s}_i)}\\
&-\Lambda_\rho^{(\mathfrak{s}_i)}\rho^{(\mathfrak{s}_i)}H^{(\mathfrak{s}_i)}\left(\left(\boldsymbol{w}^{(\mathfrak{s}_i)}-\boldsymbol{v}^{(\mathfrak{s}_i)}\right)\cdot\boldsymbol{n}^{(\mathfrak{s}_i)}\right)-\rho^{(\mathfrak{s}_i)}\boldsymbol{\Lambda}_{\boldsymbol{v}}^{(\mathfrak{s}_i)}\cdot\frac{\mathrm{d}^{(\mathfrak{s}_i)}\boldsymbol{v}^{(\mathfrak{s}_i)}}{\mathrm{d}t}\\
&+\boldsymbol{\Lambda}_{\boldsymbol{v}}^{(\mathfrak{s}_i)}\nabla^{(\mathfrak{s}_i)}\cdot\boldsymbol{T}^{(\mathfrak{s}_i)}-\boldsymbol{\Lambda}_{\boldsymbol{v}}^{(\mathfrak{s}_i)}\cdot\left(H^{(\mathfrak{s}_i)}\left(\boldsymbol{T}^{(\mathfrak{s}_i)}\cdot\boldsymbol{n}^{(\mathfrak{s}_i)}\right)\right)-\nabla^{(\mathfrak{s}_i)}\cdot\boldsymbol{q}^{(\mathfrak{s}_i)}\\
&+\operatorname{tr}\left(\boldsymbol{T}^{(\mathfrak{s}_i)}\left(\nabla^{(\mathfrak{s}_i)}\boldsymbol{v}^{(\mathfrak{s}_i)}\right)\right)+H^{(\mathfrak{s}_i)}\left(\boldsymbol{q}^{(\mathfrak{s}_i)}\cdot\boldsymbol{n}^{(\mathfrak{s}_i)}\right)\\
&-\Theta^{(\mathfrak{s}_i)}[\![\rho\left(\eta-\eta^{(\mathfrak{s})}\right)\left(\boldsymbol{w}^{(\mathfrak{s})}-\boldsymbol{v}\right)\cdot\boldsymbol{n}^{(\mathfrak{s})}\ \ -\boldsymbol{\phi}_\eta\cdot\boldsymbol{n}^{(\mathfrak{s})}]\!]^{(i)}\\
&+\Lambda_\rho^{(\mathfrak{s}_i)}[\![\rho\left(\boldsymbol{w}^{(\mathfrak{s})}-\boldsymbol{v}\right)\cdot\boldsymbol{n}^{(\mathfrak{s})}]\!]^{(i)}\\
&+\boldsymbol{\Lambda}_{\boldsymbol{v}}^{(\mathfrak{s}_i)}\cdot[\![\rho\left(\boldsymbol{v}-\boldsymbol{v}^{(\mathfrak{s})}\right)\left(\boldsymbol{w}^{(\mathfrak{s})}-\boldsymbol{v}\right)\cdot\boldsymbol{n}^{(\mathfrak{s})}+\boldsymbol{T}\cdot\boldsymbol{n}^{(\mathfrak{s})}]\!]^{(i)}\\
&+\Bigg[\!\!\Bigg[\rho\left(\left(u-u^{(\mathfrak{s})}\right)+\tfrac{1}{2}\left(\boldsymbol{v}-\boldsymbol{v}^{(\mathfrak{s})}\right)\cdot\left(\boldsymbol{v}-\boldsymbol{v}^{(\mathfrak{s})}\right)\right)\left(\left(\boldsymbol{w}^{(\mathfrak{s})}-\boldsymbol{v}\right)\cdot\boldsymbol{n}^{(\mathfrak{s})}\right)\\
&-\boldsymbol{q}\cdot\boldsymbol{n}^{(\mathfrak{s})}+\boldsymbol{T}\left(\boldsymbol{v}-\boldsymbol{v}^{(\mathfrak{s})}\right)\cdot\boldsymbol{n}^{(\mathfrak{s})}\Bigg]\!\!\Bigg]^{(i)}\\
\geq&0.
\end{aligned}
\tag{28.29}
$$

Incorporating the functional dependence of the material quantities (28.27) expressed in (28.28) into (28.29) by use of the chain rule of differentiation yields the new inequality

$$
\begin{aligned}
&\Theta^{(\mathfrak{s}_i)}\Pi^{(\mathfrak{s}_i)}=\\
&-\left(\rho^{(\mathfrak{s}_i)}\frac{\partial\psi^{(\mathfrak{s}_i)}}{\partial\rho^{(\mathfrak{s}_i)}}+\Lambda_\rho^{(\mathfrak{s}_i)}\right)\frac{\mathrm{d}^{(\mathfrak{s}_i)}\rho^{(\mathfrak{s}_i)}}{\mathrm{d}t}-\rho^{(\mathfrak{s}_i)}\boldsymbol{\Lambda}_v^{(\mathfrak{s}_i)}\cdot\frac{\mathrm{d}^{(\mathfrak{s}_i)}\boldsymbol{v}^{(\mathfrak{s}_i)}}{\mathrm{d}t}\\
&+\left(\boldsymbol{T}^{(\mathfrak{s}_i)}-\Lambda_\rho^{(\mathfrak{s}_i)}\rho^{(\mathfrak{s}_i)}\boldsymbol{I}^{(\mathfrak{s}_i)}\right)\cdot\boldsymbol{D}^{(\mathfrak{s}_i)}-\rho^{(\mathfrak{s}_i)}\left(\frac{\partial\psi^{(\mathfrak{s}_i)}}{\partial\Theta^{(\mathfrak{s}_i)}}+\eta^{(\mathfrak{s}_i)}\right)\frac{\mathrm{d}^{(\mathfrak{s}_i)}\Theta^{(\mathfrak{s}_i)}}{\mathrm{d}t}\\
&-\rho^{(\mathfrak{s}_i)}\frac{\partial\psi^{(\mathfrak{s}_i)}}{\partial\nabla^{(\mathfrak{s}_i)}\rho^{(\mathfrak{s}_i)}}\cdot\frac{\mathrm{d}^{(\mathfrak{s}_i)}\nabla^{(\mathfrak{s}_i)}\rho^{(\mathfrak{s}_i)}}{\mathrm{d}t}-\rho^{(\mathfrak{s}_i)}\frac{\partial\psi^{(\mathfrak{s}_i)}}{\partial\nabla^{(\mathfrak{s}_i)}\Theta^{(\mathfrak{s}_i)}}\cdot\frac{\mathrm{d}^{(\mathfrak{s}_i)}\nabla^{(\mathfrak{s}_i)}\Theta^{(\mathfrak{s}_i)}}{\mathrm{d}t}\\
&-\rho^{(\mathfrak{s}_i)}\frac{\partial\psi^{(\mathfrak{s}_i)}}{\partial\boldsymbol{D}^{(\mathfrak{s}_i)}}\cdot\frac{\mathrm{d}^{(\mathfrak{s}_i)}\boldsymbol{D}^{(\mathfrak{s}_i)}}{\mathrm{d}t}-\rho^{(\mathfrak{s}_i)}\frac{\partial\psi^{(\mathfrak{s}_i)}}{\partial H^{(\mathfrak{s}_i)}}\frac{\mathrm{d}^{(\mathfrak{s}_i)}H^{(\mathfrak{s}_i)}}{\mathrm{d}t}-\rho^{(\mathfrak{s}_i)}\frac{\partial\psi^{(\mathfrak{s}_i)}}{\partial\boldsymbol{W}_{\mathfrak{s}}}\cdot\frac{\mathrm{d}^{(\mathfrak{s}_i)}\boldsymbol{W}_{\mathfrak{s}}}{\mathrm{d}t}\\
&-\rho^{(\mathfrak{s}_i)}\frac{\partial\psi^{(\mathfrak{s}_i)}}{\partial\boldsymbol{W}_{\mathfrak{s}}^+}\cdot\frac{\mathrm{d}^{(\mathfrak{s}_i)}\boldsymbol{W}_{\mathfrak{s}}^+}{\mathrm{d}t}-\rho^{(\mathfrak{s}_i)}\frac{\partial\psi^{(\mathfrak{s}_i)}}{\partial\boldsymbol{W}_{\mathfrak{s}}^-}\cdot\frac{\mathrm{d}^{(\mathfrak{s}_i)}\boldsymbol{W}_{\mathfrak{s}}^-}{\mathrm{d}t}\\
&+\left(\Theta^{(\mathfrak{s}_i)}\frac{\partial\boldsymbol{\phi}_\eta^{(\mathfrak{s}_i)}}{\partial\rho^{(\mathfrak{s}_i)}}+\boldsymbol{\Lambda}_v^{(\mathfrak{s}_i)}\cdot\frac{\partial\boldsymbol{T}^{(\mathfrak{s}_i)}}{\partial\rho^{(\mathfrak{s}_i)}}-\frac{\partial\boldsymbol{q}^{(\mathfrak{s}_i)}}{\partial\rho^{(\mathfrak{s}_i)}}\right)\cdot\nabla^{(\mathfrak{s}_i)}\rho^{(\mathfrak{s}_i)}
\end{aligned}
$$

$$
\begin{aligned}
&+\left(\Theta^{(\mathfrak{s}_i)}\frac{\partial\boldsymbol{\phi}_\eta^{(\mathfrak{s}_i)}}{\partial\nabla^{(\mathfrak{s}_i)}\rho^{(\mathfrak{s}_i)}}+\boldsymbol{\Lambda}_v^{(\mathfrak{s}_i)}\cdot\frac{\partial\boldsymbol{T}^{(\mathfrak{s}_i)}}{\partial\nabla^{(\mathfrak{s}_i)}\rho^{(\mathfrak{s}_i)}}-\frac{\partial\boldsymbol{q}^{(\mathfrak{s}_i)}}{\partial\nabla^{(\mathfrak{s}_i)}\rho^{(\mathfrak{s}_i)}}\right)\cdot\nabla^{(\mathfrak{s}_i)}\left(\nabla^{(\mathfrak{s}_i)}\rho^{(\mathfrak{s}_i)}\right)\\
&+\left(\Theta^{(\mathfrak{s}_i)}\frac{\partial\boldsymbol{\phi}_\eta^{(\mathfrak{s}_i)}}{\partial\Theta^{(\mathfrak{s}_i)}}+\boldsymbol{\Lambda}_v^{(\mathfrak{s}_i)}\cdot\frac{\partial\boldsymbol{T}^{(\mathfrak{s}_i)}}{\partial\Theta^{(\mathfrak{s}_i)}}-\frac{\partial\boldsymbol{q}^{(\mathfrak{s}_i)}}{\partial\Theta^{(\mathfrak{s}_i)}}\right)\cdot\nabla^{(\mathfrak{s}_i)}\Theta^{(\mathfrak{s}_i)}\\
&+\left(\Theta^{(\mathfrak{s}_i)}\frac{\partial\boldsymbol{\phi}_\eta^{(\mathfrak{s}_i)}}{\partial\nabla^{(\mathfrak{s}_i)}\Theta^{(\mathfrak{s}_i)}}+\boldsymbol{\Lambda}_v^{(\mathfrak{s}_i)}\cdot\frac{\partial\boldsymbol{T}^{(\mathfrak{s}_i)}}{\partial\nabla^{(\mathfrak{s}_i)}\Theta^{(\mathfrak{s}_i)}}-\frac{\partial\boldsymbol{q}^{(\mathfrak{s}_i)}}{\partial\nabla^{(\mathfrak{s}_i)}\Theta^{(\mathfrak{s}_i)}}\right)\cdot\nabla^{(\mathfrak{s}_i)}\left(\nabla^{(\mathfrak{s}_i)}\Theta^{(\mathfrak{s}_i)}\right)\\
&+\left(\Theta^{(\mathfrak{s}_i)}\frac{\partial\boldsymbol{\phi}_\eta^{(\mathfrak{s}_i)}}{\partial\boldsymbol{D}^{(\mathfrak{s}_i)}}+\boldsymbol{\Lambda}_v^{(\mathfrak{s}_i)}\cdot\frac{\partial\boldsymbol{T}^{(\mathfrak{s}_i)}}{\partial\boldsymbol{D}^{(\mathfrak{s}_i)}}-\frac{\partial\boldsymbol{q}^{(\mathfrak{s}_i)}}{\partial\boldsymbol{D}^{(\mathfrak{s}_i)}}\right)\cdot\nabla^{(\mathfrak{s}_i)}\boldsymbol{D}^{(\mathfrak{s}_i)}\\
&+\left(\Theta^{(\mathfrak{s}_i)}\frac{\partial\boldsymbol{\phi}_\eta^{(\mathfrak{s}_i)}}{\partial H^{(\mathfrak{s}_i)}}+\boldsymbol{\Lambda}_v^{(\mathfrak{s}_i)}\cdot\frac{\partial\boldsymbol{T}^{(\mathfrak{s}_i)}}{\partial H^{(\mathfrak{s}_i)}}-\frac{\partial\boldsymbol{q}^{(\mathfrak{s}_i)}}{\partial H^{(\mathfrak{s}_i)}}\right)\cdot\nabla^{(\mathfrak{s}_i)}H^{(\mathfrak{s}_i)}\\
&+\left(\Theta^{(\mathfrak{s}_i)}\frac{\partial\boldsymbol{\phi}_\eta^{(\mathfrak{s}_i)}}{\partial\boldsymbol{W}_{\mathfrak{s}}}+\boldsymbol{\Lambda}_v^{(\mathfrak{s}_i)}\cdot\frac{\partial\boldsymbol{T}^{(\mathfrak{s}_i)}}{\partial\boldsymbol{W}_{\mathfrak{s}}}-\frac{\partial\boldsymbol{q}^{(\mathfrak{s}_i)}}{\partial\boldsymbol{W}_{\mathfrak{s}}}\right)\cdot\nabla^{(\mathfrak{s}_i)}\boldsymbol{W}_{\mathfrak{s}}\\
&+\left(\Theta^{(\mathfrak{s}_i)}\frac{\partial\boldsymbol{\phi}_\eta^{(\mathfrak{s}_i)}}{\partial\boldsymbol{W}_{\mathfrak{s}}^+}+\boldsymbol{\Lambda}_v^{(\mathfrak{s}_i)}\cdot\frac{\partial\boldsymbol{T}^{(\mathfrak{s}_i)}}{\partial\boldsymbol{W}_{\mathfrak{s}}^+}-\frac{\partial\boldsymbol{q}^{(\mathfrak{s}_i)}}{\partial\boldsymbol{W}_{\mathfrak{s}}^+}\right)\cdot\nabla^{(\mathfrak{s}_i)}\boldsymbol{W}_{\mathfrak{s}}^+\\
&+\left(\Theta^{(\mathfrak{s}_i)}\frac{\partial\boldsymbol{\phi}_\eta^{(\mathfrak{s}_i)}}{\partial\boldsymbol{W}_{\mathfrak{s}}^-}+\boldsymbol{\Lambda}_v^{(\mathfrak{s}_i)}\cdot\frac{\partial\boldsymbol{T}^{(\mathfrak{s}_i)}}{\partial\boldsymbol{W}_{\mathfrak{s}}^-}-\frac{\partial\boldsymbol{q}^{(\mathfrak{s}_i)}}{\partial\boldsymbol{W}_{\mathfrak{s}}^-}\right)\cdot\nabla^{(\mathfrak{s}_i)}\boldsymbol{W}_{\mathfrak{s}}^-\\
&-H^{(\mathfrak{s}_i)}\Theta^{(\mathfrak{s}_i)}\left(\boldsymbol{\phi}_\eta^{(\mathfrak{s}_i)}\cdot\boldsymbol{n}^{(\mathfrak{s}_i)}\right)-H^{(\mathfrak{s}_i)}\Lambda_\rho^{(\mathfrak{s}_i)}\rho^{(\mathfrak{s}_i)}\left(\left(\boldsymbol{w}^{(\mathfrak{s}_i)}-\boldsymbol{v}^{(\mathfrak{s}_i)}\right)\cdot\boldsymbol{n}^{(\mathfrak{s}_i)}\right)\\
&-H^{(\mathfrak{s}_i)}\boldsymbol{\Lambda}_v^{(\mathfrak{s}_i)}\cdot\left(\boldsymbol{T}^{(\mathfrak{s}_i)}\cdot\boldsymbol{n}^{(\mathfrak{s}_i)}\right)+H^{(\mathfrak{s}_i)}\left(\boldsymbol{q}^{(\mathfrak{s}_i)}\cdot\boldsymbol{n}^{(\mathfrak{s}_i)}\right)\\
&-\Theta^{(\mathfrak{s}_i)}\left\llbracket\rho\left(\eta-\eta^{(\mathfrak{s})}\right)\left(\boldsymbol{w}^{(\mathfrak{s})}-\boldsymbol{v}\right)\cdot\boldsymbol{n}^{(\mathfrak{s})}-\boldsymbol{\phi}_\eta\cdot\boldsymbol{n}^{(\mathfrak{s})}\right\rrbracket^{(i)}\\
&+\Lambda_\rho^{(\mathfrak{s}_i)}\left\llbracket\rho\left(\boldsymbol{w}^{(\mathfrak{s})}-\boldsymbol{v}\right)\cdot\boldsymbol{n}^{(\mathfrak{s})}\right\rrbracket^{(i)}\\
&+\boldsymbol{\Lambda}_v^{(\mathfrak{s}_i)}\cdot\left\llbracket\rho\left(\boldsymbol{v}-\boldsymbol{v}^{(\mathfrak{s})}\right)\left(\boldsymbol{w}^{(\mathfrak{s})}-\boldsymbol{v}\right)\cdot\boldsymbol{n}^{(\mathfrak{s})}+\boldsymbol{T}\cdot\boldsymbol{n}^{(\mathfrak{s})}\right\rrbracket^{(i)}\\
&+\Big\llbracket\rho\left(\left(u-u^{(\mathfrak{s})}\right)+\tfrac{1}{2}\left(\boldsymbol{v}-\boldsymbol{v}^{(\mathfrak{s})}\right)\cdot\left(\boldsymbol{v}-\boldsymbol{v}^{(\mathfrak{s})}\right)\right)\left(\left(\boldsymbol{w}^{(\mathfrak{s})}-\boldsymbol{v}\right)\cdot\boldsymbol{n}^{(\mathfrak{s})}\right)\\
&\qquad-\boldsymbol{q}\cdot\boldsymbol{n}^{(\mathfrak{s})}+\boldsymbol{T}\left(\boldsymbol{v}-\boldsymbol{v}^{(\mathfrak{s})}\right)\cdot\boldsymbol{n}^{(\mathfrak{s})}\Big\rrbracket^{(i)}\\
&\geq 0.
\end{aligned}
\tag{28.30}
$$

This formidable inequality is expressible as

$$
\boldsymbol{a}^{(\mathfrak{s}_i)}\cdot\boldsymbol{\alpha}^{(\mathfrak{s}_i)}+b^{(\mathfrak{s}_i)}\geq 0, \tag{28.31}
$$

where the vector $\boldsymbol{a}$ and the scalar b are functions of the variables listed in (28.28), but not of $\boldsymbol{\alpha}$, and the vector $\boldsymbol{\alpha}$ depends on time and space derivatives of these variables. Hence, inequality (28.31) is linear in $\boldsymbol{\alpha}$. It follows from Liu's theorem that $\boldsymbol{\alpha}$ is arbitrarily selectable at a fixed material point—in other words, it is possible to construct an admissible thermodynamic process having any value of $\boldsymbol{\alpha}$ we please. The inequality must hold for all fields: density, velocity, temperature, and surface curvature; and, in particular, it must hold for arbitrary values of $\boldsymbol{\alpha}$ at one point. It is concluded that all terms with the components of $\boldsymbol{\alpha}$ must vanish. Thus, necessary and sufficient conditions for (28.31) to hold are[2]

$$\boldsymbol{a}^{(\mathfrak{s}_i)} = \boldsymbol{0} \quad \text{and} \quad b^{(\mathfrak{s}_i)} \geq 0. \tag{28.32}$$

Explicitly, the entropy inequality must hold for all independent variations, indicated by the red color in (28.30), of

$$\begin{aligned}\boldsymbol{\alpha}^{(\mathfrak{s}_i)} = \Bigg\{ & \frac{\mathrm{d}^{(\mathfrak{s}_i)}\rho^{(\mathfrak{s}_i)}}{\mathrm{d}t}, \frac{\mathrm{d}^{(\mathfrak{s}_i)}\boldsymbol{v}^{(\mathfrak{s}_i)}}{\mathrm{d}t}, \frac{\mathrm{d}^{(\mathfrak{s}_i)}\Theta^{(\mathfrak{s}_i)}}{\mathrm{d}t}, \frac{\mathrm{d}^{(\mathfrak{s}_i)}\nabla^{(\mathfrak{s}_i)}\rho^{(\mathfrak{s}_i)}}{\mathrm{d}t}, \frac{\mathrm{d}^{(\mathfrak{s}_i)}\nabla^{(\mathfrak{s}_i)}\Theta^{(\mathfrak{s}_i)}}{\mathrm{d}t}, \\ & \frac{\mathrm{d}^{(\mathfrak{s}_i)}\boldsymbol{D}^{(\mathfrak{s}_i)}}{\mathrm{d}t}, \frac{\mathrm{d}^{(\mathfrak{s}_i)}H^{(\mathfrak{s}_i)}}{\mathrm{d}t}, \nabla^{(\mathfrak{s}_i)}\left(\nabla^{(\mathfrak{s}_i)}\rho^{(\mathfrak{s}_i)}\right), \nabla^{(\mathfrak{s}_i)}\left(\nabla^{(\mathfrak{s}_i)}\Theta^{(\mathfrak{s}_i)}\right), \\ & \nabla^{(\mathfrak{s}_i)}\boldsymbol{D}^{(\mathfrak{s}_i)}, \nabla^{(\mathfrak{s}_i)}H^{(\mathfrak{s}_i)}, \frac{\mathrm{d}^{(\mathfrak{s}_i)}\boldsymbol{W}_{\mathfrak{s}}}{\mathrm{d}t}, \frac{\mathrm{d}^{(\mathfrak{s}_i)}\boldsymbol{W}_{\mathfrak{s}}^{+}}{\mathrm{d}t}, \frac{\mathrm{d}^{(\mathfrak{s}_i)}\boldsymbol{W}_{\mathfrak{s}}^{-}}{\mathrm{d}t}, \\ & \nabla^{(\mathfrak{s}_i)}\boldsymbol{W}_{\mathfrak{s}}, \nabla^{(\mathfrak{s}_i)}\boldsymbol{W}_{\mathfrak{s}}^{+}, \nabla^{(\mathfrak{s}_i)}\boldsymbol{W}_{\mathfrak{s}}^{-}\Bigg\}.\end{aligned} \tag{28.33}$$

These variables appear linearly in (28.30), and thus, their coefficients must vanish. This leads to the so-called Liu identities. This implies that the following expressions must hold, respectively, for:

the Lagrange multipliers $\Lambda_{\rho}^{(\mathfrak{s}_i)}$ and $\boldsymbol{\Lambda}_{v}^{(\mathfrak{s}_i)}$

$$\Lambda_{\rho}^{(\mathfrak{s}_i)} = -\rho^{(\mathfrak{s}_i)}\frac{\partial\psi^{(\mathfrak{s}_i)}}{\partial\rho^{(\mathfrak{s}_i)}}, \quad \boldsymbol{\Lambda}_{v}^{(\mathfrak{s}_i)} = \boldsymbol{0}, \tag{28.34}$$

for the specific entropy density

$$\eta^{(\mathfrak{s}_i)} = -\frac{\partial\psi^{(\mathfrak{s}_i)}}{\partial\Theta^{(\mathfrak{s}_i)}}, \tag{28.35}$$

---

[2] This argument must be applied with caution: If $\boldsymbol{\alpha}^{(\mathfrak{s}_i)}$ has components which are symmetric, $\alpha_{k\ell}^{(\mathfrak{s}_i)} = \alpha_{\ell k}^{(\mathfrak{s}_i)}$, then the corresponding component of $\boldsymbol{a}^{(\mathfrak{s}_i)}$ must be skew-symmetric, $a_{k\ell}^{(\mathfrak{s}_i)} = -a_{\ell k}^{(\mathfrak{s}_i)}$.

for the free energy $\psi^{(\mathfrak{s}_i)}$

$$\frac{\partial \psi^{(\mathfrak{s}_i)}}{\partial \nabla^{(\mathfrak{s}_i)} \rho^{(\mathfrak{s}_i)}} = \mathbf{0}, \quad \frac{\partial \psi^{(\mathfrak{s}_i)}}{\partial \nabla^{(\mathfrak{s}_i)} \Theta^{(\mathfrak{s}_i)}} = \mathbf{0}, \quad \frac{\partial \psi^{(\mathfrak{s}_i)}}{\partial \boldsymbol{D}^{(\mathfrak{s}_i)}} = \mathbf{0}, \quad \frac{\partial \psi^{(\mathfrak{s}_i)}}{\partial H^{(\mathfrak{s}_i)}} = 0,$$
$$\frac{\partial \psi^{(\mathfrak{s}_i)}}{\partial \boldsymbol{W}_{\mathfrak{s}}} = \mathbf{0}, \quad \frac{\partial \psi^{(\mathfrak{s}_i)}}{\partial \boldsymbol{W}_{\mathfrak{s}}^{+}} = \mathbf{0}, \quad \frac{\partial \psi^{(\mathfrak{s}_i)}}{\partial \boldsymbol{W}_{\mathfrak{s}}^{-}} = \mathbf{0}, \tag{28.36}$$

and the relations among $\boldsymbol{\phi}^{(\mathfrak{s}_i)}$, $\boldsymbol{T}^{(\mathfrak{s}_i)}$, and $\boldsymbol{q}^{(\mathfrak{s}_i)}$

$$\operatorname{sym}\left(\Theta^{(\mathfrak{s}_i)} \frac{\partial \boldsymbol{\phi}_{\eta}^{(\mathfrak{s}_i)}}{\partial \nabla^{(\mathfrak{s}_i)} \rho^{(\mathfrak{s}_i)}} + \boldsymbol{\Lambda}_{v}^{(\mathfrak{s}_i)} \cdot \frac{\partial \boldsymbol{T}^{(\mathfrak{s}_i)}}{\partial \nabla^{(\mathfrak{s}_i)} \rho^{(\mathfrak{s}_i)}} - \frac{\partial \boldsymbol{q}^{(\mathfrak{s}_i)}}{\partial \nabla^{(\mathfrak{s}_i)} \rho^{(\mathfrak{s}_i)}}\right) = \mathbf{0},$$
$$\operatorname{sym}\left(\Theta^{(\mathfrak{s}_i)} \frac{\partial \boldsymbol{\phi}_{\eta}^{(\mathfrak{s}_i)}}{\partial \nabla^{(\mathfrak{s}_i)} \Theta^{(\mathfrak{s}_i)}} + \boldsymbol{\Lambda}_{v}^{(\mathfrak{s}_i)} \cdot \frac{\partial \boldsymbol{T}^{(\mathfrak{s}_i)}}{\partial \nabla^{(\mathfrak{s}_i)} \Theta^{(\mathfrak{s}_i)}} - \frac{\partial \boldsymbol{q}^{(\mathfrak{s}_i)}}{\partial \nabla^{(\mathfrak{s}_i)} \Theta^{(\mathfrak{s}_i)}}\right) = \mathbf{0},$$
$$\Theta^{(\mathfrak{s}_i)} \frac{\partial \boldsymbol{\phi}_{\eta}^{(\mathfrak{s}_i)}}{\partial \boldsymbol{D}^{(\mathfrak{s}_i)}} + \boldsymbol{\Lambda}_{v}^{(\mathfrak{s}_i)} \cdot \frac{\partial \boldsymbol{T}^{(\mathfrak{s}_i)}}{\partial \boldsymbol{D}^{(\mathfrak{s}_i)}} - \frac{\partial \boldsymbol{q}^{(\mathfrak{s}_i)}}{\partial \boldsymbol{D}^{(\mathfrak{s}_i)}} = \mathbf{0},$$
$$\Theta^{(\mathfrak{s}_i)} \frac{\partial \boldsymbol{\phi}_{\eta}^{(\mathfrak{s}_i)}}{\partial H^{(\mathfrak{s}_i)}} + \boldsymbol{\Lambda}_{v}^{(\mathfrak{s}_i)} \cdot \frac{\partial \boldsymbol{T}^{(\mathfrak{s}_i)}}{\partial H^{(\mathfrak{s}_i)}} - \frac{\partial \boldsymbol{q}^{(\mathfrak{s}_i)}}{\partial H^{(\mathfrak{s}_i)}} = \mathbf{0}, \tag{28.37}$$
$$\Theta^{(\mathfrak{s}_i)} \frac{\partial \boldsymbol{\phi}_{\eta}^{(\mathfrak{s}_i)}}{\partial \boldsymbol{W}_{\mathfrak{s}}} + \boldsymbol{\Lambda}_{v}^{(\mathfrak{s}_i)} \cdot \frac{\partial \boldsymbol{T}^{(\mathfrak{s}_i)}}{\partial \boldsymbol{W}_{\mathfrak{s}}} - \frac{\partial \boldsymbol{q}^{(\mathfrak{s}_i)}}{\partial \boldsymbol{W}_{\mathfrak{s}}} = \mathbf{0},$$
$$\Theta^{(\mathfrak{s}_i)} \frac{\partial \boldsymbol{\phi}_{\eta}^{(\mathfrak{s}_i)}}{\partial \boldsymbol{W}_{\mathfrak{s}}^{+}} + \boldsymbol{\Lambda}_{v}^{(\mathfrak{s}_i)} \cdot \frac{\partial \boldsymbol{T}^{(\mathfrak{s}_i)}}{\partial \boldsymbol{W}_{\mathfrak{s}}^{+}} - \frac{\partial \boldsymbol{q}^{(\mathfrak{s}_i)}}{\partial \boldsymbol{W}_{\mathfrak{s}}^{+}} = \mathbf{0},$$
$$\Theta^{(\mathfrak{s}_i)} \frac{\partial \boldsymbol{\phi}_{\eta}^{(\mathfrak{s}_i)}}{\partial \boldsymbol{W}_{\mathfrak{s}}^{-}} + \boldsymbol{\Lambda}_{v}^{(\mathfrak{s}_i)} \cdot \frac{\partial \boldsymbol{T}^{(\mathfrak{s}_i)}}{\partial \boldsymbol{W}_{\mathfrak{s}}^{-}} - \frac{\partial \boldsymbol{q}^{(\mathfrak{s}_i)}}{\partial \boldsymbol{W}_{\mathfrak{s}}^{-}} = \mathbf{0},$$

where $\operatorname{sym} \boldsymbol{A} = \frac{1}{2}\left(\boldsymbol{A} + \boldsymbol{A}^{T}\right)$. Equations (28.34)–(28.37) correspond to the condition $\boldsymbol{a} = \mathbf{0}$ in $(28.32)_1$.

The restrictions on the free energy (28.36) imply the reduced dependence

$$\psi^{(\mathfrak{s}_i)} = \hat{\psi}^{(\mathfrak{s}_i)}\left(\rho^{(\mathfrak{s}_i)}, \Theta^{(\mathfrak{s}_i)}\right). \tag{28.38}$$

Introducing the extra entropy flux

$$\boldsymbol{\Phi}_{\eta}^{(\mathfrak{s}_i)} = \boldsymbol{\phi}_{\eta}^{(\mathfrak{s}_i)} + \frac{1}{\Theta^{(\mathfrak{s}_i)}}\left(\boldsymbol{\Lambda}_{v}^{(\mathfrak{s}_i)} \cdot \boldsymbol{T}^{(\mathfrak{s}_i)} - \boldsymbol{q}^{(\mathfrak{s}_i)}\right) \tag{28.39}$$

and considering $(28.34)_2$, we have from (28.37)

$$
\begin{gathered}
\operatorname{sym}\left(\frac{\partial \boldsymbol{\Phi}_{\eta}^{(\mathfrak{s}_i)}}{\partial \nabla^{(\mathfrak{s}_i)} \rho^{(\mathfrak{s}_i)}}\right) = \mathbf{0}, \quad \operatorname{sym}\left(\frac{\partial \boldsymbol{\Phi}_{\eta}^{(\mathfrak{s}_i)}}{\partial \nabla^{(\mathfrak{s}_i)} \Theta^{(\mathfrak{s}_i)}}\right) = \mathbf{0}, \quad \frac{\partial \boldsymbol{\Phi}_{\eta}^{(\mathfrak{s}_i)}}{\partial \boldsymbol{D}^{(\mathfrak{s}_i)}} = \mathbf{0}, \\
\frac{\partial \boldsymbol{\Phi}_{\eta}^{(\mathfrak{s}_i)}}{\partial H^{(\mathfrak{s}_i)}} = \mathbf{0}, \quad \frac{\partial \boldsymbol{\Phi}_{\eta}^{(\mathfrak{s}_i)}}{\partial \boldsymbol{W}_{\mathfrak{s}}} = \mathbf{0}, \quad \frac{\partial \boldsymbol{\Phi}_{\eta}^{(\mathfrak{s}_i)}}{\partial \boldsymbol{W}_{\mathfrak{s}}^{+}} = \mathbf{0}, \quad \frac{\partial \boldsymbol{\Phi}_{\eta}^{(\mathfrak{s}_i)}}{\partial \boldsymbol{W}_{\mathfrak{s}}^{-}} = \mathbf{0}.
\end{gathered} \tag{28.40}
$$

Using these restrictions (28.40) on the extra entropy flux $\boldsymbol{\Phi}_{\eta}^{(\mathfrak{s}_i)}$ and the isotropy assumption it follows that

$$
\boldsymbol{\Phi}_{\eta}^{(\mathfrak{s}_i)} = \mathbf{0}. \tag{28.41}
$$

Thus, the entropy flux assumes its traditional form. It can be shown that this result will not follow, if we add the dependences $\mathrm{d}^{(\mathfrak{s}_i)}\rho^{(\mathfrak{s}_i)}/\mathrm{d}t$ and/or $\mathrm{d}^{(\mathfrak{s}_i)}\Theta^{(\mathfrak{s}_i)}/\mathrm{d}t$ to the constitutive functions (28.28). This explicitly demonstrates the physical inadequacy of the COLEMAN–NOLL approach in some cases, e.g., for materials under real thermo*dynamic* processes. This has been recognized for a long time, see, e.g., HUTTER [12], LIU and MÜLLER [22].

Returning now to the entropy inequality (28.30) and employing the above restrictions, we obtain the residual entropy inequality, corresponding to condition $(28.32)_2$, i.e., $b^{(\mathfrak{s}_i)} \geq 0$,

$$
\begin{aligned}
&\Theta^{(\mathfrak{s}_i)} \Pi^{(\mathfrak{s}_i)} \\
&= \left(\boldsymbol{T}^{(\mathfrak{s}_i)} - \sigma^{(\mathfrak{s}_i)} \boldsymbol{I}^{(\mathfrak{s}_i)}\right) \cdot \boldsymbol{D}^{(\mathfrak{s}_i)} - \frac{\boldsymbol{q}^{(\mathfrak{s}_i)} \cdot \nabla^{(\mathfrak{s}_i)} \Theta^{(\mathfrak{s}_i)}}{\Theta^{(\mathfrak{s}_i)}} \\
&\quad - H^{(\mathfrak{s}_i)} \sigma^{(\mathfrak{s}_i)} \left(\left(\boldsymbol{w}^{(\mathfrak{s}_i)} - \boldsymbol{v}^{(\mathfrak{s}_i)}\right) \cdot \boldsymbol{n}^{(\mathfrak{s}_i)}\right) \\
&\quad - \Theta^{(\mathfrak{s}_i)} [\![\rho \left(\eta - \eta^{(\mathfrak{s})}\right) \left(\boldsymbol{w}^{(\mathfrak{s})} - \boldsymbol{v}\right) \cdot \boldsymbol{n}^{(\mathfrak{s})} - \boldsymbol{\phi}_{\eta} \cdot \boldsymbol{n}^{(\mathfrak{s})}]\!]^{(i)} \\
&\quad + (\sigma^{(\mathfrak{s}_i)}/\rho^{(\mathfrak{s}_i)}) [\![\rho \left(\boldsymbol{w}^{(\mathfrak{s})} - \boldsymbol{v}\right) \cdot \boldsymbol{n}^{(\mathfrak{s})}]\!]^{(i)} \\
&\quad + [\![\rho \left(\left(u - u^{(\mathfrak{s})}\right) + \tfrac{1}{2}\left(\boldsymbol{v} - \boldsymbol{v}^{(\mathfrak{s})}\right) \cdot \left(\boldsymbol{v} - \boldsymbol{v}^{(\mathfrak{s})}\right)\right) \left(\left(\boldsymbol{w}^{(\mathfrak{s})} - \boldsymbol{v}\right) \cdot \boldsymbol{n}^{(\mathfrak{s})}\right) \\
&\qquad - \boldsymbol{q} \cdot \boldsymbol{n}^{(\mathfrak{s})} + \boldsymbol{T}\left(\boldsymbol{v} - \boldsymbol{v}^{(\mathfrak{s})}\right) \cdot \boldsymbol{n}^{(\mathfrak{s})}]\!]^{(i)} \\
&\geq 0,
\end{aligned} \tag{28.42}
$$

where we have introduced the definition of the thermodynamic surface tension [see $(28.34)_1$], viz.,

$$
\sigma^{(\mathfrak{s}_i)} := \Lambda_{\rho}^{(\mathfrak{s}_i)} = -\rho^{(\mathfrak{s}_i)2} \frac{\partial \psi^{(\mathfrak{s}_i)}}{\partial \rho^{(\mathfrak{s}_i)}}, \tag{28.43}
$$

which is identical with the well-known surface tension, as we will see later.

At this point, we should also point out that the constitutive class (28.28) is only suitable for surfaces with variable surface mass density. For density preserving surfaces,, i.e., surfaces whose mass density does not change, $\rho^{(\mathfrak{s}_i)}$ and $\nabla^{(\mathfrak{s}_i)}\rho^{(\mathfrak{s}_i)}$ are no longer independent variables within the constitutive class (28.28). In this case, returning to the initial constitutive assumption (28.28), we delete the dependences on $\rho^{(\mathfrak{s}_i)}$ and $\nabla^{(\mathfrak{s}_i)}\rho^{(\mathfrak{s}_i)}$ from the constitutive equations and repeat the above analysis. We then find the same constitutive restrictions with density preserving surfaces as before for variable surface mass density, if here $\sigma^{(\mathfrak{s}_i)} = \rho^{(\mathfrak{s}_i)}\varLambda_\rho^{(\mathfrak{s}_i)}$ is introduced, which now is an unknown (constraint) variable and can no longer be determined by the free energy $\psi^{(\mathfrak{s}_i)}$ as expressed in (28.43). We encourage the reader to repeat the details of the analysis.

Furthermore, considering relations $(28.21)_2$, (28.35), (28.38) and (28.43), we find that the surface entropy $\eta^{(\mathfrak{s}_i)}$, internal energy $u^{(\mathfrak{s}_i)}$ and tension $\sigma^{(\mathfrak{s}_i)}$ are only functions of the surface density $\rho^{(\mathfrak{s}_i)}$ and temperature $\Theta^{(\mathfrak{s}_i)}$,

$$
\begin{aligned}
\eta^{(\mathfrak{s}_i)} &= \hat{\eta}^{(\mathfrak{s}_i)}\left(\rho^{(\mathfrak{s}_i)}, \Theta^{(\mathfrak{s}_i)}\right), \\
u^{(\mathfrak{s}_i)} &= \hat{u}^{(\mathfrak{s}_i)}\left(\rho^{(\mathfrak{s}_i)}, \Theta^{(\mathfrak{s}_i)}\right), \\
\sigma^{(\mathfrak{s}_i)} &= \hat{\sigma}^{(\mathfrak{s}_i)}\left(\rho^{(\mathfrak{s}_i)}, \Theta^{(\mathfrak{s}_i)}\right).
\end{aligned}
\tag{28.44}
$$

They are related by the surfacial GIBBS equation[3]

$$
\mathrm{d}\eta^{(\mathfrak{s}_i)} = \frac{1}{\Theta^{(\mathfrak{s}_i)}}\left(\mathrm{d}u^{(\mathfrak{s}_i)} - \sigma^{(\mathfrak{s}_i)}\mathrm{d}\left(\frac{1}{\rho^{(\mathfrak{s}_i)}}\right)\right), \tag{28.45}
$$

---

[3] The surfacial GIBBS equation, (28.45), can be easily derived. By means of $(28.21)_2$ and $(28.44)_1$, one obtains

$$
\eta^{(\mathfrak{s}_i)} = \hat{\eta}^{(\mathfrak{s}_i)}\left(\rho^{(\mathfrak{s}_i)}, \Theta^{(\mathfrak{s}_i)}\right) = \frac{1}{\Theta^{(\mathfrak{s}_i)}}\left(u^{(\mathfrak{s}_i)} - \psi^{(\mathfrak{s}_i)}\right).
$$

Taking the total differential of $\eta^{(\mathfrak{s}_i)}$ yields

$$
\begin{aligned}
\mathrm{d}\eta^{(\mathfrak{s}_i)} &= -\frac{1}{(\Theta^{(\mathfrak{s}_i)})^2}\left(u^{(\mathfrak{s}_i)} - \psi^{(\mathfrak{s}_i)}\right)\mathrm{d}\Theta^{(\mathfrak{s}_i)} + \frac{1}{\Theta^{(\mathfrak{s}_i)}}\left(\mathrm{d}u^{(\mathfrak{s}_i)} - \mathrm{d}\psi^{(\mathfrak{s}_i)}\right) \\
&= -\frac{1}{(\Theta^{(\mathfrak{s}_i)})^2}\left(u^{(\mathfrak{s}_i)} - \psi^{(\mathfrak{s}_i)}\right)\mathrm{d}\Theta^{(\mathfrak{s}_i)} \\
&\quad + \frac{1}{\Theta^{(\mathfrak{s}_i)}}\left(\mathrm{d}u^{(\mathfrak{s}_i)} - \frac{\partial\psi^{(\mathfrak{s}_i)}}{\partial\rho^{(\mathfrak{s}_i)}}\mathrm{d}\rho^{(\mathfrak{s}_i)} - \frac{\partial\psi^{(\mathfrak{s}_i)}}{\partial\Theta^{(\mathfrak{s}_i)}}\mathrm{d}\Theta^{(\mathfrak{s}_i)}\right) \\
&= -\frac{1}{(\Theta^{(\mathfrak{s}_i)})^2}\left(u^{(\mathfrak{s}_i)} - \psi^{(\mathfrak{s}_i)} + \Theta^{(\mathfrak{s}_i)}\frac{\partial\psi^{(\mathfrak{s}_i)}}{\partial\Theta^{(\mathfrak{s}_i)}}\right)\mathrm{d}\Theta^{(\mathfrak{s}_i)} \\
&\quad + \frac{1}{\Theta^{(\mathfrak{s}_i)}}\mathrm{d}u^{(\mathfrak{s}_i)} + \frac{1}{\Theta^{(\mathfrak{s}_i)}}\left((\rho^{(\mathfrak{s}_i)})^2\frac{\partial\psi^{(\mathfrak{s}_i)}}{\partial\rho^{(\mathfrak{s}_i)}}\right)\mathrm{d}\left(\frac{1}{\rho^{(\mathfrak{s}_i)}}\right) \\
&= \frac{1}{\Theta^{(\mathfrak{s}_i)}}\left(\mathrm{d}u^{(\mathfrak{s}_i)} - \sigma^{(\mathfrak{s}_i)}\mathrm{d}\left(\frac{1}{\rho^{(\mathfrak{s}_i)}}\right)\right).
\end{aligned}
$$

In the last step, relations $(28.21)_2$, (28.35), and (28.43) have been used.

which expresses the total differential of the entropy as the product of the inverse of the absolute temperature times the total differential of the internal energy plus the additional term $-\sigma^{(\mathfrak{s}_i)}\mathrm{d}\left(1/\rho^{(\mathfrak{s}_i)}\right)$. This result is formally identical with the bulk GIBBS relation for a heat conducting viscous fluid, stated in (28.23).

28.3.2 Thermodynamic Equilibrium

As usual, further restrictions on the constitutive relations can be obtained from the residual inequality (28.42) in the context of thermodynamic equilibrium, which is characterized in the current local formulation by homogeneous thermodynamic field quantities and the vanishing of the entropy production rate density $\mathit{\Pi}^{(\mathfrak{s}_i)}$. In the context of the current constitutive class, (28.42) implies that the surface entropy production density $\mathit{\Pi}^{(\mathfrak{s}_i)}$ is a function of the variables

$$\boldsymbol{Y}^{(\mathfrak{s}_i)} = \left(\nabla^{(\mathfrak{s}_i)}\mathit{\Theta}^{(\mathfrak{s}_i)}, \boldsymbol{D}^{(\mathfrak{s}_i)}, \boldsymbol{W}_{\mathfrak{s}}^{+}, \boldsymbol{W}_{\mathfrak{s}}^{-}, \boldsymbol{W}_{\mathfrak{s}}\right), \tag{28.46}$$

in the form

$$\begin{aligned}
&\mathit{\Theta}^{(\mathfrak{s}_i)}\mathit{\Pi}^{(\mathfrak{s}_i)}\\
&= \left(\boldsymbol{T}^{(\mathfrak{s}_i)} - \sigma^{(\mathfrak{s}_i)}\boldsymbol{I}^{(\mathfrak{s}_i)}\right)\cdot\boldsymbol{D}^{(\mathfrak{s}_i)} - \left(1/\mathit{\Theta}^{(\mathfrak{s}_i)}\right)\boldsymbol{q}^{(\mathfrak{s}_i)}\cdot\nabla^{(\mathfrak{s}_i)}\mathit{\Theta}^{(\mathfrak{s}_i)}\\
&\quad+\left[-H^{(\mathfrak{s}_i)}\sigma^{(\mathfrak{s}_i)} + \boldsymbol{T}^{(i)} - \boldsymbol{T}^{(i-1)}\right]\boldsymbol{n}^{(\mathfrak{s}_i)}\cdot\boldsymbol{W}_{\mathfrak{s}}\\
&\quad+\Bigg[\rho^{(i)}\left(\left(u^{(i)} - u^{(\mathfrak{s}_i)}\right) + \tfrac{1}{2}\left(\boldsymbol{v}^{(i)} - \boldsymbol{v}^{(\mathfrak{s}_i)}\right)\cdot\left(\boldsymbol{v}^{(i)} - \boldsymbol{v}^{(\mathfrak{s}_i)}\right)\right)\\
&\qquad-\mathit{\Theta}^{(\mathfrak{s}_i)}\rho^{(i)}\left(\eta^{(i)} - \eta^{(\mathfrak{s}_i)}\right) + (\sigma^{(\mathfrak{s}_i)}/\rho^{(\mathfrak{s}_i)})\rho^{(i)} - \boldsymbol{T}^{(i)}\Bigg]\boldsymbol{n}^{(\mathfrak{s}_i)}\cdot\boldsymbol{W}_{\mathfrak{s}}^{+}\\
&\quad-\Bigg[\rho^{(i-1)}\left(\left(u^{(i-1)} - u^{(\mathfrak{s}_i)}\right) + \tfrac{1}{2}\left(\boldsymbol{v}^{(i-1)} - \boldsymbol{v}^{(\mathfrak{s}_i)}\right)\cdot\left(\boldsymbol{v}^{(i-1)} - \boldsymbol{v}^{(\mathfrak{s}_i)}\right)\right)\\
&\qquad-\mathit{\Theta}^{(\mathfrak{s}_i)}\rho^{(i-1)}\left(\eta^{(i-1)} - \eta^{(\mathfrak{s}_i)}\right) + (\sigma^{(\mathfrak{s}_i)}/\rho^{(\mathfrak{s}_i)})\rho^{(i-1)} - \boldsymbol{T}^{(i-1)}\Bigg]\boldsymbol{n}^{(\mathfrak{s}_i)}\cdot\boldsymbol{W}_{\mathfrak{s}}^{-}\\
&\quad+\mathit{\Theta}^{(\mathfrak{s}_i)}\left[\!\left[\boldsymbol{\phi}_{\eta}\cdot\boldsymbol{n}^{(\mathfrak{s})}\right]\!\right]^{(i)} - \left[\!\left[\boldsymbol{q}\cdot\boldsymbol{n}^{(\mathfrak{s})}\right]\!\right]^{(i)} \geq 0,
\end{aligned} \tag{28.47}$$

The surface entropy production $\mathit{\Pi}^{(\mathfrak{s}_i)}$ vanishes whenever $\boldsymbol{Y}^{(\mathfrak{s}_i)} = \boldsymbol{0}$. The condition $\boldsymbol{Y}^{(\mathfrak{s}_i)} = \boldsymbol{0}$ is called thermodynamic equilibrium and will be denoted by the index E. Obviously, in thermodynamic equilibrium, due to $\boldsymbol{W}_{\mathfrak{s}}^{+}|_E = 0$, $\boldsymbol{W}_{\mathfrak{s}}^{-}|_E = 0$, $\boldsymbol{W}_{\mathfrak{s}}|_E = 0$, hence

$$\boldsymbol{w}^{(\mathfrak{s}_i)}|_E = \boldsymbol{v}^{(\mathfrak{s}_i)}|_E = \boldsymbol{v}^{(i)}|_E = \boldsymbol{v}^{(i-1)}|_E \quad \text{on the phase interface.} \tag{28.48}$$

This means that in the defined thermodynamic equilibrium the phase interface is a material surface. Here, it has been assumed that the adjacent bulk phases $\mathfrak{B}^{(i)}$ and $\mathfrak{B}^{(i-1)}$ are also in equilibrium when the phase interface is in equilibrium, i.e., $\boldsymbol{q}^{(i)}|_E = \mathbf{0}$ and $\boldsymbol{q}^{(i-1)}|_E = \mathbf{0}$. Alternatively, we can also use the relaxed restrictions of $\left[\!\left[\boldsymbol{q} \cdot \boldsymbol{n}^{(\mathfrak{s})}\right]\!\right]^{(i)}|_E = 0$ and $[\![\Theta]\!]^{(i)}|_E = 0$. Furthermore, we have restricted our investigation only to the classical isotropic, incompressible, viscous, heat conducting fluid, for which the bulk entropy flux $\boldsymbol{\phi}_\eta^{(i)}$ can be expressed $\boldsymbol{\phi}_\eta^{(i)} = \boldsymbol{q}^{(i)}/\Theta^{(i)}$ as indicated in (28.22). We can also relax this restriction by a much weaker assumption, namely, $\left[\!\left[\boldsymbol{\phi}_\eta \cdot \boldsymbol{n}^{(\mathfrak{s})}\right]\!\right]^{(i)}|_E = 0$. In summary, we employ the restrictions

$$\left[\!\left[\boldsymbol{q} \cdot \boldsymbol{n}^{(\mathfrak{s})}\right]\!\right]^{(i)}|_E = 0, \quad [\![\Theta]\!]^{(i)}|_E = 0, \quad \left[\!\left[\boldsymbol{\phi}_\eta \cdot \boldsymbol{n}^{(\mathfrak{s})}\right]\!\right]^{(i)}|_E = 0, \tag{28.49}$$

which are physically plausible, i.e., when the phase interface is in thermodynamic equilibrium, the net heat flux and the net entropy flux from the neighboring bulk phases into the interface vanish, and the temperatures of the neighboring bulk phases at the interface are the same.

It follows that $\Pi^{(\mathfrak{s}_i)}$ has a minimum in equilibrium. Necessary conditions for this minimum are that

$$\begin{aligned} &\left.\frac{\partial \Pi^{(\mathfrak{s}_i)}}{\partial Y_k^{(\mathfrak{s}_i)}}\right|_E = 0, && Y_k^{(\mathfrak{s}_i)} \in \boldsymbol{Y}^{(\mathfrak{s}_i)}, \\ &\left.\frac{\partial^2 \Pi^{(\mathfrak{s}_i)}}{\partial Y_l^{(\mathfrak{s}_i)} \partial Y_m^{(\mathfrak{s}_i)}}\right|_E \text{ is nonnegative definite,} && Y_l^{(\mathfrak{s}_i)},\ Y_m^{(\mathfrak{s}_i)} \in \boldsymbol{Y}^{(\mathfrak{s}_i)}. \end{aligned} \tag{28.50}$$

As is well known, the first condition restricts the equilibrium forms of the dependent constitutive fields, while the second constrains the signs of material parameters. Here, we deal with the first. Applying the conditions

$$\left.\frac{\partial \Pi^{(\mathfrak{s}_i)}}{\partial \boldsymbol{D}^{(\mathfrak{s}_i)}}\right|_E = \mathbf{0}, \qquad \left.\frac{\partial \Pi^{(\mathfrak{s}_i)}}{\partial \nabla^{(\mathfrak{s}_i)} \Theta^{(\mathfrak{s}_i)}}\right|_E = \mathbf{0} \tag{28.51}$$

to the residual entropy inequality (28.47), together with condition (28.49), yields the equilibrium values of the stress, and heat flux,

$$\boldsymbol{T}_E^{(\mathfrak{s}_i)} = \sigma^{(\mathfrak{s}_i)} \boldsymbol{I}^{(\mathfrak{s}_i)}, \qquad \boldsymbol{q}_E^{(\mathfrak{s}_i)} = \mathbf{0}, \tag{28.52}$$

while the conditions

$$\left.\frac{\partial \Pi^{(\mathfrak{s}_i)}}{\partial \boldsymbol{W}_{\mathfrak{s}}^{+}}\right|_E = \mathbf{0}, \qquad \left.\frac{\partial \Pi^{(\mathfrak{s}_i)}}{\partial \boldsymbol{W}_{\mathfrak{s}}^{-}}\right|_E = \mathbf{0}, \tag{28.53}$$

together with condition (28.48) and (28.49), imply

$$\begin{aligned} & u_E^{(i-1)} - \Theta^{(\mathfrak{s}_i)} \eta_E^{(i-1)} + \frac{p^{(i-1)}}{\rho^{(i-1)}} \\ &= u_E^{(i)} - \Theta^{(\mathfrak{s}_i)} \eta_E^{(i)} + \frac{p^{(i)}}{\rho^{(i)}} \\ &= u_E^{(\mathfrak{s}_i)} - \Theta^{(\mathfrak{s}_i)} \eta_E^{(\mathfrak{s}_i)} - \frac{\sigma^{(\mathfrak{s}_i)}}{\rho^{(\mathfrak{s}_i)}} . \end{aligned} \tag{28.54}$$

The last condition $\partial \Pi^{(\mathfrak{s}_i)} / \partial \boldsymbol{W}_s |_E = \boldsymbol{0}$ yields

$$H^{(\mathfrak{s}_i)} \sigma^{(\mathfrak{s}_i)} = - [\![p]\!]^{(i)} . \tag{28.55}$$

In (28.54) and (28.55), the bulk equilibrium relations $\boldsymbol{T}^{(i)}|_E = -p^{(i)} \boldsymbol{I}$ and $\boldsymbol{T}^{(i-1)}|_E = -p^{(i-1)} \boldsymbol{I}$ have been used.

The result $(28.52)_1$ indicates that the equilibrium surface stress is isotropic and that $\sigma^{(\mathfrak{s}_i)}$ is the surface tension. Recalling the expression for $\sigma^{(\mathfrak{s}_i)}$, (28.43), we find that $\boldsymbol{T}_E^{(\mathfrak{s}_i)}$ is derivable from the free energy function. Furthermore, (28.38) and (28.43) demonstrate that, in equilibrium, the surface stress $\sigma^{(\mathfrak{s}_i)}$ is a function of the surface mass density $\rho^{(\mathfrak{s}_i)}$ and $\Theta^{(\mathfrak{s}_i)}$. This relation should be given by an equation of state. Relation $(28.52)_2$ implies in thermodynamic equilibrium a vanishing interfacial heat flux. Condition (28.55) reproduces the well-known relation of the force balance between the surface tension and the pressure on the two sides of the interface.

When $\Theta^{(\mathfrak{s}_i)} = \Theta^{(i)} = \Theta^{(i-1)}$, $\psi_E^{(i)} + p^{(i)}/\rho^{(i)} = \psi_E^{(i-1)} + p^{(i-1)}/\rho^{(i-1)}$, the first relation of (28.54) is a well-known result of thermostatics of phase equilibria and has been derived in various ways (see, e.g., BAEHR [3]). This condition means that the GIBBS functions, or the specific GIBBS free enthalpies of the phases at the interface are equal in thermodynamic equilibrium.

The second part of (28.54), $\psi_E^{(i)} + p^{(i)}/\rho^{(i)} = \psi_E^{(\mathfrak{s}_i)} - \sigma_E^{(\mathfrak{s}_i)}/\rho_E^{(\mathfrak{s}_i)}$, is new and implies important consequences for the understanding of nucleation phenomena. It contradicts the basic assumption made in classical nucleation theory, that surface tension equals the free energy of the surface per unit area, which would read $\sigma_E^{(\mathfrak{s}_i)} = \rho_E^{(\mathfrak{s}_i)} \psi_E^{(\mathfrak{s}_i)}$. We conclude that the classical nucleation theory is thermodynamically inconsistent.

28.3.3 Linear Theory for the Nonequilibrium Parts

It is assumed that the representations of the constitutive variables are composed of two parts, the equilibrium response and the dynamic or nonequilibrium response. Here we consider a linear theory in which the representations for the dynamic constitutive quantities $\boldsymbol{q}^{(\mathfrak{s}_i)} - \boldsymbol{q}_E^{(\mathfrak{s}_i)}$ and $\boldsymbol{T}^{(\mathfrak{s}_i)} - \boldsymbol{T}_E^{(\mathfrak{s}_i)}$ are linear in the nonequilibrium variables $Y_k^{(\mathfrak{s}_i)}$ defined by (28.46). Recalling the functional dependence expressed by (28.28) for $\boldsymbol{q}^{(\mathfrak{s}_i)}$ and $\boldsymbol{T}^{(\mathfrak{s}_i)}$, we then have in the linear theory

$$\boldsymbol{T}^{(\mathfrak{s}_i)} - \boldsymbol{T}_E^{(\mathfrak{s}_i)} = \lambda^{(\mathfrak{s}_i)} \left(\operatorname{tr} \boldsymbol{D}^{(\mathfrak{s}_i)}\right) \boldsymbol{I}^{(\mathfrak{s}_i)} + 2\mu^{(\mathfrak{s}_i)} \boldsymbol{D}^{(\mathfrak{s}_i)}, \tag{28.56}$$

$$\boldsymbol{q}^{(\mathfrak{s}_i)} - \boldsymbol{q}_E^{(\mathfrak{s}_i)} = -\kappa^{(\mathfrak{s}_i)} \nabla^{(\mathfrak{s}_i)} \Theta^{(\mathfrak{s}_i)} + \alpha_1^{(\mathfrak{s}_i)} \boldsymbol{W}_{\mathfrak{s}} + \alpha_2^{(\mathfrak{s}_i)} \boldsymbol{W}_{\mathfrak{s}}^{+} + \alpha_3^{(\mathfrak{s}_i)} \boldsymbol{W}_{\mathfrak{s}}^{-}, \tag{28.57}$$

where the coefficients are, in general, scalar functions as follows:

$$\begin{aligned} &\{\kappa^{(\mathfrak{s}_i)}, \lambda^{(\mathfrak{s}_i)}, \mu^{(\mathfrak{s}_i)}, \alpha_1^{(\mathfrak{s}_i)}, \alpha_2^{(\mathfrak{s}_i)}, \alpha_3^{(\mathfrak{s}_i)}\} \\ &= \{\hat{\kappa}^{(\mathfrak{s}_i)}, \hat{\lambda}^{(\mathfrak{s}_i)}, \hat{\mu}^{(\mathfrak{s}_i)}, \hat{\alpha}_1^{(\mathfrak{s}_i)}, \hat{\alpha}_2^{(\mathfrak{s}_i)}, \hat{\alpha}_3^{(\mathfrak{s}_i)}\} \left(\rho^{(\mathfrak{s}_i)}, \nabla^{(\mathfrak{s}_i)} \rho^{(\mathfrak{s}_i)}, \Theta^{(\mathfrak{s}_i)}, H^{(\mathfrak{s}_i)}\right). \end{aligned} \tag{28.58}$$

Such linear forms are indeed the simplest, and when there are not enough observations, experiments, or other physical reasons to assume that the constitutive processes involved are more complicated, it seems sensible to work with these linear forms. If necessary, more complicated constitutive assumptions for these dynamic parts can be considered.

Finally, we write the constitutive equations for $\boldsymbol{T}^{(\mathfrak{s}_i)}$ and $\boldsymbol{q}^{(\mathfrak{s}_i)}$ together

$$\boldsymbol{T}^{(\mathfrak{s}_i)} = (\sigma^{(\mathfrak{s}_i)} + \lambda^{(\mathfrak{s}_i)} \operatorname{tr} \boldsymbol{D}^{(\mathfrak{s}_i)}) \boldsymbol{I}^{(\mathfrak{s}_i)} + 2\mu^{(\mathfrak{s}_i)} \boldsymbol{D}^{(\mathfrak{s}_i)}, \tag{28.59}$$

$$\boldsymbol{q}^{(\mathfrak{s}_i)} = -\kappa^{(\mathfrak{s}_i)} \nabla^{(\mathfrak{s}_i)} \Theta^{(\mathfrak{s}_i)} + \alpha_1^{(\mathfrak{s}_i)} \boldsymbol{W}_{\mathfrak{s}} + \alpha_2^{(\mathfrak{s}_i)} \boldsymbol{W}_{\mathfrak{s}}^{+} + \alpha_3^{(\mathfrak{s}_i)} \boldsymbol{W}_{\mathfrak{s}}^{-}. \tag{28.60}$$

For variable surface mass density, the surface tension $\sigma^{(\mathfrak{s}_i)}$ can also be determined by $\psi^{(\mathfrak{s}_i)}$ in (28.43), which may be specified by an equation of state as pointed out before, while for mass density preserving surfaces, $\sigma^{(\mathfrak{s}_i)}$ is an independent variable, which can be computed by solving the field equations for the interface together with the corresponding boundary conditions.

Substituting the constitutive equations (28.59) and (28.60) into the residual entropy inequality (28.42), and evaluating the second condition of (28.50) for the minimum of the entropy production imply limitations on the material coefficients listed in (28.58). For the sake of simplicity, we evaluate this condition in index notation and assume that the stress tensor and the heat flux vector are functions of the components of $\nabla^{(\mathfrak{s}_i)} \Theta^{(\mathfrak{s}_i)}$, $\boldsymbol{W}_{\mathfrak{s}}$, $\boldsymbol{W}_{\mathfrak{s}}^{+}$, $\boldsymbol{W}_{\mathfrak{s}}^{-}$ and of six independent components of $\boldsymbol{D}^{(\mathfrak{s}_i)}$, e.g., $D_{11}^{(\mathfrak{s}_i)}$, $D_{12}^{(\mathfrak{s}_i)}$, $D_{13}^{(\mathfrak{s}_i)}$, $D_{22}^{(\mathfrak{s}_i)}$, $D_{23}^{(\mathfrak{s}_i)}$, $D_{33}^{(\mathfrak{s}_i)}$. Then, the second-order derivative is a tensor of order two, $\boldsymbol{M}^{(\mathfrak{s}_i)}$, with

$$M_{ij}^{(\mathfrak{s}_i)} = \left.\frac{\partial^2 \Pi^{(\mathfrak{s}_i)}}{\partial Z_i^{(\mathfrak{s}_i)} \partial Z_j^{(\mathfrak{s}_i)}}\right|_E, \qquad \{i, j\} \in (1, 2, \ldots, 18) \tag{28.61}$$

and

$$\begin{aligned} \boldsymbol{Z}^{(\mathfrak{s}_i)} = \Big(&\left(\nabla^{(\mathfrak{s}_i)} \Theta^{(\mathfrak{s}_i)}\right)_1, \left(\nabla^{(\mathfrak{s}_i)} \Theta^{(\mathfrak{s}_i)}\right)_2, \left(\nabla^{(\mathfrak{s}_i)} \Theta^{(\mathfrak{s}_i)}\right)_3, (\boldsymbol{W}_{\mathfrak{s}})_1, (\boldsymbol{W}_{\mathfrak{s}})_2, \\ &(\boldsymbol{W}_{\mathfrak{s}})_3, \left(\boldsymbol{W}_{\mathfrak{s}}^{+}\right)_1, \left(\boldsymbol{W}_{\mathfrak{s}}^{+}\right)_2, \left(\boldsymbol{W}_{\mathfrak{s}}^{+}\right)_3, \left(\boldsymbol{W}_{\mathfrak{s}}^{-}\right)_1, \left(\boldsymbol{W}_{\mathfrak{s}}^{-}\right)_2, \left(\boldsymbol{W}_{\mathfrak{s}}^{-}\right)_3, \\ &D_{11}^{(\mathfrak{s}_i)}, D_{12}^{(\mathfrak{s}_i)}, D_{13}^{(\mathfrak{s}_i)}, D_{22}^{(\mathfrak{s}_i)}, D_{23}^{(\mathfrak{s}_i)}, D_{33}^{(\mathfrak{s}_i)} \Big). \end{aligned} \tag{28.62}$$

Evaluating the components of $\boldsymbol{M}^{(\mathfrak{s}_i)}$ yields

$$\left.\frac{\partial^2 \Pi^{(\mathfrak{s}_i)}}{\partial\left(\nabla^{(\mathfrak{s}_i)}\Theta^{(\mathfrak{s}_i)}\right)_k \partial\left(\nabla^{(\mathfrak{s}_i)}\Theta^{(\mathfrak{s}_i)}\right)_l}\right|_E = \frac{1}{\Theta^{(\mathfrak{s}_i)}}\kappa^{(\mathfrak{s}_i)}\delta_{kl}, \tag{28.63}$$

$$\left.\frac{\partial^2 \Pi^{(\mathfrak{s}_i)}}{\partial\left(\boldsymbol{W}_{\mathfrak{s}}\right)_k \partial\left(\nabla^{(\mathfrak{s}_i)}\Theta^{(\mathfrak{s}_i)}\right)_l}\right|_E = -\frac{1}{\Theta^{(\mathfrak{s}_i)}}\alpha_1^{(\mathfrak{s}_i)}\delta_{kl}, \tag{28.64}$$

$$\left.\frac{\partial^2 \Pi^{(\mathfrak{s}_i)}}{\partial\left(\boldsymbol{W}^+_{\mathfrak{s}}\right)_k \partial\left(\nabla^{(\mathfrak{s}_i)}\Theta^{(\mathfrak{s}_i)}\right)_l}\right|_E = -\frac{1}{\Theta^{(\mathfrak{s}_i)}}\alpha_2^{(\mathfrak{s}_i)}\delta_{kl}, \tag{28.65}$$

$$\left.\frac{\partial^2 \Pi^{(\mathfrak{s}_i)}}{\partial\left(\boldsymbol{W}^-_{\mathfrak{s}}\right)_k \partial\left(\nabla^{(\mathfrak{s}_i)}\Theta^{(\mathfrak{s}_i)}\right)_l}\right|_E = -\frac{1}{\Theta^{(\mathfrak{s}_i)}}\alpha_3^{(\mathfrak{s}_i)}\delta_{kl}, \tag{28.66}$$

$$\left.\frac{\partial^2 \Pi^{(\mathfrak{s}_i)}}{\partial D_{kl}^{(\mathfrak{s}_i)} \partial D_{mn}^{(\mathfrak{s}_i)}}\right|_E = \lambda^{(\mathfrak{s}_i)}\delta_{kl} I_{mn}^{(\mathfrak{s}_i)} + \lambda^{(\mathfrak{s}_i)}\delta_{mn} I_{kl}^{(\mathfrak{s}_i)} + 4\mu^{(\mathfrak{s}_i)}\delta_{(kl)(mn)}, \tag{28.67}$$

where $\{k, l\} \in (1, 2, 3)$ and $\{m, n\} \in (1, 2, 3)$. The other components of $\boldsymbol{M}^{(\mathfrak{s}_i)}$ vanish. The condition, that the tensor $\boldsymbol{M}^{(\mathfrak{s}_i)}$ must be nonnegative definite, is equivalent to the relation $\boldsymbol{f} \cdot \boldsymbol{M}^{(\mathfrak{s}_i)} \boldsymbol{f} \geq 0$ for an arbitrary vector $\boldsymbol{f} \neq \boldsymbol{0}$. By choosing various special functions for $\boldsymbol{f}$ we obtain the following inequalities[4]

$$\kappa^{(\mathfrak{s}_i)} \geq 0, \quad \mu^{(\mathfrak{s}_i)} \geq 0, \tag{28.68}$$

$$\alpha_k^{(\mathfrak{s}_i)} = 0, \quad \lambda^{(\mathfrak{s}_i)} I_{\{kk\}}^{(\mathfrak{s}_i)} + 2\mu^{(\mathfrak{s}_i)} \geq 0, \qquad k = 1, 2, 3, \tag{28.69}$$

$$\left|\lambda^{(\mathfrak{s}_i)} I_{kl}^{(\mathfrak{s}_i)}\right| \leq \min\left\{2\left[2\mu^{(\mathfrak{s}_i)}\left(\lambda^{(\mathfrak{s}_i)} I_{\{mm\}}^{(\mathfrak{s}_i)} + 2\mu^{(\mathfrak{s}_i)}\right)\right]^{\frac{1}{2}} : m = 1, 2, 3\right\} \tag{28.70}$$
$$\text{for } (kl) = (12), (13), (23).$$

Note that in (28.69)$_2$ and (28.70) it is understood that the repeated indices $\{kk\}$ and $\{mm\}$ are not summed. Considering the validity of relations (28.69)$_2$ and (28.70) for all possible orientations of the phase interface, for which $I_{\{kk\}}^{(\mathfrak{s}_i)} \in [0, 1]$, $I_{\{mm\}}^{(\mathfrak{s}_i)} \in [0, 1]$ and $|I_{kl}^{(\mathfrak{s}_i)}| \in [0, \frac{1}{2}]$, and assuming that these material parameters are independent of the orientation of the interface yield the restrictions

$$\begin{aligned} &\lambda^{(\mathfrak{s}_i)} + 2\mu^{(\mathfrak{s}_i)} \geq 0, \\ &\left|\tfrac{1}{2}\lambda^{(\mathfrak{s}_i)}\right| \leq \min\left\{4\mu^{(\mathfrak{s}_i)}, 2\sqrt{2\mu^{(\mathfrak{s}_i)}\left(\lambda^{(\mathfrak{s}_i)} + 2\mu^{(\mathfrak{s}_i)}\right)}\right\}. \end{aligned} \tag{28.71}$$

---

[4] The derivations of the first conditions, (28.68) and (28.69)$_1$, are straight. However, the derivations of (28.69)$_2$ and (28.70) are somewhat tedious and complicated by choosing various special functions for $\boldsymbol{f}$. Here, we refrain from providing more details.

Furthermore, combining both restrictions (28.71) yields the relation

$$8(2-\sqrt{5})\mu^{(\mathfrak{s}_i)} \leq \lambda^{(\mathfrak{s}_i)} \leq 8\mu^{(\mathfrak{s}_i)}. \tag{28.72}$$

The functional forms of the coefficient functions $\kappa^{(\mathfrak{s}_i)}$, $\lambda^{(\mathfrak{s}_i)}$, $\mu^{(\mathfrak{s}_i)}$ must be determined by experiments, in general.

28.4 Constitutive Relations for the Three-Phase Contact Line

In this section, we perform an exploitation of the entropy inequality (28.18) for the three-phase contact line $\mathfrak{C}$, analogous to those corresponding processes for the phase interface demonstrated in the last section.

28.4.1 Constitutive Assumptions and Restrictions

We consider the material-dependent line variables

$$\mathcal{S} \in \{\boldsymbol{T}^{(\mathfrak{c})}, \boldsymbol{q}^{(\mathfrak{c})}, \phi_{\eta}^{(\mathfrak{c})}, \psi^{(\mathfrak{c})}, \eta^{(\mathfrak{c})}\}; \tag{28.73}$$

they are functions of the following independent line variables:

$$\mathcal{S} = \hat{\mathcal{S}}\left(\rho^{(\mathfrak{c})}, \nabla^{(\mathfrak{c})}\rho^{(\mathfrak{c})}, \Theta^{(\mathfrak{c})}, \nabla^{(\mathfrak{c})}\Theta^{(\mathfrak{c})}, \boldsymbol{D}^{(\mathfrak{c})}, \kappa^{(\mathfrak{c})}, \boldsymbol{W}_{\mathfrak{c}}, \boldsymbol{W}_{\mathfrak{c}}^{1}, \boldsymbol{W}_{\mathfrak{c}}^{2}, \boldsymbol{W}_{\mathfrak{c}}^{3}\right), \tag{28.74}$$

in which $\boldsymbol{D}^{(\mathfrak{c})} = \frac{1}{2}\left(\nabla^{(\mathfrak{c})}\boldsymbol{v}^{(\mathfrak{c})} + (\nabla^{(\mathfrak{c})}\boldsymbol{v}^{(\mathfrak{c})})^{T}\right)$ is the line stretching tensor, $\boldsymbol{W}_{\mathfrak{c}} = \boldsymbol{w}^{(\mathfrak{c})} - \boldsymbol{v}^{(\mathfrak{c})}$, and $\boldsymbol{W}_{\mathfrak{c}}^{i} = \boldsymbol{w}^{(\mathfrak{c})} - \boldsymbol{v}^{(\mathfrak{s}_i)}$ $(i \in \{1, 2, 3\})$. Here, the principle of material objectivity has been observed in the choice of the variables.

These constitutive equations must satisfy the entropy inequality (28.18). Incorporating the dependences (28.74) into (28.18) by use of the chain rule of differentiation and employing relations in $(28.19)_3$, $(28.20)_3$, and $(28.21)_3$ yields the new inequality

$$\begin{aligned}
&\Theta^{(\mathfrak{c})}\Pi^{(\mathfrak{c})} = \\
&-\left(\rho^{(\mathfrak{c})}\frac{\partial\psi^{(\mathfrak{c})}}{\partial\rho^{(\mathfrak{c})}} + \Lambda_{\rho}^{(\mathfrak{c})}\right)\frac{\mathrm{d}^{(\mathfrak{c})}\rho^{(\mathfrak{c})}}{\mathrm{d}t} - \rho^{(\mathfrak{c})}\boldsymbol{\Lambda}_{v}^{(\mathfrak{c})}\cdot\frac{\mathrm{d}^{(\mathfrak{c})}\boldsymbol{v}^{(\mathfrak{c})}}{\mathrm{d}t} \\
&+\left(\boldsymbol{T}^{(\mathfrak{c})} - \Lambda_{\rho}^{(\mathfrak{c})}\rho^{(\mathfrak{c})}\boldsymbol{I}^{(\mathfrak{c})}\right)\cdot\boldsymbol{D}^{(\mathfrak{c})} - \rho^{(\mathfrak{c})}\left(\frac{\partial\psi^{(\mathfrak{c})}}{\partial\Theta^{(\mathfrak{c})}} + \eta^{(\mathfrak{c})}\right)\frac{\mathrm{d}^{(\mathfrak{c})}\Theta^{(\mathfrak{c})}}{\mathrm{d}t} \\
&-\rho^{(\mathfrak{c})}\frac{\partial\psi^{(\mathfrak{c})}}{\partial\nabla^{(\mathfrak{c})}\rho^{(\mathfrak{c})}}\cdot\frac{\mathrm{d}^{(\mathfrak{c})}\nabla^{(\mathfrak{c})}\rho^{(\mathfrak{c})}}{\mathrm{d}t} - \rho^{(\mathfrak{c})}\frac{\partial\psi^{(\mathfrak{c})}}{\partial\nabla^{(\mathfrak{c})}\Theta^{(\mathfrak{c})}}\cdot\frac{\mathrm{d}^{(\mathfrak{c})}\nabla^{(\mathfrak{c})}\Theta^{(\mathfrak{c})}}{\mathrm{d}t}
\end{aligned}$$

$$
\begin{aligned}
&-\rho^{(\mathfrak{c})}\frac{\partial\psi^{(\mathfrak{c})}}{\partial\boldsymbol{D}^{(\mathfrak{c})}}\cdot\frac{\mathrm{d}^{(\mathfrak{c})}\boldsymbol{D}^{(\mathfrak{c})}}{\mathrm{d}t}-\rho^{(\mathfrak{c})}\frac{\partial\psi^{(\mathfrak{c})}}{\partial\kappa^{(\mathfrak{c})}}\frac{\mathrm{d}^{(\mathfrak{c})}\kappa^{(\mathfrak{c})}}{\mathrm{d}t}\\
&-\rho^{(\mathfrak{c})}\frac{\partial\psi^{(\mathfrak{c})}}{\partial\boldsymbol{W}_{\mathfrak{c}}}\cdot\frac{\mathrm{d}^{(\mathfrak{c})}\boldsymbol{W}_{\mathfrak{c}}}{\mathrm{d}t}-\sum_{i=1}^{3}\rho^{(\mathfrak{c})}\frac{\partial\psi^{(\mathfrak{c})}}{\partial\boldsymbol{W}_{\mathfrak{c}}^{i}}\cdot\frac{\mathrm{d}^{(\mathfrak{c})}\boldsymbol{W}_{\mathfrak{c}}^{i}}{\mathrm{d}t}\\
&+\left(\Theta^{(\mathfrak{c})}\frac{\partial\boldsymbol{\phi}_{\eta}^{(\mathfrak{c})}}{\partial\rho^{(\mathfrak{c})}}+\boldsymbol{\Lambda}_{v}^{(\mathfrak{c})}\cdot\frac{\partial\boldsymbol{T}^{(\mathfrak{c})}}{\partial\rho^{(\mathfrak{c})}}-\frac{\partial\boldsymbol{q}^{(\mathfrak{c})}}{\partial\rho^{(\mathfrak{c})}}\right)\cdot\nabla^{(\mathfrak{c})}\rho^{(\mathfrak{c})}\\
&+\left(\Theta^{(\mathfrak{c})}\frac{\partial\boldsymbol{\phi}_{\eta}^{(\mathfrak{c})}}{\partial\nabla^{(\mathfrak{c})}\rho^{(\mathfrak{c})}}+\boldsymbol{\Lambda}_{v}^{(\mathfrak{c})}\cdot\frac{\partial\boldsymbol{T}^{(\mathfrak{c})}}{\partial\nabla^{(\mathfrak{c})}\rho^{(\mathfrak{c})}}-\frac{\partial\boldsymbol{q}^{(\mathfrak{c})}}{\partial\nabla^{(\mathfrak{c})}\rho^{(\mathfrak{c})}}\right)\cdot\nabla^{(\mathfrak{c})}\left(\nabla^{(\mathfrak{c})}\rho^{(\mathfrak{c})}\right)\\
&+\left(\Theta^{(\mathfrak{c})}\frac{\partial\boldsymbol{\phi}_{\eta}^{(\mathfrak{c})}}{\partial\Theta^{(\mathfrak{c})}}+\boldsymbol{\Lambda}_{v}^{(\mathfrak{c})}\cdot\frac{\partial\boldsymbol{T}^{(\mathfrak{c})}}{\partial\Theta^{(\mathfrak{c})}}-\frac{\partial\boldsymbol{q}^{(\mathfrak{c})}}{\partial\Theta^{(\mathfrak{c})}}\right)\cdot\nabla^{(\mathfrak{c})}\Theta^{(\mathfrak{c})}
\end{aligned}
$$

$$
\begin{aligned}
&+\left(\Theta^{(\mathfrak{c})}\frac{\partial\boldsymbol{\phi}_{\eta}^{(\mathfrak{c})}}{\partial\nabla^{(\mathfrak{c})}\Theta^{(\mathfrak{c})}}+\boldsymbol{\Lambda}_{v}^{(\mathfrak{c})}\cdot\frac{\partial\boldsymbol{T}^{(\mathfrak{c})}}{\partial\nabla^{(\mathfrak{c})}\Theta^{(\mathfrak{c})}}-\frac{\partial\boldsymbol{q}^{(\mathfrak{c})}}{\partial\nabla^{(\mathfrak{c})}\Theta^{(\mathfrak{c})}}\right)\cdot\nabla^{(\mathfrak{c})}\left(\nabla^{(\mathfrak{c})}\Theta^{(\mathfrak{c})}\right)\\
&+\left(\Theta^{(\mathfrak{c})}\frac{\partial\boldsymbol{\phi}_{\eta}^{(\mathfrak{c})}}{\partial\boldsymbol{D}^{(\mathfrak{c})}}+\boldsymbol{\Lambda}_{v}^{(\mathfrak{c})}\cdot\frac{\partial\boldsymbol{T}^{(\mathfrak{c})}}{\partial\boldsymbol{D}^{(\mathfrak{c})}}-\frac{\partial\boldsymbol{q}^{(\mathfrak{c})}}{\partial\boldsymbol{D}^{(\mathfrak{c})}}\right)\cdot\nabla^{(\mathfrak{c})}\boldsymbol{D}^{(\mathfrak{c})}\\
&+\left(\Theta^{(\mathfrak{c})}\frac{\partial\boldsymbol{\phi}_{\eta}^{(\mathfrak{c})}}{\partial\kappa^{(\mathfrak{c})}}+\boldsymbol{\Lambda}_{v}^{(\mathfrak{c})}\cdot\frac{\partial\boldsymbol{T}^{(\mathfrak{c})}}{\partial\kappa^{(\mathfrak{c})}}-\frac{\partial\boldsymbol{q}^{(\mathfrak{c})}}{\partial\kappa^{(\mathfrak{c})}}\right)\cdot\nabla^{(\mathfrak{c})}\kappa^{(\mathfrak{c})}\\
&+\left(\Theta^{(\mathfrak{c})}\frac{\partial\boldsymbol{\phi}_{\eta}^{(\mathfrak{c})}}{\partial\boldsymbol{W}_{\mathfrak{c}}}+\boldsymbol{\Lambda}_{v}^{(\mathfrak{c})}\cdot\frac{\partial\boldsymbol{T}^{(\mathfrak{c})}}{\partial\boldsymbol{W}_{\mathfrak{c}}}-\frac{\partial\boldsymbol{q}^{(\mathfrak{c})}}{\partial\boldsymbol{W}_{\mathfrak{c}}}\right)\cdot\nabla^{(\mathfrak{c})}\boldsymbol{W}_{\mathfrak{c}}\\
&+\sum_{i=1}^{3}\left(\Theta^{(\mathfrak{c})}\frac{\partial\boldsymbol{\phi}_{\eta}^{(\mathfrak{c})}}{\partial\boldsymbol{W}_{\mathfrak{c}}^{i}}+\boldsymbol{\Lambda}_{v}^{(\mathfrak{c})}\cdot\frac{\partial\boldsymbol{T}^{(\mathfrak{c})}}{\partial\boldsymbol{W}_{\mathfrak{c}}^{i}}-\frac{\partial\boldsymbol{q}^{(\mathfrak{c})}}{\partial\boldsymbol{W}_{\mathfrak{c}}^{i}}\right)\cdot\nabla^{(\mathfrak{c})}\boldsymbol{W}_{\mathfrak{c}}^{i}\\
&-\kappa^{(\mathfrak{c})}\Theta^{(\mathfrak{c})}\left(\boldsymbol{\phi}_{\eta}^{(\mathfrak{c})}\cdot\boldsymbol{n}^{(\mathfrak{c})}\right)-\kappa^{(\mathfrak{c})}\Lambda_{\rho}^{(\mathfrak{c})}\rho^{(\mathfrak{c})}\left(\left(\boldsymbol{w}^{(\mathfrak{c})}-\boldsymbol{v}^{(\mathfrak{c})}\right)\cdot\boldsymbol{n}^{(\mathfrak{c})}\right)\\
&-\kappa^{(\mathfrak{c})}\boldsymbol{\Lambda}_{v}^{(\mathfrak{c})}\cdot\left(\boldsymbol{T}^{(\mathfrak{c})}\cdot\boldsymbol{n}^{(\mathfrak{c})}\right)+\kappa^{(\mathfrak{c})}\left(\boldsymbol{q}^{(\mathfrak{c})}\cdot\boldsymbol{n}^{(\mathfrak{c})}\right)\\
&+\sum_{i=1}^{3}\left(\rho^{(\mathfrak{s}_i)}\left(\eta^{(\mathfrak{s}_i)}-\eta^{(\mathfrak{c})}\right)\left(\boldsymbol{w}^{(\mathfrak{c})}-\boldsymbol{v}^{(\mathfrak{s}_i)}\right)\cdot\boldsymbol{s}^{(i)}-\boldsymbol{\phi}_{\eta}^{(\mathfrak{s}_i)}\cdot\boldsymbol{s}^{(i)}\right)\\
&-\Lambda_{\rho}^{(\mathfrak{c})}\sum_{i=1}^{3}\left(\rho^{(\mathfrak{s}_i)}\left(\boldsymbol{w}^{(\mathfrak{c})}-\boldsymbol{v}^{(\mathfrak{s}_i)}\right)\cdot\boldsymbol{s}^{(i)}\right)\\
&-\boldsymbol{\Lambda}_{v}^{(\mathfrak{c})}\cdot\sum_{i=1}^{3}\left(\rho^{(\mathfrak{s}_i)}\left(\boldsymbol{v}^{(\mathfrak{s}_i)}-\boldsymbol{v}^{(\mathfrak{c})}\right)\left(\boldsymbol{w}^{(\mathfrak{c})}-\boldsymbol{v}^{(\mathfrak{s}_i)}\right)\cdot\boldsymbol{s}^{(i)}+\boldsymbol{T}^{(\mathfrak{s}_i)}\cdot\boldsymbol{s}^{(i)}\right)\\
&-\sum_{i=1}^{3}\left(\rho^{(\mathfrak{s}_i)}\left(\left(u^{(\mathfrak{s}_i)}-u^{(\mathfrak{c})}\right)+\tfrac{1}{2}\left(\boldsymbol{v}^{(\mathfrak{s}_i)}-\boldsymbol{v}^{(\mathfrak{c})}\right)\cdot\left(\boldsymbol{v}^{(\mathfrak{s}_i)}-\boldsymbol{v}^{(\mathfrak{c})}\right)\right)\right.
\end{aligned}
$$

$$\begin{aligned}&\Big(\big(\boldsymbol{w}^{(\mathrm{c})}-\boldsymbol{v}^{(\mathfrak{s}_i)}\big)\cdot\boldsymbol{s}^{(i)}\Big)-\boldsymbol{q}^{(\mathfrak{s}_i)}\cdot\boldsymbol{s}^{(i)}+\Big(\boldsymbol{T}^{(\mathfrak{s}_i)}\big(\boldsymbol{v}^{(\mathfrak{s}_i)}-\boldsymbol{v}^{(\mathrm{c})}\big)\Big)\cdot\boldsymbol{s}^{(i)}\Big)\\&\geq 0.\end{aligned} \tag{28.75}$$

This inequality is linear in the new independent variables, indicated by red color in (28.75) and can be collected as follows:

$$\begin{aligned}\boldsymbol{\alpha}^{(\mathrm{c})}=\;&\bigg\{\frac{\mathrm{d}^{(\mathrm{c})}\rho^{(\mathrm{c})}}{\mathrm{d}t},\frac{\mathrm{d}^{(\mathrm{c})}\boldsymbol{v}^{(\mathrm{c})}}{\mathrm{d}t},\frac{\mathrm{d}^{(\mathrm{c})}\Theta^{(\mathrm{c})}}{\mathrm{d}t},\frac{\mathrm{d}^{(\mathrm{c})}\nabla^{(\mathrm{c})}\rho^{(\mathrm{c})}}{\mathrm{d}t},\frac{\mathrm{d}^{(\mathrm{c})}\nabla^{(\mathrm{c})}\Theta^{(\mathrm{c})}}{\mathrm{d}t},\frac{\mathrm{d}^{(\mathrm{c})}\boldsymbol{D}^{(\mathrm{c})}}{\mathrm{d}t},\\&\frac{\mathrm{d}^{(\mathrm{c})}\kappa^{(\mathrm{c})}}{\mathrm{d}t},\nabla^{(\mathrm{c})}\left(\nabla^{(\mathrm{c})}\rho^{(\mathrm{c})}\right),\nabla^{(\mathrm{c})}\left(\nabla^{(\mathrm{c})}\Theta^{(\mathrm{c})}\right),\nabla^{(\mathrm{c})}\boldsymbol{D}^{(\mathrm{c})},\nabla^{(\mathrm{c})}\kappa^{(\mathrm{c})}\\&\frac{\mathrm{d}^{(\mathrm{c})}\boldsymbol{W}_{\mathrm{c}}}{\mathrm{d}t},\frac{\mathrm{d}^{(\mathrm{c})}\boldsymbol{W}_{\mathrm{c}}^{1}}{\mathrm{d}t},\frac{\mathrm{d}^{(\mathrm{c})}\boldsymbol{W}_{\mathrm{c}}^{2}}{\mathrm{d}t},\frac{\mathrm{d}^{(\mathrm{c})}\boldsymbol{W}_{\mathrm{c}}^{3}}{\mathrm{d}t},\\&\nabla^{(\mathrm{c})}\boldsymbol{W}_{\mathrm{c}},\nabla^{(\mathrm{c})}\boldsymbol{W}_{\mathrm{c}}^{1},\nabla^{(\mathrm{c})}\boldsymbol{W}_{\mathrm{c}}^{2},\nabla^{(\mathrm{c})}\boldsymbol{W}_{\mathrm{c}}^{3},\bigg\}.\end{aligned} \tag{28.76}$$

Since thermodynamic processes, for which these variables can take any values, are admissible, the coefficients $\boldsymbol{a}^{(\mathrm{c})}$ of $\boldsymbol{a}^{(\mathrm{c})}\cdot\boldsymbol{\alpha}^{(\mathrm{c})}$ must vanish. This leads to the so-called LIU identities. It then follows that the expressions for the LAGRANGE multipliers, $\Lambda_{\rho}^{(\mathrm{c})}$ and $\boldsymbol{\Lambda}_{v}^{(\mathrm{c})}$, are

$$\Lambda_{\rho}^{(\mathrm{c})}=-\rho^{(\mathrm{c})}\frac{\partial\psi^{(\mathrm{c})}}{\partial\rho^{(\mathrm{c})}},\quad\boldsymbol{\Lambda}_{v}^{(\mathrm{c})}=\boldsymbol{0}, \tag{28.77}$$

for the specific entropy density is

$$\eta^{(\mathrm{c})}=-\frac{\partial\psi^{(\mathrm{c})}}{\partial\Theta^{(\mathrm{c})}}, \tag{28.78}$$

and for the free energy $\psi^{(\mathrm{c})}$ implies

$$\begin{aligned}&\frac{\partial\psi^{(\mathrm{c})}}{\partial\nabla^{(\mathrm{c})}\rho^{(\mathrm{c})}}=\boldsymbol{0},\quad\frac{\partial\psi^{(\mathrm{c})}}{\partial\nabla^{(\mathrm{c})}\Theta^{(\mathrm{c})}}=\boldsymbol{0},\quad\frac{\partial\psi^{(\mathrm{c})}}{\partial\boldsymbol{D}^{(\mathrm{c})}}=\boldsymbol{0},\quad\frac{\partial\psi^{(\mathrm{c})}}{\partial\kappa^{(\mathrm{c})}}=0,\\&\frac{\partial\psi^{(\mathrm{c})}}{\partial\boldsymbol{W}_{\mathrm{c}}}=\boldsymbol{0},\quad\frac{\partial\psi^{(\mathrm{c})}}{\partial\boldsymbol{W}_{\mathrm{c}}^{1}}=\boldsymbol{0},\quad\frac{\partial\psi^{(\mathrm{c})}}{\partial\boldsymbol{W}_{\mathrm{c}}^{2}}=\boldsymbol{0},\quad\frac{\partial\psi^{(\mathrm{c})}}{\partial\boldsymbol{W}_{\mathrm{c}}^{3}}=\boldsymbol{0}.\end{aligned} \tag{28.79}$$

Moreover, the relations among $\boldsymbol{\phi}^{(\mathfrak{c})}$, $\boldsymbol{T}^{(\mathfrak{c})}$, and $\boldsymbol{q}^{(\mathfrak{c})}$

$$\begin{aligned}
\operatorname{sym}\left(\Theta^{(\mathfrak{c})}\frac{\partial\boldsymbol{\phi}_\eta^{(\mathfrak{c})}}{\partial\nabla^{(\mathfrak{c})}\rho^{(\mathfrak{c})}}+\boldsymbol{\Lambda}_v^{(\mathfrak{c})}\cdot\frac{\partial\boldsymbol{T}^{(\mathfrak{c})}}{\partial\nabla^{(\mathfrak{c})}\rho^{(\mathfrak{c})}}-\frac{\partial\boldsymbol{q}^{(\mathfrak{c})}}{\partial\nabla^{(\mathfrak{c})}\rho^{(\mathfrak{c})}}\right)&=\mathbf{0},\\
\operatorname{sym}\left(\Theta^{(\mathfrak{c})}\frac{\partial\boldsymbol{\phi}_\eta^{(\mathfrak{c})}}{\partial\nabla^{(\mathfrak{c})}\Theta^{(\mathfrak{c})}}+\boldsymbol{\Lambda}_v^{(\mathfrak{c})}\cdot\frac{\partial\boldsymbol{T}^{(\mathfrak{c})}}{\partial\nabla^{(\mathfrak{c})}\Theta^{(\mathfrak{c})}}-\frac{\partial\boldsymbol{q}^{(\mathfrak{c})}}{\partial\nabla^{(\mathfrak{c})}\Theta^{(\mathfrak{c})}}\right)&=\mathbf{0},\\
\Theta^{(\mathfrak{c})}\frac{\partial\boldsymbol{\phi}_\eta^{(\mathfrak{c})}}{\partial\boldsymbol{D}^{(\mathfrak{c})}}+\boldsymbol{\Lambda}_v^{(\mathfrak{c})}\cdot\frac{\partial\boldsymbol{T}^{(\mathfrak{c})}}{\partial\boldsymbol{D}^{(\mathfrak{c})}}-\frac{\partial\boldsymbol{q}^{(\mathfrak{c})}}{\partial\boldsymbol{D}^{(\mathfrak{c})}}&=\mathbf{0},\\
\Theta^{(\mathfrak{c})}\frac{\partial\boldsymbol{\phi}_\eta^{(\mathfrak{c})}}{\partial\kappa^{(\mathfrak{c})}}+\boldsymbol{\Lambda}_v^{(\mathfrak{c})}\cdot\frac{\partial\boldsymbol{T}^{(\mathfrak{c})}}{\partial\kappa^{(\mathfrak{c})}}-\frac{\partial\boldsymbol{q}^{(\mathfrak{c})}}{\partial\kappa^{(\mathfrak{c})}}&=\mathbf{0},\\
\Theta^{(\mathfrak{c})}\frac{\partial\boldsymbol{\phi}_\eta^{(\mathfrak{c})}}{\partial\boldsymbol{W}_{\mathfrak{c}}}+\boldsymbol{\Lambda}_v^{(\mathfrak{c})}\cdot\frac{\partial\boldsymbol{T}^{(\mathfrak{c})}}{\partial\boldsymbol{W}_{\mathfrak{c}}}-\frac{\partial\boldsymbol{q}^{(\mathfrak{c})}}{\partial\boldsymbol{W}_{\mathfrak{c}}}&=\mathbf{0},\\
\Theta^{(\mathfrak{c})}\frac{\partial\boldsymbol{\phi}_\eta^{(\mathfrak{c})}}{\partial\boldsymbol{W}_{\mathfrak{c}}^1}+\boldsymbol{\Lambda}_v^{(\mathfrak{c})}\cdot\frac{\partial\boldsymbol{T}^{(\mathfrak{c})}}{\partial\boldsymbol{W}_{\mathfrak{c}}^1}-\frac{\partial\boldsymbol{q}^{(\mathfrak{c})}}{\partial\boldsymbol{W}_{\mathfrak{c}}^1}&=\mathbf{0},\\
\Theta^{(\mathfrak{c})}\frac{\partial\boldsymbol{\phi}_\eta^{(\mathfrak{c})}}{\partial\boldsymbol{W}_{\mathfrak{c}}^2}+\boldsymbol{\Lambda}_v^{(\mathfrak{c})}\cdot\frac{\partial\boldsymbol{T}^{(\mathfrak{c})}}{\partial\boldsymbol{W}_{\mathfrak{c}}^2}-\frac{\partial\boldsymbol{q}^{(\mathfrak{c})}}{\partial\boldsymbol{W}_{\mathfrak{c}}^2}&=\mathbf{0},\\
\Theta^{(\mathfrak{c})}\frac{\partial\boldsymbol{\phi}_\eta^{(\mathfrak{c})}}{\partial\boldsymbol{W}_{\mathfrak{c}}^3}+\boldsymbol{\Lambda}_v^{(\mathfrak{c})}\cdot\frac{\partial\boldsymbol{T}^{(\mathfrak{c})}}{\partial\boldsymbol{W}_{\mathfrak{c}}^3}-\frac{\partial\boldsymbol{q}^{(\mathfrak{c})}}{\partial\boldsymbol{W}_{\mathfrak{c}}^3}&=\mathbf{0},
\end{aligned}\tag{28.80}$$

must hold, where $\operatorname{sym}\boldsymbol{A}=\frac{1}{2}\left(\boldsymbol{A}+\boldsymbol{A}^T\right)$.

The restrictions on the free energy (28.79) imply the reduced dependence

$$\psi^{(\mathfrak{c})}=\hat{\psi}^{(\mathfrak{c})}\left(\rho^{(\mathfrak{c})},\Theta^{(\mathfrak{c})}\right).\tag{28.81}$$

Introducing the extra entropy flux

$$\boldsymbol{\Phi}_\eta^{(\mathfrak{c})}=\boldsymbol{\phi}_\eta^{(\mathfrak{c})}+\frac{1}{\Theta^{(\mathfrak{c})}}\left(\boldsymbol{\Lambda}_v^{(\mathfrak{c})}\cdot\boldsymbol{T}^{(\mathfrak{c})}-\boldsymbol{q}^{(\mathfrak{c})}\right)\tag{28.82}$$

and considering $(28.77)_2$, we have from (28.80)

$$\begin{gathered}
\operatorname{sym}\left(\frac{\partial\boldsymbol{\Phi}_\eta^{(\mathfrak{c})}}{\partial\nabla^{(\mathfrak{c})}\rho^{(\mathfrak{c})}}\right)=\mathbf{0},\quad\operatorname{sym}\left(\frac{\partial\boldsymbol{\Phi}_\eta^{(\mathfrak{c})}}{\partial\nabla^{(\mathfrak{c})}\Theta^{(\mathfrak{c})}}\right)=\mathbf{0},\quad\frac{\partial\boldsymbol{\Phi}_\eta^{(\mathfrak{c})}}{\partial\boldsymbol{D}^{(\mathfrak{c})}}=\mathbf{0},\\
\frac{\partial\boldsymbol{\Phi}_\eta^{(\mathfrak{c})}}{\partial\kappa^{(\mathfrak{c})}}=\mathbf{0},\quad\frac{\partial\boldsymbol{\Phi}_\eta^{(\mathfrak{c})}}{\partial\boldsymbol{W}_{\mathfrak{c}}}=\mathbf{0},\quad\frac{\partial\boldsymbol{\Phi}_\eta^{(\mathfrak{c})}}{\partial\boldsymbol{W}_{\mathfrak{c}}^1}=\mathbf{0},\quad\frac{\partial\boldsymbol{\Phi}_\eta^{(\mathfrak{c})}}{\partial\boldsymbol{W}_{\mathfrak{c}}^2}=\mathbf{0},\quad\frac{\partial\boldsymbol{\Phi}_\eta^{(\mathfrak{c})}}{\partial\boldsymbol{W}_{\mathfrak{c}}^3}=\mathbf{0}.
\end{gathered}\tag{28.83}$$

Using the restrictions (28.83) on the extra entropy flux $\boldsymbol{\Phi}_{\eta}^{(\mathrm{c})}$ and the isotropy assumption, it follows that

$$\boldsymbol{\Phi}_{\eta}^{(\mathrm{c})} = \mathbf{0}. \tag{28.84}$$

Thus, the entropy flux assumes its traditional form and equals the heat flux divided by the temperature, as presumed in the COLEMAN–NOLL approach. It can be shown that this result will not follow, if we add the dependences $\mathrm{d}^{(\mathrm{c})}\rho^{(\mathrm{c})}/\mathrm{d}t$ and/or $\mathrm{d}^{(\mathrm{c})}\Theta^{(\mathrm{c})}/\mathrm{d}t$ to the constitutive functions (28.74).

Substituting the restrictions (28.77)–(28.84) into the entropy inequality (28.75), we obtain the reduced entropy inequality in the form

$$\begin{aligned}
&\Theta^{(\mathrm{c})}\Pi^{(\mathrm{c})}\\
&= \left(\boldsymbol{T}^{(\mathrm{c})} - \tau^{(\mathrm{c})}\boldsymbol{I}^{(\mathrm{c})}\right)\cdot\boldsymbol{D}^{(\mathrm{c})} - \frac{\boldsymbol{q}^{(\mathrm{c})}\cdot\nabla^{(\mathrm{c})}\Theta^{(\mathrm{c})}}{\Theta^{(\mathrm{c})}} - \kappa^{(\mathrm{c})}\tau^{(\mathrm{c})}\left(\left(\boldsymbol{w}^{(\mathrm{c})} - \boldsymbol{v}^{(\mathrm{c})}\right)\cdot\boldsymbol{n}^{(\mathrm{c})}\right)\\
&\quad + \sum_{i=1}^{3}\left(\rho^{(\mathfrak{s}_i)}\left(\eta^{(\mathfrak{s}_i)} - \eta^{(\mathrm{c})}\right)\left(\boldsymbol{w}^{(\mathrm{c})} - \boldsymbol{v}^{(\mathfrak{s}_i)}\right)\cdot\boldsymbol{s}^{(i)} - \boldsymbol{\phi}_{\eta}^{(\mathfrak{s}_i)}\cdot\boldsymbol{s}^{(i)}\right)\\
&\quad -\tau^{(\mathrm{c})}/\rho^{(\mathrm{c})}\sum_{i=1}^{3}\left(\rho^{(\mathfrak{s}_i)}\left(\boldsymbol{w}^{(\mathrm{c})} - \boldsymbol{v}^{(\mathfrak{s}_i)}\right)\cdot\boldsymbol{s}^{(i)}\right)\\
&\quad -\sum_{i=1}^{3}\left(\rho^{(\mathfrak{s}_i)}\left(\left(u^{(\mathfrak{s}_i)} - u^{(\mathrm{c})}\right) + \tfrac{1}{2}\left(\boldsymbol{v}^{(\mathfrak{s}_i)} - \boldsymbol{v}^{(\mathrm{c})}\right)\cdot\left(\boldsymbol{v}^{(\mathfrak{s}_i)} - \boldsymbol{v}^{(\mathrm{c})}\right)\right)\right.\\
&\quad \left.\left(\left(\boldsymbol{w}^{(\mathrm{c})} - \boldsymbol{v}^{(\mathfrak{s}_i)}\right)\cdot\boldsymbol{s}^{(i)}\right) - \boldsymbol{q}^{(\mathfrak{s}_i)}\cdot\boldsymbol{s}^{(i)} + \left(\boldsymbol{T}^{(\mathfrak{s}_i)}\left(\boldsymbol{v}^{(\mathfrak{s}_i)} - \boldsymbol{v}^{(\mathrm{c})}\right)\right)\cdot\boldsymbol{s}^{(i)}\right)\\
&\geq 0,
\end{aligned} \tag{28.85}$$

where we have introduced the definition

$$\tau^{(\mathrm{c})} = -\rho^{(\mathrm{c})2}\frac{\partial\psi^{(\mathrm{c})}}{\partial\rho^{(\mathrm{c})}}. \tag{28.86}$$

We will see later that $\tau^{(\mathrm{c})}$ corresponds to the line tension.

As shown above in (28.86), when the line mass density $\rho^{(\mathrm{c})}$ is a physical variable, the line tension $\tau^{(\mathrm{c})}$ is not a field quantity and should be determined by an additional equation of state depending on the surface density and temperature (via the line free energy $\psi^{(\mathrm{c})}$). For a density preserving line, i.e., when the line density is constant, it can be demonstrated that $\tau^{(\mathrm{c})}$ is an independent field quantity and can be determined by solving the field equations in a suitably formulated boundary value problem.

It can be easily seen that the line entropy $\eta^{(\mathrm{c})}$, internal energy $u^{(\mathrm{c})}$ and tension $\tau^{(\mathrm{c})}$, which all are only functions of the line density $\rho^{(\mathrm{c})}$ and temperature $\Theta^{(\mathrm{c})}$, are related by the GIBBS equation[5]

$$\mathrm{d}\eta^{(\mathrm{c})} = \frac{1}{\Theta^{(\mathrm{c})}}\left(\mathrm{d}u^{(\mathrm{c})} - \tau^{(\mathrm{c})}\mathrm{d}\left(\frac{1}{\rho^{(\mathrm{c})}}\right)\right), \tag{28.87}$$

an equation which is analogous to the corresponding GIBBS relations in the bulk, (28.23), and on the interface, (28.45).

28.4.2 Thermodynamic Equilibrium

As usual, further restrictions on the constitutive relations can be obtained from the residual inequality (28.85) in the context of thermodynamic equilibrium, which is characterized in the current local formulation by the vanishing of the entropy production rate density $\Pi^{(\mathrm{c})}$. In the context of the current constitutive class, (28.85) implies that $\Pi^{(\mathrm{c})}$ vanishes when the independent dynamic variables

$$\boldsymbol{Y}^{(\mathrm{c})} = \left(\nabla^{(\mathrm{c})}\Theta^{(\mathrm{c})}, \boldsymbol{D}^{(\mathrm{c})}, \boldsymbol{W}_{\mathrm{c}}, \boldsymbol{W}_{\mathrm{c}}^{1}, \boldsymbol{W}_{\mathrm{c}}^{2}, \boldsymbol{W}_{\mathrm{c}}^{3}\right) \tag{28.88}$$

all vanish, where $\boldsymbol{W}_{\mathrm{c}} = \boldsymbol{w}^{(\mathrm{c})} - \boldsymbol{v}^{(\mathrm{c})}$, and $\boldsymbol{W}_{\mathrm{c}}^{i} = \boldsymbol{w}^{(\mathrm{c})} - \boldsymbol{v}^{(\mathfrak{s}_i)}$ ($i \in \{1, 2, 3\}$). We see that the line entropy production $\Pi^{(\mathrm{c})}$ has a minimum in equilibrium. Necessary conditions for this minimum are that

$$\begin{aligned} &\left.\frac{\partial \Pi^{(\mathrm{c})}}{\partial Y_k^{(\mathrm{c})}}\right|_{\boldsymbol{Y}^{(\mathrm{c})}=\boldsymbol{0}} = 0, && Y_k^{(\mathrm{c})} \in \boldsymbol{Y}^{(\mathrm{c})}, \\ &\left.\frac{\partial^2 \Pi^{(\mathrm{c})}}{\partial Y_l^{(\mathrm{c})}\partial Y_m^{(\mathrm{c})}}\right|_{\boldsymbol{Y}^{(\mathrm{c})}=\boldsymbol{0}} \text{ is nonnegative definite, } && Y_l^{(\mathrm{c})},\ Y_m^{(\mathrm{c})} \in \boldsymbol{Y}^{(\mathrm{c})}. \end{aligned} \tag{28.89}$$

As is well known, the first condition restricts the equilibrium forms of the dependent constitutive fields, while the second constrains the signs of material coefficients; here we deal only with the first. For $Y_k^{(\mathrm{c})} \in \{\boldsymbol{D}^{(\mathrm{c})}, \nabla^{(\mathrm{c})}\Theta^{(\mathrm{c})}\}$, $(28.89)_1$ yields the equilibrium values of the stress, and heat flux in the forms

$$\boldsymbol{T}_E^{(\mathrm{c})} = \tau^{(\mathrm{c})}\boldsymbol{I}^{(\mathrm{c})}, \quad \boldsymbol{q}_E^{(\mathrm{c})} = \boldsymbol{0}. \tag{28.90}$$

Recalling the expression for $\tau^{(\mathrm{c})}$, (28.86), we find that $\boldsymbol{T}_E^{(\mathrm{c})}$ is derivable from the free energy function. Furthermore, (28.90) demonstrates that, in equilibrium, the line stress $\tau^{(\mathrm{c})}$ is a function of the surface mass density $\rho^{(\mathrm{c})}$ and $\Theta^{(\mathrm{c})}$. This relation should be given by an equation of state. If the line density $\rho^{(\mathrm{c})}$ is constant, the line tension is an independent field quantity and can be determined by the field equations.

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[5] The GIBBS equation for the contact line, (28.87), can also be proved as demonstrated for the surfacial GIBBS equation, (28.45) in footnote 3 on page 429.

For $Y_k^{(\mathfrak{c})} \in \{\boldsymbol{W}_{\mathfrak{c}}\}$, $(28.89)_1$ implies

$$\kappa^{(\mathfrak{c})}\tau^{(\mathfrak{c})}\boldsymbol{n}^{(\mathfrak{c})} = -\sum_{i=1}^{3} \sigma^{(\mathfrak{s}_i)}\boldsymbol{s}^{(i)}, \tag{28.91}$$

which in case of vanishing line tension is reduced to the generalized YOUNG equation, while $(28.89)_1$ for $Y_k^{(\mathfrak{c})} \in \{\boldsymbol{W}_{\mathfrak{c}}^{i}\}$ $(i = 1, 2, 3)$ yields

$$u_E^{(\mathfrak{s}_i)} - \Theta^{(\mathfrak{c})}\eta_E^{(\mathfrak{s}_i)} - \frac{\sigma^{(\mathfrak{s}_i)}}{\rho^{(\mathfrak{s}_i)}} = u_E^{(\mathfrak{c})} - \Theta^{(\mathfrak{c})}\eta_E^{(\mathfrak{c})} - \frac{\tau^{(\mathfrak{c})}}{\rho^{(\mathfrak{c})}}, \tag{28.92}$$

or in terms of the HELMHOLTZ free energies, if it is assumed that the temperature from the interface $\mathfrak{S}^{(i)}$ to the contact line $\mathfrak{C}$ is continuous, $\Theta^{(\mathfrak{s}_i)} = \Theta^{(\mathfrak{c})}$,

$$\psi^{(\mathfrak{s}_i)} - \frac{\sigma^{(\mathfrak{s}_i)}}{\rho^{(\mathfrak{s}_i)}} = \psi^{(\mathfrak{c})} - \frac{\tau^{(\mathfrak{c})}}{\rho^{(\mathfrak{c})}}, \tag{28.93}$$

or when using equations (28.43) and (28.86) to express $\sigma^{(\mathfrak{s}_i)}$ and $\tau^{(\mathfrak{c})}$ in terms of $\psi^{(\mathfrak{s}_i)}$, respectively,

$$\frac{\partial\left(\rho^{(\mathfrak{s}_i)}\psi^{(\mathfrak{s}_i)}\right)}{\partial\rho^{(\mathfrak{s}_i)}} = \frac{\partial\left(\rho^{(\mathfrak{c})}\psi^{(\mathfrak{c})}\right)}{\partial\rho^{(\mathfrak{c})}}, \tag{28.94}$$

an equation which is impressive merely by its beauty. Substituting (28.93) into (28.91) yields

$$\kappa^{(\mathfrak{c})}\tau^{(\mathfrak{c})}\boldsymbol{n}^{(\mathfrak{c})} = -\sum_{i=1}^{3}\left\{\rho^{(\mathfrak{s}_i)}\left(\psi^{(\mathfrak{s}_i)} - \psi^{(\mathfrak{c})}\right) + \frac{\rho^{(\mathfrak{s}_i)}}{\rho^{(\mathfrak{c})}}\tau^{(\mathfrak{c})}\right\}\boldsymbol{s}^{(i)}, \tag{28.95}$$

or when expressing $\tau^{(\mathfrak{c})}$ by (28.86)

$$-\kappa^{(\mathfrak{c})}\rho^{(\mathfrak{c})}\frac{\partial\psi^{(\mathfrak{c})}}{\partial\rho^{(\mathfrak{c})}}\boldsymbol{n}^{(\mathfrak{c})} = -\sum_{i=1}^{3}\left\{\frac{\rho^{(\mathfrak{s}_i)}}{\rho^{(\mathfrak{c})}}\left(\psi^{(\mathfrak{s}_i)} - \psi^{(\mathfrak{c})}\right) - \rho^{(\mathfrak{s}_i)}\frac{\partial\psi^{(\mathfrak{c})}}{\partial\rho^{(\mathfrak{c})}}\right\}\boldsymbol{s}^{(i)}. \tag{28.96}$$

This equation expresses the unit principal normal vector $\boldsymbol{n}^{(\mathfrak{c})}$ in terms of the unit vectors normal to the boundary curve $\mathfrak{C}$ and tangential to the interfaces $\mathfrak{S}^{(i)}$, pointing exterior to $\mathfrak{S}^{(i)}$ *plus* the mass densities and the free energies of the interfaces and the contact line. This relation can be considered as another form of the generalized YOUNG equation in terms of the surface and line HELMHOLTZ free energies. In this balance, the line curvature $\kappa^{(\mathfrak{c})}$ is the only differential geometric property that enters (28.96). For straight contact lines, $\kappa^{(\mathfrak{c})}$ vanishes so that the right-hand side of (28.96) must vanish by itself.

28.4.3 Linear Theory for the Nonequilibrium Parts

Here we consider a linear theory, one of the simplest possible forms, in which the representations for $\boldsymbol{q}^{(c)} - \boldsymbol{q}_E^{(c)}$ and $\boldsymbol{T}^{(c)} - \boldsymbol{T}_E^{(c)}$ are linear in the variables $Y_k^{(c)}$ defined by (28.88). Recalling the functional dependence expressed by (28.74) for $\boldsymbol{q}^{(c)}$ and $\boldsymbol{T}^{(c)}$, we then have in the linear theory

$$\boldsymbol{T}^{(c)} - \boldsymbol{T}_E^{(c)} = \lambda^{(c)} \left(\mathrm{tr}\, \boldsymbol{D}^{(c)}\right) \boldsymbol{I}^{(c)} + 2\mu^{(c)} \boldsymbol{D}^{(c)}, \tag{28.97}$$

$$\boldsymbol{q}^{(c)} - \boldsymbol{q}_E^{(c)} = -\kappa^{(c)} \nabla^{(c)} \Theta^{(c)} + \alpha_0^{(c)} \boldsymbol{W}_c + \sum_{i=1}^{3} \alpha_i^{(c)} \boldsymbol{W}_c^i, \tag{28.98}$$

where the coefficients are, in general, scalar functions as follows:

$$\begin{aligned} &\{\kappa^{(c)}, \lambda^{(c)}, \mu^{(c)}, \alpha_0^{(c)}, \alpha_1^{(c)}, \alpha_2^{(c)}, \alpha_3^{(c)}\} \\ &= \{\hat{\kappa}^{(c)}, \hat{\lambda}^{(c)}, \hat{\mu}^{(c)}, \hat{\alpha}_0^{(c)}, \hat{\alpha}_1^{(c)}, \hat{\alpha}_2^{(c)}, \hat{\alpha}_3^{(c)}\} \left(\rho^{(c)}, \nabla^{(c)}\rho^{(c)}, \Theta^{(c)}, \kappa^{(c)}\right). \end{aligned} \tag{28.99}$$

The complete constitutive equations for $\boldsymbol{T}$ and $\boldsymbol{q}$ can be written as

$$\boldsymbol{T}^{(c)} = (\tau^{(c)} + \lambda^{(c)} \mathrm{tr}\, \boldsymbol{D}^{(c)}) \boldsymbol{I}^{(c)} + 2\mu^{(c)} \boldsymbol{D}^{(c)}, \tag{28.100}$$

$$\boldsymbol{q}^{(c)} = -\kappa^{(c)} \nabla^{(c)} \Theta^{(c)} + \alpha_0^{(c)} \boldsymbol{W}_c + \sum_{i=1}^{3} \alpha_i^{(c)} \boldsymbol{W}_c^i. \tag{28.101}$$

These constitutive relations for line quantities are fairly similar to the surface constitutive equations, given in (28.59) and (28.60). For variable line mass density, the line tension $\tau^{(c)}$ can also be determined by $\psi^{(c)}$ via (28.86), while for a density preserving line, $\tau^{(c)}$ is an independent variable, which can be computed from the momentum equation and the boundary conditions.

As obtained above the evaluation of the second condition for the minimum results in conditions on the material coefficients. For the sake of simplicity we evaluated the second condition in index notation and assumed that the stress tensor and the heat flux vector are functions of the components of $\nabla^{(c)}\Theta^{(c)}$, $\boldsymbol{W}_c$, $\boldsymbol{W}_c^j$, $j = 1, 2, 3$ and of six independent components of $\boldsymbol{D}^{(c)}$. Here we use the components $D_{11}^{(c)}$, $D_{12}^{(c)}$, $D_{13}^{(c)}$, $D_{22}^{(c)}$, $D_{23}^{(c)}$, $D_{33}^{(c)}$ of $\boldsymbol{D}^{(c)}$. Then the second derivative is a second-order tensor $\boldsymbol{M}^{(c)}$ with

$$M_{ij}^{(c)} = \left. \frac{\partial^2 \Pi^{(c)}}{\partial Z_i^{(c)} \partial Z_j^{(c)}} \right|_E, \qquad \{i, j\} \in (1, 2, \ldots, 21) \tag{28.102}$$

and

$$\begin{aligned}\boldsymbol{Z}^{(\mathrm{c})} = \Big(&\big(\nabla^{(\mathrm{c})}\Theta^{(\mathrm{c})}\big)_1, \big(\nabla^{(\mathrm{c})}\Theta^{(\mathrm{c})}\big)_2, \big(\nabla^{(\mathrm{c})}\Theta^{(\mathrm{c})}\big)_3, (\boldsymbol{W}_{\mathrm{c}})_1, (\boldsymbol{W}_{\mathrm{c}})_2, (\boldsymbol{W}_{\mathrm{c}})_3,\\ &\big(\boldsymbol{W}_{\mathrm{c}}^1\big)_1, \big(\boldsymbol{W}_{\mathrm{c}}^1\big)_2, \big(\boldsymbol{W}_{\mathrm{c}}^1\big)_3, \big(\boldsymbol{W}_{\mathrm{c}}^2\big)_1, \big(\boldsymbol{W}_{\mathrm{c}}^2\big)_2, \big(\boldsymbol{W}_{\mathrm{c}}^2\big)_3, \big(\boldsymbol{W}_{\mathrm{c}}^3\big)_1,\\ &\big(\boldsymbol{W}_{\mathrm{c}}^3\big)_2, \big(\boldsymbol{W}_{\mathrm{c}}^3\big)_3, D_{11}^{(\mathrm{c})}, D_{12}^{(\mathrm{c})}, D_{13}^{(\mathrm{c})}, D_{22}^{(\mathrm{c})}, D_{23}^{(\mathrm{c})}, D_{33}^{(\mathrm{c})}\Big).\end{aligned} \tag{28.103}$$

Evaluating the components of $\boldsymbol{M}^{(\mathrm{c})}$ yields

$$\left.\frac{\partial^2 \Pi^{(\mathrm{c})}}{\partial (\boldsymbol{W}_{\mathrm{c}})_k\, \partial \big(\nabla^{(\mathrm{c})}\Theta^{(\mathrm{c})}\big)_l}\right|_E = -\frac{1}{\Theta^{(\mathrm{c})}}\alpha_0^{(\mathrm{c})}\delta_{kl}, \tag{28.104}$$

$$\left.\frac{\partial^2 \Pi^{(\mathrm{c})}}{\partial \big(\boldsymbol{W}_{\mathrm{c}}^1\big)_k\, \partial \big(\nabla^{(\mathrm{c})}\Theta^{(\mathrm{c})}\big)_l}\right|_E = -\frac{1}{\Theta^{(\mathrm{c})}}\alpha_1^{(\mathrm{c})}\delta_{kl}, \tag{28.105}$$

$$\left.\frac{\partial^2 \Pi^{(\mathrm{c})}}{\partial \big(\boldsymbol{W}_{\mathrm{c}}^2\big)_k\, \partial \big(\nabla^{(\mathrm{c})}\Theta^{(\mathrm{c})}\big)_l}\right|_E = -\frac{1}{\Theta^{(\mathrm{c})}}\alpha_2^{(\mathrm{c})}\delta_{kl}, \tag{28.106}$$

$$\left.\frac{\partial^2 \Pi^{(\mathrm{c})}}{\partial \big(\boldsymbol{W}_{\mathrm{c}}^3\big)_k\, \partial \big(\nabla^{(\mathrm{c})}\Theta^{(\mathrm{c})}\big)_l}\right|_E = -\frac{1}{\Theta^{(\mathrm{c})}}\alpha_3^{(\mathrm{c})}\delta_{kl}, \tag{28.107}$$

$$\left.\frac{\partial^2 \Pi^{(\mathrm{c})}}{\partial \big(\nabla^{(\mathrm{c})}\Theta^{(\mathrm{c})}\big)_k\, \partial \big(\nabla^{(\mathrm{c})}\Theta^{(\mathrm{c})}\big)_l}\right|_E = \frac{1}{\Theta^{(\mathrm{c})}}\kappa^{(\mathrm{c})}\delta_{kl}, \tag{28.108}$$

$$\left.\frac{\partial^2 \Pi^{(\mathrm{c})}}{\partial D_{kl}^{(\mathrm{c})}\partial D_{mn}^{(\mathrm{c})}}\right|_E = \lambda^{(\mathrm{c})}\delta_{kl}I_{mn}^{(\mathrm{c})} + \lambda^{(\mathrm{c})}\delta_{mn}I_{kl}^{(\mathrm{c})} + 4\mu^{(\mathrm{c})}\delta_{(kl)(mn)}, \tag{28.109}$$

where $\{k, l\} \in (1, 2, 3)$ and $\{m, n\} \in (1, 2, 3)$. The other components of $\boldsymbol{M}^{(\mathrm{c})}$ are equal to zero. These components are formally similar to those for the phase interface, indicated in (28.63)–(28.67). The condition, that this tensor is positive (semi-)definite, is equivalent to the condition $\boldsymbol{f} \cdot \boldsymbol{M}^{(\mathrm{c})}\boldsymbol{f} > 0$, where $\boldsymbol{f} \neq \boldsymbol{0}$ is an arbitrary vector. For special choices of $\boldsymbol{f}$ we obtain the limitations

$$\begin{gathered}\kappa^{(\mathrm{c})} \geq 0, \qquad \alpha_0^{(\mathrm{c})} = 0, \qquad \alpha_k^{(\mathrm{c})} = 0,\\ \mu^{(\mathrm{c})} \geq 0, \qquad \lambda^{(\mathrm{c})}I_{\{kk\}}^{(\mathrm{c})} + 2\mu^{(\mathrm{c})} \geq 0\end{gathered} \tag{28.110}$$

for $k = 1, 2, 3$. Note that the repeated indices $\{kk\}$ are not summed. Due to the fact that $I_{\{kk\}}^{(\mathrm{c})} \in [0, 1]$, satisfying the restriction $(28.110)_5$ for all possible orientations of the contact line yields

$$\lambda^{(\mathrm{c})} + 2\mu^{(\mathrm{c})} \geq 0. \tag{28.111}$$

A further restriction from the semi-positivity of $\boldsymbol{M}^{(\mathrm{c})}$ is

$$\left|\lambda^{(\mathrm{c})} I_{kl}^{(\mathrm{c})}\right| \le \min\left\{2\left[2\mu^{(\mathrm{c})}\left(\lambda^{(\mathrm{c})} I_{\{mm\}}^{(\mathrm{c})} + 2\mu^{(\mathrm{c})}\right)\right]^{\frac{1}{2}}, m = 1, 2, 3\right\} \tag{28.112}$$

for $(kl) = (12), (13), (23)$. Its validity for all possible orientations of the contact line, for which $I_{\{mm\}}^{(\mathrm{c})} \in [0, 1]$ and $|I_{kl}^{(\mathrm{c})}| \in [0, \frac{1}{2}]$, reveals a relation, similar to that for the phase interface (28.72), in the form

$$8(2 - \sqrt{5})\mu^{(\mathrm{c})} \le \lambda^{(\mathrm{c})} \le 8\mu^{(\mathrm{c})}, \tag{28.113}$$

which includes relation (28.111). Hence, the restriction (28.111) is no longer necessary.

28.5 Constitutive Relations for Phase Interfaces with Memory

In Sect. 28.3 the constitutive relations for a heat conducting viscous phase interface have been investigated, whose response is characterized by the constitutive class (28.28). In this section, we will examine a more complicated case. We assume that the investigated phase interface is heat conducting viscous, and additionally with memory, e.g., for an elastic interface; moreover, its material response may also depend on its orientation. For such an interface the material behavior may be postulated by functions of the form[6]

$$\begin{aligned}\mathcal{S} = \hat{\mathcal{S}}\Big(&\rho^{(\mathfrak{s}_i)}, \dot{\rho}^{(\mathfrak{s}_i)}, \nabla^{(\mathfrak{s}_i)}\rho^{(\mathfrak{s}_i)}, \Theta^{(\mathfrak{s}_i)}, \dot{\Theta}^{(\mathfrak{s}_i)}, \nabla^{(\mathfrak{s}_i)}\Theta^{(\mathfrak{s}_i)}, \boldsymbol{D}^{(\mathfrak{s}_i)}, \dot{\boldsymbol{D}}^{(\mathfrak{s}_i)},\\ &\boldsymbol{n}^{(\mathfrak{s}_i)}, \nabla^{(\mathfrak{s}_i)}\boldsymbol{n}^{(\mathfrak{s}_i)}, \boldsymbol{W}_{\mathfrak{s}}, \boldsymbol{W}_{\mathfrak{s}}^{+}, \boldsymbol{W}_{\mathfrak{s}}^{-}\Big)\end{aligned} \tag{28.114}$$

---

[6] Here, the material historic dependence on the material time derivative $\dot{\boldsymbol{D}}^{(\mathfrak{s}_i)}$ does not satisfy the requirement of material objectivity. A more reasonable variable describing the dependence of the materially deformational history may be the material objective time derivatives of $\boldsymbol{D}^{(\mathfrak{s}_i)}$, e.g., the upper-convected time derivative (or OLDROYD derivative) $\overset{\nabla}{\mathbf{D}}{}^{(\mathfrak{s}_i)}$, the lower-convected time derivative $\overset{\triangle}{\mathbf{D}}{}^{(\mathfrak{s}_i)}$ or JAUMANN time derivatives $\overset{\circ}{\mathbf{D}}{}^{(\mathfrak{s}_i)}$, respectively, defined by

$$\begin{aligned}\text{Upper-convected time derivative}\quad \overset{\nabla}{\mathbf{D}}{}^{(\mathfrak{s}_i)} &= \dot{\mathbf{D}}^{(\mathfrak{s}_i)} - \mathbf{L}^{(\mathfrak{s}_i)}\mathbf{D}^{(\mathfrak{s}_i)} - \mathbf{D}^{(\mathfrak{s}_i)}(\mathbf{L}^{(\mathfrak{s}_i)})^T,\\ \text{Lower-convected time derivative}\quad \overset{\triangle}{\mathbf{D}}{}^{(\mathfrak{s}_i)} &= \dot{\mathbf{D}}^{(\mathfrak{s}_i)} + (\mathbf{L}^{(\mathfrak{s}_i)})^T\mathbf{D}^{(\mathfrak{s}_i)} + \mathbf{D}^{(\mathfrak{s}_i)}\mathbf{L}^{(\mathfrak{s}_i)},\\ \text{JAUMANN time derivative}\quad \overset{\circ}{\mathbf{D}}{}^{(\mathfrak{s}_i)} &= \dot{\mathbf{D}}^{(\mathfrak{s}_i)} - \mathbf{W}^{(\mathfrak{s}_i)}\mathbf{D}^{(\mathfrak{s}_i)} + \mathbf{D}^{(\mathfrak{s}_i)}\mathbf{W}^{(\mathfrak{s}_i)},\end{aligned}$$

where $\mathbf{L}^{(\mathfrak{s}_i)}$ is the velocity gradient, $\mathbf{D}^{(\mathfrak{s}_i)}$ the rate of deformation tensor and $\mathbf{W}^{(\mathfrak{s}_i)}$ is the spin tensor. If we would employ these materially objective time derivatives, the following evaluation of the entropy principle would become much more complicated, if they would be still achievable by hand. Here, we refrain doing this.

for the constitutive quantities

$$\mathcal{S} \in \left\{\boldsymbol{T}^{(\mathfrak{s}_i)}, \boldsymbol{q}^{(\mathfrak{s}_i)}, \boldsymbol{\phi}_{\eta}^{(\mathfrak{s}_i)}, \psi^{(\mathfrak{s}_i)}, \eta^{(\mathfrak{s}_i)}\right\}. \tag{28.115}$$

In comparison with (28.28) the additional dependences, $\{\dot{\rho}^{(\mathfrak{s}_i)}, \dot{\Theta}, \dot{\boldsymbol{D}}^{(\mathfrak{s}_i)}\}$, have been included into the constitutive class (28.114) to take the material memory (e.g., elastic feature) into account. The curvature of the interface, $H^{(\mathfrak{s}_i)}$, which arises in (28.28), has been removed from (28.114). Instead, in (28.114) a more general variable, $\nabla^{(\mathfrak{s}_i)}\boldsymbol{n}^{(\mathfrak{s}_i)}$, is taken into account (of which $H^{(\mathfrak{s}_i)} = \operatorname{tr}\left(\nabla^{(\mathfrak{s}_i)}\boldsymbol{n}^{(\mathfrak{s}_i)}\right)$). Moreover, the dependence on the orientation of the interface, $\boldsymbol{n}^{(\mathfrak{s}_i)}$, is also considered.

In the following, we will investigate the restrictions on the material dependences (28.114) by evaluating the entropy inequality (28.29), as done in Sect. 28.3.

28.5.1 Evaluation of the Entropy Inequality

Substituting the functional dependencies (28.114) into (28.29) and using the chain rule of differentiation yields the entropy inequality of the form

$$\Theta^{(\mathfrak{s}_i)}\Pi^{(\mathfrak{s}_i)} = \boldsymbol{a}^{(\mathfrak{s}_i)} \cdot \boldsymbol{\alpha}^{(\mathfrak{s}_i)} + b^{(\mathfrak{s}_i)} \geq 0,$$

in which

$$\begin{aligned}
\boldsymbol{\alpha}^{(\mathfrak{s}_i)} = \Bigg(& \frac{\mathrm{d}^{(\mathfrak{s}_i)}\dot{\rho}^{(\mathfrak{s}_i)}}{\mathrm{d}t}, \frac{\mathrm{d}^{(\mathfrak{s}_i)}\nabla^{(\mathfrak{s}_i)}\rho^{(\mathfrak{s}_i)}}{\mathrm{d}t}, \frac{\mathrm{d}^{(\mathfrak{s}_i)}\dot{\Theta}^{(\mathfrak{s}_i)}}{\mathrm{d}t}, \frac{\mathrm{d}^{(\mathfrak{s}_i)}\nabla^{(\mathfrak{s}_i)}\Theta^{(\mathfrak{s}_i)}}{\mathrm{d}t}, \frac{\mathrm{d}^{(\mathfrak{s}_i)}\dot{\boldsymbol{D}}^{(\mathfrak{s}_i)}}{\mathrm{d}t}, \\
& \frac{\mathrm{d}^{(\mathfrak{s}_i)}\boldsymbol{n}^{(\mathfrak{s}_i)}}{\mathrm{d}t}, \frac{\mathrm{d}^{(\mathfrak{s}_i)}\nabla^{(\mathfrak{s}_i)}\boldsymbol{n}^{(\mathfrak{s}_i)}}{\mathrm{d}t}, \frac{\mathrm{d}^{(\mathfrak{s}_i)}\boldsymbol{W}_{\mathfrak{s}}}{\mathrm{d}t}, \frac{\mathrm{d}^{(\mathfrak{s}_i)}\boldsymbol{W}_{\mathfrak{s}}^{+}}{\mathrm{d}t}, \frac{\mathrm{d}^{(\mathfrak{s}_i)}\boldsymbol{W}_{\mathfrak{s}}^{-}}{\mathrm{d}t}, \frac{\mathrm{d}^{(\mathfrak{s}_i)}\boldsymbol{v}^{(\mathfrak{s}_i)}}{\mathrm{d}t}, \\
& \nabla^{(\mathfrak{s}_i)}\left(\nabla^{(\mathfrak{s}_i)}\rho^{(\mathfrak{s}_i)}\right), \nabla^{(\mathfrak{s}_i)}\left(\nabla^{(\mathfrak{s}_i)}\Theta^{(\mathfrak{s}_i)}\right), \nabla^{(\mathfrak{s}_i)}\boldsymbol{D}^{(\mathfrak{s}_i)}, \nabla^{(\mathfrak{s}_i)}\dot{\boldsymbol{D}}^{(\mathfrak{s}_i)}, \\
& \nabla^{(\mathfrak{s}_i)}\left(\nabla^{(\mathfrak{s}_i)}\boldsymbol{n}^{(\mathfrak{s}_i)}\right), \nabla^{(\mathfrak{s}_i)}\boldsymbol{W}_{\mathfrak{s}}, \nabla^{(\mathfrak{s}_i)}\boldsymbol{W}_{\mathfrak{s}}^{+}, \nabla^{(\mathfrak{s}_i)}\boldsymbol{W}_{\mathfrak{s}}^{-}\Bigg)
\end{aligned} \tag{28.116}$$

and

$$\begin{aligned}
b^{(\mathfrak{s}_i)} = & -\left(\rho^{(\mathfrak{s}_i)}\frac{\partial\psi^{(\mathfrak{s}_i)}}{\partial\rho^{(\mathfrak{s}_i)}} + \Lambda_{\rho}^{(\mathfrak{s}_i)}\right)\frac{\mathrm{d}^{(\mathfrak{s}_i)}\rho^{(\mathfrak{s}_i)}}{\mathrm{d}t} \\
& -\left(\rho^{(\mathfrak{s}_i)}\frac{\partial\psi^{(\mathfrak{s}_i)}}{\partial\Theta^{(\mathfrak{s}_i)}} + \rho^{(\mathfrak{s}_i)}\eta^{(\mathfrak{s}_i)}\right)\frac{\mathrm{d}^{(\mathfrak{s}_i)}\Theta^{(\mathfrak{s}_i)}}{\mathrm{d}t} \\
& -\rho^{(\mathfrak{s}_i)}\frac{\partial\psi^{(\mathfrak{s}_i)}}{\partial\boldsymbol{D}^{(\mathfrak{s}_i)}} \cdot \frac{\mathrm{d}^{(\mathfrak{s}_i)}\boldsymbol{D}^{(\mathfrak{s}_i)}}{\mathrm{d}t} + \left(\boldsymbol{T}^{(\mathfrak{s}_i)} - \Lambda_{\rho}^{(\mathfrak{s}_i)}\rho^{(\mathfrak{s}_i)}\boldsymbol{I}^{(\mathfrak{s}_i)}\right) \cdot \boldsymbol{D}^{(\mathfrak{s}_i)}
\end{aligned}$$

$$
\begin{aligned}
&+\left(\Theta^{(\mathfrak{s}_i)}\frac{\partial \phi_\eta^{(\mathfrak{s}_i)}}{\partial \rho^{(\mathfrak{s}_i)}}+\boldsymbol{\Lambda}_{\boldsymbol{v}}^{(\mathfrak{s}_i)}\cdot\frac{\partial \boldsymbol{T}^{(\mathfrak{s}_i)}}{\partial \rho^{(\mathfrak{s}_i)}}-\frac{\partial \boldsymbol{q}^{(\mathfrak{s}_i)}}{\partial \rho^{(\mathfrak{s}_i)}}\right)\cdot\nabla^{(\mathfrak{s}_i)}\rho^{(\mathfrak{s}_i)}\\
&+\left(\Theta^{(\mathfrak{s}_i)}\frac{\partial \phi_\eta^{(\mathfrak{s}_i)}}{\partial \Theta^{(\mathfrak{s}_i)}}+\boldsymbol{\Lambda}_{\boldsymbol{v}}^{(\mathfrak{s}_i)}\cdot\frac{\partial \boldsymbol{T}^{(\mathfrak{s}_i)}}{\partial \Theta^{(\mathfrak{s}_i)}}-\frac{\partial \boldsymbol{q}^{(\mathfrak{s}_i)}}{\partial \Theta^{(\mathfrak{s}_i)}}\right)\cdot\nabla^{(\mathfrak{s}_i)}\Theta^{(\mathfrak{s}_i)}\\
&+\left(\Theta^{(\mathfrak{s}_i)}\frac{\partial \phi_\eta^{(\mathfrak{s}_i)}}{\partial \boldsymbol{n}^{(\mathfrak{s}_i)}}+\boldsymbol{\Lambda}_{\boldsymbol{v}}^{(\mathfrak{s}_i)}\cdot\frac{\partial \boldsymbol{T}^{(\mathfrak{s}_i)}}{\partial \boldsymbol{n}^{(\mathfrak{s}_i)}}-\frac{\partial \boldsymbol{q}^{(\mathfrak{s}_i)}}{\partial \boldsymbol{n}^{(\mathfrak{s}_i)}}\right)\cdot\nabla^{(\mathfrak{s}_i)}\boldsymbol{n}^{(\mathfrak{s}_i)}\\
&-\Theta^{(\mathfrak{s}_i)}H^{(\mathfrak{s}_i)}\left(\boldsymbol{\phi}_\eta^{(\mathfrak{s}_i)}\cdot\boldsymbol{n}^{(\mathfrak{s}_i)}\right)-\Lambda_\rho^{(\mathfrak{s}_i)}\rho^{(\mathfrak{s}_i)}H^{(\mathfrak{s}_i)}\left(\left(\boldsymbol{w}^{(\mathfrak{s}_i)}-\boldsymbol{v}^{(\mathfrak{s}_i)}\right)\cdot\boldsymbol{n}^{(\mathfrak{s}_i)}\right)\\
&-\boldsymbol{\Lambda}_{\boldsymbol{v}}^{(\mathfrak{s}_i)}\cdot\left(H^{(\mathfrak{s}_i)}\left(\boldsymbol{T}^{(\mathfrak{s}_i)}\cdot\boldsymbol{n}^{(\mathfrak{s}_i)}\right)\right)+H^{(\mathfrak{s}_i)}\left(\boldsymbol{q}^{(\mathfrak{s}_i)}\cdot\boldsymbol{n}^{(\mathfrak{s}_i)}\right)\\
&-\Theta^{(\mathfrak{s}_i)}\left\llbracket\rho\left(\eta-\eta^{(\mathfrak{s})}\right)\left(\boldsymbol{w}^{(\mathfrak{s})}-\boldsymbol{v}\right)\cdot\boldsymbol{n}^{(\mathfrak{s})}-\boldsymbol{\phi}_\eta\cdot\boldsymbol{n}^{(\mathfrak{s})}\right\rrbracket^{(i)}\\
&+\Lambda_\rho^{(\mathfrak{s}_i)}\left\llbracket\rho\left(\boldsymbol{w}^{(\mathfrak{s})}-\boldsymbol{v}\right)\cdot\boldsymbol{n}^{(\mathfrak{s})}\right\rrbracket^{(i)}\\
&+\boldsymbol{\Lambda}_{\boldsymbol{v}}^{(\mathfrak{s}_i)}\cdot\left\llbracket\rho\left(\boldsymbol{v}-\boldsymbol{v}^{(\mathfrak{s})}\right)\left(\boldsymbol{w}^{(\mathfrak{s})}-\boldsymbol{v}\right)\cdot\boldsymbol{n}^{(\mathfrak{s})}+\boldsymbol{T}\cdot\boldsymbol{n}^{(\mathfrak{s})}\right\rrbracket^{(i)}\\
&+\Bigg\llbracket\rho\left(\left(u-u^{(\mathfrak{s})}\right)+\tfrac{1}{2}\left(\boldsymbol{v}-\boldsymbol{v}^{(\mathfrak{s})}\right)\cdot\left(\boldsymbol{v}-\boldsymbol{v}^{(\mathfrak{s})}\right)\right)\left(\left(\boldsymbol{w}^{(\mathfrak{s})}-\boldsymbol{v}\right)\cdot\boldsymbol{n}^{(\mathfrak{s})}\right)\\
&\qquad-\boldsymbol{q}\cdot\boldsymbol{n}^{(\mathfrak{s})}+\boldsymbol{T}\left(\boldsymbol{v}-\boldsymbol{v}^{(\mathfrak{s})}\right)\cdot\boldsymbol{n}^{(\mathfrak{s})}\Bigg\rrbracket^{(i)}.
\end{aligned}
\tag{28.117}
$$

Since $\boldsymbol{a}^{(\mathfrak{s}_i)}$ and $b^{(\mathfrak{s}_i)}$ are independent of $\boldsymbol{\alpha}^{(\mathfrak{s}_i)}$, the inequality can be violated by arbitrary values of $\boldsymbol{\alpha}^{(\mathfrak{s}_i)}$ unless $\boldsymbol{a}^{(\mathfrak{s}_i)}=\boldsymbol{0}$ and $b^{(\mathfrak{s}_i)}\geq 0$.

The condition $\boldsymbol{a}^{(\mathfrak{s}_i)}=\boldsymbol{0}$ corresponds to the relations for the HELMHOLTZ free energy as follows:

$$
\begin{aligned}
&\frac{\partial\psi^{(\mathfrak{s}_i)}}{\partial\dot{\rho}^{(\mathfrak{s}_i)}}=0, \qquad \frac{\partial\psi^{(\mathfrak{s}_i)}}{\partial\dot{\Theta}^{(\mathfrak{s}_i)}}=0, \qquad \frac{\partial\psi^{(\mathfrak{s}_i)}}{\partial\dot{\boldsymbol{D}}^{(\mathfrak{s}_i)}}=\boldsymbol{0},\\
&\frac{\partial\psi^{(\mathfrak{s}_i)}}{\partial\boldsymbol{n}^{(\mathfrak{s}_i)}}=\boldsymbol{0}, \qquad \frac{\partial\psi^{(\mathfrak{s}_i)}}{\partial\nabla^{(\mathfrak{s}_i)}\boldsymbol{n}^{(\mathfrak{s}_i)}}=\boldsymbol{0},\\
&\frac{\partial\psi^{(\mathfrak{s}_i)}}{\partial\boldsymbol{W}_{\mathfrak{s}}}=\boldsymbol{0}, \qquad \frac{\partial\psi^{(\mathfrak{s}_i)}}{\partial\boldsymbol{W}_{\mathfrak{s}}^{+}}=\boldsymbol{0}, \qquad \frac{\partial\psi^{(\mathfrak{s}_i)}}{\partial\boldsymbol{W}_{\mathfrak{s}}^{-}}=\boldsymbol{0},
\end{aligned}
\tag{28.118}
$$

for the LAGRANGE multiplier referring to the momentum equation as

$$
\boldsymbol{\Lambda}_{\boldsymbol{v}}^{(\mathfrak{s}_i)}=\boldsymbol{0}, \tag{28.119}
$$

and for the extra entropy flux as

$$\begin{gathered}
\operatorname{sym}\left(\frac{\partial \boldsymbol{\Phi}_{\eta}^{(\mathfrak{s}_i)}}{\partial \nabla^{(\mathfrak{s}_i)} \rho^{(\mathfrak{s}_i)}}\right) = \mathbf{0}, \qquad \operatorname{sym}\left(\frac{\partial \boldsymbol{\Phi}_{\eta}^{(\mathfrak{s}_i)}}{\partial \nabla^{(\mathfrak{s}_i)} \Theta^{(\mathfrak{s}_i)}}\right) = \mathbf{0}, \\
\operatorname{sym}\left(\frac{\partial \boldsymbol{\Phi}_{\eta}^{(\mathfrak{s}_i)}}{\partial \nabla^{(\mathfrak{s}_i)} \boldsymbol{n}^{(\mathfrak{s}_i)}}\right) = \mathbf{0}, \qquad \frac{\partial \boldsymbol{\Phi}_{\eta}^{(\mathfrak{s}_i)}}{\partial \boldsymbol{D}^{(\mathfrak{s}_i)}} = \mathbf{0}, \qquad \frac{\partial \boldsymbol{\Phi}_{\eta}^{(\mathfrak{s}_i)}}{\partial \dot{\boldsymbol{D}}^{(\mathfrak{s}_i)}} = \mathbf{0}, \\
\frac{\partial \boldsymbol{\Phi}_{\eta}^{(\mathfrak{s}_i)}}{\partial \boldsymbol{W}_{\mathfrak{s}}} = \mathbf{0}, \qquad \frac{\partial \boldsymbol{\Phi}_{\eta}^{(\mathfrak{s}_i)}}{\partial \boldsymbol{W}_{\mathfrak{s}}^{+}} = \mathbf{0}, \qquad \frac{\partial \boldsymbol{\Phi}_{\eta}^{(\mathfrak{s}_i)}}{\partial \boldsymbol{W}_{\mathfrak{s}}^{-}} = \mathbf{0}, \\
\frac{\partial \boldsymbol{\Phi}_{\eta}^{(\mathfrak{s}_i)}}{\partial \dot{\rho}^{(\mathfrak{s}_i)}} - \rho^{(\mathfrak{s}_i)} \frac{\partial \psi^{(\mathfrak{s}_i)}}{\partial \nabla^{(\mathfrak{s}_i)} \rho^{(\mathfrak{s}_i)}} = \mathbf{0}, \qquad \frac{\partial \boldsymbol{\Phi}_{\eta}^{(\mathfrak{s}_i)}}{\partial \dot{\Theta}^{(\mathfrak{s}_i)}} - \rho^{(\mathfrak{s}_i)} \frac{\partial \psi^{(\mathfrak{s}_i)}}{\partial \nabla^{(\mathfrak{s}_i)} \Theta^{(\mathfrak{s}_i)}} = \mathbf{0},
\end{gathered} \tag{28.120}$$

where $\operatorname{sym}(\boldsymbol{M}) = \frac{1}{2}\left(\boldsymbol{M} + \boldsymbol{M}^{\mathsf{T}}\right)$ and the extra entropy flux is defined by

$$\begin{aligned}
\boldsymbol{\Phi}_{\eta}^{(\mathfrak{s}_i)} &:= \phi_{\eta}^{(\mathfrak{s}_i)} + \frac{1}{\Theta^{(\mathfrak{s}_i)}}\left(\boldsymbol{\Lambda}_{\boldsymbol{v}}^{(\mathfrak{s}_i)} \cdot \boldsymbol{T}^{(\mathfrak{s}_i)} - \boldsymbol{q}^{(\mathfrak{s}_i)}\right) \\
&\overset{(8.119)}{=} \phi_{\eta}^{(\mathfrak{s}_i)} - \frac{\boldsymbol{q}^{(\mathfrak{s}_i)}}{\Theta^{(\mathfrak{s}_i)}}.
\end{aligned} \tag{28.121}$$

The constraints (28.118) result in the reduced dependence of the HELMHOLTZ free energy, which now reads

$$\psi^{(\mathfrak{s}_i)} = \hat{\psi}^{(\mathfrak{s}_i)}\left(\rho^{(\mathfrak{s}_i)}, \nabla^{(\mathfrak{s}_i)} \rho^{(\mathfrak{s}_i)}, \Theta^{(\mathfrak{s}_i)}, \nabla^{(\mathfrak{s}_i)} \Theta^{(\mathfrak{s}_i)}, \boldsymbol{D}^{(\mathfrak{s}_i)}\right). \tag{28.122}$$

Using the constraints (28.120) and the isotropy assumption leads to the reduced form of the extra entropy flux

$$\boldsymbol{\Phi}_{\eta}^{(\mathfrak{s}_i)} = \xi^{(\mathfrak{s}_i)} \boldsymbol{n}^{(\mathfrak{s}_i)} \tag{28.123}$$

with $\xi^{(\mathfrak{s}_i)} = \hat{\xi}^{(\mathfrak{s}_i)}\left(\rho^{(\mathfrak{s}_i)}, \Theta^{(\mathfrak{s}_i)}, \dot{\rho}^{(\mathfrak{s}_i)}, \dot{\Theta}^{(\mathfrak{s}_i)}\right)$. From the last two conditions in (28.120), if it is further assumed that $\xi^{(\mathfrak{s}_i)} = \hat{\xi}^{(\mathfrak{s}_i)}\left(\rho^{(\mathfrak{s}_i)}, \Theta^{(\mathfrak{s}_i)}\right)$, one obtains

$$\psi^{(\mathfrak{s}_i)} = \hat{\psi}^{(\mathfrak{s}_i)}\left(\rho^{(\mathfrak{s}_i)}, \Theta^{(\mathfrak{s}_i)}, \boldsymbol{D}^{(\mathfrak{s}_i)}\right). \tag{28.124}$$

The condition (28.123) also demonstrates the difference of our results from those obtained by an evaluation of the entropy principle according to COLEMAN–NOLL, since the assumption of COLEMAN–NOLL, $\phi_{\eta}^{(\mathfrak{s}_i)} = \frac{1}{\Theta^{(\mathfrak{s}_i)}} \boldsymbol{q}^{(\mathfrak{s}_i)}$, contradicts equation (28.123). Inserting the definition $H^{(\mathfrak{s}_i)} := \operatorname{tr}\left(\nabla^{(\mathfrak{s}_i)} \boldsymbol{n}^{(\mathfrak{s}_i)}\right)$ of the surface curvature, the identity $\boldsymbol{n}^{(\mathfrak{s}_i)} \cdot \nabla^{(\mathfrak{s}_i)}(\cdot) = 0$ and the constraints (28.119), (28.123), and (28.124) into inequality (28.117) leads to the reduced entropy inequality

$$
\begin{aligned}
&\varTheta^{(\mathfrak{s}_i)}\varPi^{(\mathfrak{s}_i)}\\
={}&-\left(\rho^{(\mathfrak{s}_i)}\frac{\partial\psi^{(\mathfrak{s}_i)}}{\partial\rho^{(\mathfrak{s}_i)}}+\varLambda_{\rho}^{(\mathfrak{s}_i)}\right)\dot{\rho}^{(\mathfrak{s}_i)}-\left(\rho^{(\mathfrak{s}_i)}\frac{\partial\psi^{(\mathfrak{s}_i)}}{\partial\varTheta^{(\mathfrak{s}_i)}}+\rho^{(\mathfrak{s}_i)}\eta^{(\mathfrak{s}_i)}\right)\dot{\varTheta}^{(\mathfrak{s}_i)}\\
&+\left(\boldsymbol{T}^{(\mathfrak{s}_i)}-\sigma^{(\mathfrak{s}_i)}\boldsymbol{I}^{(\mathfrak{s}_i)}\right)\cdot\boldsymbol{D}^{(\mathfrak{s}_i)}-\rho^{(\mathfrak{s}_i)}\frac{\partial\psi^{(\mathfrak{s}_i)}}{\partial\boldsymbol{D}^{(\mathfrak{s}_i)}}\cdot\dot{\boldsymbol{D}}^{(\mathfrak{s}_i)}\\
&-\frac{1}{\varTheta^{(\mathfrak{s}_i)}}\boldsymbol{q}^{(\mathfrak{s}_i)}\cdot\nabla^{(\mathfrak{s}_i)}\varTheta^{(\mathfrak{s}_i)}-\sigma^{(\mathfrak{s}_i)}H^{(\mathfrak{s}_i)}\left(\boldsymbol{w}^{(\mathfrak{s}_i)}-\boldsymbol{v}^{(\mathfrak{s}_i)}\right)\cdot\boldsymbol{n}^{(\mathfrak{s}_i)}\\
&+\frac{\sigma^{(\mathfrak{s}_i)}}{\rho^{(\mathfrak{s}_i)}}\left\llbracket\rho\left(\boldsymbol{w}^{(\mathfrak{s})}-\boldsymbol{v}\right)\cdot\boldsymbol{n}^{(\mathfrak{s})}\right\rrbracket^{(i)}\\
&-\varTheta^{(\mathfrak{s}_i)}\left\llbracket\rho\left(\eta-\eta^{(\mathfrak{s})}\right)\left(\boldsymbol{w}^{(\mathfrak{s})}-\boldsymbol{v}\right)\cdot\boldsymbol{n}^{(\mathfrak{s})}-\boldsymbol{\phi}_{\eta}\cdot\boldsymbol{n}^{(\mathfrak{s})}\right\rrbracket^{(i)}\\
&+\Bigg\llbracket\rho\left(\left(u-u^{(\mathfrak{s})}\right)+\tfrac{1}{2}\left(\boldsymbol{v}-\boldsymbol{v}^{(\mathfrak{s})}\right)\cdot\left(\boldsymbol{v}-\boldsymbol{v}^{(\mathfrak{s})}\right)\right)\left(\left(\boldsymbol{w}^{(\mathfrak{s})}-\boldsymbol{v}\right)\cdot\boldsymbol{n}^{(\mathfrak{s})}\right)\\
&\qquad-\boldsymbol{q}\cdot\boldsymbol{n}^{(\mathfrak{s})}+\boldsymbol{T}\left(\boldsymbol{v}-\boldsymbol{v}^{(\mathfrak{s})}\right)\cdot\boldsymbol{n}^{(\mathfrak{s})}\Bigg\rrbracket^{(i)}\\
\geq{}&0,
\end{aligned}
\tag{28.125}
$$

where the definition $\sigma^{(\mathfrak{s}_i)}:=\rho^{(\mathfrak{s}_i)}\varLambda_{\rho}^{(\mathfrak{s}_i)}$ has been introduced.

28.5.2 Thermodynamic Equilibrium

From the reduced entropy inequality (28.125) we can obtain the expressions of the constitutive equations in thermodynamic equilibrium. To this end we choose a series of suitable dynamic variables $\boldsymbol{Y}^{(\mathfrak{s}_i)}$ so that $\varPi^{(\mathfrak{s}_i)}=0$ for $\boldsymbol{Y}^{(\mathfrak{s}_i)}=\boldsymbol{0}$. Then, we evaluate the minimum condition (28.50) in the context of thermodynamic equilibrium $\boldsymbol{Y}^{(\mathfrak{s}_i)}=\boldsymbol{0}$. The residual entropy inequality implies the choice

$$
\boldsymbol{Y}^{(\mathfrak{s}_i)}=\left(\dot{\rho}^{(\mathfrak{s}_i)},\dot{\varTheta}^{(\mathfrak{s}_i)},\boldsymbol{D}^{(\mathfrak{s}_i)},\dot{\boldsymbol{D}}^{(\mathfrak{s}_i)},\nabla^{(\mathfrak{s}_i)}\varTheta^{(\mathfrak{s}_i)},\boldsymbol{W}_{\mathfrak{s}},\boldsymbol{W}_{\mathfrak{s}}^{+},\boldsymbol{W}_{\mathfrak{s}}^{-}\right)
\tag{28.126}
$$

of independent nonequilibrium variables. The minimum conditions of the entropy production in thermodynamic equilibrium, $(\partial\varPi^{(\mathfrak{s}_i)}/\partial Y_k^{(\mathfrak{s}_i)})|_E=0$ for $Y_k^{(\mathfrak{s}_i)}\in\{\dot{\rho}^{(\mathfrak{s}_i)},\dot{\varTheta}^{(\mathfrak{s}_i)},\dot{\boldsymbol{D}}^{(\mathfrak{s}_i)}\}$ yield a condition for the LAGRANGE multiplier $\varLambda_{\rho}^{(\mathfrak{s}_i)}$ and conditions for the HELMHOLTZ free energy,

$$
\varLambda_{\rho}^{(\mathfrak{s}_i)}=-\rho^{(\mathfrak{s}_i)}\frac{\partial\psi^{(\mathfrak{s}_i)}}{\partial\rho^{(\mathfrak{s}_i)}},\quad\eta^{(\mathfrak{s}_i)}=-\frac{\partial\psi^{(\mathfrak{s}_i)}}{\partial\varTheta^{(\mathfrak{s}_i)}},\quad\frac{\partial\psi^{(\mathfrak{s}_i)}}{\partial\boldsymbol{D}^{(\mathfrak{s}_i)}}=\boldsymbol{0}.
\tag{28.127}
$$

The minimum conditions $(\partial \Pi^{(\mathfrak{s}_i)}/\partial Y_k^{(\mathfrak{s}_i)})|_E = 0$ for $Y_k^{(\mathfrak{s}_i)} \in \{\boldsymbol{D}^{(\mathfrak{s}_i)}, \nabla^{(\mathfrak{s}_i)}\Theta^{(\mathfrak{s}_i)}\}$ deliver the expressions of the stress and the heat flux in thermodynamic equilibrium,

$$\boldsymbol{T}_E^{(\mathfrak{s}_i)} = \sigma^{(\mathfrak{s}_i)}\boldsymbol{I}^{(\mathfrak{s}_i)}, \qquad \boldsymbol{q}_E^{(\mathfrak{s}_i)} = \boldsymbol{0}, \tag{28.128}$$

identical to (28.52).

With the assumptions $\boldsymbol{T}_E^{(i)} = -p^{(i)}\boldsymbol{I}$ and $\boldsymbol{T}_E^{(i-1)} = -p^{(i-1)}\boldsymbol{I}$ for the adjacent bulk phase subdomains, the condition $(\partial \Pi^{(\mathfrak{s}_i)}/\partial Y_k^{(\mathfrak{s}_i)})|_E = 0$ for $Y_k^{(\mathfrak{s}_i)} = \boldsymbol{W}_{\mathfrak{s}}$ results in the well-known relation

$$H^{(\mathfrak{s}_i)}\sigma^{(\mathfrak{s}_i)} = -\,[\![p]\!]^{(i)}, \tag{28.129}$$

agreeing with (28.55), while for $Y_k^{(\mathfrak{s}_i)} \in \{\boldsymbol{W}_{\mathfrak{s}}^{+}, \boldsymbol{W}_{\mathfrak{s}}^{-}\}$ it follows that

$$\begin{aligned} u^{(\mathfrak{s}_i)} - \Theta^{(\mathfrak{s}_i)}\eta^{(\mathfrak{s}_i)} - \frac{\sigma^{(\mathfrak{s}_i)}}{\rho^{(\mathfrak{s}_i)}} &= u^{(i)} - \Theta^{(\mathfrak{s}_i)}\eta^{(i)} + \frac{p^{(i)}}{\rho^{(i)}} \\ &= u^{(i-1)} - \Theta^{(\mathfrak{s}_i)}\eta^{(i-1)} + \frac{p^{(i-1)}}{\rho^{(i-1)}}. \end{aligned} \tag{28.130}$$

This agrees with (28.54), but holds now in thermodynamic nonequilibrium as well, because the surficial internal energy and entropy have been shown to be independent of the rate variables, as seen from (28.118), (28.122), and $(28.127)_3$.

Furthermore, from the condition $(28.127)_3$, it follows

$$\psi_E^{(\mathfrak{s}_i)} = \hat{\psi}_E^{(\mathfrak{s}_i)}\left(\rho^{(\mathfrak{s}_i)}, \Theta^{(\mathfrak{s}_i)}\right). \tag{28.131}$$

From relation (28.123), together with (28.121), (28.119), and $(28.128)_2$, we obtain the entropy flux in thermodynamic equilibrium

$$\phi_\eta^{(\mathfrak{s}_i)}\big|_E = \xi^{(\mathfrak{s}_i)}\boldsymbol{n}^{(\mathfrak{s}_i)}. \tag{28.132}$$

28.5.3 Isotropic Theory for the Dynamic Part

Now, we intend to employ the results obtained for the thermodynamic equilibrium to postulate an isotropic approach for the constitutive relations and derive constraints on the arising material parameters. For the sake of simplicity, we evaluate the second condition (28.50) and assume that the stress tensor and the heat flux vector are functions of the dynamic components of $\nabla^{(\mathfrak{s}_i)}\Theta^{(\mathfrak{s}_i)}$, $\boldsymbol{W}_{\mathfrak{s}}$, $\boldsymbol{W}_{\mathfrak{s}}^{+}$ and $\boldsymbol{W}_{\mathfrak{s}}^{-}$ and the six independent components of $\boldsymbol{D}^{(\mathfrak{s}_i)}$ and $\dot{\boldsymbol{D}}^{(\mathfrak{s}_i)}$, respectively.

Using only the linear generators for the isotropic representation obtained by WANG [33, 34] yields the following form for the dynamic part of the constitutive equations

$$\boldsymbol{q}^{(\mathfrak{s}_i)} = -\kappa^{(\mathfrak{s}_i)} \nabla^{(\mathfrak{s}_i)} \varTheta^{(\mathfrak{s}_i)} + \alpha_1^{(\mathfrak{s}_i)} \boldsymbol{W}_{\mathfrak{s}} + \alpha_2^{(\mathfrak{s}_i)} \boldsymbol{W}_{\mathfrak{s}}^{+} + \alpha_3^{(\mathfrak{s}_i)} \boldsymbol{W}_{\mathfrak{s}}^{-} \tag{28.133}$$

$$\boldsymbol{T}^{(\mathfrak{s}_i)} - \boldsymbol{T}_E^{(\mathfrak{s}_i)} = \lambda^{(\mathfrak{s}_i)} \boldsymbol{I}^{(\mathfrak{s}_i)} + 2\mu^{(\mathfrak{s}_i)} \boldsymbol{D}^{(\mathfrak{s}_i)} + \beta_1^{(\mathfrak{s}_i)} \dot{\boldsymbol{D}}^{(\mathfrak{s}_i)}. \tag{28.134}$$

The prefactors are assumed to be functions of the form

$$\begin{aligned} &\left\{\kappa^{(\mathfrak{s}_i)}, \mu^{(\mathfrak{s}_i)}, \lambda^{(\mathfrak{s}_i)}, \alpha_1^{(\mathfrak{s}_i)}, \alpha_2^{(\mathfrak{s}_i)}, \alpha_3^{(\mathfrak{s}_i)}\right\} \\ = &\left\{\hat{\kappa}^{(\mathfrak{s}_i)}, \hat{\mu}^{(\mathfrak{s}_i)}, \hat{\lambda}^{(\mathfrak{s}_i)}, \hat{\alpha}_1^{(\mathfrak{s}_i)}, \hat{\alpha}_1^{(\mathfrak{s}_i)}, \hat{\alpha}_1^{(\mathfrak{s}_i)}\right\} \Big(\rho^{(\mathfrak{s}_i)}, \nabla^{(\mathfrak{s}_i)} \rho^{(\mathfrak{s}_i)}, \varTheta^{(\mathfrak{s}_i)}, \nabla^{(\mathfrak{s}_i)} \varTheta^{(\mathfrak{s}_i)}, \\ &\quad \dot{\rho}^{(\mathfrak{s}_i)}, \dot{\varTheta}^{(\mathfrak{s}_i)}, \boldsymbol{D}^{(\mathfrak{s}_i)}, \dot{\boldsymbol{D}}^{(\mathfrak{s}_i)}, \boldsymbol{n}^{(\mathfrak{s}_i)}, \nabla^{(\mathfrak{s}_i)} \boldsymbol{n}^{(\mathfrak{s}_i)}, \boldsymbol{W}_{\mathfrak{s}}, \boldsymbol{W}_{\mathfrak{s}}^{+}, \boldsymbol{W}_{\mathfrak{s}}^{-}\Big). \end{aligned} \tag{28.135}$$

By inserting the constitutive equations (28.134) in the reduced entropy inequality, (28.125) takes the form

$$\begin{aligned} &\varTheta^{(\mathfrak{s}_i)} \varPi^{(\mathfrak{s}_i)} \\ =& -\left(\rho^{(\mathfrak{s}_i)} \frac{\partial \psi^{(\mathfrak{s}_i)}}{\partial \rho^{(\mathfrak{s}_i)}} + \varLambda_{\rho}^{(\mathfrak{s}_i)}\right) \dot{\rho}^{(\mathfrak{s}_i)} - \left(\rho^{(\mathfrak{s}_i)} \frac{\partial \psi^{(\mathfrak{s}_i)}}{\partial \varTheta^{(\mathfrak{s}_i)}} + \rho^{(\mathfrak{s}_i)} \eta^{(\mathfrak{s}_i)}\right) \dot{\varTheta}^{(\mathfrak{s}_i)} \\ &+ \lambda^{(\mathfrak{s}_i)} \boldsymbol{I}^{(\mathfrak{s}_i)} \cdot \boldsymbol{D}^{(\mathfrak{s}_i)} + 2\mu^{(\mathfrak{s}_i)} \boldsymbol{D}^{(\mathfrak{s}_i)} \cdot \boldsymbol{D}^{(\mathfrak{s}_i)} + \beta_1^{(\mathfrak{s}_i)} \dot{\boldsymbol{D}}^{(\mathfrak{s}_i)} \cdot \boldsymbol{D}^{(\mathfrak{s}_i)} \\ &+ \frac{1}{\varTheta^{(\mathfrak{s}_i)}} \kappa^{(\mathfrak{s}_i)} \nabla^{(\mathfrak{s}_i)} \varTheta^{(\mathfrak{s}_i)} \cdot \nabla^{(\mathfrak{s}_i)} \varTheta^{(\mathfrak{s}_i)} - \frac{1}{\varTheta^{(\mathfrak{s}_i)}} \alpha_1^{(\mathfrak{s}_i)} \boldsymbol{W}_{\mathfrak{s}}^{+} \cdot \nabla^{(\mathfrak{s}_i)} \varTheta^{(\mathfrak{s}_i)} \\ &- \frac{1}{\varTheta^{(\mathfrak{s}_i)}} \alpha_2^{(\mathfrak{s}_i)} \boldsymbol{W}_{\mathfrak{s}}^{-} \cdot \nabla^{(\mathfrak{s}_i)} \varTheta^{(\mathfrak{s}_i)} - \frac{1}{\varTheta^{(\mathfrak{s}_i)}} \alpha_3^{(\mathfrak{s}_i)} \boldsymbol{W}_{\mathfrak{s}} \cdot \nabla^{(\mathfrak{s}_i)} \varTheta^{(\mathfrak{s}_i)} \\ &- \rho^{(\mathfrak{s}_i)} \frac{\partial \psi^{(\mathfrak{s}_i)}}{\partial \boldsymbol{D}^{(\mathfrak{s}_i)}} \cdot \dot{\boldsymbol{D}}^{(\mathfrak{s}_i)} - \sigma^{(\mathfrak{s}_i)} H^{(\mathfrak{s}_i)} \left(\boldsymbol{w}^{(\mathfrak{s}_i)} - \boldsymbol{v}^{(\mathfrak{s}_i)}\right) \cdot \boldsymbol{n}^{(\mathfrak{s}_i)} \\ &- \varTheta^{(\mathfrak{s}_i)} \left\llbracket \rho \left(\eta - \eta^{(\mathfrak{s})}\right) \left(\boldsymbol{w}^{(\mathfrak{s})} - \boldsymbol{v}\right) \cdot \boldsymbol{n}^{(\mathfrak{s})} - \boldsymbol{\phi}_{\eta} \cdot n^{(\mathfrak{s})} \right\rrbracket^{(i)} \\ &+ \frac{\sigma^{(\mathfrak{s}_i)}}{\rho^{(\mathfrak{s}_i)}} \left\llbracket \rho \left(\boldsymbol{w}^{(\mathfrak{s})} - \boldsymbol{v}\right) \cdot \boldsymbol{n}^{(\mathfrak{s})} \right\rrbracket^{(i)} \\ &+ \Big\llbracket \rho \left(\left(u - u^{(\mathfrak{s})}\right) + \tfrac{1}{2} \left(\boldsymbol{v} - \boldsymbol{v}^{(\mathfrak{s})}\right) \cdot \left(\boldsymbol{v} - \boldsymbol{v}^{(\mathfrak{s})}\right)\right) \left(\boldsymbol{w}^{(\mathfrak{s})} - \boldsymbol{v}\right) \cdot \boldsymbol{n}^{(\mathfrak{s})} \\ &\qquad - \boldsymbol{q} \cdot \boldsymbol{n}^{(\mathfrak{s})} + \boldsymbol{T} \left(\boldsymbol{v} - \boldsymbol{v}^{(\mathfrak{s})}\right) \cdot \boldsymbol{n}^{(\mathfrak{s})} \Big\rrbracket^{(i)} \\ \geq& 0. \end{aligned} \tag{28.136}$$

Now, we derive all second derivatives of $\varPi^{(\mathfrak{s}_i)}$ with respect to the dynamic variables (28.126). Assuming that the matrix of the second derivatives is positive semidefinite close to thermodynamic equilibrium as mentioned in (28.50)$_2$, we obtain the conditions[7]

$$2\frac{\partial \lambda^{(\mathfrak{s}_i)}}{\partial D_{jk}^{(\mathfrak{s}_i)}} I_{jk}^{(\mathfrak{s}_i)} + 4\mu^{(\mathfrak{s}_i)} \geq 0, \tag{28.137}$$

$$\kappa^{(\mathfrak{s}_i)} \geq 0, \tag{28.138}$$

$$\alpha_1^{(\mathfrak{s}_i)} = 0, \qquad \alpha_2^{(\mathfrak{s}_i)} = 0, \qquad \alpha_3^{(\mathfrak{s}_i)} = 0, \tag{28.139}$$

$$-\rho^{(\mathfrak{s}_i)} \frac{\partial^2 \psi^{(\mathfrak{s}_i)}}{\partial \rho^{(\mathfrak{s}_i)} \partial D_{jk}^{(\mathfrak{s}_i)}} - \frac{\partial \Lambda_\rho^{(\mathfrak{s}_i)}}{\partial D_{jk}^{(\mathfrak{s}_i)}} + \frac{\partial \lambda^{(\mathfrak{s}_i)}}{\partial \dot{\rho}^{(\mathfrak{s}_i)}} I_{jk}^{(\mathfrak{s}_i)} = 0, \tag{28.140}$$

$$-\rho^{(\mathfrak{s}_i)} \frac{\partial^2 \psi^{(\mathfrak{s}_i)}}{\partial \Theta^{(\mathfrak{s}_i)} \partial D_{jk}^{(\mathfrak{s}_i)}} - \rho^{(\mathfrak{s}_i)} \frac{\partial \eta^{(\mathfrak{s}_i)}}{\partial D_{jk}^{(\mathfrak{s}_i)}} + \frac{\partial \lambda^{(\mathfrak{s}_i)}}{\partial \dot{\Theta}^{(\mathfrak{s}_i)}} I_{jk}^{(\mathfrak{s}_i)} = 0, \tag{28.141}$$

$$\begin{aligned} &\left| \frac{\partial \lambda^{(\mathfrak{s}_i)}}{\partial D_{jk}^{(\mathfrak{s}_i)}} I_{mn}^{(\mathfrak{s}_i)} + \frac{\partial \lambda^{(\mathfrak{s}_i)}}{\partial D_{mn}^{(\mathfrak{s}_i)}} I_{jk}^{(\mathfrak{s}_i)} \right| \\ &\qquad \leq 4 \left[\left(\frac{\partial \lambda^{(\mathfrak{s}_i)}}{\partial D_{jk}^{(\mathfrak{s}_i)}} I_{jk}^{(\mathfrak{s}_i)} + 2\mu^{(\mathfrak{s}_i)} \right) \left(\frac{\partial \lambda^{(\mathfrak{s}_i)}}{\partial D_{mn}^{(\mathfrak{s}_i)}} I_{mn}^{(\mathfrak{s}_i)} + 2\mu^{(\mathfrak{s}_i)} \right) \right]^{\frac{1}{2}}, \end{aligned} \tag{28.142}$$

$$\begin{aligned} &\left| \frac{\partial \lambda^{(\mathfrak{s}_i)}}{\partial \left(\nabla^{(\mathfrak{s}_i)} \Theta^{(\mathfrak{s}_i)} \right)_m} I_{jk}^{(\mathfrak{s}_i)} \right| \\ &\qquad \leq 2 \left[2 \left(\frac{\partial \lambda^{(\mathfrak{s}_i)}}{\partial D_{jk}^{(\mathfrak{s}_i)}} I_{jk}^{(\mathfrak{s}_i)} + 2\mu^{(\mathfrak{s}_i)} \right) \frac{2}{\Theta^{(\mathfrak{s}_i)}} \kappa^{(\mathfrak{s}_i)} \delta_{mm} \right]^{\frac{1}{2}}, \end{aligned} \tag{28.143}$$

$$\frac{\partial \lambda^{(\mathfrak{s}_i)}}{\partial \boldsymbol{W}_{\mathfrak{s}}} I_{jk}^{(\mathfrak{s}_i)} = -\frac{\partial \sigma^{(\mathfrak{s}_i)}}{\partial D_{jk}^{(\mathfrak{s}_i)}} H^{(\mathfrak{s}_i)} \boldsymbol{n}^{(\mathfrak{s}_i)}, \tag{28.144}$$

$$\frac{\partial \lambda^{(\mathfrak{s}_i)}}{\partial \boldsymbol{W}_{\mathfrak{s}}^{+}} I_{jk}^{(\mathfrak{s}_i)} = -\frac{\rho^{(i)}}{\rho^{(\mathfrak{s}_i)}} \frac{\partial \sigma^{(\mathfrak{s}_i)}}{\partial D_{jk}^{(\mathfrak{s}_i)}} \boldsymbol{n}^{(\mathfrak{s}_i)}, \tag{28.145}$$

$$\frac{\partial \lambda^{(\mathfrak{s}_i)}}{\partial \boldsymbol{W}_{\mathfrak{s}}^{-}} I_{jk}^{(\mathfrak{s}_i)} = -\frac{\rho^{(i-1)}}{\rho^{(\mathfrak{s}_i)}} \frac{\partial \sigma^{(\mathfrak{s}_i)}}{\partial D_{jk}^{(\mathfrak{s}_i)}} \boldsymbol{n}^{(\mathfrak{s}_i)}. \tag{28.146}$$

It is important to mention that there is no summation over piecewise occurring indices. From (28.145) and (28.146), it follows that

$$\frac{\partial \lambda^{(\mathfrak{s}_i)}}{\partial \boldsymbol{W}_{\mathfrak{s}}^{-}} = \frac{\rho^{(i-1)}}{\rho^{(i)}} \frac{\partial \lambda^{(\mathfrak{s}_i)}}{\partial \boldsymbol{W}_{\mathfrak{s}}^{+}}. \tag{28.147}$$

---

[7] These derivations are fairly tedious and complicated. Here, we refrain from providing more details.

Since the inequality (28.137) must be independent of the coordinate system, which means the inequality must be satisfied for arbitrary I_{jk}, we conclude that

$$\frac{\partial \lambda^{(\mathfrak{s}_i)}}{\partial D^{(\mathfrak{s}_i)}_{jk}} \geq -2\mu^{(\mathfrak{s}_i)} \tag{28.148}$$

must hold for $(jk) \in \{(11), (12), (13), (22), (23), (33)\}$. Due to (28.139) a dependence of the surface heat flux $\boldsymbol{q}^{(\mathfrak{s}_i)}$ on the relative velocities $\boldsymbol{W}_{\mathfrak{s}}$, $\boldsymbol{W}^{+}_{\mathfrak{s}}$, $\boldsymbol{W}^{-}_{\mathfrak{s}}$ in (28.133) cannot occur. To obtain more explicit limitations on the material parameters, further assumptions on the form of the constitutive equations are required.

28.6 Closing Summary

This chapter was devoted to the derivations of the possible forms for the constitutive relations of the material laws of phase interfaces and three-phase contact line in the context of multiphase flows. We presented the continuum description of phase interfaces and three-phase contact line associated with excess surface and line physical quantities. Starting from a fairly general postulate of constitutive functions, a simple continuum model was deduced by restrictions imposed by the rules of material frame indifference, and particularly the entropy principle paired with a few *ad hoc* assumptions.

As an example, we mention the postulation that the interfacial constitutive variables $\mathcal{S} \in \left\{\boldsymbol{T}^{(\mathfrak{s}_i)}, \boldsymbol{q}^{(\mathfrak{s}_i)}, ...\right\}$ are characterized by the constitutive functions

$$\begin{aligned}\mathcal{S} = \hat{\mathcal{S}}\ \Big(&\rho^{(\mathfrak{s}_i)}, \nabla^{(\mathfrak{s}_i)}\rho^{(\mathfrak{s}_i)}, \Theta^{(\mathfrak{s}_i)}, \nabla^{(\mathfrak{s}_i)}\Theta^{(\mathfrak{s}_i)}, \nabla^{(\mathfrak{s}_i)}\boldsymbol{v}^{(\mathfrak{s}_i)},\\ &H^{(\mathfrak{s}_i)}, \boldsymbol{v}^{(\mathfrak{s}_i)}, \boldsymbol{v}^{(i)}, \boldsymbol{v}^{(i-1)}, \boldsymbol{w}^{(\mathfrak{s}_i)}\Big).\end{aligned}$$

We employed the principle of material objectivity, evaluated the entropy inequality, and employed a linear theory for the dynamic parts of the constitutive variables. Among other results, the constitutive equations for the interfacial stress $\boldsymbol{T}^{(\mathfrak{s}_i)}$ and the interfacial heat flux $\boldsymbol{q}^{(\mathfrak{s}_i)}$ take the reduced forms

$$\begin{aligned}\boldsymbol{T}^{(\mathfrak{s}_i)} &= (\sigma^{(\mathfrak{s}_i)} + \lambda^{(\mathfrak{s}_i)}\mathrm{tr}\, \boldsymbol{D}^{(\mathfrak{s}_i)})\boldsymbol{I}^{(\mathfrak{s}_i)} + 2\mu^{(\mathfrak{s}_i)}\boldsymbol{D}^{(\mathfrak{s}_i)},\\ \boldsymbol{q}^{(\mathfrak{s}_i)} &= -\kappa^{(\mathfrak{s}_i)}\nabla^{(\mathfrak{s}_i)}\Theta^{(\mathfrak{s}_i)},\end{aligned}$$

where the following restrictions on the material parameters $\kappa^{(\mathfrak{s}_i)}$, $\lambda^{(\mathfrak{s}_i)}$ and $\mu^{(\mathfrak{s}_i)}$ must hold:

$$\kappa^{(\mathfrak{s}_i)} \geq 0, \quad \mu^{(\mathfrak{s}_i)} \geq 0, \quad 8(2-\sqrt{5})\mu^{(\mathfrak{s}_i)} \leq \lambda^{(\mathfrak{s}_i)} \leq 8\mu^{(\mathfrak{s}_i)}.$$

In case of a variable surface mass density at the interface ($\rho^{(\mathfrak{s}_i)} = \hat{\rho}^{(\mathfrak{s}_i)}\left(\boldsymbol{x}^{(\mathfrak{s}_i)}, t\right)$), the surface tension $\sigma^{(\mathfrak{s}_i)}$ should be determined by a surface thermal equation of state; it is expressed in terms of the interfacial Helmholtz free energy, as shown in (28.43). For a density preserving surface ($\rho^{(\mathfrak{s}_i)} = \text{const}$), the surface tension $\sigma^{(\mathfrak{s}_i)}$ is an unknown field quantity and must be determined by solving the field equations in a properly posed initial boundary value problem. Furthermore, the interfacial Gibbs equation, (28.45), and the relations among the interfacial Helmholtz free energy, the surface tension, as well as the Helmholtz energies and pressures of the neighboring bulk phases in thermodynamic equilibrium, (28.54), were also derived.

Similar constitutive relations for the three-phase contact line were also deduced.

These material equations seem to be fairly simple and may be applicable to explicit calculations of dynamic processes associated with the phase interfaces and the three-phase common line in multiphase flows.

28.7 Concluding Remarks

This and the previous chapter are concerned with the derivation of restrictions implied by thermodynamics of multiphase flows of bodies exhibiting moving interfaces and contact lines. In Chap. 27, the balance laws are derived for Boltzmann models of bulk, surface, and contact line continua. In this chapter then continues this problem of classical physics in three, two, and one dimensions with the presentation of the derivation of the implications that follow from Müller's entropy principle applied to these fluid continua for viscous, heat conducting, compressible or density preserving fluids. Except for the analytical-algebraic complexity of the computations, the procedures to reach the corresponding inferences are straightforward. The procedures and results of both chapters can be classified as belonging to established rules of thermodynamics. They are necessary prerequisites for a consistent application of the deduced results in fluid dynamical studies of such complex systems in initial boundary value problems. Such applications must follow the thermodynamic groundwork laid down in the two chapters.

The two chapters deal with multiphase flows with moving interfaces and contact line as a thermodynamic system, in which three-dimensional continua are separated by dynamic two-dimensional contact surfaces and a one-dimensional contact line. It is assumed that the moving interfaces have conceptually vanishing thicknesses and the contact line is similarly treated as a mathematical line possessing vanishing cross section. More complex geometric configurations are not analyzed.

The complexity of the multiphase model is, however, enhanced with respect to assumptions describing the physics of this model. The three-dimensional bulk part of the body is composed of three separate phases. They are assumed to be different Boltzmann materials, respectively, and can also be mixtures of class II, in which dilute constituent components are described by constituent mass balance laws, which can, in principle, interact via dynamic and/or chemical exchange processes, but move in consensus with the bearer fluid. The moving interfaces and the contact line are treated as two-dimensional and one-dimensional mass carrying continua, which, in principle possess distinct mass densities, velocities, temperatures, and entropies from one another and from the bulk phase. The dynamic and thermal interactions of the moving interfaces with the bulk materials and the moving interfaces with the moving contact line are exerted by the surface and line balance equations of mass, momenta, energy, and entropy that reduce to the familiar corresponding jump conditions when the surface and line mass densities are ignored.

The implication is that the moving interfaces behave essentially as *membranes* subject to surface tensions and shear forces parallel to the surface, but incapable of sustaining bending and twisting moments. Similarly, the contact line possesses the structure of a *thread* or *string*, underlying line tension and axial shear force, but again only vanishing bending and torsion.

These properties allow possible extensions of the thermodynamic model of the interfaces and the contact line to liquid *shells* and liquid *shafts* or *beams*, which would allow extensions of the descriptions of the physical behavior of the moving interfaces and contact line. In such extensions, they would fit into two-dimensional and one-dimensional COSSERAT continua, which then would interact with a BOLTZMANN bulk fluid. Such extensions then could allow accounting for the variability of the field variables across the thickness of the interfaces and the contact line by considering variations of the kinematic and thermal fields and nonzero bending and twisting moments as well as the temperature.

References

1. Alts, T., Hutter, K.: Continuum description of the dynamics and thermodynamics of phase boundaries between ice and water. Part II: thermodynamics. J. Non-Equil. Thermodyn. **13**, 250–289 (1988)
2. Alts, T., Hutter, K.: Continuum description of the dynamics and thermodynamics of phase boundaries between ice and water. Part III: Thermostatics and consequences. J. Non-Equil. Thermodyn. **13**, 301–329 (1988)
3. Baehr, H.D.: Thermodynamik. Springer, Heidelberg (2009)
4. Bargmann, S., Steinmann, P.: Classical results for a non-classical theory: remarks on thermodynamic relations in Green-Naghdi thermo-hyperelasticity. Continuum Mech. Thermodyn. **19**(1–2), 59–66 (2007)
5. Coleman, B.D., Noll, W.: The thermodynamics of elastic materials with heat condition and viscosity. Arch. Rat. Mech. Anal. **13**, 167–178 (1963)
6. Ehlers, W.: Poröse Medien, ein kontinuumsmechanisches Modell auf der Basis der Mischungstheorie. Universität-Gesamthochschule Essen, Habilitation (1989)
7. Fang, C., Wang, Y., Hutter, K.: Shearing flows of a dry granular material - hypoplastic constitutive theory and numerical simulations. Int. J. Numer. Anal. Meth. Geomech. **30**, 1409–1437 (2006)
8. Fang, C., Wang, Y., Hutter, K.: A thermo-mechanical continuum theory with internal length for cohesionless granular materials. Part I: a class of constitutive models. Continuum Mech. Thermodyn. **17**(8), 545–576 (2006)
9. Fang, C., Wang, Y., Hutter, K.: A thermo-mechanical continuum theory with internal length for cohesionless granular materials. Part II: non-equilibrium postulates and numerical simulations

of simple shear, plane Poiseuille and gravity driven problems. Continuum Mech. Thermodyn. **17**(8), 577–607 (2006)

10. Fang, C., Wang, Y., Hutter, K.: A unified evolution equation for the Cauchy stress tensor of an isotropic elasto-visco-plastic material. I. On thermodynamically consistent evolution. Continuum Mech. Thermodyn. **19**, 423–440 (2008)
11. Grad, H.: Principles of the Kinetic Theory. Handbuch der Physik XII. Springer, Berlin (1958)
12. Hutter, K.: The foundation of thermodynamics, its basic postulates and implications. Acta Mechanica **27**, 1–54 (1977)
13. Hutter, K.: The physics of ice-water phase change surfaces. In: Kosinski, W., Murdoch, A.I. (eds.): Modelling Macroscopic Phenomena at Liquid Boundaries. CISM Course 318, Springer, Vienna (1991)
14. Hutter, K., Jöhnk, K., Svendsen, B.: On interfacial transition conditions in two-phase gravity flow. Z angew. Math. Phys. **45**, 746–762 (1994)
15. Hutter, K., Jöhnk, K.: Continuum Methods of Physical Modeling. Springer, Berlin (2004)
16. Hutter, K., Wang, Y.: Phenomenological thermodynamics and entropy principles. In: Greven, A., Keller, G., Warnecke, G. (eds.) Entropy. Princeton University Press, Princeton, pp. 57–78 (2003). ISBN 0-691-11338-6
17. Hutter, K., Wang, Y.: Fluid and Thermodynamics. Volume 1: Basic Fluid Mechanics, P. 639. Springer, Berlin (2016). ISBN: 978-3319336329
18. Hutter, K., Wang, Y.: Fluid and Thermodynamics. Volume II: Advanced Fluid Mechanics and Thermodynamic Fundamentals, p. 633. Springer, Berlin (2016). ISBN: 978-3-319-33635-0
19. Kirchner, N.: Thermodynamically consistent modelling of abrasive granular materials, Part I: Non-equilibrium theory. Proc. R. Soc. Lond. A **458**, 2153–2176 (2002)
20. Kirchner, N., Teufel, A.: Thermodynamically consistent modelling of abrasive granular materials Part II: Thermodynamic equilibrium and applications to steady shear flows. Proc. R. Soc. Lond. A **458**, 3053–3077 (2002)
21. Liu, I.-Shih: Method of Lagrange multipliers for exploitation of the entropy principle. Arch. Rat. Mech. Anal. **46**, 131–148 (1972)
22. Liu, I-Shih and Müller, I.: Thermodynamics of mixtures of fluids. In: Truesdell, C. (ed): Rational thermodynamics, pp. 264–285. New York, Springer (1984)
23. Luca, I., Fang, C., Hutter, K.: A thermodynamic model of turbulent motions in a granular material. Continuum Mech. Thermodyn. **16**, 363–390 (2004)
24. Müller, I.: On the entropy inequality. Arch. Rat. Mech. Anal. **26**, 118–141 (1967)
25. Müller, I.: Die Kältefunktion, eine universelle Funktion in der Thermodynamik viskoser wärmeleitender Flüssigkeiten. Arch. Rat. Mech. Anal. **40**, 1–36 (1971)
26. Müller, I.: Thermodynamik - Grundlagen der Materialtheorie. Bertelsman Universitätsverlag, Düsseldorf (1972)
27. Müller, I.: Thermodynamics. Pitman, London (1985)
28. Sadiki, A., Bauer, W., Hutter, K.: Thermodynamically consistent coefficient calibration in nonlinear and anisotropic closure models for turbulence. Continuum Mech. Thermodyn. **12**, 131–149 (2000)
29. Spurk, J.H.: Fluid Mechanics. Springer, Berlin (1997)
30. Svendsen, B., Hutter, K.: On the thermodymics of a mixture of isotropic materials with constraints. Int. J. Eng. Sci. **33**, 2021–2054 (1995)
31. Svendsen, B., Hutter, K., Laloui, L.: Constitutive models for granular materials including quasi-static frictional behaviour: toward a thermodynamic theory of plasticity. Continuum Mech. Thermodyn. **4**, 263–275 (1999)
32. Svendsen, B., Chanda, T.: Continuum thermodynamic formulation of models for electromagnetic thermoinelastic solids with application in electromagnetic metal forming. Continuum Mech. Thermodyn. **17**, 1–16 (2005)
33. Wang, C.C.: A new representation theorem for isotropic functions: An answer to Professor G. F. Smith's criticism of my papers on representations for isotropic functions. Part I. Arch. Rat. Mech. Anal. **36**(3), 166–197 (1970)

34. Wang, C.C.: A new representation theorem for isotropic functions: An answer to Professor G.F. Smith's criticism of my papers on representations for isotropic functions. Part II. Arch. Rat. Mech. Anal. **36**(3), 198–223 (1970)
35. Wang, Y., Hutter, K.: Comparison of two entropy principles and their applications in granular flows with/without fluid. Arch. Mech. **51**, 605–632 (1999)
36. Wang, Y., Hutter, K.: Shearing flows in a Goodman-Cowin type granular material - theory and numerical results. Part. Sci. Tech. **17**, 97–124 (1999)
37. Wang, Y., Hutter, K.: A constitutive model for multi-phase mixtures and its application in shearing flows of saturated soil-fluid mixtures. Granul. Matter **1**, 163–181 (1999)
38. Wang, Y., Hutter, K.: A constitutive theory of fluid-saturated granular materials and its application in gravitational flows. Rheologica Acta **38**, 214–223 (1999)
39. Wang, Y., Oberlack, M.: A thermodynamic model of multiphase flows with moving interfaces and contact line. Continuum Mech. Thermodyn. **23**, 409–433 (2011)
40. Wang, Y., Oberlack, M., Zieleniewicz, A.: Constitutive modeling of multiphase flows with moving interfaces and contact line. Continuum Mech. Thermodyn. **25**, 705–725 (2013)
41. Wilmanski, K.: Continuum Thermodynamics, Part 1: Foundations. World Scientific Pub Co. (2009)
42. Wood, L.C.: The bogus axioms of continuum mechanics. Bull. Math. Appl. **17**, 98–102 (1981)

Chapter 29

A Granular Fluid as a Limit of a Binary Mixture Theory—Treated as a One-Constituent Goodman–Cowin-Type Material

Abstract GOODMAN and COWIN (1972) (Goodman and Cowin (1971). J. Fluid Mech. 45, 321–339. [6]) proposed a continuum theory of a dry cohesionless granular material in which the solid volume fraction ν is treated as an independent kinematic field for which an additional balance law of equilibrated forces is postulated. They motivated this additional balance law as an equation describing the kinematics of the microstructure and employed a variational formulation for its derivation. By adopting the MÜLLER–LIU approach to the exploitation of the entropy inequality we show that in a constitutive model containing ν, $\dot{\nu}$ and grad ν as independent variables, results agree with the classical COLEMAN–NOLL approach only, provided the HELMHOLTZ free energy does not depend on $\dot{\nu}$, for which the Goodman–Cowin equations are reproduced. This reduced theory is then applied to analyses of steady fully developed horizontal shearing flows and gravity flows of granular materials down an inclined plane and between parallel plates. It is demonstrated that the equations and numerical results presented by PASSMAN et al. (1980) (Passman, Nunziato, Bailey and Thomas (1980). J. Eng. Mech. Div. ASCE 106, 773–783. [15]) are false, and they are corrected. The results show that the dynamical behavior of these materials is quite different from that of a viscous fluid. In some cases, the dilatant shearing layers exist only in the narrow zones near the boundaries. They motivated this additional balance law as an equation describing the kinematics of the microstructure and employed a variational formulation for its derivation. In an appendix, we present a variational formulation, treating the translational velocity and solid volume fraction as generalized coordinates of a LAGRANGEan formulation.

Keywords Granular materials · Constitutive equations · Iteration method · Granular shearing flows

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This chapter is heavily based on the paper by WANG and HUTTER [20].

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List of Symbols

Roman Symbols

$\boldsymbol{A}$	$n \times n$ matrix in a linear equation $\boldsymbol{A\phi} = \boldsymbol{f}$
$\mathcal{A}$	Constitutive parameter for $\mathcal{A} = 2\gamma\nu\partial\psi/\partial(\operatorname{grad}\nu \cdot \operatorname{grad}\nu)$
$\boldsymbol{a}(= \boldsymbol{0})$	Liu identities
$a_0, \dots, a_3$	Parameters in the second-order approximation of $\gamma\nu\psi$, see (29.57)
$\mathcal{B}$	Material body
$\boldsymbol{b} > 0$	Residual entropy inequality
$\boldsymbol{b}$	Body force
$\boldsymbol{D}$	Strain rate (stretching) tensor
$\mathcal{E}$	Symbol for energy balance
f	Intrinsic equilibrated body force
f^D	Nonequilibrium parameter for f
f^E	Thermodynamic equilibrium value of f
$\boldsymbol{f}$	n-dimensional vector
$\boldsymbol{h}$	Equilibrated stress vector
k	Iteration index in a numerical integration method
$\boldsymbol{k}$	Extra entropy flux vector, $\boldsymbol{k} = \boldsymbol{\phi} + \frac{1}{\theta}(\boldsymbol{\lambda}^{\boldsymbol{v}} \cdot \boldsymbol{T} + \lambda^k \boldsymbol{h} - \boldsymbol{q})$
l, ℓ	External equilibrated body force
$\boldsymbol{\mathcal{M}}$	Symbol for linear momentum balance
$\mathcal{N}$	Symbol for equilibrated force balance
p	Thermodynamic pressure (see (29.39))
$\boldsymbol{q}$	Heat flux vector
$\boldsymbol{q}^E = \boldsymbol{0}$	Thermodynamic equilibrium value of $\boldsymbol{q}$
$\mathcal{R}$	Symbol for mass balance
r	Heat (energy) supply
s	Entropy supply density
S	Dimensionless parameter, see (29.66), $S = \gamma b/(2\nu_m a_0)\xi$
$\boldsymbol{T}$	CAUCHY stress tensor
$\boldsymbol{T}^E$	CAUCHY stress tensor in thermodynamic equilibrium
$u(y)$	x-component of $\boldsymbol{v}$ in a shearing problem
$\boldsymbol{v}$	Velocity vector
$\boldsymbol{w} = \operatorname{grad}\nu$	Gradient of the volume fraction
x, y, z	Cartesian coordinates, (x, y) horizontal, z vertical generally against gravity
$\bar{x}, \bar{y}, \bar{z}$	Dimensionless forms of (x, y, z)
$\boldsymbol{Y}$	Independent constitutive variables in thermodynamic nonequilibrium, $\boldsymbol{Y} = (\dot{\nu}, \operatorname{grad}\theta, \boldsymbol{D})$

Greek Symbols

$\boldsymbol{\alpha}$	Vector of physical quantities formed with derivatives of the independent constitutive variables
$\alpha(\nu)$	Coefficient function in the parameterization of $\phi(\nu)$, see (29.60)

$\alpha_0, \dots$	Coefficients in the parameterization of $\alpha(\nu)$ (dimensionless)
β	Configurational pressure, see (29.39)
γ	True density, density of the grains
ε	Internal energy
η	Entropy density per unit mass
μ	Viscosity
μ_0	Reference viscosity (see (29.61))
ν	Volume fraction
ν_m	Critical volume fraction
ν_∞	Volume fraction at densest packing
ζ	Nonequilibrium parameter for f
$\boldsymbol{\phi}$	Entropy flux
$\boldsymbol{\phi}$	$n \times n$ vector in the linear equation $\boldsymbol{A}\boldsymbol{\phi} = \boldsymbol{f}$
σ_0	Dimensionless pressure at the upper surface of the shear layer
π	Entropy production density
λ	Bulk viscosity
λ^k	LAGRANGE multiplier of the equilibrated force balance
$\boldsymbol{\lambda}^{\boldsymbol{v}}$	LAGRANGE multiplier of the momentum balance
λ^ε	LAGRANGE multiplier of the energy balance
λ^ν	LAGRANGE multiplier of the mass balance
θ	Empirical (and later) KELVIN temperature, inclination angle of a granular layer
ψ	Free energy (HELMHOLTZ free energy)
ξ	Thermodynamic nonequilibrium parameter of the CAUCHY stress tensor
$1/\xi$	Material length, $\xi^2 = a_0/\alpha_0 = [1/L^2]$
κ	Heat conductivity

Miscellaneous Symbols

$\mathrm{d}/\mathrm{d}t$	Total time derivative
∂V	Boundary of volume V
$\boldsymbol{A}^T$	Transpose of $\boldsymbol{A}$
$\boldsymbol{A}^{-T} = (\boldsymbol{A}^T)^{-1} = (\boldsymbol{A}^{-1})^T$	
$\Vert\boldsymbol{b}\Vert$	Norm of $\boldsymbol{b}$
$(\bar{\cdot})$	Dimensionless form of $(\cdot)$

29.1 Introduction

A granular material is a collection of a large number of discrete solid particles with interstices filled with a fluid or a gas. In most flows involving the granular materials, the interstitial fluid plays an insignificant role in the transportation of momentum and thus flows of such materials can be considered dispersed single phase rather than multiphase flows. A detailed review of flows of granular materials has been presented by HUTTER and RAJAGOPAL [9] and WANG and HUTTER [20, 21].

It is widely known today that granular media exhibit microstructural effects on their macroscale, which is accounted for, in general, by adding an additional dynamical equation for the solid volume fraction ν. Different authors do not unanimously agree upon the form of this equation. SVENDSEN and HUTTER [19] treated the solid volume fraction as an internal variable and write an evolution equation balancing its time rate of change with its production. WILMANSKI [22] on the other hand, using statistical arguments on the microscale demonstrated that the SVENDSEN–HUTTER equation needed to be complemented by a flux term, thus arriving at a complete balance law. On the other hand, GOODMAN and COWIN (1972) [7] introduced, on pure mathematical grounds, a balance law of equilibrated forces in which second-order time derivatives of ν, i.e., $\ddot{\nu}$ were balanced with a flux, production and supply terms. Today, it is still not clear what their motivation might have been, except, perhaps, the formal analogy with Newton's law.

In deriving their reduced constitutive relations from a class of constitutive postulates GOODMAN and COWIN used the COLEMAN–NOLL approach of thermodynamics, i.e., the linear momentum equation, the energy balance and the balance of equilibrated forces had all arbitrarily assignable external source terms, so that these balance laws would not affect the exploitation of the entropy inequality. Whereas such a procedure can be tolerated for the momentum and energy sources, it is physically utter nonsense for the balance law of equilibrated forces. This is an internal law all by itself, and at least this law must influence the thermodynamics.

This is one reason why we have rederived the thermodynamic theory, now using the MÜLLER–LIU approach in which the entropy inequality is exploited *for all thermodynamic processes*, i.e., all balance laws and boundary conditions, be these processes driven by external sources or not. We find that GOODMAN–COWIN's approach agrees with this more general approach provided the HELMHOLTZ free energy does not depend on $\dot{\nu}$. We present the general field equations that emerge in this case, study the thermodynamic equilibrium state of granular media in detail and show that in a viscous (but not plastic) model equilibrium-shear stresses can be supported by the model through the inhomogeneities of the solid volume fraction distribution. Deviations from the thermostatic equilibrium are modeled in a linear fashion as is done by GOODMAN and COWIN [7]. The analysis reproduces the GOODMAN–COWIN equations for a limited constitutive class but calls for the more general thermodynamic approach when memory effects through the $\dot{\nu}$-dependence are included in the HELMHOLTZ free energy.

As mentioned in the chapter title, we wish to interpret a granular material conceptually as a limit construction of a mixture theory of an assembly of granules—in the simplest situation of particles of one representative form and diameter—and an interstitial fluid or empty space. Different authors do not unanimously agree upon the form of this equation. SVENDSEN and HUTTER [19] treat the solid volume fraction as an internal variable and write an evolution equation, balancing its time rate of change with its production. WILMANSKI [23], on the other hand, using statistical arguments on the microscale, demonstrates that the SVENDSEN–HUTTER equation needed to be complemented by a flux term, thus arriving at a complete balance law:

$$\begin{aligned} \dot{\nu} &= \pi, && \text{Svendsen–Hutter [23]}, \\ \dot{\nu} &= \operatorname{div} \boldsymbol{h} + \pi, && \text{Wilmanski [27]}, \end{aligned} \qquad (29.1)$$

in which ν is the solid volume fraction, π its specific production, and $\boldsymbol{h}$ its flux.

Much earlier, Goodman and Cowin [7] suggested that the volume fraction of a moving granular material ought to have the form

$$\mathcal{I}\ddot{\nu} = \operatorname{div} \boldsymbol{h} + \pi, \qquad \text{Goodman–Cowin [9]}, \qquad (29.2)$$

in which $\mathcal{I}$ has the meaning of an inertia and $\ddot{\nu}$ is a volume fraction acceleration assigning to their volume fraction equation the structure of a 'volume fraction momentum balance'.

With a somewhat simplistic understanding, and with the adoption of the postulate that the granular structure can be "derived" from a scalar balance law, which typically reflects a momentum-like character, we shall now propose a model procedure. This attitude suggests that the momentum associated with the volume variation of the granules plus the pore volume may be postulated to be proportional to the acceleration of the volume fraction multiplied with a pre-factor that can be identified with a volume fraction inertia $\mathcal{I}$. This term is balanced by the volume fraction stress, the divergence of a vector-valued quantity $\boldsymbol{h}$, called the volume fraction flux, plus a scalar-valued volume fraction body force π that may be composed of an intrinsic, ρf, and an external, $\rho\ell$, contribution. Here, $\rho = \gamma\nu$ is the density and γ the true density per unit volume of the solid grains. Writing the volume fraction inertia as $\mathcal{I} = \gamma k$, in which k is a phenomenological parameter, the volume fraction momentum balance may now simply be conjectured in the form

$$\gamma k \ddot{\nu} = \operatorname{div} \boldsymbol{h} + \gamma\nu(f + \ell). \qquad (29.3)$$

Even though the motivation of this balance equation is far from being a derivation, it possesses a high potential of being able to capture a substantial part of the physics of granular materials. Ignoring the external supply part, ℓ, all remaining quantities, k, $\boldsymbol{h}$, and f have essentially constitutive character. This means that (29.3) possesses the potential of capturing a great number of physical phenomena, since all these quantities follow essentially from experimentation. The aim of the application of the second law of thermodynamics is then virtually the only tool to constrain the freedom in the selection of the functional form of k, $\boldsymbol{h}$, and f. This must be done by simultaneously accounting the balance laws of mass, momentum, and energy. As we shall see, the coupling of (29.3) with these physical laws will be enhanced by introducing working terms in the energy equation that are of the form $\boldsymbol{h} \cdot \operatorname{grad} \dot{\nu}$ and $\gamma\nu f \dot{\nu}$.

The above relatively weak motivation of the equilibrated force balance also sheds light on our preference of the entropy principle of Müller against that of Coleman–Noll: Introducing an external equilibrated force $\gamma\nu\ell$ and handling it as a "deus ex machina" to ignore (29.3) in the exploitation of the entropy principle implies that the thermodynamic interplay between (29.3) and the remaining physical balance laws is not as strong as otherwise. Therefore, to abandon the open-system exploitation of the entropy principle is a helpful step in achieving better model equations.

As the various micro-grain postulates imply distinct balance laws with distinct thermodynamically detailed results, explicit computations of flow configurations need to be deduced and compared with experimental results. We shall present results of such computations and demonstrate that the fundamental axiomatics are crucial in this regard.

In an attempt to reproduce and generalize the shear flow computations of Passman et al. (1980) [15], it was found that our reduced differential equations for the horizontal shearing flow differed in the sign of one single but important term; scrutiny apparently proved us to be correct, and recomputations generated vastly different results. Thus, in Sects. 29.5–29.7 the theory is applied to analyses of steady fully developed horizontal shearing flows and gravity flows of granular materials down an inclined plane and between vertical parallel plates, by use of a special expression of free energy used in Passman et al. [15]. Results show that the dynamical behavior of these materials is quite different from that of a viscous fluid. In some cases, the dilatant shearing layers exist only in the narrow zones near the boundaries, which is different from a viscous fluid, in which shearing exists in all flow zones. We also present the analysis of the horizontally sheared layer between two rigid plates and show that results are in this case vastly different from what Passman et al. obtained.

29.2 Thermodynamic Processes

29.2.1 Balance Relations

We shall now assume the moving material as a single-constituent material of fluid type, of which the empty pore space is dynamically acting on the motion of the grain assemblage by the microstructure equation (29.3). We shall employ the following notation:

- γ is the true mass density of the grains ($2.6 \times 10^3\,\mathrm{kg\,m^{-3}}$).
- ν is the volume fraction occupied by the grains.
- $\boldsymbol{T}$ is the Cauchy stress tensor of the grains, necessarily symmetric in a one-constituent fluid.
- $\boldsymbol{b}$ is the body force per unit mass (∼gravity force).
- The microstructural force balance is taken in the form (29.3).
- The balance of energy is extended by two additional power terms due to the flux $\boldsymbol{h}$ and the intrinsic body force $\gamma\nu f$, which are given by $\boldsymbol{h} \cdot \operatorname{grad} \dot{\nu}$ and $-\gamma\nu f \dot{\nu}$, respectively. So, the total power of working is postulated as

$$\boldsymbol{T} \cdot \boldsymbol{D} + \boldsymbol{h} \cdot \operatorname{grad} \dot{\nu} - \gamma\nu f \dot{\nu}. \tag{29.4}$$

- ε is the internal energy, $\boldsymbol{q}$ the heat flux vector, and r the radiation supply per unit mass.

With these notations, the physical balance laws of this postulated granular continuum take the forms (see this Volume Chaps. 21, 25 and 26).

- Balance of mass

$$\mathcal{R} \equiv \dot{\overline{\gamma\nu}} + \gamma\nu \operatorname{div} \boldsymbol{v} = 0, \tag{29.5}$$

- Balance of linear momentum

$$\mathcal{M} \equiv \gamma\nu\dot{\boldsymbol{v}} = \operatorname{div} \boldsymbol{T} + \gamma\nu\boldsymbol{b}, \tag{29.6}$$

- Balance of angular momentum

$$\boldsymbol{T} = \boldsymbol{T}^T, \tag{29.7}$$

- Balance of equilibrated force

$$\mathcal{N} \equiv \gamma\nu k\ddot{\nu} = \operatorname{div} \boldsymbol{h} + \gamma\nu(l + f), \tag{29.8}$$

- Balance of energy

$$\mathcal{E} \equiv \gamma\nu\dot{\varepsilon} = \boldsymbol{T} \cdot \boldsymbol{D} + \boldsymbol{h} \cdot \operatorname{grad} \dot{\nu} - \gamma\nu f \dot{\nu} - \operatorname{div} \boldsymbol{q} + \gamma\nu r. \tag{29.9}$$

The balance equations (29.5), (29.6) and (29.7) are analogous to the classical balance equations of mass, linear momentum, and angular momentum. The balance of equilibrated force is assumed in this simplest form (29.8) according to Goodman and Cowin [7]. The conservation of energy (29.9) differs from the traditional statements by the occurrence of the power terms associated with $\dot{\nu}$; here we are following Müller [14] and Goodman and Cowin [7].

29.2.2 Entropy Inequality

According to our concept of thermodynamics, following Müller [14] and Liu [13] we postulate an entropy inequality of the form

$$\pi = \gamma\nu\dot{\eta} + \operatorname{div} \boldsymbol{\phi} - \gamma\nu s, \tag{29.10}$$

η is the entropy density per unit mass, $\boldsymbol{\phi}$ its flux density, and s its production density per unit mass. π is the entropy production per unit volume, for which we require

$$\pi > 0 \tag{29.11}$$

for any thermodynamic process satisfying the balance laws (29.5)–(29.9). Following Liu [13], this can be achieved by satisfying the extended entropy inequality

$$\pi - \frac{1}{\theta}\lambda^{\nu}\mathcal{R} - \frac{1}{\theta}\boldsymbol{\lambda}^{\boldsymbol{v}} \cdot \boldsymbol{\mathcal{M}} - \frac{1}{\theta}\lambda^{k}\mathcal{N} - \lambda^{\varepsilon}\mathcal{E} > 0, \tag{29.12}$$

where λ^{ν}, $\boldsymbol{\lambda}^{\boldsymbol{v}}/\theta$, λ^{k}/θ, and λ^{ε} are the Lagrange multipliers of mass, momentum, equilibrated force balance, and energy. In the imbalance (29.12) the condition of the symmetry of the Cauchy stress tensor is not implemented, because we tacitly assume that the constitutive relation for $\boldsymbol{T}$ is postulated so as to fulfill the symmetry condition. This means that we regard the granular material as a Boltzmann continuum and thus ignore a possible intrinsic spin balance which for not too small grains may well be an oversimplification. We also have weighted in (29.12) the Lagrange parameters with $1/\theta$ (except for λ^{ε}), because ensuing calculations will be simplified, if $(\theta > 0)$ is identified with the Kelvin temperature. When substituting $\mathcal{R}$, $\boldsymbol{\mathcal{M}}$, $\mathcal{N}$ and $\mathcal{E}$ as defined in (29.5)–(29.9) into (29.12), we obtain

$$\begin{aligned}\pi = {} & \gamma\nu\dot{\eta} + \operatorname{div}\boldsymbol{\phi} - \gamma\nu s - (1/\theta)\lambda^{\nu}(\dot{\gamma}\nu + \gamma\dot{\nu} + \gamma\nu\operatorname{div}\boldsymbol{v}) \\ & -(1/\theta)\boldsymbol{\lambda}^{v}\cdot(\gamma\nu\dot{\boldsymbol{v}} - \operatorname{div}\boldsymbol{T} - \gamma\nu\boldsymbol{b}) - (1/\theta)\lambda^{k}(\gamma\nu k\ddot{\nu} - \operatorname{div}\boldsymbol{h} - \gamma\nu(l + f)) \\ & -\lambda^{\varepsilon}(\gamma\nu\dot{\varepsilon} - \boldsymbol{T}\cdot\boldsymbol{D} - \boldsymbol{h}\cdot\operatorname{grad}\dot{\nu} + \gamma\nu f\dot{\nu} + \operatorname{div}\boldsymbol{q} - \gamma\nu r) \geqslant 0.\end{aligned} \tag{29.13}$$

We will satisfy this new inequality for all (unrestricted) fields. Explicitly, the balance relations appear as constraints on the class of physically realizable processes, where λ^{ν}, $\boldsymbol{\lambda}^{v}$, λ^{k}, λ^{ε} represent the corresponding Lagrange multipliers.

Introducing the free energy

$$\psi = \varepsilon - \eta\theta \tag{29.14}$$

as well as the assumption $\lambda^{\varepsilon} = 1/\theta$ transforms the entropy inequality into the form

$$\begin{aligned}\theta\pi = {} & -\gamma\nu[\dot{\psi} + \eta\dot{\theta}] - [\gamma\lambda^{\nu} + \gamma\nu f]\dot{\nu} - \gamma\nu\boldsymbol{\lambda}^{v}\cdot\dot{\boldsymbol{v}} \\ & +\theta\operatorname{div}\boldsymbol{\phi} + \boldsymbol{\lambda}^{v}\cdot\operatorname{div}\boldsymbol{T} + \lambda^{k}\operatorname{div}\boldsymbol{h} - \operatorname{div}\boldsymbol{q} - \nu\lambda^{\nu}\dot{\gamma} \\ & +[\boldsymbol{T} - \gamma\nu\lambda^{\nu}\boldsymbol{I}]\cdot\boldsymbol{D} + \boldsymbol{h}\cdot\operatorname{grad}\dot{\nu} - \lambda^{k}\gamma\nu k\ddot{\nu} + \lambda^{k}\gamma\nu f \geqslant 0.\end{aligned} \tag{29.15}$$

In deducing it, we assumed that the material behavior is independent of the supplies, that all external source terms balance, viz.,

$$\theta\gamma\nu s - \boldsymbol{\lambda}^{v}\cdot\gamma\nu\boldsymbol{b} - \lambda^{k}\gamma\nu l - \gamma\nu r = 0, \tag{29.16}$$

which may serve as an equation that determines the entropy supply in terms of the other supply terms. The entropy and its flux as well as the Lagrange multipliers must be considered as auxiliary quantities.

This form of the entropy inequality (29.15) will be used to investigate the constitutive postulates in the next section.

29.3 Constitutive Relations

29.3.1 Constitutive Assumptions and Restrictions

We consider granular materials whose response is characterized by constitutive functions of the form

$$\mathcal{S} = \hat{\mathcal{S}}(\nu_0, \nu, \operatorname{grad}\nu, \dot{\nu}, \gamma, \theta, \operatorname{grad}\theta, \boldsymbol{v}, \operatorname{grad}\boldsymbol{v}) \tag{29.17}$$

for the material variables

$$\mathcal{S} = \{\psi, \eta, \boldsymbol{T}, \boldsymbol{h}, f, \boldsymbol{q}, \boldsymbol{\phi}\}. \tag{29.18}$$

In accordance with the assumption presented in Goodman and Cowin [7], we assumed that the response functions for granular materials depend on a reference configuration through the reference volume distribution ν_0; in this property granular materials are different from fluids. Invoking the principle of material objectivity, which implies that the response of granular materials is independent of the velocity and skew-symmetric part of the velocity gradient $\boldsymbol{W} = \frac{1}{2}(\operatorname{grad}\boldsymbol{v} - (\operatorname{grad}\boldsymbol{v})^T)$, (29.17) reduces to

$$\mathcal{S} = \hat{\mathcal{S}}(\nu_0, \nu, \operatorname{grad}\nu, \dot{\nu}, \gamma, \theta, \operatorname{grad}\theta, \boldsymbol{D}), \tag{29.19}$$

where $\boldsymbol{D} = \frac{1}{2}\left(\operatorname{grad}\boldsymbol{v} + (\operatorname{grad}\boldsymbol{v})^T\right)$ is the stretching tensor. Note that we omit $\operatorname{grad}\gamma$ as an independent constitutive variable. If the functional dependence of ψ, $\boldsymbol{T}$, $\boldsymbol{h}$, $\boldsymbol{q}$, and $\boldsymbol{\phi}$, expressed in (29.19), is incorporated in (29.15) by use of the chain rule with the identity

$$\dot{\overline{\operatorname{grad}\nu}} = \operatorname{grad}\dot{\nu} - \operatorname{grad}\nu \cdot \operatorname{grad}\boldsymbol{v}, \tag{29.20}$$

then, inequality (29.15) becomes

$$\begin{aligned}
\theta\pi = &- \left[\gamma\nu\frac{\partial\psi}{\partial\nu} + \gamma\lambda^{\nu} + \gamma\nu f\right]\dot{\nu} - \gamma\nu\boldsymbol{\lambda}^{v}\cdot\dot{\boldsymbol{v}} - \left[\gamma\nu\frac{\partial\psi}{\partial\gamma} + \nu\lambda^{\nu}\right]\dot{\gamma} \\
&+ \left[\boldsymbol{T} - \gamma\nu\lambda^{\nu}\boldsymbol{I} + \gamma\nu\frac{\partial\psi}{\partial\operatorname{grad}\nu}\otimes\operatorname{grad}\nu\right]\cdot\boldsymbol{D} + \gamma\nu\frac{\partial\psi}{\partial\operatorname{grad}\nu}\otimes\operatorname{grad}\nu\cdot\boldsymbol{W} \\
&- \gamma\nu\left[\lambda^{k}k + \frac{\partial\psi}{\partial\dot{\nu}}\right]\ddot{\nu} - \gamma\nu\left[\frac{\partial\psi}{\partial\theta} + \eta\right]\dot{\theta} \\
&+ \lambda^{k}\gamma\nu f - \gamma\nu\frac{\partial\psi}{\partial\operatorname{grad}\theta}\cdot\dot{\overline{\operatorname{grad}\theta}} + \frac{\partial\psi}{\partial\boldsymbol{D}}\cdot\dot{\boldsymbol{D}}
\end{aligned}$$

$$
\begin{aligned}
&+\left[\boldsymbol{h}-\gamma\nu\frac{\partial\psi}{\partial \operatorname{grad}\nu}+\theta\frac{\partial\phi}{\partial\dot\nu}+\boldsymbol{\Lambda}^v\cdot\frac{\partial\boldsymbol{T}}{\partial\dot\nu}+\lambda^k\frac{\partial\boldsymbol{h}}{\partial\dot\nu}-\frac{\partial\boldsymbol{q}}{\partial\dot\nu}\right]\cdot\operatorname{grad}\dot\nu\\
&+\left[\theta\frac{\partial\phi}{\partial\nu_0}+\boldsymbol{\Lambda}^v\cdot\frac{\partial\boldsymbol{T}}{\partial\nu_0}+\lambda^k\frac{\partial\boldsymbol{h}}{\partial\nu_0}-\frac{\partial\boldsymbol{q}}{\partial\nu_0}\right]\cdot\operatorname{grad}\nu_0\\
&+\left[\theta\frac{\partial\phi}{\partial\nu}+\boldsymbol{\Lambda}^v\cdot\frac{\partial\boldsymbol{T}}{\partial\nu}+\lambda^k\frac{\partial\boldsymbol{h}}{\partial\nu}-\frac{\partial\boldsymbol{q}}{\partial\nu}\right]\cdot\operatorname{grad}\nu\\
&+\left[\theta\frac{\partial\phi}{\partial \operatorname{grad}\nu}+\boldsymbol{\Lambda}^v\cdot\frac{\partial\boldsymbol{T}}{\partial \operatorname{grad}\nu}+\lambda^k\frac{\partial\boldsymbol{h}}{\partial \operatorname{grad}\nu}-\frac{\partial\boldsymbol{q}}{\partial \operatorname{grad}\nu}\right]\cdot\operatorname{grad}(\operatorname{grad}\nu)\\
&+\left[\theta\frac{\partial\phi}{\partial\gamma}+\boldsymbol{\Lambda}^v\cdot\frac{\partial\boldsymbol{T}}{\partial\gamma}+\lambda^k\frac{\partial\boldsymbol{h}}{\partial\gamma}-\frac{\partial\boldsymbol{q}}{\partial\gamma}\right]\cdot\operatorname{grad}\gamma\\
&+\left[\theta\frac{\partial\phi}{\partial\theta}+\boldsymbol{\Lambda}^v\cdot\frac{\partial\boldsymbol{T}}{\partial\theta}+\lambda^k\frac{\partial\boldsymbol{h}}{\partial\theta}-\frac{\partial\boldsymbol{q}}{\partial\theta}\right]\cdot\operatorname{grad}\theta\\
&+\left[\theta\frac{\partial\phi}{\partial \operatorname{grad}\theta}+\boldsymbol{\Lambda}^v\cdot\frac{\partial\boldsymbol{T}}{\partial \operatorname{grad}\theta}+\lambda^k\frac{\partial\boldsymbol{h}}{\partial \operatorname{grad}\theta}-\frac{\partial\boldsymbol{q}}{\partial \operatorname{grad}\theta}\right]\cdot\operatorname{grad}(\operatorname{grad}\theta)\\
&+\left[\theta\frac{\partial\phi}{\partial\boldsymbol{D}}+\boldsymbol{\Lambda}^v\cdot\frac{\partial\boldsymbol{T}}{\partial\boldsymbol{D}}+\lambda^k\frac{\partial\boldsymbol{h}}{\partial\boldsymbol{D}}-\frac{\partial\boldsymbol{q}}{\partial\boldsymbol{D}}\right]\cdot\operatorname{grad}\boldsymbol{D}\geqslant 0.
\end{aligned}
\tag{29.21}
$$

This inequality has the form

$$\boldsymbol{a}\cdot\boldsymbol{\alpha}+b\geqslant 0, \tag{29.22}$$

where the vector $\boldsymbol{a}$ and the scalar b are functions of the variables listed in (29.19), and the vector $\boldsymbol{\alpha}$ depends on time and space derivatives of these quantities. Hence, inequality (29.22) is linear in $\boldsymbol{\alpha}$ (the terms in red color in (29.21)), and since these variables can take any values, it would be able to violate it unless

$$\boldsymbol{a}=\boldsymbol{0}\text{ and }b\geqslant 0. \tag{29.23}$$

Explicitly, the entropy inequality must hold for all independent variations of $\boldsymbol{\alpha}=\{\dot\theta, \dot\gamma, \dot{\boldsymbol{v}}, \ddot\nu, \operatorname{grad}\dot\nu, \dot{\overline{\operatorname{grad}\theta}}, \dot{\boldsymbol{D}}, \operatorname{grad}\nu_0, \operatorname{grad}(\operatorname{grad}\nu_0), \operatorname{grad}(\operatorname{grad}\nu), \operatorname{grad}\gamma, \operatorname{grad}(\operatorname{grad}\theta), \operatorname{grad}\boldsymbol{D}\}$. These variables appear linearly in (29.21) and thus their coefficients must vanish. This leads to the so-called LIU identities, $\boldsymbol{a}=\boldsymbol{0}$ in $(29.23)_1$. It then follows that the expressions for the LAGRANGE multipliers $\boldsymbol{\Lambda}^v$, λ^ν, λ^k

$$\boldsymbol{\Lambda}^v=\boldsymbol{0},\quad \lambda^\nu=-\gamma\frac{\partial\psi}{\partial\gamma},\quad \lambda^k=-\frac{1}{k}\frac{\partial\psi}{\partial\dot\nu},\quad \text{(lines 1 and 3 in (29.21))} \tag{29.24}$$

for the specific entropy density

$$\eta=-\frac{\partial\psi}{\partial\theta},\quad \text{(line 3 in (29.21))} \tag{29.25}$$

for the free energy ψ

$$\frac{\partial\psi}{\partial \operatorname{grad}\theta} = \mathbf{0}, \quad \frac{\partial\psi}{\partial \boldsymbol{D}} = \mathbf{0}, \quad (textline4in\,(29.21)) \tag{29.26}$$

for the equilibrated stress vector $\boldsymbol{h}$

$$\boldsymbol{h} = \gamma\nu\frac{\partial\psi}{\partial \operatorname{grad}\nu} - \theta\frac{\partial\boldsymbol{\phi}}{\partial\dot{\nu}} - \boldsymbol{\lambda}^{v}\cdot\frac{\partial\boldsymbol{T}}{\partial\dot{\nu}} - \lambda^{k}\frac{\partial\boldsymbol{h}}{\partial\dot{\nu}} + \frac{\partial\boldsymbol{q}}{\partial\dot{\nu}} \quad \text{(line 5 in (29.21))} \tag{29.27}$$

and the relations among $\boldsymbol{\phi}$, $\boldsymbol{T}$, $\boldsymbol{h}$ and $\boldsymbol{q}$

$$\begin{aligned}
&\theta\frac{\partial\boldsymbol{\phi}}{\partial\nu_0} + \boldsymbol{\lambda}^{v}\cdot\frac{\partial\boldsymbol{T}}{\partial\nu_0} + \lambda^{k}\frac{\partial\boldsymbol{h}}{\partial\nu_0} - \frac{\partial\boldsymbol{q}}{\partial\nu_0} = \mathbf{0}, \quad \text{(line 6 in (29.21))}\\
&\theta\frac{\partial\boldsymbol{\phi}}{\partial\gamma} + \boldsymbol{\lambda}^{v}\cdot\frac{\partial\boldsymbol{T}}{\partial\gamma} + \lambda^{k}\frac{\partial\boldsymbol{h}}{\partial\gamma} - \frac{\partial\boldsymbol{q}}{\partial\gamma} = \mathbf{0}, \quad \text{(line 9 in (29.21))}\\
&\theta\frac{\partial\boldsymbol{\phi}}{\partial\boldsymbol{D}} + \boldsymbol{\lambda}^{v}\cdot\frac{\partial\boldsymbol{T}}{\partial\boldsymbol{D}} + \lambda^{k}\frac{\partial\boldsymbol{h}}{\partial\boldsymbol{D}} - \frac{\partial\boldsymbol{q}}{\partial\boldsymbol{D}} = \mathbf{0}, \quad \text{(line 12 in (29.21))}\\
&\operatorname{sym}\left[\theta\frac{\partial\boldsymbol{\phi}}{\partial \operatorname{grad}\nu} + \boldsymbol{\lambda}^{v}\cdot\frac{\partial\boldsymbol{T}}{\partial \operatorname{grad}\nu} + \lambda^{k}\frac{\partial\boldsymbol{h}}{\partial \operatorname{grad}\nu} - \frac{\partial\boldsymbol{q}}{\partial \operatorname{grad}\nu}\right] = \mathbf{0},\\
&\qquad\qquad\qquad\qquad\qquad\qquad\qquad\text{(line 8 in (29.21))}\\
&\operatorname{sym}\left[\theta\frac{\partial\boldsymbol{\phi}}{\partial \operatorname{grad}\theta} + \boldsymbol{\lambda}^{v}\cdot\frac{\partial\boldsymbol{T}}{\partial \operatorname{grad}\theta} + \lambda^{k}\frac{\partial\boldsymbol{h}}{\partial \operatorname{grad}\theta} - \frac{\partial\boldsymbol{q}}{\partial \operatorname{grad}\theta}\right] = \mathbf{0},\\
&\qquad\qquad\qquad\qquad\qquad\qquad\qquad\text{(line 11 in (29.21))}
\end{aligned} \tag{29.28}$$

must hold, where $\operatorname{sym}\boldsymbol{A} = \frac{1}{2}(\boldsymbol{A} + \boldsymbol{A}^{T})$. Equations (29.24)–(29.28) correspond to the above $\boldsymbol{a} = \mathbf{0}$.

Furthermore, to simplify our problem, we will now assume that the free energy ψ is independent of $\dot{\nu}$. We will see that under this assumption the emerging constitutive relations are in correspondence with those in GOODMAN and COWIN [7] which were gained by use of the method of COLEMAN and NOLL. By use of the assumption, it follows from $(29.24)_3$ that

$$\lambda^{k} = 0. \tag{29.29}$$

The restrictions on the free energy (29.26) imply the reduced dependence

$$\psi = \hat{\psi}(\nu_0, \nu, \operatorname{grad}\nu, \gamma, \theta), \tag{29.30}$$

or, in view of the isotropic dependence of ψ upon $\operatorname{grad}\nu$,

$$\psi = \hat{\psi}(\nu_0, \nu, \operatorname{grad}\nu\cdot\operatorname{grad}\nu, \gamma, \theta). \tag{29.31}$$

It follows from (29.31) that

$$\frac{\partial\psi}{\partial \operatorname{grad}\nu} \otimes \operatorname{grad}\nu = \left(\frac{\partial\psi}{\partial \operatorname{grad}\nu} \otimes \operatorname{grad}\nu\right)^T, \tag{29.32}$$

hence, the term in (29.21) involving $\boldsymbol{W}$ vanishes identically.

Introducing next the extra entropy flux

$$\boldsymbol{k} = \boldsymbol{\phi} + \frac{1}{\theta}\left(\boldsymbol{\lambda}^v \cdot \boldsymbol{T} + \lambda^k \boldsymbol{h} - \boldsymbol{q}\right) = \boldsymbol{\phi} - \frac{\boldsymbol{q}}{\theta} \tag{29.33}$$

and considering $(29.24)_1$ and (29.29) we have from (29.28)

$$\begin{aligned}&\frac{\partial\boldsymbol{k}}{\partial\nu_0} = 0, \quad \frac{\partial\boldsymbol{k}}{\partial\gamma} = 0, \quad \frac{\partial\boldsymbol{k}}{\partial\boldsymbol{D}} = 0,\\ &\operatorname{sym}\left(\frac{\partial\boldsymbol{k}}{\partial \operatorname{grad}\nu}\right) = 0, \quad \operatorname{sym}\left(\frac{\partial\boldsymbol{k}}{\partial \operatorname{grad}\theta}\right) = 0.\end{aligned} \tag{29.34}$$

Using the restrictions (29.34) on the extra entropy flux $\boldsymbol{k}$ and the isotropy condition[1] it follows that (GOODMAN and COWIN, [7])

$$\boldsymbol{k} = \boldsymbol{0}. \tag{29.35}$$

Thus the entropy flux takes on its traditional form. This result will not follow, when the HELMHOLTZ free energy depends also on $\dot{\nu}$. Indeed, in that case λ^k is nontrivially determined by the free energy and so the entropy flux must deviate in direction from that of the heat flux by a contribution proportional to $\boldsymbol{h}$, the equilibrated stress vector. In the COLEMAN–NOLL approach such a term, however, cannot enter since an external equilibrated body force prevents in that case the equilibrated force balance from entering the entropy inequality. *This explicitly demonstrates the physical inadequacy of the* COLEMAN–NOLL *approach in this case.*

Combining (29.35) with (29.27) and recalling the functional form (29.31) for ψ implies

$$\boldsymbol{h} = \gamma\nu\frac{\partial\psi}{\partial \operatorname{grad}\nu} = \mathcal{A}\operatorname{grad}\nu, \tag{29.36}$$

where

$$\mathcal{A} = \hat{\mathcal{A}}(\nu_0, \nu, \operatorname{grad}\nu\cdot\operatorname{grad}\nu, \gamma, \theta) = 2\gamma\nu\frac{\partial\psi}{\partial(\operatorname{grad}\nu\cdot\operatorname{grad}\nu)}. \tag{29.37}$$

Returning now to the entropy inequality (29.21) and employing these restrictions, we obtain

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[1] The isotropy condition implies that $\boldsymbol{k}$ cannot depend on $\operatorname{grad}\nu$ and $\operatorname{grad}\theta$. Thus, $\boldsymbol{k} = \boldsymbol{k}(\nu, \dot{\nu}, \theta)$, but this is only possible, if $\boldsymbol{k} \equiv \boldsymbol{0}$.

$$\begin{aligned}\theta\pi = (\boldsymbol{T} + \nu p \boldsymbol{I} + \boldsymbol{h} \otimes \operatorname{grad} \nu) \cdot \boldsymbol{D} - (\gamma \nu f - (p - \beta))\, \dot{\nu} \\ - \frac{\boldsymbol{q} \cdot \operatorname{grad} \theta}{\theta} \geqslant 0,\end{aligned} \tag{29.38}$$

where we have introduced the definitions

$$p = \gamma^2 \frac{\partial \psi}{\partial \gamma}, \quad \beta = \gamma \nu \frac{\partial \psi}{\partial \nu}, \tag{29.39}$$

which can be interpreted as the thermodynamic pressure and the configurational pressure, respectively. Equation (29.38) is the statement $(29.23)_2$.

At this point, we should also point out that the constitutive class (29.19) is only suitable for compressible granular materials. For incompressible granular materials, γ is no longer an independent variable. In this case returning to the initial constitutive assumption (29.19), we delete the dependence on γ from the constitutive equations and repeat the above analysis. We find the same constitutive restrictions for incompressible granular materials as before for compressible granular materials, if here $p = -\gamma\lambda^{\nu}$ is introduced, which now is an unknown variable and can no longer be determined by the free energy ψ as expressed in $(29.39)_1$. We leave the details of the analysis to the reader.

29.3.2 Thermodynamic Equilibrium

As usual, further restrictions on the constitutive relations can be obtained from the residual inequality (29.38) in the context of thermodynamic equilibrium, which is characterized in the current local formulation by the vanishing of the entropy production rate density π. In the context of the current constitutive class, the imbalance (29.38) implies that π vanishes when the independent dynamic variables

$$\boldsymbol{Y} = (\dot{\nu}, \operatorname{grad} \theta, \boldsymbol{D}) \tag{29.40}$$

all vanish. We see that π has a minimum in equilibrium. Necessary conditions for this minimum are that

$$\begin{aligned} &\left.\frac{\partial \pi}{\partial Y_i}\right|_{Y=0} = 0, && Y_i \in \boldsymbol{Y}, \\ &\left.\frac{\partial^2 \pi}{\partial Y_i\, \partial Y_j}\right|_{Y=0} \text{ is nonnegative definite}, && Y_i,\ Y_j \in \boldsymbol{Y}. \end{aligned} \tag{29.41}$$

As is well known, the first condition restricts the equilibrium forms of the dependent constitutive fields, while the second constrains the signs of material properties; here we deal only with the first. This condition yields the equilibrium values of the stress, intrinsic equilibrated body force and heat flux,

$$\boldsymbol{T}^E = \hat{\boldsymbol{T}}(\nu_0, \nu, \operatorname{grad}\nu, 0, \gamma, \theta, \mathbf{0}, \mathbf{0}) = -\nu p \boldsymbol{I} - \boldsymbol{h} \otimes \operatorname{grad}\nu, \tag{29.42}$$

$$f^E = \hat{f}(\nu_0, \nu, \operatorname{grad}\nu, 0, \gamma, \theta, \mathbf{0}, \mathbf{0}) = \frac{p-\beta}{\gamma\nu}, \tag{29.43}$$

$$\boldsymbol{q}^E = \hat{\boldsymbol{q}}(\nu_0, \nu, \operatorname{grad}\nu, 0, \gamma, \theta, \mathbf{0}, \mathbf{0}) = \mathbf{0}. \tag{29.44}$$

Recalling the expressions for p and β defined by (29.39) and $\mathcal{A}$ defined by (29.37), we find that $\boldsymbol{T}^E$, f^E are derivable from the free energy function. Furthermore, (29.42) demonstrates that, in equilibrium, the stress need not be a hydrostatic pressure. This shows that equilibrium properties of this material deviate from those of a classical fluid. Moreover, the result, along with (29.37), also provides some physical insight into the character of the equilibrated stress $\boldsymbol{h}$. Clearly, $\boldsymbol{h}$ will play a significant role in the theory if the system makes inhomogenerous distributions of grains important. In that case, dilatant behavior is observed and grains in close contact with each other can give rise to very high local stresses. Moreover, only the existence of $\boldsymbol{h}$ gives rise to MOHR–COULOMB friction in equilibrium (SAVAGE, [16]).

29.3.3 Linear Theory for the Nonequilibrium Parts

Here, we consider a linear theory in which the representations for $\boldsymbol{q}$, $\boldsymbol{T} - \boldsymbol{T}^E$ and $f - f^E$ are linear in the variables Y_i defined by (29.40). We also suppose $\boldsymbol{h}$ to be linear in $\operatorname{grad}\nu$; this together with (29.36) implies

$$\boldsymbol{h} = \gamma\nu \frac{\partial\psi}{\partial \operatorname{grad}\nu} = \mathcal{A} \operatorname{grad}\nu, \quad \mathcal{A} = \hat{\mathcal{A}}(\nu_0, \nu, \gamma, \theta). \tag{29.45}$$

Recalling the functional dependence expressed by (29.19) for $\boldsymbol{q}$, $\boldsymbol{T}$ and f, we then have in the linear theory

$$\boldsymbol{q} = -\kappa \operatorname{grad}\theta, \tag{29.46}$$

$$\boldsymbol{T} - \boldsymbol{T}^E = \xi\dot{\nu}\boldsymbol{I} + \lambda(\operatorname{tr}\boldsymbol{D})\boldsymbol{I} + 2\mu\boldsymbol{D}, \tag{29.47}$$

$$f - f^E = -\zeta\dot{\nu} - \delta \operatorname{tr}\boldsymbol{D}, \tag{29.48}$$

where the coefficients are, in general, scalar functions as follows:

$$\{\kappa, \xi, \lambda, \mu, \zeta, \delta\} = \{\hat{\kappa}, \hat{\xi}, \hat{\lambda}, \hat{\mu}, \hat{\zeta}, \hat{\delta}\}(\nu_0, \nu, \operatorname{grad}\nu, \gamma, \theta). \tag{29.49}$$

Such linear forms are indeed the simplest, and when there are not enough observations, experiments or other physical reasons to believe that the constitutive processes involved are more complicated, it seems sensible to work with these linear forms.

Finally, we write the constitutive equations for $\boldsymbol{T}$, f, $\boldsymbol{h}$, and $\boldsymbol{q}$ together

$$\boldsymbol{T} = [-\nu p + \lambda \operatorname{tr} \boldsymbol{D} + \xi \dot{\nu}]\boldsymbol{I} - \boldsymbol{h} \otimes \operatorname{grad} \nu + 2\mu \boldsymbol{D}, \tag{29.50}$$

$$f = \frac{p}{\gamma\nu} - \frac{\beta}{\gamma\nu} - \delta \operatorname{tr} \boldsymbol{D} - \zeta \dot{\nu}, \tag{29.51}$$

$$\boldsymbol{h} = \mathcal{A} \operatorname{grad} \nu, \tag{29.52}$$

$$\boldsymbol{q} = -\kappa \operatorname{grad} \theta. \tag{29.53}$$

where the coefficient $\mathcal{A}$ and the configurational pressure β can be determined by the free energy ψ by use of the expressions (29.37) and $(29.39)_2$. For compressible granular materials, the dynamic pressure p can also be determined by ψ in $(29.39)_1$, while for incompressible granular materials, p is an independent variable, which can be computed from the momentum equation and the boundary conditions. The coefficients κ, ξ, λ, μ, ζ, δ can be determined by experiments, in general. Note that $\mathcal{A}$ can be expressed in terms of the internal friction angle of the material (SAVAGE, [16]).

29.4 Constitutive Equations for Special Granular Materials

In this section, we will obtain the concrete forms of the constitutive equations by use of a special expression of the free energy for granular materials. It follows directly from the work of PASSMAN et al. [15]. Our interest here is in isothermal motions. Therefore, we use the purely mechanical balance relations, avoiding all thermodynamic considerations. This theory is based on balances of mass (29.5), momentum (29.6), and equilibrated force (29.8)

$$\dot{\nu} + \nu \operatorname{div} \boldsymbol{v} = 0, \tag{29.54}$$

$$\gamma\nu\dot{\boldsymbol{v}} = \operatorname{div} \boldsymbol{T} + \gamma\nu\boldsymbol{b}, \tag{29.55}$$

$$\gamma\nu k \ddot{\nu} = \operatorname{div} \boldsymbol{h} + \gamma\nu f, \tag{29.56}$$

where we have assumed that the granular material is incompressible ($\gamma = \text{const}$) and the external equilibrated body force vanishes ($l = 0$).

To obtain the explicit expressions of $\boldsymbol{T}$, $\boldsymbol{h}$, and f from (29.50)–(29.52) a representation for the specific free energy ψ is needed. We assume the specific free energy per unit volume $\gamma\nu\psi$ to be an isotropic function which is expandable in a Taylor series about $\operatorname{grad} \nu = 0$ and $\nu = \nu_m$, with ν_m interpreted as the critical volume fraction (GOODMAN and COWIN, [6]). Moreover, variations in $|\operatorname{grad} \nu|$ about zero and variations in ν about ν_m are assumed to be small. When following a second-order approximation, $\gamma\nu\psi$ can be written as

$$\gamma\nu\psi = a_0 + a_1(\nu - \nu_m) + a_2(\nu - \nu_m)^2 + a_3 \operatorname{grad} \nu \cdot \operatorname{grad} \nu, \tag{29.57}$$

where the coefficients may depend on ν_m. Requiring the free energy per unit volume to be nonnegative with a minimum, zero, at $\nu = \nu_m$ and $\operatorname{grad}\nu = 0$ implies that the coefficients are restricted by

$$a_0 = 0, \quad a_1 = 0, \quad a_2 \geqslant 0, \quad a_3 \geqslant 0. \tag{29.58}$$

Now, we write (29.57) in the form

$$\gamma\nu\psi = \phi(\nu) + \alpha(\nu)\boldsymbol{w}\cdot\boldsymbol{w}, \quad \text{with } \boldsymbol{w} = \operatorname{grad}\nu, \tag{29.59}$$

and also assume (PASSMAN et al. [15])

$$\begin{aligned} \phi(\nu) &= a_0(\nu-\nu_m)^2, & a_0 &\geqslant 0, \\ \alpha(\nu) &= \alpha_0\left(\frac{\nu_m}{\nu_\infty-\nu}\right)^2, & \alpha_0 &\geqslant 0, \end{aligned} \tag{29.60}$$

in which ν_∞ is the volume fraction corresponding to densest possible packing of the material; and ν_∞, ν_m ($\nu_\infty \geqslant \nu_m \geqslant 0$) are constants.

Substituting (29.59) and (29.60) into $(29.39)_2$, the resulting equation into (29.51), and (29.60) into (29.50) and (29.52), and selecting the representation

$$\mu = \mu_0\left(\frac{\nu_m}{\nu_\infty-\nu}\right)^8; \quad \mu_0 \geqslant 0 \tag{29.61}$$

for the viscosity μ (Savage, [16]), we obtain the constitutive equations

$$\begin{aligned} \boldsymbol{T} &= [-\nu p + \lambda \operatorname{tr}\boldsymbol{D} + \xi\dot{\nu}]\boldsymbol{I} - 2\alpha_0\left(\frac{\nu_m}{\nu_\infty-\nu}\right)^2 \boldsymbol{w}\otimes\boldsymbol{w} \\ &\quad +2\mu_0\left(\frac{\nu_m}{\nu_\infty-\nu}\right)^8 \boldsymbol{D}, \end{aligned} \tag{29.62}$$

$$\begin{aligned} f &= \frac{p}{\gamma\nu} - \frac{1}{\gamma\nu^2}\Bigg[a_0(\nu^2-\nu_m^2) \\ &\quad -\alpha_0\left(\frac{\nu_m}{\nu_\infty-\nu}\right)^2\left(\frac{3\nu-\nu_\infty}{\nu-\nu_\infty}\right)\boldsymbol{w}\cdot\boldsymbol{w}\Bigg] - \delta\operatorname{tr}\boldsymbol{D} - \zeta\dot{\nu}, \end{aligned} \tag{29.63}$$

$$\boldsymbol{h} = 2\alpha_0\left(\frac{\nu_m}{\nu_\infty-\nu}\right)^2 \boldsymbol{w}. \tag{29.64}$$

Substitution of (29.62)–(29.64) into (29.54)–(29.56) yields five scalar equations for five unknowns, p, ν, and the three components of $\boldsymbol{v}$. They fully agree with those of PASSMAN et al. [15].

In the following sections, we will numerically solve the differential equations (29.54)–(29.56) with the constitutive relations (29.62)–(29.64) subject to appropriate boundary conditions for some typical shearing field equations and gravity-flow problems, respectively.

29.5 Horizontal Shearing Flow Problem

29.5.1 Basis Equations and Boundary Conditions for Horizontal Shearing Flow

First, we discuss a steady simple shearing problem. The boundaries are two parallel, infinite plates, a fixed distance L apart. Deformation is caused by moving one plate parallel to the other. Choose fixed Cartesian coordinates with the origin on the fixed plate, x parallel to the direction of motion of the top plate, and y orthogonal to the plates, and pointing from the fixed plate toward the moving plate against the gravity field, as shown in **Fig. 29.1**.

Assume a unidirectional steady flow as follows

$$\boldsymbol{v} = [u(y), 0, 0], \qquad \nu = \nu(y), \qquad \boldsymbol{b} = [0, -b, 0]. \tag{29.65}$$

It is convenient to formulate the problem in terms of dimensionless variables. We let

$$\xi^2 = \frac{a_0}{\alpha_0} \qquad \text{and} \qquad S = \frac{\gamma b}{2\nu_m a_0 \xi}. \tag{29.66}$$

It should be noted that $1/\xi$ is a characteristic material length. Thus, increasing S corresponds to increasing either the characteristic material length or the magnitude of the gravity. We choose

$$\bar{y} = \xi y, \quad \bar{L} = \xi L, \quad \bar{\nu} = \frac{\nu}{\nu_m}, \quad \bar{\nu}_\infty = \frac{\nu_\infty}{\nu_m}, \quad \bar{u} = \frac{u}{V_0}, \quad \bar{\pi} = -\frac{T_{yy}}{a_0 \nu_m^2}. \tag{29.67}$$

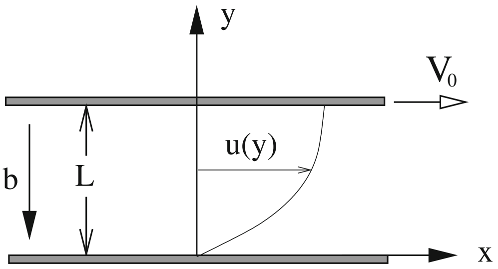


Fig. 29.1 Horizontal shearing flow and coordinate system

There is some question as to what kind of boundary conditions ought to be assigned to ν. Here we choose simply (PASSMAN et al. [15])

$$\nu(0) = \nu_0, \quad \nu(L) = \nu_0, \quad u(0) = 0, \quad u(L) = V_0, \quad T_{yy}(L) = T_0. \tag{29.68}$$

The assignment (29.68)$_5$ indicates that a stress (a pressure if $T_0 < 0$!) will be required to maintain a constant distance between the walls.

We consider steady motions. In view of the field Eqs. (29.54) and (29.56) and constitutive equations (29.62)–(29.64), the governing differential equations in terms of the nondimensional variables reduce to

$$\frac{\partial T_{yy}}{\partial y} - \gamma\nu b = 0 \longrightarrow \frac{\mathrm{d}\bar{\pi}}{\mathrm{d}\bar{y}} + 2S\bar{\nu} = 0, \tag{29.69}$$

$$\begin{aligned}\frac{\partial h_y}{\partial y} + \gamma\nu f = 0 \longrightarrow\ & \frac{\mathrm{d}}{\mathrm{d}\bar{y}}\left[\frac{2}{(\bar{\nu}_\infty - \bar{\nu})^2}\frac{\mathrm{d}\bar{\nu}}{\mathrm{d}\bar{y}}\right] \\ & + \frac{1}{\bar{\nu}}\left[\bar{\pi} + 1 - \bar{\nu}^2 - \frac{(\bar{\nu}_\infty + \bar{\nu})}{(\bar{\nu}_\infty - \bar{\nu})^3}\left(\frac{\mathrm{d}\bar{\nu}}{\mathrm{d}\bar{y}}\right)^2\right] = 0,\end{aligned} \tag{29.70}$$

$$\frac{\partial T_{xy}}{\partial y} = 0 \longrightarrow \frac{\mathrm{d}}{\mathrm{d}\bar{y}}\left[\frac{1}{(\bar{\nu}_\infty - \bar{\nu})^8}\frac{\mathrm{d}\bar{u}}{\mathrm{d}\bar{y}}\right] = 0. \tag{29.71}$$

The nondimensional boundary conditions are

$$\bar{\nu}(0) = \bar{\nu}_0, \ \bar{u}(0) = 0, \ \bar{\nu}(\bar{L}) = \bar{\nu}_0, \ \bar{u}(\bar{L}) = 1, \ \bar{\pi}(\bar{L}) = -\frac{T_0}{a_0\nu_m^2} =: \sigma_0. \tag{29.72}$$

We choose

$$\nu_\infty = 0.644, \qquad \nu_m = 0.555, \qquad \nu_0 = 0.51, \tag{29.73}$$

the values as given by SAVAGE [16], appropriate to natural angular beach sand with diameters of particles from 0.318–0.414 mm. It follows that

$$\bar{\nu}_\infty = 1.16, \qquad \bar{\nu}_0 = 0.919. \tag{29.74}$$

29.5.2 Numerical Method

Because the differential equations (29.69)–(29.71) are nonlinear, we cannot solve the boundary value problem by a direct finite-difference method. Here, we solve the nonlinear differential equation system (29.69)–(29.71) with the boundary conditions (29.72) by means of the method of successive approximation.

We describe this method for a general boundary value problem

$$F(x, y(x)) = 0, \quad x \in (a, b), \tag{29.75}$$

for which the boundary conditions are prescribed at only two points, say $x_1 = a$ and $x_2 = b$, where $a < b$,

$$V_1(x, y(x))|_{x=a} = 0, \qquad V_2(x, y(x))|_{x=b} = 0. \tag{29.76}$$

We shall only deal with the special case of boundary value problems for which the boundary conditions (29.76) are linear. In the iteration method, the nonlinear (differential) equation (29.75) is put into the form

$$L(x, y(x)) = N(x, y(x)), \tag{29.77}$$

where N is a nonlinear functional in y and L a linear functional such that the boundary value problem

$$L(x, y(x)) = r(x) \tag{29.78}$$

with the boundary conditions (29.76), which we write as

$$V_1(x, y(x))|_{x=a} = 0, \qquad V_2(x, y(x))|_{x=b} = 0 \tag{29.79}$$

can be solved readily for any well behaving right-hand side $r(x)$. If the equation (29.75) is a differential equation, we can obtain a linear equation system from (29.78) by means of the finite-difference method

$$\boldsymbol{A}\boldsymbol{\phi} = \boldsymbol{f}, \tag{29.80}$$

where $\boldsymbol{A}$ is a $n \times n$ matrix and $\boldsymbol{\phi}$ and $\boldsymbol{f}$ are vectors: $\boldsymbol{\phi} = (y(x_1), y(x_2), \ldots, y(x_n))^T$, $\boldsymbol{f} = (r(x_1), r(x_2), \ldots, r(x_n))^T$ with discrete points $a < x_1 < x_2 < \cdots < x_n < b$. In the splitting (29.77), it must be ensured that in (29.80) $\boldsymbol{A}$ is nonsingular.

If (29.75) is a differential equation of order n and, as is usually the case, the given differential equation can be solved for the highest derivate which occurs in terms of the lower derivatives, i.e., if it can be put into the form

$$y^{(n)} = \varphi(x, y, y', \ldots, y^{(n-1)}) \tag{29.81}$$

with $y^{(m)} = \mathrm{d}^m y/\mathrm{d}x^m$, then one obvious rearrangement of the form (29.77) has $L = y^{(n)}$ and $N = \varphi(x, y, y', \ldots, y^{(n-1)})$.

We can now define an iterative procedure which determines a sequence of functions $y_0(x)$, $y_1(x)$, $y_2(x)$,…in the following manner: $y_0(x)$ is chosen arbitrarily, then $y_1(x)$, $y_2(x)$, …are calculated successively as the solutions of the boundary value problems

$$\left.\begin{array}{l} L(x, y^{k+1}(x)) = N(x, y^k(x)), \\ V_1(x, y^{k+1}(x))|_{x=a} = 0, \quad V_2(x, y^{k+1}(x))|_{x=b} = 0 \end{array}\right\} \ (k = 0, 1, 2, \ldots). \tag{29.82}$$

With this generality, nothing can be asserted about the convergence of the sequence $y^k(x)$ to the solution $y(x)$ of the boundary value problem; it can happen that the sequence does not converge at all. When it does converge, the effectiveness of the method is often influenced considerably by the form of the rearrangement (29.77) of the given (differential) equation and by the choice of the starting function $y_0(x)$; the method is generally more effective the closer $y_0(x)$ is to $y(x)$.

In our calculations, to achieve a better convergence, we use the so-called method of successive over-relaxation. We solve the following boundary-value problems

$$\left.\begin{array}{l} L(x, \tilde{y}^{k+1}(x)) = N(x, y^k(x)), \\ V_1(x, \tilde{y}^{k+1}(x))|_{x=a} = 0, \quad V_2(x, \tilde{y}^{k+1}(x))|_{x=b} = 0 \end{array}\right\} \ (k = 0, 1, 2, \ldots) \tag{29.83}$$

to obtain $\tilde{y}^{k+1}$, then y^{k+1} is defined by the formulas

$$y^{k+1} = y^k + \tau(\tilde{y}^{k+1} - y^k), \quad 0 < \tau \leqslant 1, \tag{29.84}$$

where τ is a real parameter. We should choose τ so small that convergent iteration is reached. For $\tau = 1$, the successive over-relaxation method (29.83) and (29.84) is in correspondence with the simple iteration method (29.82).

For the boundary-value problem (29.69)–(29.72) the successive over-relaxation method is as follows:

We may represent the Eqs. (29.69)–(29.71) in the form

$$\bar{\pi} = \bar{\pi}_0 + 2S \int_{\bar{y}}^{\bar{L}} \bar{\nu} \, \mathrm{d}\bar{y}, \tag{29.85}$$

$$\frac{\mathrm{d}^2\bar{\nu}}{\mathrm{d}\bar{y}^2} = -\frac{(\bar{\nu}_\infty - \bar{\nu})^2}{2\bar{\nu}} \left[\bar{\pi} + 1 - \bar{\nu}^2 + \frac{3\bar{\nu} - \bar{\nu}_\infty}{(\bar{\nu}_\infty - \bar{\nu})^3} \left(\frac{\mathrm{d}^2\bar{\nu}}{\mathrm{d}\bar{y}^2} \right)^2 \right], \tag{29.86}$$

$$\frac{\mathrm{d}^2\bar{u}}{\mathrm{d}\bar{y}^2} = -\frac{8}{\bar{\nu}_\infty - \bar{\nu}} \frac{\mathrm{d}\bar{\nu}}{\mathrm{d}\bar{y}} \frac{\mathrm{d}\bar{u}}{\mathrm{d}\bar{y}}. \tag{29.87}$$

Equations (29.86) and (29.87) are obtained from Eqs. (29.70) and (29.71) by performing product differentiation of the terms on the left-hand sides and reordering the emerging equations that largest (second-order) derivatives arise on the left-hand sides. Then the iteration process is applied as follows:

$$\bar{\pi}^k = \bar{\pi}_0 + 2S \int_{\bar{y}}^{\bar{L}} \bar{\nu}^k \, \mathrm{d}\bar{y}, \tag{29.88}$$

$$\frac{\mathrm{d}^2 \tilde{\bar{\nu}}^{k+1}}{\mathrm{d}\bar{y}^2} = -\frac{(\bar{\nu}_\infty - \bar{\nu}^k)^2}{2\bar{\nu}^k} \left[\bar{\pi}^k + 1 - (\bar{\nu}^k)^2 + \frac{3\bar{\nu}^k - \bar{\nu}_\infty}{(\bar{\nu}_\infty - \bar{\nu}^k)^3} \left(\frac{\mathrm{d}^2 \bar{\nu}^k}{\mathrm{d}\bar{y}^2} \right)^2 \right], \tag{29.89}$$

$$\frac{\mathrm{d}^2 \tilde{\bar{u}}^{k+1}}{\mathrm{d}\bar{y}^2} = -\frac{8}{\bar{\nu}_\infty - \bar{\nu}^k} \frac{\mathrm{d}\bar{\nu}^k}{\mathrm{d}\bar{y}} \frac{\mathrm{d}\bar{u}^k}{\mathrm{d}\bar{y}} \tag{29.90}$$

with the boundary conditions

$$\tilde{\bar{\nu}}^{k+1}(0) = \bar{\nu}_0, \quad \tilde{\bar{\nu}}^{k+1}(\bar{L}) = \bar{\nu}_0, \quad \tilde{\bar{u}}^{k+1}(0) = 0, \quad \tilde{\bar{u}}^{k+1}(\bar{L}) = 1. \tag{29.91}$$

Then, the over-relaxation iteration is defined by the formulas

$$\left. \begin{aligned} \bar{\nu}^{k+1} &= \bar{\nu}^k + \tau(\tilde{\bar{\nu}}^{k+1} - \bar{\nu}^k), \\ \bar{u}^{k+1} &= \bar{u}^k + \tau(\tilde{\bar{u}}^{k+1} - \bar{u}^k), \end{aligned} \right\} \; 0 < \tau \leqslant 1. \tag{29.92}$$

We would like to point out that this iterative choice is not the only possible one. We can discretize the Eqs. (29.88)–(29.90) for n uniformly distributed discrete points in $\bar{y} \in [0, \bar{L}]$ by finite-difference approximations with central finite-difference quotients. In so doing, for each iterative step two tri-diagonal systems emerge, for $\tilde{\bar{\nu}}^{k+1}$ from Eq. (29.89) and for $\tilde{\bar{u}}^{k+1}$ from (29.90), respectively; these can be solved e.g. by Gaussian elimination. We start with the initial trial functions

$$\bar{\nu}^0 = \bar{\nu}_0, \qquad \bar{u}^0 = \bar{y}/\bar{L}, \tag{29.93}$$

which satisfy the boundary conditions. The iteration should be carried out until the relative differences of the computed $\bar{\nu}$ und $\bar{u}$ between two iterative steps are smaller than a given error, respectively, chosen to be 10^{-12}.

29.5.3 Numerical Results

Typical calculated results for the volume distribution, dimensionless velocity for this horizontal shearing flow problem are shown in **Figs. 29.2**, **29.3**, **29.4**, **29.5**, **29.6** and **29.7**. For convenience, the coordinate across the channel has been expressed in terms of $\bar{y}/\bar{L}$. Figure 29.2 shows the profiles of the volume fraction for various $\bar{L}$, for a fixed nondimensional normal top-wall stress σ_0 and a fixed parameter S, in this case $\sigma_0 = 0$ and $S = 0.05$. Notice that $\bar{L}$ indicates the ratio of the distance of the two horizontal plates (channel width) to the grain size. It can be seen that near the boundaries the volume fraction attains its minimum, which may lead back to the effect of dilatancy in granular materials. Relatively narrow channels (curve A) show a fairly homogeneous volume fraction profile across the channel, while, as the channel

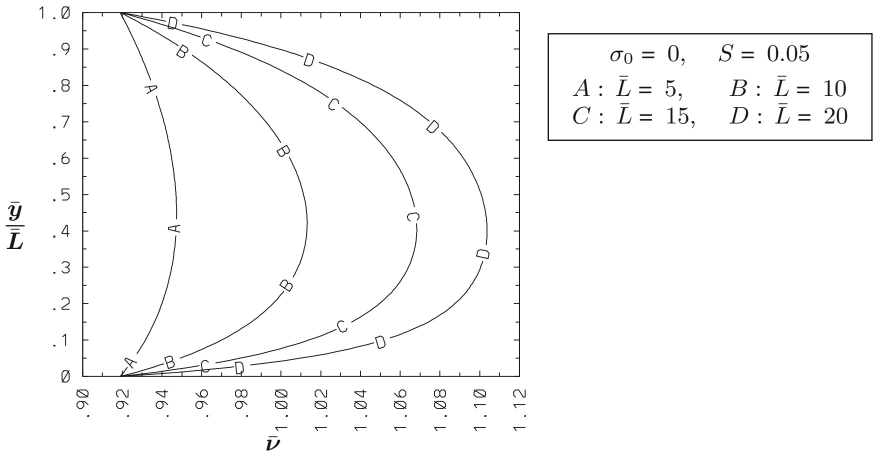


Fig. 29.2 Nondimensional volume fraction profiles for various distances of the plates for a horizontal shearing flow, from WANG and HUTTER [20]. ©Part. Sci. Technol. Taylor & Francis

width increases, there is an increasing tendency for the volume fraction evasion near the center from its fixed value on the boundaries. The corresponding velocity fields are shown in Fig. 29.3. For a narrow channel, the granular flow behaves similar to that of an incompressible NAVIER–STOKES fluid, i.e., the velocity field has a nearly linear profile across the channel. Increasing the channel width $\bar{L}$ gives an increasing tendency toward two thin regions of high shear rate near the bottom and top surfaces, and a rigid region of adherence toward the center. Thus, in channels which are narrow compared to the particle size, the shear of the moving boundary can be felt over most of the channel. In channels which are wide compared to the particle size, the shear exists only in very thin layers near the boundaries. We should also point out that this feature of granular flows occurs only for sufficiently large grain sizes. If the grain size is very small, the behavior of granular flows is more similar to a viscous fluid, as we can immediately see below.

Figures 29.4 and 29.5 show the effect of varying S on volume fraction and velocity for $\sigma_0 = 0$ and $\bar{L} = 10$; this variation expresses to some extent a dependence on grain size or on gravity. Here, a fixed $\bar{L}$ means, if the grain size varies, that the channel width should be changed accordingly. Figure 29.4 indicates the same effects of dilatancy as before; the solid volume fraction is smallest at the boundaries and increases toward the center. The corresponding velocity profiles are shown in Fig. 29.5. Fine grains (small values of S) show a velocity profile similar to that of an incompressible Navier–Stokes fluid. Increasing the grain size (increasing S) increases the manifestation of the granular character of the material. With the increasing grain size (indicated by S), if the channel width also increases to the same extent (i.e., fixed $\bar{L}$), the grain motion near the center is similar to that of an entire solid state, while the shear occurs only near the boundaries. Recalling that varying S can also be interpreted as varying the effect of gravity, Fig. 29.5 also shows that under microgravity, the behavior is close

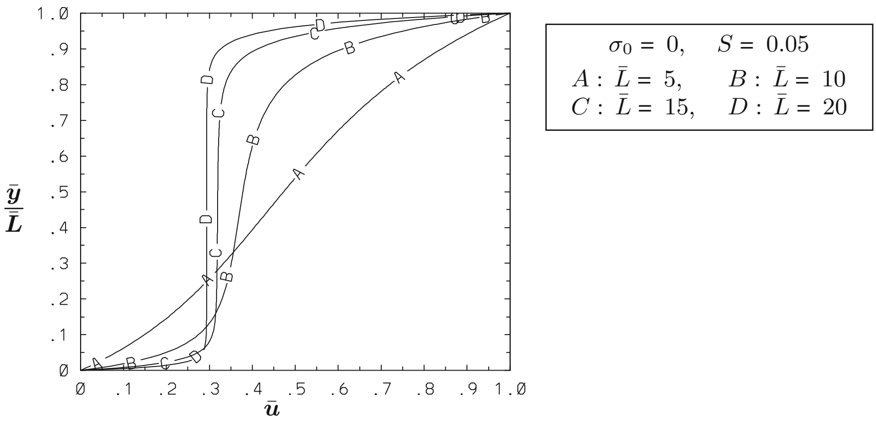


Fig. 29.3 Nondimensional velocity profiles for various distances of the plates for a horizontal shearing flow, from Wang and Hutter [20]. © Part. Sci. Technol. Taylor & Francis

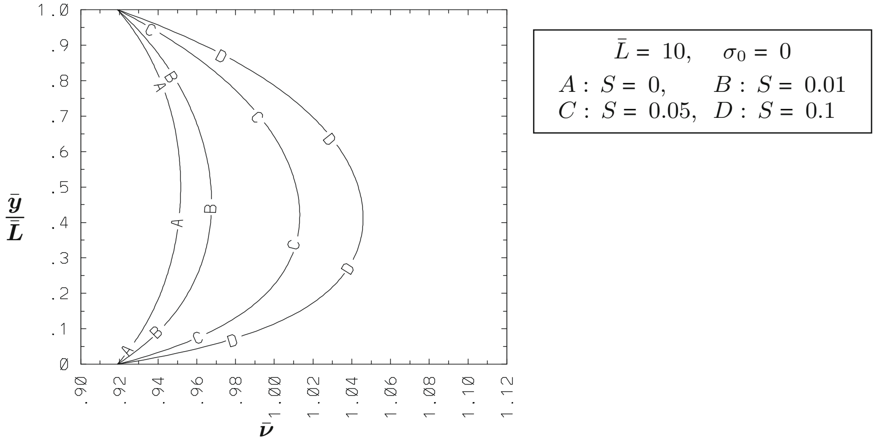


Fig. 29.4 Nondimensional volume fraction profiles for various values of parameter S for a horizontal shearing flow, from Wang and Hutter [20]. © Part. Sci. Technol. Taylor & Francis

to that of a Newtonian fluid, while strong gravity favors plug-flow behavior in the middle portion of the layer. Of course, the balance is described by the ratio of the two effects as expressed by S.

These results are vastly different from those obtained by Passman et al. [15]. One reason is the difference in sign in Eq. (29.69) mentioned before; an additional reason is the different application of boundary conditions applied here and in Passman et al. [15]. The constitutive relations give rise to normal stress effects. As a result, to maintain the distance between the two plates in this shearing motion, a transverse normal stress σ_0 must be applied. This normal stress is applied here at the top boundary and it is a pressure. We were only able to reproduce the results of Passman et al. [15],

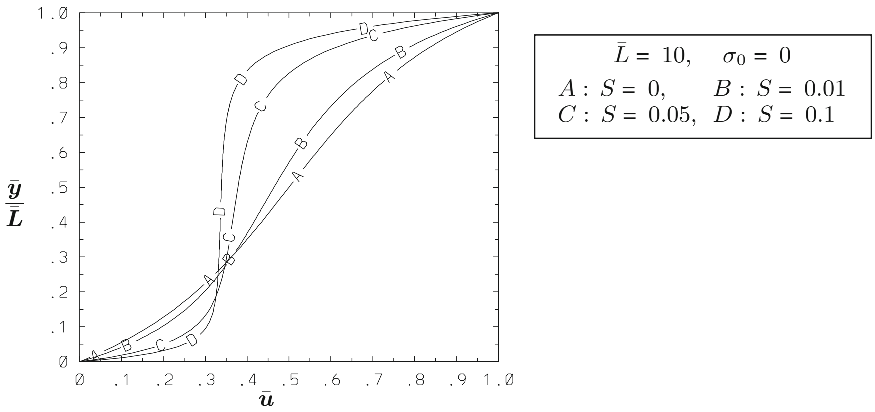


Fig. 29.5 Nondimensional velocity profiles for various values of parameter S for a horizontal shearing flow, from WANG and HUTTER [20]. © Part. Sci. Technol. Taylor & Francis

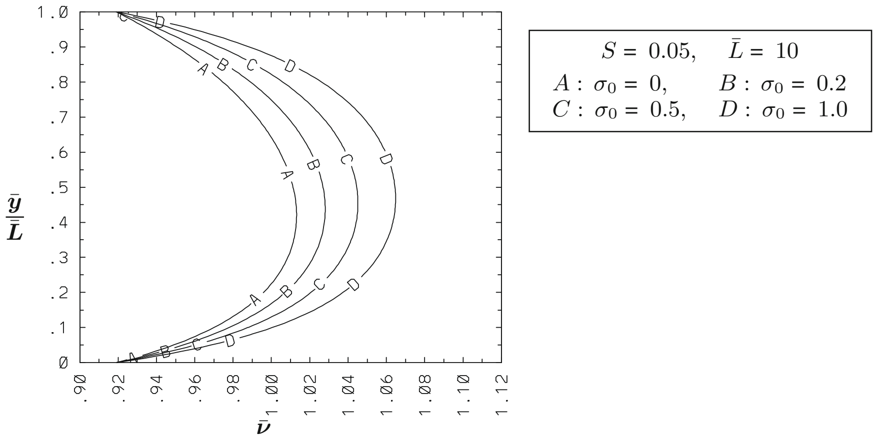


Fig. 29.6 Nondimensional volume fraction profiles for various values of the normalized top-plate pressure for a horizontal shearing flow, from WANG and HUTTER [20]. © Part. Sci. Technol. Taylor & Francis

provided their incorrect sign was corrected and the stress boundary conditions were imposed at the bottom boundary. This, they must have done, despite the difference in their statements in the text. They showed results for the bottom stress $\sigma_0 = 0$, i.e., not even the weight of the material was supported. We face difficulties in physically interpreting such conditions.

Computations have also been performed for various other values of the normal stress. Figures 29.6 and 29.7 show the effect of changing the normal top-wall stress on the horizontal granular shear flow. Increasing the normal stress will tend to cause

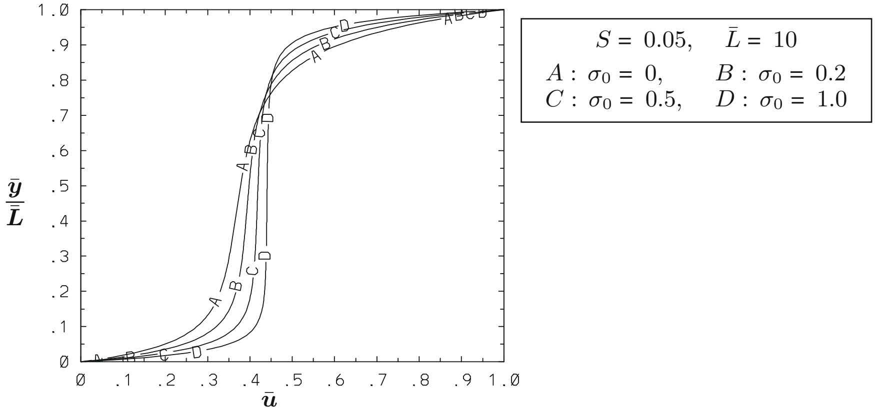


Fig. 29.7 Nondimensional velocity profiles for various values of the normalized top-plate pressure for a horizontal shearing flow, from WANG and HUTTER [20]. © Part. Sci. Technol. Taylor & Francis

the grains to interlock and increase $\bar{\nu}$ throughout the flow field. As the normal stress increases, the grain motion has an increasing tendency toward a rigid motion near the center, while the shear occurs only in the thin layers near the boundaries.

29.6 Inclined Gravity-Flow Problem

In this section, the case of steady flow of a layer of uniform thickness of a granular material down an inclined plate is analyzed. This motion is driven by gravity, a body force, rather than by a surface traction, as in the former case of simple shearing.

Consider a fully developed, two-dimensional, steady flow of a granular material of thickness L, having a tension free upper surface, down a rough plane inclined at an angle θ to the horizontal (in our computations we take $\theta = 30°$), as shown in **Fig. 29.8**. A Cartesian coordinate system, fixed to the bottom, is employed with the x axis oriented down the inclined surface, and the y axis normal to the bottom.

As in the previous problem, in view of the field equations (29.54) and (29.56) and constitutive equations (29.62)–(29.64) and employing a rectilinear flow assumption as in $(29.65)_1$, the governing differential equations for this inclined gravity-flow problem, in terms of the nondimensional variables, can be presented as follows (compare these equations with (29.69)–(29.71))

$$\frac{\mathrm{d}\bar{\pi}}{\mathrm{d}\bar{y}} + 2S\cos(\theta)\bar{\nu} = 0, \tag{29.94}$$

$$\frac{\mathrm{d}}{\mathrm{d}\bar{y}}\left[\frac{2}{(\bar{\nu}_\infty - \bar{\nu})^2}\frac{\mathrm{d}\bar{\nu}}{\mathrm{d}\bar{y}}\right] + \frac{1}{\bar{\nu}}\left[\bar{\pi} + 1 - \bar{\nu}^2 - \frac{(\bar{\nu}_\infty + \bar{\nu})}{(\bar{\nu}_\infty - \bar{\nu})^3}\left(\frac{\mathrm{d}\bar{\nu}}{\mathrm{d}\bar{y}}\right)^2\right] = 0, \tag{29.95}$$

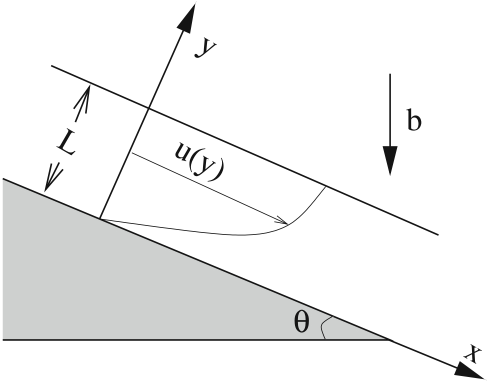


Fig. 29.8 Inclined gravity-flow and coordinate system

$$\frac{\mathrm{d}}{\mathrm{d}\bar{y}}\left[\frac{1}{(\bar{\nu}_\infty-\bar{\nu})^8}\frac{\mathrm{d}\bar{u}}{\mathrm{d}\bar{y}}\right]+2S_1\sin(\theta)\bar{\nu}=0, \tag{29.96}$$

where the dimensionless variables $\bar{\pi}$, S, $\bar{\nu}$, $\bar{u}, \ldots$ are defined as in (29.66) and (29.67); furthermore, the new parameter

$$S_1=\frac{\gamma b\nu_m}{2\mu_0 V_0\xi^2} \tag{29.97}$$

may be interpreted to represent to some extent the ratio of the gravity to the viscous friction. Equation (29.96) indicates that the value of S_1 affects only the velocity amplitude, but not its distribution across the depth. Here, because we take only an interest in the velocity distribution but not in its absolute value, we will in our computations not consider the effect of various values of S_1.

The boundary conditions for this problem are specified at the free boundary surface $\bar{y}=\bar{L}$ and along the supporting plate $\bar{y}=0$. We suppose that the upper free surface is *tension free* (GOODMAN and COWIN, 1971) and at the bottom the boundary conditions are specified such that the nondimensional boundary conditions are

$$\bar{\nu}(0)=\bar{\nu}_0,\ \bar{u}(0)=0,\qquad \frac{\mathrm{d}\bar{\nu}}{\mathrm{d}\bar{y}}(\bar{L})=0;\ \frac{\partial\bar{u}}{\partial\bar{y}}(\bar{L})=0;\ \bar{\pi}(\bar{L})=\sigma_0=0. \tag{29.98}$$

The boundary conditions on velocity and stress are physically well motivated, those on ν are, however, somewhat problematic. In an experiment, the layer thickness cannot be prescribed but must be the result of the upstream flow conditions. The total mass flux can be prescribed, and that will, through an integration of the velocity profile, essentially describe the thickness L. On the other hand, in such gravity-driven

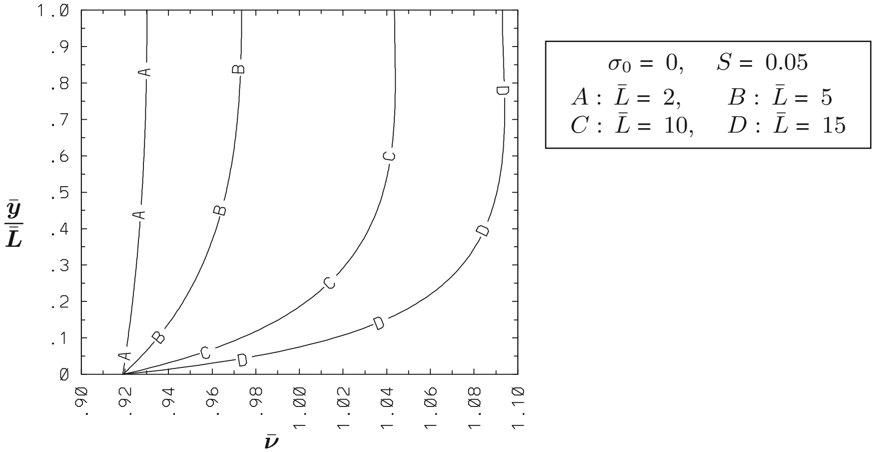


Fig. 29.9 Nondimensional volume fraction profiles for various granular depths for an inclined gravity-flow, from WANG and HUTTER [20]. © Part. Sci. Technol. Taylor & Francis

flows, often the upper most part of the granular material moves as a passive layer on top of a fluidized boundary layer. This would mean that ν should also be described at the top surface (together with $\mathrm{d}\bar{\nu}/\mathrm{d}y = 0$). If we prescribe $\bar{\nu}(0)$ in (29.98) this is tantamount to an a posteriori prescription of $\bar{\nu}(\bar{L})$.

Equations (29.94)–(29.96) with boundary conditions (29.98) can be solved as described in Sect. 29.5.2 by means of the iteration method.

Profiles of the dimensionless volume fraction and the dimensionless velocity are shown in **Figs. 29.9**, **29.10**, **29.11**, **29.12**, **29.13** and **29.14** for various values of the granular thickness $\bar{L}$, the parameter S and the normal stress σ_0, respectively. For convenience of comparison, the coordinate across the cross-section has also been expressed in terms of $\bar{y}/\bar{L}$ and the maximum velocity has been normalized. Figure 29.9 illustrates the strong dependence of the volume distribution on $\bar{L}$. A relatively thin layer thickness, i.e., $\bar{L} = 2$, shows an almost constant volume fraction across depth, while for thicker grain flow, the volume distribution decreases monotonically with depth; mainly in a relatively narrow zone near the bottom, where the shear is largest, dilation occurs, obviously due to the increased shearing. This is manifested in the velocity distribution displayed in Fig. 29.10. For small $\bar{L}$ (curve A), the velocity distribution is similar to that in an incompressible fluid theory. As $\bar{L}$ increases, there is an increasing tendency that the shear is bounded in a very narrow layer near the bottom; above the layer the velocity can be regarded as constant (curve D). This is a demonstration why for a granular flow down an inclined plane one can often assume that only a portion of the grains which is close to the base is fluidized (fluidized layer), while the upper portion is passively moving (passive layer) with the speed of the particles at the upper edge of this fluidized layer (e.g., see HUTTER et al. [10]).

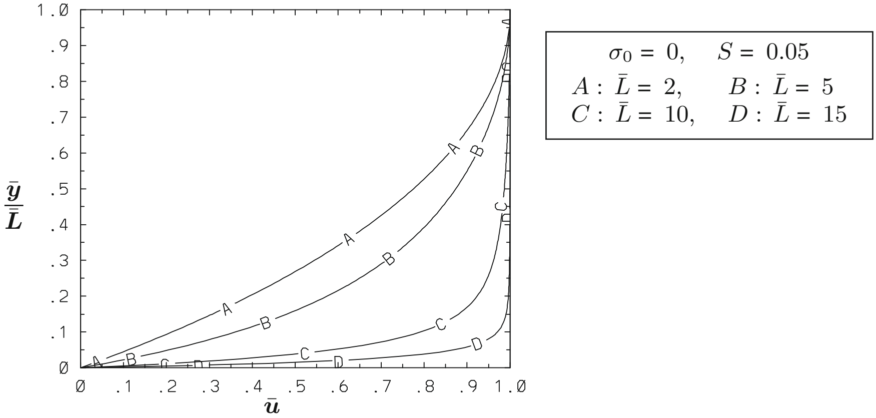


Fig. 29.10 Nondimensional velocity profiles for various granular depths for an inclined gravity-flow, from Wang and Hutter [20]. © Part. Sci. Technol. Taylor & Francis

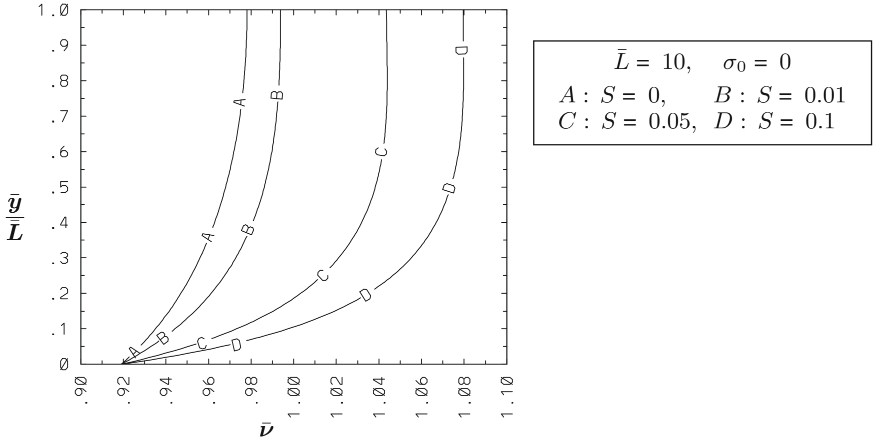


Fig. 29.11 Nondimensional volume fraction profiles for various values of parameter S for inclined gravity-flow, from Wang and Hutter [20]. © Part. Sci. Technol. Taylor & Francis

Another interesting result is, how profiles for $\bar{\nu}$ and $\bar{u}$ can change when the grain size or gravity vary. In Figs. 29.11 and 29.12 the profiles for various values of the parameter S are displayed for fixed $\bar{L}$ and σ_0. It can be seen that, as the grain size increases (i.e., S increases), the manifestation of the granular character of the material increases and the dilatancy of the granular material becomes obvious.

We also investigated the influences of the variations of the normal surface stress σ_0 for fixed $\bar{L}$ and S. Figures 29.13 and 29.14 illustrate the dependence on normal surface stress for inclined granular flow. This problem is somewhat academic as we

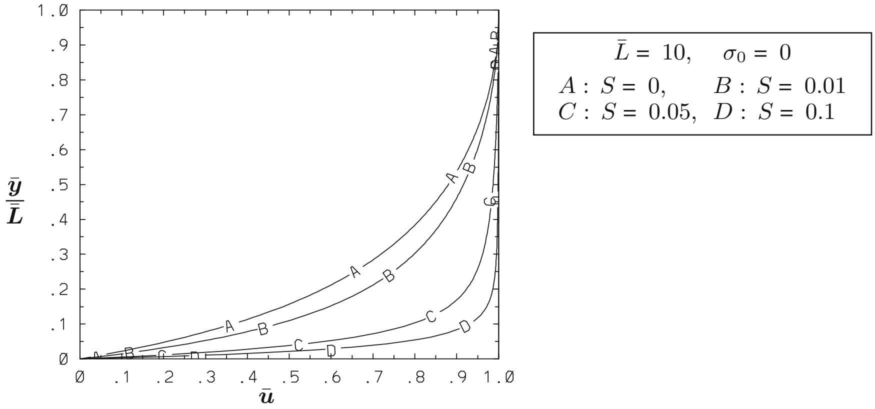


Fig. 29.12 Nondimensional velocity profiles for various values of parameter S for an inclined gravity-flow, from WANG and HUTTER [20]. © Part. Sci. Technol. Taylor & Francis

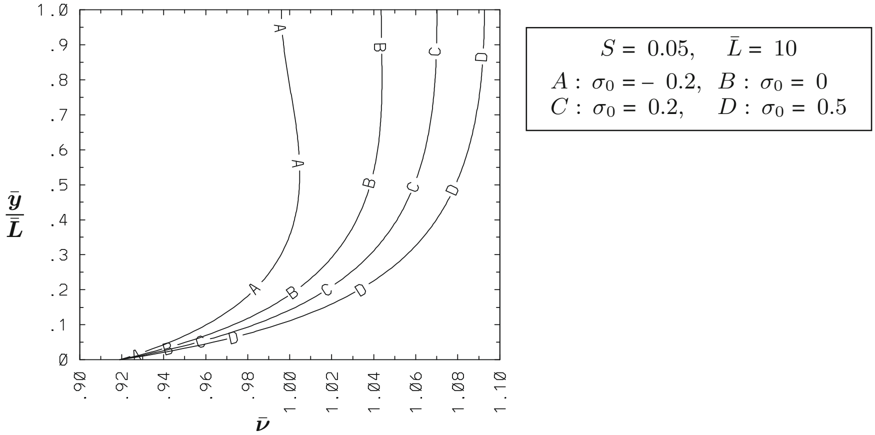


Fig. 29.13 Nondimensional volume fraction profiles for various values of the normalized surface pressure for an inclined gravity-flow, from WANG and HUTTER [20]. © Part. Sci. Technol. Taylor & Francis

previously already concluded that the surface should be stress free. However one may differently view this exercise; $\sigma_0 \neq 0$ may well represent some surface tension effects. Increasing the normal stress will tend to cause the grains to interlock, so that the material becomes denser and the shear layer becomes thinner. These figures allow for the possibility of tensile stresses on the surface.

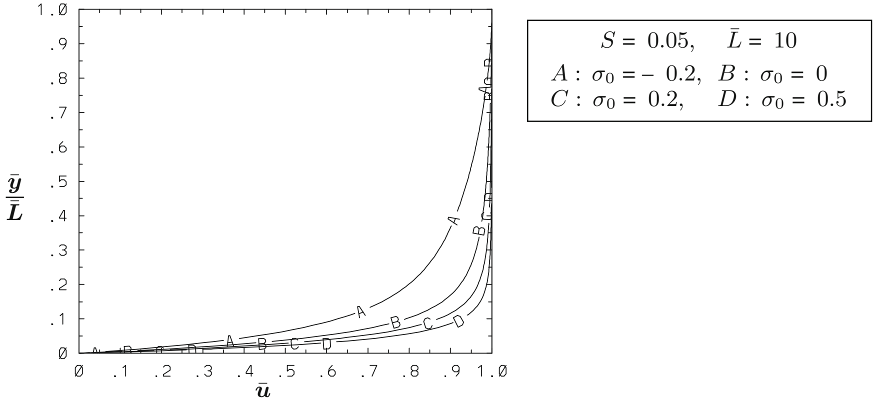


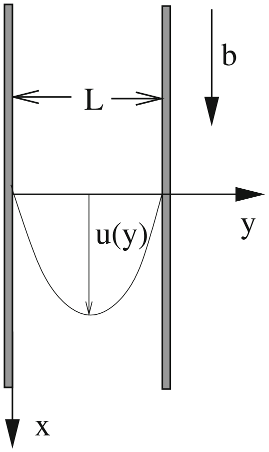
Fig. 29.14 Nondimensional velocity profiles for various values of the normalized surface pressure for an inclined gravity-flow, from WANG and HUTTER [20]. ⓒ Part. Sci. Technol. Taylor & Francis

29.7 Vertical Channel-Flow Problems

In this section, an analysis similar to that in the previous two sections is performed for the fully developed two-dimensional flow of a granular material between two rough infinite parallel flat plates of distance L aligned with the gravity field. A Cartesian coordinate system fixed to a plate is employed as shown in **Fig. 29.15**. The x axis is along the direction of flow and gravity field and the y axis is oriented normal to the plates.

The governing differential equations for this vertical channel-flow problem, in terms of the nondimensional variables, can be presented as follows

Fig. 29.15 Vertical channel-flow and coordinate system



$$\frac{\mathrm{d}}{\mathrm{d}\bar{y}}\left[\frac{2}{(\bar{\nu}_\infty-\bar{\nu})^2}\frac{\mathrm{d}\bar{\nu}}{\mathrm{d}\bar{y}}\right]+\frac{1}{\bar{\nu}}\left[\bar{\pi}+1-\bar{\nu}^2-\frac{(\bar{\nu}_\infty+\bar{\nu})}{(\bar{\nu}_\infty-\bar{\nu})^3}\left(\frac{\mathrm{d}\bar{\nu}}{\mathrm{d}\bar{y}}\right)^2\right]=0, \quad (29.99)$$

$$\frac{\mathrm{d}}{\mathrm{d}\bar{y}}\left[\frac{1}{(\bar{\nu}_\infty-\bar{\nu})^8}\frac{\mathrm{d}\bar{u}}{\mathrm{d}\bar{y}}\right]+2S_1\bar{\nu}=0 \quad (29.100)$$

with $\bar{\pi}=$ constant, where the dimensionless variables $\bar{\pi},\ S,\ S_1,\ \bar{\nu},\ \bar{u},\ldots$ are defined as in (29.66), (29.67) and (29.97).

We suppose that on two vertical flat plates the volume fraction is specified and that the no-slip condition applies. So, the nondimensional boundary conditions are

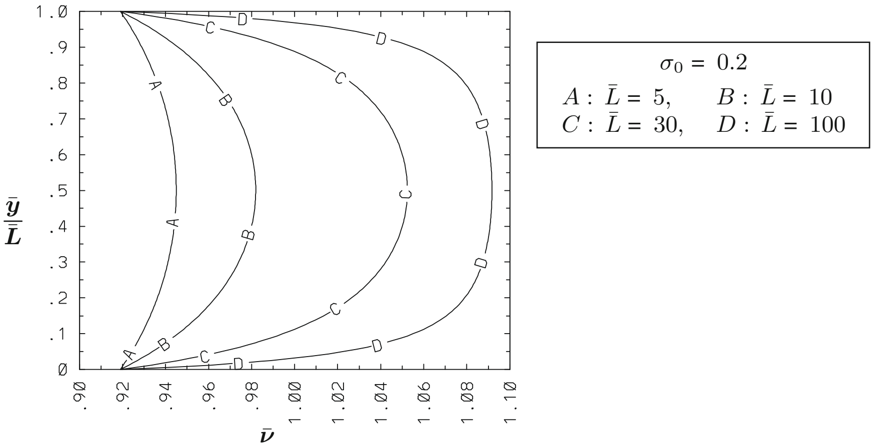


Fig. 29.16 Nondimensional volume fraction profiles for various channel widths for a vertical channel-flow, from WANG and HUTTER [20]. © Part. Sci. Technol. Taylor & Francis

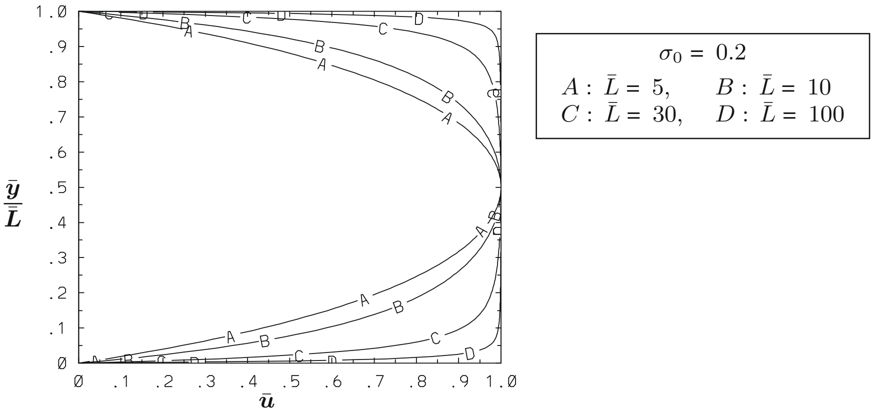


Fig. 29.17 Nondimensional velocity profiles for various channel widths for a vertical channel-flow, from WANG and HUTTER [20]. © Part. Sci. Technol. Taylor & Francis

$$\bar{\nu}(0) = \bar{\nu}(\bar{L}) = \bar{\nu}_0, \quad \bar{u}(0) = \bar{u}(\bar{L}) = 0. \tag{29.101}$$

Obviously, the symmetry conditions could also be invoked. The system of nonlinear ordinary differential equations (29.99) and (29.101) is also solved numerically by using the iteration method as described before in Sect. 29.5.2.

Dimensionless forms of the volume distribution and velocity across the complete channel are showed in **Figs. 29.16**, **29.17**, **29.18** and **29.19** for various values of $\bar{L}$ and σ_0, respectively. It can be seen that for narrow channels and small normal stress, the shear can extend from the walls to the center, which behaves as an incompressible fluid, whereas for wider channels and larger normal stress the flow structure is far

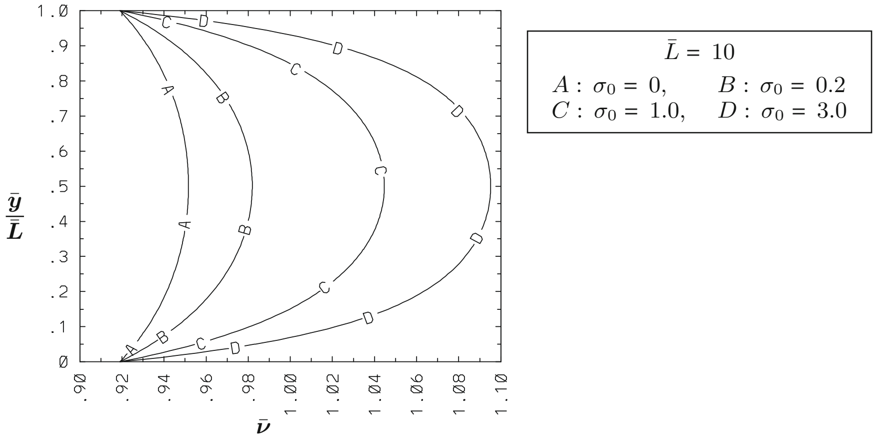


Fig. 29.18 Nondimensional volume fraction profiles for various values of the normalized pressure for a vertical channel-flow, from WANG and HUTTER [20]. © Part. Sci. Technol. Taylor & Francis

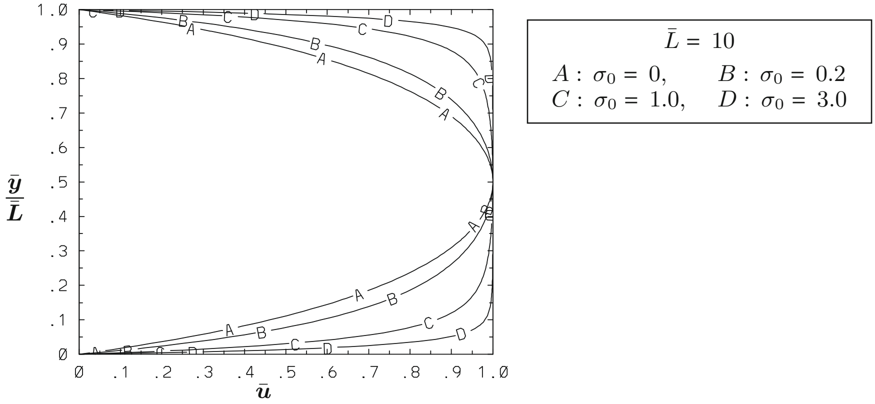


Fig. 29.19 Nondimensional velocity profiles for various values of the normalized pressure for a vertical channel-flow, from WANG and HUTTER [20]. © Part. Sci. Technol. Taylor & Francis

from an incompressible Newtonian fluid, in which in a large region near the center the grain flow is similar to that of a plug flow, with a nearly constant velocity, the shear layers close to the walls may be very thin.

29.8 Alternative Formulations

29.8.1 *Fluid Models for Cohesionless Granular Materials with Internal Length Parameter*

In the year 2006 FANG, WANG, and HUTTER [3, 4] took up the subject of the microstructural description of granular materials again by arguing that the GOODMAN–COWIN theory needed to be amended, because the balance law of equilibrated forces was dimensionally not consistent in the various terms. FANG et al. argue as follows:

- The balance law of equilibrated forces was not derived by GOODMAN and COWIN as a momentum balance, rather just motivated. It should better be interpreted as an energy balance, since $k = \frac{1}{2}\alpha\dot{\nu}^2$ looks like the traditional form of a kinetic energy. Because $\dot{\nu}^2$ has the dimension $[1/T^2]$, α would need to have the dimension $[\alpha] = [L^2]$, where T and L are time and length scales, to make k a specific kinetic energy.The parameter α should be replaced by a squared internal length ℓ^2.
- FANG et al. introduce an internal length ℓ and propose the rate of change of the "momentum associated with ν" of a granular body $\mathcal{B}$ to have the form

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathcal{B}}(\gamma\nu\ell\dot{\nu})\,\mathrm{d}v, \tag{29.102}$$

which is dimensionally correct. This proposal then leads directly to the "balance law of momentum associated with ν" as

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathcal{B}}(\gamma\nu\ell\dot{\nu})\,\mathrm{d}v = \int_{\partial\mathcal{B}}\boldsymbol{h}\cdot\boldsymbol{n}\,\mathrm{d}a + \int_{\mathcal{B}}\gamma\nu(f+\mathfrak{s})\,\mathrm{d}v, \tag{29.103}$$

in which $\boldsymbol{h}$ is its flux (corresponding to the equilibrated stress vector), f is its intrinsic body force (corresponding to its equilibrated intrinsic body force), and $\mathfrak{s}$ its supply (corresponding to its equilibrated body force) which we shall set to zero. Localizing (29.103) yields, on using the conservation of mass,

$$\gamma\nu(\ell\dot{\nu})^{\cdot} = \gamma\nu(\dot{\ell}\dot{\nu}+\ell\ddot{\nu}) = \operatorname{div}\boldsymbol{h} + \gamma\nu f. \tag{29.104}$$

This is the modified "balance of momentum associated with ν", in which the "acceleration term" has the correct dimension.

- FANG et al. then propose the energy expressions of the new formulation
  - $\frac{1}{2}(\ell\dot{\nu})^2$ as kinetic energy associated with ν,
  - $\ell\dot{\nu}\boldsymbol{h}$ as energy flux associated with ν,
  - $\rho f \ell\dot{\nu}$ as energy supply associated with ν.

It is now consequential to postulate the *total energy* by

$$E = \int_{\mathcal{B}} \rho \left\{\varepsilon + \tfrac{1}{2}\boldsymbol{v}\cdot\boldsymbol{v} + \tfrac{1}{2}(\ell\dot{\nu})^2\right\} \mathrm{d}v, \tag{29.105}$$

comprising of internal energy, $\rho\varepsilon$, traditional kinetic energy, $\frac{1}{2}\rho\boldsymbol{v}\cdot\boldsymbol{v}$ and configurational kinetic energy $\frac{1}{2}\rho(\ell\dot{\nu})^2$. Moreover, the power of working of the forces, L, may be postulated as

$$L = \int_{\mathcal{B}} \rho\left\{\boldsymbol{b}\cdot\boldsymbol{v} + f\ell\dot{\nu}\right\} \mathrm{d}v + \int_{\partial\mathcal{B}} \left(\boldsymbol{v}\boldsymbol{T}\cdot\boldsymbol{n} + \ell\dot{\nu}\boldsymbol{h}\cdot\boldsymbol{n}\right)\, \mathrm{d}a. \tag{29.106}$$

The heat added to the body from outside, Q, is as classically given by

$$Q = \int_{\mathcal{B}} \rho r \,\mathrm{d}v - \int_{\partial\mathcal{B}} \boldsymbol{q}\cdot\boldsymbol{n}\,\mathrm{d}a. \tag{29.107}$$

The balance of total energy $\mathrm{d}E/\mathrm{d}t = L + Q$ can be written as

$$\begin{aligned}
&\frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathcal{B}} \rho\left\{\varepsilon + \tfrac{1}{2}\boldsymbol{v}\cdot\boldsymbol{v} + \tfrac{1}{2}(\ell\dot{\nu})^2\right\}\mathrm{d}v \\
&= \int_{\mathcal{B}} \rho\left\{\boldsymbol{b}\cdot\boldsymbol{v} + f\ell\dot{\nu} + r\right\}\mathrm{d}v + \int_{\partial\mathcal{B}} \left\{\boldsymbol{v}\boldsymbol{T} - \boldsymbol{q} + \ell\dot{\nu}\boldsymbol{h}\right\}\cdot\boldsymbol{n}\,\mathrm{d}a,
\end{aligned} \tag{29.108}$$

which leads to the localized energy balance

$$\begin{aligned}
&\frac{\mathrm{d}}{\mathrm{d}t}\left\{\rho\left(\varepsilon + \tfrac{1}{2}\boldsymbol{v}\cdot\boldsymbol{v} + \tfrac{1}{2}(\ell\dot{\nu})^2\right)\right\} + \rho\left\{\varepsilon + \tfrac{1}{2}\boldsymbol{v}\cdot\boldsymbol{v} + \tfrac{1}{2}(\ell\dot{\nu})^2\right\}\operatorname{div}\boldsymbol{v} \\
&\overset{*}{=} \rho\dot{\varepsilon} + \tfrac{1}{2}\rho(\boldsymbol{v}\cdot\boldsymbol{v})^{\cdot} + \tfrac{1}{2}\rho\left((\ell\dot{\nu})^2\right)^{\cdot} \\
&= \operatorname{div}(\boldsymbol{v}\boldsymbol{T}) - \operatorname{div}\boldsymbol{q} + \rho r + \boldsymbol{v}\cdot\rho\boldsymbol{b} + \operatorname{div}(\ell\dot{\nu}\boldsymbol{h}) + \rho f\ell\dot{\nu},
\end{aligned} \tag{29.109}$$

in which at the step ($\overset{*}{=}$) the balance of mass has been incorporated. Using the balances of kinetic energy plus the equilibrated kinetic energy (29.104),

$$\underbrace{(\rho\dot{\boldsymbol{v}} - \operatorname{div}\boldsymbol{T} - \rho\boldsymbol{b})}_{=0}\cdot\boldsymbol{v} + \rho\underbrace{\left((\ell\dot{\nu})^{\cdot} - \operatorname{div}\boldsymbol{h} - f\right)}_{=0}\ell\dot{\nu} = 0, \tag{29.110}$$

and subtracting this expression from (29.109), finally yields

$$\rho\dot{\varepsilon} = \boldsymbol{T}\cdot\boldsymbol{D} - \operatorname{div}\boldsymbol{q} + \rho r + \boldsymbol{h}\cdot\operatorname{grad}(\ell\dot{\nu}) - \rho f\ell\dot{\nu}. \tag{29.111}$$

In these equations, only the energies of ν have been included. If the variation of the internal length ℓ is independent of the variation of ν additional energies associated with the variation of ℓ would equally have to be taken into account.

FANG et al. [3, 4] conduct thermodynamic analyses for different situations how the internal length scale is treated. They present detailed analyses for the following model assumptions:

- ℓ is a material constant (*Model I*),
- ℓ is a constitutive variable (*Model II*),
- ℓ is an independent field quantity (*Model III*),
- ℓ is an independent kinematic field quantity (*Model IV*).

The analyses for *models I and II* are straightforward, given the experience in this chapter. In [3] the balance laws of mass, momentum, modified equilibrated force, and modified energy are complemented by the entropy balance and constitutive assumptions, and the exploitation of the entropy inequality is performed in the spirit of MÜLLER–LIU. For *Model III*, an additional balance equation must be proposed to make the problem mathematically well posed. The "ℓ-associated momentum equation" is proposed as

$$\rho(\varLambda\dot{\ell})^{\cdot} = \operatorname{div}\boldsymbol{\varGamma} + \rho\varPi + \rho G, \quad \varLambda = \text{const.}, \tag{29.112}$$

where $\boldsymbol{\varGamma}$, $\varPi$, G are the flux, specific intrinsic production and an external supply term of ℓ (which we shall set to zero). These ℓ-associated quantities will also contribute to the energies

- $\frac{1}{2}\rho(\varLambda\dot{\ell})^2$ as kinetic energy, associated with ℓ,
- $\varLambda\dot{\ell}\boldsymbol{\varGamma}$ as energy flux associated with ℓ,
- $\rho\varLambda\dot{\ell}G$ as energy supply associated with ℓ.

Proceeding as above with (29.108), the first law now takes the form

$$\begin{aligned} &\frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathcal{B}}\rho\left\{\varepsilon + \tfrac{1}{2}\boldsymbol{v}\cdot\boldsymbol{v} + \tfrac{1}{2}(\ell\dot{\nu})^2 + \tfrac{1}{2}(\varLambda\dot{\ell})^2\right\}\mathrm{d}v \\ &= \int_{\mathcal{B}}\rho\left\{\boldsymbol{b}\cdot\boldsymbol{v} + f\ell\dot{\nu} + \varLambda\dot{\ell}\varPi\right\}\mathrm{d}v \\ &\quad + \int_{\partial\mathcal{B}}\left\{\boldsymbol{v}\boldsymbol{T} - \boldsymbol{q} + \ell\dot{\nu}\boldsymbol{h} + \varLambda\dot{\ell}\boldsymbol{\varGamma}\right\}\cdot\boldsymbol{n}\,\mathrm{d}a, \end{aligned} \tag{29.113}$$

from which the localized energy equation takes the form

$$\begin{aligned} \rho\dot{\varepsilon} = {}& \boldsymbol{T}\cdot\boldsymbol{D} - \operatorname{div}\boldsymbol{q} + \rho r + \boldsymbol{h}\cdot\operatorname{grad}(\ell\dot{\nu}) - \rho\ell\dot{\nu}f \\ &+ \boldsymbol{\varGamma}\cdot\operatorname{grad}(\varLambda\dot{\ell}) - \rho\varLambda\dot{\ell}\varPi, \end{aligned} \tag{29.114}$$

in which $\boldsymbol{\varGamma}$ and $\varPi$ are regarded as additional constitutive quantities. With this local form of the first law of thermodynamics the closed systems entropy principle can now be exploited by the MÜLLER–LIU method, which is done for an elastic-viscous fluid like body in [3].

In *Model IV*, the internal length ℓ is considered an independent field quantity, for which a kinematic evolution equation of the form

$$\rho\dot{\ell} = \operatorname{div} \boldsymbol{\Gamma} + \Pi \tag{29.115}$$

is proposed. The identifier "kinematic" is employed for this equation, because only the first material time derivative of ℓ occurs (and not the second). $\boldsymbol{\Gamma}$ and Π are regarded as constitutive quantities and no additional power terms involving $\boldsymbol{\Gamma}$ and Π enter the first law of thermodynamics and no additional power terms involving $\boldsymbol{\Gamma}$ and Π enter the first law of thermodynamics. The thermodynamic analysis shows for *Model IV* that heat flux and entropy flux are no longer collinear, contrary to models *I*, *II*, and *III*. This makes the model algebraically rather complicated and leads us to the conclusion that *Model IV* is not suitable for the description of the dynamics of granular materials.

29.8.2 Application to Simple Shear, Plane Poiseuille, and Gravity-Driven Flows

FANG et al. [4] deepen their analysis of the dynamic behavior of *Models I, II*, and *III* by explicitly parameterizing the constitutive variables for the CAUCHY stress $\boldsymbol{T}$, the heat flux vector $\boldsymbol{q}$, the equilibrated stress vector $\boldsymbol{h}$, the ℓ-associated flux vector $\boldsymbol{\Gamma}$, the ℓ-associated equilibrated intrinsic body force f, as well as the free energy $\gamma\nu\psi$. Their focus is to formulate the dissipative parts of the constitutive variables as linear relations of $\dot{\nu}$, $\dot{\ell}$, $\boldsymbol{D}$, $\boldsymbol{h}$, $\boldsymbol{\Gamma}$. In so doing, a complete set of constitutive equations for the constitutive quantities for each model is obtained. The implemented models are quantified by use of experimental findings of laboratory experiments and then applied to investigate typical isothermal steady granular shearing flows with density preserving grains, in particular, simple plane shearing flows, POISEUILLE flows, inclined gravity-driven flows and vertical channel flows, in particular for their *Models I* and *III*, illustrating their numerical results with graphs. Of importance are in this connection the boundary conditions. These results show that *Model III* is more appropriate than *Model I*, because *Model III* allows a better account of the motion of an individual grain. The interested reader is encouraged to consult [3, 4].

29.9 Concluding Remarks

In this chapter, a thermodynamic theory for a granular material was presented in which, besides balances for mass, momentum and energy, a balance law for equilibrated forces, as proposed by GOODMAN and COWIN, was introduced to accommodate for the dynamical effects played by the solid volume fraction, and porosity, respectively.

The form of the entropy principle was that of MÜLLER–LIU, i.e., for the prescribed constitutive class the entropy inequality was identically satisfied subject to the constraints that the balance laws of mass, momentum, energy and equilibrated forces with or without supply terms. It was shown that in comparison to a "standard" exploitation according to COLEMAN–NOLL, in which momentum, energy, and equilibrated force sources of arbitrary value must be permitted, the entropy flux is no longer collinear to the energy flux, if the time rate of change of the volume fraction is an independent variable of the HELMHOLTZ free energy. If the HELMHOLTZ free energy does not depend on $\dot{\nu}$, the two approaches yield identical results.

For such a reduced theoretical model, which agrees with that proposed by GOODMAN and COWIN [7] three typical shearing flow problems were analyzed: steady fully developed horizontal shearing flows and gravity flows of granular materials down an inclined plane and between vertical parallel plates. All three examples of granular flows display flow features different from a viscous fluid. It is shown that for a large thickness of the granular flow and large grain sizes, dilatant shearing layers exist only in narrow zones near boundaries. In the zones far away from the boundaries the shearing nearly vanishes, where the grains move as an entire solid body in a plug-flow manner, while for small thickness of the granular flow and fine grains, the behavior of the granular flows is very similar to that of a viscous fluid.

In this chapter, in which the free energy is assumed to be independent of $\dot{\nu}$, only linear thermodynamic parts of the constitutive variables $\boldsymbol{T}$, f, and $\boldsymbol{q}$ are used.

Appendix 29.A Variational Principle for a Goodman–Cowin Type Granular Material

29.A.1 Preliminaries

In this appendix, we present a variational principle providing an alternative motivation of the balance law of equilibrated forces, as introduced by GOODMAN and COWIN [7]. We shall use Cartesian tensor notation; x_i $(i = 1, 2, 3)$ and X_a $(a = 1, 2, 3)$ will be the coordinates of material points in the present and reference configurations, respectively, and t will denote the time. The volume fraction $\nu(\boldsymbol{x})$ $(0 \leqslant \nu \leqslant 1)$ and the true density $\gamma(\boldsymbol{x}) > 0$ will denote the averaged volume fraction over an RVE, filling densely the space of the body $\mathcal{B}$ so that the bulk density is expressible as

$$\rho = \gamma\nu, \tag{29.116}$$

also filling the space $\mathcal{B}$ densely.

Let us consider equilibrium states $x_i(\boldsymbol{X})$, $\nu(\boldsymbol{X})$. Neighboring such states will be denoted as $x_i(\boldsymbol{X}, \lambda)$, $\nu(\boldsymbol{X}, \lambda)$, parameterized by λ. The variations of the positions δx_i and volume fraction $\delta\nu$ may then be defined by

$$\delta x_i = \left.\frac{\mathrm{d}x_i}{\mathrm{d}\lambda}\right|_{\substack{\lambda=0\\ \boldsymbol{X}\text{ fixed}}}, \qquad \delta\nu = \left.\frac{\mathrm{d}\nu}{\mathrm{d}\lambda}\right|_{\substack{\lambda=0\\ \boldsymbol{X}\text{ fixed}}}. \tag{29.117}$$

If the volume fraction is thought of as a function of $\boldsymbol{x}$ and t, $\nu = \nu(\boldsymbol{x}, t)$ rather than $\nu(\boldsymbol{X}, t)$, the variation (29.117)$_2$ is represented by

$$\delta\nu = \left.\frac{\partial\nu}{\partial\lambda}\right|_{\substack{\lambda=0\\ \boldsymbol{x}\text{ fixed}}} + \left.\frac{\partial\nu}{\partial x_i}\frac{\partial x_i}{\partial\lambda}\right|_{\lambda=0}. \tag{29.118}$$

A variation of ν holding the spatial position $\boldsymbol{x}$ fixed is denoted by COWIN and GOODMAN [2] by

$$\Delta\nu = \left.\frac{\partial\nu}{\partial\lambda}\right|_{\substack{\lambda=0\\ \boldsymbol{x}\text{ fixed}}}. \tag{29.119}$$

Substituting (29.119) into (29.118) and using (29.117)$_1$ yields

$$\delta\nu = \Delta\nu + \nu_{,i}\delta x_i. \tag{29.120}$$

From this representation follows

$$\underbrace{(\delta\nu)_{,j}}_{\delta(\nu_{,j})+\nu_{,i}(\delta x_i)_{,j}} = \underbrace{(\Delta\nu)_{,j}}_{\Delta(\nu_{,j})} + \nu_{,ij}\delta x_i + \nu_{,i}(\delta x_i)_{,j}, \tag{29.121}$$

so that

$$\delta(\nu_{,j}) = \Delta(\nu_{,j}) + \nu_{,ij}\delta x_i. \tag{29.122}$$

The underbraced term on the left-hand side of (29.121) can be justified by the fact that $(\delta\nu)_{,j}$ differs from $(\delta\nu_{,j})$ by the convective term $\nu_{,i}(\delta x_i)_{,j}$, since $\boldsymbol{x}$ but not $\boldsymbol{X}$ is held fixed, whereas in the underbraced term on the right-hand side of (29.121) Δ is the variation holding the present configuration fixed.

29.A.2 Variational Principle

We now suppose that in the granular material the interaction of the grains is described by a scalar valued balance law that is added to the force balance by the fact that besides δx_i also $\delta \nu$ is an independent variation. So, the stored energy function W is for equilibrium states given by a function of the form $W = W(\gamma, \nu, \nu_{,i})$. It follows that the variation of the total energy function of the body can be postulated in the form

$$\begin{aligned} \delta \int_{\mathcal{B}} \gamma \nu W \, \mathrm{d}v = {} & \int_{\mathcal{B}} (\gamma \nu b_i \, \delta x_i + \gamma \nu \ell \, \delta \nu) \, \mathrm{d}v \\ & + \int_{\partial \mathcal{B}} (t_i \, \delta x_i + H \, \delta \nu) \, \mathrm{d}a. \end{aligned} \tag{29.123}$$

The volume term on the right-hand side of this equation consists of the virtual work done by the volumetric body force $\gamma \nu b_i$, subjected to the virtual displacement δx_i. In addition the scalar intrinsic equilibrated body force in GOODMAN-COWIN's terminology, performs work when being subjected to volume fraction variations $\delta \nu$. The second term on the right-hand side of (29.123) represents the associated surface work: $t_i \, \delta x_i$ is this working by the stress tractions when being subjected to the variations of the surface displacement δx_i and the variation of the equilibrated surface traction H, when being exposed to a variation of the volume fraction at the surface. This terminology follows GOODMAN and COWIN, however, (29.123) introduces the equilibrated intrinsic body force ℓ and the equilibrated traction H (both as scalar quantities). They may equally be introduced in an abstract way without specifying their meaning by a model interpretation. It is given by GOODMAN in 1969 [5].

We require the mass of a body to be conserved during variations. Thus,

$$\begin{aligned} M &= \int_{\mathcal{B}} \gamma \nu \, \mathrm{d}v \equiv \text{const.} \\ \Longrightarrow & \int_{\mathcal{B}} \delta(\gamma \nu) \, \mathrm{d}v + \int_{\mathcal{B}} \gamma \nu \, \delta(\mathrm{d}v) \equiv 0. \end{aligned} \tag{29.124}$$

Because this identity applies for all $\mathcal{B}$, also infinitesimal ones, we have

$$\delta(\gamma \nu) \, \mathrm{d}v + \gamma \nu \, \delta(\mathrm{d}v) = 0,$$

from which we deduce

$$\begin{aligned} & \delta(\gamma \nu) \, \mathrm{d}v + \gamma \nu \, \delta(x_i)_{,i} \, \mathrm{d}v = 0 \\ \Longrightarrow \; & \delta(\gamma \nu) = -\gamma \nu (\delta x_i)_{,i}. \end{aligned} \tag{29.125}$$

Similarly, $(29.124)_1$ can be multiplied with the stored energy function to yield

$$\begin{aligned} &\delta(\gamma\nu)W\,\mathrm{d}v + \gamma\nu W\,\delta(\mathrm{d}v) = 0, \\ \text{or}\quad &\int_{\mathcal{B}} \delta(\gamma\nu)W\,\mathrm{d}v + \int_{\mathcal{B}} \gamma\nu W\,\delta(\mathrm{d}v) = 0. \end{aligned} \tag{29.126}$$

These equations imply

$$\begin{aligned} \delta\int_{\mathcal{B}} \gamma\nu W\,\mathrm{d}v &= \int_{\mathcal{B}} \gamma\nu W(\delta\,\mathrm{d}v) \\ &= \underbrace{\int_{\mathcal{B}} \delta(\gamma\nu)W\,\mathrm{d}v + \int_{\mathcal{B}} \gamma\nu W\,\delta(\mathrm{d}v)}_{=0 \text{ because of mass balance}} + \int_{\mathcal{B}} \gamma\nu\,\delta W\,\mathrm{d}v \\ &= \int_{\mathcal{B}} \gamma\nu\,\delta W\,\mathrm{d}v. \end{aligned} \tag{29.127}$$

The expression on the right-hand side of (29.126) shall now alternatively be written. To this end, we observe that $W = W(\gamma, \nu, \nu_{,i})$ and obtain

$$\begin{aligned} \delta W &= \frac{\partial W}{\partial \gamma} \underbrace{\delta\gamma}_{\overset{(29.125)}{=}\left\{-\gamma(\delta x_i)_{,i} - \gamma\frac{\delta\nu}{\nu}\right\}} + \frac{\partial W}{\partial \nu}\delta\nu + \frac{\partial W}{\partial \nu_{,i}} \underbrace{\delta(\nu_{,i})}_{\overset{(29.121)}{=}\left\{(\delta\nu)_{,i} - \nu_{,k}(\delta x_k)_{,i}\right\}} \\ &= \frac{\partial W}{\partial \gamma}\left\{-\gamma(\delta x_i)_{,i} - \gamma\frac{\delta\nu}{\nu}\right\} + \frac{\partial W}{\partial \nu}\delta\nu + \frac{\partial W}{\partial \nu_{,i}}\left\{(\delta\nu)_{,i} - \nu_{,k}(\delta x_k)_{,i}\right\}. \end{aligned}$$

Multiplying this relation by $\gamma\nu$ yields

$$\begin{aligned} \gamma\nu\,\delta W = &\underbrace{-\gamma^2\nu\frac{\partial W}{\partial \gamma}(\delta x_i)_{,i} - \gamma\nu\frac{\partial W}{\partial \nu_{,i}}(\delta x_k)_{,i}\nu_{,k}}_{(i)} \\ &+ \underbrace{\gamma\nu\frac{\partial W}{\partial \nu_{,i}}(\delta\nu)_{,i}}_{(ii)} \underbrace{-\gamma^2\frac{\partial W}{\partial \gamma}\delta\nu + \gamma\nu\frac{\partial W}{\partial \nu}\delta\nu}_{(iii)}. \end{aligned} \tag{29.128}$$

Following Cowin and Goodman [2], this relation now suggests the definitions

$$\hat{p} := \gamma\nu^2\frac{\partial W}{\partial \nu}, \quad p := \gamma^2\nu\frac{\partial W}{\partial \gamma}, \quad h_i := \gamma\nu\frac{\partial W}{\partial \nu_{,i}} \tag{29.129}$$

$$P := \frac{1}{\nu}(p - \hat{p}) = \frac{1}{\nu}\left(\gamma^2\nu\frac{\partial W}{\partial \gamma} - \gamma\nu^2\frac{\partial W}{\partial \nu}\right), \tag{29.130}$$

$$T_{ij} := -p\,\delta_{ij} - h_i\nu_{,j} = -\gamma^2\nu\frac{\partial W}{\partial \gamma}\delta_{ij} - \gamma\nu\frac{\partial W}{\partial \nu_{,i}}\nu_{,j}. \tag{29.131}$$

Thus,

$$\begin{aligned}
T_{ij}(\delta x_j)_{,i} &= -\gamma^2 \nu \frac{\partial W}{\partial \gamma}(\delta x_i)_{,i} - \gamma \nu \frac{\partial W}{\partial \nu_{,i}} \nu_{,j} (\delta x_j)_{,i} && (i), \quad (29.132)\\
h_i(\delta \nu)_{,i} &= \gamma \nu \frac{\partial W}{\partial \nu_{,i}} (\delta \nu)_{,i} && (ii), \quad (29.133)\\
-P(\delta \nu) &= -\left(\gamma^2 \frac{\partial W}{\partial \gamma} - \gamma \nu \frac{\partial W}{\partial \nu}\right) \delta \nu && (iii). \quad (29.134)
\end{aligned}$$

The symbols (i), (ii), and (iii) correspond to the underscored terms in (29.128), which can now be written as

$$\begin{aligned}
\gamma \nu \, \delta W &= T_{ij}(\delta x_j)_{,i} + h_i(\delta \nu)_{,i} - P \, \delta \nu \\
&= (T_{ij} \delta x_j)_{,i} - T_{ij,i} \delta x_j + (h_i \, \delta \nu)_{,i} - h_{i,i} \, \delta \nu - P \, \delta \nu. \qquad (29.135)
\end{aligned}$$

Integrating this expression over the body $\mathcal{B}$ and using the GAUSS theorem leads to

$$\begin{aligned}
\int_{\mathcal{B}} \gamma \nu \, \delta W \, \mathrm{d}v = &- \int_{\mathcal{B}} \left\{ T_{ij,i} \, \delta x_j + (h_{i,i} + P) \delta \nu \right\} \mathrm{d}v \\
&+ \int_{\partial \mathcal{B}} \left\{ T_{ij} n_i \, \delta x_j + h_i n_i \, \delta \nu \right\} \mathrm{d}a. \qquad (29.136)
\end{aligned}$$

Next, using (29.127) in (29.123) and subsequently employing (29.136) implies

$$\begin{aligned}
&\int_{\mathcal{B}} \left\{ (T_{ij,i} + \gamma \nu b_j) \delta x_j + (h_{i,i} + P + \gamma \nu \ell) \delta \nu \right\} \mathrm{d}v \\
&+ \int_{\partial \mathcal{B}} \left\{ (t_j - T_{ij} n_i) \delta x_j + (H - h_i n_i) \right\} \delta \nu \, \mathrm{d}a \equiv 0, \qquad (29.137)
\end{aligned}$$

which must be valid for arbitrary and independent variations of δx_j and $\delta \nu$, which leads to

$$\left.\begin{aligned} T_{ij,i} + \gamma \nu b_j &= 0 \\ h_{i,i} + P + \gamma \nu \ell &= 0 \end{aligned}\right\} \text{ in } \mathcal{B}, \qquad \left.\begin{aligned} t_j &= T_{ij} n_i \\ H &= h_i n_i \end{aligned}\right\} \text{ on } \partial \mathcal{B}. \qquad (29.138)$$

These equations represent the equilibrium equations balancing the stress divergence and the body force and the equation of the balance of the equilibrated forces—divergence of the flux h_i, the volume fraction- dependent pressure P, and the intrinsic equilibrated body force $\gamma \nu \ell$. The equations on the right-hand side of (29.138) define the "stress boundary conditions", which would also follow from CAUCHY's tetrahedral argument.

COWIN and GOODMAN [2] state at this point that "given the stored energy function W as a function of $\gamma, \nu, \nu_{,i}$ the relations (29.128) and (29.129) together with the equations (29.137) constitute four equations in terms of the two unknowns γ and

ν". The system is, therefore, overdetermined as noted by JENKINS [12]. Following this author COWIN and GOODMAN then propose an equivalent alternative variational principle "which leads directly to a reduction of the equations to form a compatible system".

Alternative variational formulation (compressible granules) JENKINS [12] did not treat δx_i and $\delta\nu$ as independent fields, but δx_i and $\Delta\nu$, defined in (29.119) and related to $\delta\nu$ via (29.120). The variation of the stored energy function then takes the form

$$\gamma\nu\,\delta W = \gamma\nu\frac{\partial_W}{\partial\gamma}\delta\gamma + \gamma\nu\frac{\partial W}{\partial\nu}\delta\nu + \gamma\nu\frac{\partial W}{\partial\nu_{,i}}\delta(\nu_{,i}), \tag{29.139}$$

where

$$\begin{aligned}
&\delta\gamma = -\gamma(\delta x_i)_{,i} - \gamma\frac{\delta\nu}{\nu}, \qquad \delta\nu \overset{(29.120)}{=} \Delta\nu + \nu_{,i}\,\delta x_i,\\
&\delta(\nu_{,i}) \overset{(29.122)}{=} \Delta(\nu_{,i}) + \nu_{,ij}\,\delta x_j,
\end{aligned}$$

so that (29.139) can be written as

$$\begin{aligned}
\gamma\nu\,\delta W = {}& \gamma\nu\frac{\partial W}{\partial\gamma}\left\{-\gamma(\delta x_i)_{,i} - \gamma\frac{\delta\nu}{\nu}\right\} + \gamma\nu\frac{\partial W}{\partial\nu}\left\{\Delta\nu + \nu_{,i}\,\delta x_i\right\}\\
&+\gamma\nu\frac{\partial W}{\partial\nu_{,i}}\left\{\Delta(\nu_{,i}) + \nu_{,ij}\,\delta x_j\right\}.
\end{aligned} \tag{29.140}$$

Next, note that

$$W_{,i} = \frac{\partial W}{\partial\gamma}\gamma_{,i} + \frac{\partial W}{\partial\nu}\nu_{,i} + \frac{\partial W}{\partial\nu_{,j}}\nu_{,ji}.$$

With this and the definitions (29.129) and (29.130) for p, h_i, and P a somewhat involved but simple identification of individual terms shows that

$$\begin{aligned}
\gamma\nu\,\delta W &= \gamma\nu\left(p\left(\frac{1}{\gamma\nu}\right)_{,i} + W\right)\delta x_i \ \underbrace{-p(\delta x_i)_{,i}}_{-(p\,\delta x_i)_{,i}+p_{,i}\,\delta x_i} \ -P\Delta\nu + \underbrace{h_i(\Delta\nu)_{,i}}_{(h_i\,\Delta\nu)_{,i}-h_{,i}\,\Delta\nu}\\
&= \gamma\nu\Biggl\{\underbrace{p\left(\frac{1}{\gamma\nu}\right)_{,i} + \frac{p_{,i}}{\gamma\nu}}_{[p/(\gamma\nu)]_i} + W_{,i}\Biggr\}\delta x_i\\
&\quad -(p\,\delta x_i)_{,i} + (h_i\,\Delta\nu)_{,i} - P\,\Delta\nu - h_{i,i}\,\Delta\nu.
\end{aligned}$$

Integrating this over the body $\mathcal{B}$, and employing the divergence theorem in the last two terms on the right-hand side yield

$$\int_{\mathcal{B}} \gamma\nu\,\delta W\,\mathrm{d}v = \int_{\mathcal{B}} \left\{ \gamma\nu \left(\frac{p}{\gamma\nu} + W \right)_{,i} \delta x_i - (h_{i,i} + P)\Delta\nu \right\} \mathrm{d}v$$
$$+ \int_{\partial\mathcal{B}} \left\{ -pn_i\,\delta x_i + h_{i,i} n_i \right\} \Delta\nu\,\mathrm{d}a. \qquad (29.141)$$

The right-hand side of this expression must be identified with the right-hand side of (29.123), viz.,

$$\int_{\mathcal{B}} \left\{ \gamma\nu \left[\left(\frac{p}{\gamma\nu} + W \right)_{,i} - \ell\nu_{,i} - b_i \right] \delta x_i - \left[h_{i,i} + P + \gamma\nu\ell \right] \Delta\nu \right\} \mathrm{d}v$$
$$+ \int_{\partial\mathcal{B}} \left\{ \left(pn_i + t_i + H\nu_{,i} \right) \delta x_i + (h_i n_i - H)\Delta\nu \right\} \mathrm{d}a \equiv 0. \qquad (29.142)$$

For this to hold for all δx_i and all $\delta\nu$, we obtain

$$\left.\begin{array}{l} \dfrac{\partial}{\partial x_i}\left(\dfrac{p}{\gamma\nu} + W \right) = b_i + \ell\nu_{,i} \\ h_{i,i} + P + \gamma\nu\ell = 0 \end{array}\right\} \text{ in } \mathcal{B}, \quad \left.\begin{array}{l} -pn_i = t_i + H\nu_{,i} \\ H = h_i n_i \end{array}\right\} \text{ in } \partial\mathcal{B}. \qquad (29.143)$$

These equations possess the advantage that they can directly be integrated, if b_i and ℓ are expressed in terms of a potential as suggested by JENKINS [12]. If we choose a force potential $\Phi(x_i, \nu)$ such that

$$b_i = -\frac{\partial\Phi}{\partial x_i}, \quad \ell = -\frac{\partial\Phi}{\partial\nu}, \qquad (29.144)$$

then the field equations and boundary conditions take the forms

$$\left.\begin{array}{l} \dfrac{\partial}{\partial x_i}\left(\dfrac{p}{\gamma\nu} + W + \Phi \right) = 0 \\ \dfrac{\partial h_i}{\partial x_i} + P = \gamma\nu\dfrac{\partial\Phi}{\partial\nu} \end{array}\right\} \text{ in } \mathcal{B}, \quad \left.\begin{array}{l} -pn_i = t_i + H\nu_{,i} \\ H = h_i n_i,\ t_j = T_{ij} n_i \end{array}\right\} \text{ on } \partial\mathcal{B}. \qquad (29.145)$$

The particular form of these field equations and boundary conditions shows that they emerge naturally when one considers variations of ν by holding $\boldsymbol{x}$ fixed rather than $\boldsymbol{X}$.

29.A.3 Variational Principle for Density Preserving Granules

For a density preserving material the specific true mass is constant, $\gamma = \text{const.}$, and here, therefore, $\delta\gamma \equiv 0$. From mass balance (29.125), it then follows that

$$\delta\nu = -\nu(\delta x_i)_{,i}. \tag{29.146}$$

It follows that the variations of $\delta\nu$ and $\delta\boldsymbol{x}$ are no longer independent. Thus, the variational principle (29.123) can now be expressed as

$$\begin{aligned}\delta\int_{\mathcal{B}}\gamma\nu W\,\mathrm{d}v &= \int_{\mathcal{B}}\Big(\gamma\nu b_i\,\delta x_i - \underline{\gamma\nu^2\ell(\delta x_i)_{,i}}\Big)\,\mathrm{d}v\\ &\quad+\delta\int_{\partial\mathcal{B}}\big(t_i\,\delta x_i - \nu H(\delta x_i)_{,i}\big)\,\mathrm{d}a.\end{aligned} \tag{29.147}$$

For density preserving granules, $W = W(\nu, \nu_i)$ and, therefore,

$$\delta W = \frac{\partial W}{\partial\nu}\delta\nu + \frac{\partial W}{\partial\nu_{,i}}\delta(\nu_{,i}). \tag{29.148}$$

When using

$$\delta(\nu_{,j}) = (\delta\nu)_{,j} - \nu_{,i}(\delta x_i)_{,j}, \quad \text{see (29.121)}$$

and (29.146) in the expression (29.147) and employing the definitions (29.129)–(29.131), straightforward computations yield

$$\begin{aligned}-\gamma\nu\,\delta W &= \big(-\hat{p}\,\delta_{ij} + \nu h_{k,k}\,\delta_{ij} + h_i\nu_{,j}\big)_{,i}\ \delta x_j + \underline{[h_i\nu(\delta x_j)_{,j}]_{,i}}\\ &\quad+\underline{[\hat{p}\,\delta_{ij} - \nu h_{k,k}\,\delta_{ij} + h\nu_{,j}]_{,i}}.\end{aligned} \tag{29.149}$$

This equation is now integrated over the body; hereby, the underlined terms are transformed to surface integrals using the divergence theorem. This step leads to

$$\begin{aligned}\delta\int_{\mathcal{B}}\gamma\nu W\,\mathrm{d}v &= \int_{\mathcal{B}}\gamma\nu\,\delta W\,\mathrm{d}v\\ &= -\int_{\mathcal{B}}\big(-\hat{p}\,\delta_{ij} + \nu h_{k,k}\,\delta_{ij} - h_i\nu_{,j}\big)_{,i}\ \delta x_j\,\mathrm{d}v - \int_{\partial\mathcal{B}} h_i n_i\nu(\delta x_j)_{,j}\,\mathrm{d}v\\ &\quad+\int_{\partial\mathcal{B}} n_i\,\big(-\hat{p}\,\delta_{ij} + \nu h_{k,k}\,\delta_{ij} - h_i\nu_{,j}\big)_{,i}\ \delta x_j\,\mathrm{d}a.\end{aligned} \tag{29.150}$$

The right-hand side of this variational statement must equal the right-hand side of (29.147), in which we transform the underlined term by writing

$$\gamma\nu^2\ell(\delta x_i)_{,i} = \underline{(\gamma\nu^2\ell\,\delta x_i)_{,i}} - (\gamma\nu^2\ell)_{,i}\,\delta x_i$$

and use the divergence theorem for the first term on the right-hand side. These computations lead to

$$\begin{aligned}
&\int_{\mathcal{B}}\left\{\left[\left(\underbrace{-\hat{p}\,\delta_{ij}+\nu h_{k,k}\,\delta_{ij}-h_j\nu_{,i}+\gamma\nu^2\ell\,\delta_{ij}}_{:=T_{ij}}\right)_{,j}+\gamma\nu b_i\right]\delta x_i\right\}\mathrm{d}v\\
&+\int_{\partial\mathcal{B}}\left\{\left[t_i+\underbrace{\left(\hat{p}n_i-\nu h_{k,k}n_i+h_jn_j\nu_{,i}-\gamma\nu^2\ell n_i\right)}_{:=-T_{ij}n_j}\right]\delta x_i\right\}\mathrm{d}a\\
&+\int_{\partial\mathcal{B}}(h_in_i-H)\nu(\delta x_j)_{,j}\,\mathrm{d}a\equiv 0,
\end{aligned}\tag{29.151}$$

which must hold for all δx_i in $\mathcal{B}$ and on $\partial\mathcal{B}$. However, this requires caution in the evaluation of $(\delta x_j)_{,j}$ along the free surface $\partial\mathcal{B}$. This quantity is specified by δx_j everywhere in $\mathcal{B}\cup\partial\mathcal{B}$ except in the direction normal to the boundary $\partial\mathcal{B}$. Letting D_k be the surface gradient and $D_\perp$ the directional derivative perpendicular to $\partial\mathcal{B}$, then we have

$$(\delta x_i)_{,i}=(D_\perp n_i+D_i)\delta x_i,\quad \text{on } \partial\mathcal{B},\tag{29.152}$$

and the last term in (29.151) becomes

$$\int_{\partial\mathcal{B}}\left[(h_in_i-H)\,\nu\left(D_\perp n_j+D_j\right)\delta x_j\right]\mathrm{d}a.\tag{29.153}$$

Substituting (29.153) into (29.151) yields

$$\begin{aligned}
0\equiv&\int_{\mathcal{B}}(T_{ij,j}+\gamma\nu b_i)\delta x_i\,\mathrm{d}v\\
&+\int_{\partial\mathcal{B}}\left[(t_i-T_{ij}n_j)\delta x_i+(h_in_i-H)\nu D_\perp n_i\,\delta x_j+D_j\,\delta x_j)\right]\mathrm{d}a.
\end{aligned}\tag{29.154}$$

As the variations δx_i in $\mathcal{B}\cup\partial\mathcal{B}$ and $D_\perp\,\delta x_j$ on $\partial\mathcal{B}$ are independent, (29.154) implies

$$T_{ij,j}+\gamma\nu b_i=0,\qquad \text{in } \mathcal{B},\tag{29.155}$$

$$t_i=T_{ij}n_j,\quad H=h_in_i,\ \text{on } \partial\mathcal{B},\tag{29.156}$$

in which T_{ij} is defined in the subbraced terms of (29.151), formally,

$$T_{ij}:=-\hat{p}\,\delta_{ij}+\nu h_{k,k}\,\delta_{ij}-h_j\nu_j+\gamma\nu^2\ell\,\delta_{ij}.\tag{29.157}$$

Equation (29.155) is the classical force balance, with the stress tensor defined in (29.157) and the flux boundary conditions in (29.156). They are also given by Goodman and Cowin [7].

Alternative variational formulation (density preserving) For density preserving granules ($\delta\gamma=0$) it was shown in (29.146) that $\delta\nu=-\nu(\delta x_i)_{,i}$. With this, the variational principle (29.123) can be written as

$$\delta \int_{\mathcal{B}} \gamma \nu W \,\mathrm{d}v = \int_{\mathcal{B}} \left[\gamma b_i + \gamma \ell \nu_{,i} + (\gamma \nu \ell)_{,i}\right] \nu\, \delta x_i \,\mathrm{d}v \\ + \int_{\partial \mathcal{B}} \left[\left(t_i + H\nu_{,i} - \gamma \nu^2 \ell n_i\right) \delta x_i - H(\nu \delta x_i)_{,i}\right] \mathrm{d}a, \quad (29.158)$$

in which (29.146) and the divergence theorem have been employed. Next, using mass balance (see (29.126)) and the representation (29.148), along with (29.129)–(29.131) we obtain

$$\gamma \nu \,\delta W = \left(\frac{\hat{p}}{\nu} + \gamma W - h_{j,j}\right)_{,i} \nu\, \delta x_i \\ + \left\{\left(-\hat{p} + h_{j,j}\nu\right) \delta x_i - h_i \left(\nu\, \delta x_j\right)_{,j}\right\}_{,i}. \quad (29.159)$$

Integrating both sides of this equation over the body $\mathcal{B}$ and employing the divergence theorem in the second term in curly brackets yields

$$\int_{\mathcal{B}} \gamma \nu \,\delta W \,\mathrm{d}v = \int_{\mathcal{B}} \left\{\frac{\hat{p}}{\nu} + \gamma W - h_{j,j}\right\}_{,i} \nu\, \delta x_i \,\mathrm{d}v \\ + \int_{\partial \mathcal{B}} \left\{\left(-\hat{p} + h_{j,j}\nu\right) \delta x_i\right\} n_i \,\mathrm{d}a \\ - \int_{\partial \mathcal{B}} h_i \nu (\delta x_j)_{,j} n_i \,\mathrm{d}a. \quad (29.160)$$

This expression must equal the variation of the stored energy (29.147) expressed in terms of the power of the body forces (classical and equilibrated) plus the corresponding workings of the surface forces; this statement can be written in the form

$$0 \equiv \int_{\mathcal{B}} \left\{\gamma b_i + \gamma \ell \nu_{,i} + (\gamma \nu \ell)_{,i} - \left(\frac{\hat{p}}{\nu} + \gamma W - h_{j,j}\right)_{,i}\right\} \nu\, \delta x_i \,\mathrm{d}v \\ + \int_{\partial \mathcal{B}} \left\{t_i + H\nu_{,i} + \left(\hat{p} - h_{j,j}\nu - \gamma \nu^2 \ell\right) n_i\right\} \delta x_i \,\mathrm{d}a \\ + \int_{\partial \mathcal{B}} \left[h_i n_i - H\right] (\nu\, \delta x_j)_{,j} \,\mathrm{d}a, \quad (29.161)$$

an identity, which must hold for arbitrary δx_i in $\mathcal{B}$ and on $\partial \mathcal{B}$ as well as arbitrary gradients of $\nu \delta x_j$ perpendicular to $\partial \mathcal{B}$. Therefore,

$$\frac{\partial}{\partial x_i}\left(\frac{\hat{p}}{\nu} + \gamma W - \nu h_{j,j} - \gamma \nu \ell\right) = \gamma b_i + \gamma \ell \nu_{,i}, \qquad \text{in } \mathcal{B}, \\ t_i + H\nu_{,i} = \left(-\hat{p} + \nu h_{j,j} + \gamma \nu^2 \ell\right) n_i, \quad H = h_i n_i, \quad \text{on } \partial \mathcal{B}. \quad (29.162)$$

These field equations and boundary conditions are equivalent to (29.156), if the stress tensor (29.157) is substituted.[2]

29.A.4 Dynamic Case

To apply the principle of virtual work to the dynamic case we follow the LAGRANGEan method employed in Chap. 26 for liquid crystals with tensorial-order parameter. In this case of a granular assembly the total energy in $\mathcal{B}$ is given in (26.19) as

$$\begin{aligned} \mathcal{F} &= \int_{\mathcal{B}} F \,\mathrm{d}v, \quad \text{with} \\ F &= \rho\left(\boldsymbol{v}\cdot\boldsymbol{v} + \phi + \sigma(\rho) + \kappa(\nu,\dot{\nu}) + \chi(\nu)\right) + W(\nu, \operatorname{grad}\nu), \end{aligned} \tag{29.163}$$

in which the rank-i tensor $\mathbb{O}$ from (26.19) has been replaced by the volume fraction ν; analogous to Chap. 26:

- $\rho = \gamma\nu$ is the mass density,
- $\frac{1}{2}\boldsymbol{v}\cdot\boldsymbol{v}$, the translational kinetic energy of the grains,
- ϕ, the potential energy of the body force, $\boldsymbol{f} = -\operatorname{grad}\phi$,
- $\sigma(\rho)$, the potential energy due to the compressibility of the material,
- $\kappa(\nu, \dot{\kappa})$ the kinetic energy connected with the motion of the volume fraction,
- $\chi(\nu)$, the potential energy of the external actions on ν (which is physically nonrealistic and will be set to zero),
- W is interpreted as an "elastic" energy of the volume fraction and can be associated with the variation of the volume fraction.

Admittedly, some of these quantities are difficult to realistically identify with specific physical facts.

To evaluate the total time derivative of $\mathcal{F}$, we obtain the following individual expressions

$$\begin{aligned} \frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathcal{B}} \tfrac{1}{2}\rho(\boldsymbol{v}\cdot\boldsymbol{v})\mathrm{d}v &= \int_{\mathcal{B}} \rho\dot{\boldsymbol{v}}\cdot\boldsymbol{v}\,\mathrm{d}v, \\ \frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathcal{B}} \rho\phi\,\mathrm{d}v &= \int_{\mathcal{B}} \rho\dot{\phi}\,\mathrm{d}v = -\int_{\mathcal{B}} \rho\boldsymbol{f}\cdot\boldsymbol{v}\,\mathrm{d}v, \\ \frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathcal{B}} \rho\sigma(\rho)\,\mathrm{d}v &= \int_{\mathcal{B}} \rho\underbrace{\frac{\mathrm{d}\sigma}{\mathrm{d}\rho}}_{\sigma'}\dot{\rho}\,\mathrm{d}v = -\int_{\mathcal{B}} \rho^2\sigma'(\rho)\operatorname{div}\boldsymbol{v}\,\mathrm{d}v, \\ \frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathcal{B}} \rho\chi(\nu)\,\mathrm{d}v &= \int_{\mathcal{B}} \rho\dot{\chi}(\nu)\,\mathrm{d}v = \int_{\mathcal{B}} \rho\frac{\partial\chi}{\partial\nu}\dot{\nu}\,\mathrm{d}v, \end{aligned} \tag{29.164}$$

---

[2] COWIN and GOODMAN have a misprint in the stress boundary condition.

$$
\begin{aligned}
\frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathcal{B}} W\,\mathrm{d}v &= \int_{\mathcal{B}}\left\{\frac{\partial W}{\partial \nu}\dot{\nu} + \frac{\partial W}{\partial \operatorname{grad}\nu}(\operatorname{grad}\nu)^{\cdot} + W \operatorname{div}\boldsymbol{v}\right\}\mathrm{d}v \\
\frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathcal{B}} \rho\kappa(\nu,\dot{\nu})\,\mathrm{d}v &= \int_{\mathcal{B}}\rho\,(\kappa(\nu,\dot{\nu}))^{\cdot}\,\mathrm{d}v \overset{*}{=} \int_{\mathcal{B}}\rho\underbrace{\left\{\left(\frac{\partial\kappa}{\partial\dot{\nu}}\right)^{\cdot} - \frac{\partial\kappa}{\partial\nu}\right\}}_{\mathfrak{m}}\dot{\nu}\,\mathrm{d}v \\
&= \int_{\mathcal{B}}\rho\mathfrak{m}\dot{\nu}\,\mathrm{d}v,
\end{aligned}
$$

in which the step ($\overset{*}{=}$) follows from our basic assumption that ν and $\dot{\nu}$ are interpreted as independent generalized coordinates and velocities in a LAGRANGEan formulation (see Appendix 26.A in Chap. 26, (26.19) and 26.206), or see [1]).

Evaluating $\dot{\mathcal{F}}$, with all expressions (29.164) substituted, yields

$$
\begin{aligned}
\dot{\mathcal{F}} = \int_{\mathcal{B}}\Bigg\{&\rho\,(\dot{\boldsymbol{v}} - \boldsymbol{f})\cdot\boldsymbol{v} + \rho\mathfrak{m}\dot{\nu} + \left(\rho\frac{\partial\chi}{\partial\nu} + \frac{\partial W}{\partial\nu}\right)\dot{\nu} + \frac{\partial W}{\partial\operatorname{grad}\nu}(\operatorname{grad}\nu)^{\cdot} \\
&+ \underbrace{\big(W - \rho^2\sigma'(\rho)\big)\operatorname{div}\boldsymbol{v}}_{[(W-\rho^2\sigma')v_i]_{,i}-(W-\rho^2\sigma')_{,i}v_i} + \frac{\partial W}{\partial\operatorname{grad}\nu}\underbrace{(\operatorname{grad}\nu)^{\cdot}}_{\operatorname{grad}\dot{\nu}-\operatorname{grad}\nu\cdot\operatorname{grad}\boldsymbol{v}}\Bigg\}\mathrm{d}v \\
= \int_{\mathcal{B}}\Bigg\{&\rho(\dot{\boldsymbol{v}} - \boldsymbol{f})\cdot\boldsymbol{v} + \rho\mathfrak{m}\dot{\nu} + \left(\rho\frac{\partial\chi}{\partial\nu} + \frac{\partial W}{\partial\nu}\right)\dot{\nu} \\
&+ \underbrace{\frac{\partial W}{\partial\operatorname{grad}\nu}\operatorname{grad}\dot{\nu}}_{[1]} - \underbrace{\frac{\partial W}{\partial\operatorname{grad}\nu}\operatorname{grad}\nu\cdot\operatorname{grad}\boldsymbol{v}}_{[2]} - \big(W - \rho^2\sigma'(\rho)\big)_{,i}\,v_i\Bigg\}\mathrm{d}v \\
&+ \int_{\partial\mathcal{B}}\big[\big(W - \rho^2\sigma'\big)\,v_i\big]\,n_i\,\mathrm{d}a,
\end{aligned}
$$

in which

$$
\begin{aligned}
[1] = \int_{\mathcal{B}}\frac{\partial W}{\partial\nu_{,i}}\dot{\nu}_{,i}\,\mathrm{d}v &= \int_{\mathcal{B}}\left\{\left(\frac{\partial W}{\partial\nu_{,i}}\dot{\nu}\right)_{,i} - \left(\frac{\partial W}{\partial\nu_{,i}}\right)_{,i}\dot{\nu}\right\}\mathrm{d}v \\
&= \int_{\partial\mathcal{B}}\frac{\partial W}{\partial\operatorname{grad}\nu}\cdot\boldsymbol{n}\dot{\nu}\,\mathrm{d}a - \int_{\mathcal{B}}\operatorname{div}\left(\frac{\partial W}{\partial\operatorname{grad}\nu}\right)\dot{\nu}\,\mathrm{d}v \\
[2] = \int_{\mathcal{B}}\frac{\partial W}{\partial\nu_{,i}}\nu_{,k}v_{k,i}\,\mathrm{d}v &= \int_{\mathcal{B}}\left[\left(\frac{\partial W}{\partial\nu_{,i}}\nu_{,k}v_k\right)_{,i} - \left(\frac{\partial W}{\partial\nu_{,i}}\nu_{,k}\right)_{,i}v_k\right]\mathrm{d}v \\
&= \int_{\partial\mathcal{B}}\frac{\partial W}{\partial\nu_{,i}}\nu_{,k}v_k n_i\,\mathrm{d}a \qquad - \int_{\mathcal{B}}\left(\frac{\partial W}{\partial\nu_{,i}}\nu_{,k}\right)_{,i}v_k\,\mathrm{d}v \\
&= \int_{\partial\mathcal{B}}\left[\left(\operatorname{grad}\nu\odot\frac{\partial W}{\partial\operatorname{grad}\nu}\right)\boldsymbol{n}\cdot\boldsymbol{v}\right]\mathrm{d}a
\end{aligned}
$$

$$-\int_{\mathcal{B}} \operatorname{div}\left\{\operatorname{grad}\nu \odot \frac{\partial W}{\partial \operatorname{grad}\nu}\right\} \cdot \boldsymbol{v}\,\mathrm{d}v.$$

Recall that, if $\boldsymbol{a}, \boldsymbol{b}$ are vectors in $\mathbb{R}^3$, then $(\boldsymbol{a} \odot \boldsymbol{b})_{ik} = a_k b_i$ which equals $(\boldsymbol{a} \otimes \boldsymbol{b})^T$. Therefore,

$$\begin{aligned}
\dot{\mathcal{F}} = \int_{\mathcal{B}} \Bigg\{ & \rho(\dot{\boldsymbol{v}} - \boldsymbol{f}) \cdot \boldsymbol{v} + \rho\mathfrak{m}\dot{\nu} + \left(\rho\frac{\partial \chi}{\partial \nu} + \frac{\partial W}{\partial \nu}\right)\dot{\nu} - \operatorname{div}\left(\frac{\partial W}{\partial \operatorname{grad}\nu}\right)\dot{\nu} \\
& + \operatorname{div}\left(\operatorname{grad}\nu \odot \frac{\partial W}{\partial \operatorname{grad}\nu}\right) \cdot \boldsymbol{v} - \left(W - \rho^2\sigma'(\rho)\right)\boldsymbol{v} \Bigg\}\,\mathrm{d}v \\
& + \int_{\partial\mathcal{B}} \Bigg\{ \left[\left(W - \rho^2\sigma'\right)\boldsymbol{n} \cdot \boldsymbol{v} + \frac{\partial W}{\partial \operatorname{grad}\nu} \cdot \boldsymbol{n}\dot{\nu}\right] \\
& - \left(\operatorname{grad}\nu \odot \frac{\partial W}{\partial \operatorname{grad}\nu}\right)\boldsymbol{n} \cdot \boldsymbol{v} \Bigg\}\,\mathrm{d}a. \qquad (29.165)
\end{aligned}$$

In classical mechanics $\dot{\mathcal{F}}$ is the total power input into a mechanical system. Here, this is not so, because (29.165) contains surface terms, which may unduly constrain the potentials W and σ' without generalized surface forces. The power $\mathcal{W}^s$ of surface forces for a moving boundary $\partial\mathcal{B}$ can be written in the form

$$\mathcal{W}^s = \int_{\partial\mathcal{B}} \left\{\boldsymbol{X}^s \cdot \boldsymbol{v} + \xi^s \dot{\nu}\right\}\mathrm{d}a, \qquad (29.166)$$

in which $\boldsymbol{v}$ and $\dot{\nu}$ are independent generalized velocities. Moreover, if the surface power can be derived from a potential, i.e., if

$$\mathcal{W}^s = \frac{\mathrm{d}}{\mathrm{d}t}\int_{\partial\mathcal{B}} W^s(\boldsymbol{x}, \nu)\,\mathrm{d}a, \qquad (29.167)$$

in which W^s is a scalar potential of position and solid volume fraction, then the relations

$$\boldsymbol{X}^s = \frac{\partial W^s}{\partial \boldsymbol{x}}, \quad \text{and} \quad \xi^s = \frac{\partial W^s}{\partial \nu} \qquad (29.168)$$

ensue. Adding (29.166) to the expression (29.165) now provides the possibility to relate $\boldsymbol{X}^s$ and ξ^s to W and σ'. Explicitly, $\dot{\mathcal{F}} + \mathcal{W}^s$ can now be written as stated already in (26.29), namely as

$$\begin{aligned}
\dot{\mathcal{F}} + \mathcal{W}^s = & \int_{\mathcal{B}} \left\{\boldsymbol{X} \cdot \boldsymbol{v} + \xi^s \dot{\nu}\right\}\mathrm{d}v \\
& + \int_{\partial\mathcal{B}} \left\{\left(\boldsymbol{X}^b + \boldsymbol{X}^s\right) \cdot \boldsymbol{v} + \left(\xi^b + \xi^s\right)\dot{\nu}\right\}\mathrm{d}a, \qquad (29.169)
\end{aligned}$$

in which

$$\left.\begin{aligned} \boldsymbol{X} &= \rho(\boldsymbol{v} - \boldsymbol{f}) - \operatorname{grad}(W - \rho^2\sigma') + \operatorname{div}\left(\operatorname{grad}\nu \odot \frac{\partial W}{\partial \operatorname{grad}\nu}\right) \\ \xi &= \rho\left(\mathfrak{m} + \frac{\partial \chi}{\partial \nu}\right) + \frac{\partial W}{\partial \nu} - \operatorname{div}\left(\frac{\partial W}{\partial \operatorname{grad}\nu}\right) \end{aligned}\right\} \text{ in } \mathcal{B}, \tag{29.170}$$

$$\left.\begin{aligned} \boldsymbol{X}^b &= \left(W - \rho^2\sigma'\right)\boldsymbol{n} - \left(\operatorname{grad}\nu \odot \frac{\partial W}{\partial \operatorname{grad}\nu}\boldsymbol{n}\right) \\ \xi^b &= \frac{\partial W}{\partial \operatorname{grad}\nu} \cdot \boldsymbol{n} \end{aligned}\right\} \text{ on } \partial\mathcal{B}.$$

We repeat, as we already pointed out in Chap. 26, p. 288: It is physically significant to note that the surface integral in (29.169) with generalized forces $\boldsymbol{X}^s$ and ξ^s was introduced in (29.168). In the absence of dissipative terms we will prove that $\boldsymbol{X}^s + \boldsymbol{X}^b = \boldsymbol{0}$, $\xi^s + \xi^b = 0$. So, when $W^s \equiv 0$ then $\boldsymbol{X}^b$ and ξ^b would have to separately vanish, which would constrain the functions W and σ.

To avoid this situation, we now introduce, following Lord RAYLEIGH [18] or SONNET and VIRGA [17], see Chap. 26, (26.31), the dissipation potential as a frame indifferent functional of the stretching tensor $\boldsymbol{D}$, the volume fraction ν and its rate $\dot{\nu}$; explicitly

$$\mathcal{R} = \int_{\mathcal{B}} R \,\mathrm{d}v, \quad R = R(\nu, \dot{\nu}, \boldsymbol{D}). \tag{29.171}$$

We suppose R to be a bilinear function of $\dot{\nu}$ and $\boldsymbol{D}$; writing it in terms of $\dot{\nu}$ and $\operatorname{grad}\nu$, we have

$$\delta\mathcal{R} = \int_{\mathcal{B}} \left\{ \frac{\partial R}{\partial \dot{\nu}}\delta\dot{\nu} + \underbrace{\frac{\partial R}{\partial \operatorname{grad}\nu} \cdot \underbrace{\delta(\operatorname{grad}\boldsymbol{v})}_{\operatorname{grad}(\delta\boldsymbol{v})}}_{[1]} \right\} \mathrm{d}v,$$

where

$$[1] = \frac{\partial R}{\partial v_{i,j}}(\delta v_i)_{,j} = \left(\frac{\partial R}{\partial v_{i,j}}\delta v_i\right)_{,j} - \left(\frac{\partial R}{\partial v_{i,j}}\right)_{,j}\delta v_i,$$

implying

$$\begin{aligned} \delta\mathcal{R} &= \int_{\partial\mathcal{B}} \left(\frac{\partial R}{\partial \operatorname{grad}\boldsymbol{v}}\boldsymbol{n}\right) \cdot \delta\boldsymbol{v}\,\mathrm{d}a \\ &\quad + \int_{\mathcal{B}} \left\{ \frac{\partial R}{\partial \dot{\nu}}\,\delta\dot{\nu} - \operatorname{div}\left(\frac{\partial R}{\partial \operatorname{grad}\boldsymbol{v}}\right) \cdot \delta\boldsymbol{v} \right\} \mathrm{d}v, \end{aligned} \tag{29.172}$$

or, since $\partial R/\partial \mathrm{grad}\,\boldsymbol{v} = \partial R/\partial \boldsymbol{D}$,

$$\begin{aligned}\delta\mathcal{R} &= \int_{\partial\mathcal{B}} \left(\frac{\partial R}{\partial \boldsymbol{D}}\boldsymbol{n}\right)\cdot \delta\boldsymbol{v}\,\mathrm{d}a \\ &\quad + \int_{\mathcal{B}} \left\{\frac{\partial R}{\partial \dot{\nu}}\,\delta\dot{\nu} - \mathrm{div}\left(\frac{\partial R}{\partial \boldsymbol{D}}\right)\cdot \delta\boldsymbol{v}\right\}\mathrm{d}v.\end{aligned} \tag{29.173}$$

Here, $\boldsymbol{n}$ is the outward unit normal vector on $\partial\mathcal{B}$, and the divergence theorem has been used to obtain (29.173).

With (29.169), (29.170) and (29.173), all elements are now at disposal to apply the principle of virtual power, which requires

$$\delta(\dot{\mathcal{F}} + \mathcal{W}^s) + \delta\mathcal{R} = 0, \quad \forall\{\delta\boldsymbol{v}, \delta\dot{\nu}\}, \tag{29.174}$$

with the understanding that the generalized forces and their power of working remain constant during the variation, see also Chap. 26, Eqs. (26.8) and (26.11). Consequently, with (29.169), (29.170), and (29.173), we have

$$\left.\begin{aligned}\boldsymbol{X} - \mathrm{div}\left(\frac{\partial R}{\partial \boldsymbol{D}}\right) &= \boldsymbol{0} \\ \xi + \frac{\partial R}{\partial \dot{\nu}} &= 0\end{aligned}\right\} \quad \text{in } \mathcal{B}, \tag{29.175}$$

$$\left.\begin{aligned}&\boldsymbol{X}^b + \boldsymbol{X}^s + \frac{\partial R}{\partial \boldsymbol{D}}\cdot\boldsymbol{n} = \boldsymbol{0} \\ &\xi^b + \xi^s = 0\end{aligned}\right\} \quad \text{on } \partial\mathcal{B}. \tag{29.176}$$

These equations, with the interpretations (29.170), are the equations of motion in $\mathcal{B}$ and the boundary conditions on $\partial\mathcal{B}$. Note that $\boldsymbol{X}^b + \boldsymbol{X}^s = \boldsymbol{0}$ and $xi^b + \xi^s = 0$ if effects of dissipation are ignored. In this limited case, $\boldsymbol{X}^s$ and ξ^s are nonzero, since $\boldsymbol{X}^b \neq \boldsymbol{0}$ and $\xi^b \neq 0$. According to $(29.170)_{3,4}$, as stated earlier, their vanishing would severely constrain the potentials W and σ on the free surfaces.

Explicitly, the momentum equations $(29.175)_1$ take the forms

$$\begin{aligned}\rho\dot{\boldsymbol{v}} &= \rho\boldsymbol{f} + \mathrm{div}\,\big((W - \rho^2\sigma')\boldsymbol{I}\big) \\ &\quad -\mathrm{div}\left(\mathrm{grad}\,\nu \odot \frac{\partial W}{\partial \mathrm{grad}\,\nu}\right) + \mathrm{div}\left(\frac{\partial R}{\partial \boldsymbol{D}}\right),\end{aligned} \tag{29.177}$$

from which the stress tensor can directly be read off:

$$\boldsymbol{T} = (W - \rho^2\sigma')\boldsymbol{I} - \mathrm{grad}\,\nu \odot \frac{\partial W}{\partial \mathrm{grad}\,\nu} + \frac{\partial R}{\partial \boldsymbol{D}}. \tag{29.178}$$

Since W must be objective, it can be written as $W = \hat{W}(\nu, g)$, $g := \frac{1}{2}\mathrm{grad}\,\nu\cdot\mathrm{grad}\,\nu$; all three terms on the right-hand side of (29.178) are now symmetric, so that $\boldsymbol{T} = \boldsymbol{T}^T$.

In particular,

$$\begin{aligned}\operatorname{grad}\nu \odot \frac{\partial W}{\partial \operatorname{grad}\nu} &= \frac{\partial \hat{W}}{\partial g}\operatorname{grad}\nu \otimes \operatorname{grad}\nu \\ &\overset{\hat{W}=f(\nu)g}{=} f(\nu)\operatorname{grad}\nu \otimes \operatorname{grad}\nu. \end{aligned} \tag{29.179}$$

Moreover, the dissipative term $\partial R/\partial \boldsymbol{D}$ does not need to be restricted to NEWTONian behavior, viz.,

$$\frac{\partial R}{\partial \boldsymbol{D}} = \kappa(\operatorname{div}\boldsymbol{v})\boldsymbol{I} + 2\mu\left(\boldsymbol{D} - \tfrac{1}{3}(\operatorname{div}\boldsymbol{v})\right)\boldsymbol{I}$$

with bulk, κ, and shear, μ, viscosity. For isotropic behavior the function R in (29.171) takes the form

$$R = R(\nu, \dot{\nu}, I_{\boldsymbol{D}}, II_{\boldsymbol{D}}, III_{\boldsymbol{D}}), \tag{29.180}$$

where $I_{\boldsymbol{D}}$, $II_{\boldsymbol{D}}$, $III_{\boldsymbol{D}}$ are the invariants of the stretching tensor $\boldsymbol{D}$. It is convenient to separate the $(\nu, \dot{\nu})$-dependence of R from the dependence on $\boldsymbol{D}$. Instead of (29.180), we shall, therefore, write

$$R = r(\nu, \dot{\nu})\tilde{R}(I_{\boldsymbol{D}}, II_{\boldsymbol{D}}, III_{\boldsymbol{D}}), \tag{29.181}$$

and then may write

$$\boldsymbol{T}_{\text{diss}} = r(\nu, \dot{\nu})\left\{\frac{\partial \tilde{R}}{\partial I_{\boldsymbol{D}}}\frac{\partial I_{\boldsymbol{D}}}{\partial \boldsymbol{D}} + \frac{\partial \tilde{R}}{\partial II_{\boldsymbol{D}}}\frac{\partial II_{\boldsymbol{D}}}{\partial \boldsymbol{D}} + \frac{\partial \tilde{R}}{\partial III_{\boldsymbol{D}}}\frac{\partial III_{\boldsymbol{D}}}{\partial \boldsymbol{D}}\right\}. \tag{29.182}$$

For the principal invariants one may deduce (see HUTTER and JÖHNK [8], pp. 46–49)

$$\begin{aligned} &\frac{\partial I_{\boldsymbol{D}}}{\partial \boldsymbol{D}} = \boldsymbol{I}, \qquad \frac{\partial II_{\boldsymbol{D}}}{\partial \boldsymbol{D}} = I_{\boldsymbol{D}}\boldsymbol{I} - \boldsymbol{D}, \\ &\frac{\partial III_{\boldsymbol{D}}}{\partial \boldsymbol{D}} = \boldsymbol{D}^{-1}III_{\boldsymbol{D}} = \left\{\boldsymbol{D}^2 - I_{\boldsymbol{D}}\boldsymbol{D} + II_{\boldsymbol{D}}\boldsymbol{I}\right\}, \end{aligned} \tag{29.183}$$

in which $\boldsymbol{D}$ must be symmetric and the CALEY-HAMILTON theorem has also been used. Substituting (29.183) into (29.182) leads to the following expression for the dissipative CAUCHY stress

$$\boldsymbol{T}_{\text{diss}} = r(\nu, \dot{\nu})\left[\phi_0\boldsymbol{I} + \phi_1\boldsymbol{D} + \phi_2\boldsymbol{D}^2\right], \tag{29.184}$$

where

$$\begin{aligned}\phi_0 &= \frac{\partial\tilde{R}}{\partial I_{\boldsymbol{D}}} + \frac{\partial\tilde{R}}{\partial II_{\boldsymbol{D}}} I_{\boldsymbol{D}} + \frac{\partial\tilde{R}}{\partial III_{\boldsymbol{D}}} II_{\boldsymbol{D}},\\ \phi_1 &= -\left(\frac{\partial\tilde{R}}{\partial II_{\boldsymbol{D}}} - \partial\frac{\tilde{R}}{\partial III_{\boldsymbol{D}}} I_{\boldsymbol{D}}\right),\\ \phi_2 &= \frac{\partial\tilde{R}}{\partial III_{\boldsymbol{D}}}.\end{aligned} \tag{29.185}$$

This stress representation possesses the structure of a REINER–RIWLIN fluid. Notice that in case $\tilde{R}$ does not depend upon the third invariant $III_{\boldsymbol{D}}$, the dependence on $\boldsymbol{D}^2$ in (29.184) drops out and the ϕ-dependences simplify to

$$\phi_0 = \frac{\partial\tilde{R}}{\partial I_{\boldsymbol{D}}} + \frac{\partial\tilde{R}}{\partial II_{\boldsymbol{D}}} I_{\boldsymbol{D}}, \quad \phi_1 = \frac{\partial\tilde{R}}{\partial II_{\boldsymbol{D}}}, \quad \phi_2 = 0, \quad \text{if } \tilde{R} \neq \tilde{R}(\cdot, III_{\boldsymbol{D}}). \tag{29.186}$$

Note, moreover, a density preserving granular material ($\gamma = \text{const.}$) is not necessarily volume preserving. Its bulk viscosity is $\mu_{\text{bulk}} r(\nu, \dot{\nu})\phi_0$, while its shear viscosity is given by $\mu_{\text{shear}} = r(\nu, \dot{\nu})\phi_1$. However, if we ignore both $I_{\boldsymbol{D}}$- and $III_{\boldsymbol{D}}$-dependences of $\tilde{R}$, then the bulk viscosity vanishes. In this case, the dissipative stress reduces simply to

$$\boldsymbol{T}_{\text{diss}} = r(\nu, \dot{\nu})\phi_1 \boldsymbol{D}, \quad \phi_1 = \frac{\partial\tilde{R}}{\partial II'_{\boldsymbol{D}}} \quad II'_{\boldsymbol{D}} = \tfrac{1}{2} I_{\boldsymbol{D}^2}. \tag{29.187}$$

Except for the $r(\nu, \dot{\nu})$-dependence this law corresponds to the classical viscous shearing behavior, known in fluid mechanics as dilatant and pseudoplastic behavior (see e.g., [11], pp. 366–371). Popular examples are so-called power laws.

The second equation of motion (for the evolution of the volume fraction) is obtained by combining $(29.175)_2$ with $(29.170)_2$ and using the definition of $\mathfrak{m}$ given in (29.164). This yields

$$\gamma\nu\left\{\left(\frac{\partial\kappa}{\partial\dot{\nu}}\right)^{\cdot} - \frac{\partial\kappa}{\partial\nu}\right\} + \frac{\partial W}{\partial\nu} - \operatorname{div}\left(\frac{\partial W}{\partial \operatorname{grad}\nu}\right) + \frac{\partial R}{\partial\dot{\nu}} = 0. \tag{29.188}$$

With the stored energy function $W = \hat{W}(\nu, g)$, $g := \frac{1}{2}\operatorname{grad}\nu \cdot \operatorname{grad}\nu$ and the volume fraction kinetic energy κ given by

$$\hat{W} = \mathfrak{f}(\nu)g \quad \text{and} \quad \kappa(\nu, \dot{\nu}) = \tfrac{1}{2}k(\nu)\dot{\nu}^2, \tag{29.189}$$

(both are quadratic in grad ν and $\dot{\nu}$) one easily deduces

$$\gamma\nu\left\{k(\nu)\ddot{\nu}+\tfrac{1}{2}k'(\nu)\dot{\nu}^2\right\}-\mathfrak{f}'(\nu)g-\mathfrak{f}(\nu)\Delta\nu+\frac{\partial R}{\partial\dot{\nu}}=0. \tag{29.190}$$

The Eqs. (29.188) and (29.190) look more general than that introduced in [7],

$$\gamma\nu k\ddot{\nu}+\operatorname{div}\boldsymbol{h}-\gamma\nu f=0. \tag{29.191}$$

It is evident that the coefficient of equilibrated inertia must be a material constant as a condition to reach agreement between the field equations derived by the balance law and variational approaches. This may well be the reason why Eringen in his writings of micro-morphic continua postulates explicitly a conservation law of equilibrated inertia $k_{\mathfrak{a}}=0$ ($\mathfrak{a}=1,\dots$) in mixture formulations (see also Chap. 30, (30.5)). On the other hand, it is easy to verify that

$$\begin{aligned}\boldsymbol{h}&=-\frac{\partial\hat{W}}{\partial g}\operatorname{grad}\nu=-\mathfrak{f}(\nu)\operatorname{grad}\nu,\\ f&=\frac{1}{\gamma\nu}\frac{\partial\hat{W}}{\partial\nu}g=\tfrac{1}{2}\mathfrak{f}'(\nu)\operatorname{grad}\nu\cdot\operatorname{grad}\nu.\end{aligned} \tag{29.192}$$

Thus, there is a one-to-one correspondence of the differential equations for the fluid velocity $\boldsymbol{v}$ and the volume fraction ν between the variational and balance law derivation of the field equations. Incorporating the dissipation potential $\mathcal{R}$ the variational method has gone beyond the balance law approach, since it delivered explicit formulae for the dissipative stress given in (29.184) and (29.185). Moreover, with the introduction of the dissipative surface potential W^s, it also delivers in $(29.170)_{3,4}$ boundary conditions for the surface forces $\boldsymbol{X}^b$ and ξ^b.

References

1. Capriz, G.: Continua with Microstructure. Springer, New York (1989)
2. Cowin, S.C., Goodman, M.A.: A variational principle for granular materials. ZAMM **56**, 281–286 (1976)
3. Fang, C., Wang, Y., Hutter, K.: A thermo-mechanical continuum theory with internal length for cohesionless granular materials. Part I: a class of constitutive models. Contin. Mech. Thermodyn. **17**(8), 545–576 (2006)
4. Fang, C., Wang, Y., Hutter, K.: A thermo-mechanical continuum theory with internal length for cohesionless granular materials. Part II: non-equilibrium postulates and numerical simulations of simple shear, plane Poiseuille and gravity driven problems. Contin. Mech. Thermodyn. **17**(8), 577–607 (2006)
5. Goodman, M.A.: Continuum theory for the dynamical behaviour of granular materials. Dissertation, Tulane University (1969)
6. Goodman, M.A., Cowin, S.C.: Two problems in the gravity flow of granular materials. J. Fluid Mech. **45**, 321–339 (1971)
7. Goodman, M.A., Cowin, S.C.: A continuum theory for granular materials. Arch. Ration. Mech. Anal. **44**, 249–266 (1972)

8. Hutter, K., Jöhnk, K.: Continuum Methods of Physical Modeling, p. 635. Springer, Berlin (2004)
9. Hutter, K., Rajagopal, K.R.: On flows of granular materials. Contin. Mech. Thermodyn. **6**, 81–139 (1994)
10. Hutter, K., Szidarovsky, F., Yakowitz, S.: Plane steady flow of a cohesionless granular material down an inclined plane: a model for flow avalanches. Part II: numerical results. Acta Mech. **65**, 239–261 (1986)
11. Hutter, K., Wang, Y.: Fluid and Thermodynamics. Vol. 1: Basic Fluid Mechanics, p. 639. Springer, Berlin (2016). https://doi.org/10.1007/978-3-319.33633-6
12. Jenkins, J.T.: Static equilibrium of granular materials. J. Appl. Mech. **42**, 603–606 (1975)
13. Liu, I.-S.: Method of Lagrange multipliers for exploitation of the entropy principle. Arch. Ration. Mech. Anal. **46**, 131–148 (1972)
14. Müller, I.: Die Kältefunktion, eine universelle Funktion in der Thermodynamik viskoser wärmeleitender Flüssigkeiten Arch. Ration. Mech. Anal. https://doi.org/10.1007/BF00281528 (1971)
15. Passman, S.L., Nunziato, J.W., Bailey, P.B., Thomas, J.P.: Shearing flows of granular materials. J. Eng. Mech. Div. ASCE **106**, 773–783 (1980)
16. Savage, S.B.: Gravity flow of cohesionless granular materials in chutes and channels. J. Fluid Mech. **92**(1), 53–96 (1979)
17. Sonnet, A.M., Virga, E.G.: Dynamics of dissipative ordered fluids. Phys. Rev. E **64**(3), 031705-1-10 (2001)
18. Strutt, J.W.: (Lord Rayleigh): Some general theorems relating to vibrations. Proc. Lond. Math. Soc. **4**, 357–368 (1873)
19. Svendsen, B., Hutter, K.: On the thermodynamics of a mixture of isotropic materials with constraints. Int. J. Eng. Sci. **33**, 2021–2054 (1995)
20. Wang, Y., Hutter, K.: Shearing flows in a Goodman-Cowin type granular material - theory and numerical results. Part. Sci. Technol. **17**, 97–124 (1999)
21. Wang, Y., Hutter, K.: A constitutive model of multiphase mixtures and its application in shearing flows of saturated solid-fluid mixtures. Granul. Matter **1**, 163–181 (1999)
22. Wilmanski, K.: Macroscopic theory of evaluation of deformation textures. Int. J. Plast. **8**, 959–975 (1992)
23. Wilmanski, K.: The thermodynamical model of compressible porous materials with the balance equation of porosity. Preprint No. 310. (ed.) by Weierstra"s-Institute für Angewandte Analysis und Stochastik, Berlin (1997)

Chapter 30
A Granular Mixture Model with Goodman–Cowin-Type Microstructure and its Application to Shearing Flows in Binary Solid–Fluid Bodies

Abstract A continuum theory of a granular mixture is formulated. In the basic balance laws, we introduce an additional balance of equilibrated forces to describe the microstructural response according to GOODMAN and COWIN (Arch Rational Mech Anal, 44:249–266,1972, [10]) and PASSMAN et al. (Rational Thermodynamics, Springer, New York, pp. 286–325, 1984, [18]) for each constituent. Based on the MÜLLER–LIU form of the second law of thermodynamics, a set of constitutive equations for a viscous solid–fluid mixture with microstructure is derived. These relatively general equations are then reduced to a system of ordinary differential equations describing a steady flow of the solid–fluid mixture between two horizontal plates. The resulting boundary value problem is solved numerically and results are presented for various values of parameters and boundary conditions. It is shown that simple shearing generally does not occur. Typically, for the solid phase, in the vicinity of a boundary, if the solid volume fraction is small, a layer of high shear rate occurs, whose thickness is nearly between 5 and 15 grain diameters, while if the solid volume fraction is high, an interlock phenomenon occurs. The fluid velocity depends largely on the drag force between the constituents. If the drag coefficient is sufficiently large, the fluid flow is nearly the same as that of the solid, while for a small drag coefficient, the fluid shearing flow largely decouples from that of the solid in the entire flow region. Apart from this, there is a tendency for solid particles to accumulate in regions of low shear rate.

Keywords Granular materials · Solid–fluid mixture · GOODMAN–COWIN-type microstructure · Viscous fluid · Constitutive behavior · Shearing flows in binary mixtures

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This chapter is heavily based on the paper by WANG and HUTTER [26].

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List of Symbols

Roman Symbols

$\boldsymbol{\mathcal{A}}_\mathfrak{a}$	Tensorial parameter to evaluate $\boldsymbol{h}_\mathfrak{a}$, see (30.62), $\mathcal{A}_\mathfrak{a} = 2\rho_\mathfrak{a}\partial\psi_\mathfrak{a}/\partial(\text{grad}\,\nu_\mathfrak{a} \cdot \text{grad}\,\nu_\mathfrak{a})$, $(\mathfrak{a} = 1, \dots, N)$
a_s, (a_f)	Coefficients in the parameterizations of ϕ_s, (ϕ_f), see (30.93), (30.94)
$\boldsymbol{a} = \boldsymbol{0}$	LIU identities
$\mathfrak{a}$ $(\mathfrak{a} = 1, ..., N)$	Identifier of the $\mathfrak{a}$th constituent
$b > 0$	Residual entropy inequality
$\boldsymbol{b}_\mathfrak{a}$	Body force of constituent $\mathfrak{a}$
$\mathcal{C}$	List of dependent constitutive variables
$c_\mathfrak{a}^+$	Production rate density of the $\mathfrak{a}$th mass balance
$\boldsymbol{D}_\mathfrak{a}$	Strain rate (stretching) tensor of constituent $\mathfrak{a}$
$e_\mathfrak{a}^+$	Production rate density of the total energy of constituent $\mathfrak{a}$
$f_\mathfrak{a}$	Intrinsic equilibrated body force of constituent $\mathfrak{a}$
$f_\mathfrak{a}^E$	Equilibrium value of $f_\mathfrak{a}$
$f_\mathfrak{a}^D$	Dynamic contribution to $f_\mathfrak{a}$
$\mathcal{F}_\mathfrak{b}$	Set of independent constitutive variables of constituent $\mathfrak{a}$
$g_\mathfrak{a}^+$	Production rate density of the $\mathfrak{a}$th equilibrated force
$\boldsymbol{h}_\mathfrak{a}$	Flux vector of equilibrated force of constituent $\mathfrak{a}$
$\boldsymbol{I}$	Unit matrix (tensor) in $\mathbb{R}^2$ or in $\mathbb{R}^3$
$\boldsymbol{j}$	Mixture flux density, $\boldsymbol{j} = -\theta\boldsymbol{\phi} + \boldsymbol{q}$
$\boldsymbol{j}_\mathfrak{a}$	Constituent flux density, $\boldsymbol{j}_\mathfrak{a} = -\theta\boldsymbol{\phi}_\mathfrak{a} + \boldsymbol{q}_\mathfrak{a}$
$\boldsymbol{j}_I$	$\boldsymbol{j}_I = \sum_\mathfrak{a} \boldsymbol{j}_\mathfrak{a}$
$\boldsymbol{j}_c$	Mixture constituent flux density, see (30.29)
$k_\mathfrak{a}$	Density of equilibrated inertia of constituent $\mathfrak{a}$
$\boldsymbol{L}_\mathfrak{a}$	Velocity gradient of constituent $\mathfrak{a}$, $\boldsymbol{L}_\mathfrak{a} = \text{grad}\,\boldsymbol{v}_\mathfrak{a}$
$\ell_\mathfrak{a}$	External equilibrated force of constituent $\mathfrak{a}$
$\boldsymbol{m}_\mathfrak{a}^+$	Production rate density of linear momentum of constituent $\mathfrak{a}$
$\boldsymbol{m}_\mathfrak{a}^{+E}$	Equilibrium value of $\boldsymbol{m}_\mathfrak{a}^+$
$\boldsymbol{m}_\mathfrak{a}^{+D}$	Dynamic contribution to $\boldsymbol{m}_\mathfrak{a}^+$
m_D	Diffusion coefficient for $\boldsymbol{m}_\mathfrak{a}^{+D}$
$p_\mathfrak{a} :=$	$\gamma_\mathfrak{a}^2\partial\psi_\mathfrak{a}/\partial\gamma_\mathfrak{a}$
p_s, (p_f)	Solid (fluid) pressure
$\boldsymbol{q}_\mathfrak{a}$	Heat (energy) flux vector of constituent $\mathfrak{a}$
$\boldsymbol{q}$	Heat (energy) flux vector of the mixture
$\boldsymbol{q}^E = \boldsymbol{0}$	Equilibrium value of $\boldsymbol{q}$
$\boldsymbol{r}$	Radius vector from the coordinate origin to a particle $\mathfrak{a}$
r	Heat supply to the mixture
$r_\mathfrak{a}$	Heat supply to constituent $\mathfrak{a}$
s	Entropy supply to the mixture

$s_\mathfrak{a}$	Entropy supply to the constituent $\mathfrak{a}$
$\mathcal{S}_\mathfrak{a}$	Set of independent constitutive variables
$\boldsymbol{T}$	CAUCHY stress of the mixture
$\boldsymbol{T}_\mathfrak{a}$	CAUCHY stress tensor of constituent $\mathfrak{a}$
$\boldsymbol{T}^E_\mathfrak{a}$	Equilibrium value of $\boldsymbol{T}_\mathfrak{a}$
$\boldsymbol{T}^D_\mathfrak{a}$	Dynamic contribution of $\boldsymbol{T}_\mathfrak{a}$
$\boldsymbol{u}_\mathfrak{a} = \boldsymbol{v}_\mathfrak{a} - \boldsymbol{v}$	Diffusion velocity of constituent $\mathfrak{a}$
$\boldsymbol{v}$	Mixture velocity, $\rho\boldsymbol{v} = \sum_\mathfrak{a} \rho_\mathfrak{a}\boldsymbol{v}_\mathfrak{a}$
$\boldsymbol{v}_\mathfrak{a}$	Velocity of constituent $\mathfrak{a}$
$\boldsymbol{W}_\mathfrak{a}$	Vorticity tensor of the constituent $\mathfrak{a}$, $\boldsymbol{W}_\mathfrak{a} = \frac{1}{2}(\operatorname{grad}\boldsymbol{v}_\mathfrak{a} - (\operatorname{grad}\boldsymbol{v}_\mathfrak{a})^T)$
$\boldsymbol{W}$	Vorticity tensor of the mixture, $\boldsymbol{W} = \frac{1}{2}(\operatorname{grad}\boldsymbol{v} - (\operatorname{grad}\boldsymbol{v})^T)$
$\boldsymbol{\mathcal{W}}_\mathfrak{a} = \boldsymbol{W}_\mathfrak{a} - \boldsymbol{W}$	Objective vorticity tensor of constituent $\mathfrak{a}$
$\boldsymbol{Y}$	Nonequilibrium-independent dynamic constitutive variables.

Greek Symbols

$\boldsymbol{\alpha}$	Vector of physical quantities formed as derivatives of the independent constitutive variables
$\beta_\mathfrak{a}$	Configurational pressure, $\beta_\mathfrak{a} := \rho_\mathfrak{a}\partial\psi_\mathfrak{a}/\partial\nu_\mathfrak{a}$
$\gamma_\mathfrak{a}$	True density of constituent $\mathfrak{a}$
$\delta_{\mathfrak{a}\mathfrak{b}}$	KRONECKER delta
ε	Internal energy density of the mixture
$\varepsilon_\mathfrak{a}$	Internal energy density of the constituent $\mathfrak{a}$
$\varepsilon_I = \sum_\mathfrak{a} \xi_\mathfrak{a}\varepsilon_\mathfrak{a}$	Intrinsic internal energy of the mixture
η	Entropy density of the mixture
$\eta_\mathfrak{a}$	Entropy density of constituent $\mathfrak{a}$
$\eta^+_\mathfrak{a}$	Entropy production density of constituent $\mathfrak{a}$
θ	Empirical temperature, absolute KELVIN temperature
$\lambda_\mathfrak{a}$	Dissipation parameter for $f^D_\mathfrak{a}$, see (30.79)
$\lambda^\nu_\mathfrak{a}$	LAGRANGE multiplier of the balance law of constituent $\mathfrak{a}$
$\boldsymbol{\lambda}_\mathfrak{a}$	LAGRANGE multiplier of the momentum equation of constituent $\mathfrak{a}$
$\lambda^k_\mathfrak{a}$	LAGRANGE multiplier of the balance law of the equilibrated forces of constituent $\mathfrak{a}$
λ^ε	LAGRANGE multiplier of the mixture energy equation
$\mu_\mathfrak{a}$	Viscosity for constituent $\mathfrak{a}$
$\bar{\mu}_s$	Viscosity parameter for the parameter choice (30.90)
$\nu_\mathfrak{a}$	Volume fraction of constituent $\mathfrak{a}$
$\overset{\prime}{\nu}_\mathfrak{a}$	Time derivative of ν following the constituent $\mathfrak{a}$
ν_m	Value of ν at densest packing (≈ 0.74 for equal spheres)
ν_s	Solid volume fraction in a binary mixture
$\xi = \rho_\mathfrak{a}/\rho$	Mass fraction of constituent $\mathfrak{a}$

$\varPi$	Entropy production density of the mixture
π	LAGRANGE multiplier of the saturation condition (= saturation pressure)
$\rho = \sum_1^N \rho_{\mathfrak{a}}$	Mass density of the mixture
$\rho_{\mathfrak{a}}$	Mass density of constituent $\mathfrak{a}$
σ_s, (σ_f)	Solid (fluid) expression for $\sigma_s = -T_{s\,yy}$, $(\sigma_f = -T_{f\,yy})$
$\tau \in (0, 1]$	Iteration parameter in the method of successive approximation
$\boldsymbol{\phi}$	Entropy flux vector of the mixture
$\boldsymbol{\phi}^E = \mathbf{0}$	Equilibrium value of $\boldsymbol{\phi}$
$\boldsymbol{\phi}_{\mathfrak{a}}$	Entropy flux vector of constituent $\mathfrak{a}$
ψ_I	Mixture inner free energy
$\psi_{\mathfrak{a}}$	(HELMHOLTZ) free energy density of constituent $\mathfrak{a}$
ϕ_s, (ϕ_f)	Solid (fluid) free energy as function of ν_s (ν_f)

Miscellaneous Symbols

$\mathrm{d}/\mathrm{d}t$	Total time derivative (following the mixture particle)
$\partial\mathcal{B}$	Boundary of a material volume $\mathcal{B}$
$\overset{\prime}{(\cdot)})_{\mathfrak{a}}$	Total time derivative of $(\cdot)_{\mathfrak{a}}$
$\boldsymbol{A}^T$	Transpose of $\boldsymbol{A}$
$\boldsymbol{A}^{-T} = (\boldsymbol{A}^T)^{-1} =$	$(\boldsymbol{A}^{-1})^T$
$\Vert\boldsymbol{b}\Vert$	Norm of $\boldsymbol{b}$
$f_{[ij]}$	Skew-symmetric part of f_{ij}, $f_{[ij]} = \frac{1}{2}(f_{ij} - f_{ji})$
$f_{(ij)}$	Symmetric part of f_{ij}, $f_{(ij)} = \frac{1}{2}(f_{ij} + f_{ji})$

30.1 Introduction

Granular fluid mixture theories are of fundamental interest in many fields of engineering and natural sciences.[1] A frequent class of such multiphase flows are debris flows, groundwater flows in soils, and sediment transport in rivers and estuaries in which the granular phases may be distinguished by the different regimes of particle diameters or species characteristics (various grains of solid rocks, wood pieces, etc.). The interstitial fluids may consist of water and oil or fluid-suspended chemicals. If the different constituents arise in respectable concentrations and interact, then it is likely that their presence affects the dynamics of the neighboring solid or fluid constituents, so that the dynamics of such interacting components ought to be described not only by the common physical laws of balance of mass, momenta, and energy, but also by micromechanical balance laws, equations for each constituent by a GOODMAN–COWIN-type microstructure equation.

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[1] Such early theories have been developed by AHMADI [1, 2], BLUHM et al. [5], BOWEN [6, 7], EHLERS [8], EHLERS and KUBIK [9], HOMSY et al. [12], JOHNSON et al. [13], MASSOUDI [16], PASSMAN et al. [18, 19], SVENDSEN and HUTTER [21], and SVENDSEN [22].

It was made clear in Chap. 29 that such additional equations influencing the dynamics of each granular constituent are distinct among different specialists. It follows that unique descriptions of granular fluid mixtures do not (yet) exist; this does not come as a surprise, as different proposals pertain to distinct microstructural properties. We repeat from Chap. 29 that SVENDSEN and HUTTER [21] treat the solid volume fraction as an internal variable and write an evolution equation for it, balancing its time rate of change with its production. WILMANSKI [27], on the other hand, using statistical arguments on the microscale, demonstrated that this equation needed to be complemented by a flux term. GOODMAN and COWIN [10] based their scalar equation model on the theory of structured media, deducing thereby a balance law of equilibrated forces. The approach explains why this scalar evolution equation is reminiscent of momentum with an inertial term proportional to the second-order time derivative of the constituent volume fractions, $\ddot{\nu}_{\mathfrak{a}}$ $(\mathfrak{a} = 1, \ldots, N)$, complemented by equilibrated stress vectors $\boldsymbol{h}_{\mathfrak{a}}$ $(\mathfrak{a} = 1, \ldots, N)$ and equilibrated intrinsic interacting scalar body forces, $l_{\mathfrak{a}}$. The GOODMAN–COWIN proposal, applied for single constituent granular continua, was extended by PASSMAN et al. [18] to mixtures and will here equally be used. The reader, however, should be aware that the equilibrated force balance is also applied to the fluid. An alternative derivation for this mixture model, using LAGRANGE an dynamics in the spirit of Appendix 29.A could also be given here, see also [10, 18].

In deducing inferences for a chosen constitutive model, PASSMAN et al. [18] followed GOODMAN and COWIN's [10] procedure for dry granular materials, thereby employing the principle of equilibrated stresses and introduced additional equilibrated stress balances for all constituents to describe the microstructural response. An interstitial fluid or the porosity of the empty space is ignored. In this chapter, we shall act in the same way. However, we shall not employ the COLEMAN–NOLL approach in exploiting the entropy principle. PASSMAN et al. [18] introduced external source terms in the linear momentum equations, the energy equation and the equilibrated force balances for each constituent, which could be applied arbitrarily. It implies in the COLEMAN–NOLL approach that these balance laws do not affect the exploitation of the entropy inequality. Whereas such a procedure can in certain circumstances be tolerated for the linear momentum and energy sources, it is physically not justified for the balance laws of the equilibrated forces. These are internal laws for the body by themselves, which, as exclusive material laws, must influence the thermodynamics. This fact has already been the reason in Chap. 29 for the postulation that the sum of all external source terms in the long entropy inequality should not affect the material thermodynamic behavior. The MÜLLER–LIU approach of the exploitation of the entropy imbalance is based on this postulate: it means that all balance laws and possibly other compelling physical conditions must be accounted for in the process of exploitation of the entropy imbalance. Indeed, it will be shown that in our more general approach, additional terms beyond those of PASSMAN et al. [18], will appear in the constitutive relations, which turn out to be physically significant.

The present theory is believed to be valid for the full spectrum of two-phase solid–fluid media covering the range of variation of the solid volume fraction. The theory allows the possibility of supporting shear stresses in an equilibrium state.

This is necessary for granular media and has, e.g., been observed in the case of high concentrations in sediment transport processes, pore water flows as well as blood suspensions.

In subsequent sections, the basic laws of the motion for the constituents and the entropy imbalance for the mixture are presented. This is followed by the derivation of the constitutive equations from considerations of the first and second law of thermodynamics. This merges into the field equations of a mixture of compressible constituents. This analysis is then repeated for an assemblage of density-preserving constituents. All these field equations are in their reduced forms in conformity with the second law of thermodynamics.

In order to assess the implications of the principal equations, we then consider specific boundary value problems. To compare the emerging results with results derived by PASSMAN et al. [18], we adopt their formulas of the constituent free energy function and solve a steady fully developed horizontal shearing flow problem between two parallel plates, of which the upper one is moving with a constant speed. With the employed numerical method, it is demonstrated that the results are qualitatively similar to those of PASSMAN et al. [18], even though the constitutive equations of both models are not the same. Obviously, the results depend on boundary conditions; however, they are in qualitative agreement with experimental results on high concentration suspensions [3, 4, 11].

30.2 Thermodynamic Considerations

30.2.1 Balance Relations

We begin by assuming that the mixture consists of N constituents. The index $\mathfrak{a}$ denotes the $\mathfrak{a}$th constituent, $\mathfrak{a} = 1, \ldots, N$. The necessary thermal and mechanical field variables for each constituent are introduced as primitive quantities. Specifically, there exists a kinematic variable, the *volume fraction* or *volume distribution function* $\nu_{\mathfrak{a}}$ for each constituent $\mathfrak{a}$, introduced originally by GOODMAN and COWIN [10] for dry granular materials, that accounts for the distributions of volume of each constituent $\mathfrak{a}$ in a multiphase mixture. It is complemented by the distributed mass density (granular true mass density) $\gamma_{\mathfrak{a}}$, the CAUCHY stress tensor $\boldsymbol{T}_{\mathfrak{a}}$, body force $\boldsymbol{b}_{\mathfrak{a}}$, specific internal energy $\varepsilon_{\mathfrak{a}}$, heat flux vector $\boldsymbol{q}_{\mathfrak{a}}$, and heat supply $r_{\mathfrak{a}}$. In addition, to account for energy flux and energy supply associated with the time rate of change of volume distribution, a higher order stress and body force were introduced by GOODMAN and COWIN [10]. Such terms are expected since the volume distribution function and the motion are assumed to be kinematically independent. It is plausible, if a new independent quantity such as $\nu_{\mathfrak{a}}$ is introduced in a theory, a new equation must be introduced to determine its evolution. Following the approach of GOODMAN and COWIN [10] for dry granular materials, PASSMAN et al. [18] choose to do this for a multiphase mixture also by means of an additional equation of balance for each constituent. According to

[10, 18], an equilibrated inertia $k_{\mathfrak{a}}$, equilibrated stress vector $\boldsymbol{h}_{\mathfrak{a}}$, external equilibrated body force $l_{\mathfrak{a}}$,[2] and intrinsic equilibrated body force $f_{\mathfrak{a}}$ are introduced for each constituent. Each distributed constituent must satisfy the basic laws of motion of continuum mechanics. We write the local equations of balance for each constituent $\mathfrak{a}$ ($\mathfrak{a} = 1, \ldots, N$) of the mixture in the following forms:

- Conservation of mass

$$c^{+}_{\mathfrak{a}} = \acute{\rho}_{\mathfrak{a}} + \rho_{\mathfrak{a}} \operatorname{div} \boldsymbol{v}_{\mathfrak{a}}, \tag{30.1}$$

- Balance of linear momentum

$$\boldsymbol{m}^{+}_{\mathfrak{a}} = c^{+}_{\mathfrak{a}} \boldsymbol{v}_{\mathfrak{a}} + \rho_{\mathfrak{a}} \acute{\boldsymbol{v}}_{\mathfrak{a}} - \operatorname{div} \boldsymbol{T}_{\mathfrak{a}} - \rho_{\mathfrak{a}} \boldsymbol{b}_{\mathfrak{a}}, \tag{30.2}$$

- Balance of angular momentum

$$\boldsymbol{M}^{+}_{\mathfrak{a}} - \boldsymbol{r} \times \boldsymbol{m}^{+}_{\mathfrak{a}} = \boldsymbol{T}_{\mathfrak{a}} - \boldsymbol{T}^{T}_{\mathfrak{a}}, \tag{30.3}$$

- Balance of equilibrated force

$$g^{+}_{\mathfrak{a}} = c^{+}_{\mathfrak{a}} k_{\mathfrak{a}} \acute{\nu}_{\mathfrak{a}} + \rho_{\mathfrak{a}} (k_{\mathfrak{a}} \acute{\nu}_{\mathfrak{a}})' - \operatorname{div} \boldsymbol{h}_{\mathfrak{a}} - \rho_{\mathfrak{a}} (l_{\mathfrak{a}} + f_{\mathfrak{a}}), \tag{30.4}$$

- Conservation of equilibrated inertia

$$\acute{k}_{\mathfrak{a}} = 0, \tag{30.5}$$

- Conservation of energy

$$\begin{aligned} e^{+}_{\mathfrak{a}} = {} & c^{+}_{\mathfrak{a}} \left(\varepsilon_{\mathfrak{a}} - \tfrac{1}{2} \boldsymbol{v}_{\mathfrak{a}} \cdot \boldsymbol{v}_{\mathfrak{a}} - \tfrac{1}{2} k_{\mathfrak{a}} \acute{\nu}^{2}_{\mathfrak{a}} \right) + \boldsymbol{m}^{+}_{\mathfrak{a}} \cdot \boldsymbol{v}_{\mathfrak{a}} \\ & + g^{+}_{\mathfrak{a}} \acute{\nu}_{\mathfrak{a}} + \rho_{\mathfrak{a}} \acute{\varepsilon}_{\mathfrak{a}} - \boldsymbol{T}_{\mathfrak{a}} \cdot \boldsymbol{L}_{\mathfrak{a}} - \boldsymbol{h}_{\mathfrak{a}} \cdot \operatorname{grad} \acute{\nu}_{\mathfrak{a}} \\ & - \tfrac{1}{2} \rho_{\mathfrak{a}} \acute{k}_{\mathfrak{a}} \acute{\nu}^{2}_{\mathfrak{a}} + \rho_{\mathfrak{a}} f_{\mathfrak{a}} \acute{\nu}_{\mathfrak{a}} + \operatorname{div} \boldsymbol{q}_{\mathfrak{a}} - \rho_{\mathfrak{a}} r_{\mathfrak{a}}. \end{aligned} \tag{30.6}$$

Note that in Eq. (30.5), the conservation of equilibrated inertia is new and states that $k_{\mathfrak{a}}$ is a material constant, i.e., a quantity that remains constant when the constituent particle follows its own trajectory. This simultaneously means that "the total derivative" $(\cdot)'_{\mathfrak{a}}$ should be understood as the time derivative $\partial(\cdot)_{\mathfrak{a}}/\partial t + \operatorname{grad} (\cdot)_{a} \cdot \boldsymbol{v}_{\mathfrak{a}}$. We shall not introduce a separate symbol for the derivative $\partial(\cdot)_{\mathfrak{a}}/\partial t + \operatorname{grad} (\cdot)_{a} \cdot \cdot \boldsymbol{v}_{\mathfrak{b}}$. Moreover, $\acute{f}_{\mathfrak{a}} = \partial f/\partial t + (\operatorname{grad} f_{\mathfrak{a}}) \cdot \boldsymbol{v}_{\mathfrak{a}} = \dot{f}_{\mathfrak{a}} + (\operatorname{grad} f_{\mathfrak{a}}) \cdot \boldsymbol{u}_{\mathfrak{a}}$ is the material time derivative with respect to $\boldsymbol{v}_{\mathfrak{a}}$, $\dot{f}_{\mathfrak{a}} = \partial f/\partial t + (\operatorname{grad} f_{\mathfrak{a}}) \cdot \boldsymbol{v}$ the material time derivative with respect to the mixture velocity $\boldsymbol{v}$ and $\boldsymbol{u}_{\mathfrak{a}} = \boldsymbol{v}_{\mathfrak{a}} - \boldsymbol{v}$ the constituent diffusion velocity in the mixture; $\boldsymbol{r}$ is the position vector. $c^{+}_{\mathfrak{a}}$, $\boldsymbol{m}^{+}_{\mathfrak{a}}$, $\boldsymbol{M}^{+}_{\mathfrak{a}}$, $g^{+}_{\mathfrak{a}}$, and $e^{+}_{\mathfrak{a}}$ are, respectively, the internal growths (specific productions) of mass, linear momentum, angular

---

[2] We do not see that, physically, such an external force can exist. We keep it here for formal coincidence with [10, 18]. Our form of the second law does not depend on its existence.

momentum, equilibrated force, and energy. A derivation of the equations of balance of equilibrated force and energy and the equation of conservation of equilibrated inertia can be found in references [10, 18].

We require that the growths represent only exchanges among phases

$$\sum c_{\mathfrak{a}}^{+} = 0, \quad \sum \boldsymbol{m}_{\mathfrak{a}}^{+} = \boldsymbol{0}, \quad \sum \boldsymbol{M}_{\mathfrak{a}}^{+} = \boldsymbol{0}, \quad \sum g_{\mathfrak{a}}^{+} = 0, \quad \sum e_{\mathfrak{a}}^{+} = 0. \tag{30.7}$$

Moreover, we assume that exchanges of mass and equilibrated force do not exist, although there is no particular difficulty in relaxing this assumption,

$$c_{\mathfrak{a}}^{+} = 0, \qquad g_{\mathfrak{a}}^{+} = 0, \tag{30.8}$$

and the exchange of angular momentum happens only through the exchange of linear momentum

$$\boldsymbol{M}_{\mathfrak{a}}^{+} = \boldsymbol{r} \times \boldsymbol{m}_{\mathfrak{a}}^{+}. \tag{30.9}$$

Using these constraints (30.8) and (30.9), the equations of balance (30.1)–(30.6) can be rewritten in the forms

$$0 = \acute{\gamma}_{\mathfrak{a}}\nu_{\mathfrak{a}} + \acute{\nu}_{\mathfrak{a}}\gamma + \gamma_{\mathfrak{a}}\nu_{\mathfrak{a}}\mathrm{div}\,\boldsymbol{v}_{\mathfrak{a}}, \tag{30.10}$$

$$\boldsymbol{m}_{\mathfrak{a}}^{+} = \rho_{\mathfrak{a}}\acute{\boldsymbol{v}}_{\mathfrak{a}} - \mathrm{div}\,\boldsymbol{T}_{\mathfrak{a}} - \rho_{\mathfrak{a}}\boldsymbol{b}_{\mathfrak{a}}, \tag{30.11}$$

$$\boldsymbol{0} = \boldsymbol{T}_{\mathfrak{a}} - \boldsymbol{T}_{\mathfrak{a}}^{T}, \tag{30.12}$$

$$0 = \rho_{\mathfrak{a}}k_{\mathfrak{a}}\acute{\acute{\nu}}_{\mathfrak{a}} - \mathrm{div}\,\boldsymbol{h}_{\mathfrak{a}} - \rho_{\mathfrak{a}}(l_{\mathfrak{a}} + f_{\mathfrak{a}}), \tag{30.13}$$

$$\begin{aligned} e_{\mathfrak{a}}^{+} &= \boldsymbol{m}_{\mathfrak{a}}^{+} \cdot \boldsymbol{v}_{\mathfrak{a}} + \rho_{\mathfrak{a}}\acute{\varepsilon}_{\mathfrak{a}} - \boldsymbol{T}_{\mathfrak{a}} \cdot \boldsymbol{D}_{\mathfrak{a}} - \boldsymbol{h}_{\mathfrak{a}} \cdot \mathrm{grad}\,\acute{\nu}_{\mathfrak{a}} \\ &\quad + \rho_{\mathfrak{a}}f_{\mathfrak{a}}\acute{\nu}_{\mathfrak{a}} + \mathrm{div}\,\boldsymbol{q}_{\mathfrak{a}} - \rho_{\mathfrak{a}}r_{\mathfrak{a}}. \end{aligned} \tag{30.14}$$

The summation of (30.14) for all constituents $\mathfrak{a}$ ($\mathfrak{a} = 1, 2, \ldots, N$) forms the balance equation of energy for the mixture as a whole equivalent to

$$\begin{aligned} 0 = \rho\dot{\varepsilon} + \mathrm{div}\,\boldsymbol{q} - \boldsymbol{T} \cdot \boldsymbol{D} - \sum \boldsymbol{h}_{\mathfrak{a}} \cdot \mathrm{grad}\,\acute{\nu}_{\mathfrak{a}} \\ + \sum \rho_{\mathfrak{a}} f_{\mathfrak{a}}\acute{\nu}_{\mathfrak{a}} - \rho r, \end{aligned} \tag{30.15}$$

where the constituent and mixture fields are connected by the sum relations

$$\begin{aligned} &\rho = \sum \rho_{\mathfrak{a}}, \quad \boldsymbol{v} = \sum \xi_{\mathfrak{a}}\boldsymbol{v}_{\mathfrak{a}}, \quad \varepsilon = \varepsilon_I + \tfrac{1}{2}\sum \xi_{\mathfrak{a}}\boldsymbol{u}_{\mathfrak{a}} \cdot \boldsymbol{u}_{\mathfrak{a}}, \\ &\varepsilon_I = \sum \xi_{\mathfrak{a}}\varepsilon_{\mathfrak{a}}, \quad r = \sum \xi_{\mathfrak{a}}r_{\mathfrak{a}} \end{aligned} \tag{30.16}$$

with $\sum = \sum_{\mathfrak{a}=1}^{N}$, $\boldsymbol{u}_{\mathfrak{a}} = (\delta_{\mathfrak{a}b} - \sum \xi_{\mathfrak{b}})\boldsymbol{v}_{\mathfrak{b}}$ and the constituent mass fraction

$$\xi_{\mathfrak{a}} = \rho_{\mathfrak{a}}/\rho. \tag{30.17}$$

The mixture fluxes (stress and heat flux) take the usual forms

$$\begin{aligned}
\boldsymbol{T} &= \sum \left(\boldsymbol{T}_{\mathfrak{a}} - \rho_{\mathfrak{a}} \boldsymbol{u}_{\mathfrak{a}} \otimes \boldsymbol{u}_{\mathfrak{a}}\right), \\
\boldsymbol{q} &= \sum \left\{\boldsymbol{q}_{\mathfrak{a}} - \left[\boldsymbol{T}_{\mathfrak{a}} - \rho_{\mathfrak{a}}(\varepsilon_{\mathfrak{a}} + \tfrac{1}{2}\boldsymbol{u}_{\mathfrak{a}} \cdot \boldsymbol{u}_{\mathfrak{a}})\boldsymbol{I}\right]\boldsymbol{u}_{\mathfrak{a}}\right\}.
\end{aligned} \tag{30.18}$$

The balance laws (30.10)–(30.14) do not determine the field variables defined and interrelated by them uniquely. To that end, some fields (here $\boldsymbol{T}_{\mathfrak{a}}, \boldsymbol{h}_{\mathfrak{a}}, f_{\mathfrak{a}}, \boldsymbol{q}_{\mathfrak{a}}$) must be expressed as functionals of the others, such that the emerging equations have the potential of generating well-defined solutions. The forms of these constitutive relations are reduced or constrained by the second law of thermodynamics which is here formulated as an entropy principle.

30.2.2 Entropy Principle

There is an additive quantity for each constituent $\mathfrak{a}$, the entropy, with specific density $\eta_{\mathfrak{a}}$, flux $\boldsymbol{\phi}_{\mathfrak{a}}$, supply $s_{\mathfrak{a}}$ and growth of entropy $\eta^{+}_{\mathfrak{a}}$, for which we may write an equation of balance in the following local form:

$$\eta^{+}_{\mathfrak{a}} = \rho_{\mathfrak{a}} \acute{\eta}_{\mathfrak{a}} + \operatorname{div}\left(\boldsymbol{\phi}_{\mathfrak{a}}\right) - \rho_{\mathfrak{a}} s_{\mathfrak{a}}. \tag{30.19}$$

The summation of (30.19) over all constituents $\mathfrak{a}$ gives the equation of entropy balance for the mixture in the form

$$\Pi = \rho \dot{\eta} + \operatorname{div} \boldsymbol{\phi} - \rho s, \tag{30.20}$$

where

$$\begin{aligned}
\eta &= \sum \xi_{\mathfrak{a}} \eta_{\mathfrak{a}}, \quad \boldsymbol{\phi} = \sum \left(\boldsymbol{\phi}_{\mathfrak{a}} + \rho_{\mathfrak{a}} \eta_{\mathfrak{a}} \boldsymbol{u}_{\mathfrak{a}}\right), \\
s &= \sum \xi_{\mathfrak{a}} s_{\mathfrak{a}}, \quad \Pi = \sum \eta^{+}_{\mathfrak{a}}.
\end{aligned} \tag{30.21}$$

Following TRUESDELL [24], we do not restrict $\eta^{+}_{\mathfrak{a}}$ for each constituent except for the requirement that the total growth of entropy of the mixture be nonnegative. Formally, this so-called second law of thermodynamics represents the restriction

$$\Pi = \rho \dot{\eta} + \operatorname{div} \boldsymbol{\phi} - \rho s \geqslant 0. \tag{30.22}$$

Now, any process, which satisfies (30.22), represents a so-called admissible process. Such a process, however, must in addition satisfy the balance relations (30.10)–(30.13) and (30.15) and other additional relations, if such relations should exist. One such constraint is that of *saturation*. It states that all constituents together fill the whole mixture space,

$$\sum \nu_{\mathfrak{a}} = 1. \tag{30.23}$$

Taking the total time derivative following the mixture motion yields

$$\begin{aligned}\sum \frac{\mathrm{d}\nu_{\mathfrak{a}}}{\mathrm{d}t} &= \sum \left(\frac{\partial \nu_{\mathfrak{a}}}{\partial t} + \boldsymbol{v} \cdot \operatorname{grad} \nu_{\mathfrak{a}} \right) \\ &= \sum \Bigg(\underbrace{\frac{\partial \nu_{\mathfrak{a}}}{\partial t} + \boldsymbol{v}_{\mathfrak{a}} \cdot \operatorname{grad} \nu_{\mathfrak{a}}}_{\acute{\nu}_{\mathfrak{a}}} - \underbrace{(\boldsymbol{v}_{\mathfrak{a}} - \boldsymbol{v})}_{\boldsymbol{u}_{\mathfrak{a}}} \cdot \operatorname{grad} \nu_{\mathfrak{a}} \Bigg) \\ &= \sum \left(\acute{\nu}_{\mathfrak{a}} - \boldsymbol{u}_{\mathfrak{a}} \cdot \operatorname{grad} \nu_{\mathfrak{a}} \right) = 0. \end{aligned} \tag{30.24}$$

This equation holds for $t > 0$ and can be integrated subject to the initial condition $\sum \nu_{\mathfrak{a}} = 1$ at $t = 0$. Thus, we may replace (30.23) by

$$\sum (\acute{\nu}_{\mathfrak{a}} - \boldsymbol{u}_{\mathfrak{a}} \cdot \operatorname{grad} \nu_{\mathfrak{a}}) = 0,\ \ t > 0 \ \text{ and } \ \sum \nu_{\mathfrak{a}} = 1,\ \ t = 0. \tag{30.25}$$

In ensuing developments, we further suppose that all constituents possess the same temperature θ. Such an assumption is tantamount to the statement that thermal exchanges between the constituents occur instantaneously with no phase changes taking place in any constituent. We thus must satisfy the entropy inequality (30.22) subject to the simultaneous satisfaction of (30.10), (30.11), (30.13), (30.15), and (30.25). (The symmetry of the peculiar stress tensors is satisfied by postulating the constitutive relation accordingly). Liu [14] has shown that instead of fulfilling the entropy inequality for independent fields that are constrained by the balance laws and constraint conditions one may extend the entropy inequality by subtracting from it the products of each constraining equation with a Lagrange multiplier, viz.,

$$\begin{aligned} \varPi = {} & \rho \dot{\eta} + \operatorname{div} \boldsymbol{\phi} - \rho s \\ & -(1/\theta) \sum \lambda^{\nu}_{\mathfrak{a}} \left[\acute{\gamma}_{\mathfrak{a}} \nu_{\mathfrak{a}} + \gamma_{\mathfrak{a}} \acute{\nu}_{\mathfrak{a}} + \gamma_{\mathfrak{a}} \nu_{\mathfrak{a}} \operatorname{div} \boldsymbol{v}_{\mathfrak{a}} \right] \\ & -(1/\theta) \sum \boldsymbol{\lambda}^{v}_{\mathfrak{a}} \cdot \left[\rho_{\mathfrak{a}} \acute{\boldsymbol{v}}_{\mathfrak{a}} - \operatorname{div} \boldsymbol{T}_{\mathfrak{a}} - \rho_{\mathfrak{a}} \boldsymbol{b}_{\mathfrak{a}} - \boldsymbol{m}^{+}_{\mathfrak{a}} \right] \\ & -(1/\theta) \sum \lambda^{k}_{\mathfrak{a}} \left[\rho_{\mathfrak{a}} k_{\mathfrak{a}} \acute{\acute{\nu}}_{\mathfrak{a}} - \operatorname{div} \boldsymbol{h}_{\mathfrak{a}} - \rho_{\mathfrak{a}} (l_{\mathfrak{a}} + f_{\mathfrak{a}}) \right] \\ & -\lambda^{\varepsilon} \Big[\rho \dot{\varepsilon} + \operatorname{div} \boldsymbol{q} - \boldsymbol{T} \cdot \boldsymbol{D} - \sum \boldsymbol{h}_{\mathfrak{a}} \cdot \operatorname{grad} \acute{\nu}_{\mathfrak{a}} + \sum \rho_{\mathfrak{a}} f_{\mathfrak{a}} \acute{\nu}_{\mathfrak{a}} \\ & -\rho r \Big] - (\pi/\theta) \sum [\acute{\nu}_{\mathfrak{a}} - \boldsymbol{u}_{\mathfrak{a}} \cdot \operatorname{grad} \nu_{\mathfrak{a}}] \geqslant 0, \end{aligned} \tag{30.26}$$

where $\lambda^{\nu}_{\mathfrak{a}}$, $\boldsymbol{\lambda}^{v}_{\mathfrak{a}}$, $\lambda^{k}_{\mathfrak{a}}$, λ^{ε}, π represent the corresponding Lagrange multipliers, and satisfying this extended inequality for unrestricted-independent fields. (For convenience a factor $1/\theta$ has been extracted above from $\lambda^{\nu}_{\mathfrak{a}}$, $\boldsymbol{\lambda}^{v}_{\mathfrak{a}}$ $\lambda^{k}_{\mathfrak{a}}$ and π). These Lagrange multipliers may be constitutive quantities or independent variables. In the following evaluation of the entropy principle for a given constitutive class, we can demonstrate that the Lagrange multipliers $\lambda^{\nu}_{\mathfrak{a}}$, $\boldsymbol{\lambda}^{v}_{\mathfrak{a}}$, $\lambda^{k}_{\mathfrak{a}}$, and λ^{ε} can be given by some constitutive relations, while on π no restriction is exerted, which therefore represents an independent variable. This variable, because it is the LAGRANGE multiplier of the saturation condition (30.25), will be denoted *saturation pressure*.

Substituting the sum relations (30.16), (30.18) and (30.21) into (30.26) and introducing the mixture inner free energy

$$\psi_I = \sum \xi_\mathfrak{a} \psi_\mathfrak{a} = \varepsilon_I - \theta \eta \tag{30.27}$$

and the mixture flux density

$$\boldsymbol{j} = -\theta \boldsymbol{\phi} + \boldsymbol{q} = \boldsymbol{j}_c - \sum \left(\boldsymbol{T}_\mathfrak{a} - \tfrac{\rho_\mathfrak{a}}{2} (\boldsymbol{u}_\mathfrak{a} \cdot \boldsymbol{u}_\mathfrak{a}) \mathbf{1} \right) \boldsymbol{u}_\mathfrak{a} \tag{30.28}$$

with its constitutive part

$$\boldsymbol{j}_c := \sum \boldsymbol{j}_\mathfrak{a} + \sum \rho_\mathfrak{a} \psi_\mathfrak{a} \boldsymbol{u}_\mathfrak{a} = \boldsymbol{j}_I + \sum \rho_\mathfrak{a} \psi_\mathfrak{a} \boldsymbol{u}_\mathfrak{a}, \tag{30.29}$$

where $\boldsymbol{j}_\mathfrak{a} = -\theta \boldsymbol{\phi}_\mathfrak{a} + \boldsymbol{q}_\mathfrak{a}$, yields the form

$$\begin{aligned}
\theta \Pi = & -\rho(\dot{\psi}_I + \eta \dot{\theta}) - \sum \left[\gamma_\mathfrak{a} \lambda^\nu_\mathfrak{a} + \pi + \rho_\mathfrak{a} f_\mathfrak{a} \right] \acute{\nu}_\mathfrak{a} \\
& - \sum \rho_\mathfrak{a} \left(\boldsymbol{\lambda}^v_\mathfrak{a} + \boldsymbol{u}_\mathfrak{a} \right) \cdot \acute{\boldsymbol{v}}_\mathfrak{a} - \boldsymbol{\phi} \cdot \operatorname{grad} \theta - \operatorname{div} \boldsymbol{j}_c \\
& + \sum \left(\boldsymbol{\lambda}^v_\mathfrak{a} + \boldsymbol{u}_\mathfrak{a} \right) \cdot \operatorname{div} \boldsymbol{T}_\mathfrak{a} + \sum \left(\boldsymbol{T}_\mathfrak{a} - \gamma_\mathfrak{a} \nu_\mathfrak{a} \lambda^\nu_\mathfrak{a} \boldsymbol{I} \right) \cdot \boldsymbol{D}_\mathfrak{a} \\
& - \sum \lambda^k_\mathfrak{a} \rho_\mathfrak{a} k_\mathfrak{a} \acute{\acute{\nu}}_\mathfrak{a} + \sum \lambda^k_\mathfrak{a} \operatorname{div} \boldsymbol{h}_\mathfrak{a} + \sum \lambda^k_\mathfrak{a} \rho_\mathfrak{a} f_\mathfrak{a} \\
& - \sum \lambda^\nu_\mathfrak{a} \nu_\mathfrak{a} \acute{\gamma}_\mathfrak{a} + \sum \boldsymbol{\lambda}^v_\mathfrak{a} \cdot \boldsymbol{m}^+_\mathfrak{a} + \sum \boldsymbol{h}_\mathfrak{a} \cdot \operatorname{grad} \acute{\nu}_\mathfrak{a} \\
& + \sum \pi \boldsymbol{u}_\mathfrak{a} \cdot \operatorname{grad} \nu_\mathfrak{a} \geqslant 0
\end{aligned} \tag{30.30}$$

of the entropy inequality with the assumption $\lambda^\varepsilon = 1/\theta$. This assumption is not reasonable in cases when $\dot{\theta}$ should also be an independent constitutive variable. As we will not include such a dependence, the a priori assignment $\lambda^\varepsilon = 1/\theta$ is justifiable on the basis that MÜLLER and LIU have proved it in [15] and SVENDSEN and HUTTER could also show it in the context of [16], but did not publish the result. For single fluids or mixtures of fluids, this assumption can be directly obtained from the evaluation of the entropy inequality by use of the property of the entropy that on an ideal wall where the entropy production vanishes the normal component of the entropy flux is continuous (see e.g., [15]). In deducing (30.30), we assumed also that the material behavior is independent of the supplies, i.e., that all external source terms balance, viz.,

$$\theta \rho s - \sum \boldsymbol{\lambda}^v_\mathfrak{a} \cdot \rho_\mathfrak{a} \boldsymbol{b}_\mathfrak{a} - \sum \lambda^k_\mathfrak{a} \rho_\mathfrak{a} l_\mathfrak{a} - \rho r = 0. \tag{30.31}$$

The form (30.30) of the entropy inequality will be used to investigate the constitutive postulates in the next section.

30.3 Constitutive Modeling

We recall that the purpose of the entropy principle is to derive restrictions upon the constitutive relations. The entropy and its flux as well as the LAGRANGE multipliers must be considered as auxiliary quantities. In this section, we evaluate the entropy inequality (30.30) for a given constitutive class, which is suitable for a fluid–granular mixture.

30.3.1 Constitutive Equations

We write constitutive equations in which for each constituent $\mathfrak{a}$, the material specific dependent variables

$$\mathcal{C}_\mathfrak{a} := \left\{\psi_\mathfrak{a},\ \eta_\mathfrak{a},\ \boldsymbol{T}_\mathfrak{a},\ \boldsymbol{h}_\mathfrak{a},\ \boldsymbol{q}_\mathfrak{a},\ \phi_\mathfrak{a}\right\} \tag{30.32}$$

are functionals only of variables of the same constituent $\mathfrak{a}$ *(principle of phase separation*). We suppose here that these independent variables are

$$\mathcal{S}_\mathfrak{a} := (\nu_\mathfrak{a}, \operatorname{grad}\nu_\mathfrak{a}, \acute{\nu}_\mathfrak{a}, \gamma_\mathfrak{a}, \operatorname{grad}\gamma_\mathfrak{a}, \theta, \operatorname{grad}\theta, \boldsymbol{D}_\mathfrak{a}). \tag{30.33}$$

Quite naturally, the growths $\boldsymbol{m}_\mathfrak{a}^+$ may depend on the independent variables of all constituents, here chosen in the form $\mathcal{F}_\mathfrak{b},\ \mathfrak{b} = 1, 2, \ldots, N$,

$$\mathcal{F}_\mathfrak{b} = (\nu_\mathfrak{b}, \operatorname{grad}\nu_\mathfrak{b}, \acute{\nu}_\mathfrak{b}, \gamma_\mathfrak{b}, \operatorname{grad}\gamma_\mathfrak{b}, \theta, \operatorname{grad}\theta, \boldsymbol{D}_\mathfrak{b}, \boldsymbol{u}_\mathfrak{b}, \boldsymbol{\mathcal{W}}_\mathfrak{b}), \tag{30.34}$$

where $\boldsymbol{D}_\mathfrak{a}$ is the symmetric part, and $\boldsymbol{W}_\mathfrak{a}$ the skew-symmetric part of grad $\boldsymbol{v}_\mathfrak{a}$, representing corresponding deformation rate and vorticity tensors, respectively; $\boldsymbol{\mathcal{W}}_\mathfrak{a}$ represents the difference

$$\boldsymbol{\mathcal{W}}_\mathfrak{a} = \boldsymbol{W}_\mathfrak{a} - \boldsymbol{W}, \tag{30.35}$$

where $\boldsymbol{W} = \operatorname{skw}(\operatorname{grad}\boldsymbol{v})$. To conform with the principle of material objectivity (material frame indifference) the constitutive quantities cannot depend on all velocities of constituents $\boldsymbol{v}_\mathfrak{a}$ and the skew-symmetric parts of their gradients (except for the symmetric parts), only on the relative velocities $\boldsymbol{u}_\mathfrak{a} = \boldsymbol{v}_\mathfrak{a} - \boldsymbol{v}$ (constituent diffusion velocities) and the corresponding gradients. In short,

$$\left.\begin{aligned} &\mathcal{C}_\mathfrak{a} = \hat{\mathcal{C}}_\mathfrak{a}(\mathcal{S}_\mathfrak{a}), \\ &\boldsymbol{m}_\mathfrak{a}^+ = \hat{\boldsymbol{m}}_\mathfrak{a}^+(\mathcal{F}_\mathfrak{b},\ \mathfrak{b} = 1, \ldots, N), \end{aligned}\right\} (\mathfrak{a} = 1, \ldots, N). \tag{30.36}$$

Strictly speaking, according to the principle of equipresence [23] in TRUESDELL's original list, all the dependent constitutive variables must be functions of all the independent constitutive variables. However, for simplicity of calculation, we have replaced the principle of equipresence by the principle of phase separation, which has been adopted in many mixture theories (e.g., [1, 18]). Practically, in multiphase mixtures, the individual constituents are clearly separated physically and it is plausible to think of the mixture as phase separated. On the other hand, we ought to mention that there are also valid plausibility arguments to reject the principle of phase separation, since the different constituents in the mixture may appear as different materials in combination with the other constituents than without. A theory which imposes the principle of equipresence is far more complicated, and inferences from the entropy principle are far more difficult to draw. At last, only the results in concrete situations can decide whether the simple theory will be meaningful.

These constitutive equations must satisfy the entropy inequality (30.30). Substituting the constitutive relations (30.32)–(30.34) into (30.30), and using the identities

$$
\begin{aligned}
&\dot{\nu}_{\mathfrak{a}} = \acute{\nu}_{\mathfrak{a}} - \operatorname{grad}\nu_{\mathfrak{a}} \cdot \boldsymbol{u}_{\mathfrak{a}}, \quad (\acute{\nu}_{\mathfrak{a}})^{\cdot} = \acute{\acute{\nu}}_{\mathfrak{a}} - \operatorname{grad}\acute{\nu}_{\mathfrak{a}} \cdot \boldsymbol{u}_{\mathfrak{a}},\\
&\dot{\gamma}_{\mathfrak{a}} = \acute{\gamma}_{\mathfrak{a}} - \operatorname{grad}\gamma_{\mathfrak{a}} \cdot \boldsymbol{u}_{\mathfrak{a}},\\
&\dot{\overline{\operatorname{grad}\nu_{\mathfrak{a}}}} = \operatorname{grad}\acute{\nu}_{\mathfrak{a}} - \operatorname{grad}\nu_{\mathfrak{a}}\operatorname{grad}\boldsymbol{v}_{\mathfrak{a}} - \operatorname{grad}(\operatorname{grad}\nu_{\mathfrak{a}}) \cdot \boldsymbol{u}_{\mathfrak{a}},
\end{aligned}
\tag{30.37}
$$

yields the new inequality

$$
\begin{aligned}
\theta\varPi = {} & -\rho\left[\frac{\partial\psi_I}{\partial\theta} + \eta\right]\dot{\theta} - \rho\frac{\partial\psi_I}{\partial\operatorname{grad}\theta} \cdot \dot{\overline{\operatorname{grad}\theta}} - \sum\rho\frac{\partial\psi_I}{\partial\boldsymbol{D}_{\mathfrak{a}}} \cdot \dot{\boldsymbol{D}}_{\mathfrak{a}}\\
& -\sum\left[\rho\frac{\partial\psi_I}{\partial\gamma_{\mathfrak{a}}} + \lambda^{\nu}_{\mathfrak{a}}\nu_{\mathfrak{a}}\right]\acute{\gamma}_{\mathfrak{a}} - \sum\left[\rho\frac{\partial\psi_I}{\partial\acute{\nu}_{\mathfrak{a}}} + \lambda^{k}_{\mathfrak{a}}\rho_{\mathfrak{a}}k_{\mathfrak{a}}\right]\acute{\acute{\nu}}_{\mathfrak{a}}\\
& -\sum\left[\rho\frac{\partial\psi_I}{\partial\nu_{\mathfrak{a}}} + \gamma_{\mathfrak{a}}\lambda^{\nu}_{\mathfrak{a}} + \rho_{\mathfrak{a}}f_{\mathfrak{a}} + \pi\right]\acute{\nu}_{\mathfrak{a}}\\
& +\sum\left[\rho\frac{\partial\psi_I}{\partial\gamma_{\mathfrak{a}}}\boldsymbol{u}_{\mathfrak{a}} - \frac{\partial\boldsymbol{j}_c}{\partial\gamma_{\mathfrak{a}}}\right] \cdot \operatorname{grad}\gamma_a\\
& +\sum\left[\rho\frac{\partial\psi_I}{\partial\nu_{\mathfrak{a}}}\boldsymbol{u}_{\mathfrak{a}} + \pi\boldsymbol{u}_{\mathfrak{a}} - \frac{\partial\boldsymbol{j}_c}{\partial\nu_{\mathfrak{a}}}\right] \cdot \operatorname{grad}\nu_{\mathfrak{a}}\\
& -\sum\left[\rho\frac{\partial\psi_I}{\partial\operatorname{grad}\nu_{\mathfrak{a}}} + \rho\frac{\partial\psi_I}{\partial\acute{\nu}_{\mathfrak{a}}}\boldsymbol{u}_{\mathfrak{a}} - \frac{\partial\boldsymbol{j}_c}{\partial\acute{\nu}_{\mathfrak{a}}} - \boldsymbol{h}_{\mathfrak{a}}\right] \cdot \operatorname{grad}\acute{\nu}_{\mathfrak{a}}\\
& +\sum\rho\frac{\partial\psi_I}{\partial\operatorname{grad}\gamma_{\mathfrak{a}}} \cdot \dot{\overline{\operatorname{grad}\gamma_{\mathfrak{a}}}} - \sum\frac{\partial\boldsymbol{j}_c}{\partial\operatorname{grad}\gamma_{\mathfrak{a}}} \cdot \operatorname{grad}\operatorname{grad}\gamma_{\mathfrak{a}}\\
& +\sum\left[\boldsymbol{T}_{\mathfrak{a}} - \gamma_{\mathfrak{a}}\nu_{\mathfrak{a}}\lambda^{\nu}_{\mathfrak{a}}\boldsymbol{I} + \rho\frac{\partial\psi_I}{\partial\operatorname{grad}\nu_{\mathfrak{a}}} \otimes \operatorname{grad}\nu_{\mathfrak{a}} - \frac{\partial\boldsymbol{j}_c}{\partial\boldsymbol{v}_{\mathfrak{a}}}\right] \cdot \boldsymbol{D}_{\mathfrak{a}}\\
& +\sum\left[\rho\frac{\partial\psi_I}{\partial\operatorname{grad}\nu_{\mathfrak{a}}} \otimes \operatorname{grad}\nu_{\mathfrak{a}} - \frac{\partial\boldsymbol{j}_c}{\partial\boldsymbol{v}_{\mathfrak{a}}}\right] \cdot \boldsymbol{W}_{\mathfrak{a}}\\
& -\left[\boldsymbol{\phi} + \frac{\partial\boldsymbol{j}_c}{\partial\theta}\right] \cdot \operatorname{grad}\theta
\end{aligned}
$$

$$
\begin{aligned}
&+\sum\left[-\frac{\partial \boldsymbol{j}_c}{\partial \operatorname{grad}\nu_\mathfrak{a}}+\rho\frac{\partial\psi_I}{\partial\operatorname{grad}\nu_\mathfrak{a}}\otimes\boldsymbol{u}_\mathfrak{a}\right]\cdot{\color{red}\operatorname{grad}\left(\operatorname{grad}\nu_\mathfrak{a}\right)}\\
&-\frac{\partial \boldsymbol{j}_c}{\partial\operatorname{grad}\theta}\cdot{\color{red}\operatorname{grad}\left(\operatorname{grad}\theta\right)}-\sum\frac{\partial\boldsymbol{j}_c}{\partial\boldsymbol{D}_\mathfrak{a}}\cdot{\color{red}\operatorname{grad}\boldsymbol{D}_\mathfrak{a}}\\
&-\sum\rho_\mathfrak{a}\left(\boldsymbol{\lambda}^v_\mathfrak{a}+\boldsymbol{u}_\mathfrak{a}\right)\cdot{\color{red}\acute{\boldsymbol{v}}_\mathfrak{a}}+\sum\left(\boldsymbol{\lambda}^v_\mathfrak{a}+\boldsymbol{u}_\mathfrak{a}\right)\cdot\operatorname{div}\boldsymbol{T}_\mathfrak{a}\\
&+\sum\boldsymbol{\lambda}^v_\mathfrak{a}\cdot\boldsymbol{m}^+_\mathfrak{a}+\sum\lambda^k_\mathfrak{a}\rho_\mathfrak{a}f_\mathfrak{a}+\sum\lambda^k_\mathfrak{a}\operatorname{div}\boldsymbol{h}_\mathfrak{a}\geqslant 0.
\end{aligned}
\tag{30.38}
$$

It possesses the form

$$
\boldsymbol{a}\cdot\boldsymbol{\alpha}+b\geqslant 0,
\tag{30.39}
$$

where the vector $\boldsymbol{a}$ and the scalar b are functions of the variables listed in (30.33) and (30.34), and the vector $\boldsymbol{\alpha}$ (printed in red color) depends on time and space derivatives of these quantities. Hence, inequality (30.39) is linear in $\boldsymbol{\alpha}$, and since these variables can take any values, it would be able to violate (30.39) unless

$$
\boldsymbol{a}=\boldsymbol{0}\ \text{ and }\ b\geqslant 0.
\tag{30.40}
$$

Explicitly, the entropy inequality must hold for all independent variations of $\boldsymbol{\alpha}=\{\dot{\theta},\ \dot{\overline{\operatorname{grad}\theta}},\ \dot{\boldsymbol{D}}_\mathfrak{a},\ \acute{\gamma}_\mathfrak{a},\ \acute{\boldsymbol{v}}_\mathfrak{a},\ \acute{\acute{\nu}}_\mathfrak{a},\ \operatorname{grad}\acute{\nu}_\mathfrak{a},\ \dot{\overline{\operatorname{grad}\gamma_\mathfrak{a}}},\ \operatorname{grad}\left(\operatorname{grad}\gamma_\mathfrak{a}\right),\ \operatorname{grad}\left(\operatorname{grad}\nu_\mathfrak{a}\right),\ \operatorname{grad}\left(\operatorname{grad}\ \theta\right)$, and $\operatorname{grad}\boldsymbol{D}_\mathfrak{a}\}$. These variables appear linearly in the inequality (30.38) and thus their coefficients must vanish, leading to the so-called LIU identities. It then follows that the expressions for the LAGRANGE multipliers $\boldsymbol{\lambda}^v_\mathfrak{a}$, $\lambda^\nu_\mathfrak{a}$, $\lambda^k_\mathfrak{a}$ are given by

$$
\begin{aligned}
\boldsymbol{\lambda}^v_\mathfrak{a}&=-\boldsymbol{u}_\mathfrak{a}, &(30.41)\\
\lambda^k_\mathfrak{a}&=-\frac{\rho}{\rho_\mathfrak{a}k_\mathfrak{a}}\frac{\partial\psi_I}{\partial\acute{\nu}_\mathfrak{a}}\overset{(30.27)}{=}-\frac{1}{k_\mathfrak{a}}\frac{\partial\psi_\mathfrak{a}}{\partial\acute{\nu}_\mathfrak{a}}, &(30.42)\\
\lambda^\nu_\mathfrak{a}&=-\frac{\rho}{\nu_\mathfrak{a}}\frac{\partial\psi_I}{\partial\gamma_\mathfrak{a}}\overset{(30.27)}{=}-\gamma_\mathfrak{a}\frac{\partial\psi_\mathfrak{a}}{\partial\gamma_\mathfrak{a}}. &(30.43)
\end{aligned}
$$

To simplify our problem, we will now assume that the free energy $\psi_\mathfrak{a}$ is independent of $\acute{\nu}_\mathfrak{a}$, so the LAGRANGE multiplier $\lambda^k_\mathfrak{a}$ must vanish,

$$
\lambda^k_\mathfrak{a}=0\qquad\forall\mathfrak{a}.
\tag{30.44}
$$

The entropy inequality (30.38) implies also the following restrictions for the constitutive variables:

$$
\begin{aligned}
&\eta=-\frac{\partial\psi_I}{\partial\theta}, &(30.45)\\
&\frac{\partial\psi_I}{\partial\operatorname{grad}\theta}=\boldsymbol{0},\quad\frac{\partial\psi_I}{\partial\boldsymbol{D}_\mathfrak{a}}=\boldsymbol{0},\quad\frac{\partial\psi_I}{\partial\operatorname{grad}\gamma_\mathfrak{a}}=\boldsymbol{0}, &(30.46)
\end{aligned}
$$

$$\boldsymbol{h}_{\mathfrak{a}} = -\rho \frac{\partial \psi_I}{\partial \mathrm{grad}\, \nu_{\mathfrak{a}}} - \rho \frac{\partial \psi_I}{\partial \acute{\nu}_{\mathfrak{a}}} \boldsymbol{u}_{\mathfrak{a}} + \frac{\partial \boldsymbol{j}_c}{\partial \acute{\nu}_{\mathfrak{a}}}, \tag{30.47}$$

$$\frac{\partial \boldsymbol{j}_c}{\partial \mathrm{grad}\, \theta} \cdot \mathrm{grad}\, (\mathrm{grad}\, \theta) = 0, \tag{30.48}$$

$$\frac{\partial \boldsymbol{j}_c}{\partial \mathrm{grad}\, \gamma_{\mathfrak{a}}} \cdot \mathrm{grad}\, (\mathrm{grad}\, \gamma_{\mathfrak{a}}) = 0, \tag{30.49}$$

$$\left(\rho \frac{\partial \psi_I}{\partial \mathrm{grad}\, \nu_{\mathfrak{a}}} \otimes \boldsymbol{u}_{\mathfrak{a}} - \frac{\partial \boldsymbol{j}_c}{\partial \mathrm{grad}\, \nu_{\mathfrak{a}}}\right) \cdot \mathrm{grad}\, (\mathrm{grad}\, \nu_{\mathfrak{a}}) = 0, \tag{30.50}$$

$$\frac{\partial \boldsymbol{j}_c}{\partial \boldsymbol{D}_{\mathfrak{a}}} \cdot \mathrm{grad}\, \boldsymbol{D}_{\mathfrak{a}} = 0. \tag{30.51}$$

Equations (30.41)–(30.51) correspond to $\boldsymbol{a} \cdot \boldsymbol{\alpha} = 0$ in (30.40).

The restrictions (30.46) on the form of the mixture specific inner free energy cannot be functions of grad θ, $\boldsymbol{D}_{\mathfrak{a}}$ and grad $\gamma_{\mathfrak{a}}$; thus, ψ_I and $\psi_{\mathfrak{a}}$ take the forms

$$\begin{aligned} &\psi_I = \hat{\psi}_I(\nu_1, \ldots, \nu_N, \mathrm{grad}\, \nu_1, \ldots, \mathrm{grad}\, \nu_N, \gamma_1, \ldots, \gamma_N, \theta) \\ &\Longrightarrow \psi_{\mathfrak{a}} = \hat{\psi}_{\mathfrak{a}}(\nu_{\mathfrak{a}}, \mathrm{grad}\, \nu_{\mathfrak{a}}, \gamma_{\mathfrak{a}}, \theta). \end{aligned} \tag{30.52}$$

Using (30.29) and (30.52), one can rewrite the restrictions (30.48)–(30.50) on $\boldsymbol{j}_c$ as the restrictions on its inner parts $\boldsymbol{j}_I$ in the forms

$$\frac{\partial \boldsymbol{j}_I}{\partial \mathrm{grad}\, \theta} \cdot \mathrm{grad}\, (\mathrm{grad}\, \theta) = 0, \tag{30.53}$$

$$\frac{\partial \boldsymbol{j}_I}{\partial \mathrm{grad}\, \gamma_{\mathfrak{a}}} \cdot \mathrm{grad}\, (\mathrm{grad}\, \gamma_{\mathfrak{a}}) = 0, \tag{30.54}$$

$$\frac{\partial \boldsymbol{j}_I}{\partial \mathrm{grad}\, \nu_{\mathfrak{a}}} \cdot \mathrm{grad}\, (\mathrm{grad}\, \nu_{\mathfrak{a}}) = 0. \tag{30.55}$$

These three restrictions mean that $\partial \boldsymbol{j}_I/\partial \mathrm{grad}\, \theta$, $\partial \boldsymbol{j}_I/\partial\ \mathrm{grad}\, \gamma_{\mathfrak{a}}$, and $\partial \boldsymbol{j}_I/\partial \mathrm{grad}\, \nu_{\mathfrak{a}}$ must be skew-symmetric, which implies that $\boldsymbol{j}_I$ are collinear to grad θ, grad $\gamma_{\mathfrak{a}}$ and grad $\nu_{\mathfrak{a}}$, with the corresponding material coefficient tensors being skew-symmetric. On the other hand, the isotropy of $\boldsymbol{j}_I$ requires any such material tensors to be symmetric. To satisfy both requirements requires that these tensors must vanish, making $\boldsymbol{j}_I$ independent of grad θ, grad $\gamma_{\mathfrak{a}}$ and grad $\nu_{\mathfrak{a}}$, and takes its reduced form

$$\begin{aligned} &\boldsymbol{j}_I = \hat{\boldsymbol{j}}_I(\theta, \nu_1, \ldots, \nu_N, \acute{\nu}_1, \ldots, \acute{\nu}_N, \gamma_1, \ldots, \gamma_N, \theta, \boldsymbol{D}_1, \ldots, \boldsymbol{D}_N) \\ &\text{or} \quad \boldsymbol{j}_{\mathfrak{a}} = \hat{\boldsymbol{j}}_{\mathfrak{a}}(\theta, \nu_{\mathfrak{a}}, \acute{\nu}_{\mathfrak{a}}, \gamma_{\mathfrak{a}}, \boldsymbol{D}_{\mathfrak{a}}). \end{aligned} \tag{30.56}$$

If we restrict attention to isotropic behavior, the special form (30.56) necessarily implies $\boldsymbol{j}_{\mathfrak{a}} = \boldsymbol{0}$, $\forall \mathfrak{a}$, (there is no isotropic vectorial function of only scalars and a second rank tensor) and thus, the constituent entropy fluxes are equal to constituent heat fluxes divided by absolute temperature (see Eq. after (30.29)),

$$\boldsymbol{\phi}_{\mathfrak{a}} = \boldsymbol{q}_{\mathfrak{a}}/\theta, \tag{30.57}$$

which in the entropy principle of COLEMAN–NOLL are assumed from the outset, and

$$\boldsymbol{j}_I = \mathbf{0}. \tag{30.58}$$

In this case, $\boldsymbol{j}_c$ reduces to

$$\boldsymbol{j}_c = \sum \rho_{\mathfrak{a}} \psi_{\mathfrak{a}} \boldsymbol{u}_{\mathfrak{a}}. \tag{30.59}$$

Let $\psi_{\mathfrak{a}}$ be an isotropic function; then (30.52) implies

$$\psi_{\mathfrak{a}} = \hat{\psi}_{\mathfrak{a}}(\nu_{\mathfrak{a}}, \operatorname{grad}\nu_{\mathfrak{a}} \cdot \operatorname{grad}\nu_{\mathfrak{a}}, \gamma_{\mathfrak{a}}, \theta). \tag{30.60}$$

Substituting (30.60) and (30.59) into (30.47) asserts that the equilibrated stress $\boldsymbol{h}_{\mathfrak{a}}$ has the representation

$$\boldsymbol{h}_{\mathfrak{a}} = \rho_{\mathfrak{a}} \frac{\partial \psi_{\mathfrak{a}}}{\partial \operatorname{grad}\nu_{\mathfrak{a}}} = \mathcal{A}_{\mathfrak{a}} \operatorname{grad}\nu_{\mathfrak{a}}, \tag{30.61}$$

where

$$\mathcal{A}_{\mathfrak{a}} = \hat{\mathcal{A}}_{\mathfrak{a}}(\nu_{\mathfrak{a}}, \operatorname{grad}\nu_{\mathfrak{a}}, \gamma_{\mathfrak{a}}, \theta) = 2\rho_{\mathfrak{a}} \frac{\partial \psi_{\mathfrak{a}}}{\partial(\operatorname{grad}\nu_{\mathfrak{a}} \cdot \operatorname{grad}\nu_{\mathfrak{a}})}. \tag{30.62}$$

According to (30.59) and (30.61), the quantity

$$\left[\rho \frac{\partial \psi_I}{\partial \operatorname{grad}\nu_{\mathfrak{a}}} \otimes \operatorname{grad}\nu_{\mathfrak{a}} - \frac{\partial \boldsymbol{j}_c}{\partial \boldsymbol{v}_{\mathfrak{a}}}\right]$$

is symmetric, so that its inner product with $\boldsymbol{W}_{\mathfrak{a}}$ must vanish,

$$\left[\rho \frac{\partial \psi_I}{\partial \operatorname{grad}\nu_{\mathfrak{a}}} \otimes \operatorname{grad}\nu_{\mathfrak{a}} - \frac{\partial \boldsymbol{j}_c}{\partial \boldsymbol{v}_{\mathfrak{a}}}\right] \cdot \boldsymbol{W}_{\mathfrak{a}} = 0, \tag{30.63}$$

since $\boldsymbol{W}_{\mathfrak{a}}$ is skew-symmetric. It follows that the corresponding term in (30.38) vanishes as well.

Returning now to the entropy inequality (30.38) and employing these restrictions, and the identities from (30.59)

$$\begin{aligned}
\frac{\partial \boldsymbol{j}_c}{\partial \boldsymbol{v}_{\mathfrak{a}}} &= \rho_{\mathfrak{a}}(\psi_{\mathfrak{a}} - \psi_I)\boldsymbol{I}, \\
\frac{\partial \boldsymbol{j}_c}{\partial \nu_{\mathfrak{a}}} &= \gamma_{\mathfrak{a}}(\psi_{\mathfrak{a}} - \psi_I)\boldsymbol{u}_{\mathfrak{a}} + \rho_{\mathfrak{a}} \frac{\partial \psi_{\mathfrak{a}}}{\partial \nu_{\mathfrak{a}}} \boldsymbol{u}_{\mathfrak{a}},
\end{aligned}$$

$$\frac{\partial \boldsymbol{j}_c}{\partial \gamma_\mathfrak{a}} = \nu_\mathfrak{a}(\psi_\mathfrak{a} - \psi_I)\boldsymbol{u}_\mathfrak{a} + \rho_\mathfrak{a}\frac{\partial \psi_\mathfrak{a}}{\partial \gamma_\mathfrak{a}}\boldsymbol{u}_\mathfrak{a},$$

we obtain the reduced entropy inequality in the form

$$\begin{aligned}
\theta\Pi = &-\sum\left[\beta_\mathfrak{a} - p_\mathfrak{a} + \gamma_\mathfrak{a}\nu_\mathfrak{a} f_\mathfrak{a} + \pi\right]\acute{\nu}_\mathfrak{a}\\
&+\sum\big[(\gamma_\mathfrak{a}(\psi_I - \psi_\mathfrak{a}) + \pi)\operatorname{grad}\nu_\mathfrak{a}\\
&+\nu_\mathfrak{a}(\psi_I - \psi_\mathfrak{a})\operatorname{grad}\gamma_\mathfrak{a}\big]\cdot\boldsymbol{u}_\mathfrak{a} - \sum \boldsymbol{m}_\mathfrak{a}^{+}\cdot\boldsymbol{v}_\mathfrak{a}\\
&+\sum\big[\boldsymbol{T}_\mathfrak{a} + \nu_\mathfrak{a}\left(p_\mathfrak{a} + \gamma_\mathfrak{a}(\psi_I - \psi_\mathfrak{a})\right)\boldsymbol{I}\\
&+\mathcal{A}_\mathfrak{a}\operatorname{grad}\nu_\mathfrak{a}\otimes\operatorname{grad}\nu_\mathfrak{a}\big]\cdot\boldsymbol{D}_\mathfrak{a}\\
&-\left[\boldsymbol{\phi} + \frac{\partial \boldsymbol{j}_c}{\partial \theta}\right]\cdot\operatorname{grad}\theta \geqslant 0,
\end{aligned} \tag{30.64}$$

where $p_\mathfrak{a}$ is the *thermodynamic pressure*

$$p_\mathfrak{a} := \gamma_\mathfrak{a}^2\frac{\partial \psi_\mathfrak{a}}{\partial \gamma_\mathfrak{a}} \tag{30.65}$$

and $\beta_\mathfrak{a}$ is the *configurational pressure*

$$\beta_\mathfrak{a} := \rho_\mathfrak{a}\frac{\partial \psi_\mathfrak{a}}{\partial \nu_\mathfrak{a}}. \tag{30.66}$$

Inequality (30.64) corresponds to $b \geqslant 0$ in (30.40).

At this point, we should also point out that the constitutive class (30.33), (30.34) is suitable for mixtures with compressible constituents. For density-preserving constituents, i.e., constituents whose true mass densities do not change, $\gamma_\mathfrak{a}$ and grad $\gamma_\mathfrak{a}$ are no longer independent variables. In this case returning to the initial constitutive assumption (30.33), (30.34), we delete the dependences on $\gamma_\mathfrak{a}$ and grad $\gamma_\mathfrak{a}$ from the constitutive equations and repeat the above analysis. We find the same constitutive restrictions for mixtures with density-preserving constituents as before for compressible constituents, if here $p_\mathfrak{a} = -\gamma_\mathfrak{a}\lambda_\mathfrak{a}^{\nu}$ is introduced, which now is an unknown variable that can no longer be determined by the free energy $\psi_\mathfrak{a}$ as expressed in (30.65). We shall not repeat the details of the analysis. We further should point that inequality (30.64) looks as if entropy would be produced by the saturation pressure π by the terms in the first and second lines on the RHS of (30.64). However, this is not so, because π only contributes to the equilibrium parts of the constitutive quantities $f_\mathfrak{a}$ and $\boldsymbol{m}_\mathfrak{a}^{+}$, while the residual dissipation inequality depends only on nonequilibrium parts of these quantities as we shall demonstrate shortly.

30.3.2 Thermodynamic Equilibrium

As usual, further restrictions on the constitutive relations can be obtained from the residual inequality (30.64) in the context of thermodynamic equilibrium, which is characterized by the vanishing of the entropy production rate density Π. In the context of the current constitutive class, Π vanishes when the independent dynamic variables

$$\boldsymbol{Y} = (\acute{\nu}_1, \dots, \acute{\nu}_N, \operatorname{grad}\theta, \boldsymbol{v}_1, \dots, \boldsymbol{v}_N, \boldsymbol{D}_1, \dots, \boldsymbol{D}_N) \tag{30.67}$$

all vanish, which implies that Π assumes its minimum, zero, in thermodynamic equilibrium. Necessary conditions for this minimum are that

$$\begin{aligned} &\left.\frac{\partial \Pi}{\partial Y_i}\right|_{Y=0} = 0, && Y_i \in \boldsymbol{Y}, \\ &\left.\frac{\partial^2 \Pi}{\partial Y_i\, \partial Y_j}\right|_{Y=0} \text{ is nonnegative definite,} && Y_i,\ Y_j \in \boldsymbol{Y}. \end{aligned} \tag{30.68}$$

As is well known, the first condition restricts the equilibrium forms of the dependent constitutive fields, while the second constrains the signs of certain material parameters; here we deal only with the first:

$$\begin{aligned} &\left.\frac{\partial \Pi}{\partial \acute{\nu}_{\mathfrak{a}}}\right|_{Y=0} = 0, && \left.\frac{\partial \Pi}{\partial \operatorname{grad}\theta}\right|_{Y=0} = \boldsymbol{0}, \\ &\left.\frac{\partial \Pi}{\partial \boldsymbol{v}_{\mathfrak{a}}}\right|_{Y=0} = \boldsymbol{0}, && \left.\frac{\partial \Pi}{\partial \boldsymbol{D}_{\mathfrak{a}}}\right|_{Y=0} = \boldsymbol{0}. \end{aligned} \tag{30.69}$$

These restrictions yield the following expressions for the equilibrated internal force $f_{\mathfrak{a}}$, the entropy flux $\boldsymbol{\phi}$, the heat flux $\boldsymbol{q}$, the Cauchy stress $\boldsymbol{T}_{\mathfrak{a}}$, and the momentum exchange rate density $\boldsymbol{m}_{\mathfrak{a}}^{+}$ in thermodynamic equilibrium (denoted by the superscript E)

$$f_{\mathfrak{a}}^{E} = \frac{p_{\mathfrak{a}} - \beta_{\mathfrak{a}}}{\gamma_{\mathfrak{a}}\nu_{\mathfrak{a}}} - \frac{\pi}{\gamma_{\mathfrak{a}}\nu_{\mathfrak{a}}}, \tag{30.70}$$

$$\boldsymbol{\phi}^{E} = \boldsymbol{0}, \tag{30.71}$$

$$\boldsymbol{q}^{E} = \boldsymbol{0}, \tag{30.72}$$

$$\boldsymbol{T}_{\mathfrak{a}}^{E} = -\nu_{\mathfrak{a}}\left(p_{\mathfrak{a}} + \gamma_{\mathfrak{a}}(\psi_I - \psi_{\mathfrak{a}})\right)\boldsymbol{I} - \mathcal{A}_{\mathfrak{a}}\operatorname{grad}\nu_{\mathfrak{a}} \otimes \operatorname{grad}\nu_{\mathfrak{a}}, \tag{30.73}$$

$$\begin{aligned} \boldsymbol{m}_{\mathfrak{a}}^{+E} &= \textstyle\sum_{\mathfrak{b}} \{[\pi + \gamma_{\mathfrak{b}}(\psi_I - \psi_{\mathfrak{b}})]\operatorname{grad}\nu_{\mathfrak{b}} \\ &\qquad + \nu_{\mathfrak{b}}(\psi_I - \psi_{\mathfrak{b}})\operatorname{grad}\gamma_{\mathfrak{b}}\}\,(\delta_{\mathfrak{a}b} - \xi_{\mathfrak{a}}) \\ &= \pi\operatorname{grad}\nu_{\mathfrak{a}} + \textstyle\sum_{\mathfrak{b}}(\psi_I - \psi_{\mathfrak{b}})\operatorname{grad}(\nu_{\mathfrak{b}}\gamma_{\mathfrak{b}})(\delta_{\mathfrak{a}b} - \xi_{\mathfrak{a}}). \end{aligned} \tag{30.74}$$

It is seen from (30.70) that π does also have the meaning of a pressure. As the Lagrange multiplier associated with the saturation constraint, it is called the *saturation pressure*. This saturation pressure is an independent variable. It is observed that when only a single granular phase exists, the equilibrium constitutive equations of Goodman and Cowin [10] as well as Wang and Hutter in [25] or as contained in Chap. 29 for granular materials (with $\pi = 0$) are recovered. The existence of a nonvanishing scalar $\mathcal{A}_\mathfrak{a}$ gives rise to the possibility of supporting shear stress at zero shear rate, which is an important characteristic of granular materials, blood as well as high concentration suspensions. For low concentration suspensions $\mathcal{A}_\mathfrak{a} \to 0$ and the medium becomes incapable of supporting any shear stress at zero shear rate. It is obvious that only in this limiting situation the equilibrium properties of this granular mixture is fluid like.

Finally, it should be pointed out that the constitutive relations (30.70)–(30.74) are not in agreement with those obtained by Passman et al. [18]. Using the Coleman–Noll approach of thermodynamics, their derived constitutive relations for the thermodynamic equilibrium parts $f_\mathfrak{a}^E$ and $\boldsymbol{q}^E$ are in coincidence with the expressions (30.70) and (30.72). In their form of the entropy principle the constituent entropy fluxes are from the outset assumed to have the form $\boldsymbol{\phi}_\mathfrak{a} = \boldsymbol{q}_\mathfrak{a}/\theta$, which is equally a disadvantage of the Coleman–Noll approach, as (30.71) is automatically satisfied according to $(30.18)_2$, $(30.21)_2$ and (30.72). However, the constitutive relations for $\boldsymbol{T}_\mathfrak{a}^E$ and $\boldsymbol{m}_\mathfrak{a}^{+E}$ in [18], viz.,

$$\boldsymbol{T}_\mathfrak{a}^E = -\nu_\mathfrak{a} p_\mathfrak{a} \boldsymbol{I} - \mathcal{A}_\mathfrak{a} \operatorname{grad} \nu_\mathfrak{a} \otimes \operatorname{grad} \nu_\mathfrak{a}, \tag{30.75}$$

$$\boldsymbol{m}_\mathfrak{a}^{+E} = \pi \operatorname{grad} \nu_\mathfrak{a}, \tag{30.76}$$

do not agree with (30.73) and (30.74). Obviously, the constitutive relations (30.73), (30.74), based on the Müller–Liu thermodynamic approach, contain more terms than those obtained by a "standard" exploitation according to Coleman–Noll. The differences are significant.

30.4 Saturated Solid–Fluid Mixture with Incompressible Constituents

In this section, we specialize this mixture theory for a specific binary mixture. We consider isothermal flows of a two-phase saturated mixture of an incompressible granular solid and a fluid. Phase f represents the fluid constituent, while phase s represents the granular solid constituent.

We assume that the constituent Cauchy stresses $\boldsymbol{T}_\mathfrak{a}$, the intrinsic equilibrated body forces $f_\mathfrak{a}$ as well as the momentum exchange rate densities $\boldsymbol{m}_\mathfrak{a}^+$ may be decomposed according to

$$\boldsymbol{T}_\mathfrak{a} = \boldsymbol{T}_\mathfrak{a}^E + \boldsymbol{T}_\mathfrak{a}^D, \; f_\mathfrak{a} = f_\mathfrak{a}^E + f_\mathfrak{a}^D, \; \boldsymbol{m}_\mathfrak{a}^+ = \boldsymbol{m}_\mathfrak{a}^{+E} + \boldsymbol{m}_\mathfrak{a}^{+D}, \tag{30.77}$$

so that

$$\begin{aligned}\theta\Pi = &-\sum \gamma_{\mathfrak{a}}\nu_{\mathfrak{a}} f_{\mathfrak{a}}^{D}\acute{\nu}_{\mathfrak{a}} + \sum \boldsymbol{T}_{\mathfrak{a}}^{D}\cdot\boldsymbol{D}_{\mathfrak{a}} - \sum \boldsymbol{m}_{\mathfrak{a}}^{+D}\cdot\boldsymbol{v}_{\mathfrak{a}}\\ &+\left[\boldsymbol{\phi}+\frac{\partial \boldsymbol{j}_c}{\partial\theta}\right]\cdot\operatorname{grad}\theta \geqslant 0,\end{aligned} \tag{30.78}$$

where $\boldsymbol{T}_{\mathfrak{a}}^{E}$, $f_{\mathfrak{a}}^{E}$, and $\boldsymbol{m}_{\mathfrak{a}}^{+E}$ represent the thermodynamic equilibrium parts, as displayed in (30.70), (30.73), and (30.74), while $\boldsymbol{T}_{\mathfrak{a}}^{D}$, $f_{\mathfrak{a}}^{D}$ and $\boldsymbol{m}_{\mathfrak{a}}^{+D}$ are their dynamic contributions, which must vanish in thermodynamic equilibrium. Imbalance (30.78) is the true dissipation inequality, and it does not involve the constraint pressure. This is proof that the constraint pressure does not produce entropy for whatever the thermodynamic pressure may be. For the dynamic parts in (30.77), a very useful assumption of simplification is quasi-linearity, i.e., scalar-, vector-, and tensor-valued quantities are assumed to depend explicitly and linearly on scalar-, vector-, and tensor-valued independent dynamic variables, respectively, via scalar coefficients which themselves depend on these and on the scalar-valued independent variables. A special case of this is linearity, which arises when the scalar-valued coefficients in the quasi-linear form are assumed to depend at most on the scalar-valued independent variables. Such a form is indeed the simplest, and when there are no observations, experiments or other physical reasons to believe that the constitutive processes involved are more complicated, it seems sensible to work with this linear form. Having no such information to the contrary, and for simplicity, we assume in this work that the dynamic parts of the constituent CAUCHY stresses $\boldsymbol{T}_{\mathfrak{a}}$, the intrinsic equilibrated body force $f_{\mathfrak{a}}$ as well as the momentum exchange rate density $\boldsymbol{m}_{\mathfrak{a}}^{+}$ can be adequately represented by their linear forms.

$$\begin{aligned}\boldsymbol{T}_{\mathfrak{a}}^{D} &= 2\mu_{\mathfrak{a}}\boldsymbol{D}_{\mathfrak{a}},\\ f_{\mathfrak{a}}^{D} &= \lambda_{\mathfrak{a}}\acute{\nu}_{\mathfrak{a}},\\ \boldsymbol{m}_{\mathfrak{a}}^{+D} &= -m_D(\boldsymbol{v}_{\mathfrak{a}}-\boldsymbol{v}_{\mathfrak{b}}),\quad (a\neq b),\end{aligned} \tag{30.79}$$

where $\mu_{\mathfrak{a}}$, $\lambda_{\mathfrak{a}}$, m_D are functions of $\nu_{\mathfrak{a}}$, $\operatorname{grad}\nu_{\mathfrak{a}}\cdot\operatorname{grad}\nu_{\mathfrak{a}}$. Substituting (30.79) into the reduced entropy inequality (30.78) and exploiting $(30.68)_2$ yields the thermodynamic stability properties

$$\mu_{\mathfrak{a}} \geqslant 0,\quad \lambda_{\mathfrak{a}} \geqslant 0,\quad m_D \geqslant 0,\quad \forall\mathfrak{a}. \tag{30.80}$$

Substituting the expressions (30.70), (30.73), (30.74), and (30.79) into (30.77), and the emerging expressions into Eqs. (30.10), (30.11), and (30.13) yields the equations of conservation of mass, linear momentum, and equilibrated forces for two incompressible constituents

$$\frac{\partial\nu_s}{\partial t} + \operatorname{div}(\nu_s\boldsymbol{v}_s) = 0, \tag{30.81}$$

$$\frac{\partial\nu_f}{\partial t} + \operatorname{div}(\nu_f\boldsymbol{v}_f) = 0, \tag{30.82}$$

$$
\begin{aligned}
&\nu_s + \nu_f = 1, && (30.83)\\
&\nu_s\gamma_s\left(\frac{\partial \boldsymbol{v}_s}{\partial t} + \boldsymbol{v}_s \cdot \operatorname{grad} \boldsymbol{v}_s\right) = -\operatorname{grad}\left[\nu_s\left(p_s + \gamma_s(\psi_I - \psi_s)\right)\right] \\
&\qquad -\operatorname{div}\left[\mathcal{A}_s \operatorname{grad}\nu_s \otimes \operatorname{grad}\nu_s\right] \\
&\qquad +\operatorname{div}\left[\nu_s(\operatorname{grad}\boldsymbol{v}_s + (\operatorname{grad}\boldsymbol{v}_s)^T)\right] + \nu_s\gamma_s\boldsymbol{b}_s \\
&\qquad +\left[\pi + (1-\xi_s)\gamma_s(\psi_I - \psi_s) + \xi_s\gamma_f(\psi_I - \psi_f)\right]\operatorname{grad}\nu_s \\
&\qquad -m_D(\boldsymbol{v}_s - \boldsymbol{v}_f), && (30.84)\\
&\nu_f\gamma_f\left(\frac{\partial \boldsymbol{v}_f}{\partial t} + \boldsymbol{v}_f \cdot \operatorname{grad} \boldsymbol{v}_f\right) = -\operatorname{grad}\left[\nu_f\left(p_f + \gamma_f(\psi_I - \psi_f)\right)\right] \\
&\qquad -\operatorname{div}\left[\mathcal{A}_f \operatorname{grad}\nu_f \otimes \operatorname{grad}\nu_f\right] \\
&\qquad +\operatorname{div}\left[\nu_f(\operatorname{grad}\boldsymbol{v}_f + (\operatorname{grad}\boldsymbol{v}_f)^T)\right] + \nu_f\gamma_f\boldsymbol{b}_f \\
&\qquad +\left[\pi + (1-\xi_s)\gamma_s(\psi_I - \psi_s) + \xi_s\gamma_f(\psi_I - \psi_f)\right]\operatorname{grad}\nu_f \\
&\qquad -m_D(\boldsymbol{v}_f - \boldsymbol{v}_s), && (30.85)\\
&\nu_s\gamma_s k_s \acute{\acute{\nu}}_s = \operatorname{div}(\mathcal{A}_s \operatorname{grad}\nu_s) + (p_s - \beta_s - \pi) + \nu_s\gamma_s\lambda_s\acute{\nu}_s, && (30.86)\\
&\nu_f\gamma_f k_f \acute{\acute{\nu}}_f = \operatorname{div}(\mathcal{A}_f \operatorname{grad}\nu_f) + (p_f - \beta_f - \pi) + \nu_f\gamma_f\lambda_f\acute{\nu}_f. && (30.87)
\end{aligned}
$$

From (30.86) and (30.87), we may derive

$$
\pi = p_\alpha - \beta_\mathfrak{a} + \operatorname{div}(\mathcal{A}_\mathfrak{a} \operatorname{grad}\nu_\mathfrak{a}) - \nu_\mathfrak{a}\gamma_\mathfrak{a}k_\mathfrak{a}\acute{\acute{\nu}}_\mathfrak{a} + \nu_\mathfrak{a}\gamma_\mathfrak{a}\lambda_\mathfrak{a}\acute{\nu}_\mathfrak{a}, \qquad \mathfrak{a} = \{s, f\}, \tag{30.88}
$$

and when taking their difference to eliminate the saturation pressure π,

$$
\begin{aligned}
\beta_s - \beta_f = p_s - p_f + \operatorname{div}\left[(\mathcal{A}_s + \mathcal{A}_f)\operatorname{grad}\nu_s\right] + \nu_f\gamma_f k_f\acute{\acute{\nu}}_f \\
-\nu_s\gamma_s k_s\acute{\acute{\nu}}_s + \nu_f\gamma_f\lambda_f\acute{\nu}_f - \nu_s\gamma_s\lambda_s\acute{\nu}_s.
\end{aligned} \tag{30.89}
$$

Furthermore, we choose

$$
\mu_s = \frac{\bar{\mu}_s\nu_s^2}{(\nu_m - \nu_s)^2} \tag{30.90}
$$

according to PASSMAN et al. [19] with $\bar{\mu}_s$ a constant, in which ν_m is the volume fraction corresponding to densest possible packing of the solid particles. For uniform spheres $\nu_m \approx 0.74$, SAVAGE [20] uses essentially the same function, except an eighth power dependence on $(\nu_m - \nu_s)$. We will assess the effects of changing this power for the latter example of simple shearing flows. For the viscosity of the fluid, we let (see PASSMAN et al. [19])

$$
\mu_f = \nu_f^2\bar{\mu}_f, \tag{30.91}
$$

with $\bar{\mu}_f$ a constant. We also assume the drag coefficient m_D in the form

$$m_D = (\nu_s(1-\nu_s))^m D, \quad m = 1, \quad (\text{generally } m > 0), \tag{30.92}$$

which assures that the drag force between the constituents vanishes automatically for the limit cases $\nu_s \to 0$ and $\nu_s \to 1$.

To obtain the explicit expressions of $\boldsymbol{T}_\mathfrak{a}$, $\boldsymbol{m}^+_\mathfrak{a}$, and $f_\mathfrak{a}$, a representation for the specific free energy $\psi_\mathfrak{a}$ for each constituent $\mathfrak{a}$ is needed. We choose the simplest form according to Passman et al. [19]

$$\nu_\mathfrak{a}\gamma_\mathfrak{a}\psi_\mathfrak{a} = \phi_\mathfrak{a}(\nu_\mathfrak{a}) + \alpha_\mathfrak{a}(\operatorname{grad}\nu_\mathfrak{a}\cdot\operatorname{grad}\nu_\mathfrak{a}) \tag{30.93}$$

with the expressions

$$\begin{aligned} \phi_s &= a_s[\nu_s-\nu_c]^2, && a_s > 0 \\ \phi_f &= a_f[\nu_f-(1-\nu_c)]^2, && a_f > 0, \end{aligned} \tag{30.94}$$

where ν_c is called the *critical volume fraction for solid particles*, above which shearing of the material will cause dilatancy, below which it will cause contraction. For uniform spheres, this corresponds to a simple cubic lattice, so $\nu_c \approx 0.52$. Similarly to (30.90), we take

$$\alpha_s = \frac{\bar{\alpha}_s}{(\nu_m-\nu_s)^2} \tag{30.95}$$

for the solid constituent with $\bar{\alpha}_s$ a constant. We assume that α_f is a constant.

Substitution of the expression for the free energy (30.93) and the expressions for the viscosities of fluid and solid constituents (30.90), (30.91) into the field Eqs. (30.81)–(30.87) gives eleven scalar equations for eleven unknowns ν_s, ν_f, p_s, p_f, π, the three components of $\boldsymbol{v}_s$ and the three components of $\boldsymbol{v}_f$. In the following sections, we will numerically solve the differential equation system subject to appropriate boundary conditions for a typical shearing flow problem.

30.5 Horizontal Shearing Flow Problem

30.5.1 Basic Equations and Boundary Conditions for Horizontal Shearing Flows

First, we discuss a simple shearing problem. The boundaries are two parallel, infinite plates, a fixed distance l apart. Deformation is caused by moving one plate parallel to the other. Choose fixed Cartesian coordinates with the origin on the fixed plate, x parallel to the direction of motion of the top plate, and y orthogonal to the plates, and pointing from the fixed plate toward the moving plate against the gravity field, as shown in **Fig. 30.1**.

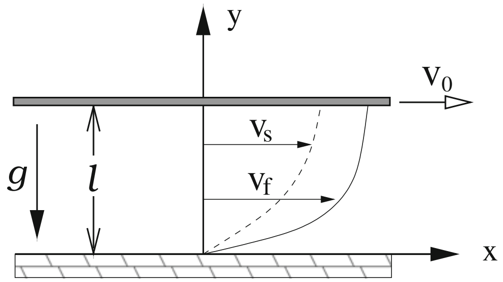

Fig. 30.1 Horizontal shearing flow and coordinate system

We consider only steady motions and assume

$$\begin{aligned}
&\boldsymbol{v}_s = [v_s(y), 0, 0], \quad \boldsymbol{v}_f = [v_f(y), 0, 0], \\
&\nu_s = \nu_s(y), \ \nu_f = \nu_f(y), \ \boldsymbol{b}_s = \boldsymbol{b}_f = [0, -g, 0], \\
&p_s = p_s(y), \ p_f = p_f(y), \ \pi = \pi(y).
\end{aligned} \tag{30.96}$$

In view of the field equations (30.81)–(30.85), (30.88), (30.89), the assumptions (30.96) and the expressions (30.90)–(30.95), the governing differential equations for this special problem reduce to

$$\nu_s + \nu_f = 1, \tag{30.97}$$

$$\begin{aligned}
&\frac{\mathrm{d}}{\mathrm{d}y}\left[\nu_s(p_s + \gamma_s(\psi_I - \psi_s)) + \mathcal{A}_s\left(\frac{\mathrm{d}\nu_s}{\mathrm{d}y}\right)^2\right] \\
&\quad -\left[\pi + (1-\xi_s)\gamma_s(\psi_I - \psi_s) + \xi_s\gamma_f(\psi_I - \psi_f)\right]\frac{\mathrm{d}\nu_s}{\mathrm{d}y} \\
&\quad + g\nu_s\gamma_s = 0,
\end{aligned} \tag{30.98}$$

$$\begin{aligned}
&\frac{\mathrm{d}}{\mathrm{d}y}\left[\nu_f(p_f + \gamma_f(\psi_I - \psi_f)) + \mathcal{A}_f\left(\frac{\mathrm{d}\nu_f}{\mathrm{d}y}\right)^2\right] \\
&\quad -\left[\pi + (1-\xi_s)\gamma_s(\psi_I - \psi_s) + \xi_s\gamma_f(\psi_I - \psi_f)\right]\frac{\mathrm{d}\nu_f}{\mathrm{d}y} \\
&\quad + g\nu_f\gamma_f = 0,
\end{aligned} \tag{30.99}$$

$$\frac{\mathrm{d}}{\mathrm{d}y}\left(\mu_s\frac{\mathrm{d}v_s}{\mathrm{d}y}\right) - D\nu_s(1-\nu_s)(v_s - v_f) = 0, \tag{30.100}$$

$$\frac{\mathrm{d}}{\mathrm{d}y}\left(\mu_f\frac{\mathrm{d}v_f}{\mathrm{d}y}\right) - D\nu_s(1-\nu_s)(v_f - v_s) = 0, \tag{30.101}$$

$$\pi = p_f - \beta_f + \frac{\mathrm{d}}{\mathrm{d}y}\left(\mathcal{A}_f\frac{\mathrm{d}\nu_f}{\mathrm{d}y}\right), \tag{30.102}$$

$$\beta_s - \beta_f = p_s - p_f + \frac{\mathrm{d}}{\mathrm{d}y}\left((\mathcal{A}_s + \mathcal{A}_f)\frac{\mathrm{d}\nu_s}{\mathrm{d}y}\right). \tag{30.103}$$

with

$$\nu_s\beta_s = a_s\left[\nu_s^2-\nu_c^2\right]+\bar{\alpha}_s\frac{3\nu_s-\nu_m}{(\nu_m-\nu_s)^3}\operatorname{grad}\nu_s\cdot\operatorname{grad}\nu_s, \tag{30.104}$$

$$\nu_f\beta_f = a_f\left[\nu_f^2-(1-\nu_c)^2\right]-\alpha_f\operatorname{grad}\nu_f\cdot\operatorname{grad}\nu_f, \tag{30.105}$$

$$\mathcal{A}_s = 2\alpha_s, \quad \mathcal{A}_f = 2\alpha_f. \tag{30.106}$$

Equation (30.97) is the saturation condition, relations (30.98), (30.99) express the equilibrated force balances of the solid and liquid constituents, while (30.100), (30.101) express the flow transverse constituent momentum balances. Finally, relations (30.102), (30.103) provide the constitutive parameterizations of the saturation pressure and the difference of the configurational pressures.

Equations (30.97)–(30.103) are a system of seven equations in the seven unknowns $\nu_s,\ \nu_f,\ \pi,\ p_s,\ p_f,\ v_s,\ v_f$, which is second order in $\nu_s,\ \nu_f,\ v_s$ and ν_f, and first order in p_s and p_f. Thus, we expect that specification of ten boundary conditions will allow us to determine ν_s, ν_f, π, p_s, p_f, v_s, v_f. We specify

$$\nu_s(0), \quad \nu_s(l), \quad \nu_f(0)(=1-\nu_s(0)), \quad \nu_f(l)(=1-\nu_s(l)), \tag{30.107}$$

consistent with (30.103) and choose no-slip boundary conditions

$$\begin{aligned} v_s(0)&=0, & v_s(l)&=1,\\ v_f(0)&=0, & v_f(l)&=1. \end{aligned} \tag{30.108}$$

Here, since Eqs. (30.100) and (30.101) are linear, v_s and v_f may be nondimensionalized by dividing them by the speed of the boundary $y=l$; so, there is no loss of generality in choosing unity for the velocity boundary conditions at $y=l$.

For simplicity, we suppose that in the upper surface the normal stress is given by

$$T_{syy}(l) = T_{fyy}(l) = -\sigma_0 \quad (\sigma_0>0). \tag{30.109}$$

We know from previous studies [17, 25] that in problems of this type, specifying the normal stress on the boundary is equivalent to specifying the flow rate.

This problem lays bare a known weakness of this theory, namely the necessity of prescribing the values of the volume fraction of the solid (and the fluid) at the plate boundaries. These are physically not controllable and thus make the solution of this problem rather academic. Other difficulties are the no-slip conditions (30.108) imposed upon the solid and the fluid. There could be a slip that might be tolerable. These difficulties call for a different parameterization of the stresses, not in terms of the volume fraction gradient, but rather on a rate-independent stretching measure. As long as parameter studies on the influence of these boundary conditions are performed, one may proceed ahead and infer consequences they imply.

30.5.2 Numerical Method

The differential equations (30.97)–(30.103) are nonlinear. Here, we solve the system of nonlinear algebra–differential equations with the boundary conditions (30.107)–(30.109) by means of the method of successive approximation. We describe this method as follows:

We may represent Eqs. (30.97)–(30.103) and the expressions (30.104)–(30.106) in the form (the numbers on the left indicate which equation is involved)

(30.97) $$\nu_f = 1 - \nu_s, \tag{30.110}$$

(30.104) $$\beta_s = a_s \frac{\nu_s^2 - \nu_c^2}{\nu_s} + \bar{\alpha}_s \frac{3\nu_s - \nu_m}{\nu_s(\nu_m - \nu_s)^3} \left(\frac{\partial \nu_s}{\partial y}\right)^2, \tag{30.111}$$

(30.105) $$\beta_f = a_f \frac{\nu_f^2 - (1-\nu_c)^2}{\nu_f} - \frac{\alpha_f}{\nu_f} \left(\frac{\partial \nu_f}{\partial y}\right)^2, \tag{30.112}$$

(30.98) $$p_s = \frac{1}{\nu_s}\sigma_s - \gamma_s(\psi_I - \psi_s) - 2\frac{\alpha_s}{\nu_s}\left(\frac{\partial \nu_s}{\partial y}\right)^2, \tag{30.113}$$

(30.99) $$p_f = \frac{1}{\nu_f}\sigma_f - \gamma_f(\psi_I - \psi_f) - 2\frac{\alpha_f}{\nu_f}\left(\frac{\partial \nu_f}{\partial y}\right)^2, \tag{30.114}$$

(30.102) $$\pi = p_f - \beta_f + \frac{\mathrm{d}}{\mathrm{d}y}\left(2\alpha_f \frac{\mathrm{d}\nu_f}{\mathrm{d}y}\right), \tag{30.115}$$

(30.98) $$\begin{aligned}\sigma_s = \sigma_0 + \int_y^l \Big\{ & -[\pi + (1-\xi_s)\gamma_s(\psi_I - \psi_s) \\ & +\xi_s \gamma_f(\psi_I - \psi_f)]\frac{\mathrm{d}\nu_s}{\mathrm{d}y} + g\nu_s\gamma_s \Big\} dy,\end{aligned} \tag{30.116}$$

(30.99) $$\begin{aligned}\sigma_f = \sigma_0 + \int_y^l \Big\{ & -[\pi + (1-\xi_s)\gamma_s(\psi_I - \psi_s) \\ & +\xi_s \gamma_f(\psi_I - \psi_f)]\frac{\mathrm{d}\nu_f}{\mathrm{d}y} + g\nu_f\gamma_f \Big\} dy,\end{aligned} \tag{30.117}$$

(30.103) $$\frac{\mathrm{d}}{\mathrm{d}y}\left[2(\alpha_s + \alpha_f)\frac{\mathrm{d}\nu_s}{\mathrm{d}y}\right] = \beta_s - \beta_f - (p_s - p_f), \tag{30.118}$$

(30.100) $$\frac{\mathrm{d}}{\mathrm{d}y}\left(\mu_s \frac{\mathrm{d}v_s}{\mathrm{d}y}\right) - D\nu_s(1-\nu_s)v_s = -D\nu_s(1-\nu_s)v_f, \tag{30.119}$$

(30.101) $$\frac{\mathrm{d}}{\mathrm{d}y}\left(\mu_f \frac{\mathrm{d}v_f}{\mathrm{d}y}\right) - D\nu_s(1-\nu_s)v_f = -D\nu_s(1-\nu_s)v_s, \tag{30.120}$$

where $\sigma_s = -T_{syy}$, $\sigma_f = -T_{fyy}$ are the normal stresses in the vertical direction. We can now define an iterative procedure which determines a sequence of functions $(\nu_s^0(y), v_s^0(y), v_f^0(y), \ldots)$, $(\nu_s^1(y), v_s^1(y), v_f^1(y), \ldots)$, $(\nu_s^2(y), v_s^2(y), v_f^2(y), \ldots)$, ... in the following manner: $(\nu_s^0(y), v_s^0(y), v_f^0(y), \ldots)$ are chosen arbitrarily, then $(\nu_s^1(y), v_s^1(y),$

$v_f^1(y)$, ...), ($\nu_s^2(y)$, $v_s^2(y)$, $v_f^2(y)$,...), ... are calculated successively as the solutions of the boundary value problem

$$\frac{\mathrm{d}}{\mathrm{d}y}\left[2(\alpha_s^k+\alpha_f)\frac{\mathrm{d}\tilde{\nu}_s^{k+1}}{\mathrm{d}y}\right]=\beta_s^k-\beta_f^k-(p_s^k-p_f^k), \tag{30.121}$$

$$\frac{\mathrm{d}}{\mathrm{d}y}\left(\mu_s^k\frac{\mathrm{d}\tilde{v}_s^{k+1}}{\mathrm{d}y}\right)-D\nu_s^k(1-\nu_s^k)\tilde{v}_s^{k+1}=-D\nu_s^k(1-\nu_s^k)v_f^k, \tag{30.122}$$

$$\frac{\mathrm{d}}{\mathrm{d}y}\left(\mu_f^k\frac{\mathrm{d}\tilde{v}_f^{k+1}}{\mathrm{d}y}\right)-D\nu_s^k(1-\nu_s^k)\tilde{v}_f^{k+1}=-D\nu_s^k(1-\nu_s^k)v_s^k \tag{30.123}$$

subject to the boundary conditions (30.107), (30.108), with the expressions

$$\nu_f^k=1-\nu_s^k, \tag{30.124}$$

$$\beta_s^k=a_s\frac{\nu_s^{k2}-\nu_c^2}{\nu_s^k}+\bar{\alpha}_s\frac{3\nu_s^k-\nu_m}{\nu_s^k(\nu_m-\nu_s^k)^3}\left(\frac{\partial\nu_s^k}{\partial y}\right)^2, \tag{30.125}$$

$$\beta_f^k=a_f\frac{\nu_f^{k2}-(1-\nu_c)^2}{\nu_f^k}-\frac{\alpha_f}{\nu_f^k}\left(\frac{\partial\nu_f^k}{\partial y}\right)^2, \tag{30.126}$$

$$p_s^k=\frac{1}{\nu_s^k}\sigma_s^k-\gamma_s(\psi_I^k-\psi_s^k)-2\frac{\bar{\alpha}_s}{\nu_s^k(\nu_m-\nu_s^k)^2}\left(\frac{\partial\nu_s^k}{\partial y}\right)^2, \tag{30.127}$$

$$p_f^k=\frac{1}{\nu_f^k}\sigma_f^k-\gamma_f(\psi_I^k-\psi_f^k)-2\frac{\alpha_f}{\nu_f^k}\left(\frac{\partial\nu_f^k}{\partial y}\right)^2, \tag{30.128}$$

$$\pi^k=p_f^k-\beta_f^k+\frac{\mathrm{d}}{\mathrm{d}y}\left(2\alpha_f\frac{\mathrm{d}\nu_f^k}{\mathrm{d}y}\right), \tag{30.129}$$

$$\begin{aligned}\sigma_s^{k+1}=\sigma_0+\int_y^l\bigg\{&-[\pi^k+(1-\xi_s^k)\gamma_s(\psi_I^k-\psi_s^k)\\&+\xi_s^k\gamma_f(\psi_I^k-\psi_f^k)]\frac{\mathrm{d}\nu_s^k}{\mathrm{d}y}+g\nu_s^k\gamma_s\bigg\}dy,\end{aligned} \tag{30.130}$$

$$\begin{aligned}\sigma_f^{k+1}=\sigma_0+\int_y^l\bigg\{&-[\pi^k+(1-\xi_s^k)\gamma_s(\psi_I^k-\psi_s^k)\\&+\xi_s^k\gamma_f(\psi_I^k-\psi_f^k)]\frac{\mathrm{d}\nu_f^k}{\mathrm{d}y}+g\nu_f^k\gamma_f\bigg\}dy.\end{aligned} \tag{30.131}$$

We can discretize Eqs. (30.121)–(30.123) for n uniformly distributed discrete points in $y\in[0,l]$ by finite-difference approximations with central finite-difference quotients. In so doing, for each iterative step three tri-diagonal systems emerge, for $\tilde{\nu}_s^{k+1}$ from Eq. (30.121), for $\tilde{v}_s^{k+1}$ from (30.122), and for $\tilde{v}_f^{k+1}$ from (30.123), respectively. We can solve this boundary value problem, e.g., by Gaussian elimination to obtain

$\tilde{\nu}_s^{k+1}$, $\tilde{v}_s^{k+1}$, and $\tilde{v}_f^{k+1}$. Then ν_s^{k+1}, v_s^{k+1}, and v_f^{k+1} are defined by the over-relaxation iteration by the formulas

$$\left.\begin{aligned} \nu_s^{k+1} &= \nu_s^k + \tau(\tilde{\nu}_s^{k+1} - \nu_s^k), \\ v_s^{k+1} &= v_s^k + \tau(\tilde{v}_s^{k+1} - v_s^k), \\ v_f^{k+1} &= v_f^k + \tau(\tilde{v}_f^{k+1} - v_f^k), \end{aligned}\right\} \quad 0 < \tau \leqslant 1, \tag{30.132}$$

where τ is a positive real parameter. We should choose τ so small that convergent iteration is reached. We would like to point out that this iterative choice is not the only possible one.

We start with the initial trial functions

$$\nu_s^0 = \nu_s(0) + \frac{y}{l}(\nu_s(l) - \nu_s(0)), \qquad v_s^0 = \frac{y}{l}, \quad v_f^0 = \frac{y}{l}, \tag{30.133}$$

which satisfy the boundary conditions. The iteration should be carried out until the relative differences of the computed ν_s, v_s, and v_f between two iterative steps are smaller than a given error, respectively, chosen to be 10^{-6}.

30.5.3 Numerical Results

We choose to investigate the case with estimated parameters corresponding to a mixture of water with natural angular beach sand (average particle diameter 0.04 cm). For this mixture, the values for $\gamma_\mathfrak{a}$, $\mu_\mathfrak{a}$, and ν_m are given according to PASSMAN et al. [19] by

$$\begin{aligned} &\gamma_s = 2200\,\mathrm{kg\,m^{-3}}, \quad &&\bar{\mu}_s = 723\,\mathrm{kg\,m^{-1}s^{-1}}, \quad &&\nu_m = 0.74, \\ &\gamma_f = 1000\,\mathrm{kg\,m^{-3}}, \quad &&\bar{\mu}_f = 0.001\,\mathrm{kg\,m^{-1}s^{-1}}. && \end{aligned} \tag{30.134}$$

The values of parameters $\alpha_\mathfrak{a}$, $a_\mathfrak{a}$ are somewhat problematic. We take as values

$$\begin{aligned} &\bar{\alpha}_s = 4.0 \times 10^{-5}\,\mathrm{kg\,m\,s^{-2}}, \quad &&\alpha_f = 3.0 \times 10^{-5}\,\mathrm{kg\,m\,s^{-2}}, \\ &a_s = 20\,\mathrm{kg\,m^{-1}s^{-2}}\ (\mathrm{Pa}), \quad &&a_f = 10\,\mathrm{kg\,m^{-1}s^{-2}}\ (\mathrm{Pa}), \end{aligned} \tag{30.135}$$

for an initial computational investigation and later assess the effects of changing them. For the drag coefficient D, we choose

$$D \in [0, 10^5]\,\mathrm{kg\ m^{-3}s^{-1}} \tag{30.136}$$

to perform our computations. It is even more problematic as to what boundary conditions to assign to $\nu_s(0)$, $\nu_s(l)$. We know of no evidence, experimental or otherwise, which would guide the choice of either of these two numbers for types of physical boundaries, which we assume, and indeed, although our numerical scheme works successfully for any $\nu_s(0) \in (0, \nu_m]$, $\nu_s(l) \in (0, \nu_m]$, our choices are essentially arbitrary. In our computations, we first take

$$\nu_s(0) = 0.7, \quad \nu_s(l) = 0.3 \tag{30.137}$$

and later assess the effect of changing them.

We have done an extensive parametric study for this problem, which is not presented in detail here. Instead, a few representative volume fraction, velocity, and normal stress profiles will be presented with a discussion of effects of the parameters.

The results for the parameter choices (30.135), (30.136) and the boundary conditions (30.108), (30.109) with $\sigma_0 = 0$ as well as (30.137) are shown in **Fig. 30.2**a–d. The solid volume fraction (Fig. 30.2a) decreases initially only very slowly from its boundary value as the distance from the bottom increases. As the distance increases, this decrease becomes more rapid, specially in the top region of the cross section. The normal stresses for the solid and the fluid (Fig. 30.2b) increase approximately linearly from their given zero boundary value at the top as the depth increases. The solid normal stress is considerably larger than that of the fluid except for the very small zone at the top. The fluid velocity profiles for various values of the drag coefficient D are shown in Fig. 30.2c. All parameters are the same as in Fig. 30.2a, b. For the case of $D = 10^5\,\mathrm{kg\,m^{-3}s^{-1}}$ the solid velocity is nearly the same as that of the fluid (for curve A in the graph), and decreasing the value of D decreases the solid velocity only very slightly so that we do not show it in the figure. The value of the fluid velocity increases considerably when the value of D is decreased, a fact that is expected as D measures the DARCY drag. For $D = 0$ the fluid constituent behaves very similar to a viscous fluid flow. On the other hand, the solid flow occurs mainly only near the top. Comparison of the solid velocity profile (curve A in Fig. 30.2c) with the solid volume fraction (Fig. 30.2a) shows that near the top the shearing of the material causes dilatancy. Qualitatively, these results are similar to those obtained by PASSMAN et al. [19], although the used constitutive equations in the two models are significantly distinct. That is to say that the additional terms in the constitutive relations obtained in the evaluation of the entropy principle following the concept of MÜLLER and LIU play not a very significant role in this numerical example of simple shearing, but we still cannot say that these terms are not important for all flow problems. We need further study in what cases these additional terms may be important.

In the above computations, we have employed an expression of the solid viscosity in the form

$$\mu_s = \frac{\bar{\mu}_s \nu_s^2}{(\nu_m - \nu_s)^n} \tag{30.138}$$

with $n = 2$ according to PASSMAN et al. [19] (see Eq. (30.90)), which is different from Savage's choice [20] with a power $n = 8$. We have also assessed the effect of the value of the power in the expression of the solid viscosity, with $n = 2,\ 4,\ 8$ instead of $n = 2$. The results are shown in Fig. 30.2d for the solid and fluid velocities

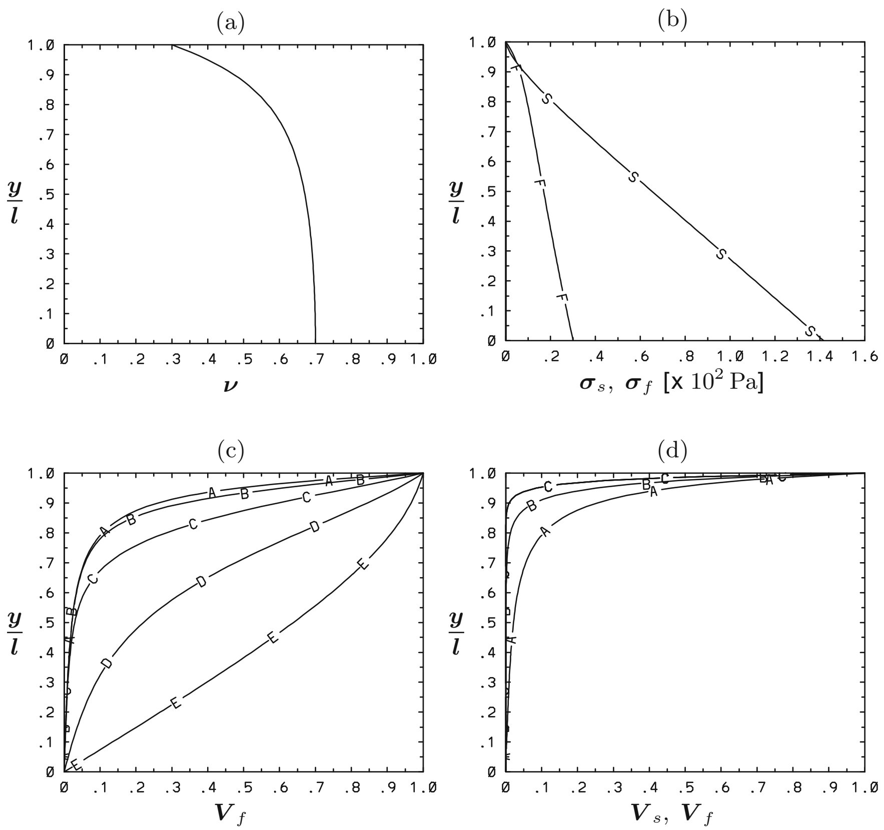

Fig. 30.2 **a** Solid volume fraction profile. **b** Normal solid and fluid stress profiles. S: Solid; F: Fluid. **c** Nondimensional fluid velocity profiles for various values of the drag coefficient D. $D = 10^5\,(A),\ 10^4\,(B),\ 10^3\,(C),\ 10^2\,(D),\ 0\,(E)\,\mathrm{kg\,m^{-3}s^{-1}}$. The solid velocity for these cases is almost the same as the fluid velocity (A). **d** Nondimensional (solid or fluid) velocity profiles for $D = 10^5\,\mathrm{kg\,m^{-3}s^{-1}}$ with various values of power $n = 2\,(A),\ 4\,(B),\ 8\,(C)$ (instead of $n = 2$ for (c)) in the function (30.90) $\mu_s = (\bar{\mu}_s \nu_s^2)/(\nu_m - \nu_s)^n$. The other parameters are $\bar{\alpha}_s = 4.0 \times 10^{-5}\,\mathrm{kg\,m\,s^{-2}}$, $\alpha_f = 3.0 \times 10^{-5}\,\mathrm{kg\,m\,s^{-2}}$, $a_s = 20\,\mathrm{kg\,m^{-1}s^{-2}}$, $a_f = 10\,\mathrm{kg\,m^{-1}s^{-2}}$, $\nu_s(0) = 0.7,\ \nu_s(l) = 0.3, \sigma_0 = 0,\ l = 0.01\,\mathrm{m}$, from WANG and HUTTER [26]

which are almost identical for $D = 10^5\,\mathrm{kg\,m^{-3}s^{-1}}$. Increasing the value of the power n tends to bound the solid flow toward a thinner layer at the top; this is not the same as obtained by PASSMAN et al. who claimed that *the exact value of this power, as long as it is positive and even, appears to have little effect on the character of the flow*. Our results disqualify this statement.

Computations have also been performed for various other values of the normal stress. **Figure** 30.3 shows the effect of changing the normal top-wall stress on the horizontal mixture shearing flow, where nothing has been changed from the case shown in Fig. 30.2a–c, except the value of the normal top-wall stress and the drag

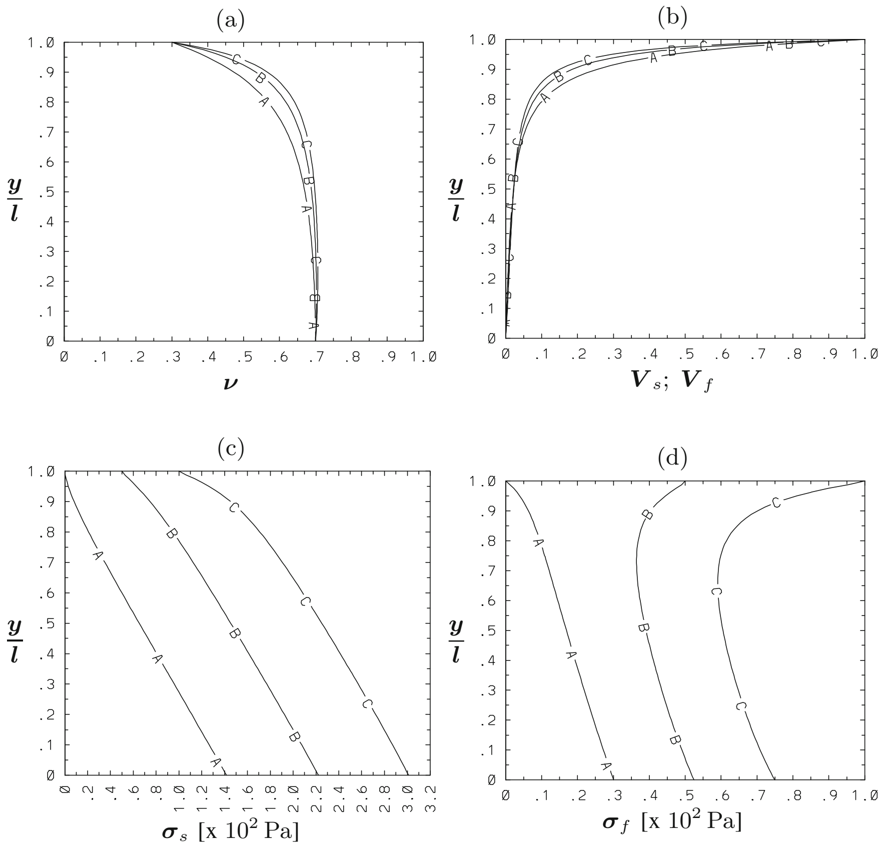

Fig. 30.3 **a** Solid volume fraction profiles. **b** Nondimensional velocity profiles. **c** Normal solid stress profiles. **d** Normal fluid stress profiles. Here nothing has been changed from the case shown in Fig. 30.2a–c for $D = 10^5\,\mathrm{kg\,m^{-3}s^{-1}}$, except various values of the normal stress at the top σ_0 (instead of $\sigma_0 = 0$): A: $\sigma_0 = 0$ Pa; B: $\sigma_0 = 50$ Pa; C: $\sigma_0 = 100$ Pa, from WANG and HUTTER [26]

coefficient is fixed at $D = 10^5\,\mathrm{kg\,m^{-3}s^{-1}}$. Increasing the normal stress will tend to cause the grains to interlock and increase ν throughout the flow field (Fig. 30.3a). For large values of D (here $D = 10^5\,\mathrm{kg\,m^{-3}s^{-1}}$), the solid and fluid velocity profiles are approximately the same (Fig. 30.3b). As the normal stress increases, the grain motion has an increasing tendency toward a rigid motion in the larger region near the bottom, while the shearing layer near the top becomes thinner. The normal solid and fluid stresses (Fig. 30.3c–d) do no longer increase approximately linearly with increasing depth as for the case with $\sigma_0 = 0$ (curve A). Specifically, for the normal fluid stress, if the normal top stress is sufficiently large, the normal fluid stress decreases initially with increasing distance from the top and then increases. There is even a case for which the normal fluid stress at the bottom is smaller than that at the top (curve C in Fig. 30.3d).

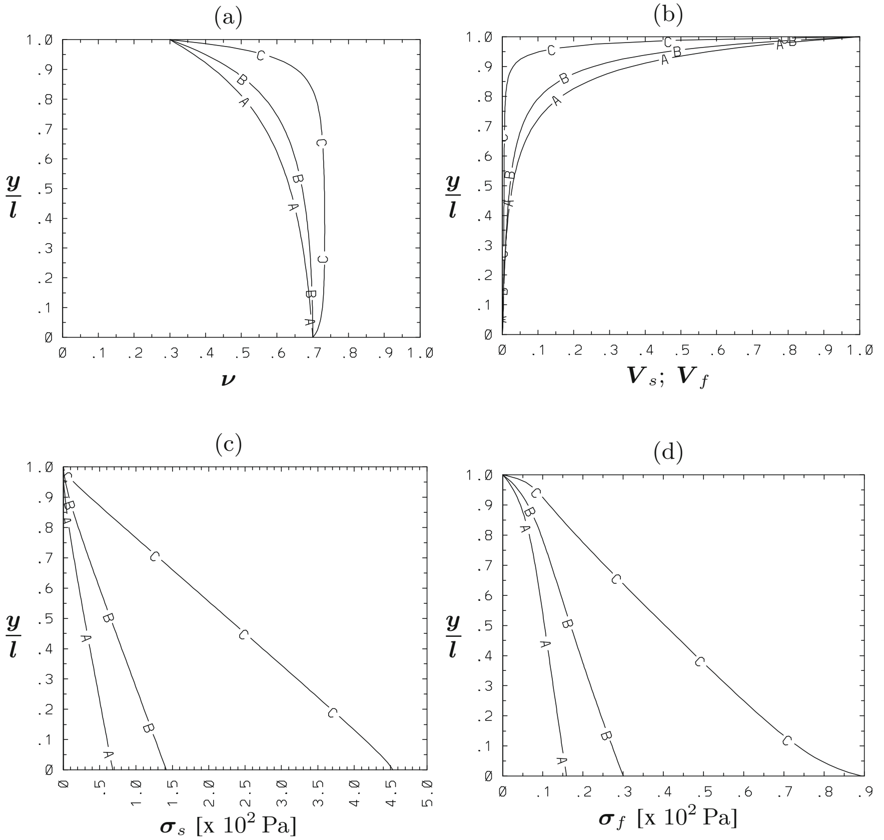

Fig. 30.4 **a** Solid volume fraction profiles. **b** Nondimensional velocity profiles. **c** Normal solid stress profiles. **d** Normal fluid stress profiles. All parameters are the same as in Fig. 30.2a–c and $D = 10^5\,\mathrm{kg\,m^{-3}s^{-1}}$, except the distance of the plates l. A: $l = 0.5$ cm; B: $l = 1.0$ cm; C: $l = 3.0$ cm, from WANG and HUTTER [26]

Figure 30.4 demonstrates the effect of varying the distance of the two plates on the volume fraction, velocity, and normal stress. It can be seen from Fig. 30.4a, b that a wide channel shows a relative large interlock layer near the bottom with an almost constant volume fraction, while, as the channel width decreases, there is an increasing tendency to extend the shearing and dilatant layer near the top. However, the absolute value of the shearing layer thickness is less influenced, which is approximately between 5 and 15 grain diameters. The normal solid and fluid stresses, shown in Fig. 30.4c, d, as expected increase when the channel width increases.

We also investigated the effect of changing α_s and α_f by changing each by factors of 0.1, 10, 100, using the case in Fig. 30.2a–c with $D = 10^5\,\mathrm{kg\,m^{-3}s^{-1}}$ as a basis. These results are displayed in **Fig. 30.5**. As the values of α_s and α_f are increased, the curvatures of the volume fraction and velocity profiles are decreased, i.e., increasing

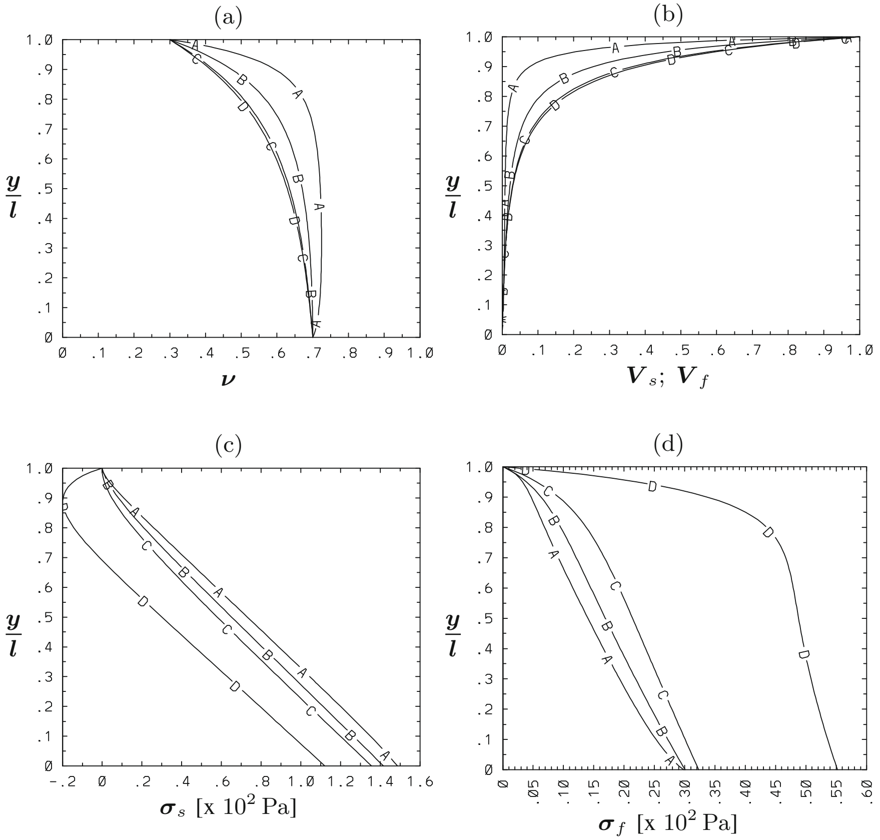

Fig. 30.5 **a** Solid volume fraction profiles. **b** Nondimensional velocity profiles. **c** Normal solid stress profiles. **d** Normal fluid stress profiles. Here nothing has been changed from the case shown in Fig. 30.2a–c for $D = 10^5\,\mathrm{kg\,m^{-3}s^{-1}}$, except the values of $\bar{\alpha}_s$, α_f. A: $(\bar{\alpha}_s, \alpha_f) = (4.0, 3.0) \times 10^{-6}\,\mathrm{kg\,m\,s^{-2}}$; B: $(\bar{\alpha}_s, \alpha_f) = (4.0, 3.0) \times 10^{-5}\,\mathrm{kg\,m\,s^{-2}}$; C: $(\bar{\alpha}_s, \alpha_f) = (4.0, 3.0) \times 10^{-4}\,\mathrm{kg\,m\,s^{-2}}$; D: $(\bar{\alpha}_s, \alpha_f) = (4.0, 3.0) \times 10^{-3}\,\mathrm{kg\,m\,s^{-2}}$, from WANG and HUTTER [26]

α_s and α_f enlarges the shearing zone near the top and reduces the interlock zone near the bottom. The shear rate at the top is, of course, decreased accordingly. It can also be seen from Fig. 30.5a, b that for sufficiently large values of α_s and α_f, ($\bar{\alpha}_s > 4.0 \times 10^{-4}\,\mathrm{kg\,m\,s^{-2}}$ and $\alpha_f > 3.0 \times 10^{-4}\,\mathrm{kg\,m\,s^{-2}}$) the volume fraction and the velocity profiles are influenced only very slightly by varying $\bar{\alpha}_s$ and α_f. Interesting is that the normal solid stress decreases by increasing $\bar{\alpha}_s$ and α_f (Fig. 30.5c), whereas the normal fluid stress changes in the reverse way (Fig. 30.5d). This behavior is also fairly different from varying the volume fraction and the velocity; the normal stresses vary still, even more, rapidly with $\bar{\alpha}_s$ and α_f for $\bar{\alpha}_s > 4.0 \times 10^{-4}\,\mathrm{kg\,m\,s^{-2}}$ and $\alpha_f > 3.0 \times 10^{-4}\,\mathrm{kg\,m\,s^{-2}}$, which we can see from Fig. 30.5c, d. A possible reason is that, for small α_s and α_f, the change of the normal stresses by varying α_s

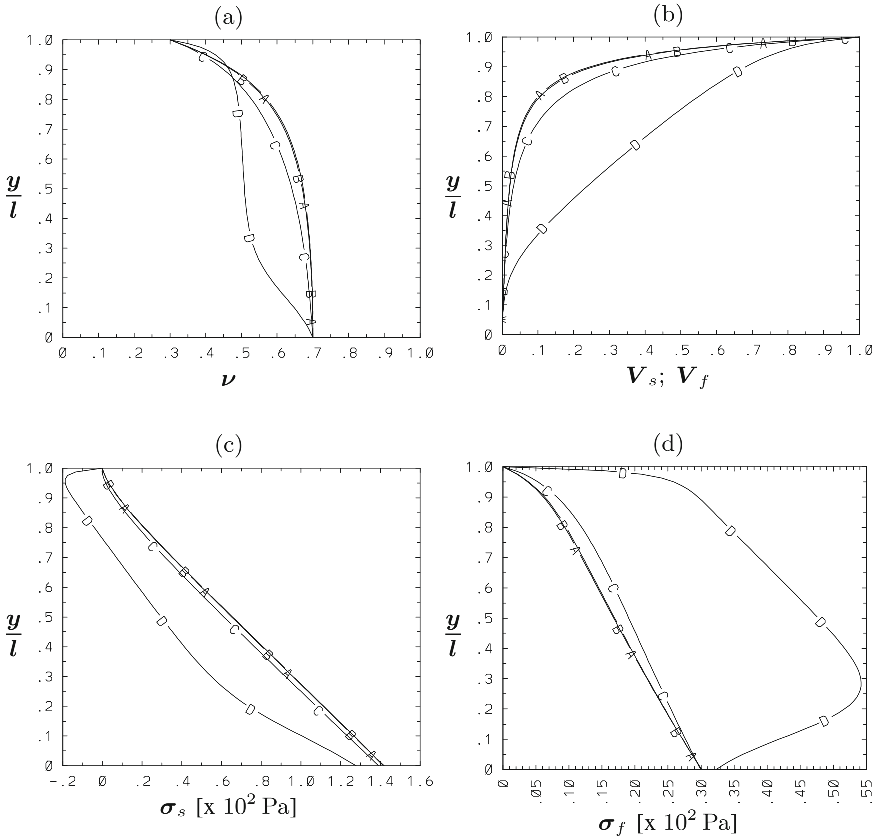

Fig. 30.6 **a** Solid volume fraction profiles. **b** Nondimensional velocity profiles. **c** Normal solid stress profiles. **d** Normal fluid stress profiles. Here nothing has been changed from the case shown in Fig. 30.2a–c for $D = 10^5\,\mathrm{kg\,m^{-3}s^{-1}}$, except the values of a_s, a_f. A: $(a_s, a_f) = (2, 1)$ Pa; B: $(a_s, a_f) = (20, 10)$ Pa; C: $(a_s, a_f) = (200, 100)$ Pa; D: $(a_s, a_f) = (2000, 1000)$ Pa, from WANG and HUTTER [26]

and α_f is compensated by a corresponding change in volume fraction. When α_s and α_f are large enough ($\bar{\alpha}_s > 4.0 \times 10^{-4}\,\mathrm{kg\,m\,s^{-2}}$ and $\alpha_f > 3.0 \times 10^{-4}\,\mathrm{kg\,m\,s^{-2}}$), the volume fraction remains nearly unchanged when α_s and α_f are varied; in this case, the influence of varying α_s and α_f manifests itself mainly in the change of the normal stresses. Besides, there exists even a negative normal solid stress (tensile) zone near the top for large $\bar{\alpha}_s$ and α_f (curve D in Fig. 30.5c), which is perhaps unphysical because the values of α_s and α_f exceed the physically reasonable range.

We also investigated the effect of changing a_s and a_f by changing the value of each variable by factors of 0.1, 10, 100, using the case in Fig. 30.2a–c with $D = 10^5\,\mathrm{kg\,m^{-3}s^{-1}}$ as a basis. It can be seen from **Fig. 30.6**a, b that decreasing a_s and a_f has the effect of causing an even larger region near the bottom where the solid volume

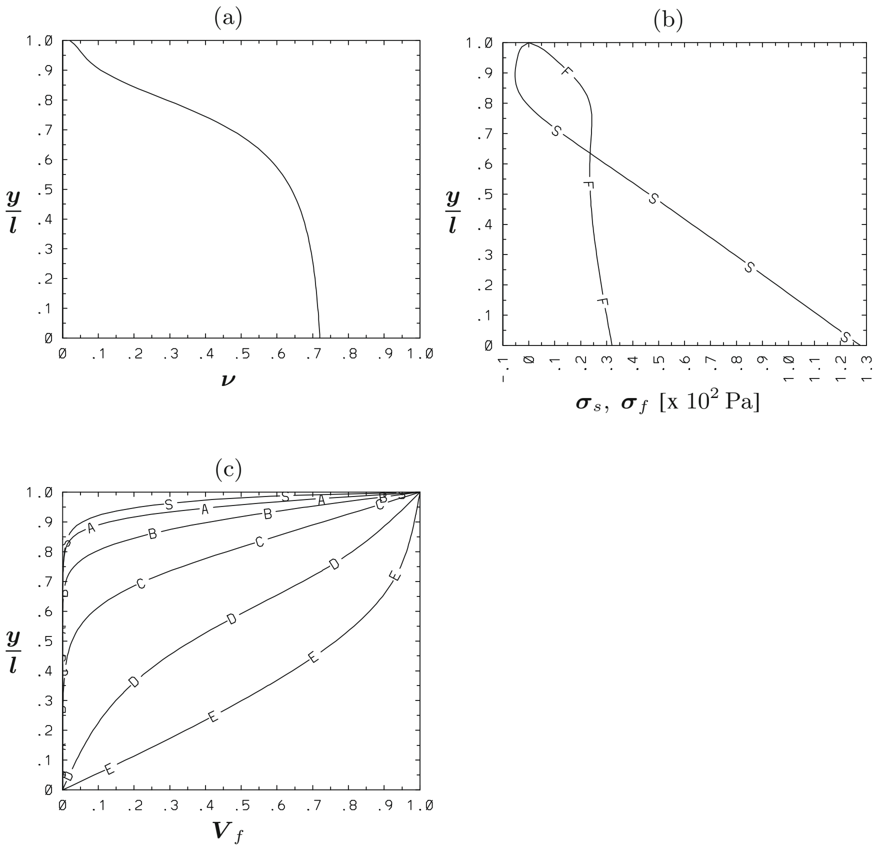

Fig. 30.7 **a** Solid volume fraction profiles. **b** Normal solid (S) and fluid (F) stress profiles. **c** Nondimensional velocity profiles. S: Solid velocity. A-E: Fluid velocity for various values of the drag coefficient D. $D = 10^5\,(A),\ 10^4\,(B),\ 10^3\,(C),\ 10^2\,(D),\ 0\,(E)\ \mathrm{kg\,m^{-3}s^{-1}}$. All parameters are the same as in Fig. 30.2a–c, except the boundary values of the volume fraction $\nu_s(0) = 0.72,\ \nu_s(l) = 0.02$, from WANG and HUTTER [26]

fraction profile remains close to constant (the boundary value), and correspondingly causing a somewhat larger region where the motion is almost rigid, with a smaller region of even higher shear rate. These features of varying a_s and a_f are very similar to those of varying α_s and α_f. The difference from those of varying α_s and α_f is that for sufficiently small values of a_s and a_f ($a_s < 20\,\mathrm{Pa}$ and $a_f < 10\,\mathrm{Pa}$) the volume fraction and the velocity profiles vary only slightly by varying a_s and a_f, which can be seen in Fig. 30.6c, d. Increasing a_s and a_f decreases the normal solid stress, but increases the normal fluid stress, which is similar to varying α_s and α_f. It is of interest to note that the normal stresses at the bottom are essentially unaffected by varying a_s, a_f.

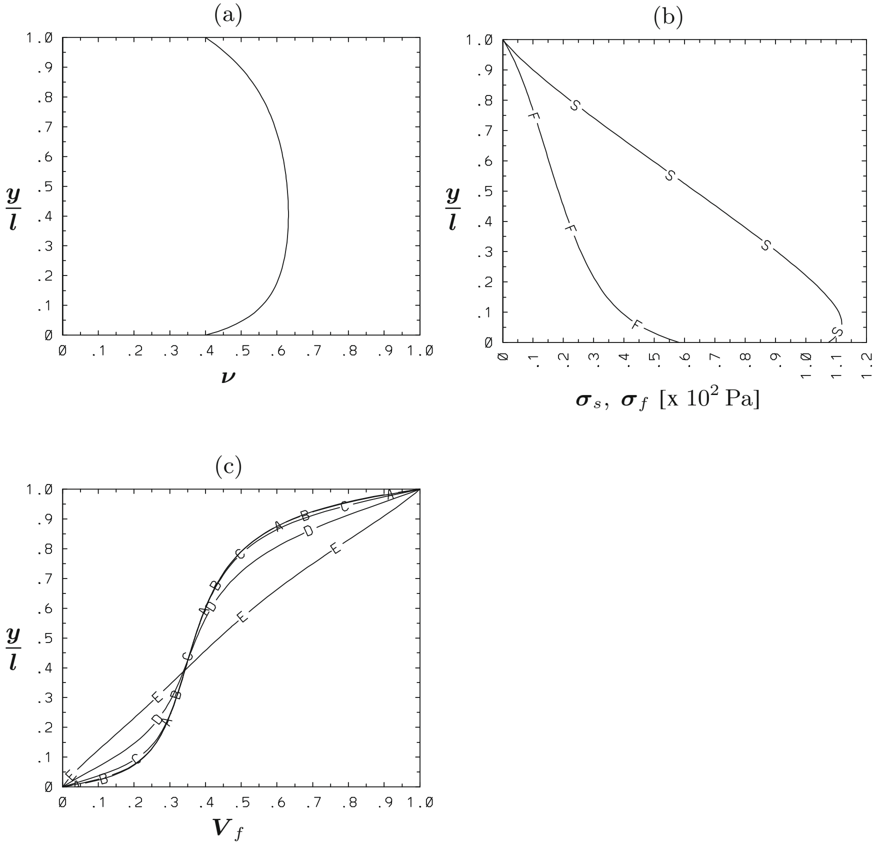

Fig. 30.8 **a** Solid volume fraction profiles. **b** Normal solid (S) and fluid (F) stress profiles. **c** Nondimensional velocity profiles for various values of the drag coefficient D. $D = 10^5\,(A),\ 10^4\,(B),\ 10^3\,(C),\ 10^2\,(D), 0\,(E)$ $\mathrm{kg\,m^{-3}s^{-1}}$. The solid velocity for these cases is almost the same as the fluid velocity (A). All parameters are the same as in Fig. 30.2a–c, except the boundary values of the volume fraction $\nu_s(0) = 0.4,\ \nu_s(l) = 0.4,$ from Wang and sc Hutter [26]

The effect of changing boundary conditions $\nu_s(0)$ and $\nu_s(l)$ is illustrated in **Figs. 30.7** and **30.8**. Here, all parameters are exactly the same as in Fig. 30.2a–c, except that the solid volume fraction at the bottom has been set equal to $\nu_s(0) = 0.72$, a value very close to ν_m, and at the top $\nu_s(l) = 0.02$, i.e., almost only fluid constituent exists (Fig. 30.7), as well as $\nu_s(0) = \nu_s(l) = 0.4$ (Fig. 30.8), respectively.

Figure 30.7a indicates that, for the case that the solid volume fraction at the bottom attains its possibly maximum and at the top nearly only fluid constituent is present, the solid volume fraction decreases only slightly from its boundary value with the distance from the bottom over approximately half of the cross section, then there is a sudden decrease and at the top one-tenths of the cross section the decrease becomes slower again. This resembles a two-layer effect: a thick solid layer near the bottom and a very thin fluid layer near the top. For this case, the normal fluid stress increases rapidly at the top two-tenths of the cross section with decreasing distance from the top, then varies only very slightly, while against it, the normal solid stress decreases only slightly at the top two-tenths of the cross section from its zero boundary value, then increases almost linearly with the increasing depth, as demonstrated in Fig. 30.7b. The corresponding solid and fluid velocity profiles are displayed in Fig. 30.7c for various values of the drag coefficient D. Because of a fairly low solid volume fraction near the top, the solid and fluid velocities are visibly different, even though $D = 10^5\,\mathrm{kg\,m^{-3}s^{-1}}$. The graph S indicates the solid velocity, which is principally independent of the value of D. A solid motion of high shear rate exists only in a very small region at the top. In the remaining large lower region, the solid motion vanishes. It clearly demonstrates the existence of an internal boundary separating a shearing region from a rigid region. The fluid motion for a large value of D is very similar to that of the solid, with appreciable values only in a thin layer near the top. Decreasing D extends the region of the fluid motion till the bottom. For very small D, the fluid constituent behaves nearly as a viscous fluid.

For the boundary conditions that the solid volume fraction at the top and at the bottom possesses the same value $\nu_s(0) = \nu_s(l) = 0.4$, it can be seen from Fig. 30.8a that, in addition to the increase in the solid volume fraction in the neighborhood of the top plate, which is similar to Fig. 30.2a, there is an increase also in the neighborhood of the bottom plate. The volume fraction diagram is, of course, unsymmetric in an obvious fashion because of gravity. In both cases, the region of the low solid volume fraction is a region of high shear rate (Fig. 30.8c as well as Fig. 30.2c), which may lead back to the effect of dilatancy in granular materials. For the high drag coefficient $D = 10^5\,\mathrm{kg\,m^{-3}s^{-1}}$, the velocities of the two constituents again are virtually indistinguishable. As before, the solid velocity is nearly independent of D (graph A), while the fluid velocity profiles become less astute with decreasing D, close to that of a viscous fluid. The normal stresses increase monotonously with increasing depth with the exception of the normal solid stress near the bottom.

30.6 Concluding Remarks

In this chapter, a thermodynamic theory for a multiphase mixture, specially for a solid–fluid mixture was presented in which, besides balances for mass, momentum, and energy, a balance law for equilibrated forces, as proposed by GOODMAN and COWIN for dry granular and then used by PASSMAN et al. for mixtures, was introduced, for each constituent of the mixture, to accommodate for the dynamical effects played by the volume fraction. The form of the entropy principle of the mixture imposed on a postulated constitutive relation was that of MÜLLER–LIU, i.e., for the prescribed constitutive class the entropy inequality was identically satisfied under the constraints that the balance laws of mass, momentum, energy, and equilibrated forces of all constituents (with or without supply terms), as well as a saturation condition be satisfied. It was shown that in comparison to a "standard" exploitation according to COLEMAN–NOLL from PASSMAN et al. [18], in which momentum, energy, and equilibrated force sources of arbitrary value are permitted, the constitutive relations based on the more general MÜLLER–LIU thermodynamic consideration are different. This theory was applied to analyses of steady fully developed horizontal shearing flows of a saturated solid–fluid mixture with incompressible constituents. The partly numerical results are in qualitative agreement with those obtained by PASSMAN et al. [19], although the used constitutive equations in the two models are not quite the same. Most results showed that the flow was divided into two regimes of behavior by the existence of an internal boundary above which the granular material deformed rapidly, but below which the granular material remained rigidly locked in place. This feature is in qualitative agreement with experimental results by HANES and INMAN [11]. Their experiments clearly demonstrate the existence of an internal boundary separating a shearing region from a rigid region. The thickness of the shearing region was measured to be between 5 and 15 grain diameters. In our computational results, the thickness of the shearing layer also lies approximately in this range.

References

1. Ahmadi, G.: On mechanics of saturated granular materials. Int. J. Non-linear Mech. **15**, 251–262 (1980)
2. Ahmadi, G.: A continuum theory for two phase media. Acta Mech. **44**, 299–317 (1982)
3. Bagnold, R.A.: Experiments on a gravity free dispersion of large solid spheres in a Newtonian fluid under shear. Proc. R. Soc. (Lond.) **A225**, 49–63 (1954)
4. Bailard, J.A.: An experimental study of granular fluid flow. Thesis, University of California, San Diego (1978)
5. Bluhm, J., de Boer, R., Wilmanski, K.: The thermodynamic structure of the two component model of porous incompressible materials with true mass densities. Mech. Res. Commun. **22**(2), 171–180 (1995)
6. Bowen, R.M.: Incompressible porous media models by use of the theory of mixtures. Int. J. Eng. Sci. **18**, 1129–1148 (1980)
7. Bowen, R.M.: Compressible porous media models by use of the theory of mixtures. Int. J. Eng. Sci. **20**, 697–735 (1982)
8. Ehlers, W.: Compressible, incompressible and hybrid two-phase models in porous media theories. In: Angel, Y.C. (ed.) Anisotropy and Inhomogeneity in Elasticity and Plasticity. AMD, vol. 158, pp. 25–38. ASME, New York (1993)
9. Ehlers, W., Kubik, J.: On finite dynamic equations for fluid-saturated porous media. Acta Mech. **105**, 101–117 (1994)
10. Goodman, M.A., Cowin, S.C.: A continuum theory for granular materials. Arch. Rational Mech. Anal. **44**, 249–266 (1972)
11. Hanes, D.M., Inman, D.L.: Observations of rapidly flowing granular-fluid materials. J. Fluid Mech. **150**, 357–380 (1985)
12. Homsy, G., Ei-Kaissay, M.M., Didwania, A.: Instability waves and theorigin of bubbles in fluidized beds, part 2: comparison with theory. Int. J. Multiph. Flow **6**, 305–318 (1980)
13. Johnson, G., Massoudi, M., Rajagopal, K.R.: Flow of a fluid-solid mixture between flat plates. Chem. Eng. Sci. **46**(7), 1713–1723 (1991)
14. Liu, I-Shih: Method of lagrange multipliers for exploitation of the entropy principle. Arch. Rational Mech. Anal. **46**, 131–148 (1972)

15. Liu, I-Shih, Müller, I.: Thermodynamics of mixtures of fluids. In: Truesdell, C. (ed.) Rational Thermodynamics, pp. 264–285. Springer, New York (1984)
16. Massoudi, M.: Stability analysis of fluidized beds. Int. J. Eng. Sci. **26**, 765–769 (1988)
17. Nunziato, J.W., Passman, S.L., Thomas, J.P.: Gravitational flow of granular materials with incompressible grains. J. Rheol. **24**, 395–420 (1980)
18. Passman, S.L., Nunziato, J.W., Walsh, E.K.: A theory of multiphase mixtures. In: Truesdell, C. (ed.) Rational Thermodynamics, pp. 286–325. Springer, New York (1984)
19. Passman, S.L., Nunziato, J.W., Bailey, P.B.: Shearing motion of a fluid-saturated granular material. J. Rheol. **30**, 167–192 (1986)
20. Savage, S.B.: Gravity flow of cohesionless granular materials in chutes and channels. J. Fluid Mech. **92**(1), 53–96 (1979)
21. Svendsen, B., Hutter, K.: On the thermodymics of a mixture of isotropic materials with constraints. Int. J. Eng. Sci. **33**, 2021–2054 (1995)
22. Svendsen, B.: A thermodynamic model for volume-fraction-based mixtures. Z. Angew. Math. Mech. **77** (1996)
23. Truesdell, C.: A new definition of a fluid, II: the Maxwellian fluid. Journal de Mathématiques Pures et Appliquées **9**(30), 111–155 (1951)
24. Truesdell, C.: Rational Thermodynamics. McGraw-Hill, New York (1969)
25. Wang, Y., Hutter, K.: Shearing flows in a Goodman-Cowin type granular material - theory and numerical results. Part. Sci. Technol. **51**, 605–632 (1999)
26. Wang, Y., Hutter, K.: A constitutive model of multiphase mixtures and its application in shearing flows of saturated solid-fluid mixtures. Granul. Matter **1**, 163–181 (1999)
27. Wilmanski, K.: The thermodynamical model of compressible porous materials with the balance equation of porosity. Preprint No. 310, Edited by Weierstra"s-Institute für Angewandte Analysis und Stochastik, Berlin (1997)

Chapter 31
Modeling of Turbulence in Rapid Granular Flows

Abstract This chapter is devoted to a phenomenological theory of granular materials subjected to slow frictional as well as rapid flows with intense collisional interactions. The microstructure of the material is taken into account by considering the solid volume fraction as a basic field. This variable enters the formulation via the balance law of configurational momentum, including corresponding contributions to the energy balance, as originally proposed by GOODMAN and COWIN (Arch Rational Mech Anal 44:249–266, 1972, [25]), but modified here by adequately introducing an internal length. The subgrid motion is interpreted as volume fraction variation in relatively moderate laminar variation *and* rapid fluctuations, which manifest themselves in correspondingly filtered equations in terms of correlation products as in turbulence theories. We applyan ergodic (REYNOLDS) filter to these equations as in classical turbulent RANS-modeling and deduce averaged balances of mass, linear and configurational momenta, energy, turbulent and configurational kinetic energy. Moreover, we postulate balance laws for the dissipation rates of the turbulent kinetic energy. All these comprise 10 evolution equations for a larger number of field variables. Closure relations are formulated for the laminar constitutive quantities and the correlation terms, all postulated to obey the material objectivity rules. To apply the entropy principle, three coldness measures are introduced for capturing material, configurational and turbulent dissipative quantities, they simplify the analysis of MÜLLER's entropy principle. The thermodynamic analysis delivers equilibrium properties of the constitutive quantities and linear expressions for the non-equilibrium closure relations.

Keywords Granular materials · Extended GOODMAN–COWIN type microstructure · Turbulent motions · REYNOLDS filtering · Laminar and turbulent constitutive modeling · Entropy principle for laminar and turbulent motions · Material, turbulent and granular temperature

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This chapter is based on the paper [40] co-authored by I. LUCA, C. FANG and K. HUTTER. We thank Prof. LUCA for her help and interest and providing us with the LaTeX file of that paper. The chapter still reflects to a large extent her style of writing. Even though our text is heavily based on that paper, extensions in the analysis should make the subject better understandable.

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List of Symbols

Roman Symbols

A	Symbol for mass balance
$\overline{A}$	Reynolds average of A
$\boldsymbol{A}\boldsymbol{x} = \boldsymbol{b}$	General form of the field equations
$\boldsymbol{a} \cdot \boldsymbol{x} + \beta \geqslant 0$	General form of the entropy inequality
$\boldsymbol{a}$	$\boldsymbol{a} = \boldsymbol{f}^K$, $(K = M, T, G, \epsilon, d) \in \mathbb{R}^{15}$, see (31.130)
a^ϵ, a^d	Coefficients in the nonequilibrium part of the Π^ϵ and Π^d parameterization, see (31.140)
$a_{ij}(i, j = 1, \dots, 5)$	Abbreviations of coefficients arising in the Hessian matrix, see (31.142)
B	Symbol for momentum balance
$\overline{B}$	Reynolds average of B
$\overline{B_i v_i} - \frac{1}{2}\overline{A v_i v_i} = 0$	Balance of modified turbulent kinetic energy
$\boldsymbol{b}, b_i$	Body force per unit mass
b^ϵ, b^d	Coefficient in the parameterization of the nonequilibrium part of Π^ϵ and Π^d
C	Symbol for configurational momentum balance, symbol for a dependent constitutive variable
$\overline{C}$	Reynolds average of C
$\overline{C\ell n} - \frac{1}{2}\overline{A\ell^2 n^2} = 0$	Balance of modified turbulent configurational kinetic energy
C^{turb}	General member of the dependent constitutive expressions
$\overline{C}_{ij}$	Turbulent configurational stress tensor, $\overline{C}_{ij} = 2\overline{\gamma\nu}\frac{\partial\psi^{\text{turb}}}{\partial\overline{g}}\frac{\partial\overline{\nu}}{\partial x_i}\frac{\partial\overline{\nu}}{\partial x_j}$
c	Coefficient in the parameterization of $\boldsymbol{k}$, see (31.103)
D	Symbol for internal energy balance
$\boldsymbol{D}$	Stretching or strain rate tensor
d	Dissipation rate due to "configurational deformations"
E	Index characterizing thermodynamic equilibrium
e	Internal energy
$\mathfrak{e}$	Modified mean internal energy ($\overline{\rho}\mathfrak{e} = \overline{\rho}\,\overline{e} + \overline{\rho' e'}$)
$\mathcal{F}$	General constitutive function
f	Intrinsic equilibrated body force per unit mass, general physical variable
G	Superscript characterizing association with configurational behavior
$\overline{g}$	$\overline{g} \equiv \frac{\partial\overline{\nu}}{\partial x_i}\frac{\partial\overline{\nu}}{\partial x_i}$
$\boldsymbol{g}$	$\boldsymbol{g} = (\operatorname{grad}\theta^M, \theta^T, \theta^G, \epsilon, d)$
H	$H = \frac{1}{\overline{\rho}}\left\{\overline{h'_j\frac{\partial\ell n'}{\partial x_j}} - \overline{\rho f'\ell n'} + \overline{\rho' f'}\ell m\right\}$, see (31.36)
H	Hessian matrix of the entropy production, see (31.142)
H_j	Turbulent configurational stress vector, $H_j = -\ell\overline{\rho n' v'_j} + \overline{\rho}\ell m m_j$, see (31.34)

$H_{(ij)}$	Symmetric part of H_{ij}, $H_{(ij)} := \frac{1}{2}(H_{ij} + H_{ji})$
$H_{[ij]}$	Skew-symmetric part of H_{ij}, $H_{[ij]} := \frac{1}{2}(H_{ij} - H_{ji})$
$\boldsymbol{h}$	Equilibrated stress vector
k	Equilibrated inertia
k	Turbulent kinetic energy, $k = \frac{1}{\overline{\rho}}\,\overline{\rho v_i' v_i'}$
$\mathfrak{k}$	Modified turbulent kinetic energy, Favre turbulent kinetic energy, $\mathfrak{k} = (k - \frac{1}{2} m_i m_i) = -\frac{1}{2\overline{\rho}} R_{ii}$
K_j^d	Flux of configurational turbulent dissipation rate
K_j^ϵ	Flux of classical turbulent dissipation rate
k_j	Extra turbulent entropy flux vector, see (31.102)
k_j^{turb}	Reduced form of the extra turbulent entropy flux vector, see (31.73)
l	External equilibrated body force
ℓ	Characteristic length of a grain, internal length in a granular material
L_{ij}	Flux arising in (31.41), $L_{ij} = \overline{\ell n'^{h_j'}} - \frac{1}{2}\overline{\rho \ell^2 n'^2 v_j'} + \overline{\rho} s m_j$
M	Superscript characterizing association to "material" behavior
m_j	Correlation value of the density-velocity product, $m_j = \overline{\rho' v_j'}$
m	Mass weighted correlation of ρ' and n', $m = \overline{\rho' n'}/\overline{\rho}$
$n \equiv \dot{\nu}$	Time rate of change of ν, "solid volume fraction velocity"
$\mathfrak{n}$	$\mathfrak{n} = \overline{n} + m = \overline{\rho n}/\overline{\rho}$
$\overline{p}$	Turbulent thermodynamic pressure, $\overline{p} \equiv \overline{\gamma}^2 \frac{\partial \psi^{\text{turb}}}{\partial \overline{\gamma}}$
$\boldsymbol{Q}$, Q_{ij}	Orthogonal rank-2 tensor, $Q_{ij} Q_{kj} = Q_{ji} Q_{jk} = \delta_{ik}$
Q_j	Turbulent heat flux (= Favre turbulent heat flux), $Q_j = \overline{\rho e' v_j'} - \overline{\rho' e'} m_j$
$\boldsymbol{q}$	Heat flux vector
$\overline{\boldsymbol{q}}$	Average material heat flux vector
$\mathbb{R}^n$	Real number space of dimension n
R_{ij}	Modified Reynolds stress tensor, see (31.30)
r	Energy supply per unit mass, radiation
s	Supply rate density of a physical variable per unit mass
s	Turbulent configurational kinetic energy, $s = \frac{1}{2\overline{\rho}}\overline{\rho \ell^2 n'^2}$
$\boldsymbol{T}$	Cauchy stress tensor
$\mathcal{T}(\overline{\boldsymbol{y}}, \boldsymbol{z})$	Closure function embracing laminar and turbulent processes
$U_i = \overline{v}_i$	ith component of the mean value of the material velocity
u_i'	Reynolds fluctuation of u_i
u_i''	Favre fluctuating part of u_i
v_j	j component of the material velocity
$\boldsymbol{v}_i$	$\boldsymbol{v}_i$ $(i = 1, \ldots, 6) = \text{grad}\,\{\overline{\gamma}, \vartheta^M, \vartheta^T, \vartheta^G \epsilon, d)\}$, see (31.102)
$x_j,\ j = 1, 2, 3$	Spatial coordinates
$\boldsymbol{z}$	Element of the turbulent state space, see (31.62)

Greek Symbols

$\alpha_i\ (i = 1, \dots, 5)$	Coefficients of contributions to the heat flux vector due to grad $(\vartheta^T, \vartheta^T, \epsilon, d)$, see (31.135)
$\beta_i\ (i = 1, \dots, 5)$	Coefficients of contributions to the vector K_j due to grad $(\vartheta^T, \vartheta^G, \epsilon, d)$, see (31.136)
$\overline{\beta}$	Turbulent configurational pressure, $\overline{\beta} = \overline{\gamma\nu}\frac{\partial\psi^{\mathrm{turb}}}{\partial\overline{\gamma}}$
γ	True density
γ'	Fluctuation of the true density
$\gamma_i\ (i = 1, \dots, 5)$	Coefficients for nonequilibrium contributions to L_j, see (31.57)
Δ_n	Principal minors of order n of a matrix of order $> n$
ϵ	$\epsilon = \frac{1}{\rho}\overline{T_{ij}\frac{\partial v'_i}{\partial x_j}}$
ζ	Viscosity of the intrinsic configurational force, see (31.134)
$\zeta_i\ (i = 1, \dots, 5)$	Coefficients of nonequilibrium contributions to K^d_j, see (31.58)
η	Entropy density
$\overline{\eta}$	Mean entropy density
θ	Temperature
ϑ	Coldness ($\vartheta = 1/\theta$)
$\vartheta^M, \vartheta^T, \vartheta^G$	Material (M), turbulent (T), configurational (G) coldness variables.
$\Lambda^{\mathfrak{a}}$	Lagrange parameters, $\Lambda^{\mathfrak{a}}(\mathfrak{a}) = (\overline{\gamma}, \overline{\nu}, U_i, \overline{e}, k, s, \epsilon, d)$, $\boldsymbol{\lambda}$
$\lambda^T (= 0)$	Turbulent bulk viscosity
λ^M	Material bulk viscosity, see (31.132)
μ^T	Turbulent shear viscosity
μ^M	Material shear viscosity, see (31.132)
ν	Volume fraction
ν_0	Reference volume fraction
ν'	Fluctuation of the volume fraction
$\xi^T (= 0)$	Turbulent volume fraction viscosity, see (31.133)
ξ^M	Material volume fraction viscosity, see (31.132)
$\xi_i\ (i = 1, \dots, 5)$	Coefficients for nonequilibrium contribution to K^ϵ_j, see (31.58)
π	Production rate of a physical variable per unit mass, entropy production (rate) per unit mass
Π^{d}	Production (rate density) of the configurational turbulent dissipation
Π^ϵ	Production (rate density) of the classical turbulent dissipation
$\overline{\pi}_E$	Mean entropy production in equilibrium
$\overline{\pi}_{\mathrm{int\,E}} = 0$	Internal turbulent dissipation
ρ	Density of mass
$\overline{\rho}$	Mean value of ρ
σ	Entropy supply density
$\boldsymbol{\phi}, \phi_i$	Flux of a general physical variable, entropy flux
$\phi^T_j = \overline{\rho}\,\overline{\eta' v'_j}$	Turbulent flux of entropy due to fluctuations of η and v_j
$\overline{\phi}_j$	Mean value of ϕ_j

ϕ_j^{turb}	Turbulent entropy flux for the mean motion, $\phi_j^{\text{turb}} = \overline{\phi}_j + \phi_j^T$
ψ^{turb}	Helmholtz free energy of granular turbulent processes, $\psi^{\text{turb}} = \overline{e} + (\theta^T/\theta^M)k + (\theta^G/\theta^M)s - \overline{\eta}/\theta^M$

Miscellaneous Symbols

$\frac{\mathrm{d}(\cdot)}{\mathrm{d}t}$	Total time derivative (following a material particle) of $(\cdot)$
$\frac{\partial(\cdot)}{\partial t}$	Partial time derivative of $(\cdot)$
$\overline{(\cdot)}$	Mean value of $(\cdot)$ in a turbulent motion
$(\cdot)'$	Fluctuation of $(\cdot)$
$\overset{\circ}{(\cdot)}$	Favre time derivative of $(\cdot)$
LES	Large eddy simulations
RANS	Reynolds averaged NS equations

31.1 Introduction

"The microstructural grain–grain interaction of a dry granular matter results from two contributions: The long-term enduring frictional contact, i.e., sliding, and the short-term elastic or inelastic collisions. Whereas a creeping flow (in a quasi-static state) and a rapid flow (in a collisional state) are defined when the dominant grain–grain interactions are relatively long and short, respectively, a flow in a dense state is characterized by the two types of interactions with equal significance [6, 7, 46, 47]. Grain–grain interactions induce temporal and spatial pulsations of the macroscopic behavior of a granular assemblage that is akin to the turbulent responses of conventional NEWTONian fluids. However, the turbulent fluctuations in dry dense materials are distinct from those in viscous fluids in three perspectives:

- They merge from grain–grain interactions by collisions rather than from flow instabilities.
- They arise also at slow speed in contrast to such responses in NEWTONian fluids, which are inherently velocity dependent, characterized by the REYNOLDS number.
- While turbulent fluctuations in viscous fluids produce kinetic energy with anisotropic eddies and destroy it essentially with isotropic eddies at the KOLMOGOROV scales, granular eddies are barely recognized from the perspective of an energy cascade and the spectrum of the frequencies of the different eddies.

These facts imply that a dense granular flow is tantamount to a complex rheological fluid continuum with significant kinetic energy dissipation, after [16].

In classical fluid dynamics of NAVIER–STOKES type, it is conjectured that the NAVIER–STOKES (NS) equations are correctly describing all motions, be these laminar or turbulent or in an intermediate range between laminar and turbulent. This has been corroborated over and over again by comparing experimental findings with results of direct numerical simulations (DNS). The Reynolds averaged NS-equations (RANS) are equations obtained from the NS equations by applying an ergodic filter to these equations and closing the deduced equations with phenomenological statements for the correlation products of fluctuating quantities. The degree of complexity of these closure schemes is in turbulence modeling known as zero-, first-, second-, and even higher order closure, and what emerges in the higher order schemes is formally a theory for averaged field quantities of a rheologically complex fluid. In large eddy simulations (LES) essentially the same procedure is taken, the difference being that the ergodicity of the filtering process is dispensed with [40].

An important detail in the derivation of turbulent model equations (either for RANS or LES) is what is called the *realizability* of the model equations (see [12, 50, 58–60]). By this is meant that the solutions of the field equations describe in some way physically realistic situations. In the turbulence literature of the past 30 years (see [1–5, 11, 42, 51–53]), this corresponds to the requirement that the averaged equations together with their parametrization for the closure quantities satisfy the second law of thermodynamics, i.e., in no process deduced from the governing field equations the irreversibility requirements are violated [40].

A source of particularly vivid and controversial discussions in the past has been the question, whether turbulent closure conditions that are analogous to the invention of material constitutive statements, ought to satisfy the principle of observer invariance, briefly stated as rule of objectivity. Presently, the common assumption is to accept this concept of invariance of the turbulent closure conditions on all levels of closure. However, it cannot be stated that the question is settled. Our present attitude is to accept the turbulent objectivity rule in this chapter as an attempt of granular laminar-turbulent motion. Incidentally, the opinion of non-objectivity of turbulent closure conditions may have emerged from the basic work of the pioneers in turbulence modeling, e.g., Prandtl, to name just him. These early authors of, say, turbulent shear flows, parametrized the shear stress $\boldsymbol{\tau}$ with an eddy viscosity $\epsilon(x, y_1, y_2)$ which depends also on $y_2 \neq y_1$, see Chap. 16 in Vol. 2 of this treatise [29]. A somewhat deeper insight into this is also given by Egolf and Hutter [13].

Granular systems, when treated as continua, are capable under slow motions of relatively smooth and ordered deformations, but are intensively fluctuating under rapid shearing because of the collisions that occur in these processes. A theoretical model that embraces both dynamical regimes has first been presented in [40]. Models for the slow creeping "laminar" flow have been developed (see [30, 61–63]) and approaches to model the collisional interaction regime have also been developed ([9, 10, 33, 34, 41, 45, 49, 50, 54, 55]), but are modeled by patching equations from the two regimes together (see [30] summarizing related literature), which is obviously unsatisfactory. The techniques applied in turbulence theory to arrive at RANS or LES models is a rational procedure by which the two regimes of distinct behavior can be bridged. It is, therefore, tempting to extend the thermodynamically consistent schemes applied in turbulence theory to the NS equations also to other fluid–solid systems. These systems are governed by other than the NS equations, supposed to be valid for smooth motions. Filtering these equations by an ergodic (Reynolds) filter will then yield corresponding averaged equations and correlation products of fluctuating quantities which serve as basis for the description of processes in which rubbing friction *and* collisional transport are equally significant. Closure conditions will be formulated and the emerging theory will have to satisfy the second law of thermodynamics, since the processes described by the averaged fields must be physically realizable.

It will be demonstrated how the splitting into a smooth "laminar" and an averaged "turbulent" set of equations can be achieved in a systematic and thermodynamically consistent way for any physical system in which the "laminar" variant is valid at all lengths and timescales—this represents the micro-behavior—while the averaged equations model the macro-behavior of the system and the filtering operations are the rules of homogenization. We shall demonstrate this with equations that describe the dynamical response of granular materials in their fluid-like regime.

In Ref. [25], GOODMAN and COWIN proposed a theory of granular materials by considering the solid volume fraction ν as a basic field variable in order to account for the microstructure of the material. They postulated a balance equation, which they called the *balance of equilibrated force*, for the quantity $k\dot{\nu}$, where the *equilibrated inertia* k has the physical dimension of L^2 and $\dot{\nu}$ denotes the total time derivative of ν,

$$\rho\frac{\mathrm{d}}{\mathrm{d}t}(k\dot{\nu}) = \frac{\partial h_j}{\partial x_j} + \rho f + \rho l, \tag{31.1}$$

in which

$$\dot{f} \equiv \frac{\partial f}{\partial t} + \frac{\partial f}{\partial x_j}v_j \equiv \frac{\mathrm{d}f}{\mathrm{d}t}.$$

The vector h_j is referred to as the *equilibrated stress vector*, while the production f and the supply l are called the *intrinsic equilibrated body force* and *external equilibrated body force*, respectively.

The first law of thermodynamics is the assertion that the total energy of a body changes at a rate balanced by the heat flow into that body and the power expended on it. Consequently, considering that the microstructure produces energy quantified as $\frac{1}{2}\rho k\dot{\nu}^2$, these authors derived the balance of internal energy in the form

$$\rho\dot{e} = \boldsymbol{T}\cdot\boldsymbol{D} + \boldsymbol{h}\cdot\operatorname{grad}\dot{\nu} - \rho f\dot{\nu} - \operatorname{div}\boldsymbol{q} + \rho r. \tag{31.2}$$

In our developments, we follow closely GOODMAN and COWIN [25], by slightly modifying the balance equation (31.1). We motivate this by the nonsymmetry of the power terms in the balance equation of internal energy (31.2). More precisely, let us focus attention on Eq. (31.1). By analyzing the physical dimension of the left-hand side, we deduce that the equilibrated stress vector h_j and the intrinsic equilibrated body force f are not at all a stress and a body force, respectively, which we expect them to be due to their names. That is why the power terms $\boldsymbol{h}\cdot\operatorname{grad}\dot{\nu}$, $\rho f\dot{\nu}$, although they clearly are the analoga of $\boldsymbol{T}\cdot\boldsymbol{D}$, have not the same structure as $\boldsymbol{T}\cdot\boldsymbol{D}$. Instead of

(31.1), in Sect. 31.2 we propose a transport equation for the so-called configurational momentum, defined as $\rho\ell\dot{\nu}$, where ℓ is a characteristic length of the material, and derive the balance law of internal energy, in which the terms mentioned before are replaced by $\boldsymbol{h} \cdot \operatorname{grad} \ell\dot{\nu}$, $\rho f \ell\dot{\nu}$.

In order to describe the fluid-like behavior of the granular material, we adopt the same constitutive assumptions as those of GOODMAN and COWIN [25] (see also WANG and HUTTER [63]) with the additional flexibility that the true density may spatially vary. The thermodynamically consistent emerging equations are accepted to be adequate for the description of the true motion of the granular fluid (and correspond to classical fluid mechanics to the NS equations).

In Sect. 31.3, the governing equations of the fully developed turbulent flows of the granular material are derived by applying an ergodic (Reynolds) filter to these equations. These equations comprise of balances of mass, linear and configurational momenta, energy, and turbulent kinetic energy as well as turbulent configurational kinetic energy. We simplify these averaged equations by ignoring fluctuations of the true density and of the solid volume fraction, however the emerging equations still involve density variations. For the dissipation rates of the turbulent kinetic energy and of the turbulent configurational kinetic energy, transport equations are postulated. Since three measures of energy enter the formulation, namely the mean internal energy, the turbulent kinetic energy, and the turbulent configurational kinetic energy, three measures of temperature or coldness are introduced as basic field variables. Finally, for the averaged constitutive quantities of the laminar flow and for the correlation terms due to the fluctuating motion closure relations are given using the rules of material and turbulent objectivity, including equipresence. Because the variables to be deduced from the field equations must describe physically realizable processes, the postulated closure relations must be made to conform with a dissipation principle.

In Sect. 31.4, therefore, we formulate for both laminar and turbulent motions an entropy principle which is used in Sect. 31.5 to restrict the generality of the closure functions postulated in the turbulent case. This task is carried out in the spirit of the MÜLLER–LIU theory. The restrictions are derived in form of the LIU equations and a residual inequality. Exploitation of the entropy principle suggests the introduction of the Helmholtz free energy and achieves determination[1] (i) of all LAGRANGE multipliers in terms of it, (ii) of all three measures of energy. Furthermore, when the HELMHOLTZ free energy is independent of the time rate of changes of the solid volume fraction, we prove a relation for the mean entropy flux analogous to the classical one. Section 31.6 deals with the restrictions on the constitutive functions in the laminar case. In Sect. 31.7, we define the thermodynamic equilibrium as a process that produces no entropy and exploit its consequences with regard to the equilibrium properties of the closure functions. We also perform its analysis in case of linear relations for the nonequilibrium parts of the closure functions.

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[1] These have to be introduced when applying the entropy principle multipliers that uses the field equations as constraints.

31.2 Laminar Motions

We introduce the mechanical and thermal field variables that are used to describe the laminar motions of a granular material: ρ – mass density, ν – solid volume fraction, v_i – velocity, ϑ – coldness, T_{ij} – stress tensor, e – internal energy, q_j – heat flux, b_j – body force, r – heat supply. We suppose $\nu \neq 0$ and define the *true* (or *distributed*) *density* γ by

$$\rho \equiv \gamma \, \nu .$$

The objective of thermodynamics of laminar motions of granular materials is then the determination of the six *basic fields*

$$\gamma, \ \nu, \ v_i, \ \vartheta. \tag{31.3}$$

To this end, the necessary equations are the balance equations complemented by closure relations. The first three of them are

- Balance of mass: $$\dot{\rho} + \rho \frac{\partial v_j}{\partial x_j} = 0, \tag{31.4}$$
- Balance of linear momentum: $$\rho \dot{v}_i = \frac{\partial T_{ij}}{\partial x_j} + \rho \, b_i, \tag{31.5}$$
- Balance of angular momentum: $$T_{ij} = T_{ji}. \tag{31.6}$$

So, as we have done it already for the granular theories in Chaps 29 and 30, the granular theory in this chapter will be based on a BOLTZMANN continuum. However, in our theory the internal energy balance does not have the traditional form, because the time derivative of the solid volume fraction produces kinetic energy. In order to deduce the appropriate form of the internal energy balance, we first propose a transport equation for the time derivative of the solid volume fraction as follows.

In this chapter the microstructure, characteristic for granular materials, will be the amended GOODMAN–COWIN model with internal length scale as developed by FANG et al. [14, 15] and explained in Sect. 29.8 of Chap. 29. To separate this kind of model from the postulated physical quantities and equations of the GOODMAN–COWIN model typified by "equilibrated forces" etc., these forces and equations will be characterized as *configurational* forces etc., In this spirit, let[2] ℓ be a characteristic length of the granular material, such as a typical particle diameter or the width of an internal boundary layer. Then, the quantity $\ell\dot{\nu}$ has the physical dimension of a velocity, so that we may call $\rho \, \ell\dot{\nu}$ the *configurational momentum.* For it we assume the following transport equation:

$$\frac{\partial}{\partial t}(\rho\ell\dot{\nu}) + \frac{\partial}{\partial x_j}(\rho\ell\dot{\nu}v_j) = \rho\frac{\mathrm{d}}{\mathrm{d}t}(\ell\dot{\nu}) = \frac{\partial h_j}{\partial x_j} + \rho f, \tag{31.7}$$

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[2] A change of the notation k, as employed in Chaps. 29 and 30, has been necessary, in order to eliminate the confusion that would result in referring to k as the turbulent kinetic energy.

in which the balance of mass has been used to obtain the expression in the middle of this chain of expressions. By analogy with the balance of linear momentum, the flux h_j may be called the *configurational stress vector* and the production f—the *configurational body force*. Note that our Eq. (31.7) does not contain any supply term, as (31.1) does. The supplies are, at least principally, sources that drive the system externally and can be controlled by measuring them. Therefore, a supply l in (31.7) has to be a measurable external quantity, but there is no indication that such a source describing the microscale effects on the macroscale would exist. In short, (31.7) is exclusively an equation describing the material properties, and source terms cannot play any role to that end.

Now we write the first law of thermodynamics by taking into account the kinetic energy produced by the microstructure of the granular material:

$$\begin{aligned}&\frac{\partial}{\partial t}\left\{\rho(e+\tfrac{1}{2}v_i v_i+\tfrac{1}{2}\,\ell^2\dot{\nu}^2)\right\}\\&+\frac{\partial}{\partial x_j}\left\{\rho(e+\tfrac{1}{2}v_i v_i+\tfrac{1}{2}\,\ell^2\dot{\nu}^2)v_j-T_{ij}\,v_i-\ell\dot{\nu}h_j+q_j\right\}=\rho\,b_i v_i+\rho\,r.\end{aligned} \tag{31.8}$$

If (31.8) is rewritten by using (31.4), and from this new expression of the first law we subtract the balance of linear momentum multiplied by v_i and the balance of configurational momentum multiplied by $\ell\dot{\nu}$, we get the balance of internal energy

$$\rho\dot{e}=T_{ij}D_{ij}+h_j\frac{\partial}{\partial x_j}(\ell\dot{\nu})-\rho\,f\ell\dot{\nu}-\frac{\partial q_j}{\partial x_j}+\rho r. \tag{31.9}$$

Here D_{ij} denotes the stretching tensor. The second and the third power terms on the right-hand side of (31.9) are quite analogous to the usual power term $T_{ij}D_{ij}$ that appears in the classical balance of internal energy. For the characteristic length ℓ, we could write an evolution equation, but we consider the simplest case, i.e., ℓ is a constant. For alternatives, see Chap. 29, Sect. 29.8.

The system (31.4)–(31.7), (31.9) is not closed in the sense that it contains too many unknowns. Besides, the temperature θ or coldness $\vartheta = 1/\theta$ does not appear explicitly as a variable in this system. That is why we must *close* it by setting in relation the field variables of the set

$$\{T_{ij},\ h_j,\ f,\ e,\ q_j\} \tag{31.10}$$

to the basic fields (31.3). Therefore, if C stands for any member of the set (31.10), then we suppose that C is given by the *closure* (*constitutive*) *relation*

$$C=\mathcal{F}\left(\nu_0,\ \nu,\ \dot{\nu},\ \frac{\partial\nu}{\partial x_i},\ \gamma,\ \frac{\partial\gamma}{\partial x_i},\ D_{ij},\ \vartheta,\ \frac{\partial\vartheta}{\partial x_i}\right), \tag{31.11}$$

where ν_0 is a reference solid volume fraction, that we take into account according to [25]. In comparison to a previous work [63], (grad γ) is added as another independent variable in order to envisage more realistic situations. The functions $\mathcal{F}$ in

(31.11) are supposed to have a common domain of definition $\mathcal{D}$, that we call the *laminar state space*. The function $\mathcal{F}$ is called a *material* or *constitutive* or *closure function*. We assume that the field variables of the set (31.10) are objective and that the corresponding material functions are frame indifferent. Occasionally for brevity we shall denote by $\boldsymbol{y}$ any member of the laminar state space, i.e.,

$$\boldsymbol{y} \equiv \left(\nu_0,\ \nu,\ \dot{\nu},\ \frac{\partial \nu}{\partial x_i},\ \gamma,\ \frac{\partial \gamma}{\partial x_i},\ D_{ij},\ \vartheta,\ \frac{\partial \vartheta}{\partial x_i} \right). \tag{31.12}$$

If we introduce the closure relations (31.10), (31.11) into (31.4)–(31.7), (31.9) we obtain the *field equations* for the determination of the basic field variables (31.3). Every solution of these field equations is called a *laminar thermodynamic process*.

31.3 Turbulent Motions

In a turbulent motion, all the field variables are decomposed into a mean part and a fluctuating part. Doing this one uses a *filter*, i.e., an averaging operator which defines the mean value $\overline{u}$ of a quantity u. We use a filter having the properties

$$\begin{aligned}
&\overline{u+v} = \overline{u} + \overline{v}, \qquad \overline{\lambda u} = \lambda \overline{u} \ \ (\lambda \in \mathbb{R}),\\
&\overline{\overline{u}} = \overline{u},\\
&\text{it commutes with the derivatives, e.g. } \overline{\frac{\partial u}{\partial x}} = \frac{\partial \overline{u}}{\partial x},\\
&\overline{u\,\overline{v}} = \overline{u}\,\overline{v}.
\end{aligned} \tag{31.13}$$

Such a filter is called an *ergodic* or a REYNOLDS *filter*. The fluctuating part of u is defined as u' and for the mean velocity we use the notation U_i, i.e., $\overline{v}_i \equiv U_i$. Thus,

$$u = \overline{u} + u' \quad \text{and} \quad v_i = U_i + v_i'.$$

Only the mean values of the field variables are relevant for the mean motion. In order to obtain the equations that relate the mean fields, we filter the balance equations. The equations that are obtained by this procedure are called the *mean balance equations*. We shall show that they can be put into the form of balance laws. Next, we derive those basic laws that model the turbulent flows of the granular materials which were introduced in Sect. 31.2.

The averaging procedure forces us to select a particular expression for the system of balance equations. The choice is unambiguous, since the balance equations are originally postulated in the form

$$\frac{\partial \rho f}{\partial t} + \frac{\partial}{\partial x_j}\left\{\rho f v_j + \Phi_j\right\} = \rho \pi + \rho s, \tag{31.14}$$

where Φ_j is the flux, π is the production, and s is the supply of f. Therefore, the starting point of averaging will be the form (31.14) of the balance laws on which the theory of laminar flows is developed. We now write down these balance laws.

- Balance of mass:

$$\frac{\partial\rho}{\partial t}+\frac{\partial\rho v_j}{\partial x_j}=0. \tag{31.15}$$

- Balance of linear momentum:

$$\frac{\partial\rho v_i}{\partial t}+\frac{\partial}{\partial x_j}\left\{\rho v_i v_j-T_{ij}\right\}-\rho b_i=0. \tag{31.16}$$

- Balance of configurational momentum:

$$\frac{\partial\rho\ell n}{\partial t}+\frac{\partial}{\partial x_j}\left\{\rho\ell n v_j-h_j\right\}-\rho f=0, \qquad n\equiv\dot{\nu}. \tag{31.17}$$

- Balance of total energy (the first law of thermodynamics):

$$\begin{aligned}&\frac{\partial}{\partial t}\left\{\rho\left(e+\tfrac{1}{2}v_i v_i+\tfrac{1}{2}\ell^2 n^2\right)\right\}\\&+\frac{\partial}{\partial x_j}\left\{\rho\left(e+\tfrac{1}{2}v_i v_i+\tfrac{1}{2}\ell^2 n^2\right)v_j-T_{ij}v_i-\ell n h_j+q_j\right\}\\&-\rho b_i v_i-\rho r=0.\end{aligned} \tag{31.18}$$

Next, we sketch the way that we follow in averaging (31.15)–(31.18). These equations can be symbolically written as

$$\begin{aligned}&A=0, \quad B_i=0, \quad C=0\,,\\&B_i v_i-\tfrac{1}{2}Av_i v_i+C\ell n-\tfrac{1}{2}A\ell^2 n^2+D=0,\end{aligned} \tag{31.19}$$

where the significance of the quantities A, B_i, C is obvious from (31.15)–(31.17), and D is given by

$$D\equiv\frac{\partial\rho e}{\partial t}+\frac{\partial\rho e v_j}{\partial x_j}-T_{ij}D_{ij}-h_j\frac{\partial\ell n}{\partial x_j}+\rho f\ell n+\frac{\partial q_j}{\partial x_j}-\rho r. \tag{31.20}$$

With the aid of (31.19), this equation can easily be verified. Note that, by rewriting (31.18) in the form $(31.19)_4$, we did not use (31.15)–(31.17), thus keeping the system (31.15)–(31.18) in its original form. By averaging (31.19) we get

$$\begin{aligned}&\overline{A}=0, \quad \overline{B_i}=0, \quad \overline{C}=0,\\&\overline{B_i v_i}-\tfrac{1}{2}\overline{Av_i v_i}+\overline{C\ell n}-\tfrac{1}{2}\overline{A\ell^2 n^2}+\overline{D}=0.\end{aligned} \tag{31.21}$$

When exploiting the system (31.21) we must take into account the relations

$$\overline{B_i v_i} = 0, \quad \overline{A v_i v_i} = 0, \quad \overline{C\ell n} = 0, \quad \overline{A\ell^2 n^2} = 0,$$

which are valid because of $(31.19)_{1-3}$; they are also independent of $(31.21)_{1-3}$. Indeed, e.g., $B_i = 0$ implies $B_i\, v_i = 0$ for any finite v_i. Thus, by definition

$$B_i v_i = \overline{(B_i\, v_i)} + (B_i\, v_i)' \quad \longrightarrow \quad \overline{(B_i\, v_i)} = \overline{\overline{B_i v_i}} + \overline{(B_i\, v_i)'},$$

implying $\overline{B_i\, v_i} = \overline{\overline{B_i v_i}}$, owing to $(31.13)_3$. Consequently, the averaging procedure applied to system (31.19) gives the set of independent equations

$$\begin{aligned} &\overline{A} = 0, \quad \overline{B}_i = 0, \quad \overline{C} = 0, \quad \overline{D} = 0, \\ &\overline{B_i v_i} = 0\,, \quad \overline{A v_i v_i} = 0, \quad \overline{C\ell n} = 0, \quad \overline{A\ell^2 n^2} = 0, \end{aligned}$$

which can be further exploited in the following manner: The terms $B_i v_i$ and $A v_i v_i$ are given by

$$\begin{aligned} B_i v_i &= \frac{\partial}{\partial t}(\rho v_i v_i) + \frac{\partial}{\partial x_j}(\rho v_i v_i v_j) - \frac{\partial}{\partial x_j}(T_{ij} v_i) + T_{ij}\frac{\partial v_i}{\partial x_j} - \rho b_i v_i \dot{v}_i, \quad (31.22)\\ A v_i v_i &= \frac{\partial}{\partial t}(\rho v_i v_i) + \frac{\partial}{\partial x_j}(\rho v_i v_i v_j) - 2\rho v_i \dot{v}_i. \end{aligned}$$

The result is that both equations $\overline{B_i v_i} = 0$ and $\overline{A v_i v_i} = 0$ contain the term $\overline{\rho v_i \dot{v}_i}$. We can eliminate it by considering the equation

$$\overline{B_i v_i} - \tfrac{1}{2}\overline{A v_i v_i} = 0. \tag{31.23}$$

Analogously, the terms $C\ell n$ and $A\ell^2 n^2$ are given by the expressions

$$\begin{aligned} C\ell n &= \frac{\partial}{\partial t}(\rho\ell^2 n^2) + \frac{\partial}{\partial x_j}\Big((\rho\ell^2 n^2 v_j) - (\ell n h_j)\Big) + h_j\frac{\partial \ell n}{\partial x_j} - \rho f \ell n - \rho\ell^2 \dot{n}, \quad (31.24)\\ A\ell^2 n^2 &= \frac{\partial}{\partial t}\Big(\rho\ell^2 n^2\Big) + \frac{\partial}{\partial x_j}(\rho\ell^2 n^2 v_j) - 2\rho\ell^2 n\dot{n}. \end{aligned}$$

From the system $\overline{C\ell n} = 0$, $\overline{A\ell^2 n^2} = 0$, we eliminate the term $\overline{\rho\ell^2 n\dot{n}}$ and deduce the relation

$$\overline{C\ell n} - \tfrac{1}{2}\overline{A\ell^2 n^2} = 0. \tag{31.25}$$

In the derivation of these results, it was assumed that ℓ is constant. Thus, we obtain in this case the following system of governing equations of the mean motion of granular materials[3] :

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[3] The specification "modified" will soon become clear.

$$\begin{aligned}
&\overline{A} = 0 && \text{(balance of mean mass),}\\
&\overline{B_i} = 0 && \text{(balance of mean linear momentum),}\\
&\overline{C} = 0 && \text{(balance of mean configurational momentum),}\\
&\overline{D} = 0 && \text{(balance of modified mean internal energy),}\\
&\overline{B_i v_i} - \tfrac{1}{2}\overline{A v_i v_i} = 0 && \text{(balance of modified turbulent kinetic energy),}\\
&\overline{C\ell n} - \tfrac{1}{2}\overline{A\ell^2 n^2} = 0 && \text{(balance of modified turbulent configurational}\\
& && \text{ kinetic energy).}
\end{aligned}$$

Now, we proceed to derive explicit expressions for these equations, by writing them in the form of balance laws. To this end, in the averaging procedure we use the properties of the chosen filter and the easily verifiable rules

$$\begin{aligned}
&\overline{uv} = \overline{u}\,\overline{v} + \overline{u'v'}, \qquad \overline{\rho u v} = \overline{\rho}\,\overline{u}\,\overline{v} + \overline{u}\,\overline{\rho' v'} + \overline{v}\,\overline{\rho' u'} + \overline{\rho u' v'},\\
&\overline{\rho u v w} = \overline{\rho}\,\overline{u}\,\overline{v}\,\overline{w} + \overline{u}\,\overline{w}\,\overline{\rho' v'} + \overline{v}\,\overline{w}\,\overline{\rho' u'} + \overline{u}\,\overline{v}\,\overline{\rho' w'} + \overline{u}\,\overline{\rho v' w'}\\
&\qquad + \overline{v}\,\overline{\rho u' w'} + \overline{w}\,\overline{\rho u' v'} + \overline{\rho u' v' w'}.
\end{aligned}$$

It is convenient to define the notation

$$U_j \equiv \overline{v}_j, \qquad \overline{\rho} m_j = \overline{\rho' v'_j} \tag{31.26}$$

for the mean velocity field $\overline{v}_j$ and mass weighted diffusion velocity m_i. These two quantities suggest the so-called FAVRE-averaged velocity

$$V_j = U_j + m_j. \tag{31.27}$$

Averaging the mass balance equation (see (31.15)) leads to the following chain of inferences:

$$\begin{aligned}
&\frac{\partial\overline{\rho}}{\partial t} + (\overline{\rho v_j})_{,j} = 0,\\
&\frac{\partial\overline{\rho}}{\partial t} + (\overline{\rho}\,\overline{v}_j)_{,j} + (\overline{\rho' v'_j})_{,j} = \frac{\partial\overline{\rho}}{\partial t} + \overline{\rho}\,\overline{v}_{j,j} + \overline{\rho}_{,j}\overline{v}_j + \underbrace{(\overline{\rho' v'_j})_{,j}}_{(\overline{\rho} m_j)_{,j}} = 0, \qquad (31.28)\\
&\underbrace{\frac{\partial\overline{\rho}}{\partial t} + \overline{\rho}_{,j}(\overline{v}_j + m_j)}_{\overset{\circ}{\overline{\rho}}} + \underbrace{\overline{\rho}(\overline{v}_j + m_j)_{,j}}_{\overline{\rho} V_{j,j}} = 0,\\
&\overset{\circ}{\overline{\rho}} + \overline{\rho} V_{j,j} = 0,
\end{aligned}$$

where the superposed ring denotes the FAVRE time derivative, i.e.,

$$\overset{\circ}{f} \equiv \frac{\partial f}{\partial t} + \frac{\partial f}{\partial x_j} V_j. \tag{31.29}$$

Equation (31.28) expresses the *balance of the mean mass*. A simple computation also shows that

$$\begin{aligned}\frac{\partial(\bar\rho f)}{\partial t} + (\bar\rho\, f\, V_j)_{,j} &= f\frac{\partial\bar\rho}{\partial t} + \bar\rho\frac{\partial f}{\partial t} + (\bar\rho\, f)_{,j} V_j + (\bar\rho\, f) V_{j,j}\\ &= f\underbrace{\left\{\left[\underbrace{\frac{\partial\bar\rho}{\partial t} + \bar\rho_{,j} V_j}_{\overset{\circ}{\bar\rho}}\right] + \bar\rho\, V_{j,j}\right\}}_{\overset{\circ}{\bar\rho}+\bar\rho\, V_{j,j}=0} + \underbrace{\bar\rho\left(\frac{\partial f}{\partial t} + f_{,j} V_j\right)}_{\bar\rho\overset{\circ}{f}},\end{aligned}$$

so that

$$\frac{\partial(\bar\rho f)}{\partial t} + \frac{\partial(\bar\rho f V_j)}{\partial x_j} = \bar\rho\,\overset{\circ}{f},$$

which will be used in the derivation of the mean balance laws, without explicitly mentioning it.

Next, by averaging the balance of linear momentum (see (31.16)) a somewhat lengthy calculation yields

$$\bar\rho\,\overset{\circ}{V}_i = \frac{\partial}{\partial x_j}(\overline{T}_{ij} + R_{ij}) + \bar\rho\,\bar b_i + \overline{\rho' b_i'}, \tag{31.30}$$

where the *modified* Reynolds *stress tensor* R_{ij} is defined[4] as

$$R_{ij} \equiv -\overline{\rho\, v_i' v_j'} + \bar\rho\, m_i m_j. \tag{31.31}$$

Details are exemplified in Appendix 31.B at the end of the chapter. Since $\bar\rho\, V_i = \overline{\rho\, v_i}$, Eq. (31.30) can be interpreted as the *balance of mean linear momentum*. Note that, in view of the formula[5]

$$\overline{\rho\, u'' v''} = \overline{\rho\, u' v'} - \frac{1}{\bar\rho}\,\overline{\rho' u'}\;\overline{\rho' v'}, \tag{31.32}$$

where u'', v'' denote the Favre fluctuating parts of u and v, respectively, and the flux R_{ij} equals the Reynolds stress tensor introduced in the Favre averaging procedure. Therefore, Eq. (31.30) is nothing else than the mean balance of linear momentum as a result of Favre filtering. In the form (31.30) it is expressed in terms of only one type of mean value, namely that introduced in (31.13). Apart from this, the Reynolds filter is preferred to the Favre filter, at least because it commutes with derivatives and the Favre filter does not.

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[4] The classical Reynolds stress tensor is given by $R_{ij} \equiv -\overline{\rho\, v_i' v_j'}$.

[5] The proof of it rests on the identity $\bar\rho(\tilde u - \bar u) = \overline{\rho' u'}$, where $\tilde u$ is the Favre (For a brief biography of Alexandre Jean Auguste Favre, see **Fig. 31.1**.) mean value of u, defined as $\bar\rho\,\tilde u \equiv \overline{\rho u}$.

Fig. 31.1 ALEXANDRE JEAN AUGUSTE FAVRE (February 23, 1911–May 25, 2005)

ALEXANDRE JEAN AUGUSTE FAVRE (Feberuary 23, 1911 Toulon–May 25, 2005 Marseille) has been an engineering physicist with specialization in turbulence. He received his basic education at Toulon and Saint-Nazaire and acquired his academic degree in engineering physics at the "École d' Ingénieurs de Marseille" from 1928–1931 with graduation in 1932. Following this period, he specialized at the "Institut de Mécanique des fluids" in Marseille, where he prepared his doctoral dissertation on air flow around airplane wings under the supervision of ANDRÉ MARCHAND.

ALEXANDRE FAVRE received in 1945 the position Maitre de Conférences (Lecturer) and in 1951 Titular Professor of Statistical Turbulence and Meteorology at the Université de la Méditerranée and simultaneously professor of Fluid Mechanics at "Ecole Central de Marseille". Here, he devoted during more than two decades his interests to the recruitment and education of students and collaborators. After several consultancies with THEODORE VON KÁRMÁN, he created in 1961 the "Institute of Statistical Mechanics and Turbulence (IMST)", where he functioned for nearly 20 years as Director. The institute's principal researches were/are supersonic flows and exchange mechanisms between the ocean and the atmosphere, which influenced developments in supersonic aviation and meteorology.

FAVRE was elected into the "Académie de Marseille" in 1968, as corresponding member of the "Académie des Sciences" in 1971 and full member in 1977.

He was "Officier de la Légion d' Honneur et de la Ordre du Mérite" and the "Commandeur des Palmes".

Professionally, FAVRE primarily worked in fluid experimentation [18], particularly in two-dimensional turbulence [20, 21] and meteorology [22]. He gained his lasting scientific recognition through the statistical averaging of the compressible NAVIER STOKES equations, where in 1965 the FAVRE averaging was introduced in lieu of REYNOLDS averaging [19, 23].

The text is based on www.wikipedia.org and [26]

We go further and average the balance of configurational momentum (see (31.17)) and obtain

$$\overline{\rho}\,\ell\,\overset{\circ}{\mathfrak{n}} = \frac{\partial}{\partial x_j}(\overline{h}_j + H_j) + \overline{\rho}\,\overline{f} + \overline{\rho' f'}, \tag{31.33}$$

where

$$\mathfrak{n} \equiv \overline{n} + m, \quad \overline{\rho}\, m \equiv \overline{\rho' n'}, \quad H_j \equiv -\ell\,\overline{\rho\, n' v'_j} + \overline{\rho}\,\ell\, m m_j. \tag{31.34}$$

Detailed calculations are shown in Appendix 31.C at the end of the chapter.

Since $\overline{\rho}\,\mathfrak{n} = \overline{\rho n}$, we interpret (31.33) as the *balance of mean configurational momentum*. The correlation H_j can be called *turbulent configurational stress vector*.

By averaging the balance of internal energy, $D = 0$ (see (31.20)), we obtain

$$\begin{aligned} \overline{\rho}\,\overset{\circ}{\mathfrak{e}} = {} & \overline{T}_{ij}\frac{\partial U_i}{\partial x_j} + \overline{h}_j\frac{\partial \ell\,\overline{n}}{\partial x_j} - \frac{\partial}{\partial x_j}(\overline{q}_j + Q_j) \\ & + \overline{\rho}\,\epsilon + \overline{\rho} H - \ell\,\mathfrak{n}(\overline{\rho}\,\overline{f} + \overline{\rho' f'}) + \overline{\rho}\,\overline{r} + \overline{\rho' r'}, \end{aligned} \tag{31.35}$$

which is derived in Appendix 31.D at the end of the chapter. The new correlation variables are defined as

$$\begin{aligned} & \overline{\rho}\mathfrak{e} \equiv \overline{\rho}\,\overline{e} + \overline{\rho' e'}, \quad Q_j \equiv \overline{\rho\, e' v'_j} - \overline{\rho' e'}\, m_j, \\ & \overline{\rho}\,\epsilon \equiv \overline{T'_{ij}\frac{\partial v'_i}{\partial x_j}}, \quad \overline{\rho} H \equiv \overline{h'_j\,\frac{\partial \ell n'}{\partial x_j}} - \overline{\rho f' \ell n'} + \overline{\rho' f'}\ell m. \end{aligned} \tag{31.36}$$

Equation (31.35) is the *balance of modified mean internal energy*[6] $\mathfrak{e}$. The correlation Q_j can be identified as *turbulent heat flux*. Using again (31.32) we recognize Q_j as being the FAVRE turbulent heat flux. The terms $\overline{\rho}\epsilon$, $\overline{\rho}H$ will be interpreted later.

Next, we exploit equation (31.23), in which we insert (31.22). By averaging we deduce that[7]

$$\begin{aligned} \overline{\rho}\,(\overset{\circ}{k} - m_i\,\overset{\circ}{m}_i + V_i\,\overset{\circ}{V}_i) = {} & R_{ij}\frac{\partial U_i}{\partial x_j} + \frac{\partial K_j}{\partial x_j} \\ & + U_i\left\{\frac{\partial}{\partial x_j}(\overline{T}_{ij} + R_{ij}) + \overline{\rho}\,\overline{b}_i + \overline{\rho' b'_i}\right\} - \overline{\rho}\epsilon + \overline{\rho}\overline{b}_i m_i + \overline{\rho\, b'_i v'_i}, \end{aligned} \tag{31.37}$$

---

[6] By definition $(31.36)_1$, $\mathfrak{e}$ is the FAVRE mean value of the internal energy density e.

[7] The above computations with explanatory details in Appendices B, C, D at the end of the chapter could be continued, but these computations will not be demonstrated; only the final result will be quoted, because the structure of the derivation is analogous to what has been demonstrated before, "only" more complex.

where the *turbulent kinetic energy* k and the flux K_j are introduced according to

$$\overline{\rho}\, k \equiv \tfrac{1}{2}\,\overline{\rho v_i' v_i'}, \qquad K_j \equiv \overline{T_{ij}' v_i'} - \tfrac{1}{2}\,\overline{\rho v_i' v_i' v_j'} + \overline{\rho}\, k\, m_j. \tag{31.38}$$

If we use the balance of mean linear momentum (31.30) in order to eliminate the term $\overline{\rho}\,\overset{\circ}{V}_i$ in (31.37), we obtain the *balance of modified turbulent kinetic energy* $\mathfrak{k}$, viz.,

$$\begin{aligned}\overline{\rho}\,\overset{\circ}{\mathfrak{k}} = R_{ij}\frac{\partial V_i}{\partial x_j} + \overline{T}_{ij}\,\frac{\partial m_i}{\partial x_j} + \frac{\partial}{\partial x_j}\left\{K_j - (\overline{T}_{ij} + R_{ij})\, m_i\right\}\\ -\overline{\rho}\,\epsilon - \overline{\rho' b_i'}\, m_i + \overline{\rho b_i' v_i'},\end{aligned} \tag{31.39}$$

where

$$\overline{\rho}\,\mathfrak{k} \equiv \overline{\rho}\,\left(k - \tfrac{1}{2}\, m_i m_i\right) = -\tfrac{1}{2} R_{ii}. \tag{31.40}$$

Hence, $\mathfrak{k}$ is the FAVRE turbulent kinetic energy. The production $\overline{\rho}\,\epsilon$ (here an annihilation) can be interpreted as the dissipation rate of $\mathfrak{k}$. If m_i is identically zero, equation (31.39) turns into the balance of the classical turbulent kinetic energy k.

Finally, we exploit Eq. (31.25). Inserting (31.24) into (31.25) and averaging, we obtain

$$\begin{aligned}&\overline{\rho}\,(\overset{\circ}{s} - \ell^2 m\, \overset{\circ}{m} + \ell^2 \mathfrak{n}\, \overset{\circ}{\mathfrak{n}})\\ &= H_j \frac{\partial \ell\, \overline{n}}{\partial x_j} + \frac{\partial L_j}{\partial x_j} + \ell\, \overline{n}\frac{\partial}{\partial x_j}(\overline{h}_j + H_j) - \overline{\rho}\, H + \ell\, \mathfrak{n}\, (\overline{\rho}\, \overline{f} + \overline{\rho' f'}),\end{aligned} \tag{31.41}$$

where the *turbulent configurational kinetic energy* s and the flux L_j are defined as

$$\overline{\rho}\, s \equiv \tfrac{1}{2}\,\overline{\rho\, \ell^2 n'^2}, \qquad L_j \equiv \overline{\ell\, n' h_j'} - \tfrac{1}{2}\overline{\rho\, \ell^2\, n'^2 v_j'} + \overline{\rho}\, s\, m_j. \tag{31.42}$$

Substitution of $\overline{\rho}\ell\, \overset{\circ}{\mathfrak{n}}$ from the balance law (31.33) into (31.41) gives the *balance of modified turbulent configurational kinetic energy* $\mathfrak{s}$, viz.,

$$\overline{\rho}\,\overset{\circ}{\mathfrak{s}} = H_j \frac{\partial \ell \mathfrak{n}}{\partial x_j} + \overline{h}_j \frac{\partial \ell m}{\partial x_j} + \frac{\partial}{\partial x_j}\left\{L_j - (\overline{h}_j + H_j)\, \ell m\right\} - \overline{\rho} H, \tag{31.43}$$

where

$$\mathfrak{s} \equiv s - \tfrac{1}{2}\, \ell^2 m^2. \tag{31.44}$$

When $m = 0$, Eq. (31.43) emerges as the balance law of the classical turbulent configurational kinetic energy s. The production $\overline{\rho} H$ (here also an annihilation) can be interpreted as the *dissipation rate* of $\mathfrak{s}$. The rates of dissipation $\overline{\rho}\,\epsilon$, $\overline{\rho} H$ also enter the balance of modified mean internal energy (31.35) with opposite sign. According to their interpretation, they should be positive and then enter as production terms in this equation. The balance law (31.35) contains yet another production /annihilation term, $\ell\mathfrak{n}(\overline{\rho}\,\overline{f} + \overline{\rho' f'})$ due to the configurational body force. Its sign is not clear at the present stage of the analysis, but intuitively should be negative.

Consider next a laminar balance equation

$$\rho\frac{\mathrm{d}\eta}{\mathrm{d}t} + \frac{\partial\phi_j}{\partial x_j} - \sigma = \pi \tag{31.45}$$

for a scalar quantity η, its flux ϕ_j, supply σ, and production π. Here, η will be identified with the entropy density, ϕ_j with its flux, σ its supply density and π its production density. REYNOLDS averaging (31.45) leads to

$$\overline{\rho}(\overset{\circ}{\overline{\eta}} + \overset{\circ}{S}) + \frac{\partial}{\partial x_j}\left(\phi_j^{\text{turb}}\right) - \overline{\sigma} = \overline{\pi}, \tag{31.46}$$

in which

$$\overline{\rho}S \equiv \overline{\rho'\eta'}, \quad \phi_j^{\text{turb}} \equiv \overline{\phi}_j + \phi_j^T, \quad \phi_j^T \equiv \overline{\rho\eta' v_j'} - \overline{\rho}Sm_j. \tag{31.47}$$

A derivation of (31.46) from (31.45) is given in Appendix 31.E to this chapter.

Now we shall simplify the analysis by assuming that

$$\gamma' = 0, \quad \nu' = 0. \tag{31.48}$$

The first of these assumptions implies that, although the true density may vary, its fluctuations are assumed to be negligible. This is reasonable, because acoustic waves in grains usually have timescales that are distant from turbulent fluctuation time scales. Thus, we still account for compressibility but do not consider its fluctuation as significant. The second assumption is physically not so obvious. It says that particle collisions may give rise to interstitial volume changes on the mean level but not to fluctuations of it. Intuitively, this seems to be a reasonable approximation even though its experimental corroboration would be difficult.

Since

$$\rho' = \overline{\gamma}\nu' + \gamma'\overline{\nu} + \gamma'\nu' - \overline{\gamma'\nu'},$$

it follows on the basis of assumptions (31.48) that $\rho' = 0$ and therefore $m_i = 0, m = 0$ (see $(31.27)_2$, $(31.34)_2$), which clearly simplifies the balance equations (31.28), (31.30), (31.33), (31.35), (31.39), (31.43). Moreover, the FAVRE time derivative (31.29) merges into the time derivative following the mean motion, U_j, viz.

$$\overset{\circ}{f} = \dot{f}, \quad \dot{f} \equiv \frac{\partial f}{\partial t} + \frac{\partial f}{\partial x_j}U_j.$$

Henceforth, this definition will be kept for the remainder of this chapter. Then the relations

$$\overline{n} = \frac{\partial \overline{\nu}}{\partial t} + \frac{\partial \overline{\nu}}{\partial x_j} U_j + \overline{\frac{\partial \nu'}{\partial x_j} v'_j}, \quad n' = \frac{\partial \nu'}{\partial t} + \frac{\partial \nu'}{\partial x_j} U_j + \frac{\partial \nu}{\partial x_j} v'_j - \overline{\frac{\partial \nu'}{\partial x_j} v'_j}$$

and assumption $(31.48)_2$ simplify to

$$\dot{\overline{\nu}} = \overline{n}, \quad n' = \frac{\partial \overline{\nu}}{\partial x_j} v'_j. \tag{31.49}$$

Thus, supposing also that there are no fluctuations of the body force, i.e., $b'_i = 0$, the balance equations (31.28), (31.30), (31.33), (31.35), (31.39), (31.43), and (31.46) take the forms

$$\dot{\overline{\rho}} + \overline{\rho} \frac{\partial U_j}{\partial x_j} = 0, \tag{31.50}$$

$$\overline{\rho} \dot{U}_i = \frac{\partial}{\partial x_j} (\overline{T}_{ij} + R_{ij}) + \overline{\rho}\, \overline{b}_i, \tag{31.51}$$

$$\ell \overline{\rho}\, \ddot{\overline{\nu}} = \frac{\partial}{\partial x_j} (\overline{h}_j + H_j) + \overline{\rho}\, \overline{f}, \tag{31.52}$$

$$\begin{aligned} \overline{\rho}\, \dot{\overline{e}} = \overline{T}_{ij} \frac{\partial U_i}{\partial x_j} + \ell\, \overline{h}_j \frac{\partial \dot{\overline{\nu}}}{\partial x_j} - \frac{\partial}{\partial x_j} (\overline{q}_j + Q_j) + \overline{\rho}\, \epsilon + \overline{\rho} H \\ -\ell\, \overline{\rho}\, \dot{\overline{\nu}} \overline{f} + \overline{\rho}\, \overline{r}, \end{aligned} \tag{31.53}$$

$$\overline{\rho} \dot{k} = R_{ij} \frac{\partial U_i}{\partial x_j} + \frac{\partial K_j}{\partial x_j} - \overline{\rho}\, \epsilon, \tag{31.54}$$

$$\overline{\rho} \dot{s} = \ell\, H_j \frac{\partial \dot{\overline{\nu}}}{\partial x_j} + \frac{\partial L_j}{\partial x_j} - \overline{\rho} H, \tag{31.55}$$

$$\overline{\rho} \dot{\eta} = -\frac{\partial \phi_j}{\partial x_j} + \sigma + \pi. \tag{31.56}$$

The quantities R_{ij}, H_j, Q_j, ϵ, H, K_j, L_j, k, s are defined in (31.31), $(31.34)_3$, $(31.36)_{2\text{–}4}$, (31.38), (31.42). We collect them here and write them by taking into account (31.49) and $\rho' = 0$:

$$\begin{aligned} R_{ij} &= -\overline{\rho}\, \overline{v'_i v'_j}, \\ H_j &= -\ell \overline{\rho} \overline{n' v'_j} \overset{(31.49)_2}{=} \ell \overline{\rho} \overline{v'_i v'_j} \frac{\partial \overline{\nu}}{\partial x_j} = \ell\, R_{ij} \frac{\partial \overline{\nu}}{\partial x_i}, \\ Q_j &= \overline{\rho}\, \overline{e' v'_j}, \qquad \overline{\rho}\, \epsilon = \overline{T'_{ij} \frac{\partial v'_i}{\partial x_j}}, \end{aligned}$$

$$
\begin{aligned}
\overline{\rho}H &= \ell\, h_i' \frac{\partial n'}{\partial x_i} - \overline{\rho\, f'\, \ell n'} = \ell \overline{h_i' \frac{\partial}{\partial x_i}\left(\frac{\partial \overline{\nu}}{\partial x_j} v_j'\right)} - \ell \overline{\rho\, f' v_j'} \frac{\partial \overline{\nu}}{\partial x_j} \\
&= \ell\, \underbrace{\overline{h_i' v_j'}}_{H_{ij}} \frac{\partial^2 \overline{\nu}}{\partial x_i \partial x_j} + \underbrace{\ell \overline{h_i' \frac{\partial \overline{\nu}}{\partial x_i} \frac{\partial v_j'}{\partial x_j}} - \ell \overline{\rho}\, \overline{f' v_j'} \frac{\partial \overline{\nu}}{\partial x_j}}_{\overline{\rho}\, d \equiv \ell\left(h_i' \frac{\partial v_i}{\partial x_j} - \overline{\rho}\, \overline{f' v_j'}\right) \frac{\partial \overline{\nu}}{\partial x_j}} \\
&= H_{(ij)} \frac{\partial^2 \overline{\nu}}{\partial x_i \partial x_j} + \overline{\rho}\, d, \qquad (31.57) \\
\overline{\rho}\, d &= \ell \left(\overline{h_i' \frac{\partial v_i}{\partial x_j}} - \overline{\rho}\, \overline{f' v_j} \right) \frac{\partial \overline{n}}{\partial x_j}, \\
\overline{\rho}\, k &= \tfrac{1}{2} \overline{\rho}\, \overline{v_i' v_i'} = -\tfrac{1}{2} R_{ii}, \\
K_j &= \overline{T_{ij}'\, v_i'} - \tfrac{1}{2} \overline{\rho\, v_i'\, v_i'\, v_j'} = \overline{T_{ij}'\, v_i'} + \tfrac{1}{2} R_{iij}, \\
\overline{\rho} s &= \tfrac{1}{2} \ell^2 \overline{\rho (n')^2} = \tfrac{1}{2} \ell^2\, \underbrace{\overline{\rho}\, \overline{v_i' v_j'}}_{-R_{ij}} \frac{\partial \overline{\nu}}{\partial x_i} \frac{\partial \overline{\nu}}{\partial x_j} = \tfrac{1}{2} \ell^2 R_{ij} \frac{\partial \overline{\nu}}{\partial x_i} \frac{\partial \overline{\nu}}{\partial x_j}, \\
L_j &= \ell \overline{n' h_j'} - \tfrac{1}{2} \ell^2 \overline{\rho (n')^2 v_j'} = \ell \overline{v_i' h_j'} \frac{\partial \overline{\nu}}{\partial x_i} - \tfrac{1}{2} \ell^2\, \underbrace{\overline{v_i'\, v_\ell'\, v_k'}}_{-R_{j\ell k}} \frac{\partial \overline{\nu}}{\partial x_k} \frac{\partial \overline{\nu}}{\partial x_\ell} \\
&= H_{ji} \frac{\partial \overline{\nu}}{\partial x_i} + \tfrac{1}{2} \ell^2 R_{j\ell k} \frac{\partial \overline{\nu}}{\partial x_k} \frac{\partial \overline{\nu}}{\partial x_\ell}, \\
\phi_j^T &= \overline{\rho \eta' v_j'},\ \phi_j^{\mathrm{turb}} = \overline{\phi_j} + \phi_j^T,
\end{aligned}
$$

in which $\overline{\rho} = \overline{\gamma}\,\overline{\nu}$. Moreover, in (31.57) round brackets enclosing tensor indices indicate that a tensor is symmetrized with respect to those indices. On noticing that the fluctuating part v_j' of the velocity field is an objective[8] vector, the quantities

$$R_{ij}, \quad Q_j, \quad H_{(ij)}, \quad K_j, \quad L_j, \quad \epsilon, \quad d$$

turn out to be equally objective.

The dissipation rates ϵ and d are considered internal variables as in classical turbulence theory of fluids; the same is also so for the "granular" dissipation rate d. Their evolutions are described by the transport equations

$$\overline{\rho}\dot{\epsilon} = \frac{\partial K_j^\epsilon}{\partial x_j} + \Pi^\epsilon, \qquad \overline{\rho}\dot{d} = \frac{\partial K_j^d}{\partial x_j} + \Pi^d, \qquad (31.58)$$

where the fluxes K_j^ϵ, K_j^d are objective vectors and the productions Π^ϵ, Π^d are objective scalars. These equations are here postulated rather than derived. They can

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[8] Let $x_i^\star = Q_{ij}(t) x_j + d_i(t)$ be a Euclidean transformation, in which $Q_{ij} Q_{kj} = \delta_{ik}$. The scalar a, vector a_i, tensor A_{ij} are called objective if $a^\star = a$, $a_i^\star = Q_{ij} a_j$, and $A_{ij}^\star = Q_{ik} A_{kl} Q_{jl}$.

also be motivated as, e.g., the Eq. (31.58)$_1$ can be suggested by means of averaging a balance law for enstrophy.[9]

The entropy principle follows here an idea by SADIKI and HUTTER [53]. They assume for turbulent motions the existence of two coldness variables ϑ^M, ϑ^T. LUCA et al. [40] took a step further and assumed the existence of three coldness variables:

> *In a turbulent motion of a granular material there exist three (empirical) temperatures θ^M, θ^T and θ^G related to the molecular motion, turbulent kinetic energy and turbulent configurational kinetic energy, respectively. Associated with these are the variables ϑ^M, ϑ^T and ϑ^G, called material, turbulent and granular coldness, respectively.*

We motivate the introduction of the third temperature as follows: (i) If we choose to relate a temperature to the turbulent kinetic energy k, as SADIKI and HUTTER [53] have done (see also HUTTER and JÖHNK [28]), then it is reasonable to relate another temperature to the turbulent configurational kinetic energy s. (ii) Eight generic balance equations (31.50)–(31.55) are at our disposal. They serve to determine the eight fields $\overline{\gamma}$, $\overline{\nu}$, U_i, ϑ^M, ϑ^T, ϑ^G. Of these, ϑ^M will be identified with the mean coldness $\overline{\vartheta} = \vartheta^M$. Moreover, (31.58) serve as two additional equations for the dissipative variables ϵ and d.

The objective of thermodynamics of turbulent motions of granular materials is now the determination of the ten *basic fields*

$$\overline{\gamma},\ \overline{\nu},\ U_i,\ \ \vartheta^M,\ \ \vartheta^T,\ \ \vartheta^G,\ \epsilon,\ d. \tag{31.59}$$

To this end, the necessary equations are the ten equations (31.50)–(31.55), (31.58) that must be supplemented by closure relations in a manner dependent on the material and the turbulence for the quantities contained in the set

$$\{\overline{T}_{ij},\ \overline{h}_j,\ \overline{f},\ \overline{e},\ \overline{q}_j,\ R_{ij},\ nQ_j,\ H_{(ij)},\ K_j,\ L_j,\ K_j^{\epsilon},\ K_j^{d},\ \Pi^{\epsilon},\ \Pi^{d}\}. \tag{31.60}$$

First, we note that the averaged value of $\boldsymbol{y}$ from (31.12) is

$$\overline{\boldsymbol{y}} = \left(\nu_0,\ \overline{\nu},\ \dot{\overline{\nu}},\ \frac{\partial\overline{\nu}}{\partial x_i},\ \overline{\gamma},\ \frac{\partial\overline{\gamma}}{\partial x_i},\ \overline{D}_{ij},\ \vartheta^M,\ \frac{\partial\vartheta^M}{\partial x_i}\right), \tag{31.61}$$

because with (31.48) we have $\overline{\dot{\nu}} = \dot{\overline{\nu}}$. We shall denote by $\boldsymbol{z}$ the independent variables that we choose, besides $\overline{\boldsymbol{y}}$, to describe the turbulence:

$$\boldsymbol{z} \equiv \left(\vartheta^T,\ \frac{\partial\vartheta^T}{\partial x_i},\ \vartheta^G,\ \frac{\partial\vartheta^G}{\partial x_i},\ \epsilon,\ \frac{\partial\epsilon}{\partial x_i},\ d,\ \frac{\partial d}{\partial x_i}\right). \tag{31.62}$$

Next, we formulate the closure relations. If C^{turb} stands for any member of the set (31.60), then

---

[9] The specific enstrophy is defined as curl $\boldsymbol{v} \cdot$ curl $\boldsymbol{v}$, where $\boldsymbol{v}$ is the velocity field. By taking the inner product of the vorticity equation with itself, a balance law for enstrophy emerges. An analogous application to curl $\boldsymbol{v}'$ yields the balance of enstrophy useful in turbulence theory.

$$C^{\text{turb}} = \mathcal{T}(\overline{\mathbf{y}}, z). \tag{31.63}$$

We refer to the functions $\mathcal{T}$ in (31.63) as *closure functions*. They are supposed to be frame indifferent (objective) and to have a common domain of definition $\mathcal{D}^{\text{turb}}$, which we call the *turbulent state space*.

When the closure relations (31.60), (31.63) are inserted into the equations of balance (31.50)–(31.58), the *field equations* for $\overline{\gamma}$, $\overline{\nu}$, U_i, ϑ^M, ϑ^T, ϑ^G, ϵ, d are obtained. Every solution of these field equations is called a *turbulent thermodynamic process*. Not all of these processes are *admissible* or *physically realizable*, however. These processes must also obey the second law of thermodynamics, which will now be formulated by an entropy principle.

31.4 Entropy Principle

The second law of thermodynamics is a statement about the irreversibility of physical processes. Many versions of the second law appeared in the literature. As an entropy principle it is used to ensure thermodynamically sound closure relations. One explicit form of the entropy principle for turbulent motions was proposed by SADIKI and HUTTER [53] (see also [28]). We reformulate this principle in order to let it be as general as possible.

Entropy principle

(1) *Every material which is able to perform laminar and turbulent motions possesses an extensive quantity* η, *called entropy*, *to which a flux* Φ_j *and a supply* σ *are assigned.*

We define the *entropy production* π as in (31.45) and when applied to turbulent processes and definitions listed in (31.158) in Appendix 31.E. When the simplified processes subject to (31.48) are considered, Eq. (31.45) reduces to

$$\pi \equiv \rho\dot{\eta} + \frac{\partial \Phi_j}{\partial x_j} - \sigma. \tag{31.64}$$

The mean entropy production $\overline{\pi}$ will then be

$$\overline{\pi} = \overline{\rho}\dot{\overline{\eta}} + \frac{\partial \Phi_j^{\text{turb}}}{\partial x_j} - \overline{\sigma}, \tag{31.65}$$

where

$$\Phi_j^{\text{turb}} \equiv \overline{\Phi}_j + \Phi_j^T, \qquad \Phi_j^T \equiv \overline{\rho}\,\overline{\eta' v_j'}.$$

(2) *The entropy* η *and the entropy flux* Φ_j *are an objective scalar and an objective vector, respectively, and both are given by closure relations. In a turbulent flow the mean entropy* $\overline{\eta}$ *and its flux* Φ_j^{turb} *must be also given by closure relations.*

We invoke TRUESDELL's principle of equipresence and assume that

$$\eta = \eta(\boldsymbol{y}), \quad \Phi_j = \Phi_j(\boldsymbol{y}), \quad \overline{\eta} = \overline{\eta}(\overline{\boldsymbol{y}}, \boldsymbol{z}), \quad \Phi_j^{\text{turb}} = \Phi_j^{\text{turb}}(\overline{\boldsymbol{y}}, \boldsymbol{z}). \tag{31.66}$$

The closure functions η, Φ_j, $\overline{\eta}$, Φ_j^{turb} are supposed to be frame indifferent.
(3) *In a supply-free body, i.e.,* $b_i = 0, r = 0, \sigma = 0,$ *the entropy production* π *is nonnegative for all laminar thermodynamic processes, and the mean entropy production* $\overline{\pi}$ *is nonnegative for all turbulent thermodynamic processes.*[10]

Thus, the requirement (3) of the entropy principle reads

$$\pi \geqslant 0 \tag{31.67}$$

for all solutions γ, ν, v_i, ϑ of the field equations that describe the laminar motion, and

$$\overline{\pi} \geqslant 0, \tag{31.68}$$

for all solutions $\overline{\gamma}$, $\overline{\nu}$, U_i, ϑ^M, ϑ^T, ϑ^G, ϵ, d of the field equations that describe the turbulent motion. By referring to a supply-free body we take the position that the supplies cannot affect the material behavior. From now on we shall consider only supply-free materials.

The entropy principle is formulated in the spirit of the MÜLLER theory [44] (see Chaps. 17 and 18 in Vol. 2 of this treatise [29]). Therefore, it will be exploited by using the method of LAGRANGE multipliers as developed by LIU [39]. This will be carried out in the next section. Before doing so we remark that, formally, the laws (31.4)–(31.7), (31.9)–(31.11), (31.64), $(31.66)_{1,2}$, (31.67) that govern the laminar motion of the granular material represent a particular case of the laws (31.50)–(31.58), (31.60), (31.63), (31.65), $(31.66)_{3,4}$, (31.68) that govern the turbulent motion of this material. To see this we must only change the notation for the field *variables*[11] as follows:

$$\begin{array}{lcl}
\boldsymbol{y} & \longrightarrow & \overline{\boldsymbol{y}}, \\
v_i & \longrightarrow & U_i, \\
T_{ij},\ h_j,\ f,\ e,\ q_j & \longrightarrow & \overline{T}_{ij},\ \overline{h}_j,\ \overline{f},\ \overline{e},\ \overline{q}_j, \\
\eta,\ \Phi_j,\ \pi & \longrightarrow & \overline{\eta},\ \Phi_j^{\text{turb}},\ \overline{\pi} \equiv \pi^M.
\end{array}$$

We then obtain the "turbulent" motion as

---

[10] Alternatively, in a body with supplies, the supplies cannot affect the material behavior and so $\sigma = \lambda_i b_i + \lambda r$, see LIU [39]. It can be shown that the two approaches are equivalent.

[11] Note that only the field variables receive an overbar, the constitutive functions remain the same. This fact must be kept in mind to avoid misinterpretations.

$$\begin{aligned}
&\overline{T}_{ij} = T_{ij}(\overline{\mathbf{y}}), \quad \overline{h}_j = h_j(\overline{\mathbf{y}}), \quad \overline{f} = f(\overline{\mathbf{y}}), \\
&\overline{e} = e(\overline{\mathbf{y}}), \quad \overline{q}_j = q_j(\overline{\mathbf{y}}), \quad \epsilon = d = 0, \\
&R_{ij} = Q_j = H_{(ij)} = K_j = L_j = \Pi^{\epsilon} = \Pi^{d} = K_j^{\epsilon} = K_j^{d} = 0, \\
&\overline{\eta} = \eta(\overline{\mathbf{y}}), \quad \Phi_j^{\text{turb}} = \Phi_j(\overline{\mathbf{y}}),
\end{aligned} \tag{31.69}$$

in which the only relevant balance equations are (31.50)–(31.53). By the entropy principle, the corresponding entropy production, denoted as in [53] by π^M, must be nonnegative for all laminar thermodynamic processes, i.e.,

$$\pi^M \geqslant 0, \tag{31.70}$$

for all solutions $\overline{\nu}$, $\overline{\gamma}$, U_i, $\overline{\vartheta} = \vartheta^M$ of the field equations that result after the insertion of (31.69) into the mean balance equations. Therefore, we have the rule:

The restrictions on the constitutive functions under laminar flow conditions can be deduced from the restrictions on the closure relations describing the turbulent flow by

- considering the case (31.69),
- omitting the overbars,
- replacing U_i by v_i.

We emphasize the logical independence of the requirements (31.70) and (31.68). Condition (31.70) restricts the constitutive functions, whilst condition (31.68) restricts the functions that appear in the closure relations assumed for turbulent motions. However, as we have already remarked, it is not necessary to exploit both (31.70) and (31.68). The restrictions on the constitutive functions are simply deduced from those obtained via (31.68) by using the rule indicated above.

31.5 Exploitation of the Entropy Inequality

As a result of (31.68) and of the definition (31.65), we obtain the *entropy inequality*

$$\overline{\rho}\dot{\overline{\eta}} + \frac{\partial \Phi_j^{\text{turb}}}{\partial x_j} \geqslant 0, \tag{31.71}$$

that must be satisfied by every turbulent thermodynamic process. To exploit it we introduce the HELMHOLTZ free energy ψ^{turb} according to

$$\vartheta^M \psi^{\text{turb}} \equiv \vartheta^M \overline{e} + \vartheta^T k + \vartheta^G s - \overline{\eta}, \tag{31.72}$$

and the extra entropy flux k_j^{turb} by

$$\Phi_j^{\text{turb}} \equiv \vartheta^M(\overline{q}_j + Q_j) - \vartheta^T K_j - \vartheta^G L_j + k_j^{\text{turb}}. \tag{31.73}$$

Notice that the definition of this HELMHOLTZ free energy involves the products "coldness times energy" for all three energy types. A similar rule "coldness times energy flux" is also introduced for the turbulent entropy flux. Substitution of $\overline{\eta}$ and Φ_j^{turb} from (31.72) and (31.73) into the entropy inequality (31.71) yields

$$\begin{aligned}
&\overline{\rho}\left(-\vartheta^M \dot{\psi}^{\text{turb}} + \vartheta^M \dot{\overline{e}} + \vartheta^T \dot{k} + \vartheta^G \dot{s}\right) + \overline{\rho}\left(\overline{e} - \psi^{\text{turb}}\right)\dot{\vartheta}^M + \overline{\rho}\, k \dot{\vartheta}^T + \overline{\rho}\, s \dot{\vartheta}^G \\
&+\vartheta^M \left(\frac{\partial \overline{q}_j}{\partial x_j} + \frac{\partial Q_j}{\partial x_j}\right) - \vartheta^T \frac{\partial K_j}{\partial x_j} - \vartheta^G \frac{\partial L_j}{\partial x_j} + \frac{\partial k_j^{\text{turb}}}{\partial x_j} \\
&+(\overline{q}_j + Q_j)\frac{\partial \vartheta^M}{\partial x_j} - K_j \frac{\partial \vartheta^T}{\partial x_j} - L_j \frac{\partial \vartheta^G}{\partial x_j} \geqslant 0.
\end{aligned} \tag{31.74}$$

We remark that, after inserting the closure relations (31.63) into Eqs. (31.50)–(31.58) and performing all differentiations by the chain rule, one obtains a system that is linear in the derivatives

$$\begin{aligned}
&\dot{U}_i,\ \frac{\partial \nu_0}{\partial x_j},\ \ddot{\overline{\nu}},\ \frac{\partial \dot{\overline{\nu}}}{\partial x_j},\ \frac{\partial^2 \overline{\nu}}{\partial x_i \partial x_j},\ \dot{\overline{\gamma}},\ \frac{\partial^2 \overline{\gamma}}{\partial x_i \partial x_j},\ \overbrace{\frac{\partial \overline{\gamma}}{\partial x_j}}^{\bullet}, \\
&\dot{\overline{D}}_{ij},\ \frac{\partial \overline{D}_{ij}}{\partial x_k},\ \dot{\vartheta}^M,\ \overbrace{\frac{\partial \vartheta}{\partial x_j}}^{\bullet},\ \frac{\partial^2 \vartheta^M}{\partial x_i \partial x_j},\ \dot{\vartheta}^T,\ \overbrace{\frac{\partial \vartheta^T}{\partial x_j}}^{\bullet},\ \frac{\partial^2 \vartheta^T}{\partial x_i \partial x_j}, \\
&\dot{\vartheta}^G,\ \overbrace{\frac{\partial \vartheta^G}{\partial x_j}}^{\bullet},\ \frac{\partial^2 \vartheta^G}{\partial x_i \partial x_j},\ \dot{\epsilon},\ \overbrace{\frac{\partial \epsilon}{\partial x_j}}^{\bullet},\ \frac{\partial^2 \epsilon}{\partial x_i \partial x_j},\ \dot{d},\ \overbrace{\frac{\partial d}{\partial x_j}}^{\bullet},\ \frac{\partial^2 d}{\partial x_i \partial x_j}.
\end{aligned} \tag{31.75}$$

Hence, it is the component formula of an equation of the type

$$\boldsymbol{A}\boldsymbol{x} = \boldsymbol{b}, \tag{31.76}$$

where $\boldsymbol{A}$ is a linear transformation from $\mathbb{R}^n$ to $\mathbb{R}^m$. In our case $n = 133$, $m = 10$ and the components of $\boldsymbol{x}$ are the derivatives (31.75).

In the entropy inequality (31.74), after explicit performance of all differentiations by the chain rule, the left-hand side, i.e., the entropy production $\overline{\pi}$, is also linear in these derivatives, hence inequality (31.74) has the form

$$\boldsymbol{a} \cdot \boldsymbol{x} + \beta \geqslant 0, \tag{31.77}$$

where $\boldsymbol{a} \cdot \boldsymbol{x}$ denotes the Euclidean inner product of $\boldsymbol{a}$ and $\boldsymbol{x}$ in $\mathbb{R}^n$, and $\beta \in \mathbb{R}$. We suppose that Eq. (31.76) has a nontrivial solution $\boldsymbol{x}$. By the entropy principle, any solution $\boldsymbol{x} \in \mathbb{R}^n$ of (31.76) must satisfy inequality (31.77). Consequently we may resort to a lemma proved by LIU [39].[12] According to this, the equation

$$\boldsymbol{A}^T \boldsymbol{\lambda} = \boldsymbol{a}, \tag{31.78}$$

where $\boldsymbol{A}^T$ denotes the transpose of $\boldsymbol{A}$, has at least one solution $\boldsymbol{\lambda} \in \mathbb{R}^m$ and any solution of (31.78) satisfies the inequality

$$\boldsymbol{b} \cdot \boldsymbol{\lambda} + \beta \geqslant 0. \tag{31.79}$$

Hence, the closure functions that define $\boldsymbol{A}$ and $\boldsymbol{a}$ are related by means of (31.78), which is called the LIU *equation*. The closure functions that define $\boldsymbol{b}$ and β must satisfy the inequality (31.79), in which $\boldsymbol{\lambda}$ is the vector that appears in (31.78). This inequality is called the *residual* (*dissipation*) *inequality*. Note that if $\boldsymbol{x}$ is a solution of (31.76) and $\boldsymbol{\lambda}$ is a solution of (31.78), then $\boldsymbol{a} \cdot \boldsymbol{x} = \boldsymbol{b} \cdot \boldsymbol{\lambda}$, such that the left-hand side in the residual inequality is nothing else than the entropy production evaluated at a thermodynamic process and expressed in terms of $\boldsymbol{\lambda}$.

Both LIU's equation and the residual inequality are referred to as *thermodynamic restrictions* on the closure functions, and the main task of the thermodynamic material theory of the MÜLLER–LIU type is to derive these restrictions. To this end, it is practically useful to start from the inequality

$$\boldsymbol{a} \cdot \boldsymbol{x} + \beta - \boldsymbol{\lambda} \cdot (\boldsymbol{A}\boldsymbol{x} - \boldsymbol{b}) \geqslant 0, \tag{31.80}$$

which is required to hold for any $\boldsymbol{x} \in \mathbb{R}^n$. Inequality (31.80) would be violated unless the "coefficient" of $\boldsymbol{x}$ is zero,[13] so that we obtain (31.78) and (31.79). LIU called the components of $\boldsymbol{\lambda}$ *Lagrange multipliers*.

In our theory, inequality (31.80) emerges in the form

$$\begin{aligned}
&\overline{\rho}\left(-\vartheta^M \dot{\psi}^{\text{turb}} + \vartheta^M \dot{\overline{e}} + \vartheta^T \dot{k} + \vartheta^G \dot{s}\right) + \overline{\rho}\left(\overline{e} - \psi^{\text{turb}}\right) \dot{\vartheta}^M \\
&+\overline{\rho}\, k \dot{\vartheta}^T + \overline{\rho}\, s \dot{\vartheta}^G + \vartheta^M \left(\frac{\partial \overline{q}_j}{\partial x_j} + \frac{\partial Q_j}{\partial x_j}\right) - \vartheta^T \frac{\partial K_j}{\partial x_j} - \vartheta^G \frac{\partial L_j}{\partial x_j} + \frac{\partial k_j^{\text{turb}}}{\partial x_j} \\
&+(\overline{q}_j + Q_j) \frac{\partial \vartheta^M}{\partial x_j} - K_j \frac{\partial \vartheta^T}{\partial x_j} - L_j \frac{\partial \vartheta^G}{\partial x_j} \\
&-\Lambda^{\overline{\gamma}} \left\{\dot{\overline{\gamma}}\, \overline{\nu} + \overline{\gamma}\, \dot{\overline{\nu}} + \overline{\gamma}\, \overline{\nu} \frac{\partial U_j}{\partial x_j}\right\} - \Lambda^{U_i} \left\{\overline{\rho} \dot{U}_i - \frac{\partial \overline{T}_{ij}}{\partial x_j} - \frac{\partial R_{ij}}{\partial x_j}\right\}
\end{aligned}$$

---

[12] Actually LIU's lemma is a special case of a much broader theorem, well known in operations research. A proof in that context can be found in SCHRIJVER [57], but the theorem dates back to FARKAS [17] and MINKOWSKI [43], see also HAUSER and KIRCHNER [27].

[13] This statement must be understood with caution: The inner product in (31.80) may contain components which can be combined as products of the form $a_{ij} x_{ji}$, where x_{ji} is a symmetric tensor. Then, $a_{ij} x_{ji} = 0$ implies that a_{ij} is skew-symmetric.

$$
\begin{aligned}
&-\Lambda^{\overline{\nu}}\left\{\ell\overline{\rho}\,\ddot{\overline{\nu}} - \frac{\partial\overline{h}_j}{\partial x_j} - \frac{\partial H_j}{\partial x_j} - \overline{\rho}\overline{f}\right\}\\
&-\Lambda^{\overline{e}}\left\{\overline{\rho}\,\dot{\overline{e}} - \overline{T}_{ij}\frac{\partial U_i}{\partial x_j} - \ell\,\overline{h}_j\frac{\partial\dot{\overline{\nu}}}{\partial x_j} + \frac{\partial\overline{q}_j}{\partial x_j} + \frac{\partial Q_j}{\partial x_j}\right.\\
&\left.-H_{(ij)}\frac{\partial^2\overline{\nu}}{\partial x_i\partial x_j} + \ell\,\overline{\rho}\,\dot{\overline{\nu}}\overline{f} - \overline{\rho}\epsilon - \overline{\rho}d\right\}\\
&-\Lambda^{k}\left\{\overline{\rho}\dot{k} - R_{ij}\frac{\partial U_i}{\partial x_j} - \frac{\partial K_j}{\partial x_j} + \overline{\rho}\epsilon\right\}\\
&-\Lambda^{s}\left\{\overline{\rho}\dot{s} - \ell\,H_j\frac{\partial\dot{\overline{\nu}}}{\partial x_j} - \frac{\partial L_j}{\partial x_j} + H_{(ij)}\frac{\partial^2\overline{\nu}}{\partial x_i\partial x_j} + \overline{\rho}\,d\right\}\\
&-\Lambda^{\epsilon}\left\{\overline{\rho}\dot{\epsilon} - \frac{\partial K^{\epsilon}}{\partial x_j} - \Pi^{\epsilon}\right\} - \Lambda^{d}\left\{\overline{\rho}\dot{d} - \frac{\partial K^{d}}{\partial x_j} - \Pi^{d}\right\} \geqslant 0,
\end{aligned}
\tag{31.81}
$$

and it must hold for all arbitrary fields (31.75). The ten LAGRANGE multipliers

$$
\Lambda^{\overline{\gamma}},\quad \Lambda^{U_i},\quad \Lambda^{\overline{\nu}},\quad \Lambda^{\overline{e}},\quad \Lambda^{k},\quad \Lambda^{s},\quad \Lambda^{\epsilon},\quad \Lambda^{d}
$$

may depend on $(\overline{\boldsymbol{y}}, \boldsymbol{z}) \in \mathcal{D}^{\text{turb}}$.

From (31.78) it is clear that any assumption on the solution $\boldsymbol{\lambda}$ is an assumption about $\boldsymbol{A}$ and $\boldsymbol{a}$ and, therefore, on the closure relations involving $\boldsymbol{A}$ and $\boldsymbol{a}$. We shall "force" $\boldsymbol{A}$ and $\boldsymbol{a}$ to be such that the identifications

$$
\Lambda^{\overline{e}} = \vartheta^{M},\quad \Lambda^{k} = \vartheta^{T},\quad \Lambda^{s} = \vartheta^{G}
$$

hold. Then, proceeding as in the exploitation of inequality (31.80), in (31.81) we set the coefficients of the derivatives (31.75) equal to zero, and thus deduce the LIU equations. Then, substituting these identifications into (31.81) and performing all differentiations of constitutive quantities according to the chain rule of differentiation and collecting terms according to the list (31.75) yields the long form of the extended inequality (31.80). Setting the coefficients of the quantities (31.75) equal to zero, thereby also observing the provisos of the above footnote, one deduces the following LIU identities:

$$
\Lambda^{\overline{\gamma}} = -\overline{\gamma}\vartheta^{M}\frac{\partial\psi^{\text{turb}}}{\partial\overline{\gamma}},\quad \Lambda^{U_i} = 0,\quad \Lambda^{\overline{\nu}} = -\frac{1}{\ell}\vartheta^{M}\frac{\partial\psi^{\text{turb}}}{\partial\dot{\overline{\nu}}},\tag{31.82}
$$

$$
\Lambda^{\overline{e}} = \vartheta^{M},\quad \Lambda^{k} = \vartheta^{T},\quad \Lambda^{s} = \vartheta^{G},\tag{31.83}
$$

$$
\Lambda^{\epsilon} = -\vartheta^{M}\frac{\partial\psi^{\text{turb}}}{\partial\epsilon},\quad \Lambda^{d} = -\vartheta^{M}\frac{\partial\psi^{\text{turb}}}{\partial d},\tag{31.84}
$$

$$
\frac{\partial\psi^{\text{turb}}}{\partial\overline{\gamma}_{,j}} = 0,\quad \frac{\partial\psi^{\text{turb}}}{\partial\overline{D}_{ij}} = 0,\quad \frac{\partial\psi^{\text{turb}}}{\partial\vartheta^{M}_{,j}} = 0,\tag{31.85}
$$

$$\frac{\partial\psi^{\text{turb}}}{\partial\vartheta^T_{,j}} = 0, \quad \frac{\partial\psi^{\text{turb}}}{\partial\vartheta^G_{,j}} = 0, \quad \frac{\partial\psi^{\text{turb}}}{\partial\epsilon_{,j}} = 0, \quad \frac{\partial\psi^{\text{turb}}}{\partial d_{,j}} = 0, \tag{31.86}$$

$$\overline{e} = \psi^{\text{turb}} + \vartheta^M \frac{\partial\psi^{\text{turb}}}{\partial\vartheta^M}, \quad k = \vartheta^M \frac{\partial\psi^{\text{turb}}}{\partial\vartheta^T}, \quad s = \vartheta^M \frac{\partial\psi^{\text{turb}}}{\partial\vartheta^G}, \tag{31.87}$$

$$\begin{aligned} &\ell\,\vartheta^M \overline{h}_j + \ell\,\vartheta^G H_j + \frac{\partial k^{\text{turb}}_j}{\partial\dot{\overline{\nu}}} + \Lambda^{\overline{\nu}} \left(\frac{\partial\overline{h}_j}{\partial\dot{\overline{\nu}}} + \frac{\partial H_j}{\partial\dot{\overline{\nu}}} \right) \\ &+ \Lambda^\epsilon \frac{\partial K^\epsilon_j}{\partial\dot{\overline{\nu}}} + \Lambda^d \frac{\partial K^d_j}{\partial\dot{\overline{\nu}}} = \overline{\gamma}\,\overline{\nu}\vartheta^M \frac{\psi^{\text{turb}}}{\partial\overline{\nu}_{,j}}, \end{aligned} \tag{31.88}$$

$$\frac{\partial k^{\text{turb}}_j}{\partial\nu_0} + \Lambda^{\overline{\nu}} \left(\frac{\partial\overline{h}_j}{\partial\nu_0} + \frac{\partial H_j}{\partial\nu_0} \right) + \Lambda^\epsilon \frac{\partial K^\epsilon_j}{\partial\nu_0} + \Lambda^d \frac{\partial K^d_j}{\partial\nu_0} = 0, \tag{31.89}$$

$$\frac{\partial k^{\text{turb}}_j}{\partial\overline{D}_{ik}} + \Lambda^{\overline{\nu}} \left(\frac{\partial\overline{h}_j}{\partial\overline{D}_{ik}} + \frac{\partial H_j}{\partial\overline{D}_{ik}} \right) + \Lambda^\epsilon \frac{\partial K^\epsilon_j}{\partial\overline{D}_{ik}} + \Lambda^d \frac{\partial K^d_j}{\partial\overline{D}_{ik}} = 0, \tag{31.90}$$

$$\begin{aligned} &\text{sym} \left\{ \frac{\partial k^{\text{turb}}_j}{\partial\overline{\nu}_{,i}} + \Lambda^{\overline{\nu}} \frac{\partial}{\partial\overline{\nu}_{,i}} \left(\overline{h}_j + H_j \right) + \Lambda^\epsilon \frac{\partial K^\epsilon_j}{\partial\overline{\nu}_{,i}} + \Lambda^d \frac{\partial K^d_j}{\partial\overline{\nu}_{,i}} \right\} \\ &= (\vartheta^G - \vartheta^M) H_{(ij)}, \end{aligned} \tag{31.91}$$

$$\text{sym} \left\{ \frac{\partial k^{\text{turb}}_j}{\partial\overline{\gamma}_{,i}} + \Lambda^{\overline{\nu}} \frac{\partial}{\partial\overline{\gamma}_{,i}} \left(\overline{h}_j + H_j \right) + \Lambda^\epsilon \frac{\partial K^\epsilon_j}{\partial\overline{\gamma}_{,i}} + \Lambda^d \frac{\partial K^d_j}{\partial\overline{\gamma}_{,i}} \right\} = 0, \tag{31.92}$$

$$\text{sym} \left\{ \frac{\partial k^{\text{turb}}_j}{\partial\vartheta^M_{,i}} + \Lambda^{\overline{\nu}} \frac{\partial}{\partial\vartheta^M_{,i}} \left(\overline{h}_j + H_j \right) + \Lambda^\epsilon \frac{\partial K^\epsilon_j}{\partial\vartheta^M_{,i}} + \Lambda^d \frac{\partial K^d_j}{\partial\vartheta^M_{,i}} \right\} = 0, \tag{31.93}$$

$$\text{sym} \left\{ \frac{\partial k^{\text{turb}}_j}{\partial\vartheta^T_{,i}} + \Lambda^{\overline{\nu}} \frac{\partial}{\partial\vartheta^T_{,i}} \left(\overline{h}_j + H_j \right) + \Lambda^\epsilon \frac{\partial K^\epsilon_j}{\partial\vartheta^T_{,i}} + \Lambda^d \frac{\partial K^d_j}{\partial\vartheta^T_{,i}} \right\} = 0, \tag{31.94}$$

$$\text{sym} \left\{ \frac{\partial k^{\text{turb}}_j}{\partial\vartheta^G_{,i}} + \Lambda^{\overline{\nu}} \frac{\partial}{\partial\vartheta^G_{,i}} \left(\overline{h}_j + H_j \right) + \Lambda^\epsilon \frac{\partial K^\epsilon_j}{\partial\vartheta^G_{,i}} + \Lambda^d \frac{\partial K^d_j}{\partial\vartheta^G_{,i}} \right\} = 0, \tag{31.95}$$

$$\text{sym} \left\{ \frac{\partial k^{\text{turb}}_j}{\partial\epsilon_{,i}} + \Lambda^{\overline{\nu}} \frac{\partial}{\partial\epsilon_{,i}} \left(\overline{h}_j + H_j \right) + \Lambda^\epsilon \frac{\partial K^\epsilon_j}{\partial\epsilon_{,i}} m + \Lambda^d \frac{\partial K^d_j}{\partial\epsilon_{,i}} \right\} = 0, \tag{31.96}$$

$$\text{sym} \left\{ \frac{\partial k^{\text{turb}}_j}{\partial d_{,i}} + \Lambda^{\overline{\nu}} \frac{\partial}{\partial d_{,i}} \left(\overline{h}_j + H_j \right) + \Lambda^\epsilon \frac{\partial K^\epsilon_j}{\partial d_{,i}} + \Lambda^d \frac{\partial K^d_j}{\partial d_{,i}} \right\} = 0 \tag{31.97}$$

and the residual inequality

$$\begin{aligned} &\left\{ \vartheta^M (\overline{T}_{ij} + \overline{C}_{ij} + \overline{\nu}\,\overline{p}\delta_{ij}) + \vartheta^T R_{ij} \right\} \overline{D}_{ij} + \vartheta^M \left\{ \overline{p} - \overline{\beta} - \ell\,\overline{\gamma}\,\overline{\nu}\overline{f} \right\} \dot{\overline{\nu}} \\ &+ \left\{ \overline{q}_j + Q_j + \frac{\partial k^{\text{turb}}_j}{\partial\vartheta^M} + \Lambda^{\overline{\nu}} \left(\frac{\partial\overline{h}_j}{\partial\vartheta^M} + \frac{\partial H_j}{\partial\vartheta^M} \right) + \Lambda^\epsilon \frac{\partial K^\epsilon_j}{\partial\vartheta^M} + \Lambda^d \frac{\partial K^d_j}{\partial\vartheta^M} \right\} \frac{\partial\vartheta^M}{\partial x_j} \end{aligned}$$

$$
\begin{aligned}
&+\left\{-K_j+\frac{\partial k_j^{\text{turb}}}{\partial \vartheta^T}+\Lambda^{\overline{\nu}}\left(\frac{\partial \overline{h}_j}{\partial \vartheta^T}+\frac{\partial H_j}{\partial \vartheta^T}\right)+\Lambda^{\epsilon}\frac{\partial K_j^{\epsilon}}{\partial \vartheta^T}+\Lambda^{d}\frac{\partial K_j^{d}}{\partial \vartheta^T}\right\}\frac{\partial \vartheta^T}{\partial x_j}\\
&+\left\{-L_j+\frac{\partial k_j^{\text{turb}}}{\partial \vartheta^G}+\Lambda^{\overline{\nu}}\left(\frac{\partial \overline{h}_j}{\partial \vartheta^G}+\frac{\partial H_j}{\partial \vartheta^G}\right)+\Lambda^{\epsilon}\frac{\partial K_j^{\epsilon}}{\partial \vartheta^G}+\Lambda^{d}\frac{\partial K_j^{d}}{\partial \vartheta^G}\right\}\frac{\partial \vartheta^G}{\partial x_j}\\
&+\left\{\frac{\partial k_j^{\text{turb}}}{\partial \epsilon}+\Lambda^{\overline{\nu}}\left(\frac{\partial \overline{h}_j}{\partial \epsilon}+\frac{\partial H_j}{\partial \epsilon}\right)+\Lambda^{\epsilon}\frac{\partial K_j^{\epsilon}}{\partial \epsilon}+\Lambda^{d}\frac{\partial K_j^{d}}{\partial \epsilon}\right\}\frac{\partial \epsilon}{\partial x_j}\\
&+\left\{\frac{\partial k_j^{\text{turb}}}{\partial d}+\Lambda^{\overline{\nu}}\left(\frac{\partial \overline{h}_j}{\partial d}+\frac{\partial H_j}{\partial d}\right)+\Lambda^{\epsilon}\frac{\partial K_j^{\epsilon}}{\partial d}+\Lambda^{d}\frac{\partial K_j^{d}}{\partial d}\right\}\frac{\partial d}{\partial x_j}\\
&+\left\{\frac{\partial k_j^{\text{turb}}}{\partial \overline{\nu}}+\Lambda^{\overline{\nu}}\left(\frac{\partial \overline{h}_j}{\partial \overline{\nu}}+\frac{\partial H_j}{\partial \overline{\nu}}\right)+\Lambda^{\epsilon}\frac{\partial K_j^{\epsilon}}{\partial \overline{\nu}}+\Lambda^{d}\frac{\partial K_j^{d}}{\partial \overline{\nu}}\right\}\frac{\partial \overline{\nu}}{\partial x_j}\\
&+\left\{\frac{\partial k_j^{\text{turb}}}{\partial \overline{\gamma}}+\Lambda^{\overline{\nu}}\left(\frac{\partial \overline{h}_j}{\partial \overline{\gamma}}+\frac{\partial H_j}{\partial \overline{\gamma}}\right)+\Lambda^{\epsilon}\frac{\partial K_j^{\epsilon}}{\partial \overline{\gamma}}+\Lambda^{d}\frac{\partial K_j^{d}}{\partial \overline{\gamma}}\right\}\frac{\partial \overline{\gamma}}{\partial x_j}\\
&+\Lambda^{\overline{\nu}}\overline{\gamma}\,\overline{\nu}\,\overline{f}+(\vartheta^M-\vartheta^T)\overline{\gamma}\,\overline{\nu}\epsilon+(\vartheta^M-\vartheta^G)\overline{\gamma}\,\overline{\nu}d+\Lambda^{\epsilon}\Pi^{\epsilon}+\Lambda^{d}\Pi^{d}\geqslant 0. \qquad (31.98)
\end{aligned}
$$

Here we have used the notations

$$
\overline{p}\equiv\overline{\gamma}^2\frac{\partial\psi^{\text{turb}}}{\partial\overline{\gamma}},\qquad \overline{\beta}\equiv\overline{\gamma}\,\overline{\nu}\frac{\partial\psi^{\text{turb}}}{\partial\overline{\nu}},\qquad \overline{C}_{ij}\equiv\overline{\gamma}\,\overline{\nu}\frac{\partial\psi^{\text{turb}}}{\partial\overline{\nu}_{,i}}\frac{\partial\overline{\nu}}{\partial x_j}. \qquad (31.99)
$$

We may refer to $\overline{p}$ as the *turbulent thermodynamic pressure*, to $\overline{\beta}$ as the *turbulent configurational pressure*, and to $\overline{C}_{ij}$ as the *turbulent configurational stress tensor*. By the isotropy condition, ψ^{turb} depends on $\overline{\nu}_{,i}$ via the scalar $\overline{g}$ defined as

$$
\overline{g}\equiv\frac{\partial\overline{\nu}}{\partial x_i}\frac{\partial\overline{\nu}}{\partial x_i}.
$$

Consequently, we have

$$
\overline{C}_{ij}=2\overline{\gamma}\,\overline{\nu}\frac{\partial\psi^{\text{turb}}}{\partial\overline{g}}\frac{\partial\overline{\nu}}{\partial x_i}\frac{\partial\overline{\nu}}{\partial x_j}=\overline{C}_{ji}.
$$

Let us next investigate the LIU equations (31.82)–(31.97). First notice that (31.82), (31.84) imply that all LAGRANGE multipliers are determined once the free energy function ψ^{turb} is prescribed as a function of its arguments. Second, (31.85) and (31.86) reduce the number of variables upon which ψ^{turb} can depend considerably. Effectively, ψ^{turb} cannot depend on $\overline{D}_{ij}$ and any gradients arising in the lists (31.61), (31.62) except $\overline{\nu}_{,i}$:

$$
\psi^{\text{turb}}=\psi^{\text{turb}}(\nu_0,\,\overline{\nu},\,\dot{\overline{\nu}},\,\overline{g},\,\overline{\gamma},\,\vartheta^M,\,\vartheta^T,\,\vartheta^G,\,\epsilon,\,d). \qquad (31.100)
$$

These are remarkable reductions. Third,via (31.87), (31.72) we obtain

$$\overline{\eta} = \vartheta^M \left(\vartheta^M \frac{\partial \psi^{\text{turb}}}{\partial \vartheta^M} + \vartheta^T \frac{\partial \psi^{\text{turb}}}{\partial \vartheta^T} + \vartheta^G \frac{\partial \psi^{\text{turb}}}{\partial \vartheta^G} \right).$$

The first member on the right-hand side is the classical expression, the second and the third are due to the turbulent and granular temperatures and reflect a similar structure.

By means of (31.82), (31.84) the LAGRANGE multipliers $\Lambda^{\overline{\gamma}}$, $\Lambda^{\overline{\nu}}$, Λ^{ϵ}, Λ^{d} depend exclusively on variables present in (31.100). That is why the restrictions (31.90), (31.92)–(31.97) can be cast into the forms

$$\frac{\partial k_j}{\partial \overline{D}_{ik}} = 0, \quad \frac{\partial k_i}{\partial v_j^A} + \frac{\partial k_j}{\partial v_i^A} = 0, \quad i,\ j,\ k \in \{1,2,3\},\ A \in \{1,\dots,6\}, \tag{31.101}$$

where the vectors $\boldsymbol{k}$ and $\boldsymbol{v}^A$ are defined by

$$\begin{aligned} &\boldsymbol{k} \equiv \boldsymbol{k}^{\text{turb}} + \Lambda^{\overline{\nu}}(\overline{\boldsymbol{h}} + \boldsymbol{H}) + \Lambda^{\epsilon}\boldsymbol{K}^{\epsilon} + \Lambda^{d}\boldsymbol{K}^{d}, \\ &\boldsymbol{v}^1 \equiv \operatorname{grad}\overline{\gamma}, \quad \boldsymbol{v}^2 \equiv \operatorname{grad}\vartheta^M, \quad \boldsymbol{v}^3 \equiv \operatorname{grad}\vartheta^T, \\ &\boldsymbol{v}^4 \equiv \operatorname{grad}\vartheta^G, \quad \boldsymbol{v}^5 \equiv \operatorname{grad}\epsilon, \quad \boldsymbol{v}^6 \equiv \operatorname{grad} d. \end{aligned} \tag{31.102}$$

Integration of the identities (31.101) gives

$$\boldsymbol{k} = \sum_{\substack{A,B=1\\ A<B}}^{6} \alpha_{AB}\, \boldsymbol{v}^A \times \boldsymbol{v}^B + \sum_{A=1}^{6} \boldsymbol{C}_A \boldsymbol{v}^A + \boldsymbol{c}, \tag{31.103}$$

where α_{AB} are scalar coefficients, $\boldsymbol{C}_A$ are skew-symmetric tensors and $\boldsymbol{c}$ is a vector. Note that α_{AB}, $\boldsymbol{C}_A$, and $\boldsymbol{c}$ may depend on ν_0, $\overline{\nu}$, $\dot{\overline{\nu}}$, $\overline{\nu}_{,j}$, $\overline{\gamma}$, ϑ^M, ϑ^T, ϑ^G, ϵ, d. Further, we recall that the entropy η and the entropy flux Φ_j are assumed to be objective quantities, so that the entropy flux Φ_j^{turb} is an objective vector. Focusing on the definition of k_j^{turb}, see (31.73), and recalling the objectivity of $\overline{q}_j$, Q_j, K_j, L_j $\overline{h}_j$, H_j, K_j^{ϵ}, K_j^{d}, $\Lambda^{\overline{\nu}}$, Λ^{ϵ}, and Λ^{d}, we infer the objectivity of the vector $\boldsymbol{k}$. Since the closure functions are frame indifferent, $\boldsymbol{k}$ turns out to be an isotropic vector-valued function. With (31.103) this is possible if and only if $\alpha_{AB} = 0$, $\boldsymbol{C}_A = \boldsymbol{0}$ and $\boldsymbol{c}$ is an isotropic vector-valued function of $\operatorname{grad}\overline{\nu}$.[14] This implies that

$$k_j = c\,\frac{\partial \overline{\nu}}{\partial x_j}, \qquad c = c\,(\nu_0,\ \overline{\nu},\ \dot{\overline{\nu}},\ \overline{g},\ \overline{\gamma}, \vartheta^M, \vartheta^T, \vartheta^G, \epsilon,\ d),$$

and therefore the extra entropy flux k_j^{turb} is given by

$$k_j^{\text{turb}} = -\Lambda^{\overline{\nu}}(\overline{h}_j + H_j) - \Lambda^{\epsilon} K_j^{\epsilon} - \Lambda^{d} K_j^{d} + c\,\frac{\partial \overline{\nu}}{\partial x_j}. \tag{31.104}$$

---

[14] See Appendix 31.F at the end of the chapter.

Now, substituting (31.104) into (31.88), (31.89), (31.91) yields

$$\begin{aligned}
&\ell\,\vartheta^M \overline{h}_j + \ell\,\vartheta^G H_j - \frac{\partial \Lambda^{\overline{\nu}}}{\partial \dot{\overline{\nu}}}\left(\overline{h}_j + H_j\right) - \frac{\partial \Lambda^{\epsilon}}{\partial \dot{\overline{\nu}}}\,K^{\epsilon}_j - \frac{\partial \Lambda^{d}}{\partial \dot{\overline{\nu}}}\,K^{d}_j + \frac{\partial c}{\partial \dot{\overline{\nu}}}\frac{\partial \overline{\nu}}{\partial x_j}\\
&\quad = \overline{\gamma}\,\overline{\nu}\vartheta^M \frac{\partial \psi^{\text{turb}}}{\partial \overline{\nu}_{,j}}, \qquad (31.105)\\
&\frac{\partial \Lambda^{\overline{\nu}}}{\partial \nu_0}\left(\overline{h}_j + H_j\right) + \frac{\partial \Lambda^{\epsilon}}{\partial \nu_0}\,K^{\epsilon}_j + \frac{\partial \Lambda^{d}}{\partial \nu_0}\,K^{d}_j - \frac{\partial c}{\partial \nu_0}\frac{\partial \overline{\nu}}{\partial x_j} = 0, \qquad (31.106)\\
&\text{sym}\left\{\frac{\partial \Lambda^{\overline{\nu}}}{\partial \overline{\nu}_{,i}}\left(\overline{h}_j + H_j\right) + \frac{\partial \Lambda^{\epsilon}}{\partial \overline{\nu}_{,i}}K^{\epsilon}_j + \frac{\partial \Lambda^{d}}{\partial \overline{\nu}_{,i}}K^{d}_j - c\,\delta_{ij} - 2\frac{\partial c}{\partial \overline{g}}\frac{\partial \overline{\nu}}{\partial x_i}\frac{\partial \overline{\nu}}{\partial x_j}\right\}\\
&\quad = (\vartheta^M - \vartheta^G)H_{(ij)}. \qquad (31.107)
\end{aligned}$$

We can simplify these restrictions if we allow the turbulent free energy to be independent of $\dot{\overline{\nu}}$,

$$\frac{\partial \psi^{\text{turb}}}{\partial \dot{\overline{\nu}}} = 0. \qquad (31.108)$$

This is an ad hoc assumption. It implies (see (31.82), (31.84))

$$\Lambda^{\overline{\nu}} = 0, \quad \frac{\partial \Lambda^{\epsilon}}{\partial \dot{\overline{\nu}}} = 0, \quad \frac{\partial \Lambda^{d}}{\partial \dot{\overline{\nu}}} = 0, \qquad (31.109)$$

so that relations (31.104)–(31.107) take the forms

$$\begin{aligned}
&k^{\text{turb}}_j = -\Lambda^{\epsilon}K^{\epsilon}_j - \Lambda^{d}K^{d}_j + c\frac{\partial \overline{\nu}}{\partial x_j}, \qquad (31.110)\\
&\overline{h}_j = \frac{1}{\ell\,\vartheta^M}\left(2\overline{\gamma}\,\overline{\nu}\vartheta^M\frac{\partial \psi^{\text{turb}}}{\partial \overline{g}}\delta_{ij} - \ell^2\,\vartheta^G R_{ij} - \frac{\partial c}{\partial \dot{\overline{\nu}}}\,\delta_{ij}\right)\frac{\partial \overline{\nu}}{\partial x_i}, \qquad (31.111)\\
&\frac{\partial \Lambda^{\epsilon}}{\partial \nu_0}\,K^{\epsilon}_j + \frac{\partial \Lambda^{d}}{\partial \nu_0}\,K^{d}_j - \frac{\partial c}{\partial \nu_0}\frac{\partial \overline{\nu}}{\partial x_j} = 0, \qquad (31.112)\\
&(\vartheta^M - \vartheta^G)H_{(ij)} = 2\,\text{sym}\left\{\left(\frac{\partial \Lambda^{\epsilon}}{\partial \overline{g}}K^{\epsilon}_j + \frac{\partial \Lambda^{d}}{\partial \overline{g}}K^{d}_j\right)\frac{\partial \overline{\nu}}{\partial x_i}\right\}\\
&\qquad -c\,\delta_{ij} - 2\frac{\partial c}{\partial \overline{g}}\frac{\partial \overline{\nu}}{\partial x_i}\frac{\partial \overline{\nu}}{\partial x_j}. \qquad (31.113)
\end{aligned}$$

In deducing (31.111), we used the expression of H_j from (31.57). This completes the exploitation of the LIU equations.

Next, with (31.109) and (31.110) the residual inequality (31.98) emerges in the form

$$\overline{\pi} = \left\{\vartheta^M(\overline{T}_{ij} + \overline{C}_{ij} + \overline{\nu}\,\overline{p}\,\delta_{ij}) + \vartheta^T R_{ij}\right\}\overline{D}_{ij} + \vartheta^M\{\overline{p} - \overline{\beta} - \ell\,\overline{\gamma}\,\overline{\nu}\,\overline{f}\}\dot{\overline{\nu}}$$

$$
\begin{aligned}
&-\left\{-\overline{q}_j - Q_j + \frac{\partial \Lambda^\epsilon}{\partial \vartheta^M} K_j^\epsilon + \frac{\partial \Lambda^d}{\partial \vartheta^M} K_j^d - \frac{\partial c}{\partial \vartheta^M}\frac{\partial \overline{\nu}}{\partial x_j}\right\}\frac{\partial \vartheta^M}{\partial x_j}\\
&-\left\{K_j + \frac{\partial \Lambda^\epsilon}{\partial \vartheta^T} K_j^\epsilon + \frac{\partial \Lambda^d}{\partial \vartheta^T} K_j^d - \frac{\partial c}{\partial \vartheta^T}\frac{\partial \overline{\nu}}{\partial x_j}\right\}\frac{\partial \vartheta^T}{\partial x_j}\\
&-\left\{L_j + \frac{\partial \Lambda^\epsilon}{\partial \vartheta^G} K_j^\epsilon + \frac{\partial \Lambda^d}{\partial \vartheta^G} K_j^d - \frac{\partial c}{\partial \vartheta^G}\frac{\partial \overline{\nu}}{\partial x_j}\right\}\frac{\partial \vartheta^G}{\partial x_j}\\
&-\left\{\frac{\partial \Lambda^\epsilon}{\partial \epsilon} K_j^\epsilon + \frac{\partial \Lambda^d}{\partial \epsilon} K_j^d - \frac{\partial c}{\partial \epsilon}\frac{\partial \overline{\nu}}{\partial x_j}\right\}\frac{\partial \epsilon}{\partial x_j}\\
&-\left\{\frac{\partial \Lambda^\epsilon}{\partial d} K_j^\epsilon + \frac{\partial \Lambda^d}{\partial d} K_j^d - \frac{\partial c}{\partial d}\frac{\partial \overline{\nu}}{\partial x_j}\right\}\frac{\partial d}{\partial x_j}\\
&+\overline{\pi}_{\text{int}} \geqslant 0,
\end{aligned}
\tag{31.114}
$$

where

$$
\begin{aligned}
\overline{\pi}_{\text{int}} \equiv &-\left\{\frac{\partial \Lambda^\epsilon}{\partial \overline{\nu}} K_j^\epsilon + \frac{\partial \Lambda^d}{\partial \overline{\nu}} K_j^d - \frac{\partial c}{\partial \overline{\nu}}\frac{\partial \overline{\nu}}{\partial x_j}\right\}\frac{\partial \overline{\nu}}{\partial x_j}\\
&-\left\{\frac{\partial \Lambda^\epsilon}{\partial \overline{\gamma}} K_j^\epsilon + \frac{\partial \Lambda^d}{\partial \overline{\gamma}} K_j^d - \frac{\partial c}{\partial \overline{\gamma}}\frac{\partial \overline{\nu}}{\partial x_j}\right\}\frac{\partial \overline{\gamma}}{\partial x_j}\\
&+(\vartheta^M - \vartheta^T)\overline{\gamma}\,\overline{\nu}\epsilon + (\vartheta^M - \vartheta^G)\overline{\gamma}\,\overline{\nu}\, d + \Lambda^\epsilon \Pi^\epsilon + \Lambda^d \Pi^d.
\end{aligned}
\tag{31.115}
$$

The quantity $\overline{\pi}_{\text{int}}$ may be called the *internal dissipation*.

31.6 Restriction to the Laminar Case

Here we use the rule indicated at the end of Sect. 31.4 in order to obtain thermodynamic restrictions in the laminar case. Thus, with

$$
\vartheta\psi \equiv \vartheta e - \eta, \quad \Phi_j \equiv \vartheta q_j + k_j,
$$

by means of (31.100), (31.82), (31.84)$_1$, (31.87), (31.104)–(31.107), we derive the following results:

$$
\begin{aligned}
&\psi = \psi(\nu_0, \nu, \dot{\nu}, g, \overline{\gamma}, \vartheta)\,, \quad g \equiv \frac{\partial \nu}{\partial x_i}\frac{\partial \nu}{\partial x_i},\\
&\Lambda^\gamma = -\gamma\vartheta\frac{\partial \psi}{\partial \gamma}, \quad \Lambda^{v_i} = 0, \quad \Lambda^\nu = -\frac{\vartheta}{\ell}\frac{\partial \psi}{\partial \dot{\nu}},\\
&\Lambda^e = \vartheta, \quad e = \psi + \vartheta\frac{\partial \psi}{\partial \vartheta},
\end{aligned}
$$

$$
\begin{aligned}
&k_j = -\Lambda^\nu h_j + c\frac{\partial \nu}{\partial x_j}, \quad c = c(\nu_0, \nu, \dot{\nu}, g, \gamma, \vartheta), \\
&\left(\ell\vartheta - \frac{\partial \Lambda^\nu}{\partial \dot{\nu}}\right) h_j + \frac{\partial c}{\partial \dot{\nu}}\frac{\partial \nu}{\partial x_j} = \rho\vartheta\frac{\partial \psi}{\partial \nu_{,j}}, \\
&\frac{\partial \Lambda^\nu}{\partial \nu_0} h_j - \frac{\partial c}{\partial \nu_0}\frac{\partial \nu}{\partial x_j} = 0, \\
&\mathrm{sym}\left\{\frac{\partial \Lambda^\nu}{\partial \nu_{,i}} h_j\right\} = c\,\delta_{ij} + 2\,\frac{\partial c}{\partial g}\frac{\partial \nu}{\partial x_i}\frac{\partial \nu}{\partial x_j}.
\end{aligned}
\tag{31.116}
$$

If we suppose that

$$
\frac{\partial \psi}{\partial \dot{\nu}} = 0,
$$

as we did in (31.108), then $\Lambda^\nu = 0$ and the last relation in (31.116) implies $c = 0$. Consequently, the extra entropy flux vanishes and the configurational stress vector is completely determined by the free energy, viz.,

$$
k_j = 0, \qquad h_j = \frac{1}{\ell}\rho\frac{\partial \psi}{\partial \nu_{,j}}.
$$

By using (31.114), the residual inequality reads

$$
\vartheta\left(T_{ij} + C_{ij} + \nu\, p\,\delta_{ij}\right) D_{ij} + \vartheta\,(p - \beta - \ell\gamma\,\nu f)\dot{\nu} + q_j\frac{\partial \vartheta}{\partial x_j} \geqslant 0, \tag{31.117}
$$

where the *thermodynamic pressure* p, the *configurational pressure* β, and the *configurational stress tensor* C_{ij} are defined as

$$
p \equiv \gamma^2\frac{\partial \psi}{\partial \gamma}, \qquad \beta \equiv \rho\,\frac{\partial \psi}{\partial \nu}, \qquad C_{ij} \equiv \rho\frac{\partial \psi}{\partial \nu_{,i}}\frac{\partial \nu}{\partial x_j}. \tag{31.118}
$$

From (31.116)–(31.118), we infer that the spatial variation of the true density may influence the thermodynamics only through the stress tensor T_{ij}, the production f and the heat flux q_j (see (31.117)).

31.7 Thermodynamic Equilibrium

We derive further restrictions on the closure relations (31.60), (31.63) by analyzing the thermodynamic equilibrium. Doing this we still account for the assumption (31.108).

By a *state of thermodynamic equilibrium* we mean a state $(\overline{\mathbf{y}}, \mathbf{z})_E$ given by (see (31.61) and (31.62))

$$(\overline{\mathbf{y}}, \mathbf{z})_E \equiv \left(\nu_0,\, \overline{\nu},\, 0,\, \frac{\partial \overline{\nu}}{\partial x_i},\, \overline{\gamma},\, \frac{\partial \overline{\gamma}}{\partial x_i},\, 0,\, \vartheta^M,\, 0,\, \vartheta^T,\, 0,\, \vartheta^G,\, 0,\, \epsilon,\, 0,\, d,\, 0\right), \tag{31.119}$$

at which the entropy production $\overline{\pi}$, given in (31.114) and (31.115), vanishes

$$\overline{\pi}_E = 0.$$

The lower index E attached to a quantity which is not $(\overline{\mathbf{y}}, \mathbf{z})$ indicates that this quantity is evaluated at $(\overline{\mathbf{y}}, \mathbf{z})_E$. Therefore, via (31.114) an equilibrium state will be a state $(\overline{\mathbf{y}}, \mathbf{z})_E$ defined by (31.119) at which the internal dissipation vanishes

$$\overline{\pi}_{\text{int}\,E} = 0. \tag{31.120}$$

We notice that owing to (31.108)

$$\psi_E^{\text{turb}} = \psi^{\text{turb}},$$

which, based on (31.109), implies that

$$\varLambda_E^{\epsilon} = \varLambda^{\epsilon}, \qquad \varLambda_E^{d} = \varLambda^{d}. \tag{31.121}$$

If we take into account definition (31.115) of $\overline{\pi}_{\text{int}}$, then condition (31.120) reads

$$\begin{aligned}
\overline{\pi}_{\text{int}\,E} \equiv & -\left\{\frac{\partial \varLambda^{\epsilon}}{\partial \overline{\nu}}\, K_{j\,E}^{\epsilon} + \frac{\partial \varLambda^{d}}{\partial \overline{\nu}}\, K_{j\,E}^{d} - \frac{\partial c_E}{\partial \overline{\nu}}\, \frac{\partial \overline{\nu}}{\partial x_j}\right\} \frac{\partial \overline{\nu}}{\partial x_j} \\
& -\left\{\frac{\partial \varLambda^{\epsilon}}{\partial \overline{\gamma}}\, K_{j\,E}^{\epsilon} + \frac{\partial \varLambda^{d}}{\partial \overline{\gamma}}\, K_{j\,E}^{d} - \frac{\partial c_E}{\partial \overline{\gamma}}\, \frac{\partial \overline{\gamma}}{\partial x_j}\right\} \frac{\partial \overline{\gamma}}{\partial x_j} \\
& +(\vartheta^M - \vartheta^T)\overline{\gamma}\,\overline{\nu}\epsilon + (\vartheta^M - \vartheta^G)\overline{\gamma}\,\overline{\nu}\, d + \varLambda^{\epsilon}\, \varPi_E^{\epsilon} + \varLambda^{d} \varPi_E^{d} \\
= {} & 0.
\end{aligned} \tag{31.122}$$

Thermodynamic equilibrium is only meaningfully defined if (31.122) holds identically. Consequently, all states $(\overline{\mathbf{y}}, \mathbf{z})_E$ are states of thermodynamic equilibrium and condition (31.122) does no longer restrict the field variables $\nu_0, \overline{\nu}, \overline{\nu}_{,i}$ $\overline{\gamma}, \overline{\gamma}_{,i}, \vartheta^M, \vartheta^T$, ϑ^G, ϵ, d, but it restricts rather the free energy ψ^{turb} through $\varLambda^{\epsilon}$, $\varLambda^{d}$, the fluxes K_j^{ϵ}, $K_j^{=d}$, the productions $\varPi^{\epsilon}$, $\varPi^{d}$, and the function c.

Note that the entropy production $\overline{\pi}$ assumes its global minimum value at an equilibrium state. Consequently, $\overline{\pi}$ can be considered a function of

$$\dot{\overline{\nu}}, \quad \overline{D}_{ij}, \quad \frac{\partial \vartheta^M}{\partial x_i}, \quad \frac{\partial \vartheta^T}{\partial x_i}, \quad \frac{\partial \vartheta^G}{\partial x_i}, \quad \frac{\partial \epsilon}{\partial x_i}, \quad \frac{\partial d}{\partial x_i},$$

having the global minimum located at $(0, \mathbf{0}, \mathbf{0}, \mathbf{0}, \mathbf{0}, \mathbf{0}, \mathbf{0})$. It follows that under sufficient smoothness properties $\overline{\pi}$ has to satisfy the conditions

$$\begin{gathered}
\left.\frac{\partial\overline{\pi}}{\partial\dot{\overline{\nu}}}\right|_E = 0, \quad \left.\frac{\partial\overline{\pi}}{\partial\overline{D}_{ij}}\right|_E = 0\,, \quad \left.\frac{\partial\overline{\pi}}{\partial\vartheta^M_{,i}}\right|_E = 0, \quad \left.\frac{\partial\overline{\pi}}{\partial\vartheta^T_{,i}}\right|_E = 0, \\
\left.\frac{\partial\overline{\pi}}{\partial\vartheta^G_{,i}}\right|_E = 0, \quad \left.\frac{\partial\overline{\pi}}{\partial\epsilon_{,i}}\right|_E = 0, \quad \left.\frac{\partial\overline{\pi}}{\partial d_{,i}}\right|_E = 0,
\end{gathered} \tag{31.123}$$

and that

$$\text{the Hessian matrix of } \overline{\pi} \text{ is positive semi-definite at } (\overline{\mathbf{y}}, z)_E. \tag{31.124}$$

Now, we investigate the necessary conditions (31.123). Inspection of the definitions of the pressures $\overline{p}$, $\overline{\beta}$ and of the configuration stress tensor $\overline{C}_{ij}$ (see (31.99)) shows that

$$\overline{p}|_E = \overline{p}, \quad \overline{\beta}|_E = \overline{\beta}, \quad \overline{C}_{ij}|_E = \overline{C}_{ij}.$$

Therefore, from (31.114) and (31.123) we obtain the following restrictions on the closure functions:

$$\begin{aligned}
\overline{f}_E &= \frac{1}{\ell\,\overline{\gamma}\,\overline{\nu}}(\overline{p} - \overline{\beta}) + \frac{1}{\ell\vartheta^M\overline{\gamma}\,\overline{\nu}} \left.\frac{\partial\overline{\pi}_{\text{int}}}{\partial\dot{\overline{\nu}}}\right|_E, \\
\left\{\vartheta^M\overline{T}_{ij} + \vartheta^T R_{ij}\right\}_E &= -\vartheta^M\overline{\nu}\,\overline{p}\,\delta_{ij} - \vartheta^M\overline{C}_{ij} - \left.\frac{\partial\overline{\pi}_{\text{int}}}{\partial\overline{D}_{ij}}\right|_E, \\
\left\{\overline{q}_j + Q_j\right\}_E &= \frac{\partial\Lambda^\epsilon}{\partial\vartheta^M}\,K^\epsilon_{j\,E} + \frac{\partial\Lambda^d}{\partial\vartheta^M}\,K^d_{j\,E} - \frac{\partial c_E}{\partial\vartheta^M}\frac{\partial\overline{\nu}}{\partial x_j} - \left.\frac{\partial\overline{\pi}_{\text{int}}}{\partial\vartheta^M_{,j}}\right|_E, \\
K_{jE} &= -\frac{\partial\Lambda^\epsilon}{\partial\vartheta^T}\,K^\epsilon_{j\,E} - \frac{\partial\Lambda^d}{\partial\vartheta^T}\,K^d_{j\,E} + \frac{\partial c_E}{\partial\vartheta^T}\frac{\partial\overline{\nu}}{\partial x_j} + \left.\frac{\partial\overline{\pi}_{\text{int}}}{\partial\vartheta^T_{,j}}\right|_E, \\
L_{jE} &= -\frac{\partial\Lambda^\epsilon}{\partial\vartheta^G}\,K^\epsilon_{j\,E} - \frac{\partial\Lambda^d}{\partial\vartheta^G}\,K^d_{j\,E} + \frac{\partial c_E}{\partial\vartheta^G}\frac{\partial\overline{\nu}}{\partial x_j} + \left.\frac{\partial\overline{\pi}_{\text{int}}}{\partial\vartheta^G_{,j}}\right|_E, \\
\frac{\partial\Lambda^\epsilon}{\partial\epsilon}\,K^\epsilon_{j\,E} + \frac{\partial\Lambda^d}{\partial\epsilon}\,K^d_{j\,E} &= \frac{\partial c_E}{\partial\epsilon}\frac{\partial\overline{\nu}}{\partial x_j} + \left.\frac{\partial\overline{\pi}_{\text{int}}}{\partial\epsilon_{,j}}\right|_E, \\
\frac{\partial\Lambda^\epsilon}{\partial d}\,K^\epsilon_{j\,E} + \frac{\partial\Lambda^d}{\partial d}\,K^d_{j\,E} &= \frac{\partial c_E}{\partial d}\frac{\partial\overline{\nu}}{\partial x_j} + \left.\frac{\partial\overline{\pi}_{\text{int}}}{\partial d_{,j}}\right|_E.
\end{aligned} \tag{31.125}$$

Further investigation of (31.122), (31.125) is of little use unless specific closure assumptions are made. For instance, if we suppose for equilibrium or nonequilibrium

$$c = 0, \quad \frac{\partial \Lambda^\epsilon}{\partial \overline{\nu}} = \frac{\partial \Lambda^d}{\partial \overline{\nu}} = 0, \quad \frac{\partial \Lambda^\epsilon}{\partial \overline{\gamma}} = \frac{\partial \Lambda^d}{\partial \overline{\gamma}} = 0, \tag{31.126}$$

then a dimensional analysis of the terms that remain in (31.122) suggests the choice

$$\begin{aligned} \Lambda^\epsilon &= \tau^\epsilon(\vartheta^M - \vartheta^T), \quad & \Lambda^d &= \tau^d(\vartheta^M - \vartheta^G)\,, \\ \Pi^\epsilon &= -\frac{1}{\tau^\epsilon}\overline{\gamma}\,\overline{\nu}\epsilon, & \Pi^d &= -\frac{1}{\tau^d}\overline{\gamma}\,\overline{\nu}d, \end{aligned} \tag{31.127}$$

with τ^ϵ, τ^d time dimensional quantities depending on $\overline{g}$, ϑ^M, ϑ^T, ϑ^G, ϵ, d. The assumptions (31.126), (31.127) imply identical satisfaction of (31.122) or

$$\overline{\pi}_{\text{int}} = 0,$$

and the restrictions $(31.125)_{1,2}$ merge into

$$\begin{aligned} &\overline{f}_E = \frac{1}{\ell\,\overline{\gamma}\,\overline{\nu}}(\overline{p} - \overline{\beta}), \\ &\left\{\vartheta^M \overline{T}_{ij} + \vartheta^T R_{ij}\right\}_E = -\vartheta^M \overline{\nu}\,\overline{p}\,\delta_{ij} - \vartheta^M \overline{C}_{ij}. \end{aligned}$$

Now, from the last two conditions (31.125), we infer that if the determinant

$$\begin{vmatrix} \dfrac{\partial \Lambda^\epsilon}{\partial \epsilon} & \dfrac{\partial \Lambda^d}{\partial \epsilon} \\ \dfrac{\partial \Lambda^\epsilon}{\partial d} & \dfrac{\partial \Lambda^d}{\partial d} \end{vmatrix} \neq 0, \tag{31.128}$$

then, since the right-hand sides of $(31.125)_{6,7}$ vanish, we have

$$K^\epsilon_{j\,E} = 0, \qquad K^d_{j\,E} = 0, \tag{31.129}$$

which implies through $(31.125)_{4,5}$ that

$$\left\{\overline{q}_j + Q_j\right\}_E = 0, \qquad K_{j\,E} = 0, \qquad L_{j\,E} = 0. \tag{31.130}$$

If at particular points of thermodynamic processes the value of the determinant (31.128) turns out to be zero, then we require, through continuity, that (31.129) equally hold and obtain (31.130). This completes the investigation of equilibrium restrictions (31.122), (31.125) in the particular case defined by (31.126)–(31.128).

31.8 Linear Deviations from Thermodynamic Equilibrium in Dynamic Processes

Next, let us turn to condition (31.124). For brevity, we write the entropy production in the form

$$\begin{aligned}\overline{\pi} = {}&\left\{\vartheta^M(\overline{T}_{ij} + \overline{C}_{ij} + \overline{\nu}\,\overline{p}\,\delta_{ij}) + \vartheta^T R_{ij}\right\}\overline{D}_{ij}\\ &+\vartheta^M\left\{\overline{p} - \overline{\beta} - \ell\,\overline{\gamma}\,\overline{\nu}\,\overline{f}\right\}\dot{\overline{\nu}} + a_j\,g_j + \overline{\pi}_{\text{int}},\end{aligned}$$

where

$$\begin{aligned}\boldsymbol{g} &\equiv (\operatorname{grad}\vartheta^M,\ \operatorname{grad}\vartheta^T, \operatorname{grad}\vartheta^G,\ \operatorname{grad}\epsilon,\ \operatorname{grad}d) \in \mathbb{R}^{15},\\ \boldsymbol{a} &\equiv (\boldsymbol{f}^M,\ \boldsymbol{f}^T,\ \boldsymbol{f}^G,\ \boldsymbol{f}^\epsilon,\ \boldsymbol{f}^d) \in \mathbb{R}^{15},\\ f_j^M &\equiv -\left\{-\overline{q}_j - Q_j + \frac{\partial\Lambda^\epsilon}{\partial\vartheta^M}K_j^\epsilon + \frac{\partial\Lambda^d}{\partial\vartheta^M}K_j^d - \frac{\partial c}{\partial\vartheta^M}\frac{\partial\overline{\nu}}{\partial x_j}\right\},\\ f_j^T &\equiv -\left\{K_j + \frac{\partial\Lambda^\epsilon}{\partial\vartheta^T}K_j^\epsilon + \frac{\partial\Lambda^d}{\partial\vartheta^T}K_j^d - \frac{\partial c}{\partial\vartheta^T}\frac{\partial\overline{\nu}}{\partial x_j}\right\},\\ f_j^G &\equiv -\left\{L_j + \frac{\partial\Lambda^\epsilon}{\partial\vartheta^G}K_j^\epsilon + \frac{\partial\Lambda^d}{\partial\vartheta^G}K_j^d - \frac{\partial c}{\partial\vartheta^G}\frac{\partial\overline{\nu}}{\partial x_j}\right\},\\ f_j^\epsilon &\equiv -\left\{\frac{\partial\Lambda^\epsilon}{\partial\epsilon}K_j^\epsilon + \frac{\partial\Lambda^d}{\partial\epsilon}K_j^d - \frac{\partial c}{\partial\epsilon}\frac{\partial\overline{\nu}}{\partial x_j}\right\},\\ f_j^d &\equiv -\left\{\frac{\partial\Lambda^\epsilon}{\partial d}K_j^\epsilon + \frac{\partial\Lambda^d}{\partial d}K_j^d - \frac{\partial c}{\partial d}\frac{\partial\overline{\nu}}{\partial x_j}\right\}.\end{aligned}$$

With this notation the (symmetric) Hessian matrix corresponding to $\overline{\pi}$ is given by

$$H = \begin{pmatrix} \dfrac{\partial^2\overline{\pi}}{\partial\dot{\overline{\nu}}^2} & \dfrac{\partial^2\overline{\pi}}{\partial\dot{\overline{\nu}}\,\partial\overline{\boldsymbol{D}}} & \dfrac{\partial^2\overline{\pi}}{\partial\dot{\overline{\nu}}\,\partial\boldsymbol{g}}\\ \dfrac{\partial^2\overline{\pi}}{\partial\overline{\boldsymbol{D}}\,\partial\dot{\overline{\nu}}} & \dfrac{\partial^2\overline{\pi}}{\partial\overline{\boldsymbol{D}}\,\partial\overline{\boldsymbol{D}}} & \dfrac{\partial^2\overline{\pi}}{\partial\overline{\boldsymbol{D}}\,\partial\boldsymbol{g}}\\ \dfrac{\partial^2\overline{\pi}}{\partial\boldsymbol{g}\,\partial\dot{\overline{\nu}}} & \dfrac{\partial^2\overline{\pi}}{\partial\boldsymbol{g}\,\partial\overline{\boldsymbol{D}}} & \dfrac{\partial^2\overline{\pi}}{\partial\boldsymbol{g}\,\partial\boldsymbol{g}} \end{pmatrix}.$$

For the entries of the matrix H_E we find

$$\begin{aligned}\left.\frac{\partial^2\overline{\pi}}{\partial\dot{\overline{\nu}}^2}\right|_E &= \left\{-2\vartheta^M\ell\,\overline{\gamma}\,\overline{\nu}\,\frac{\partial\overline{f}}{\partial\dot{\overline{\nu}}} + \frac{\partial^2\overline{\pi}_{\text{int}}}{\partial\dot{\overline{\nu}}^2}\right\}_E,\\ \left.\frac{\partial^2\overline{\pi}}{\partial\dot{\overline{\nu}}\partial\overline{D}_{ij}}\right|_E &= \left\{\vartheta^M\frac{\partial\overline{T}_{ij}}{\partial\dot{\overline{\nu}}} + \vartheta^T\frac{\partial R_{ij}}{\partial\dot{\overline{\nu}}} - \vartheta^M\ell\,\overline{\gamma}\,\overline{\nu}\,\frac{\partial\overline{f}}{\partial\overline{D}_{ij}} + \frac{\partial^2\overline{\pi}_{\text{int}}}{\partial\dot{\overline{\nu}}\partial\overline{D}_{ij}}\right\}_E,\end{aligned}$$

$$
\begin{aligned}
\left.\frac{\partial^2 \overline{\pi}}{\partial \dot{\overline{\nu}} \partial g_i}\right|_E &= \left\{ -\vartheta^M \ell\, \overline{\gamma}\, \overline{\nu}\, \frac{\partial \overline{f}}{\partial g_i} + \frac{\partial a_i}{\partial \dot{\overline{\nu}}} + \frac{\partial^2 \overline{\pi}_{\mathrm{int}}}{\partial \dot{\overline{\nu}} \partial g_i} \right\}_E , \\
\left.\frac{\partial^2 \overline{\pi}}{\partial \overline{D}_{ij}\, \partial \overline{D}_{kl}}\right|_E &= \left\{ \vartheta^M \left(\frac{\partial \overline{T}_{ij}}{\partial \overline{D}_{kl}} + \frac{\partial \overline{T}_{kl}}{\partial \overline{D}_{ij}} \right) \right. \\
&\qquad \left. + \vartheta^T \left(\frac{\partial R_{ij}}{\partial \overline{D}_{kl}} + \frac{\partial R_{kl}}{\partial \overline{D}_{ij}} \right) + \frac{\partial^2 \overline{\pi}_{\mathrm{int}}}{\partial \overline{D}_{ij}\, \partial \overline{D}_{kl}} \right\}_E , \\
\left.\frac{\partial^2 \overline{\pi}}{\partial \overline{D}_{ij}\, \partial g_k}\right|_E &= \left\{ \vartheta^M \frac{\partial \overline{T}_{ij}}{\partial g_k} + \vartheta^T \frac{\partial R_{ij}}{\partial g_k} + \frac{\partial a_k}{\partial \overline{D}_{ij}} + \frac{\partial^2 \overline{\pi}_{\mathrm{int}}}{\partial \overline{D}_{ij}\, \partial g_k} \right\}_E , \\
\left.\frac{\partial^2 \overline{\pi}}{\partial g_i\, \partial g_j}\right|_E &= \left\{ \frac{\partial a_i}{\partial g_j} + \frac{\partial a_j}{\partial g_i} + \frac{\partial^2 \overline{\pi}_{\mathrm{int}}}{\partial g_i\, \partial g_j} \right\}_E .
\end{aligned}
\tag{31.131}
$$

It is evident that without specific closure assumptions the condition on H_E of being positive semi-definite cannot be further exploited. For simplicity we assume that the stresses $\overline{T}_{ij} - \overline{T}_{ij\,E}$, $R_{ij} - R_{ij\,E}$, the productions $\overline{f} - \overline{f}_E$, $\Pi^{\epsilon} - \Pi^{\epsilon}_E$, $\Pi^d - \Pi^d_E$ and the fluxes $\overline{q}_j + Q_j$, K_j, L_j, K^{ϵ}_j, K^d_j can be approximated by linear functions of $\dot{\overline{\nu}}$, $\overline{D}_{ij}$, g_j as follows:

$$
\overline{T}_{ij} = \overline{T}_{ij\,E} + \left(\xi^M \dot{\overline{\nu}} + \lambda^M \operatorname{tr} \overline{\boldsymbol{D}} \right) \delta_{ij} + 2\mu^M \overline{D}_{ij}, \tag{31.132}
$$

$$
R_{ij} = R_{ij\,E} + \left(\xi^T \dot{\overline{\nu}} + \lambda^T \operatorname{tr} \overline{\boldsymbol{D}} \right) \delta_{ij} + 2\mu^T \overline{D}_{ij}, \tag{31.133}
$$

$$
\overline{f} = \overline{f}_E - \zeta \dot{\overline{\nu}} - \delta \operatorname{tr} \overline{\boldsymbol{D}}, \tag{31.134}
$$

$$
\begin{aligned}
\overline{q}_j + Q_j &= \overline{q}_{j\,E} + Q_j + \alpha_1 \frac{\partial \vartheta^M}{\partial x_j} + \alpha_2 \frac{\partial \vartheta^T}{\partial x_j} \\
&\quad + \alpha_3 \frac{\partial \vartheta^G}{\partial x_j} + \alpha_4 \frac{\partial \epsilon}{\partial x_j} + \alpha_5 \frac{\partial d}{\partial x_j},
\end{aligned}
\tag{31.135}
$$

$$
K_j = K_{j\,E} - \left\{ \beta_1 \frac{\partial \vartheta^M}{\partial x_j} + \beta_2 \frac{\partial \vartheta^T}{\partial x_j} + \beta_3 \frac{\partial \vartheta^G}{\partial x_j} + \beta_4 \frac{\partial \epsilon}{\partial x_j} + \beta_5 \frac{\partial d}{\partial x_j} \right\}, \tag{31.136}
$$

$$
L_j = L_{jE} - \left\{ \gamma_1 \frac{\partial \vartheta^M}{\partial x_j} + \gamma_2 \frac{\partial \vartheta^T}{\partial x_j} + \gamma_3 \frac{\partial \vartheta^G}{\partial x_j} + \gamma_4 \frac{\partial \epsilon}{\partial x_j} + \gamma_5 \frac{\partial d}{\partial x_j} \right\}, \tag{31.137}
$$

$$
K^{\epsilon}_j = K^{\epsilon}_{jE} - \left\{ \xi_1 \frac{\partial \vartheta^M}{\partial x_j} + \xi_2 \frac{\partial \vartheta^T}{\partial x_j} + \xi_3 \frac{\partial \vartheta^G}{\partial x_j} + \xi_4 \frac{\partial \epsilon}{\partial x_j} + \xi_5 \frac{\partial d}{\partial x_j} \right\}, \tag{31.138}
$$

$$
K^{d}_j = K^{d}_{jE} - \left\{ \zeta_1 \frac{\partial \vartheta^M}{\partial x_j} + \zeta_2 \frac{\partial \vartheta^T}{\partial x_j} + \zeta_3 \frac{\partial \vartheta^G}{\partial x_j} + \zeta_4 \frac{\partial \epsilon}{\partial x_j} + \zeta_5 \frac{\partial d}{\partial x_j} \right\}, \tag{31.139}
$$

$$
\Pi^{\epsilon} = \Pi^{\epsilon}_E - a^{\epsilon} \dot{\overline{\nu}} - b^{\epsilon} \operatorname{tr} \overline{\boldsymbol{D}}, \qquad \Pi^{d} = \Pi^{d}_E - a^{d} \dot{\overline{\nu}} - b^{d} \operatorname{tr} \overline{\boldsymbol{D}}. \tag{31.140}
$$

In these expressions, the scalar coefficients

$$
\xi^M, \quad \lambda^M, \quad \mu^M,
$$

$$
\begin{array}{ll}
\xi^T, \quad \lambda^T, \quad \mu^T, & \\
\zeta, \quad \delta, & \\
\alpha_j, & j = 1, \dots, 5, \\
\beta_k, & k = 1, \dots, 5, \\
\gamma_\ell, & \ell = 1, \dots, 5, \\
\xi_m, & m = 1, \dots, 5, \\
\zeta_n, & n = 1, \dots, 5, \\
a^\epsilon, b^\epsilon, & a^d, b^d,
\end{array}
$$

are 37 quantities to be specified by experiments or other means before the model equations can be applied.

We also assume that

$$
c = c_E. \tag{31.141}
$$

In general, these coefficients are scalar functions of ν_0, $\overline{\nu}$, $\overline{\nu}_{,i}$, $\overline{\gamma}$, $\overline{\gamma}_{,i}$, ϑ^M, ϑ^T, ϑ^G, ϵ, d, and the equilibrium values that appear in (31.132)–(31.141) must be restricted by (31.122) and (31.125). Moreover, combining the definitions of k and s in (31.57) with $(31.87)_{2,3}$, we may write

$$
\begin{aligned}
\overline{\rho}\, k &= -\tfrac{1}{2} R_{ii} = \overline{\rho}\vartheta^M \frac{\partial \psi^{\text{turb}}}{\partial \varepsilon}, \\
\overline{\rho}\, s &= \tfrac{1}{2}\ell^2 \, R_{ij} \frac{\partial \overline{\nu}}{\partial x_i}\frac{\partial \overline{\nu}}{\partial x_j} = \overline{\rho}\,\vartheta^M \frac{\partial \psi^{\text{turb}}}{\partial \vartheta^G}.
\end{aligned}
$$

In these expressions, since according to (31.108) ψ^{turb} is not a function of $\dot{\overline{\nu}}$, ψ^{turb} is formally the same as $\psi^{\text{turb}}|_E$, so that with (31.132) and (31.133), we obtain

$$
\begin{aligned}
&-\tfrac{1}{2}\left\{R_{ii\,E} + \xi^T \dot{\overline{\nu}} + (3\lambda^T + 2\mu^T)\operatorname{tr}\boldsymbol{D}\right\} = \underbrace{\overline{\rho}\vartheta^M \frac{\partial \psi^{\text{turb}}}{\partial \varepsilon}}_{-\frac{1}{2}R_{ii\,E}}, \\
&-\tfrac{1}{2}\ell^2\left\{R_{ij\,E} + \left(\xi^T \dot{\overline{\nu}} + \lambda^T \operatorname{tr}\boldsymbol{D}\right)\delta_{ij} + 2\mu^T\, D_{ij}\right\} \frac{\partial \overline{\nu}}{\partial x_i}\frac{\partial \overline{\nu}}{\partial x_j} = \underbrace{\overline{\rho}\vartheta^M \frac{\partial \xi^{\text{turb}}}{\partial \vartheta^G}}_{-\frac{1}{2}\ell^2 R_{ij\,E}}.
\end{aligned}
$$

These identities imply

$$
\xi^T \dot{\overline{\nu}} + (3\lambda^T + 2\mu)\operatorname{tr}\boldsymbol{D} \equiv 0,
$$

and

$$\xi^T \dot{\overline{\nu}} + \lambda^T \mathrm{tr}\boldsymbol{D} \frac{\partial \overline{\nu}}{\partial x_i} \frac{\partial \overline{\nu}}{\partial x_i} + 2\mu^T D_{ij} \frac{\partial \overline{\nu}}{\partial x_i} \frac{\partial \overline{\nu}}{\partial x_j} \equiv 0,$$

from which we deduce, since $\dot{\overline{\nu}}$, $\boldsymbol{D}$ may vary arbitrarily,

$$\begin{aligned} \xi^T &= 0, \quad 3\lambda^T + 2\mu^T = 0 \quad \text{and} \\ \xi^T &= 0, \quad \mu^T = 0 \qquad \forall \mathrm{grad}\,\overline{\nu} \neq \mathbf{0}. \end{aligned}$$

The latter result may for continuity reasons be extended to hold for all grad $\overline{\nu}$-values, including grad $\overline{\nu} = 0$. Hence, in the representation (31.132), the REYNOLDS stress tensor, when linearly depending upon the stretching tensor and the mean volume fraction speed only, cannot depend on them at all. This seems to be reasonable since the definition (31.57) of s, H_j and the restriction (31.111) on $\overline{h}_j$ show that R_{ij} is strongly related to the granular structure of the material. Furthermore, it indicates that the REYNOLDS stress tensor should nonlinearly depend on stretching, a result that is in conformity with many other granular theories.

In view of (31.115), (31.138)–(31.141), the second derivatives of $\overline{\pi}_{\mathrm{int}}$ appearing in (31.131) can be shown to vanish identically. Accordingly, insertion of (31.132)–(31.139), (31.141) into (31.131) yields the following explicit entries of the Hessian matrix H_E:

$$\begin{aligned}
\left.\frac{\partial^2 \overline{\pi}}{\partial \dot{\overline{\nu}}^2}\right|_E &= 2\vartheta^M \ell\, \overline{\gamma}\, \overline{\nu}\, \zeta \equiv a, \\
\left.\frac{\partial^2 \overline{\pi}}{\partial \dot{\overline{\nu}} \partial \overline{D}_{ij}}\right|_E &= (\vartheta^M \xi^M + \vartheta^M \ell\, \overline{\gamma}\, \overline{\nu} \delta\,)\, \delta_{ij} \equiv b\, \delta_{ij}, \\
\left.\frac{\partial^2 \overline{\pi}}{\partial \dot{\overline{\nu}} \partial g_i}\right|_E &= 0, \\
\left.\frac{\partial^2 \overline{\pi}}{\partial \overline{D}_{ij}\, \partial g_k}\right|_E &= 0, \\
\left.\frac{\partial^2 \overline{\pi}}{\partial \overline{D}_{ij}\, \partial \overline{D}_{kl}}\right|_E &= 2(\vartheta^M \lambda^M + \vartheta^T \lambda^T)\, \delta_{ij}\, \delta_{kl} + 4(\vartheta^M \mu^M + \vartheta^T \mu^T)\, \delta_{ik}\, \delta_{jl} \\
&\equiv \lambda\, \delta_{ij}\, \delta_{kl} + 2\mu \delta_{ik}\, \delta_{jl}, \\
\left.\frac{\partial^2 \overline{\pi}}{\partial \vartheta^M_{,i}\, \partial \vartheta^M_{,j}}\right|_E &= \left\{ \frac{\partial f^M_i}{\partial \vartheta^M_{,j}} + \frac{\partial f^M_j}{\partial \vartheta^M_{,i}} \right\}_E \\
&= 2\left(\alpha_1 + \frac{\partial \Lambda^\epsilon}{\partial \vartheta^M}\, \xi_1 + \frac{\partial \Lambda^d}{\partial \vartheta^M}\, \zeta_1 \right) \delta_{ij} \equiv a_{11}\, \delta_{ij}, \\
\left.\frac{\partial^2 \overline{\pi}}{\partial \vartheta^M_{,i}\, \partial \vartheta^T_{,j}}\right|_E &= \left\{ \frac{\partial f^M_i}{\partial \vartheta^T_{,j}} + \frac{\partial f^T_j}{\partial \vartheta^M_{,i}} \right\}_E
\end{aligned}$$

$$\begin{aligned}
&= \left(\alpha_2 + \frac{\partial \Lambda^\epsilon}{\partial \vartheta^M}\,\xi_2 + \frac{\partial \Lambda^d}{\partial \vartheta^M}\,\zeta_2 + \beta_1 + \frac{\partial \Lambda^\epsilon}{\partial \vartheta^T}\,\xi_1 + \frac{\partial \Lambda^d}{\partial \vartheta^T}\,\zeta_1\right)\delta_{ij} \\
&\equiv a_{12}\,\delta_{ij}, \\
\left.\frac{\partial^2 \overline{\pi}}{\partial \vartheta^M_{,i}\,\partial \vartheta^G_{,j}}\right|_E &= \left\{\frac{\partial f^M_i}{\partial \vartheta^G_{,j}} + \frac{\partial f^G_j}{\partial \vartheta^M_{,i}}\right\}_E \\
&= \left(\alpha_3 + \frac{\partial \Lambda^\epsilon}{\partial \vartheta^M}\,\xi_3 + \frac{\partial \Lambda^d}{\partial \vartheta^M}\,\zeta_3 + \gamma_1 + \frac{\partial \Lambda^\epsilon}{\partial \vartheta^G}\,\xi_1 + \frac{\partial \Lambda^d}{\partial \vartheta^G}\,\zeta_1\right)\delta_{ij} \\
&\equiv a_{13}\,\delta_{ij}, \\
\left.\frac{\partial^2 \overline{\pi}}{\partial \vartheta^M_{,i}\,\partial \epsilon_{,j}}\right|_E &= \left\{\frac{\partial f^M_i}{\partial \epsilon_{,j}} + \frac{\partial f^\epsilon_j}{\partial \vartheta^M_{,i}}\right\}_E \\
&= \left(\alpha_4 + \frac{\partial \Lambda^\epsilon}{\partial \vartheta^M}\,\xi_4 + \frac{\partial \Lambda^d}{\partial \vartheta^M}\,\zeta_4 + \frac{\partial \Lambda^\epsilon}{\partial \epsilon}\,\xi_1 + \frac{\partial \Lambda^d}{\partial \epsilon}\,\zeta_1\right)\delta_{ij} \equiv a_{14}\,\delta_{ij}, \\
\left.\frac{\partial^2 \overline{\pi}}{\partial \vartheta^M_{,i}\,\partial d_{,j}}\right|_E &= \left\{\frac{\partial f^M_i}{\partial d_{,j}} + \frac{\partial f^d_j}{\partial \vartheta^M_{,i}}\right\}_E \\
&= \left(\alpha_5 + \frac{\partial \Lambda^\epsilon}{\partial \vartheta^M}\,\xi_5 + \frac{\partial \Lambda^d}{\partial \vartheta^M}\,\zeta_5 + \frac{\partial \Lambda^\epsilon}{\partial d}\,\xi_1 + \frac{\partial \Lambda^d}{\partial d}\,\zeta_1\right)\delta_{ij} \equiv a_{15}\,\delta_{ij}, \\
\left.\frac{\partial^2 \overline{\pi}}{\partial \vartheta^T_{,i}\,\partial \vartheta^T_{,j}}\right|_E &= \left\{\frac{\partial f^T_i}{\partial \vartheta^T_{,j}} + \frac{\partial f^T_j}{\partial \vartheta^T_{,i}}\right\}_E \\
&= 2\left(\beta_2 + \frac{\partial \Lambda^\epsilon}{\partial \vartheta^T}\,\xi_2 + \frac{\partial \Lambda^d}{\partial \vartheta^T}\,\zeta_2\right)\delta_{ij} \equiv a_{22}\,\delta_{ij}, \\
\left.\frac{\partial^2 \overline{\pi}}{\partial \vartheta^T_{,i}\,\partial \vartheta^G_{,j}}\right|_E &= \left\{\frac{\partial f^T_i}{\partial \vartheta^G_{,j}} + \frac{\partial f^G_j}{\partial \vartheta^T_{,i}}\right\}_E \\
&= \left(\beta_3 + \frac{\partial \Lambda^\epsilon}{\partial \vartheta^T}\,\xi_3 + \frac{\partial \Lambda^d}{\partial \vartheta^T}\,\zeta_3 + \gamma_2 + \frac{\partial \Lambda^\epsilon}{\partial \vartheta^G}\,\xi_2 + \frac{\partial \Lambda^d}{\partial \vartheta^G}\,\zeta_2\right)\delta_{ij} \\
&\equiv a_{23}\,\delta_{ij}, \\
\left.\frac{\partial^2 \overline{\pi}}{\partial \vartheta^T_{,i}\,\partial \epsilon_{,j}}\right|_E &= \left\{\frac{\partial f^T_i}{\partial \epsilon_{,j}} + \frac{\partial f^\epsilon_j}{\partial \vartheta^T_{,i}}\right\}_E \\
&= \left(\beta_4 + \frac{\partial \Lambda^\epsilon}{\partial \vartheta^T}\,\xi_4 + \frac{\partial \Lambda^d}{\partial \vartheta^T}\,\zeta_4 + \frac{\partial \Lambda^\epsilon}{\partial \epsilon}\,\xi_2 + \frac{\partial \Lambda^d}{\partial \epsilon}\,\zeta_2\right)\delta_{ij} \equiv a_{24}\,\delta_{ij}, \\
\left.\frac{\partial^2 \overline{\pi}}{\partial \vartheta^T_{,i}\,\partial d_{,j}}\right|_E &= \left\{\frac{\partial f^T_i}{\partial d_{,j}} + \frac{\partial f^d_j}{\partial n\vartheta^T_{,i}}\right\}_E \\
&= \left(\beta_5 + \frac{\partial \Lambda^\epsilon}{\partial \vartheta^T}\,\xi_5 + \frac{\partial \Lambda^d}{\partial \vartheta^T}\,\zeta_5 + \frac{\partial \Lambda^\epsilon}{\partial d}\,\xi_2 + \frac{\partial \Lambda^d}{\partial d}\,\zeta_2\right)\delta_{ij} \equiv a_{25}\,\delta_{ij},
\end{aligned}$$

$$
\begin{aligned}
\left.\frac{\partial^2 \overline{\pi}}{\partial \vartheta^G_{,i}\,\partial \vartheta^G_{,j}}\right|_E &= \left\{\frac{\partial f^G_i}{\partial \vartheta^G_{,j}} + \frac{\partial f^G_j}{\partial t G_{,i}}\right\}_E \\
&= 2\left(\gamma_3 + \frac{\partial \Lambda^\epsilon}{\partial \vartheta^G}\,\xi_3 + \frac{\partial \Lambda^d}{\partial \vartheta^G}\,\zeta_3\right)\delta_{ij} \equiv a_{33}\,\delta_{ij}, \\
\left.\frac{\partial^2 \overline{\pi}}{\partial \vartheta^G_{,i}\,\partial \epsilon_{,j}}\right|_E &= \left\{\frac{\partial f^G_i}{\partial \epsilon_{,j}} + \frac{\partial f^\epsilon_j}{\partial \vartheta^G_{,i}}\right\}_E \\
&= \left(\gamma_4 + \frac{\partial \Lambda^\epsilon}{\partial \vartheta^G}\,\xi_4 + \frac{\partial \Lambda^d}{\partial \vartheta^G}\,\zeta_4 + \frac{\partial \Lambda^\epsilon}{\partial \epsilon}\,\xi_3 + \frac{\partial \Lambda^d}{\partial \epsilon}\,\zeta_3\right)\delta_{ij} \\
&\equiv a_{34}\,\delta_{ij}, \\
\left.\frac{\partial^2 \overline{\pi}}{\partial \vartheta^G_{,i}\,\partial d_{,j}}\right|_E &= \left\{\frac{\partial f^G_i}{\partial d_{,j}} + \frac{\partial f^d_j}{\partial \vartheta^G_{,i}}\right\}_E \\
&= \left(\gamma_5 + \frac{\partial \Lambda^\epsilon}{\partial \vartheta^G}\,\xi_5 + \frac{\partial \Lambda^d}{\partial \vartheta^G}\,\zeta_5 + \frac{\partial \Lambda^\epsilon}{\partial d}\,\xi_3 + \frac{\partial \Lambda^d}{\partial d}\,\zeta_3\right)\delta_{ij} \equiv a_{35}\,\delta_{ij}, \\
\left.\frac{\partial^2 \overline{\pi}}{\partial \epsilon_{,i}\,\partial \epsilon_{,j}}\right|_E &= \left\{\frac{\partial f^\epsilon_i}{\partial \epsilon_{,j}} + \frac{\partial f^\epsilon_j}{\partial \epsilon_{,i}}\right\}_E \\
&= 2\left(\frac{\partial \Lambda^\epsilon}{\partial \epsilon}\,\xi_4 + \frac{\partial \Lambda^d}{\partial \epsilon}\,\zeta_4\right)\delta_{ij} \equiv a_{44}\,\delta_{ij}, \\
\left.\frac{\partial^2 \overline{\pi}}{\partial \epsilon_{,i}\,\partial d_{,j}}\right|_E &= \left\{\frac{\partial f^\epsilon_i}{\partial d_{,j}} + \frac{\partial f^d_j}{\partial \epsilon_{,i}}\right\}_E \\
&= \left(\frac{\partial \Lambda^\epsilon}{\partial \epsilon}\,\xi_5 + \frac{\partial \Lambda^d}{\partial \epsilon}\,\zeta_5 + \frac{\partial \Lambda^\epsilon}{\partial d}\,\xi_4 + \frac{\partial \Lambda^d}{\partial d}\,\zeta_4\right)\delta_{ij} \equiv a_{45}\,\delta_{ij}, \\
\left.\frac{\partial^2 \overline{\pi}}{\partial d_{,i}\,\partial d_{,j}}\right|_E &= \left\{\frac{\partial f^d_i}{\partial d_{,j}} + \frac{\partial f^d_j}{\partial d_{,i}}\right\}_E \\
&= 2\left(\frac{\partial \Lambda^\epsilon}{\partial d}\xi_5 + \frac{\partial \Lambda^d}{\partial d}\,\zeta_5\right)\delta_{ij} \equiv a_{55}\,\delta_{ij}.
\end{aligned}
$$

By collecting the entries of the matrix H_E, the following bloc diagonal form for the matrix H_E is deduced

$$
H_E = \begin{pmatrix} A & 0 \\ 0 & B \end{pmatrix}, \tag{31.142}
$$

where A is the 10×10 symmetric matrix

$$A \equiv \begin{pmatrix} a & b & 0 & 0 & 0 & b & 0 & 0 & 0 & b \\ b & \lambda+2\mu & 0 & 0 & 0 & \lambda & 0 & 0 & 0 & \lambda \\ 0 & 0 & 2\mu & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 2\mu & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 2\mu & 0 & 0 & 0 & 0 & 0 \\ b & \lambda & 0 & 0 & 0 & \lambda+2\mu & 0 & 0 & 0 & \lambda \\ 0 & 0 & 0 & 0 & 0 & 0 & 2\mu & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 2\mu & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 2\mu & 0 \\ b & \lambda & 0 & 0 & 0 & \lambda & 0 & 0 & 0 & \lambda+2\mu \end{pmatrix},$$

and B is the 15×15 symmetric bloc matrix

$$B \equiv \begin{pmatrix} a_{11}I & a_{12}I & a_{13}I & a_{14}I & a_{15}I \\ a_{12}I & a_{22}I & a_{23}I & a_{24}I & a_{25}I \\ a_{13}I & a_{23}I & a_{33}I & a_{34}I & a_{35}I \\ a_{14}I & a_{24}I & a_{34}I & a_{44}I & a_{45}I \\ a_{15}I & a_{25}I & a_{35}I & a_{45}I & a_{55}I \end{pmatrix}, \quad I = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

Now, it is useful to use the SYLVESTER criterion[15]; in so doing we impose the (stronger) restriction on H_E of being positive definite. Since the determinant of a bloc matrix of the form (31.142) equals $\det A \; \det B$, using SYLVESTER's criterion we find that H_E is positive definite if and only if A and B are simultaneously positive definite. From the condition on A of being positive definite we deduce the following restrictions:

$$a > 0, \qquad \mu > 0, \qquad a(3\lambda + 2\mu) - 3b^2 > 0.$$

As a result of the corollary that is proved in Appendix 31.A of this chapter the 15×15 matrix B is positive definite if and only if the 5×5 matrix whose entries are a_{ij}, $i, j = 1, \ldots, 5$ is positive definite. This delivers restrictions upon the signs of the coefficients that appear in (31.135)–(31.139), but we refrain to write them down, since the formulae that are involved are too long.

31.9 Discussion and Conclusions

In this chapter, we presented a thermodynamically consistent derivation of the turbulent equations of a granular continuum that obeys on the laminar level equations of the GOODMAN–COWIN type. The strategy was to assume that the "laminar" equations would adequately describe the physics at all scales, and adequate reproduction of time scale features would only have to be computed with a sufficiently refined mesh.

---

[15] A real symmetric matrix $\boldsymbol{M}$ is positive definite, if and only if all the leading principal minors of $\boldsymbol{M}$ are positive (see [24] or any book on matrix algebra).

In this sense the "laminar" equations describe the granular system on the microscale, and the smoothed processes that are not resolving this microscopic fine structure are deduced by applying to the "laminar" equations a filter or smoothing operator. This operation introduces correlation products which represent the manifestation of the microscale on the macroscale. Consequently, the postulation of closure relations for these terms correspond to a homogenization procedure that could be applied to any physical or nonphysical system which gives rise to a smoothing operation in space and/or time.

An important issue that was addressed was the embedding of the postulation of material constitutive relations in a dissipation principle from which both could be reduced. We proposed an entropy principle as suggested by SADIKI and HUTTER [53] and which may be regarded as an extension or application of that proposed by MÜLLER. This entropy principle was applied in the spirit of modern rational continuum mechanics of Müller [44] and LIU [39]. The results prove us to be right in doing so, because it turned out that the turbulent heat flux and entropy flux vectors are not collinear. We derived complete reduced forms for the material equations in the laminar case and for the turbulent correlation quantities in the turbulent case. Thermodynamic equilibrium quantities and linear closure relations for nonequilibrium quantities were deduced with restrictions on the signs of the phenomenological coefficients of the latter. The final set of equations forms a complete set, from which physically realizable solutions can be deduced. One particular and interesting result is that the REYNOLDS stress tensor cannot linearly depend on the mean stretching if grad $\overline{\nu} \neq \mathbf{0}$. This points at the necessity of a nonlinear relation as it has been pointed out already by BAGNOLD [8]. However, it is interesting that this result is deduced here from pure thermodynamic arguments.

This chapter on the laminar-turbulent description of the dynamics of granular materials is based on reference [40]. It uses the entropy inequality to constrain the postulated constitutive relations such that the final field equations subject to initial-boundary conditions exclusively generate physically realizable solutions. Similar research articles of comparable complexity have been quoted, extensions capturing more complex situations are rare. Some attempts, in which hypoplastic processes are included, are given by SCHNEIDER and HUTTER [31, 32, 56], KIRCHNER and HUTTER [36], KIRCHNER and TEUFEL [37], and FANG [16], who presents a $k-\varepsilon$-model for granular turbulent behavior.

Future activities will have to concentrate on applications of the presented model to gravity-driven shear flows with free surface in two- and three-dimensional situations. This is by itself an equally interesting and nontrivial subject. A further extended problem would be the application of the turbulent averaging procedure as suggested in [40] and presented here to a binary mixture of a fluid and a solid. Such mixtures are the adequate vehicle, e.g., for the description of mudflows in which both the fluid and the solid oscillate rapidly and also interact. Correlation stresses will here enter the fluid and the solid and correlations arising from the constituent interaction terms will describe how fluid and solid fluctuations affect each other.

Appendix 31.A On Positive Definiteness of the Matrix (31.142)

In this Appendix, we shall prove the statement mentioned at the end of Sect. 31.8.

Lemma 31.1 *Let A be a $n \times n$ matrix whose entries are a_{ij}, $i, j = 1, \ldots, n$ $(n \geqslant 1)$. To A we associate the $3n \times 3n$ matrix B as follows:*

$$B \equiv \begin{pmatrix} a_{11}I & a_{12}I & \cdots & a_{1n}I \\ a_{21}I & a_{22}I & \cdots & a_{2n}I \\ \vdots & \vdots & & \vdots \\ a_{n1}I & a_{n2}I & \cdots & a_{nn}I \end{pmatrix}. \tag{31.143}$$

Here I is the 3×3 unit matrix. Then the determinant of B is given by

$$\det B = (\det A)^3. \tag{31.144}$$

■

Proof To prove the lemma we proceed by induction on n. For $n = 1$ the relation (31.144) is trivially satisfied. Now, let $n > 1$ be a given integer and suppose that (31.144) holds for any $n \times n$ matrix A. We shall have completed the proof once we have shown that (31.144)n holds for any $(n+1) \times (n+1)$ matrix A.

Hence, let A be a $(n+1) \times (n+1)$ matrix whose entries are a_{ij}, $i, j = 1, \ldots, n+1$ and let B be the associated matrix as in (31.143). Since relation (31.144) is obvious for $A = 0$ we consider the case $A \neq 0$. Without loss of generality, we may assume $a_{11} \neq 0$ and, therefore, the following calculus is permitted:

$$\det B = a_{11}^3 \begin{vmatrix} I & \frac{a_{12}}{a_{11}}I & \cdots & \frac{a_{1\,n+1}}{a_{11}}I \\ a_{21}I & a_{22}I & \cdots & a_{2\,n+1}I \\ \vdots & \vdots & & \vdots \\ a_{n+1\,1}I & a_{n+1\,2}I & \cdots & a_{n+1\,n+1}I \end{vmatrix}$$

$$= a_{11}^3 \begin{vmatrix} I & \frac{a_{12}}{a_{11}}I & \cdots & \frac{a_{1\,n+1}}{a_{11}}I \\ 0 & \left(a_{22} - a_{21}\frac{a_{12}}{a_{11}}\right)I & \cdots & \left(a_{2\,n+1} - a_{21}\frac{a_{1\,n+1}}{a_{11}}\right)I \\ \vdots & \vdots & & \vdots \\ 0 & \left(a_{n+1\,2} - a_{n+1\,1}\frac{a_{12}}{a_{11}}\right)I & \cdots & \left(a_{n+1\,n+1} - a_{n+1\,1}\frac{a_{1\,n+1}}{a_{11}}\right)I \end{vmatrix}. \tag{31.145}$$

We remark that the last determinant in (31.145) equals the determinant of a $3n \times 3n$ matrix of the form (31.143), so that we can appeal to the inductive assumption. It remains only to see that $\det B$ is nothing else than $(\det A)^3$, which completes the proof.

Lemma 31.2 *Let A and B be the matrices specified by Lemma 31.1. If B_1 and B_2 denote the principal minors of order $3n-1$ and $3n-2$, respectively, of the matrix B, then*

$$B_1 = \Delta_{n-1}^2\, \Delta_n, \quad B_2 = \Delta_{n-1}\, \Delta_n^2,$$

where Δ_{n-1}, Δ_n are the principal minors of order $n-1$ and n, respectively, of the matrix A.[16] ■

We omit the proof of Lemma 31.2 since it is similar to the proof given for Lemma 31.1.

By virtue of the two lemmas and of Sylvester's criterion we deduce the result that we need to exploit the thermodynamic equilibrium restrictions.

Corollary *Let A and B be the matrices specified by Lemma 31.1. Then the matrix B is positive definite if and only if the matrix A is positive definite.*

Appendix 31.B Derivation of Favre's Form of the Momentum Equation

By averaging the momentum equation (see (31.16)) we deduce

$$\underbrace{\overline{\frac{\partial(\rho v_i)}{\partial t} + (\rho v_i v_j)_{,j}}}_{LHS_B} = \overline{T}_{ij,j} + \overline{\rho}\overline{b}_i + \overline{\rho' b'}, \tag{31.146}$$

where

$$\begin{aligned} LHS_B &= \frac{\partial}{\partial t}\left(\overline{\rho v_i}\right) + \left(\overline{\rho v_i v_j}\right)_{,j} \\ &= \frac{\partial}{\partial t}(\overline{\rho}\,\overline{v}_i) + \frac{\partial}{\partial t}(\overline{\rho' v_i'}) \\ &\quad + \Bigg[\overline{\rho}\,\overline{v}_i\overline{v}_j + \Big(\underbrace{\overline{\rho}\overline{v_i' v_j'} + \overline{\rho' v_i' v_j'}}_{=\overline{\rho v_i' v_j'} := -R_{ij} + \overline{\rho} m_i m_j}\Big) + \underbrace{\overline{\rho' v_i'}}_{\overline{\rho} m_i}\,\overline{v}_j + \underbrace{\overline{\rho' v_j'}}_{\overline{\rho} m_j}\,\overline{v}_i\Bigg]_{,j} \end{aligned}$$

---

[16] Hence $\Delta_n = \det A$.

$$
\begin{aligned}
&= \underline{\frac{\partial}{\partial t}(\overline{\rho}\,\overline{v}_i) + \frac{\partial}{\partial t}(\overline{\rho} m_i)} \\
&\quad + \Big[\overline{\rho}\,\overline{v}_i\overline{v}_j + \underline{\overline{\rho} m_i \overline{v}_j + \overline{\rho} m_j \overline{v}_i} - R_{ij} + \overline{\rho} m_i m_j\Big]_{,j} .
\end{aligned}
\tag{31.147}
$$

Next, we introduce the definition (see (31.27))

$$\overline{v}_i = U_i = V_i - m_i$$

and evaluate the underlined terms in the above expression. This leads to

$$
\bullet \quad \frac{\partial}{\partial t}(\overline{\rho}\,\overline{v}_i) + \frac{\partial}{\partial t}(\overline{\rho} m_i) = \frac{\partial}{\partial t}\left(\overline{\rho} V_i - \overline{\rho} m_i\right) = \frac{\partial}{\partial t}(\overline{\rho} V_i),
\tag{31.148}
$$

$$
\begin{aligned}
\bullet \quad \left[\overline{\rho} m_i \overline{v}_j + \overline{\rho} m_j V_i\right]_j &= \left[\overline{\rho} m_i (V_j - m_j) + \overline{\rho} m_j (V_i - m_i)\right]_{,j} \\
&= \left[\overline{\rho} m_i V_j - \overline{\rho} m_i m_j + \overline{\rho} m_j V_i - \overline{\rho} m_i m_j\right]_{,j} \\
&= \left[\overline{\rho}\left(m_i V_j + m_j V_i - 2 m_i m_j\right)\right]_{,j} .
\end{aligned}
\tag{31.149}
$$

It follows that

$$LHS_B = \frac{\partial}{\partial t}(\overline{\rho} V_i) + \left[\overline{\rho}\,\overline{v}_i\overline{v}_j + \overline{\rho} m_i V_j + \overline{\rho} m_j V_i - \overline{\rho} m_i m_j - R_{ij}\right]_{,j} .$$

Substituting in this expression

$$\overline{\rho}\,\overline{v}_i\overline{v}_j = \overline{\rho} V_i V_j - \overline{\rho} V_i m_j - \overline{\rho} V_j m_i + \overline{\rho} m_i m_j ,$$

we obtain

$$
\begin{aligned}
LHS_B &= \frac{\partial}{\partial t}(\overline{\rho} V_i) + [\overline{\rho} V_i V_j - R_{ij}]_{,j} \\
&= \frac{\partial \overline{\rho}}{\partial t} V_i + \overline{\rho}\frac{\partial V_i}{\partial t} + \frac{\partial \overline{\rho}}{\partial x_j} V_i V_j + \underbrace{\overline{\rho}(V_i V_j)_{,j}}_{\overline{\rho} V_{j,j} V_i + \overline{\rho} V_{i,j} V_j} - R_{ij} \\
&= \underbrace{\underbrace{\left(\frac{\partial \overline{\rho}}{\partial t} + \frac{\partial \overline{\rho}}{\partial x_j} V_j\right)}_{\overset{\circ}{\overline{\rho}}} V_i + \overline{\rho} V_{j,j} V_i}_{(\underbrace{\overset{\circ}{\overline{\rho}} + \overline{\rho} V_{j,j}}_{=0}) V_i = 0} + \underbrace{\overline{\rho}\frac{\partial V_i}{\partial t} + \overline{\rho} V_{i,j} V_j}_{\overline{\rho}\overset{\circ}{V}_i} - R_{ij,j} \\
&= \overline{\rho}\,\overset{\circ}{V}_i - R_{ij,j} .
\end{aligned}
\tag{31.150}
$$

In these underbraced terms, the definition of the FAVRE derivative (see (31.29)) of $\overset{\circ}{\overline{\rho}}$ and $\overset{\circ}{V}_i$ have been used and the balance law of mass (see (31.28)) have been employed. Substituting now (31.150) into (31.146) yields

$$\overline{\rho}\,\overset{\circ}{V}_i = (\overline{T}_{ij} + R_{ij}) + \overline{\rho}\overline{b}_i + \overline{\rho' b'_i}, \tag{31.151}$$

in which R_{ij} is the modified REYNOLDS stress tensor as defined in (31.31).

Appendix 31.C Derivation of Favre's Form of the Mean Configurational Momentum Equation

In this appendix we demonstrate, how Eq. (31.33) is obtained. Starting point is the balance law of configurational momentum, (31.17), which reads

$$\ell \frac{\partial}{\partial t}(\rho n) + \ell\{\rho n v'_j\}_{,j} = h_{j,j} + \rho f, \qquad n := \dot{\nu}. \tag{31.152}$$

The right- and left-hand sides of this equation are referred to as RHS_C and LHS_C, respectively. Taking REYNOLDS averages of this equation yields

$$\begin{aligned}
\overline{LHS_C} &\equiv \ell \frac{\partial}{\partial t}(\overline{\rho n}) + \ell\left\{\overline{\rho n v_j}\right\}_{,j} = \overline{RHS_C} \equiv \overline{h}_{j,j} + \overline{\rho}\overline{f} + \overline{\rho' f'} \\
&= \ell \frac{\partial}{\partial t}(\overline{\rho}\,\overline{n}) + \ell \frac{\partial}{\partial t}\underbrace{(\overline{\rho' n'})}_{\overline{\rho}m} + \ell\Big\{\overline{\rho}\,\overline{n}\,\overline{v}_j + \overline{v}_j \underbrace{\overline{\rho' n'}}_{\overline{\rho}m} + \overline{n}\overline{\rho' v'_j} + \overline{\rho n' v'_j}\Big\}_{,j} \\
&= \ell\overline{\rho}\frac{\partial \overline{n}}{\partial t} + \ell\overline{n}\frac{\partial \overline{\rho}}{\partial t} + \ell\frac{\partial \overline{\rho}}{\partial t} m + \ell\overline{\rho}\frac{\partial m}{\partial t} \\
&\quad + \ell\Big\{\overline{\rho}_{,j}\overline{n}\,\overline{v}_j + \overline{\rho}\,\overline{n}_{,j}\overline{v}_j + \overline{\rho}\,\overline{n}\,\overline{v}_{j,j} + \overline{\rho}_{,j} m \overline{v}_j + \overline{\rho} m_{,j}\overline{v}_j + \overline{\rho} m \overline{v}_{j,j} \\
&\quad + \overline{n}_{,j}\underbrace{\overline{\rho' v'_j}}_{\overline{\rho}m_j} + \overline{n}\underbrace{(\overline{\rho' v'_j})_{,j}}_{(\overline{\rho}m_j)_{,j}} + (\overline{\rho n' v'_j})_j\Big\} \\
&= \Big\langle \ell\overline{\rho}\Big\{\Big(\underbrace{\frac{\partial \overline{n}}{\partial t} + \frac{\partial m}{\partial t}}_{\partial\mathfrak{n}/\partial t}\Big) + (\underbrace{\overline{n} + m}_{\mathfrak{n}})_{,j}\overline{v}_j\Big\}\Big\rangle \\
&\quad + \Big\langle \ell\frac{\partial \overline{\rho}}{\partial t}(\underbrace{\overline{n} + m}_{\mathfrak{n}}) + \ell\overline{\rho}_{,j}(\underbrace{\overline{n} + m}_{\mathfrak{n}})\overline{v}_j\Big\rangle \\
&\quad + \Big\langle \ell\overline{\rho}(\underbrace{\overline{n} + m}_{\mathfrak{n}})\overline{v}_{j,j} + \ell(\overline{n}\,\overline{\rho}m_j)_{,j}\Big\rangle + \underbrace{\ell\overline{(\rho n' v'_j)}_{,j}}_{-H_{j,j} + (\overline{\rho}\ell m m_j)_{,j}} \quad .
\end{aligned}$$

In this chain of equations the subbraced terms are definitions in (31.34). With these, the $\overline{LHS}_C$ transforms to the expression

$$\begin{aligned}\overline{LHS}_C &= \ell\overline{\rho}\left\{\underline{\frac{\partial\mathfrak{n}}{\partial t}} + \underline{\mathfrak{n}_{,j}V_j} - \mathfrak{n}_{,j}m_j\right\} + \left\{\underline{\ell\frac{\partial\overline{\rho}}{\partial t}\mathfrak{n} + \ell\overline{\rho}_{,j}\mathfrak{n}V_j} - \ell\overline{\rho}_{,j}\mathfrak{n}m_j\right\}\\ &\quad + \underline{\ell\overline{\rho}\mathfrak{n}V_{j,j}} - \ell\overline{\rho}\mathfrak{n}m_{j,j} + \ell(\overline{n}\,\overline{\rho}m_j)_{,j} + \ell(\overline{\rho}mm_j)_j - H_{j,j}\\ &= \underbrace{\ell\left\{\frac{\partial}{\partial t}(\overline{\rho}\mathfrak{n}) + \frac{\partial}{\partial x_j}(\overline{\rho}\mathfrak{n}V_j)_{,j}\right\}}_{\ell\overline{\rho}\mathring{\mathfrak{n}}} - H_{j,j},\end{aligned} \tag{31.153}$$

in which $\overline{v}_i$ was replaced by $V_i - m_i$. The underlined terms together define $\ell\overline{\rho}\,\mathring{\mathfrak{n}}$. The remaining terms together, except $H_{j,j}$, add up to zero.

Equating in the above expression $\overline{LHS}_C = \overline{RHS}_C$ delivers the final result

$$\ell\overline{\rho}\,\mathring{\mathfrak{n}} = \frac{\partial}{\partial x_j}(H_j + h_j) + \overline{\rho}\overline{f} + \overline{\rho' f'}, \tag{31.154}$$

stated in the main text as (31.33).

Appendix 31.D Derivation of the Modified Balance of the Mean Turbulent Energy

In this appendix, we shall corroborate Eq. (31.35), which is the balance law, $\overline{D} = 0$, for the modified Favre mean of the internal energy. The Reynolds average of (31.9) is

$$\begin{aligned}&\frac{\partial}{\partial t}(\overline{\rho e}) + \frac{\partial}{\partial x_j}(\overline{\rho e v_j}) - \overline{T_{ij}\frac{\partial v_i}{\partial x_j}} - \overline{h_j\frac{\partial(\ell n)}{\partial x_j}}\\ &+\overline{\rho f \ell n} + \frac{\partial\overline{q}_j}{\partial x_j} - \overline{\rho}\,\overline{r} - \overline{\rho' f'} \equiv 0.\end{aligned} \tag{31.155}$$

The individual terms in this equation can be written in the form[17]

---

[17] In the underbraced terms, definitions stated in (31.27) and (31.36) are used.

- $\displaystyle \frac{\partial}{\partial t}(\overline{\rho e}) = \frac{\partial}{\partial t}(\overline{\rho' e'}) + \frac{\partial}{\partial t}(\underbrace{\bar\rho\,\bar e}_{\bar\rho\mathfrak{e}-\overline{\rho' e'}}) = \frac{\partial}{\partial t}(\bar\rho\mathfrak{e}),$
- $$\begin{aligned}\frac{\partial}{\partial x_j}(\overline{\rho e v_j}) &= \frac{\partial}{\partial x_j}\Big(\bar\rho\,\bar e\,\bar v_j + \bar e\underbrace{\overline{\rho' v'_j}}_{\bar\rho m_j} + \overline{\rho' e'}\bar v_j + \underbrace{\overline{\rho e' v'_j}}_{Q_j+\overline{\rho' e'}m_j}\Big)\\ &= \frac{\partial}{\partial x_j}\Big[\Big(\bar\rho\,\bar e\underbrace{(\bar v_j + m_j)}_{V_j}\Big) + \overline{\rho' e'}\underbrace{(\bar v_j + m_j)}_{V_j} + Q_j\Big]_{,j}\\ &= \frac{\partial}{\partial x_j}\Big[\bar\rho\,\bar e V_j + \overline{\rho' e'}V_j + Q_j\Big]_{,j},\end{aligned}$$
- $\displaystyle \overline{T_{ij}\frac{\partial v_i}{\partial x_j}} = \overline{T_{ij}}\frac{\partial \bar v_i}{\partial x_j} + \underbrace{\overline{T'_{ij}\frac{\partial v'_i}{\partial x_j}}}_{\rho\epsilon} = \rho\epsilon + \overline{T}_{ij}\frac{\partial \bar v_i}{\partial x_j},$
- $\displaystyle \overline{h_j\frac{\partial \ell n}{\partial x_j}} = \bar h_j\overline{\frac{\partial \ell n}{\partial x_j}} + \underbrace{\overline{h'_j\frac{\partial \ell n'}{\partial x_j}}}_{\bar\rho H+\ell\overline{\rho f' n'}-\ell m\overline{\rho' f'}},$
- $\displaystyle \ell\overline{\rho f n} = \ell\Big\{\bar\rho\bar f\bar n + \underbrace{\overline{\rho' n'}}_{\bar\rho m}\bar f + \bar n\overline{\rho' f'} + \overline{\rho f' n'}\Big\},$
- $\displaystyle \frac{\partial \bar q_j}{\partial x_j} - \overline{\rho r} = \frac{\partial \bar q_j}{\partial x_j} - \bar\rho\,\bar r - \overline{\rho' r'}.$

Substituting these expressions into (31.155) yields

$$\begin{aligned}&\frac{\partial}{\partial t}(\bar\rho\mathfrak{e}) + \frac{\partial}{\partial x_j}(\bar\rho\,\bar e V_j) + \frac{\partial}{\partial x_j}(\overline{\rho e}V_j) + \frac{\partial}{\partial x_j}\underbrace{\Big((\overline{\rho' e'})V_j\Big)}_{(\bar\rho\mathfrak{e}-\bar\rho\,\bar e)V_j} + \frac{\partial Q_j}{\partial x_j}\\ &\quad -\bar\rho\epsilon - \overline{T_{ij}}\frac{\partial \bar v_i}{\partial x_j} - \bar h_j\overline{\frac{\partial \ell \bar n}{\partial x_j}} - \bar\rho H - \ell\overline{\rho f' n'}\\ &+ \ell m\overline{\rho' f'} + \ell\bar\rho\bar f\bar n + \ell\bar f\bar\rho m + \ell\bar n\overline{f'\rho'} + \ell\overline{\rho f' n'}\\ =\ &\bar\rho\left(\frac{\partial\mathfrak{e}}{\partial t} + \frac{\partial(\bar e V_j)}{\partial x_j}\right) + \bar{\mathfrak{e}}\frac{\partial\bar\rho}{\partial t} + \bar e V_j\frac{\partial\bar\rho}{\partial x_j} + \frac{\partial}{\partial x_j}\Big(\bar\rho\,\bar e V_j + (\overline{\rho' e'})V_j\Big)\\ &+\frac{\partial}{\partial x_j}\left[(\bar\rho\mathfrak{e} - \bar\rho\,\bar e)\,V_j\right] - \bar\rho\epsilon + \frac{\partial Q_j}{\partial x_j} - \overline{T}_{ij}\frac{\partial \bar v_j}{\partial x_j} - \ell\bar h_j\frac{\partial \bar n}{\partial x_j} - \bar\rho H\\ &-\ell\overline{\rho f' n'} + \underbrace{\ell\overline{\rho' f'}(\bar n + m)}_{\ell\mathfrak{n}\overline{f'\rho'}} + \underbrace{\ell\bar\rho\bar f\bar n + \ell\bar\rho\bar f m}_{\ell\bar\rho\bar f\mathfrak{n}} + \ell\overline{\rho f' n'} + \frac{\partial\overline{q_i}}{\partial x_j} - \bar\rho\,\bar r - \overline{\rho' r'}\\ =\ &\underbrace{\bar\rho\left(\frac{\partial\mathfrak{e}}{\partial t} + \frac{\partial\mathfrak{e}}{\partial x_j}V_j\right)}_{\bar\rho\overset{\circ}{\mathfrak{e}}} + \underbrace{\left(\bar\rho\mathfrak{e}V_{j,j} + \mathfrak{e}\frac{\partial\bar\rho}{\partial x_j}V_j + \mathfrak{e}\frac{\partial\bar\rho}{\partial t}\right)}_{\substack{\mathfrak{e}\left(\overset{\circ}{\bar\rho} + \bar\rho V_{j,j}\right) = 0\\ \text{mass balance}}} + \frac{\partial}{\partial x_j}\left(Q_j + q_j\right)\\ &+\bar\rho\epsilon - \overline{T}_{ij}\frac{\partial \bar v_j}{\partial x_j} - \ell\bar h_j\frac{\partial \bar n}{\partial x_j} - \bar\rho H + \ell\mathfrak{n}(\bar\rho\bar f + \overline{\rho' f'}) - \bar\rho\,\bar r - \overline{\rho' r'} = 0,\end{aligned}$$

implying

$$\bar\rho\,\overset{\circ}{\mathfrak{e}} = \overline{T}_{ij}\frac{\partial \bar v_i}{\partial x_j} + \ell\bar h_j\frac{\partial \bar n}{\partial x_j} - \frac{\partial}{\partial x_j}(Q_j + q_j) + \bar\rho\epsilon + \bar\rho H$$

$$-\ell\mathfrak{n}(\overline{\rho}\,\overline{f}+\overline{\rho' f'})-\overline{\rho}\,\overline{r}-\overline{\rho' r'}=0.$$

This agrees with Eq. (31.35) in the main text.

Appendix 31.E Favre's Form of the Entropy Balance

We consider the entropy balance in the form

$$\frac{\partial}{\partial t}(\rho\eta)+\frac{\partial}{\partial x_j}(\rho\eta v_j)+\phi_{j,j}-\sigma=\pi. \tag{31.156}$$

Averaging this balance law yields

$$\frac{\partial}{\partial t}(\overline{\rho}\,\overline{\eta})+\frac{\partial}{\partial x_j}(\overline{\rho\eta v_j})+\frac{\partial\overline{\phi}}{\partial x_j}-\overline{\sigma}=\overline{\pi}$$

and, using the product rules of Reynolds averaging

$$\begin{aligned}&\frac{\partial}{\partial t}(\overline{\rho}\,\overline{\eta})+\frac{\partial}{\partial t}(\overline{\rho'\eta'})\\&+\frac{\partial}{\partial x_j}\left\{\overline{\rho}\,\overline{\eta}\,\overline{v}_j+\overline{\eta}\,\overline{\rho' v_j'}+\overline{\rho'\eta'}\,\overline{v}_j+\overline{\rho\eta' v_j'}\right\}+\frac{\partial\phi_j}{\partial x_j}-\overline{\sigma}=\overline{\pi}.\end{aligned} \tag{31.157}$$

We introduce the definitions

$$\overline{\rho}S\equiv\overline{\rho'\eta'},\quad \phi_j^T\equiv\overline{\rho\eta' v_j'}-\overline{\rho}Sm_j,\quad \phi_j^{\text{turb}}=\overline{\phi}_j+\phi_j^T \tag{31.158}$$

and

$$U_j\equiv\overline{v}_j,\qquad V_j\equiv U_j+m_j. \tag{31.159}$$

Employing these expressions in (31.157) leads to the long balance expression

$$\begin{aligned}&{\color{green}\underline{\overline{\rho}\frac{\partial\overline{\eta}}{\partial t}}}+{\color{red}\underline{\overline{\eta}\frac{\partial\overline{\rho}}{\partial t}}}+{\color{blue}\underline{\overline{\rho}\frac{\partial S}{\partial t}}}+{\color{red}\underline{\underline{S\frac{\partial\overline{\rho}}{\partial t}}}}+{\color{red}\underline{\frac{\partial\overline{\rho}}{\partial x_j}\overline{\eta}U_j}}+{\color{green}\frac{\partial\overline{\eta}}{\partial x_j}\overline{\rho}U_j}+{\color{red}\overline{\rho}\,\overline{\eta}\frac{\partial U_j}{\partial x_j}}+{\color{green}\overline{\rho}m_j\frac{\partial\overline{\eta}}{\partial x_j}}\\&+{\color{red}\underline{\frac{\partial\overline{\rho}}{\partial x_j}m_j\overline{\eta}}}+{\color{red}\underline{\overline{\rho}\,\overline{\eta}\frac{\partial m_i}{\partial x_j}}}+{\color{red}\underline{\underline{\overline{\rho}S\frac{\partial U_j}{\partial x_j}}}}+{\color{blue}\underline{\overline{\rho}U_j\frac{\partial S}{\partial x_j}}}+{\color{red}\underline{\underline{\frac{\partial\overline{\rho}}{\partial x_j}U_jS}}}+\frac{\partial\phi_j}{\partial x_j}+\frac{\partial\overline{\rho}}{\partial x_j}m_jS\\&+{\color{blue}\underline{\overline{\rho}m_j\frac{\partial S}{\partial x_j}}}+{\color{red}\underline{\underline{\overline{\rho}S\frac{\partial m_j}{\partial x_j}}}}+\frac{\partial\overline{\phi}_j}{\partial x_j}-\overline{\sigma}=\overline{\pi},\end{aligned}$$

which, by reshuffling terms, as indicated by the colored underlines, can be brought to the form

$$\underbrace{\overline{\rho}\left\{\frac{\partial\overline{\eta}}{\partial t}+\frac{\partial\overline{\eta}}{\partial x_j}(\underbrace{U_j+m_j}_{V_j})\right\}}_{\overline{\rho}\overset{\circ}{\overline{\eta}}}+\underbrace{\overline{\rho}\left\{\frac{\partial S}{\partial t}+\frac{\partial S}{\partial x_j}(\underbrace{U_j+m_j}_{V_j})\right\}}_{\overline{\rho}\overset{\circ}{S}}$$

$$+\,(\overline{\eta}+S)\underbrace{\left\{\underbrace{\frac{\partial\overline{\rho}}{\partial t}+\frac{\partial\overline{\rho}}{\partial x_j}\Big(\underbrace{(U_j+m_j)}_{V_j}\Big)}_{\overset{\circ}{\overline{\rho}}}+\overline{\rho}\frac{\partial}{\partial x_j}\Big(\underbrace{U_j+m_j}_{V_j}\Big)\right\}}_{=0\ \text{(mass balance (11.28))}}$$

$$+\,\frac{\partial}{\partial x_j}\Big(\underbrace{\overline{\phi}_j+\phi_j^T}_{\phi_j^{\text{turb}}}\Big)-\overline{\sigma}=\overline{\pi},$$

or finally,

$$\overline{\rho}\left(\overset{\circ}{\overline{\eta}}+\overset{\circ}{S}\right)+\frac{\partial\phi_j^{\text{turb}}}{\partial x_j}-\overline{\sigma}=\overline{\pi}. \tag{31.160}$$

The superimposed ring denotes the FAVRE time derivative, (31.29).

Appendix 31.F Isotropic Representation of the Vector *k* in (31.103)

In this appendix, we prove that (31.103) in the main text is an isotropic vector function for $\boldsymbol{k}$, if $\boldsymbol{C}_A$ is skew-symmetric and $\alpha_{AB}=0$.

Skew-Symmetry of $\boldsymbol{C}_A$

Consider $k_i = C_{ij}v_j$, which is one single term of the middle term on the right-hand side of (31.103). Then, we have

$$\frac{\partial k_i}{\partial v_j}-\frac{\partial k_j}{\partial v_j}=0,$$

which implies

$$\frac{\partial C_{ik}v_k}{\partial v_j}+\frac{\partial C_{jk}v_k}{\partial v_i}=C_{ik}\delta_{kj}+C_{jk}\delta_{ki},=C_{ij}+C_{ji}\equiv 0 \tag{31.161}$$

expressing skew-symmetry of $\boldsymbol{C}$ and so generally of C_{ij}^A (A = 1,…,6), qed.

Demonstration that $\alpha_{AB}=0$

We sketch the proof for an isotropic vector-valued function $\boldsymbol{k}$ of three vector variables $\boldsymbol{v}^1 \equiv \boldsymbol{u}$, $\boldsymbol{v}^2 \equiv \boldsymbol{v}$, $\operatorname{grad} \overline{\nu} \equiv \boldsymbol{w}$. Similar arguments are used when many vector variables $\boldsymbol{v}^A$ are involved. Since the scalar variables are not relevant for the representation of the isotropic functions, they are left aside. Hence let $\boldsymbol{k}$ be the function defined as in (31.103) by

$$\boldsymbol{k}(\boldsymbol{u}, \boldsymbol{v}, \boldsymbol{w}) = \alpha(\boldsymbol{w})\, \boldsymbol{u} \times \boldsymbol{v} + \boldsymbol{A}(\boldsymbol{w})\boldsymbol{u} + \boldsymbol{B}(\boldsymbol{w})\boldsymbol{v} + \boldsymbol{c}(\boldsymbol{w}),$$

where $\alpha(\boldsymbol{w})$ is a scalar coefficient, $\boldsymbol{A}(\boldsymbol{w})$ and $\boldsymbol{B}(\boldsymbol{w})$ are skew-symmetric tensors and $\boldsymbol{c}(\boldsymbol{w})$ is a vector. The function $\boldsymbol{k}$ is isotropic if it satisfies the condition

$$\boldsymbol{k}(\boldsymbol{Q}\boldsymbol{u}, \boldsymbol{Q}\boldsymbol{v}, \boldsymbol{Q}\boldsymbol{w}) = \boldsymbol{Q}\, \boldsymbol{k}(\boldsymbol{u}, \boldsymbol{v}, \boldsymbol{w}) \tag{31.162}$$

for all orthogonal tensors $\boldsymbol{Q}$. If we take $\boldsymbol{u} = \boldsymbol{v} = \boldsymbol{0}$ in (31.162) we obtain that $\boldsymbol{c}$ is an isotropic vector-valued function of $\boldsymbol{w}$ and therefore $\boldsymbol{c}(\boldsymbol{w}) = c(\boldsymbol{w} \cdot \boldsymbol{w})\boldsymbol{w}$ holds. Now using this result in (31.162) and taking $\boldsymbol{v} = \boldsymbol{0}$ we obtain that $\boldsymbol{A}$ is an isotropic skew-symmetric tensor-valued function of a vector variable. Therefore $\boldsymbol{A}(\boldsymbol{w})$ turns out to be zero. Analogously, we get $\boldsymbol{B}(\boldsymbol{w}) = \boldsymbol{0}$. Finally, condition (31.162) reduces to $\alpha(\boldsymbol{Q}\boldsymbol{w}) = (\det \boldsymbol{Q})\, \alpha(\boldsymbol{w})$. In particular this implies that α is a hemitropic scalar-valued function of a vector variable. Consequently, we have $\alpha(\boldsymbol{w}) = \hat{\alpha}(\boldsymbol{w} \cdot \boldsymbol{w})$, implying $\alpha(\boldsymbol{w}) = \alpha(-\boldsymbol{w})$. On the other hand, if we choose $\boldsymbol{Q} = -\boldsymbol{1}$ in the reduced condition, we obtain $\alpha(-\boldsymbol{w}) = -\alpha(\boldsymbol{w})$ and hence $\alpha(\boldsymbol{w}) = 0$.

References

1. Ahmadi, G.: Thermodynamics of multi-temperature fluids with applications to turbulence. Appl. Math. Model. **9**, 271–274 (1985)
2. Ahmadi, G.: Thermodynamically consistent $k - Z$ models for compressible turbulent flows. Appl. Math. Model. **12**, 391–398 (1988)
3. Ahmadi, G.: A two-equation turbulence model for compressible flows based on the second law of thermodynamics. J. Non-equilib. Thermodyn. **14**, 45–49 (1989)
4. Ahmadi, G.: A thermodynamically consistent rate-dependent model for turbulence. Part I: Formulation. Int. J. Non-linear Mech. **26**, 595–606 (1991)
5. Ahmadi, G., Abu-Zaid, S.: A thermodynamically consistent stress transport model for rotating turbulent flows. Geophys. Astrophys. Fluid Dyn. **61**, 109–125 (1991)
6. Aranson, I.S., Tsimring, L.S.: Granular Patterns. Oxford University Press, Oxford (2009)
7. Ausloos, M., Lambiotte, R., Trojan, K., Koza, Z., Pekala, M.: Granular matter: a wunderfu lworld of clusters in far-from equilibrium systems. Phys. A **357**, 337–349 (2005)
8. Bagnold, R.A.: The Physics of Blown Sand and Desert Dunes, p. 265. Dover Earth Science, USA (2005). ISBN: 9780486439310
9. Campbell, C.S.: Computer simulation of rapid granular flows. In: Proceedings of the 10th National Congress on Applied Mechanics, Austin, Texas. ASME, New York (1986)
10. Campbell, C.S.: Rapid granular flows. Ann. Rev. Fluid Mech. **22**, 57–92 (1990)
11. Chowdhury, S.J., Ahmadi, G.: A thermodynamically consistent rate-dependent model for turbulence. Part I: Theory II: Computational results. Int. J. Non-lin. Mech. **27**, 705–718 (1992)
12. du Vachat, R.: Realizability inequalities in turbulent flows. Phys. Fluids **20**, 551 (1977)
13. Egolf, P., Hutter, K.: The solution of elementary turbulent shear flows. Forthcoming (2017)

14. Fang, C., Wang, Y., Hutter, K.: A thermo-mechanical continuum theory with internal length for cohesionless granular materials. Part I: a class of constitutive models. Conitn. Mech. Thermodyn. **17**(8), 545–576 (2006)
15. Fang, C., Wang, Y., Hutter, K.: A thermo-mechanical continuum theory with internal length for cohesionless granular materials. Part II: non-equilibrium postulates and numerical simulations of simple shear, plane Poiseuille and gravity driven problems. Conitn. Mech. Thermodyn. **17**(8), 577–613 (2006)
16. Fang, C.: A $k - \varepsilon$ turbulence closure model of an isothermal dry granular dense matter. Contin. Mech. Thermodyn. **28**, 1049–1069 (2016)
17. Farkas, Gy.: A Fourier-féle mechanikai elv alkalmazái. Mathematikai és Természettundományi Értesitö, **12**, 457–472 (1894)
18. Favre, A.: Contribution à l'étude expérimentale des mouvements hydrodynamiques à deux dimensions. Gautier Villars, Paris (1938)
19. Favre, A.: Equations des gaz turbulents compressible. II. Methode de vitesses moyennes; Méthode des vitesses macroscopiques pondérées par la masse volumique. J. Mec. **4**, 391 (1965)
20. Favre, A.: La turbulence en mécanique des fluides: Bases théoriques et expérimentales, méthodes statistiques. Gautier Villars, Paris (1976)
21. Favre, A.: Mesures statistiques de la correlation dans letemps, premires applications à l' études de mouvements turbulentes en suffleries, p. 67. ONERA Publication (1954)
22. Favre, A.: Turbulent Fluxes through the Sea Surface, Wave Dynamics. Plenum Press, New York (1978)
23. Favre, A.: Equations des gaz turbulents compressible I. Formes generales. J. Mec. **4**, 361–390 (1965)
24. Gilbert, G.T.: Positive definite matrices and Sivester's criterion. Am. Math. Mon. **98**(1), 44–46 (1991)
25. Goodman, M.A., Cowin, S.C.: A continuum theory for granular materials. Arch. Rational Mech. Anal. **44**, 249–266 (1972)
26. Hager, W.H.: Hydraulicians in Europe 1800-2000, Volume 2. CRC Press, Boca Raton (2009)
27. Hauser, R.A., Kirchner, N.: A historical note on the entropy principle of Müller and Liu. Conitn. Mech. Thermodyn. **14**(2), 223–226 (2002)
28. Hutter, K., Jöhnk, K.: Continuum Methods of Physical Modeling, p. 635. Springer, Berlin (2004)
29. Hutter, K., Wang, Y.: Fluid and Thermodynamics, vol. 2, p. 633. Springer, Switzerland (2016)
30. Hutter, K., Rajagopal, K.R.: On flows of granular materials. Contin. Mech. Thermodyn. **6**, 81–139 (1994)
31. Hutter, K., Schneider, L.: Important aspects in the formulation of solid-fluid debris-flow models. Part I. Thermodynamic implications. Contin. Mech. Thermodyn. **22**(5), 363–390 (2010)
32. Hutter, K., Schneider, L.: Important aspects in the formulation of solid-fluid debris-flow models. Part II. Constitutive modelling. Contin. Mech. Thermodyn. **22**(5), 391–411 (2010)
33. Jenkins, J.T., Savage, S.B.: The mean stress resulting from interparticle collisions in a rapid granular shear flow. In: Brulin, B. Hsien, R.K.T. (eds.) Proceedings of the Fourth International Conference on Continuum Models of Discrete Systems. North Holland Publishing Company, Amsterdam (1981)
34. Jenkins, J.T., Savage, S.B.: A theory for the rapid flow of identical, smooth, nearly elastic spherical particles. J. Fluid Mech. **130**, 187–202 (1981)
35. Johnson, P.C., Jackson, R.: Frictional-collisional constitutive relations for granular materials, with application to plane shearing. J. Fluid Mech. **1**(76), 67–93 (1987)
36. Kirchner, N.P., Hutter, K.: Modelling particle size segregation in granular mixtures. In: Hutter, K., Kirchner, N. (eds.) Dynamic Response of Granular and Porous Materials under Large and Catastrophic Deformation. Lecture Notes in Applied and Computational Mechanics, vol. 11, pp. 367–391. Spriner, Berlin (2003)
37. Kirchner, N.P., Teufel, T.: Thermodynamically consistent modeling of abrsasive granular materials. II: thermodynamic equilibrium and applications to steady shear flows. Proc. Royal Soc. Lond. A**458** 3053–3077 (2002)

38. Kirchner, N.: Thermodynamically consistent modeling of abrsasive granular materials. I non-equilibrium theory. I: non-equilibrium theory. Proc. Royal Soc. Lond. A**458**, 2153–2176 (2002)
39. Liu, I-Shih: Method of Lagrange multipliers for exploitation of the entropy principle. Arch. Rational Mech. Anal. **46**, 131–148 (1972)
40. Luca, I., Fang, C., Hutter, K.: A thermodynamic model of turbulent motions in a granular material. Contin. Mech. Thermodyn **16**, 363–390 (2004)
41. Lun, C.K.K., Savage, S.B., Jeffrey, D.J., Chepurny, N.: Kinetic theories for granular flow: inelastic particles in Couette flow and slightly inelastic particles in a general flow field. J. Fluid. Mech **140**, 223–256 (1984)
42. Marshall, J.S., Naghdi, P.M.: Thermodynamical theory of turbulence I. Basic developments. Philos. Trans. R. Soc. Lond. **A327**, 415–488 (1989)
43. Minkowski, H.: Geometrie der Zahlen. Teubner, Leipzig (1896)
44. Müller, I.: Thermodynamics. Pitman, New York (1985)
45. Ogawa, S.: Multitemperature theory of granular materials. Proceedings of the Continuum Mechanical and Statistical Approaches in the Mechanics of Granular Materials. In: Cowin, S.C., Satake, M. (eds) Proceedings of the Continuum Mechanical and Statistical Approaches in the Mechanics of Granular Materials, US-Japan Seminar, Sendai, Japan (1978)
46. Pöschel, T., Brillantov, N.V.: Granular Gas Dynamics. Lecture notes in Physics, vol. 624. Springer, New York (2013)
47. Rao, K.K., Nott, P.R.: Introduction to Granular Flows. Cambridge University Press, London (2008)
48. Richman, M.W.: Boundary conditions based upon a modified Maxwellian velocity distribution for flows of identical, smooth, nearly elastic spheres. Acta Mech. **75**, 227–240 (1988)
49. Richman, M.W., Marciniec, R.P.: Gravity-driven granular flows of smooth, inelastic spheres down bumpy inclines. J. Appl. Mech. **57**, 1036–1043 (1990)
50. Rung, T., Thiele, F., Fu, S.: On the realizability of non-linear stress-strain relationships for Reynolds-stress closures. Flow Turbul. Combust. **60**, 333–359 (1999)
51. Sadiki. A.: Turbulentzmodellierung und Thermodynamik. Habilitationsschrift. TU Darmstadt (1998)
52. Sadiki, A., Hutter, K.: On the frame dependence and form invariance of the transport equations for the Reynolds stress tensor and the turbulent heat flux vector: its consequences on closure models in turbulence modelling. Contin. Mech. Thermodyn. **8**, 341–349 (1996)
53. Sadiki, A., Hutter, K.: On thermodynamics of turbulence. J. Non-equilib. Thermodyn. **25**, 130–160 (2000)
54. Savage, S.B.: The mechanics of rapid granular flows. Adv. Appl. Mech. **24**, 289–366 (1984)
55. Savage, S.B., Jeffrey, D.J.: The stress tensor in a granular flow at high shear rates. J. Fluid Mech. **110**, 255–272 (1981)
56. Schneider, L., Hutter, K.: Solid Fluid Mixtures of Frictional Materials in Geophysical and Geotechnical Context Based on a Concise Thermodynamic Analysis. Advances in Geophysical and Environmental Mechanics and Mathematics. Springer, Berlin (2009)
57. Schrijver, A.: Theory of Linear and Integer Programming. Wiley-Interscience Series in Discrete Mathematics. Wiley, Chichester (1996)
58. Schumann, V.: Realizability of Reynolds stress turbulence models. Phys. Fluids **20**, 721–725 (1977)
59. Shih, T.H., Zhu, J., Lumley, J.L.: A realizable Reynolds stress algebraic equation model. NASA TM-105993 (1993)
60. Shih, T.H.: Constitutive relations and realizability of single-point turbulence closures. In: Hallbäck, M., et al. (eds.) Turbulence and Transition Modeling, pp. 155–192. Grademic Holland (1996)

61. Svendsen, B., Hutter, K., Laloui, L.: Constitutive models for granular materials including quasi-static frictional behaviour: toward a thermodynamic formulation of plasticity. Contin. Mech. Thermodyn. **11**, 263–275 (1999)
62. Wang, Y., Hutter, K.: A constitutive theory of fluid saturated granular materials and its application in gravitational flows. Rheol. Acta **38**, 214–223 (1999)
63. Wang, Y., Hutter, K.: Shearing flows in a Goodman–Cowin type granular material theory and numerical results. Part. Sci. Technol. **17**, 97–124 (1999)

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