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Field Theoretic Method in Phase Transformations

Springer

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To my father Rudolf

Contents

Chapter 1
Introduction

1.1 What Is This Book About?

Phase transitions are significant changes in the system's properties and symmetry, which happen as a result of changes of the external conditions (temperature, pressure, chemical potential, etc.). Although various phase transitions are discussed in the book as physical phenomena, the book is more about the method to study the phase transitions than about the phenomena themselves. A lot has been written about behavior of a system close to the critical point; it is characterized by special features such as scale invariance. However, these are rare cases and most of the systems spend most of their time far away from the critical points. Rephrasing Feynman we can say that there is plenty of room away from the critical point. Evolutions of the systems when they are not close to the critical points are characterized by completely different physical features, such as rate of nucleation and growth, microstructure or pattern formation, structure modification and coarsening, etc. Physical descriptions of these features require that special consideration is taken to the free energies of the phases involved in the transformations, which in many cases are known either from thermodynamic calculations or direct experimental measurements. All of that sets the stage for different approach to phase transitions, more phenomenological, which is the main subject of this book.

One of the most convenient ways of addressing the general problem of phase transformations is the *Field-Theoretic Method* (FTM) based on the Landau paradigm, which assumes that the free energy, in addition to temperature, pressure, and composition, is a continuous function of a set of internal (hidden) parameters associated with the symmetry changes, which are usually called long-range order parameters (OP). Different transitions may be laid out into the same framework if proper physical interpretations of OPs are found. Although significant strides in the direction of rigorous derivation of the basic equations of the method from the first principles have already been made (see Appendix A), this task is not finished yet.

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That is why the issue of *thermodynamic consistency* always played and still plays significant role in the development of FTM. This issue can be expressed as follows: whatever the equations of the method are, their implications should not contradict the basic laws of thermodynamics.

1.2 Who Is This Book For?

This book is for researchers who are interested in all aspects of phase transformations, especially for practitioners who are involved in theoretical studies or computer simulations of the phenomena and would like to expand their knowledge in the direction of the field theory of phase transitions. This book can be used as a textbook of a graduate or upper level undergraduate course in physics of phase transitions. The students should be familiar with the basic tenets of Physics: Thermodynamics and Statistical Mechanics, and Mathematics: Calculus and Differential Equations. Although the basic knowledge is assumed, more specific topics, critical for the subject of the book, are presented briefly in the Appendices. There is an advantage of having all the components of the method collected in one place. Please feel free to send your comments to the author via: aumantsev@gmail.com

1.3 Historical Note

Although phase transitions are always associated with some kind of singularity, application of continuum ideas in this scientific area has a very long history. The first attempts in the contemporary history to consider phase changes using continuous methods belong to Gibbs [1] who considered coexistence of phases and, in the first paragraph of his "Theory of Capillarity", delineated the main reason for the continuity between them—the finite size of the "sphere of molecular action." Although most of his treatment of the interface between the phases uses the concept of "the surface of discontinuity," he always thought of it as merely an abstraction. Later, Van der Waals [2], in his study of the equation of state of the liquid–gas transition, introduced the gradient of density contribution into the system's local energy (not entropy). This allowed him to calculate the surface tension of the system and estimate the thickness of the interfacial layer.

Path of science through history is unpredictable. No matter how much we try to control it by moral and financial support, science usually chooses serendipitous routes. The Field Theory of Phase Transformations is a case in point. The fundamental basis of what this book is about was laid out not only in 1 year but also in one city: Moscow, Russia of 1937. That year Landau [3, 4] published three papers on the theory of phase transitions and scattering of X-rays, which introduced the concept of the order parameter, started the new theoretical method, and explained how the theory should account for the system's heterogeneities. That same year

Mandelshtam and Leontovich [5] published a paper on the theory of adsorption of sound in liquids where they developed an approach to an evolving system which was pushed away from equilibrium. As if all that is not enough for a coincidence, all four papers were published in the same volume—seventh, of the same journal—Journal of Experimental and Theoretical Physics, although in different issues. It is worth mentioning here that 1937 was a very difficult year for Russia when the Stalin purges had started; very soon Landau himself fell victim of those. So, 1937 was the theory's most successful year; the crossroads of science and politics are intertwined.

The Landau's papers received significant attention in the "western" scientific community (yet the third one [4] significantly less than the first two [3]), but the Mandelshtam–Leontovich's paper [5] remains virtually unknown to this community. Although the author of this book does not know the exact reason for that, one possible explanation is that the Landau's papers were translated into English (and German) while the Mandelshtam–Leontovich's—not. That is why the author decided to publish a translation of that seminal paper in Appendix K of this book. An interesting discussion of that paper can be found in the section "Second viscosity" of Landau and Lifshitz "Fluid Mechanics" [6], the first edition of which appeared in 1944. Later on, in 1954, Landau and Khalatnikov [7] adopted the Mandelshtam– Leontovich's ideas of how to deal with disequilibrium and implemented them in their important paper.

In 1950, Ginzburg and Landau [8] expanded the early phenomenological ideas of the theory and applied them to superconductivity. However, the significance of that work for the Russian reader was not in the introduction of the gradient energy term into the free energy functional (which seems to be the main novelty of that paper for the "western" readers) but in coupling of the order parameter to the magnetic field and the method of calculating the interfacial energy between the phases. In the late 1950s, Cahn and Hilliard [9, 10] published a series of papers on the application of the continuum method to the phenomenon of spinodal decomposition and after that the whole field of the continuum theory burst in many different directions.

In the past decade, there has been inflation of theoretical and computational research using FTM when the method has become very popular in theoretical and computational studies of very different phase transitions in materials (crystallization of pure substances and alloys, precipitation in the solid state, spinodal decomposition, martensitic transformation, and grain growth), in cosmology (phase transitions in early universe) and high energy physics, in biophysics (chemotaxis, protein folding) and even in the studies of human's societies (revolutions and other social events). FTM is successful because it is

- Accurate enough to correctly predict the transition path in many different situations
- Simple enough to allow theoretical analysis
- Comprehensive enough to be interesting for practical applications
- Computationally friendly enough to be used for numerical simulations

The success of the method is due to its computational flexibility and ability to transcend the constraints of spatial/temporal scales, imposed by strictly microscopic or macroscopic methods, hence becoming a truly multiscale one with significant predictive power. However, this book is not about the numerical methods. A number of good books have been written about the method; some of them are listed below [11–16]. However, in the opinion of the author, they do not give the complete and unified approach to the method, which is the goal of this book.

1.4 Nomenclature

In addition to the standard scientific-literature designation of functional dependence: $y = \text{func}(x)$, the author uses in this book a nontraditional designation:

$$y = \text{const}(x), \tag{1.1}$$

when he means to say that the variable y is independent of the variable x. The author chooses to use the designation (1.1) instead of the traditional $y = \text{const}$ because the latter designation implies that the variable y does not vary at all, while (1.1) means that the variable y does not vary with x, although it may vary with other variables of the problem.

The chapters contain untitled introductions that provide a classical, macroscopic description of the related problem and a brief summary of the main results of the chapter. The referenced equations are numerated in each unit (Chapter or Appendix) separately with the first equation showing with the unit's number separated from the equation's number by a period, e.g., (1.1). When an equation is referenced from within the unit, the unit's number is omitted for brevity, the unit's number is restored when the reference is made form another unit [e.g., Eq. (1.1)]. The book does not have homework problems. But there are worked out examples in each chapter and in a few appendices. Important equations in the examples are referenced with the chapter number preceding letter E [e.g., (3E.7)]. Some details of derivations in the text have been left for self-analysis; they are marked throughout the text as (Why?) or (Verify!). The author suggests that the reader finishes the derivations on his/her own because no knowledge can be acquired without hard work.

Often another term, "the phase field," is used to designate practically the same method as the one considered in the book. This term was born somewhere in the mathematical community. It is time to bring this method back into the realm of physicists. In this book, different terms, which have practically same meaning, are used for the phases before and after the transition: old–new, initial–final, parent (mother)–daughter, matrix–precipitate, or nutrient–incipient (emerging). The choice is merely a literary convenience.

Many Latin and Greek letters have multiple uses in different chapters, which should not cause any confusion. Exception is made for the following list of letters, which retain the same meaning throughout the entire book.

G—Gibbs (or Landau-Gibbs) free energy of the whole system
V—volume of the whole system
g—Gibbs (or Landau-Gibbs) free energy density
x, y, z—Cartesian coordinates
η—order parameter
κ—gradient energy coefficient
σ—interfacial energy
γ—kinetic (relaxation) coefficient

The following abbreviations are used:

APB—anti-phase domain boundary
BC—boundary conditions
CAM—cellular automata method
ELE—Euler-Lagrange equation
FTM—Field-Theoretic Method
GB—grain boundaries
GHE—generalized heat equation
GL—Ginzburg–Landau
OP—order parameter
TDGLE—time-dependent Ginzburg–Landau equation

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Chapter 2
Landau Theory of Phase Transitions

In this chapter, starting with the classical approach, we define a phase as homogeneous stable matter and classify phase transitions according to the Ehrenfest classification. Then we introduce a concept of an order parameter as a hidden variable responsible for symmetry changes during the transition. We consider different thermodynamic functions and choose the Gibbs free energy as a function of temperature, pressure, and order parameter (the Landau potential) to identify the equilibrium states in open systems. Using the concept of the order parameter, the phase transitions are considered as mathematical catastrophes of the Landau potential. The "catastrophic" approach helps us to classify the phase transitions and see how different forms of the Landau potential are applicable to different cases of phase transitions. We also look at the special lines and points of the phase diagram from the point of view of the "catastrophic" changes of the order parameter. We conclude the chapter with the analysis of the external field on the phase transition, using the properties of conjugation between the field and order parameter.

2.1 A Phase and Phase Transition

There are many physical situations which may be called *phase transitions*. They are always associated with significant changes of properties in the physical system. If water is cooled below 0°C at the atmospheric pressure, it solidifies and stops flowing from one vessel to another. If a bar magnet is heated above a certain temperature, called Curie temperature (approximately 770°C for an iron magnet), it abruptly loses its property to attract small pieces of steel. If a piece of steel is quenched rapidly its hardness increases dramatically. Under the microscope one can see that characteristic plates, called martensitic, appear which have not been there before the quench. Although the concept of phase transitions was conceived and developed in the realm of physics and chemistry of materials, it has long since crossed these borders and is now used in many other branches of science (e.g., sociology and cosmology). There is one significant difference between the

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examples of phase transitions above. Water can be supercooled below 0°C and ice can be superheated above 0°C (at least slightly); however, one cannot superheat a magnet above its Curie temperature. This difference brings up a distinction between transitions of different kinds—first order and second order—discussed below. Phase transitions may also have *critical points* where the phase transition pattern changes from what it was away from this point. (Do not confuse with critical points in mathematics which occur when the first derivative of a function vanishes). For instance, in compression experiments, below the critical temperature of water there are two distinct phases, liquid and vapor, while above this temperature water changes its state (density) continuously.

For a substantive discussion of phase transitions, we need a reliable definition of *phase*. So far, we have been using an intuitive one based on the physical properties of the state of a system. However, the context of our discussion merits a rigorous definition; we suggest the following: *a phase is a homogeneous part of a system distinguishable by a set of intrinsic properties, which has attained a state of thermodynamic equilibrium under the specified external conditions.*

A few comments are in order here: (1) Of course, "a part of a system" may be the whole system; however, important is that it is "a homogeneous part." In the literature, one can find definitions of a phase that are based on the ability of phases to coexist (see Sect. 81 of ref. [1] for an example). There are two problems with such a definition: for one, some phases do not allow coexistence (e.g., in a second-order transition, see below); for another, such a definition implies that some kind of inhomogeniety is necessary for a phase to exist, which is not correct. Under certain conditions, a phase may be spatially non-uniform. For example, air in the gravitational field of Earth changes density with altitude or a dielectric material in the electrical field has inhomogeneous distribution of polarization. But these inhomogenieties are imposed on the system from outside and may be easily removed by removing the external fields. The system may have other inhomogenieties which are harder or impossible to remove, such as internal interfaces between the coexisting phases; these inhomogenieties must not be a part of the definition of a *phase*.

(2) "A thermodynamic equilibrium" does not necessarily mean globally stable equilibrium; a phase can be in the state of only local equilibrium—a *metastable phase* (see below). However, an unstable (although equilibrium) state of a system is not a phase.

(3) To be called a phase, we do not require a system (or its part) to be at equilibrium under any "external conditions," only "under the specified" ones. Certain phases may exist under specific conditions (e.g., isothermal) but not exist under others (e.g., adiabatic). For example, a solid phase that is stable in a closed system may fall apart if the system is exposed to the environment.

In thermodynamics, we define special functions of state as *entropy* S and *free energy* (Gibbs-G or Helmholtz-F) which clearly identify equilibrium states and even distinguish between the equilibrium states of different levels of stability. For example, in a system closed for thermal exchange with the environment, the *entropy must attain maximum at a stable equilibrium state*. If the system is open to the thermal exchanges, then the *equilibrium states are identified by the minima of the free energy*. One has to keep in mind that the maxima and minima of the respective thermodynamic functions are taken not with respect to the thermodynamic variables (energy E, enthalpy H, volume V, temperature T, pressure P, etc.) but with respect to the internal—hidden—variables that characterize different states for the same set of the thermodynamic variables.

As a consequence of the second law of thermodynamics, at equilibrium, the *chemical potentials* of the phases are equal. In different physical systems, the role of the chemical potential is played by different physical quantities. In an open, one-component system, which will be of primary interest for us in this book, the chemical potential is the molar Gibbs free energy G. Thus, the condition of phase equilibrium in an open, one-component system is expressed as follows:

$$G_{\text{phase}\,\alpha}(P, T) = G_{\text{phase}\,\beta}(P, T). \tag{2.1}$$

A convenient, geometrical way of describing phase transitions is with the help of a *phase diagram*—a map in the plane of the thermodynamic parameters of regions where each phase of the substance is the most stable; these regions are separated by lines known as *phase boundaries*. Equation (2.1) describes a phase boundary in the (P, T)-plane of the phase diagram; it may be expressed as the equilibrium temperature that varies with pressure:

$$T = T_{\mathrm{E}}(P) \tag{2.2a}$$

or pressure with temperature:

$$P = P_{\mathrm{E}}(T). \tag{2.2b}$$

There are different *classification systems* for phase transitions; the most popular one was introduced by Ehrenfest. It is based on the discontinuity of the appropriate thermodynamic potential—G, F, or S—with respect to the appropriate thermodynamic variable—P, T, V, or E. According to this classification, if at the transition point (phase boundary) the first derivative(s) of the thermodynamic potential with respect to its variable(s) experience discontinuity, such transition is called *first order*. If the first derivative is continuous but the second one experiences discontinuity, the transition is called the *second order*; the latter is closely associated with the critical phenomena. Such classification may not work for all transitions. However, in this book, we are using the Ehrenfest classification because it is the most convenient one. For instance, it may be expanded on the transitions of nth-order as such that the nth derivative is the first one to experience a discontinuity at the transition point.

Introducing a *jump quantity* at the transition boundary:

$$[Q] \equiv Q_{\text{phase}\,\beta}(P, T_{\mathrm{E}}) - Q_{\text{phase}\,\alpha}(P, T_{\mathrm{E}}) \tag{2.3}$$

the Ehrenfest classification may be expressed in a succinct form. For instance, for a transition to be of the first order, the *latent heat*

$$L(P, T_{\mathrm{E}}) \equiv -[H] = T_{\mathrm{E}}\left[\frac{\partial G}{\partial T}\right] = T_{\mathrm{E}}[S] \tag{2.4a}$$

and/or the *transformation volume*

$$[V] = \left[\frac{\partial G}{\partial P}\right] \tag{2.4b}$$

cannot be zero. Differentiating (2.1) along the equilibrium line (2.2a), we find the Clapeyron-Clausius equation:

$$\frac{\mathrm{d}T_{\mathrm{E}}}{\mathrm{d}P} = -T_{\mathrm{E}}\frac{[V]}{L}. \tag{2.5}$$

The jump quantity may be taken at any point of the (P, T)-plane; then, the relation (2.4a) can be expanded beyond the equilibrium line as follows:

$$L(P,\, T) = T\frac{\partial}{\partial T}[G] - [G]. \tag{2.4c}$$

As a consequence of the second law of thermodynamics, condition of stability of matter (phase) may be expressed as positivity of the *specific heat* C_{P}:

$$C_{\mathrm{P}} \equiv \left(\frac{\partial H}{\partial T}\right)_P = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_P > 0, \tag{2.6a}$$

and *isothermal* negativity of the *isothermal compression* β_{T}:

$$\beta_T \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T > 0. \tag{2.6b}$$

Then, for a transition to be of the second order, the latent heat and transformation volume must vanish but the jumps of the specific heat

$$[C_{\mathrm{P}}] = \frac{\partial}{\partial T}L = T\frac{\partial^2}{\partial T^2}[G] \tag{2.7a}$$

and/or isothermal compression

$$[\beta_T] = -\frac{1}{V_{\text{phase}\,\alpha}}\left(\frac{\partial}{\partial P}[V] + \beta_{T,\text{phase}\,\beta}[V]\right) \tag{2.7b}$$

cannot be zero at the same time.

The condition of equilibrium (2.1) is not identical with the condition of coexistence. For instance, two phases of a substance which can undergo a first-order transition may coexist under the conditions of a closed system; however, two phases of a substance that undergoes a second-order transition cannot coexist at equilibrium under any conditions.

The third law (Nernst heat theorem) basically says: at $T = 0$ K, the entropy of the most stable phase is zero. This law is more important for the low-temperature phase transitions than for those where the equilibrium temperature T_E is far away from 0 K.

Clearly, the concept of a phase transition is associated with some kind of discontinuous, nonanalytic behavior of the thermodynamic functions that describe the system. A statistical mechanical approach to phase transitions is to write down the partition function Z_N of a system of N particles interacting with each other according to a certain interparticle potential energy $u(\mathbf{r}_i, \mathbf{r}_j)$, where $\mathbf{r}_i$ is the position in space of the ith particle. Thermodynamic functions of the system can be easily expressed through the partition function. The partition function of a system that can undergo a phase transition must be such a function of its variables—volume V and temperature T—that the regions of analytic behavior are bounded by curves on which the function is not analytic. The problem of the statistical mechanics description of phase transitions is that the partition function of a finite number N of particles is a well-behaved, analytic function of its variables, hence, does not describe a phase transition. The resolution of the analyticity paradox was found in the *thermodynamic limit*, that is in the limit $(V, N) \to \infty$. The trick is that even though $Z_N(V, T)$ is analytic for every finite N, it is still possible for $z(V,T) = \lim_{N\to\infty} Z_N(V,T)/N$ to be nonanalytic.

2.2 Phase Transition as Symmetry Change: the Order Parameter

Landau [2] suggested a different approach to phase transitions, an approach that uses the concept of "*hidden variables*" in thermodynamics. A hidden variable is an internal variable which affects the properties of the system, hence its thermodynamic functions (e.g., free energy), even when the thermodynamic variables—e.g., P, T, V, E—are set by the conditions outside the system. For instance, it may be the reaction progress variable in a system where a chemical reaction occurs or the composition of a mixture of phases in a system of given pressure, temperature, and number of particles. A hidden variable can measure deviation of the system from the state of equilibrium. Then, according to the laws of thermodynamics, equilibrium state of an open system with given P and T corresponds to the minimum of Gibbs free energy. Hence, it will be found among the critical points of the free energy as a function of the hidden variable:

$$\left(\frac{\partial G}{\partial \eta}\right)_{P,T} = 0. \tag{2.8a}$$

Stability of this equilibrium is determined by the sign of the second derivative of the free energy with respect to the hidden variable:

$$\left(\frac{\partial^2 G}{\partial \eta^2}\right)_{P,T} > 0. \tag{2.8b}$$

Utility of the concept of hidden variable is also found in the fact that the first derivative of the free energy of a nonequilibrium state may be identified as a thermodynamic driving force toward the equilibrium.

In a way, Landau's idea intended to express that a phase transition looks discontinuous only in the space of the thermodynamic variables, but if you introduce another variable, inner or hidden, then the thermodynamic potentials of the system will be continuous (even analytic) functions of the set of thermodynamic and inner variables. In the theory of phase transitions, it is accustomed to call this variable an *order parameter* (OP), η, in recognition of the fact that many phase transitions are associated with some kind of ordering. It is important to understand that the OP is not equivalent to the thermodynamic variables because the latter can be set in the system arbitrarily, while the former, at the thermodynamic equilibrium, becomes a function of the latter and takes on the value, $\bar{\eta}(P, T, V, E)$, which delivers extremum to the respective potential at the given values of the thermodynamic variables—P, T, V, E. The concept of OP is very helpful in defining a phase because the "homogeneity" and "equilibrium" should be understood in the sense of OP. Then, *a phase* is defined as *a locally stable, homogeneous in the OP part of a system.*

Landau realized that many phase transitions are associated with *symmetry* changes in the system. The OP may represent a physical quantity that is, be described by a dimensional variable, or it can be defined as a measure of the symmetry difference between the phases before and after the transition. As a quantity, η, can be defined such that it is zero in the high-symmetry phase and non-zero (positive or negative) in the low-symmetry phase. The OP should describe the phase transition and its changes should reflect the symmetry changes essential for the transition. η can be a scalar, a vector, or a tensor; tensorial properties of the OP should reflect the tensorial properties of the microscopic quantity that characterizes the transition. The OP can be a complex or a multicomponent quantity, depending on the physical nature of the transition. Identification of the physical nature of the OP is the first step in the description of a phase transition. The OP is obvious for some transitions and not so obvious for others. For instance, for a martensitic transition, which has "mechanical" origin, the OP η is a crystalline lattice-parameter change; the relation $G(\eta) = G_0 + \frac{1}{2}G''(\bar{\eta})\eta^2 + \cdots$ may be interpreted as the Hooke's law and $G''(\bar{\eta})$ as the bulk modulus. For the ferromagnet/paramagnet transition, the OP represents spontaneous magnetic moment of the sample. The OP of a crystal/melt transition is not so obvious: it is the amplitude of the lattice periodic component of the density function. For a liquid–gas transition, the difference in densities of the phases plays the role of the hidden variable; however, it is not an order parameter because the symmetry of the phase does not change after the transition. Another reason not to consider density as an order parameter is that dynamically density obeys equations which differ from the dynamical equations that we will derive for the OP in Chaps. 4 and 5.

For mathematical purposes, the OP may be *scaled* and, although initially it had simple physical interpretation, after scaling the OP may lose it. Nevertheless, in many cases, the mathematical transparency outweighs the physical simplicity.

The Landau approach allows us to bridge the gap between the atomistic theories and macroscopic observations. The OP of a specific system can be derived as volume average of a microscopic quantity, which characterizes the transition—the *coarse-grained quantity* (see Appendix A). Then, thermodynamic properties of the system will be described by the coarse-grained free energy which is a function of the OP and whose minima are associated with the equilibrium states of the system, see (2.8).

Which thermodynamic potential is the most appropriate for the theory that describes the phase transition? One can choose any appropriate thermodynamic potential: the Gibbs free energy G as a function of (P, T, η), the Helmholtz free energy F as a function of (V, T, η), or the entropy of the system S as a function of its internal energy E and (V, η). For the *thermodynamic consistency* of the description of the system, the potential must obey the laws of thermodynamics. In their most natural forms, the first and second laws are expressed through the internal energy E and entropy S of the system, which may seem to indicate that these potentials should be chosen for the phase transition description. In fact, this is not the case because first, the thermodynamics provides an easy recipe for how to convert one thermodynamic potential into another—the Legendre transformation (see Appendix F). Second, the issue of intuitive clarity of the potential is paramount for the Landau theory because it is a phenomenological theory. From the standpoint of the second argument, the Gibbs free energy, $G(P, T, \eta)$, has a significant advantage in that it naturally represents an open system as opposed to $S(V, E, \eta)$—representing a closed one.

Analyticity of the thermodynamic potential means that, in the space of the thermodynamic variables plus OP, in the vicinity of the transition point the potential can be represented by a Taylor polynomial. According to Taylor's theorem, if the first $n + 1$ derivatives of the function $G(\eta)$ exist at the point $\eta = \bar{\eta}$ then

$$\begin{aligned} G(\eta) = {} & G(\bar{\eta}) + G'(\bar{\eta})(\eta - \bar{\eta}) + \frac{1}{2!}G''(\bar{\eta})(\eta - \bar{\eta})^2 \\ & + \frac{1}{3!}G'''(\bar{\eta})(\eta - \bar{\eta})^3 + \cdots + \frac{1}{n!}G^{(n)}(\bar{\eta})(\eta - \bar{\eta})^n + R_n(\eta), \end{aligned} \tag{2.9a}$$

where $R_n(\eta)$ is the nth degree remainder, which is of the order of the $(n + 1)$st derivative of G estimated at some point between $\bar{\eta}$ and η. For small values of $(\eta - \bar{\eta})$, the remainder may be dropped. How small must the difference $(\eta - \bar{\eta})$ be for this approximation to be valid? As known, the accuracy of the approximation depends on the degree of the Taylor polynomial. Although the accuracy of the approximation increases with the degree of the polynomial, its "convenience" decreases. Thus, one has to find a rational compromise to the accuracy/convenience trade-off.

This problem will be resolved only if the terms that make comparable contributions into the free energy approximation remain in the polynomial. For the point $\eta = \bar{\eta}$ to be associated with the symmetry change, it must be a critical point $(G'(\bar{\eta}) = 0)$, see (2.8a). Therefore, the linear term in the expansion (2.9a) must vanish. To take full advantage of Taylor's formula, the polynomial expansion should be truncated at the lowest possible order n_{m}. The number n_{m} determines many properties of the transition, most importantly its kind—first or second.

What is the highest degree of the polynomial n_{m} and which terms in the expansion (2.9a) should be retained?—are the core questions of the phase-transition modeling. Obviously, they cannot be covered here completely; however, some of them may be answered based on the following criterion. Often one sees in the literature a statement that "the expansion (2.9a) is valid only for small values of η" without specification of what this means. This is not accurate and must be corrected. According to Taylor's theorem, the requirement must be that the remainder $R_{n_{\mathrm{m}}}(\eta)$ is smaller than any of the nonvanishing terms of the polynomial in the interval of interest of the OP. The boundaries of the interval (η_l, η_r) are either known from the physical constraints of the problem or should be found from the mathematical analysis of the free energy. Once we have them, the criterion takes the form

$$\max_{\eta_l<\eta<\eta_r} \left| \frac{1}{n_m!} G^{(n_m)}(\bar{\eta})(\eta - \bar{\eta})^{n_m} \right| >> \max_{\eta_l<\eta<\eta_r} |R_{n_{\mathrm{m}}}(\eta)|. \tag{2.9b}$$

2.3 Phase Transition as a Catastrophe: the Free Energy

Many properties of the expansion (2.9a) can be understood on the basis of the mathematical Catastrophe theory [3]. Let us identify the minimal set of properties of a function $G(\eta)$ that can be used as the Landau–Gibbs free energy to describe a phase transition between two phases, α and β. It must have at least two minima of different magnitudes—the local (lmin) and the global (gmin)—separated by a local maximum (lmax), which represents the free-energy barrier state t:

$$G_\beta \equiv g\min_{\eta} G(\eta) \le G_\alpha \equiv l\min_{\eta} G(\eta) \le G_t \equiv l\max_{\eta} G(\eta). \tag{2.10}$$

A polynomial of the degree not less than 4th possesses these properties. Without any loss of generality, we can assume that (2.9a) is an expansion near the high-symmetry phase with $\bar{\eta} = 0$. Then, the OP can be scaled such that $G''''(\bar{\eta}) = 6$ and we obtain the *Landau potential*:

$$G(P,T,\eta) = G_0(P,T) + \frac{1}{2}A(P,T)\eta^2 - \frac{2}{3}B(P,T)\eta^3 + \frac{1}{4}\eta^4, \tag{2.11}$$

where $G_0(P,T)$ is the Gibbs free energy of the high-symmetry phase and the model coefficients $A(P,T)$, $B(P,T)$ are assumed to be smooth functions of P and T. $A(P,T)$

and $B(P, T)$ determine all the properties of the transition and can be used as the system's thermodynamic variables instead of (P, T). Hence, the equilibrium values of the OP can be found among the critical points of the Landau potential (2.12) and (2.8a) is replaced by

$$\left(\frac{\partial G}{\partial \eta}\right)_{A,B} = \bar{\eta}(A - 2B\bar{\eta} + \bar{\eta}^2) = 0. \tag{2.12}$$

Unsurprisingly, $\bar{\eta}_0 = 0$ is a solution of this equation. In addition to this root, the equilibrium set contains two more solutions:

$$\bar{\eta}_{\pm} = B \pm \sqrt{B^2 - A}. \tag{2.13}$$

Equation (2.13) has real solutions—equilibrium states—only if $A \leq B^2$. For

$$A = B^2. \tag{2.14}$$

$\bar{\eta}_+$ and $\bar{\eta}_-$ are identical and for $A > B^2$ the solutions $\bar{\eta}_{\pm}$ are complex. Thus, in the plane (B, A), the curve (2.14) separates the regions with one and three equilibrium states (see Fig. 2.1). The (B, A)-plane is an example of an equilibrium or *phase diagram* in the Landau theory. Notice that the phase diagram is symmetric with respect to the $B(P, T) = 0$ axis; indeed, if $B(P, T)$ changes sign the simple reflection $\eta \rightarrow -\eta$ will restore the Landau potential (2.11).

As known, equilibrium states may be *stable* or *unstable*. The same thermodynamic principle of the minimum Gibbs free energy provides the recipe for the stability of the states in the open system. For the Landau potential (2.11) condition of stability, (2.8b) is replaced by

$$\left(\frac{\partial^2 G}{\partial \eta^2}\right)_{A,B} = A - 4B\bar{\eta} + 3\bar{\eta}^2 > 0. \tag{2.15}$$

Analyzing (2.15), we can see that the stability of the state $\bar{\eta}_0$ depends on the sign of A only: $\bar{\eta}_0$ is stable if $A > 0$ and unstable if $A < 0$. Hence, in the (B, A)-plane, the region of stability of the state $\bar{\eta}_0$ is separated from the region of instability by the line:

$$A = 0. \tag{2.16}$$

For $B > 0$, the state $\bar{\eta}_+$ is always stable when it exists, i.e. $A < B^2$, the state $\bar{\eta}_-$ is unstable for

$$0 < A < B^2 \tag{2.17}$$

and stable for $A < 0$. [Verify (2.17)! Hint: substitute (2.13) into (2.15)]. For $B < 0$, the stability conditions for the states $\bar{\eta}_+$ and $\bar{\eta}_-$ switch places. The regions of existence and stability of the states $\bar{\eta}$ are shown in Fig. 2.1.

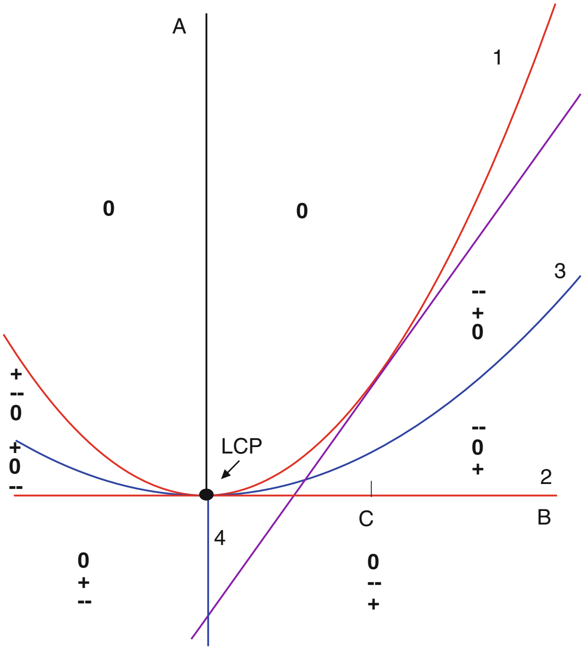


Fig. 2.1 Phase diagram of the system described by the Landau potential (2.11). The triple symbols identify levels of stability of the states in the respective regions of the phase diagram: lower symbol—globally stable; middle symbol—locally (meta-) stable; upper symbol—unstable. Curves: *red*—spinodals: 1—low symmetry, (2.14); 2—high symmetry, (2.16); *blue*—phase boundaries: 3—(2.19); 4—(2.21); *purple*—constraint of the tangential potential, (2.30). LCP—the Landau critical point

The analysis that we have conducted so far identifies only the local stability of the equilibrium states $\bar{\eta}$, i.e., stability with respect to small perturbations. However, the locally stable states may differ by the amount of free energy: the one with the least amount of energy is called *globally stable*. To determine which state, $\bar{\eta}_0$ or $\bar{\eta}_\pm$, is globally stable we need to calculate

$$\begin{aligned} G_\pm \equiv G(A,B,\bar{\eta}_\pm) &= G_0 - \frac{1}{4}\left(A - \frac{2}{3}B\bar{\eta}_\pm\right)(A - 2B\bar{\eta}_\pm) \\ &= G_0 + AB^2 - \frac{1}{4}A^2 - \frac{2}{3}B^4 \mp \frac{2}{3}B(B^2 - A)^{3/2} \end{aligned} \tag{2.18}$$

and compare it with G_0. Depending on the magnitude of B, three different cases are possible.

Case 1: $B \equiv 0$, the Landau condition. This condition may be required by the symmetry constraints of the transition. In this case, there is only one (real) solution $\bar{\eta}_0 = 0$ for $A > 0$ and three real solutions $\bar{\eta}_0 = 0$, $\bar{\eta}_\pm = \pm\sqrt{-A}$ for $A < 0$ [see (2.13)]. From (2.15), we can see that the state $\bar{\eta}_0$ is stable for $A > 0$ and unstable for $A < 0$; the states $\bar{\eta}_\pm$ are stable in the domain of their existence, i.e. $A < 0$. From (2.18), we can see that $G_\pm < G_0$, that is, the global stability of the equilibrium states is identical to the local one.

Case 2: $B > 0$. The bifurcation structure of the equilibrium diagram of the system is different from that of Case 1. The most important change is in the appearance of the domain of coexistence of the equilibrium states, $\overline{\eta}_0$ and $\overline{\eta}_\pm$, (2.17). Outside this domain, Case 2 is similar to Case 1 with only one state, $\overline{\eta}_0$, existing for $A > B^2$ and three states ($\overline{\eta}_\pm$ and $\overline{\eta}_0$) for $A < 0$. Inside the domain of coexistence, (2.17), *exchange of the global stabilities* between the states is taking place. To analyze this "process," we need to equate G_+ to G_0 in (2.18). Representing the solution in the form:

$$A = kB^2. \tag{2.19a}$$

we transform (2.18) into

$$\frac{1}{4}k^2 + \frac{2}{3}(1-k)^{3/2} - k + \frac{2}{3} = 0 \tag{2.19b}$$

which has the only solution (Verify!)

$$k = \frac{2^3}{3^2}. \tag{2.19c}$$

Thus, on the boundary $A = (8/9)B^2$, (2.19a,c), the states $\overline{\eta}_0$ and $\overline{\eta}_+$ exchange their global stabilities so that $\overline{\eta}_0$ is globally stable for $A > (8/9)B^2$ and $\overline{\eta}_+$ —for $A < (8/9)B^2$, although both states are locally stable on both sides of the boundary. Notice that on the boundary (2.19a,c) we have:

$$\overline{\eta}_+ = 2\overline{\eta}_- \tag{2.19d}$$

Let us analyze this case further. Using (2.18), we can also find the condition for the states $\overline{\eta}_+$ and $\overline{\eta}_-$ to exchange the global stabilities:

$$G_- - G_+ = \frac{4}{3}B(B^2 - A)^{3/2} = 0. \tag{2.20}$$

This equation has a true solution:

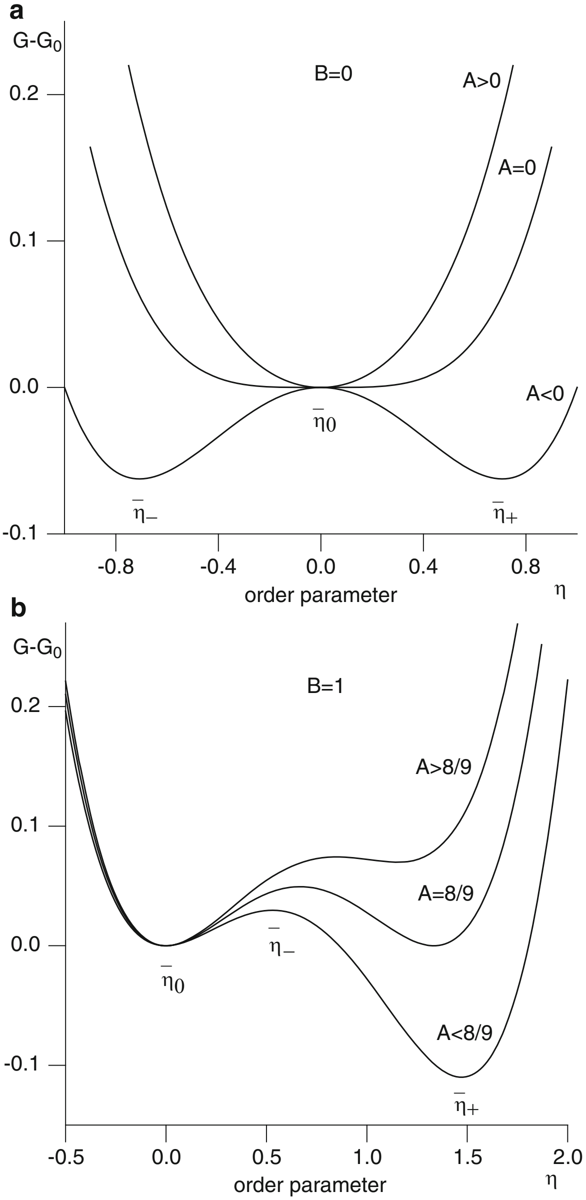
$$B = 0, \quad A \leq 0. \tag{2.21}$$

and a spurious root (2.14) because both states are unstable for $A < B^2$. Hence, (2.21) represents the true boundary of stability. The Landau potential $G(A, B, \eta)$ (2.11), as a function of the OP, is shown in Fig. 2.2 for different values of the parameters A and B.

Case 3: $B < 0$. Case 3 is analogous to Case 2 if the state $\overline{\eta}_-$ replaces the state $\overline{\eta}_+$. The substitution (2.19a) and solution (2.19c) apply to Case 3 also. (Why? Hint: $\sqrt{(x^2)} = |x|$). Equation (2.21) represents the boundary between Cases 2 and 3.

In the process of analyzing stabilities of the equilibrium states, we found two types of bifurcational loci: Type I—the states exchange their stabilities, global versus local; Type II—at least one of the states loses (or gains) the local stability.

Fig. 2.2 Landau potential, (2.11), as a function of the order parameter η for different values of the parameter A. (**a**) $B = 0$; (**b**) $B = 1$



The first type is called the *equilibrium phase boundary*, the second type is known as the *spinodal* (to be exact, the mean-field spinodal). In the case of two parameters (B, A), these loci are curves; in the case of multidimensional parameters, the loci are surfaces, or multidimensional hypersurfaces. The equilibrium phase boundaries are obtained by equating expressions (2.18) of the respective phases; the spinodals are found by equating $\partial^2 G/\partial\eta^2$ in (2.15) to zero and solving for the state of interest. Thus, for the Landau potential (2.11), the curve (2.19) is the $\bar{\eta}_0/\bar{\eta}_\pm$ phase equilibrium boundary and (2.21) is the boundary of $\bar{\eta}_+/\bar{\eta}_-$ phase equilibrium; (2.14) and (2.16) are the spinodals of the low-symmetry $\bar{\eta}_\pm$ and high-symmetry $\bar{\eta}_0$ phases, respectively (see Figs. 2.1 and 2.2). Furthermore, compare $\partial^2 G/\partial\eta^2$ for the stable and metastable phases:

$$\left(\frac{\partial^2 G}{\partial\eta^2}\right)_{A,B} = \begin{cases} A & \text{for } \eta = \bar{\eta}_0 \\ 2(B^2 - A + B\sqrt{B^2 - A}) & \text{for } \eta = \bar{\eta}_+ \end{cases} \tag{2.22}$$

and notice that $\partial^2 G/\partial\eta^2$ of the stable phase is always greater than that of the metastable phase.

When compared with Cases 2–3, Case 1 has additional symmetry, which is revealed in the degeneracy of the equilibrium. For the system described by the Landau potential (2.11), at $A > 0$ the stable state may have only one value $\bar{\eta}_0$, while at $A < 0$ the stable state (phase) is represented by two different values: $\bar{\eta}_+$ and $\bar{\eta}_-$. These conditions $A > 0$ and $A < 0$ are separated by the "Landau critical point" (see Figs. 2.1 and 2.2)

$$B \equiv 0, \quad A = 0. \tag{2.23}$$

Relevance of this point to real physical transitions has not been confirmed yet.

An auxiliary function

$$\Phi(\eta) \equiv G(\eta) - \frac{1}{2}\eta\frac{\partial G}{\partial\eta} \tag{2.24}$$

associated with the Legendre transform of the free energy G (see Appendix F) is useful in the study of the transitions. Notice that Φ and G take on equal values at the equilibrium states.

In many situations, it may be useful to express the conditions of equilibrium and boundaries of stability in the plane of the OP and one of the model parameters, A or B. Equation (2.12) expresses the first one and (2.15) (equated to zero) the second one. These conditions are depicted in Fig. 2.3.

2.4 Ehrenfest Classification

As $B(P, T)$ and $A(P, T)$ are smooth functions of P and T, the order of the transition may be determined by the jumps of the derivatives with respect to A and B, that is, the differences between the derivatives of the Landau–Gibbs free energies, $G_\pm$ and G_0, at the equilibrium lines. There are two ways to calculate these derivatives: one way is—directly by substituting the appropriate expression of $\bar{\eta}(A, B)$ into (2.11)

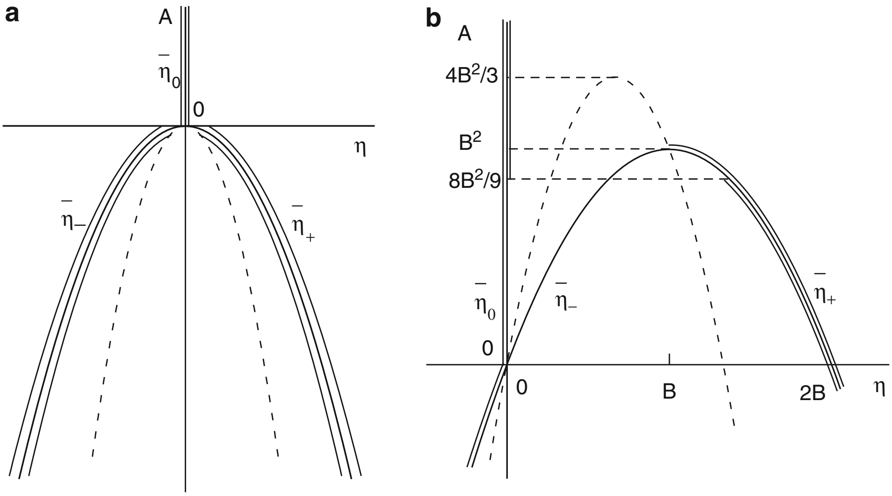


Fig. 2.3 Equilibrium state diagrams of the system described by the Landau potential, (2.11), with $B = 0$ (**a**) and $B = 1$ (**b**). *Solid lines*—the equilibrium states, *double solid lines*—the locally stable states, *triple solid lines*—the globally stable states, *dashed lines*—the local stability boundaries (spinodals)

before taking the derivative; another way—by using the expressions (2.4) and(2.7) considering $\bar{\eta}$ as a function of A and B in it. The second approach is instructive and will be demonstrated here. First, using the rule of chain differentiation we have:

$$\left(\frac{\partial G(A,B,\eta)}{\partial A}\right)_B = \left(\frac{\partial G}{\partial A}\right)_{B,\eta} + \left(\frac{\partial G}{\partial \eta}\right)_{A,B}\left(\frac{\partial \eta}{\partial A}\right)_B. \tag{2.25a}$$

Then, applying condition of equilibrium (2.12), we obtain:

$$\left(\frac{\partial G(\bar{\eta})}{\partial A}\right)_B = \left(\frac{\partial G}{\partial A}\right)_{B,\bar{\eta}}. \tag{2.25b}$$

Second, applying the same chain differentiation rule to (2.12), we have:

$$\left(\frac{\partial^2 G}{\partial A^2}\right)_B = \frac{\partial}{\partial A}\left(\left(\frac{\partial G}{\partial A}\right)_{B,\eta} + \left(\frac{\partial G}{\partial \eta}\right)_{A,B}\left(\frac{\partial \eta}{\partial A}\right)_B\right)_B = \left(\frac{\partial^2 G}{\partial A^2}\right)_{B,\eta}$$
$$+ 2\left(\frac{\partial^2 G}{\partial A \partial \eta}\right)_B\left(\frac{\partial \eta}{\partial A}\right)_B + \left(\frac{\partial G}{\partial \eta}\right)_{A,B}\left(\frac{\partial^2 \eta}{\partial A^2}\right)_B + \left(\frac{\partial^2 G}{\partial \eta^2}\right)_{A,B}\left(\frac{\partial \eta}{\partial A}\right)_B^2. \tag{2.26}$$

Table 2.1 Jumps of the derivatives at the phase transitions for different special values of the parameters A and B of the Landau potential, (2.11). Initial state is $\bar{\eta}_0$, the state after transition is $\bar{\eta}_f = \bar{\eta}_+$ or $\bar{\eta}_f = \bar{\eta}_-$

Order of transition	B	A
	$[\partial G/\partial B]$	$[\partial G/\partial A]$
$\bar{\eta}_f$	$[\partial^2 G/\partial B^2]$	$[\partial^2 G/\partial A^2]$
[G]	$[\partial^2 G/\partial A \partial B]$	$[\partial^3 G/\partial A^3]$
Zeroth order	>0	B^2
	$-2B^3/3$	$B^2/2$
$\bar{\eta}_+ = B$	$-\infty$	$-\infty$
$B^4/(3 \times 2^2)$	$+\infty$	
First order	>0	$2^3B^2/3^2$
	$-2^7B^3/3^4$	$2^3B^2/3^2$
$\bar{\eta}_+ = 2^2B/3$	$-2^7B^2/3^2$	-2
0	$2^4B/3$	
Second order	0	0
	0	0
$\bar{\eta}_\pm = 0$	0	$-1/2$
0	0	
Third order	>0	0
	0	0
$\bar{\eta}_- = 0$	0	0
0	0	$1/(2^2B^2)$

Taking the full differential of the left-hand side of the equilibrium condition (2.12) and equating it to zero, we obtain the following condition that applies to $\eta = \bar{\eta}(A, B)$:

$$\left(\frac{\partial^2 G}{\partial A \partial \eta}\right)_B + \left(\frac{\partial^2 G}{\partial \eta^2}\right)_{A,B} \left(\frac{\partial \bar{\eta}}{\partial A}\right)_B = 0. \tag{2.27a}$$

Applying (2.12) and (2.27a) to (2.26), we obtain:

$$\left(\frac{\partial^2 G(\bar{\eta})}{\partial A^2}\right)_B = \left(\frac{\partial^2 G}{\partial A^2}\right)_{B,\bar{\eta}} - \left(\frac{\partial^2 G}{\partial \eta^2}\right)_{A,B} \left(\frac{\partial \bar{\eta}}{\partial A}\right)_B^2. \tag{2.27b}$$

In (2.27b), the left-hand side is the second-order A-partial along the equilibrium line $\eta = \bar{\eta}(A, B)$, while the first term in the right-hand side is (2.27) is the second-order A-partial along the $\eta = \text{const}(A, B)$ line at the equilibrium point $\eta = \bar{\eta}(A, B)$. Importantly that these partials may not be equal. Finally, applying (2.25b) and (2.27b) to equation (2.11) we obtain expressions for the derivatives at the equilibrium line:

$$\left(\frac{\partial G(\bar{\eta})}{\partial A}\right)_B = \left(\frac{\partial G_0}{\partial A}\right)_B + \frac{1}{2}\bar{\eta}^2, \tag{2.28a}$$

$$\left(\frac{\partial^2 G(\bar{\eta})}{\partial A^2}\right)_B = \left(\frac{\partial^2 G_0}{\partial A^2}\right)_B + \bar{\eta}\left(\frac{\partial \bar{\eta}}{\partial A}\right)_B. \tag{2.28b}$$

Similar expressions can be derived for the B- and mixed AB-partials.

In Table 2.1, the jumps of the derivatives at the transition points from the state $\bar{\eta}_0$ into another state $\bar{\eta}_+$ or $\bar{\eta}_-$ are calculated using (2.28). Classification of the transitions given in Table 2.1 can be compared to the curves and points that express the special conditions on the diagram in Fig. 2.1. Namely, the Landau critical point, (2.23) is the locus of the second-order transition; (2.19) (blue line 3) is the locus of the first-order transitions. Transitions that take place on the line 3 close to the Landau critical point are called *weak first order*. In the spirit of the Erenfest classification, the low-symmetry spinodal (red line 1) may be called the line of the zeroth order and the high-symmetry spinodal (red line 2)—the line of the third-order transition. These transitions are not of the same level of significance as the first two because they are not experienced by the globally stable phases—$\bar{\eta}_0$ on line 1 and $\bar{\eta}_+$ on line 3. They occur "under the radar" of the Gibbs free energy. Yet they may appear in physical experiments or numerical simulations, and that is why they are also analyzed in this book.

2.5 The Tangential Potential

The physical nature of many phase transitions is such that the OP values of the globally stable states on both sides of the phase boundary are nearly constant, that is, do not change much as the parameters A and B vary. Crystal/melt transition is one of the examples. In this case, it is convenient to associate $\bar{\eta}_0$ with the liquid state and $\bar{\eta}_+$ with the solid one and require that the branch $\bar{\eta}_+$ does not change its value in the domain of its stability (see discussion after (2.16) and Fig. 2.3b):

$$\bar{\eta}_+ = \text{const}(A, B) \equiv C \neq 0 \quad \text{for } A < B^2. \tag{2.29}$$

Requirement (2.29) destroys independence of the parameters A and B and yields the constraint:

$$A = 2CB - C^2. \tag{2.30}$$

Then, for the free energy jump between the equilibrium states $\bar{\eta}_+$ and $\bar{\eta}_0$ we obtain:

$$[G] = G_+ - G_0 = \frac{1}{6}C^2\left(A - \frac{1}{2}C^2\right) \quad \text{for } A < C^2. \tag{2.31}$$

Great advantage of the constraint (2.30) is the simplicity of relation $[G](A, C)$, (2.31), as compared to (2.18).

Rescaling the OP

$$\eta = C\tilde{\eta}, \quad C^4 = 2W \tag{2.32}$$

we can write down the Landau–Gibbs free energy, (2.11), in the following form:

$$G(W,[G],\tilde{\eta}) = G_0 + \frac{1}{2}W\omega^2(\tilde{\eta}) + [G]v(\tilde{\eta}) \tag{2.33a}$$

where

$$\omega(x) \equiv x(1-x); \quad v(x) \equiv x^2(3-2x). \tag{2.33b}$$

Notice a useful property of the functions that make up this potential:

$$\frac{\mathrm{d}v}{\mathrm{d}x} = 6\omega(x). \tag{2.33c}$$

As we established, (2.31) is more convenient for the phase transition analysis than (2.18). But convenience comes at a price. First, the constraint (2.30) does not allow for the Landau critical point, (2.23). This means that the potential (2.30) cannot describe the second-order or weak first-order transitions. Second, as we can see on the diagram in Fig. 2.1, the purple straight line, (2.30), never crosses the red line 1, (2.14); the former is *tangent* to the latter at ($B = C$, $A = C^2$). Hence, both branches, $\bar{\eta}_\pm$, exist as stable or unstable states (i.e., are real) for all values of the parameter A. In the domain of the stability of the branch $\bar{\eta}_+$ ($B > 0, A < B^2$), the branch $\bar{\eta}_- = A/C$ is unstable. At the point of tangency, the branches $\bar{\eta}_+$ and $\bar{\eta}_-$ exchange their values so that for ($B > C, A > C^2$), the branch $\bar{\eta}_- = C$ is unstable and the branch $\bar{\eta}_+ = A/C$ is locally stable. The branch $\bar{\eta}_0 = 0$, however, remains globally stable.

For the purposes of phase transition modeling, it is more convenient to reconnect the branches $\bar{\eta}_+$ and $\bar{\eta}_-$ at the point of tangency and relabel as follows:

$$C\bar{\bar{\eta}}_1 \equiv C = \begin{cases} \bar{\eta}_+, & \text{for } A \le C^2 \\ \bar{\eta}_-, & \text{for } A \ge C^2 \end{cases}; \quad C\bar{\bar{\eta}}_t \equiv \frac{A}{C} = \begin{cases} \bar{\eta}_-, & \text{for } A \le C^2 \\ \bar{\eta}_+, & \text{for } A \ge C^2 \end{cases}. \tag{2.34a}$$

Also we redefine the free-energy jump for the reconnected branches:

$$D \equiv [G] = G_1 - G_0, \quad G_1 \equiv G(W, D, \bar{\bar{\eta}}_1). \tag{2.34b}$$

Equation (2.34b) applies in the entire domain of variation of the parameters of the potential (2.33). Equations (2.18), (2.30)–(2.32), and (2.34) establish the relations between the coefficients (W, D) and (A, B).

For the potential (2.33), (2.34), the condition of equilibrium of the phases $\bar{\bar{\eta}}_1$ and $\bar{\eta}_0$ takes the form

$$D_E = 0, \tag{2.35a}$$

It identifies the parameter D as the "driving force" for the transition. In the vicinity of the equilibrium, the two phases (stable and metastable) are separated by the unstable—*transition*—state:

$$\bar{\bar{\eta}}_t = \frac{1}{2} + 3\frac{D}{W}. \tag{2.35b}$$

At the equilibrium

$$G_t^E \equiv G(W, D_E, \bar{\bar{\eta}}_t) = G_0 + \frac{W}{32}. \tag{2.35c}$$

which shows that W is related to the free-energy barrier height between the equilibrium phases. For $\partial^2 G/\partial\eta^2$ of the stable and metastable phases we obtain:

$$\left(\frac{\partial^2 G}{\partial \eta^2}\right)_{W,D} = \begin{cases} W + 6D & \text{for } \eta = \bar{\eta}_0 \\ W - 6D & \text{for } \eta = \bar{\bar{\eta}}_1 \end{cases}. \tag{2.36}$$

Similar to the Landau potential (2.11), $\partial^2 G/\partial\eta^2$ of the stable phase is always greater than that of the metastable one. The mean-field spinodal conditions for the low-symmetry $\bar{\bar{\eta}}_1 = 1$ and high-symmetry $\bar{\eta}_0 = 0$ phases are (Verify!):

$$D_0^S = -\frac{W}{6} \text{ and } D_1^S = +\frac{W}{6}. \tag{2.37}$$

Due to the constraint (2.30), the potential (2.33)–(2.37) can be called *tangential*. In Fig. 2.4 is depicted the potential (2.33) as a function of the rescaled OP and driving force D. In Fig. 2.5a, b are depicted, respectively, projections of the surface from Fig. 2.4 on the (η, G) and (η, D) planes; the latter represents the equilibrium state diagram for this potential. Notice that inside the spinodal region and the region of equilibrium OP values ($-W/6 < D < W/6$, $0 < \eta < 1$) the two terms of the tangential potential (2.33) that depend on OP are of the same order of magnitude. This means that the remainder in the expansion (2.10) may be made arbitrarily small, which validates the truncation at $n_{\mathrm{m}} = 4$.

Sometimes it is advantageous to expand the free energy $G(\eta)$ about the unstable equilibrium state $\bar{\eta}_t$:

$$\begin{aligned} &G(\eta) = G_t + \frac{1}{2}G''_t \Delta\eta^2 + \frac{1}{6}G'''_t \Delta\eta^3 + \frac{1}{24}G''''_t\, \Delta\eta^4; \\ &\Delta\eta \equiv \eta - \bar{\eta}_t; \quad G_t^{(n)} \equiv \partial^n G(A, B, \bar{\eta}_t)/\partial\eta^n; \\ &G'_t = 0; \quad G''_t < 0, \quad G''''_t > 0. \end{aligned} \tag{2.38a}$$

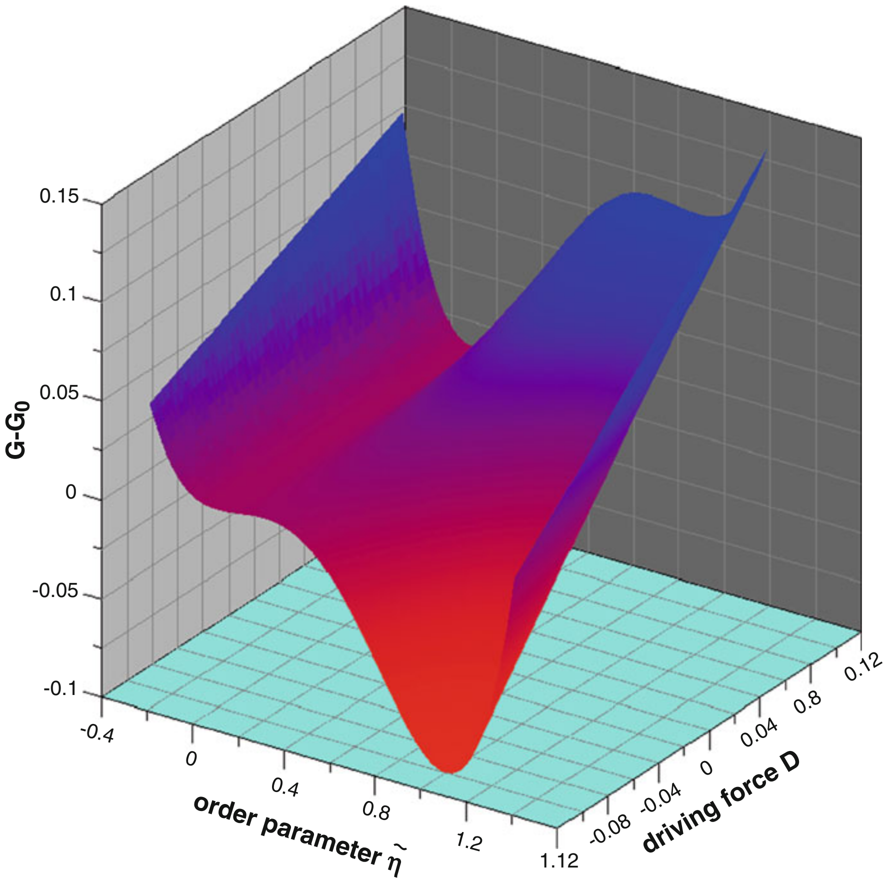


Fig. 2.4 Landau–Gibbs free-energy of the system with tangential potential, (2.33), as a function of the order parameter $\tilde{\eta}$ and driving force D

The equation of equilibrium $\partial G(\eta)/\partial\eta = 0$ has an obvious root $\Delta\eta = 0$ that corresponds to the unstable state. The other two roots, $\Delta\eta_\alpha < 0$ and $\Delta\eta_\beta > 0$:

$$G_t'' + \frac{1}{2}G_t'''\,\Delta\eta_{\alpha(\beta)} + \frac{1}{6}G_t''''\,\Delta\eta^2_{\alpha(\beta)} = 0. \tag{2.38b}$$

correspond to the local and global minima. If $G_t''' = 0$ then:

$$G_\alpha = G_\beta = G_t - \frac{3(G''_t)^2}{2G''''_t}. \tag{2.38c}$$

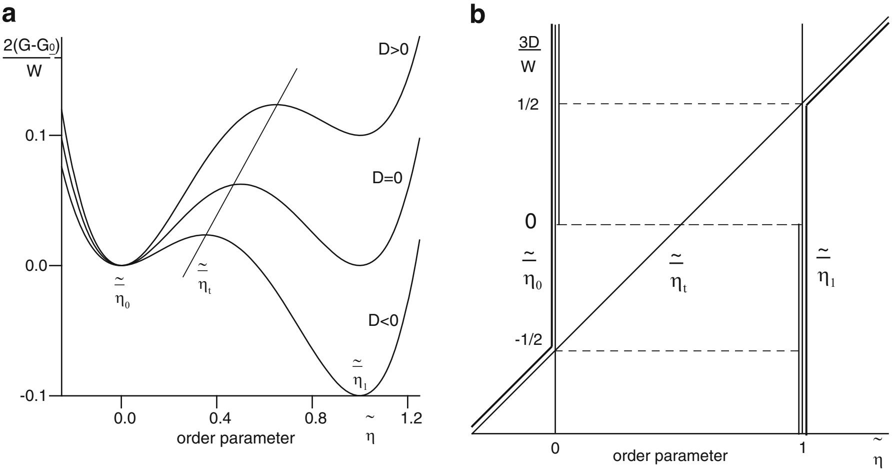


Fig. 2.5 (**a**) Projection of Fig. 2.4 on the plane ($\tilde{\eta}$, G) for different values of D. (**b**) Equilibrium state diagram of the system described by the potential from, (2.33)—projection of the lines of equilibrium from Fig. 2.4 on the plane ($\tilde{\eta}$, $3D/W$). *Solid lines*—the equilibrium states, *double solid lines*—the locally stable states, *triple solid lines*—the globally stable states

Resolving (2.38b) for $\Delta\eta_{\alpha(\beta)}$ and relating them to $\bar{\eta}_+$ and $\bar{\eta}_0$ of the Landau potential (2.11) we can establish a relationship between the coefficients (A, B) and $G_t^{(n)}$:

$$G_t'' = 2\left(B^2 - A - B\sqrt{B^2 - A}\right), \tag{2.39a}$$

$$G_t''' = 2\left(B - 3\sqrt{B^2 - A}\right), \tag{2.39b}$$

$$G_t'''' = 6. \tag{2.39c}$$

If the last relation does not hold, the OP $\Delta\eta$ can always be rescaled for this to be true.

Potentials of the order higher than the forth can also be used for the phase transition modeling. For instance, the fifth-order “10-15-6” potential has the same property as the tangential potential of preserving the values of the stable phases around the equilibrium point. However, this potential cannot be used in cases of large values of OP variations because the state with infinitely large OP value becomes globally stable. The free energy potentials of the sixth-order have more complicated phase diagrams and many new, interesting properties [4]. For instance, such a system may have a *tricritical* point where the lines of the first- and second-order transitions cross. Also notice that the free energy expansion [e.g., (2.10)] does not necessarily need to be polynomial; for instance, it can be an expansion in harmonic functions.

2.6 Phase Diagrams and Measurable Quantities

2.6.1 *First-Order Transitions*

To verify a theory of phase transitions, we need to identify in the theory the quantities which can be compared with the experimentally measurable ones. The real world experiments are not controlled by the model parameters A, B, W, D, but by the temperature and pressure. That is why we have to establish relations between (A, B) or (W, D), and (P, T). Let us concentrate, first, on the description of a first-order transition by the Landau potential (2.11). The phase equilibrium condition in the (P, T)-plane describes a line (2.2), which is isomorphous to the line (2.19a), (2.19c) in the (B, A)-plane. To resolve for $A(P, T)$ and $B(P, T)$, we need the relations for these quantities near the equilibrium line, (2.2) and (2.19). Such relation is provided by (2.18) where $G_{\pm}$ and G_0 are functions of P and T. Unfortunately, parameters A and B are convoluted in this equation, making it difficult to resolve for either one even if you assume the other one a constant. Of course, one can work backwards by assuming the functional dependence $A(P, T)$ and $B(P, T)$. But in this case, it is difficult to obtain a function equal to $G_+ - G_0 = \mathrm{func}(P, T)$ of the real substance in question (see Sect. 10.1).

For the purposes of quantitative analysis of transitions, it is more convenient to use the tangential potential of (2.33), for which the resolution problem for the parameters W and D decouples and the equilibrium line in the (P, T)-plane, (2.2), is isomorphous to the straight line, (2.35a), in the (W, D)-plane. Furthermore, thermodynamic functions, such as free energy, enthalpy, and entropy, are not measurable in phase transition experiments, but their jumps across the phase transition boundary are. The functional dependence $D = D(P, T)$ may be resolved as follows. Substituting (2.34b) into (2.4c) we obtain a differential equation

$$T\frac{\partial D}{\partial T} - D = L(P, T) \tag{2.40a}$$

which, using $D(P, T_{\mathrm{E}}) = 0$ from (2.35a) as the boundary condition, can be resolved as follows:

$$D(P, T) = T\int_{T_E}^{T} \frac{L(P, T')}{(T')^2}\,\mathrm{d}T'. \tag{2.40b}$$

For a system with

$$L = \mathrm{const}(T) \tag{2.40c}$$

we obtain:

$$D(P, T) = L(P)\frac{T - T_E(P)}{T_E(P)}. \tag{2.40d}$$

A comment needs to be made with regard to the specific heat. For a system with variable OP, the definition of the specific heat (2.6a) takes the form:

$$C_{P,\eta} \equiv \left(\frac{\partial H}{\partial T}\right)_{P,\eta} = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_{P,\eta}, \tag{2.41a}$$

Applying it to (2.27) we obtain a formula

$$C_P(T,\,\bar{\eta}) = C_{P,\bar{\eta}}(T) + T\left(\frac{\partial^2 G}{\partial \eta^2}\right)_{P,T}(\bar{\eta})\left(\frac{d\bar{\eta}}{dT}\right)_P^2, \tag{2.41b}$$

where in the left-hand side we have the specific heat of a phase along the line of equilibrium with another phase, while in the right-hand side we have the specific heat of the same phase at the same equilibrium point $\bar{\eta}$, but along the line of constant OP value, $\eta = \mathrm{const}(P, T)$. As (2.41b) indicates, in general, these quantities are not equal (cf. Figs. 2.3b and 2.5b, see also (J.5) and Appendix J). However, for a system described by the tangential potential, these quantities are equal because $(d\bar{\eta}/\partial T)_P = 0$ for the phases '0' and '1'. Also, for the system where (2.40c) is true, the specific heat jump, (2.7a), (at the equilibrium line and beyond) is zero.

On the (P, T)-phase diagram, there are two more special lines, the high-symmetry $T = T_S{}^0(P)$ and low-symmetry $T = T_S{}^1(P)$ spinodals. Using (2.35b, 2.40b) we obtain the equations for them:

$$W(P, T_S^{0/1}) = \mp 6 T_S^{0/1} \int_{T_E}^{T_S^{0/1}} \frac{L(P,\,T)}{T^2}\,\mathrm{d}T. \tag{2.42a}$$

For the system where (2.40c) is true (2.42a) turns into

$$W = \pm 6L\frac{T_E - T_S^{0/1}}{T_E}, \tag{2.42b}$$

where all quantities are functions of pressure. Equations (2.42) may be used to find $W(P,\ T)$. Unfortunately, in most of the cases the mean-field spinodals are not attainable, which renders (2.42) impractical. In this case $W(P,\ T)$ can be found from the measurements of either the interfacial quantities (Chap. 3) or thermal fluctuations (Chap. 7), see also Sect. 10.1. As we can see from (2.40), (2.42), the tangential potential has an advantage over the Landau potential for the purposes of the phase-transition modeling because it provides simple relations between its internal parameters and measurable quantities.

2.6.2 *Second-Order Transitions*

As we saw in the previous section, the constraint (2.30) does not allow for the Landau critical point; hence, the tangential potential is not adequate to represent a second-order transition. Table 2.1 indicates that the latter can be reproduced by the

Landau potential (2.11) with $B \equiv 0$. The Landau critical point may be interpreted as the temperature T_C at which $A(P, T_C)$ changes sign. Taking into account that the critical temperature may depend on pressure, $T_C = \text{func}(P)$, we obtain that $A(P, T) > 0$ for $T > T_C(P)$ and $A(P, T) < 0$ for $T < T_C(P)$. Since A is a continuous function of (P, T) and we are interested in the properties of the system in the vicinity of $T_C(P)$, it is adequate to treat $A(P, T)$ as a linear function of temperature with a zero at $T_C(P)$:

$$A(P,T) = a\tau, \quad \tau = \frac{T - T_C(P)}{T_C(P)}, \ a(P){>}0. \tag{2.43}$$

Then, using (2.13 and 2.18), the OP value and the free energy of the equilibrium states are:

$$\bar{\eta}_{\pm} = \pm\sqrt{-a\tau}, \tag{2.44a}$$

$$G_{\pm}(P,T) = G_0(P,T) - \frac{1}{4}a^2\tau^2. \tag{2.44b}$$

Equations (2.44) show that the states $\bar{\eta}_+$ and $\bar{\eta}_-$ are completely equivalent. Using (2.28), (2.44) for (2.4a), (2.7a), we find that, at the second-order transition point $A = 0$, the latent heat is zero and the jump of the specific heat is

$$[C_P] = -T_C\left(\frac{\partial A}{\partial T}\right)_P^2\left[\frac{\partial^2 G}{\partial A^2}\right] = \frac{a^2}{2T_C}. \tag{2.45}$$

However, another interesting transition may be considered in the system described by the potential (2.11), (2.21), (2.43)—transition between the states with $\bar{\eta}_+$ and $\bar{\eta}_-$. Although, from the thermodynamics point of view, these states are completely equivalent, they will be recognized as different if they occupy contiguous regions. Such regions are called *anti-phase domains* or phase variants. There are many different situations when the OP transition between the variants is possible. One of them— introduction of a conjugate field—is considered in the next section. Another one— existence of a curved boundary between them—is considered in Sects. 3.6 and 5.5.

It is possible to show that the linear-in-temperature assumption of (2.43) is equivalent to the assumptions of the mean-field theory, which states that every atom of the system "operates" in the average local field produced by all the neighbors. This approach excludes effects of the fluctuations and, as a result, makes predictions which are not confirmed precisely by experimental measurements [e.g., the finite jump $[C_P]$ (2.45) or the temperature dependence of the OP at the transition point (2.44a)]. Although it is important to know the shortcomings of the Landau theory, it is imperative to say here that this theory not only presents a correct general picture of the second-order transition, but it also provides a reasonable approach to complicated dynamical problems, which, in many cases, has not been surpassed by other approaches.

2.7 Effect of External Field on Phase Transition

If an external field conjugate to the OP is applied to the system, the phase transition will be affected by the field. The contribution of the external field into the free energy is equal to the work done by the field on the system. Conjugation of the field and the OP means that they have the same symmetry (e.g., scalar, vector, or tensor—the Curie principle). For instance, we may talk about influence of the magnetic field on ferromagnetic transition, electric field on cegnetoelectric transition, or stress on the martensitic transition. For a scalar OP and field, the field contribution is equal to $-H\eta$, where H is the field strength scaled with the volume of the system (the contribution of the field in vacuum ~ $H^2/2$ is not included because it does not have an effect on the OP). A particularly interesting example is the application of the field to a system that, without the field, can undergo a second-order transition. Then, the free energy of the system is expressed as follows:

$$G = G_0 + \frac{1}{2}A\eta^2 + \frac{1}{4}Q\eta^4 - H\eta. \tag{2.46}$$

When compared to (2.11), three changes have been made. First, we took into account that $B = 0$ in the system that can undergo the second-order transition. Second, we added the field contribution. Third, we rescaled the OP back to allow more flexibility, which resulted in appearance of the coefficient Q in front of the fourth-order term. For $H \neq 0$, although the free energy into (2.46) contains three parameters (A, Q, H), the OP can be scaled such that there will be only one free parameter left. To find the right scaling, first, we introduce the scaling factor α:

$$\eta = \alpha\tilde{\eta}. \tag{2.47a}$$

Then we plug this expression into (2.46) and transform as follows:

$$G = G_0 + \alpha H\left(\frac{\alpha A}{2H}\tilde{\eta}^2 + \frac{\alpha^3 Q}{4H}\tilde{\eta}^4 - \tilde{\eta}\right). \tag{2.47b}$$

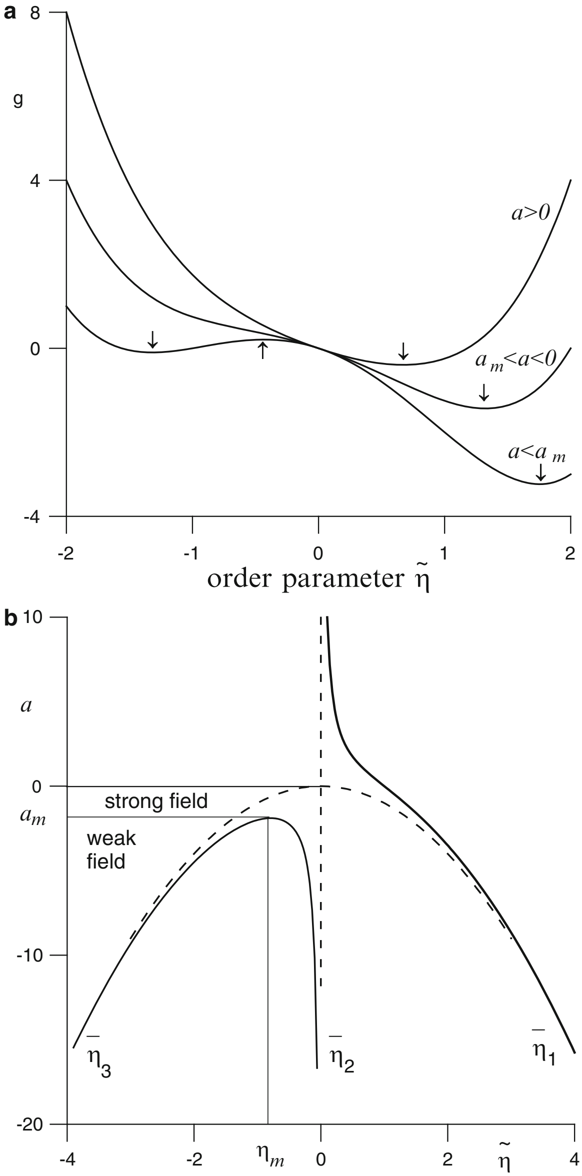
Now we can see that by selecting the proper scaling:

$$\alpha = \left(\frac{H}{Q}\right)^{1/3}; \quad g = \frac{Q^{1/3}}{H^{4/3}}(G - G_0); \quad a = \frac{A}{Q^{1/3}H^{2/3}} \tag{2.48}$$

the scaled free energy of the system will be expressed by the potential with only one dimensionless parameter a, which incorporates effects of pressure, temperature, and external field:

$$g = \frac{1}{2}a\tilde{\eta}^2 + \frac{1}{4}\tilde{\eta}^4 - \tilde{\eta}. \tag{2.49}$$

Fig. 2.6 (**a**) Scaled Landau–Gibbs free energy g of a system capable of undergoing a second-order transition and exposed to the scaled external field a, (2.49). The *arrows* show the equilibrium states. (**b**) Equilibrium state diagram of the system in (**a**). *Dashed lines* are the equilibrium states of the system without the external field



This free energy is shown in Fig. 2.6; it is instructive to compare it with Fig. 2.2, 2.3.

Simplification of the free energy, which will be helpful below in the equilibrium and stability analyses, is not the only benefit of scaling. There is a large “amount” of physics to be learned from scaling even without the use of any more mathematics. As the scaled free energy contains only one parameter, effects of different physical factors, such as temperature, pressure, and external field, may be easily assessed against one another. For instance, influence of temperature upon the transition enters the Landau expression for the free energy (2.46) through the coefficient A, which increases with the temperature, see (2.43). Then, you can see from the expression for a in (2.48) that the external field has an effect on the transition opposite to that of temperature. Hence, the field plays the role of an ordering agent, opposite to temperature—a disordering agent. Moreover, this expression allows us to quantitatively compare the effects of temperature and field: the influence of temperature is stronger than that of the field because $a \sim T$ but $a \sim H^{-2/3}$. Also notice from (2.47)–(2.49) that sign change of the field does not effect the scaled free energy but changes the sign of the OP.

The equilibrium states of the system are described by the solutions of the following equation:

$$\frac{\mathrm{d}g}{\mathrm{d}\tilde{\eta}} = a\tilde{\eta} + \tilde{\eta}^3 - 1 = 0. \tag{2.50}$$

This equation can be analyzed easily if we consider a as a function of $\tilde{\eta}$:

$$a = \frac{1 - \bar{\eta}^3}{\bar{\eta}}. \tag{2.51}$$

The maximum of this function is:

$$a_m \equiv \max_{\bar{\eta}} a(\bar{\eta}) = -\frac{3}{2^{2/3}} \approx -1.89 \tag{2.52}$$

with only one solution of (2.50) existing for $a > a_m$, two solutions for $a = a_m$, and three solutions for $a < a_m$. Resolving (2.48) and (2.52) for H allows us to find the critical value of the field

$$H_m = \frac{(A/a_m)^{3/2}}{Q^{1/2}} \tag{2.53}$$

such that there are three solutions (similar to the case of no field at all) in the region of the weak field ($0 < H < H_m, a < a_m < 0$) and only one solution in the region of the strong field ($H > H_m, 0 > a > a_m$). In the former case, the three solutions are:

$$\begin{gathered} \bar{\eta}_3 < \eta_m < \bar{\eta}_2 < 0 < \bar{\eta}_1 \\ \eta_m = -\frac{1}{2^{1/3}} \approx -0.8. \end{gathered} \tag{2.54}$$

In Fig. 2.6b, the solutions of (2.50) are depicted in the plane $(\tilde{\eta},\ a)$. Notice that, due to the ordering effect of the field, in its presence, the transition takes place at $A = A_m < 0$ ($a = a_m < 0$) that is, at a lower value than that without the field, $A = 0$.

The local stability of the equilibrium state is determined by the sign of the second derivative:

$$\frac{d^2g}{d\eta^2} = a + 3\bar{\eta}^2 = 2\frac{\bar{\eta}^3 - \eta_m^3}{\bar{\eta}}. \tag{2.55}$$

The last expression shows that the equilibrium states $\bar{\eta}_1$ and $\bar{\eta}_3$ are always locally stable, while the state $\bar{\eta}_2$ is always unstable. That is, there is no exchange of stability between the states as is in the case of the first-order transition.

The global stability of the states $\bar{\eta}_1$ and $\bar{\eta}_3$ can be assessed by comparing the free energies of the locally stable states. This can be done by using the following expression for the free energy:

$$g(\bar{\eta}) = \frac{1}{4}\left(a\bar{\eta}^2 - 3\bar{\eta}\right), \tag{2.56}$$

which is obtained by substituting (2.51) into (2.49). In the weak field ($a < a_m$):

$$g(\bar{\eta}_1) - g(\bar{\eta}_3) = \frac{1}{4}(\bar{\eta}_1 - \bar{\eta}_3)[a(\bar{\eta}_1 + \bar{\eta}_3) - 3] < 0. \tag{2.57}$$

The sign of the inequality in (2.57) follows from $\bar{\eta}_1 - \bar{\eta}_3 > 0$, $a < 0$, and $\bar{\eta}_1 + \bar{\eta}_3 = -\bar{\eta}_2 > 0$. The latter follows from the fact that the sum of the roots of a cubic equation is equal to the coefficient in front of the quadratic term, which is equal to zero as we can see from (2.50). Thus, the state $\bar{\eta}_1$ is always globally stable, meaning that the applied field effectively destroys the phase transition in the system. From the physics point of view, it is not difficult to understand why this happens. Indeed, the applied field breaks the symmetry between the two locally stable equilibrium states $\bar{\eta}_1$ and $\bar{\eta}_3$ in favor of $\bar{\eta}_1$, which has orientation in the direction of the field, see (2.47)–(2.50). As a result, this state has less free energy.

Dependence of the OP of the globally stable state on the parameters of the system can be found from (2.51):

$$\bar{\eta}_1 = \begin{cases} \dfrac{1}{a} - \dfrac{1}{a^4}, & \text{for } a \to +\infty \\ 1 - \dfrac{a}{3}, & \text{for } |a| \to 0 \\ \sqrt{|a|} + \dfrac{1}{2|a|}, & \text{for } a \to -\infty. \end{cases} \tag{2.58}$$

The scaled equilibrium values of the OP can help solve many different real-world problems. For instance, we may need to determine the strength of reaction of the system on the applied external field. This property is characterized by the isothermal susceptibility:

$$\chi \equiv \lim_{H\to 0}\left(\frac{\partial\eta}{\partial H}\right)_A. \tag{2.59}$$

Here, the fixed temperature is replaced with fixed A because, as we discussed above, the temperature dependence of the free energy enters through the coefficient A. As you can see from the scaling in (2.48), if $H \to 0 + 0$ for $A = \text{const}$, then $|a| \to \infty$ and $\operatorname{sign}(a) = \operatorname{sign}(A)$. Then from (2.48, 2.58) follows that:

$$\eta_1 \equiv \alpha\bar{\eta}_1 = \begin{cases} \dfrac{H}{A} - \dfrac{QH^3}{A^4}, & \text{for } H \to 0 \text{ and } A > 0 \\ \left(\dfrac{|A|}{Q}\right)^{1/2} + \dfrac{H}{2|A|}, & \text{for } H \to 0 \text{ and } A < 0. \end{cases} \tag{2.60}$$

Then for the susceptibility of the globally stable state we obtain:

$$\chi_1 = \begin{cases} \dfrac{1}{A}, & \text{for } A > 0 \\ \dfrac{1}{2|A|}, & \text{for } A < 0. \end{cases} \tag{2.61}$$

The jump of the susceptibility at $A = 0$ reaffirms our previous conclusion in Sect. 2.4 that, in the absence of the applied field, $A = 0$ is the locus of the second-order phase transition.

As we found in the previous section, there is another type of a transition possible in the system described by the free energy (2.46) namely between the variants $\bar{\eta}_1$ and $\bar{\eta}_3$ at $A < 0$. To analyze the properties of this transition and identify its Ehrenfest class, let us calculate the free energy difference between the variants. Using (2.46), (2.48), (2.57) we obtain:

$$[G] \equiv G(\bar{\eta}_1) - G(\bar{\eta}_3) = \frac{H^{4/3}}{4Q^{1/3}}(\bar{\eta}_1 - \bar{\eta}_3)[a(\bar{\eta}_1 + \bar{\eta}_3) - 3] < 0. \tag{2.62a}$$

For weak fields (large $|a|$): $\bar{\eta}_3 \approx -\bar{\eta}_1$. Then, using the scaling (2.48), we obtain:

$$[G] = -\frac{3}{2}H\eta_1 = -\frac{3}{2}H\sqrt{\frac{-A}{Q}}. \tag{2.62b}$$

Differentiating this expression with respect to the applied field, we find that

$$\left[\frac{\partial G}{\partial H}\right] = -\frac{3}{2}\sqrt{\frac{-A}{Q}} < 0 \tag{2.63}$$

which means that, according to the Ehrenfest classification, this is a first-order transition.

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Chapter 3
Heterogeneous Equilibrium Systems

In this chapter, we are looking at the heterogeneous equilibrium states using the classical Gibbsian approach—Theory of Capillarity and the field-theoretic one, which considers an interface as a transition region between the phases. To do that we generalize the free energy to a functional of the spatial distributions of the order parameters and introduce a gradient energy contribution into the free energy density. We analyze various forms of the gradient energy and find the square-gradient one to be preferable. Equilibrium conditions in the heterogeneous systems yield the Euler–Lagrange equation, solutions of which are called extremals. We study properties of the extremals in the systems of various physical origins and different sizes and find a bifurcation at the critical size. The results are presented in the form of the free energy landscapes. Analysis of the one-dimensional systems is particularly illuminating; it shows that, using qualitative methods of differential equations, many features of the extremals can be revealed without actually calculating them, based only on the general properties of the free energy. We find the field-theoretic expression for the interfacial energy and study its properties using different Landau potentials as examples. We introduce a concept of an instanton as a critical nucleus and study its properties in systems of different dimensionality. Multidimensional states are analyzed using the drumhead approximation and Fourier method. To analyze stability of the heterogeneous states, we introduce the Hamiltonian operator and find its eigenvalues for the extremals. Importance of the Goldstone modes and capillary waves for the stability analysis of the extremals is revealed.

3.1 Theory of Capillarity

So far we have looked at the homogeneous (one-phase) systems, which can be described by uniform spatial distributions of the OP. Let us now look at a *heterogeneous* equilibrium system composed of two or more phases. As we learned in

A. Umantsev, *Field Theoretic Method in Phase Transformations*,
Lecture Notes in Physics 840, DOI 10.1007/978-1-4614-1487-2_3,

Chap. 2, if the conditions in the system change (e.g., temperature drops) then a previously stable homogeneous state may become metastable (or even unstable) and we may want to know how this phase transforms into a stable one. In his seminal treatise, Gibbs [1] identified two different scenarios of how a metastable (or unstable) phase may transform into a stable one. Both scenarios involve reaction of the system on infinitesimal changes inspired by thermal fluctuations. In the first scenario, the critical role is played by the fluctuations—large in degree but small in extent; this scenario is called *nucleation*. In the second scenario, the critical fluctuations are infinitesimal in degree but large in extent; this is called *spinodal decomposition*. Let us take a closer look at the nucleation scenario first and consider the spinodal decomposition later (see Chap. 8).

In Chap. 2, we established that if large pieces of phases are at equilibrium with each other, then the chemical potential takes on the same value in all phases. In the case of an open system with a monatomic (one-component) substance, where the two phases α and β are separated by a plane interface, the role of the chemical potential is played by the Gibbs free energy, see (2.1). For the heterogeneous systems, this criterion must be expressed for the specific (per unit mass) free energy:

$$g_\alpha(P,T) = g_\beta(P,T). \tag{3.1}$$

If we need to calculate the *total* Gibbs free energy G of the entire two-phase system, a naïve resolution of the problem may be presented by the following formula:

$$G = g_\alpha m_\alpha + g_\beta m_\beta = g_{\alpha(\beta)} M, \tag{3.2}$$

where $m_{\alpha(\beta)}$ is mass of the phase $\alpha(\beta)$ and M is the total mass,

$$M = m_\alpha + m_\beta. \tag{3.3}$$

However, there are two problems with this formula. First, we assume that the specific Gibbs free energies of the phases α and β at equilibrium are the same as those of the noninteracting homogeneous phases α and β. When transformations affect finite amounts of matter the thermodynamic calculations become more complicated because we have to take into account variations of pressure in the transformed region. Second, the two contiguous phases are separated by an *interface*, which makes a contribution into the total free energy of the system. In the classical thermodynamics of macroscopic objects, the interface between the phases represents a sheath of finite area S and zero thickness ($M_{\text{int}} = 0$, $V_{\text{int}} = 0$), which "wraps up" a phase and separates it from the contiguous ones [1, 2]. The interface's free energy contribution is equal to the product of its area and the *interfacial energy* σ, which is the *excess* of the Gibbs free energy of the system compared to that of the homogeneous one, per unit area of the interface. To find conditions of equilibrium of the minority phase in the majority phase, let us say β in α, we present the total Gibbs free energy of the system as follows:

$$G(P,T) = F(V,T) + PV + \sigma S, \tag{3.4}$$

where P and T are the external pressure and temperature, respectively and F is the Helmholtz free energy of the system:

$$F(V,T) = m_\alpha f_\alpha(v_\alpha, T) + m_\beta f_\beta(v_\beta, T). \tag{3.5}$$

Here $v_{\alpha(\beta)}$ is the specific volume ($v = V/m$) and $f_{\alpha(\beta)}$ is specific Helmholtz free energy of the α(β) phase, respectively. Because the interface is "massless," the α → β transformation does not increase or decrease the mass of the system; hence, M in (3.3) remains unchanged. However, the total volume of the system

$$V = V_\alpha + V_\beta = m_\alpha v_\alpha + m_\beta v_\beta \tag{3.6}$$

may change because $v_\alpha \neq v_\beta$.

For the system to be at equilibrium, its total Gibbs free energy must reach minimum with respect to all independent internal variables. In addition to the external variables (P, T), the system has internal variables (v_α, v_β, m_α, m_β), see (3.4)–(3.6); however, due to the condition (3.3), not all of them are independent. We can choose (v_α, v_β, m_β) as independent variables. Then, the following partial derivatives of G are equal to zero:

$$\frac{\partial G}{\partial v_\alpha} = m_\alpha\left(\frac{\partial f_\alpha}{\partial v_\alpha} + P\right) = 0, \tag{3.7a}$$

$$\frac{\partial G}{\partial v_\beta} = m_\beta\left(\frac{\partial f_\beta}{\partial v_\beta} + P\right) + \sigma\frac{\partial S}{\partial v_\beta} = 0. \tag{3.7b}$$

$$\frac{\partial G}{\partial m_\beta} = f_\beta(v_\beta, T) + P v_\beta + \sigma\frac{\partial S}{\partial m_\beta} - f_\alpha(v_\alpha, T) - P v_\alpha = 0. \tag{3.7c}$$

Notice that out of three variations of G with respect to the independent variables only the one with respect to m_β is entirely due to the phase transition; the other two are due to the pressure changes in the respective phases.

Minimization of the total free energy also includes minimization of the interfacial energy contribution. In an *isotropic* system, this leads to the minimization of the surface area for constant volume of the nucleus (we may think of the shape of the nucleus as an independent variable). As known, the solution of this problem is a sphere. Hence, the nucleus of the minority phase takes on the shape of a sphere of radius R:

$$S = 4\pi R^2; \quad V_\beta = \frac{4\pi}{3}R^3. \tag{3.8}$$

Using (3.4) and (3.5) and the Legendre transform, (F.16)–(F.18):

$$g(P) = f(v) + Pv; \quad \frac{\mathrm{d}f}{\mathrm{d}v} = -P; \quad \frac{\mathrm{d}g}{\mathrm{d}P} = v. \tag{3.9}$$

we obtain from (3.7a) that the pressure in the majority phase is equal to the external pressure:

$$P = P_\alpha. \tag{3.10}$$

Then, taking into account that $V_\beta = m_\beta v_\beta$, from (3.7b), (3.8), (3.10) we obtain the celebrated Laplace's pressure equation for a spherical bubble:

$$P_\beta = P + \frac{2\sigma}{R}. \tag{3.11}$$

Furthermore, (3.7c) together with the Laplace's equation (3.11), tell us that the specific Gibbs free energies of the majority and minority phases are equal at equilibrium

$$g_\beta(P_\beta, T) = g_\alpha(P_\alpha, T), \tag{3.12}$$

which makes this quantity the chemical potential of the system. However, there is a difference between (3.12) and (3.1): in (3.12), the pressure in the two phases is not the same. Differentiating g_β with respect to the pressure and taking into account (3.9)–(3.11), (3.12) yields an equation:

$$\frac{2\sigma}{R} v_\beta = g_\alpha(P, T) - g_\beta(P, T). \tag{3.13}$$

Equation (3.13) allows us to find the radius of the *critical nucleus*, that is, the nucleus of the β phase which is at equilibrium with the "sea" of the α phase:

$$R_* = \frac{2\sigma}{\Delta\tilde{g}(P, T)}, \tag{3.14a}$$

where

$$\Delta\tilde{g}(P, T) \equiv \frac{g_\alpha(P, T) - g_\beta(P, T)}{v_\beta}. \tag{3.14b}$$

Notice that $R_* > 0$ only if $g_\alpha(P, T) > g_\beta(P, T)$, that is, the minority phase is stable. In this case, the majority phase is said to be supersaturated (or supercooled) and $\Delta\tilde{g}$ is called the *supersaturation*.

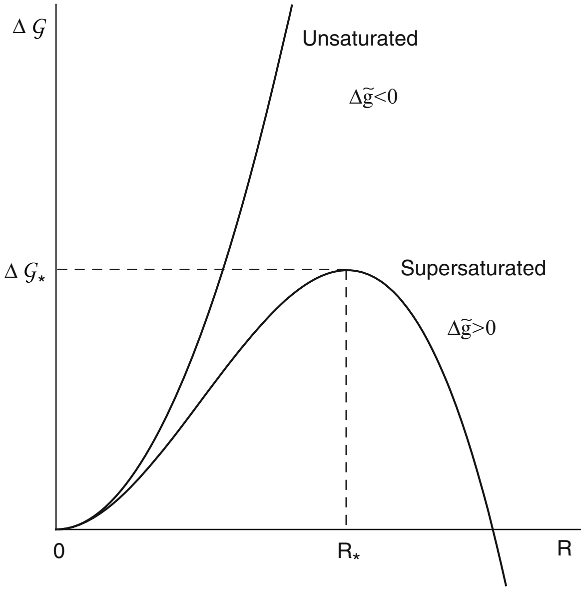


Fig. 3.1 ΔG_n of a spherical nucleus of the minority phase in the "sea" of the unsaturated ($\Delta\tilde{g}<0$) or supersaturated ($\Delta\tilde{g}>0$) majority phase as a function of its radius *R*

Now we can ask a question: How much work needs to be done on the homogeneous α phase to create in it a critical nucleus of the β phase? The answer provided by thermodynamics is that, although the specific amount of work depends on the process, the smallest amount equals the difference in the Gibbs free energies between the final and initial states:

$$\begin{aligned}\Delta G_n &= G(P,T;v_\alpha,v_\beta,m_\alpha,m_\beta) - Mg_\alpha(P,T)\\ &= m_\alpha g_\alpha(P,T) + m_\beta g_\beta(P,T) + \sigma S - (m_\alpha + m_\beta)g_\alpha(P,T)\\ &= \sigma S(R) - \Delta\tilde{g}V_\beta(R).\end{aligned} \tag{3.15}$$

The last expression in (3.15) is plotted in Fig. 3.1 as a function of *R* for different values of the supersaturation $\Delta\tilde{g}$. In the unsaturated α phase ($\Delta\tilde{g}<0$), ΔG_n is a monotonic function of R meaning that the β phase nuclei are not favorable. In the supersaturated α phase ($\Delta\tilde{g}>0$), $\Delta G_n \to 0$ for $R\to 0$ and $\Delta G_n < 0$ for $R\to\infty$, meaning that thermodynamically the system favors large nuclei of the β phase. However, as $\sigma > 0$ the function $\Delta G_n(R)$ has a maximum at the critical radius $R = R_*$:

$$\frac{\mathrm{d}\Delta G_n}{\mathrm{d}R}(R_*) = 0. \tag{3.16}$$

Using (3.8), (3.14a), and (3.15), we obtain:

$$\Delta G_* \equiv \Delta G_n(R_*) = \frac{1}{3}\sigma S(R_*) = \frac{1}{2}\Delta\tilde{g}V_\beta(R_*) = \frac{16\pi\sigma^3}{3\Delta\tilde{g}^2}. \tag{3.17}$$

This means that the favorable ($R \rightarrow \infty$, β phase) and unfavorable ($R = 0$, α phase) states of the system are separated by a "barrier" of the height ΔG_*, which needs to be overcome for the transformation to happen.

At this junction, it is important to recognize the main assumptions made in the Theory of Capillarity, which may or may not be true in a concrete problem. First, it was assumed that the minority phase is homogeneous all the way to the interface and has the specific free energy of the bulk phase β, although, at a pressure different from the external one. Second, we assume that the interface, which separates the phases, is infinitely thin. Third, we assume that the interfacial energy is isotropic and independent of the radius of the nucleus R. It is also implied in the Theory of Capillarity that the critical nucleus of the radius R_* can be formed by the thermal fluctuations in the system. This assumption will be tested in Chap. 7.

Unlike the macroscopic one, the field-theoretic approach to the problem of phase equilibrium considers an interface between the coexisting phases as a transition zone of certain thickness with spatial distribution of OPs and possibly other parameters. Hence, for the continuous description of such systems one has to know not only the average values of P, T, and OPs, but the spatial distributions of these parameters also. In this chapter, we are discussing only the equilibrium properties of the system; nonequilibrium systems will be considered in Chaps. 4 and 5.

3.2 The Free Energy

In a heterogeneous equilibrium system, some of the thermodynamic parameters turn into functions of space and the states of the system should be mathematically described by a class of functions instead of numbers. The free energy of the whole system becomes a functional of the state variables and their spatial derivatives:

$$G = \int_V \hat{g}\{P(\mathbf{x}), T(\mathbf{x}), H(\mathbf{x}), \eta_i(\mathbf{x})\}\, \mathrm{d}^3x \tag{3.18}$$

and the equilibrium states can be found as the functions that minimize this functional. In (3.18), V is the total volume occupied by the system ($V = V_\alpha + V_\beta + V_{\mathrm{int}}$) and the integrand $\hat{g}\{P, T, H, \eta\}$ may be called the Gibbs free energy density. Although in the previous section we used the specific free energy (per unit mass), most of the time in this book (unless it is specifically pointed out) for the sake of simplicity we will be using the free energy density (per unit volume). As a consequence of the inclusion of heterogeneities, we have to change the mathematical tool used to find the equilibrium states of the system: instead of the Calculus of Functions of Several Variables, we have to use the Calculus of Variations (Appendix B).

The crux of the problem of description of heterogeneous equilibrium systems by the functional (3.18) is the following question: Spatial derivatives of which thermodynamic variables must be included into the free energy density of the system?

Below we will discuss the problems associated with the inclusion of the gradients of the thermodynamic variables, such as P, T, and H into the free energy density (3.18). For now, we will be considering only the gradients of the OP.

Let us first assume that the OP of the system has only one scalar component, which is a function of $\mathbf{x}$. In principle, the density $\hat{g}$ may be a function of the spatial derivatives of the OP of all orders:

$$\hat{g} = \hat{g}\left\{P, T, H, \eta(\mathbf{x}), \frac{\partial \eta}{\partial x_i}, \frac{\partial^2 \eta}{\partial x_i \partial x_j} \cdots \right\}, \tag{3.19a}$$

where i, j are the Cartesian indexes. The density $\hat{g}$ may be expanded into a Taylor series:

$$\begin{aligned} \hat{g} = g(P, T, \eta) - H\eta + a_i \frac{\partial \eta}{\partial x_i} \\ + \frac{1}{2} b_{ij} \frac{\partial \eta}{\partial x_i} \frac{\partial \eta}{\partial x_j} + \frac{1}{2} c_{ij} \frac{\partial^2 \eta}{\partial x_i \partial x_j} \\ + \frac{1}{6} d_{ijk} \frac{\partial \eta}{\partial x_i} \frac{\partial \eta}{\partial x_j} \frac{\partial \eta}{\partial x_k} + \cdots \end{aligned} \tag{3.19b}$$

Functional dependence of the expansion coefficients a_i, b_{ij}, c_{ij}, d_{ijk}, etc. is subject to the following constraints: first, the free energy density must be invariant with respect to the transformation of the coordinates, that is a scalar; second, the continuum description is valid only if the spatial derivatives of the OP are not very large. Otherwise, the inhomogeneous part of the free energy density is much greater than the homogeneous one, and the details of the OP variations, discussed in Chap. 2, do not matter. These constraints show that the expansion coefficients may depend on the scalar quantities (P, T, H, η) and on the Euler angles θ_{ij} defined as follows:

$$\tan \theta_{ij} = \frac{\partial \eta / \partial x_i}{\partial \eta / \partial x_j}. \tag{3.20a}$$

The latter dependence causes *anisotropy*—dependence on orientation in space—of the free energy of the system. In this book we will not be considering anisotropy in greater depth and will assume that the expansion coefficients are independent of the Euler angles.

The linear term in the expansion (3.19b) is a scalar if a_is are components of a vector, so that

$$a_i \frac{\partial \eta}{\partial x_i} = \vec{a} \nabla \eta.$$

We have to ask ourselves a question: How can the free energy density of our system depend on a vector $\vec{a}$? If the system is isotropic then by definition its free energy cannot depend on an external vector $\vec{a}$. If the system's isotropy is broken by an applied external vector field, the Curie principle says that a scalar function cannot be affected by a vector field, rendering the term $\vec{a}\nabla\eta$ unphysical again.

However, there may be a case when this term makes physical sense, namely, when $\vec{a}$ is proportional to the gradient of a nonuniform, scalar, external field conjugate to the OP: $\vec{a} = \nu\nabla H$. Then, the free energy density expansion may contain an invariant linear term in the form:

$$a_i \frac{\partial\eta}{\partial x_i} = \nu\nabla H\nabla\eta. \tag{3.21}$$

But, in Sect. 3.8 on the basis of the LeChatelier–Braun principle, we analyze the consequences of inclusion of this term into the free energy density (3.19a) and conclude that

$$\nu = 0. \tag{3.22}$$

Furthermore, the two second-order-in-spatial-derivative terms in expansion (3.19b) can be reduced to each other. Indeed, let us calculate the contribution of the second second-order term into the total free energy (3.18):

$$\begin{aligned}\int_V c_{ij}\frac{\partial^2\eta}{\partial x_i\partial x_j}\,\mathrm{d}^3x &= \int_V \frac{\partial}{\partial x_i}\left(c_{ij}\frac{\partial\eta}{\partial x_j}\right)d^3x - \int_V \frac{\partial c_{ij}}{\partial\eta}\frac{\partial\eta}{\partial x_i}\frac{\partial\eta}{\partial x_j}\,\mathrm{d}^3x \\ &= \oint_\Omega c_{ij}\frac{\partial\eta}{\partial x_j}\,\mathrm{d}s_i - \int_V \frac{\partial c_{ij}}{\partial\eta}\frac{\partial\eta}{\partial x_i}\frac{\partial\eta}{\partial x_j}\,\mathrm{d}^3x.\end{aligned} \tag{3.23}$$

The Gauss theorem was used here to transform from the second expression to the third and $\oint_\Omega \mathrm{d}s_i$ means integration over the surface Ω enveloping the volume of the system V. The surface term in (3.23) is of the order of the surface free energy of the system and may be disregarded compared to the volumetric term for sufficiently large systems. For small systems, which are of great interest for nanoscience, the surface and volume terms may be of the same order. In this book, we will be considering only systems that are large enough for the surface contribution to be disregarded.

If $c_{ij} = \mathrm{const}(\eta)$, the last term in (3.23) vanishes and the entire contribution of the second second-order term in (3.19b) is zero. If $c_{ij} = \mathrm{funct}(\eta)$, the last term in (3.23) is of the same form as the first second-order term in (3.19b). Thus, the contribution of the second-order spatial derivatives into the free energy density may be expressed by the term $1/2\, b_{ij}(\partial\eta/\partial x_i)(\partial\eta/\partial x_j)$ with the properly defined second-rank tensor b_{ij}.

The free energy density, (3.19b), will be a scalar if each of the remaining irreducible terms is a scalar. For the second-order term to be a scalar, the second-rank tensor b_{ij} must be proportional to the Kronecker tensor:

$$b_{ij} = \kappa(P,T)\delta_{ij}, \quad \delta_{ij} = \begin{cases} 0, & \text{for } i \neq j \\ 1, & \text{for } i = j \end{cases}. \tag{3.24}$$

Then the total contribution of the second-order-in-spatial-derivative terms will be represented by

$$\frac{1}{2}\kappa|\nabla\eta|^2, \tag{3.25}$$

where the coefficient κ is called the *gradient energy coefficient*. The physical meaning of the gradient energy coefficient depends on the physical interpretation of the OP. For instance, if the OP represents the magnetic moment of the system, the gradient term is the exchange energy and the gradient energy coefficient is its strength.

The following must be said regarding the sign of this coefficient: if $\kappa > 0$, then the global equilibrium in the system described by the free energy, (3.18)–(3.25), will be achieved at a homogeneous state, $\eta = \text{const}(\mathbf{x})$, because any OP inhomogeneity increases the free energy of the system. If $\kappa < 0$, then the OP inhomogeneities decrease the free energy, which leads to an unphysical state of "infinite mixing" where the coexisting phases create infinite amount of infinitely sharp interfaces. To prevent our system from "going unphysical," we have to include the higher-order-in-spatial-derivative terms [e.g., the third-order ones, see (3.19b)]. In this case, you can estimate a typical scale of the OP inhomogeneity l. Indeed, the order of magnitude of the derivative is $\partial^n\eta/\partial x_i \ldots \partial x_k \sim \Delta\eta/l^n$. Then, as the second- and third-order derivatives must balance each other, we obtain $l \sim \left|\Delta\eta d_{ijk}/\kappa\right|$.

Mostly, in this book, we will be concentrating on the systems where the gradient energy coefficient is positive:

$$\kappa(P,T) > 0 \tag{3.26}$$

and the terms of the order higher than the second may be neglect, that is, $d_{ijk} = 0$. In such systems, the global equilibrium is achieved at the uniform distribution of the OP. However, except for the global equilibrium, such systems allow locally stable—metastable—heterogeneous equilibrium states.

Now we have to ask the following question: Do we need to include the gradients of the thermodynamic variables, such as P and T, into the expansion of the free energy density, (3.19a)? Let us look at the temperature gradient (∇T), first. A linear term, ($\boldsymbol{a}\nabla T$), may not be included because, as we concluded above, an isotropic system cannot support a vector $\boldsymbol{a}$. A quadratic term, $b(\nabla T)^2$, withstands the tests of isotropy and homogeneity if $b > 0$. However, it contradicts the zeroth law of thermodynamics. Indeed, according to this law any thermally isolated system must eventually come to the state of equilibrium characterized by uniform temperature distribution. But if the quadratic term is included into the free energy functional, (3.18) and (3.19a), then the state of equilibrium will allow for a heterogeneous-in-temperature equilibrium state in a thermally isolated system. This contradiction proves that the free energy density $\hat{g}$ is independent of the temperature gradient. A similar argument may be laid out with respect to the gradients of pressure.

Thus, the total free energy of a heterogeneous system with a one-component scalar OP may be expressed as follows:

$$G = \int_V \hat{g}\, \mathrm{d}^3 x \tag{3.27a}$$

$$\hat{g} \equiv g(P, T, H; \eta) + \frac{1}{2}\kappa(\nabla\eta)^2. \tag{3.27b}$$

A profound analogy may be established between our system and the Lagrangian system considered by the field theory (see Appendix D). In the framework of this analogy, the total Gibbs free energy of (3.27a) is analogous to the total energy E of the Lagrangian system, (D.18), and the Gibbs free energy density (3.27b)—to the T^{00} component of the stress-energy tensor, (D.16). This analogy hints at another quantity which may be significant for our system:

$$\breve{g} \equiv g(P, T, H, \eta) - \frac{1}{2}\kappa(\nabla\eta)^2. \tag{3.28}$$

Significance of this quantity comes from its analogy to the T^{11} component of the stress-energy tensor, which has the first integral [conservation property, see (D.19)]. Existence of the first integral is one of the consequences of the Euclidean invariance of the free-energy density (3.27b)—independence of the spatial coordinates. Another (however, not unrelated) consequence of the Euclidean invariance is existence of the Goldstone modes (Sect. 3.7).

3.3 Equilibrium States

As we discussed in Chap. 2, a thermodynamically stable equilibrium state of an open system with specified temperature and pressure must deliver minimum to the Gibbs free energy of the system. Because the free energy of the heterogeneous system is a functional, [see (3.27a)], the equation for the state η_E, either differential or integral, should be obtained by minimization of the functional, that is the variational procedure. As explained in Appendix B, the states η_E can be found among the solutions of the Euler–Lagrange equation (ELE):

$$\frac{\delta G}{\delta \eta} \equiv \left(\frac{\partial g}{\partial \eta}\right)_{P,T,H} - \kappa\nabla^2\eta = 0. \tag{3.29}$$

Solutions of ELE (3.29) are called *extremals* of the functional G (3.27a): $\eta_\mathrm{E} =$ func($\mathbf{x}$;P,T,H). There is one more parameter that is important for the extremals, this is dimensionality of the geometrical space d—the number of space variables that essentially influence it.

A physical state is not uniquely specified if we simply give the differential equations which the state must satisfy. For the extremals to describe a physical state of a system uniquely, it is necessary to set the *boundary conditions* (BC) on the surface Ω of the volume V of the system even in the thermodynamic limit: $V \to \infty$. BCs (and *initial conditions* in the case of time-dependent problems) are sets of elements of the physical behavior of the system, which are not regulated by the physical laws that entailed the equations for the system. The kind of BC that shall be used depends on the physical problem; changing BC may have dramatic effect on the properties of the state, that is, solutions of ELE (3.29). Notice in Appendix B that the variational procedure itself yields different kinds of BCs depending on the physical properties of the boundary: Dirichlet's BC on the boundary where OP is fixed (B.3):

$$\eta = F(s) \text{ on } \boldsymbol{\Omega} \tag{3.30a}$$

or the Newmann type BC on the boundary $\boldsymbol{\Omega}$ where the OP may vary (B.11):

$$\mathbf{j}_\Omega \nabla \eta = 0 \text{ on } \boldsymbol{\Omega}. \tag{3.30b}$$

Here $\mathbf{j}_\Omega$ is a unit outer vector of the boundary $\boldsymbol{\Omega}$. Solutions of ELE (3.29) that satisfy BC (3.30a) or (3.30b) represent the equilibrium states of the system:

$$\eta_E \in \{f(\mathbf{x}); P, T, H, V, d, \mathrm{BC}\}. \tag{3.31}$$

A more complicated case of a completely free boundary (Eq.(B. 17)) is also possible. In this book we will be using the Newmann type BC more often than other types. In Chap. 2, we analyzed the homogeneous (0d) equilibrium states $\bar{\eta}$; the 1d heterogeneous states will be considered in Sect. 3.4; 3d states will be considered in Sect. 3.5; the 2d states have intermediate properties between 1d and 3d.

A set of functions $\{\eta(\mathbf{x})\}$, which can generate a functional, is called a *functional space*. For our purposes, the most convenient functional space is the Hilbert space where each element is defined and continuous together with its gradients in the domain V and is characterized by its "size"—called *norm*. How can we "measure" an infinite-dimensional element of the functional space? Here is one way to do that. For each element $\eta(\mathbf{x})$ of the functional space we define four numbers: *average*

$$\langle \eta \rangle \equiv \frac{1}{V} \int_V \eta(\mathbf{x})\, \mathrm{d}^3 x, \tag{3.32a}$$

range (the largest difference between the values of the element)

$$\Pi \equiv \max_{\mathbf{x},\mathbf{x}' \in V} |\eta(\mathbf{x}) - \eta(\mathbf{x}')|, \tag{3.32b}$$

amplitude

$$N \equiv \max_V |\eta(\mathbf{x}) - \langle \eta \rangle|, \tag{3.32c}$$

and *slope*

$$\Lambda \equiv \max_V |\nabla \eta(\mathbf{x})|. \tag{3.32d}$$

Then each element of the Hilbert space $\{\eta(\mathbf{x})\}$ will be characterized by its *skew* (asymmetry):

$$\Sigma = 2N - \Pi \tag{3.32e}$$

length scale:

$$L = \frac{\Pi}{\Lambda} \tag{3.32f}$$

and the *norm*:

$$\|\eta(\mathbf{x})\| = \langle \eta \rangle + \Pi + \Lambda. \tag{3.32g}$$

For the dimensions of the terms in (3.32 g), see (B.8) and the comment after that.

To elucidate the properties of the equilibrium states $\eta_{\mathrm{E}}(\mathbf{x})$, we will derive a few other forms of the equilibrium equation useful for the analysis below. First, by partially differentiating the left-hand side of ELE (3.29) and using the fact that it does not depend explicitly on the coordinates, we find an equation for the gradient of the extremal $\eta_{\mathrm{E}}(\mathbf{x})$. In the most convenient form, this equation can be written down as

$$\hat{\mathbf{H}}(\eta_E(\mathbf{x}))\nabla \eta_E(\mathbf{x}) = 0 \tag{3.33}$$

using a linear operator

$$\hat{\mathbf{H}}(\eta_E(\mathbf{x})) \equiv \left(\frac{\partial^2 g}{\partial \eta^2}\right)_{P,T}(\eta_E) - \kappa \nabla^2 \tag{3.34}$$

called Hamiltonian, which plays an important role in the analysis of the properties of the system. An advantage of the form (3.33), (3.34) is that the properties of the Hamiltonian operator are well known from quantum mechanics (see Appendix E), where it plays a role of an operator of total energy of a particle with the term $\partial^2 g(\eta_{\mathrm{E}})/\partial \eta^2$ being analogous to the potential energy of a particle and $(-\kappa \nabla^2)$—kinetic one. Another advantage of (3.33), (3.34) is that in the case of radially symmetric extremals it is convenient to consider the Hamiltonian in the spherical polar coordinate system (see Appendix C). A disadvantage of the form (3.33), (3.34) is that the operator depends on the extremal $\eta_{\mathrm{E}}(\mathbf{x})$ itself.

Second, integrating ELE (3.29) and applying the Gauss divergence theorem with the Newmann-type BC (3.30b), we obtain an integral property of the equilibrium states:

$$\int_V \frac{\partial g}{\partial \eta} \, \mathrm{d}^3 x = 0. \tag{3.35}$$

This formula tells us that although $\partial g/\partial\eta\{\eta_{\mathrm{E}}(\mathbf{x})\}$ does not vanish everywhere, as it is the case in a homogeneous system (see Chap. 2), on average it still does.

Third, let us derive another integral form of the equilibrium equation. For this, we apply the vector-calculus formula

$$\nabla(u\nabla v) = \nabla u\nabla v + u\nabla^2 v$$

to the functions $u = v = \eta(\mathbf{x})$ and obtain

$$\nabla(\eta\nabla\eta) = (\nabla\eta)^2 + \eta\nabla^2\eta. \tag{3.36}$$

Then, multiplying all the terms of ELE (3.29) by η, using the formula (3.36), integrating over the entire volume V occupied by the system, and applying the Gauss divergence theorem, we obtain the integral form of the equilibrium equation:

$$\int_V \left[\kappa(\nabla\eta)^2 + \eta\frac{\partial g}{\partial\eta}\right]\mathrm{d}\mathbf{x} = \kappa\oint_\Omega \eta\nabla\eta\,\mathrm{d}\mathbf{s}. \tag{3.37a}$$

For the Newmann-type BC (3.30b), the integral equilibrium equation (3.37a) takes on a very appealing mathematical form:

$$\int_V \left[\kappa(\nabla\eta)^2 + \eta\frac{\partial g}{\partial\eta}\right]\mathrm{d}^3x = 0. \tag{3.37b}$$

This relation allows us to represent the total free energy of the equilibrium system in another form which involves the auxiliary function from (2.24) and does not involve the OP gradient:

$$G(\eta_E(\mathbf{x})) = \int_V \left(g - \frac{1}{2}\eta\frac{\partial g}{\partial\eta}\right)\mathrm{d}^3x. \tag{3.38a}$$

Subtracting $g(\bar{\eta})V$ from this expression and using the integral equilibrium equation (3.35) we can define the *free energy excess*

$$\Delta G_E = \int_V \left\{[g(\eta_E) - g(\bar{\eta})] - \frac{1}{2}(\eta_E - \bar{\eta})\frac{\partial g}{\partial\eta}(\eta_E)\right\}\mathrm{d}^3x \tag{3.38b}$$

which is a measure of the free energy of the state η_{E} relative to that of the homogeneous state $\bar{\eta}$.

3.4 One-Dimensional Equilibrium States

Let us first consider equilibrium states in a one-dimensional (1d) open system, which is a box with a base S, thickness X and volume $V = XS$, and where the OP depends only on one space coordinate, $\eta{=}\eta_{\mathrm{E}}(x)$. Then, ELE (3.29) takes the form:

$$\kappa \frac{\mathrm{d}^2\eta}{\mathrm{d}x^2} - \frac{\partial g}{\partial \eta} = 0, \quad 0 \le x \le X. \tag{3.39a}$$

This is an ODE of the second order, which needs two boundary conditions to identify its solution $\eta_{\mathrm{E}}(x)$ uniquely. Although in some physical situations Dirichlet's conditions may be justified, here, we will be using the Newmann's one:

$$\frac{\mathrm{d}\eta}{\mathrm{d}x} = 0 \quad \text{at } x = 0,\ x = X. \tag{3.40}$$

Instead of (3.39a), one can use the 1d version of (3.33), (3.34), which takes the form

$$-\hat{\mathbf{H}}(\eta(x))\frac{\mathrm{d}\eta}{\mathrm{d}x} \equiv \kappa \frac{\mathrm{d}^3\eta}{\mathrm{d}x^3} - \frac{\partial^2 g}{\partial \eta^2}(\eta(x))\frac{\mathrm{d}\eta}{\mathrm{d}x} = 0. \tag{3.41}$$

As we pointed out in Sect. 3.2 (see also Appendix D), the 1d-ELE (3.39a) has the first integral in the form of the conserved quantity (3.28). Because this is such an important property of the 1d-equilibrium states, we will demonstrate it again. We multiply both terms of (3.39a) by $(\mathrm{d}\eta/\mathrm{d}x)$, transform them as follows:

$$\frac{\kappa}{2}\frac{\mathrm{d}}{\mathrm{d}x}\left(\frac{\mathrm{d}\eta}{\mathrm{d}x}\right)^2 - \frac{\mathrm{d}g}{\mathrm{d}x} = 0 \tag{3.39b}$$

and integrate (3.39b) using that $\kappa(P, T) = \mathrm{const}(x)$. The first integral takes the form:

$$-\breve{g} = \frac{\kappa}{2}\left(\frac{\mathrm{d}\eta}{\mathrm{d}x}\right)^2 - g(P,T,\eta) = \mathrm{const}(x) \equiv -\mu, \tag{3.42a}$$

where

$$\mu \equiv g(P,T,\eta_l) = g(P,T,\eta_r), \tag{3.42b}$$

$$\eta_l \equiv \eta_E(0), \quad \eta_r \equiv \eta_E(X). \tag{3.42c}$$

Because of the condition (3.26), (3.42a) yields

$$\mu \le g(P,T,\eta_E(x)). \tag{3.42d}$$

According to Gibbs, the constant μ is the chemical potential of the system; its relation to the pressure, temperature, and size of the system will be discussed below. Existence of the first integral of ELE (3.29) in the form (3.42a) may be interpreted as the conservation law for the quantity $\breve{g}$. As any conservation law, it is connected to certain symmetry of the system, which will be analyzed in Chap. 6. The conservation law (3.42a) is very helpful as it allows us to analyze the equilibrium states for a general form of the potential $g(P, T, \eta)$. Unfortunately, the first integral and the conservation law exist for 1d extremals only.

Equations (3.39), (3.41), or (3.42a) plus BC (3.40) represent the boundary-value problem for the 1d equilibrium states (3.31). Let us resolve (3.42a) as follows:

$$\frac{\mathrm{d}\eta}{\mathrm{d}x} = \pm\sqrt{\frac{2}{\kappa}[g(P,T,\eta) - \mu]}. \tag{3.43}$$

This equation shows that there are two categories of 1d states: *monotonic and non-monotonic*, that is, with alternating sign of $\mathrm{d}\eta/\mathrm{d}x$. Equation (3.43) can be integrated in the domain of monotonicity of the OP. Selecting the positive branch of (3.43) and separating variables, we obtain a general solution in quadratures:

$$x = \sqrt{\frac{\kappa}{2}}\int\frac{\mathrm{d}\eta}{\sqrt{g(P,T,\eta) - \mu}}. \tag{3.44a}$$

Notice that, because of the conservative property (3.42a), the particular solution (3.44a) of the boundary-value problem, (3.39a) and (3.40), requires only one arbitrary constant, which is specified by (3.42c). Taking into account that $\eta_l<\eta_\mathrm{r}$ for the positive monotonic branch of (3.44a), we arrive at the relationship

$$X = \sqrt{\frac{\kappa}{2}}\int_{\eta_l}^{\eta_r}\frac{\mathrm{d}\eta}{\sqrt{g(P,T,\eta) - \mu}} \tag{3.44b}$$

between the size of the 1d system X, its thermodynamic parameters, P and T, and parameters of the equilibrium state $\eta_\mathrm{E}(x)$, the chemical potential μ and range $\Pi=|\eta_\mathrm{r}-\eta_l|$, (3.32b).

The non-monotonic states are periodic with a monotonic half-period $D_{1\mathrm{d}}$ and the BC, (3.40) and (3.42c), which apply on the boundaries of the domain of monotonicity $x_l < x < x_r$. In a finite-size system, the non-monotonic states are characterized by *index*—the number of half periods:

$$n_{1\mathrm{d}} \equiv \frac{X}{D_{1\mathrm{d}}},\ D_{1\mathrm{d}} \equiv x_r - x_l \tag{3.45}$$

For the monotonic states, obviously, $n_{1\mathrm{d}} = 1$.

To find the free energy of the 1d state, we substitute (3.42a) into (3.27a) and obtain:

$$G_{1\mathrm{d}} = V\mu + Sn_{1\mathrm{d}} \int_{x_l}^{x_r} \kappa \left(\frac{\mathrm{d}\eta_{1\mathrm{d}}}{\mathrm{d}x} \right)^2 \mathrm{d}x. \tag{3.46a}$$

Changing the variables of integration and using the monotonic branch of (3.43), we obtain

$$G_{1\mathrm{d}} = V\mu + Sn_{1\mathrm{d}} \int_{\eta_l}^{\eta_r} \sqrt{2\kappa[g(P,T;\eta_{1\mathrm{d}}) - \mu]}\, \mathrm{d}\eta. \tag{3.46b}$$

There is a lot that we can learn about the extremals $\eta_{\mathrm{E}}(x)$ without calculating the integrals in (3.44b) and (3.46b). The monotonic heterogeneous state must have an inflection point (x_i) and (3.39a), (3.41) with BC (3.40) help us find it. Indeed, the necessary and sufficient conditions of the inflection point of a smooth function is

$$\frac{\mathrm{d}^2\eta}{\mathrm{d}x^2}(x_i) = 0 \quad \text{and} \quad \frac{\mathrm{d}^3\eta}{\mathrm{d}x^3}(x_i) \neq 0. \tag{3.47a}$$

Then we conclude from (3.39a) and (3.41) that

$$\frac{\partial g}{\partial \eta}(\eta_i) = 0 \quad \text{and} \quad \frac{\partial^2 g}{\partial \eta^2}(\eta_i) \neq 0. \tag{3.47b}$$

Moreover, expanding the derivative near the inflection point

$$\frac{\mathrm{d}\eta}{\mathrm{d}x}(x) = \frac{\mathrm{d}\eta}{\mathrm{d}x}(x_i) + \frac{1}{2}\frac{\mathrm{d}^3\eta}{\mathrm{d}x^3}(x_i)(x - x_i)^2 + \cdots \tag{3.47c}$$

and applying the BC (3.40) to the expansion we obtain that

$$\frac{\mathrm{d}^3\eta(x_i)/\mathrm{d}x^3}{\mathrm{d}\eta(x_i)/\mathrm{d}x} < 0. \tag{3.47d}$$

Using (3.41), this yields

$$\frac{\partial^2 g}{\partial \eta^2}(\eta_i) < 0. \tag{3.47e}$$

Equation (3.47b) means that the inflection points can be found among the critical points of the potential $g(\eta)$; (3.47e) means that the inflection point η_i corresponds to the maximum of the potential $g(\eta)$, that is, unstable, transition states η_t of (2.38).

The fact that η_i is a maximum of $g(\eta)$ can also be observed from (3.42b–d) (Why?). This fact can also be used to find the length scale $L_{1\mathrm{d}}$ from (3.32f). Indeed, according to (3.43) and (3.47), the greatest value of the OP gradient is reached at the inflection point $\eta_{\mathrm{E}}(x_i){=}\eta_t$. Then [cf. (D.26)]:

$$L_{1\mathrm{d}} = \sqrt{\kappa}\frac{|\eta_r - \eta_l|}{\sqrt{2(g_t - \mu)}}. \tag{3.48}$$

3.4.1 *Classification of the States*

The 1d equilibrium states are the cornerstones of the FTM, that is why we need to study their properties in detail. To elucidate the properties of the heterogeneous states, we can use the *phase-plane method* (no relevance to the thermodynamic phase) [3, 4], which is based on the qualitative analysis of the solutions of ELE (3.39) in the plane (η, η_x) (see Fig. 3.2ii). The homogeneous equilibrium states of Chap. 2 are the rest points and the heterogeneous states are trajectories on the plane. Let us now classify the 1d heterogeneous extremals. First, let us find all possible values of the chemical potential μ that allow for solutions of the boundary-value problem (3.39a) and (3.40), using the general potential $g(P,T,\eta)$ that satisfies condition (2.10). The equation

$$g(P, T, \eta) = \mu \tag{3.49}$$

may have up to four solutions (see Fig. 3.2i). However, only the two, which are the closest to the transition-state OP η_t, are of interest for us here: $\eta_l < \eta_{\mathrm{t}}$ and $\eta_{\mathrm{r}} > \eta_{\mathrm{t}}$. Therefore, it is advantageous to expand the function $g(P, T, \eta)$ that satisfies condition (2.10) about the homogeneous transition state and truncate after the fourth-power term, see (2.38). Then, from (2.38c) we find that $g_\beta < \mu < g_t$. Also notice that if $g_\beta < g_\alpha$ then no equilibrium state is possible for $g_\beta < \mu < g_\alpha$. Then, all possible solutions of the boundary-value problem (3.39), (3.40) can be classified depending on the values of (P, T) into

$$\begin{aligned} &\text{type} - \text{e}: \quad g_\alpha = g_\beta \\ &\text{type} - \text{n}: \quad g_\alpha > g_\beta \end{aligned} \tag{3.50a}$$

and depending on the value of the chemical potential μ into

$$\begin{aligned} &\text{type}-1: \quad \mu \to g_t - 0 \\ &\text{type}-2: \quad g_\alpha < \mu < g_t \\ &\text{type}-3: \quad \mu \to g_\alpha + 0 \\ &\text{type}-4: \quad \mu = g_\alpha. \end{aligned} \tag{3.50b}$$

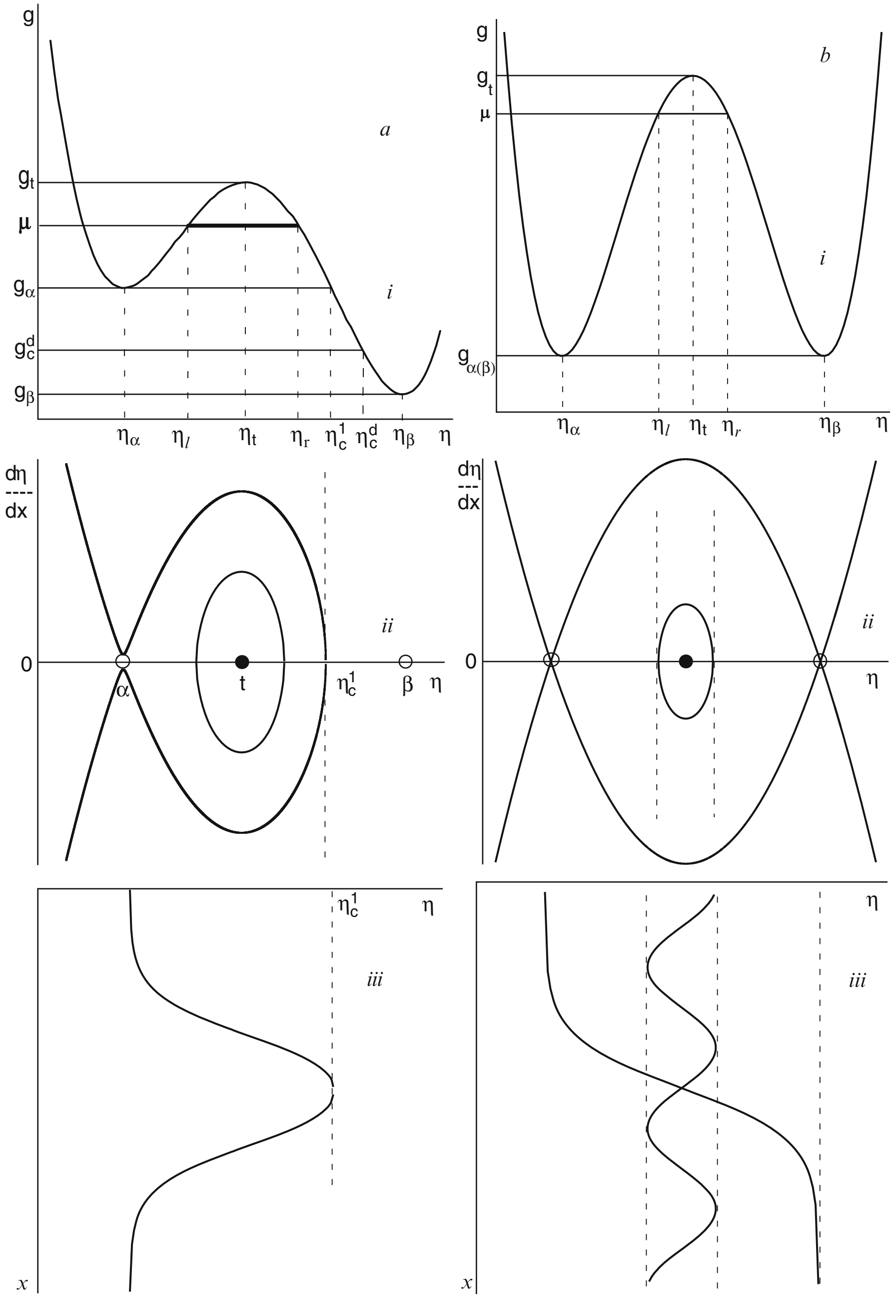


Fig. 3.2 Different types of the chemical potential μ and corresponding heterogeneous solutions of the 1d-ELE (3.39a). (**a**) -general case of (P, T)—type-n (**b**) -the symmetric case of (P, T)—type-e. (i) Potential $g = g(P, T, \eta)$; (ii) phase plane (η, η_x); (iii) heterogeneous states $\eta_E(x)$

In this classification, the numbers 1–4 combine with letters e–n to form specific types of heterogeneous states. To complete the classification, we have to distinguish between the monotonic and non-monotonic states. Different types of states, see (3.45) are depicted in Fig. 3.2.

Let us consider, first, the monotonic type-e states with different values of the chemical potential. They are generated by the symmetric potential (2.38) with

$$g_t''' = 0. \tag{3.51a}$$

This condition appears either due to the symmetry of the system (second-order transition, Sect. 2.4) or as a result of the specific external conditions (equilibrium temperature for a first-order transition). Using the phase-plane method, we can see that for the type-e states:

$$\langle \eta_{\mathrm{e}} \rangle = \eta_t, \quad \Sigma_{\mathrm{e}} = 0, \quad \mathrm{N}_{\mathrm{e}} = \frac{1}{2}\Pi_{\mathrm{e}}. \tag{3.51b}$$

Then, using the fact that in the phase plane the trajectory $\eta_e(x)$ is symmetric with respect to the transition point η_t (see Fig. 3.2bii), we can find the solutions of the boundary-value problem (3.39a), (3.40) by substituting (2.38) into (3.44a):

$$x = \sqrt{\kappa}\int \frac{\mathrm{d}\Delta\eta}{\sqrt{g''_t(\Delta\eta^2 - N_{\mathrm{e}}^2) + \frac{1}{12} g''''_t\,(\Delta\eta^4 - N_{\mathrm{e}}^4)}}, \tag{3.52}$$

where $\Delta\eta \equiv \eta_{\mathrm{e}} - \eta_t$. The end points of the solution (3.52) are $\Delta\eta_r = -\Delta\eta_l = N_{\mathrm{e}}$; they are the *turning points* of the phase plane (Why?). The solution (3.52) yields the expressions for the amplitude (3.32c) and length (3.32f) (Verify!):

$$N_{\mathrm{e}}^2 = 2m\Theta^2; \quad \Theta \equiv \sqrt{6\frac{|g''_t|}{g''''_t}}, \tag{3.53a}$$

$$L_{\mathrm{e}} = \frac{2}{\sqrt{1-m}} l; \quad l \equiv \sqrt{\frac{\kappa}{|g''_t|}}, \tag{3.53b}$$

$$m = \frac{1}{2}\left[1 - \sqrt{1 - 4\frac{g_t - \mu}{\Xi}}\right]; \quad \Xi \equiv |g_t''|\Theta^2 = 6\frac{(g''_t)^2}{g''''_t}, \tag{3.53c}$$

where m is a normalized chemical potential and Θ, l, and Ξ are the fundamental OP amplitude, length, and energy density scales, respectively. Notice that if the system approaches its spinodal point, that is $g''_t \to 0$, then $\Theta \to 0$, $\Xi \to 0$, and $l \to \infty$.

Equations (3.53) allow us to establish explicit relations between the characteristics of the state $\eta_{\mathrm{e}}(\mathrm{x})$, see (3.32). For instance, by excluding the parameter m from (3.35a) and (3.53b) we can obtain the slope as a function of the amplitude:

$$\Lambda_e = \frac{N_e}{l}\sqrt{1 - \frac{N_e^2}{2\Theta^2}}. \tag{3.53d}$$

A length scale, similar to the fundamental length l, can also be defined at a stable equilibrium state $\bar{\eta}$. It is called *correlation radius* r_C, see (7.17), because, as we will learn in Chap. 7, the OP fluctuations of the state $\bar{\eta}$ are correlated on the scale of r_C.

Now, using the substitution $u = \Delta\eta/N_e$ for (3.52), we can clarify the relationship (3.44b) for the type-e states:

$$\begin{aligned} X &= 2\sqrt{\kappa}\int\limits_0^{N_e}\frac{\mathrm{d}\Delta\eta}{\sqrt{g_t''(\Delta\eta^2 - N_e^2) + \frac{1}{12}g_t''''\ \ (\Delta\eta^4 - N_e^4)}} \\ &= \frac{2l}{\sqrt{1-m}}K\left(\sqrt{\frac{m}{1-m}}\right) = L_e K\left(\sqrt{\frac{m}{1-m}}\right), \end{aligned} \tag{3.54a}$$

where $K(k)$ is the elliptical integral of the first kind [5]

$$K(k) \equiv \int_0^1 \frac{\mathrm{d}u}{\sqrt{1-u^2}\sqrt{1-k^2u^2}} \to \begin{cases} \frac{\pi}{2}\left(1 + \frac{k^2}{4}\right), & \text{for } k \to 0+0 \\ \ln\frac{4}{\sqrt{1-k^2}}, & \text{for } k \to 1-0. \end{cases} \tag{3.54b}$$

Notice from (3.53) and (3.54a) that for the type-e states L_e is always smaller than X and the difference between the two grows as $|g_t - \mu|$ grows.

To find the free energy of a type-e state, we again use the substitution $u = \Delta\eta/N_e$ and (3.53) for (3.46b) with the potential (2.38). Then we obtain an expression for the free energy of the type-e (not necessarily monotonic) state:

$$\begin{aligned} G_e &= V\mu + S\sqrt{\frac{\kappa g''''_t}{3}}N_e^3 n_e \int_{-1}^{+1}\sqrt{(1-u^2)\left(\frac{1-m}{m} - u^2\right)}\,\mathrm{d}u \\ &= \mu V + 8\frac{\sqrt{\kappa |g''_t|^3}}{g''''_t}\Phi(m) n_e S \\ &= [g_t - \Xi m(1-m)]V + \frac{4}{3}\Xi\Phi(m) n_e S l \\ &= \left[g_{\alpha(\beta)} + \Xi\left(\frac{1}{2} - m\right)^2\right]V + \frac{4}{3}\Xi\Phi(m) n_e S l, \end{aligned} \tag{3.55a}$$

where we defined the function

$$\Phi(m) = \sqrt{1-m}\left[E\left(\sqrt{\frac{m}{1-m}}\right) - (1-2m)K\left(\sqrt{\frac{m}{1-m}}\right)\right], \tag{3.55b}$$

and $E(k)$ is the elliptical integral of the second kind [5]:

$$E(k) \equiv \int_0^1 \frac{\sqrt{1-k^2u^2}}{\sqrt{1-u^2}}\mathrm{d}u \to \begin{cases} \dfrac{\pi}{2}\left(1-\dfrac{k^2}{4}\right), & \text{for } k \to 0+0 \\ 1+\dfrac{1-k^2}{2}\left(\ln\dfrac{4}{\sqrt{1-k^2}}-\dfrac{1}{2}\right), & \text{for } k \to 1-0. \end{cases} \tag{3.55c}$$

There are two limiting cases of the function in (3.55b) which are of interest:

$$\Phi(m) \to \begin{cases} \dfrac{3\pi}{4}m, & \text{for } m \to 0+0 \\ \dfrac{1}{\sqrt{2}}\left[1-\left(\dfrac{1}{2}-m\right)\right], & \text{for } m \to \dfrac{1}{2}-0. \end{cases} \tag{3.55d}$$

The slope, amplitude, and free energy as implicit functions of the system's size are best represented in the scaled form as follows:

$$\lambda = \frac{l\Lambda_{\mathrm{e}}}{\Theta}, \quad a = \frac{N_{\mathrm{e}}}{\Theta}, \quad j = \frac{G_{\mathrm{e}} - g_{\alpha(\beta)}V}{\Xi V}; \quad s = \frac{X}{l}. \tag{3.56b}$$

Notice that j represents the dimensionless free energy excess quantity. The functions a(s) and j(s) for the monotonic states ($n_{\mathrm{e}} = 1$) are depicted in Fig. 3.3. For the non-monotonic states ($n_{\mathrm{e}}>1$) the size X is replaced in (3.56) by the length of monotonicity D_{e}, see (3.45).

3.4.2 Type-e1 Solutions: Bifurcation Off the Transition State

Although the implicit functions $j(s)$ and $a(s)$ solve the problem of the 1d extremals, it is instructive to analyze them further. For type-e1 states (3.50b), (3.53) yields:

$$m_{\mathrm{e1}} \approx \frac{g_t - \mu}{\Xi} \to 0; \quad \mathrm{N}_{\mathrm{e1}} \approx \sqrt{2\frac{g_t-\mu}{|g''_t|}} \to 0; \quad L_{\mathrm{e1}} \to 2l. \tag{3.57}$$

Notice that, while the amplitude N_{e1} of the type-e1 heterogeneous state depends strongly on the chemical potential value through ($g_{\mathrm{t}} - \mu$), the characteristic length L_{e1} is practically independent of it. Excluding the parameter m from (3.53a) and (3.54a) for type-e1 solutions we obtain:

$$N_{\mathrm{e1}} \approx 2\sqrt{2\Theta\frac{X-\tilde{X}}{\tilde{X}}}. \tag{3.58a}$$

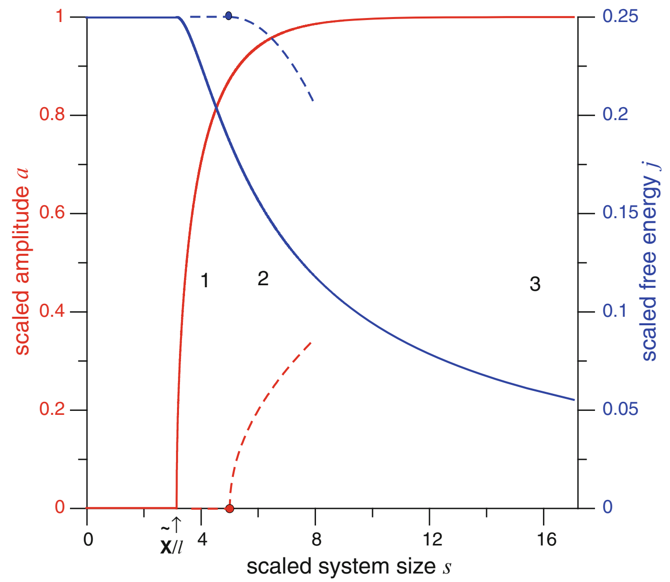


Fig. 3.3 Size-amplitude bifurcation diagram for type-e heterogeneous monotonic states. *Red lines*—scaled amplitude, *blue lines*—scaled energy; *solid lines*—1d systems, *dashed lines*—3d systems. $(\tilde{X}/l,\ 0)$—the 1d bifurcation point; *numbers*—the classification types

Equation (3.58a) shows that the heterogeneous solutions $\eta_{\mathrm{e}1}(x)$ branch away or *bifurcate* from the homogeneous transition state $\bar{\eta} = \eta_t$ at the point $X = \tilde{X}$ where

$$\tilde{X} \equiv \pi l \tag{3.58b}$$

Notice that the bifurcation length $\tilde{X}$ is of the same order of magnitude as the fundamental length l. The bifurcation (3.58) may be called "size-amplitude" (SABi). Equation (3.58a), depicted in Fig. 3.3, is the SABi diagram and $(\eta_t, \tilde{X})$ is the SABi point, near which $(X \to \tilde{X})$ the solution $\eta_{1\mathrm{e}}(x)$ is a harmonic function with the period $2\tilde{X}$ [Verify! Hint: take the integral in (3.52) or see Fig. 3.2biii].

Now, let us look at the SABi diagram from the stand point of the free energy. To do this, we exclude parameter m from (3.54a) and (3.55a) and analyze the $(\mu \to g_{\mathrm{t}}, m \to 0, X \to \tilde{X})$-limiting cases of the relationship between the free energy and the system's size $V = XS$ for the type-e1 monotonic state:

$$G_{\mathrm{e}1} = Vg_t + \Xi m S(\tilde{X} - X) = V\left[g_t - 4\Xi \frac{(X - \tilde{X})^2}{X\tilde{X}}\right]. \tag{3.59}$$

This expression is also depicted on the SABi diagram, Fig. 3.3, in the scaled form [see (3.56)].

3.4.3 Type-e3 Solutions: Approach to Thermodynamic Limit

For the type-e3 state, $\mu \rightarrow g_{\alpha(\beta)}$ and (3.50b) and (3.53) yield:

$$m_{e3} \rightarrow m_{e4} = \frac{1}{2}; \quad N_{e3} \rightarrow N_{e4} = \Theta; \quad L_{e3} \rightarrow L_{e4} = 2\sqrt{2}l. \tag{3.60}$$

Then, using properties of the elliptical integral (3.54b), we obtain the following expression for the amplitude:

$$N_{e3}^2 = \Theta^2 \left(1 - 8e^{-(2X/L_{e4})}\right). \tag{3.61}$$

Equations (3.60) and (3.61) yield that the type-e3 states appear $X \rightarrow \infty$. For the free energy of the monotonic state, (3.65) yields:

$$\begin{aligned} G_{e3} &\approx Vg_{\alpha(\beta)} + Sl\Xi\frac{2}{3}\sqrt{2}\left(1 + 4e^{-(2X/L_{e4})}\right) \\ &= V\left[g_{\alpha(\beta)} + \frac{l}{X}\Xi\frac{2}{3}\sqrt{2}\left(1 + 4e^{(-2X/L_{e4})}\right)\right]. \end{aligned} \tag{3.62}$$

The normalized free energy densities and amplitudes of the type-e1–e3 states are depicted in Fig. 3.3 as functions for the system size.

3.4.4 Type-e4 Solution: Plane Interface

As $\mu \rightarrow g_\alpha$ the elliptical integral in (3.54b) grows without bound. This means that the boundary-value problem (3.39a) and (3.40) has no type-e4 solutions in the finite domain ($X < \infty$), but may have solutions in the infinite domain ($X \rightarrow \infty$), that is, the thermodynamic limit. To find the type-e4 solutions, the phase-plane method must be supplemented with the exact calculations of the solutions $\eta_E(x)$ using quadratures of (3.52). Substituting (3.60) into (3.52) we obtain:

$$x = x_i + \frac{1}{4}L_{e4}\ln\left|\frac{\Theta + \Delta\eta_{e4}}{\Theta - \Delta\eta_{e4}}\right|, \tag{3.63a}$$

where the constant of integration, x_i, may be interpreted as the x-coordinate of the inflection point of the solution:

$$\Delta\eta_{e4}(x_i) \equiv 0. \tag{3.63b}$$

For a bounded solution, $|\Delta\eta_{4n}|<\Theta$, (3.63a) can be resolved as follows:

$$\eta_{e4} = \eta_t + \Theta \tanh\left(2\frac{x - x_i}{L_{e4}}\right). \tag{3.64}$$

In materials physics, this type of solution is called an *interface*, in the theory of micromagnetism—domain-boundary wall, in the mathematical theory of waves—kink. Although the elementary-function solution (3.64) resolves the boundary-value problem (3.39a) and (3.40) completely (see Fig. 3.2biii), it is useful for the following to analyze the properties of the solution even further:

1. Equations (3.60) and (3.52) show that for the type-e4 state $x_l \to -\infty$ and $x_r \to +\infty$.
2. Solution (3.64) is odd with respect to the point (x_i,η_t) so that $\Delta\eta(-x) = -\Delta\eta(x)$.
3. Because $X \to \infty$, BC (3.40) yields $d^2\eta/dx^2 = 0$, which, due to ELE (3.39a), results in

$$\frac{\partial g}{\partial \eta}(\eta_l) = \frac{\partial g}{\partial \eta}(\eta_r) = 0. \tag{3.65}$$

   This relation shows that the type-e4 solution connects two equilibrium phases with $\eta_l = \eta_\alpha$ and $\eta_r = \eta_\beta$.
4. The heterogeneities of the solution (3.64) are localized in an interval of x-axis of the characteristic length practically the same as that of type-e1 state: $L_{e4} = \sqrt{2}L_{e1}$, see (3.57) and (3.60). But, solution (3.64) has infinitely long "tails" in both directions, $x \to \pm\infty$.
5. Selecting the positive branch of (3.43), we may express the slope as a function of η:

$$\frac{d\eta_{e4}}{dx} = 2\frac{\Theta^2 - \Delta\eta_{e4}^2}{L_{e4}\Theta} > 0. \tag{3.66}$$

   The slope is a pulse-type function, which is essentially non-zero only on the interval of localization of heterogeneities.
6. Because the slope $(d\eta_{e4}/dx)$ does not depend on x explicitly (only through η) the solution must be translationally (with respect to the Euclidean group of spatial transformations) invariant: $\eta_{e4} = \text{func}(x - x_0)$ for arbitrary x_0. The translational invariance of the solution (3.64) was removed by setting $x_0 = x_i$.
7. We can show (Verify!) that

$$\frac{d^2\eta_{e4}}{dx^2} = -4\frac{\Delta\eta_{e4}}{L_{e4}\Theta}\frac{d\eta_{e4}}{dx}. \tag{3.67}$$

8. Using the mathematical formulae

$$\tanh(x) - \tanh(y) = \frac{\sinh(x-y)}{\cosh(x)\cosh(y)},$$
$$\frac{\mathrm{d}\tanh(x)}{\mathrm{d}x} = \frac{1}{\cosh^2(x)},$$

for solution (3.64) it is easy to show (Verify!) that

$$\eta_{e4}(x - \delta x) - \eta_{e4}(x) \approx -\delta x \frac{\mathrm{d}\eta_{e4}}{\mathrm{d}x}. \tag{3.68}$$

This relation shows that the difference between two slightly displaced solutions is equal to the shift times the slope of the unperturbed solution.

Furthermore, let us compute the free energy of the type-e4 state. Equation (3.46a) and Property 1 yield:

$$G_{e4} = Vg_{\alpha(\beta)} + S\int_{-\infty}^{+\infty} \kappa\left(\frac{\mathrm{d}\eta_{e4}}{\mathrm{d}x}\right)^2 \mathrm{d}x. \tag{3.69}$$

Compare this expression with (3.55a) and notice that G_{e4} separates into a term proportional to the volume V and the term proportional to the area S of the box, with the coefficients of proportionality independent of m and, hence, of X. This fact allows us to compare (3.69) with the free energy of the two-phase equilibrium system in the Theory of Capillarity [see Sect. 3.1, (3.1)–(3.6)] and identify the quantity:

$$\sigma \equiv \int_{-\infty}^{+\infty} \kappa\left(\frac{\mathrm{d}\eta_{e4}}{\mathrm{d}x}\right)^2 \mathrm{d}x \tag{3.70a}$$

as the interfacial energy of the system in the FTM. This expression shows that $\sigma > 0$, provided condition (3.26) is true. Notice that (3.70a) allows to interpret the Newmann-type BC, which we adopted in this book, as corresponding to the case of absence of the additional energy on the surface of the system.

The interfacial energy is an important quantity because it is measurable. This justifies more thorough analysis of expression (3.70a). Compare (3.27a) and (3.42a) with (3.70a) and see that other expressions for the interfacial energy are possible:

$$\sigma = \int_{-\infty}^{+\infty} (\hat{g} - \mu)\,\mathrm{d}x, \tag{3.70b}$$

$$\sigma = 2\int_{-\infty}^{+\infty} (g(P, T_E; \eta_{e4}) - \mu)\,\mathrm{d}x. \tag{3.70c}$$

Taking (3.37b) into account, we also find that

$$\sigma = -\int_{-\infty}^{+\infty} \eta_{e4} \frac{\partial g}{\partial \eta}(P, T_E; \eta_{e4})\, \mathrm{d}x. \tag{3.70d}$$

Using the positive branch of (3.43) we obtain another expression:

$$\sigma = \sqrt{2\kappa} \int_{\eta_\alpha}^{\eta_\beta} \sqrt{g(P, T_E; \eta_{e4}) - \mu}\, \mathrm{d}\eta. \tag{3.70e}$$

Compare (3.70e) to (D.27) and see that the interfacial energy is analogous to the abbreviated action from the Lagrangian field theory. This analogy will be addressed again in Chap. 6.

Example 3.1 Find relationships between the interfacial energy and the thermodynamic parameters for the systems with the general, Landau, and tangential potentials.

The best way to find this relationship for the general potential (2.38) is to use formula (3.70e). Then, we obtain the following relation:

$$\sigma = \sqrt{\frac{\kappa g''''_t}{12}} \int_{-\Theta}^{+\Theta} \sqrt{\left(\Theta^2 - \Delta\eta^2\right)^2}\, \mathrm{d}\Delta\eta = \frac{2}{3}\sqrt{2}\Xi l. \tag{3E.1}$$

Using the Landau potential (2.11) for (3.70e), we obtain the following relation:

$$\sigma = \sqrt{2\kappa} \int_0^{4B/3} \eta \left(\frac{2}{3}B - \frac{1}{2}\eta\right) \mathrm{d}\eta = \left(\frac{2}{3}\right)^4 \sqrt{2\kappa} B^3. \tag{3E.2}$$

For the tangential potential (2.33) first notice that, because the OP is rescaled compared to the OP of the Landau potential, the gradient-energy coefficient of the tangential potential must be rescaled too. From (3.27b), (2.32) we find that

$$\tilde{\kappa} = \kappa C^2. \tag{3E.3}$$

Then using (2.33) we find that for the tangential potential at equilibrium $|g''_t| = W/2$. Substituting this into (3.53b) and using (3.60) leads to

$$l = \sqrt{\frac{2\tilde{\kappa}}{W}}; \quad L_{e4} = 4\sqrt{\frac{\tilde{\kappa}}{W}}. \tag{3E.4}$$

Although the expression for the interfacial energy can be obtained from (3E.1), it is advantageous to derive it directly from (3.70e) using (2.33). Notice that the expression in (3.70e) is invariant to the rescaling (Why?). Then, taking into account that $\eta_\alpha = \bar{\eta}_0$, $\eta_\beta = \bar{\eta}_1$, we obtain:

$$\sigma = \sqrt{\tilde{\kappa} W} \int_0^1 \sqrt{\omega^2(\eta)}\, \mathrm{d}\eta = \frac{1}{6}\sqrt{\tilde{\kappa} W}. \tag{3E.5}$$

3.4.5 Interfacial Properties: Gibbs Adsorption Equation

The interfacial energy is an important property of a system, which deserves a closer look. At this juncture, we may ask a question: how many variables does the interfacial energy depend on? First, notice that σ can be defined properly only in the thermodynamic limit of $V \to \infty$ or at least $X \to \infty$ (dependence of the interfacial energy on the system's size is an important subject in its own rights, but we will not be looking at that in this book). At first glance, it seems that σ is a function of three variables: σ=func(P, T, μ). However, considering equilibrium conditions (3.42b), (3.65), (2.2), we find that not all of them are independent. If η_α and η_β represent different phases then five variables $(\eta_\alpha, \eta_\beta, P, T, \mu)$ are constrained by four conditions, which leave only one independent; if η_α and η_β represent the same phase then four variables are constrained by two conditions, which leave two variables independent. Thus, using (3.42b) and (3.70b) we obtain:

$$\mathrm{d}\sigma = D_T\sigma \cdot \mathrm{d}T + D_P\sigma \cdot \mathrm{d}P, \tag{3.71a}$$

where the partials of σ are

$$\begin{gathered} D_T\sigma = -\int_{-\infty}^{+\infty} (\hat{s} - s_\alpha)\,\mathrm{d}x; \\ \hat{s}(P,T,\eta) = -\frac{\partial \hat{g}}{\partial T}, \quad s_\alpha = -\frac{\partial \mu}{\partial T} = -\frac{\partial g}{\partial T}(P,T,\eta_\alpha). \end{gathered} \tag{3.71b}$$

$$\begin{gathered} D_P\sigma = \bar{\rho}\int_{-\infty}^{+\infty} (\hat{v} - v_\alpha)\,\mathrm{d}x \\ \hat{v}(P,T,\eta) = \frac{1}{\bar{\rho}}\frac{\partial \hat{g}}{\partial P}, \quad v_\alpha = \frac{1}{\bar{\rho}}\frac{\partial \mu}{\partial P} = \frac{1}{\bar{\rho}}\frac{\partial g}{\partial P}(P,T,\eta_\alpha); \end{gathered} \tag{3.71c}$$

where $\hat{s}$ is the entropy density, $\hat{v}$ is the specific volume, and $\bar{\rho} = M/V$ is the average density. If η_α and η_β represent the same phase then the partials represent the proper (that is non-diverging) quantities, the interfacial entropy and volume:

$$\chi \equiv -D_T\sigma, \quad v \equiv \frac{D_P\sigma}{\bar{\rho}}, \tag{3.72}$$

If η_α and η_β represent different phases, then according to the Clapeyron–Clausius equation (2.5)

$$[s]_\alpha^\beta\,\mathrm{d}T = \bar{\rho}[v]_\alpha^\beta\,\mathrm{d}P, \tag{3.73}$$

and:

$$\mathrm{d}\sigma = -\Gamma_s^{(v)}\,\mathrm{d}T, \tag{3.74a}$$

where the proper, non-diverging, quantity is the relative interfacial entropy:

$$\Gamma_s^{(v)} \equiv \int_{-\infty}^{+\infty} \left(\hat{s} - s_\alpha - (\hat{v} - v_\alpha) \frac{[s]_\alpha^\beta}{[v]_\alpha^\beta} \right) \mathrm{d}x. \tag{3.74b}$$

If density of the system does not change from one phase to another or is not essential for the problem, the relative interfacial entropy may be defined with respect to the OP:

$$\Gamma_s^{(\eta)} \equiv \int_{-\infty}^{+\infty} \left(\hat{s} - s_- - (\eta - \eta_-) \frac{[s]_-^+}{[\eta]_-^+} \right) \mathrm{d}x. \tag{3.74c}$$

Example 3.2 Find the fundamental length scale, interfacial energy, and entropy of the anti-phase domain boundary.

Anti-phase domain boundary (APB) is the type-e4 state that appears in the system after the second-order transition. Hence, the problem can be solved by using the Landau potential, (2.11), with $B = 0$ and $A < 0$, see Sect. 2.6.2, (2.43). Then, $\eta_t = 0$, $g_t'''' = 6$, and $g_t'' = A = a\tau$, where $\tau < 0$, which yields:

$$l = \sqrt{\frac{\kappa}{|A|}}, \quad \Theta = \sqrt{|A|}, \quad \Xi = |A|^2. \tag{3E.6}$$

For the interfacial energy, using (3E.1), we obtain:

$$\sigma = \frac{2}{3}\sqrt{2\kappa|A|^3} \tag{3E.7}$$

and for the interfacial entropy

$$\chi = \frac{1}{T_c}\sqrt{2\kappa|A|}. \tag{3E.8}$$

Notice that $\chi \gg \sigma T_C$ for $|\tau| \to 0$, that is, close to the LCP, (2.23). The type-e4 state is

$$\eta_{e4}(x) = \sqrt{|A|}\tanh\left(x\sqrt{|A|/2\kappa}\right). \tag{3E.9}$$

It is depicted in Fig. 3.4.

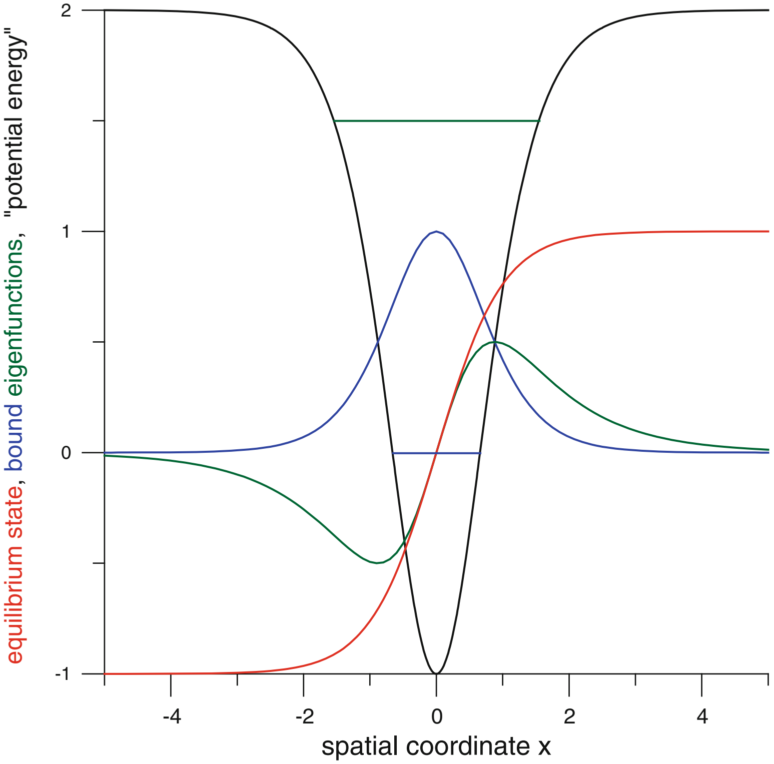


Fig. 3.4 Anti-phase domain boundary of the system with $A = -1$ and $\kappa = ½$. The equilibrium state η_{e4}, (3E.9)—*red line*, "potential energy" $\partial^2 g(\eta_{e4})/\partial\eta^2$ for this state—*black line*, and two bound eigenfunctions—*blue and green lines*. The two bound-eigenfunction energy levels are identified by the respective colors

3.4.6 Type-n4 Solution: Critical Plate—Instanton

Type-n states are more complicated; they appear when the condition (3.51a) does not hold and g'''_t becomes a measure of deviation from the phase equilibrium. The phase-plane method, however, may elucidate some of the properties of the type-n states in sufficient detail. Let us consider type-n4 state. Two comments are in order here. First, to preserve consistency with the analysis above, we will be analyzing the monotonic branch of the state. Second, it is more convenient here to use the Landau potential (2.11) instead of the general one (2.38). The relation between the two is established by (2.39), e.g.,

$$g_t''' = 2B - 6\sqrt{B^2 - A} < 0. \tag{2.39b}$$

The phase-plane method (see Fig. 3.2aii) suggests that $\eta_{\mathrm{n}4}(x)$ varies between $\eta_\alpha = 0$ and η_{c}^1 where:

$$\eta_c^1 = \frac{4}{3}B\left(1 - \sqrt{1 - \frac{9A}{8B^2}}\right). \tag{3.75}$$

Taking the integral in (3.44a), we obtain the full solution (see Fig. 3.2aiii):

$$x = \sqrt{\frac{\kappa}{A}}\left[\ln\sqrt{1 - \frac{9A}{8B^2}} - \ln\left|1 - \frac{3A}{2B\eta_{n4}}\left(1 + \sqrt{1 + \frac{3\eta_{n4}^2 - 8B\eta_{n4}}{6A}}\right)\right|\right]. \tag{3.76}$$

It has an inflection point at

$$\eta_t = \bar{\eta}_- = B - \sqrt{B^2 - A}. \tag{3.77a}$$

The characteristic length (3.48) of the solution $\eta_{n4}(x)$ is represented as follows:

$$L_{n4} = \frac{2\eta_c^1\sqrt{\kappa}}{\bar{\eta}_-\sqrt{2A - 4/3B\bar{\eta}_-}}. \tag{3.77b}$$

The "tail" of the solution in (3.76), that is, the part $0<\eta_{\mathrm{n}4}<<\bar{\eta}_-$, may be represented as $\eta_{\mathrm{n}4} \approx \mathrm{const} \times \exp(x/L_{4n})$. Notice that the characteristic length of the tail of $\eta_{\mathrm{n}4}(x)$ is different from that of $\eta_{\mathrm{e}4}(x)$ in (3.64). Another important length scale of this solution is the distance between the center (η_{c}^1) and inflection point ($\bar{\eta}_-$):

$$D_{n4} = \sqrt{\kappa}\int_{\bar{\eta}_-}^{\eta_c^1} \frac{d\eta}{\eta\sqrt{A - (4/3)B\eta + (1/2)\eta^2}}. \tag{3.78}$$

To calculate the free energy of the type-n4 state we use the Landau potential (2.11) for (3.46b) with $n_{\mathrm{n}4} = 1$ (Why?):

$$\begin{aligned} G_{n4} &= V\mu + S\sqrt{2\kappa}\int_0^{\eta_c^1} \sqrt{g(\eta) - \mu}\, d\eta \\ &= V\mu + S\sqrt{\kappa}\int_0^{\eta_c^1} \eta\sqrt{A - \frac{4}{3}B\eta + \frac{1}{2}\eta^2}\, d\eta \\ &= V\mu + S\sigma\left[3R - 2R^3 + \frac{3}{2}\left(1 - R^2\right)\ln\frac{1 - R}{1 + R}\right], \end{aligned} \tag{3.79a}$$

where

$$R = \frac{3\sqrt{A}}{2\sqrt{2}B} \tag{3.79b}$$

Notice that as $g'''_t \to 0$: $R \to 1$ and $G_{\mathrm{n}4} \to V\mu + S\sigma$.

Type-n4 represents a 1d pulse of ordering of one kind in the "sea" of ordering of another kind (e.g., β-solid in α-liquid). Notice from (3.42a) and Fig. 3.2 ai that the ordering of the "sea" is that of the metastable phase (e.g., liquid), while the ordering of the pulse comes close (although not quite there yet) to that of the stable phase (e.g., solid). For type-n4, the chemical potential, $\mu = g_{\alpha}$, corresponds to the critical value between the cases of general periodic distribution of ordering in the system and absence of the equilibrium states at all; that is why this case is called the *instanton*—a localized, critical, equilibrium excitation of the old phase with finite amount of the free-energy excess. Instanton is described by a homoclinic orbit while the kink—by the heteroclinic orbit (cf. Fig. 3.2aii and bii). In that regard, actually, (3.76) describes half-the-instanton; the whole instanton has $n_{n4} = 2$. Hence, as $R \to 1$ the total energy of the whole instanton approaches $V\mu + 2S\sigma$.

3.5 Free Energy Landscape

Various types of solutions of the 1d equilibrium boundary-value problem (3.39a) and (3.40) obtained above are in need of physical interpretation. The finite-domain solutions can be interpreted as the equilibrium states of a slab of the thickness X, while the infinite-domain solutions ($-\infty < x < +\infty$) are the equilibrium states in the thermodynamic limit, $X \to \infty$. In the infinite domain, there are periodic type-1,2,3, pulse type-n4, and kink type-e4 solutions. The periodic and pulse solutions are non-monotonic. For the periodic solution $\eta_{e2}(x)$, the right-hand side in (3.54a) describes the half-period D_{e2} and (3.45)—the index n_{e2} of the state. Type-e states correspond to the conditions of phase equilibrium, $T = T_E(P)$, when the free energies of the phases α and β are equal (see Fig. 3.2bi). For type-n states, the free energies of the homogeneous phases are different; hence, $T \neq T_E(P)$. Then, the type-e4 state can be interpreted as a two phase equilibrium state where the phases are separated by an interface and type-n4—as a 1d pulse of critical ordering (instanton).

At this stage, we have learned enough about our system to be able to understand the relationships between the physical parameters that control it. First, let us ask the question: What are the factors that may influence a state of the system $\eta_E(\boldsymbol{x})$, (3.31)? Obviously pressure P, temperature T, and the external field H do. In the previous section, we saw that the linear size X of the system's domain Ω makes a difference: the states may be finite, infinite, or semi-infinite. A less obvious factor that may change the equilibrium state is the type of the boundary conditions on the surface of the system. The latter becomes less important in the thermodynamic limit, $X \to \infty$.

In a laboratory experiment, all of the above mentioned parameters can be altered more or less independently including the dimensionality and boundary conditions. The former can be changed by preparing the samples of different shapes; the latter by changing the interaction of the system with the environment (e.g., lubricating the surface). However, the pressure P, temperature T, and system's size X are the most flexible control parameters of the system; they constitute the thermodynamic degrees of freedom of the system.

As we saw in the previous sections, there is one more parameter that influences the equilibrium states of the system: the chemical potential μ. At first glance, the chemical potential is independent of the other parameters and, hence, constitutes a thermodynamic degree of freedom. However, this perception is false. The crux of the matter is that an important factor, *stability* of the solutions, has not been taken into account yet. In the oncoming sections, we see that the stability considerations present a selection criterion for the equilibrium states. That is, when all the thermodynamic degrees of freedom are specified a unique value of the chemical potential μ will be selected based on the principle of the minimum of the free energy.

A geometrical concept of the *free energy landscape* may help us visualize distribution of the equilibrium states $\eta_E(\mathbf{x})$ in the Hilbert space $\{\eta(\mathbf{x})\}$. The free energy landscape is the "elevation" of the functional $G\{P, T, H, V, d, \mathrm{BC}; \eta(\mathbf{x})\}$, (3.27a), with respect to an arbitrary "sea" level. The extremals are the stationary points of the landscape: minima, maxima, and saddle points. How can we visualize the "real estate" of the infinite-dimensional functional space $\{\eta(\mathbf{x})\}$ over which the landscape will be constructed? This space consists of functions, which are continuous enough (usually continuous are first two partial derivatives) and satisfy the BC, e.g., (3.30b). Then the free energy functional $G\{\eta(\mathbf{x})\}$, (3.27a), may be viewed as a *hypersurface* in the functional space $\{\eta(\mathbf{x})\}$. Each element $\{\eta(\mathbf{x})\}$ is characterized by five numbers, see (3.32), (3.45). Then, each element of $\{\eta(\mathbf{x})\}$ may be represented by a point in the 4-space ($<\eta>+\Pi$, Λ, Σ, n) and the landscape will be the hypersurface over that space:

$$G = G\{\langle\eta\rangle + \Pi,\ \Lambda,\ \Sigma,\ n\}. \tag{3.80a}$$

Notice that in (3.80a) there is no explicit dependence on the system's size; it enters (3.80a) implicitly through the relationship between the range, slope, and index. Using this geometrical image, one can formulate a better idea about the equilibrium states and their stability. The equilibrium states are represented by the extremals $\eta_E(\mathbf{x})$, (3.31); they correspond to minima, maxima, or saddle points of the hypersurface (3.80a). The former means that some small deviations from the extremal $\eta_E(\mathbf{x})$ make the functional to increase while others to decrease.

We may start constructing the landscape (3.80a) with the 1d type-e monotonic states with different values of the chemical potential μ. For the landscape-dependent coordinate, we use j, see (3.56b). As $\Sigma_e = 0$ and $n_{1d} = 1$ [see (3.45, 3.51b)], we may reduce the number of the real-estate independent coordinates to two: the dimensionless slope λ and size ($<\eta>$ + N), which, for convenience, is shifted by η_t and scaled with Θ:

$$y = \frac{1}{\Theta}\left(\langle\eta\rangle + N - \eta_t\right) \tag{3.80b}$$

To visualize the landscape, we are depicting it in Fig. 3.5 and projections of its characteristic lines on the planes (y, j) and (y, λ) in Fig. 3.5a. For the homogeneous elements $\{\eta(\mathbf{x})\}$ N = 0 = Λ; they are represented by the red line.

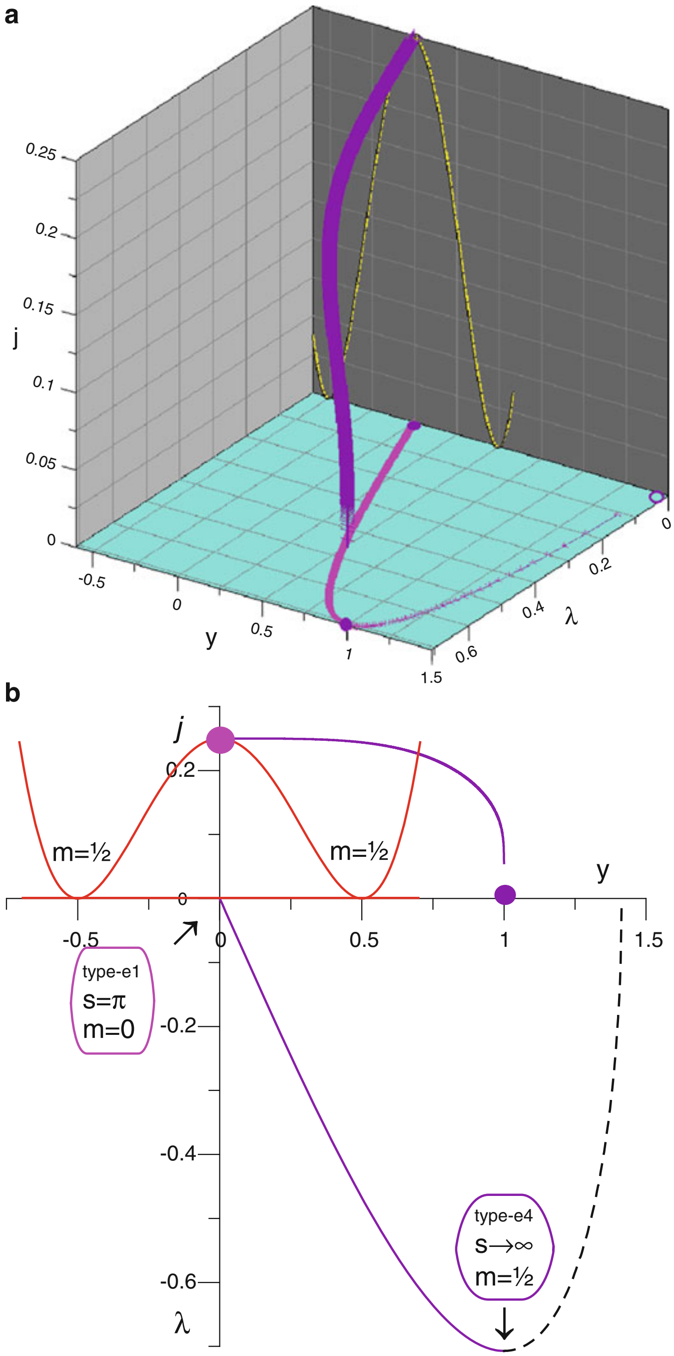


Fig. 3.5 Free energy landscape of the 1d system, $j = \text{func}(y, \lambda)$. (**a**) Projections of the free energy landscape on the planes (y, j) and (y, λ)

For the homogeneous equilibrium states $<\eta>=\eta_\alpha$ or η_t or η_β, hence, $y = -0.5$ or 0 or +0.5. For the heterogeneous equilibrium states $\mathrm{N}\neq 0\neq \Lambda$ and $<\eta>=\eta_t$, see (3.51b), and y equals a of (3.56). Then, (3.56a) expresses the projection of the line of the extremals on the plane (y, λ) and (3.53)–(3.55) on the plane (y, j). The dimensionless forms of these relations are

$$\lambda = y\sqrt{1-\frac{1}{2}y^2}, \tag{3.81a}$$

$$j = \frac{1}{4}(1-y^2) + \frac{1}{3}(2-y^2)\left[y^2 - 1 + \frac{E\left(y\big/\sqrt{2-y^2}\right)}{K\left(y\big/\sqrt{2-y^2}\right)}\right]. \tag{3.81b}$$

3.6 Multidimensional Equilibrium States

In the previous sections, we analyzed properties of the 1d equilibrium states. We may wonder now if the free-energy landscape of a thermodynamic system $G\{\eta(\mathbf{x})\}$, (3.80a), contains multidimensional equilibrium states, that is those where essential variations take place in more than one spatial direction. In fact it does and, actually, "many" (infinitely many); it is more difficult to find the multidimensional equilibrium states than the 1d ones. However, some of the multidimensional states have structures similar to those of the plane ones studied in Sect. 3.4—quasi-1d states (Sect. 3.6.1), others have spherical symmetry, which helps treating them rigorously (Sect. 3.6.2). In Sect. 3.6.3, we demonstrate how one can find multidimensional equilibrium states which can be thought of as small deviations from one of the homogeneous states, $\bar{\eta}$, studied in Chap. 2.

3.6.1 Quasi One-Dimensional States: Drumhead (Sharp Interface) Approximation

As we saw in Sect. 3.4.4, a heterogeneous equilibrium state is possible where the OP changes quickly from one bulk-phase value to another one in a plain transition zone, called interface, while remaining practically constant or changing very slowly outside this zone. This result should prompt us to search for geometrically more complicated equilibrium states that are represented by a thin transition layer where most of the OP change occurs, which, on the "outside", may have rather complicated geometrical shape, see Fig. 3.6. To find such multidimensional states, we shall introduce, instead of the Cartesian coordinates $\mathbf{x} = (x_1, x_2, x_3)$, new curvilinear coordinates $\{u = U(\mathbf{x}),\ v = V(\mathbf{x}),\ w = W(\mathbf{x})\}$ (see Appendix C). The main requirements to the new coordinates are that they are orthogonal and that the OP is a function of one coordinate only: $\eta=\eta(u)$. To eliminate the remaining arbitrariness

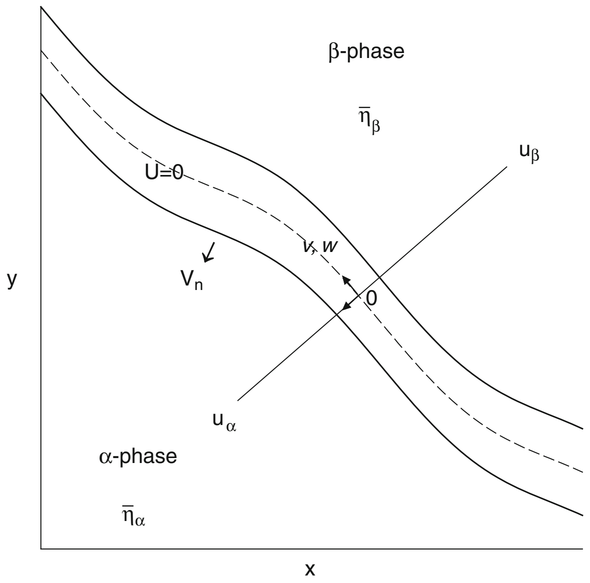


Fig. 3.6 Curvilinear coordinate system (u, v, w) associated with a curved interface. V_n—velocity of the interface motion

of the new curvilinear coordinates, we assume that the coordinate $u = U(\mathbf{x})$ obeys the eikonal equation everywhere:

$$(\nabla U)^2 = 1, \tag{C.16}$$

and we specify the level surface $U = 0$ as follows:

$$\frac{\mathrm{d}^2\eta}{\mathrm{d}u^2}(0) = 0. \tag{3.82}$$

Then, according to (3.39a), the level surface $U = 0$ corresponds to one of the equilibrium values of the OP, $\bar{\eta}$.

The level surfaces $U = \text{const}$ may be characterized by a unit normal vector:

$$\mathbf{u} \equiv \frac{\nabla\eta}{|\nabla\eta|} = \frac{1}{|\nabla\eta|}\left(\frac{\partial\eta}{\partial x_1}\mathbf{j}_1, \frac{\partial\eta}{\partial x_2}\mathbf{j}_2, \frac{\partial\eta}{\partial x_3}\mathbf{j}_3\right). \tag{C.11}$$

The unit normal $\mathbf{u}$ is invariant with respect to the rotation of the reference frame (see Appendix C). Then the curved interface may be represented by the direction cosines of $\mathbf{u}$ or by the Euler angles of inclination θ_{ij} with respect to the coordinate axis, see (C.12):

$$\tan\theta_{ij} = \frac{\partial\eta/\partial x_i}{\partial\eta/\partial x_j} = \frac{\partial u/\partial x_i}{\partial u/\partial x_j}. \tag{3.20b}$$

The unit normal **u** has many practical applications; for instance, it may be used to express the anisotropic properties of the interface, e.g., anisotropy of the interfacial energy.

Another way to characterize the curved surfaces is by describing their curvature K or radius of curvature R as a function of the curvilinear coordinates. Using the formula

$$\nabla \mathbf{u} = 2K(u, v, w) = k_1 + k_2, \tag{C.21}$$

where K is the mean curvature and k_1, k_2 are the principal curvatures of the level surface $U = \text{const}$ and expressing the Laplacian operator in the new coordinates:

$$\nabla^2 = \frac{\partial^2}{\partial u^2} + 2K(u, v, w)\frac{\partial}{\partial u}. \tag{C.23}$$

ELE (3.29) transforms as follows:

$$\kappa\frac{\mathrm{d}^2\eta}{\mathrm{d}u^2} + 2\kappa K(u, v, w)\frac{\mathrm{d}\eta}{\mathrm{d}u} - \frac{\partial g(T, \eta)}{\partial \eta} = 0. \tag{3.83}$$

The level surfaces $U = \text{const}$ are equidistant; hence the radius of curvature of these surfaces is $R = R_0(v, w) + u$. Then for the mean curvature we obtain:

$$\frac{1}{R(u, v, w)} \equiv K = K_0\left\{1 + uK_0 + u^2K_0^2 + O(u^3K_0^3)\right\}, \tag{3.84}$$

where $R_0(v, w)$ and $K_0(v, w)$ are the radius and the curvature of the level surface $U = 0$. In Sect. 3.4, we saw, (3.64), that L_{e4} is the characteristic length of variation of the OP field of the equilibrium state. Then, if:

$$Ge \equiv 2|K_0|L_{e4} << 1, \tag{3.85}$$

then (3.83) can be rewritten in the form:

$$\kappa\frac{\mathrm{d}^2\eta}{\mathrm{d}u^2} + 2\kappa K_0\frac{\mathrm{d}\eta}{\mathrm{d}u} - \frac{\partial g(T, \eta)}{\partial \eta} = 0, \tag{3.86}$$

where the coordinates u and (v, w) separate. This equation is the *drumhead* (or *sharp interface*) approximation of the ELE (3.29) and the smallness of the number Ge, called *geometric*, is the criterion of its validity. Geometrically, this means that the level surface $U = 0$ does not have very sharp folds with the radii of curvature on the scale of the interfacial thickness.

As we can see from (3.86), if the 3d equilibrium state η_E has the same internal structure as the 1d one, that is, the first and third terms add up to zero, then the mean curvature K_0 is zero everywhere. In two dimensions, this is possible only for a plain interface. In three dimensions, the mean curvature of a curved surface can be zero if the two principal curvatures at a point of the surface are equal in magnitude but of opposite sign:

$$k_1(0,v,w) = -k_2(0,v,w). \tag{3.87}$$

It is possible to construct a surface that has zero mean curvature everywhere by translating a specially designed unit cell. Such surfaces are termed “periodic minimal surfaces.”

3.6.2 Critical Droplet: 3d Spherically Symmetric Instanton

The mathematical complexity of the 3d states comes from the fact that ELE (3.29) cannot be integrated, that is, there are no first integrals that describe equilibrium for $d > 1$. However, for an isotropic system, some of the extremals may have very simple symmetry: cylindrical for $d = 2$ and spherical for $d = 3$. In a cylindrically/spherically symmetric system, the divergence operator takes the form (Appendix C):

$$\nabla^2 = \frac{\mathrm{d}^2}{\mathrm{d}r^2} + \frac{d-1}{r}\frac{\mathrm{d}}{\mathrm{d}r}, \tag{C.26}$$

where r is the spatial coordinate. The singular point $r = 0$ is called a *center* and

$$\eta_c^d \equiv \eta_E(r=0). \tag{3.88}$$

Then ELE (3.29) takes the form:

$$\kappa\left(\frac{d^2\eta}{dr^2} + \frac{d-1}{r}\frac{\mathrm{d}\eta}{\mathrm{d}r}\right) - \frac{\partial g}{\partial \eta} = 0. \tag{3.89}$$

Notice that this form also applies to a $d = 1$ system with translation invariance. Formally, it can also be applied to a $d \geq 4$ system and even to systems with fractional dimensionalities.

A physically acceptable solution has to be continuous everywhere. Thus, to avoid discontinuity at the center, the cylindrically/spherically symmetric solutions have to satisfy the following boundary condition:

$$\frac{\mathrm{d}\eta}{\mathrm{d}r} = 0 \quad \text{at } r = 0. \tag{3.90}$$

If the boundary Ω of the system is also cylindrically/spherically symmetric then (see Appendix C):

$$\mathbf{j}_\Omega = \mathbf{j}_r = \frac{\mathbf{r}}{|\mathbf{r}|}; \quad \mathbf{j}_r \nabla = \frac{\mathrm{d}}{\mathrm{d}r} \text{ on } \Omega.$$

In the thermodynamic limit, the boundary condition, (3.30b), takes the form:

$$\frac{\mathrm{d}\eta}{\mathrm{d}r} \to 0 \quad \text{at } r \to \infty. \tag{3.91}$$

One of the goals of this section is to look at the process of α → β transformation from the metastable into the stable phase of the system and compare the solutions of (3.89)–(3.91) with those of the Theory of Capillarity. The solution that we are looking for, $\eta_\mathrm{E}(r;\, \mathrm{d})$, represents a critical nucleus (instanton), that is, a localized heterogeneity in the "sea" of a homogeneous metastable phase. Thus, the third boundary condition appears:

$$\eta_E \to \eta_\alpha \quad \text{at} \quad r \to \infty \tag{3.92}$$

where η_α corresponds to the metastable phase. For $d = 1$, the nucleus has a shape of a plate, $d = 2$—a cylinder, and for $d = 3$ the nucleus is a sphere with r representing the distance from the center.

Equation (3.89) is known in the literature as a generalized Emden equation [6]. If $g(\eta)$ is a single-well parabolic function, its solution is a Bessel equation of the zeroth order. If $g(\eta)$ is a double-well function, like in (2.11) or (2.33), (3.89) is not known to have a general solution which can be expressed through elementary or special functions in a closed form. Solutions of the special cases that possess the Painlevé property (not to have movable singularities other than poles) can be expressed in quadratures.

The boundary-value problem (3.89)–(3.92) can be qualitatively analyzed using the phase-plane $(\eta, \mathrm{d}\eta/\mathrm{d}r)$. The critical nucleus solution is not a regular trajectory in the plane but a separatrix because there are three boundary conditions for a second-order ODE. Some of the properties of the critical nucleus can be deduced from the general properties of the ELE (3.89) and function $g(\eta)$ [7]. Indeed, if we multiply all terms in (3.89) by $(\mathrm{d}\eta/\mathrm{d}r)$ and integrate from r to ∞ we obtain:

$$\kappa \int_r^\infty \frac{\mathrm{d}^2\eta}{\mathrm{d}r^2}\frac{\mathrm{d}\eta}{\mathrm{d}r}\,\mathrm{d}r + \kappa(d-1)\int_r^\infty \frac{1}{r}\left(\frac{\mathrm{d}\eta}{\mathrm{d}r}\right)^2 \mathrm{d}r - \int_r^\infty \frac{\partial g}{\partial \eta}\frac{\mathrm{d}\eta}{\mathrm{d}r}\mathrm{d}r = 0. \tag{3.93}$$

Taking the BC, (3.91) and (3.92), into account we obtain [cf. with (3.42a)]:

$$-g(P,T;\eta_\alpha) = -g(P,T;\eta) + \frac{1}{2}\kappa\left(\frac{\mathrm{d}\eta}{\mathrm{d}r}\right)^2 - \kappa(d-1)\int_r^\infty \frac{\mathrm{d}r'}{r'}\left(\frac{\mathrm{d}\eta}{\mathrm{d}r'}\right)^2. \tag{3.94}$$

This relation shows that $g(P,T;\eta_\alpha)$ plays the role of the chemical potential for this type of states. Applying this relation at the center of the critical nucleus and using the BC, (3.90), we obtain:

$$\begin{aligned} g(P,T,\eta_c^d) - g(P,T,\eta_\alpha) &= -\kappa(d-1)\int_0^\infty \frac{1}{r}\left(\frac{\mathrm{d}\eta}{\mathrm{d}r}\right)^2 \mathrm{d}r \\ &= \kappa(d-1)\int_{\eta_\alpha}^{\eta_c^d} \frac{1}{r}\frac{\mathrm{d}\eta}{\mathrm{d}r}\,\mathrm{d}\eta. \qquad (3.95) \end{aligned}$$

1. From (3.95), we can see that $g(\eta_c^1) = g(\eta_\alpha)$ and $g(\eta_c^{d>1}) < g(\eta_\alpha)$, which means (see Fig. 3.2ai) that

$$\eta_\alpha < \eta_t < \eta_c^1 < \eta_c^{d>1} < \eta_\beta. \qquad (3.96)$$

From this inequality follows that the critical nuclei of the anti-phase domains are not possible because for this transition $g(\eta_\alpha) = g(\eta_\beta)$ (see Sect. 2.6.2).

2. Equation (3.95) also indicates that for $d \to \infty$: ${\eta_c}^d \to \eta_\beta$ because $g({\eta_c}^d) - g(\eta_\alpha)$ becomes more negative as $d \to \infty$. Indeed, the integral in (3.95) decreases with $d \to \infty$ but not as "fast" as $(d-1) \to \infty$.
3. If $T \to T_E(P)$ then $g(\eta_\beta) \to g(\eta_\alpha)$ and ${\eta_c}^d \to \eta_\beta$. This follows from the inequality (3.96) and the fact that ${\eta_c}^1 \to \eta_\beta$ as $g(\eta_\beta) \to g(\eta_\alpha)$ (see Fig. 3.2bi).
4. If $T \to T_E(P)$, the spatial distribution of OP becomes similar to that described by the 1d equation (3.39a) instead of (3.89). Indeed, as the critical nucleus represents the separatrix in the plane $(\eta,\ \mathrm{d}\eta/\mathrm{d}r)$, the derivative $(\mathrm{d}\eta/\mathrm{d}r)$ does not change sign in the entire domain $0 < r < \infty$ [$\mathrm{d}\eta/\mathrm{d}r < 0$ in the above considered case of $\alpha \to \beta$ transformation; cf. to the monotonic branch of (3.43)]. Then, the "multi-dimensional" term in (3.89) can be neglected, compared to the two other terms which alternate, because the former cannot balance the latter. Basically, as $T \to T_E(P)$, the critical nucleus of the field theory tends to look more like that in the Theory of Capillarity, that is, a sphere (cylinder) of the phase β in the "sea" of phase α separated by the sheath of interface; the only difference of that from the plane one is its curvature.

Now let us use the fact that $(\mathrm{d}\eta/\mathrm{d}r)^2$ is a bell-like, sharply peaked function of r that reaches maximum in $0 < r < \infty$ (cf. Fig. 3.4) and define R_d:

$$\frac{\mathrm{d}^2\eta}{\mathrm{d}r^2}(R_d) = 0. \qquad (3.97)$$

Applying the Laplace method of asymptotic expansion [8] to slowly varying functions of r, $F(r)$, and $H(r)$, we obtain:

$$\int_0^\infty \mathrm{d}r F(r)\left(\frac{\mathrm{d}\eta}{\mathrm{d}r}\right)^2 \approx F(R_d)\int_0^\infty \mathrm{d}r\left(\frac{\mathrm{d}\eta}{\mathrm{d}r}\right)^2, \qquad (3.98a)$$

$$\int_0^\infty \mathrm{d}rH(r)\int_r^\infty \mathrm{d}r'F(r')\left(\frac{\mathrm{d}\eta}{\mathrm{d}r'}\right)^2 \approx \int_r^\infty \mathrm{d}rF(r)\left(\frac{\mathrm{d}\eta}{\mathrm{d}r}\right)^2 \int_0^{R_d} \mathrm{d}rH(r). \tag{3.98b}$$

Then, replacing the lower limit of integration in (3.98a) with $(-\infty)$ and using the definition of the surface energy, (3.70a), we obtain from (3.95):

$$R_d = \frac{(d-1)\sigma}{g(\eta_\alpha) - g(\eta_c^d)}. \tag{3.99}$$

The distance R_d defined by (3.97) may be called a d-dimensional radius of the critical nucleus. In the limit $T \to T_\mathrm{E}(P)$ and $d = 3$ this expression corresponds to (3.14) for the critical nucleus R_* in the Theory of Capillarity because $g(\eta_c^d) \to g(\eta_\beta)$, but $R_3 > R_*$ if the difference $(T_\mathrm{E}-T)$ grows. Resolving (2.4c) for $L = \mathrm{const}(T)$ [see (2.40b), (2.40c)] and using it for (3.99) we obtain

$$R_d = \frac{d-1}{T_E - T}\frac{\sigma T_E}{L}, \tag{3.100}$$

which shows that $R_d \to \infty$ not only if $T \to T_\mathrm{E}(P)$ but also if $d \to \infty$ for $T = \mathrm{const}$.

Let us now introduce the total free energy *excess* due to the presence of the critical nucleus in a previously homogeneous phase α:

$$\Delta G_\mathrm{cn} \equiv \mathrm{G}\{T, P, \eta_E(\mathbf{r})\} - g(T, P, \eta_\alpha)V, \tag{3.101a}$$

$$= \int_V \left[g(T, P, \eta) + \frac{1}{2}\kappa(\nabla\eta)^2 - g(T, P, \eta_\alpha)\right] \mathrm{d}^d x. \tag{3.101b}$$

Substituting (3.94) into (3.101a) and taking into account that

$$\begin{gathered} \mathrm{d}^d x = \mathrm{d}V_d = S_d(r)\,\mathrm{d}r; \\ S_d(r) = 2\pi(d-1)r^{d-1}; \quad V_d(r) = 2\pi\frac{d-1}{d}r^d; \end{gathered} \tag{3.102}$$

where S_d and V_d are surface and volume of the d-dimensional sphere, we obtain an expression for the free energy excess of the d-dimensional, spherically symmetric critical nucleus:

$$\Delta G_{cn} = \int_0^\infty \mathrm{d}rS_d(r)\left[\kappa\left(\frac{d\eta}{dr}\right)^2 - (d-1)\int_0^\infty \frac{dr'}{r'}\kappa\left(\frac{\mathrm{d}\eta}{\mathrm{d}r'}\right)^2\right]. \tag{3.103a}$$

Again, using (3.98a), (3.98b) with the lower limit of integration replaced by $(-\infty)$ and the definition of the surface energy, (3.70a), we obtain:

$$\Delta G_{cn} = \sigma \left[S_d(R_d) - (d-1) \frac{V_d(R_d)}{R_d} \right] = \frac{1}{d} \sigma S_d(R_d). \tag{3.103b}$$

This expression corresponds to the free energy excess ΔG_*, (3.17), due to the 3d critical nucleus in the Theory of Capillarity. It also shows that the solution $\eta_E(r; \mathrm{d})$ indeed represents a d-dimensional instanton because it corresponds to the final amount of the free energy excess.

When the approximation of sharply peaked function $(\mathrm{d}\eta/\mathrm{d}r)^2$ is not valid, the free-energy excess of the critical nucleus, (3.101a), may be efficiently calculated using expression (3.38a) for the free energy:

$$\Delta G_{cn} = 2(d-1)\pi \int_0^\infty \left[g(T, P, \eta) - g(T, P, \eta_\alpha) - \frac{1}{2} \eta \frac{\partial g}{\partial \eta} \right] r^{(d-1)} \, \mathrm{d}r. \tag{3.104a}$$

Notice that the Newmann-type BC (3.91) is already accounted for in the expression (3.38a). For the Landau potential, (2.11), we obtain the following expression

$$\Delta G_{cn} = \pi(d-1) \left(\frac{2}{3} B I_3^d - \frac{1}{2} I_3^d \right), \tag{3.104b}$$

where we introduce the d-dimensional *n*th order moments of the OP distribution

$$I_n^d = \int_0^\infty \eta^n r^{d-1} \, \mathrm{d}r. \tag{3.105}$$

These moments may help us calculate many different quantities related to the critical nucleus. For instance, as the radius of the nucleus is not well defined now and $(\mathrm{d}\eta/\mathrm{d}r)^2$ is not sharply peaked, the volume of the nucleus may be defined as follows

$$\begin{aligned} V_{cn} &= \frac{1}{\eta_\beta - \eta_\alpha} \int_V (\eta - \eta_\alpha) \mathrm{d}^d x \\ &= \frac{1}{\eta_\beta - \eta_\alpha} \int_0^\infty S_d(r) \eta \, \mathrm{d}r = \frac{2\pi(d-1)}{\eta_\beta - \eta_\alpha} I_1^d. \end{aligned} \tag{3.106}$$

The moments I_n^d may be estimated analytically or calculated numerically using numeric solution of the boundary-value problem (3.89)–(3.92).

Example 3.3 Find the instantons of the tangential potential.

For the tangential potential, (2.33), the space coordinate r can be scaled as follows:

$$\tilde{r} = r\sqrt{\frac{W}{\kappa}} \tag{3E.10}$$

and the boundary-value problem, (3.89)–(3.92), takes the form:

$$\frac{\mathrm{d}^2\eta}{\mathrm{d}\tilde{r}^2} + \frac{d-1}{\tilde{r}}\frac{\mathrm{d}\eta}{\mathrm{d}\tilde{r}} + 2\eta(\eta - \eta_t)(1-\eta) = 0, \tag{3E.11}$$

$$\frac{\mathrm{d}\eta}{\mathrm{d}\tilde{r}} = 0 \quad \text{at } \tilde{r} = 0, \tag{3E.12}$$

$$\frac{\mathrm{d}\eta}{\mathrm{d}\tilde{r}} \to 0,\ \eta \to 0 \quad \text{at } \tilde{r} \to \infty, \tag{3E.13}$$

Notice that in the scaled form the problem has only one external parameter—the transition state OP:

$$\eta_t = \frac{1}{2} + 3\frac{D}{W}. \tag{2.37}$$

The 1d instanton solution can be obtained analytically similar to (3.76):

$$\begin{aligned}\tilde{r}\sqrt{2\eta_t} = \ln&\left|\frac{6\eta_t}{1+\eta_t - \sqrt{(1/2-\eta_t)(2-\eta_t)}} - \frac{4}{3}(1+\eta_t)\right| \\ &- \ln\left|4\frac{\eta_t + \sqrt{\eta_t[\eta_t - 2/3(1+\eta_t)\eta + (1/2)\eta^2]}}{\eta} - \frac{4}{3}(1+\eta_t)\right|.\end{aligned} \tag{3E.14}$$

For $d > 1$ and $\eta_t \ll 0.5$, the OP in (3E.11)–(3E.13) can be scaled as $\tilde{\eta} = \eta/\eta_t$ and the problem can be reduced to the universal (parameterless) form (Verify!). For η_t not small (~0.5), the instanton solution can be obtained numerically using the shooting method. According to this method, we pick a test value of η_c^d, present the solution as

$$\eta = \eta_c^d - \eta_c^d(\eta_c^d - \eta_t)(1-\eta_c^d)\frac{\tilde{r}^2}{d}; \quad 0<\tilde{r} \le \delta<<1, \tag{3E.15}$$

(Why?) and solve (3E.11) numerically for $\tilde{r}>>1$. If the solution satisfied the BC (3E.13) to the desired accuracy, it is declared a success; if not, the test value is adjusted and the numerical run is repeated until the BC (3E.13) is satisfied. In Fig. 3.7, the solutions for $d = 1, 2, 3$ are presented as functions of $\tilde{r}$.

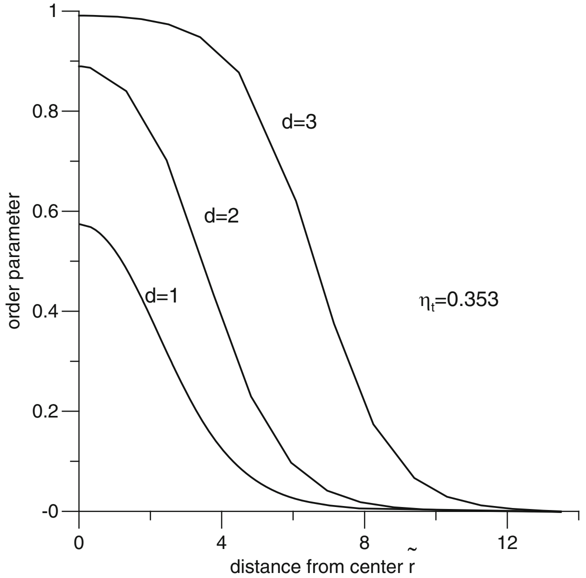


Fig. 3.7 Instantons of the tangential potential with $\eta_t = 0.353$ and different dimensionalities of the space d. For $d = 1$, the solution is (3E.14); for $d = 2, 3$, the solutions are numerical

3.6.3 Small Deviations from Homogeneous Equilibrium States: Fourier Method

Let us look for an equilibrium state $\eta_{\mathrm{E}}(\mathbf{x})$, which on average is equal to $\bar{\eta}$, that is:

$$\langle \eta_E \rangle = \bar{\eta}; \quad \Delta\eta(\mathbf{x}) \equiv \eta_E(\mathbf{x}) - \bar{\eta}. \tag{3.107}$$

Applying the equilibrium integral equations (3.37b) and (3.35), we obtain:

$$\int_V [\kappa(\nabla\Delta\eta)^2 + \frac{\partial g}{\partial \eta}(\eta_E)\Delta\eta]\,\mathrm{d}\mathbf{x} = 0. \tag{3.108a}$$

Expanding $\partial g/\partial\eta$ about $\bar{\eta}$ and taking into account (2.12), we obtain:

$$\begin{aligned}\int_V &[\kappa(\nabla\Delta\eta)^2 + \frac{\partial^2 g}{\partial \eta^2}(\bar{\eta})(\Delta\eta)^2 \\ &+ \frac{1}{2}\frac{\partial^3 g}{\partial \eta^3}(\bar{\eta})(\Delta\eta)^3 + \frac{1}{6}\frac{\partial^4 g}{\partial \eta^4}(\bar{\eta})(\Delta\eta)^4 + \cdots]\,\mathrm{d}\mathbf{x} = 0.\end{aligned} \tag{3.108b}$$

Equation (3.108b) may be analyzed using the method of Fourier transform (Appendix F). For this let us present $\Delta\eta(\mathbf{x})$ in the form of a Fourier series:

$$\Delta\eta(\mathbf{x}) = \frac{1}{\sqrt{V}} \sum_{\{\mathbf{k}\}} \Delta\hat{\eta}_{\mathbf{k}} \mathrm{e}^{i\mathbf{kx}}, \tag{3.109a}$$

where $\mathbf{k} = (k_x, k_y, k_z)$ is a separation parameter called *wave vector*. In a parallelepiped with the sides (X, Y, Z) and volume $V = XYZ$, $\mathbf{k}$ has the following components

$$\mathbf{k} = \left(\frac{\pi n_x}{X}, \frac{\pi n_y}{Y}, \frac{\pi n_z}{Z}\right), \; n_j \text{ integers}, \quad j = x, y, z. \tag{3.109b}$$

The summation in (3.109a) is over all integral-number combinations (n_x, n_y, n_z). $\Delta\hat{\eta}_{\mathbf{k}}$ are called the Fourier coefficients of $\Delta\eta(\mathbf{x})$ and can be found as:

$$\Delta\hat{\eta}_{\mathbf{k}} = \frac{1}{\sqrt{V}} \int\limits_V \Delta\eta(\mathbf{x}) \mathrm{e}^{-i\mathbf{k}\mathbf{x}}\, d\mathbf{x}. \tag{3.110}$$

Due to the condition (3.107), the $\mathbf{k} = \mathbf{0}$ Fourier mode of $\Delta\eta(\mathbf{x})$ vanishes:

$$\Delta\hat{\eta}_{\mathbf{0}} = 0 \tag{3.111}$$

If the OP field $\eta(\mathbf{x})$ is represented by real numbers (fields of different mathematical origin will be considered in Sect. 8.2) then, as you can see from (3.110), the Fourier coefficients of the opposite wave vectors $\mathbf{k}$ are complex conjugate:

$$\Delta\hat{\eta}_{-\mathbf{k}} = \Delta\hat{\eta}^*_{\mathbf{k}}. \tag{3.112}$$

Using the Fourier representation, we can express the gradient of $\Delta\eta(\mathbf{x})$ as

$$\nabla\Delta\eta(\mathbf{x}) = \frac{i}{\sqrt{V}} \sum_{\{\mathbf{k}\}} \mathbf{k}\Delta\hat{\eta}_{\mathbf{k}} \mathrm{e}^{i\mathbf{k}\mathbf{x}}. \tag{3.113}$$

Substituting (3.109a) and (3.113) into (3.108b) we obtain:

$$\begin{aligned} 0 = &\sum_{\{\mathbf{k}\}} \left[\kappa|\mathbf{k}|^2 + \frac{\partial^2 g}{\partial\eta^2}(\bar{\eta})\right] |\Delta\hat{\eta}_{\mathbf{k}}|^2 \\ &+ \frac{1}{2\sqrt{V}} \frac{\partial^3 g}{\partial\eta^3}(\bar{\eta}) \sum_{\{\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3=0\}} \Delta\hat{\eta}_{\mathbf{k}_1}\Delta\hat{\eta}_{\mathbf{k}_2}\Delta\hat{\eta}_{\mathbf{k}_3} \\ &+ \frac{1}{6V} \frac{\partial^4 g}{\partial\eta^4}(\bar{\eta}) \sum_{\{\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3+\mathbf{k}_4=0\}} \Delta\hat{\eta}_{\mathbf{k}_1}\Delta\hat{\eta}_{\mathbf{k}_2}\Delta\hat{\eta}_{\mathbf{k}_3}\Delta\hat{\eta}_{\mathbf{k}_4} + \cdots \end{aligned} \tag{3.114}$$

In the summations of the third and fourth order of the Fourier coefficients, the sums of the wave vectors add up to zero because

$$\int\limits_V \mathrm{e}^{i\mathbf{k}\mathbf{x}}\, d\mathbf{x} \to (2\pi)^3 \delta(\mathbf{k}), \quad \text{as } V \to \infty. \tag{F.10}$$

On the boundaries of the system, $\mathbf{x} = (0 \text{ or } X, y, z)$, $\mathbf{j}_\Omega=(\pm 1, 0, 0)$ or $\mathbf{x} = (x, 0 \text{ or } Y, z)$, $\mathbf{j}_\Omega=(0, \pm 1, 0)$ or $\mathbf{x} = (x, y, 0 \text{ or } Z)$, $\mathbf{j}_\Omega=(0, 0, \pm 1)$. Then, to satisfy the boundary conditions (3.30b), the Fourier coefficients must obey the following relationships (Verify!):

$$\sum_{n_j=-\infty}^{+\infty} (-1)^{n_j} n_j \Delta\hat{\eta}_{\{n_x,\, n_y,\, n_z\}} = 0. \tag{3.115a}$$

If the OP field can be represented as $\Delta\eta(\mathbf{x}) = f(x)g(y)h(z)$, the Fourier coefficients break down into products of the separate components: $\Delta\hat{\eta}_{\mathbf{k}} = \Delta\hat{\eta}_{n_x}\Delta\hat{\eta}_{n_y}\Delta\hat{\eta}_{n_z}$. In this case, condition (3.115a) may be simplified as

$$\sum_{n_j=1}^{+\infty} (-1)^{n_j} n_j \,\mathrm{Im}\left(\Delta\eta_{n_j}\right) = 0. \tag{3.115b}$$

This condition shows that the BC (3.30b) will be satisfied if all the Fourier coefficients are real. Advantage of (3.114) and (3.115a) over (3.29) or (3.37b) is that these are algebraic equations; the disadvantage is that we have to deal now with many components $\Delta\hat{\eta}_{\mathbf{k}}$ instead of one function $\Delta\eta(\mathbf{x})$.

For the state $\eta_{\mathrm{E}}(\mathbf{x})$ to be close to $\bar{\eta}$, the Fourier coefficients $\Delta\hat{\eta}_{\mathbf{k}}$ must be small. Then, (3.114) yields that the necessary condition for this is that the coefficient in front of the quadratic term vanishes

$$\kappa|\mathbf{k}|^2 + \frac{\partial^2 g}{\partial\eta^2}(\bar{\eta}) = 0. \tag{3.116a}$$

This is possible only at the point of unstable equilibrium, $\partial g(\bar{\eta})/\partial\eta<0$, that is, at the transition state $\bar{\eta} = \eta_t$. In a cube with the side X, this condition may be expressed as follows

$$X^2 = (n_x^2 + n_y^2 + n_z^2)\tilde{X}^2(P,T). \tag{3.116b}$$

As n_js are integers, this equation defines the SABi point X_d, which is a 3d analog of the 1d SABi point in (3.58b). Notice that for the 2d and 3d states the bifurcation is deferred until greater lengths, than for the 1d states, $\sqrt{2}\tilde{X}$ and $\sqrt{3}\tilde{X}$, respectively, see Fig. 3.3. Equation (3.114) can be used to find the coefficients $\Delta\hat{\eta}_{\mathbf{k}}$ beyond the SABi point.

Let us resolve (3.114) for a $\Delta\eta(\mathbf{x})$ that has

$$\mathbf{k}_1 = \mathbf{k}_2 = -\mathbf{k}_3 = -\mathbf{k}_4$$

in a system where $T = T_{\mathrm{E}}(P)$, that is, (3.51a) applies. Then the third-order summation term vanishes and the fourth-order one turns into

$$\frac{g''''_t}{2\sqrt{V}} \sum_{\{\mathbf{k}\}} \left(|\Delta\hat{\eta}_{\mathbf{k}}|^2\right)^2.$$

Then (3.114) can be resolve as follows

$$|\Delta\hat{\eta}_{\mathbf{k}}|^2 = 6V\frac{|g''_t|}{g''''_t}\left(1-\frac{X_d^2}{X^2}\right) \approx 12V\frac{|g''_t|}{g''''_t}\frac{X-X_d}{X_d}. \tag{3.117}$$

Expanding $g(\eta_{\mathrm{E}})$ in (3.27a) and substituting (3.117) into the expansion, we obtain (Verify!):

$$\begin{aligned} G_d &= Vg_t + \sum_{\{\mathbf{k}\}}\left[\frac{1}{2}(\kappa|\mathbf{k}|^2 + g''_t)\,|\Delta\hat{\eta}_{\mathbf{k}}|^2 + \frac{1}{24V}g''''_t\,\left(|\Delta\hat{\eta}_{\mathbf{k}}|^2\right)^2\right] \\ &= V\left[g_t - 6\frac{|g''_t|^2}{g''''_t}\left(\frac{X-X_d}{X_d}\right)^2\right]. \end{aligned} \tag{3.118}$$

Compare this expression with (3.59) and notice that for the extremals with $(d > 1)$

$$G_{d>1}(V) > G_1(V) \tag{3.119}$$

because of two reasons: (1) the deviation from Vg_{t} starts at the linear size X_d greater than that for $d = 1$, that is $\tilde{X}$; (2) the curvature of the deviation is d times smaller than for $d = 1$. In Fig. 3.3, the Fourier coefficients (3.117) and free energy (3.118) are expressed through a and j of (3.56) and presented in comparison with the 1d type-e extremals.

3.7 Thermodynamic Stability of States: Local Versus Global

According to the thermodynamic stability principle discussed above, only the states that correspond to the free energy minima are thermodynamically stable. A theorem from the calculus of variations (see Appendix B) says that the necessary condition for an extremal $\eta_E(\mathbf{x})$ to deliver minimum to the functional $G\{\eta(\mathbf{x})\}$ is for the second variation to be positive:

$$\delta^2 G \geq 0;\ T, P = \mathrm{const}(\mathbf{x}). \tag{3.120}$$

For the functional (3.27a), the second variation takes the form of a quadratic functional:

$$\delta^2 G = \frac{1}{2}\int_V \delta\eta\,\hat{\mathbf{H}}(\eta_E)\,\delta\eta\,\mathrm{d}v, \tag{3.121}$$

where $\hat{\mathbf{H}}$ is the Hamilton's operator from (3.33) and (3.34) and the variation $\delta\eta$ obeys the Newmann-type BC (3.30b). The linear operator $\hat{\mathbf{H}}$ has a complete set of eigenfunctions $\{\Psi_n(\mathbf{x})\}$

$$\hat{\mathbf{H}}(\eta_E)\Psi_n(\mathbf{x}) \equiv \left[\left(\frac{\partial^2 g}{\partial\eta^2}\right)_{P,T}(\eta_E) - \kappa\nabla^2\right]\Psi_n(\mathbf{x}) = \Lambda_n\Psi_n(\mathbf{x}), \tag{3.122}$$

and the variation $\delta\eta$ can be expanded in $\{\Psi_n(\mathbf{x})\}$

$$\delta\eta = \sum_n \alpha_n\Psi_n(\mathbf{x}). \tag{3.123}$$

Substituting (3.123) into (3.121), we obtain

$$\delta^2 G = \frac{1}{2}\sum_n \alpha_n^2\Lambda_n. \tag{3.124}$$

Thus, the problem of the thermodynamic stability of a state described by the extremal (3.31) is reduced to the problem of the spectrum of the eigenvalues of $\hat{\mathbf{H}}$. Indeed, if all the eigenvalues Λ_n are positive, the second variation, (3.124), is positive definite, that is, $\eta_{\mathrm{E}}(\mathbf{x})$ is a minimum. If all the eigenvalues Λ_n are negative, the second variation is negative definite, that is, $\eta_{\mathrm{E}}(\mathbf{x})$ is a maximum. Finally, if some of the eigenvalues Λ_n of $\hat{\mathbf{H}}$ are positive and some are negative, the second variation takes on a positive or negative value depending on the variation of the state $\delta\eta$. That is, the extremal $\eta_{\mathrm{E}}(\mathbf{x})$ is a saddle point. If $\eta_{\mathrm{E}} = \mathrm{const}(\mathbf{x})$ is uniform in space, then (3.122) yields that for the stability of this state we need $\Lambda = \partial^2 g(\eta_{\mathrm{E}})/\partial\eta^2 > 0$, which is precisely the criterion we used in Chap. 2.

For the nonuniform equilibrium states, $\eta_{\mathrm{E}}(\mathbf{x})$ (3.122) is analogous to the Schrödinger equation from quantum mechanics, which describes stationary motion of a particle of mass $(\hbar^2/2\kappa)$ in the potential field $\partial^2 g(\eta_E)/\partial\eta^2$. Then, $\hat{\mathbf{H}}$ is analogous to the energy operator, $\Psi_n(\mathbf{x})$ is the wave function, and (Λ_n) is the energy of the particle. Review (3.33) and (3.34) and notice that we already know d eigenfunctions of $\hat{\mathbf{H}}$ that correspond to the zero eigenvalue $\Lambda_{n*} = 0$—the d-components of the gradient of the extremal $\eta_{\mathrm{E}}(\mathbf{x})$:

$$\Psi_{i,n_*}(\mathbf{x}) = \frac{\partial\eta_E}{\partial x_i}(\mathbf{x}); \quad \Lambda_{n_*} = 0; \quad i = 1, \ldots, d. \tag{3.125a}$$

These eigenfunctions are called the *Goldstone modes*. Although very important for the stability of the state $\eta_{\mathrm{E}}(\mathbf{x})$, they do not solve the problem completely because the zero eigenvalue may not be the smallest one.

To resolve the problem of stability of the 1d equilibrium states $\eta_{\mathrm{E}}(\mathrm{x})$, motivated by the fact that they vary only in one, x-direction, we will be seeking the eigenfunctions in the form of the *capillary waves*—the Fourier modes:

$$\Psi_n(\mathbf{x}) = \psi_n(x)\mathrm{e}^{i\mathbf{k}_2\mathbf{x}_2}, \tag{3.126a}$$

where $\mathbf{k}_2 = (k_y, k_z)$, $\mathbf{x}_2 = (y, z)$, and the amplitudes satisfy the following eigenvalue problem

$$\begin{gathered}\frac{\partial^2 g}{\partial \eta^2}(\eta_E(x))\psi_n(x) - \kappa \frac{\mathrm{d}^2\psi_n(x)}{\mathrm{d}x^2} = \lambda_n \psi_n(x); \\ \frac{\mathrm{d}\psi_n(x)}{\mathrm{d}x} = 0 \quad \text{at } x = 0 \text{ and } x = X.\end{gathered} \tag{3.126b}$$

where λ_ns are the 1d-eigenvalues of $\hat{\mathbf{H}}(\eta_E(\mathbf{x}))$. Substituting (3.126a) into (3.122) we obtain the relation

$$\Lambda_n = \lambda_n + \kappa|\mathbf{k}_2|^2 \geq \lambda_n, \tag{3.127}$$

which basically shows that, for the stability of 1d-states, the capillary-wave-amplitude eigenvalue problem is the most important part because the 3d-eigenvalues Λ_ns are not less than the 1d-eigenvalues λ_ns.

3.7.1 Type-e4 State: Plane Interface

Let us start with the plane interface state $\eta_{e4}(x)$, Sect. 3.4.4. As the Goldstone mode does not solve the stability problem of this state, we need to find other eigenfunctions and eigenvalues of the Hamilton's operator (3.122) where the state η_{e4}(x) is used for the "quantum mechanical potential energy" $\partial^2 g(\eta_{e4})/\partial\eta^2$. Here we have to be more specific in the choice of the function $g(\eta)$. Let us look at the Case 1 of the Landau potential, that is, (2.11) with $B = 0$ and $A < 0$, which has the type-e4 APB equilibrium state:

$$\eta_{e4}(x) = \sqrt{-A}\,\tanh\left(x\sqrt{\frac{-A}{2\kappa}}\right). \tag{3E.9}$$

The spectrum of $\hat{\mathbf{H}}(\eta_E(\mathbf{x}))$ is discrete for $\lambda_n \leq -2A$. The 1d Goldstone mode

$$\psi_0 \propto \frac{\mathrm{d}\eta_{e4}}{\mathrm{d}x} \propto \frac{1}{\cosh^2\left(x\sqrt{\frac{-A}{2\kappa}}\right)}; \quad \lambda_0 = 0 \tag{3.125b}$$

has the smallest eigenvalue zero. There is one more bound, real eigenfunction (see (3.67) or Appendix E):

$$\psi_1 \propto \eta_{e4}(x)\sqrt{\frac{\mathrm{d}\eta_{e4}}{\mathrm{d}x}} \propto \frac{\tanh\left(x\sqrt{-A/2\kappa}\right)}{\cosh\left(x\sqrt{-A/2\kappa}\right)}; \quad \lambda_1 = -\frac{3}{2}A. \tag{3.125c}$$

Normalization of the eigenfunction does not matter because they obey a linear equation. The rest of the eigenfunctions ($n = 2, 3, \ldots$) are "scattering states" (unbound, complex valued) with $\lambda_n > -2A$. Thus, the APB is neutrally stable inhomogeneous state in the sense that it can be relocated in the x-direction to any part of the system without any additional free energy cost. Same is true about any type-e4 state (3.64), which represents the equilibrium interface. (Verify!) The equilibrium state η_{e4}, "potential energy" $\partial^2 g(\eta_{e4})/\partial\eta^2$ for this state, and bound eigenfunctions are shown in Fig. 3.4.

3.7.2 General Type-e and Type-n States

For other type-e and type-n states, exact solutions of the respective Schrödinger equations are not known and we have to look for other means to determine type of stability of these states. That is when the Sturm's comparison theorem (Appendix E) is of great help. According to that theorem, the discrete band of the spectrum of the eigenvalues $\{\lambda_n\}$ can be ordered such that the greater eigenvalue corresponds to the eigenfunction Ψ_n with greater number of zeros:

$$\begin{aligned} &n = 0,\ 1, \ldots,\ n_* - 1,\ n_*, \ldots \\ &\lambda_0 < \lambda_1 < \cdots < \lambda_{n_*-1} < \lambda_{n_*} = 0 < \cdots \\ &\psi_0,\ \psi_1, \ldots,\ \psi_{n_*-1},\ \psi_{n_*}, \ldots \end{aligned} \tag{3.128}$$

Then, (3.128) shows that $\psi_{n*}(x) = \mathrm{d}\eta_{1\mathrm{d}}/\mathrm{d}x$ is the eigenfunction with the eigenvalue $\lambda_{n*} = 0$ and all we need to know is how many zeros this function has. Indeed, if $\psi_{n*}(x)$ has at least one zero in the domain $(0, X)$ then there exists another eigenfunction $\psi_{n*-1}(x)$ with fewer zeros that corresponds to a smaller eigenvalue: $\lambda_{n*-1} < \lambda_{n*} = 0$, and the solution $\eta_{1\mathrm{d}}(x)$ is unstable. Otherwise it is stable. (3.43) and (3.50) show that $\mathrm{d}\eta_{e1}/\mathrm{d}x$, $\mathrm{d}\eta_{e2}/\mathrm{d}x$, $\mathrm{d}\eta_{e3}/\mathrm{d}x$, and $\mathrm{d}\eta_n/\mathrm{d}x$ have zeros in the domain $0 < x < X$. Hence, on the hypersurface $G\{\eta(\mathbf{x})\}$ the functions η_{e1-3} and η_n represent saddle points. Notice that because $\mathrm{d}\eta_{e4}/\mathrm{d}x$ does not have zeros in the domain $-\infty < x < +\infty$, the Sturm's comparison theorem proves our previous point that η_{e4} is a state of neutral stability.

Example 3.4 Find the 1d instanton (critical plate) and determine its stability in the system described by the following free-energy density:

$$g = g_0 + \frac{a}{2}\eta^2 - \frac{1}{4}\eta^4, \quad a > 0. \tag{3E.16}$$

This potential may be used to model a metastable state ($\bar{\eta}_m = 0$) in a system where stable states ($\bar{\eta}_s \to \pm\infty$) have much lower level of the free energy. ELE (3.29) for this system is resolved in the following form [see (3.43)]:

$$\frac{\mathrm{d}\eta}{\mathrm{d}x} = \pm\eta\sqrt{\frac{a}{\kappa}\left(1 - \frac{\eta^2}{2a}\right)}. \tag{3E.17}$$

Its instanton solution centered at $x_0 = 0$ is

$$\eta_{n4}(x) = \pm\sqrt{2a}\,\sec\mathrm{h}\left(\sqrt{\frac{a}{\kappa}}x\right). \tag{3E.18}$$

The eigenvalue equation is

$$\hat{\mathbf{H}}\psi_n(x) \equiv \left(\frac{\partial^2 g(\eta_{n4})}{\partial\eta^2} - \kappa\frac{\mathrm{d}^2}{\mathrm{d}x^2}\right)\psi_n(x) = \lambda_n\psi_n(x). \tag{3E.19}$$

The Goldstone mode of this equation is

$$\psi_0 \propto \tanh\left(\sqrt{\frac{a}{\kappa}}x\right)\sec\mathrm{h}\left(\sqrt{\frac{a}{\kappa}}x\right); \quad \lambda_0 = 0. \tag{3E.20}$$

The eigenvalue equation has one more bound eigenfunction:

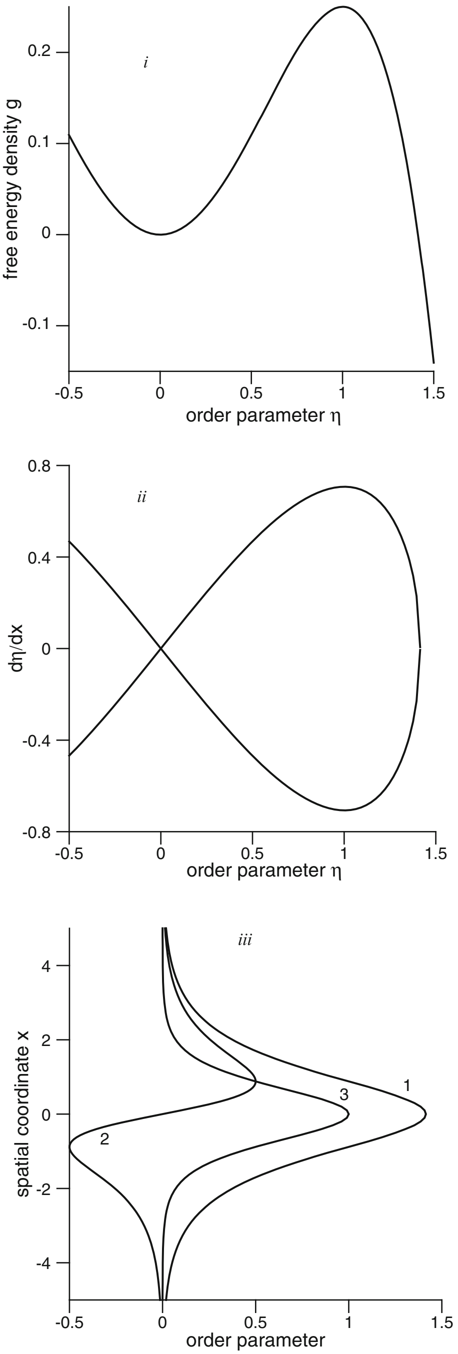
$$\psi_{-1} \propto \sec\mathrm{h}^2\left(\sqrt{\frac{a}{\kappa}}x\right); \quad \lambda_{-1} = -3a. \tag{3E.21}$$

The 1d instanton is unstable because the eigenvalue $\lambda_{-1} < 0$. Compare this example to the domain wall and notice that the Goldstone and second bound state switch their places. The potential, (3E.16), ELE (3E.17), solution, (3E.18), and the bound eigenfunctions (3E.20) and (3E.21) are shown in Fig. 3.8.

3.7.3 3d Spherically Symmetric Instanton

Now let us consider thermodynamic stability of the critical droplet—3d radially symmetric instanton (see Sect. 3.6.2). Based on the success with using the Goldstone mode and Sturm's comparison theorem for the analysis of stability of the 1d states, it is tempting to try to use the same combination for the 3d case. We will do that by presenting here the stability analysis on the "physical level of rigor," which

Fig. 3.8 A 1d system described by the free energy (3E.16). The potential (i), the phase plane (ii), and the spatial distribution of the modes (iii): 1—instanton (3E.18), 2—the Goldstone mode (3E.20), and 3—the bound eigenfunction (3E.21)



is very illuminating and sufficiently rigorous for our purposes. First, let us present the 3d Goldstone modes in the vector form:

$$\boldsymbol{\Psi}_{n_*}(\mathbf{x}) = \nabla\eta_{3d}(r) = \frac{\mathrm{d}\eta_{3d}(r)}{\mathrm{d}r}\mathbf{j}_r = \frac{\mathrm{d}\eta_{3d}(r)}{\mathrm{d}r}f_i(\vartheta,\phi)\mathbf{j}_i, \quad i = 1,\ 2,\ 3, \tag{3.129}$$

where $\mathbf{j}_i$ and f_i are the Cartesian unit vectors and projection coefficients, respectively (see Appendix C). Then, substituting (3.129) into (3.122) and using (C.27), we obtain an equation (Verify!):

$$\begin{aligned} 0 &= \hat{\mathbf{H}}(\eta_{3d}(r))\boldsymbol{\Psi}_{n_*}(\mathbf{x}) \\ &= \left\{\frac{\partial^2 g}{\partial\eta^2}(\eta_{3d}) - \kappa\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{2}{r^2}\right]\right\}\frac{\mathrm{d}\eta_{3d}(r)}{\mathrm{d}r}f_i(\vartheta,\phi)\mathbf{j}_i, \end{aligned} \tag{3.130}$$

which shows that the eigenfunction

$$\psi_{n_*}(r) \equiv \frac{\mathrm{d}\eta_{3d}(r)}{\mathrm{d}r} \tag{3.131}$$

is the zero-eigenvalue solution of the following Sturm–Liouville problem

$$\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}\psi_n}{\mathrm{d}r}\right) - \left[2 + \frac{r^2}{\kappa}\frac{\partial^2 g}{\partial\eta^2}(\eta_{3d}(r))\right]\psi_n = \lambda_n\psi_n \tag{3.132}$$

in the domain $0 \le r < \infty$. Taking into account that $\psi_{n_*}(0) = 0$ [see (3.90)] and applying the Sturm's comparison theorem (see Appendix E) we deduce that there exists an eigenfunction $\psi_0(r)$ such that it does not have zeros in $0 \le r < \infty$ and

$$\lambda_0 < \lambda_{n_*} = 0. \tag{3.133}$$

This proves that the 3d-instanton has at least one eigenfunction with negative eigenvalue, that is, this is a state of the saddle-type stability. Notice that we also proved that the "most dangerous" mode $\psi_0(r)$ has the spherical symmetry similar to that of the instanton $\eta_{\mathrm{3d}}(r)$ itself.

3.8 Gradients of Conjugate Fields

In this section, we come back to the question of inclusion of the linear term in (3.21) into the free energy density, (3.19a), and analyze its consequences. This term has proper symmetry and, comparing its contribution with the other terms in (2.45), we can see that the coefficient v has the units of length squared. This term may allow us to account for the heterogeneous variations of the applied conjugate field $H(\mathbf{x})$. Hence, in addition to the OP-field coupling terms, we have to include the "vacuum" contribution of the field—the term $\frac{1}{2}\mu H^2$, where μ is, for the time being, an undetermined field-scaling coefficient. Then

$$G = \int_V \left[g(P,T,\eta) + \frac{1}{2}\kappa(\nabla\eta)^2 - H\eta + \nu\nabla H\nabla\eta + \frac{1}{2}\mu H^2 \right] \mathrm{d}^3x. \tag{3.134}$$

Now let us apply the LeChatelier–Braun principle to a stable homogeneous equilibrium state $\bar{\eta}$, which sets in a field-free system. The principle says that the reaction of the system on small disturbances must be such as to minimize the effect of the disturbances. Variation of the functional (3.134) yields that the equilibrium distribution of the OP, which appears as a result of the applied field, is described by the ELE:

$$\frac{\partial g}{\partial \eta} - \kappa\nabla^2\eta = H + \nu\nabla^2 H. \tag{3.135}$$

Reaction of the system on the applied field can be analyzed with the help of the superposition of the plane waves with different wave vectors **k** (see Appendix F):

$$H(\mathbf{x}) = \sum_{\mathbf{k}} h_{\mathbf{k}} \mathrm{e}^{i\mathbf{kx}}; \quad \eta(\mathbf{x}) = \bar{\eta} + \sum_{\mathbf{k}} \Delta\eta_{\mathbf{k}} \mathrm{e}^{i\mathbf{kx}}, \tag{3.136}$$

where the amplitudes obey the following relations $h_{-\mathbf{k}} = h_{\mathbf{k}}^*$ and $\Delta\eta_{-\mathbf{k}} = \Delta\eta_{\mathbf{k}}^*$ because the waves represent the real fields. Substituting (3.136) into (3.135) and linearizing it (the disturbances are small) we obtain the expression for the generalized susceptibility:

$$\chi(k) \equiv \frac{\Delta\eta_{\mathbf{k}}}{h_{\mathbf{k}}} = \frac{1 - \nu k^2}{\partial^2 g(\bar{\eta})/\partial\eta^2 + \kappa^2}; \quad k = |\mathbf{k}|. \tag{3.137}$$

Now we can find the reaction of the system on the disturbance by calculating the free energy change as the result of the applied field. Substituting (3.136) and (3.137) into (3.134) we obtain (Verify!):

$$G\{P,T,H,\bar{\eta} + \Delta\eta\} \cong V\left[g(P,T,\bar{\eta}) + \sum_k |h_{\mathbf{k}}|^2 R(k) \right], \tag{3.138a}$$

where

$$2R(k) = \mu - \frac{(1 - \nu k^2)^2}{1 + l^2k^2} \left[\frac{\partial^2 g(\bar{\eta})}{\partial\eta^2} \right]^{-1} \tag{3.138b}$$

is the field amplification factor and the fundamental length l is defined in (3.53b). A homogeneous field H will be balanced by the OP changes only if $R(0) = 0$; hence, the field-scaling coefficient is

$$\mu^{-1} = \frac{\partial^2 g(\bar{\eta})}{\partial\eta^2}. \tag{3.139}$$

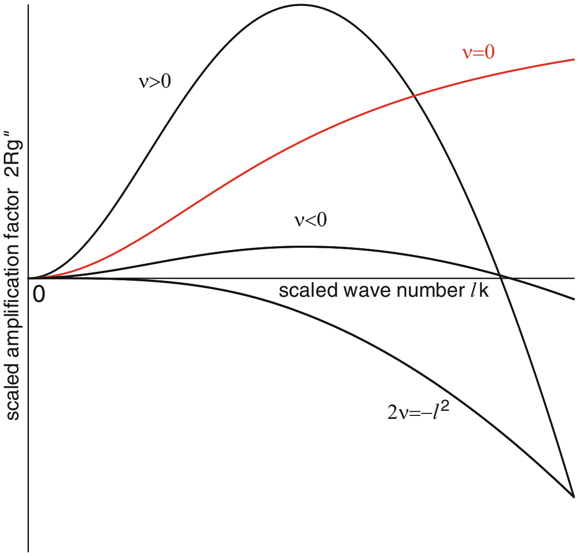


Fig. 3.9 The scaled field amplification factor R as a function of the scaled wavenumber k for different values of the coefficient ν

Then

$$R(k) = \left[\frac{\partial^2 g(\bar{\eta})}{\partial \eta^2}\right]^{-1} \frac{l^2 + 2\nu - \nu^2 k^2}{2(1 + l^2 k^2)} k^2, \tag{3.140}$$

The state $\bar{\eta}$ will remain stable and the influence of the applied field will be minimized only if $R(k) > 0$ for all values of $k > 0$. Indeed, if $R(k)$ is negative, at least for some values of k, then another state, possibly heterogeneous $\eta_{\mathrm{H}}(\mathbf{x})$, is more stable than $\bar{\eta}$, which means that a transition into that state is probable. Analysis of (3.140), see Fig. 3.9, shows that $R(k) > 0$ for all values of $k > 0$ only if $\nu = 0$. Hence (3.22) is true.

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Chapter 4
Dynamics of Homogeneous Systems

In this chapter, we conjecture the "linear ansatz" equation of evolution of the order parameter, which is consistent with the laws of thermodynamics. We analyze solutions of this equation in different situations: close to the equilibrium state, far away from it, or when the evolution is taking place close to the spinodal point. Analyzing stability of homogeneous equilibrium states we find that the criteria of their dynamic and thermodynamic stability coincide. We also take a step beyond the linear ansatz and look at the order parameter evolution in systems with memory. One of the conclusions that we arrive at is that all of the above considered cases do not describe a phase transition completely because they cannot describe overcoming of a potential barrier by the system. Hence, other forces ought to be included into the complete theory.

4.1 Evolution Equation: The Linear Ansatz

So far we have been dealing with the states of thermodynamic equilibrium. We now turn our attention to the situations when the system is initially not in one of these states. Experiments show (the Zeroth Law of Thermodynamics) that in all systems there is a tendency to evolve toward equilibrium states, which are determined by intrinsic properties of the system and not by the initial influences. Here we want to answer the following question: What is the equation that describes evolution of the OP in a nonequilibrium system? We will start with a homogeneous system.

The OP evolution equation can be conjectured based on the following arguments (see Appendix J).

First: We know that

$$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}P + \left(\frac{\partial G}{\partial \eta}\right)_{P,T}\mathrm{d}\eta. \tag{4.1}$$

A. Umantsev, *Field Theoretic Method in Phase Transformations*,
Lecture Notes in Physics 840, DOI 10.1007/978-1-4614-1487-2_4,

Then at $P = \text{const}$, $T = \text{const}$ the condition of equilibrium is expressed as following

$$\left(\frac{\partial G}{\partial \eta}\right)_{P,T} = 0. \tag{4.2}$$

Hence, deviations of the system from the equilibrium state $\bar{\eta}$ will result in the deviations of the left-hand side of (4.2) from zero. This term may be called "the driving force" of the evolution.

Second: The evolution equation should be able to describe relaxation of the system to the equilibrium state. Hence, it should contain the first-order temporal derivative of the OP. Presence of the higher-order temporal derivative of the OP is possible but not necessary.

Third: The evolution equation should be able to describe small deviations from the equilibrium state. Hence, it should contain the linear in the driving force term. The equation may contain the nonlinear in the driving force terms but not necessarily.

Fourth: The evolution equation should be consistent with the coarse-graining procedure (see Appendix A).

The four arguments discussed above suggest the following equation that describes the nonequilibrium homogeneous OP evolution [see (J.1)]

$$\frac{\mathrm{d}\eta}{\mathrm{d}t} = -\gamma\left(\frac{\partial G}{\partial \eta}\right)_{P,T}. \tag{4.3}$$

Here γ is a constant that characterizes the rate of evolution. This equation sometimes is called "the linear ansatz." Notice that the linear ansatz equation is linear only with respect to the driving force but, in general, is nonlinear with respect to the OP change.

To determine possible values of the rate constant γ, we will use the second law of thermodynamics. According to this law in the system with $P = \text{const}$, $T = \text{const}$, the equilibrium state $\bar{\eta}$ has less Gibbs free energy than any other allowed state:

$$G(\bar{\eta}) < G(\eta) \quad \text{if } \eta \neq \bar{\eta}. \tag{4.4}$$

Hence, on every evolutionary path $\eta(t) \to \bar{\eta}$ that leads to $\bar{\eta}$ it must be

$$\frac{\mathrm{d}G}{\mathrm{d}t} < 0. \tag{4.5}$$

Now let us calculate the rate of change of the Gibbs free energy G that accompanies evolution of the OP $\eta(t)$ which is a solution of (4.3). First, we have

$$\frac{\mathrm{d}G}{\mathrm{d}t} = \left(\frac{\partial G}{\partial t}\right)_{P,T,\eta} + \left(\frac{\partial G}{\partial \eta}\right)_{P,T}\frac{\mathrm{d}\eta}{\mathrm{d}t}. \tag{4.6}$$

The first term will be present in a system exposed to a time-dependent external field. In this chapter, if not indicated otherwise, we will be assuming that such fields are absent. Hence, the first term vanishes. Then, using (4.3) for (4.6) we obtain

$$\frac{\mathrm{d}G}{\mathrm{d}t} = -\gamma \left(\frac{\partial G}{\partial \eta} \right)^2_{P,T}. \tag{4.7}$$

Comparing (4.5) and (4.7) we can see that

$$\gamma > 0. \tag{4.8}$$

A few comments are in order here.

1. In the function space $\{\eta\}$ the left-hand side of (4.3) represents a flow, while the right-hand side a gradient of $G(\eta)$. Because of that, evolution of a system according to (4.3) is called *gradient flow*.
2. From (4.3) to (4.8), we can see that the free energy of the system G (strictly speaking the difference $G(\eta) - G(\bar{\eta})$) is a Lyapunov function at the equilibrium state $\bar{\eta}$. Remember that a continuous function $L(\mathbf{x})$ with continuous partial derivatives is called a *Lyapunov function* for the system of differential equations $\mathrm{d}\mathbf{x}/\mathrm{d}t = D(\mathbf{x})$, where $D(\mathbf{x} = \mathbf{0}) = 0$, if it is positive definite, i.e. such that $L(\mathbf{x} = \mathbf{0}) = 0$ and $L(\mathbf{x} \neq \mathbf{0}) > 0$, and if its total derivative due to the system $D(\mathbf{x})$ is non-positive: $(\mathrm{d}L/\mathrm{d}t)_{\mathrm{D}} = \partial L/\partial \mathbf{x} \cdot D(\mathbf{x}) \leq 0$. Existence of a Lyapunov function allows us to analyze stability of the equilibrium states of a dynamical system and distinguish between the locally stable and unstable equilibrium states. It also proves that the states of the evolutionary trajectory are time ordered and the reverse evolution is impossible, that is, the evolution is irreversible [1].
3. One may argue that the system may have evolutionary paths, which do not lead to the equilibrium state $\bar{\eta}$. However, they must lead to some other equilibrium state (e.g., local equilibrium state instead of the global one) because otherwise the zeroth law of thermodynamics is violated. Hence, (4.8) is true on this path also. This analysis helps us recognize that the domain $-\infty < \eta < +\infty$ may be broken into “basins of attraction” of different equilibrium states $\bar{\eta}_1, \bar{\eta}_2, \ldots$ (see Chap. 2).
4. A word of caution is necessary here regarding the concept of nonequilibrium free energy of the system. Rigorously speaking, Statistical Mechanics provides a recipe for how to calculate the free energy at an equilibrium state only. Then, how can we define the free energy at a nonequilibrium state? The concept of the conjugate field developed in Chap. 2 may help us clarify the concept of nonequilibrium free energy. Indeed, using (2.46), we may define the free energy at a nonequilibrium state of the OP η as equal to the free energy at the same value of the OP, which has attained equilibrium in the presence of the conjugate field H, plus H times the OP value (see Appendix J):

$$G(P, T, 0, \eta) = G(P, T, H, \bar{\eta}) + H\bar{\eta}, \quad \text{if } \eta = \bar{\eta}(P, T, H).$$

4.2 Solutions of the Linear-Ansatz Dynamic Equation

4.2.1 Evolution of Small Disturbances

Now we can analyze the general dynamic features of the linear ansatz. Let us start with the situation when in the beginning the system was slightly pulled away from the equilibrium state $\bar{\eta}$. Then we can expand the free energy near this value

$$\frac{\partial G}{\partial \eta} = \frac{\partial G(\bar{\eta})}{\partial \eta} + \frac{\partial^2 G(\bar{\eta})}{\partial \eta^2}\Delta\eta + \frac{1}{2}\frac{\partial^3 G(\bar{\eta})}{\partial \eta^3}\Delta\eta^2 + \frac{1}{6}\frac{\partial^4 G(\bar{\eta})}{\partial \eta^4}\Delta\eta^3 \cdots; \\ \Delta\eta = \eta - \bar{\eta}. \tag{4.9}$$

Taking into account that $\partial G(\bar{\eta})/\partial \eta = 0$, we obtain an equation for the small disturbances $\Delta\eta$

$$\frac{\mathrm{d}\Delta\eta}{\mathrm{d}t} \cong -\gamma \frac{\partial^2 G(\bar{\eta})}{\partial \eta^2}\Delta\eta. \tag{4.10}$$

This is a linear differential equation of the first order which has a general solution

$$\Delta\eta = \Delta\eta(0)e^{\beta_1 t}; \quad \beta_1 = -\gamma \frac{\partial^2 G(\bar{\eta})}{\partial \eta^2}. \tag{4.11}$$

Here β_1 is called the *amplification factor*. As you can see from (4.11), the sign of the amplification factor determines asymptotic behavior of the small disturbances: if $\beta_1 < 0$ then $|\Delta\eta(t)|$ decreases with time (decays)—*relaxes*, if $\beta_1 > 0$ then $|\Delta\eta(t)|$ increases with time (grows) and soon leaves the domain of validity of the expansion (4.10). If $\beta_1 = 0$ then, according to (4.11), $|\Delta\eta(t)|$ neither grows nor decays, which means that our expansion in (4.10) is not sufficient and we have to include the higher-order terms from (4.9). Given the condition, (4.8), the sign of the amplification factor β_1 is fully determined by the sign of $\partial^2 G(\bar{\eta})/\partial \eta^2$. Hence, $\partial^2 G(\bar{\eta})/\partial \eta^2$ is a very good indicator of stability of a homogeneous equilibrium state: $\partial^2 G(\bar{\eta})/\partial \eta^2 > 0$ at the stable equilibrium, $\partial^2 G(\bar{\eta})/\partial \eta^2 < 0$ at the unstable equilibrium, and $\partial^2 G(\bar{\eta})/\partial \eta^2 = 0$ at the neutral equilibrium (spinodal point).

The characteristic time scale of the relaxation

$$\tau = \frac{1}{|\beta_1|} = \frac{1}{\gamma}\left|\frac{\partial^2 G(\bar{\eta})}{\partial \eta^2}\right|^{-1} \tag{4.12}$$

determines the rate of the evolution. If the system has more than one stable equilibrium, the time scales near them may be different. For instance, for the system described by the free energy, (2.11), the time constant of the globally stable state is smaller than that of the locally stable one. If $|\partial^2 G(\bar{\eta})/\partial \eta^2| \to 0$, that is, near the spinodal points, then $\tau \to \infty$. All of these cases are depicted in Fig. 4.1.

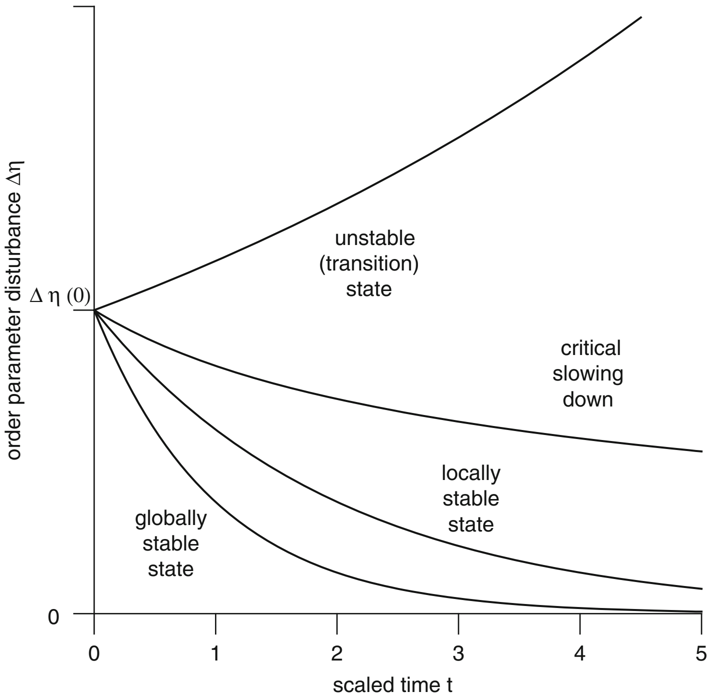

Fig. 4.1 Evolution of the system near equilibrium states according to the solutions (4.11) of the linearized dynamic equation (4.10)

The type of stability associated with β_1 is called *dynamic* because it originates from the dynamic equation. It is very closely related to the thermodynamic stability studied in Chap. 2. Indeed, $\beta_1 < 0$ for all locally stable homogeneous states and $\beta_1 > 0$ for the unstable ones. However, β_1 is not a perfect indicator of the global stability because one can envision a potential G (not considered in the previous chapters), where the curvature of the deeper well is less than that of the shallower one. The situation is even more complicated for the heterogeneous states; it will be considered in the next chapter.

4.2.2 Critical Slowing Down

As we observed from (4.10), our analysis of the dynamic stability fails at the spinodal point, that is, if $G'(\bar{\eta}) = 0$ and $G''(\bar{\eta}) = 0.$ A general effect that takes place at this point is called *critical slowing down*. But the details depend on the higher-order expansion terms in (4.9). If $G'''(\bar{\eta}) \neq 0,$ then

$$\frac{\mathrm{d}\Delta\eta}{\mathrm{d}t} \cong \beta_2 \Delta\eta^2; \quad \beta_2 = -\frac{1}{2}\gamma\frac{\partial^3 G(\bar{\eta})}{\partial\eta^3} \tag{4.13a}$$

and

$$\Delta\eta = \frac{\Delta\eta(0)}{1 - \Delta\eta(0)\beta_2 t}. \tag{4.13b}$$

Important feature of (4.13b) is that the temporal behavior of $\Delta\eta$ depends not only on the sign of $G'''(\bar{\eta})$ but also on the sign of the initial condition $\Delta\eta(0)$. Indeed, if $\Delta\eta(0)G'''(\bar{\eta})>0$, then $\Delta\eta(t)$ is a monotonically decaying function with the asymptotic behavior of t^{-1} instead of the exponential, $\exp(\beta_1 t)$. But if $\Delta\eta(0)G'''(\bar{\eta})<0$, then $\Delta\eta(t)$ increases without bound (finite-time blow-up) and quickly leaves the domain of small disturbances. The rate of this process is characterized by the blow-up time $t_2^* = (\Delta\eta(0)\beta_2)^{-1}$. Thus, if $G'''(\bar{\eta}) \neq 0$, the system is dynamically unstable because the runaway scenario is always possible: all you need to do is to choose the initial disturbance such that $\Delta\eta(0)G'''(\bar{\eta})<0$.

If $G'''(\bar{\eta}) = 0$ but $G''''(\bar{\eta}) \neq 0$, then

$$\frac{d\Delta\eta}{dt} \cong \beta_3 \Delta\eta^3; \quad \beta_3 = -\frac{1}{6}\gamma\frac{\partial^4 G(\bar{\eta})}{\partial\eta^4} \tag{4.14a}$$

and

$$\Delta\eta = \frac{\Delta\eta(0)}{\sqrt{1 - 2\Delta\eta^2(0)\beta_3 t}}. \tag{4.14b}$$

As we can see in this case the asymptotic behavior of the OP disturbance depends on the sign of $G''''(\bar{\eta})$ but is independent of the sign of $\Delta\eta(0)$. If $G''''(\bar{\eta})<0$, the system is unstable with the blow-up time $t_3^* = (2\Delta\eta^2(0)\beta_3)^{-1}$. If $G''''(\bar{\eta})>0$, the system is stable but its asymptotic approach to the equilibrium is $\Delta\eta \sim t^{-1/2}$ instead of the exponential one, that is, much slower than near the regular point of equilibrium.

4.2.3 Nonlinear Evolution

Although many features of the evolution in homogeneous systems may be understood from the analysis of the linearized equation (4.10), some of the features can be revealed only if we solve the full nonlinear equation (4.3). We will demonstrate the solution using the tangential potential of Sect 2.5. Then

$$\frac{d\eta}{dt} = 2\gamma W\eta(1-\eta)(\eta - \eta_t), \tag{4.15}$$

where η_t is the OP value of the transition state (2.35b). Taking into account that

$$\frac{1}{x(1-x)(x-a)} = \frac{1}{a(1-a)(x-a)} + \frac{1}{(1-a)(1-x)} - \frac{1}{ax},$$

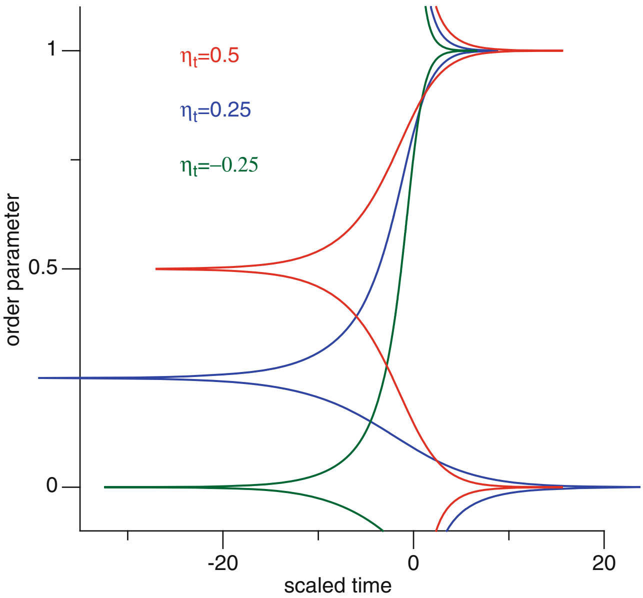

Fig. 4.2 Solutions (4.16) of the nonlinear homogeneous dynamic equation (4.15). The arrow of time is from left to right. Notice the basins of attraction of two stable states, $\bar{\eta} = 0,\ 1$, and the repulsive basins of the unstable state $\bar{\eta} = \eta_t$

we obtain a general solution of (4.15)

$$2\gamma W t = \frac{\ln|\eta - \eta_t|}{\eta_t(1-\eta_t)} - \frac{\ln|1-\eta|}{1-\eta_t} - \frac{\ln|\eta|}{\eta_t} - \text{const} \tag{4.16a}$$

where

$$\text{const} = \frac{\ln|\eta(0) - \eta_t|}{\eta_t(1-\eta_t)} - \frac{\ln|1-\eta(0)|}{1-\eta_t} - \frac{\ln|\eta(0)|}{\eta_t} \tag{4.16b}$$

and $\eta(0)$ is the OP value at $t = 0$. The solution, (4.16a), is depicted in Fig. 4.2. As we can see the equilibrium values $\bar{\eta} = 0,\ \eta_t,\ 1,$ divide the OP domain into four “watersheds”, each controlled by one manifold. Approaching the stable equilibrium state or departing from the unstable one the OP exhibits exponential tails, which have been revealed by the linearized analysis of (4.11). Compare solution (4.16a) with the Sect. G.2 of Appendix G and notice the similarities.

4.2.4 More Complicated Types of OPs

If the OP of the system is a complex variable, the driving force in (4.3) should be understood as a derivative of the analytic function $G(\eta)$. In this case, $\mathrm{Re}\partial^2 G(\bar{\eta})/\partial\eta^2$ serves as an indicator of stability and $\mathrm{Im}\partial^2 G(\bar{\eta})/\partial\eta^2$ is proportional to the frequency of oscillations. If the OP is a multicomponent variable, the linear-ansatz dynamic equation should be written for each component separately (see Appendix J, §3). The dynamic equations for the components will contain the cross-terms, which obey the Onsager symmetry relations. The cross-coefficients affect stability of the equilibrium states.

4.3 Beyond the Linear Ansatz

Now let us analyze a "nonlinear ansatz," that is, a possibility that the OP evolution equation is a nonlinear function of the driving force

$$\frac{\mathrm{d}\eta}{\mathrm{d}t} = -\Phi\left\{\left(\frac{\partial G}{\partial \eta}\right)_{P,T}\right\}. \tag{4.17}$$

The function $\Phi(x)$ is subject to the following the constraints

$$\begin{aligned} &1.\ \Phi(0) = 0 \\ &2.\ \Phi(x) - \text{analytic near } x = 0. \end{aligned} \tag{4.18a}$$

Substituting (4.17) into (4.6) and comparing it with (4.5), we find another constraint on the function $\Phi(x)$ in the domain of its definition:

$$3.\ x\Phi(x){>}0 \text{ near } x = 0. \tag{4.18b}$$

An example of a nonlinear ansatz, the function $\Phi(x){=}\gamma x{+}\alpha x^2{+}\beta x^3$, satisfies the conditions of (4.18) if $\gamma > 0$, $\alpha = 0$, and $\beta > 0$. Thus, the linear-ansatz equation (4.3) is a valid, but not the only, choice of the OP evolution equation. The nonlinear ansatz may be thought of as a system with the relaxation coefficient that depends on the OP itself—$\gamma(\eta)$. Then the conditions of (4.18) limit the allowed functional dependencies of $\gamma(\eta)$.

4.4 Relaxation with Memory

The linear and nonlinear ansatz provide instantaneous connections between the driving force and the reaction of the system. Some systems, so to speak, may have memory, that is, current reaction of the system is affected by the values of the driving force from the past. This property may be expressed by the "memory integral" over the driving force

$$\frac{\mathrm{d}\eta}{\mathrm{d}t} = -\int_{-\infty}^{t} M(t-t')\frac{\partial G}{\partial \eta}(\eta(t'))\,\mathrm{d}t', \tag{4.19}$$

where the integral kernel $M(t-t')$ is called the *memory function*. The memory integral summarizes contributions of the driving force from all the moments in time up to the current one—t. It does not spread into the future ($t'' > t$) in order not to violate causality.

Different functional forms of the memory function determine different evolutionary paths of the system.

1. If the system has "no memory":

$$M(t-t') = \gamma\delta(t-t') \tag{4.20}$$

   then (4.19) reduces to the linear-ansatz (4.3).
2. If the system has "full memory":

$$M(t-t') = \frac{1}{m} = \mathrm{const}(t,\ t') \tag{4.21}$$

   then (4.19) can be differentiated with respect to t once to yield:

$$m\frac{\mathrm{d}^2\eta}{\mathrm{d}t^2} = -\frac{\partial G}{\partial\eta}(\eta). \tag{4.22}$$

   This equation is analogous to the Newton's equation of motion of a particle of mass m in the force field $G(\eta)$, where $\eta(t)$ is the position coordinate of the particle. Solutions of this equation are known to have completely different dynamics than those of the linear-ansatz (4.3). For instance, the small deviations from a stable equilibrium $\Delta\eta$, instead of relaxation as in (4.11), represent motion of a frictionless harmonic oscillator

$$\Delta\eta(t) = A\cos(\omega t + \varphi_0); \quad \omega^2 = \frac{1}{m}\frac{\partial^2 G(\bar{\eta})}{\partial\eta^2}. \tag{4.23}$$

3. If the memory function is

$$M(t-t') = \mathrm{Re}^{-(t-t')/\tau_m} \tag{4.24}$$

   then differentiating (4.19) with respect to t we obtain (Verify!)

$$\frac{\mathrm{d}^2\eta}{\mathrm{d}t^2} + \frac{1}{\tau_m}\frac{\mathrm{d}\eta}{\mathrm{d}t} = -R\frac{\partial G}{\partial\eta}(\eta). \tag{4.25}$$

This equation has features of both equations—no memory and full memory; hence, the integral kernel, (4.24) can be called the partial-memory function. Equation (4.25) describes motion of a damped oscillator. Properties of its solutions are well known [2]. Compare (4.3, 4.22, 4.25) and notice that for the full-memory and no-memory functions to be the limiting cases of the partial-memory function it must be

$$R = 1/m, \quad \tau_m = m\gamma. \tag{4.26}$$

4.5 Other Forces

A closer inspection of Fig. 4.2 shows that starting with any initial condition $\eta(0)$ the system stays in the same basin and never crosses the divider. This means that (4.3) does not actually describe a phase transition in its entirety, only the relaxation-to-equilibrium part of the process. Neither memory nor nonlinearity can fix this problem. What changes do we need to make in (4.3) in order for it to be able to describe the phase transition?

In Chap. 2, we reached the conclusion that a phase transition implies overcoming the potential barrier, that is, moving "uphill" in the representative space of the system. This cannot be accommodated by the driving force $(\partial G/\partial \eta)$ alone because this force drives the system "downhill." We must include into the dynamic equation "other forces" that can push the system uphill:

$$\frac{\mathrm{d}\eta}{\mathrm{d}t} = -\gamma \left(\frac{\partial G}{\partial \eta}\right)_{P,T} + F. \tag{4.27}$$

One way to overcome the barrier is to include the *spatial diffusive force*, $\kappa \nabla^2 \eta$, which, as we discussed in Chap. 3, appears as a result of the gradient energy contribution. According to (3.29), the diffusive force can balance the driving force, hence push the system uphill. This will be discussed in Chap. 5.

Another possibility is to take into account *thermal fluctuations*, which arise due to the atomic/molecular nature of the physical systems, that is, microscopic degrees of freedom. In the framework of the dynamic equation, the effect of the fluctuations can be expressed by adding the so-called "Langevin force." This will be discussed in Chap. 7.

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Chapter 5
Evolution of Heterogeneous Systems

In this chapter, we apply the ideas of the previous chapters to the dynamics of heterogeneous systems and obtain the celebrated time-dependent Ginzburg-Landau equation (TDGLE) of the order parameter evolution. This equation was applied to various heterogeneous states of the system. Application of TDGLE to an equilibrium state shows that the criteria of the dynamic and local thermodynamic stability coincide. In case of a plane interface, TDGLE yields a traveling wave solution with a finite thickness and specific speed proportional to the deviation of the system from equilibrium. The drumhead approximation of this equation reveals different driving forces exerted on a moving interface and allows us to study evolution of droplets of a new phase. We extend the definition of the interfacial energy into the nonequilibrium domain of the thermodynamic parameters (phase diagram). We analyze growth dynamics of the anti-phase domains using results of FTM and the Allen-Cahn self-similarity hypothesis. The analysis reveals the coarsening regime of evolution, which was observed experimentally.

5.1 Time-Dependent Ginzburg-Landau Evolution Equation

Let us now look at the evolution of a spatially nonuniform system. In the spirit of discussion of the nonequilibrium systems in Chap. 4, we assert that the evolution equation should guide the system toward one of the equilibrium states, and the rate of change of OP should be proportional to the driving force. The only difference between the homogeneous and heterogeneous systems is that in the latter the driving force includes spatially diffuse forces. On the basis of this argument and comparing the equilibrium (2.12) with (3.29) a following evolution equation has been proposed instead of (4.3):

$$\frac{d\eta}{\mathrm{d}t} = -\gamma\left[\left(\frac{\partial g}{\partial\eta}\right)_{P,T} - \kappa\nabla^2\eta\right]. \tag{5.1}$$

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In the literature, this equation is known as the time-dependent Ginzburg-Landau equation (TDGLE). Using the expression of the variational derivative of the total free energy functional $G\{\eta\}$, with respect to the OP (see Appendix B), (5.1) can be written as follows

$$\frac{\mathrm{d}\eta}{\mathrm{d}t} = -\gamma\left(\frac{\delta G}{\delta\eta}\right)_{P,T}. \tag{5.2}$$

Comparing TDGLE in this form with the linear-ansatz (4.3), we see that the variational derivative in the former replaces the partial functional derivative in the latter. This is important for our understanding of the general properties of the evolution according to TDGLE. For instance, again it can be recognized as a gradient flow. The difference, of course, is that now the Lyapunov function(al) is the total free energy functional, (3.27), not the function $G(\eta)$. Indeed, using (5.2), we find that if (4.8) is valid then the total free energy of the system decreases (*dissipates*)

$$\frac{\mathrm{d}G}{\mathrm{d}t} = \int \frac{\delta G}{\delta\eta}\frac{\mathrm{d}\eta}{\mathrm{d}t}\mathrm{d}^3x = -\gamma\int\left(\frac{\delta G}{\delta\eta}\right)^2 \mathrm{d}^3x < 0. \tag{5.3}$$

That is why the systems described by TDGLE are called dissipative. Notice, however, that evolution of the total ordering in the system is not determined

$$\frac{\mathrm{d}}{\mathrm{d}t}\int \eta\,\mathrm{d}^3x = \int\frac{\mathrm{d}\eta}{\mathrm{d}t}\mathrm{d}^3x = -\gamma\int\frac{\delta G}{\delta\eta}\mathrm{d}^3x \gtrless 0. \tag{5.4}$$

Also, our conclusions regarding the nonlinear rate/driving force relation (Sect. 4.3) and memory function (Sect. 4.4) are valid here, if the variational derivative $\delta G/\delta\eta$ replaces partial functional derivative $\partial G/\partial\eta$.

Notwithstanding, even evolution of small disturbances in a heterogeneous system may be very different from that in a homogeneous one due to two major aspects. Firstly, in a heterogeneous system, there are small perturbations of the homogeneous equilibrium state which are spatially nonuniform; this changes the rate of their evolution. Secondly, and more significantly, in a heterogeneous system there are essentially heterogeneous equilibrium states, near which the evolution of small perturbations is significantly different from that near the homogeneous ones.

5.2 Motion of Plane Interfaces

In addition to the small perturbations of the equilibrium states, there exists another important group of solutions of the dynamic equation (5.1)—group-invariant (similarity) solutions. The idea behind these solutions is to reduce a partial differential equation (5.1) to an ordinary differential equation by using a particular symmetry of the system. Important examples of such solutions are called *traveling waves*, which use the translation invariance, expressed in the existence of the Goldstone modes (Sect. 3.7). That is, we seek a solution in the form

$$\eta(\mathbf{x}, t) = \eta(u), \quad u = \mathbf{n}\mathbf{x} - vt. \tag{5.5}$$

Here $\mathbf{n} = (\mathbf{j}_1, \mathbf{j}_2, \mathbf{j}_3)$ is a unit vector and v is a constant, the *wave speed*, which needs to be determined. A traveling wave solution of (5.5) may be visualized as a plane structure with profile given by $\eta(u)$ moving through the 3d space with speed v in the direction $\mathbf{n}$. This wave has the Goldstone mode in the direction $\mathbf{n}$ and translational symmetry in any direction perpendicular to $\mathbf{n}$. Using the chain rule of differentiation you can see that

$$\frac{\partial \eta}{\partial t} = -\frac{\mathrm{d}\eta}{\mathrm{d}u}v; \quad \nabla\eta = \frac{\mathrm{d}\eta}{\mathrm{d}u}\mathbf{n}, \tag{5.6}$$

$$\begin{aligned}\nabla^2\eta &= \frac{\mathrm{d}\eta}{\mathrm{d}u}\left(\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2}\right) + \frac{\mathrm{d}^2\eta}{\mathrm{d}u^2}\left[\left(\frac{\partial u}{\partial x}\right)^2 + \left(\frac{\partial u}{\partial y}\right)^2 + \left(\frac{\partial u}{\partial z}\right)^2\right] \\ &= \frac{\mathrm{d}^2\eta}{\mathrm{d}u^2}.\end{aligned} \tag{5.7}$$

In (5.7), the parenthesis with the second derivatives vanishes due to (5.5) and the bracket is equal to one because $|\mathbf{n}| = 1$. Using (5.6) and (5.7) for (5.1), we arrive at the ordinary differential equation

$$\kappa\frac{\mathrm{d}^2\eta}{\mathrm{d}u^2} + \frac{v}{\gamma}\frac{\mathrm{d}\eta}{\mathrm{d}u} - \left(\frac{\partial g}{\partial \eta}\right)_{P,T} = 0. \tag{5.8}$$

This is an autonomous equation, that is, an ordinary differential equation in which the independent variable does not appear explicitly. An autonomous equation is invariant under the Euclidean transformation $u \to u + a$. Since we know that the solution must be translation invariant we can reduce the order of the differential equation. First, we change the dependent variable from $\eta(u)$ to

$$q(\eta) = \frac{\mathrm{d}\eta}{\mathrm{d}u}. \tag{5.9a}$$

Second, by chain differentiation of (5.9a) we find that

$$q\frac{\mathrm{d}q}{\mathrm{d}\eta} = \frac{\mathrm{d}^2\eta}{\mathrm{d}u^2}. \tag{5.9b}$$

Third, we substitute (5.9) into (5.8) and obtain the first-order Abel-type ODE

$$q(\eta)\left(\kappa\frac{\mathrm{d}q}{\mathrm{d}\eta}+\frac{v}{\gamma}\right)=\frac{\mathrm{d}g}{\mathrm{d}\eta}. \tag{5.10}$$

In Chap. 3, we analyzed the equilibrium properties of (5.10), that is with $v=0$, and obtained an exact solution for a general function $g(P, T, \eta)$ in the form $q(\eta)=\pm\sqrt{2(g(\eta)-\mu)/\kappa}$ [see (3.43)]. In the infinite domain, the solution takes the form of (3.66) or (3.67). Unfortunately, for a moving interface ($v\neq 0$) such a general, exact solution does not exist.

However, in the case of a polynomial function $g(\eta)$ one may try to guess a solution. For instance, when $g(\eta)=P_4(\eta)$ one may try to find the solution in the form $q(\eta)=P_2(\eta)$. Indeed, let us try to solve (5.10) for the Landau free-energy potential (2.11). Using the expression, (2.13), for the stationary points (the equilibrium set) we can write

$$\left(\frac{\partial g}{\partial\eta}\right)_{P,T}=\eta(\eta-\bar{\eta}_-)(\eta-\bar{\eta}_+). \tag{5.11}$$

Then the dynamic equation (5.8) takes the form

$$q\left(\kappa\frac{dq}{d\eta}+\frac{v}{\gamma}\right)=\eta(\eta-\bar{\eta}_-)(\eta-\bar{\eta}_+). \tag{5.12a}$$

Physically, if we intend to analyze a first-order transition, we are looking for a solution of (5.12a), which approaches the equilibrium states $\eta=0$ and $\eta=\bar{\eta}_+$ far away from the wave. This motivates the following BC: (Why?)

$$q(0)=q(\bar{\eta}_+)=0. \tag{5.12b}$$

The problem (5.12) has a solution of the form

$$q=Q\eta(\eta-\bar{\eta}_+). \tag{5.13}$$

Substituting (5.13) into (5.12a) and balancing the terms of the same power in η, we find that indeed this is the case if

$$Q=\frac{\pm 1}{\sqrt{2\kappa}};\quad v=\pm\gamma\sqrt{\frac{\kappa}{2}}(\bar{\eta}_+-2\bar{\eta}_-). \tag{5.14}$$

Now $\eta(u)$ can be found by integrating (5.9a). It has the form

$$\eta_v(u)=\frac{\bar{\eta}_+}{1+\mathrm{e}^{\delta(u+a)}};\quad \delta=\bar{\eta}_+Q=\pm\frac{\bar{\eta}_+}{\sqrt{2\kappa}}, \tag{5.15}$$

where the constant of integration a is specified by the boundary or initial conditions.

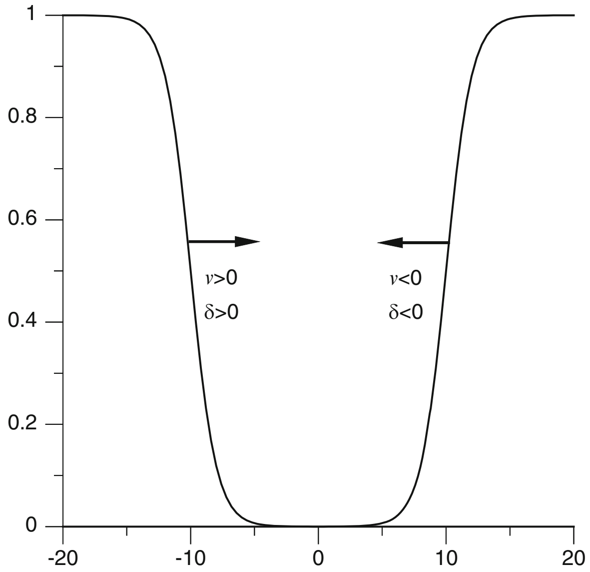

Fig. 5.1 Waves traveling in different directions

Equation (5.14) identifies the quantity $\left(\bar{\eta}_+ - 2\bar{\eta}_-\right)$ as a “driving force” for the interface and establishes the relationship between the speed v and parameters of the system. It shows that in a system with $B \neq 0$ at equilibrium ($T = T_\mathrm{E}$) the interface is not moving [see (2.19d)] and that for $T > T_\mathrm{E}$ and $T < T_\mathrm{E}$ the interface is moving in opposite directions because the quantity $\left(\bar{\eta}_+ - 2\bar{\eta}_-\right)$ has opposite signs (Verify!). However, the sign of v can be reversed not only by changing the thermodynamic conditions but also by the reflection ($Q \to -Q$). Two possible signs of Q manifest mirror symmetry of the system: for $Q > 0$ the wave is traveling in the direction of increasing u, for $Q < 0$ the opposite is true (see Fig. 5.1).

Comparison of (5.13) with (3.66) and Eq. (5.15) with (3.64) shows that the moving interface has pretty much the same structure as the stationary one. The following questions are in order here: What structural changes do occur when the interface solution “starts moving”? Does its thickness change? The thickness of the moving wave can be estimated by using the definition (3.32f). For the wave (5.15) we have

$$\frac{\mathrm{d}\eta_v}{\mathrm{d}u} = -\frac{\delta\bar{\eta}_+ \mathrm{e}^{\delta u}}{\left(1 + \mathrm{e}^{\delta u}\right)^2}. \tag{5.16a}$$

This is a bell-like function with $\max_u \left|\mathrm{d}\eta_v/\mathrm{d}u\right| = \left|\delta\bar{\eta}_+\right|/4$. Hence,

$$L_v = \frac{4}{|\delta|} = \frac{4\sqrt{2\kappa}}{\bar{\eta}_+}. \tag{5.16b}$$

As you can see the thickness of the traveling wave changes if κ or $\bar{\eta}_+$ (or both) change, that is, if (P, T) change. On the other hand, for the tangential potential $\bar{\eta}_+ = \text{const}(P, T)$; hence, if $\kappa = \text{const}(P, T)$ then $L_v = \text{const}(P, T)$, thus $L_v = \text{const}(v)$.

Equation (5.14) is very important for understanding mathematical features of our system. First, it shows that a nonlinear parabolic differential equation can support traveling wave solutions. However, unlike the linear wave equation, which is hyperbolic and propagates any wave form with the same speed, the nonlinear parabolic equation allows only certain wave profiles to propagate, each one with its own velocity. In other words, our system is not Galilean invariant (Why?). Second, (5.14) shows that the velocity is proportional to the deviation from equilibrium, for which $\left(\bar{\eta}_+ - 2\bar{\eta}_-\right)$ is a measure. Third, together with (5.15), it helps find the characteristic scales of the system: length 1/δ and time $1/\left(\gamma\bar{\eta}_+^2\right)$, and a useful expression for the velocity $v = (\gamma/2\delta)\bar{\eta}_+\left(\bar{\eta}_+ - 2\bar{\eta}_-\right)$. Fourth, the function d$\eta$/d$u$ from (5.16a) is a solution of the equation

$$\left\{\kappa\frac{\mathrm{d}^2}{\mathrm{d}u^2} + \frac{v}{\gamma}\frac{\mathrm{d}}{\mathrm{d}u} - \frac{\partial g(\eta_v)}{\partial\eta}\right\}\frac{\mathrm{d}\eta_v}{\mathrm{d}u} = 0. \tag{5.17}$$

Fifth, it is possible to resolve (5.8) or (5.10) for a more complicated potential that $g = P_4(\eta)$.

Example 5.1 Find the traveling wave solution for the anti-phase domains.

The anti-phase domain boundaries appear in the system that underwent the second-order transition (see Sects. 2.6.2, 5.5 and Example 3.2). Hence, we are looking for the solution of (5.12a) for the potential (2.11) with $B = 0$, $A < 0$ and with the BC

$$q(\bar{\eta}_-) = q(\bar{\eta}_+) = 0. \tag{5E.1}$$

This is

$$q = Q_1(\eta - \bar{\eta}_-)(\eta - \bar{\eta}_+). \tag{5E.2}$$

Substituting (5E.2) into (5.12a) and balancing the terms of the same power in η we find that

$$Q_1 = \frac{\pm 1}{\sqrt{2\kappa}}; \quad v_1 = \gamma\kappa Q_1\left(\bar{\eta}_+ + \bar{\eta}_-\right). \tag{5E.3}$$

However, after the second-order transition, see (2.44a)

$$\bar{\eta}_+ + \bar{\eta}_- = 0. \tag{5E.4}$$

Hence, a plane interface separating two variants of the same phase cannot move at all.

Example 5.2 Show that
$$q = Q_2\eta(\eta - \bar{\eta}_-) \tag{5E.5}$$

is another solutions of (5.12a) and try to find an application for it.

Example 5.3 Find the relation between the velocity v and temperature of a system described by the tangential potential.

Similar to Example 3.1, first, we find the rescaled value of the rate constant

$$\tilde{\gamma} = \frac{\gamma}{C^2}. \tag{5E.6}$$

Then, substituting $\bar{\eta}_+ = C$, $\bar{\eta}_- = C\tilde{\eta}_t$, $\tilde{\eta}_t = 1/2 + 3D/W$ from (2.34a), (2.35b), (5.37) and (3E.3), (5E.6) into (5.14) and (5.16b) we obtain

$$v = \mu(T_E - T), \quad \mu \equiv \frac{mL}{\sigma T_E}, \quad m \equiv \tilde{\gamma}\tilde{\kappa}, \tag{5E.7}$$

$$L_v = 4\sqrt{\frac{\tilde{\kappa}}{W}}. \tag{5E.8}$$

Here μ is called the kinetic coefficient (do not confuse with the chemical potential of Sect. 3.4); it is a measurable quantity in the experiments on the kinetics of phase transformations, e.g., crystallization. Notice that the mobility m and kinetic coefficient μ in (5E.7) are OP-scale invariant. Because for the tangential potential the thickness (5E.8) is velocity-independent, (5.13), (5.14), (5E.7) is also a 1d solution of (5.1) for the uniform but time-dependent temperature field $T(t)$. (Verify!)

5.3 Dynamic Stability of Equilibrium States

Dynamic stability of equilibrium states can be studied in a systematic way by analyzing evolution of *small perturbations* near these states. The perturbations are expressed as a superposition of some suitable set of *normal modes*, which must be *complete* for such a superposition to be possible, and examine equations of motion of each mode. In obtaining these equations from the relevant equations of motion of the whole system, we retain only terms which are linear in the perturbations and neglect all terms of higher order. Then, inserting

$$\eta(\mathbf{x}, t) = \eta_E(\mathbf{x}) + \Delta\eta(\mathbf{x}, t) \tag{5.18}$$

into TDGLE (5.1) and presenting $\partial g/\partial\eta$ by its Taylor series near the equilibrium state η_E we obtain:

$$\frac{1}{\gamma}\frac{\partial\Delta\eta}{\partial t} = \kappa\nabla^2\Delta\eta - \frac{\partial^2 g}{\partial\eta^2}(\eta_E)\Delta\eta - \frac{1}{2}\frac{\partial^3 g}{\partial\eta^3}(\eta_E)(\Delta\eta)^2 - \cdots \tag{5.19}$$

(Why is $\partial g(\eta_E)/\partial\eta$missing in (5.19)?) Neglecting all terms beyond the first order in $\Delta\eta$, we get the linearized problem

$$\frac{1}{\gamma}\frac{\partial\Delta\eta}{\partial t} = -\hat{\mathbf{H}}(\eta_E)\Delta\eta, \quad \hat{\mathbf{H}}(\eta_E) = \frac{\partial^2 g}{\partial\eta^2}(\eta_E) - \kappa\nabla^2. \tag{5.20}$$

Not surprisingly the problem of dynamic stability came down to the problem of the eigenvalues of the Hamilton's operator of the equilibrium state in question. We can benefit greatly from the analysis of the properties of this operator that was done in Chap. 3. Here we will repeat briefly some of the critical steps of that analysis.

5.3.1 Homogeneous Equilibrium States

Let us first consider evolution of the small perturbations $\Delta\eta$ near the homogeneous equilibrium states $\eta_E = \bar{\eta}$. In this case, (5.20) turns into a linear PDE with constant coefficients. Again, as done in Sect. 3.6.3, we use the method of Fourier transform (see Appendix F). The only difference is that now we use the integral transform instead of the discrete one. Replacing $\Delta\eta(\mathbf{x}, t)$ in (5.18) with its Fourier transform

$$\begin{aligned} \Delta\eta(\mathbf{x}, t) &= \int \Delta\hat{\eta}(\mathbf{k}, t)\, e^{i\mathbf{kx}}\, \mathrm{d}\mathbf{k} \\ \Delta\hat{\eta}(\mathbf{k}, t) &= \frac{1}{(2\pi)^3}\int \Delta\eta(\mathbf{x}, t)\, e^{-i\mathbf{kx}}\, \mathrm{d}\mathbf{x} \end{aligned} \tag{F.13}$$

we obtain the ODE for the Fourier transforms $\Delta\hat{\eta}(\mathbf{k}, t)$

$$\frac{\mathrm{d}\Delta\hat{\eta}}{\mathrm{d}t} = \beta(\mathbf{k})\Delta\hat{\eta}, \tag{5.21a}$$

$$\beta(\mathbf{k}) = -\gamma\left[\kappa|\mathbf{k}|^2 + \frac{\partial^2 g}{\partial\eta^2}(\bar{\eta})\right]. \tag{5.21b}$$

This equation can be solved as an initial value problem

$$\begin{aligned} \Delta\hat{\eta}(\mathbf{k}, t) &= \Delta\hat{\eta}_0(\mathbf{k})\, e^{\beta t}, \\ \Delta\hat{\eta}_0(\mathbf{k}) &= \frac{1}{(2\pi)^3}\int \Delta\eta(\mathbf{x}, 0)\, e^{-i\mathbf{kx}}\, \mathrm{d}\mathbf{x}, \end{aligned} \tag{5.22}$$

where the coefficients $\Delta\hat{\eta}_0(\mathbf{k})$ are the Fourier transforms of the initial condition.

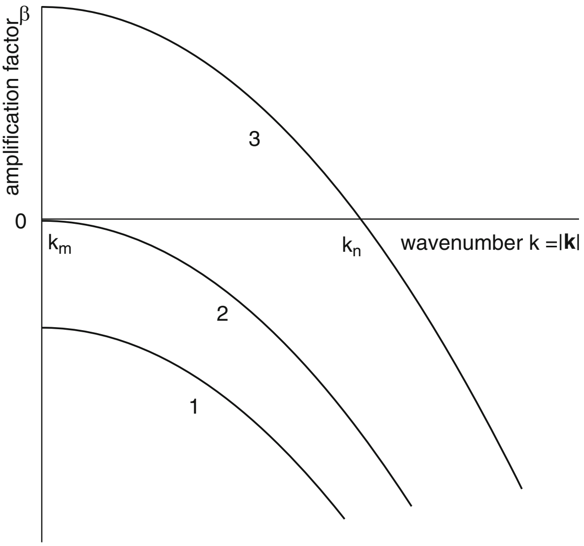

Fig. 5.2 Amplification factors for the homogeneous equilibrium states $\bar{\eta}$ in a system described by TDGLE (5.1). The state is (1) stable, (2) neutral, and (3) unstable

Same way as for the homogeneous perturbations, (4.11), the amplification factor of the small heterogeneous perturbations β determines the direction and rate of the evolution—recall that the time scale of evolution is $\tau = |\beta|^{-1}$, (4.12). Similar to the homogeneous case β is a real number for all parameters of the system and perturbations, but differs from that of the homogeneous case is that now β depends on the wave number $k = |\mathbf{k}|$ of the wavevector $\mathbf{k} = (k_x,\ k_y,\ k_z)$ of the Fourier transform $\Delta\hat{\eta}(\mathbf{k},\ t)$. If $\partial^2 g(\bar{\eta})/\partial\eta^2 > 0$ (the state $\bar{\eta}$ is stable—a phase) then $\beta < 0$ for all wavevectors; if $\partial^2 g(\bar{\eta})/\partial\eta^2 < 0$ (the state $\bar{\eta}$ is unstable) then $\beta < 0$ for the wavevectors with the wave numbers $k > k_n$, $\beta > 0$ for $0 < k < k_n$, and $\beta = 0$ for the wavevectors with the neutral wavenumber $k = k_n$

$$k_n^2 = -\frac{1}{\kappa}\frac{\partial^2 g(\bar{\eta})}{\partial\eta^2}. \tag{5.23}$$

These cases are depicted in Fig. 5.2. For instance, for the transition state $\bar{\eta}_t$ of the tangential potential (2.33)

$$k_n^t = \sqrt{\frac{W^2 - (6D)^2}{2\kappa W}}, \tag{5.24}$$

which shows that the transition state is dynamically unstable if $|D| < W/6$, that is, between the spinodal lines of the phase diagram.

It is convenient to think about individual harmonic wavemodes defined by the components of the wavevector $\mathbf{k} = (k_x, k_y, k_z)$. For instance, the "most dangerous" wavemode is the one with the greatest value of the amplification factor β. For TDGLE (5.1), it is the one with $k_m = 0$ (see Fig. 5.2). Then you can see that for TDGLE there is only one most dangerous mode $\mathbf{k}_{\mathrm{m}} = (0,\ 0,\ 0)$—uniform disturbance, but there are many neutral modes $\mathbf{k}_n = (k_{n,x},\ k_{n,y},\ k_{n,z})$ defined by the equation

$$k_{n,x}^2 + k_{n,y}^2 + k_{n,z}^2 = k_n^2 \tag{5.25}$$

As you can see from this equation, the neutral modes belong to the sphere of radius k_n centered at the origin of the Fourier space $\mathbf{k}$.

Comparing the dynamical stability analysis of this section and Sect. 4.2.1 to the thermodynamic stability analysis of Sect. 2.3, we can see that they lead to the same conclusion that the stability of the state $\bar{\eta}$ is determined by the sign of $\partial^2 g(\bar{\eta})/\partial\eta^2$. The advantage of the dynamical analysis is that we can learn more about the rate of attainment of the state in the system.

It is prudent here to make another comment regarding the normal modes; they must be not only small in amplitude, but also they cannot have very high wavenumbers, so that $|\mathbf{k}| \ll (\text{interatomic distance})^{-1}$, see (7.27) and Sect. 10.2.

5.3.2 Heterogeneous Equilibrium States

In Sect. 3.7.1, we found the plane, stationary interface $\eta_{\mathrm{E}} = \eta_{\mathrm{e4}}(x)$, which separates two phases at equilibrium, to be thermodynamically stable. Let us analyze now the dynamical stability of this state. Taking into account our success with the analysis of the thermodynamic stability of this state, we shall represent the small perturbations $\Delta\eta(x,\ y,\ z,\ t)$ in the form of the capillary waves, i.e., normal modes on the interface

$$\Delta\eta \propto \exp\left[\beta t + i(k_z z + k_y y)\right] \psi_n(x), \tag{5.26a}$$

where $\psi_n(x)$ are the eigenfunctions of the Hamilton's operator $\hat{\mathbf{H}}(\eta_{\mathrm{e4}}(x))$ with the eigenvalues λ_n. Substituting this expression into (5.20) we obtain the following dispersion relation

$$\beta = -\gamma\left[\lambda_n + \kappa\left(k_z^2 + k_y^2\right)\right]. \tag{5.26b}$$

The solution (5.26a) represents motion of transverse $(y,\ z)$-plane waves superimposed on the normal x-deformations of the interfacial structure $\eta_{\mathrm{E}} = \eta_{\mathrm{e4}}(x)$. Their evolution depends on β. As β in (5.26b) is a real number (why?), the separated solutions will diminish if $\beta < 0$, grow if $\beta > 0$, and remain stationary if $\beta = 0$. Notice from the dispersion relation (5.26b) and condition (3.26) that the second term is always negative due to the stabilizing influence of the gradient energy. This effect may be compared to the effect of the surface tension on the capillary waves on the water surface. The first term in (5.26b) is almost always negative (review Appendix E). The only other option for this term is to be equal to zero for the bound state with $n_* = 0$. Hence, our dynamic stability analysis of the domain wall (interface) shows that it is neutrally stable with the Goldstone mode ($n_* = 0$, $k_y = 0$, $k_z = 0$) being the "most unstable." This mode represents a parallel shift of the interface, which does not change the thermodynamic balance in the system because the phases on both sides of it are at equilibrium. Notice that the conclusion from the dynamic stability analysis is equivalent to that of the thermodynamic one. The significant advantage of the former is that it can reveal the rate of growth or decay of different modes.

5.3.3 Morphological Stability of Moving Plane Interface

At this juncture, it is natural to ask the following question: "Is the moving plane interface solution $\eta_v(u)$ stable with respect to the "capillary waves:" on it? To answer this question, we perturb the solution (5.15) with the capillary wave of small amplitude $N(u)$

$$\eta(\mathbf{x}, t) = \eta_v(u) + N(u)\mathrm{e}^{(\beta t + i\mathbf{k}_2\mathbf{x}_2)}, \tag{5.27a}$$

where $(\mathbf{nk}_2) = 0$ and $\mathbf{x}_2 = (0, y, z)$, and substitute (5.27a) into (5.1). After linearization, application of (5.8), and factorization of the exponential, it reduces to the following equation

$$\kappa \frac{\mathrm{d}^2 N}{\mathrm{d}u^2} + \frac{v}{\gamma}\frac{\mathrm{d}N}{\mathrm{d}u} - \left\{\frac{\partial^2 g(\eta_v)}{\partial \eta^2} + \kappa|\mathbf{k}_2|^2 + \frac{\beta}{\gamma}\right\} N = 0. \tag{5.27b}$$

Compare (5.27b) with (5.17) and notice that it has a solution

$$N = \frac{\mathrm{d}\eta_v}{\mathrm{d}u} \tag{5.27c}$$

with the solvability condition

$$\beta = -\gamma\kappa|\mathbf{k}_2|^2. \tag{5.27d}$$

The latter tells us that the moving plane interface (5.14), (5.15) is neutrally stable (see Fig. 5.2). Notice that the dispersion relation is independent of the barrier-height parameter. We may interpret this result as following: for the fixed kinetic coefficient and interfacial energy the stability criterion is independent of the interfacial thickness.

5.4 Motion of Curved Interfaces: Drumhead (Sharp Interface) Approximation

As we have seen in the previous section a plane interface moving with a constant speed may have practically the same structure as that at equilibrium. This is a result of a delicate misbalance of the "thermodynamic," $(\partial g/\partial\eta)$, and "gradient," $(\kappa\, \mathrm{d}^2\eta/\mathrm{d}u^2)$, forces, which drives the interface with speed v leaving its structure practically unchanged. We may ask a question: Is it possible that a moving *curved* interface also preserves its structure? The problem is that in addition to the forces affecting the plane interface the curved interface will experience one more force, "geometric," which can be identified through a transformation to a curvilinear coordinate system. Capitalizing on our success in Sect. 3.6.1 with the application of the curvilinear coordinates to the study of equilibrium interfaces, we introduce curvilinear *time-dependent* coordinates $\{u = U(\mathbf{x},\, t),\ v = V(\mathbf{x},\, t),\ w = W(\mathbf{x},\, t)\}$ such that during the entire process OP is a function of one coordinate only: $\eta = \eta(u)$ (see Fig. 3.6). Velocity of motion $\mathrm{v}_\mathrm{n}(v, w, t)$ of the surface $U = \text{const}$ is determined by the relation

$$\frac{\partial U}{\partial t} + v_\mathrm{n}|\nabla U| = 0, \tag{5.28}$$

where v_n defines the normal component of the velocity, that is, the component perpendicular to the level surfaces $U = \text{const}$. The tangential component of the velocity is not specified by this method. The latter may be defined separately if there is a need. In the curvilinear system of coordinates, TDGLE (5.1) takes the form

$$\kappa\frac{\mathrm{d}^2\eta}{\mathrm{d}u^2} + \left(\frac{v_\mathrm{n}}{\gamma} + 2\kappa K\right)\frac{\mathrm{d}\eta}{\mathrm{d}u} - \frac{\partial g(T,\eta)}{\partial\eta} = 0. \tag{5.29}$$

To solve (5.29), a number of different techniques may be used. We will demonstrate here how the method of *averaging* can be used to derive the evolution equation for a piece of an interface. First, we introduce the averaging operator

$$\hat{\mathbf{A}}\cdot f \equiv \int_{u_\beta}^{u_\alpha} f(\eta(u),\, u)\,\mathrm{d}u, \tag{5.30}$$

where the integration is over the thickness of the interface, that is, the interval $(u_\beta,\, u_\alpha)$ end points of which are located outside the interface zone in the regions occupied by the respective phases: $\eta(u_\beta){=}\eta_\beta$ and $\eta(u_\alpha){=}\eta_\alpha$ (see Fig. 3.6). However, straight averaging of (5.29) will eliminate the driving force term because $\int_{-\infty}^{+\infty} \partial g(T_E, \eta_{\mathrm{e}4})/\partial\eta\,\mathrm{d}u = 0$, see (3.35). Hence, proper averaging of the TDGLE should include a weight factor. As the weight factor for the averaging of (5.29) we use $\mathrm{d}\eta/\mathrm{d}u$ (for the choice of the weight factor, see Appendix D). Then, taking into account that $\mathrm{d}\eta/\mathrm{d}u$ vanishes at u_α and u_β we obtain

$$\hat{\mathbf{A}} \cdot \left(\frac{\mathrm{d}^2\eta}{\mathrm{d}u^2} \frac{\mathrm{d}\eta}{\mathrm{d}u} \right) = 0. \tag{5.31a}$$

Using the relation

$$\mathrm{d}g = \frac{\partial g}{\partial \eta}\,\mathrm{d}\eta \tag{5.31b}$$

we obtain

$$\hat{\mathbf{A}} \cdot \left(\frac{\partial g}{\partial \eta} \frac{\mathrm{d}\eta}{\mathrm{d}u} \right) = g(u_\alpha) - g(u_\beta) \cong [g]^\alpha_\beta, \tag{5.31c}$$

where $[g]^\alpha_\beta$is the jump of the free energy density from one phase to another. The difference between this quantity and the one defined in Sect. 2.1 is that now we are dealing with the phases which are not at equilibrium with each other and, hence, $[g]^\alpha_\beta \neq 0$. Furthermore, using (3.70a), the condition of the small geometrical number, (3.85), and the fact that $(\mathrm{d}\eta/\mathrm{d}u)^2$ is a bell-like, even function of u (see Sect. 3.4), we find

$$\hat{\mathbf{A}} \cdot \left\{ \left(\frac{v_\mathrm{n}}{\gamma} + 2\kappa K \right) \left(\frac{\mathrm{d}\eta}{\mathrm{d}u} \right)^2 \right\} = k_\eta \hat{\mathbf{A}} \cdot \left\{ \kappa \left(\frac{\mathrm{d}\eta}{\mathrm{d}u} \right)^2 \right\} + O\left(L_v^3 k_\eta^3 \right) \approx k_\eta \sigma, \tag{5.31d}$$

that, in the curvilinear system, the coordinates in TDGLE (5.1) separate (cf. (3.86)). In (5.31d) k_η may be called the dynamic wave number of a curved interface

$$k_\eta = \frac{v_\mathrm{n}}{m} + 2K_0. \tag{5.31e}$$

The mobility $m = \gamma\kappa$ is defined in (5E.7), and L_v is the thickness of the interface. Finally, applying the averaging operator (5.30) to the properly weighted (5.29) we obtain the equation of motion of a phase separating interface, which relates different local characteristics of the interface

$$v_\mathrm{n} = m \left(\frac{[g]^\alpha_\beta}{\sigma} - 2K_0 \right). \tag{5.32}$$

The free energy density jump in this equation depends on the temperature and/or pressure on the level surface $U = 0$ that represents the interface. Thus, all variables in this equation depend only on the local coordinates (v, w) and time t.

Equation (5.32) is an important result. First, it shows that introduction of the time-dependent curvilinear coordinates has an advantage in that the evolution of the OP field may be described by the motion of the surface $U = 0$ in space and time. Second, and most importantly, it reveals the "driving forces" for the interfacial motion: its curvature $(-2K_0)$ and the free energy density difference on both sides of the interface, $[g]_\beta^\alpha$. Compare (5.32) to Example 5.1, where we found that a plane APB cannot move, and notice that a curved APB should move toward the center of its curvature. Compare (5.32) with (5E.7) and notice that m/σ may be considered the kinetic coefficient for the driving force $[g]$.

5.4.1 Nonequilibrium Interface Energy

The integral in (5.31d), although having the form of the interface energy, actually is a more complicated quantity because it relates to a moving interface and the interface energy of the moving interface needs to be defined. The main difficulty here comes from the fact that, contrary to equilibrium, the free energy densities of phases on opposite sides of the interface are not equal. For a first-order transition, the difference between these densities constitutes the bulk driving force for the interface motion. Even if the densities of the free energy are equal, (e.g., for an APB), the interface is not flat and is moving under influence of its own curvature and surface energy.

To define the nonequilibrium surface energy, we suggest the following procedure. Let us allow the interface to move during dt and calculate the change of the Gibbs free energy in the system as a result of such motion. Using (3.27), (3.29), we obtain

$$\mathrm{d}G = \int \frac{\delta G}{\delta \eta} \delta\eta \, \mathrm{d}^3x = \mathrm{d}t \int \left[\left(\frac{\partial g}{\partial \eta} \right)_{T,P} - \kappa \nabla^2 \eta \right] \frac{\mathrm{d}\eta}{\mathrm{d}t} \mathrm{d}^3x. \tag{5.33a}$$

Noticing from (5.29) that in the curvilinear time-dependent system (u, v, w, t) the coordinates separate, we transform the coordinates and use (5.28), (C.16), (C.23). Then we find that this change is divided into two contributions

$$\mathrm{d}G = -[g]_\beta^\alpha \, \mathrm{d}t \int_{U=0} v_\mathrm{n} \, \mathrm{d}v \, \mathrm{d}w - \hat{\mathbf{A}} \cdot \left\{ \kappa \left(\frac{\mathrm{d}\eta}{\mathrm{d}u} \right)^2 \right\} \mathrm{d}t \int_{U=0} 2K_0 v_\mathrm{n} \, \mathrm{d}v \, \mathrm{d}w. \tag{5.33b}$$

The first term is proportional to the volume of the system swept over by the interface; the coefficient of proportionality in front of this term is the bulk free-energy jump that represents the driving force for the interface motion. The second term is proportional to the change of the area of the interface, which came about as a result of the motion. Hence, the coefficient of proportionality of this term may be defined as the nonequilibrium interface energy σ:

$$\sigma \equiv \int_{-\infty}^{+\infty} \kappa \left(\frac{\mathrm{d}\eta}{\mathrm{d}u}\right)^2 \mathrm{d}u. \tag{5.34}$$

Thus, the equilibrium definition of the interfacial energy, (3.70a), is extended into a nonequilibrium situation of a moving boundary. The equilibrium definition of the length scale of the interface, (3.32f), may also be extended into a nonequilibrium region.

5.4.2 *Evolution of a Spherical Droplet*

Equation (5.32) may help us understand the evolution of the droplets, which we considered in Sect. 3.1 in connection to the classical nucleation problem. Indeed, according to the definition of Sect. 3.1, the critical nucleus is the sphere of a new phase which does not grow larger or becomes smaller. Hence, its interfacial velocity is zero. Then, (5.32) yields the formula

$$\frac{1}{K_*} \equiv R_* = \frac{2\sigma}{[g]_\beta^\alpha}. \tag{5.35}$$

This expression coincides with (3.14). However, with (5.32), we can go one step further and determine the rate of evolution of the spherical droplets. Indeed, recalling that for a spherical droplet

$$R = \frac{1}{K_0}, \quad v_\mathrm{n} = \frac{\mathrm{d}R}{\mathrm{d}t} \tag{5.36a}$$

or

$$\frac{\mathrm{d}K_0}{\mathrm{d}t} = -v_\mathrm{n} K_0^2 \tag{5.36b}$$

(for simplicity we drop the subscript “0” in the radius R) we can solve the first-order ODE (5.32) and obtain the solution in the following form

$$t - t_i = \frac{R_*}{2m}\left(R - R_i + R_* \,\ln\left|\frac{R - R_*}{R_i - R_*}\right|\right), \tag{5.37}$$

where R_i is the initial radius of the droplet at $t = t_i$. This solution shows that the droplets are dynamical unstable: they grow without a limit if $R_i > R_*$ or shrink to

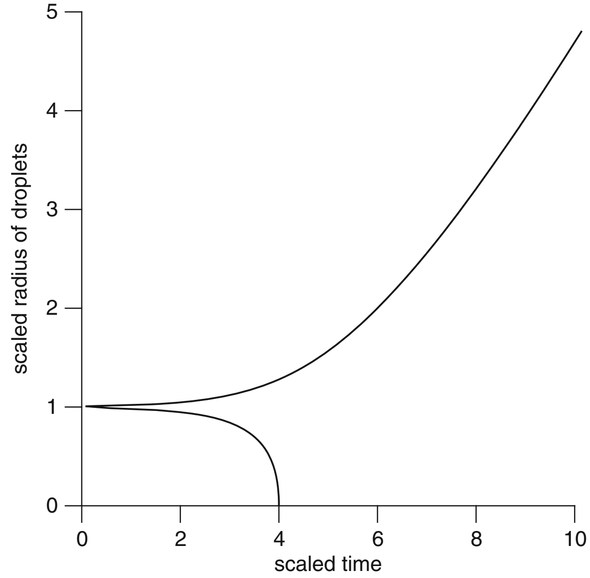

Fig. 5.3 Scaled rate of growth or shrinking of two spherical droplets with the initial radii just above and below the critical one. The latter is one

zero if $R_i < R_*$. More specifically, if the initial radius of the droplet is greater than the critical, it will be growing with a speed approaching $m[g]/\sigma$. On the other hand, if the initial radius of the droplet is smaller than the critical, it will disappear after a finite amount time, which depends on the initial radius R_i. These cases of evolution are depicted in Fig. 5.3.

5.5 Domain Growth Dynamics

Another interesting application of (5.32) comes about in systems that have undergone a second-order transition. As we discussed in Example 3.2, the interface in this case is called anti-phase domain boundary (APB) because phases that appear on both sides of the interface are not different phases; they are just different *variants* of the same phase. That is why in APB motion $[g] = 0$. Then, applying (5.32) to the APB motion we obtain

$$v_{\mathrm{n}} = -2mK_0. \tag{5.38a}$$

Hence, in APB motion, all spherical domains shrink starting with the initial size of R_i

$$R^2 = R_i^2 - 4mt. \tag{5.38b}$$

However, due to possible interconnectedness of the domains of the same variant, the problem of APB evolution is more complicated than just the rate equation (5.38a).

A full (so to speak “honest”) resolution of the problem of APB motion starting with the initial configuration of the interconnected domains is very complicated (although not entirely impossible). That is why we will be concerned here only with the evolution of the average size of the domains. Quite naturally, this size is related to the size of the separating surface, which is measured by its area. Thus, at first we have to review some of the general properties of the evolving surfaces.

Let us consider a small piece of smooth surface [without sharp corners, see condition (3.85)]. It may be represented by a tangent plane and characterized by its orientation in space. Any larger (but still small) piece of the surface is represented by a tangent sphere and characterized by its radius R and solid angle dΩ. Then for the area of this piece we obtain

$$\mathrm{d}S = R^2\,\mathrm{d}\,\Omega. \tag{5.39a}$$

Locally, evolution of this piece of surface can be described as the change of the radius ΔR. Then for the change of the area within the same solid angle dΩ we obtain

$$\Delta(\mathrm{d}S) = 2R\ \Delta R\,\mathrm{d}\ \Omega = \frac{2}{\mathrm{R}}\ \Delta R\,\mathrm{dS}. \tag{5.39b}$$

If the entire surface S is smooth then (5.39a), (5.39b) apply to every part of it and we obtain an expression for the area change

$$S \equiv \int_S \mathrm{d}s; \qquad \Delta S = \int_S \frac{2}{R}\ \Delta R\,\mathrm{d}s. \tag{5.39c}$$

As we discussed in Sect. 5.4, the temporal changes of the radius of curvature can be related to the normal velocity of the interface

$$\Delta R = v_\mathrm{n}\,\mathrm{dt}. \tag{5.39d}$$

Substituting (5.39d) into (5.39c) and replacing $(1/R)$ with the mean curvature K_0 of the surface, we arrive at the equation for the total surface area change

$$\frac{\mathrm{d}S}{\mathrm{d}t} = 2\int_S v_\mathrm{n} K_0\,\mathrm{d}s. \tag{5.40}$$

To complete the system of equations for the surface evolution, (5.32) should be used for v_n in (5.40). In the case of APB motion, substituting (5.38a) into (5.40) we obtain

$$\frac{\mathrm{d}S}{\mathrm{d}t} = -4m\int_S K_0^2\,\mathrm{d}s. \tag{5.41}$$

The integro-differential equation (5.41) shows that the total surface area of the domain boundaries monotonically decreases in time, which implies that the average domain size increases. This regime may be called "*coarsening*". Equation (5.41) does not allow us to make more detailed predictions regarding the behavior of the system.

The breakthrough may be achieved with the help of the *self-similarity* hypothesis [2]. To understand the hypothesis, let us review the length scales that characterize our system. Vanishing of the free-energy jump for APB eliminates only the time-independent length scale of the system, $R_* = 2\sigma/[g] \rightarrow \infty$, see (5.35). The system of interconnected domains has two time-dependent length scales. The product of the mobility m and time has the units of [length^2], hence, the first relevant length scale is

$$\mathrm{d}(t) = \sqrt{mt}. \tag{5.42}$$

The radius of curvature of the surface, $R = 1/K_0$, is the second relevant length scale; it characterizes locally the size of a domain occupied by one variant, e.g., α. This opens up a possibility for a self-similar regime of evolution. However, K_0 changes from place to place and to characterize the entire system we need to introduce an average quantity. Taking into account that the average curvature vanishes, $\int_S K_0\, \mathrm{d}s = 0$, we introduce the average square mean curvature of the surface

$$\bar{K}^2 \equiv \frac{1}{S} \int_S K_0^2\, \mathrm{d}s. \tag{5.43}$$

Then $\bar{R} = 1/\bar{K}$ characterizes the average domain size in the system.

Now let us see how these domains fill up the space. Imagine that entire volume of the system V is densely filled by the spheres of radius r of the variant α with the variant β filling the rest of the volume. Then we can write that

$$V = c\frac{1}{3}srN, \tag{5.44a}$$

where $s = 4\pi r^2$ is the surface of a sphere, N is the number of them, and c is the packing coefficient which depends on the arrangement of the spheres. For instance, $c = 6/\pi$ if the spheres are arranged in a simple cubic lattice. The product sN equals the total surface area in the system S. Then

$$S = \frac{3}{c}V|K_0|. \tag{5.44b}$$

As time passes, the total area S and domain curvature K change while the total volume V stays constant. If we assume that the growing or decreasing spheres always form the same type of lattice—*self-similarity regime*—then the packing coefficient $c = \text{const}$ and

$$\bar{K}(t) = \varphi S(t), \tag{5.45}$$

where $\varphi = c/(3V)$ in our example. Substituting (5.43), (5.45) into (5.41), we obtain an ODE for the average square mean curvature only

$$\frac{\mathrm{d}\bar{K}}{\mathrm{d}t} = -4m\bar{K}^3. \tag{5.46}$$

This equation has a solution

$$\bar{K}^{-2}(t) = \bar{K}^{-2}(t_0) + 4m(t - t_0), \tag{5.47}$$

where $\bar{K}(t_0)$ is the average square mean curvature at the moment in time t_0 when the self-similar regime started. Equation (5.47) shows that in the self-similarity regime the average domain size, $1/\bar{K}(t)$, monotonically increases, which justifies the term "coarsening."

For the total surface area (5.45), (5.47) yields

$$S^{-2}(t) = S^{-2}(t_0) + 4\varphi^2 m(t - t_0). \tag{5.48}$$

Initial decrease of the curvature and surface area is linear in time with the rate dependent on the initial condition

$$\begin{aligned} \bar{K}(t) &\approx \bar{K}(t_0)\left[1 - 2m\bar{K}^2(t_0)(t - t_0)\right], \\ S(t) &\approx S(t_0)\left[1 - 2m\varphi^2 S^2(t_0)(t - t_0)\right]. \end{aligned} \tag{5.49a}$$

Asymptotically the system approaches the regime when all three length scales are proportional

$$\frac{S(t)}{\mathrm{V}} \approx \bar{K}(t) \approx \frac{1}{2\sqrt{mt}} = \frac{1}{2d(t)}. \tag{5.49b}$$

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Chapter 6
Thermomechanical Analogy

A profound physical analogy can be established between the thermodynamic system undergoing a phase transition and a classical-mechanical point mass moving in a potential field. According to this analogy, the spatial coordinate, x, of a 1d thermodynamic system is analogous ($\doteq$) to the time, t, of the mechanical system; OP η is analogous to the generalized coordinate of the particle; gradient free energy coefficient is analogous to the generalized mass of the particle. In the framework of this analogy, the negative of the homogeneous density of the Gibbs–Landau free energy ($-\mathrm{g}$) is analogous to the mechanical potential function U

$$U \doteq -g(\eta), \tag{6.1}$$

while the gradient free-energy contribution is analogous to the kinetic energy of the particle, K

$$K \doteq \frac{1}{2}\kappa\left(\frac{\mathrm{d}\eta}{\mathrm{d}x}\right)^2. \tag{6.2}$$

The density of the Gibbs–Landau free energy, $\hat{g}$, (3.27), is analogous to the Lagrangian of the mechanical system and the quantity $\breve{g}$, (3.28), to the negative of the Hamiltonian. The quantity $\breve{g}$ can be obtained from the density $\hat{g}$ with the help of the Legendre transform (LT) using the OP gradient ($\mathrm{d}\eta/\mathrm{d}x$) as the variable. The OP itself (η) is not involved into the LT; that is why the homogeneous density $g(\eta)$ flips its sign when it is put into the LT (see Appendix F and Example F.2 therein). Then (3.29) corresponds to the Newtonian equation of motion of a particle in either Lagrange's or Hamilton's formulation; the condition of thermodynamic equilibrium, (3.42a), corresponds to the conservation of the mechanical energy; and negative of the chemical potential ($-\mu$) corresponds to the total mechanical energy of the system (K + U). The energy is conserved because the Hamiltonian does not depend explicitly on time, that is $\breve{g}$ does not depend explicitly on the coordinate x. The total Gibbs free energy of the thermodynamic system, G in (3.27), is analogous

A. Umantsev, *Field Theoretic Method in Phase Transformations*,
Lecture Notes in Physics 840, DOI 10.1007/978-1-4614-1487-2_6,

Table 6.1 Dictionary of the thermomechanical analogy

Continuum thermodynamics (1d systems)	Classical mechanics of many particles
Equilibrium in an open system	*Dynamics in a conservative system*
Clausius' principle	Hamilton's principle
Spatial coordinate: $x \in [\mathrm{x}_1, x_2]$	Time: $t \in [t_1, t_2]$
Thermodynamic variables: $\{\rho_i, \eta_j\}$	Generalized coordinates
Gradient free energy coefficients $\kappa_{\alpha,ij}$	Generalized masses
Negative of the homogeneous density of the free energy g	Potential function U
Density of the gradient energy	Kinetic energy K
Density of the free energy $\hat{g}$	Lagrangian
The quantity $\breve{g}$	Negative of the Hamiltonian
Equilibrium equations	Lagrange equations
Negative of the chemical potential ($-\mu$)	Total mechanical energy (K + U)
Total free energy G	Action
The interface energy	"Abbreviated action"
Relaxation dynamics	*Dissipative dynamics*
TDGLE	Lagrange equation with dissipation
Velocity over relaxation coefficient v/γ_i	Dissipative coefficient
Dissipative function F	Rayleigh's function
Non-isothermal dynamics	*Dynamics in external fields*
Temperature	Time-dependent external field

to the action of the mechanical system and the interface energy, σ in (3.70a), to the "abbreviated action" [1, 2]. Minimization of the interfacial energy is analogous to the principle of least action for the mechanical system. Table 6.1 summarizes the analogous terms in thermodynamics and classical mechanics and Fig. 6.1 shows different kinds of motion of a particle in the potential field U.

The thermomechanical analogy helps us to identify and interpret different equilibrium states in the system: the bulk phases α and β correspond to unstable (saddle-type) rest points separated by a stable (center-type) rest point γ of the mechanical system with one degree of freedom. Heterogeneous equilibrium states correspond to bound solutions of the mechanical system, e.g., periodic thermodynamic states to periodic mechanical solutions (Fig. 6.1a). Due to unboundness of the free energy, g, Fig. 3.2bi, and, hence, potential, U, (6.1), only one type of periodic motion is possible, oscillation (no rotations). The interface between the bulk phases α and β corresponds to the *heteroclinic trajectory* that connects two different rest points with equal potential energies U as shown in Fig. 6.1b (c.f. Fig. 3.2bii, iii). A critical-nucleus (instanton) corresponds to a *homoclinic orbit* that connects one rest point of lower potential energy U to itself, which is possible only for a "tipped-off" potential U (not equal depths of the wells, shown in Fig. 6.2, c.f. Fig. 3.2ai, ii, iii). Notice that due to the negative sign in (6.1) the equilibrium states switch their stabilities when "going" from the thermodynamics to mechanics. For instance, mechanical periodic solutions (Fig. 6.1a) are stable, while their thermodynamic counterparts (c.f. Fig. 3.2biii) are not. The unstable periodic states, however, do appear in the processes of phase transformations and the systems may spend a great deal of time in the vicinity of these states. Another interesting analogy can be established between the instanton

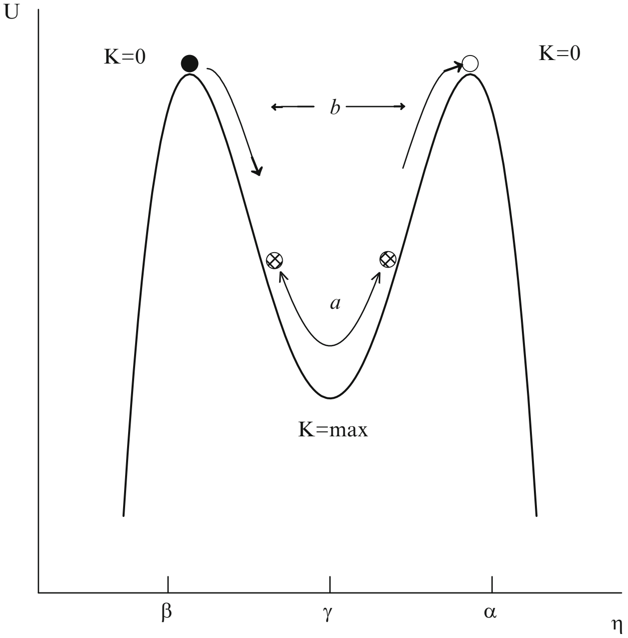

Fig. 6.1 Undamped oscillator as the mechanical analog of an equilibrium heterogeneous 1d thermodynamic system. Even potential function $U \doteq -g(\eta)$ corresponds to the thermodynamic equilibrium between phases α and β. α, β, and γ —rest points of the point mass in the potential *U*. (*a*) Periodic oscillator: the *shaded circles* indicate the turning points of the point mass. (*b*) Heteroclinic orbit: the *filled* (β) and *open* (α) *circles* indicate initial and final positions of the point mass (stable bulk phases)

described in Example 3.4 and a homoclinic orbit describing motion of a particle in one well of a double-well even potential (Verify!).

The dynamic equation (5.8) describes translation-invariant wave of OP, $\eta = \eta(x - \mathrm{v}t)$, which represents an interface between stable (β) and metastable (α) states and which travels with constant speed v. The wave cannot move at a steady pace with an arbitrary speed and have an arbitrary shape. Instead, the speed v, (5.14), and shape $\eta(u)$, (5.15), of the wave interface are *selected* as an eigenvalue/eigenfunction of the boundary problem (5.12). The thermomechanical analogy will be established if, in addition to the above described equilibrium analogy, the coefficient v/γ in (5.8) is brought into correspondence to the friction coefficient (see Table 6.1). Then the wave is analogous to the heteroclinic trajectory between two rest points with different potential energies *U*, see Fig. 6.2a. The analogy clarifies that for the friction coefficients smaller than the *critical*, trajectories are unbounded while for the coefficients that are greater—trajectories never reach the rest point (α). Hence, the selected wave-interface also possesses the "critical property," which is best revealed by the thermomechanical analogy. The thermomechanical analogy clearly shows that (5.8) has many solutions, which do not satisfy the boundary conditions, (5.12b), and only one that does.

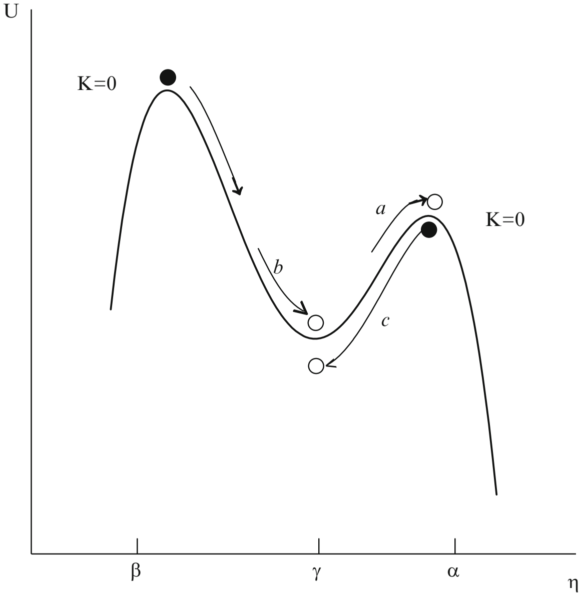

Fig. 6.2 Damped oscillator as the mechanical analog of a traveling wave in the thermodynamic system. Tipped-off potential function U corresponds to thermodynamic preference of a stable phase, β, compared to a metastable phase, α. The *filled circles* indicate the initial positions and the *open circles* indicate the final positions of the point mass. (*a*) Critically damped oscillator; (*b*) "marginally" damped oscillator; (*c*) "marginally" damped oscillator from the lower hump

The thermomechanical analogy helps us better understand the phase transitions processes by developing an intuitive approach to the dynamical problems. For instance, it clearly shows that the phase-transition dynamics destroys the equilibrium types of heterogeneous solutions: periodic, critical nucleus (instanton), and stationary interface (domain-wall), because they correspond to the conservation of the mechanical energy, and replaces them with the traveling waves with different speeds, v (c.f. Figs. 6.1 and 6.2). The thermomechanical analogy also helps interpret the *principle of selection* of such waves, that is, the answer to the question: "How can we determine the *unique* velocity of a wave that will be realized in a physical or numerical experiment with given temperature and pressure?" One example of that principle was considered above: moving interface that replaces a metastable phase with the stable one. Another example is decomposition of an unstable state γ [3]. According to (5.8), such wave may propagate with many acceptable velocities, v, which correspond to the damped oscillations of a particle about a stable rest point γ with different values of the friction coefficient, see Fig. 6.2. (Recall that the thermomechanical analogy switches stabilities between the equilibrium states of the thermodynamic system and the mechanical rest points.) The asymptotically stable traveling-wave solution, however, corresponds to the case of "marginal stability" [4, 5], that is, the waves that move slower are unstable to perturbations while those that move faster are stable. From the standpoint of the thermomechanical analogy, the asymptotically stable wave of decomposition of the unstable state into the stable one (β, Fig. 6.2b) corresponds to a particle motion with the *marginal damping*. The analogy also indicates that the unstable state may be replaced by a metastable one (α, Fig. 6.2c). The speed of the latter process is smaller than that of the former because its mechanical analog requires smaller coefficient of friction.

The thermomechanical analogy can be expanded beyond the boundaries considered above. For instance, several OPs will be analogous to several coupled mechanical point masses; however, the system must be one-dimensional for the analogy to work (Why?). The thermodynamic system at equilibrium will be analogous to a conservative (Hamiltonian) mechanical system while the 1d translation-invariant motion—to the motion of particles in a dissipative mechanical system with the frictional forces proportional to their velocities. Two- and three-dimensional equilibrium equations, (3.89), are analogous to the equation of motion of a mechanical system with the time-dependent friction coefficients. The thermomechanical analogy may be generalized on the case of a system, which is not kept at constant temperature, see Chap. 9.

The thermomechanical analogy also allows us to generalize the relaxational dynamics, TDGLE (5.1), by including the cross terms between the thermodynamic "driving forces" and responses. Such system is described by Rayleigh's dissipative function F, whose partial derivatives yield the frictional forces that should be added to the right-hand sides of the Lagrange equations [1, 2]. Then the simultaneous generalized TDGLEs take the form

$$\frac{\delta G}{\delta \eta_j} + \frac{\partial F}{\partial(\partial_t \eta_j)} = 0, \tag{6.3}$$

where F is a positive definite dissipative function:

$$\begin{aligned} F &\equiv \frac{1}{2}(\partial_t \eta_j)\tau_{jk}(\partial_t \eta_k) > 0; \\ \tau_{jk} &= \tau_{kj}; \quad \tau_{jj} = \gamma_j^{-1} > 0. \end{aligned} \tag{6.4}$$

Using (6.3) and Euler relation for homogeneous functions of the second order:

$$\begin{gathered} \text{if } Y(\alpha x_1, \alpha x_2, \alpha x_3, \ldots \alpha x_n) = \alpha^2 Y(x_1, x_2, x_3, \ldots x_n) \\ \text{then } \frac{\partial Y}{\partial x_i} x_i = 2Y, \end{gathered}$$

it is easy to see that the rate of the free-energy change in the system is

$$\frac{\mathrm{d}G}{\mathrm{d}t} \equiv \int \frac{\delta G}{\delta \eta_j} \partial_t \eta_j \, \mathrm{d}^3x = -\int 2F d^3x < 0, \tag{6.5}$$

where the last inequality follows from (6.4). For a traveling wave $\{\eta_j = \eta_j(x\text{–vt})\}$, (6.5) can be represented as follows

$$\frac{\mathrm{d}}{\mathrm{d}x}\breve{g}(\eta_i) = 2vF > 0. \tag{6.6}$$

For a thermodynamic system, (6.5) and (6.6) mean that 2F is the local rate of dissipation, which is analogous to the dissipation of the mechanical energy due to friction in a mechanical system. Thermodynamically, (6.6) can also be interpreted as that the wave speed v is proportional to the chemical potential gradient with $(2F)^{-1}$ as the mobility.

It is important to find the root cause of the analogy that we consider in this chapter. In other words, we ask a question: "What is the reason for the thermomechanical analogy to exist?" We were able to establish the analogy between the equilibrium thermodynamics of phase transition and conservative mechanics of a system of particles because both problems allow variational formulation. There is a deep connection between the Clausius' principle of thermodynamics and Hamilton's principle of mechanics. After that, we were able to match the nonequilibrium extension of the phase transition problem to the dissipative dynamics of particles because both are linear extensions of the equilibrium problems. However, we can make one step further and pose another question "What property of a system entails applicability of variational principles?" Answer to this question may be found in the connection of both theories to the Lagrangian field theory (see Appendix D). However, a more complete discussion of this problem is beyond the scope of this book [6].

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Chapter 7
Thermodynamic Fluctuations

As we noticed in Chap. 5, TDGLE is not able to describe a phase transition itself, only the evolution of the system after the transition. Obviously, something very important for the complete description of the system is missing from that scheme. What is it?

These are *fluctuations* of the thermodynamic parameters of the system, including the order parameters. Fluctuations are defined as the deviation from the average value. Several different sources of fluctuations may be pointed out; usually they are categorized as internal or external noise. Examples of the internal noise are *thermal fluctuations* and quantum mechanical ones. The former are due to the microscopic structure of matter and unpredictability of atomic hits. The latter are due to the fundamental unpredictability of Nature. Examples of the external fluctuations are noise in the electrical circuits containing ohmic resistances or electromagnets that create the magnetic fields. Surely, depending on its type, the internal and external fluctuations enter differently into the theoretical description with the former usually representing an additional "driving force" in the system, while the latter appearing as a random parameter that is coupled to the state of the system.

In this book, we are considering only the influence of the thermal (internal) fluctuations on the phase transformations. As we pointed out, this type of fluctuations originates from the atomistic structure of matter and comes into the field-theoretic description through the coarse-graining procedure (see Appendix A). From the statistical mechanics point of view, without the account of the fluctuations the system is confined to a set of parameters that corresponds to one phase. When liquid is cooled down below its freezing point the conditions for the emergence of solid phase appear but the transition may not happen. The thermodynamic fluctuations "move" the system in the phase space from one region to another "exploring" different options and "finding" the most favorable one for it.

Although this is the most significant role of the fluctuations for us, it does not exhaust the relevance of fluctuations to physical systems. Firstly, the fluctuations provide a natural framework for understanding a class of physical phenomena that

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relate the dissipative properties of a system, such as diffusion of particles in a fluid or the electrical resistance of a conductor, with the microscopic properties of the system in a state of equilibrium. This relationship was first discovered by Einstein and is often formulated in the form of the so-called *fluctuation-dissipation theorem*. Secondly, fluctuations can assume considerable significance in the neighborhood of the critical points on the phase diagrams of the systems where they obtain a high degree of spatial correlation. This gives rise to phenomena such as the critical opalescence and unlimited increase of the specific heat (the λ-point transition). Although these phenomena fall into a general category of phase transitions, they are not considered in this book in any significant depth because they require a different set of methods. From the point of view of Statistical Mechanics, different states of a system have different probabilities to be observed in the system, e.g., experimentally.

In this chapter, we look at the equilibrium distribution of fluctuations and their evolution under the influence of the stochastic environment. First we calculate the average values of the fluctuations of the OP and free energy of the system. These calculations reveal an important characteristic length scale of the fluctuations—the correlation radius, which defines the length scale of the two-point space correlation function. Then we derive the Levanyuk–Ginzburg criterion, which expresses validity of FTM in a system with fluctuations, and apply this criterion to the system undergoing the second-order transformation. To describe dynamics of fluctuating systems, we introduce irregular Langevin force, whose correlation properties obey the fluctuation-dissipation theorem. On average, evolution of the fluctuations can be described by the structure factor, which asymptotically approaches the equilibrium value. Finally, we derive the drumhead approximation of the evolution equation and apply it to analyze dynamics of the interfacial structure factor and the nucleation problem. The former reveals the length scale of the fluctuations of the interfaces. The latter allows us to find the escape time of the system and compare it with the nucleation rate of the classical nucleation theory (CNT).

7.1 Classical Nucleation Theory

Depending on the supercooling (supersaturation) of the system emergence of a new phase may take different routes. Theoretical methods for the analysis of this process may also differ depending on the magnitude of supercooling. At small supercoolings, the new phase appears in the form of small nuclei (droplets) and is characterized by the *nucleation rate*, that is, the rate of production of droplets larger than the critical size (those that will grow instead of decaying back to the old phase). According to the CNT, heterophase fluctuations in the initial phase are responsible for the nucleation of the final one; they produce a rise in the free energy excess ΔG_n [see (3.15) and Fig. 3.1]. If the initial phase is stable (unsaturated, $\Delta g < 0$, see Sect. 3.1) the probability of occurrence of these fluctuations is

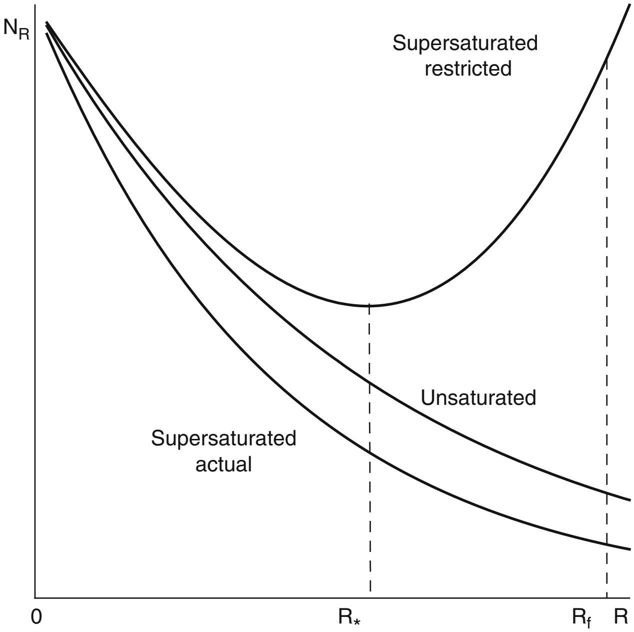


Fig. 7.1 Size distributions of embryos in the systems of different levels of saturation

proportional to exp($-\Delta G_n/k_BT$). The number of embryos (nuclei) of size R is thus given by (see Fig. 7.1)

$$N_R = N_A e^{-\Delta G_n^*(R)/k_B T} \tag{7.1}$$

where N_R is proportional to the distribution function of the nuclei of size R and N_A is a total number of atoms in the initial phase. The simplification of (7.1) is that we assume that the number of atoms in all nuclei is much smaller than N_A. Applying (7.1) to the situation when the initial phase is metastable (supersaturated, $\Delta g > 0$), we find that large heterophase fluctuations ($R > R_*$) are more probable than the small ones to the extent that all atoms should belong to very large fluctuations; this is merely the CNTs way of saying that the final phase is stable. We are interested, however, in the transformation stage, which starts with almost all the atoms in the initial phase. Thus the most probable nuclei must be excluded from the distribution. To make (7.1) applicable to the metastable initial phase, we require in CNT that no nuclei are allowed to grow beyond a limiting size R_f, which is considerably larger than the critical size R_* and the nuclei with $R \geq R_f$ are removed from the system. To preserve the total number of atoms in the system, the removed nuclei may be regarded as taken apart to individual atoms and returned into the system. Such distribution of nuclei is called restricted (see Fig. 7.1); it has a minimum at R_* while the actual nuclei size distribution should decrease to zero for large sizes.

In CNT, the nuclei are allowed to grow or shrink by adding or losing one atom at a time (impingement of nuclei is not allowed). The growth process is characterized by the nucleation rate, that is, the number of the critical nuclei formed per unit time in the entire volume V of the initial phase. The conditions of the restricted distribution produce a quasi-steady state of growing nuclei with the stationary nucleation rate of (e.g., see [1])

$$J_S = \frac{3qV}{4\pi R_*^3}\sqrt{\frac{\Delta G_*}{3\pi k_{\mathrm{B}}T}}\mathrm{e}^{-\frac{\Delta G_*}{k_{\mathrm{B}}T}}, \tag{7.2}$$

where q is the rate at which single atoms from the initial phase join the nucleus or are lost by the nucleus to the phase.

In CNT, a nucleus of a new phase is regarded as a small piece of bulk matter surrounded by a geometrical surface with a specified surface energy σ. However, even simple estimates show that the size of the nucleus is comparable with the thickness of its surface. The FTM allows us to avoid this problem.

7.2 Free Energy of Equilibrium System with Fluctuations

Let us calculate the free energy of a system at one of the homogeneous equilibrium states, $\bar{\eta}$, taking the fluctuations into account. The OP fluctuations $\Delta\eta$ are introduced as follows

$$\Delta\eta(\mathbf{r}) = \eta(\mathbf{r}) - \bar{\eta}, \tag{7.3}$$

$\eta(\mathbf{r})$ may also depend on time; we will consider this in Sect. 7.4. According to Boltzmann's principle, the probabilities of the nonequilibrium states are proportional to the factor $\exp(-G/k_{\mathrm{B}}T)$, where G is the free energy of the state, T is the temperature of the system, and k_{B} is the Boltzmann's constant. Different states of our system are described by different values of the OP, η. Thus, the distribution of probabilities of the states is

$$P(\eta) = Z\mathrm{e}^{-G(\eta)/k_{\mathrm{B}}T}, \tag{7.4}$$

where Z is the normalization constant, called the partition function. To evaluate the probabilities, we expand the free energy density of a fluctuating system about the equilibrium state

$$g(\eta) = g(\bar{\eta}) + \frac{1}{2}\frac{\partial^2 g}{\partial \eta^2}(\bar{\eta})(\Delta\eta)^2 + \cdots, \tag{7.5}$$

substitute (7.5) into (3.27) and obtain an expression

$$\begin{aligned} G(\eta) &\approx G(\bar{\eta}) + \frac{1}{2}\int_V \left[\frac{\partial^2 g}{\partial \eta^2}(\bar{\eta})(\Delta\eta)^2 + \kappa(\nabla\,\Delta\eta)^2\right] \mathrm{d}^3x, \\ G(\bar{\eta}) &\equiv g(\bar{\eta})V. \end{aligned} \tag{7.6}$$

To represent the increment $\Delta\eta$ in this expression, we will use the 3d discrete Fourier transform (Appendix F)

$$\Delta\eta(\mathbf{r}) = \sum_{\{\mathbf{k}\}} \widehat{\Delta\eta}_V(\mathbf{k})\mathrm{e}^{\mathbf{ikr}}, \tag{7.7a}$$

$$\widehat{\Delta\eta}_V(\mathbf{k}) = \frac{1}{V}\int_V \Delta\eta(\mathbf{r})\mathrm{e}^{-i\mathbf{kr}}\,\mathrm{d}\mathbf{r}, \tag{7.7b}$$

where $\{\mathbf{k}\}$ is a discrete set of wavevectors [see (F.6)] and $\widehat{\Delta\eta}_V(\mathbf{k})$ is a fluctuating variable. Notice from (7.7b) that $\widehat{\Delta\eta}_V(0)$ is the volume average of the OP fluctuations; it does not need to be zero. In a homogeneous equilibrium system, however, the ensemble averages:

$$\langle\Delta\eta(\mathbf{r})\rangle = \langle\widehat{\Delta\eta}_V(\mathbf{k})\rangle = 0. \tag{7.8}$$

Here the probabilities of different configurations, (7.4), are used for the statistical averaging.

Using Properties #3 and #5 of the 3d discrete Fourier transform (see Appendix F) for (7.6) we obtain an expression for the free energy fluctuations in the Fourier space

$$\Delta G \equiv G(\eta) - G(\bar{\eta}) \approx \frac{V}{2}\sum_{\{\mathbf{k}\}}\left[\frac{\partial^2 g}{\partial \eta^2}(\bar{\eta}) + \kappa|\mathbf{k}|^2\right]\left|\widehat{\Delta\eta}_V(\mathbf{k})\right|^2. \tag{7.9}$$

Equation (7.9) shows that the “fluctuating part” of the free energy, ΔG, can be diagonalized in the Fourier space that is, represented as a sum of the terms that depend only on one wave vector **k**. Notice that the coefficients of the terms are proportional to the amplification factor $\beta(|\mathbf{k}|)$, which we encountered in Sect. 5.3.1, where we studied evolution of the small perturbations of the equilibrium states. Applying (7.4), (7.9) to the fluctuations near the homogeneous state $\bar{\eta}$ we find that the joint probability distribution of different fluctuations

$$P(\eta) = Z\exp\left\{-\frac{V}{2k_\mathrm{B}T}\sum_{\{\mathbf{k}\}}\left[\frac{\partial^2 g}{\partial\eta^2}(\bar{\eta}) + \kappa|\mathbf{k}|^2\right]\left|\widehat{\Delta\eta}_V(\mathbf{k})\right|^2\right\} \tag{7.10}$$

can be expressed as a product of Gaussian distributions, each of which depends on the opposite wavevectors only. Hence, the individual Fourier modes $\widehat{\Delta\eta}_V(\mathbf{k})$ are statistically independent

$$\left\langle\widehat{\Delta\eta}_V(\mathbf{k})\widehat{\Delta\eta}_V(\mathbf{k}')\right\rangle = 0, \quad \text{if } \mathbf{k}+\mathbf{k}' \neq 0. \tag{7.11}$$

Evolution of the Fourier modes with $\{\mathbf{k}\}$ and $\{\mathbf{k}'{\neq}{-}\mathbf{k}\}$ may be considered independently.

Applying (7.10), Property #2 of the Fourier transform (Appendix F), and the mathematical formula

$$2\beta\int_0^\infty x^2\mathrm{e}^{-\beta x^2}\,\mathrm{d}x = \int_0^\infty \mathrm{e}^{-\beta x^2}\,\mathrm{d}x$$

to the statistically dependent modes with $\mathbf{k} + \mathbf{k}' = 0$, we obtain an expression for the average square of the Fourier mode

$$\left\langle\left|\widehat{\Delta\eta}_V(\mathbf{k})\right|^2\right\rangle = \frac{\int_0^\infty\left|\widehat{\Delta\eta}_V(\mathbf{k})\right|^2 P(\eta)\,\mathrm{d}\left|\widehat{\Delta\eta}_V(\mathbf{k})\right|}{\int_0^\infty P(\eta)\,\mathrm{d}\left|\widehat{\Delta\eta}_V(\mathbf{k})\right|} = \frac{k_\mathrm{B}T}{V\left[\partial^2 g/\partial\eta^2(\bar{\eta}) + \kappa|\mathbf{k}|^2\right]}. \tag{7.12}$$

Equation (7.12) can be used for the average square of the fluctuations only if

$$\frac{\partial^2 g}{\partial\eta^2}(\bar{\eta}) > 0 \tag{7.13}$$

because otherwise we obtain a negative expression for the mean square fluctuations of the long-wavelength modes ($|\mathbf{k}| \to 0$). This means that (7.12) is applicable at the stable equilibrium states only. Formal application of formula (7.12) at an unstable state yields an imaginary value, which may be interpreted as finite lifetime of the state. This interpretation, however, will not be used in this book.

With the help of (7.12), we can calculate the average fluctuation of the free energy (7.9)

$$\Delta G = \frac{1}{2}k_\mathrm{B}TN_{\{\mathbf{k}\}}, \tag{7.14}$$

where $N_{\{\mathbf{k}\}}$ is the number of the $\mathbf{k}$-modes in the system. Comparison of this result with the theorems of the Canonical Ensembles in the Statistical Mechanics allows us to interpret the **k**-modes as noninteracting independent degrees of freedom, $\Delta G\left(\widehat{\Delta\eta}_V(\mathbf{k})\right)$ as the effective Hamiltonian, and (7.14) as the equipartitioning of the thermal energy among the various degrees of freedom of the system. The statistical independence of the Fourier modes with $\{\mathbf{k}' + \mathbf{k} \neq 0\}$ is a result of the truncation of the expression (7.5) up to the second order, which eliminates the mode interactions. Because of that, a system described by the free energy expressions (7.6) and (7.9) is called the *free field*. The higher-order terms in (7.9) can be calculated with the help of the methods of the Statistical Mechanics [2, 3].

Using that $\widehat{\Delta\eta}_V(0)$ is the volume average of the fluctuations, we obtain from (7.12) an expression for the mean square of the fluctuations averaged over the volume of the system

$$\left\langle (\Delta\eta)_V^2 \right\rangle = \left\langle \left| \widehat{\Delta\eta}_V(0) \right|^2 \right\rangle = \frac{k_B T}{V \partial^2 g / \partial\eta^2(\bar{\eta})}. \tag{7.15}$$

This expression shows that the intensity of OP fluctuations is inversely proportional to the volume occupied by the system. The microscopic scale of the fluctuations is expressed by the factor ($k_B T/Vg$). Although under “usual” conditions, the fluctuations in (7.12) are small, there exist “unusual” conditions when the fluctuations become large. The “unusual” conditions are achieved when $V \to 0$ or simultaneously

$$\frac{\partial^2 g}{\partial\eta^2}(\bar{\eta}) \to 0 \tag{7.16a}$$

$$\text{and } |\mathbf{k}| \to 0. \tag{7.16b}$$

Condition (7.16a), as discussed in Chap. 2, means that the system approaches the critical point in the parameter space; condition (7.16b) means that the fluctuations increase for the longest wavemodes. The latter justifies the introduction of the characteristic length scale, called the *correlation radius* of fluctuations

$$r_C = \sqrt{\frac{\kappa}{\partial^2 g / \partial\eta^2(\bar{\eta})}}, \tag{7.17}$$

which plays an important role in the analysis of the fluctuations. Compare (7.17) with (3.53b) and notice that the correlation radius and fundamental lengths have similar expressions. The difference is that the former is defined at the stable state, see (7.13), while the latter at the unstable one, see (3.46e) and the comment after the equation.

Expressions (7.9) and (7.10) may be used to calculate the two-point space correlation function

$$K_\eta(\mathbf{r}_1,\mathbf{r}_2) \equiv \langle \Delta\eta(\mathbf{r}_1)\Delta\eta(\mathbf{r}_2)\rangle = \langle \eta(\mathbf{r}_1)\eta(\mathbf{r}_2)\rangle - \left\langle \eta(\mathbf{r})^2 \right\rangle, \tag{7.18}$$

where the averaging is over the thermodynamically equilibrium state of the system expressed by the joint probability $P\{\Delta\eta(\mathbf{r}_1), \Delta\eta(\mathbf{r}_2)\}$ (see Appendix G). Some of the properties of the correlator (7.18) may be pointed out right away.

1. For large distances ($|\mathbf{r}_1 - \mathbf{r}_2| \to \infty$), the correlator (7.18) breaks down into the product of the averages

$$K_\eta(\mathbf{r}_1,\mathbf{r}_2)_{|\mathbf{r}_1-\mathbf{r}_2|\to\infty} \to \langle \Delta\eta(\mathbf{r}_1)\rangle\langle\Delta\eta(\mathbf{r}_2)\rangle = 0. \tag{7.19}$$

2. At the homogeneous equilibrium state, the correlator is a function of the distance between the points only

$$K_\eta(\mathbf{r}_1,\mathbf{r}_2) = K_\eta(r), \quad r = |\mathbf{r}_1 - \mathbf{r}_2|. \tag{7.20}$$

3. Using the Fourier representation of fluctuations, the correlator (7.18) takes the form

$$K_\eta(r) = \sum_{\{\mathbf{k}\}}\sum_{\{\mathbf{k}'\}} \left\langle \widehat{\Delta\eta}_V(\mathbf{k})\widehat{\Delta\eta}_V(\mathbf{k}') \right\rangle \mathrm{e}^{i(\mathbf{k}\mathbf{r}_1+\mathbf{k}'\mathbf{r}_2)}. \tag{7.21}$$

4. As we established earlier, the $\{\mathbf{k}\}$ and $\{\mathbf{k}' \neq -\mathbf{k}\}$ Fourier modes are statistically independent. Then, using (7.11) we obtain

$$K_\eta(r) = \sum_{\{\mathbf{k}\}} \left\langle \left| \widehat{\Delta\eta}_V(\mathbf{k}) \right|^2 \right\rangle \mathrm{e}^{i\mathbf{k}\mathbf{r}}. \tag{7.22}$$

This expression shows that the mean squares of the Fourier modes of the fluctuations (7.3) are the Fourier modes of the correlator (7.18). In the Probability Theory, this statement is called the Weiner–Khinchin theorem.

Substituting (7.12) into (7.22) and taking (7.17) into account we obtain

$$K_\eta(r) = \sum_{\{\mathbf{k}\}} \frac{k_\mathrm{B} T \mathrm{e}^{i\mathbf{k}\mathbf{r}}}{V\kappa\left(r_C^{-2} + |\mathbf{k}|^2\right)}. \tag{7.23}$$

Transforming summation in (7.23) into integration ($\sum_{\mathbf{k}} \to \int_V V\,\mathrm{d}\mathbf{k}/(2\pi)^3$) we obtain

$$K_\eta(r) = \frac{k_\mathrm{B} T}{(2\pi)^3\kappa} \int_{\mathbf{k}} \frac{\mathrm{e}^{i\mathbf{k}\mathbf{r}}\,\mathrm{d}\mathbf{k}}{r_C^{-2} + |\mathbf{k}|^2}. \tag{7.24}$$

The simplest way to evaluate the integral in (7.24) is to use the Fourier transform formula (F.14). Thus,

$$K_\eta(r) = \frac{k_B T}{4\pi\kappa} \frac{e^{-r/r_C}}{r}. \tag{7.25}$$

Several comments are in order here.

1. Expression (7.25) shows that r_C determines the length scale of the decrease of the fluctuations.
2. If $r_C \to \infty$, which is the case if the critical point is approached, then $K_\eta \propto 1/r$, that is, the fluctuations in the system become correlated over very large distances.
3. Expression (7.25) can be used to obtain expression (7.15). Indeed,

$$\left\langle (\Delta\eta)_V^2 \right\rangle = \frac{1}{V^2} \int\int K_\eta(\mathbf{r}_1, \mathbf{r}_2)\, d\mathbf{r}_1\, d\mathbf{r}_2 = \frac{1}{V} \int K_\eta(r)\, d\mathbf{r}. \tag{7.26}$$

4. At $r \to 0$ we have $K_\eta \to \infty$. This result is a consequence of the fact that expression (7.12) is not applicable for very large values of the wavevector $|\mathbf{k}|$, which correspond to very small distances. The upper-$|\mathbf{k}|$ limit is due to the atomic nature of matter. Hence, expression (7.12) is applicable to the wavevectors with absolute values

$$|\mathbf{k}| \le \frac{1}{a}, \tag{7.27}$$

where a is a typical interatomic distance. Equations (7.17) and (7.27) reveal the constraint $r_C \gg a$, which presents one of the limits of applicability of the method (see Sect. 10.2).

7.3 Levanyuk–Ginzburg Criterion

In addition to the constraint (7.27), the Filed-Theoretic Method has certain limitations associated with the presence of fluctuations in the system. The principle argument may be laid out as following: For the Method to be valid the scale of the OP fluctuations must be smaller than the characteristic scale of the OP change. The natural measure of the OP change is its jump on both sides of the transition point: $[\eta] = |\bar{\eta}_+ - \bar{\eta}_0|$; the natural measure of the level of the OP fluctuations is the square root of its volume average in (7.15). However, such criterion has a caveat. First, it cannot be applied to the free field because we use the OP jump as the scale. Second, formula (7.15) shows that the scale of the OP fluctuations is inversely proportional to the volume occupied by the system. Hence, we should identify the characteristic volume for the fluctuations. Based on the analysis in the previous section, we select a cube with the correlation radius r_C on the side. Thus, the criterion formulated above can be presented as follows

$$\frac{k_B T}{r_C^3(\bar{\eta}_+)\left(\partial^2 g/\partial\eta^2(\bar{\eta}_+)\right)} \ll (\bar{\eta}_+ - \bar{\eta}_0)^2. \tag{7.28a}$$

This is called the *Levanyuk–Ginsburg criterion*. Using (7.17), it may be rewritten as follows

$$\frac{(k_B T)^2}{3}\left(\frac{\partial^2 g}{\partial\eta^2}(\bar{\eta}_+)\right) \ll (\bar{\eta}_+ - \bar{\eta}_0)^4. \tag{7.28b}$$

To analyze the role of the mode interactions let us apply criterion (7.28b) to the second-order transition in a system described by the free-energy density

$$g = g_0 + \frac{1}{2}A\eta^2 + \frac{1}{4}Q\eta^4 - H\eta \tag{2.45}$$

with $A < 0$, $Q > 0$, and $H = 0$. Then

$$\bar{\eta}_0 = 0; \bar{\eta}_\pm = \pm\sqrt{\frac{|A|}{Q}}; \quad \frac{\partial^2 g}{\partial\eta^2}(\bar{\eta}_\pm) = 2|A|. \tag{7.29}$$

Substitution of (7.29) into (7.28b) yields the criterion

$$|A| \gg \mathrm{Gi} \equiv \frac{(Qk_B T_C)^2}{\kappa^3}. \tag{7.30}$$

This criterion shows that the method based on the Landau theory of phase transitions is valid outside the region of size Gi (*Ginzburg number*) around the transition point T_C. Notice that Gi is proportional to the square of the mode-interaction coefficient Q.

7.4 Dynamics of Fluctuating Systems: Langevin Force

At this juncture, we may pose the following questions: How do the fluctuations enter into our scheme? In other words, where did we miss or omit the fluctuations in the development of the Field-Theoretic Method? How can we bring the fluctuations back into our description?

In general, the thermal fluctuations appear because a real system consists of discrete atoms and molecules and not of a continuum medium. As we explained above the OP represents the most probable evolution of the system. To bring the fluctuations back into the Field Theory, we can use the method suggested by Langevin in solving the problem of Brownian motion. To describe the incessant and random bombardment of the tiny grains of a plant pollen by the molecules of the surrounding fluid Langevin suggested to use a force that consisted of two parts: a "rapidly fluctuating" part, which averages out to zero over the interval of time long compared to the time of molecular impact and an "averaged-out" part, which represents the viscous drag. In our case, the latter is represented by the thermodynamic force ($-\gamma\delta G/\delta\eta$). Thus, the dynamic equation for the OP evolution takes the form

$$\frac{\mathrm{d}\eta}{\mathrm{d}t} = -\gamma\frac{\delta G}{\delta\eta} + \xi(\mathbf{r},t). \tag{7.31}$$

To represent the rapidly fluctuating part, we introduced Langevin force $\xi(\mathbf{r}, t)$, which averages out to zero over a long period of time $\boldsymbol{\Omega}$ at every point $\mathbf{r}$ of the system

$$\bar{\xi}_\Omega \equiv \frac{1}{\Omega}\int_0^\Omega \xi(\mathbf{r},t)\,\mathrm{d}t \to 0 \quad \text{for } \Omega \to \infty \text{ and all } \mathbf{r}. \tag{7.32}$$

To find the properties of the Langevin force, we will consider evolution of the OP near the homogeneous stable equilibrium state $\bar{\eta}$. Assuming that our system is *ergodic* (see Appendix G), we obtain the first condition on the Langevin force:

$$\langle \xi(\mathbf{r},t)\rangle = 0 \quad \text{for all } \mathbf{r} \text{ and } t, \tag{7.33a}$$

where $< \cdots >$ means averaging over the same distribution function as in (7.4), (7.10), but now the OP deviations are functions of time. Due to irregularities of the Langevin force, we may assume that it is completely uncorrelated with the thermodynamic force, that is,

$$\left\langle \frac{\delta G}{\delta\eta}(\mathbf{r}_1,t_1)\xi(\mathbf{r}_2,t_2)\right\rangle = 0 \quad \text{for all } \mathbf{r}_i \text{ and } t_i. \tag{7.33b}$$

Notice that the Langevin force does not change the dissipative property of the OP evolution. Indeed, using (7.33b) for (7.31), we obtain [c.f. (5.3)]

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\langle G\rangle = \left\langle\frac{\mathrm{d}G}{\mathrm{d}t}\right\rangle = \left\langle\frac{\delta G}{\delta\eta}\frac{\mathrm{d}\eta}{\mathrm{d}t}\mathrm{d}^3x\right\rangle = -\gamma\left\langle\int\left(\frac{\delta G}{\delta\eta}\right)^2\mathrm{d}^3x\right\rangle + \left\langle\int\frac{\delta G}{\delta\eta}\xi\,\mathrm{d}^3x\right\rangle \\ = -\gamma\int\left\langle\left(\frac{\delta G}{\delta\eta}\right)^2\right\rangle\mathrm{d}^3x < 0.\end{aligned} \tag{7.33c}$$

Now let us find the third condition on the Langevin force. To do that we consider evolution of the small deviations $\Delta\eta(\mathbf{r}, t)$, (7.3), using two different approaches: one—Statistical Mechanics (see Sect. 7.2) and another—Stochastic Dynamics, (see Appendix G). Equating the results should yield the sought condition. Linearizing (7.31) we obtain the equation for the small deviations

$$\frac{\partial \Delta\eta}{\partial t} = -\gamma \frac{\partial^2 g}{\partial \eta^2}(\bar{\eta})\ \Delta\eta + \kappa \nabla^2 \Delta\eta + \xi(\mathbf{r}, t). \tag{7.34}$$

Let us start with the analysis of the homogeneous deviations $\Delta\eta(t)$, which come from the homogeneous force $\xi(t)$. Equation (7.34) turns into an ODE, whose solution that satisfies the initial condition $\Delta\eta(t = 0) = \Delta\eta(0)$ takes the form:

$$\Delta\eta(t) = \Delta\eta(0)\mathrm{e}^{-t/\tau_0} + \mathrm{e}^{-t/\tau_0}\int_0^t \mathrm{e}^{u/\tau_0}\xi(u)\,\mathrm{d}u, \tag{7.35}$$

where the characteristic time of relaxation of the homogeneous fluctuations near the equilibrium state $\bar{\eta}$ is

$$\tau_0 = \left[\gamma \frac{\partial^2 g}{\partial \eta^2}(\bar{\eta})\right]^{-1}. \tag{4.12}$$

Deviation of the OP away from this state is a random (stochastic) process because it is driven by the Langevin force. Since $<\xi(u)> = 0$ for all u, the mean increment of the OP vanishes

$$\langle \Delta\eta(t)\rangle = \Delta\eta(0)\mathrm{e}^{-t/\tau_0} \to 0 \quad \text{for } t \to \infty.$$

For the mean square increment, we obtain

$$\begin{aligned}\langle \Delta\eta^2(t)\rangle &= \Delta\eta^2(0)\mathrm{e}^{-2t/\tau_0} + 2\Delta\eta(0)\mathrm{e}^{-2t/\tau_0}\int_0^t \mathrm{e}^{u/\tau_0}\langle\xi(u)\rangle\,\mathrm{d}u \\ &+ \mathrm{e}^{-2t/\tau_0}\int_0^t\int_0^t \mathrm{e}^{(u_1+u_2)/\tau_0}\langle\xi(u_1)\xi(u_2)\rangle\,\mathrm{d}u_1\,\mathrm{d}u_2.\end{aligned} \tag{7.36}$$

The first term on the right-hand side of this equation vanishes over time. The second term is identically zero due to (7.33a). In the third term we have a quantity

$$K_\xi(s) \equiv \langle \xi(u)\xi(u+s)\rangle \tag{7.37}$$

which is called the *autocorrelation function* of ξ and is a measure of the stochastic correlation between the value of the fluctuating variable ξ at time u_1 and its value at time $u_2 = u_1 + s$ (see Appendix G). Using the expressions (G.54) and (7.33a) for the integral in the third term, we arrive at the expression:

$$\left\langle \Delta\eta^2(t) \right\rangle = \Delta\eta^2(0)\mathrm{e}^{-2t/\tau_0} + \frac{\tau_0}{2}\left(1 - \mathrm{e}^{-2t/\tau_0}\right)\int_{-\infty}^{+\infty} K_\xi(s)\,\mathrm{d}s \underset{t\to\infty}{\to} \frac{\tau_0}{2}\int_{-\infty}^{+\infty} K_\xi(s)\,\mathrm{d}s. \tag{7.38}$$

Notice that if $\Delta\eta^2(0)$ were itself equal to the limiting expression, then $<\Delta\eta^2(t)>$ would always remain the same, which proves that *statistical equilibrium, once attained, has a natural tendency to persist.*

On the other hand, from the Statistical Mechanics analysis in Sect. 7.2, (7.15), we know that the average square of the homogeneous deviation of the OP is equal to $k_\mathrm{B}T/[V\partial^2 g(\bar{\eta})/\partial\eta^2]$. Equating it to the limiting expression in (7.38), we obtain an integral condition on the autocorrelation function of the Langevin force

$$\int_{-\infty}^{+\infty} K_\xi(s)\,\mathrm{d}s = 2\frac{\gamma k_\mathrm{B}T}{V}. \tag{7.39}$$

Now think about how properties of the Langevin force determine its autocorrelation function. If the process $\xi(t)$ has some sort of regularity then the correlator $K_\xi(s)$ extends over a range of the time interval τ_cor, defined in (G.52). On the contrary, if we assume that $\xi(t)$ is extremely irregular, then τ_cor is zero and we need to choose $K_\xi(s) \propto \delta(s)$. Thus, we obtain the third condition on the spatially homogeneous Langevin stochastic force:

$$\langle \xi(t_1)\xi(t_2) \rangle = 2\frac{\gamma k_\mathrm{B}T}{V}\delta(t_2 - t_1). \tag{7.40}$$

Next, let us analyze the autocorrelation function of the inhomogeneous Langevin force $\xi(\mathbf{r}, t)$. For a stationary process in a statistically homogeneous system, the autocorrelation function depends only on the distance in space $|\mathbf{r}|$ and time s between the points $(\mathbf{r}_1, t_1)$ and $(\mathbf{r}_2, t_2)$

$$K_\xi(\mathbf{r}, s) = \langle \xi(\mathbf{r}_1, t_1)\xi(\mathbf{r}_2, t_2) \rangle; \quad \mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1, s = t_2 - t_1, \tag{7.41}$$

where the averaging $< \cdots >$ is meant over time or the equilibrium ensemble (7.10), see (G.5) and discussion of ergodicity in Appendix G. Also in (7.41) we took into account condition (7.33a). Introducing the Fourier transform of the Langevin force

$$\xi(\mathbf{r}, t) = \sum_{\{\mathbf{k}\}} \hat{\xi}_V(\mathbf{k}, t)\mathrm{e}^{\mathrm{i}\mathbf{kr}}, \tag{7.42a}$$

$$\hat{\xi}_V(\mathbf{k}, t) = \frac{1}{V}\int_V \xi(\mathbf{r}, t)\mathrm{e}^{-\mathrm{i}\mathbf{kr}}\,\mathrm{d}\mathbf{r}, \tag{7.42b}$$

rearranging the product of the Fourier modes of the Langevin force as follows

$$\hat{\xi}_V(\mathbf{k},t_1)\hat{\xi}_V^*(\mathbf{k},t_2) = \frac{1}{V^2}\int_V\int_V \xi(\mathbf{r}_1,t_1)\xi(\mathbf{r}_2,t_2)\mathrm{e}^{-i\mathbf{k}(\mathbf{r}_2-\mathbf{r}_1)}\,\mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2$$

and averaging both sides of the equation, we obtain the relation

$$\left\langle \hat{\xi}_V(\mathbf{k},t_1)\hat{\xi}_V^*(\mathbf{k},t_2)\right\rangle = \frac{1}{V^2}\int_V\int_V K_\xi(\mathbf{r},s)\mathrm{e}^{-i\mathbf{kr}}\,\mathrm{d}\mathbf{R}\,\mathrm{d}\mathbf{r}, \tag{7.43a}$$

where $\mathbf{R} = 1/2(\mathbf{r}_1 + \mathbf{r}_2)$ and $\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2 = \mathrm{d}\mathbf{R}\mathrm{d}\mathbf{r}$. Integration over $\mathbf{R}$ in (7.43a) can be completed because the integrand is independent of this variable. The resulting relation

$$\left\langle \hat{\xi}_V(\mathbf{k},t_1)\hat{\xi}_V^*(\mathbf{k},t_2)\right\rangle = \frac{1}{V}\int_V K_\xi(\mathbf{r},s)\mathrm{e}^{-i\mathbf{kr}}\,\mathrm{d}\mathbf{r} \tag{7.43b}$$

may be rewritten in the form

$$\hat{K}_{\xi,V}(\mathbf{k},s) = \left\langle \hat{\xi}_V(\mathbf{k},t_1)\hat{\xi}_V^*(\mathbf{k},t_2)\right\rangle \tag{7.43c}$$

which shows that the Fourier transform of the two-time correlator of the Langevin force equals the averaged two-time product of the Fourier transforms of the same process. This result may be considered a space analog of the Wiener–Khinchin theorem (see Appendix G).

The properties of the Langevin-force correlator can be found from the analysis of evolution of the OP fluctuations in (7.34). In the Fourier space, it turns into the following ODE

$$\frac{\mathrm{d}\,\widehat{\Delta\eta}_{\mathrm{V}}(\mathbf{k},t)}{\mathrm{d}t} = -\gamma\left[\frac{\partial^2 g}{\partial\eta^2}(\bar{\eta}) + \kappa|\mathbf{k}|^2\right]\widehat{\Delta\eta}_{\mathrm{V}}(\mathbf{k},t) + \hat{\xi}_V(\mathbf{k},t). \tag{7.44}$$

This equation is similar to the ODE for the homogeneous deviation, if the homogeneous Langevin force $\xi(t)$ is replaced with the Fourier component of the inhomogeneous one and the relaxation time constant τ_0, (4.12), is replaced with [cf. (5.21a)]

$$\tau_{|\mathbf{k}|} = \left\{\gamma\left[\frac{\partial^2 g}{\partial\eta^2}(\bar{\eta}) + \kappa|\mathbf{k}|^2\right]\right\}^{-1} = -\frac{1}{\beta(|\mathbf{k}|)}. \tag{7.45}$$

Hence, we may write down the solution of (7.44) in the form similar to that of (7.35). Following the logic of the previous derivation, we may write down the integral condition on the Fourier modes of the Langevin force similar to that of (7.39) because the Fourier modes $\widehat{\Delta\eta}_{\mathrm{V}}(\mathbf{k},t)$ are statistically independent

$$\int_{-\infty}^{+\infty}\left\langle\hat{\xi}_V(\mathbf{k},t_1)\hat{\xi}_V^*(\mathbf{k},t_2)\right\rangle \mathrm{d}s = 2\frac{\gamma k_\mathrm{B}T}{V}. \tag{7.46a}$$

Hence,

$$\left\langle\hat{\xi}_V(\mathbf{k},t_1)\hat{\xi}_V^*(\mathbf{k},t_2)\right\rangle = 2\frac{\gamma k_\mathrm{B}T}{V}\delta(t_2-t_1). \tag{7.46b}$$

Notice that due to the equipartitioning of energy (see Sect. 7.2), the right-hand side of this equation is independent of the wavevector **k**. Let us sum up both sides of (7.46a) overall wavevectors $\{\mathbf{k}\}$ with the weight factor $\exp(\mathbf{ik}\boldsymbol{\rho})$. Then, using (7.43) we obtain

$$\int_{-\infty}^{+\infty}\sum_{\{\mathbf{k}\}}\hat{K}_{\xi,V}(\mathbf{k},s)\mathrm{e}^{\mathbf{ik}\rho}\,\mathrm{d}s = 2\frac{\gamma k_\mathrm{B}T}{V}\sum_{\{\mathbf{k}\}}\mathrm{e}^{\mathbf{ik}\rho}.$$

Using the inverse Fourier transform formula, (F.5a), and the formula

$$\sum_{\{\mathbf{k}\}}\mathrm{e}^{i\mathbf{kr}} \approx V\delta(\mathbf{r})$$

we obtain

$$\int_{-\infty}^{+\infty}K_\xi(\mathbf{r},s)\,\mathrm{d}s = 2\gamma k_B T\delta(\mathbf{r}). \tag{7.47}$$

Above we assumed total irregularity of the homogeneous process $\xi(t)$, which led to the condition, (7.40). If we assume the same irregularity for the process $\xi(\mathbf{r},t)$ at each point **r**, then we obtain the third condition on the inhomogeneous Langevin stochastic force

$$K_\xi(\mathbf{r},s) = \langle\xi(\mathbf{r}_1,t_1)\xi(\mathbf{r}_2,t_2)\rangle = 2\gamma k_\mathrm{B}T\delta(\mathbf{r}_2-\mathbf{r}_1)\delta(t_2-t_1). \tag{7.48}$$

Notice that $\delta(\mathbf{r})$ appears in (7.48) because the **k**-modes are statistically independent, $\delta(t)$—because they are irregular (no memory).

7.5 Evolution of the Structure Factor

In Sect. 7.2, we came close to introducing a very important quantity—*structure factor*. Physical significance of this quantity is in that it is experimentally measurable in the experiments on diffuse X-ray and neutron radiation scattering during the phase transformations. The structure factor $\hat{K}_{\eta,V}(\mathbf{k},\ t)$ is the Fourier transform of the two-point one-time correlation function $K_\eta(\mathbf{r}_1,\ \mathbf{r}_2,\ t)$

$$\hat{K}_{\eta,V}(\mathbf{k},\ t) = \frac{1}{V}\int_V K_\eta(\mathbf{r}_1,\ \mathbf{r}_2,\ t)\mathrm{e}^{-\mathbf{ikr}}\,\mathrm{d}\mathbf{r}, \tag{7.49a}$$

$$K_\eta(\mathbf{r}_1, \mathbf{r}_2, t) = \sum_{\{\mathbf{k}\}} \hat{K}_{\eta,V}(\mathbf{k},\ t)\mathrm{e}^{\mathbf{ikr}}. \tag{7.49b}$$

We already know something about this quantity. Indeed, compare (7.49b) to (7.12), (7.21) and notice that the equilibrium value of the structure factor at the stable homogeneous state $\bar{\eta}$ is

$$\hat{K}_{\bar{\eta},V}(\mathbf{k},\ \mathrm{t})\xrightarrow[t\to\infty]{}\langle|\widehat{\Delta\eta}_V(\mathbf{k})|^2\rangle = \frac{k_\mathrm{B}T}{V\left[\partial^2 g/\partial\eta^2(\bar{\eta}) + \kappa|\mathbf{k}|^2\right]}. \tag{7.50}$$

Let us find the expression for the structure factor away from the equilibrium. To do that we substitute (7.21) into (7.49a) and obtain

$$\hat{K}_{\bar{\eta},V}(\mathbf{k},\ t) = \frac{1}{V}\int_V \sum_{\{\mathbf{k}'\}}\sum_{\{\mathbf{k}''\}} \left\langle \widehat{\Delta\eta}_V(\mathbf{k}', t)\widehat{\Delta\eta}_V(\mathbf{k}'', t)\right\rangle \mathrm{e}^{\mathrm{i}(\mathbf{k}'\mathbf{r}_1 + \mathbf{k}''\mathbf{r}_2 - \mathbf{kr})}\,\mathrm{d}\mathbf{r}. \tag{7.51a}$$

As the averaging in this expression is over the distribution function of (7.10), the modes with $\mathbf{k}' + \mathbf{k}'' \neq 0$ are independent, hence

$$\hat{K}_{\bar{\eta},V}(\mathbf{k},\ t) = \frac{1}{V}\sum_{\{\mathbf{k}'\}}\left\langle\left|\widehat{\Delta\eta}_V(\mathbf{k}',\ t)\right|^2\right\rangle\int_V \mathrm{e}^{\mathrm{i}(\mathbf{k}'-\mathbf{k})\mathbf{r}}\,\mathrm{d}\mathbf{r}. \tag{7.51b}$$

Taking into account the mathematical formulae

$$\int_V \mathrm{e}^{\mathbf{ikr}}\,\mathrm{d}\mathbf{r}\xrightarrow[V\to\infty]{}(2\pi)^3\,\delta(\mathbf{k}), \quad \sum_{\{\mathbf{k}\}}\xrightarrow[V\to\infty]{}\frac{V}{(2\pi)^3}\int \mathrm{d}\mathbf{k}$$

we obtain that in the thermodynamic limit of $V \to \infty$

$$\hat{K}_{\bar{\eta},V} = \left\langle\left|\widehat{\Delta\eta}_V(\mathbf{k},\ t)\right|^2\right\rangle \tag{7.51c}$$

the structure factor is the averaged square of the Fourier modes of the OP fluctuations.

To derive an evolution equation for the structure factor, we differentiate (7.51c) with respect to time and use (7.44)

$$\frac{\mathrm{d}\hat{K}_{\bar{\eta},V}}{\mathrm{d}t}(\mathbf{k},\ t) = 2\beta(\mathbf{k})\hat{K}_{\bar{\eta},V}(\mathbf{k},\ t) + \left\langle \widehat{\Delta\eta}^{*}_{V}(\mathbf{k},\ t)\hat{\xi}_{V}(\mathbf{k},\ t) + \hat{\xi}^{*}_{V}(\mathbf{k},\ t)\widehat{\Delta\eta}_{V}(\mathbf{k},\ t)\right\rangle. \tag{7.52}$$

To estimate the second term in the right-hand side, we use the solution of (7.44) with the initial condition $\widehat{\Delta\eta}_{V}(\mathbf{k},\ 0)$:

$$\widehat{\Delta\eta}_{V}(\mathbf{k},\ t) = \widehat{\Delta\eta}_{V}(\mathbf{k},\ 0)\mathrm{e}^{-t/\tau_k} + \mathrm{e}^{-t/\tau_k}\int_0^t \mathrm{e}^{u/\tau_k}\hat{\xi}_{V}(\mathbf{k},\ u)\,\mathrm{d}u. \tag{7.53}$$

Substitution of (7.53) into (7.52) yields two types of averages. For the first one we obtain

$$\left\langle \widehat{\Delta\eta}^{*}_{V}(\mathbf{k},0)\hat{\xi}_{V}(\mathbf{k},\ \mathrm{t})\right\rangle = \left\langle \hat{\xi}^{*}_{V}(\mathbf{k},\ \mathrm{t})\widehat{\Delta\eta}_{V}(\mathbf{k},0)\right\rangle = 0 \tag{7.54}$$

because the initial conditions and the Langevin force are completely uncorrelated. The second type of averages was calculated in (7.46b). Then we substitute (7.46b), (7.54) into (7.52) and obtain an evolution equation for the structure factor that we sought

$$\frac{\mathrm{d}\hat{K}_{\bar{\eta},V}}{\mathrm{d}t}(\mathbf{k},\ t) = 2\beta(\mathbf{k})\hat{K}_{\eta,V}(\mathbf{k},\ t) + 4\frac{\gamma k_{\mathrm{B}}T}{V}. \tag{7.55}$$

A general solution of this equation takes the form

$$\hat{K}_{\bar{\eta},V}(\mathbf{k},\ t) = \hat{K}_{\bar{\eta},V}(\mathbf{k},\ 0)\mathrm{e}^{2\beta(\mathbf{k})t} - 2\frac{\gamma k_{\mathrm{B}}T}{V\beta(\mathbf{k})} \xrightarrow[t\to\infty]{} \frac{2k_{\mathrm{B}}T}{V\left[\partial^2 g/\partial\eta^2(\bar{\eta}) + \kappa|\mathbf{k}|^2\right]}. \tag{7.56}$$

Strictly speaking, the initial value $\left|\widehat{\Delta\eta}_{V}(\mathbf{k},\ 0)\right|^2$ is not a stochastic quantity because it is completely independent of the Langevin force (although this quantity may be random but for completely different reasons); it is presented in (7.56) as $\hat{K}_{\bar{\eta},V}(\mathbf{k},0)$ for the sake of similarity. Many features of (7.56), for instance, dependence of the structure factor on the initial value and wavenumber, can be verified experimentally.

Although (7.55) was derived for a stable homogeneous state $\bar{\eta}$, it can be used for an unstable one, but for a limited time of evolution only. The limitation comes from the magnitude of the Fourier modes $\left|\widehat{\Delta\eta}_{V}(\mathbf{k},t)\right|$. Indeed, (7.44) can be used for as long as the modes are small. Imagine a system, which was initially equilibrated at a state where (7.13) was true. The structure factor of the system is described by the asymptotic value of (7.56). After that, suddenly, we change the conditions, e.g., lower the temperature, such that condition (7.13) is no longer true. Then solution (7.56), where $\beta(\mathbf{k})$ is positive or negative depending on $|\mathbf{k}|$, can be used to describe initial stages of growth of the modes. When the modes are not small anymore, the linearized (7.44) should be replaced by the full evolution equation (7.31) in the

Fourier space. In this case, the evolution equation for the structure factor will depend on the Fourier transforms of the higher-order two-point correlation functions [4, 5].

7.6 Drumhead Approximation of the Evolution Equation

In Chap. 5, we found that theoretical analysis of the OP evolution may be significantly advanced in the situations when a thin transition layer develops in the system. In Sect. 5.5, we derived the drumhead approximation of TDGLE, see (5.32), which allowed us to identify the "driving forces" of the interfacial motion. In this section, we will apply the drumhead approximation to the fluctuating system. The starting point is the Langevin TDGLE (7.31) for the OP filed with the correlation condition (7.33a), (7.48) on the stochastic force. Let us repeat here some of the key steps of the derivation of Sect. 5.5, including the Langevin force now. Assuming that a thin layer develops in the system where the OP field changes quickly, while in the rest of the system it changes slowly, we obtain an equation (cf. (5.29) and Fig. 3.6)

$$\gamma\kappa\frac{\mathrm{d}^2\eta}{\mathrm{d}u^2}+(v_\mathrm{n}+2\gamma\kappa K)\frac{\mathrm{d}\eta}{\mathrm{d}u}-\gamma\frac{\partial g}{\partial\eta}+\xi=0, \tag{7.57}$$

where $\eta=\eta(u)$, v_n, and K depend on (v, w, t), and ξ depends on (u, v, w, t). Then, multiplying the left-hand side by $\mathrm{d}\eta/\mathrm{d}u$ and averaging it over the thickness of the layer (cf. 5.31) we obtain

$$\gamma\left(\frac{v_\mathrm{n}}{m}+2K\right)\hat{\mathbf{A}}\cdot\left\{\kappa\left(\frac{\mathrm{d}\eta}{\mathrm{d}u}\right)^2\right\}-\gamma[g]_\beta^\alpha+\zeta=0, \tag{7.58}$$

where we introduced a new stochastic force

$$\zeta(v,\ w,\ t)\equiv\hat{\mathbf{A}}\cdot\left(\xi\frac{\mathrm{d}\eta}{\mathrm{d}u}\right)=\int_{u_\beta}^{u_\alpha}\xi(u,v,w,t)\,\frac{\mathrm{d}\eta}{\mathrm{d}u}\,\mathrm{d}u. \tag{7.59}$$

The correlation properties of the force ζ need to be analyzed. Obviously [cf. (7.33a)]

$$\langle\zeta(v,\ w,\ t)\rangle=0. \tag{7.60}$$

For the autocorrelation function of ζ, we may write

$$\langle\zeta(v,\ w,\ t)\zeta(v',\ w',\ t')\rangle=\int_{u_\beta}^{u_\alpha}\mathrm{d}u\,\frac{\mathrm{d}\eta}{\mathrm{d}u}\int_{u_\beta}^{u_\alpha}\mathrm{d}u'\,\frac{\mathrm{d}\eta}{\mathrm{d}u'}\langle\xi(u,\ v,\ w,\ t)\xi(u',\ v',\ w',\ t')\rangle.$$

Then, using (7.48) we obtain

$$\begin{aligned}
&\langle \zeta(v,\ w,\ t)\zeta(v',\ w',\ t')\rangle \\
&= 2\gamma k_{\mathrm{B}} T\delta(v-v')\delta(w-w')\delta(t-t')\int_{u_\beta}^{u_\alpha}\int_{u_\beta}^{u_\alpha} \mathrm{d}u\,\mathrm{d}u' \,\frac{\mathrm{d}\eta}{\mathrm{d}u}\frac{\mathrm{d}\eta}{\mathrm{d}u'}\delta(u-u') \\
&= 2\gamma k_{\mathrm{B}} T\hat{\mathbf{A}}\cdot\left(\frac{\mathrm{d}\eta}{\mathrm{d}u}\right)^2 \delta(v-v')\delta(w-w')\delta(t-t'). \qquad (7.61)
\end{aligned}$$

In the second line of (7.61), one integration was removed by the δ-function. Using the definitions of the interfacial energy σ (3.70a) and mobility m (5E.7) we obtain from (7.57) to (7.61) the drumhead approximation of the Langevin-TDGLE

$$v_{\mathrm{n}} = m\left(\frac{[g]_\beta^\alpha}{\sigma} - 2K\right) - \frac{\kappa}{\sigma}\zeta \qquad (7.62a)$$

$$\langle \zeta(v,\ w,\ t)\rangle = 0; \qquad (7.62b)$$

$$\langle \zeta(v,\ w,\ t)\zeta(v',\ w',\ t')\rangle = 2\gamma k_{\mathrm{B}} T\frac{\sigma}{\kappa}\delta(v-v')\delta(w-w')\delta(t-t'). \qquad (7.62c)$$

In the following sections, we will use this equation for the purposes of the interfacial stability analysis and nucleation problem.

7.6.1 Evolution of the Interfacial Structure Factor

For the analysis of evolution of the capillary waves on the plane interface (see the definition in Sect. 3.7), let us use the drumhead approximation, (7.62a), instead of the method used in Sect. 5.3.2. To do that we resolve the u-coordinate equation $U(\mathbf{x}, t) = 0$ as follows

$$z = z(\mathbf{x}_2, t) = \sum_{\{\mathbf{k}_2\}} \hat{z}(\mathbf{k}_2, t)\mathrm{e}^{\mathrm{i}\mathbf{k}_2\mathbf{x}_2}, \qquad (7.63a)$$

$$\hat{z}(\mathbf{k}_2, t) = \frac{1}{S}\int_S z(\mathbf{x}_2, t)\mathrm{e}^{-\mathrm{i}\mathbf{k}_2\mathbf{x}_2}\,\mathrm{d}\mathbf{x}_2, \qquad (7.63b)$$

where z is the deflection of the drumhead interface from the plane, $\hat{z}(\mathbf{k}_2, t)$ are the Fourier transform components of the deflection, $\boldsymbol{x}_2 = (x,\ y)$, $\mathbf{k}_2 = (k_x,\ k_y)$ are the two-dimensional vectors in the geometric and Fourier spaces, and S is the area of the interface. In general (see Appendix C)

$$v_{\mathrm{n}} = \frac{\partial z}{\partial t}\boldsymbol{u}\cdot\boldsymbol{j}_z; \qquad (7.64a)$$

$$K=-\frac{1}{2}\nabla_2\left(\frac{\nabla_2 z(\mathbf{x}_2,t)}{\sqrt{1+|\nabla_2 z(\mathbf{x}_2,t)|^2}}\right);\quad \nabla_2=\left(\frac{\partial}{\partial x}\boldsymbol{j}_x,\frac{\partial}{\partial y}\boldsymbol{j}_y\right). \tag{7.64b}$$

For the capillary waves $(v, w) \approx (x, y)$ and

$$v_{\mathrm{n}}\approx\frac{\partial z}{\partial t}=\sum_{\{\mathbf{k}_2\}}\frac{\partial\hat{z}}{\partial t}(\mathbf{k}_2,t)\mathrm{e}^{\mathbf{i}\mathbf{k}_2\mathbf{x}_2} \tag{7.65a}$$

$$K\approx-\frac{1}{2}\left(\frac{\partial^2 z}{\partial x^2}+\frac{\partial^2 z}{\partial y^2}\right)=\frac{1}{2}\sum_{\{\mathbf{k}_2\}}\hat{z}(\mathbf{k}_2,\ t)|\mathbf{k}_2|^2\mathrm{e}^{\mathbf{i}\mathbf{k}_2\mathbf{x}_2}. \tag{7.65b}$$

Then, substituting (7.65) into (7.62a) we obtain an equation

$$\sum_{\{\mathbf{k}_2\}}\left(\frac{\partial\hat{z}}{\partial t}+\hat{z}m|\mathbf{k}_2|^2+\frac{\kappa}{\sigma}\hat{\zeta}\right)=0, \tag{7.66a}$$

where the Fourier components of the Langevin force ζ have the following properties

$$\left\langle\hat{\zeta}(\mathbf{k}_2,t)\right\rangle=0 \tag{7.66b}$$

$$\int_{-\infty}^{+\infty}\left\langle\hat{\zeta}(\mathbf{k}_2,t)\hat{\zeta}^*(\mathbf{k}_2,t+s)\right\rangle\mathrm{d}s=2\frac{\gamma\ \sigma k_{\mathrm{B}}T}{\kappa S}. \tag{7.66c}$$

Because each term in the sum in (7.66a) depends on the value of only one wavenumber they must vanish separately. Then, using our experience with (7.34), we obtain the solution

$$\hat{z}(\mathbf{k}_2,\ t)=\hat{z}(\mathbf{k}_2,0)\mathrm{e}^{-t/\tau_z}-\frac{\kappa}{\sigma}\mathrm{e}^{-t/\tau_z}\int_0^t\mathrm{e}^{s/\tau_z}\hat{\zeta}(\mathbf{k}_2,s)\,\mathrm{d}s \tag{7.67a}$$

$$\tau_z=\frac{1}{m|\mathbf{k}_2|^2}=-\frac{1}{\beta_z(|\mathbf{k}|)}, \tag{7.67b}$$

where $\hat{z}(\mathbf{k}_2,0)$ is the initial condition for the capillary wave and τ_z is the time scale of the evolution of the waves. Notice that the latter depends strongly on the wavenumber of the wave, diverging for the very long ones. Taking (7.62a) into account, we obtain expressions for the averaged Fourier components of the deflections

$$\langle\hat{z}(\mathbf{k}_2,\ t)\rangle=\hat{z}(\mathbf{k}_2,\ 0)\mathrm{e}^{-t/\tau_z}\xrightarrow[t\to\infty]{}0\quad\text{for all}|\mathbf{k}_2| \tag{7.68a}$$

and the two-time autocorrelation function

$$\langle \hat{z}(\mathbf{k}_2,t)\hat{z}^*(\mathbf{k}_2,0)\rangle = |\hat{z}(\mathbf{k}_2,0)|^2 \mathrm{e}^{-t/\tau_z} \xrightarrow[t\to\infty]{} 0 \quad \text{for all} |\mathbf{k}_2|. \tag{7.68b}$$

Then, introducing the interfacial structure factor

$$\hat{K}_{z,S}(\mathbf{k}_2,t) \equiv \left\langle |\hat{z}(\mathbf{k}_2,t)|^2 \right\rangle \tag{7.69}$$

we obtain an equation of its evolution

$$\begin{aligned} \hat{K}_{z,S}(\mathbf{k}_2,t) &= \hat{K}_{z,S}(\mathbf{k}_2,0)\mathrm{e}^{-2t/\tau_z} + \frac{\tau_z}{2}\left(\frac{\kappa}{\sigma}\right)^2 \left(1-\mathrm{e}^{-2t/\tau_z}\right) \int_{-\infty}^{+\infty} \left\langle \hat{\zeta}(\mathbf{k}_2,t)\hat{\zeta}^*(\mathbf{k}_2,t+s) \right\rangle \mathrm{d}s \\ &= \hat{K}_{z,S}(\mathbf{k}_2,0)\mathrm{e}^{-2t/\tau_z} + \frac{k_\mathrm{B}T}{\sigma|\mathbf{k}_2|^2 S}\left(1-\mathrm{e}^{-2t/\tau_z}\right) [\xrightarrow[t\to\infty]{}] \frac{k_\mathrm{B}T}{\sigma|\mathbf{k}_2|^2 S}. \end{aligned} \tag{7.70}$$

Equation (7.70) shows that the destabilizing effect of fluctuations and stabilizing effect of the surface tension bring up one more length scale, the *fluctuation length*

$$l_\mathrm{F} \equiv \sqrt{\frac{k_\mathrm{B}T}{\sigma}}, \tag{7.71}$$

which sets up the scale for the structure factor. Compare (7.70) with the expression for the bulk structure factor, (7.56), and notice that $\hat{K}_{z,S}(\mathbf{k}_2,t)$diverges for $|\mathbf{k}_2|\to 0$. Using the inverse Fourier transform, (7.63b), we can interpret this result to mean that the surface-average square of the long waves of the interfacial deflection grows without bound because the stabilizing influence of the surface tension for these waves vanishes.

7.6.2 Nucleation in the Drumhead Approximation

In this subsection, we will apply the stochastic drumhead equation (7.62a) to the problem of nucleation of a new phase and compare the results to those of CNT (see Sect. 7.1). One of the challenges that we have to face is to define the main quantity of CNT—rate of nucleation, using the proper fields. The approach that we are using here is to apply the field-theoretic quantity—*escape time*, which is inversely proportional to the nucleation rate. For a bistable potential, the escape time is defined as time needed for a system, which was initially in the vicinity of a minimum with higher value of the potential, to reach for the first time a vicinity of the minimum with lower value of the potential. In Appendix G, we calculated the escape time for a "particle in a bistable potential" if the Langevin equation for the particle is known. In what follows we will derive the Langevin equation for the nucleus in the drumhead approximation, calculate the escape time using the "particle in a bistable potential" formula and compare the escape time to the stationary nucleation rate of (7.2).

We assume that the transition layer has a shape of a sphere Ω_R, which surrounds a particle of the new phase. In this case

$$v_n = \frac{dR(t)}{dt}, \quad K = \frac{1}{R(t)} \text{ on } \Omega_R, \tag{5.36a}$$

where $R(t)$ is now a random variable that represents the radius of the particle. The stochastic force depends not only on time but also on the coordinates of the surface of the sphere (v, w). To eliminate this superfluous dependence, we average (7.62a) over the surface of the sphere taking into account (5.33) and that

$$\int_{\Omega_R} dv\,dw = 4\pi R^2.$$

Then

$$\frac{dR}{dt} = 2m\left(\frac{1}{R_*} - \frac{1}{R}\right) - \frac{\kappa}{4\pi R^2 \sigma}\psi(t), \tag{7.72a}$$

where R_* is the radius of the critical nucleus [cf. (5.35)] and the new force is

$$\psi(t) \equiv \int_{\Omega_R} \zeta(v, w, t)\,dv\,dw \tag{7.72b}$$

$$\langle \psi(t) \rangle = 0; \quad \langle \psi(t)\psi(t') \rangle = 8\pi\gamma k_B T \frac{\sigma}{\kappa} R^2 \delta(t - t'). \tag{7.72c}$$

Notice from (7.72) that the effect of the stochastic force is greater on smaller particles.

In principle, the particle equation (7.72) can be used for (G.40c) or (G.41c) to derive an expression for the escape time. The problem is that those formulae apply to the stochastic force that does not depend on the random variable itself, the radius $R(t)$ in this case (additive noise). To eliminate the R-dependence from the intensity and autocorrelation function of the random force, we multiply all terms of (7.72a) by $8\pi R$ and introduce a new random variable—the area of the particle's surface Ω_R

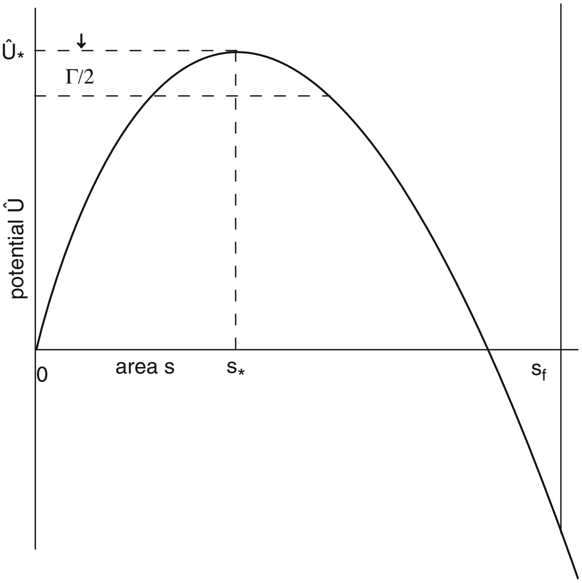
$$S = 4\pi R^2 \tag{7.73}$$

and the new force

$$\varphi(t) \equiv -\frac{2\kappa}{R\sigma}\psi(t), \tag{7.74a}$$

$$\langle \varphi(t) \rangle = 0; \quad \langle \varphi(t)\varphi(t') \rangle = \Gamma\delta(t - t'), \tag{7.74b}$$

Fig. 7.2 Bistable potential $\hat{U}(S)$, (7.76), with the two walls at $S = 0$ and $S = S_\mathrm{f}$



$$\Gamma = 32\pi \frac{m}{\sigma} k_\mathrm{B} T. \tag{7.74c}$$

Contrary to the previous subsection, S is a variable quantity now. The Langevin equation for S takes the form:

$$\frac{\mathrm{d}S}{\mathrm{d}t} = 16\pi m \left(\frac{\sqrt{S}}{\sqrt{S_*}} \right) + \varphi(t), \tag{7.75}$$

where S_* is the surface area of the critical nucleus. This equation describes "random walk of a particle" in the potential field

$$U(S) = 16\pi m \left(S - \frac{2}{3\sqrt{S_*}} S^{3/2} \right), \tag{7.76}$$

which is normalized such that $U(0) = 0$.

In the spirit of CNT, particles cannot grow to infinite sizes. To terminate the particle growth past certain size, we erect an infinitely high "wall" at $S = S_\mathrm{f}$, although precise value of S_f does not matter for as long as $S_\mathrm{f} > S_*$. Also, an infinite wall is erected at $S = 0$. The potential (7.76) with the two walls, designated as $\hat{U}(S)$, has two minima at 0 and S_f and a maximum at S_*; hence, this is a bistable potential, see Fig. 7.2. If the potential barrier is high [the fluctuations are weak, cf. (G.39)]

$$\hat{U}(S_*) \gg \Gamma. \tag{7.77}$$

then, for the escape time, we can use the expression (G.41c). Establishing the relations

$$\begin{aligned} &U(\omega_b) \to \widehat{U}(S_*) = \frac{16}{3}\pi m S_*; \quad U'(\omega_a) \to \widehat{U}'(0) = 16\pi m; \\ &U''(\omega_b) \to \widehat{U}''(S_*) = -\frac{8\pi m}{S_*^{3/2}}; \quad a_2 \to \Gamma. \end{aligned} \tag{7.78}$$

and substituting them into (G.41c) we obtain

$$\tau_{\text{of}} = \frac{1}{8m}\sqrt{\frac{k_B T S_*}{\pi\sigma}} e^{\sigma S_*/3k_B T} = \frac{\sqrt{k_B T\sigma}}{2m[g]_\beta^\alpha} e^{16\pi\sigma^3/3([g]_\beta^\alpha)^2 k_B T}. \tag{7.79}$$

The last expression in (7.79) was obtained by expressing S_* through the interfacial energy and driving force, (7.73), (5.35). Notice that this expression is independent of the cut-off radius R_f.

Comparison of (7.79) for the escape time with (7.2) for the stationary nucleation rate J_S shows that the FTM result has the correct exponential and the Zeldovich factor (the square root) but fails to reproduce the dependence on the volume of the system. The reason for that is that the presented method takes into account only spherically symmetric fluctuations of the shape, that is growth or shrinkage, and omits the shifts and distortions of the nucleus.

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Chapter 8
More Complicated Systems

Although the description presented in Chaps. 2–7 lays out a rich picture of a phase transformation, it is not rich enough to describe most of the transformations that we find around us. The problem is that so far we have been looking at the systems that can be described by a scalar, one-component order parameter while order parameters of real transformations may have many components or essential internal symmetry, not captured by a simple scalar. A few examples of more complicated systems are considered in this chapter. Specifically, we are looking at the systems where the order parameter is subject to a conservation law and go over all major steps of the method deriving the equilibrium equations in homogeneous and heterogeneous systems, dynamic equation, and analyzing the role of fluctuations. We lay out the phenomenological theory of superconductivity where the OP is a complex number and demonstrate how the method can help in calculating different properties of a superconductor. A section is devoted to a system that undergoes crystallographic transformation described by the OP that has more than one component, which interact with each other. We also look at the systems which have long time-correlation property—memory or are described by two fields of completely different symmetries.

8.1 Conservative Order Parameter: Theory of Spinodal Decomposition

8.1.1 Thermodynamic Equilibrium in a Binary System

Spinodal decomposition is a process of unmixing, i.e., spatial separation of species, which takes place in thermodynamically unstable solutions, solid or liquid. Spinodal decomposition provides an example of a phase transformation which can be described by an OP that obeys a *law of conservation*. In case of a system

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that consists of different species, it is advantageous to deal with the partial molar thermodynamic quantities instead of the densities (see Appendix H). Consider a binary solution that contains n_{A} moles of species A and n_{B} moles of species B isolated from the environment so that the total number of moles, $n = n_{\mathrm{A}} + n_{\mathrm{B}}$, and the molar fraction (*concentration*) of the species A (B), $X_{\mathrm{A}} = n_{\mathrm{A}}/n$ ($X_{\mathrm{B}} = n_{\mathrm{B}}/n$) does not change. By definition, the variables X_{A} and X_{B} are not independent as

$$X_{\mathrm{A}} + X_{\mathrm{B}} = 1. \tag{8.1}$$

A *regular solution* is a popular model of a binary system:

$$G^{\mathrm{S}} = X_{\mathrm{A}}G_{\mathrm{A}} + X_{\mathrm{B}}G_{\mathrm{B}} + RT(X_{\mathrm{A}}\ln X_{\mathrm{A}} + X_{\mathrm{B}}\ln X_{\mathrm{B}}) + \ \Omega X_{\mathrm{A}}X_{\mathrm{B}}. \tag{8.2}$$

Here R is the gas constant, G^{S} is the molar Gibbs free energy of the solution, G_{A} and G_{B} are the partial molar Gibbs free energies of the species A and B, and the total Gibbs free energy of the system is, of course, nG^{S}. The first two terms in (8.2) represent the free energy of a mechanical mixture of the components A and B. Since after mixing the atoms are in a much more random arrangement, there will be a negative entropy contribution into the free energy, called the entropy of mixing, which is the third term short of the temperature T. The fourth term represents the free energy excess (positive or negative) due to interactions of pairs of atoms of the same or different kinds. This contribution is proportional to the number of A–B pairs expressed by the product of the molar fractions with the coefficient of proportionality

$$\Omega = ZN_{Av}\omega, \quad \omega = \omega_{\mathrm{AB}} - \frac{1}{2}(\omega_{\mathrm{AA}} + \omega_{\mathrm{BB}}), \tag{8.3}$$

where Z is the coordination number of A and B, that is, the number of nearest neighbors to A or B, N_{Av} is the Avogadro number, and ω_{ij} designates the interaction energy of the i–j pair. Positive ω corresponds to the mixture where the like atoms attract more strongly than unlike atoms (attractive forces are negative, so that stronger attraction between like atoms means the ω_{AB} is a smaller negative number than the average of ω_{AA} and ω_{BB}). It is a good approximation when the atoms A and B have nearly the same radius. This model can be used for solids and liquids, although in liquids instead of Z and ω one has to use the average values.

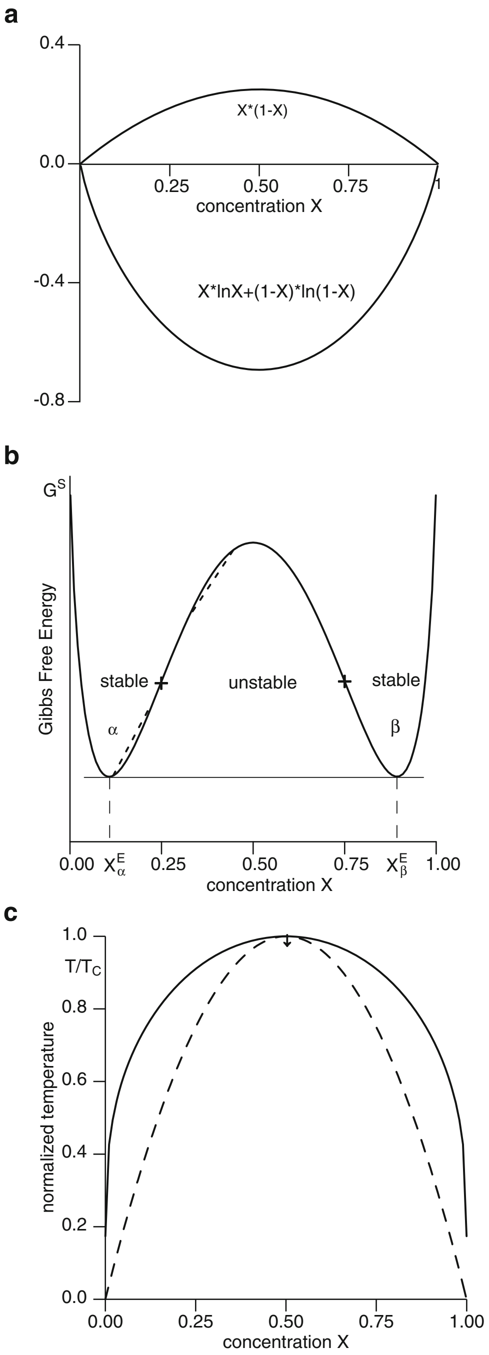
Using condition (8.1), the free energy (8.2) may be expressed as a function of one variable, e.g., $X \equiv X_{\mathrm{B}}$ (see Fig. 8.1a, b)

$$G^{\mathrm{S}}(X) = G_{\mathrm{A}} + (G_{\mathrm{B}} - G_{\mathrm{A}})X + RT[X\ln X + (1-X)\ln(1-X)] + \ \Omega X(1-X). \tag{8.4}$$

To estimate the roles of different contributions, first, notice that if $\Omega = 0$ (ideal solution) then for all compositions and all finite temperatures the free energy of the solution is less than that of the mechanical mixture of the pure components because

$$-\ln 2 \le X\ln X + (1-X)\ln(1-X) < 0 \quad \text{for } 0 < X < 1. \tag{8.5}$$

Fig. 8.1 Regular solution model of a binary system. (**a**) Contributions of entropy of mixing (negative) and energy of interactions (positive) of species into the Gibbs free energy. (**b**) Gibbs free energy of the system with $G_A \approx G_B$ at $T<T_C$. *Dashed lines* are the free energies of mixtures of the solutions. (**c**) *Solid line*—miscibility gap, (8.14); *dashed line*—spinodal curve, (8.13b); *arrow*—critical quench



This means that the first minute additions of any solute to any pure substance will always dissolve to form a solution (not necessarily an ideal one). Due to downward convexity of the ideal-solution free energy function, a single ideal solution is more stable than any mixture of the ideal solutions (Verify!).

Second, if $\Omega < 0$ (ordering solution) the situation is pretty much the same because the type of convexity of the free energy does not change. However, if $\Omega > \Omega_C > 0$ (phase-separating solution) the situation is more complicated because the free energy is not convex definite anymore (Fig. 8.1b). The critical value of the interaction parameter Ω is defined as such that changes the state of convexity of the function $G^S(X)$, (8.4), that is, the value of Ω which allows the function

$$\frac{d^2 G^S}{dX^2} = \frac{RT}{X(1-X)} - 2\,\Omega \tag{8.6}$$

to vanish exactly at one point. The latter point is called a *critical point*

$$X_C = \frac{1}{2} \tag{8.7}$$

and the critical interaction parameter value is $\Omega_C = 2RT$. It is accustomed to express the critical condition through the critical temperature of the system with the given strength of interactions Ω

$$T_C = \frac{\Omega}{2R} = \frac{Z\omega}{2k_B}. \tag{8.8}$$

Notice that T_C can be expressed through microscopic characteristics only.

Although for $T < T_C$, $G^S(X)$ looks similar to $G(\eta)$ (cf. Figs. 8.1b and 2.2a), the coordinates of the stable states in these systems have very different properties. For instance, because the overall composition of the solution X_0 must be set as the initial conditions, the molar fraction of a stable state may not correspond to a local minimum of $G^S(X)$. This does not mean that the principle of minimum of the total free energy does not apply to this system, but only that this principle must be supplemented with another condition or conditions because the physical nature of the variable X is different from that of the OP η. Most importantly, the OP value can change freely while "searching" for the free energy minimum, but the value of the variable X is influenced by *the mass conservation condition*. The latter means that in a closed system the total number of moles of a species does not change. In a binary system of A, B species, the mass conservation can be expressed as follows

$$n_A, n_B = \text{const}(t). \tag{8.9}$$

It applies equally to a system which was initially set as a heterogeneous or completely homogeneous one.

To examine the nature of the spinodal instability, let us consider an initially homogeneous system at constant temperature $T<T_C$ and concentration X_0. Because of the movement of the atoms in the solution, there are local composition fluctuations of very small values. Through these fluctuations the system or any part of it may decompose into a mixture of solutions characterized, at least initially, by compositions very close to that of the first homogeneous solution. If the Gibbs free energy of the mixture is lower than that of the homogeneous solution, then the latter is unstable and further decomposition may occur to produce states which have still lower free energy. Otherwise the decomposition will not occur. Suppose that the molar numbers and fractions of the neighboring solutions are n_α, n_β and X_α, X_β. Then

$$X_0 = \frac{n_B^\alpha + n_B^\beta}{n} = \frac{n_B^\alpha}{n^\alpha}\frac{n^\alpha}{n} + \frac{n_B^\beta}{n^\beta}\frac{n^\beta}{n} = X_\alpha x + X_\beta(1-x), \tag{8.10}$$

where x is the relative proportion (fraction) of α in the solution. Graphical representation of this result is called the *lever rule*.

The molar Gibbs free energy of the two-solution mixture is

$$G^m(X_0) = G_\alpha^S x + G_\beta^S(1-x) = G_\alpha^S \frac{X_0 - X_\beta}{X_\alpha - X_\beta} + G_\beta^S \frac{X_\alpha - X_0}{X_\alpha - X_\beta}. \tag{8.11}$$

Equation (8.11) is the equation of a straight line passing through the two points with coordinates (X_α, $G_\alpha{}^S$) and (X_β, $G_\beta{}^S$); a point on this line represents the free energy of the mixture G^m of the overall composition X_0 (Fig. 8.1b). It may be seen that if a free energy vs. concentration $G^S(X_0)$ is convex downward, the free energy of a two-solution mixture of neighboring compositions $G^m(X_0)$ is always higher than the free energy of the homogeneous solution $G^S(X_0)$. Similarly, if $G^S(X_0)$ is convex upward, $G^m(X_0)$ is lower than $G^S(X_0)$. Consequently, the solution is stable if $d^2G^S/dX^2 > 0$ and unstable if $d^2G^S/dX^2 < 0$. The inflection point,

$$\frac{d^2G^S}{dX^2} = 0, \tag{8.12}$$

separates the regions of stability and instability of the homogeneous concentration X_0 with respect to small fluctuations. According to our definition in Sect. 2.3, it is the spinodal point. The decomposition of a homogeneous solution resulting from infinitesimal fluctuations is called the spinodal decomposition.

Equations (8.4) and (8.12) yield an expression for the spinodal curve, that is, the locus of the spinodal concentrations at different temperatures

$$X_{\alpha(\beta)}^S\left(1 - X_{\alpha(\beta)}^S\right) = \frac{T}{4T_C}. \tag{8.13a}$$

Obviously, the same equation may be interpreted as an equation for the spinodal temperature T_S as a function of the concentration X_0 (Fig. 8.1c)

$$T_S = 4T_C X_0(1 - X_0). \tag{8.13b}$$

Notice that for each $T < T_C$ there are two spinodal concentrations, $X_\alpha^S < X_C$ and $X_\beta^S > X_C$, but $T_S(X_0)$ is a single-valued function.

The analysis of stability presented above may be expanded beyond the boundaries of small fluctuations of the neighboring regions (local stability) into the domain of global stability, that is, stability with respect to any compositional changes in the entire system. Indeed, applying results of the analysis of a two-phase equilibrium (Appendix H) to our system, we find that the condition of the global stability of the system is the *common tangency* between the molar fractions of the solutions X_α^E and X_β^E. Then, inspecting the calculations of (8.10)–(8.11) and Fig. 8.1b you may see that if the overall composition of the solution X_0 is between the points of common tangency, X_α^E and X_β^E, then a mixture of two solutions with these molar fractions and the relative proportion of α solution $x_\alpha^E = \left(X_0 - X_\beta^E\right) \Big/ \left(X_\alpha^E - X_\beta^E\right)$ is more stable (has less total free energy) than the homogeneous one. For a regular solution with $G_A \approx G_B$, the condition of common tangency, (H.12), is

$$\frac{dG^S}{dX}\left(X_{\alpha(\beta)}^E\right) = R\left[T \ln \frac{X_{\alpha(\beta)}^E}{1 - X_{\alpha(\beta)}^E} + 2T_C\left(1 - 2X_{\alpha(\beta)}^E\right)\right] = 0. \tag{8.14}$$

The temperature vs. concentration graph of this condition, called the solubility curve or *miscibility gap*, is depicted in Fig. 8.1c. From the stand point of the definition in Sect. 2.3, this curve represents the equilibrium phase boundary because at the points of this curve the equilibrium states, one-phase and two-phase, exchange their stabilities.

Example 8.1 Show that near the critical point:

$$\left|X_C - X_{\alpha(\beta)}^E\right| \approx \sqrt{3}\left|X_C - X_{\alpha(\beta)}^S.\right| \tag{8E.1}$$

Let us represent the solubility and spinodal curves as follows

$$X_{\alpha(\beta)}^E = X_C(1 + \varepsilon_E(T)), \quad X_{\alpha(\beta)}^S = X_C(1 + \varepsilon_S(T)). \tag{8E.2}$$

Then, taking (8.7) into account, in the vicinity of the critical point (8.13a) and (8.14) turn into

$$\frac{T}{T_C} = 1 - \varepsilon_S^2, \quad \frac{T}{T_C} = \frac{2\varepsilon_E}{\ln(1 + \varepsilon_E) - \ln(1 - \varepsilon_E)} \approx 1 - \frac{1}{3}\varepsilon_E^2. \tag{8E.3}$$

Comparing these equations we obtain the desired result. Notice that (8E.3) apply to both α and β sides of the curves.

8.1.2 Equilibrium in Inhomogeneous Systems

To describe inhomogeneities in a system that may appear as a result of the spinodal instability, Cahn and Hilliard [1] introduced a continuously varying molar fraction $X(\mathbf{r})$ and suggested to use the Ginzburg–Landau functional for the total Gibbs free energy of the system

$$G \equiv \int \left[g^{\mathrm{S}}(X) + \frac{1}{2}\kappa_{\mathrm{C}}(\nabla X)^2 \right] \mathrm{d}^3 r, \quad g^{\mathrm{S}} \equiv \frac{G^{\mathrm{S}}}{v_{\mathrm{m}}}. \tag{8.15a}$$

In (8.15a) $g^{\mathrm{S}}(X)$ is the Gibbs free energy density, v_{m} is the molar volume, κ_{C} is the concentration gradient energy coefficient, and the integration is over the entire volume of the system V. In the following v_{m} and κ_{C} will be considered constant, that is, independent of the composition of the solution.

As we know, in the state of thermodynamic equilibrium, $\bar{X}(\mathbf{r})$, the total free energy of a system that exchanges energy with environment approaches minimum: $G\{\bar{X}\} < G\{X\}$ if $\bar{X} \neq X$. However, in a closed system, where mass exchange with the environment is not allowed, this condition is subject to the species conservation constraint (8.9), which is expressed as follows

$$\int X(\mathbf{r})\, \mathrm{d}^3 r = X_0 V = \text{const.} \tag{8.16}$$

Notice from Appendix H that the proper minimization of the free energy in a closed binary system requires two species conservation constraints. In the case of a system where the molar volume is independent of the composition, the role of the second condition is played by the condition of conservation of the volume of the system

$$V \equiv \int v_{\mathrm{m}}\, \mathrm{d}n = \int \mathrm{d}^3 r = \text{const.} \tag{8.17}$$

If the molar volume depends on the composition, a whole host of other effects, including coherency strain effect, come about, none of which are of particular importance to the subject of this chapter.

Minimization of the functional G, (8.15a), under the constraints (8.16), (8.17) is called the *isoperimetric problem* in the calculus of variations (see Appendix B). From the physics stand point, the most appealing method to solve the problem is the method of Lagrange multipliers. It says that there exists a constant λ such that the functional

$$G + \lambda \int X\, \mathrm{d}^3 r \tag{8.15b}$$

approaches an unconditional minimum at $X = \bar{X}$. The volume conservation condition for a system with constant molar volume, (8.17), is trivial and does not affect the minimization procedure. Hence,

$$\frac{\delta G}{\delta X} \equiv \frac{\partial g^{\mathrm{S}}}{\partial X} - \kappa_{\mathrm{C}} \nabla^2 X = -\lambda. \tag{8.18}$$

Value of the molar fraction X on the boundaries of the system may change freely. In this case, the variational procedure yields the following boundary condition

$$\mathbf{n}\nabla X = 0 \text{ on } S. \tag{8.19}$$

To find the Lagrange multiplier λ, one needs to substitute the solution $\bar{X}(\mathbf{r})$ of (8.18), (8.19) into the conservation condition (8.16).

Let us consider now a 1d inhomogeneous binary solution of infinite size, that is, the thermodynamic limit. As we saw in Chap. 3, in this case (8.18) has the first integral, cf. (3.42a):

$$g^{\mathrm{S}}(\bar{X}) + \lambda\bar{X} - \frac{1}{2}\kappa_{\mathrm{C}}\left(\frac{\mathrm{d}\bar{X}}{\mathrm{d}x}\right)^2 = \mu = \mathrm{const}(x). \tag{8.20}$$

Because in the thermodynamic limit the boundary conditions (8.19) are placed at $x \to \pm\infty$, all higher derivatives of $\bar{X}(\mathbf{r})$ will also vanish on the boundaries. Then (8.18) yields another boundary condition

$$\frac{\partial g^{\mathrm{S}}}{\partial X} + \lambda = 0 \quad \text{for } x \to \pm\infty. \tag{8.21}$$

Hence, from (8.20), (8.21) we obtain

$$g^{\mathrm{S}}(X_-) - X_-\frac{\partial g^{\mathrm{S}}}{\partial X}(X_-) = \mu = g^{\mathrm{S}}(X_+) - X_+\frac{\partial g^{\mathrm{S}}}{\partial X(X_+)}, \tag{8.22a}$$

$$\frac{\partial g^{\mathrm{S}}}{\partial X}(X_-) = -\lambda = \frac{\partial g^{\mathrm{S}}}{\partial X(X_+)}, \tag{8.22b}$$

where $X_{\pm} = \bar{X}(\mathrm{x} \to \pm\infty)$ are the terminal (bulk) values of the molar fraction of the solutions. Comparison of (8.22) and (H.12) shows that we recovered the condition of common tangency between the terminal solutions of the system $X_{\pm}$. Consequently, they should be identified as $X^{\mathrm{E}}_{\alpha(\beta)}$. Then (8.22) can be used to find the constants λ and μ and constraint (8.16) can be used to find the X^{E}—the equilibrium fraction of α.

Furthermore, the solution of (8.20) with the boundary conditions $X_{\pm} = X^{\mathrm{E}}_{\alpha(\beta)}$ represents the transition layer between the bulk regions. It is analogous to the one studied in Chap. 3 if the OP η is replaced by the molar fraction X and functional (3.27) by (8.15b). The $\eta \leftrightarrow X$ analogy can be used for the analysis of the multidimensional solutions of (8.18).

Examples 8.2 Estimate the thickness and free energy of the transition layer between the bulk solutions of the molar fractions X^{E}_{α} and X^{E}_{β} in the regular solution with $\mathrm{G_A} \approx \mathrm{G_B}$.

First notice that in this case in (8.22)

$$\lambda = 0, \quad \mu = g^{\mathrm{S}}\left(X^{\mathrm{E}}_{\alpha(\beta)}\right). \tag{8E.4}$$

Then, adjusting the definitions of the interfacial thickness, (3.45), and energy, (3.71), to the binary system we obtain

$$l_{\mathrm{E}} \equiv \frac{\max\limits_{x,x'} |X - X'|}{\max\limits_{x} |\mathrm{d}X/\mathrm{d}x|} = \frac{\left|X_\beta^{\mathrm{E}} - X_\alpha^{\mathrm{E}}\right|}{|\mathrm{d}X/\mathrm{d}x(X_{\mathrm{C}})|} = \frac{X_\beta^{\mathrm{E}} - X_\alpha^{\mathrm{E}}}{\sqrt{2\left[g^{\mathrm{S}}(X_{\mathrm{C}}) - g^{\mathrm{S}}\left(X_{\alpha(\beta)}^{\mathrm{S}}\right)\right]/\kappa_{\mathrm{C}}}}, \tag{8E.5}$$

$$\sigma_{\mathrm{E}} \equiv \int_{-\infty}^{+\infty} \kappa_{\mathrm{C}} \left(\frac{\mathrm{d}X}{\mathrm{d}x}\right)^2 \mathrm{d}x = \int_{X_\alpha^E}^{X_\beta^E} \sqrt{2\kappa_{\mathrm{C}}\left[g^{\mathrm{S}}(X) - g^{\mathrm{S}}\left(X_{\alpha(\beta)}^{\mathrm{S}}\right)\right]}\, \mathrm{d}X. \tag{8E.6}$$

Notice in (8E.5) that the layer has the greatest slope at the critical concentration. Substitution of the expressions from (8.4), (8.8), (8.15) reveals two important scales: length and surface energy

$$l \equiv \sqrt{\frac{v_{\mathrm{m}}\kappa_{\mathrm{C}}}{RT_{\mathrm{C}}}}, \quad \sigma \equiv \sqrt{\frac{\kappa_{\mathrm{C}} RT_{\mathrm{C}}}{v_{\mathrm{m}}}}. \tag{8E.7}$$

Let us analyze two limiting cases of these expressions: $T \to 0$ and $T \to T_{\mathrm{C}}$. Applying representation (8E.2) of the equilibrium molar fractions, expanding (8.4) up to the fourth order in small ε_{E}, and then using the solution in (8E.3) we obtain

$$\frac{l_{\mathrm{E}}}{l} \to \begin{cases} 1 & \text{for } T \to 0 \\ \left(\frac{T_{\mathrm{C}} - T}{T_{\mathrm{C}}}\right)^{-1/2} & \text{for } T \to T_{\mathrm{C}} \end{cases} \tag{8E.8}$$

and

$$\frac{\sigma_{\mathrm{E}}}{\sigma} \to \begin{cases} 2\int_0^1 \sqrt{X(1-X)}\,\mathrm{d}X = \dfrac{\pi}{2} & \text{for } T \to 0 \\ X_{\mathrm{C}}\sqrt{\dfrac{T_{\mathrm{C}} - T}{T_{\mathrm{C}}}} \displaystyle\int_{-\varepsilon_E}^{+\varepsilon_E} \sqrt{\varepsilon_{\mathrm{E}}^2 - \varepsilon^2}\, \mathrm{d}\varepsilon = \dfrac{3\pi}{4}\left(\dfrac{T_{\mathrm{C}} - T}{T_{\mathrm{C}}}\right)^{3/2} & \text{for } T \to T_{\mathrm{C}}. \end{cases} \tag{8E.9}$$

Notice the typical mean-field exponents (−1/2) and (3/2) of the thickness and interfacial energy in the limit of $T \to T_{\mathrm{C}}$.

8.1.3 Dynamics of Decomposition in Binary Systems

Description of the dynamics of decomposition in mixtures should take into account the conservative nature of the variable molar fraction $X(\mathbf{r}, t)$. One way to write down an evolution equation for the system is to generalize the continuity equation [2, 3]

$$\frac{\partial X}{\partial t} = -\nabla \mathbf{J}, \tag{8.23}$$

where **J** is a flux of species B. Notice that the conservative nature of X is "automatically" taken into account by the general form of (8.23). Indeed, integrating this equation over the entire system and using the divergence theorem we obtain

$$\frac{\partial}{\partial t}\int X\,\mathrm{d}^3 r = -\oint \mathbf{nJ}\,\mathrm{d}s, \tag{8.24}$$

where integration in the second integral is over the boundary of the system S. In a closed system, that is, no mass exchange with environment, the equilibrium BC (8.19) is replaced by

$$\mathbf{nJ} = 0 \text{ on } S. \tag{8.25}$$

Hence, the surface integral in (8.24) vanishes and the total amount of the species B does not change in time. This is consistent with the conditions (8.9) and (8.16).

In the naïve theory of diffusion the flux **J** in the continuity equation (8.23) obeys the Fick's law: the flux is proportional to the gradient of concentration. To generalize this equation on the case of spinodal decomposition, notice that, in fact, the driving force for diffusion is the difference of the chemical potentials for the species at two nearby points, that is, the gradient of this quantity. Compare (8.18), (H.12) and notice that in our system the role of the chemical potential is played by the functional derivative $\delta G/\delta X$ which, according to (8.18), is equal to a constant when the system is in equilibrium. Hence, a phenomenological flux equation can be written in the form

$$\mathbf{J} = -M\nabla\frac{\delta G}{\delta \mathrm{X}}, \tag{8.26}$$

where M is called a mobility or linear response coefficient. Then, substituting (8.26) into (8.23) we obtain an equation that describes evolution of concentration in a binary system [3]

$$\frac{\partial X}{\partial t} = \nabla M \nabla \frac{\delta G}{\delta X}. \tag{8.27a}$$

Functional dependence of the linear response coefficient is a subject for discussion. Some authors suggested to use the molar-fraction dependence of the type: $M \propto X(1-X)$ to offset the infinite values of the chemical potential gradient at the concentrations approaching those of the pure A ($X \to 1$) or pure B ($X \to 0$) solutions. However, these situations are not typical for spinodal decomposition which takes place mostly inside the miscibility gap. That is why we will be considering

$$M = \text{const}(X, x). \tag{8.27b}$$

Then:

$$\frac{\partial X}{\partial t} = M\nabla^2 \frac{\delta G}{\delta X}, \quad \frac{\delta G}{\delta X} \equiv \frac{\partial g^{\mathrm{S}}}{\partial X} - \kappa_{\mathrm{C}}\nabla^2 X. \tag{8.27c}$$

To get a sense of the value of the linear response coefficient M, let us calculate the rate of the total free energy change that goes along with the evolution $X(\mathbf{r}, t)$ near the equilibrium state $\bar{X}(\mathbf{r})$

$$\frac{\mathrm{d}G}{\mathrm{d}t} = \int \frac{\delta G}{\delta X}\frac{\partial X}{\partial t}\mathrm{d}^3 r = M\int \frac{\delta G}{\delta X}\nabla^2 \frac{\delta G}{\delta X}\,\mathrm{d}^3 r.$$

Here, to obtain the final formula, we used the formula for differentiation of a functional with respect to a parameter (see Appendix B) and equation (8.27b). Then, applying a formula from the vector calculus

$$\nabla^2(uv) = u\nabla^2 v + 2\nabla u \cdot \nabla v + v\nabla^2 u$$

to $u = v = \delta G/\delta X$ and the divergence theorem we obtain

$$\frac{\mathrm{d}G}{\mathrm{d}t} = M\left[-\int\left(\nabla\frac{\delta G}{\delta X}\right)^2 \mathrm{d}^3 r + \oint \frac{\delta^*}{\delta X}\mathbf{n}\nabla\frac{\delta^*}{\delta X}\mathrm{d}s\right].$$

Applying (8.26) and BC (8.25), we obtain

$$\frac{\mathrm{d}G}{\mathrm{d}t} = -M\int\left(\nabla\frac{\delta G}{\delta X}\right)^2 \mathrm{d}^3 r. \tag{8.28a}$$

Using the fact that the integral in (8.28a) is nonnegative and that there exists an equilibrium state $\bar{X}(\mathbf{r})$, which minimizes the functional G$\{X\}$, we arrive at the condition

$$M \geq 0 \tag{8.28b}$$

because otherwise the state $\bar{X}(\mathbf{r})$ is not attainable. Also we find from (8.28a) that the functional (8.15a) is a Liapunov functional for the system described by (8.27a).

There is another way to derive (8.27c) which is of interest for us. Notice that this equation can be obtained from (5.2) by the formal substitution

$$-\gamma \Rightarrow M\nabla^2(\mathbf{r}). \tag{8.28c}$$

Equations (8.27c) and (5.2) have a common origin: these equations can be derived from the same master equation for the probability of the state characterized by $X(r_i, t)$ or $\eta(r_i, t)$ by either imposing the condition that the sum of all the changes of the variables is zero or not [4]. The common origin of the equations can be understood by considering a general relationship between the rate of the OP change $\partial\eta/\partial t$ and the driving force $\delta G/\delta\eta$

$$\frac{\partial\eta}{\partial t} = \int \Gamma(\mathbf{r} - \mathbf{r}')\frac{\delta G}{\delta X}(\mathbf{r}')\,\mathrm{d}^3 r$$

and imposing different properties, conservative or nonconservative on the kernel $\Gamma(\mathbf{r})$.

8.1.4 Evolution of Small Disturbances

To analyze dynamics of the system controlled by (8.27c), we consider first what happens to small deviations of the uniform state of concentration X_0. We write

$$X(\mathbf{r}, t) = X_0 + u(\mathbf{r}, t)$$

and then linearize (8.27c) about X_0:

$$\frac{\partial u}{\partial t} = M\nabla^2\left[\frac{\partial g^{\mathrm{S}}}{\partial X}(X_0) + \frac{\partial^2 g^{\mathrm{S}}}{\partial X^2}(X_0)u - \kappa_{\mathrm{C}}\nabla^2 u\right]. \tag{8.29a}$$

Notice that, contrary to the expansion of $\partial g/\partial\eta$ about $\bar{\eta}$ in (5.19), the term $\partial g^{\mathrm{S}}/\partial X(X_0)$ does not vanish now because X_0 may not correspond to the "bottom of the well" of $g^{\mathrm{S}}(X)$. Yet, this term does not affect behavior of $u(\mathbf{r}, t)$ because it is a constant. Hence,

$$\frac{\partial u}{\partial t} = M\left[\frac{\partial^2 g^{\mathrm{S}}(X_0)}{\partial X^2}\nabla^2 u - \kappa_{\mathrm{C}}\nabla^4 u\right]. \tag{8.29b}$$

Because of the conservation conditions (8.16) and (8.17), the average of the deviation $u(\mathbf{r}, t)$ is zero

$$\int u(\mathbf{r}, t)\,\mathrm{d}^3 r = 0. \tag{8.29c}$$

Hence, for the solutions of equation (8.29), we may try the normal modes (sine waves) of u

$$u(\mathbf{r}, t) = A\mathrm{e}^{\mathrm{i}\mathbf{kr}+\beta t}. \tag{8.30}$$

Substituting (8.30) into (8.29) we find the dispersion relation

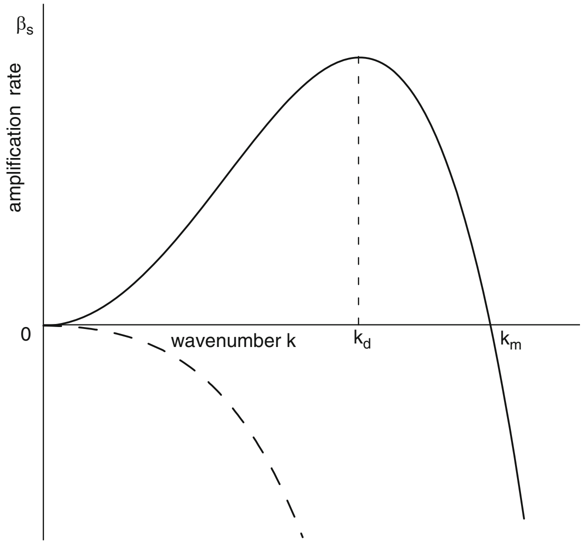


Fig. 8.2 Amplification rate β_S vs. wavenumber k of the normal modes for different values of X_0: *dashed line*—$\partial^2 g^S/\partial X_0{}^2 > 0$, the system is stable; *solid line*—$\partial^2 g^S/\partial X_0{}^2 < 0$, the system is unstable

$$\beta_S(k) = -Mk^2\left[\frac{\partial^2 g^S}{\partial X^2}(X_0) + \kappa_C k^2\right], \quad k = |\mathbf{k}|. \tag{8.31}$$

If $\partial^2 g^S/\partial X^2(X_0) > 0$ then $\beta_S(k) < 0$ for all $k > 0$, which means that the normal modes of all wavelengths decrease in amplitude: $Ae^{+\beta t} \to 0$ as $t \to \infty$. Hence, the system is stable. In this case for the normal modes with

$$k \ll \sqrt{\frac{1}{\kappa_C}\frac{\partial^2 g^S}{\partial X^2}(X_0)}$$

we can drop the gradient-energy term in (8.29b) and obtain a conventional diffusion equation

$$\frac{\partial u}{\partial t} = D_0\nabla^2 u, \quad D_0 \equiv M\frac{\partial^2 g^S}{\partial X^2}(X_0) \tag{8.32}$$

with positive diffusion coefficient D_0, see (8.28b).

On the other hand, if $\partial^2 g^S/\partial X^2(X_0) < 0$, that is, X_0 is in the spinodal region, then there are normal modes with $\beta_S(k) > 0$, that is, increase in amplitude: $Ae^{+\beta t} \to \infty$ as $t \to \infty$. Hence, the system is unstable. In this case, the dispersion relation (8.31) takes the form (Fig. 8.2):

$$\beta_S(k) = M\kappa_C k^2\left(k_m^2 - k^2\right), \quad k_m = \sqrt{-\frac{1}{\kappa_C}\frac{\partial^2 g^S}{\partial X^2}(X_0)}, \tag{8.33}$$

where k_m is the wavenumber of the marginally unstable mode for which the destabilizing (spinodal) and stabilizing (gradient-energy) contributions into the free energy cancel out.

In the case of $\partial^2 g^S / \partial {X_0}^2 < 0$, formally, the diffusion coefficient in (8.32) becomes negative—"uphill diffusion." The species acquire tendency to cluster instead of diffuse and the dynamic problem takes on an entirely different complexion. Obviously, the gradient-energy term in (8.29b) cannot be dropped because it plays the central role in opposing the clustering forces. The amplification rate β_S in (8.33) shows that the clustering prevails at small ks and spreading—at large ks. As a result, the most rapidly growing mode—"most dangerous mode"—is that for which the wavenumber is equal to

$$k_d = \frac{k_m}{\sqrt{2}}. \tag{8.34}$$

Compare (8.33) and Fig. 8.2 with (5.21a), (5.23) and Fig. 5.2 and notice that: (1) in the case of spinodal decomposition the long-wavelength disturbances grow very slowly, while in the case of a first-order transition the growth is fast—explosive; (2) in the case of spinodal decomposition, the amplification rate of the unstable modes reaches maximum at the finite wavenumber (*pattern formation*, see Sect. 9.6), while in the case of the first-order transition this wavenumber is zero (homogeneous structure formation). Presence of the finite-wavenumber maximum is a direct consequence of the conservation condition (8.16).

Using the regular-solution expression for $G^S(X)$, (8.6), (8.8), (8E.7), the marginal wavenumber k_m can be expressed as

$$k_m^2 = \frac{1}{l^2}\left[4 - \frac{T}{T_C X_0 (1 - X_0)}\right]. \tag{8.35a}$$

Comparison of this expression with (8.13b) shows that for a given composition of the solution X_0, the marginal wavenumber k_m decreases with temperature from the maximum value of $2/l$ at $T = 0$ to 0 at $T = T_S$ (Fig. 8.3). Expression (8.35a) can be resolved for the temperature

$$T = T_C\left[4 - (lk_m)^2\right]X_0(1 - X_0) \tag{8.35b}$$

and presented in the (X_0, T) plane (see Fig. 8.1c), which allows interpretation of the spinodal curve as the locus of points where $k_m = 0$.

The linear stability analysis presented above suggests the following scenarios of evolution of the concentration in the solutions starting from any almost homogeneous initial distribution $X(\mathbf{r}, t)$. If the average concentration X_0 is outside the miscibility gap, the solution is stable and will remain as an almost homogeneous state. If X_0 is between the miscibility curve $\left(X^E_{\alpha(\beta)}(T)\right)$ and spinodal

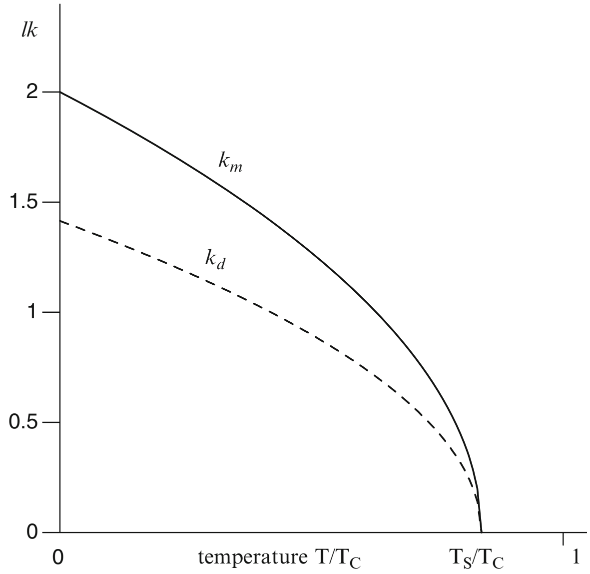


Fig. 8.3 Scaled wavenumbers of the marginally unstable k_m (*solid line*) and "most dangerous" k_d (*dashed line*) normal modes

$\left(X^\mathrm{S}_{\alpha(\beta)}(T)\right)$ the solution is still stable with respect to small variations, that is locally stable, but unstable globally that is with respect to full separation into two solutions of concentrations X^E_α and X^E_β. In this case, the process of separation will start with the formation of a small nucleus of the concentration close to, e.g., X^E_β surrounded by large region where the concentration had depleted from X_0 to X^E_α. If X_0 is inside the spinodal $\left(X^\mathrm{S}_\alpha < X_0 < X^\mathrm{S}_\beta\right)$ then the solution is unstable even with respect to small variations of concentration and the initial solution will be decomposing from the beginning. The initial deviations from the average concentration may be divided into the sine waves. Those with the wavenumbers k greater than the marginal—shrink, while those with the wavenumbers smaller—grow with the amplification factor $\beta_\mathrm{S}(k)$. Because $\beta_\mathrm{S}(k)$ has a steep maximum and because the growth rate is proportional to the exponential of $\beta_\mathrm{S}(k)$, it is possible to concentrate on the growth of the most dangerous mode k_d and those which are near that one. Such picture may be valid only for as long as the deviations u are small and the nonlinear terms in the expansion of (8.29b) can be ignored, that is, early stages of spinodal decomposition.

8.1.5 Role of Fluctuations

The experimental results, however, did not follow the latter scenario closely even when experimenters were pretty sure that they were dealing with the early stages. Among the most notable discrepancies they named the following: (1) the amplitudes of the sine waves rise much more slowly than exponentially ($Ae^{\beta t}$);

(2) the dispersion relation does not follow (8.33); (3) the observed values of k_d decrease with time. The conclusion was that the linearized thermodynamic analysis of the spinodal instability, containing many of the crucial features of the phenomenon, was missing at least one more ingredient. The key to the problem are the thermal fluctuations that may drive the system away from the linear, thermodynamic regime even on the early stages.

As we discussed in Chap. 7, a consistent way to include the thermal fluctuations into the field-theoretic method is to add the Langevin-type force to the evolution equation

$$\frac{\partial X}{\partial t} = M\nabla^2\frac{\delta G}{\delta X} + \zeta(r,t). \tag{8.36}$$

As $\zeta(\mathbf{r},\ t)$ represents the random force exerted by the rapid, thermally equilibrated modes of the system, the average value of $\zeta(\mathbf{r},\ t)$ is zero [cf. (7.33a)]. To find the autocorrelation function of $\zeta(\mathbf{r}, t)$ we may use the substitution (8.28c) for (7.48). Then

$$\langle\zeta(\mathbf{r},\ t)\zeta(\mathbf{r}_0,\ t_0)\rangle = -2Mk_\mathrm{B}T\nabla^2(r)\delta(\mathbf{r}-\mathbf{r}_0)\delta(t-t_0). \tag{8.37}$$

Equation (8.36) with G from (8.15a) and ζ calibrated by (8.37) describes evolution of the conserved quantity X, the molar fraction, in a process like the spinodal decomposition. Solutions of this equation may be obtained by direct numerical simulations.

Some key features of the solutions, however, may be revealed through the analysis of the two-point correlation function (cf. Sect. 7.5)

$$S(|\mathbf{r}-\mathbf{r}_0|,\ t) \equiv \langle u(\mathbf{r},\ t)u(\mathbf{r}_0,\ t)\rangle. \tag{8.38}$$

(In this section, instead of K, we use designation S for the correlation function and its Fourier transform, the structure factor, because this is a customary designation in the literature on the spinodal decomposition.) The averaging in (8.37) and (8.38) is performed with respect to $P\{u\}$—the probability distribution function for $u(\mathbf{r},\ t)$. Notice that the correlation function in (8.38) is assumed to be translation invariant. The Fourier transform of $S(r,\ t)$, called the structure factor $\hat{S}(k,\ t)$, is

$$\hat{S}(\mathrm{k},t) = \int S(\mathrm{r},\mathrm{t})\mathrm{e}^{-i\mathbf{kr}}\,d\mathbf{r} \tag{8.39a}$$

$$S(\mathrm{r},t) = \frac{1}{(2\pi)^3}\int \hat{S}(\mathrm{k},\mathrm{t})\mathrm{e}^{i\mathbf{kr}}\ \mathrm{d}\mathbf{k}. \tag{8.39b}$$

Expanding (8.36) about X_0, multiplying the product $u(\mathbf{r},\ t)u(\mathbf{r}_0,\ t)$ by the probability distribution function, taking the Fourier transform of the averaged quantity, and using (8.37) we obtain the evolution equation for $\hat{S}(k,\ t)$ [cf. (7.55)]:

$$\frac{\partial \hat{S}}{\partial t} = 2\beta_{\mathrm{S}}(k)\hat{S} + 2Mk_{\mathrm{B}}Tk^2 - Mk^2\left[\frac{\partial^3 g^S}{\partial X^3}(X_0)\hat{S}_3 + \frac{1}{3}\frac{\partial^4 g^S}{\partial X^4}(X_0)\hat{S}_4 + \cdots\right]. \quad (8.40)$$

Here $\beta_{\mathrm{S}}(k)$ is the amplification factor given in (8.31) and the quantities denoted by $\hat{S}_n(k,\ t)$ are the Fourier transforms of the higher-order two-point correlation functions

$$S_n(|\mathbf{r}-\mathbf{r}_0|,\ t) \equiv \left\langle u^{n-1}(\mathbf{r},\ t)u(\mathbf{r}_0,\ t)\right\rangle,$$

where the subscript is dropped for $n = 2$. Neglecting the correlation functions of orders higher than two and the fluctuation term ($2Mk_{\mathrm{B}}Tk^2$), we obtain the linear evolution equation for the structure factor, which follows from the linear evolution equation for the normal modes (8.29). Retaining the fluctuation term gives us the so-called Cook's equation [5], which is an improvement over (8.29)–(8.31) in that the stable modes with $k>k_{\mathrm{m}}$ are predicted to equilibrate at $\hat{S} = k_{\mathrm{B}}T/(k^2 - k_{\mathrm{m}}^2)$, rather than relax to zero. But the unstable modes in the Cook's approximation still exhibit unlimited exponential growth. Equation (8.40) indicates that the latter can be stopped only by the nonlinear terms of the free energy expansion that couple to the higher-order correlation functions. The problem in (8.40) is to find a physically reasonable and mathematically tractable way of relating $\hat{S}_n$ to $\hat{S}$. Langer [6] obtained an approximation, which is reasonable for the critical quench, that is, lowering the temperature from $T>T_{\mathrm{C}}$ to $T<T_{\mathrm{C}}$ at $X=X_{\mathrm{C}}$. In these conditions, we may assume that the probability distribution $P\{u\}$ is always a symmetric, Gaussian function of u, centered at $u=0$. Then, all $\hat{S}_n$s with odd numbers vanish and

$$\hat{S}_4(k,\ t) = 3S(0,\ t)\ \hat{S}(k,t). \quad (8.41)$$

where $S(0, t)=<u^2(t)>$, see (8 .38). If in (8.40) we drop the terms with $n>4$, we find that the resulting equation of motion for $\hat{S}$ has the same form as in the linear theory, but the previously constant free energy curvature $\partial^2 g^{\mathrm{S}}/\partial {X_0}^2$ is now replaced by the time-dependent expression

$$\frac{\partial^2 g^{\mathrm{S}}}{\partial X^2}(X_{\mathrm{C}}) + \frac{1}{2}\frac{\partial^4 g^{\mathrm{S}}}{\partial X^4}(X_{\mathrm{C}})\left\langle u^2(t)\right\rangle. \quad (8.42)$$

Because $\partial^4 g^{\mathrm{S}}/\partial {X_{\mathrm{C}}}^4$ is a positive constant and $<u^2(t)>$ is a positive, increasing function of time, the marginal wavenumber k_{m} in (8.33) must decrease. This implies *coarsening* of the emerging structure, which is observed in experiments and numerical simulations.

8.2 Complex Order Parameter: Ginzburg–Landau's Theory of Superconductivity

8.2.1 Order Parameter and Free Energy

There are systems where the OP should be represented by a complex function

$$\eta = |\eta| \mathrm{e}^{\mathrm{i}\Phi}. \tag{8.43}$$

Here Φ is the complex argument or phase of η. Most interesting examples of such systems are those where the quantum nature of matter is essential for its macroscopic behavior, for instance a superconducting metal. Full theory of superconductivity is very complicated and is not finished yet. In this section, we will discuss only the situations where the phenomenological Ginzburg–Landau theory is applicable [7, 8], leaving the question of the physical conditions of applicability to the end. For a superconducting phase of the material, the OP may be associated with the *wave function* of the superconducting electrons. Then, according to the quantum mechanics, the OP is a complex quantity defined with accuracy of an arbitrary additive phase and all observable quantities must depend on η and η^* (complex conjugate, CC) in such a way that they do not change if η is multiplied by a constant of the type $\mathrm{e}^{\mathrm{i}\theta}$:

$$\eta \to \eta \mathrm{e}^{\mathrm{i}\theta}, \quad \eta^* \to \eta^* \mathrm{e}^{-\mathrm{i}\theta}. \tag{8.44}$$

The OP should be normalized such that in the superconducting phase $|\eta|^2 = n_\mathrm{s}$ where n_s is the density of the "superconducting electrons."

Let us, first, consider a homogeneous superconductor outside of a magnetic field. Then η is independent of the spatial coordinates and the free energy density of a superconductor can be expanded in powers of the OP as follows

$$g(\eta, \eta^*; P, T) = g_0(P, T) + a(P, T)\eta\eta^* + \frac{1}{2} b(P, T)(\eta\eta^*)^2 + \cdots \tag{8.45}$$

where g_0 is the free energy density of a normal phase (η_n) and a, $b > 0$ are constants. The requirement of invariance to the addition of the arbitrary phase θ, (8.44), yields that the free energy expansion (8.45) cannot contain terms of the third order in η (or η^*). Hence, in the absence of the magnetic field, the superconductivity is a phase transition of the second kind.

In inhomogeneous systems, we have to account for the contributions of the components of $\nabla\eta$ into the free energy density. Taking into account that the complex OP is invariant with respect to the transformation (8.44), this contribution may be presented as const $\times |\nabla\eta|^2$. Recall that the OP η is introduced here as an effective wave function of the superconducting electrons. Then the operator $(-\hbar\nabla)$ represents the quantum mechanical operator of momentum of the particle and the contribution of the inhomogeneities into the free energy density of the system is analogous to the density of the kinetic energy in quantum mechanics. It can be presented as

$$\mathrm{const}|\nabla\eta|^2 = \frac{1}{2m}|-i\hbar\nabla\eta|^2,$$

where $\hbar = 1.05\times10^{-34}$ J s is the Plank's constant and m is an effective mass of a particle. Thus, the free energy density of an inhomogeneous system takes the form

$$\hat{g}(\eta,\eta^*,\nabla\eta;P,T) = g_0 + \frac{\hbar^2}{2m}|\nabla\eta|^2 + a|\eta|^2 + \frac{b}{2}|\eta|^4. \tag{8.46}$$

In quantum mechanics, the vectors

$$\mathbf{i} \equiv \frac{i\hbar}{2m}(\eta\nabla\eta^* - \eta^*\nabla\eta) = \frac{\hbar}{m}|\eta|^2\nabla\ \Phi \tag{8.47a}$$

$$\mathbf{j} \equiv q\mathbf{i} \tag{8.47b}$$

are identified, respectively, as the probability flux density and electrical current density due to a particle with the electrical charge q and the wave function $\eta(\mathbf{r}, t)$. These expressions can also be used in our case assuming that $\eta(\mathbf{r}, t)$, m, and $q=-|e|$ are the effective wave function, mass, and charge of the superconducting charge carries (e is the electron's charge). A few years after the introduction of the GL theory, it was discovered that the electrical current in a superconducting metal is transferred by *paired electrons*. This means that e and m in the GL theory should be replaced by $2e$ and $2m$. However, because we do not intend to present here a quantitative theory of superconductivity we will leave e and m in their original form. In a superconducting state, the conducting electrons break up into two parts, normal and superconducting, with the respective current density $\mathbf{j}_\mathrm{n}$ and $\mathbf{j}_\mathrm{s}$. Contrary to the normal current, the superconducting one does not carry heat or dissipate energy, hence, can be sustained without external sources.

So far we have been ignoring presence of the magnetic field in the material, which may appear as a result of an external source and/or the current. Now we have to ask the following questions: What will happen if the superconductor is placed into a magnetic field **H** created by the external sources? How do we introduce the magnetic field into the description of the system? What are the additional contributions into the free energy due to the presence of this field?

First, recall that in Chap. 2 discussing the influence on the transition of the external real-valued field H (which might be magnetic) we described it by the contribution ($-H\eta$) into the free energy density. However, such approach does not work for a complex OP because this contribution does not have the right symmetry. Second, as known [9], if a material is introduced into the external magnetic field of strength **H**, it will develop the magnetic moment **M** which will change the field in the material. The latter may be characterized by the magnetic induction (in CGS unit system)

$$\mathbf{B} = \mathbf{H} + 4\pi\mathbf{M}. \tag{8.48}$$

B satisfies Maxwell's equations (we consider only the case of the stationary field)

$$\nabla \times \mathbf{B} = \frac{4\pi}{c}\mathbf{j}, \tag{8.49a}$$

$$\nabla \cdot \mathbf{B} = 0. \tag{8.49b}$$

Third, to satisfy the condition of *gauge invariance* in the magnetic field, the operator ∇ must be transformed as follows [9]:

$$\nabla \to \nabla - \frac{ie}{\hbar c}\mathbf{A}, \tag{8.50}$$

where **A** is the magnetic vector potential related to the induction as

$$\mathbf{B} = \nabla \times \mathbf{A}. \tag{8.51}$$

Fourth, the work done on the material to increase the field from **B** to **B** + d**B** is **H** d**B**/4π. As the magnetic moment **M** of the normal phase (non-ferromagnetic) is practically zero, introduction of the magnetic field will change the free energy density of this phase as follows

$$g_n(P, T, \mathbf{H}) = g_0 + \frac{\mathbf{B}^2}{8\pi}. \tag{8.52}$$

The "self-contribution" of the magnetic energy density should be included into the free energy density because the magnetic field itself may be influenced by the state of ordering.

Thus the free energy density of an inhomogeneous superconductor in a stationary magnetic field is

$$\hat{g}(\eta, \eta^*, \nabla\eta; P, T, \mathbf{B}) = g_0 + \frac{\mathbf{B}^2}{8\pi} + \frac{\hbar^2}{2m}\left|\left(\nabla - \frac{ie}{\hbar c}\mathbf{A}\right)\eta\right|^2 + a|\eta|^2 + \frac{b}{2}|\eta|^4 \tag{8.52}$$

and the total free energy of the whole system is

$$\begin{aligned} G &= \int \hat{g}\, \mathrm{d}^3x \\ &= G_0(P, T) + \int \left\{ \frac{\mathbf{B}^2}{8\pi} + \frac{\hbar^2}{2m}\left|\left(\nabla - \frac{ie}{\hbar c}\mathbf{A}\right)\eta\right|^2 + a|\eta|^2 + \frac{b}{2}|\eta|^4 \right\} \mathrm{d}^3x. \end{aligned} \tag{8.54}$$

8.2.2 Equilibrium Equations

At equilibrium, the total free energy G must take on the smallest possible value. Hence, equations that describe the fields at equilibrium should be obtained by minimizing G with respect to the three independent functions (η, η^*, $\mathbf{A}$). Indeed, η and η^* are independent because a complex quantity is characterized by two real ones and $\mathbf{A}$ is independent because the OP field affects the magnetic field through the currents in the system. Varying G, (8.54), with respect to η^* and applying the Gauss theorem we obtain

$$\begin{aligned}\delta G = \int \delta\eta^* \left\{ -\frac{\hbar^2}{2m}\left(\nabla - \frac{ie}{\hbar c}\mathbf{A}\right)^2 \eta + a\eta + b|\eta|^2\eta \right\} \mathrm{d}^3x \; + \\ \frac{\hbar^2}{2m} \oint \delta\eta^* \left\{ \left(\nabla - \frac{ie}{\hbar c}\mathbf{A}\right)\eta \right\} \cdot \mathbf{n}\,\mathrm{d}s,\end{aligned} \tag{8.55}$$

where $\mathbf{n}$ is the unit vector normal to its surface and the second integral is taken over the surface of the superconductor. Setting $\delta G = 0$ and assuming that the variation $\delta\eta^*$ is arbitrary inside the superconductor and on its surface we obtain the following equation and the BC

$$-\frac{1}{2m}\left(-i\hbar\nabla - \frac{e}{c}\mathbf{A}\right)^2 \eta + a\eta + b|\eta|^2\eta = 0 \tag{8.56}$$

$$\left(-i\hbar\nabla - \frac{e}{c}\mathbf{A}\right)\eta \cdot \mathbf{n} = 0 \text{ on } S. \tag{8.57}$$

Variation of G with respect to η yields the equations which are CC to (8.56), (8.57).

Varying G, (8.54), with respect to $\mathbf{A}$, using the following formula from the vector calculus

$$\mathbf{U} \cdot (\nabla \times \mathbf{V}) - \mathbf{V} \cdot (\nabla \times \mathbf{U}) = \nabla \cdot (\mathbf{V} \times \mathbf{U})$$

and applying the Gauss theorem we obtain

$$\begin{aligned}\delta G = \int \delta\mathbf{A} \cdot \left\{ \frac{1}{4\pi}(\nabla \times \mathbf{B}) + \frac{i\hbar e}{2mc}(\eta^*\nabla\eta - \eta\nabla\eta^*) + \frac{1}{m}\left(\frac{e}{\mathrm{c}}\right)^2 \mathbf{A}|\eta|^2 \right\} \mathrm{d}^3x \\ + \frac{1}{4\pi}\oint \delta\mathbf{A} \cdot (\mathbf{B} \times \mathbf{n})\,\mathrm{d}s.\end{aligned} \tag{8.58}$$

Setting $\delta G = 0$ and assuming that the variation $\delta\mathbf{A}$ is arbitrary inside the superconductor and on its surface we obtain Maxwell's equation (8.49a) with the current density $\mathbf{j}$ [cf. (8.47), (8.50)]

$$\mathbf{j} = -\frac{e}{m}\left[\frac{i\hbar}{2}(\eta^*\nabla\eta - \eta\nabla\eta^*) + \frac{e}{\mathrm{c}}|\eta|^2\mathbf{A}\right] \tag{8.59}$$

and the BC

$$\mathbf{B} \times \mathbf{n} = 0 \text{ on } S. \tag{8.60a}$$

This is not surprising because the stationary Maxwell's equations can be derived from the variational principle of thermodynamics [9]. Notice that in (8.59) $\mathbf{j}$ represents the superconducting current only, because the normal current dies out at equilibrium.

The BC (8.60a) yields that on the boundary of the superconductor

$$B_n = 0, \quad B_t = B. \tag{8.60b}$$

Applying Maxwell's equation (8.49a) to BC (8.60a) we obtain a BC on the current

$$\frac{4\pi}{c}\mathbf{j} \cdot \mathbf{n} = (\nabla \times \mathbf{B}) \cdot \mathbf{n} = \nabla \cdot (\mathbf{B} \times \mathbf{n}) + \mathbf{B} \cdot (\nabla \times \mathbf{n}) = 0. \tag{8.60c}$$

Notice that this BC can also be derived if BC (8.57) and its CC are applied to the current defined by (8.47), (8.50). Equations (8.49a), (8.56), (8.59) with BC (8.57), (8.60a) define the distributions of the OP and magnetic fields in the superconducting material at equilibrium.

Let us analyze now the homogeneous solutions of the equilibrium equations. First, notice that if $\mathbf{B} = 0$ then we may choose the gauge $\mathbf{A} = 0$ which will allow us to define the OP in (8.56), (8.59) as a real number (e.g., the absolute value of the wave function), that is, to reduce our equations to those that have been analyzed in Chap. 2. Second, for weak but nonvanishing magnetic field, the equations take the form

$$a\eta + b|\eta|^2\eta = 0, \tag{8.61a}$$

$$\mathbf{j} = -\frac{e^2}{mc}|\eta|^2\mathbf{A}. \tag{8.61b}$$

The $\eta_n = 0$ solution of (8.61a) corresponds to the normal phase; then (8.61b) tells us that $\mathbf{j}_n = 0$. For the superconducting phase

$$n_{\mathrm{s}} = |\eta_{\mathrm{s}}|^2 = -\frac{a}{b}. \tag{8.62a}$$

This phase becomes stable when $a<0$ (see Chap. 2). Then

$$\mathbf{j}_{\mathrm{s}} = -n_{\mathrm{s}}\frac{e^2}{mc}\mathbf{A} = -\frac{|a|e^2}{bmc}\mathbf{A}. \tag{8.62b}$$

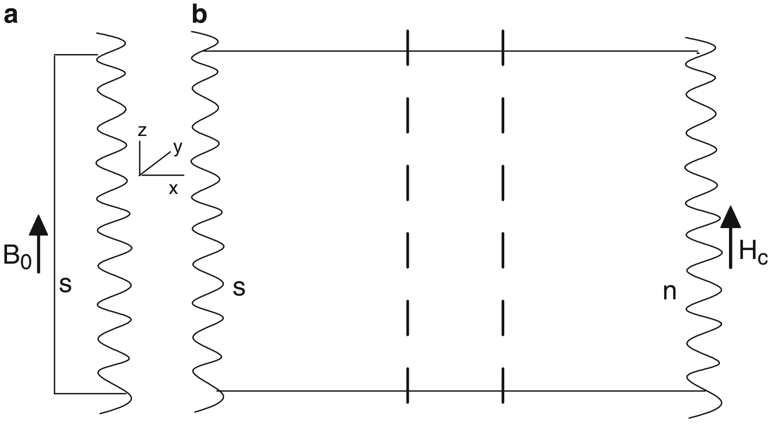


Fig. 8.4 (**a**) A boundary of a superconductor with vacuum. (**b**) Superconductor/normal phase transition layer

Applying operator $\nabla\times$ to both sides of (8.62b), using Maxwell's equations (8.49), (8.51) and the formula from vector calculus

$$\nabla\times(\nabla\times\mathbf{U})=\nabla(\nabla\cdot\mathbf{U})-\nabla^2\mathbf{U}$$

we obtain the Londons' equation [10]

$$\nabla^2\mathbf{B}=\frac{1}{\delta^2}\mathbf{B},\qquad \delta=\frac{c}{2|e|}\sqrt{\frac{bm}{\pi|a|}}=\frac{c}{2|e|}\sqrt{\frac{m}{\pi n_s}}.\tag{8.63}$$

Notice that the Londons' equation is gauge invariant.

Let us use this equation to find the magnetic field distribution close to a plane boundary of a superconductor with vacuum, which will be considered to be a *yz*-plane with the *x*-axis directed into the superconductor (see Fig. 8.4a). Then $\mathbf{B}=\mathbf{B}(x)$ and, as it follows from (8.60b), $B_x=0$, that is, only the component of the magnetic field parallel to the surface is not zero: $B_t\neq 0$. Then (8.63) and BC (8.60b) take the form $\mathrm{d}^2B_t/\mathrm{d}x^2=B_t/\delta^2$ and $B_t(0)=B_0$, where B_0 is the external field applied parallel to the surface. Hence

$$B_t=B_0\mathrm{e}^{-x/\delta}.\tag{8.64}$$

As you can see, the magnetic field penetrates only a thin surface layer of thickness δ of the superconducting sample and decays quickly below this layer. In the theory of superconductivity, this is called the Meissner effect.

Now let us calculate the free energy of a superconductor, e.g., a long cylinder, which is placed into a constant magnetic field parallel to its axis. In this case, the equilibrium equations should be obtained by minimizing not the free energy G but the following potential

$$\Phi(\{\eta\}; P, T, \mathbf{H}) = G(\{\eta\}; P, T, \mathbf{B}) - \frac{1}{4\,\pi} \int \mathbf{H} \cdot \mathbf{B}\, \mathrm{d}^3 x. \tag{8.65}$$

The integral in this potential, as we discussed above, accounts for the work done by the external forces to maintain $\mathbf{H} = \mathrm{const}(t)$. Let us call it the Gibbs magnetic potential. Equation (8.65) is an example of Legendre transformation ($\mathbf{B}$, G) → ($\mathbf{H}$, Φ), analogous to (V, F) → (P, G) (see Appendix F). As the OP is not involved into this transformation, minimization of Φ yields the same equation (8.56) and BC (8.57). Variation of the additional term in the Gibbs magnetic potential gives

$$\begin{aligned} \delta \int \mathbf{H} \cdot \mathbf{B}\, \mathrm{d}^3 x &= \int \mathbf{H} \cdot (\nabla \times \delta \mathbf{A})\, \mathrm{d}^3 x \\ &= \int \delta \mathbf{A} \cdot (\nabla \times \mathbf{H})\, \mathrm{d}^3 x + \oint (\mathbf{n} \times \mathbf{H}) \cdot \delta \mathbf{A}\, \mathrm{d}s. \end{aligned} \tag{8.65a}$$

Because there are no external currents $\mathbf{j}_{\mathrm{ext}}$, the volumetric term in this expression vanishes

$$\nabla \times \mathbf{H} = \frac{4\pi}{c} \mathbf{j}_{\mathrm{ext}} = 0. \tag{8.65b}$$

Hence, the equilibrium equation (8.59) remains the same but all parameters now should be expressed as functions of $\mathbf{H}$ instead of $\mathbf{B}$. The surface term will change the BC (8.60a) to

$$(\mathbf{B} - \mathbf{H}) \times \mathbf{n} = 0 \text{ on } S. \tag{8.60d}$$

For the normal phase: $\eta_n = 0$, $\mathbf{j}_n = 0$, $\mathbf{M}_n = 0$, and $\mathbf{B} = \mathbf{H}$. Hence,

$$\Phi_n = G_0 - \frac{H^2}{8\pi} V. \tag{8.66}$$

In the bulk of the superconducting phase: $|\eta_s| = \sqrt{|a|/b}$ and $\mathbf{B}_s = 0$. As the magnetic field penetrates only a thin surface layer of the superconducting material, the contribution of the first two terms in the integral in (8.54) is proportional to the thickness of this layer times the cross-sectional area and can be neglected compared to the contribution of the last two terms, which is proportional to the total volume of the sample V. Hence,

$$\Phi_s = \mathrm{G}_0 - \frac{a^2}{2b} V. \tag{8.67}$$

Comparing expressions (8.66) and (8.67) we can see that application of the strong enough magnetic field makes the normal phase thermodynamically more favorable than the superconducting one. As the condition of the phase equilibrium is $\Phi_s = \Phi_n$, we obtain an expression for the *critical field*, that is, the external magnetic field strength H_c that renders the superconducting phase thermodynamically (globally) unstable:

$$H_c = 2|a|\sqrt{\frac{\pi}{b}}. \tag{8.68}$$

Assuming the linear temperature dependence of the coefficient a

$$a = \alpha(T - T_c), \tag{8.69}$$

where $\alpha>0$ is a constant and T_c is the *critical temperature* of the transition (cf. Sect. 2.6.2), we obtain

$$H_c = 2\alpha\sqrt{\frac{\pi}{b}}(T_c - T). \tag{8.70}$$

This relation is applicable only to $T \to T_c - 0$ because in the derivation of (8.61) we used the condition of not strong magnetic field. Notice that our analysis of the superconducting transition yields that this is a second-order transition for $\mathbf{H} = 0$ and the first-order one for $\mathbf{H} \neq 0$.

8.2.3 Surface Tension of the Superconducting/Normal Phase Interface

As we concluded in Chap. 3, the first-order transitions allow for a state of phase coexistence, that is the state where two phases, which are at equilibrium with each other, are separated by a transition zone of particular thickness. Hence, coexistence of the superconducting and normal phases is possible at $T<T_c$ and $H=H_c$. In the theory of superconductivity, such state is called *intermediate*. We define the interfacial energy (surface tension) as the excess of the total Gibbs magnetic potential of the system with the interface, per unit area of the interface, compared to that of one of the equilibrium phases. Let us calculate the surface tension σ_{ns} and thickness of the plane *n*/*s* transition layer, which we choose to be parallel to *yz*-plane with the *x*-axis directed into the superconducting phase (see Fig. 8.4b). Then

$$\sigma_{ns} = \int_{-\infty}^{\infty} (\hat{\varphi} - \varphi_n)\,\mathrm{d}x, \tag{8.71a}$$

where all quantities depend on x only and

$$\hat{\varphi} = \hat{g} - \frac{\mathbf{H}\cdot\mathbf{B}}{4\pi} \quad \text{and} \quad \varphi_n = g_0 - \frac{a^2}{2b}. \tag{8.71b}$$

For the vector potential, which has not been “calibrated” yet, we choose the transverse (or Coulomb or London) gauge

$$\nabla \mathbf{A} = 0. \tag{8.72}$$

Then we obtain that $\mathrm{d}A_x/\mathrm{d}x = 0$ and we can choose $A_x = 0$. Remaining two components of the vector potential may be chosen as $A_z = 0$ and $A_y = A(x)$. Then $B_z = \mathrm{d}A/\mathrm{d}x$. As the term $i\mathbf{A}\nabla\eta$ in the equilibrium equation (8.56) and the free energy density (8.53) vanishes we arrive at the following boundary value problem

$$-\frac{1}{2m}\left(-\hbar^2\frac{\mathrm{d}^2\eta}{\mathrm{d}x^2} + \frac{e^2}{c^2}\mathrm{A}_y^2\eta\right) + a\eta + b|\eta|^2\eta = 0 \tag{8.73a}$$

$$\frac{d\mathrm{B}_z}{dx} = -\frac{4\pi}{c}\frac{e}{m}\left[\frac{i\hbar}{2}\left(\eta^*\frac{\mathrm{d}\eta}{\mathrm{d}x} - \eta\frac{\mathrm{d}\eta^*}{\mathrm{d}x}\right) + \frac{e}{c}|\eta|^2 A_y\right] \tag{8.73b}$$

$$x \to -\infty\text{: } n\text{ - phase,}\quad \eta = 0,\quad B_z = H_\mathrm{c} \tag{8.74a}$$

$$x \to +\infty\text{: } s\text{ - phase,}\quad |\eta|^2 = -\frac{a}{b},\quad B_z = 0. \tag{8.74b}$$

The surface tension is

$$\sigma_\mathrm{ns} = \int\left\{\frac{1}{8\pi}\left(B_z^2 - 2H_\mathrm{c}B_z\right) + \frac{\hbar^2}{2m}\left[\left|\frac{d\eta}{dx}\right|^2 + \left(\frac{e}{\hbar c}\right)^2 A_y^2|\eta|^2\right] + a|\eta|^2 + \frac{b}{2}|\eta|^4 + \frac{a^2}{2b}\right\}\mathrm{d}^3x. \tag{8.75}$$

Given the BC (8.74) and formula (8.68) it is not surprising that the integrand vanishes in the bulk of both phases. Notice that the OP in (8.73), (8.74) may be selected as a real function. Then the variables may be scaled as follows

$$\tilde{x} = \frac{x}{\delta},\quad \tilde{\eta} = \eta\sqrt{\frac{b}{|a|}},\quad \tilde{A} = \frac{A_y}{H_\mathrm{c}\delta},\quad \tilde{B} = \frac{\mathrm{d}\tilde{A}}{\mathrm{d}\tilde{x}} = \frac{B_z}{H_\mathrm{c}} \tag{8.76}$$

and (8.73), (8.74) may be represented in the scaled form

$$\frac{\mathrm{d}^2\eta}{\mathrm{d}x^2} = \kappa^2\left[\left(\frac{A^2}{2} - 1\right)\eta + \eta^3\right], \tag{8.77a}$$

$$\frac{\mathrm{d}^2A}{\mathrm{d}x^2} = A\eta^2, \tag{8.77b}$$

$$x \to -\infty,\quad \eta = 0,\quad B = \frac{\mathrm{d}A}{\mathrm{d}x} = 1,$$

$$x \to +\infty,\quad \eta = 1,\quad B = \frac{\mathrm{d}A}{\mathrm{d}x} = 0, \tag{8.78}$$

where

$$\kappa = \frac{mc}{|e|\hbar}\sqrt{\frac{b}{2\pi}} \tag{8.79}$$

and the tildes have been dropped. "These equations, unfortunately, cannot be integrated in quadratures, but we can provide its first integral" [7]

$$\frac{2}{\kappa^2}\left(\frac{\mathrm{d}\eta}{\mathrm{d}x}\right)^2 + \left(2 - A^2\right)\eta^2 - \eta^4 + \left(\frac{\mathrm{d}A}{\mathrm{d}x}\right)^2 = \mathrm{const} = 1, \tag{8.80}$$

where the value of the constant comes from the BC (8.78). Then expression (8.75) takes the form

$$\sigma_{\mathrm{ns}} = \frac{\delta H_{\mathrm{c}}^2}{8\pi}\int_{-\infty}^{\infty}\left[\frac{2}{\kappa^2}\left(\frac{\mathrm{d}\eta}{\mathrm{d}x}\right)^2 + \left(A^2 - 2\right)\eta^2 + \eta^4 + \left(\frac{\mathrm{d}A}{\mathrm{d}x} - 1\right)^2\right]\mathrm{d}x \tag{8.81}$$

$$= \frac{\delta H_{\mathrm{c}}^2}{4\pi}\int_{-\infty}^{\infty}\left[\frac{2}{\kappa^2}\left(\frac{\mathrm{d}\eta}{\mathrm{d}x}\right)^2 + \frac{\mathrm{d}A}{\mathrm{d}x}\left(\frac{\mathrm{d}A}{\mathrm{d}x} - 1\right)\right]\mathrm{d}x \tag{8.81a}$$

$$= \frac{\delta H_{\mathrm{c}}^2}{8\pi}\int_{-\infty}^{\infty}\left[\left(\frac{\mathrm{d}A}{\mathrm{d}x} - 1\right)^2 - \eta^4\right]\mathrm{d}x. \tag{8.81b}$$

(Verify (8.81a) and (8.81b)!). Notice from (8.81b) that the surface tension may vanish. One can prove (see [7]) that this takes place for the critical value of

$$\kappa^* = \frac{1}{\sqrt{2}}. \tag{8.82}$$

Vanishing of the surface tension is an important phenomenon which comes about as a result of interaction of the OP field and the magnetic field. It causes many interesting effects in superconductors, including appearance of the electromagnetic vortices.

As for the thickness of the transition zone, (8.77a) shows that the length scale of the OP variation is

$$\xi = \kappa\delta. \tag{8.83}$$

This length is equivalent to the *correlation radius* because it determines the range of statistical correlations of the OP fluctuations.

8.3 Multicomponent Order Parameter: Crystallographic Phase Transitions

Many cases of phase transitions cannot be described adequately by a scalar order parameter. They require an OP of more complicated structure, e.g. a "vector." An example in the previous section, to some extent, is a case in point. Another example is a crystallographic transition, i.e. symmetry change in a crystalline solid. In this section, we will consider only equilibrium characteristics of such transformations, which is well described by the Landau Theory of Phase Transitions.

8.3.1 Invariance to Symmetry Group

Consider a transition from a "high-symmetry" crystalline phase to a "low-symmetry" one, which may be characterized by the densities of atoms $\rho_0(\mathbf{r})$ and $\rho(\mathbf{r})$ so that

$$\rho(\mathbf{r}) = \rho_0(\mathbf{r}) + \delta\rho(\mathbf{r}). \tag{8.84}$$

The functions $\rho_0(\mathbf{r})$ and $\rho(\mathbf{r})$ have different symmetries, that is, sets (*groups*) of the transformations of the coordinates Γ with respect to which the functions are invariant. In this case, $\Gamma(\rho) = \Gamma(\delta\rho)$ is a subgroup of $\Gamma(\rho_0)$ because otherwise no symmetry change occurs at the transformation point. As known from the group theory [11], an arbitrary function may be represented as a linear combination of the base functions $\{\varphi_1, \varphi_2, \ldots\}$ which transform through each other under any transformation from the group Γ. Moreover, the base functions may be broken into a number of the linearly independent sets where the functions from each set transform through the base functions of the same set only and the number of the base functions in the set cannot be reduced any further. Such sets are called irreducible representations and play a special role in the Landau theory because the symmetry change associated with a particular transition may be described by one of the irreducible representations only. Then we represent

$$\delta\rho(\mathbf{r}) = \sum_{i=1}^{f} \eta_i \varphi_i(\mathbf{r}), \tag{8.85}$$

where $\{\varphi_i\}$ is the set of normalized base functions of the group $\Gamma(\rho_0)$ and f is the order of the representation. Because any transformation from the group $\Gamma(\rho_0)$ transforms the base functions $\{\varphi_i\}$ through each other leaving the coefficients $\{\eta_i\}$ unchanged, we may think of it as transforming $\{\eta_i\}$s leaving $\{\varphi_i\}$s unchanged.

If the set $\{\varphi_i\}$ is specified, the coarse-grained free energy G of a homogeneous crystal with the density of atoms $\rho(\mathbf{r})$ becomes a function of T, P, and $\{\eta_i\}$ and may be expanded about $\rho_0(\mathbf{r})$ if $\delta\rho(\mathbf{r})$ is small compared to $\rho_0(\mathbf{r})$. However, this is an expansion in powers of η_i as opposed to $\delta\rho(\mathbf{r})$ because the coarse-grained free energy of a homogeneous system cannot depend on the space coordinate $\mathbf{r}$. As the free energy of the crystal is independent of the choice of the coordinate system, it must be invariant with respect to the transformations of the group $\Gamma(\rho_0)$. Hence, the free energy expansion in powers of η_i should contain only invariant combinations of certain powers $I^{(n)}(\eta_i)$ and $\{\eta_i\}$ may be called a *multicomponent order parameter* (MOP).

First, notice that the expansion of G in $\{\eta_i\}$ contains no linear invariants. Indeed, existence of such, e.g., $\sum_{i=1}^{f} \alpha_i\eta_i = \text{const}$, would mean that the set of base functions $\{\varphi_i,\ i = 1,2,\ldots,f\}$ is not linearly independent, which contradicts our assumption. Second, the only invariant of the second order—a positive definite quadratic form—can always be normalized to the sum of the squares, $I^{(2)}(\eta_i) = \sum_{i=1}^{f} \eta_i^2$. Third, the invariants of different orders $I^{(n)}(\eta_i)$ are independent of each other. Hence, the free energy expansion should take the form

$$G(T,P,\{\eta_i\}) = G_0(T,P) + A(T,P)\sum_{i=1}^{f}\eta_i^2 + \sum_p B_p(T,P)I_p^{(3)}(\eta_i) + \sum_q C_q(T,P)I_q^{(4)}(\eta_i) + \cdots,$$

where $I_p^{(3)}(\eta_i)$ and $I_q^{(4)}(\eta_i)$ are invariants of the third and fourth order, respectively. Crystallographic symmetries of the system determine what invariants should be included into the expansion, which in turn determines what kinds of transitions may take place in the system. The coefficients of expansion determine the characteristics of the transition, like phase diagrams and thermodynamic quantities. Thus, the proper irreducible representation converts description of the system through the atomic density into the one through the MOP.

8.3.2 Inhomogeneous Variations

As in the case of a one-component OP, the total free energy of an inhomogeneous system is an integral over the entire volume of the system

$$G = \int_V \hat{g}\,\mathrm{d}^3x \tag{3.27a}$$

of the free energy density $\hat{g}$, which depends on the variables that characterize the state of the system and their spatial derivatives. Hence, the spatial derivatives of MOP must be included into the free energy density function

$$\hat{g}\left(T,\ P,\ \{\eta_i\},\ \left\{\frac{\partial^p\eta_i}{\partial x_k^p}\right\}\right).$$

A physically consistent functional dependence of $\hat{g}$ on $\left\{\partial^p \eta_i / \partial x_k^p\right\}$ is the subject of this subsection.

Because the equilibrium free energy comes from minimization of the integral (3.27a), two points regarding the functional dependence of $\hat{g}$ on $\left\{\partial^p \eta_i / \partial x_k^p\right\}$ should be kept in mind. First, only spatial derivatives of the first order should be included into the first approximation of $\hat{g}$ because through the integration by parts the higher derivatives can be reduced to lower derivatives plus the surface term. Second, the inhomogeneous contributions may be broken into invariant combinations and considered separately. Hence, $\hat{g}$ should not contain linear combinations of $(\partial \eta_i / \partial x_k)$ because they may be integrated into the surface term (recall the Gauss theorem). The bilinear in MOP and linear in spatial derivative terms may be divided into two contributions: symmetric

$$\eta_i \frac{\partial \eta_j}{\partial x_k} + \eta_j \frac{\partial \eta_i}{\partial x_k} = \frac{\partial \eta_i \eta_j}{\partial x_k} \tag{8.86a}$$

and antisymmetric

$$\eta_i \frac{\partial \eta_j}{\partial x_k} - \eta_j \frac{\partial \eta_i}{\partial x_k}. \tag{8.86b}$$

The former are not essential because they are perfect differentials and can also be integrated into the surface terms. The latter, called *Lifshitz invariants*, cannot be integrated out and deserve special attention. Notice that the group $\Gamma(\rho_0)$ transforms components $\{\partial \eta_k / \partial \mathrm{x_i}\}$ as the components of the position vector times the components of the MOP. Hence, the Lifshitz invariants transform as the components of the vector times the "antisymmetric square"

$$\eta_k(\mathbf{r})\eta_l(\mathbf{r}') - \eta_l(\mathbf{r})\eta_k(\mathbf{r}'). \tag{8.87}$$

This means that the Lifshitz invariants are not true scalar invariants of the group $\Gamma(\rho_0)$, but they can be linearly combined into such. If the system of interest supports only homogeneous equilibrium phases then the Lifshitz invariants must be absent because their presence does not allow a homogeneous in MOP state to minimize the total free energy. (Why?) The condition of absence of the Lifshitz invariants in the free energy expansion is equivalent to the condition that the antisymmetric square (8.87) does not transform as a vector. Crystallographic conditions for this are beyond the scope of this book, they can be found in [11]. If, on the other hand, the system of interest may sustain heterogeneous equilibrium phases (e.g., the so-called incommensurate phases), then presence of the Lifshitz invariants is warranted.

In this section, we consider systems that support the homogeneous phases only. Hence, the inhomogeneous part of the free energy density should include only the bilinear in MOP and spatial derivatives terms

$$\hat{g} = g(T, P, \{\eta_i\}) + \kappa_{ij}^{kl} \frac{\partial \eta_k}{\partial x_i} \frac{\partial \eta_l}{\partial x_j}, \tag{8.88}$$

where κ_{ij}^{kl} is the fourth rank tensor of the gradient-energy coefficients and the summation over the repeated indices is assumed. For the homogeneous state of the crystal to be stable, the inhomogeneous term should allow partitioning into positive definite invariants of the second order in the components of the gradient $\{\partial\eta_k/\partial x_i\}$. Hence, the transformation properties of the components of the gradient $\{\partial\eta_k/\partial x_i\}$ determine the symmetry of the tensor κ_{ij}^{kl}. Also, symmetry of the tensor $\kappa_{ij}^{kl}$is determined by the symmetry of the system, e.g., crystalline anisotropy [cf. (3.20a) and the discussion afterwards].

8.3.3 Equilibrium States

Equilibrium states of the system described by the free energy (8.88), (3.27a) obey the following simultaneous equations (see Appendix B)

$$\frac{\delta G}{\delta\eta_k}\equiv\frac{\partial\hat{g}}{\partial\eta_k}-\frac{\partial}{\partial x_i}\frac{\partial\hat{g}}{\partial(\partial\eta_k/\partial x_i)}=0. \tag{8.89}$$

Let us consider a system where $\kappa_{ij}^{kl}=\delta_{kl}\delta_{ij}\kappa_i^k/2$, that is

$$\hat{g}=g(T,P,\{\eta_i\})+\frac{1}{2}\kappa_i^k\left(\frac{\partial\eta_k}{\partial x_i}\right)^2. \tag{8.90}$$

Then the simultaneous equations (8.89) take the form

$$\frac{\partial g}{\partial\eta_k}-\kappa_i^k\frac{\partial^2\eta_k}{\partial x_i^2}=0,\quad k=1,\ldots,f. \tag{8.91}$$

Notice that in the second term there is no summation over k but there is summation over i (Why?).

Thermodynamic stability of a heterogeneous equilibrium state $\{\eta_k^E(\mathbf{x})\}$ is determined by the sign of the second variation of the functional

$$\delta^2G=\frac{1}{2}\int_V\delta\eta_l\hat{\mathbf{H}}\delta\eta_k\,\mathrm{d}^3x, \tag{3.121}$$

where now $\boldsymbol{\delta\eta}=(\delta\eta_k)$. The sign of the second variation is determined by the spectrum of its Hamilton's operator

$$\begin{aligned}\hat{\mathbf{H}}\,\Psi_{k,n}&=\Lambda_n\,\Psi_{k,n};\\ \hat{\mathbf{H}}&\equiv\frac{\partial^2\hat{g}}{\partial\eta_k\partial\eta_l}\left(\eta_k^E(\mathbf{x})\right)-\frac{\partial^2\hat{g}}{\partial(\partial\eta_k/\partial x_i)\partial\left(\partial\eta_l/\partial x_j\right)}\frac{\partial}{\partial x_i}\frac{\partial}{\partial x_j}.\end{aligned} \tag{8.92}$$

Same as in the case of the one-component OP, the gradient

$$\Psi_{i,k,n_*} = \frac{\partial \eta_k^E}{\partial x_i} \tag{8.93}$$

is the Goldstone mode of the equilibrium state, that is, the eigenfunction with zeroth eigenvalue: $\Lambda_n = 0$.

A particular interesting situation arises in a one-dimensional system where all variables depend on one coordinate only, e.g., $x_1 = x$. Then (8.91) take the form

$$\kappa^k \frac{\mathrm{d}^2 \eta_k}{\mathrm{d}x^2} = \frac{\partial g}{\partial \eta_k}, \quad k = 1, \ldots, f. \tag{8.94}$$

Using the thermo-mechanical analogy of Chap. 6, these equations may be interpreted as describing a conservative mechanical system of f interacting particles with x as the time, η_k—coordinate of the kth particle, κ_k—its mass, and $(-g)$ as the potential energy of the whole system. Such system has the first integral—the total mechanical energy, kinetic plus potential [12]. To see this in our case, we multiply both sides of (8.94) by $(\mathrm{d}\eta_k/\mathrm{d}x)$ and sum them up over k. Then

$$\frac{\mathrm{d}}{\mathrm{d}x}\left[\frac{1}{2}\kappa^k \left(\frac{\mathrm{d}\eta_k}{\mathrm{d}x}\right)^2\right] = \frac{\partial g}{\partial \eta_k}\frac{\mathrm{d}\eta_k}{\mathrm{d}x} = \frac{\mathrm{d}g}{\mathrm{d}x}. \tag{8.95}$$

Hence, the "conservation of mechanical energy" expression takes the form

$$\frac{1}{2}\kappa^k \left(\frac{\mathrm{d}\eta_k}{\mathrm{d}x}\right)^2 - g(T, P, \{\eta_i\}) = -\mu, \tag{8.96}$$

where μ (negative of the "total energy") is the value of g inside the homogeneous phases [cf. (3.42a)].

An interesting application of this relation appears if one wants to calculate the interfacial energy σ between two coexisting phases. As we discussed in Sect. 3.4.4

$$\sigma \equiv \int_{-\infty}^{\infty} (\hat{g} - \mu)\,\mathrm{d}x = 2\int_{-\infty}^{\infty} (g - \mu)\,\mathrm{d}x. \tag{3.70b, c}$$

Then, using (8.90) and (8.96) we obtain an expression

$$\sigma = \int_{-\infty}^{\infty} \kappa^k \left(\frac{\mathrm{d}\eta_k}{\mathrm{d}x}\right)^2 \mathrm{d}x, \tag{8.97}$$

which may be interpreted that the interfacial energy is, so to speak, a weighted sum of the squares of all the gradients of the OPs.

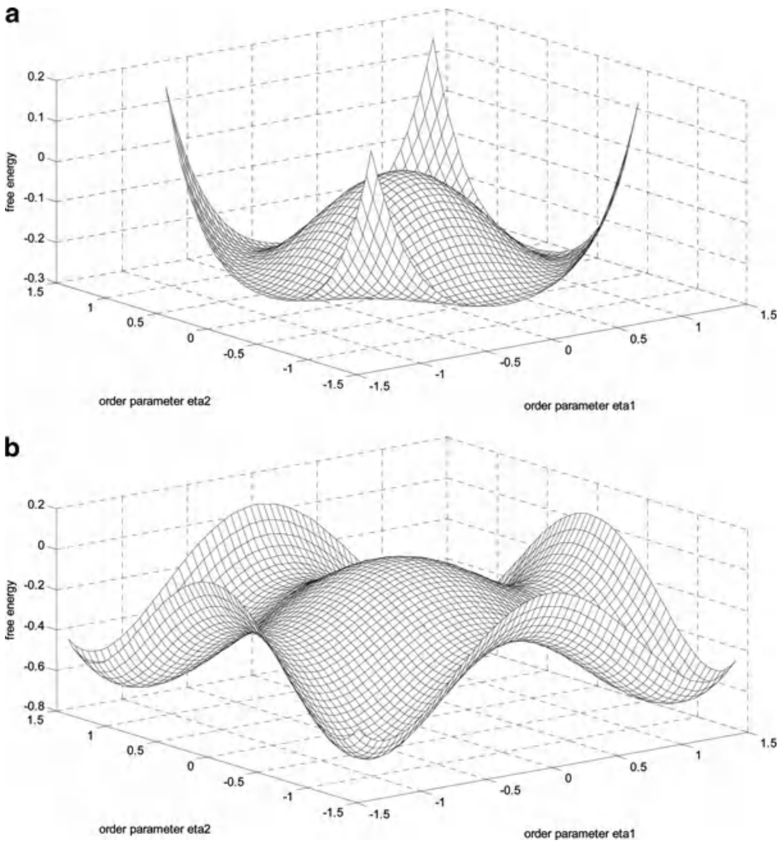


Fig. 8.5 The surfaces (g–g_0) from (8.98) as functions of (η_1, η_2) for $A = -1, C_2 = 1$ and different values of C_1: 1.25 (**a**) and -0.25 (**b**)

As an example of a system with MOP let us consider the following free energy density

$$g = g_0(T,P) + \frac{1}{2}A\left(\eta_1^2 + \eta_2^2\right) + \frac{1}{2}C_1\eta_1^2\eta_2^2 + \frac{1}{4}C_2\left(\eta_1^4 + \eta_2^4\right). \tag{8.98}$$

This potential describes transitions in a crystalline structure that belongs to the crystallographic point group D_{4h}. It may be visualized by a body-centered tetragonal Bravais lattice in which the transitions constitute displacements of the central atom away from its most symmetric position [13]. The surfaces (g–g_0) as functions of (η_1, η_2) for $A = -1$, $C_2 = 1$ and different values of C_1 are depicted in Fig. 8.5. At $C_1 = C_2$ the surface (g–g_0) is called the "Mexican hat potential" because it is a function of ($\eta_1^2 + \eta_2^2$) only.

The homogeneous equilibrium states of this system are obtained from the following system of simultaneous equations

$$\frac{\partial g}{\partial \eta_1} = \eta_1\left(A + C_1\eta_2^2 + C_2\eta_1^2\right) = 0, \tag{8.99a}$$

$$\frac{\partial g}{\partial \eta_2} = \eta_2\left(A + C_1\eta_1^2 + C_2\eta_2^2\right) = 0. \tag{8.99b}$$

The system has nine solutions, which may be divided into three groups

$$E_0 = (\bar{\eta}_1 = \bar{\eta}_2 = 0), \tag{8.100a}$$

$$E_1 = \left(\bar{\eta}_1 = 0,\ \bar{\eta}_2^2 = -\frac{A}{C_2}\right) \text{ or } \left(\bar{\eta}_1^2 = -\frac{A}{C_2},\ \bar{\eta}_2 = 0\right), \text{ and} \tag{8.100b}$$

$$E_2 = \left(\bar{\eta}_1^2 = \bar{\eta}_2^2 = -\frac{A}{C_1 + C_2}\right). \tag{8.100c}$$

In Fig. 8.6, the equilibrium states E_0, E_1, E_2 are depicted in the plane (η_1, η_2). Conditions of local stability of the equilibrium states are the following

$$D(E) \equiv \frac{\partial^2 g}{\partial \eta_1^2}\frac{\partial^2 g}{\partial \eta_2^2} - \left(\frac{\partial^2 g}{\partial \eta_1 \partial \eta_2}\right)^2 > 0 \text{ and } g_{11}(E) \equiv \frac{\partial^2 g}{\partial \eta_1^2} > 0. \tag{8.101}$$

Applying this criterion to the states (8.100) we obtain their respective regions of local stability

$$E_0 : A > 0, \tag{8.102a}$$

$$E_1 : A < 0, \quad \frac{C_1}{C_2} > 1, \tag{8.102b}$$

$$E_2 : A < 0, -1 < \frac{C_1}{C_2} < 1. \tag{8.102c}$$

For the states E_1 to be real valued in the domain of their stability it must be

$$C_2 > 0 \tag{8.102d}$$

which will be also assumed for all other cases. According to our definition of a phase as a locally stable homogeneous-in-OP state of a system (see Sect. 2.2), the states E_0, E_1, E_2 are phases in the domains (8.102a), (8.102b), (8.102c), respectively. Each phase, E_1 and E_2, has four variants of different "orientation" in the

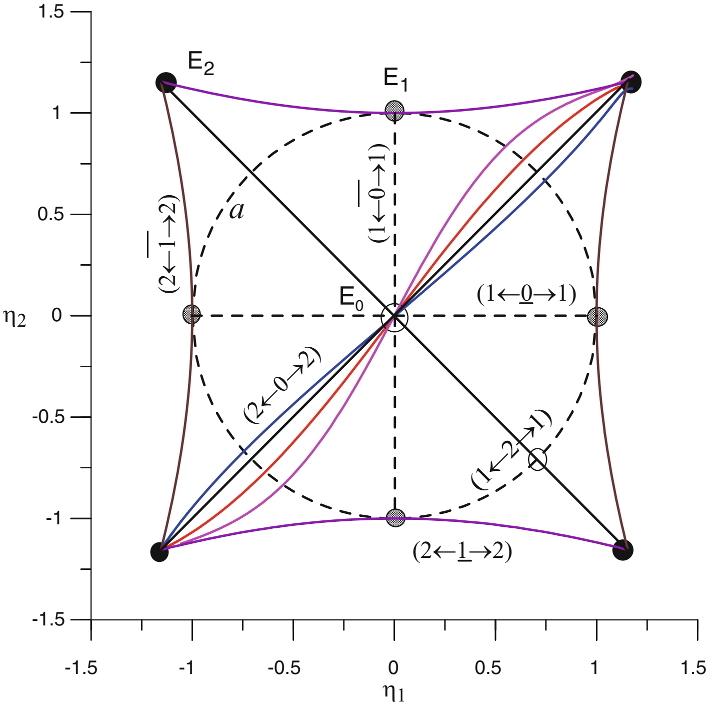


Fig. 8.6 Equilibrium states E_0, E_1, E_2 of the system with the free energy density, (8.98), for $-A/C_2 = 1$ and $C_1/C_2 = -0.25$ in the order-parameter plane (η_1, η_2). Colored trajectories are the domain-wall transition paths for different values of the gradient energy coefficients:$\kappa = 0$ (*purple*), $\kappa = 0.2$ (*pink*), $\kappa = 0.5$ (*red*), $\kappa = 1$ (*black*), $\kappa = 1.5$ (*blue*), $\kappa = \infty$ (*brown*). For $C_1 = 0$ states, E_2 will be in the corners of the square described around the *circle* "*a*"; for $C_1/C_2 = 1$—on the arch of the circle of radius equal to "*a*"; for $C_1/C_2>1$—on the circle of radius smaller than that of "*a*." *Dashed lines* are the trajectories of the domain-wall transition paths for $C_1/C_2>1$

domain of its stability. The phase diagram of the system (8.98) is presented in Fig. 8.7 for $C_2 = \text{const} > 0$. As you can see, this system has three phase transition lines: ($A=0$, $-C_2<C_1<C_2$), ($A=0$, $C_1>C_2$), and ($A<0$, $C_1=C_2$). All transitions are of the second kind because at the transition lines the stable states exchange their stabilities with the unstable ones and there are no regions of coexistence of the stable states (phases).

Analysis of inhomogeneous equilibrium states of the system presents another interesting problem for us. As we saw in Sect. 3.4, the stable 1d inhomogeneous state represents a transition zone between two phases separated by an unstable barrier state. Using the free energy (8.98) for (8.94) we obtain

$$\kappa_1 \frac{\mathrm{d}^2\eta_1}{\mathrm{d}x^2} = A\eta_1 + C_1\eta_1\eta_2^2 + C_2\eta_1^3, \tag{8.103a}$$

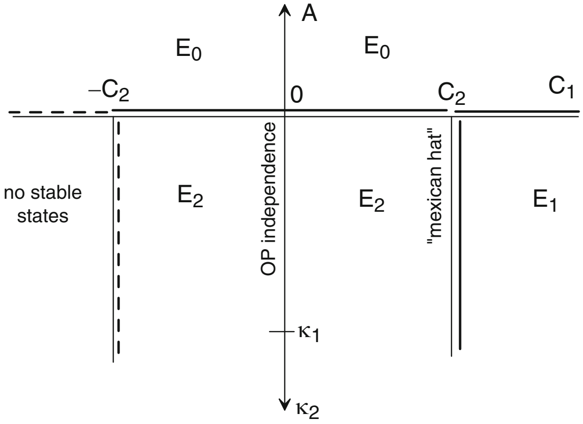


Fig. 8.7 Projection of the parameter space (A, C_1, κ_2) of the system with the free energy density (8.90), (8.98) on the plane. The phase (stability) diagram (A, C_1) for C_2=const >0

$$\kappa_2 \frac{d^2\eta_2}{dx^2} = A\eta_2 + C_1\eta_1^2\eta_2 + C_2\eta_2^3. \tag{8.103b}$$

Physically, there are two main types of the interfaces: inter-phase boundaries between two phases of different symmetries, e.g., solid/liquid or fcc/bcc, and anti-phase boundaries (APB, domain walls) between two different variants of the same phase, e.g., magnetic or order/disorder. For the system described by the free energy, (8.98) only the second type, APB, is possible. (Why?) The APBs exist only for $A < 0$ because the phase E_0 has only one variant. Six different types of APBs may be found in each phase, E_1 and E_2. Their symmetries depend on the kinds of the variants that are connected by the APB and the barrier state that separates them. The base symmetries, ($E_1 \leftarrow E_0 \rightarrow E_1$ or $E_1 \leftarrow E_2 \rightarrow E_1$) and ($E_2 \leftarrow E_0 \rightarrow E_2$ or $E_2 \leftarrow E_1 \rightarrow E_2$) are broken by the gradient-energy anisotropy. As a result, there appear six main types of the APBs, which may be found in the phase E_1 or E_2 in different modifications (see Fig. 8.6). Their interfacial energies depend on the values of C_1, C_2, and κ_1, κ_2. Effect of these parameters on the interfacial energy of the domain wall depends on its symmetry. If $C_1 = 0$, the simultaneous equations (8.103) break down into two independent equations for two different OPs. This means that the domain wall consists of two parts which coexist without interactions. In the scaled units

$$\frac{x}{\sqrt{\kappa_1/C_2}} \rightarrow x, \quad \frac{\sigma}{\sqrt{\kappa_1 C_2}} \rightarrow \sigma, \quad a = -\frac{A}{C_2}, \quad c = \frac{C_1}{C_2}, \quad \kappa = \frac{\kappa_2}{\kappa_1} \tag{8.104}$$

the dimensionless parameter κ is a measure of the gradient-energy anisotropy in the OP space (η_1, η_2).

In the isotropic E_2 phase ($\kappa = 1$), the OP symmetry is not broken and the transition path is represented by the straight-line diagonals connecting the equilibrium states in the OP plane (Fig. 8.6). The energy of the special cases of ($E_2 \leftarrow E_0 \rightarrow E_2$) interfaces are

$$\sigma_{E_2 \leftarrow E_0 \rightarrow E_2}(a, -1 < c < 1, \kappa) = \begin{cases} 2\sqrt{2}\left(1+\sqrt{\kappa}\right)a^{3/2}/3, & \text{if } c = 0 \\ 4\sqrt{2}a^{3/2}/3(1+c), & \text{if } \kappa = 1 \end{cases}. \tag{8.105a}$$

For the nonspecial cases of c and κ, the solutions may be obtained numerically using the ideas of the thermo-mechanical analogy from Chap. 6. In Fig. 8.6, the results of the computations are presented in the OP plane. Notice two features of the trajectories. First, in both cases, they pass through the state E_0 as the barrier, which is the local maximum of the free energy (see Fig. 8.5b). Second, they press to the “hard” OP axis more than to the “soft” one. (Why? Hint: think about the interfacial thicknesses of the soft and hard OPs separately). The interfacial energies of the respective domain walls are

$$\sigma_{E_2 \leftarrow E_0 \rightarrow E_2}(a = 1,\ c = -0.25,\ \kappa) = \begin{cases} 2.16, & \text{if } \kappa = 0.5 \\ 2.80, & \text{if } \kappa = 1.5. \end{cases} \tag{8.105b}$$

For the ($E_2 \leftarrow E_1 \rightarrow E_2$) interfaces, the symmetry between the OPs is broken even if $\kappa = 1$ and the transition-path trajectories are represented by the respective hyperbolae in the OP plane (Fig. 8.6). The interfacial energies of these layers are

$$\sigma_{E_2 \leftarrow E_1 \rightarrow E_2}(a, -1 < c < 1,\ \kappa) \rightarrow \begin{cases} 2\sqrt{2(1-c)}a^{3/2}/3(1+c), & \kappa \rightarrow 0 \\ 2\sqrt{2\kappa(1-c)}a^{3/2}/3(1+c), & \kappa \rightarrow \infty \end{cases}. \tag{8.106}$$

The type of the interface, ($E_2 \leftarrow E_0 \rightarrow E_2$) (8.105) or ($E_2 \leftarrow E_1 \rightarrow E_2$) (8.106), depends on the symmetries of the terminal phases that the interface connects. Both types of interfaces are thermodynamically stable, that is, their Hamilton’s operators, (8.92), do not have negative eigenvalues. In Fig. 8.8, the interfacial energies of the two types of interfaces are plotted as functions of κ. As you can see the interfaces of different types may coexist in the same phase although they have different amounts of energy.

In the E_1 phase ($c>1$), there are two types of the APBs: ($E_1 \leftarrow 0 \rightarrow E_1$) where only one OP varies while the other one is zero and ($E_1 \leftarrow 2 \rightarrow E_1$) where both OPs vary simultaneously. The symmetry of the ($E_1 \leftarrow 0 \rightarrow E_1$) interfaces is broken by the gradient-energy coefficients and the trajectories of these interfaces in the OP plane represent, respectively, the horizontal and vertical straight lines (see Fig. 8.6). Trajectories of the ($E_1 \leftarrow 2 \rightarrow E_1$) interfaces in the OP plane are arches. The interfacial energies of the ($E_1 \leftarrow 0 \rightarrow E_1$) interfaces are

$$\sigma_{E_1 \leftarrow \bar{E}_0 \rightarrow E_1}(a,\ c>1,\ \kappa) = (2\sqrt{2}/3)a^{3/2} \tag{8.107a}$$

$$\sigma_{E_1 \leftarrow \underline{E}_0 \rightarrow E_1}(a,\ c>1,\ \kappa) = (2\sqrt{2}/3)\sqrt{\kappa}a^{3/2} \tag{8.107b}$$

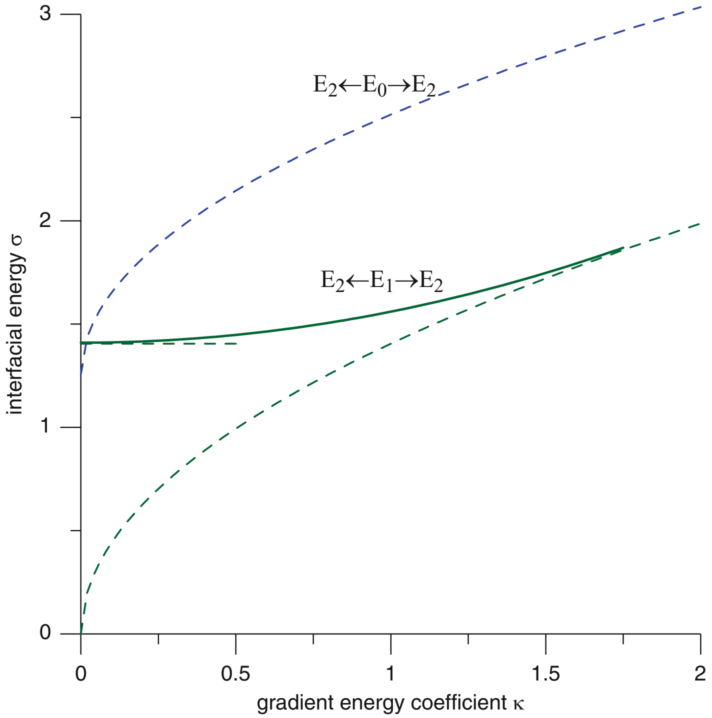


Fig. 8.8 Scaled interfacial energy σ of the domain walls in the phase E_2 at $c = -0.25$ as a function of the scaled gradient energy coefficient κ. *Blue curve*—($E_2 \leftarrow E_0 \rightarrow E_2$) type, (8.105); *green curve*—($E_2 \leftarrow E_1 \rightarrow E_2$) type, (8.106)

Example 8.3 Find the equilibrium states of the free energy density that describes transitions from fcc to $L1_0$ crystalline structure

$$\begin{aligned}\hat{g} = g_0 &+ \frac{1}{2}A\left(\eta_1^2 + \eta_2^2 + \eta_3^2\right) + \frac{1}{3}B\eta_1\eta_2\eta_3 + \frac{1}{2}C_1\left(\eta_1^2 + \eta_2^2 + \eta_3^2\right)^2 \\ &+ \frac{1}{4}C_2\left(\eta_1^4 + \eta_2^4 + \eta_3^4\right) + \frac{1}{2}\kappa\left(|\nabla\eta_1|^2 + |\nabla\eta_2|^2 + |\nabla\eta_3|^2\right).\end{aligned} \tag{8E.10}$$

8.4 Memory Effects: Non-Markovian Systems

In Chap. 7, we proposed the dynamic equation for the OP evolution (7.31) that takes into account effects of the driving force (first term in rhs) and fluctuations (second term in rhs). Let us look closer at the following property of this equation: the response of a system to the driving force is simultaneous with the application of the force. As a general rule, such simultaneity in a macroscopic theory turns out to be an approximation to causal behavior, where the response to a force comes after the application of the force. Usually simultaneity is associated with ignoring certain molecular variables. Indeed, although the time dependence of a system is governed by equations (Hamilton's or Schrödinger's) that show an instantaneous response, complete specification of the microstate of the macroscopic system requires knowledge of a very large number of molecular variables. In our mesoscopic description, the microscopic variables are coarse-grained and we deduce evolution of the system from the equations for the OPs, pretending that other variables do not chgange (see Appendix A). This is where the causality is violated. The reason why we want to reexamine the dynamic Langevin equation (7.31) instead of TDGLE (5.1) is that we would like to assess and compare the effect of causality and fluctuations at the same time. To do that, we need to derive (or at least substantiate) a causal evolution equation, which we will call the generalized Langevin equation, and then investigate the validity of simultaneity as a limiting case.

First, let us ask ourselves a question: how did simultaneity "enter" our theory? In Appendix G, we showed that the Langevin equation is equivalent to the Fokker-Plank equation (G.10), which can be derived from the master equation (G.6). In the master equation, evolution of the system depends on the transition probabilities $W(\omega|\omega')$, which depend *only* on the states between which the transition occurred and does not depend on the previous states of the system. This Markovian property is the source of simultaneity in the system.

If the Markovian condition is relaxed, evolution of the system will depend on its "history." In the Fokker-Plank equation, this will result in the jump moments a_1, a_2 being dependent on the memory effects. The Langevin equation with the memory effects takes the form

$$\frac{\mathrm{d}\eta}{\mathrm{d}t} = -\int_0^{\mathrm{t}} \Gamma(t-t')\frac{\delta G}{\delta\eta}(t')\,\mathrm{d}t' + \xi(\mathbf{r},t), \tag{8.108}$$

where $\Gamma(s)$ is the memory function, which depends on the time difference between the present t and past t' moments and assigns certain weights to the driving force applied in the different moments of the past. The instantaneous Langevin equation (7.31) can be recovered from (8.108) if the memory function has "very short memory"

$$\Gamma(t-t') = \gamma\delta(t-t'). \tag{8.109}$$

On the other hand, if the system is characterized by a finite "memory time" τ_{m}, its memory function can be written as follows

$$\Gamma(t-t') = \Gamma_0 \mathrm{e}^{-(t-t')/\tau_{\mathrm{m}}}. \tag{8.110}$$

Notice that the instantaneous case, (8.109), can be recovered from the memory case if

$$\tau_{\mathrm{m}} \to 0, \qquad \Gamma_0 \to \infty, \ \text{and} \ \tau_{\mathrm{m}}\, \Gamma_0 = \gamma. \tag{8.111}$$

(Verify! Hint: Integrate (8.109), (8.110) from t to ∞!)

Differentiating (8.108) with respect to the time (recall the rules of differentiation of integrals with respect to a parameter) we obtain

$$\frac{\mathrm{d}^2\eta}{\mathrm{d}t^2} = -\,\Gamma_0 \frac{\delta G}{\delta \eta}(t) + \frac{1}{\tau_{\mathrm{m}}} \int_0^{\mathrm{t}} \Gamma(t-t') \frac{\delta G}{\delta \eta}(t')\,\mathrm{d}t' + \frac{\mathrm{d}\xi}{\mathrm{d}t}(\mathbf{r}, t) \tag{8.112}$$

(see Appendix G regarding $\mathrm{d}\xi/\mathrm{d}t$). Excluding integrals from (8.108), (8.112) we obtain differential equation for the OP evolution in a system with memory described by the memory function (8.110)

$$\frac{\mathrm{d}^2\eta}{\mathrm{d}t^2} + \frac{1}{\tau_{\mathrm{m}}} \frac{\mathrm{d}\eta}{\mathrm{d}t} = -\,\Gamma_0 \frac{\delta G}{\delta \eta}(t) + \frac{1}{\tau_{\mathrm{m}}} \xi(\mathbf{r}, t) + \frac{\mathrm{d}\xi}{\mathrm{d}t}(\mathbf{r}, t). \tag{8.113}$$

Notice that in the limit (8.111) we recover from this equation the instantaneous case, (7.31).

As you can see from (8.113), the memory gives rise to two different effects in the system's evolution. First, the driving force ($-\delta G/\delta\eta$) "excites" not only the first derivative of the OP (speed) but also the second one (acceleration), which causes more long-term effect than in a system without memory. Second, the memory enhances the effect of fluctuations on the system by "engaging" the first derivative of the Langevin force $\xi(\mathbf{r}, t)$. Let us study these effects separately.

First, let us look at the effects of memory on small deviations from equilibrium states. For the present purposes, it will suffice to study homogeneous deviations only $\Delta\eta = \eta(t) - \bar{\eta}$ (see Sect. 4.4) because heterogeneities do not incur any new features on the system. Expanding the driving force about the stable equilibrium state $\bar{\eta}$, the evolution equation without the effect of the fluctuations will take the form

$$\ddot{\Delta\eta} + \frac{1}{\tau_{\mathrm{m}}} \dot{\Delta\eta} + \frac{1}{\tau_r^2} \Delta\eta = 0, \quad \tau_r = \left[\Gamma_0 \frac{\partial^2 g}{\partial \eta^2}(\bar{\eta})\right]^{-1/2}. \tag{8.114}$$

Using the thermo-mechanical analogy of Chap. 6, this equation describes motion of a damped linear oscillator [14]: adding the memory term is equivalent to adding mass to a dissipative system.

Equation (8.114) is a linear homogeneous ODE with constant coefficients, properties of which are very well known [15]. The nature of its solution depends on whether the characteristic equation

$$q^2 + \frac{1}{\tau_{\mathrm{m}}} q + \frac{1}{\tau_r^2} = 0 \tag{8.115}$$

has the roots

$$q_{\pm} = -\frac{1}{2\tau_{\mathrm{m}}} \pm \frac{\sqrt{\tau_r^2 - 4\tau_{\mathrm{m}}^2}}{2\tau_{\mathrm{m}}\tau_r} \tag{8.116}$$

that are real and different or coincident, or complex.

Short memory: $\tau_{\mathrm{m}} < \tau_r/2$. Both roots are real and negative: $q_- < q_+ < 0$, and the solutions of (8.114) are given by

$$\Delta\eta(t) = A\mathrm{e}^{q_+ t} + B\mathrm{e}^{q_- t}, \tag{8.117}$$

where A, B are constants. The most important difference of these solutions from those in the instantaneous case (see Sect. 4.2.1) is the dependence of the relaxation rate on the memory constant τ_{m}. Even in the case of very small memory time: $\tau_{\mathrm{m}} \ll \tau_r$, the largest relaxation time in the system, which determines its long-time properties, is $\tau_r^2/\tau_{\mathrm{m}}$. Mathematically, as one can see from (8.114), this happens because the memory constant multiplies the highest derivative of the evolution equation. Physically this means that the memory effects are always significant in the long run.

Long memory: $\tau_{\mathrm{m}} > \tau_{\mathrm{r}}/2$. The roots (8.116) are complex with negative real parts and the solutions are

$$\Delta\eta(t) = A\mathrm{e}^{-t/2\tau_{\mathrm{m}}} \cos\left(\frac{\sqrt{4\tau_{\mathrm{m}}^2 - \tau_r^2}}{2\tau_{\mathrm{m}}\tau_r} t + \alpha\right), \tag{8.118}$$

where A, α are constants. A typical solution of this type represents an oscillation about the equilibrium state $\Delta\eta = 0$ with the exponentially decreasing amplitude, decaying slower for large memory constant τ_{m}. Notice that the rate of approach to equilibrium is determined by the memory property instead of the relaxation one. In the case of very long memory: $\tau_{\mathrm{m}} \gg \tau_{\mathrm{r}}$, the system approaches equilibrium at a very slow pace, τ_{m}^{-1}, during which many oscillations about it will be made with high frequency of τ_{r}^{-1}.

Critical memory: $\tau_{\mathrm{m}} = \tau_{\mathrm{r}}/2$. In this case $q_- = q_+ = -1/2\tau_{\mathrm{m}}$. The solution

$$\Delta\eta(t) = (A + Bt)\mathrm{e}^{-t/2\tau_{\mathrm{m}}} \tag{8.119}$$

represents aperiodic approach to the equilibrium with the rate determined by the memory constant τ_{m}.

Now let us pose another question: What changes in the properties of the Langevin force $\xi(\mathbf{r}, t)$ will be caused by the memory effects in the system? To answer this question let us try to do what we have done in the case of the instantaneous response, that is, to calculate the long-time limit of the equilibrium-averaged square of the deviation of the OP from the equilibrium value. The linear generalized Langevin equation (8.113) takes the form

$$\ddot{\Delta\eta} + \frac{1}{\tau_\mathrm{m}}\dot{\Delta\eta} + \frac{1}{\tau_r^2}\Delta\eta = \frac{1}{\tau_\mathrm{m}}\xi(t) + \dot{\xi}(t). \tag{8.120}$$

The solution that satisfies the initial conditions

$$\Delta\eta(0) = \dot{\Delta\eta}(0) = 0 \tag{8.120a}$$

may be written in the Cauchy's form

$$\Delta\eta(t) = \int_0^t M(t,s)\left[\frac{1}{\tau_\mathrm{m}}\xi(s) + \dot{\xi}(s)\right]\mathrm{d}s, \tag{8.121}$$

where the kernel

$$M(t,s) = M(t-s) = \frac{\mathrm{e}^{q_+(t-s)} - \mathrm{e}^{q_-(t-s)}}{q_+ - q_-} \tag{8.121a}$$

is a one-parameter solution of the homogeneous equation (8.114), which satisfies the following initial conditions:

$$M(s,s) = 0, \quad \dot{M}(s,s) = 1. \tag{8.121b}$$

(Verify (8.121)!) The kernel M actually depends on the difference $(t-s)$ because the coefficients of its differential equation are const(t).

Integrating (8.121) by parts and taking (8.121b) into account we obtain

$$\Delta\eta(t) = -M(t)\xi(0) + \int_0^t L(t-s)\xi(s)\,\mathrm{d}s, \tag{8.122}$$

where

$$L(t) = \dot{M}(t) + \frac{1}{\tau_\mathrm{m}}M(t) = \frac{q_+\mathrm{e}^{q_-t} - q_-\mathrm{e}^{q_+t}}{q_+ - q_-}. \tag{8.122a}$$

To satisfy the BC (8.120a), we must choose $\xi(0) = 0$. Then the equilibrium-averaged square of the OP deviation (8.122) takes the form

$$\left\langle \Delta\eta^2(t)\right\rangle = \int_0^t\int_0^t L(t-s_1)L(t-s_2)\langle\xi(s_1)\xi(s_2)\rangle\,\mathrm{d}s_1\,\mathrm{d}s_2. \tag{8.123}$$

In the long-time limit, the autocorrelation function $K_\xi(s_2-s_1)=<\xi(s_1)\xi(s_2)>$ depends only on the difference (s_2-s_1), and the kernel of the double integral depends only on the sum $(s_2 + s_1)$. To verify the last statement you may consider the function

$$\mathrm{R}(t_1,t_2) \equiv (q_+ - q_-)^2 L(t_1)L(t_2) - \left[q_+ \mathrm{e}^{(q_-/2)(t_1+t_2)} - q_- \mathrm{e}^{(q_+/2)(t_1+t_2)}\right]^2$$
$$= q_+ q_- \left[2\mathrm{e}^{(q_- + q_+/2)(t_1+t_2)} - \mathrm{e}^{q_+ t_1 + q_- t_2} - \mathrm{e}^{q_- t_1 + q_+ t_2}\right]$$

and notice that

$$\frac{\mathrm{dR}}{\mathrm{d}t}(t,\ t) = R(t,\ t) = 0.$$

Then, changing the variables in (8.123) to $u = (s_2 - s_1)$, $U = t - 1/2(s_2 + s_1)$ and using the same method as in the integration of (7.36), we obtain

$$\left\langle \Delta\eta^2(\infty) \right\rangle = \int_0^\infty \left[\frac{q_+ \mathrm{e}^{q_- U} - q_- \mathrm{e}^{q_+ U}}{q_+ - q_-}\right]^2 \mathrm{d}U \int_{-\infty}^{+\infty} K_\xi(u)\, \mathrm{d}u, \tag{8.123a}$$

$$= \frac{1}{2}\tau_r \left(\frac{\tau_r}{\tau_\mathrm{m}} + \frac{\tau_\mathrm{m}}{\tau_r}\right) \int_{-\infty}^{+\infty} K_\xi(u)\, \mathrm{d}u \tag{8.123b}$$

(Verify (8.123b)!).

Regardless of the memory, in the long-time limit, the system approaches the equilibrium state where $\left\langle \Delta\eta^2 \right\rangle = k_\mathrm{B}T/[V\partial^2 g(\bar{\eta})/\partial\eta^2]$, see (7.15). Hence,

$$\int_{-\infty}^{+\infty} K_\xi(u)\, \mathrm{d}u = \frac{2k_\mathrm{B}T}{V\tau_r((\tau_r/\tau_\mathrm{m}) + (\tau_\mathrm{m}/\tau_r))\partial^2 g/\partial\eta^2(\bar{\eta})}. \tag{8.124}$$

This relationship sometimes is called the second fluctuation-dissipation theorem. It provides the foundation for a discussion of the properties of the Langevin force in the system with memory. Notice that in the asymptotic limit (8.111) we recover (7.39). However, if the characteristic memory time is very long, $\tau_\mathrm{m} \gg \tau_\mathrm{r}$, then the correlation function of fluctuations depends on the memory and is independent of the relaxation properties of the system.

If the Langevin force is irregular, the correlator K_ξ is proportional to the delta function. However, it is reasonable to assume that in a system with memory the fluctuation process is correlated over the time period equal to the time constant τ_m. Then, taking into account, the property of symmetry of the correlator [see (G.45)] and the second fluctuation-dissipation theorem, (8.124), we obtain

$$\langle \xi(t_1)\xi(t_2) \rangle = \frac{k_\mathrm{B}T}{V\left(1 + (\tau_\mathrm{m}^2/\tau_\mathrm{r}^2)\right)}\ \Gamma_0 \mathrm{e}^{-|t_2 - t_1|/\tau_\mathrm{m}}. \tag{8.125}$$

8.5 "Mechanical" Order Parameter

Consider a system, which is described by two scalar OP fields, $\psi(\mathbf{r}, t)$ and $\eta(\mathbf{r}, t)$, of different nature. The OP ψ represents generalized coordinate characterized by the mass density ρ, while the OP $\eta(\mathbf{r}, t)$ is "massless," that is, its mass density is zero. Then, in addition to the potential energy and gradient energy, the system is characterized by the kinetic energy. In the spirit of our previous discussion, we will assume that the field $\eta(\mathbf{r}, t)$ is responsible for dissipation of the mechanical energy of the system. The field $\psi(\mathbf{r}, t)$ may be called mechanical (Lagrangian) and the field $\eta(\mathbf{r}, t)$—thermodynamic. In the field theory (see Appendix D), such system is described by the Lorentz-invariant Lagrangian density

$$l\{\psi, \eta\} = \frac{1}{2}\rho\left(\frac{\partial\psi}{\partial t}\right)^2 - \frac{1}{2}\kappa_\psi(\nabla\psi)^2 - \frac{1}{2}\kappa_\eta(\nabla\eta)^2 - u(\psi, \eta), \tag{8.126}$$

where κ_ψ, κ_η are the gradient-energy coefficients of the fields $\psi(\mathbf{r}, t)$, $\eta(\mathbf{r}, t)$, and u is the potential energy density of the system, assumed to be nongravitational. For the Lagrangian density (8.126), the mechanical energy of the system is [see (D.18)]

$$E \equiv \int_\Omega \mathrm{d}^3x\left[\frac{\partial l}{\partial(\partial\psi/\partial t)}\frac{\partial\psi}{\partial t} - l\right] = \int_\Omega \mathrm{d}^3x\left[\frac{1}{2}\rho\left(\frac{\partial\psi}{\partial t}\right)^2 + \frac{1}{2}\kappa_\psi(\nabla\psi)^2 + \frac{1}{2}\kappa_\eta(\nabla\eta)^2 + u(\psi, \eta)\right]. \tag{8.127}$$

Many physical systems can be described by the fields $\psi(\mathbf{r}, t)$ and $\eta(\mathbf{r}, t)$. The following two examples are of interest for us. Martensitic transformation is a distortion of a crystalline lattice that does not need long-ranged diffusion of atoms. It is often characterized as a polymorphic (e.g., fcc-to-hcp) diffusionless transformation controlled by shear stress and strain. The field ψ may describe distribution of shear strain in the material of mass density ρ with the gradient energy coefficient κ_ψ related to the nonlocal elastic behavior of the lattice. However, the purely mechanical description does not account for the dissipative interatomic interactions, which lead to the losses of the mechanical energy. These interactions may be described by the field $\eta(\mathbf{r}, t)$. Another example comes from the area of cracks propagation in brittle materials. In this case, the Lagrangian field ψ may characterize displacement of the material perpendicular to the plane of the crack; then, displacement gradients correspond to components of strain. The dissipative field η represents defective material and distinguishes between broken (η=0) and unbroken (η=1) states.

For the equation of motion of the field $\psi(\mathbf{r}, t)$ we may try to use the Lagrange equations (D.14); their right-hand sides may be expressed as the partial functional derivatives of E, that is, with respect to the spatial variations of the respective fields. So, for the field $\psi(\mathbf{r}, t)$ we have

$$\rho \frac{\partial^2 \psi}{\partial t^2} = -\frac{\delta E}{\delta \psi}. \tag{8.128}$$

For the massless field $\eta(\mathbf{r}, t)$, the Lagrange equation of motion (D.14) turns into an equation of equilibrium, which means that the dynamical evolution of this field is not governed by the Hamilton's principle. Hence, the Lagrange equation for this field must be replaced with the dissipative one. For the massless field $\eta(\mathbf{r}, t)$ deviation of the partial functional derivative of E from zero is a measure of the deviation of the system from equilibrium, that is, the thermodynamic force. Hence, we may assume that the rate of change of the field $\eta(\mathbf{r}, t)$ is proportional to this force

$$\frac{\partial \eta}{\partial t} = -\varepsilon \frac{\delta E}{\delta \eta}. \tag{8.129}$$

This equation is analogous to TDGLE (5.2) with the mechanical energy E replacing the free energy G.

Let us calculate the rate of dissipation of the mechanical energy E. Differentiating (8.127) with respect to time as a parameter, integrating by parts and dropping the boundary term we obtain the time derivative of the mechanical energy E

$$\frac{\mathrm{d}E}{\mathrm{d}t} = \int_\Omega \mathrm{d}^3x \left[\rho \frac{\partial^2 \psi}{\partial t^2} \frac{\partial \psi}{\partial t} + \frac{\delta E}{\delta \psi} \frac{\partial \psi}{\partial t} + \frac{\delta E}{\delta \eta} \frac{\partial \eta}{\partial t} \right]. \tag{8.130}$$

Due to the equations of motion (8.128), (8.129) this is

$$\frac{\mathrm{d}E}{\mathrm{d}t} = -\varepsilon \int_\Omega \mathrm{d}^3x \left(\frac{\delta E}{\delta \eta} \right)^2. \tag{8.131}$$

Equation (8.131) shows that, indeed, changes of the field energy E occur due to evolution of the field $\eta(\mathbf{r}, t)$ only with no effect of the field $\psi(\mathbf{r}, t)$. As the energy of a mechanical system cannot be produced but may be dissipated, we conclude that $\varepsilon \geq 0$.

According to the Lagrangian field theory (Appendix D), the states of mechanical equilibrium are described by the following simultaneous equations

$$\frac{\delta E}{\delta \psi} \equiv \frac{\partial u}{\partial \psi} - \kappa_\psi \nabla^2 \psi = 0, \tag{8.132a}$$

$$\frac{\delta E}{\delta \eta} \equiv \frac{\partial u}{\partial \eta} - \kappa_\eta \nabla^2 \eta = 0. \tag{8.132b}$$

Notice that in the nongravitational system the mass density ρ has no bearing on the equilibrium states. For a homogeneous equilibrium state, (8.132) yield that

$$\frac{\partial u}{\partial \psi}(\psi,\eta)=\frac{\partial u}{\partial \eta}(\psi,\eta)=0. \tag{8.133}$$

For a heterogeneous equilibrium state let us consider an interface, that is, a 1D transition region between large regions of two different homogeneous equilibrium states (ψ_α, η_α) and (ψ_β, η_β). Such state has the first integral (D.19)

$$\frac{1}{2}\kappa_\psi\left(\frac{\mathrm{d}\psi}{\mathrm{d}x}\right)^2+\frac{1}{2}\kappa_\eta\left(\frac{\mathrm{d}\eta}{\mathrm{d}x}\right)^2-u(\psi,\eta)=\mathrm{const}(x)\equiv -v. \tag{8.134}$$

The first integral (8.134) yields that in the terminal phases

$$u(\psi_i,\eta_i)=v, \quad i=\alpha,\beta \tag{8.135}$$

because

$$\frac{\mathrm{d}\psi}{\mathrm{d}x}=\frac{\mathrm{d}\eta}{\mathrm{d}x}=0, \quad \text{at } x\rightarrow\pm\infty \tag{8.135a}$$

and

$$\frac{\mathrm{d}u}{\mathrm{d}x}(\psi_i,\eta_i)=0, \quad \text{at } x\rightarrow\pm\infty \tag{8.136}$$

because

$$\frac{\mathrm{d}u}{\mathrm{d}x}=\frac{\partial u}{\partial \eta}\frac{\mathrm{d}\eta}{\mathrm{d}x}+\frac{\partial u}{\partial \psi}\frac{\mathrm{d}\psi}{\mathrm{d}x}. \tag{8.137}$$

The interface can be characterized by the surface tension

$$\sigma=\int_{-\infty}^{+\infty}\left[\kappa_\eta\left(\frac{\mathrm{d}\eta}{\mathrm{d}x}\right)^2+\kappa_\psi\left(\frac{\mathrm{d}\psi}{\mathrm{d}x}\right)^2\right]\mathrm{d}x=\sigma_\eta+\sigma_\psi, \tag{8.138}$$

where σ_η and σ_ψ are the partial tensions

$$\sigma_\eta\equiv\int_{-\infty}^{+\infty}\left[\kappa_\eta\left(\frac{\mathrm{d}\eta}{\mathrm{d}x}\right)^2\right]\mathrm{d}x; \quad \sigma_\psi\equiv\int_{-\infty}^{+\infty}\left[\kappa_\psi\left(\frac{\mathrm{d}\psi}{\mathrm{d}x}\right)^2\right]\mathrm{d}x. \tag{8.138a}$$

To analyze the dynamical properties of the system described by (8.128), (8.129) we look first at the evolution of the small deviations of the fields from the homogeneous equilibrium $\{\psi_i, \eta_i\}$ described by (8.135)

$$\varphi = \psi(\mathbf{r}, t) - \psi_i, \quad \theta = \eta(\mathbf{r}, t) - \eta_i. \tag{8.139}$$

Expanding the potential energy function about the equilibrium state $\{\psi_i, \eta_i\}$ we obtain

$$u(\psi, \eta) = v + \frac{1}{2} u_{\psi\psi} \varphi^2 + u_{\psi\eta} \varphi\theta + \frac{1}{2} u_{\eta\eta} \theta^2 + \text{h.o.t}, \tag{8.140}$$

where

$$u_{pq} = \frac{\partial^2 u}{\partial p \partial q}(\psi_i, \eta_i); \quad p, q = \psi, \eta. \tag{8.140a}$$

Then dropping the higher-order terms (h.o.t.), (8.128), (8.129) transform to

$$\rho \frac{\partial^2 \varphi}{\partial t^2} = \kappa_\psi \nabla^2 \varphi - (u_{\psi\psi} \varphi + u_{\psi\eta} \theta), \tag{8.141a}$$

$$\frac{1}{\varepsilon} \frac{\partial \theta}{\partial t} = \kappa_\eta \nabla^2 \theta - (u_{\eta\psi} \varphi + u_{\eta\eta} \theta). \tag{8.141b}$$

Here $u_{\psi\eta}$ plays the role of the interaction coefficient in the sense that if $u_{\psi\eta} = 0$ the two fields have no linear interactions and evolve independently (to be exact—almost independently because still there may be nonlinear interactions between these fields). In this case, the independent fields ψ and η have significantly different dynamical properties: evolution of the field ψ is described by the wave equation with the phase velocity

$$c_{\text{ph}} \geq c_\psi \equiv \sqrt{\frac{\kappa_\psi}{\rho}} \tag{8.142}$$

and linear dispersion proportional to $u_{\psi\psi}$, while evolution of the field η is described by the heat equation with Newton’s cooling (or heating) proportional to $u_{\eta\eta}$, which determines growth or decrease of the field.

If the interaction coefficient is not zero, $u_{\psi\eta} \neq 0$, properties of the fields described by (8.141) change significantly. To reveal an important property that appears as a result of the interaction, we could represent the waves $\varphi(\mathbf{r}, t)$ and $\theta(\mathbf{r}, t)$ as Fourier modes and study their spectrum, as we have done that in Sect. 5.2. However, we find it here more instructive to demonstrate different method.

It will suffice to consider evolution of the homogeneous modes $\varphi(t)$ and $\theta(t)$ only. Then (8.141b) can be resolved as follows

$$\theta = \int_{-\infty}^{t} \mathrm{e}^{\varepsilon u_{\eta\eta}(t'-t)} \left[-\varepsilon u_{\eta\psi} \varphi(t')\right] \mathrm{d}t' = -\frac{u_{\eta\psi}}{u_{\eta\eta}} \sum_{n=0}^{\infty} \frac{\mathrm{d}^{(n)}\varphi/\mathrm{d}t^{(n)}}{\left(-\varepsilon u_{\eta\eta}\right)^{n}}. \tag{8.143}$$

The second equality in this expression is obtained by applying the Taylor's formula to $\varphi(t')$. Restricting the series in (8.143) by the first three terms and substituting them into (8.141a) we obtain

$$\left(\rho - \frac{u_{\psi\eta}^2}{\varepsilon^2 u_{\eta\eta}^3}\right) \frac{\mathrm{d}^2\varphi}{\mathrm{d}t^2} + \frac{u_{\psi\eta}^2}{\varepsilon u_{\eta\eta}^2} \frac{\mathrm{d}\varphi}{\mathrm{d}t} + \left(u_{\psi\psi} - \frac{u_{\psi\eta}^2}{u_{\eta\eta}}\right) \varphi = 0. \tag{8.144}$$

This equation is analogous to an equation of 1d motion of a particle with the generalized coordinate φ in a potential field $\sim\varphi^2$ and medium with a dissipative force which depends on the speed of the particle. The generalized mass of the particle and the potential function are affected by the interaction coefficient $u_{\psi\eta}$ and the dissipation coefficient

$$\alpha = \frac{u_{\psi\eta}^2}{\varepsilon u_{\eta\eta}^2} \tag{8.145}$$

is proportional to the interaction coefficient squared. Similarly, taking into account the gradient energies of the field ψ and η, we can derive from (8.141) the telegraphic equation [16], which describes propagation of the damped waves in a medium with damping proportional to the interaction coefficient squared.

The series in (8.143) can be approximated by the first three terms only if the characteristic time of oscillations of the field ψ is much greater than that of the field η. If the ψ–η interactions are not strong

$$\frac{u_{\psi\eta}^2}{u_{\psi\psi} u_{\eta\eta}} \ll 1 \tag{8.146}$$

then the former is $\sqrt{\rho/u_{\psi\psi}}$ and the latter is $\left(\varepsilon u_{\eta\eta}\right)^{-1}$, see (8.141). Hence, the condition of applicability of (8.144) is

$$\varepsilon u_{\eta\eta} \sqrt{\frac{\rho}{u_{\psi\psi}}} \gg 1. \tag{8.147}$$

This mean that the dissipation coefficient (8.145) is small

$$\alpha \ll \sqrt{\rho u_{\psi\psi}}. \tag{8.148}$$

Equations (8.144)–(8.148) shed light on the physical nature of dissipative forces in mechanical systems: they come from the interactions with other degrees of freedom, dynamics of which is dissipative.

The dynamic equations (8.128), (8.129), (8.132) support the 1d train waves traveling with speed v. The waves are described by the nonlinear equations

$$\kappa_\psi\left(1-\frac{\mathrm{v}^2}{c_\psi^2}\right)\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2}=\frac{\partial u}{\partial\psi}, \tag{8.149a}$$

$$\kappa_\eta\frac{\mathrm{d}^2\eta}{\mathrm{d}x^2}+\frac{\mathrm{v}}{\varepsilon}\frac{\mathrm{d}\eta}{\mathrm{d}x}=\frac{\partial u}{\partial\eta}. \tag{8.149b}$$

Compared to the system of two Lagrangian fields (see Appendix D) (8.149) do not have the first integral. Exact solutions of (8.149) with interacting fields ψ and η are possible but not known to the author. However, there is a lot that we can learn about the system (8.149) without solving it exactly. Let us multiply (8.149a) by $\mathrm{d}\eta/\mathrm{d}x$ and (8.149b) by $\mathrm{d}\psi/\mathrm{d}x$, add them together, and integrate the sum from $-\infty$ to $+\infty$. Then, using (8.137) we obtain the relation for the wave speed

$$\mathrm{v}=\frac{\varepsilon\kappa_\eta}{\sigma_\eta}\left[u(\eta_\alpha,\psi_\alpha)-u\left(\eta_\beta,\psi_\beta\right)\right]. \tag{8.150}$$

Notice that, contrary to the Lagrangian system of Appendix D, the selection problem—finding the unique value of the velocity of the train wave—is resolved for the system (8.149). This is a consequence of the dissipative nature of the field η. The velocity v is proportional to the potential energy difference between the equilibrium states α and β with the coefficient of proportionality that may depend on the speed v through the partial tension σ_η. However, to estimate the kinetic coefficient in (8.150), we can use an equilibrium estimate of the surface tension or abbreviated action as $\sigma_\eta l\approx\kappa_\eta\left[\eta_\alpha-\eta_\beta\right]^2$, where l is the thickness of the transition region [see (D.26), (D.28) and Example 3.1]. Then

$$\mathrm{v}\approx\varepsilon l\frac{u(\eta_\alpha,\psi_\alpha)-u\left(\eta_\beta,\psi_\beta\right)}{\left[\eta_\alpha-\eta_\beta\right]^2}. \tag{8.151}$$

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Chapter 9
Thermal Effects of Phase Transformations

A very simple set of arguments will convince you that, for the theory of phase transformations to be realistic, we have to consider the OP evolution together with other processes that take place simultaneously with the phase transformations. For instance, as we noted in Chap. 2, a phase transition of the first kind is accompanied by the release of the latent heat, which amounts to the difference of the internal energies (or enthalpies) of the phases on both sides of the transition. The heat does not remain localized at the sites where it was released, usually positions of the interfaces. Due to the mechanism of heat conduction, it will diffuse to the places with lower temperatures causing the temperature field to vary. The redistribution of heat and equilibration of temperature causes the feedback effect on the phase transition in the form of changing rate and in some cases even the direction of the transformation. Another example comes from transformations in systems of varying density, e.g., mixtures or substances in gravitational fields. Such transformations cause flow of matter, which also has a feedback effect on the transformation. Many of these processes have characteristic length and time scales longer than those of the OP variations; that's why sometimes they are called "hydrodynamics" modes. The questions that we have to answer are: How do we couple the OP evolution to these processes? What physical principles are important here? How do we maintain the thermodynamic (physical) consistency between the descriptions of all processes in the system? The main question, which is discussed in this chapter, is: How can we incorporate the mechanisms of heat release and redistribution into our method in a physically rigorous and consistent way? Another question that we will look at is: What are the new effects or features that we may expect from the transformations that are accompanied by the latent heat release? In this chapter, we review practically all aspects of the book with the energy conservation constraint included. One interesting and counterintuitive conclusion of our analysis is that the thermal effects appear even in transformations that proceed without any latent heat release.

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9.1 Equilibrium States of a Closed (Adiabatic) System

Let us consider first equilibrium states in a *closed* (*adiabatic*) *system* that is, a system that does not have heat exchange with the environment. As we know from thermodynamics, for such a system the variational principle must be changed: instead of minimizing the total free energy for the constant temperature (see Chap. 2) we must maximize the total entropy of the system keeping the total energy (enthalpy) of the system constant. Then,

$$S\{\eta\} \equiv \int_V \hat{s}(\eta, \nabla\eta)\mathrm{d}^3x \to \max, \tag{9.1}$$

for

$$E\{\eta\} \equiv \int_V \hat{e}(\eta, \nabla\eta)\mathrm{d}^3x = \text{const.} \tag{9.2}$$

Here $\hat{s}$ and $\hat{e}$ are the entropy and energy (enthalpy) densities of the system. Thus, from the viewpoint of the calculus of variations (see Appendix B), the equilibrium states in the closed system obey conditions of the *isoperimetric problem*. There exist two types of the solution of this problem (see Appendix B): type-E1: the equilibrium state *is not* an extremal of the energy functional (9.2) and type-E2: the equilibrium state *is* an extremal of the energy functional (9.2). Although in each case one has to consider both homogeneous and inhomogeneous equilibrium states, we will find that type-E2 applies to the inhomogeneous states only. Let us consider these cases separately.

9.1.1 Type-E1 States

If the sought state $\{\eta_{\mathrm{E1}}\}$ *is not* an extremal of the energy functional (9.2), then there exists a constant λ such that the state is an unconditional extremal of the functional $\int(\hat{s} + \lambda\hat{e})\,\mathrm{d}^3x$ that is, the following relation is satisfied:

$$\delta S + \lambda\,\delta E = 0. \tag{9.3}$$

Since (9.3) is true for an arbitrary variation of $\delta\eta$, $\lambda = -1/T$ where T is the absolute temperature and the state $\{\eta_{\mathrm{E1}}\}$ is an extremal of the free energy functional $G\{\eta,\ T\} = E - TS$ that is, satisfies the same necessary conditions as in the isothermal system (see Chap. 3). This hints that the Legendre transformation (see Appendix F):

$$\{E, S\} \to \left\{T = \frac{\mathrm{d}E}{\mathrm{d}S}, G = E - \frac{\mathrm{d}E}{\mathrm{d}S}S\right\} \tag{9.4}$$

may be useful here because it allows us to express the equilibrium conditions using a more convenient function of $G(T)$ instead of $S(E)$. The entropy and energy (enthalpy) densities of the system also must be Legendre transformed:

$$\hat{s} = -\left(\frac{\partial \hat{g}}{\partial T}\right)_{\eta};\, \hat{e} = \hat{g} - T\left(\frac{\partial \hat{g}}{\partial T}\right)_{\eta}. \tag{9.5}$$

Rigorously speaking in (9.4) and (9.5) we have to consider also the Legendre transformation from the volume V to pressure P, but the compression effects are not of interest here. For that matter, you may think of G as the Helmholtz function instead of the Gibbs one. It is important to note that the OP is a part of the description in both sets $\{\eta, E, S\}$ and $\{\eta, T, G\}$, but remains unaffected by the Legendre transformation.

The above obtained result that the set of the equilibrium states of the open and closed systems are the same is not surprising because it is a consequence of a more general fact that in the thermodynamic limit of $V \to \infty$ the canonical and microcanonical ensembles have the same equilibrium states [1]. However, the thermodynamic stability of the equilibrium states in the microcanonical ensembles may be different from that in the canonical one. Let us consider stability of homogeneous $\{\bar{\eta}_{\mathrm{E1}}\}$ and inhomogeneous $\{\eta_{\mathrm{E1}}(\mathbf{x})\}$ states separately.

For a homogeneous system

$$\mathrm{d}s = \frac{1}{T}\mathrm{d}e + \left(\frac{\partial s}{\partial \eta}\right)_{e}\mathrm{d}\eta \tag{9.6}$$

and the equilibrium state in a closed system is characterized by the condition

$$\left(\frac{\partial s}{\partial \eta}\right)_{e} = 0. \tag{9.7}$$

Differentiating the Legendre transformation (9.4) with respect to the OP we obtain:

$$\left(\frac{\partial g}{\partial \eta}\right)_{T} = \left(\frac{\partial e}{\partial \eta}\right)_{T} - T\left(\frac{\partial s}{\partial \eta}\right)_{T}. \tag{9.8}$$

Then, applying a mathematical formula for a partial directional derivative of a function $f(x, y)$ in the direction $h(x, y) = \text{const}$:

$$\left(\frac{\partial f}{\partial x}\right)_{h} \equiv \left.\frac{\partial f}{\partial x}\right|_{h=\text{const}} = \frac{\partial f}{\partial x} + \left.\frac{\partial f}{\partial y}\frac{\mathrm{d}y}{\mathrm{d}x}\right|_{h=\text{const}} \tag{9.9}$$

to the energy and entropy functions in (9.8) we obtain the condition of equilibrium:

$$\left(\frac{\partial g}{\partial \eta}\right)_T = -T\left(\frac{\partial s}{\partial \eta}\right)_e = 0, \tag{9.10}$$

which shows that, indeed, the closed and open systems of the same substance have the same homogeneous equilibrium states.

The condition of local thermodynamic stability in the closed system, that is, the condition that the equilibrium state corresponds to a maximum of the entropy for constant energy is

$$\left(\frac{\partial^2 s}{\partial \eta^2}\right)_e < 0. \tag{9.11}$$

Applying formula (9.9) to (9.10) we obtain

$$T\left(\frac{\partial^2 s}{\partial \eta^2}\right)_e = -\left(\frac{\partial^2 g}{\partial \eta^2}\right)_T + \left[\frac{1}{T}\left(\frac{\partial g}{\partial \eta}\right)_T - \frac{\partial^2 g}{\partial \eta \partial T}\right]\frac{\mathrm{d}T}{\mathrm{d}\eta}\bigg|_e. \tag{9.12}$$

Taking into account that the slope of the constant-energy line is

$$\frac{\mathrm{d}T}{\mathrm{d}\eta}\bigg|_e = -\frac{(\partial e/\partial \eta)_T}{(\partial e/\partial T)_\eta} = \frac{(\partial g/\partial \eta)_T - T\dfrac{\partial^2 g}{\partial \eta \partial T}}{T(\partial^2 g/\partial T^2)_\eta} \tag{9.13}$$

and that we are analyzing an equilibrium state with (9.7) and (9.10) we obtain that

$$T\left(\frac{\partial^2 s}{\partial \eta^2}\right)_e = -\left(\frac{\partial^2 g}{\partial \eta^2}\right)_T + \frac{(\partial^2 g/\partial \eta \partial T)^2}{(\partial^2 g/\partial T^2)_\eta}. \tag{9.14}$$

Hence, the condition of the local thermodynamic stability of a homogeneous equilibrium state $\{\bar{\eta}_{E1}\}$ in the closed system is

$$\left(\frac{\partial^2 g}{\partial \eta^2}\right)_T - \frac{(\partial^2 g/\partial \eta \partial T)^2}{(\partial^2 g/\partial T^2)_\eta} > 0. \tag{9.15}$$

Since the specific heat of a stable state is positive

$$C_\eta \equiv \left(\frac{\partial e}{\partial T}\right)_\eta = -T\left(\frac{\partial^2 g}{\partial T^2}\right)_\eta > 0, \tag{2.41a}$$

the condition of the local thermodynamic stability in a closed system (9.15) is less restrictive than that in the open one:

$$\left(\frac{\partial^2 g}{\partial \eta^2}\right)_T > 0. \tag{2.15}$$

In other words, a homogeneous equilibrium state may be *adiabatically stable*, that is, unstable in an open system but stable in a closed system, that is, (2.15) is not fulfilled but (9.15) is fulfilled. A necessary condition for that is $\partial^2 g/\partial T \partial \eta \neq 0$; a sufficient condition is

$$M_{\bar{\eta}}(T) \equiv \left. \frac{\left(\partial^2 g/\partial \eta \partial T\right)^2}{\left(\partial^2 g/\partial T^2\right)_\eta \left(\partial^2 g/\partial \eta^2\right)_T} \right|_{\eta=\bar{\eta}(T)} > 1, \tag{9.16}$$

where $M_{\bar{\eta}}$ is a parameter, called the *interaction module*. It determines the strength of interactions between the thermal and ordering modes of the transition. The partials that make up $M_{\bar{\eta}}$ in (9.16) should be taken at the equilibrium state in question.

An interesting interpretation of the condition of the adiabatical stability may be revealed if we find the temperature/OP slope of the line of equilibrium for this state:

$$\mathrm{d}\left(\frac{\partial g}{\partial \eta}\right)_T = \left(\frac{\partial^2 g}{\partial \eta^2}\right)_T \mathrm{d}\eta + \frac{\partial^2 g}{\partial \eta \partial T} \mathrm{d}T = 0$$

and compare it with that of the constant-energy line (9.13). Then, criterion (9.16) means

$$M_{\bar{\eta}}(T) = \frac{(\mathrm{d}T/\mathrm{d}\eta)|_e}{(\mathrm{d}T/\mathrm{d}\eta)|_{\bar{\eta}}} > 1 \tag{9.17}$$

that the slope of the constant-energy line is greater than that of the equilibrium-state line. Another application of the criterion (9.16) may be found in calculating the specific heat of the adiabatically stable state:

$$C_{\bar{\eta}(T)} \equiv \frac{\mathrm{d}e(\bar{\eta})}{\mathrm{d}T} = \left(\frac{\partial e}{\partial T}\right)_\eta + \left(\frac{\partial e}{\partial \eta}\right)_T \frac{\mathrm{d}\bar{\eta}}{\mathrm{d}T} = C_\eta (1 - M). \tag{9.18}$$

Applying (9.16) to (9.18) and (2.41a) we find that when an isothermally unstable state gains adiabatic stability its specific heat becomes negative, which means that such state is unstable in the bulk.

Two comments are in order here.

1. Equation (9.16) is only a condition of homogeneous (local) stability of the state while it may be unstable globally, that is, with respect to an inhomogeneous state, e.g., heterogeneous mixture of coexisting phases at the same temperature. This possibility is alluded to by (9.18) and the analysis that follows from it.

The global-stability analysis is more complicated. Its general conclusion is that the homogeneous state may be stable against the inhomogeneous states in a certain range of energies but only if the size of the system is below the bifurcation length $\tilde{X}$, see (3.58b) [2]. In the systems of the size less than the bifurcational creation of a phase-separating interface is not favorable and the homogeneous state turns into the global optimizer.

2. In Chap. 2 we represented the free energy of the system as a sum of the regular g_0 and singular (transition) (g–g_0) parts; in an open system, they do not "interact" with each other in the sense that g_0 does not affect the transition equations (see Sect. 2.3). This is not the case in the closed system where, as we can see from (9.15) and (9.16), the regular and singular parts are convoluted in the same equations that determine stability of the outcome of the transition. Physically, this is a result of the absence of the thermal bath in the closed system. In the open system the regular and singular parts of the free energy, so to speak, thermally interact with the bath to achieve equilibrium. In the closed system the interaction with the bath is prohibited and the regular and singular parts are "forced" to interact with each other. Because of that, we have to look at the thermal properties of the terminal phases in greater detail. Theoretically there is an advantage in dealing with a thermodynamic system with equal and temperature-independent specific heats in both high-symmetry (α) and low-symmetry (β) phases $C_\alpha = C_\beta = C = \text{const}(T)$. Technically, it is convenient to reckon the energy and entropy from the α phase at the temperature T_E of its coexistence with the β phase. Then the entropy, energy, and free energy densities of the α and β phases are

$$e_\alpha(T) = C(T - T_E),\ \ s_\alpha(T) = C\ln\frac{T}{T_E}, \tag{9.19a}$$

$$e_\beta(T) = C(T - T_E) - L,\ \ s_\beta(T) = C\ln\frac{T}{T_E} - \frac{L}{T_E}, \tag{9.19b}$$

$$g_\alpha(T) = C(T - T_E) - CT\ln\frac{T}{T_E},\ \ [g] = L\frac{T - T_E}{T_E}. \tag{9.19c}$$

The approximation of the temperature-independent specific heat simplifies our calculations in the vicinity of T_E but, apparently, cannot be extended to very low temperatures (Why?).

Example 9.1 Find conditions of the thermodynamic stability for the transition state of the tangential potential in the system with C = const(T).

The free energy density of the system is [see (9.19c), (2.33)]:

$$g = C(T - T_E) - TC\ln\frac{T}{T_E} + \frac{1}{2}W\omega^2(\eta) + L\frac{T - T_E}{T_E}\nu(\eta). \tag{9E.1}$$

Its partials are:

$$\frac{\partial^2 g}{\partial T^2}=-\frac{C}{T};\frac{\partial^2 g}{\partial T\partial\eta}=6\frac{L}{T_{\mathrm{E}}}\omega;\frac{\partial^2 g}{\partial\eta^2}=W\left(\omega'^2-2\omega\right)+6L\frac{T-T_{\mathrm{E}}}{T_{\mathrm{E}}}\omega'. \tag{9E.2}$$

Notice that the interaction modules of α and β phases are zero, which excludes any thermal effects around these states. Application of the transition-state equilibrium condition (2.35b) to (9E.2) yields (do not confuse P with pressure):

$$\frac{\partial^2 g}{\partial\eta^2}(\eta_{\mathrm{t}})=-2W\omega(\eta_{\mathrm{t}});\eta_{\mathrm{t}}=\frac{1}{2}\left(1+P\frac{T_{\mathrm{E}}-T}{T_{\mathrm{E}}}\right);P=\frac{6L}{W}. \tag{9E.3}$$

To calculate the interaction module of the state we substitute (9E.2) and (9E.3) into (9.16), which yields:

$$M_{\mathrm{t}}=3Q(1+P-2\eta_{\mathrm{t}})\omega(\eta_{\mathrm{t}});Q=\frac{L}{CT_{\mathrm{E}}}. \tag{9E.4}$$

According to (9.16) for the adiabatic stability of the state its interaction module must be greater than one. As you can see from (9E.3) and (9E.4), M_{t} varies depending on the temperature and material parameters (P, Q). Let us find the maximum value of M_{t} among all possible values of the temperature in the system. The maximum is attained at

$$\eta_{\mathrm{t}}^{\mathrm{m}}=\frac{1}{2}+\frac{P-\sqrt{3+P^2}}{6} \tag{9E.5a}$$

or

$$T^{\mathrm{m}}=\left(\frac{2}{3}+\frac{\sqrt{3+P^2}}{3P}\right)T_{\mathrm{E}}\to T_{\mathrm{E}}\text{for } P\to\infty. \tag{9E.5b}$$

Then (9E.4) and (9E.5a) yield an expression for the largest interaction module of the transition state for given parameters (P, Q):

$$M_{\mathrm{t}}^{\mathrm{m}}=\frac{1}{18}Q\left[\left(3+P^2\right)^{\frac{3}{2}}+P\left(9-P^2\right)\right] \to\begin{cases}\dfrac{1}{2\sqrt{3}}Q\left(1+\sqrt{3}P\right), & P\to 0\\ \dfrac{3}{4}QP, & P\to\infty\end{cases}. \tag{9E.6}$$

Thus, the transition state of the tangential potential may be adiabatically stable [see (9.16)] if the material properties of the system obey the following condition:

$$Q>\begin{cases}2\sqrt{3} & \text{for } P\to 0\\ \dfrac{4}{3P} & \text{for } P\to\infty\end{cases}. \tag{9E.7}$$

(Verify criterion (9.17), (9E.7) in Fig. 9.1!)

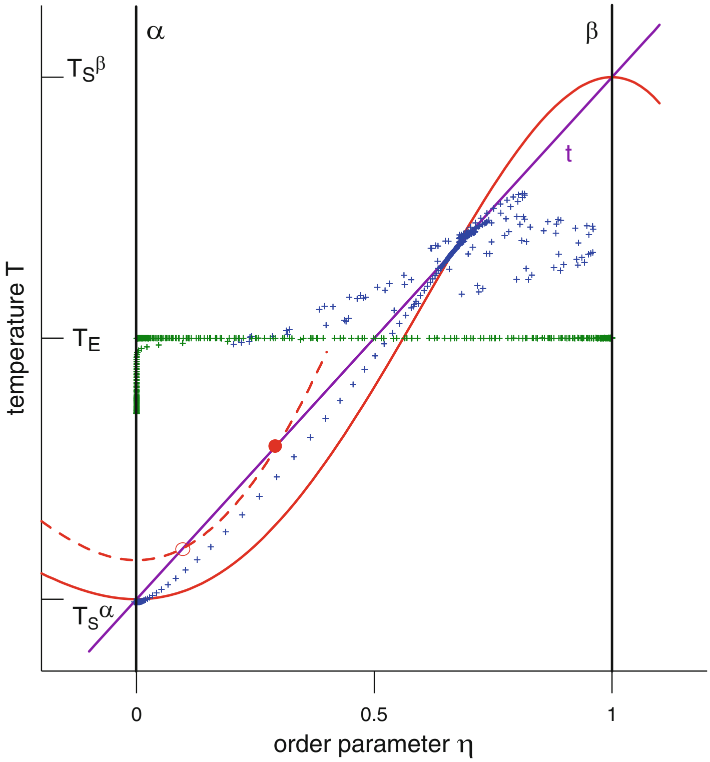


Fig. 9.1 OP–temperature plane of the equilibrium state diagram of a system described by the tangential potential with $Q = 1$ and $P = 2$. α, β, t—equilibrium states; *red lines*—constant energy trajectories (*dashed line*—for $Q = 1.1$); *circles*—equilibrium transition states of the closed (adiabatic) system (*full*—stable, *open*—unstable); *crosses*—1d nonequilibrium inhomogeneous states from the numerical simulations of (9.86) (*blue*—$t = 1{,}100$, *green*—$t = 4{,}200$)

The type-E1 inhomogeneous state $\{\eta_{E1}(\mathbf{x})\}$ of a closed system obeys the same ELE:

$$\frac{\delta G}{\delta \eta} \equiv \frac{\partial \hat{g}}{\partial \eta} - \nabla \frac{\partial \hat{g}}{\partial (\nabla \eta)} = 0. \tag{3.20}$$

To analyze the thermodynamic stability of this state we need to find the sign of the second variation of the entropy functional:

$$\delta^2 S = \frac{1}{2} \int_V \left[\frac{\partial^2 \hat{s}}{\partial \eta^2} (\ \delta\eta)^2 + 2 \frac{\partial^2 \hat{s}}{\partial T \partial \eta}\ \delta\eta \mathrm{d}T + \frac{\partial^2 \hat{s}}{\partial T^2} (\mathrm{d}T)^2 + \frac{\partial^2 \hat{s}}{\partial (\nabla \eta)^2} (\nabla\ \delta\eta)^2 \right] \mathrm{d}^3 x \tag{9.20}$$

for the variations of the OP and temperature that leave the energy functional (9.2) unchanged:

$$\Delta E \equiv E\{\eta + \delta\eta, T + \mathrm{d}T\} - E\{\eta, T\} = \delta E + \delta^2 E + \cdots = 0. \tag{9.21}$$

To find the sign of $\delta^2 S$ we may choose the variations of the OP and temperature such that the first variation of the energy functional vanishes:

$$\delta E = \int_V \left(\frac{\delta E}{\partial \eta} \delta\eta + \frac{\partial \hat{e}}{\partial T} \mathrm{d}T \right) \mathrm{d}^3 x = 0. \tag{9.22a}$$

For such variations, using (9.4) and (9.5) we obtain:

$$\begin{aligned} \mathrm{d}T &= -\frac{(\delta G/\partial\eta) - T(\partial/\partial T)(\delta G/\partial\eta)}{(\partial\hat{e}/\partial T)} \delta\eta \\ &= \frac{\nabla(\partial^2 \hat{g}/\partial T \partial(\nabla\eta)) - (\partial^2 \hat{g}/\partial T \partial\eta)}{(\partial^2 \hat{g}/\partial T^2)} \delta\eta. \end{aligned} \tag{9.22b}$$

Notice that although the variational derivative of the free energy at the equilibrium state is zero, its partial derivative with respect to temperature is not. Then (9.21) and (9.22a) yield that the second variation of the energy functional also vanishes and $\delta^2 S$ has the sign opposite to that of the second variation of the free energy functional:

$$\begin{aligned} \delta^2 G &= \delta^2 E - T\,\delta^2 S \\ &= \frac{1}{2} \int_V \left[\frac{\partial^2 \hat{g}}{\partial \eta^2} (\delta\eta)^2 + 2 \frac{\partial^2 \hat{g}}{\partial T \partial \eta} \delta\eta \mathrm{d}T + \frac{\partial^2 \hat{g}}{\partial T^2} (\mathrm{d}T)^2 + \frac{\partial^2 \hat{g}}{\partial (\nabla\eta)^2} (\nabla\,\delta\eta)^2 \right] \mathrm{d}^3 x. \end{aligned} \tag{9.23}$$

Although the sign of $\delta^2 G$ can be estimated for a general expression of the free energy we will proceed with the density in the form adopted in Chap. 3:

$$\hat{g} = g(\eta, T) + \frac{1}{2} \kappa (\nabla\eta)^2 \tag{3.27b}$$

with

$$\kappa = \mathrm{const}(T). \tag{9.24}$$

Then, integrating the last term in (9.23) by parts and substituting (9.22b) we obtain:

$$\delta^2 G = \frac{1}{2} \int_V \delta\eta \hat{\mathbf{H}}_{\mathrm{E1}} \delta\eta \mathrm{d}^3 x, \tag{9.25a}$$

$$\hat{\mathbf{H}}_{\mathrm{E1}} = \frac{\partial^2 g}{\partial \eta^2} - \frac{\left(\partial^2 g/\partial \eta \partial T\right)^2}{\left(\partial^2 g/\partial T^2\right)} - \kappa \nabla^2. \tag{9.25b}$$

Notice that the non-differential term of the Hamilton's operator in (9.25a) is greater than that in (3.34). This means that, similar to the homogeneous case, the closed system is, so to speak, more stable than the open one. To see this let us assume that $\partial^2 g/\partial T \partial \eta = \mathrm{const}(\eta)$ and consider as an eigenfunction of the operator $\hat{\mathbf{H}}_{\mathrm{E1}}(x)$ the gradient of an interface-type state [cf. (3.125b)]:

$$\Psi_*(x) = \frac{\mathrm{d}\eta_{\mathrm{e4}}}{\mathrm{d}x}(x).$$

Differentiating ELE (3.29) we obtain

$$\hat{\mathbf{H}}_{\mathrm{E1}}\ \Psi_*(x) = \frac{\mathrm{d}}{\mathrm{d}x}\frac{\delta G}{\delta \eta}(\eta_{\mathrm{e4}}) +\ \Lambda_{\mathrm{E1}*}\Psi_*(x) = \Lambda_{\mathrm{E1}*}\Psi_*(x),$$

where

$$\Lambda_{\mathrm{E1}*} = \frac{1}{C_\eta}\left(\frac{\partial^2 g}{\partial T \partial \eta}\right)^2 = \mathrm{const} > 0.$$

Because $\Lambda_{\mathrm{E1}*}$ is the smallest eigenvalue of Ψ_* (see Appendix E) the interface-type solution η_{e4} becomes absolutely stable in the closed system, as opposed to being neutrally stable (the Goldstone mode) in the open one. Physically, destruction of the Goldstone mode in a closed system is a result of elimination of the translation invariance, which in turn comes as a result of the energy conservation constraint (9.2). Indeed, any shift of the interface changes the energy balance in the system because the energy densities of the phases on the opposite sides of the interface are not equal, although their free energy densities are. Additional stabilization caused by the energy conservation constraint (9.2) may cause an unstable inhomogeneous equilibrium state of the open system to gain stability in the closed one.

9.1.2 Type-E2 States

If the sought state not only imparts a maximum on the entropy functional (9.1) but also *is* an extremal of the energy functional (9.2), then, instead of (9.3), this state satisfies the following simultaneous relations:

$$\delta S\{\eta_{\mathrm{E2}}, T_{\mathrm{E2}};\ \delta\eta,\ \delta T\} = 0, \tag{9.26a}$$

$$\delta E\{\eta_{\mathrm{E2}}, T_{\mathrm{E2}};\ \delta\eta,\ \delta T\} = 0. \tag{9.26b}$$

Importantly that because of the two variational conditions (9.26), it may not be possible to properly characterize the state with just one variable field of OP: $\{\eta_{\mathrm{E2}}(\mathbf{x})\}$. Then, another variable field, e.g., temperature $\{T_{\mathrm{E2}}(\mathbf{x})\}$, may be needed to complete the characterization of the state, so that the equilibrium state $\{\eta_{\mathrm{E2}}(\mathbf{x}),$ $T_{\mathrm{E2}}(\mathbf{x})\}$ becomes *inhomogeneous in the OP and temperature* [3].

However, the fields $\{\eta_{\mathrm{E2}}(\mathbf{x})\}$ and $\{T_{\mathrm{E2}}(\mathbf{x})\}$ are not independent because the conditions (9.26a) and (9.26b) result in a system of simultaneous equations:

$$\frac{\delta S}{\delta \eta}+\frac{\partial \hat{s}}{\partial T}\frac{\mathrm{d}T}{\mathrm{d}\eta}=0, \tag{9.27a}$$

$$\frac{\delta E}{\delta \eta}+\frac{\partial \hat{e}}{\partial T}\frac{\mathrm{d}T}{\mathrm{d}\eta}=0. \tag{9.27b}$$

where $(\delta/\delta\eta)$ is understood now as a partial functional derivative with respect to the OP for non-varying temperature field.

To better understand the properties of the state $\{\eta_{\mathrm{E2}}(\mathbf{x}), T_{\mathrm{E2}}(\mathbf{x})\}$ let us calculate the partial variational derivative of its free energy with respect to the OP:

$$\frac{\delta G}{\delta \eta}\{\eta,T\}\equiv\frac{\partial \hat{g}}{\partial \eta}-\nabla\frac{\partial \hat{g}}{\partial \nabla\eta}=\frac{\delta E}{\delta \eta}-T\frac{\delta S}{\delta \eta}+\frac{\partial \hat{s}}{\partial \nabla\eta}\nabla T. \tag{9.28a}$$

Here we used the Legendre transform (9.5) and rearranged the terms. Applying the equilibrium equations (27) we obtain:

$$\frac{\delta G}{\delta \eta}\{\eta,T\}\equiv-\left(\frac{\partial \hat{g}}{\partial T}+\hat{s}\right)\frac{\mathrm{d}T}{\mathrm{d}\eta}+\frac{\partial \hat{s}}{\partial \nabla\eta}\nabla T=-\frac{\mathrm{d}\kappa}{\mathrm{d}T}\nabla\eta\nabla T. \tag{9.28b}$$

Here we used the Legendre transform (9.5) again and (3.27b). As you can see, in general, this partial functional derivative is not zero. If the gradient energy coefficient κ is temperature independent [see (9.24)] then $\delta G/\delta\eta$ in (9.28) vanishes. However, even in this case the equilibrium state $\{\eta_{\mathrm{E2}}(\mathbf{x}), T_{\mathrm{E2}}(\mathbf{x})\}$ is different from that of type-E1 because the temperature distribution is inhomogeneous.

In order to analyze the thermodynamic stability of the state $\{\eta_{\mathrm{E2}}(\mathbf{x}), T_{\mathrm{E2}}(\mathbf{x})\}$ we need to substitute δT expressed from (9.27a) into the expression for $\delta^2 S$ in (9.20) and perform the integration by parts in the latter. This brings the second variation to the form (9.25a) and again reduces the problem of stability to the analysis of the spectrum of the respective operator $\hat{\mathbf{H}}_{\mathrm{E2}}(x)$. In a system where condition (9.24) applies this criterion takes on a particularly simple form:

$$\hat{\mathbf{H}}_{\mathrm{E2}}=\frac{\partial^2 s}{\partial \eta^2}-2\frac{\partial^2 s}{\partial T\partial \eta}\frac{\partial s/\partial \eta}{\partial s/\partial T}+\frac{\partial^2 s}{\partial T^2}\left(\frac{\partial s/\partial \eta}{\partial s/\partial T}\right)^2<0. \tag{9.29}$$

Example 9.2 Find a 1d type-E2 state of a system described by the tangential potential with C = const(T) and κ = const(T).

In the 1d case the system (9.27) reduces to

$$\frac{\mathrm{d}s}{\mathrm{d}\eta} = 0, \tag{9E.8a}$$

$$\frac{\mathrm{d}e}{\mathrm{d}\eta} - \kappa\frac{\mathrm{d}^2\eta}{\mathrm{d}x^2} = 0. \tag{9E.8b}$$

Multiplying (9E.8) by $\mathrm{d}\eta/\mathrm{d}x$ and integrating them separately we find that the equilibrium states obey the following simultaneous equations:

$$s(\eta, T) = \text{const}, \tag{9E.9a}$$

$$e(\eta, T) - \frac{\kappa}{2}\left(\frac{\mathrm{d}\eta}{\mathrm{d}x}\right)^2 = \text{const}. \tag{9E.9b}$$

The first equation shows that the state $\{\eta_{\mathrm{E2}}(\mathrm{x}), T_{\mathrm{E2}}(\mathrm{x})\}$ is isoentropic, which confirms our earlier conclusion that the temperature distribution in this state must be inhomogeneous if the OP is not uniform. The second equation shows that the regions of the system far away from the transition zone have the same energies, but not the free energies because the temperatures may be different.

For the tangential potential with (9.19), (9E.1) the entropy and energy densities are

$$s = C\ln\frac{T}{T_{\mathrm{E}}} - \frac{L}{T_{\mathrm{E}}}\nu(\eta), \tag{9E.10a}$$

$$e = C(T - T_{\mathrm{E}}) + \frac{1}{2}W\omega^2(\eta) - L\nu(\eta). \tag{9E.10b}$$

From (9E.9 and 9E.10) we find the distributions of the temperature and OP fields in the type-E2 state:

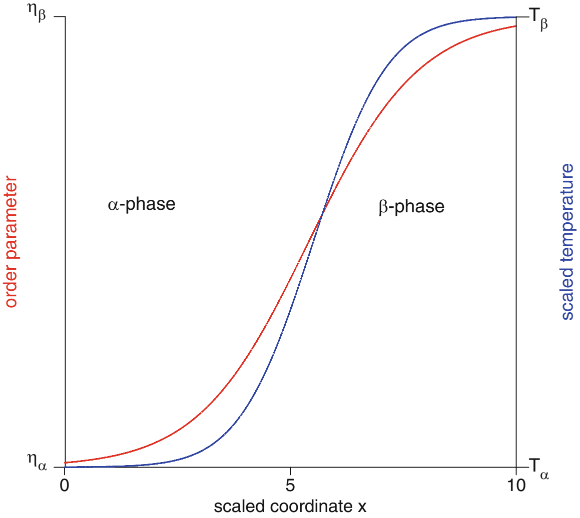
$$T = T_\alpha \exp\{Q\nu(\eta)\}, T_\alpha = T_{\mathrm{E}}\frac{Q}{\exp Q - 1}, \tag{9E.11a}$$

$$\kappa\left(\frac{\mathrm{d}\eta}{\mathrm{d}x}\right)^2 = W\omega^2(\eta) + 2L\left\{\frac{\exp[Q\nu(\eta)] - 1}{\exp Q - 1} - \nu(\eta)\right\}. \tag{9E.11b}$$

where T_α is the temperature of the α-phase. In Fig. 9.2 are depicted the scaled distributions:

$$\frac{C(T - T_\alpha)}{L} = \tilde{T}, x\sqrt{\frac{\kappa}{W}} = \tilde{x}. \tag{9E.12}$$

Fig. 9.2 Distributions of the scaled temperature (*blue*) and OP (*red*) as functions of the scaled coordinate x for the 1d type-E2 equilibrium state after a first-order transition



To analyze the thermodynamic stability of the type-E2 state (9E.11) we need to calculate the left-hand side of (9.29):

$$\hat{\mathbf{H}}_{E2} = -6CQ\left[6Q\omega^2(\eta) + \omega'(\eta)\right]. \tag{9E.13}$$

This expression is not sign definite in the domain $0 \le \eta \le 1$, which means that this state is not absolutely stable but of the saddle-type stability. Nevertheless the type-E2 states are important because the system may spend a great deal of its time in the vicinity of the state during a transformation process. The type-E2 states can be achieved in thermodynamic systems with the vanishing thermal conductivity ($\lambda \to 0$) that is, *ideal thermal insulators*.

Example 9.3 Find a type-E2 APB in a system with C = const(T) and κ = const(T).

An APB is a 1d equilibrium state, which comes about after the second-order transition, see Example 3.2. The system is described by the free energy density:

$$\hat{g} = g_0(T) + \frac{1}{2}a\eta^2\left(\frac{T - T_c}{T_c} + \frac{1}{2}\eta^2\right) + \frac{1}{2}\kappa(\nabla\eta)^2 \tag{9E.14}$$

It undergoes a second-order transition at $T = T_C$, see (2.43) and (2.44). If the temperature is lowered to $T_E < T_C$ two stable variants

$$\bar{\eta}_\pm = \pm\sqrt{-\tau}, \tau = \frac{T_E - T_c}{T_c} \tag{9E.15}$$

appear after the transition with equal likelihood. They will be separated by the transition region of the thickness of the order of magnitude

$$L_{APB} = 2\sqrt{2}l,\ l = \sqrt{\frac{\kappa}{a(-\tau)}}. \tag{9E.16}$$

If after the cooling to $T_{\mathrm{E}} < T_{\mathrm{C}}$ the system is isolated from the environment, a 1d type-E2 state may establish in the system. For such state (9.27) yield:

$$\frac{\mathrm{d}T}{\mathrm{d}\eta} = pT\eta, p = \frac{a}{CT_{\mathrm{c}}}, \tag{9E.17a}$$

$$\kappa\frac{\mathrm{d}^2\eta}{\mathrm{d}x^2} = a\eta\left(\eta^2 - 1 + \frac{T}{T_c}\right). \tag{9E.17b}$$

The BC are

$$\frac{\mathrm{d}\eta}{\mathrm{d}x}(\bar{\eta}_{\pm}) = 0, T_{\mathrm{E}} = T(\bar{\eta}_{\pm}). \tag{9E.18}$$

These equations can be integrated one after another. Integrating (9E.17a) we obtain

$$T = T_0 \mathrm{e}^{\frac{p}{2}\eta^2}, \tag{9E.19a}$$

where $T_0 = T(\eta = 0)$. Using the BC (9E.18) we obtain that

$$T = T_C(1+\tau)\mathrm{e}^{\frac{p}{2}\left(\tau+\eta^2\right)}. \tag{9E.19b}$$

Substituting (9E.19b) into (9E.17b), multiplying by $\mathrm{d}\eta/\mathrm{d}x$, integrating once, and applying the BC (9E.18) we obtain

$$l\frac{\mathrm{d}\eta}{\mathrm{d}x} = \sqrt{\eta^4 - 2\eta^2 - (\tau^2 + 2\tau) - \frac{1}{p}(1+\tau)\left[1 - \mathrm{e}^{\frac{p}{2}(\tau+\eta^2)}\right]}. \tag{9E.20}$$

Equation (9E.20) can be integrated numerically (see Fig. 9.3).

To analyze the thermodynamic stability of the type-E2 state (9E.18) and (9E.20) we calculate the left-hand side of (9.29):

$$\hat{\mathbf{H}}_{\mathrm{E2}} = -\frac{a}{T_{\mathrm{c}}}\left(1 + \alpha\eta^2\right) < 0. \tag{9E.21}$$

This expression is sign definite, which means that this state is stable, at least locally.

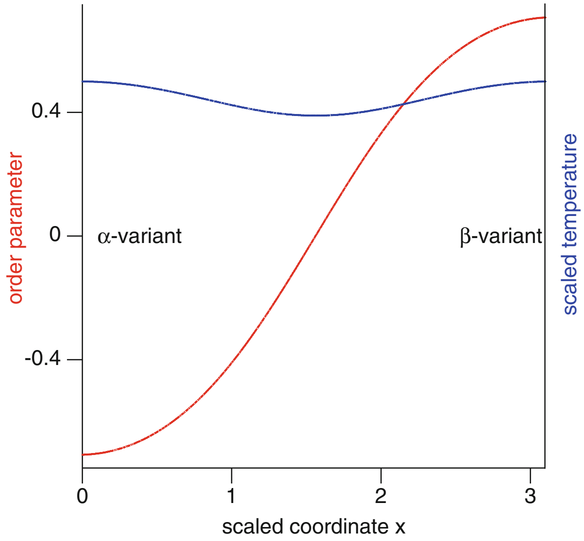


Fig. 9.3 Distributions of the scaled temperature (*blue*) and OP (*red*) as functions of the scaled coordinate x for the 1d type-E2 equilibrium state after a second-order transition

9.2 Generalized Heat Equation

As we concluded in the introduction, evolution of our system is accompanied by energy redistribution and heat propagation. Hence, in addition to TDGLE

$$\frac{\mathrm{d}\eta}{\mathrm{d}t} = -\gamma\frac{\delta G}{\delta\eta}, \quad \gamma>0, \tag{5.2}$$

our system must be described by a coupling heat equation, which takes into account heat production due to the ongoing phase transition and distribution due to the conduction. To derive such equation, we will call it *generalized heat equation* (GHE), we apply the First and Second Laws of Thermodynamics to a small volume δV of a heterogeneous nonequilibrium medium:

$$\mathrm{d}\hat{e} = \ \delta q + \ \delta w, \tag{9.30a}$$

$$\delta q = -\mathrm{div}\mathbf{J}_T\mathrm{d}t, \tag{9.30b}$$

$$\mathrm{d}\hat{s} \geq \frac{1}{T}\ \delta q. \tag{9.30c}$$

Here δw is the work done on and δq is the amount of heat given to the volume δV. Let's assume that our medium is incompressible. Then the work term vanishes and to find the GHE we have to derive the expressions for the internal energy density variation $\mathrm{d}\hat{e}$ and the heat flux $\mathbf{J}_T$ that account for nonlocal interactions in the medium, which we considered in Chap. 3. The derivation of the former is based on the calculation of a small variation of the internal energy functional E of the whole system, (9.2), which comes as a result of a small *inhomogeneous* variation of the OP $\delta\eta$:

$$\delta E = \int_{\delta V} \delta\hat{e}\, \mathrm{d}^3 x. \tag{9.31}$$

Let's assume that the variation $\delta\eta$ occurred at constant temperature and in the volume δV *independently* from neighboring volumes of the system. Such variation $\delta\eta$ vanishes everywhere outside of the considered volume. Then, using the definition of the variational derivative, we obtain:

$$\delta E = \int_{\delta V} \frac{\delta E}{\delta\eta}\, \delta\eta\, \mathrm{d}^3 x. \tag{9.32}$$

Here, as before, the variational derivative is understood as for the invariable temperature field. Finally, comparing (9.31) with (9.32) and using continuity of the variations $\delta\hat{e}(\mathbf{x})$ and $\delta\eta(\mathbf{x})$ as functions of the position, we arrive at the expression for the energy density variation:

$$\delta\hat{e} = \frac{\delta E}{\delta\eta}\, \delta\eta. \tag{9.33}$$

When the temperature varies simultaneously with OP the nonlocal energy density variation takes the form:

$$\mathrm{d}\hat{e} = \hat{C}_\eta \mathrm{d}T + \frac{\delta E}{\delta\eta}\mathrm{d}\eta. \tag{9.34a}$$

The specific heat for constant V and η per unit volume may include the gradient energy contribution:

$$\hat{C}_\eta \equiv \left(\frac{\partial\hat{e}}{\partial T}\right)_\eta. \tag{9.34b}$$

Substitution of (9.34a) into the First Law (9.30a) yields the GHE for the incompressible medium ($\mathrm{d}/\mathrm{d}t \rightarrow \partial/\partial \mathrm{t}$):

$$\hat{C}_\eta \frac{\partial T}{\partial t} = -\mathrm{div}\mathbf{J}_\mathrm{T} + Q(\mathbf{x}, t), \tag{9.35}$$

where $Q(\mathbf{x},\ t)$ is the density of instantaneous heat sources in the energy representation:

$$Q(\mathbf{x}, t) = -\frac{\delta E}{\delta\eta}\frac{\partial\eta}{\partial t} = -\left(\frac{\partial e}{\partial\eta} - \kappa_E \nabla^2 \eta\right)\frac{\partial\eta}{\partial t}, \tag{9.36a}$$

$$\kappa_{\mathrm{E}} = \kappa - T\frac{\mathrm{d}\kappa}{\mathrm{d}T}. \tag{9.36b}$$

Using the Legendre transformation [see (9.4), (9.5) and Appendix F] the heat source $Q(\mathbf{x}, t)$ may also be represented in the entropy form:

$$Q(\mathbf{x}, t) = -\left(T\frac{\delta S}{\delta \eta} + \frac{\delta G}{\delta \eta}\right)\frac{\partial \eta}{\partial t}. \tag{9.37}$$

Same variational procedure as was used in (9.31–9.34a) may be used to find the entropy variation in the volume δV:

$$\mathrm{d}\hat{s} = \frac{1}{T}\hat{C}_{\eta}\mathrm{d}T + \frac{\delta S}{\delta \eta}\mathrm{d}\eta. \tag{9.38}$$

Comparing (9.38) with (9.34a) and using the Legendre transformation (9.4) we arrive at the expression of the First Law in the form:

$$\mathrm{d}\hat{s} = \frac{1}{T}\,\delta q - \frac{1}{T}\frac{\delta G}{\delta \eta}\mathrm{d}\eta. \tag{9.39}$$

Application of the Second Law (9.30c) to (9.39) yields a constraint on the rate of OP change:

$$\frac{\delta G}{\delta \eta}\frac{\mathrm{d}\eta}{\mathrm{d}t} \leq 0. \tag{9.40}$$

Constraint (9.40) manifests the Le Chatelier–Braun principle in the nonlocal nonequilibrium medium and proves that the linear TDGLE (5.2) is acceptable, but not a unique, choice of the evolution equation for the OP. It also hints at the nonlinear extension of the TDGLE (see Sect. 4.3).

The energy (9.36a) and entropy (9.37) representations reveal many important properties of the heat source $Q(\mathbf{x}, t)$. They show that the source does not need to be sign definite that is, there may be local sinks of heat inside an overall heat source. The energy representation shows that, in addition to the homogeneous part $(\partial e/\partial \eta)$ responsible for the latent heat L (see below), the source contains the inhomogeneous part $(\kappa_{\mathrm{E}}\nabla^2\eta)$, which may affect the overall heat production in the system. The entropy representation shows that the heat source consists of the entropy contribution, which may be either positive or negative depending on the direction of the transition, and the dissipation which, due to the constraint (9.40), is proportional to the rate of the transition squared and, hence, always positive.

To complete the First Law (9.30a) we need an expression for the heat flux in the heterogeneous nonequilibrium medium. Notice from (9.30) that the expressions of the heat flux $\mathbf{J}_{\mathrm{T}}$ and heat source $Q(\mathbf{x}, t)$ are independent. The heat flux $\mathbf{J}_{\mathrm{T}}$ depends on local values of temperature, its gradients, properties of the medium, and is known to vanish with ∇T (Fourier's law). In [4] the following expression was used for the flux:

$$\mathbf{J}_\mathrm{T} = \Lambda \nabla \frac{\delta S}{\delta \hat{e}}.$$

Another possibility would be to consider an integral expression for the heat flux in a medium with the "spatial memory"; these effects are not considered in this book. Expanding the flux $\mathbf{J}_\mathrm{T}$ in ∇T and disregarding terms of the order higher than the first one, we obtain the regular expression for the heat flux:

$$\mathbf{J}_\mathrm{T} = -\lambda \nabla T, \tag{9.41}$$

where the thermal conductivity λ may be a function of T and η. Then the GHE takes the form:

$$\hat{C}_\eta \frac{\partial T}{\partial t} = \nabla(\lambda \nabla T) + Q(\mathbf{x}, t). \tag{9.42}$$

A phase transition is accompanied by the transfer of the internal energy, which is described by the energy density flux vector $\mathbf{J}_\mathrm{E}$, defined as follows:

$$\frac{\partial \hat{e}}{\partial t} = -\mathrm{div}\mathbf{J}_\mathrm{E}. \tag{9.43}$$

In order to obtain an expression for the energy density flux, we should find the partial derivative of $\hat{e}$ with respect to time:

$$\frac{\partial \hat{e}}{\partial t} = \hat{C}_\eta \frac{\partial T}{\partial t} + \frac{\delta E}{\delta \eta} \frac{\partial \eta}{\partial t} + \mathrm{div}\left(\kappa_\mathrm{E} \nabla \eta \frac{\partial \eta}{\partial t}\right). \tag{9.44}$$

Substituting the GHE in the energetic representation, (9.36a) and (9.42), into (9.44) we obtain the expression for $\mathbf{J}_\mathrm{E}$ in the incompressible motionless medium:

$$\mathbf{J}_\mathrm{E} = \mathbf{J}_\mathrm{T} - \kappa_\mathrm{E} \nabla \eta \frac{\partial \eta}{\partial t}. \tag{9.45}$$

This result shows that except for the heat flux, the expression for $\mathbf{J}_\mathrm{E}$ contains the work flux associated with the interactions that appear in the system due to inhomogeneities in a nonlocal nonequilibrium medium. The work flux entails the inhomogeneous term in the heat source, (9.36a), and is responsible for the surface creation and dissipation effect, analyzed in the next section. The work flux is analogous to the intensity of a sound wave in a fluid with η replacing the displacement of an element of fluid and κ_E replacing the adiabatic bulk modulus.

GHE (9.42) with the heat source expressed by (9.36a) or (9.37) is thermodynamically rigorous and absolutely invariant with respect to the derivation from the First or Second Laws of thermodynamics. This equation couples to TDGLE (5.2) and makes up a system of simultaneous equations that describe all stages of evolution of a phase transformation in a medium with the specified thermodynamic and kinetic properties of the system: C, κ, λ, γ, T_E (or T_C), L, W (or a). Both equations are of the diffusion type; (9.42) is characterized by the thermal diffusivity α and (5.1)—the ordering diffusivity m. The ratio of the diffusivities R:

$$R \equiv \frac{\alpha}{m} = \frac{\lambda}{C\gamma\kappa};\ \alpha = \frac{\lambda}{C},\ m = \gamma\kappa \tag{9.46}$$

is called the *kinetic number*; it determines different regimes of the evolution. As we concluded in Chap. 5, a transformation process may be loosely divided into the following stages: nucleation, growth, and coarsening. All the stages will be affected by the processes of heat release and redistribution. Let us consider the stages separately.

Example 9.4 Find the spatial distribution of the heat source in the plane interface moving through the isothermal system described by the tangential potential with $\kappa = \text{const}(T)$.

Using the transformations (5.5–5.7) for (9.36a) we obtain an expression:

$$Q(u) = v\frac{d\eta}{du}\left(\frac{\partial e}{\partial \eta} - \kappa\frac{d^2\eta}{du^2}\right). \tag{9E.22}$$

In order to use for our system the solution (5.15), which was obtained for the Landau potential, we need to scale the variable η and parameter κ in (9E.22). Using the scaling (2.32) and (3E.3), the internal energy density expression (9E.10b), and the solution (5.9b), (5.14), and (5.15) we obtain the expression for the source in the scaled variables:

$$Q(\eta) = 6vL\sqrt{\frac{W}{\kappa}}\omega^2(\eta);\ \eta(u) = \left(1 + e^{u\sqrt{W/\kappa}}\right)^{-1}, \tag{9E.23}$$

where v is the velocity of the interface

$$v = \mu(T_E - T_0) \tag{5E.2}$$

and T_0 is the temperature of the system. Notice that both branches (+ and −) of the solution (5.9b), (5.14), and (5.15) have the same expression for Q. The latter is depicted in Fig. 9.4.

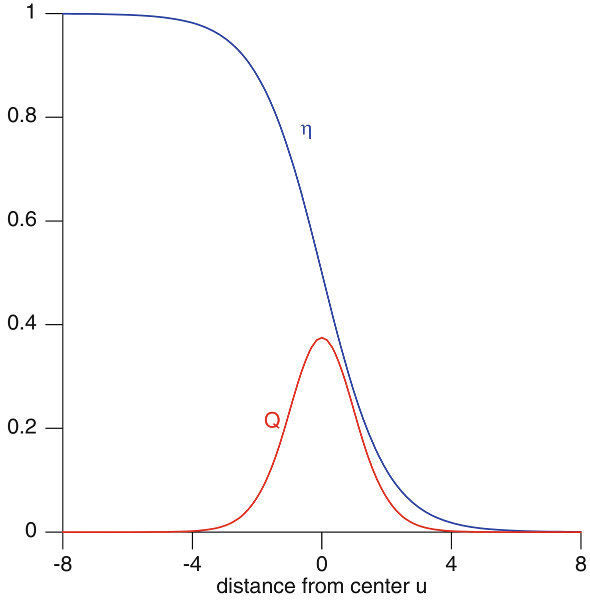


Fig. 9.4 Distributions of the OP and heat source Q in the plane interface moving through the isothermal system described by the tangential potential with $\kappa = \text{const}(T)$

9.3 Emergence of a New Phase

Heat release and redistribution may affect emergence of a new phase in many different ways. A full theory of thermal effects in nucleation is not completed yet. In this section, we will consider only one particular thermal effect of this type—the so-called *nonclassical nucleation*. It manifests when a stable phase is cooled down into a vicinity (above or below) of the spinodal point of the first-order (discontinuous) transition or undercooled below the critical temperature in the second-order (continuous) transition. Whether the small fluctuations will grow or decay depends on the stability properties of the adjacent homogeneous equilibrium states. Given our experiences in Sects. 5.3.1 and 8.1.4, let us study evolution of the small disturbances in the form of harmonic waves superimposed on an equilibrium state in question $(\bar{\eta}, \bar{T})$:

$$\eta(\mathbf{x}, t) = \bar{\eta} + \mathrm{N}\ \mathrm{e}^{\beta t + ikx}, \tag{9.47a}$$

$$T(\mathbf{x}, t) = \bar{\mathrm{T}} + \Theta \mathrm{e}^{\beta t + ikx}. \tag{9.47b}$$

Here $\mathbf{k}$ is the wave vector of the permitted perturbations and $\beta(\mathbf{k})$ is the amplification factor, which determines the "fate" of the small disturbances. When these waves are substituted into (5.1), (9.42), they yield two simultaneous equations for the small amplitudes $\{\mathrm{N}, \Theta\}$:

$$\left(\frac{\beta}{\gamma} + \overline{\frac{\partial^2 g}{\partial \eta^2}} + \kappa |\mathbf{k}|^2\right)\mathrm{N} = -\overline{\frac{\partial^2 g}{\partial \eta \partial T}}\Theta, \tag{9.48a}$$

$$\left(\lambda|\mathbf{k}|^2 - \bar{\mathrm{T}}\overline{\frac{\partial^2 g}{\partial T^2}}\beta\right)\Theta = \bar{\mathrm{T}}\overline{\frac{\partial^2 g}{\partial\eta\partial T}}\beta\mathrm{N}, \tag{9.48b}$$

where the functions with a bar should be taken at the equilibrium point $(\bar{\eta}, \bar{T})$. Not surprisingly the OP/temperature interactions depend on the mixed partial $\overline{\partial^2 g/\partial T\partial\eta}$. If this quantity is zero the simultaneous equations (9.48) break up into two independent equations for the amplitudes $\{\mathrm{N}, \Theta\}$, which means that the OP and temperature waves evolve independently. In the limit of $\lambda \to \infty$ we recover from (9.48) (5.21a), that is, the isothermal expression for the amplification factor. If λ is finite and the quantity $\overline{\partial^2 g/\partial T\partial\eta}$ is not zero the OP and temperature waves interact. In this case, the system (9.48) has nontrivial solutions only if its determinant vanishes. Then,

$$\beta^2 + \left[\gamma\left(\overline{\frac{\partial^2 g}{\partial\eta^2}} - \frac{\left(\overline{\partial^2 g/\partial\eta\partial T}\right)^2}{\overline{\partial^2 g/\partial T^2}}\right) + (\alpha + m)|\mathbf{k}|^2\right]\beta$$
$$+\ \alpha\left(\gamma\overline{\frac{\partial^2 g}{\partial\eta^2}} + m|\mathbf{k}|^2\right)|\mathbf{k}|^2 = 0. \tag{9.49}$$

This solvability condition relates the amplification rate β to the wave number **k** of the perturbations, that is, is the dispersion relation. For the equilibrium state $(\bar{\eta}, \bar{T})$ to be linearly dynamically stable, the real parts of all the roots of (9.49) must be positive. According to the Routh–Hurwitz theorem [5], the free term and the coefficient of the linear term of (9.49) must not be negative:

$$\gamma\left(\overline{\frac{\partial^2 g}{\partial\eta^2}} - \frac{\left(\overline{\partial^2 g/\partial\eta\partial T}\right)^2}{\overline{\partial^2 g/\partial T^2}}\right) + (\alpha + m)|\mathbf{k}|^2 \geq 0, \tag{9.50a}$$

$$\alpha\left(\gamma\overline{\frac{\partial^2 g}{\partial\eta^2}} + m|\mathbf{k}|^2\right)|\mathbf{k}|^2 \geq 0. \tag{9.50b}$$

Because $\alpha > 0$ and $m > 0$ condition (9.50a) is less restrictive than condition (9.50b). Then we obtain that for the linear dynamic stability of the state $(\bar{\eta},\bar{T})$ there must be

$$\overline{\frac{\partial^2 g}{\partial\eta^2}} \geq 0. \tag{9.51}$$

Hence, the criterion of the dynamical stability of the system described by (9.42), (5.1) coincides with the criterion of thermodynamic stability of the open (isothermal) system, but not the closed (adiabatic) one. This is a result of the fact that the normal modes (9.47) do not, so to speak, conserve the energy of the functional (9.2).

Now let us study the dynamical behavior of different modes of an unstable equilibrium state that is, a state where (9.10) is true but (9.51) is not. Many of the features of this behavior depend on whether (9.15) is true or not. It is more convenient to study the dispersion relation in the form where the amplification factor β and the wave number **k** are scaled as following:

$$\beta = -\gamma\overline{\frac{\partial^2 g}{\partial\eta^2}}\omega;\ |\mathbf{k}|^2 = -\frac{1}{\kappa}\frac{\partial^2 g}{\partial\eta^2}q; \tag{9.52a}$$

Then the dispersion relation takes the form:

$$\omega^2 + (M-1)\omega + (R+1)\omega q - Rq + Rq^2 = 0. \tag{9.52b}$$

Thus, different regimes of nonclassical nucleation in discontinuous transformations are determined by the kinetic number R and module M.

The left-hand side of the dispersion relation (9.52b) is a second-degree polynomial in two variables; its solutions, as known, are conics with two branches. Because the discriminant of the dispersion relation (9.52b) or (9.49) is not negative, both of its branches are real (at least for the real waves numbers q). Hence, the modes may grow ($\beta > 0$) or decay ($\beta < 0$) but cannot oscillate ($\mathrm{Im}\beta \neq 0$). The lower branch is never positive, that is, does not have unstable modes and, hence, does not present any interest for us. The upper branch, that is the one with the greater amplification factor, may have unstable modes and will be analyzed further. The wave number of the neutral mode ($\omega = 0$) is $q_0 = 0$ or 1. However, the two values may belong to two different branches. Let us find the wave number q_m of the most dangerous mode, that is, the one with the greatest amplification factor ω. For this we differentiate (9.52b) with respect to q, equate $\mathrm{d}\omega/\mathrm{d}q$ to zero, and present the result in the form:

$$M(R+1) = \frac{[1 + q_\mathrm{m}(R-1)]^2}{1 - 2q_\mathrm{m}}. \tag{9.53}$$

Depending on the values of the interaction module M and kinetic number R, several cases of instability of the equilibrium state may be found. These cases are presented in Fig. 9.5 in the plane (R, M) with the Inserts representing the dispersion relations in the dimensional form β(k).

Case a. $0 < M < (R+1)^{-1} < 1$, *weak interactions*. Equation (9.53) does not have solutions. Hence, the uniform mode ($q = 0$) is the most dangerous one: $\omega_0 = 1 - M$. This is similar to the evolution in isothermal systems, cf. (5.21a). The difference is that the amplification factor of the most dangerous mode is determined by the thermal interactions and amplification factors of other unstable modes depend on the coefficient of thermal conductivity—*semi-isothermal case*.

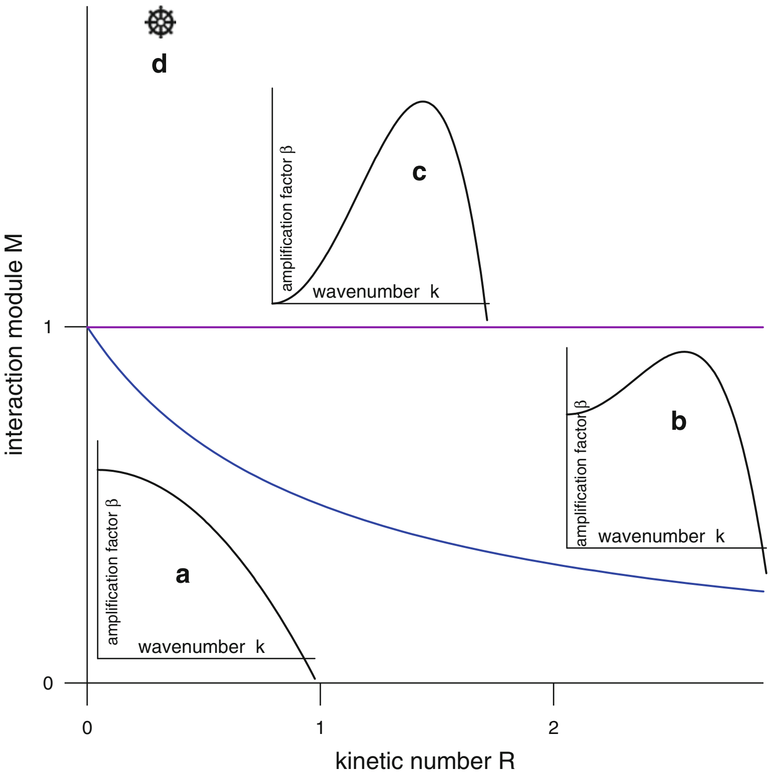


Fig. 9.5 Instability diagram in the plane (R, M). *Blue line*: $M(R + 1) = 1$. *Inserts*: the amplification factors β for the unstable branches of the dispersion relation (9.49) as functions of the wave number k for the cases (**a**)–(**c**) described in the text

Case b. $(R + 1)^{-1} < M < 1$, *medium interactions*. Equation (9.53) has solutions: the uniform wavemode is unstable but the most dangerous mode has a finite wave number—*intermediate case*.

Case c. $M > 1$, *strong interactions*. The uniform mode is neutral: $\omega_0 = 0$, and the wave number of the most dangerous mode is finite: $0 < q_m < ½$—*semi-adiabatic case*.

Case d. $M \gg 1$, *very strong interactions*. An example of this case is a system near the spinodal point $(\overline{\partial g/\partial \eta} = 0, \overline{\partial^2 g/\partial \eta^2} = 0)$, that is, the absolute stability limit of a homogeneous equilibrium state. From the stand point of thermal effects, *Case d* is the most interesting and deserves a rigorous study beyond the limit of small amplitudes. To examine the nonlinear regime of evolution of the unstable waves, we should introduce a small parameter ε, scale the modes with respect to this parameter, and balance the linear and nonlinear terms of the same order of magnitude of ε in TDGLE (5.1) and GHE (9.42). The parameter ε that we introduce here defines the departure from the spinodal point:

$$\overline{\frac{\partial^2 g}{\partial \eta^2}} = -n_1 \varepsilon^2. \tag{9.54a}$$

As the most dangerous mode is long ($k \to \infty$) and slow ($\beta \to 0$), see (9.52a) and (9.54), we scale the spatiotemporal coordinates of (9.42), (5.1):

$$X = \varepsilon x, \tau = \varepsilon^3 t \tag{9.54b}$$

and the disturbances of $\{\eta, T\}$ as follows:

$$\eta = \bar{\eta} + \varepsilon^v \xi(X, \tau), \quad T = \bar{T} + \varepsilon^{v+1} n_2 \theta(X, \tau), \quad v > 0, \tag{9.54c}$$

where the positive quantities n_i and amplitudes ξ, θ are of the order of one and the exponent v needs to be determined.

For $v > 2$, we can balance only linear terms. For $v = 2$, we can balance the nonlinear terms at the leading order of ε if we the temperature is high and the mixed partial is small:

$$\bar{T} = \frac{n_3}{\varepsilon}, \quad \overline{\frac{\partial^2 g}{\partial \eta \partial T}} = n_2 \varepsilon. \tag{9.54d}$$

Then (9.42) and (5.1) become

$$n_2^2 \theta = n_1 \xi - \frac{1}{2} \overline{\frac{\partial^3 g}{\partial \eta^3}} \xi^2 + \kappa \nabla^2 \xi, \; n_3 \frac{\partial \xi}{\partial \tau} = -\lambda \nabla^2 \theta. \tag{9.55}$$

This system governs stability of the state $(\bar{\eta}, \bar{T})$ and shows that in the early stages of its decomposition the temperature deviations are determined by the departure from equilibrium and that the heat sources are balanced by the heat conductivity in the system. Excluding θ from (9.55) and returning to the dimensional variables we obtain for the OP field the nonlinear evolution equation:

$$\frac{\mathrm{d}\eta}{\mathrm{d}t} = \frac{\lambda}{\bar{T}\left(\overline{\partial^2 g / \partial \eta \partial T}\right)^2} \nabla^2 \left[\frac{\partial g}{\partial \eta} - \kappa \nabla^2 \eta\right]. \tag{9.56}$$

This means that in this case the growing waves of the new phase obey the nonlinear Cahn–Hilliard equation from spinodal decomposition, cf. (8.27c), so that the order parameter manifests *temporary conservation law*. Using the scaling (9.54) we can see that the mobility of this regime

$$\frac{\lambda}{\bar{T}\left(\overline{\partial^2 g/\partial\eta\partial T}\right)^2} \sim \frac{1}{\varepsilon} \tag{9.56a}$$

is large and independent of the relaxation constant γ of (5.1), which means that such decomposition is totally controlled by heat transfer. The scaling (9.54) also shows that

$$M = \frac{\bar{T}\left(\overline{\partial^2 g/\partial\eta\partial T}\right)^2}{C_\eta \overline{\partial^2 g/\partial\eta^2}} \sim \frac{1}{\varepsilon}, \tag{9.56b}$$

which means that, indeed, the interactions between the OP and temperature modes are strong. The scaling (9.54d) also manifests large entropy contribution to the free energy. The scaling (9.54c) shows that in this regime the fastest modes to develop are “quasi-isothermal” because the temperature deflection is of higher order than that of the OP. This regime is characterized by modulations of the OP field; it is analogous to the spinodal decomposition in a system with a conserved OP. The difference is, first, that in the latter case modulations accompany the process from the beginning to end while in the present case the modulations are temporary and, second, that for a system with the nonconserved OP modulations are governed by the energy conservation instead of mass conservation in the spinodal decomposition.

9.4 Motion of Interfaces: Non-isothermal Drumhead (Sharp Interface) Approximation

Solution of the full problem described by TDGLE (5.1) and GHE (9.42) is complicated; it may be obtained with the help of different methods including the numerical one. However, there is plenty of information about the system’s evolution that can be gleaned from the drumhead equations. To obtain these equations we will use the averaging method similar to that used in Sect. 5.4 where, in order to derive the drumhead equation for a moving diffuse interface, we introduced the time-dependent curvilinear coordinates (u, v, w) such that in the new coordinates $\eta = \eta(u)$ (see Fig. 9.6). That allowed us to characterize the interface by the thermodynamic and kinetic properties (σ, L_v, μ) and drumhead variables (v_n, K). In this section, we will extend our analysis on the systems of varying temperature. We will derive the drumhead equations that reflect the fact that the non-isothermal interface has finite thickness and curvature. We expect these equations to reveal the physical effects due to release and redistribution of the latent heat L (2.4a), deviations from equilibrium, and multidimensionality, see Fig. 9.7.

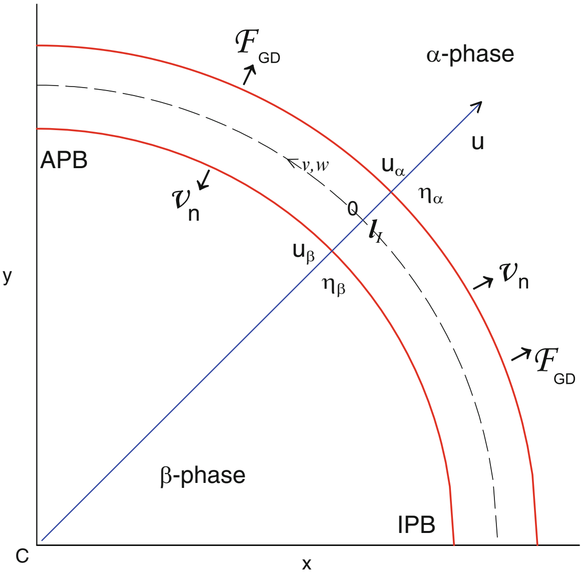


Fig. 9.6 Curvilinear coordinate system (u, v, w) associated with a curved interface. v_n—velocity of the interface motion, F_{GD}—the Gibbs–Duhem force. *APB* anti-phase boundary, *IPB* interphase boundary

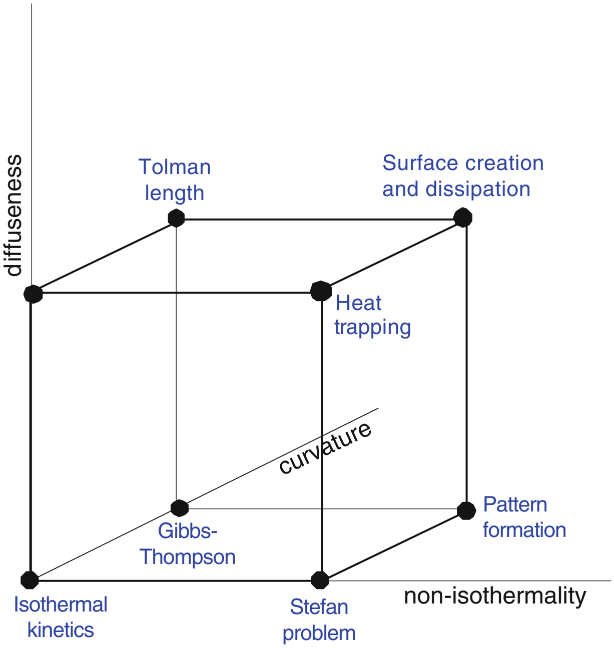


Fig. 9.7 Three characteristic properties of moving interfaces that separate phases in the first-order transformations

In order to derive the drumhead approximation of the dynamic equations for a piece of interface that moves through a variable temperature field we need to transform to the time-dependent curvilinear coordinates (u, v, w) not only TDGLE (5.1) but GHE (9.42) also. In the new coordinates $T = T(u, v, w, t)$ as opposed to $\eta = \eta(u)$. However, if the characteristic length of the thermal field l_T is much greater than that of the OP field L_v then the temperature field is "enslaved" by the OP field and we may expect that $T = T(u)$ also. For an interface moving at the speed v_n (see Appendix I):

$$l_T = \frac{\alpha}{v_n}. \tag{9.57}$$

Then the criterion for the non-isothermal drumhead approximation can be expressed with the help of the generalized Peclet number as follows:

$$\mathrm{Pe} \equiv \frac{L_v}{l_T} = \frac{v_n L_v}{\alpha} << 1. \tag{9.58}$$

The heat redistribution (Appendix I) expanded our characterization of the interface on the properties (L, α) and variable [dT/du]. The temperature gradient across the diffuse interface introduces one more interfacial (drumhead) variable:

$$[T] \equiv T_\beta - T_\alpha \approx L_v \left|\frac{dT}{du}\right|. \tag{9.59}$$

9.4.1 Generalized Stefan Heat-Balance Equation

Any heat released at the interface should be removed from it by means of thermal conduction mechanism. To obtain the heat-balance equation for a curved interface in the drumhead approximation we present GHE (9.42) for the "enslaved" temperature field in the form:

$$\lambda\left(\frac{d^2 T}{du^2} + k_T \frac{dT}{du}\right) + Q\left(T, \eta, \frac{d\eta}{du}\right) = 0, \tag{9.60}$$

where the source in the energy representation is

$$Q\left(T, \eta, \frac{d\eta}{du}\right) = v_n \left\{ \left(\frac{\partial e}{\partial \eta}\right)_T - \kappa_E \left(\frac{d^2\eta}{du^2} + 2K_0 \frac{d\eta}{du}\right) \right\} \frac{d\eta}{du} \tag{9.60a}$$

and k_T may be called the thermal wave number of a curved interface:

$$k_T = \frac{v_n C}{\lambda} + 2K_0. \tag{9.60b}$$

If we integrate the quasi-stationary GHE (9.60) from $u_\beta = -\infty$ till $u_\alpha = +\infty$ for the case of a plane interface ($K_0 = 0$) we obtain the condition of conservation of energy in the form:

$$C(T_\beta - T_\alpha) = L. \tag{9.61}$$

In the case of curved interfaces ($K_0 \neq 0$) there is no conservation of energy along the coordinate lines (u, $v = \text{const}$, $w = \text{const}$). Absence of the conservation law does not allow us to resolve the large-scale thermal problem for a curved interface like it is done for the planar one, e.g., (9.61). Instead, we average GHE (9.60) in the interval (u_β, u_α), the end points of which are in the regions of the respective phases: $\eta(u_\beta) = \eta_\beta$ and $\eta(u_\alpha) = \eta_\alpha$ (see Fig. 9.6). The difference from the isothermal case of Sect. 5.4 is that the temperature field at these points may not have reached yet its asymptotic values of $T(-\infty) = T_\beta$ or $T(+\infty) = T_\alpha$. Using the separation-of-scales condition (9.58) we can introduce the quasi-isothermal averaging operator as follows:

$$\hat{\mathbf{A}}_\mathrm{T} \cdot f \equiv \int_{u_\beta}^{u_\alpha} f(T = \text{const},\ \eta(u),\ u)\mathrm{d}u. \tag{9.62}$$

Contrary to the averaging of TDGLE (5.29), to average GHE (9.60) we do not need any weight factors because $\hat{\mathbf{A}}_\mathrm{T} \cdot Q(T_\mathrm{E}, \eta_{\mathrm{e}4})\mathrm{d}u \neq 0$. In addition to (5.31a) and (5.31d) we obtain:

$$\hat{\mathbf{A}}_\mathrm{T} \cdot \left(\frac{\mathrm{d}^2 T}{\mathrm{d}u^2}\right) = \left[\frac{\mathrm{d}T}{\mathrm{d}u}\right]; \quad \hat{\mathbf{A}}_\mathrm{T} \cdot \left(\frac{\mathrm{d}T}{\mathrm{d}u}\right) = [T]; \quad \hat{\mathbf{A}}_\mathrm{T} \cdot \left(\frac{\partial e}{\partial \eta}\frac{\mathrm{d}\eta}{\mathrm{d}u}\right) = L(T). \tag{9.63}$$

Then, application of (9.62) to (9.60) yields an equation for the jumps of temperature and temperature gradient across the interface:

$$\lambda\left\{\left[\frac{\mathrm{d}T}{\mathrm{d}u}\right] + k_\mathrm{T}[T]\right\} + (L - 2\varepsilon K_0)v_\mathrm{n} = 0, \tag{9.64a}$$

where

$$\varepsilon = \sigma - T\frac{\mathrm{d}\sigma}{\mathrm{d}T} \tag{9.64b}$$

is the interfacial internal energy. If at equilibrium an interface exists at a specific temperature only, as is the case for a first-order transition, differentiation in (9.64b) is understood in the sense of disequilibrium because expressions for the surface energy at equilibrium, (3.70a), and away from it, (5.34), coincide.

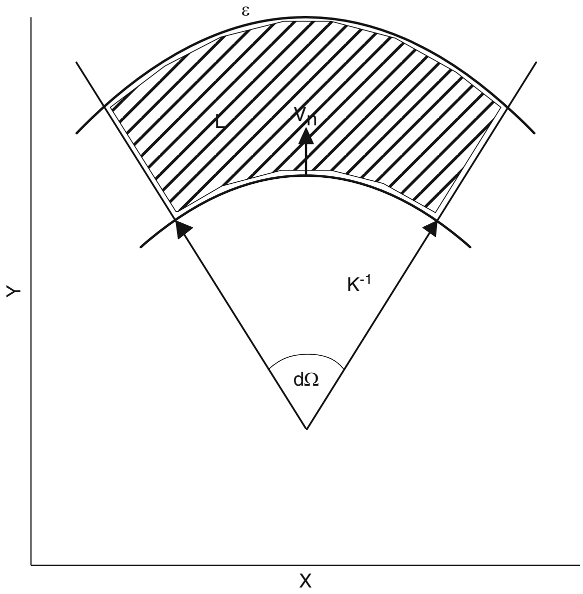


Fig. 9.8 Motion of a piece of interface bound by a fixed solid angle dΩ. K—curvature of the piece before the move, v_n—the normal component of the velocity of the interface, ε—the interfacial internal energy, L—the latent heat of transformation

The drumhead (9.64a) is a heat-balance interface condition; however, it differs from the traditional (Stefan) condition (I.2) in the terms $k_T[T]$ and $(-2\varepsilon K_0 v_n)$. The latter is due to the gradient internal energy contribution ($\sim\kappa_E$) to the heat source (9.36a); it vanishes for a flat or immobile piece of interface, i.e., when the interfacial area does not vary. To reveal this effect we may analyze the heat balance before and after a curved interface sweeps material during a first-order transition (see Fig. 9.8). The amount of heat released is called *the heat of transformation*. Traditionally, it is attributed to the product of the latent heat and the transformed volume: $\int L v_n \mathrm{d}v \mathrm{d}w \mathrm{d}t$. However, one must realize that if the moving interface is curved, the area of the interface before and after the move is different by the amount of the surface area created or destroyed: $\int 2K_0 v_n \,\mathrm{d}v \mathrm{d}w \mathrm{d}t$. As the interface carries energy, the change of the surface area will result in the positive or negative additional quantity of heat liberated at the interface. A simple way to see this difference is to consider motion of a piece of interface $\mathrm{d}X_n = v_n \mathrm{d}t$ bound by a fixed solid angle dΩ (Fig. 9.8): the area of the interface is smaller after the move if the velocity is directed toward the center of curvature of the interface and is greater if otherwise. As the latent heat is the internal energy difference of the liquid and solid phases, the additional amount of heat due to surface area difference should be proportional to the interfacial internal (not free) energy. Hence, the heat of transformation will differ from the above described amount by the amount of the surface area created or destroyed times the surface internal energy; in the boundary condition (I.2) the latent heat L must be replaced by $(L - \varepsilon K)$. This effect, which may be called the *surface creation and dissipation effect*, vanishes for a flat or immobile interface when the interfacial area does not vary.

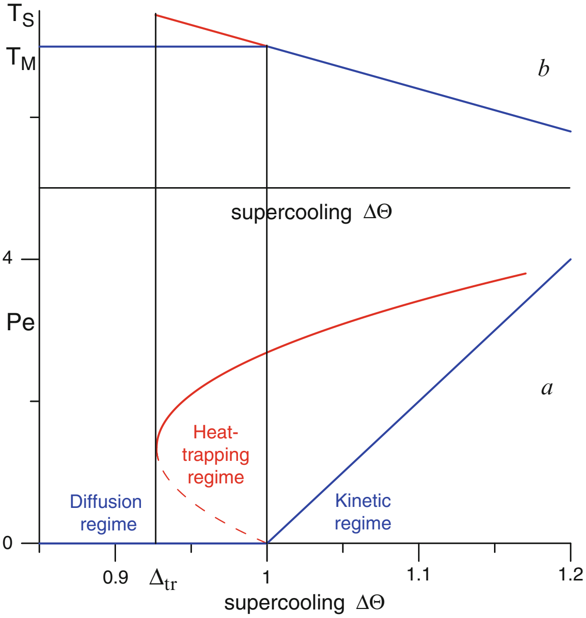


Fig. 9.9 Different regimes of motion of a plane interface separating phases α and β after a first-order phase transition. (**a**) Peclet number Pe and (**b**) final temperature of the β-phase T_β versus the initial supercooling ΔΘ of the α-phase. *Blue lines*—solution of the Stefan problem (I.9–I.11), (I.14), (I.15); *red lines*—FTM solution for a plane interface ($K_0 = 0$), (9.72)

9.4.2 Generalized Kinetic Equation

Let us summarize briefly on Fig. 9.9 what we already know about the motion of a plane phase-separating interface. If the entire system is maintained at constant temperature T_0 then the velocity of the interface is expressed by (5E.7) and the FTM allows us to relate the kinetic coefficient μ to other material properties. On the other hand, if T_0 is only the initial temperature of the parent (α) phase then motion of the interface is more complicated. In the sharp-interface approximation (see Appendix I) the velocity is

$$v = \begin{cases} \beta\sqrt{\frac{\alpha}{t}},\ \sqrt{\pi}\beta e^{\beta 2}\operatorname{erfc}\beta = \Delta\,\Theta, \ \text{if } T_E - \frac{L}{C} < T_0 < T_E & \text{(I.9 – I.11)} \\ \left(\frac{\alpha v_0}{3t}\right)^{\frac{1}{3}}, \ \text{if } T_0 = T_E - \frac{L}{C} & \text{(I.15)} \\ v_0(\Delta\,\Theta - 1), \ \text{if } T_0 < T_E - \frac{L}{C} & \text{(I.14)} \end{cases}$$

where the dimensionless supercooling and characteristic velocity are defined as follows:

$$\Delta\Theta \equiv \frac{C(T_{\mathrm{E}} - T_0)}{L}, v_0 \equiv \frac{\mu L}{C}. \tag{I.10, I.14}$$

This solution is shown in Fig. 9.9a as a blue line.

The regimes of interface motion (I.9–I.11, I.14, I.15), can be obtained without any consideration of the internal structure (diffuseness) of the interface, e.g., for a very thin interface. However, there is a group of thermal effects of motion of phase-separating interfaces, which appear as a result of the interface having the internal structure and thickness. To generalize the kinetic interface equation we average (5.29) over the thickness of the interface taking into account that the temperature is a variable. In many ways this procedure is similar to the one that led us in Sect. 5.4 to (5.32). However, an important difference exists. Because the temperature is not constant anymore (5.31b) has to be replaced by

$$dg = \frac{\partial g}{\partial \eta} d\eta + \frac{\partial g}{\partial T} dT. \tag{9.65}$$

Averaging TDGLE (5.29) we multiply all the terms of this equation by the weight factor dη/du and integrate them over the interval (u_β, u_α) (see Fig. 9.6). Taking into account that $d\eta$/du vanishes at u_β and u_α, we obtain the equation of motion for a non-isothermal phase-separating interface:

$$\hat{\mathbf{A}}_{\mathrm{T}} \cdot \left(\left(\frac{v_{\mathrm{n}}}{\gamma} + 2\kappa K \right) \left(\frac{\mathrm{d}\eta}{\mathrm{d}u} \right)^2 \right) = [g] + \hat{\mathbf{A}}_{\mathrm{T}} \cdot \left(\breve{s} \frac{\partial T}{\partial u} \right), \tag{9.66a}$$

where

$$\breve{s} = s - \frac{1}{2}\kappa_{\mathrm{s}} \left(\frac{\mathrm{d}\eta}{\mathrm{d}u} \right)^2, \kappa_{\mathrm{s}} = -\frac{\mathrm{d}\kappa}{\mathrm{d}T}. \tag{9.66b}$$

[Verify (9.66)! Hint: κ=func(T)]. Using (3.84) and the fact that (dη/du)^2 is a bell-like, even function of u (see Sect. 3.4), the left-hand side of (9.66a) may be represented as follows:

$$\sigma k_\eta + O\left(L_{\mathrm{v}}^3 k_\eta^3\right), \tag{9.67}$$

where σ is the nonequilibrium surface energy, see (5.36), and k_η was called the dynamic wave number of a curved interface:

$$k_\eta = \frac{v_{\mathrm{n}}}{m} + 2K_0. \tag{5.31e}$$

The first term in the right-hand side of (9.66a) is the free energy jump across the interface whose temperature changes together with the OP. The free energy jump in a system where the latent heat is temperature independent [see (2.40c)] can be expressed as follows:

$$[g] = L\frac{T_{\mathrm{E}} - T_{\mathrm{I}}}{T_{\mathrm{E}}} - s_{\alpha}[T] + C\left\{[T] - T_{\mathrm{I}}\ln(1 + \frac{[T]}{T_{\mathrm{I}}})\right\}. \tag{9.68}$$

where T_{I} is the average temperature of the interface, more specifically—temperature of the U=0 level surface. Substituting (9.67) and 9.68) into (9.66a) we obtain an evolution equation, which relates different local characteristics of an interface:

$$\sigma k_{\eta} = L\frac{T_{\mathrm{E}} - T_{\mathrm{I}}}{T_{\mathrm{E}}} + F_{\mathrm{GD}} + \frac{1}{2}C\frac{[T]^2}{T_{\mathrm{I}}} + O\left([T]^3, L_{\mathrm{v}}^3 k_{\eta}^3\right). \tag{9.69a}$$

$$F_{\mathrm{GD}} \equiv \hat{\mathbf{A}}_{\mathrm{T}} \cdot \left(\left(\breve{s} - s_{\alpha}\right)\frac{\partial T}{\partial u}\right). \tag{9.69b}$$

The interface condition (9.69a) reveals the “driving forces” for the interfacial motion: the free energy difference on both sides of the interface, $L(T_{\mathrm{E}} - T_{\mathrm{I}})/T_{\mathrm{E}}$, the Laplacian pressure due to the curvature ($2K_0$) (I.21), and the force, F_{GD}, (9.69b), which appears due to the temperature gradient inside the transition zone. The force F_{GD} may be called *Gibbs–Duhem force* because it may be derived from the Gibbs–Duhem relation. Notice that the driving forces in (9.69a) have units of pressure because they act on a unit area of the interface. Equations (9.64a) and (9.69a) identify the local interfacial variables v_{n}, K_0, T_{I}, $[T]$, $[\mathrm{d}T/\mathrm{d}u]$, and relate them to the thermodynamic interfacial quantities, L, σ, ε, L_{v} and kinetic properties of the medium, α, m. These equations are independent of the history and may be used as the interface conditions in long-time, long-range problems of phase transformation where heat diffusion is essential (see Sect. 9.6).

9.4.3 Gibbs–Duhem Force

To elucidate the physical meaning of this force, condition (9.61) is not enough; we need to have detailed knowledge of the temperature gradient field inside the interface, see (9.69b). Let us solve the quasi-stationary GHE (9.60) for $\mathrm{d}T/\mathrm{d}u$ inside the interface, using a method of asymptotic expansion, in the case where the temperature gradient in the final phase ($u = u_{\beta}$) is zero. In this case, obviously, $T_{\mathrm{I}} = T_{\beta}$. First, we obtain integral representations of the temperature gradient:

$$\lambda\frac{\partial T}{\partial u} = -\mathrm{e}^{-k_{\mathrm{T}}u}\int_{u_{\beta}}^{u} \mathrm{d}\tilde{u}Q(\tilde{u})\mathrm{e}^{k_{\mathrm{T}}\tilde{u}}. \tag{9.70a}$$

Then we integrate expression (9.70a) by parts:

$$\lambda \frac{\partial T}{\partial u} = -\int_{u_\beta}^{u} \mathrm{d}\tilde{u} Q(\tilde{u}) + k_{\mathrm{T}} \int_{u_\beta}^{u} \mathrm{d}\tilde{u} \int_{u_\beta}^{\tilde{u}} \mathrm{d}\tilde{\tilde{u}} Q(\tilde{\tilde{u}}) + O\left(L_{\mathrm{v}}^3 k_{\mathrm{T}}^3\right). \tag{9.70b}$$

Expansion in (9.70b) in increasing powers of k_{T} may be considered an expansion into "powers of disequilibrium." If $L_{\mathrm{v}} k_{\mathrm{T}} \ll 1$ that is, if the conditions (9.58) and (3.85) are true, expansion (9.70b) can be truncated after the second term and, for the heat-source density, we can use the energy representation (9.60a) with the equilibrium solution $\eta_{\mathrm{e4}}(u)$ (3.66). Finally, substituting (9.70b) into (9.69b) gives us the expression for the Gibbs–Duhem force (Verify!):

$$F_{\mathrm{GD}} = -\frac{v_{\mathrm{n}}}{\lambda}\left(I_1 - \frac{C}{\lambda} v_{\mathrm{n}} I_2 - 2K_0 I_3\right), \tag{9.71a}$$

where the entropy density moments I_i's are defined as follows:

$$I_1 = \hat{\mathbf{A}}_{\mathrm{T}} \cdot \left((\breve{s} - s_\alpha) p(u)\right);\ I_2 = \hat{\mathbf{A}}_{\mathrm{T}} \cdot \left((\breve{s} - s_\alpha) \int_{u_\beta}^{u} \mathrm{d}\tilde{u} p(\tilde{u})\right);$$

$$I_3 = \hat{\mathbf{A}}_{\mathrm{T}} \cdot \left((\breve{s} - s_\alpha) \int_{u_\beta}^{u} \mathrm{d}\tilde{u} \left\{\kappa_{\mathrm{E}} \left(\frac{d\eta}{d\tilde{u}}\right)^2 + p(\tilde{u})\right\}\right). \tag{9.71b}$$

$$p(u) = \breve{e} - e_\beta = T_{\mathrm{E}}(\breve{s} - s_\beta). \tag{9.71c}$$

Substitution of (9.71a) into (9.69a) yields the evolution equation for the interface motion:

$$L \frac{T_{\mathrm{E}} - T_\beta}{T_{\mathrm{E}}} + \frac{1}{2} C \frac{[T]^2}{T_\beta} = \left(\frac{\sigma}{m} + \frac{I_1}{\lambda}\right) v_{\mathrm{n}} + 2\sigma K_0 - \frac{C}{\lambda^2} I_2 v_{\mathrm{n}}^2 - \frac{2}{\lambda} I_3 v_{\mathrm{n}} K_0. \tag{9.72}$$

Exact expressions for the moments I_i's depend on the type of the potential used. However, one can see from (9.71b) that $I_3 \approx I_2 \approx I_1 L_{\mathrm{v}}$. This means [see (9.71a)] that the Gibbs–Duhem force is either parallel or antiparallel to the interfacial velocity depending on the value of the moment I_1. It is instructive to express this moment and F_{GD} using only measurable quantities that characterize an interface such as the interface energy σ, entropy χ, and latent heat L. In the medium with $\kappa = \mathrm{const}(T)$, the entropic representation of $p(u)$ in (9.71c) yields:

$$\begin{aligned} I_1 &= T_{\mathrm{E}} \hat{\mathbf{A}}_{\mathrm{T}} \cdot \left(\{s(u) - s_\alpha\} \cdot \{s(u) - s_\beta\}\right) \\ &= T_{\mathrm{E}} \hat{\mathbf{A}}_{\mathrm{T}} \cdot \left(\delta s^2 + 2 \frac{[s]}{[\eta]} (\eta_{\mathrm{e4}} - \bar{\eta})\ \delta s + [s]^2 \frac{(\eta_{\mathrm{e4}} - \eta_\beta)(\eta_{\mathrm{e4}} - \eta_\alpha)}{[\eta]^2}\right), \end{aligned} \tag{9.73}$$

where $\bar{\eta} = (\eta_\beta + \eta_\alpha)/2$. Using (3.74c) and the bell-like shape of δs we obtain:

$$\begin{aligned} &\hat{\mathbf{A}}_{\mathrm{T}} \cdot \left(\delta s^2 \right) \approx \frac{1}{L_{\mathrm{v}}} (\Gamma_{\mathrm{s}}^{(\eta)})^2; \ \hat{\mathbf{A}}_{\mathrm{T}} \cdot ((\eta_{\mathrm{e4}} - \bar{\eta})\ \delta s) \approx 0; \\ &\hat{\mathbf{A}}_{\mathrm{T}} \cdot \left(\frac{(\eta_{\mathrm{e4}} - \eta_\beta)(\eta_{\mathrm{e4}} - \eta_\alpha)}{[\eta]^2} \right) \approx -\frac{1}{6} L_{\mathrm{v}}. \end{aligned} \tag{9.74}$$

Taking into account that $[s(T_{\mathrm{E}})] = L/T_{\mathrm{E}}$, see (2.4a), and substituting (9.74) into (9.73), we obtain:

$$I_1 \approx \frac{T_{\mathrm{E}}}{L_{\mathrm{v}}} (\Gamma_{\mathrm{s}}^{(\eta)})^2 - \frac{L_{\mathrm{v}}}{6T_{\mathrm{E}}} L^2. \tag{9.75}$$

Finally, substituting (9.75) into (9.71a) we arrive at the linear approximation for the Gibbs–Duhem force:

$$F_{\mathrm{GD}} \approx \frac{v_{\mathrm{n}}}{\lambda} \left(\frac{L_{\mathrm{v}}}{6T_{\mathrm{E}}} L^2 - \frac{T_{\mathrm{E}}}{L_{\mathrm{v}}} (\Gamma_{\mathrm{s}}^{(\eta)})^2 \right). \tag{9.76}$$

Significance of this relation is in that it is expressed through measurable quantities and thermodynamic properties of a system only, yet it is applicable to many different situations. The type of transition affects the relative magnitudes of $\Gamma_{\mathrm{s}}^{(\eta)}$ and L (e.g., $L = 0$ for APB), which in turn dramatically affects the magnitude of I_1, being negative for a typical first-order transition and positive for a second-order transition. Hence, F_{GD} propels the motion of an interface that appears after the first-order transition serving as a driving force and opposes motion of an interface after the second-order transition manifesting a *drag force* [see (9.69a) and (9.76) and Fig. 9.6].

9.4.4 Interphase Boundary Motion: Heat Trapping

Now let us analyze various regimes of interface motion in the process of a phase transformation of the first order. To be specific, let us consider growth of the β-phase (e. g., crystal) replacing the α-phase (e.g., liquid). This case corresponds to the u-axis in Fig. 9.6 directed from β-phase to α-phase and the growth of the β-phase corresponds to v_{n} being positive. Then an interesting observation can be made from inspecting (9.72) and (9.75) (see Fig. 9.9). For a stationary motion of a plane interface (v_{n}=const(t), $K_0 = 0$) it is possible to have β-phase growing ($v_{\mathrm{n}} > 0$) even when its temperature after transformation is above the equilibrium value ($T_\beta > T_{\mathrm{E}}$). Mathematically, if I_1 in (9.75) is negative and large enough it is possible to balance the first term in the right-hand side of (9.72). Physically it means that if the Gibbs-Duhem force in (9.76) becomes large enough, it propels the interface against the negative bulk driving force. However, in this case looking only at the linear terms in (9.72), we obtain a wrong result that $v_{\mathrm{n}} < 0$ for $T_\beta < T_{\mathrm{E}}$ that is, the β-phase is shrinking although it is favored by the phase diagram (its temperature is below the equilibrium value). This means that, although condition (9.58) applies, in order to balance (9.72) we must take into account the nonlinear terms. This effect is called *heat trapping*.

To elucidate this effect let us analyze it in the system described by the tangential potential. First, as we can see from (9.72), for the heat trapping to be possible, the coefficient in front of the term linear in v_n must be negative. Hence, using (9.75) as an estimate, taking into account that for the tangential potential $\Gamma_s^{(\eta)} = 0$ (Verify!) and finally using (5E.7) we obtain the heat-trapping criterion:

$$\mathrm{Ht} \equiv \frac{\lambda \sigma T_\mathrm{E}}{mL^2 L_\mathrm{v}} = \frac{\lambda}{\mu L L_\mathrm{v}} < \frac{1}{6}, \tag{9.77a}$$

It may be interpreted as the upper limit on the rate of thermal conduction or the lower limit on the interfacial thickness in the system. In this equation, Ht is called the *heat-trapping number* and (5E.3) was used. Furthermore, using (9.46) and

$$L_\mathrm{v} = 4\sqrt{\frac{\kappa}{W}}, \ \sigma = \frac{1}{6}\sqrt{\kappa W}, \tag{9.3E.4, 3E.5}$$

the heat-trapping criterion can be presented as follows:

$$R < 4\frac{L^2}{WCT_\mathrm{E}}, \tag{9.77b}$$

Second, for the tangential potential the coefficients I_i of the Gibbs–Duhem force are (Verify!):

$$\begin{aligned} I_1 &= -0.1583\, L_\mathrm{v}\frac{L^2}{T_\mathrm{E}};\ I_2 = -0.0403\, L_\mathrm{v}^2\frac{L^2}{T_\mathrm{E}}; \\ I_3 &= -0.0403\, L_\mathrm{v}^2\frac{L^2}{T_\mathrm{E}} + 0.0066\, L_\mathrm{v}^2\frac{WL}{T_\mathrm{E}}. \end{aligned} \tag{9.78}$$

Now, substituting (9.78) into (9.72) with $K_0 = 0$ and taking into account (9.58), (I.10) and (9.61), which relates the final temperature of the β-phase T_β to the initial temperature of the α-phase $T_\alpha = T_0$, we can obtain an equation for the stationary velocity, v_n=const(t), of a plane interface:

$$\Delta\,\Theta = 1 + (\mathrm{Ht} - 0.1583)\mathrm{Pe} + 0.0403\mathrm{Pe}^2 - O\left(\mathrm{Pe}^3\right). \tag{9.79a}$$

If the criterion (9.77a) is not fulfilled then the stationary regime ($\mathrm{Pe} > 0$) exists for $\Delta\Theta > 1$ only and the difference from the sharp-interface case (I.14) is insignificant. If the criterion (9.77a) is fulfilled then the stationary regime ($\mathrm{Pe} > 0$) exists also for

$$1 - \frac{(\mathrm{Ht} - 0.1583)^2}{4 \times 0.0403} \equiv \Delta_\mathrm{tr} \le \Delta\,\Theta < 1. \tag{9.79b}$$

The function Pe(ΔΘ) of (9.79a) is depicted in red on Fig. 9.9a. Compare this curve with the blue line, which expresses solution of the same problem without the effects of the interfacial diffuseness taken into account. Important difference is that the diffuse-interface stationary solution does not vanish for $T_0 > T_E - L/C$ and remains positive for $T_E - L/C < T_0 < T_{tr}$. One may say that in this case the kinetic regime of growth "penetrates" the temperature domain of the diffusion regime. However, the most interesting part of the story is revealed if, using (9.61) and (9.79a), we calculate the final temperature of the β-phase after the transformation. We can see (red line in Fig. 9.9b) that this temperature is above the equilibrium point $T_\beta > T_E$. During this process the low-symmetry β-phase grows ($v_n > 0$) at the expense of the high symmetry α-phase at a temperature above the equilibrium point ($T_\beta > T_E$). In case of crystallization of water, for instance, this would have meant growth of superheated ice from supercooled water. For the crystallization of ice, however, criterion (9.77a) is not fulfilled but is quite feasible for crystallization of other substances.

Another possibility of growing β-phase ($v_n > 0$) with the temperature after transformation above the equilibrium value ($T_\beta > T_E$) is due to the Gibbs–Thompson effect that is, the change of the equilibrium temperature due to the curvature of the phase-separating interface if the center of the curvature is in the α-phase ($K_0 < 0$), see (9.72) and (I.21).

9.4.5 APB Motion: Thermal Drag

In Sect. 5.5 we considered motion of the isothermal APB, driven by its own curvature. Conventional logic dictates that APB's do not cause temperature gradients and/or thermal effects because the latent heat that generates the effects vanishes in continuous transitions: $L = 0$ [see (2.4a), (2.44b)]. What is overlooked by such logic is a contribution of the surface internal energy associated with the interface. To properly describe this effect we need to apply TDGLE (5.1) and GHE (9.42) to the APB motion (see Fig. 9.10). However, we will show here that the non-isothermal drumhead equations (9.64a) and (9.72), applied to the APB motion, describe the *temperature waves* of the amplitude [T] and average temperature gradient $\left|\overline{dT/dU}\right| = [T]/L_v$, see (9.59). Indeed, due to the symmetry of the continuous transition we may assume that [dT/du]=0 (still [T]≠0; why?). Hence, the wave represents a temperature double layer, see Fig. 9.10. Then a system of two simultaneous equations, (9.64a) and (9.72) with (9.75), for the three drumhead variables of the layer: v_n, K$_0$, [T], can be resolved as follows (Verify!):

$$[T] = \frac{2\varepsilon K_0}{C\left\{1R\frac{3}{4}(1+\tau)q\right\}};\ q = \frac{a}{CT_C} \tag{9.80a}$$

$$v_n = \frac{2\alpha K_0}{R + \frac{3}{4}(1+\tau)q}. \tag{9.80b}$$

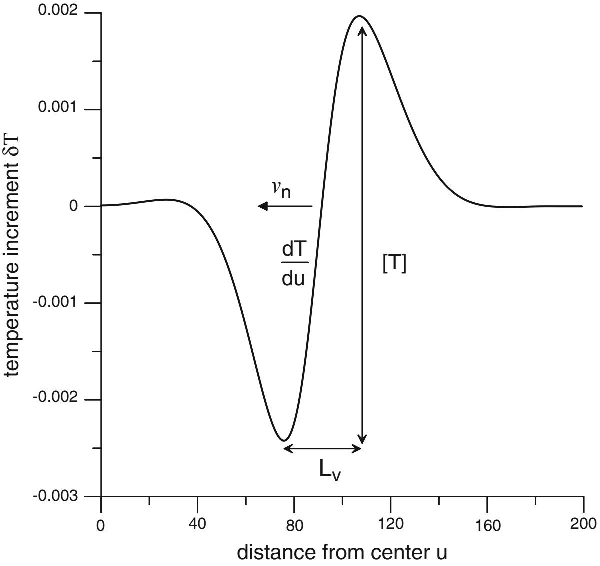


Fig. 9.10 Temperature distribution inside a curved APB moving towards its center of curvature at u=0 [calculated using TDGLE (5.1) and GHE (9.42)]

Notice that the temperature wave amplitude [T] is proportional to the curvature of the interface; for a spherical particle (9.80b) can be resolved using the bubble differential condition:

$$\dot{\kappa}_0 = V_n K_0^2. \tag{5.36}$$

Also notice that the wave amplitude [T] is critically dependent on the temperature τ. To see that we need to take into account that $\varepsilon = \sigma + T\chi \propto \sqrt{\tau}$ and recall that

$$L_{APB} = 2\sqrt{\frac{2\kappa}{a(\tau)}}, \tag{3E.6}$$

$$\sigma = \frac{2}{3}\sqrt{2a\kappa(\tau)}^{3}, \tag{3E.7}$$

$$\chi = \frac{1}{T_c}\sqrt{2a\kappa(\tau)}. \tag{3E.8}$$

Comparison of (9.80b) with (5.38a) reveals the*thermal drag effect*: a piece of the APB with the temperature gradients inside the transition region moves slower than the isothermal one. The interfacial dynamics is limited not only by the mobility of the interface*m*but also by the thermal conductivity λ of the system with the kinetic

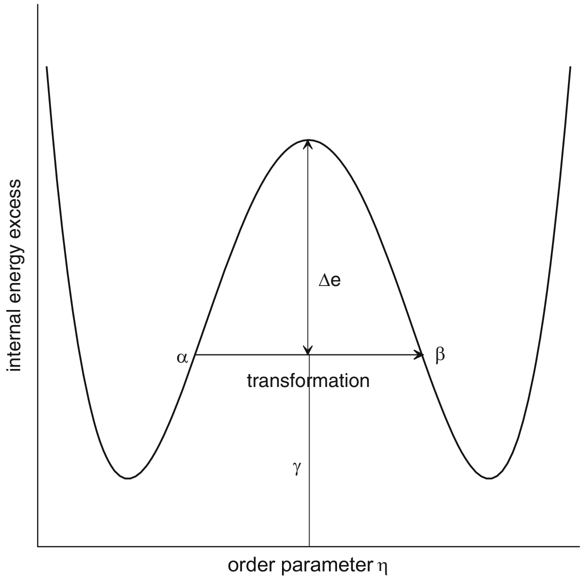


Fig. 9.11 Borrow–return mechanism. Internal energy of a substance as a function of an order parameter

number R measuring the relative roles of these processes. The thermal drag creates a temperature wave around the moving APB even when far away from the interface isothermal conditions are maintained. The drag effect is explained by the Gibbs-Duhem force being antiparallel to the boundary's velocity, hence, playing a role of a drag force (see Fig. 9.6). "Dissolution" of a small particle of a minority-variant is caused by the Laplacian pressure from the curved interface. At the same time, the Gibbs-Duhem force generates the thermal pressure in the particle that opposes the Laplacian pressure. In the ideal insulator, that is, a material with $\lambda=0$, these pressures may neutralize each other.

The FTM provides an "energetic" an explanation of the drag effect based on a *borrow–return* mechanism (see Fig. 9.11). Both variants (α, β) on either side of the interface are characterized by the same amount of internal energy density: $e_\beta = e_\alpha$. Transformation inside the interface from one variant to the other, however, requires crossing the internal energy barrier (maximum), which corresponds to the disordered phase with $\eta_\gamma = 0$. So, a small volume of substance must "borrow" a certain amount of energy proportional to $\Delta e = e_\gamma - e_\alpha$ from the neighboring volumes while moving uphill on the internal energy diagram (Fig. 9.11) and "return" it later on the downhill stage of the transformation. The borrow–return mechanism entails the internal energy flux vector (9.45) through the interface. In the non-isothermal drumhead approximation it is

$$\begin{aligned} J_\mathrm{E} = -\lambda \frac{\mathrm{d}T}{\mathrm{d}u} + \kappa_\mathrm{E} v_\mathrm{n} \left(\frac{\mathrm{d}\eta_{\mathrm{e}4}}{\mathrm{d}u}\right)^2 &= v_\mathrm{n}(\hat{e} - e_\beta) + O(\mathrm{Pe}^2 + \mathrm{PeGe}) \\ &\approx \frac{a}{4}(\eta^4 - \eta^2 - \tau^2 - \tau) v_\mathrm{n}, \end{aligned} \tag{9.81}$$

where we used the equilibrium solution $\eta_{e4}(u)$ of Example 3.2 and (2.11) and (9.42) to calculate the last expression. (Verify!) Notice that the energy flux inside the interface does not vanish even when the energy densities outside the interface are equal, $e_\beta = e_\alpha$. One can see that $\mathbf{J}_E$ is a bell-like function of space, peaked at the point where $\eta_\gamma = 0$. Such internal energy exchange requires a transport mechanism, which is served here by the heat conduction. Thus, the drag effect is due to the finite rate of heat transfer measured by the conductivity λ. Thermal drag occurs because the conversion of one variant into another is accompanied by the transmission of energy between neighboring pieces of a material, which cannot occur infinitely fast. It is important to note again that the thermal drag exists despite of the vanishing latent heat of the transition, which causes thermal effects in discontinuous transformations.

9.5 Length and Energy Scales

To better understand various features and effects of the phase transformations with varying temperature field we need to analyze different length and energy scales relevant to the process. Let us concentrate on the first-kind transformation with the tangential potential. To this end we have encountered three relevant energy scales: the thermal energy density CT_E, the latent heat L, and the free energy density barrier W. Two parameters describe their ratios: $P = 6L/W$ and $Q = L/CT_E$ (9E.3 and 9E.4). However, a unified parameter, called the *thermodynamic number*, may be defined such

$$U \equiv \frac{1}{PQ} = \frac{WCT_E}{6L^2} \tag{9.82}$$

that, together with the kinetic number R, it determines practically all different regimes of the transformations. For instance, according to (9E.6) for $P \to \infty$ the maximum value of M_t is $3/4U$, which means that all different cases of the nonclassical nucleation can be classified in terms of the numbers R and U (see Fig. 9.5). Moreover, the heat-trapping criterion (9.77a) can be expressed as $RU < 2/3$. This means that all thermodynamic systems may be divided into a few universality classes with similar thermal behavior depending on the magnitudes of U and R. For the continuous transformation there are only two relevant energy scales and their ratio $q = a/CT_C$ (9.80a) plays the role of the thermodynamic number for the continuous transformations.

On the other hand, the thermal properties of the system give rise to the capillary l_c and kinetic l_μ length scales:

$$l_c = \frac{\sigma C T_E}{L^2};\ l_\mu = \frac{\lambda}{\mu L};\ \mu = \frac{\gamma \kappa L}{T_E \sigma}, \tag{9.83}$$

which, together with the fundamental length scale $L_{\mathrm{v}} = 4\sqrt{\kappa/W}$, determine system's behavior. It is important to note that the thermodynamic and kinetic numbers may be represented as the ratios of the length scales of the system:

$$U = \frac{l_{\mathrm{c}}}{L_{\mathrm{v}}};\ R = \frac{l_{\mu}}{l_{\mathrm{c}}}. \tag{9.84}$$

Equation (9.84) makes it possible to interpret the thermal effects as an interplay of different length scales in the system.

9.6 Pattern Formation

In this section, FTM will be applied to a few of the real-life problems which result in the formation of complex structures—*patterns*. In some sense, this section is central in this book because it demonstrates many of the advantages of the Method. Up to this point all the problems that we encountered were tackled with the help of different theoretical methods. Although these methods can also be applied to the problems of pattern formation in phase transformations, we will take advantage of a very effective method of *numerical simulations*. The purpose of this section is not to present results useful for practical applications but to provide a useful framework for the theoretical and numerical analyses of the system. One of the advantages of the numerical simulations is that this approach allows intuitive, graphical analysis of the results. We will show that a combination of only two processes, phase transition described by TDGLE (5.1) and heat redistribution described by GHE (9.42), is capable of generating very complicated patterns, which are similar to those observed in experiments, specifically crystallization. These equations should be supplemented with a free energy potential that specifies the system and the boundary and initial conditions that specify the physical situation. To describe the system we use the tangential potential (9E.1). For the boundary conditions we choose thermal isolation of the system. Any realistic phase transformation starts with a nucleation stage when the first traces of the product phase emerge from the bulk of the parent phase. In this section, we do not intend to reproduce this stage adequately and the simulations start—the initial conditions—with a very small fraction of the product phase β already present in the almost uniform parent phase α at the same temperature $T_0 < T_{\mathrm{E}}$ as the phase β.

Although one can descretize these equations as they are, a more physically sound approach calls for the scaling of these equations. The latter has the following advantages. First, the scaling helps find the number of independent variables and reveal important physical quantities that determine behavior of the system. Second, computationally, it is easier to deal with dimensionless quantities than the dimensional ones. We scale the space, time and temperature as follows:

$$\tilde{x} = \sqrt{\frac{W}{\kappa}}x, \tilde{t} = \gamma W t, \tilde{T} = C\frac{T - T_0}{L}, \tag{9.85}$$

where the tilded variables are dimensionless and $\tilde{X}$ is the dimensionless size of the system. From now on we will be using only the dimensionless variables; hence, we may drop the tildes without any confusion. Then the dimensionless evolution equations for our system take the form:

$$\frac{\partial \eta}{\partial t} = \nabla^2 \eta - \omega(\eta)\left(1 - 2\eta + \frac{T - \Delta\Theta}{4U}\right), \tag{9.86a}$$

$$\frac{\partial T}{\partial t} = R\nabla^2 T + \frac{6}{P}\left[\nabla^2 \eta - \omega(\eta)(1 - 2\eta - P)\right]\frac{\partial \eta}{\partial t}, \tag{9.86b}$$

where U, P, R, and $\Delta\Theta$ are defined above. Notice that the original, dimensional system of equations (9.42), (5.2), and (9E.1) has seven independent material properties that describe the system: (C, L, T_E, W, λ, κ, γ) while the scaled system (9.86) has *irreducible* set of only three material parameters: (U, P, R). Together with the initial temperature T_0 or supercooling $\Delta\Theta$ and the system's size X, they determine different regimes of evolution of the system.

9.6.1 One-Dimensional Transformation

In Fig. 9.12 results of the numerical calculations of the discontinuous phase transformation in a simple one-component, 1d system under conditions of thermal isolation are presented. The simulations started at the state just below the α spinodal point with a small-amplitude noise added to the initial distribution of the OP. Significant advantage may be gained by looking at the simulation results against the backdrop of the equilibrium state diagram (see Fig. 9.1). The following features of the inhomogeneous transformation may be observed. On the early stage ($t < 1{,}100$, Fig. 9.12a) we observe formation of the (drumhead) interface and structural period (the OP spacing). The oscillatory mechanism emerged from the finite wavelength instability of the adiabatically stable transition state (see Fig. 9.1) and in the early stages of decomposition ($t < 1{,}500$, Fig. 9.12a) created an almost perfect periodic domain structure with the wave number described by (9.53). On the later stage ($t \sim 2{,}000$) we observe development of the *coarsening* process, which starts practically immediately after the emergence of the almost perfect periodic domain structure. The coarsening takes one of two routes: dissolution of a layer accompanied by a local temperature dip or coalescence of two neighboring layers accompanied by a temperature spike. Both types eventually lead to a new equilibrium state with the new period. On the later stage ($t > 4{,}000$, Fig. 9.12c) we observe the end of the first stage of coarsening with the formation of an almost perfect periodic structure of the β- and α-phase plates with the *doubled period.*

It is customary to view coarsening as a curvature-driven motion. In this case, there would be no coarsening in a 1d system where all boundaries are flat. In fact, coarsening is driven by the reduction of surface energy, which makes coarsening subjected to the thermal effects. Analysis of the coarsening scenario in the 1d closed system reveals the mechanism of *the sequential doubling of the structural period*,

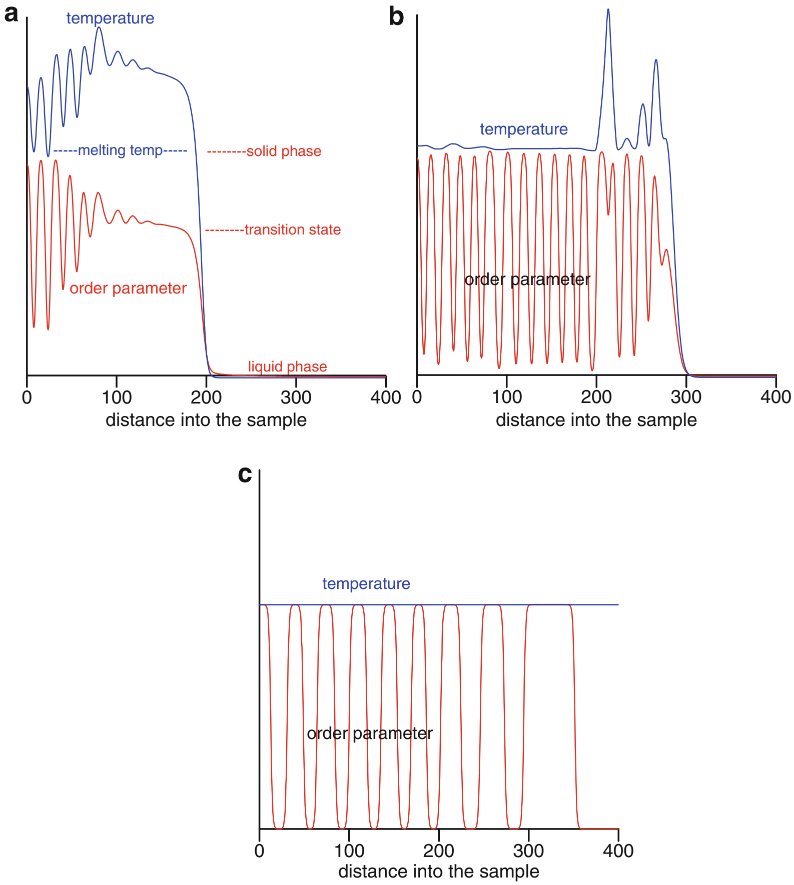


Fig. 9.12 Numerical simulation results of the 1d closed system (86) with $U = 0.5, P = 2, R = 1$, $\Delta\Theta = 0.505$: (**a**) $t = 1{,}100$, (**b**) $t = 1{,}500$, (**c**) $t = 4{,}500$

which is completely different from the traditional Lifshitz–Slezov–Wagner mechanism of coarsening.

9.6.2 *Two-Dimensional Transformation*

Even more interesting results come about in the numerical simulations of the two- and three-dimensional systems. In Fig. 9.13a, b the 2d color maps of the OP and temperature fields after long-time ($t \sim 1{,}000$) simulation of the transformations described by (9.86) in a large system of $X = 1{,}000$ for the values of ($U = 0.5$, $P = 20, R = 2, \Delta\Theta = 0.5$) are depicted. The simulations started with a small circular seed of the β-phase (initial radius equals ~$20l$) in the sea of the α-phase, all at the temperature $T_0 < T_E$. Very quickly ($t_d \sim 10$) the system develops the drumhead interface, visible in Fig. 9.13a. However, growth of a circular disk is not a stable

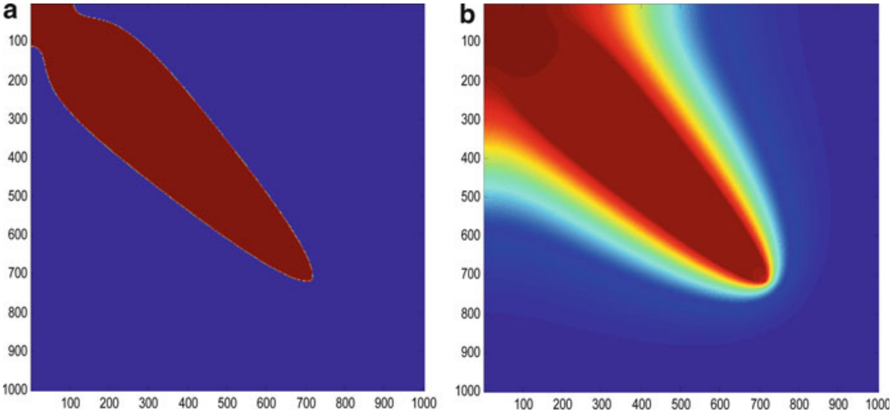


Fig. 9.13 Simulations of the growth of a spherical (circular) particle of β-phase in a sea of α-phase in the system with $U = 0.5$, $P = 20$, $R = 2.0$, $\Delta\Theta = 0.5$. (**a**) Order parameter field; (**b**) temperature field

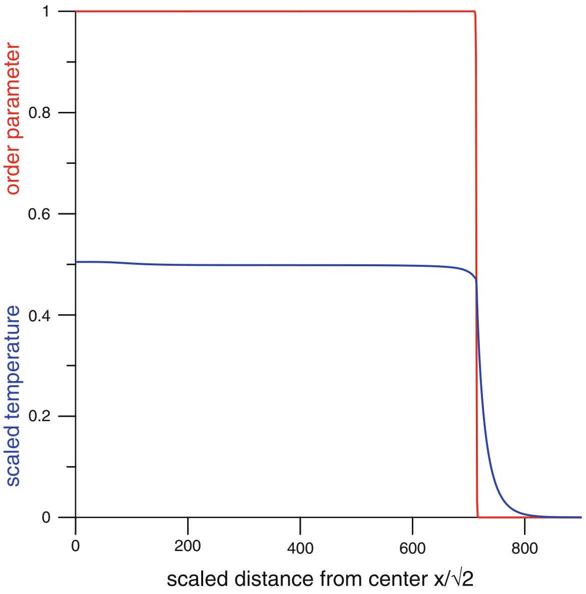


Fig. 9.14 Distribution of the temperature and OP along the axis of symmetry of the needle in Fig. 9.13 (the factor $\sqrt{2}$ is due to the diagonal direction of the needle). The equilibrium temperature corresponds to $T = 0.5$

into long needles. The process of breaking the spherical (circular) symmetry of the growing β-phase is called the Voronkov–Mullins–Sekerka instability.

In Fig. 9.14 the distribution of temperature and OP along the axis of symmetry of the needle are presented. Notice two important features of the temperature field. process and after the time $t_{\mathrm{VMS}} \sim 100$ small protrusions develop, which later on turn

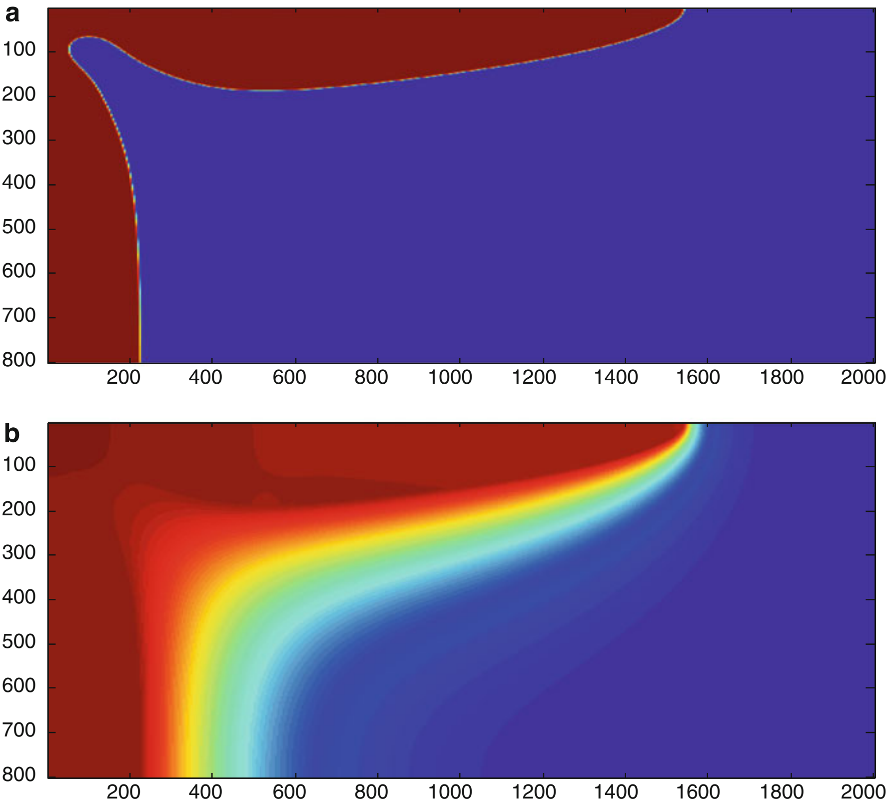


Fig. 9.15 Numerical simulations of the "dendritic forest." (**a**) Order parameter field; (**b**) temperature field

First, there is the jump of the temperature gradient across the drumhead interface at the tip of the needle due to the latent heat release. Second, there is visible overheating ($T > T_E$) at the root of the needle due to the "negative" curvature of the needle's interface close to the center (why?).

In Fig. 9.15 the 2d color maps of the OP and temperature fields of the simulations of the "dendritic forest" when the initial perturbations were placed on the plane crystal are depicted. To obtain the side branches one has to "turn on" the noise generator, which we considered in Chap. 8.

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Chapter 10
Transformations in Real Materials

We have explored many interesting properties of the Field-Theoretic Method and saw how it can help us better understand phase transformations at equilibrium and in dynamics. As the Materials Physics is moving into a new era of quantitative modeling and design of real materials, it is important to assess the challenges of the Method. One of those is obtaining reliable material parameters for it. FTM depends on a number of new parameters, which, although can be classified as material's properties, cannot be found in a table of physical and chemical constants. For example, the Method uses the Landau–Gibbs free energy of the system expanded in powers of the order parameter (Chap. 2) with the coefficients of expansion (A, B) or (W, D). A partial list of other parameters used by the method is: the gradient energy coefficient κ (Chap. 3) and the rate constant γ (Chap. 4). The problem is that these parameters cannot be easily identified in experiments and obtained through direct measurements because they are not measurable quantities, that is, do not have direct experimental meaning. In this chapter, we discuss the strategies and challenges in obtaining these parameters for realistic materials and the boundaries of applicability of the Method.

10.1 Parameters of FTM

The first attempts to find the coefficients of expansion of the Landau–Gibbs free energy consists in guessing their (T, P)-dependence, deriving the (T, P)-phase diagram of the system or its specific heat and compressibility, and comparing the theoretical results with the experimental values. This strategy seldom works for the Landau potential because of a complicated relation between the free energy and the expansion coefficients, (2.18). Identification of the material parameters was our primary motivation behind deriving the tangential potential of Sect. 2.4: for this potential, one parameter, D in (2.33), is equal to the difference of the free energies of the phases

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(not necessarily equilibrium) and can be found through the thermodynamic integration of the experimental data. Parameter W of (2.33) cannot be found from the thermodynamic measurements because the transition barrier height is not a thermodynamic (macroscopic) quantity.

One way to obtain the interfacial parameters is to derive them from the microscopic models through the coarse-graining procedure (Appendix A). This is a treacherous road, not well traveled yet. Another option is to obtain them from the experiments or atomistic (e.g., molecular dynamics) simulations. To realize this strategy, we need to identify the experimentally measurable or atomistically simulated counterparts and compare them with these parameters. For instance, the barrier-height parameter W can be found from the measurements of the interfacial energy and thickness

$$\sigma = \frac{1}{6}\sqrt{\kappa W}; \quad L_{e4} = 4\sqrt{\frac{\kappa}{W}}. \tag{3E.4, 3E.5}$$

These equations can be easily resolved for the parameters W and κ

$$\kappa = \frac{3}{2}\sigma L_{e4}; \quad W = 24\frac{\sigma}{L_{e4}}. \tag{10.1}$$

This approach has a drawback: it is difficult to extract the interfacial thickness from the experimental (or atomistic simulations) measurements.

Another strategy to identify the parameters of FTM is to use the data on the structure factor (see Sect. 7.5). This quantity is directly proportional to the intensity of the scattered radiation in any experiment on scattering of neutron, light, or X-rays. The wave vector $\mathbf{k}$ is the difference between the wave vectors of the incident and scattered radiations. The small-k (long wavelength) limit of $\hat{K}_{\bar{\eta},V}(\mathbf{k},\ t)$ can be measured by the light scattering and the large-k (short distance) part of $\hat{K}_{\bar{\eta},V}(\mathbf{k},\ t)$—by the neutron scattering. Theoretically, equilibrium value of the structure factor can be found as the long-time asymptotic limit of the following expression

$$\hat{K}_{\bar{\eta},V}(\mathbf{k},t) = \hat{K}_{\bar{\eta},V}(\mathbf{k},\ 0)\mathrm{e}^{2\beta(\mathbf{k})t} - 2\frac{\gamma k_B T}{V\beta(\mathbf{k})} \xrightarrow[t\to\infty]{} \frac{2k_B T}{V\left[\partial^2 g/\partial\eta^2(\bar{\eta}) + \kappa|\mathbf{k}|^2\right]}, \tag{7.56}$$

$$\beta(|\mathbf{k}|) = -\gamma\left[\frac{\partial^2 g}{\partial\eta^2}(\bar{\eta}) + \kappa|\mathbf{k}|^2\right]. \tag{7.45}$$

On the other hand, for the Landau potential

$$\frac{\partial^2 g}{\partial\eta^2}(\bar{\eta}) = \begin{cases} A \\ 2\left(B^2 - A + B\sqrt{B^2 - A}\right) \end{cases} \tag{2.22}$$

and for the tangential potential

$$\frac{\partial^2 g}{\partial \eta^2}(\bar{\eta}) = W(P,T) \pm 6D(P,T), \tag{2.36}$$

where the options in the right-hand side depend on the phase of the system. These relations can be resolved for the parameters of the potentials if the structure factor is measured for $\mathbf{k} = 0$ in the domains of stability of both phases separately and then extrapolated into the metastable region of at least one of them. The gradient energy coefficient can be identified as follows

$$\kappa = \frac{k_\mathrm{B}T}{V}\frac{\mathrm{d}\hat{K}^{-1}_{\bar{\eta},V}(\mathbf{k},\infty)}{\mathrm{d}|\mathbf{k}|^2}. \tag{10.2}$$

The surface tension can be extracted from the measurements of the interfacial structure factor [see (7.70)].

The rate constant γ can be extracted from the experimental (atomistic simulations) measurements of the speed of motion of the inter-phase interface in a transformation at a specified temperature below the equilibrium one T_E, and compared to the theoretical expression for the speed (5E.7). Then

$$\gamma = \frac{\sigma T_\mathrm{E}}{\kappa L}\frac{v}{T_\mathrm{E} - T}. \tag{10.3}$$

An alternative approach is to extract the rate constant γ from the expression for the dynamic structure factor, (7.56), (7.45). (Verify!).

A similar strategy can be used to extract the FTM parameters of the system with the OP conservation constraint (see Sect. 8.1). For instance, to find the concentration gradient-energy coefficient κ_C, one may identify the most pronounced wavelength of the structure, evolved in experiments or simulations, and compare it to the formula for the maximum marginal wavenumber k_d, (8.33), (8.34).

10.2 Boundaries of Applicability of the Method

One of the greatest advantages of FTM is that the method allows finding its own boundaries of applicability. They come from the thermodynamic constraints and limitations on the speed and dimensions of the evolving structures. Throughout the book we have identified several conditions of applicability. Here we will succinctly summarize these criteria.

1. Equation (2.9b) expresses limitations on the order of the polynomial expansion of the free energy in powers of the OP. It says that all essential contributions into the free energy must be accounted for.
2. The method is not applicable when the evolving structure has very fine scale. For instance, one of the limitations of the method is that the thickness of the inter-phase interface or APB is greater than the interatomic distance a

$$l \geq a \tag{10.4}$$

3. Mean-field methods do not take into account thermal fluctuations in the system. Hence, fluctuations can be added into the theory by hand. In FTM, they appear in the form of the Langevin force (see Chap. 7). Levanyuk–Ginzburg criterion, (7.28), (7.30), identifies constraints on the parameters of the theory. For instance, it says that the method is not applicable in the vicinities of the critical points, which are the high-fluctuations regions.

Chapter 11
Extensions of the Method

In the previous chapters, we demonstrated advantages of the FTM in describing phase transformations in material systems. However, the world of phase transformations is so diverse that the tools of one method may not be enough to describe all its wonders. There are many dimensions in which the method may and should be extended. First of all, we need to discuss the problem of computational efficiency of the method. Indeed, a rough estimate shows that in its full implementation the FTM is not very efficient in describing structural features of a macroscopic object because the method must naturally resolve the mesoscopic features, such as interfacial structure, which may not be critical for the overall structure and properties of the material. This problem may be resolved by using an adaptive mesh, that is, the computational grid of variable size [1]. Another strategy is to use a cellular automata method, which we discuss in this chapter. Second of all, the real-world materials manifest many features which are not directly related to phase transitions, e.g., grains and grain boundaries. These features and the problems associated with their modeling are also discussed in this chapter. We conclude this chapter and the book with an epilogue where we try to outline the challenges and future prospects of the Method.

11.1 Cellular Automata Method: "Poor Man's Phase Field"

As we saw in Sect. 5.4 not all details of the OP field are important for the global structure and rate of transformation in a material system. For instance, the fine details of the OP distribution inside the solid–liquid interface are not essential for the dendritic structure that grows from the supercooled liquid. However, being an integral part of the Field-Theoretic Method, the fine details need to be resolved in any simulation strategy, and this requires significant amount of the computational resources. To alleviate this problem many different methods were suggested; one of

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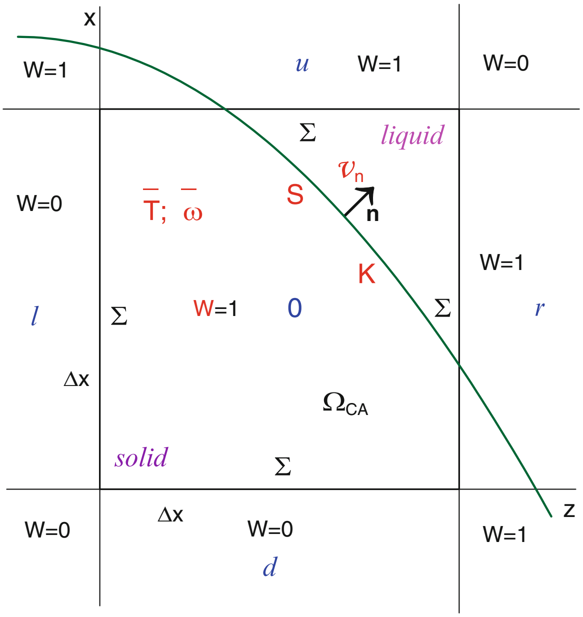

Fig. 11.1 Cellular automata method. A simulation cell with the drumhead interface that separates the phases

them, a *cellular automata method* (CAM), is essentially the Field-Theoretic Method coarse-grained one more time on the larger length scale [2, 3]. In essence, the CAM consists in dividing the whole system into cells of linear size l_{CA} and volume Ω_{CA} and averaging the field quantities in each cell (see Fig. 11.1). For the method to work, the cell size should be much larger than the interfacial thickness

$$l_{\mathrm{CA}} \gg L_v \tag{11.1}$$

but much smaller than the essential length scales of the problem in question.

To derive the CAM dynamic equations for the problem considered in Sect. 9.6.2, we will compute the thermal balance in each cell. For this, we integrate GHE (9.35) over the volume of the cell. Then

$$C\frac{\partial}{\partial t}\int_{\Omega_{\mathrm{CA}}} T\,\mathrm{d}^3x = -\oint_{\hat{\Omega}_{\mathrm{CA}}} \mathbf{J}_{\mathrm{T}}\,\mathrm{d}s + \oint_{\hat{\Omega}_{\mathrm{CA}}} Q(\mathbf{r},t)\,\mathrm{d}^3x. \tag{11.2}$$

The first integral we can present as $\bar{T}\ \Omega_{\mathrm{CA}}$, where $\bar{T}$ is the temperature averaged out over the volume of the cell. The second integral is the sum of the fluxes on all boundaries of the cell $\Sigma\hat{\Omega}_{\mathrm{CA}}\mathbf{J}_{\mathrm{T}}$. The third integral can be computed using the expression (9.36) for the heat source Q and the assumption that the OP field in the cell represents a train wave (interface), that is, it moves as a whole with the unchanging internal structure. Then, introducing the unit normal **n** directed toward the parent (liquid) phase and using (2.4a), (5.31a), we obtain

$$\int_{\Omega_{\mathrm{CA}}} Q(\mathbf{r},t)\,\mathrm{d}^3x = V_n \int_{S_0} \mathrm{d}s \int_{-\infty}^{\infty} \mathrm{d}n \left(\frac{\partial e}{\partial \eta} - \kappa_{\mathrm{E}} \frac{\partial^2 \eta}{\partial n^2}\right) \frac{\partial \eta}{\partial n} = V_n S_0 L, \tag{11.3}$$

where S_0 is the area of the piece of interface in the cell, L is the latent heat of the transformation, and V_n is the velocity of this piece in the direction of $\mathbf{n}$. Introducing a new variable, *portion of solid* in the cell

$$\bar{\varpi} \equiv \frac{\Omega_{\mathrm{S}}}{\Omega_{\mathrm{CA}}}, \tag{11.4}$$

where Ω_{S} is the volume of the solid phase in the cell Ω_{CA}, the heat-balance equation (11.1) can be rewritten as follows

$$C\frac{\partial \mathrm{T}}{\partial t} = -\,\Sigma \frac{\hat{\Omega}_{\mathrm{CA}}}{\Omega_{\mathrm{CA}}} \mathbf{J}_{\mathrm{T}} + L\frac{\partial \bar{\varpi}}{\partial t}, \tag{11.5a}$$

$$\frac{\partial \bar{\varpi}}{\partial t} = \frac{S_n}{\Omega_{\mathrm{CA}}} V_n. \tag{11.5b}$$

To obtain an equation that relates V_n to the average temperature in the cell and local curvature of the piece of interface we need to average TDGLE (5.1) over the volume of the cell. Due to (11.1), this is pretty much the same procedure that led us to (5.32). Then (disregarding the effects of heat-trapping) we obtain

$$V_n = \mu\left(T_{\mathrm{E}} - T - 2\frac{\sigma T_{\mathrm{E}}}{L} K_0\right). \tag{11.6}$$

Equations (11.4)–(11.6) are a system of simultaneous equations for the new cell variables $\bar{T}$ and $\bar{\varpi}$. However, the system is not complete—the missing information has been lost "during" the coarse graining. First, we need to compute the quantities S_0 and K_0; they can be found using values of the function $\bar{\varpi}$ in the cell of interest (0) and the surrounding cells (*front tracking*). Second, we need a *transition rule*, which indicates when (on what time step) the interface appears in 0-cell if before the cell was void of the interface. This rule can also be established based on the knowledge of the function $\bar{\varpi}$ in the surrounding cells. Hence, we can see that CAM depends heavily on the *neighborhood* of the 0-cell—$\{\varpi_i\}$. The extent (nearest neighbors, next-to-nearest, etc.) and symmetry (e.g., square or triangular lattice) of the neighborhood enriches the method at the expense of the computational resources (there is no free lunch!). The rules themselves depend on the physics of the transition process (nucleation, etc.) and properties of the system (e.g. anisotropy). They may be restored from the underlying FTM.

Let us consider a 2d system (you can think of it as being uniform in the third dimension) with crystallographic symmetry that corresponds to the square cell grid (<10> is the fastest growth direction), for which we will be using the nearest-neighbor (left, right, up, down) neighborhood (see Fig. 11.1). One may consider more complicated anisotropy of the system than its crystallography, but for the sake of simplicity we will not be doing that. Furthermore, we will rule out nucleation in front of the interface, which leaves only one mechanism of transformation—advancement of the phase interface. Then the transition rules may be realized in the CAM by introducing one more, subsidiary variable—the cell type W, which multiplies the right-hand side of (11.5b). By definition, $W_0 = 1$ if $0<\bar{\omega}_0<1$ (two-phase cell, that is with the interface inside) or if $\bar{\omega}_0 = 0$ (liquid cell) but $\bar{\omega}_i = 1$ for at least one of ($i = l, r, u, d$); all other cells, that is with $\bar{\omega}_0 = 1$ or 0, have $W_0 = 0$ (see Fig. 11.1).

There is a number of ways how the functions S_0 and K_0 can be calculated given the state of the neighborhood $\{\bar{\omega}_i\}$. For instance, one can assume that the interface describes an arch of a circle in the neighborhood and use $\{\bar{\omega}_i\}$ to deduce its length, radius, and angle of inclination in the central cell. Below, we will be using the following formulae for the curvature and slope

$$\mathrm{K}_0 = \frac{\mathrm{d}}{\mathrm{d}z}\left[\frac{(\mathrm{d}x/\mathrm{d}z)_0}{\sqrt{1+(\mathrm{d}x/\mathrm{d}z)_0^2}}\right]; \quad \left(\frac{\mathrm{d}x}{\mathrm{d}z}\right)_0 = \frac{W_0}{2}\sum_{i=l,0,r}(\bar{\omega}_{iu}-\bar{\omega}_{id}). \tag{11.7}$$

Now the system (11.4)–(11.7) can be dimensionalized using the following length, time, velocity, and temperature scales, respectively:

$$l_\mu = \frac{\lambda}{\mu L}, \quad \tau_\mu = \frac{l_\mu^2}{\alpha}, \quad v_0 = \frac{l_\mu}{\tau_\mu} = \frac{\mu L}{C}, \quad \frac{L}{C}, \tag{11.8}$$

and completely "cellularized," that is, discretized in space and time

$$\bar{T}_0^{+1} = \bar{T}_0 + a\left(\sum_{i=l,r}^{u,d}\bar{T}_i - 4\bar{T}_0\right) + \Delta\omega_0, \tag{11.9a}$$

$$\bar{\omega}_0^{+1} = \bar{\omega}_0 + \Delta\omega_0, \tag{11.9b}$$

$$\Delta\omega_0 = bW_0\xi_0\left(\Delta\Theta - \bar{T}_0 - \frac{1}{R}K_0\right), \tag{11.9c}$$

where $a = \lambda\Delta t/C\Delta X^2$, $b = v_0\Delta t/\Delta X$, $\xi_0 = S_0/l_{\mathrm{CA}}$, the supercooling $\Delta\Theta = C(T_{\mathrm{E}} - T_{\mathrm{initial}})/L$ is defined in (I.10), and kinetic number $R = \mu\sigma T_{\mathrm{E}}/\alpha L$—in (9.46), (9.83), (9.84). The system of equations (11.9) should be supplemented with BC and initial conditions. We will assume that initially the system consisted of a crystal with plane surface and a small bump with the size of a single cell on it immersed into a large volume of supercooled liquid phase at $\Delta\Theta > 0$. For the sake of simplicity for ξ_0, we will be using its isotropic average value of one. The method may be expanded to include the effects of anisotropy and presence of other components.

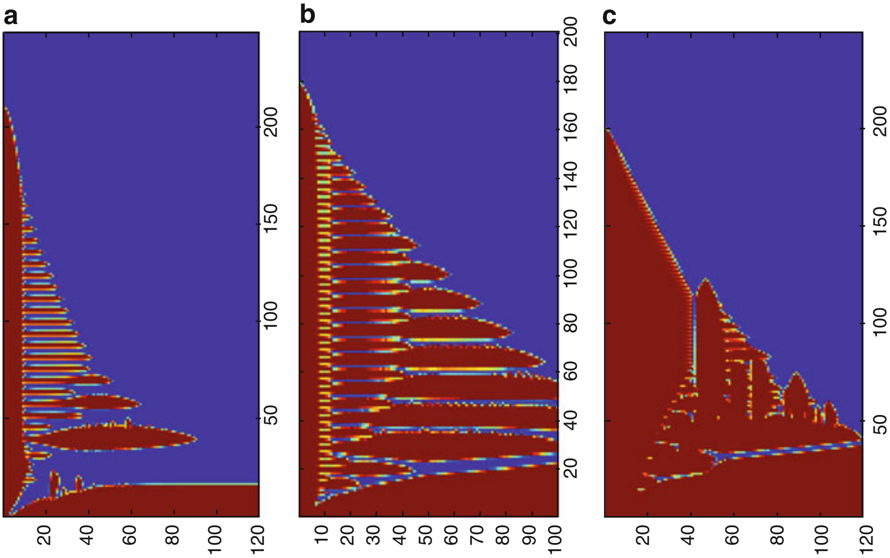

Fig. 11.2 Dendritic morphologies at different values of the supercooling: (**a**) $\Delta\Theta = 0.6$, (**b**) $\Delta\Theta = 0.85$, and (**c**) $\Delta\Theta = 1$

In Fig. 11.2 are presented numerical calculations using the system (11.9) for different parameters $\Delta\Theta$. The simulated patterns have many features of the real dendritic structures; namely, a little bump on a smooth interface turns into a long stem covered by side branches. A few interesting observations regarding the side-branch structure can be made. First, it is highly periodic with the period depending strongly on the supercooling. Second, the side-branch structure has a well-defined envelope. Third, at large supercoolings ($\Delta\Theta \geq 1$), the side branches disappear altogether; this effect is called the absolute (or second) stability. Fourth, moving away from the tip, the side-branch structure coarsens by doubling of its period. All of these features were observed experimentally.

Comparison of these results with those of the FTM presented in Sect. 9.6.1 and 9.6.2 is illuminating. First, both methods efficiently capture instability of a smooth interface to capillary-wave perturbations and "translate" this instability into long needles with rather smooth tip. However, to produce the side branches the Field Method needs an additional source of fluctuations, while CAM has, so to speak, the built-in fluctuations of sufficient amplitude to inspire the side branches. These fluctuations are related to the coarseness of the CAM grid, which also brings about grid-related anisotropy of the method. These features of the CAM do not allow it to resolve the subtle small-scale issues of the dendritic tip stability but make it an effective tool in large-scale microstructure modeling. Second, compare the process of side-branch coarsening with that of the 1d plates, which we observed in Sect. 9.6.1 and notice that in both cases the coarsening is a result of strong long-range interaction through the temperature field between the structural units of high-volume fraction; that is why both processes take similar paths of period doubling. Thus the mechanism of sequential period doubling is robust for coarsening in 1d or quasi-1d (dendritic branches) systems with a conserved quantity (energy).

11.2 Continuum Models of Grain Growth

Many solid materials consist of small crystallites called *grains*, which are domains of the same phase with different spatial orientations of their crystalline lattices. The grains are separated from each other by the grain boundaries (GB), which are 2d-extended defects with positive excess free energy and, therefore, thermodynamically unstable. Due to their global instability, curved GBs are known to move toward the centers of their curvatures. However, overall the GBs move such as to increase the average size of the grain $\bar{R}$, reduce the total GB area and thus the total free energy of the system. Simple dimensional analysis provides an approximate time dependence for $\bar{R}(t)$. Indeed, if we assume that GB energy is the only driving force for its motion then [4]

$$\frac{\mathrm{d}\bar{R}}{\mathrm{d}t} = +\frac{a}{\bar{R}}, \tag{11.10}$$

where the coefficient a is a product of the GB energy and mobility. Notice that the right-hand side of (11.10) is positive because we apply this formula to the average size $\bar{R}$ not the individual grain radii [cf. (5.36b) and (5.46)]. Solution of (11.10) is

$$\bar{R}^2 - \bar{R}_0^2 = 2at, \tag{11.11}$$

where $\bar{R}_0$ is the average grain size at $t = 0$ [cf. (5.38b) and (5.47)].

However, $\bar{R}$ is not the only characteristic that determines global evolution of the grain structure because grains of the same $\bar{R}$ can have different topological properties. The latter are characterized (in 2d case) by the topological class of a grain, k—the number of neighbors (or sides or triple junctions). Then the area of the 2d grain A obeys the following relation [5]:

$$\frac{\mathrm{d}A}{\mathrm{d}t} = \frac{a\pi}{3(k-6)}, \tag{11.12}$$

which shows that grains with more than six sides grow while those with fewer than six sides shrink.

A variety of models of grain growth have been proposed with a common feature that the GBs have zero thickness—the sharp interface models. However, recently several authors proposed rather different models of grain growth in which the GBs are assumed to be diffused, that is have finite thickness. To describe evolution of the grain structure, these models use the gradient-flow paradigm, which includes TDGLE with random forces but without the cross terms

$$\frac{\partial \eta_i}{\partial t} = -\gamma_i \frac{\delta G}{\delta \eta_i} + \xi_i(\mathbf{r}, t) \tag{7.31}$$

and the free energy functional

$$G = \int_{\Omega} \hat{g}\, \mathrm{d}^3 x \tag{3.27a}$$

with different free-energy density functions $\hat{g}$, which are the subject of discussion in this section. It is not our intention here to pass judgment on which model is better—this is a complicated question, which is still very much under consideration in the literature. Our goal here will be only to introduce the models and present their advantages and disadvantages.

11.2.1 Multiphase Field Models

Based on some similarities between the properties of the grains and antiphase domains (see Sect. 8.3). Chen et al. [6] proposed a model, in which a polycrystalline microstructure is described by a number of OP fields, $\{\eta_i(\mathbf{r}, t); i = 1..., N\}$, which designate different orientations of the grains. The free-energy density of the system is

$$\hat{g} = g\{\eta_i(\mathbf{r}, t)\} + \frac{1}{2} \sum_{i=1}^{N} \kappa_i |\nabla \eta_i|^2, \tag{11.13}$$

where κ_i are the gradient energy coefficients. The main requirement for the homogeneous part of the free-energy density is that it has degenerate minima of equal depth. A simple function which satisfies this requirement is

$$g = g_0(P, T) + A \sum_{i=1}^{N} \left(-\frac{1}{2}\eta_i^2 + \frac{1}{4}\eta_i^4 + \eta_i^2 \sum_{\substack{j=1 \\ j \neq i}}^{N} \eta_j^2 \right). \tag{11.14}$$

It has $2N$ minima located at $\{\eta_i = \pm 1; \eta_j = 0, j = 1..., i-1, i+1..., N\}$ in the N-dimensional space, each one representing a specific crystallographic orientation of a grain. The free energy of a plane GB is

$$\sigma_{\mathrm{GB}} = \int_{-\infty}^{\infty} \sum_{i=1}^{N} \left(\frac{\mathrm{d}\eta_i}{\mathrm{d}x} \right)^2 \mathrm{d}x. \tag{11.15}$$

The main contributions into the GB energy between two grains of orientations η_i and η_j come from the gradients of η_i and η_j because other OPs practically do not vary in the transition zone.

This model provides correct temporal variation of the average grain size as being asymptotically proportional to the square root of time and reasonably well reproduces evolution of the grain-size distribution function and local topological classes (number of sides) of the individual grains. However, deficiencies of the model are prominent. First, the model allows for a finite number of orientations only, while in a real material any grain orientation is possible. Second, in the model, the set of $2N$ allowed orientations is doubly degenerate and the orientations $\{\eta_i = +1; \eta_{j\neq i} = 0\}$ and $\{\eta_i = -1; \eta_{j\neq i} = 0\}$ form, so to speak, an anti-orientation GB with a finite GB energy (see Sect. 8.3), while in a real material they are totally equivalent and do not form a GB.

To describe evolution of multiphase systems, Steinbach et al. [7] developed a method where, instead of the OPs, the main field variables are partial phase contents $p_i(\mathbf{r}, t)$, $i = 1,\ldots, N$. These phase-field variables are not independent; they are defined on the Gibbsian simplex

$$\sum_{i=1}^{N} p_i(\mathbf{r}, t) = 1 \tag{11.16a}$$

and allowed to vary only between 0 and 1

$$0 \leq p_i \leq 1. \tag{11.16b}$$

The free-energy density of the system is

$$\hat{g} = \sum_{i=1}^{N} \left\{ g_i(P,T)p_i + \frac{1}{2} \sum_{j=1}^{i} \left[\alpha_{ij} p_i^2 p_j^2 + \kappa_{ij} \left(p_i \nabla p_j - p_j \nabla p_i \right)^2 \right] \right\}, \tag{11.17}$$

where $g_i(P, T)$ is the free-energy density of the individual phase i. Notice that the gradient energy contribution in (11.17) is a weighted sum of the squares of the Lifshitz invariants [see (8.86b)]. For the dynamics of the system, the authors used the relaxation ansatz (7.31).

The method has a number of inconsistencies. First and foremost, application of the relaxation ansatz (7.31) is not justified here because vanishing of the variational derivative is not the condition of equilibrium. Indeed, because the system is defined on the geometrically bounded simplex (11.16), the total free energy minimum can be achieved on its boundary where the functional (3.27a) is not differentiable. The method also has a computational disadvantage in modeling a multiphase system as it needs N field variables p_is to describe a system with N phases, while the method described in the book requires ~ $\log_2 N$ OP fields. However, the multiphase method had some success in simulations of evolution of the grain structure in monatomic systems as the average grain size was found to be proportional to time in power ~0.38.

11.2.2 Orientational Order Parameter Field Models

Morin et al. [8] introduced a model of evolution of a polycrystalline material in the d-dimensional space where the grains are characterized by a d-component vector field $\boldsymbol{\eta}(\mathbf{r}, t)$ whose magnitude represents the local crystalline order and direction represents orientation of the grain. The latter is characterized by the angle $\theta(\mathbf{r}, t) \equiv \operatorname{arcos}(\mathbf{i}\cdot\boldsymbol{\eta}/|\boldsymbol{\eta}|)$ that the vector field $\boldsymbol{\eta}(\mathbf{r}, t)$ makes with the fixed direction in space $\mathbf{i}$. The free-energy density of the system is

$$\hat{g} = f\left\{|\boldsymbol{\eta}(\mathbf{r},t)|^2,\ c(\mathbf{r},t),\ \nabla\boldsymbol{\eta},\ \nabla c,\ \cos[N\theta(\mathbf{r},t)]\right\}, \tag{11.18a}$$

where $c(\mathbf{r}, t)$ represents the local atomic concentration and N is the order of breaking the rotational symmetry of the system, that is, the number of distinguished orientations of grains. Evolution of the system is governed by d TDGLEs (7.31) for the nonconservative field $\boldsymbol{\eta}(\mathbf{r}, t)$ and a Cahn–Hilliard equation (plus the thermal fluctuations) for the conservative field $c(\mathbf{r}, t)$ [cf. (8.27)]

$$\frac{\partial c}{\partial t} = D\nabla^2\frac{\delta G}{\delta c} + \zeta(\mathbf{r},t).$$

The long-time behavior of the studied 2d system was dominated by the scaling regime when the structure factors of the concentration and ordering exhibited the so-called Porod's law, that is $S(q, t) \to q^{-(d+1)}$ for $q \to \infty$, where q is the magnitude of the Fourier wave vector. This result was attributed to the coupling between the nonconservative field $\boldsymbol{\eta}(\mathbf{r}, t)$ and the conservative field $c(\mathbf{r}, t)$. However, validity of the results may be called into question by the contribution to the free-energy density

$$\cos[N\theta(\mathbf{r},t)]\left[|\boldsymbol{\eta}(\mathbf{r},t)|^2\right]^2, \tag{11.18b}$$

which violates isotropy of the system. Indeed, just a mere rotation of the reference frame $(\mathbf{i}, \mathbf{j}, \mathbf{k})$ causes irreducible changes in the free energy differences between the grains of different orientations, which in turn should change the dynamics of the system.

Lusk [9] suggested a model where the lattices of differing orientations are distinguished by a set of lattice parameters $\{s_1, s_2, \ldots, s_N\}$, where N is the number of allowed grain orientations. However, in contrast to the previous model, these parameters do not enter into the free energy function. Instead, the free energy of the system depends on the gradients of these parameters only

$$\hat{g} = g(\eta,\ P,\ T) + \lambda(\eta)\sum_{i=1}^{N}(\nabla s_i)^2. \tag{11.19}$$

The lattice parameters obey the relaxation dynamics of the type (7.31). Using the matched asymptotic analysis, the author was able to recover the GB motion by mean curvature. He also obtained 1d analytical and numerical solutions for a stationary GB. However, this solution presents a GB as a layer of melt sandwiched between two solid crystallites—a wetted GB model, which is not the case in the polycrystalline materials far from melting point.

Kobayashi et al. [10] introduced a model of grain structure, which allows for an arbitrary orientation of grains and is invariant with respect to the reference frame. In the 2d realization of the model, the grains are characterized by two nonconservative fields, the OP field $\eta(\mathbf{r}, t)$ which is interpreted as the level of local crystalline order and the field $\theta(\mathbf{r}, t)$ which is interpreted as the local orientation of the grain lattice with respect to the fixed axis in space, say x. This is similar to the model [8]. However, what is different from the latter is that the free-energy density in this model depends only on the powers of the gradient of the field $\theta(\mathbf{r}, t)$

$$\hat{g} = g(\eta, P, T) + \alpha(\eta)|\nabla\theta| + \beta(\eta)|\nabla\theta|^2. \tag{11.20}$$

The presence of the linear term $|\nabla\theta|$ is required in the model for the localization of the GB at equilibrium. The equilibrium structure of the GB is accompanied by lowering of the value of the OP η, that is, disordering of the GB. Evolution of the ordering field is governed by the relaxation dynamics of the TDGLE type (7.31) with the relaxation coefficient that has singular dependence on η. The authors were able to reproduce some of the features of the grain structure in materials like dependence of the GB energy on GB misorientation (change in angle across the boundary), GB wetting and motion, and grain rotation (time change of orientation in the grain interior). However, due to significant singularity in the free-energy density (11.20), for its computational implementation, the method requires a number of physically unappealing fixes like the singular mobility or smoothing functions to emulate the singular term $|\nabla\theta|$. These measures also make the model computationally taxing.

11.2.3 Phase-Field Crystal

Elder et al. [11] introduced a method for modeling of transformations in materials including effects related to multiple crystal orientations. They called it the Phase-Field Crystal method because it describes phase changes as evolution of the atomic density field according to dissipative dynamics driven by minimization of the free energy of the system. The free-energy density is approximated as

$$\hat{g} = \frac{1}{2}\varphi\left[\alpha + \lambda\left(q_0^2 + \nabla^2\right)^2\right]\varphi + \frac{1}{4}\beta\varphi^4, \tag{11.21}$$

where α, β, λ, q_0 are material parameters and $\varphi(\mathbf{r}, t)$ is the deviation of the atomic density from the density of the liquid state, which is at equilibrium with the solid state at the temperature of the transformation. In the framework of this method, formation of a crystalline solid is signaled not by the value of an OP being greater than zero, but by the field $\varphi(\mathbf{r}, t)$ being unstable to the formation of a periodic structure. A full nonlinear solution of the minimization problem is very complicated even in 1d. The authors studied a one-harmonic-mode approximation of the linearized problem (the free-field problem). In the 2d small-α limit, the functional (3.27a) with the free-energy density (11.21) is minimized by the deviation

$$\varphi_{\mathrm{m}} = \bar{\varphi} + \frac{4}{5}\left(\bar{\varphi} + \frac{1}{3}\sqrt{-15\frac{\alpha}{\beta} - 36\bar{\varphi}^2}\right)\left[\cos\frac{\sqrt{3}x}{2q_0}\cos\frac{y}{2q_0} - \frac{1}{2}\cos\frac{y}{q_0}\right], \tag{11.22}$$

which represents a triangular distribution of "particles" with the reciprocal lattice vectors

$$\hat{b}_1 = \frac{1}{q_0}\left(\frac{\sqrt{3}}{2}\hat{i} + \frac{1}{2}\hat{j}\right), \quad \hat{b}_2 = \frac{1}{q_0}\hat{j}. \tag{11.23}$$

For this solution, the parameter q_0 represents the distance between the nearest-neighbor "particles," which correspond to the atomic positions.

To obtain the "phase diagram" between the average density $\bar{\varphi}$ and parameter α the authors used the Maxwell equal-area construct. Given that the field $\varphi(\mathbf{r}, t)$ is conservative and assuming that its dynamics is dissipative and driven by the minimization of the free energy, the authors used the Cahn–Hilliard equation (8.27) for the evolution of the field. Using the phase-field-crystal method, the authors obtained reasonable scenarios of evolution of the grain structure in materials, including grain growth and rotation.

11.3 Epilogue: Challenges and Future Prospects

We came to the end of our journey of studying the Field-Theoretic Method that helped us analyze various properties of phase transformations. It is the right time now to assess its pros and cons and speculate about its future. The greatest advantage of the Method is that it is on the solid theoretical footing, which allowed us on one hand to expand it on a broad variety of transformations found in materials and on the other hand to find its own limitations and boundaries of applicability. Another advantage of the Method is its transparent mathematical structure. This feature allowed us for both, to use the method as a theoretical tool and develop efficient computational schemes for practical purposes.

One of the greatest challenges of the Method is the need for parameters that correspond to the real materials or systems that undergo the transformations. These parameters cannot be measured in experiments. They can be calculated from the first principles, but this option is laborious and encounters significant difficulties. The author's hope is that these parameters will emerge from the computations, e.g., Monte Carlo or Molecular Dynamics with realistic interatomic potentials. Another challenge, particularly in computational applications, is to develop efficient algorithms that help offset the drawbacks of the method and bring the "computational cost" down. Both of these challenges need to be overcome for the successful application of FTM for quantitative modeling of material transformations in the three dimensional space.

The Method's advantages secure its great prospects. It may be expanded in many different directions. For instance, it naturally allows inclusion of the external physical fields (other than temperature and pressure), such as electric, magnetic, gravitational, into the analysis of transformations, which makes the Method more practical. Mainly in this book, we discuss the macroscopic systems of large (virtually infinite) sizes. However, the Method can be applied to systems of limited sizes, with small systems being the most interesting in this category. This is very useful because the Statistical Mechanics of Small Systems has not been developed yet. The Method is already expanding in the directions, which are not traditional for the science of phase transformations. For instance, it finds applications in biology, psychology, sociology, and even cosmology.

However, the Method experiences healthy competition from other methods, such as the Molecular Dynamics and Phase-Field Crystal. Both methods allow for microscopic resolution of the process, which on one hand is an advantage, but on the other hand, computationally slows them down considerably. We may be sure that all these challenges will make the Method stronger and more relevant to the theoretical and practical needs of the science of phase transformations.

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ERRATUM TO:

Appendix E: Eigenfunctions and Eigenvalues of the Schrödinger Equation and Sturm's Comparison Theorem

Alexander Umantsev

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On page 285, line 15, equation is incorrectly presented as:

$$\lambda < \lim_{x\to\pm\infty} \kappa(x)$$

The correct version is:

$$\lambda < \lim_{x\to\pm\infty} u(x)$$

On page 285, line 17, equation is incorrectly presented as:

$$\lambda > \lim_{x\to\pm\infty} \kappa(x)$$

The correct version is:

$$\lambda > \lim_{x\to\pm\infty} u(x)$$

The online version of the original chapter can be found at
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Appendix A: Coarse-Graining Procedure

Intention of this appendix is to show how a set of many microscopic variables can be converted into a smaller set of mesoscopic variables or even one continuous function through the procedure called *coarse-graining* (CG). There is no denial that after CG certain features of the system are lost; the hope is, however, that the essential ones are retained. We will demonstrate the CG using a simple model of ferromagnetism. Each atom in a crystal is supposed to have a magnetic moment μ_0, which may point in any direction. The concept may be clearly demonstrated on a particularly simple example of a unidirectional ferromagnetic "crystal," that is, a lattice of atoms with the magnetic moments pointing in only one of the two directions: upward or downward. Such model is called Ising model of a ferromagnet and the atomic magnetic moments—Ising spins. The state of each atom is represented by a variable σ_i ($i = 1, 2, \ldots, N$; N being the total number of atoms in the "crystal"), which takes on the values +1 or -1. Neighboring atoms in the lattice experience exchange interaction of the strength $J > 0$ and sign that depends on whether the moments are parallel or antiparallel, so that $J(\sigma_i = \sigma_j) = -J$ and $J(\sigma_i = -\sigma_j) = +J$. Therefore, the magnetic interaction energy of the atoms can be expressed by the following Hamiltonian

$$\hat{H}\{\sigma_i\} = -J \sum_{nn<ij>} \sigma_i \sigma_j, \tag{A.1}$$

where the summation is over the nearest-neighbor pairs of atoms. We will look at the one- and two-dimensional Ising models.

If the system is interacting with a heat reservoir of temperature T then each of the N Ising spins σ_i is a random variable. According to the Boltzmann's principle, the probability distribution of the microstate $\{\sigma_i\}$ is

$$P\{\sigma_i\} = \frac{1}{\hat{Z}} \mathrm{e}^{-\beta \hat{H}\{\sigma_i\}}, \tag{A.2}$$

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where $\beta = 1/k_{\mathrm{B}}T$ (k_{B} is the Boltzmann's constant) and $\hat{Z}$ is the normalization constant called the partition function

$$\hat{Z} = \sum_{\{\sigma_i\}} \mathrm{e}^{-\beta\hat{H}\{\sigma_i\}}; \quad \sum_{\{\sigma_i\}} \equiv \sum_{\{\sigma_i\}} \sum_{\{\sigma_i\}} \cdots \sum_{\sigma_N=\pm1} . \tag{A.3}$$

In (A.3), the summation is overall N Ising spins. The expectation value (average) of the spins is

$$\sigma_j = \sum_{\{\sigma_i\}} \sigma_j P\{\sigma_i\}. \tag{A.4}$$

To describe the spin dynamics, let us consider the one-dimensional array of N spins with the probability distribution $P\{\sigma_i, t\}$, which is a function of time that obeys the master equation [1]

$$\frac{\mathrm{d}}{\mathrm{d}t}P\{\sigma_i, t\} = -\left[\sum_{j=1}^{N} w_j(\sigma_j)\right] P\{\sigma_i, t\} + \sum_{j=1}^{N} w_j(-\sigma_j) P \times \left\{\sigma_1, \ldots -\sigma_j, \ldots \sigma_N, t\right\}. \tag{A.5}$$

The first term in the right-hand side describes destruction of the microstate $\{\sigma_i\}$ by a flip of any of the spins, while the second term describes creation of the microstate by the spin flip from any of the microstates $\{\sigma_1, \ldots -\sigma_j, \ldots \sigma_N\}$. If we want to describe a tendency for each spin to align itself parallel to its nearest neighbors we may chose the transition probabilities $w_j(\sigma_j)$ to be of the form

$$w_j(\sigma_j) = \frac{1}{2}\gamma\left\{1 - \frac{1}{2}\alpha\sigma_j(\sigma_{j-1} + \sigma_{j+1})\right\}. \tag{A.6}$$

Here $\gamma/2$ is the rate per unite time at which the spin flips from either state to the opposite if it were disconnected from the other spins and α describes the tendency of spins toward alignment. Positive values of α favor parallel configurations (ferromagnetism), negative values favor antiparallel configurations (antiferromagnetism), and in all cases $|\alpha| \leq 1$. Comparing the equilibrium state (A.1), (A.2) with the asymptotic state of the master equation (A.5), (A.6) we may identify

$$\alpha = \tanh\left(\frac{2J}{k_{\mathrm{B}}T}\right). \tag{A.7}$$

If we multiply both sides of the master equation (A.5) by σ_j, substitute (A.6), and sum overall values of spin variables we obtain an equation

$$\begin{aligned} \frac{1}{\gamma}\frac{\mathrm{d}\langle\sigma_j(t)\rangle}{\mathrm{d}t} &= -\langle\sigma_j(t)\rangle + \frac{1}{2}\alpha\left\{\langle\sigma_{j-1}(t)\rangle + \langle\sigma_{j+1}(t)\rangle\right\} \\ &= -(1-\alpha)\langle\sigma_j(t)\rangle + \frac{1}{2}\alpha\left\{\langle\sigma_{j-1}(t)\rangle - 2\langle\sigma_j(t)\rangle + \langle\sigma_{j+1}(t)\rangle\right\}, \end{aligned} \tag{A.8}$$

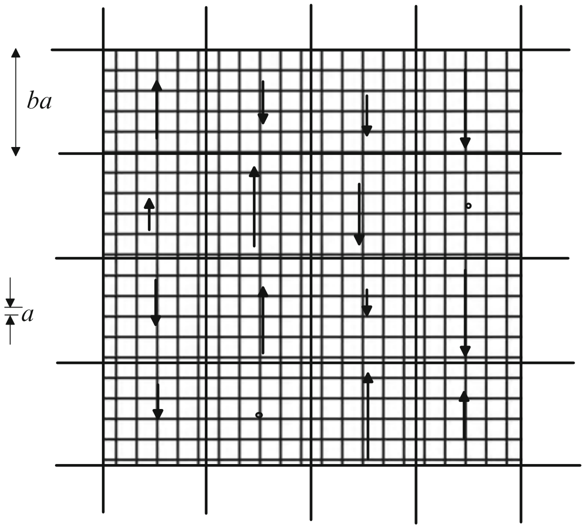

Fig. A.1 Partitioning of the lattice of the cell size *a* by the blocks of $b \times b$ cells. Each block is associated with a spin (*black arrows*) between -1 and 1

which shows that the rates of change of the average spins depend on the states of the neighbors. Extension to the 2d case is straightforward.

Unfortunately (A.1)–(A.8) are not very helpful analytically because Hamiltonian (A.1) depends on very many (N) independent variables. The number of variables of the Hamiltonian (A.1) can be significantly reduced if we are not interested in all the details of the system's behavior on the scale of the interatomic distances a. The 2d "crystal," for instance, can be divided into square blocks, each one consisting of $b \times b$ elementary cells, (see Fig. A.1). For each block, we define the block spin as a sum of b^2 Ising spins divided by b^2, that is, as the block-mean Ising spin. Designating blocks by the position vectors of their centers we obtain

$$\sigma(\mathbf{x}) = \langle\sigma\rangle_{b^2} = \frac{1}{b^2}\sum_{j=1}^{b^2}\sigma_j = \sum_{\{\sigma_j|b^2\}}\sigma_j P\{\sigma_j\}. \tag{A.9}$$

Notice the change of the structure of the independent variables. First, there are N/b^2 block spins instead of N Ising ones. Second, although the block spins are discrete variables as the Ising ones, their "degree of discreteness" changes. Indeed, while the Ising spin is just a simple binary variable, the block spin can take on $(b^2 + 1)$ different values, that is, practically becomes a continuous variable for large b. Hence, the coarse-graining smoothes out the variables at the expense of their "information content": the Ising spins describe interactions on the interatomic scale a while the block spins—on the block scale ba.

How can we find a block-spin Hamiltonian from the Hamiltonian (A.1) for the Ising spins? Let us find the probability distribution of the block spins $P\{\sigma(\mathbf{x})\}$. This can be done using simple rules of the probability theory. Consider joint probability distribution function $p(q_1, q_2)$ of two random (continuous) variables

q_1 and q_2. If we are interested only in one variable, say q_1, we can obtain its probability distribution $p'(q_1)$ by integrating $p(q_1, q_2)$ over q_2

$$p'(q_1) = \int \mathrm{d}q_2 p(q_1, q_2).$$

If we are interested in the mean value of q_1 and q_2, that is $q = (q_1 + q_2)/2$, then

$$p'(q) = \int \mathrm{d}q_1 \, \mathrm{d}q_2 p(q_1, q_2) \; \delta\Big(q - \frac{q_1 + q_2}{2}\Big) = \Big\langle \; \delta\Big(q - \frac{q_1 + q_2}{2}\Big)\Big\rangle.$$

For as long as we consider only functions of q, their average values can be calculated using $p'(q)$ or $p(q_1, q_2)$ yielding the same result because the δ-function replaces integration over q with the integration over (q_1, q_2). For instance,

$$\langle q^2 \rangle' = \int \mathrm{d}q q^2 p'(q) = \Big\langle \Big(\frac{q_1 + q_2}{2}\Big)^2 \Big\rangle.$$

Using these rules, we write the block-spin probability distribution function as follows

$$\begin{aligned} P\{\sigma(\mathbf{x})\} &= P'\{\sigma_i\} \\ &= \sum_{\{\sigma_i\}} \mathrm{e}^{-\beta \hat{H}\{\sigma_i\}} \prod_{\mathbf{x}} \; \delta\left(\sigma(\mathbf{x}) - \frac{1}{b^2}\sum_{j=1}^{b^2} \sigma_j\right) = \left\langle \prod_{\mathbf{x}} \; \delta\left(\sigma(\mathbf{x}) - \frac{1}{b^2}\sum_{j=1}^{b^2} \sigma_j\right)\right\rangle. \end{aligned} \tag{A.10}$$

Now, using the Boltzmann's principle, we can define the block-spin Hamiltonian $H\{\sigma(\mathbf{x})\}$

$$P\{\sigma(\mathbf{x})\} \equiv \frac{1}{Z} \mathrm{e}^{-\beta H\{\sigma(\mathbf{x})\}}, \tag{A.11}$$

where Z is the partition function of the CG system

$$Z = \sum_{\{\sigma_i | N/b^2\}} \mathrm{e}^{-\beta H\{\sigma(\mathbf{x})\}} \approx \frac{1}{b^2} \int_{-1}^{1} \prod_{i=1}^{N/b^2} \mathrm{d}\sigma_i \mathrm{e}^{-\beta H\{\sigma(\mathbf{x})\}}, \tag{A.12a}$$

$$\sum_{\{\sigma_i | N/b^2\}} \equiv \sum_{\sigma(\mathbf{x}_1)} \sum_{\sigma(\mathbf{x}_2)} \cdots \sum_{\sigma\left(\mathbf{x}_{N/b^2}\right) = -1}^{+1} . \tag{A.12b}$$

The procedure (A.9)–(A.12) of reducing the Ising Hamiltonian to the block Hamiltonian is called the Kadanoff transformation

$$H\{\sigma(\mathbf{x})\} = K_b \hat{H}\{\sigma_i\}, \tag{A.13}$$

where we define $K_1 = 1$. The transformation K_b can be applied multiple times with the property that $K_b K_{b'} = K_{bb'}$. Each application of the Kadanoff transformation smoothes out the spin variables at the expense of the reduction of the spatial resolution of the Hamiltonian. The block Hamiltonian $H\{\sigma(\mathbf{x})\}$ contains parameters that average out interactions of the b^2 Ising spins on the scales of the block ($\leq ba$). In this respect, the exchange interaction constant J of the Ising Hamiltonian (A.1) is the averaged out interatomic interactions on the scale $\leq a$.

There are several advantages in dealing with the smoothed, averaged variables instead of the discrete ones. First, one can use the tools of the calculus. Second, one can apply the Fourier transformation to the spin variables and represent the Hamiltonian H as a function of the Fourier components $\sigma(\mathbf{k})$. In this case, the function $H\{\sigma(\mathbf{k})\}$ contains only the components with the wave vectors $|\mathbf{k}| \leq 2\pi/ba$ because the wave vectors outside this sphere describe details of the functional behavior on the scales smaller than ba, which were eliminated from the Hamiltonian $H\{\sigma(\mathbf{x})\}$. Third, dynamics of the smoothed variables is more tractable.

As known [2], the macroscopic properties of a system can be computed from the partition function. For instance, the Helmholtz free energy is

$$F = -\frac{\ln Z}{\beta}. \tag{A.14}$$

For the stability of the system, this free energy must be a convex (concave) function of its extensive (intensive) variables, e.g., $\partial^2 F/\partial T^2 \leq 0$. Equations (A.11) and (A.14) motivate us to expect that the block Hamiltonian $H\{\sigma(\mathbf{x})\}$ possesses some properties of the free energy. Because $H\{\sigma(\mathbf{x})\}$ depends not only on the thermodynamic variables such as temperature and volume but also on the internal variables such as block spins $\{\sigma(\mathbf{x})\}$, it may not be convex (concave) function of its extensive (intensive) variables in the entire domain of definition. However, great advantage of the block Hamiltonian $H\{\sigma(\mathbf{x})\}$ over the actual free energy $F(T)$ is that it is much easier to calculate the former than the latter. In particular, this is true if the block-spin variable $\sigma(\mathbf{x})$ is transformed into a continuum, field variable defined everywhere in the space of the system.

How can we transform the block-spin variables into field variables? First, notice that

$$-\sum_{nn<ij>} \sigma_i \sigma_j = \frac{1}{2} \sum_{nn<ij>} \left(\sigma_i - \sigma_j\right)^2 + \sum_i f(\sigma_i), \tag{A.15}$$

where the function $f(\sigma_i)$ depends on the number and orientation of the nearest neighbors, that is, the symmetry of the "crystal." Also notice that the discrete quantity $(\sigma_i - \sigma_j)/a$ is the first approximation to the continuum quantity $|\nabla \sigma|$, where the gradient is taken in the direction $j \rightarrow i$. Then, replacing the summation overall the nearest-neighbor pairs by the integration over the space of the system we obtain the so-called *Ginzburg–Landau* (GL) Hamiltonian

$$H_{\mathrm{GL}}\{\sigma(\mathbf{x})\} = \int \mathrm{d}^2 x \left[f(\sigma) + \frac{\kappa}{2} |\nabla \sigma|^2 \right], \tag{A.16}$$

which is a continuum equivalent of the discrete Ising Hamiltonian (A.1). Parameter κ in (A.16) is proportional to the number of the nearest neighbors

$$\kappa \approx J N_{nn<ij>}, \tag{A.17}$$

hence, determines the radius of correlations in the system. Because the GL Hamiltonian was obtained through the Kadanoff transformation (A.13) it possesses at least some of the properties of the actual free energy F. That is why it is often called the CG free energy.

Moreover, noticing that the discrete quantity $(\sigma_{j-1} - 2\sigma_j + \sigma_{j+1})/a$ is the first approximation to the continuum quantity $\nabla^2 \sigma$, the dynamic spin-variable equation (A.8) hints at the following continuum equivalent

$$\frac{1}{\gamma} \frac{\partial \sigma(\mathbf{x},\ t)}{\partial t} = -\beta \sigma(\mathbf{x},\ t) + \frac{\alpha}{2} \nabla^2 \sigma(\mathbf{x}, t), \quad \beta > 0. \tag{A.18}$$

Further development of the continuum model may be achieved by noticing the connection between the parameters α and κ through the relations (A.7) and (A.17). However, CG may break consistency between other parts of the model, which must be restored independently.

The GL Hamiltonian (A.16) can be extended on the systems more complicated than the 2d free Ising spins. First, the system may be subjected to the external field B, which adds the contribution $\left(-\mu_0 B \sum_i \sigma_i\right)$ to the Ising Hamiltonian and $(-\mu_0 B \sigma)$ to the integrand of the GL Hamiltonian (A.16). Second, magnetization of an atom may not be directed parallel to the same axis, which makes the "spin" a vector with n components. Third, the system may vary in all three spatial directions, which changes the integration in the GL Hamiltonian. A more complicated issue of appearance of the singularities in the system associated with a phase transition is considered in the main text.

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Appendix B: Calculus of Variations and Functional Derivative

Many physical problems may be reduced to a problem of finding a function y of x (space and/or time), which delivers a maximum (or minimum) to the integral

$$I = I[y(x)] = \int_a^b F\left(x, y, \frac{\mathrm{d}y}{\mathrm{d}x}\right) \mathrm{d}x. \tag{B.1}$$

Such an integral is often called a *functional*. It is a generalization of a function in that it is a number which depends on a function rather than on another number [1, 2].

To find a maximum (or minimum) of the functional means to find a $y(x)$ such that if it is replace by $y(x) + \delta y(x)$, I is unchanged to order $\delta y(x)$, provided $\delta y(x)$ is sufficiently small. More generally, the function $y(x)$ makes the functional I stationary. To reduce this problem to the familiar one of making an ordinary function stationary, consider the replacement

$$\delta y(x) = \varepsilon u(x), \tag{B.2}$$

where ε is small and $u(x)$ is arbitrary but such that (Fig. B.1)

$$u(a) = u(b) = 0. \tag{B.3}$$

Considering $x,\ y,$ and y' as independent variables of F, we obtain

$$I(\varepsilon) = \int_a^b F(x, y + \varepsilon u, y' + \varepsilon u')\, \mathrm{d}x = I(0) + \varepsilon \int_a^b \left(\frac{\partial F}{\partial y} u + \frac{\partial F}{\partial y'} u'\right) \mathrm{d}x + O\left(\varepsilon^2\right). \tag{B.4}$$

If $I[y(x)]$ is to be stationary, then we must have

$$\frac{\mathrm{d}I}{\mathrm{d}\varepsilon}\Big|_{\varepsilon=0} = 0 \quad \text{for all } u(x).$$

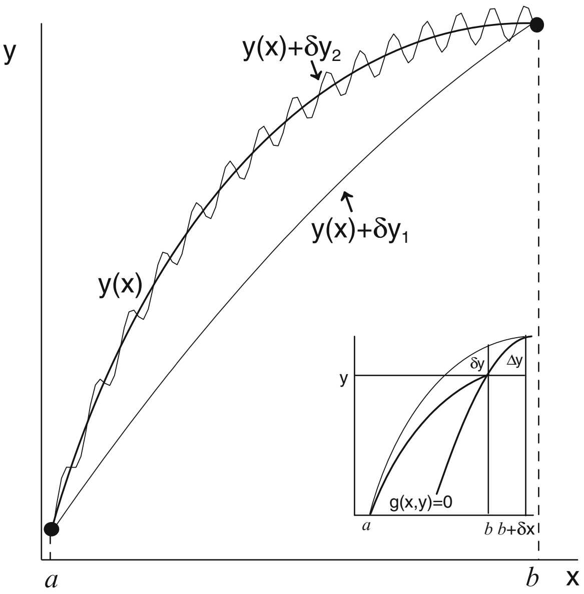

Fig. B.1 Function $y(x)$ and its variations of different smoothness, δy_1 and δy_2. Inset: transversality condition (B.12)

Thus we require that for all u

$$\int_a^b \left(\frac{\partial F}{\partial y} u + \frac{\partial F}{\partial y'} u' \right) \mathrm{d}x = 0. \tag{B.5}$$

Integrating the second term in (B.5) by parts, the equation becomes

$$\int_a^b \left(\frac{\partial F}{\partial y} - \frac{d}{dx} \frac{\partial F}{\partial y'} \right) u \, \mathrm{d}x + u \frac{\partial F}{\partial y'} \Big|_{x=a}^{x=b} = 0. \tag{B.6}$$

The integrated part vanishes because of (B.3).

The fundamental lemma of the calculus of variations says that if the integral is to vanish for *arbitrary* $u(x)$, then the term in the parenthesis must vanish [1]. Therefore, we must require

$$\frac{\partial F}{\partial y} - \frac{\mathrm{d}}{\mathrm{d}x} \frac{\partial F}{\partial y'} = 0. \tag{B.7}$$

This differential equation is called the *Euler–Lagrange* equation; solutions of this equation are called *extremals*. As expected, this equation is Euclidean invariant, i.e., invariant under the combination of translations and rotations in the space. When combined with the appropriate boundary conditions, (B.7) is equivalent to the original variational problem. The left-hand side of this equation is often written as $\delta I/\delta y$, and called the *variational*, or *functional*, derivative of I with respect to y.

There is one caveat in the derivation of the Euler–Lagrange equation (B.7). For the expansion in (B.4) to be valid, we assumed that $y(x)$ and $y(x) + \delta y(x)$ are close not only "point-by-point" but with respect to their derivatives also. This may be verified by a measure of function's magnitude, called the *norm* $\|y(x)\|$. If the norm is defined, then $\|y_1(x)-y_2(x)\|$ is a measure of the proximity of the functions. The full set of functions $y(x)$ with a norm is called a Hilbert functional space. Although a few different definitions of the norm are possible, we find the following one to be the most useful for our purposes

$$\|y(x)\| \equiv \max_{a<x<b} |y(x)| + \max_{a<x<b} |y'(x)|. \tag{B.8}$$

In Fig. B.1, for instance, the function $y(x) + \delta y_1(x)$ is close to $y(x)$ in the sense of the norm (B.8) but the function $y(x) + \delta y_2(x)$ is not. Notice that physically definition (B.8) may not be correct because it may be a sum of two quantities with different physical dimensions. Notwithstanding, it makes perfect mathematical sense as a measure of the proximity of functions.

If the integrand F does not depend on x, we can integrate the Euler–Lagrange equation once. Indeed, when multiplied by y', added and subtracted $y''(\partial F/\partial y')$, the Euler–Lagrange equation is

$$\frac{\mathrm{d}}{\mathrm{d}x}\left(F - y'\frac{\partial F}{\partial y'}\right) = 0,$$

(Why? Hint: $\partial F/\partial x = 0$) which gives a first integral in the form of the first-order equation

$$F - y'\frac{\partial F}{\partial y'} = \text{const.} \tag{B.9}$$

The following generalizations of the basic problem are possible.

Variable end points. Suppose we want to maximize the functional (B.1) but we allow $y(b)$ to be arbitrary. As before, if y is given an increment (B.2) the variation of I (change of the order not higher than the first in the small parameter ε) is

$$\delta I = \int_a^b \left(\frac{\partial F}{\partial y} - \frac{\mathrm{d}}{\mathrm{d}x}\frac{\partial F}{\partial y'}\right)\delta y\,\mathrm{d}x + \frac{\partial F}{\partial y'}\ \delta y\Big|_a^b. \tag{B.10}$$

Clearly, the Euler–Lagrange equation must still hold; otherwise, we could find a function δy with $\delta y(b) = 0$ which changed I. But in addition, if δI is to vanish for arbitrary $\delta y(b)$, we must have

$$\frac{\partial F}{\partial y'}\Big|_{x=b} = 0. \tag{B.11}$$

If both end points are free, clearly $\partial F/\partial y'$ must vanish at both ends.

Transversality condition. As another possibility, suppose y is fixed at $x = a$, but the other end point is free to lie anywhere on the curve (Inset of Fig. B.1)

$$g(x, y) = 0. \tag{B.12}$$

Now from (B.4) we obtain that

$$\delta I = \int_a^b \left(\frac{\partial F}{\partial y} - \frac{\mathrm{d}}{\mathrm{d}x}\frac{\partial F}{\partial y'}\right) \delta y \, \mathrm{d}x + \frac{\partial F}{\partial y'} \ \delta y|^b + F(b) \ \delta x. \tag{B.13}$$

Then the condition $\delta I = 0$, besides the Euler–Lagrange equation, gives the end-point condition

$$F(b) \ \delta x + \frac{\partial F}{\partial y'}(b) \ \delta y(b) = 0. \tag{B.14}$$

The coordinates of the displacement (δx, δy) of the upper end point are constraint by (B.12)

$$\frac{\partial g}{\partial x} \ \delta x + \frac{\partial g}{\partial y}\Delta y = 0. \tag{B.15}$$

Here Δy is not equal to δy of (B.14) since Δy is the increment of y when the boundary point is displaced to the position ($b + \delta x$, $y + \Delta y$) and δy is the increment of the ordinate y at the point b when going from the extremal passing through the (b, y) to the extremal passing through the ($b + \delta x$, $y + \Delta y$) (see Inset of Fig. B.1). Naturally

$$\Delta y = \ \delta y(b) + y'(b) \ \delta x. \tag{B.16}$$

Eliminating δx and δy from (B.14)–(B.16) leads to the condition

$$\left(F - y'\frac{\partial F}{\partial y'}\right)\frac{\partial g}{\partial y} - \frac{\partial F}{\partial y'}\frac{\partial g}{\partial x} = 0 \quad \text{at } x = b, \tag{B.17}$$

which is called the *transversality condition.*

Isoperimetric problem. Suppose we need to maximize *one* functional, (B.1) subject to the constraint that *another* functional be held constant

$$J[y(x)] = \int_a^b G(x, y, y')\,\mathrm{d}x = \text{const.} \tag{B.18}$$

The conventional technique for handling this problem involves the use of *Lagrange multipliers*.

The theorem [1] says that if $y(x)$ is an extremal of the functional (B.1), satisfies the constraint (B.18), but is *not* an extremal of the functional $J[y(x)]$, then there exists a constant λ such that $y(x)$ is an extremal of the functional

$$\int_a^b (F - \lambda G)\,\mathrm{d}x. \tag{B.19}$$

Inclusion of higher derivatives. Suppose we want to maximize the functional

$$I[y(x)] = \int_a^b F(x, y, y', y'')\,\mathrm{d}x \tag{B.20}$$

with y and y' held fixed at a and b. The condition is easily shown to be

$$\frac{\delta I}{\delta y} \equiv \frac{\partial F}{\partial y} - \frac{\mathrm{d}}{\mathrm{d}x}\frac{\partial F}{\partial y'} + \frac{\mathrm{d}^2}{\mathrm{d}x^2}\frac{\partial F}{\partial y''} = 0. \tag{B.21}$$

Note that we have generalized our definition of the variational derivative.

Multiple dependent variables. Suppose we want to maximize the functional

$$I[y(x), z(x)] = \int_a^b F(x, y, y', z,\ z')\,\mathrm{d}x \tag{B.22}$$

subject to fixed end-point conditions

$$y(a) = y_1 \quad y(b) = y_2, \tag{B.23a}$$

$$z(a) = z_1 \quad z(b) = z_2. \tag{B.23b}$$

We just write down an Euler–Lagrange equation for each dependent variable separately

$$\frac{\delta I}{\delta y} \equiv \frac{\partial F}{\partial y} - \frac{\mathrm{d}}{\mathrm{d}x}\frac{\partial F}{\partial y'} = 0, \tag{B.24a}$$

$$\frac{\delta I}{\delta z} \equiv \frac{\partial F}{\partial z} - \frac{\mathrm{d}}{\mathrm{d}x}\frac{\partial F}{\partial z'} = 0. \tag{B.24b}$$

Multiple independent variables. Consider the functional

$$I[z(x, y)] = \iint_{\Omega} F\big(x,\ y,\ z,\ z_x,\ z_y\big)\, \mathrm{d}x\, \mathrm{d}y, \tag{B.25}$$

where Ω is some region of the xy-plane, $z_x{=}\partial z/\partial x$ and $z_y{=}\partial z/\partial y$. The function z is to be varied in such a way that its values on the boundary of Ω remain constant. Then the condition for $I[z]$ to be stationary is

$$\frac{\delta I}{\delta z} \equiv \frac{\partial F}{\partial z} - \frac{\partial}{\partial x}\frac{\partial F}{\partial z_x} - \frac{\partial}{\partial y}\frac{\partial F}{\partial z_y} = 0. \tag{B.26}$$

Again we have extended the definition of the variational derivative.

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Appendix C: Orthogonal Curvilinear Coordinates

Depending on the symmetry of the problem, advantage may be gained by using a curvilinear coordinate system instead of the Cartesian one. Suppose that the rectangular coordinates are expressed in terms of new coordinates: u_1, u_2, u_3, by the equations

$$x_i = x_i(u_i), \quad i = 1,\ 2,\ 3 \tag{C.1}$$

and that, conversely, these relations can be inverted to express u_i in terms of x_i. Then, at least in a certain region, any point with coordinates (x_i) has corresponding coordinates (u_i). If a particle moves from point P in such a way that u_2 and u_3 are held constant and only u_1 varies, a curve in space is generated. If only one coordinate is held constant, we generate successively three surfaces passing through the point P; these surfaces intersect in the coordinate curves. It is often convenient to choose the new coordinates in such a way that the coordinate curves are mutually perpendicular at each point in space. Such coordinates are called orthogonal curvilinear coordinates.

Let $\mathbf{r}$ represent the position vector of a point P in space,

$$\mathbf{r} = x_1\mathbf{j}_1 + x_2\mathbf{j}_2 + x_3\mathbf{j}_3. \tag{C.2}$$

Then a tangent vector to the u_i curve at P is given by

$$\mathbf{U}_i = \frac{\partial \mathbf{r}}{\partial u_i} = \frac{\partial \mathbf{r}}{\partial s_i}\frac{\mathrm{d}s_i}{\mathrm{d}u_i}, \tag{C.3}$$

where s_i is the arc length along the u_i curve. Since $\partial\mathbf{r}/\partial s_i$ is a unit vector, we can write

$$\mathbf{U}_i = h_i\mathbf{u}_i, \tag{C.4}$$

where $\mathbf{u}_i$ is the unit vector tangent to the u_i curve in the direction of increasing arc length and

$$h_i = \frac{\mathrm{d}s_i}{\mathrm{d}u_i} = \left|\frac{\partial \mathbf{r}}{\partial u_i}\right| \tag{C.5}$$

is the length of U_i. These equations can be written in the differential form

$$\mathrm{d}s_i = h_i\,\mathrm{d}u_i. \tag{C.6}$$

We thus see that h_i are the scale factors that give the ratios of the differential distances to the differentials of the coordinate parameters. If the coordinate curves are orthogonal, so that

$$\mathbf{U}_i \times \mathbf{U}_{j\neq i} = 0 \tag{C.7}$$

there follows that the length of the infinitesimal line element ds is given as

$$\mathrm{d}s^2 = \sum_{i=1}^{3} \mathrm{d}x_i^2 = \sum_{j=1}^{3} h_j^2\,\mathrm{d}s_j^2, \tag{C.8}$$

the vector element of surface area on the surface $u_i = \text{const}$

$$\mathrm{d}\sigma_i = \mathbf{u}_i h_j h_k\,\mathrm{d}u_j\,\mathrm{d}u_k, \quad j,\ k \neq i, \tag{C.9}$$

the element of volume

$$\mathrm{d}\tau = h_1 h_2 h_3\,\mathrm{d}u_1\,\mathrm{d}u_2\,\mathrm{d}u_3, \tag{C.10}$$

Direction cosines of the unit vectors $\mathbf{u}_i$ with respect to the old axes $\mathbf{x}_j$ may be expressed in terms of the derivatives and the scale factors in either of the two ways

$$\gamma_{ij} = \frac{1}{h_i}\frac{\partial x_j}{\partial u_i} = h_i\frac{\partial u_i}{\partial x_j} \tag{C.11}$$

depending on whether x_i are given in terms of u_i or other way around. In two dimensions, the unit vectors are characterized by one angle φ, e.g., with axis x, such that

$$\tan\,\phi = \frac{\partial u_i/\partial y}{\partial u_i/\partial x}. \tag{C.12}$$

In the Cartesian coordinates, the gradient ∇ and Laplacian ∇^2 operators are expressed as follows

$$\nabla \equiv \mathbf{j}_1 \frac{\partial}{\partial x_1} + \mathbf{j}_2 \frac{\partial}{\partial x_2} + \mathbf{j}_3 \frac{\partial}{\partial x_3}, \tag{C.13}$$

$$\nabla^2 \equiv \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial x_3^2}. \tag{C.14}$$

In the curvilinear coordinates, the gradient of a scalar function f is

$$\nabla f = \frac{\mathbf{u}_1}{h_1} \frac{\partial f}{\partial u_1} + \frac{\mathbf{u}_2}{h_2} \frac{\partial f}{\partial u_2} + \frac{\mathbf{u}_3}{h_3} \frac{\partial f}{\partial u_3}. \tag{C.15}$$

Applying (C.15) to u_1, we find the eikonal equation

$$(\nabla u_1)^2 = \frac{1}{h_1^2}. \tag{C.16}$$

The divergence of a vector function $\mathbf{F}$ is

$$\nabla \cdot \mathbf{F} = \frac{1}{h_1 h_2 h_3} \left[\frac{\partial}{\partial u_1} (h_2 h_3 F_1) + \frac{\partial}{\partial u_2} (h_3 h_1 F_2) + \frac{\partial}{\partial u_3} (h_1 h_2 F_3) \right]. \tag{C.17}$$

By applying the vector operator in (C.17) to the vector operator ∇ of (C.15) instead of the vector function $\mathbf{F}$, we find the expression for the Laplacian operator,

$$\begin{aligned} \nabla^2 &\equiv \nabla \cdot \nabla \\ &= \frac{1}{h_1 h_2 h_3} \left[\frac{\partial}{\partial u_1} \left(\frac{h_2 h_3}{h_1} \frac{\partial}{\partial u_1} \right) + \frac{\partial}{\partial u_2} \left(\frac{h_3 h_1}{h_2} \frac{\partial}{\partial u_2} \right) + \frac{\partial}{\partial u_3} \left(\frac{h_1 h_2}{h_3} \frac{\partial}{\partial u_3} \right) \right]. \end{aligned} \tag{C.18}$$

The change in direction of the unit vectors $\mathbf{u}_i$ can be expressed in terms of the hs. For instance

$$\frac{\partial \mathbf{u}_1}{\partial u_1} = -\frac{\mathbf{u}_2}{h_2} \frac{\partial h_1}{\partial u_2} - \frac{\mathbf{u}_3}{h_3} \frac{\partial h_1}{\partial u_3}, \frac{\partial \mathbf{u}_1}{\partial u_2} = \frac{\mathbf{u}_2}{h_1} \frac{\partial h_2}{\partial u_1}. \tag{C.19}$$

Then one can define *curvature* of the u_2 coordinate line in the direction $\mathbf{u}_1$ as

$$k_2 = \frac{\mathbf{u}_2}{h_2} \frac{\partial \mathbf{u}_1}{\partial u_2} \tag{C.20}$$

and for the mean curvature K of the surface $u_1 = \text{const}$ we obtain the formula

$$2K \equiv k_2 + k_3 = \frac{\mathbf{u}_2}{h_2}\frac{\partial \mathbf{u}_1}{\partial u_2} + \frac{\mathbf{u}_3}{h_3}\frac{\partial \mathbf{u}_1}{\partial u_3} = \frac{1}{h_1 h_2 h_3}\frac{\partial}{\partial u_1}(h_2 h_3) = \nabla \cdot \mathbf{u}_1. \tag{C.21}$$

Notice that with this choice of sign in (C.20), (C.21) the curvature of a sphere is positive.

If $h_1 = \text{const}(u_1, u_2, u_3) = 1$ then the Laplacian can be represented as follows

$$\nabla^2 = \frac{\partial^2}{\partial u_1^2} + 2K\frac{\partial}{\partial u_1} + \frac{1}{h_2 h_3}\left[\frac{\partial}{\partial u_2}\left(\frac{h_3}{h_2}\frac{\partial}{\partial u_2}\right) + \frac{\partial}{\partial u_3}\left(\frac{h_2}{h_3}\frac{\partial}{\partial u_3}\right)\right]. \tag{C.22}$$

For the functions which do not depend on coordinates u_2 and u_3, expression (C.22) takes the form

$$\nabla^2 = \frac{\partial^2}{\partial u_1^2} + 2K\frac{\partial}{\partial u_1}. \tag{C.23}$$

In the spherical polar one (r, ϑ, φ) where r $(0 \le r < \infty)$ is of the absolute value of the radius vector $\mathbf{r}$ or the distance from the center of the coordinate system, ϑ $(0 \le \vartheta \le \pi)$ is the colatitude, and φ $(0 \le \varphi \le 2\pi)$ is the azimuth. Then the projection of the radius vector $\mathbf{r}$ on the Cartesian coordinates x_i can be expressed as follows

$$\begin{gathered} x_i = r f_i(\vartheta, \phi); \\ f_1 = \sin\vartheta\, \cos\phi;\ f_2 = \sin\vartheta\, \sin\phi;\ f_3 = \cos\vartheta. \end{gathered} \tag{C.24}$$

The gradient and Laplacian in the spherical coordinates take the form

$$\nabla = \mathbf{j}_r\frac{\partial}{\partial r} + \frac{\mathbf{j}_\vartheta}{r}\frac{\partial}{\partial \vartheta} + \frac{\mathbf{j}_\phi}{r\,\sin\vartheta}\frac{\partial}{\partial \phi}, \tag{C.25}$$

$$\nabla^2 = \nabla_r^2 + \frac{1}{r^2}\hat{\mathbf{L}}^2(\vartheta, \phi), \tag{C.26a}$$

$$\nabla_r^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}, \tag{C.26b}$$

$$\hat{\mathbf{L}}^2 = \frac{1}{\sin\vartheta}\frac{\partial}{\partial \vartheta}\left(\sin\vartheta\,\frac{\partial}{\partial \vartheta}\right) + \frac{1}{\sin^2\vartheta}\frac{\partial^2}{\partial \phi^2}. \tag{C.26c}$$

Here ${\nabla_r}^2$ is the radial component and $\hat{\mathbf{L}}^2$, called the Legendrian, is the angular component of the Laplacian. Compare (C.23), (C.26b) and notice that $K = 1/r$.

Also notice that the projection coefficients f_i, (C.24), are the eigenfunctions of the Legendrian with $l = 1$ and eigenvalue $-l(l + 1) = -2$ (Verify!)

$$\hat{\mathbf{L}}^2 f_i(\vartheta, \phi) = -2f_i(\vartheta, \phi). \tag{C.27}$$

In quantum mechanics, important role is played by a linear operator called Hamiltonian of a particle

$$\hat{\mathbf{H}}(\mathbf{x}) \equiv P(\mathbf{x}) - m\nabla^2, \tag{C.28}$$

where $P(\mathbf{x})$ is the potential energy of the particle of mass m. The radial component of the Laplacian represents the square of the radial component of the momentum and the Legendrian is the operator of the square of the angular momentum of a particle. The eigenfunctions of the Hamiltonian with the radially symmetric potential energy can be represented as the products of the radial and angular parts, with the latter being the eigenfunction of the Legendrian. The eigenvalues of the Hamiltonian depend on three quantum numbers, which are called the radial n_r, angular l, and magnetic m_l.

Appendix D: Lagrangian Field Theory

Fields are objects with an infinite number of degrees of freedom: the fields ψ_αs and field time/space derivatives $\partial_\mu\psi_\alpha$s at every point in space and time. A physical system at a point in space Ω at a given time $t_1 < t < t_2$ may be described by a Lagrangian density

$$l(\psi_\alpha,\ \partial_t\psi_\alpha,\ \partial_i\psi_\alpha,\ \ldots), \tag{D.1}$$

which gives rise to the Lagrangian:

$$L \equiv \int_\Omega \mathrm{d}^3x\, l(\psi_\alpha,\ \partial_t\psi_\alpha,\ \partial_i\psi_\alpha) \tag{D.2}$$

and the action

$$S \equiv \int_{t_1}^{t_2} \mathrm{d}t\, L = \int_{\Omega\times[t_1,t_2]} \mathrm{d}^4x\, l(\psi_\alpha,\ \partial_t\psi_\alpha,\ \partial_i\psi_\alpha). \tag{D.3}$$

In this section, we write the generalized time/space coordinates and field derivatives in the Lorentz-invariant form where the covariant components of the four-position-vector are

$$x^0 = t, \quad x^1 = x, \quad x^2 = y, \quad x^3 = z,$$

the contravariant time/space derivatives are

$$\partial_0 = \partial_t = \frac{\partial}{\partial t}, \quad \partial_i = \frac{\partial}{\partial x^i},\ i = 1,\ 2,\ 3$$

and the four-dimensional volume element of $\Omega \times [t_1, t_2]$ is $\mathrm{d}^4x = \mathrm{d}t\ \mathrm{d}^3x$.

A general formulation of the laws of motion of a Lagrangian system is expressed by the Hamilton's principle: *The action must be stationary for arbitrary variations of the fields* $\delta\psi_\alpha$ *that vanish on the boundary of* $\Omega\times[t_1, t_2]$. Making in (D.3) an infinitesimal transformation $\psi_\alpha \to \psi_\alpha + \delta\psi_\alpha$, we obtain

$$\delta S = \sum_\alpha \int_{\Omega\times[t_1,t_2]} \mathrm{d}^4x \left[\frac{\partial l}{\partial\psi_\alpha}\,\delta\psi_\alpha + \frac{\partial l}{\partial(\partial_\mu\psi_\alpha)}\,\delta(\partial_\mu\psi_\alpha)\right]. \tag{D.4}$$

Here and below $\mu = 0, i$ and we use the Einstein summation convention. Notice that the variations $\delta\psi_\alpha$ in (D.4) differ from the ones we use in the text and Appendix B in that now they are functions of space and time (four variations) because the action S is a functional in the four-dimensional space–time. Integrating the last term in (D.4) by parts we obtain

$$\delta S = \sum_\alpha \left\{ \int_{\Omega\times[t_1,t_2]} \mathrm{d}^4x \left[\frac{\partial l}{\partial\psi_\alpha} - \partial_\mu \frac{\partial l}{\partial(\partial_\mu\psi_\alpha)}\right]\delta\psi_\alpha + \int_{\boldsymbol{\Omega}(t_1)}^{\boldsymbol{\Omega}(t_2)} \mathrm{d}s_\mu \frac{\partial l}{\partial(\partial_\mu\psi_\alpha)}\,\delta\psi_\alpha \right\}, \tag{D.5}$$

where $\mathrm{d}s_\mu$ is the elemental four vector of the boundary hypersurface $\boldsymbol{\Omega}(t)$. The boundary term in (D.5) vanishes because $\delta\psi_\alpha[\boldsymbol{\Omega}(t)] = 0$. Using that $\delta\psi_\alpha$s are arbitrary in the interior of $\Omega\times[t_1, t_2]$ we obtain the Lagrange equations for the fields

$$\frac{\delta \mathrm{S}}{\delta\psi_\alpha} \equiv \frac{\partial l}{\partial\psi_\alpha} - \partial_t \frac{\partial l}{\partial(\partial_t\psi_\alpha)} + \partial_i \frac{\partial l}{\partial(\partial_i\psi_\alpha)} = 0. \tag{D.6}$$

Solutions of the Lagrange equations are called extremals.

In some systems, vanishing of the variations of the fields on the boundary is not justified. Instead, the variations on the boundary may also be considered arbitrary, that is, free boundary. Then for δS in (D.5) to vanish another boundary condition must be met (see details in Appendix B)

$$n_\mu \frac{\partial l}{\partial(\partial_\mu\psi_\alpha)}\Big|_{\boldsymbol{\Omega}(t)} = 0, \tag{D.7}$$

where n_μ is a unit four vector of $\mathrm{d}s_\mu$. If the fields are specified on the boundary of the time interval $[t_1, t_2]$ but not the space, e.g., spatially infinite systems, then the condition (D.7) for $\mu = i$ applies at $t = t_1$ and $t = t_2$. These boundary conditions replace the condition $\delta\psi_\alpha[\boldsymbol{\Omega}(t)] = 0$ for the extremals (D.6).

The Lagrange equations (D.6) permit the construction of a canonical stress-energy tensor

$$T^{\mu\nu} \equiv \sum_\alpha \frac{\partial l}{\partial(\partial_\mu\psi_\alpha)}\partial^\nu\psi_\alpha - \epsilon^{\mu\nu} l, \tag{D.8}$$

where the metric tensor,

$$\in^{\mu\nu} = \begin{cases} 1, & \text{if } \mu \text{ and } \nu = 0 \\ 0, & \text{if } \mu = 0 \text{ or } \nu = 0 \\ -\delta^{ij}, & \text{if } \mu = i,\ \nu = j \end{cases},$$

is used to lower or raise the Lorentz indices. The stress-energy tensor is locally conserved

$$\partial_\mu T^{\mu\nu} = 0 \tag{D.9}$$

if the Lagrangian density (D.1) does not explicitly depend on space and time. The issue of symmetry of the tensor $T^{\mu\nu}$ is not important here because we will be considering scalar fields ψ_αs only.

The local conservation of $T^{\mu\nu}$ makes possible the definition of an energy–momentum four vector

$$P^\mu \equiv \int_\Omega \mathrm{d}^3 x T^{0\mu}, \tag{D.10}$$

which is globally conserved, that is,

$$\frac{\mathrm{d}P^\mu}{\mathrm{d}t} = \int_\Omega \mathrm{d}^3 x \partial_t \mathrm{T}^{0\mu} = -\int_\Omega \mathrm{d}^3 x \partial_i \mathrm{T}^{\mathrm{i}\mu} = -\oint_\Omega \mathrm{d}s_i T^{i\mu} = 0 \tag{D.11}$$

provided that no energy or momentum escapes the volume $\boldsymbol{\Omega}$ (the last equality), e.g., at the boundary $\boldsymbol{\Omega}(t)$ the Lagrangian vanishes together with its derivatives, see (D.7). The total energy of the system is defined as

$$E \equiv P^0 = \int_\Omega \mathrm{d}^3 x T^{00}. \tag{D.12}$$

Consider a system which is described by the scalar fields $\psi_\alpha(t, \mathbf{r})$ and a Lorentz-invariant Lagrangian density

$$l(\psi_\alpha, \partial_t\psi_\alpha, \partial_i\psi_\alpha) = \frac{1}{2}\sum_\alpha \left[\rho_\alpha(\partial_t\psi_\alpha)^2 - \kappa_\alpha\left(\partial_i\psi_\alpha\partial^i\psi_\alpha\right)\right] - u(\psi_\alpha), \tag{D.13}$$

where ρ_αs are the mass densities and κ_αs are the gradient energy coefficients associated with the fields $\psi_\alpha(t, \mathbf{r})$, and $u(\psi_\alpha)$ is the potential energy density. For the Lagrangian density (D.13), equations of motion (D.6) take the form of the wave equations

$$\rho_\alpha\partial_t\partial_t\psi_\alpha = \kappa_\alpha\left(\partial_i\partial^i\psi_\alpha\right) - \frac{\partial u}{\partial\psi_\alpha}, \tag{D.14}$$

which are field analogs of the Newton's laws for particle motion. Each field ψ_α has its own characteristic wave speed

$$c_\alpha \equiv \sqrt{\frac{\kappa_\alpha}{\rho_\alpha}}. \tag{D.15}$$

The components of the stress-energy tensor (D.8) are

$$T^{00} = \frac{1}{2}\sum_\alpha \left[\rho_\alpha(\partial_t\psi_\alpha)^2 + \kappa_\alpha\left(\partial_i\psi_\alpha\partial^i\psi_\alpha\right)\right] + u(\psi_\alpha), \tag{D.16}$$

$$\begin{aligned} T^{ii} &= \frac{1}{2}\sum_\alpha \left\{\rho_\alpha(\partial_t\psi_\alpha)^2 + \kappa_\alpha\left[(\partial_i\psi_\alpha)^2 - \left(\partial_j\psi_\alpha\right)^2 - (\partial_k\psi_\alpha)^2\right]\right\} - u(\psi_\alpha), \\ & i \neq j \neq k \neq i \end{aligned} \tag{D.17}$$

and the total energy of the system (D.12) is

$$E = \int_\Omega \mathrm{d}^3x \left\{\frac{1}{2}\sum_\alpha \left[\rho_\alpha(\partial_t\psi_\alpha)^2 + \kappa_\alpha\left(\partial_i\psi_\alpha\partial^i\psi_\alpha\right)\right] + u(\psi_\alpha)\right\}. \tag{D.18}$$

This expression shows that the gradient energy coefficients κ_α cannot be negative because otherwise E would be unbounded below, which makes the system mechanically unstable.

In a stationary one-dimensional (1d) system where the fields ψ_α depend only on one space coordinate, e.g. $i = 1$, the local conservation condition (D.9) has the first integral

$$T^{11} = \frac{1}{2}\sum_\alpha \kappa_\alpha(\partial_1\psi_\alpha)^2 - u(\psi_\alpha) = \text{const} \equiv -u_\pm, \tag{D.19}$$

and the total energy is

$$E = u_\pm\ \Omega + \sigma A, \tag{D.20}$$

where A is the cross-sectional area of the volume Ω

$$A = \iint_{\Omega_2\times\Omega_3} \mathrm{d}s_1 = \iint_{\Omega_2\times\Omega_3} \mathrm{d}x^2\,\mathrm{d}x^3$$

and σ is called the abbreviated action

$$\begin{aligned} \sigma &\equiv \int_{\Omega_1} \mathrm{d}x\left[\frac{1}{2}\sum_\alpha \kappa_\alpha(\partial_1\psi_\alpha)^2 + u(\psi_\alpha) - u_\pm\right] \\ &= \int_{\Omega_1} \mathrm{d}x \sum_\alpha \kappa_\alpha(\partial_1\psi_\alpha)^2 = \sum_\alpha \sigma_\alpha; \\ \sigma_\alpha &\equiv \int_{\Omega_1} \mathrm{d}x\kappa_\alpha(\partial_1\psi_\alpha)^2. \end{aligned} \tag{D.21}$$

If the system is described by a single field ψ, we can further our analysis and resolve the first integral (D.19) for the space derivative as a function of the field

$$\partial_1\psi = \pm\sqrt{\frac{2}{\kappa}[u(\psi) - u_\pm]}. \tag{D.22}$$

By choosing one of the branches, e.g. positive, this relation can be integrated to obtain the field as a function of the coordinate

$$x = \sqrt{\frac{\kappa}{2}}\int\frac{\mathrm{d}\psi}{\sqrt{u(\psi) - u_\pm}}. \tag{D.23}$$

In the infinite system, the boundary condition (D.7) yields $\partial_1\psi(-\infty) = \partial_1\psi(+\infty) = 0$, which, together with (D.22), allows one to find $\psi_- \equiv \psi(-\infty)$ and $\psi_+ \equiv \psi(+\infty)$ as

$$u(\psi_-) = u(\psi_+) = u_\pm. \tag{D.24}$$

If $u(\psi)$ is a continuous function on $[\psi_-, \psi_+]$ then, according to Rolle's theorem, $\partial u/\partial\psi = 0$ for some value ψ_m in $[\psi_-, \psi_+]$. Then, the 1d stationary form of the Lagrange equation (D.14)

$$\kappa\frac{\partial(\partial_1\psi)}{\partial x}(x) = \frac{\partial u}{\partial\psi}(\psi) \tag{D.25}$$

shows that the functions $\partial_1\psi(x)$ and $u(\psi)$ attain maxima (or minima) at the same point in space x_m where $\psi(x_m) = \psi_m$ and that $\partial u(\psi_m)/\partial\psi = 0$. This allows us to characterize transition of the field between the values of ψ_- and ψ_+ with the characteristic length of

$$w \equiv \left|\frac{\psi_+ - \psi_-}{\partial_1\psi(x_m)}\right| = \frac{\sqrt{\kappa}|\psi_+ - \psi_-|}{\sqrt{2[u(\psi_m) - u_\pm]}}. \tag{D.26}$$

The abbreviated action (D.21) of this transition can be represented in the form of quadratures

$$\sigma = \kappa\int_{\Omega_1}\mathrm{d}x(\partial_1\psi)^2 = \kappa\int_{\Omega_1}\mathrm{d}\psi(\partial_1\psi) = \sqrt{2\kappa}\int_{\psi_-}^{\psi_+}\mathrm{d}\psi\sqrt{u(\psi) - u_\pm} \tag{D.27}$$

and estimated as follows

$$\sigma \approx \sqrt{\kappa}|\psi_+ - \psi_-|\sqrt{2[u(\psi_m) - u_\pm]}. \tag{D.28}$$

The abbreviated action (D.28) is a product of the same terms of which the length (D.26) is a quotient.

If time evolution of the fields $\psi_\alpha(t, x)$, described by the 1d dynamic Lagrange equations (D.14), can be presented as the motion of train waves with constant speed V, $\psi_\alpha(x - Vt)$, then the local conservation condition (D.9) takes the form

$$\partial_t T^{01} + \partial_1 T^{11} = \partial_1 \left(T^{11} - VT^{01} \right) = 0, \tag{D.29}$$

which yields the first integral

$$T^{11} - VT^{01} = \frac{1}{2} \sum_\alpha \kappa_\alpha \left(1 - \frac{V^2}{c_\alpha^2} \right) (\partial_1 \psi_\alpha)^2 - u(\psi_\alpha) = -u_\pm, \tag{D.30}$$

In the case of a single field, comparison of this equation with (D.22) shows that the train wave has the same spatial distribution as the stationary field but experiences the Lorentz contraction of the characteristic length

$$w_V = \sqrt{1 - \frac{V^2}{c_\psi^2}} w. \tag{D.31}$$

The speed V cannot exceed the characteristic speed c_ψ—the relativistic effect, but its actual value cannot be found from the Lagrangian and needs to be determined based on other conditions of the problem—the selection problem.

Appendix E: Eigenfunctions and Eigenvalues of the Schrödinger Equation and Sturm's Comparison Theorem

Many physical situations may be formulated in terms of the Sturm–Liouville problem where the unknown function $\Psi(x)$ obeys the Liouville equation

$$\frac{\mathrm{d}}{\mathrm{d}x}\left[\kappa(x)\frac{\mathrm{d}\Psi}{\mathrm{d}x}\right] + [\lambda - u(x)]\Psi(x) = 0 \tag{E.1}$$

with the homogeneous boundary conditions

$$\alpha_x\frac{\mathrm{d}\Psi}{\mathrm{d}x} - \beta_x\Psi = 0, \quad x = a \text{ or } x = b. \tag{E.2}$$

In (E.1), λ is an arbitrary constant, $\kappa(x) > 0$ and $u(x)$ does not have singularities in the range of x—(a, b). A solution of the Sturm–Liouville problem is called an *eigenfunction*, the constant λ—*eigenvalue*, and the set of its values that allows the solutions—*spectrum.*

According to the *Sturm's comparison theorem*, the spectrum of the Sturm–Liouville problem has the following properties:

1. If (a–b) is finite, the spectrum is discrete
2. There exists the lowest eigenvalue λ_0 of the spectrum
3. The sequence $\lambda_0 < \lambda_1 < \lambda_2 < \ldots$ can have no limit point nor any upper bound but must continue on to $+\infty$
4. The larger the eigenvalue λ, the closer together lie the zeros of the eigenfunction
5. If (a–b) is infinite, the spectrum is discrete in the half space $\lambda < \lim\limits_{x\to\pm\infty}\kappa(x)$and ##2, 3, 4 are also valid
6. For $\lambda > \lim\limits_{x\to\pm\infty}\kappa(x)$, the spectrum is continuous.

If $\kappa = \mathrm{const}(x)$ the Liouville equation is similar to the Schrödinger equation from quantum mechanics, which describes stationary motion of a particle of mass ($\hbar^2/2\kappa$) in the one-dimensional potential energy field $u(x)$, the eigenfunction $\Psi_{\mathrm{p}}{}^{(1)}(x)$ is the wave function and $\lambda = E_p{}^{(1)}$ is the total energy of the moving particle (the superscript refers to the dimensionality of the motion). In the case of infinite range, the eigenfunctions of the discrete spectrum are called *bound states* and those of the continuous spectrum—*scattering states.*

If there exists a potential function $g(\eta)$ such that the potential energy $u(x) = \partial^2 g(\tilde{\eta})/\partial\eta^2$,where $\tilde{\eta}(x)$is a heterogeneous solution of the equation

$$\kappa\frac{\mathrm{d}^2\eta}{\mathrm{d}x^2} - \frac{\partial g}{\partial\eta} = 0, \tag{E.3}$$

then the Sturm–Liouville problem (E.1), (E.2) can be reformulated as an eigenfunction/eigenvalue problem for the one-dimensional Hamiltonian operator $\hat{\mathbf{H}}$:

$$\hat{\mathbf{H}}(\tilde{\eta};\, x)\Psi_p^{(1)}(x) = E_p^{(1)}\,\Psi_p^{(1)}(x); \quad \hat{\mathbf{H}}(\tilde{\eta};\, x) \equiv \frac{\partial^2 g}{\partial\,\eta^2}(\tilde{\eta}) - \kappa\frac{\mathrm{d}^2}{\mathrm{d}x^2} \tag{E.4}$$

with at least one eigenfunction already known. Indeed, differentiating (E.3) with respect to x and noticing that neither term depends on x explicitly, we obtain

$$\kappa\frac{\mathrm{d}^2}{\mathrm{d}x^2}\left(\frac{\mathrm{d}\tilde{\eta}}{\mathrm{d}x}\right) - \frac{\partial^2 g(\tilde{\eta})}{\partial\eta^2}\frac{\mathrm{d}\tilde{\eta}}{\mathrm{d}x} = 0. \tag{E.5}$$

Comparing (E.4) and (E.5) we can find the non-normalized eigenfunction of $\hat{\mathbf{H}}(\tilde{\eta};\, x)$which corresponds to the zero eigenvalue

$$p = 1, \quad E_1^{(1)} = 0, \quad \Psi_1^{(1)}(x) \propto \frac{\mathrm{d}\tilde{\eta}}{\mathrm{d}x}. \tag{E.6}$$

This eigenfunction is the so-called Goldstone mode of the Hamiltonian.

A particular interesting situation appears in the case when

$$g(\eta) = g_0 + \frac{1}{2}\eta^2\left(a + \frac{1}{2}c\eta^2\right), \quad a<0,\ c>0. \tag{E.7}$$

In this case,

$$\tilde{\eta} = \sqrt{\frac{-a}{c}}\tanh\sqrt{\frac{-a}{2\kappa}}x \tag{E.8}$$

and, by scaling the eigenvalues and independent variable as follows

$$Q_p = \frac{2}{a}E_p^{(1)}, \quad z = \sqrt{\frac{-a}{2\kappa}}x, \quad f_p(z) = \Psi_p^{(1)}(x), \tag{E.9}$$

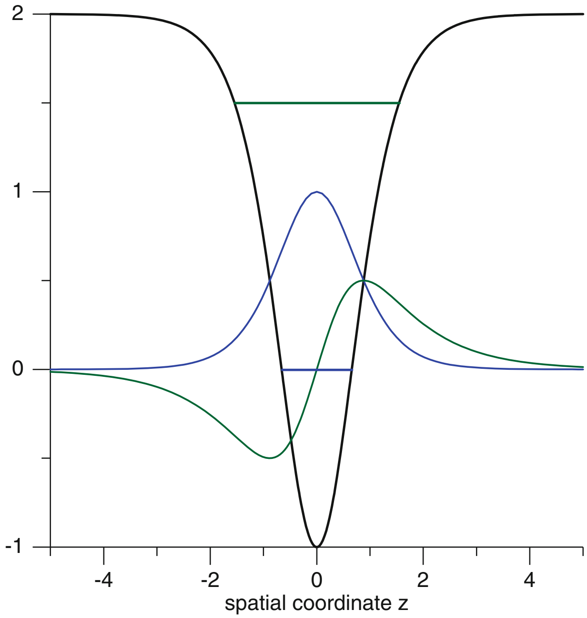

Fig. E.1 The "quantum mechanical potential energy" $u(z) = \partial^2 g(\tilde{\eta})/\partial\eta^2$ for the potential function (E.7)—*black line* and two bound states with $p = 1$—*blue line* (Goldstone mode) and $p = 2$—*green line*. The two bound-state energy levels $E_p^{(1)}$ are shown in respective colors.

the problem (E.4) can be reduced to the following

$$\left(\frac{d^2}{dz^2} + 2 - 6\tanh^2 z\right) f_p(z) = Q_p f_p(z). \tag{E.10}$$

Using representation (E.10) and the formula

$$\frac{d\tanh(x)}{dx} = \frac{1}{\cosh^2(x)} = 1 - \tanh^2(x), \tag{E.11}$$

we can find two bound states with $p = 1, 2$ and a continuum of the scattering states with $p \geq 3$ for the Hamiltonian $\hat{\mathbf{H}}$. The eigenvalues and non-normalized eigenfunctions of the bound states are (Fig. E.1)

$$\begin{aligned} p &= 1, \quad Q_1 = 0, \quad f_1 = 1 - \tanh^2 z \\ p &= 2, \quad Q_2 = -3, \quad f_2 = \tanh z\sqrt{1 - \tanh^2 z}. \end{aligned} \tag{E.12}$$

The eigenvalues and non-normalized eigenfunctions of the scattering states are

$$\begin{aligned} &p \geq 3, \quad Q_p < -4, \\ &f_p = \mathrm{e}^{i\sqrt{-Q_p-4}z}\left(-Q_p - 3 - 3\tanh^2 z + 3i\sqrt{-Q_p - 4}\tanh z\right). \end{aligned} \tag{E.13}$$

Rescaling (E.12), (E.13) back to the Hamiltonian's representation we can see that the bound state f_1 represents the Goldstone mode of $\tilde{\eta}(x)$. Using the formula

$$\tanh(y) - \tanh(x) = \frac{\sinh(y-x)}{\cosh(y)\cosh(x)}, \tag{E.14}$$

we can see that the Goldstone mode represent a small shift of $\tilde{\eta}(x)$in the normal direction. The second bound state is

$$p = 2, \quad E_2^{(1)} = -\frac{3}{2}a > 0, \quad \Psi_2^{(1)}(x) \propto \tilde{\eta}\sqrt{\frac{\mathrm{d}\tilde{\eta}}{\mathrm{d}x}}. \tag{E.15}$$

The eigenvalues of the scattering states are

$$p \geq 3, \quad E_p^{(1)} > -2a > E_2^{(1)} > E_1^{(1)} = 0. \tag{E.16}$$

Sometimes there is a need to solve an eigenfunction/eigenvalue problem for the three-dimensional Hamiltonian operator $\hat{\mathbf{H}}$. In this case, we may attempt to find particular solutions by separating the variables. If this works, a general solution can be expressed in terms of a linear combination of the separated solutions, which satisfy the boundary conditions with $|\Psi(|\mathbf{x}| \to \infty)| < \infty$. The sum of the separation constants is called the dispersion relation. For instance, for

$$\hat{\mathbf{H}}(\tilde{\eta};\, \mathbf{x}) \equiv \frac{\partial^2 g}{\partial \eta^2}(\tilde{\eta}) - \kappa\nabla^2, \quad \hat{\mathbf{H}}(\tilde{\eta};\, \mathbf{x})\Psi_{\mathbf{p}}^{(3)}(\mathbf{x}) = E_{\mathbf{p}}^{(3)}\,\Psi_{\mathbf{p}}^{(3)}(\mathbf{x}), \tag{E.17}$$

we find that

$$\Psi_{q,p}^{(3)}(\mathbf{x}) \propto \mathrm{e}^{i\mathbf{q}\mathbf{x}_2}\Psi_p^{(1)}(x); \quad E_{q,p}^{(3)} = E_p^{(1)} + \kappa q^2, \tag{E.18}$$

where $\mathbf{x}_2 = (y,\ z)$, $\mathbf{q} = (k_y,\ k_z)$, and $q = |\mathbf{q}|$. Equation (E.18) means that slight corrugations of $\tilde{\eta}(x)$are the eigenfunctions of the three-dimensional Hamiltonian operator $\hat{\mathbf{H}}$. Indeed, using the formula (E.14), the corrugation $\Delta\eta$ can be represented as

$$\begin{aligned} &\Delta\eta \equiv \tilde{\eta}[x - X(\mathbf{x}_2)] - \tilde{\eta}(x) \approx -X(\mathbf{x}_2)\Psi_1^{(1)}(x), \\ &X(\mathbf{x}_2) = \sum_{\mathbf{q}} A_{\mathbf{q}}\mathrm{e}^{i\mathbf{q}\mathbf{x}_2}. \end{aligned} \tag{E.19}$$

The eigenvalue of this eigenfunction is

$$E_{q,1}^{(3)} = \kappa \sum_{\mathbf{q}} q^2 . \tag{E.20}$$

An in-depth discussion of the solutions of the Schrödinger equation can be found in L.D. Landau, E.M. Lifshitz, “Quantum Mechanics Non-Relativistic Theory” (Elsevier, Oxford, 1958), §24 and J. Zittartz, Phys. Rev. **154** (2), 529–534 (1967).

Appendix F: Fourier and Legendre Transforms

The goal of any functional transformation is to express the information contained in the function in a more convenient way. Let $f(x)$ be a smooth (continuous, together with its derivatives) function in the interval $(-X/2, +X/2)$. Then $f(x)$ may be expanded in the Fourier series

$$f(x) = \sum_{n=-\infty}^{+\infty} \hat{f}_X(n)\mathrm{e}^{\mathrm{i}2\pi nx/X}, \tag{F.1a}$$

$$\hat{f}_X(n) = \frac{1}{X}\int_{-X/2}^{+X/2} f(x)\mathrm{e}^{-\mathrm{i}2\pi nx/X}\,\mathrm{d}x, \tag{F.1b}$$

which represents a discrete Fourier Transform (FT) in one variable. Actually, the Fourier series is defined also beyond the range $(-X/2, +X/2)$, where the function $f(x)$ is periodically continued on $(-\infty, +\infty)$ with $f_X(x + X) = f_X(x)$.

If $X \to \infty$, it is possible to replace

$$\int_{-X/2}^{+X/2} \mathrm{d}x \to \int_{-\infty}^{+\infty} \mathrm{d}x; \quad \frac{1}{X}\sum_{n=-\infty}^{+\infty} \to \frac{1}{2\pi}\int_{-\infty}^{+\infty} \mathrm{d}k; \quad k \equiv \frac{2\pi n}{X} \tag{F.2}$$

and we arrive at the Fourier integral transform in one variable

$$f(x) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} \hat{f}(k)\mathrm{e}^{\mathrm{i}kx}\,\mathrm{d}k, \tag{F.3a}$$

$$\hat{f}(k) = \int_{-\infty}^{+\infty} f(x)\mathrm{e}^{-\mathrm{i}kx}\,\mathrm{d}x. \tag{F.3b}$$

The number k is called the wavenumber, the function $\exp(\mathrm{i}kx)$—the Fourier mode, and the function $\hat{f}(k)$—the Fourier amplitude. Notice that the Fourier mode with $k = 0$ is just a const $= 1$, while the Fourier modes with large k are periodic functions with small periods.

Substituting the second equation into the first, one can derive a useful relationship

$$\delta(x - x') = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \mathrm{e}^{\mathrm{i}k(x-x')}\, \mathrm{d}k, \tag{F.4}$$

where $\delta(x)$ is a Dirac function. However, most of the time we will be using the discrete Fourier transform (F.1). Physically, the maximum value of k in the Fourier series is restricted by the interatomic distances.

If a smooth function $f(\mathbf{r})$ depends on several variables, e.g. $\mathbf{r} = (x, y, z)$, then it can be conveniently represented by its discrete FT as follows

$$f(\mathbf{r}) = \sum_{\{\mathbf{k}\}} \hat{f}_V(\mathbf{k})\mathrm{e}^{\mathrm{i}\mathbf{kr}}, \tag{F.5a}$$

$$\hat{f}_V(\mathbf{k}) = \frac{1}{V} \int_V f(\mathbf{r})\mathrm{e}^{-\mathrm{i}\mathbf{kr}}\, \mathrm{d}\mathbf{r}, \tag{F.5b}$$

where $\mathbf{k}$ turns into a wavevector (reciprocal vector)

$$\{\mathbf{k}\} \equiv \left\{k_x, k_y, k_z\right\} = \left\{\frac{2\pi n_x}{X}, \frac{2\pi n_y}{Y}, \frac{2\pi n_z}{Z}\right\} \tag{F.6}$$

and summation over $\{\mathbf{k}\}$ means triple summation over $\{-\infty < n_x < +\infty, -\infty < n_y < +\infty, -\infty < n_z < +\infty\}$.

Properties of the 3d discrete FT are

1. The uniform ($\mathbf{k} = 0$) Fourier mode of a function $f(\mathbf{r})$ represents the volume average of this function—homogeneous part of the function

$$\hat{f}_V(0) = \frac{1}{V} \int_V f(\mathbf{r})\, \mathrm{d}\mathbf{r}. \tag{F.7}$$

2. For a real-valued function $f(\mathbf{r})$, the amplitudes of the opposite reciprocal vectors are complex conjugates

$$\hat{f}_V(-\mathbf{k}) = \hat{f}_V^{\,*}(\mathbf{k}). \tag{F.8}$$

3. The gradient of $f(\mathbf{r})$ is

$$\nabla f(\mathbf{r}) = \mathrm{i} \sum_{\{\mathbf{k}\}} \mathbf{k}\hat{f}_V(\mathbf{k})\mathrm{e}^{\mathrm{i}\mathbf{kr}}. \tag{F.9}$$

4. Using (F.4) three times, one can see that as $V \to \infty$

$$\int_V \mathrm{e}^{\mathbf{ikr}}\,\mathrm{d}\mathbf{r} \to (2\pi)^3\ \delta(\mathbf{k}) = (2\pi)^3 \delta(k_x)\delta\big(k_y\big)\delta(k_z), \tag{F.10a}$$

which means that

$$\frac{\hat{V}}{(2\pi)^3} \to \delta(\mathbf{k}). \tag{F.10b}$$

5. Using properties #2 and #4 one can see that

$$\int_V f^2(\mathbf{r})\,\mathrm{d}\mathbf{r} = \int_V \sum_{\{\mathbf{k}\}}\sum_{\{\mathbf{k}\}} \hat{f}_V(\mathbf{k})\hat{f}_V(\mathbf{k}')\mathrm{e}^{\mathrm{i}(\mathbf{k}+\mathbf{k}')\mathbf{r}} d\mathbf{r}$$

$$= \sum_{\{\mathbf{k}\}}\sum_{\{\mathbf{k}\}} \hat{f}_V(\mathbf{k})\hat{f}_V(\mathbf{k}') \int_V \mathrm{e}^{\mathrm{i}(\mathbf{k}+\mathbf{k}')\mathbf{r}}\,\mathrm{d}\mathbf{r} \to_{(V\to\infty)}.$$

$$\sum_{\{\mathbf{k}\}} \frac{V}{(2\pi)^3} \int_V \hat{f}_V(\mathbf{k})\hat{f}_V(\mathbf{k}')(2\pi)^3\ \delta(\mathbf{k}+\mathbf{k}')\,\mathrm{d}\mathbf{k}'$$

$$= V\sum_{\{\mathbf{k}\}} \hat{f}_V(\mathbf{k})\hat{f}_V(-\mathbf{k}) = V\sum_{\{\mathbf{k}\}} \left|\hat{f}_V(\mathbf{k})\right|^2. \tag{F.11}$$

Similarly, if $X, Y, Z \to \infty$, it is possible to replace

$$\int_V \mathrm{d}\mathbf{r} \to \int \mathrm{d}\mathbf{r}; \quad \frac{1}{V}\sum_{\{\mathbf{k}\}} \to \frac{1}{(2\pi)^3}\int \mathrm{d}\mathbf{k}, \tag{F.12}$$

and arrive at the integral FT in three variables

$$f(\mathbf{r}) = \frac{1}{(2\pi)^3}\int \hat{f}(\mathbf{k})\mathrm{e}^{\mathbf{ikr}}\mathrm{d}\mathbf{k}, \tag{F.13}$$

$$\hat{f}(\mathbf{k}) = \int f(\mathbf{r})\mathrm{e}^{-\mathbf{ikr}}\mathrm{d}\mathbf{r}.$$

Example F.1
Find the FT of the function $\mathrm{e}^{-\alpha r}/r$*, which depends on* $|\mathbf{r}|$ *only.*

$$\int \frac{\mathrm{e}^{-\alpha r}}{r}\mathrm{e}^{-\mathrm{i}\mathbf{kr}}\,\mathrm{d}\mathbf{r} = \frac{4\pi}{\alpha^2 + |\mathbf{k}|^2}; \quad \int \frac{\mathrm{e}^{\mathrm{i}\mathbf{kr}}}{\alpha^2 + |\mathbf{k}|^2}\frac{\mathrm{d}\mathbf{k}}{(2\pi)^3} = \frac{\mathrm{e}^{-\alpha r}}{4\pi r}. \tag{F.14}$$

These relations can be obtained by noticing that the function $\varphi = \mathrm{e}^{-\alpha r}/r$ satisfies the differential equation

$$\Delta\varphi - \alpha^2\varphi = -4\pi\delta(\mathbf{r}). \tag{F.15}$$

Multiplying both sides of this equation by $\mathrm{e}^{-\mathrm{i}\mathbf{kr}}$ and integrating over the entire space we recover the previous formula.

Another way to reveal information encoded in a function $f(x)$ is through the Legendre transform (LT). If the function $f(x)$ is strictly convex (second derivative never changes sign or is zero) then the function's derivative with respect to x

$$s = \frac{\mathrm{d}f}{\mathrm{d}x}, \tag{F.16}$$

can replace x as an independent variable of the function. To reveal the symmetry associated with the LT, it is accustomed to redefine the function as follows

$$g(s) = s \cdot x(s) - f(x(s)). \tag{F.17a}$$

The redefined function $g(s)$ has the property that its derivative with respect to s is x

$$\frac{\mathrm{d}g}{\mathrm{d}s} = x(s) + s\frac{\mathrm{d}x}{\mathrm{d}s} - \frac{\mathrm{d}f}{\mathrm{d}x}\frac{\mathrm{d}x}{\mathrm{d}s} = x(s). \tag{F.18}$$

Properties of the LT are

1. The LT of an LT is the original function. To see this, it is instructive to rewrite (F.17a) in a symmetric way

$$g(s) + f(x) = sx(s). \tag{F.17b}$$

2. The extremes of the original function and the transformed one are related as follows

$$f(x_{\min}) = -g(0) \text{ and } g(s_{\min}) = -f(0). \tag{F.19}$$

3. The higher derivatives of the original and transformed functions also show symmetric relationships

$$\frac{d^2 g}{ds^2} \cdot \frac{d^2 f}{dx^2} = 1. \tag{F.20}$$

Example F.2

Find the LT of a quadratic function $f(x) = \alpha x^2/2$.

For this function, we can easily find that

$$s(x) = \alpha x, \quad x(s) = \frac{s}{\alpha}, \quad g(s) = \frac{1}{2\alpha} s^2. \tag{F.21}$$

If we substitute the first relation in (F.21) into the last one we obtain

$$g(s) = \frac{1}{2} \alpha x^2(s), \tag{F.22}$$

which shows that the LT of a quadratic function is equal to the original function expressed through the original independent variable. Of course, this is the case of a single classical particle of mass α moving with a velocity x, where $f(x)$ and $g(s)$ are the particle's kinetic energy expressed as a function of the velocity x or momentum s.

LT can be applied to a function that depends on many variables—multivariable LT. An in-depth discussion of the Legendre transform can be found in R.K. P. Zia, E.F. Redish, S.R. McKay, "Making sense of the Legendre transform", Am. J. Phys. **77**, 614 (2009).

Appendix G: Stochastic Processes

Suppose a physical system of interest can be found in different states of an *ensemble* $\Omega = \{\omega\}$ and suppose that we need to measure a quantity f that varies not only from state to state but also with time t. If the quantity f depends on other parameters, not included into the characterization of the states Ω (which is usually the case in physical systems), its values appear to be random. In this case, the quantity is said to *fluctuate*; the function $f(\Omega, t)$ is called a *stochastic process* and may be characterized by various average quantities. There are different ways to define these quantities. For instance, one may define a "time average" of f over a certain period of time T

$$\bar{f}_T \equiv \frac{1}{T} \int_0^T f(\ \Omega, t)\, \mathrm{d}t. \tag{G.1}$$

Instead of averaging over the period of time T, we may identify different states of the ensemble $\Omega = \{\omega\}$, introduce a probability density $P(\omega)$ of the state such that the probability for the system to be in the states with ($\omega < \Omega < \omega + \mathrm{d}\omega$) is

$$P(\omega)\, \mathrm{d}\omega, \tag{G.2}$$

and define the average as

$$\langle f(\omega, t) \rangle \equiv \int_{-\infty}^{+\infty} f(\omega, t) P(\omega)\, \mathrm{d}\omega. \tag{G.3}$$

Of course, the probability density $P(\omega)$ is normalized such that

$$\int_{-\infty}^{+\infty} P(\omega)\, \mathrm{d}\omega = 1. \tag{G.4}$$

The quantity (G.3) is called "ensemble average." The probability density may itself depend on time, $P(\omega, t)$, making the process time-dependent. A process is called *stationary* (do not confuse with equilibrium) if all the functions that characterize it are invariant in time, that is, do not change if every time variable t is replaced by $t + s$, where s is an arbitrary time interval. For very many systems, which are called *ergodic*, the time average over a long period of time is equal to the ensemble average

$$\bar{f}_\infty = \langle f \rangle. \tag{G.5}$$

The Master and Fokker–Plank Equations

To describe a time-dependent stochastic process, one can write an evolution equation for the probability density of the state ω, $P(\omega, t)$. In a short period of time $\mathrm{d}t$, this quantity will decrease if the system makes a transition from the state ω to one of the states between ω' and $\omega' + \mathrm{d}\omega'$; let us denote the probability of this event as $W(\omega'|\omega)\mathrm{d}\omega'\,\mathrm{d}t$. However, during the same period of time $P(\omega, t)$ will increase if one of the states between ω' and $\omega' + \mathrm{d}\omega'$ makes a transition to ω. The probability of the latter event is $W(\omega|\omega')\mathrm{d}\omega'\,\mathrm{d}t$. Here we assumed a "Markovian" property of the system expressed by the fact that "jump probability" W depends on ω and ω' but not the previous states of the system. Integrating over all states ω' we find the desired equation which is called the *master equation*

$$\frac{\partial P(\omega, t)}{\partial t} = \int_{-\infty}^{\infty} \mathrm{d}\omega' [W(\omega|\omega')P(\omega', t) - W(\omega'|\omega)P(\omega, t)]. \tag{G.6}$$

The transition probability W may be expressed as a function of the starting point and the size of the jump

$$W(\omega|\omega') = W(\omega'; \lambda), \lambda \equiv \omega - \omega'. \tag{G.7}$$

To derive the Fokker–Plank equation from (G.6), we use the basic assumption about the system that only small jumps between the neighboring states occur, that is, $W(\omega'; \lambda)$ is a sharply peaked function of λ but varies slowly with ω'. Then we may expect the solution $P(\omega, t)$ to vary slowly with ω also. It is then possible to expand the first term in the integrand of (G.6) into a Taylor series near ω and retain only the terms up to the second order in λ

$$\frac{\partial P(\omega,t)}{\partial t} = \int_{-\infty}^{\infty} \mathrm{d}\lambda \left[W(\omega;\lambda)P(\omega,t) - \lambda \frac{\partial}{\partial \omega}\{W(\omega;\lambda)P(\omega,t) + \frac{1}{2}\lambda^2 \frac{\partial^2}{\partial \omega^2}\{W(\omega;\lambda)P(\omega,t)\} - W(\omega;-\lambda)P(\omega,t) \right]. \tag{G.8}$$

Note that the dependence of $W(\omega;\,\lambda)$ on λ is fully maintained because we do not expand it with respect to this argument. Integrals of the first and fourth terms cancel. Integrals of the other terms can be written with the aid of the jump moments

$$a_\nu(\omega) \equiv \int_{-\infty}^{\infty} \lambda^\nu W(\omega;\lambda)\,\mathrm{d}\lambda. \tag{G.9}$$

The result is the Fokker–Plank equation

$$\frac{\partial P(\omega,t)}{\partial t} = -\frac{\partial}{\partial\omega}\{a_1(\omega)P(\omega,t)\} + \frac{1}{2}\frac{\partial^2}{\partial\omega^2}\{a_2(\omega)P(\omega,t)\}. \tag{G.10}$$

This equation can be presented as a continuity equation for the probability density

$$\frac{\partial P(\omega,t)}{\partial t} = -\frac{\partial J(\omega,t)}{\partial\omega} \tag{G.11}$$

and a "constitutive equation" for the probability flux $J(\omega,\,t)$

$$J(\omega,t) = a_1(\omega)P(\omega,t) - \frac{1}{2}\frac{\partial}{\partial\omega}\{a_2(\omega)P(\omega,t)\}. \tag{G.12}$$

Such representation helps interpret the first term of the flux as the drift term and the second one as the diffusion term. The Fokker–Plank equation has a stationary solution, that is, the one with $J(\omega,t) = 0$

$$P^s(\omega) = \frac{\mathrm{const}}{a_2(\omega)}\exp\left[2\int_0^{\omega}\frac{a_1(\omega)}{a_2(\omega)}\,\mathrm{d}\omega'\right]. \tag{G.13}$$

Many features of the process can be illuminated by using a potential $U(\omega)$

$$U(\omega) \equiv -\int a_1(\omega)\,\mathrm{d}\omega. \tag{G.14}$$

Using the Fokker–Plank equation, one can derive the following equations for the evolution of the average quantities

$$\frac{\mathrm{d}\langle\omega\rangle}{\mathrm{d}t} = \langle a_1(\omega)\rangle, \tag{G.15a}$$

$$\frac{\mathrm{d}\langle\omega^2\rangle}{\mathrm{d}t} = \langle a_2(\omega)\rangle + 2\langle\omega a_1(\omega)\rangle. \tag{G.15b}$$

Indeed, differentiating (G.3) with respect to time, using the Fokker–Plank equation, and integrating by parts two times we have

$$\frac{\mathrm{d}\langle\omega\rangle}{\mathrm{d}t}=\int_{-\infty}^{\infty}\omega\frac{\partial P}{\partial t}\mathrm{d}\omega=-\int_{-\infty}^{\infty}\omega\frac{\partial J}{\partial\omega}\,\mathrm{d}\omega=-\left[\omega J+\frac{1}{2}a_2P\right]_{-\infty}^{\infty}+\int_{-\infty}^{\infty}a_1P\,\mathrm{d}\omega.$$

As the flux J and density P vanish at $\pm\infty$ we obtain (G.15a). A similar procedure leads to (G.15b).

Defining the average and variance of the random variable ω as

$$\varpi\equiv\langle\omega\rangle,\quad \sigma^2\equiv\left\langle(\omega-\varpi)^2\right\rangle, \tag{G.16}$$

expanding $a_v(\omega)$ near the value of ϖ, and retaining only the leading terms one can derive a system of coupled evolution equations

$$\frac{\mathrm{d}\varpi}{\mathrm{d}t}=a_1(\varpi)+\frac{1}{2}\sigma^2\frac{\partial^2a_1}{\partial\omega^2}(\varpi), \tag{G.17a}$$

$$\frac{\mathrm{d}^2}{\mathrm{d}t}=a_2(\varpi)+2\sigma^2\frac{\partial a_1}{\partial\omega}(\varpi). \tag{G.17b}$$

Although the retained terms in (G.17a) were obtained as expansion terms of the first and second order, they can be of the same order of magnitude. This is a consequence of the fact that averaging of an alternating quantity yields greater cancelation than averaging of its square. It is important to notice here that the system (G.17) can be derived directly from the master equation (G.6), which means that these equations are accurate up to the second order at least. Equation (G.17a) shows that the evolution of the average value is not determined only by its own value, but is influenced by the fluctuations around it. The *macroscopic approximation* consists in ignoring these fluctuations, hence keeping only the first term in the expansion (G.17a). The zeroes of the first jump moment (G.9) may be called the *nodal points*. Hence, (G.17a) shows that in the macroscopic approximation of a stationary process the average value tends to one of the nodal points, if such points exist.

Equation (G.17b) shows that the tendency of the variance σ^2 to increase at a rate $a_2>0$ [see Eq.(G.9)] will be kept in check by the second term if $a_1{}'(\varpi)<0$. Then

$$\sigma^2\rightarrow\frac{a_2}{2|\partial a_1/\partial\omega|}$$

and the criterion of the validity of the macroscopic approximation becomes

$$a_2\ll4\left|\frac{a_1\partial a_1/\partial\omega}{\partial^2a_1/\partial\omega^2}\right|. \tag{G.18}$$

This criterion shows that the fluctuations are always important for the evolution of the physical system near a nodal point. However, the level of importance of the fluctuations is different in different systems. In the following sections, we will elucidated the cases of systems where the second jump moment does not vary significantly

$$a_2(\omega) = \text{const}(\omega) > 0. \tag{G.19}$$

This condition corresponds to the additive fluctuations as opposed to the multiplicative ones when the fluctuation strength depends on the stochastic variable itself. The latter case creates the so-called Ito–Stratonovich dilemma, which is beyond the scope of this book.

Decomposition of Unstable States

Consider a process of decomposition of an unstable state in a physical system. Mathematically, it can be described as switching of $\partial a_1/\partial\omega$ in (G.17) from negative to positive value so that the system finds itself in a state, which suddenly becomes unstable although it was stable before. Suppose that the first jump moment of the process vanishes at $\omega = \omega_0$ and has an essential nonlinearity

$$a_1(\omega) = a_{11}(\omega - \omega_0) + \frac{1}{2}a_{12}(\omega - \omega_0)^2, \quad a_{11} \neq 0, \quad a_{12} \neq 0. \tag{G.20a}$$

This process has two nodal points

$$\omega_0 \text{ and } \omega_1 = \omega_0 - 2\frac{a_{11}}{a_{12}}, \tag{G.20b}$$

which are the critical points of the potential $U(\omega)$, (G.14)

$$U(\omega) = \text{const} - \frac{a_{11}}{2}(\omega - \omega_0)^2 - \frac{a_{12}}{6}(\omega - \omega_0)^3. \tag{G.21}$$

Let us first analyze the process with

$$a_{11} > 0. \tag{G.22}$$

Then, introducing the scaled variables

$$\tau = a_2 t; \quad v(\tau) = \frac{a_{12}}{a_{11}}(\varpi - \omega_0); \quad w(\tau) = \frac{a_{12}^2}{a_{11}^2}\sigma^2; \tag{G.23a}$$

scaled potential

$$u(v) = \frac{a_{12}^2}{a_{11}^3} U(\omega) = -\frac{1}{2}v^2 - \frac{1}{6}v^3; \tag{G.23b}$$

and scaled parameters:

$$\alpha = \frac{a_{11}}{a_2} > 0; \quad \beta = \frac{a_{12}}{a_{11}}. \tag{G.23c}$$

we obtain the scaled form of the evolution equations (G.17)

$$\dot{v} = \frac{\alpha}{2} v(2+v) + \frac{\alpha}{2} w, \tag{G.24a}$$

$$\dot{w} = \beta^2 + 2\alpha w(1+v), \tag{G.24b}$$

where the dot means differentiation with respect to τ. In Fig. G.1 is depicted the (v,w)-phase plane of the system of equations (G.24) and the potential (G.23b).

Evolutionary system (G.24) has the stationary points ($\dot{v}_s = \dot{w}_s = 0$) that satisfy the following conditions

$$w_s = -v_s(2+v_s), \tag{G.25a}$$

$$\beta^2 = -2\alpha w_s(1+v_s). \tag{G.25b}$$

Substituting w_s in (G.25b) with (G.25a) we transform the simultaneous (G.25) into a single nonlinear equation for v_s, which is also depicted in Fig. G.1

$$z(v_s) \equiv v_s(1+v_s)(2+v_s) = \frac{\beta^2}{2\alpha}. \tag{G.26}$$

Analysis of this equation shows that there are three branches of the stationary points: $s = 0, 1, 2$. If $\beta = 0$, which is the case if $a_{12} = 0$ but $a_{11} \neq 0$, then the stationary points are

$$(v_1 = -2,\ w_1 = 0),\ (v_2 = -1,\ w_2 = 1),\ (v_0 = 0,\ w_0 = 0), \tag{G.27}$$

that is, the nodal points of (G.20a) with zero variance and the intermediate point with the finite variance (see Fig. G.1). If $\beta \neq 0$, then

$$(-2 < v_1 < v_-, w_1 > 0);\ (v_- < v_2 < -1, w_2 \sim 1);\ (v_0 > 0, w_0 < 0), \tag{G.28}$$

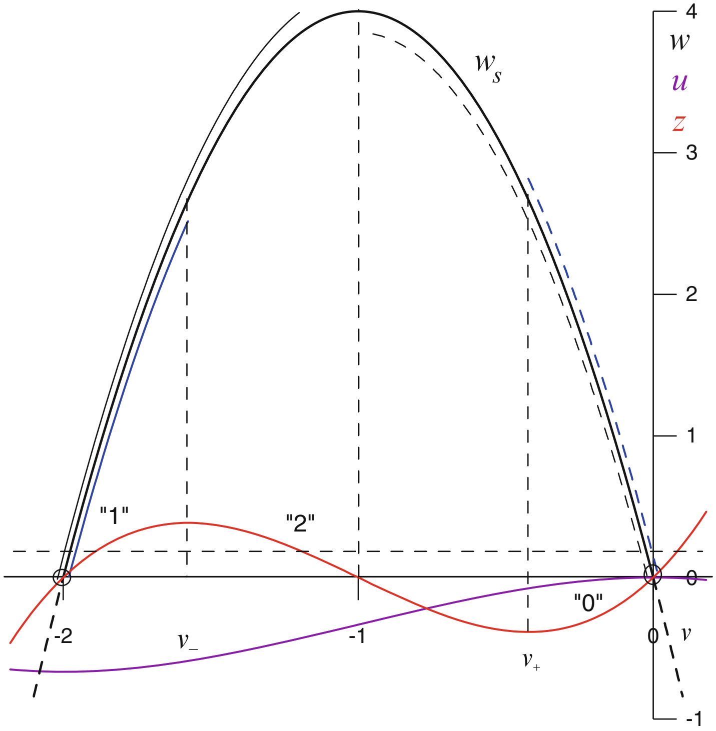

Fig. G.1 Phase plane (v, w) of the dynamical system, (G.24), with $\alpha > 0$. *Purple line*—potential u (v) (G.23b); *black line*—stationary points $w_s(v)$ (G.23b); *red line*— function z (v) (G.26); *blue lines*—stable stationary branches; *open circle*—the nodal points, *horizontal dash*—graphical solution of (G.26).

where

$$v_{\pm} = -1 \pm \frac{\sqrt{3}}{3}. \tag{G.29}$$

As $\sigma^2 > 0$, the third relation in (G.23a) yields the constraint

$$w>0, \tag{G.30}$$

which makes the "0"-branch superfluous. On the "1"-branch the average of the stationary process ϖ_1 deviates from the node ω_1. To evaluate the deviation, we need to compare it with the square root of the variance σ_1 at the stationary point. Using (G.23a) and (G.25) we obtain

$$\varpi_1 - \omega_1 = \frac{1}{(-v_1)\sqrt{-(1+v_1)}}\sqrt{\frac{\beta^2}{2\alpha}\sigma_1^2}, \tag{G.31a}$$

which means that

$$\varpi_1 - \omega_1 \ll \sqrt{\sigma_s^2} \quad \text{if } \frac{\beta^2}{2\alpha} \ll 1. \tag{G.31b}$$

There is a limit to the nonlinearity beyond which the evolutionary system (G.24) has no stationary points. Indeed, differentiating $z(v)$ and equating it to zero we obtain

$$z'(v_s) = 2 + 6v_s + 3v_s^2 = 3(v_s - v_+)(v_s - v_-) = 0. \tag{G.32}$$

Substituting the extreme values v_s into (G.26) we obtain that for $-2 < v_s < 0$

$$\beta^2 \le 2\left(\max_{-2<v_s<0} |z(v_s)|\right)\alpha = \frac{4}{3\sqrt{3}}\alpha. \tag{G.33}$$

Although σ^2 (or w) explicitly represent the fluctuations of the physical system, the stationary points of the evolutionary system (G.24) need to be analyzed on their stability because this system is an expansion of the master equation. Representing the variable as $v = v_s + \delta v$, $w = w_s + \delta w$, substituting this into (G.24), linearizing the system, and taking into account (G.26) we obtain

$$\dot{\delta v} = \alpha(1 + v_s)\ \delta v + \frac{\alpha}{2}\ \delta w, \tag{G.34a}$$

$$\dot{\delta w} = 2\alpha w_s\ \delta v + 2\alpha(1 + v_s)\ \delta w. \tag{G.34b}$$

The characteristic equation of this system is

$$k^2 - 3\alpha(1 + v_s)k + \alpha^2\left(2 + 6v_s + 3v_s^2\right) = 0. \tag{G.35}$$

Notice that the free term of the characteristic equation is proportional to $z'(v_s)$ (Why?).

As known, for the stability of a system of linear differential equations the real parts of all the roots of the characteristic equation must be negative. For (G.35) with the condition (G.22) this is the case if

$$v_s < -1, \tag{G.36a}$$

$$(v_s - v_-)(v_s - v_+) > 0. \tag{G.36b}$$

Condition (G.36a) is a simple consequence of the condition (G.30) and brings no additional restrictions on the stationary branches. Condition (G.36b) shows that the "1"-branch is stable, while the "2"-branch is unstable (see Fig. G.1). Hence

$$v_1 - \text{stable};\ v_2 - \text{unstable};\ v_0 - \text{superfluous}. \tag{G.37}$$

If the condition (G.22) is not true, the branches "1" and "0" switch the roles, while the branch "2" remains stationary unstable. Summarizing results for the decomposition process, the evolutionary system (G.24) shows that the average value of the process will be moving from ($v \approx v_0$) where it was stable before the switch toward that of the stable stationary state (v_1, w_1). For a weakly nonlinear process ($\beta \to 0$), this value (v_1) stays well inside the root-mean square range (w_1) of the nodal point ω_1 ($v_1 = -2$) while for a strongly nonlinear process this is not true. During this transition, the variance w goes through the maximum when the system is about half-way to the final state. The dimensionless time scale of the process is $1/\alpha$ and the dimensional one is $1/|a_{11}|$.

Diffusion in Bistable Potential

Consider a stochastic process that can be described by the Fokker–Plank equation (G.10) with $a_2 = \text{const}(\omega)$ as in (G.19) and the potential function $U(\omega)$ (G.14), which has three nodal points ω_a, ω_b, ω_c, of which ω_a and ω_c are locally stable and ω_b is unstable, cf. (G.21). The potential function $U(\omega)$ and stationary probability density, (G.13), are depicted in Fig. G.2. A system in ω_b would be caused to move into either ω_a or ω_c by the smallest external perturbation via a process of decomposition similar to the one described in the previous section. Potentials having such characteristics are called *bistable*. Analysis of the evolution equations (G.17) for such system shows that there is a domain of attraction D_a such that if $\varpi(0) \in D_a$ then $\varpi(t) \to \omega_a$ for $t \to \infty$. Of course, same applies to ω_c. Yet this description is not entirely correct, because even when the system is inside D_a there is still a probability, however small, for a giant fluctuation to occur, which takes it across ω_b into D_c. Thus fluctuations give rise to a macroscopic effect.

The problem of evolution of the system may be reduced to a first-passage problem: suppose at $t = 0$ a system starts out at ω_a; how long will it take it to reach the state ω_c for the first time? If at ω_c we set the absorbing boundary condition, the average or mean first passage time is called the escape time τ_{ac}. For the Fokker–Plank equation (G.10) one finds

$$\tau_{ac} = \frac{2}{a_2} \int_{\omega_a}^{\omega_c} \frac{d\omega}{P^s(\omega)} \int_{-\infty}^{\omega} P^s(\omega')\, d\omega', \tag{G.38a}$$

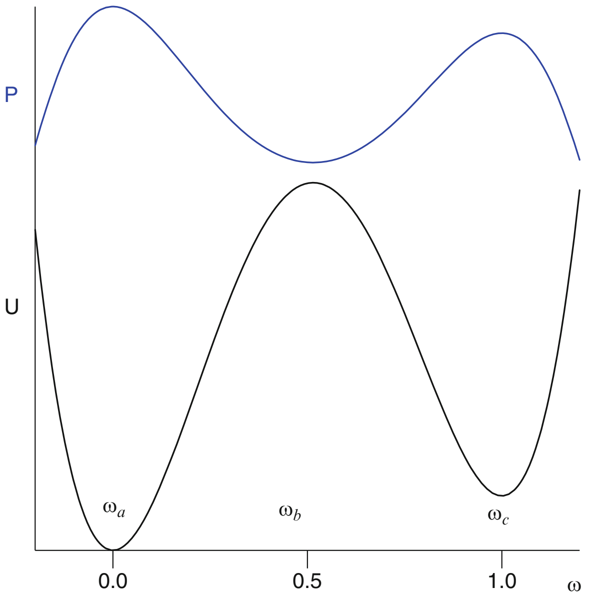

Fig. G.2 Potential U (*black line*) and probability distribution P (*blue line*) as functions of the state variable ω

where $P^s(\omega)$ should be taken from (G.13). In case of weak fluctuations

$$a_2 \ll U(\omega_b) - U(\omega_a). \tag{G.39}$$

$(P^s)^{-1}$ of (G.13) is sharply peaked at $\omega = \omega_b$, that is, the statistical probability of the unstable state $\omega = \omega_b$ is much smaller than that of the stable ones (see Fig. G.2). In this case, the escape time τ_{ac} is much longer than the time needed to establish local equilibrium in each separate valley and integration in (G.38a) can be performed using the Laplace method of asymptotic expansion [2]

$$\begin{aligned} \tau_{ac} &= \frac{2\pi_a^s}{a_2} Z e^{2U(\omega_b)/a_2} \int_{\omega_a}^{\omega_c} e^{(-1/a_2)|U''(\omega_b)|(\omega-\omega_b)^2} d\omega \\ &= 2Z\pi_a^s e^{2U(\omega_b)/a_2} \sqrt{\frac{\pi}{a_2|U''(\omega_b)|}} \end{aligned}, \tag{G.38b}$$

where

$$\pi_a^s = \frac{1}{Z} \int_{-\infty}^{\omega_b} P^s(\omega)\, d\omega \tag{G.38c}$$

is the splitting probability, that is, probability for the particle to be found left of the potential barrier at ω_b, and

$$Z = \int_{-\infty}^{+\infty} P^s(\omega)\,\mathrm{d}\omega \tag{G.38d}$$

is the normalization constant (partition function) of the distribution (G.13). In (G.38b), the exponential (Arrhenius factor) is inversely proportional to the probability of the barrier state, U'' is the second derivative of the potential and the square root (Zeldovich factor) expresses the probability for the variable ω to return back from the region beyond the barrier. In the parabolic approximation

$$U(\omega) = U(\omega_a) + \frac{1}{2}U''(\omega_a)(\omega-\omega_a)^2 + O\Big((\omega-\omega_a)^3\Big) \tag{G.40a}$$

and

$$\begin{aligned} Z\pi_a^s &= \int_{-\infty}^{\omega_b} \mathrm{e}^{-2U(\omega)/a_2}\,\mathrm{d}\omega \\ &\approx \mathrm{e}^{-2U(\omega_a)/a_2}\int_{-\infty}^{+\infty} \mathrm{e}^{-U''(\omega_a)(\omega-\omega_a)^2/a_2}\,\mathrm{d}\omega = \mathrm{e}^{-2U(\omega_a)/a_2}\sqrt{\frac{\pi a_2}{U''(\omega_a)}}. \end{aligned} \tag{G.40b}$$

Substitution of (G.40b) into (G.38b) yields

$$\tau_{ac} = \frac{2\pi}{\sqrt{U''(\omega_a)|U''(\omega_b)|}}\exp\frac{U(\omega_b)-U(\omega_a)}{a_2/2}. \tag{G.40c}$$

Notice that the escape time is very sensitive to the height of the potential barrier, $U(\omega_b)-U(\omega_a)$.

In fact, the concept of escape time can be extended on nonsmooth potentials which obey the condition (G.39). Depending on the analytical properties of the potential $U(\omega)$ at the point of minimum ω_a, the splitting probability and escape time take on different values. For the potential

$$U(\omega) = \begin{cases} U(\omega_a) + U'(\omega_a)(\omega-\omega_a) + O\Big((\omega-\omega_a)^2\Big), & \text{for } \omega \geq \omega_a \\ \infty, & \text{for } \omega < \omega_a \end{cases}, \tag{G.41a}$$

we have

$$\begin{aligned} Z\pi_a^s &= \int_{-\infty}^{\omega_b} \mathrm{e}^{-2U(\omega)/a_2}\,\mathrm{d}\omega \\ &\approx \mathrm{e}^{-2U(\omega_a)/a_2}\int_{\omega_a}^{+\infty} \mathrm{e}^{-2U'(\omega_a)(\omega-\omega_a)/a_2}\,\mathrm{d}\omega = \frac{a_2}{2U'(\omega_a)}\mathrm{e}^{-2U(\omega_a)/a_2} \end{aligned} \tag{G.41b}$$

and

$$\tau_{ac} = \frac{1}{U'(\omega_a)}\sqrt{\frac{\pi a_2}{|U''(\omega_b)|}}\exp\frac{U(\omega_b) - U(\omega_a)}{a_2/2}. \tag{G.41c}$$

Compare the expressions of the escape time, (G.40c) and (G.41c), and notice that the difference in "smoothness" of the potential $U(\omega)$ at the point of minimum ω_a, (G.40a) or (G.41a), does not change the exponential but leads to different dependences of the prefactor on the fluctuation strength a_2.

Autocorrelation Function

The average values do not characterize the stochastic processes completely. For instance, they say nothing about the internal mechanism that makes the quantity to fluctuate. We need a measure of the influence of the value of the fluctuating variable at the moment t_1 on its value at the moment $t_2 > t_1$. Such measure is expressed by the time average *autocorrelation function*

$$\overline{f(\omega_1, t_1)f(\omega_2, t_2)} \equiv \lim_{T\to\infty} \frac{1}{T}\int_0^T f(\omega_1, t_1)f(\omega_2, t_2)\,\mathrm{d}t_1. \tag{G.42}$$

One can also introduce a correlation function between two different processes $\overline{f(\omega_1, t_1)g(\omega_2, t_2)}$ but we will not need that.

The ensemble average autocorrelation function can be introduced with the help of the joint distribution function $P(\omega_1,t_1;\ \omega_2,t_2)$ such that

$$P(\omega_1, t_1;\ \omega_2, t_2)\,\mathrm{d}\omega_1\,\mathrm{d}\omega_2$$

is the probability for the system to be in the states with $(\omega_1 < \Omega < \omega_1 + \mathrm{d}\omega_1)$ at time t_1 and in the states with $(\omega_2 < \Omega < \omega_2 + \mathrm{d}\omega_2)$ at time t_2. Then

$$\langle f(\omega_1, t_1)f(\omega_2, t_2)\rangle \equiv \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} f(\omega_1, t_1)f(\omega_2, t_2)P(\omega_1, t_1; \omega_2, t_2)\,\mathrm{d}\omega_1\,\mathrm{d}\omega_2. \tag{G.43}$$

In the spirit of the ergodic hypothesis, the time average and ensemble average autocorrelation functions are equal

$$\overline{f(\omega_1, t_1)f(\omega_2, t_2)} = \langle f(\omega_1, t_1)f(\omega_2, t_2)\rangle. \tag{G.44}$$

Below are some of the properties of the autocorrelation function of a stationary process.

1. For a stationary process, the average $\langle f(\omega, t)\rangle$ is time independent and autocorrelation function $\langle f(\omega_1, t_1) f(\omega_2, t_2)\rangle$ depends only on the time interval $s = t_2 - t_1$.
2. For $s = 0$, the autocorrelation function is the mean square value of f, $\langle f^2(\omega, t)\rangle$ and, hence, must be positive definite. In a stationary system, it is independent of t that is, a constant.
3. The function $\langle f(\omega_1, t) f(\omega_2, t+s)\rangle$ is symmetric about the value $s = 0$, that is a function of $|s|$ only. Indeed,

$$\langle f(t) f(t+s)\rangle = \langle f(t-s) f(t)\rangle = \langle f(t) f(t-s)\rangle. \tag{G.45}$$

   The first equality in (G.45) is true because the system is stationary.
4. For *any* value of s, the autocorrelation function is

$$|\langle f(t) f(t+s)\rangle| \le \langle f^2(t)\rangle. \tag{G.46}$$

   Indeed, since

$$\left\langle [f(t) \pm f(t+s)]^2 \right\rangle = \langle f^2(t)\rangle + \langle f^2(t+s)\rangle \pm 2\langle f(t) f(t+s)\rangle$$
$$= 2\left[\langle f^2(t)\rangle \pm \langle f(t) f(t+s)\rangle\right] \ge 0,$$

   the function $\langle f(t) f(t+s)\rangle$ cannot go outside the limits of $\pm \langle f^2(t)\rangle$.
5. As known, the joint probability distribution function of statistically independent stochastic process factors into the product of the probability distribution functions of the individual processes. For our system, this means that if (ω_1, t_1), for some reason, is statistically independent of (ω_2, t_2) then

$$P(\omega_1, t_1; \omega_2, t_2) = P(\omega_1, t_1) P(\omega_2, t_2) \tag{G.47}$$

   and, hence,

$$\langle f(\omega_1, t_1) f(\omega_2, t_2)\rangle = \langle f(\omega_1, t_1)\rangle \langle f(\omega_2, t_2)\rangle. \tag{G.48}$$

   One may introduce a function, which is called a two-time irreducible autocorrelation function of f

$$K_f(t_1, t_2) \equiv \langle f(\omega_1, t_1) f(\omega_2, t_2)\rangle - \langle f(\omega_1, t_1)\rangle \langle f(\omega_2, t_2)\rangle. \tag{G.49}$$

   This function characterizes statistical dependence of the values of the stochastic process $f(\omega, t)$ at different moments in time. For a stationary process, it depends on $|s| = |t_2 - t_1|$ only

$$K_f(t_1, t_2) = K_f(|s|). \tag{G.50}$$

6. It statistical correlations diminish with $|s|$, that is

$$K_f(|s|) \to 0 \quad \mathit{for} \quad |s| \to \infty, \tag{G.51}$$

then the stochastic process $f(\omega, t)$ may be characterized by the correlation time τ_{cor}

$$\tau_{\text{cor}} \equiv \frac{1}{K_f(0)} \int_0^{\infty} \left|K_f(s)\right| \mathrm{d}s. \tag{G.52}$$

The magnitude of the function $K_f(s)$ is significant only when the variable s is of the same order of magnitude as τ_{cor}. In other words, as s becomes larger in comparison with τ_{cor}, the values $f(t)$ and $f(t + s)$ become uncorrelated, that is the "memory" of the physical activity during a given interval of time around t is completely lost after a laps of time large in comparison with τ_{cor}.

A useful exercise in the correlation functions is the evaluation of the double integral

$$I = \int_0^t \int_0^t \mathrm{e}^{(t_1+t_2)/\tau} K_f(t_2 - t_1)\, \mathrm{d}t_1\, \mathrm{d}t_2. \tag{G.53}$$

Changing to the variables $T = ½(t_1 + t_2)$ and $s = (t_2 - t_1)$ the integrand takes the form $\exp(2T/\tau)K_f(s)$, integration over $(\mathrm{d}t_1\, \mathrm{d}t_2)$ gets replaced by $(\mathrm{d}T\, \mathrm{d}s)$, while the limits of integration, in terms of the variables T and s, can be read from Fig. G.3; we find that, for $0 \le T \le t/2$, s goes from $-2T$ to $+2T$, while for $t/2 \le T \le t$, it goes from $-2(t - T)$ to $+2(t - T)$. Accordingly, we have

$$I = \int_0^{t/2} \mathrm{e}^{2T/\tau}\, \mathrm{d}T \int_{-2T}^{+2T} K_f(s)\, \mathrm{d}s + \int_{t/2}^{t} \mathrm{e}^{2T/\tau}\, \mathrm{d}T \int_{-2(t-T)}^{+2(t-T)} K_f(s)\, \mathrm{d}s.$$

In view of the properties #5, 6 of the function $K_f(s)$ the integrals over s draw significant contributions only from a very narrow region, of the order of τ_{cor}, around the central value $s = 0$; contributions from regions with larger values of $|s|$ are negligible. Therefore, if $t \gg \tau_{\text{cor}}$, the limits of integration for s may be replaced by $-\infty$ and $+\infty$, with the result

$$I \approx \int_0^t \mathrm{e}^{2T/\tau}\, \mathrm{d}T \int_{-\infty}^{+\infty} K_f(s)\, \mathrm{d}s = \frac{\tau}{2}(\mathrm{e}^{2t/\tau} - 1) \int_{-\infty}^{+\infty} K_f(s)\, \mathrm{d}s. \tag{G.54}$$

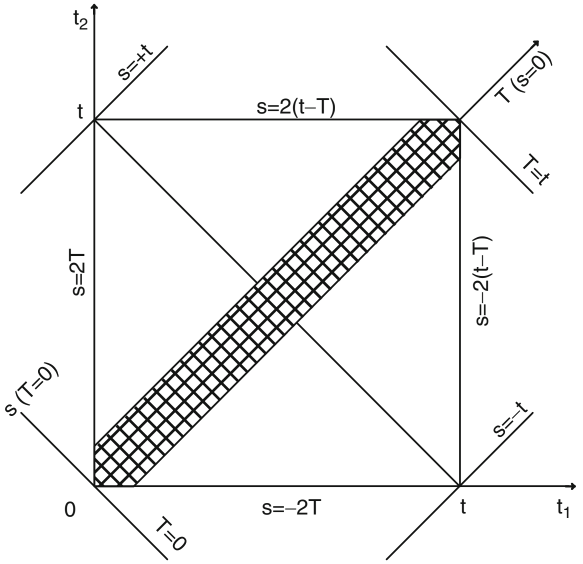

Fig. G.3 Limits of integration of the double integral in (G.53) in terms of (T, s)

The Langevin Approach

If the properties of the jump moments (G.9) are not known, an alternative way of writing an evolution equation for the time-dependent stochastic process is by including the fluctuations explicitly into the phenomenological equation for the state variable $\omega(t)$

$$\frac{d\omega}{dt} = A(\omega) + \xi(t). \tag{G.55}$$

Here $A(\omega)$ is a phenomenological force that depends on the state of the system ω and $\xi(t)$ is a fluctuating force statistically independent of A. Such equation is called the Langevin equation. We are not looking for an exact solution of the Langevin equation, only for a stochastic one. Another way to include the fluctuations into the evolutionary problem is to consider stochastic initial conditions; this alternative, however, will not be pursued in this book.

Properties of the fluctuating force can be deduced from the following calculations. An obvious short-time solution of the Langevin equation is

$$\omega(t + \Delta t) = \omega(t) + \int_t^{t+\Delta t} A(\omega(t'))\,dt' + \int_t^{t+\Delta t} \xi(t')\,dt'.$$

Hence the average of the increment $\Delta\omega$ is

$$\langle\,\Delta\omega\rangle = A(\omega(t'))dt'\;\Delta t + \langle\xi(t)\rangle\;\Delta t + O(\,\Delta t)^2. \tag{G.56}$$

This relation shows that for the phenomenological force to be representative of the dynamics of the system the ensemble average of the fluctuating force must be zero

$$\langle\xi(t)\rangle = 0. \tag{G.57}$$

Next

$$\left\langle(\,\Delta\omega)^2\right\rangle = \left\langle\left[\int_t^{t+\Delta t} A(\omega(t'))\,\mathrm{d}t'\right]^2\right\rangle + 2\int_t^{t+\Delta t}\mathrm{d}t'\int_t^{t+\Delta t}\mathrm{d}t''\langle A(\omega(t'))\xi(t'')\rangle$$
$$+\int_t^{t+\Delta t}\mathrm{d}t'\int_t^{t+\Delta t}\mathrm{d}t''\langle\xi(t')\xi(t'')\rangle.$$

The first term in the right-hand side is of order $(\Delta t)^2$; the second term vanishes due to (G.57) and the statistical independence of A and ξ; in the third term we have the autocorrelation function of ξ, $K_\xi(s) = \langle\xi(t)\xi(t+s)\rangle$, which is a measure of the stochastic correlation between the value of the fluctuating variable ξ at time t and its value at time $t + s$. If the process $\xi(t)$ has some sort of regularity then the correlator $K_\xi(s)$ would extend over a range of the time interval τ_{cor} (G.52). On the contrary, if we assume that $\xi(t)$ is extremely irregular, then τ_{cor} is zero and we may choose

$$\langle\xi(t_1)\xi(t_2)\rangle = K\;\delta(t_2 - t_1). \tag{G.58}$$

Then

$$\left\langle(\Delta\omega)^2\right\rangle = K\;\Delta t + O(\,\Delta t)^2. \tag{G.59}$$

Comparison of (G.56) with (G.15a) and (G.59) with (G.17b) shows that the Fokker–Plank and Langevin descriptions are equivalent if

$$A(\omega) = a_1(\omega);\quad K = a_2(\omega) = \mathrm{const}(\omega). \tag{G.60a}$$

Of course, if the potential function of the system $U(\omega)$ is known, the phenomenological force may be written in the form

$$A(\omega) = -\frac{\partial U(\omega)}{\partial\omega}. \tag{G.60b}$$

A comment regarding the derivative of the Langevin force is in order here. In principle, it is so irregular that its derivative is not defined. However, the rate of change of the stochastic process can be defined by its moments. This approach to the time derivative of $\xi(t)$ is used in the text.

References

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Appendix H: Two-phase Equilibrium in a Closed Binary System

Consider a closed system, which consists of two species A and B and is capable of existing as a phase α or β or a combination of both. The number of moles of different species in different phases will be designated as n_i^k, where $i, j = \mathrm{A}$ or B is the species index and $k, l = \alpha$ or β is the phase index. The fact that species do not transform into each other (no nuclear transformations) and remain in the same quantities (closed system) is expressed in the form of the species conservation conditions

$$n_i^\alpha + n_i^\beta = \mathrm{const.} \tag{H.1}$$

However, because the α ↔ β phase transformations may go, there is no conservation of the phase amounts $n_\mathrm{A}^k + n_\mathrm{B}^k \neq \mathrm{const.}$

Compositions of the phases may be described by the molar fractions of the species B in each phase

$$X^k \equiv \frac{n_\mathrm{B}^k}{n_\mathrm{A}^k + n_\mathrm{B}^k}. \tag{H.2}$$

Considering the mole numbers of different species in different phases independent of each other, we obtain

$$\frac{\partial n_i^k}{\partial n_j^l} = \delta_{ij}\,\delta_{kl}, \tag{H.3}$$

where δ_{ij} is the Kronecker's symbol. Then

$$\frac{\partial X^k}{\partial n_j^l} = \frac{p(i) - X^k}{n_\mathrm{A}^k + n_\mathrm{B}^k}\,\delta_{kl}, \quad p(i) = \begin{cases} 0, & \text{if } i = A \\ 1, & \text{if } i = B \end{cases}. \tag{H.4}$$

Each phase can be characterized by its molar Gibbs free energy G^k, which is a function of this phase's molar fraction only

$$G^k \equiv G^k(X^k). \tag{H.5}$$

The total Gibbs free energy of the whole system is

$$G^S = \left(n_\mathrm{A}^\alpha + n_\mathrm{B}^\alpha\right)G^\alpha + \left(n_\mathrm{A}^\beta + n_\mathrm{B}^\beta\right)G^\beta. \tag{H.6}$$

Then the condition of thermodynamic equilibrium of the system may be formulated in the form of a constraint extremum

$$G^S \to \min \quad \text{for } n_i^\alpha + n_i^\beta = \text{const}, \quad i = A,\ B. \tag{H.7}$$

To find the mole numbers n_i^k that deliver the constraint minimum to G^S we will be using the method of Lagrange multipliers, according to which there exist constants a and b such that the function

$$G^S + a\left(n_\mathrm{A}^\alpha + n_\mathrm{A}^\beta\right) + b\left(n_\mathrm{B}^\alpha + n_\mathrm{B}^\beta\right) \tag{H.8}$$

has unconstrained minimum with respect to the variables n_i^k. Then, differentiating function (H.8) with respect to n_i^kwe obtain

$$\frac{\partial G^S}{\partial n_i^k} + a\left(\frac{\partial n_\mathrm{A}^\alpha}{\partial n_i^k} + \frac{\partial n_\mathrm{A}^\beta}{\partial n_i^k}\right) + b\left(\frac{\partial n_\mathrm{B}^\alpha}{\partial n_i^k} + \frac{\partial n_\mathrm{B}^\beta}{\partial n_i^k}\right) = 0. \tag{H.9}$$

Using (H.3)–(H.6) for (H.9) and the relations

$$\delta_{\mathrm{A}i} + \ \delta_{\mathrm{B}i} = 1, \qquad \delta_{\alpha k} + \ \delta_{\beta k} = 1, \tag{H.10}$$

we obtain four simultaneous equations for four unknowns, X^α, X^β, a, and b

$$\begin{aligned}&\delta_{\alpha k}\left[G^\alpha + (p(i) - X^\alpha)\frac{\mathrm{d}G^\alpha}{\mathrm{d}X^\alpha}\right] + \ \delta_{\beta k}\left[G^\beta + \left(p(i) - X^\beta\right)\frac{\mathrm{d}G^\beta}{\mathrm{d}X^\beta}\right]\\ &\quad + a\ \delta_{\mathrm{A}i} + b\ \delta_{\mathrm{B}i} = 0.\end{aligned} \tag{H.11}$$

To exclude the constants a and b we first compare the equation for ($k = \alpha$, $i = \mathrm{A}$) with that for ($k = \beta$, $i = \mathrm{A}$). Then we subtract the equation for ($k{=}\alpha$, $i = \mathrm{A}$) of the equation for ($k{=}\alpha$, $i = \mathrm{B}$) and compare the difference with that of the subtraction of the equation for ($k{=}\beta$, $i = \mathrm{A}$) of the equation for ($k{=}\beta$, $i = \mathrm{B}$). The result is the system of two simultaneous equations for X^α and X^β

$$G^{\alpha} - X^{\alpha}\frac{\mathrm{d}G^{\alpha}}{\mathrm{d}X^{\alpha}} = G^{\beta} - X^{\beta}\frac{\mathrm{d}G^{\beta}}{\mathrm{d}X^{\beta}}, \tag{H.12a}$$

$$\frac{\mathrm{d}G^{\alpha}}{\mathrm{d}X^{\alpha}} = \frac{\mathrm{d}G^{\beta}}{\mathrm{d}X^{\beta}}. \tag{H.12b}$$

Mathematically, (H.12) express the condition of *common tangency* for the functions $G^{\alpha}(X^{\alpha})$ and $G^{\beta}(X^{\beta})$. Physically they mean that the chemical potentials of the species A $(-a)$ and B $(-b)$ in both phases, α and β, are equal. Notice that the derivative of the molar Gibbs free energy with respect to the fraction, see (H.12b), is the difference of the chemical potentials of the species.

Appendix I: The Stefan Problem

The Stefan problem occupies a special place in the science of phase transformations because it was the first mathematically rigorous and physically realistic, significant problem, which was solved exactly. The Stefan problem belongs to a class of so-called free-boundary problems, the essential new feature of which is the existence of a moving interface of separation between the two phases. The way in which this interface moves has to be determined. The original Stefan problem may be generalized in many different ways, some of which will be considered here.

According to the Stefan problem, a substance has a transformation point at which it changes from one phase to another with emission of absorption of heat. To clarify the ideas, we will be discussing specifically the problem of crystallization of supercooled liquid. Suppose that the melting point of the solid is T_m and that L ($\mathrm{J/m^3}$) is the latent heat of fusion of the substance. Then if the interface of separation between the solid and liquid phases is at $X(t)$, one boundary condition to be satisfied at this interface is

$$T_\mathrm{l} = T_\mathrm{s} = T_\mathrm{m}, \quad \text{at } x = X(t). \tag{I.1}$$

A second boundary condition concerns liberation of the latent heat at the interface. Suppose that the region $x > X(t)$ contains liquid at temperature $T_\mathrm{l}(x, t)$ and that the region $x < X(t)$ contains solid at temperature $T_\mathrm{s}(x, t)$. Then when the interface of separation moves a distance $\mathrm{d}X$, a quantity of heat $L\ \mathrm{d}X$ per unit area is liberated and must be removed by conduction. This requires

$$\lambda_\mathrm{s}\frac{\partial T_\mathrm{s}}{\partial x} - \lambda_\mathrm{l}\frac{\partial T_\mathrm{l}}{\partial x} = L\frac{\mathrm{d}X}{\mathrm{d}t}, \quad \text{at } x = X(t), \tag{I.2a}$$

where λ_s and λ_l are the thermal conductivities of the solid and liquid, respectively. Temperatures in the solid and liquid regions must satisfy the equations of linear flow of heat

$$C_\mathrm{s}\frac{\partial T_\mathrm{s}}{\partial t} = \lambda_\mathrm{s}\frac{\partial^2 T_\mathrm{s}}{\partial x^2}, \quad \text{when } x<X(t). \tag{I.3a}$$

$$C_\mathrm{l}\frac{\partial T_\mathrm{l}}{\partial t} = \lambda_\mathrm{l}\frac{\partial^2 T_\mathrm{l}}{\partial x^2}, \quad \text{when } x>X(t). \tag{I.3b}$$

where C_s and C_l are the specific heats of the solid and liquid, respectively.

In addition to (I.1)–(I.3), there will be initial conditions and conditions at the fixed boundaries of the regions under consideration. Suppose that the crystallization starts at the plane $x = 0$ and moves to the right and initially the regions $x > 0$ contained liquid at temperature $T_0 < T_\mathrm{m}$ (supercooled liquid) and $x < 0$ contained solid at the temperature $T_\mathrm{s} = T_\mathrm{m}$. Then the temperature of the crystallized material has to have the constant value T_m throughout and no heat will be removed through it. Temperature of the liquid will vary, but the following boundary condition will be satisfied

$$T_\mathrm{l}(x,t) \to T_0, \quad \text{as } x \to \infty. \tag{I.4}$$

First, notice that (I.2a) may be put into an alternative form by considering the curves of constant temperature $T_\mathrm{l}(x, t) = T_\mathrm{m} = T_\mathrm{s}(x, t)$ in the (x, t)-plane. On these curves

$$\frac{\partial T_\mathrm{s}}{\partial x}\,\mathrm{d}x + \frac{\partial T_\mathrm{s}}{\partial t}\,\mathrm{d}t = 0 = \frac{\partial T_\mathrm{l}}{\partial x}\,\mathrm{d}x + \frac{\partial T_\mathrm{l}}{\partial t}\,\mathrm{d}t,$$

so that (I.2a) may be written as follows

$$\lambda_\mathrm{s}\frac{\partial T_\mathrm{s}}{\partial x} - \lambda_\mathrm{l}\frac{\partial T_\mathrm{l}}{\partial x} = -L\frac{\partial T_\mathrm{s}/\partial t}{\partial T_\mathrm{s}/\partial x} = -L\frac{\partial T_\mathrm{l}/\partial t}{\partial T_\mathrm{l}/\partial x}. \tag{I.2b}$$

In this form, the nonlinearity of the Stefan problem becomes apparent. Second, analysis of the (I.3) and boundary condition (I.2b) should convince you that the Stefan problem admits *similarity* solution, that is, a solution in the form where the spatial and time variables enter in the dimensionless combination $\left(x/\sqrt{\alpha t}\right)$ and $\alpha = \lambda/C$ is called the thermal diffusivity of the respective phase. Then, substituting the similarity solution

$$T = f\left(\frac{x}{\sqrt{\alpha_l t}}\right), \tag{I.5}$$

$$X = 2\beta\sqrt{\alpha_l t} \tag{I.6}$$

where β is a constant, into (I.3), (I.4) we obtain that

$$T_{\mathrm{s}}(x,t) = T_{\mathrm{m}}, \quad \text{when } x<X, \tag{I.7a}$$

$$T_{\mathrm{l}}(x,t) = T_0 + A\operatorname{erfc}\left(\frac{x}{2\sqrt{\alpha_{\mathrm{l}}t}}\right), \quad \text{when } x>X, \tag{I.7b}$$

The error function is defined as follows

$$\operatorname{erfc}(x) = 1 - \operatorname{erf}(x) = \frac{2}{\sqrt{\pi}}\int_x^{\infty} \mathrm{e}^{-\xi^2}\,\mathrm{d}\xi.$$

The boundary conditions (I.1), (I.2a) then give an expression for the coefficient A as

$$A = \frac{T_{\mathrm{m}} - T_0}{\operatorname{erfc}\,\beta} \tag{I.8}$$

and a transcendental equation for β

$$\sqrt{\pi}\beta \exp \beta^2 \operatorname{erfc}\,\beta = \frac{C_{\mathrm{l}}(T_m - T_0)}{L}. \tag{I.9}$$

The root of (I.9) can be read from Fig. I.1 as a function of the parameter

$$\Delta\,\Theta \equiv \frac{C_{\mathrm{l}}(T_{\mathrm{m}} - T_0)}{L}, \tag{I.10}$$

which is called the dimensionless supercooling of the liquid. Differentiating (I.6) with respect to time we obtain an expression for the velocity of the interface

$$V \equiv \frac{\mathrm{d}X}{\mathrm{d}t} = \beta\sqrt{\frac{\alpha_{\mathrm{l}}}{t}}. \tag{I.11}$$

This expression has a singularity at $t \to 0$, which is due to improper initial condition. However, a greater problem of the solution (I.7)–(I.11) is that it does not work at $\Delta\Theta \geq 1$, see Fig I.1.

As we mentioned above, the original Stefan problem may be generalized in many different ways. Some of these generalizations are caused by the practical need of applications.There are also deep physical reasons for the generalization of the Stefan problem; the latter are of greater interest for us here. Notice that the roots of (I.9) exits only for $\Delta\Theta < 1$. We may ask a question: What happens if the initial supercooling of the liquid is greater than one? To answer this question, we need to look at the rate of motion of the interface.

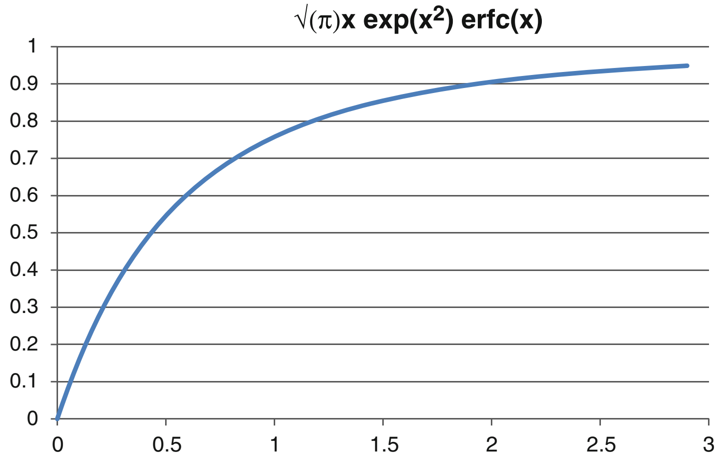

Fig. I.1 Function $y = \sqrt{\pi}x\mathrm{e}^{x^2}\mathrm{erfc}\ x$

The condition (I.1), which requires that the state of thermodynamic equilibrium is established at the interface. Clearly, an interface does not have an "incentive" to move if it is at equilibrium. Hence, to eliminate this singularity, we have to correct the boundary condition (I.1) such that it will allow for disequilibrium at the interface.

To fix this problem, a "kinetic" boundary condition was suggested [1]:

$$T_\mathrm{l} = T_\mathrm{s} = T_\mathrm{m} - \frac{V}{\mu}, \quad \text{at } x = X(t). \tag{I.12}$$

where μ was called the kinetic coefficient. The solution of the Stefan problem (I.2)–(I.4) with the generalized boundary condition (I.12) (and $C_\mathrm{l} = C_\mathrm{s}$, $\lambda_\mathrm{l} = \lambda_\mathrm{s}$) has the form

$$T_\mathrm{s}(x,t) = T_\mathrm{m} + \frac{L}{C}, \quad \text{when } x \leqslant X, \tag{I.13a}$$

$$T_\mathrm{l}(x,t) = T_0 + \frac{L}{C}\exp\left[-\frac{V}{\alpha}(x - Vt)\right], \quad \text{when } x > X, \tag{I.13b}$$

$$V = v_0(\Delta\,\Theta - 1), \quad v_0 \equiv \frac{\mu L}{C}. \tag{I.14}$$

Notice that this is not a similarity solution. This type of a solution is called a *traveling wave*.

The traveling wave solution (I.13), (I.14) supplements the solution (I.7)–(I.11) when $\Delta\Theta > 1$, but leaves the value $\Delta\Theta = 1$ open for consideration. One may say that the solution at $\Delta\Theta = 1$ was overcorrected. Another problem with the solution (I.13), (I.14) is that it was obtained by a method which is completely different from the one that led to the solution (I.7)–(I.11) and the connection of one to the other is not clear. A full solution of the Stefan problem with the "kinetic" boundary condition (I.12) may be obtained with the help of the source function of the heat equation [2]. At $\Delta\Theta = 1$, the solution for the velocity takes the form

$$V = \left(\frac{\alpha v_0}{3t}\right)^{1/3}. \tag{I.15}$$

Another shortage of the original Stefan problem is that it allows for a plane-boundary solution only while, in reality, the plane interfaces are morphologically (shape-wise) unstable and the real interfaces have a complicated three dimensional shape. To account for this discrepancy, all equations and boundary conditions must be reformulated. In three dimensions, the heat equation is

$$C_{\mathrm{s,l}}\frac{\partial T_{\mathrm{s,l}}}{\partial t} = \lambda_{\mathrm{s,l}}\Delta^2 T_{\mathrm{s,l}}, \tag{I.16}$$

and the boundary condition (I.2a) becomes

$$\lambda_{\mathrm{s}}\frac{\partial T_{\mathrm{s}}}{\partial n} - \lambda_{\mathrm{l}}\frac{\partial T_{\mathrm{l}}}{\partial n} = LV_n, \tag{I.17}$$

where $\partial/\partial n$ is a derivative in the direction normal to the interface and outward of the respective region of the solid or liquid phase and V_n is the velocity of the interface measured in the direction normal to itself. Ivantsov [3] found a mathematically beautiful and practically important solution of the three dimensional problem with the boundary conditions (I.1), (I.17). According to his solution, the solid–liquid interface may take on different shapes and move with different speeds, some of which are similar to the square-root-law of equation (I.11). However, one kind of the shape is particularly interesting because of its relevance to the dendritic growth of crystals. In this case, temperature of the solid is constant and equal to T_{m}. Temperature of the liquid varies and the isotherms are cofocal paraboloids of revolution (parabolic cylinders in the 2d case)

$$T_l(x,y,z,t) = T_0 + \frac{T_{\mathrm{m}} - T_0}{\mathrm{E}_1(\mathrm{Pe})}\mathrm{E}_1(\mathrm{Pe\ u}), \qquad \text{when } u>1, \tag{I.18}$$

where $\mathrm{E_1}(x)$ is the exponential integral function

$$\mathrm{E_1}(x) = \int_x^{\infty} \frac{\mathrm{e}^{-\xi}}{\xi}\,\mathrm{d}\xi,$$

$$u = \sqrt{\frac{x^2 + y^2}{R^2} + \left(\frac{z - Vt}{R}\right)^2} - \frac{z - Vt}{R}, \quad \mathrm{Pe} = \frac{VR}{2\alpha}, \tag{I.19}$$

The phase separating interface ($u = 1$) is the paraboloid with the radius of curvature of its vertex R and speed of motion V = const(t) in the direction of its axis (z-axis). Pe is the so-called Peclet number; it can be found from the following equation

$$\Delta\,\Theta = \mathrm{Pe}\;\mathrm{e}^{\mathrm{Pe}}\mathrm{E_1}(\mathrm{Pe}). \tag{I.20}$$

As we can see, the Ivantsov's solution allows one to find the product of V and R but does not allow to resolve them separately, that is, for the same supercooling it allows for a sharp needle (small R) to grow fast (large V) or a dull one to grow slowly. This problem became known as a problem of the operational point of a dendrite; many authors tried to solve it with the help of different selection principles. However, the theories of the dendritic growth and morphological stability of a plane interface are beyond the scope of this book.

As closing notes of this appendix, we discuss another modification of the Stefan problem. Notice that the temperature of phase equilibrium was always assumed to be constant, T_{m}. As known, however, this temperature varies if the phase separating interface is not a plane, the so-called Gibbs–Thompson effect. According to this effect, the equilibrium temperature is

$$T_{\mathrm{e}} = T_{\mathrm{m}}\left(1 - 2\frac{\sigma}{L}K\right), \tag{I.21}$$

where σ is the interfacial free energy and K is the curvature of the interface. This expression should replace T_{m} in the boundary condition (I.12).

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Appendix J: On the Theory of Adsorption of Sound in Liquids*

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Abstract: In this paper, an attempt is made to expand the ideas that explain adsorption of sound in multiatomic gasses on the case of liquids.

Previously,[1] it has been shown that a large number of phenomena, dealing with adsorption of sound can be qualitatively explained by assuming that this process is very similar to the adsorption of sound in multiatomic gasses.

In the present Letter, an attempt is made to develop this point of view for propagation of sound in liquids, formulating the problem in a most general form.

Several general remarks are in order here. We can reformulate the question as follows: How can we account for "viscosity" in hydrodynamic equations when density varies with time? As is known, the theory of viscous fluids assumes existence of two coefficients of viscosity.[2] The first one is the standard coefficient η which takes into account tangent stresses under shear, and the second coefficient η' accounts for the "viscous" stresses of uniform dilatation. Very often one assumes $\eta' = 0$ even if the density changes, e.g., in acoustics. However, in his famous work Stokes writes[3]:

> Of course, we may at once put $\eta' = 0$ if we assume that in the case of a uniform motion of dilatation the pressure at any instant depends only on the actual density and temperature at that instant, and not on the rate at which the former changes with the time. In most cases to which it would be interesting to apply the theory of viscous fluids, the density of the fluid is either constant, or may, without sensible error, be regarded as constant, or else changes slowly with the time. In the first two cases the results would be the same, and in the third

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* Zh. Eksp. Teor. Fiz. 7(3), 438–449 (1937) (in Russian).

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[1] M.A. Leontovich, Dokl. Akad. Nauk SSSR **III**, 111, (1936); Zh. Eksp. Teor. Fiz. **6**, 561 (1936).

[2] See, for example, Rayleigh, *Theory of Sound*, II, §345.

[3] G.G. Stokes, "On the theories of the internal friction of fluids in motion, and of the equilibrium and motion of elastic solids", Philos. Trans. Cambridge Soc. **8**, 287 (1849). For the quote above see page 294.

> case nearly the same, whether η' were equal to zero or not. Consequently, even if the theory and experiment agree in such cases, this should not be regarded as confirmation of the assumption that η' is equal to zero.

Thus, Stokes himself did not deem it possible to put $\eta' = 0$ in applications of the theory to the problems like sound propagation, and we doubt that the authors, who justify by referencing Stokes taking $\eta' = 0$ in the processes associated with the density changes, are correct.

The points of view expressed below to some extent can be considered as a development of the Stokes idea laid out in the first sentence of the quote above. We assume that, in addition to pressure p, density ρ, and temperature T, the equation of state contains a parameter ξ (or several parameters), which, at equilibrium, is a function of ρ and T. In a general case of absence of equilibrium, the parameter ξ obeys some kind of a "reaction" equation. Under these assumptions, as expected, the viscous stresses arise during uniform dilatation.

For sufficiently slow processes, the stresses, as it appears, can be accounted for by the second coefficient of viscosity, i.e., the processes satisfy the Stokes equation with $\eta' \neq 0$. From this follows, by the way, that the second coefficient cannot be neglected, no matter how slow the process is because we are interested in the effects of viscosity, in general. The point is that with the gradual slowing down of the process, of course, the influence of the "second viscosity" approaches zero; however, at the same time, influence of the standard viscosity tends to zero too. For instance, for the elastic waves of low frequency, the adsorption coefficient is proportional to $(4\eta/3 + \eta')\omega^2$, where ω is the frequency of the acoustic wave and, therefore, in the domain of low frequencies, the relative contribution of the "second viscosity" does not depend on frequency at all.

For the fast processes, as we will show below, the influence of viscosity cannot be accounted for just by introducing the second coefficient. For instance, for the attenuation of short acoustic waves one obtains that the adsorption coefficient is not proportional to the square of the frequency. In the simplest case, it appears that the frequency dependence of the adsorption coincides with that of the multiatomic gasses derived by Kneser et al.

§1

We assume that at a given point the state of liquid is defined not only by its temperature T and density ρ but also by a quantity ξ (or several quantities ξ_1, ξ_2, ...) which defines internal state of the liquid. The quantities ξ can be, for instance, concentrations of components that make up the liquid, concentrations of excited or associated molecules. One can suppose that ξ somehow defines the internal structure of the liquid. For the time being, it is not necessary to attribute any special meaning to these variables. At first, we will assume that the internal state of liquid can be described just by one variable ξ, similar to the case of multiatomic gasses with only one excitational degree of freedom.

We consider states away from equilibrium. That is why the state of the system is not defined just by its temperature (and density). For instance, in the Kneser case, when the gas contains the excited molecules, the state of the system depends not only on its temperature, which defines the average energy $3kT/2$ of the translational motion of molecules, but also on the concentration of excited molecules ξ,which may differ from its equilibrium value of

$$\xi_0 = \frac{\mathrm{e}^{-\varepsilon/kT}}{1 + \mathrm{e}^{-\varepsilon/kT}}.$$

This situation could be described by characterizing the nonequilibrium state of the system by two temperatures T and T_1, the latter one defining the internal energy of the system. In general as in the aforementioned example, the temperature T is related (at constant density) to the energy of the system so that its change determines change of energy of the system at the given value of ξ,

$$\Delta E = C\Delta T,$$

where C is the heat capacity *at constant* ξ (and constant density). Notice that in what follows one does not need to introduce the temperature of nonequilibrium states; instead, one can characterize the state by its energy (per unit of mass), density, and parameter ξ. For this choice of variables, the treatment and results remain the same: instead of the free energy $\Psi(T, \rho, \xi)$, one just has to use the thermodynamic function, which is appropriate for the new choice of variables, that is, entropy $S(E, \rho, \xi)$.

At equilibrium, the variable ξ has some specified value which depends on density and temperature; this value can be found from the condition of thermodynamic equilibrium

$$\frac{\partial \Psi}{\partial \xi} = 0,$$

where $\Psi(T, \rho, \xi)$is the free energy per unit mass. For the propagation of sound with vanishingly low frequency one can assume that at every moment the state of the system is consistent with the equilibrium and, therefore, the speed of the sound is defined by the static value of adiabatic compressibility. In the opposite case of very high frequencies, the internal state of liquid, that is, the quantity ξ, does not change during one period of oscillations and the speed of the sound is defined by the adiabatic compressibility at the constant value of ξ. In the crossover region of frequencies, the dispersion of sound is taking place.

To solve this problem, one has to have an equation, according to which the quantity ξ changes in the processes that take place in the fluid. This equation should correspond to the “excitation reaction equation” of the Kneser theory. It can be written based on the following ideas.

First, because we are interested in small deviations from equilibrium (small amplitudes of sound) the equation must be linear.

Second, this equation should be of the first order in the derivatives of T, ρ, and ξ with respect to time. This assumption is natural when $\xi$is concentration of a component and, hence, when the equation of interest represents the reaction rate equation. In general, this assumption means that the variation of ξ proceeds without effects of inertia.

Third, the equilibrium condition at the constant ρ and T, that is, the condition of $\xi = \text{const}$ is the equality of $\partial\Psi/\partial\xi$ to zero.

It follows from these tree requirements that the sought "reaction equation" *for the appropriate choice of the variable*ξ must have the following form

$$\overset{\bullet}{\xi} = -K\frac{\partial\Psi}{\partial\xi}, \tag{J.1}$$

where J is a constant. Here, in the expression for $\partial\Psi/\partial\xi$ we should retain only linear terms (in Ψ itself—quadratic) with respect to ΔT, $\Delta\rho$, and $\Delta\xi$, which are deviations of temperature, density, and ξ, respectively, from their equilibrium values.

We can arrive at (J.1) using the following ideas.

At constant, time independent, density and temperature, regardless of the choice of ξ the reaction equation must have the form (J.1) because, due to the assumptions made, the equation has to be linear in $\overset{\bullet}{\xi}$ and approach zero together with $\partial\Psi/\partial\xi$. In this case

$$\frac{\partial\Psi}{\partial\xi} = \Psi_{\xi\xi}\Delta\xi,$$

where $\Delta\xi = \xi - \xi_0$ and ξ_0 is the equilibrium value of ξ.

We are interested in the reaction equation when ΔT and $\Delta\rho$ are changing with time. In this case, in addition to the terms that are present when T and ρ are constant, there may be terms which depend on $\overset{\bullet}{T}$ and $\overset{\bullet}{\rho}$; in the framework of our assumption the most general form of the equation is the following

$$\overset{\bullet}{\xi} + a\overset{\bullet}{\rho} + b\overset{\bullet}{T} = -K\frac{\partial\Psi}{\partial\xi},$$

where a and b are constants.

Using the substitution $\Delta\xi + a\Delta\rho + b\Delta T$instead of $\Delta\xi$we arrive again at (J.1) where $\partial\Psi/\partial\xi$ takes the following form

$$\frac{\partial\Psi}{\partial\xi} = \Psi_{\xi\xi}\Delta\xi + \Psi_{\xi T}\Delta T + \Psi_{\xi\rho}\Delta\rho. \tag{J.1$'$}$$

In the case when the auxiliary variable somehow determines concentration of a certain component of the liquid, the parameter ξsatisfies the latter condition if ξ is chosen as a *relative* concentration of this component.

Indeed, let the volumetric concentration h to be selected initially as the auxiliary variable. At constant T and ρ, the reaction equation has the form

$$\overset{\bullet}{h} = -K' \frac{\partial \Psi}{\partial h}.$$

When density varies, in addition to the change of the amount of the component due to this equation there will be variation due to the flux of matter, and the equation takes the form

$$\overset{\bullet}{h} + \operatorname{div}(h\vec{u}) = -K' \frac{\partial \Psi}{\partial h},$$

($\vec{u}$is the velocity of liquid). Because at small velocities and small variations of h

$$\operatorname{div}(h\vec{u}) = h \operatorname{div} \vec{u} = -\frac{h}{\rho} \overset{\bullet}{\rho},$$

the equation can be rewritten as

$$\overset{\bullet}{h} - \frac{h}{\rho} \overset{\bullet}{\rho} = -\overset{\bullet}{K'} \frac{\partial \Psi}{\partial h}$$

but

$$\overset{\bullet}{h} - \frac{h}{\rho} \overset{\bullet}{\rho} = \rho \overset{\bullet}{\xi},$$

where ξ is the relative concentration $\xi = h/\rho$.

Moreover,

$$\frac{\partial \Psi}{\partial h} = \frac{\partial \Psi}{\partial \xi} \frac{\partial \xi}{\partial h} = \frac{1}{\rho} \frac{\partial \Psi}{\partial \xi},$$

so that the reaction equation takes the form of (J.1)

$$\overset{\bullet}{\xi} = -K \frac{\partial \Psi}{\partial \xi},$$

where

$$K = \frac{1}{\rho^2} K'.$$

In addition to the "reaction equation" (J.1), one has to write an energy equation. If we disregard the effects of regular viscosity and heat conductivity, whose contribution into the sound adsorption in most of the fluids, in our opinion, is several times smaller than that of the processes considered here, then the energy equation takes the following form

$$\rho \overset{\bullet}{E} - p \frac{\overset{\bullet}{\rho}}{\rho} = 0, \tag{J.2}$$

where E is the energy per unit mass and p is the pressure.

Differentiating (J.2) we obtain

$$\rho E_T \overset{\bullet}{T} + \left(\rho E_\rho - \frac{p}{\rho} \right) \overset{\bullet}{\rho} + \rho E_\xi \overset{\bullet}{\xi} = 0.$$

The second derivatives of Ψ (taken at the equilibrium state), which enter the expression for $\partial\Psi/\partial\xi$, and the derivatives of energy in the last equation can be expressed through other quantities, if we take advantage of the fact that we know the free energy as a function of T, ρ, and ξ. Then we have

$$E(T, \rho, \xi) = \Psi - T\Psi_T;$$

$$p = P(T, \rho, \xi) = \rho^2 \Psi_\rho;$$

(here $P(T, \rho, \xi)$ means the pressure as a function of T, ρ, and ξ) and, hence, at equilibrium, when $\partial\Psi/\partial\xi = \Psi_\xi = 0$

$$E_\xi = -T\Psi_{\xi T},$$

$$P_\xi = \rho^2 \Psi_{\xi\rho},$$

$$\rho^2 E_\rho - p = -TP_T.$$

Using these relations, one can bring (J.1) to the following form

$$\overset{\bullet}{\xi} = -\frac{1}{\tau} \left(\Delta\xi - \frac{E_\xi}{T\Psi_{\xi\xi}} \Delta T + \frac{P_\xi}{\rho^2 \Psi_{\xi\xi}} \Delta\rho \right), \tag{J.3}$$

where $1/\tau = K\Psi_{\xi\xi}$ and τ is a constant which determines the time of establishing equilibrium. Equation (J.2) can be rewritten in the form

$$E_\xi \overset{\bullet}{\xi} + E_T \overset{\bullet}{T} - \frac{TP_T}{\rho^2} \overset{\bullet}{\rho} = 0. \tag{J.4}$$

One has to keep in mind that the derivative E_T and P_T in this equation are taken *at constant* ξ. Hence, for instance, $C = E_T$ is the heat capacity *at constant* ξ (and at constant ρ, that is, at constant volume). This quantity is not equal to the heat capacity obtained from static measurements. Regular heat capacity c corresponds to the equilibrium state; therefore, it is equal to the derivative $(\partial E/\partial T)_\mu$ taken at a constant (and equal to zero) value of $\mu = \Psi_\xi$

$$c = \left(\frac{\partial E}{\partial T}\right)_\mu.$$

Likewise the derivative

$$P_T = \frac{\partial P(T, \rho, \xi)}{\partial T}$$

is not equal to the derivative

$$p_T = \left(\frac{\partial p}{\partial T}\right)_\mu,$$

taken at the equilibrium state.

It is easy to find the relationship between the derivatives taken at $\xi = \text{const}$ and at $\mu = \text{const}$, equal to zero. We have

$$C = E_T = \left(\frac{\partial E}{\partial T}\right)_\xi = \left(\frac{\partial E}{\partial T}\right)_\mu + \frac{\partial E}{\partial \mu}\left(\frac{\partial \mu}{\partial T}\right)_\xi = c + \frac{\partial E}{\partial \mu}\left(\frac{\partial \mu}{\partial T}\right)_\xi.$$

Taking into account, the aforementioned expression for $\Psi_{\xi T}$

$$\left(\frac{\partial \mu}{\partial T}\right)_\xi = \Psi_{\xi T} = -\frac{E_\xi}{T},$$

and

$$E_\xi = \frac{\partial E}{\partial \mu}\frac{\partial \mu}{\partial \xi} = \frac{\partial E}{\partial \mu}\Psi_{\xi\xi},$$

we obtain

$$\frac{\partial E}{\partial \mu} = \frac{E_{\xi}}{\Psi_{\xi\xi}},$$

and hence

$$C = c - \frac{E_{\xi}^{2}}{T\Psi_{\xi\xi}}. \tag{J.5}$$

Similarly, we obtain the following relations

$$P_T = \left(\frac{\partial p}{\partial T}\right)_{\xi} = \left(\frac{\partial p}{\partial T}\right)_{\mu} - \frac{P_{\xi}E_{\xi}}{T\Psi_{\xi\xi}} = p_T - \frac{P_{\xi}E_{\xi}}{T\Psi_{\xi\xi}}, \tag{J.6}$$

$$P_{\rho} = p_{\rho} + \frac{P_{\xi}^{2}}{T\Psi_{\xi\xi}}, \tag{J.7}$$

where $p(T, \rho)$ means dependence of p on T and ρ *at the equilibrium*, so that, e.g.,

$$p_T = \left(\frac{\partial p}{\partial T}\right)_{\mu}, \quad p_{\rho} = \left(\frac{\partial p}{\partial \rho}\right)_{\mu}.$$

Also notice that in the considered problem the deviations of the state of fluid from equilibrium can be accounted for in a different way, namely, as it has been done by some authors for gasses, by introducing the second temperature T_1. This can be reduced to simple change of variables. We may introduce the temperature T_1 as the temperature at which the internal state of liquid *at equilibrium* is determined by the specific value of ξ. Then, the deviation ΔT_1 of this temperature is defined by the condition

$$\frac{\partial \Psi(T_1, \rho, \xi)}{\partial \xi} = 0,$$

or

$$\Psi_{\xi\xi}\Delta_{\xi} + \Psi_{\xi T}\Delta T_1 + \Psi_{\xi\rho}\Delta\rho = 0.$$

Using this equation and introducing ΔT_1 instead of $\Delta\xi$ in (J.1) and (J.4), we obtain the following equation that determines variations of both temperatures

$$\overset{\bullet}{\underset{1}{T}} - \frac{P_{\xi}}{T\rho^{2}E_{\xi}}\,\overset{\bullet}{\rho} = \frac{1}{\tau}(\Delta T - \Delta T_1),$$

$$C\overset{\bullet}{T} + (c - C)\overset{\bullet}{\underset{1}{T}} + \frac{TP_T}{\rho^{2}}\,\overset{\bullet}{\rho} = 0.$$

§2

Considering propagation of sound wave with the frequency ω, the quantities ΔT, $\Delta\rho$, and $\Delta\xi$ are proportional to $\exp(\mathrm{i}\omega t)$ and (J.3) and (J.4) turn into

$$(1+\mathrm{i}\omega\tau)\xi = \frac{E_\xi}{T\Psi_{\xi\xi}}\Delta T - \frac{P_\xi}{\rho^2\Psi_{\xi\xi}}\Delta\rho, \tag{J.8}$$

$$E_\xi\xi = -C\Delta T + \frac{TP_T}{\rho^2}\Delta\rho. \tag{J.9}$$

Square of the complex velocity of propagation of sound is determined by the ratio of the pressure change Δp to the density change $\Delta\rho$ and is equal to

$$W^2 = \frac{\Delta p}{\Delta\rho} = P_\rho + \rho_T\frac{\Delta T}{\Delta\rho} + P_\xi\frac{\Delta\xi}{\Delta\rho}. \tag{J.10}$$

Determining the ratios $\Delta T/\Delta\rho$ and $\Delta\xi/\Delta\rho$ from (J.8) and (J.9) and substituting them into (J.10) after algebraic transformations, which use expressions (J.5), (J.6), and (J.7) and also the thermodynamic relationship

$$\frac{c_p}{c} = 1 + \frac{Tp_T^2}{c\rho^2 p_\rho},$$

we obtain

$$W^2 = V_0^2\left\{1 + \frac{\mathrm{i}\omega\tau'\left[(V_\infty/V_0)^2 - 1\right]}{1+\mathrm{i}\omega\tau'}\right\}. \tag{J.11}$$

Here,

$$V_0^2 = \frac{c_p}{c}p_\rho = p_\rho + \frac{Tp_T^2}{c\rho^2},$$

so that V_0 is the standard Laplace's speed of the sound;

$$V_\infty^2 = \frac{C_p}{C}P_\rho = P_\rho + \frac{TP_T^2}{C\rho^2},$$

that is,V_∞as $V_0$is a function of the derivatives of pressure and heat capacities, but taken at constantξ; moreover, $\tau' = \tau C/c$.

At very low frequency ω, as one can see from (J.11), W becomes real and equal to the Laplace's value V_0. With $\omega \rightarrow \infty$, W also approaches the real value, but now V_∞.

The real speed of propagation V and the attenuation coefficient per unit length α are obtained from the relations

$$\frac{1}{V} = \mathrm{Re}\,\frac{1}{W}, \quad \alpha = \omega \mathrm{Im}\,\frac{1}{W}.$$

Separating the real and imagine parts of $1/W$ and taking into account that W is always close to V_0 (V_∞/V_0 is close to one), with sufficient accuracy we obtain

$$\frac{V_0}{V} = 1 - \frac{1}{2}\,\frac{\omega^2\tau'^2\left[(V_\infty/V_0)^2 - 1\right]}{1 + \omega^2\tau'^2}, \tag{J.12}$$

$$\alpha = \frac{1}{2V_0}\,\frac{\omega^2\tau'\left[(V_\infty/V_0)^2 - 1\right]}{1 + \omega^2\tau'^2}. \tag{J.13}$$

Expressions (J.10), (J.11), and (J.12) have the same form as the corresponding expressions in the Kneser theory for gasses; they differ only in the value of the constant V_∞.

In the case of gasses,

$$\left(\frac{V_\infty}{V_0}\right)^2 = \frac{c}{C}, \tag{J.14}$$

where C is the heat capacity that corresponds to the translational motion of molecules in gasses. In our, more general case

$$\left(\frac{V_\infty}{V_0}\right)^2 - 1 = \frac{1}{\rho^2 V_0^2}\left\{\frac{P_\xi^2}{\Psi_{\xi\xi}} + \frac{T(p_T - P_\xi E_\xi/T\Psi_{\xi\xi})^2}{c - E_\xi^2/T\Psi_{\xi\xi}} - \frac{Tp_T^2}{c}\right\}. \tag{J.14$'$}$$

Thus, this quantity depends, first, on the values of c and p_T related to the equilibrium state—their values for liquids may be considered known—and, second, on the values of E_ξ and P_ξ, which define, respectively, variations of energy and pressure with the variation of ξ during the reaction. These quantities can be obtained only if certain hypotheses about the characteristic features of the processes in liquids are made. Moreover, (J.14′) includes the quantity $\Psi_{\xi\xi}$, which could be found if the magnitude of thermal fluctuations of the parameter ξ were known from some experimental observations. Indeed, the mean square of fluctuations $\overline{\Delta\xi^2}$ is equal to $kT/\Psi_{\xi\xi}$. The constant τ, which defines the magnitude of adsorption and location of the maximum of the curve adsorption-per-one-wavelength as a function of the frequency, is inversely proportional to the rate of reaction proceeding in the liquid. As known, the rate of reaction in liquids can often be estimated *qualitatively* following Smoluchowski's ideas developed in the coagulation theory of colloids. For instance, as known, the processes in fluorescent liquids can be understood from this point of view. The value of τ must be proportional to the *standard* viscosity of the liquid η. Therefore, according to (J.13), the attenuation coefficient α (at low frequency when the terms $\omega^2\tau'^2$ in the denominator can be omitted) must be approximately proportional to the standard viscosity η. Hence, in the cases when the viscosity is strongly dependent on temperature so that its variation covers over the variations of all other quantities that determine the attenuation coefficient α, the latter should be approximately proportional to the viscosity η and, with changing viscosity η, should vary proportionally to the Stokes' attenuation coefficient. Perhaps, the temperature dependence of the attenuation coefficient observed by Baumgardt[4] for water at the frequency 8×10^6 Hz can be understood from this point of view.

In a particular case of gas, where the considered reaction is excitation of particles and $\xi = n_2/n$, i.e., ξ is the relative concentration of excited molecules, we obtain

$$E_\xi = \varepsilon,$$

where ε is the energy of excitation and, due to the fact that the reaction is not accompanied by the change of the number of particles and, hence, pressure

$$P_\xi = 0.$$

Moreover, in this case

$$\Psi = RT\{\xi \ln \xi + (1-\xi)\ln(1-\xi) + \xi\Psi_1(T) + (1-\xi)\Psi_2(T) + \ln \rho\},$$

and due to (J.5),

$$\Psi_{\xi\xi} = \frac{RT}{\xi(1-\xi)} \cong \frac{RT}{\xi}, \quad c = C + \frac{\varepsilon^2}{RT^2}\xi.$$

Substituting these values into (J.14′) we find the Kneser expression (J.14).

§3

The above considered case of the nonequilibrium state of liquid that comes about with propagation of sound, which can be characterized by *one* additional parameter ξrepresents, of course, just the simplest case. Generally speaking, we have to introduce several additional parameters ξ_1,ξ_2,...

In the gas, this corresponds to the situation when one has to take into account excitations of different normal modes of a molecule, with the parameters ξ_1,ξ_2,...

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[4] E. Baumgardt, C.R. **202**, 203 (1936).

representing concentrations of molecules in various excited states. In these cases, the functional dependencies of adsorption and dispersion on the frequency as well as the dependence of adsorption on temperature can be *essentially* different from the case of one parameter. That is why we will outline briefly the way to solve this, more general problem.

Using the same ideas as above, one can come to the conclusion that for small deviations from the equilibrium state the "reactions equations," that is, equations for ξ_1,ξ_2,. . ., have to have the following form

$$\overset{\bullet}{\xi}_i = -\sum_j K_{ij} \frac{\partial \Psi}{\partial \xi_j}. \tag{J.15}$$

On the basis of the well-known general considerations,[5] coefficients K_{ij} must be symmetric: $K_{ij} = K_{ji}$. Due to this condition and with the proper choice of variables ξ_1,ξ_2,. . . the system of equations (J.15) can be reduced to a very simple form, such that every equation has only one variables ξ_i. To prove this we note, first, that if we introduce

$$2K = \sum_{ij} K_{ij} \Psi_i \Psi_j,$$

where

$$\Psi_i = \frac{\partial \Psi}{\partial \xi_i},$$

then (J.15) may be written in the following form

$$\overset{\bullet}{\underset{i}{\xi}} = -\frac{\partial K}{\partial \Psi_i}. \tag{J.16}$$

The quadratic in ΔT, $\Delta \rho$, and $\Delta \xi_i$part of Ψ, which is of interest for us, can be written as follows

$$2\Psi = \sum_{ij} \Psi_{ij} \Delta \xi_i \Delta \xi_j + 2 \sum_i \left(\frac{\partial^2 \Psi}{\partial \xi_i \partial T} \Delta \xi_i \Delta T + \frac{\partial^2 \Psi}{\partial \xi_i \partial \rho} \Delta \xi_i \Delta \rho \right), \tag{J.17}$$

where

$$\Psi_{ij} = \frac{\partial^2 \Psi}{\partial \xi_i \partial \xi_j}.$$

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[5] See, e.g., L. Onsager, Phys. Rev. **37**, 405 (1931); **38**, 2265 (1931).

The expression for Ψ in (J.17) can always be linearly transformed to the sum of the squares so that in the new variables $\Psi_{ij} = \delta_{ij}$ and Ψ has the form

$$2\Psi = \sum_i \xi_i^2 + 2\sum_i \left(\Psi_{iT}\Delta T\xi_i + \Psi_{i\rho}\Delta\rho\xi_i\right), \tag{J.17$'$}$$

where

$$\Psi_{iT} = \frac{\partial^2\Psi}{\partial\xi_i\partial T}; \quad \Psi_{i\rho} = \frac{\partial^2\Psi}{\partial\xi_i\partial\rho}; \quad \xi_i = \Delta\xi_i.$$

Now, applying the second transformation, which should be orthogonal and, therefore, keep the form of (J.17$'$) unchanged, and which transforms the quantities $\Psi_i$same way as ξ_i, we bring the quadratic form J to the following expression

$$2K = \sum_i \frac{\Psi_i^2}{\tau_i}, \tag{J.18}$$

where τ_i are some constants.

Due to (J.17) and (J.18), the reaction equation (J.16) in the latter variables takes the following form

$$\overset{\bullet}{\xi}_i = -\frac{1}{\tau_i}\left(\xi_i + \Psi_{iT}\Delta T + \Psi_{i\rho}\Delta\rho\right). \tag{J.19}$$

Energy equation takes the form quite similar to that of (J.3)

$$E_T\overset{\bullet}{T} - \frac{TP_T}{\rho^2}\overset{\bullet}{\rho} + \sum_i E_i\overset{\bullet}{\xi}_i = 0, \tag{J.20}$$

where

$$E_i = \frac{\partial E}{\partial\xi_i}.$$

For the case of propagation of sound with the frequency ω, these equations turn into

$$\xi_i(1 + \mathrm{i}\omega\tau_i) = -\left(\Psi_{iT}\Delta T + \Psi_{i\rho}\Delta\rho\right), \tag{J.21}$$

$$E_T\Delta T - \frac{TP_T}{\rho^2}\Delta\rho + \sum_i E_i\xi_i = 0. \tag{J.22}$$

Square of the complex velocity of sound propagation is equal to

$$W^2 = \frac{\Delta p}{\Delta \rho} = P_\rho + P_T \frac{\Delta T}{\Delta \rho} + \sum_i P_i \frac{\xi_i}{\Delta \rho}, \tag{J.23}$$

where

$$P_i = \frac{\partial P}{\partial \xi_i}.$$

Defining $\Delta T/\Delta \rho$ and $\xi_i/\Delta \rho$ from (J.21) and (J.22) and substituting into (J.23) we obtain

$$W^2 = P_\rho + \frac{\mathrm{i}\omega}{\rho^2} \sum_k \frac{P_k^2 \tau_k}{1 + \mathrm{i}\omega\tau_k} + \frac{T}{\rho^2} \frac{\left[P_T + 1/T \sum\limits_k P_k E_k / 1 + \mathrm{i}\omega\tau_k\right]^2}{C + 1/T \sum\limits_k E_k^2 / 1 + \mathrm{i}\omega\tau_k}. \tag{J.24}$$

For the Kneser case (excited molecules of gas) $P_k = 0$ and we obtain

$$W^2 = V_0^2 + \left(V_\infty^2 - V_0^2\right) \frac{C}{c - C} \frac{\mathrm{i}\omega/TC \sum_k E_k^2 \tau_k / 1 + \mathrm{i}\omega\tau_k}{1 - \mathrm{i}\omega/TC \sum_k E_k^2 \tau_k / 1 + \mathrm{i}\omega\tau_k}, \tag{J.25}$$

where

$$V_0^2 = p_\rho + \frac{T p_T}{c\rho} = \frac{c_p}{c} p_\rho,$$

$$V_\infty^2 = \frac{C_p}{C} p_\rho; \quad c = C + \sum_k \frac{E_k^2}{T}.$$

Discussion of these expressions will be presented elsewhere.

As mentioned above, for slow processes, the phenomena discussed here manifest in the emergence of the "volumetric viscosity." Let us show briefly how this follows from our equations, restricting ourselves to the case of one parameter ξ. Differentiating (J.3) with respect to time and then excluding the first derivative $\dot{\xi}$ from the obtained equation and (J.3), we obtain

$$\Delta\xi - \tau^2 \ddot{\xi} = \frac{E_\xi}{T\Psi_{\xi\xi}} \left(\Delta T - \tau \dot{T}\right) - \frac{P_T}{\rho^2 \Psi_{\xi\xi}} \left(\Delta\rho - \tau \dot{\rho}\right). \tag{J.26}$$

For slow processes, we drop the term $\tau^2 \ddot{\xi}$. Using (J.26), (J.4), and the relationship

$$E_\xi \Delta\xi + E_T \Delta T - \frac{TP_T}{\rho^2}\Delta\rho = 0$$

[obtained by integrating equation (J.4)], ΔT and ξ can be expressed through $\Delta\rho$ and $\overset{\bullet}{\rho}$. Substituting these expressions into Δp in (J.10) and, after some rearrangement, we obtain

$$\Delta p = V_0^2 \Delta\rho + \tau'(V_\infty^2 - V_0^2)\,\overset{\bullet}{\rho}\,.$$

Taking into account that

$$\overset{\bullet}{\rho} = -\rho \ \mathrm{div}\ \vec{u},$$

where $\vec{u}$ is the velocity of the liquid, expression for Δp can be written in the form

$$\Delta p = V_0^2 \Delta\rho - \eta' \mathrm{div}\ \vec{u},$$

where η' is the “second coefficient of viscosity,” given by

$$\eta' = \tau'\left(V_\infty^2 - V_0^2\right)\rho.$$

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