

Jimma University

College of Natural Sciences

Department of Physics

Notes on course Statistical Physics II (Phys 3092)

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After completion of this course students should be able to:

- identify simple application of classical and quantum statistics,
- apply statistical approaches in studying different properties of a system,
- derive and apply equi-partition theorem,
- explain the applications of laws of thermodynamics,
- employ Maxwell-Boltzmann, Bose-Einstein and Fermi-Dirac statistics in describing a given system,
- explain magnetic properties of substances at low temperature,
- discuss about different properties of substances related with their movement by

using kinetic theory of transport process,

- Understand the ways of incorporating the interaction term while studying dynamics of interacting particles.

UNIT-ONE

REVIEW OF THERMODYNAMICS

- After completion of this unit the learner will be able to:
 - Explain the laws of thermodynamics
 - Obtain the thermodynamics relations
 - Determine the expressions of the thermodynamic potential
 - Describe the Maxwell's thermodynamic relations

INTRODUCTION

- What is Thermodynamics?
- Thermodynamics is the study of relations among the state variables describing a thermodynamic system, and of transformations of heat into work and vice versa.
- Thermodynamic systems contain large numbers of constituent particles, and are described by a set of state variables which describe the system's properties in an average sense.

1.1 State of variable and equation of state

- State variables are classified as being either extensive or intensive.
- **Intensive variables** (independent of their size) have the same value everywhere in the system. Examples: pressure p , temperature T , chemical potential μ , density ρ , electric field E , etc Intensive variables may also be inhomogeneous.
- **Extensive variables**, such as volume V , particle number N , total internal energy E , magnetization M , etc., scale linearly with the system size.
- Extensive state variables correspond to quantities which can be determined, measured, or prescribed directly.
- Equation of state is a thermodynamics equation relating state of variables which describe the state of matter under a given set of physical conditions, such as pressure, volume, temperature (PVT), or internal energy.

$PV = nRT$ – ideal gas law

$(P + \frac{an^2}{V^2})(V - nb) = nRT$ - van der Waals equation, where a , and b are van der Waals

1.2 Laws of thermodynamics

- **Zeroth law of thermodynamics state that:** If two systems are separately in equilibrium with a third, then they must also be in equilibrium with each other. The temperature of a system in equilibrium is constant throughout the system.

First Law of Thermodynamics

- The first law of thermodynamics represents an adaptation of the law of conservation of energy to thermodynamics, where energy can be stored in internal degrees of freedom.
- The first law of thermodynamics states that energy is conserved. The change in internal energy E of a system is equal to the sum of the amount of heat energy added to the system & the amount of work done on the system.

$$dE = dQ + dW$$

Second law of thermodynamics

- The second law of thermodynamics tells us that life is not free. According to the first law we can change heat into work, apparently without limits. The second law, however, puts restrictions on this exchange. There are two versions of the second law, due to Kelvin and Claussius.

The Second law of thermodynamics-The second law can be formulated in many equivalent ways. The two statements generally considered to be the most clear are those due to Claussius and to Kelvin.

- **Claussius statement:** There exists no thermodynamic transformation whose sole effect is to transfer heat from a colder reservoir to a warmer reservoir.
- **Kelvin statement:** There exists no thermodynamic transformation whose sole effect is to extract heat from a reservoir and to convert that heat entirely into work.
- Paraphrasing, the Claussius statement expresses the common experience that heat naturally flows downhill from hot to cold, whereas the Kelvin statement says that no heat engine can be perfectly efficient. Both statements merely express facts of common experience in thermodynamic language.
- It is relatively easy to demonstrate that these alternative statements are, in fact, equivalent to each other. Although these postulates may appear somewhat mundane, their consequences are quite profound; most notably, the second law provides the basis for the thermodynamic concept of entropy.

- There exists a state function of the extensive parameters of any thermodynamic system, called entropy S , with the following properties:
 1. The values assumed by the extensive variables are those which maximize S consistent with the external constraints; and
 2. The entropy of a composite system is the sum of the entropies of its constituent subsystems.
- **Third Law of Thermodynamics:**
- The Third Law of Thermodynamics state as: The change in entropy that results from any isothermal reversible transformation of a condensed system approaches zero as the temperature approaches zero.

$$\lim_{T \rightarrow 0}(\Delta S)=0$$

1.3 Thermodynamic potential

Thermodynamic potential includes the parameters such as Helmholtz free energy (F), Enthalpy (H) & Gibbs free energy (G), where, $H=E+PV$, $F=E-TS$, & $G=F-TS+PV$

Entropy defined as: $dS = \frac{dQ}{T} \leftrightarrow TdS = dQ$

$dE = TdS - dW$, where $dW = PdV$, Then

$dE = TdS - PdV \rightarrow$ *Fundamental relation of thermodynamics*

- From $dE = TdS - PdV$, $E = E(S, V)$
- $d(PV) = PdV + VdP \Rightarrow PdV = d(PV) - VdP$
- $dE = TdS - PdV$
- $dE = TdS - d(PV) + VdP$
- $dE + d(PV) = TdS + VdP$
- $d(E + PV) = TdS + VdP$ where, $H = E + PV$ then
- **$dH = TdS + VdP \Rightarrow H = H(S, P)$ -Enthalpy**
- $dE = TdS - PdV$
- Let $d(TS) = TdS + SdT \Rightarrow TdS = d(TS) - SdT$, then

- $dE = d(TS) - SdT - pdV$
- $d(E - TS) = -SdT - pdV$, where $F = E - TS$
- **$dF = -SdT - pdV$, $F = F(T, V)$** - Helmholtz free energy

Exercise start from $dE = TdS - pdV$ show that $dG = -SdT + VdT$

1.4 Gibbs Durem's and Maxwell's relations

Maxwell's relations

- $dE = TdS - pdV$ -----(1)
 $E = E(S, V)$
- $dE = \left(\frac{dE}{dS}\right)_V dS + \left(\frac{dE}{dV}\right)_S dV$ ------(2)

Comparing equation 1 & 2

- $T = \left(\frac{dE}{dS}\right)_V$, $P = -\left(\frac{dE}{dV}\right)_S$
 $\left(\frac{dT}{dV}\right)_S = \frac{d^2E}{dVdS}$, $\left(\frac{dP}{dS}\right)_V = -\frac{d^2E}{dSdV}$ Then, $\left(\frac{dT}{dV}\right)_S = -\left(\frac{dP}{dS}\right)_V$
- The four Maxwell relations below are easily derived (verify!) for simple compressible systems.

$$E = E(S, V) \Rightarrow \left(\frac{dT}{dV}\right)_S = -\left(\frac{dP}{dS}\right)_V$$

$$H = H[S, p] \Rightarrow \left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$$

$$F = F[T, V] \Rightarrow \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$$

$$G = G[T, p] \Rightarrow \left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$$

Exercise: Derive each all the four Maxwell relations above.

Gibbs Durem's Equations

- Consider a system E, N, composed from several molecules Ni
- Systems in nature classify as:

1) Isolated system-no interaction (no exchange of energy with the environments). Energy - constant

2) Closed system- no exchange of particles (matter). N-constant, mass-constant, charge-constant

3) Open system- a system can interact with the environment. N- Vary (not constant)

$E=E(S,V,N_1,N_2, \dots, N_m)$, m-types of molecules

$S=S(E, V, N_1, N_2, \dots, N_n)$

$$dS = \left(\frac{dS}{dE}\right)_{V,N} dE + \left(\frac{dS}{dV}\right)_{E,N} dV + \sum_{i=1}^n \left(\frac{dS}{dN_i}\right)_{E,V} dN_i$$

N_i -constant

$$\mu_i = -T \left(\frac{dS}{dN_i}\right)_{E,V,N}$$

$$dS = \left(\frac{dS}{dE}\right)_{V,N} dE + \left(\frac{dS}{dV}\right)_{E,N} dV - \sum_{i=1}^n \frac{\mu_i}{T} dN_i$$

$$\left(\frac{dE}{dV}\right)_V = T \Rightarrow \left(\frac{dS}{dE}\right)_V = \frac{1}{T}$$

$$\left(\frac{dE}{dV}\right)_S = -P \Rightarrow \frac{dE}{dV} \cdot \frac{dS}{dV} = -P \cdot \frac{1}{T}, \text{ Then we get } \frac{dS}{dV} = \frac{-P}{T}$$

$$dS = \frac{dE}{T} + \frac{P}{T} dV - \sum \frac{\mu_i}{T} dN_i$$

$$TdS = dE + PdV - \sum \mu_i dN_i$$

$$dE = TdS - PdV + \sum \mu_i dN_i \rightarrow dE = d(TS) - SdT - PdV + \sum \mu_i dN_i, \text{ Then,}$$

$$dF = -SdT - PdV + \sum \mu_i dN_i$$

Again for Gibb's free energy it derives as follows:

$$dE = d(TS) - SdT - d(PV) + VdP + \sum \mu_i dN_i,$$

$$dG = -SdT + VdP + \sum \mu_i dN_i, \text{ If } S \text{ \& } V \text{ are constant}$$

$$dE = TdS - PdV + \sum \mu_i dN_i, \text{ but } dE = \sum \mu_i dN_i, \Rightarrow \mu_i = \left(\frac{dE}{dN_i}\right)_V$$

$$dF = \sum_i \mu_i dN_i \Rightarrow \mu_i = \frac{dF}{dN_i}$$

$$dG = \sum \mu_i dN_i \Rightarrow \mu_i = \frac{dG}{dN_i}$$

Therefore, $dE \neq dF \neq dG$

$G = G(T, P, N)$ - for one molecules (i-molecules)

$G = G(T, P, N_i)$, $G \propto N_i$

$$g(T, P) = \frac{G}{N_i} \Rightarrow \frac{dG}{dN_i} = \mu_i$$

Consider a system have S, N, V

$S \rightarrow \alpha S$, $V \rightarrow \alpha V$ & $N \rightarrow \alpha N$

Suppose $E(S, V, N)$

$E(\alpha S, \alpha V, \alpha N) \rightarrow \alpha E$, Assume $\alpha = 1 + \gamma$, $\gamma \ll 1$

$$E = \alpha E \Rightarrow E = E(\gamma + 1)$$

$$f(x+h) = f(x) + hf'(x) + \frac{h^2}{2} f''(x) + \dots + \frac{h^n}{n} f^n(x) = \sum f^n \frac{h^n}{n!} \text{ Taylor theorem}$$

$$E(\alpha S, \alpha V, \alpha N) = E(S, V, N) + \left(\frac{dE}{dS}\right)_{N,V} \alpha S + \left(\frac{dE}{dV}\right)_{S,N} \alpha V + \left(\frac{dE}{dN}\right)_{S,V} \alpha N$$

$$= E(S, V, N) + \alpha \left[\left(\frac{dE}{dS}\right)_{N,V} S + \left(\frac{dE}{dV}\right)_{S,N} V + \left(\frac{dE}{dN}\right)_{S,V} N_i \right]$$

$$\Rightarrow E = S \left(\frac{dE}{dS}\right)_{N,V} + V \left(\frac{dE}{dV}\right)_{S,N} + \sum N_i \left(\frac{dE}{dN_i}\right)_{S,V}$$

$$dE = TdS + SdT - PdV - VdP + \sum N_i dN_i + \sum \mu_i dN_i$$

$$dE = TdS + PdV + \sum \mu_i dN_i$$

$SdT - VdP + \sum N_i dN_i = 0 \rightarrow$ Gibb's Durem's relation

1.5) Response functions

The experimental important response functions are obtained by the second -order differential of the internal energy. Consider the entropy S expressed as a function of T, V , and N :

$$dS = \left(\frac{\partial S}{\partial T} \right)_{V,N} dT + \left(\frac{\partial S}{\partial V} \right)_{T,N} dV + \left(\frac{\partial S}{\partial N} \right)_{T,V} dN$$

Dividing by dT , multiplying by T , and assuming $dN = 0$ throughout, we have

$$C_p - C_V = T \left(\frac{\partial S}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_p$$

Appealing to a Maxwell relation derived from $F(T, V, \text{ and } N)$, and then we get:

$$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial p}{\partial T} \right)_V = - \left(\frac{\partial p}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_p.$$

This allows to writing as:

$$C_p - C_V = -T \left(\frac{\partial p}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_p^2$$

We define the response function as:

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T = -\frac{1}{V} \frac{\partial^2 G}{\partial p^2} \rightarrow \text{isothermal compressibility}$$

$$\kappa_S = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_S = -\frac{1}{V} \frac{\partial^2 \mathcal{H}}{\partial p^2} \rightarrow \text{Adiabatic compressibility}$$

$$\alpha_p = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p \rightarrow \text{thermal expansivity, thus}$$

$$C_p - C_V = V \frac{T \alpha_p^2}{\kappa_T}$$

It also interms of intensive quantity expressed as follows:

$$c_p - c_V = \frac{v T \alpha_p^2}{\kappa_T},$$

Where, as always, $v = \frac{VN_a}{N}$ is the molar volume.

This above relation generalizes to any conjugate force-displacement pair $(-p, V) \rightarrow (y, X)$:

$$\begin{aligned} C_y - C_X &= -T \left(\frac{\partial y}{\partial T} \right)_X \left(\frac{\partial X}{\partial T} \right)_y \\ &= T \left(\frac{\partial y}{\partial X} \right)_T \left(\frac{\partial X}{\partial T} \right)_y^2 . \end{aligned}$$

For example, we could have $(y, X) = (H^\alpha, M^\alpha)$

A similar relationship can be derived between the compressibility k_T and k_S . We then clearly must start with the volume, writing

$$dV = \left(\frac{\partial V}{\partial p} \right)_{S,N} dp + \left(\frac{\partial V}{\partial S} \right)_{p,N} dS + \left(\frac{\partial V}{\partial N} \right)_{S,p} dN$$

Dividing by dP , multiplying by $-V^{-1}$, and keeping N constant, we have

$$\kappa_T - \kappa_S = -\frac{1}{V} \left(\frac{\partial V}{\partial S} \right)_p \left(\frac{\partial S}{\partial p} \right)_T$$

Again we appeal to a Maxwell relation, writing

$$\left(\frac{\partial S}{\partial p} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_p ,$$

Then, after involving chain rule

$$\left(\frac{\partial V}{\partial S} \right)_p = \left(\frac{\partial V}{\partial T} \right)_p \left(\frac{\partial T}{\partial S} \right)_p = \frac{T}{C_p} \left(\frac{\partial V}{\partial T} \right)_p ,$$

We get,

$$\kappa_T - \kappa_S = \frac{v T \alpha_p^2}{c_p} .$$

Comparing the above two equations, we obtain

$$(c_p - c_V) \kappa_T = (\kappa_T - \kappa_S) c_p = v T \alpha_p^2$$

This result entails

$$\frac{c_p}{c_V} = \frac{\kappa_T}{\kappa_S}$$

The corresponding result for magnetic systems is

$$(c_H - c_M) \chi_T = (\chi_T - \chi_S) c_H = T \left(\frac{\partial m}{\partial T} \right)_H^2,$$

Where $m = M/v$ is the magnetization per mole of substance, and isothermal susceptibility:

$$\chi_T = \left(\frac{\partial M}{\partial H} \right)_T = -\frac{1}{v} \frac{\partial^2 G}{\partial H^2}$$

adiabatic susceptibility:

$$\chi_S = \left(\frac{\partial M}{\partial H} \right)_S = -\frac{1}{v} \frac{\partial^2 \mathcal{H}}{\partial H^2}$$

Here the enthalpy and Gibbs free energy are

$$\mathcal{H} = E - HM$$

$$d\mathcal{H} = T dS - M dH$$

$$G = E - TS - HM$$

$$dG = -S dT - M dH$$

Remark: The previous discussion has assumed an isotropic magnetic system where M and H are collinear, hence $H \cdot M = HM$.

$$\chi_T^{\alpha\beta} = \left(\frac{\partial M^\alpha}{\partial H^\beta} \right)_T = -\frac{1}{\nu} \frac{\partial^2 G}{\partial H^\alpha \partial H^\beta}$$

$$\chi_S^{\alpha\beta} = \left(\frac{\partial M^\alpha}{\partial H^\beta} \right)_S = -\frac{1}{\nu} \frac{\partial^2 \mathcal{H}}{\partial H^\alpha \partial H^\beta}$$

In this case, the enthalpy and Gibbs free energy are

$$\mathcal{H} = E - \mathbf{H} \cdot \mathbf{M}$$

$$d\mathcal{H} = T dS - \mathbf{M} \cdot d\mathbf{H}$$

$$G = E - TS - \mathbf{H} \cdot \mathbf{M}$$

$$dG = -S dT - \mathbf{M} \cdot d\mathbf{H}$$

1.6) Condition for equilibrium

The principle of maximum entropy requires that any spontaneous transformation of an isolated system increases its entropy. Thus, if a system begins in some arbitrary non equilibrium condition, internal changes tend to accumulate until the entropy reaches the maximum possible value compatible with the external constraints, which finally becomes the state of thermodynamic equilibrium. For the present purposes, we can consider a system to be isolated if all of its extensive quantities (such as energy, volume, and particle number) are fixed. However, the distribution of these extensive quantities is generally non uniform in some arbitrary initial configuration. Suppose that an isolated system is divided into two subsystems which share the total internal energy, volume, particle number, and any other extensive quantities needed to characterize its state, such that

$$E = E_1 + E_2$$

$$V = V_1 + V_2$$

$$N = N_1 + N_2$$

If the system is isolated, these extensive quantities are conserved, such that

$$dE=0 \Rightarrow dE_1 = -dE_2, \quad dV=0 \Rightarrow dV_1 = -dV_2, \quad \text{and} \quad dN=0 \Rightarrow dN_1 = -dN_2$$

Thus, variations of the total entropy $S = S_1 + S_2$ can then be expressed as

$$dS = \left(\left(\frac{\partial S_1}{\partial U_1} \right)_{V_1, N_1} - \left(\frac{\partial S_2}{\partial U_2} \right)_{V_2, N_2} \right) dU_1 + \left(\left(\frac{\partial S_1}{\partial V_1} \right)_{U_1, N_1} - \left(\frac{\partial S_2}{\partial V_2} \right)_{U_2, N_2} \right) dV_1 + \left(\left(\frac{\partial S_1}{\partial N_1} \right)_{V_1, U_1} - \left(\frac{\partial S_2}{\partial N_2} \right)_{V_2, U_2} \right) dN_1 + \dots$$

Thermal equilibrium between the two subsystems requires that dS be stationary with respect to first-order variations of each variable independently, such that

$$dS = 0 \implies T_1 = T_2 \quad p_1 = p_2 \quad \mu_1 = \mu_2$$

Where the fundamental relations

$T_i dS_i = dU_i + p_i dV_i - \mu_i dN_i + \dots$ are used to identify the intensive parameters T, p, μ , conjugate to the extensive variables $\{U, V, N, \dots\}$ for each subsystems. Therefore, thermal equilibrium between two systems requires equality between their intensive parameters. These intensive parameters govern the sharing of a conserved extensive quantity between interacting subsystems. Furthermore, by choosing one of the systems to be a small but macroscopic portion of a larger system, we conclude that equilibrium requires the intensive parameters like temperature, pressure, and chemical potential to be uniform throughout the system. Any local fluctuations in these parameters would induce unbalanced forces that tend to restore equilibrium by eliminating gradients in the intensive parameters. Obviously, temperature or pressure gradients would induce heat or mass flows that tend to homogenize the system.

The maximum entropy principle can also be applied to systems that are in thermal, mechanical, or chemical contact with an environment that constrains one or more of its intensive parameters. For example, we often seek to determine the equilibrium state for a system with fixed temperature and pressure instead of fixed energy and volume. Under these conditions it is useful to consider a small subsystem with energy E_1 and volume V_1 in thermal and mechanical contact with a much larger reservoir. If the initial configuration is not in equilibrium there will be exchanges of energy and volume between the subsystem and the reservoir. We assume that the reservoir is sufficiently large that small transfers of energy or volume do not change the temperature T_0 or pressure P_0 of the reservoir. The net change in entropy for the combined system can be expressed as

$$dS = dS_0 + dS_1 \geq 0$$

Where

$$dS_0 = -\frac{\delta Q}{T_0}$$

The principle of maximum entropy then requires

$$dS \geq 0 \implies dS_1 \geq T_0 dS_0$$

The increase in the entropy of the subsystem is at least as large as the decrease of the entropy of the reservoir that occurs when heat is transferred from the reservoir to the subsystem. The change in the internal energy of the subsystem can be expressed as

$$dE_1 = dQ + dW =$$

$$-T_0 dS_0 - p_0 dV_1 + \delta W' = T_0 (dS_1 - dS) - p_0 dV_1 + \delta W'$$

where it is convenient to divide the work into two contributions, $dW = -P_0 dV_1 + dW'$, where dW' is non mechanical work performed upon the subsystem in some form other than mechanical work against the constant external pressure P_0 . The requirement that the total entropy increases can now be expressed as

$$dS \geq 0 \implies dA \leq \delta W'$$

where the availability A is defined as

$$A = E_1 - T_0 S_1 + P_0 V_1 \implies dA = dE_1 - T_0 dS_1 + P_0 dV_1$$

Although this availability function strongly resembles the Gibbs free enthalpy G_1 for the subsystem, it is important to recognize that we do not require the temperature and pressure of the subsystem to match those of the environment; hence, T_0 and P_0 appear as fixed parameters in

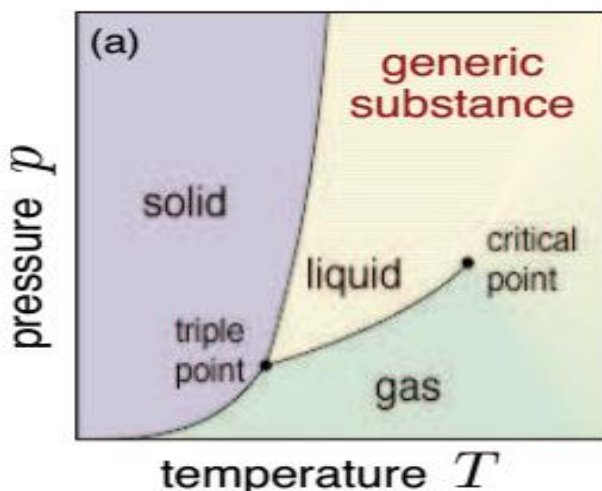
A. At equilibrium, the first derivatives of availability with respect to any of the system parameters must vanish. Furthermore, if the equilibrium is to be stable, the second derivatives must all be positive. Applying these observations to temperature and pressure, we require.

$$\left(\frac{\partial A}{\partial T}\right)_p = 0 \qquad \left(\frac{\partial^2 A}{\partial T^2}\right)_p \geq 0$$

$$\left(\frac{\partial A}{\partial p}\right)_T = 0 \qquad \left(\frac{\partial^2 A}{\partial p^2}\right)_T \geq 0$$

1.7 Thermodynamics of phase transitions

A typical phase diagram of a p-V -T system is shown in the Fig. below. The solid lines delineate boundaries between distinct thermodynamic phases. These lines are called coexistence curves. Along these curves, we can have coexistence of two phases, and the thermodynamic potentials are singular. The order of the singularity is often taken as a classification of the phase transition. i.e. if the thermodynamic potentials E, F , G, and H have discontinuous or divergent m^{th} derivatives, the transition between the respective phases is said to be m^{th} order . Modern theories of phase transitions generally only recognize two possibilities: first order transitions, where the order parameter changes discontinuously through the transition, and second order transitions , where the order parameter vanishes continuously at the boundary from ordered to disordered phases.



Chapter -Two

Simple Applications of Statistical

2.1) Partition function and their properties ideal monatomic gas

Consider a system in contact with a heat reservoir. The systems in the representative ensemble are distributed over their accessible states in accordance with the Boltzmann distribution. Thus, the probability of occurrence of some state r with energy E_r is given by

$$P_r = \frac{\exp(-\beta E_r)}{\sum_r \exp(-\beta E_r)} \quad \text{-----(2.1)}$$

The mean energy is written as

$$\bar{E} = \frac{\sum_r \exp(-\beta E_r) E_r}{\sum_r \exp(-\beta E_r)}, \quad \text{-----(2.2)}$$

where the sum is taken over all states of the system, irrespective of their energy.

Note that

$$\sum_r \exp(-\beta E_r) E_r = - \sum_r \frac{\partial}{\partial \beta} \exp(-\beta E_r) = - \frac{\partial Z}{\partial \beta}, \quad \text{-----(2.3)}$$

Where,

$$Z = \sum_r \exp(-\beta E_r) \quad \text{-----(2.4)}$$

It follows that

$$\bar{E} = - \frac{1}{Z} \frac{\partial Z}{\partial \beta} = - \frac{\partial \ln Z}{\partial \beta}, \quad \text{-----(2.5)}$$

The quantity Z , which is defined as the sum of the Boltzmann factor over all states, irrespective of their energy, is called the partition function.

It is clear that all important macroscopic quantities associated with a system can be expressed in terms of its partition function Z . Let us investigate how the partition function is related to thermodynamically quantities. Partition function is the basic parameter in statistical physics.

$$Z \propto e^{-E}$$

$$Z = \sum e^{-\beta E_r}, \quad \beta = \frac{1}{k_B T} \quad \text{-----(2.6)}$$

Recall that Z is a function of both β and x (where x is the single external parameter). Hence, $Z = Z(\beta, x)$, and we can write

$$d \ln Z = \frac{\partial \ln Z}{\partial x} dx + \frac{\partial \ln Z}{\partial \beta} d\beta \quad \text{-----}(2.7)$$

Consider a quasi-static change by which x and β change so slowly that the system stays close to equilibrium, and, thus, remains distributed according to the Boltzmann distribution.

$$d \ln Z = \beta dW - d(\bar{E} \beta) + \beta d\bar{E}, \quad \text{-----}(2.8)$$

Then, we get

$$d(\ln Z + \beta \bar{E}) = \beta(dW + d\bar{E}) \equiv \beta dQ \quad \text{-----}(2.9)$$

Hence, $S = \frac{Q}{T}$ or $dS = \frac{dQ}{T}$ -----2.10)

$$S \equiv k (\ln Z + \beta \bar{E}) \quad \text{-----}(2.11)$$

This expression enables us to calculate the entropy of a system from its partition function.

Suppose that we are dealing with a system $A^0(0)$ consisting of two systems A and A' which only interact weakly with one another. Let each state of A be denoted by an index r and have a corresponding energy E_r . Likewise, let each state of A' be denoted by an index s and have a corresponding energy E'_s . A state of the combined system A^0 is then denoted by two indices r and s . Since A and A' only interact weakly their energies are additive, and the energy of state rs is

$$E_{rs}^{(0)} = E_r + E'_s \quad \text{-----}(2.12)$$

The partition function A^0 takes the form

$$\begin{aligned}
Z^{(0)} &= \sum_{r,s} \exp[-\beta E_{rs}^{(0)}] \\
&= \sum_{r,s} \exp(-\beta [E_r + E'_s]) \\
&= \sum_{r,s} \exp(-\beta E_r) \exp(-\beta E'_s) \\
&= \left[\sum_r \exp(-\beta E_r) \right] \left[\sum_s \exp(-\beta E'_s) \right] \dots\dots\dots(2.13)
\end{aligned}$$

Hence, $Z^{(0)} = Z Z'$,(2.14)

Yields, $\ln Z^{(0)} = \ln Z + \ln Z'$ (2.15)

Where Z and Z' are the partition functions of A and A' , respectively. It follows that the mean energies of $A^{(0)}$, A , and A' are related by

$$\bar{E}^{(0)} = \bar{E} + \bar{E}' \dots\dots\dots(2.16)$$

The respective entropies of these systems are also related

$$S^{(0)} = S + S' \dots\dots\dots(2.17)$$

Hence, the partition function tells us that the extensive thermodynamic functions of two weakly interacting systems are simply additive.

2.2) Calculations of thermodynamic quantities

Consider a gas consisting of N identical monatomic molecules of mass m enclosed in a container of volume V . Let us denote the position and momentum vectors of the i^{th} molecule by r_i and p_i , respectively. Since the gas is ideal, there are no interatomic forces, and the total energy is simply the sum of the individual kinetic energies of the molecules:

$$E = \sum_{i=1}^N \frac{p_i^2}{2m}, \dots\dots\dots(2.18)$$

Let us treat the problem classically. In this approach, we divide up phase-space into cells of equal volume h_o^f . Here, f is the number of degrees of freedom, and h_o is a small constant with dimensions of angular momentum which parameterizes the precision to which the positions and momenta of molecules are determined. Each cell in phase-space corresponds to a different state. The partition function is the sum of the Boltzmann factor $\exp(-\beta E_r)$ over all possible states, where E_r is the energy of state r . Classically, we can approximate the summation over cells in phase-space as an integration over all phase-space. Thus,

$$Z = \int \cdots \int \exp(-\beta E) \frac{d^3\mathbf{r}_1 \cdots d^3\mathbf{r}_N d^3\mathbf{p}_1 \cdots d^3\mathbf{p}_N}{h_o^{3N}}, \quad \text{-----(2.19)}$$

where $3N$ is the number of degrees of freedom of a monatomic gas containing N molecules. Then, the above equation reduces to:

$$Z = \frac{V^N}{h_o^{3N}} \int \cdots \int \exp[-(\beta/2m) p_1^2] d^3\mathbf{p}_1 \cdots \exp[-(\beta/2m) p_N^2] d^3\mathbf{p}_N \quad \text{-----(2.20)}$$

Note that the integral over the coordinates of a given molecule simply yields the volume of the container, V , since the energy E is independent of the locations of the molecules in an ideal gas. There are N such integrals, so we obtain the factor V^N in the above expression. The partition function Z of the gas is made up of the product of N identical factors: i.e.,

$$Z = \zeta^N, \quad \text{-----(2.21)}$$

Where

$$\zeta = \frac{V}{h_o^3} \int \exp[-(\beta/2m) p^2] d^3\mathbf{p} \quad \text{-----(2.22)}$$

This equation is the partition function for a single molecule. Of course, this result is obvious, since we have already shown that the partition function for a system made up of a number of weakly interacting subsystems is just the product of the partition functions of the subsystems. The integral in Eq. (2.22) is easily evaluated:

$$\int \exp[-(\beta/2m) p^2] d^3\mathbf{p} = \int_{-\infty}^{\infty} \exp[-(\beta/2m) p_x^2] dp_x \int_{-\infty}^{\infty} \exp[-(\beta/2m) p_y^2] dp_y \times \int_{-\infty}^{\infty} \exp[-(\beta/2m) p_z^2] dp_z \quad \text{-----}(2.23)$$

$$= \left(\sqrt{\frac{2\pi m}{\beta}} \right)^3 \quad \text{-----}(2.24)$$

Thus,

$$\zeta = V \left(\frac{2\pi m}{h_0^2 \beta} \right)^{3/2} \quad \text{-----}(2.25)$$

And,

$$\ln Z = N \ln \zeta = N \left[\ln V - \frac{3}{2} \ln \beta + \frac{3}{2} \ln \left(\frac{2\pi m}{h_0^2} \right) \right] \quad \text{-----}(2.26)$$

Then the expression for the mean pressure yields as:

$$\bar{p} = \frac{1}{\beta} \frac{\partial \ln Z}{\partial V} = \frac{1}{\beta} \frac{N}{V}, \quad \text{-----}(2.27)$$

Which reduces to the ideal gas equation of state

$$\bar{p} V = N k T = \nu R T, \quad \text{-----}(2.28)$$

Where, $N = \nu N_A$ and $R = k N_A$, then the mean energy of the gas is obtained as:

$$\bar{E} = -\frac{\partial \ln Z}{\partial \beta} = \frac{3N}{2\beta} = \nu \frac{3}{2} R T. \quad \text{-----}(2.29)$$

Note that the internal energy is a function of temperature alone, with no dependence on volume.

The molar heat capacity at constant volume of the gas is given by

$$c_v = \frac{1}{\nu} \left(\frac{\partial \bar{E}}{\partial T} \right)_V = \frac{3}{2} R, \text{-----(2.30)}$$

Therefore, the mean energy written as

$$\bar{E} = \nu c_v T. \text{-----(2.31)}$$

Now let us use the partition function to calculate a new result. The entropy of the gas can be calculated quite simply from the expression

$$S = k (\ln Z + \beta \bar{E}). \text{-----(2.32)}$$

Thus,

$$S = \nu R \left[\ln V - \frac{3}{2} \ln \beta + \frac{3}{2} \ln \left(\frac{2\pi m}{h_0^2} \right) + \frac{3}{2} \right], \text{-----(2.33)}$$

Or
$$S = \nu R \left[\ln V + \frac{3}{2} \ln T + \sigma \right] \text{-----(2.34)}$$

Where,
$$\sigma = \frac{3}{2} \ln \left(\frac{2\pi m k}{h_0^2} \right) + \frac{3}{2}. \text{-----(2.35)}$$

2.3) Gibbs paradox

Thermodynamic quantities can be divided into two groups, extensive and intensive. Extensive quantities increase by a factor α when the size of the system under consideration is increased by the same factor. Intensive quantities stay the same. Energy and volume are typical extensive quantities. Pressure and temperature are typical intensive quantities. Entropy is very definitely an extensive quantity. Suppose that we have a system of volume V containing ν moles of ideal gas at temperature T . Doubling the size of the system is like joining two identical systems together to form a new system of volume $2V$ containing 2ν moles of gas at temperature T . Let

$$S = \nu R \left[\ln V + \frac{3}{2} \ln T + \sigma \right] \text{-----(2.36)}$$

Denote the entropy of the original system, and let

$$S' = 2\nu R \left[\ln 2V + \frac{3}{2} \ln T + \sigma \right] \text{-----}(2.37)$$

Denote the entropy of the double-sized system. Clearly, if entropy is an extensive quantity (which it is!) then we should have

$$S' = 2S \text{-----}2.38)$$

But, in fact, we find that

$$S' - 2S = 2\nu R \ln 2 \text{-----}(2.39)$$

So, the entropy of the double-sized system is more than double the entropy of the original system. Where does this extra entropy come from?

2.4) Validity of the classical approximation

Suppose the mean intermolecular separation \bar{R} can be estimated by imaging each molecule at center of a little cube of side \bar{R} , these cubes filling the available volume V . Then

$$\begin{aligned} \bar{R}^3 N &= V \\ \bar{R} &= \left(\frac{V}{N} \right)^{\frac{1}{3}} \end{aligned} \text{-----}$$

or
(2.40)

The mean momentum \bar{p} can be estimated from the known mean energy $\bar{\epsilon}$ of a molecule in the gas at temperature T .

$$\begin{aligned} \frac{1}{2m} \bar{p}^2 &\approx \bar{\epsilon} = \frac{3}{2} kT \\ \bar{p} &\approx \sqrt{3mkT} \\ \bar{\lambda} &\approx \frac{h}{\sqrt{3mkT}} \end{aligned} \text{-----}(2.41)$$

Hence the condition becomes

$$\left(\frac{V}{N}\right)^{\frac{1}{3}} \gg \frac{h}{\sqrt{3mkT}} \text{-----(2.42)}$$

2.5) Proof of equipartition

The internal energy of a monatomic ideal gas containing N particles is (3/2) N k T .This means that each particle possess, on average, (3/2) k T units of energy. Mon-atomic particles have only three translational degrees of freedom, corresponding to their motion in three dimensions. They possess no internal rotational or vibrational degrees of freedom. Thus, the mean energy per degree of freedom in a monatomic ideal gas is (1/2) k T. In fact, this is a special case of a rather general result.

Suppose that the energy of a system is determined by some f generalized coordinates q_k and corresponding f generalized momenta p_k , so that

$$E = E(q_1, \dots, q_f, p_1, \dots, p_f) \text{-----(2.43)}$$

a) The total energy splits additively into the form

$$E = \epsilon_i(p_i) + E'(q_1, \dots, p_f) \text{-----(2.44)}$$

Where ϵ_i involves only one variable p_i , and the remaining part E' does not depend on p_i .

b) The function ϵ_i is quadratic in p_i , so that

$$\epsilon_i(p_i) = b p_i^2 \text{-----(2.45)}$$

Where b is constant

The most common situation in which the above assumptions are valid is where p_i a momentum is. This is because the kinetic energy is usually a quadratic function of each momentum component, whereas the potential energy does not involve the momenta at all. However, if a coordinate q_i were to satisfy assumptions 1 and 2 then the theorem we are about to establish would hold just as well. In the classical approximation, the mean value of ϵ_i is expressed in terms of integrals over all phase-space:

$$\bar{\epsilon}_i = \frac{\int_{-\infty}^{\infty} \exp[-\beta E(q_1, \dots, p_f)] \epsilon_i dq_1 \dots dp_f}{\int_{-\infty}^{\infty} \exp[-\beta E(q_1, \dots, p_f)] dq_1 \dots dp_f} \dots\dots\dots(2.46)$$

Condition 1 gives

$$\begin{aligned} \bar{\epsilon}_i &= \frac{\int_{-\infty}^{\infty} \exp[-\beta (\epsilon_i + E')] \epsilon_i dq_1 \dots dp_f}{\int_{-\infty}^{\infty} \exp[-\beta (\epsilon_i + E')] dq_1 \dots dp_f} \\ &= \frac{\int_{-\infty}^{\infty} \exp(-\beta \epsilon_i) \epsilon_i dp_i \int_{-\infty}^{\infty} \exp(-\beta E') dq_1 \dots dp_f}{\int_{-\infty}^{\infty} \exp(-\beta \epsilon_i) dp_i \int_{-\infty}^{\infty} \exp(-\beta E') dq_1 \dots dp_f} \dots\dots\dots(2.47) \end{aligned}$$

where use has been made of the multiplicative property of the exponential function, and where the last integrals in both the numerator and denominator extend over all variables q_k and p_k except p_i . These integrals are equal and, thus, cancel. Hence

$$\bar{\epsilon}_i = \frac{\int_{-\infty}^{\infty} \exp(-\beta \epsilon_i) \epsilon_i dp_i}{\int_{-\infty}^{\infty} \exp(-\beta \epsilon_i) dp_i} \dots\dots\dots(2.48)$$

This expression can be simplified further since

$$\int_{-\infty}^{\infty} \exp(-\beta \epsilon_i) \epsilon_i dp_i \equiv -\frac{\partial}{\partial \beta} \left[\int_{-\infty}^{\infty} \exp(-\beta \epsilon_i) dp_i \right], \dots\dots\dots(2.49)$$

$$\bar{\epsilon}_i = -\frac{\partial}{\partial \beta} \ln \left[\int_{-\infty}^{\infty} \exp(-\beta \epsilon_i) dp_i \right] \dots\dots\dots(2.50)$$

According to condition 2

$$\int_{-\infty}^{\infty} \exp(-\beta \epsilon_i) dp_i = \int_{-\infty}^{\infty} \exp(-\beta b p_i^2) dp_i = \frac{1}{\sqrt{\beta}} \int_{-\infty}^{\infty} \exp(-b y^2) dy \dots\dots\dots(2.51)$$

Where $y = \sqrt{\beta} p_i$, Thus,

$$\ln \int_{-\infty}^{\infty} \exp(-\beta \epsilon_i) dp_i = -\frac{1}{2} \ln \beta + \ln \int_{-\infty}^{\infty} \exp(-b y^2) dy. \dots\dots\dots(2.52)$$

Note that the integral on the right-hand side does not depend on β at all. Then it follows from eq.(2.49)

$$\bar{\epsilon}_i = -\frac{\partial}{\partial \beta} \left(-\frac{1}{2} \ln \beta \right) = \frac{1}{2\beta} \text{-----(2.53)}$$

It gives

$$\bar{\epsilon}_i = \frac{1}{2} k T. \text{-----(2.54)}$$

This is the famous equipartition theorem of classical physics. It states that the mean value of every independent quadratic term in the energy is equal to (1/2) k T .

2.6) Simple applications

Suppose a gas of a system consists r, \vec{p} and its total kinetic energy is $K = \sum \frac{p^2}{2m} = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2)$

$$E_m = \frac{3}{2} k T \text{-----(2.52)}$$

$$E_S = N_A E_m = \frac{3}{2} N_A k T \text{-----(2.55)}$$

2.7 Specific heat of solids

Consider simple solid containing N atoms. Now, atoms in solids cannot translate (unlike those in gases), but are free to vibrate about their equilibrium positions. Such vibrations are called lattice vibrations, and can be thought of as sound waves propagating through the crystal lattice. In normal mode coordinates, the total energy of the lattice vibrations takes the particularly simple form

$$E = \frac{1}{2} \sum_{i=1}^{3N} (p_i^2 + \omega_i^2 q_i^2), \text{-----(2.56)}$$

Where ω_i is the (angular) oscillation frequency of the i^{th} normal mode. It is clear that in normal mode coordinates, the linearized lattice vibrations are equivalent to 3 N independent harmonic oscillators (of course, each oscillator corresponds to a different normal mode).

If the lattice vibrations behave classically then, according to the equipartition theorem, each normal mode of oscillation has an associated mean energy k T in equilibrium at temperature T

[(1/2) k T resides in the kinetic energy of the oscillation, and (1/2) k T resides in the potential energy]. Thus, the mean internal energy per mole of the solid is

$$\bar{E} = 3 N k T = 3 \nu R T. \text{-----}(2.57)$$

It follows that the molar heat capacity at constant volume is

$$c_V = \frac{1}{\nu} \left(\frac{\partial \bar{E}}{\partial T} \right)_V = 3 R \text{-----}(2.58)$$

We can use the quantum mechanical result for a single oscillator to write the mean energy of the solid in the form

$$\bar{E} = 3 N \hbar \omega \left(\frac{1}{2} + \frac{1}{\exp(\beta \hbar \omega) - 1} \right) \text{-----}(2.59)$$

The molar heat capacity is defined as:

$$c_V = \frac{1}{\nu} \left(\frac{\partial \bar{E}}{\partial T} \right)_V = \frac{1}{\nu} \left(\frac{\partial \bar{E}}{\partial \beta} \right)_V \frac{\partial \beta}{\partial T} = -\frac{1}{\nu k T^2} \left(\frac{\partial \bar{E}}{\partial \beta} \right)_V \text{-----}(2.60)$$

Then it gives

$$c_V = -\frac{3 N_A \hbar \omega}{k T^2} \left[-\frac{\exp(\beta \hbar \omega) \hbar \omega}{[\exp(\beta \hbar \omega) - 1]^2} \right] \text{-----}(2.61)$$

Which reduces to:

$$c_V = 3 R \left(\frac{\theta_E}{T} \right)^2 \frac{\exp(\theta_E/T)}{[\exp(\theta_E/T) - 1]^2} \text{-----}(3.62)$$

Where, $\theta_E = \frac{\hbar \omega}{k}$

2.8) General calculation of magnetism

Consider a system consisting of N non-interacting atoms in a substance in a substance at absolute temperature T and placed in an external magnetic field H pointing along the z-direction. Then the magnetic energy of an atom can be written as:

$$\boldsymbol{\varepsilon} = -\boldsymbol{\mu}\mathbf{H} \quad \text{-----(2.63)}$$

Here $\boldsymbol{\mu}$ is the magnetic moment of the atom. It is proportional to the total angular momentum $\chi\mathbf{J}$ of the atom and is conventionally written in the form:

$$\boldsymbol{\mu} = g\boldsymbol{\mu}_o\mathbf{J} \quad \text{-----(2.64)}$$

Where $\boldsymbol{\mu}_o$ is the standard unit of magnetic moment (usually the Bohr magneton $\boldsymbol{\mu}_o = e\hbar/2mc$, m is electron mass) and where g is a number of the order of unit, the so called g factor of the atom.

2.9) Maxwell's velocity distribution

Consider a molecule of a mass m in a dilute gas. The gas may consist of several different kinds of molecules, the molecules under consideration may also be polyatomic. If the external force field neglect, the energy ϵ of this molecule is equal to:

$$\epsilon = \frac{\mathbf{p}^2}{2m} + \epsilon^{(int)} \quad \text{-----(2.65)}$$

The distribution function for momenta is given by

$$g(\mathbf{p}) = \left\langle \frac{1}{N} \sum_{i=1}^N \delta(\mathbf{p}_i - \mathbf{p}) \right\rangle \quad \text{-----(2.66)}$$

Note that $g(\mathbf{p}) = \langle \delta(\mathbf{p}_i - \mathbf{p}) \rangle$ (\mathbf{p} is the same for every particle, independent of its label i). We compute the average

$\langle A \rangle = \frac{\text{Tr}(Ae^{-\beta H})}{\text{Tr} e^{-\beta H}}$. Setting $i = 1$, all the integrals other than that over P_1 divide out between numerator and denominator. We then have

$$\begin{aligned}
 g(\mathbf{p}) &= \frac{\int d^3p_1 \delta(\mathbf{p}_1 - \mathbf{p}) e^{-\beta \mathbf{p}_1^2 / 2m}}{\int d^3p_1 e^{-\beta \mathbf{p}_1^2 / 2m}} \\
 &= (2\pi m k_B T)^{-3/2} e^{-\beta \mathbf{p}^2 / 2m} \quad \text{-----(2.67)}
 \end{aligned}$$

The note commonly refer to the velocity distribution $f(\mathbf{v})$, which is related to $g(\mathbf{p})$ by

$$f(\mathbf{v}) d^3v = g(\mathbf{p}) d^3p \quad \text{-----(2.68)}$$

Hence

$$f(\mathbf{v}) = \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-m\mathbf{v}^2 / 2k_B T} \quad \text{----- (2.69)}$$

This is known as the Maxwell velocity distribution. Note that the distributions are normalized, viz.

$$\int d^3p g(\mathbf{p}) = \int d^3v f(\mathbf{v}) = 1 \quad \text{----- (2.70)}$$

If we are only interested in averaging functions of $v = |\mathbf{v}|$ which are isotropic, then we can define the Maxwell speed distribution, $\tilde{f}(v)$, as

$$\tilde{f}(v) = 4\pi v^2 f(\mathbf{v}) = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} v^2 e^{-mv^2 / 2k_B T} \quad \text{----- (2.71)}$$

Note that $\tilde{f}(v)$, is normalized according to

$$\int_0^\infty dv \tilde{f}(v) = 1 \quad \text{----- (2.72)}$$

It is convenient to represent v in units of $v_o = \sqrt{\frac{k_B T}{m}}$, in which case

$$\tilde{f}(v) = \frac{1}{v_0} \varphi(v/v_0) \quad , \quad \varphi(s) = \sqrt{\frac{2}{\pi}} s^2 e^{-s^2/2} \quad \text{----- (2.73)}$$

The distribution $\phi(s)$ is shown in fig. below. Computing averages, we have

$$C_k \equiv \langle s^k \rangle = \int_0^{\infty} ds s^k \varphi(s) = 2^{k/2} \cdot \frac{2}{\sqrt{\pi}} \Gamma\left(\frac{3}{2} + \frac{k}{2}\right) \quad \text{----- (2.74)}$$

Thus, $C_0 = 1$, $C_1 = \sqrt{\frac{8}{\pi}}$, $C_2 = 3$, etc. The speed averages are

$$\langle v^k \rangle = C_k \left(\frac{k_B T}{m} \right)^{k/2} \quad \text{----- (2.75)}$$

Note that the average velocity is $\langle v \rangle = 0$ but the average speed is $\langle v \rangle = \sqrt{\frac{8k_B T}{\pi m}}$.

The speed distribution is plotted as follows

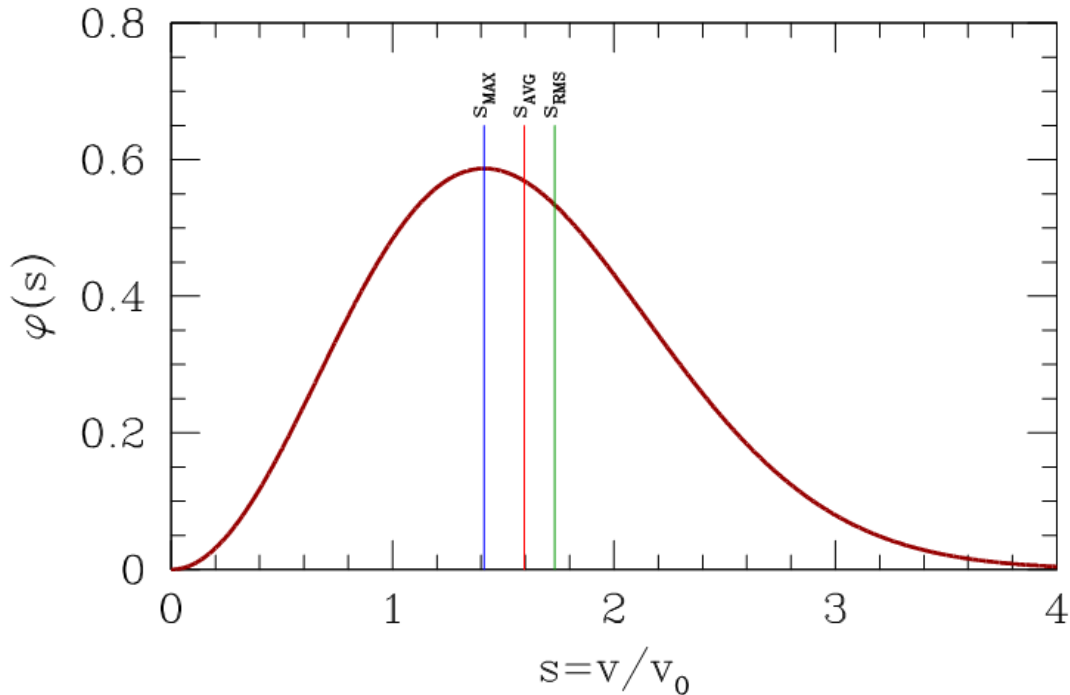


Figure 2.1: Maxwell distribution of speeds

The root mean square speed is given as:

$$v_{\text{rms}} \equiv \sqrt{\overline{v^2}} = \sqrt{\frac{3kT}{m}} \text{-----(2.76)}$$

2.10) Related velocity distribution

Consider the most probable maximum velocity \hat{v} is given as:

$$\begin{aligned} \frac{dF}{dv} &= 0 \\ 2v e^{-mv^2/2kT} + v^2 \left(-\frac{m}{kT} v \right) e^{-mv^2/2kT} &= 0 \\ v^2 &= \frac{2kT}{m} \end{aligned} \text{----- (2.77)}$$

Hence \hat{v} is obtained as

$$\hat{v} = \sqrt{\frac{2kT}{m}} \text{----- (2.78)}$$

All these various speeds are proportional to $(\frac{kT}{m})^{-1/2}$. Thus the molecular speed increases when the temperature is raised.

2.11 Number of molecule striking a surface

Consider that the container is a box in the form of parallelepiped, the area of one end wall being A . How many molecules per unit time strike this end wall? Suppose that there are n molecules per unit volume in this gas. Since they move in random direction, assume one third of them ($\frac{n}{3}$) molecules per unit volume. Half of these molecules, i.e., $\frac{n}{6}$ molecules per unit volume, have velocity in the $+z$ -direction so that they will strike the end wall under consideration. If the mean speed of the molecules is \bar{v} , these molecules cover in an infinitesimal time dt a mean distance $\bar{v}dt$. Thus the number of molecules which strike the end wall of area A in time dt is equal to the number of molecules having velocity \bar{v} , in the z -direction and contained in the cylinder of volume $A \bar{v}dt$. It is given by:

$$\Phi_o = \frac{n}{6} A \bar{v} dt \quad \text{----- (2.79)}$$

The total number Φ_o of molecules which strike unit area of the wall per unit time (i.e, the total molecular flux) is give as:

$$\Phi_o = \frac{1}{6} n \bar{v}$$

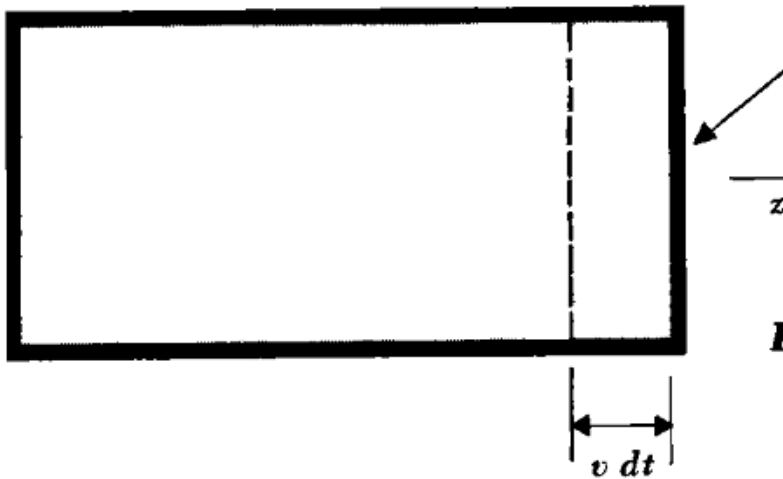


Figure 2.2 molecules colliding with walls

The dependence of Φ_o on the temperature T and mean pressure \bar{p} of the gas follows immediately :

$$\bar{p} = nkT \quad \text{or} \quad n = \frac{\bar{p}}{kT} \quad \text{-----} \quad (2.80)$$

Furthermore, by the equipartition theorem:

$$\begin{aligned} \frac{1}{2}m\bar{v}^2 &= \frac{3}{2}kT \\ \bar{v} \propto \bar{v}_{\text{rms}} &\propto \sqrt{\frac{kT}{m}} \quad \text{-----} \quad (2.81) \end{aligned}$$

Thus the above equation implies that :

$$\Phi_0 \propto \frac{\bar{p}}{\sqrt{mT}} \quad \text{-----} \quad (2.82)$$

The volume of this cylinder is $dA v dt \cos \theta$, while the number of molecules per unit volume in the velocity range is $f(\mathbf{v})d^3v$. Hence the number of molecules of this type which strike the area dA of the wall in time dt is equal to $[f(\mathbf{v})d^3v][dA v dt \cos \theta]$

Where $\Phi(\mathbf{v})d^3v \equiv$ the number of molecules, with velocity b/n v and $v + dv$, which strike a unit area of the wall per unit time.

$$\Phi(\mathbf{v}) d^3v = d^3v f(\mathbf{v})v \cos \theta \quad \text{-----} \quad (2.83)$$

In other words, we have to sum over all possible velocities v to the restriction that velocity component $v_z v \cos \theta > 0$, since molecules with $v_z < 0$ will not collide with the element of area.

$$\Phi_0 = \int_{v_z > 0} d^3v f(\mathbf{v})v \cos \theta \quad \text{-----} \quad (2.84)$$

After we goes further, the equation becomes

$$\Phi_0 = \frac{\bar{p}}{\sqrt{2\pi mkT}} \quad \text{-----} \quad (2.85)$$

2.12 Effusions

Consider a small hole or slit is made in the wall of container, the equilibrium of the gas inside the container is disturbed to a negligible extent. In the case the number of molecule which emerges through the small hole is the same as the number of molecules which strike the area occupied by the hole if the latter were closed off. The process whereby molecules emerge through such a small hole is called effusion.

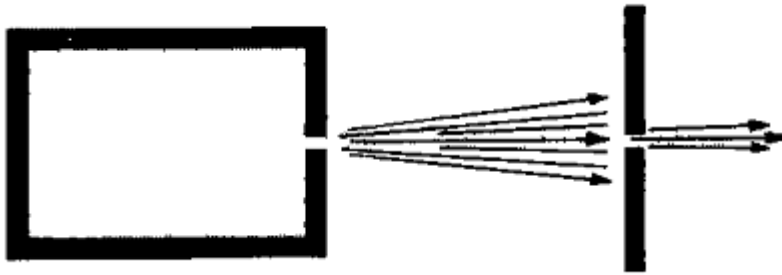


Figure 2.3 shows that formation of a molecular beam by effusing molecules.

The number of molecules which have speed in the range v and $v + dv$ and which emerge per second from a small area A into a solid angle range $d\Omega$ in the forward direction $\theta \approx 0$ is given as:

$$A\Phi(\mathbf{v}) d^3\mathbf{v} \propto A[f(v)v \cos \theta](v^2 dv d\Omega) \\ \propto f(v)v^3 dv d\Omega \propto e^{-mv^2/2kT}v^3 dv d\Omega \quad \text{----- (2.86)}$$

The number of molecules which pass per second through the hole from left to right equals the number of molecules which pass per second through the hole from right to left. This leads to the simple equality:

$$n_1\bar{v}_1 = n_2\bar{v}_2 \quad \text{----- (2.87)}$$

2.13 Pressure and momentum

We from a detailed kinetic point of view how a gas exerts a pressure. The mean force exerted on the wall of the container is due to collision of molecules with the wall. If there are a collision b/n the molecules, there will be a change of momentum.

Let denote by $G^{(+)}$ the mean molecular momentum crossing this surface dA per unit time from left to right, and by $G^{(-)}$ the mean molecular momentum crossing this surface dA per unit time from right to left.

$$\mathbf{F} = \mathbf{G}^{(+)} - \mathbf{G}^{(-)} \text{-----} (2.88)$$

Where $F = \frac{dp}{dt}$

$$\begin{aligned} \mathbf{G}^{(+)} &= \int_{v_z > 0} f(\mathbf{v}) d^3\mathbf{v} |dA v \cos \theta| (m\mathbf{v}) \text{-----} \\ \mathbf{G}^{(+)} &= dA \int_{v_z > 0} d^3\mathbf{v} f(\mathbf{v}) |v_z| (m\mathbf{v}) \end{aligned} \quad (2.89)$$

And

$$\mathbf{G}^{(-)} = dA \int_{v_z < 0} d^3\mathbf{v} f(\mathbf{v}) |v_z| (m\mathbf{v}) \text{-----} (2.90)$$

Then

$$\mathbf{F} = \mathbf{G}^{(+)} - \mathbf{G}^{(-)} = dA \int_{v_z > 0} d^3\mathbf{v} f(\mathbf{v}) v_z (m\mathbf{v}) + dA \int_{v_z < 0} d^3\mathbf{v} f(\mathbf{v}) v_z (m\mathbf{v}) \text{-----} (2.91)$$

Chapter Three

Quantum Statistics of Ideal Gases

3.1 Isolated systems: micro canonical ensembles

In statistical mechanics, there are three basic types of ensembles.

- i. Micro canonical ensemble
- ii. Canonical ensemble
- iii. Grand canonical ensemble

The micro canonical ensemble

An isolated system is both thermally insulated and mechanically undisturbed. According to the first law of thermodynamics, the internal energy of such a system is constant. We define the following ensemble to describe isolated systems:

A micro canonical ensemble is an ensemble of fixed E, V and N

The basic postulate of statistical mechanics says that every microstate of an ensemble of isolated systems occurs with equal probability. Thus, if the ensemble has W different microstates, the probability that any particular member of the ensemble is in a particular microstate is

$$P_i = \frac{1}{W} \text{-----(3.1)}$$

since the sum of all the probabilities have to add to 1 and they all must be equal. Another way to think about this equation is that the micro canonical partition function is just W .

The entropy of a micro canonical ensemble is calculated using the Boltzmann equation:

$$S = k \ln W \text{----- (3.2)}$$

3.2 System at mixed temperature

Temperature can be defined for a micro canonical ensemble using equation $T^{-1} = \left(\frac{dS}{dE}\right)_{V,N}$ To apply this equation, we first note that the number of microstates available to the system depends on the energy, so $W = W(E)$. This means that S depends on E. We can therefore write

$$T = \left[\left(\frac{dS(E)}{dE} \right)_{V,N} \right]^{-1} = \left[\left(k \frac{d \ln W(E)}{dE} \right)_{V,N} \right]^{-1} \quad \text{-----(3.3)}$$

Assume we have T; we can define other quantities that depend on it, like the Helmholtz free energy:

$$F = E - T S = E - kT \ln W \quad \text{----- (3.4)}$$

Canonical ensemble - is used to describe system in contact with a heat reservoir. The total number of particles are constant.

3.3 Grand canonical ensembles

Both the micro canonical and canonical ensembles deal with systems with a fixed number of particles N (or, in general, fixed values of the numbers of particles of each type, N_1, N_2, \dots). However, the number of molecules of a given type in a chemical system at equilibrium is not generally fixed. Due to chemical reactions, the number of molecules of each type fluctuates with time.

A grand canonical ensemble is an ensemble of fixed T, V, and μ . Suppose that the energies of the two subsystems are E_1 and E_2 , and that the numbers of molecules in each subsystem are N_1 and N_2 . Since the system is isolated, the total energy and number of molecules are conserved: $E = E_1 + E_2$ and $N = N_1 + N_2$

Note:

- i. micro-canonical ensemble have constant N, V, E number of particles, volume, and energy
- ii. canonical ensemble have constant N, V, T number of particles, volume, temperature
- iii. grand-canonical ensemble have constant μ , V, T chemical potential, volume, temperature

3.4 Identical Particles & Symmetry Requirements

Consider a system of gas consisting of N identical particle enclosed in a container of volume V. suppose the collective coordinates of the i^{th} particle is represented by Q_i and its quantum state by S_i . The state of the system of gas is then described by the set of quantum number

$$\{S_1, S_2 \dots S_N\} \text{ -----(3.5)}$$

The system of gas in this state can be described by the following wave function

$$\Psi = \Psi_{[S_1 \dots S_N]}(Q_1 \dots Q_N) \text{ -----(3.6)}$$

If the particles are distinguishable and any number of particles are allowed to be in the same state S, then the particles are said to Obey **Maxwell-Boltzmann statistics**. This is called classical description of a system and it doesn't impose symmetry requirements on the wave function when two particles are interchanged.

However, the quantum mechanical description, where identical particles are considered to be indistinguishable imposes symmetry requirements on the wave function during interchanging two particles, i-e. Interchanging two identical particles doesn't lead the whole system to a new state.

Each particle in the system has integral spin, and then the wave function of the system Ψ must be symmetric under interchanging two particles.

$$\Psi(\dots Q_i \dots Q_j \dots) = \Psi(\dots Q_j \dots Q_i \dots) \text{ ----- (3.7)}$$

Particles satisfying this symmetry condition are said to obey Bose- Einstein statistics and they are called bosons.

On the other hand if each particle in the system has half integral spin, then the wave function of the system satisfy anti symmetric condition during interchanging two particles.

$$\Psi(\dots Q_i \dots Q_j \dots) = -\Psi(\dots Q_j \dots Q_i \dots) \text{ ----- (3.8)}$$

Particles satisfying this anti symmetric condition are said to obey Fermi- Dirac Statistics & they are called fermions.

If two particles, Say i & j of the same state S are interchanged, the wave function of the system should remain the same. At the same time, if the particles have half-integral spin condition (4) must be satisfied. This leads to the conclusion that for a system containing two particles in the

same state the wave function should vanish. $\Psi \equiv 0$

Thus in the Fermi-Dirac Case there exists no state of the whole gas for which two or more particles are in the same single particle state. This is called **Pauli exclusion principle**.

3.5 Formulation of the statistical problem

Consider a system of gas consisting of N weakly interacting identical particles enclosed in a container of volume V. Suppose the system is in equilibrium at temperature T. Let n_r particles are in state r characterized by energy E_r .

The energy of the whole system which is supposed to be in state R is then given by

$$E_R = n_1 E_1 + n_2 E_2 + \dots = \sum_r n_r E_r \text{-----(3.9)}$$

The partition function of the system can be given by

$$Z = \sum_R e^{-\beta E_R} = \sum_R e^{-\beta(n_1 E_1 + n_2 E_2 + \dots)} \text{-----(3.10)}$$

The mean number of particles in a particular state r is then

$$\bar{n}_r = \frac{\sum n_r e^{-\beta(n_1 E_1 + n_2 E_2 + \dots)}}{\sum_R e^{-\beta(n_1 E_1 + n_2 E_2 + \dots)}} = \frac{1}{Z} \sum_R - \frac{1}{\beta} \frac{\partial}{\partial E_r} e^{-\beta(n_1 E_1 + n_2 E_2 + \dots)}$$

$$= \frac{1}{Z} \left(-\frac{1}{\beta}\right) \frac{\partial}{\partial E_r} \sum_R e^{-\beta(n_1 E_1 + n_2 E_2 + \dots)}$$

$$= - \frac{1}{\beta} \frac{1}{Z} \frac{\partial \ln Z}{\partial E_r} \text{-----(3.11)}$$

$$\overline{n_r^2} = \frac{\sum_R n_r^2 e^{-\beta(n_1 E_1 + n_2 E_2 + \dots)}}{\sum_R e^{-\beta(n_1 E_1 + n_2 E_2 + \dots)}} = \frac{1}{Z} \left(-\frac{1}{\beta} \frac{\partial}{\partial E_r}\right) \left(-\frac{1}{\beta} \frac{\partial}{\partial E_r}\right) \sum_R e^{-\beta(n_1 E_1 + \dots)}$$

$$= \frac{1}{\beta^2} \frac{1}{Z} \frac{\partial^2 Z}{\partial E_r^2} = \frac{1}{\beta^2} \left[\frac{\partial}{\partial E_r} \left(\frac{1}{Z} \frac{\partial Z}{\partial E_r} \right) + \frac{1}{Z^2} \left(\frac{\partial}{\partial E_r} \right)^2 \right]$$

$$\begin{aligned}
n_r^2 &= \frac{1}{\beta^2} \left[\frac{\partial}{\partial E_r} \frac{\partial \ln Z}{\partial E_r} + \left(\frac{1}{Z} \frac{\partial Z}{\partial E_r} \right)^2 \right] \\
&= \frac{1}{\beta^2} \left[\frac{\partial}{\partial E_r} \frac{\partial \ln Z}{\partial E_r} + \beta^2 n_r^{-2} \right] \\
&= \frac{1}{\beta^2} \frac{\partial^2 \ln Z}{\partial E_r^2} + n_r^{-2} \quad \text{-----(3.12)}
\end{aligned}$$

$$\triangleright \overline{(\Delta n_r)^2} = \overline{(n_r - \bar{n}_r)^2} = \overline{n_r^2} - \bar{n}_r^2 = \frac{1}{\beta^2} \frac{\partial^2 \ln Z}{\partial E_r^2} \quad \text{-----(3.13)}$$

If the particles under consideration obey Maxwell-Boltzmann statistics, partition function of the system can be obtained by eqn.(6) after summing over all possible values of n_r ($n_r=0,1,2,3\dots$) for each r provided that total no. of particles in the system is constant $\sum_r n_r = N$.

Since the particles are considered to be distinguishable, in addition to specifying the no of particles in each state, it is necessary to specify which particular particles are in which state.

In the case of Bose-Einstein statistics, the summation in equation (3.10) should be taken over all possible values of n_r for each r , and the total number of particles must be fixed. However, since the particles are considered to be indistinguishable, specifying the number of particles in each state is sufficient. A special case of Bose-Einstein statistics where total number of particles in the system is not constant, i.e, where the restriction in eq.(3.14) is lifted, is called photon statistics.

Two possible values of n_r ($n_r =0,1$) for each r , since more than one particle on particular state is not allowed, and total number of the particles must be fixed.

3.6 The quantum distribution functions

Consider a system of gas containing N particles. Let the lowest energy level of a single particle is denoted by ϵ_0 . For a system of particles that obeys BE statistics, where there is no restriction on the number of particles in any state, the lowest energy level of the whole system can be obtained by placing all the particles in the lowest energy level, and hence for the lowest energy level of the whole system we can write $E_0=N\epsilon_0$

In the case of FD statistics however, where we are not allowed to have more than one particle in any state, the lowest energy level of the whole system can only be obtained by placing one particle in each consecutive state of increasing energy starting from the lowest energy level ϵ_0 . For a system maintained at absolute temperature T, the mean number of particles in a particular state s is

$$\bar{n}_s = \frac{\sum_{n_s} n_s e^{-\beta n_s \epsilon_s} \sum_{n_1, n_2, \dots}^{(s)} e^{-\beta (n_1 \epsilon_1 + n_2 \epsilon_2 + \dots)}}{\sum_{n_s} e^{-\beta n_s \epsilon_s} \sum_{n_1, n_2, \dots}^{(s)} e^{-\beta (n_1 \epsilon_1 + n_2 \epsilon_2 + \dots)}} \quad \text{-----}(3.14)$$

Photon statistics: The summation in eq.(3.14) should be over all possible values of n_s for each s. Since there is no restriction on the total number of particles, the sums in the numerator & denominator of eq.(3.14) are the same. Hence we can write

$$\bar{n}_s = \frac{\sum_{n_s} n_s e^{-\beta n_s \epsilon_s}}{\sum_{n_s} e^{-\beta n_s \epsilon_s}} \quad \text{-----} (3.15)$$

However, the above expression can be rewritten

$$\bar{n}_s = -\frac{1}{\beta} \frac{\partial}{\partial \epsilon_s} \left(\ln \sum_{n_s} e^{-\beta n_s \epsilon_s} \right) \quad \text{-----} (3.16)$$

Now, the sum on the right-hand side of the above equation is an infinite geometric series, which can easily be evaluated. In fact,

$$\sum_{n_s=0}^{\infty} e^{-\beta n_s \epsilon_s} = 1 + e^{-\beta \epsilon_s} + e^{-2\beta \epsilon_s} + \dots = \frac{1}{1 - e^{-\beta \epsilon_s}} \quad \text{-----} (3.17)$$

Thus, eq.(3.17) gives

$$\bar{n}_s = \frac{1}{\beta} \frac{\partial}{\partial \epsilon_s} \ln(1 - e^{-\beta \epsilon_s}) = \frac{e^{-\beta \epsilon_s}}{1 - e^{-\beta \epsilon_s}} \quad \text{-----(3.18)}$$

Which is called Planck distribution.

Fermi-Dirac (FD) statistics: In this case n_r have only two values, $n_r=0, 1$ for each r and there is restriction on the total number of particles where it supposed to be fixed $\sum_r n_r=N$.

Let us introduce the function

$$Z_s(N) = \sum_{n_1, n_2, \dots}^{(s)} e^{-\beta(n_1 \epsilon_1 + n_2 \epsilon_2 + \dots)} \quad \text{----- (3.19)}$$

Which is defined as the partition function for N particles distributed over all quantum states, excluding state s , according to Fermi-Dirac statistics. By explicitly performing the sum over $n_s = 0$ and 1 , the expression (3.14) reduces to

$$\bar{n}_s = \frac{0 + e^{-\beta \epsilon_s} Z_s(N-1)}{Z_s(N) + e^{-\beta \epsilon_s} Z_s(N-1)} \quad \text{----- (3.20)}$$

Which yields

$$\bar{n}_s = \frac{1}{[Z_s(N)/Z_s(N-1)] e^{\beta \epsilon_s} + 1} \quad \text{----- (3.21)}$$

In order to make further progress, we must somehow relate $Z_s(N-1)$ to $Z_s(N)$.

Suppose that $\Delta N \ll N$. It follows that $\ln Z_s(N - \Delta N)$ can be Taylor expanded to give

$$\ln Z_s(N - \Delta N) \simeq \ln Z_s(N) - \frac{\partial \ln Z_s}{\partial N} \Delta N = \ln Z_s(N) - \alpha_s \Delta N \quad \text{----- (3.22)}$$

Where

$$\alpha_s \equiv \frac{\partial \ln Z_s}{\partial N} \quad \text{----- (3.23)}$$

Taylor expand the slowly varying function in $Z_s(N)$, rather than the rapidly varying function $Z_s(N)$, because the radius of convergence of the latter Taylor series is too small for the series to be of any practical use. Equation (3.22) can be rearranged to give

$$Z_s(N - \Delta N) = Z_s(N) e^{-\alpha_s \Delta N}. \quad \text{-----(3.24)}$$

Since $Z_s(N)$ is a sum over very many different quantum states, we would not expect the logarithm of this function to be sensitive to which particular state s is excluded from consideration. Let us, introduce the approximation that α_s is independent of s , so that we can write

$$\alpha_s \simeq \alpha \quad \text{----- (3.25)}$$

For all s , it follows that the derivative (3.23) can be expressed approximately in terms of the derivative of the full partition function $Z(N)$ (in which the N particles are distributed over all quantum states). In fact,

$$\alpha \simeq \frac{\partial \ln Z}{\partial N} \quad \text{----- (3.26)}$$

Making use of Eq. (3.24), with $\Delta N = 1$, plus the approximation (3.25), the expression (3.21) reduces to

$$\bar{n}_s = \frac{1}{e^{\alpha + \beta \epsilon_s} + 1} \quad \text{----- (3.27)}$$

This is called the Fermi-Dirac distribution. The parameter α is determined by the constraint that $\sum_r \bar{n}_r = N$: i.e.,

$$\sum_r \frac{1}{e^{\alpha + \beta \epsilon_r} + 1} = N. \quad \text{----- (3.28)}$$

Note that $\bar{n}_s \rightarrow 0$ if ϵ_s becomes sufficiently large. On the other hand, since the denominator in Eq. (3.27) can never become less than unity, no matter how small ϵ_s becomes, it follows that $\bar{n}_s \leq 1$. Thus,

$$0 \leq \bar{n}_s \leq 1 \quad \text{----- (3.29)}$$

in accordance with the Pauli exclusion principle.

Bose-Einstein statistics: The summation in eq.(3.14) is rang over all possible values of $n_r, (n_r=0,1,2,3, \dots)$, for each r and the total number of particles is restricted to be constant. Applying the concept of eq.(3.6) in eq.3.14) we can write

$$\bar{n}_s = \frac{0 + e^{-\beta \epsilon_s} Z_s(N-1) + 2 e^{-2\beta \epsilon_s} Z_s(N-2) + \dots}{Z_s(N) + e^{-\beta \epsilon_s} Z_s(N-1) + e^{-2\beta \epsilon_s} Z_s(N-2) + \dots} \quad \text{----- (3.30)}$$

Where $Z_s(N)$ is the partition function for N particles distributed over all quantum states, excluding state s, according to Bose-Einstein statistics [cf., Eq. (3.19)]. Using Eq. (3.24), and the approximation (3.25), the above equation reduces to

$$\bar{n}_s = \frac{\sum_s n_s e^{-n_s (\alpha + \beta \epsilon_s)}}{\sum_s e^{-n_s (\alpha + \beta \epsilon_s)}} \quad \text{----- (3.31)}$$

Note that this expression is identical to (3.15), except that $\beta \epsilon_s$ is replaced by $\alpha + \beta \epsilon_s$. Hence, an analogous calculation to that outlined in the previous subsection yields

$$\bar{n}_s = \frac{1}{e^{\alpha + \beta \epsilon_s} - 1} \quad \text{----- (3.32)}$$

This is called the Bose-Einstein distribution.

3.7 Maxwell-Boltzmann statistics

MB statistics- is a classical approach. The partition function is

$$Z = \sum_R e^{-\beta (n_1 \epsilon_1 + n_2 \epsilon_2 + \dots)} \quad \text{----- (3.33)}$$

Where the sum is over all distinct states R of the gas, and the particles are treated as distinguishable. For given values of n_1, n_2, \dots there are the number of possible ways of placing particles in the given states becomes $\frac{N!}{n_1! n_2! n_3! \dots}$

In these arrangements yields distinct state for the system. Hence partition function of the system becomes

$$Z = \sum_{n_1, n_2, \dots} \frac{N!}{n_1! n_2! \dots} e^{-\beta (n_1 \epsilon_1 + n_2 \epsilon_2 + \dots)} \quad \text{----- (3.34)}$$

Where the sum is over all values of $n_r = 0, 1, 2, \dots$ for each r, subject to the constraint that

$$\sum_r n_r = N. \quad \text{----- (3.35)}$$

Now, Eq. (3.34) can be written

$$Z = \sum_{n_1, n_2, \dots} \frac{N!}{n_1! n_2! \dots} (e^{-\beta \epsilon_1})^{n_1} (e^{-\beta \epsilon_2})^{n_2} \dots \quad \text{----- (3.36)}$$

Eq. (3.35) is by the result of expanding a polynomial it can be written as.

$$Z = (e^{-\beta \epsilon_1} + e^{-\beta \epsilon_2} + \dots)^N \quad \text{----- (3.37)}$$

In other word

$$\ln Z = N \ln \left(\sum_r e^{-\beta \epsilon_r} \right) \quad \text{----- (3.38)}$$

Note that the argument of the logarithm is simply the partition function for a single particle.

Equations (3.18) and (3.38) can be combined to give

$$\bar{n}_s = N \frac{e^{-\beta \epsilon_s}}{\sum_r e^{-\beta \epsilon_r}} \quad \text{----- (3.39)}$$

This is known as the Maxwell-Boltzmann distribution.

3.8 Photon statistics

We have the following relation for the partition function $Z = \sum_R e^{-\beta(n_1 \epsilon_1 + n_1 \epsilon_2 + \dots)}$

Where the summation is over all the possible state R of the whole system, or equivalently over all values of $n_r = 0, 1, 2, \dots$ for each r. We know that $\bar{n}_s = -\frac{1}{\beta} \frac{d \ln Z}{d \epsilon_s}$

$$Z = \sum_{n_1 n_2} e^{-\beta n_1 \epsilon_1} e^{-\beta n_2 \epsilon_2}$$

$$= \sum_{n_1} e^{-\beta n_1 \epsilon_1} \sum_{n_2} e^{-\beta n_2 \epsilon_2} \dots$$

$$= \left(\frac{1}{1 - e^{-\beta \epsilon_1}} \right) \left(\frac{1}{1 - e^{-\beta \epsilon_2}} \right) \dots$$

$$\Rightarrow \ln Z = \ln \sum_r \frac{1}{1 - e^{-\beta \epsilon_r}} = -\sum_r \ln(1 - e^{-\beta \epsilon_r}) \quad \text{----- (3.40)}$$

The mean number of particles in a particular state r with the corresponding energy ϵ_r

Is given by

$$\bar{n}_r = -\frac{1}{\beta} \frac{d \ln Z}{d \epsilon_r} = \frac{1}{\beta} \frac{d}{d \epsilon_r} \sum_r \ln(1 - e^{-\beta \epsilon_r}) = \frac{1}{e^{\beta \epsilon_r} - 1} \quad \text{----- (3.41)}$$

3.9 Bose-Einstein statistics

Let us now consider Bose-Einstein statistics. The particles in the system are assumed to be massive, so the total number of particles N is a fixed number. Consider the expression (3.14). For the case of massive bosons, the numbers n_1, n_2, \dots assume all values $= n_r = 0, 1, 2, \dots$ for each

r, subject to the constraint that $\sum_r n_r = N$. Performing explicitly the sum over n_s , this expression reduces to

$$\bar{n}_s = \frac{0 + e^{-\beta \epsilon_s} Z_s(N-1) + 2e^{-2\beta \epsilon_s} Z_s(N-2) + \dots}{Z_s(N) + e^{-\beta \epsilon_s} Z_s(N-1) + e^{-2\beta \epsilon_s} Z_s(N-2) + \dots} \quad \text{-----(3.42)}$$

Where $Z_s(N)$ is the partition function for N particles distributed over all quantum states, excluding state s , according to Bose-Einstein statistics

Let $Z = Z(N)$, for a system N' particles the partition function is $Z(N')$. This function is rapidly increasing function of N' , and hence multiplying it by rapidly decreasing function $e^{-\alpha N'}$ produces a function $Z(N')e^{-\alpha N'}$ which usually has a very sharp maximum. The proper choice of the positive parameter α will make the sharp maximum to occur at $N' = N$. Thus we can write

$$\sum_{N'} Z(N')e^{-\alpha N'} = Z(N)e^{-\alpha N} \Delta^* N' \quad \text{----- (3.43)}$$

Where $Z(N)e^{-\alpha N}$ is the maximum value of the summand while $\Delta^* N' \ll N$ is the width of the maximum.

$$\mathcal{Z} \equiv \sum_{N'} Z(N')e^{-\alpha N'} \quad \text{-----(3.44)}$$

Taking the logarithm of eq.(3.44), then, obtain an excellent approximation

$$\ln Z(N) = \alpha N + \ln \mathcal{Z} \quad \text{----- (3.45)}$$

Where we have neglected the term $\ln(\Delta^*)$ which is utterly negligible compared to the other terms which are of order N . Here the sum eq.(3.44) is easily performed, since it extends over all possible numbers without any restriction. The quantity \mathcal{Z} is called a grand partition function.

Now let evaluate \mathcal{Z}

$$\mathcal{Z} = \sum_R e^{-\beta(n_1 \epsilon_1 + n_2 \epsilon_2 + \dots)} e^{-\alpha(n_1 + n_2 + \dots)} \quad \text{----- (3.46)}$$

Where the sum is over all possible numbers without restriction. By regrouping terms one obtains.

$$\begin{aligned} \mathcal{Z} &= \sum_{n_1, n_2, \dots} e^{-(\alpha + \beta \epsilon_1) n_1 - (\alpha + \beta \epsilon_2) n_2 - \dots} \\ &= \left(\sum_{n_1=0}^{\infty} e^{-(\alpha + \beta \epsilon_1) n_1} \right) \left(\sum_{n_2=0}^{\infty} e^{-(\alpha + \beta \epsilon_2) n_2} \right) \end{aligned} \quad \text{----- (3.47)}$$

This is just a product of simple geometric series. Hence

$$\begin{aligned} \mathcal{Z} &= \left(\frac{1}{1 - e^{-(\alpha + \beta \epsilon_1)}} \right) \left(\frac{1}{1 - e^{-(\alpha + \beta \epsilon_2)}} \right) \\ \ln \mathcal{Z} &= - \sum_r \ln (1 - e^{-\alpha - \beta \epsilon_r}) \end{aligned} \quad \text{----- (3.48)}$$

The eq.(3.44) yields

$$\ln Z = \alpha N - \sum_r \ln (1 - e^{-\alpha - \beta \epsilon_r}) \quad \text{----- (3.49)}$$

Our argument assumed that the parameter α is to be chosen so that the function $Z(N')e^{-\alpha N'}$ has its maximum for $N'=N$, i.e, so that

$$\frac{\partial}{\partial N'} [\ln Z(N') - \alpha N'] = \frac{\partial \ln Z(N)}{\partial N} - \alpha = 0 \quad \text{----- (3.50)}$$

Since this condition involves the particular value $N'=N$, α itself must be a function of N . By the virtue of eq.(3.45), the condition eq.(3.50) is equivalent to

$$\begin{aligned} \left[\alpha + \left(N + \frac{\partial \ln \mathcal{Z}}{\partial \alpha} \right) \frac{\partial \alpha}{\partial N} \right] - \alpha &= 0 \\ N + \frac{\partial \ln \mathcal{Z}}{\partial \alpha} &= \frac{\partial \ln Z}{\partial \alpha} = 0 \end{aligned} \quad \text{----- (3.51)}$$

Using the expression of eq.(3.48), the relation of eq.(3.51) which determines α then

$$N - \sum_r \frac{e^{-\alpha-\beta\epsilon_r}}{1 - e^{-\alpha-\beta\epsilon_r}} = 0$$

$$\sum_r \frac{1}{e^{\alpha+\beta\epsilon_r} - 1} = N \quad \text{----- (3.52)}$$

By applying eq.(3.16) in to eq.(3.49), then obtains

$$\bar{n}_s = -\frac{1}{\beta} \frac{\partial \ln Z}{\partial \epsilon_s} = -\frac{1}{\beta} \left[-\frac{\beta e^{-\alpha-\beta\epsilon_s}}{1 - e^{-\alpha-\beta\epsilon_s}} + \frac{\partial \ln Z}{\partial \alpha} \frac{\partial \alpha}{\partial \epsilon_s} \right] \quad \text{----- (3.53)}$$

The last term takes into account the fact that α is a function of ϵ_s through the relation eq.(3.52). But this term vanishes by virtue of eq.(3.51). Hence it has simplify

$$\sum_r \bar{n}_r = N \quad \text{----- (3.54)}$$

The obvious requirement needed to satisfy the conservation of particles. The chemical potential of the gas is given by

$$\mu = \frac{\partial F}{\partial N} = -kT \frac{\partial \ln Z}{\partial N} = -kT\alpha$$

Then calculation of the dispersion

$$\overline{(\Delta n_s)^2} = -\frac{1}{\beta} \frac{\partial \bar{n}_s}{\partial \epsilon_s} = \frac{1}{\beta} \frac{e^{\alpha+\beta\epsilon_s}}{(e^{\alpha+\beta\epsilon_s} - 1)^2} \left(\frac{\partial \alpha}{\partial \epsilon_s} + \beta \right)$$

$$\frac{e^{\alpha+\beta\epsilon_s}}{(e^{\alpha+\beta\epsilon_s} - 1)^2} = \frac{(e^{\alpha+\beta\epsilon_s} - 1) + 1}{(e^{\alpha+\beta\epsilon_s} - 1)^2} = \bar{n}_s + \bar{n}_s^2$$

$$\overline{(\Delta n_s)^2} = \bar{n}_s(1 + \bar{n}_s) \left(1 + \frac{1}{\beta} \frac{\partial \alpha}{\partial \epsilon_s} \right) \approx \bar{n}_s(1 + \bar{n}_s) \quad \text{----- (3.55)}$$

Hence

$$\frac{\overline{(\Delta n_s)^2}}{\bar{n}_s^2} \approx \frac{1}{\bar{n}_s} + 1 \quad \text{----- (3.56)}$$

Thus the relative dispersion does not become arbitrarily small even when $\bar{n}_s \gg 1$.

3.10 Fermi-Dirac statistics

The partition function is given by

$$\begin{aligned} Z &= \sum_{n_1, n_2, n_3} e^{-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \dots) - \alpha(n_1 + n_2 + \dots)} \\ &= \left(\sum_{n_1=0}^1 e^{-(\alpha + \beta\epsilon_1)n_1} \right) \left(\sum_{n_2=0}^1 e^{-(\alpha + \beta\epsilon_2)n_2} \right) \end{aligned} \quad \text{----- (3.57)}$$

Since the summation is over the two values, then it becomes

$$\begin{aligned} Z &= (1 + e^{-\alpha - \beta\epsilon_1})(1 + e^{-\alpha - \beta\epsilon_2}) \\ \ln Z &= \sum_r \ln(1 + e^{-\alpha - \beta\epsilon_r}) \end{aligned} \quad \text{----- (3.58)}$$

Then

$$\ln Z = \alpha N + \sum_r \ln(1 + e^{-\alpha - \beta\epsilon_r}) \quad \text{----- (3.59) Except some}$$

important sign changes, this expression is the same form with the BE case. The parameter α is again to determined from the condition of eq.(3.49). Thus,

$$\begin{aligned} \frac{\partial \ln Z}{\partial \alpha} &= N - \sum_r \frac{e^{-\alpha - \beta\epsilon_r}}{1 + e^{-\alpha - \beta\epsilon_r}} = 0 \\ \sum_r \frac{1}{e^{\alpha + \beta\epsilon_r} + 1} &= N \end{aligned} \quad \text{----- (3.60)}$$

By using other equation, we can obtain

$$\bar{n}_s = - \frac{1}{\beta} \frac{\partial \ln Z}{\partial \epsilon_s} = \frac{1}{\beta} \frac{\beta e^{-\alpha - \beta\epsilon_s}}{1 + e^{-\alpha - \beta\epsilon_s}} \quad \text{----- (3.61)}$$

This expression simplified as

$$\bar{n}_s = \frac{1}{e^{\alpha + \beta \epsilon_s} + 1} \text{-----} (3.62)$$

3.10 Quantum statistics in the classical limit

The quantum statistics description of a system of ideal gas can be summarized by

$$\bar{n}_r = \frac{1}{e^{2 + \beta \epsilon_{r \pm 1}}} \text{-----} (3.63)$$

Where the +/- sign in the denominator represents FD/BE statistics & is supposed to be obtained from the relation $\sum_r \bar{n}_r = \sum_r \frac{1}{e^{2 + \beta \epsilon_{r \pm 1}}} = N$ -----(3.64)

Now we want to evaluate α under some limiting cases.

Consider a system of gas where the concentration is sufficient low. This condition (39) can be satisfied only when each term in the sum over all states is sufficiently low, $\bar{n}_r \ll 1$ or $e^{2 + \beta \epsilon_{r \pm 1}} \gg 1$ for all r.

Similarly for a system consisting of fixed number N of particles of the temperature is sufficiently large so that $\beta \epsilon_r \ll \alpha$, the parameter α must be large enough to prevent the sum from exceeding N, then we can have $e^{2 + \beta \epsilon_{r \pm 1}} \gg 1$ or $\bar{n}_r \ll 1$.

Under these conditions equation (38) becomes

$$\bar{n}_r \cong e^{-2 - \beta \epsilon_r} \text{-----} (3.65)$$

Thus the parameter α can be determined from

$$\sum_r e^{-2 - \beta \epsilon_r} = e^{-\alpha} \sum_r e^{-\beta \epsilon_r} = N$$

$$\text{➤ } e^{-\alpha} = N (\sum_r e^{-\beta \epsilon_r})^{-1} \text{-----} (3.66)$$

$$\text{➤ } \bar{n}_r \cong e^{-\alpha} e^{-\beta \epsilon_r} = N \frac{e^{-\beta \epsilon_r}}{\sum_r e^{-\beta \epsilon_r}} \text{-----} (3.67)$$

In the classical limit of sufficiently low concentration or sufficiently high temperature the quantum statistics, FD & BE statistics, reduces to MB statistics

The quantum statistics the partition function satisfy the relation

$$\ln Z = \alpha N \pm \sum_r \ln(1 \pm e^{-\beta \epsilon_r}) \text{-----(3.68)}$$

$$e^{-\alpha} e^{-\beta \epsilon_r} \ll 1$$

for $X \ll 1$

$$\ln(1+x) = x - \frac{x^2}{2!} + \frac{x^3}{3!} \dots]$$

$$\cong x$$

$$\ln Z = \alpha N \pm \sum_r \pm e^{-\alpha} e^{-\beta \epsilon_r}$$

$$\propto N + \sum_r e^{-\beta \epsilon_r}$$

$$\propto N + N \text{-----(3.69)}$$

From Equation (41)

$$-\alpha = \ln N - \ln \sum_r e^{-\beta \epsilon_r}$$

$$\alpha = -\ln N + \ln \sum_r e^{-\beta \epsilon_r}$$

Hence equation (44) becomes

$$\ln Z = N \ln N + N \ln \sum_r e^{-\beta \epsilon_r} + N \text{-----(3.70)}$$

$$= N \ln \sum_r e^{-\beta \epsilon_r} - \ln N \quad ; \ln N = N \ln N - N$$

$$= \ln Z_{MB} - \ln N! \quad ; Z_{MB} = (\sum_r e^{-\beta \epsilon_r})^N$$

$$\triangleright Z = \frac{Z_{MB}}{N!}$$

3.12 Evaluation of Partition Function

Consider a system of monatomic ideal gas. Suppose the system is in the classical limit, i.e., it has sufficiently low concentration or it is at sufficiently high temperature. The partition function of the system is then given by equation (45)

$$\begin{aligned} \ln Z &= N(-\ln N + \ln \sum_r e^{-\beta \epsilon_r} + 1) \\ &= N(-\ln N + \ln \xi + 1) \end{aligned} \quad \text{-----(3.71)}$$

Where $\xi = \sum_r e^{-\beta \epsilon_r}$ and the sum is over all possible states of a single particle. To evaluate this sum we need to know the energy of a single particle corresponding to the possible states.

A system of single non interacting particle of mass M , Position vector \vec{r} & momentum \vec{p} confined in a container of volume V can be described by a wave function $\psi(\vec{r}, t)$ of the plane wave form

$$\Psi(\vec{r}, t) = A e^{i(\vec{k} \cdot \vec{r} - \omega t)} = \Psi(\vec{r}) e^{-i\omega t} \quad \text{----- (3.72)}$$

Which propagates in the direction of the wave vector \vec{k} . The energy of these particles is then given by $\epsilon = \frac{\vec{p}^2}{2m} = \frac{\hbar^2 \vec{k}^2}{2m}$

Where the momentum \vec{p} of the particle given by de-Broglie relation

$$\vec{p} = \hbar \vec{k} \quad \text{-----(3.73)}$$

$$\Rightarrow \epsilon = \frac{\hbar^2}{2m} (k_x^2 + k_y^2 + k_z^2) \quad \text{-----(3.74)}$$

Wave function in eq.(3.72) is assumed to satisfy the periodic boundary condition, provided that dimensions of the container are large enough to the de-Broglie wave length of the particle.

$$\left. \begin{aligned} \Psi(x + L_x, y, z) &= \Psi(x, y, z) \\ \Psi(x, y + L_y, z) &= \Psi(x, y, z) \\ \Psi(x, y + L_y, z + L_z) &= \Psi(x, y, z) \end{aligned} \right\} \quad \text{----- (3.75)}$$

Where L_x , L_y , & L_z are the dimensions of the container.

$$\Psi(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} = e^{i(k_x x + k_y y + k_z z)}$$

(3.76)

Hence to satisfy the periodic boundary condition, eq.(3.75), we must have

$$\left. \begin{aligned} \kappa_x(x + L_x) &= \kappa_x x + 2\pi n_x && (n_x \text{ integral}) \\ \kappa_y &= \frac{2\pi}{L_y} n_y \\ \kappa_z &= \frac{2\pi}{L_z} n_z \end{aligned} \right\}$$

Where n_x , n_y , & n_z are integers

The eq.(3.74) can be rewritten as:

$$\epsilon = \frac{\hbar^2}{2m} (\kappa_x^2 + \kappa_y^2 + \kappa_z^2) = \frac{2\pi^2 \hbar^2}{m} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right) \quad \text{----- (3.77)}$$

$$\mathbf{Z} = \sum_r e^{-\beta \epsilon_r} = \sum_{k_x, k_y, k_z} \exp\left[\frac{\beta \hbar^2}{2m} (k_x^2 + k_y^2 + k_z^2)\right] \quad \text{----- (3.78)}$$

Successive term in a sum in eq.(3.78) correspond to a very small change like $\Delta k_x = \frac{2\pi}{L_x}$, hence a small change b/n k_x & $k_x + dk_x$ contains $\Delta n_x = \frac{L_x}{2\pi} dk_x$ terms which have nearly the same magnitude .

Chapter Four

System of Interacting Particles

4.1. Lattice Vibrations and Normal Modes

Consider a system of solid consisting of N atoms. Let the mass and position vector of the i^{th} particle are denoted by M_i and \vec{r}_i and let the equilibrium position of this atom is \vec{r}_i^0 . Since the atoms can vibrate about their equilibrium position, the kinetic energy of vibration of the system is given by

$$K = \frac{1}{2} \sum_{i=1}^N \sum_{\alpha=1}^3 M_i \dot{r}_{i\alpha}^2 = \frac{1}{2} \sum_{i=1}^N \sum_{\alpha=1}^3 M_i \dot{R}_{i\alpha}^2$$

Where α stands for x., y and z components of vector and $R_{i\alpha}^2 = r_{i\alpha} - r_{i\alpha}^0$ is displacement of the atom from equilibrium position.

If we assume a vibration over a relatively small amplitude, the potential energy $V = V_0$

$$+ \sum_{i\alpha} \left(\frac{\partial v}{\partial r_{i\alpha}} \right)_0 R_{i\alpha} + \frac{1}{2} \sum_{i\alpha, j\gamma} \left(\frac{\partial^2 v}{\partial r_{i\alpha} \partial r_{j\gamma}} \right)_0 R_{i\alpha} R_{j\gamma} + \dots$$

V_0 is the potential energy in the equilibrium configuration of the atoms. At equilibrium V must be minimum, hence we can have $\left(\frac{\partial v}{\partial r_{i\alpha}} \right)_0 = 0$

$$\Rightarrow V \cong V_0 + \frac{1}{2} \sum_{i\alpha, j\gamma} A_{i\alpha, j\gamma} R_{i\alpha} R_{j\gamma}$$

$$\text{Where, } A_{i\alpha, j\gamma} = \left(\frac{\partial^2 v}{\partial r_{i\alpha} \partial r_{j\gamma}} \right)_0$$

The total energy associated with vibrations of the atoms in the is then

$$H = V_0 + \frac{1}{2} \sum_{i\alpha} \dot{R}_{i\alpha}^2 + \frac{1}{2} \sum_{i\alpha, j\gamma} A_{i\alpha, j\gamma} R_{i\alpha} R_{j\gamma}$$

This equation can be simplified by eliminating the cross product terms in the potential energy and this can be done changing the 3N old coordinates $R_{i\alpha}$ to new set of 3N generalized coordinates q_γ by a linear transformation.

$$R_{i\alpha} = \sum_{\gamma=1}^N B_{i\alpha, \gamma} q_\gamma$$

Thus the total energy can be rewritten as

$$H = V_0 + \frac{1}{2} \sum_{r=1}^{3N} (\dot{q}_r^2 + w_r^2 q_r^2)$$

This expression is similar to that of the total energy of 3N independent 1D harmonic oscillators.

The total energy of 1D harmonic oscillator is given by

$$H_r = \frac{1}{2} (\dot{q}_r^2 + w_r^2 q_r^2)$$

The corresponding energies for the possible quantum states of this oscillator are then

$$E_r = (n_r + \frac{1}{2}) \hbar w_r, n_r = 0, 1, 2, 3, \dots$$

The total energy of a system of 3N independent harmonic oscillators, where the state of the whole system specified by $\{n_1, n_2, \dots, n_{3N}\}$, becomes

$$H = V_0 + \sum_{r=1}^{3N} E_r$$

$$E_{n_1 n_2, \dots, n_{3N}} = V_0 + \sum_{r=1}^{3N} (n_r + \frac{1}{2}) \hbar w_r$$

$$E_{n_1 n_2, \dots, n_{3N}} = V_0 + \frac{1}{2} \sum_{r=1}^{3N} \hbar w_r + \sum_{r=1}^{3N} n_r \hbar w_r$$

$$= -N\eta + \sum_{r=1}^{3N} n_r \hbar w_r$$

Where, $-N\eta = V_0 + \frac{1}{2} \sum_{r=1}^{3N} \hbar w_r$ independent of n_r

The partition function of the whole system is then

$$Z = \sum_n e^{-\beta E_n} = \sum_{n_1, n_2, \dots} e^{-\beta E_{n_1, n_2, \dots, n_{3N}}}$$

$$= \sum_{n_1, n_2, \dots} e^{-\beta(-N\eta + n_1 \hbar w_1 + n_2 \hbar w_2 + n_{3N} \hbar w_{3N})}$$

$$= e^{\beta N\eta} \sum_{n_1, n_2, \dots} e^{-\beta(n_1 \hbar w_1 + n_2 \hbar w_2 + n_{3N} \hbar w_{3N})}$$

$$= e^{\beta N\eta} \sum_{n_1=0}^{\infty} e^{-n_1 \beta \hbar w_1} \sum_{n_2=0}^{\infty} e^{-n_2 \beta \hbar w_2}$$

$$= e^{\beta N\eta} \left(\frac{1}{1 - e^{-\beta \hbar w_1}} \right) \dots \left(\frac{1}{1 - e^{-\beta \hbar w_{3N}}} \right)$$

$$\begin{aligned} \Rightarrow \ln Z &= \beta N \eta + \ln \left(\frac{1}{1 - e^{-\beta \hbar W_1}} \right) + \dots + \ln \left(\frac{1}{1 - e^{-\beta \hbar W_{3N}}} \right) \\ &= \beta N \eta - \left(\ln \left(\frac{1}{1 - e^{-\beta \hbar W_1}} \right) + \dots + \ln \left(\frac{1}{1 - e^{-\beta \hbar W_{3N}}} \right) \right) \\ &= \beta N \eta - \sum_{\gamma=1}^{3N} \ln \left(\frac{1}{1 - e^{-\beta \hbar W_{\gamma}}} \right) \end{aligned}$$

Angular frequencies W_{γ} , which also called normal mode frequencies are closely spaced. Hence, if _____ represents the number of normal modes with angular frequency in the range between ω and $\omega + d\omega$ the expression for $\ln Z$ becomes,

$$\ln Z = \beta N \eta - \int_0^{\infty} \ln(1 - e^{-\beta \hbar \omega}) \sigma(\omega) d\omega$$

The mean energy of the system is then

$$\bar{E} = -\frac{\partial \ln Z}{\partial \beta} = -N \eta + \int_0^{\infty} \frac{\hbar \omega e^{-\beta \hbar \omega}}{1 - e^{-\beta \hbar \omega}} \sigma(\omega) d\omega$$

$$= -N \eta + \int_0^{\infty} \frac{\hbar \omega}{e^{-\beta \hbar \omega} - 1} \sigma(\omega) d\omega$$

$$C_V = \left(\frac{\partial \bar{E}}{\partial T} \right)_V = \left(\frac{\partial \bar{E}}{\partial \beta} \right)_V \cdot \left(\frac{\partial \beta}{\partial T} \right)_V$$

$$\frac{\partial \beta}{\partial T} = \frac{\partial}{\partial T} \frac{1}{K_{\beta} T} = -\frac{1}{K_{\beta} T^2} = -\frac{1}{K_{\beta} T} \cdot \frac{1}{T} = -\beta \cdot K_{\beta} \beta = -K_{\beta} \beta^2$$

$$\Rightarrow C_V = -K_{\beta} \beta^2 \left(\frac{\partial \bar{E}}{\partial T} \right)_V$$

$$= -K_{\beta} \beta^2 \left(\frac{\partial}{\partial \beta} \right)_V \left[-N \eta + \int_0^{\infty} \frac{\hbar \omega}{e^{-\beta \hbar \omega} - 1} \sigma(\omega) d\omega \right]$$

$$= + K_{\beta} \beta^2 \int_0^{\infty} \frac{(\hbar \omega)^2 e^{\beta \hbar \omega}}{(e^{\beta \hbar \omega} - 1)^2} \sigma(\omega) d\omega$$

$$\text{If } \beta \hbar \omega \ll 1; e^{\beta \hbar \omega} = 1 + \beta \hbar \omega + \frac{(\beta \hbar \omega)^2}{2!} + \dots$$

$$= 1 + \beta \hbar \omega$$

$$\Rightarrow C_V = -K_{\beta} \beta^2 \int_0^{\infty} \frac{(\hbar \omega)^2 (1 + \beta \hbar \omega)}{(1 + \beta \hbar \omega - 1)^2} \sigma(\omega) d\omega$$

$$= K_{\beta} \int_0^{\infty} \frac{(\beta \hbar \omega)^2 (1 + \beta \hbar \omega)}{(\beta \hbar \omega)^2} \sigma(\omega) d\omega$$

$$= K_{\beta} \int_0^{\infty} \sigma(\omega) d\omega ; \text{ where we neglect } \beta \hbar \omega \text{ as compared to } 1.$$

$$= 3NK_{\beta} = 3 \frac{N}{N_A} N_A K_{\beta} = 3nR$$

For 1 mole of system, $n = 1$, $C_v = 3R$

4.2 Debye Approximation

By employing Debye approximation it is possible to calculate the number $\sigma(\omega)$ of normal mode frequencies. In Debye approximation the discreteness of atoms in solid is neglected and solid is treated as if it is a continuous elastic medium and these atoms are assumed to have approximately similar mass.

The approximation of treating solid as continuous elastic medium is valid when $\lambda \gg a$, where λ is the wavelength of the vibration of the elastic medium while “ a ” is mean interatomic separation in the solid.

Consider a solid which can be treated as elastic continuous medium of volume V . Let $\vec{v}(\vec{r}, t)$ denote the displacement of a point in this medium from its equilibrium position. This displacement is expected to satisfy a wave equation which describes the propagation through the medium of sound waves travelling with some effective velocity C_s .

From the previous chapter we have for a given wave vector \vec{K} the number Δn_x of possible integers n_x for which K_x lies in the range between K_x and $K_x + dK_x$ is

$$\Delta n_x = \frac{L_x}{\pi} dK_x$$

Then number of states $\rho(\vec{K}) d^3K$ for which \vec{K} lies in the range between \vec{K} and $\vec{K} + d\vec{K}$ is then

$$\rho d^3K = \Delta n_x \Delta n_y \Delta n_z = \frac{L_x L_y L_z}{\pi^3} dK_x dK_y dK_z = \frac{v}{(\pi)^3} d^3K$$

The number of states $\rho_x d_x$ for which the value of \vec{K} , $|\vec{K}|$, lies in the range between K and $K + dk$ by summing the above relation over the volume in \vec{K} space of spherical shell of inner radius k and outer radius $K + dk$,

$$\begin{aligned}\rho_x d_x &= \frac{v}{(\pi)^3} 4\pi K^2 dx \\ &= \frac{v}{(\pi)^2} K^2 dx\end{aligned}$$

Since sound wave of wave vector \vec{K} corresponds to an angular frequency, $\omega = C_s K$, the number of possible wave modes with frequency between w and $\omega + d\omega$ is then,

$$\begin{aligned}\sigma_c(\omega) d\omega &= 3 \frac{v}{(2\pi)^3} (4\pi k^2 dk) \\ &= 3 \frac{v}{(2\pi)^3} (4\pi) \left(\frac{\omega}{C_s}\right)^2 \frac{d\omega}{C_s} \\ &= 3 \frac{v}{2\pi^2 C_s^3} d\omega\end{aligned}$$

According to Debye approximation, for low frequencies w the density of modes $\sigma_c(\omega)$ for the continuous elastic medium is nearly the same as the mode density $\sigma(\omega)$ for the actual solid.

The Debye approximation, $\sigma(\omega) \approx \sigma_c(\omega)$, is valid not only for low frequencies but for all $3N$ lowest frequency modes of the elastic continuum, and it is defined by

$$\sigma_D(\omega) = \begin{cases} \sigma_c(\omega) & \text{for } \omega < \omega_D \\ 0 & \text{for } \omega > \omega_D \end{cases}$$

Where ω_D is called Debye frequency and it is chosen so that $\sigma_D(\omega)$ yields the correct total number of $3N$ normal modes.

$$\begin{aligned}\Rightarrow \int_0^\infty \sigma_D(\omega) d\omega &= \int_0^{\omega_D} \sigma_c(\omega) d\omega = 3N \\ \Rightarrow \frac{3v}{2\pi^2 C_s^3} \int_0^{\omega_D} \omega^2 d\omega &= \frac{3v}{2\pi^2 C_s^3} \frac{\omega^3}{3} \Big|_0^{\omega_D} = \frac{v}{2\pi^2 C_s^3} \omega_D^3 = 3N \\ \Rightarrow \omega_D &= \left(3N \frac{2\pi^2 C_s^3}{v}\right)^{1/3} = C_s \left(\frac{6\pi^2 N}{v}\right)^{1/3}\end{aligned}$$

4. 3. Calculation of the Partition Function for Low densities

Consider a mono atomic gas of N identical particles of mass M in a container of volume V at temperature T. Assume the system is at sufficiently high temperature and has sufficiently low density such that classical approximation is valid. The total energy of the system is then,

$$H = K + U$$

Where K is kinetic energy $K = \frac{1}{2m} \sum_{i=1}^N P_i^2$

And U is potential energy of intermolecular interaction and is a function of relative separation between the two interacting molecules.

$$U = U(R_{ij}) ; R_{ij} = |\vec{r}_i - \vec{r}_j|$$

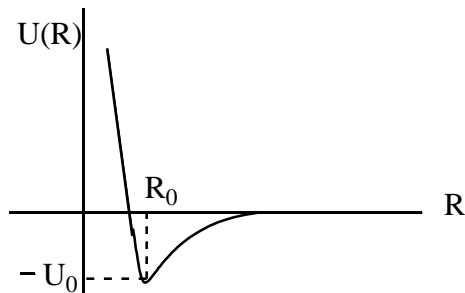
Approximately U is given by the sum of all interactions between a pair of molecules

$$U = \sum_{i=1}^N \sum_{j=1, j \neq i}^N U_{ij} = \frac{1}{2} \sum_{i=1}^N \sum_{j=1, j \neq i}^N U_{ij}$$

$$i < j \quad i \neq j$$

A semi empirical potential called Lennard-Jones potential is given by

$$U(R) = U_0 \left[\left(\frac{R_0}{R} \right)^{12} - \left(\frac{R_0}{R} \right)^6 \right]$$



The classical partition function of the system is given by

$$Z = \frac{1}{N!} \int e^{-\beta(K+U)} \frac{d^3\vec{r}_1 \dots d^3\vec{r}_N}{h^{3N}}$$

$$\begin{aligned}
&= \frac{1}{h^{3N} N!} \int e^{-\beta K(\vec{p}_1, \vec{p}_2, \dots, \vec{p}_N)} d^3 \vec{p}_1 \dots d^3 \vec{p}_N \int e^{-\beta U(r_1, r_2, \dots, r_N)} d^3 \vec{r}_1 \dots d^3 \vec{r}_N \\
&= \frac{1}{h^{3N} N!} \int e^{\frac{-\beta}{2m}(\vec{p}_1^2, \vec{p}_2^2, \dots, \vec{p}_N^2)} d^3 \vec{p}_1 \dots d^3 \vec{p}_N \int e^{-\beta U(r_1, r_2, \dots, r_N)} d^3 \vec{r}_1 \dots d^3 \vec{r}_N \\
&= \frac{1}{h^{3N} N!} \left(\int_{-\infty}^{\infty} e^{\frac{-\beta}{2m} \vec{p}^2} d^3 \vec{p} \right)^N \int e^{-\beta U(r_1, r_2, \dots, r_N)} d^3 \vec{r}_1 \dots d^3 \vec{r}_N \\
&= \frac{1}{h^{3N} N!} \left(\frac{2\pi M}{\beta} \right)^{3/2 N} \int e^{-\beta U(r_1, r_2, \dots, r_N)} d^3 \vec{r}_1 \dots d^3 \vec{r}_N \\
&= \frac{1}{N!} \left(\frac{2\pi M}{h^2 \beta} \right)^{3/2 N} Z_u
\end{aligned}$$

$$\text{Where } Z_u = \int e^{-\beta U(r_1, r_2, \dots, r_N)} d^3 \vec{r}_1 \dots d^3 \vec{r}_N$$

For ideal gas $U \approx 0$, for a system of high temperature $\beta \rightarrow 0$

In both of these limiting cases $e^{-\beta U} \rightarrow 1$, hence $Z_u \rightarrow V^N$

For a system of gas whose density is not too large one can calculate the approximate value of Z_u .

The mean potential energy of the gas is

$$\bar{U} = \frac{\int e^{-\beta U} U d^3 \vec{r}_1 \dots d^3 \vec{r}_N}{\int e^{-\beta U} d^3 \vec{r}_1 \dots d^3 \vec{r}_N} = -\frac{\partial}{\partial \beta} \ln Z_u$$

$$\Rightarrow \int_{Z_u(0)}^{Z_u(\beta)} d \ln Z_u = -\int_0^\beta \bar{U} d\beta$$

$$\Rightarrow \ln Z_u(\beta) - \ln Z_u(0) = -\int_0^\beta \bar{U}(\beta') d\beta'$$

$$\text{For } \beta = 0, Z_u(0) = V^N \Rightarrow \ln Z_u(0) = N \ln V$$

$$\Rightarrow \ln Z_u(\beta) = N \ln V - \int_0^\beta \bar{U}(\beta') d\beta'$$

For a system of N molecules, the number of pairs in the system is

$$\frac{N!}{2!(N-2)!} = \frac{N(N-1)(N-2)}{2(N-2)!} = \frac{1}{2} N(N-1) \approx \frac{1}{2} N^2 \text{ for } N \gg 1$$

$$\Rightarrow \bar{U} = \frac{1}{2} N^2 \bar{U}'$$

By approximating that the motion of any pair of molecules is not correlated appreciably with the motion of the remaining molecules, we can consider a system of pair of molecules is in thermal contact with a system containing the rest molecules (heat reservoir).

Hence mean pair potential \bar{U}' is given by

$$\bar{U}' = \frac{\int u' e^{-\beta u'} d^3 \vec{R}}{\int e^{-\beta u'} d^3 \vec{R}} = -\frac{\partial}{\partial \beta} \ln \int e^{-\beta u} d^3 \vec{R}$$

$$\int e^{-\beta u} d^3 \vec{R} = \int [1 + (e^{-\beta u} - 1)] d^3 \vec{R} = \int d^3 \vec{R} + \int (e^{-\beta u} - 1) d^3 \vec{R} = V + I = V(1 + \frac{I}{V})$$

$$\text{Where } I(\beta) = \int (e^{-\beta u} - 1) d^3 \vec{R} = \int_0^\infty (e^{-\beta u} - 1) 4\pi R^2 dR$$

$$\Rightarrow \bar{U}' = -\frac{\partial}{\partial \beta} \ln (V(1 + \frac{I}{V}))$$

$$= -\frac{\partial}{\partial \beta} \left\{ \ln V + \ln(1 + \frac{I}{V}) \right\}$$

$$= -\frac{\partial}{\partial \beta} \ln \left(1 + \frac{I}{V} \right); \text{ since } V \text{ is independent of } \beta$$

$$\text{For } I \ll V, \ln \left(1 + \frac{I}{V} \right) = \left(\frac{I}{V} + \frac{1}{2} \left(\frac{I}{V} \right)^2 \right) + \dots \approx \frac{I}{V}$$

$$\bar{U}' = -\frac{\partial}{\partial \beta} \left(\frac{I}{V} \right) = -\frac{1}{V} \frac{\partial I}{\partial \beta}$$

$$\bar{U} = \frac{1}{2} N^2 \bar{U}' = -\frac{1}{2} \frac{N^2}{V} \frac{\partial I}{\partial \beta}$$

$$\ln Z_u(\beta) = N \ln V - \int_0^\beta \frac{1}{2} \frac{N^2}{V} \frac{\partial I(\beta')}{\partial \beta'} d\beta'$$

$$= N \ln V + \frac{1}{2} \frac{N^2}{V} \int_0^\beta \frac{\partial I(\beta')}{\partial \beta'} d\beta'$$

$$= N \ln V + \frac{1}{2} \frac{N^2}{V} I(\beta); \text{ since } I(0) = 0$$

$$\Rightarrow Z_u(\beta) = V^N e^{N \sqrt{\frac{I}{V}}} \Rightarrow Z = \frac{1}{N!} \left(\frac{2\pi M}{\hbar^2 \beta} \right)^{\frac{3}{2}N} V^N e^{N \sqrt{\frac{I}{V}}}$$

4.4. Equation of State and Varial Coefficients

Mean pressure of a system can be obtained from the partition function of the system as

$$\bar{P} = \frac{1}{\beta} \frac{\partial \ln Z}{\partial V}$$

The partition function for a system of interacting particles is given by

$$Z = \frac{1}{N!} \left(\frac{2\pi M}{h^2 \beta} \right)^{\frac{3}{2}N} Z_u$$

$$\Rightarrow \ln Z = \ln \left(\frac{1}{N!} \left(\frac{2\pi M}{h^2 \beta} \right)^{\frac{3}{2}N} \right) + \ln Z_u$$

$$\Rightarrow \frac{\partial \ln Z}{\partial V} = \frac{\partial \ln Z_u}{\partial V} \Rightarrow \text{because the first term in r.h.s of the above equation is independent of } q_v.$$

$$\Rightarrow \bar{P} = \frac{1}{\beta} \frac{\partial \ln Z_u}{\partial V} = \frac{1}{\beta} \frac{\partial}{\partial V} \left(N \ln V + \frac{1}{2} \frac{N^2}{V} I \right)$$

$$= \frac{1}{\beta} \left(\frac{N}{V} - \frac{1}{2} \frac{N^2}{V^2} I \right)$$

$$\Rightarrow \beta \bar{P} = \frac{\bar{P}}{K_{\beta} T} = \frac{N}{V} - \frac{1}{2} \frac{N^2}{V^2} I = n - \frac{1}{2} n^2 I$$

For ideal gas particles, equation of state is given by

$$\bar{P} V = N K_{\beta} T$$

$$\Rightarrow \frac{\bar{P}}{K_{\beta} T} = \frac{N}{V} = n$$

The deviation of real gas equation from ideal gas can be considered by introducing correcting term in the above equation. This case is discussed by KamerlingOnnes and he introduced a virial expansion to generalize the ideal gas law.

$$\Rightarrow \frac{\bar{P}}{K_{\beta} T} = n + \beta_2(T) n^2 + B_3(T) n^3 + \dots$$

Where β_2, β_3, \dots are called virial coefficients

The second virial coefficient B_2 is then

$$\beta_2 = -\frac{1}{2} I \int_0^\infty (e^{-\beta u} - I) 4\pi R^2 dR$$

$$= -2\pi \int_0^\infty (e^{-\beta u} - I) R^2 dR$$

Let the potential U(R) is approximately given by

$$U(R) = \begin{cases} \infty & \text{for } R < R_0 \\ -U_0 \left(\frac{R_0}{R}\right)^5 & \text{for } R > R_0 \end{cases}$$

Where R_0 is the minimum possible separation between particles:

$$\text{Then } \beta_2 = -2\pi \int_0^{R_0} (e^{-\beta u} - I) R^2 dR - 2\pi \int_{R_0}^\infty (e^{-\beta u} - I) R^2 dR$$

$$\text{For } R < R_0, U(R) = \infty \Rightarrow e^{-\beta u} = 0$$

$$\Rightarrow \beta_2 = 2\pi \int_0^{R_0} R^2 dR - 2\pi \int_{R_0}^\infty (e^{-\beta u} - I) R^2 dR$$

$$= \frac{2\pi}{3} R_0^3 - 2\pi \int_{R_0}^\infty (e^{-\beta u} - I) R^2 dR$$

$$\text{If } \beta u \ll 1, e^{-\beta u} \approx 1 - \beta u$$

$$\Rightarrow \beta_2 = \frac{2\pi}{3} R_0^3 + 2\pi \int_{R_0}^\infty \beta u R^2 dR$$

$$= \frac{2\pi}{3} R_0^3 + 2\pi \beta \int_{R_0}^\infty -U_0 \left(\frac{R_0}{R}\right)^5 R^2 dR$$

$$= \frac{2\pi}{3} R_0^3 - 2\pi \beta U_0 R_0^5 \int_{R_0}^\infty \frac{dR}{R^{5-2}}$$

$$= \frac{2\pi}{3} R_0^3 - 2\pi \beta U_0 R_0^5 \frac{R^{3-5}}{3-5} \Big|_{R_0}^\infty$$

$$= \frac{2\pi}{3} R_0^3 - 2\pi \beta U_0 R_0^5 \frac{R_0^{3-5}}{5-3}$$

$$\beta_2 = \frac{2\pi}{3} R_0^3 - 2\pi \beta U_0 R_0^5 \frac{1}{5-3} \frac{1}{R_0^{5-3}}$$

$$= \frac{2\pi}{3} R_0^3 - \frac{2\pi \beta U_0 R_0^5}{5-3} \frac{1}{R_0^2} \cdot R_0^{-3}$$

$$\begin{aligned}
&= \frac{2\pi}{3} R_0^3 \frac{2\pi\beta U_0}{5-3} R_0^3 \\
&= \frac{2\pi}{3} R_0^3 \left\{ 1 - \frac{3\beta U_0}{5-3} \right\} \\
&= b' - \beta a'; \text{ where } b' = \frac{2\pi}{3} R_0^3 \text{ and } a' = \frac{3U_0}{5-3} \beta \frac{2\pi}{3} R_0^3
\end{aligned}$$

In the virial expansion, neglecting terms of order higher than n^2 yields

$$\frac{\bar{P}}{K_\beta T} = n + \beta_2 n^2$$

$$= n + (b' - \beta a') n^2$$

$$= n + \left(b' - \frac{a'}{K_\beta T} \right) n^2$$

$$\bar{P} = nK_\beta T + K_\beta T \left(b' - \frac{a'}{K_\beta T} \right) n^2$$

$$= K_\beta T + b' n^2 K_\beta T - a' n^2$$

$$\Rightarrow \bar{P} + a' n^2 = nK_\beta T (1 + b' n) = \frac{nK_\beta T}{(1 + b' n)^{-1}}$$

For very low density such that

$$(1 + b' n)^{-1} = 1 - nb' + \frac{(nb')^2}{2!} - \dots$$

$$\approx 1 - nb'$$

$$\Rightarrow \bar{P} + a' n^2 = \frac{nK_\beta T}{1 - nb'} = \frac{K_\beta T}{\frac{1}{n} - b'}$$

$$\Rightarrow (\bar{P} + a' n^2) = \left(\frac{1}{n} - b' \right) = K_\beta T$$

$$n = \frac{N}{V} = \frac{V N_A}{V} = \frac{N_A}{V_M}; \text{ where } V = \frac{N}{N_A} \text{ is number of moles}$$

where $V_M = \frac{V}{\nu}$ is molar volume

$$\Rightarrow \left(\bar{P} + \frac{a' N_A^2}{V_M^2} \right) \left(\frac{V_M}{N_A} - b' \right) = K_\beta T$$

$$\Rightarrow \left(\bar{P} + \frac{a' N_A^2}{V_M^2} \right) (V_M - N_A b') = N_A K_\beta T$$

$$\Rightarrow \left(\bar{P} + \frac{a}{V_M^2} \right) (V_M - b) = RT, \text{ where } a = N_A^2 a', \text{ } b = N_A b' \text{ and } R = N_A K_\beta$$

or $\left(\bar{P} + \frac{a}{V^2} \right) (V - Vb) = VRT \Rightarrow$ Van der Waals' equation of state a and b are called Van der Waals' constants.