

# Statistical Mechanics

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## 2.1 INTRODUCTION

Statistical mechanics is the mechanics of systems with a very large number of constituent particles, e.g., a litre of air with nearly  $10^{22}$  molecules of  $N_2$  and  $O_2$ , a cup of water with some  $10^{25}$  water molecules, a metre of copper wire with  $10^{23}$  conduction electrons. The approach here is to take a number of measurements of an observable and then to evaluate its mean value or the most probable value. Statistical mechanics makes no attempt to obtain a complete solution for complex systems. Instead, it makes predictions about certain average properties by studying the motion of a large number of identical systems, ignoring the detailed motion of individual particles.

There are classical and quantum versions of statistical mechanics. We first discuss the basic rules of classical statistical mechanics and then use them to derive Maxwell-Boltzmann's distribution law and equipartition theorem. Later we will discuss quantum statistics of Bose-Einstein and Fermi-Dirac and their applications.

## 2.2 MICROSCOPIC AND MACROSCOPIC SYSTEMS

Let us consider a gas confined in a container. It is the collection of very large number of molecules or atoms of the order of  $10^{20}$  or higher. A gas molecule or atom in a container is a *microscopic system* whereas the gas in the container is a *macroscopic system*. The detailed specification of the microscopic state or microstate of any system of  $N$  particles involves specifying the positions and velocities (in classical approach) of all the  $N$  particles and specifying wave functions of all  $N$  particles (in quantum approach). The number of particles  $N$  is so large that to write the microstate of a mole of a gas it will require more than India's total supply of paper, making it practically impossible. Fortunately, in statistical mechanics it is not attempted either. Rather, we want to know just a small number of **macroscopic variables** that are statistical averages over the many microscopic variables. For example, to specify the *macroscopic* state or *macrostate*, of a gas confined in a container, we need only to give the volume  $V$ , the number of atoms  $N$ , the total energy  $E$  and the temperature  $T$ .

## 2.4 EQUAL PROBABILITY HYPOTHESIS

The entire statistical mechanics is based on a hypothesis often called *postulate of equal probability* which states that *the probability of finding the phase point in any one region of phase space is identical with that for any other region of equal volume*. It can be shown that this hypothesis is in conformity with the Liouville's theorem. Also, the predictions based this postulate are in agreement with experimental observations justifying the postulate.

While dealing with molecules, it is convenient to consider the phase space of the molecules to be divided into a number of elementary regions, called cells, each of volume  $dq_1 dq_2 \dots dq_f dp_1 dp_2 \dots dp_f$ .

## 2.5 STATISTICAL EQUILIBRIUM

Consider a thermodynamical isolated system consisting of  $N$  particles. The energy states available to the particles are  $E_1, E_2, E_3$ , etc. These energy states may be quantized or may be continuous and are due to vibrational and rotational energy of the particles.

Suppose, that at any given instant of time,  $n_1$  particles are in state of energy  $E_1$ ,  $n_2$  particles with energy state  $E_2$ , and so on.

The total number of particles in the system is,

$$N = n_1 + n_2 + n_3 + \dots = \sum_i n_i, \quad i = 1, 2, 3, \dots \quad \dots(2.5)$$

The total energy of the system

$$E = n_1 E_1 + n_2 E_2 + n_3 E_3 + \dots$$

$$E = \sum_i n_i E_i \quad \dots(2.6)$$

Equation (2.6) refers to the total energy of a system in which the particles are non-interacting. Here, the energy of each particle depends only on the coordinates of particle in the system for an isolated system, the total energy  $E$  is constant.

For isolated system,  $E = \sum_i n_i E_i = \text{constant}$

Consider a gas having  $N$  molecules at a certain temperature and pressure. Its volume, temperature and pressure are kept constant, i.e., the system is isolated. The total energy of this system remains constant. But the molecules of the gas collide with each other and also with the walls of the container. Consequently, the number of molecules change from one energy state to the other energy state. It means that the values of  $n_1, n_2, n_3$ , etc. continuously change. It can be reasonably assumed that for each microscopic state of a system of particles, there is a particular most favoured distribution. When this distribution for the particles is reached, the system attains statistical equilibrium. For an isolated system, the values of  $n_1, n_2, n_3$ , etc. vary only near the values corresponding to the most probable distribution. Hence, the basic problem in statistical mechanics is to obtain the most probable distribution law for a given composition of the system.

In practice, three most probable distribution laws are used. They are:

- (i) Maxwell-Boltzmann Distribution Law
- (ii) Fermi-Dirac Distribution Law
- (iii) Bose-Einstein Distribution Law

Equations (2.12), (2.13) and (2.14) are the conditions to be satisfied simultaneously for the system to have the maximum probability. The most probable distribution of the molecules among various energy levels can now be obtained by Lagrange's method of undetermined multipliers. Multiplying Eq. (2.13) by  $\alpha'$  and Eq. (2.14) by  $\beta$  and then adding to Eq. (2.12), we get

$$\sum_i (\ln n_i + 1 + \alpha' + \beta E_i) dn_i = 0 \quad \dots(2.15)$$

The constant  $(1 + \alpha')$  can be replaced by another constant  $\alpha$  and as the variations  $dn_i$ 's are independent, Eq. (2.15) will be satisfied only if each term in the summation is zero. That is,

$$\ln n_i + \alpha + \beta E_i = 0$$

or 
$$\ln n_i = -(\alpha + \beta E_i)$$

or 
$$n_i = \frac{1}{\exp(\alpha + \beta E_i)} \quad \dots(2.16)$$

This is Maxwell-Boltzmann distribution law and it gives the most probable distribution of molecules among the various possible individual energy values.

It can be seen that the constant  $\beta = \frac{1}{kT}$ , where  $k$  ( $= 1.3805 \times 10^{-23}$  J/K) is the Boltzmann constant and  $T$  is temperature. Here,  $kT$  has the unit of energy (Joule). Therefore, the Maxwell Boltzmann distribution can also be expressed as

$$n_i = \frac{1}{\exp\left(\alpha + \frac{E_i}{kT}\right)} \quad \dots(2.17)$$

The constant  $\alpha$  depends on the volume and the temperature of the gas.

## 2.7 MAXWELL'S SPEED DISTRIBUTION LAW

The velocity distribution law was derived by Maxwell on the basis of kinetic theory of gases. Suppose  $n$  molecules of a gas is contained in a container of volume  $V$ . From Maxwell-Boltzmann distribution law, we have

$$n_i = e^{-\alpha} e^{-\beta E_i} \quad \dots(2.18)$$

For monoatomic gases, the value of  $e^{-\alpha}$  is given by

$$e^{-\alpha} = \frac{n dx dy dz dp_x dp_y dp_z}{V(2\pi mkT)^{3/2}} \quad \dots(2.19)$$

Substituting the values of  $e^{-\alpha}$  and  $\beta$  in Eq. (2.18), replacing  $n_i$  – the number of molecules in the  $i^{\text{th}}$  state by  $dn$  and omitting the subscript  $i$  from  $E_i$ , we get

$$dn = \frac{n \exp\left(-\frac{E}{kT}\right) dx dy dz dp_x dp_y dp_z}{V(2\pi mkT)^{3/2}} \quad \dots(2.20)$$

Integrating over the coordinates  $x, y, z$  (so that  $\iiint dx dy dz = V$ ), yields

$$dn = \frac{n \exp(-E/kT)}{(2\pi mkT)^{3/2}} dp_x dp_y dp_z \quad \dots(2.21)$$

Here,  $dn$  represents the number of molecules in the container with momentum components in the interval  $dp_x, dp_y$  and  $dp_z$ . The translational energy  $E$  of a molecule having mass  $m$  is given by

$$E = \frac{1}{2}m(v_x^2 + v_y^2 + v_z^2) \quad \dots(2.22)$$

while its momentum components can be represented as

$$p_x = mv_x, \quad p_y = mv_y, \quad p_z = mv_z \quad \dots(2.23)$$

$$\text{Therefore,} \quad dp_x dp_y dp_z = m^3 dv_x dv_y dv_z \quad \dots(2.24)$$

Substituting these in Eq. (2.21), we have

$$dn = n \left( \frac{m}{2\pi kT} \right)^{3/2} \exp \left[ \frac{-m(v_x^2 + v_y^2 + v_z^2)}{2kT} \right] dv_x dv_y dv_z \quad \dots(2.25)$$

This is *Maxwell's distribution law* for the number of molecules with velocity components in the interval  $dv_x, dv_y$  and  $dv_z$ . Writing the velocity components  $v_x, v_y$  and  $v_z$  in terms of the speed of a molecule  $v$  and changing over to polar coordinates, so that

$$v^2 = v_x^2 + v_y^2 + v_z^2 \quad \text{and} \quad dv_x dv_y dv_z = v^2 \sin \theta d\theta d\phi dv.$$

Substituting these values in Eq. (2.25), we get

$$dn = n \left( \frac{m}{2\pi kT} \right)^{3/2} \exp \left( \frac{-mv^2}{2kT} \right)^{3/2} v^2 \sin \theta d\theta d\phi dv \quad \dots(2.26)$$

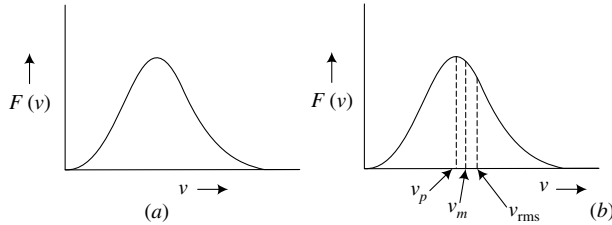
This equation gives the number of molecules with speeds between  $v$  and  $v + dv$  in a direction lying within the angular range  $\theta$  to  $\theta + d\theta$  and  $\phi$  to  $\phi + d\phi$ . Integration over the angular part gives the number of molecules with velocity between  $v$  and  $v + dv$

$$\begin{aligned} dn &= n \left( \frac{m}{2\pi kT} \right)^{3/2} \exp \left( \frac{-mv^2}{2kT} \right) v^2 dv \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi \\ &= 4\pi n \left( \frac{m}{2\pi kT} \right)^{3/2} v^2 \exp \left( \frac{-mv^2}{2kT} \right) dv \quad \dots(2.27) \end{aligned}$$

Using  $F(v)dv$  to denote the number of molecules having speeds between  $v$  and  $v + dv$ , we have

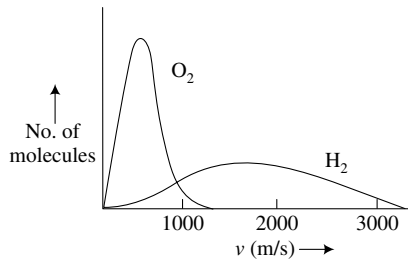
$$F(v)dv = 4\pi n \left( \frac{m}{2\pi kt} \right)^{3/2} v^2 \exp \left( \frac{-mv^2}{2kT} \right) \quad \dots(2.28)$$

The function  $F(v)dv$  is called the *Maxwell speed distribution function* derived by Maxwell before development of quantum mechanics or quantum statistics. The function  $F(v)$  is represented in Fig. 2.1.



**Fig. 2.1** (a) The Maxwell speed distribution (b) most probable speed ( $v_p$ ), mean speed ( $v_m$ ) and rms speed ( $v_{rms}$ ) marked on speed distribution.

The Maxwell speed distribution has been experimentally verified. The Maxwell speed distribution for  $O_2$  and comparatively lighter  $H_2$  molecules are shown in Fig. 2.2. In both the cases there is tail out at higher speeds, but few molecules have speeds higher than about three times the most probable speed, which would correspond to an energy nine times the most probable energy. This indicates why there is almost no hydrogen in the earth’s atmosphere. For hydrogen, the tail of the speed distribution extends beyond the earth’s escape speed ( $\approx 10$  km/s), so that any hydrogen in the earth’s atmosphere eventually leaks into the space. Smaller astronomical bodies such as moon and asteroids have such low escape velocities that all gases on their surfaces escape to space.



**Fig. 2.2**

Since the kinetic energy  $E = \frac{1}{2}mv^2$ , we can write

$$v^2 dv = \frac{(2E)^{1/2} dE}{m^{3/2}} \quad \dots(2.29)$$

Substituting these values of  $E$  and  $v^2 dv$ , Eq. (2.27) can be expressed as

$$dn = \frac{2 \pi n}{(\pi kT)^{3/2}} \exp (-E/kT) E^{1/2} dE \quad \dots(2.30)$$

which gives the number of molecules (or atoms) having energy between  $E$  and  $E + dE$ . The *most probable speed*  $v_p$  corresponds to the peak of  $F(v)$  versus curve (Fig. 2.1(b)). Using

Eq. (2.28), for  $F(v)$  to be maximum

$$\frac{d}{dv} F(v) = 4\pi n \left( \frac{m}{2\pi kT} \right)^{3/2} \left( 2v_p - v_p^3 \frac{m}{kT} \right) \exp \left( \frac{-mv^2}{2kT} \right) = 0.$$

or 
$$2v_p - v_p^3 \frac{m}{kT} = 0$$

or 
$$v_p = \sqrt{\frac{2kT}{m}} \quad \dots(2.31)$$

The *mean speed*  $v_m$  is calculated as

$$v_m = \frac{1}{n} \int_0^{\infty} v F(v) dv = \frac{1}{n} 4\pi n \left( \frac{m}{2\pi kT} \right)^{3/2} \int_0^{\infty} v^3 \exp \left( \frac{-mv^2}{2kT} \right) dv$$

Putting the value of the integral

$$v_m = 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} \cdot \frac{1}{2} \cdot \left( \frac{2kT}{m} \right)^2$$

or 
$$v_m = \sqrt{\frac{8kT}{\pi m}} \quad \dots(2.32)$$

The *root mean square speed*  $v_{rms}$  is given by

$$\begin{aligned} v_{rms}^2 = \bar{v}^2 &= \frac{1}{n} \int_0^{\infty} v^2 F(v) dv \\ &= 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} \int_0^{\infty} v^4 \exp \left( \frac{-mv^2}{2kT} \right) dv \end{aligned}$$

Putting the value of the integral

$$v_{rms}^2 = 4\pi \left( \frac{m}{2\pi kT} \right)^2 \cdot \frac{3\sqrt{\pi}}{8} \cdot \left( \frac{2kT}{m} \right)^{5/2}$$

or 
$$v_{rms} = \sqrt{\frac{3kT}{m}} \quad \dots(2.33)$$

The values of  $v_p$ ,  $v_m$  and  $v_{rms}$  are represented in Fig. 2.1 (b).

## 2.8 LAW OF EQUIPARTITION OF ENERGY

The expression for the number of molecules having coordinates in the interval  $dx$ ,  $dy$  and  $dz$  and momentum components in the interval  $dp_x$ ,  $dp_y$  and  $dp_z$ , given by Eq. (2.21) enables us to evaluate mean values in statistical mechanics. If  $A$  is any quantity which is a function of the three coordinates

and the three momenta, the mean value of  $A$ , expressed as  $\bar{A}$ , is given by

$$\bar{A} = \frac{\int \dots \int A \, dn}{\int \dots \int dn} = \frac{\int \dots \int A e^{-E/kT} \, dx \, dy \, dz \, dp_x \, dp_y \, dp_z}{\int \dots \int e^{-E/kT} \, dx \, dy \, dz \, dp_x \, dp_y \, dp_z} \quad \dots(2.34)$$

Accordingly, the average energy of molecules in a system is given by

$$\bar{E} = \frac{\int \dots \int E e^{-E/kT} \, dx \, dy \, dz \, dp_x \, dp_y \, dp_z}{\int \dots \int e^{-E/kT} \, dx \, dy \, dz \, dp_x \, dp_y \, dp_z} \quad \dots(2.35)$$

Here, it is being assumed that the energy depends on all the variables. Let us assume that the energy  $E(p_x)$  associated with momentum  $p_x$  is separable from the rest of the energy, say  $E'$ , which is dependent on all the other variables. That is,

$$E = E(p_x) + E' \quad \dots(2.36)$$

The average value of  $E(p_x)$  is

$$\bar{E}(p_x) = \frac{\int \dots \int E(p_x) e^{-E(p_x)/kT} e^{-E'/kT} \, dx \, dy \, dz \, dp_x \, dp_y \, dp_z}{\int \dots \int e^{-E(p_x)/kT} e^{-E'/kT} \, dx \, dy \, dz \, dp_x \, dp_y \, dp_z} \quad \dots(2.37)$$

Since  $E(p_x)$  depends only on the variable  $p_x$ , therefore

$$\bar{E}(p_x) = \frac{\int E(p_x) e^{-E(p_x)/kT} \, dp_x}{\int e^{-E(p_x)/kT} \, dp_x} \quad \dots(2.38)$$

Expressing the energy as a quadratic function of momenta

$$E(p_x) = a p_x^2 \quad \dots(2.39)$$

where  $a$  is a constant. Substituting this in  $E(p_x)$ , we get

$$\bar{E}(p_x) = \frac{\int_{-\infty}^{\infty} a p_x^2 e^{-ap_x^2/kT} \, dp_x}{\int_{-\infty}^{\infty} e^{-ap_x^2/kT} \, dp_x} \quad \dots(2.40)$$

The solution of the integrals on the R.H.S yields  $\frac{1}{2}kT$ . Therefore,

$$\bar{E}(p_x) = \frac{1}{2}kT \quad \dots(2.41)$$

Thus, the average (kinetic) energy associated with a variable, which contributes a quadratic term to the total energy, is  $\frac{1}{2}kT$  per molecule. This is referred to as the law of equipartition of

Hence,

$$W = \prod_i \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!} \times \text{const.} \quad \dots(2.49)$$

Taking logarithm of Eq. (2.49)

$$\ln W = \sum_i [\ln(n_i + g_i - 1)! - \ln n_i! - \ln(g_i - 1)!] + \text{const.} \quad \dots(2.50)$$

Since  $n_i$  and  $g_i$  are very large numbers using Stirling's approximation ( $\ln n_i! = n \ln n - n$ ), we have

$$\ln(g_i - 1)! = (g_i - 1) \ln(g_i - 1) - (g_i - 1) = g_i \ln g_i - g_i$$

and  $\ln(n_i + g_i - 1)! \simeq (n_i + g_i) \ln(n_i + g_i) - (n_i + g_i)$

Substituting these in Eq. (2.50), we get

$$\ln W = \sum_i [(n_i + g_i) \ln(n_i + g_i) - n_i \ln n_i - g_i \ln g_i] + \text{const.} \quad \dots(2.51)$$

The condition for the probability to be maximum is

$$d(\ln W) = 0 \quad \dots(2.52)$$

Using this condition and remembering that  $g_i$  is not a variable while  $n_i$  is a continuous variable, Eq. (2.51) gives

$$d(\ln W) = \sum_i [\ln(n_i + g_i) + (n_i + g_i) \frac{1}{(n_i + g_i)} - \ln n_i - n_i \frac{1}{n_i}] dn_i = 0$$

$$\text{or} \quad \sum_i [\ln(n_i + g_i) - \ln n_i] dn_i = 0 \quad \dots(2.52a)$$

This condition for maximum probability is subject to the conditions given by Eqs. (2.45) and (2.46). Hence, the *most probable distribution* can be obtained by the Lagrange's method of undetermined multipliers. For this, multiplying Eq. (2.45) by  $-\alpha$  and Eq. (2.46) by  $-\beta$  and then adding to Eq. (2.52), we have

$$\sum_i [\ln \frac{n_i + g_i}{n_i} - \alpha - \beta E_i] dn_i = 0 \quad \dots(2.53)$$

Since the variations  $dn_i$  are independent of each other, Eq. (2.53) will be satisfied only if the coefficient of each term in the summation is zero. That is,

$$\ln \frac{n_i + g_i}{n_i} - \alpha - \beta E_i = 0$$

$$\text{or} \quad \ln \frac{n_i + g_i}{n_i} = \alpha + \beta E_i \quad \dots(2.54)$$

Taking exponential on both sides, we get

$$\frac{n_i + g_i}{n_i} = e^{\alpha + \beta E_i}$$



or 
$$\frac{g_i}{n_i} = e^{\alpha + \beta E_i} - 1$$

or 
$$n_i = \frac{g_i}{\exp(\alpha + \beta E_i) - 1} \dots(2.55)$$

This equation represents the most probable distribution of the particles among various energy levels for a system obeying Bose-Einstein statistics and is, therefore, known as *Bose-Einstein's distribution law*.

*Bose-Einstein condensation.* In 1924, Einstein predicted that a gas of identical bosons would undergo a new kind of phase transition if cooled to a low enough temperature. He showed that *below a certain critical temperature, most of the bosons in a gas will assemble into the ground state.* This low-temperature collection of ground-state bosons is called the *Bose-Einstein condensate*.

More than 70 years after Einstein's prediction, Bose-Einstein condensation was indeed achieved in June 1995 by Carl Wieman and Eric Cornell at the University of Colorado at Boulder in a gas of rubidium 87 atoms. They were awarded Nobel Prize in physics in 2001 for their experimental work on Bose-Einstein condensation. They achieved this at a temperature of  $10^{-7}$  K in a sample of  $10^{17}$  atoms evaporated down to 2000 atoms in the laser assisted cooling process.

## 2.11 FERMI-DIRAC STATISTICS

This statistics is followed by identical and indistinguishable particles of half-integral spin (fermions) described by anti-symmetrical wave functions.

Consider a system consisting of  $n$  indistinguishable particles. Let these  $n$  particles be divided into different quantum groups such that  $n_1$  particles are in level 1 having energy  $E_1$ ,  $n_2$  are in level 2 having energy  $E_2$ ,  $n_3$  are in level 3 having energy  $E_3$ , and so on. In this distribution following hold.

- (i) The particles are indistinguishable and therefore there is no distinction in which  $n_i$  particles are chosen.
- (ii) The particles obey Pauli's exclusion principle and therefore each sub-level or cell can have 0 or 1 particle. In other words, there can be only one particle in each of the  $g_i$  wave functions. Therefore,  $g_i$  must be greater than or equal to  $n_i$  because there must be at least one wave function for every particle in the group.

The total number of particles  $n$  is a constant and the total energy  $E$  is also a constant, as given by Eqs. (2.44) and (2.46) respectively. Due to Pauli's principle, no cell can accommodate more than one particle, therefore, among  $g_i$  cells  $n_i$  is occupied and  $(g_i - n_i)$  cells are empty. The possible number of such a distribution is given by  $g_i!$  corresponding to the permutations of the  $g_i$  cells. As the particles are indistinguishable, the occupied  $n_i$  cells are similar to each other and hence  $n_i!$  permutations of occupied cells do not give distinguishable arrangement. Also  $(g_i - n_i)!$  permutations of empty cells among themselves give rise to indistinguishable arrangements. Hence, the number of distinguishable arrangements of  $n_i$  particles in  $g_i$  cells is given by

$${}_{g_i}C_{n_i} = \frac{g_i!}{n_i!(g_i - n_i)!} \dots(2.56)$$

Similarly, we can obtain expressions for other quantum states. The total number of eigenstates  $G$  for the whole system is

$$G = \frac{g_1!}{n_1!(g_1 - n_1)!} \cdot \frac{g_2!}{n_2!(g_2 - n_2)!} \cdots \frac{g_i!}{n_i!(g_i - n_i)!} \cdots$$

$$= \prod_i \frac{g_i!}{n_i!(g_i - n_i)!} \quad \dots(2.57)$$

In accordance with the postulate of equal probability of states, the probability  $W$  of the system with the specified distribution is proportional to the total number of eigenstates. That is,

$$W = \prod_i \frac{g_i!}{n_i!(g_i - n_i)!} \times \text{Constant} \quad \dots(2.58)$$

Taking logarithm on both sides,

$$\ln W = \sum_i [\ln g_i! - \ln n_i! - \ln(g_i - n_i)] + \text{const.} \quad \dots(2.59)$$

As  $n_i$ ,  $g_i$  and  $(g_i - n_i)$  are large numbers, using Stirling approximation, we have

$$\ln W = \sum_i [g_i \ln g_i - n_i \ln n_i - (g_i - n_i) \ln(g_i - n_i)] + \text{const.} \quad \dots(2.60)$$

For the probability to be maximum,  $d(\ln W) = 0$ , and remembering that  $g_i$  is not variable while  $n_i$  is, we have

$$\sum_i \left( \ln \frac{g_i - n_i}{n_i} \right) dn_i = 0 \quad \dots(2.61)$$

The conditions given by Eqs. (2.44) and (2.46a) hold in this case also. To solve by the method of Lagrange's multipliers, multiplying Eqs. (2.44) and (2.46a) by constants  $-\alpha$  and  $-\beta$  respectively and then adding to Eq. (2.61), we get

$$\sum_i \left( \ln \frac{g_i - n_i}{n_i} - \alpha - \beta E_i \right) dn_i = 0 \quad \dots(2.62)$$

As the  $dn_i$ 's are independent

$$\ln \frac{g_i - n_i}{n_i} - \alpha - \beta E_i = 0$$

$$\text{or} \quad \ln \frac{g_i - n_i}{n_i} = \alpha + \beta E_i$$

Taking exponents on both sides, we get

$$\frac{g_i - n_i}{n_i} = \exp(\alpha + \beta E_i)$$

$$\text{or} \quad \frac{g_i}{n_i} = \exp(\alpha + \beta E_i) + 1$$

$$\text{or} \quad n_i = \frac{g_i}{\exp(\alpha + \beta E_i) + 1} \quad \dots(2.63)$$

This is the most probable distribution of  $n$  indistinguishable particles among the various energy levels obeying Fermi-Dirac statistics and is therefore known as *Fermi-Dirac distribution law*.

**2.12 FERMI DISTRIBUTION FUNCTION–FERMI ENERGY**

The constants  $\alpha$  in the three distribution laws (*MB*, *BE* and *FD*) are different while the constant  $\beta$  ( $= \frac{1}{kT}$ , where  $k$  is Boltzmann constant and  $T$  is the temperature in Kelvin) is the same for all

distributions. The distribution for the Fermi-Dirac statistics, Eq. (2.63) has the form

$$n(E) = g(E) F_{FD}(E) \tag{2.64}$$

where  $n(E)$  is a distribution and  $n(E)dE$  represents the number of particles with energies between  $E$  and  $E + dE$ . The function  $g(E)$ , called the *density of states*, is the number of states available per unit energy range. The function  $n(E)/g(E)$  is *distribution function*. A comparison of Eqs. (2.63) and (2.64) and replacing  $e^\alpha$  by  $A$  gives

$$F_{FD}(E) = \frac{1}{A \exp\left(\frac{E}{kT}\right) + 1} \tag{2.65}$$

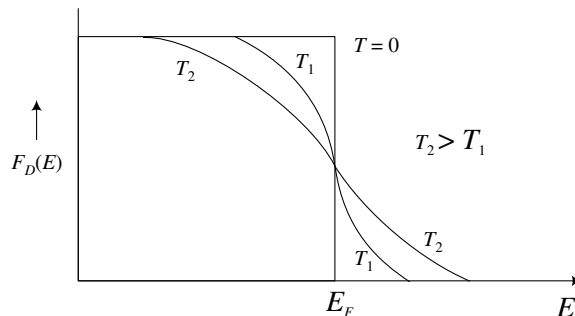
The function  $F_{FD}(E)$  is known as *Fermi-Dirac distribution function*. The constant  $A$  is strongly dependent on temperature and the dependence is exponential, given by

$$A = \exp(-E_F/kT) \tag{2.66}$$

Therefore, the Fermi-Dirac distribution is given by

$$F_{FD}(E) = \frac{1}{\exp[(E - E_F)/kT] + 1} \tag{2.67}$$

where,  $E_F$  is called Fermi energy and is a constant for a given system. The variation of  $F_{FD}(E)$  with energy  $E$  at three different temperatures is shown in Fig. 2.3. The figure shows that at  $T = 0K$ , all quantum states with energy below  $E_F$  are completely filled and those above  $E_F$  are completely empty. Consider the following cases.



**Fig. 2.3** Fermi-Dirac distribution versus energy at three different temperatures.

(a) At  $T = 0$  K: When  $E < E_F$  so that  $E - E_F$  is negative, then

$$F_{FD}(E) = \frac{1}{e^{-\infty} + 1} = \frac{1}{0 + 1} = 1$$

$\therefore F_{FD}(E) = 1$ , which implies all quantum states are completely occupied.

When  $E > E_F$  so that  $E - E_f$  is positive, then

$$F_{FD}(E) = \frac{1}{e^{+\infty} + 1} = \frac{1}{\infty} = 0$$

Which implies that all quantum states with  $E > E_F$  are empty. Thus, we can define Fermi energy as energy of the uppermost occupied level at 0 K.

(b) At  $T > 0$  K: At  $T > 0$  K electrons are excited to vacant levels above  $E_F$  (generally  $E_F \gg kT$ ), resulting in few quantum states below  $E_F$  (within energy range  $kT$ ) becoming empty and few quantum states above  $E_F$  (within energy range  $kT$ ) being occupied. Thus, the probability of finding a particle (e.g., electrons in a metal) in a state with  $E > E_F$  becomes greater than zero and the probability for the states with  $E < E_F$  becomes less than unity.

$$\text{At } T > 0 \text{ K and } E = E_F: F_{FD}(E) = \frac{1}{e^0 + 1} = \frac{1}{1 + 1} = 0.5$$

Hence, the probability of occupancy of  $E_F$  at  $T > 0$  is always 0.5. Thus, we can also define Fermi energy as the energy of the state at which the probability of occupation is  $\frac{1}{2}$  at any temperature above 0 K. At  $E \gg E_F$

$$F_{FD}(E) = \frac{1}{\exp[(E - E_F) / kT] + 1} \simeq \frac{1}{\exp(E - E_F) / kT}$$

which is Maxwell-Boltzmann distribution.

### 2.13 ENERGY OF A FERMI-DIRAC SYSTEM

Electrons in a metal are loosely bound and they obey Fermi-Dirac statistics. Therefore, the electrons in a metal can be treated as a gas of free particles. The Fermi-Dirac distribution law, given by Eq. (2.63), may be expressed in the form

$$dN = \frac{g(E)dE}{A \exp\left(\frac{E}{kT}\right) + 1} \quad \dots(2.68)$$

where,  $dN$  is the number of electrons in the energy range  $E$  and  $E + dE$ ,  $g(E)$  is the number of eigenstates in the energy range  $E$  and  $E + dE$  and  $A = e^\alpha$ . The value of  $g(E) dE$ , for the two different spin states is given by

$$g(E)dE = \frac{8\pi mV}{h^3} (2 mE)^{1/2} dE \quad \dots(2.69)$$

Therefore, Eq. (2.68) can be written as

$$dN = \frac{8\pi mV}{h^3} \frac{(2mE)^{1/2} dE}{A \exp\left(\frac{E}{kT}\right) + 1}$$

Integrating this equation, we have

$$N = \frac{8\pi mV}{h^3} (2m)^{1/2} \int_0^{\infty} \frac{E^{1/2} dE}{A \exp(E/kT) + 1} \quad \dots(2.70)$$

Total energy is given by

$$E(T) = \int E dN = \frac{8\pi mV(2m)^{1/2}}{h^3} \int_0^{\infty} \frac{E^{3/2} dE}{A \exp\left(\frac{E}{kT}\right) + 1} \quad \dots(2.71)$$

Evaluating this integral is complicated. However, at  $T = 0$  K, the Fermi-Dirac distribution function (Eq. (2.65)) is equal to unity for  $E < E_F$  and zero for  $E > E_F$ . At  $T = 0$  K, the energy of the highest occupied level is called the Fermi energy. Considering, Fermi temperature  $T_F$  given by

$$T_F = \frac{E_F}{k} \quad \dots(2.72)$$

At  $T = 0$  K, Eqs. (2.70) and (2.71) reduce to

$$N = \frac{8\pi mV(2m)^{1/2}}{h^3} \int_0^{E_F} E^{1/2} dE \quad \dots(2.73)$$

$$E(0) = \frac{8\pi mV(2m)^{1/2}}{h^3} \int_0^{E_F} E^{3/2} dE \quad \dots(2.74)$$

where  $E(0)$  is the total energy at 0 K. Evaluating the integral in Eq. (2.73) and solving for  $E_F$ , we get

$$E_F = \frac{h^2}{2m} \left( \frac{3N}{8\pi V} \right)^{2/3} = \frac{h^2}{8m} \left( \frac{3N}{\pi V} \right)^{2/3} \quad \dots(2.75)$$

The quantity  $N/V$  can be obtained from Hall effect measurement and so  $E_F$  can be calculated. The Fermi speed  $v_F$  is defined such that

$$E_F = \frac{1}{2} m v_F^2 \quad \dots(2.76)$$

Evaluation of integral in Eq. (2.74) and replacing  $E_F$  by the expression in Eq. (2.75), we get

$$E(0) = \frac{3Nh^2}{10m} \left( \frac{3N}{8\pi V} \right)^{2/3} \quad \dots(2.77)$$

It can easily be seen from Eqs. (2.77) and (2.75) that

$$E(0) = \frac{3}{5}NE_F$$

The mean energy of an electron at absolute zero  $E_m(0)$  is given by

$$E_m(0) = \frac{3}{5}E_F \quad \dots(2.78)$$

This energy is called *zero point energy*.

### Example 2.1

The density of silver is  $10.5 \text{ g/cm}^3$  and its atomic weight is 108. If each atom contributes one electron for conduction, calculate (i) the number density of conduction electrons, (ii) Fermi energy, and (iii) mean energy of the electron at 0 K.

#### Solution.

(i) Number density of conduction electrons

$$\begin{aligned} \frac{N}{V} &= \frac{\rho N_A}{M} = \frac{10.5 \text{ g/cm}^3 \times 6.02 \times 10^{23} \text{ atoms/mole}}{108 \text{ g/mole}} \\ &= 5.85 \times 10^{22} \text{ cm}^{-3} = 5.85 \times 10^{28} \text{ m}^{-3} \end{aligned}$$

(ii) Fermi energy

$$\begin{aligned} E_F &= \frac{h^2}{8m} \left( \frac{3N}{\pi V} \right)^{2/3} \\ &= \frac{(6.626 \times 10^{-34} \text{ Js})^2}{8 \times 9.1 \times 10^{-31} \text{ kg}} \left( \frac{3}{\pi} \times 5.85 \times 10^{28} \text{ m}^{-3} \right)^{2/3} \\ &= 8.816 \times 10^{-19} \text{ J} = 5.51 \text{ eV} \end{aligned}$$

(iii) Mean energy of the electron at 0 K =  $\frac{3}{5}E_F$

$$= \frac{3}{5} \times 5.51 \text{ eV} = 3.31 \text{ eV.}$$

### Example 2.2

The density of the sodium is  $0.97 \text{ g cm}^{-3}$  and its atomic weight is 23. If it has one free electron per atom, calculate its Fermi energy.

#### Solution.

$$\text{Electron density} \quad \frac{N}{V} = \frac{\rho N_A}{M} = \frac{0.97 \text{ g/cm}^3 \times 6.02 \times 10^{23} \text{ atoms/mole}}{23 \text{ g/mole}}$$