

CHAPTER

8

Statistical Mechanics

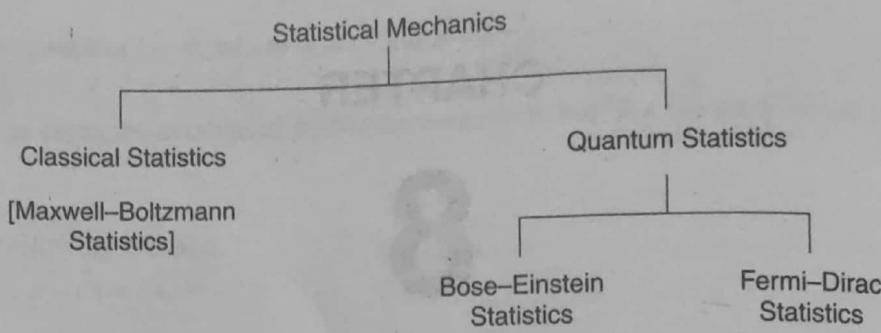
8.1 INTRODUCTION

Thermodynamics is the study of the relationship between macroscopic properties of systems, such as temperature, volume, pressure, magnetization, compressibility, etc. Statistical mechanics, also called statistical physics, is concerned with understanding how the various macroscopic properties arise as a consequence of the microscopic nature of the system. In essence, it makes macroscopic deduction from microscopic models. According to Lev Landau, statistical physics and thermodynamics together form a unit. All the concepts and quantities of thermodynamics follow most naturally, simply and rigorously from the concepts of statistical physics. Although the general statement of thermodynamics can be formulated non-statistically, their application to specific cases always requires the use of statistical physics.

Statistical approach can be applied only to such systems which contain a large number of individuals identical in some sense, but are distinguishable by means of some property. The purpose of statistical mechanics is to provide special statistical or probability laws for the distribution of identical microscopic particles (atoms and molecules) of a macroscopic system in thermal equilibrium, without considering the detailed calculation of position and velocity of individual particles and to derive all equilibrium properties of the system. Suppose, for example, 1 cm^3 of a gas under normal temperature and pressure contains 2.7×10^{19} molecules. Assuming that each molecule has three degrees of freedom, we will have to set up and solve $3 \times 2.7 \times 10^{19}$ equations of motion for 1 cm^3 of the gas. Theoretically, some equations can be solved and the solutions would be in terms of mass, position, velocity and energy of each molecule, etc., and not in terms of thermodynamic variables such as pressure, entropy, etc. Thus there is a gap between the results of classical mechanics and thermodynamics. Statistical mechanics provides the link between mechanical properties and thermodynamical properties of a system.

In statistical mechanics, the properties and laws of motion of individual atoms, molecules and elementary particles, are assumed to be known. If these laws are governed by classical mechanics, we call it classical statistics and if they are governed by quantum mechanics, we call it quantum statistics.

Classical statistics was developed by Maxwell in 1859 and then refined by Boltzmann and hence correctly called Maxwell–Boltzmann (or MB) statistics. Classical statistics is applicable to a system of identical, weakly interacting, structureless and neutral particles. Such hypothetical particles are called boltzons. Quantum particles are divided into two classes. One with integral spin (i.e., $n\hbar$) and are called Bose particles



(or simply bosons) and other with half integral spin [i.e., $\left(n + \frac{1}{2}\right)\hbar$] and are called Fermi particles (or simply fermions). Bose statistics was refined by Einstein and hence called Bose–Einstein (or BE) statistics and Fermi statistics was refined by Dirac and hence called Fermi–Dirac (or FD) statistics.

8.2 CONCEPT OF PHASE SPACE

In classical mechanics, the position of a point particle in three-dimensional space is determined by three cartesian coordinates x, y, z and its state of motion is given by the velocity components v_x, v_y and v_z . For many purposes it is more convenient to use the corresponding momenta p_x, p_y, p_z (for $m\dot{x}, m\dot{y}$ and $m\dot{z}$ where m is the mass of the particle). To describe both the positions and the state of motion of the particle, it is required to set up a six-dimensional space called the phase space, in which the six coordinates x, y, z, p_x, p_y, p_z are marked out along six mutually perpendicular axes. A point in this space describes both the position and the motion of the particle at some particular instant. Therefore, if a position of a phase point is known at any instant of time, its trajectory is also known.

8.2.1 Phase Space of N Particles System

For N particles system, the mechanical state of the whole system can be determined completely in terms of $3N$ position coordinates $q_1 \dots q_N$ and $3N$ momenta coordinates $p_1 \dots p_N$. The $6N$ -dimensional space is called the phase space or Γ space of the system. A point in Γ space represents a state of the entire system. For monoatomic gas it is also called molecular phase space or μ space.

8.2.2 Smallest Cell in Phase Space

In the μ space of particle, a volume element

$$d\tau = dx dy dz dp_x dp_y dp_z$$

is the volume of a six-dimensional cell having sides $dx, dy, dz, dp_x, dp_y, dp_z$. Such a cell of minimum volume is called a unit cell in the μ space.

So,

$$(d\tau)_{\min} = (\delta x \delta p_x)_{\min} (\delta y \delta p_y)_{\min} (\delta z \delta p_z)_{\min}$$

But uncertainty principle tells us that the minimum value of each of the products is approximately equal to Planck's constant h . Therefore,

$$(d\tau)_{\min} = (h)(h)(h) = h^3$$

In classical description, h can be chosen as an arbitrarily small constant having the dimensions of angular momentum. But quantum theory imposes a limitation on the accuracy with which a simultaneous specification

of coordinate x and its corresponding momentum p_x is possible and from uncertainty principles, phase space is actually a cell of minimum volume \hbar^3 .

8.3 CONCEPT OF ENERGY LEVELS AND ENERGY STATES

In classical mechanics, the 'state' of a system is defined by the values of the coordinates and momenta of all its constituent particles. In quantum statistics, a quantum state is a mathematical object that fully describes a quantum system. One typically imagines some experimental apparatus and procedure which prepares this quantum state; the mathematical object then reflects the set-up of the apparatus. Quantum states can be statistically mixed, corresponding to an experiment involving a random change of the parameters. States obtained in this way are called mixed states, as opposed to pure states, which cannot be described as a mixture of others. When performing a certain measurement on a quantum state, the result is in general described by probability distribution and the form that this distribution takes is completely determined by the quantum state and the observable describing the measurement. However, unlike in classical mechanics, the result of a measurement on even a pure quantum state is only determined probabilistically.

A quantum system or particle that is bound, confined spatially, can only take on certain discrete values of energy, as opposed to classical particles, which can have any energy. These are called energy levels. The term is most commonly used for energy levels of electrons in atoms or molecules, which are bound by the electric field of the nucleus. The energy spectrum of a system with energy levels is said to be quantized.

Energy levels are said to degenerate, if the same energy level is obtained by more than one quantum mechanical state. They are then called degenerate energy levels. There may be several energy states corresponding to the same energy.

8.4 MACROSTATE AND MICROSTATE

Macrostate The macrostate of a system may be defined as the number of phase points in each cell of the phase space. For a macrostate, we specify only bulk quantities which can be determined by macroscopic measurements, such as pressure, temperature, etc. Thus an isolated system consisting of a fixed number (N) of non-interacting identical particles, having a fixed internal energy (E) and occupying a fixed space of volume (V) is said to be macroscopic state or macrostate of the system. The macrostate is also called the thermodynamic state.

Microstate A state of the system in which we specify the states of all the constituent particles is called a microstate. From a dynamical point of view, each state of a system can be defined as precisely as possible by specifying all of the dynamical variables of the system. Such a state is called a microscopic state. In general, the number of different meaningful ways in which the total energy (E) of the system can be distributed among its constituent particles called microstate. One of the fundamental hypothesis of statistical mechanics is that microstates are equally probable, which means one microstate would occur as often as another over a long period of time.

Example Suppose we have four distinguishable particles a, b, c, d and we wish to distribute them into two exactly similar compartments in an open box. Since both the compartments are exactly alike, the particles have the same *a priori* probability of going into either of them. The following table will give the various macrostates and microstates.

Macrostates	Possible arrangement		No. of microstates
	Compartment 1	Compartment 2	
0, 4	Q	$abcd$	1
1, 3	a	bcd	4
	b	cda	
	c	dab	
	d	abc	
2, 2	ab	cd	6
	ac	bd	
	ad	bc	
	bc	ad	
	bd	ac	
	cd	ab	
3, 1	bcd	a	4
	cda	b	
	dab	c	
	abc	d	
4, 0	$abcd$	Q	1

Each distinct arrangement is known as the microstate of the system.

8.5 THERMODYNAMIC PROBABILITY AND ENTROPY

Thermodynamical probability is defined as the number of possible microstate corresponding to any given macrostate. Thermodynamic probability is, in general, very large, unlike mathematical probability, which when normalized, as always is less than one. In our previous example, the thermodynamic probability corresponding to the macrostate (2, 2) is equal to the number of microstates in (2, 2) which is 6.

We know that when an isolated system undergoes an irreversible process, there is a net increase of the entropy of the system. The maximum value of the entropy is reached when the system arrives at a state of equilibrium. Boltzmann related the entropy S and the thermodynamic probability W by the equation

$$S = K_B \ln \frac{W}{W_o} \quad \dots(8.1)$$

where K_B is the Boltzmann constant and W_o the initial probability. From Eq. (8.1), we have

$$\begin{aligned} S &= K_B \ln W - K_B \ln W_o \\ &= K_B \ln W - S_o \end{aligned}$$

The quantity $S_o = K_B \ln W_o$ can be taken as the zero from which the entropy is counted.
Hence,

$$(\underbrace{S = K_B \ln W}_{\text{ }}) \quad \dots(8.2)$$

8.6 EQUILIBRIUM MACROSTATE

A macroscopic state which does not tend to change in time except for random fluctuations is known as equilibrium macrostate. The macrostate of a system in equilibrium is time-independent, except for ever-present

fluctuations. The macrostate of a system can be described by certain macroscopic parameters, i.e., parameters which characterize the properties of the system on a large scale. The equilibrium macrostate of a system is independent of its past history. For example, consider an isolated gas of N molecules in a box. These molecules may originally have been confined by a partition to one half of the box. But after the partition is removed and equilibrium has been attained, the macrostate of the gas is the same in both cases; it corresponds merely to the uniform distribution of all the molecules through the entire box.

8.7 MB, BE AND FD STATISTICS

In statistical mechanics, Maxwell–Boltzmann statistics describes the statistical distribution of material particles over various energy states in thermal equilibrium, when the temperature is high enough and density is low enough to render quantum effects negligible.

Fermi–Dirac (FD) and Bose–Einstein (BE) statistics apply when quantum effects have to be taken into account. Quantum effects appear if the concentration of particles $\left(\frac{N}{V}\right) \geq n_q$ (where n_q is the quantum concentration). The quantum concentration is when the interparticle distance is equal to the thermal de Broglie wavelength, i.e., when the wave functions of the particles are touching but not overlapping.

8.8 MAXWELL – BOLTZMANN (MB) STATISTICS

8.8.1 Basic Postulates

- (i) Particles are identical and distinguishable.
- (ii) They do not possess any kind of spin.
- (iii) They do not obey the Pauli exclusion principle.

So any state can accommodate any number of particles. For example, the molecules of a gas. The particles that obey MB statistics are called boltzons. Example: Ideal gas molecules.

8.8.2 Maxwell–Boltzmann (MB) Distribution Function

Consider a system having energy levels $\varepsilon_1, \varepsilon_2, \varepsilon_3, \dots$ and the number of particles in these levels be n_1, n_2, n_3, \dots . Moreover, let each level be degenerated, i.e., let each level be associated with several sublevels. Let g_1, g_2, g_3, \dots , be the number of sublevels corresponding to the energies $\varepsilon_1, \varepsilon_2, \varepsilon_3, \dots$, respectively. So the available states of the system are the sublevels. Let us now consider the i^{th} level. The probability that a particular sublevel (or state) is occupied is $\left(\frac{1}{g_i}\right)$.

Hence the average number of particles in that state is $\left(\frac{n_i}{g_i}\right)$, which is the occupation number for the i^{th} state.

In classical statistics, the number of ways in which the total number of particles, N can be grouped into levels having respectively n_1, n_2, n_3, \dots , number of particles. The number of ways in which we can do so is equal to the number of permutations of N things, out of which n_1 are alike, n_2 others are alike, n_3 others are alike and so on. This is given by

$$M = \frac{N!}{n_1! n_2! n_3! \dots} = \frac{N!}{\prod_i n_i!} \quad \dots(8.3)$$

where \prod_i denotes the product of n_i for all values of i . Since classical particles are assumed to be distinguishable, then the total number of ways in which n_i particles occupy g_i sublevels in $g_i^{n_i}$. If $P_{\text{classical}}$ is the number of ways in which g_1 sublevels are occupied by n_1 particles, g_2 by n_2 , g_3 by n_3 and so on, then

$$P_{\text{classical}} = g_1^{n_1} g_2^{n_2} g_3^{n_3} \dots = \prod_i g_i^{n_i}$$

The total probability W of the distribution is the product of M and $P_{\text{classical}}$

$$W = \frac{N!}{\prod_i n_i!} \prod_i g_i^{n_i} = N! \prod_i \frac{g_i^{n_i}}{n_i!} \quad \dots(8.4)$$

Taking natural logarithm on both sides, we have

$$\ln W = \ln N! + \ln \prod_i \frac{g_i^{n_i}}{n_i!}$$

$$\ln W = \ln N! + \sum_i n_i \ln g_i - \sum_i \ln n_i!$$

Applying Stirling's theorem, [$\ln N! = N \ln N - N$ (where N is very large)], we have

$$\begin{aligned} \ln W &= N \ln N - N + \sum_i n_i \ln g_i - \left[\sum_i (n_i \ln n_i - n_i) \right] \\ &= N \ln N - N + \sum_i n_i \ln g_i - \sum_i n_i \ln n_i + \sum_i n_i \\ &= N \ln N - \cancel{N} + \sum_i (n_i \ln g_i - n_i \ln n_i) + \cancel{N} \\ &= N \ln N + \sum_i n_i \ln \left(\frac{g_i}{n_i} \right) \end{aligned} \quad \dots(8.5)$$

The most probable distribution can be obtained by maximizing $\ln W$, i.e., by setting

$$\delta \ln W = \sum_i \frac{\partial \ln W}{\partial n_i} \delta n_i = 0 \quad \dots(8.6)$$

subject to the constraints that the total number of particles and total energy of the system are conserved:

$$N = n_1 + n_2 + n_3 + \dots = \sum_i n_i = \text{const.}$$

$$E = n_1 \varepsilon_1 + n_2 \varepsilon_2 + \dots = \sum_i n_i \varepsilon_i = \text{const.}$$

$$\text{In differential form } \sum_i \delta n_i = 0 \quad \dots(8.7)$$

$$\text{and } \sum_i \varepsilon_i \delta n_i = 0 \quad \dots(8.8)$$

Differentiating Eq. (8.5) w.r.t. n_i , we get from Eq. (8.5)

$$\sum_i \ln \left(\frac{g_i}{n_i} \right) \delta n_i = 0 \quad \dots(8.9)$$

From Eqs (8.7), (8.8) and (8.9), we have

$$\sum_i \left(\ln \frac{g_i}{n_i} - \alpha - \beta \varepsilon_i \right) \delta n_i = 0 \quad \dots(8.10)$$

where α, β are Lagrange's multipliers. Since coefficients δn_i are arbitrary, so from Eq. (8.10) for all values of i , the term in the bracket must be zero.

Thus, $\ln \frac{g_i}{n_i} - \alpha - \beta \varepsilon_i = 0$

or, $\ln \frac{g_i}{n_i} = \alpha + \beta \varepsilon_i$

or,

$$\frac{n_i}{g_i} = e^{-(\alpha + \beta \varepsilon_i)} = \frac{1}{e^{\alpha + \beta \varepsilon_i}}$$

or,

$$n_i = \frac{g_i}{e^{\alpha + \beta \varepsilon_i}} \quad \dots(8.11)$$

This result is known as the Maxwell-Boltzmann distribution of distinguishable particles among the energy levels.

Assuming Maxwell-Boltzmann distribution, the average speed, root mean square speed, most probable speed of the molecules of an ideal gas can be calculated. The total internal energy, specific heat at constant volume of an ideal gas can also be derived very easily.

8.8.3 Limitations of Maxwell-Boltzmann Statistics

If for a given density, the temperature of a perfect gas is sufficiently low, then Boltzmann statistics is no longer applicable and a new statistics must be set up. The MB distribution function suffers from the following major objections:

- (i) The particles are assumed to be distinguishable, although in actual practice many elementary particles like electrons are indistinguishable. In BE statistics there is no restriction on the number of particles that can occupy the same energy state.
- (ii) Any number of particles are assumed to occupy the same quantum state while many particles such as electrons obey the Pauli exclusion principle which does not allow a quantum state to accept more than one particle.

These objections are removed in the distribution function known as Fermi-Dirac (FD) distribution. The particles that obey the FD statistics are called Fermions. Bose-Einstein statistics (BE) give the statistical behavior of indistinguishable particles. The particles that obey BE statistics are known as boson, e.g., photons, photons, etc.

8.9 BOSE-EINSTEIN (BE) STATISTICS

Bose-Einstein and Fermi-Dirac statistics apply when quantum effects have to be taken into account and the particles are considered indistinguishable. BE statistics was developed in 1924 by S N Bose for light quanta (photons) and generalized by A Einstein to find energy distribution among indistinguishable and identical particles, each having a spin angular momentum $m_s \hbar$ given by any of the values

$$m_s \hbar = 0, \hbar, 2\hbar, 3\hbar, \dots$$

where m_s is the spin quantum number.

8.9.1 Basic Postulates

- (i) The particles of the system are identical and indistinguishable.
- (ii) The Pauli exclusion principle is not applicable, so any quantum state can accommodate any number of particles.
- (iii) BE statistics is applicable to particles with integral spin angular momentum in units of \hbar .
- (iv) These particles have symmetric wave function.

The particles that obey BE statistics are called bosons.

Examples Photons, phonons, α -particles, π -mesons, k -mesons, higgs-boson, ${}_1\text{H}^2$, ${}_2\text{He}^4$, ${}_6\text{C}^{12}$, ${}_8\text{O}^{16}$ are examples of bosons.

8.9.2 Bose-Einstein (BE) Distribution Function

For BE statistics, since particles are indistinguishable, the number of ways in which n_i bosons can occupy g_i sublevels (no restriction on the number of particles occupying a sublevel) be obtained by taking the permutations of $\{n_i + (g_i - 1)\}$ things, out of which a group of n_i things and another group of $(g_i - 1)$ things are alike. So the number is

$$W_i = \frac{(n_i + g_i - 1)!}{n_i! (g_i - 1)!} \quad \dots(8.12)$$

The total number W of independent ways obtaining a distribution of particles among the quantum states in the various energy levels is the product of expressions given by Eq. (8.12) for $i = 1, 2, \dots, n$.

So,

$$W = \prod_i \frac{(n_i + g_i - 1)!}{n_i! (g_i - 1)!} \quad \dots(8.13)$$

Since n_i and g_i are very large numbers compared to unity so the Eq. (8.13) can be written as

$$W = \prod_i \frac{(n_i + g_i)!}{n_i! g_i!} \quad \dots(8.14)$$

Taking natural logarithm on both sides and applying Stirling's approximation, we get

$$\ln W = \sum_i [(n_i + g_i) \ln (n_i + g_i) - n_i \ln n_i - g_i \ln g_i] \quad \dots(8.15)$$

The most probable distribution can be obtained by maximizing $\ln W$, i.e., by setting $\delta \ln W = \sum_i \frac{\partial \ln W}{\partial n_i} \delta n_i = 0$ subject to the constraints that the total number of particles and total energy of the system are conserved:

$$\sum n_i = \text{const.}$$

$$\sum_i \epsilon_i n_i = \text{const.}$$

In differential form $\sum_i \delta n_i = 0$

and $\sum_i \epsilon_i \delta n_i = 0$

So by applying $\delta \ln W = 0$, Eq. (8.15) gives

$$\sum_i [\ln (n_i + g_i) \delta n_i - \ln n_i \delta n_i] = 0 \quad [\delta g_i = 0] \quad \dots(8.18)$$

Using Eqs (8.16), (8.17) and (8.18), we have

$$\sum \left[\ln \frac{n_i + g_i}{n_i} - \alpha - \beta \varepsilon_i \right] \delta n_i = 0 \quad \dots(8.19)$$

where α, β are Lagrange's multipliers.

Since coefficients δn_i are arbitrary, so from Eq. (8.19) for all values of i , the term in the bracket must be zero.

Thus, $\ln \left(\frac{n_i + g_i}{n_i} \right) - \alpha - \beta \varepsilon_i = 0$

or,

$$\frac{n_i}{g_i} = \frac{1}{e^{\alpha + \beta \varepsilon_i} - 1} \quad \dots(8.20)$$

This relation gives the most probable distribution of particles for a system obeying BE statistics and is known as Bose-Einstein distribution law.

If μ is the chemical potential and K_B is the Boltzmann constant, then in thermal equilibrium for bosons at temperature T , we can write

$$\beta = \frac{1}{K_B T} \quad \text{and} \quad \alpha = -\mu \beta$$

Substituting this value in Eq. (8.20), we obtain

$$n_i = \frac{g_i}{e^{(\varepsilon_i - \mu)/K_B T} - 1} \quad \dots(8.21)$$

The energy distribution function $f(\varepsilon_i)$ is the number of particles per quantum state in the energy level ε_i . Therefore, BE distribution function becomes (if we drop the index i)

$$f(\varepsilon) = \frac{n}{g} = \frac{1}{e^{(\varepsilon - \mu)/K_B T} - 1} \quad \dots(8.22)$$

If $\varepsilon \gg K_B T$, the BE distribution reduces to the MB distribution.

8.10 FERMI-DIRAC (FD) STATISTICS

This statistics was developed by E Fermi for electrons and its relation to quantum mechanics was established by PAM Dirac in 1926. The objective of this statistics is to find the energy distribution among indistinguishable identical particles, each having a spin angular momentum $m_s \hbar$ given by any of the values

$$m_s \hbar = \frac{1}{2} \hbar, \frac{3}{2} \hbar, \frac{5}{2} \hbar \dots$$

8.10.1 Basic Postulates

- (i) The particles of the system are identical and indistinguishable.
- (ii) The Pauli exclusion principle is applicable, so each quantum state can accommodate either no particle or only one particle.
- (iii) FD statistics is applicable to particles with $\frac{1}{2}$ integral spin angular momentum in units of \hbar .
- (iv) These particles have antisymmetric wave function.

The particles those obey FD statistics are called fermions.

Examples Protons, neutrons, electrons, μ -mesons, ${}_1^1\text{H}^3$, ${}_2^3\text{He}^3$, ${}_3^7\text{Li}^7$, ${}_6^{13}\text{C}^{13}$ are examples of fermions.

8.10.2 Fermi-Dirac (FD) Distribution Function

For FD statistics, since the particles are indistinguishable, we should know the number of ways in which n_i fermions can occupy g_i sublevels. Since fermions are governed by the Pauli exclusion principle (no two particles can occupy the same sublevel), g_i must be greater than n_i . Thus, the number of ways in which n_i fermions can occupy g_i sublevels is equal to the number of ways in which n_i things can be taken at a time from g_i different things. This is equal to ${}^g C_{n_i} = \frac{g_i!}{n_i!(g_i - n_i)!}$ considering them all, we can write the probability of the entire distribution of the particles is given by

$$W = \prod_i \frac{g_i!}{n_i!(g_i - n_i)!} \quad \dots(8.23)$$

We shall now turn to the derivation of the distribution for fermions, the FD distribution. We shall proceed exactly on the same line as in the case of MB and BE statistics. Taking logarithm of Eq. (8.23) and applying Stirling's formula, we get

$$\ln W = \sum [g_i \ln g_i - (g_i - n_i) \ln (g_i - n_i) - n_i \ln n_i] \quad \dots(8.24)$$

Under the conditions stipulated by Eqs (8.7) and (8.8), we find the maximum of the quantity $\ln W$, using Lagrange's undetermined multipliers. For this purpose, we equate to zero the derivatives of the quantity $\ln W - \alpha \sum n_i - \beta \sum n_i \varepsilon_i$ [see Eq. (8.10)].

$$\sum [\ln n_i - \ln (g_i - n_i) + \alpha + \beta \varepsilon_i] \delta n_i = 0 \quad \dots(8.25)$$

Hence, we obtain

$$\frac{n_i}{g_i} = \frac{1}{e^{\alpha + \beta \varepsilon_i} + 1} \quad \dots(8.26)$$

This relation gives the most probable distribution of particles for a system obeying FD statistics and is known as Fermi-Dirac distribution law.

For fermions in statistical equilibrium at temperature T ,

$$\alpha = -\frac{\varepsilon_f}{K_B T} \quad \text{and} \quad \beta = \frac{1}{K_B T}$$

where ε_f = Fermi energy of the system and K_B is the Boltzmann constant

Now substituting the values of β and α in Eq. (8.26), we get (if we drop the index i)

$$f(\varepsilon) = \frac{n}{g} = \frac{1}{e^{(\varepsilon - \varepsilon_f)/K_B T} + 1} \quad \dots(8.27)$$

This is known as Fermi-Dirac distribution function.

8.11 CLASSICAL STATISTICS AS A SPECIAL CASE OF QUANTUM STATISTICS

MB, BE and FD statistics can be represented by a single equation as

$$\frac{n_i}{g_i} = \frac{1}{e^{\alpha + \beta \epsilon_i} + k}$$

...(8.28)

$k = 0$ gives classical or MB statistics

$k = -1$ gives BE statistics

$k = +1$ gives FD statistics

When $e^{\alpha + \beta \epsilon_i} \gg 1$ gives $\frac{n_i}{g_i} = \frac{1}{e^{\alpha + \beta \epsilon_i}}$ which is the general form of classical distribution. The inequality in equation $e^{\alpha + \beta \epsilon_i} \gg 1$ shows that $\frac{n_i}{g_i} < 1$ which means that classical distribution is true only in the limiting case of small number of particles per quantum state. Classical distribution is thus valid only for rarefied gases.

For higher temperatures, since $\frac{n_i}{g_i} \ll 1$, we can neglect the value of k . So at higher temperatures, the three statistics gives the same result.

8.12 DENSITY OF STATES OR QUANTUM STATES IN ENERGY RANGE BETWEEN \mathcal{E} AND $\mathcal{E} + d\mathcal{E}$

The probability $g(p)$ that a molecule has a momentum between p and $p + dp$ is equal to the number of cells in phase space within which such a molecule may exist. If each cell has the infinitesimal volume h^3 , then

$$g(p) dp = \frac{\iiint dx dy dz dp_x dp_y dp_z}{h^3}$$

where the numerator is the phase space volume occupied by the particles with specified momenta.

Here $\iiint dx dy dz = V$

where V is the volume occupied by the gas in ordinary position space and

$$\iiint dp_x dp_y dp_z = 4\pi p^2 dp$$

where $4\pi p^2 dp$ is the volume of a spherical shell of radius p and thickness dp in momentum space.

Hence
$$g(p) dp = \frac{4\pi V p^2 dp}{h^3} \quad \dots(8.29)$$

Now the system contains identical particles of two types; one having a clockwise spin and another having an anticlockwise spin. If one cell contains one particle, then to accommodate them and taking spin into consideration, we need twice the number of cells. Therefore,

$$g(p) dp = 2 \frac{4\pi p^2 dp}{h^3} V = \frac{8\pi p^2 dp V}{h^3} \quad \dots(8.30)$$

Again for free particle $p = \sqrt{2m\epsilon}$, ϵ is the energy of the free particle

or,
$$p^2 = 2mE$$

...(8.31)

Differentiating Eq. (8.31), we get

$$2p dp = 2m d\epsilon \quad \dots(8.32)$$

$p dp = m d\epsilon$

or,

Substituting the values of p and $p dp$ from Eqs (8.31) and (8.32) in Eq. (8.30) we get the number of quantum states or cells lying within the energy range ε and $\varepsilon + d\varepsilon$ as $g(\varepsilon) d\varepsilon$ instead of $g(p) dp$ as

$$\begin{aligned} g(\varepsilon) d\varepsilon &= \frac{8\pi V}{h^3} \sqrt{2m\varepsilon} m d\varepsilon \\ &= \frac{8\sqrt{2}\pi V}{h^3} m^{3/2} \varepsilon^{1/2} d\varepsilon \end{aligned} \quad \dots(8.33)$$

8.13 FERMI DISTRIBUTION AT ZERO AND NON-ZERO TEMPERATURE

Figure 8.1 shows the variation of $f(\varepsilon)$ with ε for different values of temperature.

The FD distribution function which gives the average occupation of the energy level is given by

$$f(\varepsilon) = \frac{1}{e^{(\varepsilon - \varepsilon_F)/K_B T} + 1} \quad \dots(8.34)$$

Case I When $T = 0 K$ $f(\varepsilon)$ has two possible values

$$f(\varepsilon) = \frac{1}{e^{-\infty} + 1} = 1 \quad \text{if } \varepsilon < \varepsilon_F$$

and

$$= \frac{1}{e^{\infty} + 1} = 0 \quad \text{if } \varepsilon > \varepsilon_F$$

Thus, at absolute zero ($T = 0 K$) of temperature all possible quantum states of energy less than ε_F are occupied and all those of energy more than ε_F are empty.

Accordingly, the Fermi energy ε_F is defined as the energy of the highest occupied level at absolute zero.

Expanding Eq. (8.34) near $\varepsilon = \varepsilon_F$ we get at finite ($T > 0 K$) temperature as

$$f(\varepsilon) = \frac{1}{e^{(\varepsilon - \varepsilon_F)/K_B T} + 1} = \frac{1}{2} - \frac{\varepsilon - \varepsilon_F}{4K_B T} + \dots \quad \dots(8.35)$$

- (i) If $\varepsilon \leq \varepsilon_F - 2K_B T$ $f(\varepsilon) = 1$
- (ii) If $\varepsilon \geq \varepsilon_F + 2K_B T$ $f(\varepsilon) = 0$
- (iii) If $\varepsilon = \varepsilon_F$ $f(\varepsilon) = 1/2$

The spread region of Fermi distribution, i.e., the region of ε when $f(\varepsilon)$ changes from unity at zero (from $\varepsilon_F - 2K_B T$ to $\varepsilon_F + 2K_B T$) narrows as the temperature decreases and at absolute zero becomes a sharp discontinuity.

Thus, Fermi level is that energy level for which the probability of occupation at $T > 0$ is $\frac{1}{2}$, i.e., 50% of the quantum states are occupied and 50% are empty. The distribution is said to degenerate at low temperature and non-degenerate at high temperature when the step-like distribution is lost.

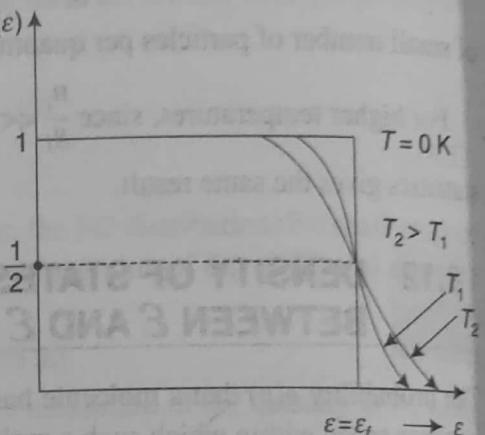


Fig. 8.1 Fermi distribution at zero and non-zero temperature.

8.13.1 Fermi Temperature

It may be defined as the ratio of the Fermi energy (ϵ_F) at absolute zero to Boltzmann constant K_B .

$$\therefore \text{Fermi temperature} \quad \theta_F = \frac{\epsilon_F}{K_B} \quad \dots(8.36)$$

8.13.2 Free Electrons in a Metal

The conduction electrons in a metal may be considered as nearly free-moving in a constant potential field, like particles of an ideal gas. Electrons have half-integral spin and hence the formula of Fermi-Dirac statistics are applicable to an ideal gas electron.

Since there can be maximum of one particle per quantum state, the function $f(\epsilon)$ is the ratio of the number of the quantum state of energy ϵ occupied by electrons to the total number of quantum states available in the energy level ϵ . From Eq. (8.27) $f(\epsilon)$ is given by

$$f(\epsilon) = \frac{1}{e^{(\epsilon - \epsilon_F)/K_B T} + 1} \quad \dots(8.37)$$

The number of particles having energies in the range between ϵ and $\epsilon + d\epsilon$ is given by

$$n(\epsilon) d\epsilon = f(\epsilon) g(\epsilon) d\epsilon \quad \dots(8.38)$$

where $g(\epsilon) d\epsilon$ is the number of quantum states of energy between ϵ and $\epsilon + d\epsilon$.

Substituting the expression for $f(\epsilon)$ in Eq. (8.38), we get

$$n(\epsilon) d\epsilon = \frac{g(\epsilon) d\epsilon}{e^{(\epsilon - \epsilon_F)/K_B T} + 1} \quad \dots(8.39)$$

The energy of an electron (non-relativistic) having momentum p is

$$\epsilon = \frac{p^2}{2m}$$

So from Eq. (8.33) we can write the number of quantum states or cells lying within the energy range ϵ and $\epsilon + d\epsilon$ is given by

$$g(\epsilon) d\epsilon = \frac{8\pi V}{h^3} \sqrt{2m\epsilon} m d\epsilon \quad \dots(8.40)$$

where V is the volume of the Fermi-phase space of conductor. So from Eqs (8.39) and (8.40), we can write

$$n(\epsilon) d\epsilon = \frac{8\pi V}{h^3} \sqrt{2m\epsilon} \times \frac{1}{e^{(\epsilon - \epsilon_F)/K_B T} + 1} \quad \dots(8.41)$$

$$\text{or, } n(\epsilon) d\epsilon = \frac{8\sqrt{2}\pi V}{h^3} \frac{m^{3/2} \epsilon^{1/2} d\epsilon}{e^{(\epsilon - \epsilon_F)/K_B T} + 1}$$

This is the Fermi-Dirac law of energy distribution for free electrons in the metal.

8.13.3 Total Number of Particles and Total Energy at Absolute Zero of Temperature

At absolute zero temperature, the total number of electrons (N) is equal to the total number of energy states occupied by the electrons from 0 to ϵ_F since each energy state can have only one electron.

Therefore,

$$\begin{aligned} N &= \int_0^{\epsilon_F} n(\epsilon) d\epsilon = \int_0^{\epsilon_F} g(\epsilon) d\epsilon \quad [\text{since } f(\epsilon) = 1] \\ &= 4\pi V \left(\frac{2m}{h^2} \right)^{3/2} \int_0^{\epsilon_F} \epsilon^{1/2} d\epsilon \quad [\text{using Eq. (8.40)}] \\ N &= \frac{8\pi V}{3} \left(\frac{2m\epsilon_F}{h^2} \right)^{3/2} \end{aligned}$$

This is the expression of total number of electrons in a metal at absolute zero.

The total energy E_t of an electron at absolute zero temperature is given by

$$E_t = \int_0^{\epsilon_F} \epsilon N(\epsilon) d\epsilon = \int_0^{\epsilon_F} \epsilon g(\epsilon) d\epsilon$$

or,

$$E_t = \int_0^{\epsilon_F} \epsilon \left(\frac{8\pi V}{h^2} \right) \sqrt{2m\epsilon} (md\epsilon) \quad [\text{by Eq. 8.40}]$$

or,

$$E_t = \frac{8\sqrt{2}\pi V m^{3/2}}{h^3} \int_0^{\epsilon_F} \epsilon^{3/2} d\epsilon$$

or,

$$E_t = \frac{8\sqrt{2}\pi V m^{3/2}}{h^3} \left(\frac{2}{5} \epsilon_F^{5/2} \right)$$

or,

$$E_t = \frac{8\pi V}{3} \left(\frac{2m\epsilon_F}{h^2} \right)^{3/2} \left(\frac{3}{5} \epsilon_F \right)$$

or,

$$E_t = \frac{3}{5} N \epsilon_F \quad \left[\because N = \frac{8\pi V}{3} \left(\frac{2m\epsilon_F}{h^2} \right)^{3/2} \right]$$

Again, N is given by

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

$$\text{or, } \epsilon_F = \frac{h^2}{2m} \left(\frac{3N}{8\pi V} \right)^{2/3} \quad \dots(8.42)$$

If $n = \frac{N}{V}$ = number of free electrons per unit volume, i.e., the free electron density, then

$$\epsilon_F = \frac{h^2}{2m} \left(\frac{3n}{8\pi V} \right)^{2/3} \quad \dots(8.43)$$

This is the expression of the Fermi energy at absolute zero temperature. Equation (8.43) shows that Fermi energy depends only on electrons concentration $\left(\frac{N}{V} \right)$ and it is totally independent on the size and volume of

the conductor. The values of ϵ_F calculated from Eq. (8.43) for a number of metals are of the order of several electron volts. But according to classical statistics all electrons in a metal at absolute zero would have zero energy. Thus we see that the results of quantum statistics are appreciably different from those of classical statistics.

8.13.4 Fermi Energy at Non-Zero Temperature

The variation of ϵ_F with temperature T is given by Sommerfeld by the following equation:

$$\epsilon_F(T) = \epsilon_F(0) \left[1 - \frac{\pi^2 K_B^2 T^2}{12 \epsilon_F^2(0)} \right] \quad \dots(8.44)$$

where $\epsilon_F(T)$ and $\epsilon_F(0)$ are Fermi energy at finite temperature T and at zero temperature. The variation of ϵ_F with temperature T is shown in Fig 8.2. It is seen that as T is increased ϵ_F decreases. But the rate of decrease with temperature is very small over a large range of temperature. Hence for all practical purposes, $\epsilon_F(T)$ may be considered constant and equal to $\epsilon_F(0)$.

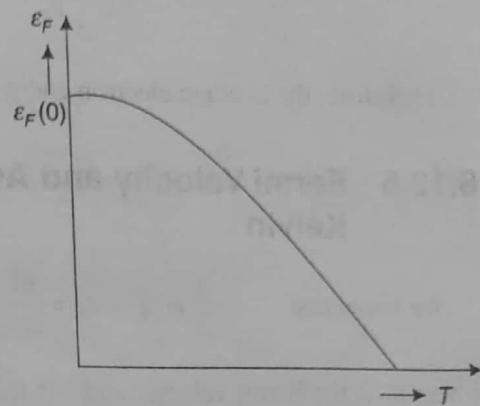


Fig. 8.2 Variation of ϵ_F with temperature for the free electrons in Cu.

8.13.5 Average Energy of Free Electrons in a Metal at Zero Kelvin

The average integral energy of free electron in a metal at absolute zero is given by

$$\begin{aligned} \bar{\epsilon} &= \frac{1}{N} \int_0^\infty \epsilon n(\epsilon) d\epsilon \quad \dots(8.45) \\ &= \frac{1}{N} \int_0^{\epsilon_F} \epsilon f(\epsilon) g(\epsilon) d\epsilon + \frac{1}{N} \int_{\epsilon_F}^\infty \epsilon f(\epsilon) g(\epsilon) d\epsilon \end{aligned}$$

Now at $T = 0$ K the value of $f(\epsilon) = 1$ if $\epsilon \leq \epsilon_F$

and at $T = 0$ K the value of $f(\epsilon) = 0$ if $\epsilon_F \geq \epsilon$

$$\text{So, } \bar{\epsilon} = \frac{1}{N} \int_0^{\epsilon_F} \epsilon g(\epsilon) d\epsilon$$

$$\text{Again } g(\epsilon) d\epsilon = 4\pi V \left(\frac{2m}{h^2} \right)^{3/2} \epsilon^{1/2} d\epsilon \quad [\text{from Eq. (8.40)}]$$

$$\begin{aligned} \text{So, } \bar{\epsilon} &= \frac{1}{N} \times 4\pi V \left(\frac{2m}{h^2} \right)^{3/2} \int_0^{\epsilon_F} \epsilon^{3/2} d\epsilon \\ &= \frac{4\pi V}{N} \left(\frac{2m}{h^2} \right)^{3/2} \times \frac{\epsilon_F^{5/2}}{5/2} \end{aligned} \quad \dots(8.46)$$

$$= \left[\frac{4\pi V}{N} \left(\frac{2m}{h^2} \right)^{3/2} \frac{2}{5} \epsilon_F^{3/2} \right] \epsilon_F$$

We know, the Fermi energy at absolute zero ($T = 0$ K)

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

or,

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

Substituting the value of $\varepsilon_F^{3/2}$ in Eq. (8.46), we have

$$\bar{\varepsilon} = \frac{3}{5} \varepsilon_F$$

Therefore, the average electron energy is equal to $\frac{3}{5}$ th of the Fermi energy at absolute zero.

8.13.6 Fermi Velocity and Average Velocity of a Free Electron at Zero Kelvin

We know that $\frac{1}{2}mv_F^2 = \varepsilon_F = \frac{h^2}{2m} \left(\frac{3n}{8\pi}\right)^{2/3}$

where v_F is the Fermi velocity and n is free electron density, i.e., $n = \frac{N}{V}$.

So $v_F = \frac{h}{m} \left(\frac{3n}{8\pi}\right)^{1/3}$

Now if \bar{v} be the average speed of an electron at 0 K, then

$$\bar{v} = \frac{1}{N} \int_0^{v_F} v n(v) dv \quad \dots(8.49)$$

where $n(v) dv$ is the number of particles within the velocity range v and $v + dv$.

Now $\varepsilon = \frac{1}{2}mv^2$ or, $d\varepsilon = mv dv$

Again at 0 K $f(\varepsilon) = 1$ if $\varepsilon \leq \varepsilon_F$

So, $n(\varepsilon) d\varepsilon = g(\varepsilon) d\varepsilon$

$$= \frac{8\pi V}{h^3} \sqrt{2m\varepsilon} m d\varepsilon$$

Therefore, $n(v) dv = 4\pi V \left(\frac{2m}{h^2}\right)^{3/2} \left(\frac{1}{2}mv^2\right)^{1/2} (mv dv)$

$$= 8\pi V \left(\frac{m}{h}\right)^3 v^2 dv.$$

So from Eq. (8.49), we have

$$\begin{aligned} \bar{v} &= \frac{1}{N} \int_0^{v_F} 8\pi V \left(\frac{m}{h}\right)^3 v^3 dv \\ &= \frac{8\pi V}{N} \left(\frac{m}{h}\right)^3 \left(\frac{v_F^4}{4}\right) \\ &= \frac{3}{4} \left(\frac{8\pi}{3n}\right) \left(\frac{m}{h}\right)^3 v_F^4 \quad \left[\text{where } \frac{N}{V} = n \text{ free electron density} \right] \end{aligned}$$

Again from Eq. (8.48)

$$v_F^3 = \left(\frac{h}{m}\right)^3 \left(\frac{3n}{8\pi}\right)$$

Hence

$$\begin{aligned} \bar{v} &= \frac{3}{4} \left(\frac{8\pi}{3h}\right) \left(\frac{m}{h}\right)^3 \left(\frac{h}{m}\right)^3 \left(\frac{3n}{8\pi}\right) v_F \\ &= \frac{3}{4} v_F \end{aligned} \quad \dots(8.50)$$

So the average speed of the electron in a metal is equal to $\frac{3}{4}$ times the Fermi velocity at absolute zero.

8.14 DERIVATION OF PLANCK'S LAW OF RADIATION FROM BE STATISTICS

Let T be the absolute temperature of a black-body chamber of volume V . The chamber is supposed to be filled with photons. Each photon has unit spin angular momentum. Hence photons are bosons and so we can use the BE statistics to derive Planck's law of radiation.

Photons are continuously emitted and absorbed by the walls of the chamber at constant temperature and constant volume. So, the number of photons is not constant. Therefore, $\sum_i n_i = \text{const.}$ or $\sum_i \delta n_i = 0$ is not valid for photon gas although the total energy of the photons remains constant. Hence the multiplier $\alpha = 0$. Thus, we have from BE distribution law [i.e., Eq. (8.20)]

$$\begin{aligned} n_i &= \frac{g_i}{e^{\beta \epsilon_i} - 1} \\ &= \frac{g_i}{e^{\epsilon_i/K_B T} - 1} \quad \text{where } \beta = \frac{1}{K_B T} \end{aligned} \quad \dots(8.51)$$

Again energy of each photon $\epsilon = hv$. So from Eq. (8.51) [omitting index i]

$$n = \frac{g}{e^{hv/K_B T} - 1}$$

The number of photon in the frequency range v and $v + dv$ is obtained by replacing g by $g(v) dv$ and n by $n(v) dv$. Hence we get from the above equation

$$n(v) dv = \frac{g(v) dv}{e^{hv/K_B T} - 1} \quad \dots(8.52)$$

where $g(v) dv$ is the number of quantum states in the frequency range v and $v + dv$.

The number of quantum states corresponding to the momenta in the range between p and $p + dp$ for particles is given by [See Eq. (8.30)]

$$g(p) dp = 2 \frac{4\pi V p^2 dp}{h^3} \quad \dots(8.53)$$

For photons of frequency v , we have

$$\text{Energy } \epsilon = hv \text{ and momentum } p = \frac{hv}{c}$$

On substituting these values in Eq. (8.53), the number of quantum states with frequency range between ν and $\nu + dv$ is given by

$$\begin{aligned} g(\nu) dv &= \frac{8\pi V \left(\frac{hv}{c}\right)^2 \frac{h}{c} dv}{h^3} \\ &= \frac{8\pi V \nu^2 dv}{c^3} \end{aligned} \quad \dots(8.54)$$

Hence, substituting the value of $g(\nu) dv$ in Eq. (8.52), we have

$$n(\nu) dv = \frac{8\pi V \nu^2 dv}{c^3} \frac{1}{e^{hv/K_B T} - 1} \quad \dots(8.55)$$

The energy of each photon = $h\nu$. The energy per unit volume or energy density, within the frequency range ν and $\nu + dv$ is given by

$$U_\nu dv = \frac{h\nu}{V} \cdot n(\nu) dv \quad \dots(8.56)$$

or,

$$\begin{aligned} U_\nu dv &= \frac{h\nu}{V} \cdot \frac{8\pi V \nu^2 dv}{c^3} \frac{1}{e^{hv/K_B T} - 1} \\ &= \frac{8\pi h \nu^3}{c^3} \frac{dv}{e^{hv/K_B T} - 1} \end{aligned} \quad \dots(8.57)$$

This is Planck's law of radiation in terms of the frequency ν . In terms of λ , Eq. (8.57) can be written as

$$U_\lambda d\lambda = \frac{8\pi hc}{\lambda^5} \frac{d\lambda}{e^{hc/\lambda K_B T} - 1} \quad \dots(8.58)$$

This is Planck's law of radiation in terms of the wavelength λ . On longer wavelength side ($\frac{hc}{\lambda} \ll K_B T$),

Eq. (8.58) becomes

$$U_\lambda d\lambda = \frac{8\pi K_B T}{\lambda^4} d\lambda \quad \dots(8.59)$$

This is the Rayleigh-Jeans formula.

On shorter wavelength side $\frac{hc}{\lambda} \gg K_B T$, Eq. (8.58) becomes

$$U_\lambda d\lambda = \frac{8\pi hc}{\lambda^5} e^{-hc/\lambda K_B T} d\lambda \quad \dots(8.60)$$

This is the Wien radiation formula.

8.15

COMPARATIVE STUDY OF THREE STATISTICAL DISTRIBUTION FUNCTIONS

	<i>MB</i>	<i>BE</i>	<i>FD</i>
Nature of particles	Identical, distinguishable,	Identical, indistinguishable	Identical, indistinguishable
Category of particles	classical (called boltzons)	(called bosons)	(called fermions)
Properties of particles	Any spin, particles adequately far apart so wave functions do not overlap	0 or integral spin (1, 2, 3, 4, ... etc.), wave functions are symmetric under interch- ange of two bosons	Half integral spin (1/2, 3/2/ 5/2,), wavefunctions are antisym- metric under interchange of two fermions
Examples	Examples: molecules of a gas	Examples: Photon, meson, muon	Examples: Proton, electron, neutron
Distribution Function	$f_{MB} = \frac{1}{e^{\alpha + \beta \epsilon_i}}$	$f_{BE} = \frac{1}{e^{\alpha + \beta \epsilon_i} - 1}$	$f_{FD} = \frac{1}{e^{\alpha + \beta \epsilon_i} + 1}$
No. of particles per energy state	No upper limit	No upper limit	Fermions obey the Pauli exclusion principle, i.e., maximum of one particle per quantum state

Worked Out Problems

Example 8.1 Distribute two particles in three different states according to (i) MB Statistics, (ii) BE statistics, and (iii) FD Statistics.

Sol. ***MB Statistics***

Since the particles are distinguishable, so total number of microstates will be

$$W = \frac{N! g_i^{n_i}}{n_i!} = 2! \frac{3^2}{2!} = 9 \text{ microstates} \quad [g_i = 3, n_i = 2, N = 2]$$

In table form:

Here *A*, *B* are two distinguishable particles.

<i>1</i>	<i>2</i>	<i>3</i>
<i>AB</i>	0	0
0	<i>AB</i>	0
0	0	<i>AB</i>
<i>A</i>	<i>B</i>	0
<i>B</i>	<i>A</i>	<i>B</i>
0	<i>A</i>	0
0	<i>B</i>	<i>A</i>
<i>A</i>	0	
<i>B</i>	0	

So total number of microstates is 9.

BE Statistics

Since the particles are indistinguishable, so total number of microstates will be

$$W = \frac{(n_i + g_i - 1)!}{n_i! (g_i - 1)!} = \frac{(2+3-1)!}{2! (3-1)!} = \frac{4!}{2! 2!} = \frac{4 \cdot 3 \cdot 2 \cdot 1}{2 \cdot 2} = 6 \text{ microstates}$$

In table form:

Here, the two particles are indistinguishable. Let us denote them both as A.

1	2	3
AA	0	0
0	AA	0
0	0	AA
A	0	A
0	A	A
A	A	0

So total number of microstates is 6.

FD Statistics

Since the particles are indistinguishable and according to the Pauli exclusion principle each state can accommodate only one particle so total number of microstates will be

$$W = \frac{g_i!}{n_i! (g_i - n_i)!} = \frac{3!}{2! (3-2)!} = 3 \text{ microstates} \quad [g_i = 3, n_i = 2]$$

In table form:

Here, the two particles are indistinguishable. Let us denote them both as A.

1	2	3
A	0	0
0	A	0
0	0	A

So total number of microstates is 3.

Example 8.2

Three distinguishable particles each of which can be in one of the $\epsilon, 2\epsilon, 3\epsilon, 4\epsilon$ energy states have total energy 6ϵ . Find all possible number of distributions of all particles in the energy states. Find the number of microstates in each case.

[WBUT 2007]

Sol. Let the particles be A, B and C. Particles are distinguishable. The possible microstates will be

Macrostate	ϵ	2ϵ	3ϵ	4ϵ	Total energy	Microstates
(2, 0, 0, 1)	AB	0	0	C	6ϵ	3
	AC	0	0	B	6ϵ	
	BC	0	0	A	6ϵ	
(0, 3, 0, 0)	0	ABC	0	0	6ϵ	1

(1, 1, 1, 0)	A	B	C	0	6 ϵ	
	B	C	A	0	6 ϵ	
	C	A	B	0	6 ϵ	
	B	A	C	0	6 ϵ	6
	A	C	B	0	6 ϵ	
	C	B	A	0	6 ϵ	

So, total number of microstates = 10 and total number of macrostates = 3.

Example 8.3 A system has non-degenerate single-particle states with 0, 1, 2, 3 energy units. Three particles are to be distributed in these states so that the total energy of the system is 3 units. Find the number of microstates if the particles obey (i) MB Statistics, (ii) BE Statistics, and (iii) FD Statistics.

Sol. (i) *MB Statistics*

[WBUT 2008, 2012]

Since the particles are distinguishable, let the particles be A, B, C. The possible microstates will be

Macrostate	0 ϵ	1 ϵ	2 ϵ	3 ϵ	Total energy	Microstates
(0, 3, 0, 0)	0	ABC	0	0	3 ϵ	1
(2, 0, 0, 1)	AB	0	0	C	3 ϵ	3
	AC	0	0	B	3 ϵ	
	BC	0	0	A	3 ϵ	
(1, 1, 1, 0)	A	B	C	0	3 ϵ	6
	A	C	B	0	3 ϵ	
	B	A	C	0	3 ϵ	
	B	C	A	0	3 ϵ	
	C	A	B	0	3 ϵ	
	C	B	A	0	3 ϵ	

So, total number of microstates = 10

(ii) *BE Statistics*

Since the particles are indistinguishable. Let us denote them as A.

Macrostate	0 ϵ	1 ϵ	2 ϵ	3 ϵ	Total energy	Microstates
(0, 3, 0, 0)	0	AAA	0	0	3 ϵ	1
(2, 0, 0, 1)	AA	0	0	A	3 ϵ	1
(1, 1, 1, 0)	A	A	A	0	3 ϵ	1

So, total number of microstates = 3

(iii) *FD Statistics*

Since the particles are indistinguishable and according to the Pauli principle, each state can accommodate only one particle, so total number of microstates will be

Macrostate	0	ϵ	2ϵ	3ϵ	Total energy	Microstates
(1, 1, 1, 0)	A	A	A	0	3ϵ	1

So total number of microstates = 1

Example 8.4 Consider a two-particle system, each of which can exist in states ϵ_1 , ϵ_2 , and ϵ_3 . What are the possible states if the particles are (i) bosons, and (ii) fermions ? [WBUT 2006]

Sol. (i) *BE Statistics*

Particles are indistinguishable and any number of particles can be accommodated in one quantum state. Let us denote them as A.

ϵ_1	ϵ_2	ϵ_3	Microstates
AA	0	0	1
0	AA	0	1
0	0	AA	1
A	A	0	1
0	A	A	1
A	0	A	1

So, total number of microstates = 6

(ii) *FD Statistics*

Particles are indistinguishable and one state can accommodate only one particle.

ϵ_1	ϵ_2	ϵ_3	Microstates
A	0	A	1
0	A	A	1
A	A	0	1

So, total number of microstates = 3

Example 8.5 Six distinguishable particles are distributed over three non-degenerate levels of energies 0, ϵ and 2ϵ . Calculate the total number of microstates of the system. Find the total energy of the distribution for which the probability is maximum.

Sol. There is only one state associated with non-degenerate energy levels. Let N_1 , N_2 and N_3 be the number of the particles in three energy states. The total number of particles $N_1 + N_2 + N_3 = 6$ (given). As the particles are distinguishable, the number of microstates, i.e., the number of ways of choosing N_1 , N_2 and N_3 particles from 6 particles is

$$W = \frac{6}{N_1! N_2! N_3!}$$

where W is the thermodynamical probability. The probability will be maximum when $N_1! N_2! N_3!$ is minimum. This is true when $N_1 = N_2 = N_3 = 2$. The corresponding total energy distribution is $0 \times N_1 + \epsilon \times N_2 + 2\epsilon \times N_3 = 2\epsilon + 4\epsilon = 6\epsilon$.

Example 8.6 Evaluate the temperature at which there is one per cent probability that a state, with an energy 0.5 eV above the Fermi energy will be occupied by an electron.

Sol. The FD distribution is $f(\varepsilon) = \frac{1}{e^{(\varepsilon - \varepsilon_F)/K_B T} + 1}$

ε_F is the Fermi energy

K_B = Boltzmann constant

Given $\varepsilon = (\varepsilon_F + 0.5)$ eV

$$\text{Thus, } f(\varepsilon) = \frac{1}{100} = \frac{1}{1 + e^{0.5/K_B T}}$$

$$\text{or, } 0.01 = \frac{1}{1 + e^x} \quad \text{where } x = \frac{0.5}{K_B T}$$

$$\text{or, } 0.01 + 0.01e^x = 1$$

$$\text{or, } e^x = \frac{0.99}{0.01} = 99$$

$$\text{or, } x = 2.303 \log_{10} 99 = \frac{0.5}{K_B T}$$

$$\text{So, } T = \frac{0.109 \times 1.6 \times 10^{-19}}{1.38 \times 10^{-23}} = 1264 \text{ K}$$

Example 8.7 Calculate the Fermi energy at 0 K of metallic silver containing one free electron per atom. The density and atomic weight of silver is 10.5 g/cm³ and 108 respectively.

$$\text{Sol. Fermi energy } \varepsilon_F = \frac{\hbar^2}{2m} \left(\frac{3N}{8\pi V} \right)^{2/3}$$

$$\text{Here } \frac{N}{V} = \frac{6.02 \times 10^{23}}{108} \times 10.5 \\ = 5.9 \times 10^{28} \text{ m}^{-3}$$

$$\text{So, } \varepsilon_F = \frac{(6.6 \times 10^{-34})^2}{2 \times 9.1 \times 10^{-31}} \times \left(\frac{3}{8 \times 3.14} \times 5.9 \times 10^{28} \right)^{2/3} \\ = 8.8 \times 10^{-19} \text{ Joules} = \frac{8.8 \times 10^{-19}}{1.6 \times 10^{-19}} \text{ eV} \\ = 5.5 \text{ eV}$$

Example 8.8 The Fermi energy of silver is 5.51 eV (i) What is the average energy of the free electrons in silver at 0 K? (ii) What is the speed of the electron corresponding to the above average energy?

Sol. The average electron energy at 0 K is

$$\bar{\varepsilon} = \frac{3}{5} \varepsilon_F \\ = \frac{3}{5} \times 5.51 = 3.306 \text{ eV.}$$

If v is the velocity of the electron, then its kinetic energy

$$\frac{1}{2}mv^2 = 3.306 \times 1.6 \times 10^{-19}$$

or,

$$v = \left(\frac{2 \times 3.306 \times 1.6 \times 10^{-19}}{9.1 \times 10^{-31}} \right)^{1/2} \text{ m/s}$$

$$= (1.16 \times 10^{12})^{1/2} = 1.08 \times 10^6 \text{ m/s}$$

Example 8.9 Consider a free electron gas at zero degree Kelvin and show that the de Broglie wavelength associated with an electron is given by

$$\lambda_F = 2 \left(\frac{\pi}{3n_0} \right)^{1/3}$$

where n_0 is the number of electrons per c.c. of the gas.

Sol. The momentum (p) of the electrons is given by

$$p = \sqrt{2m\varepsilon_F}$$

$$\text{But } \varepsilon_F = \frac{h^2}{2m} \left(\frac{3N}{8\pi V} \right)^{2/3}$$

Again, de Broglie wavelength λ_F is given by

$$\begin{aligned} \lambda_F &= \frac{h}{p} \\ &= \frac{h}{\sqrt{2m\varepsilon_F}} = \frac{h}{\sqrt{2m \frac{h^2}{2m} \left(\frac{3N}{8\pi V} \right)^{2/3}}} \\ &= \sqrt{\left(\frac{8\pi V}{3N} \right)^{2/3}} = 2 \left(\frac{\pi V}{3N} \right)^{1/3} \\ &= 2 \left(\frac{\pi}{3n_0} \right)^{1/3} \quad \left[\text{where } n_0 = \frac{N}{V} \right] \end{aligned}$$

Example 8.10 Estimate the temperature of the sun, if λ_m for the sun is 490 nm.

Sol. From Wien's displacement law of radiation, we know that

$$\lambda_m T = 0.2896$$

$$\text{Here, } T = \frac{0.2896}{\lambda_m} = \frac{0.2896}{490 \times 10^{-9}} \approx 5910 \text{ K}$$

So, the temperature of the sun is 5910 K.

Example 8.11 The Fermi energy for sodium at $T = 0$ K is 3.1 eV. Find its value for aluminum, given that the free electron density in aluminum is approximately 7 times that in sodium.

$$\frac{\text{Electron density in Al}}{\text{Electron density in Na}} = \frac{n_2}{n_1} = 7$$

For Na, Fermi energy $\epsilon_{F_1} = \frac{h^2}{2m} \left(\frac{3n_1}{8\pi} \right)^{2/3}$... (1)

For Al $\epsilon_{F_2} = \frac{h^2}{2m} \left(\frac{3n_2}{8\pi} \right)^{2/3}$... (2)

Dividing Eq. (2) by Eq. (1)

$$\frac{\epsilon_{F_2}}{\epsilon_{F_1}} = \left(\frac{n_2}{n_1} \right)^{2/3} = (7)^{2/3}$$

so,

$$\begin{aligned}\epsilon_{F_2} &= \epsilon_{F_1} \times 7^{2/3} = 3.1 \times 3.66 \\ &= 11.35 \text{ eV.}\end{aligned}$$

Review Exercises

Part 1: Multiple Choice Questions

1. Statistical methods give greater accuracy when the number of observations is
 - very large
 - very small
 - average
 - None of these
2. The relation between entropy and thermodynamical probability is given by
 - $S = \ln W$
 - $S = e^W$
 - $S = K_B \ln W$
 - None of these
3. The dimension of phase space volume are
 - (length \times momentum)³
 - (time \times momentum)³
 - (energy \times time)³
 - Both (a) and (c) are true
4. The number of macrostates for N particles in MB distribution are
 - N
 - $\frac{N}{2}$
 - $N + 1$
 - None of these
5. The number of macrostates for N particles in two compartments obeying MB statistics are
 - $\frac{N}{2}$
 - $N + 1$
 - 2^N
 - $N - 1$
6. The number of possible arrangements of two fermions in 3 cells is [WBUT 2008]
 - 9
 - 6
 - 3
 - 1
7. If n_i is the number of identical and indistinguishable particles in the i^{th} energy state with degeneracy g_i then classical statistics can be applied if [WBUT 2008]
 - $\frac{n_i}{g_i} = 1$
 - $\frac{n_i}{g_i} \ll 1$
 - $\frac{n_i}{g_i} \gg 1$
 - $g_i = 0$
8. A coin and a six-faced dice are thrown. The probability that the coin shows tail and the dice shows five is [WBUT 2005]
 - $\frac{7}{12}$
 - $\frac{1}{8}$
 - $\frac{1}{12}$
 - $\frac{1}{6}$

9. Fermi-Dirac distribution approaches Maxwell-Boltzmann distribution at
 (a) low temperature and high pressure (b) low temperature and low particle mass
 (c) high temperature and high particle mass (d) high density and low energy range
10. MB statistics is applicable for
 (a) ideal gas (b) electron (c) proton (d) photon
11. Amongst the following statements, which one is wrong? [WBUT 2006]
 (a) Maxwell-Boltzmann statistics deal with distinguishable particles.
 (b) Fermi-Dirac Statistics deal with indistinguishable particles.
 (c) Bose-Einstein statistics deal with indistinguishable particles.
 (d) Bosons are subjected to the Pauli exclusion principle.
12. Which one of the following are bosons?
 (a) Photon (b) Phonon (c) Electron (d) Both (a) and (b)
13. The spin angular momentum of photon
 (a) \hbar (b) $\frac{\hbar}{8}$ (c) 0 (d) $2\hbar$
14. The FD distribution function is expressed as
 (a) $f(\varepsilon) = \frac{1}{e^{(\varepsilon - \varepsilon_F)/K_B T} + 1}$ (b) $f(\varepsilon) = \frac{1}{e^{(\varepsilon - \varepsilon_F)/K_B T} - 1}$
 (c) $f(\varepsilon) = \frac{1}{e^{(\varepsilon - \varepsilon_F)/K_B T}}$ (d) None of these
15. Average energy $\bar{\varepsilon}$ of an electron in a metal at $T = 0$ K is [WBUT 2007]
 (a) ε_F (b) $\frac{1}{2} \varepsilon_F$ (c) $\frac{3}{5} \varepsilon_F$ (d) $\frac{5}{3} \varepsilon_F$
16. Which one of the following is a fermion?
 (a) Photon (b) Electron (c) Phonon (d) α particle
17. The number of ways in which 4 fermions can be arranged in 5 compartments is
 (a) 3 (b) 7 (c) 5 (d) 9
18. Planck's radiation law for black-body radiation can be derived from
 (a) MB statistics (b) FD statistics (c) BE statistics (d) None of these
19. The rest mass of the photon is
 (a) same as that of electron (b) zero
 (c) infinity (d) None of these
20. The maximum energy that can be occupied by an electron at $T = 0$ K is
 (a) Fermi energy (b) Bohr energy (c) chemical potential (d) None of these
21. The mathematical formula for Fermi energy at 0 K is
 (a) $\frac{\hbar^2}{8\pi V} \left(\frac{3N}{2m} \right)^{2/3}$ (b) $\frac{8\pi V}{\hbar^2} \left(\frac{3N}{2m} \right)^{2/3}$ (c) $\frac{\hbar^2}{2m} \left(\frac{3N}{8\pi V} \right)^{2/3}$ (d) None of these

22. A perfect black body is one that

 - (a) reflects all radiation
 - (b) absorbs all radiation
 - (c) transmits all radiation
 - (d) None of these

23. For $T > 0$ K, the probability of occupancy of an electron at Fermi energy level

 - (a) 1
 - (b) 0
 - (c) $\frac{1}{2}$
 - (d) 2

[Ans. 1 (a), 2 (c), 3 (d), 4 (c), 5 (c), 6 (c), 7 (b), 8 (c), 9 (c), 10 (a), 11 (d), 12 (d), 13 (a), 14 (a), 15 (c), 16 (b), 17 (c), 18 (c), 19 (b), 20 (a), 21 (c), 22 (b), 23 (c)]

Short Questions with Answers

1. Define macrostate and microstate.

Ans. Refer to Section 8.4

- ## 2. Define thermodynamical probability.

Ans. Refer to Section 8.5

- ### 3. Define phase space.

Ans. Refer to Section 8.2

- #### 4. What is an ensemble?

Ans. The collection of very large number of identical interacting macroscopic systems is called an ensemble. There are three types of ensemble (i) micro canonical ensemble – systems cannot exchange energy or matter with each other. N , V and E remain constant, (ii) Canonical ensemble – systems can exchange energy but not matter with each other. N , V and T remain constant. (iii) Grand canonical ensemble – systems can exchange both energy and matter with each other. μ , V and T remain constant, where μ is the chemical potential.

- ### 5. What is the most probable distribution?

Ans. The most probable distribution of the particles among the energy states in equilibrium is that for which the probability of occurrence is maximum. For mathematical convenience, we consider the condition for maximum value of $\ln W$. The condition for most probable distribution is

$$d \ln W = 0.$$

- ## 6. What are the limitations of MB statistics?

Ans. MB statistics are applicable only to an isolated gas of identical molecules in equilibrium. The expression for MB distribution does not give a correct expression for the entropy of an ideal gas. MB statistics cannot be applied to a system of indistinguishable particles.

7. Why may the number of photons inside an enclosure not remain constant?

Ans. The total energy of photons inside an enclosure remains constant but the total number of photons at particular temperature T may not remain constant. Photons may be absorbed and emitted by the walls of the container without any restriction. Suppose a photon of energy $2hv$ may be absorbed by the wall and two photons each of energy hv may be emitted. So the photon may be destroyed and created, i.e., the number of photons inside an enclosure may not remain constant.

Part 2: Descriptive Questions

1. Define (i) Phase space, (ii) Macrostate, and (iii) Microstate.

2. Define thermodynamical probability. Obtain a relation between entropy and thermodynamical probability.
 3. Three distinguishable particles, each of which can be in one of the $\varepsilon, 2\varepsilon, 3\varepsilon, 4\varepsilon$ energy states having total energy 6ε . Find all possible distributions of particles in energy states. Find the number of microstates in each case. [WBUT 2007]
 4. What are fermions and bosons? Give two examples of each. [WBUT 2004]
 5. (a) Sketch the Fermi distribution for $T = 0$ K and $T > 0$ K and explain.
 (b) What is the occupation probability at $\varepsilon = \varepsilon_F$?
 (c) Calculate how the degeneracy function $g(\varepsilon)$ depends on ε for a fermionic gas.
 (d) Express the Fermi level in a metal in terms of free electron density. [WBUT 2008]
 6. (a) Compare MB, BE and FD statistics mentioning at least three characteristics.
 (b) Draw the Fermi distribution curve for (i) $T = 0$ K and (ii) $T > 0$ K. Explain their significance.
 (c) Indicate which statistics will be applicable for
 (i) ${}_1\text{H}^1$ (ii) e^- (iii) π^0 (iv) photon [WBUT 2005]
- [Ans. (i) FD (ii) FD (iii) BE (iv) BE]
7. (i) What do you mean by Fermi energy? Show that it is independent of temperature.
 (ii) Prove that at 0 K the average energy is $\frac{3}{5} \varepsilon_F$.
 8. Calculate the total number of particles in a fermionic gas in terms of the Fermi level at absolute zero temperature. [WBUT 2007]
 9. Give an expression of BE statistics and hence obtain Planck's formula for black-body radiation. [WBUT 2002]

Part 3: Numerical Problems

1. Consider a two-particle system, each of which can exist in states $\varepsilon_1, \varepsilon_2, \varepsilon_3$. What are the possible states, if the particles are (i) bosons, and (ii) fermions? [WBUT 2006] [Ans. 6, 3]
2. Three identical particles can be in any of the five states. What are the number of possible ways of distributing them in various states according to MB, FD and BE statistics? [Ans. 125, 10, 35]
3. Assume in tungsten (at. wt = 183.8, density = 17.3 g/cc) there are two free electrons per atom. Calculate the Fermi energy and electron density. [Ans. 7.2 eV, 1.264×10^{23} /cc]
4. Find the Fermi level at absolute zero for Cu. Given that molar mass of Cu, $M = 63.55 \times 10^{-3}$ kg/mol. Its density $\rho = 8.93 \times 10^3$ kg/m³. Avogadro's number $N = 6.023 \times 10^{23}$ /mol. $h = 6.63 \times 10^{-34}$ Js. Mass of electron $m = 7.1 \times 10^{-31}$ kg. [Ans. 7.03 eV]
5. Find the Fermi temperature for the valance electrons in Cu. Given ε_F for copper = 7.03 eV. Boltzmann constant $K_B = 1.38 \times 10^{-23}$ J/K. [Ans. 81.5×10^3 K]
6. For silver, the electron concentration $\left(\frac{N}{V}\right)$ is 5.86×10^{28} m⁻³. Find its Fermi energy. [Ans. 5.511 eV]
7. Determine the wavelength λ_m corresponding to the maximum emissivity of a black body at temperature T equal to 300 K. [Ans. 9660 nm]