

## STATISTICAL MECHANICS

Up to the end of seventeenth century, all the observed physical phenomena were explained by using either ordinary laws of mechanics or laws of electromagnetism. But with the help of these ordinary laws, systems with many particles can't be handled due to mathematical complications. Moreover, in the last decade of seventeenth century there were some ground-breaking experiments, such as black-body radiation, which needed new theories for their explanation. As a result of these needs quantum theory came. When this theory ties its knot with statistics, we get a new branch of physics known as Statistical Mechanics capable of explaining the physical behaviour of all the systems whether composed of a single particle or composed of a large number of particles.

Statistical mechanics is basically a formalism that aims at explaining the observed physical properties of matter in bulk on the basis of dynamical behaviour of its microscopic constituents. It is applicable to any physical system in any state whatsoever. It is not concerned with the actual motion of the particles constituting a system; rather it investigates some average or most probable properties of the system without going through detail description of the constituent particles. It is noteworthy about statistical mechanics that the larger is the number of particles in a mechanical system, the more correct are the statistical predictions about the system and vice-versa. Before starting the various formalisms in statistical mechanics, let us discuss a few general considerations regarding the statistical nature of a macroscopic (observable with naked eyes) system.

### Macrostates and Microstates

Let us consider a physical system composed of  $N$  identical particles confined to a space of volume  $V$ . Typically  $N \sim 10^{23}$  for which it is customary to use *thermodynamic limit*, i.e.  $N \rightarrow \infty$ ,  $V \rightarrow \infty$ , but  $N/V$  ratio gives a finite value. In this limit, the extensive properties of the system are directly proportional to either  $N$  or  $V$ . But the intensive properties remain independent of these (i.e.  $N$  or  $V$ ). If we assume that the particles under consideration are non-interacting, the total energy  $E$  would be equal to the sum of energies  $\epsilon_i$  of the particles, i.e.,

$$E = \sum n_i \epsilon_i \dots \dots \dots (1)$$

Where  $n_i$  is the number of particles with energy  $\epsilon_i$ . Also the total number of particles is

$$N = \sum n_i \dots \dots \dots (2)$$

Under these conditions, a *macrostate* can be defined as the specification of the actual values of the system parameters  $N, V$  and  $E$ .

At the microscopic level, however, there is a large number of independent possibilities in which the macrostate  $(N, V, E)$  of the given system can be realized. In case of a non-interacting system, since the total energy  $E$  consists of a simple sum of the  $N$  single-particle energies  $\epsilon_i$ , there will obviously be a large number of different ways in which the individual  $\epsilon_i$  can be chosen so as to make the total energy equal to  $E$ . In other words, for a specific volume  $V$  of the system composed of specific number ( $N$ ) of particles, there will be a large number of different ways in which the total energy  $E$  of the system can be distributed among the  $N$  particles constituting the system. Each of these (different) ways specifies a *microstate* (or, *complexion*) of the given system. Thus corresponding to a particular macrostate, we have a large number of accessible microstates. At any time  $t$ , the macrostate of the system is *equally likely* to be in any one of its microstates which are consistent with the constrained

conditions of the given system. This assumption forms the very basis of statistical mechanics and is known as the *postulate of “equal a priori probabilities”* for all accessible microstates of the system.

The total number of accessible (i.e., consistent with the constrained conditions of the given system) microstates corresponding to a system (macrostate) is known as the *thermodynamic probability* of the system and it is generally denoted by a symbol  $\Omega(N, V, E)$ . There is a certain distinction between thermodynamic probability and mathematical probability. Mathematical probability is always less than unity, whereas thermodynamic probability (total number of microstates) is equal or more than unity. If  $S$  represents the entropy of the system,  $S$  is related to  $\Omega$  by the relation  $S = k \log_e \Omega$ .

### **Concepts of Phase-space and Density of states**

In Hamiltonian formalism in classical mechanics, we used the idea of specification of the state of a system with the help of position and momentum coordinates associated with the system. Suppose, we have a single-particle system. The instantaneous position of the system can be specified by three independent coordinates  $x, y, z$  and the instantaneous motion of the system is described conveniently by three momentum components  $p_x, p_y, p_z$ . Therefore the state of the single-particle system is then completely specified by position components  $x, y, z$  and momentum components  $p_x, p_y, p_z$ . Thus we can imagine a six dimensional space to describe the dynamical state of a single-particle system. Such a space is known as  $\mu$ -space. Now if the system contains a large number of particles such that the state of the system is represented by  $n$  independent position coordinates  $q_1, q_2, \dots, q_n$  and  $n$  independent momentum coordinates  $p_1, p_2, \dots, p_n$ , then mathematically these  $2n$  position-momentum coordinates may be allowed to define a  $2n$  dimensional space known as *phase-space* or  $\Gamma$ -space. The  $\mu$ -space is a special case of the phase-space. The instantaneous state of a system in the phase-space is represented by a point known as *phase point* or *representative point*. The number of phase points per unit volume of the phase-space is called *phase density*. The volume occupied by each phase point is known as *phase cell* which is the elementary volume in phase space. The time evolution of the state of the system can be incorporated in phase-space by movement of the same phase point in the phase-space. If we connect the instantaneous positions of the phase point in various times by some imaginary line, we get a curve known as *phase trajectory*. A phase trajectory can't intersect itself; otherwise the single point of intersection would denote two different states at two different times for the same system, which is physically unacceptable. A system (macrostate) is said to be in statistical equilibrium if the probabilities of finding the phase points in various regions of the phase-space and the average values of the properties of the system are independent of time.

In the context of phase-space there is a very fundamental statistical quantity – ***density of states which can be defined as the number of states per unit energy range.***

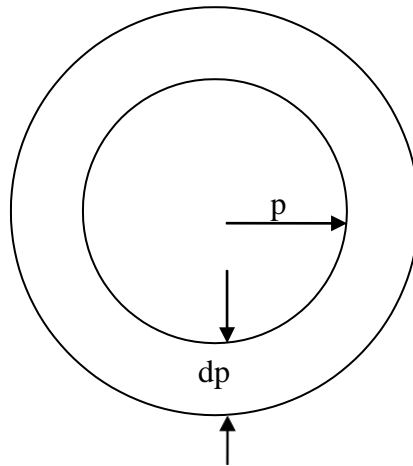
Let us calculate this for a single particle of mass  $m$  and volume  $V$ . The elementary phase volume for a single particle can be written as

$$dq_x dq_y dq_z dp_x dp_y dp_z = h^3 . \quad (\text{as } dq_i \cdot dp_i = h)$$

which is the volume of a phase cell( phase point) in phase-space. So the total volume of the phase-space is

$$\int \int \int \int \int \int dq_x dq_y dq_z dp_x dp_y dp_z$$

But  $\int \int \int dq_x dq_y dq_z = \int \int \int dx dy dz = \text{given volume } V \text{ of the particle.}$  Thus the phase



volume =  $V \int \int \int dp_x dp_y dp_z$ . Now the volume of the momentum space containing momentum between  $p$  and  $p+dp$  will be given by the volume of a spherical shell of radius  $p$  and thickness  $dp$ . Therefore,

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

Thus the volume of phase-space =  $V \cdot 4 \pi p^2 dp$

But the volume of a phase cell =  $h^3$

Therefore, total number of phase cells (microstates) in the momentum range from  $p$  to  $p+dp$  is

$$g(p)dp = V \cdot 4 \pi p^2 dp / h^3 \dots\dots\dots(3)$$

If the energy corresponding to momentum  $p$  is  $E$ ,  $E = p^2/2m$ , or  $p = (2mE)^{1/2} \dots\dots\dots(4)$

Thus total number of microstates in the energy range from  $E$  to  $E+dE$  is

$$g(E)dE = \frac{1}{h^3} 4\sqrt{2} \pi V m^{3/2} E^{1/2} dE \dots\dots\dots(5)$$

For particles having two allowed values of spin quantum number  $m_s$  (for example electron), the number of available quantum states is 2 times that given by equations (3) and (4). Also for such particles density of states becomes twice that given by eqn. (5), which is

$$g(E)dE = \frac{1}{h^3} 8\sqrt{2} \pi V m^{3/2} E^{1/2} dE \dots\dots\dots(5a)$$

### **Different formalisms in Statistical Mechanics**

The various methods of statistical mechanics are applied to discuss some average or most probable properties of large assemblies of electrons, atoms, molecules etc. Before the advent of quantum mechanics, Maxwell, Boltzmann, Gibbs etc, applied statistical methods with the help of classical physics. These methods are collectively known as **Classical Statistics or Maxwell-Boltzmann (MB) Statistics**. These statistics were proved to be successful in explaining pressure, temperature etc. of gaseous systems. But these couldn't explain some experimental results like the energy distribution in case of black-body radiation, specific heat at low temperature etc. For explaining such phenomena Satyen Bose, Albert Einstein, Enrico Fermi, Paul A. Dirac had made use of some new statistics with the help of newly discovered quantum theories. The new statistics are known as Quantum Statistics and can be divided into following two categories:-

(i) **Bose-Einstein (BE) statistics** (ii) **Fermi-Dirac (FD) statistics**

We'll discuss the various interesting features of these three (MB, BE, FD) statistics one by one in the following subsections.

## Maxwell-Boltzmann (MB) Statistics

The basic postulates of MB statistics are:-

- (i) The associated particles are distinguishable.
- (ii) Each energy state can contain any number of particles.
- (iii) Total number of particles in the entire system is constant.
- (iv) Total energy of all the particles in the entire system is constant.
- (v) Particles are spinless.

Examples: gas molecules at high temperature and low pressure.

Consider a system composed of  $N$  distinguishable, non-interacting particles. Let out of these  $N$  particles  $N_1, N_2, \dots, N_i$  particles are to be distributed in energy levels  $E_1, E_2, \dots, E_i$  respectively and these energy levels have  $g_1, g_2, \dots, g_i$  number of quantum states correspondingly. Since the total energy  $E$  and total number of particles  $N$  are constant for the system, we can write

$$\sum_i N_i E_i = E \dots \dots \dots (6)$$

$$\sum_i N_i = N \dots \dots \dots (7)$$

The number of ways in which the groups of particles  $N_1, N_2, \dots, N_i$  could be chosen from  $N$  particles is

$$W_1 = \frac{N!}{N_1! N_2! N_3! \dots N_n!} = \prod_i^n \frac{N!}{N_i!} \dots \dots \dots (8)$$

Where  $\prod$  denotes the product.

Now,  $N_i$  particles can be distributed in  $g_i$  states in  $(g_i)^{N_i}$  ways. Considering all the values of  $i$ , total number of arrangement would be

$$W_2 = \prod_i^n g_i^{N_i} \dots \dots \dots (9)$$

Therefore, the total number of ways  $W$  by which all the  $N$  particles could be distributed among the quantum states is

$$W = W_1 W_2 = \prod_i^n g_i^{N_i} \prod_i^n \frac{N!}{N_i!} \dots \dots \dots (10)$$

This is the Maxwell-Boltzmann distribution law for  $n$  distinguishable particles.

Now the Maxwell-Boltzmann distribution function can be given by,

$$f(E_i) = \frac{N_i}{g_i} = \frac{1}{e^{(\alpha + \beta E_i)}} \dots \dots \dots (11)$$

## Bose- Einstein (BE) Statistics

The basic postulates of BE statistics are:-

- (i) The associated particles are identical and *indistinguishable*.
- (ii) Each energy state can contain any number of particles.
- (iii) Total energy and total number of particles of the entire system is constant
- (iv) The particles have zero or integral spin, i.e.  $0\hbar, 1\hbar, 2\hbar, 5\hbar$  etc, where  $\hbar$  is the unit of spin.
- (v) The wave function of the system is symmetric under the positional exchange of any two particles.

Examples: photon, phonon, all mesons ( $\pi, \kappa, \eta$ ) etc., these are known as **Bosons**.

**[Note:** Symmetric and Anti-symmetric wave function

Suppose the allowed wave function for a  $n$ -particles system is  $\psi(1, 2, 3, \dots, r, s, \dots, n)$ , where the integers within the argument of  $\psi$  represent the coordinates of the  $n$ -particles relative to some fixed

origin. Now, if we interchange the positions of any two particles, say,  $r$  and  $s$ , the resulting wave function becomes  $\psi(1,2,3,\dots,s,r,\dots,n)$ . The wave function  $\psi$  is said to be symmetric when  $\psi(1,2,3,\dots,r,s,\dots,n) = \psi(1,2,3,\dots,s,r,\dots,n)$  and

anti-symmetric when  $\psi(1,2,3,\dots,r,s,\dots,n) = -\psi(1,2,3,\dots,s,r,\dots,n)$

#### Bose-Einstein Distribution Law:

Let  $N_i$  number of identical, indistinguishable, non-interacting particles are to be distributed among  $g_i$  quantum states each having energy  $E_i$ . So, in the  $i^{\text{th}}$  energy level, there are  $(N_i + g_i)$  total objects. Keeping the first quantum state fixed, the remaining  $(N_i + g_i - 1)$  objects can permute in  $(N_i + g_i - 1)!$  possible ways. But since the particles and the quantum states are indistinguishable, we have to deduct  $N_i!$  ways and  $(g_i - 1)!$  ways from the all possible ways to get effective number of arrangements. Thus total number of possible ways of arrangement for the  $i^{\text{th}}$  state is

$$W_i = \frac{(N_i + g_i - 1)!}{N_i! (g_i - 1)!} \dots \dots \dots (12)$$

Hence the total number of ways of the entire distribution of  $N$  particles in  $n$  number of energy levels of the system is

$$W = \prod_i^n \frac{(N_i + g_i - 1)!}{N_i! (g_i - 1)!} \dots \dots \dots (13)$$

Now the Bose-Einstein distribution function is given by

$$f(E_i) = \frac{N_i}{g_i} = \frac{1}{e^{(\alpha + \beta E_i)} - 1} \dots \dots \dots (14)$$

#### **Fermi-Dirac (FD) Statistics**

The basic postulates of FD statistics are:-

- (i) Particles are identical and indistinguishable.
- (ii) Total energy and total number of particles of the entire system is constant
- (iii) Particles have half-integral spin, i.e  $1/2 \hbar, 3/2 \hbar, 5/2 \hbar$  etc, where  $\hbar$  is the unit of spin
- (iv) Particles obey Pauli's exclusion principle, i.e. no two particles in a single system can have the same value for each of the four quantum numbers. In other words, a single energy state can contain at best a single particle with appropriate spin.
- (v) The wave function of the system is anti-symmetric under the positional exchange of any two particles.

Examples: electron, proton, neutron, all hyperons ( $\Lambda, \Sigma, \Xi, \Omega$ ) etc., these are known as Fermions.

#### Fermi-Dirac Distribution Law:

Consider a system of  $N$  indistinguishable, non-interacting particles obeying Pauli's exclusion principle. Let  $N_1, N_2, N_3, \dots, N_i, \dots, N_n$  Particles in the system have energies  $E_1, E_2, E_3, \dots, E_i, \dots, E_n$  respectively and let  $g_i$  is the number of degenerate quantum states in the energy level  $E_i$ . According to Pauli's exclusion principle a single quantum state can be occupied by at best one particle. Since  $N_i$  particles are to be distributed among  $g_i$  degenerate states ( $g_i \geq N_i$ ) having the same energy  $E_i$ ,  $N_i$  states will be filled up and  $(g_i - N_i)$  states will remain vacant. Now  $g_i$  states can be arranged in  $g_i!$  possible ways, . But since the particles and the quantum states are indistinguishable, we have to deduct  $N_i!$  ways and  $(g_i - N_i)!$  ways from the all possible ways to get effective number of arrangements. Thus total number of possible ways of arrangement for the  $i^{\text{th}}$  state is

$$W_i = \frac{(g_i)!}{N_i!(g_i - N_i)!} \dots \dots \dots (15)$$

Hence the total number of ways for the entire distribution of N particles in n number of energy levels of the system is

$$W = \prod_i^n \frac{(g_i)!}{N_i!(g_i - N_i)!} \dots \dots \dots (16)$$

Hence the Fermi-Dirac distribution function is given by

$$f(E_i) = \frac{N_i}{g_i} = \frac{1}{e^{(\alpha + \beta E_i)} + 1} \dots \dots \dots (17)$$

### ***Application of Fermi-Dirac statistics:***

#### **Fermi distribution at zero and non-zero temperature**

The Fermi-Dirac distribution function is

$$f(E_i) = \frac{N_i}{g_i} = \frac{1}{e^{(\alpha + \beta E_i)} + 1}$$

Now for the fermions in statistical equilibrium at absolute temperature T, it is found that  $\alpha = -E_F/kT$  and  $\beta = 1/kT$  where  $E_F$  is the Fermi energy of the system (i.e maximum energy at absolute zero) and k is Boltzmann constant =  $1.38 \times 10^{-23}$  joule/Kelvin.

Therefore F-D distribution function can be written as,

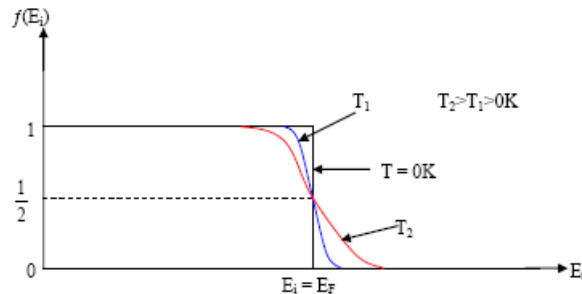
$$f(E_i) = \frac{1}{e^{(E_i - E_F)/kT} + 1} \dots \dots \dots (18)$$

Now let us discuss two distinct cases:

#### **Case I : T = 0 K**

$$\begin{aligned} f(E_i) &= 1 \text{ when } E_i < E_F \\ &= 0 \text{ when } E_i > E_F \end{aligned}$$

Thus at T = 0K,  $f(E_i)$  is a step function (see fig.below) which implies all the energy states upto  $E_i = E_F$  are filled up and the states above  $E_F$  are empty.



*Plot of Fermi-Dirac distribution function as a function of  $E_i$*

#### **Case – 2 ( T > 0 K)**

As the temperature increases beyond T= 0K, some of the electrons in the levels just below the Fermi level go to levels just above  $E_F$  resulting a gradual change in the occupation index  $f(E_i)$ . If  $E_i = E_F$ ,  $f(E_i) = 1/(e^0 + 1) = 1/2$  i.e. at a finite temperature Fermi energy of a system is that energy for which 50% energy states are filled and 50% states are vacant.

Fermi energy is the highest occupied level at absolute zero. Fermi level is the chemical potential. It is the energy level with 50% chance of being occupied at finite temperature T. The Fermi energy does not depend on temperature: the Fermi level does depend on **temperature**.

## Fermi energy for electron gas in metals

Metals are characterized by the presence of a good number of free electrons. These electrons move about at random within the metals. While moving the free electrons collide among themselves also encounter with the fixed ion cores. Such behaviour of the free electrons is similar to that of molecules of a gas. Thus metals can be treated as electron gas. Since the electrons have half-integral spin angular momenta and they obey Pauli's exclusion principle, they follow F-D statistics.

Let us consider an electron gas consisting of N electrons occupying volume V. If N is very large, the spacing between two successive energy levels becomes very small making the energy levels almost continuous. Then if the energy of the electrons ranges between E to E+dE, the number of degenerate states  $g_i$  should be replaced by  $g(E)dE$  and the total number of electrons  $N_i$  in these states should be replaced by  $N(E)dE$  in the distribution function given by equation (6). Thus the total number of electrons in the electron gas having energy between E to E+dE can be written by following eqn.(6) and eqn.(8) as

$$N(E)dE = f(E) g(E) dE = \frac{g(E)dE}{e^{\frac{E-E_F}{kT}} + 1} \dots\dots\dots (19)$$

Since the electrons have *two* allowed values of spin quantum number ( $m_s = \pm \frac{1}{2}$ ), the total number of their allowed states between energy for the energy range E to E+dE can be written by following eqn (5a),

$$g(E)dE = \frac{1}{h^3} 8\sqrt{2} \pi V m^{\frac{3}{2}} E^{\frac{1}{2}} dE$$

From fig.(7.3) it is obvious that at T = 0K, all the single-particle states upto energy  $E_F$  are filled up. Thus at T = 0K,

$$N(E)dE = \frac{g(E)dE}{e^{-\infty} + 1} = g(E)dE$$

i.e., total number of electrons is equal to the total number of single-particle energy states, hence

$$\begin{aligned} N &= \int_0^{E_F} N(E)dE = \int_0^{E_F} g(E)dE \\ &= \frac{1}{h^3} 8\sqrt{2} \pi V m^{\frac{3}{2}} \int_0^{E_F} E^{\frac{1}{2}} dE \\ \text{or, } N &= \frac{1}{3h^3} 16\sqrt{2} \pi V m^{\frac{3}{2}} E_F^{\frac{3}{2}} \end{aligned}$$

This the expression for the *total number of electrons* in the metal at T = 0K. Therefore,

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

which is the expression for *Fermi energy* of the electrons in the metal. If  $n = N/V$  denotes the concentration of the electrons in the metal, the Fermi energy of the electrons in the metal is

$$E_F = \frac{h^2}{8m} \left( \frac{3n}{\pi} \right)^{\frac{2}{3}}$$

which shows the Fermi energy of the electrons depends solely on their *concentration*

## Total energy at absolute zero temperature:

The total energy of electrons at absolute zero ( $T = 0K$ ) is given by

$$\begin{aligned}(E_0)_{tot} &= \int_0^{E_F} EN(E)dE = \int_0^{E_F} Eg(E)dE \\&= \frac{1}{h^3} 8\sqrt{2} \pi V m^{\frac{3}{2}} \int_0^{E_F} E^{\frac{3}{2}} dE \\&= \frac{1}{5h^3} 16\sqrt{2} \pi V m^{\frac{3}{2}} E_F^{\frac{5}{2}} = \frac{3}{5} NE_F\end{aligned}$$

which shows *quantum effect* because, *classically the total energy of a system at absolute zero is nothing but zero.*

The average energy per electron at  $T = 0K$  can be written as

$$\langle E_0 \rangle = (E_0)_{tot}/N = \frac{3}{5} E_F$$

which shows that at absolute zero temperature, the average energy per electron is equal to 3/5 times the Fermi energy .

## Fermi Temperature ( $T_F$ ):

Fermi temperature ( $T_F$ ) is the temperature equivalent of Fermi energy ( $E_F$ ) and it is defined as,

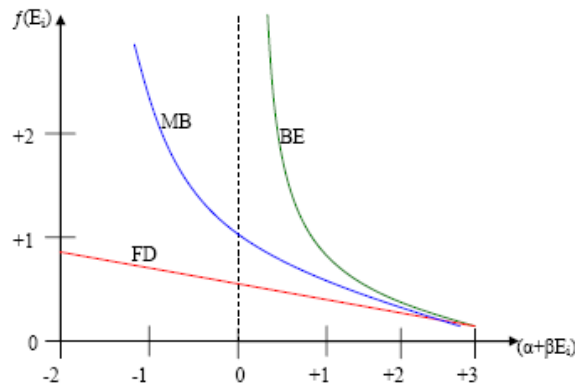
$T_F = E_F/k$ , where  $k$  is Boltzmann constant.

## *Classical Limit of Quantum Statistics*

$$f(E_i) = \frac{N_i}{g_i} = \frac{1}{e^{(\alpha+\beta E_i)}} \dots \dots \dots MB \text{ Statistics}$$

$$f(E_i) = \frac{N_i}{g_i} = \frac{1}{e^{(\alpha+\beta E_i)} + 1} \dots \dots \dots FD \text{ Statistics}$$

$$f(E_i) = \frac{N_i}{g_i} = \frac{1}{e^{(\alpha+\beta E_i)} - 1} \dots \dots \dots BE \text{ Statistics}$$



Plot of distribution function  $f(E_i)$  with  $(\alpha+\beta E_i)$  for the three statistics



Thus in general the distribution function for all the three statistics can be written as,

$$f(E_i) = \frac{N_i}{g_i} = \frac{1}{e^{(\alpha + \beta E_i)} + \delta}$$

Where  $\delta = 0$  for MB stats,

And  $\delta = -1$  for BE stats,

Lastly  $\delta = 1$  for FD stats,

It is obvious that the quantum statistics (BE and FD) would tend to the classical one (MB) only when  $e^{(\alpha + \beta E_i)} \gg 1$ , then  $\frac{N_i}{g_i} \ll 1$ . Now the parameter  $\alpha$  for both BE and FD statistics is inversely proportional to T. Thus if very high value of the temperature T corresponds to very low value of  $N_i/g_i$ , the quantum statistics reduces to the classical one.  $N_i/g_i$  is the number of particles per unit state and can be treated as the particle density. Hence *under **high temperature and low particle density** the quantum statistics tend to the classical one.*

### WORKED-OUT PROBLEMS

- Find out the different macrostates and microstates of a system of three particles distributed in three cells assuming the particles to be (i) indistinguishable, (ii) distinguishable.

Soln.: Macrostate  $\rightarrow$  specification of N,V,E

Microstate  $\rightarrow$  specification of total number of ways corresponding to a specific value of the set {N,V,E}

Here, V, E are fixed. So macrostates and microstates would be determined only by N. For *indistinguishable* particles (let,a,a,a) the all possible arrangements are shown below:

Number	Macrostates	Microstates	No. of microstates
1	111	a a a	1
2	210	aa a 0	1

3	120	a aa 0	1
4	201	aa 0 a	1
5	102	a 0 aa	1
6	021	0 aa a	1
7	012	0 a aa	1
8	300	aaa 0 0	1
9	030	0 aaa 0	1
10	003	0 0 aaa	1

For distinguishable particles (let, a,b,c) the all possible arrangements are shown below:

Number	Macrostates	Microstates	No. of microstates $\frac{n!}{n_1!n_2!n_3!}$
1	111	a b c a c b b c a b a c c a b c b a	$\frac{3!}{1!1!1!} = 6$
2	210	ab c 0 bc a 0 ca b 0	$\frac{3!}{2!1!0!} = 3$
3	120	a bc 0 b ca 0 c ab 0	$\frac{3!}{1!2!0!} = 3$
4	201	ab 0 c bc 0 a ca 0 b	$\frac{3!}{2!0!1!} = 3$
5	102	a 0 bc b 0 ca c 0 ab	$\frac{3!}{1!0!2!} = 3$
6	021	0 ab c 0 bc a 0 ca b	$\frac{3!}{0!2!1!} = 3$
7	012	0 a bc 0 b ca 0 c ab	$\frac{3!}{0!1!2!} = 3$
8	300	abc 0 0	$\frac{3!}{3!0!0!} = 1$
9	030	0 abc 0	$\frac{3!}{0!3!0!} = 1$

10	003	0 0 abc	$\frac{3!}{0!0!3!} = 1$
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2. Two particles are to be distributed in three cells. Find out the total number of possible ways both from formula and in tabular form if the particles follow (i) MB statistics (ii) BE statistics (iii) FD statistics.

Soln. The total number of possible ways (microstates) in MB, BE, FD statistics are respectively given by

$$W_{MB} = \frac{N!}{N_i!} (g_i)^{N_i}, \quad W_{BE} = \frac{(N_i + g_i - 1)!}{N_i! (g_i - 1)!}, \quad W_{FD} = \frac{(g_i)!}{N_i! (g_i - N_i)!}$$

Here,  $N = 2$ ,  $N_i = 2$ ,  $g_i = 3$ . Thus,

$$W_{MB} = \frac{2!}{2!} \cdot 3^2 = 9, \quad W_{BE} = \frac{(2 + 3 - 1)!}{2! (3 - 1)!} = \frac{4!}{2!2!} = 6, \quad W_{FD} = \frac{3!}{2! (3 - 2)!} = \frac{3!}{2!1!} = 3$$

For MB statistics, the particles are distinguishable and any state can contain any number of particles. Let the particles are a,b.

CELL-1	CELL-2	CELL-3
ab	0	0
0	ab	0
0	0	ab
a	b	0
b	a	0
0	a	b
0	b	a
a	0	b
b	0	a

For BE statistics, the particles are indistinguishable and any state can contain any number of particles. Let the particles are a,a.

CELL-1	CELL-2	CELL-3
aa	0	0
0	aa	0
0	0	aa
a	a	0
a	0	a
0	a	a

For FD statistics, the particles are indistinguishable and a single state can contain at best one particle. Let the particles are a,a.

CELL-1	CELL-2	CELL-3
a	a	0

a	0	a
0	a	a

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 such 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 (iii) FD statistics. Find the corresponding macrostates and microstates also.

Soln.

- (i) For MB statistics, let the three particles are A,B,C and the energy unit is E.

MACRO STATES	0E	1E	2E	3E	TOTAL ENERGY	MICRO STATES
(2,0,01)	AB BC CA	0 0 0	0 0 0	C A B	3E	3
(1,1,1,0)	A A B B C C	B C C A A B	C B A C B A	0 0 0 0 0 0	3E	6
(0,3,0,0)	0	ABC	0	0	3E	1

Thus for MB statistics total number of microstates is  $(3+6+1) = 9$ .

- (ii) For BE statistics, let the three particles are A,A,A and energy unit is E.

MACRO STATES	0E	1E	2E	3E	TOTAL ENERGY	MICRO STATES
(1,1,1,0)	A	A	A	0	3E	1
(2,0,0,1)	AA	0	0	A	3E	1
(0,3,0,0)	0	AAA	0	0	3E	1

Thus for BE statistics total number of microstates is  $(1+1+1) = 3$

- (iii) For FD statistics, let the three particles are A,A,A and energy unit is E.

MACRO	0E	1E	2E	3E	TOTAL	MICRO
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STATES					ENERGY	STATES
(1,1,1,0)	A	A	A	0	3E	1

Hence for FD statistics total number of microstates is 1.

4. Calculate the density of states for an electron with energy 5eV constrained to move in a cubical box of length 0.5 mm.

Soln.: The density of states of an electron is given by

$$g(E) = \frac{1}{h^3} (8\pi V \sqrt{2mE}) \quad [\text{see eqn. (7.41)}]$$

Here,  $V = (0.5 \times 10^{-3})^3 = 0.125 \times 10^{-9} \text{ m}^3$

$E = 5\text{eV} = 5 \times 1.6 \times 10^{-19} \text{ Joule} = 8 \times 10^{-19} \text{ Joule}$

$m = 9.1 \times 10^{-31} \text{ Kg}$

$h = 6.6 \times 10^{-34} \text{ Joule-Sec.}$

Therefore,  $g(E) = 1.2 \times 10^{37} \text{ states/Joule}$

Which is the required density of states for the given electron.

5. Calculate the probability of finding an electron with energy 6eV in an electron gas at  $1000^\circ\text{C}$  if the Fermi energy of the gas is 5eV.

Soln. We know that the probability of finding an electron with energy  $E_i$  is given by

$$f(E_i) = \frac{1}{e^{(E_i - E_F)/kT} + 1}$$

Here,  $E_F = 5\text{eV} = 5 \times 1.6 \times 10^{-19} \text{ Joule} = 8 \times 10^{-19} \text{ Joule}$

$E_i = 6\text{eV} = 6 \times 1.6 \times 10^{-19} \text{ Joule} = 9.6 \times 10^{-19} \text{ Joule}$

$k = 1.38 \times 10^{-23} \text{ Joule/Kelvin}$

$T = 1000^\circ\text{C} = (273 + 1000) \text{ Kelvin} = 1273 \text{ Kelvin}$

Thus

$$f(E_i) = \frac{1}{\exp\left(\frac{9.6 \times 10^{-19} - 8 \times 10^{-19}}{1.38 \times 10^{-23} \times 1273}\right) + 1} = \frac{1}{e^{9.11} + 1} = \frac{1}{9046.3} = 1.105 \times 10^{-4}$$

Hence the required probability is 0.01105 %.

6. If the probability of finding an electron of energy 6eV in an electron gas at  $1000^\circ\text{C}$  is 0.01105 %, calculate the Fermi energy of the gas.

Soln. We know that the probability of finding an electron with energy  $E_i$  is given by

$$f(E_i) = \frac{1}{e^{(E_i - E_F)/kT} + 1}$$

$$\text{Here, } f(E_i) = \frac{0.01105}{100}$$

$$E_i = 6\text{eV} = 6 \times 1.6 \times 10^{-19} \text{ Joule} = 9.6 \times 10^{-19} \text{ Joule}$$

$$k = 1.38 \times 10^{-23} \text{ Joule/Kelvin}$$

$$T = 1000^\circ\text{C} = (273 + 1000) \text{ Kelvin} = 1273 \text{ Kelvin}$$

Therefore,

$$\frac{0.01105}{100} = \frac{1}{\exp\left(\frac{9.6 \times 10^{-19} - E_F}{1.38 \times 10^{-23} \times 1273}\right) + 1}$$

which gives  $E_F \approx 8 \times 10^{-19} \text{ Joule} = 5\text{eV}$  and this is the required Fermi energy of the gas.

7. The Bose-Einstein distribution function is given by

$$f(E_i) = \frac{N_i}{g_i} = \frac{1}{e^{(\alpha + \beta E_i)} - 1}$$

If  $\alpha = -\frac{\mu}{kT}$ , where  $\mu$  represents chemical potential; show that  $\mu$  can take zero or negative values for a system of bosons.

Soln. For a system of bosons we can write

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

Since the number of states and number of particles in a state can't be negative,  $N_i \geq 0$ ,  $g_i \geq 0$ . This requires  $e^{(\alpha + \beta E_i)} \geq 1$ . If the ground state energy is assumed to be zero,  $e^\alpha \geq 1$ , i.e.,  $\alpha = -\frac{\mu}{kT} \geq 0 \Rightarrow \mu \leq 0$  and thus proved.

8. Calculate the Fermi energy for metallic silver assuming each atom of silver contains a single free electron. [ Given: Density of silver = 10.5 gm/c.c., atomic weight of silver = 108 ]

Soln. The number density of free electrons is given by

$$n = \frac{N}{V} = \frac{6.023 \times 10^{23}}{108} \times 10.5 \text{ per c.c.} = 5.9 \times 10^{28} \text{ per m}^3$$

Thus the Fermi energy is given by

$$\begin{aligned} E_F &= \frac{h^2}{8m} \left( \frac{3n}{\pi} \right)^{2/3} = \frac{(6.6 \times 10^{-34})^2}{8 \times 9.11 \times 10^{-31}} \left( \frac{3 \times 5.9 \times 10^{28}}{3.14} \right)^{2/3} \text{ Joule} \\ &= 8.8 \times 10^{-19} \text{ Joule} \\ &= \frac{8.8 \times 10^{-19}}{1.6 \times 10^{-19}} \text{ eV} = 5.5 \text{ eV.} \end{aligned}$$

9. If the Fermi energy for metallic silver is 5.5 eV. Calculate the number of free electrons per unit volume of the metallic silver.

Soln. The Fermi energy of metallic silver is given by

$$E_F = \frac{h^2}{8m} \left( \frac{3n}{\pi} \right)^{2/3} = 5.5 \text{ eV} = 5.5 \times 1.6 \times 10^{-19} \text{ Joule}$$

$$= 8.8 \times 10^{-19} \text{ Joule}$$

$$\text{or, } \frac{(6.6 \times 10^{-34})^2}{8 \times 9.11 \times 10^{-31}} \left( \frac{3n}{3.14} \right)^{2/3} = 8.8 \times 10^{-19}$$

On solving we get,

$$n \approx 5.9 \times 10^{28} \text{ per m}^3$$

which is the number of free electrons per unit volume of the metallic silver.

10. Calculate the total energy of an electron gas at absolute zero temperature for sodium containing one free electron per atom. [ Given: Density of sodium =  $9.7 \times 10^3 \text{ Kg/m}^3$ ., atomic weight of sodium = 23].

Soln. Here the number density of the free electrons is

$$n = \frac{N}{V} = \frac{6.023 \times 10^{23}}{108} \times 9.7 \times 10^3 \text{ per m}^3 = 2.54 \times 10^{29} \text{ per m}^3$$

Therefore the Fermi energy is given by

$$E_F = \frac{h^2}{8m} \left( \frac{3n}{\pi} \right)^{2/3} = \frac{(6.6 \times 10^{-34})^2}{8 \times 9.11 \times 10^{-31}} \left( \frac{3 \times 2.54 \times 10^{29}}{3.14} \right)^{2/3} \text{ Joule}$$

$$= 23.2 \times 10^{-19} \text{ Joule}$$

Hence the total energy per unit volume at absolute zero is

$$E_{tot} = \frac{1}{V} (E_0)_{tot} = \frac{3}{5} \cdot \frac{N}{V} \cdot E_F = \frac{3}{5} \cdot n \cdot E_F$$

$$= \frac{3}{5} \times 2.54 \times 10^{29} \times 23.2 \times 10^{-19} \text{ Joule/m}^3$$

$$= 35.36 \times 10^{10} \text{ Joule/m}^3$$

11. Calculate the ground-state pressure of an electron gas for sodium containing one free electron per atom. [ Given: Density of sodium =  $9.7 \times 10^3 \text{ Kg/m}^3$ ., atomic weight of sodium = 23].

Soln. The Fermi energy( $E_F$ ) and number density (n) of sodium is respectively given by

$$E_F = 23.2 \times 10^{-19} \text{ Joule}$$

$$n = 2.54 \times 10^{29} \text{ per m}^3$$

[ see Worked-out problem No. 10]

Hence the ground-state pressure is

$$\begin{aligned} P_0 &= \frac{2}{5} n E_F \\ &= \frac{2}{5} \times 2.54 \times 10^{29} \times 23.2 \times 10^{-19} \text{ Newton/m}^2 \\ &= 23.57 \times 10^{10} \text{ Newton/m}^2 \end{aligned}$$

which is the required ground-state pressure.

12. Show that sodium behaves as a metal in ordinary room temperature[ Given: Density of sodium =  $9.7 \times 10^3 \text{ Kg/m}^3$ ., atomic weight of sodium = 23].

Soln. The Fermi energy of sodium is

$$E_F = 23.2 \times 10^{-19} \text{ Joule. [see Worked-out problem No. 10]}$$

By definition , the Fermi temperature is given by

$$\begin{aligned} T_F &= E_F/k \\ &= \frac{23.2 \times 10^{-19} \text{ Joule}}{1.38 \times 10^{-23} \text{ Joule/ Kelvin}} = 16.81 \times 10^4 \text{ Kelvin} \end{aligned}$$

which is the Fermi temperature of sodium.

Since this Fermi temperature is *very very larger* than ordinary room temperature ( $\approx 300$  Kelvin), the valence band overlaps with conduction band in sodium at room temperature. Hence sodium behaves as a metal at ordinary room temperature.

13. Show that the average momentum per electron at absolute zero temperature is

$\langle p_0 \rangle = \frac{3}{4} p_F$ , where  $p_F$  is the Fermi momentum (i.e., momentum equivalent of Fermi energy).

Soln. The total momentum of electrons in an electron gas at absolute zero ( $T = 0\text{K}$ ) temperature is given by

$$(p_0)_{\text{tot}} = \int_0^{p_F} p \cdot N(p) dp \dots\dots\dots (7.60)$$

We know that at  $T = 0\text{K}$ ,

$$N(E)dE = g(E)dE \quad \quad \quad [\text{ see eqn.(7.42)}]$$

$$= \frac{1}{h^3} (8\pi V \sqrt{2mE} \text{ m})dE \quad \quad \quad [\text{ see eqn.(7.40)}]$$

$$\text{But in non-relativistic limit, } E = \frac{p^2}{2m} \dots\dots\dots (7.61)$$

$$\text{Also, } dE = \frac{p}{m} dp \dots\dots\dots (7.62)$$



And the Fermi momentum is defined as  $p_F = \frac{E_F}{2m}$  .....(7.63)

Thus using eqn.(7.60) and eqn.(7.61) we get,

$$\begin{aligned} N(p)dp &= g(p) dp \\ &= \frac{8\pi V p^2}{h^3} dp \end{aligned} \dots\dots\dots(7.64)$$

$$\begin{aligned} \text{Also from eqn.(7.43), , } N &= \frac{16\sqrt{2}\pi V m^{3/2}}{3h^3} E_F^{3/2} = \frac{16\sqrt{2}\pi V m^{3/2}}{3h^3} \left( \frac{p_F^2}{2m} \right)^{3/2} \\ &= \frac{8\pi V}{3h^3} p_F^3 \end{aligned} \dots\dots\dots(7.65)$$

Now on using eqn.(7.64) in eqn.(7.60) we get,

$$\begin{aligned} (p_0)_{tot} &= \int_0^{p_F} p \cdot \frac{8\pi V p^2}{h^3} dp \\ &= \frac{8\pi V}{h^3} \cdot \frac{p_F^4}{4} \\ &= \frac{8\pi V}{h^3} \cdot \frac{p_F}{4} \cdot p_F^3 \\ &= \frac{8\pi V}{h^3} \cdot \frac{p_F}{4} \cdot \frac{3N h^3}{8\pi V} \quad \quad \quad [\text{using eqn.(7.65)}] \\ &= \frac{3}{4} \cdot N \cdot p_F \end{aligned}$$

Therefore,

Average momentum per electron at absolute zero temperature is

$$\langle p_0 \rangle = \frac{(p_0)_{tot}}{N} = \frac{3}{4} p_F \quad \dots\dots\dots(7.66)$$

and hence proved.

#### 14. Calculate the number of photons per unit $m^3$ at 1000 Kelvin.

Soln. The number of photons per unit volume in the frequency range  $\nu$  to  $\nu+d\nu$  is given by

$$N(\nu)d\nu = \frac{8\pi}{c^3} \cdot \frac{\nu^2 d\nu}{e^{h\nu/kT} - 1} \quad \quad \quad [\text{see eqn.(7.54)}]$$

Therefore the total number of photons per unit volume having all possible energies is

$$N = \int_0^{\infty} N(\nu) d\nu = \frac{8\pi}{c^3} \int_0^{\infty} \frac{\nu^2 d\nu}{e^{h\nu/kT} - 1} \dots\dots\dots(7.67)$$

Putting  $\frac{h\nu}{kT} = x$ , such that  $d\nu = \frac{kT}{h} dx$  in eqn.(7.67) we get,

$$N = 8\pi \left( \frac{kT}{hc} \right)^3 \int_0^{\infty} \frac{x^2 dx}{e^x - 1}$$

From standard results we get,  $\int_0^{\infty} \frac{x^2 dx}{e^x - 1} = 2.405$

$$\begin{aligned} \text{Therefore,} \quad N &= 8 \times 3.14 \times \left( \frac{1.38 \times 10^{-23} \times 1000}{6.6 \times 10^{-34} \times 3 \times 10^8} \right)^3 \times 2.405 \\ &= 2.045 \times 10^{16} \text{ photons} \end{aligned}$$

which is the required number of photons per unit  $m^3$  at 1000 Kelvin.

15. Considering a relativistic particle (e.g. electron, proton etc.), calculate the density of states .

**Soln.** We know that the number of quantum states in the momentum range from  $p$  to  $p+dp$  is

$$g(p)dp = \frac{V.4\pi p^2 dp}{h^3} \quad [\text{see eqn.(7.3)}]$$

For a relativistic particle the total energy is given by

$$E^2 = m_0^2 c^4 + p^2 c^2 \dots\dots\dots(7.68)$$

where,  $m_0$  is the rest mass of the particle and  $c$  is the speed of light in free space.

So, we can write from eqn.(7.68) that

$$p^2 = (E^2 - m_0^2 c^4) / c^2 \dots\dots\dots(7.69)$$

and

$$p dp = EdE / c^2 \dots\dots\dots(7.70)$$

Hence the number of quantum states in the energy range from  $E$  to  $E+dE$  is

$$g(E)dE = \frac{4\pi V}{h^3} \frac{(E^2 - m_0^2 c^4)^{1/2}}{c} \frac{EdE}{c^2} \dots\dots\dots(7.71)$$

So, the density of states is

$$\begin{aligned} g(E) &= \frac{4\pi V E}{h^3 c^3} (E^2 - m_0^2 c^4)^{1/2} \quad \text{for } E \geq m_0 c^2 \\ &= 0 \quad \text{for } E < m_0 c^2 \dots\dots\dots(7.72) \end{aligned}$$