# STATISTICAL MECHANICS

In thermodynamics we deal with systems which ar characterized by different properties like volume, pressure, temperalture, internal energy, entropy, enthalpy etc. Thes quantities ~~are~~ have definite values when a system is in equilibrium. All these quantities or changes of these quantities are directly or indirectly measurable. The basic constituents of any thermodynamic systems are obviously the atoms or molecules and their numbers are in general very large, of the order of $10^{23}$. Hence the above systems are called macroscopic systems an the above properties or parameters are called macroscopic properties or parameters.

These macroscopic properties are related to the microscopic structure of a system, i.e. the states of the basic constituents of the systems, their motions and interactions. e.g. a) Temp is a measure of the avg translational kinetic energy of the molecules (b) The pressure of a gas is a measure of the avg rate at which the molecules transfer momentum per unit area of the wall. (c) specific heat is a measure of the avg way the molecules of a material respond to the addition of heat.

~~Thus the macroscopic properties are related to the microscopic structure of the system, i.e. the state of the basic constituents of the systems, their motion and interactions.~~

Thus the macroscopic properties are the average of the collective behaviours of all molecules in a system. But in thermodynamics the relation between macroscopic properties, on one hand, and microscopic structures on the other, are not studied.

* are discussed in Statistical mechanics.

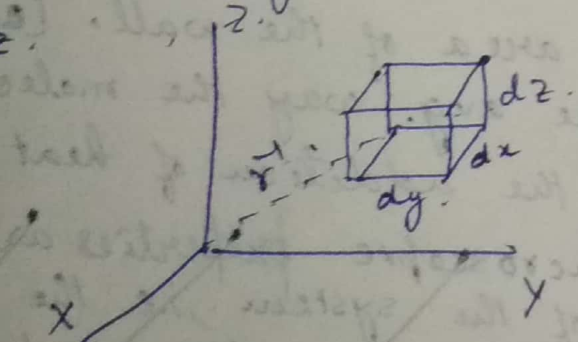
Hence, there is a necessity of theories which can relate the macroscopic properties with the microscopic structure of the system.

In statistical mechanics, attempts are made to calculate macroscopic properties of a system from the underlying microscopic structure of the system. Here theory of probability is applied to all the molecules that make up any piece of matter. As the number of molecules in any system is very large, it is possible to obtain collective or macroscopic properties of a system, without considering the detailed motion of each particle.

So in summary, in an assembly of non interacting particles, how energy is distributed among particles and how the particles are distributed over energy levels *

## Phase space of a single particle — $\mu$ Space:—

To specify the location of a particle P at any instant in 3 dimensional physical space, we require three co-ordinates $(x, y, z)$ of its position vector $\vec{r}$, the co-ordinates change as the position of the particle changes. An elementary volume at location $\vec{r}$ is $V = dx\,dy\,dz$.

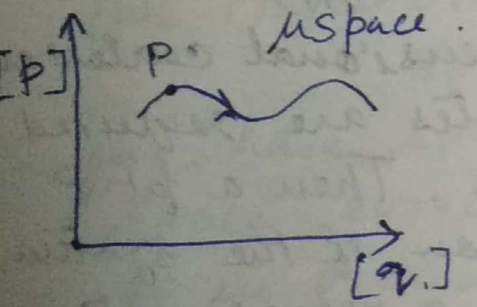


Now, If the particle moves, then to specify its state of motion we need position $(x, y, z)$ as well as momentum components $(p_x, p_y, p_z)$ at each instant.

Imagine a 6-dimensional Cartesian space in which there are 6 mutually perpendicular (orthogonal) axes and every point has six co-ords $(x, y, z, p_x, p_y, p_z)$.

Hence, at any instant, the six co-ordinates $(x, y, z, p_x, p_y, p_z)$ represent a point P in that 6-dimensional space and this point specifies both the location and the state of motion of the moving particle at that instant. As the particle moves, the location of the point P in the 6 dimensional space changes with time. The trajectory traversed by the point P in that 6-dimensional space gives the total description of the motion of the particle. Such a conceptual space giving the total description of motion of a particle is called the phase space of a single particle or μ-space.

An elementary volume of μ space $d\tau = dx\,dy\,dz\,dp_x\,dp_y$



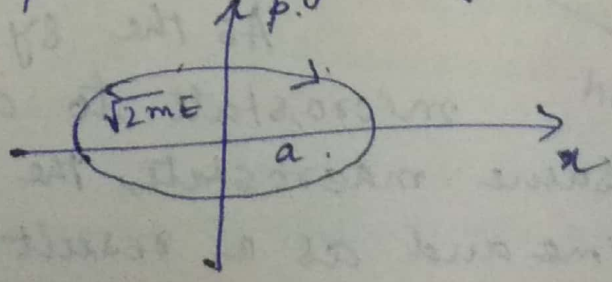
In the fig, the symbols [q] and [p] schematically represent the three co-ordinates and three momentum axes respectively and a trajectory in μ space is shown in the figure.

For a particle moving simple harmonically in a straight line, the relation between its position (x) and momentum (p) is given by,

$$\frac{x^2}{a^2} + \frac{p^2}{2mE} = 1.$$

where a, m and E are its amplitude, mass and energy respectively.

Hence, the μ-space for this particle would be two dimensional. One for position x and one for momentum p. The phase trajectory is an ellipse, a closed curve,



# Phase space of a system or $\Gamma$ space:-

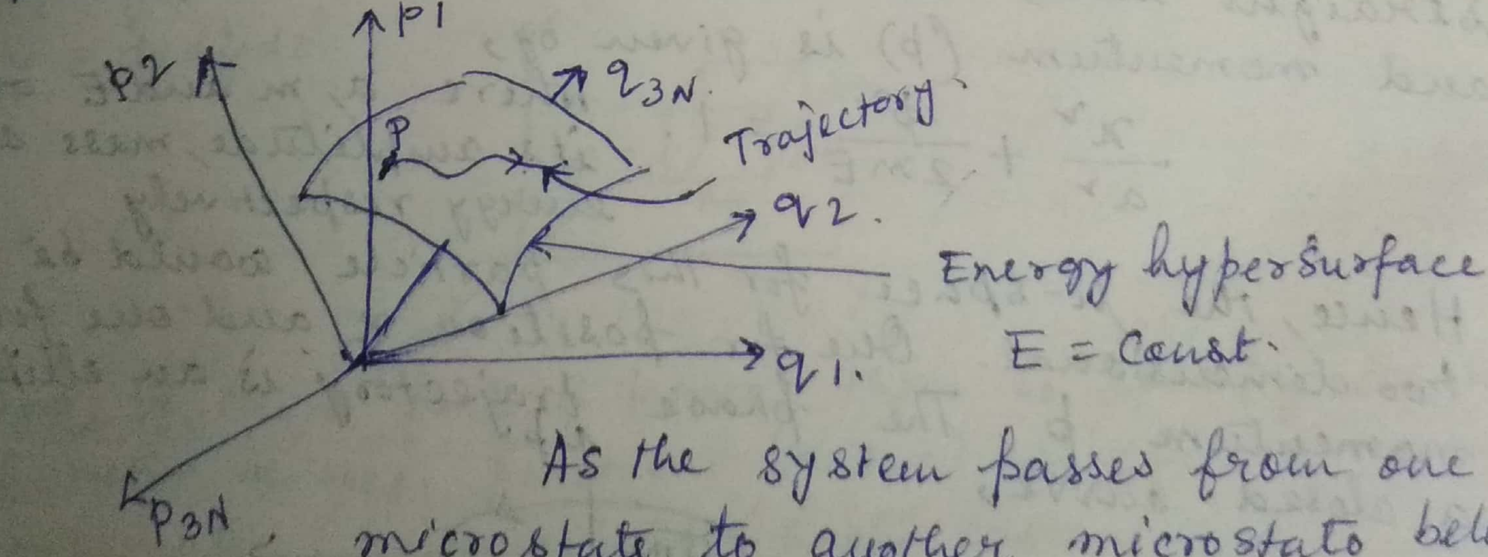
Now consider there is a system of N molecu Each one of the N molecules is moving with all possible speeds in all possible directions. To specify the system, as a whole, at a particular instant, we require six quantities for each particle. So, for the whole system we require 6N quantities;

$(x_1, y_1, z_1, x_2, y_2, z_2, \dots x_N, y_N, z_N, p_{x_1}, p_{y_1}, p_{z_1}, p_{x_2}, p_{y_2}, p_{z_2}, \dots \dots p_{x_N}, p_{y_N}, p_{z_N})$.

For convenience it can be written as,

$(q_1, q_2, q_3, \dots q_{3N}, p_1, p_2, p_3, \dots p_{3N})$

So we can imagine a 6N dimensional cartesi space, where the 6N co-ordinates are requir to specify a point in that space. Then a pt P in that space gives full description of the syste at an instant. The pt P is called a representativ point. P represents a microstate of the system.



As the system passes from one microstate to another microstate belo to the same macrostate, the 6N co-ordinates chang with time and as a result the position of the representative pt P of the system moves in that space. The path traversed by P in that space is called phase trajectory. So the phase trajectory of the point P in that space gives the full description of the time evolution of the microstate of the system.

This conceptual space, describing the variation in time of a thermodynamic system, as a whole, is called the phase space of the system or $\Gamma$ space. Trajectory of the representative pt in the phase space, never intersects with itself. If they intersect then at that point there should be two trajectories, which is never possible.

If the energy is conserved, all trajectories in phase space must lie on a surface in phase space corresponding to the constant energy. As in ordinary 3 dimensional space, we have a 2 dimensional surface, this surface in phase space is $(6N-1)$ dimensional surface in $6N$ dimensional phase space. It is called the const energy hypersurface in $\Gamma$ space.

## Macrostate:-

If the state of the system is completely specified by experimentally measurable parameters, then the state is called macrostate.

Volume (V), pressure (p), internal energy (E), number of particles (N), temperature (T), particle density ($\rho$) etc are macroscopic parameters.

## Microstate:-

The number of different meaningful ways (of the various particles in the macrostates) in which the total energy (E) of the system can be distributed among its constituent particles are called microstate. Theis a large number of microstates may lead to the same macrostates.

Eg. If we interchange velocity (but not position) of two gas molecules, the macrostate does not change, but there will be different microstate.

## Ensemble:-

A system is defined by collection of no of particles.

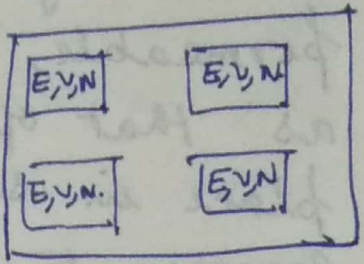
Ensemble ~~is~~ means assembly of systems.

According to Gibbs (1902) ensemble is defined as collection of large no of macroscopically identical but essentially independent system.

The classification of ensembles depends on the manner in which the system will interact. There are three types of ensembles.

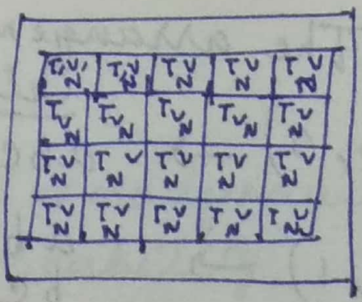
① Canonical ensemble
② Grand canonical ensemble.
③ Microcanonical ensemble.

**Microcanonical Ensemble:-** It is the collection of a large number of independent systems having same energy. E, volume V, and number of particles N. All particles are identical. The individual systems of a microcanonical ensemble are separated by rigid, impermeable and well insulated walls such that values of E, V, N for a particular system are not affected by the presence of other systems. All the members of an ensemble which are identical in features like (N, V, E) are referred to as an ensemble. The elements differ from one another in co-ordinates and momenta of the individual molecules i.e. the elements have same macroscopic state but differ in their unobservable microscopic state.



**Canonical Ensemble:-**

It is the collection of large no of independent particles/systems having same T, V and same number of identical particles N. The equality of temperature of all systems can be achieved by bringing each in thermal contact with a large heat reservoir at const temp T. The individual systems of a canonical ensemble are separated by a rigid, impermeable but conducting walls. As the walls are conducting, heat can be exchanged between the systems. As a result, all the systems will arrive at common temp T.



## Grand Canonical Ensemble:-

| | | |
|---|---|---|
| T, V, μ | T, V, μ | T, V, μ |
| T, V, μ | T, V, μ | T, V, μ |
| T, V, μ | T, V, μ | T, V, μ |

It is the collection of large number of independent systems having same T, V and chemical potential μ. The individual systems of a grand canonical ensemble are separated by rigid, permeable and conducting walls. As walls are conducting and permeable, the exchange of heat energy as well as that of particles between the system takes place in such a way that all system arrive at common temp T and chemical potential μ.

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Let, there are 4 particles. These 4 particles will be accomodated in 2 cells i and j.

So the number of possible way is —

| | | | | | |
|---|---|---|---|---|---|
| $N_i$ | 4 | 3 | 2 | 1 | 0 |
| $N_j$ | 0 | 1 | 2 | 3 | 4 |

So the no of macrostates = 5.

They are (4,0), (3,1), (2,2), (1,3), (0,4).

The arrangement of microstates :—

| | Cell i | Cell j | microstates |
|---|---|---|---|
| (4,0) → | abcd | 0 | 1 |
| (3,1) → | abc<br>bcd<br>dca<br>dab | d<br>a<br>b<br>c | 4 |

| | cell i | cell j | microstates |
|---|---|---|---|
| (2, 2) | ab | cd | |
| | ac | bd | |
| | ad | bc | 6 |
| | bc | da | |
| | bd | ac. | |
| | cd | ab. | |
| (1, 3) | a | bcd | 4 |
| | b | cda | |
| | c | dab | |
| | d | abc | |
| (0, 4) | 0 | abcd | 1. |

∴ Total no of microstates $= 1+4+6+4+1$
$= 16$

**Accessible State:**— Out of all possible microstates, the states which are actually taken by particles.

## Mathematical Probability:—

$$\frac{\text{No of microstates in the macrostate}}{\text{Total number of microstate in a system}}$$

$= P_{macro}$.

It is a fraction.

$P_{macro} \propto W$, where W is thermodynamic pobability.

## Thermodynamic Probability:—

The number of possible microstates corresponding to any given macrostate which is denoted by

## 7.5 NUMBER OF QUANTUM STATES (OR UNIT CELLS) WITHI ENERGY RANGE $E$ AND $E + dE$ IN THE PHASE SPACE O DENSITY OF STATES

Let us consider a phase space of volume containing a system of particles. A small volu element in phase space is given by

$d\tau = dx\,dy\,dz\;dp_x\,dp_y\,dp_z$ [where $(x, y, z, p_x, p_y, p_z)$ are the coordinates of a point in phase spac

So, the finite volume of the phase space available for a particle is

$$\tau = \iiiiiint dx\,dy\,dz\;dp_x\,dp_y\,dp_z \qquad \cdots(7.5.1$$

or,

$$\tau = \iiint dx\,dy\,dz \iiint dp_x\,dp_y\,dp_z \qquad \cdots(7.5.2$$

It is possible to divide the phase space into a large number of elementary cells of equ volume (i.e., size).

For quantum mechanical system, we can write using Heisenberg's uncertain principle the minimum possible value of $dx \cdot dp_x \cong h$, where $h$ is planck's constant.

So, the minimum size or volume of a unit cell for a quantum mechanical system

$$d\tau = dx\,dp_x\,dy\,dp_y\,dz\,dp_z \cong h^3 \qquad \cdots(7.5.3$$

Now, the *number of cells in the phase space* corresponding to momentum $p$ an $p + dp$ is

$$g(p)dp = \frac{\text{Volume in phase space corresponding to momentum} p \text{ and } p + dp}{h^3}$$

or,

$$g(p)dp = \frac{\iiint dxdydz \iiint dp_x\,dp_y\,dp_z}{h^3} \qquad \cdots(7.5.4$$

Now, the volume of the system of particles

$$V = \iiint dx\,dy\,dz \qquad \cdots(7.5.5$$

erefore, $g(p)dp = \frac{V}{h^3} = \iiint dp_x\,dp_y\,dp_z$ ···(7.5.6)

To evaluate, the volume of the system $\iiint dp_x\,dp_y\,dp_z)$ in momentum space corres-ponding to mentum interval $p$ and $p+dp$, let us draw a sphere [Fig. of radius $p$ such that all the points lying on the sphere e a momentum $p$ and it is given by the equation of sphere momentum space $(p_x, p_y, p_z)$ as

$$p^2 = p_x^2 + p_y^2 + p_z^2 = 2\,mE \qquad \cdots(7.5.7)$$

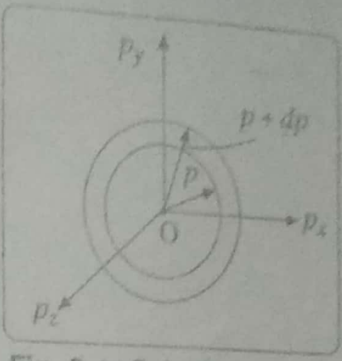

Fig. 2 ▷ Spherical shell in momentum space

ere $E$ is the energy of a particle of mass $m$.

If we draw another concentric sphere of radius $p+dp$, volume of the spherical shell enclosed between the two spheres of radius $p$ and $dp$ is given by

$\iiint dp_x\,dp_y\,dp_z$ = surface area of the sphere of radius $p \times$ thickness of the cell

$$\iiint dp_x\,dp_y\,dp_z = 4\pi p^2 dp \qquad \cdots(7.5.8)$$

Substituting this value in equation (7.5.6), we can write

$$g(p)dp = \frac{V}{h^3} 4\pi p^2 dp \qquad \cdots(7.5.9)$$

For particles having two allowed values of the spin quantum number $m_s = \pm\frac{1}{2}$, the mber of available quantum states (i.e., cells) is two times of that given by equation 5.9). So,

$$g(p)dp = \frac{2V}{h^3} 4\pi p^2 dp \qquad \cdots(7.5.10)$$

$$g(P)dp = \frac{8\pi Vp^2}{h^3} dp \qquad \cdots(7.5.11)$$

ain $p^2 = (2mE)$, where $E$ is the energy of the particle mass $m$.

fferentiating both sides, we get,

$$2p\,dP = 2m\,dE \qquad \cdots(7.5.12)$$

$$p\,dp = m\,dE$$

Substitute, $p = \sqrt{2mE}$ and $p\,dp = m\,dE$ in equation (7.5.11), we get **the number of antum states available in the phase space corresponding to energy $E$ and $E+dE$ is**

$$g(E)dE = \frac{8\pi V}{h^3} (2mE)^{1/2}\, m\,dE \qquad \cdots(7.5.13)$$

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

## 7.6 MAXWELL-BOLTZMANN STATISTICS

In statistical physics, we deal with the systems having a large number of particles the properties of the system can be deduced from a knowledge of the most probab equilibrium state.

Maxwell-Boltzmann statistics gives the statistical behaviour of distinguishable identical spinless particles of ideal gases. These particles do not obey Pauli's exclu principle.

**Basic postulates:**

1. The particles are weakly interacting identical and distinguishable.
2. They do not obey Pauli's exclusion principle. So each quantum (energy) state accomodate any number of particles.
3. The particles are spinless.

**Boltzons:** The particles those obey Maxwell-Boltzmann statistics are called Boltzo

### 7.6.1 Maxwell-Boltzmann Distribution Law

Let $N$ be the total number of distinguishable particles in an assembly. Out of these particles, we consider $N_1, N_2, N_3 \cdots N_k$ number of particles have energies $E_1, E_2,$ $\cdots, E_k$ respectively and they can be distributed in $g_1, g_2, g_3, \cdots, g_k$ number of quant states associated with the corresponding energy levels. Since, the total energy $E$ of assembly of $N$ numbers of distinguishable particles is constant we can write,

$$N_1E_1 + N_2E_2 + N_3E_3 + \cdots + N_kE_k = \sum_{i=1}^{k} N_iE_i = E \qquad \cdots(7.6.1$$

and

$$N_1 + N_2 + N_3 + \cdots + N_k = \sum_{i=1}^{k} N_i = N \qquad \cdots(7.6.1$$

If $g_i$ is the probability of locating a particle in a certain energy state $E_i$, the probabil of locating 2 particles in the same state is $g_i \times g_i = g_i^2$. Therefore, the probability for distinguishable particles to distribute in $g_i$ states (cells) is $(g_i)^{N_i}$. Hence, the to probability, for a given distribution is given by

$$W = \frac{N!\ g_1^{N_1} \cdot g_2^{N_2} \cdot g_3^{N_3} \cdots (g_k)^{N_k}}{N_1!\ N_2!\ N_3! \cdots N_k!} = N! \prod_i \frac{(g_i)^{N_i}}{N_i!} \qquad \cdots(7.6.1$$

where $\Pi$ denotes the product.

Taking natural logarithm on both sides, we have,

$$\ln W = \ln N! + \ln\left[\prod_i \frac{(g_i)^{N_i}}{N_i!}\right]$$

$$\ln W = \ln N! + \sum_i N_i \ln g_i - \sum_i \ln N_i! \qquad \cdots(7.6.1$$

Applying Stirling's approximation, $\ln x! = x \ln x - x$ (where $X$ is very large) we get equation (7.6.1.4)

$$\ln W = N \ln N - N + \sum_i N_i \ln g_i - \left[\sum_i (N_i \ln N_i - N_i)\right]$$

$$= N \ln N - N + \sum_i N_i \ln g_i - \sum_i N_i \ln N_i + \sum N_i$$

$$= N \ln N + \sum_i N_i \ln g_i - \sum_i N_i \ln N_i \quad \left[\because \sum_i N_i = N\right]$$

$$= N \ln N - \sum_i (N_i \ln N_i - N_i \ln g_i]$$

$$\mathbf{\ln W = N \ln N - \sum_i N_i \ln \frac{N_i}{g_i}} \qquad \cdots (7.6.1.5)$$

The **most probable distribution** can be obtained by evaluating the maximum value of V and then equate it to zero. Differentiating equation (7.6.1.5) *w.r.t.* $N_i$, we get from tion (7.6.1.5),

$$d[\ln W] = d(N \ln N) - \sum_i dN_i \ln \frac{N_i}{g_i} - \sum N_i \, d\left(\ln \frac{N_i}{g_i}\right)$$

$$= -\sum_i dN_i \ln \frac{N_i}{g_i} - \sum_i N_i \frac{dN_i}{N_i}$$

$$= -\sum_i dN_i \ln \frac{N_i}{g_i} - \sum_i dN_i$$

$$\mathbf{d[\ln W] = -\sum d N_i \ln \frac{N_i}{g_i}} \quad \left[\begin{array}{l} \because \sum N_i = \text{constant} \\ \therefore \sum dN_i = 0 \end{array}\right] \qquad \cdots (7.6.1.6)$$

Thus for most probable distribution, $d(\ln W) = 0$

$$\mathbf{\sum_i \ln\left(\frac{N_i}{g_i}\right) dN_i = 0} \qquad \cdots (7.6.1.7)$$

The solution of this equation is subjected to the conditions represented by equations .1.1) and (7.6.1.2)—

$$\sum_i N_i E_i = \text{constant} \;\; \text{i.e.,} \;\; \mathbf{\sum_i E_i \, dN_i = 0} \qquad \cdots (7.6.1.8)$$

$$\sum_i N_i = \text{constant} \;\; \text{or,} \;\; \mathbf{\sum dN_i = 0} \qquad \cdots (7.6$$

Multiplying equation (7.6.1.9) by $\alpha$ and equation (7.6.1.8) by $\beta$ and then addi equation (7.6.1.7) we get,

$$\sum_i \left[\ln\left(\frac{N_i}{g_i}\right) + \alpha + \beta E_i\right] dN_i = 0 \qquad \cdots(7.6.1.1$$

As the various $dN_i$ states are independent to one another, the above summati equal to zero if,

$$\ln \frac{N_i}{g_i} + \alpha + \beta E_i = 0 \text{ or, } \frac{N_i}{g_i} = e^{-\alpha - \beta E_i} \text{ or, } N_i = g_i e^{-(\alpha + \beta E_i)} \qquad \cdots(7.6.1.1$$

avg no of particle
state in
in each energy level Ei

**This equation is known as the Maxwell-Boltzmann distribution law.** This equati gives the maximum probability of distribution of particles in $g_i$-number of states wh values of $\alpha$ and $\beta$ depend upon the physical property of the system.

Now, the total number of particles

$$N = N_1 + N_2 + N_3 + \cdots$$

$$= g_1 e^{-\alpha - \beta E_1} + g_2 e^{-\alpha - \beta E_2} + g_3 e^{-\alpha - \beta E_3} + \cdots$$

$$= e^{-\alpha}\left[\sum_i g_i e^{-\beta E_i}\right]$$

or,

$$N = e^{-\alpha} Z \qquad \cdots(7.6.1.1$$

where $Z \left(= \sum_i g_i e^{-\beta E_i}\right)$ is called **the partition function.** expresses the partition of distribution energy over various energy level.

Therefore, we get from equation (7.6.1.12) $e^{-\alpha} = \frac{N}{Z}$. Thus we can write from equati (7.6.1.11) after substituting the value of $e^{-\alpha}$,

$$N_i = \left(\frac{N}{Z}\right) g_i e^{-\beta E_i} \qquad \cdots(7.6.1.1$$

This equation is also known as Maxwell-Boltzmann distribution law.

## 7.6.2 The Maxwell-Boltzmann Distribution Function

It gives the probability of a particle to occupy an energy state $E_i$ and is expressed as

$$\frac{N_i}{g_i} = \frac{1}{e^{(\alpha + \beta E_i)}} \qquad \cdots(7.6.2.$$

where $\alpha$ and $\beta$ are constants depending upon the physical property of the system.

**PROBLEM**

**A gas has two distinguishable identical particles in $k$ th energy level in which there are three quantum states according to M-B statistics.**

**i) Find the possible number of microstates,**

**ii) Find also the number of microstates in tabular form.**

*Solution*

i Since the particles are distinguishable, we can apply Maxwell-Boltzmann statistics. In that case, the total probability for this given distribution i.e., the total number of microstates,

$$W = \frac{N!\, g_k^{N_k}}{N_k!} = 2!\,\frac{3^2}{2!} \quad [\because N = 2, N_k = 2, g_k = 3] = 9 \text{ microstates.}$$

ii If the distinguishable two particles are $A$ and $B$, the number of microstates can be obtained in a tabular form as bellow (considering each quantum state can accomodate one or more than one particles) :

| Micro-states \ Q-states → | 1 | 2 | 3 |
|---|---|---|---|
| 1 | $AB$ | × | × |
| 2 | × | $AB$ | × |
| 3 | × | × | $AB$ |
| 4 | $A$ | $B$ | × |
| 5 | $B$ | $A$ | × |
| 6 | $A$ | × | $B$ |
| 7 | $B$ | × | $A$ |
| 8 | × | $A$ | $B$ |
| 9 | × | $B$ | $A$ |

So, the number of microstates are 9 .

### 7.6.3 Disadvantages of Maxwell-Boltzmann Statistics

In the Maxwell-Boltzmann statistics, it is considered that the particles of a system (e.g., ideal gas) are distinguishable. So, it can explain the energy distribution of the molecules of ideal gas to a fair degree of accuracy. But *this statistics is failed to explain the energy distribution of indistinguishable particles like electrons (so called electron gas) or photons (so called photon gas).*

These problems can be solved with the help of quantum statistics.

## 7.7 NEEDS OF QUANTUM STATISTICS

In Maxwell-Boltzmann distribution it has been assumed that

① the particles are distinguishable, but it fails to explain the energy distribution of many indistinguishable elementary particles like electrons (so called electron gas) and that of photon (so called photon gas).

② any number of particles can occupy the same quantum states. But in practice, ma particles like electrons obey Pauli's exclusion principle which states **each quantum state can accomodate only one particle.**

All these difficulties are overcome by the use of quantum statistics.

**Special Note**

Degenerate and non-degenerate states :

If $N_i$ is the number of identical particles in $g_i$ quantum states (i.e., cells) of $i$ th energy level (i.e. compartment) $E_i$ of the phase-space, the ratio of $\frac{N_i}{g_i}$ is called **occupation index.**

① If now, $\frac{N_i}{g_i} \ll 1$ (i.e., $N_i \ll g_i$), the system is called non-degenerate.

② If $\frac{N_i}{g_i} > 1$ (i.e., $N_i > g_i$), the system is called degenerate.

③ If $\frac{N_i}{g_i} \gg 1$, the system is called strongly degenerate. It is seen for Boltzons particles.

## 7.8 TYPES OF QUANTUM STATISTICS

Quantum statistics is classified into two types—

❶ Fermi-Dirac (F-D) statistics,

❷ Bose-Einstein (B-E) statistics.

It is to be noted that the **particles are indistinguishable** and **identical in both statistics.**

## 7.9 FERMI-DIRAC STATISTICS

It provides the statistical behaviour of indistinguishable and identical particles with $\frac{1}{2}$ integral spin. These particles obey Pauli's exclusion principle.

**Basic postulates:**

❶ The particles are indistinguishable and identical.

❷ They obey Pauli's exclusion principle. So, each energy state can accomodate either no particle or only one particle.

❸ These particles have $\frac{1}{2}$ integral spin (*e.g.* spin angular momentum $m_s\hbar = \frac{1}{2}\hbar, \frac{3}{2}\hbar, \frac{5}{2}\hbar$ ··· ; where $m_s$ = spin quantum number).

❹ The particles have antisymmetric wave function (as no two particles have same quantum state).

**Fermions: The particles those are indistinguishable, identical having $\frac{1}{2}$ intergral spin and obey Fermi-Dirac statistics are called fermions.**

Examples : Electrons $(m_s = \pm\frac{1}{2})$, positrons $(m_s = \pm\frac{1}{2})$, neutrons $(m_s = \pm\frac{1}{2})$, protons $(m_s = \pm\frac{1}{2})$, $\mu$ mesons $(m_s = \pm\frac{1}{2})$ are the examples of fermions. It has also observed, if the total number of nucleons of atom is odd, the atoms or molecules obey F-D statistics. So, ${}_1H^3$, ${}_2He^3$, ${}_3Li^7$, ${}_6C^{13}$ are also the examples of fermions.

## 7.9.1 Fermi-Dirac Distribution Law

Fermi-Dirac statistics is applicable for the particles those are identical, indistinguishable and obey Pauli's exclusion principle.

In order to determine the energy distribution of a system, we divide the available volume in the phase-space into a large number of quantum states. Each quantum state corresponds to a particle wave function.

Let us consider the total number of possible ways (permutations) in which '$N_i$' number of identical and indistinguishable particles can be distributed among the $g_i$ **quantum states** of energy $E_i$ such that each quantum state can accomodate only one particle. In this case, $g_i$ must be greater than $N_i$ as there must be at least one cell (quantum state) available for every particle. The number of distinguishable (or, independent) ways in which $N_i$ particles can be arranged among $g_i$ quantum states is given by

$$W_i = \frac{g_i!}{N_i!\,(g_i - N_i)!} \qquad \cdots(7.9.1.1)$$

So, the total number of independent ways, $W$, (i.e., thermodynamic probablity) of arranging $N_1, N_2, \cdots N_n$ particles in various energy levels (say, '$n$') is the product of the term given by equation (7.9.1.1). Thus the probability of the entire distribution of the particles is given by

$$W = \prod_{i=1}^{n} W_i = \prod_{i=1}^{n} \frac{g_i\,!}{N_i!\,(g_i - N_i)!} \text{ where } \prod \text{ denotes the product.} \qquad \cdots(7.9.1.2)$$

**Special Note**

The number of ways for placing a first of $N_i$ number of particles in one of the $g_i$ quantum state = $g_i$

The remaining number of quantum states after placing the first particle in a particular quantum state is $(g_i - 1)$.

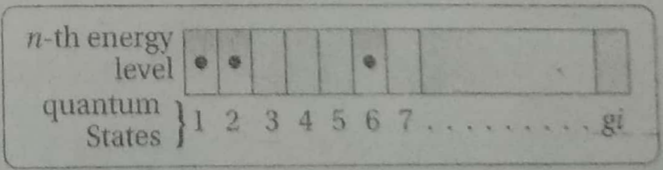

**Fig. 3** ▷ The number of ways for placing $N_i$ number particles in one of the $g_i$ quantum state

So, the number of ways of placing a second particle in $(g_i - 1)$ states = $(g_i - 1)$

Thus, the number of ways for placing $N_i$ th particle in the remaining $[g_i - (N_i - 1)]$ states = $g_i - (N_i - 1) = g_i - N_i + 1$

So, the total number of ways for placing $N_i$ particles among $g_i$ states of energy $E_i$ (keeping in mind that there is only one particle in each quantum state)

$$= g_i\,(g_i-1)(g_i-2)\quad\cdots\quad(g_i-N_i+1)$$

$$= \frac{g_i\,(g_i-1)(g_i-2)\quad\cdots\quad(g_i-N_i+1)\cdot(g_i-N_i)!}{(g_i-N_i)!}$$

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

For each of these arragements, the number for permutation of $N_i$ particles among themselves is $N_i!$ Again these permutation do not give independent arrangements of these particles due to their indistinguishable properties. So, the number of independent permutations of $N_i$ particles among $g_i$ quantum states

$$= \frac{g_i!}{N!(g_i-N_i)!}$$

Taking natural logarithm on both sides, we have

$$\ln W = \sum_{i=1}^{n} [\ln g_i! - \ln N_i! - \ln (g_i - N_i)!] \qquad \cdots(7.9.1.3)$$

Applying Stirling's approximation, $\ln x! = x \ln x - x$, (when, $x$ is large), we get from equation (7.9.1.3).

$$\ln W = \sum_i [(g_i \ln g_i - g_i) - (N_i \ln N_i - N_i) - \{(g_i - N_i) \ln (g_i - N_i) - (g_i - N_i)\}]$$

or, $$\mathbf{\ln W = \sum_i [g_i \ln g_i - N_i \ln N_i - (g_i - N_i) \ln (g_i - N_i)]} \qquad \cdots(7.9.1.4)$$

The **most probable distribution** can be obtained by evaluating the maximum value of $\ln W$. Hence differentiating equation (7.9.1.4) partially *w.r.t.* $N_i$ we get,

$$d(\ln W) = \sum_i [-N_i \cdot \frac{1}{N_i} dN_i - \ln N_i\, dN_i + (g_i - N_i)\frac{1}{(g_i - N_i)} dN_i$$

$$+ \ln (g_i - N_i)\, dN_i] \qquad [\because\ g_i \text{ is mere number, } d(g_i) = 0]$$

or, $$\mathbf{d(\ln W) = \sum_i [\ln (g_i - N_i) - \ln N_i] dN_i} \qquad \cdots(7.9.1.5)$$

So, for most probable distribution, $d(\ln W) = 0$

i.e., $\sum_i [\ln (g_i - N_i) - \ln N_i] dN_i = 0$ or, $\mathbf{\sum_i [\ln N_i - \ln (g_i - N_i)]\, dN_i = 0}$ $\cdots(7.9.1.6)$

In addition to it the system must satisfy **conservation of total number of fermions** $N$ (as no particles leave or enter into the system) and **conservation of total energy** $E$ (as the system of fermions is isolated)

$\therefore\quad N = \sum_i N_i = \text{constant}\quad$ or, $\mathbf{\sum_i dN_i = 0}$ $\cdots(7.9.1.7)$

and $E = \sum_i N_iE_i$ = constant or $\sum_i E_i\, dN_i = 0$ ···(7.9.1.8)

Multiplying equation (7.9.1.7) by $\alpha$ and equation (7.9.1.8) by $\beta$ and then adding them to equation (7.9.1.6) we have,

$$\sum_i [\ln N_i - \ln(g_i - N_i) + \alpha + \beta E_i]\, dN_i = 0 \qquad \cdots(7.9.1.9)$$

where $\alpha$ and $\beta$ are Lagrange's undetermined multiplier.

As various $dN_i$ states are independent of one another, the above summation is equal to zero if

$$\ln N_i - \ln(g_i - N_i) + \alpha + \beta E_i = 0$$

or, $$\ln\frac{g_i - N_i}{N_i} = \alpha + \beta E_i \qquad \text{or,} \qquad \frac{g_i - N_i}{N_i} = e^{\alpha + \beta E_i}$$

or, $$\frac{g_i}{N_i} - 1 = e^{\alpha + \beta E_i} \qquad \text{or,} \qquad \frac{g_i}{N_i} = 1 + e^{\alpha + \beta E_i}$$

or, $$N_i = \frac{g_i}{e^{\alpha + \beta E_i} + 1} \qquad \cdots(7.9.1.10)$$

This equation is Fermi-Dirac distribution law.

For fermions in statistical equilibrium at temperature $T$, $\alpha = -\frac{E_f}{kT}$ (i.e., the value of $\alpha$ is negative) and $\beta = \frac{1}{kT}$ where $E_F$ = Fermi energy of the system and

$k$ = Boltzmann's constant = $1.38 \times 10^{-23}\ \text{J} \cdot \text{K}^{-1}$

$$N_i = \frac{g_i}{e^{(E_i - E_f)/kT} + 1} \qquad \cdots(7.9.1.11)$$

So, the F-D distribution function thus becomes

$$f(E) = \frac{N_i}{g_i} = \frac{1}{1 + e^{(E_i - E_f)/kT}} \qquad \cdots(7.9.1.12)$$

### 7.9.2 Fermi-Dirac Distribution Function

This gives the probability of a fermion to occupy an energy state $E_i$ at absolute temperature $T$ and is expressed as

$$f(E) = \frac{1}{1 + e^{(E_i - E_f)/kT}} \qquad \cdots(7.9.2.1)$$

where $E_f$ = the Fermi energy and $k$ = Boltzmann's constant = $8.62 \times 10^{-5}\ \text{eV} \cdot \text{K}^{-1}$ = $1.3805 \times 10^{-23}\ \text{J} \cdot \text{K}^{-1}$

same, indep. Co onetical

### 7.9.3 Fermi Distribution at Zero and Non-zero Temperature

If we draw a graph between $f(E)$ against $E_i$ at different temperature we get the adjacent graph [Fig. 4]. At $T = 0\text{K}$, we get a curve as shown by full line whereas at higher temperature $T > 0\text{K}$, the corresponding Fermi distribution curve is shown in Fig. 4. We find from equation, (7.9.1.11), $N_i$ decreases rapidly for $E_i > E_f$ at low temperature.

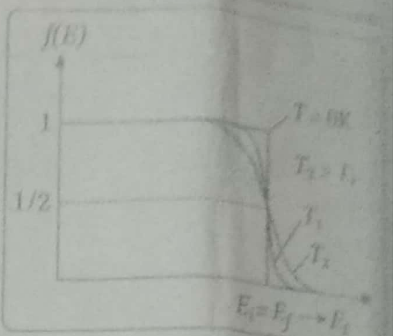

Fig. 4 ▷ The Fermi-Dirac distribution function

Analyzing this curve the following cases are observed.

**Case 1** If $T > 0$ K and $E_i = E_f$,

$$f(E) = \frac{1}{1+e^{(E_f-E_f)/kT}} = \frac{1}{1+e^0} = \frac{1}{2}$$

Thus, for Fermi energy level the probability of occupation of a fermion is $\frac{1}{2}$ for any temperature greater than 0 K.

**Case 2**

❶ If $T = 0,\ E_i < E_f;\ f(E) = \frac{1}{1+e^{-\infty}} = \frac{1}{1+0} = 1$

i.e., *All energy states having* $E_i < E_f$ *are occupied by a single* fermion (i.e., electron).

❷ if $T = 0,\ E_i > E_f;\ f(E) = \frac{1}{1+e^{\infty}} = \frac{1}{1+\infty} = 0$

i.e., *All energy states having* $E_i > E_f$ *are unoccupied.*

At $T = 0$ K, Fermi energy ($E_f = \varepsilon_f$, say) is that energy level upto which all the energy states are filled up by fermions and all the energy states above it are empty. The Fermi energy level is the highest occupied energy level of fermions at $T = 0$ K. **Thus, Fermi energy is the maximum energy that can be occupied by a fermion (i.e., electron) at 0 K.**

### 7.9.4 Fermi Temperature ($\theta_f$)

**It may be defined as the ratio of the fermi energy ($\varepsilon_f$) at absolute zero to Boltzmann's constant $k$ and its corresponding absolute temperature.**

So, Fermi temperature $\theta_f = \varepsilon_f/kT$.

**PROBLEM**

**1 A gas has two indistinguishable identical particles in $k$ th energy level in which there are three quantum states according to F-D statistics.**

**(i) Find the possible number of microstates, and**

**(ii) Show the number of microstates in tabular form.**

**Solution**

i The total number of microstates considering each indistinguishable quantum state can accomodate only one particle.

Dirac distribution

mi-Dirac distribution
ved to have half-
in unit of
Fermions

$$W = \frac{g_k!}{N_k!\,(g_k - N_k)!} = \frac{3!}{2!\,(3-2)!}$$

$$= 3 \text{ microstates } [\because g_k = 3,\ N_k = 2].$$

8 Let each indistinguishable particle be $A$. Therefore, the number of microstates can be given in the following table:

| Micro-states \ Q-states → | 1 | 2 | 3 |
|---|---|---|---|
| 1 | $A$ | $A$ | × |
| 2 | $A$ | × | $A$ |
| 3 | × | $A$ | $A$ |

nce, the number of microstates are 3.

**BLEM**

**Find the probability of an electron to occupy an energy state of 6.125eV at temperature 991°C (Given : The Fermi energy level of the atom is 5.6 eV).**

**lution]** The probability of an electron to occupy an energy state $E$ is given by,

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

re $E = 6.125$ eV, $E_f = 5.6$ eV,

$$k = 1.38 \times 10^{-23}\ \mathrm{J \cdot K^{-1}} = 8.62 \times 10^{-5}\ \mathrm{eV \cdot K^{-1}}$$

$$T = 991 + 273 = 1264\ \mathrm{K}$$

$$f(E) = \frac{1}{1 + e^{(6.125 - 5.6)/8.62 \times 10^{-5} \times 1264}}$$

$$= \frac{1}{1 + e^{4.818}} = \frac{1}{1 + 123.77} = \frac{1}{124.77}$$

So, the probability to occupy an energy state with energy 6.125 eV is 0.008 (i.e., 0.8% ≈ (1%)).

**BLEM**

**The probability of an electron to occupy an energy state of 6.125 eV is 1% at temperature 991°C. Find the Fermi energy.**

**ution]** Here $f(E) = \frac{1}{e^{(E - E_f)/(kT)} + 1}$

$$\frac{1}{100} = \frac{1}{e^{(6.125 - E_f)/8.62 \times 10^{-5} \times 1264} + 1} \quad [991^\circ\mathrm{C} = 1264\ \mathrm{K}]$$

$$E_f = 5.625\ \mathrm{eV}$$

nce, the Fermi energy is 5.625 eV.

## 7.9.5 Electron Gas in Metal

In metal, there is an overlapping between valance band and conduction band. Due to th reason, a large no of free electrons are observed in metals. Thus metal becomes a ve good conductor. These free electrons move freely in the metal and continuously colli with the atoms. So they behave like a gas, called electron gas.

Electrons are elementary particles with $\frac{1}{2}$ integral spin. In a metal electrons have the quantised energy level and obeys Pauli's exclusion principle. So, they are called fermi as they obey Fermi-Dirac statistics.

If we consider a continuous distribution of energy among '$N$' number of f electrons in electron gas then for the electrons with their energy range $E$ and $E+dE$, s replaced by $g(E)\,dE$ and $n_i$ is replaced by $n(E)\,dE$ in equation (7.9.1.11).

So, the total number of electrons in metal within the energy range $E$ and $E+dE$ be written from equation (7.9.1.12) as,

$$n(E)\,dE = \frac{g(E)\,dE}{e^{(E-E_f)/kT}+1} \quad \text{---(7.9}$$

## 7.9.6 Fermi-Dirac Law of Energy Distribution for Free Electrons in Meta

If $n(E)\,dE$ is the total number electrons within the energy range $E$ and $E+dE$, the can write from equation (7.9.5.1)

$$n(E)\,dE = \frac{g(E)\,dE}{e^{(E-E_f)/kT}+1} \quad \text{---(7.9}$$

where $g(E)\,dE$ is the number of energy states within the energy range $E$ and $E+dE$ is the volume of the Fermi-phase space of conductor, the value of $g(E)\,dE$ can be w in terms of momentum as

$$g(p)\,dp = \frac{8\pi V}{h^3}\cdot p^2\,dp = \frac{8\pi V}{h^3}\cdot p(p\,dp) \quad \text{---(7.}$$

Now, for non-relativistic case, the energy of an electron moving with velocity $v$,

$$E = \frac{1}{2}mv^2 = \frac{p^2}{2m} \quad (\text{since } p = mv) \quad \text{---(7}$$

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

Differentiating, $2p\,dp = 2m\,dE$ or, $p\,dp = m\,dE$ ---(7

Substituting the value of $p$ and $p\,dp$ we get from equation (7.9.6.2)

$$g(E)\,dE = \frac{8\pi V}{h^3}(2mE)^{1/2}m\,dE \quad \text{---(7}$$

From equation (7.9.6.1) we can write

$$n(E)\,dE = \frac{8\sqrt{2}\pi V}{h^3} = \frac{m^{3/2}E^{1/2}dE}{e^{(E-E_f)/kT}+1} \quad \text{---(}$$

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

## 7.9.7 Value of Total Energy (Fermi Energy) and Total Number of Electrons in Metal at Absolute Zero

At absolute temperature ($T = 0$ K), the total number of electrons is equal to the total number of energy states occupied by the electrons from the energy range 0 to $\varepsilon_f$ (Fermi energy).

Electrons are fermions. Therefore, each energy state has only one electron. Thus, at temperature $T = 0$ K, the number of electrons ($N$) is equal to the total number of energy states occupied by the electrons for the energy from 0 to $\varepsilon_f$. Thus from equation (7.9.6.5) we get,

$$N = \int_0^{\varepsilon_f} g(E)\, dE = \frac{8\sqrt{2}\pi V m^{3/2}}{h^3} \int_0^{\varepsilon_f} E^{1/2} dE = \frac{8\sqrt{2}\pi V m^{3/2}}{h^3} \varepsilon_f^{3/2} \times \frac{2}{3}$$

$$N = \frac{16\sqrt{2}\pi V m^{3/2}}{3h^3} \varepsilon_f^{3/2} \qquad \cdots(7.9.7.1)$$

**This is the expression of total number of electrons in a metal at absolute zero.** So, the **Fermi energy at absolute zero can** be written from equation (7.9.7.1).

$$\varepsilon_f = \frac{h^2}{8m}\left(\frac{3N}{\pi V}\right)^{2/3} \qquad \cdots(7.9.7.2)$$

**So Fermi energy depends only on electrons concentration $\left(\frac{N}{V}\right)$ and it is independent on the size and volume of the conductor.**

**PROBLEM**

**For silver, the electron concentration $\left(\frac{N}{V}\right)$ is $5.86 \times 10^{28}$ m$^{-3}$. Find its Fermi energy.**

**Solution** Given, electron concentration of silver, $\frac{N}{V} = 5.86 \times 10^{28}$ m$^{-3}$

So, the Fermi energy at, $T = 0$ K

$$\varepsilon_f = \frac{h^2}{8m}\left(\frac{3}{\pi}\frac{N}{V}\right)^{2/3} = \frac{(6.624 \times 10^{-34})^2}{8 \times 9.1 \times 10^{-31}} \left[\frac{3}{3.14} \times (5.86 \times 10^{28})\right]^{2/3} \text{J}$$

$$\simeq 9 \times 10^{-19}\,\text{J} = \frac{9 \times 10^{-19}}{1.6 \times 10^{-19}}\,\text{eV} = 5.625\,\text{eV}$$

So, the maximum kinetic energy of free elctrons in silver at absolute zero temperature is 5.625 eV.

**PROBLEM**

**If the atomic weight and density of silver is 108 g·mol-1 and 10.50 g·cm-3 respectively, find the Fermi energy level of silver at 0 K (considering there is 1 free electron per atom).**

**Solution** We know, Fermi energy at $T = 0$ K, $\varepsilon_f = \frac{h^2}{8m}\left(\frac{3N}{\pi V}\right)^{2/3}$

---

- At absolute zero, the highest energy occupied by valence electron is equal to Fermi energy.

Here, electron concentration of silver can be written as

$$\frac{N}{V} = \frac{\text{Avogadro number}}{\text{atomic weight}} \times \text{density}$$

$$= \left(\frac{6.023 \times 10^{23} \text{ atom mole}^{-1}}{108 \text{ g mol}^{-1}}\right) \times (10.50 \text{ g} \cdot \text{cm}^{-3}) = 5.86 \times 10^{28} \text{ m}^{-3}$$

$$\therefore \quad \varepsilon_f = \frac{h^2}{8m}\left(\frac{3}{\pi} \cdot \frac{N}{V}\right)^{2/3} = \frac{(6.624 \times 10^{-34})^2}{8 \times 9.1 \times 10^{-31}} \left[\frac{3}{3.14}(5.86 \times 10^{28})\right]^{2/3}$$

$$\simeq 9 \times 10^{-19} \text{ J} = \frac{9 \times 10^{-19}}{1.6 \times 10^{-19}} \text{ eV} = 5.625 \text{ eV}.$$

**PROBLEM 3** **If the Fermi energy at 0 K of metalic silver is 5.5 eV, find the electron concentration of silver atom. Given, the atomic weight of silver is 108 and the number of free electron per atom is 1.**

**Solution** We know, Fermi energy at absolute zero

$$\varepsilon_f = \frac{h^2}{8m}\left(\frac{3N}{\pi V}\right)^{2/3}; \quad \text{where } \frac{N}{V} = \text{electron concentration}$$

or, $$5.5 \times 1.6 \times 10^{-19} = \frac{(6.6 \times 10^{-34} \text{ J} \cdot \text{s})^2}{8 \times 9.1 \times 10^{-31} \text{kg}} \left(\frac{3}{3.14}\right)^{2/3} \cdot \left(\frac{N}{V}\right)^{2/3}$$

or, $$\frac{640.64 \times 10^{-50}}{(6.6 \times 10^{-34})^2} = \left(\frac{3}{3.14}\right)^{2/3} \cdot \left(\frac{N}{V}\right)^{2/3}$$

or, $$(14.70 \times 10^{18})^{3/2} = \frac{3}{3.14} \times \frac{N}{V}$$

or, $$\frac{N}{V} = 5.89 \times 10^{28} \times \frac{3.14}{3} = 5.89 \times 10^{28} \text{ m}^{-3}$$

So, the free electron concentration (or density) = $5.86 \times 10^{28}$ m$^{-3}$.

## 7.10 BOSE-EINSTEIN STATISTICS

It gives the statistical behaviour of indistinguishable and identical particles with inte
spin. These particles do not obey Pauli's exclusion principle.

**Basic postulates:**

❶ The particles are indistinguishable and identical.

❷ They do not obey Pauli's exclusion principle. So, each quantum (energy) state c
accomodate any number of particles.

❸ These particles have zero or integral spin (i.e., spin angular momentum $m_s\hbar$
$\hbar, 2\hbar, 3\hbar \cdots$, where $m_s$ = spin quantum number).

❹ These particles have symmetric wave function.

**Bosons: The particles those are indistinguishable, identical having integral sp
(i.e., $m_s\hbar = 0, \hbar, 2\hbar$) and obey Bose-Einstein statistics are called as bosons.**

***Examples:*** phonons, photons ($m_s = 1$), $\pi$-mesons ($m_s = 0$), $\alpha$-particles ($m_s = 0$),
mesons, $\eta$-mesons.

If the total number of nucleons of atom is even, the atoms or molecules obey B
statistics. So, ${}_1H^2$, ${}_2He^4$, ${}_6C^{12}$, ${}_8O^{16}$, etc. atoms are also the examples of bosons.

### 7.10.1 Bose-Einstein Distribution Law

Bose-Einstein theory is applicable for the particles those are identical, indistinguishab
and each quantum state can be occupied by any number of particles.

In order to find the energy distribution among indistinguishable identical partic
(each having spin angular momentum $m_s\hbar = 0, \frac{1}{2}\hbar, \frac{3}{2}\hbar, \cdots$)❸, we divide the availab
volume in the phase space into a large number of quantum states.

Let us consider the total number of ways in which $N_i$ number of identic
indistinguishable particles can be distributed among $g_i$ quantum states of energy $E_i$ su
that each quantum state (cell of the phase space) can be occupied by any number
particles.

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❸ $m_s$ = spin quantum number and $m_s\hbar$ = spin angular momentum.

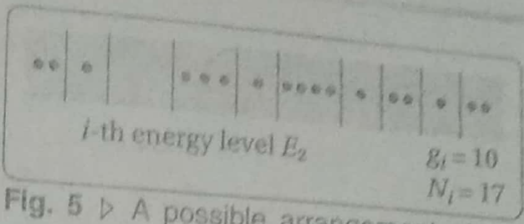

**Fig. 5** ▷ A possible arrangement of $N_i$ particles among $g_i$ number of degenerate quantum states of energy $E_i$ (i.e., in the $i$-th energy state)

Suppose, $N_i$ identical particles are arranged a row and distributed among $g_i$ quantum ates with $(g_i - 1)$ partitions in between to give e distinct arrangements [Fig. 5].

The number of possible distinguishable and tinct arrangements of $N_i$ particles with 1) partitions can be given as

$$W_i = \frac{(N_i + g_i - 1)\,!}{N_i!\,(g_i - 1)\,!} \qquad \cdots(7.10.1.1)$$

So, the total number of distinguishable and distinct ways $(W)$ of arranging $N_1$, $N_2$, $\cdots$ $N_n$ particles in '$n$' energy level is the product of expression given in equation 10.1.1) for $i = 1, 2, \cdots n$.

$$W = \prod_{i=1}^{n} W_i = \prod_{i=1}^{n} \frac{(N_i + g_i - 1)\,!}{N_i!\,(g_i - 1)\,!} \quad \text{where } \prod \text{ denotes the product.} \qquad \cdots(7.10.1.2)$$

**Most probable macrostate:** It corresponds to the state of maximum thermo-dynamic bability. We know, $N_i$ and $g_i$ are very large numbers compared to unity. Hence, the ation (7.10.1.2) can be written as

$$W = \frac{\prod_{i=1}^{n} (N_i + g_i)\,!}{N_i!\,g_i!} \qquad \cdots(7.10.1.3)$$

ing natural logarithm on both sides, we have

$$\ln W = \sum_i \ln(N_i + g_i)\,! - \ln N_i - \ln g_i\,! \qquad \cdots(7.10.1.4)$$

Applying Stirling's approximation, $\ln x! = x \ln x - x$ (where $x$ is very large) get from equation (7.10.1.4),

$$\ln W = \sum_i [\{(N_i + g_i)\ \ln(N_i + g_i) - (N_i + g_i)\}$$
$$-\{N_i \ln N_i - N_i\} - \{g_i \ln g_i - g_i\}]$$

$$\ln W = \sum_i [(N_i + g_i) \ln(N_i + g_i) - N_i \ln N_i - g_i \ln g_i] \qquad \cdots(7.10.1.5)$$

The most probable distribution can be obtained by evaluating the maximum value of $W$. Hence, differentiating the equation (7.10.1.5), we get,

$$d(\ln W) = \sum_i [\ln(N_i + g_i)\, dN_i + (N_i + g_i)\, \frac{1}{(N_i + g_i)}\, dN_i$$
$$-N_i \frac{1}{N_i} dN_i - \ln N_i\, dN_i] \quad [g_i \text{ is mere number } d(g_i) = 0]$$

state in the … average … …stein … …wing result: … …tion 4.10.1 … Total number of microstates in the mom… range from $p$ to $p+dp$ is … named the pa… bosons.

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or,
$$d(\ln W) = \sum_i [\ln(N_i+g_i)\,dN_i - \ln N_i\,dN_i] \quad \cdots(7.10.$$

Thus, for *most probable distribution*, $d(\ln W) = 0$

i.e.,
$$\sum_i [\ln(N_i+g_i)\,dN_i - \ln N_i\,dN_i] = 0$$

or,
$$\sum_i [\ln N_i - \ln(N_i+g_i)]\,dN_i = 0 \quad \cdots(7.10.1$$

As the system must satisfy **(i)** conservation of total number of bosons $N$ … **(ii)** conservation of total energy of the system,

∴
$$N = \sum_i N_i = \text{constant} \quad \text{or,} \quad \sum_i dN_i = 0 \quad \cdots(7.10.1$$

and
$$E = \sum_i N_i E_i = \text{constant} \quad \text{or,} \quad \sum_i E_i\,dN_i = 0 \quad \cdots(7.10.1$$

Multiplying equation (7.10.1.8) by $\alpha$ and equation (7.10.1.9) $\beta$ and then addin… equation (7.10.1.7), we have

$$\sum_i [\ln N_i - \ln(N_i+g_i) + \alpha + \beta E_i]\,dN_i = 0 \quad \cdots(7.10.1.1$$

As the variation $dN_i$ are independent to one another, the above summation is equ… to zero if

$$\ln N_i - \ln(N_i+g_i) + \alpha + \beta E_i = 0$$

or,
$$\ln\frac{N_i+g_i}{N_i} = \alpha + \beta E_i \quad \text{or,} \quad \frac{N_i+g_i}{N_i} = e^{\alpha+\beta E_i}$$

or,
$$1 + \frac{g_i}{N_i} = e^{\alpha+\beta E_i} \quad \text{or,} \quad \frac{g_i}{N_i} = e^{\alpha+\beta E_i} - 1$$

or,
$$N_i = \frac{g_i}{e^{\alpha+\beta E_i} - 1} \quad \cdots(7.10.1.1$$

This **equation is Bose-Einstein distribution law.** Thus, it gives the most prob… distribution of bosons among the various energy levels (i.e., compartments).

In thermal equilibrium for bosons at temperature $T$, if $\mu$ is the chemical potentia… the system and $k$ is the Boltzmann's constant, we can write

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

Thus, we get from equation (7.10.1.11),

$$N_i = \frac{g_i}{e^{(E_i-\mu)/kT} - 1} \quad \cdots(7.10.1.1$$

So, the Bose-Einstein distribution function becomes

$$f(E) = \frac{N_i}{g_i} \quad \text{or} \quad f(E) = \frac{1}{e^{(E_i-\mu)/kT} - 1} \qquad \cdots(7.10.1.13)$$

If $E_i \gg kT$, the B-E distribution reduces to M-B distribution.

## 7.10.2 Bose-Einstein Distribution Function

This gives the probability of a boson to occupy an energy state ($E_i$) at absolute temperature ($T$) and is expressed as

$$f(E) = \frac{1}{e^{(E_i-\mu)/kT} - 1} \qquad \cdots(7.10.2.1)$$

where

$\mu$ = chemical potential of the gas

$k$ = Boltzmann's constant = $8.62 \times 10^{-5}\,\text{eV}\cdot\text{K}^{-1}$ $(= 1.3805 \times 10^{-23}\,\text{J}\cdot\text{K}^{-1})$

**PROBLEM 1**

**A gas has two indistinguishable identical particles in $k$th energy level in which there are three seperate quantum states according to B-E statistics.**

**(i) Find the possible number of microstates.**

**(ii) Show the individual microstates in a tabular form.**

**Solution**

1. In B-E statistics each quantum state can accomodate one or more than one indistinguishable identical particles.

According to B-E statistics, the total number of microstates considering the two particles are in $k$th energy level and the other levels are empty

$$W = \frac{(N_k + g_k - 1)!}{N_k!\,(g_k - 1)!} = \frac{(2+3-1)!}{2!\,(3-1)!} \qquad [\because N_k = 2,\ g_k = 3]$$

$$= \frac{4!}{2!\,2!} = \frac{4\cdot 3\cdot 2\cdot 1}{2\cdot 2} = 6 \text{ microstates}$$

2. If the two indistinguishable identical particles are represented by $A$, the number of microstates can be given below in tabular form :

| Q-states → <br> Micro-states ↓ | 1 | 2 | 3 |
|---|---|---|---|
| 1 | AA | × | × |
| 2 | × | AA | × |
| 3 | × | × | AA |

---

* If the energy levels of the system is very closely packed, the number of bosons having energy range $E$ and $E + dE$ is given by

$$n(E)\,dE = \frac{g(E)\,dE}{(E_i - \mu)/kT}$$

### 4.7.4 *Photon gas*

Now we shall apply B-E distribution law to a particular kind of bosons, namely photons. We know that photons have spin 1 and zero rest mass and have energy $E = h\nu$, $h$ is Planck's constant and $\nu$ is its frequency and it moves with universal speed $c$ in vacuum. Frequency and hence energy is now a continuous variable.

We consider an enclosure of volume $V$ maintained at a constant temperature $T$.

We suppose that the photons are contained in $V$ in equilibrium. We can call that collection of photons as *photon gas*. In the language of classical electromagnetic theory it is nothing but electromagnetic waves confined in that enclosure.

A very important property of photons is that all bodies at all temperatures emit and absorb photons. Hence number of photons $N$ in an enclosure kept at a constant temperature $T$ is *not constant.*

In the derivation of the above formula, the parameter $\alpha$ is introduced to ensure that $N$ is constant. But in this case $N$ is not constant.

$\therefore \alpha = 0 \quad \therefore e^{\alpha} = 1$

$\therefore$ From the above eqn. we can write the following.

Number of photons having energy between $E$ and $E + dE$, contained in a volume $V$ in equilibrium at temperature $T$ is given by

$$n(E)dE = \frac{g(E)dE}{e^{\frac{E}{kT}} - 1} \quad \text{............}(4.19)$$

Here $g$ $(E)dE$ is the number of states within the energy interval $E$ to $E + dE$. This number is to be found by elaborate calculation we get

$$g(E)dE = \frac{8\pi V}{c^3}\frac{E^2 dE}{h^3}.$$

[Calculation of $g(E)dE$ : In section 4.10.1 below we found the following result:

Total number of microstates in the momentum range from $p$ to $p + dp$ is

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

For photons we have relations : $E = pc$

$\therefore dE = cdp.$

Also photons have two spin states in transverse direction ; therefore to get the number of photon states we have to multiply the above by 2.

$\therefore$ Total number of photon states in the momentum range from $E$ to $E + dE$ is

$$g(E)dE = 2 \times V\frac{4\pi}{h^3}\frac{E^2}{c^2}\frac{dE}{c} = 2 \times V\frac{4\pi}{h^3c^3}E^2\,dE$$

$\therefore$ From 4.19, we get

$$n(E)dE = \frac{8\pi V}{c^3}\frac{E^2dE}{h^3}\frac{1}{e^{\frac{E}{kT}}-1}.$$

Dividing this by $V$ and multiplying by $E$, we get the energy per unit volume of the photon gas in the energy range $E$ and $E + dE$ in equilibrium at temperature $T$ to be

$$u_T(E)dE = \frac{8\pi}{c^3}\frac{E^3dE}{h^3}\frac{1}{e^{\frac{E}{kT}}-1} \quad \text{.............(4.20)}$$

Substituting $E = h\nu$ and $dE = hd\nu$ in eqn. 4.20, we get the energy density within a photon gas in equilibrium at temperature $T$ in the frequency range $\nu$ and $\nu + d\nu$ to given by

$$u_T(\nu)d\nu = \frac{8\pi}{c^3h^3}\frac{h^3\nu^3}{e^{h\nu/kT}-1}hd\nu$$

$$= \frac{8\pi h}{c^3}\frac{\nu^3d\nu}{e^{h\nu/kT}-1} \quad \text{..........(4.21)}$$

This is the well known Planck's law of radiation; we learned in the previous chapter.

It should be mentioned that Max Planck did not arrived at the above formula by this method. He derived it by an ad hoc assumption about radiation from oscillators in a blackbody, as we have seen in the previous chapter. The idea of photon was developed much later by Einstein and others. The credit for the above derivation goes to Professor Satyen Bose (1920). His basic idea in the derivation of the above relation was developed further and generalised by Einstein and we get the Bose-Einstein statistics. To honour Bose's contribution to Bose-Einstein statistics, Paul Dirac