→ Statistical Physics Be → 10 – 14 marks

Chapter-16

Date 10[29
Page 3

Classical statistical physics

* **Phase space** :- A combination of position space and momentum space is called phase space. It has 6 dimensions, i.e. three position co-ordinates and three momentum co-ordinates, all mutually perp. to each other. The position of a particle in phase space is specified by a point with six coordinates x, y, z, P_x, P_y, P_z. A small element in phase space is denoted by $d\tau$ and is given by

$$d\tau = (dx\,dy\,dz)(dP_x\,dP_y\,dP_z)$$

Volume of phase space :-

Volume of phase space is given as

$$d\tau = dP_x\,dP_y\,dP_z\,dx\,dy\,dz$$

From Heisenberg's uncertainty's principle,

$$dP_x\,dx \geq h$$

$$dP_y\,dy \geq h$$

$$dP_z\,dz \geq h$$

Where h is called planck's constant.

Then, $d\tau \geq h^3$

$\therefore$ Volume $= h^3$

Microstates and Macrostates :

The specification of a molecule in a cell is called microstate. The individual molecules if remain always in the same region of cell there is no change in microstate

Specification of number of molecules in a cell is called macrostate. If no. of molecules always remain same in the confined region of phase space whichever may be the molecule, the macrostate remain sam.

Let us design three phase space i.e. three cells A, B and C carrying molecules (a, b, c), (p, q) and f respectively. Molecules a, b and c if they are specified in cell A is called microstate of cell. There are three molecules in A is the macrostate of the cell A.

A	a, b, c	a, b, q	a q
B	p, q	p, c	b, c, p
C	f	f	f

Similarly, specification of molecules p in cell B and f in cell c are their respective microstate. The total number of molecules in cell B is two and c is one refers to macrostate of cell B and c respectively.

* **Ensemble** :- Each gas molecules constitutes a system. The collection of gas molecules from an assembly. The random collection of identical and independent assemblies is called ensemble. It has three types. they are

(1) Microconical ensemble
(2) Conical ensemble
(3) Grand-conical ensemble.

* **Constraint**

A restriction imposed upon the momentum or position of a particle due to geometrical condition is called constraint. For eg: The beads of an abacus are constraint to move 1-Dimension motion by supporting wires.

* **Thermodynamic probability** :- Two system are said to in thermodynamic probability if it satisfies the following two conditions.

(i) The probabilityes of finding of phase point in various region of phase should be independent of time.

(ii) The average values for the properties of system in various region of phase should be independent buth can be written ~~mathe~~ mathematically as,

$$\left(\frac{d\rho}{dt}\right)_{pq} = \text{constant}$$

where, ρ = density function
q = position
p = Momentum

* Fundamental postulates of classical statistical mechanics

The application of statistical mechanics to gases, certain fundamental postulates are mad. These are

(I) Any gas is composed by molecules, which are in motion and behave like very small elastic spheres.

(II) The size of each phase cell is same.

(III) All accessible macrostates corresponding to the possible macrostates are equally probable.

(IV) The total number of molecules is constant.

Total energy of the system is constant. Let there are n_1 molecules of energy ε_1, n_2 of ε_2 etc. then from the law of conservation of energy

$$E = n_1\varepsilon_1 + n_2\varepsilon_2 + \ldots \Rightarrow E = \sum_i n_i\varepsilon_i$$

(V) The equillibrium state of a gas corresponds to the microstate of maximum probability.

* **Partition function :** Volume in phase space occupied by cononical ensemble is called partition function. It is the energy partition that determines how the particles are distributed in difference energy range. It behaves in statistial mechanics as ψ behaves in quantum mechanics.

It is denoted by Z and is given as

$$Z = e^{-\beta A}$$

where, $\beta = \frac{1}{K_B T}$ Boltzmann's factor.

A = Helmohltz energy

Partition function is dimensionless quantity. Its value depend on molecular weight, temperature and intermolecular distance.

* **Division of phase space into cells :**

Let 2f dimensional phase space defined by position co-ordinates $q_1, q_2, \ldots q_i \ldots q_f$ and momentum co-ordinates $P_1, P_2 \ldots P_i \ldots P_f$, an element of phase volume may be represented by

$$d\tau = (\Delta q_1, \Delta q_2 \ldots \Delta q_f)(\Delta P_1, \Delta P_2 \ldots \Delta P_f)$$

Let us divide any finite volume of phase space into a charge no. of cells. Let the size of each cell be h^f.

But $h = \delta P_i, \delta q_i$

∴ The no. of microstates in this volume element

$$= \frac{\Delta q_1 \Delta q_2 \ldots \Delta q_i \ldots \Delta q_f \Delta p_1 \Delta p_2 \ldots \Delta p_i \ldots \Delta p_f}{h^f}$$

* Relation between Entropy and probability

Boltzmann derived the relationship between entropy and probability. Consider two cell A and B having entropies S_1 and S_2 having probability Ω_1 & Ω_2 respectively.

Then from Boltzmann relation,

$$S_1 = f(\Omega_1)$$
$$S_2 = f(\Omega_2)$$

Since, entropy is extensive quantity so,

$$S = S_1 + S_2 \longrightarrow (I)$$

Also,

$$\Omega = \Omega_1 \Omega_2$$

or, $f(\Omega) = f(\Omega_1 \Omega_2) \longrightarrow (II)$

Taking partial derivative of eqn. (II), we get

$$f'(\Omega_1) = \Omega_2 f'(\Omega_1 \Omega_2) \longrightarrow (III)$$
$$f'(\Omega_2) = \Omega_1 f'(\Omega_1 \Omega_2) \longrightarrow (IV)$$

Dividing eqn. (III) by (IV)

$$\frac{f'(\Omega_1)}{f'(\Omega_2)} = \frac{\Omega_2}{\Omega_1}$$

$$\therefore \Omega_1 f'(\Omega_1) = \Omega_2 f'(\Omega_2) = K$$

Where K is constant. Then,

$\Omega_1 f'(\Omega_1) = K$

$f'(\Omega_1) = \frac{K}{\Omega_1}$

Integrating, we get

$\int f'(\Omega_1)\, d(\Omega_1) = \int \frac{K\, d\Omega_1}{\Omega_1}$

$f(\Omega_1) = K \log \Omega_1 + C_1 \longrightarrow (v)$

Similarly,

$f(\Omega_2) = K \log \Omega_2 + C_2 \longrightarrow (vi)$

From experimental observations $K = 1.4 \times 10^{-23}$ J/K called Boltzmann constant. After applying the boundary condition, the constant c_1 and c_2 vanish.

$\therefore$ The general relation between the entropy and probability is

$s = K \log \Omega.$

* Boltzmann Cannonical distribution law

Let $n_1, n_2 --- n_i$ be the no. of particle in the energy state $\varepsilon_1, \varepsilon_2 --- \varepsilon_i$ respectively.

(I) From conservation of mass

i.e. $n_1 + n_2 + --- + n_i = N$

or, $\delta n_1 + \delta n_2 + --- + \delta n_i = \delta N = 0 \longrightarrow (1)$

(II) From conservation of energy

i.e. $\varepsilon_1 n_1 + \varepsilon_2 n_2 + --- + \varepsilon_i n_i = E$

$\varepsilon\delta n_1 + \varepsilon_2\delta n_2 + \dots + \varepsilon_i\delta n_i = 0 \longrightarrow (II)$

Now,

probability, $\Omega = \dfrac{N!}{n_1!\,n_2!\,n_3!\dots n_i!}$

Taking log on both sides, we get

$\log\Omega = \log N! - \log n_1! - \log n_2! - \dots - \log n_i! \longrightarrow (III)$

Using Strilling theorem,

$\log x! = x\log x - x$ if x is large

Then eqn. (III) becomes

$\log\Omega = N\log N - N - n_1\log n_1 + n_1 - n_2\log n_2 + n_2 - \dots - n_i\log n_i + n_i \longrightarrow (IV)$

For maximum probability $\delta(\log\Omega) = 0$

From eqn. (IV), we get

$\delta\log\Omega = \delta(N\log N) - \delta N - \delta(n_1\log n_1) + \delta n_1 - \delta(n_2\log n_2) + \delta n_2 - \dots$
$- \delta(n_i\log n_i) + \delta n_i$

or, $0 = 0 - 0 - n_1\cdot\frac{1}{n_1}\delta n_1 - \delta n_1\log n_1 + \delta n_1 - n_2\cdot\frac{1}{n_2}\delta n_2 - \delta n_2\log n_2 + \delta n_2$
$- \dots - n_i\cdot\frac{1}{n_i}\delta n_i - \delta n_i\log n_i + \delta n_i$

or, $0 = \delta n_1\log n_1 + \delta n_2\log n_2 - \dots + \delta n_i\log n_i \longrightarrow (VI)$

Multiply eqn. (I) by α and eqn. (II) by β and add with eqn. (VI), we get

$\alpha\delta n_1 + \alpha\delta n_2 + \dots + \beta\varepsilon_1\delta n_1 + \beta\varepsilon_2\delta n_2 + \dots + \log n_1\delta n_1 + \log n_2\delta n_2$
$+ \dots = 0$

or, $(\alpha + \beta\varepsilon_1 + \log n_1)\delta n_1 + (\alpha + \beta\varepsilon_2 + \log n_2)\delta n_2 + \dots = 0$

or, $\sum_i (\alpha+\beta\epsilon_i+\log n_i)\,\delta n_i = 0$

or, $\alpha+\beta\epsilon_i+\log n_i = 0$

or, $\log n_i = -\alpha-\beta\epsilon_i$

or, $n_i = e^{-\alpha-\beta\epsilon_i}$

or, $n_i = e^{-\alpha}.e^{-\beta\epsilon_i}$

$\therefore n_i = A.e^{-\beta\epsilon_i} \longrightarrow (VII)$

Where $A = e^{-\alpha}$ is constant. $\beta = \frac{1}{K_BT}$

This eqn (VII) is known as Boltzmann conical distribution law.

* Maxwell's distribution law of velocities:

We have from Boltzmann canonical distribution law,

$$n_i = Ae^{-\beta\epsilon_i}, \quad \beta = \frac{1}{K_BT}$$

The no. of molecules n having energy E and position position co-ordinates bet x and $x+dx$, y and $y+dy$, z and $z+dz$ and velocity components v_x and v_x+dv_x, v_y and v_y+dv_y, v_z and v_z+dv_z is given by

$$n\,dx\,dy\,dz\,dv_x\,dv_y\,dv_z = Ae^{-\beta[\frac{1}{2}m(v_x^2+v_y^2+v_z^2)]}\,dx\,dy\,dz\,dv_x\,dv_y\,dv_z \longrightarrow (I)$$

Integrating eqn (I), we get

$$N = \int\!\!\int\!\!\int\!\!\int\!\!\int\!\!\int Ae^{-\beta\frac{1}{2}m(v_x^2+v_y^2+v_z^2)}\,dx\,dy\,dz\,dv_x\,dv_y\,dv_z$$

$$= \iiint dx\,dy\,dz \iiint A e^{-m\beta\left[\frac{1}{2}(v_x^2+v_y^2+v_z^2)\right]} dv_x\,dv_y\,dv_z.$$

$$= AV\int e^{-\frac{m\beta}{2}v_x^2}dv_x \int e^{-\frac{m\beta}{2}v_y^2}dv_y \int e^{-\frac{m\beta}{2}v_z^2}dv_z$$

Using standard integral,

$$N = AV\int_{-\infty}^{+\infty} e^{-\frac{m\beta}{2}v_x^2}dv_x \int_{-\infty}^{+\infty} e^{-\frac{m\beta}{2}v_y^2}dv_y \int_{-\infty}^{+\infty} e^{-\frac{m\beta}{2}v_z^2}dv_z \rightarrow \text{(II)}$$

Using standard definite integrals, we have

$$\int_{-\infty}^{+\infty} e^{-\frac{m\beta}{2}v_x^2}dv_x = \sqrt{\frac{2\pi}{m\beta}}$$

$$\int_{-\infty}^{+\infty} e^{-\frac{m\beta}{2}v_y^2}dv_y = \sqrt{\frac{2\pi}{m\beta}}$$

$$\int_{-\infty}^{+\infty} e^{-\frac{m\beta}{2}v_z^2}dv_z = \sqrt{\frac{2\pi}{m\beta}}$$

From (II), we have

$$N = AV\sqrt{\frac{2\pi}{m\beta}}\cdot\sqrt{\frac{2\pi}{m\beta}}\cdot\sqrt{\frac{2\pi}{m\beta}}$$

$$N = AV\left(\frac{2\pi}{m\beta}\right)^{3/2}$$

$$A = \frac{N}{V}\left(\frac{m\beta}{2\pi}\right)^{3/2}$$

$$A = \frac{N}{V}\left(\frac{m}{2\pi K_BT}\right) \quad \left[\because \beta = \frac{1}{K_BT}\right]$$

Now, substituting values of A and B in eq^{n} (I)

$$n_i\,dx\,dy\,dz\,dv_x\,dv_y\,dv_z = \frac{N}{V}\left(\frac{m}{2\pi K_BT}\right)^{3/2} e^{-\frac{m(v_x^2+v_y^2+v_z^2)}{2K_BT}}\,dx\,dy\,dz\,dv_x\,dv_y\,dv_z$$

The no. of molecules having velocity co-ordinates v_x and v_x+dv_x, v_y and v_y+dv_y, v_z and v_z+dv_z can be found by integrating eq^{n} (IV) w.r. to co-ordinates (irrespective of co-ordinates)

$$n_i\,dv_x\,dv_y\,dv_z = \iiint \frac{N}{V}\left(\frac{m}{2\pi K_BT}\right)^{3/2} e^{-\frac{m}{2K_BT}(v_x^2+v_y^2+v_z^2)}\,dx\,dy\,dz\;dv_x\,dv_y\,dv_z$$

$$= \frac{N}{V}\left(\frac{m}{2\pi K_BT}\right)^{3/2} e^{-\frac{m}{2K_BT}(v_x^2+v_y^2+v_z^2)}\,V\,dv_x\,dv_y\,dv_z$$

$$\therefore n_i\,dv_x\,dv_y\,dv_z = N\left(\frac{m}{2\pi K_BT}\right)^{3/2} e^{-\frac{m}{2K_BT}(v_x^2+v_y^2+v_z^2)}\,dv_x\,dv_y\,dv_z \longrightarrow (III)$$

The no. of molecules having velocity components v_x and v_x and v_x+dv_x irrespective of v_y, v_z, x, y, z, can be found by integrating eq^{n} (III) w.r. to v_y and v_z.

i.e. $$n_i\,dv_x = N\left(\frac{m}{2\pi K_BT}\right)^{3/2}\iint e^{-\frac{m}{2K_BT}(v_x^2+v_y^2+v_z^2)}\,dv_x\,dv_y\,dv_z$$

$$= Ne^{-\frac{m}{2K_BT}v_x^2}\left(\frac{m}{2K_BT}\right)^{3/2}\left(\frac{2\pi K_BT}{m}\right)^{1/2}\left(\frac{2\pi K_BT}{m}\right)^{1/2} dv_x$$

$$= Ne^{-\frac{m}{2K_BT}v_x^2}\left(\frac{m}{2\pi K_BT}\right)^{1/2} dv_x$$

$$n_i\,dv_x = Ne^{-\frac{mv_x^2}{2K_BT}}\left(\frac{m}{2\pi K_BT}\right)^{1/2} dv_x \longrightarrow (IV)$$

The probability that a molecule will have x-component of velocity in the range v_x to $v_x + dv_x$ is given by

$$p(v_x)\,dv_x = \frac{n(v_x)}{N}\,dv_x = \left(\frac{m}{2\pi K_B T}\right)^{1/2} e^{-\frac{mv_x^2}{2K_BT}}\,dv_x \quad \text{(V)}$$

Equations (IV) and (V) represent Maxwell's distribution law of velocities.

* Maxwell's Boltzmann distribution law

Following are the conditions of Maxwell Boltzmann statistics :

1. Any no. of particles ($n = 0, 1, 2, 3 \ldots$) can be accommodated in a quantum state.
2. The particles are considered to be distinguishable.
3. The sum of particles in each quantum state is the total no. of particles (conservation of mass)
4. The sum of the energy of each particle in the quantum state is the total energy (conservation of energy)

Let us consider a system of N-particles $n_1, n_2, \ldots n_i$ consisting energy $\varepsilon_1, \varepsilon_2 \ldots \varepsilon_i \ldots$ The no. of particles can exchange the state so that the particles in each state be the same.

The probability of given eigen state of the N particle is

$$G = \frac{N!\, g_1^{n_1} g_2^{n_2} g_i^{n_i}}{n_1!\, n_2!\, n_3!} = N! \prod_i \frac{g_i^{n_i}}{n_i!} \longrightarrow (I)$$

The probability of given state is,

$$\Omega = N! \prod_i \frac{g_i^{n_i}}{n_1!\, n_2! \ldots n_i!} \times \text{constant} \longrightarrow (II)$$

Taking log on both sides, (II)

$$\log \Omega = \log N! + \sum_i (n_i \log g_i - \log n_i \quad n_i) + \text{constant}$$

$$= \text{constant} - \sum_i [n_i \log n_i - n_i \log g_i!]$$

$$\delta \log \Omega = -\sum_i \left[n_i \frac{1}{n_i} \delta n_i + \log n_i \delta n_i - \log g_i \delta n_i\right]$$

$$= -\sum_i \left[\log \frac{n_i}{g_i} + 1\right] \delta n_i$$

For maxima, $\delta \log \Omega = 0$ or $\sum_i \left[\log \frac{n_i}{g_i} + 1\right] \delta n_i = 0 \longrightarrow (III)$

Now, $\sum \delta n_i = 0 \longrightarrow (IV)$

and $\sum E_i \delta n_i = 0 \longrightarrow (V)$

Multiply (IV) by α and (V) by β and adding with (III),

$$\sum_i \left[\log \frac{n_i}{g_i} + 1\right] \delta n_i + \sum_i \alpha \delta n_i + \sum_i \beta E_i \delta n_i = 0$$

or, $$\sum_i \left[\log \frac{n_i}{g_i} + \alpha + \beta E_i\right]\delta n_i = 0$$

for each independent δn_i, $\log \frac{n_i}{g_i} + \alpha + \beta E_i = 0.$

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

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

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

$$n_i = g_i e^{-(\alpha+\beta E_i)} = \frac{g_i}{e^{\alpha+\beta E_i}} \longrightarrow (VI)$$

This gives the number of particles in i^{th} cell following the maxwell's Boltzmann Statistics. This is Maxwell Boltzmann distribution law.

* Law of equipartition of energy.

The degree of freedom of a dynamical system may be defined as the total no. of independent co-ordinates required to specify completely its position and configuration. A molecule in a gas can move along any of the three co-ordinates axes. It has three degree of freedom. A rigid body has six degree of freedom (three rotational and three translational)

According to the kinetic theory of gas, the mean K.E of a temperature T is given as

$$\frac{1}{2}mc^2 = \frac{3}{2}KT$$

Where K is Boltzmann constant and c is root mean square speed.

But $c^2 = u^2+v^2+w^2$

As x,y,z are all equivalent, the mean square velocities along the three axes are equal i.e. $u^2 = v^2 = w^2$

$$\therefore \frac{1}{2}mu^2 = \frac{1}{2}mv^2 = \frac{1}{2}mw^2$$

$$\therefore \frac{1}{2}mc^2 = 3\left[\frac{1}{2}mu^2\right] = 3\left[\frac{1}{2}mv^2\right] = 3\left[\frac{1}{2}mw^2\right] = \frac{3}{2}KT$$

$$\therefore \frac{1}{2}mu^2 = \frac{1}{2}KT$$

$$\frac{1}{2}mv^2 = \frac{1}{2}KT$$

$$\frac{1}{2}mw^2 = \frac{1}{2}KT$$

Thus the average energy associated with each degree of freedom (whether translatory or rotatory)

$$= \frac{1}{2}KT$$

⑤ Chapter-16 : Quantum statistical physics

* Bose Einstein Statistics

Following are the conditions of Bose-Einstein statistics:

(I) particles are identical and indistinguishable.
(II) particles doesn't obey pauli exclusion principle
(III) The sum of particles in each quantum state is the total no. of particles.
(IV) The sum of energy of each particle in the quantum state is the total energy.

Let us consider a system of N-particles $n_1, n_2 \ldots n_i$ consisting energy $\varepsilon_1, \varepsilon_2, \ldots \varepsilon_i$. Let g is the degeneracy factor.

Suppose n_i particles are arranged in a raw and distributed among g_i quantum states with $(g_i - 1)$ particles in between. The total no. of possible arrangements of particles and partitions is equal to the total no. of permutations of $(n_i + g_i - 1)$ objects in a row. Therefore the total possible ways of arranging n_i particles with $(g_i - 1)$ partitions $= (n_i + g_i - 1)!$

As the particles are identical and indistinguishable the possible no. of distinct arrangements

$$= \frac{(n_i+g_i-1)!}{n_i!\,(g_i-1)!}.$$

The total no. of different and distinguishable ways of arranging N particles in all the available energy states is given as

$$\Omega = \frac{(n_1+g_1-1)!}{n_1!\,(g_1-1)!} \times \frac{(n_2+g_2-1)!}{n_2!\,(g_2-1)!} \times \ldots$$

$$\therefore \Omega = \prod_i \frac{(n_i+g_i-1)!}{n_i!\,(g_i-1)!} \longrightarrow (I)$$

Also, we have, $\log x! = x\log x - x$ for large x

From (I),

$$\log \Omega = \sum_i \left[\log(n_i+g_i-1)! - \log n_i! - \log(g_i-1)!\right]$$

$$= \sum_i (n_i+g_i-1)\log(n_i+g_i-1) - (n_i+g_i-1) - \left[n_i\log n_i - n_i\right] - \left[(g_i-1)\log(g_i-1) - (g_i-1)\right]$$

$$\therefore \log_e\Omega = \sum_i \left[(n_i+g_i-1)\log_e(n_i+g_i-1) - n_i\log_e n_i - (g_i-1)\log_e(g_i-1)\right] \longrightarrow (II)$$

$$\therefore \delta\log_e\Omega = \sum_i \left[\log_e(n_i+g_i-1)\delta n_i - \log_e n_i\,\delta n_i\right] = 0 \text{ for max.}$$

$$\therefore \sum_i \left[-\log_e(n_i+g_i-1) + \log_e n_i\right]\delta n_i = 0 \longrightarrow (III)$$

Also, $\sum_i \delta n_i = 0$ and $\longrightarrow$ (IV)

$\sum_i \varepsilon_i\,\delta n_i = 0 \longrightarrow$ (V)

Multiplying (IV) by α and (V) by β and adding to (III), we get

$$\sum_i \left[-\log_e(n_i+g_i-1) + \log_e n_i + \alpha + \beta\varepsilon_i\right]\delta n_i = 0$$

or, $-\log_e(n_i+g_i-1) + \log_e n_i + \alpha + \beta\varepsilon_i = 0$

∴ $-\log_e(n_i+g_i) + \log_e n_i + \alpha + \beta\varepsilon_i = 0$

[1 can be neglected compared with (n_i+g_i)]

∴ $\log_e\left(\frac{n_i}{n_i+g_i}\right) = -\alpha - \beta\varepsilon_i$

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

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

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

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

This is Bose Einstein distribution law.

* Fermi Dirac Statistics

The conditions for fermi dirac statistics are given as

(I) The sub levels consists only $n_i = 0$ or 1 i.e. the particles obey pauli exclusion principle.

(II) The particles are identical and indistinguishable.

(III) The sum of energy possessed by a particles in each sub-levels of different energy levels is the total energy. Let g be the degeneracy factor.

Let us consider a system of N-partisles $n_1, n_2, \ldots n_i$ consisting energy $\varepsilon_1, \varepsilon_2 \ldots \varepsilon_i$.

Thus, the total no. of different ways of arranging n_i particles among the g_i states with energy level ε_i is

$$g_i(g_i-1)\ldots[g_i-(n_i-1)]$$

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

Also, the total no. of different and distinguishable ways is

$$\frac{g_i!}{n_i!\,(g_i-n_i)!}$$

Now,

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

Taking log on bothsides, we get

$\log \Omega = \sum_i [\log g_i! - \log n_i! - \log (g_i - n_i)!]$

We have,

$\log x! = x \log x - x$ for large x

or, $\log \Omega = \sum_i [g_i \log g_i - g_i - n_i \log n_i + n_i - (g_i - n_i) \log (g_i - n_i) + g_i - n_i]$

or, $\log \Omega = \sum_i [g_i \log g_i - n_i \log n_i - (g_i - n_i) \log (g_i - n_i)]$

$\therefore \delta \log \Omega = \sum_i [\log n_i - \log (g_i - n_i)] \delta n_i$

For maximum $\delta(\log \Omega) = 0$

$\Rightarrow \sum_i [\log n_i - \log (g_i - n_i)] \delta n_i = 0 \longrightarrow (I)$

But,

$\sum_i \delta n_i = 0$ and $\longrightarrow (II)$

$\sum \varepsilon_i \delta n_i = 0 \longrightarrow (III)$

Multiplying (II) by α and (III) by β and add to (I), we get

$\therefore \sum_i \log n_i - \log (g_i - n_i) + \alpha + \beta \varepsilon_i] \delta n_i = 0$

or, $\log n_i - \log (g_i - n_i) + \alpha + \beta \varepsilon_i = 0$

or, $\log\left(\frac{n_i}{g_i - n_i}\right) = -\alpha - \beta\varepsilon_i$

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

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

$\therefore n_i = \frac{g_i}{e^{+\alpha+\beta\varepsilon_i}+1}$

This is fermi dirac distribution law.

* Results of three statistics

The expression for the most probable distributions in the three statistics are

(1) Maxwell's Boltzmann statistics:

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

Where α, β are constant, g is the degeneracy of ith level and n_i are the no. of particles for energy ε_i.

(2) Bose Einstein Statistics:

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

(3) fermi dirac statistics:

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

It is to be noted that if $\frac{g_i}{n_i}$ is very large in comparison to unity we may write,

$$\frac{g_i}{n_i} \approx \frac{g_i}{n_i} + 1 \approx \frac{g_i}{n_i} - 1$$

i.e. for large values of $\frac{g_i}{n_i}$ Bose Einstein and fermi Dirac distributions approach the Maxwell-Boltzmann distribution. This is the case for normal existence of gases when the temperature is not too low and pressure is not too high.