UNIT - V. STATISTICAL PHYSICS

Phase - space - Maxwell - Boltzmann distribution law - Fermi Dirac destribution law - Application to electron gas - Bose - Einstein distribution law - Application to photon gas - Radiation Laws - Comparison of three statistics.

Statistical mechanics can be divided into two main classes.

1. Classical statistics or Maxwell - Boltzmann statistics
2. Quantum statistics.

⇒ classical statistics interpreted successfully many ordinary observed phenomena such as temp., pressure, energy etc., But it failed to account for several other experimentally observed phenomena such as black body radiation, photoelectric effect, specific heat capacity at low temps etc.

This failure of classical statistics forces the issue in favour of the new quantum idea of discrete exchange of energy between systems. Thus a new quantum statistics was investigated. There are two types of quantum statistics:

1. Bose - Einstein Statistics
2. Fermi - Dirac Statistics.

1. <u>Bose - Einstein statistics</u>: This is applicable to the identical, indistinguishable particles of zero or integral spin. These particles are called <u>bosons</u>.
2. <u>Fermi - Dirac statistics</u>: This is applicable to identical, indistinguishable particles of half spin. These particles obey Pauli exclusion Principle and are called <u>fermions</u>.

கட்ட வெளி

Phase space

To specify the position as well as energy of a molecule inside a gas. We must specify ~~coord~~, Three space coordinates x, y, z and Three momentum cordinates P_x, P_y, P_z.

This six dimensional space for a single molecule is called phase space or μ - space.

(x, y, z, P_x, P_y, P_z)

$\Delta x, \Delta y, \Delta z\ \Delta P_x, \Delta P_y, \Delta P_z.$

$\Delta x, \Delta y\ \Delta z\ \Delta P_x\ \Delta P_y\ \Delta P_z = h^3$

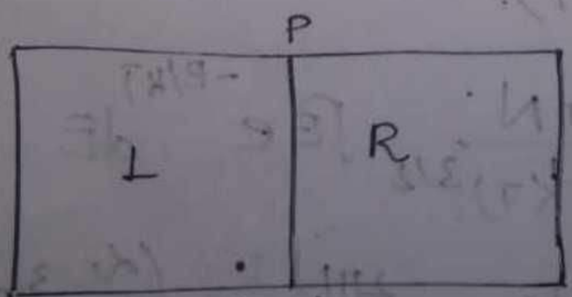
$\Delta x\ \Delta P_x \geq h.$

W

Micro and Macro States:

நுண் நிலையும் பெரு நிலையும்.

a, b, c and d.



(4, 0), (3, 1) (2, 2), (1, 3) and (0, 4)

abc	d
abd	c
acd	b
bcd	a

1. 4 particle in L & 0 in R.
2. 3 particles in L 1 " in R.
3. 2 particles in L & 2 particles in R
4. 1 particle in L 3 in R.
5. 0 in L & 4 in R.

Derivation of Maxwell - Boltzmann distribution law:

Consider a system of N distinguishable molecules of a gas.

Suppose n_1 of them have energy E_1,

n_2 have energy E_2, ...

n_i have energy E_i and so on.

Thus the entire assembly of molecules can be divided into different energy states with energies $E_1, E_2, E_3 \ldots E_i$ and having $n_1, n_2, n_3 \ldots n_i$ molecules.

(1) The total no. of molecules N is constant.

Hence, $N = n_1 + n_2 + n_3 + \ldots + n_i + \ldots = \text{Constant}$

or $\delta N = \delta n_1 + \delta n_2 + \delta n_3 + \ldots + \delta n_i + \ldots = 0$

i.e., $\sum_i \delta n_i = 0$ —— (1)

(2) The total energy E of the gas molecules is constant.

$$E = E_1 n_1 + E_2 n_2 + E_3 n_3 + \ldots + E_i n_i + \ldots = \text{Constant}$$

$$\delta E = E_1 \delta n_1 + E_2 \delta n_2 + E_3 \delta n_3 + \ldots + E_i \delta n_i + \ldots = 0$$

i.e., $\sum_i E_i \delta n_i = 0$ —— (2)

(3) Suppose there are g_i cells with the energy E_i. The total no. of ways in which n_i molecules can have the energy E_i is $(g_i)^{n_i}$

(4)

Hence the total no. of ways in which N molecules can be distributed among the various energies is

$$W_1 = (g_1)^{n_1} (g_2)^{n_2} (g_3)^{n_3} \cdots (g_i)^{n_i} \cdots$$

The no. of ways in which the groups of $n_1, n_2, n_3 \cdots n_i \cdots$ particles can be chosen from N particles is given by

$$W_2 = \frac{N!}{n_1!\, n_2!\, n_3!}$$

The no. of distinguishable ways in which N molecules can be distributed among the possible energy level is

$$W = W_1 W_2 = \frac{N!}{n_1!\, n_2!\, n_3! \cdots} (g_1)^{n_1} (g_2)^{n_2} (g_3)^{n_3} \quad \text{--- (3)}$$

The quantity W is called the thermodynamic probability for the system.

For the most probable distribution, W is a maximum subject to the restriction that the total no. of particles N and the total energy E are constant.

The natural logarithm of Eq. (3) is

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

By Stirling's Theorem, $\ln n! = n \ln n - n$

$$\ln W = N \ln N - N - \Sigma n_i \ln n_i - \Sigma n_i + \Sigma n_i \ln g_i$$

$$\ln W = N \ln N - \Sigma n_i \ln n_i + \Sigma n_i \ln g_i \quad \text{--- (4)}$$

From Eq. (4), We have for maximum W

$$\delta \ln W_{max} = \cancel{-\Sigma n_i \frac{1}{n_i}\delta n_i +} = -\Sigma(\ln n_i)\delta n_i + \Sigma(\ln g_i)\delta n_i = 0$$

(or)

$$-\Sigma(\ln n_i)\delta n_i + \Sigma(\ln g_i)\delta n_i = 0 \quad [\because \Sigma \delta n_i = 0] \quad \text{— (5)}$$

Equ (1) & (2) can be incorporated into equ (5) by making use of Lagrange's method of undetermined multipliers. Multiplying Eq. (1) by $-\alpha$ and Eq (2) by $-\beta$ and adding to Eq. (5), we get,

$$\Sigma(-\ln n_i + \ln g_i - \alpha - \beta E_i)\delta n_i = 0 \quad \text{— (6)}$$

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

$$n_i = g_i e^{-\alpha} e^{-\beta E_i} \quad \text{— (7)}$$

Equ (7) is called Maxwell - Boltzmann distribution law.

Derivation of Bose - Einstein distribution law.

Consider an assembly of N bosons.
They are identical and indistinguishable.
No restriction is imposed as to the no. of particles That may occupy a given cell.

Let us now consider a box divided into g_i sections by $(g_i - 1)$ partitions and n_i indistinguishable particle to be distributed among these sections.

The permutations of n_i particles and $(g_i - 1)$ partitions simultaneously is given by $(n_i + g_i - 1)!$.

But this includes also the permutations of n_i particles among themselves and also $(g_i - 1)$ partitions among themselves, as both these groups are internally indistinguishable.

Hence the actual no. of ways in which n_i particles are to be distributed in g_i sub levels is.

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

$\therefore$ the total no. of distinguishable and distinct ways of arranging N particles in all the available energy state is give by

$$W = \prod \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!} \quad \text{— (1)}$$

n_i and g_i are large numbers.

Hence we may neglect 1 in the above expression.

$$W = \prod \frac{(n_i + g_i)!}{n_i!\, g_i!} \quad \text{— (2)}$$

$$\ln W = \sum \left[\ln (n_i + g_i)! - \ln n_i! - \ln g_i! \right]$$

As n_i and g_i are large numbers, We can use Stirling approximation.

$$\therefore \ln W = \sum (n_i + g_i) \ln (n_i + g_i) - n_i \ln n_i - g_i \ln g_i \quad \text{— (3)}$$

Here, g_i is not subject to variation and n_i varies continuously.

For most probable distribution, $\delta \ln W_{max} = 0$

Hence, if the W of Equ. (3) represents a maximum,

$$\delta \ln W_{max} = \sum \left[\ln (n_i + g_i) - \ln n_i \right] \delta n_i = 0 \quad \text{— (4)}$$

The total no. of particles and total energy are constants

$$\therefore \sum \delta n_i = 0 \quad \text{— (5)}$$

$$\sum E_i \delta n_i = 0 \qquad — (6)$$

multiplying Eq.(5) by $-\alpha$, Eq.(6) by $-\beta$ and adding to Eq. (4)

$$\sum \left[\ln(n_i + g_i) - \ln n_i - \alpha - \beta E_i\right] \delta n_i = 0$$

The variations δn_i are independent of each other. Hence we get,

$$\ln\left[\frac{n_i + g_i}{n_i}\right] - \alpha - \beta E_i = 0 \qquad — (7)$$

$$n_i = \frac{g_i}{(e^{\alpha + \beta E_i}) - 1} \qquad — (8)$$

$$n_i = \frac{g_i}{(e^{\alpha} e^{E_i/KT}) - 1} \qquad — (8)$$

This is known as Bose - Einstein distribution law.

Let us define a quantity $f(E_1) = \frac{n_1}{g_1}$

$f(E_1)$ is called the occupation 'index' of a state of energy E_1.

$$f_{BE}(E_1) = \frac{1}{(e^{\alpha} e^{E_1/KT}) - 1}$$

we will refer to $f(E)$ as the occupation probability on the distribution function.

Derivation of Fermi - Dirac distribution law:

Fermi - Dirac statistics is obeyed by indistinguishable particles of half-integral spin that have antisymmetric wave functions and obey Pauli exclusion principle.

Consider N fermions with the total energy E. Suppose that n_1 particles occupy the first energy level with energy E_1, n_2 particles occupy the second energy level with energy E_2 and so on.

Let us now find out the total no. of ways in which n_i particles can be distributed in g_i cells having the same energy E_i.

The no. of distinguishable arrangements of n_i particles in g_i cells is,

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

The total no. of Eigen states for the whole system is given by $[\ln n! = n\ln n - n]$

$$W = \prod_{i=1}^{n} \frac{g_i!}{n_i!(g_i - n_i)!} \qquad (1)$$

Taking the natural logarithm of both sides

$$\ln W = \Sigma \left[\ln g_i! - \ln n_i! - \ln(g_i - n_i)!\right]$$

Applying Stirling's approximation.

$$\ln W = \Sigma \left[g_i \ln g_i - g_i - n_i \ln n_i + n_i \right.$$
$$\left. (-g_i - n_i)\ln(g_i - n_i) + (g_i - n_i)\right]$$

$$\ln W = \sum\left[g_i \ln g_i - n_i \ln n_i - (g_i - n_i)\ln(g_i - n_i)\right] \quad \text{--- (2)}$$

Here g_i is not subject to variation and n_i varies continuously.

For most probable distribution, $\delta \ln W_{max} = 0$.

$$\delta \ln W_{max} = \sum\left[-\ln n_i + \ln(g_i - n_i)\right]\delta n_i = 0 \quad \text{--- (3)}$$

$$\sum \delta n_i = 0 \quad \text{--- (4)}$$

$$\sum E_i \delta n_i = 0 \quad \text{--- (5)}$$

multiplying Eq (4) by $-\alpha$ Eq (5) by $-\beta$ and adding to Eq. (3).

(4) $\Rightarrow \sum \delta n_i(-\alpha)$

(5) $\Rightarrow \sum E_i \delta n_i(-\beta)$

Equ (3) $\Rightarrow \sum\left[-\ln n_i + \ln(g_i - n_i) - \alpha - \beta E_i\right]\delta n_i = 0$

As the variation δn_i are independent of each other, we get

$$\ln\left[\frac{g_i - n_i}{n_i}\right] - \alpha - \beta E_i = 0$$

$$n_i = \frac{g_i}{(e^{\alpha} e^{\beta E_i}) + 1} \quad \text{--- (6)}$$

This known as Fermi-Dirac Distribution law.

$\beta = 1/kT$ and $\alpha = -E_F/kT$ where E_F is Fermi energy

$$E_F = -\alpha kT$$

$$n_i = \frac{g_i}{(e^{\alpha} e^{E_i/kT}) + 1} \quad \text{—} (7)$$

Definition of Fermi energy:

At the absolute zero of temperature the maximum K.E that a free electron can have is called the Fermi energy E_F.

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

The F.D distribution function is

$$f_{FD}(E_i) = \frac{1}{e^{\alpha} e^{E/kT} + 1}$$

APPLICATION OF FERMI DIRAC STATISTICS:

Theory of Fermi-Gas and Fermi energy:

Various properties of the metals such as electrical and thermal conductivities can be explained on the assumption that the electron in the metal are free to move exactly like the particles of a gas.

Metals have free electrons which are free to move inside metal surface but are not free to come out and leave the surface due to surface barrier (Coulomb potential well).

Electrons are fermions. Thus such a system with a large no. of electrons moving freely inside, is an example of Fermi gas. We can study the behaviour of the electrons on the basis of F-D statistics by considering them to form an electron gas in the metal.

Expression for Fermi energy:

The "free electron gas" in a solid obeys Fermi - Dirac Statistics.

$M(E)$ allowed quantum states in an energy range between E and $E+dE$ and $N(E)$ is the no. of particles in the same range.

Then $N(E)$ quantum states are filled and $M(E) - N(E)$ are vacant.

The F-D distribution function $f(E)$ is

$$f(E) = \frac{N(E)}{M(E)} = \frac{1}{1+e^{(E-E_f)/KT}}.$$

It is defined as the probability that the level E is occupied by an electron.

If the level is certainly empty, then $f(E) = 0$

If the level is certainly full, then $f(E) = 1$.

$f(E)$ has a value between zero and unity.

The distribution function for electrons at $T = 0k$ has the form

$f(E) = 1$ when $E < E_f$

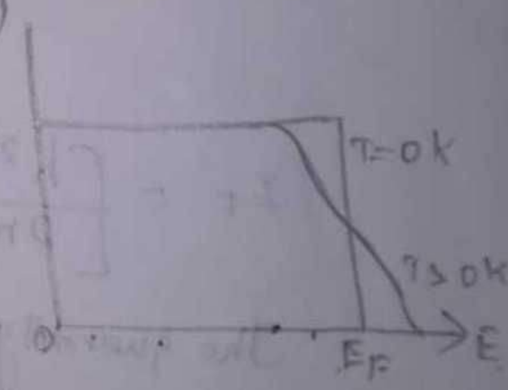
$f(E) = 0$ when $E > E_f$.

The all levels below E_f are completely filled and all levels above E_f are completely empty.

For $E = E_f$, $f(E) = \frac{1}{1+e^0}$

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

at all temperatures.



The probability of finding an electron with energy equal to the Fermi-energy in a metal is $1/2$ at any temp.

$g(E)\,dE$ be the no. of quantum states available to electrons with energies between E and E + dE.

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

m - mass of the electron and V is the volume of the electron gas.

$$N = \int_0^{E_F} g(E)\, dE$$

$$= \frac{8\sqrt{2}\pi V m^{3/2}}{h^3} \int_0^{E_F} E^{1/2}\, dE$$

$$N = \frac{16\sqrt{2}\pi V m^{3/2}}{3h^3} \cdot E_F^{3/2}$$

$$E_F = \left[\frac{h^2}{2m}\right]\left[\frac{3N}{8\pi V}\right]^{2/3}$$

The quantity N/V is the density of free electrons. N/V represents the no. of free electrons per unit volume of the metal.

An effective temp of the electron gas, known as the Fermi-temp is defined by

$$T_F = E_F / K.$$