Lecture Notes of B.Sc.(HONS.) PHYSICS ,Part-III, Paper -VI

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TOPIC:-------Maxwell Boltzmann Distribution Law

Postulates of Maxwell Boltzmann Distribution Law:

The Assemblies consists of in general three kinds of particles:-

1. Identical but distinguishable, particles of any spin. The molecules of a gas are the particles of this kind.
2. Identical and indistinguishable particles of zero or integral spin. The Helium atoms at low temperature and the photons are the particles of this kind. These are called **Bose particles** and they don't obey the Pauli's exclusion principle.
3. Identical and indistinguishable particles of spin half. They obey Pauli's exclusion principle and are called **Fermi particles**, example are electron, proton, neutron etc.

The particles of first kind obey Maxwell Boltzmann distribution law which tells us how a total fixed amount of energy is distributed among various members of an assembly of identical particles in the most probable distribution.

Consider a system of N similar, but distinguishable molecules of a gas. We know that the instantaneous state of a molecule is represented by a phase point in the phase space. Let the phase space is divided into a large no. of cells 1,2,3….i…k. Let $n_1, n_2, n_3, \ldots\ldots n_k$ be the no. of gas molecules whose phase points lie in cells 1,2,3….k respectively in the equilibrium state. As the gas molecules are moving continuously, therefore n_i's will change continuously in many different ways, but will always keep values close to those for the state of equilibrium i.e. the most probable state. Let us suppose n_i's change obeying the fundamental postulates of statistical mechanics.

1. **Total number of molecules is constant.**

$$N=n_1+n_2+n_3+n_4 \ldots\ldots\ldots\ldots +n_k =\text{constant} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1a)$$

$\delta N = \delta n_1 + \delta n_2 + \delta n_3 + \delta n_4 \ldots\ldots\ldots + \delta n_k = 0$ ……………………………....(1b)

2. **The total energy of the system is constant.**

   $E = \epsilon_1 n_1 + \epsilon_2 n_2 + \epsilon_3 n_3 + \epsilon_4 n_4 \ldots\ldots\ldots + \epsilon_k n_k$ ………………………………(2a)

   $\delta E = \epsilon_1 \delta n_1 + \epsilon_2 \delta n_2 + \epsilon_3 \delta n_3 + \epsilon_4 \delta n_4 \ldots\ldots\ldots + \epsilon_k \delta n_k = 0$ ……………………(2b)

3. when gas is in equilibrium the probability is maximum (most probable distribution). Thus $\delta P = 0$, i.e. when P =max., log P is max. and

   $\delta(\log P) = 0.$ ……………………………………………………..(3)

But $P = \frac{N!}{n_1! n_2! \ldots\ldots\ldots n_k!} (g_1)^{n_1} (g_2)^{n_2} (g_3)^{n_3} \ldots \ldots \ldots \ldots (g_k)^{k}$

Where g_i is the priori probability for a molecule to have the energy ϵ_i.

Taking logarithm of above equation ,we get

$\log P = \log N! - \sum_i \log n_i! + \sum_i n_i \log g_i$

Using Stirling's formula, we get

$\log P = N \log N - N - \sum_i n_i \log n_i + \sum_i n_i + \sum_i n_i \log g_i$

But $\sum_i n_i = N$, therefore

$\log P = N \log N - \sum_i n_i \log n_i + \sum_i n_i \log g_i$

Therefore ,according to eqn. (3),we get

$\delta(\log P) = 0 - \sum_i n_i \, \delta(\log n_i) - \sum_i \log n_i \delta n_i + \sum_i \log g_i \delta n_i = 0$ ……………(4)

(Since N log N is constant)

But $n_i \, \delta(\log n_i) = n_i \times \frac{1}{n_i} \delta n_i = \delta n_i$

$\sum_i n_i \, \delta(\log n_i) = \sum_i \delta n_i = 0$ ……………………………….using eqn.(1)

Therefore eqn.(4) gives

$\sum_i \log n_i \delta n_i + \sum_i \log g_i \delta n_i = 0$ …………………………………………...(5)

Let us now use the method of Lagrangian undetermined multiplier. For this purpose multiplying equations [1(b) and 2(b) by α and β respectively where α and β are undetermined quantities independent of n_i's and then adding the resulting expression to eqn. no.(5) we get,

$\sum_i \log n_i \delta n_i + \sum_i \log g_i \delta n_i + \sum_i \alpha \, \delta n_i + \sum_i \beta \epsilon_i \, \delta n_i = 0$

$\sum_i[\log n_i - \log g_i + \alpha + \beta\epsilon_i]\ \delta n_i = 0$ ……………………………..…………(6)

As δn_i's are independent variables ,therefore for the validity of eqn. no. (6)

$\log n_i - \log g_i + \alpha + \beta\epsilon_i = 0$

i.e. $n_i = g_i\, e^{-\alpha}\, e^{-\beta\epsilon_i}\epsilon$

$n_i = A\, g_i\, e^{-\beta\epsilon_i}$ …………………………………….…………….……(7)

where A= $e^{-\alpha}$ is constant.

This results determines the most probable distribution of molecules among the various possible individual states and is known as **Maxwell Boltzmann Distribution Law.**

Evaluation of constants A and β

For evaluating A and β it is convenient to consider continuous distribution of molecular energies rather than discrete energies $\epsilon_1, \epsilon_2, \epsilon_3, \ldots\ldots\ldots, \epsilon_k$

Then eqn. (7) becomes

$n(\epsilon)d\epsilon = Ag(\epsilon)e^{-\beta\epsilon}d\epsilon$ ………………………………………….…..…………..(8)

Here $n(\epsilon)$ represents the no. of molecules having energies between ϵ and ϵ+d ϵ. If p is the molecular momentum, then

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

So that eqn. (8) may be written as

$$n(p)dp = Ag(p)e^{-\beta\frac{p^2}{2m}}dp$$

Here represents the no. of molecules having momentum between p and p+dp. Thus the priori probability that a molecule have momentum between p and p+dp is equal to the no. of cells in the phase space within which such a a molecule may exist . If each cell has infinitesimal volume h^3, then

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

Where the no. represents the volume of the phase space occupied by the particles with the specified momenta.

If V is the volume occupied by the gas in ordinary position space, then

$$\iiint dxdydz = V. \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(11)$$

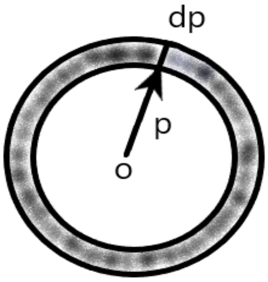

Fig.(1)

Let us imagine that p_x,p_y, and p_z are along three mutually perpendicular axes and draw a sphere of radius p about the origin. Then the surface of the radius drawn will contain all the points for which $p_x^2 + p_y^2 + p_z^2 = p^2$. Now let us draw another sphere of radius p+dp concentric with the first as shown in fig.(1). The volume between two sphere of radii p and p+dp will contain all the molecule in the momentum having momenta between p and p+dp. The volume between two sphere is given by,

$$\iiint dp_x dp_y dp_z = \frac{4}{3}\pi(p+dp)^3 - \frac{4}{3}\pi(p)^3$$

$$= \frac{4}{3}\pi\, 3p^2 dp$$

$$= 4\pi\, p^2 dp \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(12)$$

Substituting values from eqn.(11) and (12) in eqn.(10), we get

$$g(p)dp = \frac{V\, 4\pi\, p^2 dp}{h^3} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(13)$$

$$n(p)dp = \frac{V\, 4\pi\, p^2 A e^{-\beta\frac{p^2}{2m}}\, dp}{h^3} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(14)$$

Since total no. of molecules is N, i.e.

$$\int_0^\infty n(p)dp = N \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(15)$$

the integral of eqn.(14) yields

$$N = \frac{V\, 4\pi A}{h^3}\int_0^\infty p^2 e^{-\beta\frac{p^2}{2m}}\, dp \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(16)$$

Since standard definite integral $\int_0^\infty x^2 e^{-ax^2}\, dx = \frac{1}{4}\sqrt{\left(\frac{\pi}{a^3}\right)}$

$$\therefore \int_0^\infty p^2 e^{-\beta\frac{p^2}{2m}}\, dp = \frac{1}{4}\sqrt{\left(\frac{8m^3\pi}{\beta^3}\right)} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(17)$$

Substituting the value of integral (17) in (16),we get

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

$A=\frac{Nh^3}{V}\,(\frac{\beta}{2\pi m})^{3/2}$ ……………………………………………………………(18)

Substituting this value in eqn. (14), we get

$\therefore n(p)dp = 4\pi N(\frac{\beta}{2\pi m})^{3/2} p^2 e^{-\beta\frac{p^2}{2m}}$ dp ……………………………………………(19)

In order to calculate the value of β, we compute the total energy of the system of molecules.

Since $p^2= 2m\epsilon$ and $dp=\frac{md\epsilon}{\sqrt{2m\epsilon}}$, we may write eqn.(19) as

$n(\epsilon)d\epsilon= 4\pi N(\frac{\beta}{2\pi m})^{3/2} 2m\epsilon\, e^{-\beta\epsilon}\,\frac{md\epsilon}{\sqrt{2m\epsilon}}$

$=2\pi N\left(\frac{\beta}{\pi}\right)^{3/2} \epsilon^{1/2}\, e^{-\beta\epsilon}\, d\epsilon$ ……………………………………………(20)

The total energy E is given by

$E=\int_0^\infty \epsilon\, n(\epsilon)d\epsilon =\int_0^\infty 2\pi N\left(\frac{\beta}{\pi}\right)^{3/2} \epsilon^{3/2}\, e^{-\beta\epsilon}\, d\epsilon$

$E=2\pi N\left(\frac{\beta}{\pi}\right)^{\frac{3}{2}}\frac{3}{4}\sqrt{\left(\frac{\pi}{\beta^5}\right)}=\frac{3}{2}\frac{N}{\beta}$ ……………………………………………………(21)

{using standard definite integral $\int_0^\infty \epsilon^{3/2}\, e^{-\beta\epsilon}\, d\epsilon =\frac{3}{4}\sqrt{\left(\frac{\pi}{\beta^5}\right)}$ }

As we are considering the noninteracting (ideal), gas molecules according to kinetic theory of gases the total energy E of N molecules of an ideal gas at absolute temperature T is

$\therefore E =\frac{3}{2}$ NkT ……………………………………………………………(22)

Where k is Boltzmann’s Constant =1.38 x10^{-23} joule/kelvin

Comparing eqn.(21) and (22), we get

$\frac{3}{2}\frac{N}{\beta} = \frac{3}{2}$ NkT

i.e. $\beta =\frac{1}{kT}$ ……………………………………………………………(23)

substituting this value in eqn.(19) and (20),we get

$$n(p)dp = 4\pi N\left(\frac{1}{2\pi mkT}\right)^{3/2} p^2 e^{-\frac{p^2}{2mKT}}\,\mathrm{dp} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(24)$$

$$n(\epsilon)d\epsilon = 2\pi N\left(\frac{1}{\pi kT}\right)^{3/2} \epsilon^{1/2} e^{-\epsilon/KT}\, d\epsilon \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(25)$$

Eqn.(24) represents the no. of molecules with momenta between p and p+dp in an assembly of an ideal gas containing N molecules at absolute temp. T and is called the Maxwell-Boltzmann Distribution Law of momenta.

Eqn.(25) represents the no. of molecules with energies between ϵ and $\epsilon + d\epsilon$ in the same assembly of an ideal gas and is called the Maxwell-Boltzmann Distribution Law of energies. For small values of ϵ the term $e^{-\epsilon/kT}$ is nearly unity and hence n(ϵ) i.e. the no. molecules with energy ϵ is proportional to $\epsilon^{1/2}$ and so for ϵ =0, n(ϵ) =0.Fpr large values of ϵ the term $e^{-\epsilon/kT}$dominates over $\epsilon^{1/2}$ therefore n(ϵ) is proportional to $e^{-\epsilon/kT}$. Thus if n(ϵ) is plotted against ϵ, the energy distribution curve first rises due to the term $\epsilon^{1/2}$, reaches a maximum and then falls according to $e^{-\epsilon/kT}$.The Maxwell-Boltzmann energy distribution at two different temperatures T_1 and T_2 ($T_1 < T_2$) is shown in Fig.(2).

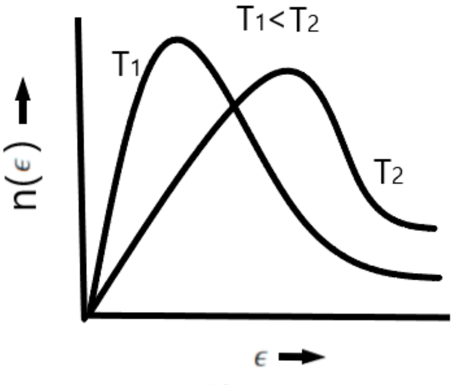

Fig.(2)