Classical Statistical mechanics

(Core course : 13)

Mr. Arindam Changder*
Department Of Physics
Raniganj Girls' College
(Affiliated to Kazi Nazrul University)
*Email : changderarindam96@gmail.com

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Classical Statistical mechanics (MB-Stat.):-

*. Derivation of Maxwell-Boltzmann Statistical distribution law:-

Assumptions:-

1. Particles are distinguishable and there is no Symmetry Consideration.
2. Particles are non-interacting.
3. A given energy state Can accomodate any no. of particles.
4. Total number of particles is Const. i.e. $N = \sum_j N_j$ = Const.
5. Total energy of the System of N non-interacting particles is also Const.

i.e. $E = \sum_j n_j \epsilon_j$ = Const.

Let us divide, the entire phase space into large no. of cells of approx. Const. energies $\epsilon_1, \epsilon_2, \epsilon_3, \dots, \epsilon_j, \cdots$ with $n_1, n_2, \cdots n_j, \cdots$ respectively no. of particles.

Let, each Cell Contains a no of Sub cells and j^{th} cell with energy ϵ_j to $(\epsilon_j + d\epsilon_j)$ Contains g_j no of Single particle quantum States.

It is also called the degeneracy of the j^{th} cell. (In general, $g_j >> n_j$)

*. g_j is proportional to the volume of the phase cell.

In MB-Statistics- particles are distinguishable and non-interacting. There is also no restrictions on the no of particles in any given energy state. Therefore, the no of different independent ways in which N no of particles in different cells may be arranged, keeping the total numbers in each cells fixed is, $^{N}C_{n_1} \cdot {}^{N-n_1}C_{n_2} \cdot {}^{N-n_1-n_2}C_{n_3} \cdots = \frac{N!}{n_1! \cdot n_2! \cdots} = \frac{N!}{\prod_{j=1}^{\infty} n_j!}$

Total no of distinct ways, called the intrinsic probability in which n_j particles can be distributed among g_j quantum states of the j^{th} cell is $g_j^{n_j}$. Considering all cells this no is, $\prod_{j=1}^{\infty} g_j^{n_j}$.

Hence, the total no of microstates for the above distribution is,

$$\Omega = N! \prod_{j=1}^{\infty} \frac{g_j^{n_j}}{n_j!} \quad \text{——} \quad (1)$$

N! different arrangement is equivalent to unity as the particles are identical. So, a division by N! in the above expression is necessary. → 'Correct Boltzmann Counting'

$$\therefore \Omega^{MB} = \prod_{j=1}^{\infty} \frac{g_j^{n_j}}{n_j!} \quad \text{——} \quad (2)$$

In eq$^{\underline{m}}$ the distribution attains most probable distribution which contains maximum no of microstates. Thus for most probable distribution, $S/K = \ln\Omega = \text{maximum}$ (where, S = entropy; K = Boltzmann's const.)

$$\text{or, } \delta(S/K) = \delta(\ln\Omega) = 0 \quad \text{—— (3)}$$

$$\text{or, } \sum_j \frac{\partial}{\partial n_j}(S/K)\,\delta n_j = 0 \quad \text{—— (4)}$$

From the assumptions, we have,

$$\left.\begin{aligned} N &= \sum_j n_j = \text{Const.}\\ \text{and, } E &= \sum_j n_j\epsilon_j = \text{Const.}\end{aligned}\right\} \text{—— (5)}$$

$$\therefore \delta N = \sum_j \delta n_j = 0 \quad \text{— (6)}$$

$$\& \ \delta E = \sum_j \epsilon_j\,\delta n_j = 0 \quad \text{— (7)}$$

We multiply eq$^{\underline{n}}$ (6) by unknown parameters $(-\alpha)$ and eq$^{\underline{n}}$ (7) by $(-\beta)$ and adding with eq$^{\underline{n}}$ (4), *

*Lagrange's method of undetermined multipliers,

$$\sum_j\left[\frac{\partial}{\partial n_j}(S/K) - (\alpha+\beta\epsilon_j)\right]\delta n_j = 0 \quad \text{— (8)}$$

As δn_j is arbitrary, we have,

$$\frac{\partial}{\partial n_j}(S/K) = \alpha+\beta\epsilon_j \quad \text{—— (9)}$$

In MB-Statistics, $(S/K)^{MB} = \ln\Omega^{MB}$

$$\text{or, } (S/K)^{MB} = \ln\left(\prod_{j=1}^{\infty}\frac{g_j^{n_j}}{n_j!}\right) = \sum_{j=1}^{\infty}\left(n_j\ln g_j - \ln n_j!\right)$$

using Stirling approx$^{\underline{n}}$: $\ln N! = N\ln N - N$

$$\therefore (S/K)^{MB} = \sum_{j=1}^{\infty}\left[n_j\ln g_j - n_j\ln n_j + n_j\right]$$

$$= \sum_{j=1}^{\infty}\left[n_j\ln\left(\frac{g_j}{n_j}\right) + n_j\right]$$

$$\text{or, } S^{MB} = K\sum_{j=1}^{\infty} n_j\left[\ln\left(\frac{g_j}{n_j}\right) + 1\right] \quad \text{—— (10)} \leftarrow \text{Entropy in MB-Stat.}$$

As, $(S/k)^{MB} = \sum_{j=1}^{\alpha} [n_j \ln g_j - n_j \ln n_j + n_j]$

$\therefore \frac{\partial}{\partial n_j}(S/k)^{MB} = \frac{\partial}{\partial n_j}\sum_{j=1}^{\alpha} [n_j \ln g_j - n_j \ln n_j + n_j]$

$= \ln g_j - n_j \cdot \frac{1}{n_j} - \ln n_j \cdot 1 + 1$

$= \ln g_j - \ln n_j$

$\therefore \frac{\partial}{\partial n_j}(S/k)^{MB} = \ln\left(\frac{g_j}{n_j}\right)$ —— (11)

From eqn. (9), $\frac{\partial}{\partial n_j}(S/k)^{MB} = \alpha + \beta\epsilon_j$

or, $\ln\left(\frac{g_j}{n_j}\right) = \alpha + \beta\epsilon_j$

or, $\frac{g_j}{n_j} = e^{\alpha + \beta\epsilon_j}$

or, $n_j = \frac{g_j}{e^{\alpha + \beta\epsilon_j}}$

or, $n_j = \frac{g_j}{e^{\alpha} \cdot e^{\beta\epsilon_j}} = \frac{g_j}{f} e^{-\beta\epsilon_j}$ —— (12)

Where, $f = e^{\alpha}$ is called degeneracy parameter.

$\therefore$ Total no of particles of the System is,

$N = \sum_j n_j = \frac{1}{f}\sum_j g_j e^{-\beta\epsilon_j} = AZ$

Where. $A = \frac{1}{f} = e^{-\alpha}$ and $Z = \sum_j g_j e^{-\beta\epsilon_j}$

Z is known as the partition function of the MB-Statistics. It represents how the particles of the System are distributed in various energy States.

When the energy varies Continuously then, $Z = \int g(\epsilon) e^{-\beta\epsilon} d\epsilon$

'Z' → Sum Over States or in German '**ZustandSumme**'.

Evaluation of α and β :-

As. $\delta S = \sum_j \frac{\partial S}{\partial n_j}\delta n_j$

But, for most probable distribution,

$$\frac{\partial}{\partial n_j}(S/K) = \alpha + \beta\epsilon_j$$

or, $\frac{\partial S}{\partial n_j} = K(\alpha+\beta\epsilon_j)$

or, $\sum_j \frac{\partial S}{\partial n_j}\delta n_j = \sum_j K(\alpha+\beta\epsilon_j)\delta n_j$

or, $\delta S = K\alpha\delta N + K\beta\delta E$ —(13)

As, $\delta N = \sum_j \delta n_j$ and $\delta E = \sum_j \epsilon_j \delta n_j$

Again, we have, $T\delta S = \delta E + p\delta V - \mu\delta N$

$$\therefore \delta S = \frac{\delta E}{T} + \frac{p}{T}\delta V - \frac{\mu}{T}\delta N$$

μ is the chemical potential.

At Const. volume, $\delta V = 0$

$$\therefore \delta S = \frac{\delta E}{T} - \frac{\mu}{T}\delta N \quad \text{——} (14)$$

Comparing equations (13) and (14),

$K\beta = \frac{1}{T}$ and $-\frac{\mu}{T} = K\alpha$

or, $\beta = \frac{1}{KT}$

or, $\alpha = -\frac{\mu}{KT}$

or, $\alpha = -\mu\beta$

$\therefore$ The average no of particles per quantum state,

$$\langle n_{MB}\rangle \text{ or } \overline{n}_{MB} = \frac{n_j}{g_j} = \frac{1}{e^{\alpha+\beta\epsilon_j}}$$

$$= \frac{1}{e^{-\mu\beta+\beta\epsilon_j}} = \frac{1}{e^{\beta(\epsilon_j-\mu)}}$$

or, $\boxed{\langle n_{MB}\rangle = \frac{1}{e^{\frac{(\epsilon_j-\mu)}{KT}}}}$

Application of Classical Statistics (for ideal gas):-

Let us Consider, a System of N non-interacting gas particles in a volume V at temperature T and total energy E.

The volume of the phase space in the energy range ϵ to $(\epsilon+d\epsilon)$ is,

$$\Gamma(\epsilon)d\epsilon = \iiint dx\,dy\,dz \iiint dp_x\,dp_y\,dp_z$$

$$= V\cdot 4\pi p^2 dp = 2\pi V(2m)^{3/2}\epsilon^{1/2}d\epsilon \text{ --- (1)}$$

As, $\epsilon = p^2/2m$

$\therefore d\epsilon = \frac{p\,dp}{m}$

$\therefore dp = \frac{m\,d\epsilon}{\sqrt{2m\epsilon}}$

$\therefore$ The no of microstates in the energy range ϵ to $(\epsilon+d\epsilon)$ and in volume V,

$$g(\epsilon)d\epsilon = \frac{\Gamma(\epsilon)d\epsilon}{h^3} = 2\pi V\left(\frac{2m}{h^2}\right)^{3/2}\epsilon^{1/2}d\epsilon \text{ --- (2)}$$

where, h^3 is the volume of unit phase cell.

$g(\epsilon)d\epsilon$ is the no of single particle quantum State in the energy range ϵ to $(\epsilon+d\epsilon)$ and in volume V.

According to MB statistics, the no of particles in the energy range ϵ to $(\epsilon+d\epsilon)$ and in the volume V is,

$$\left[\because n_j = \frac{g_j}{e^{\frac{(\epsilon_j-\mu)}{kT}}}\right]$$

$$n(\epsilon)d\epsilon = \frac{g(\epsilon)d\epsilon}{f}e^{-\beta\epsilon} = \frac{2\pi V}{f}\left(\frac{2m}{h^2}\right)^{3/2}\epsilon^{1/2}e^{-\beta\epsilon}d\epsilon \text{ --- (3)}$$

where, $f = e^{\alpha}$ = degeneracy parameter; $\alpha = -\mu\beta$ and $\beta = 1/kT$

Here, the total no of particles in the microcanonical ensemble is,

$$N=\int_0^\infty n(\epsilon)\,d\epsilon$$

$$\text{or, } N=\frac{2\pi V}{f}\left(\frac{2m}{h^2}\right)^{3/2}\int_0^\infty \epsilon^{1/2}e^{-\beta\epsilon}\,d\epsilon$$

Put, $\beta\epsilon = x$

$$\therefore d\epsilon=\frac{dx}{\beta}$$

$$\therefore N=\frac{2\pi V}{f}\left(\frac{2m}{h^2}\right)^{3/2}\beta^{-3/2}\int_0^\infty x^{1/2}e^{-x}\,dx$$

$$=\frac{2\pi V}{f}\left(\frac{2m}{h^2}\right)^{3/2}\beta^{-3/2}\,\Gamma(3/2)\qquad\left(\because \beta=\frac{1}{KT}\right)$$

$$=\frac{2\pi V}{f}\left(\frac{2m}{h^2}\right)^{3/2}(KT)^{3/2}\,\frac{1}{2}\cdot\Gamma(1/2)$$

$$[\because \Gamma(1/2)=\sqrt{\pi}]$$

$$=\frac{2\pi V}{f}\left(\frac{2m}{h^2}\right)^{3/2}(KT)^{3/2}\,1/2\cdot\sqrt{\pi}$$

$$\text{or, } N=\frac{V}{f}\left(\frac{2\pi mKT}{h^2}\right)^{3/2}\text{ ——(4)}$$

The degeneracy parameter is,

$$f=e^{\alpha}=\frac{V}{N}\left(\frac{2\pi mKT}{h^2}\right)^{3/2}\text{ ——(5)}$$

$$\therefore \text{The partition function, } Z=Nf=V\left(\frac{2\pi mKT}{h^2}\right)^{3/2}\text{ —(6)}$$

Hence, from eq$^{\underline{n}}$ (3), the no of molecules in the energy range ϵ to $(\epsilon+d\epsilon)$ at temperature T is,

$$n(\epsilon)\,d\epsilon=\frac{2\pi N}{(\pi KT)^{3/2}}\,\epsilon^{1/2}e^{-\beta\epsilon}\,d\epsilon\text{ —(7)}$$

[using eq$^{\underline{n}}$ (4)]

This is the MB-dist. law of energy dist. among the ideal gas molecules.

Let, c be the velocity of a molecule.

$$\therefore \text{K.E, } \epsilon=\frac{1}{2}mc^2\quad\therefore d\epsilon=mc\,dc$$

∴ The no of molecules in the velocity range c to (c+dc) at temp. T in the vol. V is,

$$n(c)\,dc=\frac{2\pi N}{(\pi KT)^{3/2}\sqrt{\frac{m}{2}}}\cdot c\,e^{-\frac{mc^2}{2KT}}\,mc\,dc$$

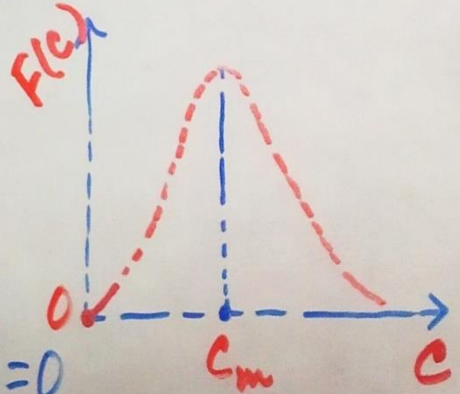
$$\text{or, } n(c)\,dc=4\pi N\left(\frac{m}{2\pi KT}\right)^{3/2}e^{-\frac{mc^2}{2KT}}c^2\,dc\text{ —(8)}$$

This is Maxwell's velocity distribution law.

$$\therefore \frac{n(c)\,dc}{N} = 4\pi\left(\frac{m}{2\pi KT}\right)^{3/2} e^{-\frac{mc^2}{2KT}} c^2\,dc$$

or, $\frac{n(c)\,dc}{N} = F(c)\,dc$

where, $F(c) = \frac{n(c)}{N} = 4\pi\left(\frac{m}{2\pi KT}\right)^{3/2} e^{-\frac{mc^2}{2KT}} c^2$ = velocity distribution function.



$c_m \to$ most probable velocity.

Thus. $\left.\frac{dF(c)}{dc}\right|_{c=c_m} = 0$

or, $4\pi\left(\frac{m}{2\pi KT}\right)^{3/2}\left[e^{-\frac{mc_m^2}{2KT}}\,2c_m + c_m^2\, e^{-\frac{mc_m^2}{2KT}}\cdot\left(-\frac{m}{2KT}\right)\cdot 2c_m\right] = 0$

or, $2c_m\, e^{-\frac{mc_m^2}{2KT}}\left[1 - c_m^2\cdot\frac{m}{2KT}\right] = 0$

$\therefore 1 - c_m^2\cdot\frac{m}{2KT} = 0$

or. $c_m^2 = \frac{2KT}{m}$

or, $\boxed{c_m = \sqrt{\frac{2KT}{m}}}$

Average velocity:-

$\therefore \bar{c}$ or $\langle c\rangle = \frac{1}{N}\int_0^\infty c\,n(c)\,dc$

or, $\bar{c} = 4\pi\left(\frac{m}{2\pi KT}\right)^{3/2}\int_0^\infty c^3 e^{-\frac{mc^2}{2KT}}\,dc$

or, $\boxed{\bar{c} = \sqrt{\frac{8KT}{m\pi}}}$ $\left[\because \int_0^\infty x^3 e^{-ax^2}\,dx = \frac{1}{2a^4}\right]$

Root mean Square velocity (r.m.s velocity) :-

It is defined as the Square root of the mean of the Squares of the velocities of all the gas molecules.

$$\therefore \overline{c^2} = \frac{1}{N}\int_0^\infty c^2 n(c)\,dc$$

$$= 4\pi\left(\frac{m}{2\pi KT}\right)^{3/2}\int_0^\infty c^4 e^{-\frac{mc^2}{2KT}}\,dc$$

$$= 4\pi\cdot\frac{1}{\pi^{3/2}}\cdot(b^2)^{3/2}\int_0^\infty c^4 e^{-b^2c^2}\,dc$$

$$= \frac{4b^3}{\sqrt{\pi}}\int_0^\infty e^{-z}\,\frac{z^2}{b^4}\,\frac{dz}{2b\sqrt{z}}$$

$$= \frac{4b^3}{\sqrt{\pi}}\int_0^\infty e^{-z} z^{3/2}\cdot\frac{1}{2b^5}\,dz$$

$$= \frac{4b^3}{\sqrt{\pi}}\cdot\frac{1}{2b^5}\int_0^\infty e^{-z} z^{(5/2-1)}\,dz$$

$$= \frac{2}{\sqrt{\pi}\cdot b^2}\,\Gamma(5/2) = \frac{\cancel{2}}{\cancel{\sqrt{\pi}}\cdot b^2}\cdot\frac{3}{\cancel{2}}\cdot\frac{1}{2}\cdot\cancel{\sqrt{\pi}} = \frac{3}{2}\cdot\frac{1}{b^2} = \frac{3}{\cancel{2}}\cdot\frac{2KT}{m} = \frac{3KT}{m}$$

Let, $b^2 = \frac{m}{2KT}$

or, $b = \left(\frac{m}{2KT}\right)^{1/2}$

Let, $b^2c^2 = z$

or, $dz = 2b^2c\,dc$

or, $dc = \frac{dz}{2b\cdot bc}$

or, $dc = \frac{dz}{2b\sqrt{z}}$

$$\boxed{\therefore c_{r.m.s} = \sqrt{\overline{c^2}} = \sqrt{\frac{3KT}{m}}}$$

Laws of equipartition of energy :-

It states that total K.E of a dynamical System Consisting of large no of particles in thermal equilibrium is equally divided among its all degrees of freedom and the energy associated with one molecule per degree of freedom is equal to ½KT.

'K' → Boltzmann's Const.
'T' → Absolute temp. of the gas.

Proof :-

The total energy of the System is, $E = \sum_j n_j \epsilon_j$ —— (1)

For a Continuous System, $E = \int_0^\infty \epsilon\, n(\epsilon)\, d\epsilon = \frac{2\pi N}{(\pi KT)^{3/2}} \int_0^\infty \epsilon^{3/2} e^{-\beta\epsilon}\, d\epsilon$

Put, $\beta\epsilon = x \quad \therefore d\epsilon = \frac{dx}{\beta}$

$$\therefore E = \frac{2\pi N}{(\pi KT)^{3/2}} \beta^{-5/2} \int_0^\infty x^{3/2} e^{-x}\, dx$$

$$= \frac{2\pi N}{(\pi KT)^{3/2}} \beta^{-5/2}\, \Gamma(5/2)$$

Or, $E = \frac{2\pi N}{(\pi KT)^{3/2}} (KT)^{5/2} \frac{3}{2} \cdot \frac{1}{2} \cdot \sqrt{\pi} = \frac{3}{2} NKT$

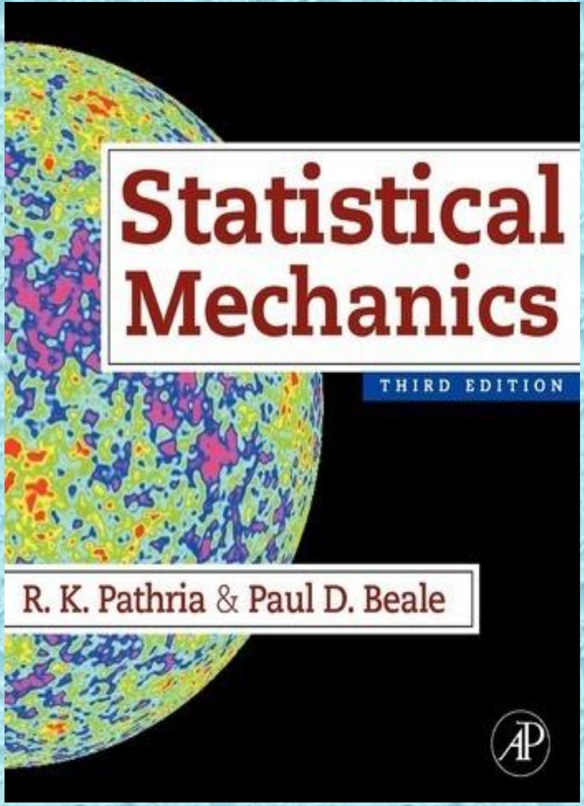
∴ Average energy of an ideal gas molecule is, $\langle E\rangle' = \frac{E}{N} = \frac{3}{2} KT$

Now, each molecule has 3 degrees of translational motion. So, the average energy per degree of freedom of an ideal gas molecule is,

$$\boxed{\langle E\rangle = \frac{\langle E\rangle'}{3} = \frac{1}{2} KT}$$

***A little task for the students: Evaluate the thermodynamic quantites for ideal monatomic gases.

If necessary, then you may take a qualitative support from the reference books.



Reference Books