// Statistical Mechanics //

- Microscopic System : of the order of atomic dimension.
- Macroscopic System : observable in large scale.

- Def. : It is the study of macroscopic parameters of an equilibrium system from the known properties of microscopic states of the particles using mechanical laws.

- Probability Calculation :

  N: Distinguishable Particle.

  n: No. of container.

  N_1 : ~~Partic~~ Particles in 1st container

  N_2 : " " 2nd " and so on.

Initially, assuming two containers only, and $N = N_1 + N_2$.

For, 1st container, the distribution is given by:

$$^{N}C_{N_1} = \frac{N!}{N_1!(N-N_1)!} = \frac{N!}{N_1!\,N_2!} \quad \text{---(1)}$$

Assuming, the 2nd container is having two parts with particles n_1 and n_2;

$$n_1 + n_2 = N_2 = N - N_1 \quad \text{---(2)}$$

From eqⁿ. 1

$$N_2 C_{n_1} = \frac{N_2!}{n_1!(N_2-n_1)!} = \frac{N_2!}{n_1!\,n_2!} \quad \text{— (2)}$$

So the whole system can be assumed as one with three partitions. 1st containing N_1 particles, 2nd with n_1 and 3rd with n_2 particles,

Here, the total no. of ways for this distribution is:

$$^{N}C_{N_1} \cdot {}^{N_2}C_{n_1} = \frac{N!}{N_1!\,N_2!} \cdot \frac{N_2!}{n_1!\,n_2!} = \frac{N!}{N_1!\,n_1!\,n_2!} \quad \text{— (3)}$$

Hence, it can be generalized as:

$$W = \frac{N!}{N_1!\,N_2!\,N_3!\ldots N_n!} = \frac{N!}{\prod_{i=1}^{n} N_i!} \quad \text{— (4)}$$

Total no. of cases: n^N.

$$\text{Probability} = \frac{W}{n^N} = \frac{N!}{\prod_{i=1}^{n} N_i!}\, n^{-N}. \quad \text{— (5)}$$

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When N is large, eqn (4) can be simplified as.

Stirling's approxn. $N! = N(\ln N - 1)$ ——(6).

$$\ln N! = \ln 1 + \ln 2 + \ln 3 + \dots + \ln N.$$

and $\ln N^N = \ln N + \ln N + \dots + \ln N.$

Hence, $\ln\left(\frac{N!}{N^N}\right) = \ln(1/N) + \ln(2/N) + \dots + \ln(N/N)$

$$= \sum_{x=1}^{N} (\ln x - \ln N)$$

By replacing summation with integration

$$\ln(N!/N^N) = \int_{x=1}^{N} (\ln x - \ln N)$$

$$= \ln N - N + 1.$$

$$\therefore \ln N! = N\ln N + \ln N - N + 1 \simeq N(\ln N - 1)$$

from (4) $\ln W = N(\ln N - 1) - \sum_{i=1}^{n} N_i(\ln N_i - 1)$

$$= N\ln N - \sum_{i=1}^{n} N_i \ln N_i \quad \text{——(7)}$$

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• Phase space and density of states:

Position co-ordinate: (x, y, z)

Momentum : (p_x, p_y, p_z)

Phase space: (x, y, z, p_x, p_y, p_z)

$\delta x \, \delta p_x = h_0$. (where h_0: constant having angular momentum dimension)

Volume of each cell in phase space: $\delta x \, \delta y \, \delta z \, \delta p_x \, \delta p_y \, \delta p_z$

$$= h_0^3 .$$

Energy of quantized particle:

$$\epsilon = \frac{\hbar^2}{2m}\left(k_x^2 + k_y^2 + k_z^2\right) \; ; \text{ where } k = \frac{2\pi n}{L} .$$

$$= \frac{2\pi^2\hbar^2}{m} \cdot \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right) . \quad \text{—— (8)}$$

Again, Allowed values of p_x, p_y, and p_z are,

$$p_x = \frac{h n_x}{L_x} . \quad p_y = \frac{h n_y}{L_y} . \quad p_z = \frac{h n_z}{L_z} .$$

$n_x \rightarrow n_x + \Delta n_x$.

$p_x \rightarrow p_x + dp_x$.

$$\Delta n_x = \frac{L_x}{h} \, dp_x .$$

For 3-D space:

$$\Delta n_x \, \Delta n_y \, \Delta n_z = \frac{L_x L_y L_z}{h^3} \cdot dp_x \, dp_y \, dp_z$$

$$= \frac{V}{h^3} dp_x \, dp_y \, dp_z. \quad \text{---(9)}$$

No. of quantum states $g(E)\,dE$ within E and $E+dE$ is found to be:

$$g(E)\,dE = \frac{V}{h^3} 4\pi p^2 \, dp \quad \text{---(10)}$$

$$g(E)\,dE = \frac{2\pi V}{h^3} \cdot (2m)^{3/2} E^{1/2} \, dE \quad \text{---(11)}$$

no. of states / energy range ie

$\boxed{\text{DENSITY OF STATES}}$

Distribution function:

$$W_1 = \frac{N!}{\prod_{i=1}^{n} N_i!}$$

$$W_2 = \prod_{i=1}^{n} g_i^{N_i}$$ [g_i: no. of degenerate states.
N_i particle may occupy g_i states.

Total no. of ways W

$$W = W_1 W_2 = \frac{N!}{\prod_{i=1}^{n} N_i!} \prod_{i=1}^{n} g_i^{N_i}$$

$$\ln W = N \ln N + \sum_{i=1}^{n} N_i \ln g_i - \sum_{i=1}^{n} N_i \ln N_i$$

It can be shown that,

$$f(E_i) = \frac{N_i}{g_i} = e^{\alpha + \beta E}$$; (α, β: Lagrange's multipliers) —— (12)

where, $f(E_i)$ = Distribution function
ie, ratio of N_i with g_i states.

Eq.n (12) is referred as <u>Maxwell-Boltzmann Distribution</u>

- Entropy :

from 1st law of thermodynamics:

$$\delta u = \delta Q - p\,\delta V. \qquad \text{—(13)}$$

$$u = \sum_i N_i \epsilon_i \;;$$

$$\delta u = \sum_i \epsilon_i\,\delta N_i + \sum_i N_i\,\delta \epsilon_i \qquad \text{—(14).}$$

$$\Downarrow$$

$$\sum_i N_i \frac{\partial \epsilon_i}{\delta V}\,\delta V = -p\,\delta V.$$

$$p = -\frac{\partial u}{\partial V}.$$

$$\delta Q = \sum_i \epsilon_i\,\delta N_i \qquad \text{—(15).}$$

Again, $\delta \ln W = -\beta \sum_i \epsilon_i\,\delta N_i = -\beta\,\delta Q.$

$$\beta = -1/k_B T.$$

$$\cancel{K_B}\; K_B\,\delta \ln W = \frac{\delta Q}{T} = \delta S.$$

Entropy $\boxed{S = k_B \ln W + \text{Constant.}}$ —(16)

where, $k_B = 1.38 \times 10^{-23}\ \mathrm{J/K}.$

- MB - Distribution:

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

$$N(E)\,dE = e^{\alpha}\, e^{-E/K_BT}\, g(E)\,dE.$$

Total no. of particles:

$$N = \int_0^\infty N(E)\,dE = e^{\alpha} \int_0^\infty g(E)\, e^{-E/K_BT}\,dE.$$

MB distribution function can be shown as:

$$f(E) = e^{\alpha}\, e^{-E/K_BT} = \frac{N}{2V}\left(\frac{h^2}{2\pi M K_BT}\right)^{3/2} e^{-E/K_BT}$$

$$f(E) = \frac{N}{F}\, e^{-E/K_BT}$$

where $F = \sum_i g_i\, e^{-E/K_BT}$.