

# A.R COACHING CENTRE

PG-TRB, POLYTECHNIC-TRB, SET COACHING FOR PHYSICS  
Kallakurichi Dst, Contact-8667737887.

## PG TRB - 2019

### Unit IV - Statistical Mechanics

#### Maxwell Boltzmann statistics:- (or) Classical statistics:

##### Basics:

- ▶ The statistical methods are applied only to physical systems containing a very large number of particles.
- ▶ Types of statistics:
  - (1) Classical Statistics
    - (i) Maxwell-Boltzmann statistics (Ex: gas molecule).
  - (2) Quantum Statistics
    - (i) Bose-Einstein statistics (Bosons  $\rightarrow$  zero or integral spin, Ex: photon).
    - (ii) Fermi-Dirac statistics (Fermions  $\rightarrow$  half integral spin, Ex: Electron).

##### Phase-Space:

To specify the state of gas from the molecular point of view we require the position and velocity (or more conveniently momentum) of each of its molecules, (i.e) we must specify six quantities  $x, y, z, p_x, p_y, p_z$  for each of the molecules.

The state of the point in the space will be described by a set of six co-ordinate  $x, y, z, p_x, p_y, p_z$ . This six-dimensional space is called phase-space and element of volume in the space is termed as a cell.

$\therefore$  Six dimensional phase space for a single particle is called molecular phase-space (or)  $\mu$ -space and  $6N$  dimensional phase space is called  $\tau$ -space (or)  $\gamma$ -space.

##### Note:-

- ▶ The dimension of the volume element are  $(length \times momentum)^f = (joule \ second)^f$ .
- ▶ The size of the cell (each) be  $h^f$ .
- $h \rightarrow$  constant has the dimension of  $joule \ second$ .

##### Microstates:- ( $2^n$ )

We must state to which cell each molecule of the system belongs temporarily.

Example: In the 4 particles, the total number of microstates =  $2^n = 2^4 = 16$ .

##### Macrostates:- ( $n + 1$ )

The specification of the number of molecules (or) phase points in each cell of phase space.

Example: In the 4 particles, the total number of macrostates =  $(n + 1) = (4 + 1) = 5$ .

- ▶ Many different microstates may correspond to the same macrostate.
- ▶ The microstates which are allowed under given restrictions are called accessible microstates.

##### Ensemble:-

A collection of large number of identical independent system is called an ensemble. In an ensemble the systems play the same role as molecule in a gas.

► Accessible states: are the states consistent with the given constraints of the system.

### Thermodynamic probability:-

The number of microstates corresponding to that macrostate.

Example: The thermodynamical probability for the macrostate  $N_i = 3, N_j = 1$  is 4. (i.e)  $\Omega = 4$ .

cell  $i$     abc    abd    acd    bcd

cell  $j$     d    c    b    a

► The thermodynamic probability

$$\Omega = \frac{N!}{n_1! n_2! n_3!}$$

► Number of meaning arrangements =  $\frac{n!}{r! (n-r)!} = {}^n C_r$ .

Example:

A system of 4 distinguishable, for a macrostate (1,3),  $r = 1, (n-r) = 3$  and  $n = 4$  the number of microstate.

$$\therefore \text{Thermodynamic probability } (\Omega)_{(r,n-r)} = \frac{n!}{r! (n-r)!} = \frac{4!}{1! 3!} = 4.$$

### Fundamental postulate of statistical mechanics:-

1. All the cells in the phase space are of equal size.
2. All the accessible microstate corresponding to possible macrostates are equally probable. (i.e) The probability of all microstates of the system are equal.
3. The equilibrium state of a gas corresponds to the macrostate of maximum probability.
4. The total number of molecules is constant ( $N$ ).
5. The total number of the system is constant ( $E$ ).

$$h = \delta p_i \delta q_i$$

### ENSEMBLE:-

An ensemble is defined as a collection of a large number of macroscopically identical but essentially independent system.

The condition of equilibrium between two systems in thermal contact - The  $\beta$ - parameter:-

Two systems which are capable of exchanging heat between one another, are said to be in thermal contact.

According to statistical mechanics the two systems in thermal contact will be in equilibrium if their functions  $\left[ \frac{\partial}{\partial E} \log \Omega \right]$  are equal.

$$\left[ \frac{\partial}{\partial E} \log \Omega(E) = \frac{\partial}{\partial E'} \log \Omega'(E') \right]$$

- The function  $\left[ \frac{\partial}{\partial E} \log \Omega \right]$  is generally represented by  $\beta$ ,  
 $\beta \rightarrow$  has the dimensions of reciprocal energy for thermally equilibrium we have,

$$\frac{1}{\beta} = KT \quad (\text{or}) \quad \beta = \frac{1}{KT} = \frac{\partial}{\partial E} \log \Omega(E)$$

$K \rightarrow$  is a Boltzmann's constant (dimension  $\rightarrow \text{joule deg}^{-1}$ ) (or)  $J K^{-1}$ .

$$K = \frac{R}{N} \quad \text{where, } R \rightarrow \text{gas constant for 1 Kg mol, } N \rightarrow \text{Avogadro number.}$$

### Relation between entropy and probability:-

- The probability of the system in equilibrium state is maximum. But from the thermodynamical point of view the equilibrium state of a system is the state of maximum entropy.  
 ►  $S = K \log_e \Omega$   $S \rightarrow$  Entropy,  $\Omega \rightarrow$  Probability.

The above equation state that the entropy of a system is proportional to the logarithm of probability of that system. (i.e)  $S \propto \log_e \Omega$

### Boltzmann's canonical distribution law:-

- The number of molecules in each cell as a function of energy associated with each particle in that cell.

$$n_i = A e^{-\beta \epsilon_i}; \quad n_i = \frac{1}{e^{\alpha + \beta \epsilon_i}}; \quad n_i = \exp[-\alpha - \beta \epsilon_i]$$

### Partition function:-

The quantity  $z$  is called the Boltzmann partition function or simply the partition function.

$$z = \frac{N}{A} = \sum_i g_i e^{-\epsilon_i / KT} \quad (\text{or}) \quad z = \sum_i e^{-\beta \epsilon_i}$$

$z \rightarrow$  the gas molecules of an assembly are distributed (or) partitioned among the various energy levels. (Sum of state of the system)

### Kinetic theory of gases:-

1. Pressure of gas  $P = \frac{1}{3} \rho c^2$ ;  $\rho = nm \rightarrow$  density.
2.  $P = \frac{2}{3}$  Kinetic energy.
3. Kinetic energy of temperature (one mole of an ideal monoatomic gas)  $E = \frac{3}{2} KT$ ;  
 $K = \frac{R}{N}$ ;  $K = 1.38 \times 10^{-23} \text{ joule/K}$ ;  $E \propto T$ ;  $E = \frac{3}{2} RT$
4. The mean square velocity of a molecules is directly proportional to the absolute temperature  $\overline{V^2} \propto T$
5. Boyle's law  $PV = \frac{2}{3} N$ ;  $V \propto \frac{1}{P}$  (or)  $PV = \text{constant}$ .
6. Charle's law:  $V \propto T$  at constant value of  $P \rightarrow$  (or)  $\frac{V}{T} = \text{constant}$ .
7. Gas equation:  $PV = RT$ .

**Classical Maxwell-Boltzmann Distribution law:-**

The assemblies, in general, consist of three types of particles:

1. Identical but distinguishable particles:-

Molecules of a gas are the particles of the kind. The particles obey Maxwell-Boltzmann distribution law.

2. Identical but indistinguishable particle of Zero (or) Integral spin:-

Photons are the particles of this kind. The particle obey Bose-Einstein statistics and hence known as Bose particle (Bosons).

3. Identical but indistinguishable particle of 1/2 integral spin:-

Electron, proton, neutron are the particle of this kind. They obey the pauli's exclusion principle and Fermi-Dirac statistics. This particle are known as fermions.

**Evaluation of constant in the Maxwell-Boltzmann distribution law:**

$$E = \frac{3N}{2\beta} ; \quad E = \frac{3}{2} RT = \frac{3}{2} nKT .$$

$$C = \frac{1}{(2\pi mKT)^{3/2} V}$$

**Maxwell - Boltzmann distribution law (statistics):-**

1. The total number of particles in the entire system is always constant.

2. The probability of a given distribution,  $P = \frac{1}{N!} \prod_{i=1}^k \left( \frac{g_i^{n_i}}{n_i} \right)$ .

3. The condition for most probable distribution (or) maximum probability,

$$d(\log p) = 0 \text{ (or) } \sum \left[ \log \left( \frac{n_i}{g_i} \right) \right] dn_i = 0 .$$

4. The M-B distribution law is,  $n_i = g_i e^{-\alpha} e^{-\beta E_i}$  (or)  $n_i = \frac{g_i}{e^{\alpha + \beta E_i}}$  (or)  $\frac{n_i}{g_i} = \frac{1}{e^{\alpha + \beta E_i}}$

$$\text{(i.e) } \frac{n_i}{g_i} = \frac{1}{\exp \left( \frac{\epsilon_i - \mu}{K_B T} \right)}$$

5. The different ways of their distribution in for energy levels =  $g_i^{n_i}$  .

6. Entropy of a perfect crystal is zero.

7. The probability of finding one particle in the  $s^{th}$  state is  $\bar{n}_s = e^{(\mu - \epsilon_s)/KT}$  .

8. At equilibrium, the chemical potential will be the same for all substances  $\sum \bar{n}_s = N$  .

9. For classical behaviour,  $e^{\mu/KT} \ll 1$  .

Exercise:  $g_i = 4, n_i = 3$   $\therefore$  Number of ways  $g_i^{n_i} = 4^3 = 64$  .

**M-B energy distribution :**

$$\blacktriangleright \log \left( \frac{n_i}{g_i} \right) = -\alpha - \beta E_i \quad (\text{or}) \quad n_i = g_i e^{(-\alpha - \beta E_i)} \quad (\text{or}) \quad n_i = g_i e^{-\alpha} e^{-\beta E_i}$$

$$(\text{or}) \quad n_i = g_i e^{-\alpha} e^{-E_i/KT} \quad \therefore \beta = \frac{1}{KT}$$

where,  $i = 1, 2, 3, \dots, K$

$K \rightarrow$  Boltzmann constant ;  $T \rightarrow$  Absolute temperature.

$\blacktriangleright$  The quantity  $e^{-E_i/KT}$  is known as the Boltzmann factor.

$\blacktriangleright$  The quantity  $\sum g_i e^{-E_i/KT}$  is the sum over all states of the system and is called the partition function of the system ( $Z$ ).

$$Z = \sum g_i e^{-E_i/KT}$$

$$n_i = \frac{N}{Z} g_i e^{-E_i/KT}$$

**M-B energy distribution function:**

The general energy distribution function  $f(E_i)$  is the average number of particles per quantum state in the  $i^{\text{th}}$  energy level  $E_i$ . It is given by,

$$f(E_i) = \frac{n_i}{g_i} ; \quad \boxed{f(E_i) = e^{-\alpha} e^{-E_i/KT}}$$

**M-B Energy distribution function for an ideal gas:-**

$\blacktriangleright$  An ideal gas consisting of free particle with no spin  $g(E) dE$  is

$$g(E) dE = 2\pi V \left( \frac{2m}{h^2} \right) E^{1/2} dE$$

The M-B energy distribution law for the particles of ideal gas,

$$\boxed{n(E) dE = \frac{2N}{\sqrt{\pi}} \left( \frac{1}{KT} \right)^{3/2} E^{1/2} e^{-E/KT} dE}$$

$\blacktriangleright e^{-\alpha} = \frac{V}{N} \left( \frac{2\pi mKT}{h^2} \right)^{3/2} \rightarrow$  is called the degeneracy parameter.

**Condition for application of M-B statistics:**

$\blacktriangleright$  The M-B statistics is applicable to a system of particles for which the mean distance between the particle is greater than the thermal De-Broglie wavelength of the particles.

$\blacktriangleright$  The volume of per particle =  $\left( \frac{V}{N} \right)$

$\therefore$  The mean distance between the particle =  $\left( \frac{V}{N} \right)^{1/3}$

$\blacktriangleright$  The de-Broglie wavelength associated is given by ( $\lambda$ ),  $\lambda = \left( \frac{h^2}{2\pi mKT} \right)^{1/2}$

Thus, the condition for M-B statistical to become applicable is,

$$\left( \frac{V}{N} \right)^{1/3} \geq \left( \frac{h^2}{2\pi mKT} \right)^{1/2} \quad (\text{or}) \quad \left( \frac{V}{N} \right) \geq \left( \frac{h^2}{2\pi mKT} \right)^{3/2}$$

$$\left(\frac{V}{N}\right) \left(\frac{2\pi mKT}{h^2}\right)^{3/2} \geq 1 \quad (\text{or}) \quad e^\alpha \geq 1$$

**Three cases:****Case (i):**

When the degeneracy parameter  $e^\alpha$  statistics this condition the gas is said to be non-degenerate (i.e)  $e^\alpha \geq 1$ .

**Case (ii):**

When  $e^\alpha > 1$ , but not too large, the gas is said to be weakly degenerate.

**Case (iii):**

When  $e^\alpha < 1$ , the gas is said to be strongly degenerate. The M-B statistics is valid for systems at high temperature, at low densities  $\left(\frac{N}{V}\right)$  has a low value.

**M-B law of distribution of momentum:**

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

**Application of M-B distribution law:**

1. Total internal energy and specific heat at constant volume of an ideal gas.

$$U = \frac{3}{2} KT ; \quad C_v = \frac{3}{2} R$$

2. Maxwell - Boltzmann speed distribution:

- M-B law of speed distribution

$$n(v) dv = 4\pi N \left(\frac{m}{2\pi KT}\right)^{3/2} v^2 e^{-mv^2/2KT} dv$$

- $g_i$  = Number of cells in the zone under consideration.

$$g_i = \frac{\text{Volume of the zone in the phase space}}{\text{Volume of one cell}}$$

$$g_i = \frac{\int \int \int \int \int \int dx dy dz dp_x dp_y dp_z}{h^3}$$

$$g_i = \frac{4\pi V p^2 dp}{h^3}$$

Maxwell's distribution law,

$$N(V) dV = BV^2 e^{-mV^2/2KT} dV$$

**Three cases:**

- (i) If  $V = 0$  ;  $N(V) = 0$ . It means no molecule has a zero speed.

- (ii) For a small values of  $V$ ,  $\frac{mV^2}{2KT} \ll 1$  and  $e^{-mV^2/2KT} = 1$  ;  $\therefore N(V) \propto V^2$ .

Thus, attains a maximum value for a value of  $V$ .

(iii) For large values of  $V$ ,  $N(V) \propto e^{-mV^2/2KT}$  Thus value of  $N(V)$  decreases exponentially with increasing of value  $V$ .

### Maxwell's distribution law of velocities:

Maxwell's distribution law of velocities,

$$n(\nu_x) d\nu_x = N \left( \frac{m}{2\pi KT} \right)^{1/2} e^{-m\nu_x^2/2KT} d\nu_x$$

$$p(V_x) dV_x = N \left( \frac{m}{2\pi KT} \right)^{1/2} e^{-mV_x^2/2KT} dV_x$$

### Limitation of M-B method:

1. It is applicable only to an isolated gas of identical molecules in equilibrium.
    - (a) The mean potential energy due to mutual interaction between the molecule is very small compared to their mean kinetic energy (under this condition the gas is said to be ideal).
    - (b) The gas is dilute (i.e) the number of molecule per unit volume is small. So that the average separation between the molecules is large and hence individual molecules can be distinguished. (Under this condition the gas is said to be non-degenerate).
  2. The expression for M-B could does not give correct expression for the entropy  $S$  of an ideal gas and thus leads to the Gibb's paradox.
  3. It cannot be applied to as system of indistinguishable particles.
  4. From M-B distribution, we get the expression for the emission current density  $J = A_o T^{1/2} e^{-\phi/KT}$  which is not correct, and correct is  $J = A_o T^2 e^{-\phi/KT}$
- Experimental verification of Maxwell's distribution of molecular speed experimentally arranged by I.F.Zartman and C.C.Ko (Bismuth).

(to be continue... )

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