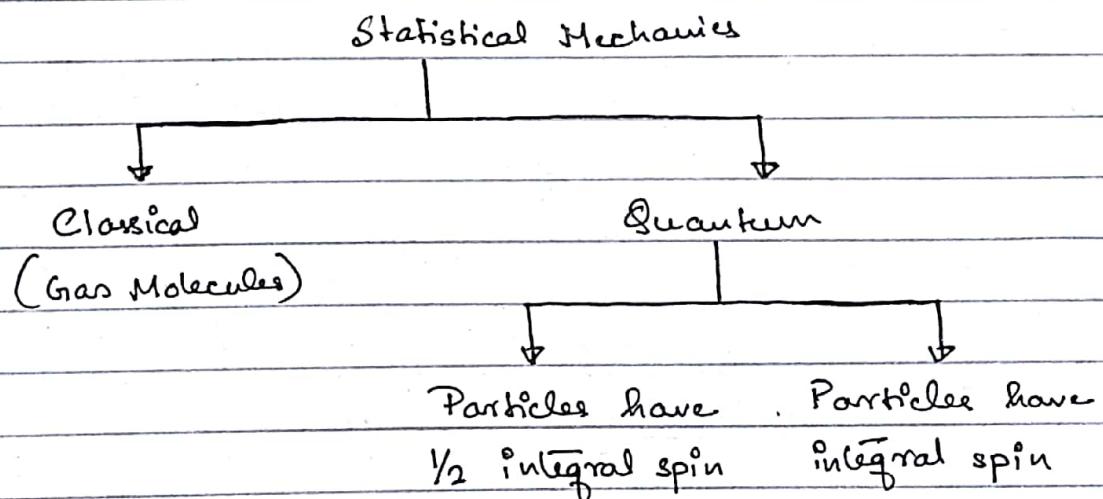


Introduction to Statistical Mechanics

It deals with the mechanical systems that are in thermal equilibrium. It is statistical because it makes a statistical prediction for a large number of particles which are free and random and may be classical or quantum. It is that branch of physics which studies macroscopic quantities of a system from the molecular or microscopic particles.

It provides the link between classical mechanics (mechanical properties) and thermodynamics (thermal properties). It has been applied to liquids, gases, metals, polymers and bio-systems (DNA, etc.). Main purpose is to establish the law governing the behaviour of macroscopic quantities of a system by using the law governing the behaviour of molecular quantities of the system.



Classical particles which are far enough to distinguish obey Maxwell-Boltzmann Statistics, and quantum particles with $\frac{1}{2}$ integral spin obey Fermi-Dirac Statistics and those with integral spin obey Bose-Einstein Statistics.

Energy Levels, Energy / Quantum States, Degeneracy.

For a bound electron

$$E_n = \frac{-me^4 z^2}{8\epsilon_0^2 n^2 h^2} = -\frac{13.6 z^2}{n^2} \text{ eV.}$$

Energy level.	n	l	m _l	m _s	Energy States
2	2	0	0, 1	$\pm \frac{1}{2}, \mp \frac{1}{2}$	$(2, 0, 0, 1/2), (2, 0, 0, -1/2)$,
		1	0, -1	$\pm \frac{1}{2}, \mp \frac{1}{2}$	$(2, 1, 1, 1/2), (2, 1, 1, -1/2)$, $(2, 1, 0, 1/2), (2, 1, 0, -1/2)$ $(2, 1, -1, 1/2), (2, 1, -1, -1/2)$

Different Energy States may correspond to one Energy level.

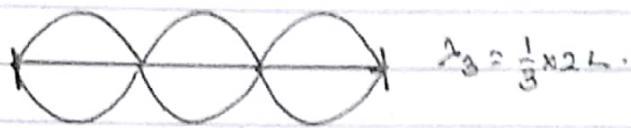
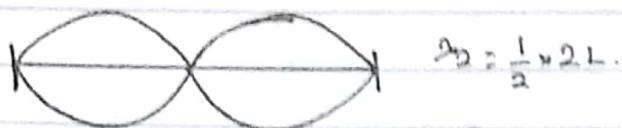
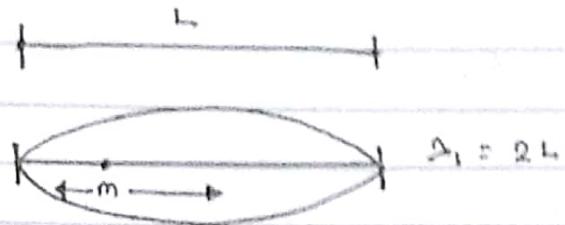
The number of Energy States in one Energy level is known as Degeneracy Number (g_i) for the ith Energy level.

All energy states in one level have same energy.

If $g_i = 1$, then non-degenerate energy level.

If $g_i > 1$, then degenerate energy level.

form a free particle.



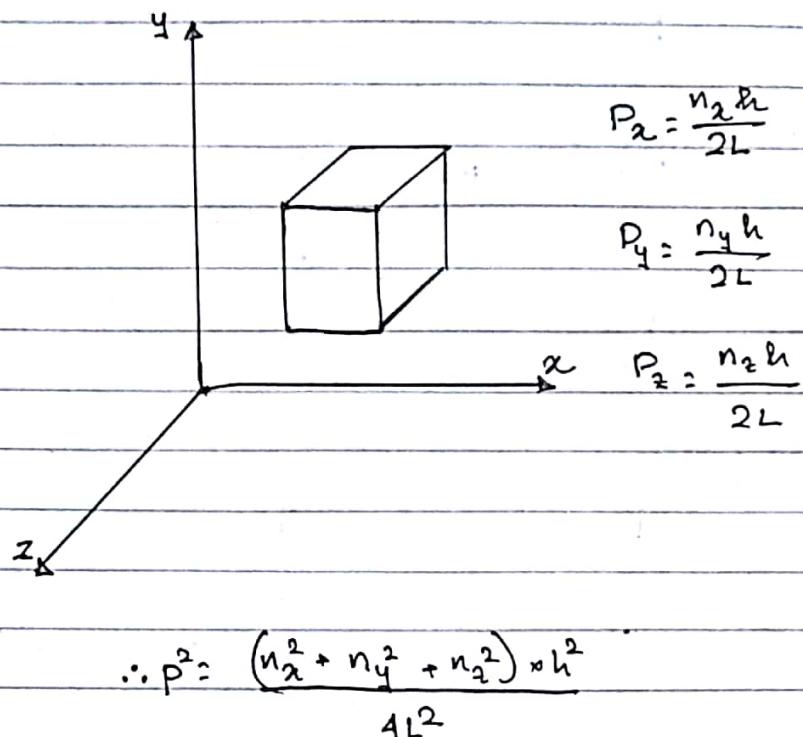
∴ For this stretched string.

$$\lambda_i^o = \frac{1}{n_i^o} \times 2L \quad (n_i^o = 1, 2, 3, \dots)$$

If we had a free particle moving to and fro in a certain length L then a matter wave travels with L . Mode of vibration keeps altering and for some mode i , wavelength $\lambda_i^o = \frac{1}{n_i^o} \times 2L$

$$\therefore P_i^o = \frac{\hbar}{\lambda_i^o} = \frac{n_i^o \hbar}{2L}$$

In a cube, a free particle.



and we have.

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

$$\therefore E = \frac{(n_x^2 + n_y^2 + n_z^2) h^2}{8mL^2}$$

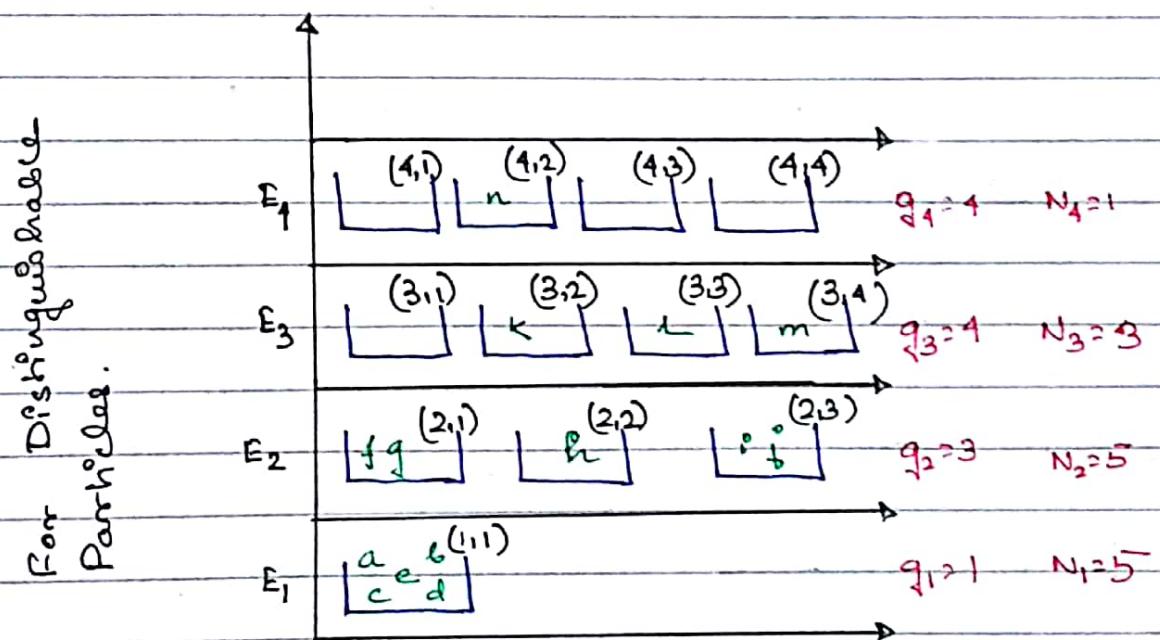
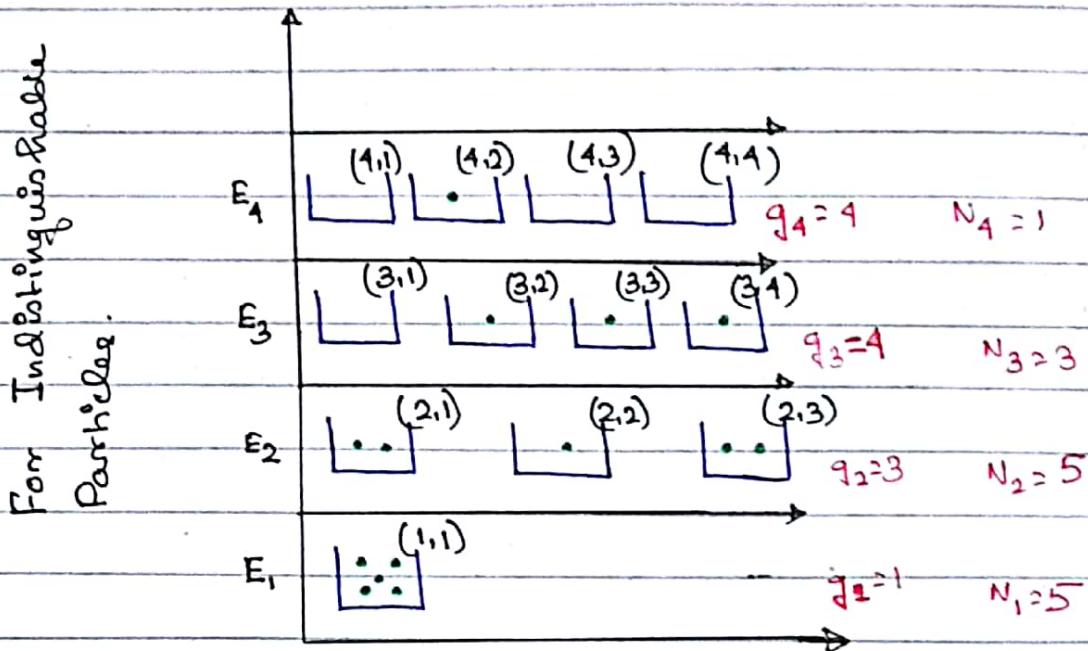
Since $n_x, n_y, n_z \geq 1$,

\therefore Minimum value of

$$E = \frac{3h^2}{8mL^2}$$

Energy Level	Energy Value,	n_x	n_y	n_z	Energy States	Degeneracy (g_i)
Ground State	$\frac{3h^2}{8mL^2}$	1	1	1	(1,1,1)	1 (Non-Degenerate)
1st Excited State	$\frac{6h^2}{8mL^2}$	2	1	1	(2,1,1)	3
		1	2	1	(1,2,1)	(Degenerate.)
		1	1	2	(1,1,2)	
2nd Excited State	$\frac{9h^2}{8mL^2}$	2	2	1	(2,2,1)	3
		2	1	2	(2,1,2)	(Degenerate)
		1	2	2	(1,2,2)	
3rd Excited State	$\frac{11h^2}{8mL^2}$	3	1	1	(3,1,1)	3
		1	3	1	(1,3,1)	(Degenerate)
		1	1	3	(1,1,3)	
4th Excited State	$\frac{12h^2}{8mL^2}$	2	2	2	(2,2,2)	1 (Non-Degenerate)

Schematic representation of Energy Levels, Energy States and Degeneracy.



Occupation Number (N_i):- The number of particles in each energy level is known as the Occupation Number.

Total number of Particles of the system :

$$N = N_1 + N_2 + N_3 + \dots + N_i = \sum N_i$$

For a closed system $N = \sum N_i = \text{Constant}$

Each particle in the i th energy level has energy E_i^0 irrespective of the energy state it occupies at that energy level. The total energy of the system

$$U = N_1 E_1 + N_2 E_2 + \dots + N_i E_i$$

For an isolated system

$$U = \sum_{i=1}^n N_i E_i = \text{Constant}$$

Macrostate :— Whether the particles are distinguishable or not, the specification of the set of the number of particles in each energy level of the system is defined as the macrostate of the system. It is denoted by M .

$$M = \{N_1, N_2, N_3, \dots, N_i\}.$$

For last two examples $M = \{5, 5, 3, 1\}$ or $M(5, 5, 3, 1)$.

Microstate :— If the particles are indistinguishable, a specification of the set of the number of particles in each energy state of the system is defined as the microstate of the system.

Ex:- (1,1) has 5 particles

(2,1) has 2 particles.

If the particles are distinguishable, a specification of the quantum state in each particle of the system is defined as the microstate of the system.

- Ex:-
- (1.1) state contains (a,b,c,d,e)
 - (2.1) state contains (f,g)
 - (2.2) state contains (h)

- Each particle can only be in one quantum state at a time. The system as a whole taken can only be one microstate at a time.
- If any particle changes its quantum state, the system takes another microstate.
- There are large number of ways in which particles can be transferred without changing the macrostate of the system.

The number of microstates corresponding to a particular macrostate is called **Thermodynamic Probability** of the given microstate and is denoted by w .

Note:- For Indistinguishable particles change from one Energy state to another Energy State doesn't give new microstate.

There maybe a large number of macrostates. For each of these macrostates, corresponding to each of these (M_k), There are large number of microstates (w_k).

Total number of microstates of a system is the **Thermodynamic Probability (Ω)** of the system.

Fundamental postulate of Statistical Mechanics states that all the microstates of a system are equally possible.

Probability of a Microstate :- $P = \left(\frac{1}{N}\right)$

Probability of a Macrostate :- $P_{M_k} = \left(\frac{W_k}{N}\right)$

The most probable state is simply the macrostate which has the maximum number of microstates.

Maxwell-Boltzmann Constant

Basic Postulates :-

- * 1. Particles are considered to be identical and distinguishable.
- 2. Net number of particles of the system is constant, or system is closed.

$$N = \sum N_i = \text{Constant}$$

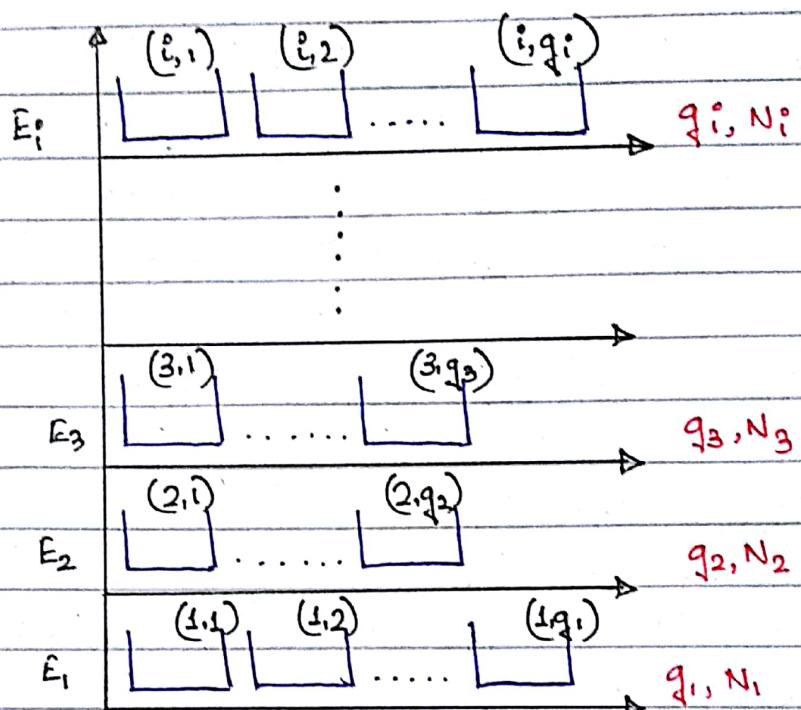
- 3. Net Energy of the system is constant.

$$U = \sum E_i^0 N_i = \text{Constant}$$

or, the system is isolated.

- * 4. Particles don't obey Pauli's Exclusion Principle.
- * 5. Particles don't obey Heisenberg's Uncertainty Principle.
- 6. Examples:- Gas molecules.

Now, we calculate the number of microstates possible (Thermodynamic Probability) corresponding to a macrostate $M = \{N_1, N_2, \dots, N_i\}$ for a system of particles (gas molecules) obeying Maxwell Boltzmann Statistics



The Number of ways to collect N_1 particles from N particles is

$${}^N C_{N_1} \text{ ways}$$

Similarly, the number of ways to collect N_2 particles from $(N - N_1)$ particles is

$${}^{N-N_1} C_{N_2} \text{ ways}$$

So for collecting N_i particles from remaining particles, we have

$$N - \sum_{j=1}^{i-1} N_j^o C_{N_i} \text{ ways.}$$

∴ The total number of ways to collect N_1, N_2, \dots, N_i particles in E_1, E_2, \dots, E_i energy level is

$$N_{C_{N_1}} \cdot N_{-N_1} C_{N_2} \cdot \dots \cdot N_{- \sum_{j=1}^{i-1} N_j} C_{N_i}$$

$$= \frac{N!}{N_1! (N-N_1)!} \cdot \frac{(N-N_1)!}{N_2! (N-N_1-N_2)!} \cdot \dots$$

$$= \frac{N!}{N_1! \cdot N_2! \cdots N_i!} = \frac{N!}{\prod_{j=1}^i N_j!}$$

Now,

Number of ways to arrange N_1 particles among g_1 Energy States in E_1 is

$g_1^{N_1}$ ways

Similarly, the number of ways to arrange N_i particles among g_i Energy states in E_i is

$g_i^{N_i}$ ways.

∴ The Total Number of ways to arrange $N_1, N_2, N_3, \dots, N_i$ particles among $g_1, g_2, g_3, \dots, g_i$ Energy States in $E_1, E_2, E_3, \dots, E_i$ is

$g_1^{N_1} \cdot g_2^{N_2} \cdot g_3^{N_3} \cdots \cdots \cdot g_i^{N_i}$ ways

$= \prod_{j=1}^i g_j^{N_j}$ ways.

∴ The Effective Number of Ways to distribute N particles corresponding to a macrostate $M = \{N_i^o\}$ under Maxwell Boltzmann Statistics is

$W = \text{Collect Part} \times \text{Arrange Part}$

$$= \frac{N!}{N_1! N_2! \dots N_i!} \times q_1^{N_1} q_2^{N_2} \dots q_i^{N_i}$$

$$= N! \cdot \prod_{j=1}^i \frac{q_j^{N_j}}{N_j!}$$

$$\therefore W = N! \times \prod_{j=1}^i \frac{q_j^{N_j}}{N_j!}$$

Fermi Dirac Statistics

Basic Properties

* 1. Particles are identical and indistinguishable.

2. Net number of particles of the system is constant or system is closed.

$$N = \sum N_i = \text{Constant.}$$

3. Net Energy of the system is constant or the system is isolated.

$$U = \sum E_i N_i = \text{Constant}$$

4. Particles have half integral spin.

* 5. Particles have asymmetric wave function. So

They obey Pauli's Exclusion Principle.

* 6. Particles obey Heisenberg's Uncertainty Principle

7. Examples: - e^- , p^+ , n^0 , He_2^3 are all also called Fermions.

Number of ways to collect N_1, N_2, \dots, N_i fermions in E_1, E_2, \dots, E_i levels is

$$1 \times 1 \times 1 \times \dots \times 1 \quad (\text{i times})$$

This is because the particles are identical.

Number of ways to arrange N_1 particles among g_1 Energy states in E_1 level is

$$\frac{g_1!}{N_1! (g_1 - N_1)!}$$

Similarly, Number of ways to arrange N_i particles among g_i^o Energy States in E_i^o level is

$$g_i^o C_{N_i}^o$$

∴ Effective Number of ways to distribute N Fermions is:-

$$W = \text{Collect Part} \times \text{Arrange Part}$$

$$= 1 \times g_1^o C_{N_1}^o \cdot g_2^o C_{N_2}^o \cdots g_i^o C_{N_i}^o$$

$$W = \prod_{f=1}^L g_f^o C_{N_f}^o$$

$$\therefore W = \prod_{f=1}^L g_f^o C_{N_f}^o$$

Bose Einstein Statistics

Basic Properties

- ① 1. Particles are identical and indistinguishable.
- 2. Net number of particles of the system is constant as the system is closed.
$$N = \sum N_i = \text{Constant}$$
- 3. Net Energy of the system is constant as the system is isolated.
$$U = \sum E_i^0 N_i = \text{Constant.}$$
- 4. Particles have integral spin.
- 5. The particles have have symmetric wave functions.
- ② 6. They do not obey Pauli's Exclusion Principle
- 7. Examples:- BOSONS (photons, He⁺ atoms, etc)

Total number of ways to collect $N_1, N_2, N_3, \dots, N_i$ particles from $E_1, E_2, E_3, \dots, E_i$ level is

$$1 \times 1 \times 1 \times \dots \times 1 \quad (\text{i times}) \\ = 1 \text{ way.}$$

Number of Energy States: - g_1

Number of Particles: - N_1

∴ Total number of objects is $(g_1 + N_1)$

The first state can be chosen in g_1 ways and corresponding to each way, permutations of remaining objects $(g_1 + N_1 - 1)$ among themselves is

$$g_1 \cdot (g_1 + N_1 - 1)!$$

Now, the total number of ways to arrange N_1 distinguishable particles among g_1 distinguishable states is

$$g_1 \cdot (g_1 + N_1 - 1)!$$

But in B.E. statistics, both particles and states are indistinguishable. So the number of ways is

$$\frac{g_1 \cdot (g_1 + N_1 - 1)!}{g_1! N_1!} = \binom{g_1 + N_1 - 1}{N_1}$$

\therefore Effective Number of ways to distribute N Bosons

$W = \text{Collect Part} \times \text{Arrange Part}$

$$= 1 \times \binom{g_1 + N_1 - 1}{N_1} \times \binom{g_2 + N_2 - 1}{N_2} \times \dots \times \binom{g_i + N_i - 1}{N_i}$$

$$\therefore W = \prod_{i=1}^o \frac{(N_i^o + g_i^o - 1)!}{N_i^o! (g_i^o - 1)!} = \prod_{j=1}^o \binom{g_j^o + N_j^o - 1}{N_j^o}$$

$\therefore W_{B.E.} = \prod_{j=1}^o \binom{g_j^o + N_j^o - 1}{N_j^o}$
--

Q. 4 particles are distributed in 3 levels having energies $0, E, 3E$, so that total energy is $4E$. If the levels have degeneracy 1, 2 and 3 respectively, find all possible distribution of particles in the system.

Ans:- Given $N = 4$ and $U = 4E$

$E_3 = 3E$		$g_3 = 3$
$E_2 = E$		$g_2 = 2$
$E_1 = 0$		$g_1 = 1$

The possible macrostates are:-

$$i. M_1 = \{2, 1, 1\}$$

$$ii. M_2 = \{0, 4, 0\}$$

∴ For Maxwell Boltzmann Statistics

$$W_1 = \frac{4! \times (1^2 \times 2^1 \times 3^1)}{1! \times 2! \times 1!} = 72$$

$$1! \times 2! \times 1!$$

$$W_2 = \frac{4! \times (4^1)}{2!} = 48$$

For Bose-Einstein Statistics

$$W_1 = 2C_2 \times 2C_4 \times 3C_1 = 6$$

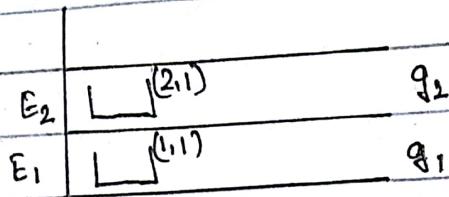
$$W_2 = {}^0C_0 \times {}^5C_4 \times {}^2C_0 = 5$$

For Fermi-Dirac Statistics, we cannot solve this as

$$\sum N_i > \sum g_i$$

Q. 4 distinguishable particles are distributed over 2 non-degradable energy levels. Calculate the micro and macrostates of the system.

Ans:-



Possible Macrostates

$$M_1 = \{4, 0\}, M_2 = \{3, 1\}, M_3 = \{2, 2\}, M_4 = \{1, 3\}, M_5 = \{0, 4\}$$

For Distinguishable
Particles

$$\text{For } M_1, W_1 = 1$$

$$\text{For } M_2, W_2 = 4$$

$$\text{For } M_3, W_3 = 6$$

$$\text{For } M_4, W_4 = 4$$

$$\text{For } M_5, W_5 = 1$$

$$\therefore \Sigma = 16$$

For Indistinguishable
Particles

$$\text{For } M_1, W_1 = 1$$

$$\text{For } M_2, W_2 = 1$$

$$\text{For } M_3, W_3 = 1$$

$$\text{For } M_4, W_4 = 1$$

$$\text{For } M_5, W_5 = 1$$

$$\therefore \Sigma = 5$$

Distribution Law

For Maxwell-Boltzmann Law

$$N = \sum N_i^0 = \text{Constant}$$

$$U = \sum E_i N_i^0 = \text{Constant}$$

$$W = N! \prod_i \frac{N_i^0}{N_i!}$$

$$\therefore \ln W = \ln N! + \sum_i (N_i^0 \ln g_i - \ln N_i!)$$

Using Stirling's Approximation.

$$\ln x! \approx x \ln x - x \quad (\text{for large } n)$$

$$\therefore \ln W = N \ln N + \sum_i (N_i^0 \ln g_i - N_i^0 \ln N_i + N_i)$$

For most probable state

- W is maximum
- $\ln W$ is maximum

Using Lagrange Multiplier method, we can write it as

$$\partial (\ln W - \alpha \sum N_i^0 - \beta \sum N_i E_i) = 0$$

$$\Rightarrow \partial (N \ln N - N + \sum_i (N_i^0 \ln g_i - N_i^0 \ln N_i + N_i) - \alpha \sum N_i^0 - \beta \sum N_i E_i) = 0$$

$$\Rightarrow \partial (\ln W_{\max}) - \alpha \sum N_i^0 - \beta \sum N_i E_i = 0$$

$$\sum (\ln(\frac{q_i^0}{N_i^0}) - \alpha - \beta E_i) dN_i = 0$$

Each term of the summation is independent of each other so each is equal to zero.

$$[\ln(\frac{q_i^0}{N_i^0}) - \alpha - \beta E_i] dN_i = 0$$

But $dN_i \neq 0$ as $N_i^0 \neq$ constant.

$$\text{So } \ln\left(\frac{q_i^0}{N_i^0}\right) - \alpha - \beta E_i = 0$$

$$\Rightarrow \ln\left(\frac{q_i^0}{N_i^0}\right) = \alpha + \beta E_i$$

$$\Rightarrow \frac{q_i^0}{N_i^0} = e^{\alpha + \beta E_i}$$

$$\Rightarrow \frac{N_i^0}{q_i^0} = \frac{1}{e^{\alpha + \beta E_i}}$$

For Quasi-Continuous Energy levels

$$N(E)dE = \frac{q(E)dE}{e^{\alpha + \beta E}} \rightarrow ①$$

This is the number of particles in the energy interval E and $E+dE$.

And so,

$$\int_0^\infty N(E)dE = N$$

① is the distribution law for Maxwell Boltzmann Statistics

For Fermi-Dirac Statistics

$$N(E)dE = \frac{g(E)dE}{e^{(E-\mu)/kT} + 1}$$

For Bose-Einstein Statistics

$$N(E)dE = \frac{g(E)dE}{e^{(E-\mu)/kT} - 1}$$

Calculation of $g(E)dE$:

Phase Space:— Combination of position and Momentum Space.

Ex:- For a 1D Harmonic Oscillator

$$E = \frac{P_x^2}{2m} + \frac{1}{2}Kx^2$$

$$\Rightarrow \frac{P_x^2}{2mE} + \frac{Kx^2}{2E/K} = 1$$

This equation denotes the equation of a ellipse. With greater Energy, the ellipse increases in size.

For 1D Phase Space, we have

- 1D position space
- 1D momentum space

For 4D Phase Space, we have

- 2D position space (x, y)
- 2D momentum space (p_x, p_y)

For 6D Phase Space, we have

- 3D position space (x, y, z)
- 3D momentum space (p_x, p_y, p_z)

Let us consider a 2D phase space

Each cell is a quantum or Energy state.

let us choose a cell. Its area is $dq \cdot dp$

$dq \cdot dp = \hbar$ [Value as small as we like for classical mechanical description]

But for Quantum Mechanical Description

$dq \cdot dp > \hbar$ [Planck's Constant]

For a 6D Phase space, the volume of each such cell is

$$\begin{aligned} &= (dx dy dz) (dp_x dp_y dp_z) \\ &= (dx dp_x) \cdot (dy dp_y) \cdot (dz dp_z) \\ &= \hbar^3 \end{aligned}$$

Total Volume of Phase Space

$$= \iiint \iiint dx dy dz dP_x dP_y dP_z.$$

$$= \iiint dx dy dz \cdot \iiint dP_x dP_y dP_z$$

$$= V \iiint dP_x dP_y dP_z$$

The volume of the space within momentum p to $p+dp$ is $V \cdot 4\pi p^2 dp$ (we consider this as a spherical shell with inner radius p and thickness dp)

∴ The number of energy states within the momentum range p to $p+dp$ is given by

$$\mathfrak{f}(p) dp = \frac{V \cdot 4\pi p^2 dp}{h^3}$$

From the thermodynamical identity to change in particle number

$$dU = dQ - PdV - \mu dN \rightarrow (1)$$

where μ is the chemical potential. It is the form of energy that can be released or absorbed due to change in the numbers of particles of a system.

Chemical Equilibrium $\Delta\mu = 0$

\therefore Particles diffuse until $\Delta\mu = 0$

From (1)

$$dU = TdS - PdV - \mu dN \rightarrow (2)$$

$$\text{As } U = f(S, V, N)$$

$$dU = \frac{\partial U}{\partial S} dS + \frac{\partial U}{\partial V} dV + \frac{\partial U}{\partial N} dN \rightarrow (3)$$

$$\frac{\partial U}{\partial S} = T, \quad \frac{\partial U}{\partial N} = \mu.$$

It is apparent that $S \propto W$

For most probable state $S \propto W_{max}$.

or $S \propto \ln W_{max}$.

$$S = k \ln W_{max}$$

Now the Lagrangian Multipliers

$$\alpha = \frac{\partial \ln W_{max}}{\partial N} = \frac{1}{k} \cdot \frac{\partial S}{\partial N}$$

$$= \frac{1}{k} \frac{\partial S}{\partial U} \cdot \frac{\partial U}{\partial N}$$

$$= \frac{1}{k} \cdot \frac{1}{T} \cdot (-\mu)$$

$$\therefore \alpha = \frac{-\mu}{kT}$$

$$\beta = \frac{\partial \ln W_{max}}{\partial U} = \frac{1}{k} \cdot \frac{\partial S}{\partial U}$$

$$= \frac{1}{k} \cdot \frac{1}{T}$$

$$\therefore \beta = \frac{1}{kT}$$

Maxwell Boltzmann Statistics

$$N(E)dE = \frac{g(E)dE}{e^{\alpha + \beta E}}$$

$$\text{or, } N(E)dE = e^{-\alpha} e^{-\beta E} g(E)dE$$

$$\Rightarrow N(E)dE = e^{\frac{\mu}{kT}} e^{-\frac{E}{kT}} 2\pi v \left(\frac{2m}{h^2}\right)^{3/2} E^{1/2} dE$$

$$\therefore N = \int_0^\infty N(E)dE$$

$$= e^{\frac{\mu}{kT}} \cdot 2\pi v \left(\frac{2m}{h^2}\right)^{3/2} \int_0^\infty e^{-\frac{E}{kT}} E^{1/2} dE$$

Let $e^{-E/kT} = e^{-x}$ and then using gamma function,

$$N = e^{\mu/kT} \cdot 2\pi V \left(\frac{2m}{h^2} \right)^{3/2} (kT)^{3/2} \int_0^\infty e^{-x} x^{1/2} dx.$$

$$\Rightarrow N = e^{\mu/kT} \cdot 2\pi V \left(\frac{2m}{h^2} \right)^{3/2} (kT)^{3/2} \frac{1}{\sqrt{\pi}}$$

$$\Rightarrow N = e^{\mu/kT} \cdot V \cdot \left(\frac{2\pi m kT}{h^2} \right)^{3/2}.$$

$$\therefore \boxed{e^{\mu/kT} = \frac{N}{V \cdot \left(\frac{2\pi m kT}{h^2} \right)^{3/2}}}$$

MB Distribution Law

$$\begin{aligned} N(E)dE &= e^{\mu/kT} \cdot e^{-E/kT} \cdot 2\pi V \left(\frac{2m}{h^2} \right)^{3/2} E^{1/2} dE \\ &= \frac{N \cdot 2\pi V \cdot \left(\frac{2m}{h^2} \right)^{3/2}}{V \cdot \left(\frac{2\pi m kT}{h^2} \right)^{3/2}} \cdot e^{-E/kT} \frac{\sqrt{2\pi}}{E^{1/2}} dE \\ &= \frac{2\pi N}{(\pi kT)^{3/2}} \cdot e^{-E/kT} \cdot E^{1/2} dE \end{aligned}$$

$$\therefore \boxed{N(E)dE = \frac{2\pi N}{(\pi kT)^{3/2}} e^{-E/kT} \cdot E^{1/2} dE}$$

Total Energy of Gas Molecules

$$U = \int_0^{\infty} E \cdot N(E) dE$$

$$= \frac{2\pi N}{(\pi kT)^{3/2}} \int_0^{\infty} e^{-E/kT} \cdot E^{1/2} dE$$

Let $E/kT = x$.

$$= \frac{2\pi N}{(\pi kT)^{3/2}} (kT)^{5/2} \int_0^{\infty} e^{-x} \cdot x^{3/2} dx$$

$$= \frac{2\pi N kT}{\pi^{3/2}} \cdot \frac{3}{2} \cdot \frac{1}{2} \sqrt{\pi}$$

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

$$\therefore U = \frac{3NkT}{2}$$

Average Energy of Gas molecules per degree of freedom
is: —

$$\frac{\bar{U}}{3} = \frac{1}{3} \frac{U}{N} = \frac{1}{3} \frac{3}{2} \frac{NkT}{2}$$

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

Maxwell Boltzmann Speed Distribution Law

We know,

$$N(E)dE = \left[\frac{2\pi N}{(\pi kT)^{3/2}} \right] e^{-E/kT} \cdot E^{1/2} dE$$

$$\text{Here } E = \frac{1}{2}mv^2$$

$$\Rightarrow dE = mv dv$$

$$\begin{aligned} N(v)dv &= \left[\frac{2\pi N}{(\pi kT)^{3/2}} \right] \frac{1}{\sqrt{2}} m^{1/2} m e^{-\frac{mv^2}{2kT}} v^2 dv \\ &= \left[\sqrt{2}\pi N \left(\frac{m}{\pi kT} \right)^{3/2} \right] e^{-\frac{mv^2}{2kT}} \cdot v^2 dv \end{aligned}$$

$$\bullet \bar{v} = \frac{\int_0^\infty N(v)dv \cdot v}{N} = \frac{1}{N} \int_0^\infty v \cdot N(v)dv$$

$$= \left[\frac{1}{N} \sqrt{2}\pi N \left(\frac{m}{\pi kT} \right)^{3/2} \right] \cdot \int_0^\infty e^{-\frac{mv^2}{2kT}} \cdot v^3 dv$$

$$\text{let } \frac{mv^2}{2kT} = x$$

$$\Rightarrow \frac{mv dv}{kT} = dx$$

$$\Rightarrow \bar{v} = \sqrt{2}\pi \left(\frac{m}{\pi kT} \right)^{3/2} \left(\frac{2kT}{m} \right) \left(\frac{kT}{m} \right) \int_0^\infty e^{-x} x dx$$

$$= \sqrt{2}\pi \left(\frac{m}{\pi kT} \right)^{3/2} \left(\frac{2kT}{m} \right) \left(\frac{kT}{m} \right)$$

$$\therefore \bar{v} = \sqrt{\frac{8kT}{\pi m}}$$

- $v_{rms} = \sqrt{\frac{\int_0^\infty v^2 N(v) dv}{N}}$

$$\therefore v_{rms} = \sqrt{\frac{3kT}{m}}$$

- v_p

From MB Speed Distribution Law

$$N(v) = \left[\sqrt{2\pi} N \left(\frac{m}{\pi kT} \right)^{3/2} \right] e^{-\frac{mv^2}{2kT}} v^2$$

\equiv no. of gas molecules per unit velocity
within the velocity interval v to $v+dv$

Taking ln on both sides

$$\ln[N(v)] = \ln A - \frac{mv^2}{2kT} + 2mv.$$

$$\Rightarrow \frac{d}{dv} \left[\ln[N(v)] \right] = -\frac{mv}{kT} + \frac{2}{v}$$

Differentiating w.r.t v ,

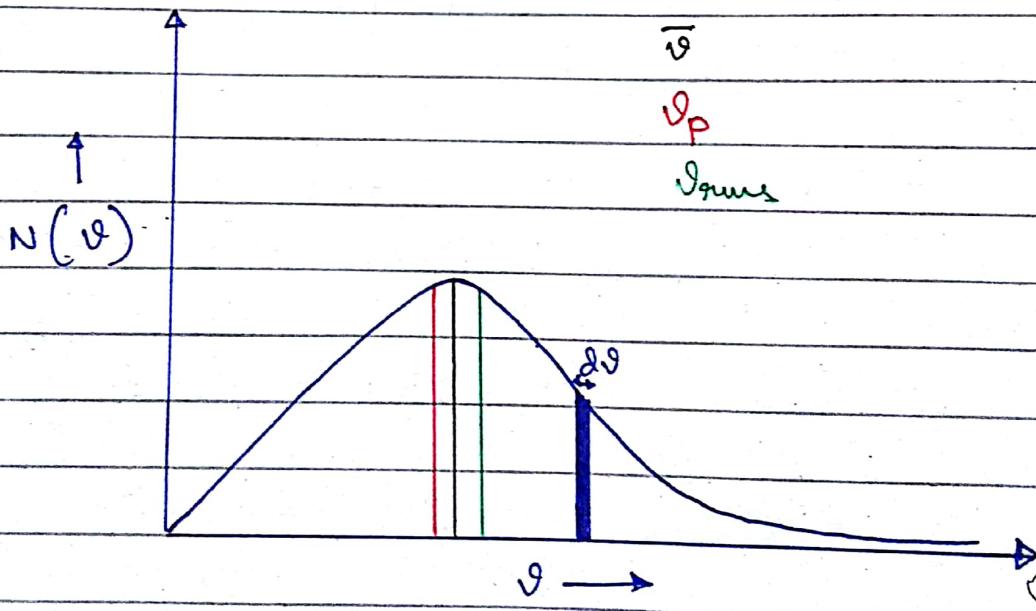
$$\frac{d}{dv} \left[\ln[N(v)] \right] = -\frac{mv}{kT} + \frac{2}{v}.$$

At $v=v_p$, mv is maximum

$$\therefore \frac{d}{dv} \left[\ln[N(v)] \right] \Big|_{v=v_p} = 0$$

$$\Rightarrow -\frac{mv_p}{kT} + \frac{2}{v_p} = 0$$

$$\therefore v_p = \sqrt{\frac{2kT}{m}}$$



Total area under the curve $N = \int_0^\infty N(v) dv$

Fermi-Dimac Statistics

- $N(E)dE = \frac{g(E)dE}{e^{\frac{\epsilon + \beta E}{kT}} + 1}$

- $g(E)dE = 2\pi v \left(\frac{2m}{h^2}\right)^{3/2} \cdot E^{1/2} dE$

Here, we have not considered the spin of the particle.
For fermions, we have 2 spin degeneracy.

A fermion in one energy state can have 2 allowable quantum states. Taking spin into consideration, no. of energy states within E and $E+dE$ is given by:-

$$g(E)dE = (2) \cdot 2\pi v \left(\frac{2m}{h^2}\right)^{3/2} E^{1/2} dE$$

- $\alpha = -\frac{\mu}{kT}$, where μ is the chemical potential

- $\mu(T=0)$ is the Fermi Energy (E_F) and
 $\mu(T=300K) = 0.9998E_F$

$$\mu \propto T^{-1}$$

- $\beta = \frac{1}{kT}$

Fermi-Dimc Distribution Function:-

$$f(E) = \frac{N(E)}{g(E)} = \frac{\text{Number of particles per unit energy within } E \text{ and } E+dE}{\text{Number of states per unit energy within } E \text{ and } E+dE}$$

$$\approx \frac{1}{e^{q+\beta E} + 1} = \frac{1}{e^{(E-E_F)/kT} + 1}$$

$$\therefore f(E) = \frac{1}{e^{(E-E_F)/kT} + 1}$$

$$f(E) \Big|_{T=0} \text{ in metals}$$

Case 1: $E < E_F$ at $T=0$

$$f(E) = \frac{1}{e^{-(E_F-E)/kT} + 1} = \frac{1}{e^{\infty} + 1} = 1.$$

$$\therefore \frac{N(E)}{g(E)} \geq 1$$

$$\Rightarrow N(E) \geq g(E).$$

\therefore All states are fully occupied at $T=0$ and $E < E_F$ (i.e below E_F).

Case 2: $E > E_F$ at $T=0$

$$f(E) = \frac{1}{e^{\infty} + 1} = \frac{1}{\infty + 1} = 0$$

\therefore Number of fermions above E_F in all states at 0K is zero. All states are unoccupied.

At $T=0\text{K}$, Fermi Level E_F is the energy level below which all states are fully occupied and above which all are completely unoccupied.

Case 3: $E = E_F$ at $T > 0$

$$f(E) = \frac{1}{e^0 + 1} = \frac{1}{2}$$

At $T > 0\text{K}$, Fermi level E_F is the energy level which is occupied half. $f(E)$ is termed as the occupancy and it is the fraction of occupied energy states at energy level E .

Let fraction of occupied quantum states in Energy level x units above E_F

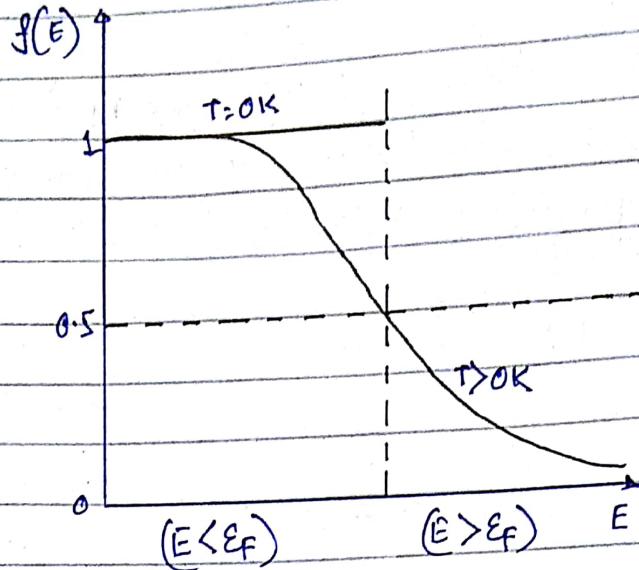
$$E = E_F + x.$$

$$\therefore f(E) : f(E_F + x) = \frac{1}{e^{x/kT} + 1}$$

For unoccupied quantum states $E' = E_F - x$.

$$f(E') : f(E_F - x) = 1 - [f(E_F + x)] = \frac{1}{e^{x/kT} + 1}$$

Q. Plot $f(E)$ v/s E at $T=0K$ and $T>0K$ in metals.



We know,

$$N = \int_0^{\infty} N(E) dE = \int_0^{\infty} f(E) g(E) dE$$

$$= \underbrace{\int_0^{E_F} f(E) g(E) dE}_1 + \underbrace{\int_{E_F}^{\infty} f(E) g(E) dE}_0$$

$$= \int_0^{E_F} 4\pi V \left(\frac{2m}{h^2} \right)^{3/2} E^{1/2} dE$$

$$= 4\pi V \left(\frac{2m}{h^2} \right)^{3/2} \cdot \frac{2}{3} E_F^{3/2}$$

~~∴~~ $\therefore E_F = \left(\frac{3N}{8\pi V} \right)^{2/3} \left(\frac{h^2}{2m} \right)^{3/2}$ → ①

Here N/V is the concentration of free electrons in the metal.

Average kinetic energy of an electron at T=0K in metals

$$\bar{E} = \frac{\text{Total Energy}}{\text{No. of free electrons}} = \frac{\int_0^{\epsilon_F} E N(E) dE}{N}$$

$$= \frac{1}{N} \int_0^{\epsilon_F} E g(E) dE \quad \text{as } f(E) = 1.$$

$$= \frac{4\pi V}{N} \left(\frac{2m}{h^2} \right)^{3/2} \int_0^{\epsilon_F} E^{3/2} dE$$

$$= \frac{4\pi V}{N} \left(\frac{2m}{h^2} \right)^{3/2} \cdot \frac{2}{5} \cdot \epsilon_F^{5/2}$$

Replacing the value of $\epsilon_F^{3/2}$ from ①

$$= \frac{4\pi V}{N} \left(\frac{2m}{h^2} \right)^{3/2} \cdot \frac{2}{5} \left(\frac{3N}{8\pi V} \right) \left(\frac{h^2}{2m} \right)^{3/2} \cdot \epsilon_F$$

$$= \frac{3}{5} \epsilon_F$$

$\therefore \bar{E} = \frac{3}{5} \epsilon_F$

Fermi Velocity :- It is the velocity of an electron corresponding to the energy value of E_F

$$\frac{1}{2} m v_f^2 = E_F$$

$$\Rightarrow v_f^2 = \frac{2E_F}{m}$$

$$= \frac{g}{m} \cdot \left(\frac{\hbar^2}{2m} \right) \cdot \left(\frac{3N}{8\pi V} \right)^{2/3}$$

$$\therefore v_f = \left(\frac{\hbar}{m} \right) \cdot \left(\frac{3N}{8\pi V} \right)^{1/3}$$

Average velocity of electrons in metals at $T=0K$

$$\bar{v} = \frac{1}{N} \int v N(v) dv = \frac{1}{N} \int v g(v) dv$$

$$\text{We know, } f(E) = \frac{N(E)}{g(E)}$$

$$\text{and } g(E) dE = 4\pi V \left(\frac{2m}{\hbar^2} \right)^{3/2} E^{1/2} dE$$

$$\text{Putting } E = \frac{1}{2} mv^2$$

$$\Rightarrow dE = mv^2 dv$$

$$\therefore g(v) dv = 4\pi V \cdot \left(\frac{2m}{\hbar^2} \right)^{3/2} \cdot \frac{1}{\sqrt{2}} \sqrt{m} v \cdot mv^2 dv$$

$$\bar{v} = \frac{1}{N} 2\sqrt{2}\pi V \frac{2\sqrt{2}}{\hbar^3} m^3 \int v^3 dv$$

$$= \frac{3}{4} \bar{\theta}_f$$

$$\therefore \boxed{\bar{\theta} = \frac{3}{4} \bar{\theta}_f}$$

Fermi Temperature :- It is the temperature of an electron corresponding to the E_F .

$$\frac{1}{2} k T_F = E_F.$$

$$\Rightarrow T_F = \frac{2E_F}{K}$$

$$\therefore \boxed{T_F = \frac{2E_F}{K}}$$

This is not the actual temperature but a convenient notation applicable for classical nature.

Bose-Einstein Statistics

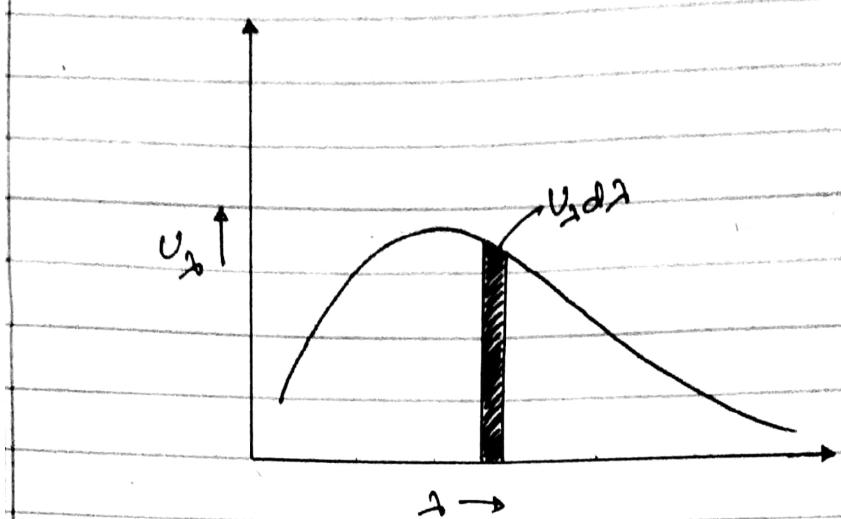
$$\text{We know, } N(E) dE = \frac{g(E) dE}{e^{\frac{E}{kT}} - 1}$$

We assume a particle as a photon.

The number of photons within the frequency range ν to $\nu + d\nu$ is given by

$$N(\nu) d\nu = \frac{g(\nu) d\nu}{e^{\frac{h\nu}{kT}} - 1}$$

Planck's Black Body Radiation Law using BE Statistics



At a given temperature, a blackbody consists of a large number of photons. The total number of photons need not be conserved while the total energy remains constant. Unlike gas molecules and electrons, photons may be created or destroyed.

For instance, 2 photons, each of $h\nu$ energy can be emitted simultaneously by the absorption of a single photon of energy $2h\nu$.

$$\therefore N(\nu) d\nu = \frac{g(\nu) d\nu}{e^{h\nu/kT} - 1}$$

$$g(P) dP = \frac{V \times 4\pi P^2 dP}{h^3}$$

Photons have two states of polarisation (LCP and RCP). Taking states of polarisation into consideration.

$$g(P) dP = \frac{2 \times V \times 4\pi P^2 dP}{h^3}$$

$$\text{we know, } P = \frac{h\nu}{c}.$$

$$\Rightarrow dP = \frac{h\nu}{c} d\nu$$

$$\therefore q(\nu) d\nu = \frac{8\pi\nu}{h\nu^3} \cdot \frac{h^2}{c^2} \nu^2 \frac{\nu}{c} d\nu$$

$$\therefore q(\nu) d\nu = \frac{8\pi\nu}{c^3} \cdot \nu^2 d\nu$$

The Energy Density of Black Body radiation within the frequency interval ν to $\nu + d\nu$ is given by

$$U_\nu d\nu = \frac{N(\nu) d\nu \times h\nu}{V}$$

$$\Rightarrow U_\nu d\nu = \frac{1}{V} \cdot h\nu \cdot \frac{q(\nu) d\nu}{e^{h\nu/kT} - 1}$$

$$\Rightarrow U_\nu d\nu = \frac{h\nu}{V} \cdot \frac{8\pi\nu}{c^3} \frac{\nu^2 d\nu}{e^{h\nu/kT} - 1}$$

$$\therefore U_\nu d\nu = \frac{8\pi h\nu^3 d\nu}{c^3 (e^{h\nu/kT} - 1)}$$

$$U_\lambda d\lambda = -U_\nu d\nu = -\frac{8\pi h\nu^3 d\nu}{c^3 [e^{h\nu/kT} - 1]}$$

$$\nu = c/\lambda, d\nu = -\frac{c}{\lambda^2} d\lambda$$

$$\therefore U_\lambda d\lambda = \frac{8\pi h c d\lambda}{\lambda^5 [e^{hc/\lambda kT} - 1]}$$