

# **Statistical Mechanics**

# Black Body Radiation

All objects radiate electromagnetic energy continuously regardless of their temperatures.

Though which frequencies will predominate, depends on the **temperature**.

At room temperature most of the radiation is in **infrared part** of the spectrum and hence is **invisible**.

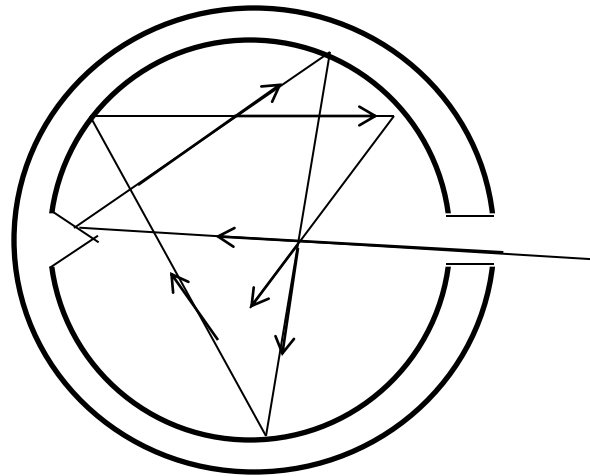
The ability of a body to radiate is closely related to its ability to absorb radiation.

A body at a constant temperature is in thermal equilibrium with its surroundings and must absorb energy from them at the same rate as it emits energy.

A perfectly **black body** is the one which absorbs completely all the radiation, of whatever wavelength, incident on it.

Since it neither transmits any radiation, it **appears black whatever the color of the incident radiation** may be.

There is no surface available in practice which will absorb all the radiation falling on it. **BUT** a metallic cavity can work as perfect black body.

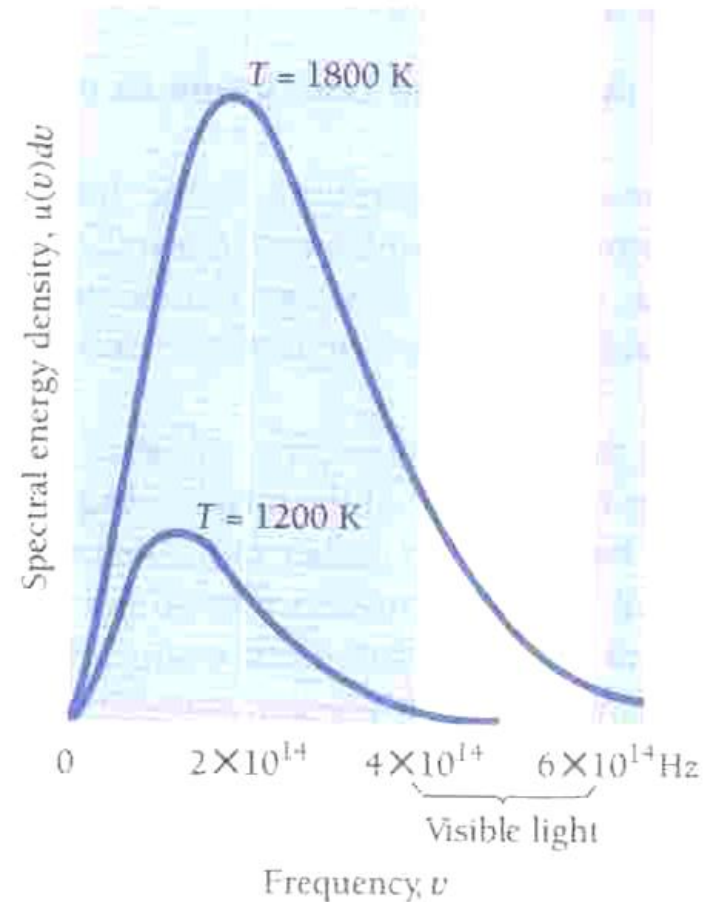


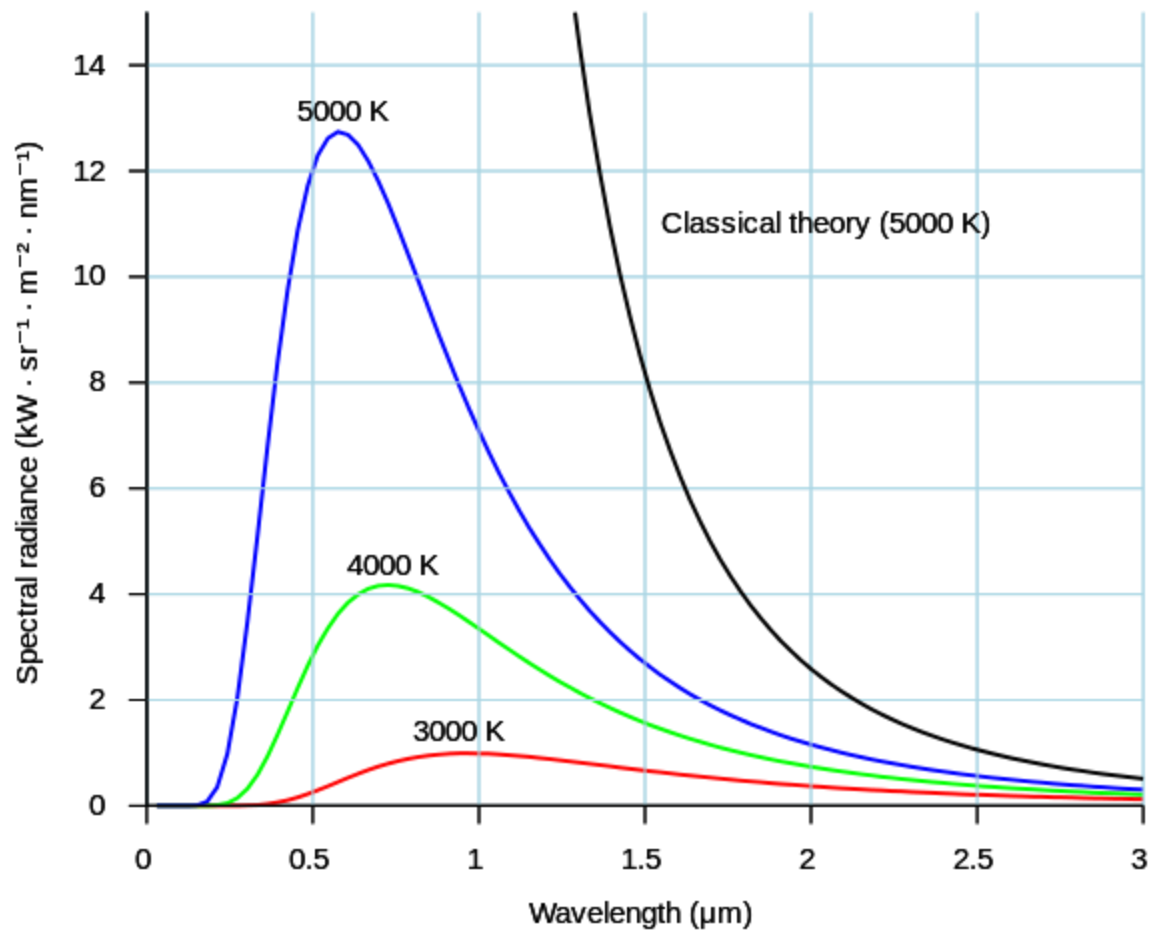
The cavity walls are constantly emitting and absorbing radiation, and this radiation is known as black body radiation.

# Characteristics of Black Body Radiation

- (i) The total energy emitted per second per unit area (radiancy  $E$  or area under curve) increases rapidly with increasing temperature.
- (ii) At a particular temperature, the spectral radiance is maximum at a particular frequency.
- (iii) The frequency (or wavelength,  $\lambda_m$ ) for maximum spectral radiance decreases in direct proportion to the increase in temperature. This is called “Wien’s displacement law”

$$\lambda_m \times T = \text{constant } (2.898 \times 10^{-3} \text{ m.K})$$





## Statistical Mechanics

- ***Every solid, liquid or gas*** is an assembly of enormous number of **microscopic** particles.
- Similarly, **radiation** is an assembly of photons.
- It is impossible to study the movement of **individual particle/ photon**.
- However the **MACROSCOPIC** properties of such assemblies can be explained in terms of the **statistical distributions**.

# Statistical Distribution

This expresses **the most probable way** in which a certain **total amount of energy 'E'** is distributed among the **'N' members of a system of particles** in thermal equilibrium at absolute temperature, T.

Thus Statistical Mechanics reflects **overall behavior of system of many particles.**

Suppose  $n(\epsilon)$  is the no. of particles having energy,  $\epsilon$

$$\text{then } n(\epsilon) = g(\epsilon)f(\epsilon)$$

where  $g(\epsilon)$  = **no. of states of energy  $\epsilon$**  or statistical weight corresponding to energy  $\epsilon$  (or simply **density of states**)

$f(\epsilon)$  = **distribution function**

= average no. of particles in each state of energy  $\epsilon$

= probability of occupancy of each state of energy  $\epsilon$

Usually, we are interested, how the fixed amount of energy is distributed among the various identical particles of an assembly. **There are 3 kinds of identical particles-**

1. Identical particles that are sufficiently far apart to be **distinguishable**.

Example: molecules of a gas.

Negligible overlapping of  $\psi$

**Maxwell-Boltzmann Statistics is used.**

2. Indistinguishable identical particles of '0' or integral spin.

Example: Bosons (Photons, Phonons, alpha particles) (don't obey the Pauli exclusion principle)

Overlapping of  $\psi$

**Bose-Einstein Statistics is used.**

3. Indistinguishable identical particles with odd-half integral spin ( $1/2, 3/2, 5/2 \dots$ ).

Example: Fermions (Electrons, Protons, Neutrons) (obey the exclusion principle)

**Fermi-Dirac Statistics is used.**



- Every kind of Statistics, is characterized by its **DISTRIBUTION FUNCTION**.
- Which means- **number of particles inside a state of energy  $\epsilon$**

- DISTRIBUTION FUNCTION for MB Statistics-

$$f_{M.B.}(\epsilon) = Ae^{-\epsilon/kT}$$

- DISTRIBUTION FUNCTION for BE Statistics-

$$f_{B.E.}(\epsilon) = \frac{1}{e^{\alpha} e^{\epsilon/kT} - 1}$$

- DISTRIBUTION FUNCTION for FD Statistics-

- 

$$f_{F.D.}(\epsilon) = \frac{1}{e^{\alpha} e^{\epsilon/kT} + 1}$$

# Maxwell-Boltzmann Statistics

According to this law number of identical and distinguishable particles in a system at temperature, T having energy  $\epsilon$  is

$n(\epsilon) = (\text{No. of states of energy } \epsilon) \cdot (\text{average no. of particles in a state of energy } \epsilon)$

$$n(\epsilon) = g(\epsilon) \cdot A e^{-\epsilon/kT} \quad (\text{i})$$

Here A is a constant and  $f_{M.B.}(\epsilon) = A e^{-\epsilon/kT}$

**Equation (i) represents the Maxwell-Boltzmann Distribution Law**

This law cannot explain the behavior of photons (Black body radiation) or of electrons in metals (specific heat, conductivity)

# Applications of M.B. Statistics

## (i) Molecular energies in ideal gas

No. of molecules having energies between  $\epsilon$  and  $\epsilon + d\epsilon$  is given by

$$n(\epsilon)d\epsilon = \{g(\epsilon)d\epsilon\} \{f(\epsilon)\}$$

$$n(\epsilon)d\epsilon = Ag(\epsilon)e^{-\epsilon/kT}d\epsilon \quad (i)$$

The momentum of a molecule having energy  $\epsilon$  is given by

$$p = \sqrt{2m\epsilon} \quad \Rightarrow \quad dp = \frac{m d\epsilon}{\sqrt{2m\epsilon}}$$

No. of states in momentum space having momentum between  $p$  and  $p + dp$  is proportional to the volume element i.e.

$$\alpha \iiint dp_x dp_y dp_z$$

$$\propto \frac{4}{3} \pi (p + dp)^3 - \frac{4}{3} \pi p^3$$

$$\propto 4\pi p^2 dp$$

$$g(p)dp \propto 4\pi p^2 dp$$

$$g(p)dp = Bp^2 dp \quad \text{B is a constant}$$

Each momentum corresponds to a single  $\epsilon$

$$g(\epsilon)d\epsilon = Bp^2 dp$$

$$g(\epsilon)d\epsilon = B.2m\epsilon. \frac{m d\epsilon}{\sqrt{2m\epsilon}}$$

$$g(\varepsilon)d\varepsilon = 2m^{3/2}B\sqrt{\varepsilon}d\varepsilon$$

Put in (i)

No. of molecules with energy between  $\epsilon$  and  $\epsilon + d\epsilon$

$$n(\varepsilon)d\varepsilon = 2m^{3/2}BA\sqrt{\varepsilon}e^{-\varepsilon/kT}d\varepsilon$$

$$n(\varepsilon)d\varepsilon = C\sqrt{\varepsilon}e^{-\varepsilon/kT}d\varepsilon \quad (\text{ii})$$

Total No. of molecules is N

$$N = \int_0^{\infty} n(\varepsilon)d\varepsilon = C \int_0^{\infty} \sqrt{\varepsilon}e^{-\varepsilon/kT}d\varepsilon$$

Using identity

$$\int_0^{\infty} x^{1/2} e^{-ax} dx = \frac{1}{2a} \sqrt{\frac{\pi}{a}}$$

$$C = \frac{2\pi N}{(\pi kT)^{3/2}}$$

Put value of C in equation (ii)

$$n(\varepsilon) d\varepsilon = \frac{2\pi N}{(\pi kT)^{3/2}} \sqrt{\varepsilon} e^{-\varepsilon/kT} d\varepsilon$$

above equation gives the **number** of molecules with energies between  $\epsilon$  and  $\epsilon + d\epsilon$  in an ideal gas that contains N molecules and whose absolute temperature is T. **It is called molecular energy distribution equation.**

## Average Molecular Energy

Total energy of the system  $E = \int_0^{\infty} \varepsilon n(\varepsilon) d\varepsilon$

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

Using

$$\int_0^{\infty} x^{3/2} e^{-ax} dx = \frac{3}{4a^2} \sqrt{\frac{\pi}{a}}$$

$$E = \frac{2\pi N}{(\pi kT)^{3/2}} \left[ \frac{3}{4} (kT)^2 \sqrt{\pi kT} \right]$$

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

$$\text{Average energy per molecule} = \bar{\mathcal{E}} = \frac{E}{N}$$

$$\bar{\mathcal{E}} = \frac{3}{2} kT$$

This is the average molecular energy and is independent of the molecular mass

At Room Temperature its value is 0.04 eV.



# Equipartition of Energy: Equipartition Theorem

Average Kinetic Energy associated with each degree of freedom of a molecule is

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

**(In statistics, the number of values in a study that are free to vary are known as degree of freedom.)**

## Distribution of molecular speed

$$K.E. \Rightarrow \varepsilon = \frac{1}{2}mv^2$$

$$\Rightarrow d\varepsilon = mv dv$$

Put this in molecular energy distribution equation

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

It is called molecular speed distribution formula.

## RMS Speed

$$v_{rms} = \sqrt{\overline{v^2}}$$

It is the square root of the average squared molecular speed

$$\overline{\varepsilon} = \frac{1}{2} m \overline{v^2} = \frac{3}{2} kT$$

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

## Average Speed

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

$$= 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} \int_0^{\infty} v^3 e^{-mv^2/2kT} dv$$

Using

$$\int_0^{\infty} x^3 e^{-ax^2} dx = \frac{1}{2a^2}$$

$$\bar{v} = 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} \cdot \left( \frac{4k^2 T^2}{2m^2} \right) = \sqrt{\frac{8kT}{\pi m}}$$

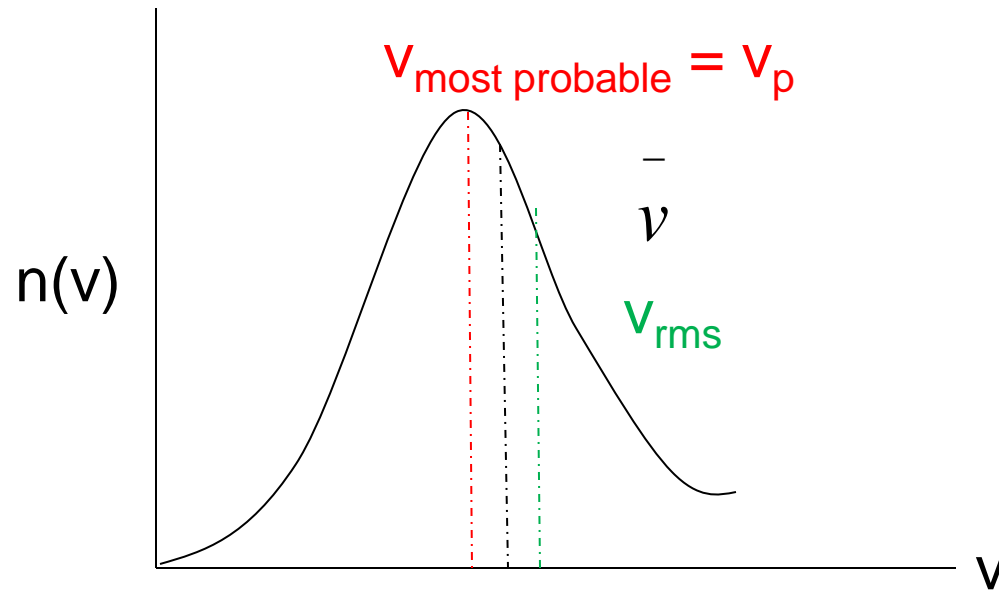
## Most Probable Speed

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

$$\frac{dn(v)}{dv} = 4\pi N \left( \frac{m}{2\pi kT} \right)^{3/2} \frac{d}{dv} \left[ v^2 e^{-mv^2/2kT} \right] = 0$$

$$4\pi N \left( \frac{m}{2\pi kT} \right)^{3/2} \neq 0$$

$$\frac{d}{dv} \left[ v^2 e^{-mv^2/2kT} \right] = 0 \quad \Rightarrow \quad v_p = \sqrt{\frac{2kT}{m}}$$



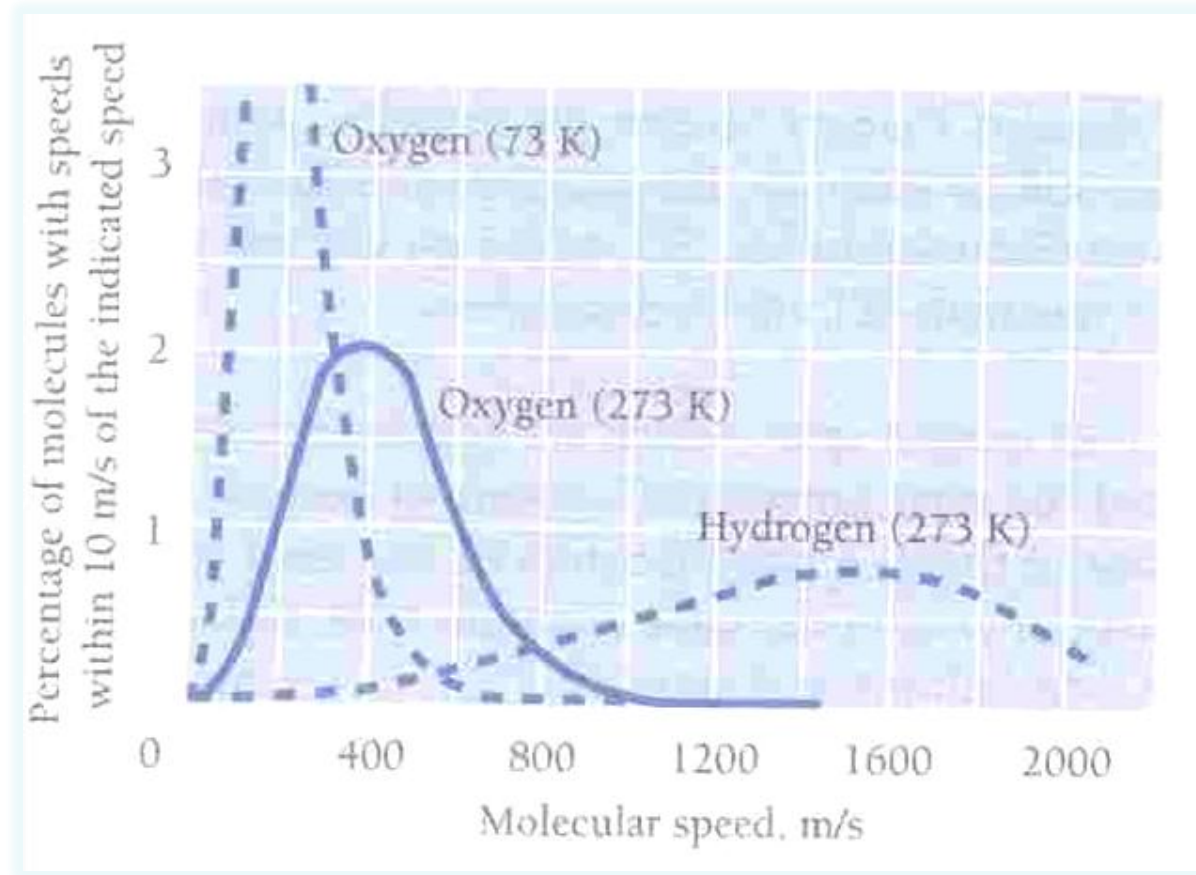
M.B. Speed Distribution Curve

(i) Speed distribution is not symmetrical

(ii) 
$$v_p < \bar{v} < v_{rms}$$

$$\sqrt{\frac{2kT}{m}} < \sqrt{\frac{8kT}{\pi m}} < \sqrt{\frac{3kT}{m}}$$

# Variation in molecular speed with 'T' and ' molecular mass'



This curve suggests that most probable speed  $\propto \sqrt{T}$

Also the most probable speed  $\propto 1/\sqrt{m}$

# Quantum Statistics (Indistinguishable identical particles)

## Bosons

1. '0' or integral spin
2. Do not obey exclusion principle
3. Symmetric wave function
4. Any number of bosons can exist in the same quantum state of the system

## Fermions

1. Odd half integral spin
2. Obey exclusion principle
3. Anti-symmetric wave function
4. Only one fermion can exist in a particular quantum state of the system

Consider a system of two particles, 1 and 2, one of which is in state 'a' and the other in state 'b'.

When particles are distinguishable then

$$\psi' = \psi_a(1)\psi_b(2)$$

$$\psi'' = \psi_a(2)\psi_b(1)$$

When particles are indistinguishable then

$$\text{For Bosons, } \psi_B = \frac{1}{\sqrt{2}} [\psi_a(1)\psi_b(2) + \psi_a(2)\psi_b(1)]$$

symmetric

$$\text{For Fermions, } \psi_F = \frac{1}{\sqrt{2}} [\psi_a(1)\psi_b(2) - \psi_a(2)\psi_b(1)]$$

anti-symmetric



$\psi_F$  becomes zero when 'a' is replaced with 'b' i.e.

$$\psi_F = \frac{1}{\sqrt{2}} [\psi_a(1)\psi_a(2) - \psi_a(2)\psi_a(1)] = 0$$

Thus two Fermions can't exist in same state (Obey Exclusion Principle)

# Bose-Einstein Statistics

Any number of particles can exist in one quantum state.

Distribution function can be given by

$$f_{B.E.}(\varepsilon) = \frac{1}{e^{\alpha} e^{\varepsilon/kT} - 1}$$

where  $\alpha$  may be a function of temperature, T.

For Photon gas  $\alpha = 0 \Rightarrow e^{\alpha} = 1$

-1 in denominator indicates multiple occupancy of an energy state by Bosons

# Bose-Einstein Condensation

If the temperature of any gas is reduced, the wave packets grow larger as the atoms lose momentum according to uncertainty principle.

When the gas becomes very cold, the dimensions of the wave packets exceeds the average atomic spacing resulting into overlapping of the wave packets. If the atoms are bosons, eventually, all the atoms fall into the lowest possible energy state resulting into a single wave packet. This is called Bose-Einstein condensation.

The atoms in such a Bose-Einstein condensate are barely moving, are indistinguishable, and form one entity – a superatom.

# Bose Einstein Statistics

(Indistinguishable identical particles- BOSONS)

1. '0' or integral spin
2. Do not obey exclusion principle
3. Symmetric wave function

( Means if we have two particles, THERE WILL BE NO CHANGE IN THE WAVEFUNCTION IF WE EXCHANGE THE LOCATION FOR BOTH THE PARTICLES)

4. Any number of bosons can exist in the same quantum state of the system.

## 5. Distribution function

$$f_{B.E.}(\varepsilon) = \frac{1}{e^{\alpha} e^{\varepsilon/kT} - 1}$$

# Planck's Radiation Law

Planck assumed that the atoms of the walls of cavity radiator (black body) behave as oscillators with energy

$$\varepsilon_n = nh\nu \quad n = 0, 1, 2, 3, \dots$$

The average energy of an oscillator is

$$\bar{\varepsilon} = \frac{\varepsilon}{N} \quad \text{N is total no. of Oscillators}$$

$$\bar{\varepsilon} = \frac{h\nu}{e^{h\nu/kT} - 1} \quad (i)$$

Thus the energy density ( $u_\nu$ ) of radiation in the frequency range  $\nu$  to  $\nu + d\nu$  is

$$u_\nu d\nu = \frac{8\pi\nu^2 d\nu}{c^3} \times \bar{\varepsilon}$$

here  $G(\nu) d\nu = \frac{8\pi\nu^2 d\nu}{c^3}$  represents the density of standing waves in a cavity

$$u_\nu d\nu = \frac{8\pi\nu^2 d\nu}{c^3} \left( \frac{h\nu}{e^{h\nu/kT} - 1} \right)$$

$$u_\nu d\nu = \frac{8\pi h\nu^3}{c^3} \frac{d\nu}{e^{h\nu/kT} - 1}$$

This is Planck's Radiation formula in terms of frequency.

In terms of wavelength

$$u_\lambda d\lambda = \frac{8\pi hc}{\lambda^5} \frac{d\lambda}{e^{hc/\lambda kT} - 1}$$

This is Planck's Radiation formula in terms of wavelength.

## Case I : (Rayleigh-Jeans Law)

$$u_{\lambda} d\lambda = \frac{8\pi hc}{\lambda^5} \frac{d\lambda}{e^{hc/\lambda kT} - 1}$$

When  $\lambda$  is large then  $e^{hc/\lambda kT} \approx 1 + \frac{hc}{\lambda kT}$

$$u_{\lambda} d\lambda = \frac{8\pi hc}{\lambda^5 \left( 1 + \frac{hc}{\lambda kT} - 1 \right)} d\lambda$$

$$u_{\lambda} d\lambda = \frac{8\pi kT}{\lambda^4} d\lambda$$

This is Rayleigh-Jeans Law for longer  $\lambda$ 's.

## Case II : (Wein's Law)

$$u_{\lambda} d\lambda = \frac{8\pi hc}{\lambda^5} \frac{d\lambda}{e^{hc/\lambda kT} - 1}$$

When  $\lambda$  is very small then  $e^{hc/\lambda kT} \gg 1$

$$u_{\lambda} d\lambda = \frac{8\pi hc}{\lambda^5} e^{-hc/\lambda kT} d\lambda$$

This is Wein's Law for small  $\lambda$ 's.

$$u_{\lambda} d\lambda = \frac{A}{\lambda^5} e^{B/\lambda kT} d\lambda$$

This is another form of Wein's Law..

Here A and B are constants.



# **Application of the BE Statistics for understanding the specific heat of solids**

- Specific heat is the heat required to raise the temperature of one gram of a substance by one degree centigrade.
- Earlier we had Dulong-Petit's law for the theoretical prediction of the specific heat of solids.
- This law is not in the good agreement with experiments for lighter elements.

# **Specific Heat of Solids: The answer comes from Statistical Mechanics**

## **A- Classical Approach-**

In case of solids total average energy per atom per degree of freedom is  $kT$ .

Each atom in the solid should have total energy =  $3kT$  (3 degrees of freedom).

For one mole of solid, total energy,  $E = 3N_0kT$  (classically)

Here  $N_0$  is the Avogadro number.

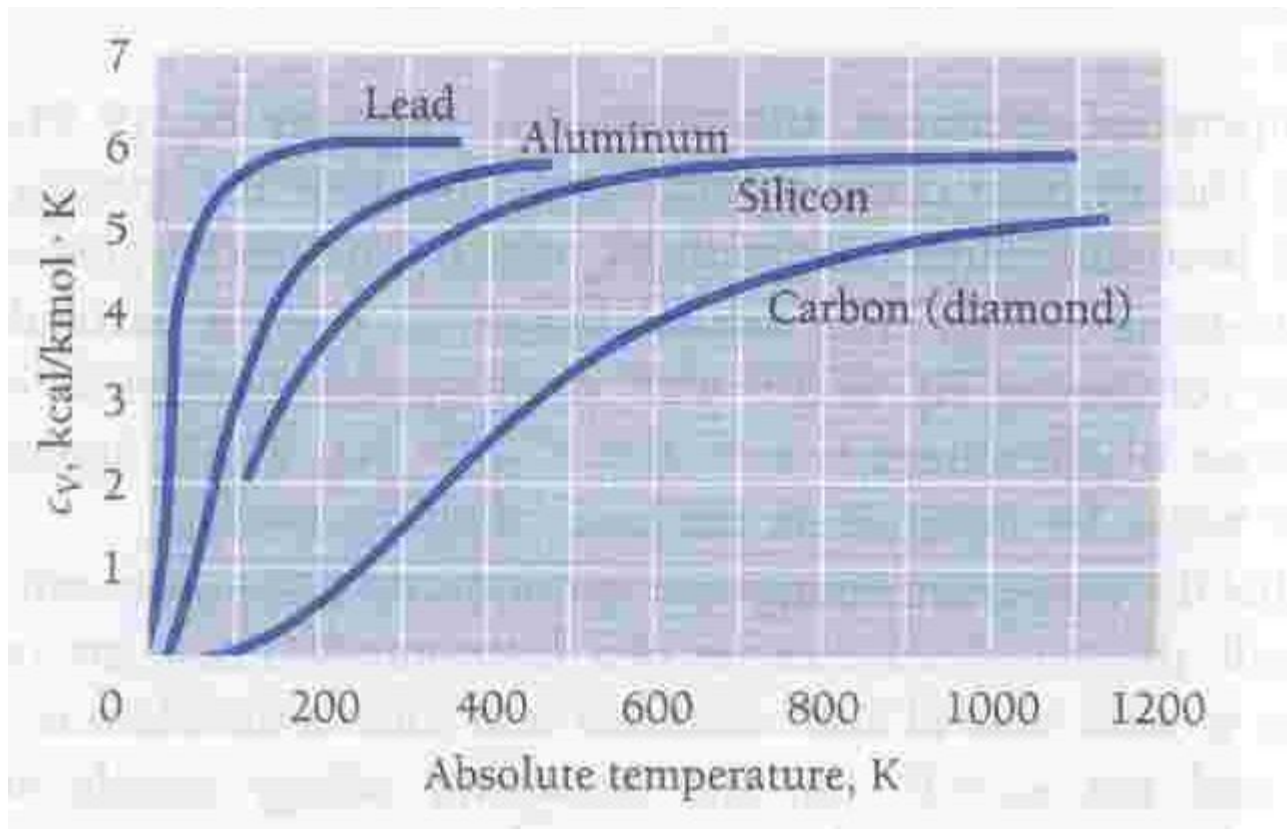
$$E = 3RT$$

Specific heat at constant volume is

$$C_v = \left( \frac{\partial E}{\partial T} \right)_v = 3R \quad \sim 6 \text{ kcal/kmol.K}$$

**This is Dulong & Petit's Law.**

This means that atomic specific heat (at constant volume) for all solids is approx 6 kcal/kmol.K and is independent of T.



**Dulong and Petit's Law fails for light elements such as B, Be and C.**

*Also it is not applicable at low temperatures for all solids.*

## B- Einstein's Approach of Specific Heat of Solids

According to it the motion of the atoms in a solid is oscillatory.

The average energy per oscillator atom) is

$$\bar{\varepsilon} = \frac{h\nu}{e^{h\nu/kT} - 1}$$

The total energy for one mole of solid in three degrees of freedom.

$$E = 3N_o \frac{h\nu}{e^{h\nu/kT} - 1}$$

The molar specific heat of solid is  $C_v = \left( \frac{\partial E}{\partial T} \right)_v$

$$C_v = 3N_o hv \left( \frac{hv}{kT^2} \right) \frac{e^{hv/kT}}{(e^{hv/kT} - 1)^2} = 3N_o k \left( \frac{hv}{kT} \right)^2 \frac{e^{hv/kT}}{(e^{hv/kT} - 1)^2}$$

$$C_v = 3R \left( \frac{hv}{kT} \right)^2 \frac{e^{hv/kT}}{(e^{hv/kT} - 1)^2}$$

This is Einstein's specific heat formula.

Case I:

At high T,  $kT \gg hv$  then

$$e^{hv/kT} \approx 1 + \frac{hv}{kT}$$

$$C_v \approx 3R \left( \frac{h\nu}{kT} \right)^2 \frac{\left( 1 + \frac{h\nu}{kT} \right)}{\left( 1 + \frac{h\nu}{kT} - 1 \right)^2}$$

$$C_v \approx 3R \left( 1 + \frac{h\nu}{kT} \right)$$

$$C_v \approx 3R \quad (\because kT \gg h\nu)$$

This is in agreement with Dulong & Petit's Law at high T.

Case II:

At low  $T$ ,  $h\nu \gg kT$  then  $e^{h\nu/kT} \gg 1$

$$C_v \approx 3R \left( \frac{h\nu}{kT} \right)^2 e^{-h\nu/kT}$$

This implies that as  $T \rightarrow 0, C_v \rightarrow 0$

i.e. is in agreement with experimental results at low  $T$ .

# Fermi-Dirac Statistics

Obey Pauli's exclusion Principle

Distribution function can be given by

$$f_{F.D.}(\epsilon) = \frac{1}{e^{\alpha} e^{\epsilon/kT} + 1}$$

$f(\epsilon)$  can never exceed 1, whatever be the value of  $\alpha$ ,  $\epsilon$  and  $T$ . So only one particle can exist in one quantum state. (Pauli's Principle)

$\alpha$  is given by

$$\alpha = -\frac{\epsilon_F}{kT}$$

where  $\epsilon_F$  is the **Fermi Energy** and represents the energy of highest occupied energy state at absolute zero temperature.



Thus at  $T = 0$ , For  $\epsilon < \epsilon_F$  all energy states from  $\epsilon = 0$  to  $\epsilon_F$  are occupied as

$$f_{F.D.}(\epsilon) = 1$$

Thus at  $T = 0$ , all energy states for which  $\epsilon > \epsilon_F$  are vacant.

$$f_{F.D.}(\epsilon) = 0$$

Case II:

$$T > 0$$

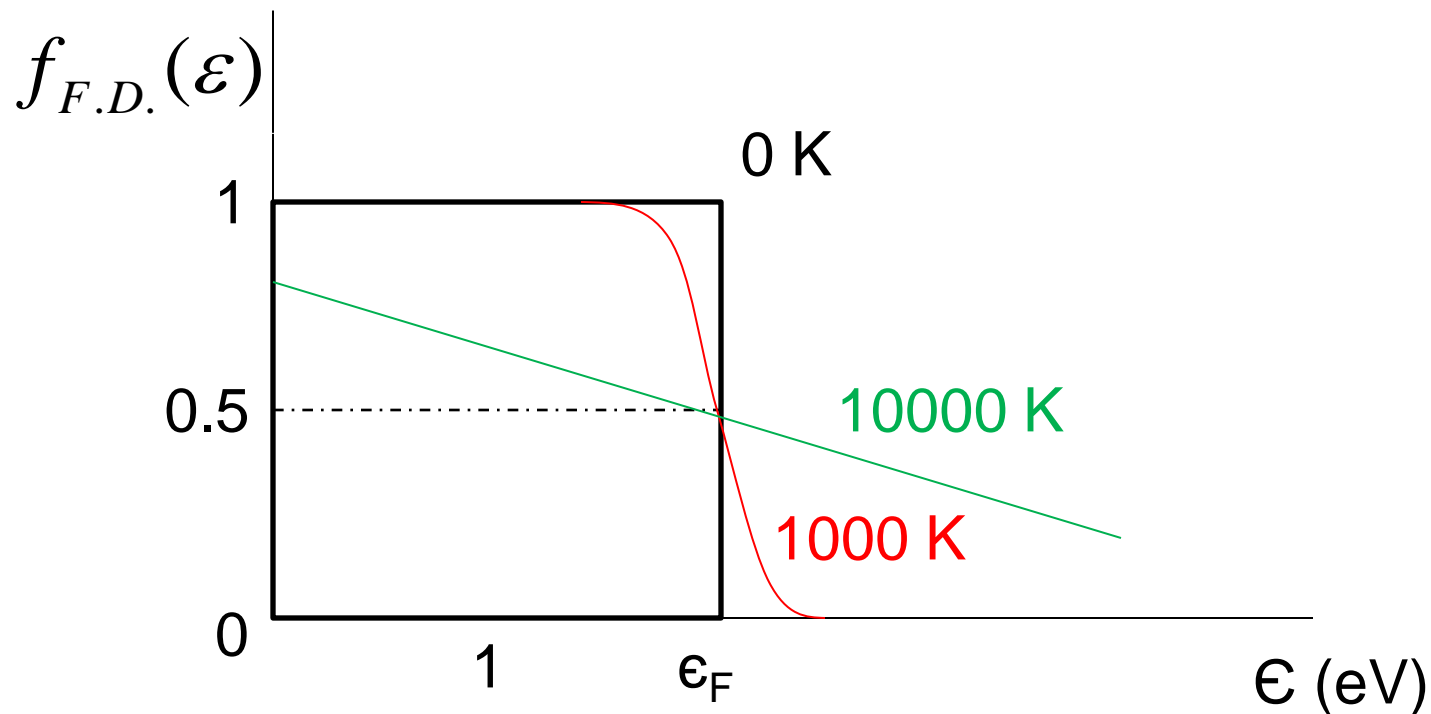
Some of the filled states just below  $\epsilon_F$  becomes vacant while some just above  $\epsilon_F$  become occupied.

Case III:

At  $\epsilon = \epsilon_F$

$$f_{F.D.}(\epsilon) = \frac{1}{e^0 + 1} = \frac{1}{2} \quad \text{For all } T$$

Probability of finding a fermion (i.e. electron in metal) having energy equal to fermi energy ( $\epsilon_F$ ) is  $\frac{1}{2}$  at any temperature.



# Free electrons in a metal

Typically, one metal atom gives one electron.

One mole atoms gives one mole of free electrons, ( $N_o$ )

If each free electron can behave like molecules of an ideal gas.  
Then

Average K.E. for 1 mole of electron gas,  $E_e = \frac{3}{2} N_o kT = \frac{3}{2} RT$

Molar specific heat of electron gas,  $(C_v)_e = \left( \frac{\partial E_e}{\partial T} \right)_v = \frac{3}{2} R$

Then total specific heat in metals at high T should be

$$C_v = 3R + \frac{3}{2} R = \frac{9}{2} R$$

But experimentally at high T  $C_v \approx 3R$

**It means free electrons are not contributing in the specific heat.**

By definition highest state of energy to be filled by a free electron at  $T = 0$  is obtained at  $\epsilon = \epsilon_F$

The no. of electrons having energy  $\epsilon$  is

$$N = \int_0^{\epsilon_F} n(\epsilon) d\epsilon \quad \text{where} \quad n(\epsilon) d\epsilon = \frac{8\sqrt{2}\pi V m^{3/2}}{h^3} \sqrt{\epsilon} d\epsilon$$

Here V is the volume of the metal

$$N = \frac{8\sqrt{2}\pi V m^{3/2}}{h^3} \int_0^{\varepsilon_F} \sqrt{\varepsilon} d\varepsilon = \frac{16\sqrt{2}\pi V m^{3/2}}{3h^3} \varepsilon_F^{3/2}$$

$$\Rightarrow \varepsilon_F = \frac{h^2}{2m} \left( \frac{3N}{8\pi V} \right)^{2/3} \quad (\text{i})$$

where  $N/V$  is the density of free electrons.

## Electron energy distribution

No. of electrons in the electron gas having energy between  $\varepsilon$  and  $\varepsilon + d\varepsilon$  is

$$n(\varepsilon)d\varepsilon = g(\varepsilon)f(\varepsilon)d\varepsilon$$

$$n(\varepsilon)d\varepsilon = \frac{8\sqrt{2}\pi V m^{3/2}}{h^3} \frac{\varepsilon^{3/2} \sqrt{\varepsilon}}{e^{(\varepsilon - \varepsilon_F)/kT} + 1} d\varepsilon$$

using (i)

$$n(\varepsilon)d\varepsilon = \left( \frac{3N}{2} \right) \frac{\varepsilon^{-3/2} \sqrt{\varepsilon}}{e^{(\varepsilon - \varepsilon_F)/kT} + 1} d\varepsilon$$

This is electron energy distribution formula, according to which distribution of electrons can be found at different temperatures.

# Average electron energy at 0K

Total energy at 0K is

$$E_o = \int_0^{\epsilon_F} \epsilon n(\epsilon) d\epsilon$$

Since at 0K all electrons have energy less than or equal to  $\epsilon_F$

$$e^{(\epsilon - \epsilon_F)/kT} = e^{-\infty} = 0$$

$$E_o = \frac{3N}{2} \epsilon_F^{-3/2} \int_0^{\epsilon_F} \epsilon^{3/2} d\epsilon = \frac{3N}{5} \epsilon_F$$

Then average electron energy

$$\left( \bar{\epsilon}_o \right) = \frac{E_o}{N} = \frac{3}{5} \epsilon_F \quad \text{at 0K.}$$