UNIT – III

5.Elements Of Statistical Mechanics

Introduction:Statistical mechanics provides the mathematical language for understanding the nature of materials and applies to microstates and ultimately to arrive at the bulk property estimation. Statistical mechanics mainly deals with the distribution of identical, distinguishable and indistinguishable particles of a system in different states of the system.

Phase space or hyper space or μ - space:Consider a system consisting of a large number of particles. The state of the particle at an instant can be represented with 3 position and 3 momentum coordinates.To specify the position and momentum of a particle in a system,a 6-dimentional space called phase space or hyper space or μ - space is used. Any point in this space can be represented with 3 position coordinates x, y, z and the 3 momentum coordinates P_x,P_y,P_z. The space points in this space are called phase points or representative points. The space can be divided into large number of small elements called cells or groups. The volume of each element is dx, dy, dz, dp_x ,dp_y,dp_z and is equal to h^3.

Maxwell – Boltzman Distribution (Classical Statistics) :This distribution is applied to a macroscopic system consisting of a large number of identical but distinguishable particles such as gas molecules in a container. This distribution tells us the way of distribution of total energy E of the system among the various identical particles.

The main assumptions of Maxwell –Boltzman statistics are:
1.The particles are identical and distinguishable.
2.Any number of particles can occupy a single cell in phase space ie., there is no limit on the number of particles which can occupy a phase space cell or an energy level .
3.The particles have any value of the spin ie., any spin is possible.
4.Energy levels are continuous.

Consider a system consisting of n_1 particles in E_1 level, n_2 particles in E_2 level, …. , n_i particles in E_i level ,etc.

The total number of particles in the system is constant

$$\text{ie .,} \sum n_i = N \quad \text{……. (1)}$$

The total energy (E)of the system is constant .

$$\text{ie.,} \sum n_i E_i = E \quad \text{……. (2)}$$

Let g_1, g_2, g_3, …., g_i be the number of electron states called degeneracy parameter .

The probability of distribution of particles in different energy levels is given by

$$W = (N! g_i^{n_i})/(n_1! n_2! .... n_i!) \quad \text{…… (3)}$$

Applying logarithm on both sides we get,

$$\log W = \log N! - (\log n_1! + \log n_2! + ….. + \log n_i!) + (n_1 \log g_1 + n_2 \log g_2 + …. + n_i \log g_i)$$

Using Sterling's approximation , $\log x! = x \log x - x$

$$\log W = (N\log N - N) - \{(n_1\log n_1 - n_1 + n_2\log n_2 - n_2 + \ldots + n_i\log n_i - n_i)\} + (n_1\log g_1 + n_2\log g_2 + \ldots + n_i\log g_i)$$

Differentiating on both sides w.r.t n and N and g are constants

$$0 = -\{n_1\, dn_1/n_1 + \log n_1\, dn_1 + \ldots.. + n_i\ dn_i/n_i + \log n_i\, dni\} + \{\log g_1 dn_1 + \ldots. + \log g_i\, dn_i\}$$

$$0 = dni\,(1+\log n_1 - \log g_1) + dn_2\,(1+\log n_2 - \log g_2) + \ldots. + dn_i\,(1 + \log n_i - \log g_i) \quad \ldots\ldots\ldots..(4)$$

We know that

$$n_1+n_2+\ldots.+n_i = N \quad \ldots\ldots\ldots\ldots\ldots.(5)$$

$$dn_1+dn_2+\ldots.+dn_i = 0 \quad \ldots\ldots\ldots\ldots.(6)$$

and also $n_1 E_1+n_2E_2+\ldots..+n_iE_i = E \quad \ldots\ldots\ldots..(7)$

$$E_1dn_1+E_2dn_2+ \ldots..+E_idn_i = 0 \quad \ldots\ldots\ldots..(8)$$

To solve equation (4) multiply equation (6) by α and equation(8) by β and add to (4) where α and β are constants known as Lagrangean multipliers.

Bose Einstein Distribution:The Bose Einstein Distribution deals with the distribution of identical indistinguishable particles like photons or phonons called Bonons. They do not obey Pauli's Principle.

The assumptions of Bose Einstein statistics are :
1.Particles are identical and indistinguishable.
2.There is no limit to the number of particles per state.
3.They have integral multiples of $h/2\pi$.
4.Energy states are discrete.

Consider a system consisting of N identical indistinguishable particles. Let n_1 number of particles have each of energy E_1 which has g_1 states and n_2 number of particles have each of energy E_2 which has g_2 states and so on. The g_i states will have $(g_i - 1)$ partitions.

Fermi-Dirac Distribution:The Fermi-Dirac Distribution deals with the indistinguishable particles like electrons called Fermions. They obey Pauli's Principle (no two electrons in an atom have the same quantum state).

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Black Body Radiation : A body that completely absorbs all wavelengths of radiation incident on it at low temperatures or emits different wavelengths of radiation at higher temperatures is known as a black body.

A graph has been plotted between intensity versus wavelength of radiation from a black body.The temperature of the body is raised to different values and distribution curves are plotted for different temperatures.

From graph,

1. The intensity of radiation increases for each wavelength as the temperature of the body increases.
2. At any given temperature , the intensity of radiation from the body is maximum for a particular wavelength represented as λ_{1m}, λ_{2m}, λ_{3m},……. This wavelength shifts towards shorter wavelength region with increase of temperature.
3. The area under the curve is proportional to the total radiation energy emitted by the body in unit time.

(a) Wien's Law:Wien showed that the maximum energy ,E_m of the emitted radiation from black body is proportional to fifth power of absolute temperature (T^5).

$$\text{i.e,} \quad E_m \alpha T^5 \qquad \text{or} \qquad E_m = \text{constant} \times T^5$$

Wien deduced the relation between the wavelength of emission and the temperature of the body as

$$U_\lambda \, d\lambda = (c_1 / \lambda^5) \, e^{-(c2/\lambda T)} \, d\lambda$$

$$= (8 \pi c h / \lambda^5) \{ 1 / [e^{(hc/\lambda K_B T)} - 1] \} d\lambda$$

Where $U_\lambda d\lambda$ is the energy per unit volume in the wavelength range λ and $\lambda+d\lambda$.Here c_1 and c_2 are constants.Wien's law is valid at lower wavelength region,whereas it deviates from experimental values at higher wavelength regions.

(b) Rayleigh-Jeans Law: Rayleigh deduced an equation for the black body radiation based on the principle of equipartition of energy,each mode of vibration has assigned an average energy of K_BT.The number of vibrations per unit volume in the wavelength range λ and $\lambda+d\lambda$ is given by $8 \pi \lambda^{-4} d\lambda$.

The vibration energy per unit volume in the range of λ and $\lambda+d\lambda$ is

$$U_\lambda \, d\lambda = 8 \pi K_B T \lambda^{-4} d\lambda$$

This is Rayleigh-Jeans equation.This law correctly predicts the fall of intensity in the longer wavelength side.However,it fails to explain the lower wavelength side of the spectrum.

(c) Planck's Law: Planck assumed that the walls of the black body consists of a large number of electrical oscillators,vibrating with their own natural frequencies.An

oscillator possesses an energy equal to $h\upsilon$ where h is Planck's constant and υ is the frequency of the oscillator.

An oscillator may lose or gain energy by emitting or by absorbing photons respectively.Planck derived an equation for the energy per unit volume of black body in the entire spectrum of black body radiation and is given by

$$U_\lambda \, d\lambda = 8\pi h c / \lambda^5 \{ [1 / e^{(h\upsilon / K_B T)}] - 1 \} d\lambda$$

Concept of Electron gas and Fermi Energy:

(a) Electron gas: A metal consists of immobile positive ions and free electrons.These free electrons are very large in metals.They move in random directions inside a metal like the gas molecules in a container.They are referred as free electron gas or electron gas.

When an electric field is applied on metals,the free electrons drift in a direction opposite to the applied field.They obey gas laws.

(b)Fermi Energy: The electron gas obey Fermi-Dirac distribution.Let g(E) be the density of electron states i.e,the number of available electron states per unit volume of metal in unit range of energies E.

Let the number of electron filled states be N(E) in g(E).

Then the Fermi-Dirac distribution function F(E) is

$$F(E) = N(E) / g(E) = 1 / [1 + \exp (E - E_F / K_B T)]$$

The distribution function F(E) is defined as the probability that an energy level E is occupied by an electron.

Suppose,if the level is empty then F(E) = 0 or if the level is filled ,then F(E) = 1.

In general the value of F(E) lies in between 0 and 1.

At 0K, F(E) = 1 for $E < E_F$

] ……..(2)

= 0 for $E > E_F$

This shows that all states below E_F are completely filled and all states above E_F are completely empty.As temperature increases , then F(E) decreases below E_F .At higher temperatures the curve passes through a point at which the probability of the electron being in the conduction or valence band is 0.5.The energy at which the probability of occupation is 0.5 at all temperatures is called Fermi energy.Alternatively,the highest energy possessed by an electron at absolute zero of temperature (0K) in a metal is called Fermi energy.



Density of States: To calculate the carrier concentration ie, the number of electrons per unit volume in a given energy range :
Let us consider the product of the density of states Z(E) and occupancy probability F(E)

$$\text{i.e,} \quad n_c = \int Z(E)\, F(E)\, dE \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

The number of energy states with a particular value of E depends on how many combinations of quantum numbers result in the same value of n (degeneracy).

To calculate the number of energy states with all possible energies,with n as radius (where $n^2 = n_1^{\,2} + n_2^{\,2} + n_3^{\,2}$) a sphere is constructed in 3-dimensional space and every point (n_1, n_2 , n_3) within this space represents an energy state.

And also as every integer represents one energy state,unit volume of this space contains exactly one state.Hence the number of states in any volume is equal to the volume expressed in units of cubes of lattice parameters.

$\therefore$ The number of energy states within a sphere of radius n = $(4 / 3) \pi n^3$

Since n_1, n_2 , n_3 can have only positive integer values,we have to consider only one octant of the sphere.

Hence available energy states = $(1 / 8) (4 \pi n^3 / 3)$

In order to calculate the number of states within a small energy interval E and E+dE ,we have to construct two spheres with radii n and (n+dn) and calculate the space occupied within these two spheres.

Thus the number of energy states having energy values between E and E+dE is given by

$$Z(E)\, dE = (1 / 8) (4 \pi / 3) (n+dn)^3 - (1 / 8) (4 \pi n^3 / 3)$$

$$= (\pi n^2 / 2)\, dn \qquad \ldots\ldots\ldots\ldots\ldots\ldots(2)$$

(neglecting higher powers of dn as it is very small)

The expression for the energy of electron is given by

$$E = n^2 h^2 / 8 m L^2$$

$$n^2 = 8 m L^2 E / h^2$$

$$n = [8 m L^2 E / h^2]^{1/2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

Differentiating n^2 ,we get

$$2n\, dn = 8 m L^2 dE / h^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

$$dn = 8 m L^2 dE / 2n h^2$$

$$= (8 m L^2 / h^2) (1 / 2) (h^2 / 8 m L^2)^{½} (dE / E^{1/2})$$

$$= (1 / 2) (8 m L^2 / h^2)^{1/2} (dE / E^{1/2})$$

……(5)

Substituting the values of n^2 and dn in eq (2) , we get

$$Z(E)\, dE = (\pi / 2) (8 m L^2 E / h^2) (1 / 2) [8 m L^2 / h^2]^{1/2} (dE / E^{1/2})$$

$$= (\pi / 4) (8 m L^2 / h^2)^{3/2} E^{1/2} dE$$

According to Pauli's exclusion principle two electrons of opposite spin can occupy each state and hence the number of energy states available for electron occupancy is given by

$$Z(E)\, dE = 2 \times (\pi / 4) (8 m L^2 / h^2)^{3/2} E^{1/2} dE$$

$$= (4 \pi / h^3) (2 m)^{3/2} L^3 E^{1/2} dE \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(6)$$

Density of energy states is given by number of energy states per unit volume

i.e, density of states = $Z(E)\, dE = (4 \pi / h^3) (2 m)^{3/2} E^{1/2} dE$ ……..(7)

Free electron density in metals:
Substituting the values F(E) and Z(E) in eq(1) for calculation of electron density,

$$n_c = \int Z(E) F(E)\, dE$$

$$= (4 \pi / h^3) (2 m)^{3/2} \int E^{1/2} \{1 / [1 + \exp (E - E_F / K_B T)] \} dE \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(8)$$

This is the expression for free carriers ie, electron density at any temperature.This can be used to calculate the free electron density in metals and carrier concentration in semiconductors.