SYSTEM OF HARMONIC OSCILATOR UNDER C.E

- **Let's** consider a practically independent system of N harmonic oscillators.

  One of the best example of canonical ensemble formulation,

  The topic serves as the basis of , **(a)** Theory of black body radiation

  (b) Theory of lattice vibrations

  Resp. called as S.M of photons and S.M of phonons.

- **If** the harmonic oscillator is treated classically then it's total energy is expressed as,

$$H(q_i\, p_i) = \frac{1}{2} m\omega^2 q_i^{\,2} + \frac{p_i^{\,2}}{2m} \quad \ldots\ldots\ldots\{i = 1,2,\ldots\ldots\ldots,N\} \qquad (1)$$

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Let, $Q_1(\beta)$ be the Partition function of single oscillator then,

$$Q_1(\beta) = \int_{-\alpha}^{\alpha}\int_{-\alpha}^{\alpha}\{\ e^{-\beta[H(q_i\,p_i\,)]}\ \}\ \frac{dp\,dq}{h} \qquad \text{..............} \ (2)$$

$$\therefore \quad Q_1(\beta) = \int_{-\alpha}^{\alpha}\int_{-\alpha}^{\alpha}\{\ e^{-\beta[\frac{1}{2}m\omega^2 q^{\,2}\ +\ \frac{p^2}{2m}]}\ \}\ \frac{dp\,dq}{h}$$

Using formula, $\int_{-\alpha}^{\alpha} e^{-a x^{\,2}} dx = (\pi/a)^{1/2}$

$$\therefore \quad Q_1(\beta) = \frac{1}{h}\left(\frac{2\pi}{\beta m\omega^2}\right)^{1/2}\left(\frac{2\pi m}{\beta}\right)^{1/2} = \frac{2\pi}{h\beta\omega} = \frac{1}{\beta\hbar\omega} = \frac{\mathbf{KT}}{\boldsymbol{\hbar\omega}} \qquad \text{................}(3)$$

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The partition function of the N – Oscillators can be extended as,

$$\therefore \quad Q_N(\beta) = [Q_1(\beta)]^N = \left(\frac{1}{\beta\hbar\omega}\right)^N = \left(\frac{\mathbf{KT}}{\boldsymbol{\hbar\omega}}\right)^{\mathbf{N}} \qquad \text{…………………(4)}$$

It is assumed that the Oscillators are "Distinguishable" .

- **Helmholtz free energy** of the system is expressible as,

$$\therefore \qquad A = -KT\log[Q_N(\beta)] = -KT\log\left(\frac{KT}{\hbar\omega}\right)^N$$

$$\therefore \qquad \boxed{\mathbf{A = NKTlog}\left(\frac{\boldsymbol{\hbar\omega}}{\mathbf{KT}}\right)} \qquad \text{………………. (5)}$$

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- **Chemical energy ,**

$$\mu = \left(\frac{dA}{dN}\right)_{V,T}$$

Using eq.5,

$$\therefore \quad \mu = \frac{d}{dN}\left[NKT\log\left(\frac{\hbar\omega}{KT}\right)\right]$$

$$\therefore \quad \boldsymbol{\mu = KT\log\left(\frac{\hbar\omega}{KT}\right)} \qquad \text{..................} \ (6)$$

- **Pressure,** $P = -\left(\frac{dA}{dV}\right)_{N,T} = \frac{d}{dV}\left[NKT\log\left(\frac{\hbar\omega}{KT}\right)\right] = 0 \qquad \text{..................} \ (7)$

SYSTEM OF HARMONIC OSCILATOR UNDER C.E

- **Entropy,**

$$S = -\left(\frac{dA}{dT}\right)_{N,V}$$

Using eq.5,

$$\therefore \quad S = -\frac{d}{dT}\left[-\text{NKTlog}\left(\frac{\text{KT}}{\hbar\omega}\right)\right] = \text{NKlog}\left(\frac{\text{KT}}{\hbar\omega}\right) + \text{NKT}.\frac{\hbar\omega}{\text{KT}}\cdot\frac{\text{K}}{\hbar\omega}$$

$$\therefore \quad \boxed{\mathbf{S = NK\left[\log\left(\frac{KT}{\hbar\omega}\right) + 1\right]}} \qquad \text{………………. (8)}$$

SYSTEM OF HARMONIC OSCILATOR UNDER C.E

- **Internal energy,**

$$U = A + TS$$

$$\therefore \quad U = -NKT\log\left(\frac{KT}{\hbar\omega}\right) + TNK\left[\log\left(\frac{KT}{\hbar\omega}\right) + 1\right]$$

$$\therefore \quad \boxed{\mathbf{U = NKT}} \quad \text{.................. (9)}$$

- **Heat capacity,**

$$C_p = C_v = \frac{\partial U}{\partial T}$$

Using eq. 9

$$\therefore \quad \boxed{\boldsymbol{C_p = C_v = NK}} \quad \text{..........(10)}$$

The Statistics of Paramagnetism

- **A** system of N magnetic dipoles , each having a magnetic moment μ . In the presence of an external magnetic field H , the dipoles will experience a torque tending to align them in the direction of the field.
- **T**hermal agitation in the system offers resistance to the tendency of alignment i.e. because of thermal agitation it is difficult to get complete magnetization (saturation magnetization).
- **A**s $T \rightarrow 0K$, thermal agitation becomes ineffective and the system exhibits a complete orientation of the dipole moments. While at $T \rightarrow \infty$, we approach a state of randomization which implies a vanishing magnetization.
- **A**t intermediate temperature the process of paramagnetism is governed by parameter $\left(\frac{\mu H}{KT}\right)$.

The Statistics of Paramagnetism

- **The** total energy of all the dipoles is expressible as,

$$E = \sum_{i=1}^{N} \overline{\mu_i} \,.\, \overline{H} = -\mu H \sum_{i=1}^{N} Cos\theta_i \qquad ....(1)$$

The P.F = $Q_N(\beta) = [Q_1(\beta)]^N$ ....(2)

where, $Q_1(\beta) = \sum_{\theta_i} e^{-\beta(-\mu H Cos\theta)}$

- **The** "mean magnetic moment" M of the system will be the direction of field H for its magnitude we shall have,

$$M_Z = N < \mu\, Cos\theta > = \frac{N \sum_{\theta} \mu Cos\theta e^{\beta \mu H Cos\theta}}{\sum_{\theta} e^{\beta \mu H Cos\theta}} \qquad ....(3)$$

The Statistics of Paramagnetism

- The **H.F.E.** is,

$$A = -NKT \log[Q_1(\beta)] \qquad \textbf{where, } Q_1(\beta) = \sum_\theta e^{\beta\mu H Cos\theta}$$

$$\therefore -\left(\frac{\partial A}{\partial H}\right)_T = -\frac{\partial}{\partial H}\{-NKT \log[Q_1(\beta)]\} = \frac{\partial}{\partial H}\{NKT \log[\sum_\theta e^{\beta\mu H Cos\theta}]\}$$

$$\therefore \quad = \frac{NKT \sum_\theta \beta\mu Cos\theta e^{\beta\mu H Cos\theta}}{\sum_\theta e^{\beta\mu H Cos\theta}} = NKT\beta \left[\frac{\sum_\theta \mu Cos\theta e^{\beta\mu H Cos\theta}}{\sum_\theta e^{\beta\mu H Cos\theta}}\right]$$

$$\therefore \quad = N < \mu Cos\theta > \; = \; M_Z$$

$$\therefore \quad \boldsymbol{M_Z = -\left(\frac{\partial A}{\partial H}\right)_T} \qquad \textbf{...............(4)}$$

The Statistics of Paramagnetism

- **The** single dipole partition function is expressible as,

$$Q_1(\beta) = \int_0^{2\pi}\int_0^{\pi} e^{\beta H\mu Cos\theta}\, Sin\theta d\theta d\varphi \qquad \text{..............} (5)$$

where, $\int\int Sin\theta d\theta d\varphi$ = Solid angle

let, $x = \beta H\mu Cos\theta$

$dx = -\beta H\mu\, Sin\theta d\theta$

$\sin\theta d\theta = \frac{dx}{\beta H\mu}$

$$\therefore \qquad Q_1(\beta) = \int_0^{2\pi}\left[\int_0^{\pi} \frac{e^{x}(-dx)}{\beta H\mu}\right] d\varphi = -\frac{2\pi}{\beta H\mu}\left[e^{\beta H\mu Cos\theta}\right]_0^{\pi}$$

$$\therefore \qquad = \frac{4\pi}{\beta H\mu}\left[\frac{e^{\beta H\mu} - e^{\beta H\mu}}{2}\right] = \frac{4\pi}{\beta H\mu}\left[Sinh\beta H\mu\right] \qquad \text{..............}(6)$$

The Statistics of Paramagnetism

- Using eq.(4)

$$M_z = N < \mu Cos\Theta > = N\mu_z$$

$$\therefore \quad \mu_z = \frac{M_z}{N} = -\frac{1}{N}\left(\frac{\partial A}{\partial H}\right) = -\frac{1}{N}\frac{\partial}{\partial H}\{-NKT \log[Q_1(\beta)]\}$$

$$\therefore = KT \frac{\partial}{\partial H}\left\{\log\left[\frac{4\pi\, Sinh\beta H\mu}{\beta H\mu}\right]\right\} = KT\frac{\partial}{\partial H}[\log 4\pi + \log(Sinh\beta H\mu) - \log(\beta H\mu)]$$

$$\therefore = KT\left[0 + \frac{\cosh\beta H\mu}{\sinh\beta H\mu}.\beta\mu - \frac{1}{\beta H\mu}.\beta\mu\right] = \beta\mu KT\left[\coth\beta H\mu - \frac{1}{\beta H\mu}\right] = \mu\, L(\beta H\mu) \quad \text{..........(7)}$$

where, $L(x)$ = **Langevin function**

$$L(x) = \left[\coth x - \frac{1}{x}\right] \quad , \; x = \beta H\mu \qquad \text{................(8)}$$

The Statistics of Paramagnetism

Case 1: for strong magnetic field at very low temperature $x >> 1$,hence $L(x) \rightarrow 1$ the system then acquires a state of magnetic saturation.

$$\overline{\mu_z} \text{ tending to } \mu \; (\overline{\mu_z} \rightarrow \mu) \qquad \text{.................(9)}$$

Almost all the dipoles are align in the direction of external magnetic field i.e. the state of saturation magnetization.

Case2: If field is week & temperature is high i.e. $x \ll 1$ then the $L(x)$ is expressible in terms of series,

$$L(x) = \frac{x}{3} - \frac{x^3}{45} + \ldots\ldots\ldots\ldots. \qquad \text{.................(10)}$$

for small value of x,

$$L(x) \approx \frac{x}{3}$$

The Statistics of Paramagnetism

$\therefore \quad L(x) = \frac{H\mu}{3KT}$ where, $x = \beta H\mu$ ……………(11)

from eq. (7) , $\mu_z = \mu L(x)$

$\therefore \quad \mu_z = \frac{H\mu^2}{3KT}$ ……………….(12)

$\therefore$ for lowest approximation,

$M_z = N_0\mu_z = \frac{N_0 H\mu^2}{3KT}$ ……………….(13)

where, N_0 = number of dipoles per unit volume

The high temperature isothermal susceptibility is expressed as,

$$\chi_T = \lim_{H \to 0}\left(\frac{\partial M_z}{\partial H}\right) = \frac{N_0\mu^2}{3KT} = \frac{C}{T}$$ ………………..(14)

eq.13 is curie law of paramagnetism , and C is curie constant.

Quantum mechanical treatment of Paramagnetism

- The magnetic dipole moment μ and its component μ_z in the direction of field is Quantized they can not have arbitrary values.

The $\vec{\mu}$ & $\vec{l}$ are related as,

$$\vec{\mu} = \left(g \frac{e}{2mc}\right)\vec{l} \qquad \ldots\ldots\ldots\ldots(1)$$

$$l^2 = J(J+1)\hbar^2 \qquad J = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots\ldots\ldots \text{or } 0,1,2\ldots.. \qquad \ldots\ldots\ldots\ldots(2)$$

$g\frac{e}{2mc}$ is called gyromagnetic ratio and ‘g’ is called lande’s ‘g’ factor.

❖ If the net angular momentum of the dipole is due solely to electron spin ,then g=2.

❖ If it is solely due to orbital motion ,then g=1.

Quantum mechanical treatment of Paramagnetism

In general,

$$g = \frac{3}{2} + \frac{s(s+1)-L(L+1)}{2J(J+1)} \quad \text{...............(3)}$$

From eq.1 & eq.2 we have,

$$\mu^2 = \left(g\,\frac{e}{2mc}\right)^2 l^2$$

$$\therefore \quad \mu^2 = \left(g\,\frac{e}{2mc}\right)^2 J^2(J+1)\hbar^2$$

$$\therefore \quad \mu^2 = g^2\mu_\beta^2(J+1)J \quad \text{...............(4)}$$

$\mu_\beta = \frac{e\hbar}{2mc}$, is the " Bohr magneton" .

$$\mu_Z = g\mu_\beta m \; ; \; m = -J \,..........\, +J \quad \text{...............(5)}$$

$\therefore$ μ_Z is quantized.

Quantum mechanical treatment of Paramagnetism

Now , $Q_1(\beta)$ can expressed as

$$Q_1(\beta) = \sum_{m=-J}^{J} e^{(\beta g \mu_\beta m H)} \qquad \text{....................(6)}$$

let, $\beta g J \mu_\beta H = x$ ....(7)

Using eq.6 & 7

$$Q_1(\beta) = \sum_{m=-J}^{J} e^{\frac{mx}{J}} = \frac{e^{-x}\left\{e^{\frac{(2J+1)x}{J}} - 1\right\}}{e^{\frac{x}{J}} - 1}$$

$$\therefore \quad Q_1(\beta) = \frac{\left\{e^{\frac{(2J+1)x}{2J}} - e^{\frac{-(2J+1)x}{2J}}\right\}}{e^{\frac{x}{2J}} - e^{\frac{-x}{2J}}} = \frac{\sinh\left\{\left(1+\frac{1}{2J}\right)x\right\}}{\sinh\left\{\left(\frac{1}{2J}\right)x\right\}} \qquad \text{...............(8)}$$

Quantum mechanical treatment of Paramagnetism

$$\therefore \frac{\partial}{\partial H}\{\log[Q_1(\beta)]\} = \frac{\partial}{\partial H}\left[log\left(\frac{\sinh\left\{\left(1+\frac{1}{2J}\right)x\right\}}{\sinh\left\{\left(\frac{1}{2J}\right)x\right\}}\right)\right]$$

$\therefore$ substitute $x = \beta g J \mu_\beta H$,from eq.7

$$\therefore \frac{\partial}{\partial H}\{\log[Q_1(\beta)]\} = \frac{\partial}{\partial H}\left[log\left(\frac{\sinh\left\{\left(1+\frac{1}{2J}\right)\beta g J \mu_\beta H\right\}}{\sinh\left\{\left(\frac{1}{2J}\right)\beta g J \mu_\beta H\right\}}\right)\right]$$

$$\therefore \quad = \coth\left[\left(1+\frac{1}{2J}\right)\beta g J \mu_\beta H\right].\left(1+\frac{1}{2J}\right).\ \beta g J \mu_\beta - \coth\left[\left(\frac{1}{2J}\right)\beta g J \mu_\beta H\right].\left(\frac{1}{2J}\right).\ \beta g J \mu_\beta$$

$$\therefore \quad = \coth\left[\left(1+\frac{1}{2J}\right)x\right].\left(1+\frac{1}{2J}\right).\ \beta g J \mu_\beta - \coth\left[\left(\frac{1}{2J}\right)x\right].\left(\frac{1}{2J}\right).\ \beta g J \mu_\beta \quad \text{.............(9)}$$

Quantum mechanical treatment of Paramagnetism

$\therefore$ The magnetization, $M_Z = N\overline{\mu_Z} = \frac{N}{\beta}\frac{\partial}{\partial H}\{\log[Q_1(\beta)]\}$

$$\therefore M_Z = N(gJ\mu_\beta)\left\{\left(1+\frac{1}{2J}\right)\coth\left[\left(1+\frac{1}{2J}\right)x\right] - \left(\frac{1}{2J}\right)\coth\left[\left(\frac{1}{2J}\right)x\right]\right\}$$

$\therefore \overline{\mu_Z} = (gJ\mu_\beta)\, B_J(x)$ ……………(10)

where, $B_J(x) = \left\{\left(1+\frac{1}{2J}\right)\coth\left[\left(1+\frac{1}{2J}\right)x\right] - \left(\frac{1}{2J}\right)\coth\left[\left(\frac{1}{2J}\right)x\right]\right\}$…………(11)

$B_J(x)$ is "Brillouin function" of the order J.

Case 1.

For $x>>1$ i.e. for low temperature & High field.

$B_J \rightarrow 1$ i.e. saturation magnetization ………….(12)

Quantum mechanical treatment of Paramagnetism

Case 2.

For x<<1 i.e. for high temperature & Low field .

i.e. expression reduce to ,

$$B_J = \frac{1}{3}\left(1 + \frac{1}{J}\right)x + \cdots \qquad \text{................(13)}$$

So, $\mu_Z = (gJ\mu_\beta)\,\frac{1}{3}\left(1 + \frac{1}{J}\right)\beta gJ\mu_\beta H = \left(\frac{gJ\mu_\beta}{3KT}\right)^2\left(\frac{J+1}{J}\right)H = \frac{g^2{\mu_\beta}^2 J(J+1)}{3KT}H$

..............(14)

Curie constant ,

$$C_J = \frac{N_0 g^2{\mu_\beta}^2 J(J+1)}{3K} = \frac{N_0\mu^2}{3K} \qquad \text{................(15)}$$