Qu. Debye model to determine sp. heat of solid at high and low temperature.

Ans. Debye improve the theory of sp. heat of solid and remove the shortcoming of the Einstein model proposing that the solid is assembly of large number of atoms situated at lattice point . Debye assume that system vibrates as a whole and free vibration of the system are elastic solid vibration associated with elastic wave propagated through continuum medium. Which is characteristics of the substance.

In quantum theory the normal mode of vibration of the atoms in the form of elastic waves associated with sound waves called ‘phonon’. The quantum state of a crystal lattice near its ground state can therefore be specified by the number of phonon present. At very low temperatures a solid can be considered as a volume full of non-interacting phonon gas. If the wave length of the elastic wave travelling in the solid is large compared to the interatomic distances then, the solid can be considered as a continuum and has continuous distribution of normal frequencies. According to Debye

$$\int_0^{\upsilon_D} g(\upsilon)\, d\upsilon = 3N, \qquad \upsilon > \upsilon_D, \quad \text{and}$$
$$= 0, \qquad 0 < \upsilon_D \tag{1}$$

Let us now calculate the total number of phonons of each type lying in a volume **V**. The total number of states in the momentum range p and p + dp , lying in a volume v is given as

$$g(p)\, dp = \frac{4\pi V\, p^2 dp}{h^3} \tag{2}$$

where h is the Planck’s constant. From de-Broglie relations

$$p = \frac{h}{\lambda}$$

$$p = \frac{h\upsilon}{\lambda\upsilon}$$

$$p = \frac{h\upsilon}{C}$$

Hence Eq.(2) reduces to

$$g(\upsilon)d\upsilon = \frac{4\pi V \left(\frac{h\upsilon}{C}\right)^2 d\left(\frac{h\upsilon}{C}\right)}{h^3} \tag{3}$$

$$g(\upsilon)d\upsilon = \frac{4\pi V\, \upsilon^2 d\upsilon}{C^3} \tag{4}$$

The total modes of vibration in the frequency range υ and $\upsilon + d\upsilon$ have the component one longitudinal and two transverse wave, hence Eq. (4) written as

$$g(\upsilon)d\upsilon = 4\pi V \left(\frac{1}{C_l^3} + \frac{1}{C_t^3}\right) \upsilon^2 \, d\upsilon \tag{5}$$

The Eq. (5) integrated for Debye frequency as

$$\int_0^{\upsilon_D} g(\upsilon)d\upsilon = 4\pi V \left(\frac{1}{C_l^3} + \frac{1}{C_t^3}\right) \int_0^{\upsilon_D} \upsilon^2 d\upsilon$$

$$= 4\pi V \left(\frac{1}{C_l^3} + \frac{1}{C_t^3}\right) \frac{\upsilon_D^3}{3} \tag{6}$$

According to Debye approach this is equal to 3N, then Eq.(6) reduces to

$$= 4\pi V \left(\frac{1}{C_l^3} + \frac{1}{C_t^3}\right) \frac{\upsilon_D^3}{3} = 3N$$

$$\text{or} \quad \left(\frac{1}{C_l^3} + \frac{1}{C_t^3}\right) = \frac{9N}{4\pi V \, \upsilon_D^3} \tag{7}$$

Putting this value in Eq. (6), we get

$$\int_0^{\upsilon_D} g(\upsilon)d\upsilon = 4\pi V \left(\frac{9N}{4\pi V \upsilon_D^3}\right) \int_0^{\upsilon_D} \upsilon^2 d\upsilon$$

or

$$\int_0^{\upsilon_D} g(\upsilon)d\upsilon = \left(\frac{9N}{\upsilon_D^3}\right) \int_0^{\upsilon_D} \upsilon^2 d\upsilon \tag{8}$$

According to Debye model the average energy of the whole oscillator is given as

$$\overline{\varepsilon} = \int_0^{\upsilon_D} g(\upsilon)d\upsilon . \, \overline{\varepsilon}_V$$

$\overline{\varepsilon}_V$ = mean energy of the oscillator calculated by Einstein.

Hence

$$\overline{\varepsilon} = \int_0^{\upsilon_D} g(\upsilon)d\upsilon . \, h\upsilon\left(\frac{1}{2} + \frac{1}{e^{\frac{h\upsilon}{kT}} - 1}\right)$$

$$= \frac{9N}{\upsilon_D^3} . \int_0^{\upsilon_D} \upsilon^2 d\upsilon \, . \, h\upsilon\left(\frac{1}{2} + \frac{1}{e^{\frac{h\upsilon}{kT}} - 1}\right)$$

$$= \frac{9Nh}{\upsilon_D^3} . \int_0^{\upsilon_D} \upsilon^3 d\upsilon \, . \left(\frac{1}{2} + \frac{1}{e^{\frac{h\upsilon}{kT}} - 1} \right)$$

$$= \frac{9Nh}{2\upsilon_D^3} . \int_0^{\upsilon_D} \upsilon^3 d\upsilon + \frac{9Nh}{\upsilon_D^3} . \int_0^{\upsilon_D} \upsilon^3 d\upsilon \left(\frac{1}{e^{\frac{h\upsilon}{kT}} - 1} \right)$$

$$= \frac{9Nh\upsilon_D^4}{8\upsilon_D^3} + \frac{9Nh}{\upsilon_D^3} . \int_0^{\upsilon_D} \frac{\upsilon^3 d\upsilon}{e^{\frac{h\upsilon}{kT}} - 1}$$

$$\bar{\varepsilon} = \frac{9Nh\upsilon_D}{8} + \frac{9Nh}{\upsilon_D^3} . \int_0^{\upsilon_D} \frac{\upsilon^3 d\upsilon}{e^{\frac{h\upsilon}{kT}} - 1} \qquad (10)$$

The 1st term of the Eq.(1) is free from temperature which is zero point energy of the oscillator. The 2nd term as integral part evaluated as

$$= \frac{9Nh}{\upsilon_D^3} . \int_0^{\upsilon_D} \frac{\upsilon^3 d\upsilon}{e^{\frac{h\upsilon}{kT}} - 1} \qquad (11)$$

The Eq.(11) adjusted for evaluation as

$$= \frac{9Nh}{\upsilon_D^3} . \int_0^{\frac{h\upsilon_D}{kT}} \frac{\left(\frac{h\upsilon}{kT}\right)^3 \frac{k^3T^3}{h^2} d\left(\frac{h\upsilon}{kT}\right) . \left(\frac{KT}{h}\right)}{\left(e^{\frac{h\upsilon}{kT}} - 1\right)} \qquad (12)$$

Let, $x = \frac{h\upsilon}{kT}$ and $u = \frac{h\upsilon_D}{kT}$, we get

$$= \frac{9Nh\, k^4T^4}{\upsilon_D^3 h^3} . \int_0^u \frac{(x)^3 dx}{(e^x - 1)}$$

$$= \frac{3NkT. \quad 3\, k^3T^3}{\upsilon_D^3 h^3} . \int_0^u \frac{(x)^3 dx}{(e^x - 1)}$$

$$= 3NkT . \frac{3}{u^3} . \int_0^u \frac{(x)^3 dx}{(e^x - 1)}$$

Therefore

$$\bar{\varepsilon} = \frac{9Nh\upsilon_D}{8} + 3NkT \; D(u) \qquad (13)$$

Where

$$D(u) = \frac{3}{u^3} \int_0^u \frac{(x)^3 dx}{(e^x - 1)} \quad (14)$$

In Eq.(13) 1st term is the zero point energy and 2nd term is the Debye function which is evaluated at high and low temperature.

At high temperature:

In Eq.(14), the value

$x = \frac{h\upsilon}{kT}$ and $u = \frac{h\upsilon_D}{kT} = \frac{\theta_D}{T}$, θ_D is known as Debye temperature.

If $T >> \theta_D$, then exponential term expand as

$$e^x - 1 = 1 + x + \frac{x^2}{2!} +, ..., -1$$

The value 1 is cancelled and taking only 1st order term, we get

$e^x - 1 = x$, hence Eq.(10) written as

$$D(u) = \frac{3}{u^3} \int_0^u \frac{(x)^3 dx}{(e^x - 1)}$$

$$D(u) = \frac{3}{u^3} \int_0^u \frac{(x)^3 dx}{x} = \frac{3}{u^3} \int_0^u x^2 dx = \frac{3}{u^3} . \frac{u^3}{3} = 1 \quad (15)$$

Putting this value in Eq.(13), we get

$$\bar{\varepsilon} = \frac{9Nh\upsilon_D}{8} + 3NkT \quad (16)$$

The sp. heat

$$C_V = (\frac{d\bar{\varepsilon}}{dT})_V$$

Or

$$C_V \simeq 3Nk = 3R_0 \quad (17)$$

The sp. heat calculated by Debye at high temperature is agree with experimental results.

At low temperature:

At low temperature

T << θ_D

i.e

x >> 1, In first approximation the upper limit of the integration replaced by ∞ , the Debye integration is written as

$$D(u) = \frac{3}{u^3} \int_0^\infty \frac{(x)^3 dx}{(e^x - 1)}$$

$$= \frac{\pi^4}{5} (\frac{T}{\theta_D})^3$$

Hence,

$$\bar{\varepsilon} = \frac{9Nh\upsilon_D}{8} + 3NkT \cdot \frac{\pi^4}{5} (\frac{T}{\theta_D})^3 \qquad (18)$$

Now,

$$C_V = (\frac{d\bar{\varepsilon}}{dT})_V$$

$$C_V = 12Nk \frac{\pi^4}{5} (\frac{T}{\theta_D})^3$$

$$C_V \propto T^3$$

This is known as Debye T^3 law, in the limit $T \to 0,\ C_V \to 0.$ The theoretical value agree with experimental value at low temperature also. Hence Debye theory appreciable for determining sp. heat of solid.

Discussion with graph

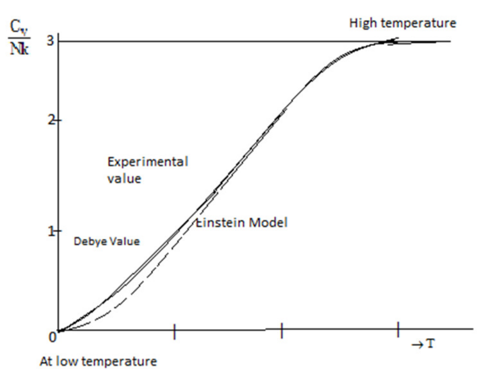

Fig.(1) Comparison of Debye calculated Sp. heat with experimental results and Einstein.

The calculated value of sp. heat by Debye at high temperature and low temperature is shown in Fig.(1) with experimental results. Which is agree with high temperature and low temperature also decrease with temperature.

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