

# *Einstein's Theory of specific heat of solids*

In 1931, Einstein put forward his theory to explain the specific heat of solids. This theory is based upon the following assumptions.

- 1) Atoms in the crystal may be treated as the identical harmonic oscillators.
- 2) There are  $3N$  one dimensional oscillators in the crystal corresponding to  $N$  atoms.
- 3) The oscillators have discrete values of energy in accordance with quantum mechanical approach.
- 4) All the  $3N$  oscillators have the same natural frequency  $\nu$  of vibrations because each of them has identical surroundings.
- 5) Any no. Of atoms may occupy a given energy state.
- 6) The energy distribution of the system is given by Maxwell Boltzmann law.

## *Expression:-*

Making use of Maxwell-Boltzmann distribution of energies, the average energy of one dimensional oscillator is given by

$$\langle E \rangle = \frac{\sum_{n=0}^{\infty} E_n e^{-E_n/k_B T}}{\sum_{n=0}^{\infty} e^{-E_n/k_B T}}$$

where  $E_n$  is the energy of  $n$ th state,  $k_B$  is Boltzmann constant and  $T$  is absolute temperature. For a quantum mechanical oscillator, the energy of  $n$ th state is given by

of vibrations.

$$E_n = \left(n + \frac{1}{2}\right) h\nu, \quad \text{where } h \text{ is planck's constant and } \nu \text{ is frequency}$$

$$\therefore \langle E \rangle = \frac{\sum_{n=0}^{\infty} \left(n + \frac{1}{2}\right) h\nu e^{-\left(n + \frac{1}{2}\right) h\nu/k_B T}}{\sum_{n=0}^{\infty} e^{-\left(n + \frac{1}{2}\right) h\nu/k_B T}} \quad \dots(1)$$

Put  $-\frac{h\nu}{k_B T} = x$  ... (2)

Therefore, equation (2) becomes

$$\langle E \rangle = \frac{\sum_{n=0}^{\infty} \left(n + \frac{1}{2}\right) h\nu e^{\left(n + \frac{1}{2}\right) x}}{\sum_{n=0}^{\infty} e^{\left(n + \frac{1}{2}\right) x}} = \frac{h\nu \sum_{n=0}^{\infty} \left(n + \frac{1}{2}\right) e^{\left(n + \frac{1}{2}\right) x}}{\sum_{n=0}^{\infty} e^{\left(n + \frac{1}{2}\right) x}}$$

$$\Rightarrow \langle E \rangle = \frac{h\nu \left( \frac{1}{2} e^{x/2} + \frac{3}{2} e^{3x/2} + \frac{5}{2} e^{5x/2} + \dots \right)}{e^{x/2} + e^{3x/2} + e^{5x/2} + \dots} \quad \dots(3(a))$$

But  $\frac{d}{dx} \log_e (e^{x/2} + e^{3x/2} + e^{5x/2} + \dots)$

$$= \frac{\frac{1}{2} e^{x/2} + \frac{3}{2} e^{3x/2} + \frac{5}{2} e^{5x/2} + \dots}{e^{x/2} + e^{3x/2} + e^{5x/2} + \dots}$$



Therefore, equation (3) can be written as

$$\begin{aligned} \langle E \rangle &= hv \frac{d}{dx} [\log_e (e^{x/2} + e^{3x/2} + e^{5x/2} + \dots)] \\ &= hv \frac{d}{dx} [\log_e \{e^{x/2} (1 + e^x + e^{2x} + \dots)\}] \\ &= hv \left[ \frac{d}{dx} (\log_e e^{x/2}) + \frac{d}{dx} \{\log_e (1 + e^x + e^{2x} + \dots)\} \right] \end{aligned}$$

or 
$$\langle E \rangle = hv \left[ \frac{1}{2} + \frac{d}{dx} \{\log_e (1 + e^x + e^{2x} + \dots)\} \right] \quad \dots(3(b))$$

Now using Binomial theorem,

$$1 + e^x + e^{2x} + e^{3x} + \dots = (1 - e^x)^{-1}$$

Therefore, equation 3(b) can be written as

$$\begin{aligned} \langle E \rangle &= hv \left[ \frac{1}{2} + \frac{d}{dx} \log_e (1 - e^x)^{-1} \right] \\ &= hv \left[ \frac{1}{2} - \frac{d}{dx} \log_e (1 - e^x) \right] \\ &= hv \left[ \frac{1}{2} + \frac{e^x}{1 - e^x} \right] = hv \left[ \frac{1}{2} + \frac{1}{\frac{1}{e^x} - 1} \right] \end{aligned}$$

$$\Rightarrow \langle E \rangle = hv \left[ \frac{1}{2} + \frac{1}{e^{-x} - 1} \right] = hv \left[ \frac{1}{2} + \frac{1}{e^{hv/k_B T} - 1} \right] \quad [\text{using eqn. (2)}]$$

Since there are  $3N$  oscillators corresponding to  $N$  atoms of crystal, the average energy of the crystal (solid) is

$$U = 3N \langle E \rangle = 3N hv \left[ \frac{1}{2} + \frac{1}{e^{hv/k_B T} - 1} \right] \quad \dots(4)$$

Now the molar specific heat of the solid is given by

$$C_V = \frac{dU}{dT} \quad (\text{for one mole})$$

$$= \frac{d}{dT} \left[ 3N hv \left[ \frac{1}{2} + \frac{1}{e^{hv/k_B T} - 1} \right] \right] \quad (\text{Using eqn. (4)})$$

$$= 3N hv \left[ \frac{-e^{hv/k_B T}}{(e^{hv/k_B T} - 1)^2} = \frac{d}{dT} \left( \frac{hv}{k_B T} \right) \right] = \frac{3N hv e^{hv/k_B T}}{(e^{hv/k_B T} - 1)^2} \cdot \frac{hv}{k_B T^2}$$



or

$$C_v = 3N k_B \left( \frac{h\nu}{k_B T} \right)^2 \frac{e^{h\nu/k_B T}}{(e^{h\nu/k_B T} - 1)^2} \quad \dots(5)$$

For one mole,

$$Nk_B = R$$

where R is the universal gas constant.

Therefore, eqn. (6) becomes

$$C_v = 3R \left( \frac{h\nu}{k_B T} \right)^2 \frac{e^{h\nu/k_B T}}{(e^{h\nu/k_B T} - 1)^2}$$

Let

$$\frac{h\nu}{k_B} = \theta_E \text{ is the Einstein temperature.}$$

$$C_v = 3R \left( \frac{\theta_E}{T} \right)^2 \frac{e^{\theta_E/T}}{(e^{\theta_E/T} - 1)^2} \quad \dots(6)$$

Eqn. (6) gives the molar specific heat of solid in terms of temperature. Two cases can be discussed.

**Case 1.** If the temperature is very high in comparison to  $\theta_E$  i.e.,  $T \gg \theta_E$ . Then  $\frac{\theta_E}{T}$  is quite small.

$$e^{\theta_E/T} \approx 1 + \frac{\theta_E}{T}$$

Therefore eqn. (6) becomes,

$$C_v = \frac{3R \left( \frac{\theta_E}{T} \right)^2 \left( 1 + \frac{\theta_E}{T} \right)}{\left( \frac{\theta_E}{T} \right)^2} = 3R \left( 1 + \frac{\theta_E}{T} \right)$$

But

$$1 + \frac{\theta_E}{T} \approx 1$$

$\therefore$

$$C_v = 3R.$$

which is the Dulong and Petit's Law. Therefore, at high temperatures, Dulong and Petit's law is obeyed.

**Case 2.** If the temperature is low in comparison to  $\theta_E$  i.e.,  $T \ll \theta_E$ , then  $\frac{\theta_E}{T} \gg 1$ .

i.e.

$$e^{\theta_E/T} + 1 \approx e^{\theta_E/T}$$

Therefore from eqn. (6),

$$C_v = 3R \left( \frac{\theta_E}{T} \right)^2 \frac{e^{\theta_E/T}}{(e^{\theta_E/T})^2} = 3R \left( \frac{\theta_E}{T} \right)^2 e^{-\theta_E/T}$$



Thus, for  $T \ll \theta_E$ , the specific heat is proportional to  $e^{\theta_E/T}$ . This implies that the specific heat of solids decreases with the decrease in temperature. The variation of  $C_v$  with  $T$  is in good agreement with the experimental result at high temperatures, but does not give exact results at very low temperatures. It is due to the reason that the approach used is over simplified with the assumption that the oscillators are independent of each other and still oscillate with a common frequency. In actual lattice, all the harmonic oscillators are coupled together and cannot vibrate independently. A modification in this regard was made by Debye in his theory of specific heat of solids.

# ***Drawbacks of Einstein's model of specific heat***

The reason for the discrepancy between the theory and the low temperature experimental results are due to over simplified model by Einstein that all the atomic Oscillators vibrate independently at the same frequency. In fact, they are couple together relative to their neighbors in the lattice and are capable of producing a spectrum of frequencies rather than a single frequency  $\nu$ . Later on, the discrepancy between theory and the low temperature experimental values was removed and in general, fit to experimental data was removed by Debye in 1912.