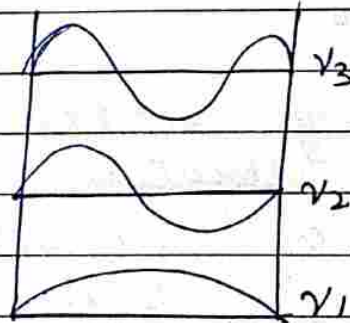


## Debye theory of lattice heat capacity

### Assumptions:-

1. The atoms in a solid are not independent but they move under the effect of neighbouring atoms. Therefore, a crystal cannot be considered as a system of independent H.O.s (atoms) but it is system of coupled H.O.'s.
2. Motion of one atom anywhere in a solid affect all other atoms in a crystal. As a result a wave is produced in a crystal called as lattice wave.
3. Therefore, crystal can propagate elastic waves of freq. ranging from low freq (sound waves) to high freq corresponding to infrared absorption.
4. Thus, a crystal can have number of modes of vibrations, i.e. A crystal can vibrate in various modes with different frequencies & no. of vibrational modes per unit frequency range is called density of modes.



Each  $\nu$  is a different mode.

5. A crystal can support a coupled mode.

Coupled mode means superposition of various modes.

6 The maximum freq. of oscillation is called Debye frequency ( $\omega_D$ ). & Minimum freq. is zero for a wave of infinite wavelength.

$$0 < \omega < \omega_D \quad \text{--- (1)}$$

or  $\rightarrow$  This is the highest freq. propagating through a crystal.  
 $0 < \nu < \nu_D$

The number of vibrational modes in the frequency range  $\nu$  &  $\nu + \nu$  is given as  $g(\nu) d\nu$

$\therefore$  The total number of modes of vibration is  $\int_0^{\nu_D} g(\nu) d\nu$ . --- (2)

but we know that total number of modes of vibration is  $3N$  in a crystal lattice,

$$\int_0^{\nu_D} g(\nu) d\nu = 3N \quad \text{--- (3)}$$

Now, In any continuous solid subjected to elastic vibrations, we encounter two types of vibrational modes i.e. longitudinal vibrational mode and transverse vibrational mode.

$$g(\nu) d\nu = 4\pi V \left( \frac{1}{c_l^3} + \frac{2}{c_t^3} \right) \nu^2 d\nu \quad (4)$$

$c_l$  = velocity of long. vibrations (1 dir)

$c_t$  = " " transverse vibrations (2 dir)

\* [Note: In eq (4), I have used a direct result.]

Putting in eq (2)

$$\int_0^{\nu_D} g(\nu) d\nu = 3N$$

$$\int_0^{\nu_D} 4\pi V \left( \frac{1}{c_l^3} + \frac{2}{c_t^3} \right) \nu^2 d\nu = 3N$$

$$4\pi V \left( \frac{1}{c_l^3} + \frac{2}{c_t^3} \right) \int_0^{\nu_D} \nu^2 d\nu = 3N$$

$$4\pi V \left( \frac{1}{c_l^3} + \frac{2}{c_t^3} \right) \frac{\nu_D^3}{3} = 3N \quad (5)$$

$$\nu_D = \left[ \frac{9N}{4\pi V \left( \frac{1}{c_l^3} + \frac{2}{c_t^3} \right)} \right]^{1/3} \quad (6)$$

Now the average energy of an oscillator having frequency  $\nu$  at a temperature  $T$  is given by

$$\bar{e} = \frac{h\nu}{e^{h\nu/k_B T} - 1} \quad (7)$$

The Energy of solid in the range  $\nu$  &  $\nu + d\nu$

$$dE = (\text{average energy per mode}) \times (\text{no. of modes in the range } \nu \text{ to } \nu + d\nu)$$

Total energy of the crystal

$$E = \int_0^{\nu_D} dE = \int_0^{\nu_D} \bar{E} g(\nu) d\nu$$

$$E = \int_0^{\nu_D} 4\pi V \left( \frac{1}{c^3} + \frac{2}{ct^3} \right) \nu^2 \frac{h\nu}{e^{h\nu/k_B T} - 1} d\nu$$

$$= 4\pi V \left( \frac{1}{c^3} + \frac{2}{ct^3} \right) \int_0^{\nu_D} \frac{h\nu^3}{e^{h\nu/k_B T} - 1} d\nu$$

from eq. (6)

$$= \frac{9Nk}{\nu_D^3} \int_0^{\nu_D} \frac{h^3}{e^{h\nu/k_B T} - 1} d\nu \quad \text{--- (7)}$$

$$\text{Let } x = \frac{h\nu}{k_B T} \quad \nu = \frac{x k_B T}{h}$$

$$d\nu = \frac{k_B T}{h} dx$$

also,  $x_D = \frac{h\nu_D}{k_B T}$ , Now Define a qty

$$\theta_D = \frac{h\nu_D}{k_B} \quad \text{called } \underline{\underline{\text{Debye temp.}}}$$

(8)

$$\therefore x_D = \frac{\theta_D}{T}$$

$$E = \frac{9N h^3}{v_D^3} \int_0^{x_D} \frac{\left(\frac{x k_B T}{h}\right)^3 \left(\frac{h^3}{v_D}\right) dx}{e^x - 1}$$

$$E = \frac{9N h^3}{v_D^3} \left(\frac{k_B T}{h}\right)^3 \int_0^{x_D} \frac{x^3 dx}{e^x - 1}$$

$$E = 9N k_B T \underbrace{\left(\frac{k_B}{h v_D}\right)^3}_{1/\theta_D^3} T^3 \int_0^{x_D} \frac{x^3 dx}{e^x - 1}$$

$$E = 9N k_B T \left(\frac{T}{\theta_D}\right)^3 \int_0^{x_D} \frac{x^3 dx}{e^x - 1} \quad \text{--- (9)}$$

Now, let us discuss the two cases:

1) High temperature case:

$$T \gg \theta_D \quad x = \frac{h\nu}{k_B T}$$

$\therefore x$  is very small

$$\therefore e^x \sim 1 + x \quad \left\{ \begin{array}{l} x \\ e^x = 1 + x + \frac{x^2}{2} + \dots \\ \text{neglecting higher} \\ \text{order terms like} \\ x^2, x^3, \dots \end{array} \right.$$

Putting in eq (9)

$$E = 9N k_B T \left(\frac{T}{\theta_D}\right)^3 \int_0^{x_D} \frac{x^3 dx}{1+x-1}$$

$$E = 9N k_B T \left(\frac{T}{\theta_D}\right)^3 \int_0^{x_D} x^2 dx$$

$$E = 9NK_B T \left( \frac{T}{\theta_D} \right)^3 \int_0^{\theta_D} x^2 dx$$

$$E = \cancel{9} NK_B T \left( \frac{T}{\theta_D} \right)^3 \frac{x_D^3}{\cancel{3}}$$

$$E = 3NK_B T \left( \frac{T}{\theta_D} \right)^3 \left( \frac{\theta_D}{T} \right)^3$$

$$E = 3NK_B T = 3RT$$

$\left\{ \begin{array}{l} \because NK_B = R \\ \text{for } N = N_A \end{array} \right.$

$$C_V = \left( \frac{\partial E}{\partial T} \right)_V = 3R$$

→ same as Dulong & Petit's law.

∴ At high temp, the Debye's theory also obeys the Dulong & Petit's law as obeyed by classical & Einstein's theory.

2) Low temperature case:  $T \ll \theta_D$

$$x = \frac{\theta_D}{T} \rightarrow \infty$$

eq (9) becomes

$$E = 9NK_B T \left( \frac{T}{\theta_D} \right)^3 \int_0^{\infty} \frac{x^3 dx}{e^x - 1}$$

$$\text{Now, } \int_0^{\infty} \frac{x^3 dx}{e^x - 1} = \frac{\pi^4}{15}$$

(7)

$$E = 9 N K_B T \left( \frac{T}{\Theta_D} \right)^3 \cdot \frac{\pi^4}{15}$$

$$E = \frac{3}{5} \frac{N K_B \pi^4 T^4}{\Theta_D^3}$$

$$E = \frac{3 \pi^4 N K_B T^4}{5 \Theta_D^3} \rightarrow \text{Note } E \propto T^4$$

$$C_V = \left( \frac{\partial E}{\partial T} \right)_V$$

$$C_V = \frac{3}{5} \pi^4 \frac{N K_B}{\Theta_D^3} 4 \cdot T^3$$

$$C_V = \frac{12}{5} \pi^4 \frac{N K_B}{\Theta_D^3} \cdot T^3$$

$$C_V = \frac{12}{5} \pi^4 N K_B \left( \frac{T}{\Theta_D} \right)^3$$

$$\downarrow \text{ or } C_V = \frac{12}{5} \pi^4 R \left( \frac{T}{\Theta_D} \right)^3 \quad \left\{ \begin{array}{l} \text{for } \\ N = N_a \\ N K_B = R \end{array} \right\}$$

This is known as Debye's  $T^3$  law for sp. heat of solids.

This shows that, at very low temperature, the specific heat of solid varies as  $T^3$  & this law holds for  $T \leq \frac{\Theta}{10}$ .

whereas, In Einstein's theory

at low temp, decrease in specific heat was exponentially & the decrease was much rapid than observed from Debye's theory ( $T^3$  law).

Hence, the agreement with experimentally observed curve was much better for Debye's theory.

— x —