

# 3 Thermal Properties of Solids

## \* Classical Theory of lattice heat capacity (Dulong - Petit law)

1819 French Physicist

According to classical theory the atoms in a solids are in a constant thermal vibration. this one dimensional motion can be identified with that of simple harmonic oscillator.

The energy of harmonic oscillator is given by

$$E = E_{kin} + E_{pot} \\ = \frac{P^2}{2m} + V(x) \dots \dots \dots (1)$$

$$V(x) = \frac{1}{2} m \omega^2 x^2$$

where  $m$  is mass of atom,  $\omega$  is natural frequency of oscillator &  $x$  displacement of atom from their equilibrium position.

In solid several atoms will be constantly vibrating with different velocity. In order to estimate the average energy  $\langle E \rangle$  of any oscillator we have treat this assembly of atomic oscillator using statistical mechanics

According to classical Maxwell-Boltzmann's statistics that the oscillator will have the energy  $E$  at temperature  $T$  is given by the Boltzmann factor  $e^{-E/KT}$ . So its average energy is found by integrating  $E \cdot e^{-E/KT}$  over all

possible energy and divide by the integral by  $\exp^{-E/KT}$  to normalise the result.

$$\langle \bar{E} \rangle = \frac{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} E \cdot \exp^{-E/KT} dp dx}{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp^{-E/KT} dp dx} \quad (2)$$

From equation (1)

$$E = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2$$

Therefore equation (2) becomes

$$\langle \bar{E} \rangle = \frac{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \left[ \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2 \right] \cdot \exp \left[ \frac{-\frac{p^2}{2m} - \frac{1}{2}m\omega^2 x^2}{KT} \right] dp dx}{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp \left[ \frac{-\frac{p^2}{2m} - \frac{1}{2}m\omega^2 x^2}{KT} \right] dp dx}$$

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp \left[ \frac{-\frac{p^2}{2m} - \frac{1}{2}m\omega^2 x^2}{KT} \right] dp dx$$

$$= \int_{-\infty}^{\infty} \frac{p^2}{2m} \cdot \exp \left[ \frac{-p^2}{2mKT} \right] dp$$

$$\int_{-\infty}^{\infty} \exp \left[ \frac{-p^2}{2mKT} \right] dp$$

$$+ \int_{-\infty}^{\infty} \frac{1}{2} m \omega^2 x^2 \exp \frac{-m \omega^2 x^2}{2kT} dx$$

$$\int_{-\infty}^{+\infty} \exp \frac{-m \omega^2 x^2}{2kT} dx \quad (3)$$

$$= \frac{1}{2m} \int_{-\infty}^{\infty} p^2 \exp \frac{-p^2}{2mkT} dp$$

$$\int_{-\infty}^{\infty} \exp \frac{-p^2}{2mkT} dp$$

$$+ \frac{m \omega^2}{2} \int_{-\infty}^{\infty} x^2 \exp \frac{-m \omega^2 x^2}{2kT} dx$$

$$\int_{-\infty}^{\infty} \exp \frac{-m \omega^2 x^2}{2kT} dx$$

(4)

To solve above integral by using standard integral.

$$(i) \int_0^{\infty} \exp(-du) du = \frac{1}{2} \left( \frac{\pi}{d} \right)^{1/2}$$

$$(ii) \int_0^{\infty} u^2 \exp(-du^2) du = \frac{1}{4} \left( \frac{\pi}{d} \right)^{1/2}$$

Let  $d = \frac{1}{2mkT}$

$$u^2 = p^2$$

First integral term in equation (4)  
we have

$$\frac{1}{2m} \int_{-\infty}^{\infty} p^2 \exp\left(-\frac{p^2}{2mkT}\right) dp$$

$$\int_{-\infty}^{\infty} \exp\left(-\frac{p^2}{2mkT}\right) dp$$

To solve above by using standard integral and substitution

$$= 2 \times \frac{1}{2m} \times \frac{1}{4} \left[ \frac{\pi}{(\frac{1}{2}mkT)^3} \right]^{\frac{1}{2}}$$

$$\frac{2 \times \frac{1}{2} \left[ \frac{\pi}{\frac{1}{2}mkT} \right]^{\frac{1}{2}}}{2}$$

$$= \frac{2 \times \frac{1}{2m} \cdot \frac{1}{4} \left[ \pi (2mkT)^3 \right]^{\frac{1}{2}}}{2 \times \frac{1}{2} \left[ \pi (2mkT) \right]^{\frac{1}{2}}}$$

$$\frac{2 \times \frac{1}{2m} \cdot \frac{1}{4} \left[ \pi (2mkT)^3 \right]^{\frac{1}{2}}}{2 \times \frac{1}{2} \left[ \pi (2mkT) \right]^{\frac{1}{2}}}$$

$$= \frac{2 \times \frac{1}{2m} \cdot \frac{1}{4} \left[ \pi \cdot 2^3 m^3 k^3 T^3 \right]^{\frac{1}{2}}}{2 \times \frac{1}{2} \left[ \pi \cdot 2 m k T \right]^{\frac{1}{2}}}$$

$$\frac{2 \times \frac{1}{2m} \left[ \pi \cdot 2^3 m^3 k^3 T^3 \right]^{\frac{1}{2}}}{2 \times \frac{1}{2} \left[ \pi \cdot 2 m k T \right]^{\frac{1}{2}}}$$

$$= \frac{1}{4m} \left[ 4 m^2 k^2 T^2 \right]^{\frac{1}{2}}$$

$$= \frac{1}{2} \cdot \frac{1}{\pi} \cdot \frac{1}{2} \cdot \pi K T$$

$$= \frac{K T}{2} \quad \text{--- (5)}$$

Second integral

$$\frac{m \omega^2}{2} \int_{-\infty}^{\infty} x^2 \exp \left[ \frac{-m \omega^2 x^2}{2 K T} \right] dx$$

$$\int_{-\infty}^{\infty} \exp \left[ \frac{-m \omega^2 x^2}{2 K T} \right] dx$$

After solving this using standard integral and substitution we get

$$= \frac{K T}{2} \quad \text{--- (6)}$$

Substitute this value in equation (4)

$$\langle E \rangle = \frac{K T}{2} + \frac{K T}{2} = K T \quad \text{--- (7)}$$

The oscillators can vibrate about three mutually perpendicular axes and hence mean energy

$$\langle E \rangle = 3 K T$$

If there are  $N$  atoms in a molecule then internal energy

$$U = 3 N K T$$

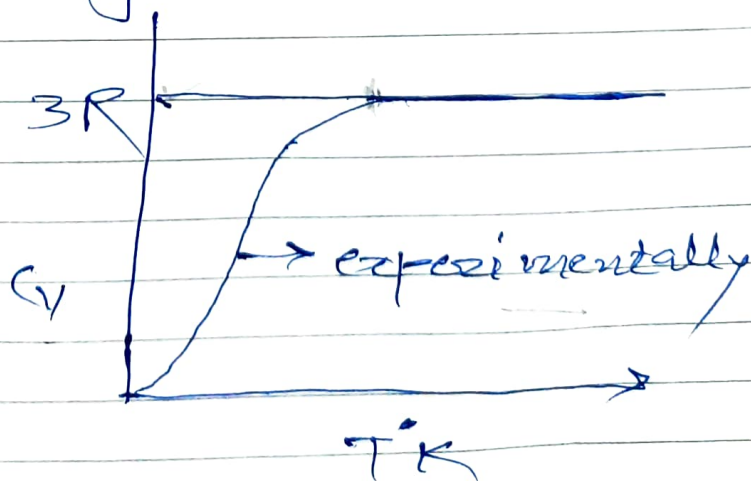
$$U = 3RT$$

$\therefore NK = R$  is universal gas constant.

$$\therefore C_V = \left( \frac{dU}{dT} \right)_V = 3R = 5.96 \frac{\text{cal}}{\text{mole}^\circ\text{K}}$$

The classical theory thus shows that the heat capacity of all the solid elements should be constant, independent of temperature and for a mole of any solid element always equal to about 6 calories. This is known as Dulong-Petit law. This is fairly correct for the element with atomic weight greater than 40 and at above room temperature.

This law is break down seriously at low temperature range. In the lower temperature range the sp. heat of all the substances is found to approach zero as shown in figure



# Einstein's Theory of Lattice Heat Capacity (1906)

classmate

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Einstein in 1906 by applying Planck's quantum theory, classically the atoms of solids were considered to be simple harmonic oscillator having continuous energy. Einstein assumed that atoms are again identical independent harmonic oscillator with same natural frequency  $\nu$  but their energies are not continuous. The energies are quantised and they have only the discrete values:

$$\text{i.e. } h\nu, 2h\nu, 3h\nu, \dots, nh\nu$$

where  $n$  is quantum number,  $h$  is Planck's constant and  $\nu$  is frequency of oscillators.

The possible energy of oscillator may be represented by

$$E_n = nh\nu$$

$$n = 0, 1, 2, \dots$$

$$E_n = n \frac{h}{2\pi} \cdot 2\pi\nu$$

$$= nh\omega \quad \dots \quad (1)$$

$$h = \frac{h}{2\pi} \cdot 2\pi, \quad h - \text{Planck's constant}$$

$\omega = 2\pi\nu$  angular frequency.

According to quantum mechanics energy of an harmonic oscillator is given by

$$E = E_0 + E_n \\ = \frac{1}{2}h\omega + nh\omega$$

$$= (n + \frac{1}{2}) \hbar \omega \quad \text{--- (2)}$$

$E_0 = \frac{1}{2} \hbar \omega$  is known as zero point energy of an oscillator

From Maxwell-Boltzmann statistics mean energy of the oscillator is given by

$$\bar{E} = \sum_{n=0}^{\infty} (n + \frac{1}{2}) \hbar \omega \cdot \exp \left[ \frac{-(n + \frac{1}{2}) \hbar \omega}{KT} \right]$$

$$\sum_{n=0}^{\infty} \exp \left[ \frac{-(n + \frac{1}{2}) \hbar \omega}{KT} \right]$$

Let  $x = -\frac{\hbar \omega}{KT}$

$$= \hbar \omega \sum_{n=0}^{\infty} (n + \frac{1}{2}) \cdot e^{[(n + \frac{1}{2}) x]}$$

$$\sum_{n=0}^{\infty} e^{[(n + \frac{1}{2}) x]}$$

$n = 0, 1, 2, 3, \dots$

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

$$= \hbar \omega \cdot \frac{d}{dx} \log (e^{\frac{1}{2}x} + e^{\frac{3}{2}x} + \dots)$$

$$= \hbar \omega \frac{d}{dx} \log [e^{\frac{1}{2}x} (1 + e^x + e^{2x} + \dots)]$$

$$= \hbar \omega \frac{d}{dx} \left[ \log e^{\frac{1}{2}x} + \log (1 - e^{-x}) \right]$$



$$= \hbar\omega \frac{d}{dx} \left[ \frac{1}{2}x - \log(1 - e^x) \right]$$

$$= \hbar\omega \left[ \frac{1}{2} - \frac{1}{1 - e^x} x - e^x \right]$$

$$= \hbar\omega \left[ \frac{1}{2} + \frac{e^x}{1 - e^x} \right]$$

$$= \hbar\omega \left[ \frac{1}{2} + \frac{e^x/e^x}{1 - e^x/e^x} \right]$$

$$= \hbar\omega \left[ \frac{1}{2} + \frac{1}{e^{-x} - 1} \right]$$

$$\because x = -\frac{\hbar\omega}{KT}$$

$$= \hbar\omega \left[ \frac{1}{2} + \frac{1}{e^{\frac{\hbar\omega}{KT}} - 1} \right] \quad \text{--- (4)}$$

$$\bar{E} = \frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\frac{\hbar\omega}{KT}} - 1} \quad \text{--- (5)}$$

If  $N$  is no. of oscillator in a mole of solid and oscillators are vibrating along three mutually perpendicular axes, then net energy associated with the mole of the solid is

$$U = 3N\bar{E}$$

$$= \frac{3N\hbar\omega}{2} + \frac{3N\hbar\omega}{e^{\frac{\hbar\omega}{KT}} - 1} \quad \text{--- (6)}$$

the specific heat at constant vol.  
may be

$$\begin{aligned}
 C_V &= \left( \frac{dU}{dT} \right)_V = \frac{d}{dT} \left[ \frac{3NkT\omega}{2} + \frac{3NkT\omega}{\left[ e^{\left( \frac{h\omega}{kT} \right)} - 1 \right]} \right] \\
 &= 3Nk\omega (-1) \exp \left[ \left( \frac{h\omega}{kT} \right) \right]^{-2} \\
 &\quad \cdot \exp \frac{h\omega}{kT} \cdot \frac{h\omega}{k} \left( -\frac{1}{T^2} \right) \\
 &= \frac{3Nk\omega \left( \frac{h\omega}{k} \right) \cdot e^{\left( \frac{h\omega}{kT} \right)} \cdot \frac{1}{T^2}}{\left[ e^{\frac{h\omega}{kT}} - 1 \right]^2}
 \end{aligned}$$

Multiply and divided by  $k$

$$\begin{aligned}
 C_V &= \frac{3Nk \frac{h\omega}{k} \frac{h\omega}{k} \cdot e^{\frac{h\omega}{kT}} \cdot \frac{1}{T^2}}{\left[ e^{\frac{h\omega}{kT}} - 1 \right]^2} \\
 &= \frac{3Nk \left( \frac{h\omega}{k} \right)^2 \cdot e^{\frac{h\omega}{kT}}}{\left[ e^{\frac{h\omega}{kT}} - 1 \right]^2} \quad \text{--- (7)}
 \end{aligned}$$

It is convenient to express above results in a simple way by defining characteristic temp.

$\Theta_E$  is called Einstein's temp.

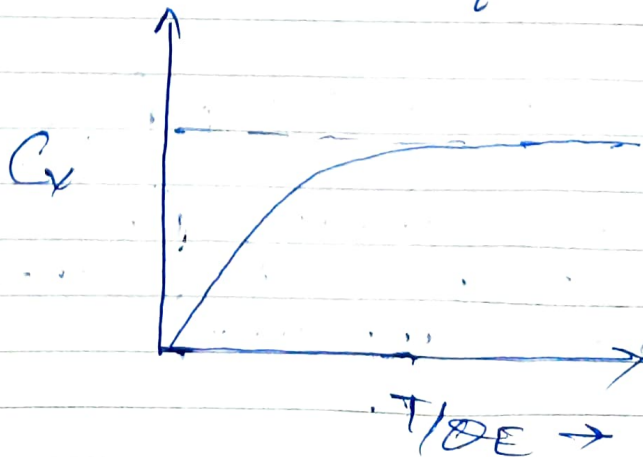
$$h\nu = k\Theta_E$$

$\therefore$  substitute this in above eq<sup>n</sup>.  
we get

$$C_V = \frac{3Nk \left( \frac{k\Theta_E}{kT} \right)^2 e^{-\frac{k\Theta_E}{kT}}}{\left[ \exp\left( \frac{k\Theta_E}{kT} \right) - 1 \right]^2}$$

$$= \frac{3Nk \left( \frac{\Theta_E}{T} \right)^2 e^{-\frac{\Theta_E}{T}}}{\left[ \exp\left( \frac{\Theta_E}{T} \right) - 1 \right]^2} \quad \text{--- (8)}$$

This equation gives the values for those value of  $\Theta$  which agree well with experimental values over wide range of temp. in which heat capacity varies appreciably with temp.



For high temperature

$$T \gg \Theta_E \Rightarrow \exp\left(\frac{\Theta_E}{T}\right) \approx 1,$$

$$\exp\left(\frac{\Theta_E}{T}\right) = 1 + \frac{\Theta_E}{T}$$

$$\therefore C_V = 3NK = 3R = 5.96 \frac{\text{cal}}{\text{mole} \cdot \text{K}}$$

which is classical results  
Dulong-Petit law.

For low temperature

$$T \ll \Theta_E$$

$$\exp\left(\frac{\Theta_E}{T}\right) \gg 1$$

i.e. exponential term is large. Hence unity in the denominator in the equation (8) can be neglected.

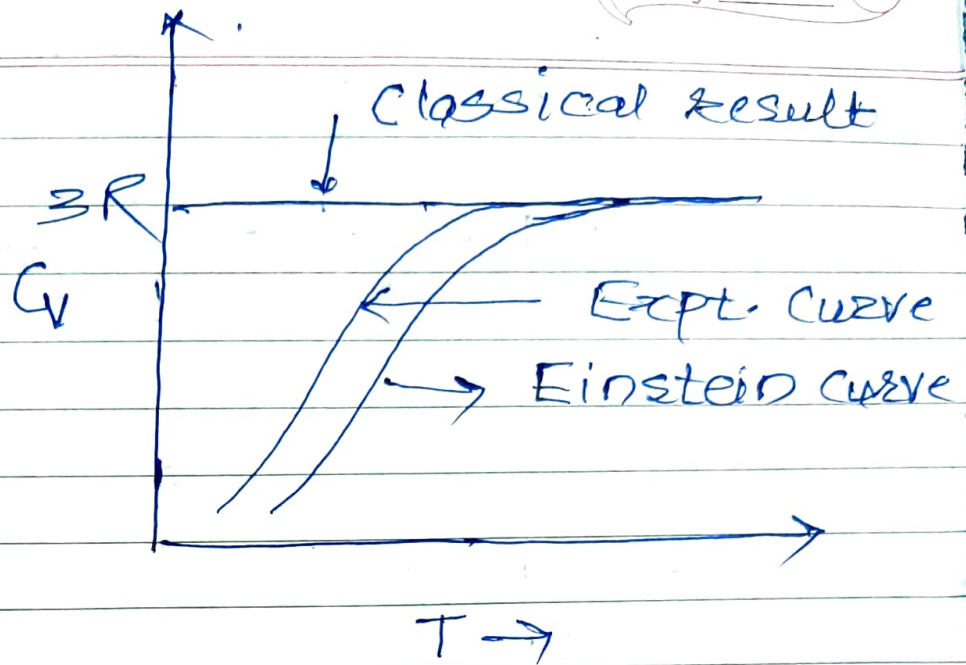
This gives

$$C_V = 3NK \left(\frac{\Theta_E}{T}\right)^2 \cdot \exp\left(\frac{\Theta_E}{T}\right)$$

$$\frac{\exp\left(\frac{\Theta_E}{T}\right)^2}{\exp\left(\frac{\Theta_E}{T}\right)^2}$$

$$= 3NK \left(\frac{\Theta_E}{T}\right)^2 \cdot \exp\left(-\frac{\Theta_E}{T}\right) \quad \text{--- (9)}$$

From equation (9) it is clear that sp. heat  $C_V$  approaches zero as  $T$  approaches zero



For high temp

$$C_V = 3NK \left( \frac{Q_E}{T} \right)^2 \cdot \frac{1}{\left( 1 + \frac{Q_E}{T} - 1 \right)^2}$$

$$e^x = 1 + x$$

$$e^{\frac{Q_E}{T}} = 1 + \frac{Q_E}{T}$$

$$C_V = 3NK$$

$$= 3R = 5.96 \text{ cal.}$$

# Debye's Model of lattice heat capacity

classmate

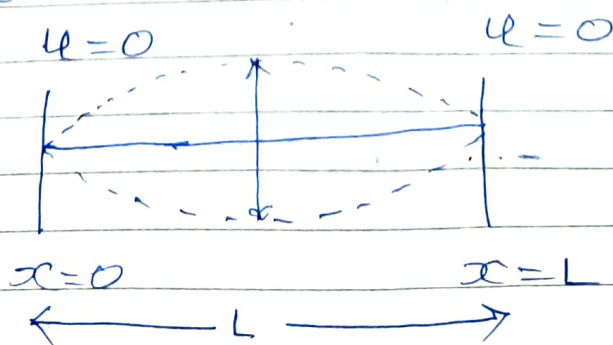
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The essential difference between Debye model and Einstein's model is that, Debye consider the vibrational modes of crystal as whole, where as Einstein consider the vibration of single atom and atomic vibrations to be independent to each other. For dealing with vibrational modes of solids as a whole, Debye apply the theory of vibrational modes of continuous medium.

Debye in 1912 proposed that, solid can be continuous elastic body and wave can be propagated through the solid. In fact vibrational modes of solids cover wide range of frequencies because atomic vibration in the crystal are strongly coupled and are not independent. The basic assumptions on which the theory is based.

1. solid consist of strings of atoms
2. oscillation are not independent
3. The length of string is equal to the length of solid
4. string oscillates if their ends are fixed.



## Density of modes of vibration

Let us consider a one dimensional continuous string of length  $L$  to be vibrating with its end is fixed. Consider  $u(x, t)$  be the displacement of the string at instant  $t$ . The differential equation of wave is

$$\begin{aligned} \frac{d^2 u}{dx^2} &= \frac{d^2 u}{dt^2} \cdot \frac{dt^2}{dx^2} = \frac{d^2 u}{dt^2} \cdot \frac{1}{\frac{dx}{dt}} \cdot \frac{1}{\frac{dx}{dt}} \\ &= \frac{d^2 u}{dt^2} \cdot \frac{1}{c_s^2} \quad \text{--- (1)} \end{aligned}$$

where  $c_s = \frac{dx}{dt}$  is velocity of wave in a string

The general solution of this equation is given by

$$u(x, t) = A \sin Kx \cos \omega t \quad \text{--- (2)}$$

where  $K$  is the wave number  
 $\omega = 2\pi f$  angular frequency

$$\begin{aligned} \frac{du}{dx} &= A \cos Kx \cdot K \cos \omega t \\ &= AK \cos Kx \cos \omega t \end{aligned}$$

$$\begin{aligned} \frac{d^2 u}{dx^2} &= -AK \sin Kx \cdot K \cos \omega t \\ &= -AK^2 \sin Kx \cos \omega t \\ &= -K^2 u \end{aligned}$$

Now

$$\frac{du}{dt} = -A \sin Kx \sin \omega t \cdot \omega$$

$$\frac{d^2 u}{dt^2} = -A \sin Kx \cos \omega t \cdot \omega \cdot \omega$$

$$= -A\omega^2 \sin kx \cos \omega t$$

$$= -\omega^2 u$$

keeping this value in equation (1) we get

$$-k^2 u = -\omega^2 u \cdot \frac{1}{c_s^2}$$

$$k^2 = \frac{\omega^2}{c_s^2}$$

$$k_x = \frac{\omega}{c_s} \quad \text{or} \quad k_x = \frac{\omega}{c_s}$$

Now the boundary conditions

$$x=0 \quad x=L$$

$$u=0 \quad u=0$$

Apply this boundary condition to equation (2) we have

$$A \sin kL \cos \omega t = 0$$

$$A \cos \omega t \neq 0 \quad \text{then} \quad \sin kL = 0$$

$$kL = n\pi \Rightarrow k = \frac{n\pi}{L}$$

$$k_x = \frac{n_x \pi}{L}$$

Similarly wave equation in 3D

$$\frac{d^2 u}{dx^2} + \frac{d^2 u}{dy^2} + \frac{d^2 u}{dz^2} = \frac{1}{c_s^2} \cdot \frac{d^2 u}{dt^2} \quad \text{--- (3)}$$

The solution of the wave equation is given by



$$u(x, y, z, t) = A \sin k_x x \sin k_y y \sin k_z z \cos \omega t$$

where  $k_x$ ,  $k_y$  &  $k_z$  are the wave vectors in the direction of  $x, y, z$  by applying boundary conditions we get

$$k_x = \frac{n_x \pi}{L}, \quad k_y = \frac{n_y \pi}{L}, \quad k_z = \frac{n_z \pi}{L}$$

$$k_x^2 + k_y^2 + k_z^2 = \frac{\omega^2}{c^2} = \frac{(2\pi\nu)^2}{c^2}$$

$$k_x^2 + k_y^2 + k_z^2 = \frac{4\pi^2 \nu^2}{c^2}$$

$$\frac{n_x^2 \pi^2}{L^2} + \frac{n_y^2 \pi^2}{L^2} + \frac{n_z^2 \pi^2}{L^2} = \frac{4\pi^2 \nu^2}{c^2}$$

$$\frac{\pi^2}{L^2} (n_x^2 + n_y^2 + n_z^2) = \frac{4\pi^2 \nu^2}{c^2}$$

$$n_x^2 + n_y^2 + n_z^2 = \frac{4L^2 \nu^2}{c^2}$$

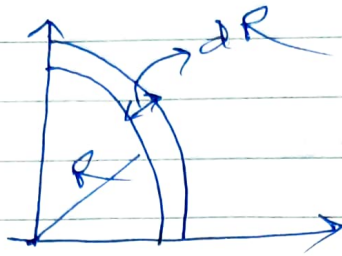
$$n_x^2 + n_y^2 + n_z^2 = R \text{ (says)} = \frac{4L^2 \nu^2}{c^2}$$

$$\therefore R = \frac{2L}{c} \nu \quad \text{--- (4)}$$

$$dR = \frac{2L}{c} \cdot d\nu \quad \text{--- (5)}$$

Let us now find out possible modes of vibration  $z(\nu)d\nu$  in the frequency range  $\nu$  and  $\nu+d\nu$  for this

consider two dimensional case



Area of strip whose inner radius  $R$  and thickness  $dR$

$$\frac{2\pi R dR}{4}$$

The vol. occupied by shell is

$$\frac{4\pi}{3} (R+dR)^3 - \frac{4\pi}{3} R^3$$

$$\frac{4\pi}{3} [(R+dR)^3 - R^3]$$

$$\frac{4\pi}{3} [R^3 + 3R^2 dR + 3R dR^2 + dR^3 - R^3]$$

Higher order term in  $dR$  is neglected

$$\frac{4\pi}{3} \cdot 3R^2 dR = 4\pi R^2 dR$$

$$\frac{4\pi}{8} R^2 dR \quad \text{this is volume}$$

occupied by shell

From equation (4) & (5) we get

$$\frac{4\pi}{8} \cdot \frac{4L^2 D^2}{C_s^2} \cdot \frac{2L \cdot dD}{C_s}$$

$$\frac{4}{3} \pi L^3 \nu^2 d\nu$$

$$\frac{4\pi L^3 \nu^2 d\nu}{c_s^3}$$

$$\frac{4\pi V}{c_s^3} \nu^2 d\nu \quad \text{--- (6)}$$

$c_s^3$  is the vol. occupied by the spherical shell

$L^3 = V$  the vol. of solid.

since there is one longitudinal and two transverse mode then vol. occupied by the space is

$$4\pi V \left\{ \frac{2}{c_t^3} + \frac{1}{c_l^3} \right\} \nu^2 d\nu \quad \text{--- (7)}$$

$c_t$  &  $c_l$  is the velocity of transverse and longitudinal modes then the possible modes of vibration is

$$Z(\nu) d\nu = 4\pi V \left\{ \frac{2}{c_t^3} + \frac{1}{c_l^3} \right\} \nu^2 d\nu \quad \text{--- (8)}$$

## Debye equation of sp. heat of solid.

While dealing with the vibrational modes of solids, crystal consist atoms the total no. of vibrational modes are  $3N$  where  $N$  is total number of atoms in the solid.

If  $\nu_D$  is the maximum frequency or Debye frequency which is common to both transverse and longitudinal modes, then

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

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

$$\frac{9N}{4\pi V} = \left\{ \frac{2}{c_t^3} + \frac{1}{c_l^3} \right\} \nu_D^3 \quad \text{--- (10)}$$

By using Planck's theorem the average energy of an oscillator having frequency  $\nu$  at temperature  $T$  is given by

$$\bar{E} = \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1} \quad \text{--- (11)}$$

$\therefore$  Total energy of oscillator

$$U = 3N \bar{E}$$

$$= 4\pi V \left\{ \frac{2}{c^3} + \frac{1}{c^3} \right\} \int_0^{\nu_D} \nu^2 d\nu \cdot \frac{h\nu}{e^{\frac{h\nu}{KT}} - 1}$$

substitute the value of square bracket

$$U = \int_0^{\nu_D} 4\pi V \cdot \frac{9N}{4\pi V \nu^3} \cdot \frac{\nu^2 d\nu \cdot h\nu}{e^{\frac{h\nu}{KT}} - 1}$$

$$= \int_0^{\nu_D} \frac{9Nh\nu^3 d\nu}{\nu^3 e^{\frac{h\nu}{KT}} - 1}$$

Let  $\frac{h\nu}{KT} = x$

$h\nu = KT x$

$\nu = \frac{KT}{h} \cdot x \quad d\nu = \frac{KT}{h} \cdot dx$

$$U = \int_0^{\nu_D} \frac{9Nh \left(\frac{KT}{h}\right)^3 x^3 \cdot \frac{KT}{h} dx}{\left(\frac{KT}{h}\right)^3 \frac{x^3}{e^x - 1}}$$

$$= 9NKT \cdot \left(\frac{KT}{h\nu_D}\right)^3 \int_0^{\nu_D} \frac{x^3 dx}{e^x - 1} \quad \text{--- (12)}$$

then sp. heat of solid may be

$$C_v = \frac{d(U)}{dT} = \frac{d}{dT} \left[ 9NKT \cdot \left(\frac{KT}{h\nu_D}\right)^3 \int_0^{\nu_D} \frac{x^3 dx}{e^x - 1} \right] \quad \text{--- (13)}$$

Case (I)

sp. heat at higher temperature

$$h\nu \ll kT, \quad \frac{h\nu}{kT} \ll 1$$

$$\therefore e^x = 1 + x$$

$$C_V = \frac{dU}{dT} = \frac{d}{dT} \left[ 3NkT \left( \frac{kT}{h\nu} \right)^3 \int_0^{\infty} \frac{x^2}{1+x} dx \right]$$

$$= \frac{d}{dT} \left[ 3NkT \left( \frac{kT}{h\nu} \right)^3 \left[ \frac{x^3}{3} \right]_0^{\infty} \right]$$

$$= \frac{d}{dT} \left[ 3NkT \left( \frac{kT}{h\nu} \right)^3 x^3 \right]$$

$$\because x = \frac{h\nu}{kT} = \frac{h\nu_D}{kT}$$

$$= \frac{d}{dT} \left[ 3NkT \left( \frac{kT}{h\nu_D} \right)^3 \left( \frac{h\nu_D}{kT} \right)^3 \right]$$

$$= \frac{d}{dT} [3NkT]$$

$$= \frac{d}{dT} [3RT] \quad \because Nk = R$$

$$C_V = 3R = 5.96 \text{ cal.} \quad \text{--- (14)}$$

Case (II) At low temperature

$$kT \ll h\nu$$

$$\frac{h\nu}{kT} \gg 1$$

$$C_V = \frac{d}{dT} \left[ 9NKT \cdot \left( \frac{KT}{h\nu_D} \right)^3 \int \frac{x^3 dx}{e^x - 1} \right]$$

$$= \frac{d}{dT} \left[ 9NKT^4 \cdot \left( \frac{K}{h\nu_D} \right)^3 \cdot \frac{\pi^4}{15} \right]$$

$$= \frac{d}{dT} \left[ \frac{3}{5} NK \pi^4 \left( \frac{K}{h\nu_D} \right)^3 \cdot T^4 \right]$$

$$= \left[ \frac{3}{5} NK \pi^4 \left( \frac{K}{h\nu_D} \right)^3 \cdot 4T^3 \right]$$

$$= \frac{12}{5} NK \pi^4 \left( \frac{K}{h\nu_D} \right)^3 T^3 \quad \text{--- (15)}$$

This is Debye  $T^3$  law.

At low temperatures the lattice sp. heat varies as  $T^3$ .