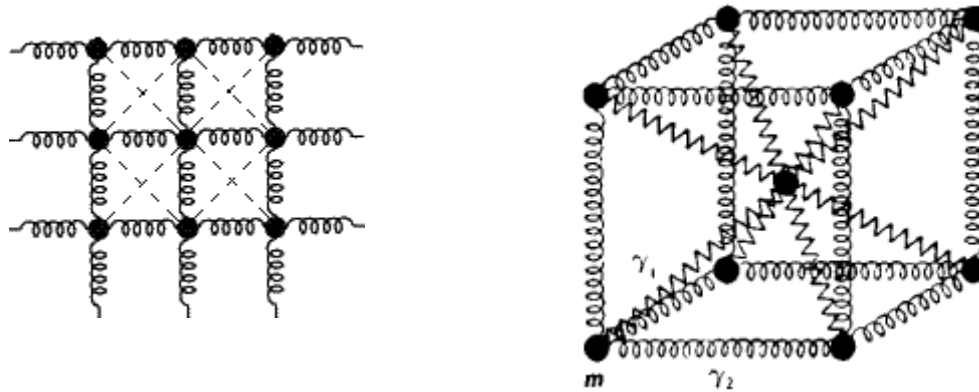


## Elementary Lattice Dynamics

*Syllabus:* Lattice Vibrations and Phonons: Linear Monoatomic and Diatomic Chains. Acoustical and Optical Phonons. Qualitative Description of the Phonon Spectrum in Solids. Dulong and Petit's Law, Einstein and Debye theories of specific heat of solids.  $T^3$  law.

### 1. Introduction:

Every atom in a crystal is surrounded by other atoms by the influence of attractive force. If an atom is displaced from its equilibrium position, the force due to other atoms comes into act to restore its equilibrium position. The lattice structure can be modeled as the atoms are connected with each other by spring in three dimensions. A schematic structure in two and three dimensions are shown here.

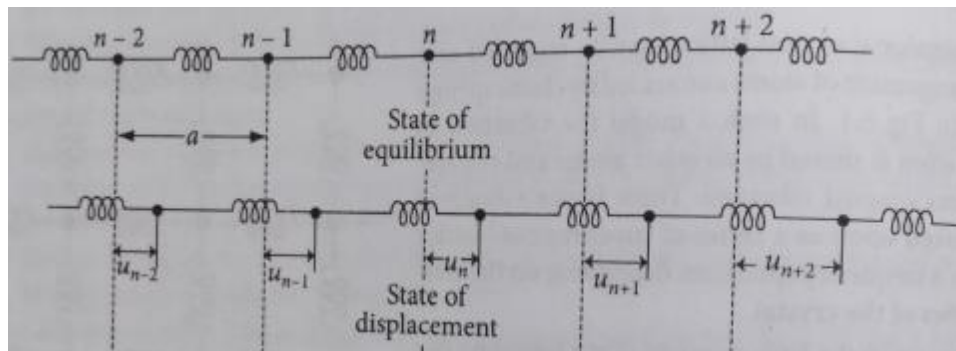


If the position of an atom is displaced by some means, it will cause displacement of neighbourhood atoms i.e., the vibration of an atom in the crystal is coupled vibration. The vibration in crystal may originate from thermal motion – the atoms vibrate in normal modes that yields thermal properties of solids like the specific heat, thermal conductivity. Another type of vibration in crystal is forced vibration which is caused due to the propagation of acoustic wave or the electromagnetic wave through the crystal that yields acoustical and some optical properties of solids. We will study such coupled vibration in one dimensional chain of lattice; we will discuss a monoatomic chain of lattice and a diatomic chain of lattice.

Here are few assumptions necessary for the study:

1. Motion of one atom is experienced by the nearest neighbouring atom only
2. The motion follows Hooke's law – that is the motion is simple harmonic  $F = -\beta u$
3. Only longitudinal motion is considered.

### 2. Linear Monoatomic Lattice Chain:



Equation of Motion:

$$F_n = \beta(u_{n+1} - u_n) - \beta(u_n - u_{n-1})$$

$$\Rightarrow m\ddot{u}_n = \beta(u_{n+1} + u_{n-1} - 2u_n) \dots (1)$$

Here one motion is resistive and the other motion is supportive. So  $-ve$  sign come between two relative displacements.  $F_n = -ve$  will make it a restoring type force.

Trial solution:

$$u_n = u_0 e^{i(\omega t - kna)}$$

$$u_{n-1} = u_0 e^{i(\omega t - k(n-1)a)} = u_n e^{-ika}$$

$$\ddot{u}_n = -\omega^2 u_0 e^{i(\omega t - kna)}$$

Substituting the trial solution in equation (1)

$$-m\omega^2 = \beta(e^{ika} + e^{-ika} - 2) = \beta \left( e^{\frac{ika}{2}} - e^{-\frac{ika}{2}} \right)^2$$

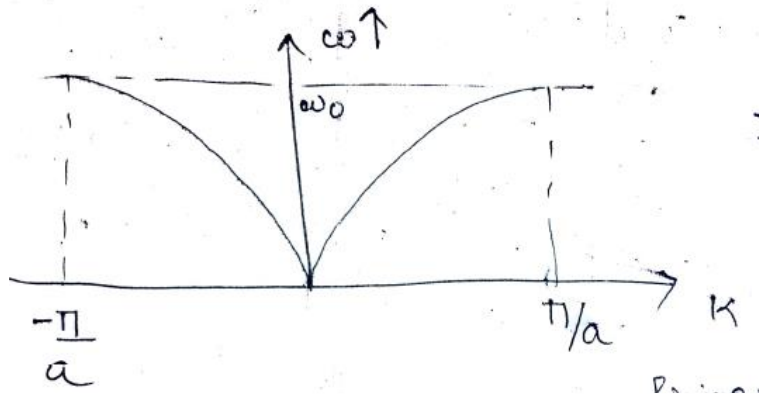
$$\Rightarrow -m\omega^2 = -4\beta \sin^2 ka/2$$

or,  $\omega^2 = \frac{4\beta}{m} \sin^2 \frac{ka}{2} \Rightarrow \omega = \pm \sqrt{\frac{4\beta}{m}} \sin \frac{ka}{2} = \pm \omega_0 \sin \frac{ka}{2} \dots (2)$

The longitudinal stiffness factor and linear mass density are respectively defined as  $C = \beta a$  and  $\rho = m/a$ . Thus equation (2) can be rewritten as (substituting  $\beta/m = c/\rho a^2$ )

$$\omega = \pm \frac{2}{a} \sqrt{\frac{C}{\rho}} \sin \frac{ka}{2} = \pm \frac{2}{a} v_s \sin \frac{ka}{2}$$

where  $v_s = \sqrt{C/\rho}$  is constant and has the dimension of velocity.



Phase velocity:

$$v_p = \frac{\omega}{k} = \frac{\omega_0}{k} \sin \frac{ka}{2}$$

Group velocity:

$$v_g = \frac{d\omega}{dk} = \omega_0 \frac{d}{dk} \sin \frac{ka}{2} = \frac{\omega_0 a}{2} \cos \frac{ka}{2}$$

Case 1: If the value of  $k$  is small (i.e., wavelength  $\lambda$  is large, or frequency is small)

$$\lim_{k \rightarrow 0} v_p \approx \frac{\omega_0 ka}{k \cdot 2} = \frac{\omega_0 a}{2} = \lim_{k \rightarrow 0} v_g$$

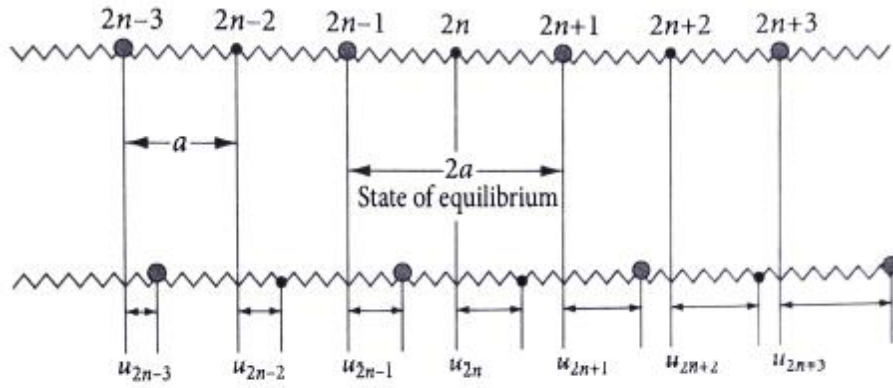
Thus for  $k \rightarrow 0$  the group velocity and the phase velocity are same which signifies that the medium will not act as dispersive medium for the long wavelength limit ( $\lambda$  large, frequency small). If acoustic wave passes the medium then it will not be dispersive as  $v_p = v_g$ .

Case 2: For a larger value of  $k$ , the group velocity differs from the phase velocity ( $v_p \neq v_g$ ). The medium thus behaves as dispersive medium for relatively shorter wavelength.

$$\text{If } \omega = \omega_0, \quad \sin \frac{ka}{2} = 1 \Rightarrow k_n = \pm \frac{n\pi}{a}, n = 1, 2, 3, \dots$$

In this case we get standing wave energy will be confined in a region. Energy will not pass through medium. Group velocity  $v_g = 0$  here as energy is not carried out through the medium.

### 3. Linear Diatomic Lattice Chain:



**Fig. 6.5:** Linear diatomic lattice in the equilibrium and disturbed states  
 $[u_{2n+3} > u_{2n+2} > u_{2n+1} > u_{2n} > u_{2n-1} > u_{2n-2} > u_{2n-3}]$

Figure: Solid State Physics by S. P. Kuila

Equations of motion:

$$\begin{aligned} F_{2n} &= m\ddot{u}_{2n} = \beta(u_{2n+1} - u_{2n}) - (u_{2n} - u_{2n-1}) \\ &= \beta(u_{2n+1} + u_{2n-1} - 2u_{2n}) \dots (1) \end{aligned}$$

$$F_{2n+1} = M\ddot{u}_{2n+1} = \beta(u_{2n+2} + u_{2n} - 2u_{2n+1}) \dots (2)$$

Trial solution:

$$\begin{aligned} u_{2n} &= Ae^{i(\omega t - k \cdot 2n \cdot a)} \\ u_{2n+1} &= Be^{i(\omega t - k \cdot \overline{2n+1} \cdot a)} \\ u_{2n+2} &= Ae^{i(\omega t - k \cdot \overline{2n+2} \cdot a)} \\ u_{2n-1} &= Be^{i(\omega t - k \cdot \overline{2n-1} \cdot a)} \end{aligned}$$

Substituting the trial solutions in equations (1) and (2), we have

$$\begin{aligned}
m(-\omega^2 A) &= \beta\{B(e^{ika} + e^{-ika}) - 2A\} \\
\text{or, } -m\omega^2 A &= \beta(2B \cos ka - 2A) \\
\Rightarrow (2\beta - m\omega^2)A - 2\beta \cos ka B &= 0 \dots (3)
\end{aligned}$$

and

$$\begin{aligned}
M(-\omega^2 B) &= \beta\{A(e^{ika} + e^{-ika}) - 2B\} \\
\text{or, } -M\omega^2 B &= \beta(2A \cos ka - 2B) \\
\Rightarrow 2\beta \cos ka A - (2\beta - M\omega^2)B &= 0 \dots (4)
\end{aligned}$$

Equations (3) and (4) yield nontrivial solutions for  $A$  and  $B$  if

$$\begin{aligned}
\begin{vmatrix} 2\beta - m\omega^2 & -2\beta \cos ka \\ 2\beta \cos ka & -2\beta + M\omega^2 \end{vmatrix} &= 0 \\
\text{or, } (2\beta - m\omega^2)(M\omega^2 - 2\beta) + (2\beta \cos ka)^2 &= 0 \\
\text{or, } -4\beta^2 + 2\beta M\omega^2 + 2\beta m\omega^2 + Mm\omega^4 + 4\beta^2 \cos^2 ka &= 0 \\
\Rightarrow Mm\omega^4 - 2\beta(M + m)\omega^2 + 4\beta^2 \sin^2 ka &= 0 \\
\Rightarrow \omega^4 - 2\beta \left(\frac{1}{M} + \frac{1}{m}\right)\omega^2 + \frac{4\beta^2}{Mm} \sin^2 ka &= 0 \dots (5)
\end{aligned}$$

$$\begin{aligned}
\therefore \omega^2 &= \frac{1}{2} \left[ 2\beta \left(\frac{1}{M} + \frac{1}{m}\right) \pm \sqrt{4\beta^2 \left(\frac{1}{M} + \frac{1}{m}\right)^2 - \frac{16\beta^2}{Mm} \sin^2 ka} \right] \\
&= \beta \left[ \left(\frac{1}{M} + \frac{1}{m}\right) \pm \sqrt{\left(\frac{1}{M} + \frac{1}{m}\right)^2 - \frac{4}{Mm} \sin^2 ka} \right] \dots (6)
\end{aligned}$$

Equation (5) yields two roots (two frequency relations between  $\omega$  and  $k$  – the dispersion relations) as in equation (6):

$$\omega_+^2 = \beta \left[ \left(\frac{1}{M} + \frac{1}{m}\right) + \sqrt{\left(\frac{1}{M} + \frac{1}{m}\right)^2 - \frac{4}{Mm} \sin^2 ka} \right] \dots (7)$$

$$\omega_-^2 = \beta \left[ \left(\frac{1}{M} + \frac{1}{m}\right) - \sqrt{\left(\frac{1}{M} + \frac{1}{m}\right)^2 - \frac{4}{Mm} \sin^2 ka} \right] \dots (8)$$

$\omega_+$  corresponds to optical mode of vibration while  $\omega_-$  corresponds to the acoustic mode of vibration (as the optical frequency is very large corresponds to acoustic frequency  $\omega_+ \gg \omega_-$ ).

Case 1: Let us now consider a special case  $ka \rightarrow 0$ ,  $\sin ka \approx 0$  – at the center of the Brillouin zone.

(a) Optical Branch: In this case ( $ka \rightarrow 0$ ,  $\sin ka \approx 0$ ) equation (7) yields

$$\omega_+ = \sqrt{2\beta \left(\frac{1}{M} + \frac{1}{m}\right)}$$

(b) Acoustic Branch: In this case ( $ka \rightarrow 0, \sin ka \approx ka$ ) equation (8) yields

$$\begin{aligned}
 \omega_-^2 &= \beta \left[ \left( \frac{1}{M} + \frac{1}{m} \right) - \sqrt{\left( \frac{1}{M} + \frac{1}{m} \right)^2 - \frac{4k^2 a^2}{Mm}} \right] \\
 &= \beta \left[ \frac{1}{\mu} - \sqrt{\frac{1}{\mu^2} - \frac{4k^2 a^2}{Mm}} \right] \text{ where } \left( \frac{1}{M} + \frac{1}{m} = \frac{1}{\mu} \right) \\
 &= \frac{\beta}{\mu} \left[ 1 - \sqrt{1 - \frac{4\mu^2 k^2 a^2}{Mm}} \right] \approx \frac{\beta}{\mu} \left[ 1 - \left( 1 - \frac{2\mu^2 k^2 a^2}{Mm} \right) \right] \\
 &= \frac{2\beta\mu k^2 a^2}{Mm} = \frac{2\beta k^2 a^2}{M+m} \\
 \therefore \omega_- &= \sqrt{\frac{2\beta}{M+m}} ka
 \end{aligned}$$

If  $k = 0$  (at the center of Brillouin Zone) then the acoustic mode will disappear, optical mode will remain.

Case 2: Let  $ka \rightarrow \pi/2, \sin ka \approx 1$  – at the boundary of the Brillouin Zone

(a) Optical Branch: In this case ( $ka \rightarrow \pi/2, \sin ka \approx 1$ ) equation (7) yields

$$\begin{aligned}
 \omega_+^2 &= \beta \left[ \left( \frac{1}{M} + \frac{1}{m} \right) + \sqrt{\left( \frac{1}{M} + \frac{1}{m} \right)^2 - \frac{4}{mM}} \right] \\
 &= \beta \left[ \left( \frac{1}{M} + \frac{1}{m} \right) + \left( -\frac{1}{M} + \frac{1}{m} \right) \right] = \beta \left( \frac{2}{m} \right) \\
 \Rightarrow \omega_+ &= \sqrt{\frac{2\beta}{m}}
 \end{aligned}$$

(b) Acoustic Branch: In this case ( $ka \rightarrow \pi/2, \sin ka \approx 1$ ) equation (8) yields

$$\begin{aligned}
 \omega_-^2 &= \beta \left[ \left( \frac{1}{M} + \frac{1}{m} \right) - \sqrt{\left( \frac{1}{M} + \frac{1}{m} \right)^2 - \frac{4}{mM}} \right] \\
 &= \beta \left[ \left( \frac{1}{M} + \frac{1}{m} \right) - \left( -\frac{1}{M} + \frac{1}{m} \right) \right] = \beta \left( \frac{2}{M} \right) \\
 \Rightarrow \omega_- &= \sqrt{\frac{2\beta}{M}}
 \end{aligned}$$

Relative amplitudes and phases for optical and acoustic mode of vibration:

Let,  $k \rightarrow 0, \cos ka \rightarrow 1$ .

$$\omega_+ = \sqrt{2\beta \left( \frac{1}{M} + \frac{1}{m} \right)}, \quad \omega_- = \sqrt{\frac{2\beta}{M+m}} ka$$

For  $\omega = \omega_+$ , we have from equation (3)

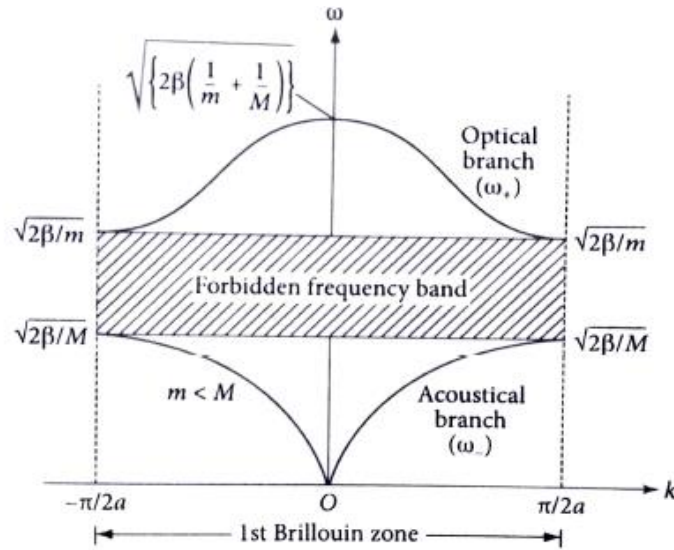
$$\begin{aligned} (2\beta - m\omega_+^2)A - 2\beta \cos ka B &= 0 \\ \Rightarrow \left[ 2\beta - m2\beta \left( \frac{1}{M} + \frac{1}{m} \right) \right] A - 2\beta B &= 0 \\ \Rightarrow -\frac{2m}{M} \beta A = 2\beta B \Rightarrow \frac{A}{B} &= -\frac{M}{m} \end{aligned}$$

Thus the atoms move out of phase in optical mode of vibration.

For  $\omega = \omega_-$ , we have from equation (3)

$$\begin{aligned} (2\beta - m\omega_-^2)A - 2\beta \cos ka B &= 0 \\ \Rightarrow \left[ 2\beta - m \frac{2\beta}{M+m} k^2 a^2 \right] A - 2\beta B &= 0 \\ \Rightarrow A &= B \end{aligned}$$

In acoustic mode of vibration, both atoms vibrate with same amplitude and in same phase.

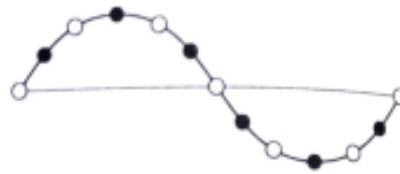


**Fig. 6.6:** Acoustical and optical branches due to a linear diatomic lattice

MODE OF VIBRATION.



**Fig. 6.7 (a):** Optical mode



**Fig. 6.7 (b):** Acoustical mode

Figure: Solid State Physics by S. P. Kuila

## Specific heat of solids

The specific heat of solids is defined as  $C_v = dU/dT$  where  $U$  is the energy of the system.

### A. Dulong–Petit Law:

Specific heats of all solids are same and that is  $6\text{cal/mol}^\circ\text{C}$

This law is based on the classical explanation and the law of equipartition energy. It assumes the atoms in a crystal as 3 dimensional harmonic oscillators. By the theorem of equipartition of energy, the average kinetic energy of 3D oscillators is  $3KT/2$ . Therefore, the total average energy of an oscillator is  $3KT$ . (average potential energy of a harmonic oscillator is same as the average kinetic energy).

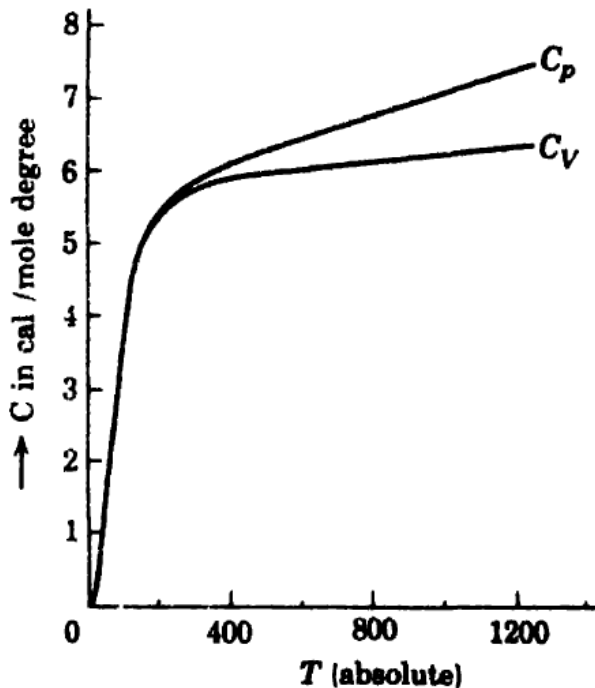
Therefore, the molar energy

$$U = 3N_AKT = 3RT$$
$$\Rightarrow C_v = \frac{dU}{dT} = 3R = 6 \text{ cal/mol}^\circ\text{C}$$

This is the same for all solids and independent of temperature. In practice, the observation is different. Dulong–Petit law is consistent at higher temperatures only.

### Limitations:

- (i) Dulong–Petit law is consistent with experimental observation at room temperature or above. At lower temperature  $C_v$  varies with  $T$ .
- (ii)  $C_v$  below the room temperature depends on the material.



$$C_p - C_v = -T \left( \frac{\partial V}{\partial T} \right)_p^2 \left( \frac{\partial p}{\partial V} \right)_T$$

## B. Einstein Model:

**Phonons:** Quantum of the vibrational energy. Energy of phonon  $E_n = nh\nu = n\hbar\omega$

It follows the similar property as photon does.

Momentum  $p = h\nu/c = \hbar\omega/c$  where  $c$  is the speed of the acoustic wave.

No of states between  $\omega$  and  $\omega + d\omega$ :

$$\begin{aligned} N(\omega)d\omega &= \frac{4\pi V (\hbar\omega)^2 \hbar}{h^3 c^2 c} d\omega \\ &= \frac{4\pi V}{8\pi^3 c^3} \omega^2 d\omega = \frac{V}{2\pi^2 c^3} \omega^2 d\omega \end{aligned}$$

No of states between  $\nu$  and  $\nu + d\nu$ :

$$\begin{aligned} N(\nu)d\nu &= \frac{4\pi V (h\nu)^2 h}{h^3 c^2 c} d\nu \\ &= \frac{4\pi V}{c^3} \nu^2 d\nu \end{aligned}$$

In Einstein model, the energy is calculated in the semi-classical approach as follows. It uses the MB statistics and phonon hypothesis.

$$\begin{aligned} N_n &= N_0 e^{-\epsilon_n/kT} = N_0 e^{-nh\nu/kT} \\ \bar{\epsilon} &= \frac{\sum_{n=0}^{\infty} \epsilon_n N_n}{\sum_{n=0}^{\infty} N_n} = \frac{\sum_{n=0}^{\infty} nh\nu e^{-nh\nu/kT}}{\sum_{n=0}^{\infty} e^{-nh\nu/kT}} = \frac{h\nu}{e^{h\nu/kT} - 1} \end{aligned}$$

Molar energy

$$\begin{aligned} U &= N_A \bar{\epsilon} = N_A \frac{h\nu}{e^{h\nu/kT} - 1} \\ \therefore C_V &= \frac{dU}{dT} = \frac{h\nu N_A (-1) e^{h\nu/kT} h\nu}{(e^{h\nu/kT} - 1)^2} \frac{1}{K} \left( -\frac{1}{T^2} \right) \end{aligned}$$

This is for one dimensional oscillator.

For a 3D oscillator

$$C_V = 3 \frac{dU}{dT} = 3N_A K \left( \frac{h\nu}{KT} \right)^2 \frac{e^{h\nu/KT}}{(e^{h\nu/KT} - 1)^2}$$

$h\nu/K$  dimensionally represents a temperature, say  $\theta_E$ . the Einstein temperature.

$$\therefore C_V = 3R(\theta_E/T)^2 \frac{e^{\theta_E/T}}{(e^{\theta_E/T} - 1)^2}$$

Note that, if quantum mechanical expression of the energy were taken  $\epsilon_n = (n + 1/2)h\nu$ , the average energy would be

$$\bar{\epsilon} = \frac{h\nu}{e^{h\nu/kT} - 1} + \frac{h\nu}{2}$$

However, the zero point energy ( $h\nu/2$ ) would not contribute to the specific heat as it is independent of temperature.



### High temperature limit:

Let the temperature is large and hence  $h\nu/KT$  is small.

$$\begin{aligned}\therefore e^{h\nu/KT} &\approx 1 + \frac{h\nu}{KT} \\ \Rightarrow \bar{\epsilon} &= \frac{h\nu}{e^{h\nu/KT} - 1} = KT \\ \Rightarrow U &= 3N_A \bar{\epsilon} = 3N_A KT = 3RT \\ \therefore C_V &= \frac{\partial U}{\partial T} = 3R\end{aligned}$$

### Low temperature limit:

At the low temperature,  $h\nu/KT$  is large and hence  $e^{h\nu/KT} \gg 1$ .

$$\begin{aligned}\therefore \bar{\epsilon} &= \frac{h\nu}{e^{h\nu/KT} - 1} \approx h\nu e^{-h\nu/KT} \\ \Rightarrow U &= 3N_A \bar{\epsilon} = 3N_A h\nu e^{-h\nu/KT} \\ \therefore C_V &= \frac{dU}{dT} = 3N_A h\nu e^{-h\nu/KT} \left(-\frac{h\nu}{K}\right) \left(-\frac{1}{T^2}\right) \\ &= 3N_A K \left(\frac{h\nu}{KT}\right)^2 e^{-h\nu/KT} \\ &= 3R \left(\frac{\theta_E}{T}\right)^2 e^{-\theta_E/T}\end{aligned}$$

### Experimental Evidences

(i) The specific heat of solid at very low temperature follows a  $T^3$  law that is  $C_V \propto T^3$  at low temperature.

### C. Debye's Theory:

Debye assumed that the vibration of solid should be consider as a whole, rather than the vibration of a single atom (as Einstein did) because the atoms in the solid form a coupled system.

Since the vibration of a solid as a whole is considered, corresponding to every longitudinal mode there will be two transverse modes of vibration. Thus the number of modes corresponding to the frequency between  $\nu$  and  $\nu + d\nu$  is

$$Z(\nu)d\nu = \frac{4\pi V}{c^3} \nu^2 d\nu$$

Let longitudinal wave speed is  $c_l$  while the transverse wave speed is  $c_t$ . Thus total number of modes considering one longitudinal and two transverse modes of vibration between the frequency range  $\nu$  and  $\nu + d\nu$  is

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

Debye pointed out that the maximum frequency must be restricted due to the fact that total number of modes of vibration must be  $3N_A$  ( $N_A$  is the Avogadro number) i.e. there is a cut off frequency called the Debye frequency  $\nu_D$ .

$$\begin{aligned}
\int_0^{\nu_D} Z(\nu) d\nu &= 3N_A \\
\Rightarrow 4\pi V \left( \frac{1}{c_l^3} + \frac{2}{c_t^3} \right) \int_0^{\nu_D} \nu^2 d\nu &= 3N_A \\
\Rightarrow \frac{4\pi V}{3} \left( \frac{1}{c_l^3} + \frac{2}{c_t^3} \right) \nu_D^3 &= 3N_A \\
\text{or, } \nu_D^3 &= \frac{9N_A}{4\pi V} \left( \frac{1}{c_l^3} + \frac{2}{c_t^3} \right)^{-1} \dots (2)
\end{aligned}$$

Equation (2) represents the expression for the Debye cut off frequency  $\nu_D$ .

Debye took the expression for average energy as calculated by Einstein, i.e.

$$\bar{\epsilon} = \frac{h\nu}{e^{h\nu/KT} - 1}$$

Thus, the total energy

$$\begin{aligned}
U &= \int_0^{\nu_D} Z(\nu) \bar{\epsilon} d\nu \\
&= 4\pi V \left( \frac{1}{c_l^3} + \frac{2}{c_t^3} \right) \int_0^{\nu_D} \frac{h\nu}{e^{h\nu/KT} - 1} \nu^2 d\nu \\
&= \frac{9N_A h}{\nu_D^3} \int_0^{\nu_D} \frac{\nu^3 d\nu}{e^{h\nu/KT} - 1} \dots (3)
\end{aligned}$$

Specific heat:

$$\begin{aligned}
C_V &= \frac{dU}{dT} = \frac{9N_A h}{\nu_D^3} \int_0^{\nu_D} \frac{\nu^3 d\nu (-1) e^{h\nu/KT}}{(e^{h\nu/KT} - 1)^2} \frac{h\nu}{K} \left( -\frac{1}{T^2} \right) \\
&= \frac{9N_A h}{\nu_D^3} \int_0^{\nu_D} \left( \frac{h}{KT^2} \right) \frac{e^{h\nu/KT} \nu^4}{(e^{h\nu/KT} - 1)^2} d\nu \dots (4)
\end{aligned}$$

Let  $h\nu/KT = x$ , Note that  $h\nu/K$  dimensionally represents a temperature. For  $\nu = \nu_D$ , let  $h\nu_D/K = \theta_D$  – the Debye temperature. Thus  $x = x_m = h\nu_D/KT = \theta_D/T$ . Substituting in equation (4), we have

$$\begin{aligned}
C_V &= \frac{9N_A h}{\nu_D^3} \int_0^{x_m} \left( \frac{h}{KT^2} \right) \frac{e^x x^4}{(e^x - 1)^2} \left( \frac{KT}{h} \right)^4 \left( \frac{KT}{h} \right) dx \\
&= \frac{9N_A h}{\nu_D^3} \int_0^{x_m} \left( \frac{K^4 T^3}{h^4} \right) \frac{e^x x^4}{(e^x - 1)^2} dx \\
&= 9N_A K \left( \frac{KT}{h\nu_D} \right)^3 \int_0^{x_m} \frac{e^x}{(e^x - 1)^2} x^4 dx
\end{aligned}$$

$$= 3R \left( \frac{3}{x_m^3} \right) \int_0^{x_m} \frac{e^x}{(e^x - 1)^2} x^4 dx = 3RD(x) \dots (5)$$

where,  $D(x)$  is called the Debye function and is defined as

$$D(x) = \left( \frac{3}{x_m^3} \right) \int_0^{x_m} \frac{e^x}{(e^x - 1)^2} x^4 dx \dots (6)$$

For large temperature  $C_V \approx 3R$ , and thus from equation (5) it is clear that the limiting value of the Debye function in this case is 1 i.e.  $D(x \rightarrow 0) \approx 1$ .

**High temperature limit:**  $T \rightarrow$  large,  $x = hv/KT \rightarrow$  small.

$$e^x \approx 1 + x \Rightarrow e^x - 1 \approx x$$

From equation (5)

$$D(x) = \left( \frac{3}{x_m^3} \right) \int_0^{x_m} \frac{1}{x^2} x^4 dx = 1$$

$\therefore$  From equation (4),  $C_V = 3R$ .

Alternative approach: For higher temperature,  $hv/KT$  is small and hence

$$e^{hv/KT} \approx 1 + \frac{hv}{KT}$$

Thus from equation (3)

$$\begin{aligned} U &= \frac{9N_A h}{v_D^3} \int_0^{v_D} \frac{v^3 dv}{e^{hv/KT} - 1} \approx \frac{9N_A h}{v_D^3} \int_0^{v_D} \frac{v^3 dv}{(hv/KT)} \\ &= \frac{9N_A}{v_D^3} KT \int_0^{v_D} v^2 dv = 3RT \\ \therefore C_V &= \frac{dU}{dT} = 3R \end{aligned}$$

**Low temperature limit:**

Recall  $x = hv/KT$ ,  $x_m = hv_D/KT$ . For low temperature,  $x_m \rightarrow \infty$ . From equation (3), we have

$$\begin{aligned} U &= \frac{9N_A h}{v_D^3} \int_0^{v_D} \frac{v^3 dv}{e^{\frac{hv}{KT}} - 1} = \frac{9N_A h}{v_D^3} \int_0^{x_m} \left( \frac{KT}{h} \right)^4 \frac{x^3 dx}{e^x - 1} \\ &= \frac{9N_A h}{v_D^3} \left( \frac{KT}{h} \right)^4 \int_0^{\infty} \frac{x^3 dx}{e^x - 1} = \frac{9N_A h}{v_D^3} \left( \frac{KT}{h} \right)^4 \left( \frac{\pi^4}{15} \right) \\ \therefore C_V &= \frac{dU}{dT} = \frac{9N_A h}{v_D^3} \left( \frac{K}{h} \right)^4 \left( \frac{\pi^4}{15} \right) 4T^3 \end{aligned}$$

$\therefore C_V \propto T^3 \rightarrow$  at very low temperature as observed experimentally.

This is the famous Debye's  $T^3$  law and it agrees well with the experimental result at low temperature. However, as  $T \rightarrow 0$  K this law fails. In that region  $C_V$  is found to vary linearly with  $T$  i.e.  $C_V \propto T$  as  $T \rightarrow 0$ .

This is not due to the lattice vibration. It is the electronic contribution of specific heat at very low temperature. At low temperature  $C_V = AT + BT^3$ .

### Difference between the Einstein and the Debye Models:

Limitations of the Debye model

1. Debye assumed continuum model of solid which is approximately true only for long wavelength vibrational modes. This assumption does not hold for short wavelength.
2. Debye assumed that the frequency of various modes of vibration is independent of temperature of solid which is also not true.
3. It is assumed that  $c_l$  and  $c_t$  are independent of frequency of vibration that means we assumed a non-dispersive medium which is not true in general.
4. Debye assumed that the total number of modes of vibration should be restricted to  $3N_A$ . However, there is no justification behind this assumption in a continuum model.
5. Debye did not consider the interaction between the atoms and the contribution of electrons to this specific heat.

