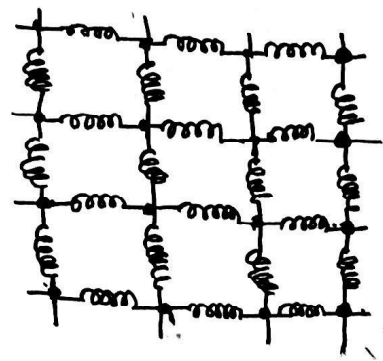


UNIT - IV

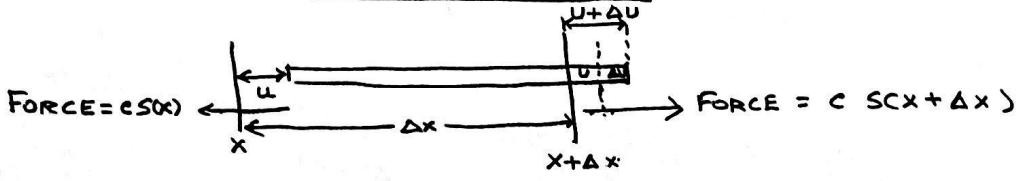
THEORY OF ELASTIC VIBRATIONS.

INTRODUCTION:



- * A lattice is usually regarded as an array of atoms connected with each other by elastic strings.
- * When an external forces are applied, motion of every atom would be shared by all the atoms and thus x would "vibrate as a whole".

ELASTIC VIBRATIONS OF 1D LINE: (HOMOGENEOUS ISOTROPIC)



- * Consider an element of a homogeneous isotropic length Δx .
- * In the presence of stress, an elastic strain is produced.
- * \therefore The elastic strain $s(x) = \frac{\partial u}{\partial x}$. — (1)
- * Let 'c' be longitudinal stiffness constant, then force is given by.

$$F(x) = c s(x) \quad \left[\because \text{In 1D, Stress} = \text{Force} \right]$$

$$+ F(x+\Delta x) = c s(x+\Delta x)$$

$$= c \left[s(x) + \frac{\partial s}{\partial x} \Delta x \right]$$

[Using Taylor's expansion $f(x) = f(a) + \frac{f'(a)}{1!} (x-a) + \frac{f''(a)}{2!} (x-a)^2 + \dots$

$$= \sum_{n=0}^{\infty} \frac{f^{(n)}(a)}{n!} (x-a)^n$$

$f^{(n)}(a)$ - is the n^{th} derivative of f at point a]

Net force $F(x+\Delta x) - F(x) = c \left(\frac{\partial s}{\partial x} \right) \Delta x$.

Related to Newton's law $c \left(\frac{\partial s}{\partial x} \right) \Delta x = m a$. — (2)

If ρ is the mass/unit length, then $\rho = m \Delta x$ & $a = \frac{\partial^2 u}{\partial t^2}$ — (3)

From eqn (1) $S(x) = \frac{\partial u}{\partial x}$.

then $\frac{\partial S}{\partial x} = \frac{\partial^2 u}{\partial x^2}$ — (4)

using (3) & (4) in eqn (2)

$$c \left(\frac{\partial^2 u}{\partial x^2} \right) \Delta x = m \frac{\partial^2 u}{\partial t^2}$$

$$c \frac{\partial^2 u}{\partial x^2} = \frac{m}{\Delta x} \frac{\partial^2 u}{\partial t^2}$$

$$\frac{\partial^2 u}{\partial x^2} = \frac{\rho}{c} \frac{\partial^2 u}{\partial t^2}$$

writing $\Rightarrow \frac{\rho}{c} = \frac{1}{v^2}$ then — (5)

$$\frac{\partial^2 u}{\partial x^2} = \frac{1}{v^2} \frac{\partial^2 u}{\partial t^2}$$

(6) — 1D Eqn of wave elastic (or) Wave Equation.

The solution of the wave equation is given by.

$$u = u_0 e^{i(\omega t - 2\pi x/\lambda)} = u_0 e^{i(\omega t - kx)}$$
 — (7)

where $k = \frac{2\pi}{\lambda}$
 $\omega = 2\pi \nu$

ω & k are related by

$$\frac{\omega}{k} = \frac{2\pi \nu}{2\pi/\lambda} = \nu \lambda = v$$

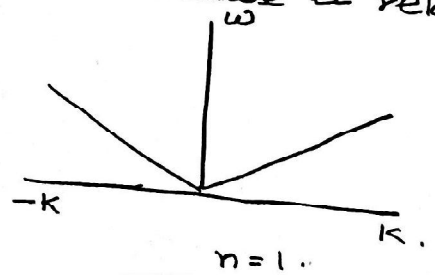
$$\frac{1}{v^2} = \frac{\rho}{c}$$

$$v = \sqrt{c/\rho}$$

$$\omega = k \sqrt{\frac{c}{\rho}}$$
 — (8)

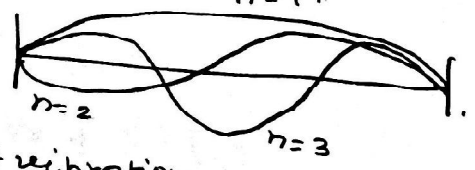
This is known as dispersion relation because it relates frequency & wavelength.

Phase velocity $v_p = \frac{\omega}{k}$
 $v_g = \frac{d\omega}{dk}$



$u = u_0 \sin kx \sin \omega t$

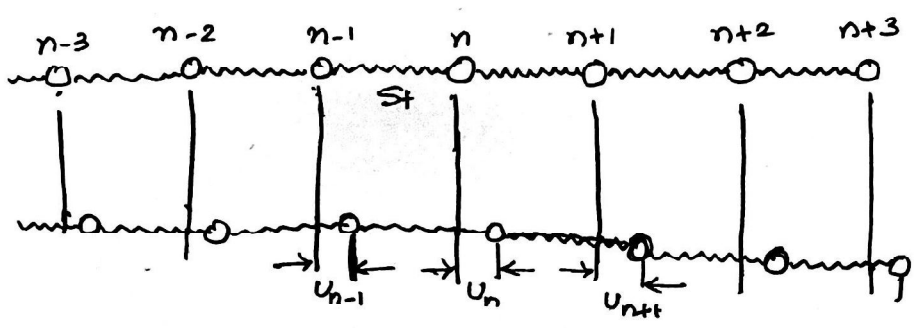
$k = \frac{\pi}{L}, \frac{2\pi}{L}, \frac{3\pi}{L}, \dots, \frac{n\pi}{L}$ n-modes of vibration.



THEORY OF ELASTIC VIBRATIONS OF MONOATOMIC LATTICES:

(Non-homogeneous medium)

* Consider a 1D chain of identical atoms each of mass 'm', Connected by Hook's law springs as shown in Fig .



* At equilibrium the atoms will be situated on equally spaced (a) site atn-1, n, n+1,..... with co-ordinates ... (n-1)a, na, (n+1)a.....

* When the vibrational motion is excited, they will execute periodic motion about their equilibrium position.

* To set up a force equations, the following assumptions are made

- a) The forces between neighbouring atoms are linear.
- b) The force required to produce the displacement is directly ppl to displacement itself.
- c) The only significant forces between atoms are due to direct nearest-neighbour interactions.

∴ The force acting on the 'n' atom due to the two springs which bind it to (n-1) + (n+1) as .

$$\begin{aligned}
 F_n &= \beta (u_{n+1} - u_n) - \beta (u_n - u_{n-1}) \\
 &= \beta (u_{n+1} + u_{n-1} - 2u_n) \quad \text{--- (1)}
 \end{aligned}$$

where β is the spring constant.

Applying Newton's second law to obtain equation of motion

$$m \frac{d^2 u_n}{dt^2} = \beta (u_{n+1} + u_{n-1} - 2u_n) \quad \text{--- (2)}$$

Periodic solution to this wave equation:

$$u_n = u_0 e^{i(\omega t - kna)} \quad \text{--- (3)}$$

Similarly for u_{n+1} & u_{n-1} ,

$$u_{n+1} = u_0 e^{i[\omega t - k(n+1)a]} \quad \text{--- (4)}$$

$$u_{n-1} = u_0 e^{i[\omega t - k(n-1)a]} \quad \text{--- (4)}$$

Substitution solutions (3) & (4) in eqn (2) we get

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

$$m\omega^2 = \beta [2 - \exp(ika) - \exp(-ika)]$$

$$\omega^2 = \frac{2\beta}{m} [1 - \cos ka] \quad \because \cos ka = \frac{e^{ika} + e^{-ika}}{2}$$

$$\omega^2 = \frac{4\beta}{m} \sin^2 \frac{ka}{2} \quad \text{--- (5)}$$

In terms of ρ and c . The dispersion equation can be written as

$$\rho = \frac{m}{a} ; \beta = \frac{c}{a} \quad \text{(or) writing } \rho = ma \text{ and } \beta = ca$$

$$\omega = \pm \frac{2}{a} \sqrt{\frac{c}{\rho}} \sin\left(\frac{ka}{2}\right) \quad \text{--- (6)}$$

ω is related k ($2\pi/\lambda$) by the above equation is known as

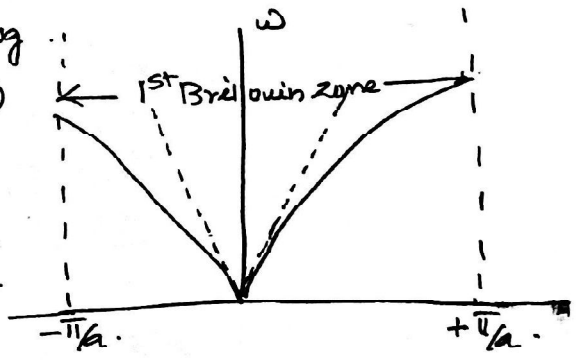
dispersion relation and is plotted in Fig

Case i: At low frequencies ($k \rightarrow 0$ i.e long w.L)

$$\sin \frac{ka}{2} \Rightarrow \frac{ka}{2}$$

$$\therefore \omega = \frac{2}{a} v_s \frac{ka}{2} = v_s k$$

Very similar to homogeneous, continuous line/medium. Phase and group velocity equal to v_s .



Case (ii) : At higher frequencies, (λ is low, κ is high) the phase velocity and group velocity are not equal

$$\left. \begin{aligned} v_g &= \frac{d\omega}{dk} = v_s \cos \frac{\kappa a}{2} \\ v_p &= \frac{\omega}{\kappa} = \frac{2v_s}{\kappa a} \sin \frac{\kappa a}{2} \end{aligned} \right\} \text{--- (8)}$$

Case (iii) : when $\kappa = \frac{\pi}{a}$, then eqn (6) becomes $\left[\kappa = \frac{2\pi}{\lambda} = \frac{\pi}{a} \text{ or } \lambda = 2a \right]$

$$\omega = \sqrt{\frac{4B}{m}} \left[\text{because } \sin \frac{1}{2} \kappa a = \sin \frac{1}{2} \left(\frac{\pi}{a} \right) a = \sin \frac{\pi}{2} = 1 \right]$$

This is called limiting frequency i.e., no signal or energy is propagated and the wave is a "standing wave".

At this condition $\kappa = \frac{\pi}{a}$, where $\kappa = \frac{2\pi}{\lambda}$

$$\left. \begin{aligned} \therefore \lambda &= 2a \\ \& \quad v_g &= 0 \quad \& \quad v_p \rightarrow \text{finite.} \end{aligned} \right\} \text{--- (9)}$$

This is equivalent to Bragg reflection of x-rays from successive planes of atoms in a crystal. ($\lambda = 2d$)

Above this frequency the lattice vibration won't exist.

(OR) The frequencies $\omega \leq \sqrt{\frac{4B}{m}} = \frac{2v_s}{a}$ will propagate down a lattice. Thus lattice act as a low-pass filter which transmits only frequency range between 0 and $2v_s/a$

Case (iv) : Associated with this limited freq (ω_0) there are many possible values of κ as shown in Fig. i.e., lattice can propagate several wavelengths at the same frequency ω_0 . The atomic displacement pattern associated with certain value of κ , say κ_1 , in the range

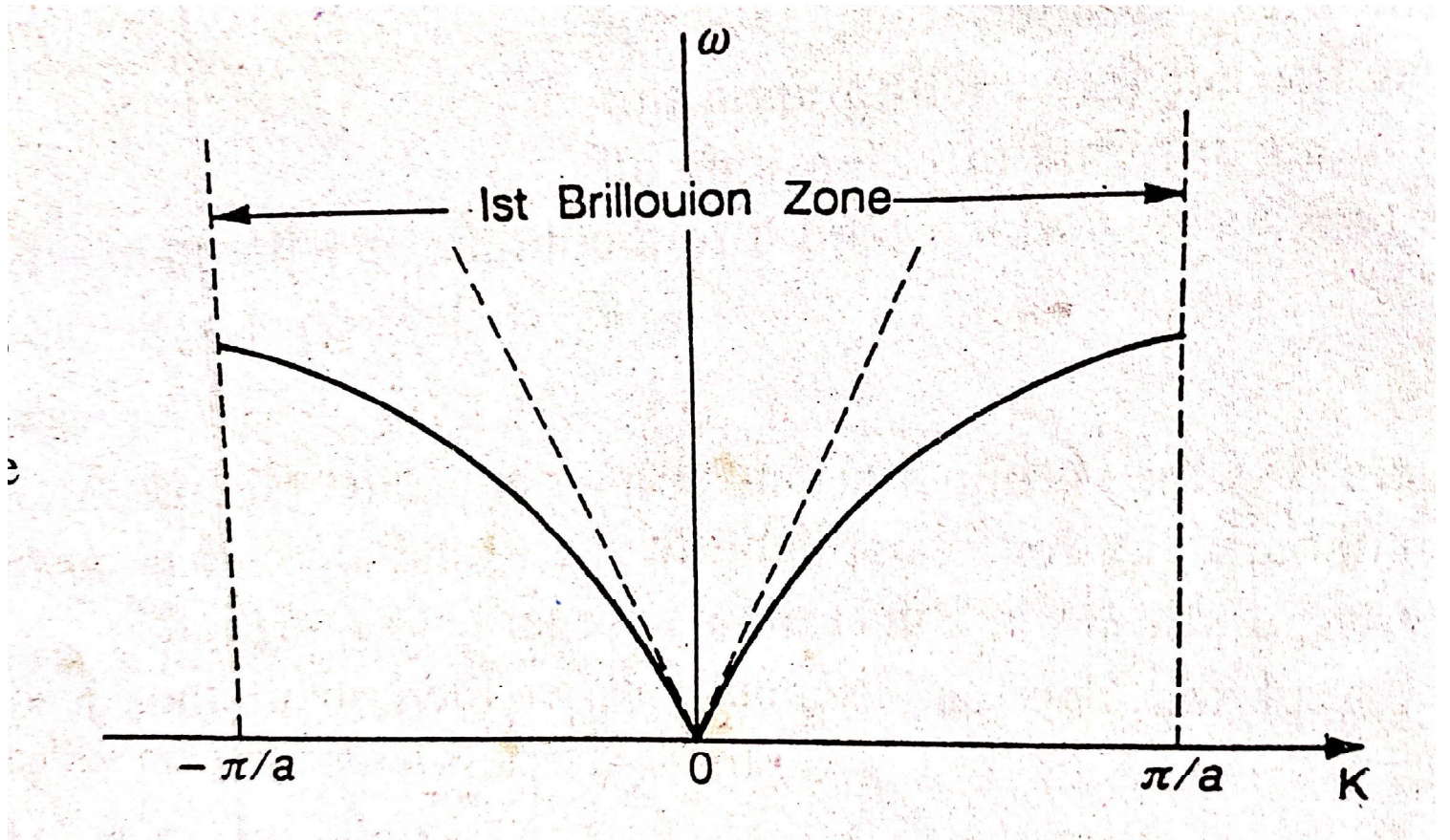
$$\boxed{-\frac{\pi}{a} < \kappa_1 < \frac{\pi}{a}}$$

BRILLOUIN ZONES:

The plot of ω vs \vec{k} shows different periods, say the central region $-\frac{\pi}{a} < k < +\frac{\pi}{a}$ marked 1 and 1' there are only two possible values: $k = \pm k_1$. The next set of region has two more possible values: $k = \pm k_2$, ... by $k = \pm k_3, \pm k_4, \dots$ marked as 2nd, 3rd, ... regions which are called Brillouin zones. (Fig. 8).

For a particular frequency ω_0 , there can be several \vec{k} values associated and hence different values of λ . From Fig. 9, same set of atomic displacements represents two waves of different wavelengths, but having the same frequency ω_0 .

The relationship between these different values of k for the same frequency ω_0 is represented as "Brillouin Zones".



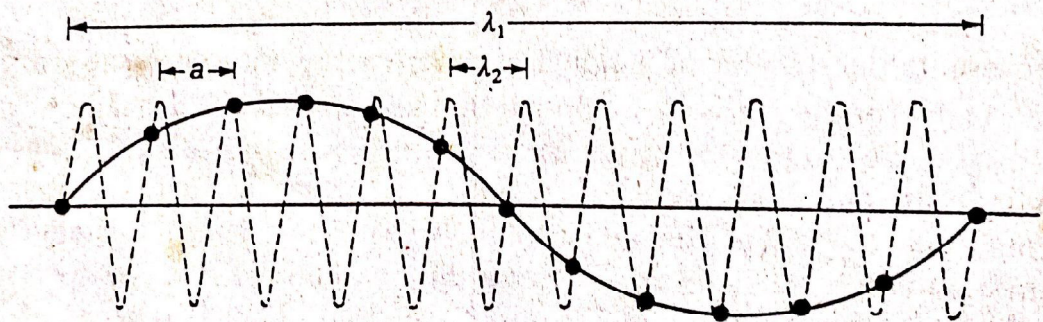
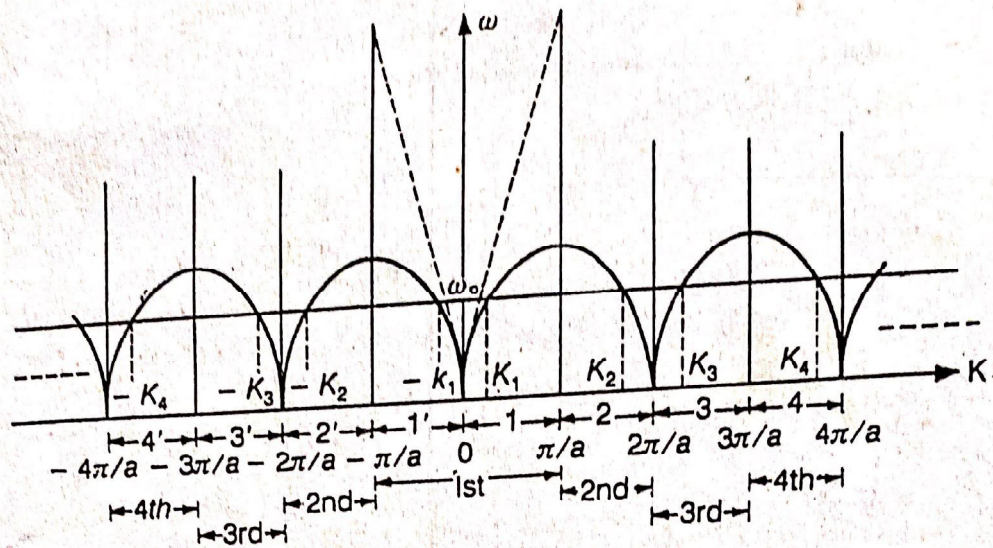


Fig. 2. A simple example of a wave packet.

PHONONS: (Unit or quantum of energy)

- * The energy in a lattice vibration is quantized.
- * The quantized energy in a particular mode 'n' is given by

$$E = n \hbar \omega$$

n - +ive integer
 $\hbar = h/2\pi = 1.05 \times 10^{-27}$ → Planck's Const.
 $\omega = 2\pi \nu$ → angular freq.

- * The energy of a particular mode of vibration is equal to integral multiple of $\hbar \omega$ (phonon).

This unit ($\hbar \omega$) is called a "phonon".

- * The no. of phonons in a ~~given~~ mode is given by

Boltzmann relation

$$\bar{n} = \frac{1}{\exp(\hbar \omega / k_B T) - 1} = \left[e^{\hbar \omega / k_B T} - 1 \right]^{-1}$$

k_B - Boltzmann Const.
 T - absolute Temp.

Consequence of Quantization: Because of the quantization,

the energy changes only to adjacent allowed values (under first order approximation), we must have

$$\Delta E = \pm \hbar \omega$$

Corresponding to $\Delta n = \pm 1$.

- * + refers to gain of one unit of energy
- refers to loss of one unit of energy.

i.e., In a neutron scattering, the change in the energy of the incident neutron must be $\pm \hbar \omega$ in each scattering

i.e., it must lose or gain only one phonon in each event.

Phonon Momentum: using de Broglie relation $p = \frac{h}{\lambda} = \frac{h(2\pi)}{2\pi \lambda} = \hbar \vec{k}$

where \vec{k} is the wave vector of the phonon & $\hbar \vec{k}$ is called the crystal momentum.

Character Chart - ELASTIC VIBRATIONS

1) Stress - Force/unit area

2) Strain - change in dimension/original dimension

3) Hooke's Law - Strain & Stress ; $F = c \Delta x$.

4) Newton's IInd Law - $F = ma$. F - Force; m - mass.
 a - acceleration.

5) Taylor's expansion/series : $f(x) = f(a) + \frac{f'(a)}{1!} (x-a) + \frac{f''(a)}{2!} (x-a)^2 + \dots$
 $= \sum_{n=0}^{\infty} \frac{f^{(n)}(a)}{n!} (x-a)^n$

6) velocity of a wave in a medium of density ρ is $v_s = \sqrt{\frac{E}{\rho}}$

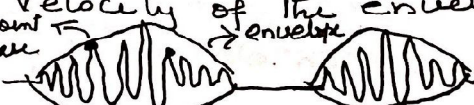
7) 1D wave equation of elastic wave : $\frac{\partial^2 u}{\partial x^2} = \frac{1}{v^2} \frac{\partial^2 u}{\partial t^2}$

8) Solution of the wave equation : $u = u_0 e^{i(\omega t - kx)}$

9) Wave vector $\vec{k} = \frac{2\pi}{\lambda}$ + ang. freq $\omega = 2\pi\nu$

10) Relation between ω , \vec{k} & v : $\frac{\omega}{k} = \frac{2\pi\nu}{2\pi/\lambda} = \nu\lambda = v$

11) Phase velocity : velocity of a point (or phase) on a wave.
 $v_p = \omega/k$

12) Group velocity : Velocity of the envelope (amplitude) or phase
 $v_g = \frac{d\omega}{dk}$

13) Solution of a Standing wave : $u = u_0 \sin kx \sin \omega t$.

14) Dispersion relation for 1D lattice vibrations : $\beta = \frac{c}{a}$; $\rho = \frac{m}{a}$

$$\omega = \sqrt{\frac{4B}{m}} \left| \sin \frac{1}{2} ka \right| = \frac{2}{a} v_s \left| \sin \frac{1}{2} ka \right|$$

15) Brillouin zone: The lattice can propagate several wavelengths for the same freq ω . (i.e.) physically express as $-\frac{\pi}{a} < k < \frac{\pi}{a}$.

16) Phonon: quantization of lattice vibration $E = n \hbar \omega$
 n - integer or zero; $\hbar \omega$ - phonon (1 quanta of vib. energy)

17) Boltzmann Distribution: Average no. of phonons in a particular mode is \bar{n} by $\bar{n} = \frac{1}{\exp(\frac{\hbar \omega}{k_B T}) - 1} = \left[e^{\frac{\hbar \omega}{k_B T}} - 1 \right]^{-1}$

18) Phonon Momentum: $p = \frac{h}{\lambda} = \frac{h}{2\pi} \frac{2\pi}{\lambda} = \hbar k \Rightarrow x^{\text{th}} \text{ momentum}$.

The Linear Diatomic Lattice

We now consider a linear lattice of two different kinds of atoms, arranged alternately as shown in fig. 11, that is, a lattice with a basis of two atoms in the primitive cell. Let each atom be separated from

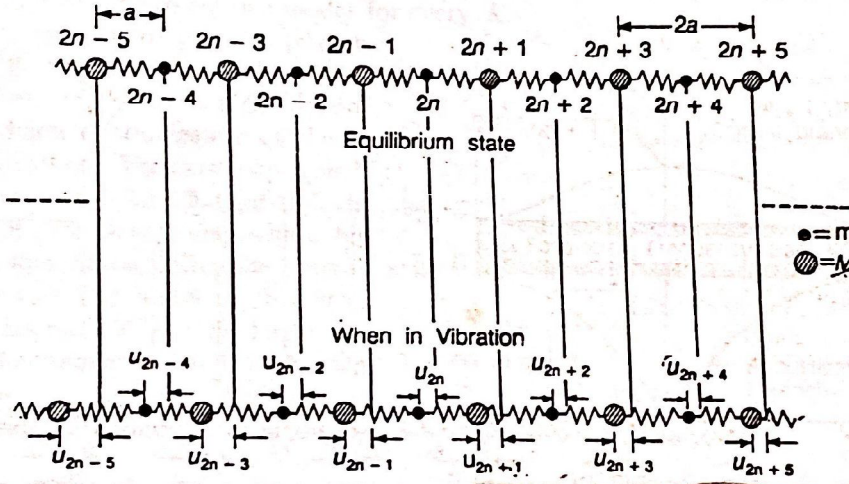


Fig. 11.

its two nearest neighbours by a distance 'a' and that the mass of the lighter atom is 'm' and of the heavier atom 'M', assuming the two kinds of atoms have different masses. We shall analyse the motion just as we did in the mono-atomic case writing, of course, separate equations of motion for the light and the heavy atoms :

$$\left. \begin{aligned} F_{2n} &= m \frac{d^2 u_{2n}}{dt^2} = \beta (u_{2n+1} - 2u_{2n} + u_{2n-1}) \\ F_{2n+1} &= M \frac{d^2 u_{2n+1}}{dt^2} = \beta (u_{2n+2} - 2u_{2n+1} + u_{2n}) \end{aligned} \right\} \dots(25)$$

under the assumption that each atom interacts only with its nearest neighbours and that the force constants are identical between all pairs of nearest neighbours. We must seek running wave solutions of the type :

$$\left. \begin{aligned} u_{2n} &= A e^{i(\omega t - 2Kna)} \\ u_{2n+1} &= B e^{i[\omega t - (2n+1)Ka]} \end{aligned} \right\} \dots(26)$$

where K is the wavevector of a particular mode of vibration. Note that the frequency of the two types of atoms is being taken the same. This is because both types of atoms participate in the single wave motion K . Amplitudes are, however, different because of the difference in their masses. Writing similarly the expressions for u_{2n+2} and u_{2n-1} and substituting them into (25), we get the two equations

$$\left. \begin{aligned} -m\omega^2 A &= \beta B (e^{-iKa} + e^{iKa}) - 2\beta A \\ -M\omega^2 B &= \beta A (e^{-iKa} + e^{iKa}) - 2\beta B \end{aligned} \right\} \dots(27)$$

Writing $2 \cos Ka$ for $(e^{-iKa} + e^{iKa})$, and rearranging the terms, we have

$$\left. \begin{aligned} (2\beta - \omega^2 m) A - (2\beta \cos Ka) B &= 0 \\ (-2\beta \cos Ka) A + (2\beta - \omega^2 M) B &= 0 \end{aligned} \right\} \dots(28)$$

This set of homogeneous linear equations has a non-vanishing solution for A and B only if the determinant of the coefficients of A and B vanishes, i.e.

$$\begin{vmatrix} 2\beta - m\omega^2 & -2\beta \cos Ka \\ -2\beta \cos Ka & 2\beta - M\omega^2 \end{vmatrix} = 0$$

or

$$(2\beta - M\omega^2)(2\beta - m\omega^2) - 4\beta^2 \cos^2 Ka = 0$$

or

$$\omega^4 - \frac{2\beta(m+M)}{mM} \omega^2 + \frac{4\beta^2 \sin^2 Ka}{mM} = 0$$

giving finally

$$\omega^2 = \beta \left(\frac{1}{m} + \frac{1}{M} \right) \pm \beta \sqrt{\left[\left(\frac{1}{m} + \frac{1}{M} \right)^2 - \frac{4 \sin^2 Ka}{Mm} \right]} \dots(29)$$

This is the dispersion relation for the linear diatomic lattice. This may be compared with the corresponding relation for the linear monatomic lattice (11) :

$$\omega^2 = \frac{4\beta}{m} \sin^2 \frac{Ka}{2}$$

The diatomic case evidently has two values of ω corresponding to a single value of the wave vector K (considering only the positive values of ω). We may denote these two values of ω by ω_+ and ω_- corresponding to whether the + or - sign is taken in (29). We consider first ω_+ . For $K \rightarrow 0$ we can neglect the sine term. So we have

$$\omega_+ = \sqrt{\left[2\beta \left(\frac{1}{m} + \frac{1}{M} \right) \right]} \dots(30)$$

For $K \rightarrow \frac{\pi}{2a}$, the sine term becomes $\frac{-4}{Mm}$ and we have

$$\omega_+ = \sqrt{\left(\frac{2\beta}{m} \right)} \dots(31)$$

We now consider ω_- . For $K \rightarrow 0$ the sine term becomes $(4K^2 a^2 / Mm)$. (In this case we cannot neglect it because it proves to be the only non-zero term). We get

$$\begin{aligned} \omega^2 &= \beta \left(\frac{1}{M} + \frac{1}{m} \right) - \beta \left(\frac{1}{m} + \frac{1}{M} \right) \sqrt{\left(1 - \frac{Mm}{(M+m)^2} 4K^2 a^2 \right)} \\ &= \beta \left(\frac{1}{m} + \frac{1}{M} \right) \left[1 - \sqrt{\left(1 - \frac{Mm}{(M+m)^2} 4K^2 a^2 \right)} \right] \end{aligned}$$

$$= \beta \left(\frac{1}{m} + \frac{1}{M} \right) \left[1 - 1 + \frac{mM}{(M+m)^2} 2K^2 a^2 \right]$$

$$= \frac{2\beta}{M+m} K^2 a^2.$$

$$\therefore \omega_- = Ka \sqrt{\left(\frac{2\beta}{M+m} \right)}. \quad \dots(32)$$

For $K \rightarrow (\pi/2a)$, the solution is similar to (31) except that m is replaced by M :

$$\omega_- = \sqrt{\left(\frac{2\beta}{M} \right)}. \quad \dots(33)$$

The solution (29) is plotted in fig. 12 together with the other derived solutions (30), (31), (32) and (33). We observe :

(1) The allowed frequency range of propagation is split into an upper branch called the optical branch and a lower branch called the acoustical branch. The acoustical branch looks qualitatively similar to the dispersion relation for a monatomic lattice, but the optical branch represents a completely different type of wave motion. Anyway, there are two modes for every K .

(2) There is a band of frequencies (shown shaded) between the two branches for which the wave-like solutions (of the form (26)) do not exist. This is a characteristic feature of elastic waves in diatomic lattices. The existence of such a band would mean that it is not possible to excite vibrations of a frequency lying within this band. It is, due to this reason, called the 'forbidden frequency band'. The width of this band depends on the mass ratio M/m —the larger this ratio, the wider the frequency band. If the two masses are equal, the two branches join at $K = \pm(\pi/2a)$ and the forbidden band disappears.

(3) The first Brillouin zone goes in this case from $K = -(\pi/2a)$ to $K = +(\pi/2a)$. Therefore the smallest possible wavelength of this Brillouin zone is $4a$, corresponding to the value $\pi/2a$ of K at the zone boundary.

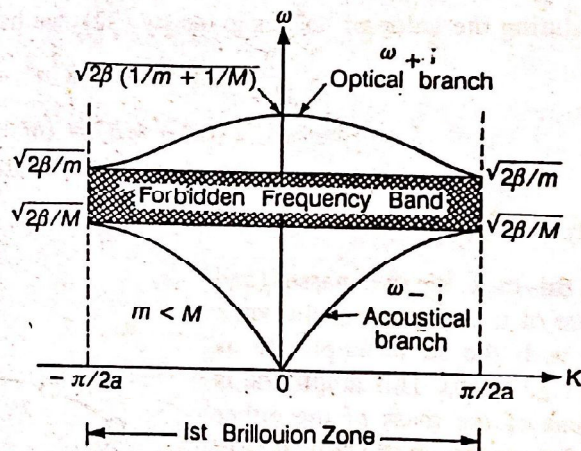


Fig. 12.

Now one might ask what is the physical significance of the forbidden frequency band?

HEAT CAPACITY

(8)

Ist LAW OF THERMODYNAMICS!

The amount of heat dq added to a system must be equal to the increase in energy dE plus the amount of work done by the system.

$$dq = dE + P dv$$

Then specific heat at constant volume is

$$C_v = \left[\frac{\partial Q}{\partial E} \right]_v = \left[\frac{\partial E}{\partial T} \right]_v$$

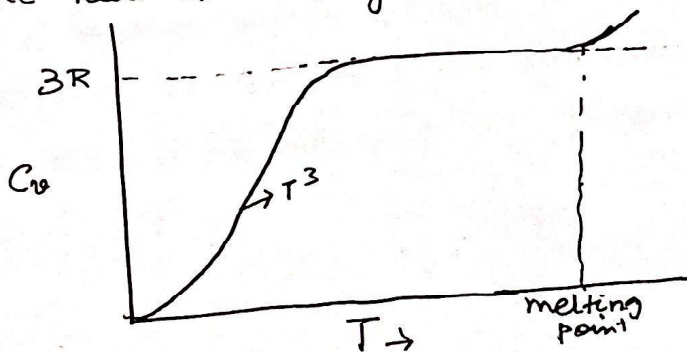
HEAT CAPACITY OF A SUBSTANCE! It is the amount of heat energy required to raise the temperature of the substance by 1K.

SPECIFIC HEAT CAPACITY! It is the amount of heat energy required to raise the 1 kg of substance by 1 K.

There are 2 types of sp. heat capacities (i) C_v & (ii) C_p . i.e., sp. heat capacities at constant volume (C_v) and at constant pressure (C_p)

C_v can be obtained from the energy of the system immediately and is more useful.

* The heat capacity / kg mol of a substance is called molar heat capacity and is obtained by multiplying the specific heat C_v (or C_p) by the mol-wt of the substance.



* Figure Shows the experimental Variation of molar sp. heat of some typical Solids as a function of temp. The following observations were noted:

(i) At elevated temps C_v is flat (or) Constant (i.e., independent of temp) and equal to 3 times gas Constant R (KJ/mol) per kmol. This is called Dulong - Petit law. It holds to just below melting point.

(ii) At low temperatures C_v begins to fall off and approaches zero as $T \rightarrow 0$.

(iii) As temperature approaches near zero, the C_v obeys T^3 law. i.e. $C_v = \text{Const} \times T^3$.

CLASSICAL THEORY OF LATTICE SP. HEAT CAPACITY:

- Assumptions of the theory: (i) Solid x^L s are assembly of atoms held together by binding forces. (Stretched String)
 - (ii) Atoms are free to vibrate about their equilibrium positions subject to the constraining forces which obey Hooke's law
 - (iii) The effect of temp (or) thermal energy would set these atoms to vibrate as harmonic oscillators.
- " \therefore Each atom is a classical 3D harmonic oscillator which vibrates independently of all other atoms in a x^L ."

The above assumptions are common to all theories of sp. heat and the distinction/difference between them is based on their frequency spectrum or energy choices.

(10)

* In classical theory, 1D harmonic oscillator is treated first and then extended it to 3N 1D harmonic oscillator.

* The energy of a harmonic oscillator of ang. freq. ω may be written

$$E = \frac{p^2}{2m} + \frac{m\omega^2 x^2}{2} \quad \text{--- (1)}$$

\downarrow \downarrow
 K.E P.E.

p - momentum.
 x - displacement from equilibrium position.

The average energy of a harmonic oscillator according to Classical mechanics is given by

$$\bar{E} = \frac{\int_0^\infty E e^{-E/K_B T} dE}{\int_0^\infty e^{-E/K_B T} dE}$$

$$\bar{E} = K_B T. \quad \text{--- (2)}$$

T - absolute Temp
 K - Boltzmann const

Then vibrational energy of N atoms is classically equal to

$$E = 3NKT. \quad \text{--- (3)}$$

$$\text{Then } C_v = \frac{dE}{dT} = 3Nk = 3R = 5.96 \text{ cal/deg/mol.} \quad \text{--- (4)}$$

where R - gas constant. If the solid contains N atoms of 'A' and N atoms of 'B', the sp. heat/mole would be 6R.

* This result is in quantitative agreement with expt at high temps. only.

* It does not explain the decrease of the sp. heat at low temp as experimentally observed.

This drawback is removed when quantum theory is used.

EINSTEIN THEORY!

ASSUMPTIONS: (i) X^l is regarded as an aggregate of atomic oscillators.

(ii) All of them vibrate independently with same natural frequency ω_0 instead of classical harmonic oscillator i.e. quantum harmonic oscillator.

(iii) These quantum harmonic oscillators have only discrete energy values i.e. $E_n = n h \omega_0$ with $n = 0, 1, 2, 3, \dots$ (5)

(iv) Based on thermal properties, the vibration of N atoms is represented by $3N$ one dimensional independent harmonic oscillators, whose energy levels are given by eqn (5).

Let us write the no of such oscillators at energy E is ppl to $\exp(-E/k_B T)$. Then the average energy is (6)

$$\bar{E} = \frac{\sum_{n=0}^{\infty} E_n \exp(-E_n/k_B T)}{\sum_{n=0}^{\infty} \exp(-E_n/k_B T)} = \frac{h \omega_0 \sum_{n=0}^{\infty} n \exp(-E_n/k_B T)}{\sum_{n=0}^{\infty} \exp(-E_n/k_B T)}$$

Sub (5) in (6)

$$\bar{E} = \frac{h \omega_0 [\exp(-h \omega_0/k_B T) + 2 \exp(-2h \omega_0/k_B T) + \dots]}{[1 + \exp(-h \omega_0/k_B T) + \exp(-2h \omega_0/k_B T) + \dots]}$$

Writing $x = -h \omega_0/k_B T$, we have.

$$\begin{aligned} \bar{E} &= \frac{h \omega_0 (e^x + 2e^{2x} + \dots)}{(1 + e^x + e^{2x} + \dots)} \\ &= h \omega_0 \frac{d}{dx} \left[\log(1 + e^x + e^{2x} + \dots) \right] \\ &= h \omega_0 \frac{d}{dx} \left\{ \log(1 - e^x)^{-1} \right\} = \frac{h \omega_0}{(e^{-x} - 1)} \end{aligned}$$

$$\bar{E} = \frac{h \omega_0}{e^{h \omega_0/k_B T} - 1} \quad \text{--- (7)}$$

On Comparison with classical theory expression for $\bar{E} = k_B T$ [eqn (1)], the eqn (2) contains the frequency of the oscillator.

The internal energy of the x^l is obtained by multiplying the average energy (\bar{E}) by the no. of oscillators $3N$, then

$$E = \frac{3N \hbar \omega_0}{\left[\exp\left(\frac{\hbar \omega_0}{k_B T}\right) - 1 \right]}$$

$$\left[\frac{d}{dT} \left[\frac{1}{e^{\hbar \omega_0 / k_B T} - 1} \right] = \frac{d}{dT} \left[e^{\hbar \omega_0 / k_B T} - 1 \right]^{-1} \right]$$

$$C_v = \left(\frac{dE}{dT} \right)_v = 3N k_B \left(\frac{\hbar \omega_0}{k_B T} \right)^2 \frac{\exp(\hbar \omega_0 / k_B T)}{\left[\exp(\hbar \omega_0 / k_B T) - 1 \right]^2} \quad \text{--- (8)}$$

Eqn (8) can be written by using Einstein temp θ_E i.e., in eqn (8) substituting $\theta_E = \frac{\hbar \omega_0}{k_B}$, then

$$C_v = 3N k_B \left(\frac{\theta_E}{T} \right)^2 \frac{\exp(\theta_E / T)}{\left[\exp(\theta_E / T) - 1 \right]^2} \quad \text{--- (10)}$$

Case (i): For higher temp $T \gg \theta_E$ $\exp \frac{\theta_E}{T} \approx 1 + \frac{\theta_E}{T}$ + eqn (10) becomes

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

$C_v \approx 3N k_B \Rightarrow$ Dulong + Petit's value.

Case (ii): For low temp $T \ll \theta_E$ $\exp(\frac{\theta_E}{T}) \gg 1$, then eqn (10) can be approximated to

$$C_v = 3N k_B \left(\frac{\theta_E}{T} \right)^2 \exp(-\theta_E / T) \quad \text{--- (11)}$$

C_v approaches zero as $T \rightarrow 0$ in the low temp region. It decreases exponentially with 'T' but not as T^3 at very low temp. Hence Einstein theory fails to explain T^3 law at low temp when it approaches zero. Hence it needs some modification.

CHARACTERS CHART

1) 1ST LAW OF THERMODYNAMICS: $dQ = dE + P dv$
 ↓ ↓ ↓
 Energy Gn to Increase Work done
 System in Energy by the system.

2) SP. HEAT AT CONSTANT VOLUME (C_v) = $\left(\frac{dQ}{dT}\right)_v = \left(\frac{dE}{dT}\right)_{dv=0}$

3) HEAT CAPACITY: Amount of heat energy required to raise the temp of the substance by 1K.

4) Specific Heat Capacity: Heat energy required to raise 1 kg of substance by 1K.

5) Mol. Sp. Heat Capacity: Mol. wt x Sp. Heat.

6) DULONG-PETIT LAW: At elevated temps, the C_v is const and is $\approx 3R$.
 R is gas const. $R = Nk_B$.

7) T³ LAW: At low temp (very close to zero) the C_v decreases rapidly to the 3rd power of temp. $C_v \propto T^3$.

8) Energy of a harmonic oscillator: $E = \frac{p^2}{2m} + \frac{m\omega^2 x^2}{2}$
 ↓ ↓
 K.E P.E
 p - momentum
 ω - ang. freq
 x - displacement of atom.
 m - mass

9) No of atoms having energy E is $\bar{n} = \int_0^{\infty} e^{-E/k_B T} dE$

10) Average energy $\bar{E} = \frac{\text{energy} \times \text{no of atoms}}{\text{no of atoms}} = \frac{\int_0^{\infty} E e^{-E/k_B T} dE}{\int_0^{\infty} e^{-E/k_B T} dE}$

11) Classical Theory: $E_v = 3Nk_B T$; $C_v = \frac{dE}{dT} = 3Nk_B \approx 3R = 5.96 \frac{\text{Joule}}{\text{mol}}$

12) Energy of a quantum harmonic oscillator: $E_n = n \hbar \omega_0$ [$n = 0, 1, 2, 3, \dots$]

13) quantum energy of an oscillator: $\bar{E} = \frac{\hbar \omega_0}{e^{\hbar \omega_0 / k_B T} - 1}$

14) Einstein temp (θ_E): $\theta_E = \frac{\hbar \omega_0}{k_B}$ ⇒ Temp above which C_v behaves at high temp; Below which it obey T or T³ laws.

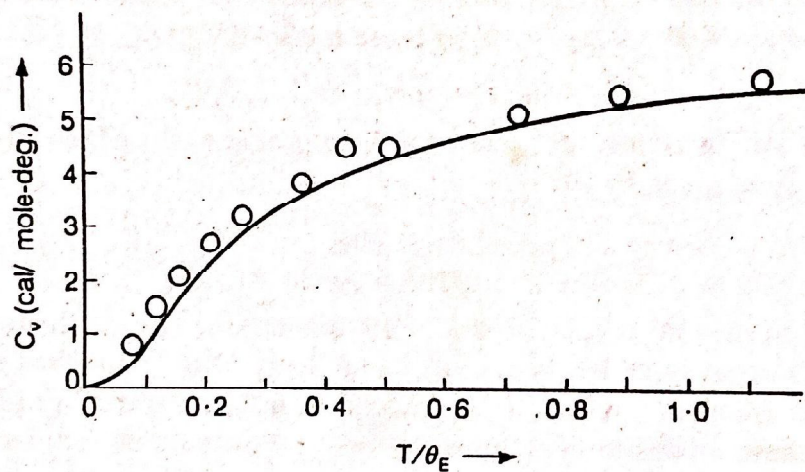


Fig. 5. Comparison of experimental heat capacity with that calculated from the Einstein's theory for diamond,

DEBYE THEORY

- ASSUMPTIONS: (i) The atoms of the crystal are treated as harmonic oscillators. (ii) But they are incapable of vibrating independently i.e. they are coupled together strongly and oscillate relative to their neighbouring lattice. (iii) The atoms are capable of propagating elastic waves whose frequency might vary over a wide range of values ($\nu \pm d\nu$). Therefore the vibrational motion of the crystal is considered as whole (or continuum) rather than vibration motion of single atom. The total no. of vibrational modes be $3N$, N being the no. of atoms.

In other words, Debye model suggest that the frequency spectrum corresponding to a perfect continuum (whole crystal) is cut off so as to comply with $3N$ modes. This assumption leads to Debye cut off frequency ω_D , which is defined as

$$\int_0^{\omega_D} D(\omega) d\omega = 4\pi V \left(\frac{2}{c_l^3} + \frac{1}{c_t^3} \right) \int_0^{\omega_D} \omega^3 d\omega = 3N \quad \text{--- (1)}$$

where $D(\omega) d\omega$ is the no. of possible modes of vibration in the frequency interval between $\omega + \omega + d\omega$ called density of frequency states.

The allowed energy levels of each mode is given by.

$$E_n = n h \omega \quad \text{where } n = 0, 1, 2, 3 \quad \text{--- (2)}$$

According to Maxwell-Boltzmann distribution law, their average energy is given by.

$$\bar{E} = \frac{h\omega}{\exp(h\omega/k_B T) - 1} \quad \text{--- (3)}$$

The contribution made by the density of frequency states $D(\omega) d\omega$ to the internal energy is then written as.

$$dE = \bar{E} D(\omega) d\omega \quad \text{--- (4)}$$

The total internal energy of the x^l is obtained by integrating eqn (4) over ω between the limits 0 to ω_D so as to include all the $3N$ normal modes of vibrations.

$$E = \int_0^{\omega_D} \bar{E} D(\omega) d\omega = \int_0^{\omega_D} D(\omega) \frac{\hbar\omega}{\exp(\hbar\omega/k_B T) - 1} d\omega$$

$$= 9N \left(\frac{k_B T}{\hbar\omega_D}\right)^3 k_B T \int_0^{x_m} \frac{x^3 dx}{e^x - 1} \rightarrow (5)$$

Where $x = \frac{\hbar\omega}{k_B T}$ + $x_m = \frac{\hbar\omega_D}{k_B T}$; It is convenient to introduce a characteristic temperature known as Debye temperature θ_D by $\theta_D = \frac{\hbar\omega_D}{k_B}$, then eqn (5) becomes

$$E = 9N k_B T \left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{x^3}{e^x - 1} dx \quad (6)$$

By differentiating (6) w.r.t. $\frac{T}{\theta_D}$ gives C_v ,

$$C_v = 9N k_B \cdot \left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx \quad (7)$$

This is the Debye formula for heat capacities of solids.

Case i: At high temp $T \gg \theta_D$, x is very small (i.e. $x \ll 1$), then

$e^x - 1 \approx 1 + \frac{x}{1!} + \dots - 1 = x$; substituting eqn (6)

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

$$= 3N k_B T$$

$C_v = 3N k_B \Rightarrow$ Dulong-Petit Law.

Case ii: At low temp $T \ll \theta_D$, the upper limit becomes infinity (∞)

and $\int_0^{\infty} \frac{x^3}{e^x - 1} dx = \frac{\pi^4}{15}$; Then eqn (6) becomes.

$$E = 9N k_B T \left(\frac{T}{\theta_D}\right)^3 \frac{\pi^4}{15}$$

$$C_v = \frac{12\pi^4}{5} N k_B \left(\frac{T}{\theta_D}\right)^3$$

$$= 234 N k_B \left(\frac{T}{\theta_D}\right)^3 \Rightarrow \text{DEBYE } T^3 \text{ LAW}$$

Thus the Debye theory satisfactorily account for the variation of heat capacity in the low temp region.

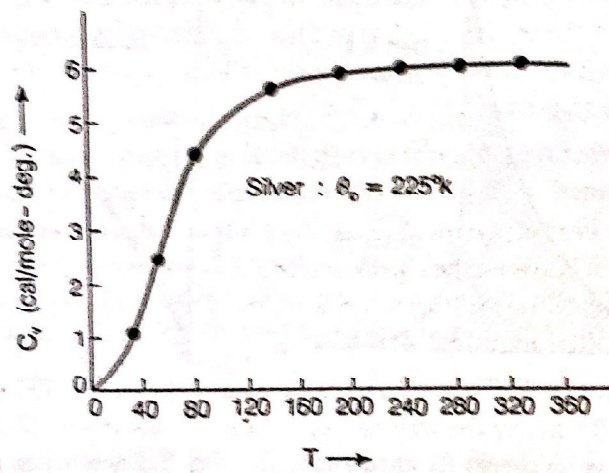
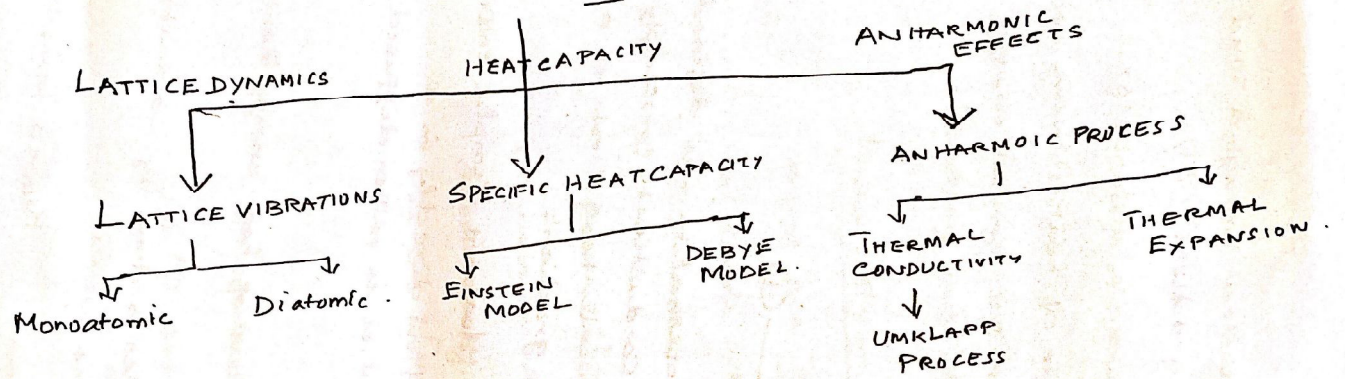


Fig. 9. Comparison of the Debye heat capacity curve (eqn. 32) with the observed values (dots) for silver.

UNIT - IV



THERMAL CONDUCTIVITY

- * All solids conduct heat.
- * The rate at which heat is conducted through a solid depends upon the temperature gradient ($\Delta T/\Delta x$).
i.e., temp diff (ΔT) exist between a distance (Δx).
- * Suppose ΔQ be the magnitude of heat flowing over an area A in a time Δt , then the thermal energy flux is expressed as $\frac{1}{A} \frac{\Delta Q}{\Delta t}$.

From the above two statements

$$\frac{1}{A} \frac{\Delta Q}{\Delta t} \propto \frac{\Delta T}{\Delta x}$$

$$\boxed{\frac{1}{A} \frac{\Delta Q}{\Delta t} = -k \frac{\Delta T}{\Delta x}} \quad \text{--- (1)}$$

where k is the constant of proportionality + is defined as the co-efficient of thermal conductivity (or) simply thermal conductivity. - sign indicates heat flows in a direction opposite to that of the gradient.

- * This implies that thermal energy does not simply enter one end of the specimen and flow directly in a straight path to the other end, but it is rather diffused through the specimen.
- * In normal insulators the process of heat energy transfer is done by lattice waves.
- * In metals, the energy transfer is done by conduction electrons as well as by lattice waves.

$$\therefore K_{\text{total}} = K_{\text{phonon}} + K_{\text{electron}} \quad \left[K_{\text{elec}} = 0 \text{ for insulators} \right]$$

└ (2)

Using Debye model, the thermal conductivity k is defined by the relation

$$\boxed{k = \frac{1}{3} C_v \lambda \bar{c}} \quad \text{--- (3)}$$

λ is the mean free path between phonon-phonon collisions and \bar{c} is average phonon velocity.

MEAN PHONON / FREE PATH (λ):

λ is determined by two principal processes (i) geometrical scattering & (ii) Phonon-phonon scattering.

Geometrical scattering - arises only when lattice vibrations are purely harmonic, there are no collisions between different phonons and the collisions of phonons ~~are~~ only with xL boundary and the lattice imperfections.

Phonon-phonon scattering - arises when the forces between atoms are "anharmonic". It is the only mechanism in solids which may bring about the distributions of phonons locally in to thermal equilibrium.

Phonon-phonon collisions would tend to restore the equilibrium and the rate of this restoring process is described by the selection rules as given below:

If two phonons 1 and 2 collide it will produce 5^{th} phonon

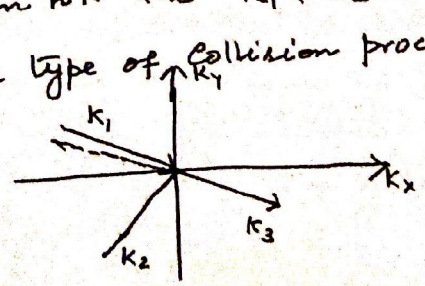
$$\therefore \omega_1 + \omega_2 = \omega_3 \quad \text{--- (1)}$$

$$k_1 + k_2 = k_3 + G \quad \text{--- (2) where } G \text{ is the}$$

2π times of the R.L. vector.

Eqn (1) expresses the conservation of energy $\hbar\omega$: two phonons of energies $\hbar\omega_1$ & $\hbar\omega_2$ may give rise to a single phonon of energy $\hbar\omega_3$ which is equal to sum of individual phonon energies.

Eqn (2), on assuming $G=0$ leads to conservation of momentum $\hbar k$ i.e. $k_1 + k_2 = k_3$. Periodic lattices or crystals. These type of collision process are called normal or N process



N-process
 $k_1 + k_2 = k_3$

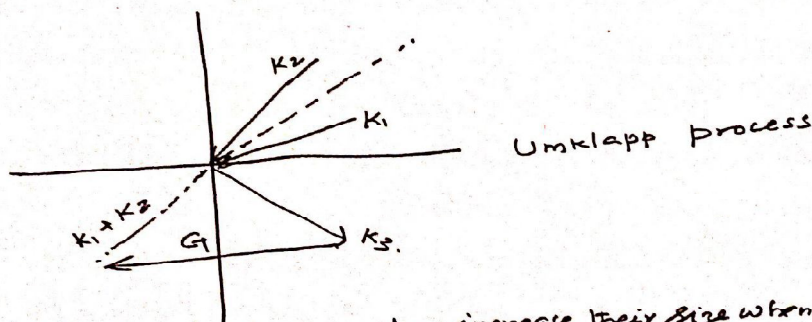
UMKLAPP PROCESS:

Any collision process which satisfy the selection rules $\omega_1 + \omega_2 = \omega_3$

$$k_1 + k_2 = k_3 + q \quad \text{where } q \neq 0$$

and there is no conservation of momentum and the direction of energy flow is changed after the collision.

These collision process are responsible for "Thermal resistance" in solids. This process of collision is called U-process or Umklapp process.



Thermal Expansion: (i) All solids expand or increase their size when heated

Co-efficient linear Expansion (α) is defined as the ratio of the increase in length of solid per degree rise of temp to original length. If l_1 & l_2 are the lengths at two temps $t_1^\circ C$ & $t_2^\circ C$, then

$$\alpha = \frac{l_2 - l_1}{l_1 (t_2 - t_1)}$$

If l_0 is the length at $0^\circ C$ + l_t at $t^\circ C$

$$\text{then } \alpha = \frac{l_t - l_0}{l_0 t} = \frac{1}{l} \frac{dl}{dt}$$

linear expansion is related superficial expansion (β) and volume expansion (γ) through the relations

$$\beta = 2\alpha \quad \text{and} \quad \gamma = 3\alpha \quad (\text{for isotropic solids})$$

$$\gamma = \alpha_1 + \alpha_2 + \alpha_3 \quad (\text{for anisotropic solids})$$

to an increase in the average interatomic distance corresponding to thermal expansion.

If the oscillators are purely harmonic— that is, if the potential energy of an oscillator is a parabolic function of its position— the average positions of different oscillators would not be the functions of temperature (or energy) despite increasing amplitudes, as is illustrated by fig. 17 (a). No change in the

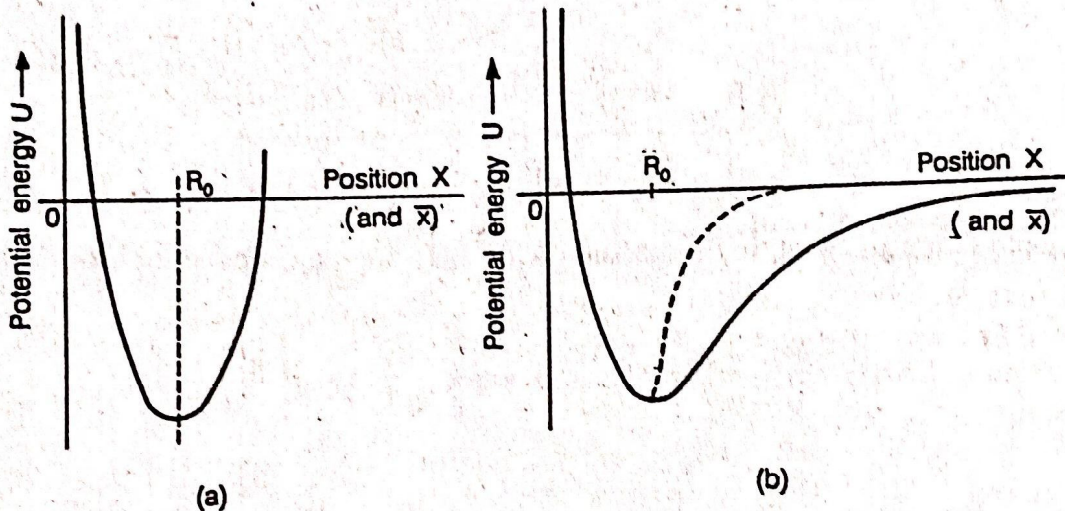


Fig. 17. Potential energy U vs. position X curves (continuous) and potential energy vs. average position \bar{x} curves (discontinuous) for a harmonic oscillator in (a), and for an anharmonic oscillator in (b). Note that in (a) the average position is at the zero-temperature lattice constant R_0 at all temperatures (or energies), while in (b) it moves away from R_0 as the temperature is increased. The situation (b) clearly leads to thermal expansion, and (a) does not.

average interatomic distance would thus occur with the energy increase, and no thermal expansion whatever. On the other hand, if the oscillators are anharmonic— that is, if the potential energy of an oscillator is an asymmetric function of its position— the average positions of different oscillators would obviously be the functions of temperature, as is illustrated in fig. 17 (b). Here, the average interatomic distance would thus be greater than the zero-temperature lattice constant, and the thermal expansion is observed. By the way of conclusion we may say that the thermal expansion of solids is due essentially to the anharmonicity of the lattice oscillations ; if the anharmonicity were not there in the lattice oscillations, there would be no thermal expansion. It may be remembered that the thermal conductivity is another effect related to the anharmonicity of lattice vibrations.

We now find an expression for the coefficient of thermal expansion α . To start with, we shall first calculate the average value of x , as appearing in the expression

$$U(x) = \underbrace{ax^2}_{\text{harmonic term}} - \underbrace{(gx^3 - fx^4)}_{\text{anharmonic terms}} \quad \dots(59)$$

This expression approximates the true potential energy of an atom (oscillator) as a function of position, with the origin of energy and position taken at R_0 , the lattice constant at $T = 0$; x is therefore a displacement representing the increase in the lattice constant, or the thermal expansion. Using now the relation $\alpha = \frac{\partial \bar{x}}{\partial T}$, where \bar{x} is the average value of x , we shall calculate α . A little thinking will convince that $\alpha = \frac{\partial \bar{x}}{\partial T}$ is essentially equivalent to (58).

It is worthwhile to note that the term involving x^3 steepens the left side and flattens the right side of the potential energy curve; it therefore accentuates the effect of the repulsive forces of the atoms. The term involving x^4 flattens the bottom of the curve and represents softening of the vibrations at large amplitudes since it reduces the energy necessary to produce a displacement.

Using the statistical definition of averages and the Boltzmann distribution function, which weighs all the possible values of x according to their thermodynamic probability, we calculate \bar{x} , the average value of x , as

$$\bar{x} = \frac{\int_{-\infty}^{\infty} x \exp[-(ax^2 - gx^3 - fx^4)/k_B T] dx}{\int_{-\infty}^{\infty} \exp[-(ax^2 - gx^3 - fx^4)/k_B T] dx} \quad \dots(60)$$

If the anharmonic terms are small in comparison with $k_B T$, we may expand the exponential function in (60) as

$$\begin{aligned} \exp\left[\frac{-(ax^2 - gx^3 - fx^4)}{k_B T}\right] &\rightarrow \exp\left[\frac{-ax^2}{k_B T}\right] \exp\left[\frac{gx^3 + fx^4}{k_B T}\right] \\ &= \exp\left[\frac{-ax^2}{k_B T}\right] \left[1 + \frac{gx^3}{k_B T} + \frac{fx^4}{k_B T}\right] \end{aligned}$$

and have

$$\bar{x} = \frac{\int_{-\infty}^{\infty} \exp(-ax^2/k_B T) (x + gx^4/k_B T + fx^5/k_B T) dx}{\int_{-\infty}^{\infty} \exp(-ax^2/k_B T) dx} \quad \dots(61)$$

in place of (60). In writing this expression we have neglected the anharmonic terms of denominator. Looking now the various integrals from the table of standard integrals, we have from (61):

$$\bar{x} = \frac{0 + \frac{3}{4} \cdot \frac{g}{k_B T} \cdot \sqrt{\left(\frac{\pi k_B^5 T^5}{a^5}\right)} + 0}{\sqrt{\left(\frac{\pi k_B T}{a}\right)}} = \frac{3}{4} \frac{g}{a^2} \cdot k_B T \quad \dots(62)$$

Thus

$$\alpha = \frac{\partial \bar{x}}{\partial T} = \frac{3}{4} \frac{g k_B}{a^2} \quad \dots(63)$$

According to these calculations, we find that the thermal expansion is directly proportional to the temperature, and the coefficient of thermal expansion is independent of temperature. This is what has actually been observed experimentally for most solids but only in the room temperature range and above, and not at low temperatures. At low temperatures, however, the observed thermal expansion coefficient for most solids becomes much smaller than the above predicted value and indeed approaches zero as $T \rightarrow 0$. Thus, the expression (63) is not a perfect one.

It appears that here again the classical picture of atomic oscillations (used in the above calculations) breaks down, and the atoms of the crystal must be regarded as quantum oscillators rather than classical ones. Let us obtain the corresponding quantum-mechanical results and see whether they agree with the experimental observations. The approximate results are obtained simply by substituting for $k_B T$ in (62) the expression (9). This is because what the quantity $k_B T$ represents for a classical oscillator, the same the quantity (9) represents for a quantum oscillator. We thus have

$$\bar{x} = \frac{3g}{4a^2} \cdot \frac{\hbar\omega_0}{\exp(\hbar\omega_0/k_B T) - 1},$$

in place (62). At high temperatures, this reduces essentially to (62), but as $T \rightarrow 0$, we have

$$\bar{x} = \frac{3g}{4a^2} \hbar\omega_0 \exp(-\hbar\omega_0/k_B T), \quad \dots(64)$$

whence

$$\alpha = \frac{\partial \bar{x}}{\partial T} = \frac{3gk_B}{4a^2} \left(\frac{\hbar\omega_0}{k_B T} \right)^2 \exp(-\hbar\omega_0/k_B T). \quad \dots(65)$$

It is obvious that the coefficient of thermal expansion now approaches zero as $T \rightarrow 0$. Further, (65) gives results which are in reasonably good agreement with experiments over a wide range of low temperatures. Thus, the result (65), combined with (63), gives an expression for α which may be taken as satisfactory for describing the experiments on thermal expansion.