UNIT - III

THERMAL PROPERTIES OF SOLIDS

* Specific heat of gases :

According to law of equipartition of energy in a dynamical system in thermal equilibrium, the energy is equally distributed between the various degrees of freedom and for each of them it is equal to $\frac{1}{2}kT$, where k is Boltzmann's constant given by $k = R/N$, R is the gas constant and N is Avogadro number and T is the absolute temperature.

In a monatomic gas, the molecules and atoms are considered to be identical free particles. If an atom be assumed to be a point particle then each molecule will have three degrees of freedom. Thus a system having a gram-molecules of the gas will consist of 3N degrees of freedom, where N is the number of molecules in a gas. The molecules have no potential energy in the state of a perfect gas. Hence, the energy of a gram-molecule of a monatomic gas will be given by

$$E = 3N \frac{1}{2} kT = \frac{3}{2} NkT$$

Hence the molar specific heat at constant volume is given by

$$C_V = \frac{dE}{dT} = \frac{3}{2} Nk = \frac{3}{2} R$$

$$= 2.98 \text{ cal/degree}$$

For perfect gas, we have

$$C_p - C_v = R$$

$$C_p = C_v + R$$

$$= \frac{3}{2} R + R = \frac{5}{2} R$$

$$= 4.6 \text{ cal/degree.}$$

Then the ratio of the two specific heats,

$$\gamma = \frac{C_p}{C_v} = \frac{5/2\,R}{3/2\,R} = \frac{5}{3} = 1.6 \quad \text{-----(1)}$$

These theoretical values are found to agree with the experimental results for monatomic gases like argon helium etc.

In diatomic gases, the molecules are considered to be ~~points~~, made up of two similar atoms connected with each other like a dumbell. If we again consider the atoms to be points, the molecule will have three degrees of freedom of translation and two of rotation about the two axes $\perp$r to the line joining the atoms. Thus the total energy of a gram-molecule of a perfect diatomic gas will be,

$$E = 5N \times \frac{1}{2}kT = \frac{5}{2}NkT = \frac{5}{2}RT$$

Thus the molar specific heat at constant volume is

$$C_v = \frac{dE}{dT} = \frac{5}{2}R$$

Hence $C_p = C_v + R$

$$= \frac{5}{2}R + R = \frac{7}{2}R$$

and

$$\gamma = \frac{C_p}{C_v} = \frac{7/2\,R}{5/2\,R} = \frac{7}{5} = 1.4 \quad \text{-----(2)}$$

This agrees with the experimental values of gases like H_2, N_2 etc

In a triatomic molecules, there will be three translational degrees of freedom and three rotational. Hence

$$\cancel{E = 6N\,\frac{1}{2}kT = 3NkT}$$

$$E = 3RT$$

The molar specific heat at constant volume is

$$C_v = \frac{dE}{dT} = 3R$$

Hence, $C_p = C_v + R$

$$= 3R + R$$

$$= 4R$$

and $\gamma = \frac{C_p}{C_v} = \frac{4R}{3R} = \frac{4}{3} = 1.33$ ----- (3)

The energy due to internal vibrations of polyatomic molecules cannot be easily calculated because the vibrations are very much restricted and are not free and full.

* Specific Heat of Solids

The specific heat of a substance is defined as the heat required to raise the temperature of one gram molecule of the substance through 1°C i.e

$$C = \frac{dQ}{dT} \quad \text{-------} \ (1)$$

where dQ is the amount of heat added to a system to raise its temperature from T to T+dT. The quantity of heat required to increase the temperature of a body is different under different conditions; one can have various types of specific heats. For example, the specific heat at constant pressure (C_p), is generally different from the specific heat at constant volume (C_v). C_p is always greater than C_v i.e $C_p > C_v$.

According to the first law of thermodynamics, the heat added to a system is used up into two ways; firstly, to increase the internal energy of the system, thereby raising its temperature, and secondly, to do some work on the system to increase its volume against an external pressure. If the system expands against a constant pressure, then the first law can be written as

$$dQ = dE + pdV \quad \text{-------------} (2)$$

The first term on the right hand side represents the change in internal energy of the system and second term represents the work done to change the volume by an amount dv at a pressure p. If heat is added to the system at constant volume, the second term in eq.(2) vanishes and the specific heat at constant volume may be expressed as

$$C_V = \left(\frac{dQ}{dT}\right)_V = \left(\frac{\partial E}{\partial T}\right)_V \quad \text{-----------} (3)$$

similarly, the specific heat at constant pressure as

$$C_p = \left(\frac{dQ}{dT}\right)_p \quad \text{--------} (4)$$

The increase in internal energy of a solid may be due to two ways

(i) The atoms vibrate freely about their equilibrium position. As temperature increases they are set into rigorous vibrations.

(ii) The free electrons in case of metals and semiconductors get thermally excited to higher energy states.

The first contribution arises from the atomic vibrations and is called lattice specific heat. The second contribution arises from the electronic system and is relatively small contribution. Thus, in general, the specific heat of solid may be expressed as

$$C_{solid} = C_{lat.} + C_{elect.} \quad \text{-------} (5)$$

* Classical Theory of Lattice Heat capacity:

A crystal consists of atoms which are arranged in a periodic manner and are bound together by strong binding forces. Each atom is free to vibrate about its equilibrium position and constitutes a three-dimensional harmonic oscillator. The effect of imparting thermal energy to a solid is to increase its internal energy in the form of vibrational energy of these harmonic oscillators.

In the classical theory it is assumed that each atom of a crystal acts as a three-dimensional harmonic oscillator and all the atoms vibrate independent of one another. A system of N vibrating atoms is equavalent to a system of 3N identical and independent one-dimensional harmonic oscillators. This is because each vibrating atom has three independent vibrational degrees of freedom and according to the principle of equipartion of energy, the vibrational energy is distributed equally among all the three degrees of freedom. Thus, each vibrational degree of freedom can be regarded as a one-dimensional harmonic oscillator.

Assuming that each harmonic oscillator vibrates with its natural frequency ω_0. However, the energies of these oscillators may be different because they may vibrate with different amplitudes. Also, each oscillator may acquire any value of energy ranging continuously from zero to infinity. In order to determine the heat capacity of a solid, we find out the average thermal energy of one-dimensional harmonic oscillator, multiply it by 3N.

The energy E of a one-dimensional harmonic oscillator of mass m and angular frequency ω_0 is given by

$$E = \frac{p^2}{2m} + V(x)$$

$$E = \frac{p^2}{2m} + \frac{1}{2} m\omega_0^2 x^2 \quad \text{-------} \quad (1)$$

where $p^2/2m$ represents the kinetic energy, p is the momentum and $V(x)$ is the potential energy at a displacement x from the mean position. The average energy of each harmonic oscillator is given by

$$\bar{E} = \frac{\int E \, e^{-E/kT} \, dE}{\int e^{-E/kT} \, dE} \quad \text{-------} \quad (2)$$

Using eq^n (1), we get

$$\bar{E} = \frac{\iint_{px} \left(\frac{p^2}{2m} + \frac{1}{2} m\omega_0^2 x^2\right) e^{\left(-p^2/2mkT\right)} \cdot e^{\left(-\frac{m\omega_0^2 x^2}{2kT}\right)} \, dp\,dx}{\iint_{px} e^{\left(-\frac{p^2}{2mkT}\right)} \cdot e^{\left(-\frac{m\omega_0^2 x^2}{2kT}\right)} \, dp\,dx}$$

$$\bar{E} = \frac{\iint_{px} \left(\frac{p^2}{2m}\right) e^{\left(-p^2/2mkT\right)} \cdot e^{\left(-\frac{m\omega_0^2 x^2}{2kT}\right)} \, dp\,dx}{\iint_{px} e^{\left(-\frac{p^2}{2mkT}\right)} \cdot e^{\left(-\frac{m\omega_0^2 x^2}{2kT}\right)} \, dp\,dx} + \frac{\iint_{px} \left(\frac{m\omega_0^2 x^2}{2}\right) e^{\left(-\frac{p^2}{2mkT}\right)} \cdot e^{\left(-\frac{m\omega_0^2 x^2}{2kT}\right)} \, dp\,dx}{\iint_{px} e^{\left(-\frac{p^2}{2mkT}\right)} \cdot e^{\left(-\frac{m\omega_0^2 x^2}{2kT}\right)} \, dp\,dx}$$

$$= \frac{\int_p \left(\frac{p^2}{2m}\right) e^{\left(-\frac{p^2}{2mkT}\right)} dp}{\int_p e^{\left(-p^2/2mkT\right)} dp} + \frac{\int_x \left(\frac{m\omega_0^2 x^2}{2}\right) e^{\left(-\frac{m\omega_0^2 x^2}{2kT}\right)} dx}{\int_x e^{\left(-\frac{m\omega_0^2 x^2}{2kT}\right)} dx} \qquad \text{---(3)}$$

Now $$\int_0^\infty u^2 e^{-au^2} du = \frac{1}{4}\sqrt{\frac{\pi}{a^3}} \qquad \text{-------(4)}$$

and $$\int_0^\infty e^{-au^2} du = \frac{1}{2}\sqrt{\frac{\pi}{a}} \qquad \text{-------(5)}$$

$$\therefore \quad \bar{E} = \frac{1}{2m} \cdot \frac{\frac{1}{4}\left[\pi(2mkT)^3\right]^{1/2}}{\frac{1}{2}\left[\pi(2mkT)\right]^{1/2}} + \frac{1}{2}m\omega_0^2 \, \frac{\frac{1}{4}\left[\pi\left(\frac{2kT}{m\omega_0^2}\right)^3\right]^{\frac{1}{2}}}{\frac{1}{2}\left[\pi\left(\frac{2kT}{m\omega_0^2}\right)\right]^{\frac{1}{2}}}$$

$$\bar{E} = \frac{1}{2}kT + \frac{1}{2}kT$$

$$\therefore \quad \bar{E} = kT \qquad \text{---------(6)}$$

Thus the total vibrational energy of a crystal ~~is~~ containing N identical atoms or 3N one-dimensional harmonic oscillator becomes

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

$$E = 3NkT \qquad \text{-----------(7)}$$

The total vibrational energy of a crystal is independent of the type of frequency distribution of oscillators assumed in this model. The energy E depends only on the temperature provided the volume remains constant.

The specific heat of a solid containing of N atoms is

$$C_v = \left(\frac{\partial E}{\partial T}\right) = 3Nk \qquad \text{-----(8)}$$

$$C_v = 3R = 5.96 \text{ cal/mole-K} \qquad \text{-----(9)}$$

According to the classical theory, the molar heat capacity of all solids is constant and is independent of temperature and frequency. This is called Dulong and Petits law.

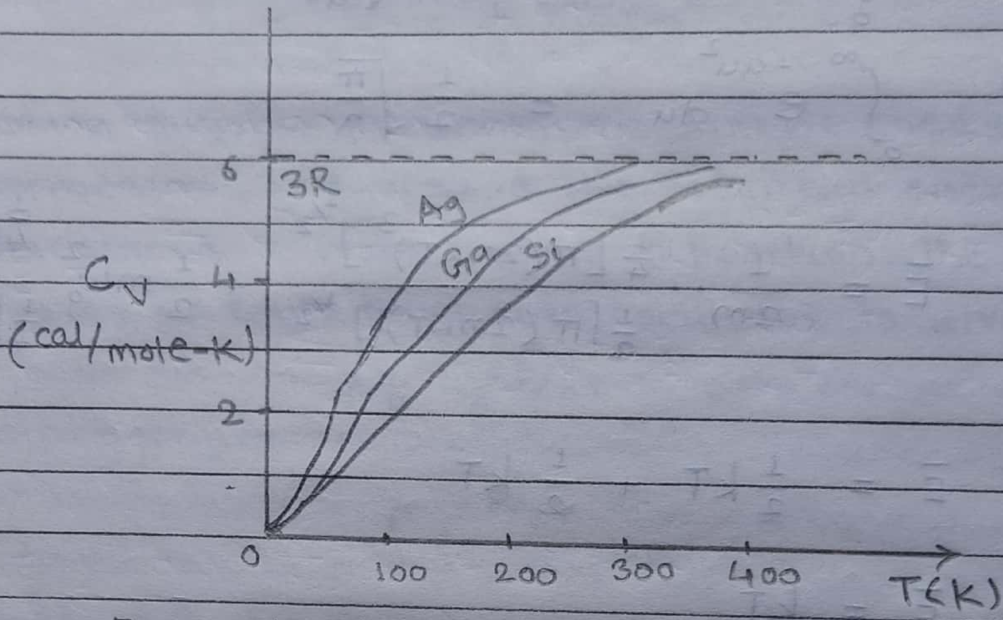

Fig. 1 Heat capacity of silver, germanium and silicon as a function of temperature

As shown in above Fig. 1, the heat capacity approaches zero for Ag, Ge and Si as T approaches zero. This discripancy was resolved first by Einstein and then by Debye by using the quantum theory.

* Einstein's Theory of Lattice Heat Capacity:

Einstein, in 1911, attempted to resolve the descrepancies of the classical theory of specific heat by applying the Plank's quantum theory. The silent features of the Einstein's theory are as below -

(i) A crystal consists of atoms which are regarded as identical and independent harmonic oscillators.

(ii) A solid consisting of N atoms is equivalent to 3N one-dimensional harmonic oscillators.

(iii) All the oscillators vibrate with same natural frequency.

(iv) The oscillators are quantum oscillators and have discrete energy spectrum rather than continuous one.

(v) Any number of oscillators may be present in the same quantum state.

(vi) The atomic oscillators from an assembly of the systems obey the Maxwell-Boltzmann distribution of energies.

Consider the Plank's quantum theory, the discrete energy values of an oscillator with frequency ν are given by

$$E_n = nh\nu = n\hbar\omega_0 \quad \text{-------- (1)}$$

where $n = 0, 1, 2, 3, \ldots$ is called the quantum number. The energy levels of the harmonic oscillators as

$$E_n = \left(n+\frac{1}{2}\right)h\nu = \left(n+\frac{1}{2}\right)\hbar\omega_0 \quad \text{---(2)}$$

where $\frac{1}{2}\hbar\omega_0$ is the temperature independent zero point energy contribution to the internal energy of the oscillator. To calculate the average energy of an oscillator, we replace integration by summation in the

expression for the Maxwell-Boltzmann distribut
of energy and obtain

$$\bar{E} = \frac{\sum_{n=0}^{\infty} E_n \exp\left(-\frac{E_n}{kT}\right)}{\sum_{n=0}^{\infty} \exp\left(-\frac{E_n}{kT}\right)} \quad \text{---------- (3)}$$

Using equation (2), we get

$$\bar{E} = \frac{\sum_{n=0}^{\infty} \left(n+\frac{1}{2}\right)\hbar\omega_0 \exp\left[-\left(n+\frac{1}{2}\right)\frac{\hbar\omega_0}{kT}\right]}{\sum_{n=0}^{\infty} \exp\left[-\left(n+\frac{1}{2}\right)\frac{\hbar\omega_0}{kT}\right]}$$

$$\bar{E} = \frac{\hbar\omega_0 \sum_{n=0}^{\infty} \left(n+\frac{1}{2}\right) \exp\left[\left(n+\frac{1}{2}\right)x\right]}{\sum_{n=0}^{\infty} \exp\left[\left(n+\frac{1}{2}\right)x\right]} \quad \text{---- (4}$$

where $x = -\frac{\hbar\omega_0}{kT}$

$$\therefore \bar{E} = \frac{\hbar\omega_0\left[\frac{1}{2}e^{x/2} + \frac{3}{2}e^{3x/2} + \frac{5}{2}e^{5x/2} + \cdots\right]}{\left[e^{x/2} + e^{3x/2} + e^{5x/2} + \cdots\right]}$$

$$= \hbar\omega_0 \frac{d}{dx} \log\left[e^{x/2} + e^{3x/2} + e^{5x/2} + \cdots\right]$$

$$= \hbar\omega_0 \frac{d}{dx} \log\left[e^{x/2}\left(1 + e^{x} + e^{2x} + \cdots\right)\right]$$

Now $\log(1 + e^{x} + e^{2x} + \cdots) = -\log(1-e^{x})$

$$\therefore \bar{E} = \hbar\omega_0 \frac{d}{dx}\left[\frac{x}{2} - \log(1-e^{x})\right]$$

$$= \hbar\omega_0\left[\frac{1}{2}+\frac{e^{x}}{1-e^{x}}\right] = \hbar\omega_0\left[\frac{1}{2}+\frac{1}{e^{-x}-1}\right]$$

$$= \hbar\omega_0\left[\frac{1}{2}+\frac{1}{e^{\hbar\omega_0/kT}-1}\right]$$

$$\therefore \bar{E} = \frac{1}{2}\hbar\omega_0 + \frac{\hbar\omega_0}{\exp\left(\frac{\hbar\omega_0}{kT}\right)-1} \quad \text{------.(5)}$$

The expression for the internal energy of the crystal becomes

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

$$\therefore E = 3N\left[\frac{1}{2}\hbar\omega_0 + \frac{\hbar\omega_0}{\exp\left(\frac{\hbar\omega_0}{kT}\right)-1}\right]$$

$$= \frac{3}{2}N\hbar\omega_0 + \frac{3N\hbar\omega_0}{\exp\left(\frac{\hbar\omega_0}{kT}\right)-1} \quad \text{------(6)}$$

$$\therefore C_V = \left(\frac{\partial E}{\partial T}\right)_V = 3Nk\left(\frac{\hbar\omega_0}{kT}\right)^2 \frac{e^{\frac{\hbar\omega_0}{kT}}}{\left(e^{(\hbar\omega_0/kT)}-1\right)^2} \quad \text{----(7)}$$

Let $\theta_E = \frac{\hbar\omega_0}{k}$ -------- (8)

where θ_E is the characteristic temperature known as the Einstein temperature

$$\therefore C_V = 3Nk\left(\frac{\theta_E}{T}\right)^2 \frac{e^{\frac{\theta_E}{T}}}{\left(e^{\theta_E/T}-1\right)^2} \quad \text{----(9)}$$

we now consider the following cases :

⟨I⟩ High temperature behaviour

For high temperatures such that

$kT >> \hbar\omega_0$ or $T >> \theta_E$

we can write

$$e^{\hbar\omega_0/kT} - 1 = 1 + \frac{\hbar\omega_0}{kT} + \cdots - 1$$

$$\therefore e^{\hbar\omega_0/kT} - 1 = \frac{\hbar\omega_0}{kT} \quad \text{------- (10)}$$

$$\therefore C_v = 3Nk\left(\frac{\hbar\omega_0}{kT}\right)^2 \frac{\left(1 + \frac{\hbar\omega_0}{kT}\right)}{\left(\frac{\hbar\omega_0}{kT}\right)^2}$$

$$= 3Nk\left(1 + \frac{\hbar\omega_0}{kT}\right)$$

For large T $\hbar\omega_0/kT \rightarrow 0$ and we get

$$C_v = 3Nk = 3R$$

which is the Dulong and petits law as obtained from classical theory.

⟨II⟩ Low temperature behaviour

For low temperatures such that

$kT << \hbar\omega_0$ or $T << \theta_E$

we can write

$$e^{\hbar\omega_0/kT} - 1 \cong e^{\hbar\omega_0/kT}$$

At low temperatures, the average vibrational energy decreases exponentially with decrease in temperature

$$\therefore C_v = 3Nk\left(\frac{\hbar\omega_0}{kT}\right)^2 e^{-\hbar\omega/kT}$$

or in terms of θ_E, it becomes

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

Thus, for $T << \theta_E$, the heat capacity is proportional to $e^{-\theta_E/T}$ which is the dominating factor. However, experimentally it is found to vary as T^3 for most of the solids.

Limitations of Einstein's theory

Although the Einstein's model provides a much better explanation for the variation of heat capacity with temperature than the classical theory but

(i) it fails to account for the values of specific heat at very low temperatures.

(ii) Another weak point in Einstein's deduction is that ν and θ are obtained empirically and cannot be verified from any other independent physical data.

(iii) Einstein himself recognised that the assumption of monochromatic vibrations did not correspond to actual facts.

(iv) Einstein considered the atomic oscillators to vibrate independently at the same frequency but in fact these oscillators are coupled together and there may be a number of possible vibrational frequencies rather than a single frequency ω_0.

The discrepancy between theory and the low temperature experimental values was removed and the experimental data was improved by Debye in 1912.

* Debye's Theory of Specific Heat of Solids:

The Einstein's theory assumed that the atoms of a crystal vibrate totally independent of one another. The all atoms vibrate with the same frequency ω_o which is the natural frequency. ~~of~~

Debye in 1912, put forward his model of lattice heat capacity. Debye assumed that the atoms are bound together in a crystal and form a system of coupled harmonic oscillators which can not vibrate independently. The waves could be propogated through solids and their wavelengths raged from low frequencies (sound waves) to high frequencies corresponding to infrared absorption. He considered the vibrational modes of a crystal as a whole while Einstein considered the vibration of a single atom. The number of vibrational modes per unit frequency range is called density of mode $z(\nu)$. We now determine the density of vibrational modes of crystal treating it as a continuous medium

o Density of Modes

consider a one dimensional continuous string of length L. Let it vibrate in a longitudinal mode with both ends fixed. Let x be the position of a line element and $u(x,t)$ its displacement from the mean position at any time t, therefore, the one dimensional wave equation is

$$\frac{\partial^2 u}{\partial x^2} = \frac{1}{\nu_s^2}\frac{\partial^2 u}{\partial t^2} \quad \text{-----------} (1)$$

Now considering the three-dimensional wave equation is

$$\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2} = \frac{1}{\nu_s^2}\frac{\partial^2 u}{\partial t^2} \quad \text{----} (2)$$

The three-dimensional continuous medium can be taken as a cube of side L whose faces are fixed. The standing wave solutions of the wave equation (2) is

$$u(x,y,z,t) = A\sin\left(\frac{n_x\pi}{L}x\right).\sin\left(\frac{n_y\pi}{L}y\right).\sin\left(\frac{n_z\pi}{L}\right).\cos 2\pi\nu t \quad \text{------- (3)}$$

where n_x, n_y, n_z are positive integers ≥ 1. substituting this solution into equation (2), we obtain

$$\frac{\pi^2}{L^2}\left(n_x^2+n_y^2+n_z^2\right) = \frac{4\pi^2\nu^2}{v_s^2} \quad \text{-------(4)}$$

$$\text{or} \quad \left(n_x^2+n_y^2+n_z^2\right) = \frac{4L^2\nu^2}{v_s^2} \quad \text{------- (5)}$$

This equation gives the possible modes of vibration. The integers n_x, n_y and n_z determine the possible frequencies or wavelength. In order to determine the number of possible modes of vibration, $Z(\nu)\,d\nu$, present in the frequency range ν and $\nu+d\nu$, we consider a network of points in the space defined by three positive integral co-ordinates n_x, n_y and n_z. The radius vector R of any point from the origin is given by

$$R^2 = n_x^2+n_y^2+n_z^2 = \frac{4L^2\nu^2}{v_s^2} \quad \text{------- (6)}$$

This is the equation of a sphere of volume

$$V' = \frac{4}{3}\pi R^3$$

Differentiating it, we get

$$dV' = 4\pi R^2 dR \quad \text{------- (7)}$$

The number of modes present in the frequency range ν and $\nu+d\nu$ should be the same as number of points lying in the volume interval V' and $V'+dV'$ or in the range R and R+dR of the radius vector. since each point occupies, on an average, a unit volume in the space of integers, the number of points presents in the volume dv' of the spherical shell is equal to the volume of the shell i.e

$$dn = 4\pi R^2 dR \quad \text{-------------} (8)$$

But since a mode of vibration is always determined by the positive values of n_x, n_y and n_z only, we must consider the number of points lying in the octant defined by these positive integers only. Thus the number of possible modes of vibration is

$$Z(\nu)d\nu = \frac{1}{8}(4\pi R^2 dR)$$

$$= \frac{1}{8}\, 4\pi\, \frac{4L^2\nu^2}{v_s^2}\, \frac{2L}{v_s}\, d\nu$$

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

$$\therefore \quad Z(\nu)d\nu = \left(\frac{4\pi V}{v_s^3}\right)\nu^2 d\nu \quad \text{-------------} (9)$$

where $V = L^3$ is the volume of the solid cube.

In general, the elastic waves propogating in a solid are of two types - transverse waves and longitudinal waves. The velocity of propogation of transverse wave ~~is~~ (v_t) is different from the velocity of longitudinal waves (v_l). The transverse waves have two vibrational modes ⊥r to the direction of propogation whereas the longitudinal waves have only one mode. For such a case, the total number of vibrational modes is expressed as

$$Z(\nu)d\nu = 4\pi V\left[\frac{2}{v_t^3} + \frac{1}{v_l^3}\right]\nu^2 d\nu \quad \text{-----} (10)$$

* The Debye Approximation

If the interatomic distance is small as compared to the wavelength of elastic waves, the crystal can be regarded as a continuum from the point of view of the waves. The highest frequency propogating through a crystal is called the Debye frequency, ν_D. It is common to transverse and longitudinal modes of vibrations. For the total number of vibrational modes with frequencies ranging from zero to ν_D, we can write

$$\int_0^{\nu_D} Z(\nu)\,d\nu = 3N \quad \text{------}(1)$$

But

$$Z(\nu)\,d\nu = 4\pi V\left[\frac{2}{v_t^3}+\frac{1}{v_l^3}\right]\nu^2 d\nu$$

$$\therefore \int_0^{\nu_D} 4\pi V\left[\frac{2}{v_t^3}+\frac{1}{v_l^3}\right]\nu^2 d\nu = 3N$$

$$4\pi V\left[\frac{2}{v_t^3}+\frac{1}{v_l^3}\right]\int_0^{\nu_D}\nu^2 d\nu = 3N$$

$$\therefore 4\pi V\left[\frac{2}{v_t^3}+\frac{1}{v_l^3}\right]\frac{\nu_D^3}{3} = 3N$$

$$\therefore \nu_D^3 = \frac{9N}{4\pi V}\left[\frac{2}{v_t^3}+\frac{1}{v_l^3}\right]^{-1} \quad \text{-------}(2)$$

The vibrational energy of a crystal is determined by using the Plank's theory. The average energy of an oscillator having frequency ν at a temperature T is given by

$$\bar{E} = \frac{h\nu}{e^{h\nu/KT}-1} \quad \text{-------}(3)$$

Thus the vibrational energy of the crystal is given by

$$E = \int_0^{\nu_D} \bar{E}\, Z(\nu)\, d\nu$$

$$\therefore \quad E = \int_0^{\nu_D} 4\pi V\left[\frac{2}{v_t^3}+\frac{1}{v_l^3}\right]\frac{h\nu^3}{e^{h\nu/kT}-1}\, d\nu$$

$$= 4\pi V h\left[\frac{2}{v_t^3}+\frac{1}{v_l^3}\right]\int_0^{\nu_D}\frac{\nu^3\, d\nu}{e^{h\nu/kT}-1}$$

But we know that

$$4\pi V\left[\frac{2}{v_t^3}+\frac{1}{v_l^3}\right] = \frac{9N}{\nu_D^3}$$

$$\therefore \quad E = \frac{9Nh}{\nu_D^3}\int_0^{\nu_D}\frac{\nu^3\, d\nu}{e^{h\nu/kT}-1} \quad \text{-------- (4)}$$

Putting $\frac{h\nu}{kT} = x$ and $\frac{h\nu_D}{kT} = x_m$ we get

$$\nu = \frac{xkT}{h}$$

$$d\nu = \frac{kT}{h}\, dx$$

so, equation (4) becomes

$$E = \frac{9Nh}{\nu_D^3}\left(\frac{kT}{h}\right)^4\int_0^{x_m}\frac{x^3\, dx}{e^x-1}$$

$$E = 9N\left(\frac{kT}{h\nu_D}\right)^3 kT\int_0^{x_m}\frac{x^3\, dx}{e^x-1} \quad \text{------- (5)}$$

As in the Einstein's theory, we introduce here a characteristic temperature, Θ_D, called the Debye temperature defined as

$$\Theta_D = \frac{h\nu_D}{k} \quad \text{so} \quad x_m = \frac{\Theta_D}{T} \quad \text{------ (6)}$$

Equation (5) becomes

$$E = 9NkT\left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} \frac{x^3 dx}{e^x - 1} \quad \text{-------- (7)}$$

The specific heat is given by

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

$$= 9Nk\left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} \frac{e^x x^4}{(e^x - 1)^2} dx \quad \text{---- (8)}$$

$$= 3R\left(\Theta_D/T\right) F_D \quad (\text{for } N = N_a)$$

The function F_D is called the Debye function and is expressed as

$$F_D = 3\left(\frac{T}{\Theta_D}\right)^4 \int_0^{\Theta_D/T} \frac{e^x x^4}{(e^x - 1)^2} dx \quad \text{----- (9)}$$

Now considering the high and low temperature cases

(I) High Temperature case

For $T >> \Theta_D$, x is small compared with unity for the complete range of integration. Therefore, we can write

~~$e^x \approx$~~ $$e^x - 1 \cong x$$

So, equation $E = 9kTN\left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} \frac{x^3 dx}{e^x - 1}$ becomes

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

$$= 9NkT\left(\frac{T}{\theta_D}\right)^3 \cdot \left[\frac{x^3}{3}\right]_0^{\theta_D/T}$$

$$= 9NkT\left(\frac{T}{\theta_D}\right)^3 \cdot \frac{1}{3}\left(\frac{\theta_D}{T}\right)^3$$

$$E = 3NkT \quad \text{-----------} (10)$$

$$\therefore \; C_v = \left(\frac{\partial E}{\partial T}\right)$$

$$= 3Nk$$

$$\therefore \; C_v = 3R$$

Thus at high temperatures, the Debye's theory also obeys the Dulong and Petits law.

⟨II⟩ At Low Temperature Case

For $T << \theta_D$, $x_m = \frac{\theta_D}{T} \rightarrow \infty$

Therefore equation

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

becomes

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

Now

$$\int_0^{\infty} \frac{x^3\,dx}{e^x - 1} = \frac{\pi^4}{15} \quad \text{-----------} (11)$$

$$\therefore \; E = 9NkT\left(\frac{T}{\theta_D}\right)^3 \cdot \frac{\pi^4}{15}$$

$$\therefore \; E = \frac{3}{5}\pi^4 Nk \frac{T^4}{\theta_D^3} \quad \text{-----------} (12)$$

The expression for specific heat is

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

$$\therefore \quad C_V = \frac{3}{5}\pi^4 Nk \; \frac{4T^3}{\theta_D{}^3}$$

$$\therefore \quad C_V = \frac{12}{5}\pi^4 Nk \left(\frac{T}{\theta_D}\right)^3$$

$$\therefore \quad C_V = \frac{12}{5}\pi^4 R \left(\frac{T}{\theta_D}\right)^3 \quad \text{--------- (13)}$$

Thus, at very low temperature, the specific heat is proportional to T^3. This is called the Debye T^3 law and holds for $T \leq \frac{\theta_D}{10}$.

→ Limitations of the Debye Model

(i) The Debye's continuum model is valid for long wavelengths (only for low frequencies).

(ii) The total number of vibrational modes are assumed to be 3N.

(iii) The cut off frequencies is assumed to be the same for both longitudinal and transverse waves.

(iv) According to the Debye's theory, θ_D is independent of temperatures, whereas actually it is found to vary up to an extent of 10% or even more.

(v) The theory does not take into account the actual crystalline nature of the solid. The theory cannot be applied to crystals comprising more than one type of atom.

(vi) The theory completely ignores the interaction among the atoms and the contribution of electrons to the specific heat.