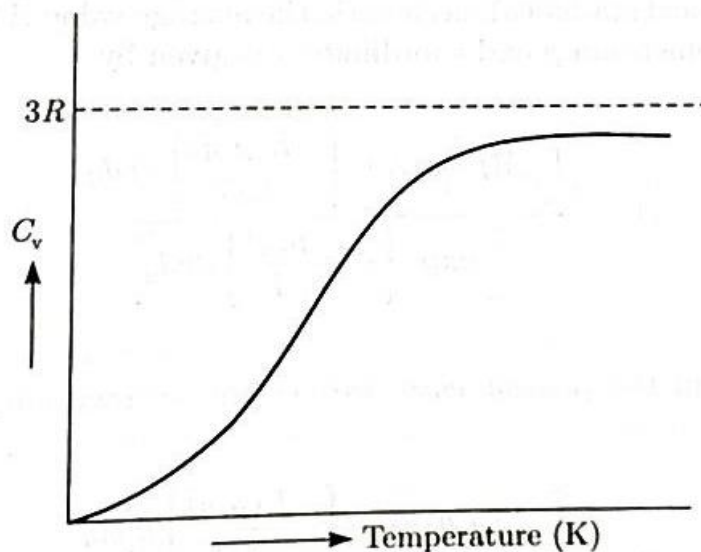


## Module 6.3

### 1. Introduction

The thermal properties of solids are mainly concerned with the flow of heat through a solid. The two main carriers of heat are the quanta of lattice vibration the ‘phonons’ and the ‘electrons’. The total heat transferred is shared by these two. Depending upon the temperature, thone may dominate the other. Usually, the former predominates at the lower temperature and the latter at the higher temperatures.

The specific heat of solids plays an important role in their thermal behaviour. The molar specific heat of a solid at constant volume ( $C_v$ ) is the amount of heat required to raise the temperature of its 1 mole by  $1^\circ\text{C}$  at constant volume. On the other hand, the molar specific heat of a solid at constant pressure ( $C_p$ ) is the amount of heat required to raise the temperature of its one mole by  $1^\circ\text{C}$  at constant pressure.  $C_p$  is somewhat higher the  $C_v$  in solids as it includes the work associated with a volume change as well as the change in internal energy. Based on classical theory, Dulong and Petit, in 1819, showed that the molar specific heat of all solids at constant volume is 5.96 calories per degree Kelvin, irrespective of their nature. This law is valid only in the high-temperature region. At low temperature, however, the specific heat drops sharply and approaches 0 as  $T$  approaches 0 K, as shown in figure 6.1



**Figure 6.1:** Variation of specific heat of a solid with temperature.

The variation of specific heat in the low-temperature region was first explained by Einstein who assumed the aggregate crystal to be composed of atomic oscillators, all of which vibrate with the same natural frequency. The allowed energy states of these oscillators are an integral multiple of  $h\nu$ , where  $h$  is the Planck's constant and  $\nu$  is the frequency of oscillation. Using the Boltzmann's

theorem and the idea of quantum oscillators, the variation of specific heat with temperature in the low-temperature region could be explained. Although Einstein's theory predicts that  $C_v \rightarrow 0$  as  $T \rightarrow 0$  K, the theoretical and experimental curves do not agree too well.

Later, Debye improved Einstein's theory by modifying Einstein's assumption of the constant frequency of oscillators and gave a satisfactory explanation to the  $T^3$  - law, shown by most metals.

## 2 Classical Theory of Specific Heat

Classically, a crystal can be visualized as an assembly of a large number of atoms, held together in a periodic array by certain binding forces and vibrations about their mean positions. The internal energy of a crystal resides in the vibrations of its constituent atoms. These vibrations may be resolved along three mutually perpendicular axes so that we may represent each atom by three harmonic oscillators. All the oscillators have the same frequency, but their energies are different as they vibrate with different amplitudes.

The energy of a harmonic oscillator is composed of its kinetic and potential energies and is given by

$$E = p^2/2m + \frac{1}{2} m\omega^2_0 q^2 \quad (1)$$

Where the symbols have their usual meaning.

According to the classical statistical mechanics, the average value of  $A$  of any quantity  $A(p,q)$  which is a function of momentum  $p$  and coordinate  $q$  is given by

$$\bar{A} = \frac{\int_{-\infty}^{+\infty} A(p,q) \exp\left[-\frac{E(p,q)}{k_B T}\right] dp dq}{\int_{-\infty}^{+\infty} \exp\left[-\frac{E(p,q)}{k_B T}\right] dp dq} \quad (2)$$

Applying this in the present case, we get the average energy of an oscillator in thermal equilibrium as

$$\bar{E} = \frac{\int_{-\infty}^{+\infty} E(p,q) \exp\left[-\frac{E(p,q)}{k_B T}\right] dp dq}{\int_{-\infty}^{+\infty} \exp\left[-\frac{E(p,q)}{k_B T}\right] dp dq} \quad (3)$$

Using equations (1) and (3) can be expressed as

$$\bar{E} = \frac{\int_{-\infty}^{+\infty} \left( \frac{p^2}{2m} + \frac{1}{2} m \omega_0^2 q^2 \right) \exp \cdot \left[ -\frac{\left( \frac{p^2}{2m} + \frac{1}{2} m \omega_0^2 q^2 \right)}{k_B T} \right] dp dq}{\int_{-\infty}^{+\infty} \exp \cdot \left[ -\frac{\left( \frac{p^2}{2m} + \frac{1}{2} m \omega_0^2 q^2 \right)}{k_B T} \right] dp dq}$$

$$\bar{E} = \frac{\int_{-\infty}^{+\infty} \left( \frac{p^2}{2m} \right) \exp \cdot \left[ -\frac{p^2}{2m k_B T} \right] dp}{\int_{-\infty}^{+\infty} \exp \cdot \left[ -\frac{p^2}{2m k_B T} \right] dp} + \frac{\int_{-\infty}^{+\infty} \left( \frac{1}{2} m \omega_0^2 q^2 \right) \exp \cdot \left[ -\frac{(m \omega_0^2 q^2)}{2 k_B T} \right] dq}{\int_{-\infty}^{+\infty} \exp \cdot \left[ -\frac{(m \omega_0^2 q^2)}{2 k_B T} \right] dq}$$

$$\bar{E} = \frac{k_B T}{2} + \frac{k_B T}{2}$$

$$\bar{E} = k_B T \quad (4)$$

Where we have the result of standard integrals.

Each oscillator has thus an average energy of  $k_B T$ . Since each atom can be represented by three harmonic oscillators, the total average energy of each atom is  $3k_B T$ . If there are  $N$  atoms in 1 mole of the substance then the total internal energy associated with 1 mole of the substance will be

$$E = 3Nk_B T = 3RT$$

The molar specific heat at constant volume is, therefore,

$$C_v = \left( \frac{\partial E}{\partial T} \right)_v = 3Nk_B = 3R$$

$$C_v = 5.96 \text{ cal/mol-K}$$

The molar specific heat of all solids is, therefore, 5.96 cal/mol-K and is independent of temperature. This is known as Dulong and Petit's law. This law, however, fails in case of light elements such as boron, beryllium and carbon for which the Debye's temperature is much above 300 K.

Dulong and Petit's law is found to be in good agreement with the experimental values obtained for many solids including metals at room temperature and above. But, at low temperatures, the specific heat capacity falls off rapidly and approaches 0 as  $T \rightarrow 0$  K.

A possible explanation for the variation of specific heat of solids at low temperatures can now be given. As the temperature is lowered, some of the oscillators stop oscillating and do not contribute to the specific heat. At 0 K, all the oscillators stop oscillating and therefore, specific

heat drops down to zero. But, why will an oscillator not oscillate? Since  $C_v$  is independent of temperature, we are not at all concerned with the amplitude of oscillation approaching 0 as  $T \rightarrow 0$  K. we have, therefore, to consider the inability of some of the oscillators to oscillate at all at low temperatures.

The discrepancy between the theoretical and experimental results was explained by Einstein by applying quantum theory.

### **3. Heat capacities of solids**

Any theory used to calculate lattice vibration heat capacities of crystalline solids must explain two things:

- i. Near room temperature, the heat capacity of most solids is around  $3k$  per atom (the molar heat capacity for a solid consisting of  $n$ -atom molecules is  $\sim 3nR$ ). This is the well-known Dulong and Petit law.
- ii. At low temperatures,  $C_v$  decreases, becoming zero at  $T=0$ . Heat capacities have a temperature dependence of the form  $\alpha T^3 + \gamma T$ , where the  $T^3$  term arises from lattice vibrations and the linear term from conduction electrons.

Classical mechanics would predict  $C_v = 3R$  at all temperatures, in violation of both experiment and the third law of thermodynamics.

### **4. Einstein's theory of heat capacities:**

Einstein treated the atoms in a crystal as  $N$  simple harmonic oscillators, all having the same frequency  $\nu E$ . The frequency  $\nu E$  depends on the strength of the restoring force acting on the atom, i.e. the strength of the chemical bonds within the solid. Since the equation of motion for each atom decomposes into three independent equations for the  $x$ ,  $y$  and  $z$  components of displacement, and  $N$ - atom solid is equivalent to  $3N$  harmonic oscillators, each vibrating independently at frequency  $\nu E$ .

Note that this treatment is a gross approximation since, in reality, the lattice vibrations are very complicated coupled oscillations. The energy levels of the harmonic oscillators are given by

$$\epsilon_v = h\nu E(v + 1/2), v = 0, 1, 2, \dots$$

Assuming the oscillators are in thermal equilibrium at temperature  $T$ , the partition function for a single oscillator is

$$q = \sum_{v=0}^{\infty} \exp[-\beta \epsilon_v] = \sum_{v=0}^{\infty} \exp[-\beta h\nu E(v + \frac{1}{2})] = e^{-x/2} \sum_{v=0}^{\infty} e^{-xv} = \frac{e^{-x/2}}{1 - e^{-x}}$$

Where  $x = \beta h\nu E$ .

In the above, we have used the fact that  $\sum_{n=0}^{\infty} x^n = \frac{1}{1-x}$

The mean energy per oscillator is then

$$u = -\frac{d \ln q}{d\beta} = \frac{d}{d\beta} \left[ \frac{\beta h\nu_E}{2} + \ln(1 - e^{-\beta h\nu_E}) \right] = \frac{h\nu_E}{2} + \frac{h\nu}{e^{\beta h\nu_E} - 1}$$

The first term above,  $h\nu/2$ , is simply the zero-point energy. Using the fact that energy is an extensive property, the energy of the  $3N$  oscillators in the  $N$ -atom solid is

$$U = 3N_u = 3N \left( \frac{h\nu_E}{2} + \frac{h\nu}{e^{\beta h\nu_E} - 1} \right)$$

The heat capacity at constant volume is therefore

$$C_U = \left( \frac{\partial U}{\partial T} \right)_v = 3N \left( \frac{\partial U}{\partial T} \right)_v \frac{\partial \beta}{\partial T} = 3Nk \frac{x^2 e^x}{(e^x - 1)^2}$$

$$\text{Where } x = \frac{h\nu_E}{kT} = \frac{\theta_E}{T}$$

$\theta_E$  is the ‘Einstein temperature’, which is different for each solid, and reflects the rigidity of the lattice.

At the high-temperature limit, when  $T \gg \theta_E$  (and  $x \ll 1$ ), the Einstein heat capacity reduces to  $C_v = 3Nk$ , the Dulong and Petit law [prove by setting  $e^x \sim 1+x$  in the denominator].

At the low-temperature limit, when  $T \ll \theta_E$  (and  $x \gg 1$ ),  $C_v \propto 0$  as  $T \propto 0$ , as required by the third law of thermodynamics. [Prove by setting  $e^x - 1 \sim e^x$  in the denominator for large  $x$ ].

## **5. Debye’s theory of heat capacities:**

Debye improved on Einstein’s theory by treating the coupled vibrations of the solid in terms of  $3N$  normal modes of vibration of the whole system, each with its frequency. The lattice vibrations are therefore equivalent to  $3N$  independent harmonic oscillators with these normal mode frequencies. For low-frequency vibrations, defined as those for which the wavelength is much greater than the atomic spacing,  $\lambda \gg a$  the crystal may be treated as a homogeneous elastic medium. The normal modes are the frequencies of the standing waves that are possible in the medium. Debye derived an expression for the number of modes with the frequency between  $\nu$  and  $\nu+d\nu$  in such a medium.

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

Where  $V$  is the crystal volume and  $\nu$  is the propagation velocity of the wave. As outlined above, this expression applies only to low-frequency vibrations in a crystal. Debye used the approximation that it applied to all frequencies, and introduced a maximum frequency  $\nu_D$  (the Debye frequency) such that there were  $3N$  modes in total.

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

The Debye frequency corresponds to  $\lambda = 2a$  when neighbouring atoms vibrate in antiphase with each other. With this approximation in place, Debye integrated over all of the frequencies to find the internal energy of the crystal, and then calculated the heat capacity using  $C_v = \left(\frac{\partial U}{\partial T}\right)_V$ . The resulting expression is given below.

$$c_v = 3Nk \left[ \frac{3}{x_D^3} \int_0^{x_D} \frac{x^4 e^x dx}{(e^x - 1)^2} \right]$$

Where  $x = \frac{h\nu}{kT}$ , and  $x_D = \frac{h\nu_D}{kT} = \frac{\theta_D}{T}$ . The Debye heat capacity depends only on the Debye temperature  $\theta_D$ . The integral cannot be evaluated analytically, but the bracketed function is tabulated.

At high temperatures ( $T \gg \theta_D$ ,  $x_D \ll 1$ ), we may rewrite the integrand as follows:

$$\frac{x^4 e^x}{(e^x - 1)^2} = \frac{x^4}{(e^x - 1)(1 - e^{-x})} = \frac{x^4}{2(\cosh(x) - 1)} = \frac{x^4}{2(x^2/2! + x^4/4! - \dots)}$$

Retaining only the  $x^2$  term in the denominator gives

$$c_v = 3Nk \left[ \frac{3}{x_D^3} \int_0^{x_D} x^2 dx \right] = 3Nk$$

To determine the low-temperature limit ( $T \ll \theta_D$ ,  $x_D \gg 1$ ), we note that the integrand tends towards zero rapidly for large  $x$ . This allows us to replace the upper limit by  $\infty$  and turn the integral into a standard integral, to give

$$C_v = 3Nk \left(\frac{T}{\theta_D}\right)^3 \left(3 \int_0^\infty \frac{x^4 e^x}{(e^x - 1)^2} dx\right) = \frac{12}{5} \pi^4 Nk \left(\frac{T}{\theta_D}\right)^3$$

We see that the Debye heat capacity decreases as  $T^3$  at low temperatures, in agreement with experimental observation. This is a marked improvement in Einstein's theory.

## **6 LIMITATIONS OF DEBYE MODEL**

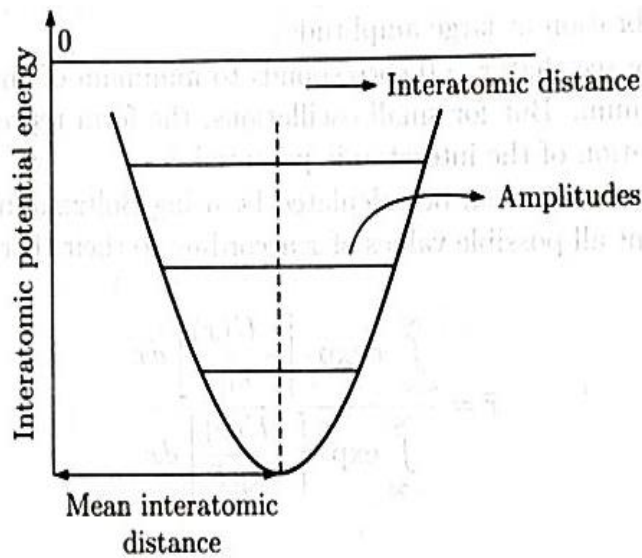
1. The theory completely ignores the interactions among the atoms and the contributions of electrons to the specific heat.
2. Debye temperature  $\theta_D$  is independent of temperature whereas it is found to vary up to an extent of 10% or more.
3. This theory does not take into account the actual crystalline nature of the solid. The theory cannot be applied to the crystals containing more than one type of atoms.
4. Debye model is valid for long-wavelength or shorter frequencies only.
5. Cut off frequency is the same for both transverse and longitudinal waves, while the velocities of longitudinal and transverse waves have different values for different frequencies.

## Module 6.3

### 1. Thermal Expansion

Almost all solids, as we know, expand on heating. This expansion takes place due to an increase in the average interatomic distance. As the temperature increases, the amplitude of lattice vibrations increases. At the melting point, this increase is about 12% of the interatomic spacing.

If we assume that the lattice vibrations are purely harmonic, we get the potential curve as shown in Figure 6.4 which is a parabola. As the temperature increases, the energy of the oscillators also increases, but their mean positions remain the same. The result is that there is no increase in atomic spacing and consequently, no expansion on heating which is contrary to observation.



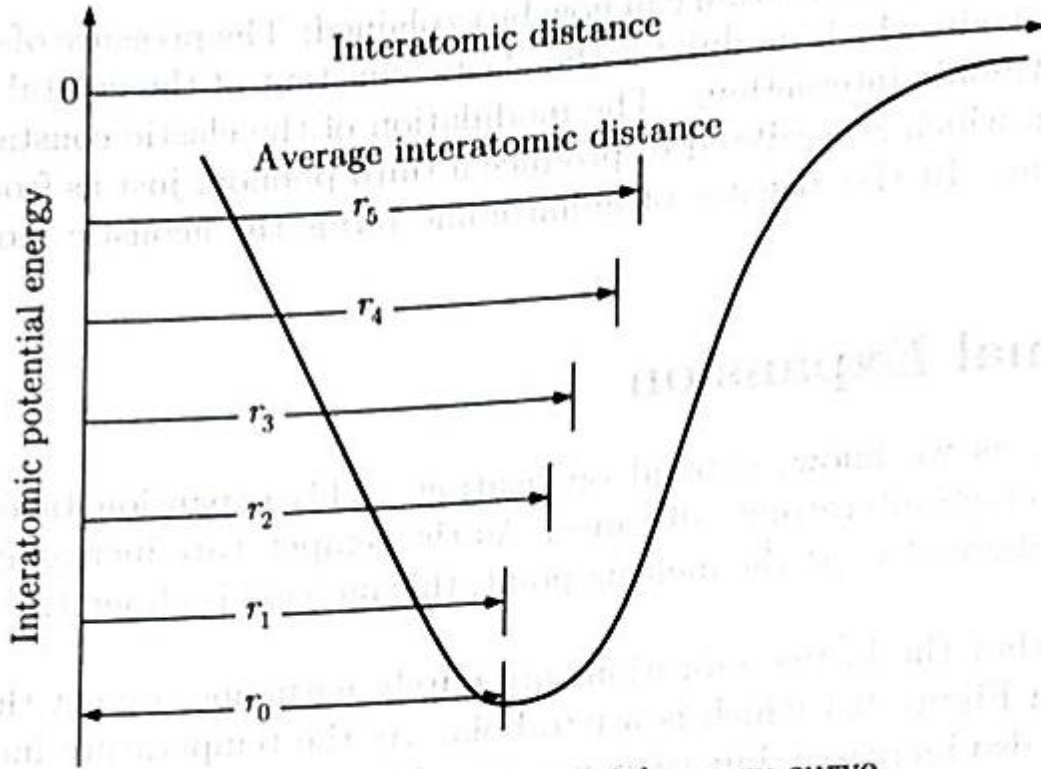
**Figure 6.4:** Potential energy curve, taking the lattice vibrations as perfectly harmonic.

In reality, however, the potential energy curve is not exactly parabolic but has the shape as shown in Figure 6.5. As the temperature increases, the energy of the oscillators also increases, but their mean positions do not remain the same. The result is that the interatomic distance increases and hence, the solid expand.

The thermal expansion may be explained by taking into account the effect of anharmonic terms in the expression for potential energy. The potential energy of the atoms at a displacement  $x$  from their equilibrium separation  $0$  K may be expressed as

$$U(x) = cx^2 - gx^3 - fx^4 \quad (1)$$

Where  $c$ ,  $g$  and  $f$  are positive constants. The term representing  $x^2$  containing the harmonic term and the other two terms represent the anharmonic terms. The term containing  $x^3$  comes in because of the asymmetry of the mutual repulsions of the atoms and term in  $x^4$  represents the softening of the vibration at large amplitudes.



**Figure 6.5: Actual potential energy curve.**

From equation (1) we see that  $x = 0$  corresponds to the minimum of energy which, however, is not the absolute minimum. But for small oscillations, the form represented by Eq. (1) is an adequate representation of the interatomic potential.

The average displacement  $x$  can be calculated by using Boltzmann's distribution function which takes into account all possible values of  $x$  according to their thermodynamic probability and is given by

$$\bar{x} = \frac{\int_{-\infty}^{\infty} x \cdot \exp\left[-\frac{U(x)}{k_B T}\right] dx}{\int_{-\infty}^{\infty} \exp\left[-\frac{U(x)}{k_B T}\right] dx} \quad (2)$$

Now,

$$U(x) = cx^2 - gx^3 - fx^4$$

$$\rightarrow \exp\left[-\frac{U(x)}{k_B T}\right] = \exp\left(-\frac{cx^2 - gx^3 - fx^4}{k_B T}\right)$$

$$\rightarrow \exp\left[-\frac{U(x)}{k_B T}\right] = \exp\left(-\frac{cx^2}{k_B T}\right) \cdot \exp\left(\frac{gx^3 + fx^4}{k_B T}\right)$$



If the anharmonic terms in energy are small compared to  $k_B T$ , then the above equation can be approximated as

$$\exp. \left[ -\frac{U(x)}{k_B T} \right] = \exp. \left( -\frac{cx^2}{k_B T} \right) \cdot \left[ 1 + \frac{gx^3 + fx^4}{k_B T} \right] \quad (3)$$

Using Eq. (3), Eq. (2) can be expressed as

$$\begin{aligned} \bar{x} &= \frac{\int_{-\infty}^{\infty} x \left[ 1 + \frac{gx^3 + fx^4}{k_B T} \right] \cdot \exp. \left( -\frac{cx^2}{k_B T} \right) dx}{\int_{-\infty}^{\infty} \left[ 1 + \frac{gx^3 + fx^4}{k_B T} \right] \cdot \exp. \left( -\frac{cx^2}{k_B T} \right) dx} \\ \rightarrow \bar{x} &\approx \frac{\int_{-\infty}^{\infty} \left[ x + \frac{gx^4 + fx^5}{k_B T} \right] \cdot \exp. \left( -\frac{cx^2}{k_B T} \right) dx}{\int_{-\infty}^{\infty} \exp. \left( -\frac{cx^2}{k_B T} \right) dx}, \text{ as } 1 \gg \frac{gx^3 + fx^4}{k_B T} \\ \rightarrow \bar{x} &= \frac{\int_{-\infty}^{\infty} \left[ \frac{g}{k_B T} \right] x^4 \cdot \exp. \left( -\frac{cx^2}{k_B T} \right) dx + \int_{-\infty}^{\infty} \left[ x + \frac{fx^5}{k_B T} \right] \cdot \exp. \left( -\frac{cx^2}{k_B T} \right) dx}{\int_{-\infty}^{\infty} \exp. \left( -\frac{cx^2}{k_B T} \right) dx} \quad (4) \end{aligned}$$

where we have neglected the anharmonic terms in the denominator.

Since

$$\int_{-\infty}^{\infty} \text{odd function} = 0$$

Equation (4) gives

$$\begin{aligned} \bar{x} &= \frac{\left( \frac{g}{k_B T} \right) \int_{-\infty}^{\infty} [x^4] \cdot \exp. \left( -\frac{cx^2}{k_B T} \right) dx}{\int_{-\infty}^{\infty} \exp. \left( -\frac{cx^2}{k_B T} \right) dx} \\ \rightarrow \bar{x} &= \frac{\left( \frac{g}{k_B T} \right) \left( \frac{k_B T}{c} \right)^{5/2} \cdot \left( \frac{3\sqrt{\pi}}{4} \right)}{\sqrt{\frac{\pi k_B T}{c}}} \\ \rightarrow \bar{x} &= \left( \frac{3g}{4k_B T} \right) \left( \frac{k_B T}{c} \right)^2 \\ \rightarrow \bar{x} &= \frac{3g}{4c^2} k_B T \quad (5) \end{aligned}$$

Since  $k_B T$  represents classically the mean energy  $\bar{E}$  of oscillators in harmonic approximation, Eq. (5) takes the form

$$\bar{x} = \frac{3g}{4c^2} \cdot \bar{E} = \frac{3g}{4c^2} k_B T \quad (6)$$

The thermal expansion coefficient is given by

$$\alpha = \frac{\partial \bar{x}}{\partial T} = \frac{3g k_B}{4c^2} \quad (7)$$

The thermal expansion coefficient is, thus independent of temperature. The result is obtained without taking into account the quantization of energy. Hence, at high temperatures, the system is similar to the classical one.

Quantum mechanically, the average energy of an oscillator of frequency  $\vartheta$  is given by

$$\bar{E} = \frac{h\vartheta}{\exp\left(\frac{h\vartheta}{k_B T}\right) - 1}$$

and hence, the average displacement  $\bar{x}$  is

$$\bar{x} = \frac{3g}{4c^2} \cdot \bar{E} = \left(\frac{3g}{4c^2}\right) \cdot \left[\frac{h\vartheta}{\exp\left(\frac{h\vartheta}{k_B T}\right) - 1}\right] \quad (8)$$

As  $T \rightarrow 0$  K, the exponential term in the denominator of Eq. (8) becomes much greater than unity and, therefore, (8) can be approximated as

$$\begin{aligned} \bar{x} &= \left(\frac{3g}{4c^2}\right) \cdot \frac{h\vartheta}{\exp\left(\frac{h\vartheta}{k_B T}\right)} \\ \rightarrow \quad \bar{x} &= \frac{3g}{4c^2} \cdot h\vartheta \cdot \exp\left(-\frac{h\vartheta}{k_B T}\right) \end{aligned} \quad (9)$$

and

$$\begin{aligned} \bar{\alpha} &= \frac{\partial \bar{x}}{\partial T} = \frac{3g}{4c^2} \cdot h\vartheta \cdot \left(\frac{h\vartheta}{k_B T^2}\right) \cdot \left(-\frac{h\vartheta}{k_B T}\right) \\ \rightarrow \quad \bar{\alpha} &= \frac{3gk}{4c^2} \cdot \left(\frac{h\vartheta}{k_B T}\right)^2 \cdot \exp\left(-\frac{h\vartheta}{k_B T}\right) \end{aligned} \quad (10)$$

It follows from Eq. (10) that as  $T \rightarrow 0$  K,  $\alpha \rightarrow 0$ , as required by the third law of thermodynamics which, by the way, also requires that  $C_v \rightarrow 0$  as  $T \rightarrow 0$  K.

## 2. Thermal Conductivity of Solids

Theory of thermal conductivity of solids can be developed by knowing the rate at which the energy is transferred across the solid by electrons and photons which get scattered by collisions among themselves as well as by impurities and imperfections in the solid. In crystals the phonons move with the velocity of sound and, therefore, heat conduction also takes place with the velocity of sound. In the present case, we limit our discussion to conduction by phonons, leaving the conduction by electrons to be discussed later. Then theory will, therefore, apply only to insulators.

The amount of heat  $Q$  that flows through a unit cross-sectional area of a solid per second where the temperature gradient is  $\frac{d\theta}{dx}$  is given by

$$Q = -K \frac{d\theta}{dx} \quad (11)$$

where  $K$  is the thermal conductivity. The negative sign in Eq. (11) is used to indicate that as the distance  $x$  increases, the temperature  $\theta$  decreases.

The thermal conductivity of solids can most easily be explained if we regard the solid to be a container enclosing a phonon gas which is found to behave like an ideal monatomic gas. We shall, therefore, first derive an expression for the thermal conductivity of a monatomic gas and shall then apply it to the lattice of a crystalline solid.

Let us find the number of particles of an ideal gas having velocity lying between  $v$  and  $v + dv$  and crossing an elementary area  $ds$  per second from a direction lying between angle  $\theta$  and  $\theta + d\theta$ . Referring to Figure 6.6, we see that this number will be just half the number of particles within this velocity range inside a column of cross-sectional area  $ds \cos \theta$  and length  $v$ , because the other half may go in the opposite direction.

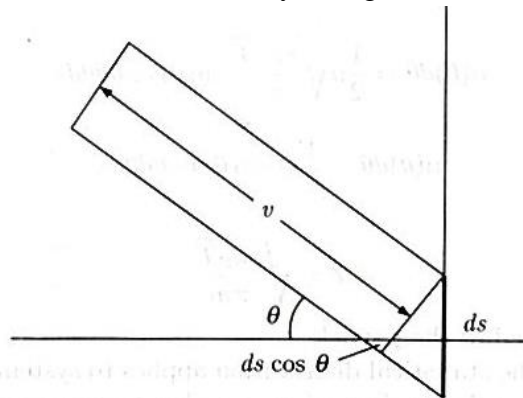


Figure 6.6: Particles striking an elementary area from a direction of  $\theta$  with velocities lying between  $v$  and  $v + dv$ .

If  $n(\vartheta)d\vartheta$  be the number of molecules per unit volume having velocity lying between  $\vartheta$  and  $\vartheta + d\vartheta$ , then the number of molecules crossing the area  $dscos\theta$  in a direction lying between angle  $\theta$  and  $\theta + d\theta$  is

$$dn = \frac{1}{2} \vartheta \cdot n(\vartheta) d\vartheta \cdot \frac{4\pi \sin\theta d\theta}{4\pi} \cdot dscos\theta$$

$$\rightarrow dn = \frac{1}{2} \vartheta \cdot n(\vartheta) \cdot \sin\theta \cos\theta dv ds \quad (12)$$

Where  $\left(\frac{4\pi \sin\theta d\theta}{4\pi}\right)$  represents the solid angle subtended by the element  $d\theta$  about  $\theta$  to the solid angle  $4\pi$  subtended by the entire space around it.

From Maxwell-Boltzmann distribution law, we have

$$n(\vartheta)d\vartheta = 4\pi n \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} \vartheta^2 \exp\left(-\frac{m\vartheta^2}{2k_B T}\right) d\vartheta$$

Substituting this value of  $n(\vartheta)d\vartheta$  in Eq. (6.70) and integrating over  $(\vartheta)$  (remembering that the velocity distribution is independent of angle  $\theta$ ) we get the number of molecules striking the elementary area  $ds$  per second from a direction lying between  $\theta$  and  $\theta + d\theta$  as

$$\rightarrow n(\theta)d\theta = \frac{1}{2} \cdot 4\pi n \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} \cdot \frac{1}{2} \left(\frac{2k_B T}{m}\right)^2 \sin\theta \cos\theta d\theta ds$$

$$\rightarrow n(\theta)d\theta = \frac{\pi n}{\pi^{3/2}} \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} \cdot \left(\frac{2k_B T}{m}\right)^2 \sin\theta \cos\theta d\theta ds$$

$$\rightarrow n(\theta)d\theta = n \cdot \sqrt{\frac{2k_B T}{\pi m}} \sin\theta \cos\theta d\theta ds$$

$$\rightarrow n(\theta)d\theta = \frac{1}{2} \cdot 2n \cdot \sqrt{\frac{2k_B T}{\pi m}} \sin\theta \cos\theta d\theta ds$$

$$\rightarrow n(\theta)d\theta = \frac{1}{2} n \cdot \sqrt{\frac{8k_B T}{\pi m}} \sin\theta \cos\theta d\theta ds$$

$$\rightarrow n(\theta)d\theta = \frac{1}{2}n\bar{c}.\sin\theta\cos\theta d\theta ds \quad (13)$$

Where

$$\bar{c} = \sqrt{\frac{8k_B T}{\pi m}} \quad (14)$$

It is the average thermal speed of the particle.

It may be noted that the statistical distribution applies to systems in thermal equilibrium. The thermal conduction involves a flow of energy due to temperature gradient and so, we are dealing here with a system which is not in thermal equilibrium. The use of statistical distribution in this case, therefore, only an approximation.