UNIT 8   THERMAL PROPERTIES

Structure

8.1   INTRODUCTION

You know that atoms in solids are held together by interatomic forces. These forces oppose any attempt to displace atoms from their equilibrium positions. This description of solids enables us to understand their elastic properties. Further, you have also learnt that when an external dynamical force is applied on a solid, the atoms vibrate about their equilibrium positions giving rise to lattice waves. In Units 6 and 7, you have learnt that the nature of lattice waves, characterised by its dispersion relation, depends on the assumption whether the solid is considered as a homogeneous continuous elastic medium or as a collection of atoms arranged along a periodic lattice. In this unit, you will learn how the concept of lattice waves can be used to understand thermal properties such as heat capacity of solids.

Heat capacity is an important thermal property of solids and has been of special interest to physicists for long. A complete explanation of heat capacity measurement data necessitates the use of quantum physics. You may, however, recall the basics of heat capacity including the Dulong-Petit law from your school physics. In Sec. 8.2, you will learn to explain it on the basis of vibration of atoms, that is, on the basis of atomic oscillator model and classical statistical mechanics. But to account for the fact that heat capacity decreases with temperature, Einstein and Debye developed theories using quantum ideas. You will learn these theories of heat capacity in Sec. 8.3 and 8.4. In quantum theories, the atomic oscillators in a solid are assumed to behave like harmonic oscillators. The harmonic oscillator model, however, fails to provide satisfactory explanation of thermal properties such as thermal expansion of solids. The theoretical explanation of thermal expansion is beyond the scope of this course.

In this Block, thermal properties of solids have been discussed under the assumption that electrons are tightly bound to their parent atom. This model of a solid does not help to understand electrical properties of metals and semiconductors. In the next unit, you will learn the free electron theory of metals, which assumes that electrons influence their physical properties.

Objectives

After studying this unit, you should be able to:

- explain the physical basis of Dulong-Petit law;
- state the differences between predictions of the classical theory and observed behaviour of heat capacity;
- derive an expression for the heat capacity based on Einstein's model of a solid and explain its limitations at low temperatures; and
- derive an expression for the heat capacity on the basis of Debye's model of a solid and explain how it successfully explains the low temperature behaviour.

8.2 HEAT CAPACITY

You are familiar with the concept of heat capacity from school physics. You also learnt about it in your Thermodynamics and Statistical Mechanics course (PHE-06). We know that when we supply thermal energy to a body, its temperature increases. The ratio of the amount of heat, ΔQ absorbed by a body to the corresponding change in its temperature, ΔT is known as heat capacity. It is usually denoted by the letter C. Expressed mathematically, we can write

$$C = \frac{\Delta Q}{\Delta T}.$$

(8.1)

Can you recall the parameters which determine the magnitude of C. If your guess is that heat capacity of a body is determined by its mass, chemical composition, nature of bonding and the conditions under which body is heated, you are thinking correctly. For example, when a body is heated at constant volume, we define *heat capacity at constant volume* (C_v). Similarly, when pressure on a body is kept constant during heating process, we define *heat capacity at constant pressure* (C_p). For gases, the values of heat capacities at constant volume and at constant pressure differ significantly even at ordinary temperatures. This is because gases can be compressed due to large intratomic separation and weak interatomic forces. On the other hand, for liquids and solids, which are almost incompressible, the values of C_p and C_v are almost the same upto about 300K. At higher temperatures, measurable difference has been reported in some cases (Fig. 8.1). Since it is more difficult to keep the volume of a solid constant when thermal energy is supplied to it, the experimental observations enable us to measure C_p. But, theoretically it is simpler to calculate C_v. Thus, for simplicity, we shall confine our discussion in this Unit to heat capacity at constant
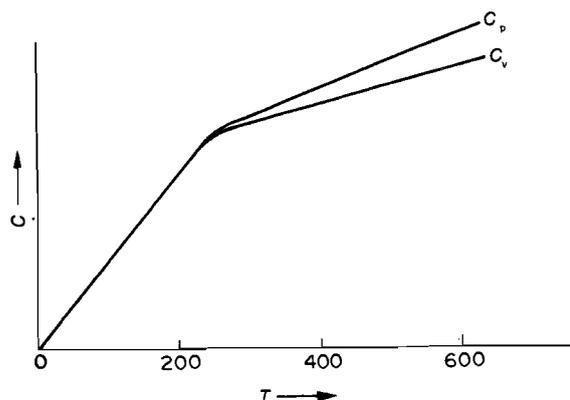

Fig. 8.1: Temperature variation of C_v and C_p for copper

Since the coefficient of volume expansion is three times the coefficient of linear expansion, α_L, Eq. (8.2) can be rewritten as:

$$C_p - C_v = \frac{9TV\alpha_L^2}{K_T}$$

volume but you may ask: How we explain observed results theoretically? This is achieved by taking recourse to thermodynamics. From PHE-06 course you will recall that the first and second laws of thermodynamics describe all processes which involve thermal energy. You may recall the thermodynamic relation connecting C_p and C_v :

$$C_p - C_v = \frac{TV\alpha^2}{K_T},$$

(8.2)

where α is the coefficient of volume expansion and K_T is isothermal compressibility.

You may like to pause for a while and ask: What information do experiments provide us about heat capacity of solids? What is the current status of our theoretical understanding, and so on? You will discover answers to all such questions as you read through this unit. We begin our discussion with the classical findings of Dulong and Petit.

8.2.1 Dulong-Petit Law

In early 19th century, Dulong and Petit conducted a series of classical experiments to measure heat capacities of solids at different temperatures. Fig. 8.2a shows a typical temperature versus heat capacity curve obtained by Dulong and Petit. Fig. 8.2b shows the temperature dependence of heat capacity of silver and germanium, respectively a metal and a semiconductor. Note that

* *at high temperatures, heat capacity is independent of temperature and is equal to 3 R for all solids,* where R is the universal gas constant. Its value is 8.3 JK^{-1}. This is known as *Dulong-Petit law*.

* as temperature decreases, heat capacity decreases almost exponentially and approaches zero as $T \to$ 0K.
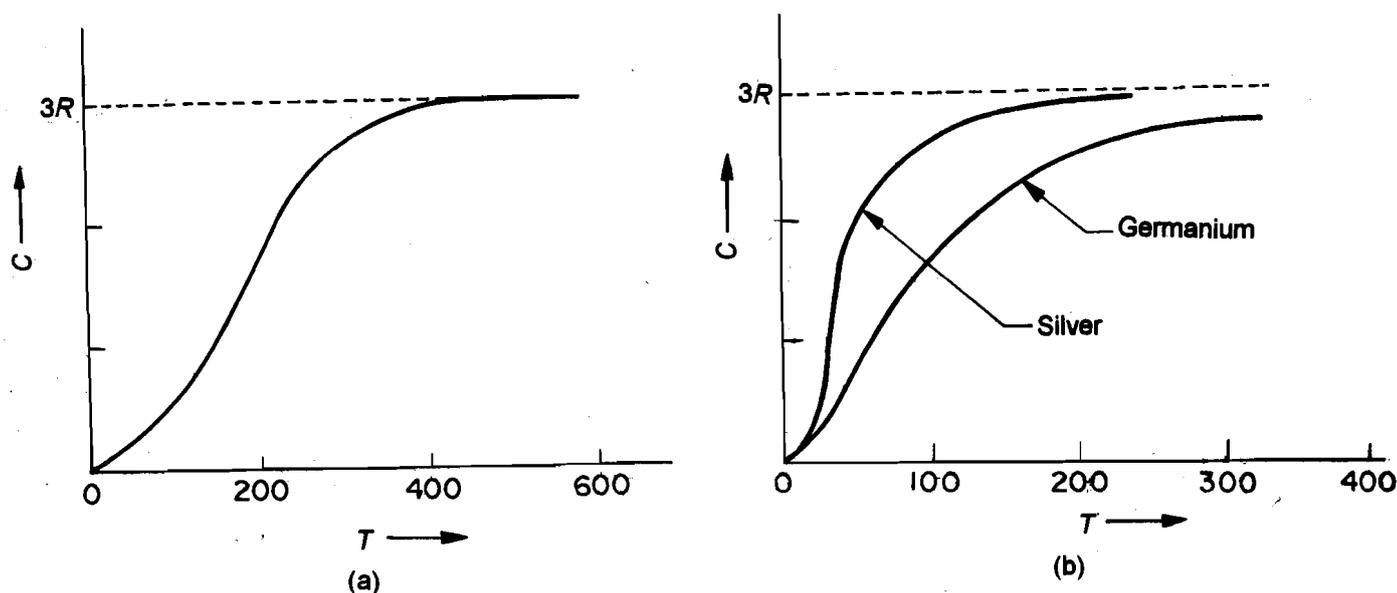

Fig. 8.2: a) Typical temperature dependence of heat capacity of solids; and b) heat capacity versus temperature curves for silver and germanium

Now, you may like to know: What is the theoretical basis for the observed temperature dependence of heat capacity? Let us first understand the observations qualitatively. You know that a solid is a collection of atoms arranged along a periodic lattice. Since we confine our discussion to heat capacity at constant volume, it is logical to think that the (heat) energy supplied to a solid will be *completely* used in increasing its internal energy. This can happen via two mechanisms. Firstly, atoms can oscillate about their equilibrium positions much more vigorously by absorbing heat energy. Secondly, in metals and semiconductors, the heat energy can also be absorbed by electrons in outer orbits and be excited to higher energy states. Corresponding to these mechanisms of absorption of heat energy, we have lattice and electronic contributions to the heat capacity. In this unit, however, we limit our discussion to lattice heat capacity.

Early attempts to explain Dulong-Petit law were made on the basis of classical notions about the energy of vibrating atoms based on Maxwell-Boltzmann (M-B) distribution law. It gave rise to the classical theory of heat capacity which you will learn now.

8.2.2 Classical Theory of Heat Capacity

This theory is based on the assumption that atoms in a periodic lattice vibrate about their equilibrium sites and obey Hookes' law. *That is, each atom is bound to its equilibrium site by a harmonic force and when thermal energy is supplied, it vibrates like an harmonic oscillator.* It is further assumed that each atom is equivalent to a

classical three-dimensional (3-D) harmonic oscillator and vibrates independently. This means that a solid consisting of N atoms can be treated as a collection of as many three-dimensional, independent harmonic oscillators. Equivalently, N vibrating atoms can be considered as a collection of $3N$, one-dimensional (1-D) independent harmonic oscillators. And, to obtain an expression for the heat capacity of a solid, we need to know the average energy of a 1-D harmonic oscillator and multiply it by $3N$. Therefore, our problem reduces to obtaining an expression for the average energy of a 1-D harmonic oscillator.

The equivalence of N, 3-D harmonic oscillators and $3N$, 1-D harmonic oscillators follows from the principle of equipartition of energy which you have learnt in PHE-06. According to this principle, vibrational energy of an atom is distributed equally among its three degrees of freedom-one along each coordinate axes. Therefore, an atom (or a 3-D harmonic oscillator) is equivalent to three 1-D harmonic oscillators.

You may recall from Oscillations and Waves course (PHE-02) that the total energy of a 1-D harmonic oscillator is written as

$$\varepsilon = \text{Kinetic energy} + \text{Potential energy}$$

$$= \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2, \tag{8.3}$$

where m, p, ω and x respectively denote mass, momentum, angular frequency and displacement from equilibrium position of an atom. According to classical mechanics, *energy of an oscillator can take any value between zero and infinity*. To calculate the average energy, we note that energy distribution of a classical system is governed by M-B distribution. *The M-B distribution function, which gives the probability that an oscillator will have energy* ε, is given by

$$f(\varepsilon) = A \exp\left[-\frac{\varepsilon}{k_B T}\right], \tag{8.4}$$

where A is an arbitrary constant and k_B is Boltzmann constant. Thus, the average energy of a 1-D oscillator will be given by

$$<\varepsilon> = \frac{\int_0^\infty \varepsilon\, f(\varepsilon)\, d\varepsilon}{\int_0^\infty f(\varepsilon)\, d\varepsilon} = k_B T. \tag{8.5}$$

You should solve the following SAQ to verify this result.

SAQ 1

Verify the result contained in Eq. (8.5).

Since a solid having N atoms is equivalent to $3N$ one-dimensional harmonic oscillators, its total energy is given by

$$E = 3 N k_B T \tag{8.6}$$

and the heat capacity is given by

$$C_v = \left(\frac{\partial E}{\partial T}\right)_v = 3N k_B. \tag{8.7}$$

If we consider one mole of a substance, the total number of atoms will be equal to the Avogadro number, N_A, and the heat capacity per mole or the *molar heat capacity* will be equal to

$$C_v = 3 N_A k_B = 3R \text{ mole}^{-1}, \tag{8.8}$$

where $R = N_A k_B$ is the universal gas constant. Let us pause for a while and try to understand the significance of this result. It shows that heat capacity of solids is constant, equal to $3R$ and independent of temperature. This explains Dulong-Petit law, which holds rather well at room temperature and above. However, as it became possible to carry out measurements at lower temperatures, it was observed that heat capacity decreases with temperature for almost all solids. Physically, it implies that as temperature decreases, the atomic motion is constrained and at absolute zero, all motion should cease. The classical theory, which predicts temperature independent heat capacity, fails to explain why heat capacity tends to zero as temperature approaches absolute zero and is not consistent with the third law of thermodynamics. This posed an interesting challenge to the physicists in the twentieth century. First successful attempt to explain this behaviour was made by Einstein on the basis of quantum ideas. You will learn it now.

8.3 EINSTEIN THEORY

Einstein developed the quantum theory of heat capacity and proposed that atoms in a solid should be treated as Planck oscillators characterised by a constant frequency. This implies that energy (ε_n) of a quantum oscillator is $nh\nu$, where n is a positive integer, h is Planck constant and ν is frequency of oscillation. *Note that Einstein assumed that all oscillators vibrate with the same frequency.*

According to Einstein's theory, a solid made of N atoms is equivalent to $3N$, 1-D independent harmonic oscillators. To obtain an expression for the heat capacity, Einstein assumed that the probability of an oscillator possessing energy $nh\nu$, when the system is at temperature T, is proportional to $\exp\left[-\dfrac{nh\nu}{k_B T}\right]$. That is, Einstein also used M-B distribution law probably because the oscillators are distinguishable from each other due to their location at different lattice sites. *Thus, in Einstein's theory, we analyse the statistical behaviour of quantum oscillators using classical (M-B) distribution law.* Since the energy is quantised, we obtain the average energy of an oscillator by summation, rather than by integration (as we did in classical theory). Under these conditions, we may write the average energy of a quantum harmonic oscillator as:

$$<\varepsilon> = \frac{\displaystyle\sum_{n=0}^{\infty} \varepsilon_n \exp\left[-\frac{\varepsilon_n}{k_B T}\right]}{\displaystyle\sum_{n=0}^{\infty} \exp\left[-\frac{\varepsilon_n}{k_B T}\right]}.$$

Substituting $\varepsilon_n = nh\nu$ in this expression, we get

$$<\varepsilon> = \frac{h\nu \displaystyle\sum_{n=0}^{\infty} n \exp\left[-\frac{nh\nu}{k_B T}\right]}{\displaystyle\sum_{n=0}^{\infty} \exp\left[-\frac{nh\nu}{k_B T}\right]}. \qquad (8.9)$$

To evaluate the RHS of Eq. (8.9), we introduce a change of variable and write $\dfrac{h\nu}{k_B T} = x$. Then, expression for average energy simplifies to

A quantum oscillator can exchange energy with its surroundings only in units of a minimum quantum. In order to oscillate, an oscillator must have at least one quantum or unit of energy. *If this condition is invoked, it is obvious that at low temperatures, there may not be enough thermal energy to give at least one quantum of energy to each and every atomic oscillator in a solid. This may cause decrease in heat capacity as temperature decreases.*

$$< \varepsilon > = \frac{h\nu \sum_{n=0}^{\infty} ne^{-nx}}{\sum_{n=0}^{\infty} e^{-nx}} = \frac{h\nu\left[e^{-x} + 2e^{-2x} + 3e^{-3x} + ...\right]}{\left[1 + e^{-x} + e^{-2x} + e^{-3x} + ...\right]}$$

$$= \frac{h\nu N}{D}. \tag{8.10}$$

Now let us first consider the expression in the numerator:

$$N = e^{-x} + 2e^{-2x} + 3e^{-3x} + ... \tag{8.11a}$$

Multiply by e^x on both sides. This gives

$$e^x N = 1 + 2e^{-x} + 3e^{-2x} + ... \tag{8.11b}$$

On subtracting the expression in Eq. (8.11a) from that in Eq. (8.11b), we get

$$\left(e^x - 1\right)N = 1 + e^{-x} + e^{-2x} + ... \tag{8.11c}$$

The right hand side in this expression is an infinite geometric series with common ratio e^{-x} and is simply identical to the denominator in Eq. (8.10). Hence

$$\frac{N}{D} = \frac{1}{e^x - 1} \tag{8.12}$$

and the expression for average energy of an Einstenian harmonic oscillator simplifies to

$$< \varepsilon > = \frac{h\nu}{e^x - 1} = \frac{h\nu}{\exp\left[\dfrac{h\nu}{k_B T}\right] - 1}. \tag{8.13}$$

If a solid consists of $3N$ one-dimensional oscillators, the expression for its total energy is obtained by multiplying Eq. (8.13) by $3N$:

$$E = \frac{3Nh\nu}{\exp\left[\dfrac{h\nu}{k_B T}\right] - 1} \tag{8.14}$$

so that the heat capacity is given by

$$C_v = 3Nk_B \left(\frac{h\nu}{k_B T}\right)^2 \frac{\exp\left[\dfrac{h\nu}{k_B T}\right]}{\left(\exp\left[\dfrac{h\nu}{k_B T}\right] - 1\right)^2}. \tag{8.15}$$

If we take one mole of the solid, N is replaced by N_A in this expression to obtain molar heat capacity:

$$C_v = 3R \left(\frac{hv}{k_B T} \right)^2 \frac{\exp \left[\dfrac{hv}{k_B T} \right]}{\left(\exp \left[\dfrac{hv}{k_B T} \right] - 1 \right)^2}. \qquad (8.16)$$

This result shows that heat capacity is a function of temperature – a feature missing in the classical theory. Note that the key to success of Einstein's theory is the concept of quantisation of energy.

To compare the predictions of this theory with experimental results, we need to know the frequency of the oscillators so that the theoretical value of C_v at a given temperature can be obtained using Eq. (8.16). The question is: How to estimate the value of frequency? *This difficulty is overcome by choosing such a value of frequency for which Eq. (8.16) fits the experimental curve. That is, it is assumed that each solid has a characteristic frequency, called* **Einstein frequency**, v_E. It is customary to write

$$hv_E = k_B T_E, \qquad (8.17)$$

where T_E denotes the **Einstein temperature**. Like the characteristic frequency, T_E will have a fixed value for a given solid. In terms of Einstein temperature, the expression in Eq. (8.16) for heat capacity takes the form

$$C_v = 3R \left(\frac{T_E}{T} \right)^2 \frac{\exp \left[\dfrac{T_E}{T} \right]}{\left(\exp \left[\dfrac{T_E}{T} \right] - 1 \right)^2}. \qquad (8.18)$$

Note that C_v is a function of (T_E/T). You may now like to investigate the nature of temperature dependence. For copper, a plot of Eq. (8.18) is shown in Fig. 8.3. You will note that this relation reproduces all the general features of the observed curve. Now, let us consider the nature of temperature dependence in two limiting cases: at high temperatures $(T \gg T_E)$ and at low temperatures $(T \ll T_E)$.

High temperature limit $(T \gg T_E)$

In this case, $(T_E / T) \ll 1$ and we can write the exponential term as

$$\exp \left[\frac{T_E}{T} \right] = 1 + \frac{T_E}{T} + \frac{1}{2!} \left(\frac{T_E}{T} \right)^2 + \ \cdots$$

Using this expansion in Eq. (8.18), we get

$$C_v = 3R \left(\frac{T_E}{T} \right)^2 \frac{\left(1 + \dfrac{T_E}{T} + \dfrac{1}{2!} \left(\dfrac{T_E}{T} \right)^2 + \cdots \right)}{\left[\dfrac{T_E}{T} + \dfrac{1}{2!} \left(\dfrac{T_E}{T} \right)^2 + \dfrac{1}{3!} \left(\dfrac{T_E}{T} \right)^3 + \cdots \right]^2}$$

You can readily simplify this expression to obtain

$$C_v = 3R \left[1 - \frac{1}{12} \left(\frac{T_E}{T} \right)^2 + \cdots \right]. \qquad (8.19)$$
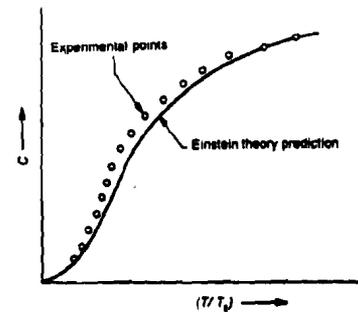

Fig. 8.3: Heat capacity versus temperature plot for copper at low temperatures as predicted by Einstein's theory and as obtained experimentally

$$\exp (x) = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \cdots$$
$$\text{for } x \ll 1$$

so that

$$\exp (x) - 1 = x + \frac{x^2}{2!} + \frac{x^3}{3!} + \cdots$$

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For many materials, molar heat capacity at $T_E \sim 200$ K and high temperatures will approach $3R$. From this we can conclude that Einstein's theory provides sound basis for validity of Dulong-Petit law.

Low temperature limit $(T \ll T_E)$

For $(T_E / T) \gg 1$, we can ignore unity in comparison to the exponential term in the denominator of Eq. (8.18) and write:

$$C_v = 3R \left(\frac{T_E}{T}\right)^2 \exp\left[-\frac{T_E}{T}\right]. \tag{8.20}$$

You may now ask: What does Eq. (8.20) signify physically in relation to temperature dependence of heat capacity? We know that exponential function changes more rapidly than any power of x. Therefore, Einstein theory predicts that heat capacity at low temperatures will decay exponentially and approach zero as temperature tends to absolute zero. This prediction of Einstein led to a lot of experimental activity on measurement of heat capacity at low temperatures and results for several solids were reported. Again refer to Fig. 8.3 which depicts the temperature variation of heat capacity of copper as predicted by Einstein's theory alongwith experimentally observed curve. *Note that, at low temperatures, the exponential decrease predicted by Einstein is much faster compared to experimental result.* We may, therefore, conclude that *Einstein's theory is qualitative,* particularly at low temperatures, as it fails to explain experimental observations near absolute zero for most solids.

The discrepancy between experimental curve and Einstein's predication could possibly be due to Einstein's assumption that all the atomic oscillators in a solid are identical, independent of each other and vibrate with the same characteristic frequency. Indeed, arguing along these lines, Debye modified Einstein's oversimplified model by assigning *a range of frequencies* to atomic oscillators. But, before you learn these details, pause for a moment and answer the following SAQ.

Spend 2 min.

SAQ 2

Mark the following statements as True or False:

a) According to the classical theory of heat capacity, average energy of an atomic oscillator is independent of temperature.

b) According to Einstein theory, heat capacity decreases exponentially with temperature at low temperatures.

c) Einstein theory predicts that the average energy of an atomic oscillator depends on its frequency.

d) Einstein theory assumes that the energy values which an atomic oscillator can acquire form a discrete set.

8.4 DEBYE THEORY

To overcome the limitations of Einstein theory, Debye suggested that it is unrealistic to assume that all atoms in a solid vibrate with one frequency and independent of each other. According to him, motion of one atom influences the motion of all other atoms. *Debye, therefore, proposed that a solid should be treated as a collection of coupled harmonic oscillators having a spectrum of frequencies.* However, following Einstein, Debye assumed that each mode (way of oscillation) of vibration of a crystal lattice is equivalent to a harmonic oscillator whose average energy is given by Eq. (8.13).

You have seen that in Einstein's theory, the total energy of a solid is obtained by multiplying average energy of an oscillator by the number of modes (that is, $3N$). Bu

writing expression for total energy of a solid for Debye model is not straightforward because

- enumeration of number of modes is quite difficult for a system of coupled oscillators, and
- exact knowledge of the distribution of frequencies among different modes is not easy to obtain.

Thus, to write an expression for total energy, Debye introduced a parameter called *density of modes* or *density of states*, which gives the number of modes per unit frequency range. We denote it by the symbol $g(v)$ and write the total vibrational energy of a solid as:

$$E = \int \langle \varepsilon(v) \rangle g(v) dv, \qquad (8.20)$$

where integral is over all the allowed values of frequencies and $g(v) dv$ gives the number of modes whose frequencies are in the range v and $v + dv$.

Debye assumed that all waves (generated by the system of coupled oscillators constituting a solid) with frequencies in a certain range, $0 < v < v_{max}$, could propagate through the solid. And for a 3-D solid, he showed that the number of allowed vibrational modes between frequencies v and $v+dv$ is given by

$$g(v) dv = \frac{9N}{v_{max}^3} v^2 dv \qquad 0 < v < v_{max} \qquad (8.21)$$

$$= 0. \qquad v > v_{max}$$

Note that the total number of modes is defined by

$$\int_0^{v_{max}} g(v) dv = 3N, \qquad (8.22)$$

where v_{max} is the maximum allowed frequency, also called **Debye frequency**. On substituting for average energy and density of states from Eqs. (8.13) and (8.21), respectively in Eq. (8.20), we can write the total energy of the solid as

$$E = \frac{9Nh}{v_{max}^3} \int_0^{v_{max}} \frac{v^3 dv}{\exp\left[\dfrac{hv}{k_B T}\right] - 1}. \qquad (8.23)$$

To simplify, we rewrite Eq. (8.23) in terms of the energy of an elastic wave by defining

$$\xi = hv$$

so that

$$d\xi = hdv$$

and

$$v^3 dv = \frac{\xi^3 d\xi}{h^4}.$$

On inserting these results in Eq. (8.23), we get

$$E = \frac{9N}{\xi_{max}^3} \int_0^{\xi_{max}} \frac{\xi^3 d\xi}{\exp\left[\dfrac{\xi}{k_B T}\right] - 1} . \qquad (8.24)$$

where ξ_{max} is the maximum energy.

The heat capacity is therefore given by

$$C_v = \left(\frac{dE}{dT}\right)_v = \frac{9N}{\xi_{max}^3} \int_0^{\xi_{max}} \frac{\xi^4 \, d\xi \, \exp\left[\dfrac{\xi}{k_B T}\right]}{k_B T^2 \left[\exp\left[\dfrac{\xi}{k_B T}\right] - 1\right]^2}$$

$$= \frac{9N}{(k_B T_D)^3} \int_0^{k_B T_D} \frac{\xi^4 \exp\left[\dfrac{\xi}{k_B T}\right] d\xi}{k_B T^2 \left[\exp\left[\dfrac{\xi}{k_B T}\right] - 1\right]^2} ,$$

where $T_D = \dfrac{\xi_{max}}{k_B}$ is **Debye temperature**.

Integrating by parts, we get

$$C_v = \frac{9N}{(k_B T_D)^3} \frac{1}{T} \left[-\frac{(k_B T_D)^4}{\left[\exp\left[T_D / T\right] - 1\right]} + \int_0^{k_B T_D} \frac{4\xi^3 d\xi}{\left[\exp\left[\dfrac{\xi}{k_B T}\right] - 1\right]} \right] .$$

$$(8.25)$$

To simplify this expression, we introduce a dimensionless variable through the

relation $x = \dfrac{\xi}{k_B T}$. Note that as $\xi \to 0$, $x \to 0$ and the lower limit of integration will

remain zero. However, as $\xi \to \xi_{max}$, $x \to \dfrac{T_D}{T}$ so that $x_{max} = \left(\dfrac{T_D}{T}\right)$ gives the upper

limit of integration. Thus, we can write

$$C_v = 3N k_B \, f_D\left(\frac{T_D}{T}\right), \qquad (8.26)$$

where

$$f_D\left(\frac{T_D}{T}\right) = \frac{1}{x_{max}^3} \left[12 \int_0^{x_{max}} \frac{x^3 dx}{[\exp[x]-1]} - \frac{3x_{max}^4}{[\exp[x_{max}]-1]} \right]. \qquad (8.27)$$

Eq. (8.26) is the **Debye formula** for heat capacity of solids. Here f_D is known as **Debye function** and can not be evaluated analytically for general values of x. Therefore, the value of heat capacity has to be obtained numerically at different temperatures. However, the expression for f_D can be evaluated in the limiting cases. Let us now examine the nature of Debye formula in high and low temperature regions.

In high temperature limit, $x \left(= T_D / T\right)$ is very small and we may write $\exp[x] \cong 1 + x$, so that $\exp[x] - 1 = x$, if we ignore powers of x higher than one. Thus, in the first order approximation, Eq. (8.26) reduces to

$$C_v = 9Nk_B \frac{1}{x_{max}^3} \left[12 \cdot \frac{x_{max}^3}{3} - 3x_{max}^3 \right]$$

$$= 3Nk_B. \tag{8.28}$$

This shows that Debye theory conforms to Dulong-Petit law at high temperatures. This convergence can be understood physically. At high temperatures, there is sufficient thermal energy available in the solid so that each and every mode receives energy equal to classical value $k_B T$. And since the density of states is $3N$, we write total energy of the solid as

$$E = 3N k_B T$$

which gives $C_v = 3Nk_B$. However, from the above, you may be justified in concluding that it is not a special achievement of the Debye's theory because high temperature heat capacity is pretty well explained by classical as well as Einstein's theories. You may obviously like to know as to how this theory explains low temperature behaviour of heat capacity.

Low temperature limit ($T \ll T_D$ or $x_{max} \gg 1$)

For $\dfrac{T}{T_D} \ll 1$, the exponential term in Eq. (8.26) increases faster than any power of x.

Therefore, the quantity $\dfrac{x_{max}^n}{\exp[x_{max}] - 1}$ will tend to zero as $x_{max} \to \infty$. That is, the second term in the Debye function approaches zero. Further, in the integral occurring in Debye function (Eq. (8.27)), we may replace x_{max} by infinity without introducing much error. Then Eq. (8.27) simplifies to

$$f_D(x_{max}) = \frac{12}{x_{max}^3} \int_0^\infty \frac{x^3 \, dx}{\exp[x] - 1}.$$

Integral in this expression for $f_D\left(\dfrac{T_D}{T}\right)$ is of the form of a standard integral given as

$$\int_0^\infty \frac{x^{p-1} \, dx}{\exp[x] - 1} = (p-1)! \sum_{n=1}^\infty \frac{1}{n^p}.$$

So, we can write

$$f_D\left(\frac{T_D}{T}\right) = \frac{12}{x_{max}^3} \int_0^\infty \frac{x^{4-1} \, dx}{\exp[x] - 1}$$

$$= \frac{12}{x_{max}^3} (3)! \sum_{n=1}^\infty \frac{1}{n^4}$$

$$= \frac{72}{x_{max}^3} \sum_{n=1}^\infty \frac{1}{n^4}.$$

The summation term in the above expression represents Riemann Zeta function of order 4, that is,

$$\sum_{n=1}^{\infty} \frac{1}{n^4} = \zeta(4)$$

and its value is equal to $\frac{\pi^4}{90}$. Thus, the expression for Debye function simplifies to

$$f_D\left(\frac{T_D}{T}\right) = \frac{72}{x_{max}^3} \times \frac{\pi^4}{90} = \frac{4}{5} \frac{\pi^4}{x_{max}^3}.$$

Substituting this value of $f_D\left(\frac{T_D}{T}\right)$ in Eq. (8.26), we get

$$C_v = \frac{12\pi^4}{5} N k_B \left(\frac{T}{T_D}\right)^3 \qquad\qquad (8.29)$$
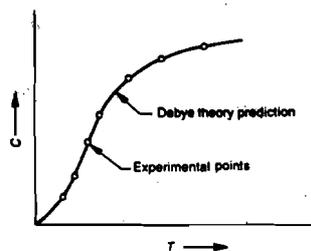

Fig. 8.4: Comparison of temperature variation of heat capacity as per Debye's theory and experimental observation

This result shows that at low temperatures, heat capacity varies as T^3. This is known as *Debye T^3- law*. Debye's theory successfully explains heat capacity at low temperatures for most solids (Fig. 8.4).

Note that Debye's theory uses phenomenological model for frequency distribution function. *It is based on the approximation that solids can be treated as isotropic homogeneous media whose dispersion relations are linear.* You may, however, recall from Unit 7 that the dispersion curves for monatomic and diatomic crystal lattices are not linear for the entire frequency range. At some stage, you may like to consider such refinements in Debye model by modifying the expression for density of states. However, such theories of heat capacity are beyond the scope of this course.

Before we close our discussion, a special mention about the **heat capacity of metals** will be appropriate here. In metals, thermal energy is absorbed by crystal lattice as well as by free electrons. Therefore, we should also expect an electronic contribution to the heat capacity. At normal temperatures, this contribution is negligible compared to the contribution due to lattice vibrations and may be ignored. At low temperatures, however, the lattice heat capacity decreases very rapidly (Debye T^3- law), whereas the heat capacity due to electrons decreases linearly with T. As a consequence, electronic heat capacity dominates. Therefore, heat capacity of a metal at low temperatures will be given by the expression

$$C = aT + bT^3, \qquad\qquad (8.30)$$

where a and b are constants. You will learn the details of electronic heat capacity in Unit 9 of this course.

Yet another point which you should note is that in the theories of heat capacity discussed in this Unit, we have consistently assumed that vibrating atoms in a solid are analogous to harmonic oscillators. This is known as *harmonic oscillator approximation* and it has served us well in case of heat capacity. There are, however, many other thermal properties of solids, such as thermal expansion, which cannot be explained on the basis of harmonic approximation. To explain those thermal properties, we must take into account what is known as **anharmonic interactions** between the atoms of a solid. You will learn about this in higher level courses on solid state physics.

Now, let us sum up what you have learnt in this Unit.

8.5 SUMMARY

- **Dulong-Petit law** states that heat capacity of solids is constant and independent of temperature: $C_v = 3R$ mol^{-1}.

- **Classical theory of heat capacity** assumes that atoms in a solid behave like harmonic oscillators. A solid consisting of N atoms can be treated as equivalent to $3N$, one-dimensional independent harmonic oscillators. Average energy of a 1-D oscillator is equal to $k_B T$ and the heat capacity is given by

$$C_v = \frac{\partial E}{\partial T} = \frac{\partial}{\partial T}\left(3N k_B T\right) = 3N k_B .$$

- Classical theory conforms to Dulong-Petit law, but it fails to explain temperature dependence of heat capacity at low temperatures.

- **Einstein theory of heat capacity** uses the concept of quantisation of energy. The average energy of a quantum oscillator is given by

$$< \varepsilon >= \frac{hv}{\exp\left[\dfrac{hv}{k_B T}\right] - 1}$$

and the molar heat capacity is given by

$$C_v = 3R \left(\frac{T_E}{T}\right)^2 \frac{\exp\left[\dfrac{T_E}{T}\right]}{\left(\exp\left(\dfrac{T_E}{T}\right) - 1\right)^2} ,$$

where T_E denotes **Einstein temperature**: $T_E = \dfrac{hv_E}{k_B}$, and v_E is called **Einstein frequency**. Einstein's theory predicts that heat capacity decreases exponentially at low temperatures and reduces to zero at absolute zero. This explains experimental observations only qualitativly.

- **Debye theory** is based on the assumptions that a solid behaves as an isotropic homogenous substance, and its dispersion relation is linear. The total energy of a solid as per Debye theory is given by

$$E = \int \langle \varepsilon(v) \rangle g(v)\, dv ,$$

where density of states, $g(v)$, is given by

$$g(v) = \frac{9N}{v_{max}^3} v^2 dv \qquad\qquad 0 < v < v_{max}$$

$$= 0 \qquad . \qquad\qquad v > v_{max}$$

- According to Debye theory, the expression for heat capacity is given by

$$C_v = 3Nk_B f_D\left(\frac{T_D}{T}\right),$$

where T_D is **Debye temperature,** defined as $T_D = \dfrac{h\nu_D}{k_B}$, ν_D is **Debye**

frequency, and $f_D\left(\dfrac{T_D}{T}\right) = \dfrac{1}{x_{max}^3}\left[12\int\limits_0^{\nu_{max}}\dfrac{x^3 dx}{\exp[x]-1} - \dfrac{3x_{max}^4}{\exp[x_{max}]-1}\right]$ is **Debye**

function with $x = \dfrac{h\nu}{k_B T}$, a dimensionless parameter.

- Debye theory conforms to Dulong-Petit law at high temperature ($T \gg T_D$). At low temperature, it predicts that heat capacity varies as T^3:

$$C_v = \frac{12\pi^4}{5}Nk_B\left(\frac{T}{T_D}\right)^3,$$

which is known as **Debye T^3 – law.**

8.6 TERMINAL QUESTIONS   *Spend 15 min.*

1. Debye temperature for aluminium is 418 K. Calculate the frequency of highest possible lattice vibration in aluminium. Also calculate the molar heat capacity of aluminium at 20K.

2. Debye temperature for copper is 445 K. Calculate the thermal energy of one mole of copper at Debye temperature on the basis of classical theory of heat capacity.

8.7 SOLUTIONS AND ANSWERS

Self-Assessment Questions (SAQs)

1. Substituting Eq. (8.4) in Eq. (8.5), we get

$$\langle\varepsilon\rangle = \frac{\displaystyle\int_0^\infty \varepsilon\exp\left[-\frac{\varepsilon}{k_B T}\right]d\varepsilon}{\displaystyle\int_0^\infty \exp\left[-\frac{\varepsilon}{k_B T}\right]d\varepsilon}$$

Let us introduce a change of variable as

$$x = \frac{\varepsilon}{k_B T}$$

so that

$$d\varepsilon = (k_B T)dx$$

and

$$\varepsilon\,d\varepsilon = (k_B T)^2\,x\,dx$$

Thus, we can write:

$$\langle\varepsilon\rangle = \frac{(k_B T)^2\displaystyle\int_0^\infty x\exp[-x]dx}{(k_B T)\displaystyle\int_0^\infty \exp[-x]dx}$$

$$= \frac{(k_B T) \int_0^\infty x \exp[-x] dx}{[\exp[-x]]_0^\infty}$$

$$= (k_B T) \left[x \exp[-x] \Big|_0^\infty - \int_0^\infty \exp[-x] dx \right]$$

$$= k_B T$$

2. a) False; b) True; c) True; d) True

Terminal Questions (TQs)

1. We know that

$$\nu_D = k_B T_D$$

Given $T_D = 418$ K

$$H = 6.62 \times 10^{-34} \text{ Js}$$

$$k_B = 1.38 \times 10^{-23} \text{ JK}^{-1}$$

Thus, frequency of highest possible lattice vibration

$$\nu_D = \frac{k_B T_D}{h} = \frac{(1.38 \times 10^{-23} \text{ JK}^{-1}) \times (418 \text{ K})}{6.62 \times 10^{-34} \text{ Js}}$$

$$= 5.49 \times 10^{-15} \text{ s}^{-1}$$

For calculating molar heat capacity at 20 K, we note that T << T_D, and hence we can use Eq. (8.29)

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

$$= \frac{12 \times (3.14)^4 \times (6.02 \times 10^{23} \text{ mol}^{-1}) \times (1.38 \times 10^{-23} \text{ JK}^{-1})}{5} \times \left(\frac{20 \text{ K}}{418 \text{ K}} \right)^3$$

$$= 0.04 \text{ JK}^{-1} \text{ mol}^{-1}.$$

2. According to the classical theory, thermal energy of a solid at temperature T is given by Eq. (8.7)

$$E = 3Nk_B T.$$

For one mole of copper, $N = N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$

and

$$T = T_D = 445 \text{ K}.$$

Thus,

$$E = 3 \times (6.02 \times 10^{23} \text{ mol}^{-1}) \times (1.38 \times 10^{-23} \text{ JK}^{-1}) \times (445 \text{ K})$$

$$= 1.1 \times 10^4 \text{ J}$$