

Chapter 3 The Vibrational Heat Capacity of Solids

In a solid material, the heat capacity is often made up of several sources. If the material contains two state systems such as in the case of a paramagnetic solid considered in the last chapter, there is energy associated with orienting these systems with respect to an external field, and this gives rise to the characteristic peaked Schottky anomaly in the heat capacity over a relatively small range of temperatures. If the material is a conductor, it turns out that there is a contribution to the heat capacity due to the conduction electrons. In this chapter we shall study what is perhaps the most important contribution to the heat capacity of solids at moderate temperatures, namely the energy that is due to the vibrations of the atoms or molecules within the crystal lattice.

3.1 Experimental Data

Let us discuss first what we are seeking to explain using the theory. The heat capacity (at constant volume) C_V of many solid materials lie on the curve shown in Figure 3.1 once the temperature axis has been scaled appropriately by an amount depending on the material. We notice that

- At **high** temperatures, the heat capacity tends to $3Nk$ where N is the number of atoms in the material. This is called the law of Dulong and Petit. It turns out that this can be understood classically in terms of the equipartition theorem. Unfortunately, classical mechanics also predicts that the heat capacity should be independent of temperature. Despite many heroic efforts, no satisfactory classical explanation for the way in which the specific heat varies with temperature has ever been found and Maxwell recognized this as a very severe problem for classical mechanics.
- At **low** temperatures the heat capacity decreases to zero. This can be regarded as a consequence of the third law of thermodynamics which states that the entropy of a system tends to zero when the temperature is reduced to zero. At constant volume, we know that $dQ = dE = C_V(T) dT$. If we consider a reversible process taking a system from state 0 at zero temperature to state 1 at temperature $T = T_1$,

$$S_1 - S_0 = \int_0^{T_1} \frac{dQ}{T} = \int_0^{T_1} \frac{C_V(T)}{T} dT$$

In order for this difference to be finite, the integrand cannot diverge at zero too rapidly. If we assume that for small T we can approximate $C_V(T)$ by the power-law T^p , we see that the integrand is proportional to T^{p-1} . The integral diverges unless $p > 0$. If we suppose that $p > 0$, then $C_V(T) \rightarrow 0$ as $T \rightarrow 0$.

Even though we can argue from rather general principles that C_V must tend to zero as T becomes small, we shall see that the explanation for this arises from the discreteness of the energy levels. It was Einstein who first showed (in 1907) that quantum mechanics could resolve this outstanding problem and explain the approximate temperature dependence of the heat capacity. The first part of this chapter will be concerned with Einstein's theory.

Despite the successes of Einstein's theory, it failed to predict in detail the way in which the heat capacity actually approaches zero as $T \rightarrow 0$. In order to examine the low-temperature region in more detail, it is preferable to plot C_V/T rather than T . It is found experimentally that if C_V/T is plotted as a function of T^2 , the graph is essentially a straight line at low temperatures. This means that at low temperatures

$$\frac{C_V}{T} = \alpha T^2 + \gamma$$

or

$$C_V = \alpha T^3 + \gamma T$$

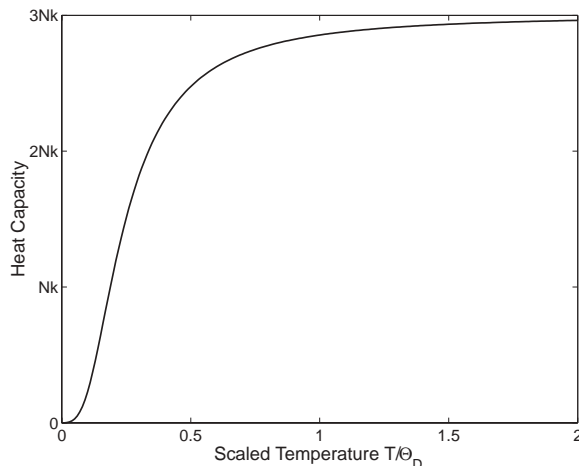


Figure 3.1 Heat capacity of a solid as a function of temperature.

It is found that for **insulators**, only the cubic term is present, whereas for **conductors**, the linear term is also present. It turns out that the linear term is due to the effects of conduction electrons, whereas the cubic term can be understood in terms of a more refined theory of lattice vibrations. It is this theory (due to Debye) which we shall consider in the second part of this chapter.

3.2 Einstein's Theory

In terms of our development of statistical mechanics, we have so far dealt with a collection of N distinguishable (by their positions) but independent particles, each of which can be in one of two energy eigenstates. In this section, we again consider N distinguishable, independent particles, but now, each particle has infinitely many energy eigenstates.

In Einstein's model for the lattice vibrations in a solid, each atom is regarded as a three-dimensional simple harmonic oscillator which oscillates about its equilibrium position in accordance with the equation of motion

$$\frac{d^2\mathbf{r}}{dt^2} = -\omega_E^2\mathbf{r} \quad (3.1)$$

where all the oscillators are assumed to be **independent** and the vibration frequency ω_E of all the oscillators are assumed to be equal. In order to proceed, we first need to work out the energy levels (i.e., the energy eigenstates) of a single three dimensional harmonic oscillator. Schrödinger's equation for the spatial part of the energy eigenfunction $u(x)$ of such an oscillator reads

$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2} \right) + \frac{1}{2} m \omega_E^2 (x^2 + y^2 + z^2) u = E u \quad (3.2)$$

It turns out that there are three quantum numbers r_1 , r_2 and r_3 that label the energy eigenstates. The energy eigenvalues are

$$E_{r_1, r_2, r_3} = \left(r_1 + r_2 + r_3 + \frac{3}{2} \right) \hbar \omega_E \quad (3.3)$$

where each of r_1 , r_2 and r_3 comes from the set $\{0, 1, 2, 3, \dots\}$. Although we shall not need these, the corresponding energy eigenstates are

$$u_{r_1, r_2, r_3}(x, y, z) = f_{r_1}(x) f_{r_2}(y) f_{r_3}(z) \quad (3.4)$$

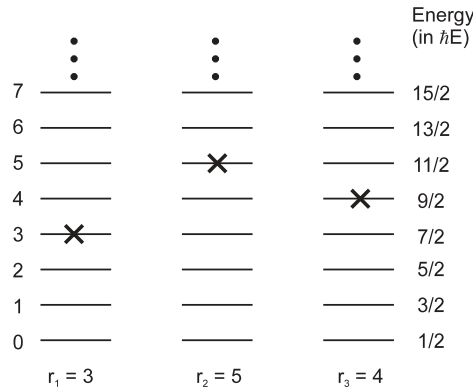


Figure 3.2 Ladders showing energy eigenstates of a single three-dimensional harmonic oscillator. The oscillator shown is in eigenstate $\mathbf{r} = (3, 5, 4)$ whose energy is $13\frac{1}{2}\hbar\omega_E$.

where $f_r(x)$ is the r 'th eigenfunction of the one-dimensional harmonic oscillator. Recall that the r 'th energy eigenstate of the one-dimensional oscillator has energy $(r + \frac{1}{2})\hbar\omega_E$ and so a single three-dimensional harmonic oscillator may be thought of as three independent one-dimensional oscillators with the same spring constant.

We may represent the three quantum numbers associated with a **single** three-dimensional harmonic oscillator as points on the rungs of three ladders (see Figure 3.2). The energy of the particle is related to the sum of the rung numbers.

If we now consider N atoms, we have to think of $3N$ separate ladders. An energy eigenstate (i.e., a single microstate) of the N atoms together is labelled by the $3N$ non-negative integers $\mathbf{r} \equiv (r_1, r_2, \dots, r_{3N})$, and the energy of this eigenstate is

$$E_{\mathbf{r}} = \left[\left(r_1 + \frac{1}{2} \right) + \left(r_2 + \frac{1}{2} \right) + \dots + \left(r_{3N} + \frac{1}{2} \right) \right] \hbar\omega_E \quad (3.5)$$

In order to do statistical mechanics, we simply (!) need to count the states.

3.2.1 The Partition Function

Let us suppose that the system of N atoms is in thermal contact with a heat bath at temperature $T = (k\beta)^{-1}$. By definition, the partition function is

$$Z = \sum_r \exp(-\beta E_r) \quad (3.6)$$

where the each state index r is really a list of $3N$ quantum numbers $(r_1, r_2, \dots, r_{3N})$. Since the $3N$ ladders have the same energy levels and are independent, we can compute the partition function for a single ladder and raise the result to the power $3N$. This requires the ladders to refer to distinguishable entities, which they do since each particle is assumed to occupy a fixed location.

For one ladder, we have a single integer index r which can range from zero to infinity. The energy associated with the r 'th level is $E_r = (r + \frac{1}{2})\hbar\omega_E$. Hence for one ladder,

$$\begin{aligned} Z_{1 \text{ ladder}} &= \sum_{r=0}^{\infty} \exp \left[-\beta \left(r + \frac{1}{2} \right) \hbar\omega_E \right] \\ &= \exp \left(-\frac{x}{2} \right) \sum_{r=0}^{\infty} \exp(-rx) \end{aligned} \quad (3.7)$$

where $x = \beta\hbar\omega_E = \Theta_E/T$, where $\Theta_E = \hbar\omega_E/k$ is known as the **Einstein temperature**. We can compute the sum of the infinite series to obtain

$$Z_{1 \text{ ladder}} = \frac{e^{-x/2}}{1 - e^{-x}}. \quad (3.8)$$

For the whole system of N atoms, where there are $3N$ ladders,

$$Z = \left(\frac{e^{-x/2}}{1 - e^{-x}} \right)^{3N} \quad (3.9)$$

From this partition function it is straightforward to compute the thermodynamic quantities of interest.

3.2.2 Mean Energy

As usual we compute

$$\begin{aligned} \bar{E} &= -\frac{\partial}{\partial \beta} (\log Z) \\ &= -3N \left[\frac{\partial}{\partial x} \left(-\frac{x}{2} - \log(1 - e^{-x}) \right) \right] \frac{\partial x}{\partial \beta} \\ &= \frac{3}{2} N \hbar \omega_E \left(\frac{e^x + 1}{e^x - 1} \right) \end{aligned} \quad (3.10)$$

3.2.3 Heat Capacity

Recall from the previous chapter that

$$C_V = \left(\frac{\partial \bar{E}}{\partial T} \right)_V = k \beta^2 \left(\frac{\partial^2}{\partial \beta^2} \log Z \right)_V \quad (3.11)$$

Substituting the expression for Z and simplifying, we find

$$\begin{aligned} C_V &= k \left(\frac{x}{\hbar \omega_E} \right)^2 \frac{\partial^2}{\partial x^2} \left[3N \left(-\frac{x}{2} - \log(1 - e^{-x}) \right) \right] \left(\frac{\partial x}{\partial \beta} \right)^2 \\ &= 3kN \frac{x^2 e^x}{(e^x - 1)^2} \end{aligned} \quad (3.12)$$

At high temperatures, $x \rightarrow 0$,

$$C_V \approx 3kN \left[\frac{x^2 e^x}{\left(x + \frac{x^2}{2!} + \dots \right)^2} \right]_{x \rightarrow 0} = 3kN \quad (3.13)$$

and so we recover the law of Dulong and Petit. At low temperatures, x is large and

$$C_V \approx 3kN \frac{x^2 e^x}{e^{2x}} = 3kN x^2 e^{-x} \quad (3.14)$$

$$= 3kN \left[\frac{\Theta_E^2}{T^2} \exp \left(-\frac{\Theta_E}{T} \right) \right] \quad (3.15)$$

This tends to zero as $T \rightarrow 0$. Graphs of the mean energy and the heat capacity are shown as the solid and dashed lines respectively in Figure 3.3. In the classical limit, energy is not quantized and we have a continuum of levels. We can achieve a similar effect by supposing $\hbar \omega_E \rightarrow 0$, so that Θ_E is zero. In this case, $C_V = 3Nk$ for all temperatures, as expected by the law of Dulong and Petit. In the classical theory, the energy rises linearly with temperature so that the slope of the E vs T curve (which is the heat capacity) is constant.

From the true graph of energy versus temperature seen as the dashed line of Figure 3.3, we see that at low temperatures where $T/\Theta_E < 1$ (or where $kT < \hbar \omega_E$), the linear relationship between E and T does not hold. Instead of tending to zero at zero temperature, the energy tends to $\frac{3}{2} Nk\Theta_E$ or $\frac{3}{2} N\hbar \omega_E$. This is the **ground state energy** of the system of harmonic oscillators, since there are $3N$ ladders, each of which has ground state energy $\frac{1}{2} \hbar \omega_E$. The ground state energy of a harmonic oscillator is a quantum mechanical phenomenon,

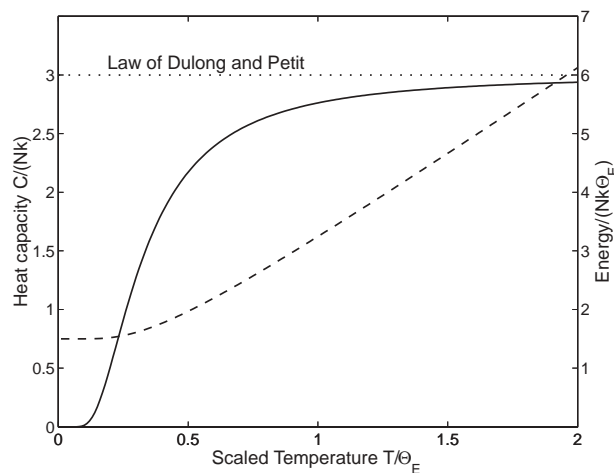


Figure 3.3 Vibrational heat capacity (solid line) and energy (dashed line) of a solid according to Einstein's theory. Dotted line shows classical result (law of Dulong and Petit).

which may be considered as a manifestation of Heisenberg's uncertainty principle, since the classical idea of an oscillator of zero energy which is a particle at rest at a precisely known position is not possible in quantum mechanics.

Due to the flattening out of the energy versus temperature graph at low temperatures, the heat capacity tends to zero at zero temperature, instead of remaining constant as the classical theory would predict. This phenomenon is sometimes referred to as the “freezing out” of the degrees of freedom of the system. Another way of thinking about this is to say that when the thermal energy is much less than the spacing between the rungs of the ladder for the oscillators ($kT \ll \hbar\omega_E$), the particles tend to sit in the ground state and are unable to “see” the higher rungs of the ladder as the probability to excite them up the ladder is very small. They thus do not contribute to the heat capacity of the system. Classically of course, the rungs form a continuum, and it is always possible to climb up no matter how low the temperature is.

Let us now try to see what parameters of the material affect the value of Θ_E which is essentially the only parameter needed to draw the graph of C versus T . We construct a very crude model and suppose that the solid consists of atoms of mass m separated from each other by distance a . If we displace one of the atoms by a distance x , we would like to estimate the restoring force so that we can fit this to the force law which defines ω_E , namely

$$f = -m\omega_E^2 x \quad (3.16)$$

The macroscopic quantity which we can measure that relates the restoring force to the displacement in a solid is its **Young's modulus**. The strain ε associated with a displacement of x is the fractional change in length which is of order x/a . The stress σ is the force per unit area which is of order f/a^2 . The Young's modulus E is the ratio

$$E = \frac{\sigma}{\varepsilon} = \frac{f/a^2}{x/a} = \frac{f}{ax} = \frac{m\omega_E^2}{a} \quad (3.17)$$

Hence we may write

$$\omega_E \approx A \left(\frac{aE}{m} \right)^{1/2} \quad (3.18)$$

where A is a fudge factor of order unity (it is actually closer to 2) which compensates for our carelessness in treating the geometrical factors. The inter-atomic spacing may be estimated with the help of the density since

$$\rho \approx m/a^3 \quad (3.19)$$

and so we have

$$\omega_E = \frac{k\Theta_E}{\hbar} \approx A \left(\frac{E^{1/2}}{m^{1/3}\rho^{1/6}} \right) \quad (3.20)$$

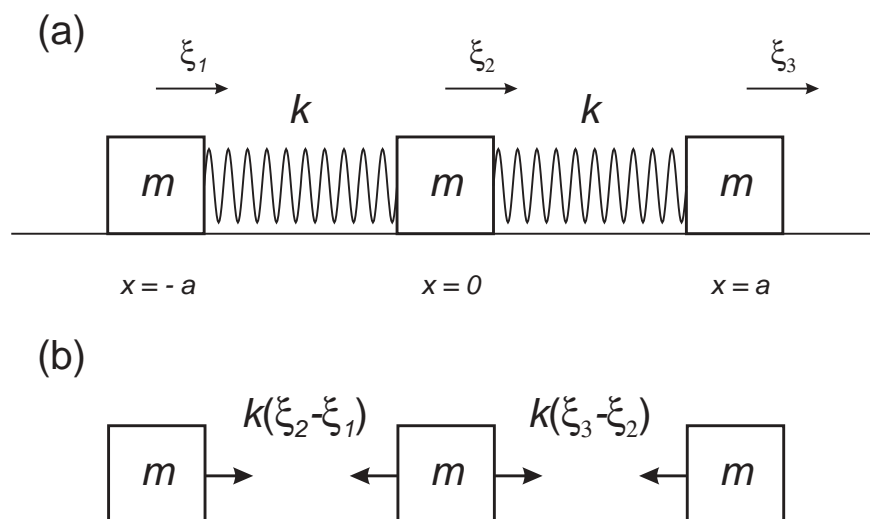


Figure 3.4 Three masses coupled by springs (a) shows the definitions of the displacements and (b) shows the forces on each mass.

So for large ω_E , we want a very rigid material (high E) with low mass and density. Conversely, for small ω_E , we want an easily deformable material (low E) with high mass and density. Indeed, it is found that diamond has a large ω_E , lead has a small ω_E and aluminium has an intermediate value. In our text, a quantitative comparison is made and the agreement with experiment is remarkably good, considering the crudeness of our models.

3.3 Debye's theory

As mentioned in the introduction, although Einstein's theory gives an explanation of the gross behaviour of the heat capacity with temperature and with the material properties, its detailed prediction of the way in which C behaves at low temperatures is not consistent with experiment which shows that $C \propto T^3$ for insulators. Debye's theory is able to explain this dependence and it is this theory that we shall now consider.

3.3.1 Modes of Vibration

In Einstein's theory, each atom is taken to be an independent three-dimensional oscillator, and all the oscillators have the same frequency. In a real solid, all the atoms are coupled to each other and cannot be treated independently. However, an important mathematical trick allows us to treat **linear coupled** systems as if they were made of independent "virtual" oscillators. These virtual oscillators generally have different oscillation frequencies however, so that instead of dealing with $3N$ ladders with the same spacing between energy levels, we still have $3N$ ladders, but the energy level spacings of these will differ.

Let us start with a one-dimensional model of coupled oscillators. Suppose we have three particles of mass m connected by two springs of spring constant k as shown in Figure 3.4. Let a be the equilibrium lengths of the springs, so that when the system is at rest and the springs are at their equilibrium lengths, the masses are at $x = -a$, $x = 0$ and $x = a$. Let ξ_1 , ξ_2 and ξ_3 denote the displacements of the masses from their equilibrium positions. By considering Newton's second law for each mass, we can write down the force on each and

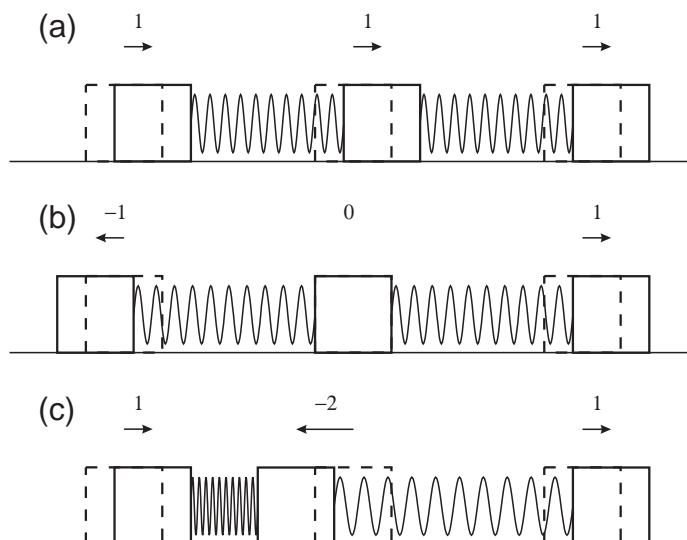


Figure 3.5 Normal modes of vibration of three coupled masses. (a) shows translation at zero frequency, (b) shows oscillations at $\omega = \sqrt{k/m}$ and (c) shows oscillations at $\omega = \sqrt{3k/m}$.

equate this to the acceleration. This yields

$$\begin{aligned} m\ddot{\xi}_1 &= k(\xi_2 - \xi_1) \\ m\ddot{\xi}_2 &= k(\xi_3 - \xi_2) - k(\xi_2 - \xi_1) \\ m\ddot{\xi}_3 &= -k(\xi_3 - \xi_2) \end{aligned}$$

which may be written in matrix form as

$$\frac{d^2}{dt^2} \begin{pmatrix} \xi_1 \\ \xi_2 \\ \xi_3 \end{pmatrix} = -\underbrace{\frac{k}{m} \begin{pmatrix} 1 & -1 & 0 \\ -1 & 2 & -1 \\ 0 & -1 & 1 \end{pmatrix}}_{\mathbf{A}} \begin{pmatrix} \xi_1 \\ \xi_2 \\ \xi_3 \end{pmatrix} \quad (3.21)$$

In general the motion of the system is such that the motion of each mass is a rather complicated function of time. However, this complexity is superficial, as any general motion can be split into the sum of three **normal modes**. The characteristic of a normal mode is that when the system is in a normal mode, all the masses move with the same frequency. It turns out that the normal mode angular frequencies are the square roots of the eigenvalues of the matrix \mathbf{A} . These are

$$\omega_1 = 0, \quad \omega_2 = \sqrt{\frac{k}{m}} \quad \text{and} \quad \omega_3 = \sqrt{\frac{3k}{m}} \quad (3.22)$$

The corresponding eigenvectors are

$$\mathbf{v}_1 = \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix}, \quad \mathbf{v}_2 = \begin{pmatrix} -1 \\ 0 \\ 1 \end{pmatrix} \quad \text{and} \quad \mathbf{v}_3 = \begin{pmatrix} 1 \\ -2 \\ 1 \end{pmatrix} \quad (3.23)$$

These indicate how each of the masses move for the three normal modes. As shown in Figure 3.5, the first normal mode (at zero frequency) corresponds to equal translation of all the masses, and so is not strictly a mode of vibration. The second mode (at angular frequency $\sqrt{k/m}$) corresponds to the central mass remaining stationary and the two end masses vibrating antisymmetrically, while the third mode (at angular frequency $\sqrt{3k/m}$) corresponds to the vibration shown in Figure 3.5(c) where the oscillation amplitude of the centre mass is out of phase with and twice that of the outer masses.

For the system of three coupled masses in one dimension, there are three “virtual oscillators” at the normal mode frequencies. These virtual oscillators are independent, and we can assign amplitudes (and phases) to each. Each choice of amplitudes and phases for the virtual oscillators defines an actual motion of the coupled system (namely the appropriate sum of the normal modes).

3.3.2 Normal Modes of a Rod

Let us now progress to a system of N coupled oscillators in one dimension which is the obvious extension of the problem so far considered. The equations of motion are now

$$\frac{d^2}{dt^2} \begin{pmatrix} \xi_1 \\ \xi_2 \\ \vdots \\ \xi_{N-1} \\ \xi_N \end{pmatrix} = -\frac{k}{m} \underbrace{\begin{pmatrix} 1 & -1 & & & \\ -1 & 2 & -1 & & \\ & \ddots & \ddots & \ddots & \\ & & & -1 & 2 & -1 \\ & & & & -1 & 1 \end{pmatrix}}_{\mathbf{A}} \begin{pmatrix} \xi_1 \\ \xi_2 \\ \vdots \\ \xi_{N-1} \\ \xi_N \end{pmatrix} \quad (3.24)$$

If we suppose that the masses and springs may be approximated by a continuum (e.g. a steel rod or a rod of jelly), so that the initial separation a between the masses is small, and $\xi(x, t)$ now represents the displacement at time t of a particle which was initially at position x within the material, we can turn this large system of ordinary differential equations into a single **partial differential equation**. Let us consider a typical equation in the system, for the k 'th mass that was initially at x_k :

$$\frac{d^2 \xi_k}{dt^2} = \frac{k}{m} (\xi_{k-1} - 2\xi_k + \xi_{k+1}) \quad (3.25)$$

$$\frac{\partial^2 \xi}{\partial t^2}(x_k, t) = \frac{k}{m} [\xi(x_k - a, t) - 2\xi(x_k, t) + \xi(x_k + a, t)] \quad (3.26)$$

where we have switched to partial derivative notation since ξ is a now function of two variables. Since a is small, we may use Taylor's theorem to write

$$\xi(x_k \pm a, t) \approx \xi(x_k, t) \pm a \frac{\partial \xi}{\partial x}(x_k, t) + \frac{1}{2} a^2 \frac{\partial^2 \xi}{\partial x^2}(x_k, t) \quad (3.27)$$

so that

$$\xi(x_k - a, t) - 2\xi(x_k, t) + \xi(x_k + a, t) \approx a^2 \frac{\partial^2 \xi}{\partial x^2}(x_k, t) \quad (3.28)$$

Substituting back into (3.26), we see that

$$\frac{\partial^2 \xi}{\partial t^2}(x_k, t) = \frac{ka^2}{m} \frac{\partial^2 \xi}{\partial x^2}(x_k, t) \quad (3.29)$$

We see that this is precisely the **wave equation** for propagation of longitudinal (i.e., sound) waves at speed $c^2 = ka^2/m$, namely

$$\frac{\partial^2 \xi}{\partial t^2} = c^2 \frac{\partial^2 \xi}{\partial x^2}. \quad (3.30)$$

As we take the process to the continuum limit, we must let a and m approach zero in such a way that c remains finite. Note that this equation holds at each mass except those at the very ends, so the partial differential equation holds within the body of the material.

Let us now think about the boundary conditions. The first equation of (3.24) is

$$\frac{d^2 \xi_1}{dt^2} = \frac{k}{m} (\xi_2 - \xi_1) \quad (3.31)$$

Substituting the Taylor expansion (to first order) of ξ about the left-hand endpoint $x = x_1$ yields

$$\frac{\partial^2 \xi}{\partial t^2}(x_1, t) = \frac{ka}{m} \frac{\partial \xi}{\partial x}(x_1, t) \quad (3.32)$$

or

$$\frac{\partial \xi}{\partial x}(x_1, t) = \frac{m}{ka} \frac{\partial^2 \xi}{\partial t^2}(x_1, t). \quad (3.33)$$

Remember that we are going to let a and m both approach zero in such a way that $c = ka^2/m$ remains finite. The coefficient $m/(ka)$ in front of the expression on the right-hand side may be written as a/c . As

a and m both tend to zero, it is clear that a/c must tend to zero. Thus we obtain the left-hand boundary condition that

$$\frac{\partial \xi}{\partial x}(x_1, t) = 0 \quad (3.34)$$

and similarly, for the right-hand side,

$$\frac{\partial \xi}{\partial x}(x_N, t) = 0. \quad (3.35)$$

We are thus led to the conclusion that in order to find the modes of vibration in the continuum limit for a one-dimensional body, we should consider the **waves** that can propagate within the material in such a way as to satisfy the Neumann boundary conditions (i.e., vanishing derivatives at the endpoints). This means that there must be an integer number of half wavelengths between the boundaries. The normal mode frequencies are found from the admissible wavelengths using the usual relationship $\omega = 2\pi c/\lambda$. For a one dimensional rod of length L , we see that

$$\frac{n\lambda_n}{2} = L \Rightarrow \lambda_n = \frac{2L}{n} \Rightarrow \omega_n = \frac{2\pi c}{\lambda_n} = \frac{n\pi c}{L} \quad (3.36)$$

So the **spectrum** of normal mode frequencies for the one dimensional rod consists of equally-spaced frequencies, separated by angular frequency $\pi c/L$.

In the true continuum limit, the levels keep on going for ever, but if there are only N particles moving in one dimension, there can only be N normal modes. In the Debye theory, we simply truncate the list of modes, retaining the ones with the lowest N frequencies. This is actually quite a coarse approximation, since at such high mode numbers, adjacent particles are moving essentially in opposite directions and the continuum approximation based on Taylor's expansion of ξ in terms of x breaks down. Nevertheless, as we shall see, the theory does give good results.

3.3.3 Normal Modes of a Solid

For the vibrational modes of a solid, we have to consider the three-dimensional wave equation and consider the waves which can propagate within the material while being consistent with the boundary conditions. An additional complication arises since we have more than just longitudinal waves when we deal with three dimensions. Indeed, for each direction of propagation of the wave (labelled by its propagation vector \mathbf{k}) it is possible to have one **longitudinal** wave and two **transverse** waves (corresponding to different states of polarization). The longitudinal waves propagate at one speed c_L (which is the speed of sound in the material) whereas the transverse waves (which are also known as **shear waves**) propagate at a different speed c_T .

Apart from these complications, the procedure is very similar to that used above. We need to find the frequencies of the $3N$ independent "virtual oscillators" which represent the normal modes of our coupled vibrating system. If we consider a cube of material of length L , we first determine the different propagation vectors \mathbf{k} which are consistent with fitting an integer number of half wavelengths in each direction. Each propagation vector may be labelled by three integers n_x , n_y and n_z such that

$$\mathbf{k} = (k_x, k_y, k_z) \text{ where } k_x = \frac{n_x\pi}{L}, k_y = \frac{n_y\pi}{L} \text{ and } k_z = \frac{n_z\pi}{L}. \quad (3.37)$$

Corresponding to this value of \mathbf{k} , the angular frequency of the wave is $\omega = kc$ where $k = |\mathbf{k}|$ and c is the wave velocity. We would like to count the number of normal modes which correspond to a specified range of k values. Since n_x , n_y and n_z are integers, the permitted values of \mathbf{k} lie on a lattice. A given value of k corresponds to a sphere in \mathbf{k} space, and we need to count the number of lattice points lying in this sphere. In fact we only consider the positive octant of the sphere since all the n values are non-negative. A convenient way of counting is to divide the volume of the octant of the sphere by the volume occupied by a lattice site.

$$\# \text{ (Lattice sites with } |\mathbf{k}| \leq k) \approx \frac{\frac{1}{8}(\frac{4}{3}\pi k^3)}{(\pi/L)^3} = \frac{k^3 L^3}{6\pi^2} \quad (3.38)$$

By differentiating this expression with respect to k , we find the number of lattice sites with $k \leq |\mathbf{k}| < k + dk$. This yields

$$f(k) dk = \# \text{ (Lattice sites with } k \leq |\mathbf{k}| < k + dk) = \frac{k^2 V}{2\pi^2} dk \quad (3.39)$$

where we have written V for the volume of the cube. It can be shown that our result is in fact independent of the shape of the volume.

Since $\omega = kc$, we can readily convert this to an expression for the number of lattice sites with frequency between ω and $\omega + d\omega$. Using the symbol $f(\omega)$ for this purpose as well (even though this is a *different function* to $f(k)$ above),

$$f(\omega) d\omega = \frac{\omega^2 V}{2\pi^2 c^3} d\omega. \quad (3.40)$$

We must now remember that corresponding to each permitted wave propagation vector \mathbf{k} , there are three possible waves, one longitudinal and two transverse. If these all had the same velocity, we would simply multiply the above result by three. We note however that since the longitudinal wave travels at speed c_L while the two transverse waves travel at c_T , the density of normal modes for an elastic solid is

$$f(\omega) d\omega = \frac{\omega^2 V}{2\pi^2} \left(\frac{1}{c_L^3} + \frac{2}{c_T^3} \right) d\omega \quad (3.41)$$

$$= \frac{3\omega^2 V}{2\pi^2 \bar{c}^3} d\omega \quad (3.42)$$

where we have written

$$\frac{3}{\bar{c}^3} = \frac{1}{c_L^3} + \frac{2}{c_T^3} \quad (3.43)$$

so that \bar{c} plays the role of an average wave speed. Note that once again, $f(\omega)$ is a different function to those given previously. We shall continue to use the same symbol for the density of modes appropriate for each new problem.

3.3.4 Partition function and Mean Energy for Vibrational Modes of a Solid

What we have found so far are the normal mode frequencies which correspond to the “virtual oscillators” into which we shall decompose the vibrations of our solid. In reality, the virtual oscillator frequencies ω_α form a discrete set of $3N$ frequencies, but our continuum model discussed above has replaced the closely spaced frequencies by a density of modes $f(\omega)$. Since it is important that we have a finite number of oscillators, we shall suppose that we can replace a sum over all the virtual oscillator frequencies with an integral

$$\sum_{\omega_\alpha} \rightarrow \int_0^{\omega_D} d\omega f(\omega) \quad (3.44)$$

where the upper limit ω_D called the **Debye (angular) frequency** is chosen so that

$$\int_0^{\omega_D} d\omega f(\omega) = 3N \quad (3.45)$$

Thus, we artificially chop off the integral at the maximum frequency needed to give us the correct number of modes. Substituting for $f(\omega)$ and performing the integral, we see that

$$3N = \int_0^{\omega_D} \frac{3\omega^2 V}{2\pi^2 \bar{c}^3} d\omega \quad (3.46)$$

or

$$\omega_D^3 = \frac{6\pi^2 N \bar{c}^3}{V}. \quad (3.47)$$

We may rewrite $f(\omega)$ in terms of ω_D to give

$$f(\omega) = \frac{9N\omega^2}{\omega_D^3}.$$

Corresponding to each virtual oscillator of frequency ω_α , there is a ladder with rung spacing $\hbar\omega_\alpha$. These oscillators are independent and so the partition function of the collection will be the product of the single-oscillator partition functions. From equation (3.8) for a single ladder with rung spacing $\hbar\omega_\alpha$, we have

$$Z_{1 \text{ ladder}} = \frac{\exp(-\beta\hbar\omega_\alpha/2)}{1 - \exp(-\beta\hbar\omega_\alpha)}. \quad (3.48)$$

For all $3N$ ladders, we obtain

$$Z = \prod_{\alpha=1}^{3N} \frac{\exp(-\beta\hbar\omega_\alpha/2)}{1 - \exp(-\beta\hbar\omega_\alpha)} \quad (3.49)$$

Taking logarithms to turn the product into a sum, we obtain

$$\log Z = \sum_{\alpha=1}^{3N} -\frac{\beta\hbar\omega_\alpha}{2} - \log[1 - \exp(-\beta\hbar\omega_\alpha)] \quad (3.50)$$

We now use the continuum approximation to replace the sum by an integral. This gives

$$\log Z \approx - \int_0^{\omega_D} f(\omega) \left\{ \frac{\beta\hbar\omega}{2} + \log[1 - \exp(-\beta\hbar\omega)] \right\} d\omega \quad (3.51)$$

$$= - \int_0^{\omega_D} \frac{9N\omega^2}{\omega_D^3} \left\{ \frac{\beta\hbar\omega}{2} + \log[1 - \exp(-\beta\hbar\omega)] \right\} d\omega \quad (3.52)$$

$$= -\frac{9}{8}N\beta\hbar\omega_D - \frac{9N}{\omega_D^3} \int_0^{\omega_D} \omega^2 \log[1 - \exp(-\beta\hbar\omega)] d\omega \quad (3.53)$$

From the partition function, the mean energy is given straightforwardly by using

$$\bar{E} = -\frac{\partial}{\partial\beta} (\log Z) \quad (3.54)$$

$$= \frac{9}{8}N\hbar\omega_D + \frac{9N\hbar}{\omega_D^3} \int_0^{\omega_D} \frac{\omega^3}{\exp(\beta\hbar\omega) - 1} d\omega \quad (3.55)$$

It is convenient to write $x = \beta\hbar\omega$ and $x_D = \beta\hbar\omega_D$ in the last integral to obtain the simpler form

$$\bar{E} = \frac{9}{8}N\hbar\omega_D + \frac{9NkT}{x_D^3} \int_0^{x_D} \frac{x^3}{e^x - 1} dx \quad (3.56)$$

The heat capacity at constant V is found by differentiating \bar{E} with respect to T . It is easier to start from (3.54) since the only dependence on temperature is through β in the denominator of the integrand. We find

$$C_V = \frac{\partial \bar{E}}{\partial T} = \frac{9Nk}{x_D^3} \int_0^{x_D} \frac{x^4 e^x}{(e^x - 1)^2} dx \quad (3.57)$$

The last integral cannot be evaluated in closed form, but may readily be found numerically. We may also introduce the **Debye temperature** Θ_D such that $k\Theta_D = \hbar\omega_D$. With this definition, $x_D = \Theta_D/T$.

We can get a feeling for the behaviour of C_V by evaluating it in the limits of high and low temperatures. At high temperatures, i.e., if $T \gg \Theta_D$, x_D is small and we can replace the integrand by its value near zero. This is most simply done by expanding the exponentials in a power series in x ,

$$\frac{x^4 e^x}{(e^x - 1)^2} = \frac{x^4 (1 + x + \dots)}{(x + \frac{1}{2}x^2 + \dots)^2} = x^2 + \dots \quad (3.58)$$

Thus

$$C_V \approx \frac{9Nk}{x_D^3} \int_0^{x_D} x^2 dx = 3Nk \quad (3.59)$$

Not surprisingly, we recover the law of Dulong and Petit in the high temperature limit. On the other hand, at low temperatures, $T \ll \Theta_D$, and x_D becomes large. If we replace the upper limit of the integral by infinity, we find that

$$\int_0^\infty \frac{x^4 e^x}{(e^x - 1)^2} dx = \frac{4}{15}\pi^4 \quad (3.60)$$

This result is derived in appendix A of Mandl, but for our purposes, it is just some number. We thus see that

$$C_V = \frac{9Nk}{x_D^3} \left(\frac{4}{15} \pi^4 \right) = \frac{12}{5} Nk \pi^4 \left(\frac{T}{\Theta_D} \right)^3 \quad (3.61)$$

which shows the dependence of C_V on T^3 , in agreement with experiment.

A very appealing feature of the Debye theory is that it predicts that the vibrational heat capacity of all solids follows essentially the same law, with only a single parameter Θ_D which is the Debye temperature. Furthermore, we have found an explicit formula for ω_D , namely

$$\omega_D^3 = \frac{6\pi^2 N \bar{c}^3}{V} \quad (3.62)$$

which may be rearranged to give Θ_D in terms of readily measured quantities such as the number density of atoms N/V and the average speed of elastic waves in the medium \bar{c} ,

$$\Theta_D = \frac{\hbar \bar{c}}{k} \left(\frac{6\pi^2 N}{V} \right)^{1/3}. \quad (3.63)$$

In our text, the experimentally determined values of Θ_D from heat capacity measurements are compared with those calculated using this formula. A remarkably good agreement is found.