

26

The Harmonic Solid

It is not knowledge, but the act of learning, not possession but the act of getting there, which grants the greatest enjoyment.

Johann Carl Friedrich Gauss, German mathematician (1777–1855)

In this chapter we return to calculating the contributions to the specific heat of a crystal from the vibrations of the atoms. We have previously discussed a cruder approximation, the Einstein model, in Section 24.11 of Chapter 24. The harmonic solid is a model of lattice vibrations that goes beyond the Einstein model in that it allows all the atoms in the crystal to move simultaneously.

To simplify the mathematics, we will consider only a one-dimensional model in this book. The general extension to three dimensions does bring in some new phenomena, but it complicates the notation unnecessarily at this point. We will go into three dimensions only for particularly simple cases, in which the extension of the theory does not present any difficulties.

After going through the discussion in this chapter, it should be easy to follow the mathematics of the general three-dimensional case in any good textbook on solid-state physics.

26.1 Model of a Harmonic Solid

A one-dimensional model of a crystal lattice is described by uniformly spaced points along a line,

$$R_j = ja. \quad (26.1)$$

The spacing a is called the lattice constant and the index j is an integer. Atoms are located at points

$$r_j = R_j + x_j = ja + x_j, \quad (26.2)$$

where x_j is the deviation of the position of an atom relative to its associated lattice point.

To write an expression for the kinetic energy we will need the time derivative of x_j which we will indicate by a dot over the variable,

$$\dot{x}_j \equiv \frac{\partial x_j}{\partial t} = \frac{\partial r_j}{\partial t} = \dot{r}_j. \quad (26.3)$$

The energy of a microscopic state is given by the following expression:

$$\begin{aligned} E &= \frac{1}{2}m \sum_j \dot{r}_j^2 + \frac{1}{2}K \sum_j (a + r_j - r_{j+1})^2 \\ &= \frac{1}{2}m \sum_j \dot{x}_j^2 + \frac{1}{2}K \sum_j (x_j - x_{j+1})^2. \end{aligned} \quad (26.4)$$

The potential energy is a minimum for nearest-neighbor separations equal to the lattice constant, a , and is quadratic in the deviations from this optimum separation. As we will see, it is the assumption of a quadratic potential energy that makes this model tractable.

The general strategy to solve for the properties of the harmonic crystal is to transform the problem from N interacting particles to N independent simple harmonic oscillators, which enables us to factorize the partition function as discussed in Section 24.7. Once we have made this transformation, we need only copy the results for quantum SHOs from Section 24.10, and we have solved for the properties of the harmonic solid.

26.2 Normal Modes

The key to reducing the problem to independent oscillators is to Fourier transform¹ the position variables to find the normal modes. The Fourier transform of the positions of the particles is given by

$$\tilde{x}_k = N^{-1/2} \sum_j x_j \exp(-ikR_j), \quad (26.5)$$

where k is the (one-dimensional) wave vector or wave number. We can anticipate that the wave number is related to the wavelength λ by

$$k = \frac{2\pi}{\lambda}. \quad (26.6)$$

An obvious property of the Fourier transformed variables \tilde{x}_k is that

$$\tilde{x}_{-k} = \tilde{x}_k^*, \quad (26.7)$$

where the superscript $*$ indicates the complex conjugate.

¹ Jean Baptiste Joseph Fourier, French mathematician and physicist (1768–1830).

26.2.1 Inverse Fourier Transformation

The inverse of the Fourier transformation in eq. (26.5) is

$$x_j = N^{-1/2} \sum_k \tilde{x}_k \exp(ikR_j), \quad (26.8)$$

which we can confirm by direct substitution,

$$\begin{aligned} \tilde{x}_k &= N^{-1/2} \sum_j x_j \exp(-ikR_j) \\ &= N^{-1/2} \sum_j N^{-1/2} \sum_{k'} \tilde{x}_{k'} \exp(ik'R_j) \exp(-ikR_j) \\ &= \sum_{k'} \tilde{x}_{k'} N^{-1} \sum_j \exp(i(k' - k)R_j) \\ &= \sum_{k'} \tilde{x}_{k'} \delta_{k,k'} = \tilde{x}_k. \end{aligned} \quad (26.9)$$

The identity

$$\sum_j \exp(i(k' - k)R_j) = N\delta_{k,k'}, \quad (26.10)$$

which was used in deriving eq. (26.9), will often prove useful in statistical mechanics. The validity of eq. (26.10) can be easily shown,

$$\begin{aligned} \sum_j \exp(i(k' - k)R_j) &= \sum_j \exp\left(i(n' - n)\frac{2\pi}{L}ja\right) \\ &= \sum_j \exp\left(2\pi i(n' - n)\frac{j}{N}\right). \end{aligned} \quad (26.11)$$

If $n' = n$, so that $k' = k$, then the sum is clearly equal to N . If $n' - n = 1$, the sum is simply adding up the N complex roots of -1 . Since they are uniformly distributed around the unit circle in the complex plane, they sum to zero. If $n' - n$ is any other integer (excepting a multiple of N), the angle between each root is multiplied by the same amount, they are still distributed uniformly, and they still sum to zero.

To complete the Fourier transform, we must specify the boundary conditions. There are two kinds of boundary condition in general use. Since they each have their own advantages, we will discuss them both in detail.

26.2.2 Pinned Boundary Conditions

Pinned boundary conditions for the harmonic solid are similar to the boundary conditions we used for black-body radiation. In that problem, the transverse electric field

vanished at the boundaries of the metal box. For pinned boundary conditions, the vibrations vanish at the boundaries of the system.

To implement pinned boundary conditions, first extend the number of atoms in the model from N to $N + 2$ by adding atoms with indices 0 and $N + 1$. These two atoms enforce the boundary conditions by being fixed ('pinned') at the positions $R_0 = 0$ and $R_{N+1} = (N + 1)a$.

The two solutions $\exp(ikR_j)$ and $\exp(-ikR_j)$ can be combined to give $\tilde{x}_k \propto \sin(kR_j)$ to satisfy the boundary condition that $x_0 = 0$ at $R_0 = 0$. From the other boundary condition that $x_{N+1} = 0$ at $R_{N+1} = (N + 1)a = L$, we need

$$kL = k(N + 1)a = n\pi, \quad (26.12)$$

or,

$$k = k(n) = \frac{n\pi}{L}, \quad (26.13)$$

for some integer n .

Since we have N atoms in the system, we expect to find N independent solutions. If we define

$$K \equiv \frac{2\pi}{a}, \quad (26.14)$$

we can see that k and $k + K$ correspond to the same solution:

$$\begin{aligned} \sin((k + K)R_j) &= \sin(kR_j + jaK) \\ &= \sin\left(kR_j + ja\frac{2\pi}{a}\right) \\ &= \sin(kR_j + 2\pi j) \\ &= \sin(kR_j). \end{aligned} \quad (26.15)$$

Adding any integer multiple of K to k also produces the same solution.

For calculations, the standard choice for pinned boundary conditions is to use only those solutions corresponding to values of n from 1 to N .

26.2.3 Periodic Boundary Conditions

The other possible boundary conditions are periodic. In one dimension, this might be thought of as bending the line of atoms into a circle and tying the ends together, so that

$$R_{j+N} = R_j. \quad (26.16)$$

Note that the length of a system with periodic boundary conditions is

$$L = Na, \quad (26.17)$$

in contrast to the length of $(N + 1)a$ for pinned boundary conditions.

In two dimensions, a rectangular lattice with periodic boundary conditions can be viewed as a torus. It is rather difficult to visualize periodic boundary conditions in three dimensions (it is called a Klein bottle), but the mathematics is no more difficult.

The great advantage of periodic boundary conditions is that the system becomes invariant under translations of any multiple of the lattice constant a . The system has no ends in one dimension (and no borders or surfaces in two or three dimensions).

For periodic boundary conditions, we will take solutions of the form $\exp(ikR_j)$. The condition that the system is periodic means that

$$\exp(ik(R_j + L)) = \exp(ikR_j), \quad (26.18)$$

which implies that

$$kL = 2n\pi, \quad (26.19)$$

or

$$k = k(n) = \frac{2n\pi}{L}, \quad (26.20)$$

for some integer value of n . Note that the values of k given in eq. (26.20) for periodic boundary conditions are spaced twice as far apart as the values of k for pinned boundary conditions given in eq. (26.13).

As was the case for pinned boundary conditions, the solution corresponding to k is identical to the solution corresponding to $k + K$, where K is given by eq. (26.14). We can confirm that k and $k + K$ correspond to the same solution,

$$\begin{aligned} \exp(i(k + K)R_j) &= \exp\left(ikR_j + i\frac{2\pi}{a}ja\right) \\ &= \exp(ikR_j + i2\pi j) \\ &= \exp(ikR_j). \end{aligned} \quad (26.21)$$

In eq. (26.21), do not forget that j is an integer index, while $i = \sqrt{-1}$.

Note that $n = 0$ is a solution for periodic boundary conditions, while it is not for pinned boundary conditions because $\sin(0) = 0$. The solution for $n = 0$ corresponds to moving all atoms together in the same direction.

It is customary to take both positive and negative values of $k(n)$, so that the central values of n we will use are

$$n = 0, \pm 1, \pm 2, \dots, \pm(N-1)/2 \text{ for } N \text{ odd,} \quad (26.22)$$

and

$$n = 0, \pm 1, \pm 2, \dots, \pm(N/2-1), N/2 \text{ for } N \text{ even.} \quad (26.23)$$

For even values of N , the state corresponding to $-N/2$ is identical to the state corresponding to $N/2$.

For periodic boundary conditions, the values of k lie at symmetric points in k -space, and the only independent states lie between $k = -K/2$ and $k = K/2$. This region is called the Brillouin Zone in honor of Léon Nicolas Brillouin (French physicist, 1889–1969, American citizen after 1949). All information in the Brillouin Zone is repeated throughout k -space with a periodicity of $K = 2\pi/a$.

When you take a course in solid state physics, you will find that three-dimensional Brillouin Zones can be rather complicated—and much more interesting. They are essential in understanding important properties of real materials, but they go beyond the scope of this book.

26.3 Transformation of the Energy

If we apply the Fourier transform in eq. (26.8) to the energy of the harmonic crystal given in eq. (26.4), we find that each Fourier mode is independent. This is the great simplification that justifies the bother of introducing Fourier transforms, because it enables us to factorize the partition function.

We will treat the kinetic and potential energy terms separately, beginning with the kinetic terms. The kinetic terms are, of course, already diagonal before the Fourier transform, but we have to demonstrate that they are also diagonal after the Fourier transform.

26.3.1 Kinetic Energy

Using the time derivative of eq. (26.8),

$$\dot{x}_j = N^{-1/2} \sum_k \dot{\tilde{x}}_k \exp(ikR_j), \quad (26.24)$$

we can carry out a Fourier transform of the kinetic energy term in eq. (26.4),

$$\begin{aligned}
 \text{K.E.} &= \frac{1}{2}m \sum_j \dot{x}_j^2 = \frac{1}{2}m \sum_j \dot{x}_j \dot{x}_j \\
 &= \frac{1}{2}m \sum_j \left(N^{-1/2} \sum_k \dot{\tilde{x}}_k \exp(ikR_j) \right) \left(N^{-1/2} \sum_{k'} \dot{\tilde{x}}_{k'} \exp(ik'R_j) \right) \\
 &= N^{-1} \frac{1}{2}m \sum_k \sum_{k'} \dot{\tilde{x}}_k \dot{\tilde{x}}_{k'} \sum_j \exp(i(k+k')R_j) \\
 &= N^{-1} \frac{1}{2}m \sum_k \sum_{k'} \dot{\tilde{x}}_k \dot{\tilde{x}}_{k'} N \delta_{k+k',0} \\
 &= \frac{1}{2}m \sum_k \dot{\tilde{x}}_k \dot{\tilde{x}}_{-k} = \frac{1}{2}m \sum_k |\dot{\tilde{x}}_k|^2.
 \end{aligned} \tag{26.25}$$

For the last equality, we have used eq. (26.7).

26.3.2 Potential Energy

For the potential energy term in eq. (26.4), separate the factors of $(x_j - x_{j+1})$ in the sum and use eq. (26.24) to introduce \tilde{x}_k ,

$$\begin{aligned}
 \text{P.E.} &= \frac{1}{2}K \sum_j (x_j - x_{j+1})^2 = \frac{1}{2}K \sum_j (x_j - x_{j+1})(x_j - x_{j+1}) \\
 &= \frac{1}{2}K \sum_j \left(N^{-1/2} \sum_k \tilde{x}_k (\exp(ikR_j) - \exp(ikR_{j+1})) \right) \\
 &\quad \times \left(N^{-1/2} \sum_{k'} \tilde{x}_{k'} (\exp(ik'R_j) - \exp(ik'R_{j+1})) \right) \\
 &= \frac{1}{2}K \sum_j \left(N^{-1/2} \sum_k \tilde{x}_k \exp(ikja) (1 - \exp(ika)) \right) \\
 &\quad \times \left(N^{-1/2} \sum_{k'} \tilde{x}_{k'} \exp(ik'ja) (1 - \exp(ik'a)) \right)
 \end{aligned} \tag{26.26}$$

Next, collect terms and simplify using the identity eq. (26.10):

$$\begin{aligned}
 \text{P.E.} &= \frac{1}{2}KN^{-1} \sum_k \sum_{k'} \tilde{x}_k \tilde{x}_{k'} (1 - \exp(ika)) (1 - \exp(ik'a)) \\
 &\quad \times \sum_j \exp(i(k - k')ja) \\
 &= \frac{1}{2}K \sum_k \tilde{x}_k \tilde{x}_{-k} (1 - \exp(ika)) (1 - \exp(-ika)) \\
 &= \frac{1}{2} \sum_k K(k) |\tilde{x}_k|^2.
 \end{aligned} \tag{26.27}$$

The function

$$K(k) = K(1 - \exp(ika))(1 - \exp(-ika)) \tag{26.28}$$

gives the effective spring constant for the mode with wave number k .

Adding eqs. (26.25) and (26.27) together, we find the energy of the harmonic crystal from eq. (26.4) in terms of the Fourier transformed variables

$$E = \frac{1}{2}m \sum_k |\dot{\tilde{x}}_k|^2 + \frac{1}{2} \sum_k K(k) |\tilde{x}_k|^2 = \sum_k \left(\frac{1}{2}m |\dot{\tilde{x}}_k|^2 + \frac{1}{2}K(k) |\tilde{x}_k|^2 \right). \tag{26.29}$$

The problem has been transformed from one with N variables (the positions of the atoms) to N problems, each with a single variable (the amplitude of the mode \tilde{x}_k with wave number k). Each mode represents a simple harmonic oscillator with mass m (the same as the original atomic mass) and spring constant $K(k)$. For each mode, the square of the frequency is given by the usual ratio of the spring constant to the mass,

$$\omega^2(k) = \frac{K(k)}{m}. \tag{26.30}$$

26.4 The Frequency Spectrum

To analyze the spectrum of frequencies, $\omega(k)$, we can rewrite eq. (26.28) for $K(k)$ in a more convenient form:

$$\begin{aligned}
 K(k) &= K(1 - \exp(ika))(1 - \exp(-ika)) \\
 &= K(1 - \exp(ika) - \exp(-ika) + 1) \\
 &= 2K(1 - \cos(ka)) \\
 &= 4K \sin^2(ka/2).
 \end{aligned} \tag{26.31}$$

The angular frequency is then given by

$$\omega^2(k) = \frac{4K \sin^2(ka/2)}{m}, \quad (26.32)$$

or,

$$\omega(k) = 2\tilde{\omega} \left| \sin\left(\frac{ka}{2}\right) \right|, \quad (26.33)$$

where $\tilde{\omega} = \sqrt{K/m}$. This spectrum is plotted in Fig. 26.1.

For small wave number ($k \ll \pi/a$), the frequency of a mode in eq. (26.33) becomes linear in the wave number k ,

$$\omega(k) = 2\tilde{\omega} |\sin(ka/2)| \approx \tilde{\omega} ka. \quad (26.34)$$

The speed of a sound wave $v(k)$ is given by the product of the frequency $\nu(k)$ times the wavelength for long wavelengths (small k). From eq. (26.34), we see that the speed of a sound waves is a constant,

$$\frac{\omega(k)}{k} = \frac{2\pi \nu(k)}{2\pi/\lambda} = \nu(k)\lambda = v(k) = a\sqrt{\frac{K}{m}}. \quad (26.35)$$

The linearity of the function $\omega(k)$ can also be seen near the origin in Fig. 26.1.

The generalization of these calculations to a three-dimensional harmonic crystal is not particularly difficult, although the mathematics becomes rather more messy because of the necessary introduction of vector notation. The three-dimensional form of the Brillouin Zone is also somewhat more complicated. However, the generalization of the frequency spectrum to three dimensions has a particularly simple form,

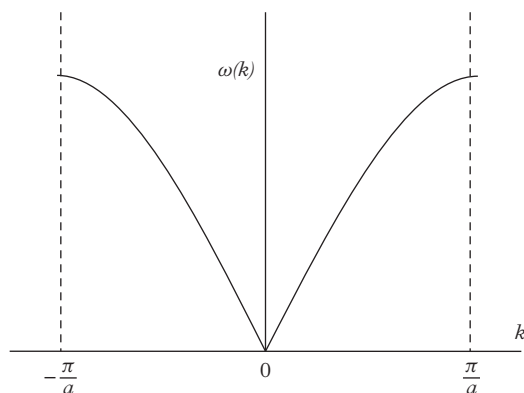


Fig. 26.1 Frequency spectrum of a one-dimensional harmonic solid, as given in eq. (26.33).

$$\omega^2(\vec{k}) = 2K \sum_{\vec{\delta}} \sin^2 \left(\frac{\vec{k} \cdot \vec{\delta}}{2} \right). \quad (26.36)$$

The sum in this equation goes over the vectors $\vec{\delta}$ connecting a site to its nearest neighbors. Eq. (26.36) is valid for all lattices with nearest-neighbor harmonic interactions.

Interactions with more distant neighbors requires only a small change in eq. (26.36),

$$\omega^2(\vec{k}) = 2K \sum_{\alpha} \sum_{\vec{\delta}_{\alpha}} \sin^2 \left(\frac{\vec{k} \cdot \vec{\delta}_{\alpha}}{2} \right). \quad (26.37)$$

The index α goes over more distant types of neighbors.

26.5 Alternate Derivation: Equations of Motion

An alternative derivation of the frequency spectrum of the harmonic solid is given by the equations of motion. This approach is somewhat more flexible in dealing with problems involving multiple sublattices or nonuniform interactions, such as Problems 26.2 and 26.3 at the end of this chapter.

Consider the equation of motion for the coordinate x_j ,

$$m\ddot{x}_j = -K(x_j - x_{j-1} + x_j - x_{j+1}). \quad (26.38)$$

Look for solutions of the form

$$x_j = X \exp(ik2aj) \exp(-i\omega t). \quad (26.39)$$

Substituting this into the equation of motion, we find

$$-m\omega^2 X = -K(X - X \exp(-ika) + X - X \exp(+ika)), \quad (26.40)$$

or,

$$m\omega^2 = K(2 - 2\cos(ka)). \quad (26.41)$$

This can be simplified further to

$$\omega^2 = \frac{4K \sin^2(ka/2)}{m}, \quad (26.42)$$

which agrees with eq. (26.32).

26.6 The Energy in the Classical Model

Since the SHOs in eq. (26.29) are not particles that can move from one system to another, the classical partition function given here does not contain a factor of $1/N!$

$$Z_{class} = \frac{1}{h^N} \int dp \int dq \exp(-\beta H). \quad (26.43)$$

The limits for the integrals in eq. (26.43) have been omitted (which is not usually a good idea) because they all go from $-\infty$ to ∞ .

Because of the diagonal form of the Fourier transformed energy, the partition function factors. Since all the integrals are gaussian, we can evaluate them immediately,

$$Z_{class} = \prod_k \frac{1}{h} \left[(2\pi m k_B T)^{1/2} (2\pi k_B T / K(k))^{1/2} \right]. \quad (26.44)$$

Simplifying this expression, we find

$$Z_{class} = \prod_k \left[\frac{2\pi}{h} k_B T \left(\frac{m}{K(k)} \right)^{1/2} \right] = \prod_k (\beta \hbar \omega(k))^{-1}, \quad (26.45)$$

where

$$\omega(k) = \sqrt{\frac{K(k)}{m}}, \quad (26.46)$$

is the frequency of the k -th mode.

As usual, the average energy is found by taking a derivative with respect to β ,

$$\begin{aligned} U &= \frac{\partial(\beta F)}{\partial \beta} \\ &= - \frac{\partial(\ln Z_{class})}{\partial \beta} \\ &= - \frac{\partial}{\partial \beta} \left[-N \ln \beta - \sum_k \ln(\hbar \omega(k)) \right] \\ &= N \frac{1}{\beta} = N k_B T. \end{aligned} \quad (26.47)$$

As expected, the specific heat has the constant value of k_B , which is the Law of Dulong and Petit.

For a classical harmonic crystal, the spectrum of frequencies as a function of the wave number k is unimportant for equilibrium properties. In the next section we will see that this is not the case for a quantum mechanical harmonic crystal.

26.7 The Quantum Harmonic Crystal

Formal expressions for the quantum mechanical properties of a harmonic lattice are obtained just as easily as the classical properties—though their evaluation is rather more challenging. Because the system factorizes into N SHOs, the partition function is found by inserting the results from Section 24.10,

$$Z_{QM} = \prod_k \left[\exp(-\beta \hbar \omega(k)/2) (1 - \exp(-\beta \hbar \omega(k)))^{-1} \right]. \quad (26.48)$$

The energy of the system is just the sum of the energies of the individual modes, which can be confirmed by taking the negative logarithmic derivative of eq. (26.48) with respect to β , as in eq. (24.12),

$$U_{QM} = \sum_k \left[\frac{1}{2} \hbar \omega(k) + \frac{\hbar \omega(k)}{\exp(\beta \hbar \omega(k)) - 1} \right]. \quad (26.49)$$

Because the wave numbers are closely spaced, eq. (26.49) can be turned into an integral without introducing a significant error,

$$U_{QM} = \frac{L}{\pi} \int_{-\pi/a}^{\pi/a} dk \left[\frac{1}{2} \hbar \omega(k) + \frac{\hbar \omega(k)}{\exp(\beta \hbar \omega(k)) - 1} \right]. \quad (26.50)$$

For high temperatures ($k_B T \gg \hbar \omega_k$ for all modes), the average energy of every mode goes to $k_B T$, and we recover the classical answer and the Law of Dulong and Petit.

For low temperatures the situation is more complicated, because different modes have different frequencies. The contribution of each mode to the specific heat depends on the ratio $\hbar \omega_k / k_B T$; when the ratio is small, the contribution to the specific heat is k_B , but when the ratio is large, the contribution becomes very small. As the temperature is lowered, the contributions to the specific heat from a larger fraction of the modes becomes negligible, and the total specific heat goes to zero.

To calculate how the specific heat of the harmonic crystal goes to zero, we need the frequency spectrum found in Section 26.4. The formal solution for the specific heat is found by substituting eq. (26.33) into eq. (26.49) and differentiating with respect to temperature. This procedure is easily carried out numerically on a modern computer.

On the other hand, it turns out to be both useful and enlightening to develop an approximation that allows us to investigate the low-temperature behavior analytically, as we will do in the following section on the Debye approximation.

26.8 Debye Approximation

We mentioned previously that the Brillouin Zone is very simple in one dimension; it is just the region from $k = -\pi/a$ to π/a . In three dimensions it takes on more complicated forms that reflect the symmetry of the particular lattice: face-centered cubic, body-centered cubic, hexagonal, and so on. This makes it necessary to perform a three-dimensional integral over the Brillouin Zone.

When the theory of the quantum mechanical harmonic lattice was first developed in the early part of the twentieth century, computers were non-existent; all calculations had to be accomplished by hand. This made it very important to simplify calculations as much as possible, and led to the approximation that we will discuss in this section.

However, even today, when we can easily and rapidly evaluate eq. (26.50) and its generalization to three dimensions on a computer, there is still considerable value in simplifying the calculation as an aid to understanding its significance. Such simplifying approximations will also show the relationship of the harmonic crystal to black-body radiation, which might otherwise be much less obvious.

The Debye approximation—named after its inventor, the Dutch physicist Peter Joseph William Debye (born Petrus Josephus Wilhelmus Debye, 1884–1966)—can be viewed as a kind of interpolation between the known high- and low-temperature regions.

For low temperatures, only low-energy modes will be excited significantly because the high-energy modes will be cut off by the exponential term $\exp(\beta\hbar\omega(k))$ in the denominator of the integrand in eq. (26.50). Therefore, we only need to look at the low-frequency region of the energy spectrum. As shown in Section 26.4, the low-frequency spectrum is given by a simple linear relation

$$\epsilon(\vec{k}) = \hbar\omega(\vec{k}) \approx \hbar v |\vec{k}|. \quad (26.51)$$

In this equation, v is the speed of sound, and we have generalized the result to an arbitrary number of dimensions.

Eq. (26.51) is a very nice result because it is spherically symmetric. If the Brillouin Zone were also spherically symmetric, we could use that symmetry to reduce the three-dimensional integral for the energy to a one-dimensional integral. For this reason, Debye introduced an approximation that does exactly that. He approximated the energy spectrum by $\epsilon(\vec{k}) = \hbar v |\vec{k}|$ and the true shape of the Brillouin Zone by a sphere!

It's easy to see how Debye got away with this approximation at low temperatures. Only the low-energy modes made a significant contribution to the average energy, and eq. (26.51) was an excellent approximation for those modes. The high-energy modes that would be affected by true functional form of $\omega(\vec{k})$ and the shape of the Brillouin Zone did not contribute anyway, so that distortion did not matter.

However, at high temperatures neither of these two arguments is valid. The high-energy modes are important, and they do not have the form given in eq. (26.51). Fortunately, a different argument comes into play to save the approximation.

Recall that for high temperatures, when $k_B T \gg \hbar \omega(\vec{k})$, the energy of each mode is just given by the classical value of $k_B T$. Since each mode contributes $k_B T$, the energy spectrum is irrelevant; the only thing that matters is *how many modes there are*. For this reason, Debye fixed the size of his (approximate) spherical Brillouin Zone so that it had exactly $3N$ modes—the same as the true Brillouin Zone.

The radius of the approximate Brillouin Zone is most easily found by going back into n -space, in which the points are distributed uniformly with a density equal to one. Each point in the positive octant (n_x, n_y, n_z are all positive) represents three modes (two for the transverse modes, and one for the longitudinal mode). The total number of modes must equal $3N$,

$$3N = \frac{3}{8} \int_0^{n_D} 4\pi n^2 dn = \frac{3}{8} \frac{4}{3} \pi n_D^3 = \frac{1}{2} \pi n_D^3. \quad (26.52)$$

The Debye radius in \vec{n} -space is

$$n_D = \left(\frac{6N}{\pi} \right)^{1/3}. \quad (26.53)$$

This also gives us results for the corresponding values of the Debye wave number and the Debye energy,

$$k_D = \frac{\pi}{L} \left(\frac{6N}{\pi} \right)^{1/3} \quad (26.54)$$

$$\epsilon_D = \frac{\pi}{L} \left(\frac{6N}{\pi} \right)^{1/3} \hbar v. \quad (26.55)$$

Note that v in eq. (26.55) is the speed of sound, as in eq. (26.51).

Since the ground-state energy plays no role in the thermodynamics of the harmonic solid, we will ignore it and write the energy in the Debye approximation for a three-dimensional harmonic crystal as a one-dimensional integral,

$$U_{Debye} = \frac{3\pi}{2} \int_0^{n_D} n^2 dn \frac{\hbar \omega(n)}{\exp(\beta \hbar \omega(n)) - 1}. \quad (26.56)$$

At this point we will follow the same procedure for simplifying the integral that we used in Section 25.6 for black-body radiation. We define a dimensionless integration variable to transform the integral in eq. (26.56) to a more convenient form,

$$x = \beta \hbar \omega(n) = \left(\frac{\pi \hbar v}{L k_B T} \right) n. \quad (26.57)$$

The upper limit of the integral in eq. (26.56) will become

$$x_d = \frac{\Theta_D}{T}, \quad (26.58)$$

where the Debye temperature, Θ_D , is given by

$$\Theta_D = \frac{\hbar v}{k_B} \left(\frac{6\pi^2 N}{L^3} \right)^{1/3}. \quad (26.59)$$

Using these substitutions, eq. (26.56) takes on the following form:

$$\begin{aligned} U_{Debye} &= \frac{3\pi}{2} \left(\frac{Lk_B T}{\pi \hbar v} \right)^3 k_B T \int_0^{\Theta_D/T} dx x^3 (\exp(x) - 1)^{-1} \\ &= \frac{3L^3 (k_B T)^4}{2\pi^2 \hbar^3 v^3} \int_0^{\Theta_D/T} dx x^3 (\exp(x) - 1)^{-1}. \end{aligned} \quad (26.60)$$

The great advantage of eq. (26.60) when Debye first derived it was that it could be evaluated numerically with pencil and paper (and a bit of effort). However, even today Debye's equation remains very useful for gaining insights into the behavior of a crystal at both high and low temperatures, as we will show in the following subsections.

26.8.1 Debye Approximation for $T \gg \Theta_D$

At high temperatures we expect the energy to go to $U \approx 3Nk_B T$, because that was how we selected the size of the spherical Brillouin Zone. But it is always good to check to make sure that we did not make an error in the calculation.

For high temperatures, $\Theta_D/T \ll 1$, so that the upper limit of the integral in eq. (26.60) is small. For small values of x in the integrand, we can make the approximation

$$x^3 (\exp(x) - 1)^{-1} \approx x^3 (1 + x - 1)^{-1} = x^2, \quad (26.61)$$

which is easy to integrate. Inserting this approximation into eq. (26.60), we find

$$\begin{aligned} U_{Debye} &\approx \frac{3L^3 (k_B T)^4}{2\pi^2 \hbar^3 v^3} \int_0^{\Theta_D/T} dx x^2 \\ &= \frac{3L^3 (k_B T)^4}{2\pi^2 \hbar^3 v^3} \frac{1}{3} \left(\frac{\Theta_D}{T} \right)^3 \end{aligned} \quad (26.62)$$

$$\begin{aligned}
&= \frac{3L^3(k_B T)^4}{2\pi^2 \hbar^3 v^3} \frac{1}{3} \left(\frac{\hbar v}{k_B} \left(\frac{6\pi^2 N}{L^3} \right)^{1/3} \frac{1}{T} \right)^3 \\
&= \frac{L^3(k_B T)^4}{2\pi^2 \hbar^3 v^3} \frac{\hbar^3 v^3}{k_B^3} \left(\frac{6\pi^2 N}{L^3 T^3} \right) \\
&= 3Nk_B T.
\end{aligned}$$

Since the Debye temperature was chosen to include $3N$ modes in the spherical approximate Brillouin Zone, the high-temperature expression for the energy is as expected, and the specific heat is $3k_B$, consistent with the Law of Dulong and Petit.

26.8.2 Debye Approximation for $T \ll \Theta_D$

For low temperatures, $\Theta_D/T \gg 1$, and the upper limit of eq. (26.60) is large. Since the integrand goes to zero as $x^3 \exp(-x)$, taking the upper limit to be infinite is a good approximation,

$$U_{Debye} \approx \frac{3L^3(k_B T)^4}{2\pi^2 \hbar^3 v^3} \int_0^\infty dx x^3 (\exp(x) - 1)^{-1}. \quad (26.63)$$

The integral in eq. (26.63) should be familiar. It is exactly the same as the integral we found in eq. (25.29) during the analysis of black-body radiation. This is not a coincidence, as discussed next,

$$\int_0^\infty dx \frac{x^3}{e^x - 1} = \frac{\pi^4}{15}. \quad (26.64)$$

Inserting the value of the integral into eq. (26.63), we find the low-temperature behavior of the energy of the harmonic lattice in closed form,

$$\begin{aligned}
U_{Debye} &\approx \frac{3L^3(k_B T)^4}{2\pi^2 \hbar^3 v^3} \frac{\pi^4}{15} \\
&= L^3 \frac{\pi^2}{10 \hbar^3 v^3} (k_B T)^4 \\
&= V \frac{\pi^2}{10 \hbar^3 v^3} (k_B T)^4.
\end{aligned} \quad (26.65)$$

The energy per unit volume is then given by

$$\frac{U}{V} = u = \left(\frac{\pi^2}{10 \hbar^3 v^3} \right) (k_B T)^4. \quad (26.66)$$

The energy of the harmonic crystal at low temperatures, for which the Debye approximation is accurate, is very similar to the energy of black-body radiation. Recall eq. (25.30) from Chapter 25 for the energy per unit volume of black-body radiation

$$\frac{U_{BB}}{V} = u = \left(\frac{\pi^2}{15\hbar^3 c^3} \right) (k_B T)^4. \quad (26.67)$$

The form of eqs. (26.66) and (26.67) is the same, because for both black-body radiation and the low-temperature harmonic crystal, the energy spectrum is linear in the wave number: $\omega = vk$ for the harmonic solid, and $\omega = ck$ for black-body radiation (light waves).

There are only two differences between eq. (26.66) for the low-temperature behavior of the harmonic solid and eq. (25.30) or (26.67) for black-body radiation. The expression for the harmonic crystal contains the speed of sound v , instead of the speed of light c , and the factor in the denominator is 10 instead of 15 because there are three polarizations for sound, but only two for light.

From eq. (26.66) we see that the energy of a harmonic crystal is proportional to T^4 , which is analogous to the T^4 factor in the Stefan–Boltzmann Law, eq. (25.31). Taking a derivative of the energy with respect to temperature, we see that the specific heat is proportional to T^3 , which is observed to be the correct behavior of insulating crystals at low temperatures.

The specific heats of metallic crystals, on the other hand, are linear in the temperature. The origin of this difference between conductors and insulators will be discussed in Chapter 29.

26.8.3 Summary of the Debye Approximation

There are three steps in deriving the Debye approximation.

1. Replace the true energy spectrum with an approximate spectrum that is linear in the wave number, k , and spherically symmetric: $\epsilon(\vec{k}) = \hbar v |\vec{k}|$.
2. Replace the true Brillouin Zone by a spherically symmetric Brillouin Zone.
3. Choose the size of the spherically symmetric Brillouin Zone so that it contains exactly N k -values and $3N$ modes.

The Debye approximation is excellent at both high and low temperatures. Do not be fooled, however: in between, it is only mediocre. The qualitative behavior of the contributions to the specific heat from lattice vibrations in real crystals is monotonically increasing with temperature, starting from T^3 -behavior at low temperatures and going to the constant value $3k_B$ (Law of Dulong and Petit) at high temperatures. The detailed form of the function depends on details of the true energy spectrum and the shape of the

true Brillouin Zone. Fortunately, the full, three-dimensional integrals are easy to do on a computer, so that we need not rely on the Debye approximation as much as researchers did in the middle of the last century.

26.9 Problems

PROBLEM 26.1

Fourier transform of the particle positions

In Section 26.2 an argument was given for the validity of eq. (26.10),

$$\sum_j \exp(i(k' - k)R_j) = N\delta_{k,k'}.$$

This argument can be made into a proof by carrying out the sum exactly.

1. Extend the derivation of the infinite sum $\sum_{n=0}^{\infty} x^n$ to calculate the finite sum $\sum_{n=0}^N x^n$.
2. Carry out the proof for periodic boundary conditions with odd N .

PROBLEM 26.2

The harmonic crystal

1. Show that for a harmonic crystal the integral

$$\int_0^{\infty} [C_V(\infty) - C_V(T)] dT$$

is exactly equal to the zero-point energy of the solid.

2. Interpret the result graphically. It might help to relate this result to an earlier assignment on the properties of quantum SHOs.

PROBLEM 26.3

The harmonic crystal with alternating spring constants

Most crystals contain more than one kind of atom. This leads to both quantitative and qualitative differences in the vibration spectrum from the results derived in class. These differences occur whenever the periodicity is altered, whether by changing the masses of the atoms or changing the spring constants.

As an example of the kinds of differences that can arise when the periodicity changes, consider the problem of a one-dimensional lattice with alternating spring constants K_1 and K_2 . For simplicity, you can assume that all the masses are equal to m .

1. If the distance between atoms is a , the periodicity is $2a$. What is the size of the Brillouin Zone?

2. Calculate the vibration spectrum of the lattice. You might find it more convenient to write down equations of motion for the two sublattices.
3. Sketch the vibration spectrum in the Brillouin Zone based on your calculations.
4. Sometimes the vibration spectrum of a crystal with more than one kind of atom is approximated by a combination of an Einstein model and a Debye model. Explain why this might make sense and, give appropriate parameters for such a description in the present case. In answering this question, consider the high- and low-temperature behavior of the specific heat of this model.

PROBLEM 26.4

The harmonic crystal with alternating masses

Most crystals contain more than one kind of atom. This leads to both quantitative and qualitative differences in the vibration spectrum from the results derived in class. These differences occur whenever the periodicity is altered, whether by changing the masses of the atoms or changing the spring constants.

As an example of the kinds of differences that can arise when the periodicity changes, consider the problem of a one-dimensional lattice with alternating masses m_1 and m_2 .

1. If the distance between atoms is a , the periodicity is $2a$. What is the size of the Brillouin Zone?
 2. Calculate the vibration spectrum of the lattice. You might find it more convenient to write down equations of motion for the two sublattices.
 3. Sketch the vibration spectrum in the Brillouin Zone based on your calculations.
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