

Lattice Vibrations

2.1 Monatomic Linear Chain

So far, in our discussion of the crystalline nature of solids we have assumed that the atoms sat at lattice sites. This is not actually the case; even at the lowest temperatures the atoms perform small vibrations about their equilibrium positions. In this chapter we shall investigate the vibrations of the atoms in solids. Many of the significant features of lattice vibrations can be understood on the basis of a simple one-dimensional model, a monatomic linear chain. For that reason we shall first study the linear chain in some detail.

We consider a linear chain composed of N identical atoms of mass M (see Fig. 2.1). Let the positions of the atoms be denoted by the parameters R_i , $i = 1, 2, \dots, N$. Here, we assume an infinite crystal of vanishing surface to volume ratio, and apply *periodic boundary conditions*. That is, the chain contains N atoms and the N th atom is connected to the first atom so that

$$R_{i+N} = R_i. \quad (2.1)$$

The atoms interact with one another (e.g., through electrostatic forces, core repulsion, etc.). The potential energy of the array of atoms will obviously be a function of the parameters R_i , i.e.,

$$U = U(R_1, R_2, \dots, R_N). \quad (2.2)$$

We shall assume that U has a minimum $U(R_1^0, R_2^0, \dots, R_N^0)$ for some particular set of values $(R_1^0, R_2^0, \dots, R_N^0)$, corresponding to the equilibrium state of the linear chain. Define $u_i = R_i - R_i^0$ to be the deviation of the i th atom from its equilibrium position. Now expand U about its equilibrium value to obtain

$$\begin{aligned} U(R_1, R_2, \dots, R_N) &= U(R_1^0, R_2^0, \dots, R_N^0) + \sum_i \left(\frac{\partial U}{\partial R_i} \right)_0 u_i \\ &+ \frac{1}{2!} \sum_{i,j} \left(\frac{\partial^2 U}{\partial R_i \partial R_j} \right)_0 u_i u_j + \frac{1}{3!} \sum_{i,j,k} \left(\frac{\partial^3 U}{\partial R_i \partial R_j \partial R_k} \right)_0 u_i u_j u_k + \dots \end{aligned} \quad (2.3)$$

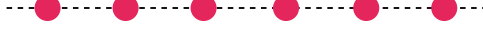


Fig. 2.1. Linear chain of N identical atoms of mass M

The first term is a constant which can simply be absorbed in setting the zero of energy. By the definition of equilibrium, the second term must vanish (the subscript zero on the derivative means that the derivative is evaluated at $u_1, u_2, \dots, u_n = 0$). Therefore, we can write

$$U(R_1, R_2, \dots, R_N) = \frac{1}{2!} \sum_{i,j} c_{ij} u_i u_j + \frac{1}{3!} \sum_{i,j,k} d_{ijk} u_i u_j u_k + \dots, \quad (2.4)$$

where

$$\begin{aligned} c_{ij} &= \left(\frac{\partial^2 U}{\partial R_i \partial R_j} \right)_0, \\ d_{ijk} &= \left(\frac{\partial^3 U}{\partial R_i \partial R_j \partial R_k} \right)_0. \end{aligned} \quad (2.5)$$

For the present, we will consider only the first term in (2.4); this is called *the harmonic approximation*. The Hamiltonian in the harmonic approximation is

$$H = \sum_i \frac{P_i^2}{2M} + \frac{1}{2} \sum_{i,j} c_{ij} u_i u_j. \quad (2.6)$$

Here, P_i is the momentum and u_i the displacement from the equilibrium position of the i th atom.

Equation of Motion

Hamilton's equations

$$\begin{aligned} \dot{P}_i &= -\frac{\partial H}{\partial u_i} = -\sum_j c_{ij} u_j, \\ \dot{u}_i &= \frac{\partial H}{\partial P_i} = \frac{P_i}{M} \end{aligned} \quad (2.7)$$

can be combined to yield the equation of motion

$$M\ddot{u}_i = -\sum_j c_{ij} u_j. \quad (2.8)$$

In writing down the equation for \dot{P}_i , we made use of the fact that c_{ij} actually depends only on the relative positions of atoms i and j , i.e., on $|i - j|$. Notice that $-c_{ij} u_j$ is simply the force on the i th atom due to the displacement u_j of the j th atom from its equilibrium position. Now let $R_n^0 = na$, so that $R_n^0 - R_m^0 = (n - m)a$. We assume a solution of the coupled differential equations

of motion, (2.8), of the form

$$u_n(t) = \xi_q e^{i(qna - \omega_q t)}. \quad (2.9)$$

By substituting (2.9) into (2.8) we find

$$M\omega_q^2 = \sum_m c_{nm} e^{iq(m-n)a}. \quad (2.10)$$

Because c_{nm} depends only on $l = m - n$, we can rewrite (2.10) as

$$M\omega_q^2 = \sum_{l=1}^N c(l) e^{iqla}. \quad (2.11)$$

Boundary Conditions

We apply periodic boundary conditions to our chain; this means that the chain contains N atoms and that the N th atom is connected to the first atom (Fig. 2.2). This means that the $(n + N)$ th atom is the same atom as the n th atom, so that $u_n = u_{n+N}$. Since $u_n \propto e^{iqna}$, the condition means that

$$e^{iqNa} = 1, \quad (2.12)$$

or that $q = \frac{2\pi}{Na} \times p$ where $p = 0, \pm 1, \pm 2, \dots$. However, not all of these values of q are independent. In fact, there are only N independent values of q since there are only N degrees of freedom. If two different values of q , say q and q' give identical displacements for every atom, they are equivalent. It is easy to see that

$$e^{iqna} = e^{iq'na} \quad (2.13)$$

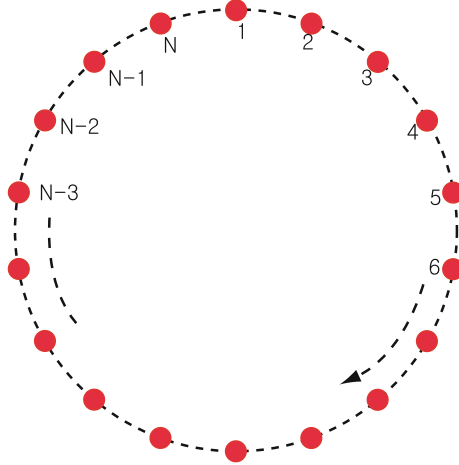


Fig. 2.2. Periodic boundary conditions on a linear chain of N identical atoms

for all values of n if $q' - q = \frac{2\pi}{a}l$, where $l = 0, \pm 1, \pm 2, \dots$. The set of independent values of q are usually taken to be the N values satisfying $q = \frac{2\pi}{L}p$, where $-\frac{N}{2} \leq p \leq \frac{N}{2}$. We will see later that in three dimensions the independent values of \mathbf{q} are values whose components (q_1, q_2, q_3) satisfy $q_i = \frac{2\pi}{L_i}p$, and which lie in the first Brillouin zone, the Wigner-Seitz unit cell of the reciprocal lattice.

Long Wave Length Limit

Let us look at the long wave length limit, where the wave number q tends to zero. Then $u_n(t) = \xi_0 e^{-i\omega_{q=0}t}$ for all values of n . Thus, the entire crystal is uniformly displaced (or the entire crystal is translated). This takes no energy if it is done very very slowly, so it requires $M\omega^2(0) = \sum_{l=1}^N c(l) = 0$, or $\omega(q=0) = 0$. In addition, it is not difficult to see that since $c(l)$ depends only on the magnitude of l that

$$M\omega^2(-q) = \sum_l c(l)e^{-iqla} = \sum_{l'} c(l')e^{iq'l'a} = M\omega^2(q). \quad (2.14)$$

In the last step in this equation, we replaced the dummy variable l by l' and used the fact that $c(-l') = c(l')$. Equation (2.14) tells us that $\omega^2(q)$ is an even function of q which vanishes at $q = 0$. If we make a power series expansion for small q , then $\omega^2(q)$ must be of the form

$$\omega^2(q) = s^2 q^2 + \dots \quad (2.15)$$

The constant s is called the *velocity of sound*.

Nearest Neighbor Forces: An Example

So far, we have not specified the interaction law among the atoms; (2.15) is valid in general. To obtain $\omega(q)$ for all values of q , we must know the interaction between atoms. A simple but useful example is that of nearest neighbor forces. In that case, the equation of motion is

$$M\omega^2(q) = \sum_{l=1}^1 c_l e^{iqla} = c_{-1}e^{-iqa} + c_0 + c_1 e^{iqa}. \quad (2.16)$$

Knowing that $\omega(0) = 0$ and that $c_{-l} = c_l$ gives the relation $c_1 = c_{-1} = -\frac{1}{2}c_0$. Therefore, (2.16) is simplified to

$$M\omega^2(q) = c_0 \left[1 - \left(\frac{e^{iqa} + e^{-iqa}}{2} \right) \right]. \quad (2.17)$$

Since $1 - \cos x = 2 \sin^2 \frac{x}{2}$, (2.17) can be expressed as

$$\omega^2(q) = \frac{2c_0}{M} \sin^2 \frac{qa}{2}, \quad (2.18)$$

which is displayed in Fig. 2.3. By looking at the long wave length limit, the coupling constant is determined by $c_0 = \frac{2Ms^2}{a^2}$, where s is the velocity of sound.

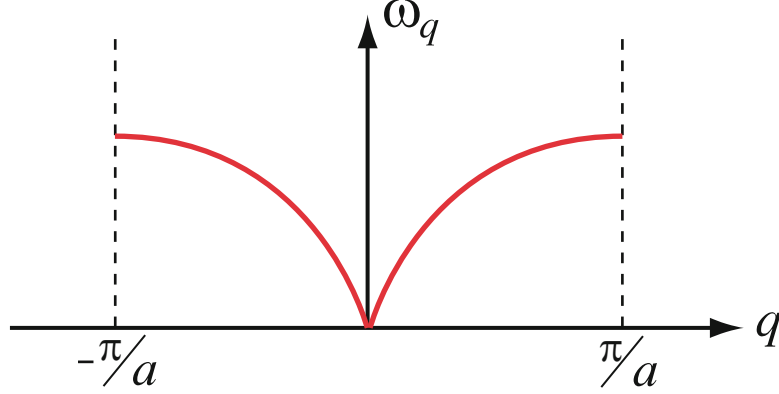


Fig. 2.3. Dispersion relation of the lattice vibration in a monatomic linear chain

2.2 Normal Modes

The general solution for the motion of the n th atom will be a linear combination of solutions of the form of (2.9). We can write the general solution as

$$u_n(t) = \sum_q [\xi_q e^{iqna - i\omega t} + \text{cc}], \quad (2.19)$$

where cc means the complex conjugate of the previous term. The form of (2.19) assures the reality of $u_n(t)$, and the $2N$ parameters (real and imaginary parts of ξ_q) are determined from the initial values of the position and velocity of the N atoms which specify the initial state of the system.

In most problems involving small vibrations in classical mechanics, we seek new coordinates p_k and q_k in terms of which the Hamiltonian can be written as

$$H = \sum_k H_k = \sum_k \left[\frac{1}{2M} p_k p_k^* + \frac{1}{2} M \omega_k^2 q_k q_k^* \right]. \quad (2.20)$$

In terms of these normal coordinates p_k and q_k , the Hamiltonian is a sum of N independent simple harmonic oscillator Hamiltonians. Because we use running waves of the form $e^{iqna - i\omega_q t}$ the new coordinates q_k and p_k can be complex, but the Hamiltonian must be real. This dictates the form of (2.20).

The normal coordinates turn out to be

$$q_k = N^{-1/2} \sum_n u_n e^{-ikna}, \quad (2.21)$$

and

$$p_k = N^{-1/2} \sum_n P_n e^{+ikna}. \quad (2.22)$$

We will demonstrate this for q_k and leave it for the student to do the same for p_k . We can write (2.19) as

$$u_n(t) = \alpha \sum_k \xi_k(t) e^{ikna}, \quad (2.23)$$

where ξ_k is complex and satisfies $\xi_{-k}^* = \xi_k$. With this condition $u_n(t)$, given by (2.23), is real and α is simply a constant to be determined. We can write the potential energy $U = \frac{1}{2} \sum_{mn} c_{mn} u_m u_n$ in terms of the new coordinates ξ_k as follows.

$$U = \frac{1}{2} |\alpha|^2 \sum_{mn} c_{mn} \sum_k \xi_k e^{ikma} \sum_{k'} \xi_{k'} e^{ik'na}. \quad (2.24)$$

Now, let us use $k' = q - k$ to rewrite (2.24) as

$$U = \frac{1}{2} |\alpha|^2 \sum_{nkq} \left[\sum_m c_{mn} e^{ik(m-n)a} \right] \xi_k \xi_{q-k} e^{iqna}. \quad (2.25)$$

From (2.10) one can see that the quantity in the square bracket in (2.25) is equal to $M\omega_k^2$. Thus, U becomes

$$U = \frac{1}{2} |\alpha|^2 \sum_{nkq} M\omega_k^2 \xi_k \xi_{q-k}^* e^{iqna}. \quad (2.26)$$

The only factor in (2.26) that depends on n is e^{iqna} . It is not difficult to prove that $\sum_n e^{iqna} = N\delta_{q,0}$. We do this as follows: Define $S_N = 1 + x + x^2 + \cdots + x^{N-1}$; then $xS_N = x + x^2 + \cdots + x^N$ is equal to $S_N - 1 + x^N$.

$$xS_N = S_N - 1 + x^N. \quad (2.27)$$

Solving for S_N gives

$$S_N = \frac{1 - x^N}{1 - x}. \quad (2.28)$$

Now, let $x = e^{iqa}$. Then, (2.28) says

$$\sum_{n=0}^{N-1} (e^{iqa})^n = \frac{1 - e^{iqaN}}{1 - e^{iqa}}. \quad (2.29)$$

Remember that the allowed values of q were given by $q = \frac{2\pi}{Na} \times \text{integer}$. Therefore, $iqaN = i\frac{2\pi}{Na}aN \times \text{integer}$, and $e^{iqaN} = e^{2\pi i \times \text{integer}} = 1$. Therefore, the numerator vanishes. The denominator does not vanish unless $q = 0$. When $q = 0$, $e^{iqa} = 1$ and the sum gives N . This proves that $\sum_n e^{iqna} = N\delta(q, 0)$ when $q = \frac{2\pi}{Na} \times \text{integer}$. Using this result in (2.26) gives

$$U = \frac{1}{2} |\alpha|^2 \sum_k M \omega_k^2 \xi_k \xi_k^* N. \quad (2.30)$$

Choosing $\alpha = N^{-1/2}$ puts U into the form of the potential energy for N simple harmonic oscillators labeled by the k value. By assuming that P_n is proportional to $\sum_k p_k e^{-ikna}$ with $p_{-k}^* = p_k$, it is not difficult to show that (2.22) gives the kinetic energy in the desired form $\sum_k \frac{p_k p_k^*}{2M}$. The inverse of (2.21) and (2.22) are easily determined to be

$$u_n = N^{-1/2} \sum_k q_k e^{ikna}, \quad (2.31)$$

and

$$P_n = N^{-1/2} \sum_k p_k e^{-ikna}. \quad (2.32)$$

Quantization

Up to this point our treatment has been completely classical. We quantize the system in the standard way. The dynamical variables q_k and p_k are replaced by quantum mechanical operators \hat{q}_k and \hat{p}_k which satisfy the commutation relation

$$[p_k, q_{k'}] = -i\hbar \delta_{k,k'}. \quad (2.33)$$

The quantum mechanical Hamiltonian is given by $H = \sum_k H_k$, where

$$H_k = \frac{\hat{p}_k \hat{p}_k^\dagger}{2M} + \frac{1}{2} M \omega_k^2 \hat{q}_k \hat{q}_k^\dagger. \quad (2.34)$$

\hat{p}_k^\dagger and \hat{q}_k^\dagger are the Hermitian conjugates of \hat{p}_k and \hat{q}_k , respectively. They are necessary in (2.34) to assure that the Hamiltonian is a Hermitian operator. The Hamiltonian of the one-dimensional chain is simply the sum of N independent simple Harmonic oscillator Hamiltonians. As with the simple Harmonic oscillator, it is convenient to introduce the operators a_k and its Hermitian conjugate a_k^\dagger , which are defined by

$$q_k = \left(\frac{\hbar}{2M\omega_k} \right)^{1/2} (a_k + a_{-k}^\dagger), \quad (2.35)$$

$$p_k = i \left(\frac{\hbar M \omega_k}{2} \right)^{1/2} (a_k^\dagger - a_{-k}). \quad (2.36)$$

The commutation relations satisfied by the a_k 's and a_k^\dagger 's are

$$[a_k, a_{k'}^\dagger]_- = \delta_{k,k'} \text{ and } [a_k, a_{k'}]_- = [a_k^\dagger, a_{k'}^\dagger]_- = 0. \quad (2.37)$$

The displacement of the n th atom and its momentum can be written

$$u_n = \sum_k \left(\frac{\hbar}{2MN\omega_k} \right)^{1/2} e^{ikna} (a_k + a_{-k}^\dagger), \quad (2.38)$$

$$P_n = \sum_k i \left(\frac{\hbar\omega_k M}{2N} \right)^{1/2} e^{-ikna} (a_k^\dagger - a_{-k}). \quad (2.39)$$

The Hamiltonian of the linear chain of atoms can be written

$$H = \sum_k \hbar\omega_k \left(a_k^\dagger a_k + \frac{1}{2} \right), \quad (2.40)$$

and its eigenfunctions and eigenvalues are

$$|n_1, n_2, \dots, n_N\rangle = \frac{(a_{k_1}^\dagger)^{n_1}}{\sqrt{n_1!}} \dots \frac{(a_{k_N}^\dagger)^{n_N}}{\sqrt{n_N!}} |0\rangle, \quad (2.41)$$

and

$$E_{n_1, n_2, \dots, n_N} = \sum_i \hbar\omega_{k_i} \left(n_i + \frac{1}{2} \right). \quad (2.42)$$

In (2.41), $|0\rangle = |0_1\rangle |0_2\rangle \dots |0_N\rangle$ is the ground state of the entire system; it is a product of ground state wave functions for each harmonic oscillator. It is convenient to think of the energy $\hbar\omega_k$ as being carried by an *elementary excitations* or *quasiparticle*. In lattice dynamics, these elementary excitations are called *phonons*. In the ground state, no phonons are present in any of the harmonic oscillators. In an arbitrary state, such as (2.41), n_1 phonons are in oscillator k_1 , n_2 in k_2 , ..., n_N in k_N . We can rewrite (2.41) as $|n_1, n_2, \dots, n_N\rangle = |n_1\rangle |n_2\rangle \dots |n_N\rangle$, a product of kets for each oscillator.

2.3 Mössbauer Effect

With the simple one-dimensional harmonic approximation, we have the tools necessary to understand the physics of some interesting effects. One example is *the Mössbauer effect*.¹ This effect involves the decay of a nuclear excited state via γ -ray emission (see Fig. 2.4). First, let us discuss the decay of a nucleus in a free atom; to be explicit, let us consider the decay of the excited state of Fe^{57} via emission of a 14.4 keV γ -ray.

$$\text{Fe}^{57*} \longrightarrow \text{Fe}^{57} + \gamma \quad (2.43)$$

The excited state of Fe^{57} has a lifetime of roughly 10^{-7} s. The uncertainty principle tells us that by virtue of the finite lifetime $\Delta t = \tau = 10^{-7}$ s, there

¹ R. L. Mössbauer, D.H. Sharp, Rev. Mod. Phys. **36**, 410 (1964).

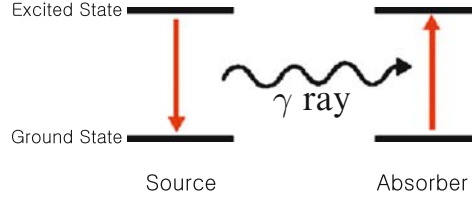


Fig. 2.4. The exact transition energy is required to be reabsorbed because of the very sharply defined nuclear energy states

is an uncertainty ΔE in the energy of the excited state (or a natural linewidth for the γ -ray) given by $\Delta E = \frac{\hbar}{\Delta t}$. Using $\Delta t = 10^{-7}$ s gives $\Delta\omega = 10^7 \text{ s}^{-1}$ or $\Delta(\hbar\omega) \simeq 6 \times 10^{-9} \text{ eV}$. Thus, the ratio of the linewidth $\Delta\omega$ to the frequency ω is $\frac{\Delta\omega}{\omega} \simeq 4 \times 10^{-13}$.

In a resonance experiment, the γ -ray source emits and the target resonantly absorbs the γ -rays. Unfortunately, when a γ -ray is emitted or absorbed by a nucleus, the nucleus must recoil to conserve momentum. The momentum of the γ -ray is $p_\gamma = \frac{\hbar\omega}{c}$, so that the nucleus must recoil with momentum $\hbar K = p_\gamma$ or energy $E(K) = \frac{\hbar^2 K^2}{2M}$ where M is the mass of the atom. The recoil energy is given by $E(K) = \frac{\hbar^2 \omega^2}{2Mc^2} = \frac{(\hbar\omega)^2}{2(M/m)mc^2}$. But $mc^2 \simeq 0.5 \times 10^6 \text{ eV}$ and the ratio of the mass of Fe^{57} to the electron mass m is $\sim 2.3 \times 10^5$, giving $E(K) \simeq 2 \times 10^{-3} \text{ eV}$. This recoil energy is much larger than the energy uncertainty of the γ -ray ($6 \times 10^{-9} \text{ eV}$). Because of the recoil on emission and absorption, the γ -ray is short by $4 \times 10^{-3} \text{ eV}$ of energy necessary for resonance absorption. Mössbauer had the idea that if the nucleus that underwent decay was bound in a crystal (containing $\sim 10^{23}$ atoms) the recoil of the entire crystal would carry negligible energy since the crystal mass would replace the atomic mass of a single Fe^{57} atom. However, the quantum mechanical state of the crystal might change in the emission process (via emission of phonons). A typical phonon has a frequency of the order of 10^{13} s^{-1} , much larger than $\Delta\omega = 10^7 \text{ s}^{-1}$ the natural line width. Therefore, in order for resonance absorption to occur, the γ -ray must be emitted without simultaneous emission of phonons. This *no phonon γ -ray emission* occurs a certain fraction of the time and is referred to as *recoil free fraction*. We would like to estimate the recoil free fraction.

As far as the recoil-nucleus is concerned, the effect of the γ -ray emission can be represented by an operator H' defined by

$$H' = Ce^{i\mathbf{K} \cdot \hat{\mathbf{R}}_N}, \quad (2.44)$$

where C is some constant, $\hbar K$ is the recoil momentum, and \hat{R}_N is the position operator of the decaying nucleus. This expression can be derived using the semiclassical theory of radiation, but we simply state it and demonstrate that it is plausible by considering a free nucleus.

Recoil of a Free Nucleus

The Hamiltonian describing the motion of the center of mass of a free atom is

$$H_0 = \frac{P^2}{2M}. \quad (2.45)$$

The eigenstates of H_0 are plane waves

$$|k\rangle = V^{-1/2} e^{i\mathbf{k} \cdot \mathbf{R}_N}$$

whose energy is

$$E(k) = \frac{\hbar^2 k^2}{2M}.$$

Operating on an initial state $|k\rangle$ with H' gives a new eigenstate proportional to $|k + K\rangle$. The change in energy (i.e., the recoil energy) is

$$\Delta E = E(k + K) - E(k) = \frac{\hbar^2}{2M} (2\mathbf{k} \cdot \mathbf{K} + K^2).$$

For a nucleus that is initially at rest, $\Delta E = \frac{\hbar^2 K^2}{2M}$, exactly what we had given previously.

Mössbauer Recoil Free Fraction

When the atom whose nucleus emits the γ -ray is bound in the crystal, the initial and final eigenstates must describe the entire crystal. Suppose the initial eigenstate is

$$|n_1, n_2, \dots, n_N\rangle = \prod_i n_i^{-1/2} \left(a_{k_i}^\dagger \right)^{n_i} |0\rangle.$$

In evaluating H' operating on this state, we write $R_N = R_N^0 + u_N$ to describe the center of mass of the nucleus which emits the γ -ray. We can choose the origin of our coordinate system at the position R_N^0 and write

$$R_N = u_N = \sum_k \left(\frac{\hbar}{2MN\omega_k} \right)^{1/2} (a_k + a_{-k}^\dagger). \quad (2.46)$$

Because k is a dummy variable to be summed over, and because $\omega_k = \omega_{-k}$, we can replace a_{-k}^\dagger by a_k^\dagger in (2.46).

The probability of a transition from initial state $|n_i\rangle = |n_1, n_2, \dots, n_N\rangle$ to final state $|m_f\rangle = |m_1, m_2, \dots, m_N\rangle$ is proportional to the square of the matrix element $\langle m_f | H' | n_i \rangle$. This result can be established by using time dependent perturbation theory with H' as the perturbation. Let us write this probability as $P(m_f, n_i)$. Then $P(m_f, n_i)$ can be expressed as

$$P(m_f, n_i) = \alpha \left| \langle m_f | C e^{i\mathbf{K} \cdot \mathbf{R}_N} | n_i \rangle \right|^2. \quad (2.47)$$

In (2.47) α is simply a proportional constant, and we have set $H' = Ce^{i\mathbf{K}\cdot\mathbf{R}_N}$. Because $P(m_f, n_i)$ is the probability of going from $|n_i\rangle$ to $|m_f\rangle$, $\sum_{m_f} P(m_f, n_i) = 1$. This condition gives the relation

$$\alpha|C|^2 \sum_{m_f} \langle m_f | e^{i\mathbf{K}\cdot\mathbf{R}_N} | n_i \rangle^* \langle m_f | e^{i\mathbf{K}\cdot\mathbf{R}_N} | n_i \rangle = 1. \quad (2.48)$$

Because $e^{i\mathbf{K}\cdot\mathbf{R}_N}$ is Hermitian, $\langle m_f | e^{i\mathbf{K}\cdot\mathbf{R}_N} | n_i \rangle^*$ is equal to $\langle n_i | e^{-i\mathbf{K}\cdot\mathbf{R}_N} | m_f \rangle$. We use this result in (2.48) and make use of the fact that $|m_f\rangle$ is part of a complete orthonormal set so that $\sum_{m_f} |m_f\rangle\langle m_f|$ is the unit operator to obtain

$$\alpha|C|^2 [\langle n_i | e^{-i\mathbf{K}\cdot\mathbf{R}_N} \times e^{i\mathbf{K}\cdot\mathbf{R}_N} | n_i \rangle]^2 = 1.$$

This is satisfied only if $\alpha|C|^2 = 1$, establishing the result

$$P(m_f, n_i) = |\langle m_f | e^{i\mathbf{K}\cdot\mathbf{R}_N} | n_i \rangle|^2. \quad (2.49)$$

Evaluation of $P(n_i, n_i)$

The probability of γ -ray emission without any change in the state of the lattice is simply $P(n_i, n_i)$. We can write R_N in (2.49) as

$$R_N = \sum_k \beta_k (a_k + a_k^\dagger), \quad (2.50)$$

where we have introduced $\beta_k = \left(\frac{\hbar}{2MN\omega_k}\right)^{1/2}$. If we write $|n_i\rangle = |n_1\rangle |n_2\rangle \cdots |n_N\rangle$, then

$$\langle n_i | e^{i\mathbf{K}\cdot\mathbf{R}_N} | n_i \rangle = \langle n_1 | \langle n_2 | \cdots \langle n_N | [e^{iK \sum_k \beta_k (a_k + a_k^\dagger)}] | n_1 \rangle | n_2 \rangle \cdots | n_N \rangle. \quad (2.51)$$

The operator a_k and a_k^\dagger operates only on the k th harmonic oscillator, so that (2.51) can be rewritten

$$\langle n_i | e^{i\mathbf{K}\cdot\mathbf{R}_N} | n_i \rangle = \prod_k \langle n_k | e^{iK\beta_k(a_k + a_k^\dagger)} | n_k \rangle. \quad (2.52)$$

Each factor in the product can be evaluated by expanding the exponential in power series. This gives

$$\begin{aligned} \langle n_k | e^{iK\beta_k(a_k + a_k^\dagger)} | n_k \rangle &= 1 + \frac{(iK\beta_k)^2}{2!} \langle n_k | a_k a_k^\dagger + a_k^\dagger a_k | n_k \rangle \\ &\quad + \frac{(iK\beta_k)^4}{4!} \langle n_k | (a_k + a_k^\dagger)^4 | n_k \rangle + \cdots \end{aligned} \quad (2.53)$$

The result for this matrix element is

$$\langle n_k | e^{iK\beta_k(a_k + a_k^\dagger)} | n_k \rangle = 1 - \frac{E(K)}{\hbar\omega_k} \frac{n_k + \frac{1}{2}}{N} + O(N^{-2}). \quad (2.54)$$

We shall neglect terms of order N^{-2} , N^{-3} , ..., etc. in this expansion. With this approximation we can write

$$\langle n_i | e^{i\mathbf{K} \cdot \mathbf{R}_N} | n_i \rangle \simeq \prod_k \left[1 - \frac{E(K)}{\hbar\omega_k} \frac{n_k + \frac{1}{2}}{N} \right]. \quad (2.55)$$

To terms of order N^{-1} , the product appearing on the right-hand side of (2.55) is equivalent to $e^{-\frac{E(K)}{N} \sum_k \frac{n_k + \frac{1}{2}}{\hbar\omega_k}}$ to the same order. Thus, for the recoil free fraction, we find

$$P(n_i, n_i) = e^{-2 \frac{E(K)}{N} \sum_k \frac{n_k + \frac{1}{2}}{\hbar\omega_k}}. \quad (2.56)$$

Although we have derived (2.56) for a simple one-dimensional model, the result is valid for a real crystal if sum over k is replaced by a three-dimensional sum over all \mathbf{k} and over the three polarizations. We will return to the evaluation of the sum later, after we have considered models for the phonon spectrum in real crystals.

2.4 Optical Modes

So far, we have restricted our consideration to a monatomic linear chain. Later on, we shall consider three-dimensional solids (the added complication is not serious). For the present, let us stick with the one-dimensional chain, but let us generalize to the case of two atoms per unit cell (Fig. 2.5).

If atoms A and B are identical, the primitive translation vector of the lattice is a , and the smallest reciprocal vector is $K = \frac{2\pi}{a}$. If A and B are distinguishable (e.g. of slightly different mass) then the smallest translation vector is $2a$ and the smallest reciprocal lattice vector is $K = \frac{2\pi}{2a} = \frac{\pi}{a}$. In this case, the part of the ω vs. q curve lying outside the region $|q| \leq \frac{\pi}{2a}$ must be translated (or folded back) into the first Brillouin zone (region between $-\frac{\pi}{2a}$ and $\frac{\pi}{2a}$) by adding or subtracting the reciprocal lattice vector $\frac{\pi}{a}$. This results in the spectrum shown in Fig. 2.6. Thus, for a non-Bravais lattice, the phonon spectrum has more than one branch. If there are p atoms per primitive unit cell, there will be p branches of the spectrum in a one-dimensional crystal. One branch, which satisfies the condition that $\omega(q) \rightarrow 0$ as $q \rightarrow 0$ is called the *acoustic branch* or *acoustic mode*. The other $(p-1)$ branches are called *optical branches* or *optical modes*. Due to the difference between the



Fig. 2.5. Linear chain with two atoms per unit cell

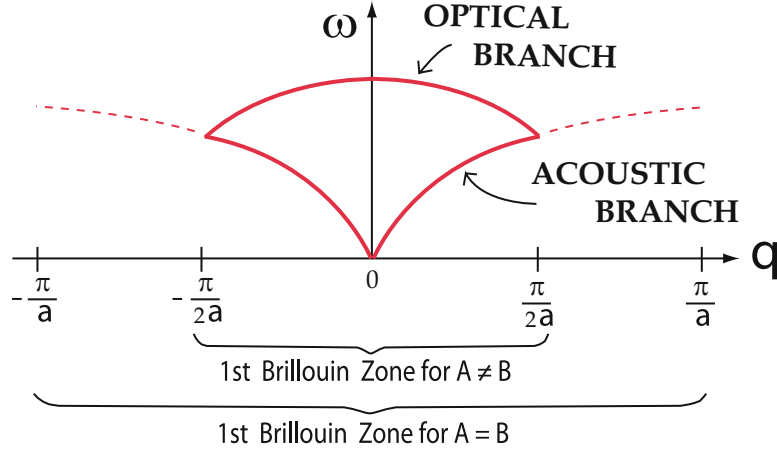


Fig. 2.6. Dispersion curves for the lattice vibration in a linear chain with two atoms per unit cell

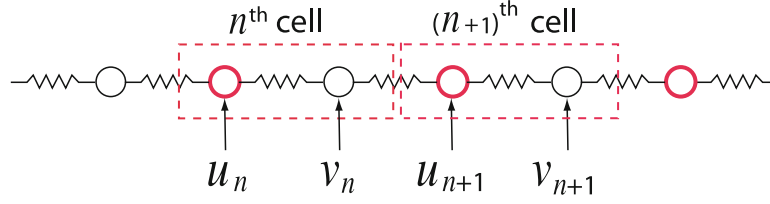


Fig. 2.7. Unit cells of a linear chain with two atoms per cell

pair of atoms in the unit cell when $A \neq B$, the degeneracy of the acoustic and optical modes at $q = \pm \frac{q}{2a}$ is usually removed. Let us consider a simple example, the linear chain with nearest neighbor interactions but with atoms of mass M_1 and M_2 in each unit cell. Let u_n be the displacement from its equilibrium position of the atom of mass M_1 in the n th unit cell; let v_n be the corresponding quantity for the atom of mass M_2 . Then, the equations of motion are

$$M_1 \ddot{u}_n = K [(v_n - u_n) - (u_n - v_{n-1})], \quad (2.57)$$

$$M_2 \ddot{v}_n = K [(u_{n+1} - v_n) - (v_n - u_n)]. \quad (2.58)$$

In Fig. 2.7, we show unit cells n and $n+1$. We assume solutions of (2.57) and (2.58) of the form

$$u_n = u_q e^{iq2an - i\omega_q t}, \quad (2.59)$$

$$v_n = v_q e^{iq(2an+a) - i\omega_q t}. \quad (2.60)$$

where u_q and v_q are constants. Substituting (2.59) and (2.60) into the equations of motion gives the following matrix equation.

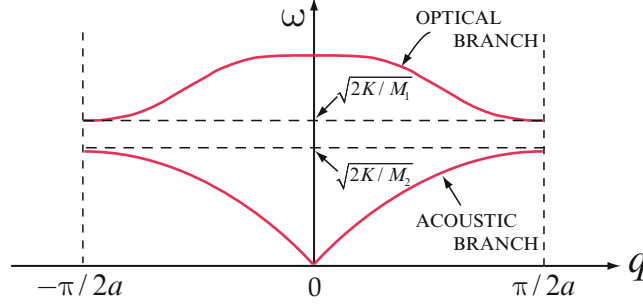


Fig. 2.8. Dispersion relations for the acoustical and optical modes of a diatomic linear chain

$$\begin{bmatrix} -M_1\omega^2 + 2K & -2K \cos qa \\ -2K \cos qa & -M_2\omega^2 + 2K \end{bmatrix} \begin{bmatrix} u_q \\ v_q \end{bmatrix} = 0. \quad (2.61)$$

The nontrivial solutions are obtained by setting the determinant of the 2×2 matrix multiplying the column vector $\begin{bmatrix} u_q \\ v_q \end{bmatrix}$ equal to zero. The roots are

$$\omega_{\pm}^2(q) = \frac{K}{M_1 M_2} \left\{ M_1 + M_2 \mp [(M_1 + M_2)^2 - 4M_1 M_2 \sin^2 qa]^{1/2} \right\}. \quad (2.62)$$

We shall assume that $M_1 < M_2$. Then at $q = \pm \frac{\pi}{2a}$, the two roots are $\omega_{\text{OP}}^2(q = \frac{\pi}{2a}) = \frac{2K}{M_1}$ and $\omega_{\text{AC}}^2(q = \frac{\pi}{2a}) = \frac{2K}{M_2}$. At $q \approx 0$, the two roots are given by $\omega_{\text{AC}}^2(q) \simeq \frac{2Ka^2}{M_1 + M_2} q^2$ and $\omega_{\text{OP}}^2(q) = \frac{2K(M_1 + M_2)}{M_1 M_2} \left[1 - \frac{M_1 M_2}{(M_1 + M_2)^2} q^2 a^2 \right]$. The dispersion relations for both modes are sketched in Fig. 2.8.

2.5 Lattice Vibrations in Three Dimensions

Now let us consider a primitive unit cell in three dimensions defined by the translation vectors \mathbf{a}_1 , \mathbf{a}_2 , and \mathbf{a}_3 . We will apply periodic boundary conditions such that N_i steps in the direction \mathbf{a}_i will return us to the original lattice site. The Hamiltonian in the harmonic approximation can be written as

$$H = \sum_i \frac{\mathbf{P}_i^2}{2M} + \frac{1}{2} \sum_{i,j} \mathbf{u}_i \cdot \underline{C}_{ij} \cdot \mathbf{u}_j. \quad (2.63)$$

Here, the tensor \underline{C}_{ij} (i and j refer to the i th and j th atoms and \underline{C}_{ij} is a three-dimensional tensor for each value of i and j) is given by

$$\underline{C}_{ij} = [\nabla_{R_i} \nabla_{R_j} U(\mathbf{R}_1, \mathbf{R}_2, \dots)]_{R_i^0 R_j^0}. \quad (2.64)$$

In obtaining (2.63) we have expanded $U(\mathbf{R}_1, \mathbf{R}_2, \dots)$ in powers of $\mathbf{u}_i = \mathbf{R}_i - \mathbf{R}_i^0$, the deviation from the equilibrium position, and we have used the definition of equilibrium to eliminate the term that is linear in \mathbf{u}_i .

From Hamilton's equation we obtain the equation of motion

$$M\ddot{\mathbf{u}}_n = - \sum_j \underline{C}_{ij} \cdot \mathbf{u}_j. \quad (2.65)$$

We assume a solution to (2.65) of the form

$$\mathbf{u}_n = \boldsymbol{\xi}_{\mathbf{k}} e^{i\mathbf{k} \cdot \mathbf{R}_n^0 - i\omega_{\mathbf{k}} t}. \quad (2.66)$$

Here, $\boldsymbol{\xi}_{\mathbf{k}}$ is a vector whose magnitude gives the size of the displacement associated with wave vector \mathbf{k} and whose direction gives the direction of the displacement. It is convenient to write

$$\boldsymbol{\xi}_{\mathbf{k}} = \hat{\boldsymbol{\varepsilon}}_{\mathbf{k}} q_{\mathbf{k}}, \quad (2.67)$$

where $\hat{\boldsymbol{\varepsilon}}_{\mathbf{k}}$ is a unit polarization vector (a unit vector in the direction of $\boldsymbol{\xi}_{\mathbf{k}}$) and $q_{\mathbf{k}}$ is the amplitude. Substituting the assumed solution into the equation of motion gives

$$M\omega_{\mathbf{k}}^2 \boldsymbol{\varepsilon}_{\mathbf{k}} = \sum_j \underline{C}_{ij} \cdot \hat{\boldsymbol{\varepsilon}}_{\mathbf{k}} e^{i\mathbf{k} \cdot (\mathbf{R}_j^0 - \mathbf{R}_i^0)}. \quad (2.68)$$

Because (2.68) is a vector equation, it must have three solutions for each value of \mathbf{k} . This is apparent if we define the tensor $\underline{F}(\mathbf{k})$ by

$$\underline{F}(\mathbf{k}) = - \sum_j e^{i\mathbf{k} \cdot (\mathbf{R}_j^0 - \mathbf{R}_i^0)} \underline{C}_{ij}. \quad (2.69)$$

Then, (2.68) can be written as a matrix equation

$$\begin{pmatrix} M\omega_{\mathbf{k}}^2 + F_{xx} & F_{xy} & F_{xz} \\ F_{yx} & M\omega_{\mathbf{k}}^2 + F_{yy} & F_{yz} \\ F_{zx} & F_{zy} & M\omega_{\mathbf{k}}^2 + F_{zz} \end{pmatrix} \begin{pmatrix} \hat{\varepsilon}_{\mathbf{k}x} \\ \hat{\varepsilon}_{\mathbf{k}y} \\ \hat{\varepsilon}_{\mathbf{k}z} \end{pmatrix} = 0. \quad (2.70)$$

The three solutions of the three by three secular equation for a given value of \mathbf{k} can be labeled by a *polarization index* λ . The eigenvalues of (2.70) will be $\omega_{\mathbf{k}\lambda}^2$ and the eigenfunctions will be

$$\hat{\boldsymbol{\varepsilon}}_{\mathbf{k}\lambda} = (\hat{\varepsilon}_{\mathbf{k}\lambda}^x, \hat{\varepsilon}_{\mathbf{k}\lambda}^y, \hat{\varepsilon}_{\mathbf{k}\lambda}^z)$$

with $\lambda = 1, 2, 3$.

When we apply periodic boundary conditions, then we must have the condition

$$e^{ik_i N_i a_i} = 1 \quad (2.71)$$

satisfied for $i = 1, 2, 3$ the three primitive translation directions. In (2.71), k_i is the component of \mathbf{k} in the direction of \mathbf{a}_i and N_i is the period associated

with the periodic boundary conditions in this direction. From the condition (2.71), it is clear that the allowed values of the wave vector \mathbf{k} must be of the form

$$\mathbf{k} = 2\pi \left(\frac{n_1}{N_1} \mathbf{b}_1 + \frac{n_2}{N_2} \mathbf{b}_2 + \frac{n_3}{N_3} \mathbf{b}_3 \right), \quad (2.72)$$

where n_1 , n_2 , and n_3 are integers, and \mathbf{b}_1 , \mathbf{b}_2 , \mathbf{b}_3 are primitive translation vectors of the reciprocal lattice. As in the one-dimensional case, not all of the values of \mathbf{k} given by (2.72) are independent. It is customary to choose as independent values of \mathbf{k} those which satisfy (2.72) and the condition

$$-\frac{N_i}{2} \leq n_i \leq \frac{N_i}{2}. \quad (2.73)$$

This set of \mathbf{k} values is restricted to the first Brillouin zone, the set of all values of \mathbf{k} satisfying (2.72) that are closer to the origin in reciprocal space than to any other reciprocal lattice point. The total number of \mathbf{k} values in the first Brillouin zone is $N = N_1 N_2 N_3$, and there are three normal modes (three polarizations λ) for each \mathbf{k} value. This gives a total of $3N$ normal modes, the number required to describe a system of $N = N_1 N_2 N_3$ atoms each having three degrees of freedom. For \mathbf{k} values that lie outside the Brillouin zone, one simply adds a reciprocal lattice vector \mathbf{K} to obtain an equivalent \mathbf{k} value inside the Brillouin zone.

2.5.1 Normal Modes

As we did in the one-dimensional case, we can define new coordinates $q_{\mathbf{k}\lambda}$ and $p_{\mathbf{k}\lambda}$ as

$$\mathbf{u}_n = N^{-1/2} \sum_{\mathbf{k}\lambda} \hat{\varepsilon}_{\mathbf{k}\lambda} q_{\mathbf{k}\lambda} e^{i\mathbf{k} \cdot \mathbf{R}_n^0}, \quad (2.74)$$

$$\mathbf{P}_n = N^{-1/2} \sum_{\mathbf{k}\lambda} \hat{\varepsilon}_{\mathbf{k}\lambda} p_{\mathbf{k}\lambda} e^{-i\mathbf{k} \cdot \mathbf{R}_n^0}. \quad (2.75)$$

The Hamiltonian becomes

$$H = \sum_{\mathbf{k}\lambda} H_{\mathbf{k}\lambda} = \sum_{\mathbf{k}\lambda} \left[\frac{1}{2M} p_{\mathbf{k}\lambda} p_{\mathbf{k}\lambda}^* + \frac{1}{2} M \omega_{\mathbf{k}\lambda}^2 q_{\mathbf{k}\lambda} q_{\mathbf{k}\lambda}^* \right]. \quad (2.76)$$

It is customary to define the polarization vectors $\hat{\varepsilon}_{\mathbf{k}\lambda}$ to satisfy $\hat{\varepsilon}_{-\mathbf{k}\lambda} = -\hat{\varepsilon}_{\mathbf{k}\lambda}$ and $\hat{\varepsilon}_{\mathbf{k}\lambda} \cdot \hat{\varepsilon}_{\mathbf{k}\lambda'} = \delta_{\lambda\lambda'}$. Remembering that $\sum_n e^{i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{R}_n^0} = N \delta_{\mathbf{k},\mathbf{k}'}$, one can see immediately that

$$\sum_n \hat{\varepsilon}_{\mathbf{k}\lambda} \cdot \hat{\varepsilon}_{\mathbf{k}'\lambda'} e^{i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{R}_n^0} = N \delta_{\mathbf{k},\mathbf{k}'} \delta_{\lambda\lambda'}. \quad (2.77)$$

The conditions resulting from requiring \mathbf{P}_n and \mathbf{u}_n to be real are

$$\mathbf{p}_{\mathbf{k}\lambda}^* = \mathbf{p}_{-\mathbf{k}\lambda} \quad \text{and} \quad \mathbf{q}_{\mathbf{k}\lambda}^* = \mathbf{q}_{-\mathbf{k}\lambda} \quad (2.78)$$

where $\mathbf{p}_{\mathbf{k}\lambda} = \hat{\varepsilon}_{\mathbf{k}\lambda} p_{\mathbf{k}\lambda}$ and $\mathbf{q}_{\mathbf{k}\lambda} = \hat{\varepsilon}_{\mathbf{k}\lambda} q_{\mathbf{k}\lambda}$. The condition on the scalar quantities $p_{\mathbf{k}\lambda}$ and $q_{\mathbf{k}\lambda}$ differs by a minus sign from the vector relation (2.78) because $\hat{\varepsilon}_{\mathbf{k}\lambda}$ changes sign when \mathbf{k} goes to $-\mathbf{k}$.

2.5.2 Quantization

To quantize, the dynamical variables $p_{\mathbf{k}\lambda}$ and $q_{\mathbf{k}\lambda}$ are replaced by quantum mechanical operators $\hat{p}_{\mathbf{k}\lambda}$ and $\hat{q}_{\mathbf{k}\lambda}$ which satisfy the commutation relations

$$[\hat{p}_{\mathbf{k}\lambda}, \hat{q}_{\mathbf{k}'\lambda'}]_- = -i\hbar\delta_{\mathbf{k}\mathbf{k}'}\delta_{\lambda\lambda'}. \quad (2.79)$$

It is again convenient to introduce creation and annihilation operators $a_{\mathbf{k}\lambda}^\dagger$ and $a_{\mathbf{k}\lambda}$ defined by

$$q_{\mathbf{k}\lambda} = \left(\frac{\hbar}{2M\omega_{\mathbf{k}\lambda}} \right)^{1/2} (a_{\mathbf{k}\lambda} - a_{-\mathbf{k}\lambda}^\dagger), \quad (2.80)$$

$$p_{\mathbf{k}\lambda} = i \left(\frac{\hbar M\omega_{\mathbf{k}\lambda}}{2} \right)^{1/2} (a_{\mathbf{k}\lambda}^\dagger + a_{-\mathbf{k}\lambda}). \quad (2.81)$$

The differences in sign from one-dimensional case result from using scalar quantities $q_{\mathbf{k}\lambda}$ and $p_{\mathbf{k}\lambda}$ in defining $a_{\mathbf{k}\lambda}$ and $a_{\mathbf{k}\lambda}^\dagger$. The operators $a_{\mathbf{k}\lambda}$ and $a_{\mathbf{k}'\lambda'}$ satisfy the commutation relations

$$[a_{\mathbf{k}\lambda}, a_{\mathbf{k}'\lambda'}^\dagger]_- = \delta_{\mathbf{k}\mathbf{k}'}\delta_{\lambda\lambda'}, \quad (2.82)$$

$$[a_{\mathbf{k}\lambda}, a_{\mathbf{k}'\lambda'}]_- = [a_{\mathbf{k}\lambda}^\dagger, a_{\mathbf{k}'\lambda'}^\dagger]_- = 0. \quad (2.83)$$

The Hamiltonian is given by

$$H = \sum_{\mathbf{k}\lambda} \hbar\omega_{\mathbf{k}\lambda} \left(a_{\mathbf{k}\lambda}^\dagger a_{\mathbf{k}\lambda} + \frac{1}{2} \right). \quad (2.84)$$

From this point on the analysis is essentially identical to that of the one-dimensional case which we have treated in detail already. In the three-dimensional case, we can write the displacement \mathbf{u}_n and momentum \mathbf{P}_n of the n th atom as the quantum mechanical operators given below:

$$\mathbf{u}_n = \sum_{\mathbf{k}\lambda} \left(\frac{\hbar}{2MN\omega_{\mathbf{k}\lambda}} \right)^{1/2} \hat{\varepsilon}_{\mathbf{k}\lambda} e^{i\mathbf{k}\cdot\mathbf{R}_n^0} (a_{\mathbf{k}\lambda} - a_{-\mathbf{k}\lambda}^\dagger), \quad (2.85)$$

$$\mathbf{P}_n = \sum_{\mathbf{k}\lambda} i \left(\frac{\hbar M\omega_{\mathbf{k}\lambda}}{2N} \right)^{1/2} \hat{\varepsilon}_{\mathbf{k}\lambda} e^{-i\mathbf{k}\cdot\mathbf{R}_n^0} (a_{\mathbf{k}\lambda}^\dagger + a_{-\mathbf{k}\lambda}). \quad (2.86)$$

Mean Squared Displacement of an Atom

As an example of how to use the quantum mechanical eigenstates and the operator describing dynamical variables, let us evaluate the mean squared displacement of an atom from its equilibrium position in a three-dimensional crystal. We can write

$$\mathbf{u}_n \cdot \mathbf{u}_n = \sum_{\mathbf{k}\lambda, \mathbf{k}'\lambda'} \left(\frac{\hbar}{2MN} \right) (\omega_{\mathbf{k}\lambda} \omega_{\mathbf{k}'\lambda'})^{-1/2} \hat{\varepsilon}_{\mathbf{k}\lambda} \cdot \hat{\varepsilon}_{\mathbf{k}'\lambda'} (a_{\mathbf{k}\lambda} + a_{\mathbf{k}\lambda}^\dagger) (a_{\mathbf{k}'\lambda'} + a_{\mathbf{k}'\lambda'}^\dagger). \quad (2.87)$$

Here, we have again chosen the origin at the equilibrium position of the n^{th} atom so that $R_n^0 = 0$. Then, we can replace $\hat{\varepsilon}_{\mathbf{k}\lambda} a_{-\mathbf{k}\lambda}^\dagger$ by $-\hat{\varepsilon}_{\mathbf{k}\lambda} a_{\mathbf{k}\lambda}^\dagger$ in (2.85). This was done in obtaining (2.87). If we assume the eigenstate of the lattice is $|n_{\mathbf{k}_1\lambda_1}, n_{\mathbf{k}_2\lambda_2}, \dots\rangle$, it is not difficult to see that

$$\langle \mathbf{u}_n \rangle = \langle n_{\mathbf{k}_1\lambda_1}, n_{\mathbf{k}_2\lambda_2}, \dots | \mathbf{u}_n | n_{\mathbf{k}_1\lambda_1}, n_{\mathbf{k}_2\lambda_2}, \dots \rangle = 0, \quad (2.88)$$

and that

$$\langle \mathbf{u}_n \cdot \mathbf{u}_n \rangle = \sum_{\mathbf{k}\lambda} \left(\frac{\hbar}{2MN\omega_{\mathbf{k}\lambda}} \right) (2n_{\mathbf{k}\lambda} + 1). \quad (2.89)$$

2.6 Heat Capacity of Solids

In the nineteenth century, it was known from experiment that at room temperature the specific heat of a solid was given by the Dulong–Petit law which said

$$C_v = 3R, \quad (2.90)$$

where $R = N_A k_B$, and $N_A = \text{Avogadro number} (=6.03 \times 10^{23} \text{ atoms/mole})$ and $k_B = \text{Boltzmann's constant} (=1.38 \times 10^{-16} \text{ ergs/}^\circ\text{K})$. Recall that 1 calorie = 4.18 joule = 4.18×10^7 ergs. Thus, (2.90) gave the result

$$C_v \simeq 6 \text{ cal/deg mole}. \quad (2.91)$$

The explanation of the Dulong–Petit law is based on the equipartition theorem of classical statistical mechanics. This theorem assumes that each atom oscillates harmonically about its equilibrium position, and that the energy of one atom is

$$E = \frac{p^2}{2m} + \frac{1}{2}kr^2 = \frac{1}{2m} (p_x^2 + p_y^2 + p_z^2) + \frac{1}{2}k (x^2 + y^2 + z^2). \quad (2.92)$$

The equipartition theorem states that for a classical system in equilibrium $\left\langle \frac{p_x^2}{2m} \right\rangle = \frac{1}{2}k_B T$. The same is true for the other terms in (2.92), so that the energy per atom at temperature T is $E = 3k_B T$. The energy of 1 mole is

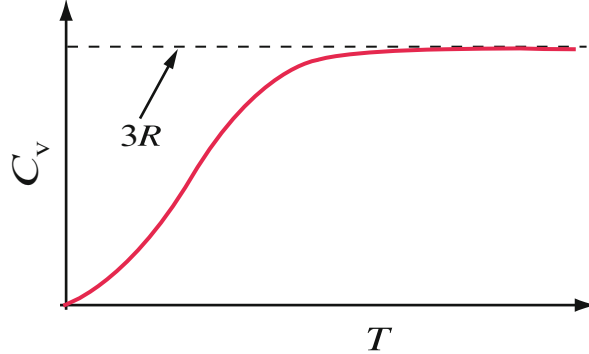


Fig. 2.9. Temperature dependence of the specific heat of a typical solid

$$U = 3N_A k_B T = 3RT. \quad (2.93)$$

It follows immediately that C_v , which is equal to $(\frac{\partial U}{\partial T})_v$ is given by (2.90). It was later discovered that the Dulong–Petit law was valid only at sufficiently high temperature. The temperature dependence of C_v for a typical solid was found to behave as shown in Fig. 2.9.

2.6.1 Einstein Model

To explain why the specific heat decreased as the temperature was lowered, Einstein made the assumption that the atomic vibrations were quantized. By this we mean that if one assumes that the motion of each atom is described by a harmonic oscillator, then the allowed energy values are given by $\varepsilon_n = (n + \frac{1}{2})\hbar\omega$, where $n = 0, 1, 2, \dots$, and ω is the oscillator frequency.² Einstein used a very simple model in which each atom vibrated with the same frequency ω . The probability p_n that an oscillator has energy ε_n is proportional to $e^{-\varepsilon_n/k_B T}$. Because p_n is a probability and $\sum_{n=0}^{\infty} p_n = 1$, we find that it is convenient to write

$$p_n = Z^{-1} e^{-\varepsilon_n/k_B T}, \quad (2.94)$$

and to determine the constant Z from the condition $\sum_{n=0}^{\infty} p_n = 1$. Doing so gives

$$Z = e^{-\hbar\omega/2k_B T} \sum_{n=0}^{\infty} \left(e^{-\hbar\omega/k_B T} \right)^n. \quad (2.95)$$

The power series expansion of $(1 - x)^{-1}$ is equal to $\sum_{n=0}^{\infty} x^n$. Making use of this result in (2.95) gives

² See Appendix A for a quantum mechanical solution of a harmonic oscillator problem.

$$Z = \frac{e^{-\hbar\omega/2k_B T}}{1 - e^{-\hbar\omega/k_B T}} = \frac{e^{\hbar\omega/2k_B T}}{e^{\hbar\omega/k_B T} - 1}. \quad (2.96)$$

The mean value of the energy of one oscillator at temperature T is given by $\bar{\varepsilon} = \sum_n \varepsilon_n p_n$. Making use of (2.94) and (2.95) and the formula $\sum_n n e^{-nx} = -\frac{\partial}{\partial x} \sum_n e^{-nx}$ gives

$$\bar{\varepsilon} = \frac{\hbar\omega}{2} + \bar{n}\hbar\omega. \quad (2.97)$$

Here, \bar{n} is the thermal average of n ; it is given by

$$\bar{n} = \frac{1}{e^{\hbar\omega/k_B T} - 1}, \quad (2.98)$$

and is called the *Bose-Einstein distribution function*. The internal energy of a lattice containing N atoms is simply $U = 3N\hbar\omega (\bar{n} + \frac{1}{2})$, where \bar{n} is given by (2.98). If N is the Avogadro number, then the specific heat is given by

$$C_v = \left(\frac{\partial U}{\partial T} \right)_v = 3Nk_B F_E \left(\frac{\hbar\omega}{k_B T} \right), \quad (2.99)$$

where the *Einstein function* $F_E(x)$ is defined by

$$F_E(x) = \frac{x^2}{(e^x - 1)(1 - e^{-x})}. \quad (2.100)$$

It is useful to define the *Einstein temperature* T_E by $\hbar\omega = k_B T_E$. Then the x appearing in $F_E(x)$ is $\frac{T_E}{T}$.

In the high-temperature limit ($T \gg T_E$), x is very small compared to unity. Expanding $F_E(x)$ for small x gives

$$F_E(x) = 1 - \frac{1}{12}x^2 + \dots, \quad (2.101)$$

and

$$C_v = 3Nk_B \left[1 - \frac{1}{12} \left(\frac{T_E}{T} \right)^2 + \dots \right]. \quad (2.102)$$

This agrees with the classical Dulong-Petit law at very high temperature and it falls off with decreasing T .

In the low temperature limit ($T \ll T_E$), x is very large compared to unity. In this limit,

$$F_E(x) \simeq x^2 e^{-x}, \quad (2.103)$$

and

$$C_v = 3Nk_B \left(\frac{T_E}{T} \right)^2 e^{-T_E/T}. \quad (2.104)$$

The Einstein temperature was treated as a parameter to be determined by comparison with experiment. The Einstein model reproduced the Dulong–Petit law at high temperature and showed that C_v decreased as the temperature was lowered. Careful comparison of experimental data with the model showed that the low temperature behavior was not quite correct. The experimental data fit a T^3 law at low temperature (i.e., $C_v \propto T^3$) instead of decreasing exponentially as predicted by the simple Einstein model.

2.6.2 Modern Theory of the Specific Heat of Solids

We know from our study of lattice vibrations that Einstein’s assumption that each atom in the crystal oscillated at a single frequency ω is too great a simplification. In fact, the normal modes of vibration have a spectrum $\omega_{\mathbf{q}\lambda}$, where \mathbf{q} is a wave vector restricted to the first Brillouin zone and λ is a label that defines the polarization of the mode. The energy of the crystal at temperature T is given by

$$U = \sum_{\mathbf{q}\lambda} \left(\bar{n}_{\mathbf{q}\lambda} + \frac{1}{2} \right) \hbar \omega_{\mathbf{q}\lambda}. \quad (2.105)$$

In (2.105), $\bar{n}_{\mathbf{q}\lambda}$ is given by

$$\bar{n}_{\mathbf{q}\lambda} = \frac{1}{e^{\hbar \omega_{\mathbf{q}\lambda} / k_B T} - 1}. \quad (2.106)$$

From (2.105), the specific heat can be obtained; it is given by

$$C_v = \left(\frac{\partial U}{\partial T} \right)_v = k_B \sum_{\mathbf{q}\lambda} \left(\frac{\hbar \omega_{\mathbf{q}\lambda}}{k_B T} \right)^2 \left(e^{\frac{\hbar \omega_{\mathbf{q}\lambda}}{k_B T}} - 1 \right)^{-1} \left(1 - e^{-\frac{\hbar \omega_{\mathbf{q}\lambda}}{k_B T}} \right)^{-1}. \quad (2.107)$$

To carry out the summation appearing in (2.107), we must have either more information or some model describing how $\omega_{\mathbf{q}\lambda}$ depends on \mathbf{q} and λ is needed.

Density of States

Recall that the allowed values of \mathbf{q} were given by

$$\mathbf{q} = 2\pi \left(\frac{n_1}{N_1} \mathbf{b}_1 + \frac{n_2}{N_2} \mathbf{b}_2 + \frac{n_3}{N_3} \mathbf{b}_3 \right), \quad (2.108)$$

where \mathbf{b}_i were primitive translations of the reciprocal lattice, n_i were integers, and N_i were the number of steps in the direction i that were required before the periodic boundary conditions returned one to the initial lattice site. For simplicity, let us consider a simple cubic lattice. Then $\mathbf{b}_i = a^{-1} \hat{x}_i$, where a is the lattice spacing and \hat{x}_i is a unit vector (in the x , y , or z direction). The allowed (independent) values of \mathbf{q} are restricted to the first Brillouin zone. In this case, that implies that $-\frac{1}{2}N_i \leq n_i \leq \frac{1}{2}N_i$. Then, the summations over

q_x , q_y , and q_z can be converted to integrals as follows:

$$\sum_{q_x} \Rightarrow \frac{\int dq_x}{2\pi/N_x a} \Rightarrow \frac{L_x}{2\pi} \int dq_x. \quad (2.109)$$

Therefore, the three-dimensional sum $\sum_{\mathbf{q}}$ becomes

$$\sum_{\mathbf{q}} = \frac{L_x L_y L_z}{(2\pi)^3} \int d^3 q = \frac{V}{(2\pi)^3} \int d^3 q. \quad (2.110)$$

In these equations L_x , L_y , and L_z are equal to the length of the crystal in the x , y , and z directions, and $V = L_x L_y L_z$ is the crystal volume. For any function $f(\mathbf{q})$, we can write

$$\sum_{\mathbf{q}} f(\mathbf{q}) = \frac{V}{(2\pi)^3} \int d^3 q f(\mathbf{q}). \quad (2.111)$$

Now, it is convenient to introduce the *density of states* $g(\omega)$ defined by

$$g(\omega)d\omega = \left\{ \begin{array}{l} \text{The number of normal modes per unit volume} \\ \text{whose frequency } \omega_{\mathbf{q}\lambda} \text{ satisfies } \omega < \omega_{\mathbf{q}\lambda} < \omega + d\omega. \end{array} \right. \quad (2.112)$$

From this definition, it follows that

$$g(\omega)d\omega = \frac{1}{V} \sum_{\substack{\mathbf{q}\lambda \\ \omega < \omega_{\mathbf{q}\lambda} < \omega + d\omega}} 1 = \frac{1}{(2\pi)^3} \sum_{\lambda} \int_{\omega < \omega_{\mathbf{q}\lambda} < \omega + d\omega} d^3 q. \quad (2.113)$$

Let $S_{\lambda}(\omega)$ be the surface in three-dimensional wave vector space on which $\omega_{\mathbf{q}\lambda}$ has the value ω . Then $dS_{\lambda}(\omega)$ is an infinitesimal element of this surface of constant frequency (see Fig. 2.10). The frequency change $d\omega$ in going from the surface $S_{\lambda}(\omega)$ to the surface $S_{\lambda}(\omega + d\omega)$ can be expressed in terms of $d\mathbf{q}$, an infinitesimal displacement in \mathbf{q} space as

$$d\omega = d\mathbf{q} \cdot [\nabla_{\mathbf{q}} \omega_{\mathbf{q}\lambda}]_{\omega_{\mathbf{q}\lambda}=\omega} \quad \text{or} \quad d\omega = dq_{\perp} |\nabla_{\mathbf{q}} \omega_{\mathbf{q}\lambda}|_{\omega_{\mathbf{q}\lambda}=\omega}. \quad (2.114)$$

Here, dq_{\perp} is the component of $d\mathbf{q}$ normal to the surface of constant frequency $S_{\lambda}(\omega)$. The volume element $d^3 q$ in wave vector space can be written $dq_{\perp} dS_{\lambda}(\omega)$, and using (2.114) allows us to write

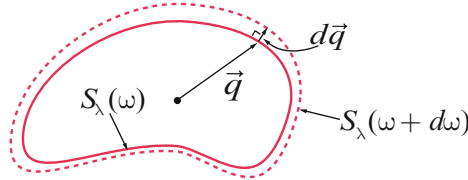


Fig. 2.10. Constant frequency surfaces in three-dimensional wave vector space

$$d^3q = \frac{d\omega}{|\nabla_{\mathbf{q}}\omega_{\mathbf{q}\lambda}|_{\omega_{\mathbf{q}\lambda}=\omega}} dS_{\lambda}(\omega). \quad (2.115)$$

With this result, we can express the density of states as

$$g(\omega) = \frac{1}{(2\pi)^3} \sum_{\lambda} \int \frac{dS_{\lambda}(\omega)}{|\nabla_{\mathbf{q}}\omega_{\mathbf{q}\lambda}|_{\omega}}. \quad (2.116)$$

In (2.116) the integration is performed over the surface of constant frequency $S_{\lambda}(\omega)$. The denominator contains the magnitude of the gradient of $\omega_{\mathbf{q}\lambda}$ (with respect to \mathbf{q}) evaluated at $\omega_{\mathbf{q}\lambda} = \omega$.

2.6.3 Debye Model

To evaluate (2.107) and obtain the specific heat, Debye³ introduced a simple assumption about the phonon spectrum. He took $\omega_{\mathbf{q}\lambda} = s_{\lambda} |\mathbf{q}|$ for all values of \mathbf{q} in the first Brillouin zone. Then, the surfaces of constant energy are spheres (i.e., $S_{\lambda}(\omega)$ is a sphere in \mathbf{q} space of radius $q = \frac{\omega}{s_{\lambda}}$). In addition, Debye replaced the Brillouin zone by a sphere of the same volume. Since $\sum_{\mathbf{q} \in 1^{\text{st}} \text{BZ}} 1 = N$, we can write

$$N = \left(\frac{L}{2\pi}\right)^3 \int_{|\mathbf{q}| < q_D} d^3q = \frac{V}{(2\pi)^3} \frac{4}{3} \pi q_D^3. \quad (2.117)$$

In (2.117) we have introduced q_D , the *Debye wave vector*. A sphere of radius q_D contains the N independent values of \mathbf{q} associated with a crystal containing N atoms. From (2.117), $q_D^3 = 6\pi^2 N/V$, where V is the volume of the crystal.

The density of states for the Debye model is very simple since $|\nabla_{\mathbf{q}} \omega_{\mathbf{q}\lambda}| = s_{\lambda}$. Substituting this result into (2.116) gives

$$g(\omega) = \frac{1}{(2\pi)^3} \sum_{\lambda} \left[\frac{4\pi q^2}{s_{\lambda}} \right]_{q=\frac{\omega}{s_{\lambda}}}^{q=q_D}. \quad (2.118)$$

If we introduce the unit step function $\theta(x) = 1$ for $x > 0$ and $\theta(x) = 0$ for $x < 0$, $g(\omega)$ can be expressed

$$g(\omega) = \frac{\omega^2}{2\pi^2} \left[\frac{\theta(s_l k_D - \omega)}{s_l^3} + \frac{2\theta(s_t k_D - \omega)}{s_t^3} \right]. \quad (2.119)$$

Here, of course, s_l and s_t are the speed of a longitudinal and of a transverse sound wave. Figure 2.11 shows the frequency dependence of the three-dimensional density of states in the Debye model. Any summation over allowed values of wave vector can be converted into an integral over frequency by using the relation

³ P. Debye, *Annalen der Physik* **39**, 789 (1912).

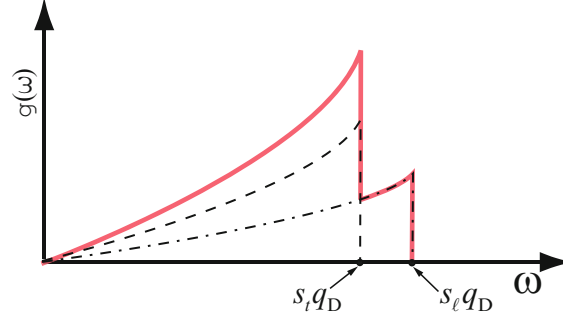


Fig. 2.11. Three-dimensional density of states in the Debye model

$$\sum_{\mathbf{q}\lambda} f(\omega_{\mathbf{q}\lambda}) = V \int d\omega g(\omega) f(\omega). \quad (2.120)$$

Here, $f(\omega_{\mathbf{q}\lambda})$ is an arbitrary function of the normal mode frequencies $\omega_{\mathbf{q}\lambda}$. Making use of (2.120), the expression for the specific heat [(2.107)] can be written

$$C_v = k_B V \int d\omega \left(\frac{\hbar\omega}{\Theta} \right)^2 \left(e^{\hbar\omega/\Theta} - 1 \right)^{-1} \left(1 - e^{-\hbar\omega/\Theta} \right)^{-1} g(\omega). \quad (2.121)$$

Here, we have introduced $\Theta = k_B T$. We define the *Debye temperature* T_D by $\Theta_D = k_B T_D = \hbar s_l q_D$. Remembering that $V = 6\pi^2 N q_D^{-3}$ and that the integral $\int d\omega$ goes from $\omega = 0$ to $\omega = \omega_D = s_l q_D$ for longitudinal waves and from $\omega = 0$ to $\omega = s_t q_D = \frac{s_t}{s_l} \omega_D$ for transverse waves, it is not difficult to demonstrate that

$$C_v = 3Nk_B \left[\frac{1}{3} F_D \left(\frac{\Theta_D}{\Theta} \right) + \frac{2}{3} F_D \left(\frac{s_t \Theta_D}{s_l \Theta} \right) \right], \quad (2.122)$$

where the *Debye function* $F_D(x)$ is defined by

$$F_D(x) = \frac{3}{x^3} \int_0^x \frac{z^4 dz}{(e^z - 1)(1 - e^{-z})}. \quad (2.123)$$

Behavior at $\Theta \gg \Theta_D$

In this limit, x which equals $\frac{\Theta_D}{\Theta}$ or $\frac{s_t \Theta_D}{s_l \Theta}$ is much smaller than unity. Therefore, we can expand the exponentials for small argument to obtain

$$F_D(x) \simeq \frac{3}{x^3} \int_0^x \frac{z^4 dz}{z^2} \approx 1. \quad (2.124)$$

In this limit, $C_v = 3Nk_B$, in agreement with the classical Dulong–Petit law.

Behavior at $\Theta \ll \Theta_D$

In this limit, x is much larger than unity, and because of the exponential in the denominator of the integral little error arises from replacing the upper limit by infinity. This gives

$$F_D(x) \simeq \frac{3}{x^3} \int_0^\infty \frac{z^4 dz}{(e^z - 1)(1 - e^{-z})}. \quad (2.125)$$

The integral is simply a constant. Its value can be obtained analytically

$$\int_0^\infty \frac{z^4 dz}{(e^z - 1)(1 - e^{-z})} = \frac{4}{15} \pi^4. \quad (2.126)$$

The result for C_v at very low temperature is

$$C_v = \frac{4}{5} \pi^4 N k_B \left[1 + 2 \left(\frac{s_l}{s_t} \right)^3 \right] \left(\frac{\Theta}{\Theta_D} \right)^3. \quad (2.127)$$

This agrees with the observed behavior of the specific heat at very low temperature, viz. $C_v = AT^3$, where A is a constant.

2.6.4 Evaluation of Summations over Normal Modes for the Debye Model

In our calculation of the recoil free fraction in the Mössbauer effect (See (2.56)), and in the evaluation of (2.89), the mean square displacement $\langle \mathbf{u}_n \cdot \mathbf{u}_n \rangle$ of an atom from its equilibrium position, we encountered sums of the form

$$I = N^{-1} \sum_{\mathbf{q}\lambda} \frac{\bar{n}_{\mathbf{q}\lambda} + \frac{1}{2}}{\hbar \omega_{\mathbf{q}\lambda}}. \quad (2.128)$$

These sums can be performed by converting the sums to integrals through the standard prescription

$$\sum_{\mathbf{q}} f(\omega_{\mathbf{q}\lambda}) \rightarrow \frac{V}{(2\pi)^3} \int d^3q f(\omega_{\mathbf{q}\lambda}), \quad (2.129)$$

or by making use of the density of states $g(\omega)$ and the result that

$$\sum_{\mathbf{q}\lambda} f(\omega_{\mathbf{q}\lambda}) = V \int d\omega g(\omega) f(\omega). \quad (2.130)$$

For simplicity, we will use a Debye model with the velocity of transverse and longitudinal waves both equal to s . Then

$$g(\omega) = \frac{3\omega^2}{2\pi^2 s^3} \theta(sk_D - \omega). \quad (2.131)$$

The summation in (2.128) can then be written as

$$I = \frac{V}{N} \int_0^{\omega_D} d\omega \frac{3\omega^2}{2\pi^2 s^3} \frac{1}{\hbar\omega} \left[\frac{1}{2} + \frac{1}{e^{\hbar\omega/\Theta} - 1} \right]. \quad (2.132)$$

Let $z = \frac{\hbar\omega}{\Theta}$, and make use of $k_D^3 = 6\pi^2 \frac{N}{V}$. Then (2.132) can be rewritten

$$I = \frac{9}{\Theta_D} \left(\frac{\Theta}{\Theta_D} \right)^2 \int_0^{\Theta_D/\Theta} dz \, z \left[\frac{1}{2} + \frac{1}{e^z - 1} \right]. \quad (2.133)$$

First, let us look at the high temperature limit of (2.133). If $\Theta \gg \Theta_D$, then for values of z appearing in the integrand $\frac{1}{e^z - 1} \simeq \frac{1}{z}$. This corresponds to the classical equipartition of energy since the energy of a mode of frequency $\omega_{\mathbf{q}\lambda}$ is given by

$$\hbar\omega_{\mathbf{q}\lambda} \left[\frac{1}{e^{\hbar\omega_{\mathbf{q}\lambda}/\Theta} - 1} + \frac{1}{2} \right] \simeq \hbar\omega_{\mathbf{q}\lambda} \left[\frac{\Theta}{\hbar\omega_{\mathbf{q}\lambda}} + \frac{1}{2} \right],$$

and this is equal to Θ for every mode (the $\frac{1}{2}$ is negligible if $\Theta \gg \hbar\omega_{\mathbf{q}\lambda}$) as required by classical statistical mechanics. With this approximation

$$I \simeq \frac{9}{\Theta_D} \left(\frac{\Theta}{\Theta_D} \right)^2 \int_0^{\Theta_D/\Theta} dz = \frac{9\Theta}{\Theta_D^2}. \quad (2.134)$$

At very low temperature, $\Theta \ll \Theta_D$, we can approximate the upper limit by ∞ in the term proportional to $(e^z - 1)^{-1}$, since the contribution from very large values of z is very small. This gives

$$I = \frac{9}{\Theta_D} \left(\frac{\Theta}{\Theta_D} \right)^2 \left[\int_0^\infty \frac{dz \, z}{e^z - 1} + \int_0^{\Theta_D/\Theta} dz \, \frac{z}{2} \right]. \quad (2.135)$$

The first integral in the square bracket is a constant, while the second is $\frac{1}{4} \left(\frac{\Theta_D}{\Theta} \right)^2$. The second term is much larger than the first for $\Theta \ll \Theta_D$, so it is a reasonable approximation to take

$$I = \frac{9}{4\Theta_D}. \quad (2.136)$$

(see, for example, Fig. 2.12).

2.6.5 Estimate of Recoil Free Fraction in Mössbauer Effect

Equation (2.56) gave the probability of starting in a lattice state $|n_i\rangle = |n_1, n_2, \dots, n_N\rangle$ and ending, after the γ -ray emission, in the same state. If we assume that the crystal is in thermal equilibrium at a temperature Θ , then (2.56) is simply

$$P(\bar{n}_i, \bar{n}_i) = e^{-2E(K)I}, \quad (2.137)$$

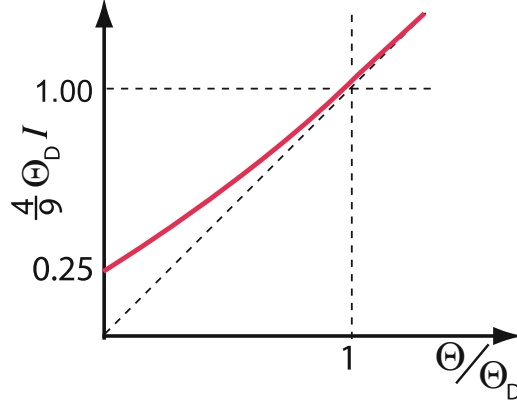


Fig. 2.12. Behavior of an integral I for $\Theta \leq \Theta_D$

where \bar{n}_i is the *Bose–Einstein distribution function*, $E(K)$ is the recoil energy, and I is given by (2.132). We have just evaluated I using a simplified Debye model at both high ($\Theta \gg \Theta_D$) and low ($\Theta \ll \Theta_D$) temperatures. If we use (2.134) and (2.137), we find that at ($\Theta_D \gg \Theta$), $P \simeq e^{-\frac{9E(K)}{2\Theta_D}}$. Remember that $E(K) \simeq 2 \times 10^{-3}$ eV. For a typical crystal $\Theta_D \simeq 300\text{K} \cdot k_B \approx 2.5 \times 10^{-2}$ eV, giving for P , $P \simeq e^{-\frac{1}{3}} \approx 0.7$. This means that at very low temperature, 70% of the γ rays are emitted without any change in the number of phonons in the crystal.

At high temperature (let us take $\Theta = 400\text{K}$, larger than but not much larger than $\Theta_D \simeq 300\text{K}$) $I \simeq \frac{9\Theta}{\Theta_D^2}$ giving $P(\bar{n}_i, \bar{n}_i) \simeq e^{-\frac{9E(K)}{2\Theta_D} \cdot \frac{4\Theta}{\Theta_D}}$. This gives $P(\bar{n}_i, \bar{n}_i)$ at $\Theta = 400\text{K}$ of roughly 0.14, so that, even at room temperature the Mössbauer recoil free fraction is reasonably large.

2.6.6 Lindemann Melting Formula

The *Lindemann melting formula* is based on the idea that melting will occur when the amplitude of the atomic vibrations (i.e., $\langle (\delta R)^2 \rangle^{1/2}$) becomes equal to some fraction γ of the interatomic spacing. Recall that $\langle \mathbf{u}_n \cdot \mathbf{u}_n \rangle = \frac{\hbar^2}{M} I$ where I is given by (2.128) (see (2.89)). We can use the $\Theta \gg \Theta_D$ limit for I to write

$$\langle (\delta R)^2 \rangle \simeq \frac{9\hbar^2 \Theta}{M \Theta_D^2}. \quad (2.138)$$

The melting temperature is assumed to be given by $\Theta_{\text{Melting}} = \frac{M \Theta_D^2}{9\hbar^2} \gamma^2 r_0^2$, where r_0 is the atomic spacing and γ is a constant in the range ($0.2 \leq \gamma \leq 0.25$). This result is only very qualitative since it is based on a very much oversimplified model.

Some Remarks on the Debye Model

One can obtain an intuitive picture of the temperature dependence of the specific heat by applying the idea of classical equipartition of energy, but only to modes for which $\hbar\omega < \Theta$. By this we mean that only modes whose energy $\hbar\omega$ is smaller than $\Theta = k_B T$ can be thermally excited at a temperature Θ and make a contribution to the internal energy U , and such modes contribute an energy Θ . Thus, we can write for U

$$U = \sum_{\mathbf{q}\lambda} \left(\bar{n}_{\mathbf{q}\lambda} + \frac{1}{2} \right) \hbar\omega_{\mathbf{q}\lambda} \simeq 3 \frac{V}{(2\pi)^3} \int_0^{\Theta/\hbar s} \Theta \, 4\pi q^2 \, dq. \quad (2.139)$$

In writing (2.139) we have omitted the zero point energy since it does not depend on temperature and put $\hbar\omega[\bar{n}(\omega)] \simeq \Theta$ for all modes of energy less than Θ . This gives (using $V = \frac{6\pi^2 N}{k_D^3}$ and $\hbar s k_D = \Theta_D$)

$$U = 3N \left(\frac{\Theta}{\Theta_D} \right)^3 \Theta. \quad (2.140)$$

Differentiating with respect to T gives

$$C_v = 12Nk_B \left(\frac{\Theta}{\Theta_D} \right)^3. \quad (2.141)$$

This rough approximation gives the correct T^3 temperature dependence, but the coefficient is not correct as might be expected from such a simple picture.

Experimental Data

Experimentalists measure the specific heat as a function of temperature over a wide range of temperatures. They often use the Debye model to fit their data, taking the Debye temperature as an adjustable parameter to be determined by fitting the data to (2.122) or some generalization of it. Thus, if you see a plot of Θ_D as a function of temperature, it only means that at that particular temperature T one needs to take $\Theta_D = \Theta_D(T)$ for that value of T to fit the data to a Debye model. It is always found that at very low T and at very high T the correct Debye temperature $\Theta_D = \hbar s \left(\frac{6\pi^2 N}{V} \right)^{1/3}$ agrees with the experiment. At intermediate temperatures there might be fluctuations in Θ_D of the order of 10% from the correct value. The reason for this is that $g(\omega)$, the density of states, for the Debye model is a considerable simplification of the actual $g(\omega)$ for real crystals. This can be illustrated by considering briefly the critical points in the phonon spectrum.

2.6.7 Critical Points in the Phonon Spectrum

Remember that the general expression for the density of states was given by (2.116). Points at which $\nabla_{\mathbf{q}}\omega_{\mathbf{q}\lambda} = 0$ are called *critical points*; the integrand in (2.116) becomes infinite at such points.

Suppose that \mathbf{q}_c is a critical point in the phonon spectrum. Let $\boldsymbol{\xi} = \mathbf{q} - \mathbf{q}_c$; then for points in the neighborhood of \mathbf{q}_c we can write

$$\omega_{\mathbf{q}} = \omega_c + \alpha_1 \xi_1^2 + \alpha_2 \xi_2^2 + \alpha_3 \xi_3^2, \quad (2.142)$$

where ξ_i are the components of $\boldsymbol{\xi}$, and $\omega_c = \omega(q_c)$. If α_1 , α_2 , and α_3 are all negative, by substituting into the expression for $g(\omega)$ and evaluating in the neighborhood of q_c , one obtains

$$g(\omega) = \begin{cases} 0 & \text{if } \omega > \omega_c, \\ \text{constant } (\omega_c - \omega)^{1/2} & \text{if } \omega < \omega_c. \end{cases} \quad (2.143)$$

Thus, although $g(\omega)$ is continuous at a critical point, its first derivative is discontinuous.

In three dimensions there are four kinds of critical points:

1. *Maxima*: Points at which all three α_i are negative.
2. *Minima*: Points at which all three α_i are positive.
3. *Saddle Points of the First Kind*: Points at which two α_i 's are positive and one is negative.
4. *Saddle Points of the Second Kind*: Points at which one α_i is positive and the other two are negative.

The critical points all show up as points at which $\frac{dg(\omega)}{d\omega}$ is discontinuous. A rough sketch of $g(\omega)$ vs. ω showing several critical points is shown in Fig. 2.13. It is not too difficult to demonstrate that in three dimensions the phonon spectrum must have at least one maximum, one minimum, three saddle points of each kind. As an example, we look at the simpler case of two dimensions. Then

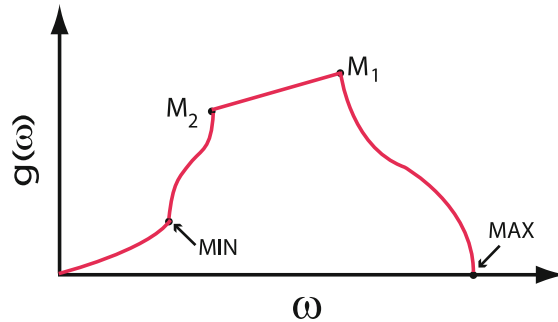


Fig. 2.13. Behavior of the density of states at various critical points

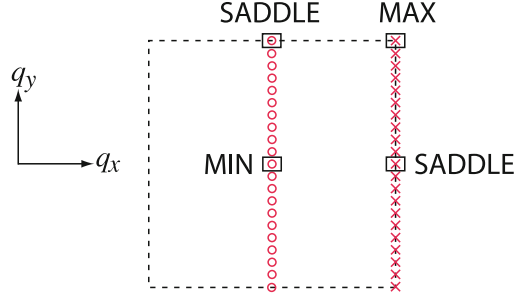


Fig. 2.14. Behavior of critical points in two dimensions

the phonon spectrum must have at least one maximum, one minimum, and two saddle points (there is only one kind of saddle point in two dimensions) (see Fig. 2.14). This can be demonstrated as follows:

1. We know $\omega_{\mathbf{q}}$ is a periodic function of \mathbf{q} ; values of \mathbf{q} which differ by a reciprocal lattice vector \mathbf{K} give the same $\omega_{\mathbf{q}}$.
2. For a Brillouin zone of a two-dimensional square, we can consider $\omega(q_x, q_y)$ as a function of q_x for a sequence of different fixed values of q_y . Because $\omega(q_x, q_y)$ is a periodic function of q_x there must be at least one maximum and one minimum on each line $q_y = \text{constant}$.
3. Consider the locus of all maxima (represented by X's in Fig. 2.14). Along this locus $\omega(\mathbf{q})$ must have at least one maximum and one minimum as a function of q_y . These points will be an absolute maximum and a saddle point.
4. Doing the same for the locus of all minima (represented by O's in Fig. 2.14) gives one absolute minimum and another saddle point.

Because of the critical points, the phonon spectrum of a real solid looks quite different from that of the Debye model. However, the Debye model is constructed so that

1. The low frequency behavior of $g(\omega)$ is correct because for very small ω , $\omega_{\mathbf{q}\lambda} = s_{\lambda} |q|$ is a very accurate approximation.
2. The total area under the curve $g(\omega)$ is correct since k_D , the Debye wave vector is chosen so that there are exactly the correct total number of modes $3N$.

Because of this, the Debye model is good at very low temperature (where only very low frequency modes are important) and at very high temperature (where only the total number of modes and equipartition of energy are important). In Fig. 2.15 we compare $g(\omega)$ for a Debye model with that of a real crystal. We note that $\int g_{\text{Debye}}(\omega) d\omega \approx \int g_{\text{Actual}}(\omega) d\omega$.

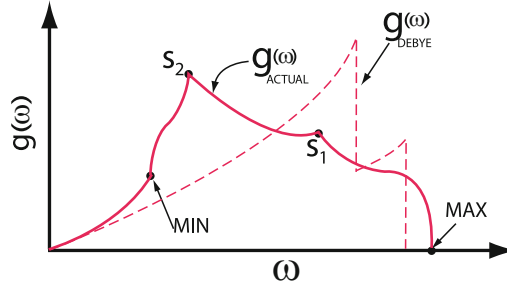


Fig. 2.15. Comparison of the density of states $g(\omega)$ for a Debye model and that of a real crystal

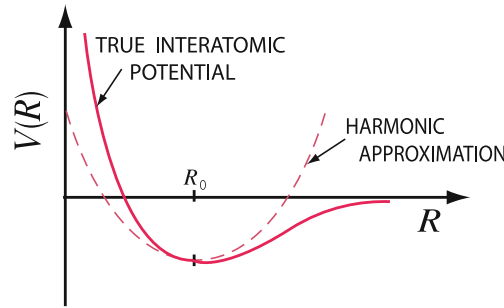


Fig. 2.16. Comparison of the potential felt by an atom and the harmonic approximation to it

2.7 Qualitative Description of Thermal Expansion

We have approximated the interatomic potential in a crystal by

$$V(R) = V(R_0) + \sum_{ij} c_{ij} u_i u_j + \text{higher terms.} \quad (2.144)$$

In Fig. 2.16 we show a sketch of the potential felt by one atom and the harmonic approximation to it. There are two main differences in the two potentials:

1. The true interatomic potential has a very strong repulsion at $u = R - R_0$ negative (i.e., close approach of the pair of atoms).
2. The true potential levels off as R becomes very large (i.e., for large positive u).

For a simple one-dimensional model we can write $x = x_0 + u$, where x_0 is the equilibrium separation between a pair of atoms and $u = x - x_0$ is the deviation from equilibrium. Then, we can model the behavior shown in Fig. 2.16 by assuming that

$$V(x) = V_0 + cu^2 - gu^3 - fu^4. \quad (2.145)$$

Here, g and f are positive constants. The fu^4 term simply accounts for the fact that the harmonic approximation rises too quickly for large u . The gu^3 term accounts for the asymmetry in the potential for u greater than or less than zero. When u is negative, $-gu^3$ is positive making the short range repulsion larger; when u is positive, $-gu^3$ is negative softening the interatomic repulsion for large R .

Now let us evaluate the expectation value of u at a temperature $k_B T = \beta^{-1}$.

$$\langle u \rangle = \frac{\int_{-\infty}^{\infty} du u e^{-\beta V}}{\int_{-\infty}^{\infty} du e^{-\beta V}}. \quad (2.146)$$

But, $V = V_0 + cu^2 - gu^3 - fu^4$, and we can expand $e^{\beta(gu^3 + fu^4)}$, for small values of u , to obtain

$$e^{-\beta V} = e^{-\beta(V_0 + cu^2)} (1 + \beta gu^3 + \beta fu^4). \quad (2.147)$$

The integrals in the numerator and denominator of (2.146) can be evaluated. Because of the factor $e^{-\beta cu^2}$, we do not have to worry about the behavior of the integrand for very large values of $|u|$ so there is little error in taking the limit as $u = \pm\infty$. We can easily see that

$$\int_{-\infty}^{\infty} du e^{-\beta V} = e^{-\beta V_0} \int_{-\infty}^{\infty} du e^{-\beta cu^2} (1 + \beta gu^3 + \beta fu^4). \quad (2.148)$$

The βgu^3 term vanishes because it is an odd function of u ; the βfu^4 gives a small correction to the first term so it can be neglected. This results in

$$\int_{-\infty}^{\infty} du e^{-\beta V} \simeq e^{-\beta V_0} \left(\frac{\pi}{\beta c} \right)^{1/2}. \quad (2.149)$$

In writing down (2.149) we have made use of the result $\int_{-\infty}^{\infty} dz e^{-z^2} = \sqrt{\pi}$. The integral in the numerator of (2.146) becomes

$$\int_{-\infty}^{\infty} du u e^{-\beta V} = e^{-\beta V_0} \int_{-\infty}^{\infty} du u e^{-\beta cu^2} (1 + \beta gu^3 + \beta fu^4). \quad (2.150)$$

Only the βgu^3 term in the square bracket contributes to the integral. The result is

$$\int_{-\infty}^{\infty} du u e^{-\beta V} \simeq e^{-\beta V_0} \frac{3\sqrt{\pi}}{4} \beta g (\beta c)^{-5/2}. \quad (2.151)$$

In obtaining (2.151) we have made use of the result $\int_{-\infty}^{\infty} dz z^4 e^{-z^2} = \frac{3\sqrt{\pi}}{4}$. Substituting it back in (2.146) gives

$$\langle u \rangle = \frac{1}{\beta} \frac{3g}{4c^2} = \frac{3g}{4c^2} k_B T. \quad (2.152)$$

The displacement from equilibrium is positive and increases with temperature. This suggests why a crystal expands with increasing temperature.

2.8 Anharmonic Effects

To get some idea about how one would go about treating *anharmonic effect*, let us go back to the simple one-dimensional model and include terms that we have neglected (up to this time) in the expansion of the potential energy. We can write $H = H_{\text{Harmonic}} + H'$, where H' is given by

$$H' = \frac{1}{3!} \sum_{lmn} d_{lmn} u_l u_m u_n + \frac{1}{4!} \sum_{lmnp} f_{lmnp} u_l u_m u_n u_p + \dots \quad (2.153)$$

As a first approximation, let us keep only the cubic anharmonic term and make use of

$$u_m = \sum_k \left(\frac{\hbar}{2MN\omega_k} \right)^{1/2} (a_k + a_{-k}^\dagger) e^{ikma}. \quad (2.154)$$

Substituting (2.154) in (2.153) gives

$$\begin{aligned} H'_3 = \frac{1}{3!} \sum_{lmn} d_{lmn} \sum_{kk'k''} \left(\frac{\hbar}{2MN} \right)^{3/2} (\omega_k \omega_{k'} \omega_{k''})^{-1/2} \\ \times (a_k + a_{-k}^\dagger) (a_{k'} + a_{-k'}^\dagger) (a_{k''} + a_{-k''}^\dagger) e^{ikna} e^{ik'ma} e^{ik''la}. \end{aligned} \quad (2.155)$$

As before, d_{lmn} does not depend on l, m, n individually, but on their relative positions. We can, therefore, write $d_{lmn} = d(n-m, n-l)$. Now introduce $g = n-m$ and $j = n-l$ and sum over all values of g, j , and n instead of l, m , and n . This gives for the cubic anharmonic correction to the Hamiltonian

$$\begin{aligned} H'_3 = \frac{1}{3!} \sum_{ngj} d(g, j) \sum_{kk'k''} \left(\frac{\hbar}{2MN} \right)^{3/2} (\omega_k \omega_{k'} \omega_{k''})^{-1/2} \\ \times (a_k + a_{-k}^\dagger) (a_{k'} + a_{-k'}^\dagger) (a_{k''} + a_{-k''}^\dagger) e^{ikna} e^{ik'(n-g)a} e^{ik''(n-j)a}. \end{aligned} \quad (2.156)$$

The only factor depending on n is $e^{i(k+k'+k'')na}$, and

$$\sum_n e^{i(k+k'+k'')na} = N \delta(k+k'+k'', K). \quad (2.157)$$

Here, K is a reciprocal lattice vector; the value of K is uniquely determined since k, k', k'' must all lie within the first Brillouin zone. Eliminate k'' remembering that if $-(k+k')$ lies outside the first Brillouin zone, one must add a reciprocal lattice vector K to k'' to satisfy (2.157). With this H'_3 becomes

$$\begin{aligned} H'_3 = N \sum_{kk'} \frac{1}{3!} \sum_{gj} d(g, j) e^{-ik'ga} e^{i(k+k')ja} \left(\frac{\hbar}{2MN} \right)^{3/2} \\ \times (\omega_k \omega_{k'} \omega_{k+k'})^{-1/2} (a_k + a_{-k}^\dagger) (a_{k'} + a_{-k'}^\dagger) (a_{-(k+k')} + a_{k+k'}^\dagger). \end{aligned} \quad (2.158)$$

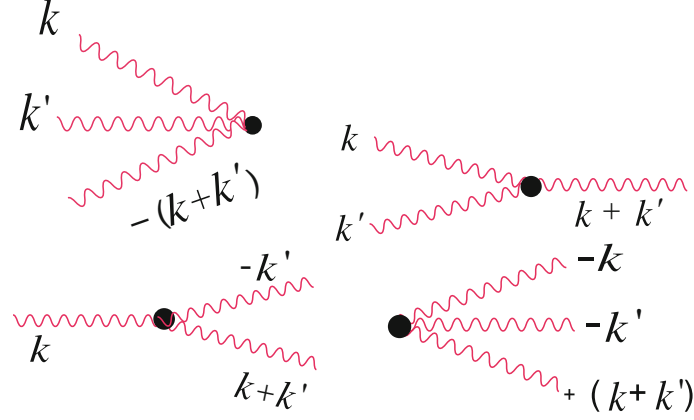


Fig. 2.17. Scattering of phonons: (a) annihilation of three phonons, (b) annihilation of two phonons and creation of a third phonon, (c) annihilation of one phonon and creation of two phonons, (d) creation of three phonons

Now define

$$G(k, k') = \frac{1}{3!} \sum_{gj} d(g, j) e^{ikja} e^{ik'(j-g)a} \left(\frac{\hbar^3}{2^3 M^3 N \omega_k \omega_{k'} \omega_{k+k'}} \right)^{1/2}. \quad (2.159)$$

Then, H'_3 is simply

$$H'_3 = \sum_{kk'} G(k, k') \left(a_k + a_{-k}^\dagger \right) \left(a_{k'} + a_{-k'}^\dagger \right) \left(a_{-(k+k')} + a_{k+k'}^\dagger \right). \quad (2.160)$$

Feynman Diagrams

In keeping track of the results obtained by applying H' to a state of the harmonic crystal, it is useful to use *Feynman diagrams*. A wavy line will represent a phonon propagating to the right (time increases to the right). The interaction (i.e., the result of applying H'_3) is represented by a point into (or out of) which three wavy lines run. There are four fundamentally different kinds of diagrams (see Fig. 2.17):

1. $a_k a_{k'} a_{-(k+k')}$ annihilates three phonons (Fig. 2.17a).
2. $a_k a_{k'} a_{k+k'}^\dagger$ annihilates two phonons and creates a third phonon (Fig. 2.17b).
3. $a_k a_{-k'}^\dagger a_{k+k'}^\dagger$ annihilates a phonon but creates two phonons (Fig. 2.17c).
4. $a_{-k}^\dagger a_{-k'}^\dagger a_{k+k'}^\dagger$ creates three phonons (Fig. 2.17d).

Due to the existence of anharmonic terms (cubic, quartic, etc. in the displacements from equilibrium) the simple harmonic oscillators which describe

the normal modes in the harmonic approximation are coupled. This anharmonicity leads to a number of interesting results (e.g., thermal expansion, phonon-phonon scattering, phonon lifetime, etc.) We will not have space to take up these effects in this book. However, one should be aware that the harmonic approximation is an approximation. It ignores all the interesting effects resulting from anharmonicity.

2.9 Thermal Conductivity of an Insulator

When one part of a crystal is heated, a temperature gradient is set up. In the presence of the temperature gradient heat will flow from the hotter to the cooler region. The ratio of this heat current density to the magnitude of the temperature gradient is called the *thermal conductivity* κ_T .

In an insulating crystal (i.e., one whose electrical conductivity is very small at low temperatures as a result of the absence of nearly free electrons) the heat is transported by phonons. Let us define $u(x)$ as the internal energy per unit volume in a small region about the position x in the crystal. We assume that $u(x)$ depends on position because there is a temperature gradient $\frac{\partial T}{\partial x}$ in the x -direction. Because the temperature T depends on x , the local thermal equilibrium phonon density $\bar{n}_{q\lambda} = [e^{\hbar\omega_{q\lambda}/\Theta} - 1]^{-1}$ will also depend on x . This takes a little explanation. In our discussion of phonons up until now, a phonon of wave vector \mathbf{k} was not localized anywhere in the crystal. In fact, all of the atoms in the crystal vibrated with an amplitude u_k and different phases $e^{ikna - i\omega_k t}$. In light of this, a phonon is everywhere in the crystal, and it seems difficult to think about difference in phonon density at different positions. In order to do so, we must construct wave packets with a spread in k values, Δk , chosen such that $(\Delta k)^{-1}$ is much larger than the atomic spacing but much smaller than the distance Δx over which the temperature changes appreciably. Then, by a phonon of wavenumber k we will mean a wavepacket centered at wavenumber k . The wavepacket can then be localized to a region Δx of the order $(\Delta k)^{-1}$. If the temperature at position x is different from that at some other position, the phonon will transport energy from the warmer to the cooler region. The thermal current density at position x can be written

$$j_T(x) = \int \frac{d\Omega}{4\pi} s \cos \theta u(x - l \cos \theta). \quad (2.161)$$

In this equation $u(x)$ is the internal energy per unit volume at position x , s is the sound velocity, l is the phonon mean free path ($l = s\tau$, where τ is the average time between phonon collisions), and θ is the angle between the direction of propagation of the phonon and the direction of the temperature gradient (see Fig. 2.18). A phonon reaching position x at angle θ (as shown in Fig. 2.18) had its last collision, on the average, at $x' = x - l \cos \theta$. But the phonons carry internal energy characteristic of the position where they had

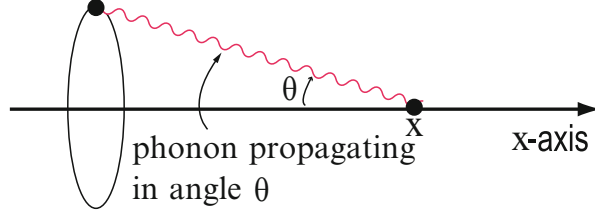


Fig. 2.18. Phonon propagation in the presence of a temperature gradient in the x -direction

their last collision, so such phonons carry internal energy $u(x - l \cos \theta)$. We can expand $u(x - l \cos \theta)$ as $u(x) - \frac{\partial u}{\partial x} l \cos \theta$, and integrate over $d\Omega = 2\pi \sin \theta d\theta$. This gives the result

$$j_T(x) = -\frac{1}{3} s l \frac{\partial u}{\partial x}. \quad (2.162)$$

Of course the internal energy depends on x because of the temperature gradient, so we can write $\frac{\partial u}{\partial x} = \frac{\partial u}{\partial T} \frac{\partial T}{\partial x}$. The result for the *thermal conductivity* $\kappa_T = -j_T \left(\frac{\partial T}{\partial x} \right)^{-1}$ is

$$\kappa_T = \frac{1}{3} s^2 \tau C_v. \quad (2.163)$$

In (2.163), we have set $l = s\tau$ and $\frac{\partial u}{\partial T} = C_v$, the specific heat of the solid.

2.10 Phonon Collision Rate

The collision rate τ^{-1} of phonons depends on

1. Anharmonic effects which cause phonon–phonon scattering
2. Defects and impurities which can scatter phonons and
3. The surfaces of the crystal which can also scatter phonons

Only the phonon–phonon collisions are very sensitive to temperature, since the phonon density available to scatter one phonon varies with temperature. For a perfect infinite crystal, defects, impurities, and surfaces can be ignored.

Phonon–phonon scattering can degrade the thermal current, but at very low temperature, where only low frequency ($\omega \ll \omega_D$ or $k \ll k_D$) phonons are excited, most phonon–phonon scattering conserves *crystal momentum*. By this we mean that in the real scattering processes shown in Fig. 2.19, no reciprocal lattice vector \mathbf{K} is needed in the conservation of crystal momentum, and Fig. 2.19a would contain a delta function $\delta(\mathbf{k}_1 + \mathbf{k}_2 - \mathbf{k}_3)$, Fig. 2.19b a $\delta(\mathbf{k}_1 - \mathbf{k}_2 - \mathbf{k}_3)$, and Fig. 2.19c a $\delta(\mathbf{k}_1 + \mathbf{k}_2 - \mathbf{k}_3 - \mathbf{k}_4)$. This occurs because each k -value is very small compared to the smallest reciprocal lattice vector \mathbf{K} . These scattering processes are called *N-processes* (for normal scattering processes), and they do not degrade the thermal current.

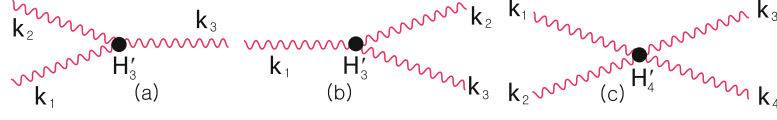


Fig. 2.19. Phonon–phonon scattering (a) Scattering of two phonons into one phonon, (b) Scattering of one phonon into two phonons, (c) Scattering of two phonons into two phonons

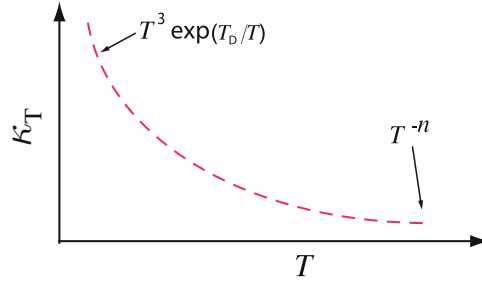


Fig. 2.20. Temperature dependence of the thermal conductivity of an insulator

At high temperatures phonons with k values close to a reciprocal lattice vector K will be thermally excited. In this case, the sum of \mathbf{k}_1 and \mathbf{k}_2 in Fig. 2.19a might be outside the first Brillouin zone so that $\mathbf{k}_3 = \mathbf{k}_1 + \mathbf{k}_2 - \mathbf{K}$. It turns out that these processes, *U-processes* (for Umklapp processes) do degrade the thermal current. At high temperatures it is found that τ is proportional to temperature to the $-n$ power, where $1 \leq n \leq 2$. The high temperature specific heat is the constant Dulong–Petit value, so that according to (2.163) $\kappa_T \propto T^{-n}$ at high temperature.

At low temperature, only U-processes limit the thermal conductivity (or contribute to the thermal resistivity). But few phonons with $k \approx k_D$ are present at low temperature. A rough estimate would give $e^{-\hbar\omega_D/\Theta}$ for the probability of U-scattering at low temperature. Therefore, τ_U , the scattering time for U-processes is proportional to $e^{\Theta_D/\Theta}$. Since the low temperature specific heat varies as T^3 , (2.163) would predict $\kappa_T \propto T^3 e^{T_D/T}$ for the thermal conductivity at low temperature. The result for the temperature dependence of thermal conductivity of an insulator is sketched in Fig. 2.20.

2.11 Phonon Gas

Landau introduced the concept of thinking of elementary excitations as particles. He suggested that it was possible to have a gas of phonons in a crystal whose properties were analogous to those of a classical gas. Both the atoms or molecules of a classical gas and the phonons in a crystal undergo collisions. For the former, the collisions are molecule–molecule collisions or molecule–wall of container collisions. For the latter they are phonon–phonon,

phonon–imperfection or phonon–surface collisions. Energy is conserved in these collisions. Momentum is conserved in molecule–molecule collisions in a classical gas and in N-process phonon–phonon collisions in a *phonon gas*. Of course, the number of particles is conserved in the molecule–molecule collisions of a classical gas, but phonons can be created or annihilated in phonon–phonon collisions, so their number is not a conserved quantity.

The sound waves of a classical gas are oscillations of the particle density. They occur if $\omega\tau \ll 1$, so that thermal equilibrium is established very quickly compared to the period of the sound wave. They also require that momentum be conserved in the collision process.

Landau⁴ called normal sound waves in a gas *first sound*. He proposed an oscillation of the phonon density in a phonon gas that named *second sound*. This oscillation of the phonon density (or energy density) occurred in a crystal if $\omega\tau_N \ll 1$ (as in first sound) but $\omega\tau_U \gg 1$ so that crystal momentum is conserved. Second sound has been observed in He⁴ and in a few crystals.

⁴ L. Landau, J. Phys. U.S.S.R. **5**, 71 (1941).

Problems

2.1. Consider a three-dimensional Einstein model in which each degree of freedom of each atom has a vibrational frequency ω_0 .

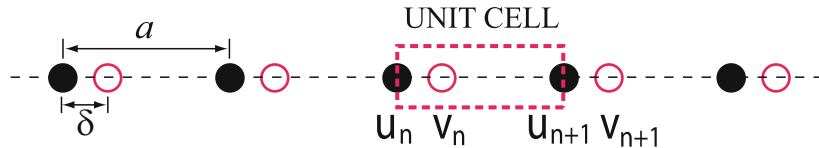
- Evaluate $G(\omega)$, the number of modes per unit volume whose frequency is less than ω .
- Evaluate $g(\omega) = \frac{dG(\omega)}{d\omega}$.
- Make a rough sketch of both $G(\omega)$ and $g(\omega)$ as a function of ω .

2.2. For a one-dimensional lattice a phonon of wave number k has frequency $\omega_k = \omega_0 \sin \frac{|k|a}{2}$ for a nearest neighbor coupling model. Now approximate this model by a Debye model with $\omega = s|k|$.

- Determine the value of s , the sound speed, and k_D , the Debye wave vector.
- Sketch ω as a function of k for each model over the entire Brillouin zone.
- Evaluate $g(\omega)$ for each model and make a sketch of $g(\omega)$ vs. ω for each.

2.3. Consider a diatomic linear chain. Evaluate u_q/v_q for the acoustic and optical modes at $q = 0$ and at $q = \frac{\pi}{2a}$.

2.4. Consider a linear chain with two atoms per unit cell (each of mass M) located at 0 and δ , where $\delta < \frac{a}{2}$, a being the primitive translation vector. Let C_1 be the force constant between nearest neighbors and C_2 the force constant between next nearest neighbors. Determine $\omega_{\pm}(k=0)$ and $\omega_{\pm}(k=\frac{\pi}{a})$.



2.5. Show that the normal mode density (for small ω) in a d -dimensional harmonic crystal varies as ω^{d-1} . Use this result to determine the temperature dependence of the specific heat.

2.6. In a linear chain with nearest neighbor interactions $\omega_k = \omega_0 \sin \frac{|k|a}{2}$. Show that $g(\omega) \simeq \left(\frac{2}{\pi a}\right) \frac{1}{\sqrt{\omega_0^2 - \omega^2}}$.

2.7. For a certain three-dimensional simple cubic lattice the phonon spectrum is independent of polarization λ and is given by

$$\omega(k_x, k_y, k_z) = \omega_0 \left[\sin^2 \left(\frac{k_x a}{2} \right) + \sin^2 \left(\frac{k_y a}{2} \right) + \sin^2 \left(\frac{k_z a}{2} \right) \right]^{1/2}.$$

- (a) Sketch a graph of ω vs. k for
 1. $k_y = k_z = 0$ and $0 \leq k_x \leq \frac{\pi}{a}$ (i.e., along $\Gamma \rightarrow X$),
 2. $k_z = 0$ and $k_x = k_y = \frac{k}{\sqrt{2}}$ for $0 \leq k \leq \frac{\sqrt{2}\pi}{a}$ (i.e., along $\Gamma \rightarrow K$),
 3. $k_x = k_y = k_z = \frac{k}{\sqrt{3}}$ for $0 \leq k \leq \frac{\sqrt{3}\pi}{a}$ (i.e., along $\Gamma \rightarrow L$).
- (b) Draw the ω vs. k curve for the Debye approximation to these dispersion curves as dashes lines on the diagram used in part (a).
- (c) What are the critical points of this phonon spectrum? How many are there?
- (d) Make a rough sketch of the Debye density of states $g(\omega)$. How will the actual density of states differ from the Debye approximation?
- (e) Using this example, discuss the shortcomings and the successes of the Debye model in predicting the thermodynamic properties (like specific heat) of solids.

2.8. For a two-dimensional crystal a simple Debye model takes $\omega = sk$ for the longitudinal and the single transverse modes for all allowed k values up to the Debye wave number k_D .

- (a) Determine k_D as a function of $\frac{N}{L^2}$, where N is the number of atoms and L^2 is the area of the crystal.
- (b) Determine $g(\omega)$, the density of normal modes per unit area.
- (c) Find the expression for the internal energy at a temperature T as an integral over the density of states times an appropriate function of frequency and temperature.
- (d) From the result of part (c) determine the specific heat c_v .
- (e) Evaluate c_v for $k_B T \ll \hbar\omega_D = \hbar sk_D$.

Summary

In this chapter, we discussed the vibrations of the atoms in solids. Quantum mechanical treatment of lattice dynamics and dispersion curves of the normal modes are described.

The Hamiltonian of a linear chain is written, in the harmonic approximation, as $H = \sum_i \frac{P_i^2}{2M} + \frac{1}{2} \sum_{i,j} c_{ij} u_i u_j$, where P_i is the momentum and $u_i = R_i - R_i^0$ is the deviation of the i th atom from its equilibrium position. A general dispersion relation of the normal modes is $M\omega_q^2 = \sum_{l=1}^N c(l)e^{iqla}$. The normal coordinates are given by

$$q_k = N^{-1/2} \sum_n u_n e^{-ikna}; \quad p_k = N^{-1/2} \sum_n P_n e^{+ikna}.$$

The inverse of q_k and p_k are $u_n = N^{-1/2} \sum_k q_k e^{ikna}$; $P_n = N^{-1/2} \sum_k p_k e^{-ikna}$.

The quantum mechanical Hamiltonian is given by $H = \sum_k H_k$, where

$$H_k = \frac{\hat{p}_k \hat{p}_k^\dagger}{2M} + \frac{1}{2} M \omega_k^2 \hat{q}_k \hat{q}_k^\dagger.$$

The dynamical variables q_k and p_k are replaced by quantum mechanical operators \hat{q}_k and \hat{p}_k which satisfy the commutation relation $[p_k, q_{k'}] = -i\hbar \delta_{k,k'}$. It is convenient to rewrite \hat{q}_k and \hat{p}_k in terms of the operators a_k and a_k^\dagger , which are defined by

$$q_k = \left(\frac{\hbar}{2M\omega_k} \right)^{1/2} (a_k + a_{-k}^\dagger); \quad p_k = i \left(\frac{\hbar M \omega_k}{2} \right)^{1/2} (a_k^\dagger - a_{-k}).$$

The a_k 's and a_k^\dagger 's satisfy $[a_k, a_{k'}^\dagger]_- = \delta_{k,k'}$ and $[a_k, a_{k'}]_- = [a_k^\dagger, a_{k'}^\dagger]_- = 0$.

The displacement of the n th atom and its momentum can be written

$$u_n = \sum_k \left(\frac{\hbar}{2MN\omega_k} \right)^{1/2} e^{ikna} (a_k + a_{-k}^\dagger),$$

$$P_n = \sum_k i \left(\frac{\hbar \omega_k M}{2N} \right)^{1/2} e^{-ikna} (a_k^\dagger - a_{-k}).$$

The Hamiltonian of the linear chain of atoms can be written

$$H = \sum_k \hbar \omega_k \left(a_k^\dagger a_k + \frac{1}{2} \right),$$

and its eigenfunctions and eigenvalues are

$$|n_1, n_2, \dots, n_N\rangle = \frac{(a_{k_1}^\dagger)^{n_1}}{\sqrt{n_1!}} \cdots \frac{(a_{k_N}^\dagger)^{n_N}}{\sqrt{n_N!}} |0\rangle$$

and $E_{n_1, n_2, \dots, n_N} = \sum_i \hbar \omega_{k_i} (n_i + \frac{1}{2})$.

In the three-dimensional case, the Hamiltonian is given by

$$H = \sum_{\mathbf{k}\lambda} \hbar\omega_{\mathbf{k}\lambda} \left(a_{\mathbf{k}\lambda}^\dagger a_{\mathbf{k}\lambda} + \frac{1}{2} \right).$$

The allowed values of \mathbf{k} are given by $\mathbf{k} = 2\pi \left(\frac{n_1}{N_1} \mathbf{b}_1 + \frac{n_2}{N_2} \mathbf{b}_2 + \frac{n_3}{N_3} \mathbf{b}_3 \right)$. The displacement \mathbf{u}_n and momentum \mathbf{P}_n of the n th atom are written, respectively, as

$$\begin{aligned} \mathbf{u}_n &= \sum_{\mathbf{k}\lambda} \left(\frac{\hbar}{2MN\omega_{\mathbf{k}\lambda}} \right)^{1/2} \hat{\epsilon}_{\mathbf{k}\lambda} e^{i\mathbf{k}\cdot\mathbf{R}_n^0} \left(a_{\mathbf{k}\lambda} - a_{-\mathbf{k}\lambda}^\dagger \right) \\ \mathbf{P}_n &= \sum_{\mathbf{k}\lambda} i \left(\frac{\hbar M\omega_{\mathbf{k}\lambda}}{2N} \right)^{1/2} \hat{\epsilon}_{\mathbf{k}\lambda} e^{-i\mathbf{k}\cdot\mathbf{R}_n^0} \left(a_{\mathbf{k}\lambda}^\dagger + a_{-\mathbf{k}\lambda} \right). \end{aligned}$$

The energy of the crystal is given by $U = \sum_{\mathbf{q}\lambda} \left(\bar{n}_{\mathbf{q}\lambda} + \frac{1}{2} \right) \hbar\omega_{\mathbf{q}\lambda}$, where $\bar{n}_{\mathbf{q}\lambda}$ is given by $\bar{n}_{\mathbf{q}\lambda} = \frac{1}{e^{\hbar\omega_{\mathbf{q}\lambda}/k_B T} - 1}$. The lattice heat capacity is written as

$$C_v = \left(\frac{\partial U}{\partial T} \right)_v = k_B \sum_{\mathbf{q}\lambda} \left(\frac{\hbar\omega_{\mathbf{q}\lambda}}{k_B T} \right)^2 \left(e^{\frac{\hbar\omega_{\mathbf{q}\lambda}}{k_B T}} - 1 \right)^{-1} \left(1 - e^{-\frac{\hbar\omega_{\mathbf{q}\lambda}}{k_B T}} \right)^{-1}.$$

The *density of states* $g(\omega)$ defined by

$$g(\omega)d\omega = \begin{cases} \text{The number of normal modes per unit volume} \\ \text{whose frequency } \omega_{\mathbf{q}\lambda} \text{ satisfies } \omega < \omega_{\mathbf{q}\lambda} < \omega + d\omega. \end{cases}$$

Then we have $g(\omega) = \frac{1}{(2\pi)^3} \sum_{\lambda} \int \frac{dS_{\lambda}(\omega)}{|\nabla_{\mathbf{q}} \omega_{\mathbf{q}\lambda}|_{\omega}}$. Here, $dS_{\lambda}(\omega)$ is an infinitesimal element of the surface of constant frequency in three-dimensional wave vector space on which $\omega_{\mathbf{q}\lambda}$ has the value ω . Near a critical point \mathbf{q}_c , at which $\nabla_{\mathbf{q}} \omega_{\mathbf{q}\lambda} = 0$, in the phonon spectrum, we can write

$$\omega_q = \omega_c + \alpha_1 \xi_1^2 + \alpha_2 \xi_2^2 + \alpha_3 \xi_3^2,$$

where ξ_i are the components of $\xi = \mathbf{q} - \mathbf{q}_c$, and $\omega_c = \omega(q_c)$. In three dimensions, there are four kinds of critical points:

1. *Maxima*: points at which all three α_i are negative.
2. *Minima*: points at which all three α_i are positive.
3. *Saddle Points of the First Kind*: Points at which two α_i 's are positive and one is negative.
4. *Saddle Points of the Second Kind*: Points at which one α_i is positive and the other two are negative.

The density of states for the Debye model is expressed as

$$g(\omega) = \frac{\omega^2}{2\pi^2} \left[\frac{\theta(s_l k_D - \omega)}{s_l^3} + \frac{2\theta(s_t k_D - \omega)}{s_t^3} \right].$$

Here, s_l and s_t are the speed of a longitudinal and of a transverse sound wave.



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