Phonons and Lattice Vibrations

CHAPTER OUTLINE

2.1 LATTICE DYNAMICS

2.1.1 Theory

In a crystalline solid, at finite temperatures, the ions or the atoms are not stationary but vibrate around an equilibrium position. In 1907, Einstein proposed a theory of the heat capacity of a solid based on Planck's quantum hypothesis. He assumed that each atom of the solid vibrates around its equilibrium position with a frequency ν_E, known as the Einstein frequency. Each atom vibrates like a simple harmonic oscillator that is in the potential well of the force field of its neighbors. The atoms have the same frequency ν_E and vibrate independent of the other atoms. Thus, a mole of solid with N atoms is assumed to have $3N$ independent harmonic oscillators. The excitation spectrum of the crystalline solid is composed of levels that are spaced at a distance $\hbar\nu_E$ from each other.

The basic assumption of the Einstein model was that the atoms vibrate independent of each other, which could be justified only if the temperature is very high. However, at normal temperatures this assumption breaks down, because if two or more atoms move in unison, the restoring forces between them, which tend to restore each of them to their equilibrium position, would be reduced. In such a scenario, the required energy to excite a quantum would be reduced. In fact, the correlation between the motion of the adjacent atoms would play a significant role in solving the problem of lattice vibrations.

We consider the ground state of the lattice with a basis as the state at zero temperature, where each ion or atom of mass M_n is located at the equilibrium position $\mathbf{d}_n$, which is a vector connecting the local origin of the cell with a basis to the atom or ion of mass M_n. We assume that if the lattice has only one atom per unit cell, the atom is located at the lattice point and $\mathbf{d}_n = 0$. At a finite temperature, the displacement of the nth atom or the ion in the ith unit cell (the local origin of which is located at the direct lattice vector $\mathbf{R}_i$, and we have assumed that the origin of the lattice is one of the lattice points) from its equilibrium position at $\mathbf{d}_n$ is the vector $\mathbf{u}_{ni}$. The definition of the vector $\mathbf{u}_{ni}$ is schematically shown in Figure 2.1. We note that $\mathbf{u}_{ni}$ can also be written as

$$\mathbf{u}_{ni} = \mathbf{r} - \mathbf{R}_i - \mathbf{d}_n, \tag{2.1}$$

where $\mathbf{r}$ is the instantaneous position of the atom or ion of mass M_n located in the unit cell of which the local origin is at $\mathbf{R}_i$.

The kinetic energy of the crystalline lattice can be written as

$$T = \sum_{ni} \frac{1}{2} M_n |\dot{\mathbf{u}}_{ni}|^2. \tag{2.2}$$

The potential energy of the crystal depends on the structure of the cell as well as the interatomic forces. However, we assume that at any given instant, the function $V(\mathbf{u}_{ni})$ describes the potential energy of the crystal in terms of the instantaneous positions of all atoms, i.e., in terms of their actual displacements from the equilibrium positions. In addition, it is assumed that the perfect lattice is a configuration of stable equilibrium. The study of phonons is based on the assumption that the deviation $\mathbf{u}_{ni}$ of the ions or atoms from their equilibrium position $\mathbf{R}_i + \mathbf{d}_n$ is so small that one can make a Taylor expansion in powers of the variables $\mathbf{u}_{ni}$. Thus, we can write

$$V = V_0 + \sum_{ni\alpha} \left[\frac{\partial V}{\partial u_{ni}^\alpha} \right]_0 u_{ni}^\alpha + \frac{1}{2} \sum_{nn'} \sum_{ii'} \sum_{\alpha\beta} \left[\frac{\partial^2 V}{\partial u_{ni}^\alpha \partial u_{n'i'}^\beta} \right]_0 u_{ni}^\alpha u_{n'i'}^\beta + ..., \tag{2.3}$$
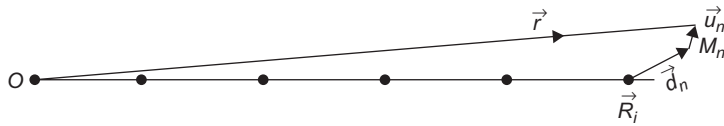

FIGURE 2.1

Definition of $\mathbf{u}_{ni}$ for a lattice with a basis.

where u_{ni}^{α} are the Cartesian components of $\mathbf{u}_{ni}$ and α and β are Cartesian indices running over the basis vectors of three-dimensional space.

The first term V_0 is essentially the cohesive energy of the crystal, but for the present purpose it is a constant term that can be neglected without affecting the calculation. Because the lowest energy state is a minimum as a function of the locations of the ions or atoms, the linear term in Eq. (2.3) must vanish near equilibrium. The first important term in Eq. (2.3) is the quadratic term in Eq. (2.3). This is known as the harmonic approximation. If one considers the higher-order terms for study of certain properties of the crystal, those are known anharmonic terms. However, in the present discussion, we shall restrict ourselves to the harmonic approximation.

We follow the Lagrangian procedure in classical mechanics to solve Eqs. (2.2) and (2.3). If we define the Lagrangian function (Symon, 1971, p. 366)

$$L = T - V, \tag{2.4}$$

the Lagrangian equations are

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_k}\right) - \frac{\partial L}{\partial q_k} = 0, \quad k = 1, \ldots, 3N. \tag{2.5}$$

From Eqs. (2.2), (2.3), and (2.5), we obtain (Problem 2.1)

$$M_n \, \ddot{u}_{ni}^{\alpha} = -\sum_{n'i'\beta} \left[\frac{\partial^2 V}{\partial u_{ni}^{\alpha} \partial u_{n'i'}^{\beta}}\right]_0 \mathbf{u}_{n'i'}^{\beta}. \tag{2.6}$$

We define a Cartesian tensor Φ such that its components are obtained by the relation

$$\Phi_{ni;n'i'}^{\alpha\beta} \equiv \left[\frac{\partial^2 V}{\partial u_{ni}^{\alpha} \partial u_{n'i'}^{\beta}}\right]_0. \tag{2.7}$$

From Eqs. (2.6) and (2.7), we obtain the vector equation

$$M_n \, \ddot{u}_{ni} = -\sum_{n'i'} \Phi_{ni;n'i'} \cdot \mathbf{u}_{n'i'}. \tag{2.8}$$

Eq. (2.8) can be interpreted as the force acting on the nth atom in the ith cell (the cell of which the local origin is at a distance $\mathbf{R}_i$ from the origin of the lattice, where $\mathbf{R}_i$ is a direct lattice vector) due to the displacement $\mathbf{u}_{n'i'}$ of the atom on the n'th site of the i'th cell. In fact, much of the theory of phonons can be developed without considering how to calculate $\Phi_{ni;n'i'}$. However, $\Phi_{ni;n'i'}$ cannot depend on the absolute position of $\mathbf{R}_i$ and $\mathbf{R}_{i'}$ in the crystalline lattice. Thus, the tensor Φ has to be a function of their relative position $\mathbf{R}_i$ and $\mathbf{R}_{i'}$. If we write

$$\mathbf{R}_{i'} - \mathbf{R}_i = \mathbf{R}_l, \tag{2.9}$$

the Cartesian tensor can be expressed in the alternate form

$$\Phi_{ni,n'i'} = \Phi_{nn'}(\mathbf{R}_l). \tag{2.10}$$

From Eqs. (2.8) and (2.10), we obtain

$$M_n\ddot{\mathbf{u}}_{ni} = -\sum_{n'l}\Phi_{nn'}(\mathbf{R}_l)\cdot\mathbf{u}_{n',i+l}. \tag{2.11}$$

Here, $\mathbf{u}_{n,i+l}$ denotes the instantaneous displacement of the nth atom in the $i+l$th cell. We note that because the summation over the direct lattice vector $\mathbf{R}_l$ spans the entire lattice, Eq. (2.11) is translationally invariant. For example, if we change the label $\mathbf{R}_l$ to $\mathbf{R}_{l'}$, we obtain

$$M_n\ddot{\mathbf{u}}_{ni} = -\sum_{n'l'}\Phi_{nn'}(\mathbf{R}_{l'})\cdot\mathbf{u}_{n',i+l'}, \tag{2.12}$$

which yields the same set of equations as Eq. (2.11). We also note another property of the tensor Φ is that the energy of the crystal cannot change if all the ions (or atoms) are displaced by a single vector, i.e.,

$$\sum_{l'}\Phi_{nn'}(\mathbf{R}_{l'}) = 0. \tag{2.13}$$

Because Eq. (2.11) must satisfy Bloch's theorem, if the set of functions of the time that describes the value of $\mathbf{u}_{ni}(t)$ for each value of $\mathbf{R}_i$ has been found, then according to the Bloch condition, there would be a wave vector $\mathbf{q}$ such that

$$\mathbf{u}_{ni}(t) = e^{i\mathbf{q}\cdot\mathbf{R}_i}\mathbf{u}_{n,0}(t), \tag{2.14}$$

where $\mathbf{u}_{n,0}(t)$ is the displacement of the nth atom in the cell that has been chosen as the origin for the direct lattice vectors $\mathbf{R}_i$. It is obvious from Eq. (2.14) that the atom or ion located at every site $\mathbf{d}_n$ (measured from the local origin of the unit cell, as shown in Figure 2.1) moves with the same amplitude and direction. However, the phase would vary for each cell. From Eqs. (2.11) and (2.14), we obtain

$$M_n\ddot{\mathbf{u}}_{n,0}e^{i\mathbf{q}\cdot\mathbf{R}_i} = -\sum_{n'l}\Phi_{nn'}(\mathbf{R}_l)\cdot\mathbf{u}_{n',0}e^{i\mathbf{q}\cdot\mathbf{R}_l}e^{i\mathbf{q}\cdot\mathbf{R}_i}. \tag{2.15}$$

In Eq. (2.15), we cancel the $e^{i\mathbf{q}\cdot\mathbf{R}_i}$ from both sides, and because the origin 0 is arbitrary, we consider a solution with a definite value of $\mathbf{q}$ by writing

$$\mathbf{u}_{n,0} = \mathbf{U}_{n,\mathbf{q}}, \tag{2.16}$$

and obtain

$$M_n\ddot{\mathbf{U}}_{n,\mathbf{q}} = -\sum_{n'}\left[\sum_l\Phi_{nn'}(\mathbf{R}_l)e^{i\mathbf{q}\cdot\mathbf{R}_l}\right]\cdot\ddot{\mathbf{U}}_{n',\mathbf{q}}. \tag{2.17}$$

We define the Fourier transform of the force tensor Φ as

$$\Phi_{nn'}(\mathbf{q}) \equiv \sum_l\Phi_{nn'}(\mathbf{R}_l)e^{i\mathbf{q}\cdot\mathbf{R}_l}, \tag{2.18}$$

and rewrite Eq. (2.17) as

$$M_n\ddot{\mathbf{U}}_{n,\mathbf{q}} = -\sum_{n'}\Phi_{nn'}(\mathbf{q})\cdot\mathbf{U}_{n',\mathbf{q}}, \tag{2.19}$$

Eq. (2.19) is a set of $3m$ equations (assuming that there are m atoms per unit cell and there are three component equations—due to the three Cartesian components of the vectors—for each of the m values of n) in contrast to Eq. (2.8), which had a set of $3mN$ equations. This enormous simplification was possible because of the translational invariance.

Using the classical theory of vibrations,

$$U_{n,\mathbf{q}}^{\alpha}(t) = U_{n,\mathbf{q}}^{\alpha}e^{i\omega t}, \tag{2.20}$$

we obtain from Eqs. (2.19) and (2.20),

$$\sum_{n'\beta}[\Phi_{nn'}^{\alpha\beta}(\mathbf{q}) - \omega^2 M_n\delta_{nn'}\delta_{\alpha\beta}]U_{n',\mathbf{q}}^{\alpha} = 0. \tag{2.21}$$

Eq. (2.21) is an eigenvalue equation with $3m$ solutions that are solved by finding the roots of the equation in ω^2 when the determinant of the matrix [ ] is equal to zero. In a sense, we are solving $3m$ normal modes of vibration of m atoms in a unit cell that are assumed to interact via the force tensor $\Phi_{nn'}(\mathbf{q})$. This force tensor, $\Phi_{nn'}(\mathbf{q})$, which is different for each value of $\mathbf{q}$, is a sum of interactions of all n-type atoms (those atoms located at site n in each unit cell) with all the atoms on site n', and includes the effect of their relative phases.

2.1.2 Normal Modes of a One-Dimensional Monoatomic Lattice

We consider a set of ions of mass M (we have been using ions and atoms interchangeably for the lattice vibrations) located at the lattice points separated by a distance a. The one-dimensional Bravais lattice vectors are $\mathbf{R}_i = n_i a$. In this one-dimensional chain of lattice, one atom (or ion) of the same type is located at the lattice point. If the lattice 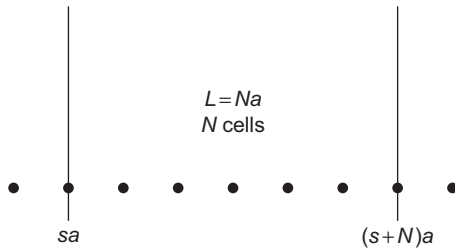constant is a, we define $L = Na$ such that periodic boundary conditions are applied to the linear chain. This boundary condition requires that the atoms located at s and at $s+N$ vibrate with the same amplitude and phase. The linear chain is shown in Figure 2.2.

The linear boundary condition is best illustrated if we construct an endless circular chain of lattice points. This endless circular chain is illustrated in Figure 2.3. We note that although this illustration is possible for a one-dimensional lattice, such periodic boundary conditions have to be imagined for a three-dimensional lattice.

FIGURE 2.2

A linear chain of lattice points with periodic boundary conditions.
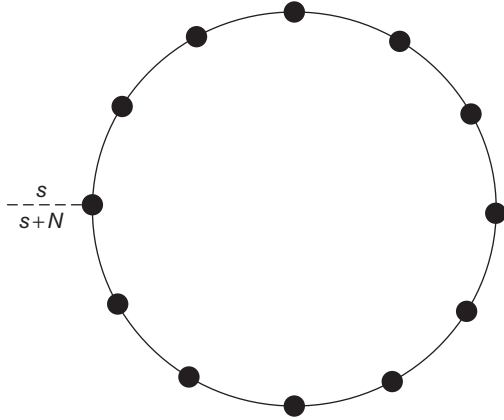
FIGURE 2.3

An endless circular chain of lattice points.
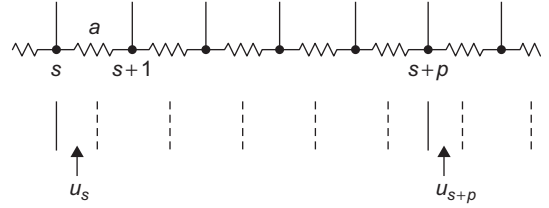
FIGURE 2.4

A linear chain of identical atoms, each located at a lattice point.

Figure 2.4 shows a linear chain of atoms of identical point mass m in a linear lattice of lattice constant a. The atoms are located at the lattice points. The atom (or ion) of which the equilibrium position is sa is displaced from equilibrium by an amount u_s, as shown in Figure 2.4.

For simplicity, we consider only nearest-neighbor interactions between the atoms (ions). The potential energy V in Eq. (2.3) is of the form

$$V^{harm} = \frac{1}{2} K \sum_s [u(sa) - u([s+1]a)]^2, \tag{2.22}$$

where K is the interaction energy of two ions (popularly known as the spring constant) $-\Phi_{i,i+1}$. Φ_{ii} is determined by the condition set in Eq. (2.13). The equations of motion are obtained from Eq. (2.22) as

$$M\ddot{u}(sa) = -\frac{\partial V^{harm}}{\partial u(sa)} = -K[(u(sa) - 2u([s-1]a) - u([(s+1]a)]. \tag{2.23}$$

The solution of Eq. (2.23) is of the type

$$u(sa, t) = Ae^{i(qsa-\omega t)}. \tag{2.24}$$

Using the periodic boundary condition (Figure 2.3),

$$e^{iqNa} = 1, \tag{2.25}$$

we obtain the expression for q,

$$q = \frac{s}{N} \frac{2\pi}{a}, \tag{2.26}$$

where s is an integer and a is the lattice constant of the one-dimensional lattice. The q values lie between $-\frac{\pi}{a}$ and $\frac{\pi}{a}$. Substituting Eq. (2.24) in Eq. (2.23), we obtain

$$M\omega^2 = 2K(1-\cos qa) = 4K\,\sin^2(qa/2), \tag{2.27}$$

which leads to the solution

$$\omega(q) = 2\sqrt{\frac{K}{M}}\,\sin\left(\frac{qa}{2}\right), \tag{2.28}$$

where we have taken only the positive root of Eq. (2.27) because ω is an even function of q. We plotted ω as a function of q in Figure 2.5. We note that there is a maximum vibrational frequency $\omega = 2\sqrt{\frac{K}{M}}$ and the behavior is periodic with period $2\pi/a$. In fact, all possible vibrations are given by values of q in the range

$$-\frac{\pi}{a} < q \le \frac{\pi}{a}, \tag{2.29}$$

which is the Brillouin zone (we will discuss the Brillouin zone in detail in Chapter 4 by using the nearly free electron model in a periodic lattice potential) for a linear lattice.

One can also count the number of modes in the following way. From Eq. (2.26), we obtain an expression for the density of modes in one-dimensional **q** space as

$$\frac{Na}{2\pi} = \frac{L}{2\pi}, \tag{2.30}$$

where L is the length of the sample. We also note that when $qa \ll 1$,

$$\frac{d\omega}{dq} = \frac{\omega}{q} = \sqrt{\frac{K}{M}}\,a = \text{constant}. \tag{2.31}$$
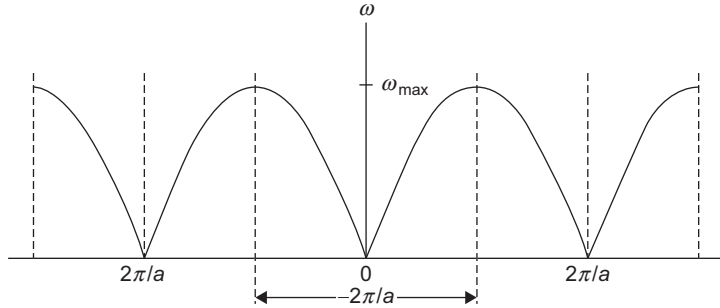

FIGURE 2.5

The vibrational frequencies of a linear chain of identical point masses.

Thus, the group velocity is equal to the phase velocity, and this proportionality of frequency to the wave number is also the property of the ordinary elastic waves in a continuum. This is also the velocity of sound waves and is known as the acoustic mode. However, at large values of q, the velocity of the wave is not constant. In fact, when $q = \pi/a = 2\pi/\lambda$, i.e., when the wavelength $\lambda = 2a$, ω_q bends over to a horizontal tangent (see Figure 2.5). This shows the property of dispersion.

2.1.3 Normal Modes of a One-Dimensional Chain with a Basis

We consider a one-dimensional Bravais lattice of lattice constant a with two ions or atoms of masses M_1 and M_2 per unit cell. This is shown in Figure 2.6. The basic assumption is that each ion interacts only with the nearest neighbors, which are at a distance $a/2$ from each other, and $M_1 > M_2$. Thus, the lattice constant of the linear chain is a.

If K is the force constant, from Eq. (2.21) we obtain

$$V^{harm} = \frac{K}{2} \sum_s [u_1(sa) - u_2(sa)]^2 + \frac{K}{2} \sum_s [u_2(sa) - u_1[s+1]a]^2, \tag{2.32}$$

where $u_1(sa)$ is the displacement of the ion that oscillates about the site sa and $u_2(sa)$ is the displacement of the ion that oscillates around $sa + d$. The equations of motion are

$$M_1\,\ddot{u}_1(sa) = -\frac{\partial V^{harm}}{\partial u_1(sa)} = -K[2u_1(sa) - u_2(sa) - u_2([s-1]a)],$$

$$\tag{2.33}$$

$$M_2\,\ddot{u}_2(sa) = -\frac{\partial V^{harm}}{\partial u_2(sa)} = -K[2u_2(sa) - u_1(sa) - u_1([s+1]a)].$$

The solutions of Eq. (2.33) are of the type

$$u_1(sa, t) = \in_1 e^{i(qsa-\omega t)}$$

and

$$u_2(sa, t) = \in_2 e^{i(qsa-\omega t)}. \tag{2.34}$$

Substituting Eq. (2.34) in Eq. (2.33), we obtain

$$-\omega^2 M_1 \in_1 e^{i(qsa-\omega t)} = K(\in_2 - 2\in_1 + \in_2 e^{-iqa})\, e^{i(qsa-\omega t)}$$

and

$$-\omega^2 M_2 \in_2 e^{i(qsa-\omega t)} = K(\in_1 e^{iqa} - 2\in_2 + \in_1)\, e^{i(qsa-\omega t)}. \tag{2.35}$$

FIGURE 2.6

Diatomic linear chain of masses M_1 and M_2.

We cancel the $e^{i(qsa-\omega t)}$ term from both sides and solve the determinantal equation

$$\begin{vmatrix} 2K - M_1\omega^2 & -K(1 + e^{-iqa}) \\ -K(1 + e^{iqa}) & 2K - M_2\omega^2 \end{vmatrix} = 0. \tag{2.36}$$

There are two roots of the solution of Eq. (2.36), which yields (Problem 2.4)

$$\omega_{\pm}^2 = K\left(\frac{1}{M_1} + \frac{1}{M_2}\right) \pm K\sqrt{\left[\left(\frac{1}{M_1} + \frac{1}{M_2}\right)^2 - \frac{4\sin^2(qa/2)}{M_1 M_2}\right]}. \tag{2.37}$$

The two solutions of Eq. (2.37) are the two branches of the phonon dispersion relation. For small q, the two roots of Eq. (2.37) are

$$\omega_- = \sqrt{\frac{K}{2(M_1 + M_2)}}qa \tag{2.38}$$

and

$$\omega_+ = \sqrt{\frac{2K(M_1 + M_2)}{M_1 M_2}}. \tag{2.39}$$

We also note from Eq. (2.37) that if $qa = \pm\pi$ (the Brillouin zone boundary), the expressions for $\omega_{\pm}$ reduce to

$$\omega_{\pm}^2 = \left(K\left[\frac{1}{M_1} + \frac{1}{M_2}\right] \pm K\left[\frac{1}{M_2} - \frac{1}{M_1}\right]\right). \tag{2.40}$$

Thus, we obtain

$$\omega_+ = \sqrt{\frac{2K}{M_2}} \tag{2.41}$$

and

$$\omega_- = \sqrt{\frac{2K}{M_1}}. \tag{2.42}$$

At the Brillouin zone boundary, $q = \pm\frac{\pi}{a}$. We also note that because $M_1 > M_2, \omega_+ > \omega_-$. Another interesting point to note is that from Eq. (2.34), u_1 and u_2 are periodic with $q = \pm 2\pi/a$. Therefore, the dispersion relation repeats itself for each Brillouin zone. From the previous discussions, we obtain the following results.

The vibrational frequency of a diatomic linear chain of mass M_1 and M_2 is shown in Figure 2.7.

The first branch, ω_-, which tends to become zero at $q = 0$, is known as the acoustic mode.
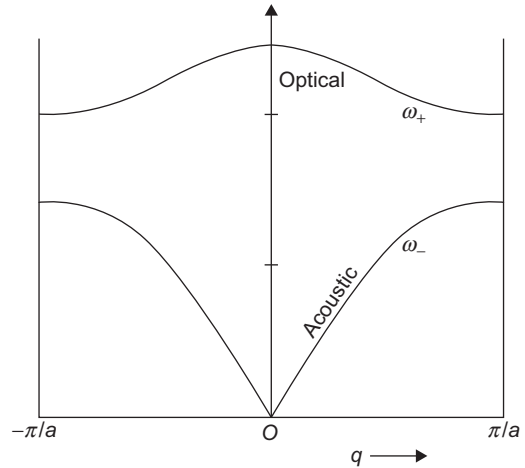

FIGURE 2.7

Optical and acoustic phonon branches of a diatomic linear chain.

It is in fact the analogue of a long-wavelength vibration of the linear chain, conceived as an elastic continuum. The normal value of the velocity of sound is reproduced in this case just as in the case of a monoatomic lattice. In the acoustic mode, the atoms vibrate in unison, whereas in the optical mode, the atoms in the unit cell vibrate out of phase. Essentially, the two sublattices of the two types of atoms move rigidly in opposition to one another. This can also be stated in the alternate form that the diatomic molecules vibrate as if they are independent of the neighbors. If these crystals are ionic crystals, the two types of atoms are of opposite electric charge. This yields an oscillating dipole moment that is optically active. We also note that if the masses of the two atoms in the linear chain were equal ($M_1 = M_2$), there would be no gap at the zone boundaries.

The configuration of atoms in the acoustic and optical modes in the diatomic linear chain is shown in Figure 2.8. In the acoustic mode, atoms within a unit cell move in concert, whereas in the optical mode they vibrate against each other.

In the previous example, we discussed only a linear chain of atoms. Thus, we obtained dispersion relation for longitudinal acoustic (LA) and longitudinal optical (LO) phonons. However, if we consider two atoms per primitive cell in a three-dimensional lattice, as in the NaCl or diamond structure, for each polarization mode in a direction of propagation, there are two branches in the dispersion relation ω versus q. In addition to LA and LO phonons, of which the dispersion relations are essentially the same as shown in Figure 2.7, one obtains transverse acoustical (TA) and transverse optical (TO) phonons. Figure 2.9 shows the TA and TO modes for a diatomic linear lattice at the same wavelength.

The optical modes of oscillation of individual ions in both transverse and longitudinal modes are shown in Figure 2.10.
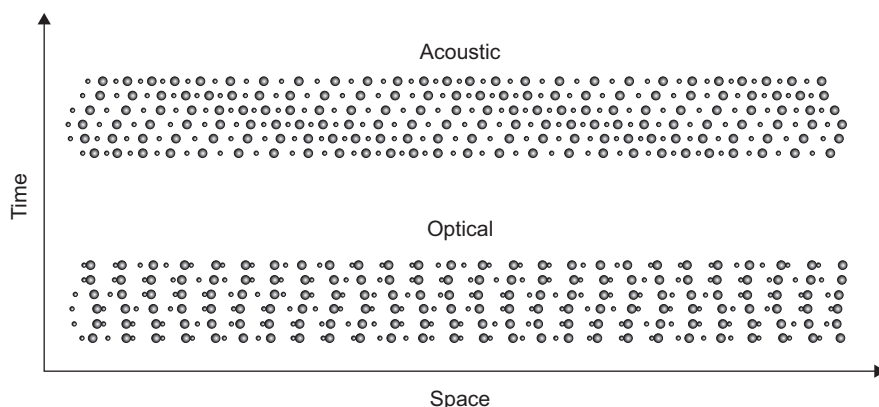

FIGURE 2.8

Configuration of atoms in acoustic and optical modes in the diatomic linear chain.
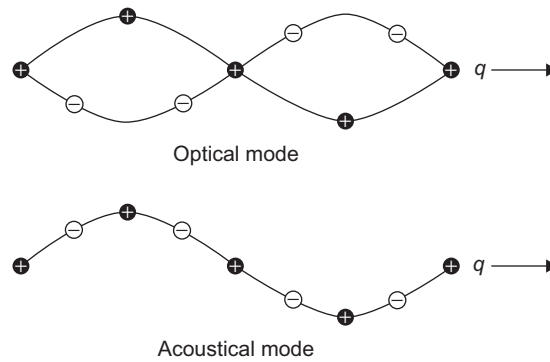
FIGURE 2.9

Transverse optical and acoustical waves for the same wavelength in a diatomic linear lattice.
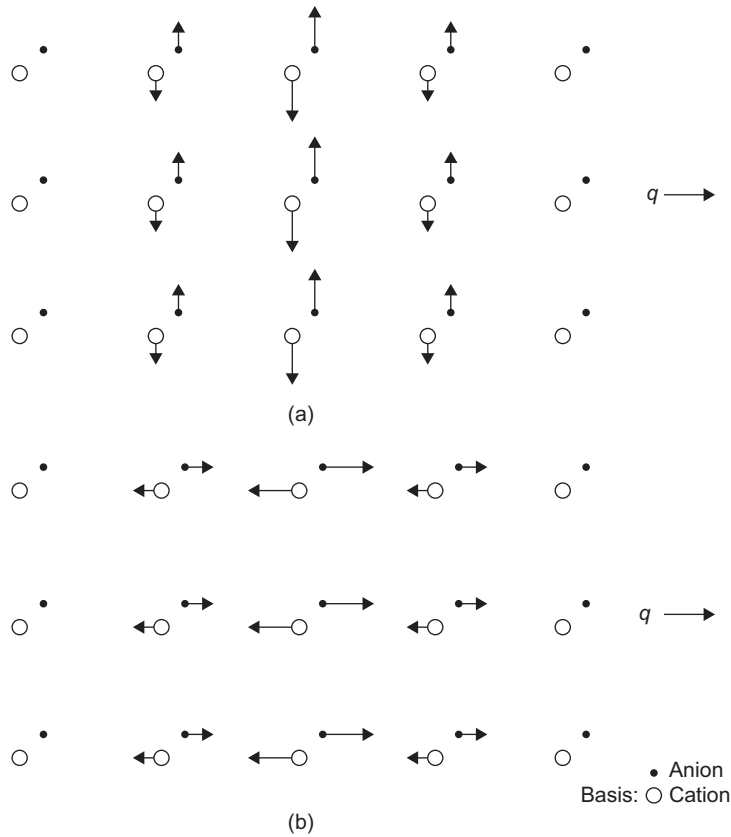

FIGURE 2.10

The direction of displacement of individual ions in (a) transverse optical (TO) and (b) longitudinal optical (LO) modes of oscillation.

2.2 LATTICE SPECIFIC HEAT

2.2.1 Theory

The thermal excitation of the lattice contributes to the specific heat of solids. To calculate the lattice specific heat, one has to use quantum mechanical operators instead of the classical coordinates $\mathbf{u}_{ni}$ and their momenta. In the earlier formulation of the theory of lattice vibrations, we obtained a set of equations of motion that are those of an assembly of independent simple harmonic oscillators. However, in a quantum mechanical treatment, the excitations are of the Bose–Einstein type. We introduced the term *phonons* to describe the normal modes of the crystal in the same manner the term *photons* was introduced to describe the quantum theory of electromagnetic field. In that theory, a normal mode of the radiation field in a cavity is given by $(n + \frac{1}{2})\hbar\omega$, where ω is the angular frequency of the mode. The *photons* are the quanta of radiation field that describes classical light. Similarly, the *phonons* are the quanta of the ions' displacement field that describes classical sound. The nomenclature of normal modes and phonons are equivalent although the latter is much more convenient.

If we want to specify the energy levels of an N-ion harmonic crystal that can be regarded as $3N$ independent oscillators, the contribution to the energy $\varepsilon_{\mathbf{q}s}$ of a particular normal mode with angular frequency $\omega_s(\mathbf{q})$ can have the discrete set of values

$$\varepsilon_{\mathbf{q}s} = \left(n_{\mathbf{q}s} + \frac{1}{2}\right)\hbar\omega_s(\mathbf{q}), \tag{2.43}$$

where there are $n_{\mathbf{q}s}$ phonons of type s with wave vector $\mathbf{q}$ present in the crystal. We note that an equivalent classical description would be that the normal mode of branch s with wave vector $\mathbf{q}$ is in its $n_{\mathbf{q}s}$th excited state. We note that the total energy E is the sum of the energies of the individual normal modes,

$$E = \sum_{\mathbf{q}s}\left(n_{\mathbf{q}s} + \frac{1}{2}\right)\hbar\omega_s(\mathbf{q}). \tag{2.44}$$

When we consider an assembly of independent simple harmonic oscillators, the excitations must be bosons. From the theory of Bose–Einstein statistics, $\overline{n}_{\mathbf{q}s}$, the mean number of bosons with energy $\hbar\omega_s(\mathbf{q})$ in thermal equilibrium at temperature T, when the chemical potential μ is taken to be zero ($\mu = 0$ because the total number of phonons in thermal equilibrium is determined by the temperature and hence is not an independent variable), is given by

$$\overline{n}_{\mathbf{q}s} = \frac{1}{e^{\beta\hbar\omega_s(\mathbf{q})} - 1}, \tag{2.45}$$

where

$$\beta = 1/k_B T. \tag{2.46}$$

The quanta in the $\mathbf{q}$th mode will contribute an energy

$$\overline{\varepsilon}_{\mathbf{q}s} = \left(\overline{n}_{\mathbf{q}s} + \frac{1}{2}\right)\hbar\omega_s(\mathbf{q}), \tag{2.47}$$

which includes the zero-point energy. From Eqs. (2.45) and (2.47), the average total energy of the system (neglecting the zero-point energy) is

$$\bar{\varepsilon} = \sum_{\mathbf{q}s} \frac{\hbar\omega_s(\mathbf{q})}{e^{\beta\hbar\omega_s(\mathbf{q})}-1}. \tag{2.48}$$

Here, the summation is over all polarizations s and different modes $\mathbf{q}$. Thus, the specific heat is given by

$$C_V = \frac{1}{V}\frac{\partial\bar{\varepsilon}}{\partial T} = \frac{1}{V}\sum_{\mathbf{q}s}\frac{\partial}{\partial T}\frac{\hbar\omega_s(\mathbf{q})}{e^{\beta\hbar\omega_s(\mathbf{q})}-1}, \tag{2.49}$$

where V is the volume of the crystal. We will now evaluate the specific heat in the high-temperature and intermediate-temperature. We will evaluate low-temperature limits in Problem 2.5.

1. In the high-temperature limit, $k_B T/\hbar$ is large compared with all the phonon frequencies. Thus, if we write $x = \frac{\hbar\omega}{k_B T} \ll 1$,

$$\frac{1}{e^x-1} \approx \frac{1}{x}\left[1-\frac{x}{2}+\frac{x^2}{12}+\cdots\right]. \tag{2.50}$$

From Eqs. (2.49) and (2.50), we obtain

$$C_V \simeq \frac{3N}{V}, \tag{2.51}$$

which is the classical law of Dulong and Petit. The higher-order terms in Eq. (2.50) yield the quantum corrections to the classical Dulong and Petit law.

2. In intermediate-temperature limits, both the Debye and Einstein models of specific heat are obtained by making different approximations. We note that in a large crystal, we can replace the sum in Eq. (2.49) by an integration over the wave vectors $\mathbf{q}$ that satisfy the Born–von Karman boundary conditions. Thus, Eq. (2.49) can be expressed as

$$C_V = \frac{\partial}{\partial T}\sum_s\int\frac{d\mathbf{q}}{(2\pi)^3}\frac{\hbar\omega_s(\mathbf{q})}{e^{\beta\hbar\omega_s(\mathbf{q})}-1}, \tag{2.52}$$

where the integral is over the first Brillouin zone. We can retrieve both the Debye and the Einstein models of specific heat of solids from Eq. (2.52), although they were originally derived under very different assumptions.

2.2.2 The Debye Model of Specific Heat

The Debye model of specific heat can be obtained by making two basic assumptions. First, all branches of the vibration spectrum are replaced with three branches of the acoustic mode such that the linear dispersion

$$\omega(q) = sq, \tag{2.53}$$

where s is the velocity of sound. Second, the integral over the first Brillouin zone is replaced by an integral over a sphere of the same volume and radius q_D in reciprocal space. It is assumed that the sphere contains exactly N allowed wave vectors just as in the case of the first Brillouin zone. Thus, the radius of the Debye sphere, q_D, is such that

$$N = \frac{V}{8\pi^3} \frac{4}{3}\pi q_D^3, \tag{2.54}$$

and hence

$$q_D = \left(\frac{6\pi^2}{v_c}\right)^{1/3}, \tag{2.55}$$

where v_c is the volume of the Wigner–Seitz cell, which can be written in the alternate form

$$N = \frac{q_D^3}{6\pi^2}, \tag{2.56}$$

where n is the density of ions. From Eqs. (2.53) through (2.55), we obtain

$$C_V = \frac{\partial}{\partial T} \frac{3\hbar c}{2\pi^2} \int_0^{q_D} \frac{q^2 dq}{e^{\beta\hbar sq}-1}. \tag{2.57}$$

We define a Debye frequency

$$\omega_D = q_D s \tag{2.58}$$

and a Debye temperature

$$\Theta_D = \hbar\omega_D/k_B. \tag{2.59}$$

If we write

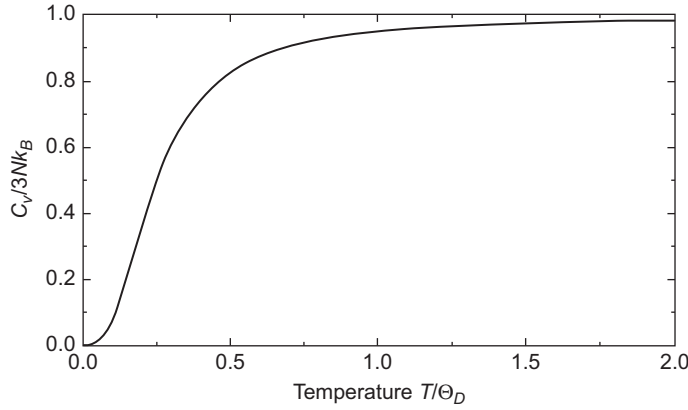$$x = \hbar sq/k_B T, \tag{2.60}$$

Eq. (2.57) can be written as

$$C_V = 9Nk_B \left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} \frac{x^4 e^x dx}{(x-1)^2}. \tag{2.61}$$

where N is the number of cells in the crystal. At low temperatures, the upper limit of the integral Θ_D/T tends to infinity, in which case the integral

$$\int_0^\infty \frac{x^4 e^x dx}{(x-1)^2} = \frac{4\pi^4}{5}. \tag{2.62}$$

FIGURE 2.11

Specific heat in the Debye approximation.

Thus, we obtain from Eqs. (2.61) and (2.62),

$$C_V \approx \frac{12\pi^4}{5} N k_B \left(\frac{T}{\Theta_D}\right)^3,$$

(2.63)

which is the Debye's T^3—*law of lattice specific heats*. The Debye law of specific heat is shown schematically in Figure 2.11.

The Debye's theory of specific heat works very well for solids. However, the Debye temperature, Θ_D, is often interpolated from the observed specific heat, thereby allowing it to depend on the temperature T. In fact, from Eqs. (2.58) and (2.59), Θ_D is related to the velocity of sound, s, by the relation,

$$\Theta_D = \frac{\hbar q_D s}{k_B},$$

(2.64)

and therefore should be calculated directly for a solid. In any case, Θ_D for most solids is listed in tables.

It is interesting to note that at temperatures well above Θ_D, the integrand form in Eq. (2.61) can be replaced by its form for small x and one obtains Dulong and Petit's law. Therefore, the Debye temperature, Θ_D, is a measure of the temperature separating the low-temperature region where quantum statistics is used from the high-temperature region where classical mechanics can be used.

However, Debye's theory of specific heat has its limitations. In most cases, the sharp cutoff frequency $\omega_D = \frac{k_B \Theta_D}{\hbar}$ is not justified. In general, there is a spread with several peaks that correspond to the modes of different polarization, which have different velocities. In addition, there is a peak at high frequencies due to the strong dispersion near the zone boundary. The contrast between the Debye spectrum and an actual lattice spectrum is shown in Figure 2.12.
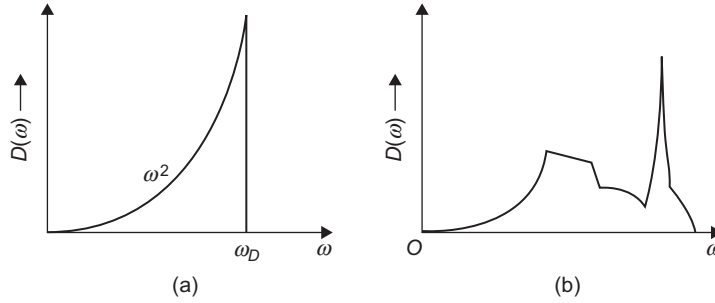
FIGURE 2.12

(a) Debye spectrum; (b) actual lattice spectrum.

2.2.3 The Einstein Model of Specific Heat

As we noted earlier, in a lattice with a basis, there are both acoustic modes and optical modes. The three acoustic modes can be easily treated by the Debye model. The optical modes can be treated by the Einstein model in which each mode has the same frequency, ω_E, which is independent of **q**. Therefore, from Eq. (2.45), we obtain that each optical branch will contribute to the thermal energy density in the Einstein approximation,

$$\varepsilon = \frac{N\hbar\omega_E}{e^{\beta\hbar\omega_E}-1}, \tag{2.65}$$

and if there are p such branches,

$$C_V^{optical} = \frac{1}{V}\frac{\partial E}{\partial T} = pNk_B\frac{(\beta\hbar\omega_E)^2\,e^{\beta\hbar\omega_E}}{(e^{\beta\hbar\omega_E}-1)^2}. \tag{2.66}$$

We can also define an *Einstein temperature* Θ_E by

$$\Theta_E = \frac{\hbar\omega_E}{k_B}. \tag{2.67}$$

It should be noted that Einstein was the first to derive the theory of specific heat of solids by using quantum statistics instead of classical statistics. From Eq. (2.66), we note that when $T \gg \Theta_E$, $\beta\hbar\omega_E \equiv \frac{\Theta_E}{T}$ is very small and we can write

$$C_V^{optical} = pNk_B, \tag{2.68}$$

so that each optical mode contributes k_B/V, as required by Dulong and Petit's law. However, when $T \ll \Theta_E$, $\beta\hbar\omega_E$ is very large so that the
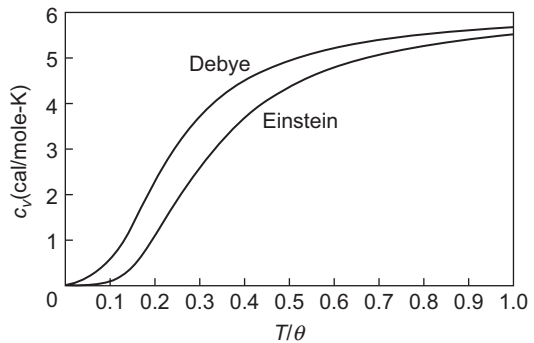

FIGURE 2.13

Comparison of Debye's and Einstein's specific heat as a function of $\frac{T}{\Theta}$.

contribution to C_V drops exponentially. Thus, it is very difficult to excite the optical modes at low temperatures.

A comparison of Debye's and Einstein's expressions for specific heat as a function of $\frac{T}{\Theta}$ is shown in Figure 2.13.

2.3 SECOND QUANTIZATION

2.3.1 Occupation Number Representation

The behavior of systems with a very large number of particles is studied in statistical physics. Suppose we have a system of N noninteracting particles that are found in states with wave functions $\varphi_1, \varphi_2, ..., \varphi_N$ which form a complete orthonormal set. For noninteracting particles, the wave function φ_i corresponds to one of the plane wave states

$$\varphi_{\mathbf{k}} = e^{i\mathbf{k}\cdot\mathbf{r}}. \tag{2.69}$$

They obey the orthonormality condition,

$$\int d\mathbf{r}\, \varphi_i^*(\mathbf{r})\varphi_j(\mathbf{r}) = \delta_{i,j}, \tag{2.70}$$

as well as

$$\sum_i \varphi_i^*(\mathbf{r})\varphi_j(\mathbf{r}') = \delta(\mathbf{r}-\mathbf{r}'). \tag{2.71}$$

The system can evidently be described by specifying the number of particles in states $\varphi_1, \varphi_2, ..., \varphi_N$. The complete wave function can be specified by using a new representation. We represent the basis function in the many-body wave function as

$$|n_1, n_2, n_3, ..., n_k ... >, \tag{2.72}$$

with n_k as the number of particles in state φ_k. The total number of particles

$$\sum n_i = N. \tag{2.73}$$

For Fermions (electrons, protons, neutrons, and He[3] atoms), which obey Fermi–Dirac statistics, the restriction is that

$$n_i = 0, \text{or } 1. \tag{2.74}$$

For bosons (photons, phonons, and He$_4$ atoms), which obey Bose–Einstein statistics, there is *no restriction* for n_i. For photons and phonons,

$$\sum_i n_i = N(T), \tag{2.75}$$

where $N(T)$ depends on the temperature T. Further,

$$N = 0 \text{ at } T = 0$$

and

$$N \neq 0 \text{ at } T \neq 0. \tag{2.76}$$

2.3.2 Creation and Annihilation Operators

(a) Bosons

We will first consider the *creation and annihilation operators* for bosons. We define the operators a_k and $a_k^\dagger$ by

$$a_k \,|n_1, n_{2,} ..., n_k, ... > = \sqrt{n_k}\,|n_1, n_2, ..., n_k - 1, ... > \tag{2.77}$$

and

$$a_k^\dagger \,|n_1 \cdot n_2, ..., n_k, ... > = \sqrt{n_k + 1}\,|n_1, n_2, ..., n_k + 1, ... >. \tag{2.78}$$

Here, a_k is the *annihilation operator* because it decreases

$$n_k \rightarrow n_k - 1, \tag{2.79}$$

and $a_k^\dagger$ is the *creation operator* because it increases

$$n_k \rightarrow n_k + 1. \tag{2.80}$$

The vacuum state is defined as

$$|0, 0, ..., 0, ... >, \tag{2.81}$$

whereas the other occupation numbers remain unchanged. From Eqs. (2.77) and (2.78), we obtain

$$\begin{aligned} a_k^\dagger a_k \,|n_1, n_2, ..., n_k, ... > &= \sqrt{n_k}\, a_k^\dagger \,|n_1, n_{2,} ..., n_k - 1, ... > \\ &= n_k \,|n_1, n_2, ..., n_k, ... >. \end{aligned} \tag{2.82}$$

From Eq. (2.82), we obtain that $a_k^\dagger a_k \Rightarrow n_k$ is the number operator in state **k**. Similarly, we obtain

$$\begin{aligned} a_k a_k^\dagger \,|n_1, n_{2,} ..., n_k, ... > &= \sqrt{n_k + 1}\, a_k \,|n_1, n_2, ..., n_k + 1, ... > \\ &= (n_k + 1) \,|n_1, n_2, ..., n_k, ... >. \end{aligned} \tag{2.83}$$

Subtracting Eq. (2.82) from Eq. (2.83), we obtain

$$(a_k a_k^\dagger - a_k^\dagger a_k) \, |n_1, n_2, ..., n_k, ... > \, = \, |n_1, n_2, ..., n_k, ... >. \tag{2.84}$$

Eq. (2.84) implies that

$$a_k a_k^\dagger - a_k^\dagger a_k = 1, \tag{2.85}$$

which can be written in the alternate form

$$[a_k, a_k^\dagger]_- = 1, \tag{2.86}$$

where $[A, B]_-$ is the commutator

$$[A, B]_- = AB - BA. \tag{2.87}$$

If $k \neq k'$,

$$\begin{aligned}
a_{k'}^\dagger a_k \, |n_1, n_2, ..., n_{k'}, ..., n_k, ... > &= \sqrt{n_k} \, a_{k'}^\dagger \, |n_1, n_2, ..., n_{k'}, ..., n_{k-1}, ... > \\
&= \sqrt{n_k} \, \sqrt{n_{k'} + 1} \, |n_1, n_2, ..., n_{k'+1}, ..., n_{k-1} ... >.
\end{aligned} \tag{2.88}$$

$$\begin{aligned}
a_k a_{k'}^\dagger \, |n_1, n_2, ..., n_{k'}, ..., n_k, ... > &= a_k \sqrt{n_{k'} + 1} \, |n_1, n_2, ..., n_{k'+1}, ..., n_k ... > \\
&= \sqrt{n_k} \, \sqrt{n_{k'} + 1} \, |n_1 \cdot n_2, ..., n_{k'+1}, ..., n_k ... >.
\end{aligned} \tag{2.89}$$

Subtracting Eq. (2.89) from Eq. (2.88), we obtain

$$(a_{k'}^\dagger a_k - a_k a_{k'}^\dagger)|n_1, n_2, ..., n_{k'+1}, ..., n_k, ... > \, = 0. \tag{2.90}$$

From Eqs. (2.86) and (2.90), we obtain the commutation relation between the creation and annihilation operators of bosons,

$$[a_k, a_{k'}^\dagger]_- = \delta_{k,k'}, \tag{2.91}$$

where $\delta_{k,k'}$ is the Kronecker delta function, i.e.,

$$\delta_{k,k'} = 1 \text{ if } k = k', \text{ and } \delta_{k,k'} = 0 \text{ if } k \neq k'. \tag{2.92}$$

Similarly, we can obtain the other commutation relations for bosons,

$$[a_k, a_{k'}]_- = 0,$$

and

$$[a_k^\dagger, a_{k'}^\dagger]_- = 0. \tag{2.93}$$

Eqs. (2.91) and (2.93) are the three commutation relations for bosons. The total number of bosons like He^4 atoms,

$$\sum_k <n_k> = N, \tag{2.94}$$

where $<n_k>$ is the thermally average occupation number representation in state **k** at temperature T or, equivalently, the number of particles in state **k** at temperature T. According to the Bose–Einstein distribution function,

$$<n_k> = \frac{1}{e^{\beta(\varepsilon_k - \mu)} - 1}, \tag{2.95}$$

where

$$\varepsilon_k = \hbar^2 k^2 / 2m, \tag{2.96}$$

and $\mu = $ chemical potential. For He^4 atoms, $\mu \neq 0$ at high temperatures. However, for photons and phonons,

$$\varepsilon_k = sk \text{ and } \mu \equiv 0. \tag{2.97}$$

In Eq. (2.97),

$$s = c = \text{speed of light for photons,}$$

and

$$s = \text{speed of sound for phonons.}$$

(b) Fermions

The creation and destruction operators for Fermions obey very different commutation relations because the total number of particles in a level n_i can be 0 or 1.

The basis function in the many-body representation is

$$|n_1, n_2, ..., n_i, ... >, \tag{2.98}$$

with the constraint, $n_i = 0$, or $n_i = 1$. The Fermion operators a_i and $a_i^\dagger$ are defined as

$$a_i |n_1, n_2, ..., n_i, ... > = \sqrt{n_i} \, (-1)^m |n_1, n_2, ..., n_i - 1, ... >, \tag{2.99}$$

where

$$m = \sum_{j<i} n_j \tag{2.100}$$

and

$$a_i^\dagger |n_1, n_2, ..., n_i, ... > = \sqrt{1 - n_i} \, (-1)^m |n_1, n_2, ..., n_i + 1, ... >. \tag{2.101}$$

Here, the function $(-1)^m$ comes from the requirement that the wave function is antisymmetric for Fermions. From Eqs. (2.99) and (2.101), we obtain

$$a_i^\dagger a_i |n_1, n_2, ..., n_i, ...> = \sqrt{n_i}(-1)^m a_i^\dagger |n_1, n_2, ..., n_i - 1, ...>$$
$$= \sqrt{n_i}\sqrt{2-n_i}(-1)^{2m}|n_1, n_2, ..., n_i ...>. \tag{2.102}$$

Similarly,

$$a_i a_i^\dagger |n_1, n_2, ..., n_i ...> = \sqrt{1-n_i}(-1)^m a_i |n_1, n_2, ..., n_i + 1, ...>$$
$$= \sqrt{1-n_i}\sqrt{1+n_i}(-1)^{2m}|n_1, n_2, ..., n_i, ...>. \tag{2.103}$$

If $n_i = 0$, we obtain from Eqs. (2.102) and (2.103),

$$(a_i^\dagger a_i + a_i a_i^\dagger)|n_1, n_2, ..., n_i, ...> = |n_1, n_2, ..., n_i, ...>. \tag{2.104}$$

Similarly, if $n_i = 1$, we obtain from Eqs. (2.102) and (2.103),

$$(a_i^\dagger a_i + a_i a_i^\dagger)|n_1, n_2, ..., n_i, ...> = |n_1, n_2, ..., n_i, ...>. \tag{2.105}$$

From Eqs. (2.104) and (2.105), we obtain

$$a_i^\dagger a_i + a_i a_i^\dagger = 1, \tag{2.106}$$

which can be written in the alternate form

$$[a_i, a_i^\dagger]_+ = 1. \tag{2.107}$$

In general, we can show that

$$[a_i, a_j^j]_+ = 0, \quad i \neq j,$$

and

$$[a_i, a_j]_+ = [a_i^\dagger, a_j^\dagger]_+ = 0. \tag{2.108}$$

From Eqs. (2.107) and (2.108), the commutation relations for Fermions can be written as

$$[a_i, a_j^\dagger]_+ = \delta_{ij},$$

and

$$[a_i, a_j]_+ = [a_i^\dagger, a_j^\dagger]_+ = 0. \tag{2.109}$$

We also obtain from Eq. (2.102),

$$a_i^\dagger a_i = \sqrt{n_i}\sqrt{2-n_i} = \overline{n}_i, \tag{2.110}$$

because if

$$n_i = 0, \quad \overline{n}_i = 0$$

and if

$$n_i = 1, \quad \overline{n}_i = 1. \tag{2.111}$$

Thus, $a_i^\dagger a_i = \overline{n}_i = n_i$ is the number operator for state i. From the Fermi–Dirac distribution function, we obtain the expression for the average number of particles in state k at temperature T,

$$<a_k^\dagger a_k> = <n_k> = \frac{1}{e^{\beta(\varepsilon_k - \mu)} + 1}. \tag{2.112}$$

2.3.3 Field Operators and the Hamiltonian

Here, we introduce the operators of a *field of particles*:

$$\psi(\xi) = \sum_i \varphi_i(\xi) a_i \tag{2.113}$$

and

$$\psi^\dagger(\xi) = \sum_i \varphi_i^{\,*}(\xi) a_i^\dagger. \tag{2.114}$$

Here, a_i and $a_i^\dagger$ are the second quantization operators, and $\varphi_i(\xi)$ is the particle in the state i. If a_i and $a_i^\dagger$ are operators for bosons,

$$\psi(\xi)\psi^\dagger(\xi') - \psi^\dagger(\xi')\psi(\xi) = \sum_{i,j} \varphi_i(\xi)\varphi_j^*(\xi')[a_i a_j^\dagger - a_j^\dagger a_i]. \tag{2.115}$$

From Eqs. (2.91) and (2.115), we obtain

$$\psi(\xi)\psi^\dagger(\xi') - \psi^\dagger(\xi')\psi(\xi) = \sum_i \varphi_i(\xi)\varphi_i^*(\xi). \tag{2.116}$$

We note that because $\varphi_i(\xi) \Rightarrow \varphi_1(\xi), \varphi_2(\xi), \varphi_3(\xi), \dots$, forms a complete orthonormal set, it satisfies

$$\sum_i \varphi_i(\xi)\varphi_i^*(\xi) = \delta(\xi - \xi'). \tag{2.117}$$

From Eqs. (2.116) and (2.117), we obtain

$$[\psi(\xi), \psi^\dagger(\xi')]_- = \delta(\xi - \xi') \tag{2.118}$$

By using a similar procedure, we can easily derive

$$[\psi(\xi), \psi(\xi')]_- = [\psi^\dagger(\xi), \psi^\dagger(\xi')]_- = 0. \tag{2.119}$$

If a_i and $a_i^\dagger$ are Fermion operators, we can derive, by using a similar procedure,

$$[\psi(\xi), \psi^\dagger(\xi')]_+ = \delta(\xi - \xi'), \tag{2.120}$$

and

$$[\psi(\xi), \psi(\xi')]_+ = [\psi^\dagger(\xi), \psi^\dagger(\xi')]_+ = 0. \tag{2.121}$$

We will now consider the Hamiltonian that describes a system of interacting particles (for example, the electrons in a solid):

$$H = \sum_i \frac{1}{2m} p_i^2 + \sum_i V(\mathbf{r}_i) + \frac{1}{2} \sum_{i \neq j} V^{(2)}(\mathbf{r}_i - \mathbf{r}_j). \tag{2.122}$$

Here, $p_j = -i\hbar\nabla_j = -i\hbar\frac{\partial}{\partial \mathbf{r}_j}$ is the momentum operator for the jth particle, $V(\mathbf{r}_i)$ is the periodic potential, and $V^{(2)}(\mathbf{r}_i - \mathbf{r}_j)$ is the interaction energy between the ith particle and the jth particle. We will denote $p_i^2/2m$ and $V(\mathbf{r}_i)$ as single-particle operators and $V^{(2)}(\mathbf{r}_i - \mathbf{r}_j)$ as two-particle operators.

The Hamiltonian in Eq. (2.122) can be expressed in terms of the second quantization operators

$$H = \sum_\alpha \int \left[-\frac{\hbar^2}{2m} \psi_\alpha^\dagger(\mathbf{r})\nabla^2\psi_\alpha(\mathbf{r}) + V(\mathbf{r})\psi_\alpha^\dagger(\mathbf{r})\psi_\alpha(\mathbf{r}) \right] d\mathbf{r}$$

$$+ \frac{1}{2} \sum_{\alpha\beta} \int\int \psi_\alpha^\dagger(\mathbf{r})\psi_\beta^\dagger(\mathbf{r}')V^{(2)}(\mathbf{r}-\mathbf{r}')\psi_\beta(\mathbf{r}')\psi_\alpha(\mathbf{r}) \, d\mathbf{r} \, d\mathbf{r}'. \tag{2.123}$$

In Eq. (2.123), we have written

$$\psi(\xi) = \psi_\alpha(\mathbf{r}),$$

where α is the spin index and $\mathbf{r}$ is the coordinate.

The expression for the Hamiltonian given by Eq. (2.123) is equivalent to the corresponding expression in Eq. (2.122). We also note that the total number of particles

$$N = \langle N \rangle = \sum_k n_k = \sum_k \frac{1}{e^{\beta(\varepsilon_k - \mu)} + 1}. \tag{2.124}$$

The chemical potential μ is determined by the condition that when

$$T = 0, \quad \mu = \varepsilon_F = \text{the Fermi energy}. \tag{2.125}$$

We consider a system of free particles moving in space. The single-particle wave function can be written as

$$\varphi_\mathbf{k}(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{r}}. \tag{2.126}$$

This leads to the free-particle Schrodinger equation,

$$\frac{-\hbar^2}{2m}\nabla^2\varphi_\mathbf{k}(\mathbf{r}) = \varepsilon_\mathbf{k}\varphi_\mathbf{k}(\mathbf{r}) = \frac{\hbar^2 k^2}{2m}\varphi_\mathbf{k}(\mathbf{r}). \tag{2.127}$$

Here, $\mathbf{k}$ is the momentum of the particle, and its kinetic energy is $\frac{\hbar^2 k^2}{2m}$. For different $\mathbf{k}$ values, we have different states. Thus, the field operators become

$$\psi(\mathbf{r}) = \frac{1}{\sqrt{V}} \sum_{\mathbf{k}} a_{\mathbf{k}} e^{i\mathbf{k} \cdot \mathbf{r}} \tag{2.128}$$

and

$$\psi^{\dagger}(\mathbf{r}) = \frac{1}{\sqrt{V}} \sum a_{\mathbf{k}}^{\dagger} e^{-i\mathbf{k} \cdot \mathbf{r}}. \tag{2.129}$$

In Eqs. (2.128) and (2.129), the spin indices are neglected for the present. Substituting Eqs. (2.128) and (2.129) in Eq. (2.123), and letting $V = 1$, we obtain

$$H = \sum_{\mathbf{k}} \frac{\hbar^2 k^2}{2m} a_{\mathbf{k}}^{\dagger} a_{\mathbf{k}} + \sum_{\mathbf{kq}} V(\mathbf{q}) \, a_{\mathbf{k+q}}^{\dagger} a_{\mathbf{k}} + \frac{1}{2} \sum_{\mathbf{kpq}} V^{(2)}(\mathbf{q}) \, a_{\mathbf{k-q}}^{\dagger} a_{\mathbf{p+q}}^{\dagger} a_{\mathbf{p}} \, a_{\mathbf{q}}. \tag{2.130}$$

We note that if $V(\mathbf{q}) = V^{(2)}(\mathbf{q}) = 0$, the Hamiltonian is diagonalized and Eq. (2.130) reduces to

$$H = \sum_{\mathbf{k}} \varepsilon_{\mathbf{k}} \, a_{\mathbf{k}}^{\dagger} \, a_{\mathbf{k}} = \sum_{\mathbf{k}} \varepsilon_{\mathbf{k}} n_{\mathbf{k}}. \tag{2.131}$$

Eq. (2.131) reduces to the previous result

$$a_{\mathbf{k}}^{\dagger} a_{\mathbf{k}} = n_{\mathbf{k}}. \tag{2.132}$$

If we define $V(\mathbf{q})$ as the Fourier transform of $V(\mathbf{r})$,

$$V(\mathbf{q}) = \int V(\mathbf{r}) e^{i\mathbf{q} \cdot \mathbf{r}} \, d\mathbf{r}, \tag{2.133}$$

and the interaction $V(\mathbf{q}) \, a_{\mathbf{k+q}}^{\dagger} a_{\mathbf{k}}$ can be represented by Figure 2.14.

Similarly, we define the Fourier transform of $V^{(2)}(\mathbf{r})$ as

$$V^{(2)}(\mathbf{q}) = \int V^{(2)}(\mathbf{r}) \, e^{i\mathbf{q} \cdot \mathbf{r}} \, d\mathbf{r}. \tag{2.134}$$

For example, if

$$V^{(2)}(\mathbf{r}) = \frac{e^2}{r}, \tag{2.135}$$

$$V^{(2)}(\mathbf{q}) = \frac{4\pi e^2}{q^2}. \tag{2.136}$$

The interaction $V^{(2)}(\mathbf{q}) \, a_{\mathbf{k+q}}^{\dagger} \, a_{\mathbf{p-q}}^{\dagger} \, a_{\mathbf{p}} \, a_{\mathbf{k}}$ can be represented by Figure 2.15.
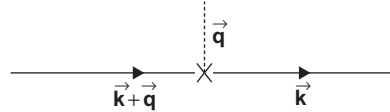

FIGURE 2.14

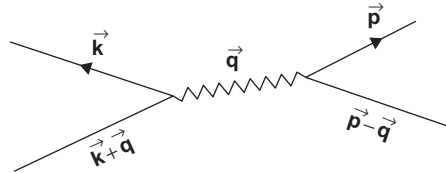$V(\mathbf{q}) \, a_{\mathbf{k+q}}^{\dagger} a_{\mathbf{k}}.$

FIGURE 2.15

$V^{(2)}(\mathbf{q}) \, a_{\mathbf{k+q}}^{\dagger} a_{\mathbf{p-q}}^{\dagger} a_{\mathbf{p}} a_{\mathbf{k}}.$

2.4 **QUANTIZATION OF LATTICE WAVES**

2.4.1 **Formulation**

We consider a cubic lattice of lattice constant a. We assume that at each lattice site, we have atoms with mass M vibrating around this site. The Hamiltonian that describes this system of atoms is

$$H = \sum_i \frac{p_i^2}{2M} + \sum_{i \neq j} \frac{1}{2} V(\mathbf{d}_i - \mathbf{d}_j), \tag{2.137}$$

where $V(\mathbf{d}_i - \mathbf{d}_j)$ is the interaction potential energy between atoms at the sites $\mathbf{d}_i$ and $\mathbf{d}_j$. Here, $\mathbf{d}_i = \mathbf{R}_i + \mathbf{u}_i$ and $\mathbf{d}_j = \mathbf{R}_j + \mathbf{u}_j$, where $\mathbf{u}_i$ and $\mathbf{u}_j$ are the displacements of the atoms from the lattice sites located at $\mathbf{R}_i$ and $\mathbf{R}_j$. Figure 2.16 shows these displacements, for convenience, on the surface of a cubic lattice.

For small $\mathbf{u}_i$ and $\mathbf{u}_j (\mathbf{u}_i \text{ and } \mathbf{u}_j \ll a)$, we have

$$\sum_{i \neq j} V(\mathbf{d}_i - \mathbf{d}_j) \approx \sum_{i \neq j} V(\mathbf{R}_i - \mathbf{R}_j) + \sum_{i \neq j} \mathbf{u}_i \cdot \frac{\partial^2 V}{\partial \mathbf{R}_i \partial \mathbf{R}_j} \cdot \mathbf{u}_j. \tag{2.138}$$

The first term on the right side of Eq. (2.138) is a constant term and can be ignored. If we define the tensor

$$\overset{\leftrightarrow}{\mathbf{G}} \equiv \frac{\partial^2 V}{\partial \mathbf{R}_i \partial \mathbf{R}_j}, \tag{2.139}$$

Eq. (2.138) can be written in the alternate form

$$\sum_{i \neq j} V(\mathbf{d}_i - \mathbf{d}_j) = \sum_{i \neq j} \frac{1}{2} \mathbf{u}_i \cdot \overset{\leftrightarrow}{\mathbf{G}} \cdot \mathbf{u}_j. \tag{2.140}$$
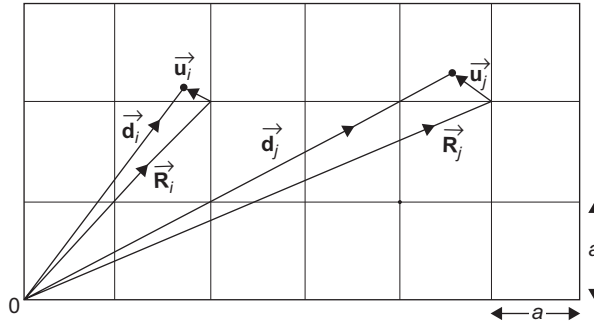

FIGURE 2.16

Definitions of $\mathbf{d}_i$ and $\mathbf{u}_i$ in a cubic lattice of lattice constant a.

Thus, the Hamiltonian can be written as

$$H = \sum_i \frac{P_i^2}{2M} + \sum_{i \neq j} \frac{1}{2} \mathbf{u}_i \cdot \overset{\leftrightarrow}{\mathbf{G}} \cdot \mathbf{u}_j = T + V. \tag{2.141}$$

In Eq. (2.141),

$$\mathbf{P}_i = M \dot{\mathbf{u}}_i. \tag{2.142}$$

From Lagrange's equation of motion,

$$L = T - V \tag{2.143}$$

and

$$\frac{d}{dt} \frac{\partial L}{\partial \dot{\mathbf{u}}_l} - \frac{\partial L}{\partial \mathbf{u}_l} = 0, \tag{2.144}$$

we obtain from Eq. (2.141),

$$M \ddot{\mathbf{u}}_l = -\sum_{l'} \overset{\leftrightarrow}{\mathbf{G}}_{ll'} \cdot \dot{\mathbf{u}}_{l'}. \tag{2.145}$$

We make a Fourier transformation,

$$\mathbf{u}_l = \sum_q \mathbf{U}_q \, e^{i\mathbf{q} \cdot \mathbf{l}}, \tag{2.146}$$

and obtain from Eqs. (2.145) and (2.146),

$$M \sum_q \ddot{\mathbf{U}}_l \, e^{i\mathbf{q} \cdot \mathbf{l}} = -\sum_{l'} \overset{\leftrightarrow}{\mathbf{G}}_{ll'} \cdot \sum_q \mathbf{U}_q e^{i\mathbf{q} \cdot \mathbf{l}'}, \tag{2.147}$$

which can be written in the alternate form

$$\sum_q \left[M \ddot{\mathbf{U}}_q \, e^{i\mathbf{q} \cdot \mathbf{l}} + \sum_{l'} \overset{\leftrightarrow}{\mathbf{G}}_{ll'} \cdot \mathbf{U}_q e^{i\mathbf{q} \cdot \mathbf{l}'} \right] = 0. \tag{2.148}$$

Eq. (2.148) implies

$$M \ddot{\mathbf{U}}_q + \sum_{l'} \overset{\leftrightarrow}{\mathbf{G}}_{ll'} \cdot \mathbf{U}_q e^{i\mathbf{q} \cdot (\mathbf{l}' - \mathbf{l})} = 0. \tag{2.149}$$

If we write

$$\mathbf{U}_q(t) = \mathbf{U}_q e^{i\omega_q t}, \tag{2.150}$$

Eq. (2.149) can be written as

$$M \omega_q^2 \hat{\in}_q = \sum_{l'} \overset{\leftrightarrow}{\mathbf{G}}_{ll'} \cdot \hat{\in}_q \, e^{i\mathbf{q} \cdot (\mathbf{l} - \mathbf{l}')}. \tag{2.151}$$

Here,

$$\hat{\epsilon}_q = \frac{\mathbf{U}_q}{|\mathbf{U}_q|} = \text{unit vector along } \mathbf{U}_q \tag{2.152}$$
$$= \text{polarization vector.}$$

$\hat{\epsilon}_q$ could be along $\lambda = x, y, z$ directions. Thus,

$$\hat{\epsilon}_{q\lambda} \Rightarrow \omega_{q\lambda}. \tag{2.153}$$

Thus, Eq. (2.151) can be written in the alternate form

$$M\omega_{q\lambda}^2 \hat{\epsilon}_{q\lambda} = \sum_{l'} \overset{\leftrightarrow}{\mathbf{G}}_{ll'} \cdot \hat{\epsilon}_{q\lambda} e^{i\mathbf{q} \cdot (\mathbf{l}-\mathbf{l'})} = \overset{\leftrightarrow}{\mathbf{G}}(q) \cdot \hat{\epsilon}_{q\lambda}. \tag{2.154}$$

From Eqs. (2.141) and (2.154), we can write the Hamiltonian in the alternate form

$$H = \sum_l \frac{P_l^2}{2m} + \frac{1}{2} \sum_{l \neq l'} \mathbf{u}_l \cdot \overset{\leftrightarrow}{\mathbf{G}}_{ll'} \cdot \mathbf{u}_{l'}. \tag{2.155}$$

We can express

$$\mathbf{P}_l = \sqrt{\frac{M}{N}} \sum_{k\lambda} \hat{\epsilon}_{k\lambda} P_{k\lambda} e^{-i\mathbf{k} \cdot \mathbf{l}}, \tag{2.156}$$

where

$$\hat{\epsilon}_{kx} \perp \hat{\epsilon}_{ky} \perp \hat{\epsilon}_{kz}.$$

We also write

$$\mathbf{u_l} = \sum_k \mathbf{U}_k e^{i\mathbf{k} \cdot \mathbf{l}}. \tag{2.157}$$

Here,

$$\mathbf{U}_k = \frac{1}{\sqrt{MN}} \hat{\epsilon}_{k\lambda} Q_{k\lambda}, \tag{2.158}$$

where N is the number of lattice sites (or atoms). From Eqs. (2.157) and (2.158), we obtain

$$\mathbf{u}_l = \frac{1}{\sqrt{MN}} \sum_k \hat{\epsilon}_{k\lambda} Q_{k\lambda} e^{i\mathbf{k} \cdot \mathbf{l}}. \tag{2.159}$$

From Eq. (2.156), we obtain

$$\sum_l \frac{P_l^2}{2M} = \frac{1}{2N} \sum_{k\lambda, k'\lambda',} \hat{\epsilon}_{k'\lambda'} \cdot \hat{\epsilon}_{k\lambda} P_{k'\lambda'} P_{k\lambda} \sum_l e^{-(\mathbf{k}+\mathbf{k'}) \cdot \mathbf{l}}. \tag{2.160}$$

Using the relation

$$\sum_l e^{-i(\mathbf{k}+\mathbf{k'}) \cdot \mathbf{l}} = N \delta_{\mathbf{k},-\mathbf{k'}}, \tag{2.161}$$

we can write Eq. (2.160) in the alternate form

$$\sum_l \frac{P_l^2}{2M} = \frac{1}{2} \sum_{k,\lambda,\lambda'} \hat{\in}_{-k\lambda'} \cdot \hat{\in}_{k\lambda} P_{-k\lambda'} P_{k\lambda}. \tag{2.162}$$

Because

$$\omega_{k\lambda} = \omega_{-k\lambda}, \tag{2.163}$$

$$\hat{\in}_{k\lambda'} = \hat{\in}_{-k\lambda'}. \tag{2.164}$$

Further,

$$\hat{\in}_{k\lambda'} \cdot \hat{\in}_{k\lambda} = \delta_{\lambda\lambda'}, \tag{2.165}$$

and we can substitute

$$P_{-k\lambda} = P_{k\lambda}^\dagger.$$

Substituting Eq. (2.164) in Eq. (2.162), we obtain

$$\sum_l \frac{P_l^2}{2M} = \frac{1}{2} \sum_{k\lambda} P_{k\lambda}^\dagger P_{k\lambda}. \tag{2.166}$$

We now consider the term

$$\frac{1}{2} \sum_{ll'} \mathbf{u}_l \cdot \overset{\leftrightarrow}{\mathbf{G}}_{ll'} \cdot \mathbf{u}_{l'} = \frac{1}{2MN} \sum_{k\lambda,\kappa'\lambda',ll'} \hat{\in}_{k\lambda} Q_{k\lambda} \cdot \overset{\leftrightarrow}{\mathbf{G}}_{ll'} \cdot \hat{\in}_{k'\lambda'} Q_{k'\lambda'} e^{i\mathbf{k}\cdot\mathbf{l}+i\mathbf{k'}\cdot\mathbf{l'}}. \tag{2.167}$$

We can write

$$e^{i\mathbf{k}\cdot\mathbf{l}+i\mathbf{k'}\cdot\mathbf{l'}} = e^{i\mathbf{k'}\cdot(\mathbf{l'-l})} e^{i(\mathbf{k+k'})\cdot\mathbf{l}}. \tag{2.168}$$

Eq. (2.154) can be written in the alternate form (by changing q to k', and λ to λ')

$$M\omega_{k'\lambda'}^2 \hat{\in}_{k'\lambda'} = \sum_{l'} \mathbf{G}_{ll'} \cdot \hat{\in}_{k'\lambda'} e^{i\mathbf{k'}\cdot(\mathbf{l'-l})}. \tag{2.169}$$

Further,

$$\sum_l e^{i(\mathbf{k+k'})\cdot\mathbf{l}} = N\delta_{\mathbf{k,-k'}}. \tag{2.170}$$

From Eqs. (2.167) through (2.170), we obtain

$$\frac{1}{2} \sum_{ll'} \mathbf{u}_l \cdot \overset{\leftrightarrow}{\mathbf{G}}_{ll'} \cdot \mathbf{u}_{l'} = \frac{1}{2} \sum_{k\lambda,k'\lambda'} \hat{\in}_{k\lambda} \cdot \hat{\in}_{k'\lambda'} Q_{k\lambda} Q_{k'\lambda'} \delta_{\mathbf{k,-k'}} \omega_{k'\lambda'}^2, \tag{2.171}$$

$$= \frac{1}{2} \sum_{k,\lambda,\lambda'} \hat{\in}_{k\lambda} \cdot \hat{\in}_{-k\lambda'} Q_{k\lambda} Q_{-k\lambda'} \omega_{-k\lambda'}^2. \tag{2.172}$$

We use the identities

$$\begin{aligned}
\hat{\epsilon}_{-k\lambda'} &= \hat{\epsilon}_{k\lambda'} \\
\hat{\epsilon}_{k\lambda} \cdot \hat{\epsilon}_{k\lambda'} &= \delta_{\lambda\lambda'} \\
\omega_{-k\lambda} &= \omega_{k\lambda},
\end{aligned} \tag{2.173}$$

in Eq. (2.172), and obtain

$$\frac{1}{2}\sum_{ll'} \mathbf{u}_l \cdot \overleftrightarrow{\mathbf{G}}_{ll'} \cdot \mathbf{u}_{l'} = \frac{1}{2}\sum_{k\lambda} \omega_{k\lambda}^2 Q_{k\lambda} Q_{-k\lambda} = \frac{1}{2}\sum_{k\lambda} \omega_{k\lambda}^2 Q_{k\lambda}^\dagger Q_{k\lambda}. \tag{2.174}$$

From Eqs. (2.155), (2.166), and (2.174), we obtain

$$H = \frac{1}{2}\sum_{k\lambda} P_{k\lambda}^\dagger P_{k\lambda} + \frac{1}{2}\sum_{k\lambda} \omega_{k\lambda}^2 Q_{k\lambda}^\dagger Q_{k\lambda}. \tag{2.175}$$

In Eq. (2.175), we have expressed the Hamiltonian in normal coordinates $P_{k\lambda}$ and $Q_{k\lambda}$.

2.4.2 **Quantization of Lattice Waves**

The quantization of lattice waves starts from the fundamental ideas of quantum mechanics. If we define

$$[A, B] = AB - BA, \tag{2.176}$$

$$\mathbf{P}_l = (P_l^x, P_l^y, P_l^z), \tag{2.177}$$

and

$$\mathbf{u}_l = (u_l^x, u_l^y, u_l^z), \tag{2.178}$$

we have the commutation relations

$$[P_l^\alpha, u_{l'}^\beta] = \frac{\hbar}{i}\, \delta_{ll'}\delta_{\alpha\beta}, \quad \alpha, \beta = x, y, z \tag{2.179}$$

$$[P_l^\alpha, P_{l'}^\beta] = [u_l^\alpha, u_{l'}^\beta] = 0. \tag{2.180}$$

Introducing the creation and annihilation operators, $a_{k\lambda}^\dagger$ and $a_{k\lambda}$, and substituting

$$P_{k\lambda} = \left(\frac{\hbar\omega_{k\lambda}}{2}\right)^{\frac{1}{2}} i(a_{k\lambda}^\dagger - a_{-k\lambda}) \tag{2.181}$$

and

$$Q_{k\lambda} = \left(\frac{\hbar}{2\omega_{k\lambda}}\right)^{\frac{1}{2}} (a_{k\lambda} + a_{-k\lambda}^\dagger), \tag{2.182}$$

and using the commutation relations from Problem 2.9, we obtain

$$[a_{k\lambda}, a^{\dagger}_{k'\lambda'}] = \delta_{kk'\delta_{\lambda\lambda'}}. \tag{2.183}$$

and

$$[a_{k\lambda}, a_{k'\lambda'}] = [a^{\dagger}_{k\lambda}, a^{\dagger}_{k'\lambda'}] = 0. \tag{2.184}$$

These operators satisfy the commutation relations for bosons. Substituting Eqs. (2.181) and (2.182) in Eq. (2.175), we obtain (Problem 2.10)

$$H = \sum_{k\lambda} \hbar\omega_{k\lambda}\left(a^{\dagger}_{k\lambda} a_{k\lambda} + \frac{1}{2}\right). \tag{2.185}$$

We denote $a^{\dagger}_{k\lambda}a_{k\lambda} = n_{k\lambda}$, as the occupation number operator for phonons with energy $\hbar\omega_{k\lambda}$. Here, $\omega_{k\lambda}$ is the vibrational frequency in the state k and polarization λ. The term $\frac{1}{2}\sum_{k\lambda} \hbar\omega_{k\lambda}$ in H is the zero-point vibrational energy. The other definitions are

$$\begin{aligned}
|n_k> &= \text{the state with } n_k \text{ phonons,} \\
a^{\dagger}_k a_k |n_k> &= |n_k>, \\
a_k |n_k> &= \sqrt{n_k} \ |n_k-1>, \\
a^{\dagger}_k |n_k> &= \sqrt{n_k+1} \ |n_k+1>, \\
a_k |0> &= 0, \text{ no phonons to destroy.}
\end{aligned} \tag{2.186}$$

PROBLEMS

2.1. Derive Eq. (2.6) from Eqs. (2.2), (2.3), and (2.5).

2.2. Derive Eq. (2.21) from Eq. (2.20).

2.3. Derive Eq. (2.28) from Eq. (2.27).

2.4. Derive Eq. (2.37) from Eq. (2.36).

2.5. The general expression for specific heat of solids is given in Eq. (2.52):

$$C_v = \frac{\partial}{\partial T} \sum_s \int \frac{d\mathbf{q}}{(2\pi)^3} \frac{\hbar\omega_s(\mathbf{q})}{e^{\beta\hbar\omega_s(\mathbf{q})}-1}, \tag{1}$$

where the integration is over the first Brillouin zone. Show that at very low temperatures, where the optical modes can be neglected, the three acoustic branches can be written as $\omega = \omega_s(\mathbf{q}) = c_s(\hat{\mathbf{q}})q$ ($c_s(\hat{\mathbf{q}})$ are the long-wavelength phase velocities of the acoustic mode), and the k-space integration over the first Brillouin zone can be replaced by an integration over all space,

$$C_v = \frac{\partial}{\partial T} \sum_s \int \frac{d\mathbf{q}}{(2\pi)^3} \frac{\hbar c_s(\hat{\mathbf{q}})q}{e^{\beta\hbar c_s(\hat{\mathbf{q}})q}-1}. \tag{2}$$

In spherical coordinates, $d\mathbf{q} = q^2 dq\, d\Omega$. By writing $z \equiv \beta\hbar c_s(\hat{\mathbf{q}})q$, show that Eq. (2) can be written as

$$C_v = \frac{\partial}{\partial T}\, \frac{(k_B T)^4}{(\hbar s)^3}\, \frac{3}{2\pi^2} \int_0^\infty \frac{z^3 dz}{e^z - 1}, \tag{3}$$

where $\frac{1}{s^3}$ is the average of the third power of the long-wavelength phase velocities,

$$\frac{1}{s^3} = \frac{1}{3}\sum_s \int \frac{d\Omega}{4\pi}\, \frac{1}{c_s(\hat{\mathbf{q}})^3}. \tag{4}$$

Using the result of the integral,

$$\int_0^\infty \frac{x^3 dx}{e^x - 1} = \frac{\pi^4}{15}, \tag{5}$$

show from Eqs. (3) and (5) that at very low temperatures,

$$C_v = \frac{2\pi^2}{5} k_B \left(\frac{1}{\beta\hbar c}\right)^3. \tag{6}$$

2.6. The lattice specific heat is of the form Eq. (2.52) or Eq. (1) in Problem 2.5,

$$C_v = \frac{\partial}{\partial T}\sum_s \int \frac{d\mathbf{q}}{(2\pi)^3}\, F(\omega_s(\mathbf{q})). \tag{1}$$

Show that Eq. (1) can be written in the alternate form

$$C_v = \frac{\partial}{\partial T}\int D(\omega)F(\omega)d\omega, \tag{2}$$

where $D(\omega)$ is the density of normal modes per unit volume, i.e., the phonon density of levels. Hence, $D(\omega)d\omega$ is the total number of modes between ω and $\omega + d\omega$ in the crystal divided by its volume. Show that

$$D(\omega) = \sum_s \int \frac{d\mathbf{q}}{(2\pi)^3}\, \delta(\omega - \omega_s(\mathbf{q})). \tag{3}$$

It can also be shown that

$$D(\omega) = \sum_s \int \frac{d\Omega}{(2\pi)^3}\, \frac{1}{|\nabla\omega_s(\mathbf{q})|}, \tag{4}$$

where the integral is over the surface of the first Brillouin zone on which $\omega_s(\mathbf{q}) \equiv \omega$.

2.7. In the Debye approximation, all the wave vectors of the normal modes lie within a sphere of radius q_D, and in all three branches of the spectrum the linear dispersion relation $\omega = cq$. Show by using Eq. (3) of Problem 2.6 that the density of normal modes, $D(\omega)$, is given by

$$D(\omega) = \left\{ \frac{3}{2\pi^2} \frac{\omega^2}{s^3} \right\}, \quad \omega = \omega_D = q_D c_s(\mathbf{q}),$$
$$= 0, \quad \omega > \omega_D.$$

2.8. Derive Eq. (2.145) from Eqs. (2.141), (2.143), and (2.144).

2.9. Using the expressions

$$\mathbf{P}_l = \sqrt{\frac{M}{N}} \sum_{k\lambda} \hat{\in}_{k\lambda} P_{k\lambda} e^{-\mathbf{k} \cdot \mathbf{l}} \tag{1}$$

and

$$\mathbf{Q}_l = \frac{1}{\sqrt{MN}} \sum_{k\lambda} \hat{\in}_{k\lambda} Q_{k\lambda} e^{i\mathbf{k} \cdot \mathbf{l}}, \tag{2}$$

show that

$$[P_{k\lambda}, Q_{k'\lambda'}] = \frac{\hbar}{i} \delta_{kk'} \delta_{\lambda\lambda'}, \tag{3}$$

and

$$[P_{k\lambda}, P_{k'\lambda'}] = [Q_{k\lambda}, Q_{k'\lambda'}] \equiv 0. \tag{4}$$

2.10. Substituting Eqs. (2.181) and (2.182) in Eq. (2.175), show that

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

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