Lattice Dynamics

2.1. INTRODUCTION

This chapter presents the thermal properties and lattice dynamics of solids. In thermal equilibrium, the mass centers or the nuclei of the atoms in a solid are not at rest but instead they vibrate with respect to their equilibrium positions. In fact, many thermal properties of solids are determined by the amplitude and phase factor of the atomic vibrations. For example, the specific heat of an insulator is due entirely to its lattice vibrations. Solid argon, which is perhaps the simplest solid of all, consists of a regular array of neutral atoms with tightly bound closed-shell electrons. These electrons are held together primarily by the van der Waal force, and hence interact only with their nearest-neighbor atoms. The physical properties of such a solid are due entirely to the thermal vibrations of its atoms with respect to their equilibrium positions. Therefore, the specific heat for such a solid is constituted entirely from its lattice vibrations. On the other hand, the specific heat for metals is dominated by the lattice specific heat at high temperatures, and by the electronic specific heat at very low temperatures. The most important effect of the lattice vibration on metals or intrinsic semiconductors is that it is the main scattering source that limits the carrier mobility in these materials. In fact, the interaction between the electrons and lattice vibrations is usually responsible for the temperature dependence of the resistivity and carrier mobility in metals or lightly doped semiconductors. Furthermore, such interactions may also play an important role in the thermoelectric effects of metals and semiconductors.

According to the classical Dulong and Petit law, the lattice specific heat for a solid is constant and equal to 3R (=5.96 cal/mol°C). The Dulong and Petit law gives correct prediction of lattice specific heat for most solids at high temperatures but fails at very low temperatures. The lattice specific heat can be derived from the classical statistics as follows.

Consider a solid with $N$ identical atoms that are bounded together by an elastic force. If each atom has three degrees of freedom, then there will be $3N$ degrees of freedom for the $N$ atoms to produce $3N$ independent vibration modes, each with the same vibration frequency. According to classical statistics, the mean energy for each lattice
vibration mode is $k_B T$, and hence the total energy $U$ for $3N$ vibration modes in a solid is equal to $3Nk_B T$. Thus, the lattice specific heat under constant volume condition is given by

$$C_v = \frac{dU}{dT} = 3Nk_B = 3R$$

(2.1)

where $R$ ($=Nk_B$) is the ideal gas constant, and $k_B$ is the Boltzmann constant (=1.38x10$^{-23}$ joule/K). For an ideal gas system, by substituting $N = 6.025x10^{23}$ atoms/g-mol (Avogadro’s number) into Eq. (2.1) one finds that $C_v$ is equal to 5.96 cal/mol·°C. This value is in good agreement with the experimental data for the solids at high temperatures. However, Eq. (2.1) fails to predict correctly the lattice specific heat for most solids at very low temperatures. This is due to the fact that at very low temperatures, atoms in a solid are no longer vibrating independently with one another. Instead, the lattice vibration modes can be considered as quasi-continuum with a broad spectrum of vibration frequencies from very low frequencies up to a maximum frequency determined by the number of vibration modes available in the lattice.

In Section 2.2, the expressions for the dispersion relations of a one-dimensional (1-D) monatomic linear chain and a diatomic linear chain are derived and depicted. The dispersion relation for a three-dimensional (3-D) lattice is derived and discussed in Section 2.3. The concept of phonons (i.e. quantized lattice vibration modes) in crystalline solids is depicted in Section 2.4. In Section 2.5, the phonon density of states function is derived, and the lattice spectra for some metals and semiconductors are presented. The Debye model for predicting the lattice specific heat of a solid over the entire range of temperature is depicted in Section 2.6.

2.2. THE ONE-DIMENSIONAL LINEAR CHAIN

To understand the thermal and physical properties associated with atomic (lattice) vibrations in a solid, it is useful to consider two simple cases, namely, (i) the one-dimensional (1-D) monatomic linear chain and (ii) the 1-D diatomic linear chain. These are discussed as follows:

(i) The Monatomic Linear Chain: In a 1-D monatomic linear chain, there is one atom per unit cell. If only the nearest-neighbor interaction is considered, then the linear chain can be represented by a string of identical masses connecting to one another by the same massless spring, as is illustrated in Figure 2.1. In this case, the equation of motion for the atomic displacement can be easily derived using Hooke’s law. According to this classical law, the force acting on the $n$th atom with mass $m$ can be expressed as
\[ F_n = m \frac{\partial^2 u_n}{\partial t^2} = -\beta (u_n - u_{n+1}) - \beta (u_n - u_{n-1}) \quad (2.2) \]

Where \( \beta \) is the force constant between two adjacent atoms, and \( u_n, u_{n-1}, u_{n+1} \) denote the displacement of the \( n^{th} \), \( (n-1)^{th} \), and \( (n+1)^{th} \) atoms, respectively. The solution of Eq. (2.2) has the form of a travelling wave, which is given by

\[ u_n = u_q e^{i(na - \omega t)} \quad (2.3) \]

Where \( q \) is the wave vector \( (q = 2\pi/\lambda) \) of the lattice wave, \( a \) is the lattice constant, and \( n \) is an integer. Note that \( u_q \) denotes the amplitude function of the lattice wave, which is also a function of wave vector \( q \). Substituting Eq. (2.3) into Eq.(2.2), one obtains

\[ m \omega^2 = -2\beta (\cos qa - 1) \quad (2.4) \]

Equation (2.4) is the solution for a simple harmonic oscillator, which has a dispersion relation \( (\omega \text{ vs. } q) \) given by

\[ \omega = 2\sqrt{\frac{\beta}{m}} \sin(qa / 2) = \omega_m \sin(qa / 2) \quad (2.5) \]

Where \( \omega_m = 2(\beta/m)^{1/2} \) is the maximum frequency of the lattice vibration modes. Figure 2.2 shows a plot of the dispersion relation for a 1-D monatomic linear chain obtained from Eq. (2.5). As shown in this figure, the dispersion curve has a period of \( 2\pi/a \).

The dispersion relation given by Eq.(2.5) for a 1-D monatomic linear chain exemplifies several fundamental physical properties of lattice dynamics in a solid. First, all the possible lattice vibration modes are limited by the allowed values of wave vector \( q \), which fall in the range of \(-\pi/a \leq q \leq \pi/a\). This range is known as the first Brillouin zone for the dispersion curve of a 1-D monatomic linear chain. There are \( n \) independent wave vectors within the first Brillouin zone representing \( n \) (i.e., \( n = N \), where \( N \) is the total number of atoms) independent vibration modes. Each atomic displacement contributes to one lattice vibration mode. The maximum wave number \( q_{\text{max}} \), which occurs at the zone boundary, is given by

\[ q_{\text{max}} = \pi / a \approx 10^3 \, \text{cm}^{-1} \quad (2.6) \]

Where \( a \) is the lattice constant. Since the frequency \( \omega \) is a periodic function of wave vector \( q \) in \( q \)-space, for any given wave vector \( q' \) outside the first Brillouin zone there is a corresponding wave vector \( q \) in the first Brillouin zone, which can be obtained by translational operation (i.e., \( q' = q \pm K \), where \( K \) is the reciprocal lattice vector).
The translational symmetry operation in a crystal lattice has been discussed in detail in Chapter 1. At the zone boundaries, the solution of Eq. (2.3) does not represent a traveling wave but a standing wave. Thus, at the zone boundaries, \( q_{\text{max}} = \pm (n \pi / a) \), and \( u_n \) is given by

\[
\begin{align*}
    u_n &= u_{q_{\text{max}}} e^{i(n\pi - qa)} = u_{q_{\text{max}}} e^{-i\omega \tau} \cos(n\pi) \\
\end{align*}
\]

(2.7)

Equation (2.7) shows that at the zone boundaries, \( \cos n\pi = \pm 1 \), depending on whether \( n \) is an even or an odd integer. This implies that the vibration modes for the alternate atoms are out of phase at the zone boundaries. The group velocity of the lattice wave packet is defined by

\[
    v_g = \frac{d\omega}{dq} 
\]

(2.8)

Solving Eqs. (2.5) and (2.8) yields an expression for the group velocity, which is

\[
    v_g = (\beta / m)^{1/2} a \cos(qa / 2) 
\]

(2.9)

From Eq. (2.9), it is noted that at the zone boundaries where \( q_{\text{max}} = \pm \pi / a \), the group velocity \( v_g \) is equal to zero. Thus, the lattice wave is a standing wave packet at the zone boundaries, and the incident and reflected lattice waves have the same amplitude but travel in the opposite directions.

In the long-wavelength limit (i.e., for \( qa \to 0 \)), Eq. (2.5) reduces to

\[
    \omega = (\beta / m)^{1/2} aq 
\]

(2.10)

Which shows that for \( qa \to 0 \), the vibration frequency, \( \omega \), of the lattice waves is directly proportional to the wave vector, \( q \). This corresponds to the common property of ordinary elastic waves in a continuum medium. In this case, the group velocity (\( v_g = d\omega / dq \)) and the phase velocity (\( v_p = \omega / q \)) are equal, and their values can be determined from the slope of the dispersion curve at small \( q \) value, as is shown in Figure 2.2. Using \( a = 3 \text{ Å} \) and \( v_s = 10^5 \text{ cm/sec} \), one obtains value of \( (\beta / m)^{1/2} \approx 3 \times 10^{12} \text{ s}^{-1} \), and the maximum vibration frequency that a lattice can support is \( \omega_{\text{max}} = 2 (\beta / m)^{1/2} = 6 \times 10^{12} \text{ s}^{-1} \); this value falls in the infrared spectral regime of electromagnetic radiation spectrum.

(ii) The Diatomic Linear Chain: The dispersion relation for the case of a 1-D diatomic linear chain will be derived and discussed next. Figure 2.3 shows a 1-D diatomic linear chain, which contains two types of atoms with different masses per unit cell. The atoms are equally spaced, but with different masses placed in alternate positions along the linear chain. If one assumes that only the nearest-neighbor interactions are important, then the force
constant, $\beta$, between the two different mass atoms is the same throughout the entire linear chain. Therefore, there are two atoms per unit cell with masses of $m_1$ and $m_2$. Using Hooke’s law, the equations of motion for the $2n^{th}$ and $(2n+1)^{th}$ atoms of the 1-D diatomic linear chain can be written as

$$m_1 \frac{\partial^2 u_{2n}}{\partial t^2} = \beta(u_{2n+1} + u_{2n-1} - 2u_{2n})$$  \hspace{1cm} (2.11)$$

$$m_2 \frac{\partial^2 u_{2n+1}}{\partial t^2} = \beta(u_{2n+2} + u_{2n} - 2u_{2n+1})$$  \hspace{1cm} (2.12)$$

Solutions of Eqs. (2.11) and (2.12) can be expressed respectively as

$$u_{2n} = u_a e^{i(2naq - \omega t)}$$  \hspace{1cm} (2.13)$$

$$u_{2n+1} = u_a e^{i[(2n+1)aq - \omega t]}$$  \hspace{1cm} (2.14)$$

Where $u_{2n}$ and $u_{2n+1}$ are the displacements for the $2n^{th}$ and $(2n+1)^{th}$ atoms, respectively. Now, substituting Eqs. (2.13) and (2.14) into Eqs. (2.11) and (2.12) one obtains

$$2\beta u_a - m_1 \omega^2 u_a - 2\beta u_a \cos qa = 0$$  \hspace{1cm} (2.15)$$

$$2\beta u_a - m_2 \omega^2 u_a - 2\beta u_a \cos qa = 0$$  \hspace{1cm} (2.16)$$

Equations (2.15) and (2.16) will have a nontrivial solution if and only if the determinant for the coefficients of $u_a$ and $u_a$ in both equations is set equal to zero. Thus, the frequency $\omega$ must satisfy the secular equation given by

$$\begin{vmatrix} 2\beta - m_1 \omega^2 & -2\beta \cos(qa) \\ -2\beta \cos(qa) & 2\beta - m_2 \omega^2 \end{vmatrix} = 0$$  \hspace{1cm} (2.17)$$

Solving Eq. (2.17) for $\omega$ yields

$$\omega^2 = \beta \left\{ \frac{1}{m_1} + \frac{1}{m_2} \right\} \pm \sqrt{ \left\{ \frac{1}{m_1} + \frac{1}{m_2} \right\}^2 - \frac{4\sin^2(aq)}{m_1m_2} }$$  \hspace{1cm} (2.18)$$

Using the same argument as in the case of a monatomic linear chain, one finds that the allowed values of $|q|$ for the diatomic linear chain is given by

$$|q| = \frac{n\pi}{Na}$$  \hspace{1cm} (2.19)$$
Where $N$ is the total number of unit cells in the linear chain and $n$ is an integer. Since the period of a diatomic linear chain is equal to $2a$, the first Brillouin zone is defined by

$$\frac{-\pi}{2a} \leq q \leq \frac{\pi}{2a}$$  \hspace{1cm} (2.20)$$

Which is a factor of 2 smaller than the first Brillouin zone of the 1-D monatomic linear chain. Figure 2.4 shows the dispersion curves for the 1-D diatomic linear chain with $m_1 > m_2$. The upper curve shown in Figure 2.4 corresponds to the plus sign given by Eq. (2.18), and is called the optical branch. The lower curve, which corresponds to the minus sign in Eq. (2.18), is known as the acoustical branch. The lattice vibration modes in the optical branch can usually be excited by the infrared optical radiation, which has frequencies in the range from $10^{12}$ to $10^{14}$ Hz. For the acoustical branch, the lattice vibration modes can be excited if the crystal is connected to an acoustical wave transducer that produces pressure waves throughout the crystal. In general, the dispersion curves for a solid with two atoms per unit cell contain both the acoustical and optical branches. For example, the dispersion curves for an alkali-halide crystal such as NaCl consist of both acoustical and optical branches, contributing by the positively and negatively charged ions (i.e., Na⁺, Cl⁻) in the crystal.

The physical insights for the dispersion curves of a diatomic linear chain can be best explained by considering two limiting cases, namely, (i) the long-wavelength limit (i.e., $qa \to 0$) and (ii) near the zone boundaries (i.e., $q \to \pm \pi/2a$). These are discussed as follows.

(i) **The Acoustical Branch:** For $qa \to 0$, using the minus sign in Eq. (2.18) for the acoustical branch, one obtains

$$\omega = \left[ \frac{2\beta}{(m_1 + m_2)} \right]^{1/2} \frac{q}{a}$$  \hspace{1cm} (2.21)$$

Equation (2.21) shows that in the long-wavelength limit, $\omega$ is directly proportional to the wave vector $q$. This result is identical to the monatomic linear chain discussed in the previous section. Furthermore, from Eq. (2.16), and for $qa \to 0$, the ratio of the amplitude of two different mass atoms is given by

$$\frac{u_2}{u_o} = 1$$  \hspace{1cm} (2.22)$$

Which implies that in the long-wavelength limit, atoms at odd and even lattice sites are moving in phase with equal amplitude. From the above analysis, it is obvious that in the long-wavelength limit the dispersion curve in the
acoustical branch for a diatomic linear chain will reduce to that of a monatomic linear chain if the masses of two
different mass atoms are equal (i.e., $m_1 = m_2 = m$).

(ii) The Optical Branch: The optical branch for the 1-D diatomic linear chain is shown by the upper curve of Figure 2.4. In the long-wavelength limit, when $q a$ approaches zero, one obtains

$$\omega = \left[ \frac{2\beta (m_1 + m_2)}{m_1 m_2} \right]^{1/2}$$

Equation (2.23) shows that in the optical branch as $q a \to 0$, the frequency $\omega$ becomes a constant and independent of the wave vector $q$. Thus, the lattice vibration mode at $q a = 0$ represents a standing wave. The ratio of the amplitude factor given by Eq. (2.24) reveals that the lattice vibration modes of alternate masses are out of phase, and the amplitude of the vibration modes is inversely proportional to the mass ratio of the alternate atoms. This can be best explained by considering the alkali-halide crystal. The two types of ions in an alkali-halide crystal (e.g., NaCl) are oppositely charged, and hence will experience opposing forces when an electric field is applied to the crystal. As a result, the motion of atoms in alternate lattice sites is out of phase with each other with an amplitude ratio inversely proportional to their mass ratio. If electromagnetic waves with frequencies corresponding to the frequencies of optical lattice vibration modes are applied to the crystal, resonant absorption takes place. Since the frequencies in which the lattice vibration modes are excited in this branch usually fall in the infrared spectral range, it is referred to as the optical branch.

Another feature of the dispersion curves shown in Figure 2.4 is the existence of a forbidden gap between $\omega_+ = (2\beta/m_1)^{1/2}$ and $\omega_- = (2\beta/m_2)^{1/2}$ at the zone boundaries (i.e. $q_{\text{max}} = \pm \pi / 2a$). The forbidden region corresponds to frequencies in which lattice waves cannot propagate through the linear chain without attenuation. This can be easily verified by substituting a value of $\omega$, which falls in the forbidden region of the dispersion curve shown in Figure 2.4 into Eq. (2.18). In this case, the wave vector $q$ becomes a complex number, and the lattice waves with frequencies falling in the forbidden zone will attenuate when they propagate through the linear chain. It is interesting to note that a similar situation also exists in the energy band scheme of a semiconductor in which a forbidden band gap exists.
between the valence band and the conduction band at the zone boundaries of the first Brillouin zone. This will be discussed in detail in Chapter 4.

2.3. DISPERSION RELATION FOR A THREE-DIMENSIONAL LATTICE

The dispersion relation for the 1-D linear chain derived in Section 2.2 can be easily extended to the 2-D and 3-D lattices by considering the lattice vibration modes as simple harmonic oscillators. As frequently encountered in quantum mechanics, the displacement of atoms can be expressed in terms of the normal coordinates and normal modes of quantum oscillators. According to quantum mechanics, the lattice vibration modes generated by the atomic vibrations in their equilibrium positions can be represented by the harmonic oscillators, with each vibration mode having its own characteristic frequency $\omega$ and wave vector $q$. According to quantum theory, the equation of motion for a 3-D harmonic oscillator is given by

$$\ddot{Q}_{q,s} + \omega(q,s)^2 Q_{q,s} = 0$$ (2.25)

Where $Q_{q,s}$ is the normal coordinate and $\omega(q,s)$ denotes the normal frequency. For a 3-D lattice both $Q_{q,s}$ and $\omega(q,s)$ are functions of wave vector $q$ and polarization index $s$ (i.e., $s = 1, 2, 3$).

In general, if a crystal contains only one atom per unit cell, then there are three possible polarizations for each wave vector $q$, one longitudinal and two transverse modes of polarization. In the longitudinal mode of lattice vibration, the motion of atoms is along the direction of wave propagation, while for the transverse modes the motion of atoms is in the plane perpendicular to the direction of wave propagation. If a crystal contains $N$ atoms per unit cell, then the index $n$ varies from 1 to $3N$. For example, if $N = 2$ and $s = 3$, then there are three polarizations (i.e., $s = 3$; one longitudinal and two transverse modes) in the acoustical branch and three polarizations in the optical branch (i.e., $s = 4, 5, \text{ and } 6$).

Figure 2.5a, b, and c show the measured lattice dispersion curves for silicon, GaAs, and aluminum, respectively, obtained from the inelastic slow neutron experiment.\(^{1-3}\) As can be seen in this figure, the dispersion curves for these materials are strongly dependent on the crystal orientations. This is due to the fact that lattice vibration modes depend strongly on crystal symmetry and atomic spacing along a particular crystal orientation. For example, the atomic spacing for a silicon crystal along the (100) axis is different from those along (111) and (110) axes. As a result, the dispersion relations for the silicon lattice are different along (100), (110), and (111) orientations. A similar situation exists in GaAs and aluminum. In general, the dispersion curves for most solids can
be determined from the inelastic slow neutron experiment. In this experiment, the energy losses of a slow neutron due to scattering by the lattice vibrations and the change of wave vector during scattering can be determined experimentally by the conservation of energy and conservation of momentum. A slow neutron impinging upon a crystal sees the crystal lattice mainly by interacting with the nuclei of the atoms. The momentum conservation for the slow neutron scattering by a lattice vibration mode can be described by

\[ \vec{k} = \vec{k'} \pm \vec{q} + \vec{K} \]  

(2.26)

Where \( \vec{k} \) is the wave vector of the incident neutron, \( \vec{k'} \) is the wave vector of the scattered neutron, \( \vec{q} \) is the phonon wave vector, and \( \vec{K} \) is the reciprocal lattice vector. The plus sign in Eq. (2.26) denotes the creation of a phonon, while the minus sign is for annihilation of a phonon. Note that we have introduced here the terminology “phonon” to represent the quantized lattice vibration.

The conservation of energy for scattering of a slow neutron by a lattice atom is given by

\[ \frac{h^2 k^2}{2M_n} = \frac{h^2 k'^2}{2M_n} \pm \hbar \omega_q \]  

(2.27)

Where \( \hbar \omega_q \) is the phonon energy. In Eq. (2.27), the plus sign is for phonon emission and the minus sign is for phonon absorption. The dispersion relation for the lattice vibration modes of a crystalline solid can be determined by Eqs.(2.26) and (2.27) using the energy gain and loss of the scattered neutrons as a function of the scattering direction (i.e., \( \vec{k} - \vec{k'} \)) from the slow neutron experiment. This method has been widely used in determining the phonon spectra of the metals, insulators, and semiconductors. The concept of phonon will be discussed next.

### 2.4. THE CONCEPT OF PHONONS

The dispersion relations derived in Section 2.2 for the 1-D monatomic and diatomic linear chains are based on Hooke’s law. The results of this classical approach provide a good insight concerning the physical properties of lattice waves, which is important to the understanding of the specific heat of a solid. However, it is not a common practice to use the wave concept of lattice vibrations to deal with the problems of interactions between electrons and lattice waves in a crystalline solid, such as scattering of electrons by the lattice waves in a semiconductor or a metal. Instead the quantum mechanical approach is usually used to solve the problems of scattering of electrons by the lattice vibrations in a solid. In the framework of quantum mechanics, each lattice vibration mode is quantized, and
can be treated as a quantum oscillator with a characteristic frequency $\omega$ and a wave vector $q$. This quantized lattice vibration mode is usually referred to as the “phonon”, analogous to referring “photon” as a quantum unit of the electromagnetic radiation. Therefore, it is appropriate to introduce here the concept of “phonons” to represent the quantized lattice vibration modes in a crystalline solid.

In Section 2.3, the normal coordinates and normal modes are introduced to describe the quantum oscillators for the 3-D lattice vibration modes in a crystalline solid. A quantized lattice vibration mode (phonon) can be represented by a harmonic oscillator, which has a characteristic frequency $\omega$, wave vector $q$, and polarization index $s$. According to quantum theory, the energy of a harmonic oscillator is given by

$$E_n = (n + 1/2)\hbar \omega$$  \hspace{1cm} (2.28)

Where $n = 0, 1, 2, 3,... \; \hbar = h/2\pi; \; h$ is the Planck constant, and $\omega$ is the characteristic frequency of the quantum oscillator. Using Eq. (2.28), the phonon energy can be written as

$$E_n(q,s) = (n_{q,s} + 1/2)\hbar \omega(q,s)$$  \hspace{1cm} (2.29)

Where $n_{q,s} = 1/[\exp(\hbar \omega/k_B T) – 1]$ is the average phonon occupation number, which can be derived using Bose-Einstein statistics to be discussed in Chapter 3. The quantity $\hbar \omega/2$ on the right-hand side of Eq. (2.29) represents the zero-point phonon energy (i.e., $n_{q,s} = 0$). It should be noted that the zero-point energy does not affect the phonon distribution function in any way, nor does it contribute to the average internal energy and the specific heat of a solid at temperatures above the absolute zero degree Kelvin. A large value of $n_{q,s}$ in Eq. (2.29) corresponds to phonons with large amplitude, and vice versa. In the dispersion curves shown in Section 2.2, the acoustical branch consists of both the longitudinal and transverse acoustical (LA and TA) phonons, while the optical branch is composed of longitudinal and transverse optical (LO and TO) phonons.

It should be noted that phonon scatterings are usually the dominant scattering mechanisms in the intrinsic and lightly doped semiconductors, and hence they control the carrier mobilities in these semiconductors. This will be discussed further in Chapter 7 and Chapter 8.

### 2.5. THE DENSITY OF STATES AND LATTICE SPECTRUM

The density of states function for phonons in a crystalline solid can be derived using the periodic boundary conditions of the crystalline solids. For a 3-D cubic lattice, if the length of each side of the cubic unit cell is equal to
Then the density of states function can be derived using the periodic boundary conditions over the \( N \) atoms within the cubic unit cell with a volume of \( L^3 \). Values of the phonon wave vector \( q \) are determined by using the 3-D periodic boundary conditions given by

\[
e^{i (q_x x + q_y y + q_z z)} = e^{i [q_x (x + L) + q_y (y + L) + q_z (z + L)]}
\]

(2.30)

which is reduced to

\[
e^{i (q_x + q_y + q_z) L} = 1
\]

(2.31)

From Eq. (2.31), one obtains \( q_x, q_y, q_z = 0, \pm 2\pi/L, \pm 4\pi/L; \ldots; N\pi/L \). Therefore, there is one allowed value of \( q \) per unit volume \((2\pi/L)^3\) in the reciprocal space (i.e., the \( q \)-space). To find a general expression of the phonon density of states function \( D(\omega) \) for a 3-D crystal lattice, the total number of states per unit volume with frequencies between \( \omega \) and \( \omega + d\omega \) can be expressed by

\[
D(\omega) d\omega = \left( \frac{L}{2\pi} \right)^3 \int_{\text{shell}} d^3q
\]

(2.32)

The integrand of Eq. (2.32) represents the total number of states available within a spherical shell in \( q \)-space with frequencies varying between \( \omega \) and \( \omega + d\omega \), and \((2\pi/L)^3\) is the volume of the unit cell in \( q \)-space. As shown in Figure 2.6, \( dS_\omega \) is the area element of the constant frequency surface in \( q \)-space, and \( d^3q \) is the volume element, which can be expressed as

\[
d^3q = dS_\omega dq_\perp
\]

(2.33)

Now substituting Eq. (2.33) into Eq. (2.32) and using the relation that \( dq_\perp = d\omega /|\nabla_q \omega| \), one obtains a general expression for the phonon density of states function as

\[
D(\omega) = \left( \frac{L}{2\pi} \right)^3 \int_{\text{shell}} \frac{dS_\omega}{|\nabla_q \omega|}
\]

(2.34)

Or

\[
D(\omega) = \left( \frac{L}{2\pi} \right)^3 \int \frac{dS_\omega}{v_g}
\]

(2.35)

where \( v_g = |\nabla_q \omega| \) is the group velocity of phonon. Note that integration of Eq. (2.34) is carried out over the constant frequency surface in \( q \)-space.
It is clear that an expression for the phonon density of states function can be derived from Eq. (2.34) provided that the dispersion relation between $\omega$ and $q$ is known. Figure 2.7a shows the plot of phonon density of states as a function of frequency for copper, and Figure 2.7b illustrates the corresponding density of states function derived by using a dispersionless relation, $\omega = u_s q$, in Eq. (2.34), where $u_s$ is the velocity of sound.

The phonon density of states plot shown in Figure 2.7a for the copper crystal was obtained from the numerical analysis of the measured dispersion curve. In general, if the constant frequency surface in $q$-space is spherical, then in the long-wavelength limit, the density of states function $D(\omega)$ is proportional to the square of the frequency. It should be noted that Eq. (2.34) could be applied to the derivation of the density of states function for electrons in the conduction band or for holes in the valence band of a semiconductor. This can be achieved by including the spin degeneracy factor (=2) due to the Pauli’s exclusion principle and by replacing the frequency of phonons by the energy of electrons or holes in Eq. (2.34), as will be discussed further in Chapter 4.

2.6. LATTICE SPECIFIC HEAT

The classical Dulong and Petit law described in Section 2.1 fails to predict correctly the temperature dependence of the lattice specific heat of solids at very low temperatures. The reason for its failure arises from the fact that Dulong and Petit’s law does not consider all lattice vibration modes with different vibration frequencies, particularly the long-wavelength phonons, which are the dominant vibration modes at low temperatures. In deriving the lattice specific heat for solids, Debye uses a continuum model to account for all the possible lattice vibration modes. This assumption is valid as long as the wavelength of phonons is large compared to the interatomic spacing. In this respect, a solid is considered as a continuous medium to the lattice phonons. Furthermore, the number of vibration modes is limited by the total number of constituent atoms in the crystal, which is equal to $N$. Therefore, for $N$ atoms each with three degrees of freedom the total number of vibration modes is equal to $3N$. In other words, the frequency spectrum corresponding to a perfect continuum is cutoff so as to comply with a total of $3N$ vibration modes. The Debye cutoff frequency, $\omega_D$, corresponds to a maximum frequency in which the transverse and longitudinal vibration modes can support. The Debye model for the lattice specific heat of a solid is discussed next.

To derive the lattice specific heat of a crystalline solid, it is necessary to find the total internal energy due to the thermal vibrations of lattice atoms. Using Eq. (2.29) for the average phonon energy ($= n_{\scriptscriptstyle ph} \hbar \omega$) and ignoring the
zero-point energy, the total energy of the lattice phonons with frequencies varying from zero to a cutoff frequency $\omega_D$ is given by

$$ U = \int_0^{\omega_D} D(\omega) \hbar \omega d\omega \left( e^{\frac{\hbar \omega k_B T}{\epsilon}} - 1 \right) \quad (2.36) $$

Where $D(\omega)$ is the density of states function per unit frequency given by Eq. (2.34). To find the solution of Eq. (2.36), the expression for $D(\omega)$ and the dispersion relation between $\omega$ and $q$ must be first derived. In the Debye model, it is assumed that the solid under consideration is an isotropic dispersionless continuum medium, and hence the relation between $\omega$ and $q$ is given by

$$\omega = v_g q = v_p q = u_s q \quad (2.37)$$

Where $v_g$, $v_p$, and $u_s$ denote the group velocity, phase velocity, and the velocity of sound in a solid, respectively. From Eq. (2.37), it is noted that the group and phase velocities are equal to the velocity of sound in a dispersionless continuum medium. Furthermore, in an isotropic medium, the phase velocity of phonons is independent of the direction of wave vector $q$. To derive the phonon density of states function, one can consider the spherical shell in $q$-space as shown in Figure 2.6. From Eqs. (2.34) through (2.37) one can determine the number of vibration modes within the spherical shell for frequencies between $\omega$ and $\omega + d\omega$, and the result yields

$$ D(\omega) d\omega = \left( \frac{L}{2\pi} \right)^3 \int dS_{\omega} d\omega = \left( \frac{3V \omega^2}{2\pi^2 u_s^2} \right) d\omega \quad (2.38) $$

Where $V = L^3$ is the volume of the cubic unit cell, and the surface integral ($\int dS_{\omega}$) is equal to $4\pi q^2$ or $4\pi \omega^2 / u_s^2$. A typical Debye spectrum calculated from Eq. (2.38) is shown in Fig. 2.7b. A factor of 3 is included in Eq. (2.38) to account for the three components of polarizations (i.e., two transverse and one longitudinal) per wave vector. In general, the propagation velocities for the transverse-mode phonons and the longitudinal-mode phonons are not equal (i.e., $v_t \neq v_l$), and hence Eq. (2.38) must be replaced by

$$ D(\omega) d\omega = \left( \frac{V}{2\pi^2} \right) \left( \frac{2}{v_t^2} + \frac{1}{v_l^2} \right) \omega^2 d\omega \quad (2.39) $$

The Debye cutoff frequency, $\omega_D$, can be obtained by integrating Eq. (2.39) for frequencies from 0 to $\omega_D$, and using the fact that there are $3N$ total vibration modes in the crystal. Thus, the total number of vibration modes is given by
\[
\int_0^{\omega_D} D(\omega) \, d\omega = 3N
\]  
(2.40)

Now, substituting Eq.(2.38) for \(D(\omega)\) into Eq.(2.40), and the result yields

\[
\omega_D = (6\pi^2n)^{1/3} u_s
\]  
(2.41)

Where \(n = N/V\) is the number of atoms per unit volume and \(u_s\) is given by

\[
u_s = \left[ \frac{1}{3} \left( \frac{2}{v_t^3} + \frac{1}{v_f^3} \right) \right]^{-1/3}
\]  
(2.42)

Where \(u_s\) is the average velocity of phonons in the solid. The total energy of phonons can be obtained by substituting Eq. (2.38) into Eq. (2.36) and integrating Eq. (2.36) from \(\omega = 0\) to \(\omega = \omega_D\) which yields

\[
U = \left( \frac{3V}{2\pi^2 u_s^2} \right) \int_0^{\omega_D} \frac{h \omega^3 \, d\omega}{(e^{\hbar \omega/k_BT} - 1)}
\]

(2.43)

Where \(x = \hbar \omega/k_BT, x_m = \hbar \omega_D/k_BT = T_D/T,\) and \(T_D = \hbar \omega_D/k_B\) is called the Debye temperature. The lattice specific heat under constant volume can be obtained from Eq. (2.43) by differentiating the total energy \(U\) with respect to temperature, which yields

\[
C_v = \frac{dU}{dT} = 9Nk_B \left( \frac{T}{T_D} \right)^\frac{3}{2} \int_0^{T_0/T_D} \frac{e^x x^4 \, dx}{(e^x - 1)^2}
\]  
(2.44)

Where \(T_0 = \hbar \omega_D/k_B = (h u_s / k_B L)(6\pi^2 N)^{1/3}\) is used in Eq.(2.44). It is noted that an analytical expression valid over the entire temperature range could not be obtained from Eq. (2.44). However, an analytical expression may be derived for two limiting cases, namely, for \(T > T_D\) and \(T < T_D\). They are depicted as follows:

(i) The high temperature regime (\(T > T_D\) or \(x \ll 1\)):

In the high temperature regime, Eq. (2.44) can be simplified to

\[
C_v \approx 9Nk_B \left( \frac{T}{T_D} \right)^\frac{3}{2} \int_0^{T_0/T_D} \frac{x^4 \, dx}{x^2} = 3Nk_B = 3R
\]  
(2.45)

Which is identical to the result predicted by the classical Dulong and Petit’s law for the lattice specific heat of solids.

(ii) The low temperature regime (\(T < T_D\) or \(x \gg 1\)):
In this case, the upper limit of the integral in Eq. (2.43) for the total energy of phonons may be replaced by infinity, and the definite integral is given by

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

(2.46)

Now, substituting Eq. (2.46) into Eq. (2.43) and differentiating the total energy $U$ with respect to $T$ one obtains the lattice specific heat as

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

(2.47)

Equation (2.47) shows that the lattice specific heat of a crystalline solid is proportional to $T^3$ at low temperatures.

The result given by Eq. (2.47) provides a correct prediction of the temperature dependence of the lattice specific heat for both semiconductors and insulators at low temperatures. The reason for the good agreement is attributed to the fact that Debye model takes into account the contribution of the long-wavelength acoustical phonons to the lattice specific heat, which is dominant at low temperatures. Figure 2.8 shows a comparison of the lattice specific heat versus temperature predicted by the Debye model and by Dulong and Petit’s law.

Although Debye model generally gives a correct prediction of the lattice specific heat for both insulators and semiconductors over a wide range of temperatures, the Debye temperature used in theoretical fitting of the experimental data varies from material to material. For example, the Debye temperature is $T_D = 640$ K for silicon and $370$ K for germanium.

In spite of the success of Debye model for predicting the correct temperature behavior of lattice specific heat of semiconductors and insulators over a wide range of temperatures, it fails, however, to predict the correct temperature dependence of the specific heat of metals at very low temperatures. The reason for its failure stems from the fact that the electronic specific heat, which is contributed by the total kinetic energy of electrons in a metal, becomes dominant at very low temperatures. In fact, the specific heat of a metal is dominated by the electronic specific heat rather than by the lattice specific heat at very low temperatures. Using Fermi-Dirac statistics it can be shown that the electronic specific heat for a metal varies linearly with temperature at very low temperatures, which is in good agreement with the experimental observation of the specific heat of metals at very low temperatures.

Thus, the total specific heat for a metal consists of the lattice specific heat and the electronic specific heat, which can be expressed by
\[ C_v = C_l + C_e = \alpha T^3 + \beta T \]  

(2.48)

Where \( C_l \) and \( C_e \) denote the lattice- and electronic- specific heat, respectively. Both \( \alpha \) and \( \beta \) are constants which can be determined from the \( C_v/T \) versus \( T^2 \) plot. From the slope of this plot one can determine the constant \( \alpha \), and the intercept, when extrapolated to \( T = 0 \) K, yields the constant \( \beta \). It is noted that at very low temperatures the electronic specific heat prevails in the metals and the second term in Eq. (2.48) becomes dominant. Therefore, the specific heat of metals varies linearly with temperature at very low temperatures. Derivation of the electronic specific heat for a metal can be made using Fermi-Dirac statistics to be discussed in Chapter 3.

**PROBLEMS**

2.1. (a) Considering only the nearest-neighbor interaction, find the dispersion relation for the diatomic linear chain of a silicon lattice along the (111) crystal axis. Note that the mass of the silicon atoms is identical, and the positions of the nearest-neighbor atoms in the (111) axis are located at \( (0,0,0) \), \( (a/4, a/4, a/4) \), and \( (a, a, a) \) inside the unit cell. Assume that the force constant between the nearest-neighbor atoms is equal to \( \beta \).

(b) Plot the dispersion curves (\( \omega \) vs. \( q \)) from the result obtained in (a).

(c) Sketch the atomic displacement for the longitudinal and transverse optical lattice vibration modes at \( q = \pi / 4\sqrt{3}a, \pi / 2\sqrt{3}a, \text{ and } \pi / \sqrt{3}a \).

2.2. Using Einstein model, derive the lattice specific heat for a 3-D crystal lattice. (Hint: The Einstein model is similar to the Debye model except that it assumes a single vibration frequency \( \omega_E \) and energy, \( E = h\omega_E \) for all lattice phonons. The phonon distribution function is \( <n> = 1/(e^{\hbar\omega_E/\kappa T} - 1) \). Based on this assumption you can derive the average phonon energy and the lattice specific heat.)

2.3. (a) For a 1-D monatomic linear chain with fixed end boundary condition, show that the density of states function can be expressed by

\[
D(\omega) = \frac{L}{\pi} \frac{d\omega}{d\omega} \\
= \left( \frac{2L}{\pi a} \right) \frac{1}{(\omega_w^2 - \omega^2)^{1/2}} 
\]
[Hint: Use the dispersion relation given by Eq. (2.5) to derive $D(\omega)$ for the 1-D case.]

(b) Apply the Debye model to this 1-D linear chain, and show that the density of states function can be expressed by

$$D(\omega) = \frac{L}{\pi v_s}$$

Where $L$ is the length of the linear chain.

(c) Plot $D(\omega)$ versus $\omega$ for (a) and (b), and explain the difference.

2.4. Using the Debye model derive the specific heat for a 1-D monatomic linear chain with only nearest-neighbor interaction, and show that at low temperatures the specific heat varies linearly with temperature. What is the cutoff frequency for this case?

2.5 (a) Write down the equations of motion for a 1-D linear chain of identical masses but are connected to each other by springs of two different force constants, $\beta_1$ and $\beta_2$, in alternating positions. Find the dispersion relation for this linear chain.

(b) Plot the dispersion curve for the linear chain given in (a).

2.6. (a) Write down the equation of motion for a 2-D square lattice with spacing $a$ and atomic mass $M$. The nearest-neighbor force constant is given by $\beta$.

(b) Assume that the solution of (a) is given by

$$u_{lm} = u(0) \exp[(lk/a + mk/a - \omega t)]$$

Where $u_{lm}$ denotes the displacement normal to the plane of the square lattice for the atom in the $l$th column and $m$th row. Find the dispersion relation in (a).

(c) Plot the dispersion curve for a square lattice based on the result obtained in (b).

2.7. Derive the density of states function $D(\omega)$ for a 1-D linear chain of length $L$ carrying $N + 1$ particles with a spacing of $a$ for the following cases:

(a) The particles $s = 0$ and $s = N$ at the ends of the linear chain are held fixed (i.e., fixed boundary condition).

(b) The linear chain is allowed to form a ring, so that the periodic boundary condition can be applied to the problem [i.e., $u(sa) = u(sa + L)$].

(c) What are the allowed values of the wave vector $q$ in cases (a) and (b)?
2.8. One common method used in determining the phonon spectra of a solid is the slow neutron scattering experiment. Give an example to explain this technique for determining the phonon spectra in a crystal. [See the paper by A. D. B. Woods et al., Phys. Rev. 131, 1025 (1963); see also Woods et al., Phys. Rev. 119, 980 (1960).]

REFERENCES


BIBLIOGRAPHY


