Phonons and Thermal Properties

6

6.1 Phonons and Thermal Properties

6.1.1 Introduction

In the previous chapters, we have considered the electrons in a crystal that consisted of a rigid lattice of atoms. This represented a good approximation because the mass of an atom is more than 2000 of the mass of an electron. However, such assumptions founder when considering specific heat, thermal expansion, the temperature dependence of electron relaxation time, and thermal conductivity. In order to interpret these phenomena involving electrons and atoms, a more refined model needs to be considered, in which the atoms are allowed to move and vibrate around their equilibrium positions in the lattice. In this chapter, we will present a simple yet relatively accurate mathematical model to describe the mechanical vibrations of atoms in a crystal. We will first cover one-dimensional monatomic and diatomic crystals followed by three-dimensional crystals. We will then consider the collective movement or excitations of the atoms in a crystal, the so-called phonons, and conclude with a section on the velocity of sound in a medium.

6.1.2 Interaction of Atoms in Crystals: Origin and Formalism

We saw in Sect. 1.5, when discussing the formation of bonds in solids, that these equilibrium positions were achieved by balancing attractive and repulsive forces between individual atoms. We assumed that the attractive and repulsive forces always canceled each other and that the masses were infinite. The resulting potential $U(R)$ curve for an atom as a function of its distance R from a neighboring atom is shown in Fig. 6.1. This figure shows a minimum energy for a specific atomic separation, which we understood was true at all time.

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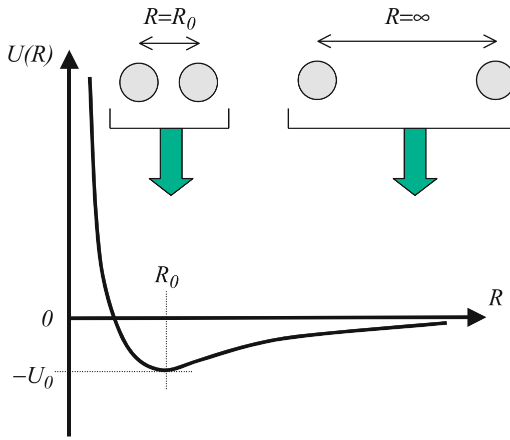


Fig. 6.1 Potential energy of two neighboring atoms in a crystal as a function of the interatomic spacing. When the two atoms are very far away from each other, they do not interact, and the interaction potential energy is near zero. When they get closer to one another, they are attracted to each other to form a bond, which leads to a lowering of the potential energy. However, when they are very close, the electrostatic repulsion from the nuclear charge of each atom leads to a repulsive interaction and an increase in the potential energy

The origin of these forces lies in the electrostatic interaction between the electrical charges (nuclei and electron clouds) in the two neighboring atoms. Classically, the electrons are constantly moving in an atom, in a non-deterministic manner (thus the name "cloud"). One can easily understand that the attractive and repulsive forces do not balance each other at all times but rather the attractive force would be stronger than the repulsive force at a certain time and then weaker shortly afterward. On average, a balance of forces is still achieved. We therefore realize that the positions of atoms in a lattice are not fixed in time but that small deviations do occur around the equilibrium positions. Such vibrations are also more intense at higher temperatures. Note that this is a fully classical analysis of why these lattice vibrations exist. The quantum mechanical description is quite different. In quantum mechanics, the electrons do not move about the lattice in a cloud but occupy energy levels inside allowed energy bands. The lattice atoms have kinetic and potential energy, and the wavefunction for lattice vibrations must also obey Schrödinger equation. The solutions to Schrödinger equation give one the eigenfunctions and allowed energy levels of the lattice vibrations. These allowed energy levels of lattice vibrations are called phonons. In the quantum mechanical description, the lattice is never at rest, even at 0 K. The atoms always move, or oscillate, because the Heisenberg uncertainty principle does not allow the atoms to have a definite position in space. If the atoms were stationary, then their momentum would be indeterminate. The quantum compromise for this scenario is called the zero-point energy which naturally derives from Schrödinger equation and gives the lattice vibrational modes a minimum amount of spatial uncertainty called the zero-point motion. To this zero-point motion, there is a zero-point energy. This observation is already true for the simple diatomic molecule, for which the vibrational modes are the solutions of the harmonic oscillator problem in quantum mechanics. Instead of solving Schrödinger equation for lattice vibrations, it is much easier and more convenient to first study the allowed classical modes of vibration. It turns out that the classical treatment survives the quantum treatment. The classical bands change into the true quantum lattice energy bands through a simple transformation. We will therefore continue with the more intuitive classical description knowing that the classical results can be taken over in the quantum limit.

Let us now develop a simple mathematical model for such atomic vibrations and introduce the formalism that will be used in the rest of the text. We start by considering the two neighboring atoms, one at the origin ($R = 0$) and the other at a distance R, while its equilibrium position is at $R = R_0$. A one-dimensional analysis will be considered at this time. The potential energy $U(R)$ in Fig. 6.1 of the second atom can be conveniently expressed with respect to the equilibrium values at R_0 through what is called the Taylor expansion (see Appendix A.5):

$$U(R) = U(R_0) + \left(\frac{dU}{dR}\right)_{R_0}(R - R_0) + \frac{1}{2}\left(\frac{d^2U}{dR^2}\right)_{R_0}(R - R_0)^2 + \frac{1}{6}\left(\frac{d^3U}{dR^3}\right)_{R_0}(R - R_0)^3 + \dots \tag{6.1}$$

where $\left(\frac{dU}{dR}\right)_{R_0}$, $\left(\frac{d^2U}{dR^2}\right)_{R_0}$, $\left(\frac{d^3U}{dR^3}\right)_{R_0}$ are the first, second, and third derivatives of $U(r)$, respectively, evaluated at $r = R_0$. $(R{-}R_0)$ is called the displacement. The first derivative $\left(\frac{dU}{dR}\right)_{R_0}$ is in fact equal to zero, because it is calculated at the equilibrium position $r = R_0$, which is where the potential $U(r)$ reaches a minimum. Therefore, only the displacement terms $(R{-}R_0)^n$ with an exponent n larger than or equal to 2 are left. The usefulness of the Taylor expansion resides in the fact that at small deviations from equilibrium, i.e., $(R{-}R_0) << R_0$, it is reasonable to approximate $U(R)$ with only the first few terms of the expansion in Eq. (6.1).

By denoting $U_0 = -U(R_0)$ and $x = R - R_0$ the displacement, Eq. (6.1) can be rewritten as:

$$U(x) + U_0 = \frac{1}{2}C_1x^2 + C_2x^3 + \dots \tag{6.2}$$

where $C_1 = \left(\frac{d^2U}{dR^2}\right)_{R_0}$ and $C_2 = \frac{1}{6}\left(\frac{d^3U}{dR^3}\right)_{R_0}$ are constants of the model, determined by the nature of the atoms considered. The first term in the right-hand side of Eq. (6.2), $\frac{1}{2}C_1x^2$, is in fact the potential energy associated with an elastic force equal to $F = -\frac{d}{dx}\left(\frac{1}{2}C_1x^2\right) = -C_1x$, where C_1 is the elastic force constant. The negative sign means that F acts as a restoring force, i.e., in the direction opposite to the displacement u of the atom.

In the following sections, we will limit the analysis to the first term in the expansion in Eq. (6.2) and denote $C = C_1$:

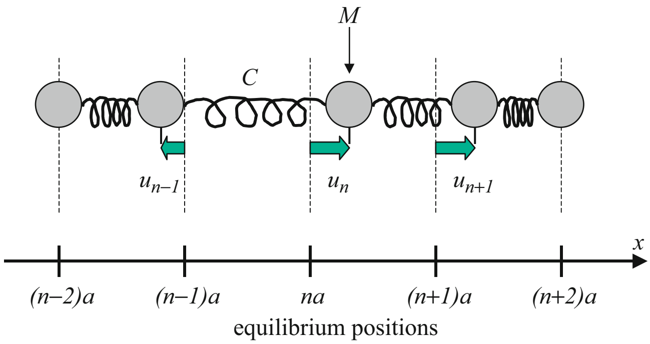


Fig. 6.2 Model for the interaction of identical atoms in a harmonic crystal. The relative movement of the atoms is modeled by a spring such that atoms displaced from their equilibrium positions are forced back by the neighboring atoms. The displacement can travel like a wave throughout the lattice

$$U(x) + U_0 \approx \frac{1}{2}Cx^2 \tag{6.3}$$

Because the atomic vibrations described by this potential only involve second-order displacements, such a solid is generally referred as a harmonic crystal in which the interactions between atoms can be modeled by a spring. This formalism is valid in solids up to all reasonable temperatures. We will apply this formalism to two cases of one-dimensional lattice, extend it to a three-dimensional lattice, and derive a few macroscopic physical properties of crystals.

6.1.3 One-Dimensional Monatomic Harmonic Crystal

In this simple model, we consider a one-dimensional (linear) lattice with a period a and with identical atoms of mass M, vibrating around each lattice point, as depicted in Fig. 6.2. Each atom is indexed by an integer n, and its displacement from its equilibrium position is denoted u_n. The atoms are taken to oscillate in the same direction as the lattice (i.e., longitudinal vibration). All the results obtained for this artificial one-dimensional model prove to be true for three-dimensional lattices as well.

Traveling Wave Formalism

In this one-dimensional case, we will take into account only the interaction between nearest neighbors, an assumption that has little effect on the final results. When considering two neighboring atoms, the forces that are exerted on each one can be modeled as resulting from a spring which links the interacting atoms, as the one shown in Fig. 6.2. In other words, the force acted on the n^{th} atom:

- By the $(n\text{-}1)^{th}$ atom is $F_{n,\,n-1} = -C(u_n - u_{n-1})$
- By the $(n+1)^{th}$ atom is $F_{n,\,n+1} = -C(u_n - u_{n+1})$

where C is the quasi-elastic force constant, a characteristic of the spring. Although this spring formalism is obviously crude, it nevertheless describes the interaction between atoms rather well. This is because the elastic force constant C arises from Eq. (6.3) and corresponds to the first level of approximation for the interactions between atoms. The resultant force acting on the n^{th} atom is therefore:

$$F_n = F_{n,n-1} + F_{n,n+1} = -C(2u_n - u_{n-1} - u_{n+1}) \tag{6.4}$$

The equation of motion for the n^{th} atom is then expressed using classical mechanics like Newton's law:

$$M\frac{d^2u_n}{dt^2} = F_n = -C(2u_n - u_{n-1} - u_{n+1}) \tag{6.5}$$

where M is the mass and $\frac{d^2u_n}{dt^2}$ is the acceleration of the n^{th} atom. We thus obtain a large number of coupled differential equations, where the unknown functions are the displacements $u_n(t)$. We seek solutions to the Eq. (6.5) in the form of traveling waves such as:

$$u_n(t) = A\exp[i(kan - \omega t)] \tag{6.6}$$

where A is the amplitude of the displacement, k is the wavenumber of the wave, and ω its angular frequency. This expression is typical of a traveling wave because it satisfies the relation:

$$\begin{aligned} u_{n+1}(t) &= A\exp[i(ka(n+1) - \omega t)] = A\exp\left[i\left(kan - \omega\left(t - \frac{ka}{\omega}\right)\right)\right] \\ &= u_n\left(t - \frac{ka}{\omega}\right) \end{aligned} \tag{6.7}$$

which shows that the value of the displacement $u_{n+1}(t)$ at the $(n+1)^{th}$ atom at a time t is the same as the displacement $u_n(t)$ at the n^{th} atom at an earlier time $\left(t - \frac{ka}{\omega}\right)$. This means that the magnitude of the displacement is like a wave that is traveling a distance a in space during a time $\frac{ka}{\omega}$. The velocity at which the wave is traveling is therefore equal to:

$$\frac{a}{{}^{ka}/_{\omega}} = \frac{\omega}{k} \tag{6.8}$$

The wavelength λ and frequency υ of the traveling wave are related to the wavenumber or angular frequency through the defined relations:

$$\begin{cases} \lambda = \dfrac{2\pi}{k} \\ \upsilon = \dfrac{\omega}{2\pi} \end{cases} \tag{6.9}$$

Boundary Conditions

Before solving the equation of motion in Eq. (6.5), we must introduce the boundary condition that the linear array of atoms is finite and consists of N atoms with the first and last atoms being equivalent, i.e., $u_{n+N}(t) = u_n(t)$. This is the periodic or Born-von Karman boundary conditions which we have already encountered in Sect. 5.3. This is a reasonable assumption because macroscopic crystal specimens consist of a very large number of atoms. And since the interaction forces are significant only between neighboring atoms, the motion of boundary atoms on the "surface" of the specimen does not affect the motion of all other atoms inside the sample.

Because of the general exponential expression of $u_n(t)$ (Eq. (6.6)), these conditions lead to the discretization of the wavenumber k, similar to what was obtained in Chap. 5:

$$k = k_m = \frac{2\pi}{a}\frac{m}{N} \tag{6.10}$$

where $m = 0, \pm 1\ldots$ is an integer. In fact, only N different values of wavenumber k are necessary. Indeed, if two wavenumbers k and k' differ from each other by an integer times $\frac{2\pi}{a}$ (e.g., $k' = k + \frac{2\pi}{a}$), which is equivalent to say that their corresponding integers m and m' differ by an integer times N (e.g., $m' = m + N$), then they lead to the same function $u_n(t)$ as seen through the simple calculation:

$$\begin{aligned} u_n{}'(t) &= A\exp\left[i\left(k'an - \omega t\right)\right] \\ &= A\exp[i2\pi n + i(kan - \omega t)] = u_n(t) \end{aligned} \tag{6.11}$$

which is valid for any point (na) and any time (t). This means that k and k' are physically indistinguishable. In other words, the basic interval of variation of k can be chosen as:

$$\frac{1}{2}\left(-\frac{2\pi}{a}\right) \le k \le \frac{1}{2}\left(\frac{2\pi}{a}\right) \tag{6.12}$$

And all the physical properties of our one-dimensional crystal that depends on the wavenumber k must be periodic with a period $\frac{2\pi}{a}$. Again, we arrive at the concept of the first Brillouin zone introduced in Chap. 5 and Sect. 5.4.1 for electronic states. And the quantity $\frac{2\pi}{a}$ is a reciprocal lattice period. Of course, we can (and must) always choose the number of atoms N so large that the variation of k could be considered as quasi-continuous.

Phonon Dispersion Relation

Now we can solve the equation of motion in Eq. (6.5), by substitutingEq. (6.6) into it:

$$-M\omega^2 A\exp[i(kan - \omega t)] = -C\left(2 - e^{-ika} - e^{ika}\right)A\exp[i(kan - \omega t)]$$

which successively becomes, after simplification of the exponential and the constant A:

$$-M\omega^2 = -C\left(2 - e^{-ika} - e^{ika}\right)$$

or:

$$\omega^2 = \frac{2C}{M}(1 - \cos ka) = \frac{4C}{M}\sin^2\frac{ka}{2} \tag{6.13}$$

where we have made use of the trigonometric relation: $1 - \cos x = 2\sin^2\frac{x}{2}$. This last expression can also be rewritten as:

$$\omega = \omega_{\max}\left|\sin\frac{ka}{2}\right| \tag{6.14}$$

where $\omega_{\max} = \sqrt{\frac{4C}{M}}$. This relation is called the phonon dispersion relation and is plotted in Fig. 6.3.

We see that the solutions of Eq. (6.5) of the traveling wave type exist only if the relation in Eq. (6.14) is satisfied by the wavenumber k and the angular frequency ω of the traveling wave. The frequency and wavenumber of the traveling wave

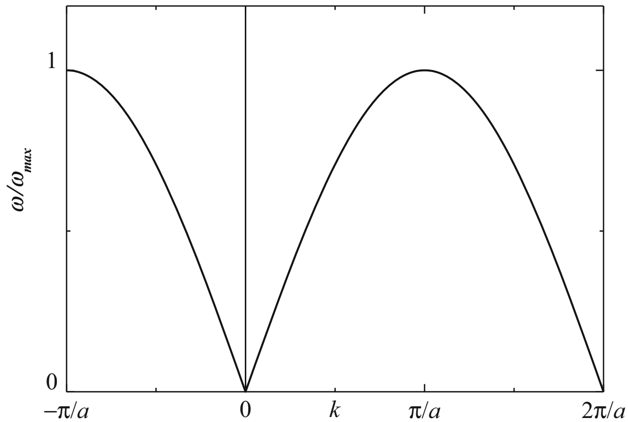


Fig. 6.3 Phonon dispersion relation in a one-dimensional monatomic harmonic crystal, expressed through the dependence of the angular frequency as a function of the wavenumber k

characterizing the lattice vibrations are not specific to one particular atom but are rather a property of the entire lattice. As such, the term phonon is used to designate lattice vibrations, and a frequency and a wavenumber are associated with each phonon. A more detailed discussion on phonons can be found in Sect. 6.1.6.

For a small wavenumber ($k \to 0$), i.e., in the long wave limit, Eq. (6.14) becomes:

$$\omega = \omega_{\max}\frac{a}{2}k \tag{6.15}$$

where we have used the approximation for the sine function, $\sin(x) \approx x$, for $x \to 0$, which is in fact the Taylor expansion of the sine function near zero (see Eq. (6.1)). Equation (6.15) means that the angular frequency ω is proportional to the wavenumber k in the long wave limit. Neighboring atoms have similar displacements in this region.

In the short wavelength limit, as k increases, the slope of ω decreases and becomes flat at the zone boundaries $k = \pm\pi/a$. At this point, the atoms in adjacent cells are vibrating with opposite phase. In other words, alternate springs are compressed and stretched, giving rise to maximum atomic displacement and frequencies of vibration.

6.1.4 One-Dimensional Diatomic Harmonic Crystal

Formalism

In the previous sections, we have discussed the motion of atoms in a one-dimensional monatomic crystal where all the atoms are identical, with a mass M, and their equilibrium positions are equally spaced (spacing a). In crystallography terms, we considered a basis of one atom per unit cell. A more general description of atomic motion in a crystal involves a basis with more than one atom.

In this section, we will consider a one-dimensional diatomic harmonic crystal. Ionic crystals such as NaCl and CsCl, atomic crystals such as Si and Ge, and binaries such as GaAs and InP are examples of lattices whose unit cells contain two atoms each. The following parameters need to be introduced for a complete diatomic model. The masses of the two different atoms (labeled 1 and 2) in a unit cell will be denoted M_1 and M_2, respectively, with $M_1 > M_2$. The equilibrium distance between the two atoms in a unit cell is generally arbitrary, but we will choose it to be half the primitive unit cell length for simplicity, i.e., $a/2$. In addition, the elastic force constant C, as defined inEq. (6.2), should be different depending on if an atom interacts with its front or its back neighbor. But for simplicity, we will consider only one force constant C. In spite of these simplifications, the discussion and the results will not lose their generality, even if the mathematical steps will be significantly simpler.

Each diatomic basis will be indexed by an integer n. The displacement of atom 1 from its equilibrium position will be denoted $u_n(t)$, while the displacement of atom 2 will be denoted $v_n(t)$. The atoms are taken to oscillate in the same direction as the

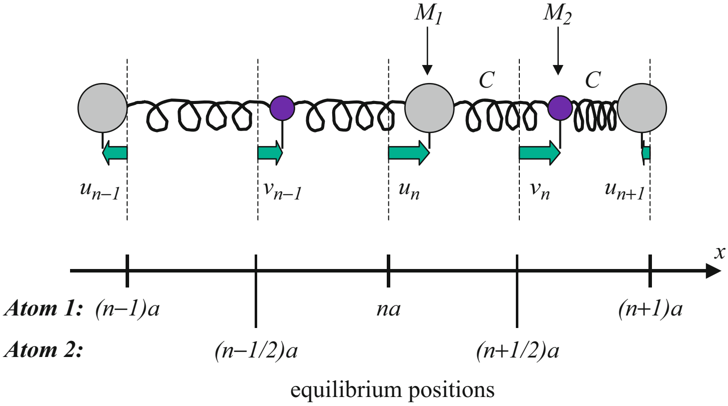


Fig. 6.4 One-dimensional model for the interaction of atoms in a diatomic harmonic crystal structure with atom masses M_1 and M_2. It is assumed here that all the springs have the same constant

lattice (i.e., longitudinal vibration). All these parameters and their simplifications are summarized in Fig. 6.4.

Two coupled sets of equations of motion, similar to Eq. (6.5), need to be considered; one for the displacement of the n^{th} atom 1 and one for the displacement of the n^{th} atom 2:

$$\begin{cases} M_1 \dfrac{d^2 u_n}{dt^2} = -C(2u_n - v_{n-1} - v_n) \\ M_2 \dfrac{d^2 v_n}{dt^2} = -C(2v_n - u_n - u_{n+1}) \end{cases} \tag{6.16}$$

Here again, we seek solutions to the set of Eq. (6.16) in the form of traveling waves with the same wavenumber k and angular frequency ω:

$$\begin{cases} u_n(t) = A\exp[i(kan - \omega t)] \\ v_n(t) = B\exp[i(ka(n + ½) - \omega t)] \end{cases} \tag{6.17}$$

where A and B are the amplitude of the displacements.

Phonon Dispersion Relation

Substituting these traveling wave expressions into Eq. (6.16), we obtain:

$$\begin{cases} -M_1\omega^2 A\exp[i(kan - \omega t)] \\ = -C(2A\exp[i(kan - \omega t)] - B\exp[i(ka(n - {}^1\!/_2) - \omega t)] - B\exp[i(ka(n + {}^1\!/_2) - \omega t)]) \\ -M_2\omega^2 B\exp[i(ka(n + {}^1\!/_2) - \omega t)] \\ = -C(2B\exp[i(ka(n + {}^1\!/_2) - \omega t)] - A\exp[i(kan - \omega t)] - A\exp[i(ka(n + 1) - \omega t)]) \end{cases}$$

Dividing by $\exp[i(kan - \omega t)]$ the first expression and $\exp[i(ka(n + ½) - \omega t)]$ the second expression, we get:

$$\begin{cases} -M_1\omega^2 A = -C\left(2A - B\exp\left(-\frac{ika}{2}\right) - B\exp\left(+\frac{ika}{2}\right)\right) \\ -M_2\omega^2 B = -C\left(2B - A\exp\left(-\frac{ika}{2}\right) - A\exp\left(+\frac{ika}{2}\right)\right) \end{cases}$$

After rearranging the terms with A and those with B:

$$\begin{cases} A[2C - M_1\omega^2] - BC\left[\exp\left(-\frac{ika}{2}\right) + \exp\left(+\frac{ika}{2}\right)\right] = 0 \\ -AC\left[\exp\left(-\frac{ika}{2}\right) + \exp\left(+\frac{ika}{2}\right)\right] + B[2C - M_2\omega^2] = 0 \end{cases}$$

Expressing the sum of exponentials with trigonometric functions, we get:

$$\begin{cases} A[2C - M_1\omega^2] - B\left[2C\cos\left(\frac{ka}{2}\right)\right] = 0 \\ -A\left[2C\cos\left(\frac{ka}{2}\right)\right] + B[2C - M_2\omega^2] = 0 \end{cases} \tag{6.18}$$

This system of equation has a nonzero solution, i.e., A and B not both equal to zero, if and only if the determinant of the system is zero:

$$\left[2C - M_1\omega^2\right]\left[2C - M_2\omega^2\right] - \left[2C\cos\left(\frac{ka}{2}\right)\right]\left[2C\cos\left(\frac{ka}{2}\right)\right] = 0 \tag{6.19}$$

which, after developing the products, becomes:

$$M_1M_2\omega^4 - 2C(M_1 + M_2)\omega^2 + 4C^2 - 4C^2\cos^2\left(\frac{ka}{2}\right) = 0$$

or:

$$M_1M_2\omega^4 - 2C(M_1 + M_2)\omega^2 + 4C^2\sin^2\left(\frac{ka}{2}\right) = 0 \tag{6.20}$$

This equation is of the form $\alpha\omega^4 - 2\beta\omega^2 + \gamma = 0$, with α, β, and $\gamma > 0$, and has two solutions for ω^2, denoted ω_+^2, and ω_-^2 such that:

$$\omega_\pm^2 = \frac{\beta \pm \sqrt{\beta^2 - \alpha\gamma}}{\alpha} \tag{6.21}$$

Therefore, the solutions of Eq. (6.20) are:

$$\omega_{\pm}^{2}(k)=\frac{C(M_1+M_2)\pm\sqrt{C^2(M_1+M_2)^2-4C^2M_1M\sin^2\left(\frac{ka}{2}\right)}}{M_1M_2}$$

which can be simplified into:

$$\omega_{\pm}^{2}=C\left(\frac{M_1+M_2}{M_1M_2}\right)\pm C\sqrt{\left(\frac{M_1+M_2}{M_1M_2}\right)^2-\frac{4\sin^2\left(\frac{ka}{2}\right)}{M_1M_2}}$$

Using the trigonometric identity $\cos(2x) = 1 - 2\sin^2(x)$, this equation becomes:

$$\omega_{\pm}^{2}(k)=C\left(\frac{M_1+M_2}{M_1M_2}\right)\left[1\pm\sqrt{1-\frac{2M_1M_2}{(M_1+M_2)^2}(1-\cos(ka))}\right]\tag{6.22}$$

which constitutes the phonon dispersion relation in the model considered, similar to that obtained in Eq. (6.14). This expression always has a meaning since the argument of the square root is always positive because we have, for any value of masses M_1 and M_2 and value of wavenumber k:

$$0\leq(1-\cos(ka))\leq 2$$

and therefore:

$$0\leq\frac{2M_1M_2}{(M_1+M_2)^2}(1-\cos(ka))\leq\frac{4M_1M_2}{(M_1+M_2)^2}\leq 1$$

There are thus two possible dispersion relations, denoted $\omega_{+}(k)$ and $\omega_{-}(k)$, relating the angular frequency to the wavenumber. Both are plotted in the first Brillouin zone in Fig. 6.5. These plots represent the so-called phonon spectrum of a one-dimensional diatomic harmonic crystal.

The values for $\omega_{+}(k)$ and $\omega_{-}(k)$ at $k = 0$ and $k=\pm\frac{\pi}{a}$ can be easily calculated from Eq. (6.22) (note that we have chosen $M_1 > M_2$). The top curve in Fig. 6.5 corresponds to $\omega_{+}(k)$ and is called the optical phonon branch or simply optical phonon, while the bottom branch corresponds to $\omega_{-}(k)$ and is called the acoustic phonon branch or simply acoustic phonon.

Now, for small values of wavenumber ($k \to 0$), an approximate expression can be derived from Eq. (6.22). To do so, we start by using an approximate expression for the cosine function in the Eq. (6.22):

$$\cos(ka)\approx 1-\frac{1}{2}(ka)^2$$

This approximation is in fact the Taylor expansion of the cosine function near zero (see Eq. (6.1)). We therefore obtain successively:

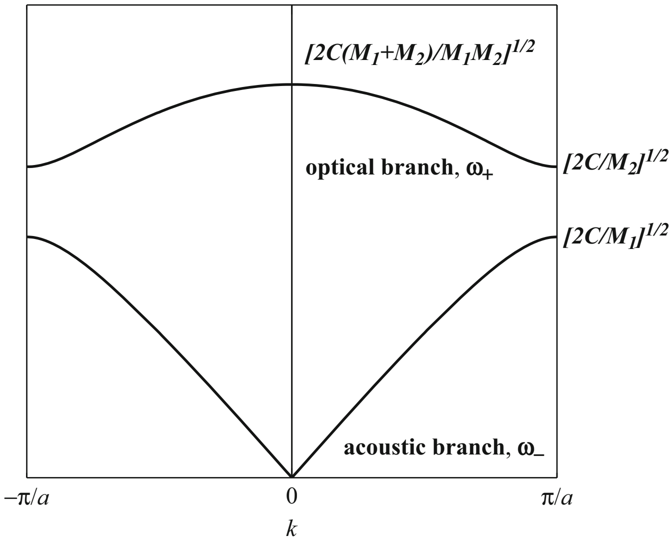


Fig. 6.5 Optical and acoustic branches in the dispersion relation

$$1 - \cos(ka) \approx \frac{1}{2}(ka)^2$$

$$\sqrt{1 - \frac{2M_1M_2}{(M_1+M_2)^2}(1 - \cos(ka))} \approx \sqrt{1 - \frac{M_1M_2}{(M_1+M_2)^2}(ka)^2}$$

$$\text{and } \sqrt{1 - \frac{2M_1M_2}{(M_1+M_2)^2}(1 - \cos(ka))} \approx 1 - \frac{M_1M_2}{2(M_1+M_2)^2}(ka)^2$$

by using the approximation $\sqrt{1-x} \approx 1 - \frac{1}{2}x$ for $x \to 0$ (again this comes from the Taylor expansion of $\sqrt{1-x}$ for small values of x). Equation (6.22) can then be approximated by the following expression:

$$\omega_{\pm}^2(k) \approx C\left(\frac{M_1+M_2}{M_1M_2}\right)\left[1 \pm \left(1 - \frac{M_1M_2}{2(M_1+M_2)^2}(ka)^2\right)\right] \tag{6.23}$$

Consequently, in the long wave limit, the angular frequency of the acoustic phonon branch can be written as:

$$\omega_{-}^2(k) \approx C\left(\frac{M_1+M_2}{M_1M_2}\right)\left[\frac{M_1M_2}{2(M_1+M_2)^2}(ka)^2\right]$$

$$\omega_-(k) \approx k\sqrt{\frac{Ca^2}{2(M_1 + M_2)}} \tag{6.24}$$

which means that the angular frequency $\omega_-(k)$ in the acoustic phonon branch is proportional to the wavenumber k, similar to the result obtained in Eq. (6.15). The shape of the acoustic branch is similar, but the increased mass lowers the frequency. For the acoustic branch in the long wave limit, the traveling wave is equivalent to the elastic wave of a one-dimensional atomic chain regarded as a continuous media. The nature of the vibrations in this region is just like sound waves. The two atoms in the unit cell move in the same direction, and over a small region, it seems as if the entire crystal has been compresses or stretched. This is why the $\omega_-(k)$ branch is called the acoustic branch.

In the same limit ($k \to 0$), the angular frequency of the optical phonon branch can be expressed from Eq. (6.23):

$$\omega_+^2(k) \approx C\left(\frac{M_1 + M_2}{M_1M_2}\right)[1 + 1] = 2C\left(\frac{M_1 + M_2}{M_1M_2}\right) \tag{6.25}$$

which shows that the angular frequency $\omega_+(k)$ in the optical phonon branch is constant in the long wave limit. The nature of the vibrations in this region is that the two atoms in the unit cell move in opposite directions. This is similar to the top of the band in the monatomic case, where there is maximum distortion and frequency of vibration. The angular frequency in the limit ($k \to \pi/a$) for the optical and acoustic branches is left as an exercise at the end of the chapter.

Furthermore, the ratio of the displacement amplitudes A and B defined in Eq. (6.17) can be taken for two different values, depending on the branch chosen, calculated from either one of Eq. (6.18):

$$\left(\frac{B}{A}\right)_\pm = \frac{2C - M_1\omega_\pm^2}{2C\cos\left(\frac{ka}{2}\right)} \tag{6.26}$$

Again, in the long wave limit ($k \to 0$) and for the acoustic phonon branch, we have $\omega_-(k) \to 0$ as seen from Eq. (6.24) and $\cos\left(\frac{ka}{2}\right) \to 1$ so that:

$$\left(\frac{B}{A}\right)_- \to \frac{2C}{2C} = 1 \tag{6.27}$$

which demonstrates that, in this case, the vibrations of the two atoms in one primitive unit cell have exactly the same amplitude and phase (i.e., direction), as shown in Fig. 6.6.

In the long wave limit ($k \to 0$) for the optical phonon branch, we have $\omega_+ \to \sqrt{\frac{2C}{\left(\frac{M_1M_2}{M_1+M_2}\right)}}$ from Eq. (6.25), and therefore, by substituting into Eq. (6.):

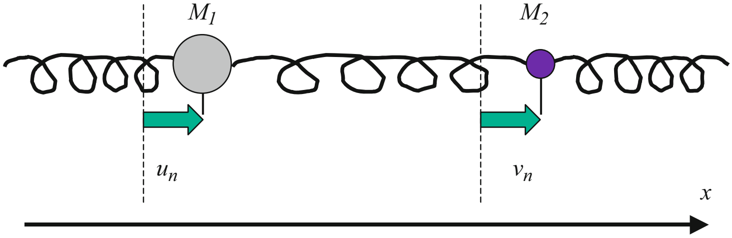


Fig. 6.6 Atomic vibrations in a one-dimensional diatomic harmonic crystal, corresponding to the acoustic phonon branch. In this configuration, the two atoms forming the unit cell move in the same direction at the same time

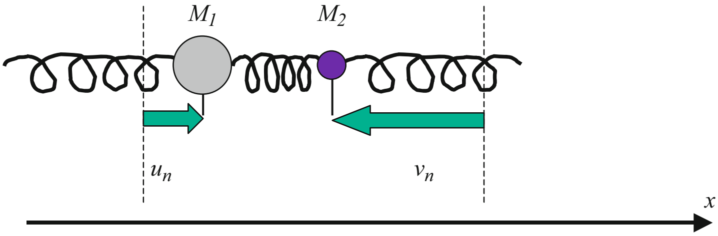


Fig. 6.7 Atomic vibrations in a one-dimensional diatomic harmonic crystal, corresponding to the optical phonon branch. In this configuration, the two atoms forming the unit cell move in opposite directions at the same time

$$\left(\frac{B}{A}\right)_+ \rightarrow \frac{2C - M_1 \frac{2C}{\left(\frac{M_1 M_2}{M_1+M_2}\right)}}{2C} = -\frac{M_1}{M_2} \tag{6.28}$$

which shows that, in the long wave limit of the optical branch, the vibrations of the two atoms in one primitive unit cell have a specific amplitude ratio and opposite phases (i.e., directions), as shown in Fig. 6.7. Thus, optical phonons are described by the oscillations of two atoms about a center of mass, while acoustic phonons are described by the movement of the two atoms center of mass. The amplitude ratio in the limit ($k \rightarrow \pi/a$) is left as an exercise at the end of the chapter.

Actually, the ratio of the amplitudes is such that the vibrations of the two atoms in a primitive unit cell leave the position of their center of gravity unchanged. Therefore, if the two atoms are ions of opposite charges, such as in the case of GaAs or NaCl, these oscillations result in a periodic oscillation of the amplitude of the dipole moment formed by these two charged ions, as discussed in Sect. 1.5.6. Such oscillations of the dipole moment are frequently optically active, i.e., are involved in the absorption or emission of electromagnetic (infrared mostly) radiation. This explains the use of the term “optical” for the $\omega_+(k)$ branch of lattice vibrations.

One can use the dispersion relation for phonons and photons to examine the conservation of energy and momentum that applies to the interaction of phonons and

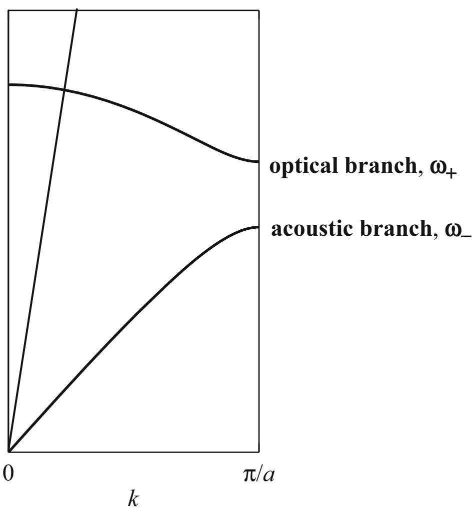


Fig. 6.8 The dispersion curves for a photon and an acoustic and optical phonon. The optical branch crosses with the photon branch, allowing for energy and momentum conservation

photons. Figure 6.8 shows the crossing of the dispersion relation for both acoustic and optical phonons with a photon. Because the photon and optical phonon curves cross, energy and momentum can be exchanged. An optical phonon can be created or annihilated with a photon. Since the acoustic mode never crosses the photon dispersion, they cannot interact. For example, in NaCl, its optical mode is excited by light because an electric field can displace the two oppositely charged ions in different directions. In a Ge crystal, the two atoms in the unit cell have similar charges and cannot be excited by an electric field.

6.1.5 Extension to Three-Dimensional Case

Formalism

So far, we have only considered a one-dimensional atomic crystal. A real crystal expands in all three dimensions of space, and lattice vibrations are more complicated. For example, the vibrations can occur in all three directions, regardless of the equilibrium position alignment of the atoms, and need to be expressed using a displacement vector $\vec{u}_{\vec{R}}(t)$. Moreover, a wavevector $\vec{k}$ must be used, similarly to the way it was done in Chap. 5 for three-dimensional electronic band structures. This wavevector $\vec{k}$ also indicates the direction of propagation of the traveling wave. The expression of the displacement, given for the one-dimensional case in Eq. (6.6), becomes in the three-dimensional case now:

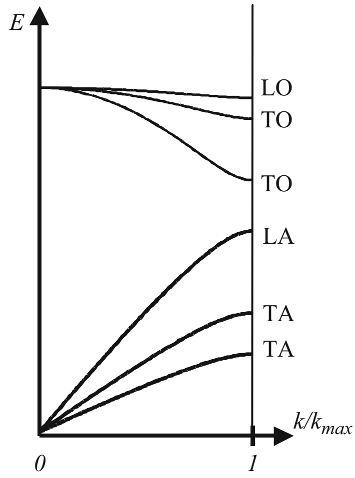


Fig. 6.9 Typical phonon dispersion spectrum for a three-dimensional diatomic lattice ($s = 2$)

$$\vec{u}_{\vec{R}}(t) = \vec{A} \exp\left[i\left(\vec{k} \cdot \vec{R} - \omega t\right)\right] \tag{6.29}$$

where $\vec{A}$ is the amplitude vector of the displacement and $\vec{k} \cdot \vec{R}$ is the dot product between the wavevector and the equilibrium position $\vec{R}$ of the atom considered.

In spite of this increased complexity, all the features obtained in the present simplified study remain valid. In particular, there still exist two types of phonons, as shown in the example of dispersion spectrum in Fig. 6.9: acoustic phonons, for which the vibration frequency goes to zero in the long wave limit ($\left|\vec{k}\right| \to 0$), and optical phonons, for which the frequency goes to a nonzero finite value in the long wave limit. Each type of phonons is further divided into two main categories: transversal and longitudinal phonons. The terms "transversal" and "longitudinal" refer to the direction of atomic displacements $\vec{u}(t)$ with respect to direction of propagation $\vec{k}$: perpendicular for transversal and parallel for longitudinal. There are generally two transverse and one longitudinal branch for each optical and acoustic phonons. Furthermore, the dispersion relations are not always isotropic, meaning that the phonon dispersion relations are different for different symmetry directions within the crystal.

For example, in Fig. 6.9, the transversal acoustic (TA), longitudinal acoustic (LA), transversal optical (TO), and longitudinal optical (LO) phonon branches are shown. Notice that the longitudinal branches are higher in energy than the transverse branches. In general, for a three-dimensional crystal with s atoms per unit cell, there are always three acoustic branches, two transversal and one longitudinal. There are also $3s-3$ optical branches. Figure 6.9 shows a typical example for $s = 2$. A monatomic Bravais lattice ($s = 1$) can only have acoustic phonon branches.

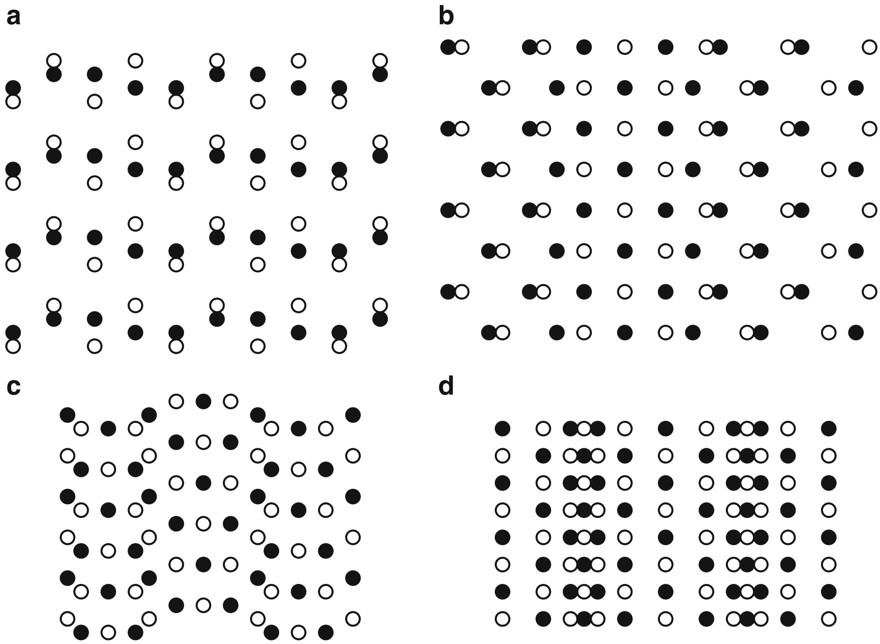


Fig. 6.10 The propagation of the four different phonon modes through a lattice: (**a**) transverse optic, (**b**) longitudinal optic, (**c**) transverse acoustic, and (**d**) longitudinal acoustic

Figure 6.10 shows the movement of (a) transverse optic (TO), (b) longitudinal optic (LO), (c) transverse acoustic (TA), and (d) longitudinal acoustic (LA) phonons in a lattice. The black circles represent the atoms with smaller mass, such as the gallium atoms in gallium arsenide. The white circles represent the heavier atoms, such as the arsenic atoms in gallium arsenide.

TO phonons propagate by the lighter atoms (black) being displaced perpendicular to the direction of the wave traveling. The heavier atoms (white) remain somewhat stationary within the lattice. For LO phonons, the heavier atoms remain somewhat stationary within the lattice, while the lighter atoms move parallel to the propagation of the traveling wave. As you can see, both optic modes produce a change in dipole movement, or the movement of the atoms about their center of mass. The heavier atoms remain fixed in the lattice, while the lighter atoms move and carry the wave through the medium. TA modes propagate similar to a pulse moving along a string after it has been jerked. The wave propagates through the movement of both the heavier and lighter atoms. Lastly, LA phonons propagate through the movement of a pair of atoms toward and away from another pair of atoms. Both acoustic modes correspond to the movement of the center of mass of two atoms. The distance between a heavier and lighter atoms remains fixed, while the pair as a whole is displaced relative to other atom pairs.

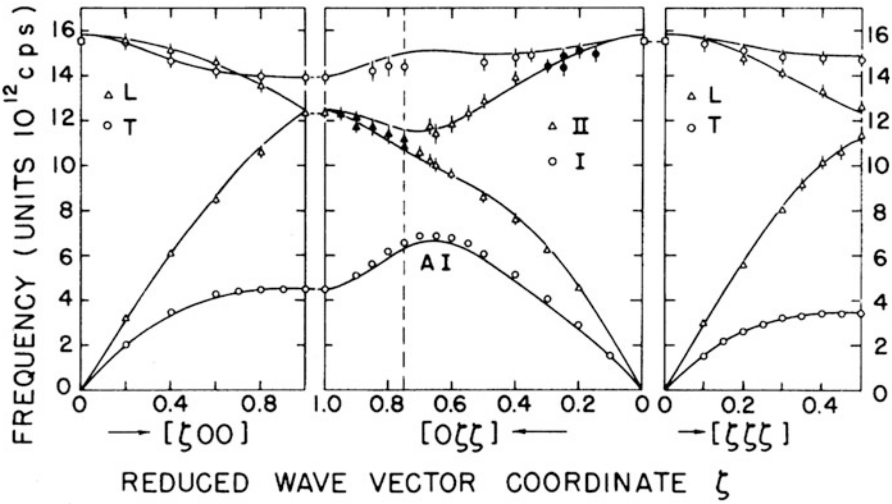


Fig. 6.11 Phonon dispersion relation for silicon in three crystal directions. Solid lines are calculated. Data points: open circles represent transverse (T) modes, open triangles longitudinal (L) modes, and solid points undetermined polarization modes (Reprinted with permission from Dolling 1963, Fig. 1. Copyright 1963, International Atomic Energy Association)

Silicon

Silicon crystals only have two identical atoms in their unit cell and bonds in the diamond structure. This results in the LO and TO energies being degenerate at the zone center. Since both atoms are identical, the bonds do not carry any electronegativity, and there is no restoring force like that in GaAs (Fig. 6.11).

Gallium Arsenide

In GaAs, the LO phonons have higher energy than the TO phonons near the zone center. This results from the ionic nature of the bonding in zinc-blende crystals. In GaAs, the arsenic atoms contribute five electrons to the bonds compared to gallium atoms, which contribute three. Consequently, the electrons spend on average more time near the arsenic atoms resulting the arsenic atoms to be slightly more negative, while the gallium atoms are slightly positive. This difference in electronegativity produces a restoring force for a propagating LO mode but not a TO mode. This increase in energy gives the LO modes a higher frequency (Fig. 6.12).

6.1.6 Phonons

In Chap. 5, the treatment of the electrons in a crystal led to energy levels and momenta that do not correspond to those of individual atoms but are properties of the lattice as a whole. Earlier in this chapter, we have hinted that the characteristics of the traveling waves arising from lattice vibrations are not specific to one particular

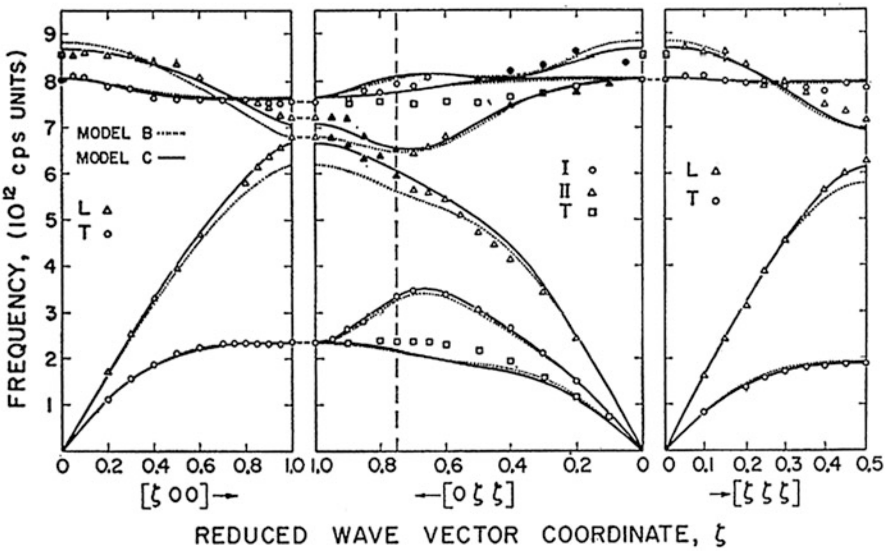


Fig. 6.12 Phonon dispersion relation for gallium arsenide in three crystal directions. Dotted and solid lines denote calculated values. Solid points denote undetermined polarization modes (Reprinted figure with permission from Waugh and Dolling 1963, Fig. 1. Copyright 1963 by the American Physical Society)

atom but are rather a property of the entire lattice too. We thus have to consider the collective excitation of the crystal as a whole and talk about a lattice wave. Each type of vibration is called a vibrational mode and is characterized by a wavevector $\vec{k}$ and a frequency $\omega(\vec{k})$.

The previous sections of this chapter dealt with a classical analysis of lattice vibrations. In a quantum mechanical treatment, especially when lattice waves interact with other objects (e.g., electrons, electromagnetic waves, or photons), it is convenient to regard a lattice wave as a quasiparticle or phonon with a momentum and a (quantized) energy such that:

$$\begin{cases} \vec{p} = \hbar\,\vec{k} \\ E = \hbar\omega(\vec{k}) \end{cases} \tag{6.30}$$

This is analogous to the quantization of the electromagnetic field discussed in Chap. 4. The energy in Eq. (6.30) is the quantum unit of vibrational energy at that frequency. Because phonons involve vibrational energy stored in the crystal, phonons can interact with other waves or particles such as electrons, photons, and phonons. These types of interactions lead to the experimentally observable physical properties of crystals.

The velocity of a phonon is given by the group velocity of the corresponding traveling wave, defined as the gradient of the frequency with respect to the wavevector:

$$\vec{v}_g = \frac{\partial \omega(\vec{k})}{\partial \vec{k}} = \nabla_{\vec{k}}\omega(\vec{k}) \tag{6.31}$$

In Cartesian coordinates with unit vectors $(\vec{x}, \vec{y}, \vec{z})$, this relation can be written as:

$$\vec{v}_g = \frac{\partial \omega(k_x, k_y, k_z)}{\partial k_x}\vec{x} + \frac{\partial \omega(k_x, k_y, k_z)}{\partial k_y}\vec{y} + \frac{\partial \omega(k_x, k_y, k_z)}{\partial k_z}\vec{z} \tag{6.32}$$

In this quantum picture, the propagation of harmonic lattice waves, i.e., up to the second-order term in Eq. (6.2), is equivalent to the free movement of non-interacting phonon quasiparticles, also called "phonon gas," and their description is similar to that of photons.

In particular, any number of identical phonons may be present simultaneously in the lattice, in any of the phonon mode characterized by a wavevector $\vec{k}$ for a given temperature. A phonon gas thus obeys the Bose-Einstein statistics which says that the average number of phonons in a given mode $(\vec{k})$ is then determined by:

$$N_{\vec{k}} = \frac{1}{\exp\left(\frac{\hbar\omega(\vec{k})}{k_b T}\right) - 1} \tag{6.33}$$

where $k_b$is the Boltzmann constant and T is the absolute temperature. At high temperatures, i.e., $k_b T >> \hbar\omega(\vec{k})$, the exponential in Eq. (6.33) can be approximated by:

$$\exp\left(\frac{\hbar\omega(\vec{k})}{k_b T}\right) \approx 1 + \frac{\hbar\omega(\vec{k})}{k_b T} \tag{6.34}$$

where we have used the approximation $\exp(x) \approx 1 + x$ for $x \rightarrow 0$ (again this comes from the Taylor expansion of $\exp(x) \approx 1 + x$ for small values of x). Therefore, $N_{\vec{k}} \approx \frac{k_b T}{\hbar\omega(\vec{k})}$, which expresses that the average number of phonons in a given mode is proportional to the temperature, at high temperatures.

As mentioned earlier, phonons can interact with other phonons. Such interaction would correspond to anharmonic vibrations in the classical wave picture, which arise from cubic and higher order terms in Eqs. (6.1 and 6.2).

Example

Q Estimate the average number of phonons in a given mode at low temperatures.

A The average number of phonons $N(E)$ with an energy E is given by: $N(E) = \frac{1}{\exp\left(\frac{E}{k_b T}\right) - 1}$. At low temperatures, we have $\exp\left(\frac{E}{k_b T}\right) >> 1$, and the expression for $N(E)$ can be simplified into: $N(E) \approx \exp\left(-\frac{E}{k_b T}\right)$.

6.1.7 Sound Velocity

It is known that a solid can transmit sound. This is in fact accomplished through the vibrations of atoms similar to the ones discussed in earlier sections. The sound velocity is the speed at which sound propagates and is related to velocity of a traveling wave as discussed below.

In Sect. 6.1.3, we have already hinted that the velocity of the traveling wave was given by the ratio of the angular frequency to the wavenumber in Eq. (6.8):

$$v_{\mathrm{ph}} = \frac{\omega}{k} \tag{6.35}$$

Using Eqs. (6.13 and 6.14), we obtain:

$$v_{\mathrm{ph}} = \sqrt{\frac{4C}{M}}\left|\frac{\sin\left({}^{ka}\!/_{2}\right)}{k}\right| = a\sqrt{\frac{C}{M}}\left|\frac{\sin\left({}^{ka}\!/_{2}\right)}{{}^{ka}\!/_{2}}\right| = v_0\left|\frac{\sin\left({}^{ka}\!/_{2}\right)}{{}^{ka}\!/_{2}}\right| \tag{6.36}$$

where:

$$v_0 = a\sqrt{\frac{C}{M}} \tag{6.37}$$

Therefore:

$$v_{\mathrm{ph}} = v_0\left|\frac{\sin\left({}^{ka}\!/_{2}\right)}{{}^{ka}\!/_{2}}\right| \tag{6.38}$$

This quantity is called the phase velocity because it represents the velocity of the phase of the wave or, in other words, the speed at which the peak of the wave travels in space. The phase velocity is plotted in Fig. 6.13, and we see that it never reaches zero.

There is another quantity of interest which is the group velocity of a traveling wave which represents the velocity of a wave packet and therefore of the wave energy and is defined as:

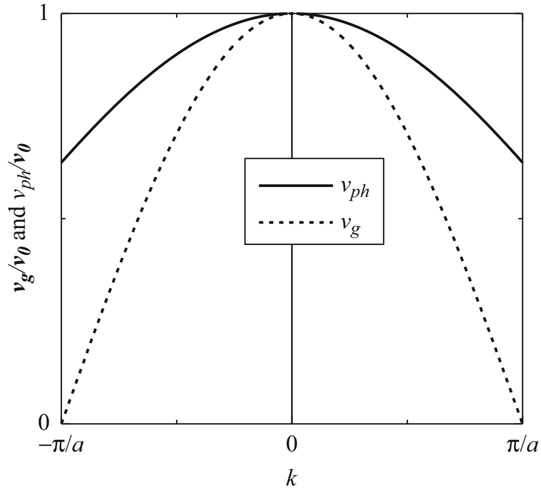


Fig. 6.13 Phase and group velocities versus wavenumber k

$$v_g = \left|\frac{d\omega}{dk}\right| \tag{6.39}$$

Using Eqs. (6.13 and 6.14), we obtain:

$$v_g = \sqrt{\frac{4C}{M}}\frac{a}{2}\left|\cos\left({}^{ka}\!/_{2}\right)\right| = a\sqrt{\frac{C}{M}}\left|\cos\left({}^{ka}\!/_{2}\right)\right| \tag{6.40}$$

and therefore:

$$v_g = v_0\left|\cos\left({}^{ak}\!/_{2}\right)\right| \tag{6.41}$$

The group velocity is also plotted in Fig. 6.6. We see that this quantity drops to zero when $k \longrightarrow \frac{\pi}{a}$, i.e., at boundary of the first Brillouin zone.

Example

Q Estimate the order of magnitude for the elastic constant C of silicon, given that the sound velocity in silicon is 2.2×10^5 cm·s^{-1}.

A Starting from the expression for the sound velocity, $v_0 = a\sqrt{\frac{C}{M}}$, where $a = 5.43$ Å and $M = 28M_p$ are the lattice constant and mass of a silicon atom, respectively. We thus have:

$$C = M\frac{v_0^2}{a^2} = \left(28 \times 1.67264 \times 10^{-27}\right) \times \frac{\left(2.2 \times 10^3\right)^2}{\left(5.43 \times 10^{-10}\right)^2}$$
$$\approx 0.77\,N.m^{-1}$$

From Eq. (6.37), we see that the speed of sound in a medium is proportional to the inverse square root of M, the atomic mass, and the square root of C, the elastic constant of the material. A generalized form for the speed of sound in a medium is:

$$v_s = \sqrt{\frac{B}{\rho}} \tag{6.42}$$

where B is the bulk modulus of the material and ρ is the density, given by its mass divided by its volume.

The bulk modulus is the property that determines the extent to which a medium changes its volume in response to an applied pressure. A generalized expression for the bulk modulus of a material is given by:

$$B = -\frac{\Delta p}{\frac{\Delta V}{V}} \tag{6.43}$$

where p is an applied pressure and V is the medium's volume. $\Delta V/V$ is the percent change in volume produced by a change in pressure Δp. The minus sign is included because whenever we increase the pressure, the volume decreases and vice versa. The minus sign allows what is under the radical in Eq. (6.42) to be positive.

Just as phonon modes can be anisotropic in a crystal, the bulk modulus is also directional within a crystal, and the velocity of sound is dependent upon what direction the sound is traveling in a material. A medium's bulk modulus generally takes on a tensor form and can be significantly different in the Γ, X, and L directions. This results from the crystal structure (e.g., cubic, tetragonal, orthorhombic, etc.) having different bonding lengths on different sides of each atom.

6.1.8 Summary

In this chapter, we have described the basic formalism for treating the interaction between atoms in a crystal, through the simple examples of one-dimensional monatomic and diatomic harmonic lattices. Several important concepts have been introduced such as the lattice vibrational modes, traveling waves, dispersion relations, acoustic and optical branches, longitudinal and transversal branches, and sound velocity. We realized that these lattice vibrations could be quantized in the same manner as the electromagnetic field and can thus be considered as quasiparticles, or phonons, with a momentum and energy and which obey Bose-Einstein statistics.

6.2 Thermal Properties of Crystals

6.2.1 Introduction

In Chap. 6 Part 1, we built simple mathematical models to describe the vibrations of atoms, first in a one-dimensional system and then extended to a three-dimensional harmonic crystal. These models, in the quantum description, led us to introduce a quasiparticle called the phonon, with an associated momentum and energy spectrum. Many of the phenomena measured in crystals can be traced back to phonons.

In this chapter, we will employ the results of the phonon formalism used in Chap. 6 to interpret the thermal properties of crystals, in particular their heat capacity, thermal expansion, and thermal conductivity.

6.2.2 Phonon Density of States (Debye Model)

Debye Model

The Debye model was developed in the early stages of the quantum theory of lattice vibration in an effort to describe the observed heat capacity of solids (Sect. 6.1.3). The model relies on a simplification of the phonon dispersion relation (see, e.g., Eq. (6.22), Fig. 6.5, or Fig. 6.8). In the Debye model, all the phonon branches are replaced with three acoustic branches, one longitudinal (l) and two transversal (t), with corresponding phonon spectra:

$$\omega_n\left(\vec{k}\right) = v_n\left|\vec{k}\right| = v_n k \tag{6.44}$$

where n ($= l$ or t) is an index, k is the norm or length of the wavevector $\vec{k}$, and v_l and v_t are the longitudinal and transversal sound velocities, respectively. This model corresponds to a linearization of the phonon spectrum as shown in Fig. 6.4. But this linearization implies that the phonon frequencies depend solely on the norm of the wavevector. Some boundary conditions therefore need to be changed in this model (Fig. 6.14).

Indeed, we remember that the range for the wavevector was restricted to the first Brillouin zone in the real phonon dispersion relation. The Born-von Karman boundary conditions of Sect. 5.3 limited the total number of allowed values for $\vec{k}$ to the number N of atoms in the crystal of volume V considered. We saw in Sect. 5.3 that the volume occupied by each wavevector was $\frac{(2\pi)^3}{V}$. The volume of the first Brillouin zone is then $\frac{2(\pi)^3 N}{V}$ and must be equal to $\frac{4\pi}{3}k_D^3$ where k_D is the Debye wavenumber such that the relation (7.1) is valid in the range $0 \leq k \leq k_D$. We thus obtain:

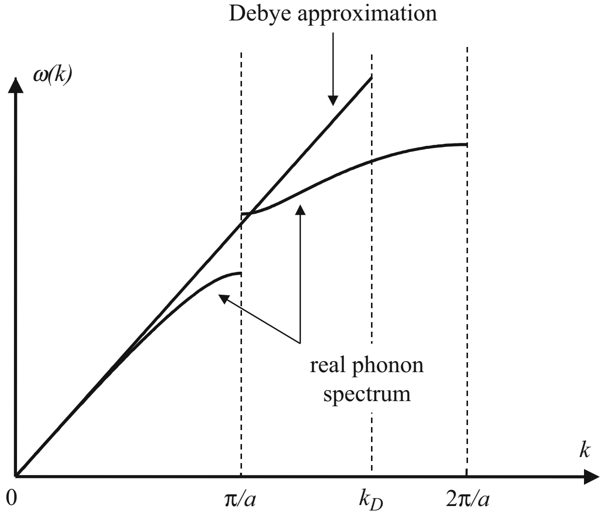


Fig. 6.14 Illustration of the Debye model in the phonon dispersion curve. In the Debye model, all the phonon branches are replaced with three acoustic branches. This corresponds to a simplification of the phonon dispersion spectrum, through a linearization of the phonon branches. A sphere is defined in momentum space with radius k_D, the Debye wavevector, such that the total number of modes inside the Debye sphere now matches the total number of modes in the real system

$$k_D^3 = \frac{6\pi^2 N}{V} \tag{6.45}$$

This wavenumber corresponds to a Debye frequency ω_D defined by:

$$\hbar\omega_D = \hbar\nu_0 k_D \tag{6.46}$$

where ν_0 is the sound velocity in the material. The Debye frequency is characteristic of a particular solid material and is approximately equal to the maximum frequency of lattice vibrations. It is also useful to define the Debye temperature Θ_D such that:

$$k_b\Theta_D = \hbar\omega_D = \hbar\nu_0 k_D \tag{6.47}$$

The significance of Θ_D will become clear in the following discussion. However, it follows that every solid will have its own characteristic phonon spectrum and therefore its own Debye temperature. The Debye temperatures for a few solids are listed in Table 6.1.

Example

Q Calculate the Debye wavelength for GaAs, given that the density of GaAs is $d = 5.32 \times 10^3$ kg·m^{-3}.

A We make use of the expression giving the Debye wavenumber $k_D^3 = \frac{6\pi^2 N}{V}$, which is related to the Debye wavelength through $\lambda_D = \frac{2\pi}{k_D} = 2\pi\left(\frac{6\pi^2 N}{V}\right)^{-1/3}$, where N is the number of atoms in the volume V. By definition of the density,

Table 6.1 Debye temperatures of a few solids (Grigoriev and Meilikhov 1997)

Material	Θ_D (K)
Pb	105
Au	162
Ag	227
NaCl	275
GaAs	345
Cu	347
Ge	373
W	383
Al	433
Fe	477
Si	650
BN	1900
C (diamond)	2250

we have $d = \frac{1}{V}\frac{N}{2}(M_{Ga} + M_{As})$, where M_{Ga} and M_{As} are the masses of a Ga and an As atom, respectively. The factor 2 arises from the fact that half of the atoms in the volume are Ga atoms and the other half are As atoms.

Therefore, we can write:

$$\lambda_D = 2\pi\left(6\pi^2 \frac{2d}{(M_{Ga}+M_{As})}\right)^{-1/3}$$
$$= 2\pi\left(6\pi^2 \frac{2\times 5.32\times 10^3}{(69.7+74.9)\times 1.67264\times 10^{-27}}\right)^{-1/3}$$

or $\lambda_D = 4.57\,\text{Å}$.

Phonon Density of States

The phonon density of states $g(\omega)$ is the number of phonon modes $\vec{k}$ per unit frequency interval which have a frequency $\omega\left(\vec{k}\right)$ equal to a given value ω. It can be calculated in a way similar to that used for the electron density of states in Sect. 6.1.3:

$$g(\omega) = \sum_{\vec{k},n} \delta\left[\omega_n\left(\vec{k}\right) - \omega\right] \tag{6.48}$$

where the summation is performed over all phonon modes $\vec{k}$ and phonon branches labeled n. Because the crystal has macroscopic sizes, the strictly discrete wavevector $\vec{k}$ can be considered quasi-continuous, as was done in Chap. 6 Eq. 6.44, and the discrete summation can be replaced by an integral:

$$\sum_{\vec{k}} \Upsilon(\vec{k}) \equiv \frac{V}{(2\pi)^3} \int_k \Upsilon(\vec{k}) d\vec{k} = \frac{V}{(2\pi)^3} \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \Upsilon(k_x, k_y, k_z) dk_x dk_y dk_z \quad (6.49)$$

where V is the volume of the crystal considered. The summation here is actually performed over all values of $\vec{k}$ in the first Brillouin zone. Equation (6.48) then becomes:

$$g(\omega) = \frac{V}{(2\pi)^3} \sum_n \iiint_k \delta\left[\omega_n(\vec{k}) - \omega\right] d\vec{k} \quad (6.50)$$

We now make use of Eq. (5.37):

$$d\vec{k} = d\left(\frac{4\pi}{3}k^3\right) = 4\pi k^2 dk$$

where k is the norm or length of the wavevector $\vec{k}$. Therefore, Eq. (6.50) becomes:

$$g(\omega) = \frac{4\pi V}{(2\pi)^3} \sum_n \int_0^{k_D} \delta\left[\omega_n(\vec{k}) - \omega\right] k^2 dk \quad (6.51)$$

where the integration is now from 0 to the Debye wavenumber k_D, in agreement with the Debye model described earlier. Substituting (6.46), we get successively:

$$g(\omega) = \frac{V}{2\pi^2} \sum_n \int_0^{k_D} \delta[v_n k - \omega] k^2 dk \quad (6.52)$$

or:

$$g(\omega) = \frac{V}{2\pi^2} \sum_n \int_0^{k_D} \delta[x - \omega] \frac{x^2}{v_n^3} dx \quad (6.53)$$

after the change of variable $x = v_n k$ (and thus $dx = v_n dk$). There is a nonzero solution only if there is a wavenumber k between 0 and k_D such that $x = v_n k = \omega$, and:

$$\begin{cases} g(\omega) = \dfrac{V}{2\pi^2} \sum_n \dfrac{\omega^2}{v_n^3} & for\, 0 \le \omega \le \omega_D \\ g(\omega) = 0 & for\, \omega_D \le \omega \end{cases} \quad (6.54)$$

Remembering that the Debye model takes into account one longitudinal (l) and two transversal (t) modes, we obtain:

$$\begin{cases} g(\omega) = \dfrac{V}{2\pi^2}\left(\dfrac{\omega^2}{v_l^3} + 2\dfrac{\omega^2}{v_t^3}\right) & for\, 0 \leq \omega \leq \omega_D \\ g(\omega) = 0 & for\, \omega_D \leq \omega \end{cases} \tag{6.55}$$

which can also be rewritten as:

$$\begin{cases} g(\omega) = \dfrac{3V\omega^2}{2\pi^2 v_0^3} & for\, 0 \leq \omega \leq \omega_D \\ g(\omega) = 0 & for\, \omega_D \leq \omega \end{cases} \tag{6.56}$$

where:

$$\frac{1}{v_0^3} = \frac{1}{3}\left(\frac{1}{v_l^3} + \frac{2}{v_t^3}\right) \tag{6.57}$$

is the inverse average sound velocity. This phonon density of states is illustrated in Fig. 6.15 where we have a parabolic relation. Although the Debye model is a simple approximation, the choice of k_D ensures that the area under the curve of $g(\omega)$ is the same as for the real curve for the density of states. Moreover, this expression is precise enough to determine the lattice contribution to the heat capacity both at high and low temperatures.

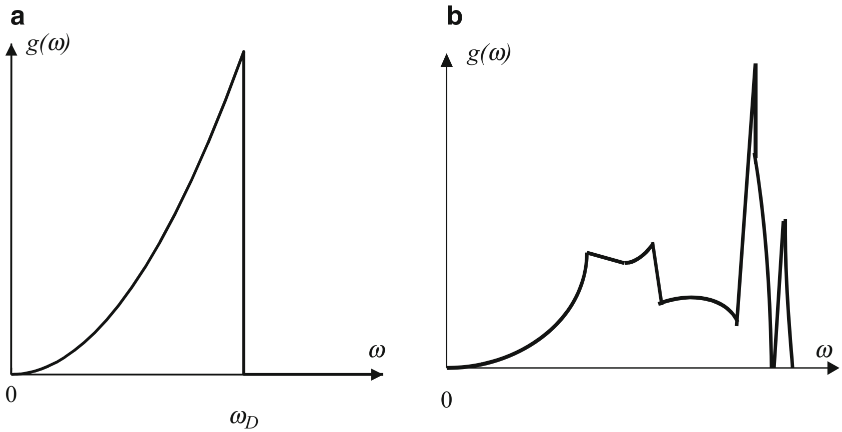


Fig. 6.15 (**a**) Illustration of the phonon density of states in the Debye model, where the relationship is parabolic until the Debye frequency is reached, after which the density of states is equal to zero. (**b**) Illustration of a typical phonon spectrum of a real crystal with discontinuities due to singularities in the spectrum. The singularities are due to zeroes in the group velocity

Heat Capacity

Lattice Contribution to the Heat Capacity (Debye Model)

When heat is transferred to a solid, its temperature increases. Heat has a mechanical equivalent which is an energy and is generally expressed in units of calorie with 1 calorie corresponding to 4.184 joules. Different substances need different amounts of heat energy to raise their temperature by a set amount. For example, it takes 1 calorie to raise 1 g of water by 1 degree K. The same amount of energy, however, raises 1 g of copper by about 11 K.

The heat capacity, C, of a material is a measure of the ability with which a substance can store this heat energy and is described by the ratio of the energy dE transferred to a substance to raise its temperature by an amount dT. The greater a given material's heat capacity, the more energy must be added to change its temperature. The heat capacity is characteristic of a given substance, and its units are cal·K^{-1} or J·K^{-1}. The heat capacity is defined as:

$$C_v = \left(\frac{dE}{dT}\right)_v \tag{6.58}$$

subscripts denoting which variable (volume or pressure) is held constant.

The specific heat capacity, often known simply as the specific heat and denoted by a lowercase c, of a material is the heat capacity per unit the mass. The specific heat of a given substance has units or cal·g^{-1}·K^{-1} or J·kg^{-1}·K^{-1} and is thus specific to a particular material and independent of the quantity of material. A few values of specific heat for elements in the periodic table are given in Fig. A. in Appendix A.3.

Both heat capacity and specific heat phenomena are closely related to phonons because, when a solid is heated, the atomic vibrations become more intense and more phonons or vibrational modes are accessible. A measure of the heat energy received by a solid is therefore the change in the total energy carried by the lattice vibrations. This total energy E can be easily expressed using the following integral, knowing the average number of phonons $N(\omega)$) (Eq. 6.33), the phonon density of states $g(\omega)$, and that a phonon with frequency ω has an energy $\hbar\omega$ (Eq. 6.30):

$$E = \int_0^\infty N(\omega) g(\omega) \hbar\omega d\omega \tag{6.59}$$

In the Debye model, we can use Eq. (6.56) for $g(\omega)$ and rewrite Eq. (6.59) as:

$$E = \int_0^{\omega_D} \frac{1}{\exp\left(\frac{\hbar\omega}{k_b T}\right) - 1} \frac{3V\omega^2}{2\pi^2 v_0^3} \hbar\omega d\omega$$

or:

$$E = \frac{3V\hbar}{2\pi^2 v_0^3} \int_0^{\omega_D} \frac{\omega^3}{\exp\left(\frac{\hbar\omega}{k_b T}\right) - 1} d\omega \tag{6.60}$$

Note that the previous integral is performed only up to the Debye frequency, as the phonon density of states is equal to zero beyond that point. Using the change of variable $x = \frac{\hbar\omega}{k_b T}$ (and thus $dx = \frac{\hbar}{k_b T} d\omega$), this equation becomes:

$$E = \frac{3V\hbar}{2\pi^2 v_0^3} \left(\frac{k_b T}{\hbar}\right)^4 \int_0^{\frac{\hbar\omega_D}{k_b T}} \frac{x^3}{e^x - 1} dx \tag{6.61}$$

Let us now make use of the Debye temperature Θ_D defined in Eq. (6.46) and the Debye wavenumber k_D in Eq. (6.47) to express:

$$\frac{1}{(\Theta_D)^3} = \frac{1}{k_D^3} \left(\frac{k_b}{\hbar\nu_0}\right)^3 = \frac{V}{6\pi^2 N} \left(\frac{k_b}{\hbar\nu_0}\right)^3$$

Using Eq. (6.46) for the boundary of the integral, Eq. (6.61) can then be rewritten as:

$$E = 9Nk_b \frac{1}{(\Theta_D)^3} T^4 \int_0^{\frac{\Theta_D}{T}} \frac{x^3}{e^x - 1} dx \tag{6.62}$$

For *high temperatures*, where $k_b T \gg \hbar\omega_D$ or simply $T \gg \Theta_D$, the integral in Eq. (6.62) is evaluated close to zero, i.e., $0 < x < \frac{\Theta_D}{T} << 1$. The function in the integral can thus be approximated as follows:

$$\frac{x^3}{e^x - 1} \approx \frac{x^3}{(1 + x) - 1} = x^2$$

where we have used the approximation $\exp(x) \approx 1 + x$ for $x \to 0$. As a result, Eq. (6.62) becomes successively:

$$\begin{aligned} E &\approx 9Nk_b \frac{1}{(\Theta_D)^3} T^4 \int_0^{\frac{\Theta_D}{T}} x^2 dx \\ &= 9Nk_b \frac{1}{(\Theta_D)^3} T^4 \left[\frac{x^3}{3}\right]_0^{\frac{\Theta_D}{T}} \\ &= 3Nk_b \frac{1}{(\Theta_D)^3} T^4 \left(\frac{\Theta_D}{T}\right)^3 \end{aligned}$$

and finally:

$$E \approx 3Nk_bT \tag{6.63}$$

The heat capacity is thus obtained after differentiating this expression with respect to the temperature as in Eq. (6.63):

$$C_v = \left(\frac{dE}{dT}\right)_v = 3Nk_b \tag{6.64}$$

This relation shows that, for high temperatures, i.e., $T \gg \Theta_D$, the heat capacity is independent of temperature. In fact, this could have been easily calculated using classical theory. Indeed, in classical statistical thermodynamics, each mode of vibration is associated with a thermal energy equal to k_bT. Therefore, for a solid with N atoms, each having three vibrational degrees of freedom, we get $3\,N$ modes; the total thermal energy is then $3Nk_bT$, as derived in Eq. (6.63); and the heat capacity is found to be equal to Eq. (6.64). This is known as the law of Dulong and Petit, which is based on classical theory. The molar heat capacity, that is, the value of the heat capacity for 1 mole of atoms, is calculated for N equal to the Avogadro number $N_A = 6.02204 \times 10^{23}$ mol^{-1} and is $C_v = 3\mathcal{N}_A k_b = 24.95$ J·mol^{-1}·K^{-1} = 5.96 cal·mol^{-1}·K^{-1}.

This shows that, at high temperatures $T \gg \Theta_D$, the Debye model fits the classical model. For *low temperatures*, however, where $k_bT \ll \hbar\omega_D$ or simply $T \ll \Theta_D$, the heat capacity is not constant with temperature anymore. This is where the quantum theory of phonons is needed and where the accuracy of the Debye model is best appreciated. In this case, the integral in Eq. (6.61) can be extended up to infinity without much error. Moreover, the exponential fraction in the integral can be expressed as:

$$\begin{aligned} \frac{1}{e^x - 1} &= \left(\frac{1}{e^x}\right)\left(\frac{1}{1 - e^{-x}}\right) \\ &= \frac{1}{e^x}\sum_{n=0}^{\infty}(e^{-x})^n = \sum_{n=1}^{\infty}(e^{-x})^n = \sum_{n=1}^{\infty} e^{-nx} \end{aligned} \tag{6.65}$$

because $x > 0$ and $e^{-x} < 1$. Therefore, the integral in Eq. (6.61) becomes:

$$\begin{aligned} \int_0^{\frac{\Theta_D}{T}} \frac{x^3}{e^x - 1}dx &\approx \int_0^{\infty} \frac{x^3}{e^x - 1}dx \\ &= \int_0^{\infty}\left(\sum_{n=1}^{\infty} x^3 e^{-nx}\right)dx \\ &= \sum_{n=1}^{\infty}\left(\int_0^{\infty} x^3 e^{-nx}dx\right) \\ &= \sum_{n=1}^{\infty} I_n \end{aligned} \tag{6.66}$$

where the integral I_n can be simplified after the following successive integration by parts:

$$\begin{aligned}
I_n &= \int_0^\infty x^3 e^{-nx} dx \\
&= \left[-x^3 \tfrac{e^{-nx}}{n}\right]_0^\infty + \int_0^\infty 3x^2 \frac{e^{-nx}}{n} dx \qquad = 0 + \frac{3}{n}\int_0^\infty x^2 e^{-nx} dx \\
&= \frac{3}{n}\left[-x^2 \frac{e^{-nx}}{n}\right]_0^\infty + \frac{3}{n}\int_0^\infty 2x \frac{e^{-nx}}{n} dx \quad = 0 + \frac{6}{n^2}\int_0^\infty x^2 e^{-nx} dx \\
&= \frac{6}{n^2}\left[-x \frac{e^{-nx}}{n}\right]_0^\infty + \frac{6}{n^2}\int_0^\infty \frac{e^{-nx}}{n} dx \quad = 0 + \frac{6}{n^3}\int_0^\infty e^{-nx} dx \\
&= \frac{6}{n^3}\left[-\frac{e^{-nx}}{n}\right]_0^\infty \\
&= \frac{6}{n^4}
\end{aligned}$$

Thus, Eq. (6.66) can be rewritten as:

$$\int_0^{\frac{\Theta_D}{T}} \frac{x^3}{e^x - 1} dx \approx 6 \sum_{n=1}^{\infty} \frac{1}{n^4} \tag{6.67}$$

The sum in this expression corresponds to $\zeta(4)$, which is called the Riemann zeta function evaluated at 4, and is equal to:

$$\zeta(4) = \sum_{n=1}^{\infty} \frac{1}{n^4} = \frac{\pi^4}{90} \tag{6.68}$$

And Eq. (6.62) becomes:

$$E = 9Nk_b \frac{1}{(\Theta_D)^3} T^4 \frac{6\pi^4}{90}$$

or:

$$E = \frac{3\pi^4}{5} Nk_b \frac{T^4}{(\Theta_D)^3} \tag{6.69}$$

To determine the heat capacity, we must differentiate this expression with respect to the temperature as in Eq. (6.69):

$$C_v = \left(\frac{dE}{dT}\right)_v = \frac{d}{dT}\left(\frac{3\pi^4}{5}Nk_b\frac{T^4}{(\Theta_D)^3}\right)$$

or:

$$C_v = \frac{12\pi^4}{5}Nk_b\left(\frac{T}{\Theta_D}\right)^3 \tag{6.70}$$

where N is the number of atoms in the crystal. This relation shows that, for low temperatures, i.e., $T << \Theta_D$, the heat capacity is proportional to T^3. The experimentally measured molar heat capacity is shown in Fig. 6.16 for a few solids as a function of temperature.

The figure shows that the Debye model is in good agreement with experimental observations, both in the high-temperature and the low-temperature regions.

Example

Q Calculate the Debye temperature for InP, given that the $v_l = 4.594 \times 10^3$ m·s^{-1}, $v_t = 3.085 \times 10^3$ m·s^{-1}, and the mass density of InP is $d = 4.81 \times 10^3$ kg·m^{-3}.

A We make use of the expression giving the Debye temperature, $\Theta_D = \frac{\hbar\omega D}{k_b}$, where the Debye frequency $\omega_D = v_0 k_D$ is calculated knowing $\frac{1}{v_0^3} = \frac{1}{3}\left(\frac{1}{v_l^3} + \frac{2}{v_t^3}\right)$ and

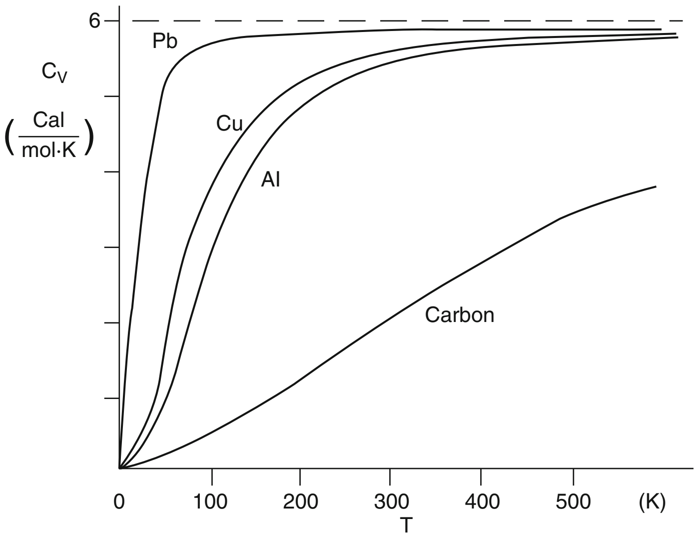


Fig. 6.16 Temperature dependence of the molar heat capacity C_v of some materials. At low temperatures, the heat capacity follows a T^3 relation (Hummel 1993, Fig. 19.1. © 1985, 1993 by Springer-Verlag Berlin Heidelberg. With kind permission of Springer Science and Business Media)

$k_D^3 = \frac{6\pi^2 N}{V} = 6\pi^2\left(\frac{2d}{M_{In} + M_P}\right)$ similarly to the previous example. Numerically, we successively obtain:

$$v_0 = \left[\frac{1}{3}\left(\frac{1}{v_l^3} + \frac{2}{v_t^3}\right)\right]^{-1/3} = \left[\frac{1}{3}\left(\frac{1}{\left(4.594\times 10^3\right)^3} + \frac{2}{\left(3.085\times 10^3\right)^3}\right)\right]^{-1/3} \text{ or:}$$

$$v_0 = 3.37 \times 10^3\,\mathrm{m \cdot s^{-1}}.$$

In addition, we have:

$$k_D = \left(6\pi^2\left(\frac{2 \times 4.81 \times 10^3}{(114.8 + 31) \times 1.67264 \times 10^{-27}}\right)\right)^{1/3} \text{ or}$$

$$k_D = 1.33 \times 10^{10}\,\mathrm{m^{-1}}$$

which leads to:

$$\omega_D = 4.47 \times 10^{13}\,\mathrm{Hz}\,\text{and}$$

$$\Theta_D = \frac{\left(1.05458 \times 10^{-34}\right)\left(4.47 \times 10^{-13}\right)}{1.38066 \times 10^{-23}} = 341.5\,K$$

Throughout this discussion, we realized that the Debye temperature Θ_D played a significant role in the heat capacity of a material. It indicates the separation between the high-temperature region where classical theory is valid and the low-temperature region where quantum theory is needed. The Debye temperature can be measured by fitting the experimental data of Fig. 6.16 to Eq. (6.70).

Electronic Contribution to the Heat Capacity

The previous discussion has considered the contribution of lattice vibrations or phonons to the heat capacity. This is valid for dielectric, i.e., insulating, materials. But, unlike dielectric materials, metals have a large number of free electrons, N_f, which can also absorb thermal energy, thus increasing the overall heat capacity of the metal. The contribution of electrons to the total heat capacity, denoted C_v^{el}, can be found as:

$$C_v^{el} = \frac{\pi^2}{2}\frac{N_f k_b^2}{E_F}T \tag{6.71}$$

$$C_v^{el} = \gamma T$$

where N_f is the total number of free electrons in the crystal, E_F is the Fermi energy, k_b the Boltzmann constant, and T the absolute temperature. The mathematical steps involved in the calculation of C_v^{el} are quite challenging and are beyond the scope of this textbook. Only a few defining equations will be listed here. The heat capacity C_v^{el} is defined by:

$$C_v^{el} = \left(\frac{dE}{dT}\right)_{N_f} \tag{6.72}$$

where E is the energy of all the electrons in the crystal and is given by:

$$E = \int_0^\infty \varepsilon g_{3D}(\varepsilon) f_e(\varepsilon) d\varepsilon \tag{6.73}$$

where $f_e(\varepsilon)$ is the Fermi-Dirac distribution defined in Eq. (5.28) and $g_{3D}(\varepsilon)$ is the three-dimensional electronic density of states of free electrons given by:

$$g_{3D}(\varepsilon) = \frac{1}{2\pi^2}\left(\frac{2m^*}{\hbar^2}\right)^{3/2} \sqrt{(\varepsilon)} \tag{6.74}$$

with m^* being the electron effective mass. The temperature dependence of E is included in the Fermi-Dirac distribution function.

We can see from Eq. (6.71) that the electronic contribution C_v^{el} to the heat capacity depends linearly on temperature and thus can be discriminated from the T^3 dependence of the lattice or phonon contribution denoted C_v^{ph} (Eq. 6.70) at low temperatures. It is interesting to consider the ratio of C_v^{el} to C_v^{ph}:

$$\frac{C_v^{el}}{C_v^{ph}} = \frac{\frac{\pi^2}{2}\frac{N_f k_b^2}{E_F} T}{\frac{12\pi^4}{5} N k_b \left(\frac{T}{\Theta_D}\right)^3} = \frac{5}{24\pi^2}\frac{N_f}{N}\frac{k_b}{E_F}\frac{\Theta_D^3}{T^2} \tag{6.75}$$

where Θ_D is the Debye temperature. By introducing the Fermi temperature T_F such that:

$$E_F = k_b T_F \tag{6.76}$$

And Eq. (6.75) becomes:

$$\frac{C_v^{el}}{C_v^{ph}} = \frac{5}{24\pi^2}\frac{N_f}{N}\frac{\Theta_D^3}{T^2 T_F} \tag{6.77}$$

The ratio $\frac{N_f}{N}$ expresses the average number of free electrons that each atom contributes to the crystal. Equation (6.77) shows that, as the temperature is increased, the contribution of the lattice to the heat capacity exceeds that of electrons. This occurs at a temperature T_0 such that $C_v^{el} = C_v^{ph}$ or:

$$T_0 = \sqrt{\frac{5}{24\pi^2}\frac{N_f}{N}\frac{\Theta_D^3}{T_F}} \tag{6.78}$$

Numerically, one can find that this temperature is only a few percent of the Debye temperature, i.e., a few degrees K (Table 6.1). This means that the contribution of electrons to the heat capacity can only be observed at very low temperatures.

Example

Q Calculate the ratio of C_v^{el}/C_v^{ph} at 4.2, 30, 77, and 296 K for Cu (assume $\Theta_D = 340\,K$ and $E_F = 7$ eV).

A We start from the expression for the above ratio: $\frac{C_v^{el}}{C_v^{ph}} = \frac{5}{24\pi^2}\frac{N_f}{N}\frac{k_b}{E_F}\frac{\Theta_D^3}{T^2}$. Since Cu has two free electrons per atom, we can write $\frac{N_f}{N} = 2$. This leads to: $\frac{C_v^{el}}{C_v^{ph}} = \frac{5}{24\pi^2} \times 2 \times \frac{1.38066 \times 10^{-23}}{7 \times 1.60218 \times 10^{-19}}\frac{340^3}{T^2} = \frac{20.43}{T^2}$

which gives:

$$\frac{C_v^{el}}{C_v^{ph}} = 1.16\ (4.2\text{K}), 0.023\ (30\text{K}), 0.034\ (77\text{K}), 0.00023\ (296\text{K}).$$

6.2.3 Thermal Expansion

Beside a few notable exceptions, it is commonly known that the volume of a heated solid increases. This phenomenon is called thermal expansion.

If a material of length L is heated through a *small* temperature change ΔT, the change in length ΔL is proportional to the original length and to the change in temperature. The coefficient of linear expansion α_L is called the thermal expansion coefficient and is defined by the following relationship:

$$\frac{\Delta L}{L} = \alpha_L \Delta T \tag{6.79}$$

The linear expansion coefficients of a few solids are shown in Table 6.2.

As Eq. (6.79) describes, an isotropic material exhibits equal thermal expansion in all directions. Some cases in the real world, however, can be more complex than implied by Eq. (6.79). The coefficient α_L can vary with temperature, so that the amount of expansion not only depends upon the temperature change but also upon the absolute temperature of the material.

Some materials are not isotropic and have a different value for the coefficient of linear expansion dependent upon the axis along which the expansion is measured.

Table 6.2 Thermal expansion coefficients of a few solids (Chemical Rubber Company 1997; Grigoriev and Meilikhov 1997)

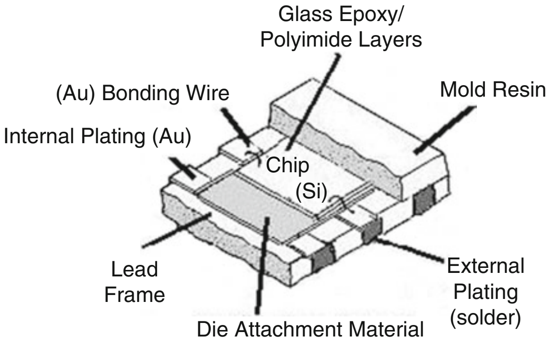
Solid	α_L ($\times 10^{-5}$ K^{-1})
NaCl	3.96
Pb	2.89
Al	2.31
Ag	1.89
Cu	1.65
Au	1.42
Fe	1.18
C (diamond)	1.18
Ordinary glass	0.90
Ge	0.582
GaAs	0.54
InSb	0.47
Si	0.468
AlAs	0.35
Si_3N_4	0.27
Pyrex glass	0.32
Invar	0.07
Quartz glass	0.05

For instance, with increasing temperature, calcite ($CaCO_3$) crystals expand along one crystal axis and contract ($\alpha_L < 0$) along another axis.

Engineers in the semiconductor field are often extremely concerned about the thermal expansion rate of a material when designing a device or system that must operate over a range of temperatures. Improperly packaging a semiconductor device without giving careful consideration to the thermal expansion properties of the materials can result in reliability problems and reduced lifetime of the device. As a result, most companies perform thermal cycling tests of their devices to determine whether or not thermal expansion is a possible failure mechanism.

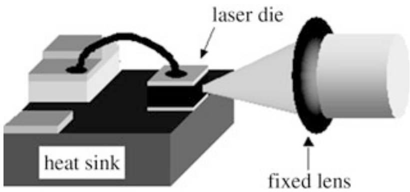
The problems associated with thermal expansion are most severe when two materials of different thermal expansion coefficients are permanently bonded together, such as in integrated circuits. For example, if the thermal expansion properties of a metal heat sink are not properly matched to the thermal expansion properties of the semiconductor material, the brittle semiconductor can crack as the device is heated and cooled. In fact, copper and other metals exhibit thermal expansion properties that are an order of magnitude greater than that of semiconductors such as Si and GaAs, making it very problematic to attach these materials directly. In order to address this issue, many semiconductor devices are packaged using intermediate die attachment materials as well as advanced solder alloys and optimized package materials as illustrated in Fig. 6.17. Some examples of advanced packaging processes that rely on optimizing the coefficient of thermal expansion are high-power RF-electronics and lasers (Fig. 6.17).

Fig. 6.17 Cutaway illustration of an advanced semiconductor device package. To avoid cracking and stresses and for devices where alignment is critical, packaging materials must be chosen with compatible thermal expansion coefficients



Example

Q A semiconductor laser is affixed to a copper heat sink and sealed into a package inside of a factory clean room environment where the ambient temperature is 20 °C. The lasers are then installed in scientific equipment monitoring gas emissions from a volcano in Hawaii.



The package also contains a collimating lens that is fixed in place and aligned with the central axis of the laser beam. If the ambient temperature in Hawaii is48 °C, how far off axis will the laser be when the device is in operation? (Assume that thermal expansion has a negligible effect on the in-plane expansion of the heat sink. Also assume that the heat sink is 3 mm long on each side and 1 mm tall).

A Equation (6.79) describes the linear expansion of a material: $\frac{\Delta L}{L} = \alpha_L \Delta T$. Cu has a coefficient of linear expansion, α_L, equal to 1.67 × 10^{-5} K^{-1}. The heat sink is originally 1mm tall (L), and the temperature difference, ΔT, is equal to 48 °C−20 °C = 28 °C = 28 K.

Thus, the change in length of the heat sink is equal to:$\Delta L = (1.67 \times 10^{-5} K^{-1})(28K)(1\ \ mm) = 4.68 \times 10^{-4} mm$
or 0.468 μm.

Thermal expansion means that the average distance between atoms increases when the temperature goes up and is therefore related to atomic vibrations or phonons in a solid. It can be easily understood that at a higher temperature, the atomic vibrations will be more intense, the distances between atoms will be higher, and therefore the overall solid volume will be larger. The mathematical treatment of this relationship is beyond the scope of the discussion. We will merely give a brief and simple description of the phenomenon.

We saw in Sect. 6.1.2 that the *equilibrium* interatomic distance $r = R_0$ is determined by the minimum of the atomic interaction potential energy $U(r)$. In thermodynamics, for such a system at thermal equilibrium at a temperature T, the *average* interatomic distance is denoted $<R>$ and is given by the Maxwell-Boltzmann distribution:

$$\langle R \rangle = \frac{\int_{-\infty}^{\infty} R e^{-\frac{U(R)}{k_b T}} dR}{\int_{-\infty}^{\infty} e^{-\frac{U(R)}{k_b T}} dR} \tag{6.80a}$$

By introducing the displacement $x = R - R_0$ and expressing $U(R)$ as a function of x as was done in Sect. 6.1.2 (Eq. 6.2), we can rewrite this equation as:

$$\langle R \rangle = \frac{\int_{-\infty}^{\infty} (R_0 + (R - R_0)) e^{-\frac{U(R)}{k_b T}} dR}{\int_{-\infty}^{\infty} e^{-\frac{U(R)}{k_b T}} dR} = R_0 \frac{\int_{-\infty}^{\infty} e^{-\frac{U(R)}{k_b T}} dR}{\int_{-\infty}^{\infty} e^{-\frac{U(R)}{k_b T}} dR} + \frac{\int_{-\infty}^{\infty} x e^{-\frac{U(x)}{k_b T}} dx}{\int_{-\infty}^{\infty} e^{-\frac{U(x)}{k_b T}} dx}$$

or:

$$\langle R \rangle = R_0 + \frac{\int_{-\infty}^{\infty} x e^{-\frac{U(x)}{k_b T}} dx}{\int_{-\infty}^{\infty} e^{-\frac{U(x)}{k_b T}} dx} \tag{6.80b}$$

For low temperatures and thus small vibrational amplitudes ($x < <R_0$), one can approximate the potential energy $U(x)$ with terms up to the second order in x (i.e., x^2) as was done in Eq. (6.3). This is the harmonic approximation. In this case, the exponential $e^{-\frac{U(x)}{k_b T}}$ is an even function of x, $x e^{-\frac{U(x)}{k_b T}}$ is an odd function of x, and therefore $\int_{-\infty}^{\infty} x e^{-\frac{U(x)}{k_b T}} dx = 0$ and $\langle R \rangle = R_0$. This means that, in the harmonic case, the average interatomic distance $<R>$ is exactly R_0, the distance corresponding to the potential energy minimum.

At higher temperatures, the atomic displacement x is large enough so that higher order terms in Eq. (6.2) need to be included (e.g., x^3), causing anharmonic effects. In this case, the exponential $e^{-\frac{U(x)}{k_b T}}$ is not an even or odd function of x anymore, and the integral fraction in Eq. (6.38) is strictly positive. As a result, $\langle R \rangle > R_0$ which means that the average interatomic distance becomes larger than R_0, i.e., there is thermal expansion. We see that thermal expansion is a direct result of anharmonic effects in the atomic interaction potential.

6.2.4 Thermal Conductivity

In the previous few sections, we saw that a lattice could receive and store thermal energy, heat through lattice vibrations, i.e., by creating more phonons, or through free electrons in a metal by gaining more kinetic energy. The lattice vibrations generate waves that can propagate, while free electrons can move in a metal. The thermal energy can thus be transported from one end of the solid to another. This characteristic is called thermal conductivity and is also an important parameter when designing a device or system.

Depending on the thermal conductivity of the materials used, heat may build up from the operation of the device and lead to failure of the device or system. Removal of excess heat has become a very critical issue in semiconductor design in recent years, especially in the design of modern high-density computer chips and high-power optoelectronic semiconductors. In the semiconductor industry, Moore's law has predicted that the number of transistors on a chip doubles every 18 months. This has led to both a reduction of the size of transistors and an increase in the packing density. The increase in transistor density has also lead to a significant increase in the power density (heat) in the same area that needs to be removed from the chip.

The thermal conductivity of a solid is quantified through a positive parameter called the thermal conductivity coefficient K (read "kappa") which is defined as:

$$J_T = -\kappa \frac{dT}{dx} \tag{6.81}$$

where J_T is the thermal current density, i.e., the thermal energy transported across a unit area per unit time. This is expressed in units of J·cm^{-2}·s^{-1} or W·cm^{-2}. $\frac{dT}{dx}$ is the temperature gradient, which is the rate at which the temperature changes from one region of the solid to another. The thermal conductivity coefficient thus has the units of W·cm^{-1}·K^{-1} (or W·m^{-1}·K^{-1}). Values of the thermal conductivity of a few materials are given below in Table 6.3 and Fig. A. in Appendix A.3.

Equation (6.81) expresses that there is a flux of thermal energy within the solid as a result of a difference of temperature between two regions. The minus sign means that the thermal energy flows from the higher-temperature region to the lower-temperature region. This relation is analogous to the electrical current which originates from a difference in electrical potential. In Eq. (6.39), we assumed that the thermal current and the temperature gradient occurred along one direction. In a three-dimensional case, the current and the gradient would be simply replaced by vectors. The simplification here does not reduce the generality of the physical concepts which will be derived. Moreover, in this section, we will only be interested

Table 6.3 Thermal conductivities of a few solids (Chemical Rubber Company 1997; Adachi 2004)

Solid	κ ($W \cdot m^{-1} \cdot K^{-1}$)
Pyrex glass	1.1
NaCl	6.4
Pb	35
GaAs	56
Ge	64
GaP	77
Fe	80
AlN	82
InP	68
Si	124
BeO	210
Al	237
Au	317
Cu	401
Ag	429
C (diamond)	1000

in the qualitative properties of the thermal conductivity. An exhaustive mathematical treatment can therefore be avoided.

Copper has become the material of choice for most heat-spreading applications in microelectronics because it is a material with one of the highest thermal conductivities and affordable costs. In some cutting edge devices, however, even copper is falling short of adequately removing heat from semiconductor devices, and the engineers and materials scientists have had to think of alternative approaches. One such approach has been to use diamond because it has a thermal conductivity several times larger than that of copper. Commercial manufacturing of diamond heat-spreading materials through the use of chemical vapor deposition (CVD) has reduced the material's cost and improved availability and made diamond heat spreaders a viable solution for high-heat load applications, such as power laser diodes.

Thermal conductivity can be viewed as the result of phonons (quasiparticle) moving from a hotter to a colder region and undergoing collisions with one another or against material imperfections (defects, boundaries) so that their energy can be transferred in space. These collisions are also often referred to by using the more general term scattering. The mathematical model commonly followed makes use of the kinetic theory of gases, in which (i) each quasiparticle is modeled as a free moving particle in space with a momentum and an energy, (ii) each quasiparticle is subject to instantaneous collision events with other particles, (iii) the probability for a collision to occur during an interval of time dt is proportional to dt, and (iv) the particles reach thermal equilibrium only through these collisions.

Similar to the heat capacity, there are two contributions to the thermal conductivity: a lattice contribution (phonons) denoted κ_{ph} and an electronic contribution (electrons) denoted κ_e.

The lattice contribution κ_{ph} can be regarded as the thermal conductivity of a phonon gas. Using the kinetic theory of gases, the following expression can be derived for the lattice contribution:

$$\kappa_{ph} = \frac{1}{3}\left(\frac{C_v^{ph}}{V}\right)v_0\Lambda \tag{6.82}$$

where $\left(\frac{C_v^{ph}}{V}\right)$ is the heat capacity per unit volume of the solid considered and v_0 is the average phonon velocity. The parameter Λ is the mean free path of a phonon between two consecutive collisions and is central to the thermal conductivity process.

There are two types of phonon-phonon interactions in crystals. The first one involves what is called normal processes which conserve the overall phonon momentum, $\vec{k_1} + \vec{k_2} + \vec{k_3} = 0$, but not phonon number (phonons are bosons and are not subject to particle number conservation) where $\vec{k_1}$, $\vec{k_2}$, and $\vec{k_3}$ are the momenta of three interacting phonons. The second type is called umklapp processes and is such that $\vec{k_1} + \vec{k_2} + \vec{k_3} = n\vec{K}$, where $n = 1, 2, 3\ldots$ is an integer and $\vec{K}$ is a reciprocal lattice vector. We recall from Chaps. 4 and 5 that electron and lattice momentum in a crystal is only conserved give or take a reciprocal lattice vector. Equation (6.40) was first applied by Debye to describe thermal conductivity in dielectric (insulating) solids.

At very low temperatures, i.e., $T \ll \Theta_D$, the average number of phonons given in Eq. (6.33) tends toward zero. The phonon-phonon scattering becomes negligible, and the mean free path Λ is determined by the scattering of phonons against the solid imperfections or even the solid boundaries. Λ thus increases until it is equal to the geometrical size of the sample. Then, the thermal conductivity behaves as the heat capacity C_v^{ph} and has a T^3 dependence (Eq. (6.80)). In particular, $\kappa_{ph} \to 0$ when $T \to 0$. These are shown in Fig. 6.18a for Λ and Fig. 6.18b for κ_{ph}.

For higher temperatures, i.e., $T \gg \Theta_D$, we saw in Sect. 6.1.6 that the average number of phonons is proportional to T. Thus, phonon-phonon interactions become increasingly dominant as the temperature increases. Since the collision frequency should be proportional to the number of phonons with which a phonon can collide, Λ ends up being proportional to $1/T$ at higher temperatures, as shown in Fig. 6.18a. At the same time, we saw that in the heat capacity C_v^{ph} saturates at high temperatures (Eq. 6.71). The thermal conductivity κ_{ph} therefore has a $1/T$ dependence in this regime, as shown in Fig. 6.18b.

Another contribution to the thermal conductivity arises from electrons and mainly concerns metals which have a large concentration of free electrons. Here, again, the kinetic theory of gases leads to an expression of the electronic contribution κ_{el} similar to Eq. (6.82):

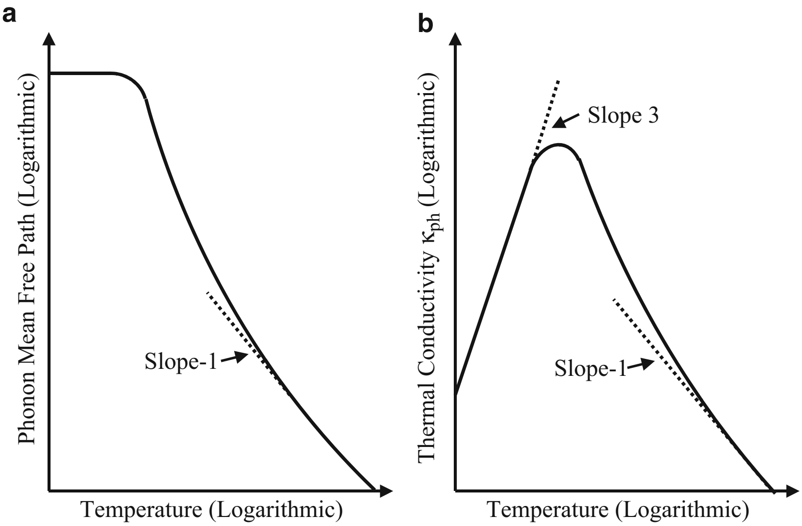


Fig. 6.18 Variation of (**a**) phonon mean free path and (**b**) lattice thermal conductivity as a function of temperature. At low temperatures, as the phonon-phonon interaction and scattering decrease, the phonon mean free path is determined by crystal imperfections which are independent of temperature, and the thermal conductivity follows a T^3 dependence. At high temperatures, phonon-phonon scattering increases, and both the phonon mean free path and the thermal conductivity decrease as T^{-1}

$$\kappa_{el} = \frac{1}{3}\left(\frac{C_v^{el}}{V}\right)v_e\Lambda_e \tag{6.83a}$$

where $\left(\frac{C_v^{el}}{V}\right)$ is the electronic contribution to the heat capacity per unit volume of the solid considered and v_e is the average electron velocity. The parameter Λ_e is the mean free path of an electron and describes how far an electron can travel on average between two consecutive collisions. We will not in this chapter discuss the various scattering mechanisms for an electron because of their large number and complexity. Electronic transport and relaxation times will be discussed in more details in Chap. 8. An interesting relationship can be derived linking the thermal conductivity and electrical conductivity (σ_{el}) of the free electron gas using Eqs. 6.71 and 6.83. This is known as the Wiedemann-Franz law and can be written as:

$$\kappa_{el} = \frac{\pi^2 k_b^2}{3q^2}T\sigma_{el} \tag{6.83b}$$

The electrical conductivity σ_{el} has not yet been discussed and is treated in detail in Chap. 8, Sect. 8.2. It is measured in units of siemens/m or S/m.

We will conclude by providing a numerical estimate of this contribution and compare it to the lattice contribution. At room temperature, on the one hand, a typical phonon has a mean free path of 3×10^{-6} cm, a velocity of 10^5 cm·s^{-1}, and a heat capacity of 25 J·K^{-1}·mol^{-1}, yielding a thermal conductivity of $\kappa_{ph} \approx 2.5$ W·cm^{-1}·K^{-1}. On the other hand, for a pure (perfect) metal, an electron has a mean free path of 10^{-5} cm, a velocity of 10^8 cm·s^{-1}, and a heat capacity of 0.5 J·K^{-1}·mol^{-1}, yielding a thermal conductivity of $\kappa_{ph} \approx 250$ W·cm^{-1}·K^{-1}. This clearly shows that the electrons in a pure metal are responsible for almost all the heat transfer. However, if the metal has many defects, the phonon contribution may be comparable with the electron contribution.

6.2.5 Summary

In this chapter, we have shown that phonons in solids are responsible for important contributions to the thermal properties of crystals. This includes heat capacity, thermal expansion, and thermal conductivity. The Debye model of phonons was presented, and it was shown that, despite the considerable simplifications made to the spectrum, the model still accurately describes the temperature dependence of the heat capacity and the thermal conductivity coefficients as measured experimentally in crystals. The subject of thermal conductivity has acquired more importance recently in view of the work on thermoelectricity and heat energy harvesting. Thermal transport and how to control it are treated in detail in Chap. 12 of this book.

Problems for Phonons and Thermal Properties

1. Explain why there is no optical phonon in the dispersion curve for the one-dimensional monatomic chain of atoms.
2. Explain why there is a forbidden range of vibration energies between the optical and acoustic phonon branches. Solve Eq. (6.22) for the case when $k = \pi/a$.
3. The one-dimensional monatomic harmonic crystal (Sect. 6.1.3) is in fact a particular case of the diatomic model described in Sect. 6.1.4, for which the two atoms are identical. To prove this, show that the expression for the diatomic harmonic crystal can be transformed into an expression similar to the monatomic crystal. Solve Eq. (6.22) in the limit $M_1 = M_2 = M$. What considerations do you have to take into account to do this?
4. In the chapter, the phonon frequencies at the center of the zone $k = 0$ were determined for the diatomic molecule. Calculate the phonon frequencies at the zone boundary $k = \pi/a$.
5. Plot the shapes of the optical and acoustic branches in the dispersion relation for four different ratios of masses: $\frac{M_1}{M_2} = 10, 5, 2$, and 1. Show that, in the case of two identical atoms, there is actually only one acoustic branch and no optical branch for the dispersion relation.
6. In Sect. 6.1.4, we calculated the ratio of the displacement amplitudes A and B for the long wave limit ($k \to 0$) for both the optical and acoustic phonon branches

and then determined the displacement of the atoms with respect to each other. Calculate Eq. (6.26), the ratio of the displacement amplitudes, in the short wave limit ($k \to \pi/a$), and draw the displacement of the atoms with respect to each other.

7. Suppose that a light wave of wavelength 3 μm is absorbed by a one-dimensional diatomic harmonic chain with atoms of mass 4×10^{-26} kg and 5×10^{-26} kg and atomic spacing of 4.5 Å. What is the force constant in MKS units?
8. From the figures for the phonon dispersion curves for Si and GaAs plus the equations for optical and acoustic phonons, explain why the energy for the Si curves is higher in energy than the curves for GaAs? Assume that the elastic constant is about the same for both materials. Also, why do the optical and acoustic phonon branches cross at the zone boundary for Si but not for GaAs?
9. Plot the average number of phonons $N(\omega) = \frac{1}{\exp\left(\frac{\hbar\omega}{k_bT}\right) - 1}$ for at least five values of

   T to show its evolution with increasing temperatures. For each one, plot the function $F(\omega) = \frac{k_bT}{\hbar\omega}$, and show that it is a good approximation for $N(\omega)$ for high temperatures, i.e., $k_bT > > \hbar\omega$.
10. Let us model a rigid bar as a linear monatomic chain of atoms, as in Sect. 6.1.3 with the same notations. We further assume that the equilibrium interatomic separation is a and that its cross section is a^2. Its Young's modulus E_Y is defined as the ratio of the stress applied in one direction divided by the relative elongation in this same direction. The stress is the ratio of the interatomic force ($F_{n,n-1}$) divided by the cross-sectional area (a^2) on which this force is applied. The relative elongation is the interatomic displacement divided by the equilibrium separation. The Young's modulus has the dimension of a pressure and is expressed in Pa (Pascal). The solid density M_V is the ratio of the mass of the solid to its volume. Here, we assume that the mass of an atom is M and that there is only one atom in a volume of a^3.

    Show that the sound velocity, defined in Sect. 6.1.7, is equal to the ratio: $\sqrt{\frac{E_Y}{M_V}}$.
11. From the speed of sound equation, $\nu = (B/\rho)^{½}$, calculate the speed of sound in silicon and compare with the speed of sound in gallium arsenide. Assuming that the largest effect on the velocity comes from the density, why is this result expected?

Problems for Thermal Properties of Crystals

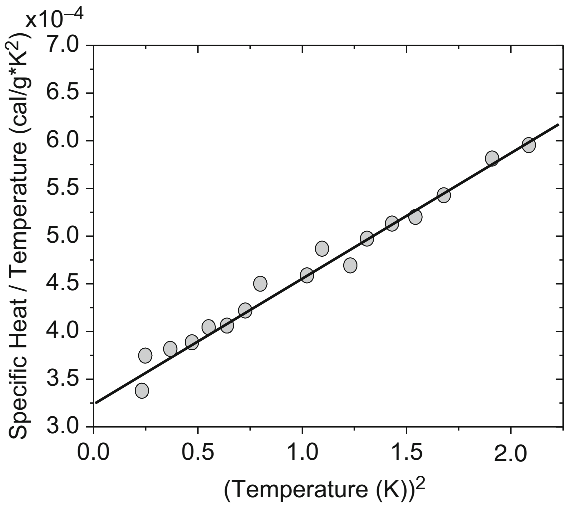
1. In your own words, describe the meaning of the phonon density of states.
2. In your own words, describe the meaning of the Debye frequency and the Debye temperature. Develop a simple equation relating the Debye frequency, Debye temperature, and Debye wavelength.
3. Determine the Debye temperature Θ_D, Debye wavelength, and the Debye frequency ω_D for diamond given that the lattice constant for this material is

3.56 Å, the density of diamond is 3.52×10^3 kg·m^{-3}, and the speed of sound in diamond is 12,000 m·s^{-1}.

4. In your own words, describe the meaning of heat capacity. How is heat capacity related to specific heat?
5. Starting from the expression of the total energy carried by the lattice vibrations in Eq. (6.60), show that the heat capacity $C_v = \left(\frac{dE}{dT}\right)_v$ can be written as:

$$C_v = 9Nk_b\left(\frac{T}{\Theta_D}\right)^3 \int_0^{\frac{\Theta_D}{T}} \frac{x^4 e^x}{(e^x - 1)^2} dx$$

6. It takes 450 cal to raise the temperature of a metallic sample from 20 to 35 °C. What is the heat capacity of the metal sample? If the sample has a mass of 78 g, what is the specific heat of the sample?
7. The specific heat of metals is dominated by the electronic contribution at low temperatures and by phonons at high temperatures. At what temperature are the two contributions equal in rubidium? Note that $\gamma = 2.41$ mJ/(mole K^2) for rubidium. Briefly describe your thinking.
8. The figure below illustrates measurements of the specific heat (plotted as C/T versus T^2) for a crystalline element. Use what you know about the origins and temperature dependence of the specific heat capacity to determine whether the element is Na or Si. Discuss both possibilities.



Experimental data of the specific heat of an unknown element.

9. In your own words, describe the meaning of thermal expansion in solid-state engineering.
10. Look up in tables or reference books the room temperature lattice constants for the following crystals: aluminum, copper, iron, silicon, germanium, and diamond. Using the coefficients of linear expansion, plot the values of the lattice constants up to a temperature of 1000 °C.
11. In your own words, briefly describe the meaning of thermal conductivity and the physical processes that influence the thermal conductivity.
12. Diamond is an electrical nonconductor; however, the thermal conductivity of diamond is greater than the thermal conductivity of copper for $T > 40$ K. How can this be explained?

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