

TOPIC 4: LATTICE VIBRATIONSPRIMARY READING ASSIGNMENT

“Dynamics of Crystal Lattices”, from *Solid State and Semiconductor Physics*, J.P. McKelvey

SUPPLEMENTARY REFERENCE

“Phonons I: Crystal Vibrations” from *Introduction to Solid State Physics*, Charles Kittel

LECTURE PROGRAM

1. Elastic Vibrations of Continuous Media
 - a. Stress, strain
 - b. Hooke's law, elastic modulus
 - c. Wave equation
 - d. Solutions to the wave equation
 - e. Phase velocity
2. Group Velocity of Harmonic Wave Trains
 - a. Superposition of sinusoids of ω , k and $\omega+d\omega$, $k+dk$
 - b. Group velocity
 - c. Dispersion
3. Wave Motion on a One-dimensional Atomic Lattice
 - a. Displacement of the n^{th} atom
 - b. Equation of motion, and solutions to the equation
 - c. Dispersion relation
 - d. Phase velocity
 - e. Group velocity
 - f. Limiting case of $k \ll \pi/a$ ($\lambda \gg 2a$)
 - g. Significance of $k = \pi/a$ ($\lambda = 2a$)
 - h. Normal modes
4. One-dimensional Diatomic Lattice
 - a. Atomic displacement and equations of motion
 - b. Dispersion relation
 - c. Acoustic branch
 - d. Optical branch
5. Forbidden Frequency Region
6. Three-Dimensional Lattices
7. Optical Excitation of Lattice Vibrations in Ionic Crystals

CHAPTER 3

DYNAMICS OF CRYSTAL LATTICES

3.1 ELASTIC VIBRATIONS OF CONTINUOUS MEDIA

We now must investigate the characteristics of elastic vibrational motion of crystal lattices. We shall find that there are important differences between elastic waves in lattice structures composed of discrete atoms and waves in completely continuous and homogeneous elastic media. In order to be able to appreciate these differences clearly we shall first briefly review some of the major features of elastic waves in homogeneous, isotropic, linear elastic substances. We shall discuss only one-dimensional wave motion in detail, but we shall try to indicate wherever necessary how the results may be extended to describe two- and three-dimensional systems.

Consider an element of a homogeneous, isotropic elastic substance of length Δx and of uniform cross-sectional area $\Delta y \Delta z$. In the absence of elastic strain, this element extends from x to $x + \Delta x$ along the x -axis, as shown in Figure 3.1. In the

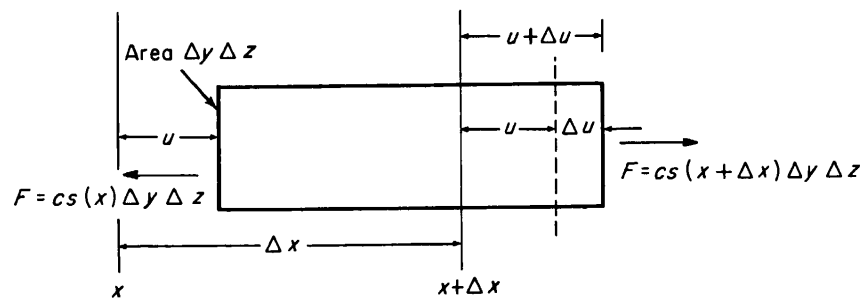


FIGURE 3.1. Displacement and extensional strain of a volume element which originally extended from x to $x + \Delta x$. In the strained condition the element extends from $x + u$ to $x + \Delta x + u + \Delta u$.

presence of a stress, an elastic strain is produced, the equilibrium position of the left-hand end of the element being displaced a distance u along the x -axis, and the right-hand end of the element being displaced a distance $u + \Delta u$. If the elastic medium is a linear one, the applied stress and the resulting strain are related linearly by Hooke's law. The strain s is defined as the elastic extension of the element per unit length, that is,

$$s(x) = \lim_{\Delta x \rightarrow 0} \frac{\Delta u}{\Delta x} = \frac{\partial u}{\partial x}, \quad (3.1-1)$$

whereas the stress is the force per unit area acting on the element. According to

Hooke's law, then, if $F(x)$ is the total force acting at point x ,

$$F(x) = cs(x)\Delta y \Delta z, \quad (3.1-2)$$

where c is the elastic modulus of the material. Likewise, at the point $x + \Delta x$,

$$F(x + \Delta x) = cs(x + \Delta x)\Delta y \Delta z. \quad (3.1-3)$$

The total force on the element must be related to the acceleration of the element by Newton's law, whereby

$$F(x + \Delta x) - F(x) = c[s(x + \Delta x) - s(x)]\Delta y \Delta z = ma, \quad (3.1-4)$$

where m is the mass of the element and a its acceleration. Expanding $s(x + \Delta x)$ in a Taylor's series about the point x and neglecting terms of second order and higher in Δx , which will in any case vanish in the limit as $\Delta x \rightarrow 0$, we find

$$c \frac{\partial s}{\partial x} \Delta x \Delta y \Delta z = ma. \quad (3.1-5)$$

But the mass of the element is its density ρ times the volume $\Delta x \Delta y \Delta z$, the acceleration is $\partial^2 u / \partial t^2$, and the strain, according to the definition (3.1-1) is $\partial u / \partial x$. Making these substitutions, (3.1-5) becomes

$$\frac{\partial^2 u}{\partial x^2} = \frac{\rho}{c} \frac{\partial^2 u}{\partial t^2}. \quad (3.1-6)$$

This is the *wave equation* for the amplitude of elastic waves in a linear homogeneous medium as a function of x and t , where the elastic strain is confined to the x -direction.

Solutions to this equation may be written in the form

$$u(x, t) = Ae^{i(\omega t - 2\pi x/\lambda)} = Ae^{i(\omega t - kx)}, \quad (3.1-7)$$

where

$$k = 2\pi/\lambda. \quad (3.1-8)$$

The solution (3.1-7) represents a sinusoidal disturbance of frequency ω and wavelength λ which is propagated along the positive x -axis. It is usually more convenient to express the results of calculations involving harmonic vibrations in terms of the *propagation constant* k than in terms of λ itself. The propagation direction of the wave is reversed by changing the sign of k . If the solution (3.1-7) is differentiated and substituted back into the wave equation (3.1-6), it will be seen that in order for (3.1-6) to be satisfied, ω and k must be related by

$$\omega = k\sqrt{c/\rho}. \quad (3.1-9)$$

The phase velocity of a wave is the rate of advance of a point of constant phase along the propagation direction of the wave. To determine the phase velocity, we may examine the motion of a point of constant phase, and for convenience let us

choose that point to be the point of *zero* phase. Since the phase angle, according to (3.1-7) is $\omega t - kx$, the equation of motion of the zero-phase point is

$$\omega t - kx = 0$$

or,
$$x = \frac{\omega}{k} t = v_p t. \quad (3.1-10)$$

The phase point is seen to advance at constant phase velocity v_p equal to ω/k . According to (3.1-9) the phase velocity for these waves may be expressed as

$$v_p = \omega/k = \sqrt{c/\rho}, \quad (3.1-11)$$

whence it is clear that the wave equation (3.1-6) can be written in the form

$$\frac{\partial^2 u}{\partial x^2} = \frac{1}{v_p^2} \frac{\partial^2 u}{\partial t^2}. \quad (3.1-12)$$

For this particular case the phase velocity is *independent* of frequency and wavelength, and depends only upon the physical constants c and ρ associated with the elastic medium.

3.2 GROUP VELOCITY OF HARMONIC WAVE TRAINS

Let us now investigate what happens when two wave trains, one of frequency ω and propagation constant k , the other of slightly different frequency $\omega + d\omega$ and propagation constant $k + dk$, are superposed. We shall assume for simplicity that the maximum amplitudes of the two wave trains are the same, in which case the two amplitudes may be written

$$\begin{aligned} u_1 &= A \cos(\omega t - kx) \\ u_2 &= A \cos[(\omega + d\omega)t - (k + dk)x]. \end{aligned} \quad (3.2-1)$$

The amplitude of the superposition is then

$$u_1 + u_2 = A[\cos(\omega t - kx) + \cos[(\omega + d\omega)t - (k + dk)x]] = A[\cos \alpha + \cos \beta]. \quad (3.2-2)$$

But from elementary trigonometry,

$$\cos \alpha + \cos \beta = 2 \cos \frac{1}{2}(\alpha - \beta) \cos \frac{1}{2}(\alpha + \beta), \quad (3.2-3)$$

and from (3.2-2) we have

$$\alpha + \beta = 2\omega t - 2kx + t d\omega - x dk \cong 2(\omega t - kx), \quad (3.2-4)$$

and

$$\alpha - \beta = x dk - t d\omega. \quad (3.2-5)$$

In (3.2-4) the differential terms $t d\omega$ and $x dk$ may be neglected as small in comparison with the other terms; in (3.2-5) there are no "large" terms, and the differential terms are important. Substituting (3.2-4) and (3.2-5) into (3.2-2), we find

$$u_1 + u_2 = 2A \cos(\omega t - kx) \cos\left(\frac{1}{2}x dk - \frac{1}{2}t d\omega\right). \quad (3.2-6)$$

This superposition represents a wave characterized by the original values of ω and k multiplied by a sinusoidal envelope of much longer wavelength $4\pi/dk$, called an "envelope of beats," as shown in Figure 3.2. The motion of this envelope can be

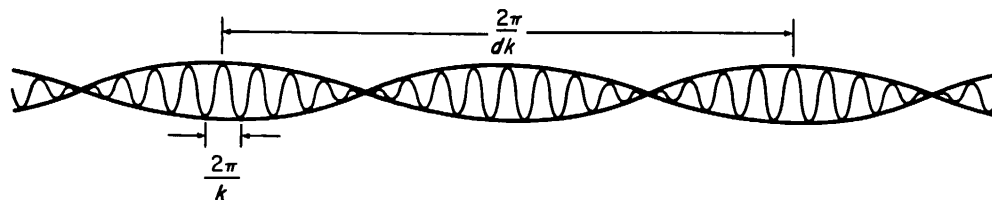


FIGURE 3.2. Wave train formed by superposing two sinusoidal waves of frequencies ω and $\omega + d\omega$ and propagation constants k and $k + dk$.

examined, and in particular the phase velocity of the *envelope* (corresponding to the velocity of the groups or "beats" along the propagation direction) determined by the same procedure used for a simple harmonic wave in Section 3.1. The equation of motion of the zero-phase point of the envelope is thus

$$x dk - t d\omega = 0,$$

or,

$$x = \frac{d\omega}{dk} t = v_g t. \quad (3.2-7)$$

The envelope, or the groups of waves, are thus seen to move with a velocity $d\omega/dk$; this velocity is termed the *group* velocity v_g associated with the waves. It can be shown that the velocity with which the wave transmits energy along the propagation direction is this group velocity.¹ It can readily be seen that this is physically reasonable; for example, in the wave train of Figure 3.2, no energy can ever flow past a node, since the medium at the nodal point is absolutely motionless. The energy must thus be transmitted with the velocity with which the nodes themselves move, that is, the group velocity. For the case of a standing wave, the group velocity is zero, and it is clear that there is no net energy flow in this case.

For the elastic waves in a homogeneous medium which were discussed in Section 3.1, the phase velocity and group velocity are exactly the same, according to equation (3.1-9). This is true because ω is a *linear* function of k , whereby ω/k and $d\omega/dk$ are equal. The same result is true for electromagnetic waves in vacuo, because there again the velocity is a constant independent of frequency and wavelength. The phase velocity and group velocity may *differ* only when the phase velocity ω/k is a function

¹ L. Brillouin, *Wave Propagation in Periodic Structures*, Dover Publications, Inc., New York (1953).

of the frequency ω , thus only when ω itself is *other than a linear function* of k . This situation arises, for example, when light passes through a medium where the index of refraction (and hence the phase velocity) is a function of frequency; the phenomenon is called *dispersion*, and such a medium is referred to as a *dispersive* medium. As we shall soon see, it also arises for the case of elastic waves in a medium which is composed of discrete atoms bound together by Hooke's law forces, especially when the wavelengths involved are not much greater than the interatomic distances.

3.3 WAVE MOTION ON A ONE-DIMENSIONAL ATOMIC LATTICE

We now wish to discuss the longitudinal vibrational motion of a one-dimensional chain of identical atoms of mass m which are bound to one another by linear forces as shown in Figure 3.3. At equilibrium the atoms will be situated on equally spaced equilibrium sites, but when vibrational motion is excited, they will execute periodic motions about these equilibrium positions, the actual displacement of the n th atom

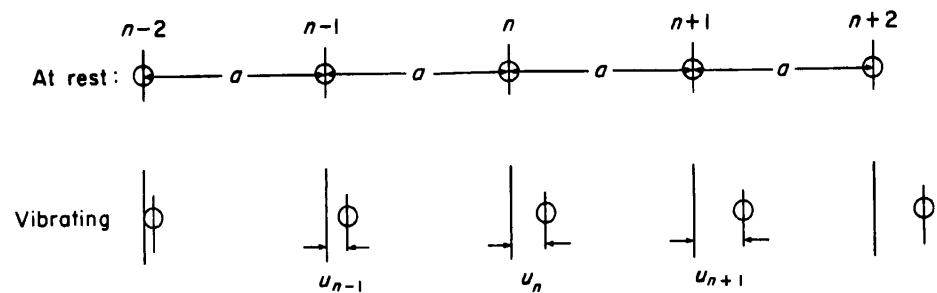


FIGURE 3.3. Geometry of the monatomic linear lattice of Section 3.3.

from its equilibrium position being given by the amplitude u_n . It is assumed that the forces between neighboring atoms are Hooke's law forces, as if the atoms were bound together by ideal springs, and it is further assumed that the only significant force interactions between atoms are direct nearest-neighbor interactions. The direct influence of atoms $n+2$, $n+3$, $n+4 \dots$ upon atom n is thus regarded as negligible, although the behavior of atom $n+2$, for example, may indirectly influence atom n insofar as it directly affects atom $n+1$, which in turn acts upon n . Under these assumptions the net force acting upon the n th atom can be written, in terms of the extension of the two "springs" which bind it to atoms $n+1$ and $n-1$, as

$$\begin{aligned} F_n &= \beta(u_{n+1} - u_n) - \beta(u_n - u_{n-1}) \\ &= \beta(u_{n+1} + u_{n-1} - 2u_n), \end{aligned} \quad (3.3-1)$$

where β is the Hooke's law constant which expresses the proportionality between the force required to produce an atomic displacement and the displacement itself.

According to Newton's second law, this force can be expressed as the product of

the mass m of the n th atom times its acceleration, whereby we obtain the equation of motion

$$m \frac{d^2 u_n}{dt^2} = \beta(u_{n+1} + u_{n-1} - 2u_n). \quad (3.3-2)$$

We are seeking periodic solutions to this equation, which we may expect to have the form

$$u_n = A e^{i(\omega t - k n a)}, \quad (3.3-3)$$

in analogy with (3.1-7). In (3.3-3), however, we must represent the coefficient of k in the exponent as the x -coordinate of the n th atom of the chain, i.e., na . According to this scheme, we should then expect that

$$u_{n+1} = A e^{i[\omega t - k(n+1)a]}$$

and

$$u_{n-1} = A e^{i[\omega t - k(n-1)a]}. \quad (3.3-4)$$

If the solution (3.3-3) is now differentiated twice with respect to time, and, along with (3.3-4), substituted back into the equation of motion (3.3-2), the result is

$$\begin{aligned} -m\omega^2 &= \beta(e^{ika} + e^{-ika} - 2) \\ &= 2\beta(\cos ka - 1). \end{aligned} \quad (3.3-5)$$

However, since

$$1 - \cos \theta = 2 \sin^2 \frac{1}{2}\theta, \quad (3.3-6)$$

this may be expressed in the form

$$\omega = \sqrt{4\beta/m} |\sin \frac{1}{2}ka|. \quad (3.3-7)$$

The absolute value signs are needed in (3.3-7) only because we must regard the frequency as an essentially positive quantity, regardless of whether k is positive or negative, that is, regardless of whether the wave is propagated to the right or to the left along the chain.

We see, thus, that there are solutions of the form (3.3-3) provided that ω is related to k by (3.3-7). It is evident that in this case ω is not a linear function of k , so that the medium we are dealing with is a dispersive one; a relation such as (3.3-7) which gives ω as a function of k is called a *dispersion relation*. Figure 3.4 shows a plot of ω vs. k , as given by (3.3-7). From this (and from (3.3-7)) it will be noted that if we restrict ourselves to values of k which are much less than π/a , and thus to values of λ which are much greater than twice the interatomic distance a , ω is approximately linear with k , since then $\sin \frac{1}{2}ka \cong \frac{1}{2}ka$ and

$$\omega \cong ka \sqrt{\beta/m}. \quad (3.3-8)$$

In this long-wavelength limit the phase velocity will be essentially constant, since

$$v_p = \omega/k = a \sqrt{\beta/m} = v_0. \quad (3.3-9)$$

In this same limit the group velocity is seen to be

$$v_g = d\omega/dk = a\sqrt{\beta/m} = v_0, \quad (3.3-10)$$

thus constant and equal to the phase velocity under these conditions. For very long wavelengths, then, the dispersion effects are negligible and the medium acts like

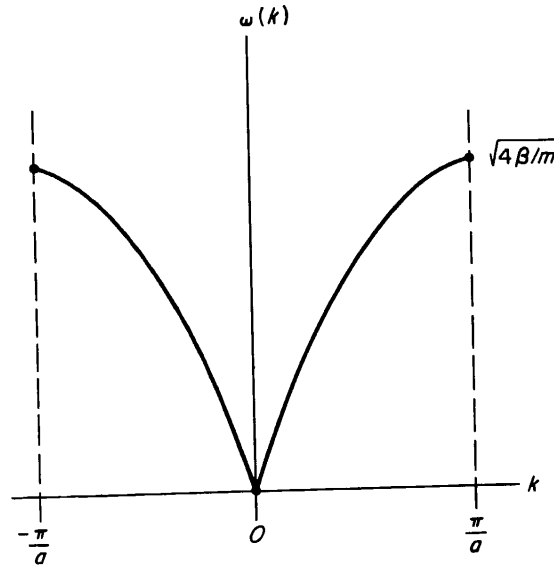


FIGURE 3.4. Dispersion relation for the monatomic linear lattice of Section 3.3.

continuous and homogeneous elastic medium. This is, of course, most reasonable from a physical point of view, since for such long wavelengths the "atomic" nature of the chain is of little importance insofar as the dynamical behavior of the system is concerned. As k increases, however, the dispersion effects become more important and ω no longer varies linearly with k . Under these conditions, we find from (3.3-7) that

$$v_p = \omega/k = v_0 \frac{|\sin \frac{1}{2}ka|}{\frac{1}{2}ka} \quad (3.3-11)$$

and

$$v_g = d\omega/dk = v_0 |\cos \frac{1}{2}ka|, \quad (3.3-12)$$

where $v_0 = a\sqrt{\beta/m}$ is the long wavelength limit of both v_p and v_g , as shown by (3.3-9) and (3.3-10). Figures 3.5 and 3.6 show plots of v_p and v_g as functions of k .

It will be observed from Figure 3.6 that $v_g \rightarrow 0$ as $k \rightarrow \pi/a$ and thus as $\lambda \rightarrow 2a$, in this case the phase of vibration of neighboring atoms differ by π radians, and the character of the motion is simply a standing wave. This condition also corresponds to Bragg reflection of the elastic vibrations from successive atoms of the crystal; for this geometry the Bragg angle θ of the Bragg equation (2.1-1) is $\pi/2$, corresponding to normal incidence, in which case the Bragg equation reduces to $\lambda = 2d$ for the first order of reflection. The actual physical character of the motion is illustrated by Figure 3.7 for the long wavelength case and for the condition $\lambda = 2a$ in which the standing

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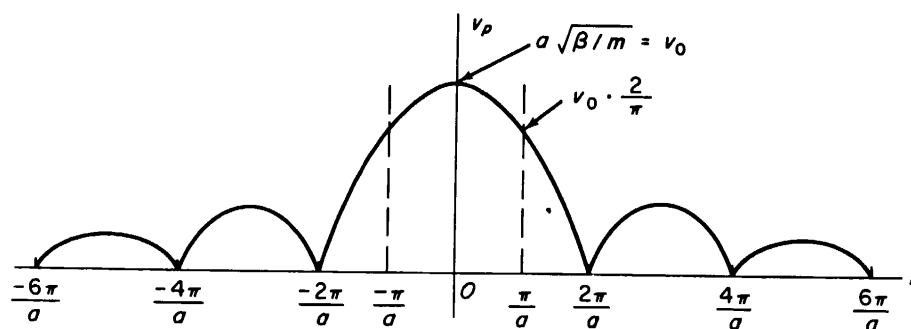


FIGURE 3.5. Phase velocity as a function of the propagation constant k for the monatomic linear lattice. [After L. Brillouin, *Wave Propagation in Periodic Structures*, McGraw-Hill, New York (1946), with permission.]

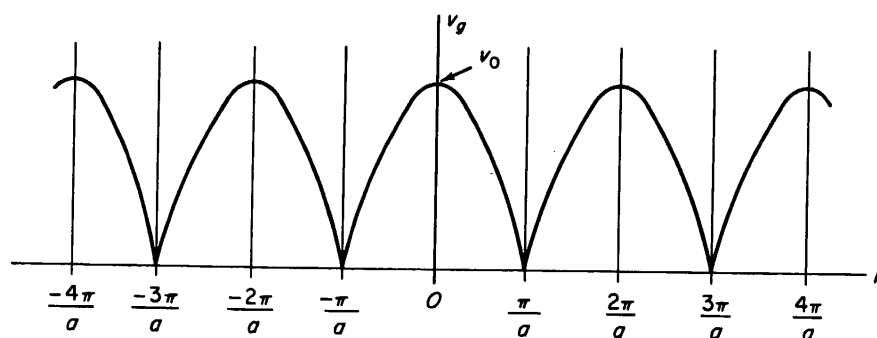


FIGURE 3.6. Group velocity as a function of the propagation constant k for the monatomic linear lattice.

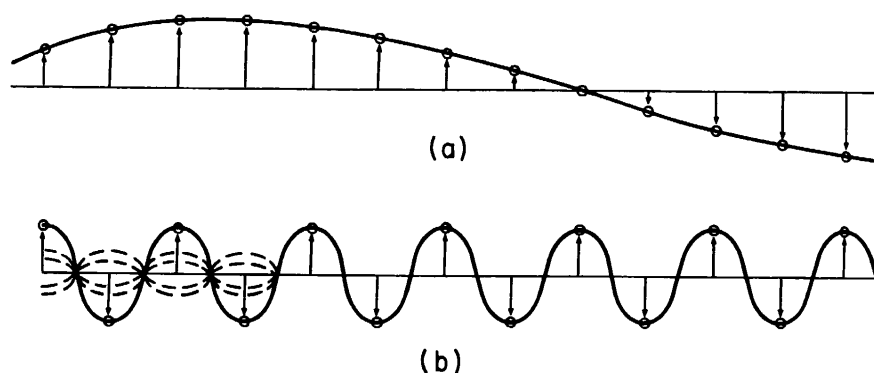


FIGURE 3.7. Atomic displacements on the monatomic linear lattice (a) for wavelength much larger than the interatomic spacing, (b) in the limit where $\lambda = 2a$. The displacements are shown as transverse ones for the sake of clarity in representation, but it should be remembered that the actual displacements which are discussed in the text are *longitudinal*. [After Brillouin.]

waves are set up. In these figures the atomic displacements are represented as transverse displacements for convenience of illustration, although, of course, the actual atomic motions which are we discussing are assumed to be *longitudinal* ones in which the actual atomic displacements are along the chain, rather than normal to it.

For any given value of k in the region $-\pi/a < k < \pi/a$ there will be a vibrational motion involving certain possible atomic displacements, as shown by Figure 3.8. However, as also shown in that figure, the *same* set of displacements of atoms as that associated with this wave can *also* be associated with a wave of larger k (thus smaller

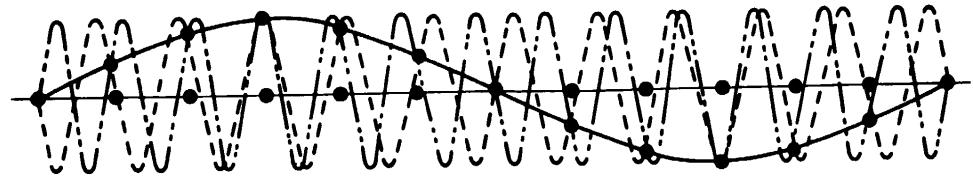


FIGURE 3.8. A single set of atomic displacements represented by several sinusoidal waves of various wavelengths. [From L. Brillouin, *Wave Propagation in Periodic Structures*, McGraw-Hill, New York (1946).]

λ), and with still another of even larger k . In other words, there may be many representations of the same atomic displacement pattern, each involving a different value of k and hence a different value of λ . These different representations can be shown to be associated with different periods of the ω vs. k plot. Each of the possible representations must have the same value of ω ; therefore on a plot of ω vs. k showing several periods of the curve, such as Figure 3.9, there will be many possible values

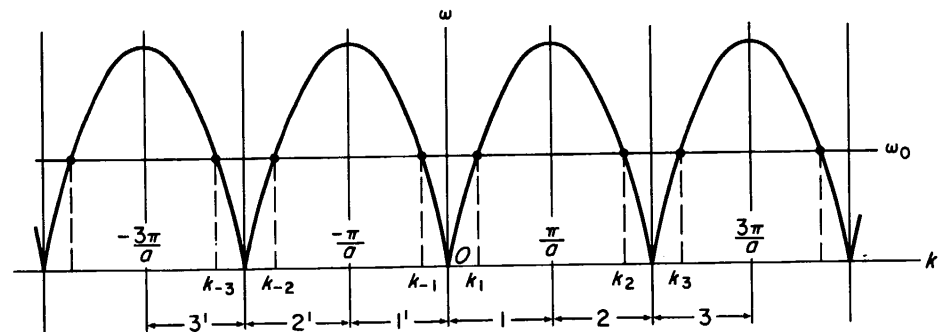


FIGURE 3.9. Several periods of the dispersion relation for the linear monatomic lattice. Note that many values of k may be associated with any given frequency within the allowed range.

of k corresponding to the same ω . In the central region, extending from $-\pi/a$ to π/a there are only two possibilities, a wave propagating to the right with propagation constant k_1 , and one propagating to the left with propagation constant $k_{-1} = -k_1$. The regions marked 2 and 2' in the figure, which contain two more possible solutions, k_2 and $k_{-2} = -k_2$, can be superimposed upon the central region by translating region 2 to the left a distance $2\pi/a$ and translating region 2' to the right a distance $2\pi/a$. The character of the possible solutions in region 2 is the same as that for the possible solutions in region 1', except for a difference in k -values of $2\pi/a$; the same can be said for regions 2' and 1. Likewise, the regions 3 and 3', containing two possible solutions, for which $k = k_3$ and $k = k_{-3} = -k_3$, can be superimposed upon the central region $-\pi/a < k < \pi/a$ by translating region 3 to the left a distance $2\pi/a$ and 3' to the right a distance $2\pi/a$; the physical character of the solutions in these regions thus coincides with those in the central region except for differences in k -values of $2\pi/a$. Similar

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relations may be observed for higher zones. The physical fact of importance is that any possible arrangement of atomic positions which is compatible with a sinusoidal solution of *any* wavelength, however short, can be represented as, or *reduced* to a sinusoidal solution for which $-\pi/a < k < \pi/a$, and which thus belongs to the central zone. For this reason, it is not necessary in this case to consider vibrations other than those belonging to the central zone $-\pi/a < k < \pi/a$. This central region (1 and 1' in Figure 3.9) is called the *first Brillouin Zone*; the regions 2 and 2', 3 and 3', etc., for each of which the physical character of solutions is the same as that for the first zone except for a translation along the k -axis by a distance equal to an integral multiple of $2\pi/a$, are referred to as the second, third, etc., Brillouin Zones, respectively. We shall have further occasion to use the concept of Brillouin Zones in connection with the quantum mechanical behavior of electrons in periodic lattices.²

We must also determine how many possible *normal modes* of vibration (in other words, how many independent solutions of the wave equation which satisfy a given set of boundary conditions) can be associated with a linear chain of atoms. Suppose, for example, we consider a chain which is rigidly fixed at both ends. If the chain, which we shall take to be of length L , were a homogeneous and continuous medium, then any vibration of the form

$$u(x,t) = A \sin k_n x \sin \omega t \quad (3.3-13)$$

with

$$k_n = n\pi/L, \quad (3.3-14)$$

where n is an integer, would satisfy the boundary conditions that the displacement u at the two ends of the chain at $x = 0$ and $x = L$ must vanish, and hence would qualify as a normal mode of vibration of the system. This situation is illustrated in Figure 3.10. If the chain, however, is made up of discrete atoms, then the maximum value

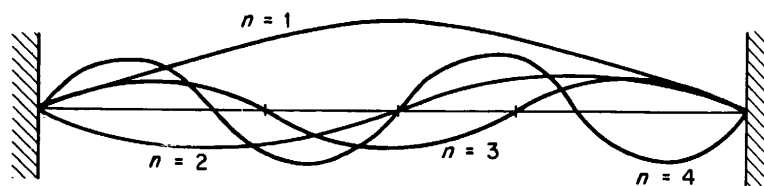


FIGURE 3.10. A set of sinusoidal displacements of a transversely vibrating string, all of which satisfy the boundary condition that the displacement vanish at both ends. These various sinusoidal configurations may be regarded as *normal modes* for the system under this particular boundary condition.

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of k is given by π/a , which corresponds to a minimum value of wavelength of $2a$, as shown by Figure 3.7(b). Any larger value of k or any smaller value of λ corresponds simply to a repetition of some configuration which can be described by a value of k within the central zone. The possible values of k for such a system are, according to (3.3-14) $k = \pi/L, 2\pi/L, 3\pi/L, \dots \pi/a$. But if there are N atoms in a chain of length L , each separated from its neighbor by a distance a , then $a = L/(N - 1)$, and hence the

² It should be noted that the phase velocities of equivalent waves in different Brillouin Zones differ, but this fact has no direct physical import.

permitted values of k for normal vibrations of this type are $k = \pi/L, 2\pi/L, 3\pi/L, \dots, (N-1)\pi/L$, giving a total of $N-1$ modes. The mode for which $k = (N-1)\pi/L$ ($\lambda = 2a$), however, must be excluded in this case, because it cannot be excited unless the end atoms move, which is forbidden by the boundary conditions. The actual number of normal modes of vibration under these boundary conditions is then $N-2$; that is, the number of atoms in the chain less two. Of course, if N is a very large number, it makes very little difference whether the number of normal modes is regarded as $N-2$ or simply N .

We should note that it is the physical boundary conditions which are imposed upon the system which limit the possible values of k to a certain finite number out of the continuum of possible values between $-\pi/a$ and π/a which are permitted by the solutions of the differential equations of motion of the system. As the above discussion shows, when we hold the ends of the chain rigidly fixed, we select a set of $N-2$ possible values of k corresponding to solutions which satisfy these boundary conditions, out of this infinite set of possible values. In any actual problem we must, however, select *some* boundary conditions on the elastic waves, and as far as the *number* of possible normal modes is concerned, it turns out that it makes little difference precisely what set of physically reasonable boundary conditions are selected. In each case there will be essentially N possible normal modes of vibration which satisfy the boundary conditions which have been picked, provided the number of atoms N is much larger than unity. This result is found also to apply to two- and three-dimensional systems.

It will be useful in many instances to select as a boundary condition the requirement that the vibrational amplitude of the N th atom be precisely the same as that of the first atom. Physically this would correspond to a linear chain which is bent into the form of a ring, the N th atom joining on to the first to close the chain. Boundary conditions of this sort are called *periodic* boundary conditions; the application of these boundary conditions to the solutions (3.3-3) of the equations of motion will yield the same result—that there can be essentially N solutions of the equations of motion which *also* satisfy the periodic boundary conditions. The details of proving this result are assigned as an exercise for the reader.

3.4 THE ONE-DIMENSIONAL DIATOMIC LATTICE

So far, in our examination of the dynamical properties of crystal lattices, we have concerned ourselves with the case where all the atoms of the lattice are identical. Since many common crystals are diatomic compounds, which contain atoms of two distinct chemical species, and since the dynamical characteristics of their lattices differ in a number of important ways from those of monatomic crystals, we must now address ourselves to a study of elastic vibrations in crystals of this type.

Consider now a lattice in which atoms of two species are arranged alternately, each atom being separated from its two neighbors by a distance a , as shown in Figure 3.11. The mass of the lighter atom is denoted by m , that of the heavier atom by M . The assumptions of Section 3.3 in regard to Hooke's law forces between atoms and the direct consideration of nearest neighbor interactions only are made here also. It is now necessary to write separate equations of motion for the light and heavy atoms;

this may be done in exact analogy with the procedure of Section 3.3, the result being

$$F_{2n} = m \frac{d^2 u_{2n}}{dt^2} = \beta(u_{2n+1} + u_{2n-1} - 2u_{2n}),$$

$$F_{2n+1} = M \frac{d^2 u_{2n+1}}{dt^2} = \beta(u_{2n+2} + u_{2n} - 2u_{2n+1}).$$
(3.4-1)

Again, we must seek solutions of the form $(\text{const.})e^{i(\omega t - kx)}$, representing the x -coordinate of the atom in terms of its position along the chain as in (3.3-3) and (3.3-4).

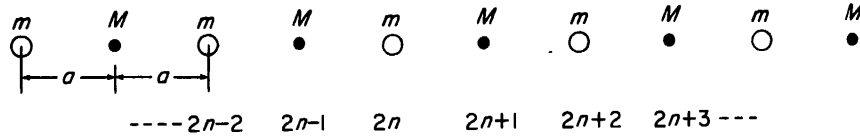


FIGURE 3.11. Geometry of the diatomic linear lattice of Section 3.4.

Since the two kinds of atoms have different masses, their respective vibration amplitudes will not, in general, be equal, nor is it perfectly clear at this point that their frequencies are the same, although, as we shall see, this turns out to be the case. We thus assume solutions of the form

$$u_{2n} = Ae^{i(\omega_1 t - 2kna)}$$

and

$$u_{2n+1} = Be^{i(\omega_2 t - [2n+1]ka)}. \quad (3.4-2)$$

If u_{2n} and u_{2n+1} are given by these expressions, then according to the rule that the coefficient of k in the exponent must represent the x -coordinate of the atom in question, we must also have

$$u_{2n+2} = Ae^{i(\omega_1 t - [2n+2]ka)} = u_{2n} e^{-2ika}$$

$$u_{2n-1} = Be^{i(\omega_2 t - [2n-1]ka)} = u_{2n+1} e^{2ika}.$$
(3.4-3)

Differentiating the solutions (3.4-2) twice with respect to time and substituting back into the equations of motion (3.4-1), using (3.4-3) to express all displacements in terms of u_{2n} and u_{2n+1} , we find

$$-m\omega_1^2 u_{2n} = \beta[(1 + e^{2ika})u_{2n+1} - 2u_{2n}]$$

$$-M\omega_2^2 u_{2n+1} = \beta[(1 + e^{-2ika})u_{2n} - 2u_{2n+1}].$$
(3.4-4)

Solving the second of these equations for u_{2n+1} , we see that

$$u_{2n+1} = \frac{\beta(1 + e^{-2ika})}{2\beta - M\omega_2^2} u_{2n}. \quad (3.4-5)$$

The equations of motion require that this relation be satisfied for all values of time. However, if the values for u_{2n} and u_{2n+1} as given by (3.4-2) are substituted into (3.4-5),

it is clear that this requirement can be satisfied for all values of t only if ω_1 and ω_2 are equal. Accordingly, taking

$$\omega_1 = \omega_2 = \omega, \quad (3.4-6)$$

then substituting (3.4-5) into the first of Equations (3.4-4), expressing the exponentials in terms of trigonometric functions and simplifying, it is found that

$$(2\beta - M\omega^2)(2\beta - m\omega^2) - 4\beta^2 \cos^2 ka = 0. \quad (3.4-7)$$

Rearranging this equation, collecting like powers of ω , we obtain, finally

$$\omega^4 - \frac{2\beta(m+M)}{mM} \omega^2 + \frac{4\beta^2 \sin^2 ka}{mM} = 0. \quad (3.4-8)$$

This quadratic equation in ω^2 can easily be solved by the quadratic formula to give *two* solutions for ω^2 , which we shall call ω_+^2 and ω_-^2 , according to whether the + or - sign in the quadratic formula is chosen. The result is

$$\omega_{\pm}^2 = \frac{\beta(m+M)}{mM} \left[1 \pm \sqrt{1 - \frac{4mM \sin^2 ka}{(m+M)^2}} \right]. \quad (3.4-9)$$

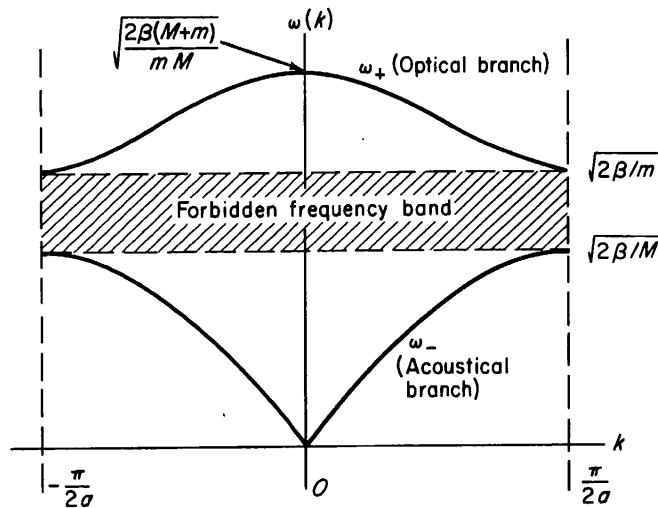


FIGURE 3.12. Dispersion relation for the diatomic linear lattice, showing acoustical and optical branches.

A plot of this result is shown in Figure 3.12. There are two branches of the ω vs. k curve, corresponding to whether the + or - sign is taken in (3.4-9). The upper branch, $\omega_+(k)$, is called the *optical* branch, while the lower one, $\omega_-(k)$, is called the *acoustical* branch. The significance of this terminology will become apparent in due course. For *small* values of k , $\sin ka \cong ka$, and the two roots become

$$\omega_+(0) = \sqrt{\frac{2\beta(m+M)}{mM}} \quad (3.4-10)$$

ω_1 and ω_2

(3.4-6)

exponentials

(3.4-7)

(3.4-8)

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(3.4-9)

and

$$\omega_-(k) = ka \sqrt{\frac{2\beta}{m+M}} \quad (ka \ll \pi/2). \quad (3.4-11)$$

To obtain (3.4-11) one must expand the square root of (3.4-9) in a binomial expansion for small values of the argument.

The smallest possible wavelength of the first Brillouin Zone is twice the unit cell distance of the lattice, which here is $2a$. This gives a minimum wavelength of $4a$, corresponding to a maximum value of k of $\pi/2a$, at the boundary of the first zone. For this value of k , (3.4-9) yields

$$\omega_+ = \sqrt{2\beta/m} \quad (3.4-12)$$

and

$$\omega_- = \sqrt{2\beta/M}.$$

We may better understand the physical characteristics of the motion by examining what happens when $k \rightarrow 0$. For this case, the ratio of the amplitudes B/A is readily obtained from (3.4-5), the result being

$$\lim_{k \rightarrow 0} \frac{u_{2n+1}}{u_{2n}} = \frac{B}{A} = \frac{2\beta}{2\beta - M\omega_{\pm}^2}. \quad (3.4-13)$$

For the acoustical branch, $\omega = \omega_-$, as given by (3.4-11), and as $k \rightarrow 0$, $\omega_- \rightarrow 0$, whereby $B/A = 1$. Hence, for the acoustical mode of vibration, the two types of atoms move in the same direction with the same amplitude, as shown in Figure 3.13(a). For

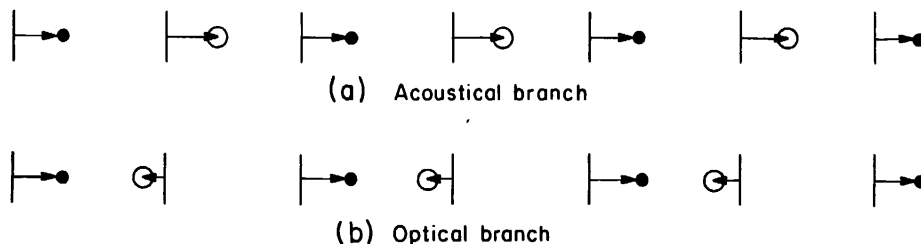


FIGURE 3.13. Physical displacements associated with long wavelength vibrations belonging to (a) acoustical branch, (b) optical branch.

the optical branch, $\omega = \omega_+$ in (3.4-13), and using (3.4-10) it is readily seen that in this instance, $B/A = -m/M$. For the optical branch at $k = 0$, then, the vibrations of the atoms are in *opposite* directions and the amplitudes are inversely in the ratio of the masses, so that the center of mass of the unit cell remains fixed during the period of the motion, as shown in Figure 3.13(b). These characteristics are typical of the optical and acoustical branch in general. The optical mode vibrations in ionic crystals where the two types of atoms are oppositely charged, can be excited by an electric field, which tends to move the ions in opposite directions. Specifically, in ionic substances, this mode can be excited by the electric field associated with a light wave, from which the term *optical* mode vibrations is derived.

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3.5 THE FORBIDDEN FREQUENCY REGION

According to Figure 3.12, there exists a band of frequencies $2\beta/M < \omega^2 < 2\beta/m$ where no solutions of the form (3.4-2) exist. It turns out that frequencies in this range simply cannot be propagated as continuous undamped harmonic vibrations of the lattice. If one attempts to excite vibrations of a frequency lying within this band the vibrations are *attenuated* or damped by the lattice, the attenuation coefficient depending upon the frequency, the atomic masses, and the force constant.

To see this more clearly, let us write (3.4-7) in the form

$$\begin{aligned}\cos ka &= \sqrt{\left(1 - \frac{m\omega^2}{2\beta}\right)\left(1 - \frac{M\omega^2}{2\beta}\right)} \\ &= i\sqrt{\left(1 - \frac{m\omega^2}{2\beta}\right)\left(\frac{M\omega^2}{2\beta} - 1\right)} = i\delta.\end{aligned}\quad (3.5-1)$$

Since in the region $2\beta/M < \omega^2 < 2\beta/m$ the first factor in the top equation of (3.5-1) is positive and the second negative, it is clear that $\cos ka$ must be imaginary in this region of frequency, whereby ka itself must be a complex number. If the square root is written in the second form above, $\cos ka$ is expressed as an imaginary quantity $i\delta$, where δ is a *real* number in the frequency range of interest.

The cosine of a complex number may be expressed as the sum of real and imaginary parts by a simple calculation using Euler's theorem, as follows:

$$\cos z = \cos(x + iy) = \cos x \cosh y - i \sin x \sinh y. \quad (3.5-2)$$

Setting this equal to $i\delta$, as required by (3.5-1), and equating real and imaginary parts of the resulting equation, one obtains

$$\cos x \cosh y = 0, \quad (3.5-3)$$

$$\sin x \sinh y = -\delta. \quad (3.5-4)$$

In (3.5-3), $\cosh y$ is never zero for any value of y , hence $\cos x = 0$ and $x = \pm\pi/2$, whereby $\sin x = \pm 1$. Substituting this value into (3.5-4), it is clear that

$$y = \mp \sinh^{-1} \delta, \quad (3.5-5)$$

$$\text{whence} \quad z = ka = x + iy = \pm \frac{\pi}{2} \mp i \sinh^{-1} \delta \quad (3.5-6)$$

and the solutions of the wave equation (3.4-2) become

$$\begin{aligned}u_{2n} &= Ae^{i\omega t} e^{-2ikna} = Ae^{i\omega t} e^{-2ni(\pm\pi/2 \mp i \sinh^{-1} \delta)} = \pm Ae^{i\omega t \mp 2n \sinh^{-1} \delta} \\ &= \pm Ae^{i\omega t} e^{\mp 2na \cdot a^{-1} \sinh^{-1} \delta}.\end{aligned}\quad (3.5-7)$$

These are attenuated or damped oscillations; the minus sign in the exponent must be

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chosen for the physically real case of damped waves (the plus sign represents growing waves whose amplitude increases exponentially along the chain). The attenuation constant κ , defined by writing the solution (3.5-7) as

$$u_{2n} = Ae^{i\omega t}e^{-2\kappa na} \quad (3.5-8)$$

is given by

$$\kappa = \frac{1}{a} \sinh^{-1} \delta, \quad (3.5-9)$$

where δ , in turn, is given by (3.5-1). The same general situation is found to prevail for values of ω in excess of $\omega_+(0)$ as given by (3.4-10), and also in the case of the monatomic chain for values of ω in excess of $\sqrt{4\beta/m}$; in each case it is found that the lattice simply cannot propagate frequencies in these ranges, and that any such disturbance must be damped or attenuated by the lattice.

We have so far discussed only longitudinal waves in one-dimensional lattices; it should, however, be understood that it is also possible to excite *transverse* vibrations in which the atomic displacements are perpendicular to the chain, rather than along it. The characteristics of these transverse waves are in general very similar to those of the longitudinal waves; the phenomenon of dispersion, the acoustical and optical modes of vibration for diatomic lattices, and the forbidden frequency bands all occur in much the same way as they do for longitudinal waves. Since the transverse waves involve atomic displacements normal to those associated with the longitudinal vibrations, transverse and longitudinal waves may be excited simultaneously and (to a first order of approximation) independently of one another. Likewise, since there are two possible orthogonal and independent displacement directions for transverse waves, two independent transverse oscillations may be excited simultaneously.

3.6 OPTICAL EXCITATION OF LATTICE VIBRATIONS IN IONIC CRYSTALS

In an ionic crystal such as NaCl, the sodium and chlorine atoms are ionized, the sodium atom bearing a charge e and the chlorine atom a charge $-e$. In such crystals, the electric vector of a light wave can excite optical mode vibrations, since an electric field exerts forces on the positive and negative charges which are in opposite directions. In this discussion, we shall assume that we are dealing with a diatomic linear lattice of oppositely charged atoms, extending along the x -direction, and that the light is incident in a direction perpendicular to the atomic chain in such a way that the electric vector of the wave oscillates along the x -axis. Under these conditions, at any given instant of time, all the atoms of the crystal experience the same electric field, neighboring positive and negative ions being subjected to exactly equal but opposite forces. The effect of an exciting field of this type will be to set up *forced* longitudinal vibrations in the crystal lattice, *at the frequency of the exciting source*, that is, the incident light wave. Since the electric field is the same everywhere on the lattice at a given time,

the type of vibration which will be excited will be that of Figure 3.13(b), thus an optical vibration of infinitely long wavelength, for which $k = 0$.

In the presence of such a field, the force on a positive ion is $eE_0e^{i\omega_0 t}$; and on a negative ion, $-eE_0e^{i\omega_0 t}$, where ω_0 is the light frequency and E_0 is the magnitude of the electric vector of the light wave. Accordingly, a force term $eE_0e^{i\omega_0 t}$ should be added to the right-hand side of the first of the equations of motion (3.4-1) and a term $-eE_0e^{i\omega_0 t}$ to the second. If, now, solutions of the form

$$u_{2n} = Ae^{i(\omega_0 t - 2kna)} \quad (3.6-1)$$

$$u_{2n+1} = Be^{i(\omega_0 t - [2n+1]ka)}$$

are assumed, the vibrations thus being assumed to be at the forcing frequency, and the steps leading to Equations (3.4-4) repeated, one obtains

$$\begin{aligned} -m\omega_0^2 u_{2n} &= \beta[(1 + e^{2ika})u_{2n+1} - 2u_{2n}] + eE_0e^{i\omega_0 t} \\ -M\omega_0^2 u_{2n+1} &= \beta[(1 + e^{-2ika})u_{2n} - 2u_{2n+1}] - eE_0e^{i\omega_0 t}. \end{aligned} \quad (3.6-2)$$

Since, physically, the optical vibration which is excited by the light wave is one for which $k = 0$, the above set of equations reduce to

$$\begin{aligned} (2\beta - m\omega_0^2)u_{2n} - 2\beta u_{2n+1} &= eE_0e^{i\omega_0 t} \\ -2\beta u_{2n} + (2\beta - M\omega_0^2)u_{2n+1} &= -eE_0e^{i\omega_0 t}. \end{aligned} \quad (3.6-3)$$

This set of simultaneous equations may be solved for the vibration amplitudes u_{2n} and u_{2n+1} , the result being

$$\begin{aligned} u_{2n} &= \frac{(-eE_0/m)}{\omega_0^2 - \omega_+^2(0)} e^{i\omega_0 t} \\ u_{2n+1} &= \frac{(eE_0/M)}{\omega_0^2 - \omega_+^2(0)} e^{i\omega_0 t}, \end{aligned} \quad (3.6-4)$$

where $\omega_+(0)$ is the long-wavelength limit of the optical branch frequency, as given by (3.4-10).

According to these results, when the incident light frequency is equal to the natural frequency of the lattice for long wavelength optical mode vibrations, $\omega_+(0)$, a resonance effect should be observed, the vibration amplitudes becoming very large. We should expect the very large vibration amplitudes of the charged ions at resonance to give rise to a strong *reradiation* of electromagnetic energy at the resonant frequency. This phenomenon is actually observed for ionic crystals, a single strong peak in the optical reflectivity of the crystal occurring in the far infrared region of the spectrum, typically in the 40 to 100 μ wavelength region. It is possible, knowing the elastic constants of the crystal to arrive at an estimate of the force constant β ; if the atomic masses m and M are then known, the resonance frequency $\omega_+(0)$ as predicted by (3.4-10) can be calculated and compared with the optical frequency at which the reflectivity maximum is observed experimentally. The agreement found in this way is quite good for most simple ionic crystals.

If radiation from a continuous-spectrum infrared source is reflected several times by a given ionic crystal, the resulting residual radiation will be nearly monochromatic light of the lattice resonance frequency, since at other frequencies the reflectivity of the crystal will be rather small, and after several reflections such light will be strongly attenuated. This effect has led to the terminology *residual rays*, or, as the German puts it, *Reststrahlen*, referring to the reflected radiation from an ionic crystal at the reflectivity peak. The presence or absence of the characteristic Reststrahl effect serves to indicate whether a crystal is ionic or covalent, since optical mode vibrations cannot be excited in this manner in a covalent crystal in which the atoms bear no net charge. The intensity of the Reststrahl peak in a mixed ionic-covalent crystal likewise gives a quantitative estimate of the relative strength of the ionic component of the crystal binding.

Associated with the reflectivity peak, of course, is a minimum in the optical *transmission* of the crystal. Although in the simple calculation we have made, we included no provision in the form of damping terms in the equations of motion to account for energy losses from the crystal, in actual fact energy is lost. This energy loss is due not only to the reradiation of the reflected beam, but also for other reasons, the most important of which is that the *anharmonicity* of the lattice vibrations which sets in at the large amplitudes that occur near resonance causes the excitation of other modes of vibration of the lattice.

3.7 BINDING ENERGY OF IONIC CRYSTAL LATTICES³

In an ionic crystal, the forces which hold the crystal together arise primarily from simple electrostatic interactions between the positive and negative ions of the crystal. For this type of binding it is relatively simple to calculate the binding energy of the crystal lattice on a semiempirical basis. The original treatment of this subject is due to Madelung and Born.^{4,5,6}

Let us consider as a specific example a crystal of the NaCl structure, as illustrated in Figure 1.7(a), and let U_{ij} be the potential energy of interaction between ions i and j of the crystal. The total energy of interaction between ion i and all other ions of the crystal will then be

$$U_i = \sum_j' U_{ij}. \quad (3.7-1)$$

The prime on the summation indicates that the term for which $j = i$ is to be *excluded* from the sum, there being obviously no binding interaction between the ion i and itself. In addition to the Coulomb energy of interaction $\pm e^2/r_{ij}$, where r_{ij} is the distance between ions i and j , one must assume that there is a *repulsive* force which becomes

³ This section follows in a general way the treatment given by C. Kittel in *Introduction to Solid State Physics*, John Wiley & Sons, New York (1956).

⁴ E. Madelung, *Physik. Zeitschr.* **11**, 898 (1910).

⁵ M. Born, *Atomtheorie des Festen Zustandes*, Teubner, Leipzig (1923).

⁶ M. Born and M. Göppert-Mayer, *Handbuch der Physik* **24/2**, 623 (1933).

large only for very small interionic distances. This short-range repulsive force arises in effect, simply because when the atoms are close together, they resist any further attempt to force them to occupy the same space. If this force were not present, the crystal would *always* have a net Coulomb attractive energy between oppositely charged ions which would be greater than the Coulomb repulsive energy between ions of like charge, and the crystal would collapse to essentially zero volume! The energy of interaction between ions i and j due to this force is represented empirically by a term A/r_{ij}^n . If the exponent n is a reasonably large number, this repulsive interaction will be very small at large distances, becoming appreciable only at quite small interatomic spacings.

We may write the total energy of interaction between the two ions i and j as the sum of the Coulomb and short-range repulsive interactions in the form

$$U_{ij} = \frac{A}{r_{ij}^n} \pm \frac{e^2}{r_{ij}}. \quad (3.7-2)$$

It should be noted that the *force* arising from the short-range repulsive interaction is given by the negative derivative of the corresponding interaction energy with respect to r_{ij} , nA/r_{ij}^{n+1} . In (3.7-2) the $+$ sign applies to interactions between ions of like sign, the $-$ sign to interactions between ions of opposite charge. The constant A simply expresses the proportionality between the short-range repulsive energy and r_{ij}^n . If we regard the crystal as being composed of N positive ions and N negative ions, the total binding energy of the lattice, U , may be written

$$U = NU_i. \quad (3.7-3)$$

Although the total number of ions in the crystal is $2N$, in determining the total binding energy we must count the contribution from each pair of ij interactions only once; had we written (3.7-3) with this factor of 2 on the right-hand side, we would have been incorrectly counting interactions U_{ij} and U_{ji} of (3.7-1) as separate entities. The energy U_{ij} as given by (3.7-2) is seen to be the amount of energy required to separate the ions i and j from an initial distance r_{ij} until they are infinitely far apart. The total lattice energy U is thus the energy required to convert a crystal whose nearest neighbor atoms are initially a distance r apart into separate ions, each of which is essentially infinitely far from all the others.

If, now, the dimensionless quantities x_{ij} are defined, such that

$$x_{ij} = r_{ij}/r, \quad (3.7-4)$$

where r is the distance between nearest neighbor atoms in the crystal, then (3.7-2) can be written

$$U_{ij} = \frac{A}{r^n x_{ij}^n} \pm \frac{e^2}{rx_{ij}}, \quad (3.7-5)$$

and

$$U_i(r) = \sum_j' U_{ij} = \sum_j' \frac{A}{r^n x_{ij}^n} \pm \sum_j' \frac{e^2}{rx_{ij}}. \quad (3.7-6)$$

However, in (3.7-6) r is now independent of the summation index j , whereby

$$U_i(r) = \frac{A}{r^n} \sum_j' \frac{1}{x_{ij}^n} \pm \frac{e^2}{r} \sum_j' \frac{1}{x_{ij}}, \quad (3.7-7)$$

which we shall write as

$$U_i(r) = \frac{B_n}{r^n} - \frac{\alpha e^2}{r}, \quad (3.7-8)$$

with

$$B_n = A \sum_j' 1/x_{ij}^n \quad (3.7-9)$$

and

$$\alpha = \sum_j' \mp 1/x_{ij}. \quad (3.7-10)$$

Figure 3.14 shows a plot of relation (3.7-8) giving U_i as a function of the nearest neighbor distance r . If the distance between neighboring atoms is large, then the

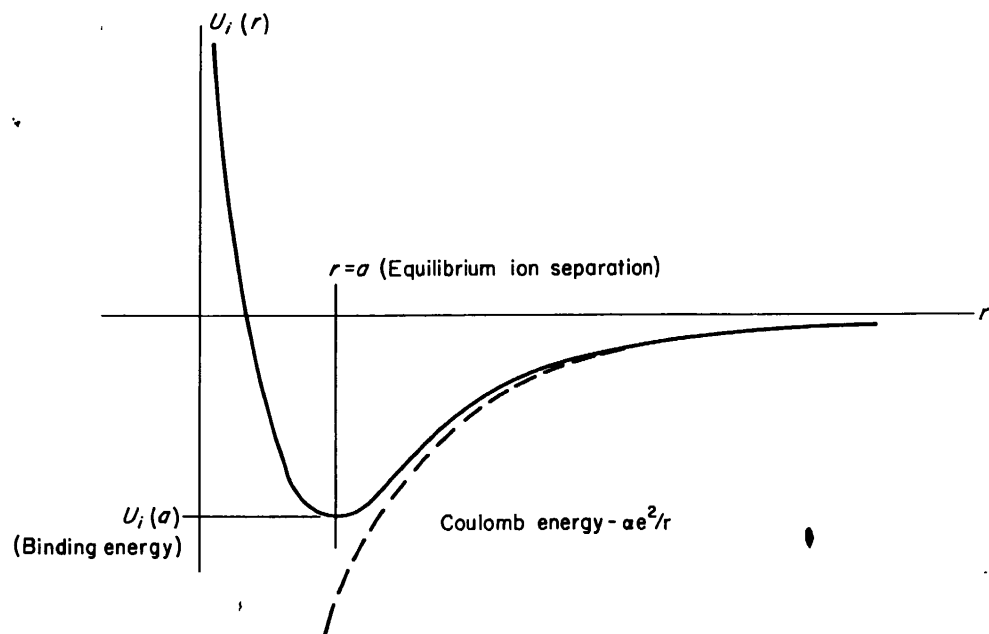


FIGURE 3.14. Potential energy of an ion in an ionic crystal as a function of the interatomic distance r . The crystal is in equilibrium when this energy is a minimum, corresponding to an interatomic separation equal to the equilibrium lattice distance a .

short-range repulsion is negligible and the binding energy is essentially the excess Coulomb energy of attraction, which approaches zero as r goes to infinity. At shorter distances the positive short-range repulsive energy becomes important, and exceeds the negative Coulomb energy, increasing rapidly as r becomes small. There is a position of minimum energy for the system, as indicated in the diagram, and this point represents the equilibrium condition of the crystal. The value of r associated with this point is simply the equilibrium nearest neighbor interatomic distance a . At this point

the Coulomb attractive force between ions is just balanced by the short-range repulsion, the net force on an atom, given by $-\partial U_i/\partial r$, being zero.

The constant α of Equation (3.7-8), which is called the Madelung constant, is a number which is determined completely by the lattice structure of the crystal. The constant B depends upon the repulsive energy coefficient A as well as the lattice structure. It can, however, be determined in terms of the equilibrium nearest neighbor distance a . To do this, one evaluates the derivative of $U_i(r)$ at $r = a$, which according to the above discussion must be zero, since the minimum point of the potential energy curve occurs at $r = a$. We have then,

$$-\frac{nB_n}{a^{n+1}} + \frac{\alpha e^2}{a^2} = 0,$$

whereby

$$B_n = \alpha e^2 a^{n-1}/n. \quad (3.7-11)$$

Substituting this value of B_n into (3.7-8), using (3.7-3) we find for the total binding energy at equilibrium

$$U_0 = NU_i(a) = -\frac{N\alpha e^2}{a} \left(1 - \frac{1}{n}\right). \quad (3.7-12)$$

In this formula, initially, we know neither α nor n . We can, in principle, however, calculate α by evaluating the sum (3.7-10) over all atoms of the crystal. In this equation, the upper sign refers to interactions between like charges, the lower to interactions between opposite ones. If, therefore, the origin is chosen as a negative ion site, the positive sign in (3.7-10) will refer to interactions with positive ions and the negative sign to interactions with negative ions. For a one-dimensional chain of atoms of alternating charge, each atom of which is separated by a distance a from its neighbors, we have, choosing a negative ion as the origin and using (3.7-10)

$$\alpha = \sum_j' \mp 1/x_{ij} = 2 \left[1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \dots \right]. \quad (3.7-13)$$

The factor 2 is necessary because contributions from atoms to the left of the origin as well as atoms to the right of the origin must be included in the sum. From the series expansion

$$\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \dots \quad (3.7-14)$$

the series of (3.7-13) can be obtained by setting $x = 1$, whence, for this case

$$\alpha = 2 \ln 2. \quad (3.7-15)$$

The evaluation of the Madelung constant proves to be a rather simple exercise for this simple example. When the same methods are applied to actual three-dimensional crystal lattices, however, it is found that the sum converges so slowly that it is a very difficult matter to evaluate α directly in this manner. It is instructive to write

out the Madelung sum for nearest neighbors, next nearest neighbors, third nearest neighbors, etc., in the NaCl structure, to exhibit the nature of these convergence difficulties. There are various mathematical schemes which can be used to circumvent these difficulties, the best known of which are due to Evjen⁷ and Ewald.⁸ We shall not go into the details of these methods, but merely quote the results for a few of the structures of interest. It is found that for the

NaCl structure	$\alpha = 1.7476$
CsCl structure	1.7627
Zincblende structure	1.6381

The tendency of ionic compounds to crystallize in structures which have large Madelung constants is well known. The reason for this is that a maximum value of α , according to (3.7-12) minimizes the energy of the system, giving a crystal with maximum (negative) binding energy. Highly ionic crystals thus rarely crystallize in the zincblende structure.

The constant n in (3.7-12), which is really the exponent associated with the short-range repulsive potential, can be expressed in terms of the *adiabatic compressibility* of the crystal, which is experimentally measurable. In order to do this, we may begin with the First Law of Thermodynamics, which states that

$$dQ = dU + p dV = T dS, \quad (3.7-16)$$

the symbols having their usual thermodynamic meanings. The internal energy U is assumed to consist entirely of potential energy of interaction between the ions of the crystal, as given by (3.7-12). This means that the temperature is assumed to be much less than the melting temperature on an absolute scale, for as the temperature increases the ions acquire, in addition to their potential energy, more and more *kinetic* energy of vibration, which at the melting point exceeds the potential energy of interaction between the ions and thus destroys the stability of the crystal lattice. For an adiabatic process $dQ = 0$, whereby $dS = 0$ and $dU = -p dV$, giving

$$p = -\left(\frac{dU}{dV}\right)_s \quad \text{and} \quad \left(\frac{dp}{dV}\right)_s = -\left(\frac{d^2U}{dV^2}\right)_s. \quad (3.7-17)$$

The adiabatic compressibility (compressibility measured under such conditions that no heat is exchanged with surroundings) may be defined as

$$K = -\frac{1}{V} \left(\frac{dV}{dp}\right)_s, \quad (3.7-18)$$

in which case, from (3.7-17) ' ,

$$\frac{1}{K} = -V \left(\frac{dp}{dV}\right)_s = V \left(\frac{d^2U}{dV^2}\right)_s. \quad (3.7-19)$$

⁷ H. M. Evjen, *Phys. Rev.* **39**, 675 (1932).

⁸ P. P. Ewald, *Ann. d. Physik* **64**, 253 (1921).

Also,

$$\frac{dU}{dV} = \frac{dU}{dr} \frac{dr}{dV}$$

and

$$\begin{aligned} \frac{d^2U}{dV^2} &= \frac{d}{dV} \left(\frac{dU}{dV} \right) = \frac{d}{dV} \left(\frac{dU}{dr} \frac{dr}{dV} \right) = \frac{dU}{dr} \frac{d^2r}{dV^2} + \frac{dr}{dV} \frac{d}{dV} \left(\frac{dU}{dr} \right) \\ &= \frac{dU}{dr} \frac{d^2r}{dV^2} + \left(\frac{dr}{dV} \right)^2 \frac{d^2U}{dr^2}. \end{aligned} \quad (3.7-20)$$

But the volume of the unit cell of NaCl, containing 4 Na atoms and 4 Cl atoms, as shown in Figure 1.7(a), is $8r^3$; the volume per Na atom (or per Cl atom) is thus $2r^3$, and the total volume of a large crystal containing N Na ions and N Cl ions will be found to be

$$V = 2Nr^3, \quad (3.7-21)$$

whereby

$$\frac{dr}{dV} = \frac{1}{6Nr^2} \quad (3.7-22)$$

and

$$\frac{d^2r}{dV^2} = \frac{d}{dV} \left(\frac{1}{6Nr^2} \right) = \frac{d}{dr} \left(\frac{1}{6Nr^2} \right) \frac{dr}{dV} = -\frac{1}{18N^2r^5}. \quad (3.7-23)$$

According to (3.7-20), (3.7-22), and (3.7-23), then,

$$\frac{d^2U}{dV^2} = \frac{-1}{18N^2r^5} \frac{dU}{dr} + \frac{1}{36N^2r^4} \frac{d^2U}{dr^2}, \quad (3.7-24)$$

As we have already seen, $dU/dr = 0$ at $r = a$, whence from (3.7-24) we must have

$$\left(\frac{d^2U}{dV^2} \right)_{r=a} = \frac{1}{36N^2a^4} \left(\frac{d^2U}{dr^2} \right)_{r=a}, \quad (3.7-25)$$

from which, recalling (3.7-19),

$$\frac{1}{K} = \left(V \frac{d^2U}{dV^2} \right)_{r=a} = \frac{1}{18Na} \left(\frac{d^2U}{dr^2} \right)_{r=a}. \quad (3.7-26)$$

From (3.7-8), $U(r)$ can be written

$$U(r) = NU_i(r) = N \left[\frac{B_n}{r^n} - \frac{\alpha e^2}{r} \right], \quad (3.7-27)$$

whence

$$\frac{d^2U}{dr^2} = N \left[\frac{n(n+1)B_n}{r^{n+2}} - \frac{2\alpha e^2}{r^3} \right], \quad (3.7-28)$$

B_n being given by (3.7-11). Substituting for B_n from the latter equation into (3.7-28)

and simplifying, letting $r = a$, we obtain finally

$$\left(\frac{d^2U}{dr^2}\right)_{r=a} = \frac{N\alpha e^2(n-1)}{a^3} = \frac{18Na}{K}, \quad (3.7-29)$$

whence, solving for n ,

$$n = 1 + \frac{18a^4}{K\alpha e^2}. \quad (3.7-30)$$

For NaCl, the measured value of the adiabatic compressibility K is about 4×10^{-12} cm²/dyne, while $a = 2.8 \times 10^{-8}$ cm. Substituting these values into (3.7-30) gives the result $n \cong 8$, whereby, in this case, according to (3.7-12) we should expect $U_0 \cong -0.9N\alpha e^2/a$. It would appear, then, that approximately 90 per cent of the binding energy of the lattice is accounted for by the first term in (3.7-12), which represents the excess of Coulomb attraction energy between ions of opposite charge over Coulomb repulsion energy between ions of like charge, while the second term, representing the short-range repulsive contribution represents only about 10 per cent of the total. The fact that n turns out to be a rather large number is consistent with our original assumptions regarding the form of the short-range repulsive potential, and in fact serves to a degree to validate those assumptions.

The cohesive energy of most of the highly ionic I-VII type crystals calculated in this manner from (3.7-12) and (3.7-30) agree quite well with experimentally determined values, as shown in Table 3.1.⁹ The agreement with experiment is not quite so

TABLE 3.1.

Theoretical and Experimental Binding Energies
of Ionic Crystals

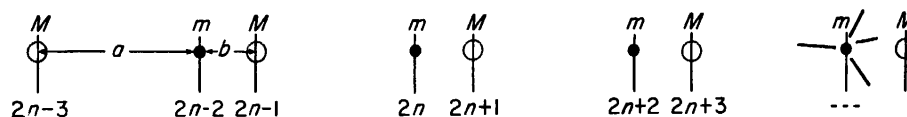
Substance	U_0 (calc.) kcal./mole	U_0 (exp.) kcal./mole	Repulsive exponent, n
LiCl	193.3	198.1	7.0
NaCl	180.4	182.8	8.0
KCl	164.4	164.4	9.0
RbCl	158.9	160.5	9.5
CsCl	148.9	155.1	10.5
NaBr	171.7	173.3	8.5
KBr	157.8	156.2	9.5
NaI	160.8	166.4	9.5
KI	149.0	151.5	10.5
RbI	144.2	149.0	11.0
ZnS (Zincblende)	819.0	851.0	9.0
ZnSe	790.0	845.0	9.5
PbS	705.0	731.0	10.5
PbSe	684.0	735.0	11.0

⁹ The values quoted here are taken from F. Seitz, *Modern Theory of Solids*, McGraw-Hill, New York (1940), Tables XXIV and XXVI, pp. 80-83.

good for the less completely ionic II-VI compounds, as one might expect. We should bear in mind the fact that these calculations are to a degree empirical ones, which relate one set of experimentally determined quantities (lattice spacing and compressibility) to another (repulsive potential exponent and binding energy). A really fundamental calculation of crystal binding energy would proceed from the known wave-mechanical properties of the positive and negative ions, and would *predict*, rather than utilize, the values of the lattice constant and the compressibilities; the only measured quantities which would appear in such a formulation would be e , m , h , etc. Calculations of this type, the results of which are in fairly good agreement with experiment have been made by Löwdin.¹⁰ A discussion of the details is unfortunately beyond the scope of the present work. The simpler Born-Madelung theory, nevertheless, is of considerable value because it verifies the simple conceptual model of ionic binding with which we started, and because it enables us to understand fairly simply the role of both Coulomb and short-range repulsive forces in determining the binding energy of ionic substances.

EXERCISES

1. For the monatomic linear lattice of Section 3.3, find the attenuation coefficient for waves of frequency greater than $\sqrt{4\beta/m}$.
2. Derive the equation of motion for transverse waves on the monatomic linear lattice of Section 3.3; compare your result with the equation of motion for longitudinal waves.
3. Find the phase velocity and group velocity for waves of both optical and acoustical branches for the diatomic lattice of Section 3.4. Plot your results as a function of k .
4. The zincblende lattice can be regarded as a series of (111) planes of alternate spacing $a, a/3, a, a/3, a, a/3, \dots$, where a is one quarter of the edge of the cubic unit cell. Each plane contains atoms of only one type, so that the atomic species in successive planes alternate thus: Zn, S, Zn, S, Zn, \dots . The planes are held together alternately by one covalent bond per atom, normal to the (111) plane, and three such bonds per atom at an angle to the [111] direction whose cosine is $1/3$, so that the same amount of force per unit displacement is involved in stretching a single bond or a system of three bonds disposed at this angle, when an atom is displaced along the [111] direction. By considering a diatomic lattice of the type shown in the figure below, with a force constant β which is the same for any displacement, set up and



solve the equations of motion for longitudinal waves in the [111] direction in zincblende, and plot the resulting ω vs. k relation in the first Brillouin Zone. Where is the edge of this first zone? *Hint:* For zincblende, $b = a/3$, $m \neq M$ in the figure above.

5. Solve Problem 4 to obtain the ω vs. k relations for longitudinal waves in the [111] direction for the *diamond* lattice. Does the fact that diamond has only one species of atom mean that there is no "optical" branch for this structure? Compare your results generally with those of Problem 4.
6. If the elastic stiffness coefficient c for NaCl is 5×10^{11} dynes/cm², find the force constant β and calculate the Reststrahl frequency for this crystal.

¹⁰ P. Löwdin, *Ark. Mat. Astron. Fysik* **35A**, Nos. 9, 30 (1947).

7. Suppose that longitudinal vibrations in a linear chain of N identical atoms are constrained to obey periodic boundary conditions, so that the motion of the first and last atom of the chain is identical. Find the number of normal modes of vibration for this system.

8. Find the Madelung constant for the linear chain of Problem 4, assuming the atoms of mass m to have a positive charge and those of mass M an equal negative charge.

9. Suppose that a homogeneous, isotropic fluid of dielectric constant κ were poured into the interatomic spaces of an ionic crystal, so that the Coulomb interaction is reduced by a factor $1/\kappa$. Assuming that the short-range repulsive potential is unchanged, calculate the new lattice spacing and the new binding energy in terms of the old spacing and the old binding energy.

10. Discuss the optical reflection characteristics of Ge, CdS, KBr, and GaAs in the far infrared region of the spectrum. Explain your predictions physically.

11. The imposition of periodic boundary conditions on a one-dimensional chain of atoms corresponds physically to the case where the head and tail of the chain are joined to form a continuous *ring* of atoms. To what physical system does a two-dimensional square net of atoms obeying periodic boundary conditions at opposite edges of the net correspond? Discuss the topological implications of a three-dimensional cubical lattice obeying periodic boundary conditions on opposite sample faces.

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	Name	Field
	Electron	—
	Photon	Electromagnetic wave
	Phonon	Elastic wave
	Plasmon	Collective electron wave
	Magnon	Magnetization wave
—	Polaron	Electron + elastic deformation
—	Exciton	Polarization wave

Figure 1 Important elementary excitations in solids. The origins of the concepts and the names of the excitations are discussed by C. T. Walker and G. A. Slack, Am. J. Phys. 38, 1380 (1970).

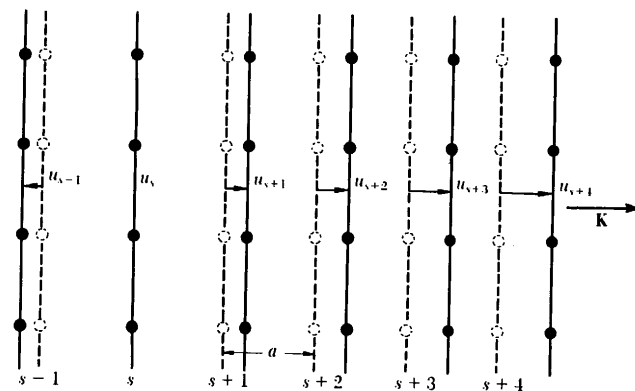


Figure 2 (Dashed lines) Planes of atoms when in equilibrium. (Solid lines) Planes of atoms when displaced as for a longitudinal wave. The coordinate u measures the displacement of the planes.

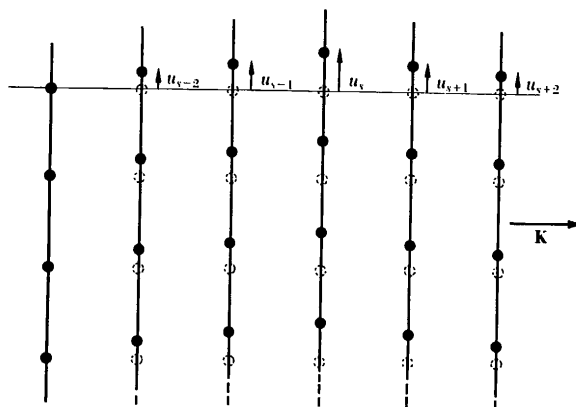


Figure 3 Planes of atoms as displaced during passage of a transverse wave.

VIBRATIONS OF CRYSTALS WITH MONATOMIC BASIS

Consider the elastic vibrations of a crystal with one atom in the primitive cell. We want to find the frequency of an elastic wave in terms of the wavevector that describes the wave and in terms of the elastic constants.

The mathematical solution is simplest in the [100], [110], and [111] propagation directions in cubic crystals. These are the directions of the cube edge, face diagonal, and body diagonal. When a wave propagates along one of these directions, entire planes of atoms move in phase with displacements either parallel or perpendicular to the direction of the wavevector. We can describe with a single coordinate u_s the displacement of the plane s from its equilibrium position. The problem is then one dimensional. For each wavevector there are three modes, one of longitudinal polarization (Fig. 2) and two of transverse polarization (Fig. 3).

We assume that the elastic response of the crystal is a linear function of the forces. That is equivalent to the assumption that the elastic energy is a quadratic function of the relative displacement of any two points in the crystal. Terms in the energy that are linear will vanish in equilibrium—see the minimum in Fig. 3.6. Cubic and higher order terms may be neglected for sufficiently small elastic deformations, but play some role at high temperatures, as we see in Chapter 5.

We assume accordingly that the force on the plane s caused by the displacement of the plane $s + p$ is proportional to the difference $u_{s+p} - u_s$ of their displacements. For brevity we consider only nearest-neighbor interactions, so that $p = \pm 1$. The total force on s comes from planes $s \pm 1$:

$$F_s = C(u_{s+1} - u_s) + C(u_{s-1} - u_s) . \quad (1)$$

This expression is linear in the displacements and is of the form of Hooke's law.

The constant C is the force constant between nearest-neighbor planes and will differ for longitudinal and transverse waves. It is convenient hereafter to regard C as defined for one atom of the plane, so that F_s is the force on one atom in the plane s .

The equation of motion of the plane s is

$$M \frac{d^2 u_s}{dt^2} = C(u_{s+1} + u_{s-1} - 2u_s) , \quad (2)$$

where M is the mass of an atom. We look for solutions with all displacements

having the time dependence $\exp(-i\omega t)$. Then $d^2u_s/dt^2 = -\omega^2 u_s$, and (2) becomes

$$-M\omega^2 u_s = C(u_{s+1} + u_{s-1} - 2u_s) . \quad (3)$$

This is a difference equation in the displacements u and has traveling wave solutions of the form:

$$u_{s\pm 1} = u \exp(\pm iKa) , \quad (4)$$

where a is the spacing between planes and K is the wavevector. The value to use for a will depend on the direction of K .

With (4), we have from (3):

$$-\omega^2 M u \exp(isKa) = C\{\exp[i(s+1)Ka] + \exp[i(s-1)Ka] - 2 \exp(isKa)\} . \quad (5)$$

We cancel $u \exp(isKa)$ from both sides, to leave

$$\omega^2 M = -C[\exp(iKa) + \exp(-iKa) - 2] . \quad (6)$$

With the identity $2 \cos Ka = \exp(iKa) + \exp(-iKa)$, we have the dispersion relation connecting ω and K :

$$\omega^2 = (2C/M)(1 - \cos Ka) . \quad (7)$$

The boundary of the first Brillouin zone lies at $K = \pm \pi/a$. We show from (7) that the slope of ω versus K is zero at the zone boundary:

$$d\omega^2/dK = (2Ca/M) \sin Ka = 0 \quad (8)$$

at $K = \pm \pi/a$, for here $\sin Ka = \sin(\pm \pi) = 0$. The special significance of phonon wavevectors that lie on the zone boundary is developed in (12) below.

By a trigonometric identity (7) may be written as

$$\omega^2 = (4C/M) \sin^2 \frac{1}{2} Ka ; \quad \omega = (4C/M)^{1/2} |\sin \frac{1}{2} Ka| . \quad (9)$$

A plot of ω versus K is given in Fig. 4.

First Brillouin Zone

What range of K is physically significant for elastic waves? Only those in the first Brillouin zone. From (4) the ratio of the displacements of two successive planes is given by

$$\frac{u_{s+1}}{u_s} = \frac{u \exp[i(s+1)Ka]}{u \exp(isKa)} = \exp(iKa) . \quad (10)$$

The range $-\pi$ to $+\pi$ for the phase Ka covers all independent values of the exponential.

There is absolutely no point in saying that two adjacent atoms are out of phase by more than π : a relative phase of 1.2π is physically identical with a

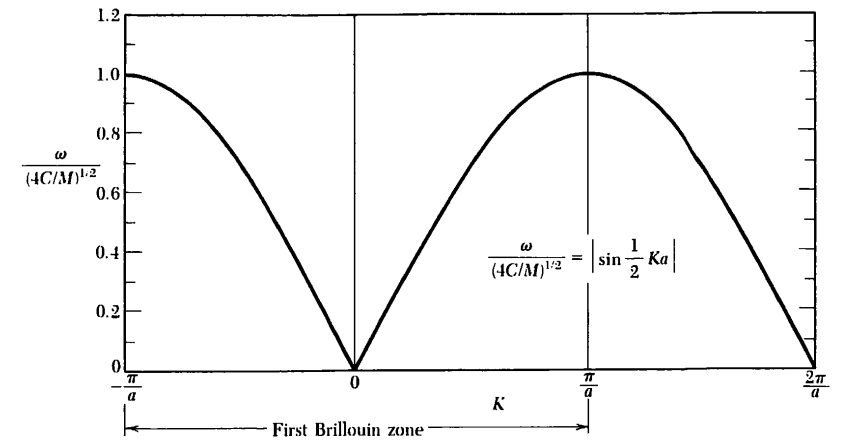


Figure 4 Plot of ω versus K . The region of $K \ll 1/a$ or $\lambda \gg a$ corresponds to the continuum approximation; here ω is directly proportional to K .

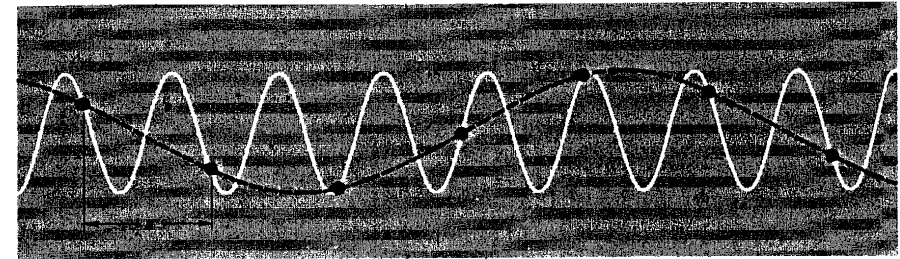


Figure 5 The wave represented by the solid curve conveys no information not given by the dashed curve. Only wavelengths longer than $2a$ are needed to represent the motion.

relative phase of -0.8π , and a relative phase of 4.2π is identical with 0.2π . We need both positive and negative values of K because waves can propagate to the right or to the left.

The range of independent values of K is specified by

$$-\pi \leq Ka \leq \pi , \quad \text{or} \quad -\frac{\pi}{a} \leq K \leq \frac{\pi}{a} .$$

This range is the first Brillouin zone of the linear lattice, as defined in Chapter 2. The extreme values are $K_{\max} = \pm \pi/a$.

There is a real difference here from an elastic continuum: in the continuum limit $a \rightarrow 0$ and $K_{\max} \rightarrow \pm \infty$. Values of K outside of the first Brillouin zone (Fig. 5) merely reproduce lattice motions described by values within the limits $\pm \pi/a$.

We may treat a value of K outside these limits by subtracting the integral multiple of $2\pi/a$ that will give a wavevector inside these limits. Suppose K lies

outside the first zone, but a related wavevector K' defined by $K' \equiv K - 2\pi n/a$ lies within the first zone, where n is an integer. Then the displacement ratio (10) becomes

$$u_{s+1}/u_s = \exp(iKa) \equiv \exp(i2\pi n) \exp[i(Ka - 2\pi n)] \equiv \exp(iK'a) , \quad (11)$$

because $\exp(i2\pi n) = 1$. Thus the displacement can always be described by a wavevector within the first zone. We note that $2\pi n/a$ is a reciprocal lattice vector because $2\pi/a$ is a reciprocal lattice vector. Thus by subtraction of an appropriate reciprocal lattice vector from K , we always obtain an equivalent wavevector in the first zone.

At the boundaries $K_{\max} = \pm \pi/a$ of the Brillouin zone the solution $u_s = u \exp(isKa)$ does not represent a traveling wave, but a standing wave. At the zone boundaries $sK_{\max}a = \pm s\pi$, whence

$$u_s = u \exp(\pm is\pi) = u (-1)^s . \quad (12)$$

This is a standing wave: alternate atoms oscillate in opposite phases, because $u_s = \pm 1$ according to whether s is an even or an odd integer. The wave moves neither to the right nor to the left.

This situation is equivalent to Bragg reflection of x-rays: when the Bragg condition is satisfied a traveling wave cannot propagate in a lattice, but through successive reflections back and forth, a standing wave is set up.

The critical value $K_{\max} = \pm \pi/a$ found here satisfies the Bragg condition $2d \sin \theta = n\lambda$: we have $\theta = \frac{1}{2}\pi$, $d = a$, $K = 2\pi/\lambda$, $n = 1$, so that $\lambda = 2a$. With x-rays it is possible to have n equal to other integers besides unity because the amplitude of the electromagnetic wave has a meaning in the space between atoms, but the displacement amplitude of an elastic wave usually has a meaning only at the atoms themselves.

Group Velocity

The transmission velocity of a wave packet is the group velocity, given as

$$v_g = d\omega/dK ,$$

or

$$\mathbf{v}_g = \text{grad}_{\mathbf{K}} \omega(\mathbf{K}) , \quad (13)$$

the gradient of the frequency with respect to \mathbf{K} . This is the velocity of energy propagation in the medium.

With the particular dispersion relation (9), the group velocity (Fig. 6) is

$$v_g = (Ca^2/M)^{1/2} \cos \frac{1}{2}Ka . \quad (14)$$

This is zero at the edge of the zone where $K = \pi/a$. Here the wave is a standing wave, as in (12), and we expect zero net transmission velocity for a standing wave.

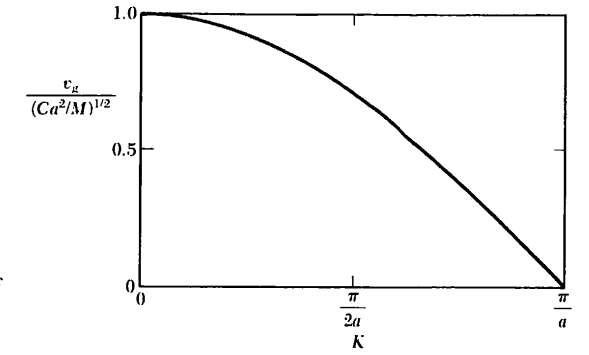


Figure 6 Group velocity v_g versus K , for model of Fig. 4. At the zone boundary the group velocity is zero.

Long Wavelength Limit

When $Ka \ll 1$ we expand $\cos Ka \approx 1 - \frac{1}{2}(Ka)^2$, so that the dispersion relation (7) becomes

$$\omega^2 = (C/M)K^2a^2 . \quad (15)$$

The result that the frequency is directly proportional to the wavevector in the long wavelength limit is equivalent to the statement that the velocity of sound is independent of frequency in this limit. Thus $v = \omega/K$, exactly as in the continuum theory of elastic waves—in the continuum limit $a = 0$ and thus $Ka = 0$.

Derivation of Force Constants from Experiment

In metals the effective forces may be of quite long range, carried from ion to ion through the conduction electron sea (Chapter 10). Interactions have been found between planes of atoms separated by as many as 20 planes. We can make a statement about the range of the forces from the observed dispersion relation for ω . The generalization of the dispersion relation (7) to p nearest planes is easily found to be

$$\omega^2 = (2/M) \sum_{p>0} C_p (1 - \cos pKa) . \quad (16a)$$

We solve for the interplanar force constants C_p by multiplying both sides by $\cos rKa$, where r is an integer, and integrating over the range of independent values of K :

$$\begin{aligned} M \int_{-\pi/a}^{\pi/a} dK \omega_K^2 \cos rKa &= 2 \sum_{p>0} C_p \int_{-\pi/a}^{\pi/a} dK (1 - \cos pKa) \cos rKa \\ &= -2\pi C_{r/a} . \end{aligned} \quad (16b)$$

The integral vanishes except for $p = r$. Thus

$$C_p = -\frac{Ma}{2\pi} \int_{-\pi/a}^{\pi/a} dK \omega_K^2 \cos pKa \quad (17)$$

gives the force constant at range pa , for a structure with a monatomic basis.

TWO ATOMS PER PRIMITIVE BASIS

The phonon dispersion relation shows new features in crystals with two or more atoms per primitive basis. Consider, for example, the NaCl or diamond structures, with two atoms in the primitive cell. For each polarization mode in a given propagation direction the dispersion relation ω versus K develops two branches, known as the acoustical and optical branches. We have longitudinal LA and transverse acoustical TA modes, and longitudinal LO and transverse optical TO modes, as in Fig. 7.

If there are p atoms in the primitive cell, there are $3p$ branches to the dispersion relation: 3 acoustical branches and $3p - 3$ optical branches. Thus germanium (Fig. 8a) and KBr (Fig. 8b), each with two atoms in a primitive cell, have six branches: one LA, one LO, two TA, and two TO.

The numerology of the branches follows from the number of degrees of freedom of the atoms. With p atoms in the primitive cell and N primitive cells, there are pN atoms. Each atom has three degrees of freedom, one for each of the x, y, z directions, making a total of $3pN$ degrees of freedom for the crystal. The number of allowed K values in a single branch is just N for one Brillouin zone.¹ Thus the LA and the two TA branches have a total of $3N$ modes, thereby accounting for $3N$ of the total degrees of freedom. The remaining $(3p - 3)N$ degrees of freedom are accommodated by the optical branches.

We consider a cubic crystal where atoms of mass M_1 lie on one set of planes and atoms of mass M_2 lie on planes interleaved between those of the first set (Fig. 9). It is not essential that the masses be different, but either the force constants or the masses will be different if the two atoms of the basis are in nonequivalent sites. Let a denote the repeat distance of the lattice in the direction normal to the lattice planes considered. We treat waves that propagate in a symmetry direction for which a single plane contains only a single type of ion; such directions are $[111]$ in the NaCl structure and $[100]$ in the CsCl structure.

We write the equations of motion under the assumption that each plane interacts only with its nearest-neighbor planes and that the force constants are identical between all pairs of nearest-neighbor planes. We refer to Fig. 9 to obtain

$$\begin{aligned} M_1 \frac{d^2 u_s}{dt^2} &= C(v_s + v_{s-1} - 2u_s) ; \\ M_2 \frac{d^2 v_s}{dt^2} &= C(u_{s+1} + u_s - 2v_s) . \end{aligned} \quad (18)$$

¹We show in Chapter 5 by application of periodic boundary conditions to the modes of the crystal of volume V that there is one K value in the volume $(2\pi)^3/V$ in Fourier space. The volume of a Brillouin zone is $(2\pi)^3/V_c$, where V_c is the volume of a crystal primitive cell. Thus the number of allowed K values in a Brillouin zone is V/V_c , which is just N , the number of primitive cells in the crystal.

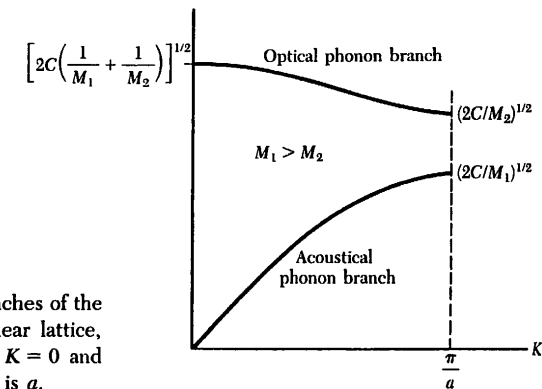


Figure 7 Optical and acoustical branches of the dispersion relation for a diatomic linear lattice, showing the limiting frequencies at $K = 0$ and $K = K_{\max} = \pi/a$. The lattice constant is a .

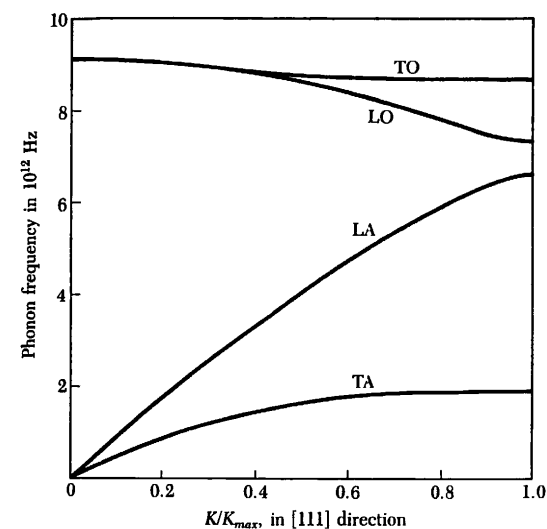


Figure 8a Phonon dispersion relations in the $[111]$ direction in germanium at 80 K. The two TA phonon branches are horizontal at the zone boundary position, $K_{\max} = (2\pi/a)(\frac{1}{2}\frac{1}{2}\frac{1}{2})$. The LO and TO branches coincide at $K = 0$; this also is a consequence of the crystal symmetry of Ge. The results were obtained with neutron inelastic scattering by G. Nilsson and G. Nelin.

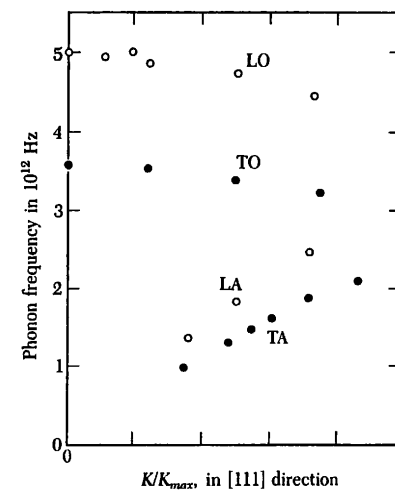


Figure 8b Dispersion curves in the $[111]$ direction in KBr at 90 K, after A. D. B. Woods, B. N. Brockhouse, R. A. Cowley, and W. Cochran. The extrapolation to $K = 0$ of the TO, LO branches are called ω_T, ω_L ; these are discussed in Chapter 10.

We look for a solution in the form of a traveling wave, now with different amplitudes u, v on alternate planes:

$$u_s = u \exp(isKa) \exp(-i\omega t) ; \quad v_s = v \exp(isKa) \exp(-i\omega t) . \quad (19)$$

Recall the definition of a in Fig. 9 as the distance between nearest identical planes, not nearest-neighbor planes.

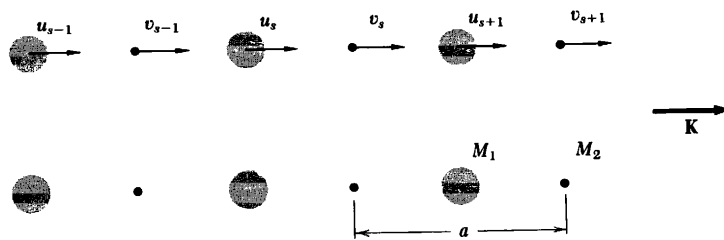


Figure 9 A diatomic crystal structure with masses M_1, M_2 connected by force constant C between adjacent planes. The displacements of atoms M_1 are denoted by $u_{s-1}, u_s, u_{s+1}, \dots$, and of atoms M_2 by v_{s-1}, v_s, v_{s+1} . The repeat distance is a in the direction of the wavevector K . The atoms are shown in their undisplaced positions.

On substitution of (19) in (18) we have

$$\begin{aligned} -\omega^2 M_1 u &= Cv[1 + \exp(-iKa)] - 2Cu; \\ -\omega^2 M_2 v &= Cu[\exp(iKa) + 1] - 2Cv. \end{aligned} \quad (20)$$

The homogeneous linear equations have a solution only if the determinant of the coefficients of the unknowns u, v vanishes:

$$\begin{vmatrix} 2C - M_1 \omega^2 & -C[1 + \exp(-iKa)] \\ -C[1 + \exp(iKa)] & 2C - M_2 \omega^2 \end{vmatrix} = 0, \quad (21)$$

or

$$M_1 M_2 \omega^4 - 2C(M_1 + M_2)\omega^2 + 2C^2(1 - \cos Ka) = 0. \quad (22)$$

We can solve this equation exactly for ω^2 , but it is simpler to examine the limiting cases $Ka \ll 1$ and $Ka = \pm\pi$ at the zone boundary. For small Ka we have $\cos Ka \approx 1 - \frac{1}{2}K^2 a^2 + \dots$, and the two roots are

$$\omega^2 \approx 2C \left(\frac{1}{M_1} + \frac{1}{M_2} \right) \quad (\text{optical branch}); \quad (23)$$

$$\omega^2 \approx \frac{\frac{1}{2}C}{M_1 + M_2} K^2 a^2 \quad (\text{acoustical branch}). \quad (24)$$

The extent of the first Brillouin zone is $-\pi/a \leq K \leq \pi/a$, where a is the repeat distance of the lattice. At $K_{\max} = \pm\pi/a$ the roots are

$$\omega^2 = 2C/M_1; \quad \omega^2 = 2C/M_2. \quad (25)$$

The dependence of ω on K is shown in Fig. 7 for $M_1 > M_2$.

The particle displacements in the transverse acoustical (TA) and transverse optical (TO) branches are shown in Fig. 10. For the optical branch at $K = 0$ we find, on substitution of (23) in (20),

$$\frac{u}{v} = -\frac{M_2}{M_1}. \quad (26)$$

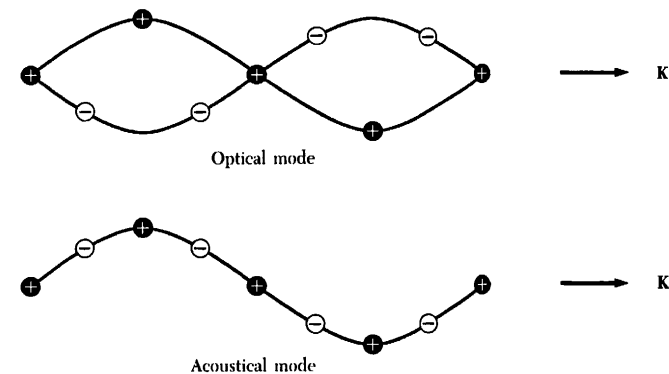


Figure 10 Transverse optical and transverse acoustical waves in a diatomic linear lattice, illustrated by the particle displacements for the two modes at the same wavelength.

The atoms vibrate against each other, but their center of mass is fixed. If the two atoms carry opposite charges, as in Fig. 10, we may excite a motion of this type with the electric field of a light wave, so that the branch is called the optical branch. At a general K the ratio u/v will be complex, as follows from either of the equations (20). Another solution for the amplitude ratio at small K is $u = v$, obtained as the $K = 0$ limit of (24). The atoms (and their center of mass) move together, as in long wavelength acoustical vibrations, whence the term acoustical branch.

Wavelike solutions do not exist for certain frequencies, here between $(2C/M_1)^{1/2}$ and $(2C/M_2)^{1/2}$. This is a characteristic feature of elastic waves in polyatomic lattices. There is a frequency gap at the boundary $K_{\max} = \pm\pi/a$ of the first Brillouin zone. If we look for solutions in the gap with ω real, then the wavevector K will be complex, so that the wave is damped in space.

QUANTIZATION OF ELASTIC WAVES

The energy of a lattice vibration is quantized. The quantum of energy is called a **phonon** in analogy with the photon of the electromagnetic wave. Elastic waves in crystals are made up of phonons. Thermal vibrations in crystals are thermally excited phonons, like the thermally excited photons of black-body electromagnetic radiation in a cavity.

The energy of an elastic mode of angular frequency ω is

$$\epsilon = (n + \frac{1}{2})\hbar\omega \quad (27)$$

when the mode is excited to quantum number n ; that is, when the mode is occupied by n phonons. The term $\frac{1}{2}\hbar\omega$ is the zero point energy of the mode. It occurs for both phonons and photons as a consequence of their equivalence to a quantum harmonic oscillator of frequency ω , for which the energy eigenvalues are also $(n + \frac{1}{2})\hbar\omega$. The quantum theory of phonons is developed in Appendix C.

We can easily quantize the mean square phonon amplitude. Consider the standing wave mode of amplitude

$$u = u_0 \cos Kx \cos \omega t .$$

Here u is the displacement of a volume element from its equilibrium position at x in the crystal.

The energy in the mode, as in any harmonic oscillator, is half kinetic energy and half potential energy, when averaged over time. The kinetic energy density is $\frac{1}{2}\rho(\partial u/\partial t)^2$, where ρ is the mass density. In a crystal of volume V , the volume integral of the kinetic energy is $\frac{1}{4}\rho V\omega^2 u_0^2 \cos^2 \omega t$. The time average kinetic energy is

$$\frac{1}{8}\rho V\omega^2 u_0^2 = \frac{1}{2}(n + \frac{1}{2})\hbar\omega , \quad (28)$$

and the square of the amplitude is

$$u_0^2 = 4(n + \frac{1}{2})\hbar/\rho V\omega . \quad (29)$$

This relates the displacement in a given mode to the phonon occupancy n of the mode.

What is the sign of ω ? The equations of motion such as (2) are equations for ω^2 , and if this is positive then ω can have either sign, $+$ or $-$. But the energy of a phonon must be positive, so it is conventional and suitable to view ω as positive. (For circularly polarized waves both signs are often used, to distinguish one sense of rotation from the other.) If the crystal structure is unstable, or becomes unstable through an unusual temperature dependence of the force constants (Chapter 13), then ω^2 will be negative and ω will be imaginary.

A mode with ω imaginary will be unstable, at least if the real part of ω is negative. The crystal will transform spontaneously to a more stable structure. An optical mode with ω close to zero is called a soft mode, and these are often involved in phase transitions, as in ferroelectric crystals.

PHONON MOMENTUM

A phonon of wavevector K will interact with particles such as photons, neutrons, and electrons as if it had a momentum $\hbar K$. However, a phonon does not carry physical momentum.

The reason that phonons on a lattice do not carry momentum is that a phonon coordinate (except for $K = 0$) involves relative coordinates of the atoms. Thus in an H_2 molecule the internuclear vibrational coordinate $r_1 - r_2$ is a relative coordinate and does not carry linear momentum; the center of mass coordinate $\frac{1}{2}(r_1 + r_2)$ corresponds to the uniform mode $K = 0$ and can carry linear momentum.

The physical momentum of a crystal is

$$p = M(d/dt) \sum u_s . \quad (30)$$

When the crystal carries a phonon K ,

$$p = M(du/dt) \sum_s \exp(isKa) = M(du/dt)[1 - \exp(iNKa)] / [1 - \exp(iKa)] , \quad (31)$$

where s runs over the N atoms. We have used the series

$$\sum_{s=0}^{N-1} x^s = (1 - x^N)/(1 - x) . \quad (32)$$

In the next chapter we enumerate the discrete values of K compatible with the boundary conditions, to find that $K = \pm 2\pi r/Na$, where r is an integer. Thus $\exp(iNKa) = \exp(\pm i2\pi r) = 1$, and from (31) it follows that the crystal momentum is zero:

$$p = M(du/dt) \sum_s \exp(isKa) = 0 . \quad (33)$$

The only exception to (33) is the uniform mode $K = 0$, for which all u_s equal u , so that $p = NM(du/dt)$. This mode represents a uniform translation of the crystal as a whole, and such a translation does carry momentum.

All the same, for most practical purposes a phonon acts as if its momentum were $\hbar K$, sometimes called the **crystal momentum**. In crystals there exist wavevector selection rules for allowed transitions between quantum states. We saw that the elastic scattering of an x-ray photon by a crystal is governed by the wavevector selection rule

$$\mathbf{k}' = \mathbf{k} + \mathbf{G} , \quad (34)$$

where \mathbf{G} is a vector in the reciprocal lattice; \mathbf{k} is the wavevector of the incident photon, and \mathbf{k}' is the wavevector of the scattered photon. In the reflection process the crystal as a whole will recoil with momentum $-\hbar\mathbf{G}$, but this uniform mode momentum is rarely considered explicitly.

Equation (34) is an example of the rule that the total wavevector of interacting waves is conserved in a periodic lattice, with the possible addition of a reciprocal lattice vector \mathbf{G} . The true momentum of the whole system always is rigorously conserved.

If the scattering of the photon is inelastic, with the creation of a phonon of wavevector \mathbf{K} , then the wavevector selection rule becomes

$$\mathbf{k}' + \mathbf{K} = \mathbf{k} + \mathbf{G} . \quad (35)$$

If a phonon \mathbf{K} is absorbed in the process, we have instead the relation

$$\mathbf{k}' = \mathbf{k} + \mathbf{K} + \mathbf{G} . \quad (36)$$

Relations (35) and (36) are the natural extensions of (34).

We exhibit the mathematics involved in the wavevector selection rule. Suppose two phonons \mathbf{K}_1 , \mathbf{K}_2 interact through cubic terms in the elastic energy to create a third phonon \mathbf{K}_3 . The probability of the collision will involve the product of the three phonon wave amplitudes, summed over all lattice sites: (phonon \mathbf{K}_1 in)(phonon \mathbf{K}_2 in)(phonon \mathbf{K}_3 out) \propto

$$\sum_n \exp(-i\mathbf{K}_1 \cdot \mathbf{r}_n) \exp(-i\mathbf{K}_2 \cdot \mathbf{r}_n) \exp(i\mathbf{K}_3 \cdot \mathbf{r}_n) = \sum_n \exp[i(\mathbf{K}_3 - \mathbf{K}_1 - \mathbf{K}_2) \cdot \mathbf{r}_n] .$$

This sum in the limit of a large number of lattice sites approaches zero unless $\mathbf{K}_3 = \mathbf{K}_1 + \mathbf{K}_2$ or $\mathbf{K}_3 = \mathbf{K}_1 + \mathbf{K}_2 + \mathbf{G}$. If either of these conditions is satisfied, of which the first is merely a special case of the second, the sum is equal to the number of lattice sites N . A similar sum was considered in Problem 2.4.

INELASTIC SCATTERING BY PHONONS

Phonon dispersion relations $\omega(\mathbf{K})$ are most often determined by the inelastic scattering of neutrons with the emission or absorption of a phonon. Further, the angular width of the scattered neutron beam gives information bearing on the lifetime of phonons.

A neutron sees the crystal lattice chiefly by interaction with the nuclei of the atoms. The kinematics of the scattering of a neutron beam by a crystal lattice are described by the general wavevector selection rule:

$$\mathbf{k} + \mathbf{G} = \mathbf{k}' \pm \mathbf{K} , \quad (37)$$

and by the requirement of conservation of energy. Here \mathbf{K} is the wavevector of the phonon created (+) or absorbed (−) in the process, and \mathbf{G} is any reciprocal lattice vector. For a phonon we choose \mathbf{G} such that \mathbf{K} lies in the first Brillouin zone.

The kinetic energy of the incident neutron is $p^2/2M_n$, where M_n is the mass of the neutron. The momentum \mathbf{p} is given by $\hbar\mathbf{k}$, where \mathbf{k} is the wavevector of the neutron. Thus $\hbar^2 k^2/2M_n$ is the kinetic energy of the incident neutron. If \mathbf{k}' is the wavevector of the scattered neutron, the energy of the scattered neutron is $\hbar^2 k'^2/2M_n$. The statement of conservation of energy is

$$\frac{\hbar^2 k^2}{2M_n} = \frac{\hbar^2 k'^2}{2M_n} \pm \hbar\omega , \quad (38)$$

where $\hbar\omega$ is the energy of the phonon created (+) or absorbed (−) in the process.

To determine the dispersion relation using (37) and (38) it is necessary in the experiment to find the energy gain or loss of the scattered neutrons as a function of the scattering direction $\mathbf{k} - \mathbf{k}'$. Results for germanium and KBr are

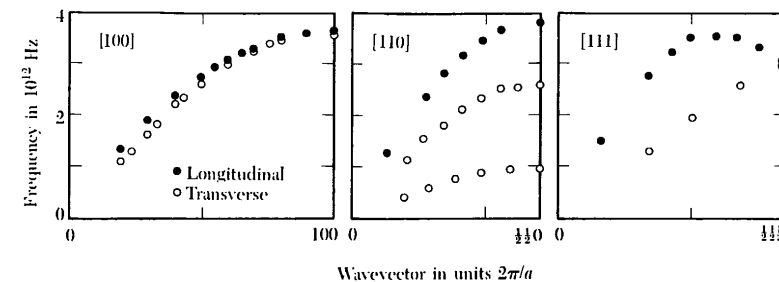


Figure 11 The dispersion curves of sodium for phonons propagating in the [001], [110], and [111] directions at 90 K, as determined by inelastic scattering of neutrons, by Woods, Brockhouse, March and Bowers.

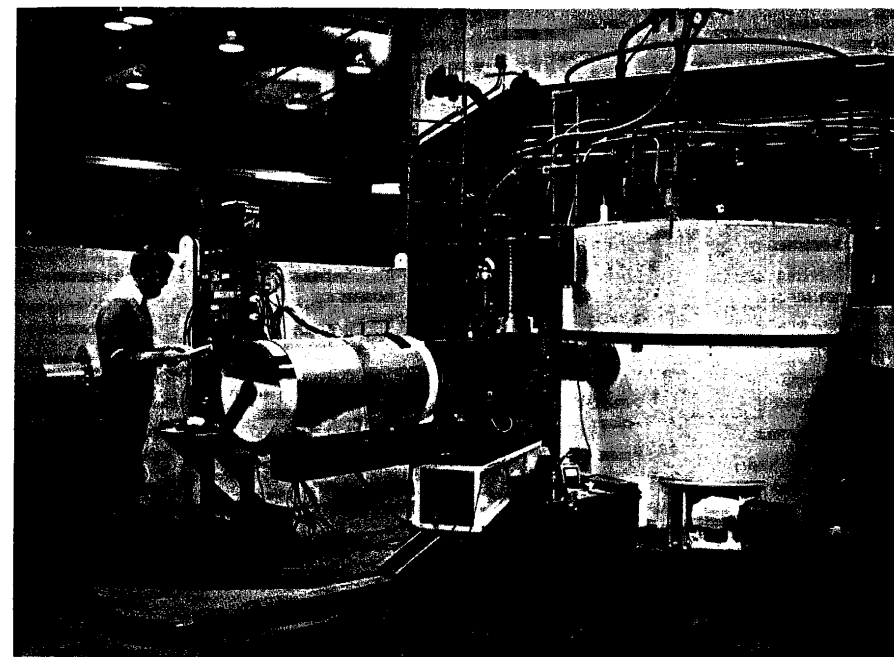


Figure 12 A triple axis neutron spectrometer at Brookhaven. (Courtesy of B. H. Grier.)

given in Fig. 8; results for sodium are given in Fig. 11. A spectrometer used for phonon studies is shown in Fig. 12.

Recently the concept of “mirror symmetry” has been introduced into the study of alkali-halide ion dynamics.² The idea is to consider the crystal that would be formed if the signs of the ions in A^+B^- were reversed. Now A^-B^+ does not exist, but a nearest mass pair that does exist will have, it turns out experimentally, a phonon dispersion relation remarkably similar to that of A^+B^- . Thus KF is the approximate mirror image of NaCl, for K^+ is isoelectronic with Cl^- and F^- is isoelectronic with Na^+ .

²L. L. Foldy and B. Segall, Phys. Rev. **B25**, 1260 (1982); L. L. Foldy and T. A. Witten, Solid State Commun. **37**, 709 (1981).

SUMMARY

- The quantum unit of a crystal vibration is a phonon. If the angular frequency is ω , the energy of the phonon is $\hbar\omega$.
- When a phonon of wavevector \mathbf{K} is created by the inelastic scattering of a photon or neutron from wavevector \mathbf{k} to \mathbf{k}' , the wavevector selection rule that governs the process is

$$\mathbf{k} = \mathbf{k}' + \mathbf{K} + \mathbf{G} ,$$

where \mathbf{G} is a reciprocal lattice vector.

- All elastic waves can be described by wavevectors that lie within the first Brillouin zone in reciprocal space.
- If there are p atoms in the primitive cell, the phonon dispersion relation will have 3 acoustical phonon branches and $3p - 3$ optical phonon branches.

Problems

1. **Vibrations of square lattice.** We consider transverse vibrations of a planar square lattice of rows and columns of identical atoms, and let $u_{l,m}$ denote the displacement normal to the plane of the lattice of the atom in the l th column and m th row (Fig. 13). The mass of each atom is M , and C is the force constant for nearest neighbor atoms.
 - (a) Show that the equation of motion is

$$M(d^2u_{lm}/dt^2) = C[(u_{l+1,m} + u_{l-1,m} - 2u_{lm}) + (u_{l,m+1} + u_{l,m-1} - 2u_{lm})] .$$

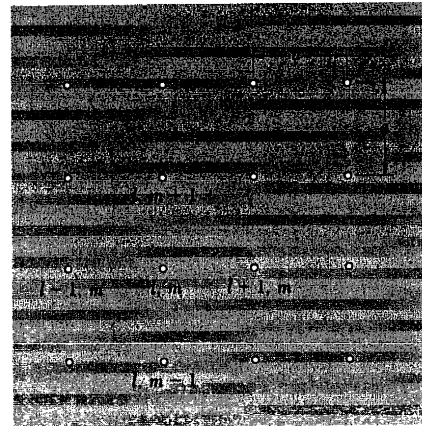


Figure 13 Square array of lattice constant a . The displacements considered are normal to the plane of the lattice.

- (b) Assume solutions of the form

$$u_{lm} = u(0) \exp[i(lK_x a + mK_y a - \omega t)] ,$$

where a is the spacing between nearest-neighbor atoms. Show that the equation of

motion is satisfied if

$$\omega^2 M = 2C(2 - \cos K_x a - \cos K_y a) .$$

This is the dispersion relation for the problem. (c) Show that the region of \mathbf{K} space for which independent solutions exist may be taken as a square of side $2\pi/a$. This is the first Brillouin zone of the square lattice. Sketch ω versus K for $K = K_x$ with $K_y = 0$, and for $K_x = K_y$. (d) For $Ka \ll 1$, show that

$$\omega = (Ca^2/M)^{1/2}(K_x^2 + K_y^2)^{1/2} = (Ca^2/M)^{1/2}K ,$$

so that in this limit the velocity is constant.

2. **Monatomic linear lattice.** Consider a longitudinal wave

$$u_s = u \cos(\omega t - sKa)$$

which propagates in a monatomic linear lattice of atoms of mass M , spacing a , and nearest-neighbor interaction C .

- (a) Show that the total energy of the wave is

$$E = \frac{1}{2}M \sum_s (du_s/dt)^2 + \frac{1}{2}C \sum_s (u_s - u_{s+1})^2 ,$$

where s runs over all atoms.

- (b) By substitution of u_s in this expression, show that the time-average total energy per atom is

$$\frac{1}{2}M\omega^2 u^2 + \frac{1}{2}C(1 - \cos Ka)u^2 = \frac{1}{2}M\omega^2 u^2 ,$$

where in the last step we have used the dispersion relation (9) for this problem.

3. **Continuum wave equation.** Show that for long wavelengths the equation of motion (2) reduces to the continuum elastic wave equation

$$\frac{\partial^2 u}{\partial t^2} = v^2 \frac{\partial^2 u}{\partial x^2} ,$$

where v is the velocity of sound.

4. **Basis of two unlike atoms.** For the problem treated by (18) to (26), find the amplitude ratios u/v for the two branches at $K_{\max} = \pi/a$. Show that at this value of K the two lattices act as if decoupled: one lattice remains at rest while the other lattice moves.

5. **Kohn anomaly.** We suppose that the interplanar force constant C_p between planes s and $s + p$ is of the form

$$C_p = A \frac{\sin pk_0 a}{pa} ,$$

where A and k_0 are constants and p runs over all integers. Such a form is expected in metals. Use this and Eq. (16a) to find an expression for ω^2 and also for $\partial\omega^2/\partial K$. Prove that $\partial\omega^2/\partial K$ is infinite when $K = k_0$. Thus a plot of ω^2 versus K or of ω versus K has a vertical tangent at k_0 : there is a kink at k_0 in the phonon dispersion relation $\omega(K)$.

6. *Diatomic chain.* Consider the normal modes of a linear chain in which the force constants between nearest-neighbor atoms are alternately C and $10C$. Let the masses be equal, and let the nearest-neighbor separation be $a/2$. Find $\omega(K)$ at $K = 0$ and $K = \pi/a$. Sketch in the dispersion relation by eye. This problem simulates a crystal of diatomic molecules such as H_2 .

7. *Atomic vibrations in a metal.* Consider point ions of mass M and charge e immersed in a uniform sea of conduction electrons. The ions are imagined to be in stable equilibrium when at regular lattice points. If one ion is displaced a small distance r from its equilibrium position, the restoring force is largely due to the electric charge within the sphere of radius r centered at the equilibrium position. Take the number density of ions (or of conduction electrons) as $3/4\pi R^3$, which defines R . (a) Show that the frequency of a single ion set into oscillation is $\omega = (e^2/MR^3)^{1/2}$. (b) Estimate the value of this frequency for sodium, roughly. (c) From (a), (b), and some common sense, estimate the order of magnitude of the velocity of sound in the metal.

*8. *Soft phonon modes.* Consider a line of ions of equal mass but alternating in charge, with $e_p = e(-1)^p$ as the charge on the p th ion. The interatomic potential is the sum of two contributions: (1) a short-range interaction of force constant $C_{1R} = \gamma$ that acts between nearest neighbors only, and (2) a coulomb interaction between all ions. (a) Show that the contribution of the coulomb interaction to the atomic force constants is $C_{pC} = 2(-1)^p e^2/p^3 a^3$, where a is the equilibrium nearest-neighbor distance. (b) From (16a) show that the dispersion relation may be written as

$$\omega^2/\omega_0^2 = \sin^2 \frac{1}{2}Ka + \sigma \sum_{p=1}^{\infty} (-1)^p (1 - \cos pKa)p^{-3},$$

where $\omega_0^2 \equiv 4\gamma/M$ and $\sigma = e^2/\gamma a^3$. (c) Show that ω^2 is negative (unstable mode) at the zone boundary $Ka = \pi$ if $\sigma > 0.475$ or $4/7\zeta(3)$, where ζ is a Riemann zeta function. Show further that the speed of sound at small Ka is imaginary if $\sigma > (2 \ln 2)^{-1} = 0.721$. Thus ω^2 goes to zero and the lattice is unstable for some value of Ka in the interval $(0, \pi)$ if $0.475 < \sigma < 0.721$. Notice that the phonon spectrum is not that of a diatomic lattice because the interaction of any ion with its neighbors is the same as that of any other ion.

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*This problem is rather difficult.

5
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