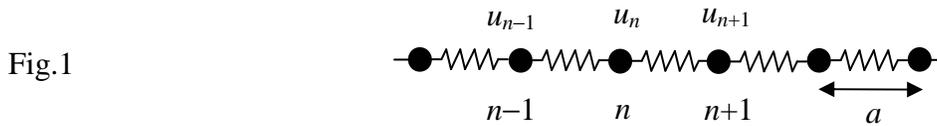


Section 5: Lattice Vibrations

So far we have been discussing equilibrium properties of crystal lattices. When the lattice is at equilibrium each atom is positioned exactly at its lattice site. Now suppose that an atom is displaced from its equilibrium site by a small amount. Due to force acting on this atom, it will tend to return to its equilibrium position. This results in lattice vibrations. Due to interactions between atoms, various atoms move simultaneously, so we have to consider the motion of the entire lattice.

One-dimensional lattice

For simplicity we consider, first, a one-dimensional crystal lattice and assume that the forces between the atoms in this lattice are proportional to relative displacements from the equilibrium positions.



This is known as the *harmonic approximation*, which holds well provided that the displacements are small. One might think about the atoms in the lattice as interconnected by elastic springs. Therefore, the force exerted on n -th atom in the lattice is given by

$$F_n = C(u_{n+1} - u_n) + C(u_{n-1} - u_n), \quad (5.1)$$

where C is the interatomic force (elastic) constant. Applying Newton's second law to the motion of the n -th atom we obtain

$$M \frac{d^2 u_n}{dt^2} = F_n = C(u_{n+1} - u_n) + C(u_{n-1} - u_n) = -C(2u_n - u_{n+1} - u_{n-1}), \quad (5.2)$$

where M is the mass of the atom. Note that we neglected here by the interaction of the n -th atom with all but its nearest neighbors. A similar equation should be written for each atom in the lattice, resulting in N coupled differential equations, which should be solved simultaneously (N is the total number of atoms in the lattice). In addition the boundary conditions applied to the end atom in the lattice should be taken into account.

Now let us attempt a solution of the form

$$u_n = A e^{i(qx_n - \omega t)} \quad (5.3)$$

where x_n is the equilibrium position of the n -th atom so that $x_n = na$. This equation represents a traveling wave, in which all the atoms oscillate with the same frequency ω and the same amplitude A and have wavevector q . Note that a solution of the form (5.3) is only possible because of the translational symmetry of the lattice.

Now substituting Eq.(5.3) into Eq.(5.2) and canceling the common quantities (the amplitude and the time-dependent factor) we obtain

$$M(-\omega^2) e^{iqna} = -C \left[2e^{iqna} - e^{iq(n+1)a} - e^{iq(n-1)a} \right] \quad (5.4)$$

This equation can be further simplified by canceling the common factor e^{iqna} , which leads to

$$M\omega^2 = C(2 - e^{iqa} - e^{-iqa}) = 2C(1 - \cos qa) = 4C \sin^2 \frac{qa}{2}. \quad (5.5)$$

We find therefore the dispersion relation for the frequency

$$\omega = \sqrt{\frac{4C}{M}} \left| \sin \frac{qa}{2} \right|, \quad (5.6)$$

which is the relationship between the frequency of vibrations and the wavevector q . This dispersion relation has a number of important properties.

(i) *Reducing to the first Brillouin zone.* The frequency (5.6) and the displacement of the atoms (5.3) do not change when we change q by $q+2\pi/a$. This means that these solutions are physically identical. This allows us to set the range of independent values of q within the first Brillouin zone, i.e.

$$-\frac{\pi}{a} \leq q \leq \frac{\pi}{a}. \quad (5.7)$$

Within this range of q the ω versus q is shown in Fig.2.

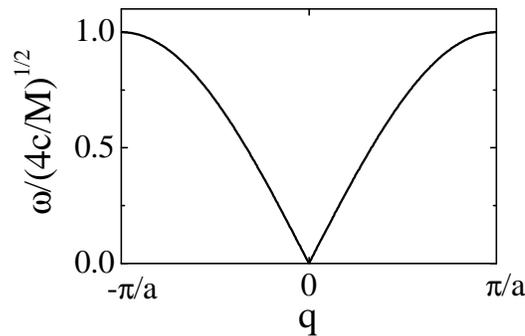


Fig.2

The maximum frequency is $\sqrt{4C/M}$. The frequency is symmetric with respect to the sign change in q , i.e. $\omega(q) = \omega(-q)$. This is not surprising because a mode with positive q corresponds to the wave traveling in the lattice from the left to the right and a mode with a negative q corresponds to the wave traveling from the right to the left. Since these two directions are equivalent in the lattice the frequency does not change with the sign change in q .

At the boundaries of the Brillouin zone $q = \pm\pi/a$ the solution represents a standing wave $u_n = A(-1)^n e^{-i\omega t}$: atoms oscillate in the opposite phases depending on whether n is even or odd. The wave moves neither right nor left.

(ii) *Phase and group velocity.* The phase velocity is defined by

$$v_p = \frac{\omega}{q} \quad (5.8)$$

and the group velocity by

$$v_g = \frac{d\omega}{dq}. \quad (5.9)$$

The physical distinction between the two velocities is that v_p is the velocity of the propagation of the plane wave, whereas the v_g is the velocity of the propagation of the wave packet. The latter is the velocity for the propagation of energy in the medium.

For the particular dispersion relation (5.6) the group velocity is given by

$$v_g = \sqrt{\frac{Ca^2}{M}} \cos \frac{qa}{2}. \quad (5.10)$$

As is seen from Eq.(5.10) the group velocity is zero at the edge of the zone where $q=\pm\pi/a$. Here the wave is standing and therefore the transmission velocity for the energy is zero.

(iii) *Long wavelength limit.* The long wavelength limit implies that $\lambda \gg a$. In this limit $qa \ll 1$. We can then expand the sine in Eq.(5.6) and obtain for the positive frequencies:

$$\omega = \sqrt{\frac{C}{M}} qa. \quad (5.11)$$

We see that the frequency of vibration is proportional to the wavevector. This is equivalent to the statement that velocity is independent of frequency. In this case

$$v_p = \frac{\omega}{q} = \sqrt{\frac{C}{M}} a. \quad (5.12)$$

This is the velocity of sound for the one dimensional lattice which is consistent with the expression we obtained earlier for elastic waves.

Diatomic 1D lattice

Now we consider a one-dimensional lattice with two non-equivalent atoms in a unit cell. It appears that the diatomic lattice exhibit important features different from the monoatomic case. Fig.3 shows a diatomic lattice with the unit cell composed of two atoms of masses M_1 and M_2 with the distance between two neighboring atoms a .

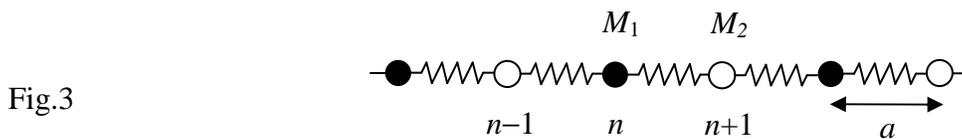


Fig.3

We can treat the motion of this lattice in a similar fashion as for monoatomic lattice. However, in this case because we have two different kinds of atoms, we should write two equations of motion:

$$\begin{aligned} M_1 \frac{d^2 u_n}{dt^2} &= -C(2u_n - u_{n+1} - u_{n-1}) \\ M_2 \frac{d^2 u_{n+1}}{dt^2} &= -C(2u_{n+1} - u_{n+2} - u_n) \end{aligned} \quad (5.13)$$

In analogy with the monoatomic lattice we are looking for the solution in the form of traveling mode for the two atoms:

$$\begin{bmatrix} u_n \\ u_{n+1} \end{bmatrix} = \begin{bmatrix} A_1 e^{iqna} \\ A_2 e^{iq(n+1)a} \end{bmatrix} e^{-i\omega t}, \quad (5.14)$$

which is written in the obvious matrix form. Substituting this solution to Eq.(5.13) we obtain

$$\begin{bmatrix} 2C - M_1 \omega^2 & -2C \cos qa \\ -2C \cos qa & 2C - M_2 \omega^2 \end{bmatrix} \begin{bmatrix} A_1 \\ A_2 \end{bmatrix} = 0. \quad (5.15)$$

This is a system of linear homogeneous equations for the unknowns A_1 and A_2 . A nontrivial solution exists only if the determinant of the matrix is zero. This leads to the secular equation

$$(2C - M_1 \omega^2)(2C - M_2 \omega^2) - 4C^2 \cos^2 qa = 0. \quad (5.16)$$

This is a quadratic equation, which can be readily solved:

$$\omega^2 = C \left(\frac{1}{M_1} + \frac{1}{M_2} \right) \pm C \sqrt{\left(\frac{1}{M_1} + \frac{1}{M_2} \right)^2 - \frac{4 \sin^2 qa}{M_1 M_2}}. \quad (5.17)$$

Depending on sign in this formula there are two different solutions corresponding to two different dispersion curves, as is shown in Fig.4:

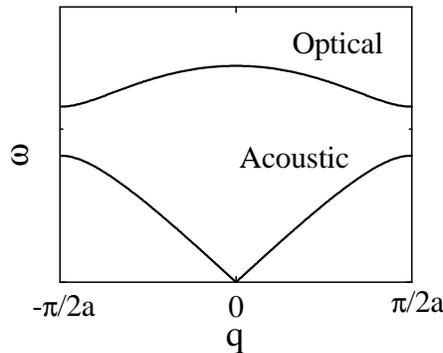


Fig.4

The lower curve is called the *acoustic branch*, while the upper curve is called the *optical branch*. The optical branch begins at $q=0$ and $\omega=0$. Then with increasing q the frequency increases in a linear fashion. This is why this branch is called acoustic: it corresponds to elastic waves or sound. Eventually this curve saturates at the edge of the Brillouin zone. On the other hand, the optical branch has a non-zero frequency at zero q

$$\omega_0 = \sqrt{2C \left(\frac{1}{M_1} + \frac{1}{M_2} \right)}. \quad (5.18)$$

and it does not change much with q .

The distinction between the acoustic and optical branches of lattice vibrations can be seen most clearly by comparing them at $q=0$ (infinite wavelength). As follows from Eq.(5.15), for the acoustic branch $\omega=0$ and $A_1=A_2$. So in this limit the two atoms in the cell have the same amplitude and the phase. Therefore, the molecule oscillates as a rigid body, as shown in Fig.5 for the acoustic mode.

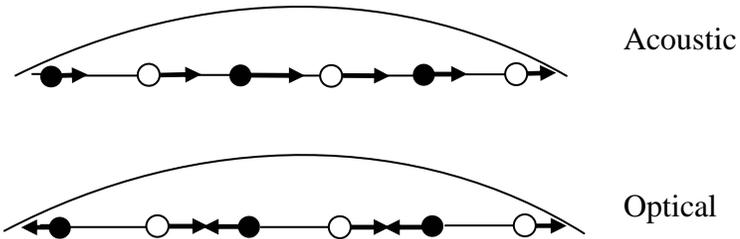


Fig.5

On the other hand, for the optical vibrations, substituting Eq.(5.18) to Eq.(5.15), we obtain for $q=0$:

$$M_1 A_1 + M_2 A_2 = 0. \quad (5.19)$$

It implies that the optical oscillation takes place in such a way that the center of mass of a molecule remains fixed. The two atoms move in out of phase as shown in Fig.5. The frequency of these vibrations lies in infrared region which is the reason for referring to this branch as optical.

Three dimensional lattice

These considerations can be extended to the three-dimensional lattice. To avoid mathematical details we shall present only a qualitative discussion. Consider, first, the monatomic Bravais lattice, in which each unit cell has a single atom. The equation of motion of each atom can be written in a manner similar to that of Eq.(5.2). The solution of this equation in three dimensions can be represented in terms of *normal modes*

$$\mathbf{u} = \mathbf{A} e^{i(\mathbf{q}\mathbf{r} - \omega t)} \quad (5.20)$$

where the wave vector \mathbf{q} specifies both the wavelength and direction of propagation. The vector \mathbf{A} determines the amplitude as well as the direction of vibration of the atoms. Thus this vector specifies the *polarization* of the wave, i.e., whether the wave is *longitudinal* (\mathbf{A} parallel to \mathbf{q}) or *transverse* (\mathbf{A} perpendicular to \mathbf{q}).

When we substitute Eq.(5.20) into the equation of motion, we obtain three simultaneous equations involving A_x , A_y , and A_z , the components of \mathbf{A} . These equations are coupled together and are equivalent to a 3×3 matrix equation. The roots of this equation lead to three different dispersion relations, or three dispersion curves, as shown in Fig.6. All three branches pass through the origin, which means all the branches are acoustic. This is of course to be expected, since we are dealing with a *monatomic* Bravais lattice.

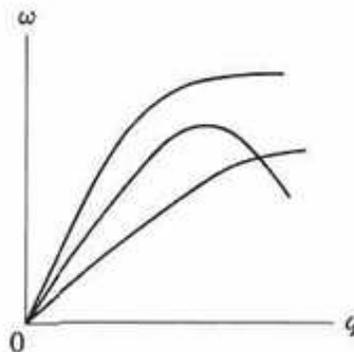


Fig.6

The three branches in Fig.6 differ in their polarization. When \mathbf{q} lies along a direction of high symmetry - for example, the [100] or [110] directions - these waves may be classified as either pure longitudinal or pure transverse waves. In that case, two of the branches are transverse and one is longitudinal. One usually refers to these as the TA - *transverse acoustic* and LA - *longitudinal acoustic* branches, respectively. However, along non-symmetry directions the waves may not be pure longitudinal or pure transverse, but have a mixed character.

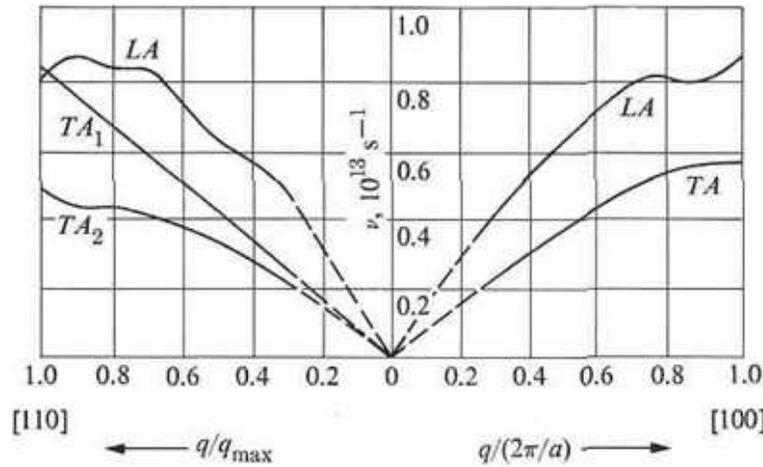


Fig.7

Figure 7 shows the dispersion curves for Al in the [100] and [110] directions. Note that in certain high-symmetry directions, such as the [100] in Al, the two transverse branches coincide. The branches are then said to be *degenerate*.

We turn our attention now to the non-Bravais three-dimensional lattice. Here the unit cell contains two or more atoms. If there are s atoms per cell, then on the basis of our previous experience we conclude that there are $3s$ dispersion curves. Of these, *three* branches are acoustic, and the remaining $(3s - 3)$ are optical. The mathematical justification for this assertion is as follows: We write the equation of motion for each atom in the cell, which results in s equations. Since these are vector equations, they are equivalent to $3s$ scalar equations, which have $3s$ roots. It can be shown that three of these roots always vanish at $q = 0$, which results in three acoustic branches. The remaining $(3s - 3)$ roots, therefore, belong to the optical branches, as stated above.

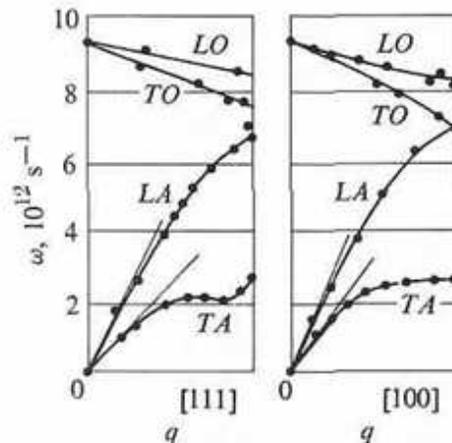


Fig.8

The acoustic branches may be classified, as before, by their polarizations as TA_1 , TA_2 , and LA. The *optical* branches can also be classified as longitudinal or transverse when q lies along a high-symmetry direction, and one speaks of LO and TO branches. As in the one-dimensional case, one can also show that, for an optical branch, the atoms in the unit cell vibrate out of phase relative to each other. As an example of a non-Bravais lattice, the dispersion curves for Ge are shown in Fig.8. Since there are two atoms per unit cell in germanium, there are six branches: three acoustic and three optical. Note that the two transverse branches are degenerate along the [100] direction, as indicated earlier.

Phonons

So far we discussed a classical approach to the lattice vibrations. As we know from quantum mechanics the energy levels of the harmonic oscillator are quantized. Similarly the energy levels of lattice vibrations are quantized. The quantum of vibration is called a *phonon* in analogy with the photon, which is the quantum of the electromagnetic wave.

We know that the allowed energy levels of the harmonic oscillator are given by

$$E = (n + 1/2)\hbar\omega \quad (5.21)$$

where n is the quantum number. A normal vibration mode in a crystal of frequency ω is given by Eq.(5.20). If the energy of this mode is given by Eq.(5.21) we can say that this mode is occupied by n *phonons* of energy $\hbar\omega$. The term $1/2\hbar\omega$ is the zero point energy of the mode.

Let me now make a comparison between the classical and quantum solutions in one-dimensional case. Consider a normal vibration

$$u = Ae^{i(qx - \omega t)} \quad (5.22)$$

where u is the displacement of an atom from its equilibrium position x and A is the amplitude. The energy of this vibrational mode averaged over time is (see Problem 4.1):

$$E = 1/2 M \omega^2 A^2 = (n + 1/2)\hbar\omega. \quad (5.23)$$

We see that there is a relationship between the amplitude of vibration and the frequency and the phonon occupation of the mode. In classical mechanics any amplitude of vibration is possible, whereas in quantum mechanics on discrete values are allowed. This is shown in Fig.9

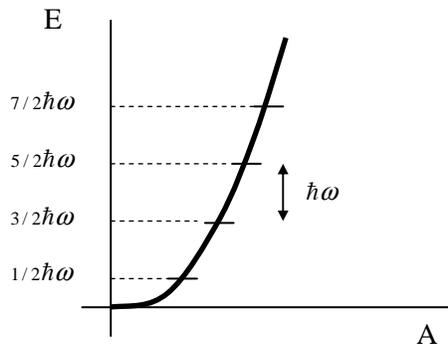


Fig.9

The lattice with s atoms in a unit cell is described by $3s$ independent oscillators. The frequencies of normal modes of these oscillators will be given by the solution of $3s$ linear equations as we discussed before. They are $\omega_p(\mathbf{q})$, where p denotes a particular mode, i.e. $p=1, \dots, 3s$. The energy of this mode is given by

$$E_{q_p} = (n_{q_p} + 1/2)\hbar\omega_p(\mathbf{q}), \quad (5.24)$$

where n_{q_p} is the occupation number of the normal mode and is an integer. A vibrational state of the entire crystal is specified by giving the occupation numbers for each of the $3s$ modes. The total vibrational energy of the crystal is the sum of the energies of the individual modes, so that

$$E = \sum_{q_p} E_{q_p} = \sum_{q_p} (n_{q_p} + 1/2)\hbar\omega_p(\mathbf{q}). \quad (5.25)$$

Phonons can interact with other particles such as photons, neutrons and electrons. This interaction occurs such as if photon had a momentum $\hbar\mathbf{q}$. However, a phonon does not carry real physical momentum. The reason is that the center of mass of the crystal does not change its position under vibrations (except $q=0$).

In crystals there exist 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 $\mathbf{k}' = \mathbf{k} + \mathbf{G}$, 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. This equation can be considered as a condition for the conservation of the momentum of the whole system, in which the lattice acquires a momentum $-\hbar\mathbf{G}$.

If the scattering of a photon is inelastic and is accompanied by the excitation or absorption of a phonon the selection rule becomes

$$\mathbf{k}' = \mathbf{k} \pm \mathbf{q} + \mathbf{G}, \quad (5.26)$$

where sign (+) corresponds to creation of a phonon and sign (−) corresponds to absorption of a phonon.

Phonon dispersion relations $\omega_p(\mathbf{q})$ can be determined by the inelastic scattering of neutrons with emission or absorption of phonons. In this case in addition to the condition of momentum conservation we have the requirement of conservation of energy. The latter condition can be written as

$$\frac{\hbar^2 k^2}{2M} = \frac{\hbar^2 k'^2}{2M} \pm \hbar\omega \quad (5.27)$$

where M is the mass of the neutron and $\hbar\mathbf{k}$ and $\hbar\mathbf{k}'$ are the momenta of the incident and scattered neutron. Once we know in an experiment the kinetic energy of the incident and scattered neutrons from Eq.(5.27) we can determine the frequency of the emitted or absorbed phonon. Then experimentally we need to determine those directions, which are characterized by the highest intensity of the scattered beam. For these directions the conditions (5.26) are satisfied and therefore from Eqs.(5.26) we can find the wavevector of the phonon. Therefore, this is the way to obtain the dispersion conditions for the frequency of phonons which we discussed before.