

## Lecture 4: Elastic constants and phonons

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In the previous chapter, we learned that crystals could form by minimizing the binding energy. After obtaining the expression for the binding energy, we can then calculate the equilibrium separation and equilibrium energy. Near the minimum point, we can expand the energy of the system using the power series:

$$U(r) = U_0 + \left. \frac{\partial U}{\partial r} \right|_{r_0} (r - r_0) + \frac{1}{2} \left. \frac{\partial^2 U}{\partial r^2} \right|_{r_0} (r - r_0)^2 + \mathcal{O}((r - r_0)^3).$$

Since  $r_0$  is the equilibrium separation by construction, the second term is zero. Therefore, the  $r$ -dependent leading term is the third term. We will let  $C = \left. \frac{\partial^2 U}{\partial r^2} \right|_{r_0}$  (the elastic constant) and  $u = r - r_0$  is the displacement from the equilibrium separation. We can then rewrite the above equation as:

$$\Delta U = U(r) - U_0 = \frac{1}{2} C u^2,$$

which is expression for the potential energy of the simple harmonic oscillators. Hence, we expect the atoms inside the crystals to oscillate around its equilibrium separation. In this chapter, we will study this lattice vibration, which we call phonons, and their contributions to the physical phenomena that we can measure.

### 4.1 Elastic waves in crystals

As we have seen in the introduction, the binding energy of atoms in the crystal can be expanded using a power series and the non-zero leading term is a parabolic function in the displacement from the equilibrium position. The implication of this term is the oscillating motion of the atoms which gives rise to the vibrational wave traveling through the crystal, which we call **phonons** to emphasize their similar characteristics with the electromagnetic wave or photons.

#### 4.1.1 Vibrational wave in monatomic crystal

We will start off by considering the simplest case, that is, the harmonic oscillation in the lattice with one atom per a unit cell. To further simplify our problem, we will consider the oscillation of  $N$  planes of atoms with respect to each other and will let the 'spring constant'  $C$  between these planes be the same. The planes are a distance  $a$  apart. Now let label one plane the  $s^{\text{th}}$  plane, the plane to its left the  $(s + 1)^{\text{th}}$  plane, and the plane to its right the  $(s - 1)^{\text{th}}$  plane. We will also assume that the lattice is very large and the effect of the boundary can be ignored. However, for simplicity in the calculation, we will assume a **periodic boundary** condition, that is, the  $N^{\text{th}}$  plane is connected back to the  $0^{\text{th}}$  plane. Letting  $u$  be the displacement from the equilibrium position  $na$  ( $n$  is an integer), we can write the equation of motion of the  $n^{\text{th}}$  plane as

$$M \frac{\partial^2 u_s}{\partial t^2} = -C [2u_s - u_{s+1} - u_{s-1}] \quad (4.1)$$

with the boundary condition

$$u(Na) = u(0).$$

For the time dependent part, we have

$$u_s(t) = u(sa)e^{-i\omega t}.$$

Therefore, the left hand side of Eq. 4.1 becomes

$$M \frac{\partial^2 u_s}{\partial t^2} = -M\omega^2 u_s(t). \quad (4.2)$$

And for the spatial dependent part, due to the periodicity of the crystal we have

$$u(sa) = u_0 e^{iKsa},$$

using Bloch Theorem that we will prove in Lecture 7. Therefore, the right hand side of Eq. 4.1 becomes

$$\begin{aligned} -C[2u_s(t) - u_{s+1}(t) - u_{s-1}(t)] &= -Cu_0 e^{-i\omega t} [2e^{iKsa} - e^{iKa(s+1)} - e^{iKa(s-1)}] \\ &= -Cu_0 e^{-i\omega t} e^{iKsa} [2 - e^{iKa} - e^{-iKa}] \\ &= -2Cu_s(t) [1 - \cos(Ka)] \end{aligned} \quad (4.3)$$

After combining Eqs.4.2 and 4.3, we obtain the dispersion relation that shows the expression of  $\omega$  as a function of  $K$  as

$$\begin{aligned} \omega^2(K) &= \frac{2C}{M} [1 - \cos(Ka)] \\ &= \frac{4C}{M} \sin^2\left(\frac{Ka}{2}\right), \end{aligned}$$

or

$$\omega = \left| \sqrt{\frac{4C}{M}} \sin\left(\frac{Ka}{2}\right) \right|$$

From this equation, we can immediately see that the frequency of the lattice vibration can have a value between 0 and  $\sqrt{\frac{4C}{M}}$  and the whole range of frequency is contained inside the first Brillouin zone between  $K = -\frac{\pi}{a}$  and  $\frac{\pi}{a}$ . Analogously, in three dimensional lattices, we can specify all phonon excitations in the first Brillouin zone. The region near the zone edge corresponds to the short-distance interaction (short-wavelength limit) while the region near the origin corresponds to the long distance interaction (long-wavelength limit).

We can calculate the group velocity  $v_g$  of this vibrational wave of the lattice using  $v_g = \frac{d\omega}{dK}$ , which we obtain

$$v_g = a \sqrt{\frac{C}{M}} \cos\left(\frac{Ka}{2}\right).$$

We can see that  $v_g$  goes to zero as  $K$  approaches the zone boundary. We can think of this phenomenon as standing wave at the zone edge. This situation is similar to the condition for the Bragg peak. When the condition for the Bragg diffraction is met, the wave cannot transverse through the sample, that is, the vibrations wave or phonons cannot travel through the sample; hence the wave velocity is zero.

On the other hand near the origin or for the continuum limit, where  $\lambda \gg a$ , that is,  $Ka \ll 1$ , we have

$$\sin\left(\frac{Ka}{2}\right) \simeq \frac{1}{2}Ka$$

Therefore, for the small  $K$  the dispersion relation becomes

$$\omega = a\sqrt{\frac{C}{M}}K \equiv vK,$$

and the group velocity becomes

$$v_g = v = a\sqrt{\frac{C}{M}}.$$

This is in fact the velocity of sound since sound propagates through solid by means of lattice vibration.

**Determination of the spring constant from experiment** In our calculations, we have only included the nearest-neighbor interaction but in fact in some crystals such as in metals the attractive force due to the delocalization of electrons that holds atoms together are quite long-range. In some case, it has been experimentally shown that the interactions can be as long as 20 lattice constants. Therefore, we have to modify the dispersion relation to include the long-range nature of the interaction. For  $p$  nearest planes, the dispersion relation becomes

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

We then can solve for  $C_p$  by multiplying both sides by  $\cos(rKa)$  and integrating over the Brillouin zone:

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

Therefore,

$$C_r = -\frac{Ma}{2\pi} \int_{-\pi/a}^{\pi/a} dK \omega_K^2 \cos(rKa).$$

Once we know the dispersion relation  $\omega_K$  from an experiment, we can calculate the spring constant at range  $ra$  using this formula.

In the three-dimensional lattice, we have three vibrational modes of the lattice.

- **One longitudinal mode:** In this mode, the vibration is along the traveling direction of the wave.
- **Two transverse modes:** For these modes, the vibration is perpendicular to the direction of the traveling wave.

We note that the dispersion and wave velocity of these three modes can be different due to the difference in the elastic constant  $C$  along those directions.

### 4.1.2 Vibrational wave in the diatomic crystal

In this section, we will use the same mathematical method to calculate the dispersion relation of the vibrational wave or phonons in the crystal where a basis has two atoms or the diatomic crystal.

We will again consider the vibration of lattice planes in one dimension. However, now we have two types of lattices planes, which we will called  $A$  and  $B$ , consisted of different patterns of atoms. Since the plane separation between lattice planes could be different, we have two displacement variables  $u_s$  and  $v_s$  for the  $s^{th}$  plane of the first kind of lattice planes  $A$  and the  $s^{th}$  plane of the second kind of lattice planes  $B$ , respectively.  $u_s$  and  $v_s$  are defined to be a

distance from the equilibrium position. For simplicity, we will assume that the spring constants are all the same. In reality, the spring constants between two adjacent planes to the left and the right can be different.

We can again write down a set of the equations of motion for  $u_s$  and  $v_s$  as the following:

$$\begin{aligned} M_B \frac{d^2 u_s}{dt^2} &= -C [2u_s - v_s - v_{s-1}] \\ M_A \frac{d^2 v_s}{dt^2} &= -C [2v_s - u_s - u_{s+1}], \end{aligned}$$

where  $M_A$  and  $M_B$  are the masses of lattices of types  $A$  and  $B$ , respectively. The solution for these equations are similar to the solution to the monatomic crystal, that is,

$$u_s(t) = u_0 e^{-i\omega t} e^{iKsa}$$

and

$$v_s(t) = v_0 e^{-i\omega t} e^{iKsa}.$$

We can substitute these solutions back to the equations of motion to obtain:

$$\begin{aligned} -\omega^2 M_B u_0 &= C v_0 (1 + e^{-iKa}) - 2C u_0 \\ -\omega^2 M_A v_0 &= C u_0 (1 + e^{iKa}) - 2C v_0 \end{aligned} \quad (4.4)$$

In order to solve this set of equations, we will rewrite them in a matrix form.

$$\begin{bmatrix} 2C - \omega^2 M_B & -C(1 + e^{-iKa}) \\ -C(1 + e^{iKa}) & 2C - \omega^2 M_A \end{bmatrix} \begin{bmatrix} u_0 \\ v_0 \end{bmatrix} = 0.$$

We will then define the matrix  $M$  to be

$$M = \begin{bmatrix} 2C - \omega^2 M_B & -C(1 + e^{-iKa}) \\ -C(1 + e^{iKa}) & 2C - \omega^2 M_A \end{bmatrix}.$$

From your linear algebra class, you might have learned that the set of equations 4.4 can be solved by finding the determinant of  $M$  and setting it to zero, that is,  $\det M = 0$ , from which we will get

$$\omega^4 M_A M_B - 2\omega^2 C (M_B + M_A) + 2C^2 (1 - \cos(Ka)) = 0.$$

We can rewrite the last term  $2C^2 (1 - \cos(Ka)) = 4C^2 \sin^2 \frac{Ka}{2}$ . The above equation is a quadratic equation and can be solved readily:

$$\omega^2 = C \left( \frac{M_A + M_B}{M_A M_B} \right) \pm C \left[ \left( \frac{M_B + M_B}{M_A M_B} \right)^2 - \frac{4 \sin^2 \frac{Ka}{2}}{M_A M_B} \right]^{1/2}.$$

We can rewrite this equation using a reduced mass

$$\frac{1}{\mu} = \frac{1}{M_A} + \frac{1}{M_B} \Rightarrow \mu = \frac{M_A M_B}{M_A + M_B}$$

and let  $M = M_A + M_B$ . With these substitutions, we obtain

$$\omega^2 = \frac{C}{\mu} \pm \frac{C}{\mu} \left[ 1 - \frac{4\mu}{M} \sin^2 \frac{Ka}{2} \right]^{1/2}.$$

From this expression, we can see right away that there are two solutions corresponding to the  $\pm$  sign in front of the second term. This means, there are two branches of the dispersion relation for each value of  $K$ .

Again, let us first consider the case of the continuum limit or the long wavelength limit, that is,  $Ka \ll 1$ . We can approximate  $\sin^2 \frac{Ka}{2} \approx \left(\frac{Ka}{2}\right)^2$ . Therefore, the expression for  $\omega^2$  becomes

$$\omega^2(K) = \begin{cases} \frac{2C}{\mu} - \frac{1}{2} \frac{C}{M} K^2 a^2 & \text{for +} \\ \frac{1}{2} \frac{C}{M} K^2 a^2 & \text{for -} \end{cases}$$

If we let  $K$  goes to zero, then  $\frac{C}{\mu} \gg \frac{C}{M} K^2 a^2$  and  $\omega^2(K)$  becomes

$$\omega^2(K) = \begin{cases} \frac{2C}{\mu} & \text{for +} \\ \frac{1}{2} \frac{C}{M} K^2 a^2 & \text{for -} \end{cases}$$

The phonon excitations in the case of the negative sign is the same as those in the case of monatomic crystal, that is, it goes to zero as  $K$  goes to zero and for small  $K$ ,  $\omega$  is linearly proportional to  $K$ . We will call this mode the **acoustic mode**. This mode is due to the relative motion between atoms in different unit cells just like in the monatomic case. In the case of positive sign, as  $K$  goes to zero, the energy of this branch instead goes to a finite value. If the value of  $\frac{Ca^2}{M}$  is small, this mode becomes relative flat (weakly dispersive) compared to the acoustic mode. We call this mode the **optical mode**. It is due to the relative motion between atoms in the same unit cell.

In the other limit, if  $K$  obtains its maximum value possible. That is, if  $K = \pi$ , then  $\sin^2 \frac{\pi}{2} = 1$ . The expression for  $\omega$  becomes

$$\omega^2 = \frac{C}{\mu} \pm \frac{C}{\mu} \left[ 1 - \frac{4\mu}{M} \right]^{1/2}.$$

But we have

$$1 - \frac{4\mu}{M} = \frac{(M_A - M_B)^2}{(M_A + M_B)^2}$$

Therefore, we can rewrite the equation for  $\omega$  in terms of  $M_A$  and  $M_B$  as

$$\omega^2 = C \frac{M_A + M_B}{M_A M_B} \pm C \left| \frac{M_A - M_B}{M_A M_B} \right|.$$

$$\Rightarrow \omega^2(K) = \begin{cases} \frac{2C}{M_A} & \text{for +} \\ \frac{2C}{M_B} & \text{for -} \end{cases}$$

This expression indicates the energy of phonons at the zone edge. We can see that if  $M_A \neq M_B$ , then there is a energy gap of phonons at the zone edge, where no  $\omega$  is allowed.

Similar to the acoustic mode, the optical mode also has three modes or three polarizations, two transverse modes and one longitudinal mode. For the transverse modes, the difference between the transverse acoustic mode (TA) and transverse optical mode (TO) is that the atoms in TA form a single wave while those in TO form node-antinode configuration. For the TO mode at  $K = 0$ , the displacement  $u$  and  $v$  will have a ratio:

$$\frac{u}{v} = -\frac{M_A}{M_B},$$

which means the two types of atoms will vibrate out-of-phase with each other due to the minus sign. It turns out that if the two types of atoms happen to carry charges, then this mode of vibration can be excited using light. That is the reason why this mode is called the optical mode.

On the other hand, for the acoustic mode at  $K = 0$ ,  $\omega^2$  is also equal to zero. Therefore, from Eq.4.4, we have

$$2Cu - 2Cv = 0$$

$$u = v,$$

which means the atoms in Planes  $A$  and  $B$  will move together and their vibration motion with respect to other sets of Planes  $A$  and  $B$  in different unit cells give rise to the acoustic phonons.

For the  $p$ -atom crystal in  $d$  dimensional space, there are  $pd$  normal modes of phonons. In three-dimensional space, each branch has three polarizations; one longitudinal and two transverse. There can only be one acoustic branch, which means that there can only be three acoustic modes. The rest of the normal modes, which is equal to  $3(p-1)$ , are the optical mode, out of which  $p-1$  modes are optical longitudinal and  $2(p-1)$  are optical transverse.

**Phonon momentum** We will think of phonons as if it carries the momentum of  $\hbar\vec{K}$ , which is sometimes called **crystal momentum**. We have learned in the previous chapter when we talked about the diffraction (elastic scattering) that the change in the wave vectors  $\vec{k}$  of the incident beam and  $\vec{k}'$  of the scattered beam is equal to the reciprocal lattice vector  $\vec{G}$ , which represent the momentum of the lattice. In this case,  $\vec{G}$  represents the crystal momentum as the whole crystal or its center mass moves due to the recoil. However, this change in momentum is quite small and we do not actually observe the recoil motion.

In order to measure phonons, we will need to perform an inelastic scattering, which means there is a transfer of energy to the crystal and hence both direction and magnitude of the wave momentum have to change. We can think of the inelastic scattering as two processes. In the first process, a phonon is created and the equation for the momentum transfer is

$$\vec{k}' + \vec{K} = \vec{k} + \vec{G}.$$

In the second process, a phonon is destroyed or created; the equation of the momentum transfer becomes

$$\vec{k}' = \vec{k} + \vec{K} + \vec{G}.$$

Since we can also measure the energy transfer of the scattering process, we can obtain the dispersion relation of phonons. To measure the dispersion relation of phonons, we can use x-ray or neutron beams since both light and neutrons can excite the vibration mode of the crystal.

For neutron scattering, the conservation of energy and momentum gives the following equation for the energy and momentum transfers:

$$\begin{aligned} \vec{k}' \pm \vec{K} &= \vec{k} + \vec{G} \\ \frac{\hbar^2 k^2}{2m_n} &= \frac{\hbar^2 k'^2}{2m_n} \pm \hbar\omega, \end{aligned}$$

where  $m_n$  is the neutron mass, the  $\pm$  sign indicates whether a phonon is created or destroyed, and  $\hbar\omega$  is the the phonon energy.

## References

- [1] Kittel, C.: Introduction to Solid State Physics 7<sup>th</sup> Edition (Chapter 3), John Wiley & Sons, Inc. (1996).
- [2] Ashcroft, N. W. and Mermin, N. D.: Solid State Physics (Chapter 20), Thomson Learning, Inc. (1976).