

## Chapter 5

# The one-dimensional monatomic solid

In the first few chapters we found that our simple models of solids, and electrons in solids, were insufficient in several ways. In order to improve our understanding, we now need to take the periodic microstructure of crystals more seriously. To get a qualitative understanding of the effects of the periodic lattice, it is frequently sufficient to think in terms of simple one dimensional systems.

### 5.1 Forces between atoms: Compressibility, Sound, and Thermal Expansion

In the last chapter we discussed bonding between atoms. We found, particularly in the discussion of covalent bonding, that the lowest energy configuration would have the atoms at some optimal distance between (See figure 4.7, for example). Given this shape of the energy as a function of distance between atoms we will be able to come to some interesting conclusions.

For simplicity, let us imagine a 1-dimensional system of atoms (atoms in a single line). The potential  $V(x)$  between the atoms is drawn in the Figure 5.1.

The classical equilibrium position is the position at the bottom of the well (marked  $x_{eq}$  in the figure). The distance between atoms at low temperature should then be  $x_{eq}$ . (As a homework assignment we will consider how quantum mechanics can change this value and increase it a little bit!).

Now, let us Taylor expand the potential around its minimum.

$$V(x) \approx V(x_{eq}) + \frac{\kappa}{2}(x - x_{eq})^2 + \frac{\kappa_3}{3!}(x - x_{eq})^3 + \dots$$

Note that there is no linear term (if there were a linear term, then the position  $x_{eq}$  would not be the minimum). If there are only small deviations from the position  $x_{eq}$  the higher terms are much much smaller than the leading quadratic term and we can throw these terms out. This is a rather crucial general principle that *any* potential, close enough to its minimum, is quadratic.

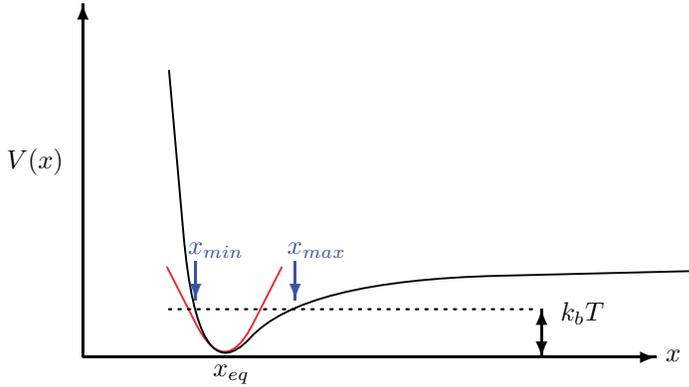


Figure 5.1: Potential Between Neighboring Atoms (black). The red curve is a quadratic approximation to the minimum (it may look crooked but in fact the red curve is symmetric and the black curve is asymmetric). The equilibrium position is  $x_{eq}$ . At finite temperature  $T$ , the system can oscillate between  $x_{max}$  and  $x_{min}$  which are not symmetric around the minimum. Thus as  $T$  increases the *average* position moves out to larger distance and the system expands.

### Compressibility (or Elasticity)

We thus have a simple Hooke's law quadratic potential around the minimum. If we apply a force to compress the system (i.e., apply a pressure to our model one dimensional solid) we find

$$-\kappa(\delta x_{eq}) = F$$

where the sign is so that a positive (compressive) pressure reduces the distance between atoms. This is obviously just a description of the compressibility (or elasticity) of a solid. The usual description of compressibility is

$$\beta = -\frac{1}{V} \frac{\partial V}{\partial P}$$

(one should ideally specify if this is measured at fixed  $T$  or at fixed  $S$ . Here, we are working at  $T = S = 0$  for simplicity). In the 1d case, we write the compressibility as

$$\beta = -\frac{1}{L} \frac{\partial L}{\partial F} = \frac{1}{\kappa x_{eq}} = \frac{1}{\kappa a} \quad (5.1)$$

with  $L$  the length of the system and  $x_{eq}$  is the spacing between atoms. Here we make the conventional definition that the equilibrium distance between identical atoms in a system (the so-called lattice constant) is written as  $a$ .

### Sound

You may recall from your fluids course that in an isotropic compressible fluid, one predicts sound waves with velocity

$$v = \sqrt{\frac{B}{\rho}} = \sqrt{\frac{1}{\rho\beta}} \quad (5.2)$$

Here  $\rho$  is the mass density of the fluid,  $B$  is the bulk modulus, which is  $B = 1/\beta$  with  $\beta$  the (adiabatic) compressibility.

While in a real solid the compressibility is anisotropic and the speed of sound depends in detail on the direction of propagation, in our model 1d solid this is not a problem and we can calculate that the the density is  $m/a$  with  $m$  the mass of each particle and  $a$  the equilibrium spacing between particles.

Thus using our result from above, we predict a sound wave with velocity

$$v = \sqrt{\frac{\kappa a^2}{m}} \quad (5.3)$$

Shortly (in section 5.2.2) we will re-derive this expression from a microscopic equations of motion for the atoms in the 1d solid.

### Thermal Expansion

So far we have been working at zero temperature, but it is worth thinking at least a little bit about thermal expansion. This will be fleshed out more completely in a homework assignment. (In fact even in the homework assignment the treatment of thermal expansion will be very crude, but that should still be enough to give us the general idea of the phenomenon<sup>1</sup>).

Let us consider again figure 5.1 but now at finite temperature. We can imagine the potential as a function of distance between atoms as being like a ball rolling around in a potential. At zero energy, the ball sits at the the minimum of the distribution. But if we give the ball some finite temperature (i.e, some energy) it will oscillate around the minimum. At fixed energy  $k_b T$  the ball rolls back and forth between the points  $x_{min}$  and  $x_{max}$  where  $V(x_{min}) = V(x_{max}) = k_b T$ . But away from the minimum the potential is asymmetric, so  $|x_{max} - x_{eq}| > |x_{min} - x_{eq}|$  so on average the particle has a position  $\langle x \rangle > x_{eq}(T = 0)$ . This is in essence the reason for thermal expansion! We will obtain positive thermal expansion for any system where  $\kappa_3 < 0$  (i.e., at small  $x$  the potential is steeper) which almost always is true for real solids.

### Summary

- Forces between atoms determine ground state structure.
- These same forces, perturbing around the ground state, determine elasticity, sound velocity, and thermal expansion.
- Thermal expansion comes from the non-quadratic part of the interatomic potential.

## 5.2 Microscopic Model of Vibrations in 1d

In chapter 2 we considered the Boltzmann, Einstein, and Debye models of vibrations in solids. In this section we will consider a detailed model of vibration in a solid, first classically, and then quantum mechanically. We will be able to better understand what these early attempts to understand vibrations achieved and we will be able to better understand their shortcomings.

---

<sup>1</sup>Although this description is an annoyingly crude discussion of thermal expansion, we are mandated by the IOP to teach something on this subject. Explaining it more correctly, is unfortunately, rather messy!

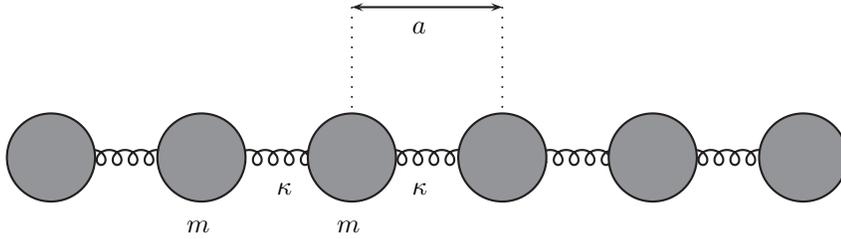
Let us consider a chain of identical atoms of mass  $m$  where the equilibrium spacing between atoms is  $a$ . Let us define the position of the  $n^{\text{th}}$  atom to be  $x_n$  and the equilibrium position of the  $n^{\text{th}}$  atom to be  $x_n^{\text{eq}} = na$ .

Once we allow motion of the atoms, we will have  $x_n$  deviating from its equilibrium position, so we define the small variable

$$\delta x_n = x_n - x_n^{\text{eq}}$$

Note that in our simple model we are allowing motion of the masses only in one dimension (i.e., we are allowing longitudinal motion of the chain, not transverse motion).

As discussed in the previous section, if the system is at low enough temperature we can consider the potential holding the atoms together to be quadratic. Thus, our model of a solid is chain of masses held together with springs as show in this figure



With this quadratic interatomic potential, we can write the total potential energy of the chain to be

$$\begin{aligned} V_{\text{tot}} &= \sum_i V(x_i - x_{i+1}) \\ &= V_{\text{eq}} + \sum_i \frac{\kappa}{2} (\delta x_i - \delta x_{i+1})^2 \end{aligned}$$

The force on the  $n^{\text{th}}$  mass on the chain is then given by

$$F_n = \frac{\partial V_{\text{tot}}}{\partial x_n} = \kappa(\delta x_{n+1} - \delta x_n) + \kappa(\delta x_{n-1} - \delta x_n)$$

Thus we have Newton's equation of motion

$$m(\delta \ddot{x}_n) = F_n = \kappa(\delta x_{n+1} + \delta x_{n-1} - 2\delta x_n) \quad (5.4)$$

To remind the reader, for any coupled system system, a *normal mode* is defined to be a collective oscillation where all particles move at the same frequency. We now attempt a solution to Newton's equations by using an ansatz that describes the normal modes as waves

$$\delta x_n = A e^{i\omega t - ikx_n^{\text{eq}}} = A e^{i\omega t - ikna}$$

where  $A$  is an amplitude of oscillation.

Now the reader might be confused about how it is that we are considering complex values of  $\delta x_n$ . Here we are using complex numbers for convenience but actually we implicitly mean to

take the real part. (This is analogous to what one does in circuit theory with oscillating currents!). Since we are taking the real part, it is sufficient to consider only  $\omega \geq 0$ , however, we must be careful that  $k$  can then have either sign, and these are inequivalent once we have specified that  $\omega$  is positive.

Plugging our ansatz into Eq. 5.4 we obtain

$$-m\omega^2 A e^{i\omega t - ikna} = \kappa A e^{i\omega t} \left[ e^{-ika(n+1)} + e^{-ika(n-1)} - 2e^{-ikan} \right]$$

or

$$m\omega^2 = 2\kappa[1 - \cos(ka)] = 4\kappa \sin^2(ka/2) \quad (5.5)$$

We thus obtain the result

$$\omega = 2\sqrt{\frac{\kappa}{m}} \left| \sin\left(\frac{ka}{2}\right) \right| \quad (5.6)$$

In general a relationship between a frequency (or energy) and a wavevector (or momentum) is known as a *dispersion relation*. This particular dispersion relation is shown in Fig. 5.2

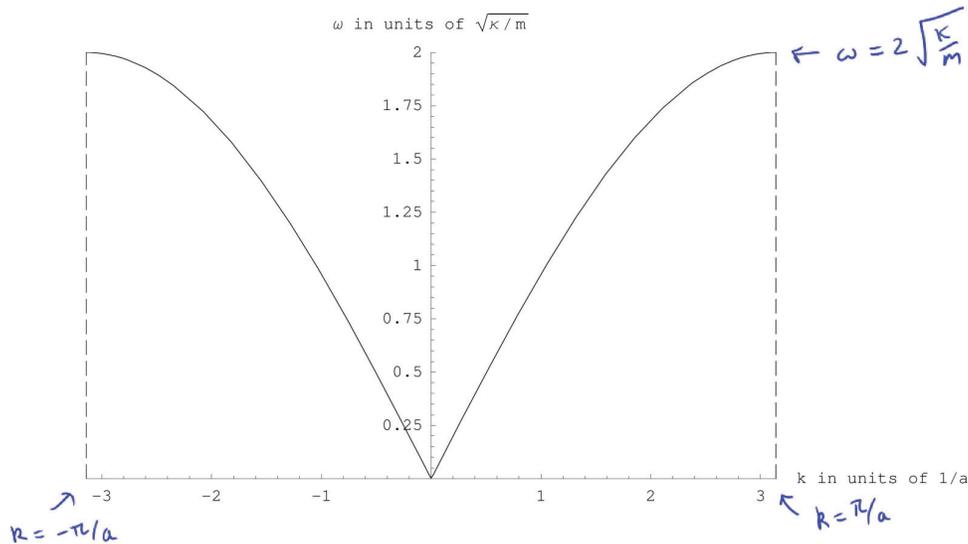


Figure 5.2: Dispersion relation of the 1d harmonic chain. The dispersion is periodic in  $k \rightarrow k + 2\pi/a$

### 5.2.1 First Exposure to the Reciprocal Lattice

Note that in the figure Fig. 5.2 we have only plotted the dispersion for  $-\pi/a \leq k \leq \pi/a$ . The reason for this is obvious from Eq. 5.6 — the dispersion relation is actually periodic in  $k \rightarrow k + 2\pi/a$ . In fact this is a very important general principle:

**Principle 5.2.1:** A system which is periodic in real space with a periodicity  $a$  will be periodic in reciprocal space with periodicity  $2\pi/a$ .

In this principle we have used the word *reciprocal* space which means  $k$ -space. In other words this principle tells us that if a system looks the same when  $x \rightarrow x + a$  then in  $k$ -space the dispersion will look the same when  $k \rightarrow k + 2\pi/a$ . We will return to this principle many times in later chapters.

The periodic unit (the “unit cell”) in  $k$ -space is conventionally known as the *Brillouin Zone*<sup>2,3</sup>. This is your first exposure to the concept of a Brillouin zone, but it again will play a very central role in later chapters. The “First Brillouin Zone” is a unit cell in  $k$ -space centered around the point  $k = 0$ . Thus in Fig. 5.2 we have shown only the first Brillouin zone, with the understanding that the dispersion is periodic for higher  $k$ . The points  $k = \pm\pi/a$  are known as the *Brillouin-Zone boundary* and are defined in this case as being points which are symmetric around  $k = 0$  and are separated by  $2\pi/a$ .

It is worth pausing for a second and asking why we expect that the dispersion curve should be periodic in  $k \rightarrow k + 2\pi/a$ . Recall that we defined our vibration mode to be of the form

$$\delta x_n = Ae^{i\omega t - ikna} \quad (5.7)$$

If we take  $k \rightarrow k + 2\pi/a$  we obtain

$$\delta x_n = Ae^{i\omega t - i(k+2\pi/a)na} = Ae^{i\omega t - ikna} e^{-i2\pi n} = Ae^{i\omega t - ikna}$$

where here we have used

$$e^{-i2\pi n} = 1$$

for any integer  $n$ . What we have found here is that shifting  $k \rightarrow k + 2\pi/a$  gives us back exactly the same oscillation mode the we had before we shifted  $k$ . The two are physically exactly equivalent!

In fact, it is similarly clear that shifting  $k$  by any  $k + 2\pi p/a$  with  $p$  an integer since, will give us back exactly the same wave also since

$$e^{-i2\pi np} = 1$$

as well. We can thus define a set of points in  $k$ -space (reciprocal space) which are all physically equivalent to the point  $k = 0$ . This set of points is known as the *reciprocal lattice*. The original periodic set of points  $x_n = na$  is known as the *direct lattice* or *real-space lattice* to distinguish it from the reciprocal lattice, when necessary.

The concept of the reciprocal lattice will extremely important later on. We can see the analogy between the direct lattice and the reciprocal lattice as follows:

$$\begin{array}{ll} \text{Direct lattice:} & x_n = \dots \quad -2a, \quad -a, \quad 0, \quad a, \quad 2a, \quad \dots \\ \text{Reciprocal lattice:} & G_n = \dots \quad -2\left(\frac{2\pi}{a}\right), \quad -\frac{2\pi}{a}, \quad 0, \quad \frac{2\pi}{a}, \quad 2\left(\frac{2\pi}{a}\right), \quad \dots \end{array}$$

Note that the defining property of the reciprocal lattice in terms of the points in the real lattice can be given as

$$e^{iG_m x_n} = 1 \quad (5.8)$$

A point  $G_m$  is a member of the reciprocal lattice iff Eq. 5.8 is true for all  $x_n$  in the real lattice.

<sup>2</sup>Leon Brillouin was one of Sommerfeld’s students. He is famous for many things including for being the “B” in the “WKB” approximation. I’m not sure if WKB is on your syllabus, but it really should be if it is not already!

<sup>3</sup>The pronunciation of “Brillouin” is something that gives English speakers a great deal of difficulty. If you speak French you will probably cringe at the way this name is butchered. (I did badly in French in school, so I’m probably one of the worst offenders.) According to online dictionaries it is properly pronounced somewhere between the following words: brēwan, bree-wah, breel-wahn, bree(y)wa(n), and bree-l(uh)-wahn. At any rate, the “l” and the “n” should both be very weak.

### 5.2.2 Properties of the Dispersion of the 1d chain

We now return to more carefully examine the properties of the dispersion we calculated (Eq. 5.6).

#### Sound Waves:

Recall that sound wave<sup>4</sup> is a vibration that has a long wavelength (compared to the inter-atomic spacing). In this long wavelength regime, we find the dispersion we just calculated to be linear with wavevector  $\omega = v_{sound}k$  as expected for sound with

$$v_{sound} = a\sqrt{\frac{\kappa}{m}}.$$

(To see this, just expand the sin in Eq. 5.6). Note that this sound velocity matches the velocity predicted from Eq. 5.3.

However, we note that at larger  $k$ , the dispersion is no longer linear. This is in disagreement with what Debye assumed in his calculation in section 2.2. So clearly this is a shortcoming of the Debye theory. In reality the dispersion of normal modes of vibration is linear only at long wavelength.

At shorter wavelength (larger  $k$ ) one typically defines two different velocities: The *group velocity*, the speed at which a wavepacket moves, is given by

$$v_{group} = d\omega/dk$$

And the *phase velocity*, the speed at which the individual maxima and minima move, is given by

$$v_{phase} = \omega/k$$

These two match in the case of a linear dispersion, but otherwise are different. Note that the group velocity becomes zero at the Brillouin zone boundaries  $k = \pm\pi/a$  (i.e., the dispersion is flat). As we will see many times later on, this is a general principle!

#### Counting Normal Modes:

Let us now ask how many normal modes there are in our system. Naively it would appear that we can put any  $k$  such that  $-\pi/a \leq k < \pi/a$  into Eq. 5.6 and obtain a new normal mode with wavevector  $k$  and frequency  $\omega(k)$ . However this is not precisely correct.

Let us assume our system has exactly  $N$  masses in a row, and for simplicity let us assume that our system has periodic boundary conditions i.e., particle  $x_0$  has particle  $x_1$  to its right and particle  $x_{N-1}$  to its left. Another way to say this is to let,  $x_{n+N} = x_n$ , i.e., this one dimensional system forms a big circle. In this case we must be careful that the wave ansatz Eq. 5.7 makes sense as we go all the way around the circle. We must therefore have

$$e^{i\omega t - ikna} = e^{i\omega t - ik(N+n)a}$$

Or equivalently we must have

$$e^{ikNa} = 1$$

---

<sup>4</sup>For reference it is good to remember that humans can hear sound wavelengths roughly between 1cm and 10m. Both of these are very long wavelength compared to interatomic spacings.

This requirement restricts the possible values of  $k$  to be of the form

$$k = \frac{2\pi p}{Na} = \frac{2\pi p}{L}$$

where  $p$  is an integer and  $L$  is the total length of the system. Thus  $k$  becomes quantized rather than a continuous variable. This means that the  $k$ -axis in Figure 5.2 is actually a discrete set of many many individual points; the spacing between two of these consecutive points being  $2\pi/(Na)$ .

Let us now count how many normal modes we have. As mentioned above in our discussion of the Brillouin zone, adding  $2\pi/a$  to  $k$  brings one back to exactly the same physical wave. Thus we only ever need consider  $k$  values within the first Brillouin zone (i.e.,  $-\pi/a \leq k < \pi/a$  (since  $\pi/a$  is the same as  $-\pi/a$  we choose to count one but not the other)). Thus the total number of normal modes is

$$\text{Total Number of Modes} = \frac{\text{Range of } k}{\text{Spacing between neighboring } k} = \frac{2\pi/a}{2\pi/(Na)} = N \quad (5.9)$$

There is precisely one normal mode per mass in the system — that is, one normal mode per degree of freedom in the whole system. This is what Debye insightfully predicted in order to cut off his divergent integrals in section 2.2.3 above!

### 5.2.3 Quantum Modes: Phonons

We now make a rather important leap from classical to quantum physics.

**Quantum Correspondence:** If a classical harmonic system (i.e., any quadratic hamiltonian) has a normal oscillation mode at frequency  $\omega$  the corresponding quantum system will have eigenstates with energy Presumably

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right) \quad (5.10)$$

you know this well in the case of a single harmonic oscillator. The only thing different here is that the harmonic oscillator is a collective normal mode not just motion of a single particle. This quantum correspondence principle will be the subject of a homework assignment.

Thus at a given wavevector  $k$ , there are many possible eigenstates, the ground state being the  $n = 0$  eigenstate which has only the zero-point energy  $\hbar\omega(k)/2$ . The lowest energy excitation is of energy  $\hbar\omega(k)$  greater than the ground state corresponding to the excited  $n = 1$  eigenstate. Generally all excitations at this wavevector occur in energy units of  $\hbar\omega(k)$ , and the higher values of energy correspond classically to oscillations of increasing amplitude.

Each excitation of this “normal mode” by step up the harmonic oscillator excitation ladder (increasing the quantum number  $n$ ) is known as a “phonon”.

**Definition 5.2.1.** A *phonon* is a discrete quanta of vibration<sup>5</sup>

This is entirely analogous to defining a single quanta of light as a photon. As is the case with the photon, we may think of the phonon as actually being a particle, or we can think of the phonon as being a quantized wave.

<sup>5</sup>I do not like the definition of a phonon as “a quanta of vibrational energy” which many books use. The vibration does carry indeed energy, but it carries other quantum numbers (such as crystal momentum) as well, so why specify energy only?

If we think about the phonon as being a particle (as with the photon) then we see that we can put many phonons in the same state (ie., the quantum number  $n$  in Eq. 5.10 can be increased to any value), thus we conclude that phonons, like photons, are bosons. As with photons, at finite temperature there will be a nonzero number of phonons (i.e.,  $n$  will be on average nonzero) as given by the Bose occupation factor.

$$n_B(\beta\omega) = \frac{1}{e^{\beta\omega} - 1}$$

with  $\beta = 1/(k_bT)$  and  $\omega$  the oscillation frequency.

Thus, the expectation of the phonons at wavevector  $k$  is given by

$$E_k = \hbar\omega(k) \left( n_B(\beta\omega(k)) + \frac{1}{2} \right)$$

We can use this type of expression to calculate the heat capacity of our 1d model<sup>6</sup>

$$U_{total} = \sum_k \hbar\omega(k) \left( n_B(\beta\omega(k)) + \frac{1}{2} \right)$$

where the sum over  $k$  here is over all possible normal modes, i.e,  $k = 2\pi p/(Na)$  such that  $-\pi/a \leq k < \pi/a$ . Thus we really mean

$$\sum_k \rightarrow \sum_{p=-N/2}^{N/2-1} |_{k=(2\pi p)/(Na)}$$

Since for a large system, the  $k$  points are very close together, we can convert the discrete sum into an integral (something we should be very familiar with by now) to obtain

$$\sum_k \rightarrow \frac{Na}{2\pi} \int_{-\pi/a}^{\pi/a} dk$$

Note that we can use this continuum integral to count the total number of modes in the system

$$\frac{Na}{2\pi} \int_{-\pi/a}^{\pi/a} dk = N$$

as predicted by Debye.

Using this integral form of the sum we have the total energy given by

$$U_{total} = \frac{N}{2\pi} \int_{-\pi/a}^{\pi/a} dk \hbar\omega(k) \left( n_B(\beta\omega(k)) + \frac{1}{2} \right)$$

from this we could calculate specific heat as  $dU/dT$ .

These two previous expressions look exactly like what Debye would have obtained from his calculation (for a 1d version of his model)! The only difference lies in our expression for  $\omega(k)$ . Debye only knew about sound where  $\omega = vk$ , is linear in wavevector. We, on the other hand, have

<sup>6</sup>The observant reader will note that we are calculating  $C_V = dU/dT$  the heat capacity at constant volume. Why constant volume? As we saw above when we studied thermal expansion, the crystal does not expand unless we include third order (or higher) order terms in the interatomic potential, which are not in this model!

just calculated that for our microscopic ball and spring model  $\omega$  is not linear in  $k$ . In fact, Einstein's calculation of specific heat can be phrased in exactly the same language. Only for Einstein's model  $\omega = \omega_0$  is constant for all  $k$ . We thus see Einstein's model, Debye's model, and our microscopic harmonic model in a very unified light. The only difference between the three is what we use for a dispersion relation.

One final comment is that it is frequently useful to further replace integrals over  $k$  with integrals over frequency (we did this when we studied the Debye model above). We obtain generally

$$\frac{Na}{2\pi} \int_{-\pi/a}^{\pi/a} dk = \int d\omega g(\omega)$$

where<sup>7</sup>

$$g(\omega) = 2 \frac{Na}{2\pi} |dk/d\omega|$$

Note that in the (1d) Debye model this density of states is constant from  $\omega = 0$  to  $\omega = \omega_{Debye} = v\pi/a$ . In our model, as we have calculated above, the density of states is not a constant, but becomes zero at frequency above the maximum frequency  $2\sqrt{\kappa/m}$ . (In a homework problem we calculate this density of states explicitly). Finally in the Einstein model, this density of states is a delta-function at frequency  $\omega_0$ .

## 5.2.4 Comments on Reciprocal Space II: Crystal Momentum

As mentioned above, the wavevector of a phonon is defined only modulo the reciprocal lattice. In other words,  $k$  is the same as  $k + G_m$  where  $G_m = 2\pi m/a$  is a point in the reciprocal lattice. Now we are supposed to think of these phonons as particles – and we like to think of our particles as having energy  $\hbar\omega$  and a momentum  $\hbar k$ . But we cannot define a phonon's momentum this way because physically it is the same phonon whether we describe it as  $\hbar k$  or  $\hbar(k + G_m)$ . We thus instead define a concept known as the *crystal momentum* which is the momentum modulo the reciprocal lattice — or equivalently we agree that we must always describe  $k$  within the first Brillouin zone.

In fact, this idea of crystal momentum is extremely powerful. Since we are thinking about phonons as being particles, it is actually possible for two (or more) phonons to bump into each other and scatter from each other — the same way particles do<sup>8</sup>. In such a collision, energy is conserved and *crystal momentum is conserved!* For example three phonons each with crystal momentum  $\hbar(2/3)\pi/a$  can scatter off of each other to produce three phonons each with crystal momentum  $-\hbar(2/3)\pi/a$ . This is allowed since the initial and final states have the same energy and

$$3 \times (2/3)\pi/a = 3 \times (-2/3)\pi/a \pmod{2\pi/a}$$

During these collisions although momentum  $\hbar k$  is not conserved, crystal momentum is<sup>9</sup>. In fact, the situation is similar when, for example, phonons scatter from electrons in a periodic lattice –

<sup>7</sup>The factor of 2 out front comes from the fact that each  $\omega$  occurs for the two possible values of  $\pm k$ .

<sup>8</sup>In the harmonic model we have considered phonons do not scatter from each other. We know this because the phonons are eigenstates of the system, so their occupation does not change with time. However, if we add anharmonic (cubic and higher) terms to the inter-atomic potential, this corresponds to perturbing the phonon hamiltonian and can be interpreted as allowing phonons to scatter from each other.

<sup>9</sup>This thing we have defined  $\hbar k$  has dimensions of momentum, but is not conserved. However, as we will discuss below in chapter 10, if a particle, like a photon, enters a crystal with a given momentum and undergoes a process that conserves crystal momentum but not momentum, when the photon exits the crystal we will find that total momentum of the system is indeed conserved, with the momentum of the entire crystal accounting for any momentum that is missing from the photon. See footnote 5 in section 10.1.1

crystal momentum becomes the conserved quantity rather than momentum. This is an extremely important principle which we will encounter again and again. In fact, it is a main cornerstone of solid-state physics.

Aside: There is a very fundamental reason for the conservation of crystal momentum. Conserved quantities are results of symmetries (this is a deep and general statement known as Noether's theorem<sup>10</sup>). For example, conservation of momentum is a result of the translational invariance of space. If space is not the same from point to point, for example if there is a potential  $V(x)$  which is different at different places, then momentum is not conserved. The conservation of crystal momentum correspondingly results from space being invariant under translations of  $a$ , giving us momentum that is conserved modulo  $2\pi/a$ .

### 5.3 Summary of the one-dimensional chain

A number of very crucial new ideas have been introduced in this section. Many of these will return again and again in later chapters.

- Normal modes are collective oscillations where all particles move at the same frequency.
- If a system is periodic in space with periodicity  $\Delta x = a$ , then in reciprocal space ( $k$ -space) the system is periodic with periodicity  $\Delta k = 2\pi/a$ .
- Values of  $k$  which differ by multiples of  $2\pi/a$  are physically equivalent. The set of points in  $k$ -space which are equivalent to  $k = 0$  are known as the reciprocal lattice.
- Any values of  $k$  is equivalent to some  $k$  in the first Brillouin-zone,  $-\pi/a \leq k < \pi/a$  (in 1d).
- The sound velocity is the slope of the dispersion in the small  $k$  limit (group = phase velocity in this limit).
- A classical normal mode of frequency  $\omega$  gets translated into quantum mechanical eigenstates  $E_n = \hbar\omega(n + \frac{1}{2})$ . If the system is in the  $n^{\text{th}}$  eigenstate, we say that it is occupied by  $n$  phonons.
- Phonons can be thought of as particles, like photons, that obey Bose statistics.

#### References

Sound and compressibility:

- Goodstein, section 3.2b.
- Ibach and Luth, beginning of section 4.5
- Hook and Hall, section 2.2

Thermal Expansion (Most references go into *way* too much depth on thermal expansion):

- Kittel chapter 5, section on thermal expansion.

---

<sup>10</sup>Emmy Noether has been described by Einstein, among others, as the most important woman in the history of mathematics.

Normal Modes of Monatomic Chain and introduction to phonons:

- Kittel, beginning of chapter 4
- Goodstein, beginning of section 3.3
- Hook and Hall, section 2.3.1
- Burns, section 12.1-12.2
- Ashcroft and Mermin, beginning of chapter 22.

## Chapter 6

# The one-dimensional diatomic solid

In the previous chapter we studied in detail a one dimensional model of a solid where every atom is identical to every other atom. However, in real materials not every atom is the same (for example, in Sodium Chloride, we have two types of atoms!). We thus intend to generalize our previous discussion of the one dimension solid to a one dimensional solid with two types of atoms. Much of this will follow the outline set in the previous chapter, but we will see that several fundamentally new features will now emerge.

### 6.1 Diatomic Crystal Structure: Some useful definitions

Consider the following model system

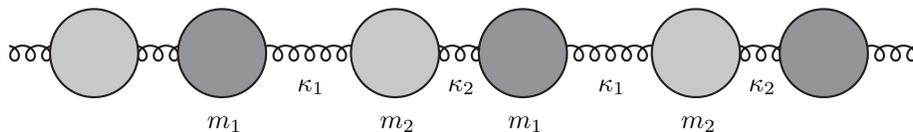


Fig. 6.1.1

Which represents a periodic arrangement of two different types of atoms. Here we have given them two masses  $m_1$  and  $m_2$  and the springs which alternate along the 1-dimensional chain. The springs connecting the atoms have spring constants  $\kappa_1$  and  $\kappa_2$  and also alternate.

In this circumstance with more than one type of atom, we first would like to identify the so-called *unit cell* which is the repeated motif in the arrangement of atoms. In this picture, we have put a box around the unit cell. The length of the unit cell in 1d is known as the *lattice constant*

and it is labeled  $a$ .

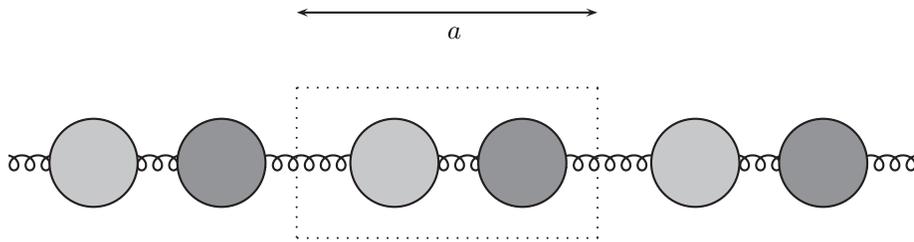


Fig. 6.1.2

Note however, that the definition of the unit cell is extremely non-unique. We could just as well have chosen (for example) the unit cell to be as follows.

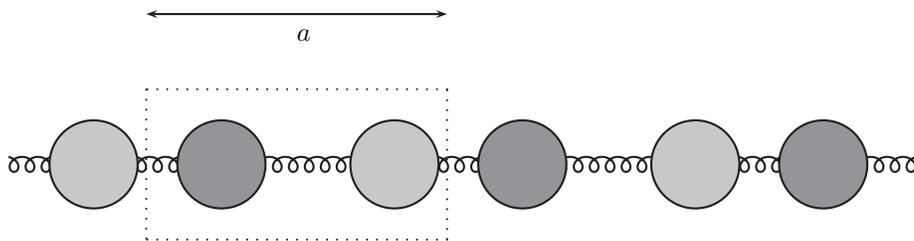


Fig. 6.1.3

The important thing in defining a periodic system is to choose *some* unit cell and then construct the full system by reproducing the same unit cell over and over. (In other words, make a definition of the unit cell and stick with that definition!).

It is sometimes useful to pick some reference point inside each unit cell. This set of reference points makes a simple *lattice* (we will define the term “lattice” more closely in later chapters – but for now the point is that a lattice has only one type of point in it – not two different types of points). So in this figure, we have marked our reference point in each unit cell with an **X** (again, the choice of this reference point is arbitrary).

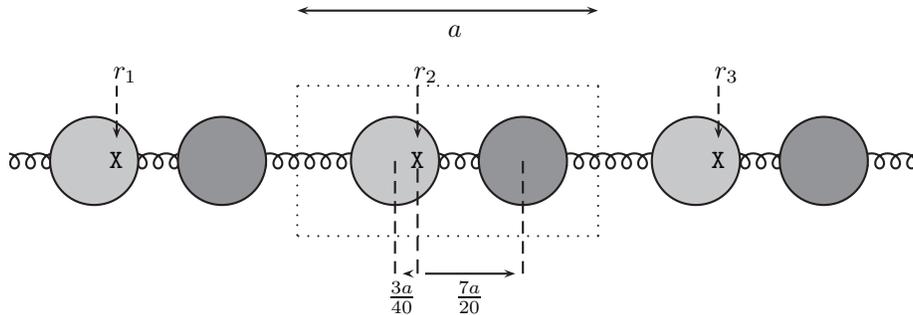


Fig. 6.1.4

Given the reference lattice point in the unit cell, the description of all of the atoms in the unit cell with respect to this reference point is known as a *basis*. In this case we might describe our basis as

- light gray atom      centered at position  $3a/40$  to left of reference lattice point
- dark gray atom      centered at position  $7a/20$  to right of reference lattice point

Thus if the reference lattice point in unit cell  $n$  is called  $r_n$  (and the spacing between the lattice points is  $a$ ) we can set

$$r_n = an$$

with  $a$  the size of the unit cell. Then the (equilibrium) position of the light gray atom in the  $n^{th}$  unit cell is

$$x_n^{eq} = an - 3a/40$$

whereas the (equilibrium) position of the dark gray atom in the  $n^{th}$  unit cell is

$$y_n^{eq} = an + 7a/20$$

## 6.2 Normal Modes of the Diatomic Solid

For simplicity, let us focus on the case where all of the masses along our chain are the same  $m_1 = m_2 = m$  but the two spring constants  $\kappa_1$  and  $\kappa_2$  are different. (For homework we will consider the case where the masses are different, but the spring constants are the same!).

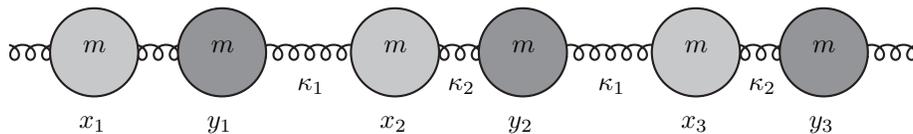


Fig. 6.2.1

Given the spring constants in the picture, we can write down Newton's equations of motion for the deviations of the positions of the masses from their equilibrium positions. We obtain

$$m \ddot{\delta x}_n = \kappa_2(\delta y_n - \delta x_n) + \kappa_1(\delta y_{n-1} - \delta x_n) \quad (6.1)$$

$$m \ddot{\delta y}_n = \kappa_1(\delta x_{n+1} - \delta y_n) + \kappa_2(\delta x_n - \delta y_n) \quad (6.2)$$

Analogous to the one dimensional case we propose ansätze<sup>1</sup> for these quantities that have the form of a wave

$$\delta x_n = A_x e^{i\omega t - ikna} \quad (6.3)$$

$$\delta y_n = A_y e^{i\omega t - ikna} \quad (6.4)$$

where, as in the previous chapter, we implicitly mean to take the real part of the complex number. As such, we can always choose to take  $\omega > 0$  as long as we consider  $k$  to be either positive and negative

As we saw in the previous chapter, values of  $k$  that differ by  $2\pi/a$  are physically equivalent. We can thus focus our attention to the first Brillouin zone  $-\pi/a \leq k < \pi/a$ . Note that the important length here is the unit cell length or lattice constant  $a$ . Any  $k$  outside the first Brillouin zone is redundant with some other  $k$  inside the zone.

As we found in the previous chapter, if our system has  $N$  unit cells, then (putting periodic boundary conditions on the system)  $k$  will be quantized in units of  $2\pi/(Na) = 2\pi/L$ . Note that here the important quantity is  $N$ , the number of unit cells, not the number of atoms ( $2N$ ).

Dividing the range of  $k$  in the first Brillouin zone by the spacing between neighboring  $k$ 's, we obtain exactly  $N$  different possible values of  $k$  exactly as we did in Eq. 5.9. In other words, we have exactly one value of  $k$  per unit cell.

We might recall at this point the intuition that Debye used — that there should be exactly one possible excitation mode per degree of freedom of the system. Here we obviously have two degrees of freedom per unit cell, but we obtain only one possible value of  $k$  per unit cell. The resolution, as we will see in a moment, is that there will be two possible oscillation modes for each wavevector  $k$ .

We now proceed by plugging in our ansätze (Eq. 6.3 and 6.4) into our equations of motion (Eq. 6.1 and 6.2). We obtain

$$\begin{aligned} -\omega^2 m A_x e^{i\omega t - ikna} &= \kappa_2 A_y e^{i\omega t - ikna} + \kappa_1 A_y e^{i\omega t - ik(n-1)a} - (\kappa_1 + \kappa_2) A_x e^{i\omega t - ikna} \\ -\omega^2 m A_y e^{i\omega t - ikna} &= \kappa_1 A_x e^{i\omega t - ik(n+1)a} + \kappa_2 A_x e^{i\omega t - ikna} - (\kappa_1 + \kappa_2) A_y e^{i\omega t - ikna} \end{aligned}$$

which simplifies to

$$\begin{aligned} -\omega^2 m A_x &= \kappa_2 A_y + \kappa_1 A_y e^{ika} - (\kappa_1 + \kappa_2) A_x \\ -\omega^2 m A_y &= \kappa_1 A_x e^{-ika} + \kappa_2 A_x - (\kappa_1 + \kappa_2) A_y \end{aligned}$$

This can be rewritten conveniently as an eigenvalue equation

$$m\omega^2 \begin{pmatrix} A_x \\ A_y \end{pmatrix} = \begin{pmatrix} (\kappa_1 + \kappa_2) & -\kappa_2 - \kappa_1 e^{ika} \\ -\kappa_2 - \kappa_1 e^{-ika} & (\kappa_1 + \kappa_2) \end{pmatrix} \begin{pmatrix} A_x \\ A_y \end{pmatrix} \quad (6.5)$$

The solutions of this are obtained by finding the zeros of the secular determinant

$$0 = \begin{vmatrix} (\kappa_1 + \kappa_2) - m\omega^2 & -\kappa_2 - \kappa_1 e^{ika} \\ -\kappa_2 - \kappa_1 e^{-ika} & (\kappa_1 + \kappa_2) - m\omega^2 \end{vmatrix} = |(\kappa_1 + \kappa_2) - m\omega^2|^2 - |\kappa_2 + \kappa_1 e^{ika}|^2$$

---

<sup>1</sup>I believe this is the proper pluralization of ansatz.

The roots of which are clearly given by

$$m\omega^2 = (\kappa_1 + \kappa_2) \pm |\kappa_1 + \kappa_2 e^{ika}|$$

The second term needs to be simplified

$$|\kappa_1 + \kappa_2 e^{ika}| = \sqrt{(\kappa_1 + \kappa_2 e^{ika})(\kappa_1 + \kappa_2 e^{-ika})} = \sqrt{\kappa_1^2 + \kappa_2^2 + 2\kappa_1\kappa_2 \cos(ka)}$$

So we finally obtain

$$\omega_{\pm} = \sqrt{\frac{\kappa_1 + \kappa_2}{m} \pm \frac{1}{m} \sqrt{\kappa_1^2 + \kappa_2^2 + 2\kappa_1\kappa_2 \cos(ka)}} \quad (6.6)$$

Note in particular that for each  $k$  we find two normal modes — thus since there are  $N$  different  $k$  values, we obtain  $2N$  modes total (if there are  $N$  unit cells in the entire system). This is in agreement with our above discussion that we should have exactly one normal mode per degree of freedom in our system.

The dispersion of these two modes is shown in Figure 6.1.

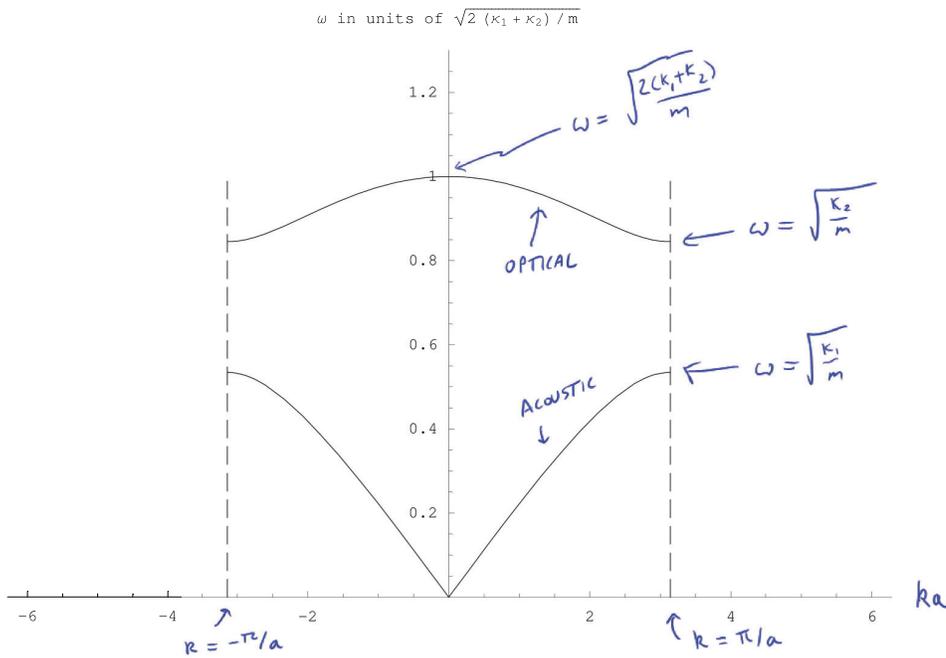


Figure 6.1: Dispersion relation of the 1d diatomic chain. The dispersion is periodic in  $k \rightarrow k + 2\pi/a$ . Here the dispersion is shown for the case of  $\kappa_2 = 1.4\kappa_1$ . This scheme of plotting dispersions, putting all normal modes within the first Brillouin zone, is the *reduced zone scheme*. Compare this to Fig. 6.2 below.

A few things to note about this dispersion. First of all we note that there is a long wavelength low energy mode with linear dispersion (corresponding to  $\omega_-$  in Eq. 6.6). This is the sound wave, or acoustic mode. Generally the definition of an *acoustic mode* is any mode that has linear dispersion as  $k \rightarrow 0$ . These correspond to sound waves.

By expanding Eq. 6.6 for small  $k$  it is easy to check that the sound velocity is

$$v_{\text{sound}} = \frac{d\omega_-}{dk} = \sqrt{\frac{a^2\kappa_1\kappa_2}{2m(\kappa_1 + \kappa_2)}} \quad (6.7)$$

In fact, we could have calculated this sound velocity on general principles analogous to what we did in Eq. 5.2. The density of the chain is  $2m/a$ . The effective spring constant of two springs  $\kappa_1$  and  $\kappa_2$  in series is  $\tilde{\kappa} = (\kappa_1 + \kappa_2)/(\kappa_1\kappa_2)$  so the compressibility of the chain is  $\beta = 1/(\tilde{\kappa}a)$  (See Eq. 5.1). Then plugging into Eq. 5.2 gives exactly the same sound velocity as we calculate here in Eq. 6.7.

The higher energy branch of excitations is known as the *optical* mode. It is easy to check that in this case the optical mode goes to frequency  $\sqrt{2(\kappa_1 + \kappa_2)/m}$  at  $k = 0$ , and also has zero group velocity at  $k = 0$ . The reason for the nomenclature “optical” will become clearer later in the course when we study scattering of light from solids. However, here is a very simplified description of why it is named this way: Consider a solid being exposed to light. It is possible for the light to be absorbed by the solid, but energy and momentum must both be conserved. However, light travels at a very high velocity  $c$ , so  $\omega = ck$  is a very large number. Since phonons have a maximum frequency, this means that photons can only be absorbed for very small  $k$ . However, for small  $k$ , acoustic phonons have energy  $vk \ll ck$  so that energy and momentum cannot be conserved. On the other hand, optical phonons have energy  $\omega_{\text{optical}}$  which is finite for small  $k$  so that at some value of small  $k$ , we have  $\omega_{\text{optical}} = ck$  and one can match the energy and momentum of the photon to that of the phonon.<sup>2</sup> Thus, whenever phonons interact with light, it is inevitably the optical phonons that are involved.

Let us examine a bit more closely the acoustic and the optical mode as  $k \rightarrow 0$ . Examining our eigenvalue problem Eq. 6.5, we see that in this limit the matrix to be diagonalized takes the simple form

$$\omega^2 \begin{pmatrix} A_x \\ A_y \end{pmatrix} = \frac{\kappa_1 + \kappa_2}{m} \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix} \begin{pmatrix} A_x \\ A_y \end{pmatrix} \quad (6.8)$$

The acoustic mode (which has frequency 0) is solved by the eigenvector

$$\begin{pmatrix} A_x \\ A_y \end{pmatrix} = \begin{pmatrix} 1 \\ 1 \end{pmatrix}$$

This tells us that the two masses in the unit cell (at positions  $x$  and  $y$ ) move together for the case of the acoustic mode in the long wavelength limit. This is not surprising considering our understanding of sound waves as being very long wavelength compressions and rarifications. This is depicted in Figure 6.2.2. Note in the figure that the amplitude of the compression is slowly modulated, but always the two atoms in the unit cell move almost exactly the same way.

---

<sup>2</sup>From this naive argument, one might think that the process where one photon with frequency  $\omega_{\text{optical}}$  is absorbed while emitting a phonon is an allowed process. This is not true since the photons carry spin and spin must also be conserved. Much more typically the interaction between photons and phonons is one where a photon is absorbed and then re-emitted. I.e., it is inelastically scattered. We will discuss this later on.

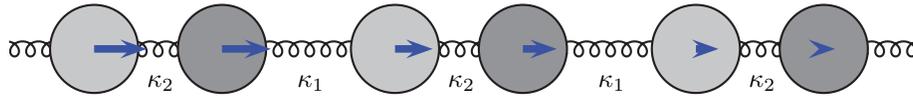


Fig. 6.2.2

A long wavelength acoustic mode

On the other hand, the optical mode at  $k = 0$ , having frequency  $\omega^2 = \frac{2(\kappa_1 + \kappa_2)}{m}$ , has the eigenvector

$$\begin{pmatrix} A_x \\ A_y \end{pmatrix} = \begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

which describes the two masses in the unit cell moving in *opposite* directions, for the optical mode. This is depicted in Figure 6.2.3. Note in the figure that the amplitude of the compression is slowly modulated, but always the two atoms in the unit cell move almost exactly the opposite way.

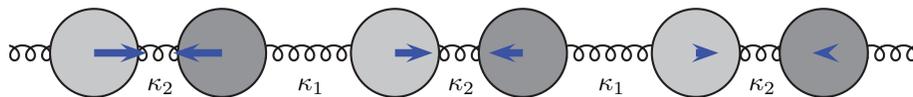


Fig. 6.2.3

A long wavelength optical mode

In order to get a better idea of how motion occurs for both the optical and acoustic modes, it is useful to see animations, which you can find on the web. Another good resource is to download the program “ChainPlot” from Professor Mike Glazer’s web site (<http://www.amg122.com/programs>)<sup>3</sup>

In this example we had two atoms per unit cell and we obtained two modes per distinct value of  $k$ . One of these modes is acoustic and one is optical. More generally if there are  $M$  atoms per unit cell (in one dimension) we will have  $M$  modes per distinct value of  $k$ , of which one mode will be acoustic (goes to zero energy at  $k = 0$ ) and all of the remaining modes are optical (do not go to zero energy at  $k = 0$ ).

**Caution:** We have been careful to discuss a true one dimensional system, where the atoms are allowed to move only along the one dimensional line. Thus each atom has only one degree of freedom. However, if we allow atoms to move in other directions (transverse to the 1d line) we will have more degrees of freedom per atom. When we get to the 3d solid we should expect 3 degrees of freedom per atom. And there should be 3 different acoustic modes at each  $k$  at long wavelength. (In 3d, if there are  $n$  atoms per unit cell, there will be  $3(n - 1)$  optical modes but always 3 acoustic modes totalling  $3n$  degrees of freedom per unit cell.)

<sup>3</sup>Note in particular the comment on this website about most books getting the form of the acoustic mode incorrect!

One thing that we should study closely is the behavior at the Brillouin zone boundary. It is also easy to check that the frequencies  $\omega_{\pm}$  at the zone boundary ( $k = \pm\pi/a$ ) are  $\sqrt{\kappa_1/m}$  and  $\sqrt{\kappa_2/m}$ , the larger of the two being  $\omega_+$ . We can also check that the group velocity  $d\omega/dk$  of both modes goes to zero at the zone boundary (Similarly the optical mode has zero group velocity at  $k = 0$ ).

In Fig. 6.1 above, we have shown both modes at each value of  $k$ , such that we only need to show  $k$  within the first Brillouin zone. This is known as the *reduced zone scheme*. Another way to plot exactly the same dispersions is shown in Fig. 6.2 and is known as the *extended zone scheme*. Essentially you can think of this as “unfolding” the dispersions such that there is only one mode at each value of  $k$ . In this picture we have defined (for the first time) the *second Brillouin zone*.

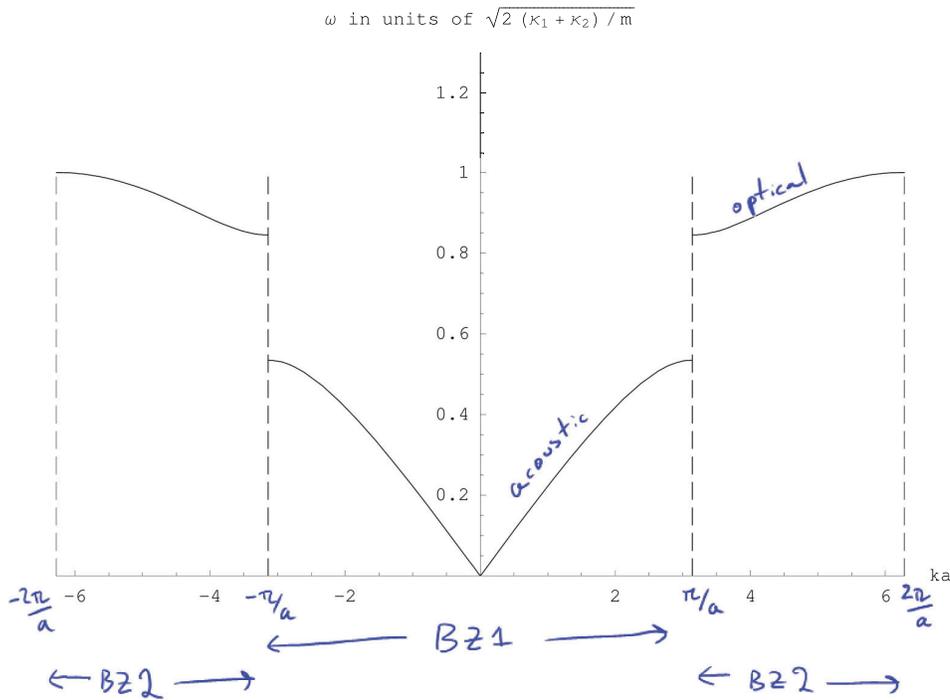


Figure 6.2: Dispersion relation of the 1d diatomic chain in the extended zone scheme (Again choosing  $\kappa_2 = 1.4\kappa_1$ ). Compare this to Fig. 6.1 above. The first Brillouin zone is labeled BZ1 and the second Brillouin zone is labeled BZ2.

Recall the first zone in 1d is defined as  $|k| \leq \pi/a$ . Analogously the second Brillouin zone is now  $\pi/a \leq |k| \leq 2\pi/a$ . In later chapters we will define the Brillouin zones more generally.

Here is an example where it is very useful to think using the extended zone scheme. We have been considering with  $\kappa_2 > \kappa_1$ , now let us consider what would happen if we take the limit of  $\kappa_2 \rightarrow \kappa_1$ . When the two spring constants become the same, then in fact the two atoms in the unit cell become identical, and we have a simple monatomic chain (which we discussed at length in the previous chapter). As such we should define a new smaller unit cell with lattice constant  $a/2$ , and the dispersion curve is now just a simple  $|\sin|$  as it was in chapter Ref. 5.2.

Thus it is frequently useful if the two atoms in a unit cell are not too different from each

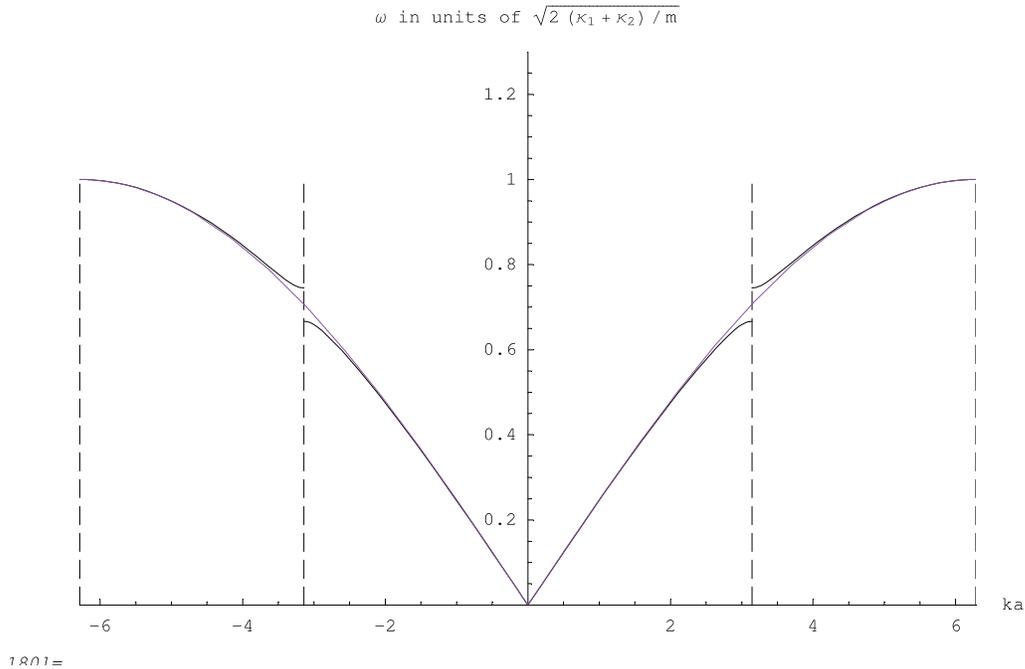


Figure 6.3: (black) Dispersion relation of the 1d diatomic chain in the extended zone scheme with  $\kappa_2$  not too different from  $\kappa_1$ . (blue) Dispersion relation when  $\kappa_2 = \kappa_1$ . In this case, the two atoms become exactly the same, and we have a monatomic chain with lattice spacing  $a/2$ . This single band dispersion precisely matches that calculated in chapter 5.2 above, only with the lattice constant redefined to  $a/2$ .

other, to think about the dispersion as being a small perturbation to a situation where all atoms are identical. When the atoms are made slightly different, a small gap opens up at the zone boundary, but the rest of the dispersion continues to look mostly as if it is the dispersion of the monatomic chain.

### 6.3 Summary of the diatomic solid

A number of key concepts are introduced in this chapter as well

- A unit cell is the repeated motif that comprises a crystal
- The basis is the description of the unit cell with respect to a reference lattice
- The lattice constant is the size of the unit cell (in 1d)
- If there are  $M$  atoms per unit cell we will find  $M$  normal modes at each wavevector  $k$
- One of these modes is an acoustic mode, meaning that it has linear dispersion at small  $k$ , whereas the remaining  $M - 1$  are optical meaning they have finite frequency at  $k = 0$ .

- For the acoustic mode, all atoms in the unit cell move in-phase with each other, whereas for optical modes, they move out of phase with each other
- Except for the acoustic mode, all other excitation branches have zero group velocity for  $k = n\pi/a$  for any  $n$ .
- If all of the dispersion curves are plotted within the first Brillouin zone  $|k| \leq \pi/a$  we call this the reduced zone scheme. If we “unfold” the curves such that there is only one excitation plotted per  $k$ , but we use more than one Brillouin zone, we call this the extended zone scheme.
  
- If the two atoms in the unit cell become identical, the new unit cell is half the size of the old unit cell. It is convenient to describe this limit in the extended zone scheme.

### References

- Ashcroft and Mermin, chapter 22 (but not the 3d part)
- Ibach and Luth, section 4.3
- Kittel, chapter 4
- Hook and Hall, sections 2.3.2, 2.4, 2.5
- Burns, section 12.3