Lecture 10:

- **Review: waves in cubic crystals from top-down approach**
- **Lecture: Atomic vibrations in crystals**

Review

Consider inhomogenously **stressed** cube and collect all of the stresses in the x-direction. A uniform (homogenous) stress will not produce a propagating wave.

We express forces in terms of elements of the elastic stiffness matrix (C) multiplied by strains (e).

Then, we use earlier expressions for the strains in terms of derivatives of displacement variables in the x, y, and z direction which are call u, v, and w

$$\rho\frac{\partial^2 u}{\partial t^2} = C_{11}\frac{\partial^2 u}{\partial x^2} + C_{44}\left(\frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2}\right) + (C_{12} + C_{44})\left(\frac{\partial^2 v}{\partial y \partial x} + \frac{\partial^2 w}{\partial z \partial x}\right)$$

This equation has all the trappings of the PDE for a wave (2nd time derivative on one side, 2nd spatial derivative on the other side). To solve this problem we consider special cases of the propagation direction (which determines the factors in the exponent) and the direction of particle motion (which determines if we drop u, v, w or none of these). Then we solve for ω as a function of k. For example, for a wave propagating in the [100] direction in a crystal and particle motion also in the [100] direction (longitudinal wave) we use a 'guessed' solution of the form:

$$u = u_0 e^{i(Kx-\omega t)}$$

Which yields a solution

$$\omega^2\rho = C_{11}K^2$$

And a propagation velocity

$$v_s = \sqrt{\frac{C_{11}}{\rho}}$$

Note that the velocity is the same for all k.

We can also get a transverse wave (particle motion orthogonal to propagation direction) by 'guessing' the solution:

$$v = v_0 e^{i(Kx-\omega t)}$$

When we substitute this into the wave equation we get:

$$\omega^2\rho = C_{44}K^2$$

$$v_s = \sqrt{\frac{C_{44}}{\rho}}$$

Again, propagation velocity is independent of k.

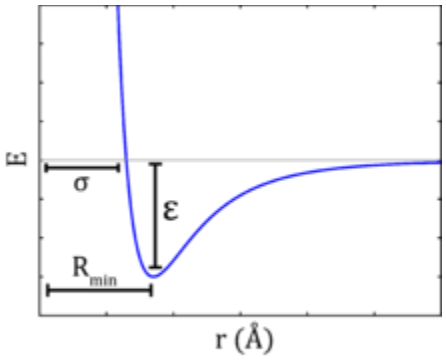
Atomic potentials

In the previous chapter we derived expressions for the atomic potentials due to van der waals bonding and ionic bonding.

Van der waals (Lennard Jones potential):

$$U(R) = 4\epsilon[\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^{6}]$$

(each atom feels this potential energy as a function of distance from its neighbor)

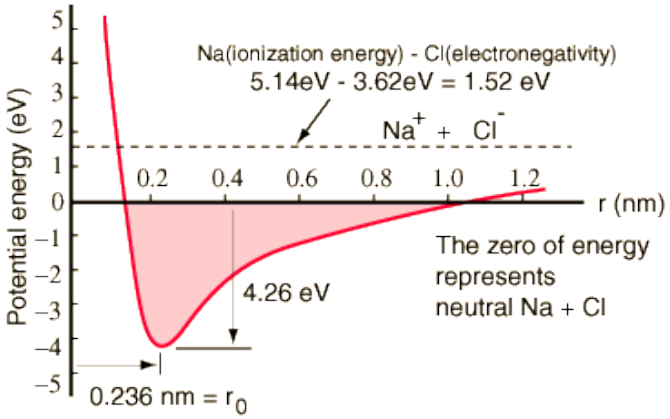


Ionic solid atomic potential:

$$U_{tot} = N(z\lambda e^{-\frac{R}{\rho}} - \frac{\alpha q^2}{R})$$

Where z is the number of nearest neighbors an ion in the crystal has, N is the number of total ion pairs, and α is the **madelung constant**.

$\alpha \equiv \sum_j \frac{(\pm)}{p_{ij}}$ (sum includes nearest neighbors)

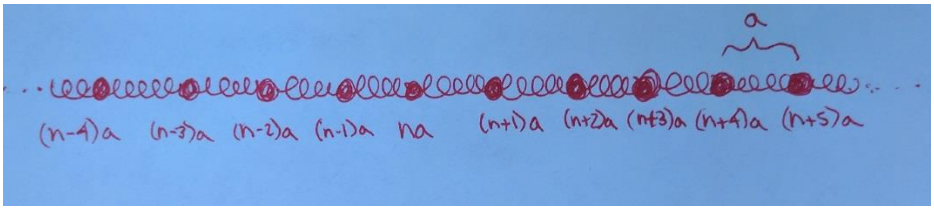


What both of these potentials (and any other one with a local minimum) have in common is that close to the equilibrium atomic spacing (R_0), $U \sim k(r - R_0)^2$. That is to say, for small amounts of atomic

motion, the potential looks like that of a harmonic oscillator. Thus, when we model the atoms of a solid as masses on springs, there is some physical motivation for that model.

Model: infinite one dimensional line of masses connected by springs

Consider a line of identical masses, m, a distance a apart connected by springs.



The position of each mass is labeled as in the image below, with some central mass chosen to have the position label na (n is an integer).

When a mass is displaced from its equilibrium position, we call this **displacement** $u(va)$, where v is an integer. For the n-th atom, this small but arbitrary displacement has the label u(na)

When all of the atoms are subjected to small but arbitrary dispacements, the total potential energy is given by:

$$U_{tot} = \frac{1}{2}C\sum_{n}[u(na) - u([n+1]a)]^2$$

Here, the term in parenthesis after the sum measures how far a given **spring** has been stretch and compressed. It is for this reason that we only count the neighbor to the right of each atom. Now, write equation of motion **for atom located at position na**

$$ma = F$$

$$m\frac{\partial^2 u(na)}{\partial t^2} = -\frac{\partial U_{tot}}{\partial u(na)}$$

For the expression on the right side of the equation, we only consider u(na) terms in U_{tot}:

$$U_{tot,containing\ u(na)} = \frac{1}{2}C[u(na) - u([n+1]a)]^2 + \frac{1}{2}C[u([n-1]a) - u(na)]^2$$

$$= \frac{1}{2}C[2u(na)^2 - 2u(na)u([n+1]a) - 2u(na)u([n-1]a) + u([n+1]a)^2 + u([n-1]a)^2$$

Plugging this into the equation of motion above:

$$m\frac{\partial^2 u(na)}{\partial t^2} = -C[2u(na) - u([n-1]a) - u([n+1]a)]$$

We are seeking wave-like solutions, which have the form:

$$u(na,t) \propto e^{i(kna-\omega t)}$$

As in the previous lecture, ω is the angular frequency of the wave, and k is the wavevector (which encodes information about wavelength and propagation direction). Since we are considering a 100% 1-

dimensonal system at this point, so direction is not explicitly included, but we plug in x=na for that variable.

Substitute the solution $u(na,t) \propto e^{i(kna-\omega t)}$ into the equation of motion:

$$-m\omega^2 e^{i(kna-\omega t)} = -C\left[2e^{i(kna-\omega t)} - e^{i[k(n-1)a-\omega t)]} - e^{i[k(n+1)a-\omega t)]}\right]$$
$$-m\omega^2 e^{i(kna-\omega t)} = -C[2 - e^{-ika} - e^{ika}]e^{i(kna-\omega t)}$$
$$m\omega^2 = C[2 - 2coska]$$

Solve for dispersion relation ($\omega\ vs\ k$

$$\omega = \sqrt{\frac{2C(1-coska)}{m}}$$

Use the trig identity $\sin^2\frac{\theta}{2} = \frac{1-cos\theta}{2}$

$$\omega = 2\sqrt{\frac{C}{m}}\left|sin\frac{ka}{2}\right|$$

The absolute value appears around the sine to ensure that ω is positive

This solution describe a propagating wave with

Phase velocity: $v_p = \omega/k$

Group velocity: $v_g = \frac{\partial\omega}{\partial k}$

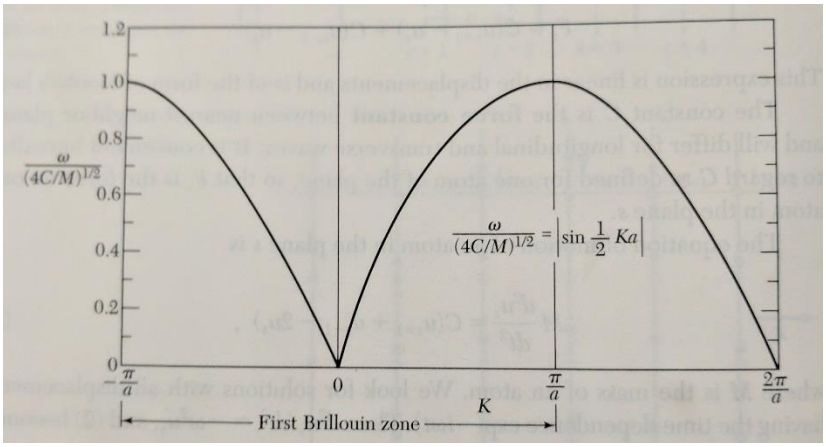
For the dispersion relation for this propagating wave, we consider small k where $sin\theta \sim \theta$

$$\omega \approx 2\sqrt{\frac{C}{m}}\left|\frac{ka}{2}\right|$$

$$\frac{\partial\omega}{\partial k} = v_{g,small\ k} = a\sqrt{\frac{C}{m}}$$

A plot of the dispersion relation is shown below:

Question: what is the velocity at $k = \pi/a$?



Since the frequency goes as the absolute value of the sine of momentum (k), the dispersion relation is a function which repeats infinitely. However, beyond the **first brillouin zone**, the information is redundant.

As a reminder, the first brillouin zone is defined as:

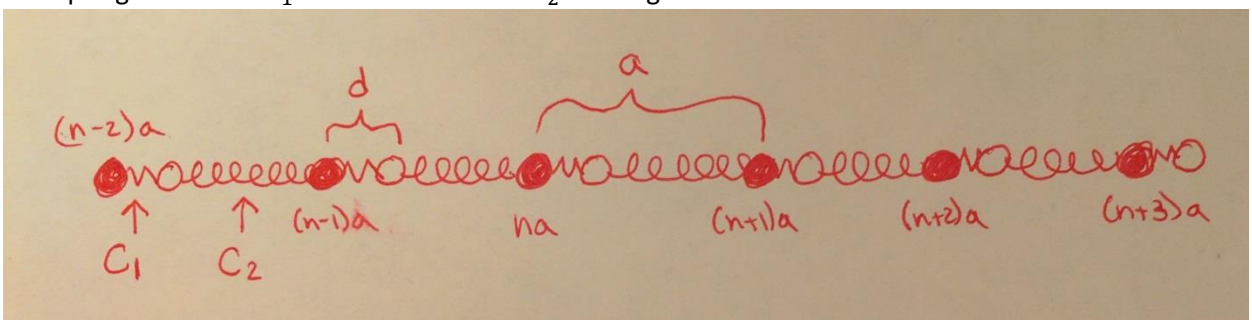
- Minimum volume containing all wavevectors, k, that can be bragg reflected by the crystal
- The wigner-seitz cell (see Ch1 of textbook) in reciprocal space (see Ch2), defined by drawing lines between a central reciprocal lattice point and each of its neighbors, drawing planes (lines in 2D or 1D) that are perpendicular bisectors of these lines, and taking the smallest volume enclosed by these planes

For a 1D lattice with unit cell dimension a, the reciprocal lattice is given by vectors $\boldsymbol{b_1} = \frac{2\pi}{a}\hat{\boldsymbol{x}}$ and every reciprocal lattice point can be reached with an integer multiple of **b1.**

Setting one reciprocal lattice point at the origin, the bisectors between the origin and the closest two lattice points are located at $= \pm\frac{\pi}{a}$. **This sets the boundary of the brillouin zone in 1 dimension**. Any k' outside these limits is equivalent to $k' - \frac{2\pi n}{a}$ which translates that point back into the first brillouin zone (n is an integer).

One dimensional lattice with a basis

Now we consider a 1 dimensional system with two (identical) atoms in the basis. Equilibrium positions of the atoms are given by na and na+d, where $d \leq \frac{a}{2}$. The lattice spacing is still given by a. There are two spring constants: C_1 for short bond and C_2 for longer bond.



$$U_{tot} = \frac{C_1}{2}\sum_n [u(na) - v(na)]^2 + \frac{C_2}{2}\sum_n [v(na) - u([n+1]a)]^2$$

(the position index na refers to both atoms in a given unit cell; u is the displacement of the atoms to the left of spring C1 (colored in above) and v is the displacement of the atoms to the left of spring C2 (open circles above))

$$m\frac{\partial^2 u(na)}{\partial t^2} = -\frac{\partial U_{tot}}{\partial u(na)}$$

$$m\frac{\partial^2 u(na)}{\partial t^2} = -\frac{C_1}{2}[2u(na) - 2v(na)] - \frac{C_2}{2}[2u(na) - 2v([n-1]a)]$$

$$m\frac{\partial^2 v(na)}{\partial t^2} = -\frac{\partial U_{tot}}{\partial v(na)}$$

$$m\frac{\partial^2 v(na)}{\partial t^2} = -\frac{C_1}{2}[2v(na) - 2u(na)] - \frac{C_2}{2}[2v(na) - 2u([n+1]a)]$$

Again, let's guess wavelike solutions of the form:

$$u(na) = \epsilon_1 e^{i(kna-\omega t)}$$

$$v(na) = \epsilon_2 e^{i(kna-\omega t)}$$

Where ϵ_1 and ϵ_2 are constants to be determined latter.

Plug our solutions into the equations of motion above and cancel out common factors of $e^{i(kna-\omega t)}$

Equation for u: $-m\omega^2\epsilon_1 = -C_1[\epsilon_1 - \epsilon_2] - C_2[\epsilon_1 - \epsilon_2 e^{-ika}]$

Equation for v: $-m\omega^2\epsilon_2 = -C_1[\epsilon_2 - \epsilon_1] - C_2[\epsilon_2 - \epsilon_1 e^{ika}]$

Rewrite equations grouping ϵ_1's and $\epsilon_2's$ together:

$$0 = \epsilon_1[-C_1 - C_2 + m\omega^2] + \epsilon_2[C_1 + C_2 e^{-ika}]$$

$$0 = \epsilon_1\left[C_1 + C_2 e^{ika}\right] + \epsilon_2[-C_1 - C_2 + m\omega^2]$$

This system of equations can be rewritten in matrix form

$$0 = \begin{pmatrix} -C_1 - C_2 + m\omega^2 & C_1 + C_2 e^{-ika} \\ C_1 + C_2 e^{ika} & -C_1 - C_2 + m\omega^2 \end{pmatrix} \begin{pmatrix} \epsilon_1 \\ \epsilon_2 \end{pmatrix}$$

The nontrivial solution is achieved if the determinant of the matrix is equal to zero.

$$(m\omega^2 - (C_1 + C_2))^2 - \left(C_1^2 + C_1 C_2 e^{-ika} + C_1 C_2 e^{ika} + C_2^2\right) = 0$$

$$(m\omega^2 - (C_1 + C_2))^2 = C_1^2 + 2C_1 C_2 coska + C_2^2$$

$$m\omega^2 - (C_1 + C_2) = \pm\sqrt{C_1^2 + 2C_1 C_2 coska + C_2^2}$$

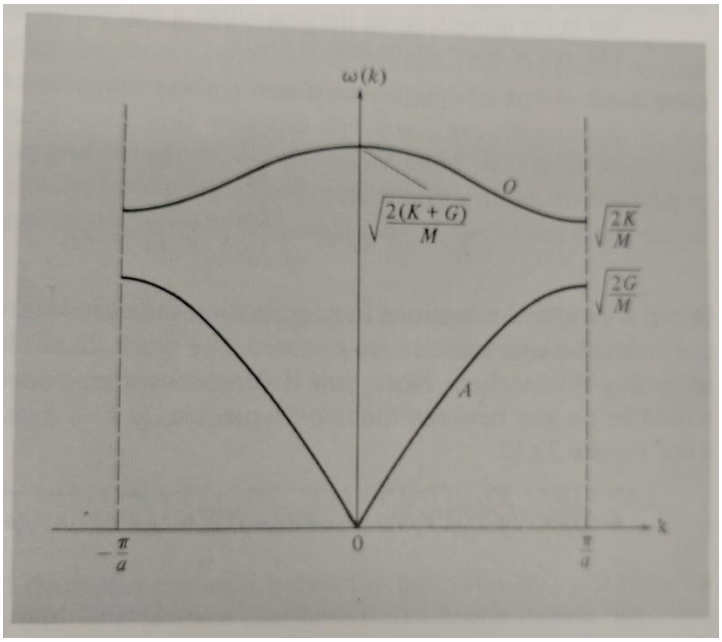
$$\omega^2 = \frac{(C_1 + C_2)}{m} \pm \frac{1}{m}\sqrt{C_1^2 + 2C_1 C_2 coska + C_2^2}$$

When we plug this expression for ω^2 back into one of the equations (use the 2nd one) we used to derive it, we can get a ratio for $\frac{\epsilon_2}{\epsilon_1}$. This is useful for quantifying the amplitudes of the two wave solutions we have.

$$\frac{\epsilon_2}{\epsilon_1} = \frac{C_1 + C_2 e^{ika}}{\mp\sqrt{C_1^2 + 2C_1C_2 coska + C_2^2}}$$

$$\frac{\epsilon_2}{\epsilon_1} = \frac{C_1 + C_2 e^{ika}}{\mp|C_1 + C_2 e^{ika}|}$$

We plot dispersion relations (first brillouin zone only) for the 2 roots of $\omega(k)$, and then we write simpler expressions for the roots in certain limits. Note that the book that the figure was taken from uses different notation, so substitute $K \to C_1$, $G \to C_2$. Note that there are now **two** dispersions, one like we had before, and a new one which has finite energy at k=0. The former is called an acoustic dispersion (A) and the latter is called an optical dispersion (O). The physical origin of this language is that the acoustic branch is a traveling wave, like sound, and the optical branch can couple to light because light which has energy comparable to these waves in solids also has really small momentum $k = \frac{\nu}{c}$



Limit 1: $k \sim 0$

In the limit of small k, $coska \approx 1 - \frac{1}{2}(ka)^2$

And

$$\omega^2 \approx \frac{(C_1 + C_2)}{m} \pm \frac{1}{m}\sqrt{C_1^2 + 2C_1C_2 - C_1C_2(ka)^2 + C_2^2} \approx \frac{(C_1 + C_2)}{m} \pm \frac{(C_1 + C_2)}{m}\sqrt{1 - \frac{C_1C_2(ka)^2}{(C_1 + C_2)^2}}$$

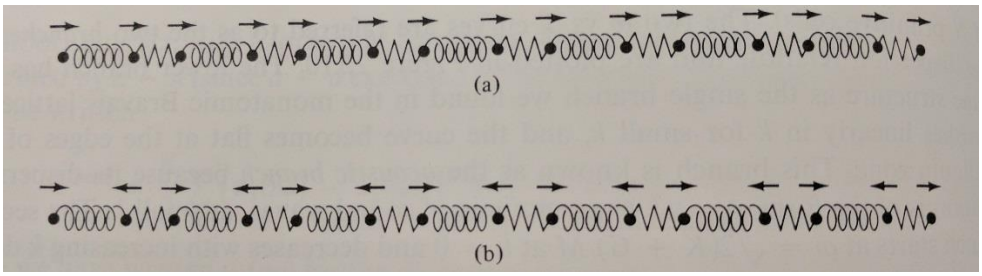
Also, remember that the expansion of $\sqrt{1+x}$ about x=0 $\approx 1+\frac{1}{2}x$

And the roots of ω are:

- (positive root) $\omega = \sqrt{\frac{(C_1+C_2)}{m} - \frac{C_1C_2(ka)^2}{2m(C_1+C_2)}}$
- (negative root) $\omega = ka\sqrt{\frac{C_1C_2}{2m(C_1+C_2)}}$

The negative root belongs to the acoustic branch and the positive root belongs to the optical branch. Physically, the acoustic mode at k~0 corresponds to a longitudinal wave traveling across the spring chain at velocity $\frac{\partial\omega}{\partial k} \sim a\sqrt{\frac{C_1C_2}{2m(C_1+C_2)}}$

The positive root belongs to the optical branch, and physically what this looks like (at k~0) is adjacent pairs of atoms oscillating out of phase with the next pair. The physical picture is found by considering the relative values of ϵ_1, ϵ_2 in each regime.



Limit 2: $k \sim \pi/a$

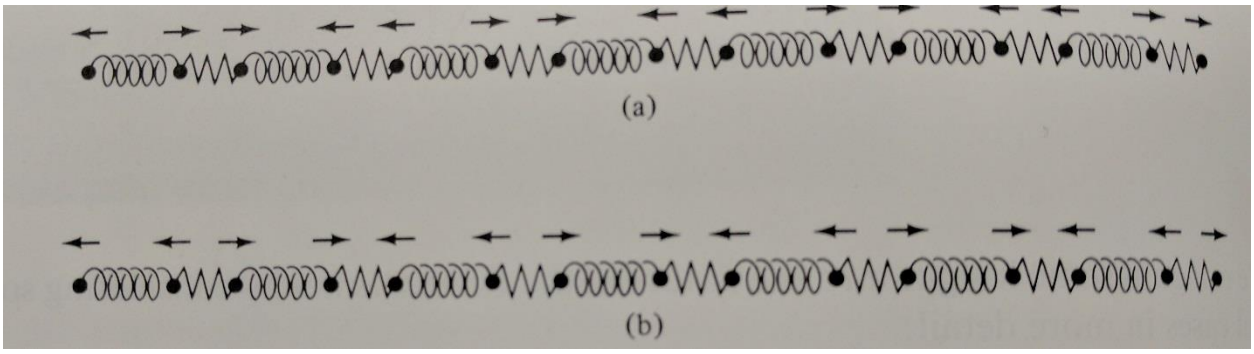
Here, $coska \sim -1$

The two roots are:

- (positive root) $\omega = \sqrt{\frac{2C_1}{m}}$
- (negative root) $\omega = \sqrt{\frac{2C_2}{m}}$

One thing to notice is that neither of these roots have a factor of k in them, so the derivative of ω with respect to k gives **zero**. Thus, these are not traveling waves.

Another thing to notice is that each root only involves **one** spring constant. Thus, these solutions correspond to situations where only **one** of the springs is stretched at a time.



In this derivation, I showed how to get optical and acoustic waves in a line of masses on springs where the 2 masses in the basis are the same but the spring constant are different. Kittel derives the same qualitative result using a line of masses on springs where the 2 masses in the basis are **different** but the spring constants are the same. You can derive the most general result, which has the same qualitative information of two types of waves, using a toy problem where the masses and the spring constants are both different.

Next lecture:

- How to get transverse waves
- Quantization of elastic waves