Summary of chapter 4.

The discussion at the end of chapter 3 is only correct for elastic waves that have a wavelength much longer than twice the periodicity of the lattice. Notice that we treated the material as a continuous medium. Of course this approach brakes down on an atomistic level: The density and elastic compliance constants are no longer homogeneous on an atomistic level: the density peaks at the average nucleus position and the elastic compliance constants describe the coupling between oscillating nuclei in the periodic crystal structure. The elastic wave is only defined at the position of the atoms and is not a continuous function but a series, i.e. a row of numbers that indicate the position of a row of atoms. In mathematics we refer to such function as a discrete function (see Fig. 1 below). The displacement of the wave between the atoms has no meaning.
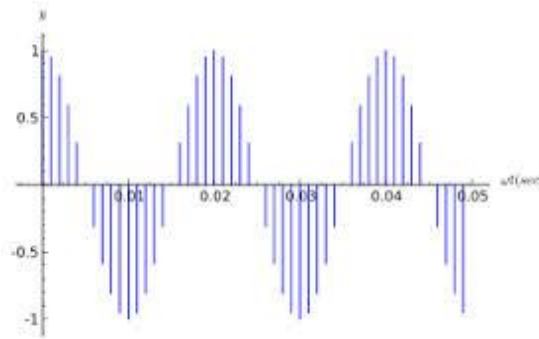

Fig. 1: Elastic wave represented by discrete function

Elastic waves are best analyzed and understood by looking to the propagation in certain directions in the crystal. For example for the cubic crystal structure waves propagating in the [100], [110], and [111] directions entire planes of atoms move in phase with displacement either parallel or perpendicular to the direction of the wave-vector. The wave can be described by a single coordinate, the displacement parallel (longitudinal mode) or perpendicular to the wave-vector (two transverse modes).

In this chapter we re-did the analysis of the phonon waves using the granular structure of the individual atoms. Our approach is based on (a) elastic response is a linear function of the forces, i.e. Hooke's law; (2) we only considered nearest neighbor interactions, i.e.

$$F_s = M \frac{d^2 u_{s,t}}{dt^2} = C\left(u_{s+1,t} - u_{s,t}\right) - C\left(u_{s,t} - u_{s-1,t}\right) \qquad [1]$$

Where F_s is the net force acting on atom plane s. C is the force constant in N/m. I added an extra subscript t to indicate that u depends on both the plane number s and the time t. Also note that equation [1] differs from equation (56) of chapter 3 in three ways: (1) the constants M and C in equation [1] refer to the atom mass (kg) and the force constant (N/m) while ρ and C_{11} of equation (56) refer to density (kg/m^3) and elastic compliance constants (N/m^2); (2) equation [1] is in terms of force (N) and displacement ($u_{s,t}$) while equation (56) is stated in terms of stress (N/m^2) and strain (dimension less); (3) the strain and stress in equation (56) were continuous functions while $u_{s,t}$ and F_s in equation [1] are discrete functions.

Note furthermore that equation [1] is actually a whole set of equations, one for each atom plane. Since we are looking for waves we expect the solution of equation [1] to consist of a time dependent part, i.e.

$e^{-i\omega t}$ and a position dependent part, i.e. u_s. So separation of variables gives the following time independent difference equation:

$$-M\omega^2\, u_s = C\left(u_{s+1} + u_{s-1} - 2u_s\right)$$ [2]

To solve a <u>difference equation</u> we normally use a trial solution of the form m^s. Since we are interested in wave properties it might be better to write m as e^{iKa} where a is the distance between two atom planes, so to use as a trial solution $u_o e^{iKas}$ where K is the wave-vector of the wave:

$$-M\omega^2\, \mathrm{u}_o e^{iKas} = C\left(u_o e^{iKa(s+1)} + u_o e^{iKa(s-1)} - 2u_o e^{iKas}\right) \Leftrightarrow$$
$$M\omega^2\, e^{iKa} = -C\left(e^{iKa2} + 1 - 2e^{iKa}\right) \Leftrightarrow$$
$$M\omega^2 = -C\left(e^{iKa} + e^{-iKa} - 2\right) \Leftrightarrow$$
$$\omega^2 = \frac{2C}{M}\left(1 - \cos(Ka)\right)$$ [3]

This is the dispersion relation, i.e. relation between wave-vector and frequency, for elastic waves. In Fig. 4 of chapter 4 the ω is plotted as a function of K. We see that the function is periodic. The slope of the dispersion relation is the speed of the wave. You can see that the speed is more or less constant for small wave-vectors and then the speed decreases as the wave-vector approaches π/a. A wave-vector of π/a corresponds with a wave that has a wavelength equal to 2 times the lattice constant. The waves beyond π/a are the same waves as the waves below π/a. Kittel illustrates this in Fig. 5. Note that the wave is a discrete function so, the displacement is only defined at the position of the atoms, i.e. at positions s*a where a is the distance between the atoms: this are the black dots in Fig. 5 of Kittel. Two waves are sketched in Fig. 5 that both have the same displacements at the atom positions and which thus should be the same elastic waves. The white wave has a period that is a little bit smaller than a, while the dashed wave has a period that is 5a (see also the figure below). For both waves the ratio of the displacement of two successive planes is the same. This ratio given by:

$$\frac{u_{s+1}}{u_s} = \frac{e^{iKa(s+1)}}{e^{iKas}} = e^{iKa}$$ [4]

So both waves are identical. The wave-vectors between $-\pi < Ka < \pi$ are repeated between $\pi/a < Ka < 3\pi/a$ etc. So we only have to consider the wave-vectors between $-\pi/a$ and π/a. This is called the first Brillouin zone. A wave with a wave-vector K' in the 2nd Brillouin zone can be described by a wave in the first Brillouin zone at K=K'-2π/a. The boundaries of the first Brillouin zone, K=π/a and K=-π/a, are referred to as the zone boundaries. Note that a wave with this wave-vector has zero speed so is a standing wave.
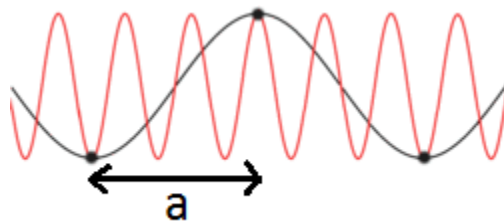

Fig. 2: Black dots are atom positions. The lattice constant is identified by a. Both periodic functions describe the elastic wave. The red (black) wave has a wave-vector in the 2nd (first) Brillouin zone.

So because of the atoms we expect a dispersion relation that looks like the function sketched by Kittel in Fig. 4 of chapter 4. We also expect the speed of the elastic waves to be dependent on the frequency and be smaller for higher frequencies. Furthermore the wavelength of an elastic wave is limited by the lattice parameter, or $K_{max}=\pi/a$ with a the lattice parameter.

Above discussion is too simple for most crystal structures. First of all in 3D we expect three different dispersion curves for each direction in the crystal, one for each mode, i.e. one longitudinal and two transverse branches. Since the lattice parameters can be different in different directions, we expect the dispersion relation to depend on the direction of the wave-vector. Also most materials have crystal structures with more than just one atom per base. This will lead to more branches in the phonon dispersion. For example for NaCl the base consists of a Na ion and Cl ion. Both ions can move 180 degrees out of phase with each other or in phase with each other leading to two different waves. The former waves are referred to as optical modes while the latter are referred to as acoustical modes (see also Fig. 3 below). Note that for the optical mode in an oxide or salt the elastic wave has an electric dipole moment that changes as a function of the position. This provides a direct coupling between the elastic wave and an EM wave. Optical phonon modes can therefore be detected by infrared transmission or reflection measurements and we refer to them as being infrared active. Acoustical phonons can also interact with photons but only indirectly. They are referred to Raman active phonons: A photon is in-elastically scattered and the scattered phonon has a different energy of the incident photon. Note that we have several Raman setups in the physics department at Texas State.
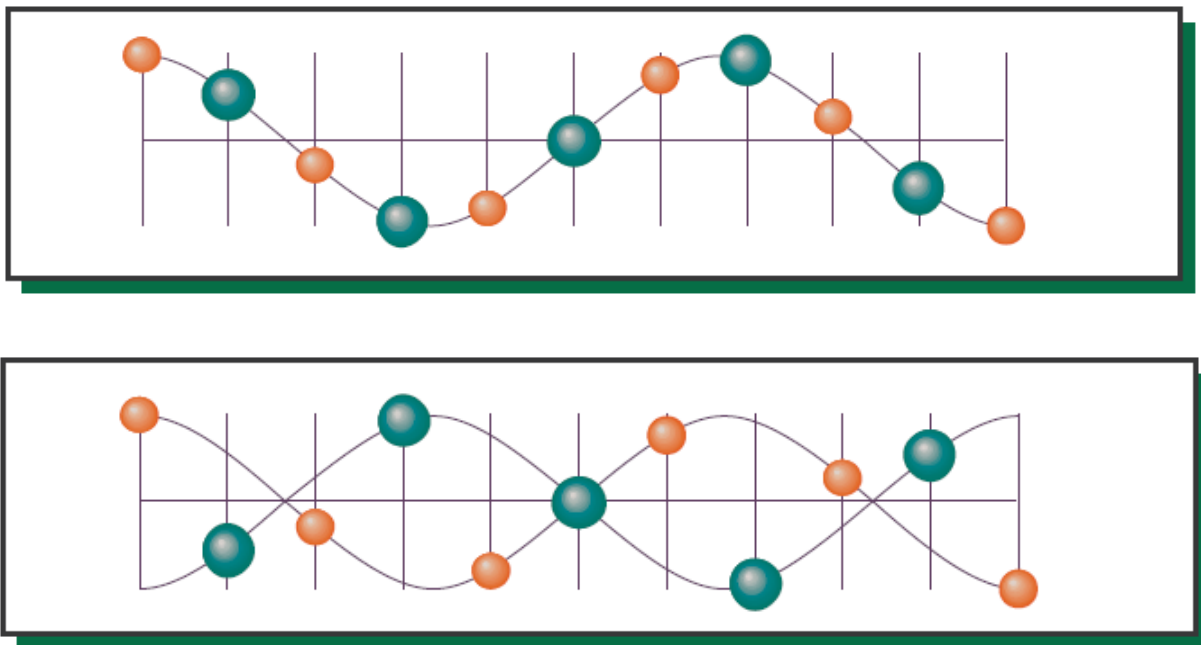

Fig. 3: Acoustic (top) and Optical phonon mode.

For a material with p atoms in the base we expect 3p branches, i.e. 3 acoustical branches and 3p-3 optical branches. The factor 3 is because for each direction we have 2 transverse and 1 longitudinal branch.

Kittel treats the phonon dispersion of a 2 atoms per basis crystal in a direction for which atom planes perpendicular to the K-vector only contain a single type of ion: for example NaCl is the [111] direction or CsCl in the [100] direction. For such system we have now two sets of difference equations, i.e.

$$M_1 \frac{d^2 u_{s,t}}{dt^2} = C\left(v_{s,t} + v_{s-1,t} - 2u_{s,t}\right)$$

$$M_2 \frac{d^2 v_{s,t}}{dt^2} = C\left(u_{s+1,t} + u_{s,t} - 2v_{s,t}\right)$$

[5]

Where $u_{s,t}$ is the displacement of the Na ions and $v_{s,t}$ the displacement of the Cl ions. Using an approach similar as above we find for the time independent set of equations:

$$-\omega^2 M_1 u_s = C\left(v_s + v_{s-1} - 2u_s\right)$$

$$-\omega^2 M_2 v_s = C\left(u_{s+1} + u_s - 2v_s\right)$$

[6]

To solve this set of difference equations similar to the 1 atom base case discussed above we use as trial solutions $v_s = v_o e^{iska}$, $u_s = u_o e^{iska}$. On substitution of those trial solutions in equation [6] we get:

$$-\omega^2 M_1 u_o = Cv_o\left[1 - e^{-iKa}\right] - 2Cu_o$$

$$-\omega^2 M_2 v = Cu_o\left[e^{iKa} + 1\right] - 2Cv_o$$

[7]

So non-trivial solutions require the determinant to be zero, so we find for the dispersion relation:

$$M_1 M_2 \omega^4 - 2C(M_1 + M_2)\omega^2 + 2C^2\left(1 - \cos(Ka)\right) = 0$$

[8]

This equation has four roots, i.e. two with positive K and two with negative K. The low w-roots are the acoustical branches and the high w-roots are the optical branches. The dispersion relation is printed in Fig. 7 and 8 on page 96 of Kittel. Note that a band-gap exists, i.e. there are no phonon modes with a frequency between $\sqrt{2C/M_1}$ and $\sqrt{2C/M_2}$. For those particular frequencies an acoustic wave will not be able to propagate without loss through the crystal.

Although Kittel treats the elastic waves classical, starting from Newton's 2nd law, we could treat elastic waves quantum mechanically. If one does that one will find that for a certain oscillation mode ω_K, the energy is quantized and given by:

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega_{\vec{K}}$$

[9]

We can use equation [9] to determine the square of the amplitude of a certain phonon mode:

$$u_o^2 = 4\left(n + \frac{1}{2}\right)\frac{\hbar}{\rho V \omega}$$

[10]

Where n is the occupancy of the phonon mode.

At the end of chapter 4 Kittel discusses the interaction of phonons with particles including photons, neutrons, and electrons. Although phonons do not carry momentum, we saw in chapter 2 that when a particle scatters of a crystal the incident and the scattered particles will obey the following selection rule:

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

[11]

Where G is a vector of the reciprocal lattice and **k'** and **k** are the wave-vector of the scattered and incident particle. The change of momentum of the particles will result in the complete crystal to recoil with a momentum $-\hbar\vec{G}$, so momentum conservation is still obeyed. In the case the scattering of the particles is inelastic and a phonon is created the selection rule will become:

$$\vec{k}'=\vec{k}+\vec{K}+\vec{G} \qquad\qquad\qquad [12]$$

Where K is the momentum of the created phonon. Of course also energy need to be conserved. For neutrons:

$$\frac{\hbar^2 K^2}{2M_n}=\frac{\hbar^2 k'^2}{2M_n}+\hbar\omega \qquad\qquad\qquad [13]$$

1. By measuring the energy and momentum of incident and scattered neutrons one can determine the dispersion relation of the phonons in different materials.
2. Photons can interact with phonons. Interaction of photons with acoustical phonons is called Brillouin scattering and interaction of photons with optical phonons is called Raman scattering. The scattering can result in the absorption or emission a phonon resulting in a scattered photon that has a higher or lower energy than the incident photon.
3. Photons can also directly interact with the optical phonons in the Infrared. With the right polarization it is possible to detect the transverse and longitudinal optical phonons. It is not possible to see the dispersion and the momentum of photons is small and we only see transitions near K=0.

[1] For movies of a transverse and longitudinal elastic wave see: https://www.nde-ed.org/EducationResources/CommunityCollege/Ultrasonics/Physics/wavepropagation.htm

[2] For a movie of a surface acoustical wave see: https://www.nde-ed.org/EducationResources/CommunityCollege/Ultrasonics/Physics/modepropagation.htm

[3] For a movie of an optical phonon in PbTe: https://www.youtube.com/watch?v=RV2rciEvxvI

[4] For a movie of an acoustical phonon in PbTe: https://www.youtube.com/watch?v=6qgIiyKKgvQ

[5] The right side of equation [2] is proportional to an approximation for the curvature since

$$\frac{d^2u}{dx^2}=\frac{d\left(\frac{du}{dx}\right)}{dx}\approx\frac{\frac{u_{s+1}-u_s}{1}-\frac{u_s-u_{s-1}}{1}}{1}$$

Or equation [2] reads a discrete function u_s (left side) that is proportional to its 2nd derivative (right side), and of course the solution should be an exponential discrete function in s.