MONATOMIC LATTICE VIBRATIONS

For monatomic gases we can model heat energy as the kinetic energy of the atoms. This model leads to the ideal gas law, and the model can be expanded to include other gas molecules. For solids, we can model **heat energy as the energy in lattice vibrations**. This model should then lead to predictions about heat capacity, thermal conductivity, and thermal expansion of solids. We first look at longitudinal oscillations (oscillations in the direction of the wave). Homework problems will look at transverse oscillations (oscillations perpendicular to the direction of the wave).

1. Start with $\Sigma \mathbf{F} = m\mathbf{a}$ (Newton's Second Law).

Newton's Second Law applies to individual atoms, so we must look at one atom (or in 3-D, look at one plane of atoms) which we will label with the subscript, s. This atom (or plane) is bound with "spring-like" bindings to neighboring atoms (or planes) with "spring constants", C_1.

Because the atoms are bound with electrical forces rather than springs, our atom s is also bound with "spring-like" forces to atoms further away than its nearest neighbor. These forces will have weaker binding forces, and hence weaker "spring constants" which we label C_p.

We label the displacement of atom s from its lattice position by u_s, and the displacements from their lattice positions of the atoms further up and down the line by $u_{s\pm p}$.

Due to the nature of the binding, if $u_s = 0$, and if $u_{s+1} = 0$ also, then there will be no force between the two (the two are at their equilibrium distance: if they were closer they would repel; if they were farther apart, they would attract).

Now consider the case when $u_s = 0$: if $u_{s+1} > 0$, then there would be a pulling force on u_s pulling u_s toward u_{s+1}. Likewise, if $u_{s+1} < 0$, then there would be a pushing force on u_s pushing u_s away from u_{s+1}.

Now consider the case when $u_{s+1} = 0$: if $u_s > 0$, then it would be closer than normal to u_{s+1} and so would be repelled away from u_{s+1}. Likewise, if $u_s < 0$, then it would be further than normal from u_{s+1} and there would be a pulling force on u_s pulling it toward u_{s+1}.

If BOTH u_s and u_{s+1} are not zero, then we have to look and see where both are to see if there will be a pushing force, pulling force, or no force on u_s. The result of this leads us to write the force between these two as:

$$F_{\text{between s and s+1}} = C_1 (u_{s+1} - u_s).$$

A similar argument holds for the force between s and s+p in general:

$$F_{\text{between s and s+p}} = C_p (u_{s+p} - u_s).$$

What about the force between s and s-1 (that is, between an atom and the atom behind it)? Consider the case when $u_s = 0$: if $u_{s-1} > 0$, then u_{s-1} is closer to u_s than normal and will push it away (in the forward direction). This is equivalent to u_{s+1} pulling u_s toward it in the forward direction. In fact, the above force relations hold for p BOTH positive (atoms ahead of atom s) and negative (atoms behind atom s)!

Putting this altogether gives:

$$\mathbf{\Sigma F_{on\ s} = {}_p\Sigma\, C_p (u_{s+p} - u_s) = m_s\, d^2u_s/dt^2.}$$

2. Solving the time part of Newton's Second Law.

First let's consider the time dependence of u_s and the u_{s+p}. Note the existence of $-u_s$ in every term on the force side and the d^2u_s/dt^2 on the right side. What function when you take the second derivative gives itself back again with a minus sign? The sine and cosine function (or equivalently, the $e^{i\Omega t}$ function).

[Note: Sine, cosine, and exponential functions here have to be functions of time, but the arguments of these functions can not have units. The Ω factor multiplying the t will include units of radians/sec to make this happen. We will use Ω for the oscillations of the lattice and use ω for the electromagnetic wave oscillations.] And since the u_{s+p} functions are just like the u_s functions except displaced in space from the u_s, we could expect that they would have the same time dependence.

Therefore, let's "**guess**" that the time dependence of u_s is of the form: $\mathbf{u_s(t) = u_{s*}e^{i\Omega t}}$ where u_{s*} is the amplitude of the oscillation for u_s and does not depend on time. This can be seen in a standing wave, and we only get appreciable amplitudes (and so appreciate energy) with waves that bounce back and forth if they form standing waves.
Newton's Second Law then gives:

$$\mathbf{{}_p\Sigma\, C_p\,(u_{s+p*} - u_{s*}) \;=\; m_s(-\Omega^2)u_{s*}}$$

where the $e^{i\Omega t}$ factor cancels out since it is in every term

3. Solving the spatial part of Newton's Second Law.

What we are left with is a **difference** equation: that is, recognize that $(u_{s+p*}-u_{s*}) = \Delta u$ is a difference that is related to u_{s*}. This difference equation can be made to look like an ordinary differential equation if we divide both sides by $\Delta x = (s+p)a - sa$ [recall a = normal spacing between lattice points, so $x_s=sa$, $x_{s+p}=(s+p)a$]. We cannot in fact take the limit as $\Delta x \to 0$ because we do not have a continuous medium but rather a discrete one. However, we can look at the solution of the differential equation that is similar to this difference equation and then see if we can try to "guess" a solution to the difference equation based on this.

The differential equation that is similar to our difference equation looks like:

$\beta dy/dx = -\alpha y$ which has the solution: $y(x) = Ae^{-(\alpha/\beta)x}$.

Further, we might expect some oscillation in space, so we might expect:

$$\mathbf{guess:}\quad \mathbf{u_{s+p*} \;=\; u_o e^{iK(s+p)a}}$$

where $K = 2\pi/\lambda$ with λ being the wavelength of the oscillation [we used $k = 2\pi/\lambda$ for the x-rays, so here we'll use $K = 2\pi/\lambda$ for the oscillations of the atoms]; $x_{s+p} = (s+p)a$ where the constant, a, is the normal separation between lattice points; and u_o is some constant amplitude. Now we substitute our guess solution into the difference equation to get:

$$ {}_p\Sigma\, C_p\,(u_o e^{iK(s+p)a} - u_o e^{iKsa}) \;=\; -m_s\Omega^2 u_o e^{iKsa}$$

or factoring out the $u_o e^{iKsa}$ factor from each term, and noting all atoms have the same mass ($m=m_s=m_{s+p}$) and the same amplitude, u_o:

$$-m\Omega^2 \;=\; {}_p\Sigma\, C_p\,(e^{iKpa} - 1)\ .$$

Let's now break the ${}_p\Sigma$ into three parts: ${}_{p<0}\Sigma$, p=0 term, and ${}_{p>0}\Sigma$.
[Recall that we sum over all p's including both positive and negative - indicating atoms both ahead and behind the s atom.]

Note that the p=0 term is zero (as it should since the s atom cannot have a force on itself!).

Note that $C_{p<0} = C_{p>0}$. This is due to the repeating nature of the lattice. The atom p places ahead is exactly equivalent to the atom p places behind. Therefore, we can replace the sum over -p with a sum over +p just reversing the sign on the p in the exponent:

$$ {}_{p<0}\Sigma\, C_{p<0}\,(e^{iKpa} - 1) \;=\; {}_{p>0}\Sigma\, C_{p>0}\,(e^{-iKpa} - 1)\ ,$$

so that our equation now becomes:

$$-m\Omega^2 \;=\; {}_{p>0}\Sigma\, C_p\,(e^{ipKa} - 1 + e^{-ipKa} - 1) \;=\; {}_{p>0}\Sigma\, C_p\,(e^{ipKa} + e^{-ipKa} - 2)\ .$$

Now recalling that $e^{\pm ipKa} = \cos(pKa) \pm i\sin(pKa)$, we can recognize that

$e^{ipKa} + e^{-ipKa} = 2\cos(pKa)$, so that our equation ends up as:

$$-m\Omega^2 \;=\; {}_{p>0}\Sigma\, 2C_p\,(\cos[pKa] - 1)\ ,$$

which **relates Ω to K**, so we recognize this as the **dispersion relation** for the monatomic lattice vibrations:

$$\mathbf{\Omega^2 \;=\; (2/m)\ {}_{p>0}\Sigma\, C_p\,[1 - \cos(pKa)]}\ .$$

4. We can play with this a little bit: we can use a trig identity: $\cos(\theta+\phi) = \cos(\theta)\cos(\phi) - \sin(\theta)\sin(\phi)$ so $\cos(2\theta) = \cos^2(\theta) - \sin^2(\theta) = [1 - \sin^2(\theta)] - \sin^2(\theta) = 1 - 2\sin^2(\theta)$, or **$1 - \cos(2\theta) = 2\sin^2(\theta)$** so:

$[1 - \cos(pKa)] = 2\sin^2(\frac{1}{2}pKa)$ to put the dispersion relation into the form:

$$\Omega^2 = (4/m)\sum_{p>0} C_p \sin^2(\tfrac{1}{2}pKa) .$$

5. Phase velocity: $v_{phase} = \lambda f = \lambda/T = (2\pi/T)/(2\pi/\lambda) = \Omega/K$.

$v_{phase} = \Omega/K = [(4/m)\sum_{p>0} C_p \sin^2(\frac{1}{2}pKa)]^{1/2}/K$, or playing around

[i.e., multiplying numerator and denominator by a and then bringing the denominator of Ka inside the square root] :

$$v_{phase} = [(a^2/m)\sum_{p>0} C_p \{\sin(\tfrac{1}{2}pKa)/(\tfrac{1}{2}Ka)\}^2]^{1/2} .$$

6. Group velocity: $v_{group} = d\Omega/dK$

Since our dispersion relation is in the form of $\Omega^2(K)$ instead of $\Omega(K)$, let's first consider $d(\Omega^2)/dK = d(\Omega^2)/d(\Omega) * d(\Omega)/dK = 2\Omega(d\Omega/dK)$, so $v_{group} = d\Omega/dK = [d(\Omega^2)/dK]/2\Omega$ and from the dispersion relation on the previous page:

$$d(\Omega^2)/dK = d\{(2/m)\sum_{p>0} C_p [1-\cos(pKa)]\}/dK = (2/m)\sum_{p>0} paC_p \sin(pKa)$$

thus the group velocity is

$$v_{group} = [d(\Omega^2)/dK]/2\Omega = (2/m)\sum_{p>0} paC_p \sin(pKa)/2\Omega = (a/\Omega m)\sum_{p>0} pC_p \sin(pKa).$$

This says that whenever $Ka = n\pi$ (where n is any integer), $v_{group} = 0$. Thus **$v_{group} = 0$ when $K = \pi/a$** which is **when $K = \frac{1}{2}(2\pi/a) = \frac{1}{2}G$** , i.e., **$v_{group} = 0$ when K is at the Brillouin zone boundary!**

Actually $v_{group} = 0$ whenever $K=n\pi/a$, but we'll see in the next section (7) that $K=n\pi/a$ is really no different than $K=\pi/a$.

Oscillations for which $v_{group} = 0$ are called **standing waves** which only oscillate in place and do not propagate (no transmission); if an x-ray has this k, it will try to set up the same K for the lattice vibration. If the lattice K cannot be transmitted, then the x-ray cannot be transmitted and will only diffract. Hence, this is another interpretation of the Bragg diffraction condition.

7. Limits on K:

Consider the ratio: $\{u_{s+1}/u_s\} = \{u_o e^{iK(s+1)a}/u_o e^{iKsa}\} = e^{iKa}$

If we replace K with $K' = K + n(2\pi/a)$, then the ratio becomes:

$$\{u_{s+1}/u_s\} = \{u_o e^{iK'(s+1)a}/u_o e^{iK'sa}\} = e^{iK'a} = e^{i[Ka + n(2\pi/a)a]} = e^{iKa} * e^{in2\pi} = e^{iKa}$$

which means that **for both K and K', adjacent atoms have the same phase difference, and hence K and K' describe the same oscillation pattern!** Hence the range for K of $\{0 < Ka < 2\pi\}$, or $\{-\pi < Ka < +\pi\}$, or equivalently: $\{(-\pi/a) < K < (+\pi/a)\}$ covers all the different oscillations. *See the excel spreadsheet on the course web page for this section (OscBZone.xlsx).*

This says that only those K's in the first Brillouin zone

$$[-\tfrac{1}{2}(2\pi/a) < K < \tfrac{1}{2}(2\pi/a) , \quad \text{or} \quad -\tfrac{1}{2}G < K < +\tfrac{1}{2}G]$$

are needed to completely describe the oscillations of the lattice!

Since **K has a maximum value (π/a),** and since $K = 2\pi/\lambda$, then λ has a minimum value of: $2\pi/\lambda_{min} = K_{max} = \pi/a$, or **$\lambda_{min} = 2a$** . Since K does not have a minimum value, λ does not have a maximum value. In the continuum limit, $a \to 0$ so $K_{max} \to \infty$ and $y_{min} \to 0$.

Homework problem 9 *asks you to demonstrate this via a diagram.* *[Hint: see excel spreadsheet mentioned above]*

8. Special case of nearest neighbor interactions only:

For nearest neighbor interactions only, we only keep the p=1 term and the dispersion relation

$$\Omega^2 = (4/m)\sum_{p>0} C_p \sin^2(\tfrac{1}{2}pKa)$$

simplifies to:

$$\Omega^2 = (4C/m)\sin^2(\tfrac{1}{2}Ka), \quad \text{or} \quad \Omega = 2(C/m)^{1/2}\sin(\tfrac{1}{2}Ka)$$

Therefore, $v_{phase} = \Omega/K = a(C/m)^{1/2}\sin(\tfrac{1}{2}Ka)/(\tfrac{1}{2}Ka)$, and

$$v_{group} = d\Omega/dK = a(C/m)^{1/2}\cos(\tfrac{1}{2}Ka).$$

If we **consider only small K** (large λ and small Ω), then since for small angles we have $\sin(\theta) \approx \theta$, and $\cos(\theta) \approx 1$, we get the following approximations:

$$v_{phase} \approx a(C/m)^{1/2} = \text{constant}, \quad \text{and} \quad v_{group} \approx v_{phase}.$$

9. Finding C_p :

If we can **experimentally** determine Ω(K), then we can try to determine the C_p by the method of Fourier Analysis. Consider the following (where r is a particular integer):

$$\int_{-\frac{1}{2}\pi/a}^{+\frac{1}{2}\pi/a} \Omega^2(K)\cos(rKa)\,dK \quad \text{with} \quad \Omega^2(K) = (2/m)\sum_{p>0} C_p[1-\cos(pKa)] \text{ (from part 3 above)}$$

becomes:

$$\int_{-\frac{1}{2}\pi/a}^{+\frac{1}{2}\pi/a} (2/m)\sum_{p>0} C_p[1-\cos(pKa)]\cos(rKa)\,dK = \int_{-\frac{1}{2}\pi/a}^{+\frac{1}{2}\pi/a} (2/m)\sum_{p>0} C_p[\cos(rKa) - \cos(pKa)\cos(rKa)]\,dK$$

$= 0$ if $p \neq r$, since integral of cos(θ) over one cycle is zero and cos(nθ)cos(mθ) over one cycle is also 0 unless n=m.

$= -2\pi C_r/ma$ if $p = r$. (This holds only for monatomic lattices.)

or finally:

$$C_r = (ma/2\pi)\int_{-\frac{1}{2}\pi/a}^{+\frac{1}{2}\pi/a} \Omega^2(K)\cos(rKa)\,dK.$$

Thus if we can empirically come up with Ω(K), we can determine the C_p's for monatomic lattices.

Homework problems 10, 11, and 12 *have you work with transverse waves on a 2-D lattice of monatomic atoms. You should be able to follow similar steps to the above for these three problems.*

Homework problem 13 *considers the energy in a longitudinal wave (the kind of wave we dealt with in this section).*

10. Review

We started with Newton's 2nd law and showed that waves will propagate in a solid as long as the frequency of the wave is related to its wavelength by what we call the **dispersion relation**:

$$\Omega^2 = (4/m)\sum_{p>0} C_p \sin^2(\tfrac{1}{2}pKa).$$

Since the crest of a wave (as well as all the other phases of a wave) moves with a phase speed that is related to the frequency and wavelength by $v_{phase} = \Omega/K$, we were able to see how the phase velocity (speed of oscillations which is the speed of sound in the solid) depends on the properties of the solid:

$$v_{phase} = [(a^2/m)\sum_{p>0} C_p\{\sin(\tfrac{1}{2}pKa)/(\tfrac{1}{2}Ka)\}^2]^{1/2}.$$

Also from the dispersion relation, we can get the group velocity of waves in the solid:

$$v_{group} = (a/\Omega m)\sum_{p>0} pC_p \sin(pKa).$$

From this, we can see that when $K = \pi/a$, that is, **when $K = \frac{1}{2}(2\pi/a) = \frac{1}{2}G$**, we have $v_{group} = 0$, or **standing waves** which only oscillate in place and do not propagate (no transmission).