

§4 – Vibrations

4.1 Vibrations

This is a sizeable subject, which leads to powerful predictions about the thermal properties of solids. When considering the counting of modes, we will see how reciprocal space notation is a useful tool.

We will start by considering simple models of vibrations and progress towards a more general case. Although strictly necessary, we will not study elasticity theory.

Probably the simplest model of lattice vibrations is a 1-dimensional monoatomic infinite chain of identical particles.

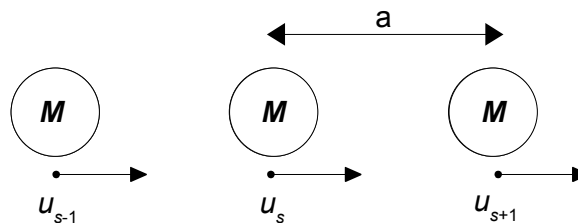


Figure 4.1: Monoatomic crystal comprising atoms of mass M connected by force constant C separated by repeat distance a .

a) 1D Monoatomic Chain

From Fig 4.1, we can see that the force (to the right) of a mass at a point s on the chain, M_s is given by:

$$F_s = M \frac{d^2 u_s}{dt^2} = C(u_{s-1} - u_s) + C(u_{s+1} - u_s) = C(u_{s+1} + u_{s-1} - 2u_s) \quad (4.1)$$

This equation has a wave solution. As usual, we have an amplitude equal to the value at $t = 0$ and a complex exponential term:

$$u_s = (u_s)_0 e^{-i\omega t} \quad (4.2)$$

We can drop the “0” after substituting into equation (4.1) without losing information:

$$-M \omega^2 u_s = C(u_{s+1} + u_{s-1} - 2u_s) \quad (4.3)$$

This is now simply a recurrence relation. If we assume that u_s has a wave-like space dependence, we can simplify this further:

$$u_s = u e^{iK(sa)} \quad (4.4)$$

Where K is some wavenumber, s is an integer (the number of the particle along the chain) and a is the lattice spacing. In other words, sa corresponds to distance along the chain.

Thus, equation (4.3) becomes:

$$-M\omega^2 e^{iKsa} = C e^{iKsa} \left(\underbrace{e^{iKa}}_{(s+1)} + \underbrace{e^{-iKa}}_{(s-1)} - 2 \right) \quad (4.5)$$

Using the standard identity, $\cos x \equiv \frac{1}{2}(e^{ix} + e^{-ix})$ gives:

$$-M\omega^2 = 2C(\cos Ka - 1)$$

$$\Rightarrow \omega^2 = 2\frac{C}{M}(1 - \cos Ka)$$

$$\omega^2 = \frac{4C}{M} \sin^2\left(\frac{1}{2}Ka\right) \quad (4.6)$$

This is known as a **dispersion relation**. It tells us how the frequency of the wave changes with the wavenumber. Every value of K can be a solution.

4.2 First Brillouin Zone

The wavenumber has units $[L]^{-1}$, which suggests that there may be a link between the wavenumber and reciprocal space.

If we plot ω against K , we can see that $\omega(K)$ is periodic in K .

We can see the First Brillouin Zone as the first set of unique solutions of $\omega(K)$ about $K = 0$. The value of K at the zone boundary can be found by writing e^{iKsa} as:

$$e^{iKsa} = e^{iKsa} e^{2\pi is} = e^{i\left(K + \frac{2\pi}{a}\right)sa}$$

So, we have unique solutions in the range $-\frac{\pi}{a} \leq K \leq \frac{\pi}{a}$. But, K can be positive or negative, so the zone boundary occurs at:

$$K_{zB} = \pm \frac{\pi}{a} \quad (4.7)$$

This is a very important result.

We can see from the picture that the high-frequency wave, corresponding to K beyond the zone boundary, is *indistinguishable* from a lower frequency wave within the FBZ:

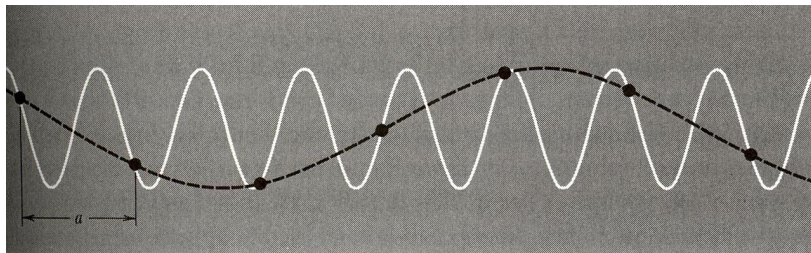


Figure 4.2: The wave represented by the solid curve conveys no further information than the dashed curve at the atom positions. Only wavelengths longer than $2a$ are needed to represent the motion.

It is possible to distinguish the positive and negative states at the zone boundary, but only because of the time-dependence of u_s :

$$u_s(t) = (u_s)_0 e^{iKsa} e^{-i\omega t} = (u_s)_0 e^{i(Ksa - \omega t)} \quad (4.8)$$

The *phase velocity* is given by:

$$v_p = \frac{\omega}{K} \quad (4.9)$$

The phase velocity can be positive or negative.

However, at the zone boundary, $K = \pm \frac{\pi}{a}$, we lose this sense of direction:

$$u_s(t)_{K=\pi/a} = (u_s)_0 \exp(i(\pm\pi s - \omega t)) = (u_s)_0 (-1)^s e^{-i\omega t} \quad (4.10)$$

Equation (4.10) represents a standing wave with alternate atoms oscillating in opposite phase. So, at the zone boundary, we no longer have a travelling wave.

4.3 Group Velocity

A generally more useful measure of velocity is the **group velocity**, which represents the movement of the wave packets. This is defined as the rate of change of angular velocity with wavenumber:

$$v_g = \frac{d\omega}{dK} = \frac{d}{dK} \left[2 \left(\frac{C}{M} \right)^{\frac{1}{2}} \sin \left(\frac{Ka}{2} \right) \right] = a \left(\frac{C}{M} \right)^{\frac{1}{2}} \cos \left(\frac{Ka}{2} \right) \quad (4.11)$$

The group velocity falls smoothly to zero at the zone boundary.

If we take the long wavelength limit, then $K \ll \frac{\pi}{a}$ and $\cos \left(\frac{Ka}{2} \right) \approx 1$.

Thus, the long-wavelength group velocity is:

$$v_g \approx a \left(\frac{C}{M} \right)^{\frac{1}{2}} = \text{const.} \quad (4.12)$$

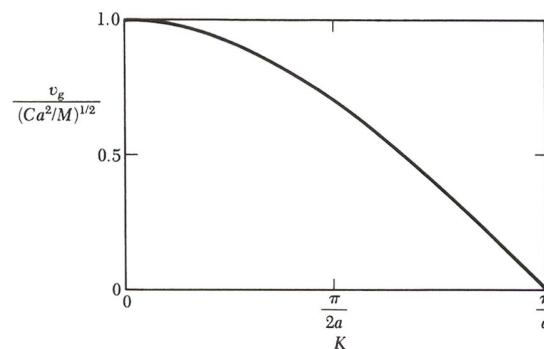


Figure 4.3: Group velocity v_g versus K , for a 1-dimensional monoatomic chain.

This can also be interpreted as the linear region of the dispersion relation.

The angular frequency in this case is given by:

$$\omega = 2 \left(\frac{C}{M} \right)^{\frac{1}{2}} \left| \sin \left(\frac{Ka}{2} \right) \right| \approx 2 \left(\frac{C}{M} \right)^{\frac{1}{2}} \frac{a}{2} |K|$$

The long-wavelength group velocity is then:

$$v_p = \frac{\omega}{K} = a \left(\frac{C}{M} \right)^{\frac{1}{2}} = v_g \quad (4.13)$$

This is the velocity of long-wavelength elastic waves in the solid, commonly called the *speed of sound* in the material:

$$v_s \approx v_p \approx v_g \quad (4.14)$$

A non-dispersive medium has $v_g = v_p$.

Dispersion effects set in near the zone boundary. We can consider this as interference with a Bragg-diffracted wave travelling in the opposite direction, slowing down the wave packets until they eventually form a standing wave at the zone boundary.

It is easy to generalise these results to three dimensions by replacing the wavenumber K with the 3-dimensional wavevector \vec{K} :

Dispersion Relation:

$$\omega(K) \rightarrow \omega(\vec{K})$$

Group Velocity:

$$v_g \rightarrow \vec{v}_g = \nabla_K \omega(\vec{K})$$

Where: ∇_K is the gradient (del) operator in wavevector space, which is a vector.

In the long-wavelength limit, an isotropic medium (e.g. cubic structure) has the same v_g value in all directions.

There are two types of polarization: *longitudinal* and *transverse*, denoted by L and T . Altogether, there are 3 modes, 1 L mode and 2 T modes.

Typical values for the constants are:

$$M = Z m_p \sim 50 \times 10^{-27} \text{ kg}$$

$$a \sim 0.3 \text{ nm}$$

$$v_s \sim 10^4 \text{ m s}^{-1}$$

Using these values gives a spring constant of:

$$C = M \left(\frac{v_s}{a} \right)^2 = 5 \times 10^{-26} \cdot (3 \times 10^{13})^2 = 50 \text{ N m}^{-1}$$

This is a typical macroscopic value for a light spring.

4.4 Structure with a Basis

So far, we have considered the 1-dimensional primitive lattice. The next level of complexity is a two-atom basis, or equivalently, a basis with two spring constants. An example of this is the [1 1 1] planes of a NaCl structure.

This time, we have two coupled equations of motion:

$$M_1 \frac{d^2 u_s}{dt^2} = C(v_s + v_{s-1} - 2u_s) \quad (4.15)$$

$$M_2 \frac{d^2 v_s}{dt^2} = C(u_{s+1} + u_s - 2v_s) \quad (4.16)$$

Again, the solution will be a wave, but there will be different amplitudes for the two masses. There will be the same frequency and wavenumber for each wave-mode of the system:

$$u_s = u e^{-i\omega t} e^{iK(sa)} \quad (4.17)$$

$$v_s = v e^{-i\omega t} e^{iK(sa)} \quad (4.18)$$

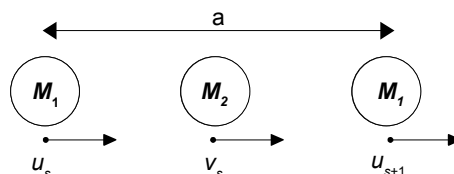


Figure 4.4: Diatomic crystal structure with masses M_1 and M_2 connected by force constant C . The repeat distance a is twice that of the monoatomic crystal.

We can substitute and cancel the common factors of the exponentials:

$$-\omega^2 M_1 u = C(v + v e^{-iKa} - 2u) \quad (4.19)$$

$$-\omega^2 M_2 v = C(u e^{iKa} + u - 2v) \quad (4.20)$$

We can write the coupled bilinear equations (4.19) and (4.20) in terms of a matrix:

$$\begin{pmatrix} 2C - \omega^2 M_1 & -C(1 + \exp[-iKa]) \\ -C(\exp[iKa] + 1) & 2C - \omega^2 M_2 \end{pmatrix} \begin{pmatrix} u \\ v \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} \quad (4.21)$$

This is an eigenvalue problem. As with all eigenvalue problems (in matrix form), the determinant of the matrix must be zero in order to obtain solutions:

$$\omega^4 M_1 M_2 - \omega^2 (2C M_1 + 2C M_2) + 4C^2 - C^2 (1 + \exp[-iKa])(\exp[iKa] + 1) = 0$$

Using the identity $2 \cos x = e^x + e^{-x}$:

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

Finally, completing the square gives solutions to ω^2 as:

$$\omega^2 = \frac{2C(M_1 + M_2) \pm \sqrt{4C^2(M_1 + M_2)^2 - 8M_1 M_2 C^2(1 - \cos(Ka))}}{2M_1 M_2} \quad (4.22)$$

There are two frequencies for each K wavenumber. This corresponds to the two “branches” of the dispersion relation.

Before we plot this result, it will be useful to examine the limits of this solution.

a) Small- K Limit

In this case, $K \ll \frac{\pi}{a}$, so $1 - \cos Ka \approx \frac{1}{2} K^2 a^2$.

So, we have:

$$M_1 M_2 \omega^4 - 2C(M_1 + M_2)\omega^2 + C^2 K^2 a^2 = 0$$

Let us look at the general equation for the roots of a quadratic in the limit $c \rightarrow 0$:

For the negative solution:

$$\lim_{c \rightarrow 0} \left[\frac{-b - \sqrt{b^2 - 4ac}}{2a} \right] = \frac{-b - \sqrt{b^2}}{2a} = -\frac{b}{a} \quad (4.23)$$

The positive solution is slightly more complicated, but we can use a series expansion of the form

$$(x+y)^{1/2} = x^{1/2} \left(1 + \frac{y}{x} \right)^{1/2} = x^{1/2} \left(1 + \frac{1}{2} \frac{y}{x} + O\left(\frac{y}{x}\right)^2 \right) :$$

$$\frac{-b + \sqrt{b^2 - 4ac}}{2a} \approx \frac{-b + b(1 - (4ac)/(2b^2))}{2a} = \frac{c}{b} \quad (4.24)$$

Thus the two small- K solutions are:

$$\omega_1^2 = \frac{2C(M_1 + M_2)}{M_1 M_2} = 2C \left(\frac{1}{M_1} + \frac{1}{M_2} \right) \quad (4.25)$$

$$\omega_2^2 = \frac{C^2 K^2 a^2}{2C(M_1 + M_2)} = \frac{C}{2(M_1 + M_2)} K^2 a^2 \quad (4.26)$$

Equation (4.25) is proportional to the reciprocal of the reduced mass $\mu = \frac{M_1 M_2}{(M_1 + M_2)}$. There is also no dispersion in this branch.

Equation (4.26) is like the solution to the monoatomic problem, where the group velocity incorporates both masses:

$$v_g = a \left(\frac{C}{M} \right)^{1/2} \rightarrow a \left(\frac{C}{2(M_1 + M_2)} \right)^{1/2}$$

b) Zone Boundary

At the zone boundary, we know that $K = \frac{\pm \pi}{a}$. Since the solutions at these two limits will be equivalent, but with opposite sign, we will just consider the positive limit. At $K = \frac{\pi}{a}$ we have $\cos K a = -1$, which gives:

$$M_1 M_2 \omega^4 - 2C(M_1 + M_2)\omega^2 + 4C^2 = 0$$

So, solving for ω^2 gives:

$$\omega^2 = \frac{2C(M_1 + M_2) \pm \sqrt{4C^2(M_1 + M_2)^2 - 16C^2(M_1 M_2)}}{2M_1 M_2}$$

Take the term in the square root:

$$4C^2(M_1 + M_2)^2 - 16C^2(M_1 M_2) = 4C^2(M_1^2 + 2M_1 M_2 + M_2^2 - 4M_1 M_2)$$

$$4C^2(M_1 + M_2)^2 - 16C^2(M_1 M_2) = 4C^2(M_1^2 - 2M_1 M_2 + M_2^2) = 4C^2(M_1 - M_2)^2$$

Thus, the solutions of ω^2 are:

$$\omega^2 = \frac{2C(M_1 + M_2) \pm 2C(M_1 - M_2)}{2M_1 M_2} = \frac{C}{M_1 M_2} [(M_1 + M_2) \pm (M_1 - M_2)] \quad (4.27)$$

This clearly has two solutions, given by:

$$\omega_1 = \sqrt{\frac{2C}{M_1}} \quad (4.28)$$

$$\omega_2 = \sqrt{\frac{2C}{M_2}} \quad (4.29)$$

So, at the zone boundary, the branches separate into solutions related to an individual mass.

We can use these limit solutions to project the final curves:

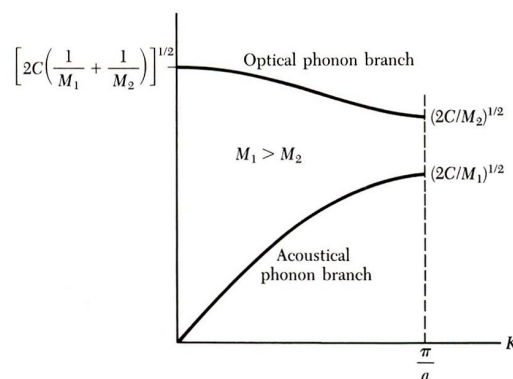


Figure 4.5: Optical and acoustic branches of the dispersion relation of a diatomic linear lattice in the positive half of the first Brillouin zone. Here, a is the lattice constant.

As before, we do not consider states outside $\pm \frac{\pi}{a}$, since for discrete atoms, these will be identical to those shown.

4.5 Nature of Branches

The splitting of the dispersion relation into optical and acoustic branches is a fundamental paradigm of solid state physics.

We can determine the nature of the modes from the eigenvalues of the matrix equation.

In the **optical** mode, u and v have **opposite** sign.

In the **acoustic** mode, u and v have the **same** sign.

The ratio of u and v varies with K .

We saw before that a wave appears to have a low-frequency and high-frequency modes. For transverse waves, these correspond to the acoustic and optical modes respectively.

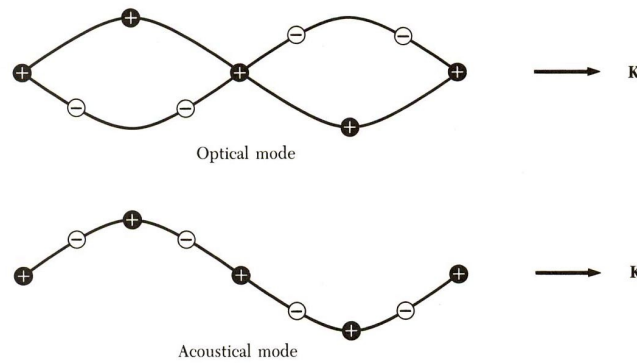


Figure 4.6: Transverse optical and acoustic waves in a diatomic linear lattice. Both modes have the same wavelength.

At the zone centre ($K = 0$) of the optical mode, the wave is flat.

At the zone boundary, only one of the ions oscillates.

We have not shown how the 2-branch dispersion evolves into a single branch when the two masses are equal.

The problem is that we used a in both cases. However, **these are not the same**. Once the masses become the same, the diatomic length is twice the monoatomic length as defined in Fig. 4.1 and 4.4.

We can shift the negative section of the optical branch into a doubled Brillouin Zone.

We can close the gap between the acoustic branch and shifted part of the optical branch by setting $M_1 = M_2$.

Let us check the frequencies:

$$\omega_c = \sqrt{2C \left(\frac{1}{M_1} + \frac{1}{M_2} \right)}$$
 for a diatomic chain.

If $M_1 = M_2$, then:

$$\omega_c = \sqrt{\frac{4C}{M}}$$
 for a monoatomic chain.

General Case:

In a general 3-dimensional monoatomic system, there will be always be 3 acoustic branches:

Transverse – 2 modes

Longitudinal – 1 mode

This means there are three angular frequencies for each value of the wavevector \vec{k} .

For a 2-atom basis, there will be twice this number of modes. However, since there are always 3 acoustic modes, these extra 3 modes will be optical modes.

For a p -atom basis, there will be $p \times 3$ number of total modes.

It is clear that the most general case of an n -dimensional system with a p -atom basis, will have:

$n(p-1)$ optical modes

n acoustic modes

Where the optical modes will be of mixed polarisation.

4.6 Quantisation of Vibrations

A mechanical oscillator has discrete excitation energies. We have shown in quantum mechanics, that the energy, ϵ of an oscillator, with quantum number n (corresponding to the energy level) and angular frequency ω is given by:

$$\epsilon = \left(n + \frac{1}{2} \right) \hbar \omega \quad (4.30)$$

Where n is a non-negative integer.

Mechanical vibrations correspond to bosons, which means that any number of them can occupy an energy state, i.e. n can be **any** non-negative integer.

The quanta of mechanical excitation are called **phonons**, by an obvious analogy with the quanta of optical oscillation: the photons.

If $n = 0$, then we have the lowest energy state, which has **zero-point energy**, which we can see from equation (4.30) is equal to $\frac{1}{2} \hbar \omega$.

The zero-point energy is a result of Heisenberg's uncertainty principle: the angular frequency has units of inverse time, and we know that the uncertainty between energy and time is given by:

$$\Delta \epsilon \Delta t \geq \frac{\hbar}{2} .$$

Each K -value of the excitation of the crystal corresponds to a different mode, like an independent oscillator.

We will show later that the eigenvectors for all values of K are orthogonal to one another. We can write the energy as a function of K , since ω is a function of K :

$$\epsilon_K = \left(n + \frac{1}{2} \right) \hbar \omega(K)$$

We can consider the phonon to be a particle inside the crystal (because of wave-particle duality). Thus, we can consider the phonon to have a momentum:

$$\vec{p}_K = \hbar \vec{K} \tag{4.31}$$

Note:

This is not a physical momentum in the standard sense. We call it the *crystal momentum* and can be seen as a “potential momentum” which can be gained or lost by interacting with an external probe, such as a photon or neutron.

Since neutrons are electrically neutral, they are much more effective at measuring the phonon dispersion relation than other methods, such as photon scattering.

A neutron's energy is given by $\epsilon_n = \frac{1}{2} m v^2$. This energy can be gained or lost when interacting with a crystal.

$$\frac{1}{2} m v^2 = \frac{\hbar^2}{2 m} k^2 \tag{4.32}$$

This is an *inelastic* scattering, meaning that the neutron's energy is not conserved.

However, since energy cannot be created or destroyed, we can use the conservation of energy and momentum to relate the initial (E, \vec{k}) and final (E', \vec{k}') energy-momentum:

From the conservation of energy:

$$E' = E \pm \hbar \omega(K) \tag{4.33}$$

And, from the conservation of “momentum”:

$$\vec{k}' = \vec{k} + \vec{G} \pm \vec{K} \tag{4.34}$$

Where lowercase k represents neutron wavenumber and uppercase K represents phonon wavenumber.

Thus, we can reconstruct both \vec{K} and $\omega(\vec{K})$.

We can use the results from the measurement of the neutron's final energy and momentum, with equations (4.33) and (4.34) to plot the experimental dispersion curves shown below for Sodium, Silicon and Germanium.

