This week we continue our study of phonons by considering more realistic 3D solids. We will, however, continue to assume that only nearest-neighbour, harmonic interactions are important.

We will use four key words to describe phonon modes in three dimensions. We have already met the distinction between optic and acoustic modes (see week 8 notes); we will now also need to distinguish between longitudinal modes, in which the atomic displacements are parallel to the wavevector, and transverse modes, in which they are perpendicular to it.

Let’s first consider a very simple 3D solid with the simple cubic structure. For clarity we will only show a single plane of atoms.

In order to draw a phonon dispersion curve, we have to choose a direction for our wavevector; let’s choose a simple example and consider \( \mathbf{k} \) parallel to the \((100)\) direction. This means that all the atoms in each plane perpendicular to \((100)\) (two of which are shown in blue) will move together. If we consider any atom in one of these planes, say the one highlighted in dark blue, it is connected to the nearest-neighbour plane by a spring with force constant \( J \). If the displacement is longitudinal, this is just a collection of monoatomic chains of the sort we have already considered, and we would expect the dispersion curve for this branch of phonons to look exactly like we derived last week for the monoatomic case. (We will worry about transverse vibrations in this model a little later.)

Let’s then consider a more realistic model: a face-centred cubic solid. For clarity we show only two planes of atoms, with the plane at \( z = \frac{1}{2} \) indicated by thicker circles.

This time our chosen atom, again highlighted in blue, has four nearest neighbours in the neighbouring plane in the \((100)\) direction: they are at vectors of \((\frac{1}{2}, \pm\frac{1}{2}, 0)\) and \((\frac{1}{2}, 0, \pm\frac{1}{2})\). What we want to do is somehow to add up the effects of these four springs into a single effective spring constant between this atom and the neighbouring plane. Again, we will begin by considering longitudinal motion.

In order to do this, we will need to work out what happens when a harmonic spring is distorted in a direction that is not along its length. We will assume that our potentials are completely isotropic; that is, that they
can be written as $E(r)$ where as usual $r^2 = x^2 + y^2 + z^2$. The spring constant for motion along the direction of the spring is $J = \frac{\partial^2 E}{\partial r^2}$. Let’s set up our coordinate system so that we really want to know the spring constant for motion in the $x$ direction, $\frac{\partial^2 E}{\partial x^2}$. We proceed as follows.

Implicitly differentiating the definition of $r$ above gives

$$2x = 2r \frac{\partial r}{\partial x}.$$ 

Now by the chain rule

$$\frac{\partial E}{\partial x} = \frac{\partial E}{\partial r} \frac{\partial r}{\partial x}$$

$$\frac{\partial^2 E}{\partial x^2} = \frac{\partial^2 E}{\partial r^2} \left( \frac{\partial r}{\partial x} \right)^2 + \frac{\partial E}{\partial r} \frac{\partial^2 r}{\partial x^2}.$$ 

Since we are expanding about a minimum, $\frac{\partial E}{\partial r} = 0$ and we are left with the rather neat expression

$$\frac{\partial^2 E}{\partial x^2} = \frac{\partial^2 E}{\partial r^2} \left( \frac{\partial r}{\partial x} \right)^2 = \frac{x^2 \partial^2 E}{r^2 \partial r^2}.$$ 

Let’s apply this to the spring connecting our chosen atom to the atom a vector $(\frac{1}{2}, \frac{1}{2}, 0)$ away. We have

$$J_{(\frac{1}{2}, \frac{1}{2}, 0)} = \frac{\left(\frac{1}{2}\right)^2}{(\frac{1}{2})^2 + (\frac{1}{2})^2} J = \frac{1}{2} J.$$ 

It is easy to see that in fact this result will be the same for each of the four nearest neighbours, so that the effective spring constant between these planes is $J_{\text{eff}} = 4 \times \frac{1}{2} J = 2J$ for longitudinal motion.

What about vibrations in a transverse direction? By an exactly analogous argument (or simply by relabelling our axes!) we find that

$$\frac{\partial^2 E}{\partial y^2} = \frac{\partial^2 E}{\partial r^2} \left( \frac{\partial r}{\partial y} \right)^2 = \frac{y^2 \partial^2 E}{r^2 \partial r^2}.$$ 

Applying this to the atoms at $(\frac{1}{2}, \pm \frac{1}{2}, 0)$ gives $J_{(\frac{1}{2}, \pm \frac{1}{2}, 0)} = \frac{1}{2} J$ as before. However, applying this formula to the atoms at $(\frac{1}{2}, 0, \pm \frac{1}{2})$ gives $J_{(\frac{1}{2}, 0, \pm \frac{1}{2})} = 0$. In other words, the nearest neighbours with the same $y$ coordinate do not provide any resistance to motion in the $y$ direction (within the harmonic approximation). One way of rationalising this is to realise that this motion would be possible even if these springs were replaced by rigid rods with no ability to stretch at all! Summing up the spring constants thus gives $J_{\text{eff}} = 2 \times \frac{1}{2} J = J$ for transverse motion.

Putting all of this together, our prediction is that the dispersion curve for a face-centred cubic solid in the $(100)$ direction should have the same functional form as a monoatomic 1D chain. Furthermore, it should have a transverse mode that rises to $1/\sqrt{2}$ of the frequency of the longitudinal mode at the Brillouin zone boundary. (In fact, it should have two such transverse modes, with exactly the same energy, since there are two directions transverse to $(100)$: $y$ and $z$.) And indeed if we look at the experimental dispersion curve of neon, an fcc solid, we see exactly that:
Fig. 8.7 Acoustic mode dispersion curves for neon (ccp structure) measured by inelastic neutron scattering. L and T denote longitudinal and transverse modes respectively. For the [001] and [111] directions the two transverse modes are degenerate (as indicated by the label 2T). Along the [110] direction, the (x,y) and (z) labels indicate the directions of the atomic motions. (Data taken from Endoh et al., Phys. Rev. B 11, 1681, 1975.)

This diagram is Figure 8.7 in Dove. The portion we have just derived is the left section, labelled (0, 0, \(\xi\)). This notation, where multiplication by the reciprocal lattice vectors is implied, is sometimes referred to as reduced wavevector.

Returning to our initial simple cubic example, we can now see that for transverse vibrations our model predicts no spring constant at all! In other words, this structure is unstable to transverse (shear) motion of the planes. This is one reason why this structure is so uncommon in nature.

We will spend some time in class repeating these calculations for other structures (such as body-centred cubic) and other directions of \(\mathbf{k}\). Our aim will be to understand the experimentally determined phonon dispersion curves of real materials including neon (above), potassium (body-centred cubic), and sodium chloride. Each of these experimental curves (and many others besides) can be found in Dove.

Next topic: how are these phonon modes occupied at a given temperature?
Revision questions for week 9a

A51. What is the difference between a longitudinal and a transverse mode?

A52. How many branches in total would we expect in the phonon dispersion curve of a material with the following structures? How many of these would be transverse optic, longitudinal optic, transverse acoustic, and longitudinal acoustic?
   (a) Body-centred cubic
   (b) Sodium chloride
   (c) Diamond

The following two questions refer to the experimental dispersion curve of neon, which can be found on p.3 of the notes above.

A53. How many branches would we expect in the phonon dispersion curve of a monatomic solid like neon? Why are this many branches not visible at every point of the experimental curve?

A54. Estimate the speed of longitudinal sound waves travelling in the [111] direction in neon. Take the cell parameter to be \( a = 4.43 \text{ Å} \).

A55. The following set of atomic displacements in a primitive cubic solid can be described by a wavevector \( k \) within the first Brillouin zone and displacement direction (transverse or longitudinal) in two possible ways. Give both. What is special about this wavevector that allows these two different descriptions?

B56. A two-dimensional close-packed layer, of the sort found in the crystal structures of many metals, is shown below. The lattice vectors \( \mathbf{a} \) and \( \mathbf{b} \) are as shown, and the motif consists of a single atom.

(a) Draw the reciprocal lattice vectors \( \mathbf{a}^* \) and \( \mathbf{b}^* \).

In this problem, we will consider vibrations with wavevector \( \mathbf{k} \) parallel to \( \mathbf{x} \) in the coordinate system defined below. As usual, we consider only harmonic interactions between nearest-neighbour atoms, which we model as ideal springs with force constant \( J \). The wavefronts, and the “springs” between one atom and its neighbours in the next plane, are indicated below.

(b) Write down the interatomic vectors between nearest neighbours \( \mathbf{r}_1 \) and \( \mathbf{r}_2 \) in terms of the cell parameter \( a \), using the \( x, y \) coordinate system.

(c) Hence calculate the effective spring constant \( J_{\text{eff}} \) between nearest-neighbour planes, in terms of \( J \), for (i) longitudinal and (ii) transverse vibrations.

(d) Hence sketch the dispersion curve for waves in this direction, in enough detail to show the results of your previous calculations.

(e) Suppose that we excite a longitudinal mode at the Brillouin zone boundary. Draw a sketch of this structure in which each atom is labelled with an arrow to show its displacement.

(f) Show – perhaps using an appropriate diagram – that this set of displacements could equally well be interpreted as a transverse mode with wavevector parallel to \( y \).