

## Day 6: Monday – 50 minutes

## Recap:

Found dispersion relations for diatomic and monatomic chains. Learned about boundary conditions

**Application to solids:**

How does our study of chains of spring-coupled masses relate to real solids?

The chemical bonds that hold atoms together in solids can be modeled by springs. They can be stretched, compressed or bent and, for small displacements, the necessary force is proportional to the displacement – that is, they obey Hooke's law. Much of what we have learned about 1-D chains applies to 3-D crystals, but there are also new features that appear:

(1) The number of atoms ( $N$ ) in a macroscopic crystal is very large – on the order of  $10^{28}$  per  $\text{m}^3$ . This means that there are an enormous number of modes, and their wavevector and frequency values are very closely spaced. We can often treat  $k_q$  and  $\omega_q$  as continuous variables,  $k$  and  $\omega$ .

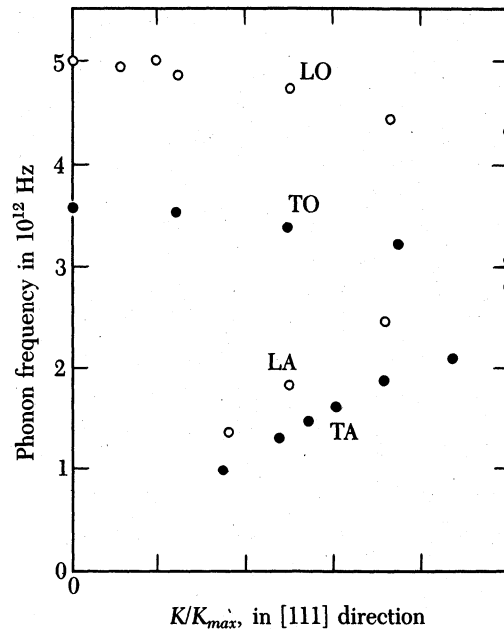
(2) The “wavevector”  $k$  becomes a true, 3-D vector  $\vec{k}$  with components  $k_x$ ,  $k_y$  and  $k_z$ . The Brillouin zone was a line segment in 1-D on the  $k$ -axis. In 3-D it becomes a polyhedron enclosing a region of 3-D “k-space.”

(3) For waves propagating in any particular direction, we now have to consider 3 “polarizations”:

(i) a longitudinal wave in which the atoms move in the direction of wave propagation (similar to the modes we have analyzed on chains)

(ii) two transverse waves in which the atoms move perpendicularly to the direction of wave propagation. There are two transverse modes because there are two orthogonal directions perpendicular to propagation. For example, if the propagation is in the  $z$ -direction, transverse motion could occur in either the  $x$ - or  $y$ -directions.

The lessons of the diatomic chain apply qualitatively to the modes of a binary compound. This is illustrated by the dispersion relations for a crystal of potassium bromide, KBr, shown below. As we discuss later, dispersion relations like these can be determined experimentally by scattering neutrons off the crystal.



(KBr at 90 K, after Woods, Brockhouse, Cowley, and Cochran, 1963)

For each polarization, longitudinal and transverse, there is an acoustic branch and an optic branch (the two transverse branches happen to be identical for KBr as a result of the cubic symmetry of this particular crystal structure – not true in general).

The experimental dispersion relations contain a lot of information and allow us to draw some basic conclusions about the “springs” (chemical bonds) that hold KBr together.

For example, for any  $k$ -value, we see that the frequencies of the longitudinal waves are higher than those of the transverse waves. Thus, the “springs” are stiffer (higher effective  $\kappa$ ) for compression or stretching than for flexing.

We can use the 1-D result to estimate the “spring constant” of the chemical bond. The frequency of the optic mode at  $k = 0$  is given by

$$\omega_{opt} = \sqrt{2\kappa \left( \frac{1}{M} + \frac{1}{m} \right)}$$

The experimental dispersion relation yields  $\frac{\omega_{opt}}{2\pi} = 5 \times 10^{12}$  Hz for longitudinal waves. From  $M = 79.9$  g/mole (Br) and  $m = 39.1$  g/mole (K) we can calculate  $\kappa \approx 20$  N/m. The spring constant for the transverse modes would be about 30 % lower.

We can also estimate the speed of sound (acoustic waves) in the crystal. In the limit  $ka \ll 1$ , the dispersion relation becomes  $\omega = \sqrt{\frac{2\kappa}{M+m}} \left( \frac{a}{2} \right) k$ . This has just the form of the dispersion relation for ordinary sound:

$$\lambda v = v_s \Rightarrow \frac{2\pi}{k} \cdot \frac{\omega}{2\pi} = v_s \Rightarrow \omega = v_s k$$

Thus, we can write  $v_s = \sqrt{\frac{2\kappa}{M+m}} \left( \frac{a}{2} \right)$ .

Evaluating with our value of  $\kappa$  for longitudinal waves and  $a = 6.6 \times 10^{-10}$  m (lattice constant of KBr), we get  $v_s \approx 7 \times 10^3$  m/s. This is a typical value for the speed of acoustic waves in solids.

We don't need expensive neutron scattering data to get information about interatomic interactions. From direct measurements of the speed of sound in a crystal, we could do the calculation the other way round and find  $\kappa$ . Still another possibility is to use continuum theory

$$\text{speed of sound} = (\text{bulk modulus/density})^{1/2}$$

and obtain the speed of sound and, hence  $\kappa$ , from measurements of the bulk modulus and the density of the crystal. The point is that an understanding of the fundamental vibrational properties of a solid allows us to obtain microscopic, atomic scale information from measurements of macroscopic properties like the speed of sound or the bulk modulus.

## Phonons

The normal mode vibrations of solids are referred to as PHONONS.

Phonons are important because they

1. Are the mechanism for sound conduction
2. Relate to the elastic properties of solids
3. Interact with other “-ons” in the solid (electrons, magnons, plasmons) to modify properties (for example, they are responsible for superconductivity).
4. Contribute to heat conduction and heat capacity

### What, exactly, is a phonon?

Recall that the vibrational properties of the 2-mass coupled oscillator can be viewed in terms of two independent simple harmonic oscillators, one with frequency  $\omega_{\text{low}}$  and one with frequency  $\omega_{\text{high}}$ . They are independent in the sense that if only one normal mode is excited, there will be no transfer of energy into the other mode. Similarly, the normal modes of a crystal lattice can be viewed as a set of (many) independent harmonic oscillators.

A classical harmonic oscillator can be excited with any amount of energy -- up to a reasonable maximum where Hooke's Law no longer applies, or the spring breaks, or the masses hit each other, etc. If we give the masses a bigger push or larger displacement at  $t = 0$ , the energy and amplitude will be larger, but any “reasonable” value is possible.

The oscillators representing the normal modes of a crystal lattice obey the rules of quantum mechanics. (This is because the “masses” (atoms) are so much lighter than those encountered in classical mechanical oscillators.) The energy of a quantum harmonic oscillator is “quantized” -- only certain values of the energy are allowed. For an oscillator with frequency  $\omega$ , the rule is

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

where  $n$  is an integer ( $n = 0, 1, 2, \dots$ ) and  $\hbar$  is (Planck's constant)/ $2\pi$ . In analogy with the particle description of electromagnetic radiation (photon), a little bundle of vibrational energy in a lattice can be viewed as a "particle" of energy  $\hbar\omega$  and momentum  $\hbar\vec{k}$ . Such a "particle" is a **phonon**.

When a particular lattice mode is excited to a high energy (high  $n$ ), we would say that there are many phonons of this particular  $\omega$  and  $\vec{k}$ . If  $n$  is low, then there are few phonons of this type. Thus, for example, instead of describing the a particular motion as a superposition of a large amplitude low frequency vibration and a small amplitude high frequency vibration, we talk of a solid as having many low frequency phonons and a few high frequency phonons. We will see that the temperature of the crystal has a big influence on how many phonons are present and what their frequencies are.

The description of lattice vibrations in terms of phonons makes it easier to analyze processes in which other particles (photons, neutrons, electrons, etc.) interact with the crystal. For example, if we pass light through a crystal, it is possible for photons to be destroyed and phonons created. Such a process must conserve energy and momentum:

$$\omega_{phonon} = \omega_{photon}$$

$$k_{phonon} = k_{photon}$$

In order for such a process to be effective, there must be a coupling between the photon and the lattice vibrations. The coupling is very strong for the optic modes of an ionic solid like KBr. Because neighboring atoms have opposite electric charges, the electric field of the light moves  $K^+$  and  $Br^-$  ions in opposite directions. But this is exactly the anti-phase motion associated with the "optic modes". (This is, in fact, how these modes got their name.) So it is easy for the oscillating electric fields of light (photons) to create phonons of the optic modes in ionic crystals just so long as the conservation conditions are met.

What is the wavelength of light that excites optic modes in ionic crystals? Our dispersion relation for KBr shows, for example, that the frequency of the longitudinal optic mode is about  $5 \times 10^{12}$  Hz. (Why do

we use the frequency near  $k = 0$ ?). The wavelength of electromagnetic radiation of this frequency is

$$\lambda_{\text{photon}} = \frac{c}{\nu_{\text{photon}}} = \frac{3 \times 10^8 \text{ m/s}}{5 \times 10^{12} \text{ Hz}} = 6 \times 10^{-5} \text{ m} = 60 \text{ } \mu\text{m}$$

This wavelength corresponds to infrared light. The optic modes of ionic compounds like KBr can be studied experimentally by infrared spectroscopy – as we scan the wavelength of light transmitted by such crystals, there are dips in the transmission (peaks in the absorption) when the energy and momentum of the photons match those of the optic modes.

When a beam of neutrons is passed through a crystal, the neutrons gain or lose energy and momentum by creating or destroying phonons. By analyzing the outgoing neutrons and using the conservation conditions, it is possible to determine the energy and momenta ( $\omega$  and  $\vec{k}$ ) of the phonons. This is how the dispersion relation for KBr was determined.

Phonons can also interact with electrons – scattering processes thus limit the electron motion, and are an important part of why materials have finite electrical resistance. As the temperature increases, the lattice vibrates more strongly (there are more phonons), and thus the interaction with the electrons is stronger, and the resistance goes up. This is very clear in a metal. The same effect occurs in a semiconductor, but in this case, there is a competing effect – carrier generation – that overshadows it. For semiconductors, resistivity goes down with temperature.

Phonons are important for the thermal properties of solids. The lattice vibrations are the largest “reservoir” of thermal energy, i.e. the largest contributors to the internal energy of a solid. We’ll be interested in calculating heat capacity due to phonons. Phonons also conduct heat – when one side of a lattice is hotter than another, the phonons transfer thermal energy from one side to another to bring the crystal to equilibrium.