Chapter 2

VIBRATIONAL PROPERTIES OF SOLIDS

2.1 From chains to solids

In Chapter 1 we examined the classical vibrational properties of one-dimensional chains of masses connected by springs. How does this relate to the behavior of real, three-dimensional solid materials? The surprising answer to this question is that many of the features of vibrational waves on classical chains have a close counterpart in solids. The reason is that the chemical bonds that hold atoms together in solids can be modeled very well by springs. Bonds can be stretched, compressed or bent and, for small displacements of the atoms, the necessary force is proportional to the displacement – that is, chemical bonds obey Hooke's law.   Still, there are also some new features that appear in 3-D solids:

> (1) The number of atoms (N) in a macroscopic crystal is very large – on the order of 10^{28} per 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 ω_q as **continuous variables, k and ω.**

> (2) The "wavevector" k becomes a true, 3-D vector, , 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 <u>two</u> transverse modes because there are two orthogonal directions perpendicular to propagation. For example, if a wave propagates in the *z*-direction, transverse motion could occur in both the *x*- and *y*-directions.

The lessons of the diatomic chain apply qualitatively to the vibrational 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 a crystal.
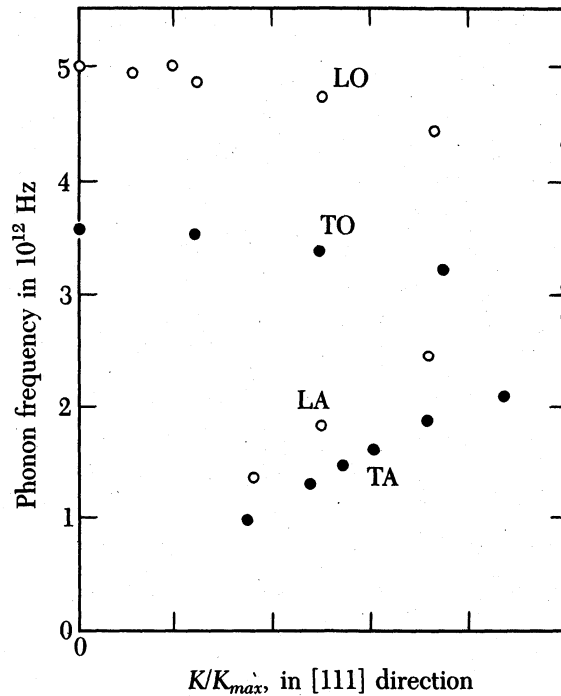
Figure 2.X.   Dispersion relations for KBr at 90 K, after Woods, Brockhouse, Cowley, and Cochran (1963). [From Kittel, need alternate figure??]

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

The experimental dispersion relations contain a lot of information and allow us to draw some basic conclusions about the springs-like 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 κ) for compression or stretching than for flexing.

Next, we can use the 1-D result to estimate the "spring constant" of the chemical bond. Recall that the general result for the dispersion of acoustic and optic modes on a diatomic chain is given by

$$\omega^2 = \kappa\left(\frac{1}{M}+\frac{1}{m}\right) \pm \left[\left(\frac{1}{M}+\frac{1}{m}\right)^2 - \frac{4}{Mm}\sin^2\left(\frac{ka}{2}\right)\right]^{1/2}$$

Taking the plus-sign, we find that the frequency of the optic mode at $k = 0$ is given by

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

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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:

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

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

We don't really 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 κ. Still another possibility is to use continuum theory
$$\text{speed of sound} = (\text{bulk modulus/density})^{1/2} \qquad \text{(XX)}$$

and obtain the speed of sound and, hence κ, 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.

2.2   Phonons

The normal mode vibrations of solids are referred to as **phonons**. They plan an important role in determining many fundamental physical properties of solids:

   (i) **Conduction of sound**. The long-wavelength propagating acoustic modes of atomic displacements are, in fact, what we call "sound" in solids. They provide the mechanism

for conduction of vibrational energy from one part of a solid to another. We have seen that the velocity of sound propagation is directly related to the dispersion relation for the acoustic modes at low frequency/long wavelength.

(ii) **Elastic properties**. Strain induced in a solid by external forces (compression, tension, shear) requires motions of atoms relative to their neighbors. Wave-like vibrational excitations of a lattice also involve such atomic motion. It is not surprising, therefore, that a bulk elastic property like the bulk modulus is closely related to a vibrational property (speed of sound) as in Eq. Xx.

(iii) **Thermal properties**. Phonons are usually the largest reservoir of thermal energy in solids. The exceptions occur at very low temperatures where the amplitudes of lattice vibrations have been reduced to the point where other forms of energy become dominant. Examples of such other forms include magnetic energy or the kinetic energy of electrons. At "ordinary temperatures" such as room temperature, phonons provide the mechanism for conduction of heat. That is, when one side of a solid is hotter than the other, phonons provide a mechanism for transfer of heat from the hot side to the cold side. Phonons are also the largest contributor to internal energy and, hence, the heat capacity.

(iv) **Interactions with other excitations**. Phonons are the most important example of the "–ons," the various fundamental carriers of energy a solid. Other examples are electrons, magnons (magnetic excitations), and plasmons (combined electronic-ionic vibrational excitations). Some very important physical properties depend on interactions between different " –ons." Superconductivity, for example, occurs in most cases because of interactions between electrons and phonons.

2.2.1 What, exactly, is a phonon?

A more detailed examination of the lattice vibrations of a solid requires us to consider the quantum mechanical properties of the lattice modes. We will see that a quantum picture explains why we describe lattice vibrations with a word, phonon, that suggests a particle, i.e. something like an electr**on**, prot**on**, mes**on**, phot**on**, etc.

Recall that the vibrational properties of the 2-mass coupled oscillator can be viewed in terms of two <u>independent</u> simple harmonic oscillators, one with frequency ω_{low} and one with frequency ω_{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 <u>any</u> 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 initially give the masses a bigger push or larger displacement, the energy and amplitude will be larger, but any "reasonable" value is possible.
The situation is different for the normal modes of a crystal lattice because they 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 ω, the rule is

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

where n is an integer ($n = 0, 1, 2 , \ldots$) and $\hbar$ is (Planck's constant)/2π. 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 called 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 ω 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.

2.2.2 Interaction of phonons with light – optic modes

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 an interaction or **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 near $k = 0$ is about 5 x 10^{12} Hz.

The wavelength of electromagnetic radiation of this frequency is

$$\lambda_{photon} = \frac{c}{\nu_{photon}} = \frac{3\times10^8 \, \text{m/s}}{5\times10^{12} \, \text{Hz}} = 7.5 \times 10^{-5} \, \text{m} = 75 \, \mu\text{m}$$

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.

2.2.3 Interaction of phonons with other particles – neutrons and electrons

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 (ω and $\vec{k}$) of the phonons. This is how the dispersion relation for KBr was determined.

Phonons can also interact with electrons. Phonons temporarily disrupt the symmetries of an otherwise perfect crystal. This disorder scatters electrons, limiting their motion, and is 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.

2.3   Thermal properties of solids

The lattice vibrations are usually the largest "reservoir" of thermal energy, i.e. the largest contributors to the internal energy of a solid. Phonons are therefore very important for the heat capacity of solids. In this section we will consider the contributions of phonons to the heat capacity of a solid

2.3.1 Density of states and distributions functions

The specific heat is defined at the change in energy per unit temperature:

$$C = \left. \frac{\partial E_{tot}}{\partial T} \right|_{V \, or \, P}$$

or, in different notation,

$$C = \left.\frac{\partial U}{\partial T}\right|_{V \, or \, P}.$$

Thus a calculation of the heat capacity requires that we first calculate the total energy. We can then take the derivative with respect to temperature to obtain the heat capacity.

To calculate the total energy of the system quantum particles (any quantum particles), we need three things:

(i) the spectrum of **energy states** of the system, including any degeneracies;

(ii) a **distribution function** that tells us whether a particular state contributes to the total energy of the system, *i.e.* whether the state is occupied by one or more particles;

(iii) a prescription for adding up the energies of the occupied states – a quantity called the **density of energy states**.

We will eventually discuss the energy spectrum, the distribution function, and the density of states appropriate for phonons. But first we will consider a simpler example drawn from elementary quantum mechanics, the one-dimensional infinite square well.

The infinite square well potential in 1-D.

The energy spectrum:

Solving Schrödinger's equation (PH424) for an electron in a one-dimensional infinite square well gives us the energy spectrum
$$E_n = n^2 E_0$$
where *n* is an integer, $n = 1, 2, 3, \ldots\ldots$.

Now, let's suppose that many electrons are in such a 1-D well, but they don't "know" that the other electrons are there. Stated more properly, this means that we are neglecting the electrostatic and magnetic interactions between electrons. This sounds like an unreasonable assumption, especially when we consider the strong electrostatic mutual repulsion of electrons. Surprisingly, however, this actually works pretty well for metals! The model of non-interacting electrons simply ensures that the potential energy well seen by any one electron is not modified by the presence of other electrons. We will also assume, for simplicity, that our electrons have no spin. The only rule is that an electron may not be characterized by the same quantum number as another (the Pauli Exclusion Principle). In the present example, an electron is described by one of the state functions of the 1-D well – but only one such state may be assigned to each electron. The states are assigned to the electrons using the "fairness principle" you learned about in PH423.

In a 1-D world of spin-less electrons, the electrons would then be characterized by quantum numbers 1 through 10, say, and the function that describes whether the state contributes to the total energy or not is $P_n = \begin{matrix} 1 & n \leq 10 \\ 0 & n > 10 \end{matrix}$. We will see shortly that use of this particular P_n amounts to assuming that our system is at absolute temperature $T = 0$.

Now we simply add up the energies of the occupied states:

$$E_{tot} = \sum_{n=1}^{\infty} E_n P_n = \sum_{n=1}^{10} n^2 E_0$$

This is a very easy sum to do using the formula for the sum of the squares of the first m integers:

$$\sum_{n=1}^{m} n^2 = \frac{m(m+1)(2m+1)}{6} \implies E_{tot} = E_0 \sum_{n=1}^{10} n^2 = \frac{10 \cdot 11 \cdot 21}{6} \cdot E_0 = 385 E_0$$

There are, however, many times when the sum is not so easy to perform, and it is mathematically simpler to approximate the sum by an integral. What if we approximated the previous sum by an integral? In that case, we would have

$$E_{tot} = \int_{n=0}^{\infty} E(n)P(n)dn = \int_{n=0}^{10} n^2 E_0 dn = \frac{1000}{3} E_0 = 333 E_0.$$

The integral approximation introduced an error ($333 E_0$ versus the exact result $385 E_0$), but you can convince yourself that the error becomes ever smaller as the number of states involved increases. In the spirit of the infinitesimals of calculus, e.g. dn, the approximation becomes better and better as the energy spacing between the states becomes a small fraction of the total energy involved. This is almost always the case in solids where the number of atoms (and energy states) approaches 10^{23}.

The distribution function:

The sum and integral we have been considering is not temperature dependent, because we picked a particular distribution function $P(n)$ that corresponds to $T = 0$. In general, the probability function P_n (or "occupation function" or "distribution function") is different for different temperatures. In fact, most of the temperature dependence of the total energy usually comes from this function. At $T = 0$, only the lowest available energy states are occupied, but at higher temperatures, higher energy states can be occupied, even if lower states are not. This increases the entropy of the system.

In the literature, the distribution function is usually given the symbol f, so we'll use that from now on. Its dependence on the quantum state and temperature is denoted thus: $f(n,T)$. The distribution functions most frequently encountered are shown below:

Distribution functions:

Maxwell-Boltzmann distribution function: $f_{MB}(n,T) = \exp\left(-E(n)/k_B T\right)$

Fermi-Dirac distribution function: $f_{FD}(n,T) = \dfrac{1}{\exp\left(\left[E(n) - E_F\right]/k_B T\right) + 1}$

Bose-Einstein distribution function: $f_{BE}(n,T) = \dfrac{1}{\exp\left(E(n)/k_B T\right) - 1}$

The correct choice of distribution functions depends on the system under consideration.

The Density of States:

Often, the quantum number *n* isn't a convenient counter for the quantum states. We may prefer to label states by their energy, or by their wave vector, or something else. The label doesn't matter as long as we count all the states properly. If we labeled states by their energies, could we simply write (remember we changed from *P* to *f*)

$$E_{tot} = \int_{E=0}^{\infty} E f(E,T) dE \quad ? \textbf{ NO!!!}$$

Why not? The answer is that the states are not equally distributed in energy space (not to mention that the dimensions are wrong!). We have not considered how many states might exist in a given energy interval dn. For example, consider our 1-D particle in a box for which the energy states are given by $E_n = n^2 E_0$. The allowed energies $E_0, 4E_0, 9E_0, 16E_0, 25E_0$.. become ever more widely separated as energy increases. Thus it's <u>not fair</u> to weight every energy interval *dE* the same. The correct expression is

$$E_{tot} = \int_{E=E_{lowest}}^{E_{highest}} E f(E,T) D(E) dE$$

where *D(E),* called the **density of states**, is the **number of states per unit energy interval**. Note that *D(E)* is a <u>number per unit energy interval</u>, not a spatial density. You can easily see that for this 1-dimensional case, $D(E) = \dfrac{dn}{dE}$ but this does not hold in two or more dimensions! We'll return to two and more dimensions later.