

6. LATTICE VIBRATIONS.

Aim: To study simple models for the vibrations of the atoms in crystals. We introduce new concepts, namely phonons, dispersion relations and density of states.

This lecture marks the beginning of a new part of the course. We will now be concerned with physical properties related to the atoms, and in particular to their vibrational modes. The models we will study are purely classical in the first part; only later will we introduce the quantum mechanical concept of phonons.

We will mainly consider one-dimensional, linear models. This is a good approximation in certain symmetry directions, i.e. the [100], [110] and [111] directions in cubic structures. In these directions whole planes of atoms move in phase, K p.90-91. The vibrations are called longitudinal if the displacement of the atoms is parallel to the wavevector (i.e. to the direction) of the propagating elastic wave. A transversal vibration has the wavevector orthogonal to the atomic displacements.

1. Continuum model.

We first briefly review longitudinal elastic waves in the continuum. Consider a rod with length L in equilibrium. When excited by a longitudinal wave, the instantaneous length becomes $L+u$, and a volume element dx becomes $d(x+u)$. The longitudinal oscillations are described by **the wave equation**:

$$d^2u/dt^2 = v^2 d^2u/dx^2,$$

where Y is the bulk modulus and ρ is the density. The velocity of propagation of the wave (i.e. of sound) is $v = \sqrt{Y/\rho}$. In order to solve the wave equation, we assume a plane wave solution $u \sim \exp[i(kx - \omega t)]$, from which we directly obtain by substitution $\omega = vk$. This relation between the frequency and magnitude of the wavevector is called **the dispersion relation**. The phase velocity $v_f = \omega/k$ and the group velocity $v_g = d\omega/dk$ of the wave are equal. The behaviour becomes very different when we take into account the discrete atomic structure of crystalline solids.

2. Monatomic linear chain (K p. 91-94).

Here we consider a one-dimensional lattice in the x -direction. One atom (mass M) is sitting at each lattice point, $x = (s+p)a$ (a is the lattice constant), and there is no basis. The force between any two atoms is assumed to be proportional to the difference between their displacements (**the harmonic approximation**), compare Hooke's law. The force on atom s becomes:

$$F_s = \sum_p c_p (u_{s+p} - u_s), \text{ leading to the equation of motion,}$$

$$M d^2u_s/dt^2 = \sum_p c_p (u_{s+p} - u_s).$$

Here we have summed the interactions over all atoms at $p \neq s$ in the chain. Kittel keeps only the nearest-neighbor ones. We again make a plane wave ansatz for the solution and follow the

derivation in K p. 91-92. The complete expression for **the dispersion relation** becomes (note that $c_p = c_{-p}$ by symmetry):

$$\omega^2 = (2/M) \sum_{p>0} c_p (1 - \cos(kpa)) = (4/M) \sum_{p>0} c_p \sin^2(kpa/2).$$

The relation given by Kittel follows by neglecting all $p>1$, and is illustrated in K fig. 4, p. 92. The dispersion relation is periodic in k with period $2\pi/a$. All information about the vibrations is present in the **first Brillouin zone** of the reciprocal lattice (k -space), i.e. for k -values between $-\pi/a$ and π/a . The wavelength is $2\pi/k$; hence k -values outside of these limits represent wavelengths less than $2a$. Vibrations with so short wavelengths are seen to include unphysical oscillations (nodes between the atoms), K fig.5, p. 93.

The continuum model holds only in the long wavelength limit as $k \rightarrow 0$. For large k the phase and group velocities are no longer equal. At $k = \pm\pi/a$ the group velocity is zero; we have a **standing wave**.

We consider now a linear chain with N atoms and of length $L = Na$. The finite length gives rise to a finite number of vibrational modes and hence a finite number of allowed k -values. We treat the finiteness of real crystals by the method of **periodic boundary conditions** (K p.110). In our one-dimensional case we put $u(x) = u(x+L)$. For a plane wave solution this leads to the condition $\exp(ikNa) = 1$, which is satisfied only when $k = n2\pi/Na$, with $n = 0, \pm 1, \pm 2, \pm 3, \dots, \pm(N/2-1), (N/2)$. There are N allowed k -values (modes) within the first Brillouin zone. The distance between two modes is $\Delta k = 2\pi/Na = 2\pi/L$. The number of modes per unit $|k|$ -range is the inverse of this, but multiplied with two to take into account both positive and negative k . The **density of states**, the number of modes per unit frequency range is now obtained from

$$D(\omega) d\omega = (L/\pi) (dk/d\omega) d\omega, \text{ and hence } D(\omega) = L/\pi v_g.$$

3. Diatomic linear chain (K p.95-99).

Here we consider a linear lattice with a basis of two atoms having masses M_1 and M_2 . They are positioned at $x = (s+p)a$ and $x = (s+p+1/2)a$, respectively. Their displacements are denoted u and v , respectively. Considering only nearest-neighbor interactions, the equations of motion are given by K, eq. (18), p. 97, but to the index on the v 's should be added a term $1/2$ (also in eq. (19)). The derivation is analogous to the one in Kittel. However, the final results, eq. (22)-(26) in Kittel are the same as with our notation.

The dispersion relation now exhibits two branches, one with optical modes and one with acoustic modes (K fig. 7, p. 96). The nature of the vibrations at $k=0$ is shown in Kittel, fig. 10, p. 98. The optical mode at $k=0$ has a frequency falling in the infrared range. For ionic crystals, such a transverse optical mode can be excited by infrared radiation of this frequency ω_{TO} . The acoustic branch approaches zero as $k \rightarrow 0$, in this limit it has a "velocity of sound". At $k = \pm\pi/a$, the sub-lattices vibrate independent of one another, they do not couple to one another.

This model is a good approximation for ionic crystals, A^+B^- , for waves propagating in directions where an atomic plane contains only A^+ or only B^- ions.

Link to applet showing the dispersion relation:

4. Three dimensional crystals (K p.111-112, 117-119).

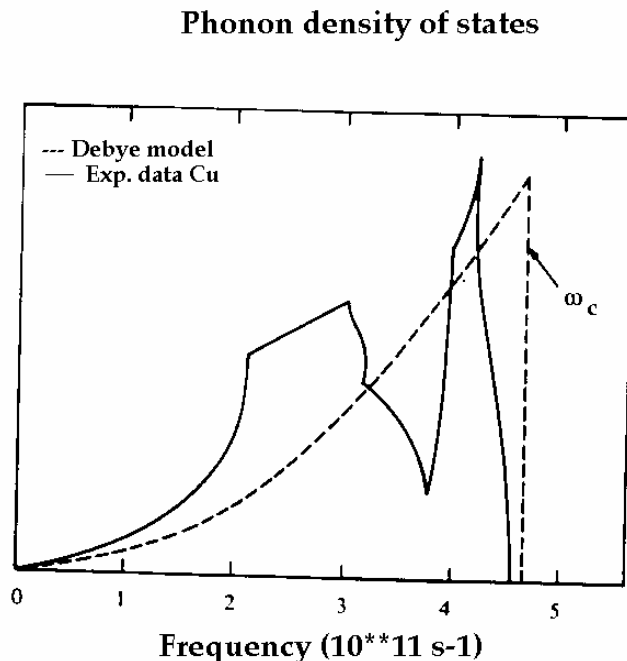
In this case each atom has three degrees of freedom. When there is no basis, there exist three (acoustic) branches, one longitudinal and two transverse ones. In the case of a basis of p atoms, there exists in total $3p$ branches of which three are acoustic and $3(p-1)$ are optic ones. Each branch contains N modes as above, where N now is the number of primitive cells.

Note that \mathbf{k} is now a vector and its allowed values are within the first Brillouin zone of the three-dimensional reciprocal lattice. In general, the dispersion relations, $\omega(\mathbf{k})$, have to be calculated numerically. They are usually depicted only in certain symmetry directions in the Brillouin zone. Some general relations for the density of states can be obtained, though.

To obtain the density of states we first apply periodic boundary conditions in x -, y - and z -directions, leading to $D(\mathbf{k})=V/8\pi^3$ for each branch of modes. We use the notation $k=|\mathbf{k}|$. We first consider the so called **Debye approximation**. We assume that the dispersion relation is $\omega = vk$ just as for a continuum, but with an upper cutoff so that the number of modes in the branch becomes N (K p.112). Hence $D(\omega) \sim \omega^2$, which follows from the spherical symmetry of the constant frequency surfaces in k -space. This approximation is reasonable in many cases.

A general expression for the density of states is expressed as an integral over a surface of constant frequency in k -space (K p. 117-119).

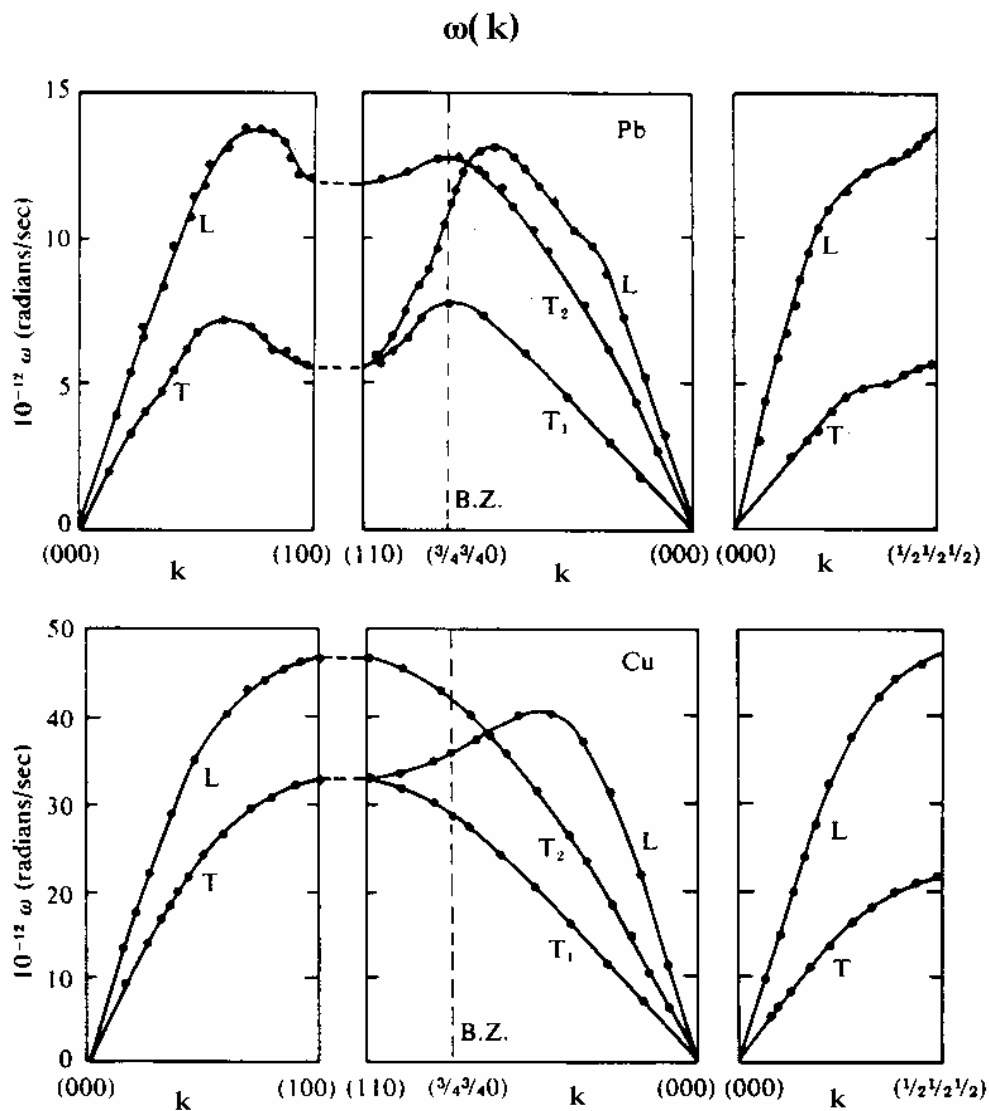
The figure below shows the experimental vibrational density of states for Cu as compared to the Debye approximation:



It is seen that the general trend is similar, but there is more structure in the experimental curve. The sharp peaks and kinks in the curve arise from points in the Brillouin zone where the group velocity is zero. They are called van Hove singularities.

The next figure depicts the dispersion relations for lead and copper, in certain symmetry direction. We observe three branches, two transverse and one longitudinal. The force constants for the transverse ones are generally lower than for the longitudinal, hence $\omega_T(k) < \omega_L(k)$. The local maxima in some of the curves are due to interactions between atoms further apart than the nearest neighbours.

Phonon dispersion curves for Pb and Cu



Oneatomic: Three branches (1 LA and 2 TA)

5. Phonons (K p. 107-110, 117-118)

The energy of the lattice vibrations is quantized. The quanta (quasiparticles) are called phonons. The energy of a vibrational mode is described with a harmonic oscillator model, K p.99. The mode can be occupied with any number, n , of phonons. The average occupancy, $\langle n \rangle$, depends on the frequency and is given by the **Planck distribution** function, K p. 107-108. The phonons are bosons and so their number is not conserved.

The phonon pseudomomentum or crystal momentum is treated in Kittel p. 100-102. The phonons are due to relative motions (vibrations) in the crystal, hence they do not impart momentum to the crystal as a whole. The phonon however acts if it has momentum $\mathbf{p} = (\hbar/2\pi)\mathbf{k}$, leading to conservation rules for the \mathbf{k} -vector in scattering processes. These conservation rules must include the reciprocal lattice vector \mathbf{G} , since scattering might lead to \mathbf{k} -values outside the first Brillouin zone and a \mathbf{G} is needed to get back to the first zone (compare diffraction where $\mathbf{k} = \mathbf{k}' + \mathbf{G}$). These are the basis of various experimental methods to study the lattice vibrations.

6. Experimental methods.

(Survey only)

a) Infrared spectroscopy.

As noted above, infrared radiation can be used to excite transversal optical (TO) phonons close to $\mathbf{k}=0$ in ionic solids. The ions in the TO branch vibrate in opposite directions and the resulting dipole moment can couple to electromagnetic radiation. Only transverse vibrations can be excited since light is a transverse wave motion. The wavelengths of infrared radiation are of the order of $10\ \mu\text{m}$, which is several orders of magnitude larger than the lattice constant, a . Hence the wavevector of the photon is very much less than π/a in magnitude and is close to $\mathbf{k}=0$ in the Brillouin zone.

We have an incoming photon (\mathbf{k}) that is absorbed and gives rise to a phonon of wavevector \mathbf{q} . The \mathbf{k} -conservation rule becomes $\mathbf{k} = \mathbf{q}$. The absorption is centred around the TO frequency and is described by the **Lorentz model**:

$$M \frac{d^2 u}{dt^2} + \gamma \frac{du}{dt} + Ku = -eE.$$

Here M is the reduced mass, γ is the damping, K is the force constant and E is the local electric field.

The infrared absorption by optical phonons has practical consequences. By Kirchhoff's law the absorption at each wavelength is equal to the thermal emittance of heat radiation at that wavelength. In certain applications a high emittance is desired, often in combination with a low absorption of solar radiation. a) The equilibrium temperature of a spacecraft needs to be quite close to room temperature due to the needs of the electronics. Surface coatings with high emittance can help to regulate the temperature of the spacecraft. b) On earth, surfaces can be cooled to 10-20 degrees below ambient temperature in dry climates, by utilizing a material with tailored infrared absorption (emission). This is sometimes a nuisance (the frost on your car window even if the temperature has been a few degrees above zero) but might also be used in certain places for simple cool storage, in building design and for promoting dew condensation.

b) Inelastic phonon scattering.

To analyse inelastic scattering we need to consider the conservation of energy and k-vector. Energy conservation gives

$$\omega = \omega_0 \pm \omega_q.$$

And k-conservation:

$$\mathbf{k} = \mathbf{k}_0 \pm \mathbf{q} + \mathbf{G}.$$

The index 0 refers to the incoming photon and q to the created or absorbed phonon. In this technique the scattering of visible laser light is commonly used. Scattering can occur from acoustic phonons (**Brillouin scattering**) or optical phonons (**Raman scattering**).

c) Inelastic neutron scattering (K p. 100-102).

The energy of thermal neutrons is of the same order as that of the phonons. This means that the energy losses during scattering are easily measurable. Measurements of the energy change and the scattering direction are used to experimentally determine the dispersion relation. Unlike the photon based techniques we are not restricted to $k \approx 0$ here. A schematic picture of a triple-axis neutron spectrometer is shown below (adapted from Myers). A monochromatic beam is obtained by Bragg diffraction from a crystal, and the beam impinges on a sample. The scattered beams are analysed in another crystal using Bragg diffraction to determine the wavelengths. The whole apparatus can be rotated around M, also the analyzer can be rotated around S and the detector around A. This is a method to get a very detailed determination of the dispersion relation

