Motion of the atoms: Lattice vibrations

- Properties of solids can be divided (roughly) into phenomena that are related to motion of the atoms (around their equilibrium position) and those determined by electrons. This division is justifiable since the motion of the nuclei is much slower (larger mass) than electron motions (e\(^{-}\) remain in ground state).

- From Heisenberg’s uncertainty principle it is clear that even at absolute zero, the atoms must vibrate around their equilibrium position (“zero point energy”).

- For many phenomena electron motion leads to transport phenomena (bands, scattering, thermoelectric effects). These are not considered here.

Lattice vibrations can explain:

- Sound velocity

**Thermal properties** such as

- Heat capacity
- Specific heat
- Thermal expansion
- Thermal conductivity (for insulators and semiconductors)

**Elastic properties** such as

- Temperature dependence of elastic constants
- Hardness

**Optical properties** such as

- Infrared absorption
Linear chain of coupled harmonic oscillators

Key assumptions:
Periodic boundary conditions
Only nearest neighbor interactions
Small displacements (harmonic oscillations: $F \sim x$, $V \sim x^2$)
Dispersion $\omega(k)$ for linear atomic chain

- $k'$ and $k$ are physically equivalent: $\bar{k}' = \bar{k} + \frac{2\pi}{a}m$ (m integer)

- Only wavelengths longer than $2a$ are needed.

- All physical information (all frequencies, group velocities) are contained in the interval of $-\frac{\pi}{a} < \bar{k} \leq \frac{\pi}{a}$

This corresponds to the first Brillouin zone!
Group velocity

From the solution it follows that the Group velocity is

\[ v_g = \frac{d\omega}{dk} = \sqrt{\frac{Ca^2}{M}} \cos \left( \frac{ka}{2} \right) \]

Note that:

1. There is a frequency maximum:

   \[ \omega = 2 \sqrt{\frac{C}{M}} \]

2. On the edge of the Brillouin zone

   \[ v_g = \frac{d\omega}{dk} = 0 \quad \text{The wave is a standing wave hence no energy is transmitted!} \]

3. Long wavelength limit:
   For \( ka << 1 \) the group velocity does not depend on \( k \).

No dispersion! The velocity of sound does not depend on frequency.
Summary last time

• We looked at lattice vibrations for a linear chain of identical masses $M$ (classically) coupled harmonically by the force constant $C$.

• The displacement can be described as a wave $u_n = Ae^{i(kna-\omega t)}$

• It is sufficient to only consider $k$-vectors in the 1st Brillouin zone.

• There are $N$ normal modes, the frequency is $\omega = a\sqrt{\frac{C}{M}}\cos\left(\frac{ka}{2}\right)$

• There is a maximum frequency:

  $\omega_{\text{max}} = 2\sqrt{\frac{C}{M}}$ at $k=\pi/a$

• The group velocity on the edge of the Brillouin zone disappears $\rightarrow$ standing waves (no transport of energy).

• For long wavelengths ($ka\ll1$ : typically sound waves) the group velocity does not depend on $k$ ("no dispersion").

  $v_g = \frac{d\omega}{dk} = \sqrt{\frac{Ca^2}{M}}\cos\left(\frac{ka}{2}\right)^{ka\ll1} \rightarrow v_g = \frac{\omega}{k} \approx a\sqrt{\frac{C}{M}} = \text{const.}$
Diatomic of coupled harmonic oscillators

Longitudinal waves

Same assumptions:
Periodic boundary conditions
Only nearest neighbor interactions
Small displacements (*harmonic oscillations*: $F \sim x$, $V \sim x^2$)

Solving the two equations of motion yields

$$
\omega^2 = C \frac{m + M}{mM} \pm C \sqrt{\left(\frac{m + M}{mM}\right)^2 - \frac{2}{mM} (1 - \cos(ka))}
$$
Lattice vibrations for diatomic chain

\[ \omega^2 = C \frac{m + M}{mM} \pm C \sqrt{ \left( \frac{m + M}{mM} \right)^2 - \frac{2}{mM} (1 - \cos(ka)) } \]

For each \( k \) value there are two values of \( \omega \). The “branches” of \( \omega(k) \)

**Nomenclature:**

The branches are referred to as “**acoustic**” and “**optical**” branches.

Only one branch behaves like sound waves (\( \omega/k \rightarrow \text{const. For } k \rightarrow 0 \)). For the optical branch the atoms are oscillating in antiphase and in an ionic crystal these charge oscillations (magnetic dipole moment) couple to electromagnetic radiation (optical waves).

**Definition:** All branches that have \( \omega \neq 0 \) at \( k=0 \) are **optical**. *This does not necessarily mean optical activity!*

What do the different branches mean? Our detailed calculation shows:
Phonons

- The energy of lattice vibrations is quantized!

- The quants of lattice vibrations are called **phonons** (similar to photons the quants of the electromagnetic field).

Experimental proof:
- Inelastic neutron scattering
  \( \Delta E \text{ and } \Delta k \) of neutrons are multiples of phonon energies.

- Energy modes of quantum harmonic oscillator:
  \[ E_n = \left(n + \frac{1}{2}\right)\hbar \omega \quad n = 0, 1, 2, \ldots \]

Consider the state of energy \( E_n \) as state with \( n \) phonons, each with energy \( \hbar \omega \)

- Phonons are bosons with spin 0. \[ \langle N_e \rangle = g_i \left(e^{\frac{E-\mu}{k_B T}} \pm 1\right)^{-1} \quad + \text{Fermi-Bose} \]

  Many quants can have same energy!
  \( g_i \) is degree of degeneracy

  \[ \rightarrow g_i e^{-\frac{(E-\mu)}{k_B T}} \quad \text{Boltzmann} \]

- Phonon number \( n \) may take any value and change with time.

**Remember:**
Why do we need phonons to explain indirect band transitions?
Experiments to determine phonon properties $\omega(k)$

I. Scattering with Neutrons

II. Scattering with electromagnetic radiation (visible light):

If you would scatter with E&M radiation, which wavelength do you suggest?
What do you think of inelastic X-ray scattering for determining $\omega(k)$?

- Brillouin scattering (off acoustic phonons)
- Raman scattering (off optical phonons)

Which part of $\omega(k)$ can one determine?

III. Direct absorption of E&M radiation

Which wavelength would you use?
Experiments in real materials

Theory

our (simple) model for diatomic base

\[ \left( \frac{1}{M_1} + \frac{1}{M_2} \right)^{1/2} \]

Optical phonon branch

\[ \frac{(2G/M_1)^{1/2}}{a} \]

Acoustical phonon branch

\[ \frac{\pi}{a} \]

General case in 3D:

- \( p \) atoms/unit cell
- We expect 3 acoustic and 3(p-1) optical branches.
- What do we find experimentally?

Experiments: 1. Neutron scattering

Neutrons excite lattice vibrations: measure \( \Delta E \) and \( \Delta k \) of neutrons (transfer to crystal)

Ge [111] direction, T=80K

KBr in [111] direction, 90K

Expect 3 acoust. & 3 opt. Branches

Some branches are degenerated!
More experiments

2. Raman scattering

![Raman scattering diagram](image)