Crystal Vibrations

Physics
Univ. of Central Florida

Outlines
1. Vibrations of crystals with monatomic basis
2. Two atoms per primitive basis
3. Quantization of elastic waves
4. Phonon momentum
5. Inelastic scattering by phonons

In Units 2,3&4 we discuss lattice structures and binding of atoms. Those are zero temperature properties. Now we want to know what happen when \( T > 0 \). We can see that at finite temperature, the atoms will vibrate. The attractive force in a crystal can be described by the spring-mass system. So the lattice vibration can be treated as a 3D network of springs connected all atoms together. The use of the spring-mass system (SHO model) can be justified by looking at the potential between two atoms inside a crystal.

For each wave-vector, there are three modes, one longitudinal and two transverse. Assume that there is no net force on atom \( S \) when all atoms are at the equilibrium position. So the net force on S-atom is

\[
F_s = \sum_p C_p (u_{s+p} - u_s) \quad (p \text{ can be positive or negative})
\]

where \( u \) is the deviation from equilibrium position

\[
F_s = m \frac{d^2 u_s}{dt^2} = \sum_p C_p (u_{s+p} - u_s)
\]

Assume \( u_s \propto e^{-i\omega t} \)

\[-m\omega^2 u_s = \sum_p C_p (u_{s+p} - u_s) \quad \text{Eq. (1)}\]

Assume only the nearest neighbor interactions

\[-m\omega^2 u_s = C_1 (u_{s+1} - u_s) + C_{-1} (u_{s-1} - u_s)\]

Let \( C_1 = C_{-1} \)

\[-m\omega^2 u_s = C (u_{s+1} + u_{s-1} - 2u_s) \quad \text{Eq. (2)}\]

This equation has a solution of the form

\[u_s = \mathbf{u} \cdot e^{i(k \cdot d)} \quad \text{Eq. (3)}\]

This comes from the Bloch theorem, namely the solution that satisfies the Schrödinger equation must have this form

\[
\psi_S (r) = e^{i(k \cdot r)} u_k (r)
\]

Where \( u_k (r) \) has the periodicity of the lattice.

\[u_k (r) = u_k (r + \mathbf{d})\]
Now substitute eq. (3) into (2),

\[-m\omega^2 u_0 = C[e^{ik_a} + e^{-ik_a} - 2]u_0\]

\[\omega^2 = \frac{2C}{m}[1 - \cos ka] = \frac{4C}{m} \sin^2 \left(\frac{ka}{2}\right)\]

\[\omega = \sqrt{\frac{4C}{m} \sin^2 \left(\frac{ka}{2}\right)}\]

Eq. (4)

Comments on the previous figure.

1. \(\omega\) vs. \(k\) relationship is called dispersion relation.
2. In our current case, \(\omega \ll k\) for \(k \to 0\). Since lattice vibration is just sound wave in solid. \(\omega = V_s k\), where \(V_s\) is the velocity of the sound. We can see that as \(k \to 0\), \(V_s = \text{constant}\).
3. Since the curve repeats itself for large \(k\). Usually we only defined the dispersion curve in the 1st Brillouin zone.
4. At the zone boundary, \(\omega = 0\). The slope is the group velocity of the sound wave. The group velocity at zone boundary is zero. (Standing wave, no energy transmitted).
5. In general, if more than nearest neighbor planes are involved,

\[\omega^2 = \frac{2}{m} \sum_{l \neq 0} C_p(1 - \cos pk_a)\]

(5)

First Brillouin Zone

Here we want to argue that the range of \(K\) that is meaningful is within \(-\frac{\pi}{a} < K \leq \frac{\pi}{a}\), as shown on p7. This situation is similar to the real lattice structure where Wigner-Seitz cell contains all necessary information. In reciprocal space, all the useful information contains in the First Brillouin zone (which is W-S cell in the \(k\)-space).

For example, when we look at the ratio of lattice displacement,

\[\frac{u_{n+1}}{u_n} = e^{(k_{n+1} - k_n)a} = e^{\Delta k a}\]

Since \(e^{2\pi n} = 1\), we can write the eq. as

\[\frac{u_{n+1}}{u_n} = e^{(k_{n+1} - k_n)a} = e^{\Delta k a}\]

where \(k' = k + n \cdot \frac{2\pi}{a}\)

What does that means?

See figure 4.

At the boundary, \(K_{\text{max}} = \pm \frac{\pi}{a}\), the vibration is not a traveling wave any more, it becomes a standing wave and does not transmit energy or information.

See figure 5

Group velocity and long wavelength limit

We learned in E&M that the group velocity of a wave packet is given by

\[v_g = \frac{d\omega}{dK} \quad \text{1D} \quad \text{v}_g = \nabla_k \omega(K) \quad \text{3D}\]

So if we use the dispersion relation on p7, we end up with

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

At zone boundary, no transmission. For small wavevector,

\[\omega = \sqrt{\frac{Ca}{M}Ka}\]

Derivation of Force constant

From the previous equation, we can derive the force constant from experiment. In metal, because of the conduction electrons, the interaction range is quite long, sometimes, as many as twenty layers need to be taken into account. We solve the previous equation for \(C_p\) by times both sides by \(\cos(qka)\) and integrate over \(k\).

\[\int_{-\pi/a}^{\pi/a} \frac{\omega^2 \cos(qka)dk}{a^2} = 2 \sum_{l \neq 0} \int_{-\pi/a}^{\pi/a} (1 - \cos(pka)) \cos(qka)dk\]

\[-2\pi \frac{C_l}{a} = \frac{ma}{2\pi} \int_{-\pi/a}^{\pi/a} \omega^2 \cos(pka)dk\]

(6)
Two atoms per primitive basis

When we have two atoms per primitive cell, each polarization will have two branches, acoustical, and optical.

For p atoms per primitive cell, we have 3 acoustical polarization, and (3p-3) optical polarization.

Assume atoms only have nearest neighbor interaction:

\[ \frac{d^2u_1}{dt^2} = C(v_1 - u_1) \quad (7.1) \]
\[ \frac{d^2v_1}{dt^2} = C(u_{s+1} + u_s - 2V_s) \quad (7.2) \]

From the Bloch theorem

\[ u_s = u_0 e^{i k_0 a} e^{-i \omega t} \quad (8.1) \]
\[ v_s = v_0 e^{i k_0 a} e^{-i \omega t} \quad (8.2) \]

where \( a \) is the distance between identical atoms (see p10).

Substitute (8.1, 8.2) into (7.1, 7.2), we end up with

\[ -\omega^2 m_1 u_0 = Cv_0 (1 + e^{-ika}) - 2Cu_0 \]
\[ -\omega^2 m_2 v_0 = Cu_0 (1 + e^{ika}) - 2Cv_0 \]

A non-trivial solution exists only when the determinant is equal to zero.

It reduces into

\[ m_1 m_2 \omega^4 - 2C(m_1 + m_2) \omega^2 + 2C^2 (1 - \cos ka) = 0 \quad (10) \]

For \( ka \ll 1 \)

\[ \cos ka \equiv 1 - \frac{1}{2} (ka)^2 \]

\[ \omega^4 - 2C \frac{m_1 + m_2}{m_1 m_2} \omega^2 + \frac{C^2 k^2 a^2}{m_1 m_2} = 0 \]

\[ \omega^2 = \frac{2C}{m_1} \quad \text{or} \quad \omega^2 = \frac{2C}{m_2} \]

So the dispersion relation

The optical mode and acoustic mode of lattice vibration shown in real space.

For the same momentum, optical mode carries much more energy than the acoustic mode.

Special cases

(1) If \( m_1 \to \infty \)

\( m_1 \) is always fixed in space. This implies standing wave and no energy transmitted. The system only oscillates at one frequency.

Einstein model of solid
(2) If \( m_2 \to 0 \)

Optical mode will disappear. The dispersion relation goes back to the one atom model.

(3) If \( m_1 \to m_2 \)

Band gap gradually disappears and lattice goes back to monatomic lattice. The lattice spacing changes from \( a \) to \( a/2 \).

(4) In general when \( m_1 \neq m_2 \), we have an energy gap, which means no vibration can exist in this gap. This is called forbidden gap.

(5) If there is no lattice, \( (a \to 0) \), we end up with continuum model and recover the classical sound wave in air.

**Examples of experimental phonon dispersion relation**

**Quantization of lattice vibration**

The energy of the lattice vibration can be quantized. The quantum of energy is called phonon similar to photon in the E&M theory. From the SHO model, we described previously, we can see that

\[
\epsilon = \left( n + \frac{1}{2} \right) \hbar \omega
\]

This can be derived from the Hamiltonian of the system

\[
H = \sum_{k=1}^{n} \left( \frac{1}{2Mk} P_k^2 + \frac{1}{2} C (Q_k+Q_{k+1})^2 \right) \quad \text{(wave)}
\]

It can be shown that the above \( H \) can be transform into

\[
H = \sum_{k} \left\{ \frac{1}{2M} P_k^2 - \frac{1}{2} M \omega_0^2 Q_k Q_{-k} \right\} \quad \text{(Phonon)}
\]

**Phonon satisfies the Bose-Einstein statistics, where**

\[
\langle n_k \rangle = \frac{1}{e^{\beta \omega_k} - 1} \quad \text{and} \quad \langle e_k \rangle = \frac{\hbar \omega_k}{e^{\beta \omega_k} - 1}
\]

If we let \( u = u_0 \cdot \cos kx \cdot \cos \omega t \)

The kinetic energy density of the crystal is

\[
\frac{1}{2} \rho \left( \frac{\partial u_0}{\partial t} \right)^2 = \frac{1}{8} \rho V \omega^2 u_0^2 = \frac{1}{2} \left( n + \frac{1}{2} \right) \hbar \omega
\]

Which equal to \( \frac{3}{8} \) of the total energy of SHO

\[
u_0^2 = \frac{4 \left( n + \frac{1}{2} \right)^2}{\rho V \omega}
\]

**Phonon momentum**

Phonons satisfy Bose-Einstein statistics and the dispersion relation is similar to photon

\[
\omega = c k
\]

where \( \hbar \omega \) is the phonon momentum, and \( c \) is the speed of phonon.

A phonon can interact with photons, neutrons, or electrons, but the phonon momentum is not exactly like a “physical momentum” of a mass particle.

Phonon momentum involves relative coordinates, so the net physical momentum is zero, except for the \( K = 0 \) mode.


\[ \vec{F} = h \vec{k} = \sum_m \frac{d}{dt} \left( \sum_s u_s \right) = m \frac{d}{dt} \left( \sum_s \exp(i\vec{k}\cdot\vec{s}) \right) \quad (\text{Bloch theorem}) \]

Since \( \exp(i\vec{k}\cdot\vec{s}) = \exp(i\vec{k}\cdot\vec{s} + \vec{\Delta}) = 1 \)

\[ \vec{F} = 0 \quad (\text{Physical Momentum equal to zero.}) \]

We can see that for every \( \vec{k} \) phonon, there exists a \(-\vec{k}\) phonon inside the solid, such that the net physical momentum is equal to zero. (Except for the \( \vec{k} = 0 \) mode, which corresponds to the translation of the center of the mass.

Elastic scattering of X-ray (Bragg scattering)

\[ \vec{k}' = \vec{k} + \vec{\Delta} \]

\( \vec{k} \) is the wavevector of the incident photon, \( \vec{k}' \) is the wavevector of the scattered photon. The crystal recoils as a whole by \(-h\vec{\Delta}\).

Inelastic scattering

1. A phonon is created.
\[ \vec{k} + \vec{\Delta} = \vec{k}' + \vec{K} \]

2. A phonon is destroyed
\[ \vec{k} + \vec{\Delta} = \vec{k}' - \vec{K} \]

Why neutron scattering is a very important tool in the investigation of phonon spectrum?

Wavelength of a phonon ~ order of lattice constant ~ 1Å
Energy of a phonon ~ \( 10^{-1} \) to \( 10^{-2} \) eV

\[ h\omega = h \cdot v \cdot k = 1.054 \cdot 10^{-34} \cdot 3000 \cdot 6 \cdot 10^{10} / 1.6 \cdot 10^{-19} = 0.12 \text{ eV} \]

For photon with \( \lambda = 1 \sim 10 \text{ Å} \), energy \( \sim 10^4 \sim 10^3 \text{ eV} \)

The change in energy for photon is too small to observed. If we use infrared the energy is ok but the wavelength is too large as compared to lattice constant.

The infrared can only probe a very small portion of the dispersion relation curve.