Crystal Vibrations

Vibrations of atoms in a crystal give us waves (sound waves). This lecture studies these sound waves.

Model: consider atoms as points (sites) and consider a crystal as points connected by springs.

### 3.1. Vibrations of crystals with monotonic basis

#### 3.1.1. Displacement and Force

Consider a 1D crystal with one atom per unit cell. Here we label the sites (atoms) using an integer \(s = 1, 2, \ldots, N\).

Displacement of site \(s\): how far the site moves away from its equilibrium position: \(u_s = R_s - R_s^{(0)}\) where \(R_s\) is the position of the site \(s\) and \(R_s^{(0)}\) is the equilibrium position.

Force on site \(s\): \(F_s = C(u_{s+1} - u_s) + C(u_s - u_{s-1}) = C(u_{s+1} + u_{s-1} - 2u_s)\) (3.1)

Here we assume each spring follows the Hooke’s law and \(C\) is the spring constant \(F = C \Delta L\) (assuming higher order terms are small).

#### 3.1.2. Equation of motion

\[
m \frac{d^2 u_s}{dt^2} = F_s = C(u_{s+1} - u_s) + C(u_s - u_{s-1}) = C(u_{s+1} + u_{s-1} - 2u_s)
\]

(3.2)

#### 3.1.3. Sound waves

To solve this equation, we consider a plane wave:

\[u_s = u \exp(i K s a) \exp(-i \omega t)\] (3.3)

This \(u_s\) is complex and the real part of it is the true displacement.

Here the amplitude of this wave is \(u\). The wavevector is \(K = 2\pi / \lambda\). \(a\) is the lattice constant. The frequency of this wave is \(\omega\). For this wave, the equation of motion turns into

\[-m \omega^2 u \exp(i K s a) \exp(-i \omega t) = C[\exp(i K a) + \exp(-i K a) - 2] u \exp(i K s a) \exp(-i \omega t)\] (3.4)
Here we used the following relations:

\[ u_s = u \exp(i K a) \exp(-i \omega t) \]  
\[ u_{s+1} = u \exp(i K (s + 1) a) \exp(-i \omega t) = u \exp(i K s a) \exp(-i \omega t) \exp(i K a) \]  
\[ u_{s-1} = u \exp(i K (s - 1) a) \exp(-i \omega t) = u \exp(i K s a) \exp(-i \omega t) \exp(-i K a) \]  
\[ \frac{d^2 u_s}{dt^2} = u \exp(i K s a) \frac{d^2}{dt^2} \exp(-i \omega t) = -\omega^2 u \exp(i K s a) \exp(-i \omega t) \]

We can simplify the EOM:

\[ -m \omega^2 = C \{ \exp(i K a) + \exp(-i K a) - 2 \} = 2 \{ \cos(K a) - 1 \} \]

So

\[ \omega^2 = \frac{2}{m} - [1 - \cos(K a)] \]

and thus

\[ \omega = 2 \sqrt{\frac{C}{m}} \sqrt{\frac{1 - \cos(K a)}{2}} \]

Using the trigonometric identity \( \sqrt{\frac{1 - \cos a}{2}} = | \sin \frac{a}{2} | \)

\[ \omega = 2 \sqrt{\frac{C}{m}} | \sin \frac{K a}{2} | \]

Fig. 2. \( \omega \) as a function of \( K \).

### 3.1.4. the long wave length limit

At small momentum (very small \( K, K a << 1 \)), \( \sin \frac{K a}{2} = \frac{K a}{2} + O\left(\frac{(K a)^2}{2}\right) \), so

\[ \omega \approx a \sqrt{\frac{C}{m}} \]

This limit is known as “the long wavelength limit”, becomes small \( K \) means very large wavelength (\( \lambda = 2 \pi / K \to \infty \) when \( K \to 0 \))
Here, the frequency is a linear function of the wavevector and at \( K = 0, \omega = 0 \). This type of sound waves with \( \omega \propto K \) are known as “acoustic sounds”.

For an acoustic sound mode, the relation between \( \omega \) and \( K \) is very similar to the corresponding relation for light. For light, we have \( \omega = c K \) where \( c \) is the speed of light. Here, we have \( \omega = v K \) where \( v = a \sqrt{C/m} \) is the speed of this sound wave.

### 3.1.5. The continuum limit

If we set the lattice spacing to be very small (\( a \to 0 \)), when this lattice model should recover the continuum limit. Here, the continuum limit is the same as the long wave length limit, because both these two limit have \( k a \ll 1 \), so

\[
\omega = 2 \sqrt{\frac{C}{m}} \left| \sin \frac{K a}{2} \right| \approx a \sqrt{\frac{C}{m}} K
\]  \( \text{(3.14)} \)

### 3.1.6. Brillouin zone boundary \( K = \pi / a \)

At \( K = \pi / a \)

\[
u_s = u \exp(i K s a) \exp(-i \omega t) = u \exp(i \pi s) \exp(-i \omega t) = (-1)^s u \exp(-i \omega t)
\]  \( \text{(3.15)} \)

This is a standing wave, where even sites and odd sites move in the opposite way.

### 3.2. Quantization of sound waves

Quantum mechanics tells us that for a wave with frequency \( \omega \) and wavevector \( k \), we can consider it as a beam of particles with energy \( E = h \omega \) and momentum \( P = h K \).

For EM waves (light), the corresponding particles are photons.

For sound waves, the corresponding particles are called "phonons".

The energy of a phone is \( E =h \omega \) and we know that

\[
E = 2 \hbar \sqrt{\frac{C}{m}} \left| \sin \frac{P a}{2 \hbar} \right|
\]  \( \text{(3.16)} \)

At small momentum (very small \( P, P a / 2 \hbar \ll 1 \)), we have

\[
E = a \sqrt{\frac{C}{m}} P
\]  \( \text{(3.17)} \)

### 3.3. Sound velocities: phase velocity and group velocity

#### 3.3.1. Phase velocity

The phase velocity of a wave is

\[
\nu_p = \frac{\omega}{K}
\]  \( \text{(3.18)} \)

For this sound wave, \( \omega = 2 \sqrt{\frac{C}{m}} \left| \sin \frac{K a}{2} \right| \), so we have

\[
\nu_p = \frac{\omega}{K} = 2 \sqrt{\frac{C}{m}} \left| \sin \frac{K a}{2} \right| K
\]  \( \text{(3.19)} \)

at small \( K \) (the long wavelength limit).
\[ v_p = \omega K = 2 \sqrt{\frac{C}{m} \sin \frac{K a}{2}} = 2 \sqrt{\frac{C}{m} K} = \sqrt{\frac{C}{m} a} \] (3.20)

### 3.3.2. Group velocity

The group velocity measures the velocity of a wave packet. It is defined as:

\[ v_g = \frac{d \omega}{d K} \] (3.21)

For this sound wave, \( \omega = 2 \sqrt{\frac{C}{m} \sin \frac{K a}{2}} \). For the first Brillouin zone \((-\pi/a < K < \pi/a)\), \( \omega = 2 \sqrt{\frac{C}{m} \sin \frac{K a}{2}} \), because in this region \( \sin \frac{K a}{2} \geq 0 \)

\[ v_g = \frac{d \omega}{d K} = 2 \sqrt{\frac{C}{m} \sin \frac{K a}{2}} = \frac{a C}{m} \cos \frac{K a}{2} = \sqrt{\frac{C}{m} a} \] (3.22)

At small \( K \) (the long wavelength limit), \( v_g \approx v_p \)

\[ v_g = a \sqrt{\frac{C}{m} \cos \frac{K a}{2}} = a \sqrt{\frac{C}{m}} \] (3.23)

which is the same as \( v_p \) at small \( K \)

At the edge of the Brillouin zone, \( K = \pi/a, \)

\[ v_g = a \sqrt{\frac{C}{m} \cos \frac{\pi}{2}} = 0 \] (3.24)

Zero group velocity means that there is no energy flow. As discussed above, \( K = \pi/a \) has a standing wave, which indeed has no energy flow.

### 3.4. two atoms per primitive basis

![Fig. 3. A 1D crystal formed by two different types of atoms](image)

**3.4.1. Equations of motion**

Two types of atoms, ABABABABAB...

- Use an integer \( s \) to label each unit cell (each unit cell contains two atoms: 1 A atom and 1 B atom)
- Use \( u_i \) to describe the displacement of A atoms
- Use \( v_j \) to describe the displacement of B atoms

The equations of motion is
\[
M_1 \frac{d^2 u_i}{dt^2} = F_S = C(\nu_i - u_i) + C(\nu_{i-1} - u_i) = C(\nu_i + \nu_{i-1} - 2u_i) \tag{3.25}
\]
\[
M_2 \frac{d^2 v_i}{dt^2} = F_S = C(u_{i+1} - v_i) + C(u_i - v_i) = C(u_{i+1} + u_i - 2v_i) \tag{3.26}
\]
Here \( M_1 \) and \( M_2 \) are the masses for atoms A and B respectively.

So we have
\[
M_1 \frac{d^2 u_i}{dt^2} = C(\nu_i + \nu_{i-1} - 2u_i) \tag{3.27}
\]
\[
M_2 \frac{d^2 v_i}{dt^2} = C(u_{i+1} + u_i - 2v_i) \tag{3.28}
\]

### 3.4.2. Sound wave solutions

Let’s consider sound waves
\[
u_i = u \exp(i ka) \exp(-i \omega t) \tag{3.29}
\]
\[
v_i = v \exp(i ka) \exp(-i \omega t) \tag{3.30}
\]
Here, \( a \) is the lattice constant (the size of a unit cell. NOT the distance between neighboring A and B atoms).

Now, the EOM will take the form
\[
-M_1 \omega^2 u \exp(i ka) \exp(-i \omega t) = C(\nu_i + \nu_{i-1} e^{-iKa} - 2u) \exp(i ka) \exp(-i \omega t) \tag{3.31}
\]
\[
-M_2 \omega^2 v \exp(i ka) \exp(-i \omega t) = C(u_{i+1} e^{iKa} + u_i - 2v) \exp(i ka) \exp(-i \omega t) \tag{3.32}
\]

So
\[
M_1 \omega^2 u = -C(\nu + v e^{-iKa} - 2u) \tag{3.33}
\]
\[
M_2 \omega^2 v = -C(u e^{iKa} + u - 2v) \tag{3.34}
\]

So
\[
(M_1 \omega^2 - 2C) u + C(1 + e^{-iKa}) v = 0 \tag{3.35}
\]
\[
C(e^{iKa} + 1) u + (M_2 \omega^2 - 2C) v = 0 \tag{3.36}
\]

We can write these two equations into a matrix form
\[
\begin{pmatrix}
M_1 \omega^2 - 2C & C(1 + e^{-iKa}) \\
C(e^{iKa} + 1) & M_2 \omega^2 - 2C
\end{pmatrix}
\begin{pmatrix}
u \\
v
\end{pmatrix}
= \begin{pmatrix} 0 \\
0
\end{pmatrix} \tag{3.37}
\]

where \( u \) and \( v \) are the two unknowns for these two equations.

For this type of linear equations, to have nontrivial solution (\( u \) and \( v \) being nonzero), we must have
\[
\det\begin{pmatrix}
M_1 \omega^2 - 2C & C(1 + e^{-iKa}) \\
C(e^{iKa} + 1) & M_2 \omega^2 - 2C
\end{pmatrix} = 0 \tag{3.38}
\]

This condition give us a relation between \( \omega \) and \( K \)
\[
\det\begin{pmatrix}
M_1 \omega^2 - 2C & C(1 + e^{-iKa}) \\
C(e^{iKa} + 1) & M_2 \omega^2 - 2C
\end{pmatrix} = (M_1 \omega^2 - 2C)(M_2 \omega^2 - 2C) - C^2(1 + e^{-iKa})(e^{iKa} + 1) =
\]
\[
(M_1 M_2 \omega^2 + 4C^2 - 2C M_1 \omega^2 - 2C M_2 \omega^2) - C^2(2 + e^{-iKa} + e^{iKa}) =
\]
\[
(M_1 M_2 \omega^2 + 4C^2 - 2C M_1 \omega^2 - 2C M_2 \omega^2) - 2C^2(1 + \cos K a) = 0 \tag{3.39}
\]

So
\[ M_1 M_2 \omega^3 - (2C M_1 + 2CM_2) \omega^2 + 2C^2 (1 - \cos K a) = 0 \]  

(3.40)

The solution to this equation is:

\[
\omega^2 = \frac{2C M_1 + 2CM_2 \pm \sqrt{(2C M_1 + 2CM_2)^2 - 8M_1 M_2 C^2 (1 - \cos K a)}}{2M_1 M_2} = \frac{C M_1 + C M_2 \pm \sqrt{(C M_1 + C M_2)^2 - 2M_1 M_2 C^2 (1 - \cos K a)}}{M_1 M_2} 
\]

(3.41)

where the “+” solution is known as the optical branch and the “-” one is known as the acoustic branch.

![Diagram](image.png)

Fig. 4. \( \omega \) as a function of \( K \). Notice that there are two branches of solutions. The low branch is called acoustic branch and the upper one is the optical branch.

### 3.4.3. the long wave length limit \((K \approx 0)\)

In the long wave length limit (or the continuum limit), where \( K a \ll 1 \), we can set \( \cos K a = 1 \) for the optical branch

\[
\omega^2 = \frac{C M_1 + C M_2 + \sqrt{(C M_1 + C M_2)^2}}{M_1 M_2} = \frac{2C M_1 + 2CM_2}{M_1 M_2} = 2 \left( \frac{1}{M_1} + \frac{1}{M_2} \right) 
\]

(3.42)

For the acoustic branch, setting \( \cos K a = 1 \) will give us \( \omega^2 = 0 \), which is not good enough. So we need to keep higher order terms here and set \( \cos K a = 1 - (K a)^2 / 2 \). Then we have,

\[
\omega^2 = \frac{C M_1 + C M_2 - \sqrt{(C M_1 + C M_2)^2 - M_1 M_2 C^2 K^2 a^2}}{M_1 M_2} = \frac{C M_1 + C M_2}{M_1 M_2} \left( 1 - \frac{M_1 M_2 C^2 K^2 a^2}{(C M_1 + C M_2)^2} \right) = \frac{C M_1 + C M_2}{M_1 M_2} \left( 1 - \frac{1}{2} \frac{M_1 M_2 C^2 K^2 a^2}{(C M_1 + C M_2)^2} \right)
\]

(3.43)

So

\[
\omega = \sqrt{\frac{1 - \frac{C}{2 \frac{M_1 M_2}{a}} K}{K}} 
\]

(3.44)

The acoustic mode has \( \omega \propto K \), so we have \( \omega = 0 \) at \( K = 0 \). But the optical mode has finite \( \omega \) at \( K = 0 \).
3.4.4. the edge of the zone \( K = \pi / a \)
At zone edge \( K = \pi / a \), \( \cos K a = -1 \)
\[
\omega^2 = \frac{C M_1 + C M_2 \pm \sqrt{(C M_1 + C M_2)^2 - 4 M_1 M_2 C^2}}{M_1 M_2} = \frac{C M_1 + C M_2 \pm \sqrt{(C M_1 - C M_2)^2}}{M_1 M_2} = \frac{C M_1 + C M_2 \pm (C M_1 - C M_2)}{M_1 M_2}
\] (3.45)

So,
\[
\omega^2 = 2 \frac{C}{M_1} \quad \text{or} \quad \omega^2 = 2 \frac{C}{M_2}
\] (3.46)

Here, one of the modes only involves the motion of A atoms (with mass \( M_1 \)) and the other mode only involves the motion of the B atoms (with mass \( M_2 \)).

3.4.5. Energy gap
Notice that between the acoustic and optical branches, there is a range of frequency which cannot be reached, regardless of the momentum \( K \) (the equation has no solution). This range is called an “energy gap”.

3.4.6. Questions: Why at \( K = \pi / a \), the frequency of the acoustic phonon mode only relies on \( M_1 \), but is independent of \( M_2 \). For the optical phonon model, why it frequency only depends on \( M_2 \) but not \( M_1 \) at \( K = \pi / a \)?
Answer: at \( K = \pi / a \), for the acoustic mode, only atoms with mass \( M_1 \) moves. For the optical modes only atoms with mass \( M_2 \) moves.

3.5. Longitudinal and transverse phonon modes

In higher dimensions, the deformation \( u_s \) becomes a vector \( \bar{u}_s \) and the wavevector \( K \) becomes a vector \( \bar{K} \). Depending on the angle between \( \bar{u} \) and \( \bar{K} \), we can distinguish two different types of sound waves:

Longitudinal modes: \( \bar{u} \) is parallel to \( \bar{K} \)

Transverse modes: \( \bar{u} \) is perpendicular to \( \bar{K} \)

In a \( D \)-dimensional space, there will be 1 longitudinal acoustic branch and \( D-1 \) transverse acoustic branches.
3.6. Number of phonon modes

For a lattice with \( n \) atoms per unit cell, there are \((n - 1) d\) optical phonons and \(d\) acoustic phonon modes.

For these \(d\) acoustic phonon modes, one of them is longitudinal and the other \(d - 1\) modes are transverse acoustic modes.

In each unit cell (\(n\) atoms per unit cell), there are \(nd\) degrees of freedom, this number matches the number of phonon modes (acoustic+optical).