Lecture 8 - Crystal Vibrations

**Outline**

- Vibrations of atoms in crystals
- Normal modes of harmonic crystal - exact solution of the problem of an infinite number of coupled oscillators with a few lines of algebra
- Relation to sound waves for long wavelength
- Role of Brillouin Zone - relation to Bragg Diffraction
- Quantization and Phonons

(Read Kittel Ch 4)

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### Phonons I - Crystal Vibrations (Kittel Ch. 4)

**Vibration of atoms in a linear chain**

Consider atoms in a line restricted to move along the line

- Equilibrium positions: \( R_n^0 = n a \)
- Displacements: \( \Delta R_n = u_n a \)

Plot of displacements \( u \)

\[
\begin{array}{cccccccccccc}
\text{un-3} & \text{un-2} & \text{un-1} & \text{un} & \text{un+1} & \text{un+2} & \text{un+3} & \text{un+4} & \text{un+5} & \text{un+6} \\
\end{array}
\]

More later on this

**Energy due to Displacements**

- The energy of the crystal changes if the atoms are displaced.
- Analogous to springs between the atoms
- Suppose there is a spring between each pair of atoms in the chain. For each spring the change in energy is:

\[
\Delta E = \frac{1}{2} C (u_{n+1} - u_n)^2
\]

- Note: There are no linear terms if we consider small changes \( u \) from the equilibrium positions

**Force due to Displacements**

- The force on atom \( n \) is due to the two springs on the right and left sides of the atom

\[
F_n = C \left[ (u_{n+1} - u_n) - (u_n - u_{n-1}) \right]
= C \left[ u_{n+1} + u_{n-1} - 2 u_n \right]
\]

- The right spring is compressed more than the left one. Thus the force on atom \( n \) is to the left

- Note: For simplicity we consider only springs connecting nearest neighbors -- in general there can be interactions with more distant neighbors

**Oscillations of linear chain**

- Newton's Law:

\[
M \frac{d^2 u_n}{dt^2} = F_n = C \left[ u_{n+1} + u_{n-1} - 2 u_n \right]
\]

- Time dependence: Let \( u_n(t) = u_n \exp(-i \omega t) \)

### More on this

(sin(\omega t)) or cos(\omega t) are also correct but harder to use

Then

\[
M \omega^2 u_n = C \left[ u_{n+1} + u_{n-1} - 2 u_n \right]
\]

- How to solve? Looks complicated - an infinite number of coupled oscillators!
Lecture 8 - Crystal Vibrations

Oscillations of linear chain

- Since the equation is the same at each atom i, the solution must have the same form at each i differing only by a phase factor. This is most easily written
  \[ u_n = u \exp(i k n a) \]
- Then
  \[ M \omega^2 u = C [\exp(ika) + \exp(-ika) - 2] u \]
  or
  \[ \omega^2 = \left( \frac{C}{M} \right) [2 \cos(ka) - 2] \]

- A more convenient form is
  \[ \omega^2 = \left( \frac{C}{M} \right) [2 \cos(ka) - 2] = 4 \left( \frac{C}{M} \right) \sin^2(ka/2) \]
  (using \( \cos(x) = \cos(x/2) - \sin^2(x/2) = 1 - 2 \sin^2(x/2) \))
- Finally:
  \[ \omega = 2 \left( \frac{C}{M} \right)^{1/2} |\sin(ka/2)| \]

Brillouin Zone

- Consider k ranging over all reciprocal space. The expression for \( \omega_k \) is periodic
  \[ \omega_k = 2 \left( \frac{C}{M} \right)^{1/2} |\sin(ka/2)| \]
- All the information is in the first Brillouin Zone - the rest is repeated with periodicity 2\( \pi/a \) - that is, the frequencies are the same for \( \omega_k \) and \( \omega_{k+G} \) where G is any reciprocal lattice vector \( G = \) integer times 2\( \pi/a \)
- What does this mean?

Meaning of Periodicity in Reciprocal space

- In fact the motion of atoms with wavevector k is identical to the motion with wavevector \( k + G \)
- All independent vibrations are described by k inside BZ

Meaning of Periodicity in Reciprocal space -- II

- This is a general result valid in all crystals in all dimensions (more later on 2 and 3 dimensions)
- The vibrations are an example of excitations. The atoms are not in their lowest energy positions but are vibrating.
- The excitations are labeled by a wavevector k and are periodic functions of k in reciprocal space.
- All the excitations are counted if one considers only k inside the Brillouin zone (BZ). The excitations for k outside the BZ are identical to those inside and are not independent excitations.
**Group velocity of vibration wave**
- The wave $u_n = u \exp(ik(na) - i\omega t)$ is a traveling wave.
- Group velocity $v_k = d\omega_k / dk = \text{slope of } \omega_k \text{ vs } k$

\[\omega_k = 2 \left( \frac{C}{M} \right)^{1/2} \sin \left( \frac{ka}{2} \right)\]

**Sound Velocity**
- In the long wavelength (small $k$) limit the atomic vibration wave $u_n = u \exp(ik(na) - i\omega t)$ is an elastic wave.
- Atoms act like a continuum for $ka = 2\pi/a \ll 1$.
- Speed of sound: $v_k = d\omega_k / dk = \omega_k / k = v$ independent of $k$ for small $k$.
- From previous slide: $v_{\text{sound}} = a \left( \frac{C}{M} \right)^{1/2}$
- Homework to show the relation to elastic waves

**What is significance of zero Group velocity at BZ Boundary?**
- Fundamentally different from elastic wave in a continuum.
- Since $\omega_k$ is periodic in $k$ it must have $v_k = d\omega_k / dk = 0$ somewhere.
- Occurs at BZ boundary because $\omega_k$ must be symmetric about the points on the boundary.

**Vibration at the BZ Boundary**
At the boundary of the Brillouin Zone in one dimension $k = \pi/a$
- The displacement is $u_n = u \exp(ikn) = u \exp(in\pi)$

**Two atoms per cell - Linear chain**
- To illustrate the effect of having two different atoms per cell, consider the simplest case atoms in a line with nearest neighbor forces only.
- Now we must calculate force and acceleration of each of the atoms in the cell.

\[F_{n1} = K \left[ u_{n2}^2 + u_{n1}^2 - 2u_{n1}u_{n2} \right] = M_1 \frac{d^2 u_{n1}}{dt^2}\]

\[F_{n2} = K \left[ u_{n3}^2 + u_{n2}^2 - 2u_{n2}u_{n3} \right] = M_2 \frac{d^2 u_{n2}}{dt^2}\]
Oscillations with two atoms per cell

- Since the equation is the same for each cell \( n \), the solution must have the same form at each \( n \) differing only by a phase factor. This is most easily written
  \[
  u_1^n = u_1 \exp(ik (n a) - k o t)
  \]
  \[
  u_2^n = u_2 \exp(ik (n a) - k o t)
  \]
- Inserting in Newton's equations gives the coupled equations
  \[
  -M_1 \omega^2 u_1 = K \left[ (\exp(-ik a) + 1) u_2 - 2 u_1 \right]
  \]
  and
  \[
  -M_2 \omega^2 u_2 = K \left[ (\exp(ik a) + 1) u_1 - 2 u_2 \right]
  \]
- Or
  \[
  [2 K - M_1 \omega^2] u_1 - K (\exp(-ik a) + 1) u_2 = 0
  \]
  and
  \[
  [2 K - M_2 \omega^2] u_2 - K (\exp(ik a) + 1) u_1 = 0
  \]

Oscillations with two atoms per cell

- From the previous slide
  \[
  2 K - M_1 \omega^2 u_1' + K (\exp(-ik a) + 1) u_2' = 0
  \]
  and
  \[
  2 K - M_2 \omega^2 u_2' - K (\exp(ik a) + 1) u_1' = 0
  \]
These two equations can be written in matrix form:

\[
\begin{bmatrix}
2 K - M_1 \omega^2 & - K (\exp(-ik a) + 1) \\
- K (\exp(ik a) + 1) & 2 K - M_2 \omega^2
\end{bmatrix}
\begin{bmatrix}
u_1' \\
u_2'
\end{bmatrix}
= 0
\]

- The solution is that the determinant must vanish:

\[
\begin{bmatrix}
2 K - M_1 \omega^2 & - K (\exp(-ik a) + 1) \\
- K (\exp(ik a) + 1) & 2 K - M_2 \omega^2
\end{bmatrix}
= 0
\]

Oscillations with two atoms per cell

- There are two solutions for each wave vector \( k \)

- Limits:
  - \( k \approx 0 \)
    - Acoustic: \( \omega^2 = \frac{1}{2} \frac{K}{(M_1 + M_2)} k^2 a^2 \)
    - Optic: \( \omega^2 = \frac{2 K}{\left(\frac{1}{M_1} + \frac{1}{M_2}\right)} = \frac{2 K}{\mu} \)
  - \( k = \pi/a \)
    - Acoustic: \( \omega^2 = \frac{2 K}{M_{\text{large}}} \)
    - Optic: \( \omega^2 = \frac{2 K}{M_{\text{small}}} \)

Modes for \( k \) near 0

- Acoustic at \( k \) near 0 - motion of cell as a whole
- Optic at \( k = 0 \) - opposed motion - larger displacement of smaller mass

Modes for \( k \) at BZ boundary

- Each type of atom moves in opposite directions in adjacent cells
- Leads to two modes, each with only one type of atoms moving
  - Acoustic at \( k = \pi/a \) - motion of larger mass
  - Optic at \( k = \pi/a \) - motion of smaller mass

Atom 2 does not move because there are no forces on it!
Vibration waves in 2 or 3 dimensions

• The position \( \mathbf{R}_n \) and displacement \( \mathbf{u}_n \) are vectors \( \mathbf{R}_n = \mathbf{R}_n^0 + \mathbf{u}_n \).
• The force on an atom is a vector \( \mathbf{F}_n \) that depends upon the displacements of all the neighbors.

Looks complicated

Each atom exerts forces on each of its neighbors

How do we deal with this?

Vibration waves in 2 or 3 dimensions

• Every atom in a plane has the same displacement \( \mathbf{u}_n \) and the same force \( \mathbf{F}_n \) on it.
• Thus it is sufficient to solve equations for one atom in each plane – all the others obey the same equations.

Vibration waves in 2 or 3 dimensions

• Normal modes of vibrations in any crystal can be described as waves in which planes move rigidly (Note that there are different sets of planes for different directions of the \( \mathbf{k} \) vector!)
• The forces between planes can be described by an effective spring constant \( C_{\text{eff}} \) – we will discuss how to determine the effective constant next time.
• Then Newton’s equations become
  \[
  M \frac{d^2 \mathbf{u}_n}{dt^2} = \mathbf{F}_n = C_{\text{eff}} \left( \mathbf{u}_{n+1} + \mathbf{u}_{n-1} - 2 \mathbf{u}_n \right)
  \]
• Note: \( n \) denotes a plane of atoms, \( n+1 \) and \( n-1 \) denote the neighboring planes.
• \( \mathbf{u}_n \) is an atom in plane \( n \); \( \mathbf{u}_{n+1} \) an atom in plane \( n+1 \), etc.
• The same as a one-dimensional problem!

Vibration waves in 2 or 3 dimensions

• We can understand vibrations waves in 2 and 3 dimensional crystals using the same ideas as for vibrations of atoms in a line.
  A wave is defined by the direction of propagation of the wave – \( \mathbf{k} \)-vector
  Planes of atoms perpendicular to \( \mathbf{k} \) move together
  Like a one-dimensional problem!

Vibration waves in 2 or 3 dimensions

• Thus all normal modes of vibrations in any crystal can be described in the same way as a one dimensional chain – but be careful to interpret the results properly!
  • There are different sets of planes for different directions of the \( \mathbf{k} \) vector.
  • The effective spring constant \( C_{\text{eff}} \) must be determined – it is different for different directions of \( \mathbf{k} \) and for different types of motion.
  • In 2 and 3 dimensions there can be longitudinal and transverse motions.
Vibration waves in 2 or 3 dimensions

- It is easier to visualize if we turn the crystal to orient the planes vertical and the k vector horizontal
  - Longitudinal motion
  - Transverse motion

Oscillations in higher dimensions

- Simplest example: Simple cubic with central forces
- For k in x direction each atom in the vertical planes moves the same:
  \[ u_n = u_n = u \exp(\mathbf{k} \cdot \mathbf{n} \cdot \mathbf{a} - i \omega t) \]

- **Longitudinal motion:** for \( u_n \) in x direction: the problem is exactly the same as a linear chain
  \[ \omega \rangle \approx 2 \left( \frac{C_L^{\text{eff}}}{M} \right)^{1/2} | \sin(ka/2) | \text{ where } C_L^{\text{eff}} = C \]

- **Transverse motion:** k in x direction; motion \( v_n \) in y direction
  \[ v_n = v_n = v \exp(\mathbf{k} \cdot \mathbf{n} \cdot \mathbf{a} - i \omega t) \]

- Central forces give no restoring force! Unstable!
- Need other forces - non-central or second neighbor

Meaning of Periodicity in Reciprocal space -- Again

- The same logic that we used for one dimension applies to 2 and 3 dimensions
- The vibrations are an example of excitations. The atoms are not in their lowest energy positions but are vibrating.
- The excitations are labeled by a wavevector k and are periodic functions of k in reciprocal space.
- All the excitations are counted if one considers only k inside the Brillouin zone (BZ). The excitations for k outside the BZ are identical to those inside and are not independent excitations.
- This is a general result valid in all crystals in all dimensions

Diffraction and the Brillouin Zone

- Brillouin Zone formed by perpendicular bisectors of G vectors
- Consequence: No diffraction for any k inside the first Brillouin Zone

- Special Role of Brillouin Zone (Wigner-Seitz cell of recip. lat.) as opposed to any other primitive cell
- Important later in course -- Here we have example for vibrations -- later for electrons
Summary

• Normal modes of vibrations in a crystal with harmonic forces:
  • Independent oscillators are labeled by wavevector $\mathbf{k}$ and have frequency $\omega_k$.
  • The relation $\omega_k$ as a function of $\mathbf{k}$ is called a dispersion curve.
  • $\omega_k$ periodic as a function of $\mathbf{k}$ in reciprocal space.
  • All independent oscillations are described by wavevectors $\mathbf{k}$ inside the Brillouin Zone.
  • For more than one atom per cell there are acoustic and optic modes of vibration.

• Sound waves are long wavelength (small $k$) acoustic modes.
• Group velocity of the waves vanish at BZ boundary.
  • Bragg scattering!
• Linear chain, planes in crystals – more next time.

Next time

• Why do vibrations in crystals act like atoms connected by springs?
• How do we determine the effective spring constant from the forces that bind the atoms together?
• Quantization and Phonons
• Is phonon "momentum" real?
• Experimental Measurements
• (Read Kittel Ch 4)