Lecture 9 - Crystal Vibrations continued - Phonons I

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

View of triple axis neutron scattering facility at National Research Council of Canada
http://neutron.nrc.ca/welcome.htm

Outline

- Examples in higher dimensions
- How many modes are there?
- Quantization and Phonons
- Experimental observation by inelastic scattering
- (Read Kittel Ch 4)

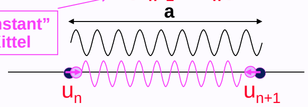
From last lecture

Energy due to Displacements

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

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

C = "spring constant" Notation in Kittel



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

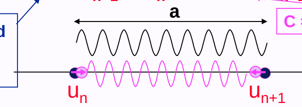
What determines the "spring constant"

- The energy of the crystal changes if the atoms are displaced – because the atoms are bound together!
- Example: Atoms in a line with binding of each pair of atoms that depends of the distance $\phi(|\underline{R}_{n+1} - \underline{R}_n|)$
- For each bond the change is energy is:

$\Delta E = \frac{1}{2} \phi'' (u_{n+1} - u_n)^2 = \frac{1}{2} C (u_{n+1} - u_n)^2$

ϕ'' = second derivative of $\phi(r)$

C = "spring constant"



- **Examples: Coulomb, Van der Waals attraction, replusive terms, etc. given before**

From last lecture

Vibration waves in 2 or 3 dimensions

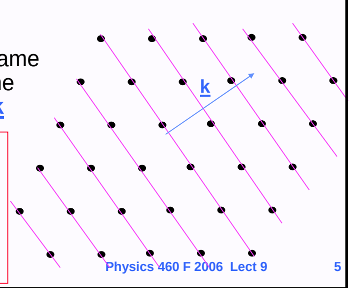
- Newton's Law: $M\, d^2 \underline{u}_n / dt^2 = \underline{F}_n$
- General Solution:

$\underline{u}_n(t) = \Delta\underline{u} \exp(i\underline{k} \cdot \underline{R}_n - i\omega t)$

Vector dot product - same for all atoms in plane perpendicular to $\underline{k}$

Consider the motion to be vibrations of planes of atoms

Like a chain in one dimension!

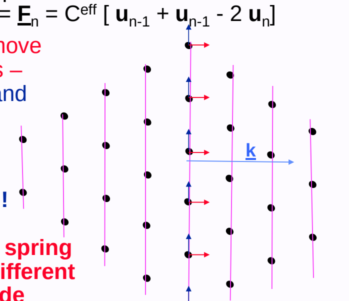


Vibration waves in 2 or 3 dimensions

- Easier to see with planes vertical and k vector horizontal
- Then Newton's equations become

$M\, d^2 \underline{u}_n / dt^2 = \underline{F}_n = C^{eff} [\, \mathbf{u}_{n-1} + \mathbf{u}_{n-1} - 2\, \mathbf{u}_n]$

- Each plane can move in three directions – one longitudinal and two transverse



Like one dimension!

But the effective spring constant C^{eff} is different for each mode

How do we find C^{eff} ?

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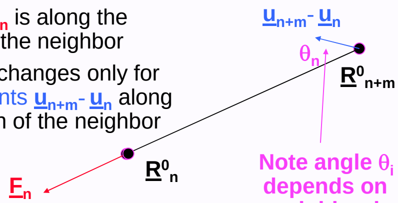
Central Forces

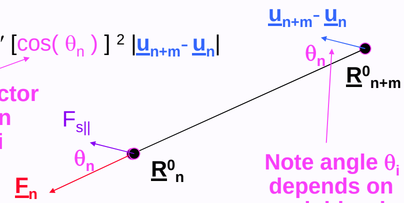
- For Central Forces the depends only on the distance between the atoms
- The energy per atom is
  $E = (1/2(1/N)\ \Sigma_{nm}\ \phi_{nm}\ (|\ \underline{\mathbf{R}}_n - \underline{\mathbf{R}}_{n+m}\ |)$
  $= E_0 + (1/4N)\ \Sigma_{nm}\ \phi_{nm}''\ (\Delta|\ \underline{\mathbf{R}}_n - \underline{\mathbf{R}}_{n+m}\ |)^2 + \ldots.$
- The force $\underline{\mathbf{F}}_n$ is along the direction of the neighbor
- The length changes only for displacements $\underline{\mathbf{u}}_{n+m} - \underline{\mathbf{u}}_n$ along the direction of the neighbor



Geometric factors for Central Forces

- We will consider waves with each atom displaced in the same direction – for simplicity – then we always need the force in the direction of the motion $F_{n||}$
- $F_{s||} = -\ \Sigma_i\ \phi_i''\ [\cos(\ \theta_n\ )\ ]^2\ |\underline{\mathbf{u}}_{n+m} - \underline{\mathbf{u}}_n|$

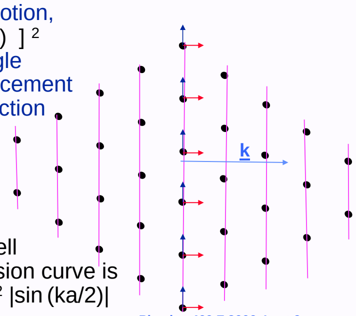
Geometric factor depends on neighbor i



Vibration waves in 2 or 3 dimensions

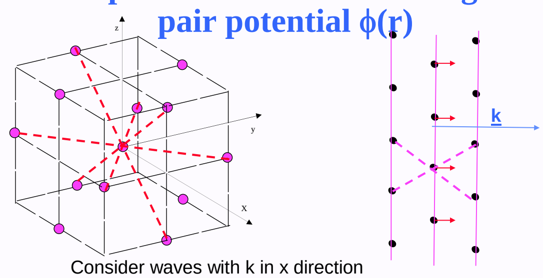
- Newton's equations
  $M\ d^2\ \underline{\mathbf{u}}_n / dt^2 = \underline{\mathbf{F}}_n = C^{eff}\ [\ \mathbf{u}_{n+1} + \mathbf{u}_{n-1} - 2\ \mathbf{u}_n]$

For each type of motion,
$C^{eff} = \Sigma_i\ \phi_i''\ [\cos(\ \theta_i\ )\ ]^2$
where θ_i is the angle between the displacement vector and the direction to neighbor i



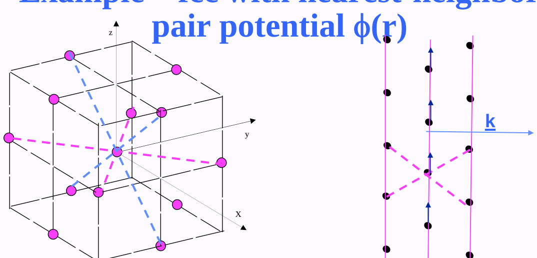
For one atom per cell the resulting dispersion curve is
$\omega_k = 2\ (C^{eff} / M\ )^{1/2}\ |\sin (ka/2)|$

Example – fcc with nearest-neighbor pair potential $\phi(r)$



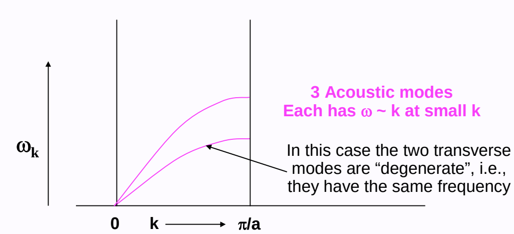
Consider waves with k in x direction
Longitudinal motion in x direction
Each atom has 4 neighbors in each of the two neighboring planes with $\cos(\theta)^2 = ½$
$C^{eff} = 4\ \phi_i''/2 \qquad \omega_k = 2^{3/2}\ (\phi_i''/M\ )^{1/2}\ |\sin (ka/2)|$

Example – fcc with nearest-neighbor pair potential $\phi(r)$



Consider waves with k in x direction
Transverse motion in y direction
Each atom has 2 neighbors in each of the two neighboring planes with $\cos(\theta)^2 = ½$ and 2 neighbors with $\cos(\theta) = 0$
$C^{eff} = 2\ \phi_i''/2 \qquad \omega_k = 2\ (\phi_i''/M\ )^{1/2}\ |\sin (ka/2)|$

Waves traveling in x direction in fcc crystal with one atom per cell



In the case of nearest neighbor forces, the longitudinal ω_k is higher than the transverse ω_k by the factor $2^{1/2}$

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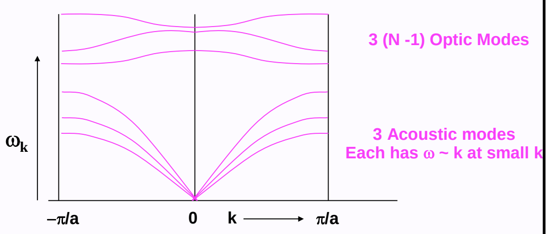
Oscillations in general 3 dimensional crystal with N atoms per cell



Quantization of Vibration waves

- **Max Planck - The beginning of quantum mechanics in 1901**
- **There were observations and experimental facts that showed there were serious issues that classical mechanics failed to explain**
- **One was radiation – the laws of classical mechanics predicted that light radiated from hot bodies would be more intense for higher frequency (blue and ultraviolet) – totally wrong!**
- **Planck proposed that light was emitted in "quanta" – units with energy $E = h\nu = \hbar\omega$**
- **Planck's constant h --- "h bar" = $\hbar = h/2\pi$**
- **The birth of quantum mechanics**
- **Applies to all waves!**

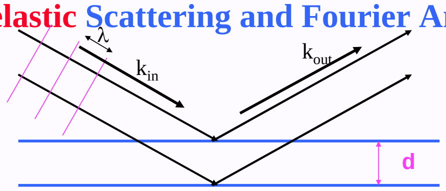
Quantization of Vibration waves

- Each independent harmonic oscillator has quantized energies:
  $e_n = (n + 1/2)\, h\nu = (n + 1/2)\hbar\omega$
- We can use this here because we have shown that vibrations in a crystal are independent waves, each labeled by **k** (and index for the type of mode - 3N indices in a 3 dimen. crystal with N atoms per cell)
- Since the energy of an oscillator is 1/2 kinetic and 1/2 potential, the mean square displacement is given by $(1/2)\, M\, \omega^2 u^2 = (1/2)\,(n + 1/2)\, \hbar\omega$
  where M and u are appropriate to the particular mode (e.g. total mass for acoustic modes, reduced mass for optic modes , ….)

Quantization of Vibration waves

- Quanta are called phonons
- Each phonon carries energy $\hbar\omega$
- For each independent oscillator (i.e., for each independent wave in a crystal), there can be any integer number of phonons
- These can be viewed as particles
- They can be detected experimentally as creation or destruction of quantized particles
- Later we will see they can transport energy just like a gas of ordinary particles (like molecules in a gas).

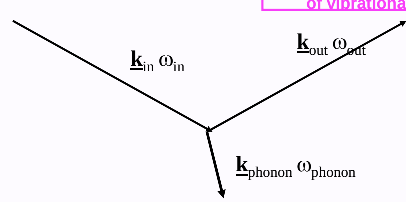
Inelastic Scattering and Fourier Analysis



- The in and out waves have the form:
  $\exp(i\,\mathbf{k}_{in}\cdot \mathbf{r} - i\,\omega_{in} t)$ and $\exp(i\,\mathbf{k}_{out}\cdot \mathbf{r} - i\,\omega_{out} t)$
- For elastic scattering we found that diffraction occurs only for $\mathbf{k}_{in} - \mathbf{k}_{out} = \mathbf{G}$
- For inelastic scattering the lattice planes are vibrating and the phonon supplies wavevector $\mathbf{k}_{phonon}$ and frequency ω_{phonon}

Inelastic Scattering and Fourier Analysis

- Result:
- Inelastic diffraction occurs for
  $\mathbf{k}_{in} - \mathbf{k}_{out} = \mathbf{G} \pm \mathbf{k}_{phonon}$
  $\omega_{in} - \omega_{out} = \pm\, \omega_{phonon}$ or $E_n - E_{out} = \pm\, \hbar\omega_{phonon}$
  Create or destroy quanta of vibrational energy



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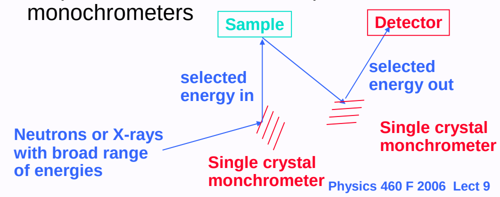
Experimental Measurements of Dispersion Curves

- Dispersion curves ω as a function of k are measured by inelastic diffraction
- If the atoms are vibrating then diffraction can occur with energy loss or gain by scattering particle
- In principle, can use any particle - neutrons from a reactor, X-rays from a synchrotron, He atoms which scatter from surfaces, ……

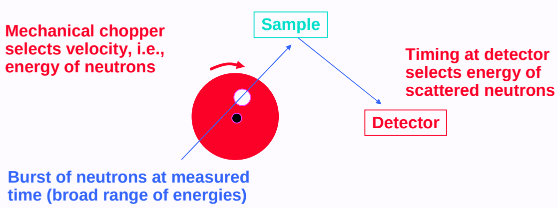
Experimental Measurements of Dispersion Curves

- Neutrons are most useful for vibrations
  For λ ~ atomic size, energies ~ vibration energies
  BUT requires very large crystals (weak scattering)
- X-ray - only recently has it been possible to have enough resolution (meV resolution with KeV X-rays!)
- "Triple Axis" - rotation of sample and two monochrometers



Experimental Measurements of Dispersion Curves

- Alternate approach for Neutrons
  Use neutrons from a sudden burst, e.g., at the new "spallation" source at Oak Ridge
  (Largest science project in the US this century!)
- Measure in and out energies by "time of flight"



More on Phonons as Particles

- Quanta are called phonons, each with energy $\hbar\omega$
- **k** can be interpreted as "momentum"
- What does this mean?
  NOT really momentum - a phonon does not change the total momentum of the crystal
  But **k** is "conserved" almost like real momentum - when a phonon is scattered it transfers "**k**" plus any reciprocal lattice vector, i.e.,
  $$\sum \mathbf{k}_{before} = \sum \mathbf{k}_{after} + \mathbf{G}$$
- Example : scattering of particles
  $$\mathbf{k}_{in} = \mathbf{k}_{out} + \mathbf{G} \pm \mathbf{k}_{phonon}$$
  where + means a phonon is created, - means a phonon is destroyed

Summary

- Normal modes of harmonic crystal
  Independent oscillators labeled by wavevector k and having frequency ω_k
- The relation ω_k as a function of k is called a dispersion curve - 3N curves for N atoms/cell in 3 dimensions
- Quantized energies (n + 1/2) h ω_k
- Can be viewed as particles that can be created or destroyed - each carries energy and "momentum"
- "Momentum" conserved modulo any **G** vector
- Measured directly by inelastic diffraction - difference in in and out energies is the quantized phonon energy
- Neutrons, X-rays, …..

Next time

- **Phonon Heat Capacity**
- **One of the early mysteries solved by quantum mechanics - obey Bose-Einstein Statistics**
- **Density of states of phonons**
- **Debye and Einstein Models**
- **(Read Kittel Ch 5)**