Review:

$$\mathbf{R} = \mathbf{R}' - \mathbf{\bar{G}}$$

$$\mathbf{R} \cdot (\frac{1}{2} \mathbf{G}) = \left( \frac{1}{2} \mathbf{G} \right)^2$$

$$2 \mathbf{G} \sin \theta = n \lambda$$

$$\mathbf{R}$$ must go from origin of reciprocal space to $$BZ$$!

$$I(\mathbf{h} \mathbf{k} \mathbf{\ell}) \propto |S(\mathbf{h} \mathbf{k} \mathbf{\ell})|^2$$

$$S(\mathbf{G}) = \int_{\text{unit cell}} V(\mathbf{x}) \mathbf{e}^{i \mathbf{G} \cdot \mathbf{x}} \, d\mathbf{x}$$

$$= \int \sum_{j} f_j \mathbf{e}^{i \mathbf{G} \cdot \mathbf{r}_j}$$

Atomic form factor

[$$\text{Structure factor of the basis}$$]

$$C_{CsCl}:$$

$$S(\mathbf{h} \mathbf{k} \mathbf{\ell}) = f_{Cs} + f_{Cl} (-1)^{h+k+l}$$
Cesium bcc

Basis

\[ C_5 = [0, 0, 0] \]
\[ C_5 = [\frac{1}{2}, \frac{1}{2}, \frac{1}{2}] \]

\[ S(\mathbf{h} \mathbf{k} \mathbf{e}) = f_{C_5} e^{i \mathbf{C} \cdot \mathbf{h}} + f_{C_5} e^{i \mathbf{C} \cdot (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})} \]
\[ = f_{C_5} e^{i \mathbf{C} \cdot -\mathbf{h}} + f_{C_5} e^{i \mathbf{C} \cdot (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})} \]
\[ = f_{C_5} (1 + e^{i \pi (\mathbf{h} \cdot \mathbf{F})}) \]
\[ = f_{C_5} (1 + (-1)^{\mathbf{h} \cdot \mathbf{F}}) \]

\[ = \begin{cases} 
2f_{C_5} & \text{h+k+l = even} \\
0 & \text{h+k+l = odd} \rightarrow \text{Systematic Absence} 
\end{cases} \]

Here \( \mathbf{C} = 0 \),
if we look
at \( \mathbf{d} = \frac{1}{2} \) plane,
we get fcc!!
bcc is being viewed in conventional cubic unit cell, z plane

of atoms sit half way between octra to cause destructive

interference.

N.B. If (hkl) doesn't lead to diffraction, then
this means it isn't a reciprocal lattice vector.
Here, (100) is not a z, since we're relating the z
n the sc lattice & it's not in 1-1 corr. w/ a family of lattice planes.

(100) was
\[ \lambda = \frac{2\pi}{a} \]

(200) was
\[ \lambda = \frac{2\pi}{2a} = \frac{1}{2} \left( \frac{2\pi}{a} \right) \checkmark \]

Copper Fcc:

Basis:

\( \begin{align*} & [0,0,0] \\
& [h,0,h] \\
& [h, h, 0] \\
& [0, h, h] \end{align*} \)

\[ S \left( \frac{1}{2} \right) = S_{\text{Cu}} \left( 1 + e^{i\pi(4m+1)} + e^{i\pi(3h)} + e^{i\pi(4m+3h)} \right) \]

Selection Rules:

\[ \begin{align*} & \text{sc} \quad \text{all } h, k, l \text{ allowed} \\
& \text{bcc} \quad h + h + l = \text{even} \\
& \text{fcc} \quad h, k, l \text{ all odd or even \quad \text{w/ } } \frac{\sqrt{3}}{2} \text{ or \( 111 \) } \quad \frac{\sqrt{3}}{2} \text{ or \( 222 \) or \( 100 \)) \end{align*} \]

Don't require all axes of lattice to have same length.
Diamond: fcc w/ basis

\[ \{0,0,0\}, \{\frac{1}{2}, \frac{1}{2}, 0\}, \{\frac{1}{2}, 0, \frac{1}{2}\}, \{0, \frac{1}{2}, \frac{1}{2}\} \]

\[ u + [u_x, u_y, u_z] \quad v + \vec{v} \quad w + \vec{w} \]

\[ S_{\text{fcc}}(h,k,l) = \sum_c e^{i \mathbf{G} \cdot \mathbf{r}_c} \]

where \( \mathbf{G} = h\mathbf{a}_1 + k\mathbf{a}_2 + l\mathbf{a}_3 \)

\[ = \sum_c \left( 1 + e^{i \mathbf{G} \cdot \mathbf{r}_c} \right) \times \left( 1 + e^{i \mathbf{G} \cdot \mathbf{r}_c + \mathbf{G} \cdot \mathbf{G} / 2} \right) \]

for an fcc lattice.

This was also the case for fcc bcc lattices viewed from sc lattice, though the \( S_{\text{fcc}} = 1 \) for an sc lattice.

Methods of Scattering Experiments:

- Laue Method: Single crystal, very \( K \)
- Powder Crystal Method: Ample specimen
- Powder Diffraction: Debye-Scherrer Method
Example \[
\text{PrO}_2: \quad \text{Pr} \to [0,0,0] \\
0 \to [1,y,1,y] \\
[1,y,1,y] \\
[1,y,1,y] \\
\]

The multiplicity of plane leads to:

\[
I_{\text{E}4\text{h}3} \times N_{\text{E}4\text{h}3} \left| S_{\text{E}4\text{h}3} \right|^2
\]

\[
d_{\text{E}_4\text{h}3} = \frac{a}{2 \sin \theta} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}
\]

\[
\frac{a^2}{d^2} = h^2 + k^2 + l^2 = N
\]

\[
d_{\text{E}_4\text{h}3} = \frac{h^2 + k^2 + l^2}{h^2 + k^2 + l^2} = \frac{N}{N_a}
\]

Guess \( N_a \) so other \( N_a \)'s are integers.

\[
N_a = 3
\]

This gives us \( N_a \)'s, which gives \( \text{E}4\text{h}3 \), & also gives \( a \).

What about measured intensities?

These can be explained by the scattering amplitude.

\[
I_{\text{E}4\text{h}3} = CM_{\text{E}4\text{h}3} \left[ b_{\text{Pr}} + b_{0} \left( e^{i(\pi)(4+n+2e)} + e^{\frac{i\pi}{2}(4+n+3e)} \right) \right]^2
\]

use (une) \( b \) agree w/ measured. Can also infer \( b_{\text{Pr}} ^{\prime} b_{0} \) value(scatting length).
Final conclusion scattering:

It's the method for determining the atomic structure of materials:

- X-rays
  - Penicillin (1964)
  - Bacillus (1976)
  - Photosynthetic proteins (1988)
  - Ribosome (2007)

Inelastic scattering:

\[
\frac{1}{Q} = \vec{R} - \vec{R}' + \delta \\
E(Q) = E(\vec{R}) - E(\vec{R}')
\]

Thermodynamic dispersion:

\[
E(Q)
\]
Review:

$$S_{\text{cube}} = \sum_i f_i e^{2\pi i (h x + k y + l z)}$$

Selection Rules:

- SC: all $$h, k, l$$ allowed
- bcc: $$h + k + l = \text{even}$$
- ccc: $$h, k, l = \text{all even or all odd}$$

Lattice + Basis:

$$S_{\text{cube}} = S_{\text{f.c.c.}} \times S_{\text{basis}}$$

Example: Diamond

$$S_{\text{cube}} = f_c \left( 1 + e^{i\pi (hN + kT + lU)} \right) x (1 + e^{i\pi (hN + kT + lU) + 2\pi (hN + kT + lU)})$$

$$f_c$$: lattice

Diffraction Methods:

- Debye-Scherrer or Powder Method

$$I \propto M \propto |S_{\text{cube}}|^2$$

\[ \text{multiplicity} \]

- Lattice
- Lattice constant
- Atomic form factors
Let's consider vibrations of crystals,

**Vibrations in a 1D Monatomic Chain:**

In a 1D crystal, vibrations can propagate as waves longitudinally or transversely:

1. Longitudinal mode
2. Transverse modes

Here, entire planes of waves move together in phase. We can learn much from the 1D case:

\[ S_{X_n} = X_n - x_n \quad \text{then} \quad m \ddot{x}_n = -2kS_{X_n} + k_{\parallel}(S_{X_n+1} + S_{X_n-1}) \]

Growth in time, \( S_{X_n} = Ae^{-i(k_{\parallel}x_n - \omega t)} \)

N.B. X-position only defined at \( X = n \cdot a \), so we will get alternating where \( k + 2\pi n \)

Since random motion at \( K \), so we can distinguish than \( x \) by \( K \) is relevant.

Thus,

\[ -m \omega^2 x e^{-i(k_{\parallel}x_n - \omega t)} = -2kS_{X_n} x e^{-i(k_{\parallel}x_n - \omega t)} + k_{\parallel}(S_{X_n+1} x e^{-i(k_{\parallel}x_{n+1} - \omega t)} + S_{X_n-1} x e^{-i(k_{\parallel}x_{n-1} - \omega t)}) \]

\[ = kS_{X_n} x e^{-i(k_{\parallel}x_n - \omega t)} [\omega^2 + 2x \omega i k_{\parallel} x + x^2 k_{\parallel}^2] \]
Canceling common factor $k$ using Euler's Eq.  

$$m\omega^2 = k_0 \left(2 - 2\cos(ka)\right)$$

$$\omega^2 = \frac{2k_0}{m} \left(1 - \cos(ka)\right)$$

$$= \frac{4k_0}{m} \sin^2 \left(\frac{ka}{2}\right)$$

$$\omega_n^2 = 2\sqrt{\frac{k_0}{m}} \left|\sin \left(\frac{ka}{2}\right)\right|$$

From $\omega^2$ expression, it is most clear that $\omega^2(k+\gamma_n) = \omega^2(k)$ when $\gamma_n = \frac{2\pi n}{a}$.

So

$$S\chi_n (k+\gamma_n) = A e^{-i ((k+\gamma_n) \cdot r - \omega (k+\gamma_n) t}$$

$$= A e^{-i (k \cdot r - \omega t)}$$

$$= S\chi_n (k)$$

Here, although $\lambda$, but are the same physically.

Thus only relevant $K \in \Gamma/\mathbb{Z}$. 

\[ w(h) \]
Remarks:

At BZ edge, \( k = \pm \frac{\pi}{a} \) gives standing waves.

\[
Sx_n = Ae^{i\left(\frac{2\pi}{a} na - \omega t\right)} \Rightarrow \begin{cases} \frac{\pi}{a} na - \omega t \end{cases}
\]

Also recall that \( k = \pm \frac{\pi}{a} \) satisfy Bragg-Laue diffraction conditions.

So this gives us another view of diffraction: \( \vec{k} \) that diffract don't propagate or waves through crystals.

\( \Delta \vec{n} = \frac{\vec{c}}{n} \)

In long wavelength limit:

\[
\lambda \ll \frac{1}{k} \Rightarrow 1 \quad \text{or} \quad k \ll 1
\]

\[
\omega(k) = 2 \sqrt{\frac{k z}{m}} \left| \sin \left( \frac{k z}{2} \right) \right|
\]

\[
\simeq a \sqrt{\frac{k z}{m}} \cdot k
\]

\[
= V_{\text{sound}} \cdot k
\]
where the group (speed of wave packet) \( V_g \) and phase (speed of individual min or max) velocities are equal:

\[
V_g = \frac{\text{dw}}{dn} = V_{\text{sound}}
\]

\[
V_p = \frac{\omega}{k} = V_{\text{sound}}
\]

\[\Delta \theta \left( \frac{\pm \pi}{a} \right) = 0\]

**Counting Normal Modes:**

- **Normal Numbers:**
  - \( N \) degrees of freedom
  - \( N \) modes for 1D system
  - \( 3N \) if there are \( N \) layers
  - \( 3 \) POF overall

\[
\sum_{j} e^{i(k_{\text{aq}} - \omega t)} = e^{i(\mathbf{k} \cdot \mathbf{n} a - \omega t)} = e^{i(k_{\text{aq}} - \omega t)} - e^{-i(k_{\text{aq}} - \omega t)}
\]

\[e^{-i(k_{\text{aq}} - \omega t)} = 1\]

\[k \cdot Na = 2\pi n\]

\[
k_n = \frac{2\pi}{Na} \cdot n = \frac{2\pi}{L} \cdot n
\]
So each mode occupies
\[ \delta k = \frac{\pi}{N \cdot \alpha} = \left(\frac{N \cdot \alpha}{2 \pi}\right)^{-1} \]
of \( K \)-space.

The density of states is then:
\[ \text{DOS}_k = \left(\frac{N \cdot \alpha}{2 \pi}\right) = \frac{L}{2 \pi} \]

In the \( 1 \)st \( BZ \), which has width \( \frac{2 \pi}{a} \), there are
\[ \left(\frac{N \cdot \alpha}{2 \pi}\right) \cdot \frac{2 \pi}{a} = N \text{ modes} \]

\[ \checkmark = \sum_k = \frac{N_h}{2 \pi} \int_0^{\frac{2 \pi}{a}} dh \]

Van Hove singularity

\[ D(\omega) = \frac{\text{\# states}}{\Delta \omega \times \text{interval in freq. space}} \]

\[ = \frac{\text{DOS}_k \cdot \Delta k}{\Delta \omega} \]

\[ D(\omega) = \frac{2}{\pi} \left(\frac{L}{2 \pi}\right) \left| \frac{1}{d\omega/dk} \right| \]

[ Density of States in Frequency ]
Physics 410/810 - Solid State Physics
Spring 2015

Friday, Week 4:

Preview:

\[ \omega(k) = 2\sqrt{\frac{\hbar k}{m}} \left| \sin \left( \frac{ka}{2} \right) \right| \]

\[ \omega(k) = 2\sqrt{\frac{\hbar k}{m}} \left| \sin \left( \frac{ka}{2} \right) \right| \]

\[ \sum_{n} A e^{i(k_{n} + \alpha)a - \omega b} = A e^{i(k_{n} - \omega^2)} \]

\[ K_{n}a = \frac{2\pi}{L} \cdot n \]

\[ K_{n} = \frac{2\pi}{Na} \cdot n \]

\[ \frac{2\pi}{La} \cdot n \]

Density of States:

\[ D(k) = \frac{Na}{2\pi} = \frac{L}{2\pi} \]

\[ D(\omega) = 2 \left( \frac{L}{2\pi} \right) \frac{1}{|dw/dk|} \]
Quantum Modes: Phonons

- Quantum Correspondence: A classical quadratic Hamiltonian mode \( w \) with frequency \( \omega \) has energy eigenstates:

\[
E_n = \hbar \omega (n + \frac{1}{2}) \quad n \in \mathbb{Z}^+
\]

High \( n \) = large amplitude

Phonons:
Each excitation by a step up the harmonic oscillator ladder is a "photon.

A phonon is a discrete quantum of vibration.

Like photons, phonons are bosons so the occupation \( \rho \) of a mode of freq. \( \omega(k) \) is

\[
\rho_n (\rho + \hbar\omega) = \frac{1}{e^{\hbar\omega/kT} - 1}
\]

so

\[
\rho = \frac{1}{kT} \quad \text{[Bose occupation factor]}
\]
Thus the energy of a mode is:

\[ E_n = \hbar \omega(n) \left( N_0 \left( p_{\nu} \omega(n) \right) + \frac{1}{2} \right) \]

and the total energy:

\[ U_{\text{total}} = \sum n \hbar \omega(n) \left( N_0 \left( p_{\nu} \omega(n) \right) + \frac{1}{2} \right) \]

\[ = \frac{N_0}{2\pi} \int_{-\pi}^{\pi} \hbar \omega(k) \left( N_0 \left( p_{\nu} \omega(k) \right) + \frac{1}{2} \right) dk \]

Later we will see Dohya & Einstein models for \( U_{\text{total}} \) differ in what the dispersion relation is:

\[ \omega(k) = \omega_q(k) \quad \text{(Dohya)} \]

\[ \omega(n) = \omega_0 \quad \text{(Einstein)} \]

Where we also note,

\[ \sum n = \frac{N_0}{2\pi} \int_{-\pi}^{\pi} \omega(k) \omega(k) dk \]

\[ = \frac{1}{2\pi} \int \omega(k) dk \]

Crystal Momentum (Phonon momentum):

The momentum of a photon is \( \hbar \hat{k} \), so it is tempting to write the phonon momentum as

\[ \hbar \hat{k} \]

But the phonon mode is the same physically for \( \hat{k} + \frac{\pi}{a} \), so \( \hbar \hat{k} \) is ambiguous. In a crystal, the quantity \( \hbar \hat{k} \) is known as the crystal momentum \( \hat{K} \); it is conserved modulo \( \frac{2\pi}{a} \):

\[ \hbar \hat{K} = \hbar \hat{k} + \hbar \frac{2\pi}{a} \text{ for some } \frac{2\pi}{a} \]

However, energy is conserved.
\[ \begin{align*}
\kappa &= \frac{2\pi n}{\sqrt{3}} \\
\kappa &= -\frac{2\pi n}{\sqrt{3}} \quad \leftarrow \quad \rightarrow \\
\varepsilon_k &= \pi / a \\
\varepsilon_\perp &= -\pi / a
\end{align*} \]

However, energy will always be conserved:

\[ \varepsilon_{\text{in}} = \varepsilon_{\text{out}} + \frac{2\pi n}{a} \]

*Vibrations of a 1D Diatomic Chain:*

Assume masses are equal:

\[ 
\begin{align*}
\mathbf{m} \, \ddot{x}_n &= -(k_1 + k_2) x_n + k_1 x_{n-1} + k_2 x_{n+1} \\
\mathbf{m} \, \ddot{y}_n &= -(k_1 + k_2) y_n + k_1 y_{n-1} + k_2 y_{n+1}
\end{align*} \]

Now \( x_n, y_n \) may have different amplitudes:

\[ 
\begin{align*}
x_n &= A_x e^{-i(k - a - \omega t)} \\
y_n &= A_y e^{-i(k - a - \omega t)}
\end{align*} \]

\[ 
\begin{align*}
-\mathbf{m} \, \omega^2 A_x e^{-i(k - a - \omega t)} &= -(k_1 + k_2) A_x e^{-i(k - a - \omega t)} + k_1 A_y e^{i(k - a - \omega t)} e^{i\kappa a} + k_2 A_y e^{-i(k - a - \omega t)} \\
-\mathbf{m} \, \omega^2 A_y e^{-i(k - a - \omega t)} &= -(k_1 + k_2) A_y e^{-i(k - a - \omega t)} + k_1 A_x e^{i(k - a - \omega t)} e^{i\kappa a} + k_2 A_x e^{-i(k - a - \omega t)}
\end{align*} \]
Cancelling common factors, we have,

\[-m w^2 A_x = -(k_1 + k_2) A_x + k_1 A_y e^{i\kappa a} + k_2 A_y\]

\[-m w^2 A_y = -(k_1 + k_2) A_y + k_1 A_x e^{-i\kappa a} + k_2 A_x\]

or in matrix form,

\[
mw^2 \begin{pmatrix} A_x \\ A_y \end{pmatrix} = \begin{pmatrix} k_1 + k_2 & -k_1 e^{i\kappa a} - k_2 \\ -k_1 e^{-i\kappa a} - k_2 & k_1 + k_2 \end{pmatrix} \begin{pmatrix} A_x \\ A_y \end{pmatrix}
\]

A solution is found by the det = 0:

\[
\begin{vmatrix} (k_1 + k_2) - mw^2 & -k_1 - k_1 e^{i\kappa a} \\
-k_1 e^{-i\kappa a} - k_2 & (k_1 + k_2) - mw^2 \end{vmatrix} = 0
\]

\[
mw^2 = (k_1 + k_2) \pm \left| k_1 + k_2 e^{i\kappa a} \right|
\]

\[
= \sqrt{\left(k_1 + k_2 e^{i\kappa a}\right)\left(k_1 + k_2 e^{-i\kappa a}\right)} = \sqrt{k_1^2 + k_2^2 + 2k_1 k_2 \cos(\kappa a)}
\]

\[
W \pm = \left(\frac{k_1 + k_2}{m} \pm \frac{1}{m} \sqrt{k_1^2 + k_2^2 + 2k_1 k_2 \cos(\kappa a)}\right)^{1/2}
\]

Let's evaluate \(W_+\) @ \(\kappa = 0\) & \(\kappa = \frac{2\pi}{a}\):

\[
W_+(0) = \left(\frac{k_1 + k_2}{m} \pm \frac{1}{m} \sqrt{(k_1 + k_2)^2}\right)^{1/2} = \left(\frac{k_1 + k_2}{m} \pm k_1 + k_2\right)^{1/2}
\]

\[
= \left\{ \begin{array}{l}
0 \\
\frac{1}{m} \sqrt{2(k_1 + k_2)}
\end{array} \right. +
\]

\[
\frac{1}{m} \sqrt{2(k_1 + k_2)}
\]
\[ w_{\pm} \left( \frac{3\pi}{a} \right) = \left( \frac{k_{1} + k_{2}}{m} \pm \frac{k_{2} - k_{1}}{m} \right)^{1/2} \]

Assume \( k_{2} > k_{1} \)

[Graph showing dispersion relations with labels for acoustic and optical branches]

**Remarks:**

- For the 2-atom basis, there are 2 unique values of \( w(W) \) per \( k \).
  These are called dispersion branches.

- In general, the number of dispersion branches will equal the number of DOF of the unit cell, but there will only be one acoustic branch per DOF of an atom (up to 3), i.e., the rest will be optical branches:

  \[
  \begin{align*}
  \text{# of Acoustic Branches} &= 3 \\
  \text{# of Optical Modes} &= 3(n-1)
  \end{align*}
  \]

  \( n \) basis atoms

- Allowed \( k \)-vectors still determined by Banerjee-Hamann & Luttinger:

  \[ k_{z} = \frac{2\pi n}{N_{a}} \quad n = \frac{2\pi L}{L} \]
• The optical branch has a finite \( W @ K \to 0, \lambda \to \infty \). It's name arises because

\[
W_{\text{photon}} = c \cdot K
\]

\[
W_{\text{phonon}} = \sum \frac{W_0}{v_{\text{mode}}} \quad \text{optical} \quad K \to 0
\]

\[
W_{\text{phonon}} = \sum \frac{W_0}{v_{\text{mode}}} \quad \text{acoustic}
\]

Since \( CK > W_{\text{mode}} \) for all \( K \), we cannot get conservation of energy by coupling to the acoustic modes.

For the optical mode, we can find some \( K \) such that,

\[
c \cdot K = W_0
\]

So photons will interact with optical phonons.

• Viewing \( W(K) \) in the extended zone scheme (or by going up the \( W \) first, then the optical branch from \( \pm \frac{\pi}{a} \)) we see that the Bragg condition is not for vibrational waves at the edge of the 1st \& 2nd BZ.

Here \( \frac{\partial W}{\partial K} = 0 \)

So no waves can propagate.

• There is a \( \Delta W \) gap at \( K = \pm \frac{\pi}{a} \):

\[
\Delta W = \sqrt{\frac{2k_F}{m}} - \sqrt{\frac{2k_F}{m}}
\]

\( k = k_1 \to k_2 \quad \Delta W = 0 \)

But we get a monochromatic beam with \( a_{\text{monoch}} = \frac{a}{2} \) so \( K = \pm \frac{2\pi}{a} \) is 1st BZ.