Chapter 2
Reciprocal Lattice

Phys 175A
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Crystal Lattice

- Periodic \( f(r + T) = f(r) \) for any observable functions such as electronic density, electric potential, etc. which means they are all periodic functions because of the translational properties of the lattice vectors.
Fourier Transform

- Fourier series (1D): \( f(r) = \sum_n A_n e^{i2\pi nr/a} \)
  
  where the period is \( a \).
  
  such that \( f(r + ua) = f(r) \); \( u \) is an integer.

- Or write \( f(r) \equiv \sum_G A_G e^{iGr} \)
  
  where \( G = 2\pi n/a \) (for 1D lattice)
  
  and \( A_G = (1/a) \int_{\text{cell}} f(r) e^{-iGr} \, dr \)
1D Translational Invariance

\[ f(r + T) = \sum_G A_G e^{iG(r+T)} = \sum_G A_G e^{iGr} e^{iGT} \]
\[ = f(r) = \sum_G A_G e^{iGr} \]

i.e. \[ e^{iGT} = 1 \]

For example, if \( T = ua \) (1D), then \( GT = 2\pi un = 2\pi \cdot \text{(integer)} \) and \( e^{iGT} = 1 \).
3D Translational Invariance

- For 3D lattice, \( e^{iG \cdot T} = 1 \)
  
  and \( T = u_1a_1 + u_2a_2 + u_3a_3 \) is the translational vector or the lattice vector

- Define “reciprocal primitive vectors”

- \( b_1 = (2\pi/V) a_2 \times a_3 \)
- \( b_2 = (2\pi/V) a_3 \times a_1 \)
- \( b_3 = (2\pi/V) a_1 \times a_2 \)

  where \( V \) is the volume of the primitive lattice cell
  \( V = |a_1 \cdot a_2 \times a_3| \), such that \( b_i \cdot a_j = 2\pi\delta_{ij} \)
  and \( \delta_{ij} \) is the kronecker delta function.

  Note: \( \{a\}'s \) don’t have to be orthogonal.
Reciprocal Lattice Vectors

Define \( \mathbf{G} = v_1 \mathbf{b}_1 + v_2 \mathbf{b}_2 + v_3 \mathbf{b}_3 \)
where the \( v \)'s are integers so that
so that
\[ \mathbf{G} \cdot \mathbf{T} = 2\pi ( u_1 v_1 + u_2 v_2 + u_3 v_3) = 2\pi \cdot \text{(integer)} \]
[because \( \mathbf{b}_i \cdot \mathbf{a}_j = 2\pi \delta_{ij} \)]
and \( e^{i \mathbf{G} \cdot \mathbf{T}} = 1 \)

In other words, because of the translational invariance property of the crystal, there exist a set of vector \( \mathbf{G} \) such that \( \mathbf{G} \cdot \mathbf{T} = 2\pi \cdot \text{(integer)} \). This set of vector defines another set of lattice point in the Reciprocal Space.
Reciprocal Vector Space

- G has a unit of 1/length. Similar to the wave-vector k in the plane wave expression $e^{i\mathbf{k} \cdot \mathbf{r}}$.
- G has a meaning in Fourier transform, k-space, or momentum space.
- It defines a set of lattice points in the k-space.
Direct and Reciprocal Lattice

- For every crystal, there is a set of space lattice (crystal lattice) – location of lattice points in real space where atoms and molecules are.
- There is also a set of reciprocal lattice in the momentum space (k-space) – something we see in diffraction measurement. However, there is no physical object present at the reciprocal lattice sites.
Light Microscopy vs X-ray Crystallography

\[ \lambda \sim 500 \text{ nm} \quad \lambda \sim 0.1 \text{ nm} \]

(a) Enlarged image
see real space

(b) Electron density map
see reciprocal space
Tunneling Microscope vs X-Ray Diffraction

“see” Direct Lattice (surface only)

Reciprocal Lattice (volume)
Reciprocal nature of diffraction pattern

Bragg’s law: \[ 2d \sin \theta = n \lambda \]

\[ d \propto \frac{1}{\sin \theta} \]

Diffraction maximum can be specified by the Miller indices \([hkl]\)
What do we learn from x-ray?

- Lattice parameters (Space Group)
- Symmetry (Point Group)
- Miller Index (h,k,l) for each point
- Intensity (square of structural factor) of each reflection
Properties of $G$ – reciprocal lattice

- Each $G$ is normal to a lattice plane in real space.
- $G \cdot T = 2\pi n$. For a fixed $G$ and $n$, there are many $T$ vectors satisfied this equation. But they all lie on the plane perpendicular to $G$. 

Diagram:

- Crystal plane
- G
- T
Distance between planes $= 2\pi/G$

- If $G$ has no common factor (prime #), then the distance between crystal plane perpendicular to the $G$ is $2\pi/G$.
- $d = T \cos \theta = 2\pi n/G$
- $d' = T' \cos \theta' = 2\pi (n+1)/G$
- Separation of planes $= d' - d = 2\pi/G$
- and $G$ must be the smallest reciprocal lattice for a given direction in $k$-space (prime #).
Small G dominates

- The larger the G, the closer the crystal plane, and less atoms on the plane.
- For example, in sc, separation of (100) is $a$, of (110) is $a/\sqrt{2} = 0.71a$
Volume of the reciprocal cell

If the volume of a unit cell of the direct lattice is $V$, then the volume of a unit cell of the reciprocal lattice is $(2\pi)^D/V$ where $D$ is the dimension of the lattice, usually 3.

3D:

$$V_g = |\mathbf{b}_1 \cdot \mathbf{b}_2 \times \mathbf{b}_3|$$

$$= (2\pi/V)^3 \left\{ (\mathbf{a}_2 \times \mathbf{a}_3) \cdot (\mathbf{a}_3 \times \mathbf{a}_1) \times (\mathbf{a}_1 \times \mathbf{a}_2) \right\}$$

$$= (2\pi/V)^3 \left\{ (\mathbf{a}_2 \times \mathbf{a}_3) \cdot \left[ \mathbf{a}_3 \cdot (\mathbf{a}_1 \times \mathbf{a}_2) \right] \mathbf{a}_1 - \left[ \mathbf{a}_1 \cdot (\mathbf{a}_1 \times \mathbf{a}_2) \right] \mathbf{a}_3 \right\}$$

$$= (2\pi/V)^3 \left\{ (\mathbf{a}_2 \times \mathbf{a}_3) \cdot \left[ \mathbf{a}_3 \cdot (\mathbf{a}_1 \times \mathbf{a}_2) \right] \mathbf{a}_1 \right\}$$

$$= (2\pi/V)^3 \left\{ (\mathbf{a}_2 \times \mathbf{a}_3) \cdot V \mathbf{a}_1 \right\}$$

$$= (2\pi)^3/V^2 \left\{ (\mathbf{a}_2 \times \mathbf{a}_3) \cdot \mathbf{a}_1 \right\}$$

$$= (2\pi)^3/V$$
Reciprocal of Reciprocal

- The direct lattice is the reciprocal of its own reciprocal lattice
- \( \mathbf{b}_1 = (2\pi/V) \mathbf{a}_2 \times \mathbf{a}_3 \)
- \( \mathbf{b}_2 = (2\pi/V) \mathbf{a}_3 \times \mathbf{a}_1 \)
- \( \mathbf{b}_3 = (2\pi/V) \mathbf{a}_1 \times \mathbf{a}_2 \)
- reciprocal \( \mathbf{c}_1 = (2\pi/V_g) \mathbf{b}_2 \times \mathbf{b}_3 \)
  \[= \frac{V}{(2\pi)^2} \left( \frac{2\pi}{V} \right)^2 (\mathbf{a}_3 \times \mathbf{a}_1) \times (\mathbf{a}_1 \times \mathbf{a}_2)\]
  \[= (1/V) \{ [\mathbf{a}_3 \cdot (\mathbf{a}_1 \times \mathbf{a}_2)] \mathbf{a}_1 - [\mathbf{a}_1 \cdot (\mathbf{a}_1 \times \mathbf{a}_2)] \mathbf{a}_3 \}\]
  \[= (1/V) \{ [\mathbf{a}_3 \cdot (\mathbf{a}_1 \times \mathbf{a}_2)] \mathbf{a}_1 \}\]
  \[= \mathbf{a}_1 \]
The Wigner-Seitz cell of the reciprocal lattice is called the Brillouin Zone.
### Cubic – reciprocal lattice

<table>
<thead>
<tr>
<th>Crystal Structure</th>
<th>Direct Lattice</th>
<th>Reciprocal Lattice</th>
<th>Volume (k-space)</th>
</tr>
</thead>
</table>
| SC                | \[
\begin{align*}
\vec{a}_1 &= a\hat{x} \\
\vec{a}_2 &= a\hat{y} \\
\vec{a}_3 &= a\hat{z}
\end{align*}
\] | \[
\begin{align*}
\vec{b}_1 &= (2\pi/a)\hat{x} \\
\vec{b}_2 &= (2\pi/a)\hat{y} \\
\vec{b}_3 &= (2\pi/a)\hat{z}
\end{align*}
\] | \[(2\pi/a)^3\] |
| FCC               | \[
\begin{align*}
\vec{a}_1 &= \frac{1}{2}a(\hat{x} + \hat{y}) \\
\vec{a}_2 &= \frac{1}{2}a(\hat{y} + \hat{z}) \\
\vec{a}_3 &= \frac{1}{2}a(\hat{z} + \hat{x})
\end{align*}
\] | \[
\begin{align*}
\vec{b}_1 &= \frac{2\pi}{a}(\hat{x} + \hat{y} - \hat{z}) \\
\vec{b}_2 &= \frac{2\pi}{a}(-\hat{x} + \hat{y} + \hat{z}) \\
\vec{b}_3 &= \frac{2\pi}{a}(\hat{x} - \hat{y} + \hat{z})
\end{align*}
\] | \[4(2\pi/a)^3\] |
| BCC               | \[
\begin{align*}
\vec{a}_1 &= \frac{1}{2}a(\hat{x} + \hat{y} - \hat{z}) \\
\vec{a}_2 &= \frac{1}{2}a(-\hat{x} + \hat{y} + \hat{z}) \\
\vec{a}_3 &= \frac{1}{2}a(\hat{x} - \hat{y} + \hat{z})
\end{align*}
\] | \[
\begin{align*}
\vec{b}_1 &= \frac{2\pi}{a}(\hat{x} + \hat{y}) \\
\vec{b}_2 &= \frac{2\pi}{a}(\hat{y} + \hat{z}) \\
\vec{b}_3 &= \frac{2\pi}{a}(\hat{z} + \hat{x})
\end{align*}
\] | \[2(2\pi/a)^3\] |
Hexagonal - homework

Derive the reciprocal vectors for a 2D hexagonal lattice.

Real space

Reciprocal space

Real and reciprocal lattices appear to be rotated from one another!
**1D - Reciprocal Lattice**

\[ \mathbf{b}_i \cdot \mathbf{a}_j = 2\pi \delta_{ij} \text{ means } \mathbf{b} \cdot \mathbf{a} = 2\pi \]

so \( \mathbf{b} = \frac{2\pi}{a} \) along the same direction

First BZ

Direct Lattice

Reciprocal Lattice
2D Reciprocal Lattice

Direct Lattice

Reciprocal Lattice

\[ \vec{a}_1 = a_1 \hat{x} \]
\[ \vec{a}_2 = a_2 \hat{y} \]

\[ \vec{b}_1 = \frac{2\pi}{a_1} \hat{x} \]
\[ \vec{b}_2 = \frac{2\pi}{a_2} \hat{y} \]

\[ \vec{b}_i \cdot \vec{a}_j = 2\pi \delta_{ij} \]
\[ \vec{b}_1 \cdot \vec{a}_1 = 2\pi; \quad \vec{b}_1 \cdot \vec{a}_2 = 0 \]
\[ \vec{b}_2 \cdot \vec{a}_1 = 0; \quad \vec{b}_2 \cdot \vec{a}_2 = 2\pi \]
Diffraction in quantum mechanic description: (Born approx)

The transitional amplitude to scatter from k-state to k’-state = $M_{kk'} = \langle k'|V(r)|k \rangle = \int \Psi^*(r) V(r) \Psi(r) \, dr$

$\Psi(r) = e^{ik \cdot r}$ is the plane wave (think of the Bragg scattering plane incident & diffracted waves)

In Fourier series, $V(r) = \sum V_G e^{iG \cdot r}$ (with the translational property of the lattice)

$M_{kk'} = \sum V_G \int e^{i(G + k - k') \cdot r} \, dr = \sum V_G \delta(G - \Delta k)$

= $V_G$ if $G = \Delta k$, $M_{kk'} = 0$ otherwise.

So the condition for Bragg scattering becomes $G = \Delta k = k' - k$
For elastic scattering, frequency $\omega = ck$ is unchanged. Speed of light is the same before & after scattering off the target, so $|k| = |k'|$.

Write $k + G = k'$ and square both sides gives $2k \cdot G + G^2 = 0$,

$$2k \cdot G = 2kG \cos \alpha = -G^2$$
$$-2k \cos \beta = -G$$
$$2k \sin \theta = G$$
$$2(2\pi/\lambda) \sin \theta = 2\pi n/d$$
$$2d \sin \theta = n\lambda$$

which is the Bragg condition.
X-ray data

Calcite - France Stone
Random/Backpack
March 24, 1993
40 kv, 30 ma
0.005 deg steps; 0.25 sec/step
15 pt. filter

D: 39.37 deg
2.287 ang

E:

C: 23.04 deg
3.86 ang

A:

B:
Bragg Conditions

\[ 2 \vec{k} \cdot \vec{G} + G^2 = 0 \]
\[ |\vec{k} \cdot \vec{G}| = G/2 \]

Can use different \( k \) to probe the same \( G \). Different circles, different \( k \) and angles.

Or similarly, all \( k \) end on the perpendicular bisecting plane of \( G \) would give Bragg diffraction. (BZ !!)
Laue Equations

- \( \mathbf{G} = \Delta \mathbf{k} = \nu_1 \mathbf{b}_1 + \nu_2 \mathbf{b}_2 + \nu_3 \mathbf{b}_3 \)
- \( \mathbf{b}_i \cdot \mathbf{a}_j = 2\pi \delta_{ij} \)
- \( \mathbf{a}_j \cdot \Delta \mathbf{k} = 2\pi \nu_j \) define sets of cones around \( \{\mathbf{a}\} \)

Allowed diffraction when the cones intersect. Note: Cone height is discrete, not a continue spectrum. Zero height is allowed) - different integers \( \nu \)'s.
Ewald Sphere

A sphere with radius $k$. Any point lands on the surface of the sphere is an allowed $G$ value, i.e. diffraction occurs at that particular angle & $k$. In principle, it can map out the whole reciprocal lattice using different $k$. 

![Ewald Sphere Diagram](image)
Example

Note:
\[ a_1 \cdot b_2 = 0 \]
\[ a_2 \cdot b_1 = 0 \]

Here \( \{a\} \) are the direct lattice vectors & \( \{b\} \) are the reciprocal lattice vectors.
RECIPROCAL LATTICE

REAL LATTICE

length = 1/d_{0,1}

(0,0) planes
Note: length is longer than (0,1) since spacing between (1,1) planes is smaller.
real lattice

\( \mathbf{a}_1 \)
\( \mathbf{a}_2 \)

reciprocal lattice

\( \mathbf{b}_1 \)
\( \mathbf{b}_2 \)

length = \( \frac{1}{d_{2,1}} \)

(0,0)

(2,1) planes
RECIProCAL LATTICE

REAL LATTICE

length = 1/d_{3,1}

(3,1) planes
RECIPIROCAL LATTICE

REAL LATTICE

(0,0) planes
(1,1) planes
(2,1) planes
(3,1) planes
REAL LATTICE

RECIPIROCAL LATTICE

with basis, for example
RECI PROCAL LATTICE

REAL LATTICE

length = 1/d_{2,2}

(2,2) planes
How do we orient the crystal to observe diffraction from the (0,1) reflection?
Bragg condition-- upper beam has to be an integral number of wavelengths from the lower beam for constructive interference.
$n\lambda = 2d \sin \theta$
(2,1) planes
Interpretation of the observed diffraction pattern

The reciprocal lattice can be constructed.
Diffraction by a monatomic lattice

Bragg condition:
In phase to get constructive interference (+ + + +)
Zero reflection otherwise (+ - + - + -)

From here we got:
\[ \mathbf{G} = \Delta \mathbf{k} // \mathbf{d} \]
\[ G = 2\pi/d \]
Bragg diffraction
Laude Equations
Construction of reciprocal lattice from EACH diffraction observed
i.e. each reciprocal lattice point gives a spot on the screen
Diffraction by a lattice with a Basis

For diatomic lattice (assume identical atoms) ALL in phase to get max amplitude (+ +  + +)
Zero amplitude if the reflection from the basis cancel (− +  − +).
Likewise, if the basis reflections are in phase, but the lattice reflections are out-of-phase, amplitude still cancels (+ +  − −)
i.e. to get max Bragg scattering, both lattice reflections and basis reflections should be in phase. Amplitude is less if they are partially in phase or out-of-phase.

With multiple atoms, or non-identical atoms, scattering amplitude would not be uniform. There are partial cancellations.
The resulting reciprocal lattice of the direct lattice would be modified.
Fourier Analysis of a Basis

- Scattering amplitude

\[ M_{kk'} = <k'|V(r)|k> = \int \Psi^*(r) V(r) \Psi(r) \, dr \]

where \( \Psi(r) = e^{i k \cdot r} \)

\[ V(r) = \sum_j V(r-r_j) = \sum G,j \, V_G \, e^{i G \cdot (r-r_j)} \]

\( r_j \) is the position of the \( j^{\text{th}} \) atom in the unit cell.

- \( M_{kk'} = \sum V_G \int e^{i (G + k - k') \cdot (r-r_j)} \, dr \]

\[ = \sum_G \sum_j e^{-i G \cdot r_j} \left[ V_G \int e^{i (G + k - k') \cdot r} \, dr \right] \]

Define \( S_G = \sum_j e^{-i G \cdot r_j} f_j \) the Structure Factor and \( f_j \) is the Atomic Form Factor such that \( M_{kk'} \propto S_G \)
Now if we specify $\mathbf{G}$ and $\mathbf{r}_j$ as
$$
\mathbf{G} = \nu_1 \mathbf{b}_1 + \nu_2 \mathbf{b}_2 + \nu_3 \mathbf{b}_3 \quad \text{and} \quad \mathbf{r}_j = x_j \mathbf{a}_1 + y_j \mathbf{a}_2 + z_j \mathbf{a}_3
$$
we get:
$$
S_G = \sum_{j=1}^{s} f_j e^{-2\pi i (x_j \nu_1 + y_j \nu_2 + z_j \nu_3)}
$$

Note that $S_G$ can be complex, because the scattering intensity involves the magnitude squared of $S_G$.

The evaluation of atomic form factor is complicated but for spherically-symmetric electron density, it can be written as (Kittel)
$$
f_j = 4\pi \int_{0}^{\infty} n_j(r) r^2 \frac{\sin(Gr)}{Gr} dr
$$
Example – bcc

primitive cell
bcc
$V = \frac{a^3}{2}$

reciprocal cell
fcc
$V = \frac{(4\pi/a)^3}{4}$
* see primitive vectors

• lattice cell sc
• w/ 2-pts basis
• $V = a^3$

• reciprocal lattice sc
• $V = (2\pi/a)^3$ [8x smaller than the cube $(4\pi/a)^3$]
• extra lattice points
• extra diffraction spots?
For a BCC lattice, \( r_j = (000) \) and \((\frac{1}{2} \frac{1}{2} \frac{1}{2})\). The structure factor is then:

\[
S_G = \left[1 + e^{-\pi i (v_1 + v_2 + v_3)}\right]f
\]

The structure factor is maximum \( S_G = 2f \) when the sum of the indices is even, i.e. \( v_1 + v_2 + v_3 = 2n \).

The structure factor is \( S_G = 0 \) when the sum of the indices is odd, i.e. \( v_1 + v_2 + v_3 = 2n + 1 \).

The only \( G \) show up in diffraction pattern are the ones fit the fcc lattice points.

Same physical measurement regardless how the cell was defined.
Example – fcc

- **Primitive cell**
  - fcc
  - $V = \frac{a^3}{4}$

- **Reciprocal cell**
  - bcc
  - $V = (4\pi/a)^3/2$
  * see primitive vectors

- **Lattice cell sc**
  - w/ 4-pts basis
  - $V = a^3$

- **Reciprocal lattice sc**
  - $V = (2\pi/a)^3$ [8x smaller than the cube $(4\pi/a)^3$]
  - extra lattice points
  - extra diffraction spots?
For a FCC lattice, we have four atoms per init cell located at (000), (0 ½ ½), (½ 0 ½) and (½ ½ 0). The structure factor is then:

\[ S_G = \left[ 1 + e^{-\pi i (v_1 + v_2)} + e^{-\pi i (v_1 + v_3)} + e^{-\pi i (v_2 + v_3)} \right] f \]

When all indices are even or odd, then \( S_G = 4f \).
When the indices are partially even and partially odd, then \( S_G = 0 \).

The only G show up in diffraction pattern are the ones fit the bcc lattice points.
Same physical measurement regardless how the cell was defined.
Homework

- Problem # 1, 2
- Problem # 5, 6, 7