Handout 5
Reciprocal Space

Useful concepts for the analysis of diffraction data

Chem 4850/6850/8850
X-ray Crystallography
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“Reflection from lattice planes” is just a concept that helps us to visualize what is happening in a diffraction experiment.

In reality, X-rays are scattered by the electrons in the atoms:
- X-ray wavelength is similar to size of electron cloud
- a periodic crystal corresponds to a periodic variation in electron density
- the scattering event leads to a phase change of $180^\circ$

Neutrons are scattered by nuclei:
- nuclei are much smaller than the neutron wavelength
- neutrons can also interact with magnetic moments in a material
Phase change on scattering

What do we actually measure?

- We measure the intensity distribution of scattered radiation as a function of scattering angle
  - for single crystals, we get 3D resolution
  - for powder experiments, all information is compressed into 1D

- The intensity distribution of scattered radiation is a result of the electron density distribution inside the crystal
  - the electron density distribution is the same in each unit cell
    ⇒ periodic array of electron density
Reciprocal space

- We do not see the periodic electron density directly during a diffraction experiment
  - we only observe the intensity distribution of X-ray scattering from the crystal(s)

- The diffraction intensity is correlated to the electron density in the crystal by a Fourier transform
  - often referred to as direct space and reciprocal space

- This means that we sample reciprocal space with our diffraction experiments
  - we can define a reciprocal lattice that corresponds to the direct (crystal) lattice
Real and reciprocal space

FIGURE 3.11. Relationships between a crystal (in crystal space) and its reciprocal lattice (in diffraction space).

The reciprocal lattice

- The reciprocal lattice has the same symmetry as the crystal lattice
- It can be derived from the crystal lattice graphically
  - draw lattice planes
  - pick an origin and draw normals to the lattice planes
  - mark points along the normals spaced $d^*(hkl)$ from the origin, where $d^*(hkl) = 1/d(hkl)$
- The reciprocal lattice constants $a^*$, $b^*$ and $c^*$ are defined so that they correspond to $d^*(100)$, $d^*(010)$ and $d^*(001)$
  - note that the direction of $a^*$, $b^*$ and $c^*$ will only coincide with that of $a$, $b$ and $c$ if the crystal lattice has $\alpha = \beta = \gamma = 90^\circ$
The reciprocal lattice – graphical construction

“Structure Determination by X-ray Crystallography”,

FIGURE 2.15. Direct and reciprocal lattices: (a) monoclinic $P$, as seen in projection along $b$, showing three families of planes; (b) corresponding reciprocal lattice.
The mathematical definition of the reciprocal lattice constants is

\[
\begin{align*}
\mathbf{a}^* &= \frac{\mathbf{b} \times \mathbf{c}}{\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})} \\
\mathbf{b}^* &= \frac{\mathbf{c} \times \mathbf{a}}{\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})} \\
\mathbf{c}^* &= \frac{\mathbf{a} \times \mathbf{b}}{\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})}
\end{align*}
\]

where \( \mathbf{a} \cdot (\mathbf{b} \times \mathbf{c}) = V \)

\( V = \text{volume of the unit cell} \)

Note that the cross product returns a vector, while the dot product gives a scalar!
Scattering from a material

Assumption: Incoming beam is a plane wave, phase change on scattering is identical for all rays

According to vector algebra:
- $\Delta l_1 = \mathbf{r} \cdot \mathbf{s}_0$
- $\Delta l_2 = \mathbf{r} \cdot \mathbf{s}$
- total path difference: $\Delta l = \Delta l_1 - \Delta l_2 = \mathbf{r} \cdot (\mathbf{s} - \mathbf{s}_0)$

$\mathbf{s}_0$: Unit vector of incoming beam
$\mathbf{s}$: Unit vector of scattered beam
Scattering from a material (2)

Define: Scattering vector

\[ S = s - s_0 \]

The phase difference \( \phi \) is given by

\[ \phi = 2\pi \frac{\Delta l}{\lambda} = \frac{2\pi}{\lambda} S \cdot r = K \cdot r \]

The change in scattering amplitude, \( dA(s) \), is given by the phase difference and the electron density in the volume element \( dV_r \)

\[ dA(s) = e^{-iK \cdot r} \rho(r) dV_r \]

\[ A(s) = \int_{V_r} e^{-iK \cdot r} \rho(r) dV_r \quad \text{Fourier transform!} \]
The relationship between $A$ and $\rho$

- The scattering amplitude, $A(s)$, and the electron density, $\rho(r)$, are correlated by a Fourier transform

$$A(s) = \int_{V_r} e^{-iK \cdot r} \rho(r) dV_r$$

$$\rho(r) = \int_{V_r} e^{iK \cdot r} A(s) dV_r$$

- Problem: We cannot measure $A(s)$, but only the intensity $I$, which is given by

$$I = A(s) \cdot A^*(s)$$

- Note that these equations are valid for any material, we have not yet made any assumptions about periodicity!
Scattering from crystals

To describe the electron density distribution in a crystal, we only need to describe it in one unit cell:

$$\rho(r) = \rho(r_0 + \tau_1), \text{where } \tau_1 = m_1a + m_2b + m_3c$$

Over all space, this gives us

$$A(s) = \int_{V_r}^{\infty} e^{-iK \cdot (r_0 + \tau_1)} \rho(r_0) dV_r$$

or

$$A(s) = \left[ \int_{V_r}^{\infty} e^{-iK \cdot r_0} \rho(r_0) dV_r \right] \sum_{m_1} e^{-iK \cdot m_1a} \sum_{m_2} e^{-iK \cdot m_2b} \sum_{m_3} e^{-iK \cdot m_3c}$$
A crystal’s interference function

The summation part in the formula for the scattering amplitude describes a crystal’s interference function:

\[ \sum_{m_1} e^{-iK \cdot m_1 \mathbf{a}} \sum_{m_2} e^{-iK \cdot m_2 \mathbf{b}} \sum_{m_3} e^{-iK \cdot m_3 \mathbf{c}} \]

remember that

\[ e^{-i \frac{2\pi m_1}{\lambda} \cdot \mathbf{S} \cdot \mathbf{a}} = \cos \left( \frac{2\pi m_1}{\lambda} \cdot \mathbf{S} \cdot \mathbf{a} \right) - i \sin \left( \frac{2\pi m_1}{\lambda} \cdot \mathbf{S} \cdot \mathbf{a} \right) \]

This will lead to reinforcement for

\[ \mathbf{a} \cdot \mathbf{S} = n_1 \lambda \quad \mathbf{b} \cdot \mathbf{S} = n_2 \lambda \quad \mathbf{c} \cdot \mathbf{S} = n_3 \lambda \]

or, using unit vectors

\[ \frac{\mathbf{a} \cdot \mathbf{S}}{\lambda} = \frac{n_1}{\mathbf{a}} \quad \frac{\mathbf{b} \cdot \mathbf{S}}{\lambda} = \frac{n_2}{\mathbf{b}} \quad \frac{\mathbf{c} \cdot \mathbf{S}}{\lambda} = \frac{n_3}{\mathbf{c}} \]

Laue conditions!
A crystal’s interference function (2)

- Each of these conditions describes a family of planes spaced $1/a$ ($1/b$, $1/c$) as a solution for $S$
  - for a one dimensional array of scatterers, the solutions are planes
  - for a two dimensional array, the solutions are lines
  - for a three dimensional array, the solution consists of points: The reciprocal lattice points

Ray Young, X-ray Monograph
The Ewald sphere

- Remember that we defined
  \[ S = s - s_0 \]
  where \( s \) and \( s_0 \) were unit vectors

- We can choose a frame of reference in which \( s_0 \) is fixed, and the end point of the vector \( s_0/\lambda \) is the origin of reciprocal space

- This allows us to define an *Ewald sphere*, also known as *sphere of reflection*, with radius \( 1/\lambda \) around the crystal

Ray Young, X-ray Monograph
Fulfilling four conditions

- The Ewald construction is also known as *wavelength condition*. 
- The three Laue conditions and the wavelength condition must be fulfilled simultaneously for diffraction to occur.
- This means that a reciprocal lattice point must lie on the Ewald sphere for diffraction to occur.
- Rotation of crystal is equivalent to rotation of reciprocal lattice.

Bragg’s law in reciprocal space

- If we define the distance of a lattice point from the origin of reciprocal space as \( d^* \), we get

\[
d^* = \frac{S}{\lambda}
\]

- We can also show that

\[
\frac{2\sin \theta}{|d^*|} = \lambda
\]

- It follows that

\[
|d| = \frac{1}{|d^*|}
\]

Ray Young, X-ray Monograph
Calculating d-spacings

- The distance of reciprocal lattice points from the origin of the reciprocal lattice is given by

\[ d^* = h \cdot \mathbf{a}^* + k \cdot \mathbf{b}^* + l \cdot \mathbf{c}^* \]

- \( h, k \) and \( l \) are the Miller indices

- By definition, \( d \) can be calculated from \( d^* \) by

\[ |d| = \frac{1}{|d^*|} \]

- Calculation is only straightforward for orthogonal crystal lattices
### d-spacing formulae

**TABLE 2.4. Expressions for \(d^*(hkl)\) and \(d(hkl)\) in the Seven Crystal Systems**

<table>
<thead>
<tr>
<th>System</th>
<th>(d^2(hkl))</th>
<th>(d^2(hkl))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triclinic</td>
<td>(h^2a^<em>+k^2b^</em>+l^2c^<em>+2hkb</em>c^<em>\cos\alpha^</em>+2hlc<em>a^</em>\cos\beta^<em>+2hka</em>b^<em>\cos\gamma^</em>)</td>
<td>(K^2/d^2(hkl))</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>(h^2a^<em>+k^2b^</em>+l^2c^<em>+2hla</em>c^<em>\cos\beta^</em>)</td>
<td>(\left{\frac{1}{\sin^2\beta}\left[\frac{h^2}{a^2}+\frac{k^2}{b^2}+\frac{l^2}{c^2}a \cos \beta \right] + \frac{k^2}{b^2}\right}^{-1})</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>(h^2a^<em>+k^2b^</em>+l^2c^*)</td>
<td>(\left{\frac{k^2}{a^2}+\frac{l^2}{b^2}+\frac{l^2}{c^2}\right}^{-1})</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>((h^2+k^2)a^<em>+l^2c^</em>)</td>
<td>(\left{\frac{h^2+k^2}{a^2}+\frac{l^2}{c^2}\right}^{-1})</td>
</tr>
<tr>
<td>Hexagonal and trigonal ((P))</td>
<td>((h^2+k^2+hk)a^<em>+l^2c^</em>)</td>
<td>(\left{\frac{4(h^2+k^2+hk)}{3a^2}+\frac{l^2}{c^2}\right}^{-1})</td>
</tr>
<tr>
<td>Trigonal ((R)) (rhombohedral)</td>
<td>([h^2+k^2+l^2+2(hk+kl+hl)(\cos\alpha^<em>)]a^</em>)</td>
<td>(a^2(\text{TR})^{-1}), where (T=h^2+k^2+l^2+2(hk+kl+hl)[(\cos^2\alpha - \cos\alpha)/\sin^2\alpha]) and (R=(\sin^2\alpha)/(1 - 3\cos^2\alpha + 2\cos^3\alpha))</td>
</tr>
<tr>
<td>Cubic</td>
<td>((h^2+k^2+l^2)a^*)</td>
<td>(\left{\frac{h^2+k^2+l^2}{a^2}\right}^{-1} = \frac{a^2}{h^2+k^2+l^2})</td>
</tr>
</tbody>
</table>

*In the monoclinic system, \(d(100) = a\sin\beta, d(001) = c\sin\beta\), and hence \(a = K/(a^*\sin\beta^*)\) and \(c = K/(c^*\sin\beta^*)\).*

*In the hexagonal system (and trigonal \(P\)), \(a = b = K/(a^*\sin\gamma^*) = K/(c^*\sqrt{3}/2)\).*

*In general, the expressions for \(d^*^2\) are simpler in form than the corresponding expressions for \(d^2\).*

Observations from single crystals and powders

- For a single crystal, there is one orientation in real space, resulting in one orientation of the reciprocal lattice
  - reciprocal lattice points are resolved and will result in diffraction intensity when they touch the Ewald sphere

- A powder sample consists of many crystallites with random orientations
  - we get many overlapping reciprocal lattices, resulting in a “sphere” of reciprocal lattice points that fulfill the Bragg condition at a given $2\theta$
  - the sphere will intersect the Ewald sphere in a circle
  - we will observe “powder rings”
If we assume an infinite number of randomly oriented crystallites, every point $P_n$ at distance $d^*$ from the origin of reciprocal space fulfills the Laue conditions.