Structure Factors

How to get more than unit cell sizes from your diffraction data

http://homepages.utoledo.edu/clind/

Yet again… expanding convenient concepts

✦ First concept introduced: Reflection from lattice planes
  - facilitates derivation of Bragg’s law
  - explains the location of spots on the observed diffraction pattern

✦ Second concept introduced: Scattering from atoms, all the electron density was assumed to be concentrated in a “lattice point” (e.g., origin of the unit cell)
  - gave the correct locations for spots in the diffraction pattern

✦ But what about atoms that are located “between lattice planes”? 
  - any atom can scatter an X-ray that hits it
  - what does this imply for the overall scattering amplitude?
Atoms “between lattice planes”

- “Atoms between lattice planes” will always scatter X-rays so that the resulting wave is partially out of phase with X-rays scattered from the “lattice planes”
  - the “lattice planes” can be envisioned as atoms located in the plane

![Diagram of X-ray scattering](image)

“Structure Determination by X-ray Crystallography”,

Description of a plane

- Point P can be described by the vector \( \mathbf{p} \), which is perpendicular to the plane LMN, or by the coordinates \((X,Y,Z)\)
  - the intercept equation of the plane is given by
    \[
    \frac{X}{a_p} + \frac{Y}{b_p} + \frac{Z}{c_p} = 1
    \]
  - this can be rearranged to
    \[
    X \cos \chi + Y \cos \psi + Z \cos \omega = p
    \]
  - describes family of parallel planes that are located at distance \(|p|\) from 0

![Diagram of plane description](image)

“Structure Determination by X-ray Crystallography”,
Path difference

\[ X \cos \chi + Y \cos \psi + Z \cos \omega = p \]

For plane O': \[ p = d_{hkl}; \quad a_p = a/h; \quad b_p = b/k; \quad c_p = c/l \]
\[ \cos \chi = d_{hkl}/(a/h); \quad \cos \psi = d_{hkl}/(b/k); \quad \cos \omega = d_{hkl}/(c/l) \]

For plane A: \[ p_A = d_A; \quad \text{atom at } (X_A, Y_A, Z_A) \]
\[ \Rightarrow d_A = X_A \cdot \frac{d_{hkl}}{a/h} + Y_A \cdot \frac{d_{hkl}}{b/k} + Z_A \cdot \frac{d_{hkl}}{c/l} \]
\[ d_A = (hx_A + ky_A + lz_A)d_{hkl} \quad \text{using fractional coordinates} \]

According to Bragg’s law, the path difference between O and A is
\[ \delta_A = 2d_A \sin \theta_{hkl} = 2d_{hkl} \sin \theta_{hkl} (hx_A + ky_A + lz_A) \]
\[ \Rightarrow \delta_A = \lambda (hx_A + ky_A + lz_A) \]

Using wave equations instead

We can describe a wave as
\[ W_0 = f \cdot \cos(2\pi X/\lambda) \quad \text{or} \quad W_0 = f \cdot \cos(\alpha) \]
where \( W_0 \) is the transverse displacement of a wave moving in the X direction, the maximum amplitude is \( f \) at \( t=0 \) and \( X=0 \).

For other waves with a maximum at \( t=t_n \) and \( X=X_n \), we can write
\[ W_n = f_n \cdot \cos(2\pi X_n/\lambda) \quad \text{where} \quad \phi_n = 2\pi X_n/\lambda \]

Two arbitrary waves of same frequency can then be represented as
\[ W_1 = f_1 \cdot \cos(\alpha - \phi_1) = f_1 \cdot [\cos(\alpha \cos(\phi_1) + \sin(\alpha) \sin(\phi_1))] \]
\[ W_2 = f_2 \cdot \cos(\alpha - \phi_2) = f_2 \cdot [\cos(\alpha \cos(\phi_2) + \sin(\alpha) \sin(\phi_2))] \]

Sum: \[ W = W_1 + W_2 = \cos(\alpha) \cdot (f_1 \cdot \cos(\phi_1) + f_2 \cdot \cos(\phi_2)) + \sin(\alpha) \cdot (f_1 \cdot \sin(\phi_1) + f_2 \cdot \sin(\phi_2)) \]
Wave equations continued

We know that we can write any wave as

$$W = F \cos(\alpha - \phi) = F [\cos(\alpha) \cos(\phi) + \sin(\alpha) \sin(\phi)]$$

Comparison with the equations on the last slide gives

$$F \cos(\phi) = f_1 \cos(\phi_1) + f_2 \cos(\phi_2)$$
$$F \sin(\phi) = f_1 \sin(\phi_1) + f_2 \sin(\phi_2)$$

$F$ can be calculated as

$$F = [(f_1 \cos(\phi_1) + f_2 \cos(\phi_2))^2 + (f_1 \sin(\phi_1) + f_2 \sin(\phi_2))^2]^{1/2}$$

Argand diagrams

- Waves can be represented as vectors in an Argand diagram
  - represented with real and imaginary components
  - allows for straightforward wave addition
  - For any given wave, we can write
    $$F = |F|e^{i\alpha} = |F| e^{i(\alpha_1 + \alpha_2)}$$
    (compare to slide 9 of handout 6!)

Wave addition using Argand diagrams

- Any number of waves can be added using an Argand diagram
  - For \( N \) waves, \( F \cos(\phi) = \sum_{j=1}^{N} f_j \cos(\phi_j); \ F \sin(\phi) = \sum_{j=1}^{N} f_j \sin(\phi_j) \)
  - Alternatively, we can write \( F = \sum_{j=1}^{N} f_j e^{i\phi_j} = |F| e^{i\phi} \)

Phase difference

- From our treatment of path differences of waves scattered by arbitrary atoms, we obtained
  \[ \delta_A = \lambda (hx_A + ky_A + lz_A) \]

- The corresponding phase difference can be written as
  \[ \phi_j = (2\pi / \lambda) \delta_j = 2\pi (hx_j + ky_j + lz_j) \]

- This implies that our expression for \( F \) depends on the diffraction direction as described by the Miller indices \( hkl \) (or the diffraction angle, if you prefer)
Structure factors

- **F** should be more properly written as \( F(hkl) \) or \( F_{hkl} \) to express its dependence on the diffraction angle.
- There will be a unique \( F(hkl) \) corresponding to each reflection in a diffraction pattern.
  - note – and remember! – that all atoms in a crystal contribute to every \( F(hkl) \)!
- \( F(hkl) \) is called the **structure factor** for the \((hkl)\) reflection.
- Can be broken down in its real and imaginary components:
  \[
  F(hkl) = A(hkl) + iB(hkl)
  \]
  where
  \[
  A(hkl) = \sum_{j=1}^{N} f_j \cos(2\pi(hx_j + ky_j + lz_j)) \quad B(hkl) = \sum_{j=1}^{N} f_j \sin(2\pi(hx_j + ky_j + lz_j))
  \]

Atomic scattering factors

- The individual atomic components, \( f_j \), are called **atomic scattering factors**.
  - depend on nature of atom, direction of scattering, and X-ray wavelength
  - provide a measure of how efficiently an atom scatters X-rays compared to an electron
  - usually written as \( f_j \), although they should be written as \( f_{j,\theta,\lambda} \)
  - listed as a function of \( \sin(\phi)/\lambda \) for each atom in the International Tables
  - maximum value of \( f_j \) is \( Z_j \), the number of electrons of the \( j^{th} \) atom
Intensity and structure factors

- We cannot measure structure factors, instead, we will measure the intensity of diffracted beams

\[ I(hkl) \propto F(hkl)F^*(hkl) \]

\[ F^*(hkl) = |F(hkl)|e^{-i\phi} \]

\[ |F(hkl)|^2 = A^2(hkl) + B^2(hkl) \]

- The phase is given by

\[ \tan(\phi) = B(hkl)/A(hkl) \]

- Problem: We lose the phase information when measuring intensities!

Factors between I and F

- There are several factors between I and F that will change the measured intensity:
  - thermal vibration of the atoms: exp[-B_0(sin^2(\theta)/\lambda)^2]
  - Lorentz factor, for normal 4 circle diffractometers: 1/sin(2\theta)
  - absorption: e^{-\mu t}, where \mu is the linear absorption coefficient and t the thickness of the specimen
  - polarization: p = (1+cos^2(2\theta))/2
  - scale factor
Thermal vibration

- Thermal vibration "smears out" the electron cloud surrounding an atom
  - we see time average over all configurations
  - displacement of atoms leads to slight phase difference for atoms in neighboring unit cells
  - \( f = f_0 \exp[-B_j \sin^2(\theta) \lambda^2] \)
  - \( B_j = 8\pi^2 \langle u^2 \rangle \)
  - \( \langle u^2 \rangle \) is the mean square amplitude of displacement

Systematic absences

- Some reflections will be systematically absent from your diffraction pattern
- These absences are a result of
  - lattice centering
  - glide planes
  - screw axes
- Note that simple rotations and mirror planes to not give systematic absences!
- Space groups can be assigned based on systematic absences
### Table 4.1. Limiting Conditions for Unit-Cell Type

<table>
<thead>
<tr>
<th>Unit-cell type</th>
<th>Limiting conditions</th>
<th>Translations associated with the unit-cell type</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>A</td>
<td>h + k + l = 2n</td>
<td>a/2 + b/2</td>
</tr>
<tr>
<td>B</td>
<td>h + k + l = 2n</td>
<td>a/2 + c/2</td>
</tr>
<tr>
<td>C</td>
<td>h + k + l = 2n</td>
<td>a/2 + b/2</td>
</tr>
<tr>
<td>I</td>
<td>h + k + l = 2n</td>
<td>a/2 + b/2 + c/2</td>
</tr>
<tr>
<td>F</td>
<td>h + k + l = 2n</td>
<td>a/2 + b/2</td>
</tr>
<tr>
<td></td>
<td>h + k + l = 2n</td>
<td>a/2 + c/2</td>
</tr>
<tr>
<td></td>
<td>h + k + l = 2n</td>
<td>a/2 + b/2 + c/2</td>
</tr>
<tr>
<td>R_{int}</td>
<td>h + k + l = 3n (rev)</td>
<td>[a/2 + b/3 + c/3</td>
</tr>
</tbody>
</table>

*This condition is not independent of the other two, as may be shown easily.

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### Table 4.2. Limiting Conditions for Screw Axes

<table>
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<th>Screw axis</th>
<th>Orientation</th>
<th>Limiting condition</th>
<th>Translation component</th>
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<tbody>
<tr>
<td>21</td>
<td>[100]</td>
<td>h = 2n</td>
<td>a/2</td>
</tr>
<tr>
<td>21</td>
<td>[100]</td>
<td>h = 2n</td>
<td>b/2</td>
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<tr>
<td>21</td>
<td>[100]</td>
<td>h = 2n</td>
<td>c/2</td>
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<td>[100]</td>
<td>l = 2n</td>
<td>b/2</td>
</tr>
<tr>
<td>21</td>
<td>[100]</td>
<td>l = 2n</td>
<td>c/2</td>
</tr>
<tr>
<td>41</td>
<td>[100]</td>
<td>i = 3n</td>
<td>c1/2</td>
</tr>
<tr>
<td>41</td>
<td>[100]</td>
<td>i = 3n</td>
<td>2c1/2</td>
</tr>
<tr>
<td>61 or 26</td>
<td>[100]</td>
<td>i = 6n</td>
<td>c/2</td>
</tr>
<tr>
<td>61 or 26</td>
<td>[100]</td>
<td>i = 6n</td>
<td>2c1/2</td>
</tr>
<tr>
<td>61 or 26</td>
<td>[100]</td>
<td>i = 6n</td>
<td>3c1/2</td>
</tr>
<tr>
<td>61 or 26</td>
<td>[100]</td>
<td>i = 6n</td>
<td>4c1/2</td>
</tr>
<tr>
<td>61 or 26</td>
<td>[100]</td>
<td>i = 6n</td>
<td>5c1/2</td>
</tr>
</tbody>
</table>

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### Table 4.3. Limiting Conditions for Glide Planes

<table>
<thead>
<tr>
<th>Glide plane</th>
<th>Orientation</th>
<th>Limiting condition</th>
<th>Translation component</th>
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<tbody>
<tr>
<td>a</td>
<td>[100]</td>
<td>h = 2n</td>
<td>a/2</td>
</tr>
<tr>
<td>a</td>
<td>[110]</td>
<td>h = 2n</td>
<td>a/2</td>
</tr>
<tr>
<td>b</td>
<td>[100]</td>
<td>k = 2n</td>
<td>b/2</td>
</tr>
<tr>
<td>b</td>
<td>[110]</td>
<td>k = 2n</td>
<td>b/2</td>
</tr>
<tr>
<td>c</td>
<td>[100]</td>
<td>l = 2n</td>
<td>c/2</td>
</tr>
<tr>
<td>c</td>
<td>[110]</td>
<td>l = 2n</td>
<td>c/2</td>
</tr>
<tr>
<td>n</td>
<td>[100]</td>
<td>h + l = 2n</td>
<td>b/2 + c/2</td>
</tr>
<tr>
<td>n</td>
<td>[100]</td>
<td>h + k = 2n</td>
<td>a/2 + b/2</td>
</tr>
</tbody>
</table>

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