Basic Principles of Scattering and Diffraction

Efrain E. Rodriguez
Chemistry and Biochemistry
University of Maryland, College Park
Acknowledgements

Sunil Sinha
UC San Diego

Roger Pynn
U. Indiana

Jacob Tosado
U. Maryland
Acknowledgements
Outline

1. Scattering geometry basics: Plane waves and Fourier transforms

2. Scattering cross sections for neutrons and x-rays

3. Scattering from ensemble of atoms and diffraction
Scattering geometry basics

Plane waves and Fourier transforms
Scattering geometry basics: The sinusoidal wave

\[ A \sin \theta \]
\[ A \cos \theta \]

\[ A = \text{amplitude} \]
\[ \theta = \text{angle} \]
\[ \phi = \text{phase difference} \]

\[ \cos \theta = \sin(\theta + \pi/2) \]

\[ \psi = A \sin(\theta + \phi) \]
Scattering geometry basics: The wavenumber $k$

\[ \psi = A \sin(\theta + \phi) \]

$k = \text{wavenumber}$

$x = \text{position}$

$\lambda = \text{wavelength}$

\[ k = \frac{2\pi}{\lambda} \]

$k$ has SI units of rad m$^{-1}$

\[ \psi = A \sin(kx + \phi) \]
Scattering geometry basics: The travelling wave

Wave moves in $x$-direction with time, $t$

$$\psi = A \sin(kx + \phi)$$

$\phi_0$ = initial phase angle
$\phi$ = phase after time $t$
$\omega$ = angular frequency

$$\omega = 2\pi v$$

$$\phi = \phi_0 - \omega t$$

$$\psi = A \sin(kx - \omega t + \phi_0)$$
We define a plane wave:
Amplitude in the \( z \)-direction,
Propagates in \( y \)- and \( x \)-directions.

\[ \vec{r} = \text{direction of propagation} \]
\[ \vec{k} = \text{wavevector} \]
\[ |\vec{k}| = \frac{2\pi}{\lambda} \]

\[ \psi = A \sin(\vec{k} \cdot \vec{r} - \omega t + \phi_0) \]
Scattering geometry basics: The traveling plane wave

Plane wave in $x$-direction only

Plane wave in $xy$-direction

Animation courtesy of Dr. Dan Russell, Grad. Prog. Acoustics, Penn State
Scattering geometry basics: Complex numbers

- Useful to work with exponential over sinusoidal waves
- Complex numbers allow us to simplify wavefunction equations

$$e^{i\theta} = \cos \theta + i \sin \theta$$

$$\psi = A \sin(\vec{k} \cdot \vec{r} - \omega t + \phi_0)$$

$$\psi = Ae^{i(\vec{k} \cdot \vec{r} - \omega t)}$$
Scattering geometry basics: The Fourier series

- We approximate a periodic structure through a sum of cosines and sines.
- Let $f(x)$ be a function expanded by a Fourier series

$$f(x) \approx a_0 + a_1 \cos(kx) + a_2 \cos(2kx) + a_3 \cos(3kx) + \cdots$$

$$+ b_1 \sin(kx) + b_2 \sin(2kx) + b_3 \sin(3kx) + \cdots$$

$n = 1$, fundamental harmonic

$n = 3$, higher harmonics included

Goes to zero if $f(x) = f(-x)$
The Fourier coefficients

- We write sum more efficiently if we pick the coefficients correctly.
- Now a definition and not approximation.

\[ f(x) = \sum_{n=-\infty}^{\infty} c_n e^{in \omega x} \]

where \( c_{-n} = c_n^* \)

\[ c_n = \frac{1}{\lambda} \int_{0}^{\lambda} f(x) e^{-in \omega x} \, dx \]

- We extend the analysis to a non-periodic function
- The Fourier coefficients become continuous functions we call \( F(k) \)

\[ c_n = \frac{1}{\sqrt{2\pi}} F(k) \Delta k \]
The Fourier transform

The limiting case is $\lambda \to \infty$ and $\Delta k \to 0$

- We call $F(k)$ the Fourier transform of $f(x)$, and vice versa
- We can toggle between real space ($x$) and reciprocal space ($k$)

\[
f(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} F(k) e^{ikx} \, dk
\]

\[
F(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(x) e^{-ikx} \, dx
\]

Argand diagram for real and imaginary components

Credit: Dr. David Cowtan, University of York
Fourier optics: Young’s double slit experiment

\[ q = k \sin \theta \]

\[ |\vec{k}| = \frac{2\pi}{\lambda} \]
An important Fourier transform: Young’s double slit

\[ A(x) = \delta \left( x - \frac{d}{2} \right) + \delta \left( x + \frac{d}{2} \right) \]

\[ \psi(q) = \psi_0 \left( e^{iqd/2} + e^{-iqd/2} \right) \]

\[ \psi(q) = \psi_0 2 \cos \left( \frac{qd}{2} \right) \]

\[ q = \frac{2\pi \sin \theta}{\lambda} \]
We don’t see the transform, but its amplitude squared

\[ I(q) \propto \left[ \cos \left( \frac{qd}{2} \right) \right]^2 \]

\[ I(q) \propto 1 + \cos(qd) \]

\( I(q) \) is our intensity or diffraction function

- Graph showing \( A(x) \) and \( d \)
- Graph showing \( I(q) \) and \( \frac{2\pi}{d} \)
Bragg’s law from Fourier transform of a diffraction grating

\[ A(x) = \sum_{m=-\infty}^{\infty} \delta(x - md) \]

\[ I(q) \propto \sum_{n=-\infty}^{\infty} \delta(q - nq_0) \]

\[ \frac{2\pi n}{d} = \frac{2\pi \sin \theta}{\lambda} \]

\[ n\lambda = d \sin \theta \]

\[ \frac{2\pi}{d} \]
The phase problem with cats and ducks

animals in real space

animals in reciprocal space

Credit: Dr. David Cowtan, University of York
The phase problem, mixing phases and amplitudes

amplitudes from original animal, but phases from opposite animal

Credit: Dr. David Cowtan, University of York
Scattering cross sections
neutrons and x-rays
The differential cross-section

When neutrons (or X-rays) scattered by the sample, we use $\sigma$ to represent number scattered particles

$$d\Omega = \frac{dS}{r^2}$$

We are after the differential cross-section

$$\frac{d\sigma}{d\Omega}$$
Flux of particles from beam and scattering at a solid angle

$$\Phi = \text{Flux of incoming particles}$$

Number per unit time per unit area \((s^{-1} \text{ cm}^{-2})\)

Scattering occurs within the plane by \(2\theta\) and out by angle \(\phi\)

We can define the solid angle as \(\Delta \Omega\)
The differential and double differential cross section

\[ \Phi = \text{number of incident neutrons per cm}^2 \text{ per second} \]
\[ \sigma = \text{total number of neutrons scattered per second} / \Phi \]
\[ \frac{d\sigma}{d\Omega} = \frac{\text{number of neutrons scattered per second into } d\Omega}{\Phi \ d\Omega} \]
\[ \frac{d^2\sigma}{d\Omega dE} = \frac{\text{number of neutrons scattered per second into } d\Omega \ & \ dE}{\Phi \ d\Omega \ dE} \]
Plane waves impinge on a single atom

Top-down view of incident plane wave arriving at atomic center.

\[ \psi_i = \psi_0 e^{ikz} \]

\[ \psi_f = \psi_0 f(\lambda, \theta) \frac{e^{ikx}}{r} \]
The ‘aperture’ function $f(\lambda, \theta)$ for scattering a plane wave

- We approximate $f(\lambda, \theta)$ as a constant for neutron scattering as a fixed point.
- For x-rays, we cannot make this approximation which affects $f(\lambda, \theta)$

Increasing slit-size means that the scattered wave has more $2\theta$-dependence
Intensity drops off at higher scattering angles

GIFs of plane wave arriving at a slit
The neutron scattering length

- In neutron scattering, the nucleus is a point source.
- $f(\lambda, \theta)$ is therefore a constant
- $f(\lambda, \theta) = b$ where $b$ is known as the scattering length

$$\psi_f = \psi_0 f(\lambda, \theta) \frac{e^{ikx}}{r}$$

- Note that $f(\lambda, \theta)$ and $b$ must have units of length since it is divided by $r$
- Typical $b$ are in fm or $10^{-15}$ m
- Can be positive or negative!
The neutron scattering cross section

\[ R = \frac{\Phi}{\text{incident flux} \times \text{cross-sectional area}} \]

\[ \sigma = 4\pi|b|^2 \]

\[ |\psi_0|^2 = \Phi \]
\[ |\psi_f|^2 = \frac{\Phi}{r^2} |f(\lambda, \theta)|^2 \]

\[ R = \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} |\psi_f|^2 \, d\Sigma \]

\[ \sigma = 2\pi \int_{\theta=0}^{\pi} |f(\lambda, \theta)|^2 \sin 2\theta \, d2\theta \]
Neutron scattering length for hydrogen

- Units given in barns, where 1 barn = $10^{-28}$ m$^2$
- These are isotope specific and will depend on the orientation of nuclear spin with respect to the neutron
- Example hydrogen vs. deuterium
- H has triplet and singlet from proton

\[
\langle b \rangle = \frac{3}{4} b^+ + \frac{1}{4} b^- \\
\langle b \rangle = -0.374 \times 10^{-14} m \\
\Delta b = \sqrt{\langle b^2 \rangle - \langle b \rangle^2} \\
\Delta b = 2.527 \times 10^{-14} m
\]

\[
b^+ = 1.085 \times 10^{-14} m \\
b^- = -4.750 \times 10^{-14} m
\]
Neutron scattering length for deuterium

- Deuterium has a quartet and doublet from proton and neutron in its nucleus
- 2/3 of states are quartet, 1/3 are doublet

\[ \langle b \rangle = \frac{2}{3} b^+ + \frac{1}{3} b^- \]
\[ \langle b \rangle = 0.668 \times 10^{-14} m \]
\[ \Delta b = 0.403 \times 10^{-14} m^2 \]

\[ \sigma = 4\pi|b|^2 \]
\[ \langle b^2 \rangle = \langle b \rangle^2 + (\Delta b)^2 \]
\[ \langle \sigma \rangle = \sigma_{coh} + \sigma_{inc} \]

<table>
<thead>
<tr>
<th>(barns)</th>
<th>( \sigma_{coh} = 4\pi\langle b \rangle^2 )</th>
<th>( \sigma_{incoh} = 4\pi(\Delta b)^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>1.76</td>
<td>80.27</td>
</tr>
<tr>
<td>Deuterium</td>
<td>5.59</td>
<td>2.05</td>
</tr>
</tbody>
</table>
The intrinsic cross section for x-rays

- The x-ray is a electromagnetic radiation with the electric field $E_{in}$ oscillating normal to the wave’s propagation.

- The electrons in the atomic center will oscillate with the x-ray and re-emit the x-ray with the oscillating field $E_{rad}$

Thompson scattering length of the electron

$$r_0 = \frac{e^2}{4\pi \varepsilon_0 mc^2} = 2.82 \times 10^{-15} \text{ m}$$
The cross section for x-rays

Measured intensity (i.e. number of x-ray photons) $\alpha$ energy/sec

Energy per unit area of beam $\alpha E^2$;

$$\Rightarrow \frac{\text{intensity measured in detector}}{\text{incident intensity}} = \frac{I_{sc}}{I_0} = \frac{|E_{rad}|^2 R^2 \Delta \Omega}{|E_{in}|^2 A}$$

differential cross section $= \frac{d\sigma}{d\Omega} = \frac{\text{number of x-rays scattered per sec in } \Delta \Omega}{\text{(number of incident x-rays per area) } \times \Delta \Omega}$

$$\frac{d\sigma}{d\Omega} = \frac{I_{sc}}{(I_0 / A) \Delta \Omega} = \frac{|E_{rad}|^2 R^2}{|E_{in}|^2} = r_0^2 \cos^2 \psi$$
The atomic form factor for x-rays

Atomic Form Factor: \[ f^0(\vec{q}) = \int \rho(\vec{r}) e^{i\vec{q} \cdot \vec{r}} \, dV \]

\[ f^0(q = 0) = Z \]

\[ f^0(q \to \infty) = 0 \]

Atomic Form Factor with Dispersion Corrections:

\[ f(\vec{q}, \hbar \omega) = f^0(\vec{q}) + f'(\hbar \omega) + i f''(\hbar \omega) \]
Scattering from multiple atoms

Diffraction from a crystal
The scattering triangle

- $k_i$ is the incident wavevector and $k_f$ is the scattered wavevector.
- Useful to work with another vector besides $k_i$ or $k_f$.
- We define $Q$, as our momentum transfer.

\[ \vec{Q} = \vec{k}_i - \vec{k}_f \]
Momentum transfer, or Q-space

\[ \mathbf{Q} = \mathbf{k}_i - \mathbf{k}_f \quad \text{or} \quad \mathbf{Q} = \mathbf{k}_f - \mathbf{k}_i \]

\[ |\mathbf{k}| = \frac{2\pi}{\lambda} \]

For elastic scattering, no energy transfer

\[ |\mathbf{k}_i| = |\mathbf{k}_f| \]

\[ |\mathbf{Q}| = \frac{4\pi \sin \theta}{\lambda} \]
Scattering from an ensemble of atoms

\[ |\mathbf{Q}| = \frac{4\pi \sin \theta}{\lambda} \]

\[ \mathbf{Q} = \mathbf{k}_f - \mathbf{k}_i \]

Waves scattered can add up in phase
Adding up the waves scattered from different centers

At a scattering center located at $\vec{R}_i$, the incident wave is $e^{i \vec{k}_0 \cdot \vec{R}_i}$

so the scattered wave at $\vec{r}$ is $\psi_{\text{scat}} = \sum e^{i \vec{k}_0 \cdot \vec{R}_i} \left[ -\frac{b_i}{|\vec{r} - \vec{R}_i|} e^{i \vec{k}' \cdot (\vec{r} - \vec{R}_i)} \right]$

\[
\therefore \frac{d\sigma}{d\Omega} = \frac{vdS}{vd\Omega} \left| \psi_{\text{scat}} \right|^2 = \frac{dS}{d\Omega} b_i e^{i \vec{k}' \cdot \vec{r}} \sum \frac{1}{|\vec{r} - \vec{R}_i|} e^{i (\vec{k}_0 - \vec{k}') \cdot \vec{R}_i} \right|^2
\]

\[
\frac{d\sigma}{d\Omega} = \sum_{i,j} b_i b_j e^{i (\vec{k}_0 - \vec{k}') \cdot (\vec{R}_i - \vec{R}_j)} = \sum_{i,j} b_i b_j e^{-i \vec{Q} \cdot (\vec{R}_i - \vec{R}_j)}
\]

For x-rays: $\frac{d\sigma}{d\Omega} = r_0^2 \sum_{i,j} e^{i (\vec{k}_0 - \vec{k}') \cdot (\vec{R}_i - \vec{R}_j)} \left\{ \frac{1 - \cos^2 2\theta}{2} \right\}$
A crystal has translational symmetry
Relationship between real and reciprocal space in crystals

**Reciprocal Lattice:**

\[
V_c = \frac{\bar{a}_1 \cdot (\bar{a}_2 \times \bar{a}_3)}{2\pi}
\]

\[
\bar{a}_1^* = \frac{2\pi}{V_c} \bar{a}_2 \times \bar{a}_3
\]

\[
\bar{a}_2^* = \frac{2\pi}{V_c} \bar{a}_3 \times \bar{a}_1
\]

\[
\bar{a}_3^* = \frac{2\pi}{V_c} \bar{a}_1 \times \bar{a}_2
\]
Diffraction and Bragg’s law

\[ \mathbf{G}_{hkl} = \frac{2\pi}{d_{hkl}} \]

\( h, k \) and \( l \) are called Miller indices

- \((hkl)\) describes a set of planes perpendicular to \( \mathbf{G}_{hkl} \), separated by \( d_{hkl} \)
- \( \{hkl\} \) represents a set of symmetry-related lattice planes
- \([hkl]\) describes a crystallographic direction
- \(<hkl>\) describes a set of symmetry equivalent crystallographic directions

\[ \frac{2\pi n}{d_{hkl}} \sin \theta = \frac{4\pi \sin \theta}{\lambda} \]

\[ n \lambda = 2d_{hkl} \sin \theta \]
Example: diffraction from a crystal – the fcc lattice

- A monochromatic (single $\lambda$) neutron beam is diffracted by a single crystal only if specific geometrical conditions are fulfilled.

- Useful $\lambda$ are typically between 0.4 Å and 2.5 Å.

- These conditions can be expressed in several ways:
  - Laue’s conditions: with $h$, $k$, and $l$ as integers
  - Bragg’s Law:
  - Ewald’s construction

- Diffraction tells us about:
  - The dimensions of the unit cell
  - The symmetry of the crystal
  - The positions of atoms within the unit cell
  - The extent of thermal vibrations of atoms in various directions

Lattice in real space
Relationship between real and reciprocal space
Beam of neutrons or x-rays scattered from planes

Real Space

Reciprocal Space
Bragg reflections from crystallographic planes
Centering operations lead to systematic absences

{001} family of planes are systematically absent
Other allowed reflections in fcc lattice
[111] view of the (220) reflection
The Ewald sphere and scattering triangle

The Ewald Sphere
Radius is $2\pi/\lambda$
Reciprocal Lattice

Lowest Harmonics in the Scattering Plane

Momentum Change (1-24-2)

Crystallographic Planes

Plane Normal
Summary

For x-ray and neutron scattering, we are dealing with the scattering of plane waves by atoms and nuclei.

\[ F(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(x)e^{-ikx} \, dx \]

For neutrons:

\[ \frac{d\sigma}{d\Omega} = \sum_{i,j} b_i b_j e^{-Q \cdot (R_i - R_j)} \]

For x-rays:

\[ \frac{d\sigma}{d\Omega} = r_0^2 \sum_{i,j} |f(Q)|^2 e^{-Q \cdot (R_i - R_j)} P(2\theta) \]

\[ |\vec{Q}| = \frac{4\pi \sin \theta}{\lambda} \]

When \( G_{hkl} = Q \), Bragg’s Law

\[ n\lambda = 2dhkl \sin \theta \]
Questions?

neutron scattering