Neutron scattering presentation series

(1) Basic concepts and neutron diffraction

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<table>
<thead>
<tr>
<th>Type</th>
<th>Technique</th>
<th>Length scale</th>
<th>Time scale</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Reciprocal space (Q/Å⁻¹)</td>
<td>Real space (r/nm)</td>
</tr>
<tr>
<td>Static scattering</td>
<td>Ultra-Small Angle Neutron Scattering (USANS)</td>
<td>5x10⁻⁶ ~ 0.005</td>
<td>100 ~ 10⁵</td>
</tr>
<tr>
<td></td>
<td>Small Angle Neutron Scattering (SANS)</td>
<td>0.001 ~ 0.5</td>
<td>1 ~ 500</td>
</tr>
<tr>
<td></td>
<td>Neutron Diffraction</td>
<td>0.1 ~ 20</td>
<td>0.05 ~ 5</td>
</tr>
<tr>
<td></td>
<td>Neutron Reflectometry</td>
<td>0.001 ~ 0.5</td>
<td>1 ~ 500</td>
</tr>
<tr>
<td>Dynamic scattering</td>
<td>Neutron Spin Echo (NSE)</td>
<td>0.01 ~ 0.5</td>
<td>1 ~ 50</td>
</tr>
<tr>
<td></td>
<td>Quasi-Elastic Neutron Scattering (QENS)</td>
<td>0.1 ~ 10</td>
<td>0.05 ~ 5</td>
</tr>
<tr>
<td></td>
<td>Inelastic Neutron Scattering (INS)</td>
<td>0.1 ~ 10</td>
<td>0.05 ~ 5</td>
</tr>
<tr>
<td>( \lambda = 0.1 \sim 10 \text{ Å} )</td>
<td>Source</td>
<td>Measurement time</td>
<td>Sample size</td>
</tr>
<tr>
<td>---</td>
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<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Neutron</td>
<td>Reactor Spallation source</td>
<td>min \sim,\text{hour}</td>
<td>cm, mL</td>
</tr>
<tr>
<td>X-ray</td>
<td>Synchrotron</td>
<td>(\mu s \sim \text{ms})</td>
<td>mm, (\mu\text{L})</td>
</tr>
<tr>
<td></td>
<td>In-house</td>
<td>min \sim,\text{hour}</td>
<td></td>
</tr>
</tbody>
</table>
Advantages and Disadvantages of Scattering Techniques

Advantages:
1. Dynamical and structural information in several orders
2. Ensemble sampling
3. Non-destructive penetration
4. Contrast variation available
5. Sensitive to magnetic fields (neutron)

Disadvantages:
1. Inverse problem
2. Ensemble sampling
3. Radiation resistance (X-ray)
4. Sample amount
5. Beamtime accessibility (neutron)
Outline

Basic concepts:
1. Scattering cross section
2. Scattering length and scattering length density
3. Coherent and incoherent scattering
4. Reciprocal space
5. Spatial and time correlation functions

Neutron diffraction:
1. Single crystal diffraction
2. Powder diffraction
3. Rietveld refinement method
4. Pair distribution function (PDF) method
Cross Section – Scattering Ability

Number of incident neutrons: \( I \)
Number of scattered neutrons: \( \Theta \)
Number density of scatterers in the sample: \( N \ [L^{-3}] \)
Beam size: \( A \ [L^2] \)
Sample thickness: \( \Delta x \ [L] \)
Solid angle: \( \Omega \)

Scattering probability:

\[
\frac{\Theta}{I} \propto \frac{NA\Delta x}{A} = N\Delta x
\]

\[
\frac{\Theta}{I} = N\Delta x \sigma \quad \frac{1}{I} \frac{d\Theta}{d\Omega} = \frac{N\Delta x d\sigma/d\Omega}{\Omega} = N\Delta x \sigma(\theta)
\]
Cross Section and Scattering Length

\[ \frac{\Theta}{I} = N\Delta x \sigma \quad \frac{1}{I} \frac{d\Theta}{d\Omega} = N\Delta x \frac{d\sigma}{d\Omega} = N\Delta x \sigma(\theta) \]

\( \sigma [L^2] \) (microscopic cross section): describes the scattering ability of the material.

For neutrons scattered by the nuclei:

\[ \sigma(\theta) = \frac{d\sigma}{d\Omega} = b L^2 \]

\( b [L] \): constant, scattering length

\[ \sigma = \int \sigma(\theta) d\Omega = 4\pi b L^2 \]

Units: \( \sigma \): 1 barn = 10^{-24} \text{ cm}^2 = 10^{-28} \text{ m}^2

\( b \): 1 fm = 10^{-15} \text{ m} = 10^{-5} \text{ Å} \)
1. X-ray sensitive to heavy atoms (high electron density)
2. Neutrons sensitive to light nuclei
3. Hydrogen: negative neutron scattering length (isotope substitution)
4. Chlorine and sulfur in the solvent strongly scatter X-ray
5. Boron: neutron absorption
Example 1: scattering by 1mm thick water

Mass density: 0.99997 g/cm$^3$

Cross section: H: 82.02 barn, O: 4.232 barn

\[
T\downarrow n = 1 - \frac{\Theta}{I} = 1 - N \Delta \sigma H \Delta x H = 1 - N \Delta \sigma H \Delta x (2\sigma H + \sigma O) = 1 - \frac{0.99997}{18.01528 \times 6.0221413 \times 10^{23}} \times 0.1 \times (2 \times 82.02 + 4.232) \times 10^{-24} = 0.4375
\]
Contrast comes from the scattering length density.

\[ \rho = \frac{1}{V} \sum_i b_i \]

Unit: $10^{-10}$ cm$^{-2}$ = $10^{-6}$ Å$^{-2}$

Scattering Length Density

(Pynn IUB lecture 2006)
Example 2: scattering length density of water

Mass density: 0.99997 g/cm$^3$
Scattering length: H: $-3.7423$ fm, O: $5.805$ fm

\[
\rho_H O = \text{mass density/molecular weight } N A \sum_i b_i = \text{mass density/molecular weight } N A (2 b_H + b_O ) = 0.99997/18.01528 \times 6.0221413 \times 10^{23} \times 1/10^{24} \times (-2 \times 3.7423 + 5.805) \times 10^{-5} = -0.5614 \times 10^{-6}
\]

($\text{Å}^{-2}$)
## Scattering Length Density (cont’d)

<table>
<thead>
<tr>
<th>materials</th>
<th>SLD ($10^{-6}$ Å$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O</td>
<td>-0.56</td>
</tr>
<tr>
<td>D$_2$O</td>
<td>6.39</td>
</tr>
<tr>
<td>h-styrene</td>
<td>1.413</td>
</tr>
<tr>
<td>d-styrene</td>
<td>6.5</td>
</tr>
<tr>
<td>h-cyclohexane</td>
<td>-0.24</td>
</tr>
<tr>
<td>d-cyclohexane</td>
<td>6.01</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>4.186</td>
</tr>
</tbody>
</table>

---

The graph shows the scattering length density ($10^{10}$ cm$^{-2}$) as a function of %D$_2$O. The materials are color-coded as follows:
- **Water**: Blue
- **Lipid**: Green
- **Protein**: Pink
- **DNA**: Cyan

(Pynn IUB lecture 2006)
Scattering Length Density Profile

\[ \rho \text{ [Å}^2\text{]} \]

Depth (y) into the sample [Å]

\( \Delta = 20 \text{ nm} \)

Fitzsimmons lecture 2005)

Coherent and Incoherent Scattering

The neutron scattering length depends on the nuclear isotope, spin relative to the neutron, and nuclear eigenstate.

For a single nucleus of a species,

\[ b_{\downarrow i} = \langle b \rangle + \delta b_{\downarrow i} \]

where \( \langle \delta b_{\downarrow i} \rangle = 0 \)

For the correlation between two nuclei,

\[ b_{\downarrow i} b_{\downarrow j} = \langle b \rangle^2 + (\delta b_{\downarrow i} + \delta b_{\downarrow j})\langle b \rangle + \delta b_{\downarrow i}\delta b_{\downarrow j} \]

Average over the whole group of nuclei,

\[ \langle \delta b_{\downarrow i} + \delta b_{\downarrow j} \rangle = 0 \]

\[ \langle \delta b_{\downarrow i}\delta b_{\downarrow j} \rangle = 0 \& (i \neq j) \& ((\delta b_{\downarrow i}) \tau_2 ) = (b \tau_2 ) - (b \tau_2 \& (i=j)) \]
For the correlation between two nuclei,

\[ b_{ij} b_{lj} = \langle b \rangle^2 + \delta b_{ij} \delta b_{lj} \]

Therefore, the correlation between all nuclei,

\[ \frac{d\sigma}{d\Omega} = \sum_{i,j=1}^{N} b_{ij} e^{iQ \cdot (R_i - R_j)} = \langle b \rangle^2 \sum_{i,j=1}^{N} b_{ij} e^{iQ \cdot (R_i - R_j)} + N(\langle b^2 \rangle - \langle b \rangle^2) \]
Coherent and Incoherent Scattering (cont’d)

\[
\frac{d\sigma}{d\Omega} = \langle b \rangle^2 \sum_{ij=1}^N b_i b_j e^{-iQ \cdot (R \downarrow_i - R \downarrow_j)} + N((b \downarrow^2) - \langle b \rangle^2
\]

- **Coherent scattering**: Correlation between relative spatial positions
- **Incoherent scattering**: Individual scattering contribution
### Coherent and Incoherent Scattering (cont’d)

\[ \langle b \rangle^2 \]

**Coherent scattering cross section**

**Incoherent scattering cross section**

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>( b_{\text{coh}} ) (fm)</th>
<th>( \sigma_{\text{coh}} ) (barn)</th>
<th>( \sigma_{\text{inc}} ) (barn)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>-3.472</td>
<td>1.8</td>
<td>80.2</td>
</tr>
<tr>
<td>D</td>
<td>6.674</td>
<td>5.6</td>
<td>2</td>
</tr>
<tr>
<td>C</td>
<td>6.65</td>
<td>5.55</td>
<td>0.001</td>
</tr>
<tr>
<td>O</td>
<td>5.805</td>
<td>4.2</td>
<td>0.0008</td>
</tr>
<tr>
<td>V</td>
<td>-0.443</td>
<td>0.02</td>
<td>5</td>
</tr>
</tbody>
</table>

![Graph showing scattering cross sections]
Reciprocal Space – Spatial Frequency

(a) 1D
(b) 2D
(c) 3D

Real lattice

Reciprocal lattice

Real lattice

Reciprocal lattice

Signal amplitude

Time domain

Frequency domain
Reciprocal Space – Spatial Frequency (cont’d)

Time space shape: $f(t)$

Frequency space shape: $F(\omega)$

$\mathcal{F}[f(t)] = F(\omega)$

$\mathcal{F}^{-1}[F(\omega)] = f(t)$

$\omega T = 2\pi$

Fourier transform:

$\mathcal{F}[f(t)] = \int_{-\infty}^{\infty} f(t) e^{-i\omega t} \, dt = F(\omega)$

$\mathcal{F}[f(r)] = \int V f(r) e^{-i\cdot Q \cdot r} \, dV = F(Q)$
Reciprocal Space – Spatial Frequency (cont’d)

Time space shape:

Frequency space spectrum:

\[ \mathcal{F}[f(t)] = F(\omega) \]

\[ \mathcal{F}^{-1}[F(\omega)] = f(t) \]

\[ \omega T = 2\pi \]

Real space distribution:

Reciprocal space spectrum:

\[ \mathcal{F}[f(r)] = F(Q) \]

\[ \mathcal{F}^{-1}[F(Q)] = f(r) \]

\[ Qd = 2\pi \]
Reciprocal Space – Spatial Frequency (cont’d)

\[ 2d \sin \theta = n \lambda \]
Reciprocal Space – Spatial Frequency (cont’d)
Neutron/X-ray/light scattering measures different mathematical transforms (Fourier, Abel) of two-point correlation functions (Debye, van Hove) in different spaces \((r/Q, t/\omega)\) and different time or length scales \((\lambda, 2\theta)\).
Correlation Functions (cont’d)

Interference between two scattered waves:
\[
\Psi_{\downarrow i} \Psi_{\downarrow j} \star = b_{\downarrow i} b_{\downarrow j} e^{\star -iQ \cdot (R_{\downarrow i} - R_{\downarrow j})}
\]

Sum over all scatterers:
\[
d\sigma/d\Omega = \sum_{i,j=1}^{N} b_{\downarrow i} b_{\downarrow j} e^{\star -iQ \cdot (R_{\downarrow i} - R_{\downarrow j})}
\]
Correlation Functions (cont’d)

\[
d\sigma/d\Omega = \sum_{i,j=1}^{N} b_i \Psi_j \Psi_j^* = \sum_{i,j=1}^{N} b_i b_j e^{-iQ \cdot (R_i - R_j)}
\]

Debye correlation function (structure)

\[\gamma(r) = \int V \rho(r') \rho(r + r') d^3 r'\]

van Hove pair correlation function (dynamic)

\[G(r,t) = \frac{1}{N} \sum_{i,j=1}^{N} \delta(r - r_i(t) + r_j(0))\]

Pair distribution function (structure)

\[g(r) = \frac{V}{N^2} \sum_{i,j=1}^{N} \delta(r - r_i + r_j)\]

Self time correlation function (dynamic)

\[G_s(r,t) = \frac{1}{N} \sum_{i=1}^{N} \delta(r_i(0)) \delta(r - r_i(t))\]
Correlation Functions (cont’d)

**Debye correlation function (structure)**

\[ \gamma(r) = \int V \rho(r') \rho(r + r') \, dr' \]

\[ I(Q) = \mathcal{F} [\gamma(r)] \quad \text{(SANS, USANS, ND, NR)} \]

\[ G(z) = \mathcal{A} [\gamma(r)] \quad \text{(SESANS)} \]

**Pair distribution function (structure)**

\[ g(r) = V/N \sum_{i,j} \delta(r - r_{ij}) \]

\[ S(Q) = \mathcal{F} [g(r)] \quad \text{(SANS, USANS)} \]

**van Hove pair correlation function (dynamic)**

\[ G(r,t) = 1/N \sum_{i,j} \delta(r - r_{ij}(t) + r_{ij}(0)) \]

\[ I(Q,t) = \mathcal{F} \downarrow Q [G(r,t)] \quad \text{(NSE)} \]

\[ S(Q,\omega) = \mathcal{F} \downarrow Q,\omega [G(r,t)] \quad \text{(INS)} \]

**Self time correlation function (dynamic)**

\[ G_{\text{s}}(r,t) = 1/N \sum_{i,j} \delta(r_{ij}(0)) \delta(r - r_{ij}(t)) \]

\[ S_{\text{s}}(Q,\omega) = \mathcal{F} \downarrow Q,\omega [G_{\text{s}}(r,t)] \quad \text{(QENS, incoh)} \]
Neutron Diffraction

\[ |k \downarrow f| = |k \downarrow i| = \frac{2\pi}{\lambda} \]

\[ Q \downarrow d = 2n\pi \]

\[ Q : \text{Momentum transfer} \]

\[ Q = k \downarrow f - k \downarrow i \]

\[ n\lambda = 2d \sin \theta \]

Bragg's Law

Constructive interference when

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

Scattering triangle

\[ Q = |Q| = 2|k \downarrow i| \sin \theta = \frac{4\pi}{\lambda} \sin \theta \]
Neutron Diffraction (cont’d)

Two axis diffractometer

Diffraction – Where the atoms are:
Clifford Shull, 1994 Nobel Prize (1/2)
**Notations**

- **Crystal lattice**
  \[ R = m_1 \mathbf{a}_1 \downarrow + m_2 \mathbf{a}_2 \downarrow + m_3 \mathbf{a}_3 \downarrow \]

- **Reciprocal lattice**
  \[ G \downarrow hkl = h \mathbf{a}_1 \uparrow^* + k \mathbf{a}_2 \uparrow^* + l \mathbf{a}_3 \uparrow^* \]

- **Miller indices**
  \[ h, k, l \]

- **(hkl)**: a set of planes perpendicular to \( G \downarrow hkl \), separated by \( 2\pi / |G \downarrow hkl| \)

- **[hkl]**: a specific crystallographic direction

- **{hkl]**: a set of symmetry-related lattice planes

- **⟨hkl⟩**: a set of symmetry-equivalent crystallographic directions

\[ a \downarrow 1 \uparrow^* = 2\pi / V \quad a \downarrow 2 \times a \downarrow 3 \]

\[ a \downarrow 2 \uparrow^* = 2\pi / V \quad a \downarrow 3 \times a \downarrow 1 \]

\[ a \downarrow 1 \times a \downarrow 3 = 2\pi \delta \downarrow ij \]

\[ V = a \downarrow 2 \times (a \downarrow 2 \times a \downarrow 3) \]
Ewald Sphere

Laue’s condition

\[ Q = G \downarrow hkl \]

\[ Q \cdot a_1 = 2\pi h, \quad Q \cdot a_2 = 2\pi k, \quad Q \cdot a_3 = 2\pi l \]
Powder Diffraction

- Phase identification
- Crystallinity
- Lattice parameters
- Crystallite size
- Orientation
Rietveld Refinement Method

\[ I = I_0 \sum h^{\uparrow} k^{\downarrow} m^{\downarrow} L^{\downarrow} F_{\downarrow h^{\downarrow} k^{\downarrow} l^{\downarrow}} P(\Delta h^{\downarrow}) + I^{\downarrow b} \]

- \( I_0 \): incident intensity
- \( k^{\downarrow h} \): scale factor for particular phase
- \( m^{\downarrow h} \): reflection multiplicity
- \( L^{\downarrow h} \): correction factors on intensity (texture...)
- \( F_{\downarrow h^{\downarrow} k^{\downarrow} l^{\downarrow}} \): structure factor for a particular reflection
  \[ F_{hkl} = \sum i^{\uparrow} b_{il} e^{\uparrow - iQ \cdot R \downarrow l} e^{\uparrow - W \downarrow l} \]
- \( P(\Delta h^{\downarrow}) \): peak shape function (instrument resolution function, crystallite size, strain, defects)
- \( I^{\downarrow b} \): background intensity
Example: Polymer Diffraction

- Phase identification
- Crystallinity
  \[ x_{cr} = A_{cr} / A_{cr} + K A_{am} \]
- Lattice parameters
  \[ d = 2\pi/Q \]
- Crystallite size
  \[ L_{hkl} = 0.89\lambda / (FWHM - \Delta\theta)\cos\theta \]
- Orientation
  \[ f_{\phi} = 1/2 (3(\cos^2\phi) - 1) \]
Crystal Structure and Hydrogen Bonding System in Cellulose I\textsubscript{a} from Synchrotron X-ray and Neutron Fiber Diffraction

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Example: Polymer Diffraction (cont’d)