neutron scattering

Basic Introduction to Small Angle Scattering

by Roger Pynn
We Measure Neutrons Scattered from a Sample

Φ = number of incident neutrons per cm² per second

σ = total number of neutrons scattered per second / Φ

\[
\frac{d\sigma}{d\Omega} = \frac{\text{number of neutrons scattered per second into } d\Omega}{\Phi d\Omega}
\]

\[
\frac{d^2\sigma}{d\Omega dE} = \frac{\text{number of neutrons scattered per second into } d\Omega \text{ & } dE}{\Phi d\Omega dE}
\]

σ measured in barns:
1 barn = 10⁻²⁴ cm²

Attenuation = \( \exp(-N\sigma t) \)
N = # of atoms/unit volume
t = thickness
Scattering from Many Atoms

• Neutrons are scattered by nuclei
  – The range of nuclear forces is femtometers – much less than the neutron wavelength so the scattering is point like (ripples on a pond)

• Energy of (thermal) neutron is too small to change nuclear energy
  – If the nucleus is fixed, the scattering is elastic

• We can add up the (elastic) scattering from an assembly of nuclei:

\[
\frac{d\sigma}{d\Omega} = \sum_{i,j} b_i b_j e^{i(k_0 - k')(\vec{R}_i - \vec{R}_j)} = \sum_{i,j} b_i b_j e^{-i\vec{Q} (\vec{R}_i - \vec{R}_j)}
\]

where the wavevector transfer \( Q \) is defined by \( \vec{Q} = \vec{k}' - \vec{k}_0 \)

  – \( b_i \) is called the coherent scattering length of nucleus \( i \)
  – \( k \) is the incident neutron wavevector \( (2\pi/\lambda) \); \( k' \) is the scattered wavevector
  – The calculation assumes the scattering is weak (called Born Approximation)
The Success of Neutron Scattering is Rooted in the Neutron’s Interactions with Matter

- Interact with nuclei not electrons
- Isotopic sensitivity (especially D and H)
- Penetrates sample containment
- Sensitive to bulk and buried structure
- Simple interpretation – provides statistical averages, not single instances
- Wavelength similar to inter-atomic spacings
- Energy similar to thermal energies in matter
- Nuclear and magnetic interactions of similar strength
Scattering Triangle

Neutron diffraction measures the differential scattering cross section \( d\sigma/d\Omega \) as a function of the scattering wavevector \( Q \).

For elastic scattering, \( k = k' \) so \( Q = 2 \ k \sin \theta = (2 \ \pi/\lambda) \sin \theta \).

The distance probed in the sample is: \( d = 2\pi / Q \).

(Combining the two equations gives Bragg’s Law: \( \lambda = 2 \ d \sin \theta \))
Small Angle Neutron Scattering (SANS) is used to measure large objects (~10 nm to ~1 μm).

Small Q => large d (because $d = \frac{2\pi}{Q}$)

Large d => small $\theta$ (because $\lambda = 2d \sin \theta$)

Scattering at small angles probes large length scales.

Typical scattering angles for SANS are ~ 0.3° to 5°
Two Views of the Components of a Typical Reactor-based SANS Diffractometer

Note that SANS, like other diffraction methods, probes material structure in the direction of (vector) \( \mathbf{Q} \)
The NIST 30m SANS Instrument Under Construction
Where Does SANS Fit As a Structural Probe?
Typical SANS Applications

• Biology
  – Organization of biomolecular complexes in solution
  – Conformation changes affecting function of proteins, enzymes, protein/DNA complexes, membranes etc
  – Mechanisms and pathways for protein folding and DNA supercoiling

• Polymers
  – Conformation of polymer molecules in solution and in the bulk
  – Structure of microphase separated block copolymers
  – Factors affecting miscibility of polymer blends

• Chemistry
  – Structure and interactions in colloid suspensions, microemulsions, surfactant phases etc
  – Mechanisms of molecular self-assembly in solutions
Scattering Length Density

• Remember
  \[ \frac{d\sigma}{d\Omega} = b_{coh}^2 \left( \left| \int d\vec{r} e^{-i\vec{Q} \cdot \vec{r}} n_{nucl}(\vec{r}) \right|^2 \right) \]

• What happens if Q is very small?
  – The phase factor will not change significantly between neighboring atoms
  – We can average the nuclear scattering potential over length scales \( \sim 2\pi/10Q \)
  – This average is called the scattering length density and denoted \( \rho(\vec{r}) \)

• How do we calculate the SLD?
  – By hand: let us calculate the scattering length density for quartz – SiO\(_2\)
  – Density is 2.66 gm.cm\(^{-3}\); Molecular weight is 60.08 gm. mole\(^{-1}\)
  – Number of molecules per Å\(^3\) = \( N = 10^{-24}(2.66/60.08) \times N_{avagadro} = 0.0267 \) molecules per Å\(^3\)
  – SLD=\( \Sigma b/volume = N(b_{Si} + 2b_O) = 0.0267(4.15 + 11.6) \times 10^{-5} \) Å\(^{-2}\) = 4.21 \times 10^{-6} \) Å\(^{-2}\)

• A uniform SLD causes scattering only at Q=0; spatial variations in the SLD cause scattering at finite values of Q
### SLD Calculation

- [www.ncnr.nist.gov/resources/sldcalc.html](http://www.ncnr.nist.gov/resources/sldcalc.html)
- Need to know chemical formula and density
- Not relevant for SLD
- Enter

<table>
<thead>
<tr>
<th>Compound</th>
<th>Density (g/cm³)</th>
<th>Wavelength (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆H₁₂</td>
<td>0.86</td>
<td>6</td>
</tr>
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</table>

#### X-ray values

<table>
<thead>
<tr>
<th>Neutron SLD</th>
<th>Cu Ka SLD</th>
<th>Mo Ka SLD</th>
</tr>
</thead>
<tbody>
<tr>
<td>-3.07E-7 (Å⁻²)</td>
<td>8.34E-6 + 9.36E-9i (Å⁻²)</td>
<td>8.33E-6 + 2.08E-9i (Å⁻²)</td>
</tr>
</tbody>
</table>

#### Background

<table>
<thead>
<tr>
<th>Neutron Inc. XS</th>
<th>Neutron Abs. XS</th>
<th>Neutron 1/e length</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.93; 33.4 (cm⁻¹)</td>
<td>0.0823 (cm⁻¹)</td>
<td>0.166 (cm)</td>
</tr>
</tbody>
</table>

Determine best sample thickness

Note units of the cross section – this is cross section per unit volume of sample.
SANS Measures Particle Shapes and Inter-particle Correlations

\[
\frac{d\sigma}{d\Omega} = \left\langle b \right\rangle^2 \int_{\text{space}} d^3r \int_{\text{space}} d^3r' n_N (\vec{r}) n_N (\vec{r}') e^{i\vec{Q} \cdot (\vec{r} - \vec{r}')} \\
= \int_{\text{space}} d^3R \int_{\text{space}} d^3R' \left\langle n_P (\vec{R}) n_P (\vec{R}') \right\rangle e^{i\vec{Q} \cdot (\vec{R} - \vec{R}')} \left\langle (\rho - \rho_0) \int_{\text{particle}} d^3x e^{i\vec{Q} \cdot \vec{x}} \right\rangle^2
\]

\[
\frac{d\sigma}{d\Omega} = (\rho - \rho_0)^2 \left| F(\vec{Q}) \right|^2 V_p^2 N_p \int_{\text{space}} d^3R G_p (\vec{R}) e^{i\vec{Q} \cdot \vec{R}}
\]

where \( G_p \) is the particle - particle correlation function (the probability that there is a particle at \( \vec{R} \) if there's one at the origin) and \( \left| F(\vec{Q}) \right|^2 \) is the particle form factor :

\[
\left| F(\vec{Q}) \right|^2 = \frac{1}{V_p^2} \left\langle \left| \int_{\text{particle}} d^3x e^{i\vec{Q} \cdot \vec{x}} \right|^2 \right\rangle
\]
Scattering from Independent Particles

Scattered intensity per unit volume of sample = \[ I(\vec{Q}) = \frac{1}{V} \frac{d\sigma}{d\Omega} = \frac{1}{V} \left| \int \rho(\vec{r}) e^{i\vec{Q} \cdot \vec{r}} d\vec{r} \right|^2 \]

For identical particles

\[ I(Q) = \frac{N}{V} (\rho_p - \rho_0)^2 V_p^2 \left\langle \frac{1}{V_p} \int e^{iQ \cdot \vec{r}} d\vec{r} \right\rangle^2 \]

contrast factor \hspace{1cm} particle form factor \( |F(\vec{Q})|^2 \)

Note that \[ I(0) = \frac{N}{V} (\rho_p - \rho_0)^2 V_p^2 \]

Particle concentration \( c = NV_p / V \) and particle molecular weight \( M_w = \rho V_p N_A \)

where \( \rho \) is the particle mass density and \( N_A \) is Avagadro's number

so \[ I(0) = \frac{cM_w}{\rho N_A} (\rho_p - \rho_0)^2 \] provides a way to find the particle molecular weight
Scattering for Spherical Particles

The particle form factor \( \left| F(\vec{Q}) \right|^2 = \left| \int_V d\vec{r} e^{i\vec{Q} \cdot \vec{r}} \right|^2 \) is determined by the particle shape.

For a sphere of radius \( R \), \( F(Q) \) only depends on the magnitude of \( Q \): 

\[
F_{\text{sphere}}(Q) = 3V_0 \left[ \frac{\sin QR - QR \cos QR}{(QR)^3} \right] \equiv \frac{3V_0}{QR} j_1(QR) \rightarrow V_0 \text{ at } Q = 0
\]

Thus, as \( Q \to 0 \), the total scattering from an assembly of uncorrelated spherical particles [i.e. when \( G(\vec{r}) \to \delta(\vec{r}) \)] is proportional to the square of the particle volume times the number of particles.

![Graph of 3j_1(x)/x]
Radius of Gyration Is the Particle “Size” Usually Deduced From SANS Measurements

If we measure $\bar{r}$ from the centroid of the particle and expand the exponential in the definition of the form factor at small $Q$:

$$F(Q) = \int \bar{r} e^{iQ \cdot \bar{r}} \approx V_0 + i \int Q \cdot \bar{r} d^3 r - \frac{1}{2} \int (Q \cdot \bar{r})^2 d^3 r + \ldots$$

$$= V_0 \left[ 1 - \frac{Q^2}{2} \frac{\int \cos^2 \theta \sin \theta d\theta \int r^2 d^3 r}{\int d^3 r} + \ldots \right] = V_0 \left[ 1 - \frac{Q^2 r_g^2}{6} + \ldots \right] \approx V_0 e^{-\frac{Q^2 r_g^2}{6}}$$

where $r_g$ is the radius of gyration is $r_g = \int R^2 d^3 r / \int d^3 r$. It is usually obtained from a fit to SANS data at low $Q$ (in the so-called Guinier region) or by plotting $\ln(\text{Intensity}) \propto Q^2$. The slope of the data at the lowest values of $Q$ is $r_g^2/3$. It is easily verified that the expression for the form factor of a sphere is a special case of this general result.
Incoherent Background and Absorption

- In addition to coherent (Q-dependent) scattering, neutrons may be scattered incoherently.
- Incoherent scattering is not directionally (Q) dependent.
  - In SANS (or reflectometry) measurements it is a uniform background.
- Incoherent scattering arises from two sources:
  - Spin incoherent scattering (the neutron-nucleus state can be singlet or triplet and these have different scattering lengths).
  - Isotopic incoherent scattering.
- Look up incoherent scattering lengths (included in NIST SLD calculator – see next VG).
- Neutrons may also be absorbed by some nuclei.
Calculating Form Factors

- www.ncnr.nist.gov/resources/simulator.html
- Note: \( T(1 \text{ mm } \text{H}_2\text{O}) = 0.5; \ T(1 \text{ mm } \text{D}_2\text{O}) = 0.9 \)
  \[ \frac{d\sigma}{d\Omega} (\text{H}_2\text{O}) = 1 \text{ cm}^{-1}; \ \frac{d\sigma}{d\Omega} (\text{D}_2\text{O}) = 0.06 \text{ cm}^{-1} \)

No background

H\text{2}O background
Both tubes contain borosilicate beads + pyrex fibers + solvent. (A) solvent refractive index matched to pyrex; (B) solvent index different from both beads and fibers – scattering from fibers dominates

* Chart courtesy of Rex Hjelm
Contrast Variation

\[ \text{Scattering Length Density (} 10^{10} \text{ cm}^{-2} \) \]

- \( \text{CD}_2 \)
- Deuterated RNA
- Deuterated Protein
- Water
- RNA
- DNA
- Protein
- Lipid Head Group
- \( \text{CH}_2 \)

\[ \Delta \rho \]

% \( \text{D}_2\text{O} \) in Solvent
# Isotopic Contrast for Neutrons

<table>
<thead>
<tr>
<th>Hydrogen Isotope</th>
<th>Scattering Length $b$ (fm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1$H</td>
<td>-3.7409 (11)</td>
</tr>
<tr>
<td>$^2$D</td>
<td>6.674 (6)</td>
</tr>
<tr>
<td>$^3$T</td>
<td>4.792 (27)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Nickel Isotope</th>
<th>Scattering Lengths $b$ (fm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{58}$Ni</td>
<td>15.0 (5)</td>
</tr>
<tr>
<td>$^{60}$Ni</td>
<td>2.8 (1)</td>
</tr>
<tr>
<td>$^{61}$Ni</td>
<td>7.60 (6)</td>
</tr>
<tr>
<td>$^{62}$Ni</td>
<td>-8.7 (2)</td>
</tr>
<tr>
<td>$^{64}$Ni</td>
<td>-0.38 (7)</td>
</tr>
</tbody>
</table>
Using Contrast Variation to Study Compound Particles

Examples include nucleosomes (protein/DNA) and ribosomes (proteins/RNA)

\[ I_1(Q) = (\rho_1 - \rho_2)^2 F_1^2 \]

\[ I_2(Q) = (\rho_2 - \rho_1)^2 F_2^2 \]

\[ I_3(Q) = \frac{(\rho_1 - \rho_0)^2}{(\rho_1 - \rho_2)^2} I_1(Q) - \frac{(\rho_2 - \rho_0)^2}{(\rho_1 - \rho_2)^2} I_2(Q) \]

\[ = 2(\rho_1 - \rho_0)(\rho_2 - \rho_0) F_1 F_2 \frac{\sin(QR_{12})}{QR_{12}} \]

\[ = 0 \text{ at } Q = \pi/R_{12} \]

Viewgraph from Charles Glinka (NIST)
What can we Learn from SANS?

Zero Q intercept - gives particle volume if concentration is known

Guinier region (slope = \(-r_g^{2/3}\) gives particle “size”)

Dimensionality of particle (slope = -1 for rods, -2 for sheets, \(-D_f\) for a mass fractal)

Porod region - gives surface area and surface fractal dimension 
{slope = -(6-D_s)}
Sample Requirements for SANS

- Monodisperse particles, non-interacting to measure shape
- Concentration: 1-5 mg/ml
- Volume: 350-700 μl per sample
- Data collection time: 0.5-6 hrs per sample
- Typical biology experiment: 2-4 days
- Deuterated solvent is highly desirable
- Multiple concentrations are usually necessary.
- Specific deuteration may be necessary.
- Multiple solvents of different deuteration are highly desirable → contrast variation.
References

• Viewgraphs describing the NIST 30-m SANS instrument

• SANS data can be simulated for various particle shapes using the programs available at:

• To choose instrument parameters for a SANS experiment at NIST go to:
  – www.ncnr.nist.gov/resources/sansplan.html

• A very good description of SANS experiments can be found at:
  http://www.strubi.ox.ac.uk/people/gilbert/sans.html
END