Analysis of SANS and USANS Data

Steve Kline

NCNR Summer School

Neutron Small Angle Scattering and Reflectometry

June 26-30, 2006
Outline

• Basic Equations
• Model-independent methods
  Guinier, Porod, Invariant
• Non-Linear Model Fitting
  Particles, Polymers, Materials
• Global Fitting
• Anisotropic Scattering
• Transforms
• Ab initio modeling

Easy

More involved
The Basics

Starting from: \[
\frac{d\sigma}{d\Omega}(\vec{q}) = \frac{1}{N} \left| \sum_{i}^{N} b_i e^{i\vec{q} \cdot \vec{r}_i} \right|^2
\]

- We can replace the sum over atoms with an integral over the scattering length density \[\sum_{i}^{N} b_i \rightarrow \int \rho(\vec{r}) d\vec{r}\]

- Normalizing by sample volume and introducing scattering length density

\[
\frac{d\Sigma}{d\Omega}(\vec{q}) = \frac{N}{V} \frac{d\sigma}{d\Omega}(\vec{q}) = \frac{1}{V} \left| \int_{V} \rho(\vec{r}) e^{i\vec{q} \cdot \vec{r}} d\vec{r} \right|^2
\]

- Inhomogeneities in \(\rho(\vec{r})\) give rise to small angle scattering

\[\Sigma = \sigma/V\] is the “macroscopic cross section”
Scattering Basis

Different systems each have a natural basis - and all are equivalent.

- This is especially true if the scattering is from “countable” units.

\[ \left( \int_{V} f(\mathbf{r}) \, d\mathbf{r} \right)^2 \rightarrow \sum_{i}^{N} \sum_{j}^{N} f(\mathbf{r}_i - \mathbf{r}_j) \]

Polymers monomer unit
Particulates per particle
Proteins polypeptide subunits

- A statistical description may also be appropriate

\[ \rho(r) \rightarrow \gamma(r) \]

Non-particle correlation function
Measured Intensity

After reducing the raw data - you will typically have:

I(Q) vs. Q
Units of intensity are cm\(^{-1}\) ster\(^{-1}\)
Units of Q are length\(^{-1}\)

\[ I(Q) = \frac{8\pi\xi^3 (\Delta \rho)^2 \phi(1 - \phi)}{(1 + (Q\xi)^2)^2} \]

\[ I(Q) = \frac{\phi}{V_p} \left[ 3V_p (\Delta \rho) (\sin(QR) - QR \cos(QR)) \right]^2 \]

\[ I(Q) = \frac{2\phi(\Delta \rho)^2 Zv_m (e^{-x} + x - 1)}{x^2} \quad x = (QR_g)^2 \]
Model Independent Analysis

What information can you obtain?

• Invariant
  - volume fraction, data consistency

• Porod Limit
  - specific surface area, surfactant head group area

• Guinier Analysis
  - general or specific dimensions

• I(Q=0)
  - particle volume, molecular weight
Scattering Invariant

10% black
90% white
in each square

- Scattered intensity for each would certainly be different

\[ Q_I = \int_{0}^{\infty} q^2 \frac{d\Sigma}{d\Omega} (q) \, dq \]

- For an incompressible, two-phase system:

\[ Q_I = 2\pi^2 \Delta \rho^2 \phi (1 - \phi) \]

- Domains can be in any arrangement

*Guinier and Fournet, pp. 75-81.

**Need “wide” Q-range to do integration
Porod Scattering

• At large $q$: $I(q) \propto q^{-4}$

\[
\lim_{q \to \infty} \frac{d\Sigma}{d\Omega} (q) = C_p / q^4 = 2\pi \Delta \rho^2 S_v / q^4
\]

$S_v = \text{specific surface area of sample}$

*Glatter and Kratky, pp. 30-31.

**Need “sharp” interface and “high” $Q$
Guinier Analysis

Guinier Approximation:
\[ I(Q) \approx I(0)e^{-\frac{1}{3}R_g^2Q^2} \]

Guinier Plot:
\[ \ln[I(Q)] = \ln[I(0)] - Q^2R_G^2/3 \]

Guinier Radius = \( R_g \)
= RMS distance from “center of scattering density”

Sphere:
\[ R_g^2 = \frac{3}{5} R^2 \]

Cylinder:
\[ R_g^2 = \frac{L^2}{12} + \frac{d^2}{8} \]

Gaussian Coil:
\[ R_g^2 = \frac{1}{6} \langle L^2 \rangle \]

**Need “dilute” particles and “low” Q**
Zero angle scattering

\[ I(Q = 0) = \frac{1}{V} \left( \int_V \rho(\vec{r}) d\vec{r} \right)^2 \]

becomes

\[ I(Q = 0) = \frac{N}{V} (\rho_p - \rho_o)^2 V_p^2 \]

for \( N \) uniform particles in volume \( V \), each with SLD \( \rho_p \) and volume \( V_p \)

In terms of concentration:

\[ c(\text{mg/ml}) = \frac{N}{V} \rho V_p \]

\[ M_w = \rho V_p N_A \]

\( \rho = \text{mass density} \)

\[ I(Q = 0) = \frac{c M_w}{\rho N_A} (\rho_p - \rho_o)^2 \]

**Need “dilute” particles and “low” Q**
Determining the Contrast Match Point

\[ I(Q = 0) = \frac{N}{V} (\rho_p - \rho_o)^2 V_p^2 \]

- Make several measurements at different solvent SLDs
- Keep the same concentration
- Extrapolate data to \( I(Q=0) \)
- Plot \( \sqrt{I(Q=0)} \) vs. SLD
- Don’t forget to correct for the incoherent background contribution
- For composite particles, \( I(Q=0) \) will never reach zero - but it will be a minimum at the average particle contrast

**Need “dilute” particles and “low” Q**
Non-Linear Model Fitting

One of the most commonly used methods
- a “forward” calculation
- many structures and interactions to choose from

- propose a structural model
- calculate I(Q)
- adjust structural parameters
- repeat until done
Resolution

All measured data is affected to some extent by the instrument configuration = “Resolution Smearing”

“True” $I(Q) \rightarrow I_s(Q)$

$Q = \frac{4\pi}{\lambda} \sin(\theta/2)$

- SANS uses pinhole collimation
- USANS uses slit collimation (more significant smearing)

Resolution effects should NEVER be ignored during analysis

- NCNR tools make it easy to include resolution
Non-Linear Model Fitting

- Non-linear least squares fitting to experimental data
- Use all the information you can to reduce the number of free model parameters
  - SLD’s
  - Concentrations
  - Lengths
- A “good” fit does not necessarily guarantee a perfect representation of the structure in the sample

**Need knowledge of sample and model**

<table>
<thead>
<tr>
<th>Point</th>
<th>parameters_sf</th>
<th>coef_sf</th>
<th>smear_coef_sf</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>scale</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>1</td>
<td>Radius (Å)</td>
<td>55</td>
<td>55</td>
</tr>
<tr>
<td>2</td>
<td>contrast (Å-2)</td>
<td>2e-06</td>
<td>2e-06</td>
</tr>
<tr>
<td>3</td>
<td>bkgd (cm-1)</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
Contrast Variation

Contrast Matching
reduce the number of phases “visible”

\[ \text{solvent} = \text{core} \]

\[ \text{solvent} = \text{shell} \]

- The two distinct two - phase systems can be easily understood
Global Fitting

Contrast variation
- same particles, different solvent
- $R$, $d_p$, $d$ are the same
- $d_{solv}$, background are different

SANS + USANS data
- same sample (same cell)
- all parameters are the same
- smearing, scaling different

**Need “correct” model**
Anisotropic Scattering

Elongated particles aligned by shear

Magnetic domains under an applied field

\[ I(Q) \propto (\Delta \rho^2 + \Delta M^2 \sin^2 \phi)P(Q)S(Q) \]

\[ \Box \text{M} = \text{magnetic contrast} \]

Analyze as a 2D pattern \( I(Q,\Box) \)
Transforms - $p(r)$

$p(r)$ is the probability that 2 randomly chosen points are at a distance $r$ apart.

If $I(Q)$ is measured over a wide enough Q-range, then one can compute $p(r)$ as the inverse transform:

$$p(r) = \frac{1}{2\pi^2} \int_0^\infty I(Q)Qr \sin(Qr) dQ$$

For a sphere:

$$p(r) = 12x^2(2 - 3x + x^3) \quad x = r/D$$

*See: D. Svergun, O. Glatter

**Need “dilute” particles and “wide” Q-range**
Ab initio methods

- Calculate $I(Q)$ for complex structures
- Biological molecules made up of subunits
- non-standard geometric shapes

$$I(Q) = \sum_{i=1}^{n} I_i(Q) + 2 \sum_{i \neq j} F_i(Q) F_j(Q) \frac{\sin(Qr_{ij})}{Qr_{ij}}$$

- fill volume with spheres on a grid
- need distance between every pair
- can be computationally intensive
- can optimize shape

**Need “dilute” particles and “burly” computer**
Summary

• Start Simple

• Work up to more complex

• Must use all other information available
• Must always make physical sense
• Must always check that approximations are valid
  - dilute, random, length scales, etc.

• Many tools available at the NCNR
• Many tools available on the web