Small Angle Neutron Scattering (SANS)

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• Common Features of SANS
• Scattering Principle
• SANS Instrument & Data Reduction
• Contrast
• Dilute Particulate Systems – Form Factor
  Data analysis
  Examples
• Concentrated Particulate Systems – Structure Factor
  Data analysis
  Examples
• Dilute Polymer Solutions
  Analysis for Gaussian Chain – Debye Function
  More Generalized Analysis – Zimm Plot
• Small Angle Diffraction Analysis
• Model Independent Scaling Method Analysis
• Summary
1. The $Q$ range of SANS: between 0.002 and 0.6 Å$^{-1}$ – achievable with long wavelengths of neutrons and low detecting angles

2. A powerful technique for *in-situ* study on the *global* structures of *isotropic* samples

3. Easy to play contrast with isotope substitution

4. Data analysis:
   (A) Model dependent: well-defined particulate systems (possible non-unique solutions)
   (B) Model independent: general feature of the structure
**Neutron Scattering Principle - I**

**General Equation**

\[
\frac{d^2\sigma}{d\Omega dE} = \frac{\text{neutron flux of the incident beam} \cdot d\Omega dE}{\text{The number of neutrons scattered per second into a solid angle } d\Omega \text{ with the final energy between } E \text{ and } E+dE}
\]

**For Elastic Scattering**

We do not analyze the energy but only count the number of the scattered neutrons

\[
\frac{d\sigma}{d\Omega} = \int_0^{\infty} \frac{d^2\sigma}{d\Omega dE} dE = \frac{\text{neutron flux of the incident beam} \cdot d\Omega}{\text{The number of neutrons scattered per second into a solid angle } d\Omega}
\]

[time\(^{-1}\)] [area\(^{-1}\)]

**Differential cross section**
Scattering vector, \( Q \)

\[
|Q| = |k_o - k_i| = \frac{4\pi}{\lambda} \sin\frac{\theta}{2}
\]

The measured intensity at \( Q \) (or \( \theta \)), \( I_m(Q) \) can be expressed as

\[
I_m(Q) = I_F \cdot \Omega_o \cdot \varepsilon \cdot T \cdot \frac{d\sigma}{d\Omega} \cdot (\frac{d\sigma}{d\Omega})_v \cdot A \cdot t
\]

- **Flux**
- **Solid angle**
- **Detector efficiency**
- **Sample transmission**
- **Differential cross-section**
- **Beam area on the sample**
- **Path length**

\[
\frac{d\sigma}{d\Omega}_{v,\text{sam}} = \left(\frac{d\sigma}{d\Omega}\right)_{v,\text{std}} \frac{I_{m,\text{sam}}(Q) \cdot A_{\text{std}} \cdot t_{\text{std}} \cdot T_{\text{std}}}{I_{m,\text{std}}(Q) \cdot A_{\text{sam}} \cdot t_{\text{sam}} \cdot T_{\text{sam}}}
\]
For $\lambda = 8$ Å and $\theta_{\text{min}} \sim 0.25^\circ$, $Q_{\text{min}} \sim 0.003$ Å$^{-1}$. Max. attainable length scale $= 2\pi/Q_{\text{min}} \sim 2000$ Å.
Current CNBC SANS Setup

M.-P. Nieh Y. Yamani, N. Kučerka and J. Katsaras

\[ Q_{\text{min}} \sim 0.006 \text{ Å}^{-1}: \text{Max. attainable length} = \frac{2\pi}{Q_{\text{min}}} \sim 1000 \text{ Å}. \]
Contrast — A Key Parameter

$$\left( \frac{d\sigma}{d\Omega} \right)_V = \frac{N}{V} \left( \rho_p - \rho_o \right)^2 V_p \rho \left( \rho \right)$$

Scattering intensity is proportional to “the square of the scattering length density difference between studied materials and medium” (known as “contrast factor”).

Ideally, we would like to increase the contrast yet without changing the chemical properties of the system. This is one of the greatest advantages using neutron scattering, since the neutron scattering lengths of isotopes can be very different.

<table>
<thead>
<tr>
<th>Biomaterials</th>
<th>( \rho, \text{Å}^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pepsin</td>
<td>7.0 E-06</td>
</tr>
<tr>
<td>Phosphorylase</td>
<td>5.6 E-06</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>3.0 E-06</td>
</tr>
<tr>
<td>H2O</td>
<td>1.0 E-06</td>
</tr>
<tr>
<td>D2O</td>
<td>-1.0 E-06</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Atom</th>
<th>Nucleus</th>
<th>( b_c ) ( (10^{-12} \text{ cm}) )</th>
<th>( \sigma_c ) ( (10^{-24} \text{ cm}^2) )</th>
<th>( \sigma_i ) ( (10^{-24} \text{ cm}^2) )</th>
<th>( \sigma_{abs} ) ( (10^{-24} \text{ cm}^2) )</th>
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</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>( ^1\text{H} )</td>
<td>-0.374</td>
<td>1.76</td>
<td>79.7</td>
<td>0.33</td>
</tr>
<tr>
<td>Deuterium</td>
<td>( ^2\text{H} )</td>
<td>0.667</td>
<td>5.59</td>
<td>2.01</td>
<td>0</td>
</tr>
<tr>
<td>Carbon</td>
<td>( ^{12}\text{C} )</td>
<td>0.665</td>
<td>5.56</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>( ^{14}\text{N} )</td>
<td>0.930</td>
<td>11.1</td>
<td>0</td>
<td>1.88</td>
</tr>
<tr>
<td>Oxygen</td>
<td>( ^{15}\text{O} )</td>
<td>0.580</td>
<td>4.23</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Fluorine</td>
<td>( ^{19}\text{F} )</td>
<td>0.556</td>
<td>4.03</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Phosphorous</td>
<td>( ^{31}\text{P} )</td>
<td>0.513</td>
<td>3.31</td>
<td>0</td>
<td>0.17</td>
</tr>
<tr>
<td>Chlorine</td>
<td>( ^{35}\text{Cl} )</td>
<td>0.958</td>
<td>11.53</td>
<td>5.9</td>
<td>33.6</td>
</tr>
</tbody>
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J. Pencer, V. N. P. Anghel, N. Kučerka and J. Katsaras,
SANS Analysis – Dilute Particulate Systems

\[
\left( \frac{d\sigma}{d\Omega} \right)_v = \frac{N}{V} (\rho_p - \rho_o)^2 V_p^2 P(\vec{Q}) S(\vec{Q})
\]

**orientational average**

\[
\left( \frac{d\sigma}{d\Omega} \right)_v = \frac{N}{V} \int \int \rho(\vec{r}_1)\rho(\vec{r}_2) \langle e^{-i\vec{Q} \cdot (\vec{r}_1 - \vec{r}_2)} \rangle d\vec{r}_1 d\vec{r}_2
\]

\[
= \frac{N}{V} \left| \int_{V_p} \Delta\rho(\vec{r}) \cdot \langle e^{-i\vec{Q} \cdot \vec{r}} \rangle d\vec{r} \right|^2
\]

\[
= \frac{N}{V} (\rho_p - \rho_o)^2 \cdot V_p^2 \cdot P(\vec{Q})
\]

\[
= \frac{(\rho_p - \rho_o)^2 N}{V} \sum_{k=1}^\infty \left| A_k(\vec{Q}) \right|^2
\]

**Particle Form Factor**

\[
A_k(\vec{Q}) = \int_{\text{particle } k} \langle e^{-i\vec{Q} \cdot \vec{r}} \rangle d\vec{r}
\]

**Amplitude of the Form Factor**

The form factor is determined by the structure of the particle.
Simulation of a particular system - Spheres

Since spheres are isotropic, there is no need to do orientational average.

\[ P(q) = \frac{1}{V_{\text{sphere}}} \left| \iiint_{V_{\text{sphere}}} e^{-i\vec{Q} \cdot \vec{r}} \, d\vec{r} \right|^2 \]

\[ = \frac{1}{V_{\text{sphere}}} \left| \int_{r=0}^{R} \int_{\theta=0}^{\pi} \int_{\varphi=0}^{2\pi} e^{-iQr\cos\theta} r^2 \sin\theta \, d\varphi \, d\theta \, dr \right|^2 \]

\[ = \frac{9}{(QR)^6} \left[ \sin(QR) - qR\cos(QR) \right]^2 \]

\[ \left( \frac{d\sigma}{d\Omega} \right)_v = \frac{N}{V} (\rho_{\text{sphere}} - \rho_o)^2 \cdot V_{\text{sphere}}^2 \cdot P(\vec{Q}) \]

\[ = \phi_{\text{sphere}} \cdot V_{\text{sphere}} \cdot \Delta\rho^2 \cdot \frac{9}{(QR)^6} \left[ \sin(QR) - QR\cos(QR) \right]^2 \]
# SANS Analysis – Dilute Particulate Systems

## Common form factors of particulate systems

<table>
<thead>
<tr>
<th>Morphologies</th>
<th>P(Q)</th>
<th>Morphologies</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Spheres</strong> (radius : R)</td>
<td>( \frac{9}{(QR)^6} [\sin(QR) - QR \cdot \cos(QR)]^2 = A_{sph}(QR) )</td>
<td><img src="image" alt="Spheres" /></td>
</tr>
<tr>
<td><strong>Spherical shells</strong> (outer radius: R₁, inner radius: R₂)</td>
<td>( \frac{\left[ R_1^3 \cdot A_{sph}(QR_1) - R_2^3 \cdot A_{sph}(QR_2) \right]^2}{(R_1^3 - R_2^3)^2} )</td>
<td><img src="image" alt="Spherical Shells" /></td>
</tr>
<tr>
<td><strong>Triaxial ellipsoids</strong> (semiaxes: a,b,c)</td>
<td>( \int_0^1 \int_0^1 A_{sph}^2 [Q \sqrt{a^2 \cos^2(\pi x/2) + b^2 \sin^2(\pi x/2)(1-y^2) + c^2 y^2}] , dx , dy )</td>
<td><img src="image" alt="Triaxial Ellipsoids" /></td>
</tr>
<tr>
<td><strong>Cylinders</strong> (radius: R, length: L)</td>
<td>( 4 \int_0^1 \frac{J_1^2[QR\sqrt{1-x^2}]}{[QR\sqrt{1-x^2}]^2} \frac{\sin^2(QLx/2)}{(QLx/2)^2} , dx )</td>
<td><img src="image" alt="Cylinders" /></td>
</tr>
<tr>
<td><strong>Thin disk</strong> (radius: R)</td>
<td>By setting L = 0 ( \frac{2 - J_1(2QR)/QR}{Q^2 R^2} )</td>
<td><img src="image" alt="Thin Disk" /></td>
</tr>
<tr>
<td><strong>Long rod</strong> (length: L)</td>
<td>By setting R = 0 ( \frac{2}{QL} \int_0^Q \frac{\sin(t)}{t} , dt - \frac{\sin^2(QL/2)}{(QL/2)^2} )</td>
<td><img src="image" alt="Long Rod" /></td>
</tr>
</tbody>
</table>

“Structure Analysis by Small Angle X-Ray and Neutron Scattering” L. A. Feigen and D. I. Svergun
**Procedure of Data Analysis**

1. Select a model for possible structure of the aggregates
2. Fit the experimental data using the selected model (Fix the values of any “known” physical parameters as many as possible)
3. Is it a good fit?
   - Yes: A Possible Structure
   - No: Change the model
Examples of A Dilute Particulate System

Sample: A mixture of dimyristoyl and dihexanoyl phosphatidylcholine (DMPC, DHPC), and dimyristoyl phosphatidylglycerol (DMPG) in D$_2$O; total lipid conc. = 0.1 wt.%

In these cases, the known (or constrained) physical parameters are SLDs of lipid and D$_2$O and the bilayer thickness. Thus, there are only 2 parameters to be determined through fitting in each case.

Oblate shells: $a=180$ Å, $b=62$ Å
Spherical shells: $R=133$ Å, $p=0.15$
Bilayer disks: $R=156$ Å, $L=45$ Å
SANS Analysis – Concentrated Particulate Systems

\[
\left( \frac{d\sigma}{d\Omega} \right)_v = \frac{N}{V} (\rho_p - \rho_o)^2 V_p^2 P(\mathbf{Q}) S(\mathbf{Q})
\]

\[
\frac{d\sigma}{d\Omega} = \frac{N}{V} \int \int \rho(\mathbf{r}_1) \rho(\mathbf{r}_2) \langle e^{-i\mathbf{Q} \cdot (\mathbf{r}_1 - \mathbf{r}_2)} \rangle \, d\mathbf{r}_1 d\mathbf{r}_2
\]

\[
= \frac{1}{V} \sum_{k=1}^{N} < |A_k(\mathbf{Q})|^2 >
\]

\[
+ \frac{1}{V} \left< \sum_{k=1}^{N} \sum_{j \neq k} A_k(\mathbf{Q}) A_j^*(\mathbf{Q}) e^{-i\mathbf{Q} \cdot (\mathbf{R}_k - \mathbf{R}_j)} \right>
\]

\[
\sim \frac{1}{V} \sum_{k=1}^{N} < |A_k(\mathbf{Q})|^2 > \left\{ 1 + \sum_{j \neq k} \langle e^{-i\mathbf{Q} \cdot (\mathbf{R}_k - \mathbf{R}_j)} \rangle \right\}
\]

\[
= \frac{N}{V} (\rho_p - \rho_o)^2 V_p^2 \cdot P(\mathbf{Q}) \cdot S(\mathbf{Q})
\]

Structure Factor

In dilute solution, \( S(\mathbf{Q}) = 1 \)
SANS Analysis – Concentrated Particulate Systems

Models for $S(Q)$

- Hard Sphere
- Square Well Attraction
- Coulomb Repulsion

$S(Q=0) = kT(\partial N/\partial \pi)$

Osmotic compressibility

$S(0)>1$ more compressible
$S(0)<1$ less compressible

CNBC June 5, 2013
Simulation Result using Coulomb Repulsive Model

\[ Q_{\text{max}} \propto \phi^{\frac{1}{3}} \]

Fixed, due to \( P(Q) \)

- \( R = 50 \, \text{Å} \)
- \( Q = 50 \)
- \( C_{\text{salt}} = 0.001\text{M} \)

\( I(\text{cm}^{-1}) \) vs. \( Q(\text{Å}^{-1}) \)
“Bicelles” composed of DMPC/DHPC and small amount of Tm$^{3+}$

### SANS Analysis – Concentrated Particulate Systems

![Graph showing SANS analysis with data points and a trend line for different total lipid concentrations.](image-url)
“Gaussian Chain” Model: The effective bond length, $a$, of one step (composed of several segments of the chain) has a Gaussian distribution.

$$a^2 = \sum_{n=1}^{N} \frac{|\overrightarrow{R}_n - \overrightarrow{R}_{n-1}|^2}{N}$$

The distribution vector between any two “steps” $m$, $n$, i.e., $(\overrightarrow{R}_n - \overrightarrow{R}_m)$ is Gaussian

$$\Phi(\overrightarrow{R}_n - \overrightarrow{R}_m, n-m) = \left[ \frac{3}{2\pi a^2 |n-m|} \right]^{3/2} \exp\left[ - \frac{3(\overrightarrow{R}_n - \overrightarrow{R}_m)^2}{2a^2 |n-m|} \right]$$

This model is adequate for describing long polymer chains in a theta solvent, where the segment-segment and segment-solvent interaction and the excluded volume effect are canceled out. Such polymer chains are also known as “phantom” chains.

The scattering from a Gaussian Chain can be described as a Debye function

\[
\frac{d\sigma}{d\Omega} = N_p \Phi_p (\rho_p - \rho_o)^2 V_M \left( \frac{2}{Q^4 R_G^4} (e^{-Q^2 R_G^2} - 1 + Q^2 R_G^2) \right)
\]

Debye Function

- \(V_M\): molecular volume of monomer
- \(N_p\): degree of polymerization

Radius of Gyration, \(R_G^2 = \frac{1}{2N^2} \sum_{m,n} (R_n - R_m)^2\)
Debye function is not always adequate to describe the polymer conformation!
An example is that as polymers are in a good solvent, the intensity at high Q regime will decay with $Q^{-5/3}$ instead of $Q^{-2}$.

### Polylactide in CD$_2$Cl$_2$

<table>
<thead>
<tr>
<th>$\phi_p$</th>
<th>$N_p$</th>
<th>$R_G$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1%</td>
<td>111</td>
<td>39</td>
</tr>
<tr>
<td>2%</td>
<td>74</td>
<td>32</td>
</tr>
<tr>
<td>4%</td>
<td>42</td>
<td>27</td>
</tr>
</tbody>
</table>

deviation from the data!
For dilute polymer solutions, the scattering intensity at low q regime (i.e., $q \cdot R_G < 1$) can be expressed as a function of $R_G$, $M_W$ (molecular weight), $A_2$ (second virial coefficient) and $\phi_p$ (volume fraction of the polymer)

$$\frac{V_m \phi_p \Delta \rho^2}{I(Q)} = (1 + Q^2 R_G^2/3 + \ldots)(\frac{1}{N_p} + 2\phi_p A_2 + \ldots)$$

$V_m$ is the molecular volume of the monomer

$N_p$ is the degree of polymerization

$R_G$, $N_p$ and $A_2$ can be obtained by Zimm plot, where

$$\frac{V_m \phi_p \Delta \rho^2}{I(Q)}$$

is plotted against $(Q^2 + c\phi_p)$ and two extrapolation lines

for $Q=0$ and $\phi=0$ are also obtained ($c$ is an arbitrary number.).

The slope of the extrapolation line for $\phi_p = 0$ is $R_G^2/3N_p$.

The slope of the extrapolation line for $Q = 0$ is $2A_2/c$.

The intercept of both extrapolation lines is $1/N_p$. 

Zimm Plot

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June 5, 2013
Polylactide in CD$_2$Cl$_2$

Application of Zimm Plot

N$_p$ = 387
R$_G$ = 79 Å
A$_2$ = 88.6

Compared to the result obtained from Debye fitting:

<table>
<thead>
<tr>
<th>$\phi_p$</th>
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<th>R$_G$ (Å)</th>
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<td>4%</td>
<td>42</td>
<td>27</td>
</tr>
</tbody>
</table>

It requires at least two concentrations to make up a Zimm plot.
**Guinier regime** – low-Q scattering

\[
\left( \frac{d\sigma}{d\Omega} \right)_v = \frac{N}{V} (\rho_p - \rho_o)^2 \cdot V_p^2 \cdot [1 - (QR_G)^2/3 + \ldots]
\]

\[
\sim \phi_p (\rho_p - \rho_o)^2 V_p e^{-Q^2 R_G^2/3}
\]

\[
\ln\left[ \left( \frac{d\sigma}{d\Omega} \right)_v \right] = \ln(I_o) - Q^2 R_G^2/3
\]
Porod regime – high-Q (with respect to the length scale) scattering

The form factor of a sphere (radius of R)

\[
\begin{align*}
\left( \frac{d\sigma}{d\Omega} \right)_v &= \phi_{sphere} V_{sphere} \Delta\rho^2 \left( \frac{9}{(QR)^6} \right) \sin(QR) - QR \cdot \cos(QR) \right)^2
\end{align*}
\]

For QR>>1, i.e., focusing at smooth interface between two bulks 3-dimensionally

\[
\begin{align*}
\left( \frac{d\sigma}{d\Omega} \right)_v &\sim \frac{N_{sphere} V_{sphere}^2 \Delta\rho^2}{V} \frac{9}{2(QR)^4} = \frac{2\pi \Delta\rho^2 S_T}{VQ^4} \quad \text{total surface area}
\end{align*}
\]

For P = 0, 1, and 2, the scattering intensity is proportional to 1/Q, Q^2, and Q^4, respectively.

**Graph**

```
log I = \frac{2\pi \Delta\rho^2 S_T}{V}
```

-4

“Polymers and Neutron Scattering” J. S. Higgins and H. C. Benoit
If $I_m(Q)$ scales with $Q^{-n}$ over a wide range of $Q$. The “possible” structure can be obtained with some knowledge of the systems.

<table>
<thead>
<tr>
<th>particles</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Long Rigid rod</td>
<td>1</td>
</tr>
<tr>
<td>• Smooth 2-D Objects</td>
<td>2</td>
</tr>
<tr>
<td>• Linear Gaussian Chain</td>
<td>2</td>
</tr>
<tr>
<td>• Chain with Excluded Volume</td>
<td>5/3</td>
</tr>
<tr>
<td>• Interfacial Scattering from 3-D Objects with Smooth Surface (Porod regime)</td>
<td>4</td>
</tr>
<tr>
<td>with fractal Surface</td>
<td>3 ~ 4</td>
</tr>
</tbody>
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“Polymers and Neutron Scattering” J. S. Higgins and H. C. Benoit
Small Angle Diffraction

DOPC

\[ \frac{hQ}{2\pi} = \frac{h}{d} = \frac{2h \sin\left(\frac{\theta}{2}\right)}{\lambda} \]

\[ I \propto |F(Q)|^2 = \left| \sum b_i e^{-iQz_i} \right|^2 \]

\[ \rho(z) = \rho_0 + \sum_{h=1}^{h_{\text{max}}} F_h \cos\left(2\pi \frac{h z}{d}\right) \]
Example: Orientation of Cholesterol in Biomembrane

Take Home Messages

• SANS is a powerful tool to study the **global structures** of isotropic systems in the length scales ranging from 10 to 1000 Å.

• It is easy to vary the contrast in a neutron scattering experiment without significantly changing the chemical properties of the systems.

• The scattering function is proportional to the product of **contrast factor**, **form factor** (intraparticle scattering function) and **structure factor** (interparticle interaction).

• Structural parameters can be obtained through model dependent approaches, while model independent scaling law can also reveal possible morphology of the studied system.