Exploring the Nanoworld with Small-Angle Scattering

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1. Bragg's Law and wave interference
2. Why do Small-Angle Scattering?
3. Imaging vs. Scattering
4. Basic Concepts
   a) Cross Section
   b) Scattering Vector, Fourier Transform
   c) Scattering Length Density
5. Particle Scattering
   a) Guinier Approximation
   b) Porod's Law
6. Fractal Structures
7. Nanocomposites

SAXS & SANS: $\theta \leq 6^\circ$

Source of x-rays, light or neutrons

Methods of X-Ray and Neutron Scattering in Polymer Science

Ryong-Joon Roe
Crystals: Bragg’s Law and the scattering vector, $q$

\[ d = \frac{2}{q} \sin \left( \frac{\theta}{2} \right) \]

1. Ordered Structures give peaks in “reciprocal” Space.
2. Large structures scatter at small angles.
3. The relevant size scale is determined by \( 2\pi/q \)
4. $q$ is a vector.
5. You can’t always determine the real space structure from the scattering data.

Problem: Nanomaterials are seldom ordered
Disordered Structures in “Real Space”

Agglomerates

Precipitated Silica

\((\text{NaO}) (\text{SiO}_2)_{3.3} + \text{HCl} \rightarrow \text{SiO}_2 + \text{NaCl}\)

Water Glass

Aggregates

Complex
Hierarchical
Disordered

Difficult to quantify structure from images.

Primary Particles
Hierarchical Structure from Scattering

Four Length Scales
Four Morphology Classes

\[ q = \frac{2\pi}{d_{\text{Bragg}}} = \frac{4\pi}{\lambda} \sin\left(\frac{\theta}{2}\right) \]

USAS
SAS

Exponents related to morphology

\[ q [\text{Å}^{-1}] \sim \text{Length}^{-1} \sim \sin(\theta/2) \]
Why Reciprocal Space?

Isotactic polystyrene foams prepared by TIPS

Jim Aubert, SNL

Characterizing Disordered Systems in Real Space

Electron Density Distribution

\[ n(r) \]

Throw out phase information

Correlation Function of the Electron Density Distribution

\[ \Gamma_n(r) = \int n(u)n(u + r)du \]

Real space

\[ r \]

\[ \xi \]

Depends on latitude and longitude. Too much information to be useful.

Depends on separation distance. Retains statistically significant info.

Resolution problems at small \( r \)
Opacity problems for large \( r \)
2-dimensional
Operator prejudice

Problems with real space analysis
Imaging vs. Scattering

\[ \Gamma_n(r) = \int n(u) n(u + r) du \]

\[ I_{\text{scatt}}(q) = n(r) e^{iqr} dr \]


Anodized Aluminum

Why is there a peak?
What is the meaning of the peak position?
Why did the peak disappear for the 64° curve.
What is the meaning of “Intensity (cm⁻¹)”
Angle dependence

$q$

$\phi = 0^\circ$

$\phi = 64^\circ$

$\phi = 53^\circ$

$\phi = 45^\circ$

$\phi = 0^\circ$

Intensity (cm$^{-1}$)

$q$ (Å$^{-1}$)
Intensity and Differential Scattering Cross Section

\[ J \equiv \frac{d}{d} \left( \frac{\text{cm}^2}{\text{str}} \right) \] differential scattering cross section

Energy of a wave \( \sim \) Intensity \( \sim \) Amplitude\(^2 = |\mathbf{A}|^2\)

Plane wave: \( J_0 \)

Spherical wave: \( J_\Omega \)

Spherical wave:
\[
J_\Omega = \text{energy/unit solid angle/s} \quad \text{or} \quad \text{photons/unit solid angle/s}
\]

Plane wave:
\[
J_0 = \text{energy/unit area/s} \quad \text{or} \quad \text{photons/unit area/s}
\]
What is “Intensity?” What do we really measure?

\[
\frac{J}{J_A} \equiv \frac{d}{d} \left( \frac{\text{cm}^2}{\text{str}} \right) = \frac{\text{detected photons/solid angle/s}}{\text{incident photons/area/s}} = \frac{\text{cm}^2}{\text{str}} \sim V = \text{sample volume}
\]

\[
\frac{J(q)}{J_A V} \equiv \frac{J(q)}{J_A \cdot \text{area} \cdot \text{length}} = \frac{\text{detected photons/str/s}}{\text{incident photons} \cdot \text{area} \cdot \text{length/area/s}} = \frac{1}{\text{length} \cdot \text{str}}
\]

\[
= \frac{\text{fraction of the photons scattered into unit solid angle}}{\text{unit sample length}}
\]

\[
= \frac{d}{Vd} \left[ \text{cm}^{-1} \right] \quad \text{often called the scattering cross section or the intensity}
\]

Intensity = \( \frac{J}{J_0} \equiv \frac{d}{d} \left( \frac{\text{cm}^2}{\text{str}} \right) \)  \quad \text{Roe}

Intensity = \( \frac{J}{VJ_0} = \frac{d}{Vd} \left( \frac{1}{\text{cm}} \right) \)  \quad \text{Experimentalists, Irena, Indra}

Intensity = (arbitrary constant) \times J  \quad \text{Common Usage}
Generalized Bragg’s Law for Disordered System

What is the relationship between real space and reciprocal space when there are no crystal planes?

$$\mathcal{A} e^{i2\pi(\nu t - x/\lambda)}$$

Scattering from 2 atoms

2 atoms

many atoms
Scattering from two atoms

\[ A_0 e^{i2\pi(ut-x/\lambda)} \]

\[ \hat{S}_0 \times r \]

\[ 1 = \hat{S}_0 \times r \]

\[ 2 = \hat{S} \times r \]

Difference in path length

\[ \frac{\text{const} \times A_0}{r} e^{i2\pi(ut-(x+\delta)/\lambda)} = \frac{2}{r} \]

What are the units of \( \text{const} \)?

Instrument (\( q \))

\[ = \frac{2}{r} \left( \hat{S}_0 \times r - \hat{S} \times r \right) \]

Sample (\( r \))
Scattering vectors $s$ and $q$

\[ s = \frac{\hat{S} - \hat{S}_0}{\lambda} \text{ Called the scattering vector} \]

\[ |s| = s = \frac{|\hat{S} - \hat{S}_0|}{\lambda} = \frac{2\sin \theta}{\lambda} \]

\[ q = 2\pi s \text{ Also called the scattering vector} \]

\[ q = 2 \quad s = 4\sin \frac{\theta}{2} \]
Combine the two waves

Total Scattered Wave

$$\mathcal{A} = \mathcal{A}_1 + \mathcal{A}_2 = \frac{b}{R} \mathcal{A}_0 e^{i2\pi(\nu t - x/\lambda)} + \frac{b}{R} \mathcal{A}_0 e^{i2\pi(\nu t - x/\lambda) - 2\pi s r}$$

$$= \frac{b}{R} \mathcal{A}_0 e^{i2\pi(\nu t - x/\lambda)} (1 + e^{-i2\pi s r})$$

drops out

$$J = \mathcal{A} \mathcal{A}^* = (b \mathcal{A}_0)^2 (1 + e^{-i2\pi s r})(1 + e^{i2\pi s r})$$

scattering power, $b$, of an atom has the units of length
Adding up the Phases

\[ \mathcal{A}(s, r) = (b \mathcal{A}_0) \times \left( 1 + e^{-i2\pi s \cdot r} \right) \]

Two electrons

\[ \mathcal{A}(s, r_{1\ldots N}) = (b \mathcal{A}_0) \sum_{j=0}^{N} e^{-i2\pi s \cdot r_j} \]

Many electrons

Amplitude is the Fourier transform of the SLD distribution (almost)

Electron density distribution

\[ n(r) = \text{number of atoms in a volume element } dr = dx \, dy \, dz \text{ around point } r. \]

\[ \frac{\text{atoms}}{cm^3} \]

Scattering length density distribution

\[ \rho(r) = \text{scattering length in a volume element } dr = dx \, dy \, dz \text{ around point } r. \]

\[ \frac{\text{atoms}}{cm^3} \quad \frac{cm}{\text{atom}} = cm^2 \]
Scattering Length Density (SLD) Distribution

Fourier transform of the scattering length density distribution

\[
\frac{\mathcal{A}(q)}{\mathcal{A}_0} = \int b(r)n(r) e^{-iqr} dr = \int \rho(r) e^{-iqr} dr
\]

Can’t be measured

What we measure: Square of the Fourier transform of the SLD distribution

\[
I_{\text{scatt}}(q) = \frac{J_\Omega(q)}{J_0} = |\mathcal{A}(q)|^2 = \left| \int \rho(r) e^{-iqr} dr \right|^2
\]

Can’t be inverted

What we measure: Square of the Fourier transform of the SLD distribution

\[
I_{\text{scatt}} = n(r) e^{iqr} dr \quad \Gamma_n(r) = \int n(u)n(u + r) du
\]

q \quad 0

See slide 43
Scattering from Spherical Particle(s)

\[ A_1(q) = \frac{A(q)}{A_0} = \int \rho(r) e^{-iqr} \, dr \]

\[ = \int_0^\infty \rho(r) 4\pi r^2 \frac{\sin qr}{qr} \, dr \]

\[ = \frac{\rho_0 4\pi}{q} \int_0^R r \sin(qr) \, dr \]

\[ = \rho_0 4\pi R^3 \frac{(\sin qR - qR \cos qR)}{(qR)^3} \]

\[ N = \text{particle volume} \]

\[ = \rho_0 \frac{4\pi R^3}{3} \frac{3(\sin qR - qR \cos qR)}{(qR)^3} \]

\[ = \rho_0 N \frac{3(\sin qR - qR \cos qR)}{(qR)^3} \]

\[ I_N(q) = N \rho_0^2 v^2 \left[ \frac{3(\sin qR - qR \cos qR)}{(qR)^3} \right]^2 \]

N particles

\[ I(q) \sim N(\rho - \rho_0)^2 v^2 P(q) \]

solvent SLD
Particle in Dilute Solution

\[ A(q) = \frac{4\pi}{q} \left( \rho_2 - \rho_1 \right) \int_0^R r \sin(qr) \, dr + \rho_1 \int_0^{R_v} r \sin(qr) \, dr \]

\[ = \Delta\rho \left( \frac{3(\sin qR - qR \cos qR)}{(qR)^3} \right) + \rho_1 V \left( \frac{3(\sin qR_v - qR_v \cos qR_v)}{(qR_v)^3} \right) \]

\[ = 0 \text{ unless } qR \leq 1 \]
Small-Angle Scattering from Spheres

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

Large object scatter at small angles

Guinier Regime
Diameter = 140 Å

Porod (power-law) Regime

Silica in Polyurethane

Guinier Radius

Initial curvature is a measure of length

\[ \mathcal{I}(q) = \frac{A(q)}{A_0} = \int (r) e^{i q r} \, dr \]

\[ I(q) = |A(q)|^2 = rv^2 \left[ 1 - \frac{1}{3} q^2 R_g^2 + \cdots \right] \]

\[ R_g^2 = \frac{1}{v} \int r^2 (r) \, dr \text{ for any shape} \]

\[ (r) = \begin{cases} 1 & r < R \\ 0 & r > R \end{cases} \text{ sphere} \]

\[ R_g = \sqrt{\frac{3}{5}} R_{\text{hard}} \]
Guinier Fits

$I(q) \sim \exp \left( -\frac{1}{3} q^2 R_G^2 \right) + \cdots$

$R_G \xrightarrow{\text{dilute}} R_g$

Guinier radius    Radius-of-Gyration
Dense packing: Correlated Particles

Packing Factor = \( k = 8 \phi \)

Packing Factor \( \approx 6 \)
Colloidal Silica in Epoxy

EPON 862 + Cure W+ Silica


8/15/2013
NX School 24
Using $R_G$: Agglomerate Dispersion

Light Scattering

Hierarchical Structure from Scattering

Four Length Scales
Four Morphology Classes

\[ q = \frac{2\pi}{d_{\text{Bragg}}} = \frac{4\pi}{\lambda} \sin\left(\frac{\theta}{2}\right) \]

Exponents related to morphology

Intensity

USAXS
SAXS

\[ q [\text{Å}^{-1}] \sim \text{Length}^{-1} \sim \sin(\theta/2) \]

100,000 nm 200 nm 10 nm 0.5 nm

Agglomerate Aggregate Primary Particle Network “Polymer”
Fractal description of disordered objects

Real Space

\[ M \sim V \sim R^3 \]

\[ M \sim V \sim R^2 \]

\[ M \sim V \sim R \]

\[ M \sim V \sim R^{2.2} \]

Mass Fractal Dimension = \( d \)
Surface Fractal Dimension

Sharp interface

$S \sim R^2$

fractal or self-affine surface

$S \sim R^{ds}$
Scattering from Fractal Objects: Porod Slopes

\[ d = \text{Mass Fractal Dimension} \]
\[ d_s = \text{Surface Fractal Dimension} \]

\[ M \sim v \sim R^3 \quad \text{solid particle} \]
\[ M \sim v \sim Nv_u \sim R^d v_u \quad \text{mass fractal} \]
\[ S = R^2 \quad \text{solid particle} \]
\[ S \sim R^{d_s} \quad \text{surface fractal} \]

Small \( q \)
\[ I(q = 0) \sim v^2 \sim (Nv_u)^2 \sim R^{2d} \]

Large \( q \)
\[ I_p(qR \gg 1) \sim \frac{S_v}{q^x} \sim \frac{R^{d_s}}{q^x} \sim \left(\frac{R^{d_s+x}}{(qR)^x}\right) \]
Match at \( qR = 1 \)
\[ R^{d_s+x} \sim R^{2d} \]
\[ x = 2d - d_s \]

\[ I(q) \sim q^{-(2d-d_s)} \]
<table>
<thead>
<tr>
<th>Structure</th>
<th>Scaling Relation</th>
<th>Porod Slope: $d_s - 2d_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smooth Surface</td>
<td>$d_m = 3$</td>
<td>$qR &gt;&gt; 1$</td>
</tr>
<tr>
<td></td>
<td>$d_s = 2$</td>
<td>$-4$</td>
</tr>
<tr>
<td>Rough Surface</td>
<td>$d_m = 3$</td>
<td>$2 &lt; d_s \leq 3$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$-3 \leq \text{Slope} \leq -4$</td>
</tr>
<tr>
<td>Mass Fractal</td>
<td>$1 \leq d_s = d_m \leq 3$</td>
<td>$-1 \leq \text{Slope} \leq -3$</td>
</tr>
</tbody>
</table>

$I(q) = q^{d_s - 2d_m}$
Scattering from colloidal aggregates

Precipitated Silica

$R$, $r$

$log q$, $log I$

$qR = 1$

$qr = 1$

$q^{-d}$

$q^{-4}$
Morphology of Dimosil® Tire-Tread Silica

Two Agglomerate length Scales

- Soft = Chemically Bonded
- Hard = Physically Bonded

Light Scattering and USAXS analysis showing two distinct length scales:
- 116 µm
- 7.1 µm
- 3.2 µm
- 300 nm
- 126 Å

Dispersion and Reinforcement

Graph showing intensity vs. q (Å⁻¹)
Aggregates are robust

\[ R_{agg} = \frac{1}{q} \]

What is the ideal aggregate size?
Exploring the Nanoworld

1-d
Tubes
Carbon Nanotubes

2-d
Sheets
Layered Silicates

3-d
Spheres
Colloidal Silica

How valid are the cartoons?
What are the implications of morphology for material properties?

Answers come from Small-Angle Scattering.

The Promise of Nanotube Reinforcement

\[ E_\delta = \frac{E_{\text{composite}}}{E_{\text{matrix}}} \]

\[ E_\delta = 1 + 2.5\phi \]
\[ = 1 + 2\alpha\phi \approx 1 + 2000\phi \]
\[ = 1 + 0.4\alpha\phi \approx 1 + 400\phi \]

\( \alpha = \text{aspect ratio} \)
0.01% Loading CNTs in Bismaleimide Resin

\[
\frac{d\Sigma}{V dq} (\text{cm}^{-1})
\]

- **Simplified Tube**
  - \( r_o = 450 \, \text{Å} \)
  - \( L = 1 \times 10^6 \, \text{Å} \)
  - \( T = 100 \, \text{Å} \)

Graph showing intensity vs. \( q (\text{Å}^{-1}) \):
- **LIGHT**: -1
- **SAXS**: -4
- **PD**:

Scanning Electron Microscope (SEM) image showing nanotube structures.
0.05% Carbon in Bismaleimide Resin

Worm-like branched cluster

\[ \alpha = \frac{L_p}{r} = 4.5 \]

Intensity (cm\(^{-1}\))

- Wormlike Cluster
  - \( r = 450 \text{ Å} \)
  - \( T = 100 \text{ Å} \)
  - \( L_p = 2000 \text{ Å} \)
  - \( d_m = 2.85 \)

- Tube
  - \( r = 450 \text{ Å} \)
  - \( T = 100 \text{ Å} \)

0.05%
TEM of Nanocomposites

Hyperion MWNT in Polycarbonate

Pegel et al. Polymer (2009) vol. 50 (9) pp. 2123-2132
Morphology and Mechanical Properties

Halpin-Tsai, random, short, rigid fiber limit

\[ E = \frac{E_c}{E_m} = 1 + 0.4 \]\n\[ = 4.5 \]

No better than spheres

Assumes no connectivity
\( \alpha = 4.5 \)
Don’t Believe the Cartoons

1-d
Tubes

2-d
Sheets

3-d
Spheres

Carbon Nanotubes

Layered Silicates

Colloidal Silica

Conclusion

If you want to determine the morphology of a disordered material use small-angle scattering.
Extras
Correlation Functions

\[ I(q) = \langle |\mathcal{A}(q)|^2 \rangle = \left\langle \left| \int \rho(r) e^{-iqr} \, dr \right|^2 \right\rangle \]

\[ = \left\langle \left[ \int \rho(u) e^{-iqu} \, du \right] \left[ \int \rho(v) e^{iqv} \, dv \right] \right\rangle \]

\[ r = u - v \]

\[ = \int_{\text{volume}} \left\langle \left[ \int \rho(u) \rho(u+r) \, du \right] \right\rangle e^{-iqr} \, dr \]

\[ \Gamma_{\Delta \rho}(r) \text{ is the autocorrelation function of the fluctuation of scattering length density = Patterson function} \]

\[ \text{Scattering cross section is the Fourier transform of the ensemble average of the correlation function of the fluctuation of scattering length density.} \]
Not really a Fourier Transform

**Problem!**
Must know sample geometry

\[ I(q) = \int_V \Gamma_\rho(r) e^{-i\mathbf{q} \cdot \mathbf{r}} d\mathbf{r} \neq \int_{-\infty}^{\infty} \Gamma_\rho(r) e^{-i\mathbf{q} \cdot \mathbf{r}} d\mathbf{r} \]

\[ (0) = \langle \mathbf{v} \rangle \langle \mathbf{v} \rangle d\mathbf{v} = \langle \mathbf{v}^2 \rangle V \]

\[ (\mathbf{v}) = \langle \mathbf{v} \rangle \langle \mathbf{v} + \mathbf{v} \rangle d\mathbf{v} = \langle \mathbf{v} \rangle \langle \mathbf{v} \rangle V = \langle \mathbf{v} \rangle^2 V \]

\[ I(q) = \langle \mathbf{r} \rangle e^{i\mathbf{q} \cdot \mathbf{r}} d\mathbf{r} = \]
Extending to infinite integrals

\[ I(q) = \sqrt{\langle r \rangle e^{iqr} dr} = \sqrt{\langle r \rangle \langle \hat{V} \rangle^2 + \langle \hat{V} \rangle^2} e^{iqr} dr \]

\[ = \langle r \rangle \langle \hat{V} \rangle^2 e^{iqr} dr + \langle \hat{V} \rangle^2 e^{iqr} dr \]

\[ (r)e^{iqr} dr \quad q \neq 0 \]

\[ \eta(r) = \rho(r) - \langle \rho \rangle \]

Γ_η = Autocorrelation of the fluctuation of the scattering length density.

Scattering is determined by fluctuations of the density from the average

\[ \delta(q) = \int e^{-iqx} dx \]

A dilute gas does not “diffract” (scatter coherently).
SAXS from Polymers

Gaussian probability distribution

\[ w(N,r)dr = \frac{3}{2Nl^2} \exp\left(\frac{3r^2}{2Nl^2}\right)dr \]
Scattering from Polymer Coils

N bonds of length \( l \), \( N+1 \) beads of volume \( v_u \)
scattering length of one bead = \( \rho_0 v_u \)

\[
I(q) = \sum_{j=0}^{N} \left( \frac{v_u}{\rho_0} \right)^2 e^{i\mathbf{q} \cdot \mathbf{r}_{jk}} = \sum_{j=0}^{N} \left( \frac{v_u}{\rho_0} \right)^2 P(r) e^{i\mathbf{q} \cdot \mathbf{r}} d\mathbf{r}
\]

\[
P(r) = 2 \left( N + 1 \right) K \left( \frac{3}{2} \frac{2}{K l^2} \right)^{3/2} \exp \left( \frac{3 r^2}{2 K l^2} \right)
\]

\( l \) = bond length

Number of walks of \( K \) steps

\( e\cdot e \) distribution for a walk of \( K \) steps

\[
I(q) = \left( \frac{v_u}{\rho_0} \right)^2 \frac{2 \left( e \frac{x}{6} + x \frac{1}{x^2} \right)}{x^2}; \quad x = \frac{q^2 N l^2}{6} = q^2 \left\langle R_g \right\rangle^2
\]

Debye form factor

Form Factor

\( R_g = 100 \text{ Å} \)

Slope = -2
Worm-like Chain

Persistence Length, $L$

Rod like on short length scales $d = 1$

Gaussian on large length scales $d = 2$

$\log I(q) \sim \frac{2}{L}$

$\log q$
Correlation Functions

\[
\frac{d\sigma}{d\Omega} = I_{\text{scatt}}(q) = \frac{J(q)}{J_0} = \langle |A(q)|^2 \rangle = \left\langle \int \rho(r) e^{-iqr} dr \right\rangle^2 \quad \text{Ensemble Average} < >
\]

\[
I(q) = \left\langle \left[ (u) e^{iq\cdot u} du \right] \left[ (v) e^{iq\cdot v} dv \right] \right\rangle
\]

\[
r = u - v
\]

\[
I(q) = \left\langle \left[ (u) (u + r) du \right] e^{iqr} dr \right\rangle
\]

\[
(r) = \left\langle \left[ (u) (u + r) du \right] \right\rangle
\]

\[
\Gamma_\rho(r) \text{ is the autocorrelation function of the scattering length density}
\]

Scattering Cross section is the Fourier Transform of the ensemble average of the correlation function of the scattering length density (Patterson Function)