Everything You Ever Wanted to Know About SAXS But Were Afraid to Ask

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When should I use the Scattering Technique?
**Ideal Studies for Scattering**

Scattering good for:
- Global parameters, distributions; 1\textsuperscript{st} order
- Different sample states
- In-situ transitional studies
- Non destructive sample preparation

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Solid  
Melted & Sheared  
Recrystallized
Ideal Studies for Microscopy

Microscopy good for:

- Local detail
- Surface detail
- Faithfully represents local complexities

E.g. if objective is to monitor the degree to which Mickey’s nose(s) and ears hold to a circular micromorphology… use microscopy not scattering
Forming a bi-continuous porous network with ligament width on the nanoscale by removing the less noble element from a binary alloy, in this case Ag-Au.
Scattering: Neutrons or Photons?

X-rays
- Sensitive to electron density contrast

Neutrons
- Sensitive to nuclear scattering length contrast

Neutron scattering: Deuteration allows species selection

Advantages of X-ray scattering:
- Relatively small sample quantities required
- Relatively fast data acquisition times - allows time resolved effects to be characterized
Scattering: Neutrons or Photons?

Neutrons: Deuteration allows species selection

This essentially permits a dramatic alteration to the ‘visibility’ of the tagged elements in terms of their contribution to the reciprocal space scattering pattern.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Scattering length ($x 10^{12}$ cm²)</th>
<th>Incoherent scattering ($x 10^{24}$ cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1$H</td>
<td>-0.374</td>
<td>80</td>
</tr>
<tr>
<td>$^2$D</td>
<td>0.667</td>
<td>2</td>
</tr>
</tbody>
</table>
Scattering: Neutrons or Photons?

Photos of deformation

SANS patterns

\[ \lambda = 0\% \quad \lambda = 300\% \]
Scattering: Neutrons or Photons?

X-rays: Order of magnitude better spatial resolution
Fast data acquisition times for time resolved data

Oscillatory Shearing of lyotropic HPC – a liquid crystal polymer
X-ray Scattering: Transmission or Reflection?

Need to be conscious of:
Constituent elements, i.e. absorption cutoffs
Multiple scattering
Area of interest: surface effect or bulk effect

Transmission geometry appropriate for:
• Extracting bulk parameters, especially in deformation
• Weakly scattering samples: can vary path length
X-ray Scattering: Transmission or Reflection?

Reflection geometry appropriate for:
- Films on a substrate (whether opaque or not)
- Probing surface interactions
X-ray Scattering: SAXS or WAXS?

No fundamental difference in physics: a consequence of chemistry

WAXS patterns contain data concerning correlations on an intra-molecular, inter-atomic level (0.1-1 nm)

SAXS patterns contain data concerning correlations on an inter-molecular level: necessarily samples where there is macromolecular or aggregate order (1-100 nm)

As synthesis design/control improves, SAXS becomes more relevant than ever before
X-ray Scattering: SAXS or WAXS?

Experimental consequences

WAXS: Detector close to sample, consider:
• Distortion of reciprocal space mapping
• Thermal effects when heating sample
• No ion chamber for absorption

SAXS: Detector far from sample, consider:
• Absorption from intermediate space
• Interception of appropriate q range
What can I Learn from a SAXS Pattern?
Recognizing Reciprocal Space Patterns: Indexing

Face centered cubic pattern from diblock copolymer gel
Recognizing Reciprocal Space Patterns: Indexing

Real space packing

Face centered cubic

Body centered cubic

Hexagonal

Reciprocal space image (unoriented domains)

Normalized peak positions

\[ \equiv 1; \ = \sqrt{4/3}; \ = \sqrt{8/3} \]

\[ \equiv 1; \ = \sqrt{2}; \ = \sqrt{3} \]

\[ \equiv 1; \ = \sqrt{3}; \ = \sqrt{4} \]
Recognizing Reciprocal Space Patterns: $R_g$

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Dendrimers designed as poragens for nano-porous media: interest in monodispersity and density distribution per poragen

$$R_g^2 \propto \ln I(q) / q^2$$
Modeling Radial Density of Isomer Architectures

Relate the internal density (and thus functionality as nano-electronic application) of dendrimer isomer to the design architecture, modelling as a star with f arms. Can predict size and density of sphere from architectural model.

Model: \( \rho(r) = \int f^{(3\nu-1)/2\nu} r^{(1-3\nu)/\nu} \, dr \)
Recognizing Reciprocal Space Patterns: Preferential Orientation

Real space packing

Reciprocal space image

Randomly aligned rods

Preferentially aligned rods

Hydrated DNA
Extracting Physical Parameters from X-ray data

\[ I(q) \]

\[ I(\phi) \]
Extracting Physical Parameters from X-ray data

Molecular size: Radius of gyration ($R_g$)

Guinier plot

\[
\ln I(q) = \ln I(0) \exp \left[ -q^2 R_g^2 / 3 \right]
\]

\[
R_g^2 \propto \ln I(q) / q^2
\]

Guinier region: $q < 1 / R_g$
Extracting Physical Parameters from X-ray data

Molecular conformation: Scaling exponent

Gradient of profile in intermediate region implies fractal dimension of scattering unit
Molecular Conformation in Dentin

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SAXS pattern

DEJ  pulp
Molecular Conformation in Dentin

![Graph showing Scaling exponent vs Distance from pulp (mm) with markers for 16G213, 16G224, and 17G246]

- Scaling exponent plotted against Distance from pulp (mm)
- Markers indicate data points for different groups:
  - 16G213
  - 16G224
  - 17G246
**Molecular Conformation in Dentin**

Shape change of mineral crystallites from needle-like to plate-like from pulp to dentin-enamel junction (DEJ).

Dentinogenesis imperfecta (DI) teeth shown to exhibit impaired development of intrafibrillar mineral: characteristic scattering peaks are absent from the diseased tooth.
Extracting Physical Parameters from X-ray data

Molecular conformation: Persistence length of coiled chain

\[ I(q) = q^2 \]

Kratky plot

\[ q^* = \frac{6}{\pi q^*} \]
Extracting Physical Parameters from X-ray data

Molecular orientation: Orientation parameter $P_2$

$$<P_{2n}(\cos \phi)> = \frac{\int I(s,\phi) P_{2n}(\cos \phi) \sin \phi \, d\phi}{\int I(s,\phi) \sin \phi \, d\phi}$$

Normalized:

$$-0.5 < P_2 < 1$$
Molecular Orientation in Injection Moldings

Measuring the degree and inclination of preferential molecular orientation in a piece of injection molded plastic (e.g. hip replacement joints). ~ 1500 WAXS patterns

Orientation parameters: $0 < P_2 < 0.3$  

Marks the injection point

Axis of orientation
What can the SAXS beamline at SSRL do?
GENERIC SYNCHROTRON LAYOUT

LINAC
E ~ 0.01 GeV

BOOSTER
Radius ~ 5m
E ~ 2.5 GeV

STORAGE RING
Radius ~ 10m
E ~ 3 GeV
I ~ 200 mA (10^{-19}.10^{16}.10^{2})
e- velocity ~ c

BEAMLINE

Electron frame

Laboratory frame
**Beamline 1-4: Materials Science Scattering**

Unfocused $\phi \sim 4 \times 10^{11} \text{ h} \text{v s}^{-1} \text{ mA}^{-1}$

**Source size:** 8 000 $\mu$m$^2$

**Min q ~ 0.015 nm$^{-1}$**

**Max d ~ 400 nm**

SPEAR3 bend magnet

$I = 500 \text{ mA}, E = 8333 \text{ eV}$

$\sigma(x), \sigma(y) 160 \times 50 \mu$m

Bent mirror, V focus

Bent, offcut Xtl mono, H focus

Optical chamber: The “Coffin”
Beamline 1-4 upstream optics: The ‘Coffin’

Helium filled drift tank: The ‘Coffin’

Beamline 1-4 (early design)

Beamline 1-5

X-rays
Inside the ‘Coffin’:
Three jaw slit

Cu side shielding
Cu Upper slit
Cu Side slit
Cu Lower slit

X-rays
Inside the ‘Coffin’: Cu cooled Bent Mirror M0

- Finger comb pressing contact onto M0
- Copper contact bar
- Bending rods
- Cu terminus block
- M0 SiO₂ block
- Cu braid, welded to bar
- X-rays
Helium exit for Mono cooling
M0 cooling
Cu braid

Inside the ‘Coffin’:
He Cooled Si Mono

Si [111] crystal

1-4 mono assembly

M0 cooling
Cu terminus

Mono cooling

Si [111] crystal

1-4 mono assembly
Monochromator cooling assembly

He Outlet onto mono

Cu coils around He drift tubes

Intake

Chiller

Recirculating bath

Helium filled ‘Coffin’

Fan
Beamline 1-4 stoppers

Inside 1-4 stopper tank

Each stopper:
- 1.25” Cu
- 2 x 3/16” Pb

Stopper 1
- Mono crystal

Stopper 2
- ‘Coffin’

Experimental Hutch

X-rays
Experimental Hutch

- Ion chamber readout
- Motor position encoders
- Hutch stopper control
- Electronics control chassis
- Motor control chassis
- Beamline control computer
- Sample temperature control
Sample Environments: Goniometer

Used for Reflection X-ray geometries

Huber 410 Goniometer

Two axes angular translation
Two axes linear translation
Sample Environments: X-Y drivable flat mount

Four sample positions

$x$ and $y$ drives $\pm 2.25\mu m$

$x$ and $y$ throw $\sim 100mm$

Adaptor to hold fluid cells

Fluid cell with flow feeds
Sample Environments: Oven

Temp $T$: $25^\circ C < T < 450^\circ C$

stability $\pm 2^\circ C$

Feed for inert gas

10 soldering iron

core heaters

Fit for fluid

holder cells
Sample Environments: Oven

Fluid holder cells: assemble as three parts with windows
Sample volume ~ 2.5 cc
Optical path length = 1 mm
Material: 5 each of
Polytetrafluoroethylene (Teflon); Aluminum & Steel

Teflon cells have flow couplings for in-situ titration
Sample Environments: Tensiometer

**Extension rate** $E$:

$0.001 \text{ mm s}^{-1} < E < 25 \text{ mm s}^{-1}$

**Oven Temp** $T$: $25^\circ C < T < 100^\circ C$

**Temp stability** $\pm 2^\circ C$

**Elastomeric Polypropylene sample at 300% extension**
**Principal Parameters for Scattering Experiments**

\[ q_{\text{min}}: 0.03 \text{ nm}^{-1} \quad (\text{c.f. pre 2004 } q_{\text{min}} = 0.07 \text{ nm}^{-1}) \]

*Can observe features* \( d_{\text{max}} \sim 200 \text{ nm} \quad (\text{c.f. pre-2004 } d_{\text{max}} = 90 \text{ nm})

*Focused Flux* \( \Phi \sim 1 \times 10^{10} \text{ h} \nu \text{ s}^{-1} \text{ mA}^{-1} \)

*Source size* = 18 nm/rad  
(c.f. pre 2004 = 130 nm/rad)  

*Sample to detector distance* \( D = 3 \text{ m} \quad (\text{c.f. pre 2004 } D = 1.2 \text{ m}) \)