Introduction to Small Angle X-ray Scattering for Nanomaterials

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Outline

• Introduction
• Experimental Setups
• Fundamentals of X-ray Scattering
• Theory and Applications of Small Angle X-ray Scattering
• Applications
Researchers come to the APS from:
• 50 states plus Puerto Rico and the District of Columbia
• 33 countries
• 150 companies
• 250 universities

ADVANCED PHOTON SOURCE

5300 researchers each year
Sources of scientific discovery and technological innovation

A critical component of maintaining U.S. leadership in the physical sciences
Length Scales Probed by SAS and Other Characterization Techniques

**Crystallography**
- Atomic Structures

**Microstructure**
- Proteins
- Micelles
- Porous Media
- Polymers
- Precipitates

**Structure**
- Viruses
- Bacteria
- Grain Structures

**DIFFRACTION**
- TEM
- USAXS, USANS

**OPTICAL MICROSCOPY**
- Light scattering

**WAXS**
- DLS

Length Scales Probed:
- 0.1 Å
- 1 Å
- 1 nm
- 100 nm
- 1 μm
- 10 μm
- 1 mm

**DIFFRACTION**
- X-ray, n, e⁻
1. X-ray Scattering Setup
   - Storage-Ring synchrotron
   - X-ray scattering setup
X-ray Scattering Setup Configuration

Transmission Mode
Transmission x-ray scattering

X-ray scattering setup with X-ray, Sample, and detector.

Reflection Mode
Grazing incidence (GI) x-ray scattering

Grazing incidence x-ray scattering setup with X-ray, Sample, and detector.
Real space vs Reciprocal space

• Properties

• Unit in length $^{-1}$

• Length in reciprocal space is $1/\text{length in real space}$

• Volume of reciprocal space is $1/\text{volume in real space}$
When do you need synchrotron x-ray source?
1. High flux: high background exp
2. Small beam size: small amount of sample, etc
3. Fast data collection: in-situ, fast kinetics
Figure 3. SAXS data of BCC SL of 15nm gold spherical particles linked with DNA. The same sample were measured with APS and Lab sources.
New SAXS/WAXS Setup at Beamline 12ID-B of Argonne

- From 1 to 150 nm
- High flux, one measurement less than 0.1 s
- In situ SAXS study: high temperature (up to 1500°C) and high pressure (up to 20,000 psi)
- Element specific information from ASAXS
- Can be combined with many other techniques such as IR and other spectroscopy
Fundamentals of X-ray Scattering

- X-ray scattering and interference
- Form factor: size & shape
- Size polydispersity
- Structure factor
- X-ray contrast
Atomic Form Factor

Electron cloud in atoms has radial density distribution $\rho(r)$

$$f(q) = 4\pi \int \rho(r) r^2 \frac{\sin(qr)}{qr} \, dr$$

- Atomic form factors are fundamental parameters for X-ray techniques.
- $f(0)=Z$ : the total electron of the atom, scattering length.
- Atoms with higher Z will scatter stronger.

Data taken from *International Tables for Crystallography*, Vol. C, Table 6.1.1.1
Polydispersity: Size Distribution
Scattering for an ensemble with different sizes:

- Size polydispersity smears/dampens fine features in scattering profile.
Spheres of different sizes

![Graph showing the relationship between P(Q) and Q (Å⁻¹) for spheres of different sizes.](image)
“Long & thin” cylinder

\[ P(Q) \]

\[ Q^{-1} \]

\[ Q (\text{Å}^{-1}) \]

\[ P(Q) \]

\[ Q^{-1} \]
Particle Correlation: Structure Factor

Dilute, randomly distributed particles:

\[ I(q) = NP(q) \]

Correlated particles:

\[ I(q) = NP(q)S(q) \]

S(q) structure factor
Structure Factor: Common Spacing(s) between Scatterers

\[ S(q) = 1 + 4\pi \frac{N}{V} \int_0^\infty r^2 [g(r) - 1] \frac{\sin qr}{qr} dr \]

- \( g(r) \): radial particle distribution function
- Low concentration, \( S(q) = 1 \)
- Higher concentration, \( S(q) \) oscillates about 1

\[ I(q) = NP(q)S(q) \]
Theory and Applications of SAXS

- Guinier Approximation
- Porod Law
- Invariant
- Hierarchical structural Information
Guinier Equation

When \( q \to 0 \),

\[
I(q) \approx I(0) \exp\left(-\frac{R_g^2 q^2}{3}\right)
\]

\( R_g \): radius of gyration
\( I(0) \): forward scattering

Guinier analysis for compact particles

\[
I_0 = 0.0034855 \pm 1.4397 \times 10^{-06}
\]

\[
R_g = 20.683 \pm 0.012413 \text{ Å}
\]

\[
Q_{max} \times R_g = 1.3007
\]

To get reliable Guinier plot / \( R_g \) analysis:

➢ \( q_{max} \times R_g < 1.3 \) for globular; <0.8 for enlongate
➢ \( q_{min} \leq \pi/D_{max} \)
➢ Multiple (≥5???) data points in linear fashion
Guinier Plot: Data Evaluation & Sample Condition

Mono-dispersed
Normal / linear

Poly-dispersed aggregates
Curve-up

Repulsion
Curve-down

Porod Law

**Generalized form:**

\[ I(q) \propto q^{-\alpha} \]

\[ \alpha = \begin{align*} 
1 & \text{ rod-like} \\
2 & \text{ lamellar/disc} \\
4 & \text{ sphere} \\
\text{fraction: fractals} 
\end{align*} \]

- Can provide morphology information
- May not be valid in atomic length region
- Could be misled by inaccurate background subtraction
Porod Invariant and Porod Volume

Porod Invariant $Q$:

$$ Q = \int_{0}^{\infty} q^2 I(q) dq = 2\pi^2 (\Delta \rho)^2 V $$

For uniform particles:

$$ I(0) = (\Delta \rho V)^2 $$

Porod volume:

$$ V = \frac{2\pi^2 I(0)}{Q} $$

- The invariant measures the total electrons, does not depend on morphology.
- The volume of a molecule can be estimated solely from scattering data.
- Calculation of particle volume does not require absolute data scaling.
Anatomy of SAXS Profile

One characteristic length:
all dimensions similar
aspect ratio: $d_{\text{max},A}/d_{\text{max},B} \sim 1$

A,B dimension

Two characteristic lengths:
$L >> 2R$

$R=20 \text{ A}, L = 800 \text{ A}$

$qR \sim 1$
Pair Distance Distribution Function (PDDF)

\[ p(r) = \frac{r^2}{2\pi^2} \int_0^\infty q^2 I(q) \frac{\sin qr}{qr} dq \]  

--- reverse FT of \( I(q) \)

- The PDDF of a molecule is the (net-electrons and distance) weighted atom-pair distance histogram.

\[ p(r) \sim \sum_{|\vec{r}_j - \vec{r}_k| < r + dr} 1 \times \Delta n(\vec{r}_j) \times \Delta n(\vec{r}_k) \times r^2 \]

excess electrons of atom \( j \) over solvent
Combination of SAXS & PDDF for Shape Determination

SAXS Instruments at 12ID
**Setup**

Heated capillary flow cell

Heating up to 1500 °C

GISAXS cell for high temperature and pressure reactions
Combined SAXS with other technique

- **a)**
  - Structure
  - UV-vis
  - Processing
  - Properties
  - X-rays

- **b)**
  - XRF detector
  - X-ray
  - levitated sample
  - acoustic levitator
  - CCD

- **c)**
  - Copper heating tube
  - X-ray
  - WAXS detector
  - SAXS detector
  - Mixer
  - Pump
  - Quartz Capillary
  - Ion chamber
  - XAS I₀
  - Furnace
  - X-ray

- **d)**
  - WAXS detector
  - Photodiode
  - (XAS I₀)
  - Furnace
  - Sample Cell
  - X-ray
SAXS and SANS

In situ SAXS/WAXS

(a) Intensity (cm$^{-1}$) vs. Time (s)

(b) Intensity (a.u.) vs. Time (s)

(c) TEM image of PtSn nanoparticles, scale bar = 20 nm

(d) Diagram showing the reaction sequence:
- $\text{Pt}^{2+}$ and $\text{Sn}^{4+}$ react to form Pt
- Pt interacts with PtSn to form PtSn

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*Nano Lett.*, **18**(6), pp 4053–4057
SAXS of Au-DNA Superlattice

Science 2011, 334, 204–208
P(r) of dimmer structure

Cis I

Cis II

Cis III

Cis data

Cis I

Cis II

Cis III

Lithium Ion Battery

Lithium ion batteries are powering the world.
The Nobel Prize in Chemistry 2019

John B. Goodenough
Prize share: 1/3

M. Stanley Whittingham
Prize share: 1/3

Akira Yoshino
Prize share: 1/3
How to characterize the electrolyte in the solution?

Co-solvent: aggregates or single molecule?

• EC/PC form no aggregates
• EC/DEC, EC/MC, EC/DMC form ~ 2 nm aggregates
• Cryo-EM, MD simulation: structures

MD Study of LiTFSI Solvation Structure

**Figure. Experimental and calculated SAXS data for 20 m LiTFSI in water.**

(Left) Peaks highlighted with black arrows indicate TFSI⁻ aggregates. (Right) MD simulations show the heterogeneous structure of the electrolyte comprises percolating networks of ion and water domains consistent with experimental SAXS data.

SAXS/WAXS Study of LiTFSI Solvation Structure

**Peak a:** TFSI− solvated structure

**Peak b:** TFSI− network (water molecules act as bridging bond)

Feature in SAXS is due to TFSI-TFSI

TFSI-H₂O and H₂O-H₂O also evolve with concentration change

SAXS/WAXS Study of Different Anions

(a) BNTI

(b) BETI

(c) TFSI

(d) FSI

SAXS/WAXS Study of NaTFSI in Water

SAXS/WAXS Study of Mg(TFSI)$_2$ in Water

SAXS of LITFSI in Different Solvents

Molecular Aggregation in Catholyte Redoxmer Solutions

Collaborator: Shkrob (ANL), Odom (Kentucky), Ewoldt (UIUC), Assary (ANL), L. Zhang (UIUC), Carino (ANL)

Correlation peaks indicative of redoxmer clustering are observed in concentrated solutions of some redoxmers but not the others, depending on subtle structural variations.

- SAXS studies demonstrate aggregation and microscopic phase separation in crowded redoxmer solutions
- Aggregation is shown to affect stability of charged redoxmers
- It strongly affects viscosity and conductivity

Tao and Erik as co-author
1. Journal of Physical Chemistry B, 2020, 124, 45, 10226-10236;
2. Journal of Physical Chemistry B, 2020, 124, 46, 10409-10418;
Supported Metal Catalysts by Atomic Layer Deposition

Lu, Junling; Elam, Jeffrey W.; Stair, Peter C. Accounts of Chemical Research (2013), 46(8), 1806-1815
ALD Overcoated Catalyst with Enhanced Stability

- Dramatically improved yield and lifetime with ALD overcoat
- Without overcoat, coke formed in <30 min, zero yield
- With overcoat, virtually no coking, >20% yield
- Lifetime enhancement: >100x

45c Al₂O₃ Over-coating on Pd/Al₂O₃ Catalyst

Collaborated with Peter Stair, Northwestern University

Science, 2012, 9, 1205–1208
The fitting shows that the average particle size is 6.7 nm, consistent with BJH Model data 7.1 nm.
Gamma-Al₂O₃ support has no change before and after heating.
For 45ALD coated samples, the intensity increases, indicating the pore.
Average pore radius 1.7 nm

Tao Li as co-author. ACS Catalysis, 2020, 10 (23), 13957-13967.
Combined SAXS/WAXS of TiO$_2$ Overcoat

5 nm ALD TiO$_2$ overcoat on spherical nanodur  Heat in air 20°C/min to 1000°C

- APS (12 ID-B)
- Linkam stage (RT to 1500 °C)

- SAXS: pore size.
- WAXS: crystallization.

In Situ SAXS/XAS of Al₂O₃ Overcoat on Nanodour

1% wt Pt on Al₂O₃

Pt Nanoparticles

Al₂O₃ Support

Al₂O₃ ALD
5, 15, or 25 cycles

High Temperature Treatment

X-ray Fluorescence

Scattered X-rays

ALD-overcoated Supported Metal Nanoparticles

SAXS detector

Fluorescence detector

XANES

15c ALD Pt
20°C/min

SAXS

15c ALD Pt
20°C/min
Integrating Photocatalysis and Thermocatalysis to Enable Efficient Dry Reforming of Methane (DRM)

Collaborator: Ying Li (TAMU)

L. Fang, Z. Feng, L. Cheng, R. Winans, Tao Li*. Small Methods, 2020, 2000315.
Collaborator: Byeongdu Lee (ANL), Wenyu Huang (ISU/Ames)
Multiple Techniques to Observe Structure under Real Conditions
(If you can do it in the lab, we can do it on the beamline)

Five sectors provide a suite of in-situ techniques including X-ray scattering and spectroscopy at:

1-ID (high energy SAXS/WAXS (PDF))
9-ID-D(USAXS/SAXS)
9-BM, 20-BM (XAS)
10-ID (XAS)
11-BM (Hi res powder diff)
11-ID-B,C (PDF)
12-BM (XAS/SAXS)
12-ID-B, C (SAXS/WAXS, and GISAXS/GIWAXS)
Also - Imaging and Microscopy (2-BM, 32-ID-BC)

X-ray scattering and spectroscopy combined with FTIR and Raman to study in situ catalysis on a flat surface.
Software and useful website

http://smallangle.org/content/Software

- Fit2D or Nika for data reduction.
- SASfit, Irena, SasView
- Crysol
- GIXSGUI and FitGISAXS

Irena and Nika software course
Beyond Rg Materials
Beyond Rg Bio
BioSAS: Advanced Applications
THANK YOU