Small-angle Neutron Scattering lecture

Lisa DeBeer-Schmitt
NXSchool July 2022
Outline:

- What is SANS?
- Instruments at ORNL
- Sample Environment capabilities
- Science Cases
  - Polymers
  - Magnetic ordering (diffraction)
  - Engineering materials
- New Directions
Small-angle neutron scattering (SANS)

\[ I(Q) = A \Delta \rho^2 n V^2 P(Q) S(Q) \]

A powerful tool for studying nanophase bulk materials

Probes lengths of 0.5 – 700 nm
Using angles of \( \theta = 0.1 \text{ to } 45^\circ \)
SANS with other techniques

Microscopy: Direct but limited

SAS: Indirect and model-dependent but in-situ
Why Neutrons?

- **Low Energy**: (E=80meV for 1 Å neutrons vs. 12.42 keV for x-rays. **No radiation damage**.)
- **High Penetration of cold neutrons** – bulk samples
- **Large difference in the scattering cross-section for the hydrogen and deuterium** contrast variation capability.
  - Solute or solvent can be deuterated to vary the contrast ($\rho_{\text{H}_2\text{O}} = -0.56 \times 10^{10}\text{cm}^{-2}$, $\rho_{\text{D}_2\text{O}} = 6.334 \times 10^{10}\text{cm}^{-2}$)
  - Study of multicomponent systems through selective deuteration and contrast matching with H/D mixtures.
- **Sensitive to substantial difference in scattering length density in transition metals**
- **MAGNETISM**.
  - Neutron has a magnetic moment and spin which give contrast

Magnetic domains in Fe\textsubscript{2}O\textsubscript{4}
L. Kish et al in preparation

Data from NXschool experiment

Copper precipitate growth in steel
Neutron and x-ray scattering cross-sections

X-ray and neutron scattering are essentially the same concept, except...

- X-rays scatter from electrons
- Neutrons scatter from nuclei

C. Metting, Dissertation University of Maryland 2011

[Diagram showing X-ray scattering factors and neutron scattering lengths for various elements, with negative and positive scattering cross-sections indicated.]
SANS from hierarchical structures

SANS is a structural technique that probes a wide array of length scales.
## ORNL SANS instrument specifications.

<table>
<thead>
<tr>
<th></th>
<th>GP-SANS</th>
<th>Bio-SANS</th>
<th>EO-SANS</th>
<th>USANS</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Moderator</strong></td>
<td>Supercritical hydrogen</td>
<td>Supercritical hydrogen</td>
<td>Coupled, supercritical hydrogen</td>
<td>Decoupled, poisoned hydrogen</td>
</tr>
<tr>
<td><strong>Source</strong></td>
<td>Reactor, continuous</td>
<td>Reactor, continuous</td>
<td>Spallation, 60 or 30 Hz, TOF</td>
<td>Spallation, 60 Hz, TOF</td>
</tr>
<tr>
<td><strong>Sample-to-detector distance</strong></td>
<td>1.1–20 m</td>
<td>1.1–15.5 m</td>
<td>1.0–9 m</td>
<td>N/A</td>
</tr>
<tr>
<td><strong>Beam size</strong></td>
<td>Up to 20 mm diameter</td>
<td>Up to 20 mm diameter</td>
<td>Up to 15 mm diameter</td>
<td>Up to 40 mm by 40 mm</td>
</tr>
<tr>
<td><strong>Q range</strong></td>
<td>$7 \times 10^{-4}$ to 1 Å$^{-1}$</td>
<td>$9 \times 10^{-4}$ to 1 Å$^{-1}$</td>
<td>$2 \times 10^{-3}$ to 6 Å$^{-1}$</td>
<td>$7 \times 10^{-6}$ to $5 \times 10^{-3}$ Å$^{-1}$</td>
</tr>
<tr>
<td><strong>Incident wavelength</strong></td>
<td>4–25 Å</td>
<td>6–25 Å</td>
<td>0.5–20 Å</td>
<td>3.6, 1.8, 1.2 and 0.9 Å</td>
</tr>
<tr>
<td><strong>$\Delta \lambda/\lambda$</strong></td>
<td>9–45%</td>
<td>9–45%</td>
<td>$&lt;1$–20%†</td>
<td>Monochromated with crystals</td>
</tr>
<tr>
<td><strong>Detector type</strong></td>
<td>$^3$He LPSD array</td>
<td>$^3$He LPSD array</td>
<td>$^3$He LPSD array</td>
<td>$^3$He</td>
</tr>
</tbody>
</table>

† The resolution of EO-SANS is wavelength dependent and also depends on the binning used in the software. The upper end of the range indicated is for the shortest wavelength used in the current data reduction.
Sample Environments:

Current Sample environment options:

- A suite of changers that can be configured to hold from 8 - 18 samples
- Peltier system that goes from -10 to 120 °C with 0.01 degree control and holds 12 samples.
- HiDRA load frame; rheometer
- Shared furnace capable of temperature up to 200 °C
- New controlled atmosphere furnace and vacuum furnace to > 1000 °C
- Horizontal 11 T recondensing magnet allowing users to utilize 11 T at 30 mK. (3/2016), 5 T horizontal open bore magnet (5/2017) and 8 T vertical magnet with temps 30 mK to 300 K
  - Electric field and current can also be applied to the samples
- SANS dedicated cryostat with sapphire windows
- Pressure cells (McHugh 2kBar and 1kBar changer)

Future upgrades:

- Strain cell to apply in-situ compression or tension (11 T and 5 T magnets)
- In-situ reaction vessel
- Load frame for stretching polymers
Science cases

- Diblock copolymers
- Skyrmion in thin films
- Novel Steels for reactor
Influence of Cleavage of Photosensitive Group on Micellization and Gelation of a Doubly Responsive Diblock Copolymer

Lilin He\textsuperscript{1}, Bin Hu\textsuperscript{2}, Daniel M. Henn\textsuperscript{2}, and Bin Zhao\textsuperscript{2}

\textsuperscript{1}Large Scale Structure Group, Neutron Scattering Division, Oak Ridge National Laboratory

\textsuperscript{2}Department of Chemistry, University of Tennessee: Knoxville
Influence of Cleavage of Photosensitive Group on Micellization and Gelation of a Doubly Responsive Diblock Copolymer

Block Copolymers have wide technical applications owning to their capabilities to self-assemble into nanostructures under different conditions.

Challenge: To precisely tune and control the molecular characteristics of the block copolymers under appropriate conditions.

Mark A. Ward, Theoni K. Georgiou, Polymers 2011, 3(3), 1215-1242;
Thermal- and light-sensitive diblock copolymer PEO-b-P(TEGEA-co-NBA)

Brown-red color due to the photochemical reaction

Multiple transitions

Flowing Fluid

(a) 20 °C → (b) 33 °C → (c) 52 °C

Irradiated with 365 nm UV light

33 °C → (d) 40 °C → (f) 52 °C

“living”/controlled radical polymerization

Irradiated for 6 days with 365nm UV light

Block 1 Block 2

Rheological Results

- Dynamic storage modulus $G'$, loss modulus $G''$, versus temperature
- 25wt % D$_2$O solution of PEO-$b$-P(TEGEA-co-NBA).
- A heating rate of 3°C/min.
- A strain amplitude of 1%
- An oscillation frequency of 1 Hz.

- Reversible sol-gel-soft gel transitions is achieved;
- Gel is composed of packed micelles;
- UV irradiation leads to a narrower gel state window.

Rheological Properties ✅ Microstructure ✅
SANS results: Unimer State

- Guinier Approximation at low-q:
  - $I(Q) = I(0) \exp(-Q^2R_g^2/3)$
  - $\ln[I(Q)]$.vs.$Q^2$ plot where $Q.R_g<1.0$
  - $R_g = \sqrt{(3.\text{slope})}$
  - $M=(1000.I(0).d^2.Na)/(C.\Delta p^2)$

- Power-law at high q

**Real Space**

<table>
<thead>
<tr>
<th>Structure</th>
<th>Scaling Relation</th>
<th>darda</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M \sim V \sim R^3$</td>
<td>$d_m = 3$</td>
<td>$d = 3$</td>
</tr>
<tr>
<td>$M \sim V \sim R^2$</td>
<td>$d_s = 2$</td>
<td>$d = 2$</td>
</tr>
<tr>
<td>$M \sim V \sim R^1$</td>
<td>$2 &lt; d_s \leq 3$</td>
<td>$1 &lt; d_s \leq d_m \leq 3$</td>
</tr>
</tbody>
</table>

**Smooth Surface**

- $2 < d_s \leq 3$

**Rough Surface**

- $1 < d_s \leq d_m \leq 3$

**Mass Fractal**

- $-2.5$

- $-1$

- $-2$

**Dispersion**

- $3 \leq \text{Slope} \leq 4$

- $q^{d_s-2d} = 3$


Dale Shaefer: Nxschool talk 2017
Both solutions contain single chains and loosely-assembled clusters.

The chains are more stretched after UV irradiation.

- 0.02 wt%
- 15 °C

A model for polymers with excluded volume fraction yields Rg and Porod exponent:

**Before UV**
- \( R_g = 25.5 \AA \)
- Porod exponent = 1.94

**After UV**
- \( R_g = 31.1 \AA \)
- Porod exponent = 1.59

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Micelles form above critical micelle temperature

Cleaving the light sensitive group defers the formation of the micelles

0.02wt%

Before UV

After UV

Temperature Effect: Concentrated solution

- Micelles grows with temperature;
- Possible sphere to rod transition at 55°C for the UV exposed sample.

25 wt%

Model Fitting: Polycoreshell model

Material Balance Calculation

\[
\begin{align*}
N_{ag}(131*V_{TN}+113*V_{PEO}+f)+30*c &= \frac{4\pi}{3} R_A^3 \\
N_{ag}*113*V_{PEO}(1-f)+30*d &= \frac{4\pi}{3} (R_B^3 - R_A^3) \\
N_{ag}(131*b_{TN}+113*b_{PEO}*f)+191*c &= \frac{4\pi}{3} R_A^3 * \rho_A \\
N_{ag}*113*b_{PEO}(1-f)+191*d &= \frac{4\pi}{3} (R_B^3 - R_A^3) * \rho_B
\end{align*}
\]

\[\frac{d\Sigma(Q)}{d\Omega} = \Delta \rho^2 \phi \ V_p \ P(Q) \ S(Q)\]

Percus-Yevick closure of the Ornstein-Zernike equation

- Micelle size (core and corona) and volume fraction
- Size polydispersity
- SLDs in core and corona
- Aggregation number
- Number of D_2O molecules in core and corona
- Fraction of PEO chains in core and corona
• The core size increases while the corona width remains;
• The slight shrinkage of corona at high temperatures is attributed to the loss of water, which is caused by the reduced miscibility of water and PEO.
Micelle effective volume fraction agrees the viscoelastic properties of solutions;

Delayed gel formation in irradiated sample due to higher LCST transition;

Critical value $0.53 \pm 0.02$
Summary of Polymer Micellization

Unimers and clusters → Mixture of micelles and unimers → “well-defined” micelles (Micellar solution)

Ordered micelles (Micellar gel) → Micellar solution (Less overlapping and entangled chains) → Rodlike micelles (for irradiated sample only)
Realization of magnetic skyrmions in thin films at ambient conditions

Ryan Desautels, Lisa DeBeer-Schmitt, Sergio Montoya, Julie Borchers, Soong-Guen Je, Nan Tang, Mi-Young Im, Micheal Fitzsimmons, Eric Fullerton, Dustin Gilbert
Skyrmions: a brief introduction

Tony Skyrme
Nuc. Phys. 13, 556 (1962)

Science 323, 915 (2009)

Igor Dzyaloshinskii
Soviet Physocs Jetc. 5, 1259 (1957)
Toru Moriya
Phys. Rev. 120, 91 (1960)

Predicted in magnetic systems
(Phys. Rev. Lett. 87, 037203 (2001))


Nature Mater. 10, 106 (2011)

DM Interaction Prefers 90° Orientation
Defines a ‘handedness’

Direct Exchange Prefers Parallel Alignment
\( E \propto J (\vec{S}_1 \cdot \vec{S}_2) \)
Skyrmions: a brief introduction

Néel (hedgehog)

Bloch

(arrows indicate magnetic spins)

Circularity (CW and CCW)

Polarity (Core-up, Core-down)

anti-parallel to perimeter


Changing between topological classes requires irreversible processes
Skyrmions: a brief introduction


Frequently form hexagonally packed arrays with long-range ordering
Magnetism effects on Skymrion stability

Imagine if we didn’t have this long-range ordering…

Origin of the long-range order is in magneto-crystalline coupling

We are interested in skyrmion systems which have weak magnetocrystalline coupling

Fert, Nat. Nanotechnol. 8, 152 (2013)

Fe/Gd Multilayer Thin Films: The Ingredients for Skyrmions at Ambient Conditions

Ferrimagnetic construction with perpendicular magnetic anisotropy

Dipole-stabilized skyrmions

Limited/no DMI

No in-plane structure to cement a long-range orientation
From saturation, worm domain remanent state

Break up into chiral bubbles, no chirality control, no long range order

Generating an Artificial Striped Phase

Tilting the sample imparts an in-plane field which breaks the symmetry.

Artificial Stripe Domain

Labyrinth (or worm) domains
Generating an Artificial Striped Phase

Desautels et al., *Under Review*
Skyrmion lattice Stability Envelope

- Stable at room temperature and zero field!
Implications of Chirality Control on the stability of Skyrmion Lattices

TEM indicates Bloch-type structure with no circularity control

Bubbles with opposite chirality will coalesce and annihilate to become a biskyrmion, but not hexagonal arrays

Strong repulsive interactions between bubbles with identical chirality

Hexagonally Ordered Arrays
Implications of Chirality Control on the stability of Skyrmion Lattices

Side view

Appears as Néel Skyrmion, not Bloch (as observed with TEM)

Maybe Neel on the top and bottom, Bloch in the middle

Without DMI, the Bloch region has no net chirality (as observed in TEM)

Assumed these are flux-closure domains with no defined chirality

Strong Repulsive Interaction

Repulsive interactions due to surface features, which have their chirality defined by the dipole fields
Thin Films studies at GP-SANS

Mag-G

a) Background

b) Stripes

Mag-H

c) Mag-G

d) Mag-H
Use of Small-Angle Neutron Scattering to Characterize Novel Steels for Reactor Applications

Kevin G. Field¹, Kenneth C. Littrell¹*, and Samuel A. Briggs²

¹Oak Ridge National Laboratory
²Sandia National Laboratories
Oxidation of cladding is key towards core degradation during a coolant-limited accident scenario.

- Normal Operation: 345°C
- Zr cladding Balloon & Burst: 800°C
- Rapid Zr Cladding Oxidation: 1000°C+
- Stainless Steel Melting: 1850°C
- Zr-alloy Melting: 2200°C+
- UO₂ Melting: 2000°C+
Oxidation of cladding is key towards core degradation during a coolant-limited accident scenario.

- Normal Operation
- Zr-cladding Balloon & Burst
- Rapid Zr Cladding Oxidation
- Zr-alloy Melting
- UO₂ Melting
- Stainless Steel Melting
- Oxidation Resistant Cladding
- Zr-Based Cladding
- Zirc-4, 1 bar steam 1500°C
- APM, 1 bar steam 1500°C

Temperatures:
- 345°C
- 800°C
- 1000°C+
- 1500°C
- 1850°C
- 2200°C+
SANS Scattered Intensity: Local Monodisperssed Approximation

\[
\frac{d\sigma}{d\Omega}(q) = \Delta \rho^2 \int_0^\infty \phi(q, R)^2 S[q, R_{HS}(R)]N(R) \, dR + Aq^{-B} + C
\]

- Contrast: \(\Delta \rho^2 = (\rho_{\text{particle}} - \rho_{\text{matrix}})^2\)
- Form factor (for spheres):
  \[
  \phi(q, R) = 3V_0[\sin(qR) - qR\cos(qR)]/(qR)^3
  \]
- Structure factor:
  \[
  S[q, R_{HS}(R)] = [1 + 24\eta_{HS}G(R_{HS}q)/(R_{HS}q)]^{-1}
  \]
- Size distribution (Weibull density function):
  \[
  N(R) = (R/R_\bar{R})^{b-1}\exp[-(R/R_\bar{R})^b]
  \]
- Low-q power-law: \(Aq^{-B}\)
- Background: \(C\)

Magnetic Shielded-SANS measurements: Contrast from Neutrons

1. **Nuclear contrast:**
\[ \Delta \rho_{\text{nucl}}^2 = (\rho_{\text{nucl}, \text{particle}} - \rho_{\text{nucl}, \text{matrix}})^2 \]

2. **Magnetic contrast:**
\[ \Delta \rho_{\text{mag}}^2 = (\rho_{\text{mag}, \text{particle}} - \rho_{\text{mag}, \text{matrix}})^2 \]

\[
\frac{d\sigma}{d\Omega}(q) = \Delta \rho^2 \int_0^\infty \phi(q, R)^2 \ldots \]

\[ [\Delta \rho_{\text{nucl}}^2 + \Delta \rho_{\text{mag}}^2 \sin^2 \alpha] \]

*Can exploit magnetization to extract composition*
Radiation tolerance of FeCrAl alloys is analogous to FeCr alloys under similar irradiation conditions.

- Dispersed barrier hardening (DBH) has linked radiation-hardening in FeCrAl alloys to formation of Cr-rich $\alpha'$ and dislocation loops after neutron irradiation to 1.8 dpa at 382°C.

Need exists to understand the role of composition and temperature on the formation and progression of Cr-rich $\alpha'$ in FeCrAl alloys.

---

A large amount of FeCrAl samples have been irradiated and/or tested over the past 5 years...

...how do we characterize α' from these efficiently?
Magnetic Shielded-SANS measurements: Role of temperature and composition on α'

- Selected FeCrAl alloys irradiated in HFIR to determine temperature, composition, and microstructure trends

<table>
<thead>
<tr>
<th>Capsule ID</th>
<th>Number</th>
<th>Neutron Flux (n/cm²)</th>
<th>Neutron Fluence (n/cm²)</th>
<th>Dose Rate (dpa/s)</th>
<th>Dose (dpa)</th>
<th>Irradiation Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FCAT-01</td>
<td>45</td>
<td>$1.10 \times 10^{15}$</td>
<td>$2.17 \times 10^{21}$</td>
<td>$9.6 \times 10^{-7}$</td>
<td>1.9</td>
<td>194.5 ± 37.9</td>
</tr>
<tr>
<td>FCAT-02</td>
<td>45</td>
<td>$1.04 \times 10^{15}$</td>
<td>$2.05 \times 10^{21}$</td>
<td>$9.1 \times 10^{-7}$</td>
<td>1.8</td>
<td>362.7 ± 21.2</td>
</tr>
<tr>
<td>FCAT-03</td>
<td>45</td>
<td>$1.10 \times 10^{15}$</td>
<td>$2.17 \times 10^{21}$</td>
<td>$9.6 \times 10^{-7}$</td>
<td>1.8</td>
<td>559.4 ± 28.1</td>
</tr>
</tbody>
</table>

- Measurements performed at CG-2 general purpose SANS beamline at HFIR
- Data collected on broken tensile heads in magnetic shielded SANS configuration
Magnetic Shielded-SANS measurements: Role of temperature and composition on $\alpha'$

Scattering Variable $Q$ (Å$^{-1}$)

Scattering Intensity (cm$^{-1}$)

Increasing Temp.

C06M  C35M  C37M  C35MN  C35M10TC

Magnetic Shielded - SANS measurements:

Role of temperature and composition on $\alpha'$

C06M  C35M  C37M  C35MN  C35M10TC

Not Measured

Not Measured
Magnetic Shielded-SANS measurements: Role of temperature and composition on $\alpha'$

- Increasing irradiation temperature increases mean radius and distribution width
- Cr stronger than Al in control in $\alpha'$ precipitation
- Microstructure (precipitates/grain size) can play a role in $\alpha'$ precipitation

$\rho_{\text{avg}} = 54.9 \times 10^{23} \text{ m}^3$

$f_{\text{avg}} = 3.8 \pm 3.2\%$

$\rho_{\text{avg}} = 5.0 \times 10^{23} \text{ m}^3$

$f_{\text{avg}} = 0.2 \pm 0.1\%$

$\rho_{\text{avg}} = 4.1 \times 10^{23} \text{ m}^3$

$f_{\text{avg}} = 3.7 \pm 0.4\%$

$\rho_{\text{avg}} = 19.9 \times 10^{23} \text{ m}^3$

$f_{\text{avg}} = 7.8 \pm 0.9\%$

$\rho_{\text{avg}} = 5.8 \times 10^{23} \text{ m}^3$

$f_{\text{avg}} = 4.0 \pm 0.4\%$

$\rho_{\text{avg}} = 13.3 \times 10^{23} \text{ m}^3$

$f_{\text{avg}} = 6.6 \pm 1.2\%$

$\rho_{\text{avg}} = 31.3 \times 10^{23} \text{ m}^3$

$f_{\text{avg}} = 5.6 \pm 1.2\%$

$\rho_{\text{avg}} = 7.2 \times 10^{23} \text{ m}^3$

$f_{\text{avg}} = 1.9 \pm 0.3\%$

$\rho_{\text{avg}} = 55.1 \times 10^{23} \text{ m}^3$

$f_{\text{avg}} = 9.6 \pm 3.7\%$

$\rho_{\text{avg}} = 7.9 \times 10^{23} \text{ m}^3$

$f_{\text{avg}} = 3.5 \pm 0.4\%$
Magnetic Shielded-SANS measurements: Role of temperature and composition on ρ'

\[ \frac{d\sigma}{d\Omega}(q) = \Delta \rho^2 \int_0^\infty \phi(q, R)^2 \ldots \] 

\[ [\Delta \rho^2_{nucl} + \Delta \rho^2_{mag} \sin^2 \alpha] \]

\[ A - ratio = \frac{\Delta \rho^2_{mag+nucl}}{\Delta \rho^2_{nucl}} \]

- Magnetic shielded SANS reveals that irradiations below 500°C form primarily ρ'
  - Typically lower Cr content in 195°C irradiations
- Above 500°C, scattering could be from nano-cavity formation
Practical Application of Ex-situ SANS results: 
\( \alpha' \) concern for normal operation, but can be tuned

- \( \alpha' \) has strong dependencies on composition, starting microstructure, and irradiation temperature
New Directions with SANS

- Time-resolved SANS
- GI-SANS
Time-resolved SANS (TR-SANS)

- Additively manufactured steels
- Data collected during ramp, 5 hour anneal, and cooling (not shown)
- SANS and SAX data taken under same heat treatment
- SANS sees metastable magnetic domain changes, but SAXS is only sensitive to the microstructure evolution

C. Fancher et al. In preparation
GI-SANS

- Being developed at ORNL at EQ-SANS but GP-SANS, BIO-SANS can do this technique.
- Measuring the specular and off-specular versus sample angle encodes both in-plane and out-of-plane structure of the systems.

Fe/Gd multilayers measured with a large (195 mT) out-of-plane field in the skyrmion phase

WLNC Liyanage et. al in preparation


Experts at ORNL on GI-SANS:
- Shuo Qian
- Changwoo Do
- Valeria Lauter
Thank you for your attention.

- SANS is a powerful tool for probing mesoscale structures in a multitude of systems
- ORNL SANS have a wide variety of sample environments to enable your science

Questions?

Instrument Teams:

**GP-SANS**
- Lisa DeBeer-Schmitt
- Ken Littrell
- Lilin He
- Cody Pratt

**USANS**
- Wei-ren Chen
- Yingrui Shang
- Carrie Gao
- Changwoo Do

**Bio-SANS**
- Venky Pingali
- Wellington Leite
- Volker Urban
- Luke Heroux

**EQ-SANS**
- Carrie Gao
- Changwoo Do
- William Heller
- Gergely Nagy
As you can clearly see in slide 397...

GAAAAH!

"Powerpoint" poisoning.