Small Angle Scattering on Metals with Neutrons and X-rays
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3-6-2015
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Outline

• Introduction:
  Nanoscale structures in metals

• Experimental Methods:
  Summary SAS
  When to use SAS
  Comparison SANS & SAXS

• Examples:
  SANS on precipitates
  SAXS on precipitates
  Small-angle diffraction with SANS
Improved functionality by nanostructuring materials

Precipitation hardening Al-Cu (4 at.%) 

Figure 11.25 Schematic depiction of several stages in the formation of the equilibrium precipitate ($\theta$) phase. (a) A supersaturated $\alpha$ solid solution. (b) A transition, $\theta'$, precipitate phase. (c) The equilibrium $\theta$ phase, within the $\alpha$-matrix phase.

Precipitation

Strength during aging

Murray, 
Structure evolution during phase transformations in structural materials

Nucleation: formation of new phase particles
- nm size clusters
- occurs on short time scales
- positioned within bulk materials
- strongly dependent on interface/defect properties

Growth: increase in size of nucleated grain
- controlled by diffusion of alloying elements and/or heat
- interaction between neighboring growing particles
- dependent on microstructure of the parent phase

Need for time-dependent in-situ measurements
Nanoscale probes

**Small-Angle X-ray Scattering**

**Small-Angle Neutron Scattering**

**Transmission Electron Microscopy**

**Atom probe Tomography**

Nanoscale probes

**Small-Angle X-ray Scattering**
- Non destructive
- In situ / time resolved
- Contrast near absorption edge
- High flux
  - Sample thickness heavy elements
  - No spatial information
  - Indirect chemical information

**Small-Angle Neutron Scattering**
- Non destructive
- In situ / time resolved
- Magnetic information
- Can probe a large volume
  - Flux limited
  - No spatial information
  - Indirect chemical information

**Transmission Electron Microscopy**
- Up to atomic spatial resolution
- Can provide chemical information
  - Destructive
  - Probes limited volume

**Atom probe Tomography**
- Near atomic spatial resolution
- Precise chemical information
  - Destructive
  - Probes limited volume

Combining techniques will provide complementary information
Small Angle Scattering: Elastic Scattering

Momentum conservation:
\[ \mathbf{p}_{\text{out}} = \mathbf{p}_{\text{in}} + \Delta \mathbf{p} \]
\[ \hbar \mathbf{k}_{\text{out}} = \hbar \mathbf{k}_{\text{in}} + \hbar \mathbf{Q} \]
\[ \mathbf{Q} = \mathbf{k}_{\text{out}} - \mathbf{k}_{\text{in}} \]

Energy conservation:
\[ E_{\text{out}} = E_{\text{in}} + \Delta E = E_{\text{in}} \]

Neutrons:
\[ \frac{\Delta \mathbf{p}^2}{2m} = \frac{\mathbf{p}_{\text{in}}^2}{2m} \rightarrow \mathbf{p}_{\text{out}} = \mathbf{p}_{\text{in}} \]

X-rays:
\[ c |\mathbf{p}_{\text{out}}| = c |\mathbf{p}_{\text{in}}| \rightarrow |\mathbf{p}_{\text{out}}| = |\mathbf{p}_{\text{in}}| \]

\[ |\mathbf{k}_{\text{out}}| = |\mathbf{k}_{\text{in}}| = k = \frac{2\pi}{\lambda} \]

Wave vector transfer:
\[ \mathbf{Q} = \frac{4\pi}{\lambda} \sin(\theta) \]

- \( k \) = wave vector
- \( Q \) = wave vector transfer
- \( \lambda \) = wavelength
- \( 2\theta \) = scattering angle
Interference pattern: \( I(Q) \propto |f(Q)|^2 \)

Fourier transform of object \( f(Q) = \int \rho(r) e^{iQr} d^3r \)

- **sphere**
  - \( 2R \)
  - \( |f(Q)|^2 \)
  - \( Q_z \), \( Q_y \)

- **cube**
  - \( L \)
  - \( |f(Q)|^2 \)
  - \( Q_z \), \( Q_y \)

- **block**
  - \( 2L \)
  - \( |f(Q)|^2 \)
  - \( Q_z \), \( Q_y \)

Note: patterns are in log scale
Scattered Intensity:

\[
\frac{d\Sigma}{d\Omega}(Q) = (\Delta \rho)^2 \int_0^\infty D_N(R) V^2(R) P(Q, R) dR
\]

Contrast:

\[
(\Delta \rho)^2 = (\rho_{\text{particle}} - \rho_{\text{matrix}})^2
\]

Orientation-averaged square of formfactor:

\[
P(Q, R) = \int_0^{\pi/2} |f|^2 \sin(\alpha) d\alpha
\]

Particle volume:

\[V(R)\]

Number distribution of size particles:

\[D_N(R)\]

Assumptions:

1. dilute limit (low volume fraction of particles within the matrix)
2. weak scattering (<10% of the X-rays or neutrons are scattered)
Contrast X-rays:

\[
(\Delta \rho)^2 = (\rho_{\text{particle}} - \rho_{\text{matrix}})^2
\]

Sensitive to variations in:
- Chemical composition
- Density
**Contrast Neutrons:**

**Nuclear contrast:**

\[
(\Delta \rho)^2 = \left( \rho_{\text{particle}} - \rho_{\text{matrix}} \right)^2
\]

with \( \rho = \sum_i N_0 b_c^i \)

- \( N_0 \) = number density
- \( b_c \) = scattering length
- \( \rho \) = scattering length density

**Sensitive to variations in:**
- Chemical composition
- Density

**Magnetic contrast:**

\[
(\Delta \rho)^2 = p_0^2 \left( M_{\text{particle}}^\perp - M_{\text{matrix}}^\perp \right)^2 = p_0^2 \left( M_{\text{particle}} - M_{\text{matrix}} \right)^2 \sin^2 \alpha
\]

with \( M = \sum_i N_0 \mu_i \)

- \( N_0 \) = number density
- \( \mu \) = magnetic moment
- \( M \) = magnetisation

**Sensitive to variations in:**
- Size magnetic moment
- Density
- Orientation magnetic moment
Considerations SAXS on metals

**Anomalous SAXS:**
Close to an absorption edge X-ray scattering depends on the energy:

\[ f = f^0(Q) + f'(E) + if''(E) \]

This gives additional contrast and can provide additional chemical information.

**Sample transmission:**
The transmission X-rays with \( E < 30 \) keV leads to restrictions in the allowed sample thickness (especially for heavy elements).

**Additional scattering for crystalline materials (metals):**
X-rays with 10-30 keV have a wavelength of \( \lambda = 0.4\text{-}1.2 \) Å. This allows for a possible diffraction signal.
Considerations SANS on metals

**Magnetic SANS:**
For magnetic materials the particles have both nuclear and magnetic contrast that probe the sample particle size distribution. The ratio between them may provide chemical information.

**Contrast:**
As the coherent scattering length strongly varies from element to element the contrast strongly depends on the composition.

**Sample transmission:**
The large penetrating power of neutrons generally allow a large sample thickness (and sample volume to be probed).

**No additional diffraction signal:**
In SANS neutrons have a wavelength of $\lambda = 6\text{-}10\ \text{Å}$. This generally does not allow Bragg scattering.
Data analysis

Data reduction:
Transform the raw intensity data on the 2D detector $I(x,y)$ into instrument independent 1D SAS data of $(d\Sigma/d\Omega)(Q)$ versus $Q$.

Model fitting: (SASfit, Grasp, GNOM, …)
Construct a model of the scattering objects and obtain the relevant model parameters by fitting. Additional information from other methods (TEM, Atom probe) is generally very useful to obtain reliable results.
Example:
SANS on Cu precipitation in deformed Fe-Cu alloys
Scattering from inhomogeneities

1. Nuclear contrast: scattering length density $\rho$
   \[ \Delta \rho^2 = (\rho_p - \rho_m)^2 \]
   particle matrix

2. Magnetic contrast: magnetisation $M$
   \[ \Delta M^2 = (M_p - M_m)^2 \]
   particle matrix

Neutron Intensity: $I(Q) \propto (\Delta \rho^2 + p_0^2 \Delta M^2 \sin^2 \alpha) \left| f(Q) \right|^2$

Magnetic scattering from $\Delta M \perp Q$ only!
SyNeW School 2 June 2015: Small-Angle Scattering

Fe-Cu, AQ, 8% deformed, aged for 96h at 550°C

SANS 2D Patterns with & without Magnetic Field

Fe-Cu, AQ, 8% deformed, aged for 96h at 550°C
Isotropic (nuclear) & anisotropic (magnetic) SANS intensity before/after aging at 550 °C for 12 h with 0% and 24% deformation.
TEM after 12 h of aging at 550 °C

0% deformation

8% deformation

He et al.,
Phase fraction of Cu precipitates

Invariant: \( Q_{0,i} = \int_0^\infty \left( \frac{d\Sigma}{d\Omega} \right)_i Q^2 dQ = 2\pi^2 (\Delta \rho_i)^2 f_V (1 - f_V) \)
Profile fitting of the SANS curve

\[
\left( \frac{d\Sigma}{d\Omega} \right)(Q) = (\Delta \rho)^2 \left[ \int_{0}^{\infty} D_N(R) V^2(R) P(Q, R) dR \right]
\]

Theoretical estimate contrast:
- Nuclear: \((\Delta \rho_{NUC})^2 = 2.2 \times 10^{28} \text{ m}^4\)
- Magnetic: \((\Delta \rho_{MAG})^2 = 15.5 \times 10^{28} \text{ m}^4\)

\((\Delta \rho_{MAG})^2 \gg (\Delta \rho_{NUC})^2\)

Particle volume: \(V(R) = \frac{4\pi R^3}{3}\)

Log-normal number distribution of particles:

\[
D_N(R) = \frac{N_p}{R\sigma \sqrt{2\pi}} \exp \left( -\frac{[\ln(R) - \ln(R_m)]^2}{2\sigma^2} \right)
\]

Square of formfactor:

\[
P(Q, R) = |F(Q, R)|^2 = \left(3 \frac{\sin(QR) - (QR)\cos(QR)}{(QR)^3}\right)^2
\]
Time-resolved SANS measurements Fe-Cu

Fe-Cu
24% pre-strain

$D_v (\text{nm}^{-1})$

$R (\text{nm})$

0.000
0.001
0.002
0.003
0.004

0.5h
1h
2h
3h
4h
5h
6h
7h
8h
9h
12h
**Time-resolved SANS measurements Fe-Cu**

Structure evolution Cu precipitates during growth:

\[ \text{bcc} \rightarrow 9R \rightarrow 3R \rightarrow fcc \]

**bcc**: \( R < 5 \text{ nm} \)

**9R**: \( 5 \text{ nm} < R < 16 \text{ nm} \)

**3R & fcc**: \( R > 16 \text{ nm} \)
Time-resolved SANS measurements Fe-Cu

Network of Cu along dislocations/interfaces

Porod constant $K_p$: $\lim_{Q \to \infty} [I(Q)] = K_p Q^{-4} + B$

![Graph showing the relationship between aging time and $K_p$.]

$K_p = 2\pi(\Delta \rho)^2 S_v$

with specific surface:

$S_v = \frac{\text{interface area}}{\text{volume}}$

Pre-strain leads to a strong Cu precipitation at dislocations/interfaces
Time-resolved ASAXS measurements of undeformed Fe-Cu (8x enhanced contrast)

E = 7.106 keV
L = 20-30 μm

Perez et al.,
Example:
SANS on Au precipitation in deformed Fe-Au alloys
Au precipitation in deformed Fe-Au (1 at.%)

Initial state

After 12 h at 550 °C

Nuclear SANS

Magnetic SANS

Zhang et al.,
TEM of Au precipitates in Fe-Au after aging

- **Undeformed:** only along grain boundaries
- **Deformed:**
  1. along grain boundaries
  2. disk-like, closely connected to the dislocations

Disk-shaped precipitates

\[
\left( \frac{d\Sigma}{d\Omega} \right)(Q) = \begin{cases} 
\text{constant} & \text{for } 0 \leq Q < \frac{\pi}{R} \\
Q^{-2} & \text{for } \frac{\pi}{R} \leq Q < \frac{2\pi}{L} \\
Q^{-4} & \text{for } \frac{2\pi}{L} \leq Q \leq \infty
\end{cases}
\]
Phase fraction of Au precipitates

Invariant: \( Q_{0,i} = \int_{0}^{\infty} \left( \frac{d \Sigma}{d \Omega} \right)_i Q^2 dQ = 2\pi^2 (\Delta \rho_i)^2 f_V (1 - f_V) \)
Specific surface \((S/V)\) circular caps Au precipitates

For disk-shaped precipitates with \(\pi / R \ll Q \ll 2\pi / L\):

\[
\left( \frac{d\Sigma}{d\Omega} \right)(Q) = C_2 Q^{-2} + C_0 \quad \text{where} \quad C_2 = 4\pi (\Delta \rho)^2 \frac{f_v}{S_{vc}}
\]

Specific surface for monodisperse disks:

\[
S_{vc} = 2\pi R^2 N_p = 2 f_v / L \rightarrow C_2 = 2\pi (\Delta \rho)^2 f_v L
\]
Profile fitting of the SANS curve

\[
\frac{d\Sigma}{d\Omega}(Q) = (\Delta \rho)^2 \int_0^\infty D_N(R)V^2(R)P(Q,R)dR
\]

Particle volume: \( V(R) = \pi R^2 L = 2\pi R^3 / \varepsilon \) with aspect ratio \( \varepsilon = 2R / L \)

Log-normal number distribution of particles:

\[
D_N(R) = \frac{N_p}{R\sigma\sqrt{2\pi}} \exp\left(-\frac{\left[\ln(R) - \ln(R_m)\right]^2}{2\sigma^2}\right)
\]

Orientation-averaged square of formfactor:

\[
P(Q,R) = \frac{\pi}{2} \int_0^{\pi/2} |F|^2 \sin(\alpha) d\alpha = \int_0^{\pi/2} \left(\frac{2J_1(QR\sin(\alpha))}{QR\sin(\alpha)}\frac{\sin(QL\sin(\alpha)/2)}{QL\sin(\alpha)/2}\right)^2 \sin(\alpha) d\alpha
\]
Profile fitting of the SANS curve

\[ \varepsilon = \frac{2R}{L} \approx 8 \]

**SANS**

- 12 h at 550 °C
- 24% deformation

**TEM**

- 12 h at 550 °C
- 24% deformation

(a) SANS

(b) TEM
Au segregation at (sub)grain boundaries

For Porod scattering: $Q \gg \pi / R$ and $Q \gg 2\pi / L$:

$$\left( \frac{d\Sigma}{d\Omega} \right)(Q) = C_2 Q^{-4} + C_0 \quad \text{where} \quad C_4 = 2\pi (\Delta\rho)^2 S_v$$

Specific surface $S_v = \text{interfacial area per unit volume}$

![Graph showing specific surface $S_v$ and constant $C_4$ as a function of aging time for different pre-strains.](image)
Example:
SAXS on (Fe,Cr)$_7$C$_3$ carbides and dislocation structures in low-Cr steel
SAXS pattern:

\[ E = 17 \text{ keV} \]
\[ \lambda = 0.729 \text{ Å} \]

Heat treatment:

Isotropic → precipitate
Streaks → dislocations

Gözde Dere et al.,
Isotropic SAXS profile

Lognormal size distribution:

\[ f(R) = \frac{1}{s R (2\pi)^{1/2}} \exp \left\{ -\frac{1}{2} \left[ \frac{\ln(R/R_m)}{s} \right]^2 \right\} \]

<table>
<thead>
<tr>
<th>$R_m$ (nm)</th>
<th>$s$</th>
<th>$f_v$ (%)</th>
<th>$N$ (m$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT</td>
<td>4.74</td>
<td>0.33</td>
<td>$2.98 \times 10^{22}$</td>
</tr>
<tr>
<td>823 K</td>
<td>5.25</td>
<td>0.26</td>
<td>$1.64 \times 10^{22}$</td>
</tr>
</tbody>
</table>

Streaks in SAXS profiles
Small-angle scattering from dislocations


$$I = A^2 \left[ cL + F_t(Q_t, L) F_w(Q_w, L) \right]$$

- StrONGLY anisotropic scattering along $(Q_w)$ and perpendicular $(Q_t)$ to the wall.
Streaks in SAXS profiles
Correlation to simultaneous X-ray Diffraction

The data provide direct information that links:
the matrix phase structure, dislocations and nucleated precipitate.

Gözde Dere et al.,
Streaks in SAXS profiles
Correlation to simultaneous X-ray Diffraction

Gözde Dere et al.,
Example:
SANS on the magnetic flux-line lattice of superconducting UPt$_3$
Small Angle Neutron Scattering

Magnetic flux-line lattice in superconductor

Diffraction pattern (superconducting Nb)

\[ I(Q) \propto |f(Q)|^2 \]

\[ f(Q) = \text{form factor field profile} \]
Magnetic Flux-Line Lattice

Flux quantum: $\Phi_0 = \hbar/2e = 2.07 \times 10^{-15}$ Tm$^2$

$$S = \Phi_0/B = (\sqrt{3}/2) \ a^2 = (2/\sqrt{3}) \ d_{10}^2$$

$$d_{10} = \sqrt{\sqrt{3}/2}(\Phi_0/B) = 423.4 \ \text{Å}/\sqrt{B} \ [T]$$

Flux quantum: $\Phi_0 = \hbar/2e = 2.07 \times 10^{-15}$ Tm$^2$
Unconventional superconductivity in UPt$_3$

Flux-Line Lattice $\text{UPt}_3$ ($B \parallel c$)

**Normal State**

**Zero-Field Cooled**

**Field Cooled**

$T_Q = 475 \text{ mK}$

Further reading SAXS/ SANS on metals:


SANS instrument under development in Delft