Grazing Incidence Small Angle X-ray Scattering

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Outline

- Grazing Incidence Small Angle X-ray Scattering (GISAXS) beamline and setup
- Key knowledge to interpret GISAXS
  - Fourier Transform
  - Shape, size, and orientation of particles and lattices
- The effect of a small incident angle
  - Reflection
    - Experimental examples: Crystalline nano particles.
  - Penetration depth
    - Experimental examples: Block copolymer films
  - Refraction
- Grazing Incidence Small Angle X-ray Diffraction
  - Ewald sphere
    - Experimental examples: Block copolymer films
- Quantitative calculation
  - Distorted wave Born approximation
  - Snell’s law and Fresnel’s law
Beamstop with a photodiode (phd)

Sample-to-detector distance

Sample

Fast shutter

Guard slit

I0 monitor (IC, etc.)

Beam defining slit
Beamstop with a photodiode \((phd)\)

Pilatus2M(SAXS)

Pilatus300(WAXS)

Fast shutter

\(\theta\)

\(\phi\)

\(sah\)

\(sav\)
12ID-B beamline at APS
Why GISAXS?

Advantage for the grazing incidence geometry for thin film.
1. Several orders larger scattering volume
2. Scatterings from oriented samples
Scattering and Fourier Transform

Electron density

$|\text{FT(Electron density)}|^2$
The Bragg equation: $q = \frac{2\pi}{D}$
1. The Bragg equation: $q = \frac{2\pi}{D}$
2. Orientation
Polydispersity
1. Scattering from a flat surface
2. Particle shape
Octahedron

Real space

Reciprocal space
When the structure factor is applied
2D cylinders

Height  10nm  20nm  50nm  100nm  500nm
lattices
Note

- So far, the intensities have been calculated NUMERICALLY

\[ I(q) = \left| \sum_{i=1}^{N} F_i(q) \right|^2 \]

- Takes a long time to model and calculate.

- Analytical ways will follow
How to split the form factor and the structure factor

\[ I(q) = \left| \sum_{i=1}^{N} F_i(q) \right|^2 = P(q)S(q) \]

- Decoupling approximation (DA)
- Local Monodisperse Approximation (LMA)
The form factor

\[ F(q) = \rho \int_V e^{-jq \cdot r} \, dr \]

\[ P(q) = \langle |F(q)|^2 \rangle \]

\[ = \sum_{l=1}^{N_p} \frac{N_l}{N_p} \langle |F_l(q)|^2 \rangle \]

\[ = \int n(r) \langle |F_l(q)|^2 \rangle \, dr \]
The form factor models from Babonneau’s software
Rods laid down on a substrate

B. Lee et al. Langmuir, 2007, 23 (22), pp 11157–11163
The size distribution model

- Gaussian
- Double Gaussian for the bimodal distribution.
- Log-normal
- Double Log-normal for the bimodal distribution.
- Weibull
- Schultz-Zimm function
The structure factors from Babonneau’s software

- Random organization: $S(q) = 1$
- Percus-Yevick 3D: Hard sphere potential
- Percus-Yevick 2D
- Paracrystal 1D
- Paracrystal 2D rectangular
- Paracrystal 2D hexagonal
- And many others.. See IsGISAXS manuals.
Reciprocal space or scattering vector $q$

- The scattering vector $q$ is not a scalar but a vector. ($qx$, $qy$, $qz$)

- When a lattice (or a sample) rotate, the reciprocal lattice (or the scattering from the sample) rotates.

- The Bragg condition is not only $q = 2\pi/d$. 
Ewald sphere
Definitions of angles and the q space
Note

- Effects due to the grazing incidence geometry
  - Absorption
  - Reflection
  - Refraction

- These effects are highly depending on the sample.
  - Supported island.
  - Buried particles.
  - Sandwiched particles.
  - ...

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In GISAXS, you can measure only the upper half.
- Substrate absorbs the downward scattering.
At the incident angle, 0

At the incident angle $> 0$
The effect of a small incident angle
1. Reflection causes an additional incident beam

\[ \alpha_i < \alpha_c \]
$\alpha_i \sim \alpha_c$
\[ \alpha_i > \alpha_c \]
Effect of wave amplitudes

\[
\frac{d\sigma}{d\Omega} = r^2 \psi_{sc}(r) \psi_{sc}^*(r)
\]

\[
= A \left| T_i T_f F(q_{||}, q_{z,t}) + T_i R_f F(q_{||}, -q_{z,t}) + R_i T_f F(q_{||}, q_{z,t}) + R_i R_f F(q_{||}, -q_{z,t}) \right|^2
\]
GISAXS from a sphere / log scale image
Example

A facetted Pt/W(211) sample annealed at 1340 K

Measured at different azimuth angles

Measured at different incident angles: (a) 0.1°, (b) 0.22°, (c) 0.42°, (d) 0.68°.

C. Revenant et al., Surface Science, 601, 16, 3431
0.8 nm Co/1.1 ML Pt/W after an annealing during (a) 3 min at 920–1000 K, (b) 3 min at 1020–1100 K, (c) 3 min at 1140–1210 K. Respective simulated 2D GISAXS patterns from (d) to (f).

C. Revenant et al., Surface Science, 601, 16, 3431
Shape changes with Ag nanoparticles in propylene epoxidation

Under ~1 atm. pressure of 1.0% propylene and 0.5% oxygen in He

On 6 cycle Al₂O₃ over SiO₂/Si

Shape changes with Ag nanoparticles in propylene epoxidation

Under ~1 atm. pressure of 1.0% propylene and 0.5% oxygen in He
On 6 cycle Al2O3 over SiO2/Si with an initial cluster size ~6nm

- Change of the wetting angle
- Onset of change of aspect ratio
- Particle shape transformation to spherical form
- Particles remain spherical after 4 hrs reaction and cooling back to 23 C
The effect of small incidence angle

2. Critical angle

\[
\alpha_c = \frac{\lambda (r_e \bar{\rho} / \pi)^{1/2}}
\]

Electron density | Critical angle at 8keV
--- | ---
0.32 e/Å³ | 0.150 degree
0.70 e/Å³ | 0.223 degree
Critical angles

\[ \alpha_i \]
Vary the incident angle!!

X-ray energy: 7.38keV  
Critical angles of PS and PS-PI block copolymer film and Si wafer ~ 0.16° and 0.25°, respectively.

As long as the incident angle is smaller than the critical angle of substrate, particle scattering will be detected. If overshothing is not an issue, the smaller incident angle is the better because smaller q is accessible.

If the incident angle is smaller than the critical angle of film, x-ray can only scan top surface of film. If the exit angle is smaller than the critical angle of film, scattered x-ray practically cannot be detected.

The effect of a small incident angle
3. Refraction

\[
\alpha_i \quad \tilde{\alpha}_i \quad \tilde{\alpha}_f \quad \alpha_f
\]

\[
n_f = 1 - \delta + i\beta \equiv 1 - \alpha_c^2/2 + i\beta
\]

\[
\alpha_c = \lambda (r_e \bar{\rho}/\pi)^{1/2}
\]

\[
n_f \cos \tilde{\alpha} = \cos \alpha
\]
How much x-ray will be refracted in a polymer film

Figure 6. Relations between $q_z$ and $\alpha_f$ of the diffraction due to the reflected (circles) and transmitted (squares) beams: the filled and open symbols denote the diffraction peaks without and with correction for the refraction effect, respectively.

B. Lee et al. Macromolecules, 2005, 38 (10), pp 4311–4323
Penetration depth

\[
\alpha_c = \lambda \left( \frac{r_e \bar{\rho}}{\pi} \right)^{1/2}
\]

Figure 21. Universal curves of the variation of scattering depth \( \Lambda \) with incidence and exit angles \( \alpha_i \) and \( \alpha_f \), expressed as multiples of \( \alpha_c \). The units of the vertical scale depend in general on the photoelectric absorption of the sample, but have been calculated here for gold at \( \lambda = 1.5 \) \( \text{Å} \) using equation (49).

Quiz
GISAXS vs SAXS : 40nm AuNp
Diffraction from lattice
2D powder
BCC - 100 vs 110 orientation

$\alpha_i$, $k_i$, $\phi$, $x$, $y$, $z$, $\alpha_f$, $2\theta_f$, $\phi$.

Ewald sphere

Photodiode/Beamstop

Detector plane

Pixel(H)

Pixel(V)

Two reciprocal spaces

$q_x$, $q_y$, $q_z$, $q_{z,T}$, $q_{z,R}$
BCC 110 orientation

Along z axis

Along y axis
Ewald sphere

Two-beam effect
Refraction correction
Crystal orientation matrix
Penetration depth
BCC : 100 vs 110
BCC : 100 vs 110
BCC : 100 vs 110

**Diffractions from block copolymer films**

Hexagonal Cylinder  
Hexagonally perforated layer  
Gyroid : Cubic(Ia3d)

Lee et al. Macromolecules, 2005, 38, 4311


Facet analysis

112 orientation
111 : 19.5, 61.9, and 90°
110 : dotted arrows

2D powder with 112 orientation
Octahedron
Truncated Octahedron
Octahedron scattering in the reciprocal space
Quantitative calculation
\[
\begin{pmatrix}
q_x \\
q_y \\
q_z, X
\end{pmatrix} = n_f k_0 \begin{pmatrix}
\cos \tilde{\alpha}_f \cos 2\theta_f - \cos \tilde{\alpha}_i \\
\cos \tilde{\alpha}_f \sin 2\theta_f \\
\sin \tilde{\alpha}_f \pm \sin \tilde{\alpha}_i
\end{pmatrix}
\]

where \(X = t\) or \(r\) for \(+\) or \(−\), and the tilde indicates the refracted angle.
Definition of $q$: Four $q$’s in GISAXS due to the reflection

$$q = k_f - k_i$$

For GISAXS:

- **A**: $q_z = k_{f,z} - k_{i,z}$
  - $q_x = k_{f,x} - k_{i,x}$

- **B**: $q_z = -k_{f,z} - k_{i,z}$
  - $-k_{f,z}$

- **C**: $q_z = k_{f,z} + k_{i,z}$
  - $-k_{i,z}$

- **D**: $q_z = -k_{f,z} + k_{i,z}$
  - $-k_{f,z}$
Full DWBA formulae

\[
\frac{d\sigma}{d\Omega} = r^2 \psi_{sc}(r) \psi_{sc}^*(r) \\
= A \left| T_i T_f F(q_{||}, q_{z,t}) + T_i R_f F(q_{||}, -q_{z,r}) + R_i T_f F(q_{||}, q_{z,r}) + R_i R_f F(q_{||}, -q_{z,t}) \right|^2
\]

\[
q_t = (q_{||}, q_{z,t}) \\
q_r = (q_{||}, q_{z,r})
\]
Fresnel’s law (wave amplitude) and Snell’s law (wave vector)

\[ m = \frac{1}{2} \]

\[ \begin{align*}
T_i & = k_{z,i} \\
R_i & = -k_{z,i}
\end{align*} \]

\[ z = z_1 \]

\[ z_1 = 0 \text{ and } z_m \neq 1 < 0 \]

\[ d_m = z_{m-1} - z_m > 0. \]

\[ \psi_i(\alpha_i) = T_i e^{ik_{z,i}z} + R_i e^{-ik_{z,i}z} \]

\[ k_{z,i,m} = -k_0 \sqrt{n_m^2 - \cos^2 \alpha_i} \]

\[ \psi_f(\alpha_f) = (T_f e^{-ik_{z,f}z} + R_i e^{ik_{z,f}z})^* \]

\[ k_{z,f,m} = k_0 \sqrt{n_m^2 - \cos^2 \alpha_f} \]

\[ T_1 = 1 \text{ and } R_N = 0. \]

Lee et al. Macromolecules, 2005, 38, 4311
Fresnel’s law (wave amplitude) and Snell’s law (wave vector)

The Fresnel coefficients at the interface between layers $m$ and $m+1$ are

$$\begin{align*}
r_{m,m+1} & = \frac{k_{z,m} - k_{z,m+1}}{k_{z,m} + k_{z,m+1}} \\
t_{m,m+1} & = \frac{2k_{z,m}}{k_{z,m} + k_{z,m+1}}
\end{align*}$$

\[X_m = \frac{R_m}{T_m} = e^{2ik_{z,m}z_m} \left( \frac{r_{m,m+1} + X_{m+1}e^{2ik_{z,m+1}z_m}}{1 + r_{m,m+1}X_{m+1}e^{-2ik_{z,m+1}z_m}} \right)\]

\[R_{m+1} = \frac{1}{t_{m+1,m}} \left( T_{m}r_{m+1,m}e^{i(k_{z,m+1}+k_{z,m})z_m} + R_{m}e^{i(k_{z,m+1}-k_{z,m})z_m} \right)\]

\[T_{m+1} = \frac{1}{t_{m+1,m}} \left( T_{m}e^{-i(k_{z,m+1}-k_{z,m})z_m} + R_{m}r_{m+1,m}e^{-i(k_{z,m+1}+k_{z,m})z_m} \right)\]
Intensity and scattering vectors

\[ \Psi_{sc,m}(R) = -\frac{e^{ik_0R}}{R} \int \Psi_{f,m}^*(r)V(r)\Psi_{i,m}(r)dr, \]

\[ \Psi_{sc,m}(R) = \frac{e^{ik_0R}}{R} \Phi_m(q), \]

\[ \Phi_m(q) = T_{i,m}T_{f,m}A(q_{||},m,q_{t,z},m) + T_{i,m}R_{f,m}A(q_{||},m,-q_{r,z},m) \]
\[ + R_{i,m}T_{f,m}A(q_{||},m,q_{r,z},m) + R_{i,m}R_{f,m}A(q_{||},m,-q_{t,z},m), \]

where \( A(q) \) is the Fourier transform of \( V(r) \)

\[ I(q) = \sum_m R^2\Psi_{sc,m}(R)\Psi_{sc,m}^*(R) = \sum_m \Phi_m(q)\Phi_m^*(q) \]
Effect of wave amplitudes

\[
\frac{d\sigma}{d\Omega} = r^2 \psi_{sc}(r) \psi_{sc}^*(r) = A \left| T_i T_f F(q_\parallel, q_{z,t}) + T_i R_f F(q_\parallel, -q_{z,r}) + R_i T_f F(q_\parallel, q_{z,r}) + R_i R_f F(q_\parallel, -q_{z,t}) \right|^2
\]

Lee et al. Macromolecules, 2005, 38, 4311
References

Probing surfaces and interfaces morphology with Grazing Incidence Small Angle X-Ray Scattering
G. Renaud et al., Surface Science Reports, 64(8), 255-380 (2009).

Structural Analysis of Block Copolymer Thin Films with Grazing Incidence Small-Angle X-ray Scattering

Softwares
http://www.chemie.uni-hamburg.de/pw/sfoerster/software.html
http://sites.google.com/site/byeongdu/software