Grazing Incidence X-ray Scattering and Diffraction
Theory and applications

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Outline

• Experimental considerations

• Brief introduction to the Distorted Wave Born Approximation

• Example GISAXS

• GIWAXS + example
Transmission vs Gracing incidence geometry

Transmission:

X-rays

Sample

Gracing incidence:

\( q (\text{nm}^{-1}) \)

Intensity (a.u.)

\( q_i (\text{nm}^{-1}) \)

Si\(_2\)O\(_2\) R=25nm

monodisperse

polydisperse

\( q_i (\text{nm}^{-1}) \)

Intensity (a.u.)
GISAXS and GIWAXS applications

- Long-range ordering of block copolymers for dense data storage
- Composite membranes for artificial photosynthesis
- Inorganic nanocomposites for electrochromic windows
- Batteries & fuel cells
- OPV BHJ materials
- Lithographic patterning
- Self-assembly of nanoparticles in block copolymer thin films
- Nanocomposites for solar cells
- Virus nanofiber tissue engineering materials
- Block copolymer self-assembly
Probing polymers and soft matter length scales
Ideally, beam as small as possible vertically and parallel
Grazing Incident Small Angle X-ray Scattering

Characterization of nanoscale density correlations and/or the shape of nanoscopic objects at surfaces, at buried interfaces, or in thin films

- Surface sensitive (minimum penetration depth 10 nm)
- High scattering intensity ideal to perform in-situ and time-resolved study
- Complex data analysis

\[
q_{x,y,z} = \frac{2\pi}{\lambda} \left[ \frac{\cos(\alpha_f) \cos(2\theta_f) - \cos(\alpha_i)}{\cos(\alpha_f) \sin(2\theta_f) \sin(\alpha_f) + \sin(\alpha_i)} \right]
\]

Image: Prof. Andreas Meyer, Uni Hambourg
X-ray reflectivity (XRR)

- Measure strictly only along $q_z = \frac{4\pi}{\lambda} \sin(\alpha)$
- Point detector with collimator
- Information about $\rho_e(z)$, roughness, thickness

Usually in GIXS $\alpha_c$ (polym) < $\alpha_i$ < $\alpha_c$ (sub)
Regimes for GISAXS analysis

\[ \alpha_i < \alpha_c \text{ (polymer)} \quad : \quad \text{evanescent regime} \]

\[ \alpha_c \text{ (polymer)} < \alpha_i < \alpha_c \text{ (substrate)} \quad : \quad \text{dynamic regime} \]

\[ \alpha_i > \alpha_c \text{ (substrate)} \quad : \quad \text{kinematic regime} \]

In the kinematic regime:

\[
\frac{d\sigma}{d\Omega}(q) = \frac{1}{N} \sum_i \sum_j F^i(q)F^{j,*}(q)\exp[iq(R^i_\parallel - R^j_\parallel)]
\]

In the simple Born Approximation (BA):

\[
F^i = \int_V \rho(r)\exp(iq \cdot r)\,dr
\]
Experimental considerations

Footprint of the beam:

Beam 300 μm:
\[ \alpha_i = 0.1^\circ \rightarrow 17 \text{ cm} \]
\[ \alpha_i = 0.5^\circ \rightarrow 3.4 \text{ cm} \]
Surface scattering – reflection and refraction

Light

Index of refraction: $n \geq 1$

Snell’s law: $n_1 \sin \alpha = n_2 \sin \alpha'$

X-ray

Index of refraction: $n = 1 - \delta + i\beta$

Snell’s law: $n_1 \cos \alpha = n_2 \cos \alpha'$

Total reflection
Surface sensitivity (penetration depth)

Limited penetration into the sample → enhanced surface sensitivity

Snell’s law: \( \cos \alpha = n \cos \alpha' \)

Critical angle: \( \alpha_c = \sqrt{2\delta} = \lambda \sqrt{\frac{\rho}{\pi}} \)

For \( \alpha_i \leq \alpha_c \)

Evanescent regime

Penetration depth - \( \Lambda \) (Å)

Snell’s law:
\[
\cos \alpha = n \cos \alpha' 
\]

Critical angle:
\[
\alpha_c = \sqrt{2\delta} = \lambda \sqrt{\frac{\rho}{\pi}} 
\]

For \( \alpha_i \leq \alpha_c \)

Evanescent regime

Penetration depth - \( \Lambda \) (Å)

- Si
- Au
- PP

12 keV (\( \lambda = 1.033 \) Å)
Reflection and Transmission coefficients

For the bare substrate:

\[ E(r, k) = E_0 e^{-i k || r ||} \begin{cases} e^{-i k_{i,z} z} + r e^{i k_{i,z} z} & \text{for } z > 0 \\ t e^{-i k_{t,z} z} & \text{for } z < 0 \end{cases} \]

Fresnel reflectivity: \[ R_F = |r|^2 \]

Fresnel transmission: \[ T_F = |t|^2 \]

\[ r = \frac{k_{i,z} - k_{t,z}}{k_{i,z} + k_{t,z}} \]

\[ t = \frac{2 k_{t,z}}{k_{i,z} + k_{t,z}} \]

\[ n = 1 - \delta + i \beta \]
Nano-objects supported on a substrate

\[
\frac{d\sigma}{d\Omega} = r_e^2 |\Delta \rho|^2 |\mathcal{F}(q_\parallel, k^i_z, k^f_z)|^2
\]

\[
q = k_f - k_i
\]

\[
\mathcal{F}(q_\parallel, k^i_z, k^f_z) = F(q_\parallel, q^1_z) + r(\alpha_i)F(q_\parallel, q^2_z) + r(\alpha_f)F(q_\parallel, q^3_z) + r(\alpha_i)r(\alpha_f)F(q_\parallel, q^4_z)
\]

Classican Born Approx. (SAXS)

1. \(q^1_z = k^f_z - k^i_z\)

2. \(q^2_z = k^f_z + k^i_z\)

3. \(q^3_z = -k^f_z - k^i_z\)

4. \(q^4_z = -k^f_z + k^i_z\)
Distorted Wave Born Approximation - DWBA

For a simple sphere:

\[ F_{sphere}(q, R) = 4\pi R^3 \frac{\sin(qR) - qR\cos(qR)}{(qR)^3} e^{iqzr} \]

Classical SAXS
Nano-objects supported on a substrate

Yoneda peak for Si substrate: $\alpha_f = \alpha_c$
Nano-objects supported on a substrate: effect of increasing $\alpha_i$

Au nanoparticles $R = 25$nm on glass substrate

For supported nano-object the maximum scattered intensity is at the critical angle of the substrate
Particle shape sensitivity

\[
q_{x,y,z} = \frac{2\pi}{\lambda} \left[ \begin{array}{c} \cos(\alpha_f) \cos(2\theta_f) - \cos(\alpha_i) \\ \cos(\alpha_f) \sin(2\theta_f) \\ \sin(\alpha_f) + \sin(\alpha_i) \end{array} \right]
\]

Calculations performed using the IsGISAXS software (R. Lazzari)
Calculated form factors under the DWBA

Now with spatial correlation between nano-objects

If spatial correlation exists between objects, an interference function has to be considered:

**Decoupling approximation (DA):**

\[
I(q) \propto I_a(q) + |\langle F(q) \rangle|^2 S(q)
\]

**Local monodisperse approximation (LMA):**

\[
I(q) \propto \langle |F(q)|^2 \rangle S(q)
\]

**PS cylinders with 2D hexagonal lattice**

**PS spheres with 2D hexagonal lattice**
Supported nanoparticles: Pt deposit on MgO (001)

Disks with 1D paracrystalline lattice

Au clusters on a substrate

@BM26B

Au clusters with R = 3nm and H/R = 1.6
GISAXS from a monolayer of core-shell gold-PNIPAM nanoparticles

Spheroidal Gold cores
R = 25nm

2D Hex with a = 230 nm
High resolution GISAXS (GIUSAXS)

Au linear assembly

AFM

GIUSAXS

$q^* = 0.0048 \text{ nm}^{-1} \rightarrow d = 1.3 \text{ \mu m}$
Several possible geometries

Buried interfaces: Pb clusters implanted in Si substrate

\[ \alpha_i \sim \alpha_c \text{ (substrate)} \]

\[ \alpha_i \gg \alpha_c \text{ (substrate)} \]

\[ D_{\text{intercluster}} = 9 \text{nm} \]
Scattering from facets: pyramid

X-rays \( \zeta = 0^\circ \)

X-rays \( \zeta = 45^\circ \)
Scattering from facets: Ge/Si(001) quantum dots

Bragg rod is proportional to the facet area
**In-situ GISAXS: study of LIPSS formation**

Laser Induced Periodic Surface Structures (LIPSS)

- Interference of the incident and reflected light at the interface produces ripples with a period $L$:
  $$\Lambda = \frac{\lambda}{n \pm \sin \Theta_i}$$

- Roughness:
  $$\sigma = \sqrt{\sigma_0^2 + \frac{kT}{2\pi \gamma} \ln\left(\frac{\lambda_l}{\lambda_s}\right)}$$

  $\sigma_0$: Molecular Roughness
  $\lambda_l$: longest wavelength
  $\lambda_s$: shortest wavelength

Poly(triethylene terephthalate) (PTT)
Set-up @ BM26, ESRF

Sample
Laser
Mirrors
I: Iris
A: Attenuator
Sample
AFM

F=7 mJ/cm² @ N pulses (8ns)

N pulses (8ns)

Final height about 50nm, periodicity about 200 nm

(a) Non-irrad.
(b) 100
(c) 300

(a) Non-irrad.
(b) 100
(c) 300

AFM

F=7 mJ/cm² @ N pulses (8ns)

N pulses (8ns)
GISAXS at the liquid-air interface

Deflecting crystal

Adjustable z-table

Colloidal CdSe/CdS nanorods

GIWAXS – crystallinity and orientation

Isotropic:

Textured – slightly oriented:

Highly oriented:
Maps of constant $q_r$ values in pixel space

$$q_r = \sqrt{q_x^2 + q_y^2}$$

$$q = \sqrt{q_r^2 + q_z^2}$$
P3HT:PCBM:P3HT-b-P4VP blends

- **Why P3HT- b -P4VP:** non-covalent supramolecular interactions between P4VP and P3HT-b-P4VP is blended with P3HT:PCBM
- **Inverted OPV devices**
  - Glass/ITO/TiOx/active layer/MoO$_3$/Ag
- **Goal:**
  - Exploit the PCBM - P4VP interactions to trigger the morphology and improve the power conversion efficiency (PCE)

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Prof. G. Hadziioannou (Uni Bordeaux)
GIWAXS (1) - Block-copolymer additives in OPVs

**P3HT- b** -**P4VP** as nanostructuring agent in the **P3HT:PCBM** blend

Upon **P3HT- b** -**P4VP** incorporation:

- PCBM is less aggregated → more interfaces for exciton dissociation
- Minor decrease in the crystallinity of P3HT
- Increase in the population of the face-on oriented P3HT crystallites

* Adv. Mat. 2012, 24, 2196-2201
GIWAXS (2) – Ordering in organic thin film transistors

- Yoneda peak
- (001) peak
- (002) peak
- Low angle diffuse scattering

GISAXS

GIWAXS

$q_y (\text{nm}^{-1})$ vs. $q_z (\text{nm}^{-1})$ intensity (a.u.)
Ordering in organic thin film transistors

MM1320 (5 nm)

MM1322 (15 nm)

MM1325 (50 nm)

GIWAXS (2)
Software for DWBA

• IsGISAXS from R. Lazzary (Windows)

• FitGISAXS from D. Babboneau (Igor Pro)

• BornAgain (Python)
  C. Durniak et al, (Juelich)
Books and references


Conclusions

- GISAXS and GIWAXS are powerful tools to obtain statistical structural information on sub-monolayers, monolayers and multilayers of soft and hard condensed matter

- GISAXS $\rightarrow$ 1-100 (1000) nm

- GIWAXS $\rightarrow$ down to 0.1 nm

- Surface sensitivity

- High intensity allows for in-situ study

Thank you for your attention!

Questions?