GISAXS/GIWAXS Data Analysis: Thinking in Reciprocal-Space

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What to do with data?

- Qualitative inspection
- Linecuts
- Peak indexing
- Modeling (comparison)
- Fitting

Workflow:

Detector image → Calibrated 2D data

Physical insight → Analysis
Scattering Geometry
Scattering Geometry

- X-ray beam hits sample

\[
|k_i| = \frac{2\pi}{\lambda}
\]
Scattering Geometry

- X-ray beam scatters at a certain angle

\[ |\vec{k}_i| = \frac{2\pi}{\lambda} \]
Scattering Geometry

- Consider the difference between the incident and scattered vectors

\[ |\vec{k}_i| = \frac{2\pi}{\lambda} \]
Scattering Geometry

- We define $q$ to be the momentum transfer

$$\vec{q} = \vec{k}_o - \vec{k}_i$$
Reciprocal-space

- $q$ is a vector in **reciprocal-space** ($k$ and $q$ have units of 1/distance)
Reciprocal-space

- $q$ is always on a sphere

$$|\vec{q}| = q = \frac{4\pi}{\lambda} \sin \theta$$

$Ewald$ sphere
Reciprocal-space

Detector records the intersection between the Ewald sphere and the reciprocal-space

\[ \left| \mathbf{q} \right| = q = \frac{4\pi}{\lambda} \sin \theta \]

For SAXS, it’s almost a plane...
Reciprocal lattice

- Reciprocal-space is the Fourier transform of the realspace structure
- Peaks in reciprocal-space correspond to some repeat spacing in realspace
- $q = 2\pi/d$
Reciprocal lattice

- You observe a peak on the detector when the reciprocal lattice is aligned such that the Ewald sphere intersects the peak.
Reciprocal lattice examples

- Peaks come from repeating structures
- Distance is inverted: $d = \frac{2\pi}{q}$
3D Reciprocal-space

- Aligned

- Isotropic
3D Reciprocal-space

- In-plane powder

- Bimodal
3D Reciprocal-space

- ?

[Diagram of striped objects on a surface]
Reciprocal lattice exercise

- What lattice will be generated?
Reciprocal lattice exercise

- Identify realspace planes
Reciprocal lattice exercise

- This repeating structure yields a peak normal to the planes
Reciprocal lattice exercise

- Reciprocal-space is centro-symmetric
Reciprocal lattice exercise

- Another set of planes...
Reciprocal lattice exercise

- Another set of planes...
- ... another set of peaks.
Reciprocal lattice exercise

- Reciprocal peaks are arranged in hexagonal lattice
- But note the orientation!
- Also: no peak corresponds to the particle-particle distance...
Reciprocal lattice exercise

- We also get higher-order peaks
- We’ve neglected peak intensities and shape, which encode all the details of the structure (finite size $\rightarrow$ peak width, electron density distribution $\rightarrow$ peak intensities, disorder $\rightarrow$ peak falloff, ...)

![Diagram of reciprocal lattice exercise](image)
GISAXS

- GISAXS makes this more complicated:
  - Refraction shifts and distorts reciprocal-space
GISAXS

- GISAXS makes this more complicated:
  - Refraction shifts and distorts reciprocal-space
  - Reflection leads to two sets of peaks

You can use DWBA to predict peak positions
So, you can index all the peaks, ...

Singh *ACS Nano* 2012, 17, 10335
Examples

- Block-copolymer cylinder phase

Note two rings

Disordered
Qualitative

- Diffuse scattering comes from disorder, roughness...
- Halo usually means amorphous, sharp rings means good order (crystal?)
- Intensity along ring tells orientation
- Peaks becomes speckled as the grain size becomes very large
- An array of distinct peaks means crystal is well-oriented w.r.t. substrate
- If the peaks appear/disappear when you rotate, you may have a single crystal

![Disordered](disordered.png) ![Some Ordering](some-ordering.png) ![ Oriented, Textured](oriented-textured.png) ![Single Crystal](single-crystal.png)

less order more order
Linecut

- Calibration converts from pixel to $q$
  - Detector distance
  - X-ray energy
  - Beam position
  - Detector orientation/tilt
- Adjust intensity
  - Beam flux and measurement time
  - Polarization, pixel acceptance, ...
- Linecuts:
  - 1D radial average
  - Radial (in-plane, out-of-plane, other)
  - “Straight” (qz or qr)
  - Along an arc
- Binning:
  - Average multiple pixels to improve SNR
  - Don’t smear-out real features! (e.g. peak width)
  - Account for background!
Linecut: what can it tell you?

- \( q \)-position \( \Rightarrow d = \frac{2\pi}{q} \)
  - But don’t forget about unit-cell symmetry!

- \( q \)-positions \( \Rightarrow \) Unit cell symmetry, dimensions and distortion

- Peak width \( \Rightarrow \) \( \zeta = \frac{2\pi K}{\Delta q} \)
  - Must account for instrumental resolution
  - Many things can affect peak width (microstrain, faults, ...)

- Intensity \( \Rightarrow \) Population analysis (amount of material)
  - Must account for various factors: peak multiplicity, sample symmetry, experimental (flux, acceptance), ...
  - Comparing between samples can be tricky (sample size/thickness, \( e^- \) contrast)
  - Use relative comparisons or internal standards

Smilgies J. Appl. Cryst. 2009, 42, 1030
Peak width

- Peak width can be anisotropic:
  - Width in each direction is telling you the ‘grain size’ in that direction
- Remember: distance is inverted $\xi = \frac{2\pi K}{\Delta q}$
  - Narrow peak $\rightarrow$ big grains
  - Broad peak $\rightarrow$ small grains

Width along qr gives the in-plane grain size

Extended streaks along vertical: This means the ‘size’ in the vertical is very small (thickness of a very thin film)
P3HT: poly 3-hexylthiophene

- Lamellar repeat: 1.6 nm
- π-π stacking: 0.39 nm
- PCBM halo: ~0.5 nm
- P3HT (010): ~1.6 nm
- P3HT π-π (010): ~0.4 nm
• Intensity along ring tells orientation

Edge-on
\[ \alpha_h \approx 0.0002 \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \]

Face-on
\[ \alpha_h \approx 0.1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \]

• How to quantify?
Analysis

- Account for Bragg angle
- Think in terms of how the Ewald sphere intersects reciprocal-space
- Subtract background

Data doesn’t start at 0

Exclude Yoneda and sub-horizon data

Baker *Langmuir* 2010, 26, 9146
Analysis

- Account for in-plane powder symmetry

\[ I_c = I \times \sin \chi \]
What about in-plane alignment?

- Chains align with the grooves
- Not an in-plane powder!

Johnston *ACS Nano* 2014, 8, 243
In-plane aligned

- Rotate sample, accumulated images to reconstruct 3D reciprocal-space
- Use $\phi$ rocking scan (and correct intensities)
- If very well-aligned: just use intensity at $\phi = 0^\circ$
2D Nanoparticle Assembly

- Nanoparticles attracted to air-water (due to charge)
- Nanoparticle organization controlled by DNA coronas

Srivastava JACS 2014, ASAP
2D Nanoparticle Assembly

- Brute-force modeling...

\[ P(q, r) = \int_0^{2\pi} |F(q_x, q_y)|^2 \, d\phi \]

\[ = \int_0^{2\pi} \rho(r) e^{iqr} \, dV \, d\phi \]

\[ = \int_0^{2\pi} \left[ \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \rho(x, y) e^{iqr \sin(\phi)x} e^{iqr \cos(\phi)y} \, dx \, dy \right]^2 \, d\phi \]

\[ = \int_0^{2\pi} \left[ \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \rho(x, y) e^{iqr \sin(\phi)x} e^{iqr \cos(\phi)y} \, dx \, dy \right]^2 \, d\phi \]
Conventional GISAXS

- Thin film scattering: GISAXS
Conventional GISAXS

- GISAXS blocked below horizon
- TSAXS attenuated at high angle
New geometry

- What if beam hits near edge of substrate?
- Scattering exits from edge...
New concept: GTSAXS

- Grazing-incidence Transmission Small-Angle X-ray Scattering

Scattering exits from edge (between horizon and sample corner)

Lu *J Appl Cryst* 2013, 46, 165
BCP pattern

(a) $\alpha_i = 0.10^\circ$
(b) $\alpha_i = 0.16^\circ$
(c) $\alpha_i = 0.50^\circ$

(d) [Image of a pattern with 50 nm scale]

(e) [Graph showing intensity vs. $q_z (\text{Å}^{-1})$ with lines for $\alpha_i = 0.10^\circ$, $\alpha_i = 0.16^\circ$, and $\alpha_i = 0.50^\circ$.]
GTSAXS

- New geometry makes data much simpler to analyze:
  - Reflection terms nearly zero
  - Refraction is small and linear (and independent of angle)
- Simple scattering theory (Born approximation) now sufficient to fit data!
- All that is required is (representative) sample near edge
Conclusion

• Analysing GISAXS data can be tricky...

• But it’s worth doing:
  • In principle, everything about the sample’s structure is encoded in the data

• Thinking in terms of **reciprocal-space** can help

• Questions?
Exercises

What's this intense rod?
Why are there oscillations along the rod?
What does this peak tell you?
Exercises

What’s this stuff?

Lots of peaks!

What kind of sample is this?
Exercises

What does this ring tell you?

High background... why?

What’s this?
Exercises

How would you analyze this sample?