Probing 3-D Orientation in Templated Self-Assembly using Rotational SANS

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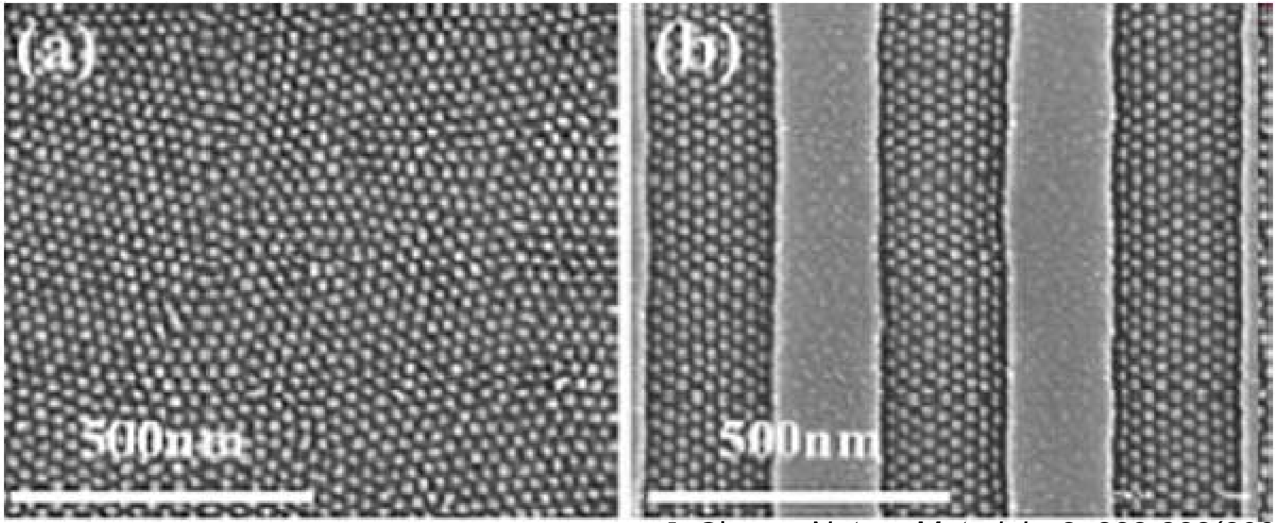
Templated Self Assembly of Block Copolymers

Challenges

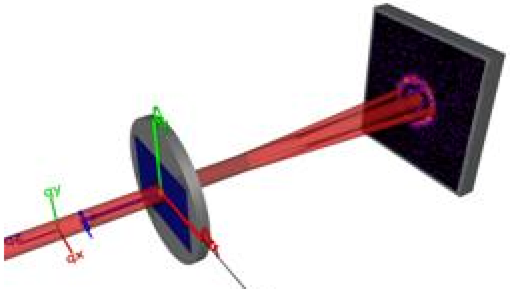
•Difficult to “see” below the top surface

•Other applications will focus on complex 3-dimensional structures (Nanostructured membranes for energy applications, hierarchical assembly)

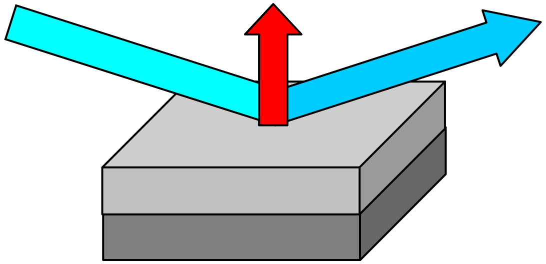


J. Cheng, *Nature Materials*, 3, 823-828(2004)

SANS vs. NR of Thin Films



Small Angle Neutron Scattering



Specular Neutron Reflectivity

•Measures structure parallel to the substrate

•Measures structure perpendicular to the substrate

SANS + NR together can provide parrallel vs. perpendicular orientation map

•Substrate must be neutron transparent with low adsorbtion, no SANS structure

•Optimal film thickness is on the order of mm’s, but 10 nm is possible.

•Analysis is performed in the limit of the Born Approximation

•Q vector is relative to beam only, substrate plane is irrelevant.

•Substrate is smooth and flat, has relatively high scattering length density

•Characterization becomes challenging as film thickness > 200 nm.

•Limit of high interaction at low angle to limit of Born Approximation at very high angles

•Q vector is effectively defined by substrate plane.

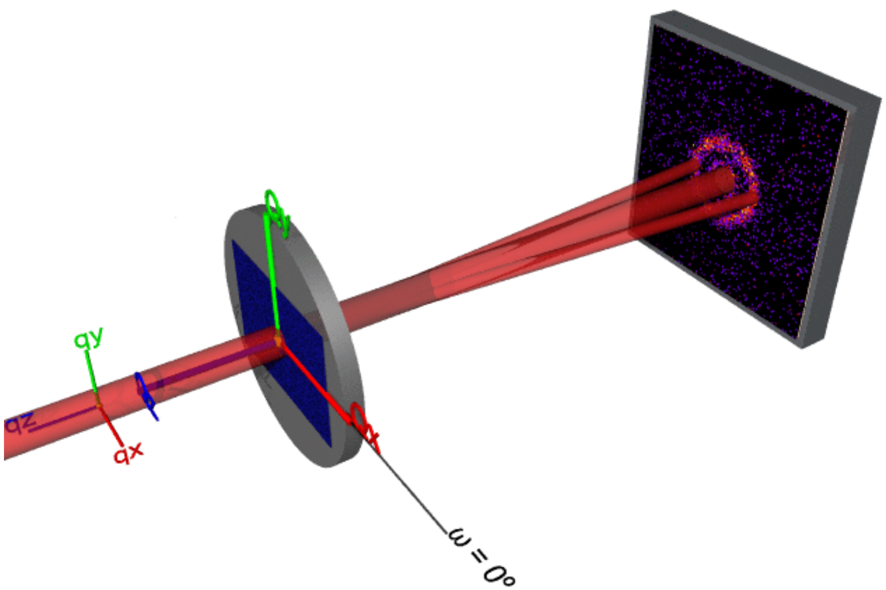
Rotational Small Angle Neutron Scattering

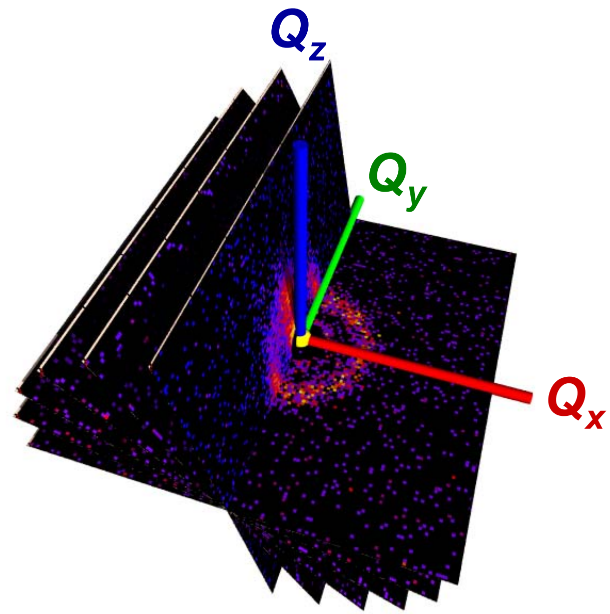
- We convert from beam-coordinates (q_x,q_y,q_z) to sample-coordinates (Q_x,Q_y,Q_z) using a rotation matrix

$$Q_x = q_x \cos\omega - q_z \sin\omega$$

$$Q_y = q_y$$

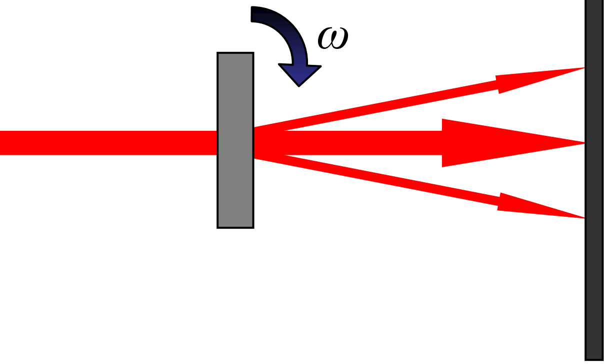
$$Q_z = q_x \sin\omega + q_z \cos\omega$$

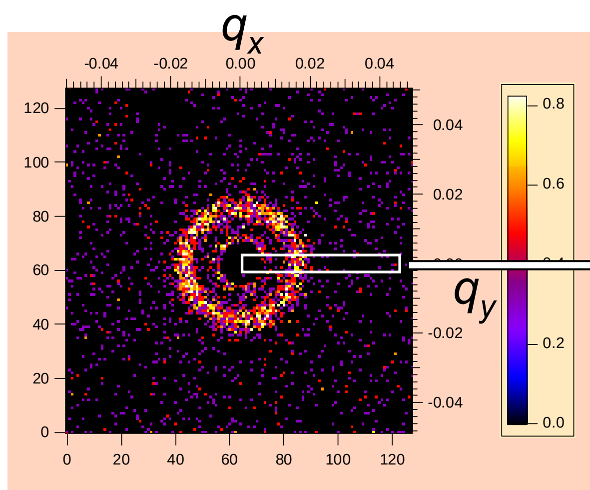


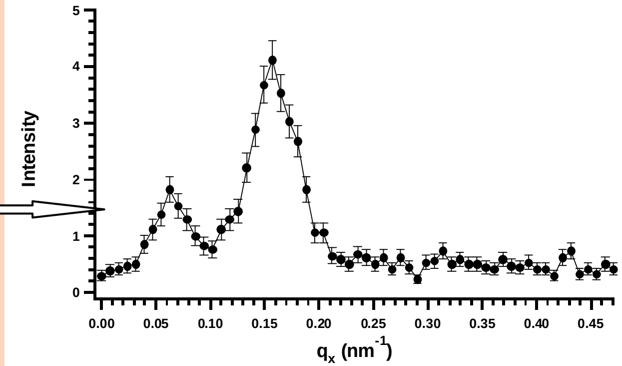


Rotational Small Angle Neutron Scattering

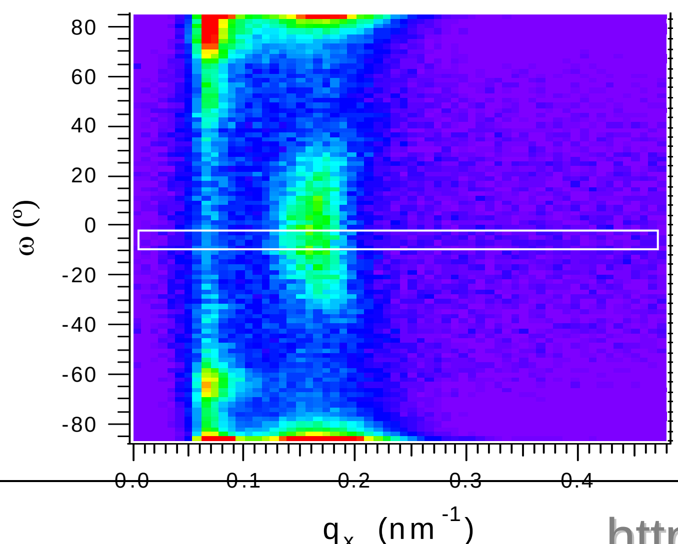
a) For each ω:
- Get SANS image
- Box average q_x



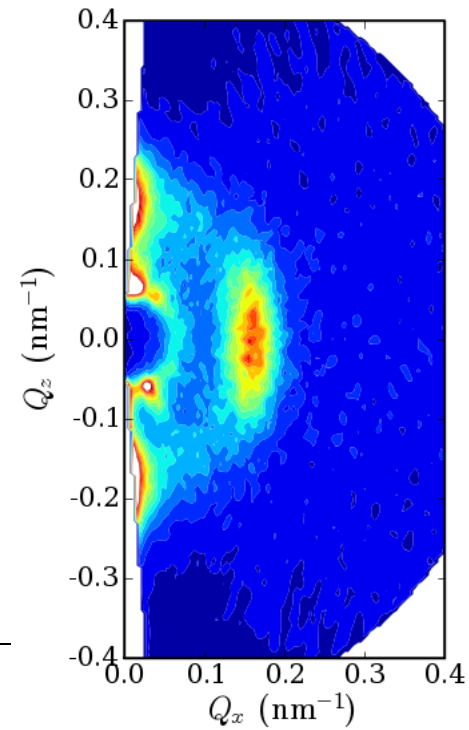




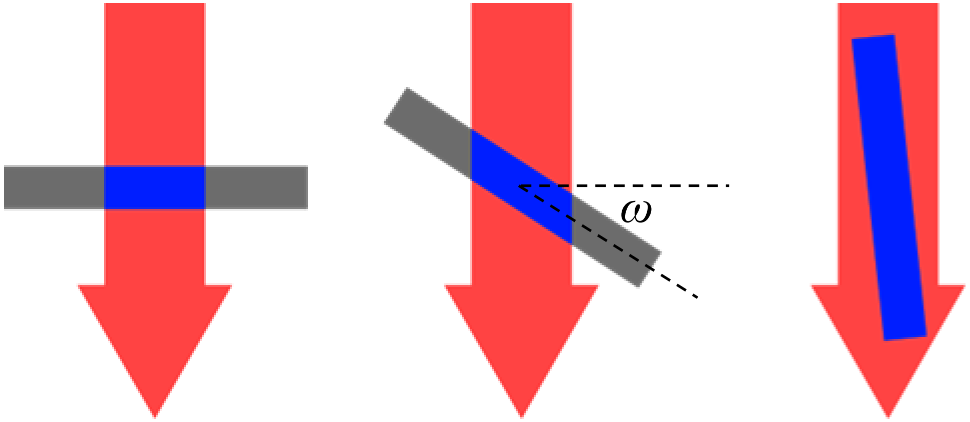
b) Assemble the 1D slices:



c) Convert to sample reciprocal space



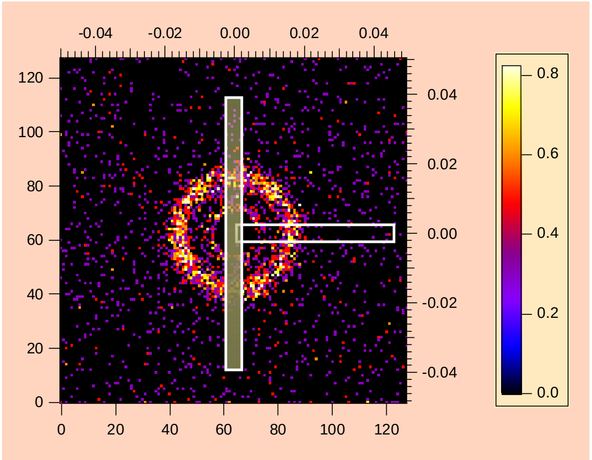
Normalization of Scattering Volume



Path Length increases as sample is rotated

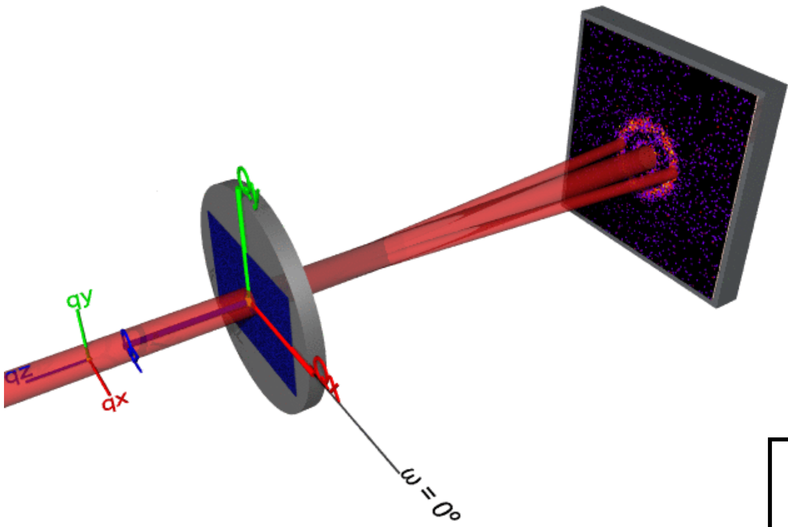
Implications:

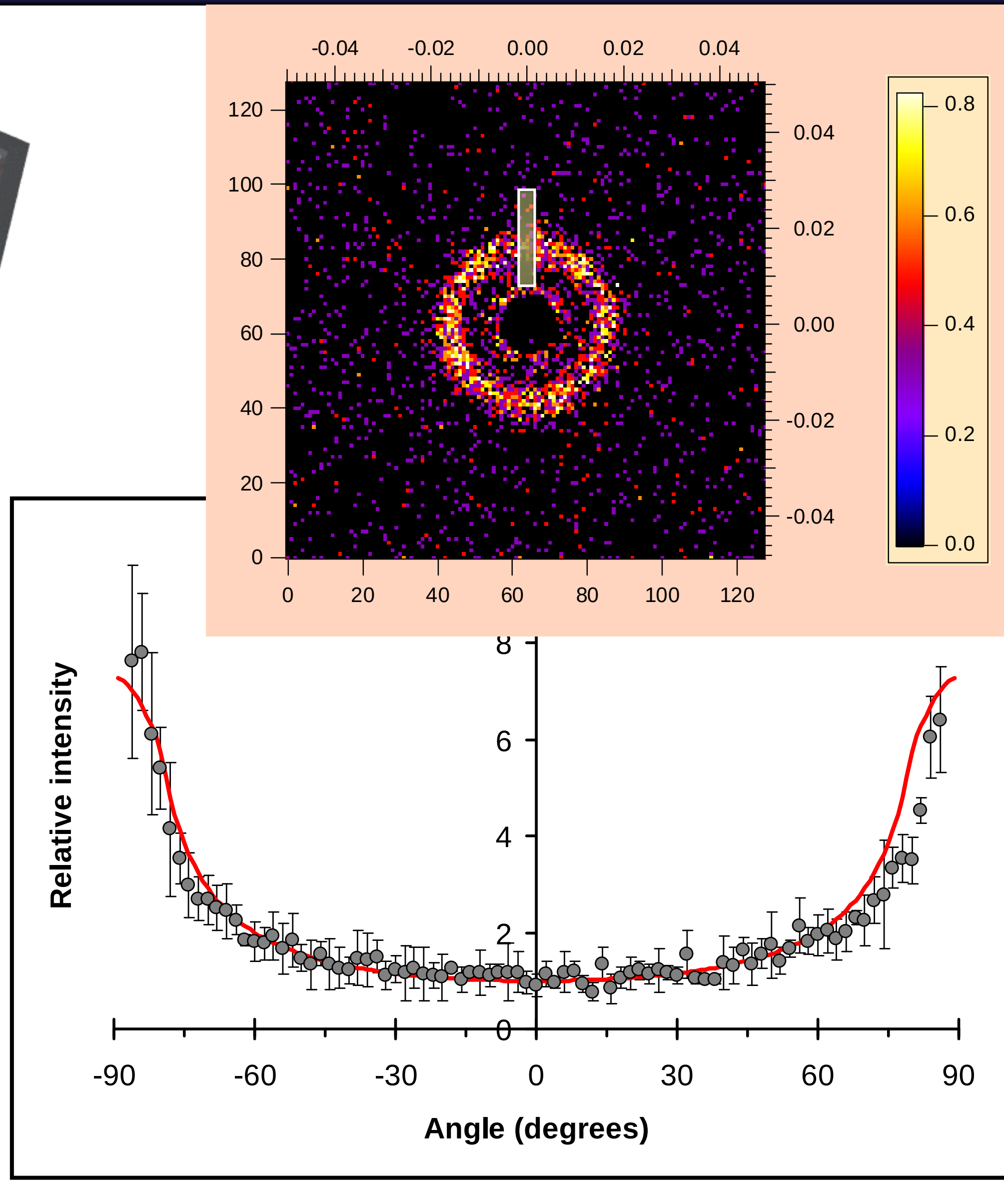
1. Sample area measured is not constant
2. At high angles, reflection will no longer be negligible
3. Sample volume is increasing and must be normalized



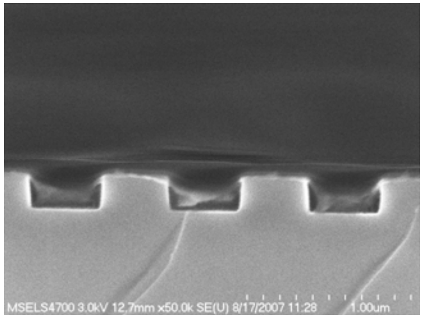
Use invariance of I(qy) to normalize path length changes

Scattering Volume Normalization





Lets look at a sample – Templated Assembly



dPS-b-PMMA

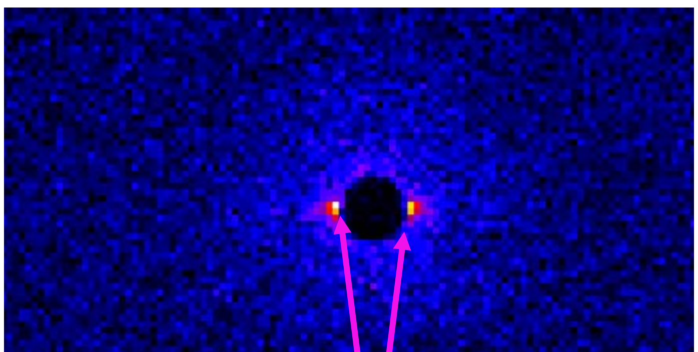
Lamellar Forming Morphology

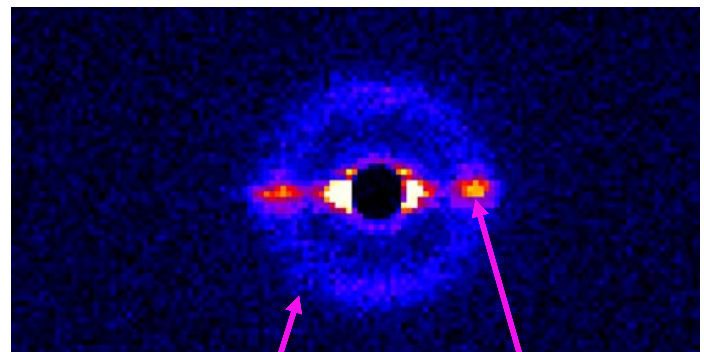
Forms domains of approx. 20 nm size

Repeat period approx. 40 nm

BCP-filled Template as cast

BCP-filled Template after anneal @ T=160C for 1 hr





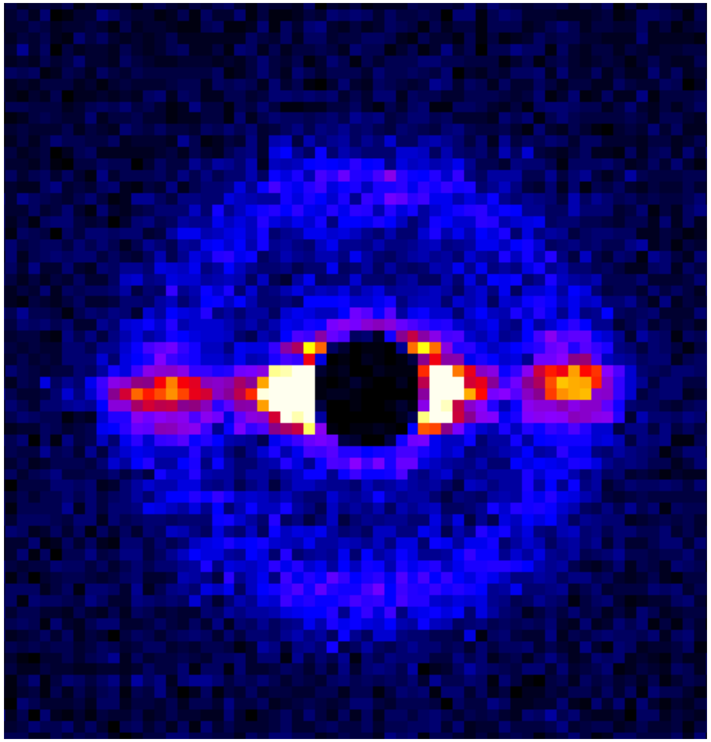
Diffraction Spots from template

Diffraction Spot from aligned BCP

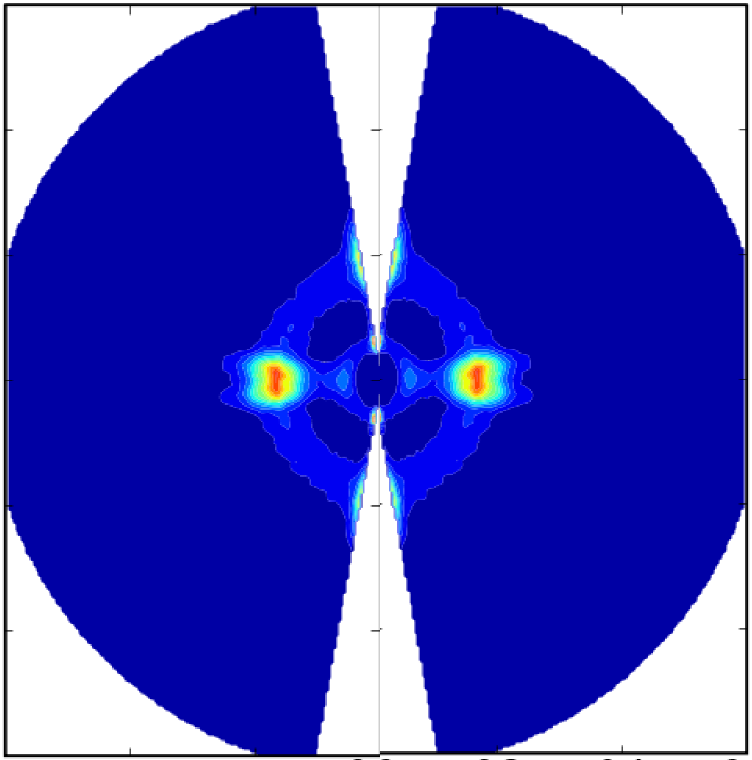
Unaligned BCP

“Top” and “Side” views from R-SANS

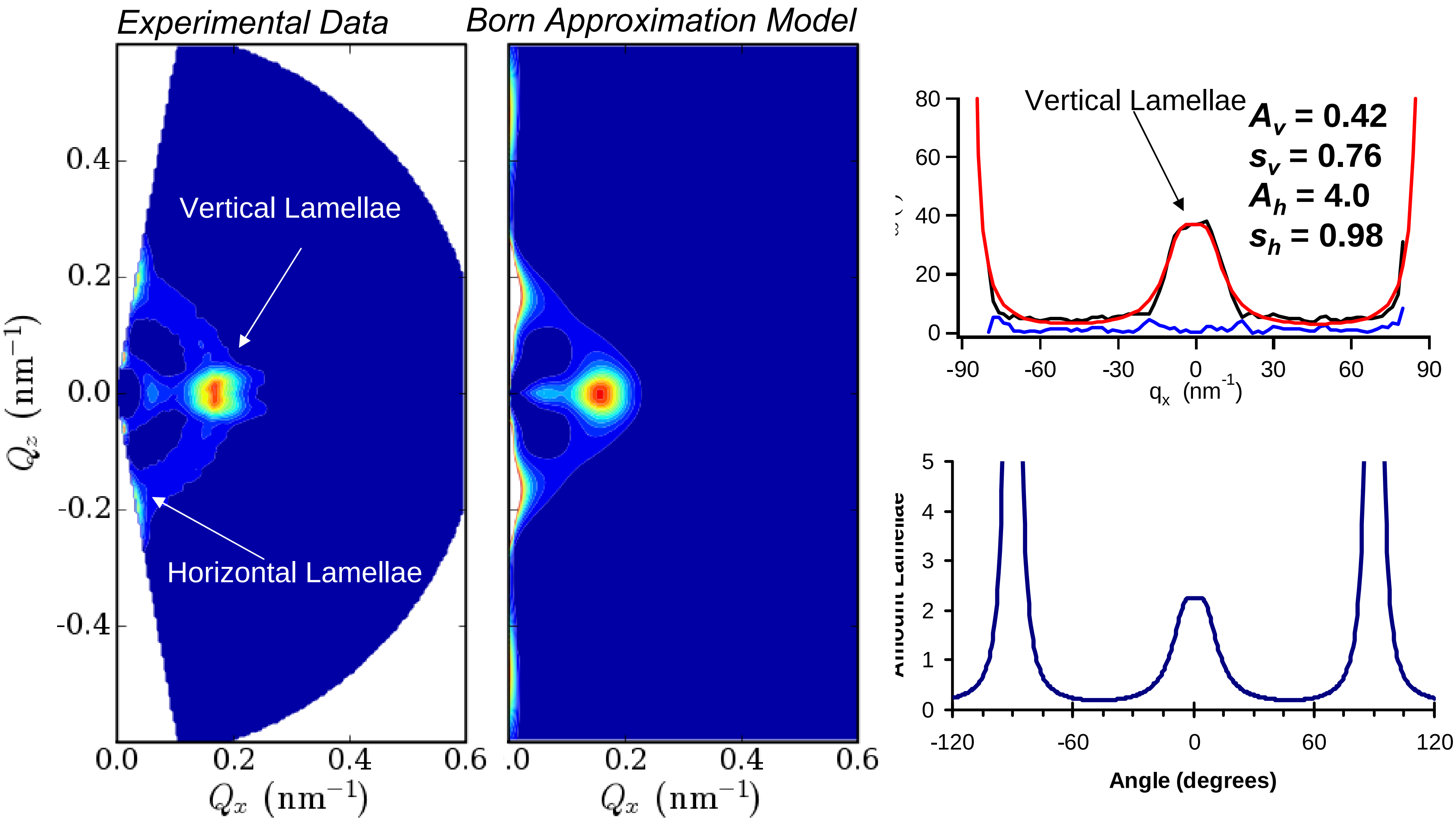
Normal Incidence (Qx-Qy plane)



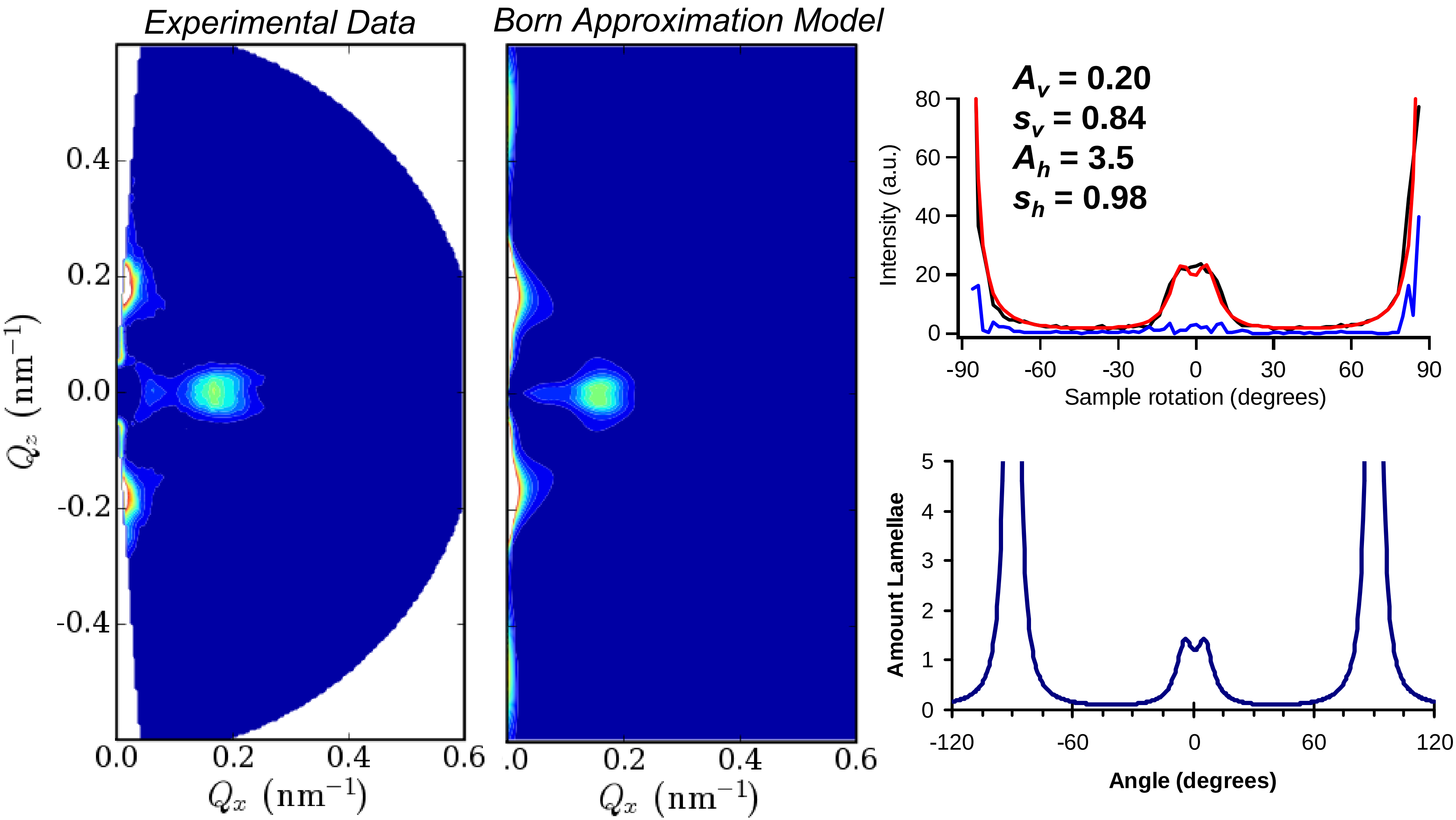
Cross Section (Qx-Qz plane)



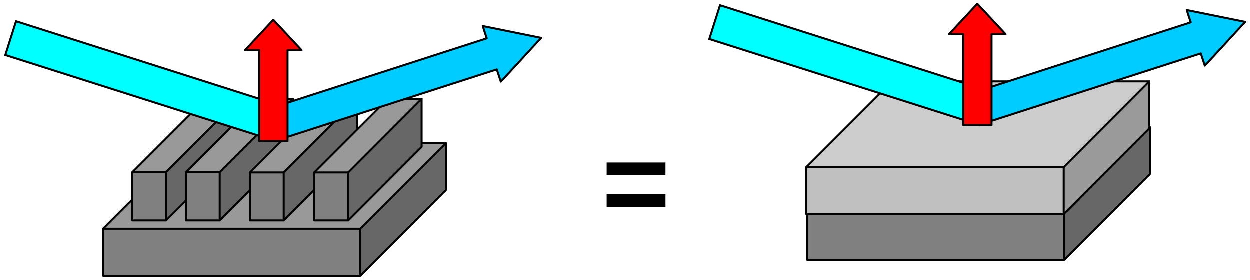
Templated Lamellae – 35 minutes



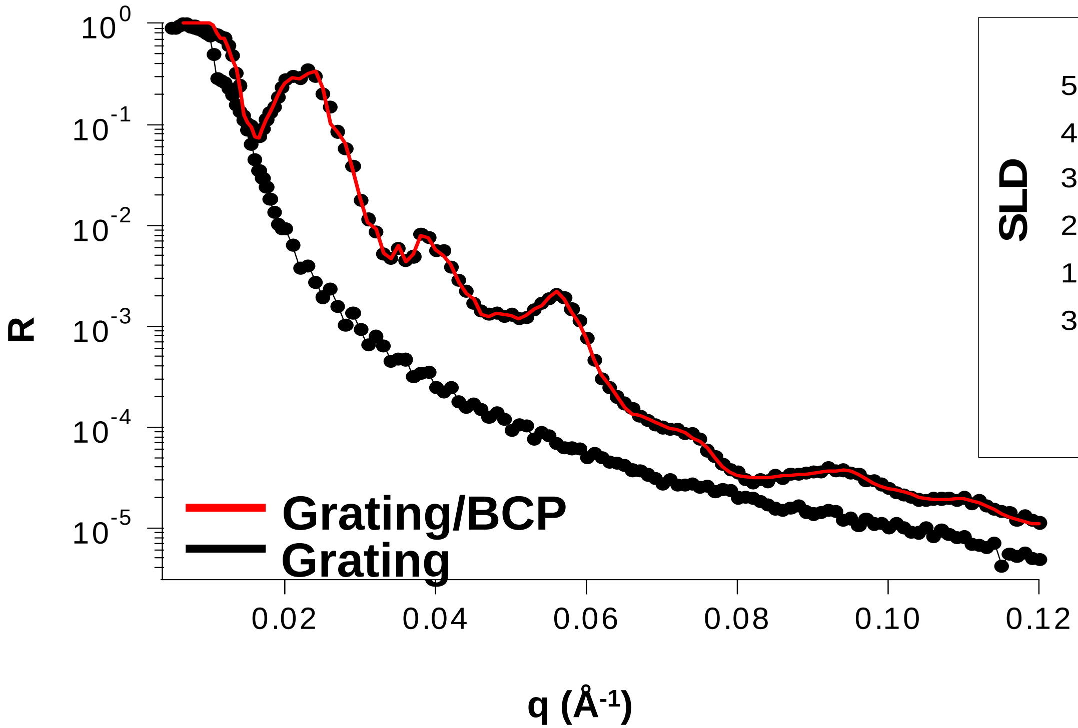
Templated Lamellae – 8 hours

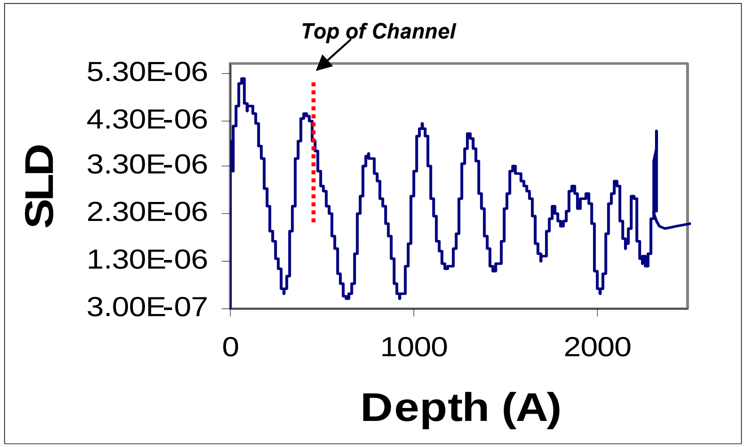


Neutron Reflectivity of Templated Assembly

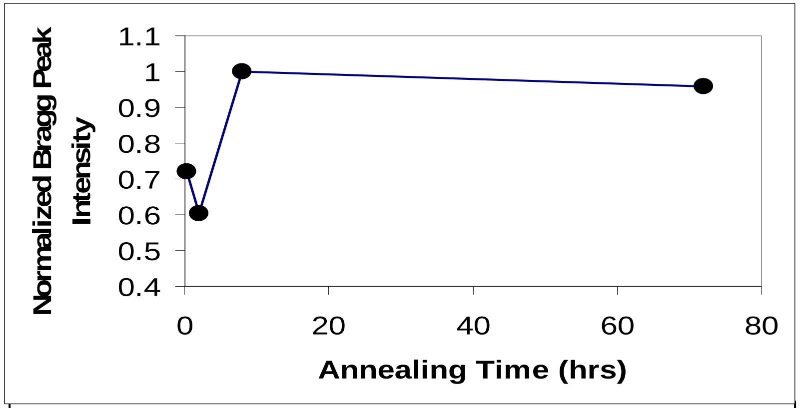


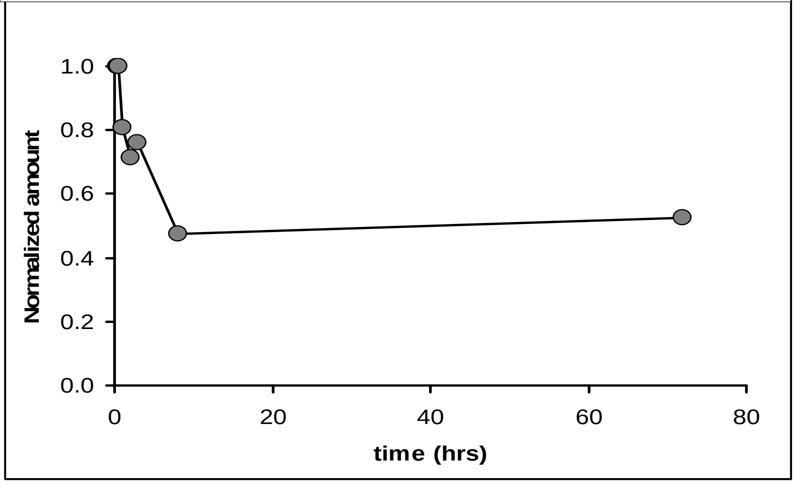
XR techniques developed by Hae-Jeong Lee et al.

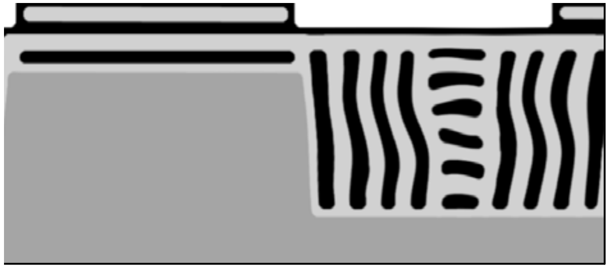




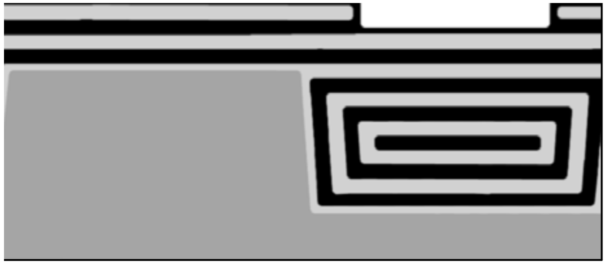
Kinetics of Ordering Lamellae







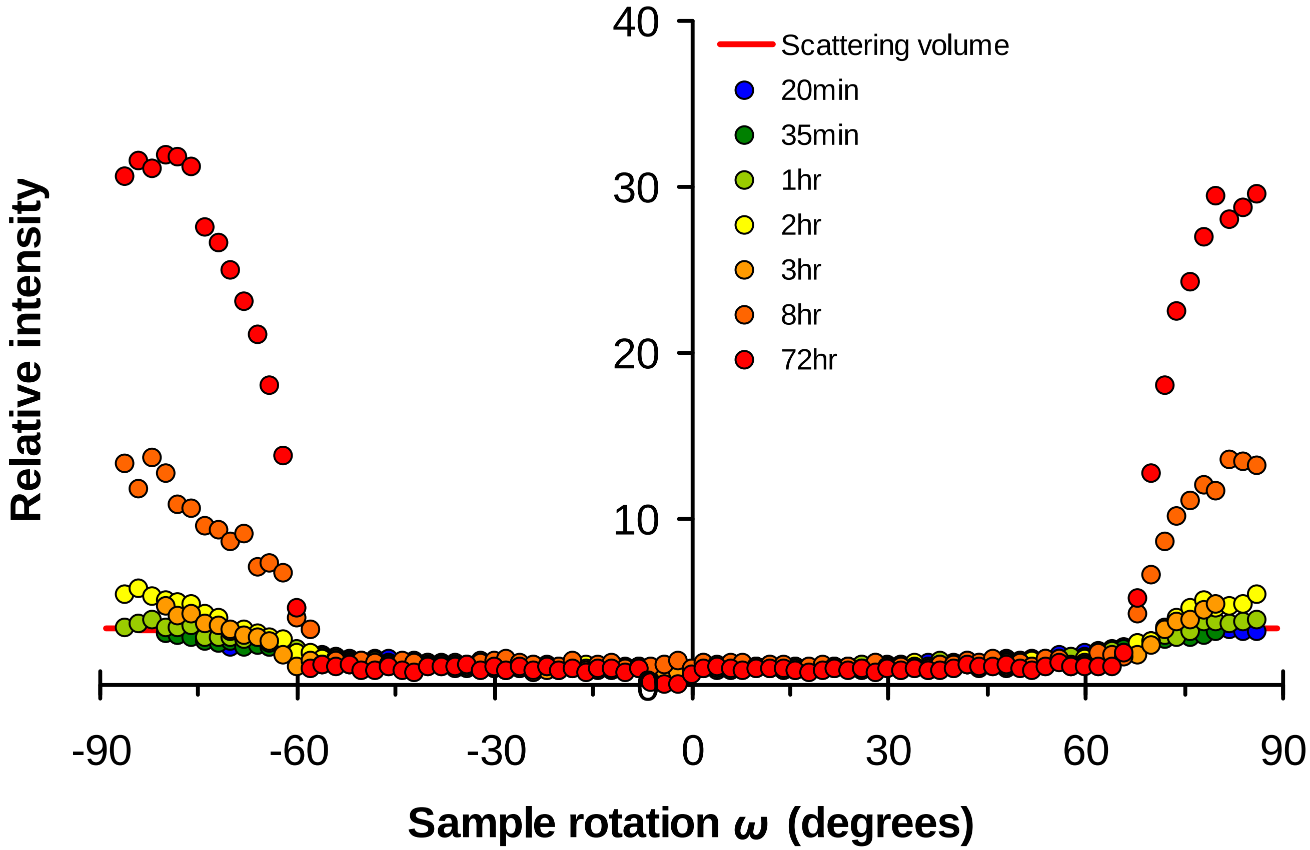
Short Anneal

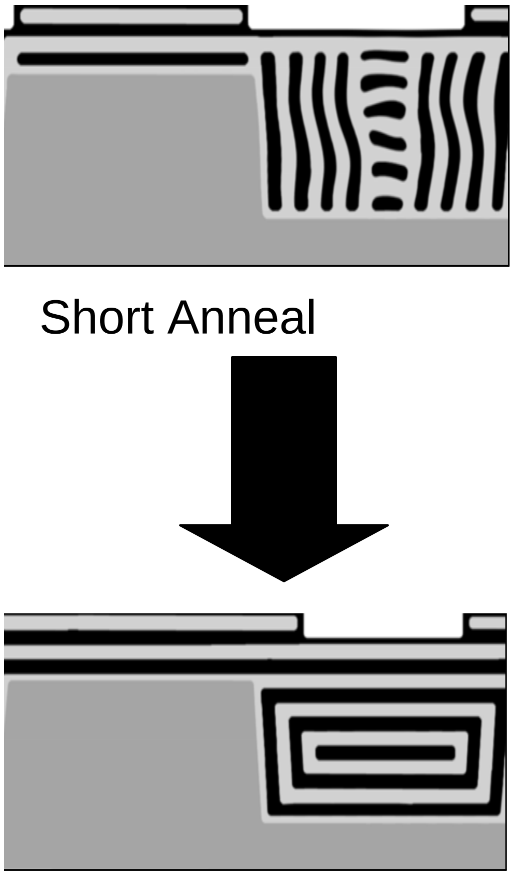


Long Anneal

Problem: Need to fill in missing “wedge” of data for more accuracy.

“Invariant” Scattering – I(qy)





Short Anneal

Long Anneal

Final Thoughts

Rotational SANS
•Developing Integral Equation model to describe I(q) for all rotation angles
	•Wen-li Wu

•Filling in “Missing Wedge” with Off-specular Neutron Reflectivity
	•Brian Maranville, Sushil Satija, Chuck Majkrzak

•Striving to assess the role of dynamic scattering, substrate waveguiding, etc. to create quantitatively accurate models

•Potential to utilize the enhanced transmission scattering to measure confined systems with low S/N