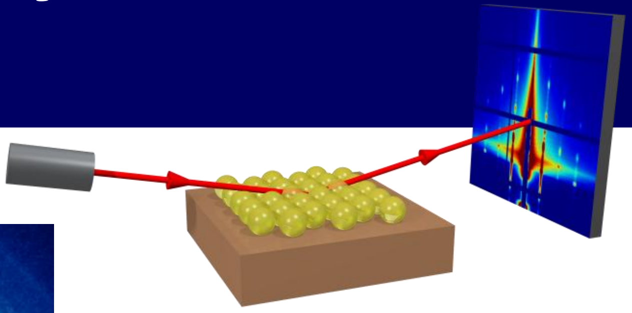
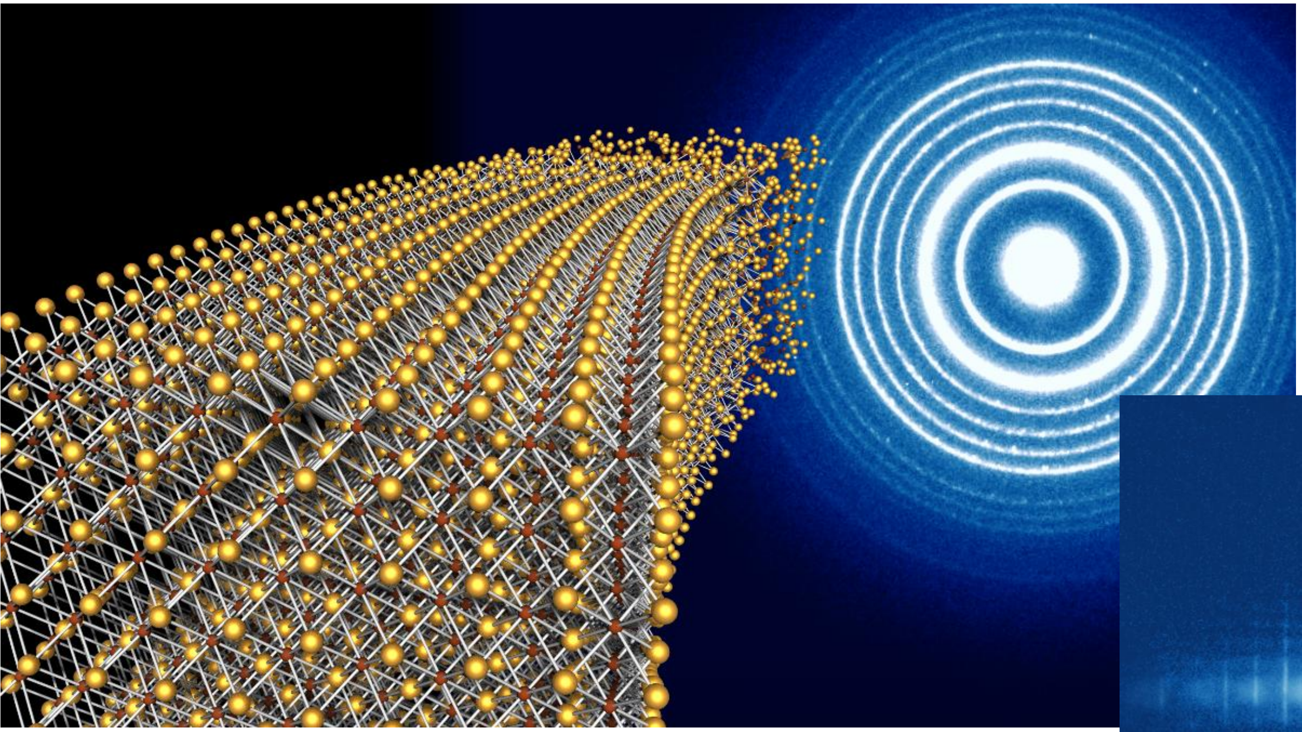
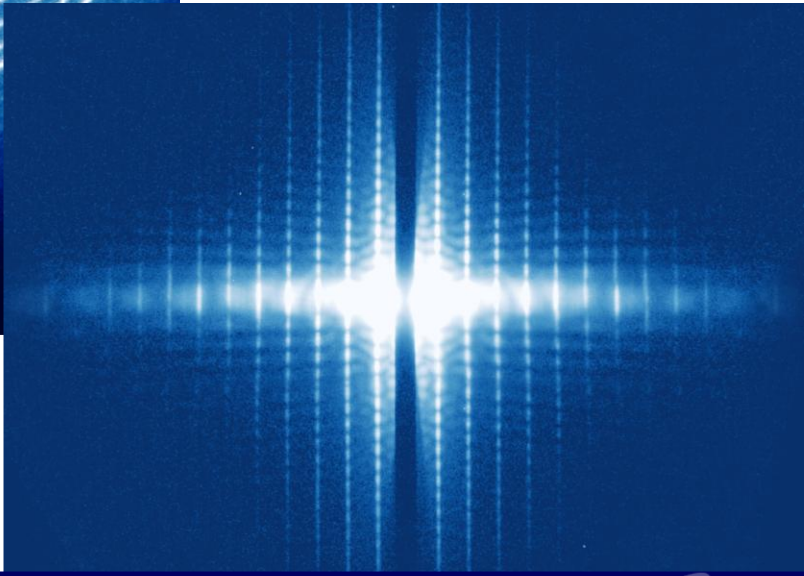
Synchrotron Scattering for Study of Soft Systems







Kevin G. Yager

BROOKHAVEN NATIONAL LABORATORY

Outline

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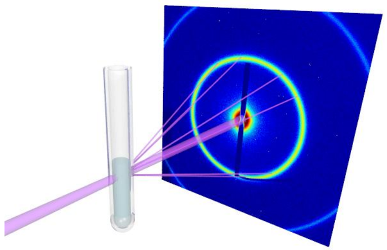
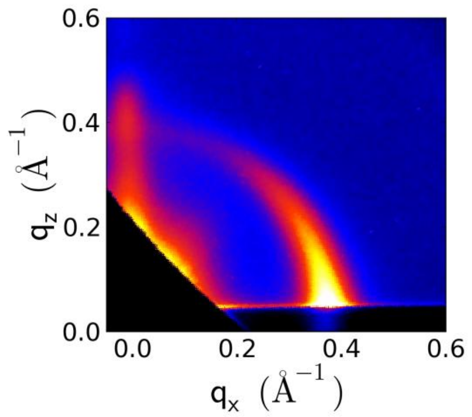
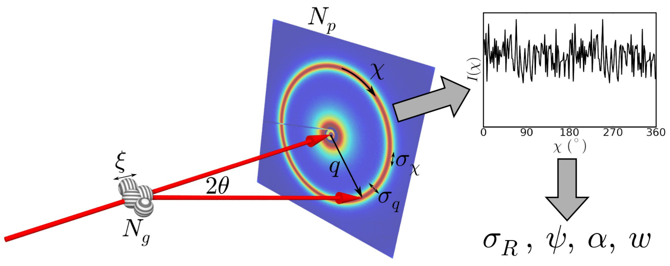
- X-ray scattering for nanoscience



- Experimental examples:
  - P3HT
  - Block-copolymers
  - 2D nanoparticle assembly



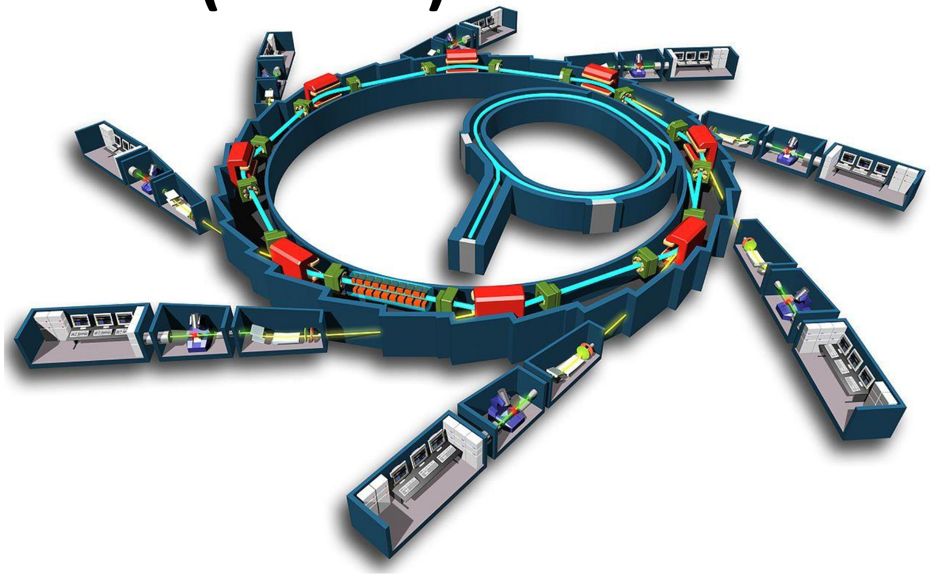
- New techniques:
  - Variance scattering
  - GTSAXS
  - Nano-lattice model



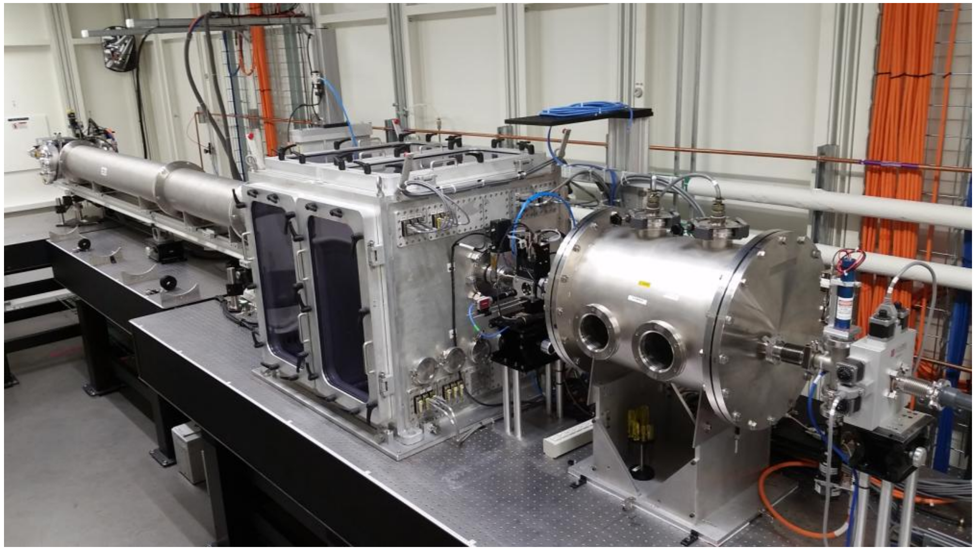
Synchrotron

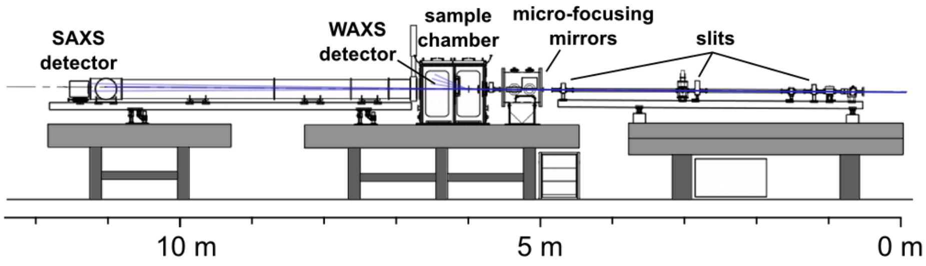
NSLS-II (USA)

SOLEIL (France)



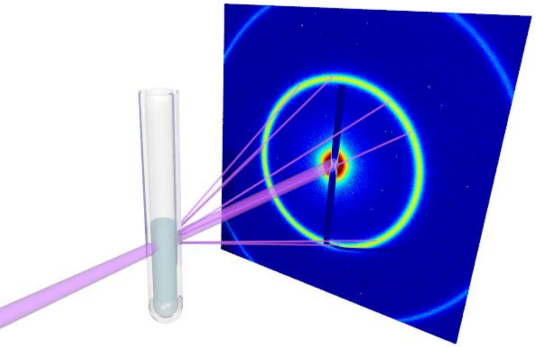
CMS beamline at NSLS-II

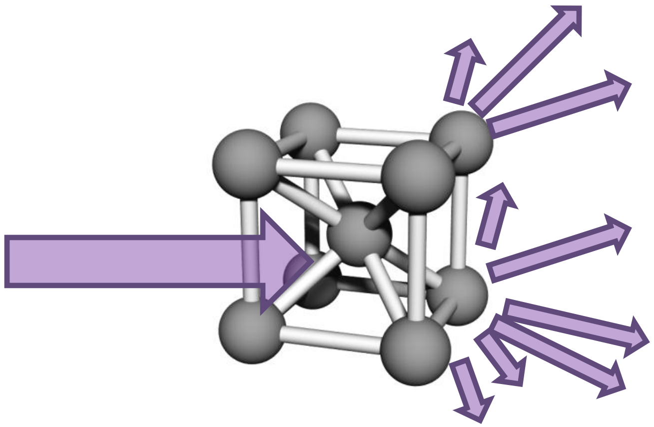


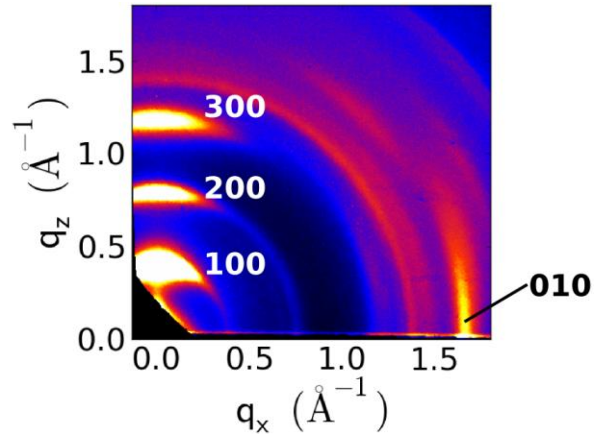


X-ray Scattering

- X-rays scatter off of all the atoms/particles in the sample

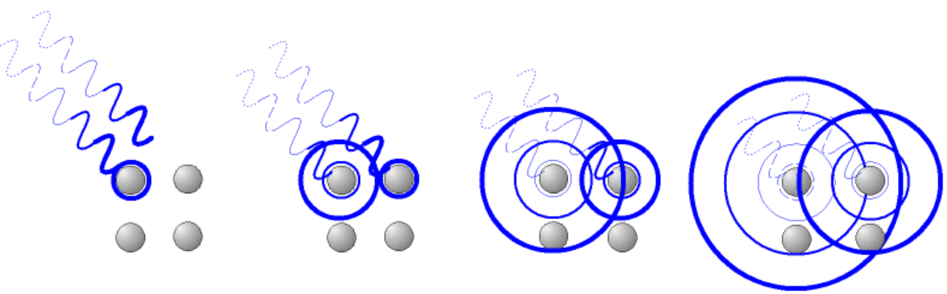


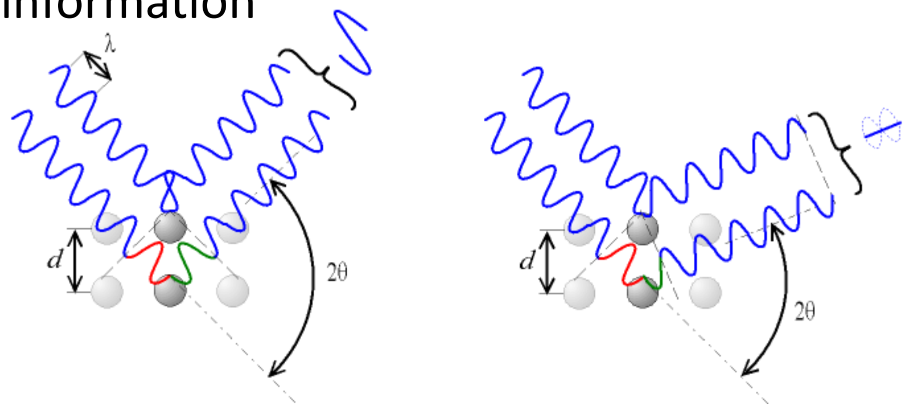




- Interfere of scattered waves produces distinct spots or rings at angles that encode structural information

$$n\lambda = 2d\sin\theta$$





- Wide-angles: atomic/molecular
- Small-angles: nano

"Kinds" of Scattering

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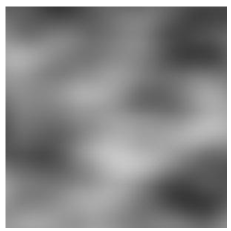
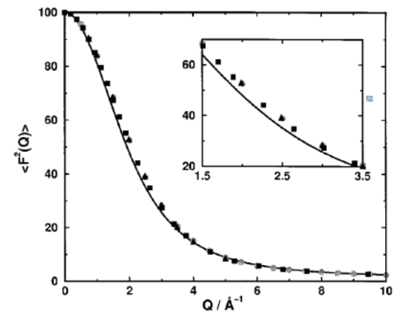
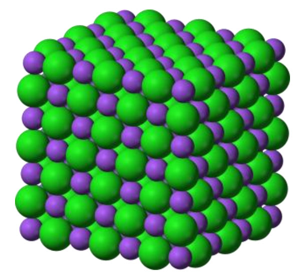
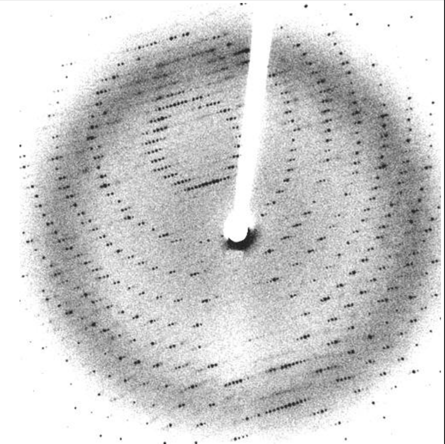
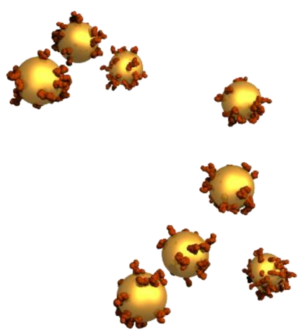
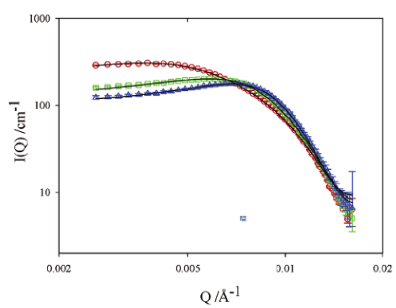
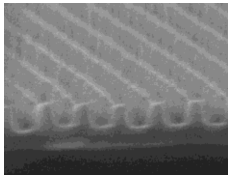
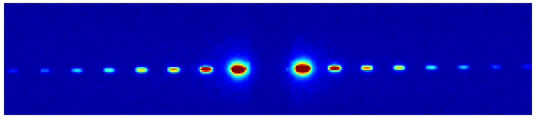
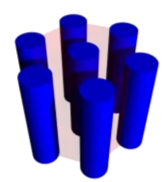
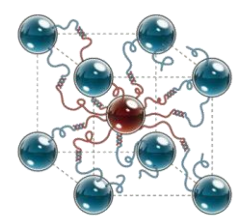
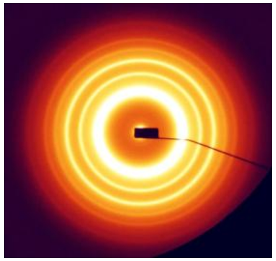
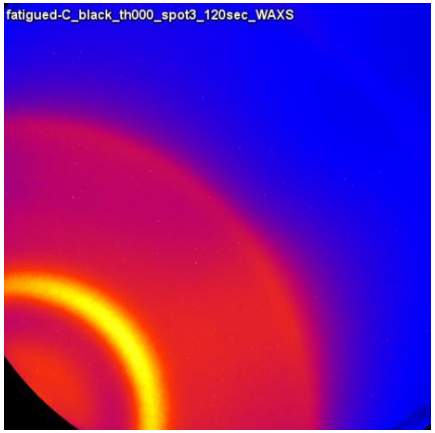
Organization of constituents ("Structure Factor")

Constituents ("Form Factor")	Random	Periodic
Simple	Gases, liquids, glasses, …  	Crystals, …  
Arbitrary	Colloids, proteins in solution, …  	Lithography, nano-particle lattices, …     

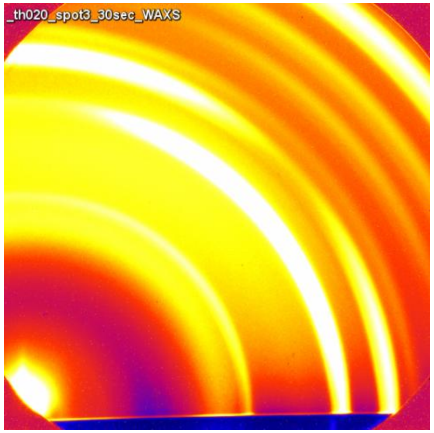
X-ray Scattering

- Qualitative: assess order

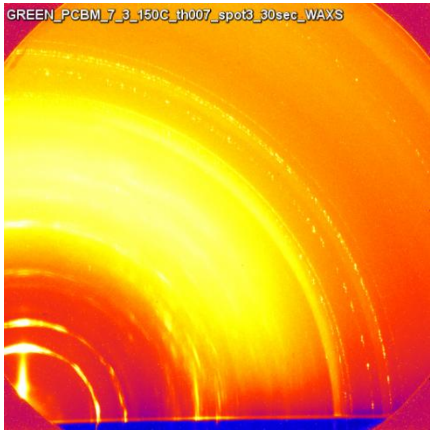
- Peak positions: quantify *d*-spacing
    - Multiple peaks: determine symmetry, solve for unit cell
- Peak width: calculate grain size
- Intensity: quantify amounts of populations
- Intensity along arcs: determine orientation distribution



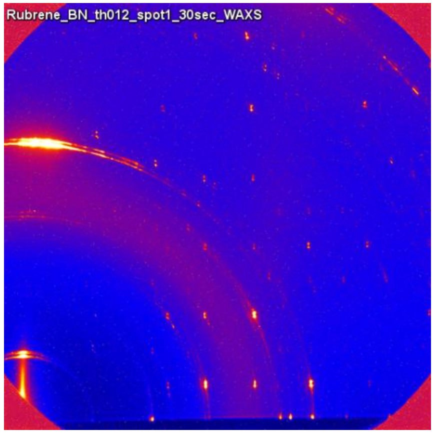
disordered



some ordering



oriented, textured

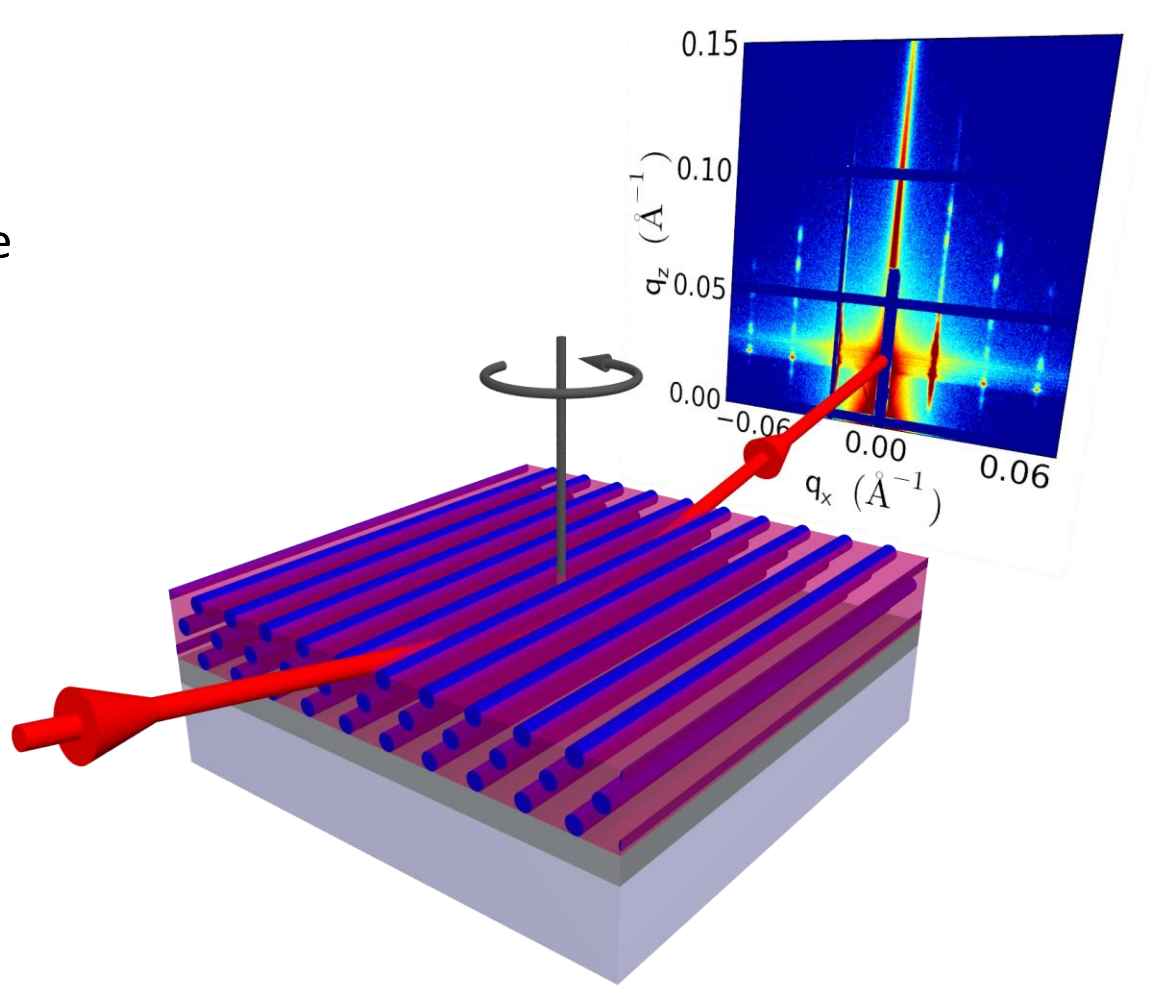


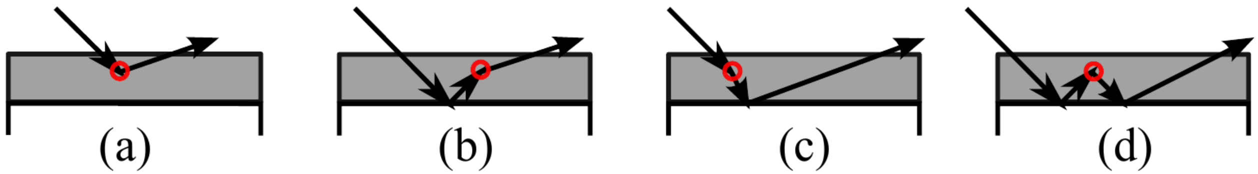
single crystal

less order ⟷ more order

GISAXS

- **G**razing-**I**ncidence **S**mall-**A**ngle **X**-ray **S**cattering
- Strong signal:
  - Beam projection on sample
  - Reflection-mode enhances E-field in film
- In-plane and out-of-place structure
- Analysis complicated:
  - Refraction and reflection shifts *q*-space
  - Data is sum of many possible reflection/ scattering terms





Outline

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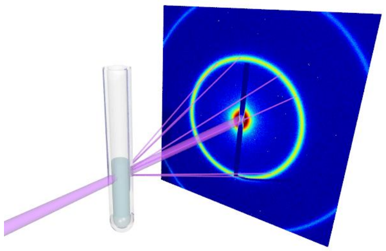
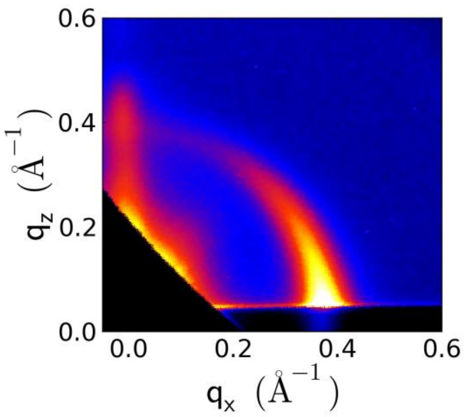
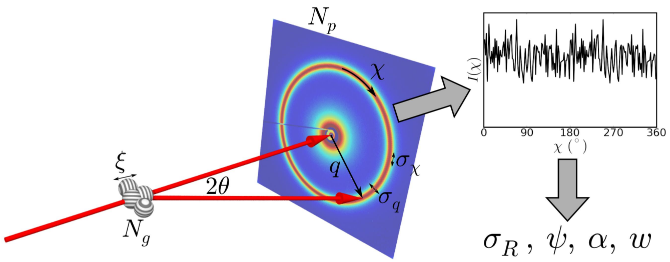
- X-ray scattering for nanoscience



- Experimental examples:
  - P3HT
  - Block-copolymers
  - 2D nanoparticle assembly

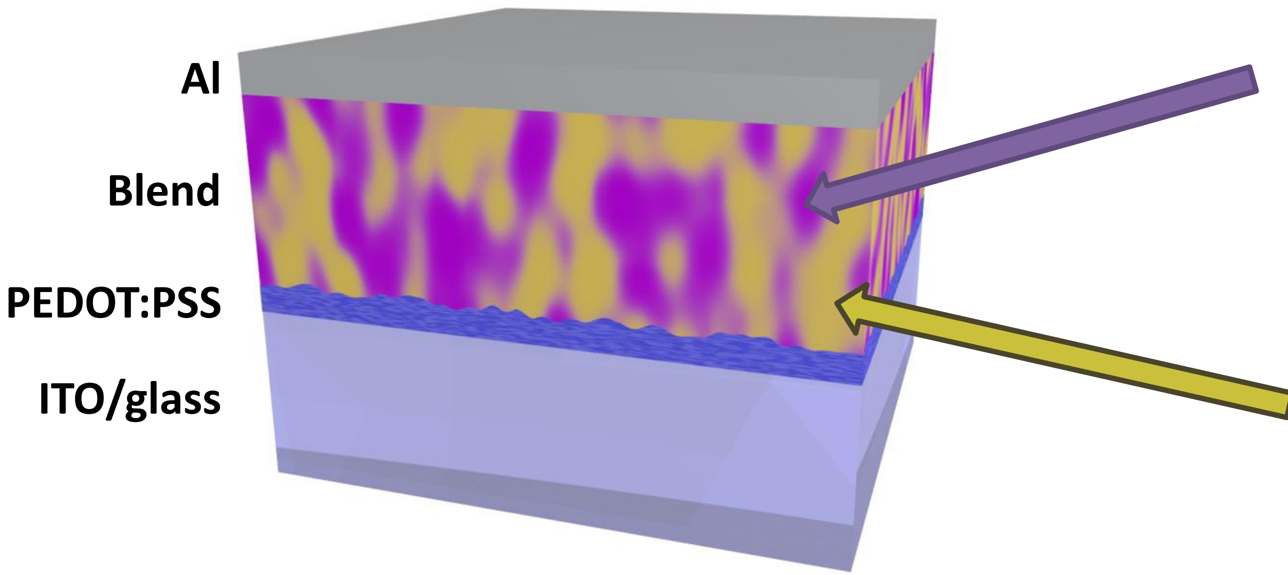


- New techniques:
  - Variance scattering
  - GTSAXS
  - Nano-lattice model

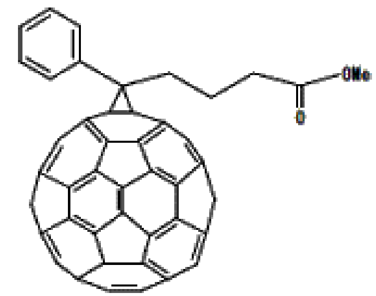


Organic Photo-voltaic

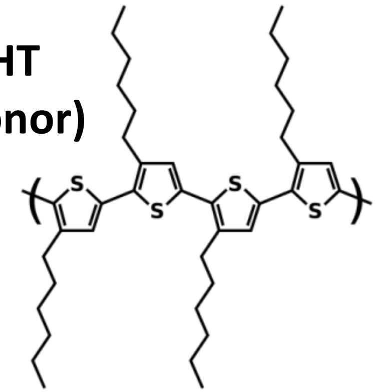
- Prototypical OPV: P3HT/PCBM bulk-heterojunction



PCBM (acceptor)



P3HT (donor)



- Exciton diffusion length ≈ 10-20 nm
- Film thickness ≈ 100 nm

- Need network for charge transport, but small domains to avoid recombination
- Ideal morphology is actually trapped in a non-equilibrium state (control and stability issues!)

P3HT: poly 3-hexylthiophene

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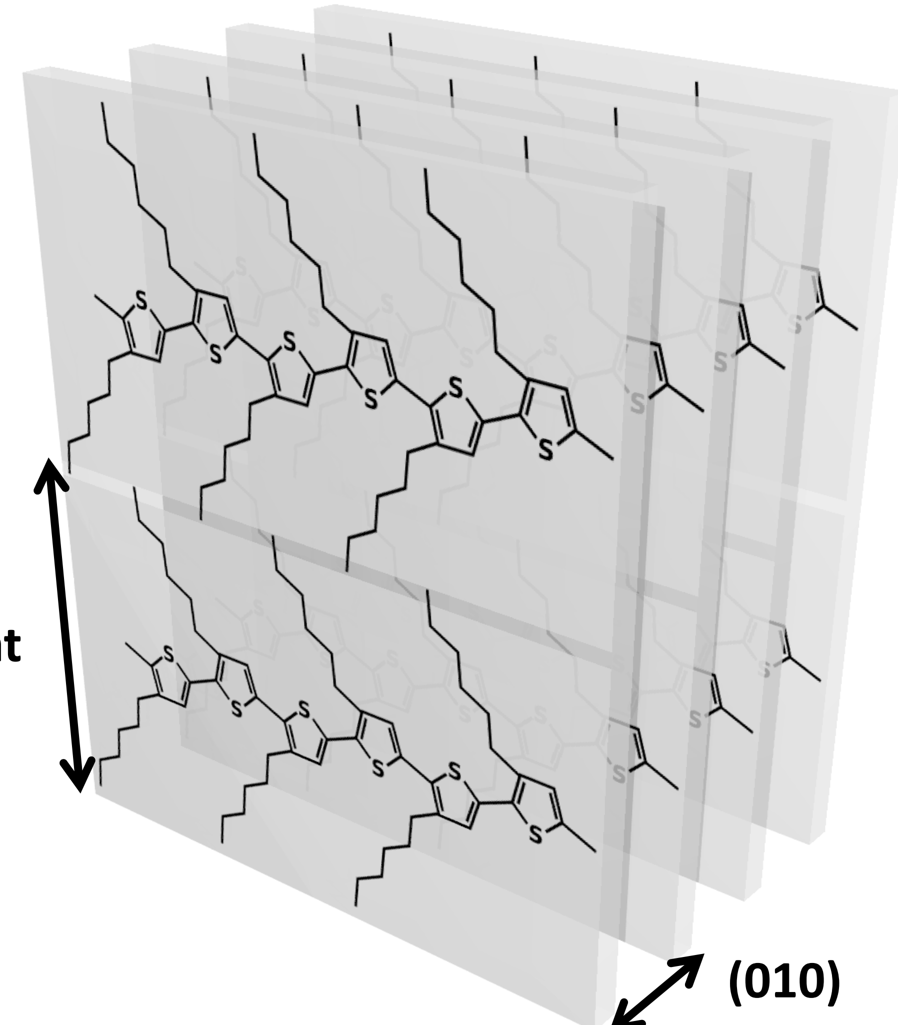
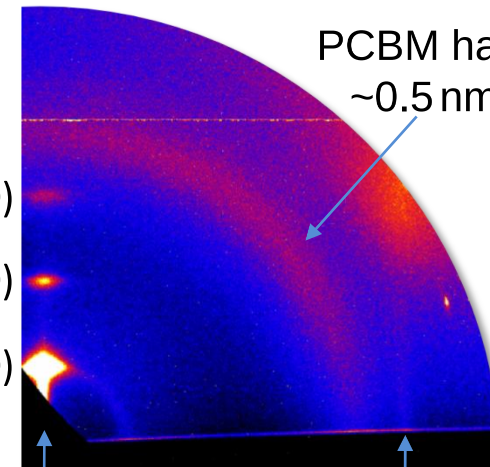
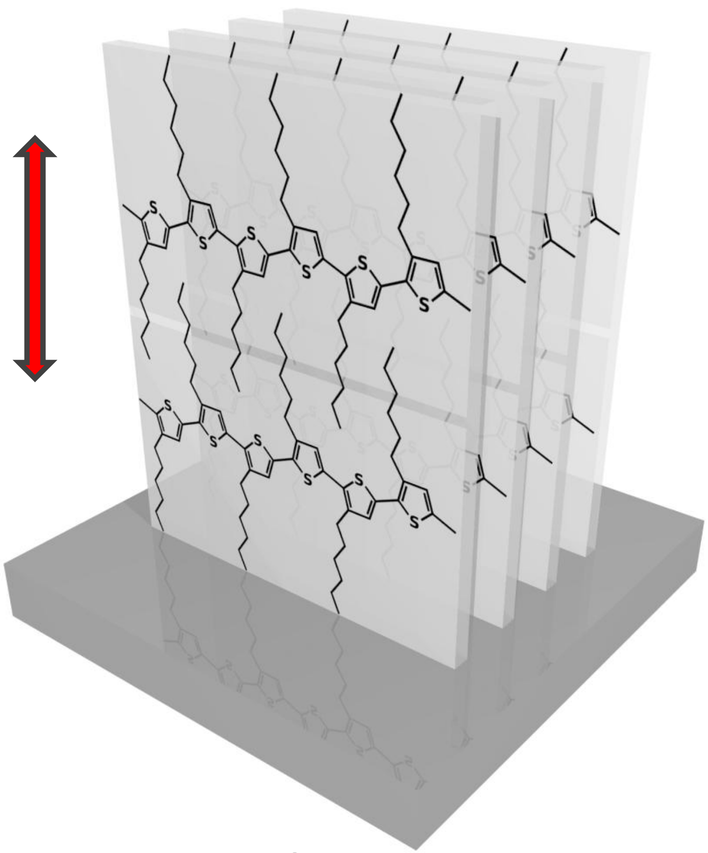




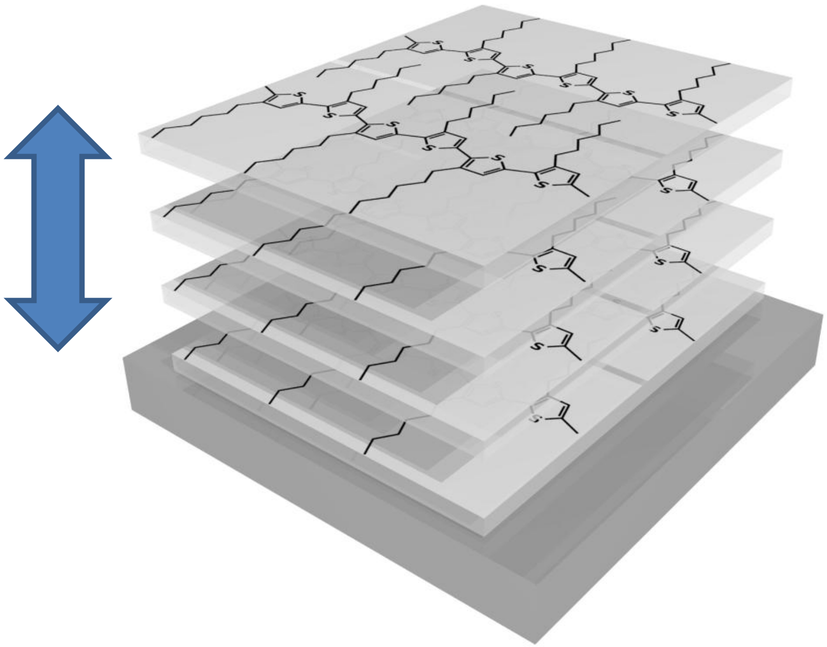
Anisotropic Conduction

- Face-on orientation would be ~300× better



Edge-on

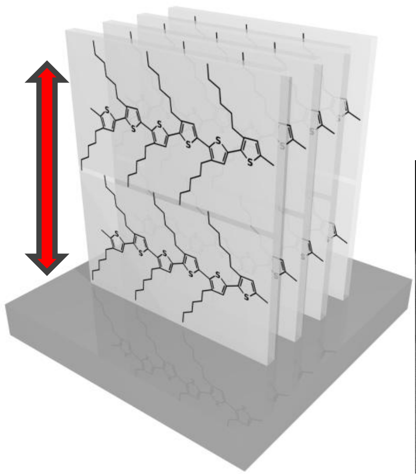
$\alpha_h \approx 0.0002\ \mathrm{cm^2V^{-1}s^{-1}}$

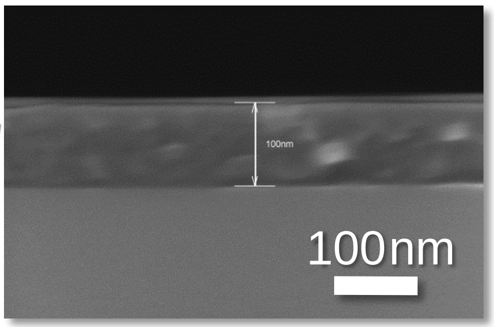


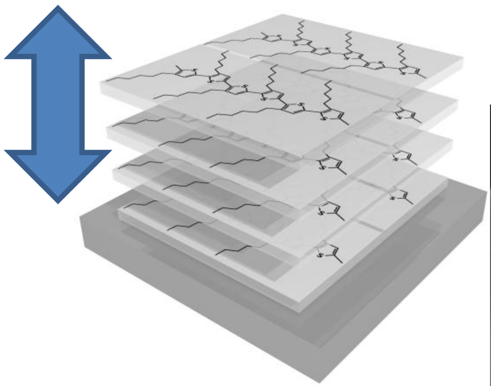
Face-on

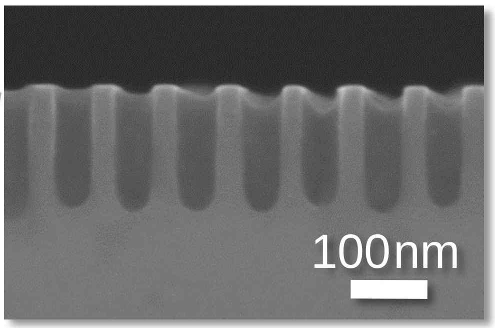
$\alpha_h \approx 0.1\ \mathrm{cm^2V^{-1}s^{-1}}$

P3HT Orientation









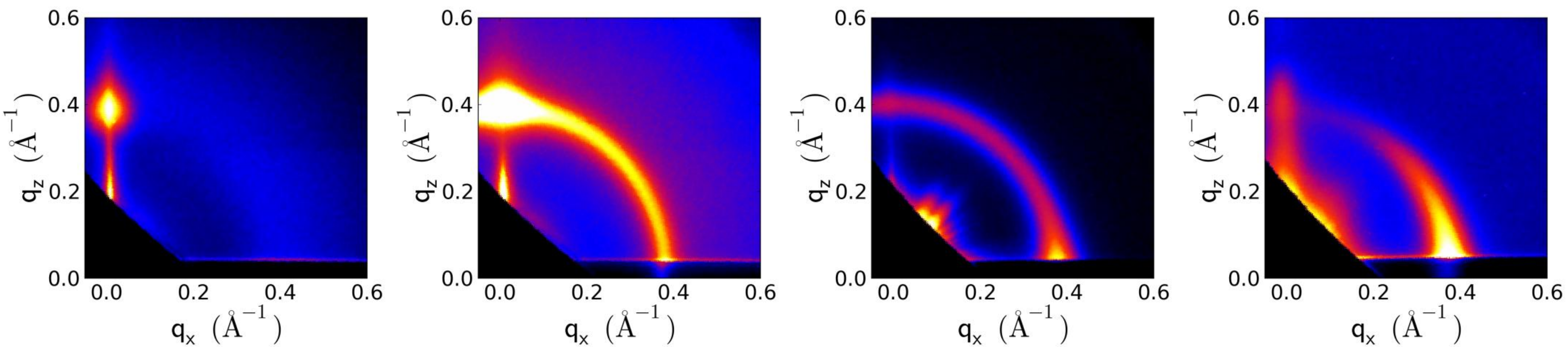
Edge-on

$\alpha_h \approx 0.0002\ \mathrm{cm^2V^{-1}s^{-1}}$

Face-on

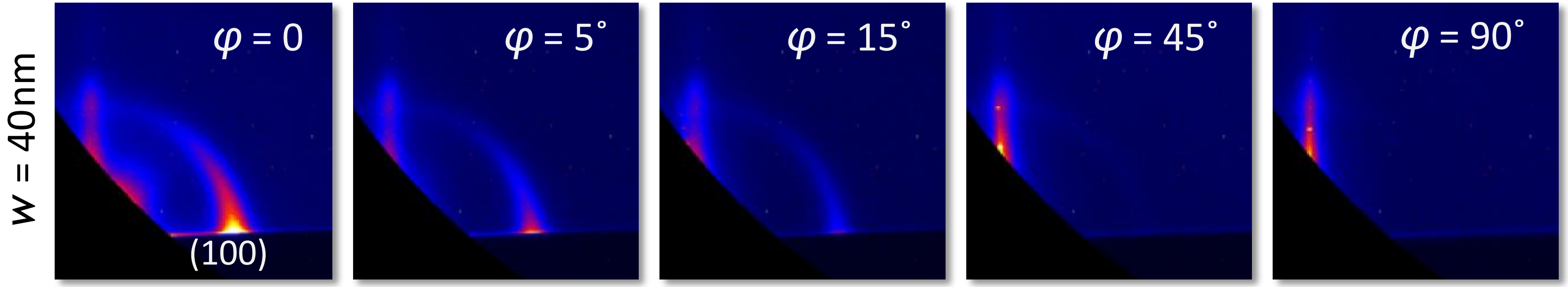
$\alpha_h \approx 0.1\ \mathrm{cm^2V^{-1}s^{-1}}$

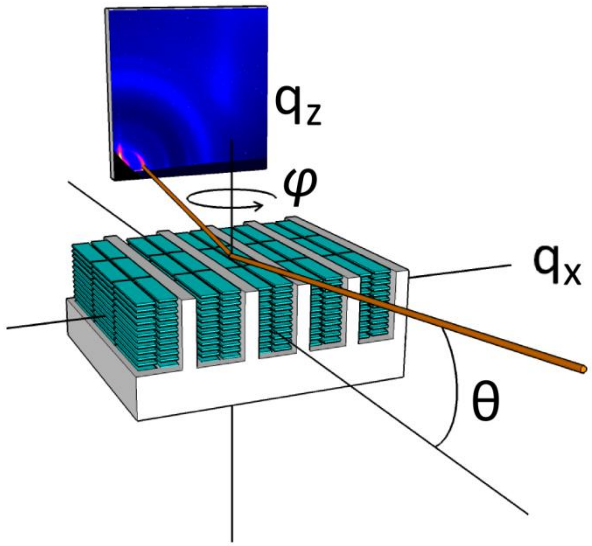
- Intensity along ring tells orientation

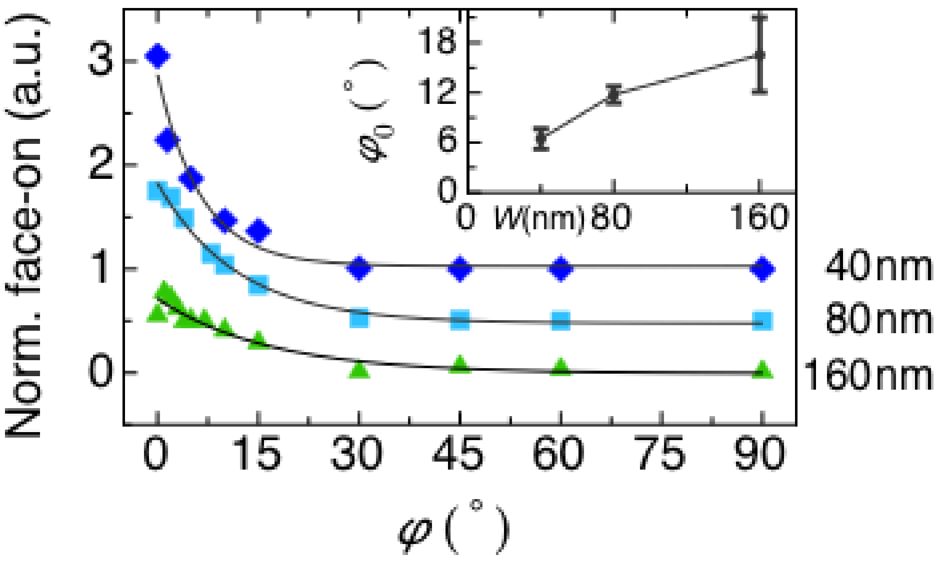


In-plane Alignment

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

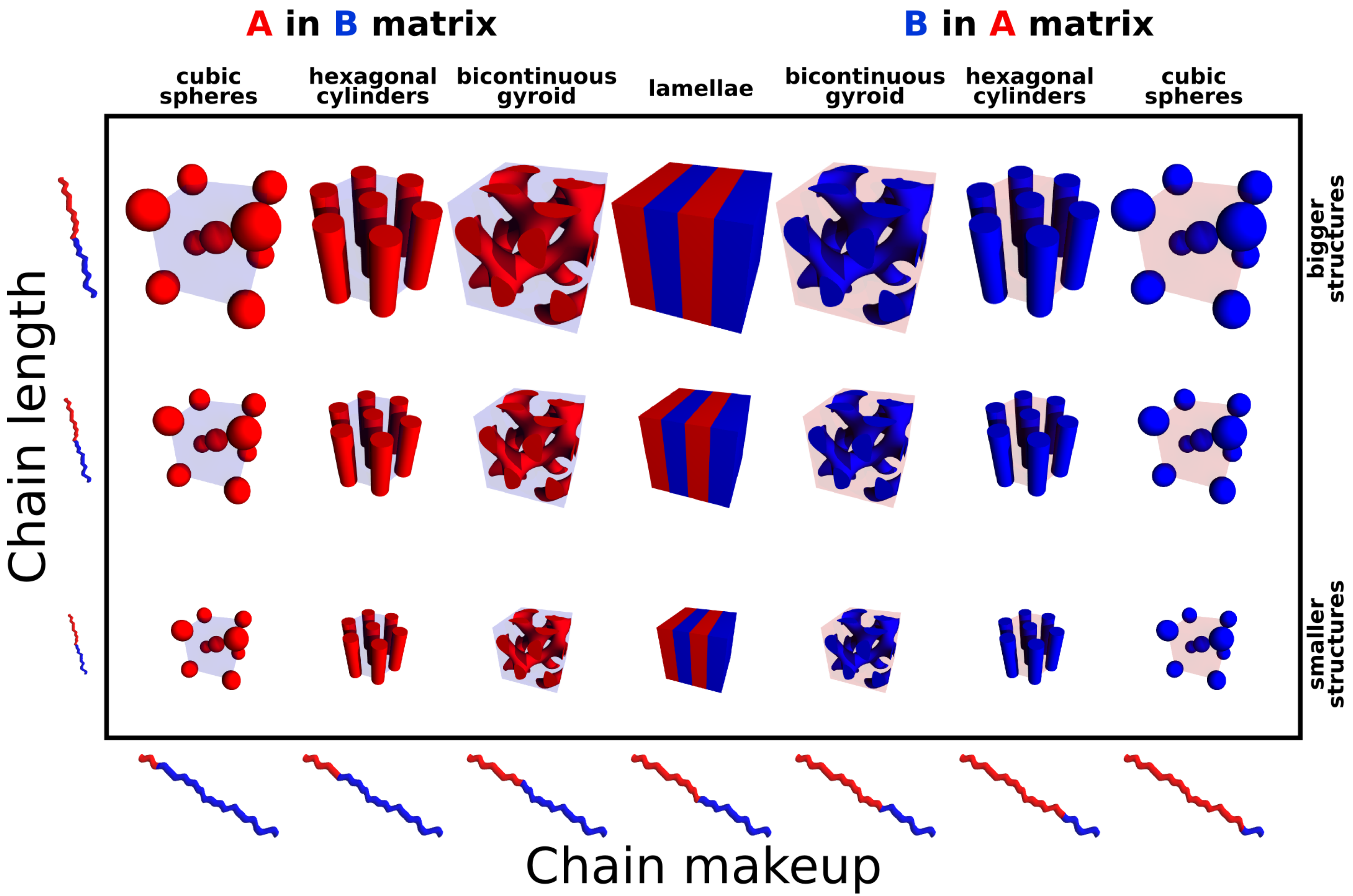






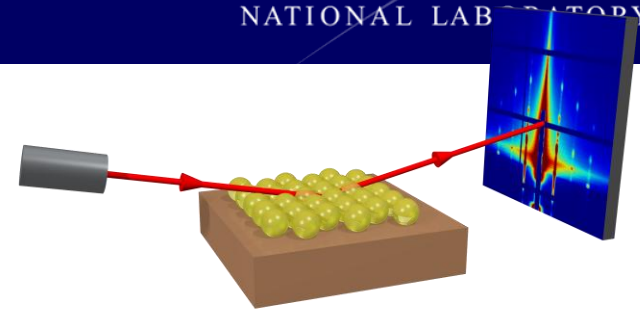
Johnston *ACS Nano* **2014**, 8, 243

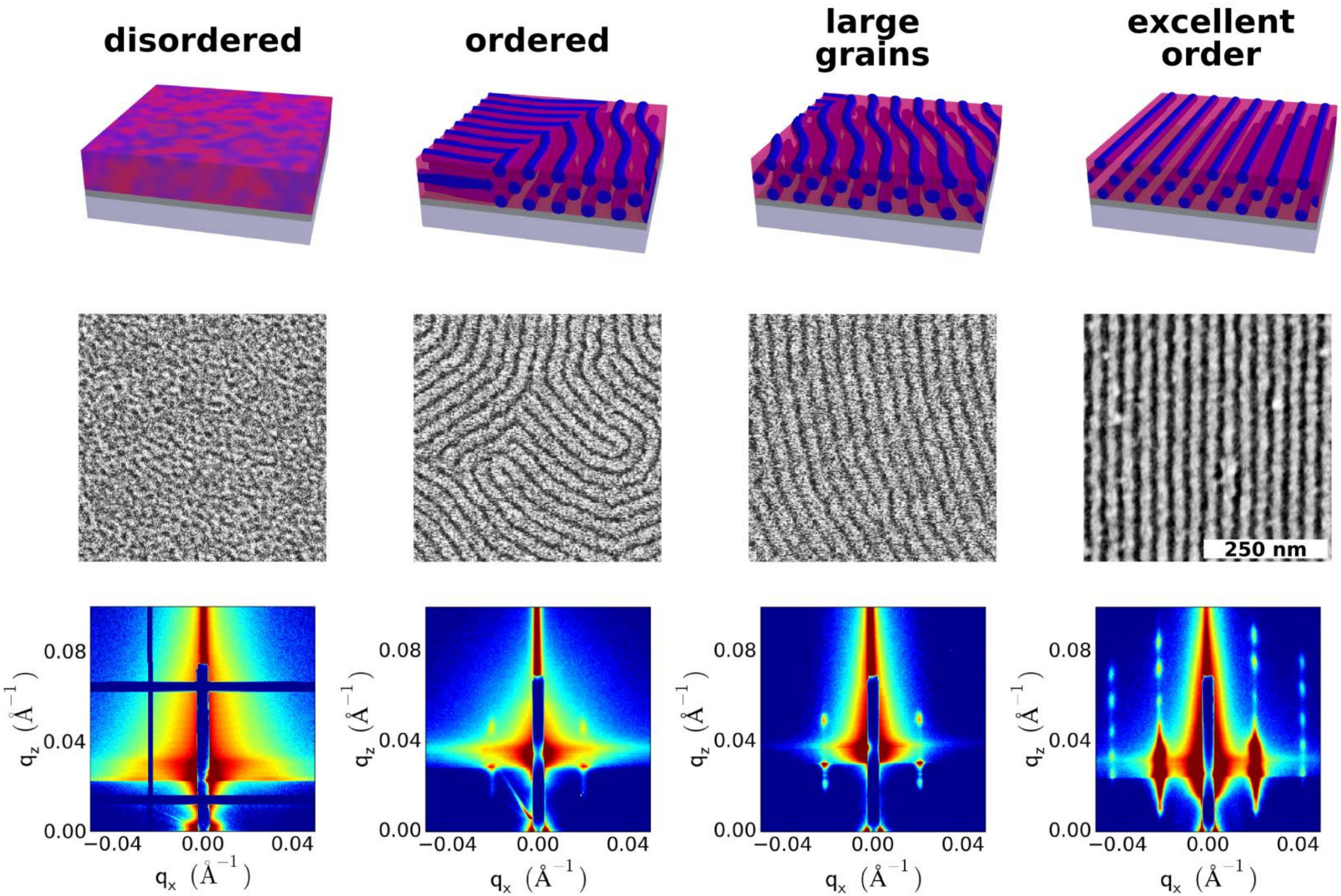
Block copolymers



GISAXS of BCP

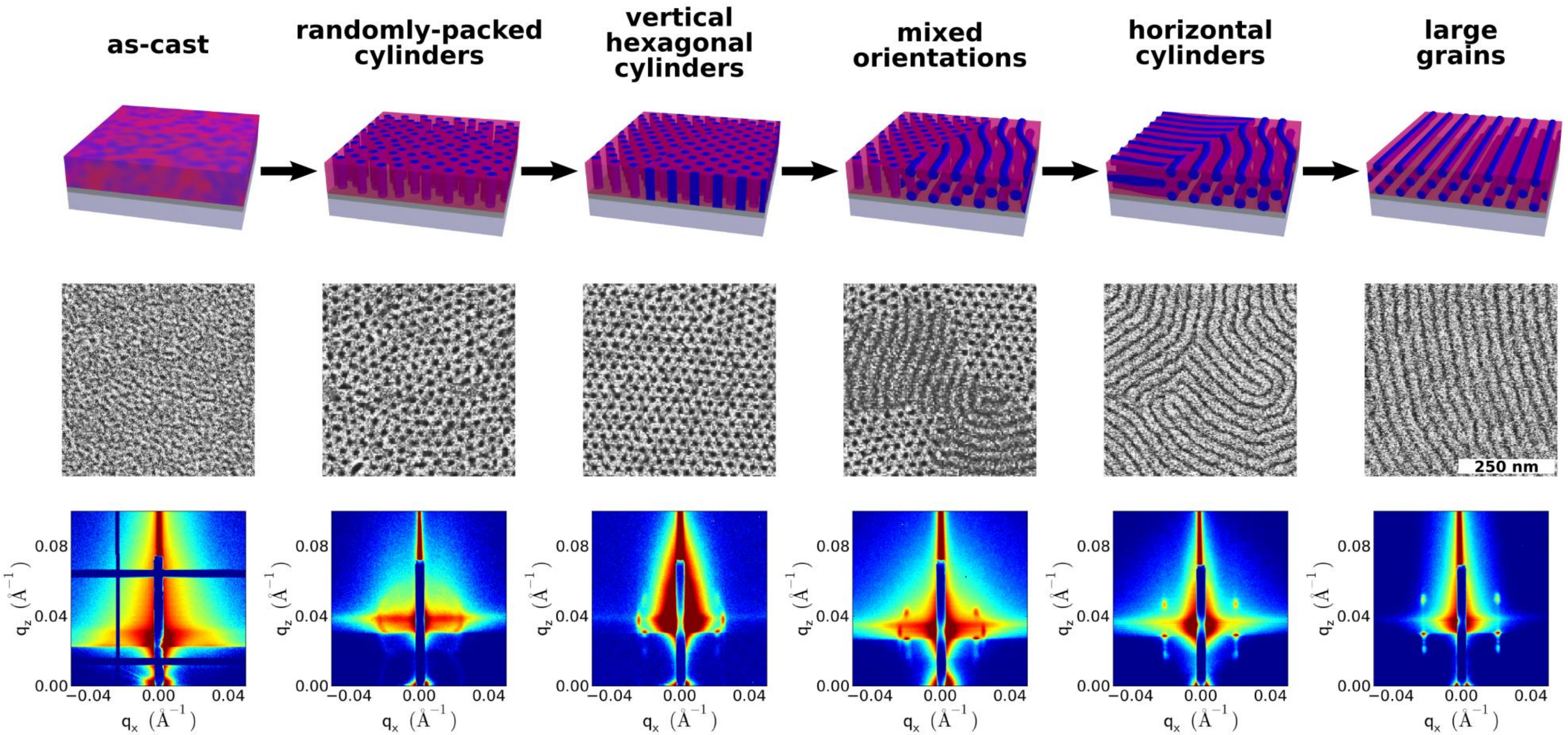
- Determine morphology, grain size, orientation, …





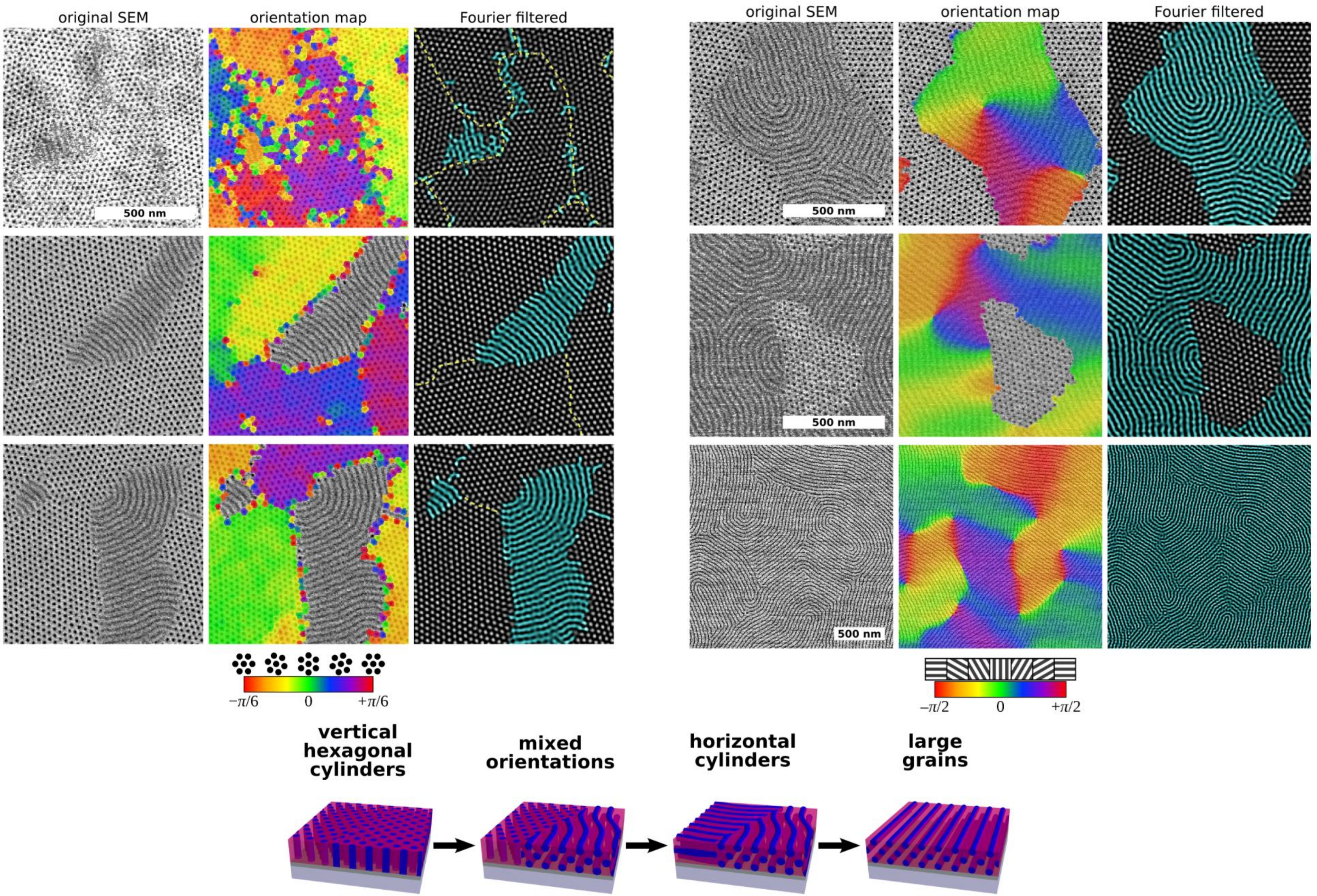
Reordering Transitions

- Transient states may appear during assembly



Majewski and Yager *Soft Matter* **2016**, *12*, 281

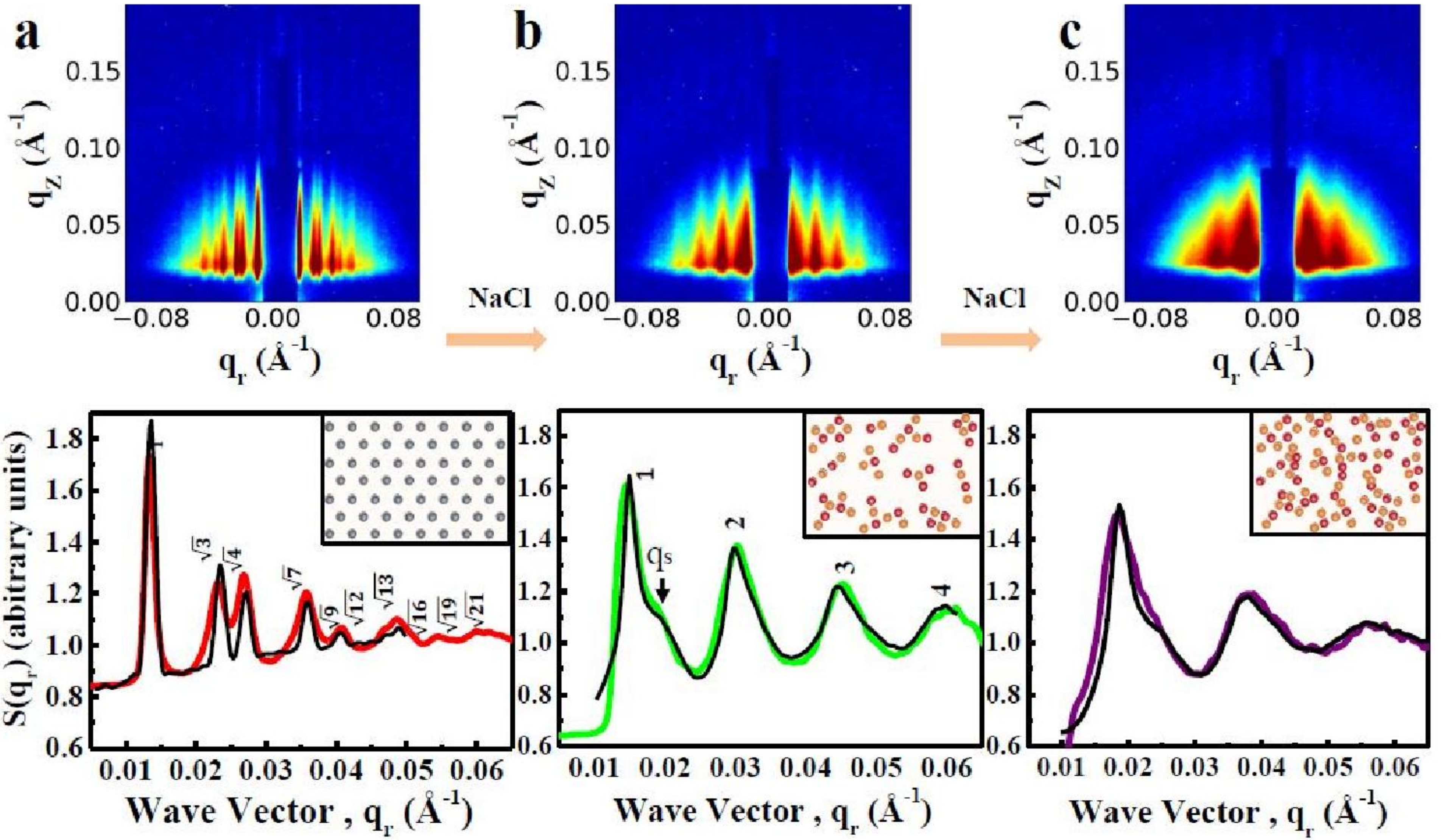
Reorientation Transition



2-D Nanoparticle Assembly

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

Srivastava *JACS* **2014**



2-D Nanoparticle Assembly

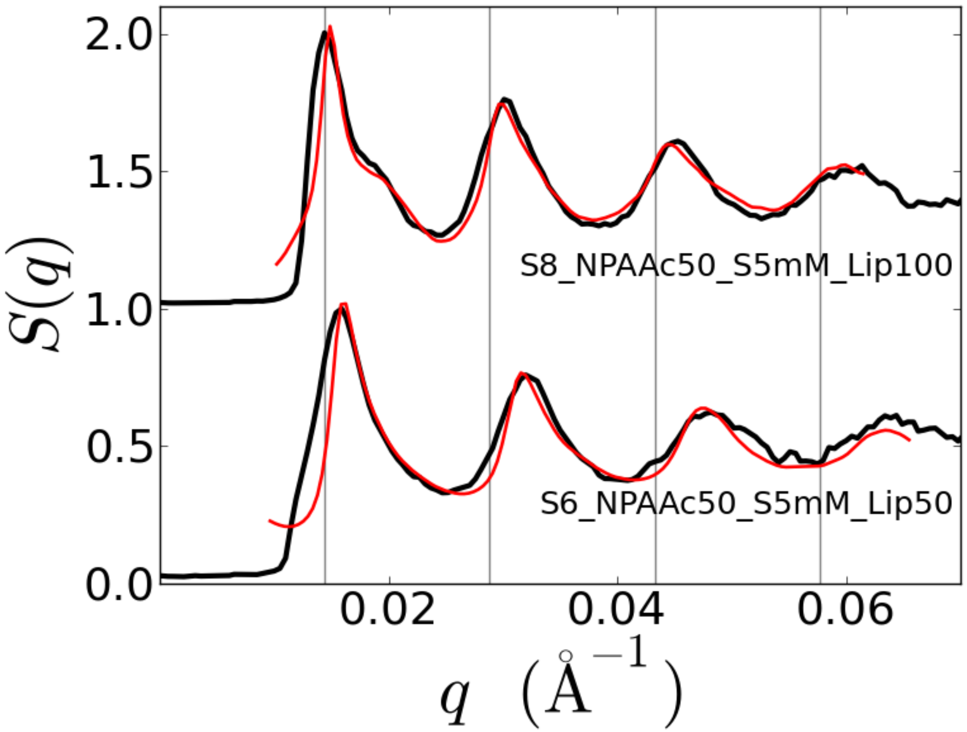
- Brute-force modeling…

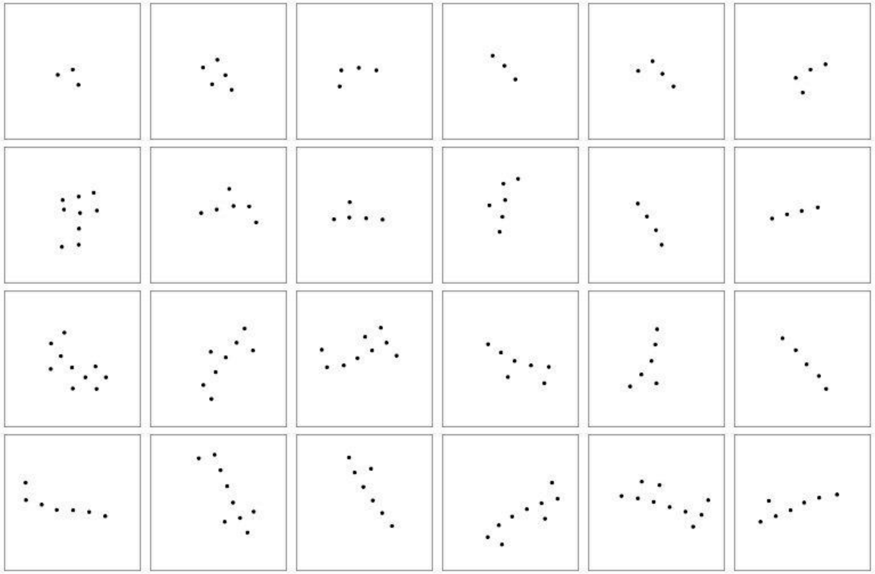
$$P(q_r) = \int_0^{2\pi} \left|F(q_x, q_y)\right|^2 d\phi$$

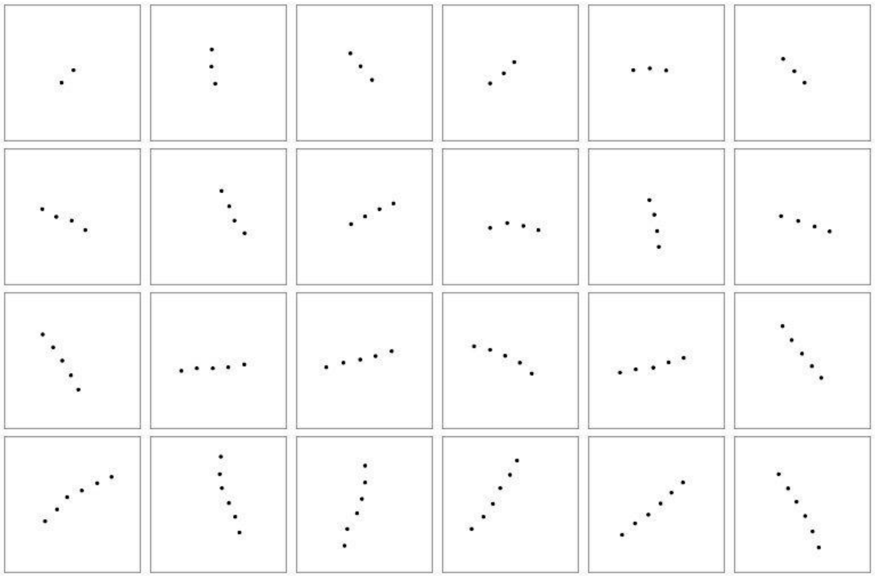
$$= \int_0^{2\pi} \left|\rho\,(r) e^{iq.r}\, dV\right|^2 d\phi$$

$$= \int_0^{2\pi} \left|\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \rho(x,y) e^{iq_x x} e^{iq_y y}\, dx\, dy\right|^2 d\phi$$

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







Outline

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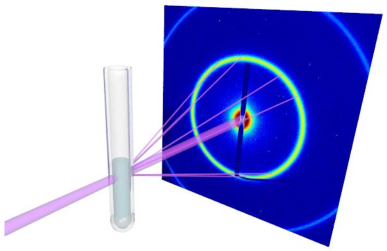
- X-ray scattering for nanoscience



- Experimental examples:
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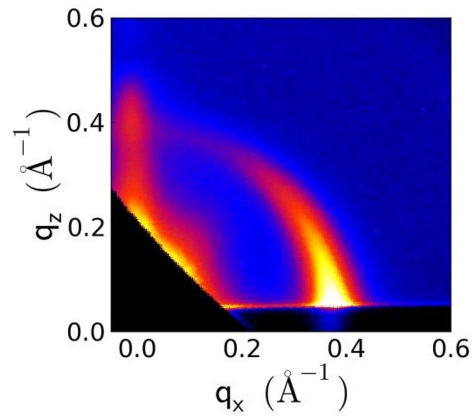
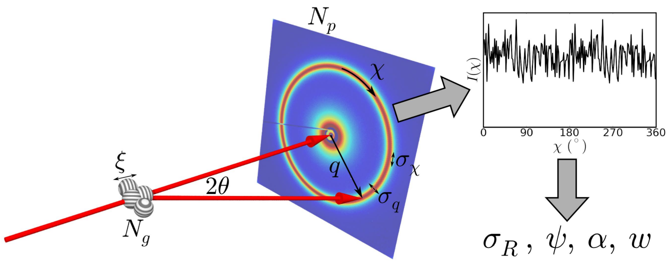
  - 2D nanoparticle assembly

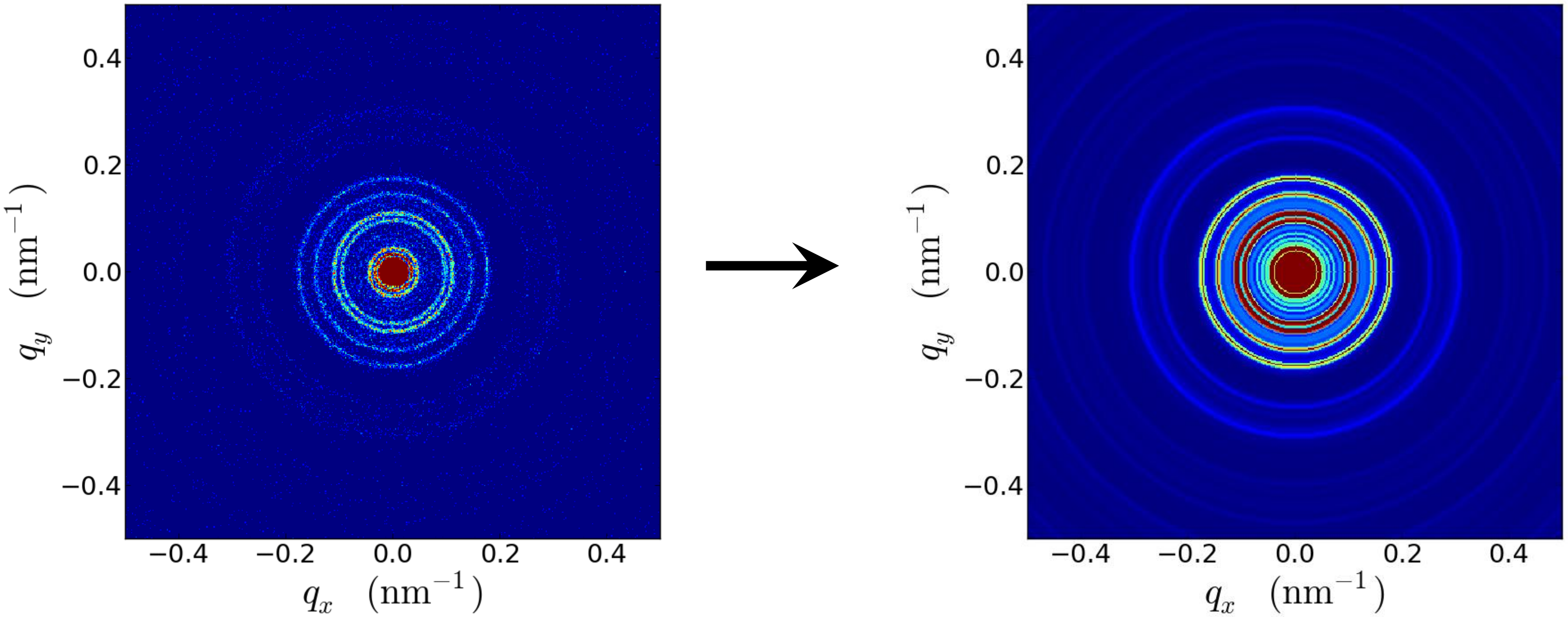


- New techniques:
  - Variance scattering
  - GTSAXS
  - Nano-lattice model



‘Variance Scattering’

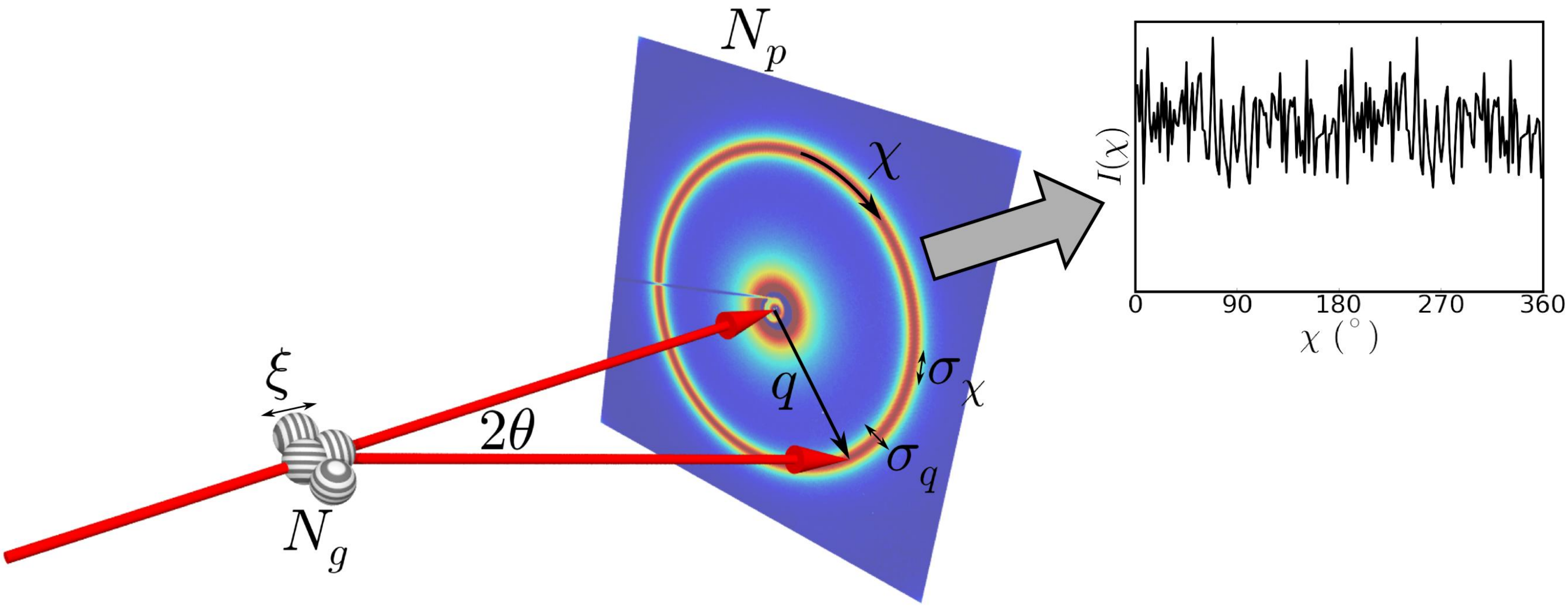
- Conventionally, when we measure a scattering pattern, we accumulate data over a large area and time, to average-out random fluctuations…



- What if, instead of ignoring those variations, you **emphasize** them, and **monitor** them?

Scattering Ring

- A scattering ring is a summation of many peaks
- Each set of *m* peaks comes from a different grain in the sample

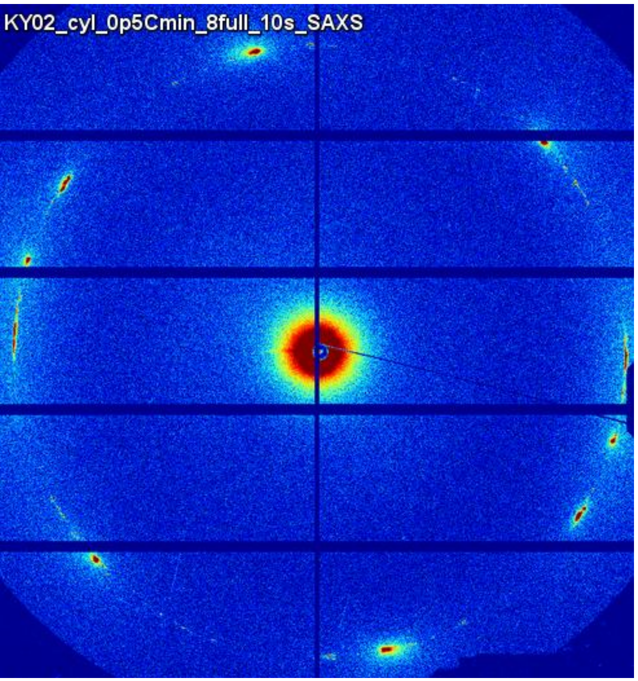


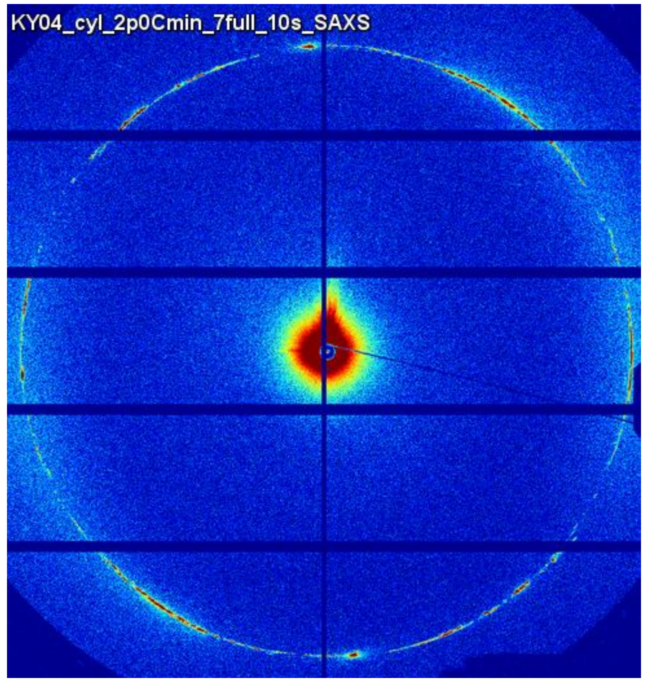
- The more grains probed by the beam, the more uniform the ring becomes

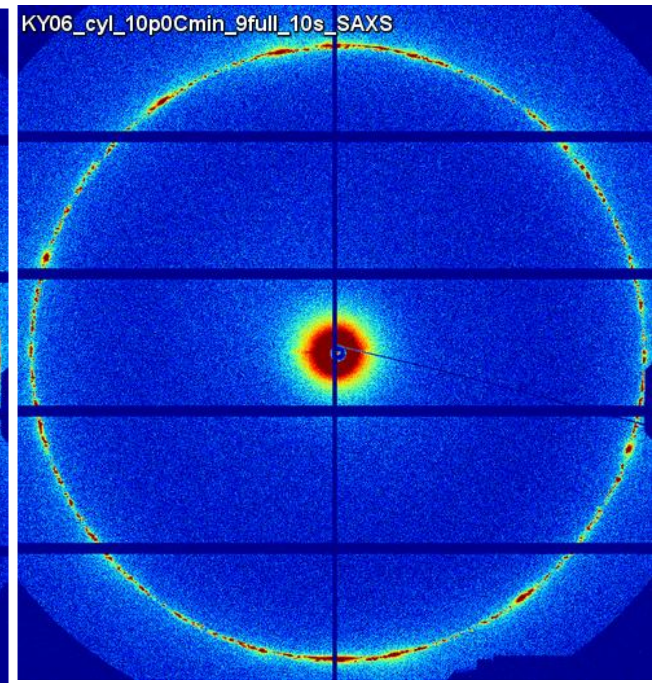
Yager and Majewski, J. Appl. Cryst. 2014, 47, 1855.

Scattering Ring

- The more grains probed by the beam, the more uniform the ring becomes
- The detector probes only a fraction of the peaks in reciprocal-space







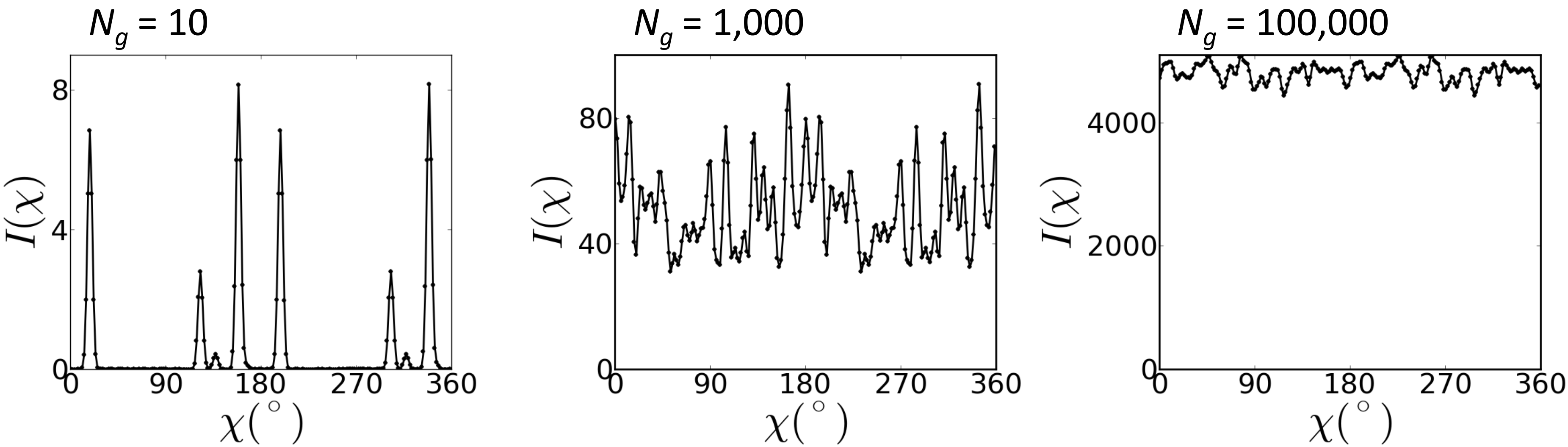
$$f_{\text{Ewald}} = \frac{\pi 2q \times (\sqrt{2\pi}\sigma_q) \times (\sqrt{2\pi}\sigma_q)}{4\pi q^2 \times (\sqrt{2\pi}\sigma_q)} = \frac{\sqrt{2\pi}\sigma_q}{2q}$$

$$N_p = m f_{\text{Ewald}} f_\chi N_g = \frac{m\sqrt{2\pi}\sigma_q f_\chi}{2q} N_g$$

$$N_g = \frac{2q}{m\sqrt{2\pi}\sigma_q f_\chi} N_p$$

Ring Graininess

- Simulations are used to generate scattering rings for different number of grains (N_g)



- We can quantify the variation…

Ring Graininess

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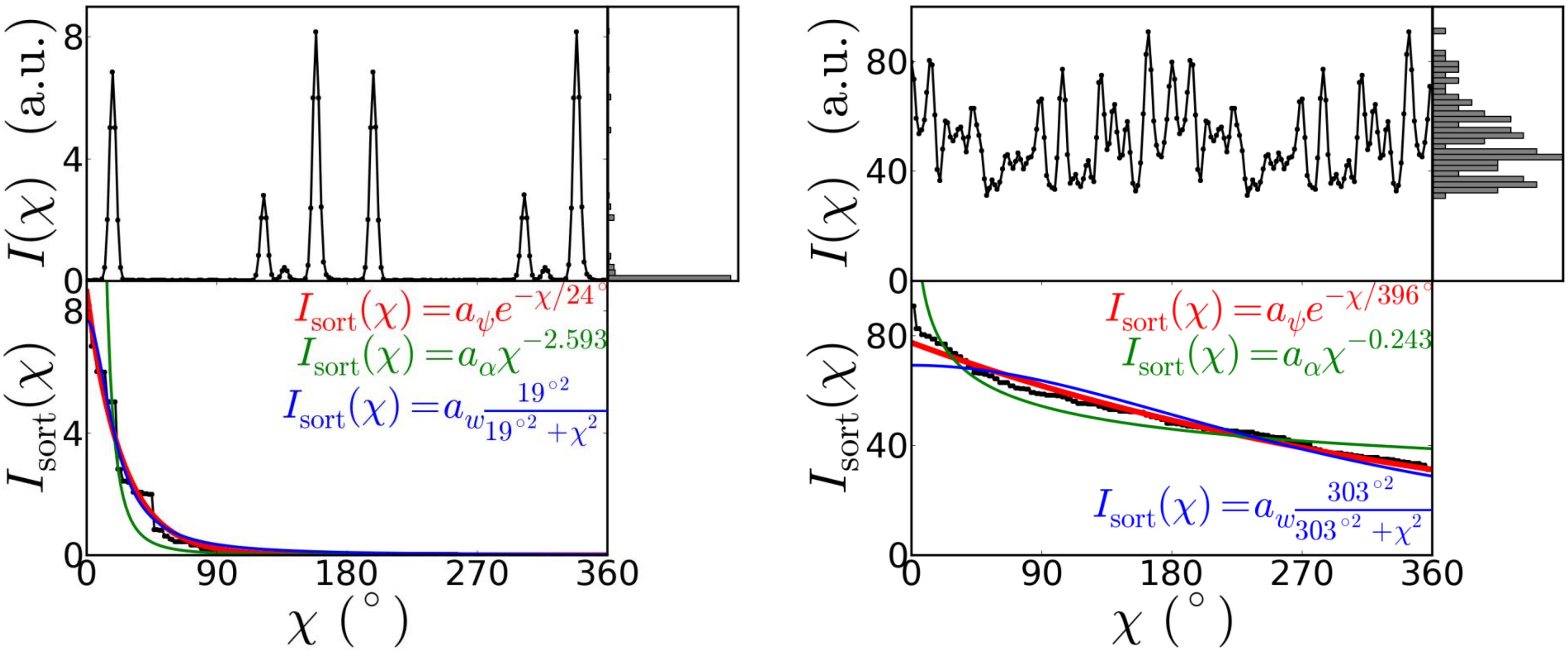
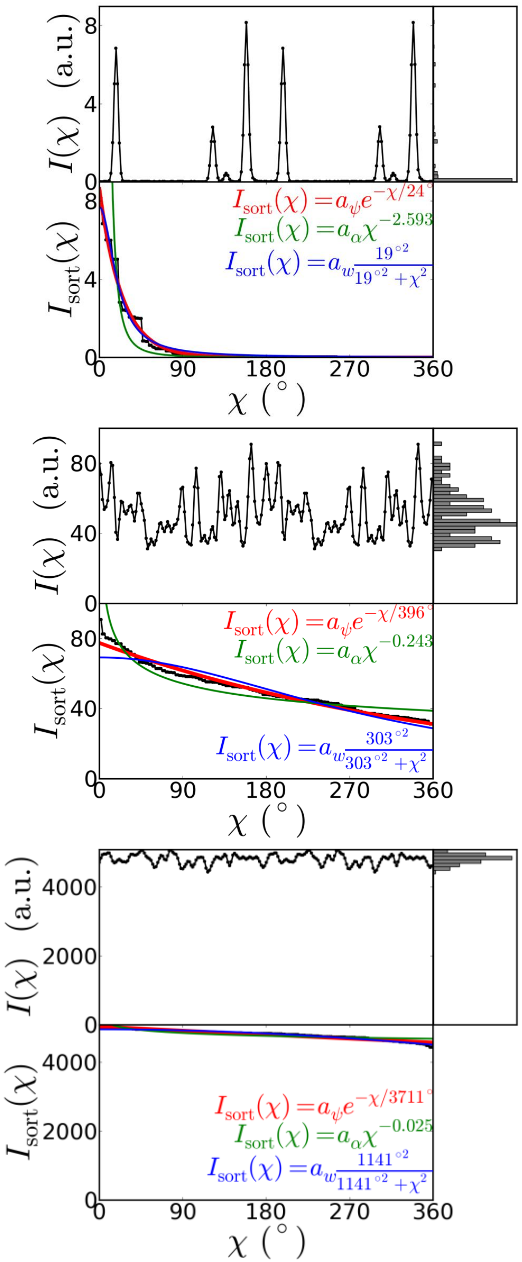
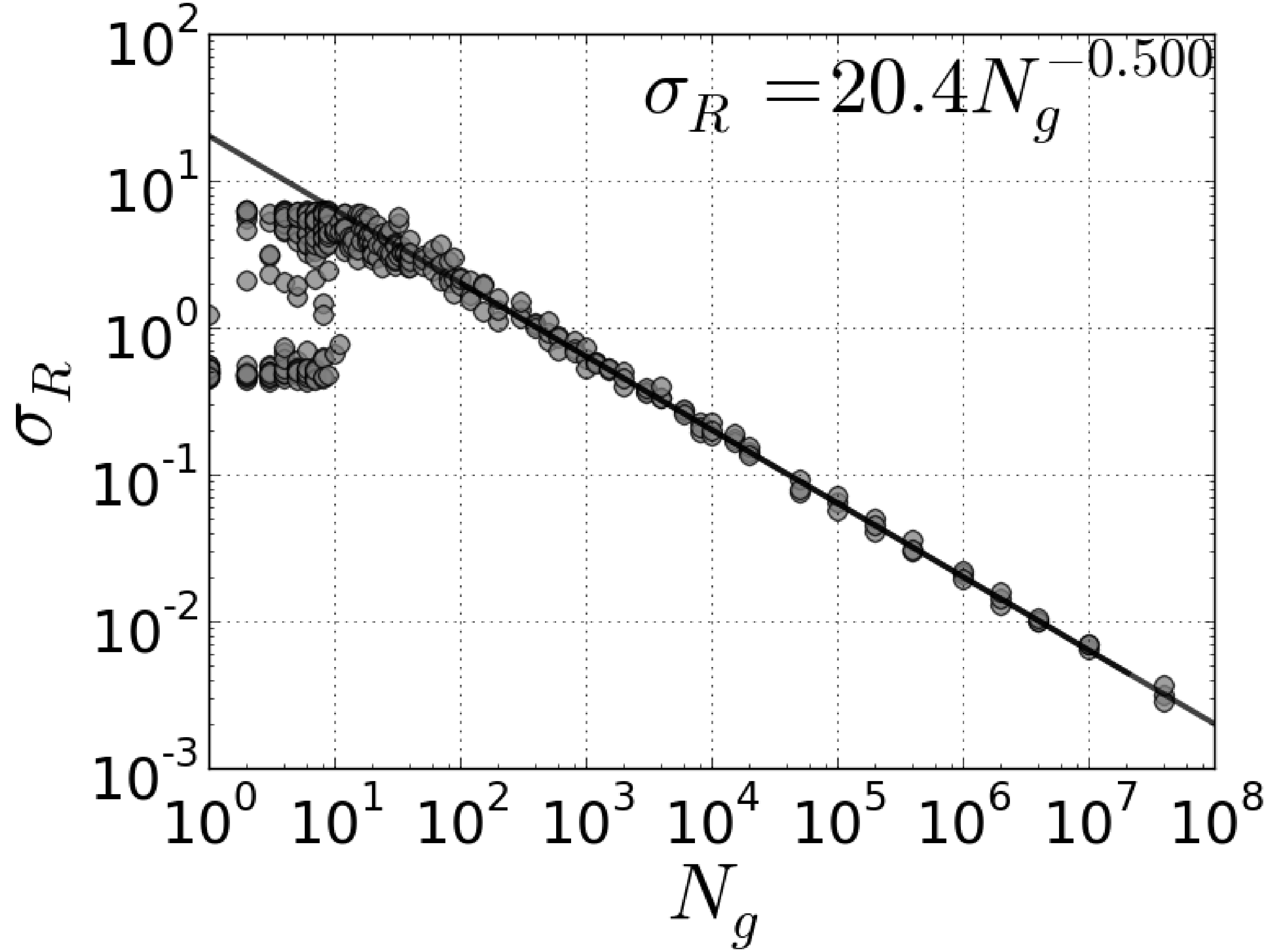
- One simple metric is the relative **standard deviation** of the intensity



- The decay of the “sorted” curve also encodes how many peaks were in the signal
- We can fit the decay of the “sorted” curve

σ_R metric





Experimental: liquid crystal

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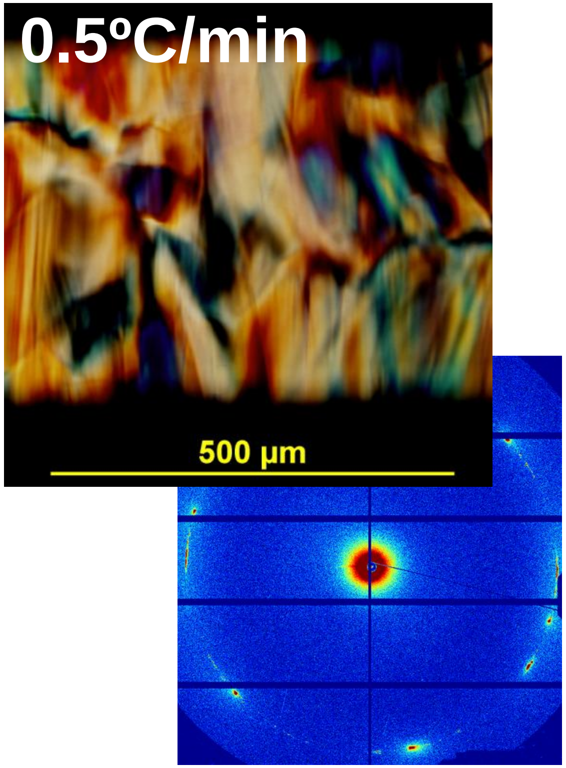
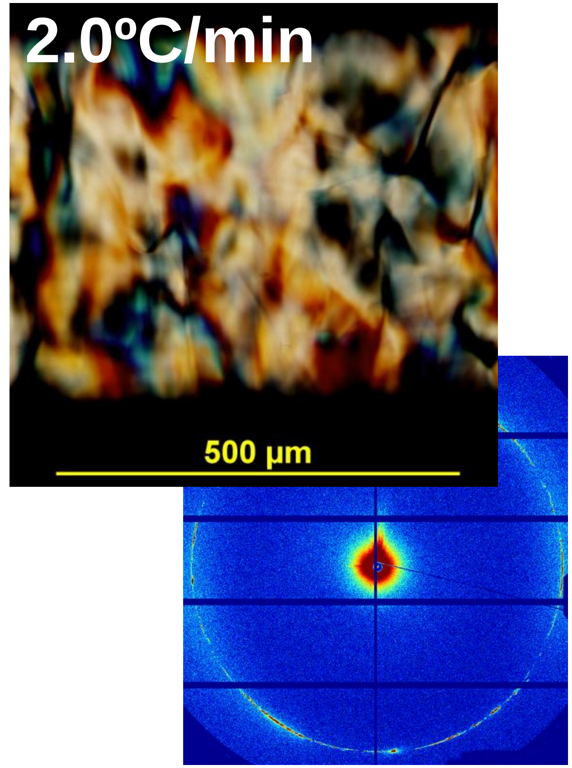
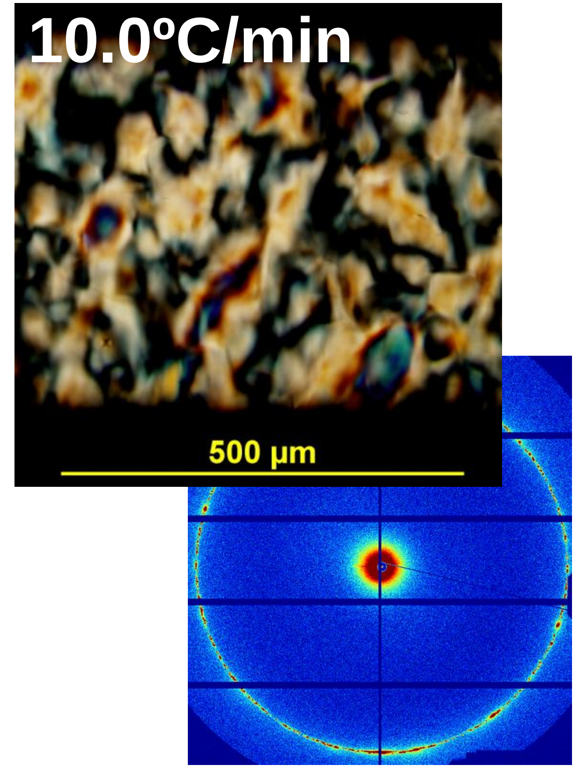
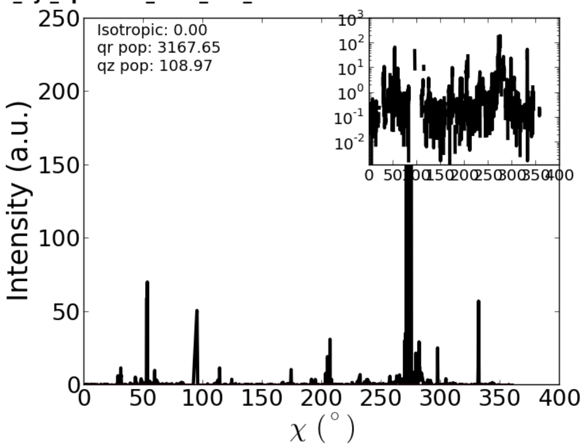


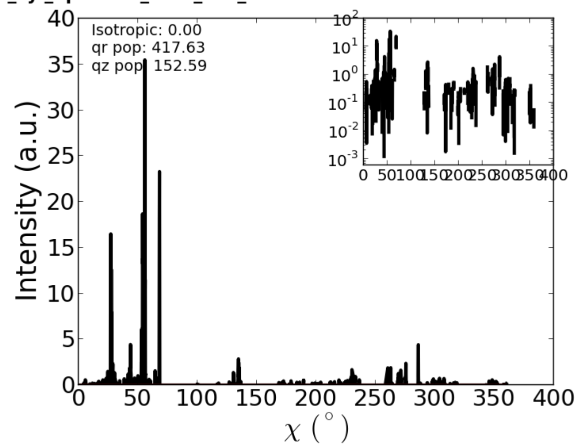




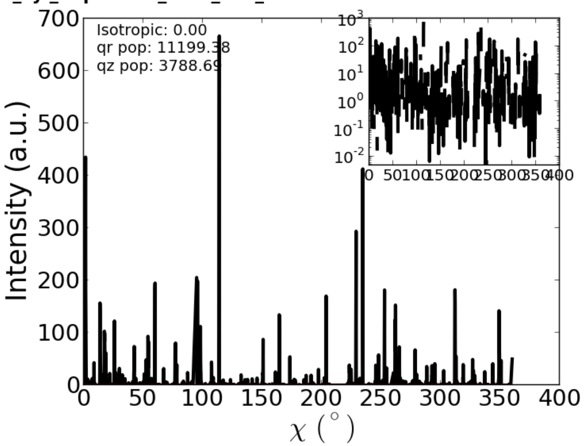
KY02_cyl_0p5Cmin_6full_10s_SAXS-linecut



KY04_cyl_2p0Cmin_5full_10s_SAXS-linecut



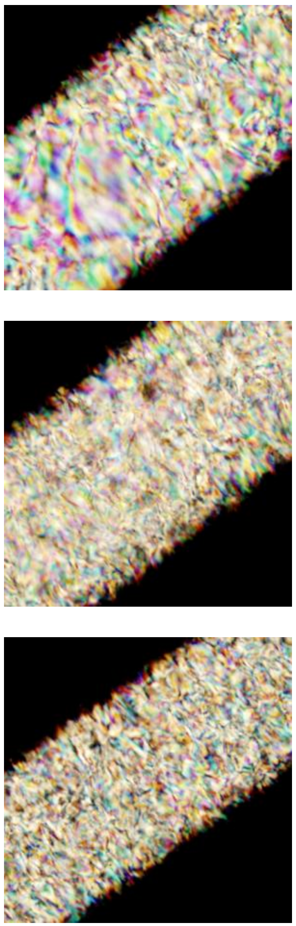
KY06_cyl_10p0Cmin_7full_10s_SAXS-linecut

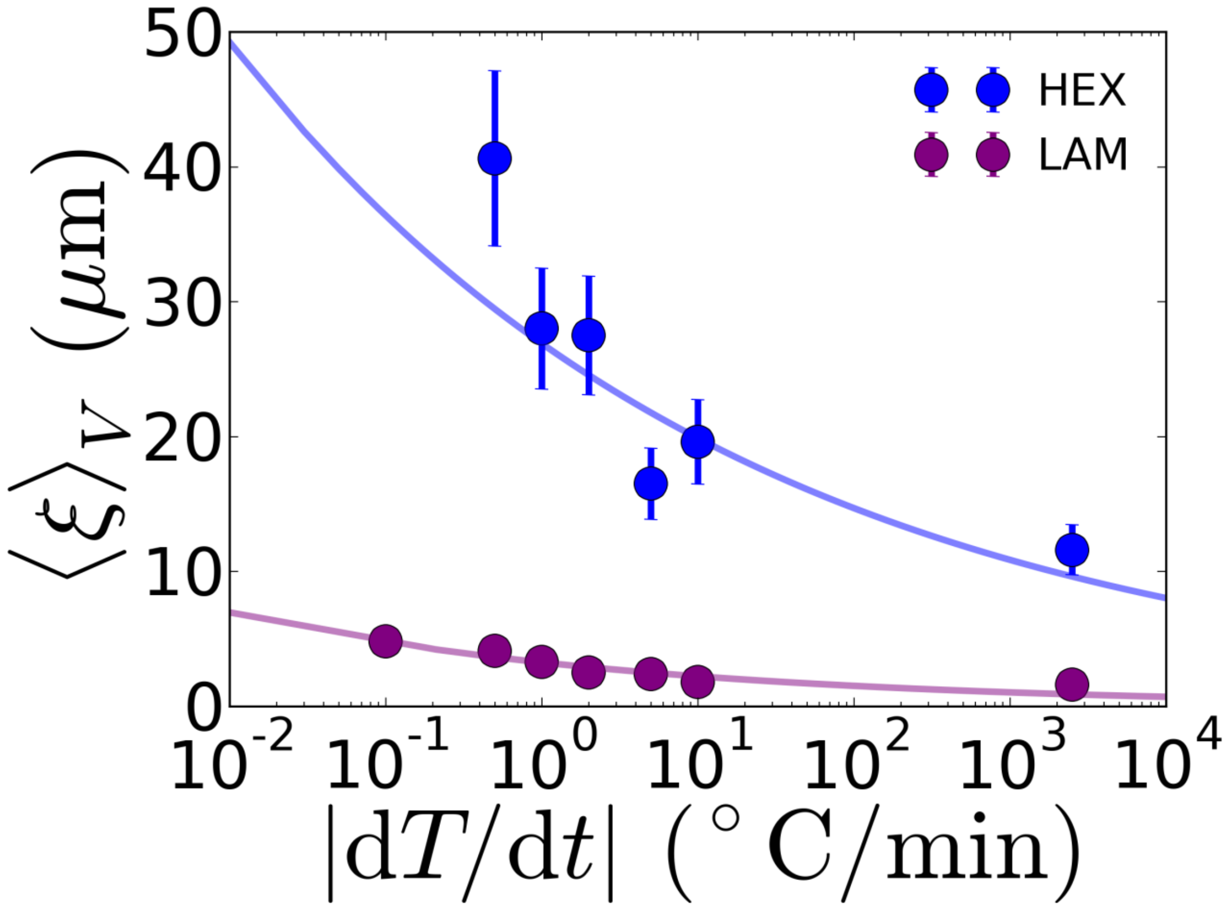


Experimental

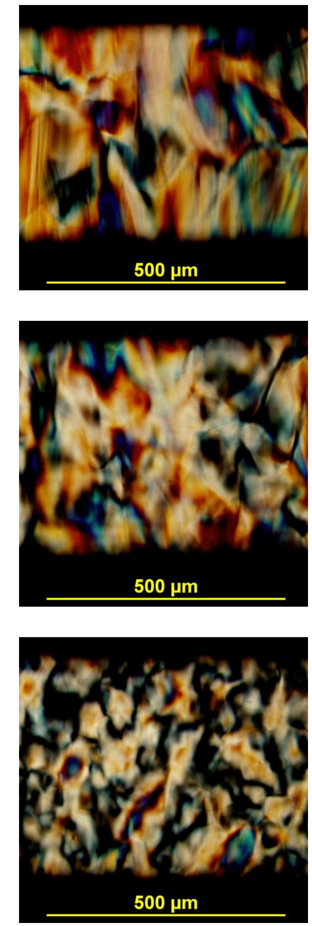
- We can measure variation in micron-sized grains, as a function of quench rate…

lamellar



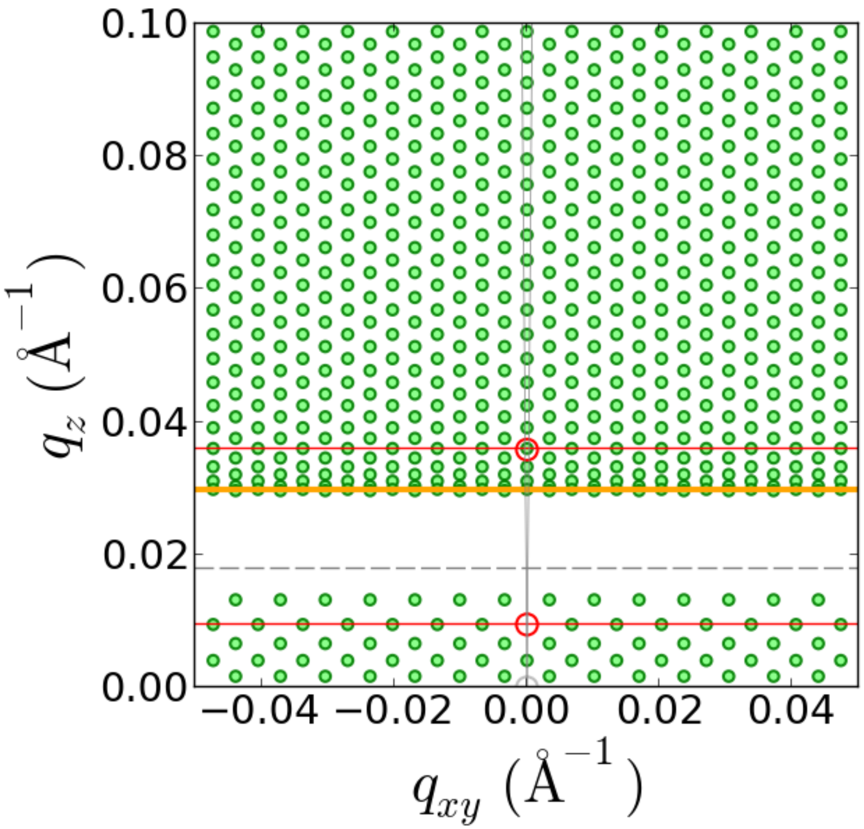


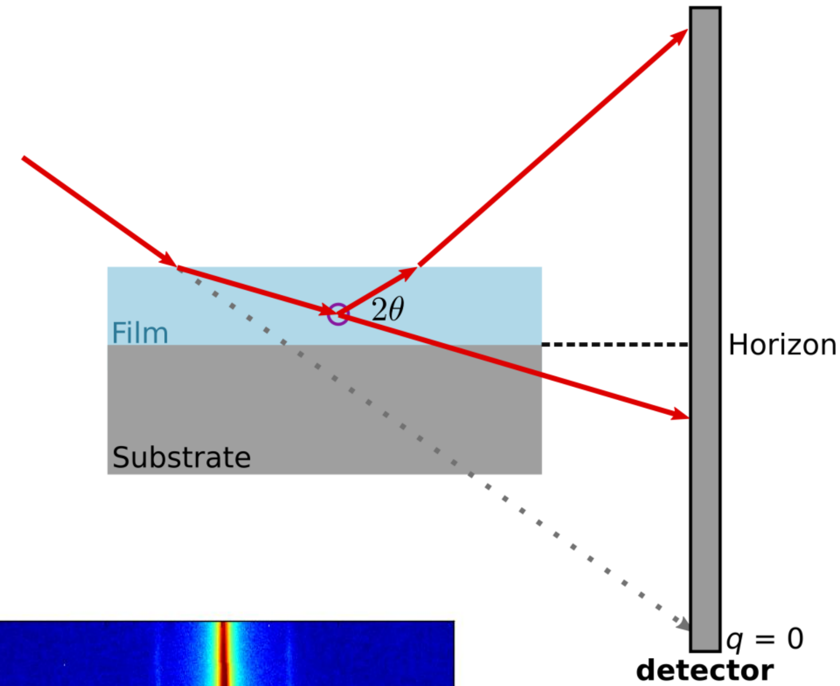
hexagonal

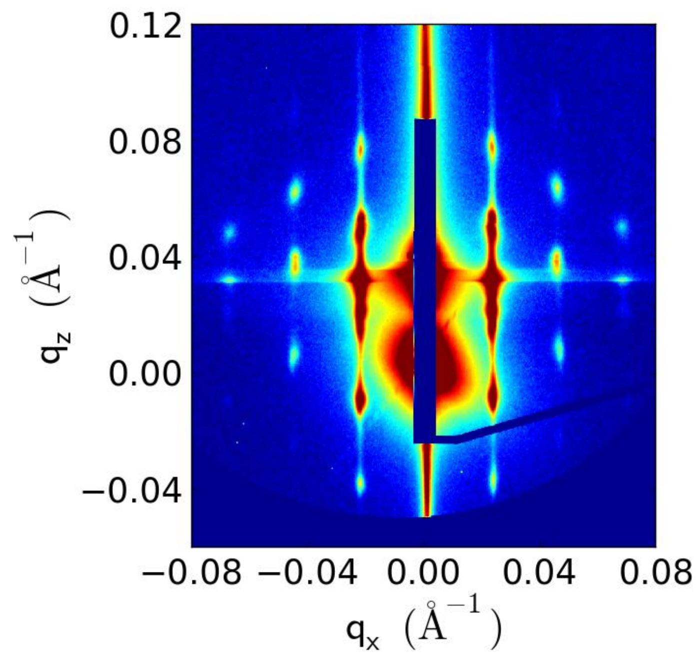


GISAXS

- Refraction shifts and distorts reciprocal-space

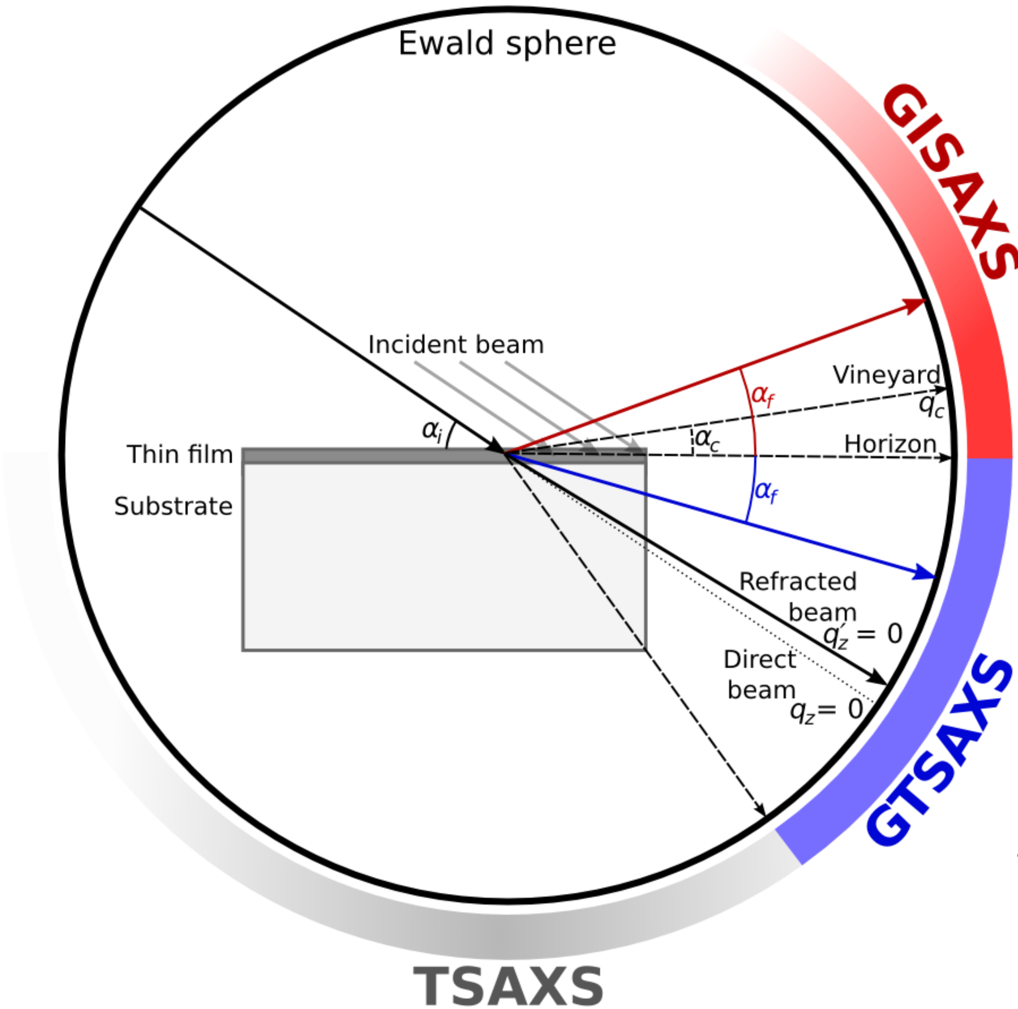






New concept: GTSAXS

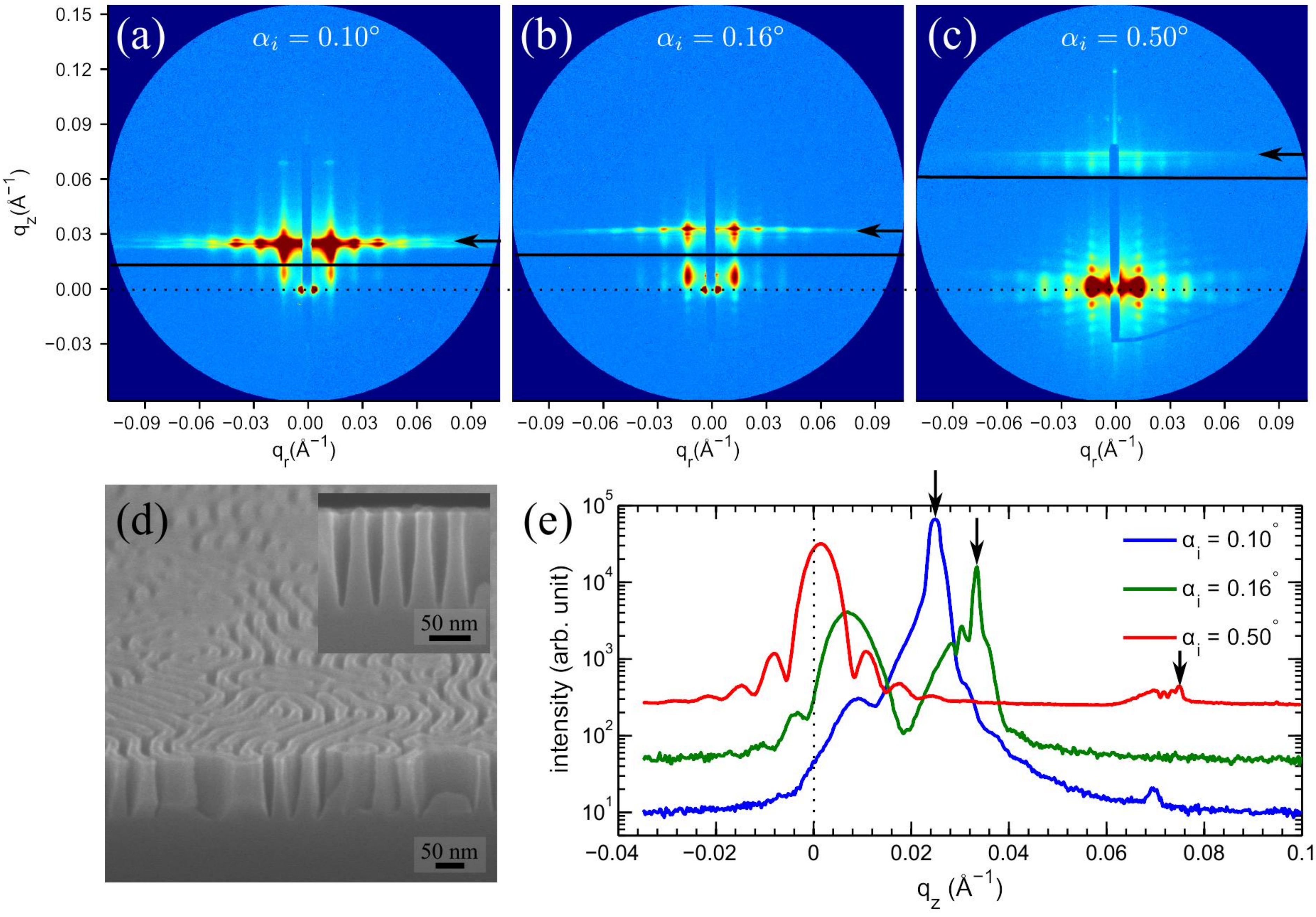
- **G**razing-incidence **T**ransmission **S**mall-**A**ngle **X**-ray **S**cattering



Scattering exits from edge (between horizon and sample corner)

Lu et al. J. Appl. Cryst. 2013, 46, 165.

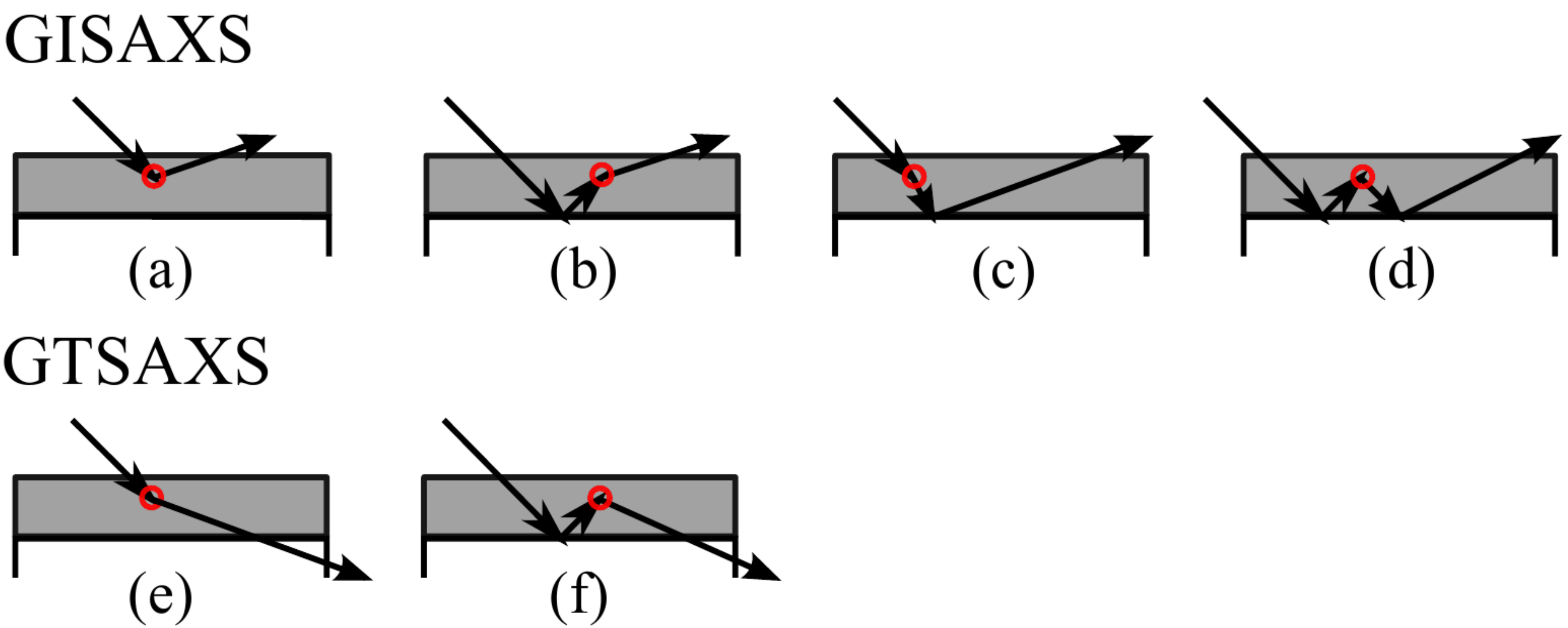
BCP pattern



(a) $\alpha_i = 0.10°$
(b) $\alpha_i = 0.16°$
(c) $\alpha_i = 0.50°$
$q_z(Å^{-1})$
$q_r(Å^{-1})$
(d)
50 nm
50 nm
(e)
intensity (arb. unit)
q_z ($Å^{-1}$)
α_i = 0.10°
α_i = 0.16°
α_i = 0.50°

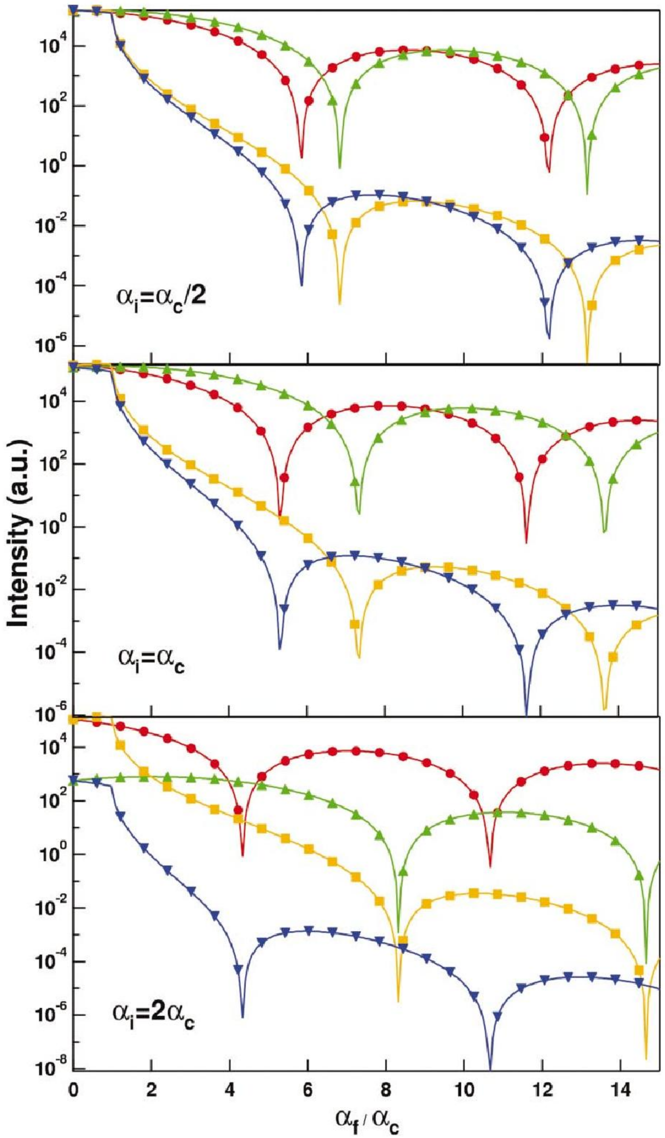
Modeling

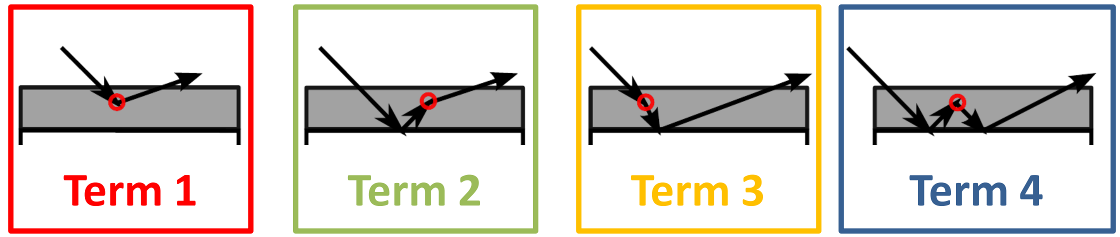
- Distorted-Wave Born Approximation (DWBA) considers 4 possible reflection-scattering events
- Born Approximation (BA) is much simpler: just a single scattering term



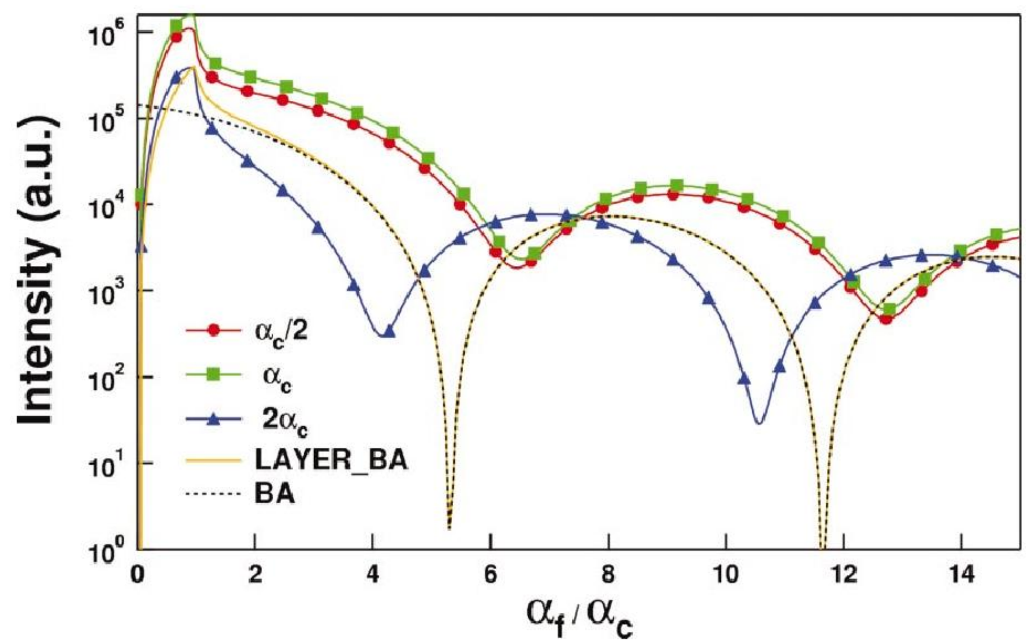
Multiple Terms

- 4 terms of DWBA have different phases





Smears the minima of the BA



Lazzari, J. Appl. Cryst. 2002, 35, 406.

Refraction correction

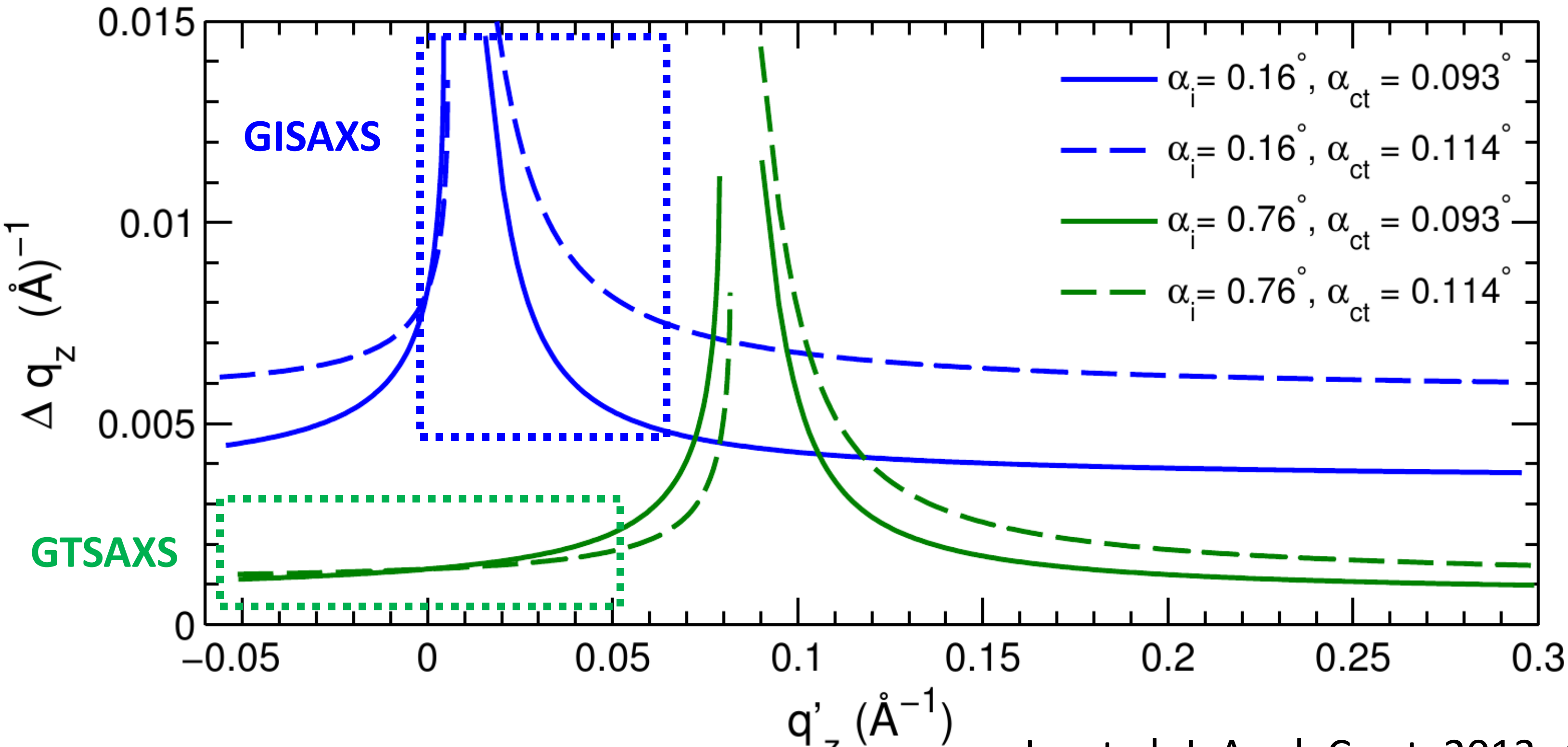
- Correction in GISAXS is large and nonlinear
- Correction in GTSAXS is just a small offset

GISAXS

$$q'_z = k_0 \left(\sqrt{\sin\alpha_i^2 - \sin\alpha_{ct}^2} + \sqrt{\sin\alpha_f^2 - \sin\alpha_{ct}^2} \right)$$
$$= k_0 \left(\sqrt{\sin\alpha_i^2 - \sin\alpha_{ct}^2} + \sqrt{\left(\frac{q_z}{k_0} - \sin\alpha_i\right)^2 - \sin\alpha_{ct}^2} \right)$$

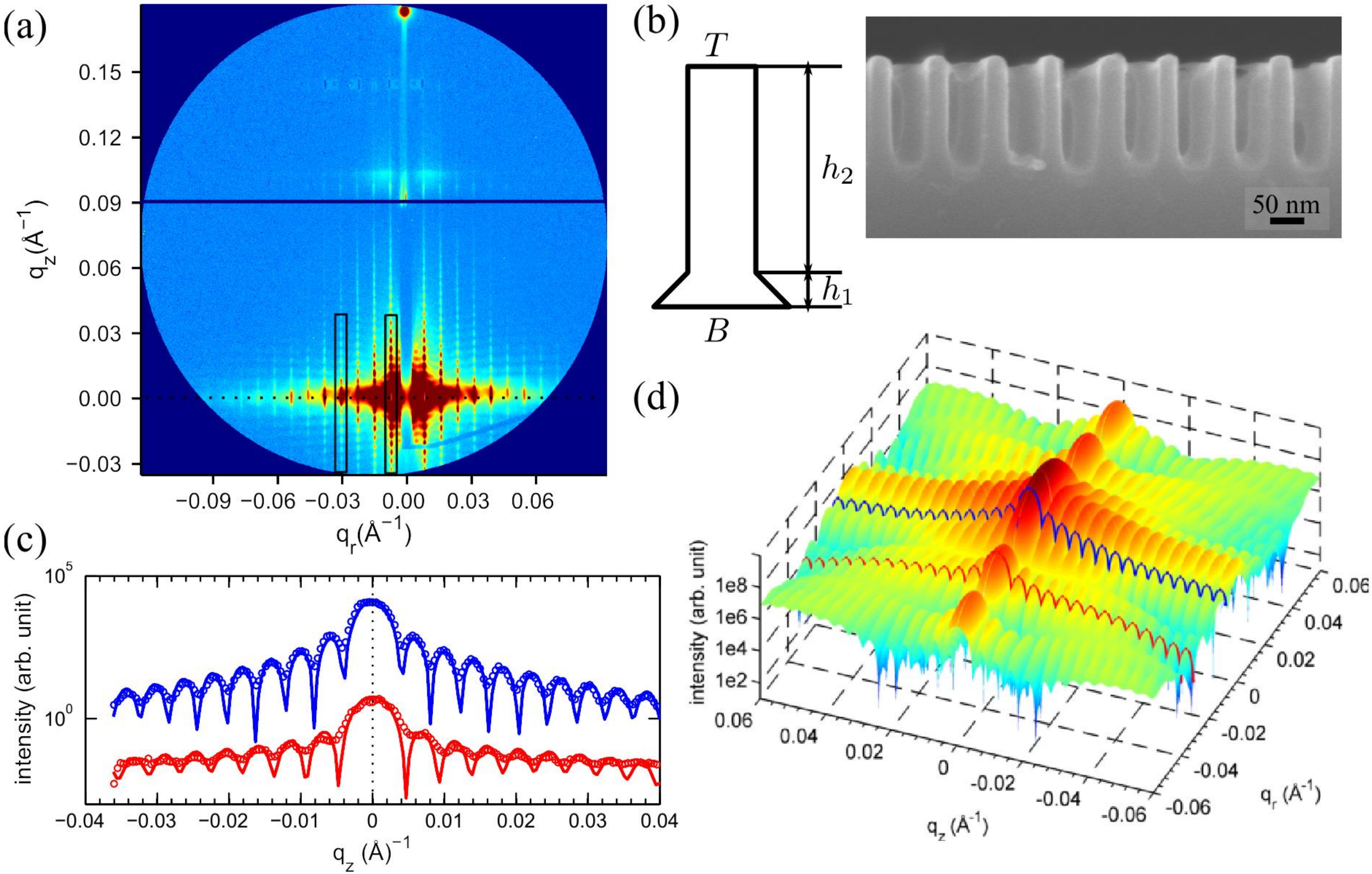
GTSAXS

$$q'_z = k_0 \left(\sqrt{\sin\alpha_i^2 - \sin\alpha_{ct}^2} - \sqrt{\sin\alpha_f^2 + \sin\alpha_{\mathrm{Si}}^2 - \sin\alpha_{ct}^2} \right)$$
$$= k_0 \left(\sqrt{\sin\alpha_i^2 - \sin\alpha_{ct}^2} - \sqrt{\left(\frac{q_z}{k_0} - \sin\alpha_i\right)^2 + \sin\alpha_{\mathrm{Si}}^2 - \sin\alpha_{ct}^2} \right)$$



Lu et al. J. Appl. Cryst. 2013, 46, 165.

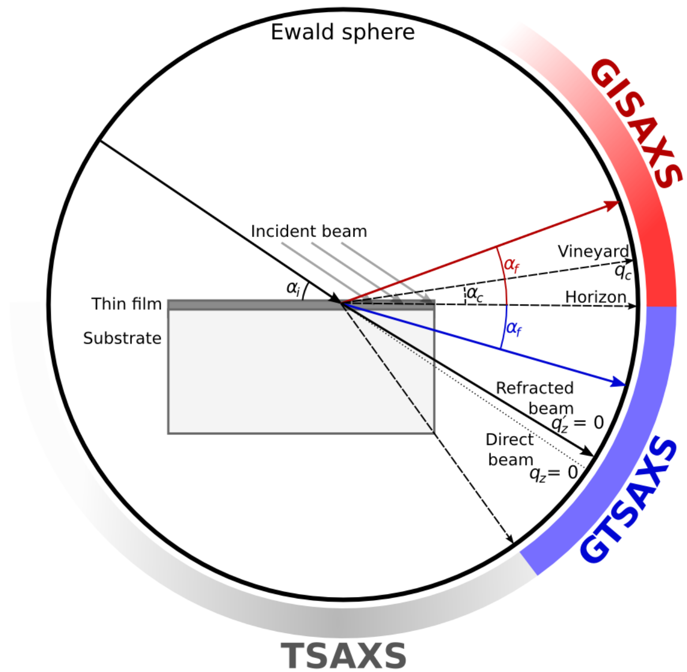
Lithographic line grating

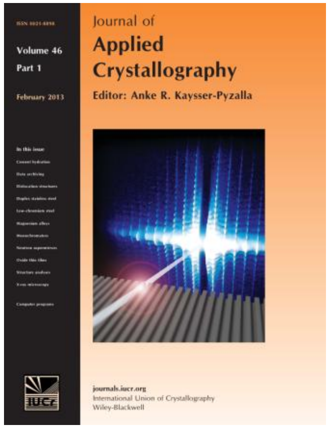


Lu et al. J. Appl. Cryst. 2013, 46, 165.

GTSAXS Comparison

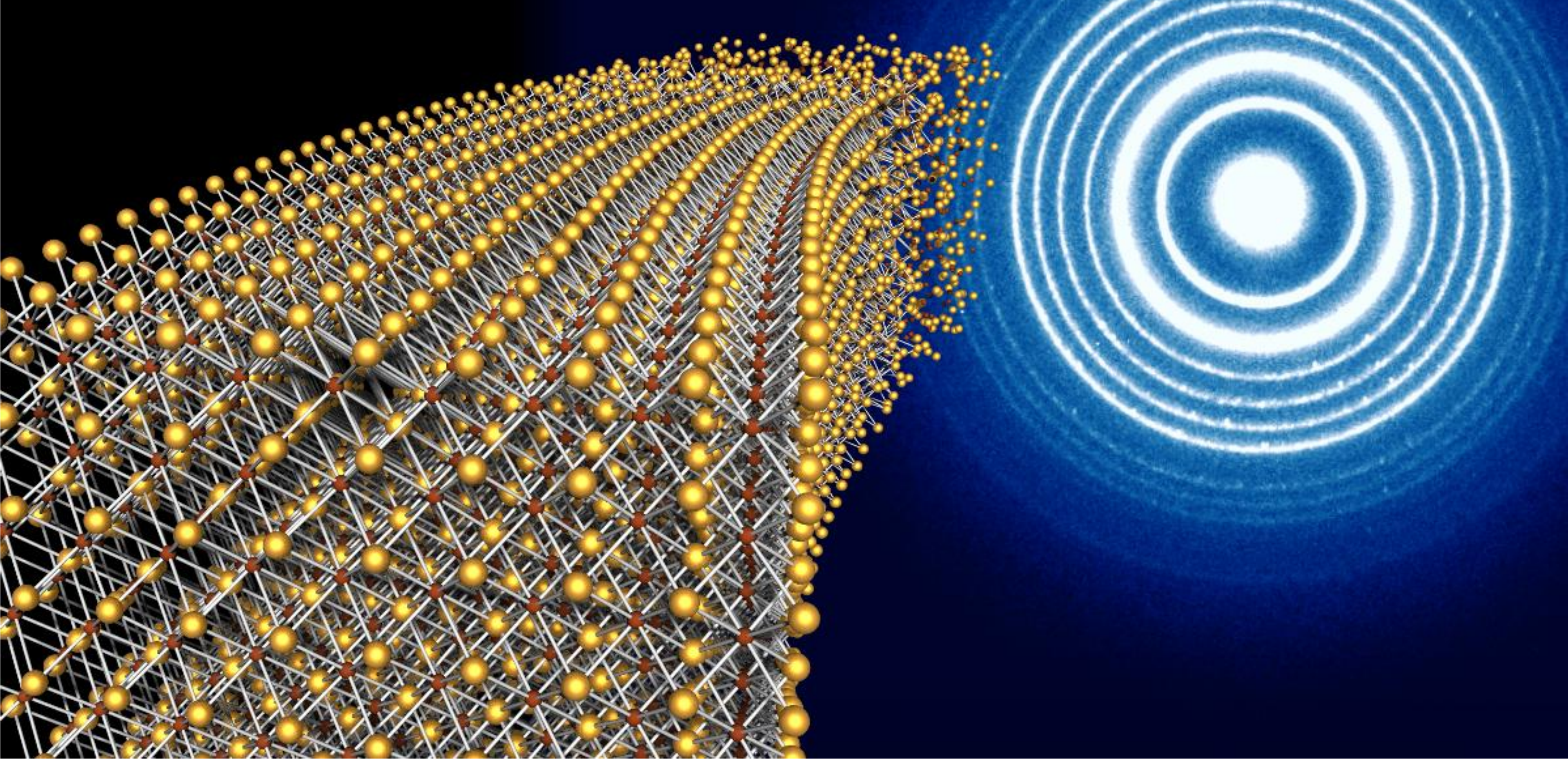
	TSAXS	GTSAXS	GISAXS
Requirements	Thin substrate	Thin film Flat substrate <u>Sample near edge</u> Focused beam <u>Beam near edge</u> <u>Sufficient incident angle</u>	Thin film Flat substrate Focused beam Low incident angle
Advantages	Simple analysis	Strong signal qz data Simple analysis	Strong signal qz data
Disadvantages	Thin substrate Weak signal Limited qz data	Sample constraints	Complex analysis

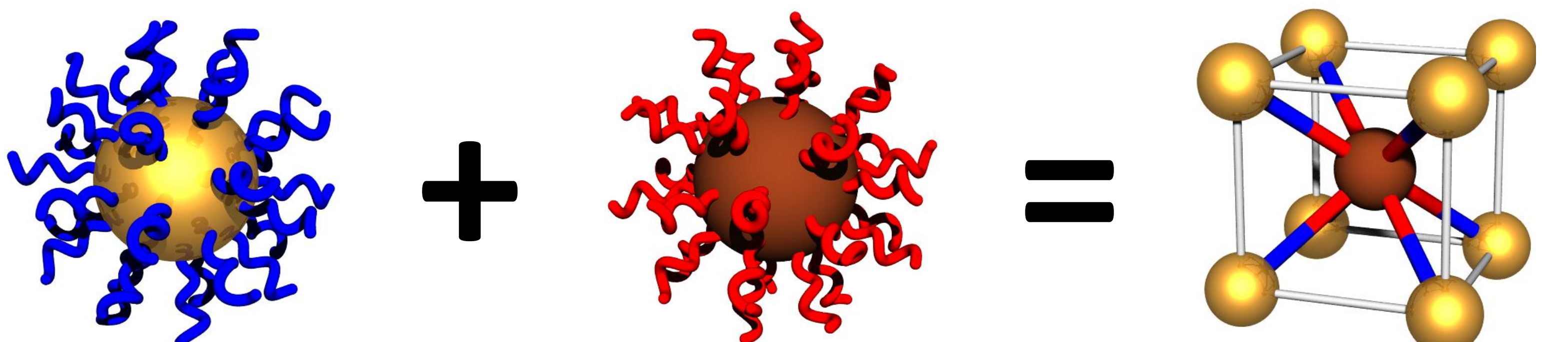




Lu et al. J. Appl. Cryst. 2013, 46, 165.

Nanoparticle superlattices





Nano-lattice x-ray model

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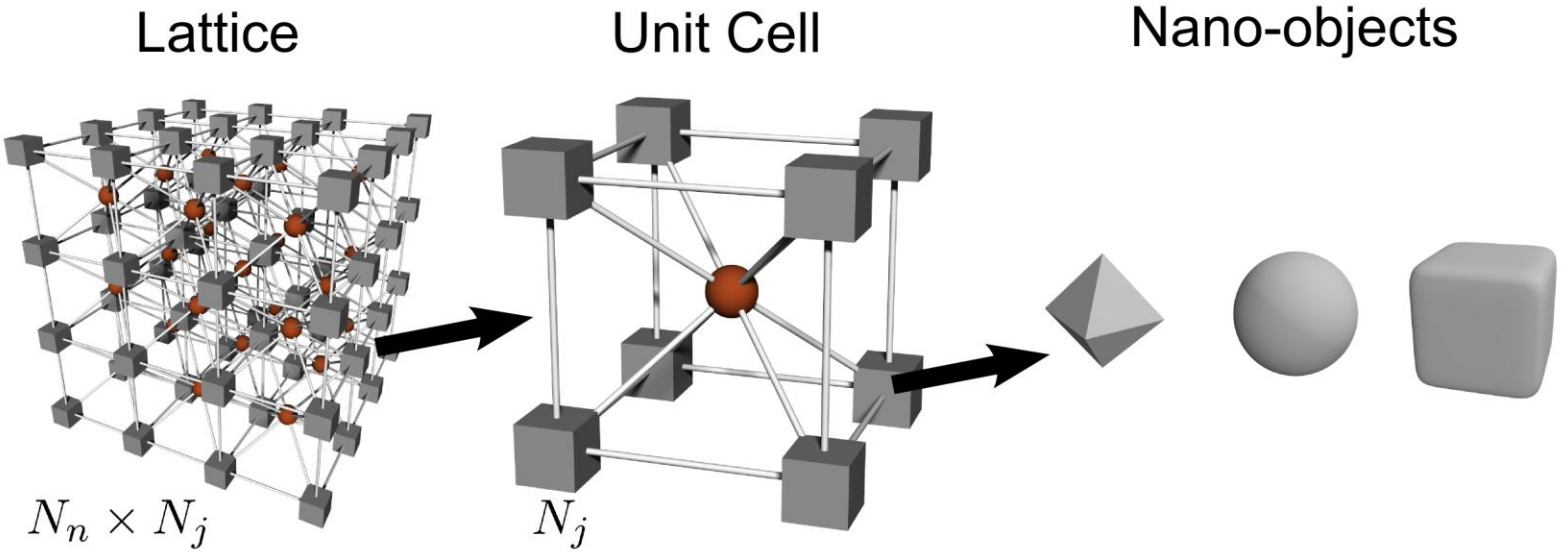
- Derived a very general scattering formalism
- Allows for arbitrary lattice of arbitrary nano-objects

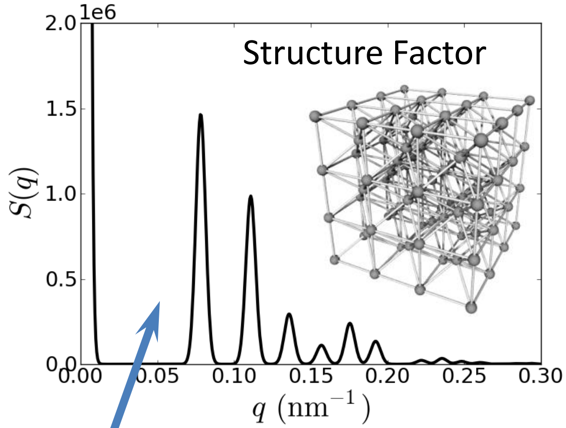


Variables			
structural	grain size (ξ)	symmetry ($a, b, c, \alpha, \beta, \gamma$)	shape (p, ...), material ($\Delta\rho$), size (R), orientation (M_j)
disorder	substitutional, vacancy, ...	positional (σ_D)	polydispersity (σ_R/R), orientational
Compute	$I(q), S(q)$	$Z_0(q)$	$F_j(\mathbf{q}), P_j(q)$

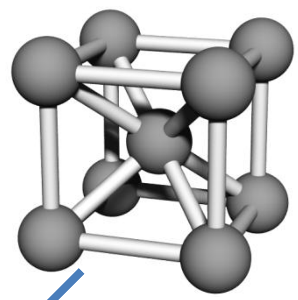
Yager, J. Appl. Cryst. 2014, 47, 118.

Formalism

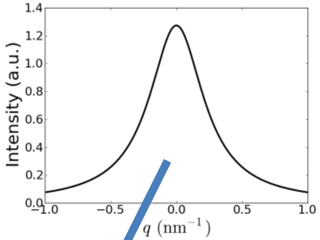
Structure Factor



Lattice Unit Cell



Peak Shape

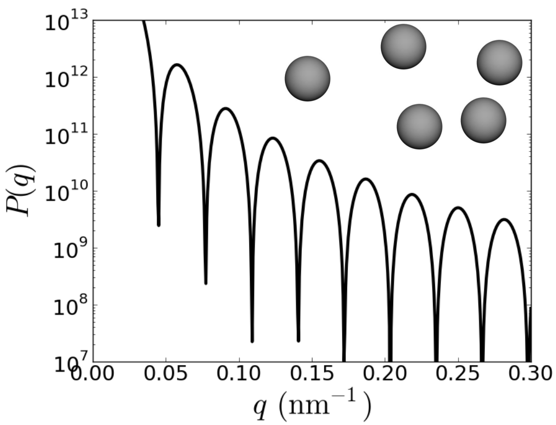


Debye-Waller (thermal disorder)

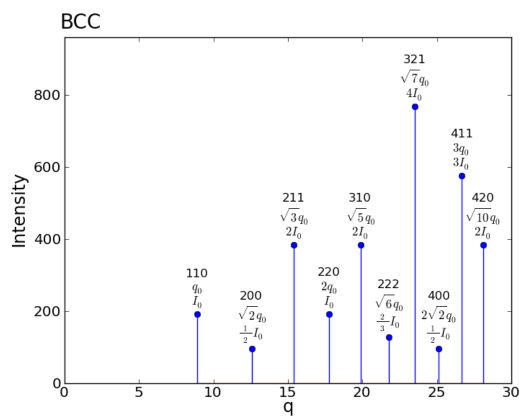
Plane Wave

$$S(q) = \frac{c}{q_{hkl}^2 P(q_{hkl})} \sum_{\{hkl\}}^{m_{hkl}} \left| \sum_{j=1}^{n_c} F_j(M \cdot \mathbf{q}_{hkl}) e^{2\pi i (x_j h + y_j k + z_j l)} \right|^2 e^{-\sigma_D^2 q_{hkl}^2 a^2} L_{hkl}(q - q_{hkl})$$

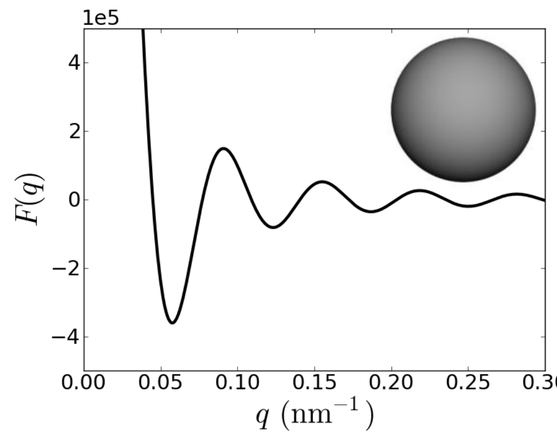
Isotropic Form Factor



Reciprocal-space Peaks

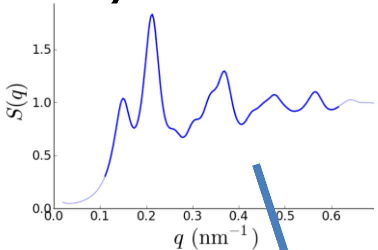


Particle Form Factor

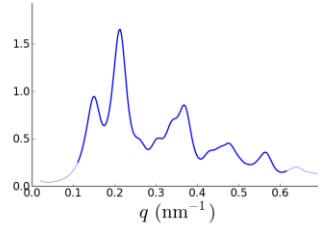


Disorder

- Real systems are disordered



Structural Peaks



Particle Size Polydispersity

$$\beta_j(q) = \frac{|\langle F_j(\mathbf{q})\rangle|^2}{\left\langle |F_j(\mathbf{q})|^2 \right\rangle} = \frac{|\langle F_j(\mathbf{q})\rangle|^2}{\overline{P}_j(q)}$$

$$I(q) = P(q)S(q)$$

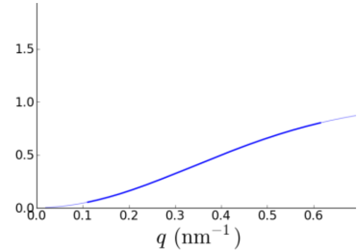
$$= P(q)\left[\frac{cZ_0(q)}{P(q)}G(q) + 1 - \beta(q)G(q)\right]$$

Peak shape/width *L* (contained within *Z*) accounts for finite grain size

Diffuse Scattering

Debye-Waller (thermal disorder)

$$G(q) = e^{-\sigma_D^2 q^2 a^2}$$



- Particle size polydispersity
- Grain size (correlation length)
- Positional disorder (DW)

Fitting data

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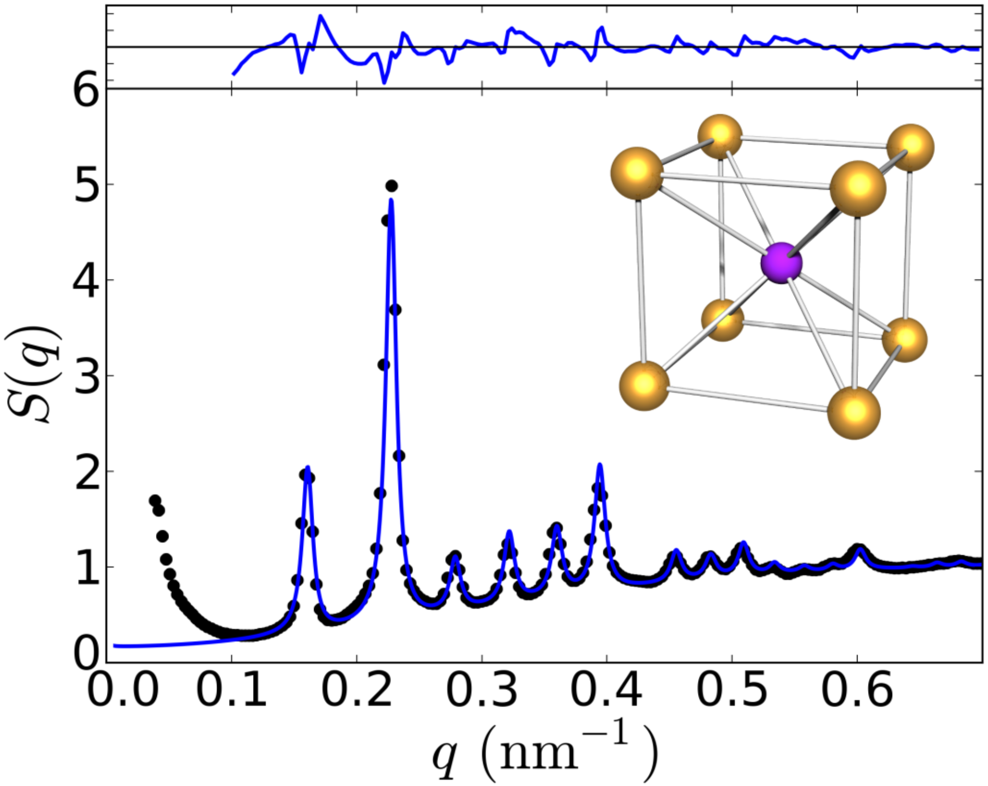
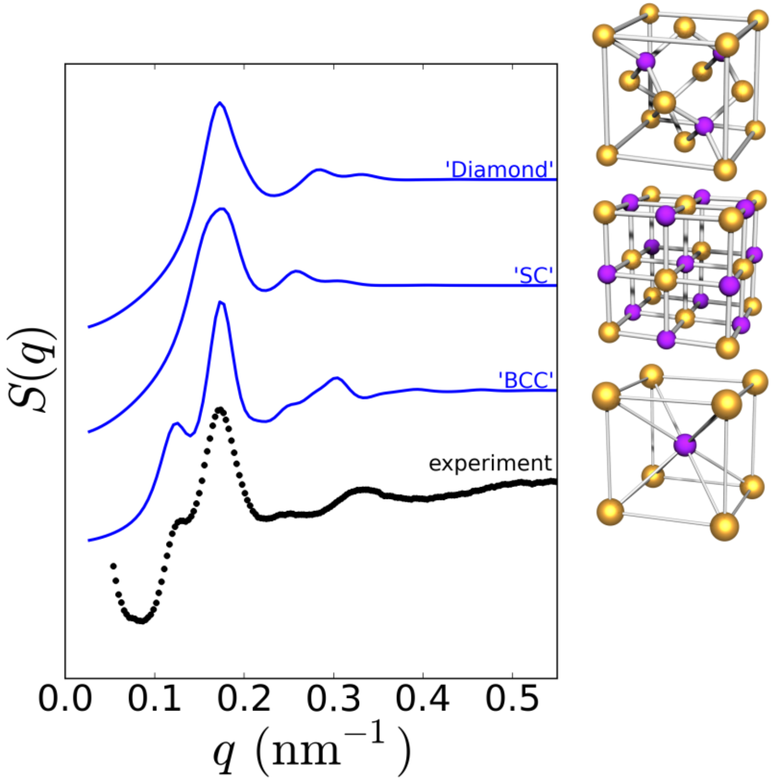
- Can fit experimental data quantitatively, extracting parameters of interest
- Constraining parameters (e.g. via SEM) helps
- Many parameters can be fit uniquely

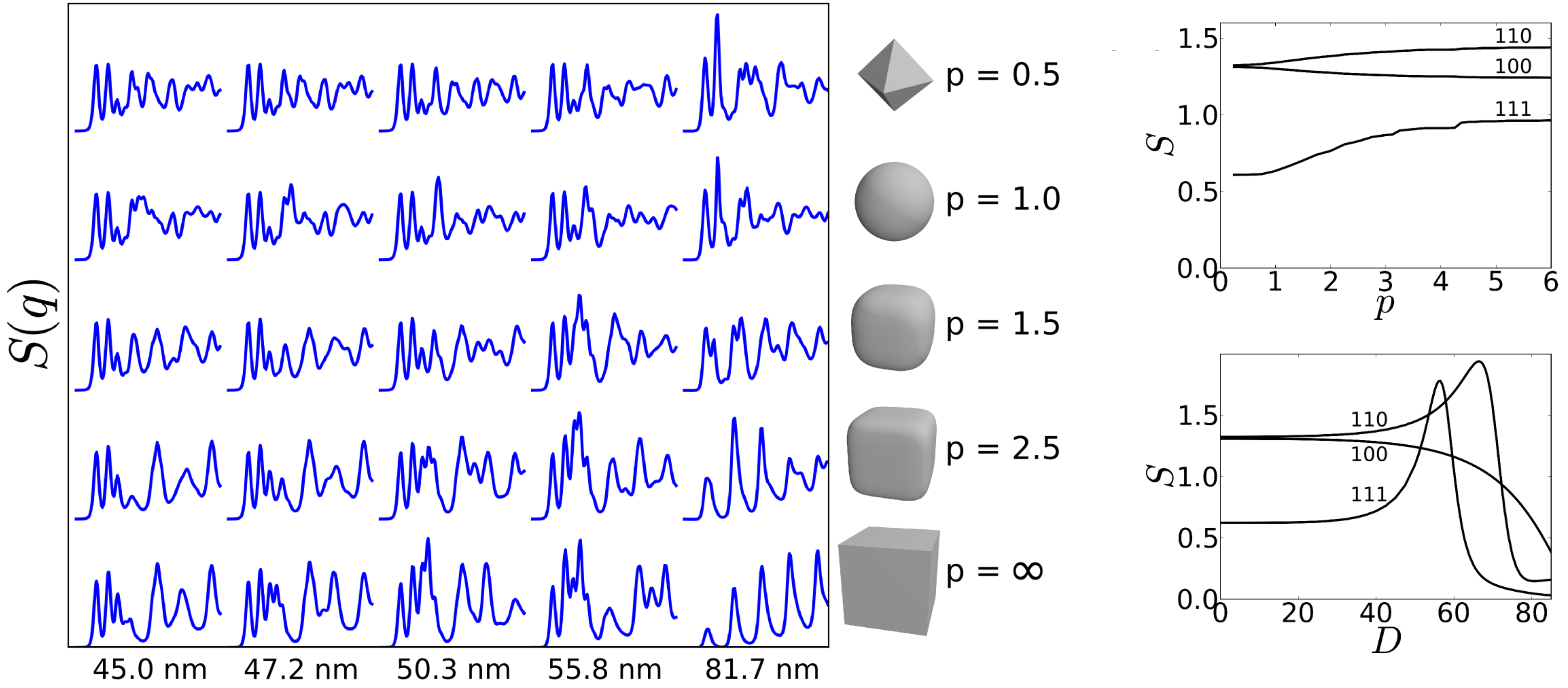




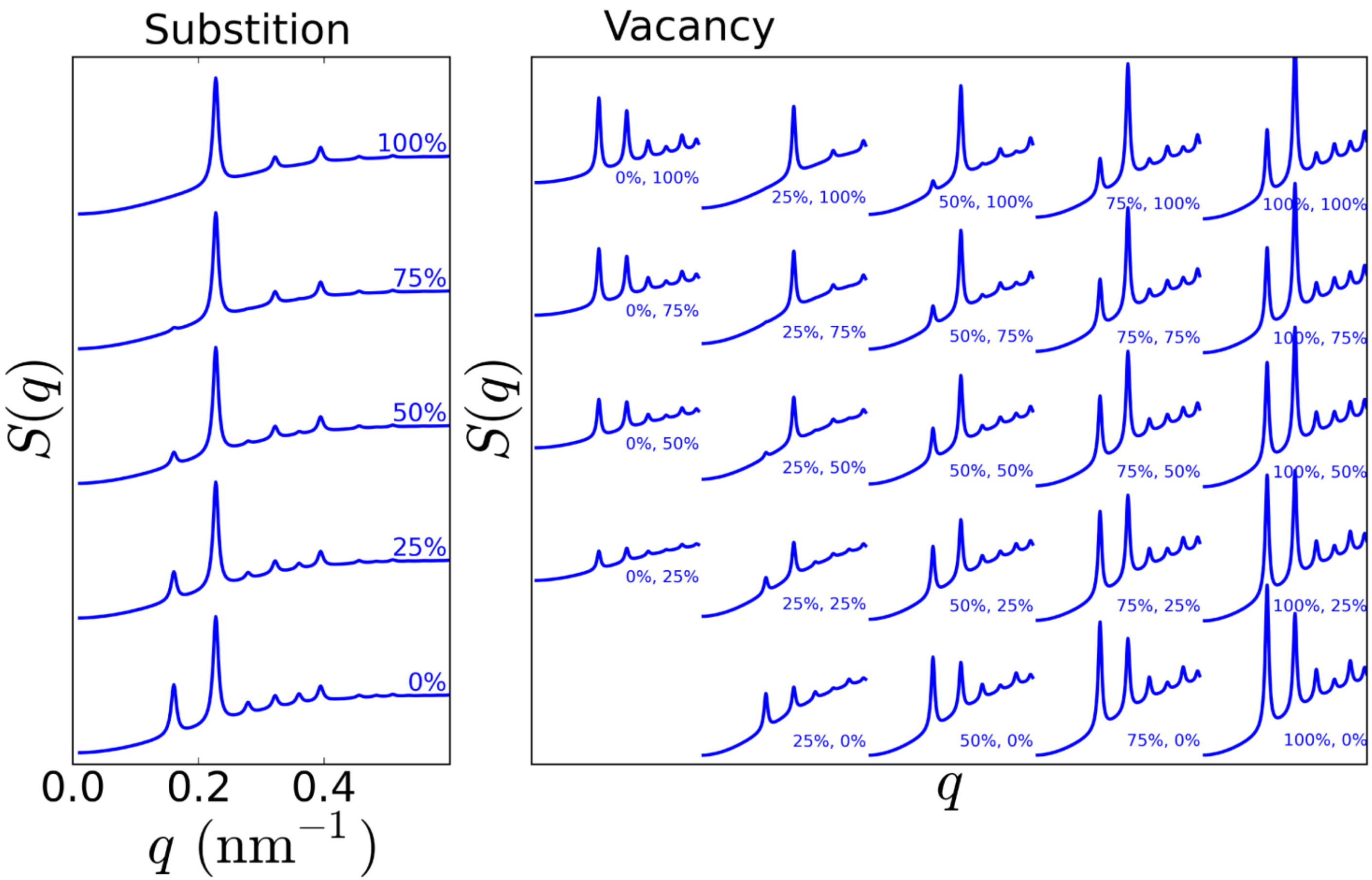
- Even in highly disordered systems, we can deduce structure…

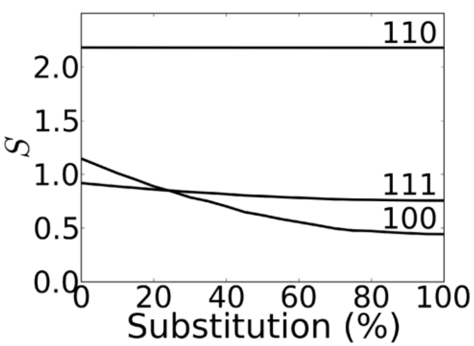
Particle Properties

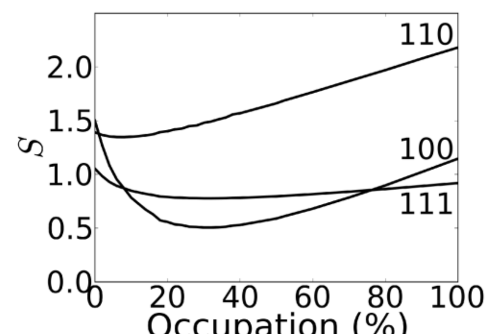
- Nano-object size and shape modulates peak heights
- Can substantially alter prediction



Lattice Site Defects

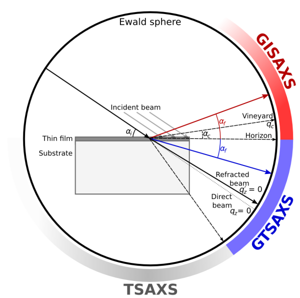




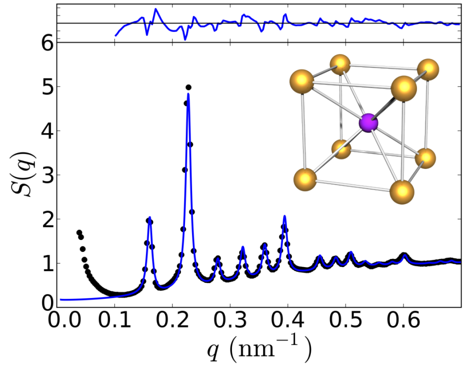


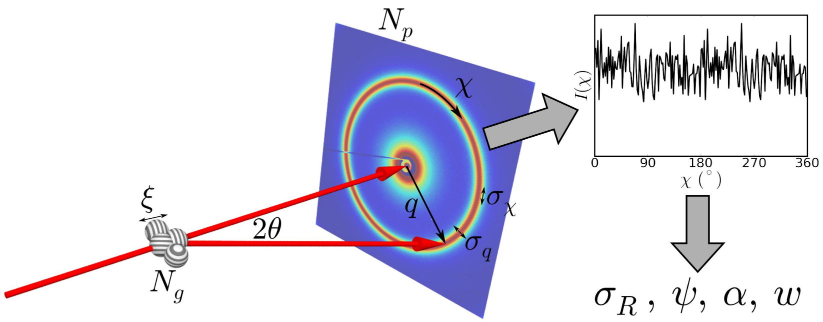
Conclusions

- X-ray scattering a powerful way to measure nanostructured thin films



- New techniques being used to analyze more complex systems:
  - Variance scattering for grain size & distribution
  - GTSAXS for complex nanostructures
  - New models for data fitting





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