GISAXS/GIWAXS Data Analysis: Thinking in Reciprocal-Space

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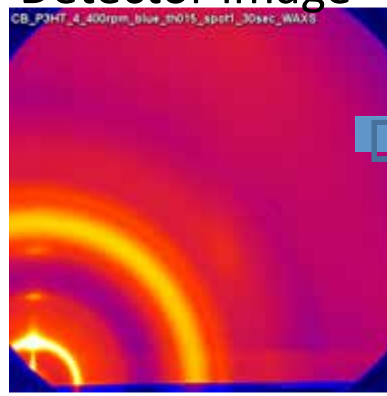
nsls
IR UV X

What to do with data?

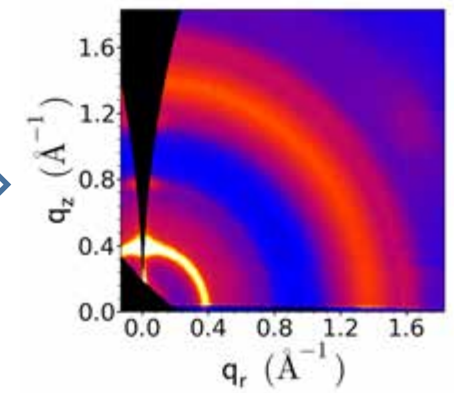
- Qualitative inspection
- Linecuts
- Peak indexing
- Modeling (comparison)
- Fitting

Workflow

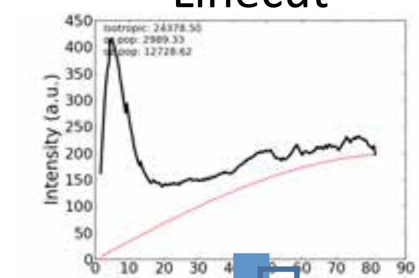
Detector image



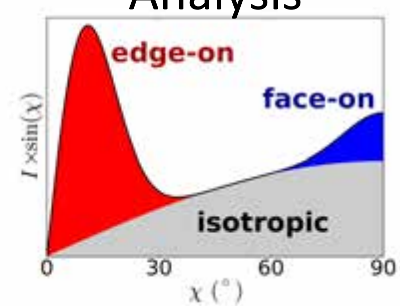
Calibrated 2D data



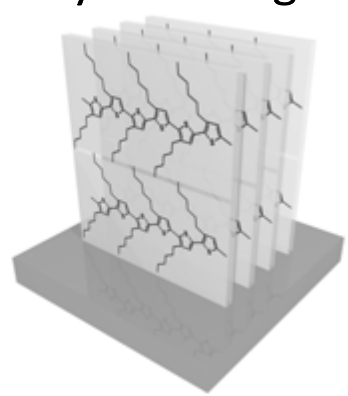
Linecut



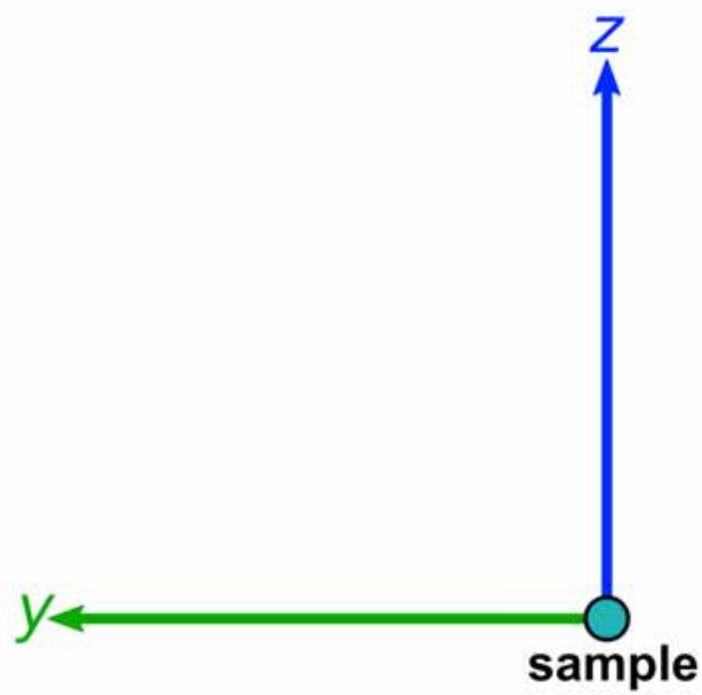
Analysis



Physical insight

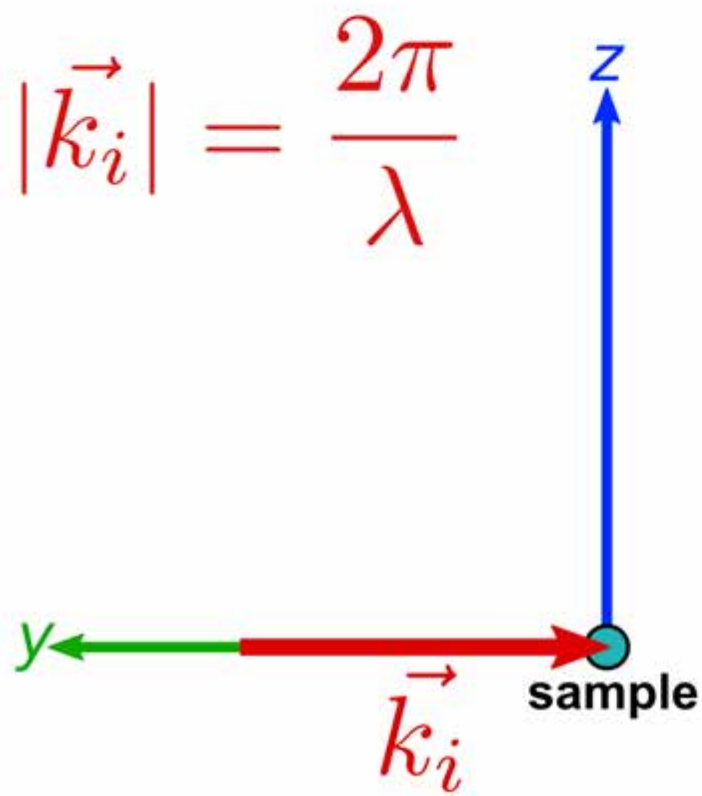


Scattering Geometry



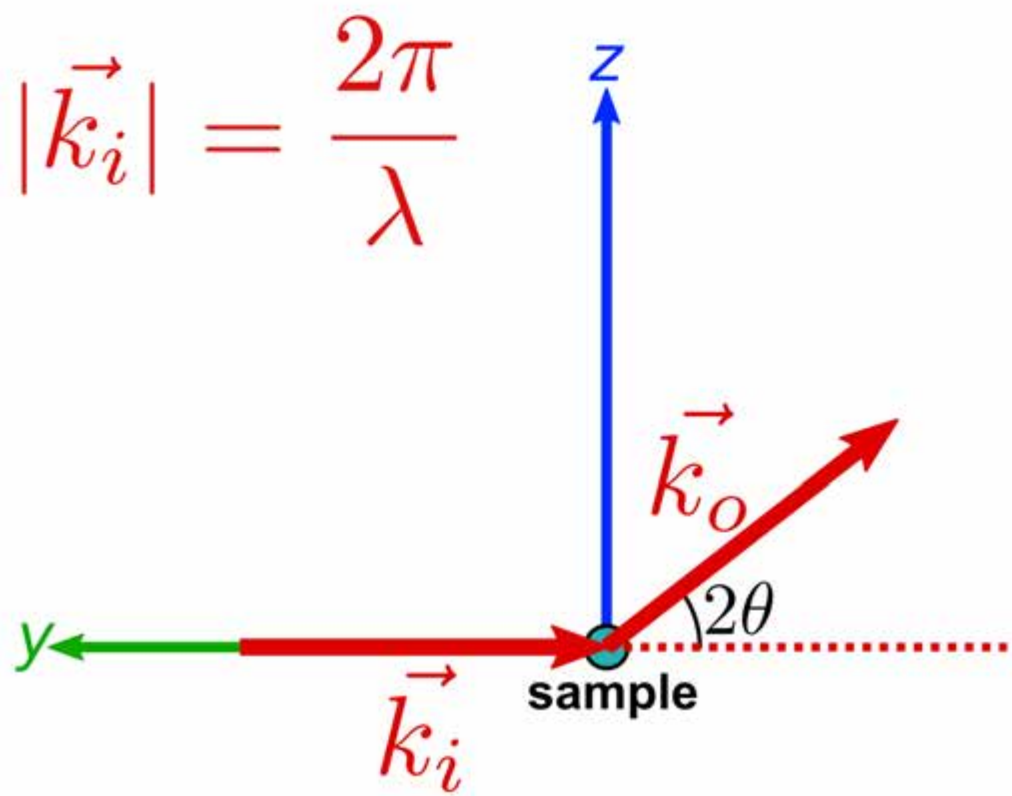
Scattering Geometry

- X-ray beam hits sample



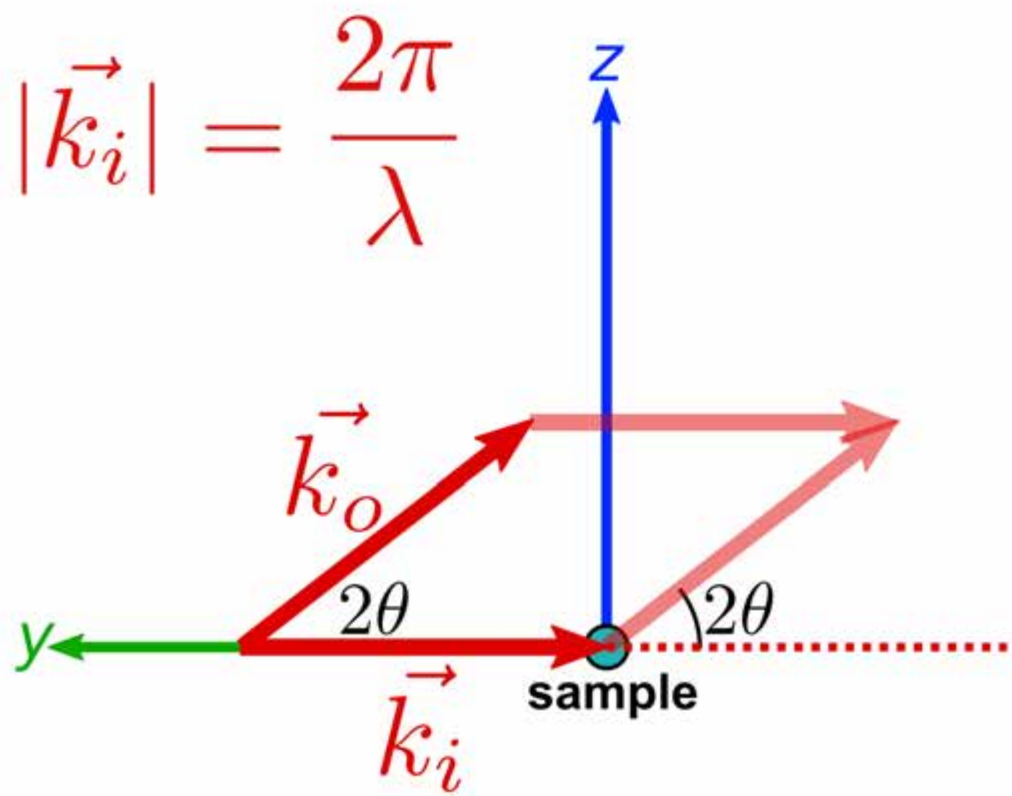
Scattering Geometry

- X-ray beam scatters at a certain angle



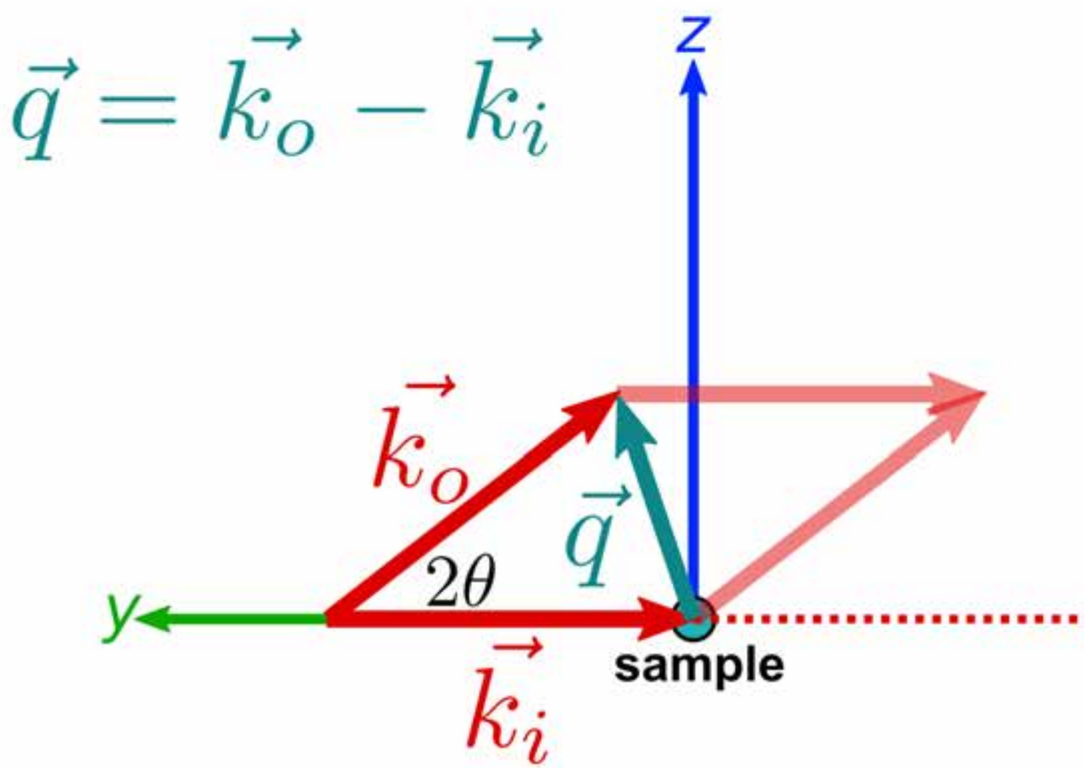
Scattering Geometry

- Consider the difference between the incident and scattered vectors



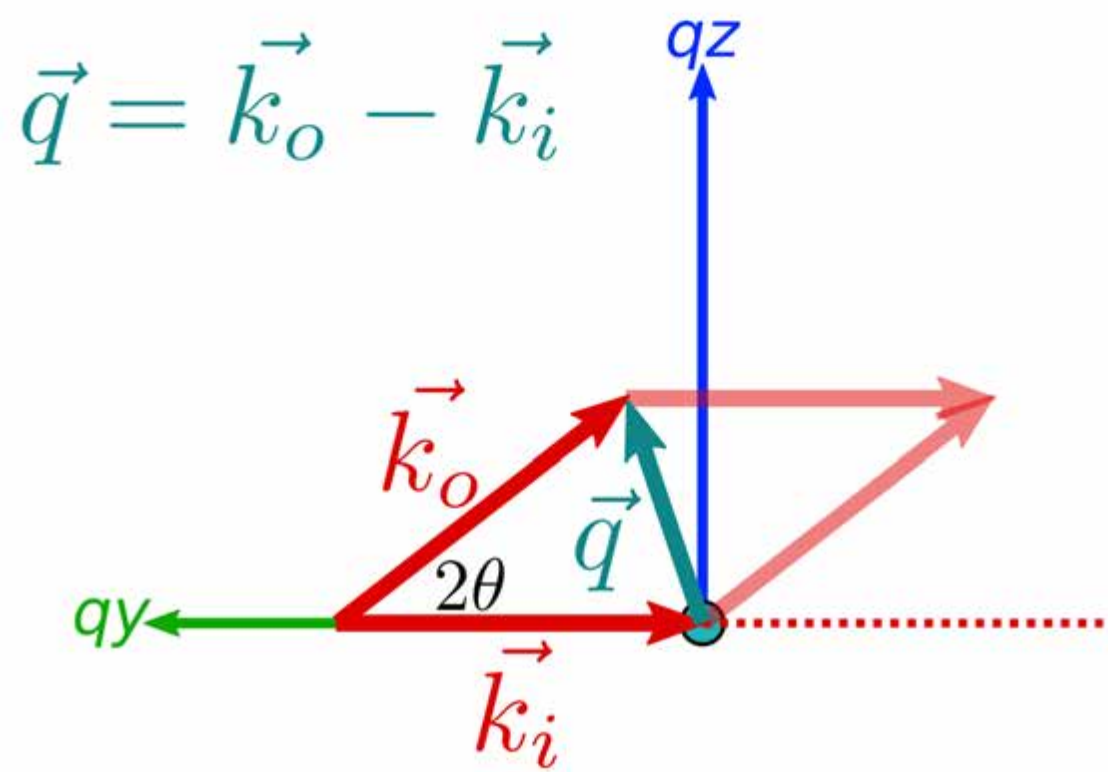
Scattering Geometry

- We define *q* to be the momentum transfer



Reciprocal-space

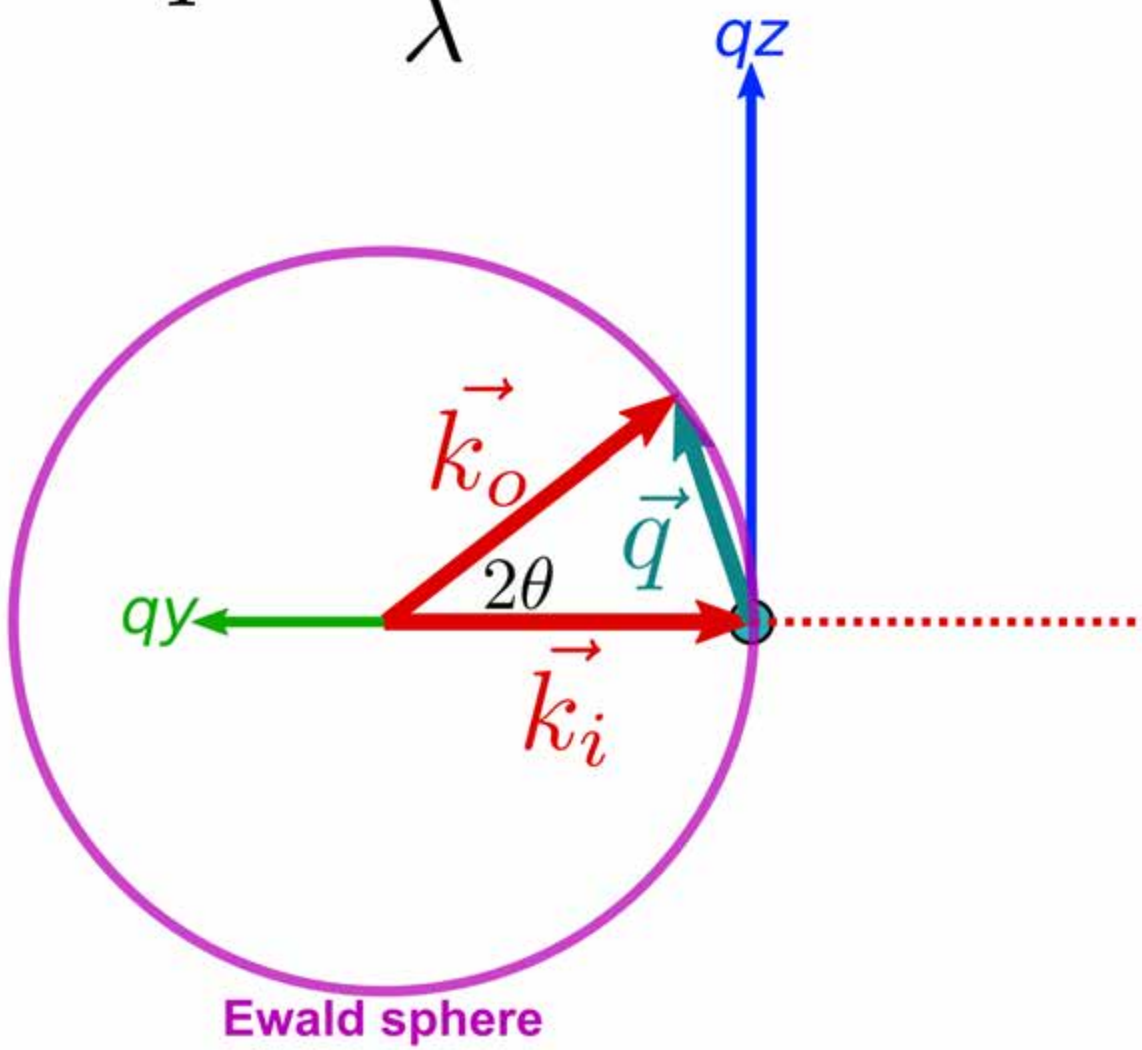
- q is a vector in **reciprocal-space** (k and q have units of 1/distance)



Reciprocal-space

- *q* is always on a sphere

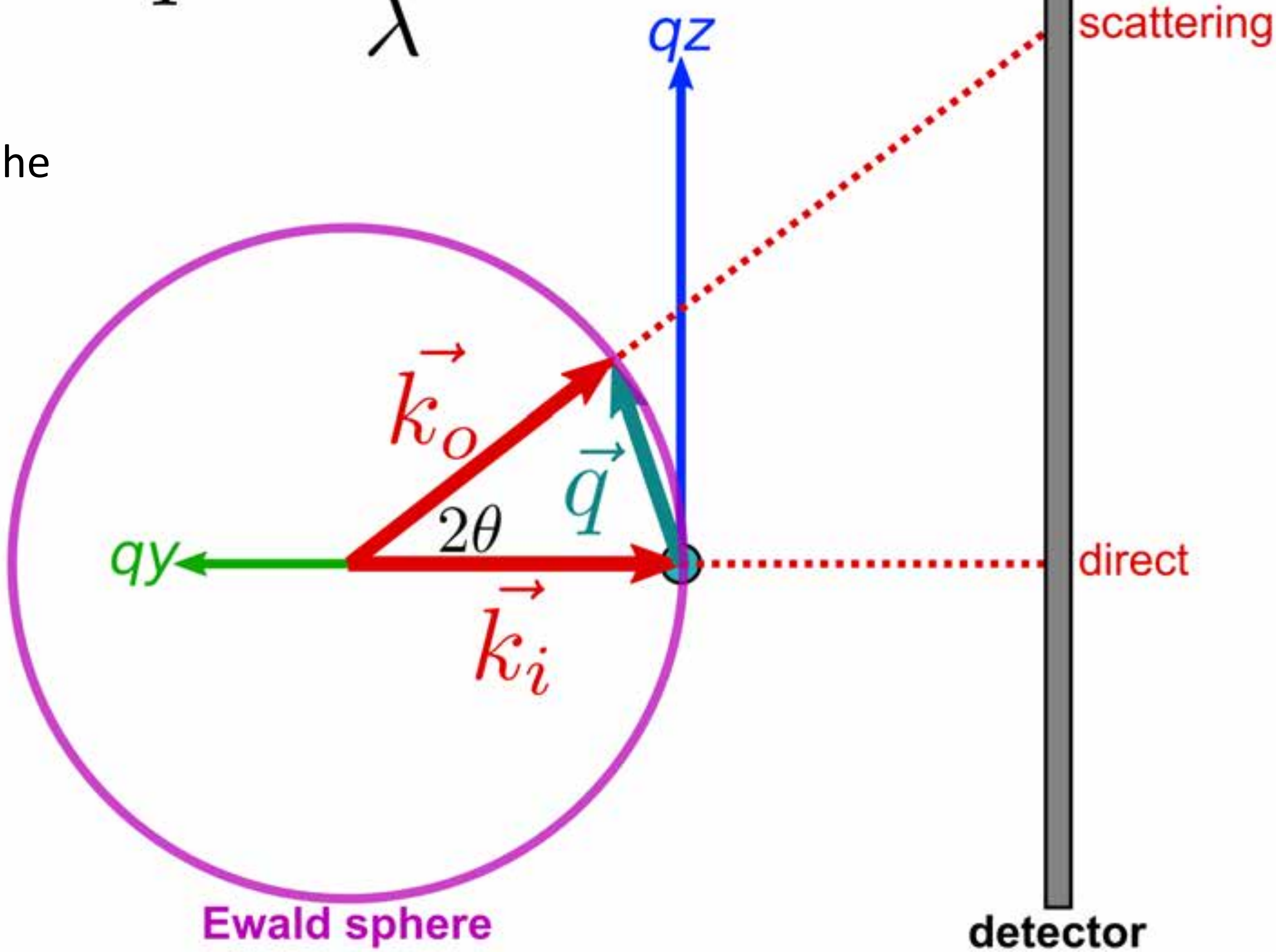
$$|\vec{q}| = q = \frac{4\pi}{\lambda} \sin\theta$$



Reciprocal-space

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

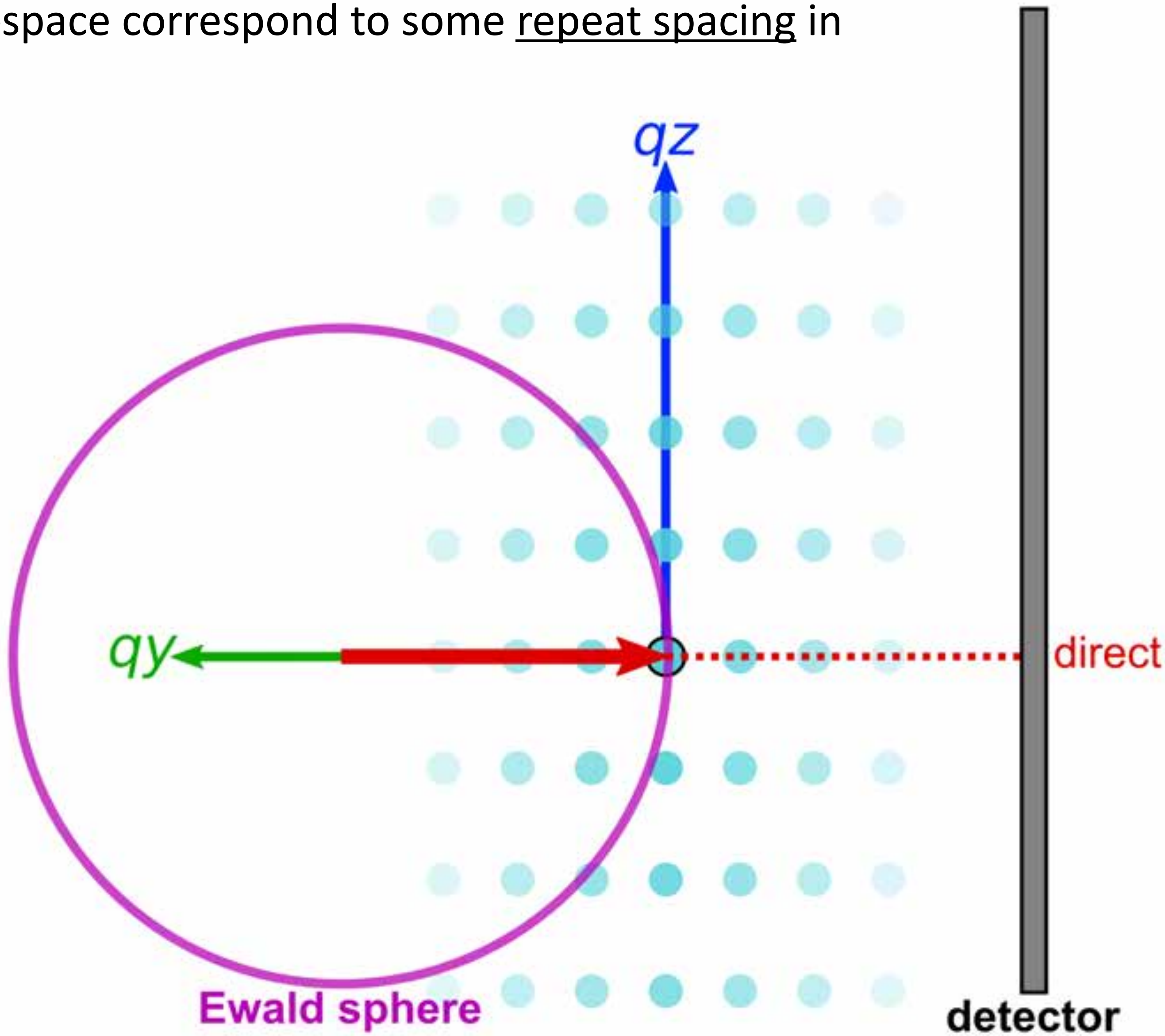
Detector records the intersection between the Ewald sphere and the reciprocal-space



For SAXS, it's almost a plane…

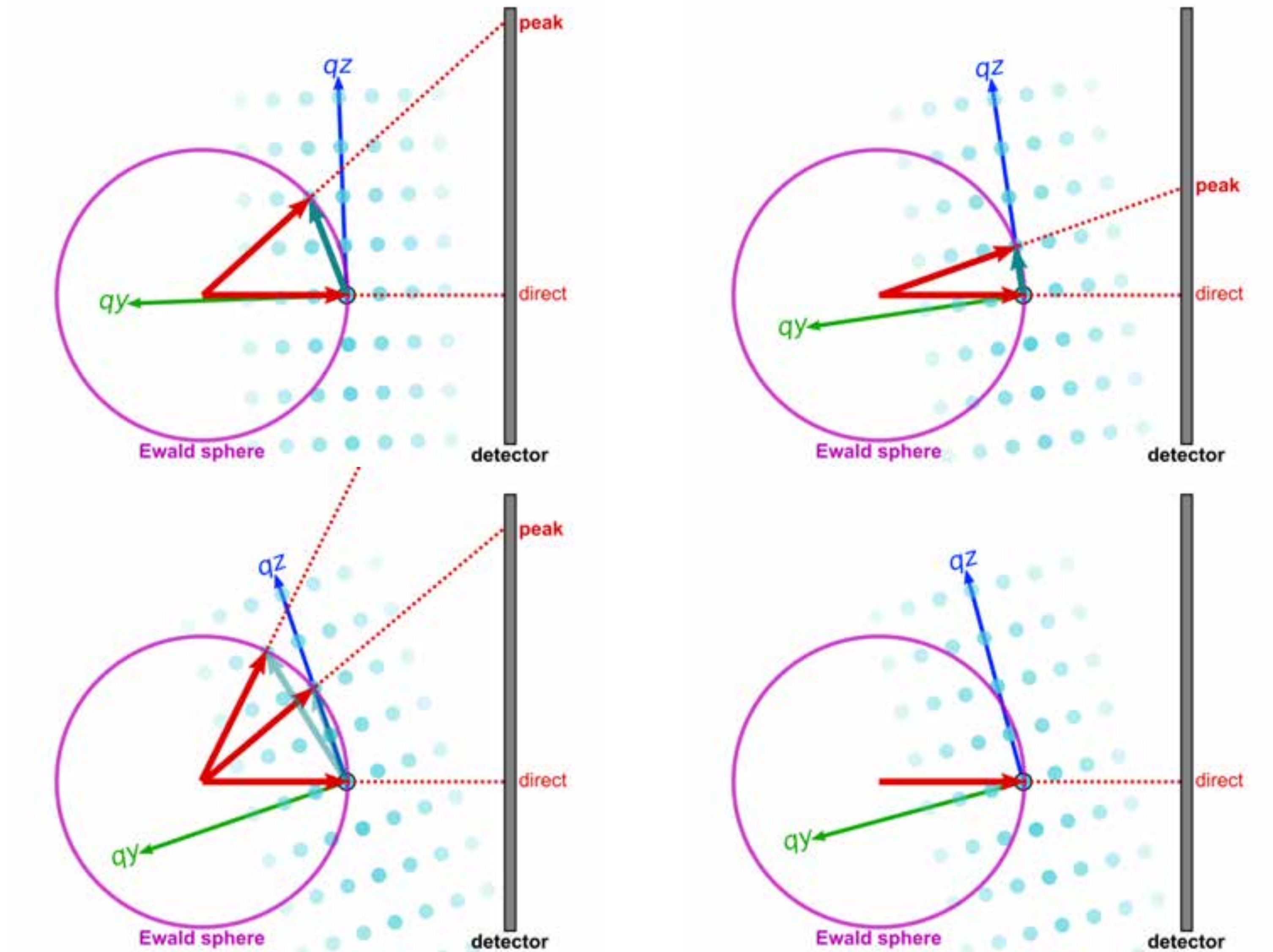
Reciprocal lattice

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



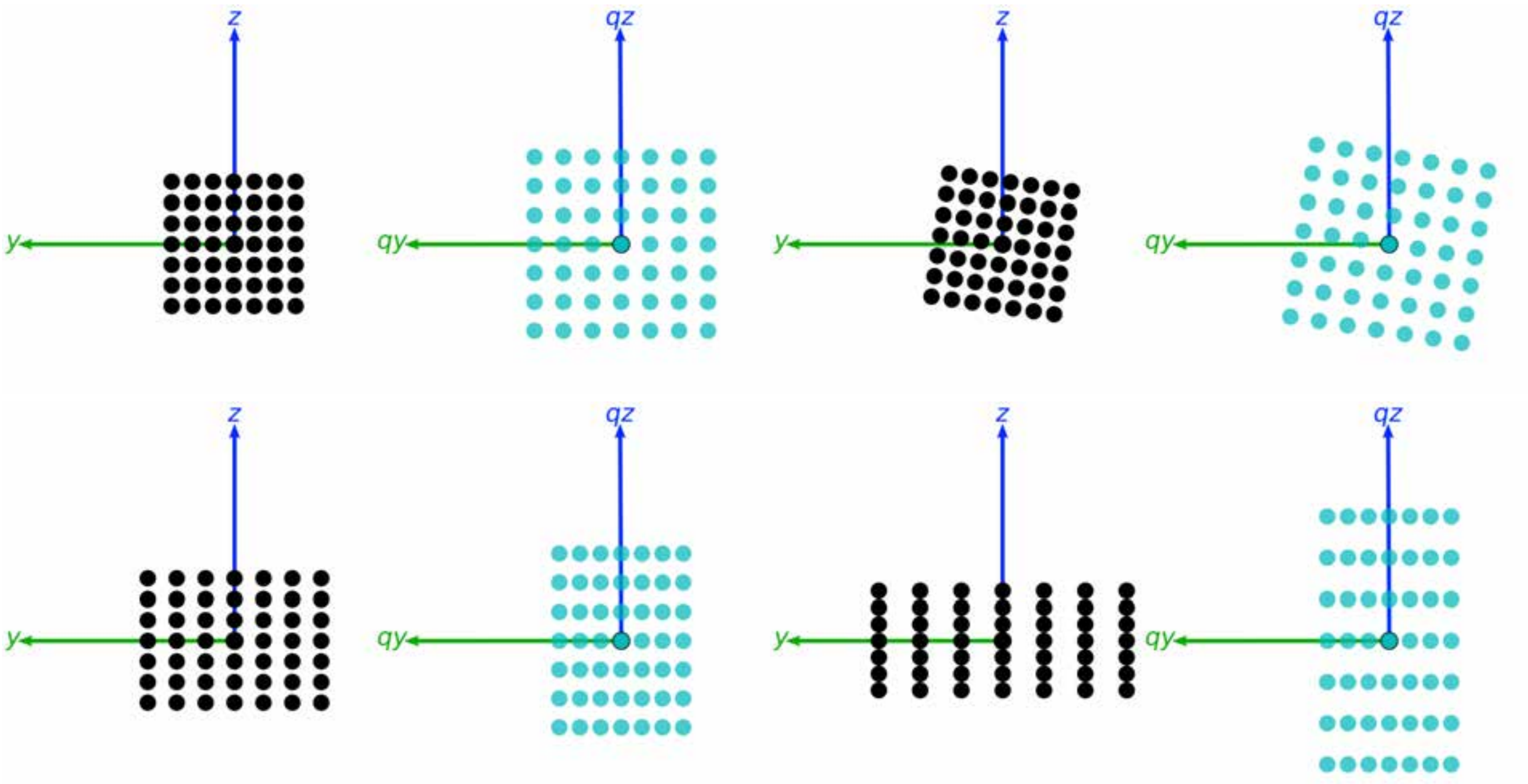
Reciprocal lattice

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



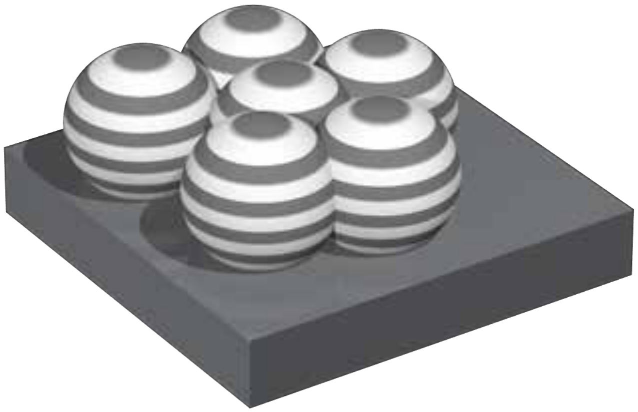
Reciprocal lattice examples

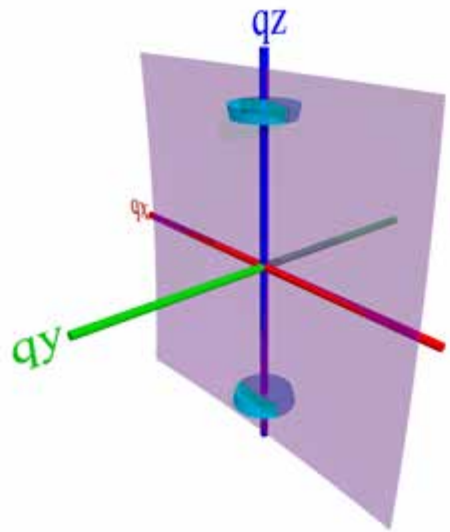
- Peaks come from repeating structures
- Distance is inverted: $d = 2\pi/q$

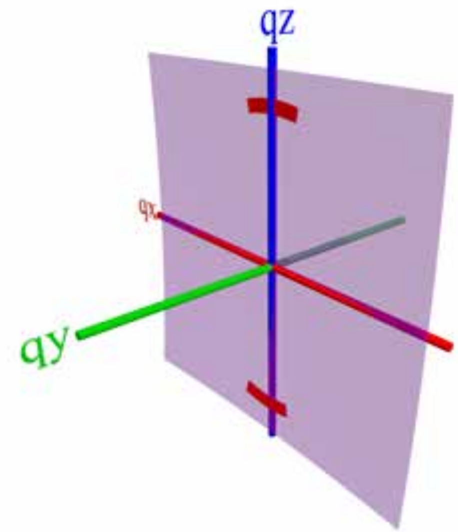


3D Reciprocal-space

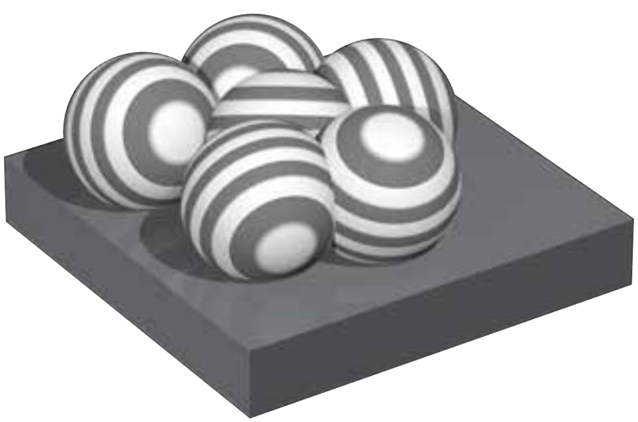
- Aligned

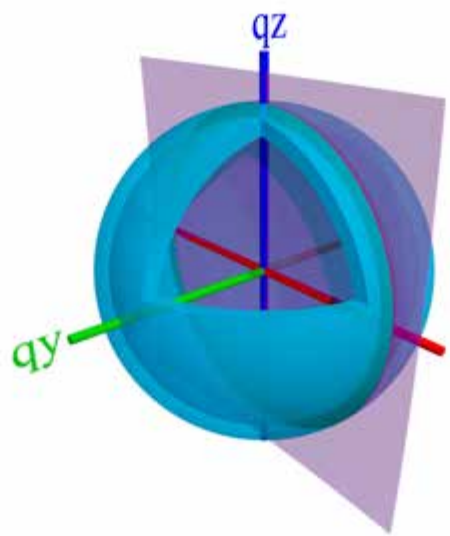


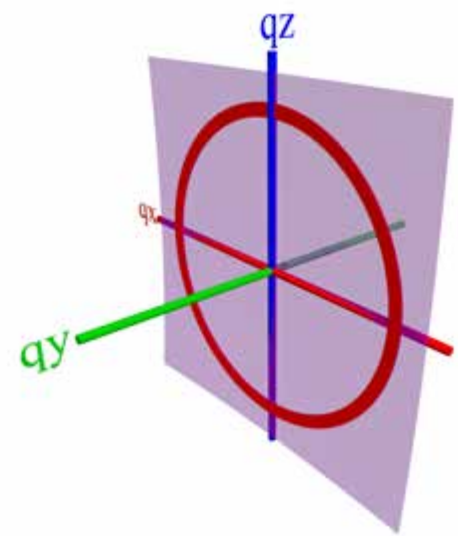




- Isotropic

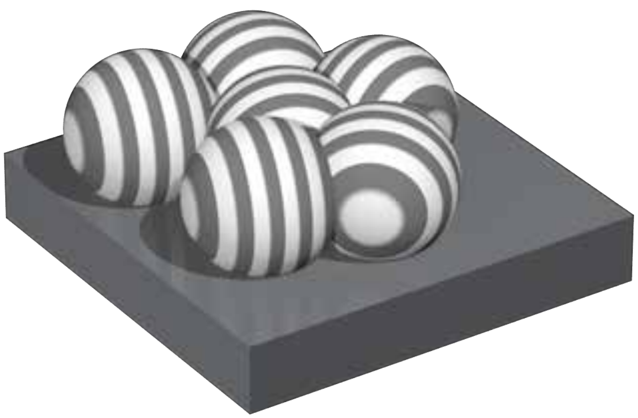


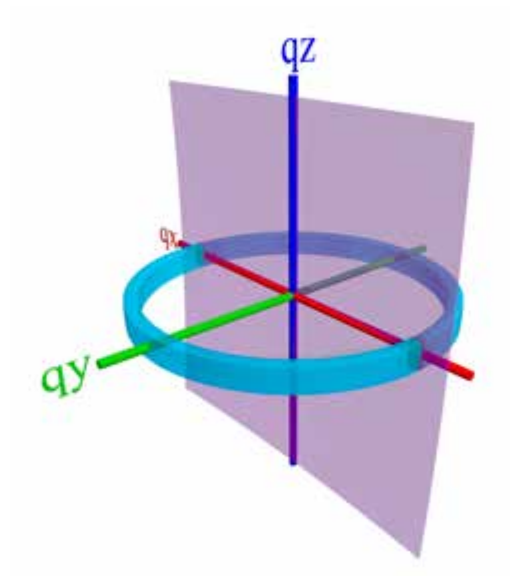


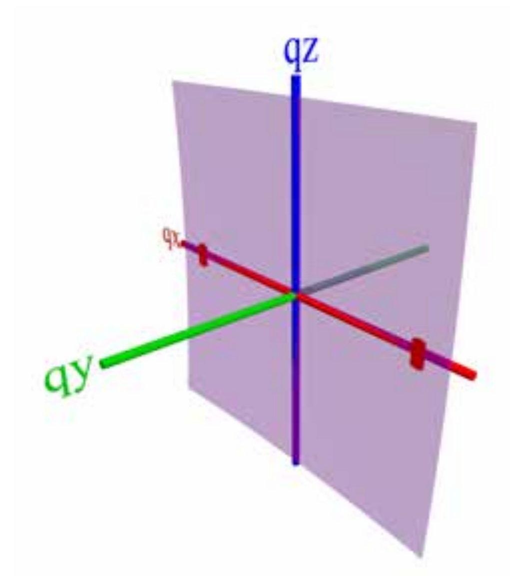


3D Reciprocal-space

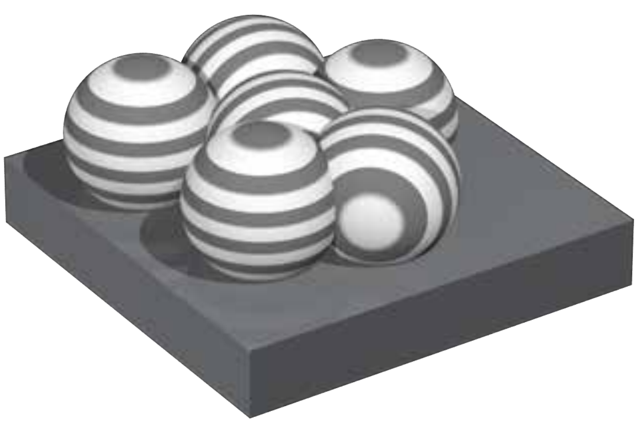
- In-plane powder

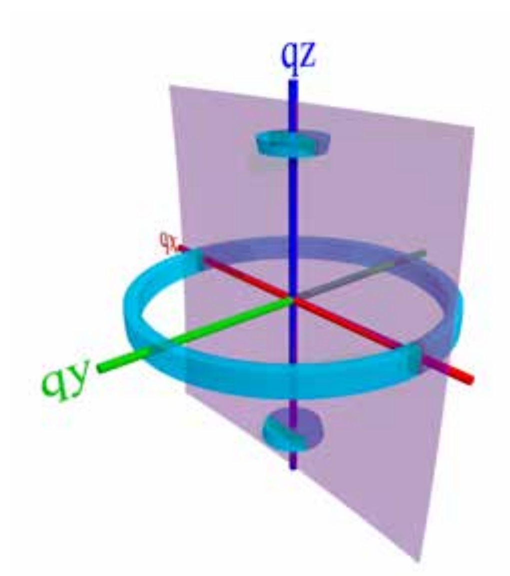


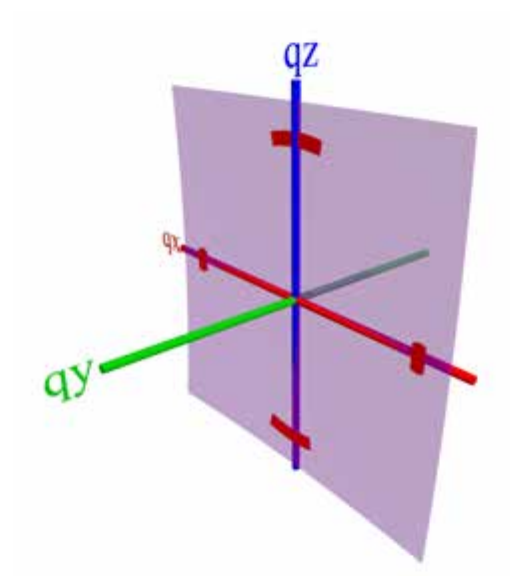




- Bimodal

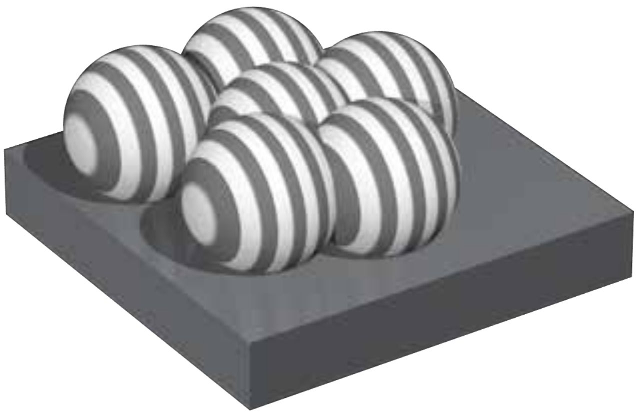






3D Reciprocal-space

- ?



Reciprocal lattice exercise

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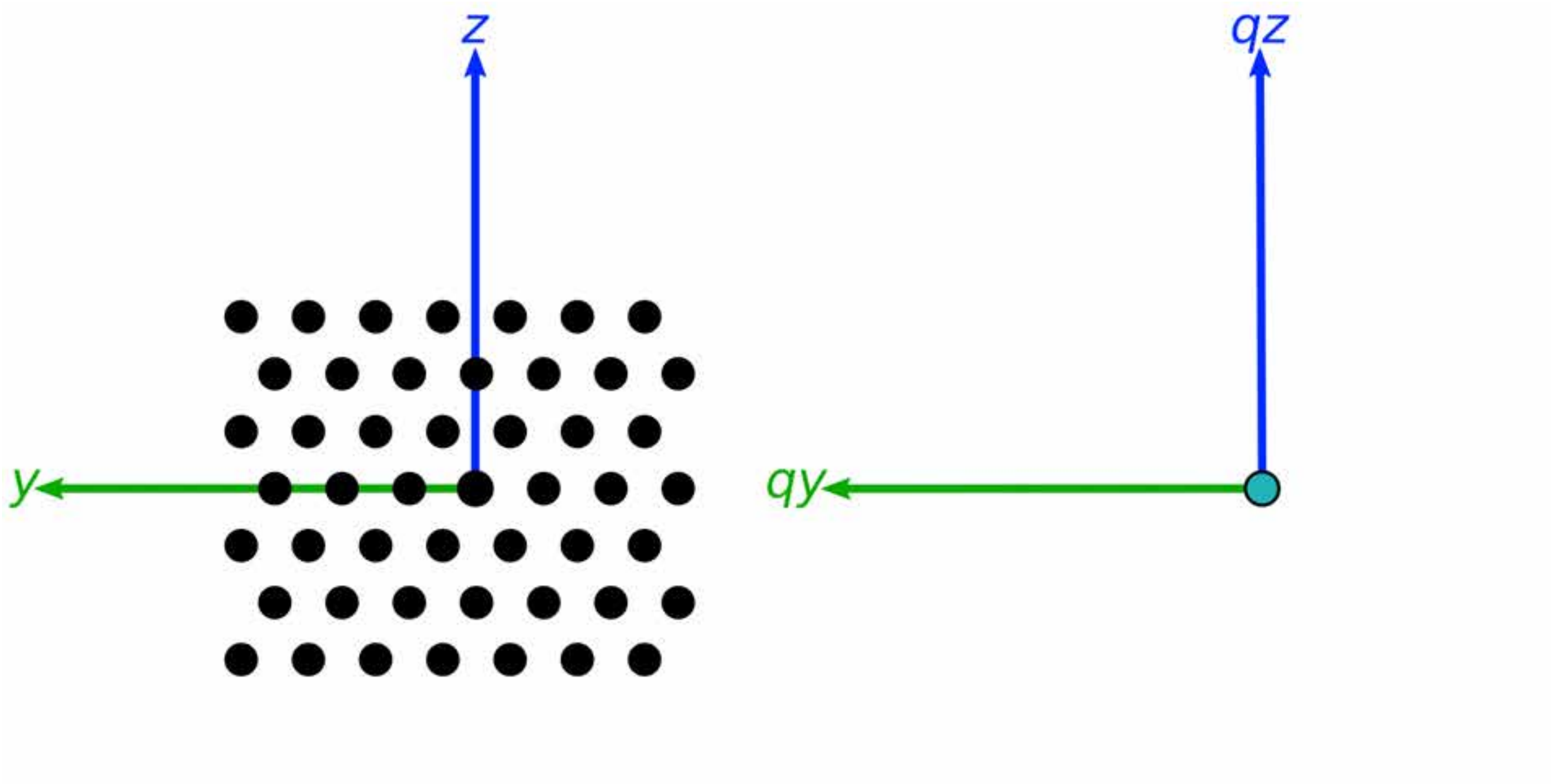
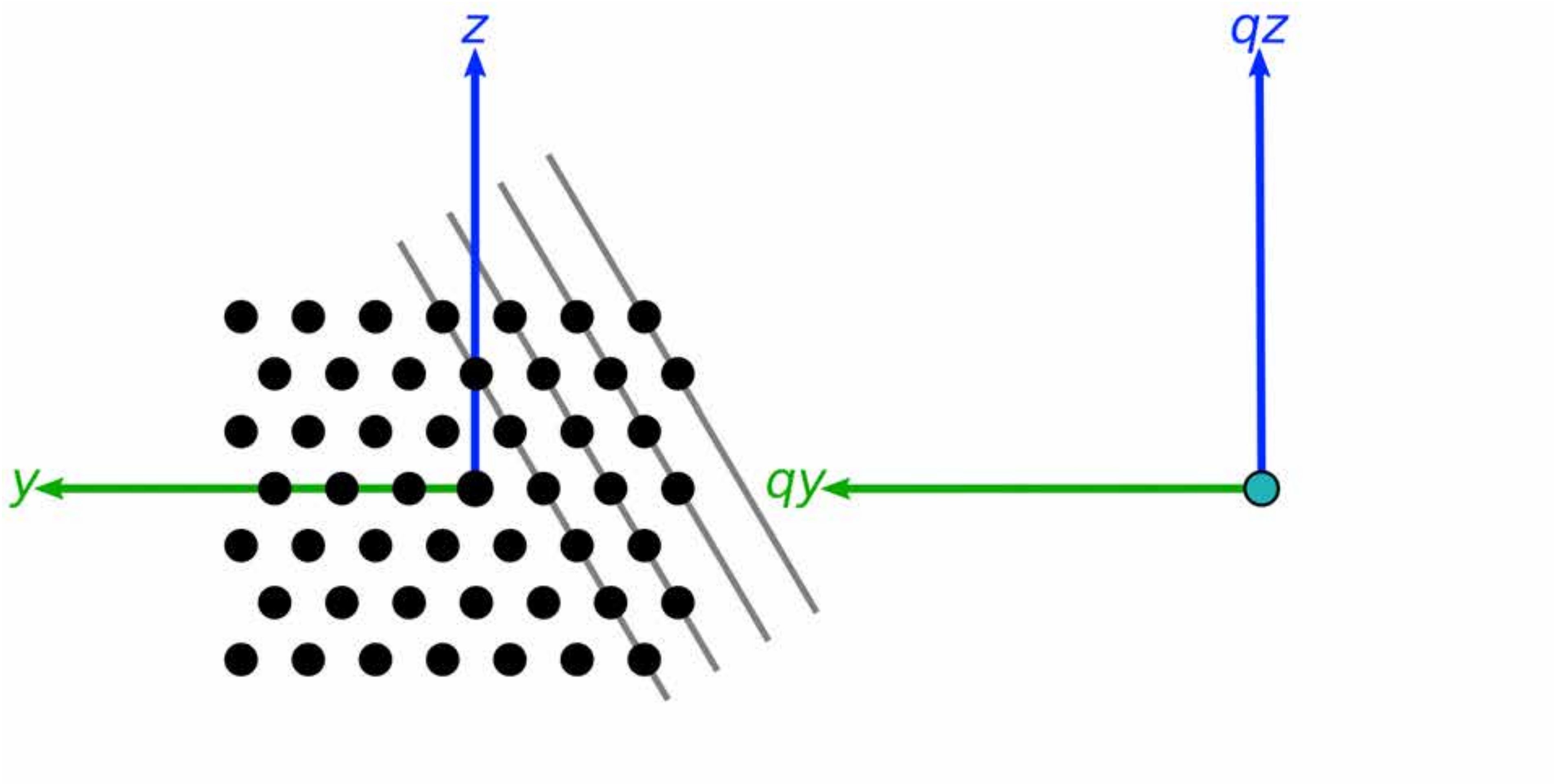
- What lattice will be generated?



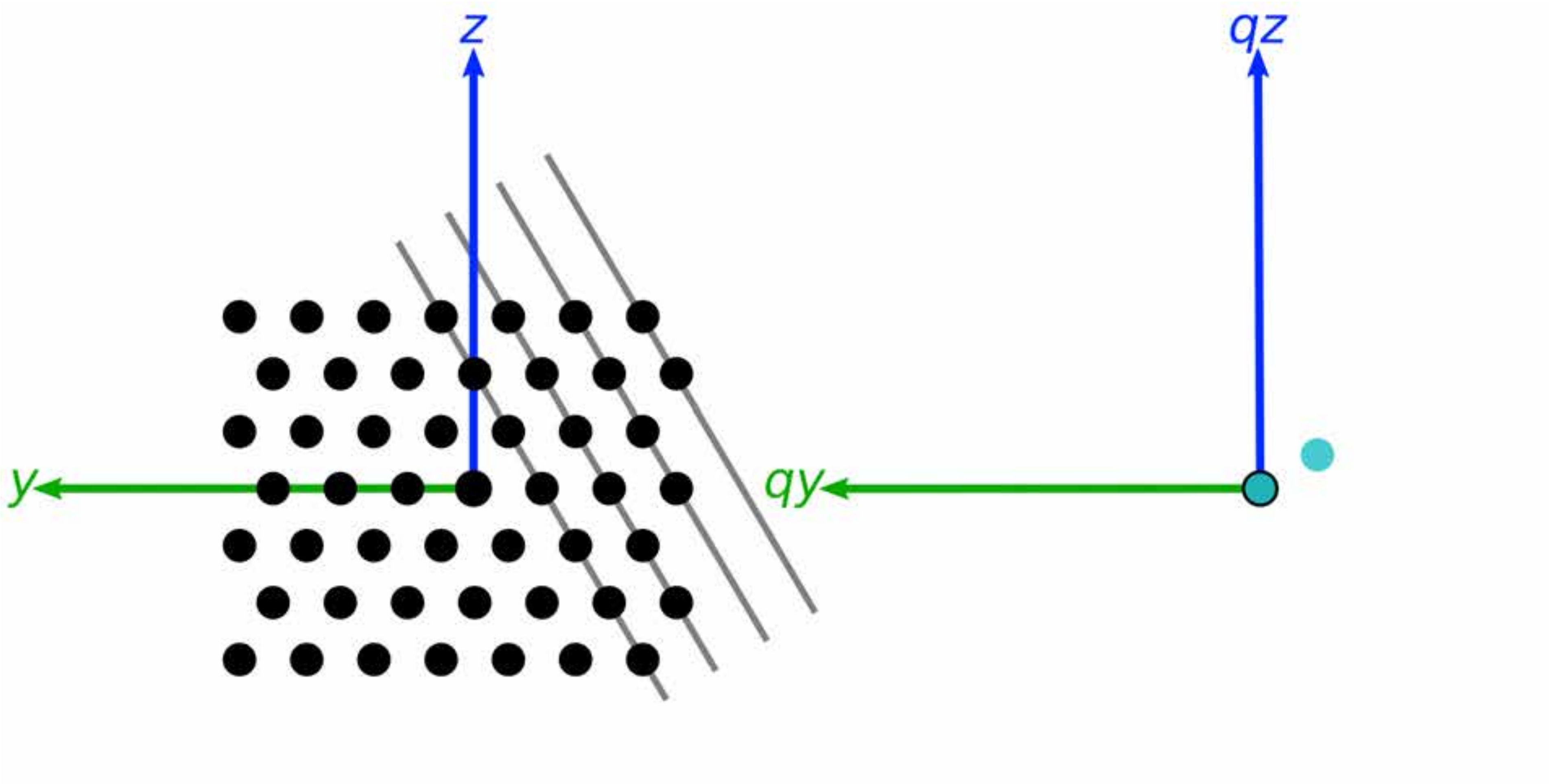
Reciprocal lattice exercise

- Identify realspace planes



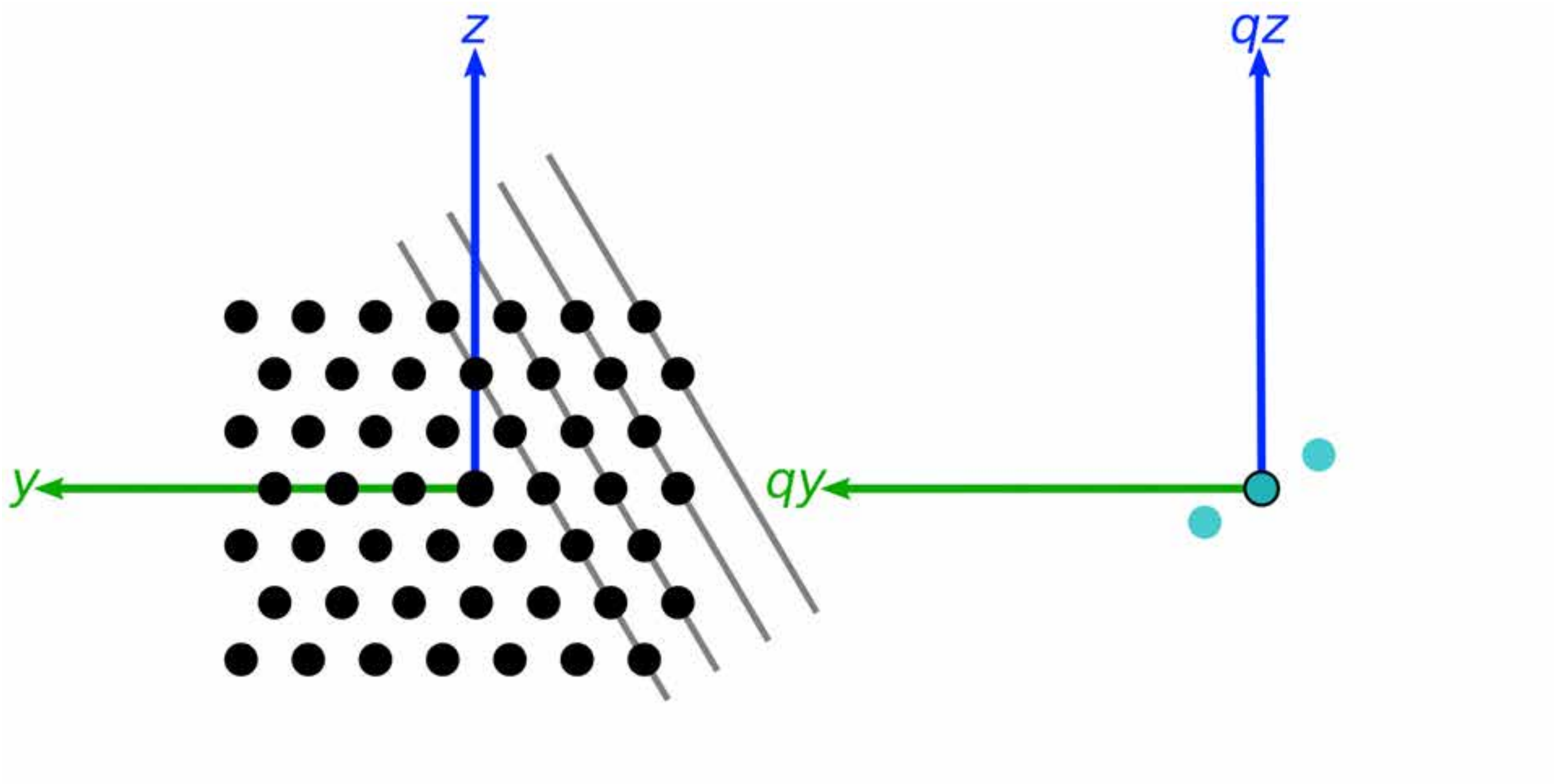
Reciprocal lattice exercise

- This repeating structure yields a peak normal to the planes



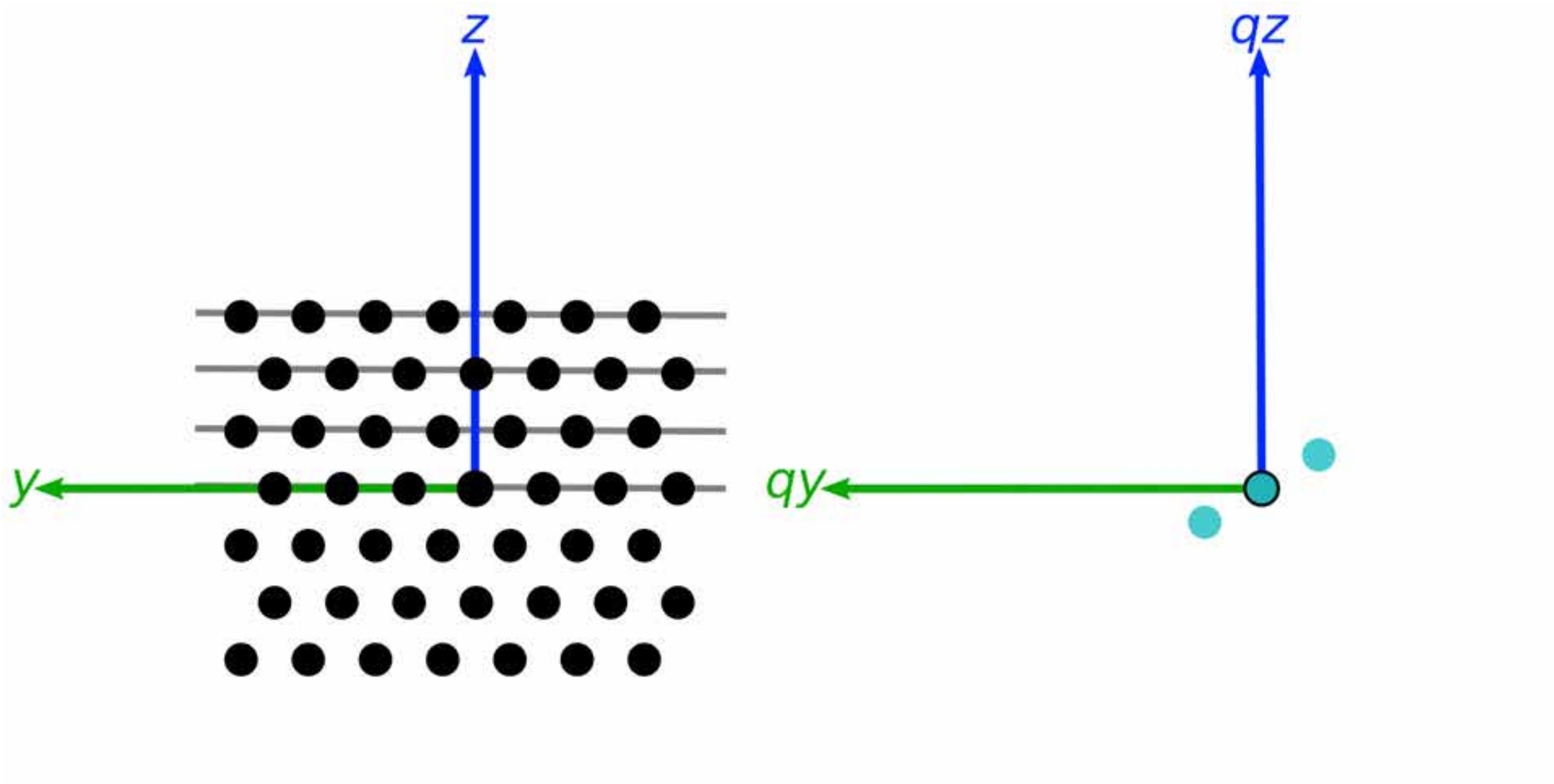
Reciprocal lattice exercise

- Reciprocal-space is centro-symmetric



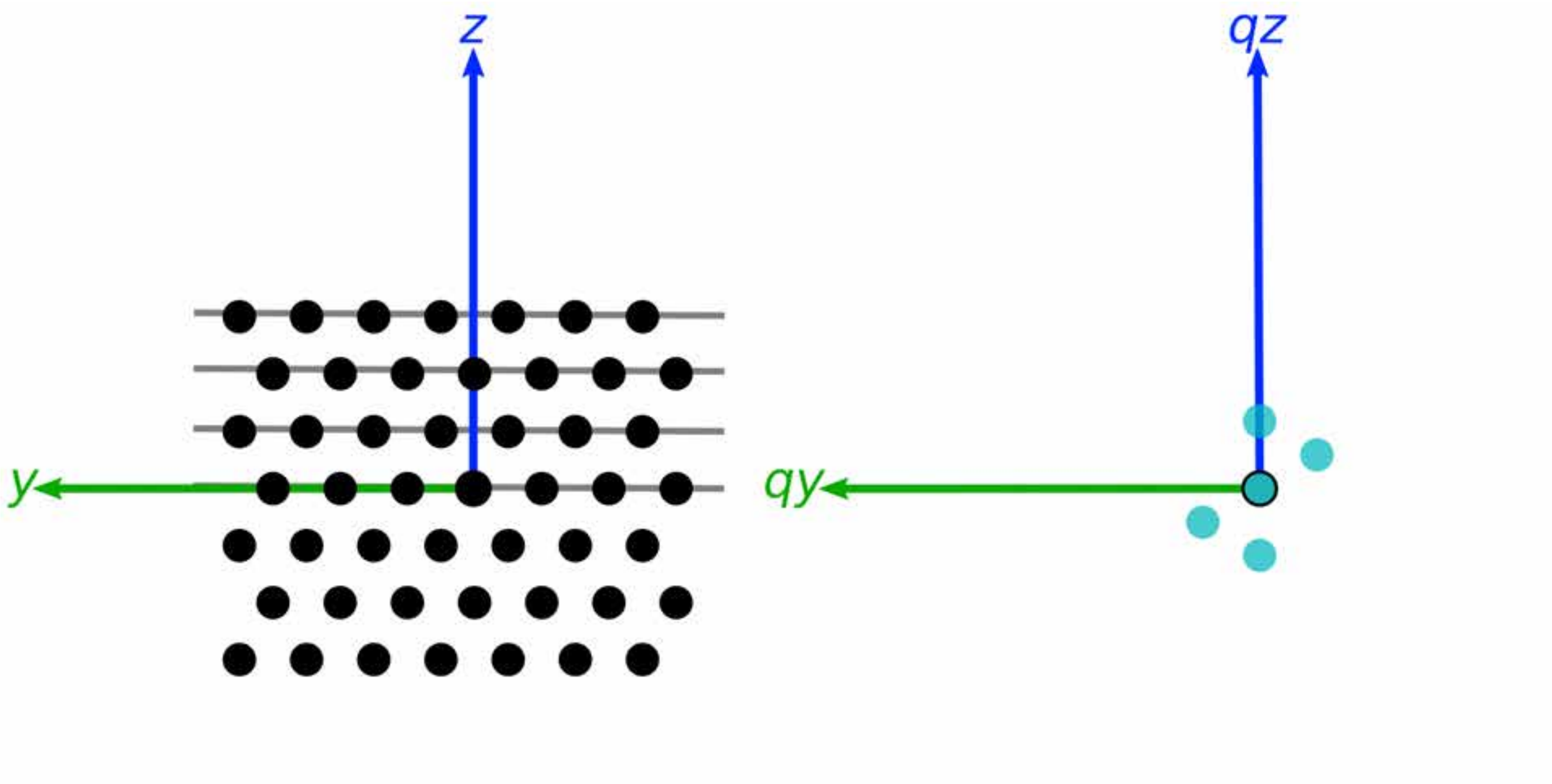
Reciprocal lattice exercise

- Another set of planes…



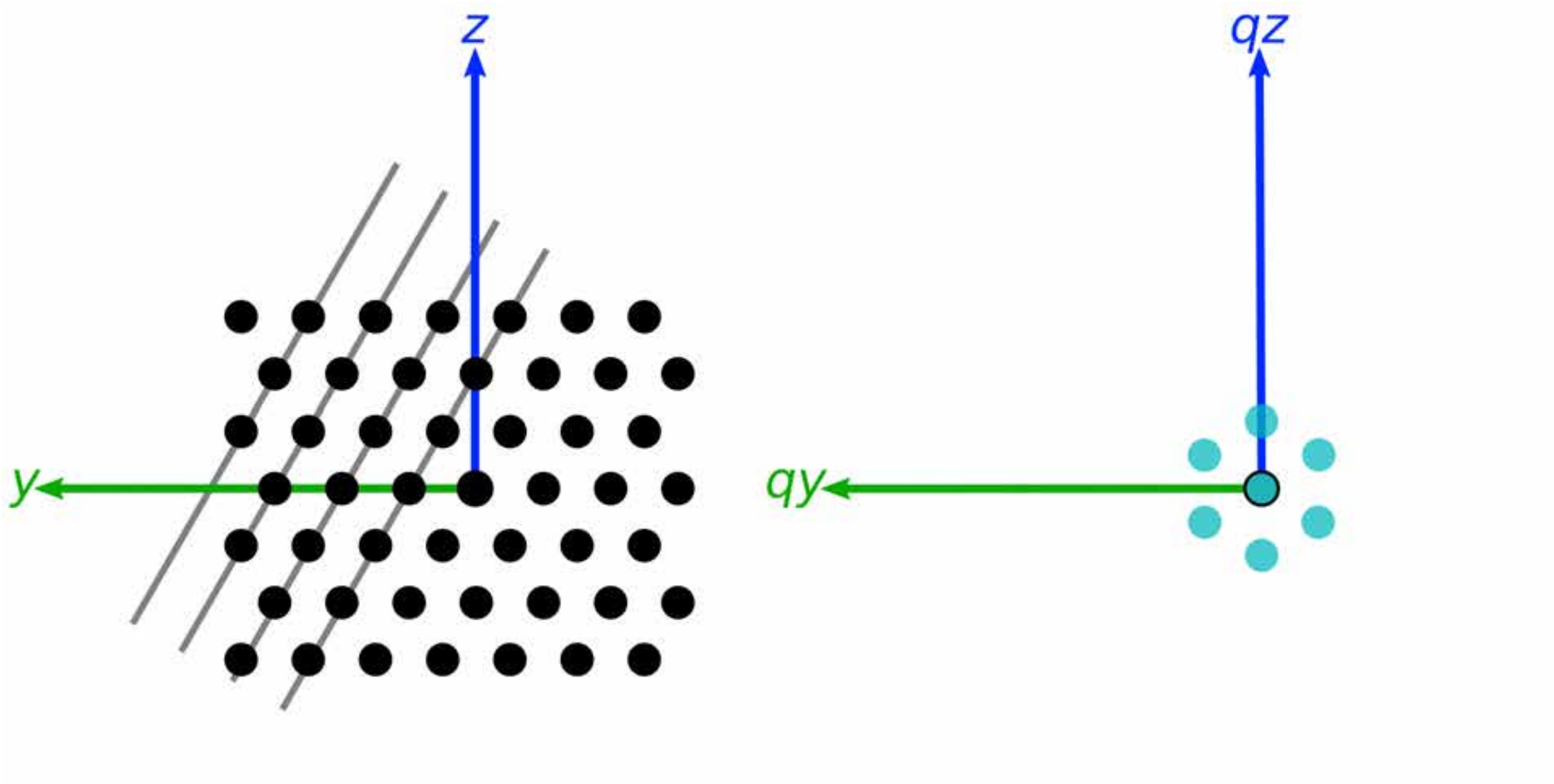
Reciprocal lattice exercise

- Another set of planes…
- … another set of peaks.



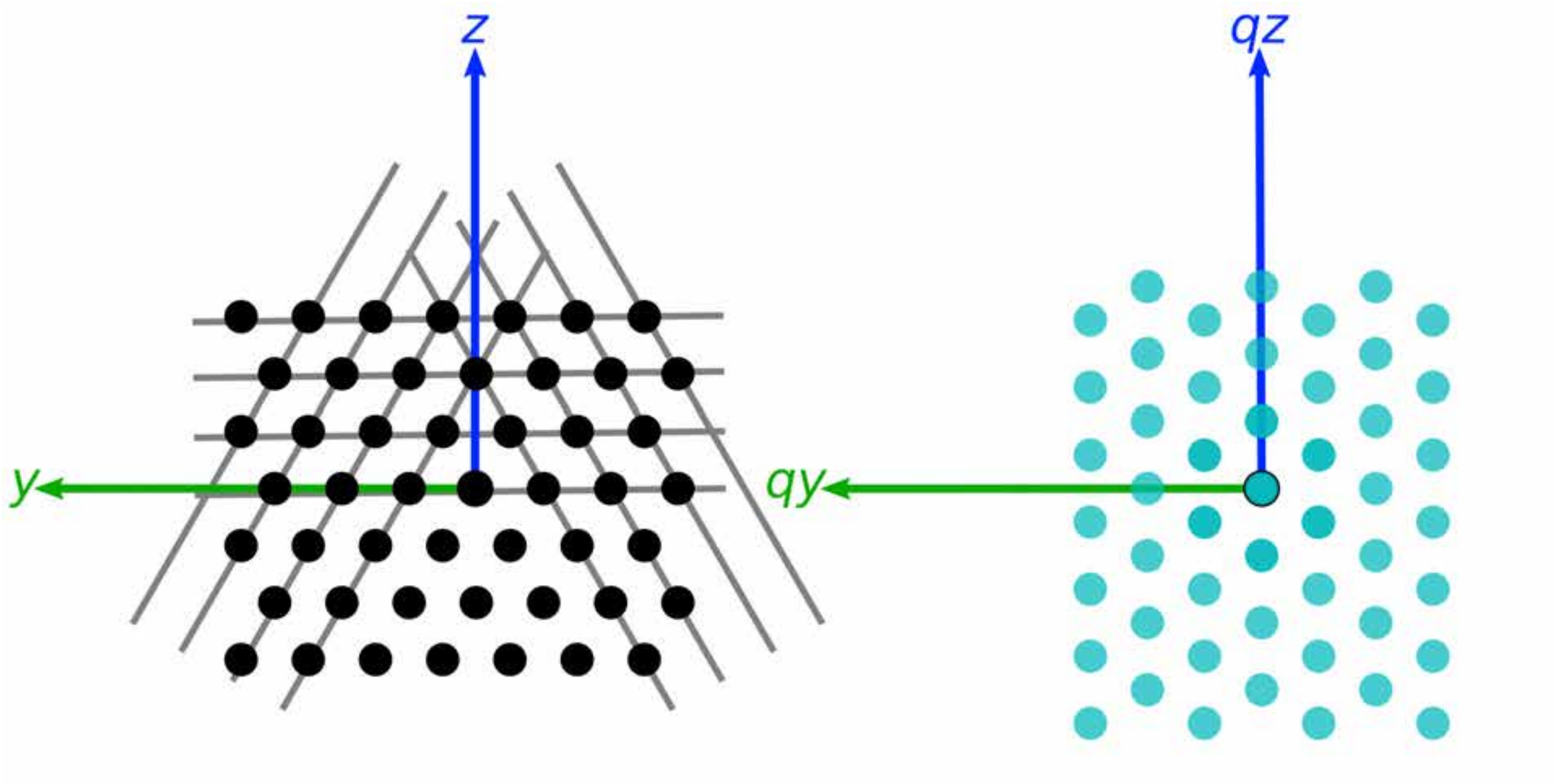
Reciprocal lattice exercise

- 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 gets higher-order peaks
- We've neglected peak intensities and shape, which encode all the details of the structure (finite size → peak width, electron density distribution → peak intensities, disorder → peak falloff, …)



GISAXS

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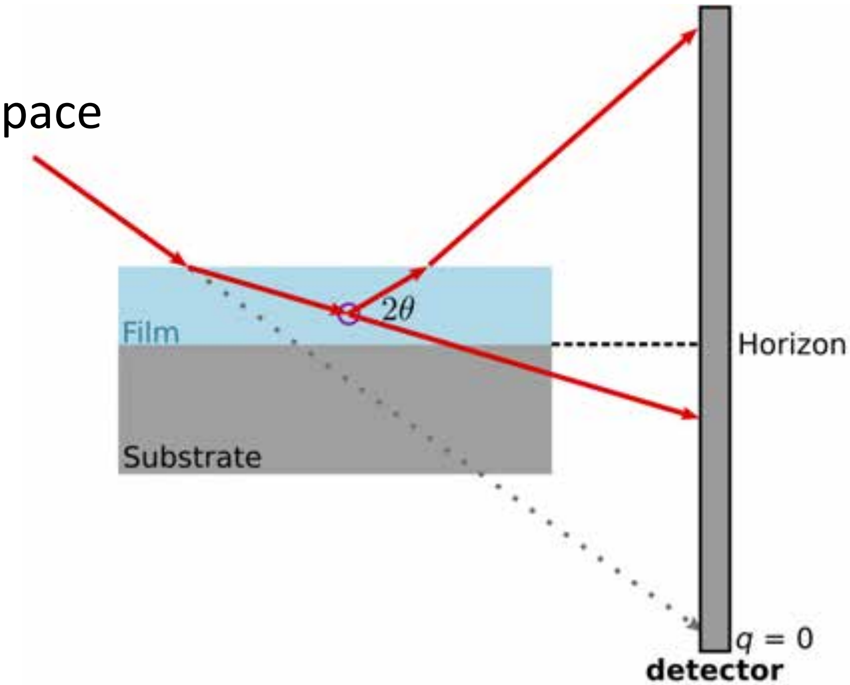
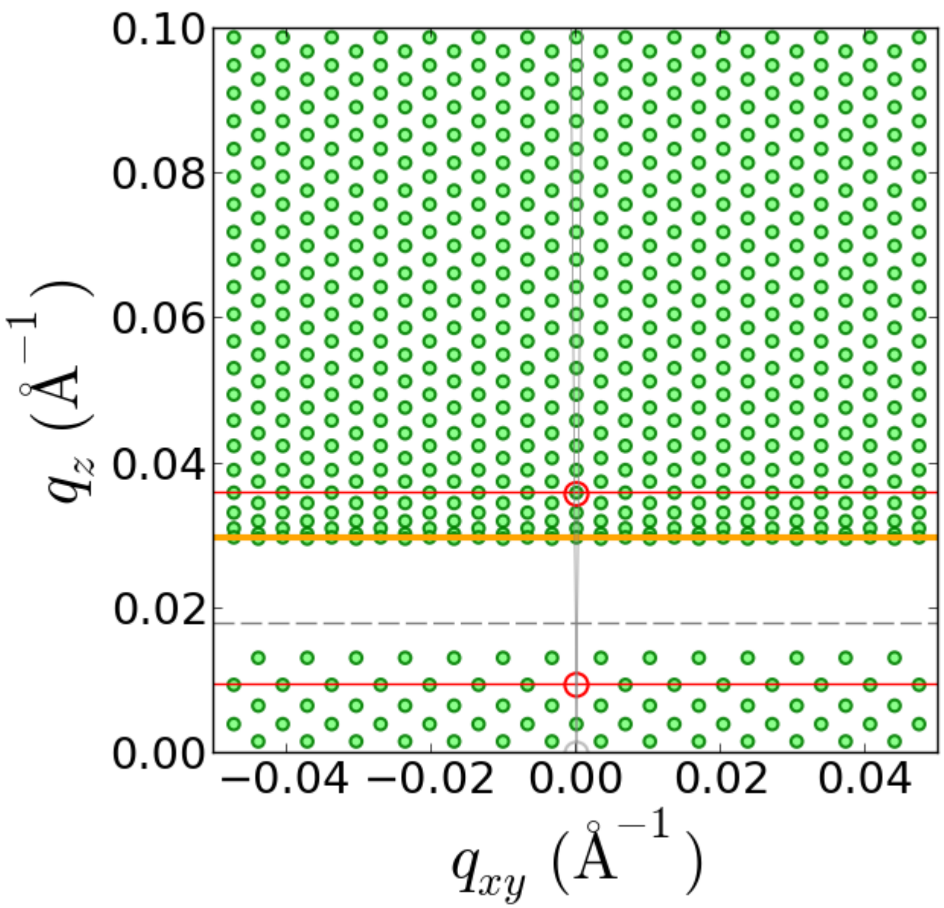
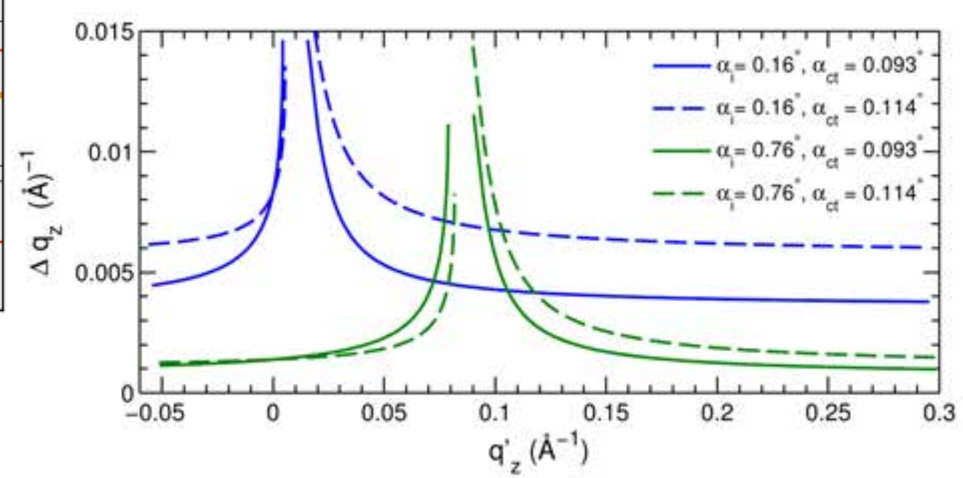
- GISAXS makes this more complicated:
  - Refraction shifts and distorts reciprocal-space







GISAXS

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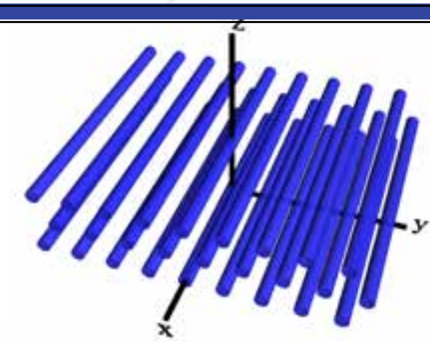
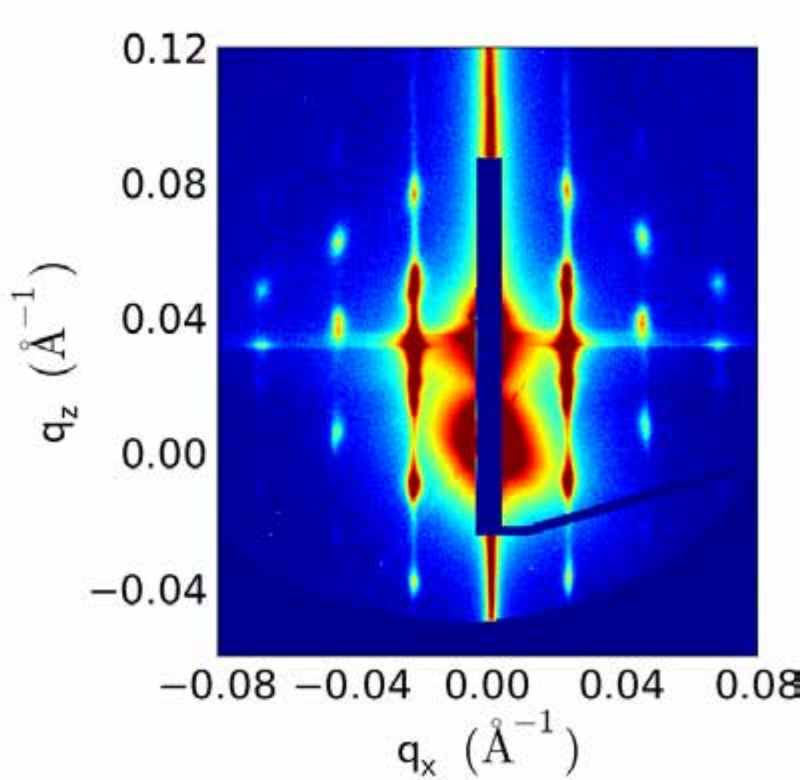
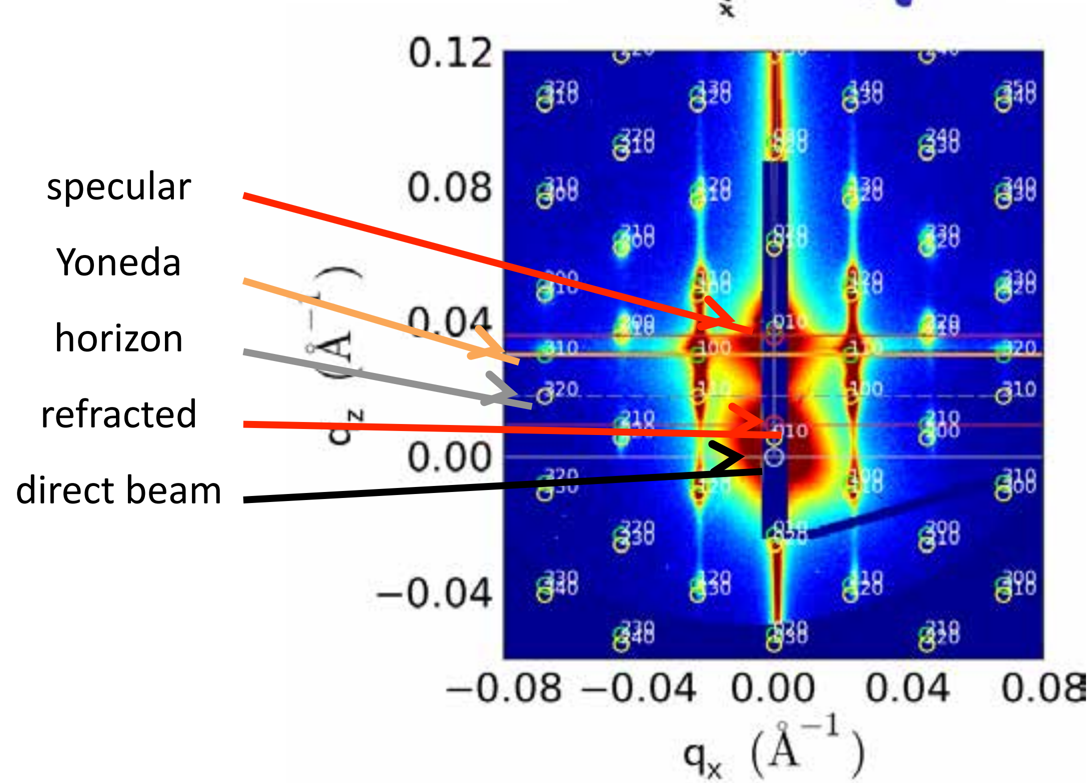
- GISAXS makes this more complicated:
    - Refraction shifts and distorts reciprocal-space
    - Reflection leads to two sets of peaks





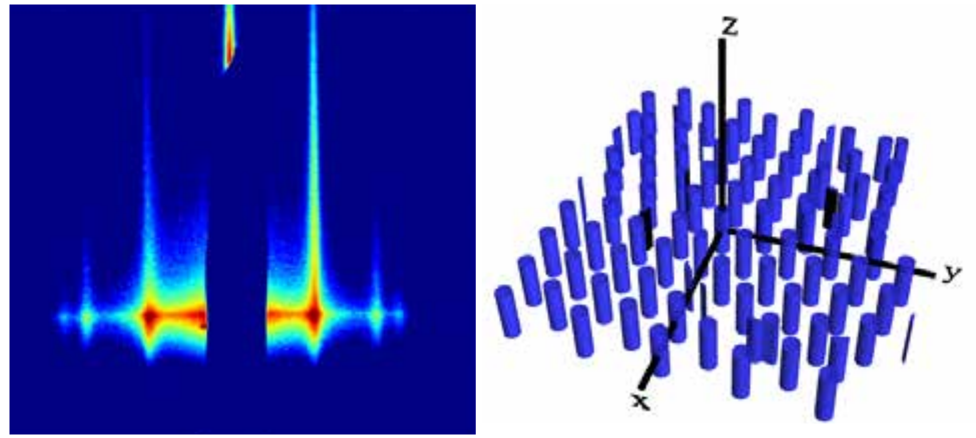


- You can use DWBA to predict peak positions
- So, you can index all the peaks, …

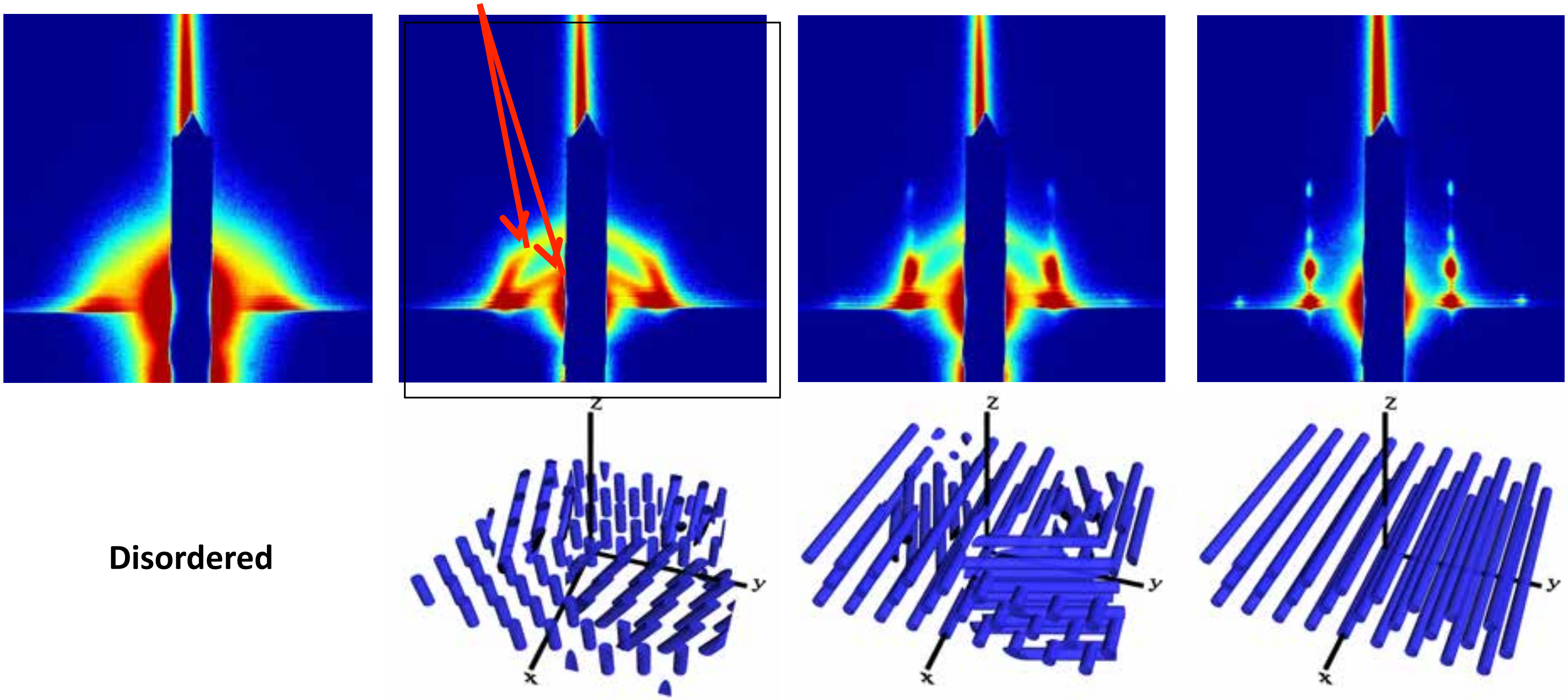
Singh *ACS Nano* **2012**, 17, 10335

Examples

- Block-copolymer cylinder phase

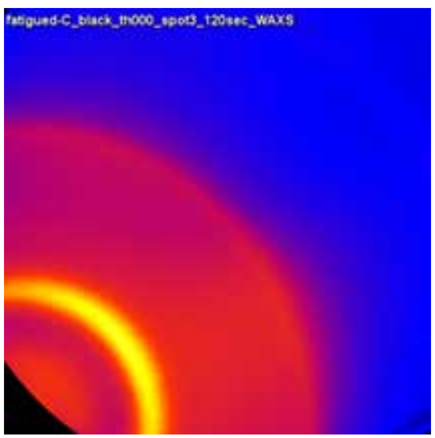


Note two rings

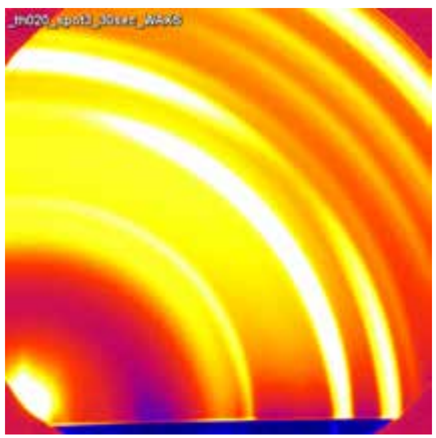


Qualitative

- 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

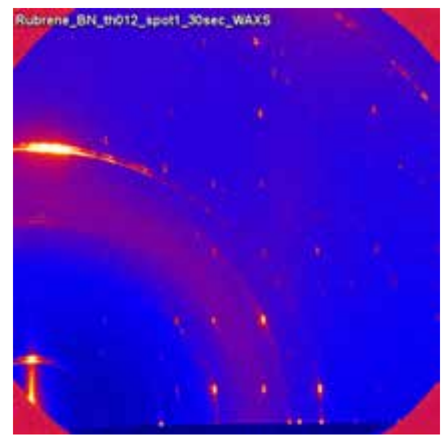


disordered



some ordering

oriented, textured

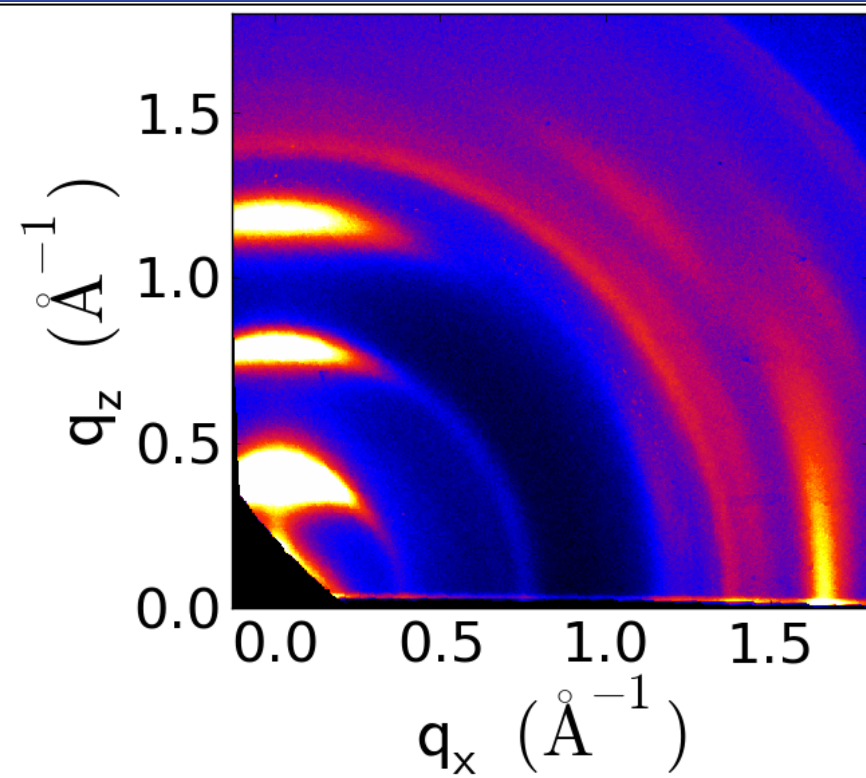


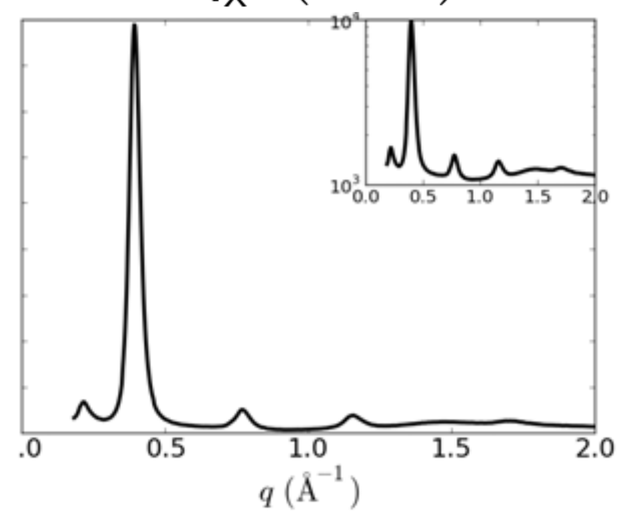
single crystal

less order ⟷ more order

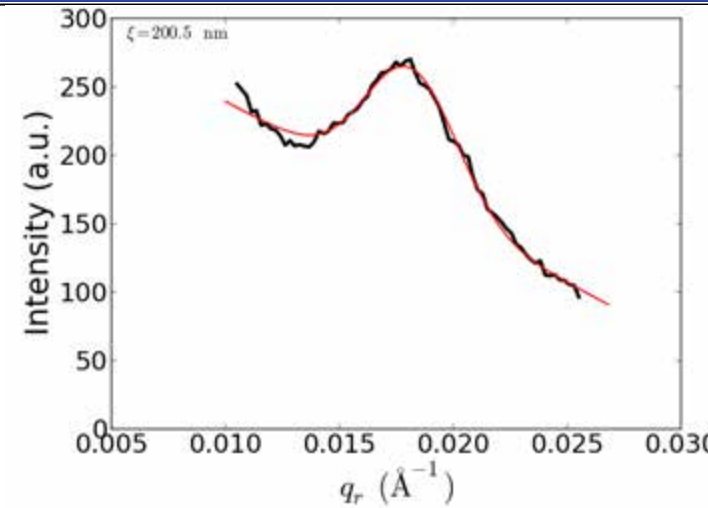
Linecut

- 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 <u>background</u>!





Linecut: what can it tell you?

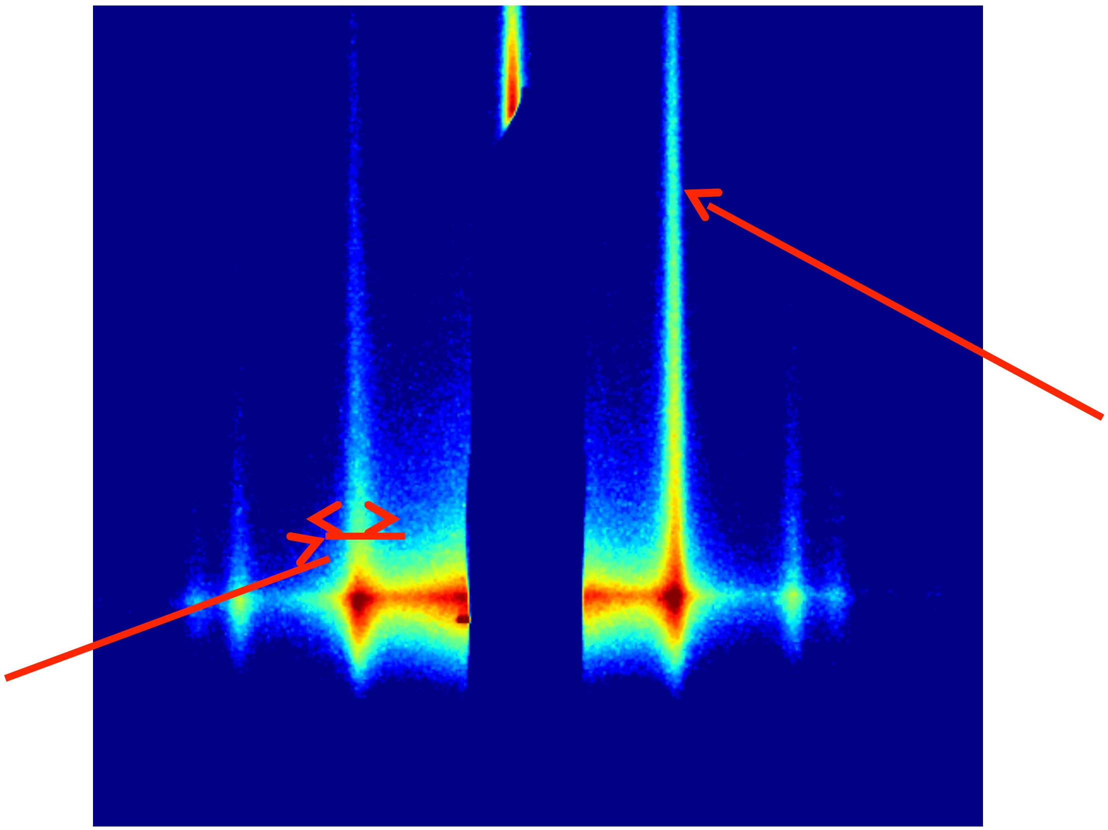


Smilgies *J. Appl. Cryst.* **2009,** 42, 1030

- *q*-position → $d = 2\pi/q$
  - But don't forget about unit-cell symmetry!
- *q*-positio<u>**s**</u> → Unit cell symmetry, dimensions and distortion
- Peak width → $\xi = 2\pi K/\Delta q$
  - Must account for instrumental resolution
  - Many things can affect peak width (microstrain, faults, …)
- Intensity → 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

Peak width

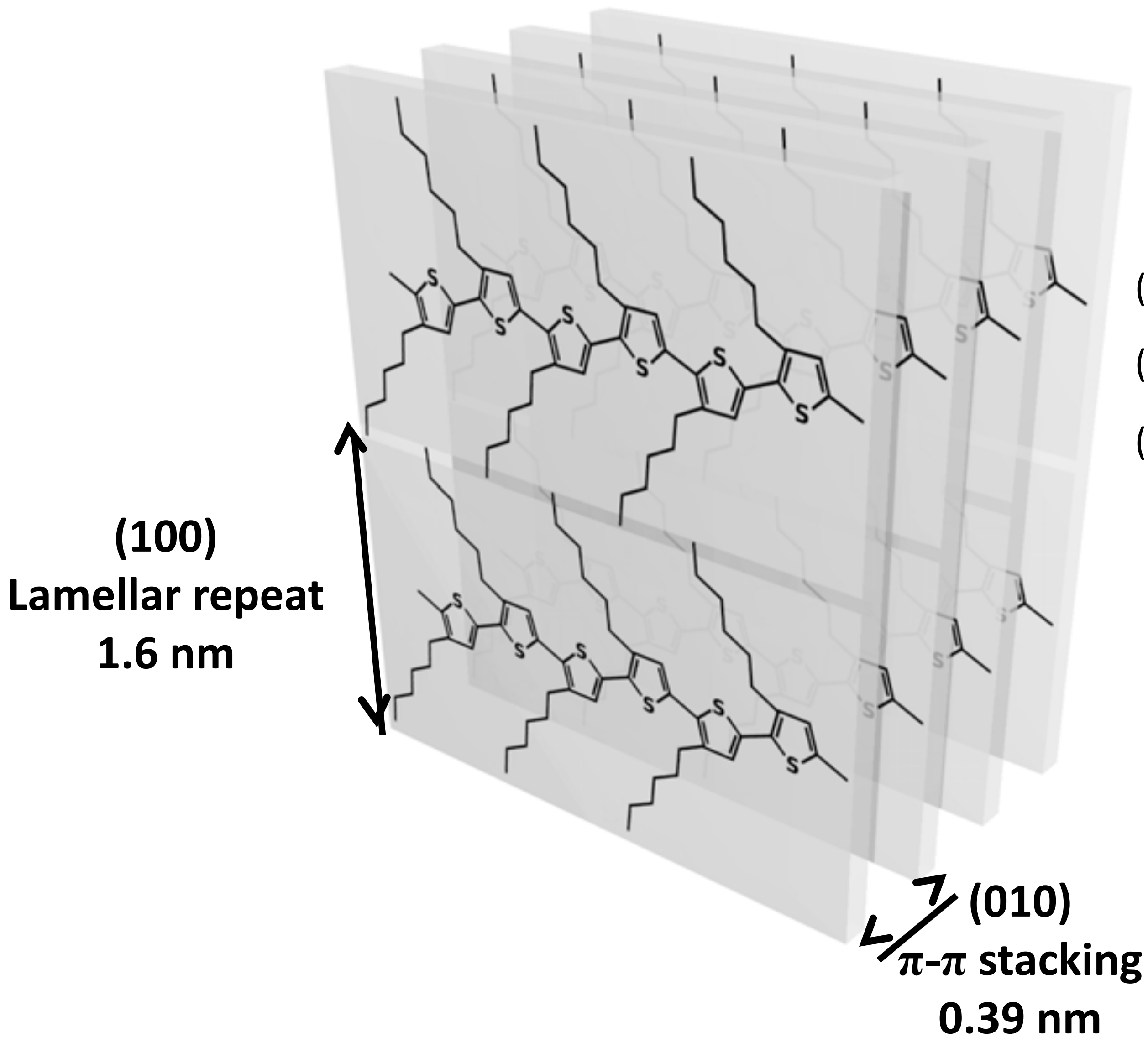
- Peak width can be anisotropic:
  - Width in each direction is telling you the 'grain size' in that direction
- Remember: distance is inverted $\xi = 2\pi K/\Delta q$
  - Narrow peak → big grains
  - Broad peak → small grains

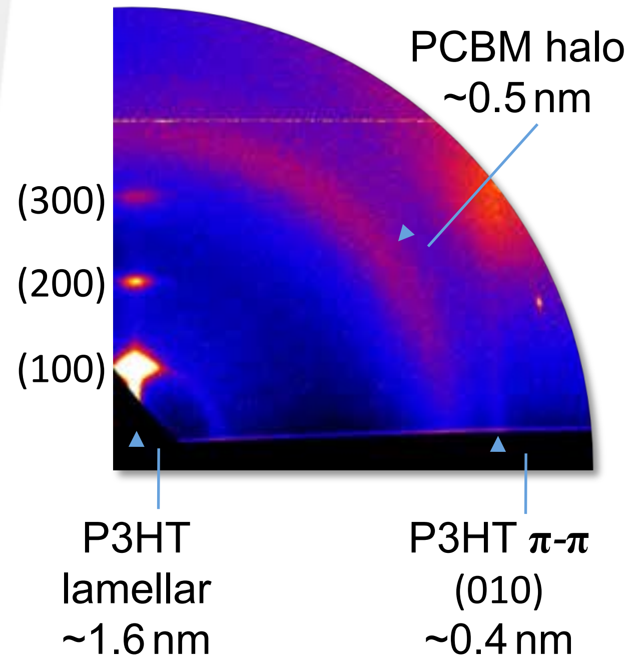


Width along qr gives the in-plane grain size

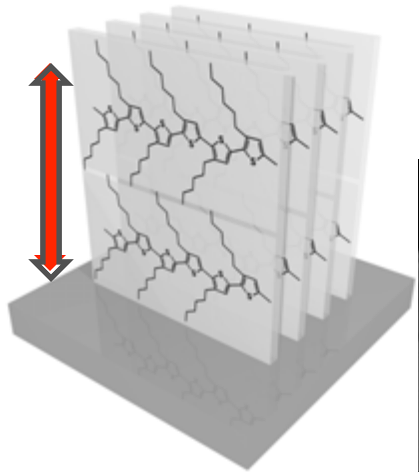
Extended streaks along vertical: This means the 'size' in the vertical is very small (thickness of a very thin film)

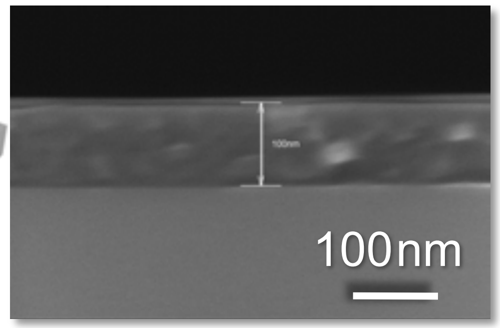
P3HT: poly 3-hexylthiophene

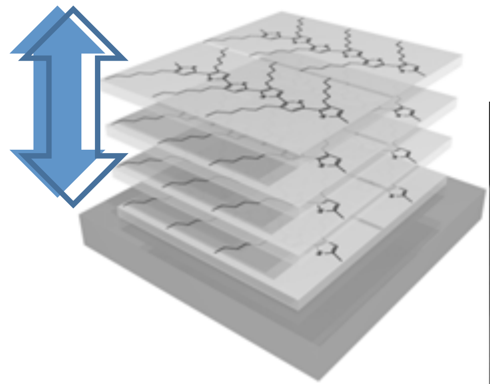


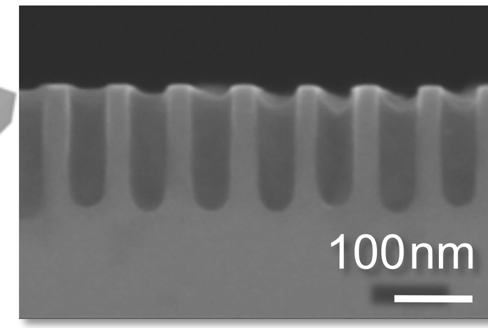


P3HT orientation









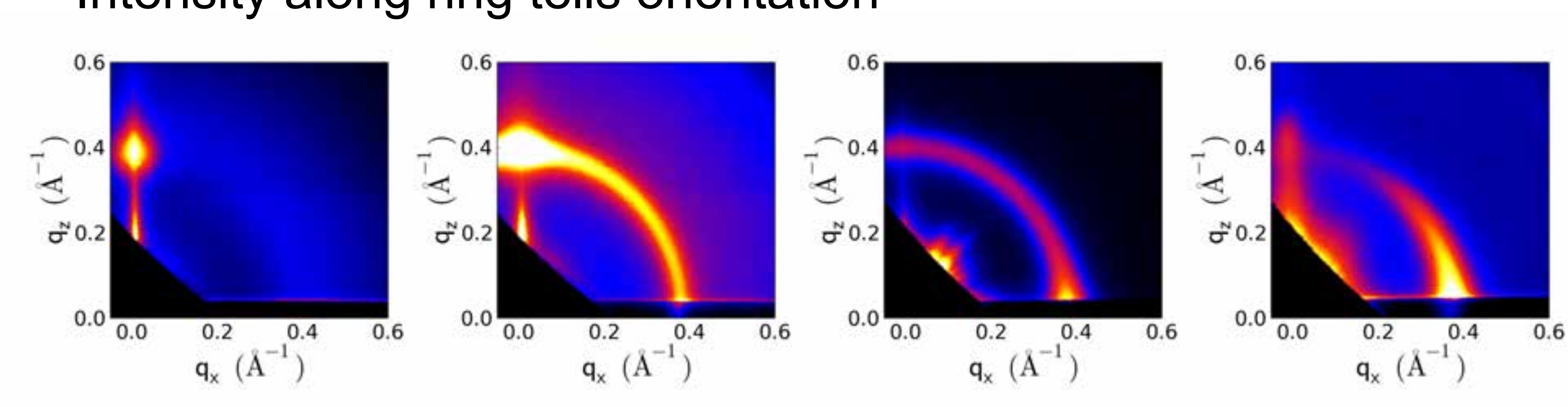
Edge-on

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

Face-on

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

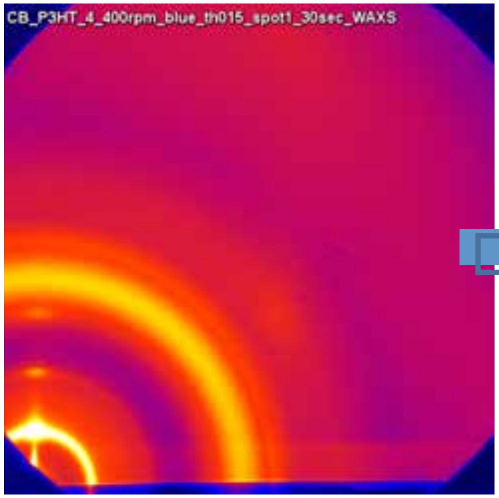
- Intensity along ring tells orientation

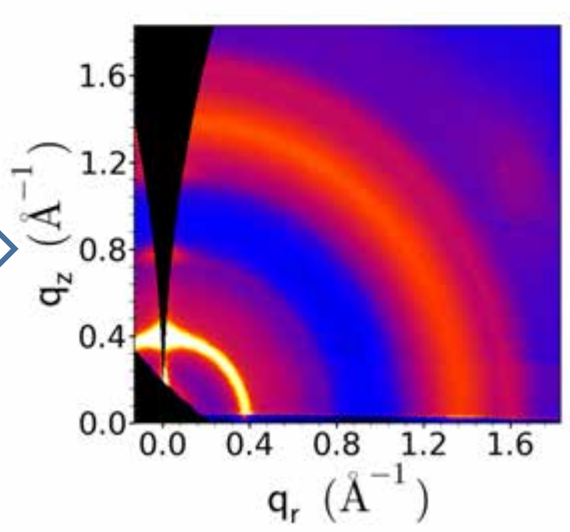


- How to quantify?

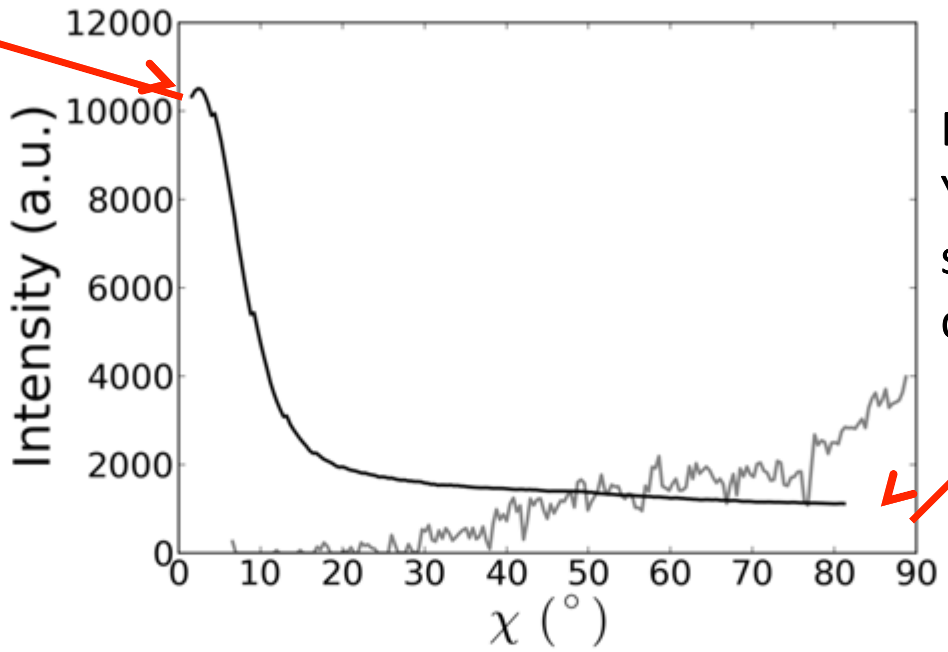
Analysis

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

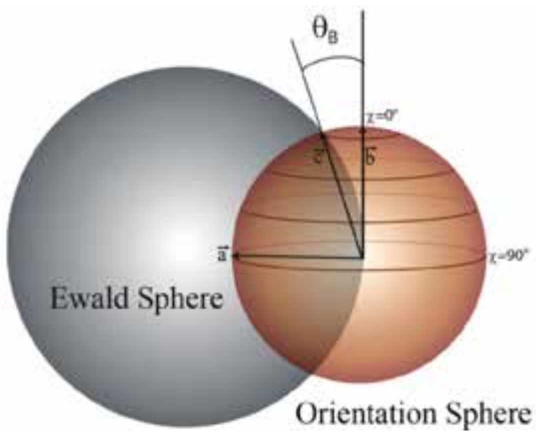




Data doesn't start at 0



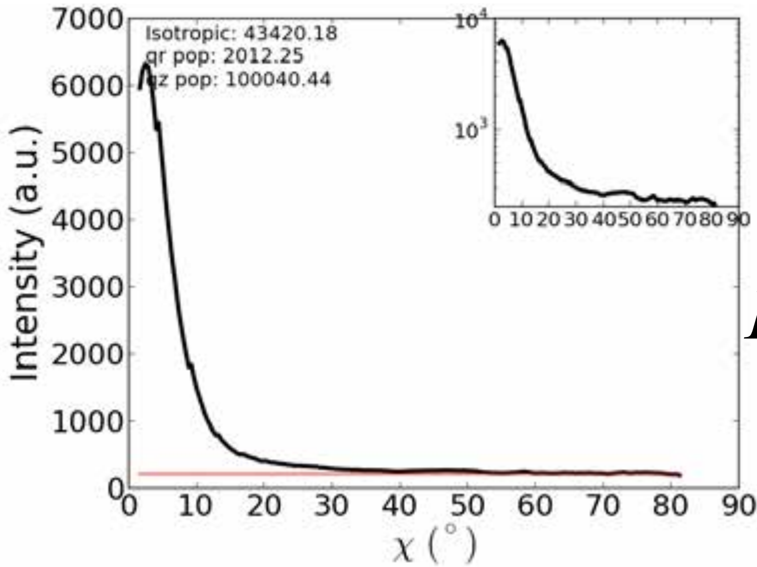
Exclude Yoneda and sub-horizon data



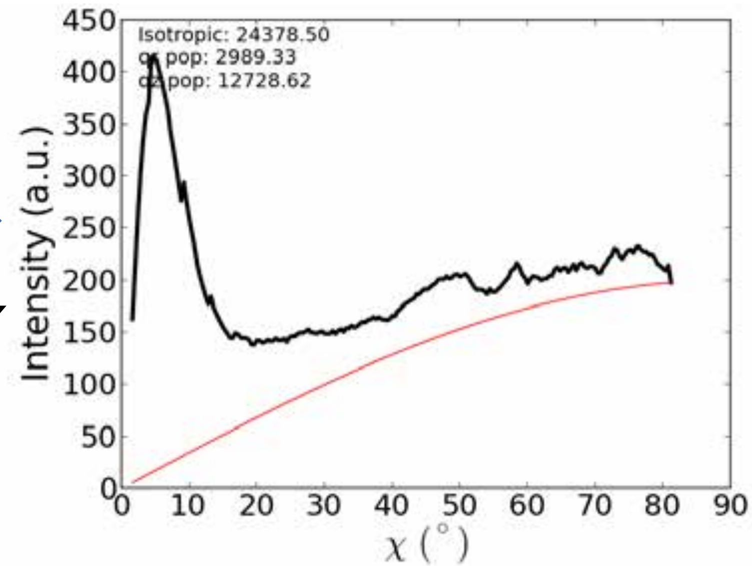
Baker *Langmuir* **2010**, 26, 9146

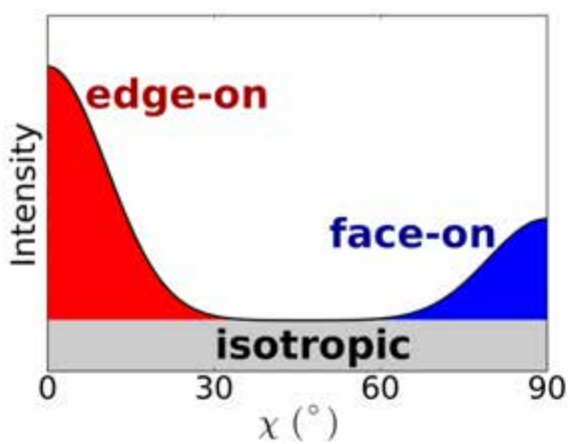
Analysis

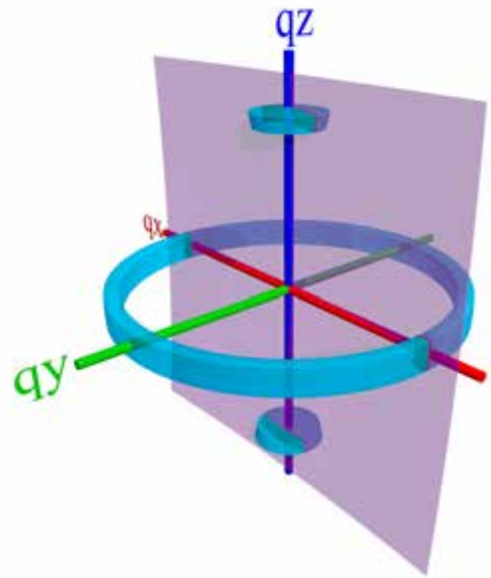
- Account for in-plane powder symmetry

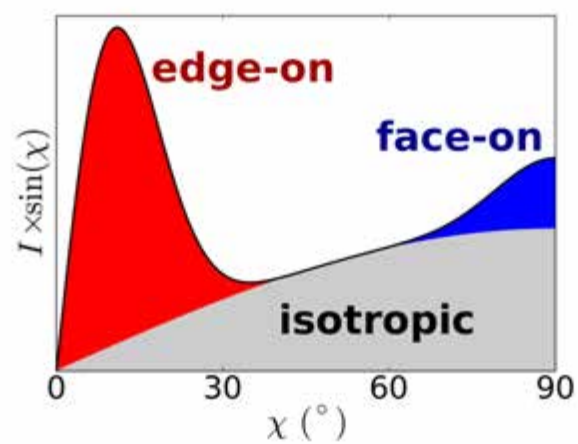


$$I_c = I \times \sin\chi$$



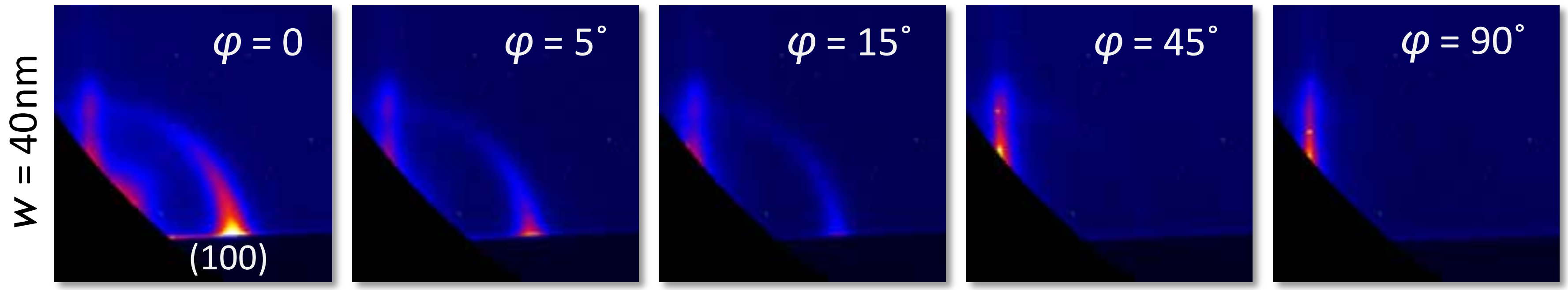


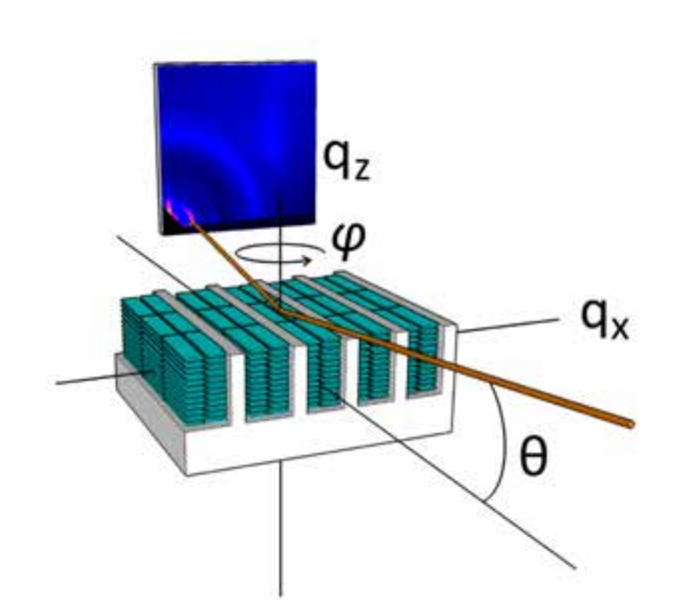


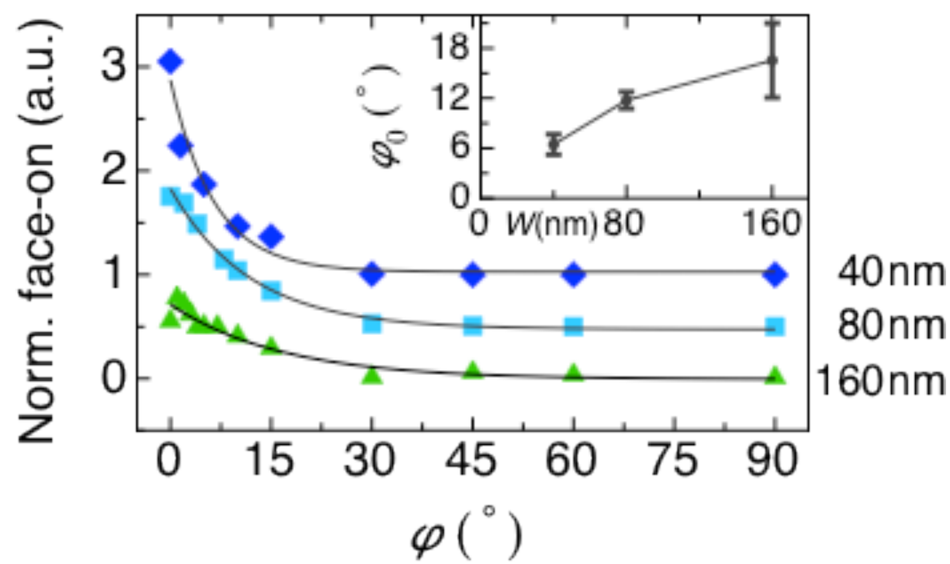


What about in-plane alignment?

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



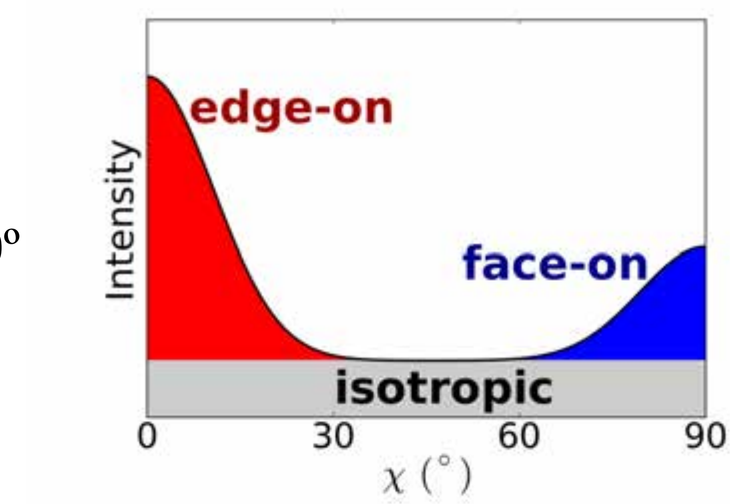


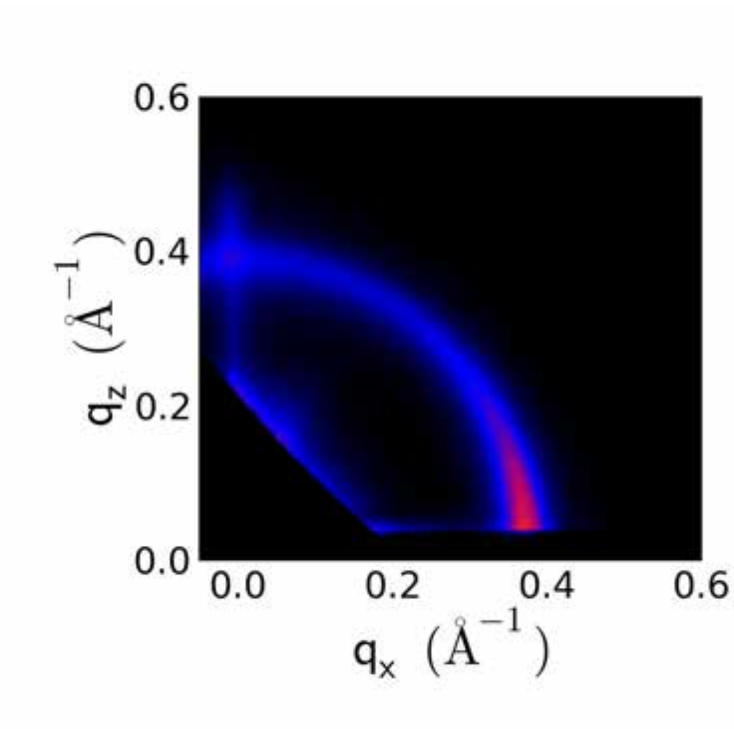


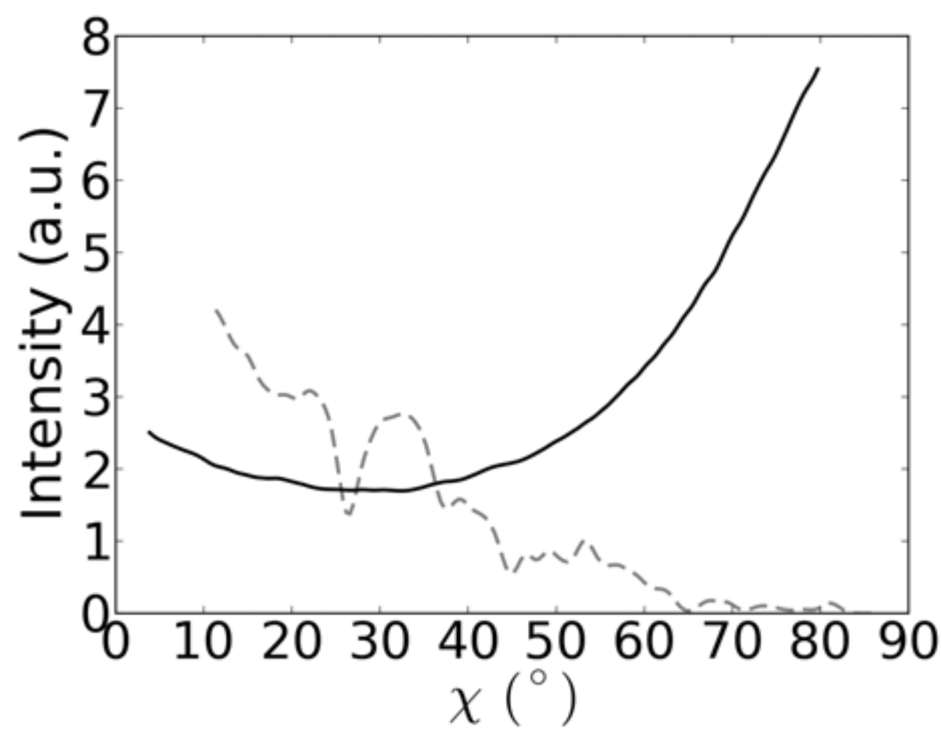
Johnston *ACS Nano* **2014**, 8, 243

In-plane aligned

- Rotate sample, accumulated images to reconstruct 3D reciprocal-space
- Use ϕ rocking scan (and correct intensities)
- If very well-aligned: just use intensity at ϕ = 0º



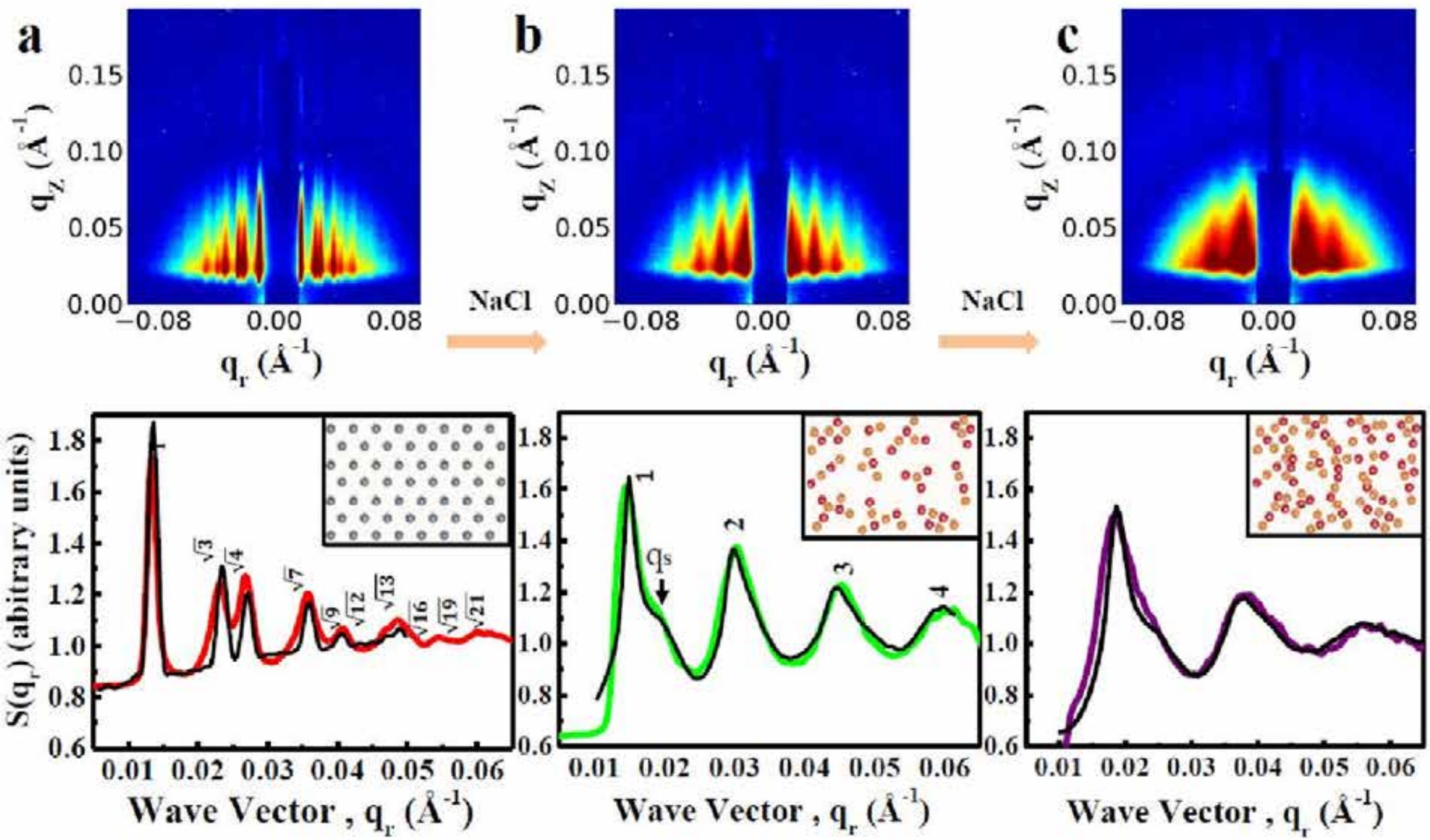




2D Nanoparticle Assembly

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

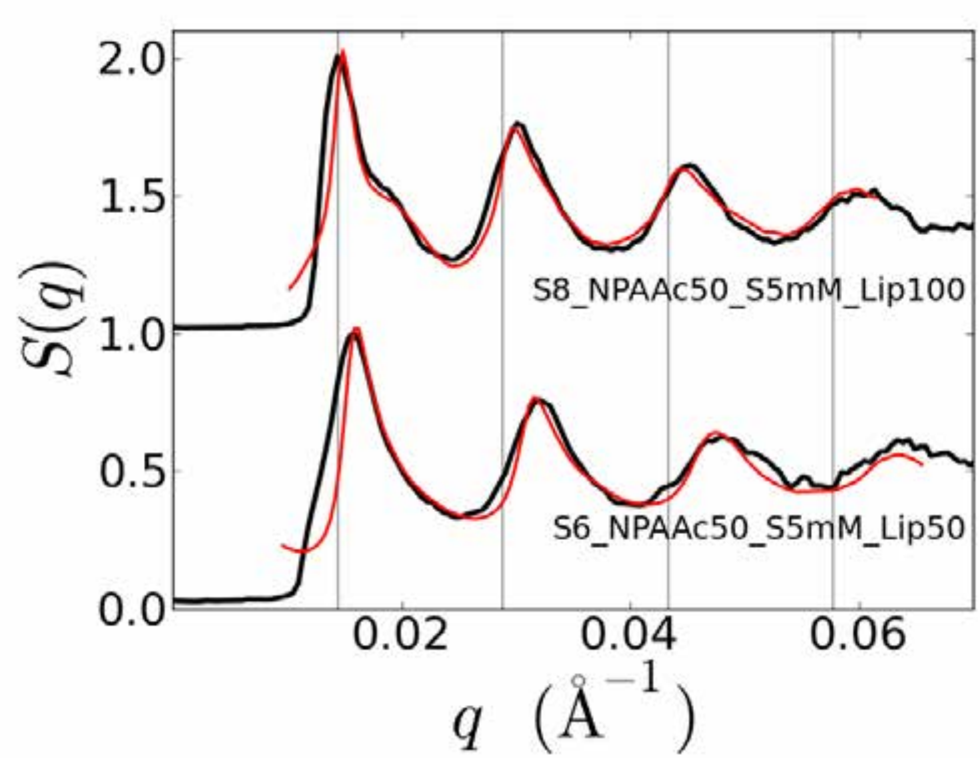
Srivastava *JACS* **2014**, ASAP

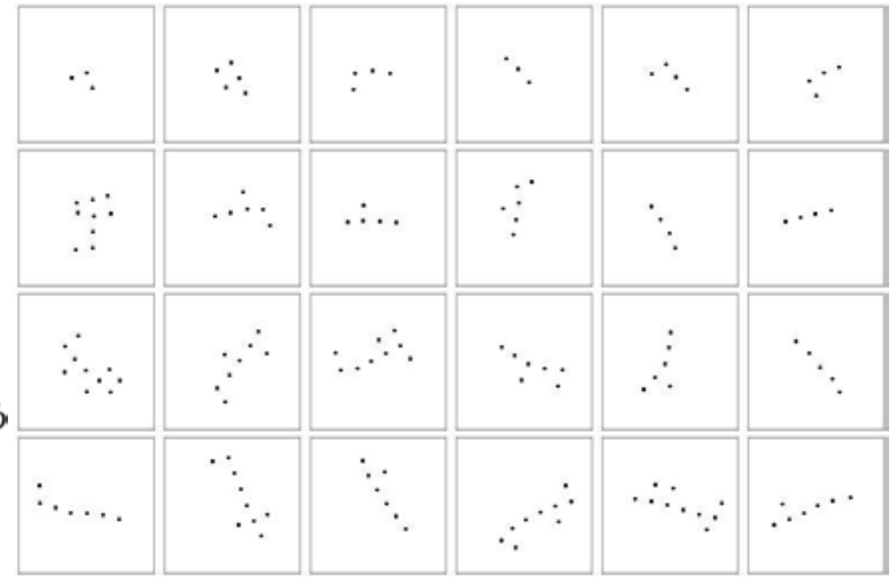


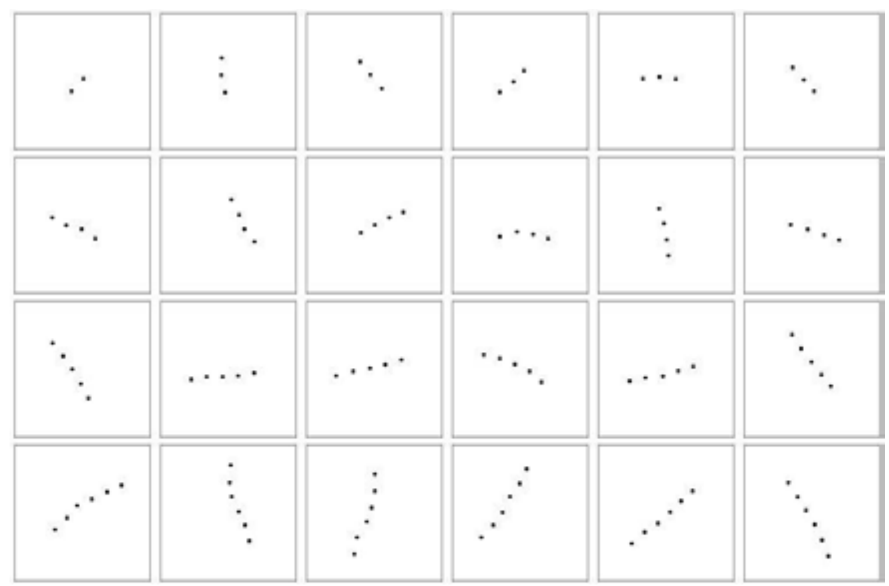
2D Nanoparticle Assembly

- Brute-force modeling…

$$
\begin{aligned}
P(q_r) &= \int_0^{2\pi} \left|F(q_x, q_y)\right|^2 d\phi \\
&= \int_0^{2\pi} \left|\rho\,(r) e^{iq.r}\, dV\right|^2 d\phi \\
&= \int_0^{2\pi} \left|\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \rho(x,y) e^{iq_x x} e^{iq_y y}\, dx\, dy\right|^2 d\phi \\
&= \int_0^{2\pi} \left|\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \rho(x,y) e^{iq_r sin(\phi) x} e^{iq_r cos(\phi) y}\, dx\, dy\right|^2 d\phi
\end{aligned}
$$

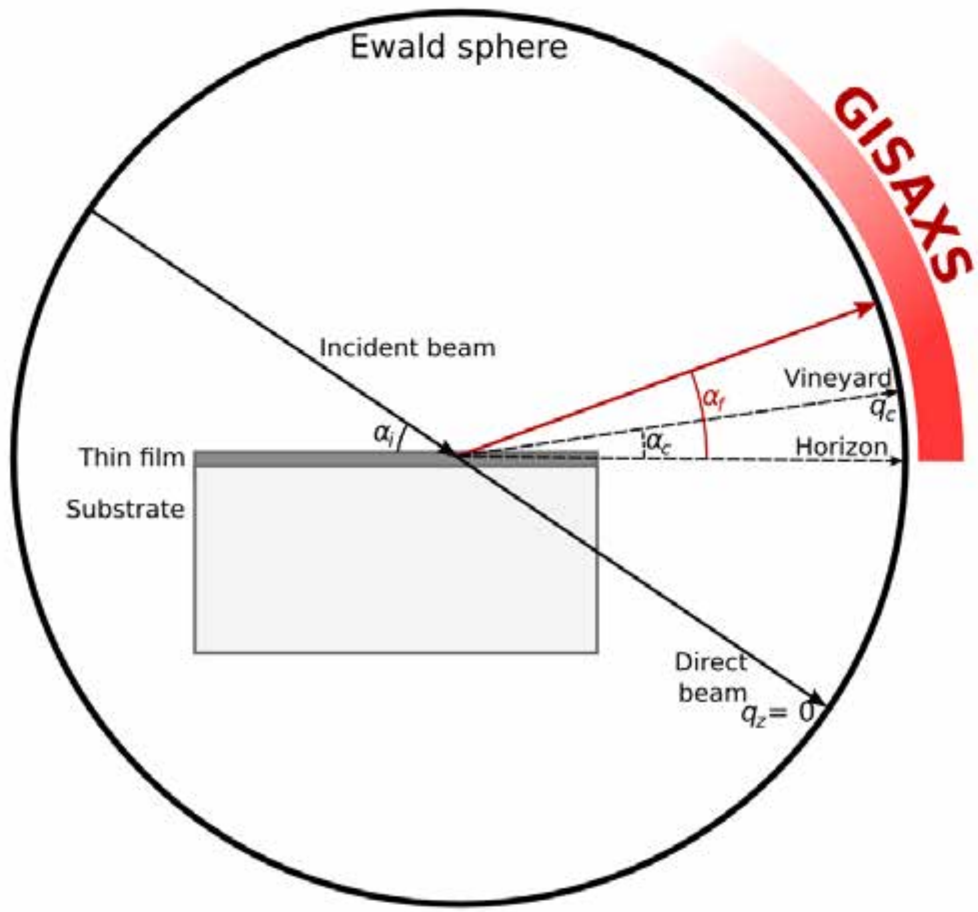






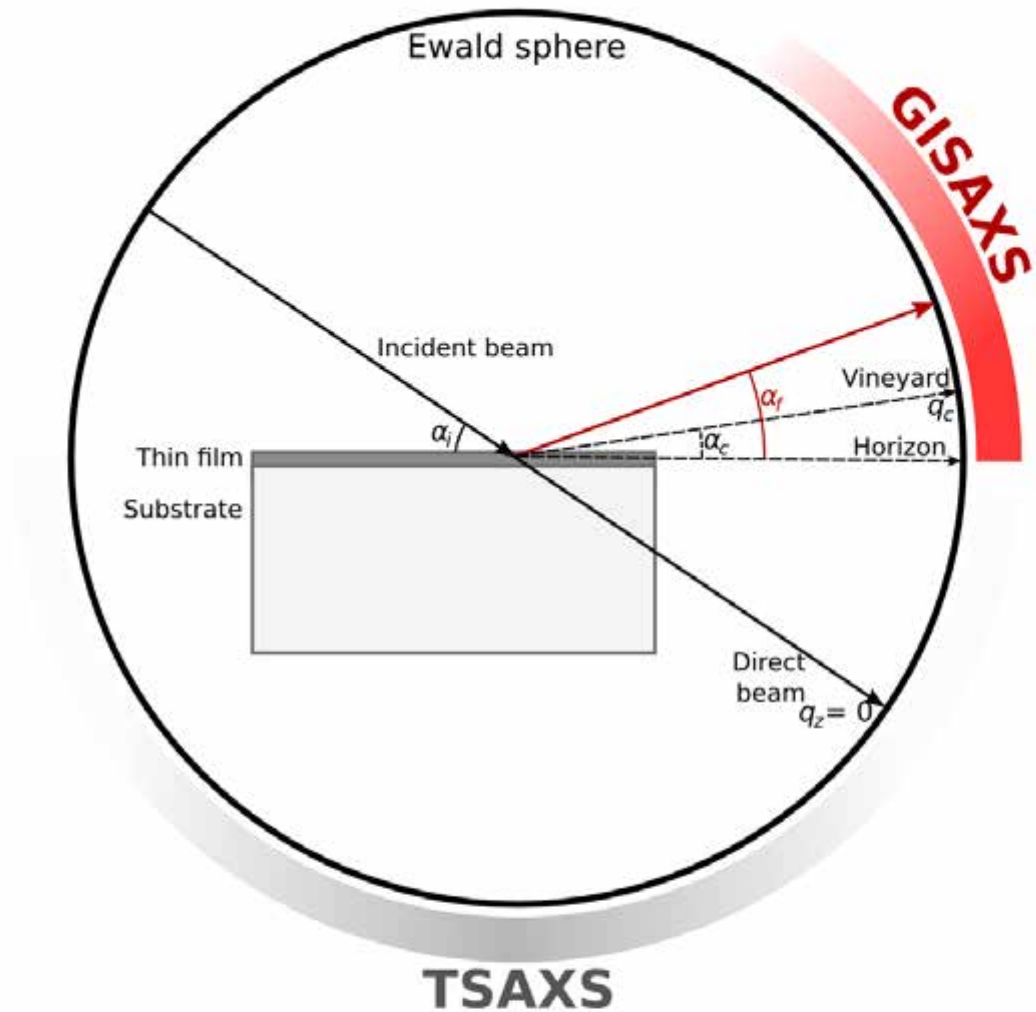
Conventional GISAXS

- Thin film scattering: GISAXS



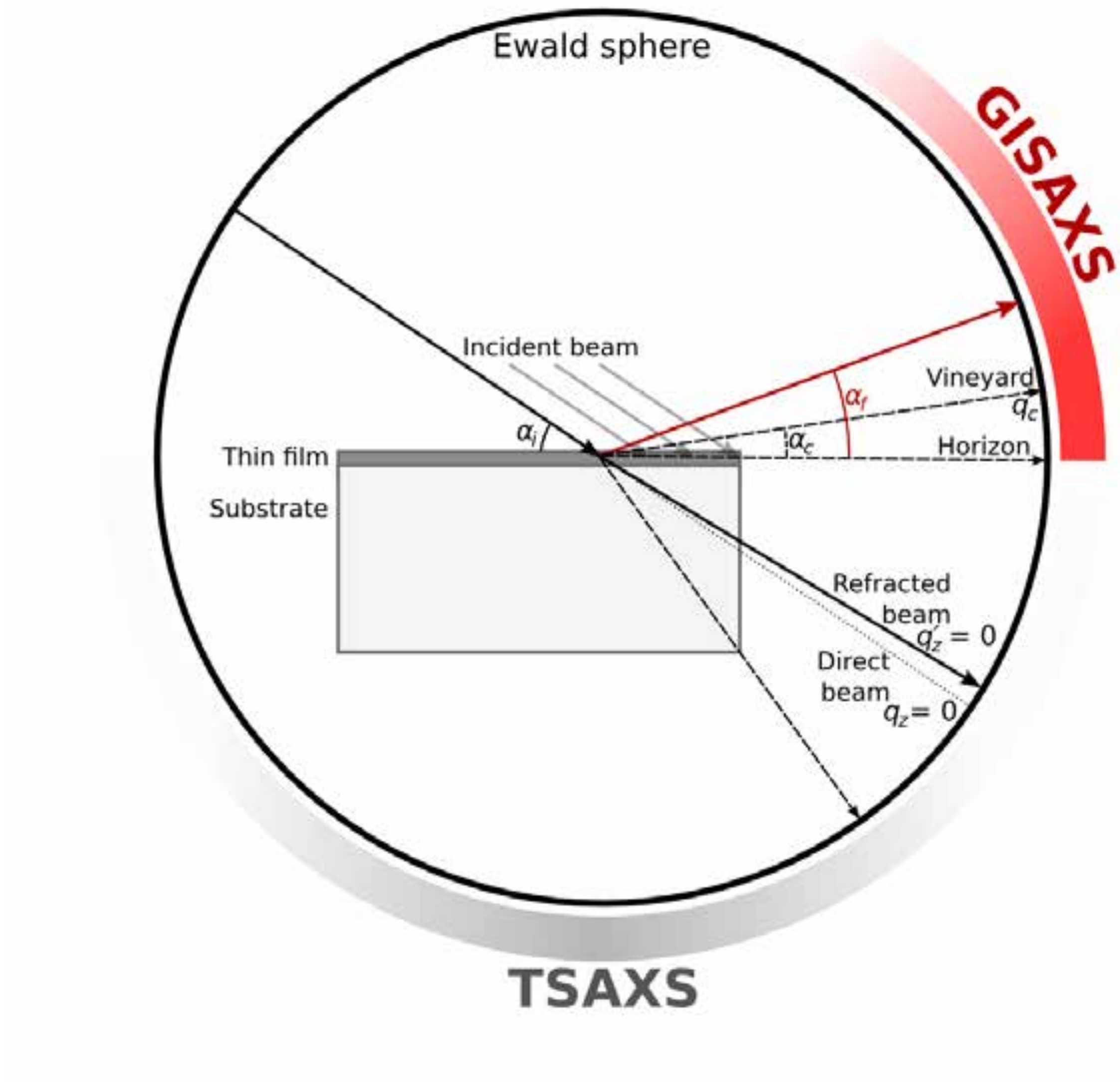
Conventional GISAXS

- GISAXS blocked below horizon
- TSAXS attenuated at high angle



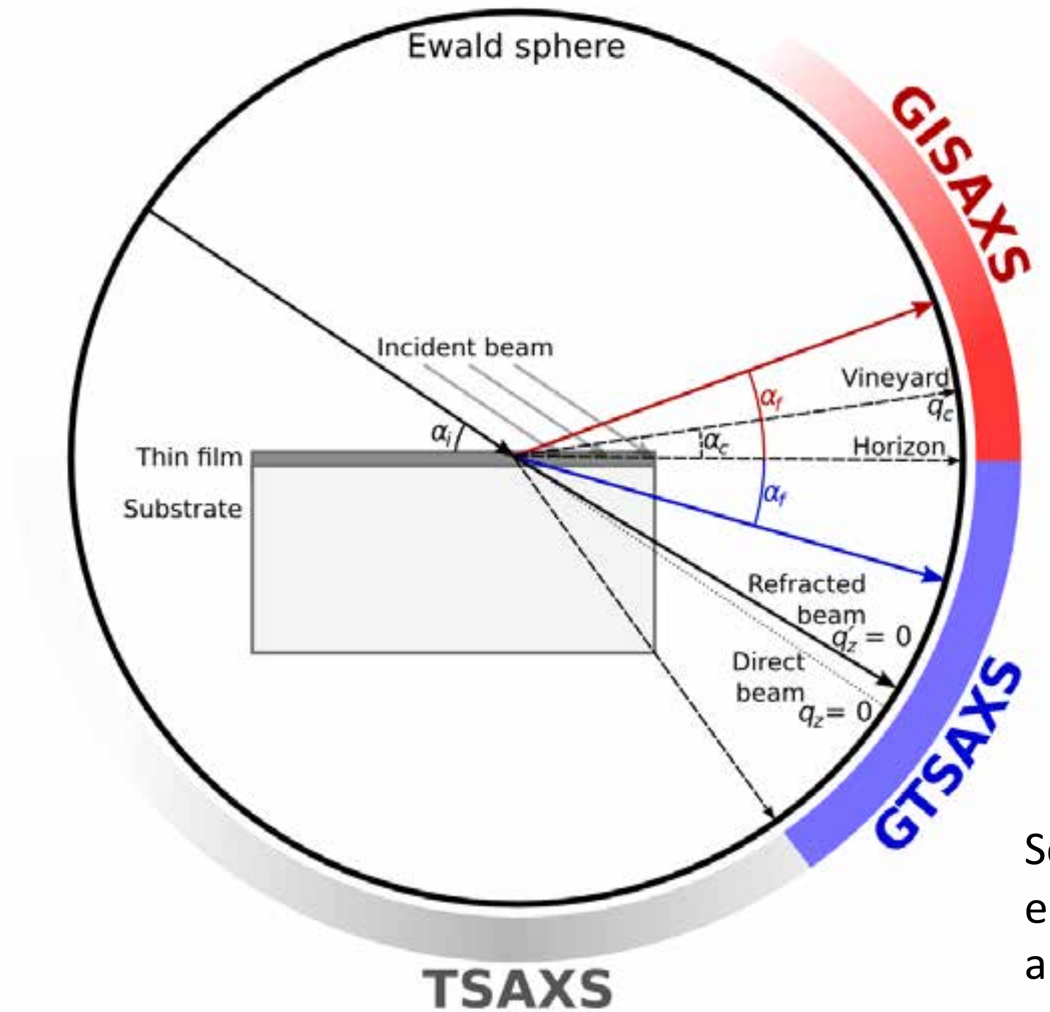
New geometry

- What if beam hits near edge of substrate?
- Scattering exits from edge…



New concept: GTSAXS

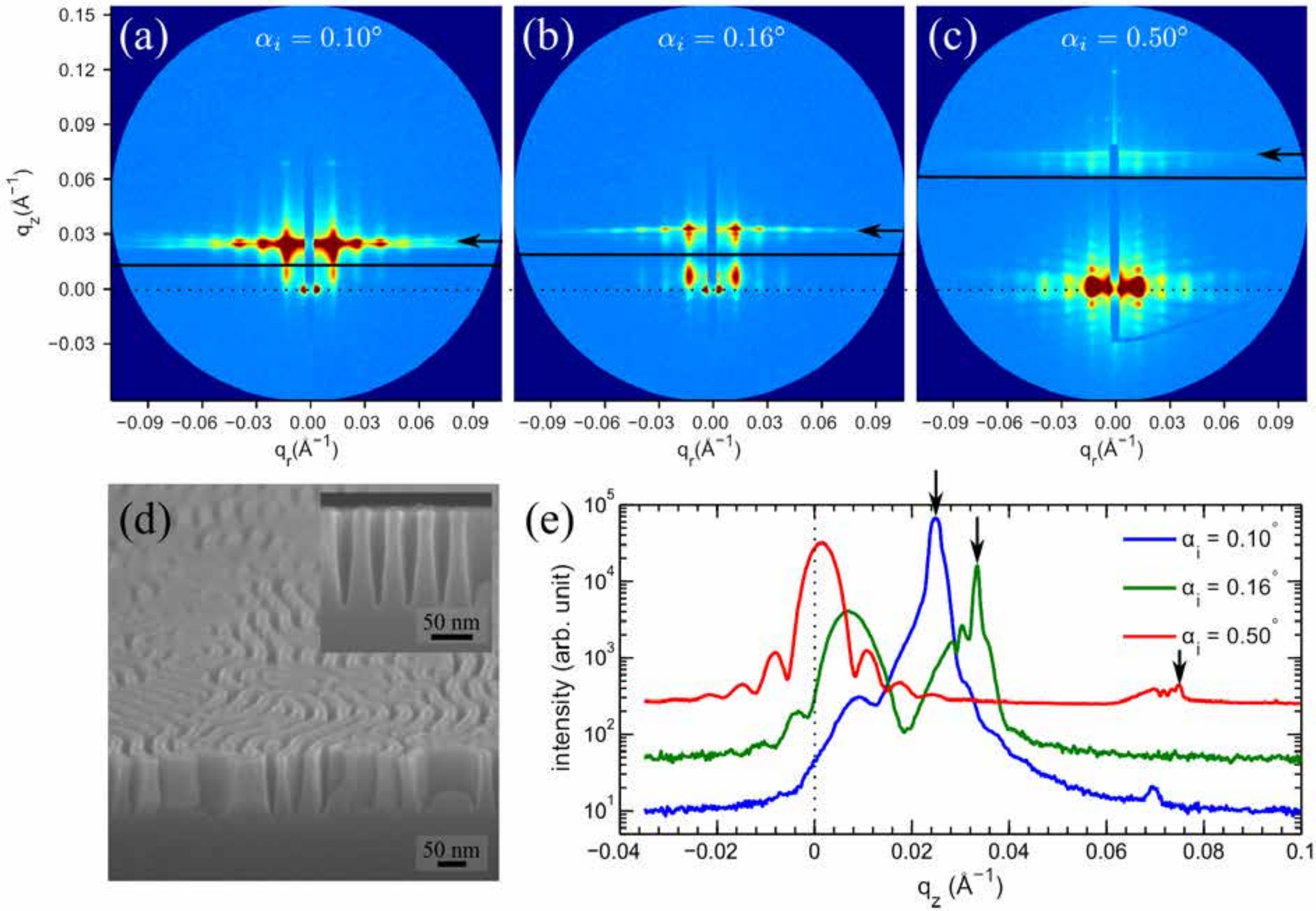
- **G**razing-incidence **T**ransmission **S**mall-**A**ngle **X**-ray **S**cattering



Scattering exits from edge (between horizon and sample corner)

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

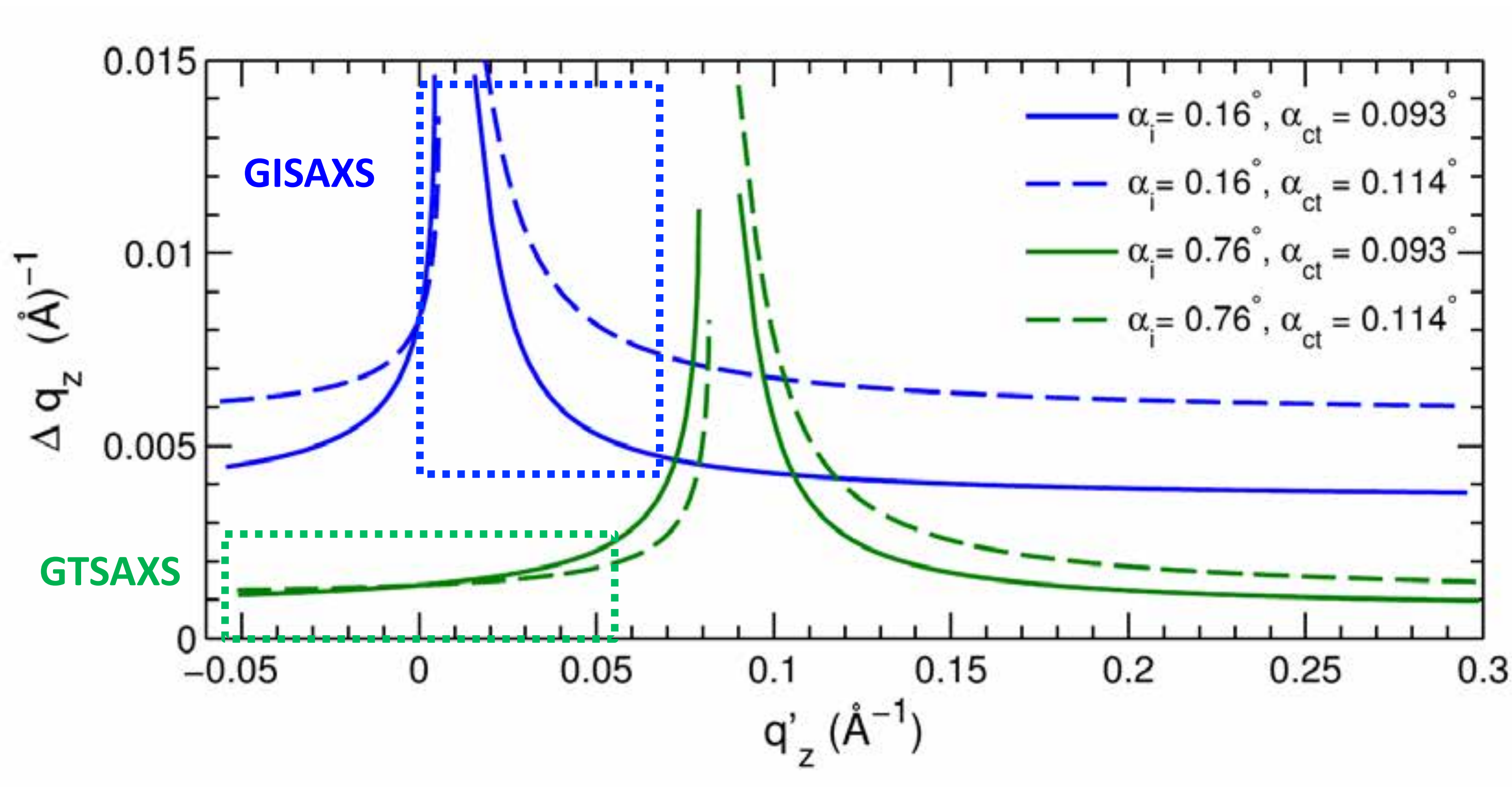
BCP pattern



(a)
$\alpha_i = 0.10°$
(b)
$\alpha_i = 0.16°$
(c)
$\alpha_i = 0.50°$
$q_z(Å^{-1})$
0.15
0.12
0.09
0.06
0.03
0.00
−0.03
−0.09 −0.06 −0.03 0.00 0.03 0.06 0.09
$q_r(Å^{-1})$
(d)
50 nm
50 nm
(e)
$\alpha_i = 0.10°$
$\alpha_i = 0.16°$
$\alpha_i = 0.50°$
intensity (arb. unit)
10^5
10^4
10^3
10^2
10^1
−0.04 −0.02 0 0.02 0.04 0.06 0.08 0.1
$q_z (Å^{-1})$

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

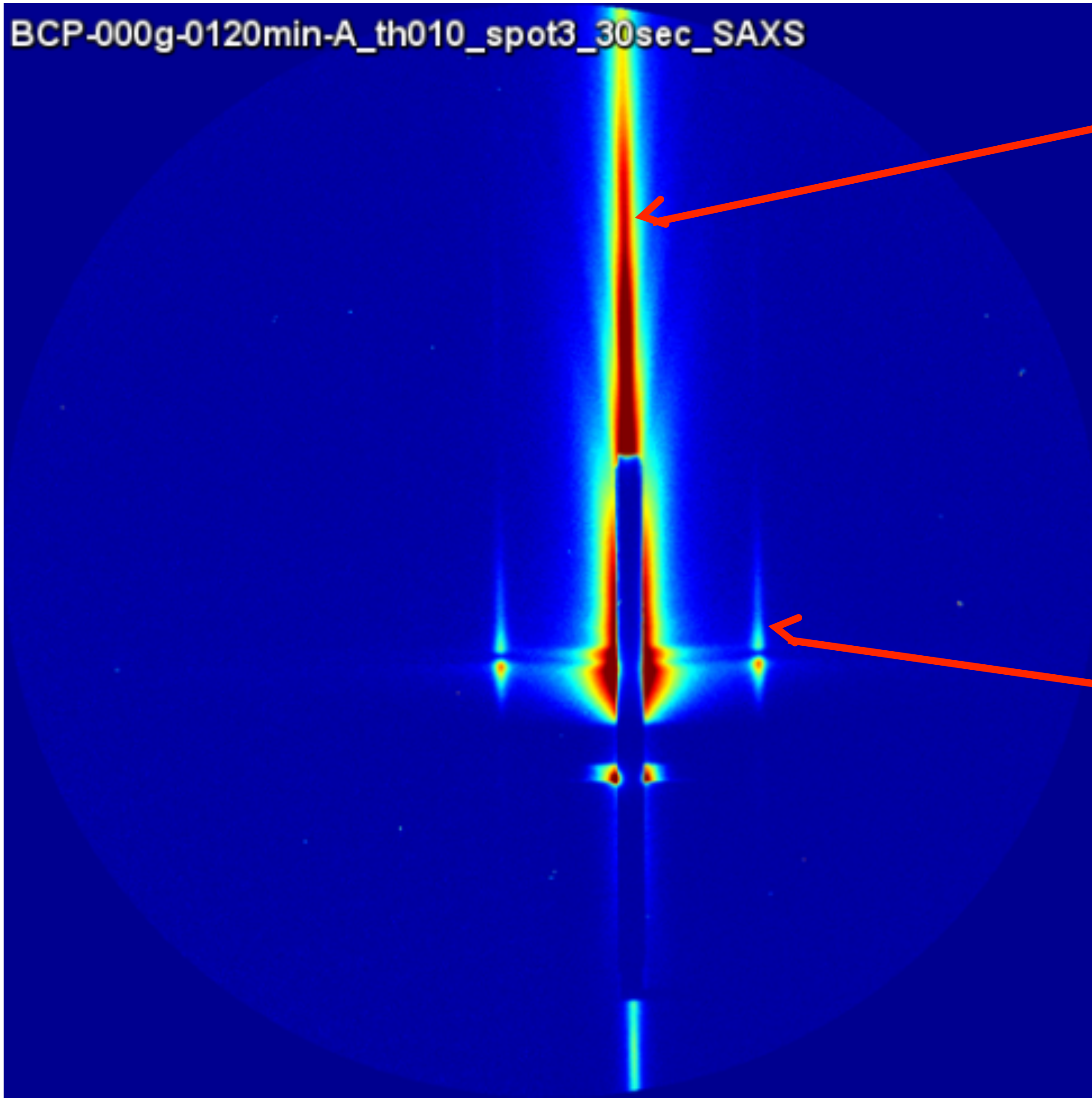
- Analysing GISAXS data can be tricky…

- 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

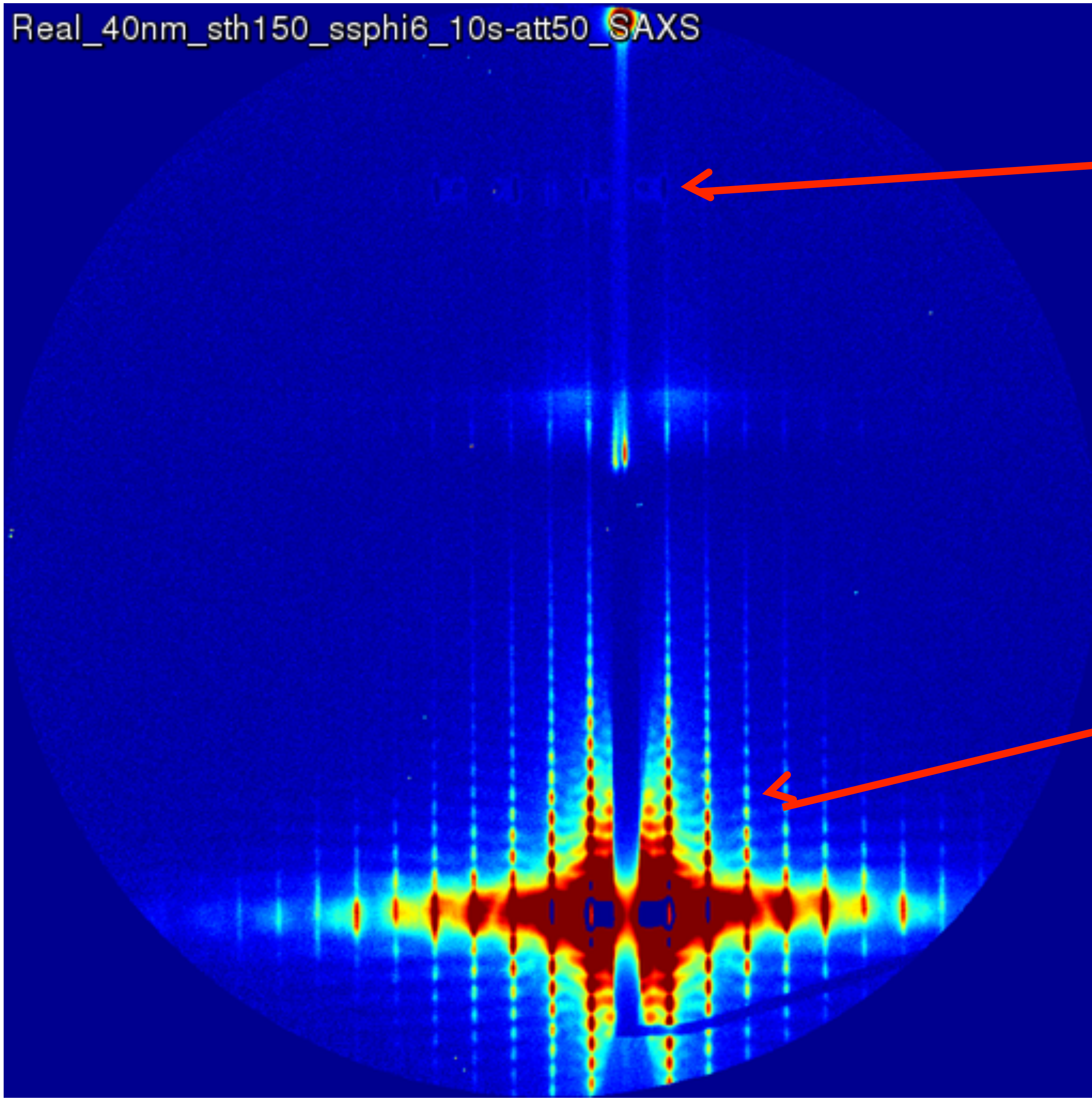


What's this intense rod?

Why are there oscillations along the rod?

What does this peak tell you?

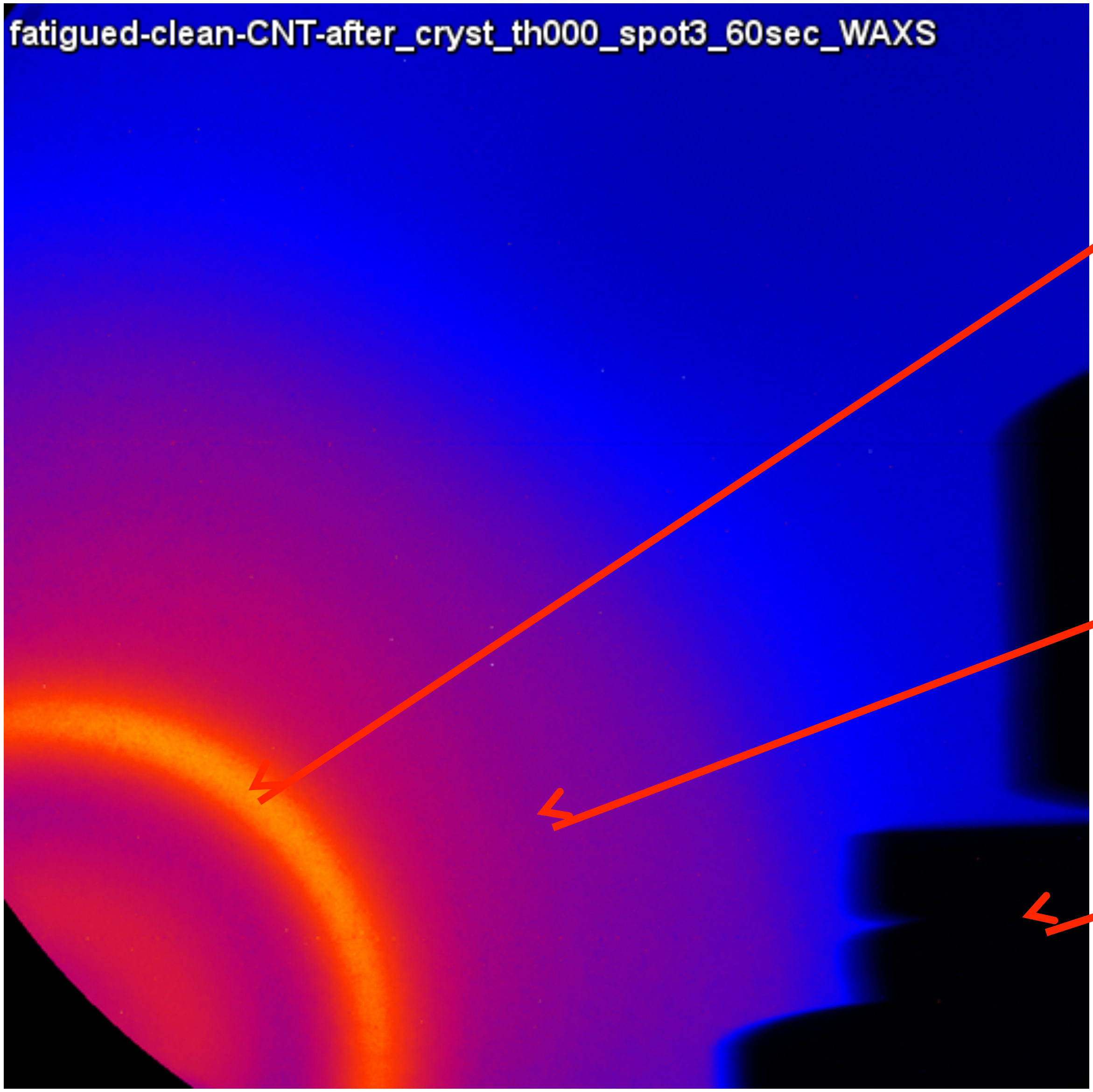
Exercises



What's this stuff?

Lots of peaks! What kind of sample is this?

Exercises

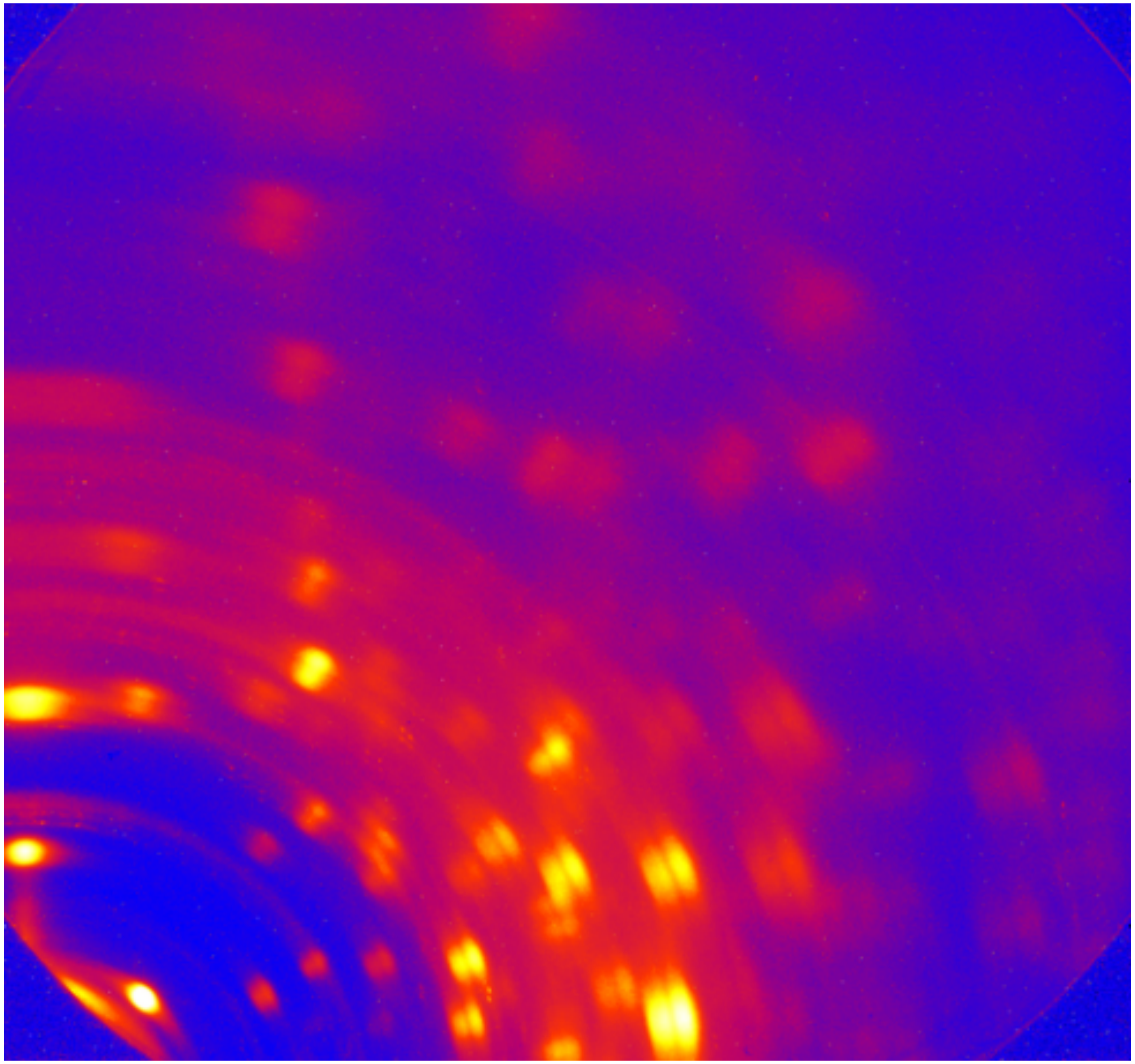


What does this ring tell you?

High background… why?

What's this?

Exercises



How would you analyze this sample?