Structural indexing and texture in films by GISAXS

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Probing surface and interface morphology with Grazing Incidence Small Angle X-Ray Scattering

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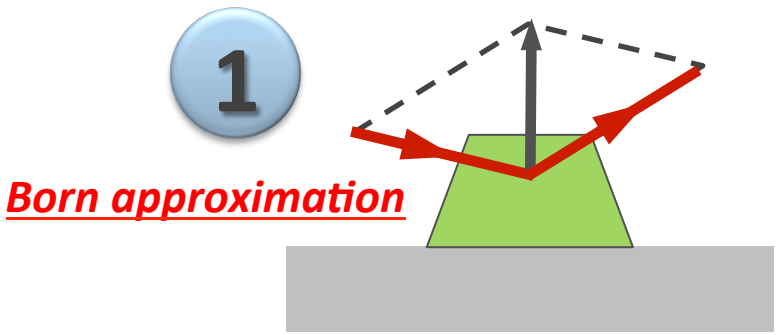
GISAXS from supported nano-objects

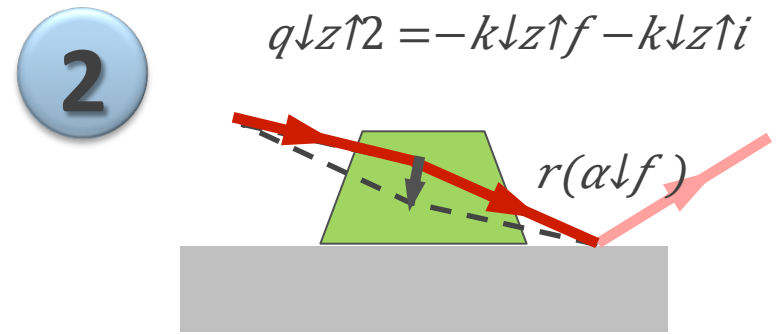
$$(d\sigma/d\Omega)_{diff} = r_e^2 \, |\Delta\rho|^2 \, |\mathcal{F}(q_{||}, k_{z,i}, k_{z,f})|^2$$

$$\mathcal{F}(q_{||}, k_{z,i}, k_{z,f}) = F(q_{||}, q_{z,1}) + r(\alpha_f) F(q_{||}, q_{z,2}) + r(\alpha_i) F(q_{||}, q_{z,3}) + r($$

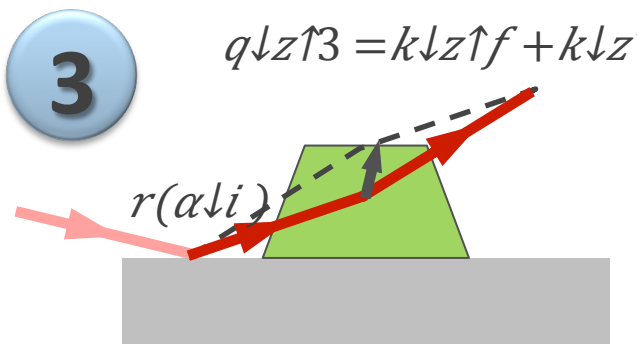
$$q_{z,1} = k_{z,f} - k_{z,i}$$



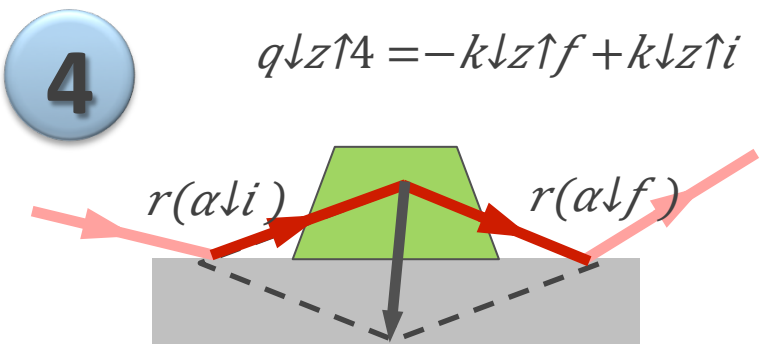
$$q_{z,2} = -k_{z,f} - k_{z,i}$$



$$q_{z,3} = k_{z,f} + k_{z,i}$$



$$q_{z,4} = -k_{z,f} + k_{z,i}$$



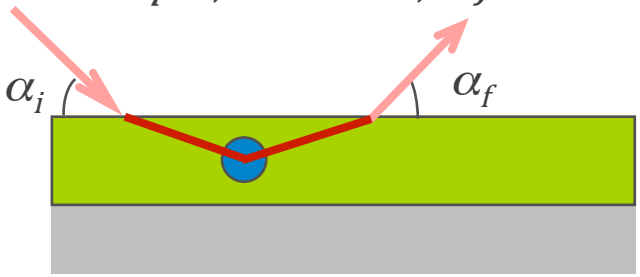
GISAXS from buried structures in films

$$\psi(\boldsymbol{r},\boldsymbol{k}) = e^{i\boldsymbol{k}_{\parallel}\cdot\boldsymbol{r}_{\parallel}} \begin{cases} e^{-ik_{z,1}z} + R_1 e^{ik_{z,1}z} & \text{for } z>0 \\ T_2 e^{-ik_{z,2}z} + R_2 e^{\ldots} & \text{for } -d<z<0 \\ \ldots & \text{for } z<-d \end{cases}$$

$$\mathcal{F}(q_{\parallel}, k_{z,1}^{i}, k_{z,1}^{f}) = T_2(k_{z,2}^{f}) T_2(k_{z,2}^{i}) F(q_{\parallel}, q_{z,2}^{1}) + R_2(k_{z,2}^{f}) T_2(\ldots$$
$$+ T_2(k_{z,2}^{f}) R_2(k_{z,2}^{i}) F(q_{\parallel}, q_{z,2}^{3}) + R_2(k_{z,2}^{f}) R_2(k_{z,2}^{i}) F(q_{\parallel}, q_{z,2}^{4})$$

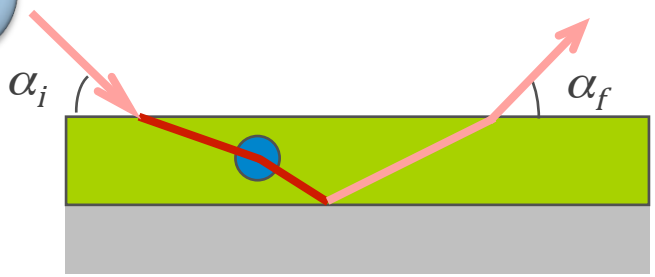
1

$$q_{z,2}^{1} = k_{z,2}^{f} - k_{z,2}^{i}$$



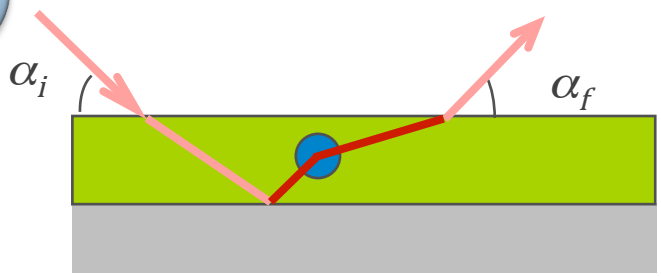
2

$$q_{z,2}^{2} = -k_{z,2}^{f} - k_{z,2}^{i}$$



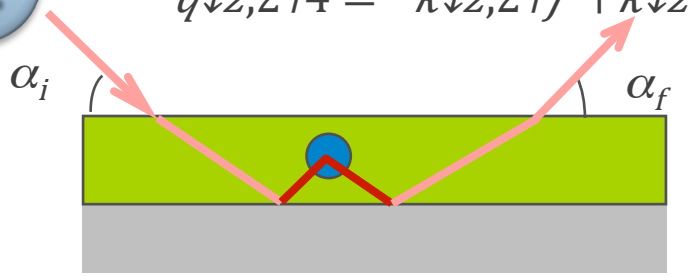
3

$$q_{z,2}^{3} = k_{z,2}^{f} + k_{z,2}^{i}$$



4

$$q_{z,2}^{4} = -k_{z,2}^{f} + k_{z,2}^{i}$$



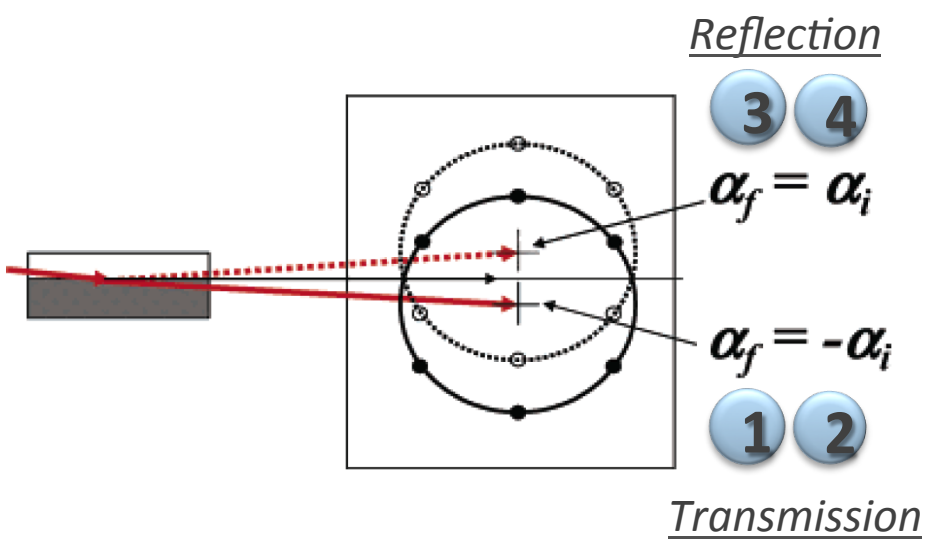
Transmission and reflection channels

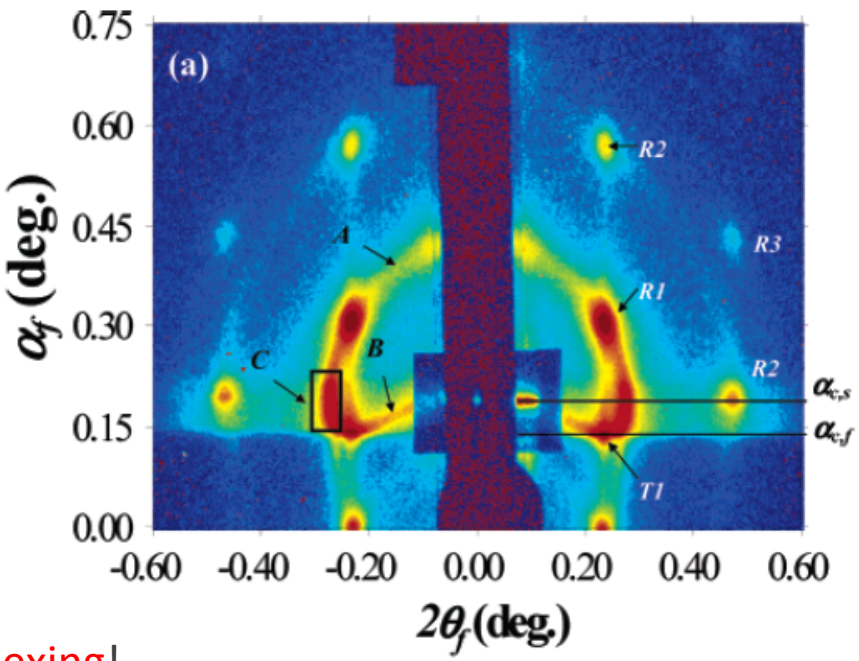
1 2

$$\alpha_f = \arcsin\sqrt{\left(\frac{q_z}{k}\right)^2 + \sin^2\alpha_i - \frac{2q_z}{k}\sqrt{n^2 - 1 + \sin^2\alpha_i}}$$

3 4

$$\alpha_f = \arcsin\sqrt{\left(\frac{q_z}{k}\right)^2 + \sin^2\alpha_i + \frac{2q_z}{k}\sqrt{n^2 - 1 + \sin^2\alpha_i}}$$





Important for substrate supported 3D structure indexing!

B. Lee et al, Macromolecules 38, 4316 (2005)

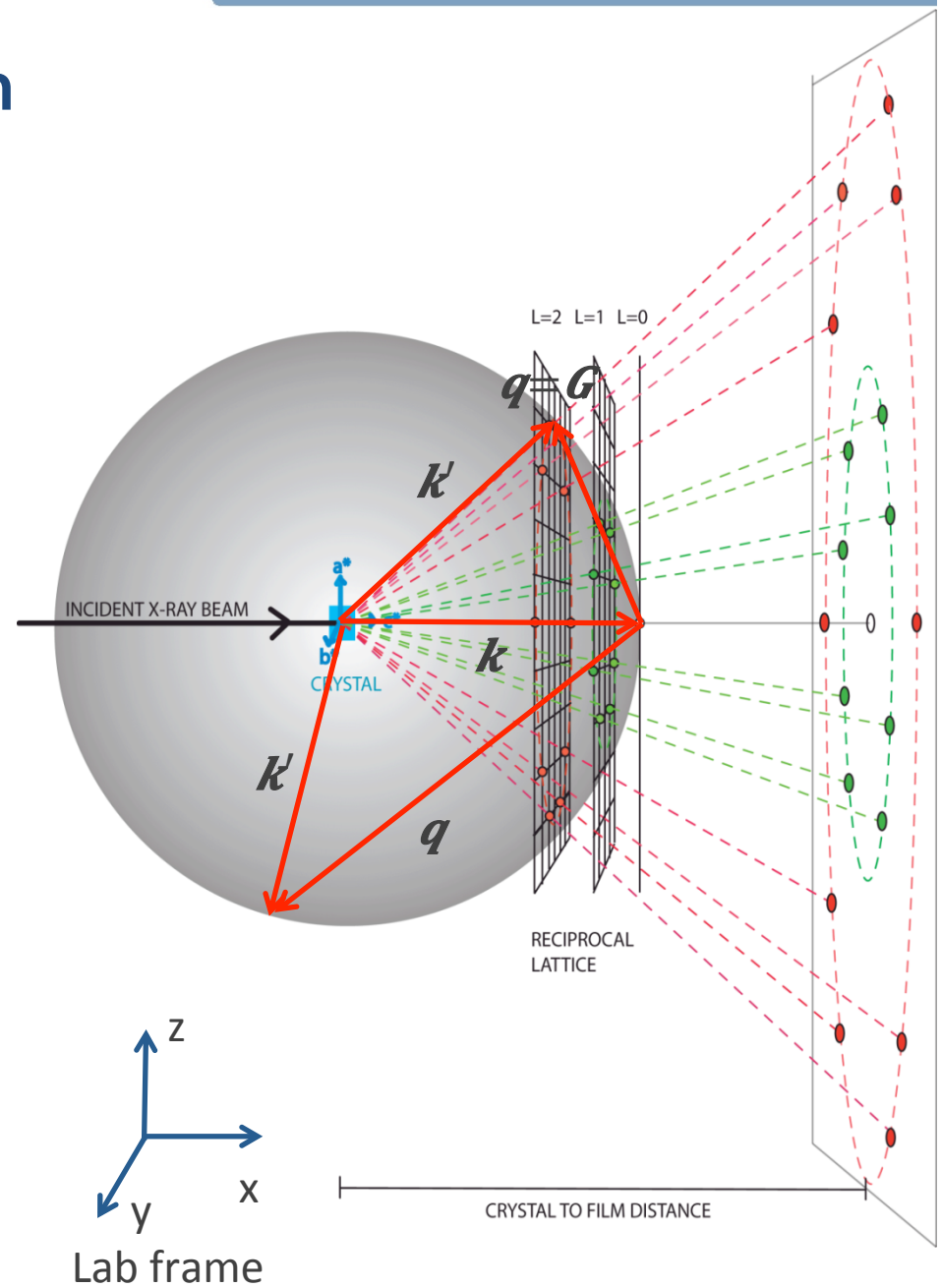
Ewald sphere Construction

- Diffraction occurs when Laue condition is fulfilled

$$\boldsymbol{q} = \boldsymbol{G}$$

$\boldsymbol{q} = \boldsymbol{k}' - \boldsymbol{k}$: wave vector transfer
$\boldsymbol{G}$: reciprocal lattice vector

- Ewald sphere construction
  - Draw a sphere with radius $|k|$ centered at the sample position (in the lab frame)
  - Superimpose the reciprocal space with its origin at the intersection of the incident beam and the Ewald sphere surface.
  - Reciprocal lattices falling on the sphere surface give diffractions.



3D structure indexing in supported organized films

- Ewald sphere is defined in the lab frame; reciprocal space lattices are conveniently defined in the sample frame. The two frames are related by an incident angle dependent rotation matrix

$$R_y(\alpha)=\begin{bmatrix}\cos\alpha & 0 & \sin\alpha \\ 0 & 1 & 0 \\ -\sin\alpha & 0 & \cos\alpha\end{bmatrix}$$

- Reciprocal lattice vector in the lab frame is obtained from the sample frame through a rotation operation

$$(G_x, G_y, G_z) = R_y \boldsymbol{G} = R_y (h\boldsymbol{a}_1^* + k\boldsymbol{a}_2^* + l\boldsymbol{a}_3^*).$$

- Allowed diffractions for lattice points on Ewald sphere surface

$$|\boldsymbol{G}_{lab} - \boldsymbol{k}|^2 - |\boldsymbol{k}|^2 = (G_x - k)^2 + G_y^2 + G_z^2 - k^2 \le \Delta G^2$$

ΔG accounts for the finite size of Bragg peak in the reciprocal space and any mosaicity of the domains.

- Wave vector transfer (q_x, q_y, q_z) is defined in the sample frame

3D structure indexing in supported organized films

- Domains of surface supported structures often have a statistical orientation distribution with respect to surface normal. Assume the orientation is isotropic in the surface plane, which is often true for most self-assembled structures; thus the reciprocal lattice points become a set of rings (2D powers), dependent only on in-plane $q_{\parallel} = \sqrt{q_x^2 + q_y^2}$
- Laue condition and the rotation operation of q are given by

$$G_x^2 + G_y^2 + G_z^2 - q_{\parallel}^2 + q_z^2 + q_z (G_x \sin\alpha - G_z \cos\alpha) = 0$$
$$-G_x \sin\alpha + G_z \cos\alpha = q_z$$

- Solve these equations simultaneously for $(q_{\parallel}, q_z)$. Thus the outgoing angles are

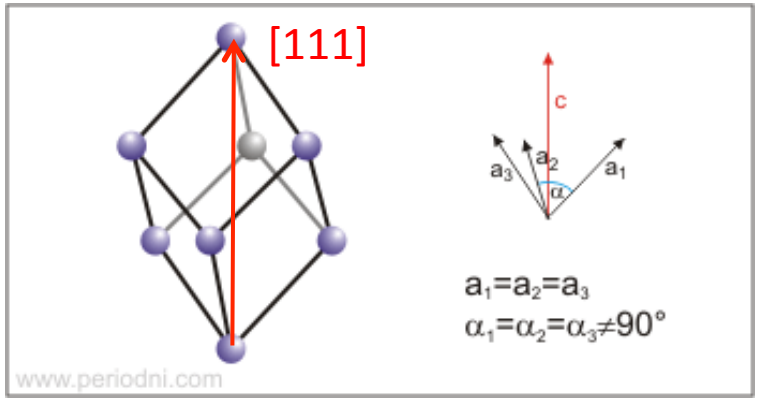
$$\alpha_f = \arcsin\sqrt{\left(\frac{q_z}{k}\right)^2 + \sin^2\alpha_i - \frac{2q_z}{k}\sqrt{n^2 - 1 + \sin^2\alpha_i}}$$ Exit angle (reflection)

$$\alpha_f = \arcsin\sqrt{\left(\frac{q_z}{k}\right)^2 + \sin^2\alpha_i + \frac{2q_z}{k}\sqrt{n^2 - 1 + \sin^2\alpha_i}}$$ Exit angle (transmission)

$$2\theta = \arccos(\cos^2\alpha_f + \cos^2\alpha_i - (q_{\parallel}/k)^2 - 2\cos\alpha_f \cos\alpha_i)$$ In-plane angle

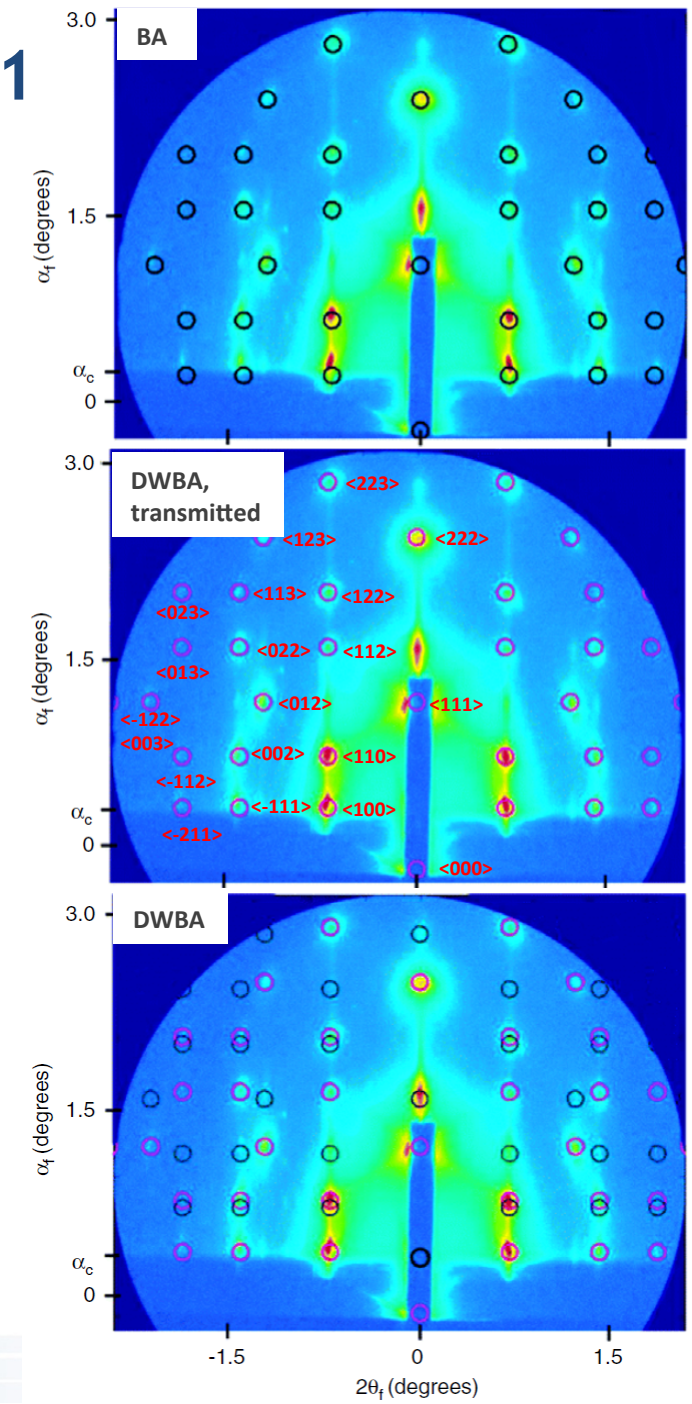
- Softwares: NanoCell (Mathematica, Hillhouse at Washington U.), GIXSGUI (Matlab, 8ID/APS/ANL), and Byeongdu Lee (APS/ANL)'s code.

3D structure indexing - example #1

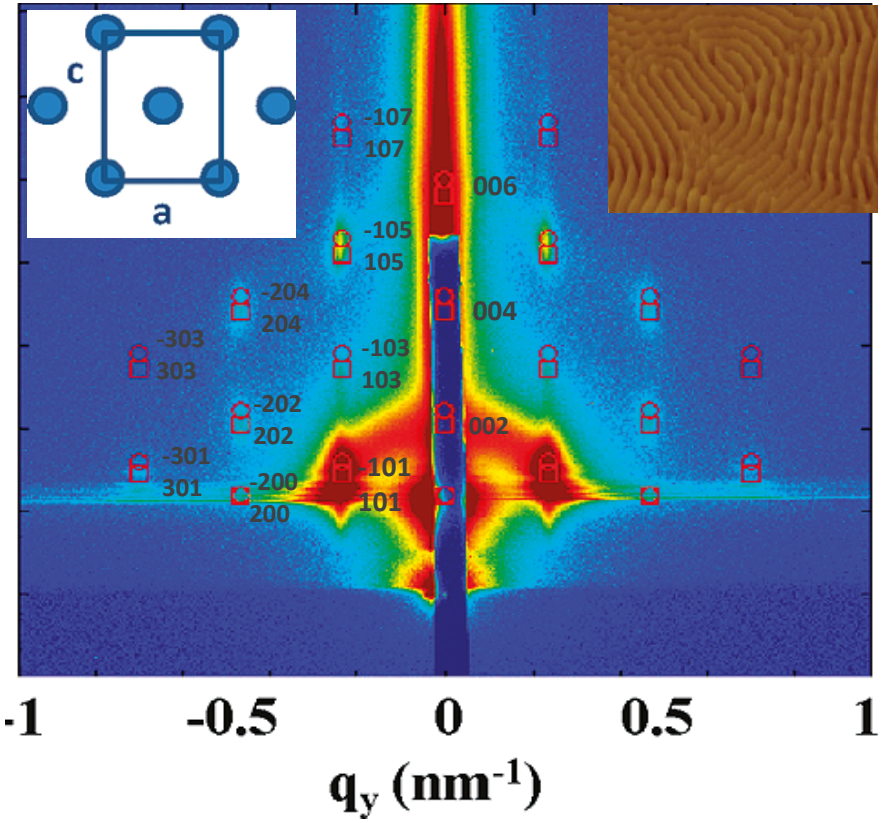


- Rhombohedral nanoporous silica thin film with R-3m symmetry, a=114 A and α=87°
- [111] direction perpendicular to the silicon substrate
- E=7.35 KeV, and incident angle is 0.23°
- Born approximation does not work well when exit angle is close to the critical angle.
- Born approximation does not predict some peaks which arises from the transmitted and reflected scattering channels.

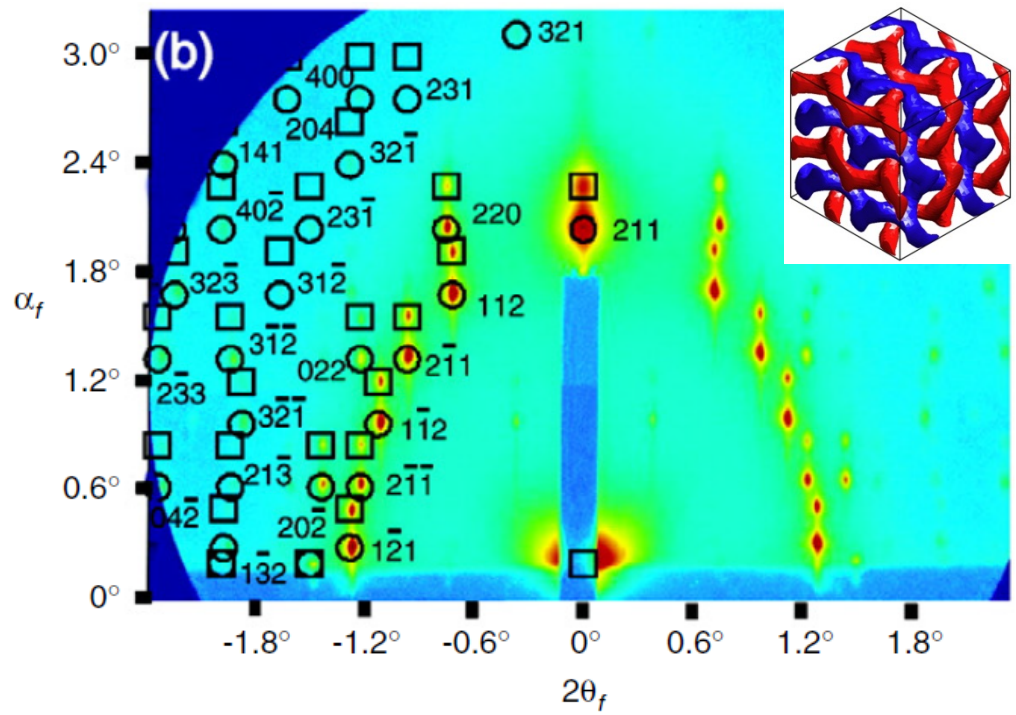
M. Tate et al., JPCB 110, 9882 (2006)



3D structure indexing – more examples



Hexagonally closely packed (HCP) cylinders self-assembled in PtBMA-PMMA block-copolymer films
Y. Sun, et al., Macromolecules 44, 6525 (2011)



Double-gyroid porous film on FTO substrate
V. Urade et al., Chem. Mater. 19, 768 (2007)

Textured films

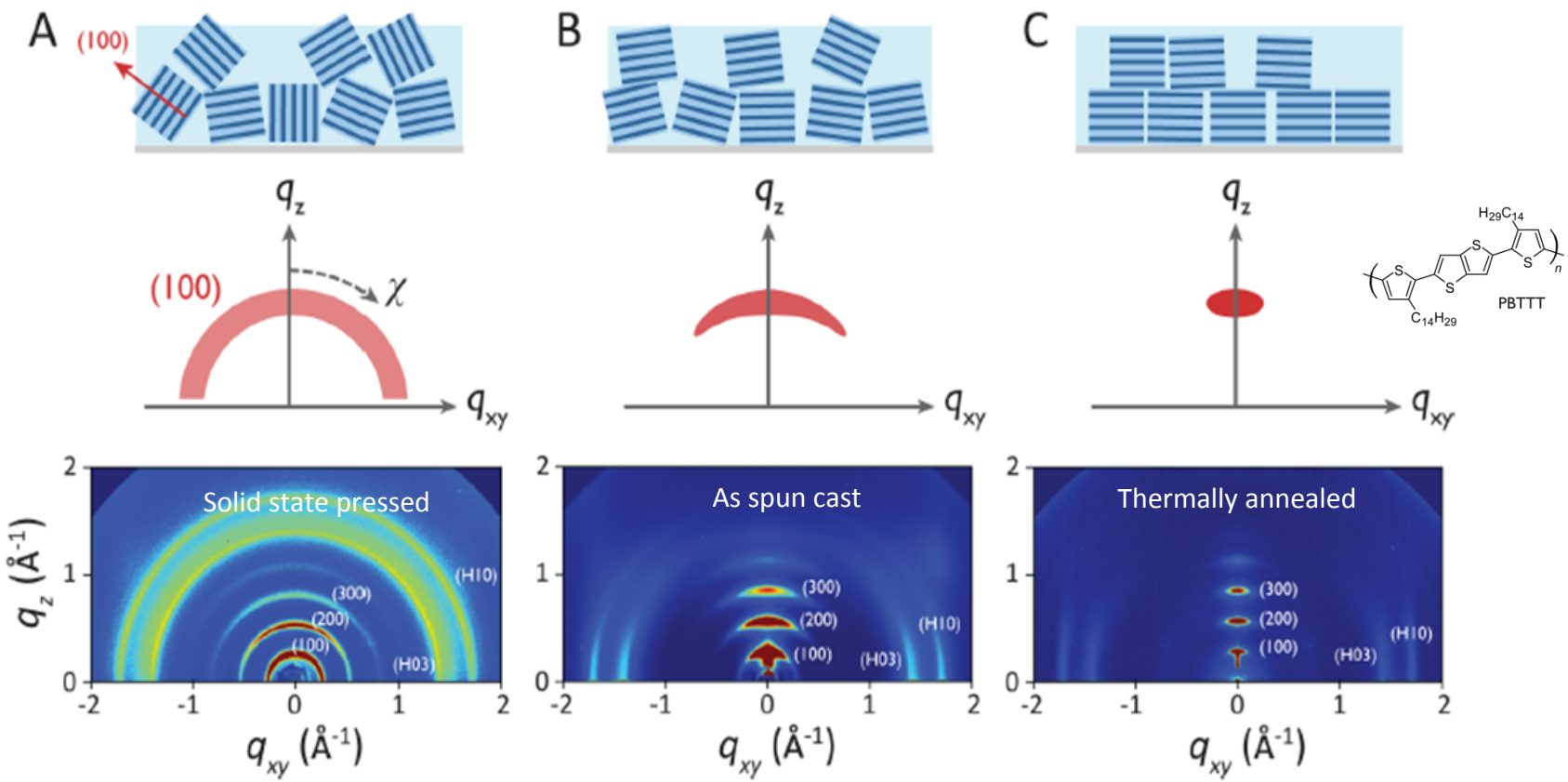
- In 2D powders, a well-aligned axis is perpendicular to the substrate and rotational averaging with respect to the surface normal results in a rotationally homogeneous scattering intensity.
- In textured films, further ordering may exist, and structures may show a preferential orientation with respect to the substrate.
- Textured appear more often in thin films of self-assembled organic small molecules where fine crystallites form and exhibit varying degrees of order and preferred orientation.
- For detailed formula, refer to Dag W. Breiby, et al., Simulating X-ray diffraction of textured films, J. Appl. Cryst. (2008). 41, 262–271

Textured films

Randomly oriented crystals

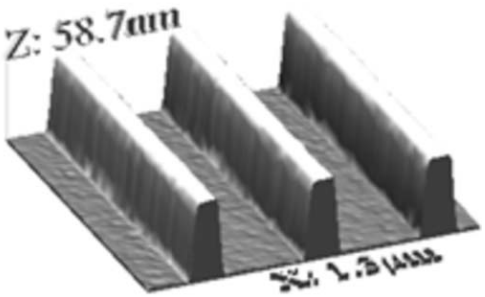
Broad distribution of crystal orientation

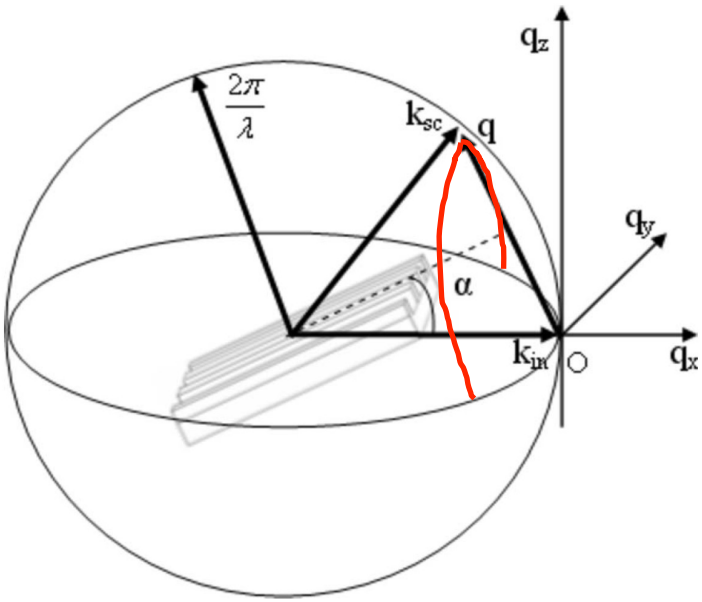
Highly oriented



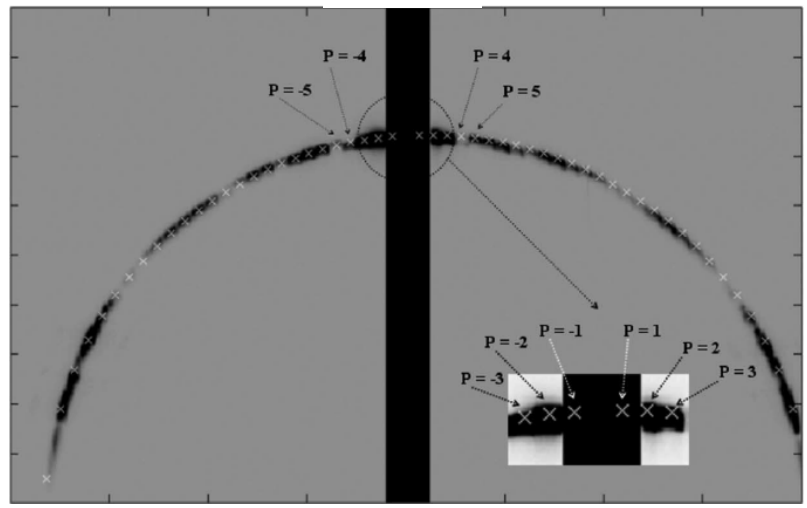
J. Rivnay, et al., Chem. Rev. 112, 5488 (2012)

Thin film gratings

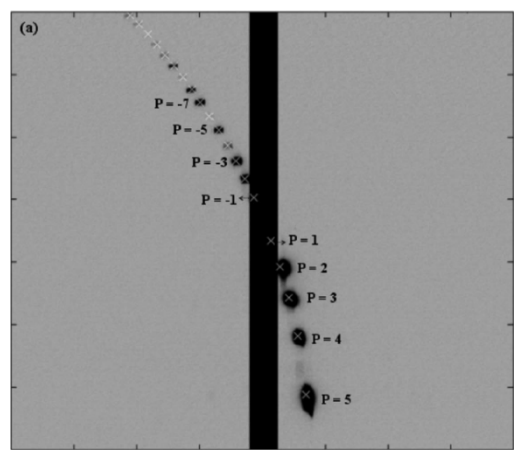




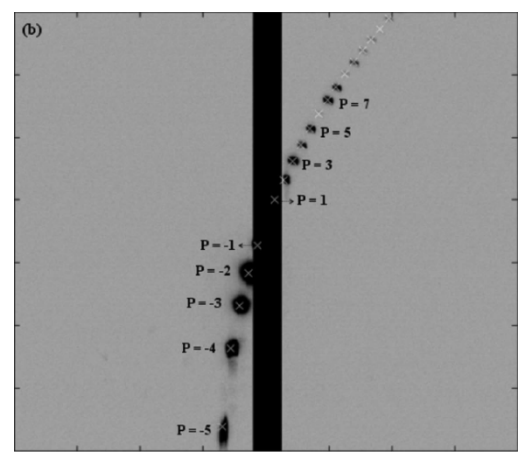
$\varphi = 0^\circ$

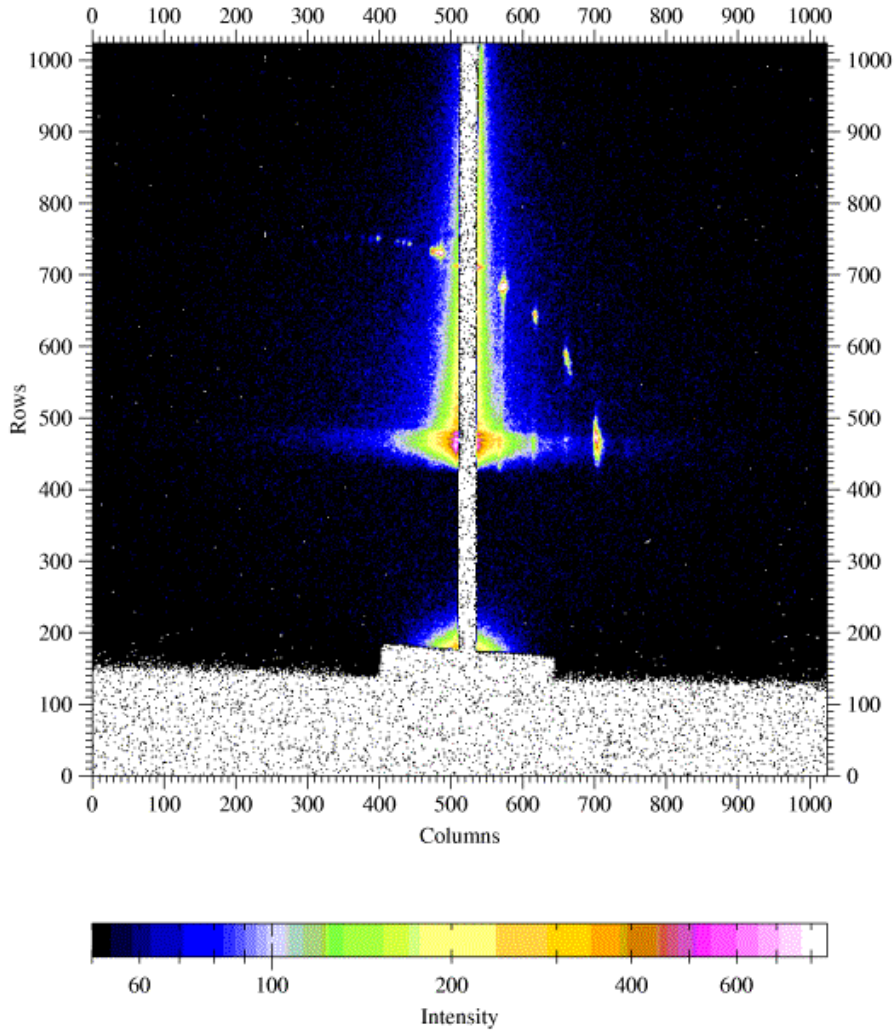


$\varphi = -1^\circ$



$\varphi = 1^\circ$



Minhao Yan and Alain Gibaud,
J. Appl. Cryst. 40, 1051 (2007)

Block copolymer thin film gratings on patterned substrates