Introduction to GISAXS

Joseph Strzalka
Time-Resolved Research
X-Ray Science Division

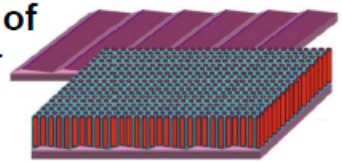
With material adapted from Zhang Jiang

Outline

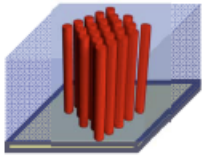
- GISAXS: Grazing Incidence SAXS
  - Motivation
  - Description
  - Experimental requirements
- Surface Sensitivity
- Complications from Surface Scattering

GISAXS Applications

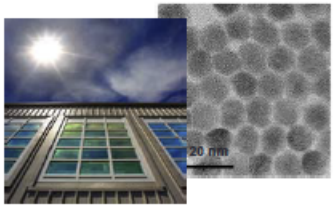
Long-range ordering of block copolymers for dense data storage
(Russell, UMass Amherst & Xu, UCB/MSD)



Composite membranes for artificial photosynthesis
(Segalman, UCB/MSD; Weber, EETD)

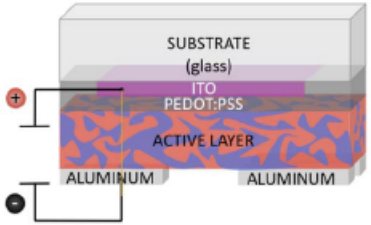


Inorganic nanocomposites for electrochromic windows (Milliron, Foundry)

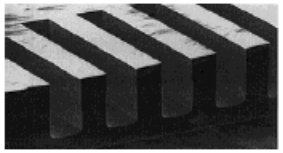


Batteries & fuel cells
(Balsara, UCB/MSD/EETD)

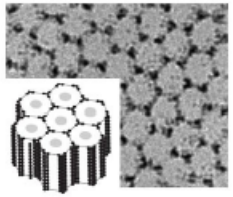
OPV BHJ materials
(McGehee, Stanford; Toney, SSRL/SLAC; Gomez, PSU; Kline, NIST; Liu, TMF; Ade, NCSU; Kramer, UCSB; Russell, UMass Amherst; Amassian, KAUST)



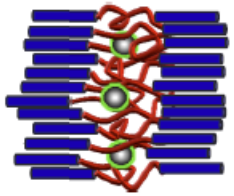
Lithographic patterning
(Soles, NIST; Ocko, BNL)



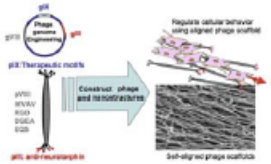
Self-assembly of nanoparticles in block copolymer thin films
(Xu, UCB/MSD)



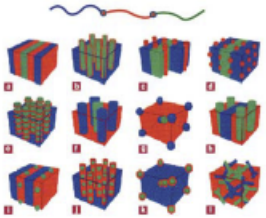
Nanocomposites for solar cells (Segalman, UCB/MSD & Urban, Foundry)



Virus nanofiber tissue engineering materials
(Lee, UCB/PBD)



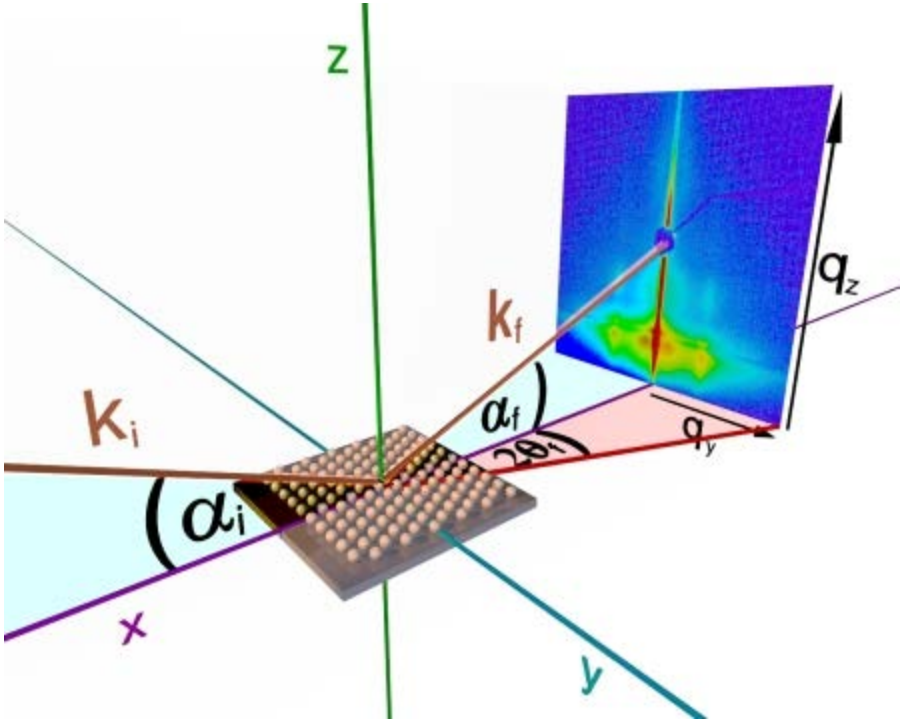
Block copolymer self-assembly
(Kramer, UCSB; Russell, UMass Amherst; Xu, UCB/MSD)



Elaine Chan, ALS and Jema Technologies LLC

Grazing Incidence X-ray Scattering (GIXS): what is it?

- Means of studying electron density contrast variations (structure) near surfaces and interfaces
- X-rays incident at grazing incidence
  - Limited penetration into sample means enhanced surface sensitivity
- Scattered x-rays observed with an area detector

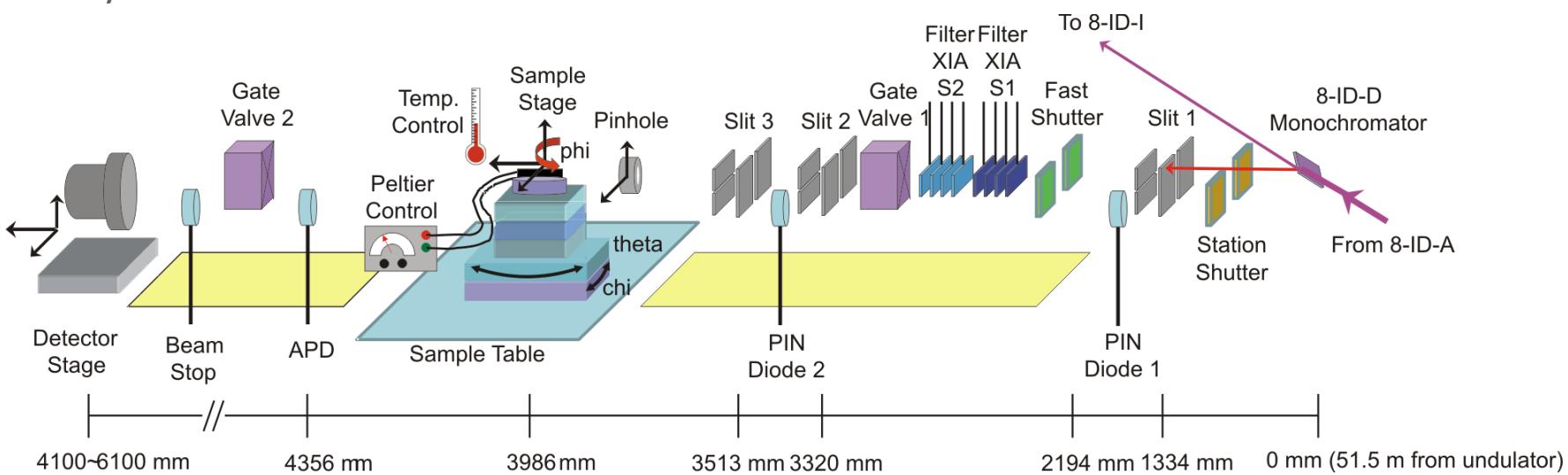


$$q_{x,y,z} = \frac{2\pi}{\lambda}\begin{bmatrix} \cos(\alpha_f)\cos(2\theta_f) - \cos(\alpha_i) \\ \cos(\alpha_f)\sin(2\theta_f) \\ \sin(\alpha_f) + \sin(\alpha_i) \end{bmatrix}$$

Images:
Prof. Andreas Meyer, U. Hamburg, www.gisaxs.de

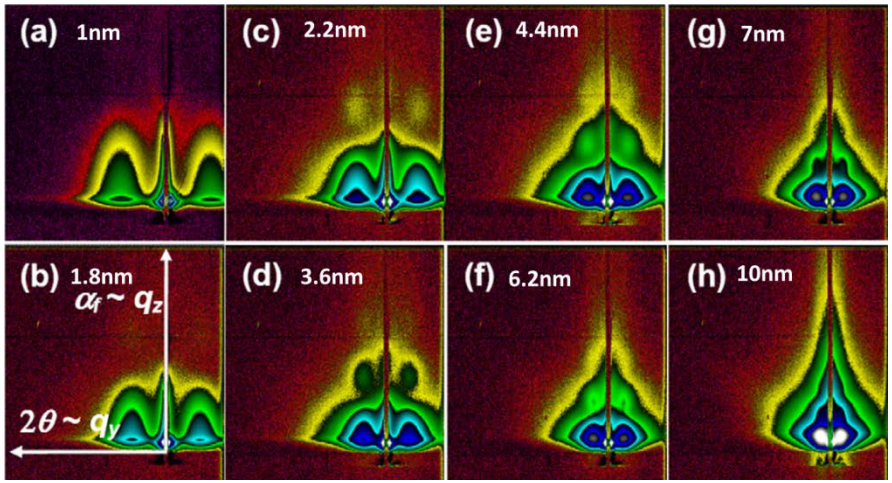
GISAXS Experimental Requirements

- Beam-defining and guard slits
- Area detector
- Diffractometer for sample positioning: 6 degrees of freedom:
  - x, y, z
  - Θ, χ, ϕ (pitch, roll, yaw)
- Extended beamstop
- Fast (point) detector for alignment
- Synchrotron source



GISAXS Advantages

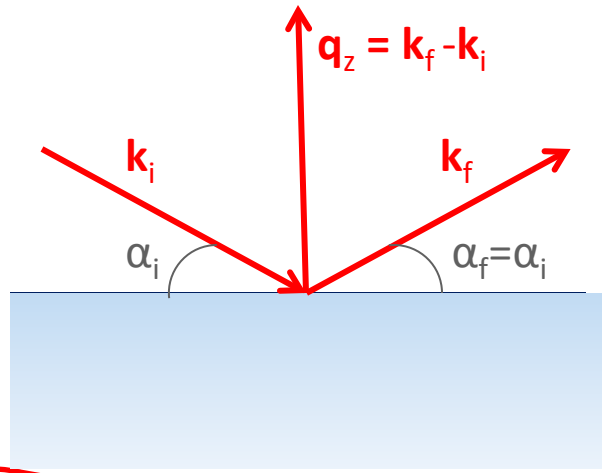
- In situ measurements
- No Scanning: time-resolved measurements
- Study buried structures
- Non destructive
- Probe statistically relevant sample areas (mm^2)



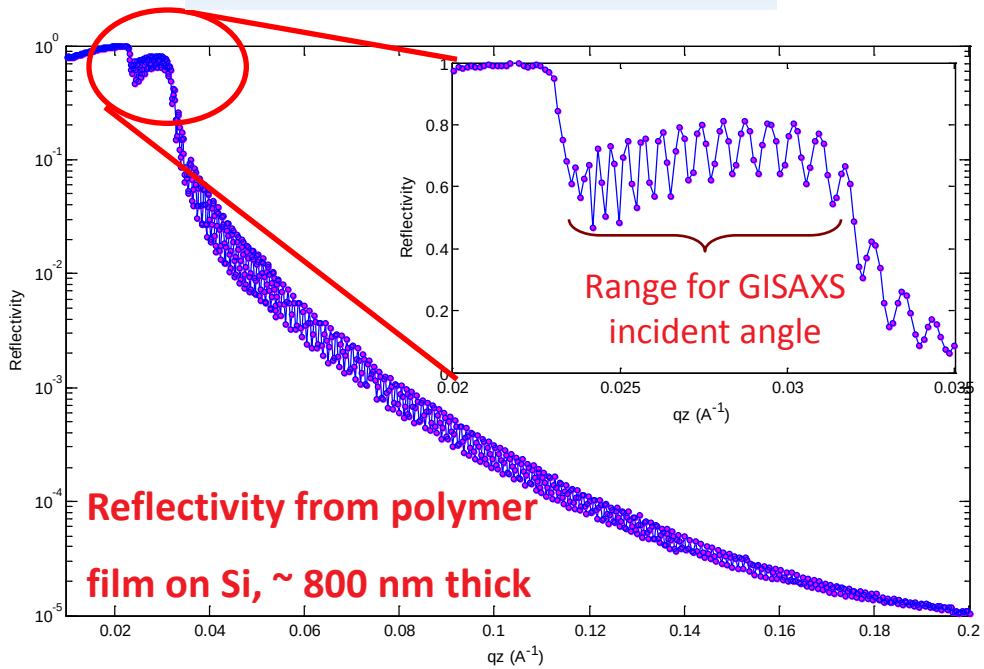
Growth of Ag nano-island on MgO(001) surface studied by GISAXS

Revenant et al., PRB, 79, 1 (2009)

X-ray reflectivity gives GISAXS surface sensitivity



- Point detector and collimation measure strictly along $q_z = (4\pi/\lambda)\sin(\alpha)$
- Resolution constant over entire q-range



- Total external reflection occurs at small angles (grazing incidence)
  - One critical angle for the polymer film α_{cp}
  - One critical angle for the Si support α_{cSi}
  - GIXS usually $\alpha_{cp} < \alpha_i < \alpha_{cSi}$ (penetrate thin film but not substrate → surface sensitivity)
- Reflectivity from a ~800nm polymer film supported on Si

Review of surface scattering basics - reflection and refraction

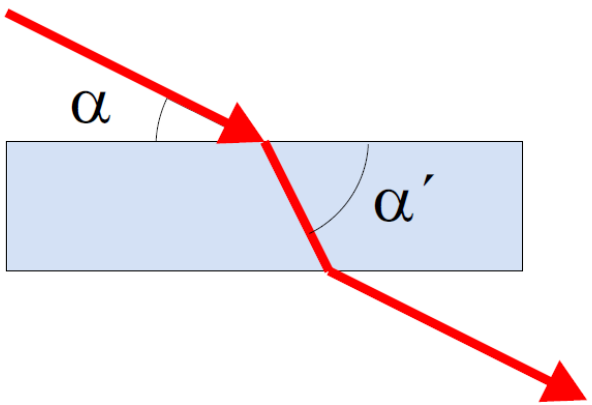
Index of refraction

$n \geq 1$

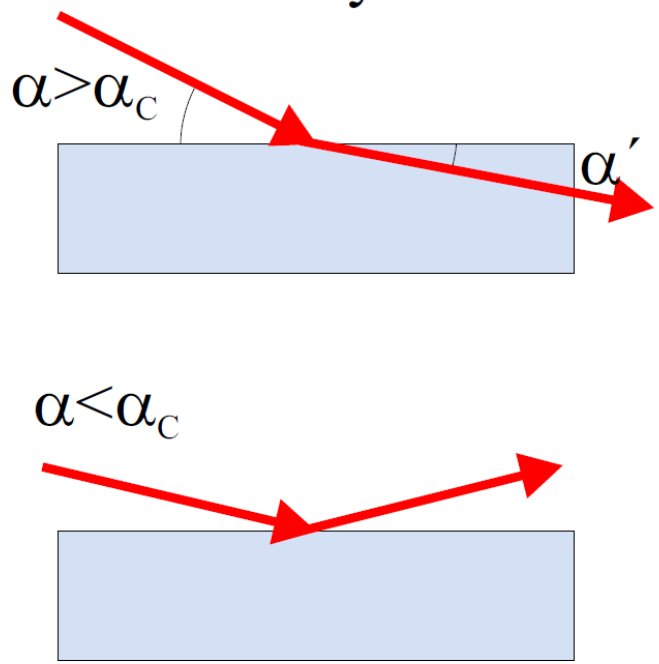
$n = 1 - \delta + i\beta$

$0 < \mathrm{Real}[n] \leq 1$

Light

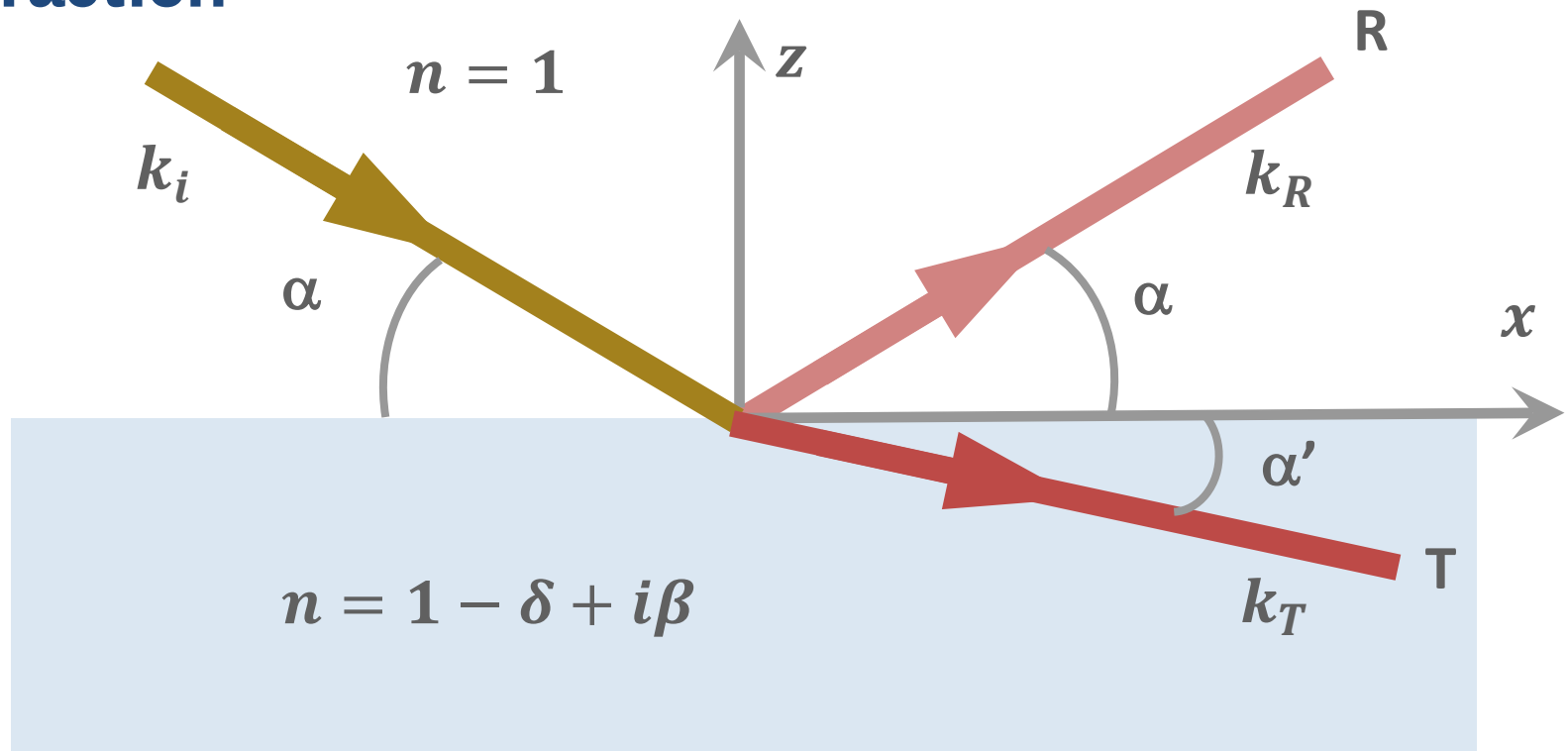


X-rays



Total external reflection

Review of surface scattering basics - reflection and refraction



Snell's law: $\cos\alpha = n\cos\alpha'$

Critical angle for total external reflection (α'=0):

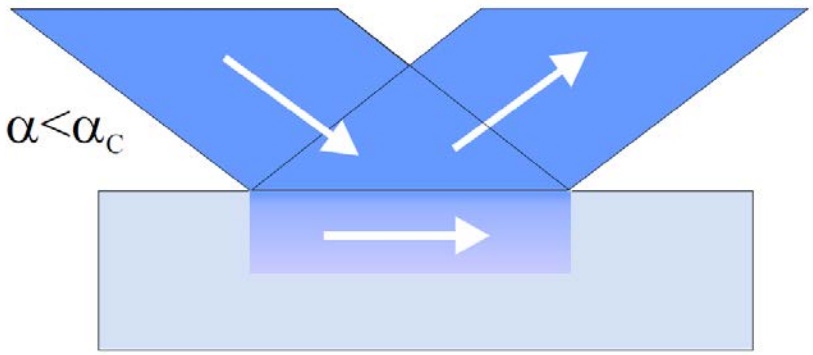
$$\alpha_c = \cos^{-1} n \approx \sqrt{2\delta}$$
$$= \lambda\sqrt{r_e\rho/\pi}$$

Typical $\delta \sim 10^{-5}$, so $\alpha_c \sim 0.1° - 0.5°$

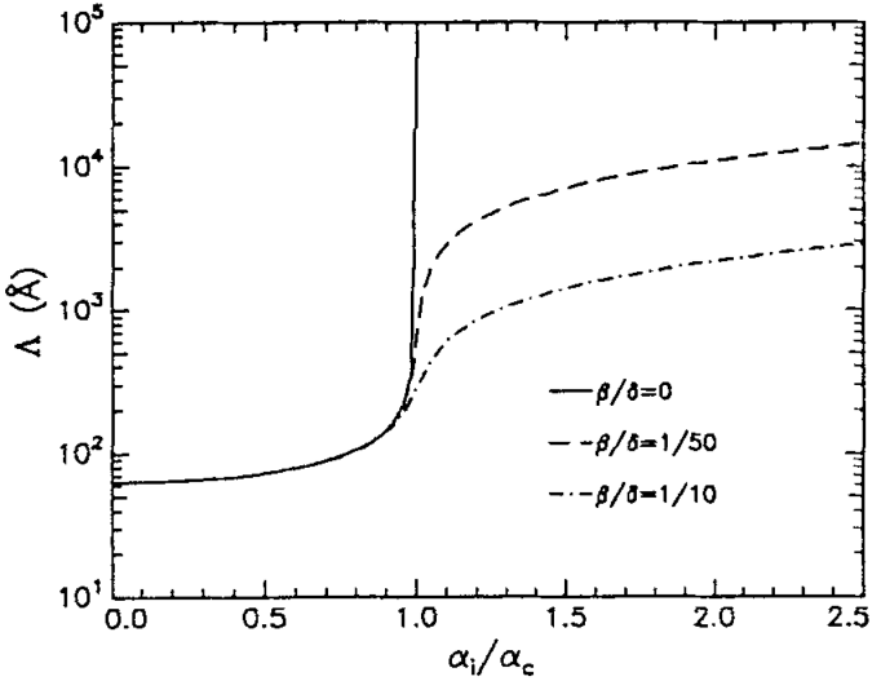
r_e: *e*- radius; ρ: *e*- density

Wave vector transfer for reflected beam $q_z = 2ksin(\alpha)$

Review of surface scattering basics - evanescent wave and penetration depth



Penetration depth on Si surface with λ=1.54A



- The reflection is almost 100%, and x-ray only penetrates a typical depth of a few nanometer.
- By tuning the incident angle, x-ray can be a *surface* sensitive technique

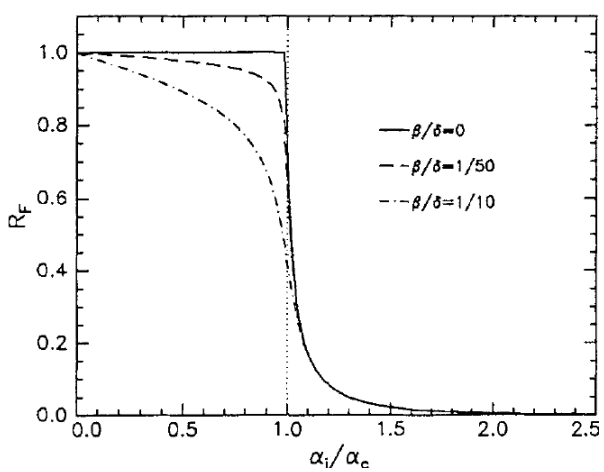
Review of surface scattering basics - Fresnel reflectivity and transmission

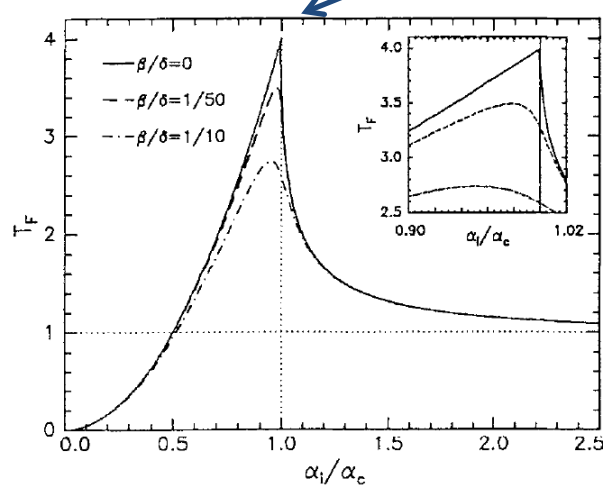
- Fresnel formulas: reflection and transmission coefficients

$$\begin{cases} r = \dfrac{k_{i,z} - k_{t,z}}{k_{i,z} + k_{t,z}} \\ t = \dfrac{2k_{t,z}}{k_{i,z} + k_{t,z}} \end{cases}$$

- Fresnel reflectivity: $R_F = |r|^2$
- Fresnel transmission: $T_F = |t|^2$

Yoneda peak





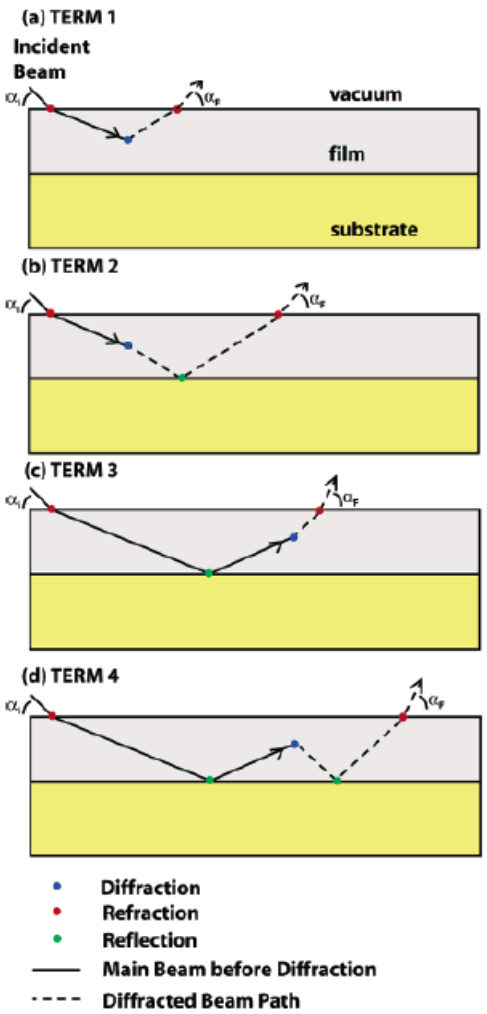
For silicon/vacuum interface, λ=1.54 A

- For reflectivity from multilayers, use recursive method of Parratt

Distorted Wave Born Approximation

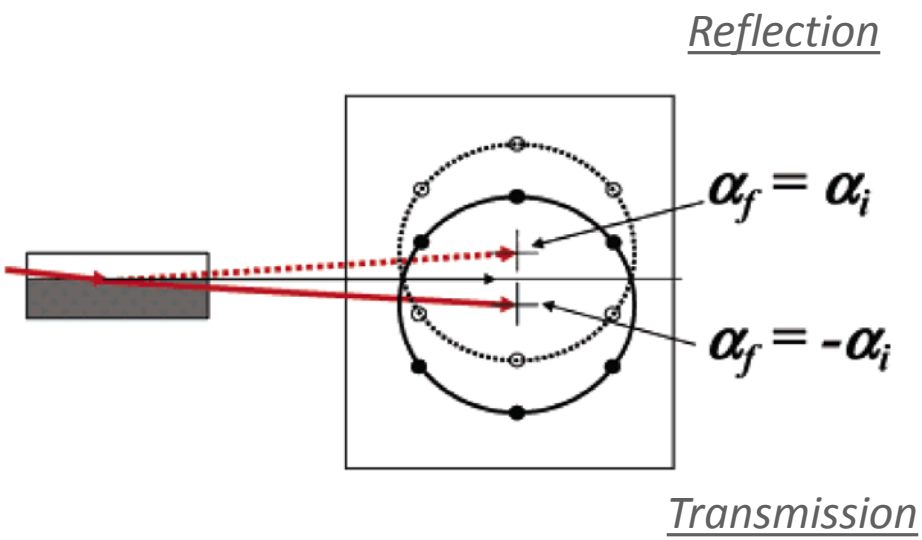
- Born approximation, used in SAXS, is insufficient for calculating scattering from surfaces
- Treat scattering from buried structures as perturbations of the incident, reflected and refracted waves
- Four terms to describe the scattering from surfaces

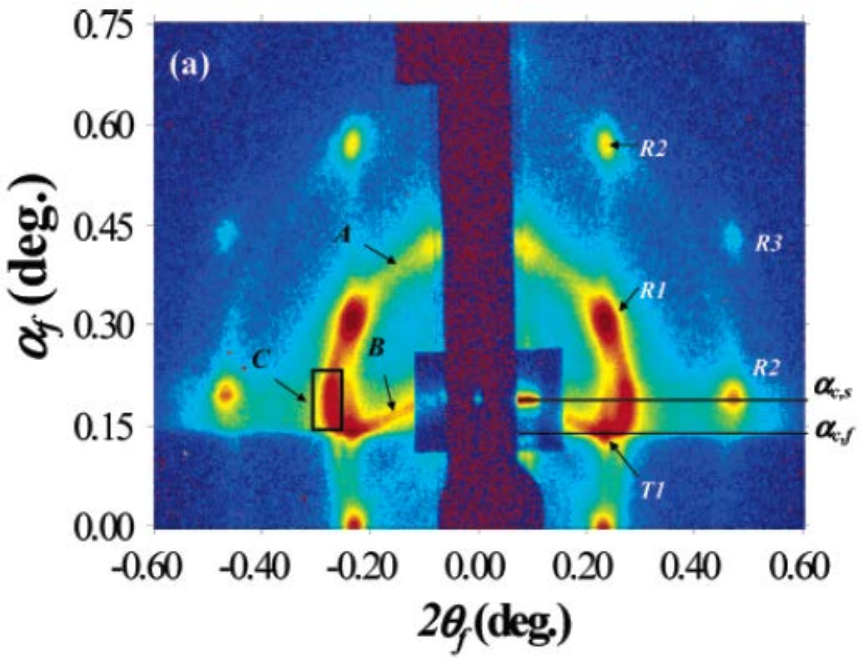
$$q_{z,1} = k_{f,z} - k_{i,z}$$
$$q_{z,2} = -k_{f,z} - k_{i,z}$$
$$q_{z,3} = k_{f,z} + k_{i,z}$$
$$q_{z,4} = -k_{f,z} + k_{i,z}$$



Transmission and reflection channels

Both transmitted and reflected beams contribute to observed scattering.





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

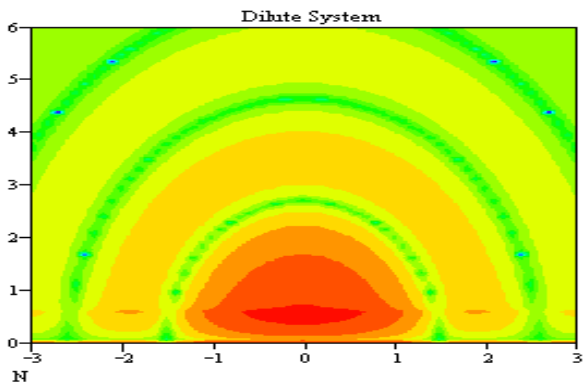
Form factor and structure factor

- For samples with statistical distribution of particle size and positions (not gratings, not single crystals) – such as self-assembled block-copolymers on flat surfaces, statistical averaging is applied

$$\left(\frac{d\sigma}{d\Omega}\right) \propto \left\langle \left|\sum_{\boldsymbol{r}_j} f_j(\boldsymbol{Q}) e^{i\boldsymbol{Q}\cdot\boldsymbol{r}}\right|^2 \left|\sum_{\boldsymbol{R}_n} e^{i\boldsymbol{Q}\cdot\boldsymbol{R}_n}\right|^2 \right\rangle = \langle |F(\boldsymbol{Q})|^2 \rangle S(\boldsymbol{Q})$$

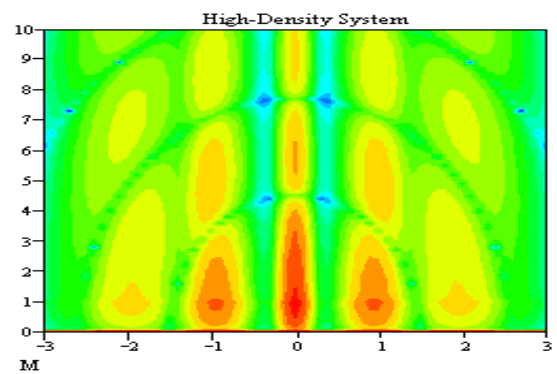
- F is the form factor; S is the structure factor to describe the statistical position correlation between particles.

Dilute nanoparticles



Byeongdu Lee

2D monolayer of nanoparticles



Zhang Jiang

D. Smilgies, http://staff.chess.cornell.edu/~smilgies/gisaxs/GISAXS.php