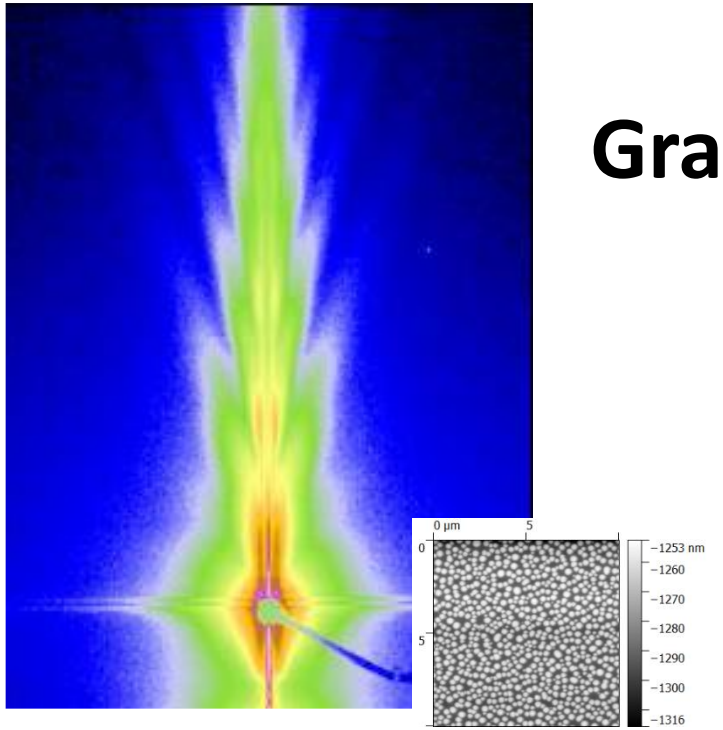
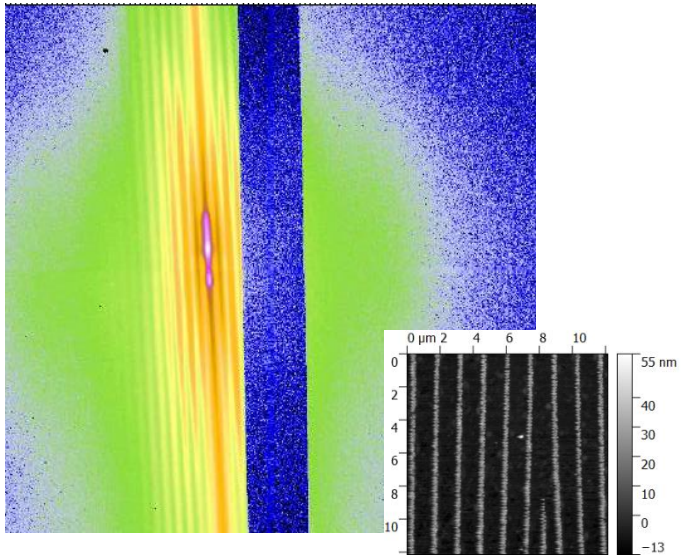


Grazing Incidence X-ray Scattering and Diffraction

Theory and applications

Giuseppe Portale
NWO, DUBBLE@ESRF
European Synchrotron Radiation Facility
Grenoble (France)



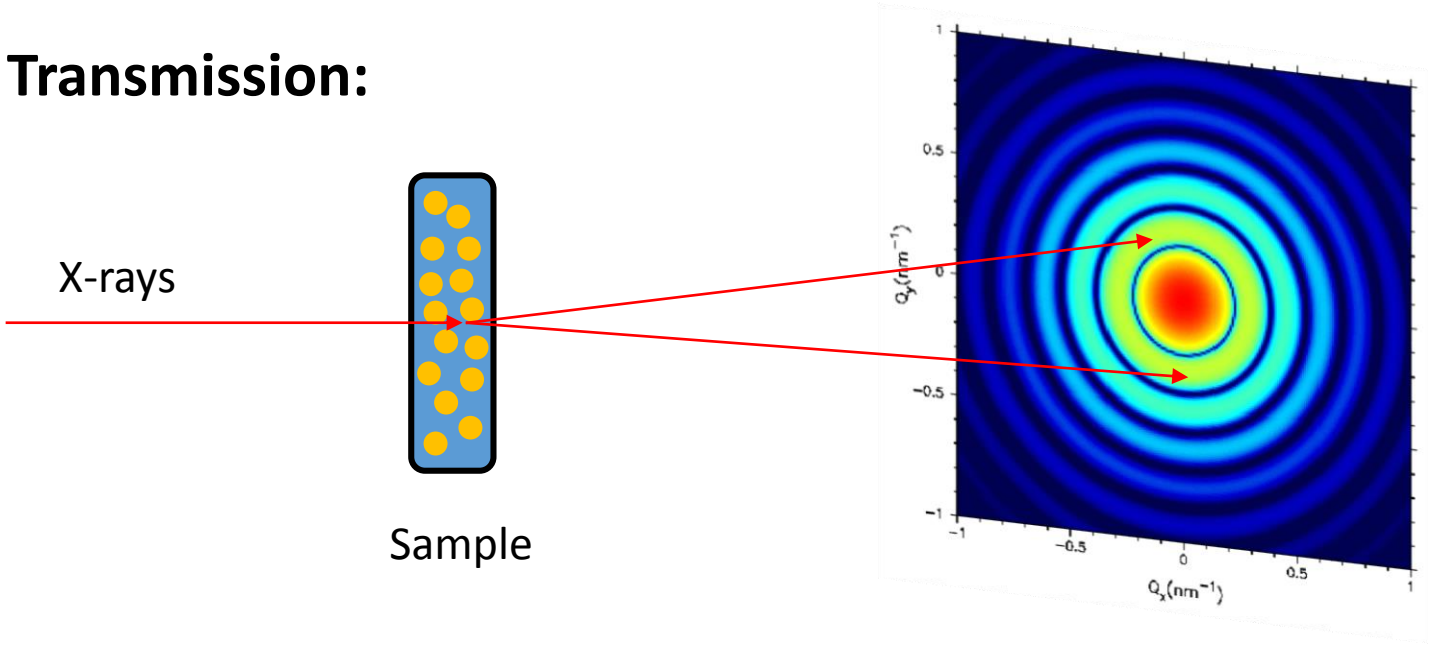
SyNeW 2015 Mini-school, Uthecht June 2, 2015

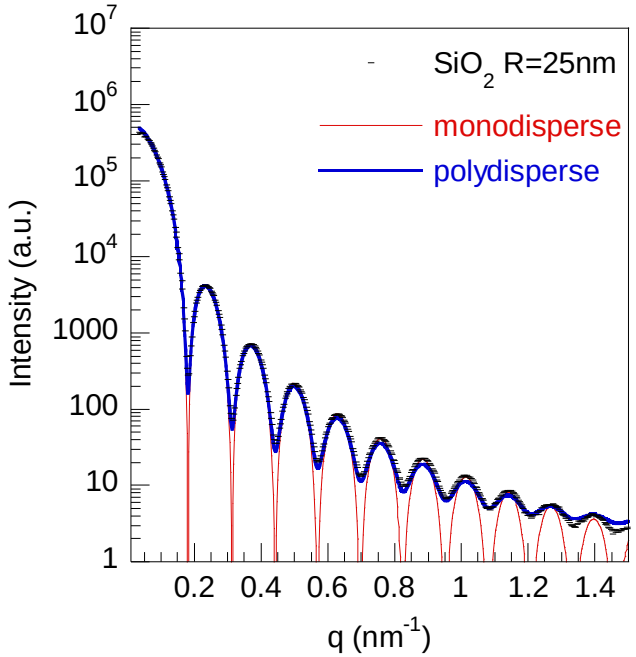
Outline

- **Experimental considerations**
- **Brief introduction to the Distorted Wave Born Approximation**
- **Example GISAXS**
- **GIWAXS + example**

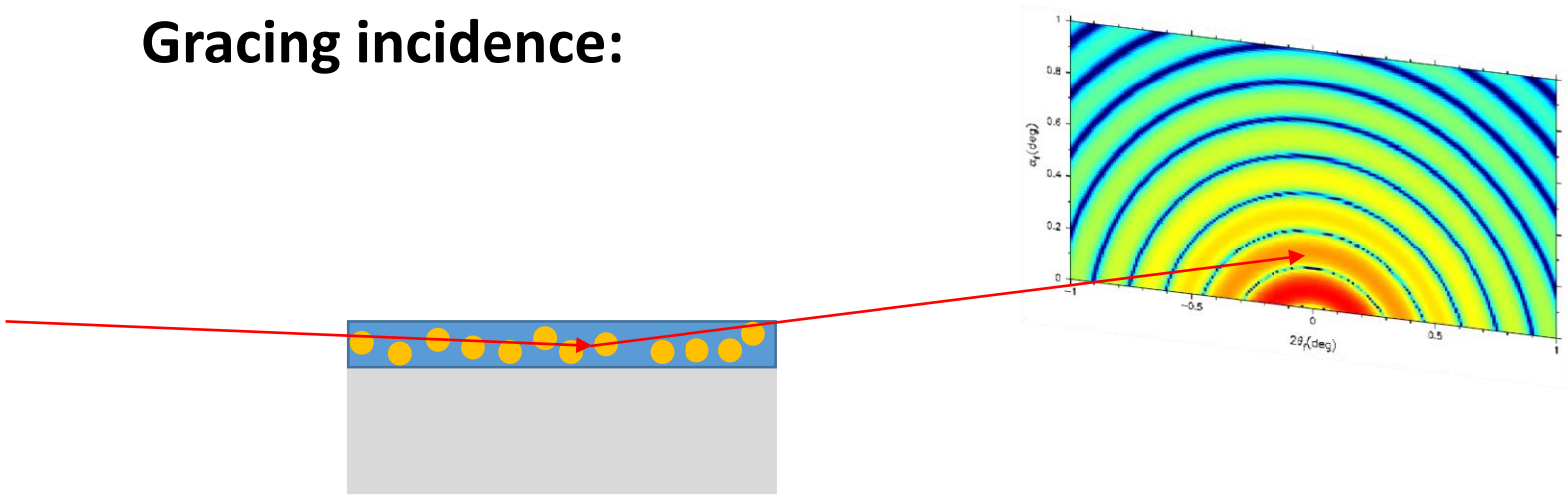
Transmission vs Gracing incidence geometry

Transmission:



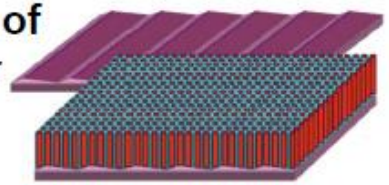


Gracing incidence:

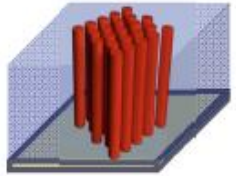


GISAXS and GIWAXS applications

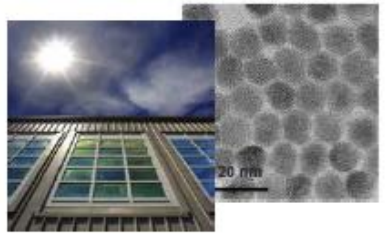
Long-range ordering of block copolymers for dense data storage



Composite membranes for artificial photosynthesis

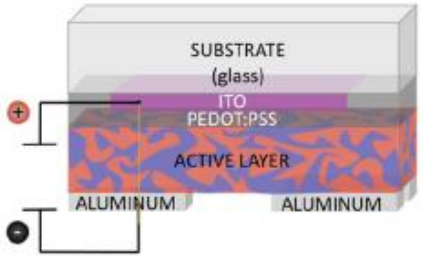


Inorganic nanocomposites for electrochromic windows

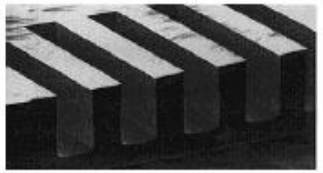


Batteries & fuel cells

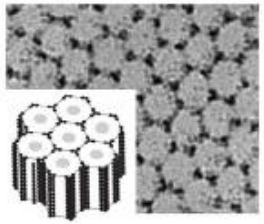
OPV BHJ materials



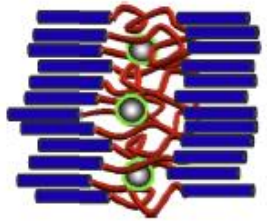
Lithographic patterning



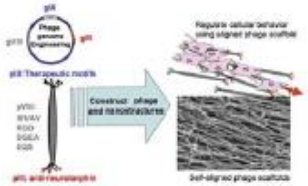
Self-assembly of nanoparticles in block copolymer thin films



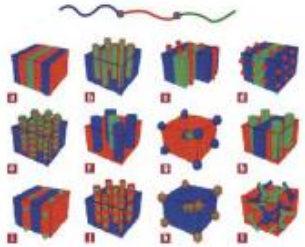
Nanocomposites for solar cells



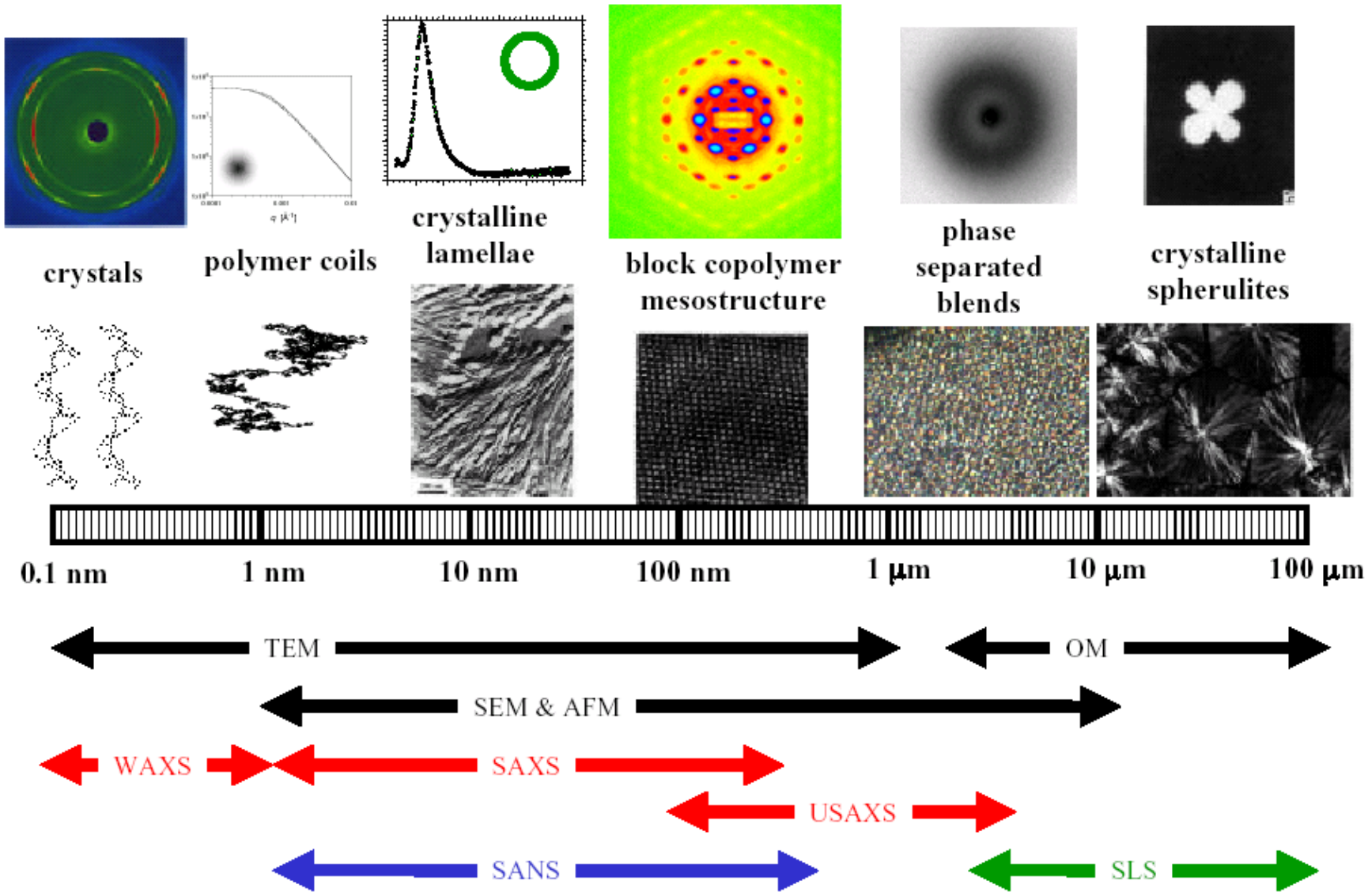
Virus nanofiber tissue engineering materials



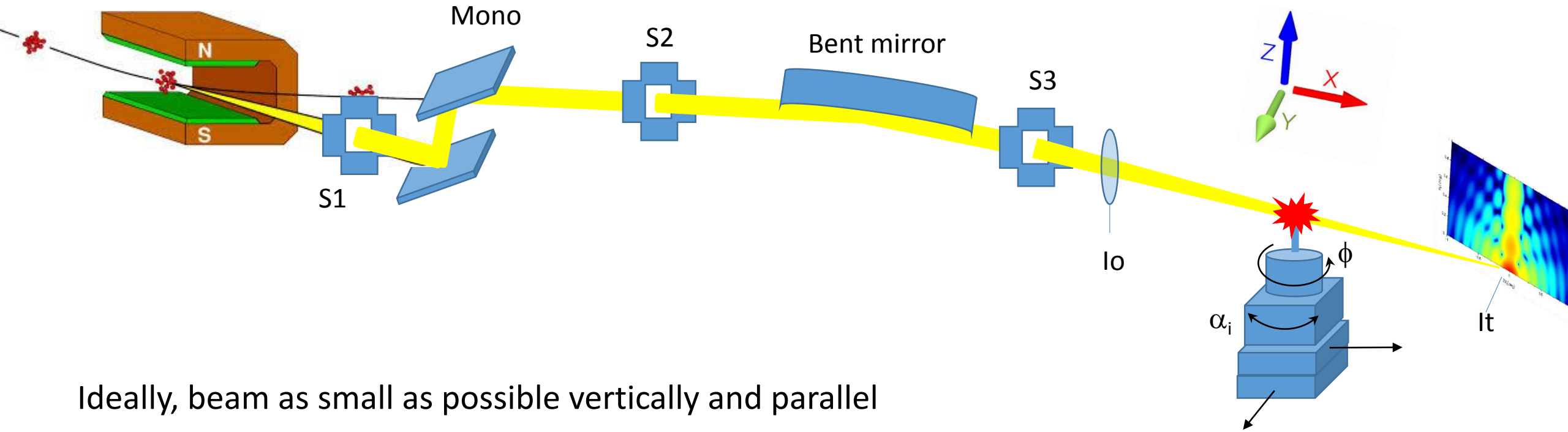
Block copolymer self-assembly



Probing polymers and soft matter length scales



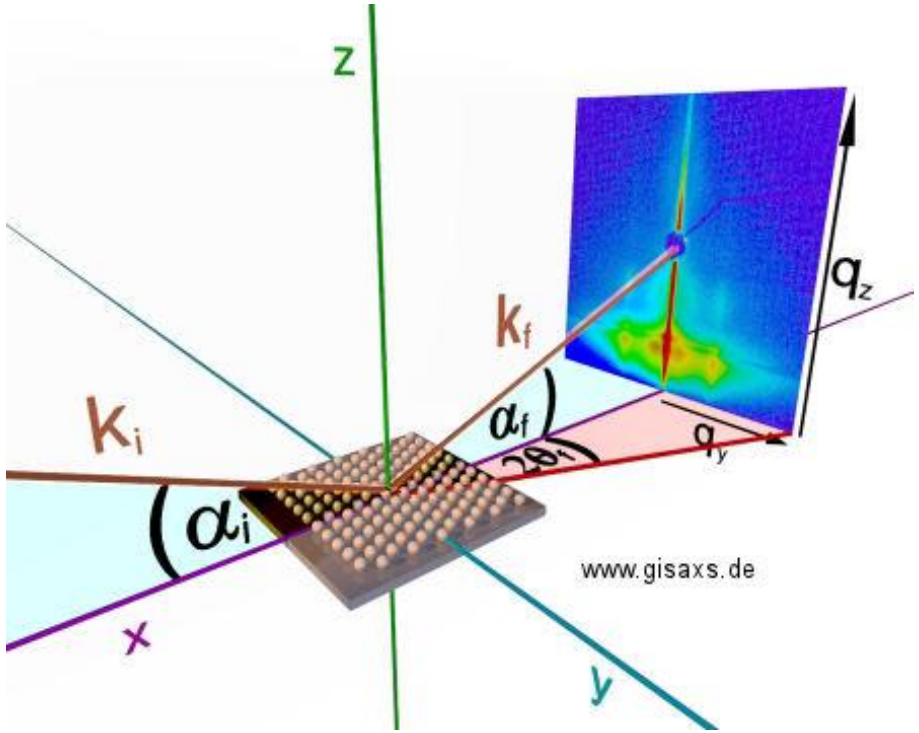
Experimental setup & conventions



Ideally, beam as small as possible vertically and parallel

Grazing Incident Small Angle X-ray Scattering

Characterization of **nanoscale density correlations** and/or the **shape of nanoscopic objects** at surfaces, at buried interfaces, or in thin films

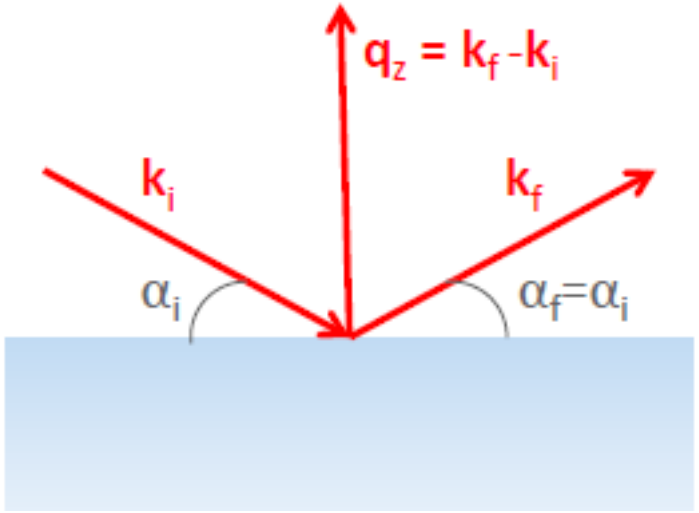


$$q_{x,y,z} = \frac{2\pi}{\lambda}\begin{bmatrix}\cos(\alpha_f)\cos(2\theta_f) - \cos(\alpha_i) \\ \cos(\alpha_f)\sin(2\theta_f) \\ \sin(\alpha_f) + \sin(\alpha_i)\end{bmatrix}$$

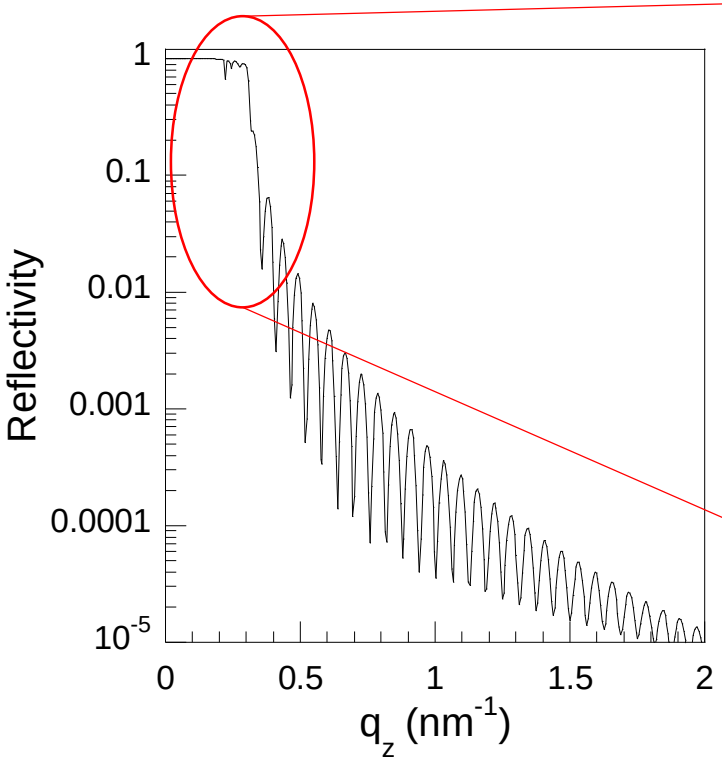
- 🙂 Surface sensitive – possibility to study structures at the interfaces
- 🙂 Surface sensitive (minimum penetration depth 10 nm)
- 🙂 High scattering intensity ideal to perform in-situ and time-resolved study
- 🙂 2D-GISAXS: lateral and normal ordering probed at the same time
- ☹ Complex data analysis

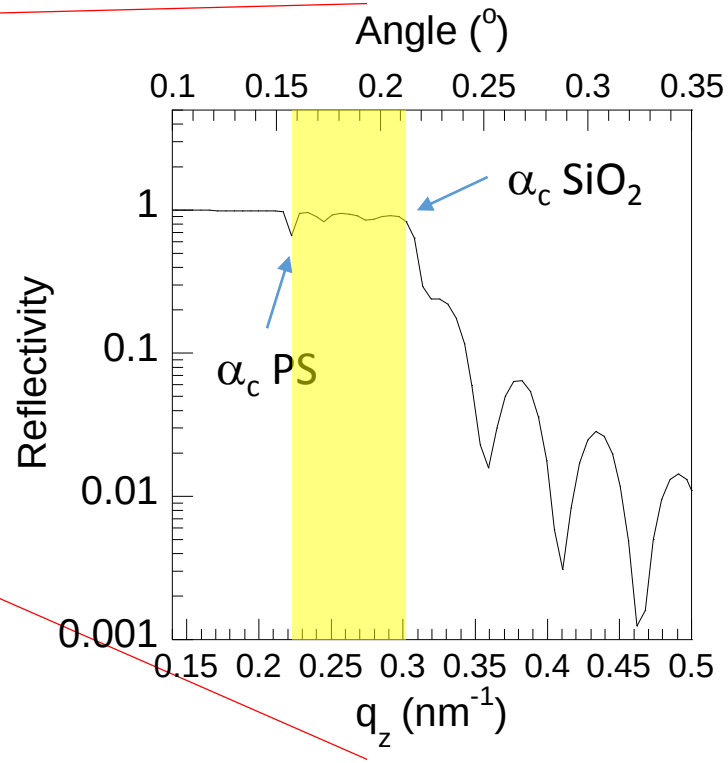
Image: Prof. Andreas Meyer, Uni Hambourg

X-ray reflectivity (XRR)



- Measure strictly only along $q_z = \frac{4\pi}{\lambda}\sin(\alpha)$
- Point detector with collimator
- Information about $\rho_e(z)$, roughness, thickness





Usually in GIXS α_c (polym) < α_i < α_c (sub)

Regimes for GISAXS analysis

$\alpha_i < \alpha_c$ (polymer)	:	evanescent regime
α_c (polymer) $< \alpha_i < \alpha_c$ (substrate)	:	dynamic regime
$\alpha_i > \alpha_c$ (substrate)	:	kinematic regime

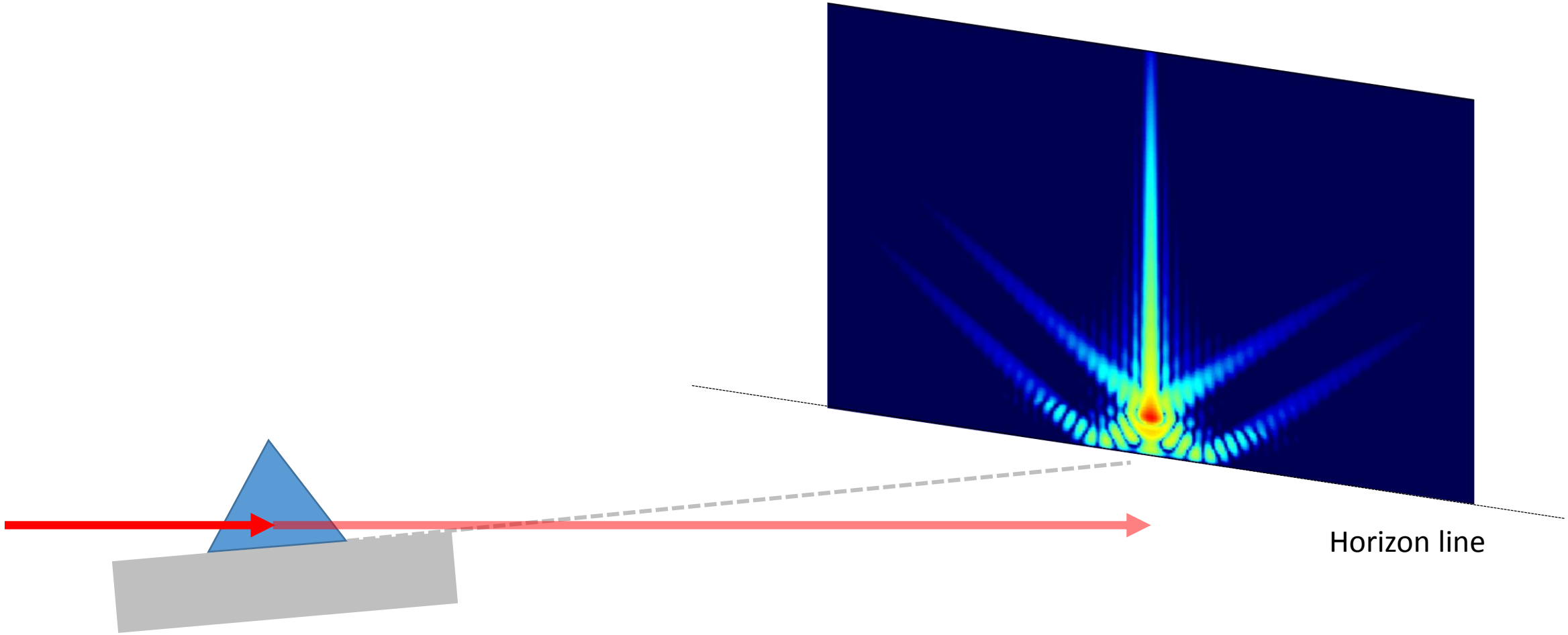
In the kinematic regime:

$$\frac{d\sigma}{d\Omega}(\boldsymbol{q}) = \frac{1}{N}\sum_i \sum_j F^i(\boldsymbol{q}) F^{j,*}(\boldsymbol{q}) exp\left[i\boldsymbol{q}(\boldsymbol{R}_{\parallel}^i - \boldsymbol{R}_{\parallel}^j)\right]$$

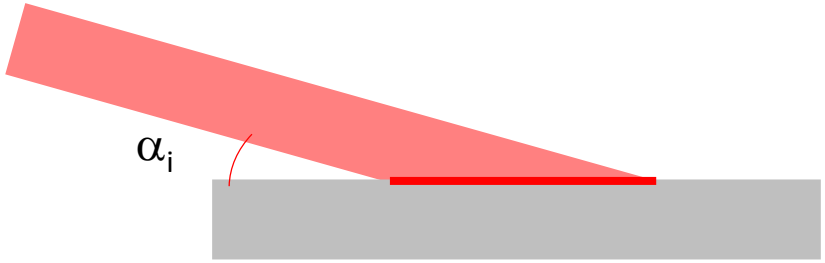
In the simple Born Approximation (BA):

$$F^i = \int_V \rho(\mathbf{r}) \exp(i\boldsymbol{q} \cdot \boldsymbol{r})\, d\boldsymbol{r}$$

Experimental considerations



Footprint of the beam:

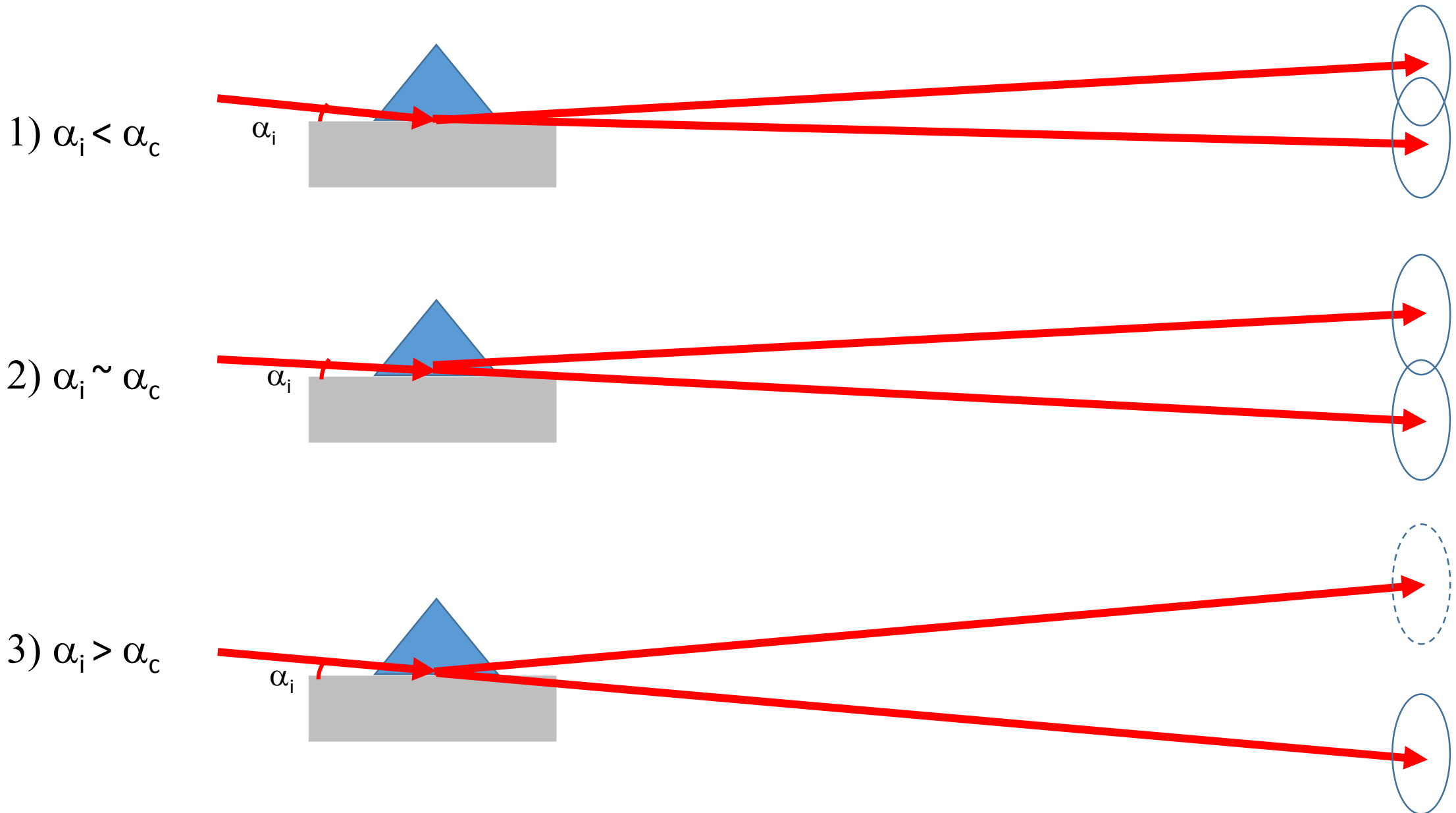


Beam 300 μm:

α_i = 0.1° → 17 cm

α_i = 0.5° → 3.4 cm

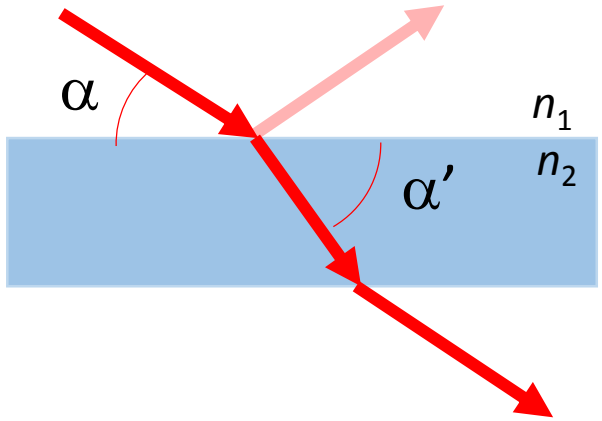
Effect of using a small incident angle



Surface scattering – reflection and refraction

Light

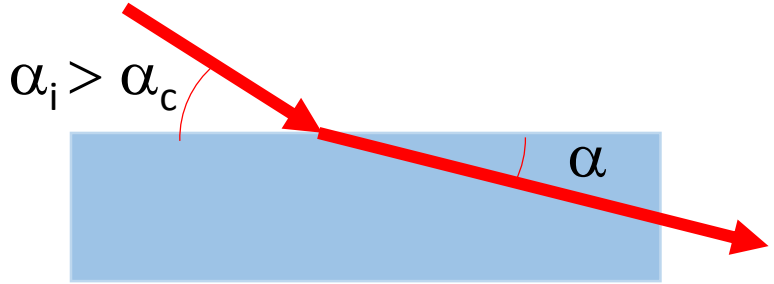
Index of refraction: $n \geq 1$



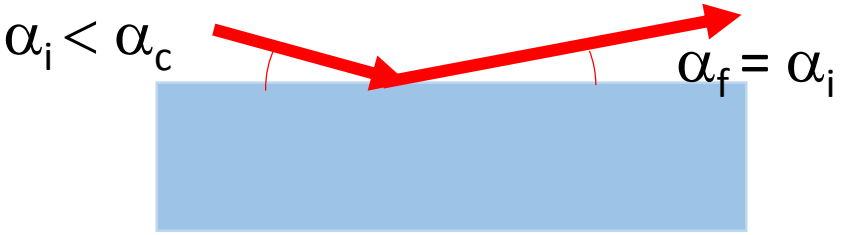
Snell's law: $n_1 \sin \alpha = n_2 \sin \alpha'$

X-ray

Index of refraction: $n = 1 - \delta + i\beta$



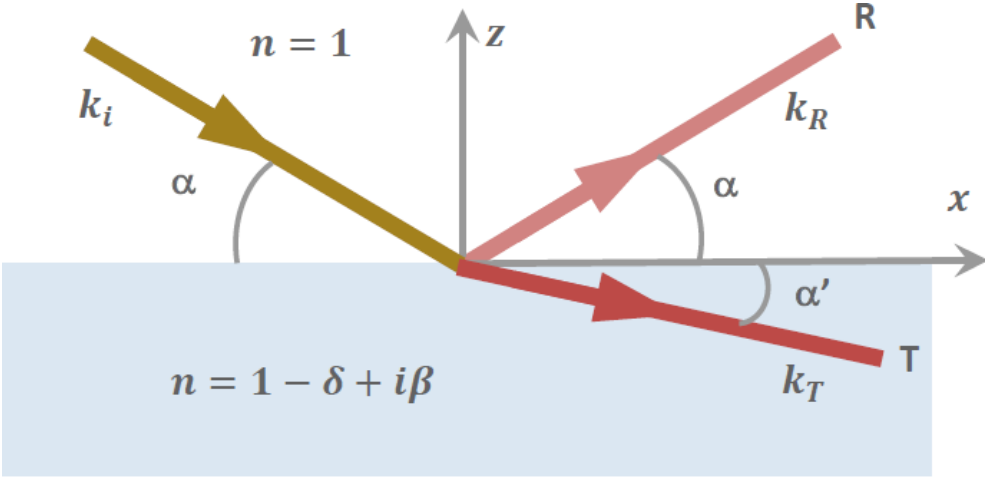
Snell's law: $n_1 \cos \alpha = n_2 \cos \alpha'$



Total reflection

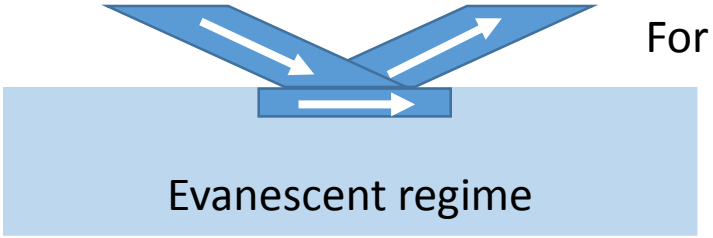
Surface sensitivity (penetration depth)

Limited penetration into the sample → enhanced surface sensitivity

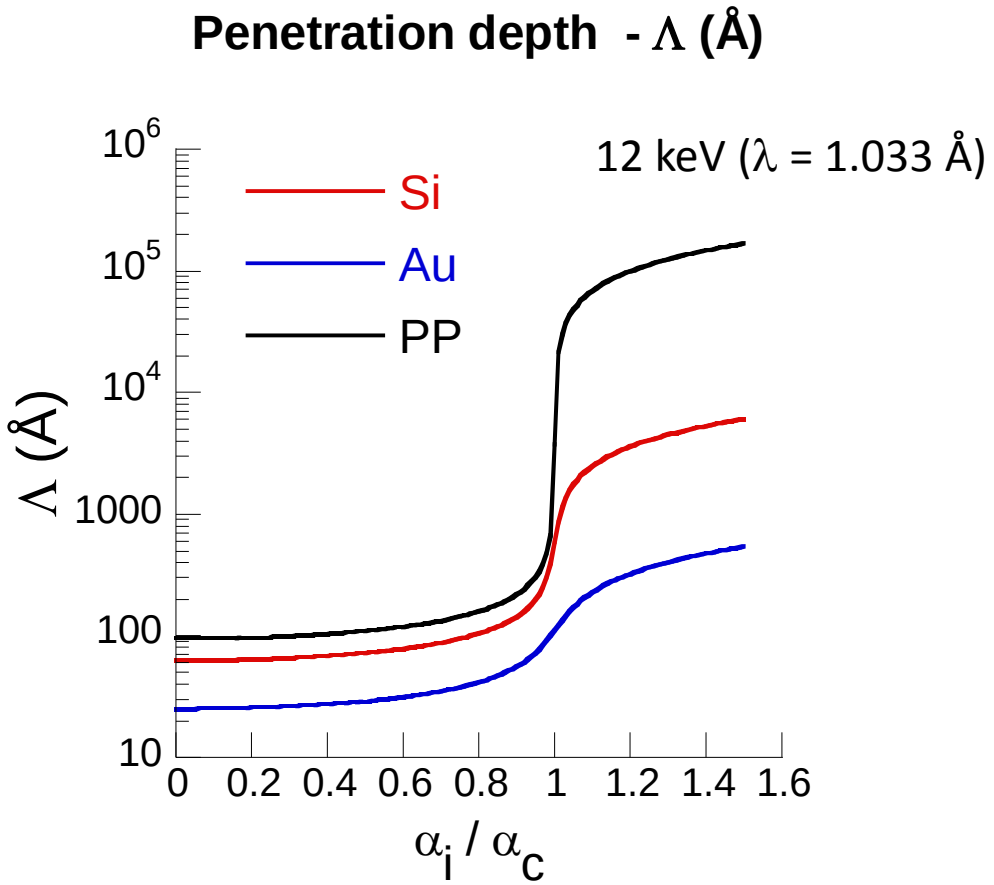


Snell's law: $\cos\alpha = n\cos\alpha'$

Critical angle: $\alpha_c = \sqrt{2\delta} = \lambda\sqrt{r_e\rho/\pi}$



For $\alpha_i \leq \alpha_c$



Reflection and Transmission coefficients

For the bare substrate:

$$\mathrm{E}(\mathrm{r},\mathrm{k}) = E_0 e^{-ik_{\parallel}r_{\parallel}} \begin{cases} e^{-ik_{i,z}z} + re^{ik_{i,z}z} & for\ z > 0 \\ te^{-ik_{\mathrm{t},z}z} & for\ z < 0 \end{cases}$$

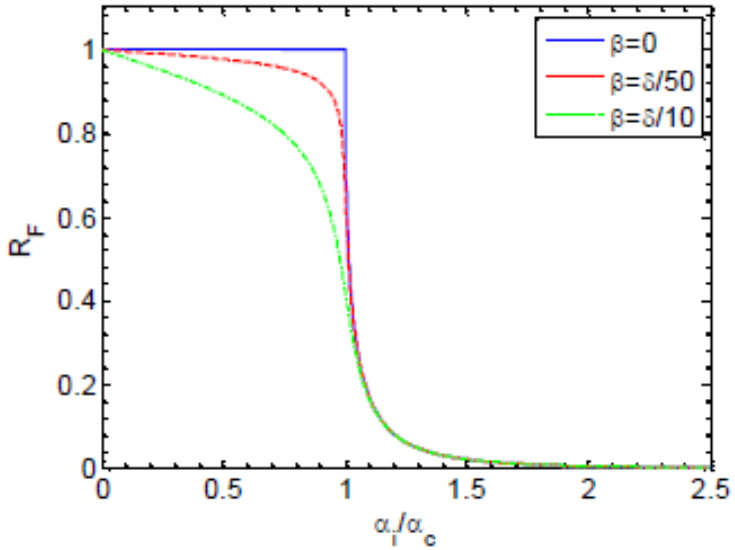
$$r = \frac{k_{i,z} - k_{t,z}}{k_{i,z} + k_{t,z}}$$

Fresnel reflectivity: $R_F = |r|^2$

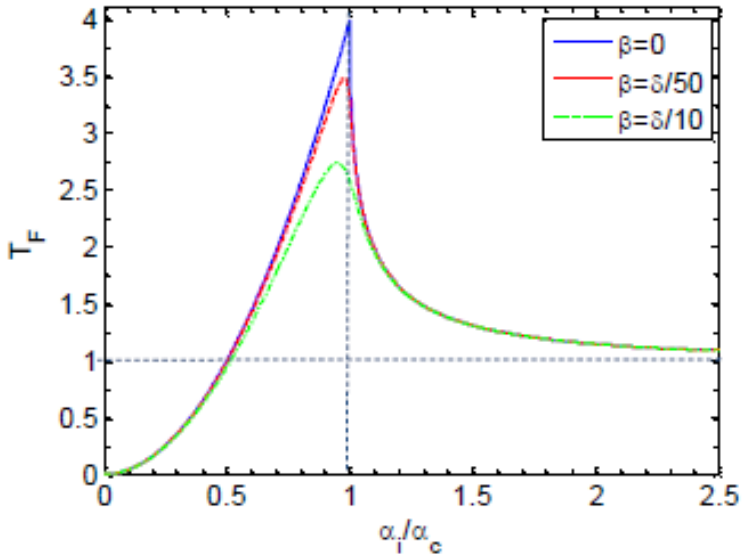
$$t = \frac{2k_{t,z}}{k_{i,z} + k_{t,z}}$$

Fresnel transmission: $T_F = |t|^2$

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



Yoneda peak

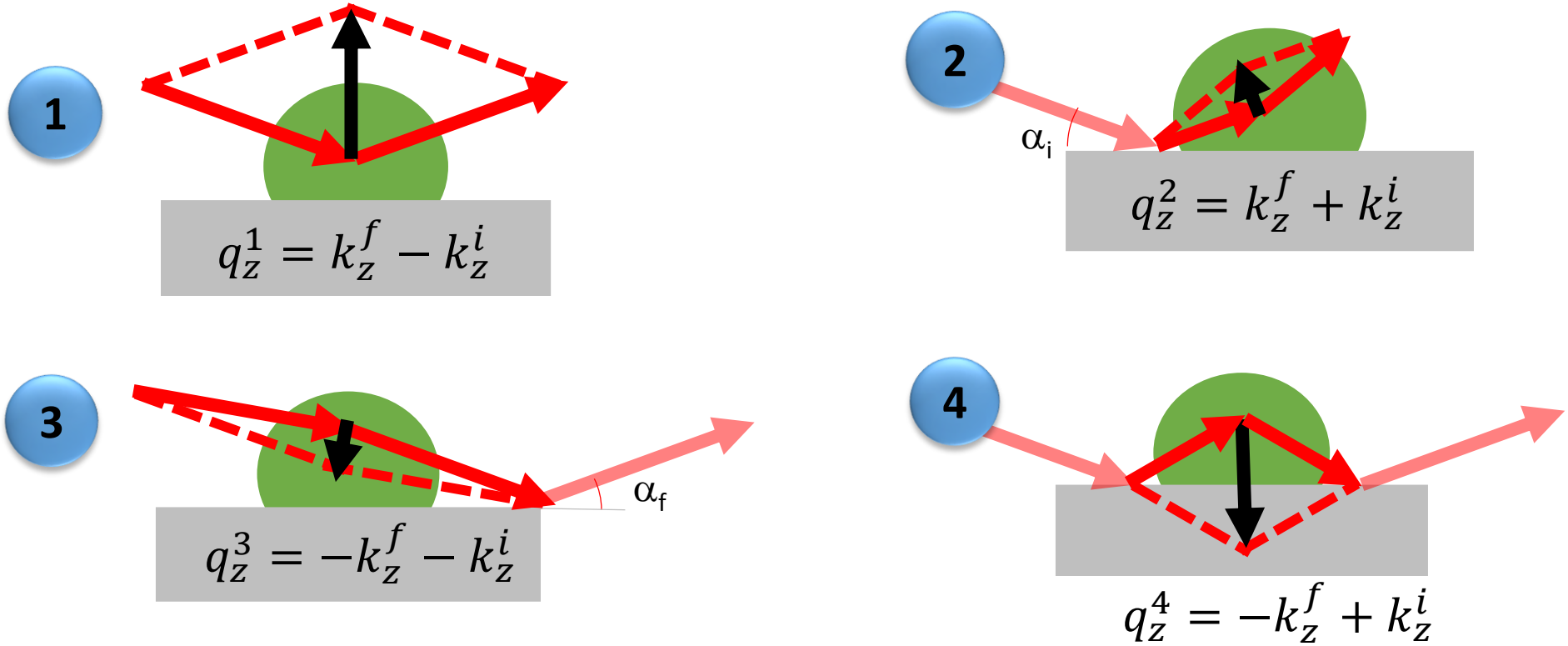


Nano-objects supported on a substrate

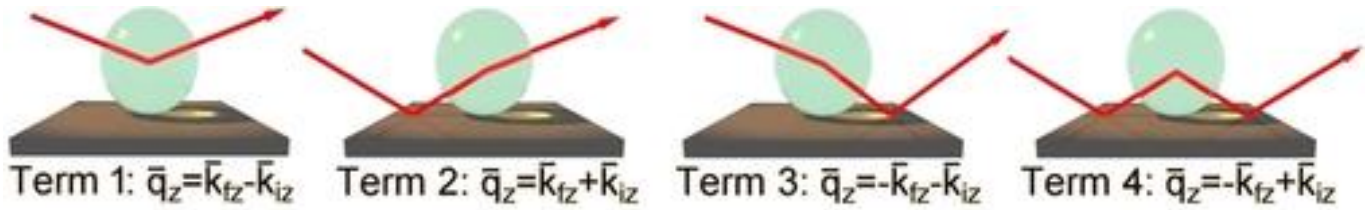
$$\frac{d\sigma}{d\Omega} = r_e^2 |\Delta\rho|^2 \left|\mathcal{F}(\boldsymbol{q}_\parallel, k_z^i, k_z^f)\right|^2 \qquad \boldsymbol{q} = \boldsymbol{k}_f - \boldsymbol{k}_i$$

$$\mathcal{F}\left(\boldsymbol{q}_\parallel, k_z^i, k_z^f\right) = F(\boldsymbol{q}_\parallel, q_z^1) + r(\alpha_i)F(\boldsymbol{q}_\parallel, q_z^2) + r(\alpha_f)F(\boldsymbol{q}_\parallel, q_z^3) + r(\alpha_i)r(\alpha_f)F(\boldsymbol{q}_\parallel, q_z^2)$$

Classican Born Approx. (SAXS)



Distorted Wave Born Approximation - DWBA

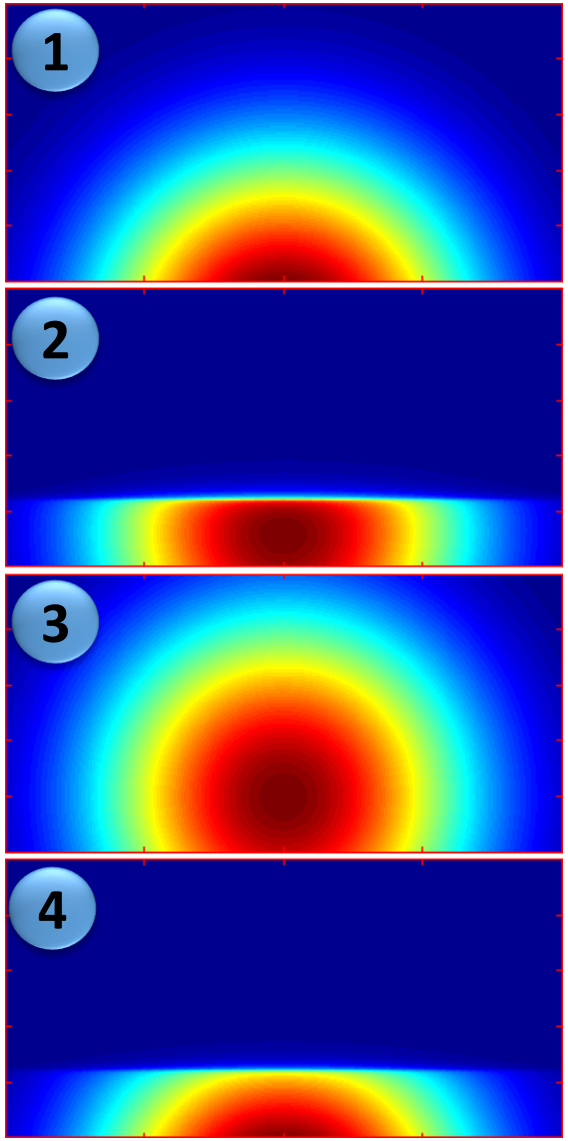


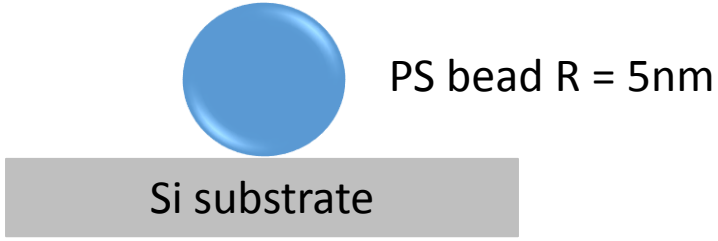
For a simple sphere:

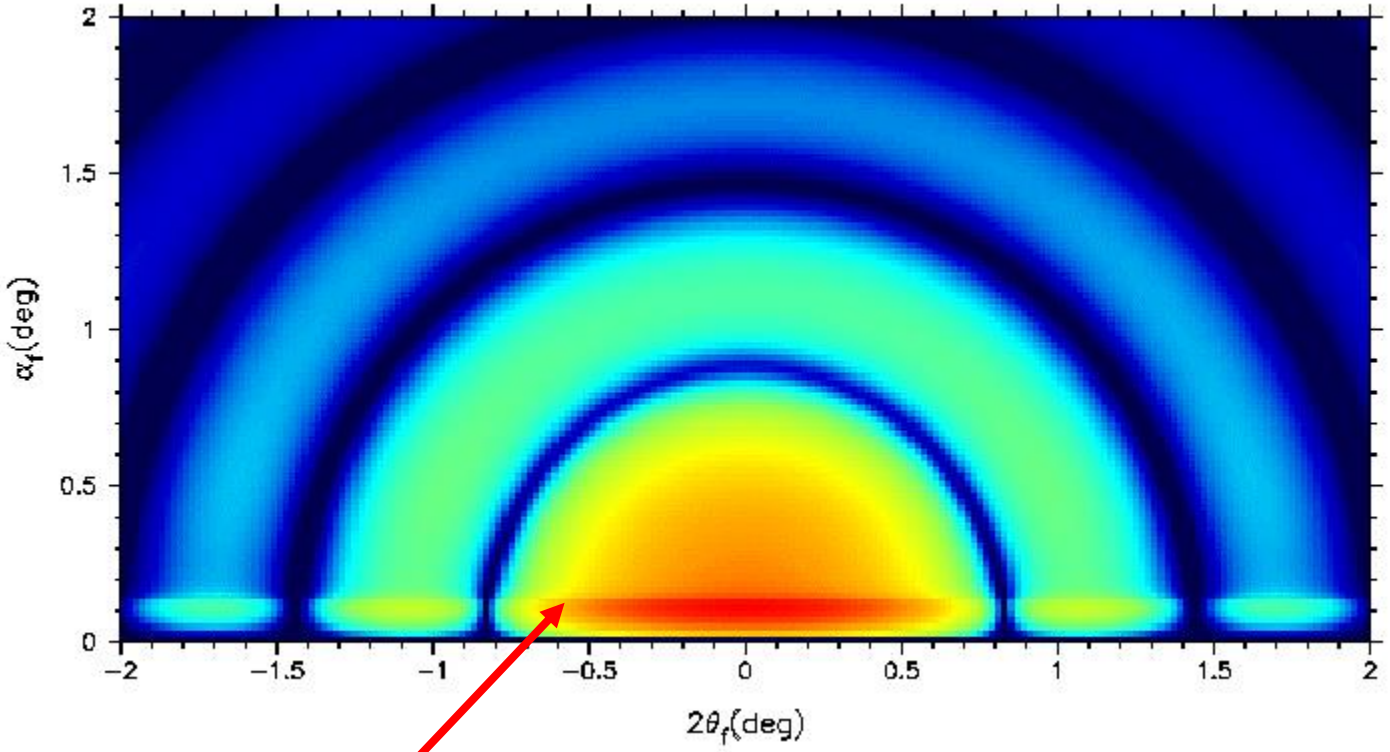
$$F_{sphere}(q,R) = \boxed{4\pi R^3 \frac{\sin(qR) - qRcos(qR)}{(qR)^3}} e^{iq_z r}$$

Classical SAXS

Nano-objects supported on a substrate



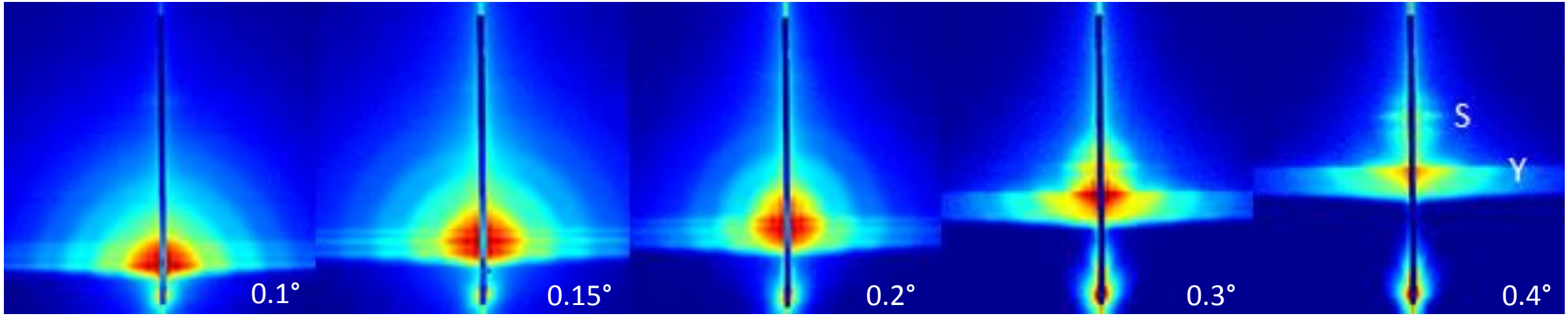




Yoneda peak for Si substrate: $\alpha_f = \alpha_c$

Nano-objects supported on a substrate: effect of increasing α_i

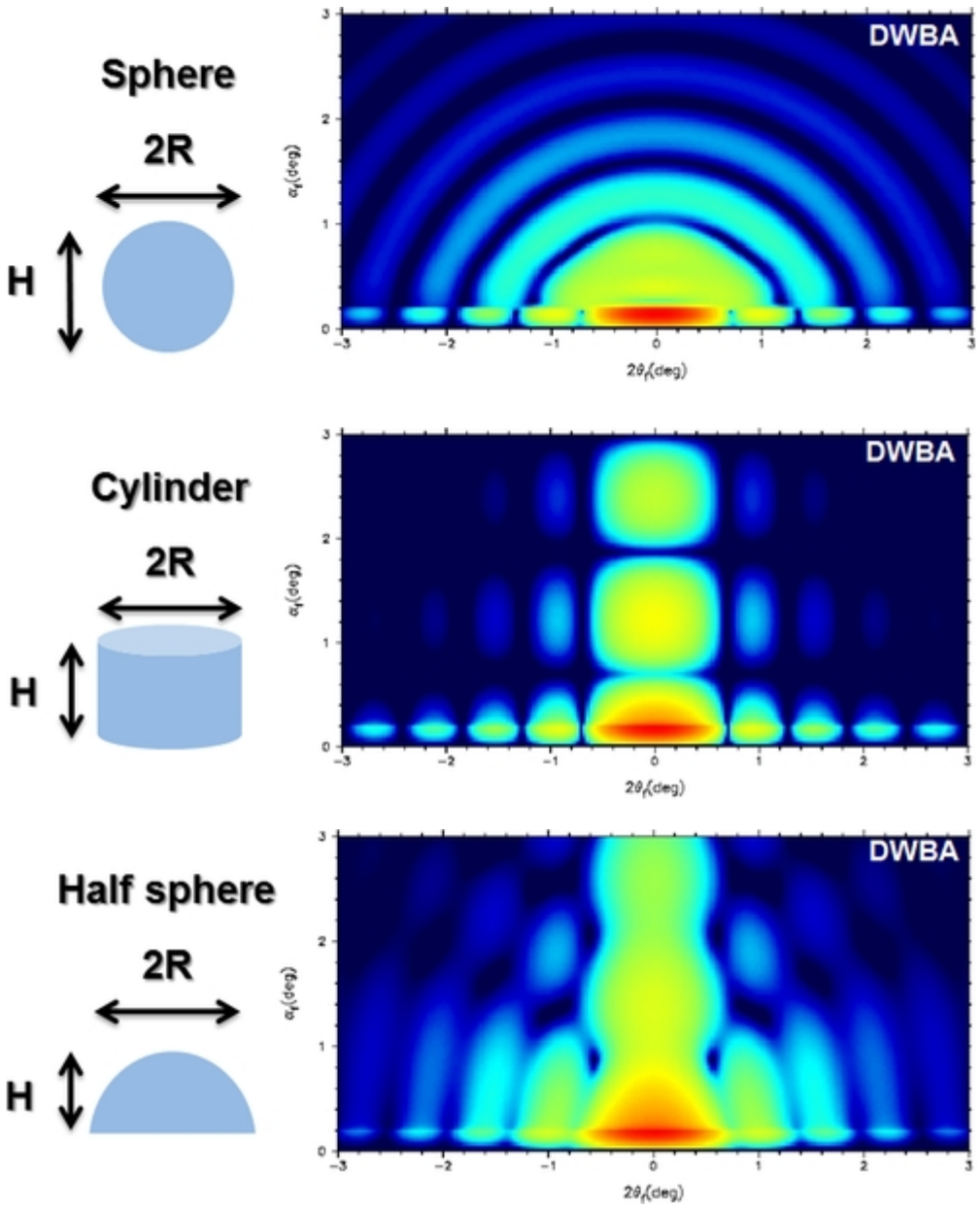
Au nanoparticles R = 25nm on glass substrate



For supported nano-object the maximum scattered intensity is at the critical angle of the substrate

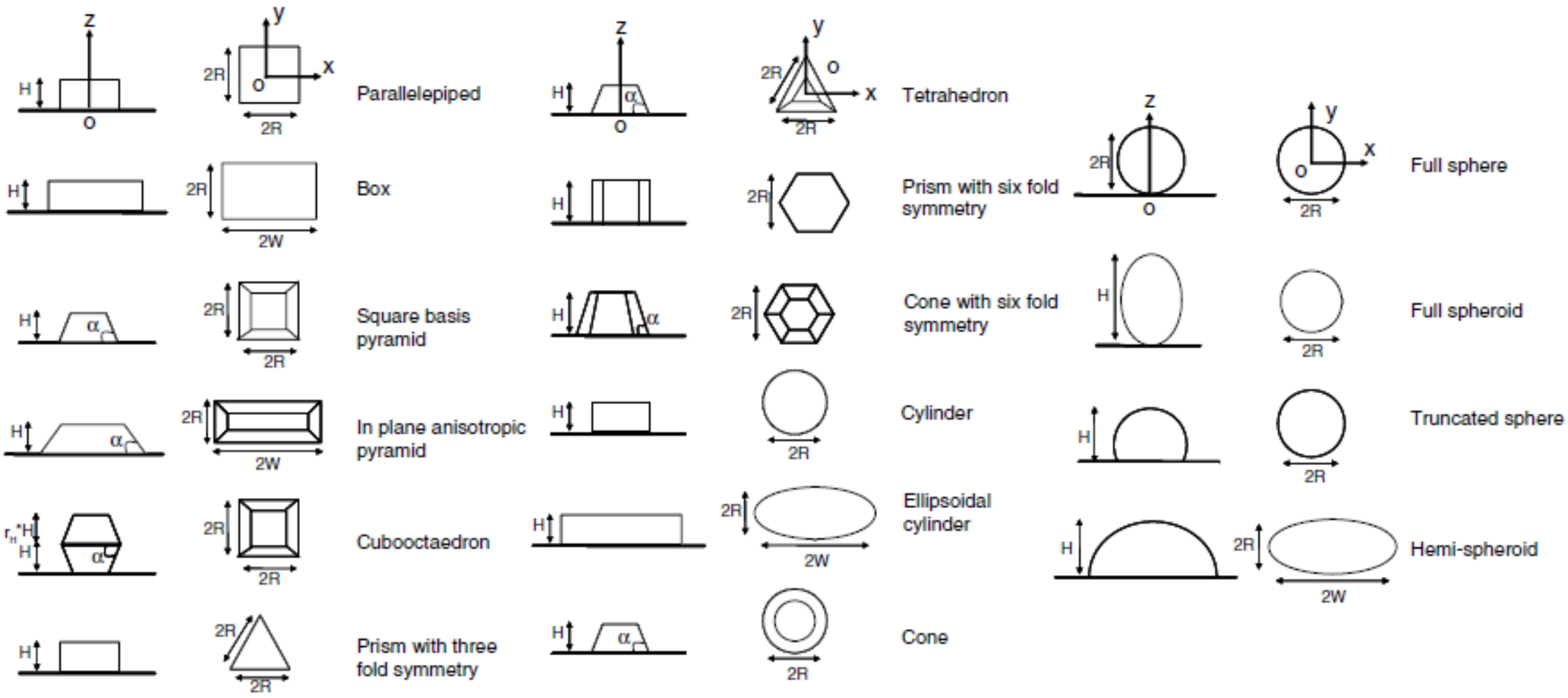
Particle shape sensitivity

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



Calculations performed using the IsGISAXS software (R. Lazzari)

Calculated form factors under the DWBA



Renaud G., Lazzari R., Leroy F., *Surf. Sci Rep.* 64 (2009), 255-380

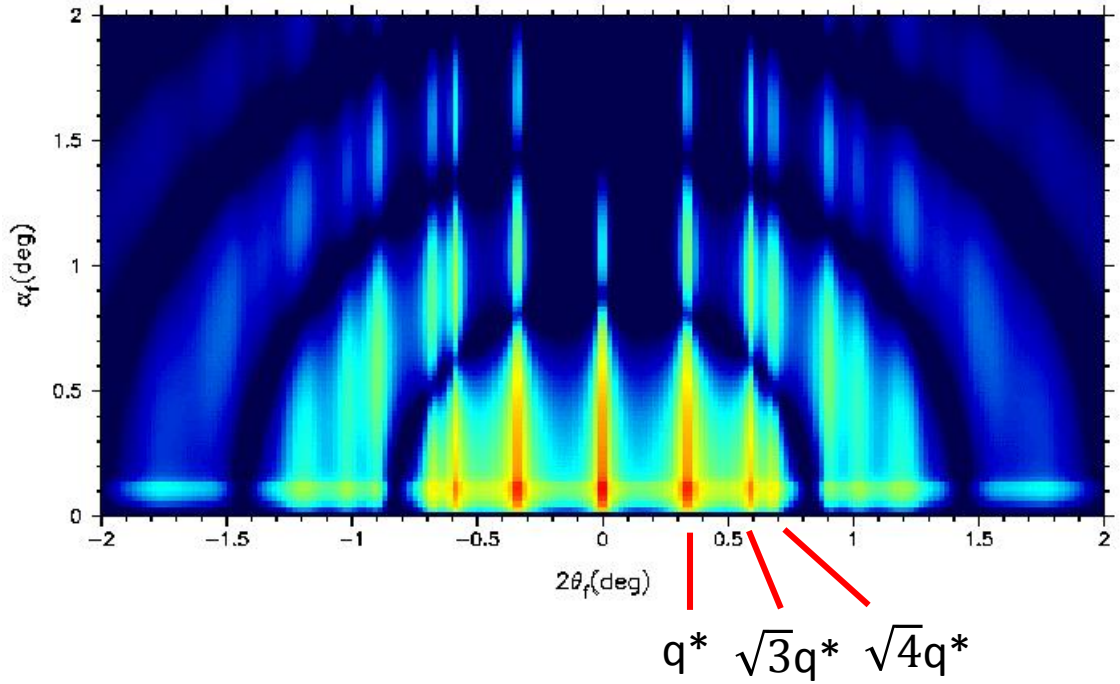
Now with spatial correlation between nano-objects

If spatial correlation exists between objects, an interference function has to be considered:

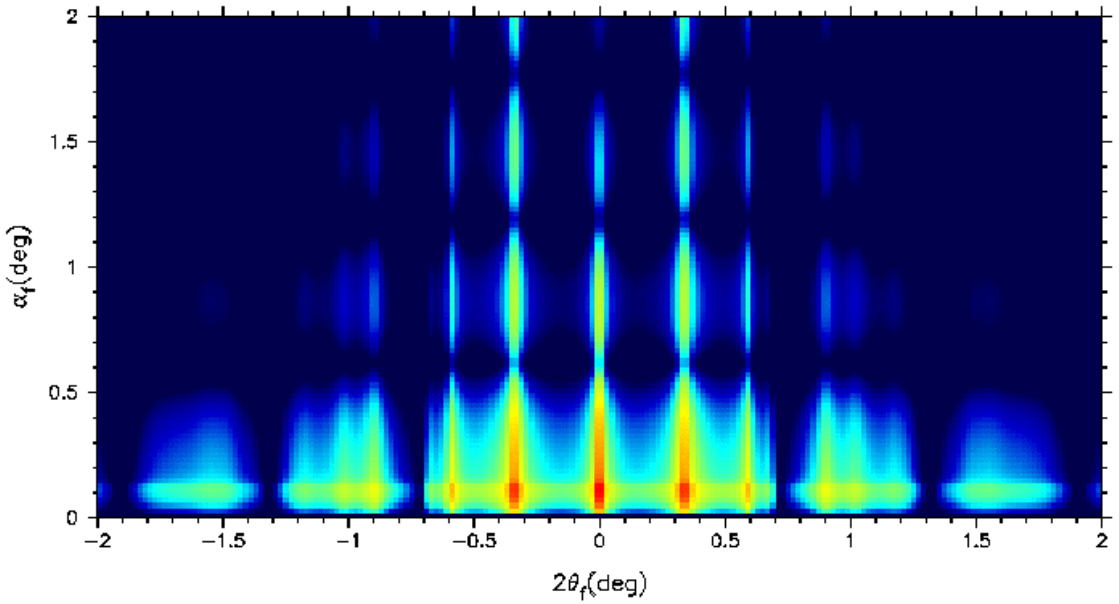
Decoupling approximation (DA): $I(q) \propto I_d(q) + |\langle F(q) \rangle|^2 S(q)$

Local monodisperse approximation (LMA): $I(q) \propto \langle |F(q)|^2 \rangle S(q)$

PS spheres with 2D hexagonal lattice

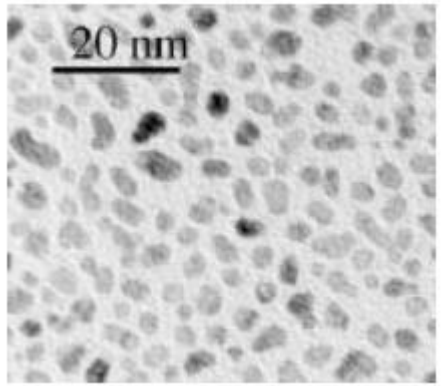


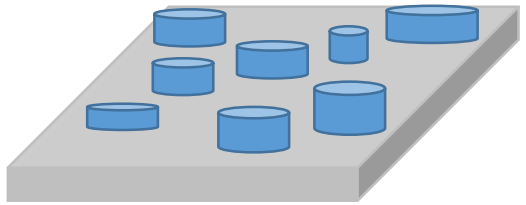
PS cylinders with 2D hexagonal lattice



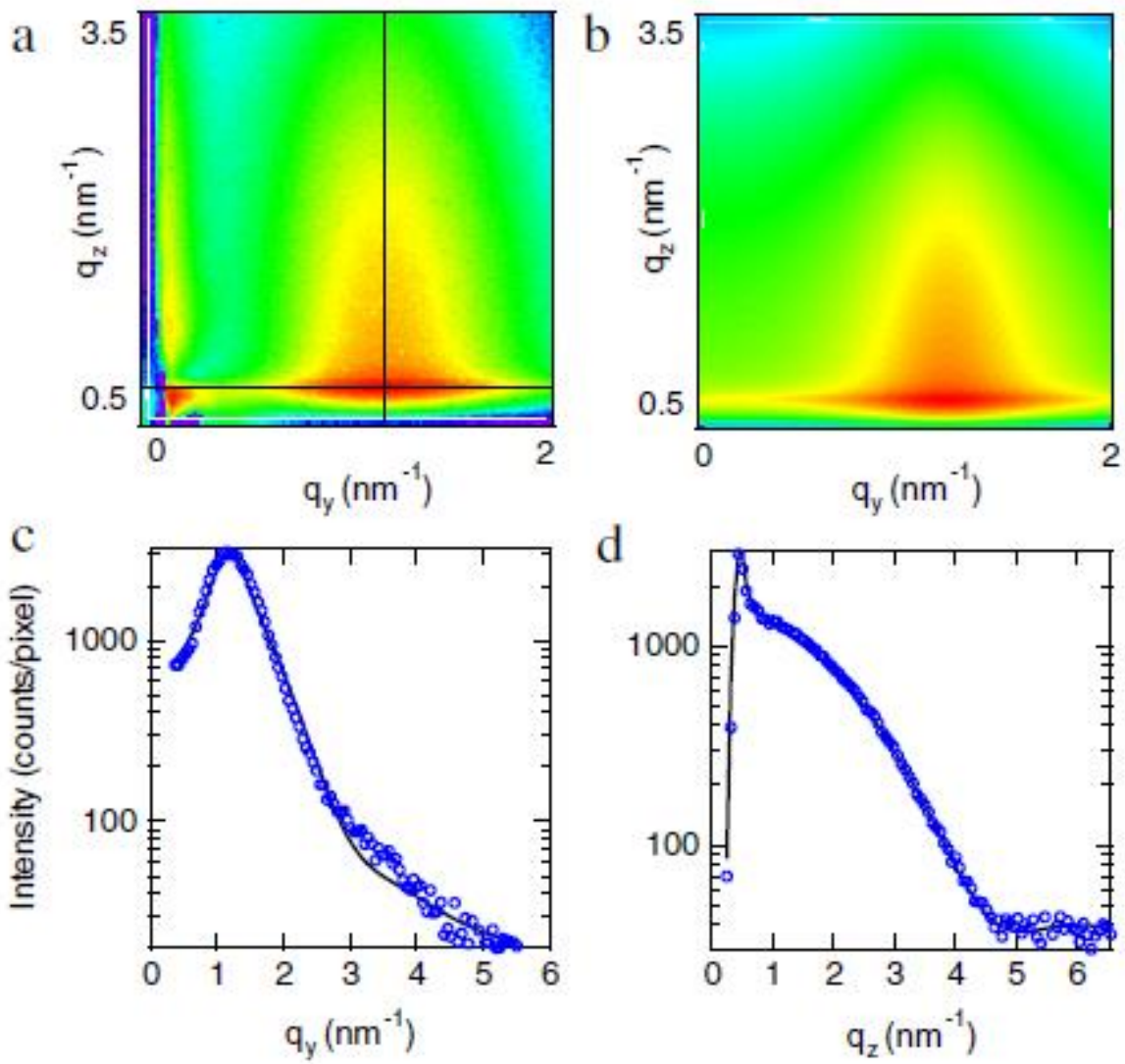
Supported nanoparticles: Pt deposit on MgO (001)

TEM





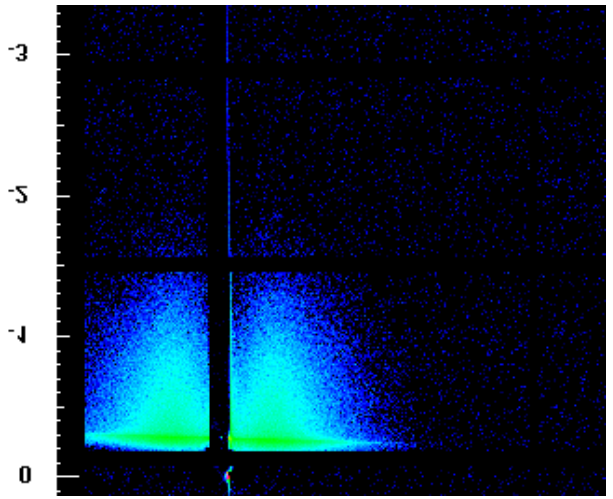
Disks with 1D paracrystalline lattice

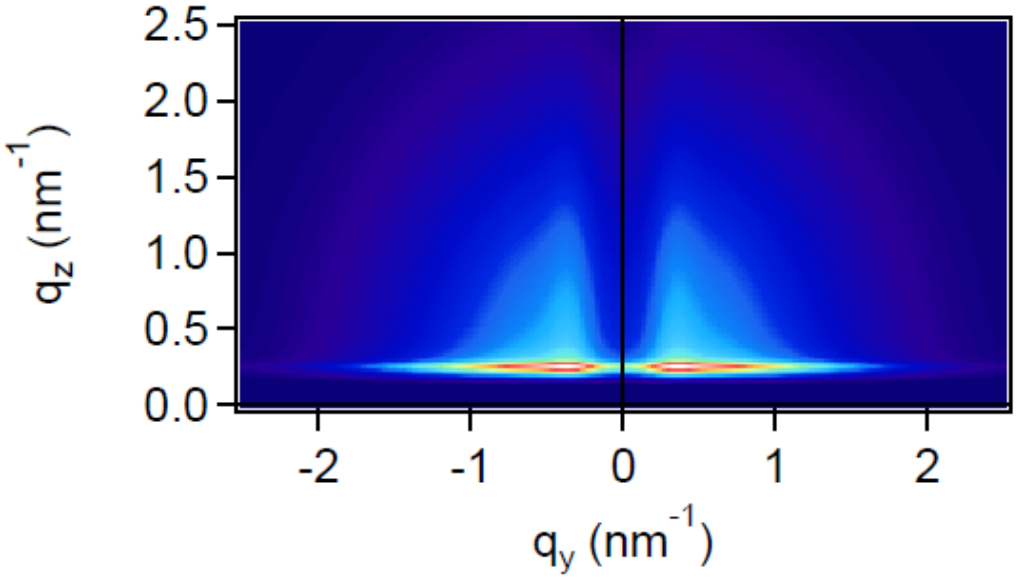


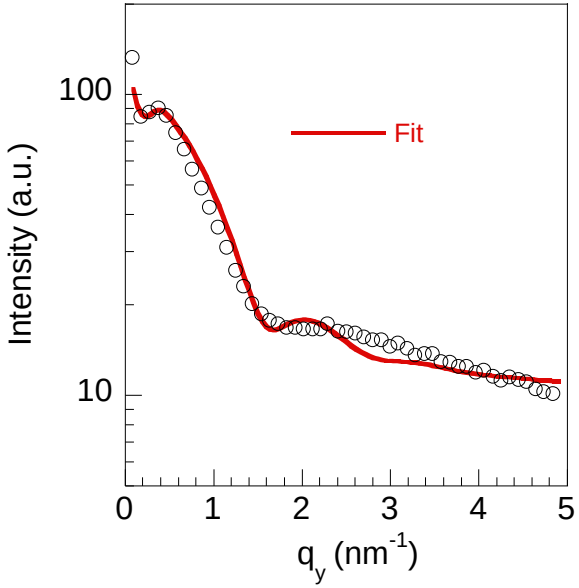
J. Olander et al. Phys. Rev. B 76 (2007) 075409.

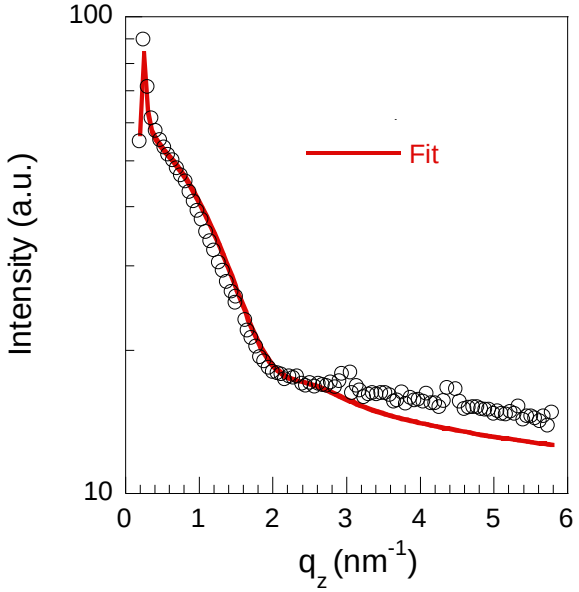
Au clusters on a substrate

@BM26B

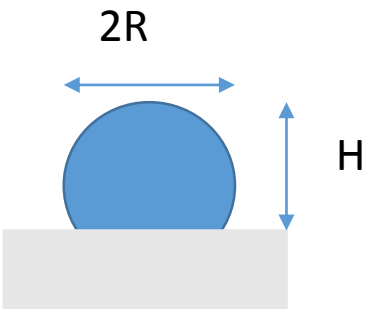




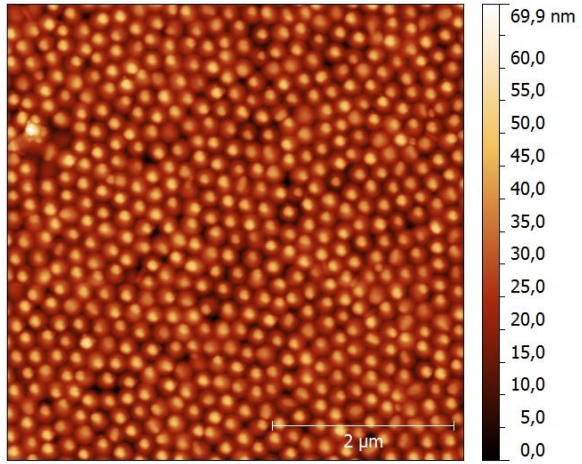


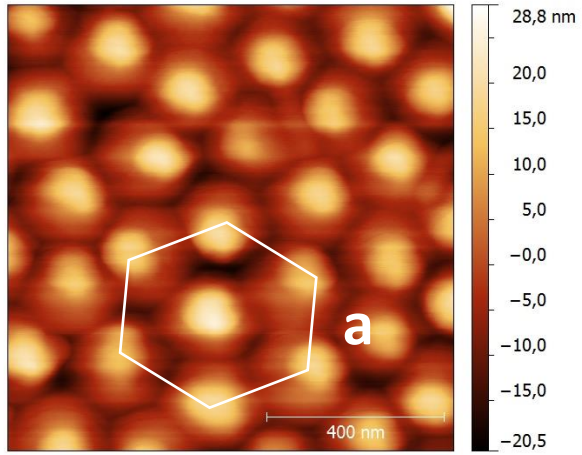


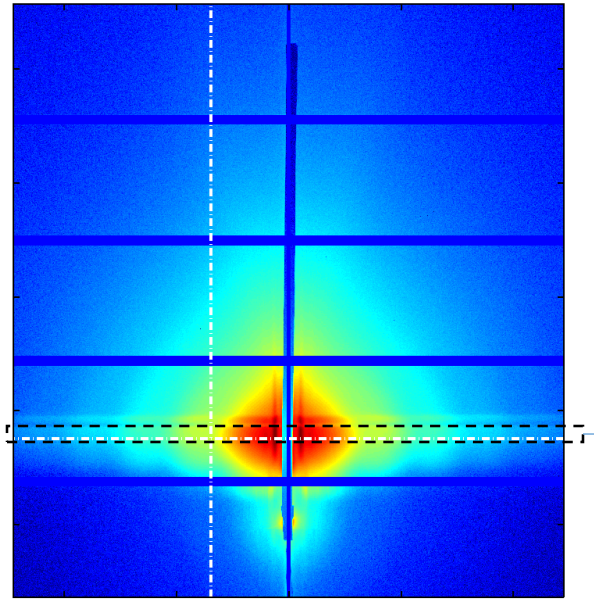
Au clusters with R = 3nm and H/R = 1.6

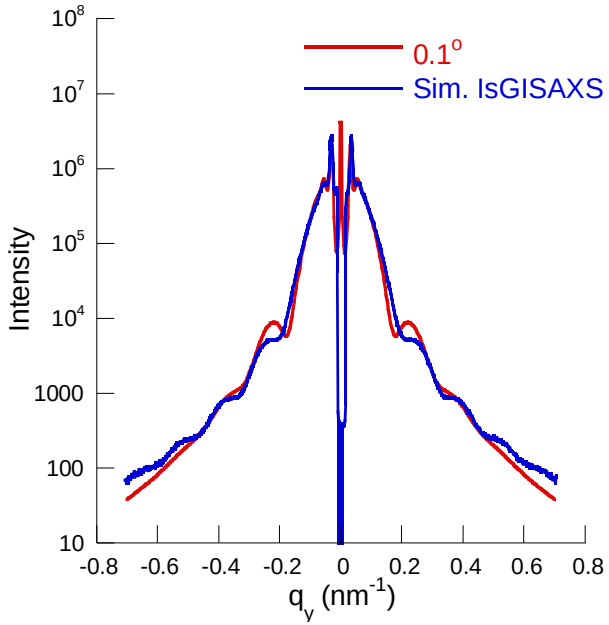


GISAXS from a monolayer of core-shell gold-PNIPAM nanoparticles









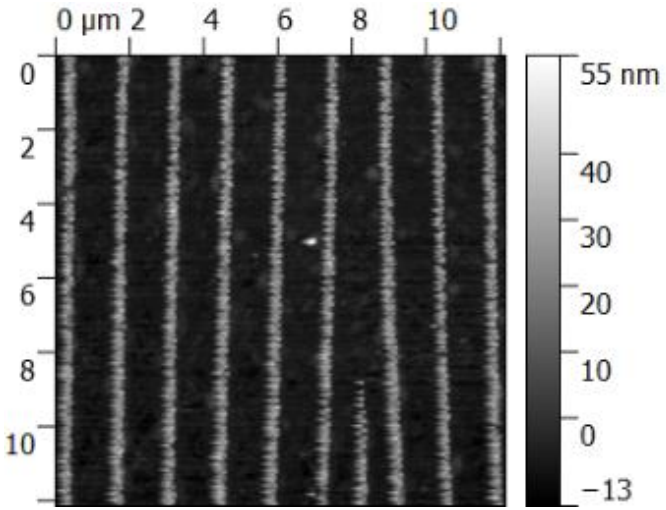
Spheroidal Gold cores
R = 25nm

2D Hex with
a = 230 nm

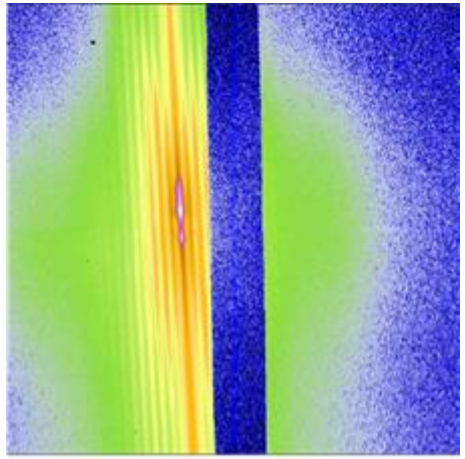
High resolution GISAXS (GIUSAXS)

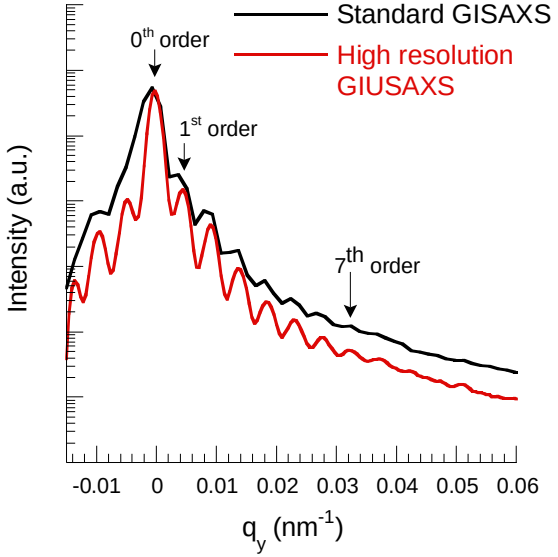
Au linear assembly

AFM



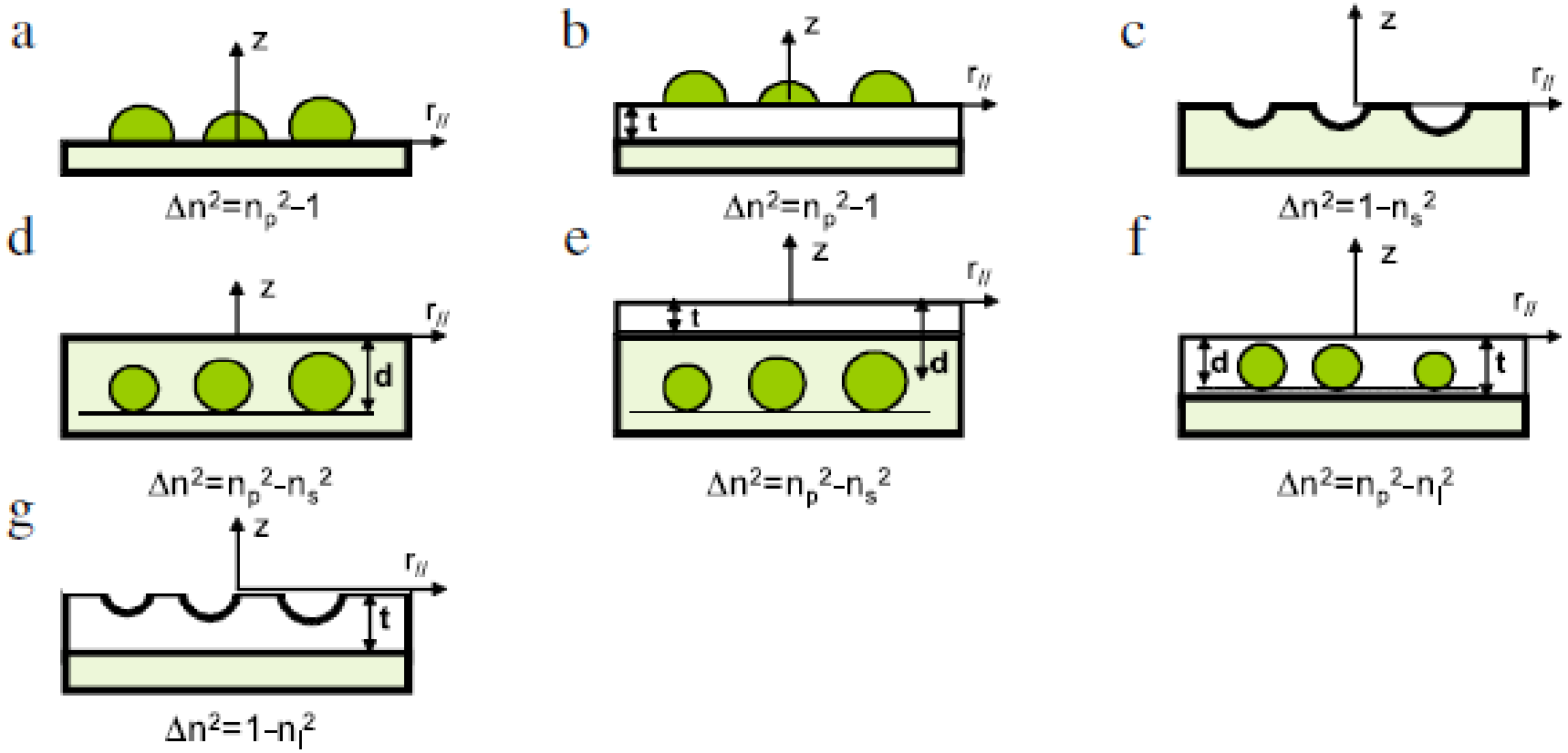
GIUSAXS





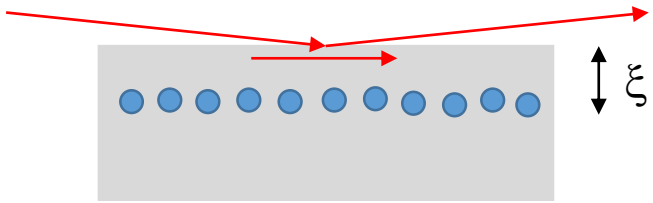
$q^* = 0.0048\ nm^{-1} \rightarrow d = 1.3\ \mu m$

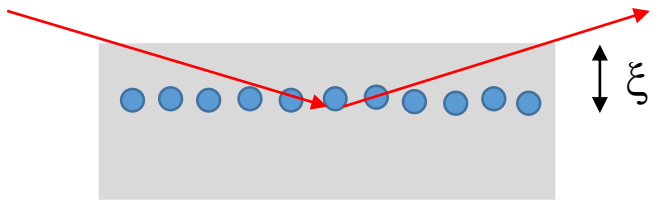
Several possible geometries

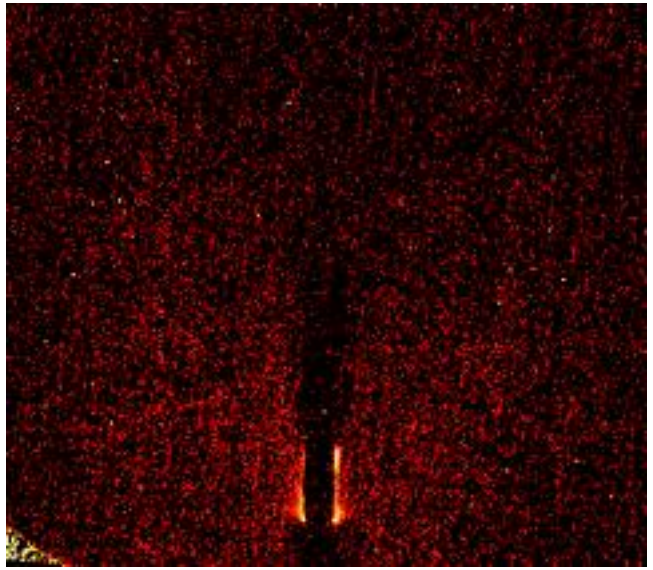


Renaud G., Lazzari R., Leroy F., *Surf. Sci Rep.* 64 (2009), 255-380

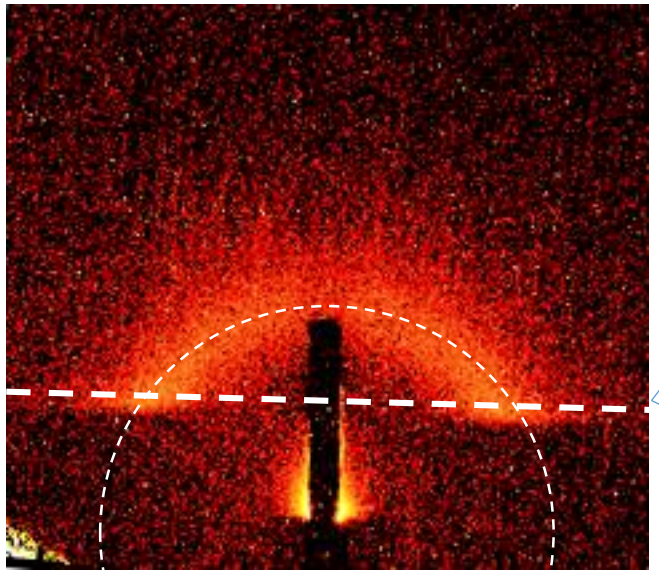
Buried interfaces: Pb clusters implanted in Si substrate



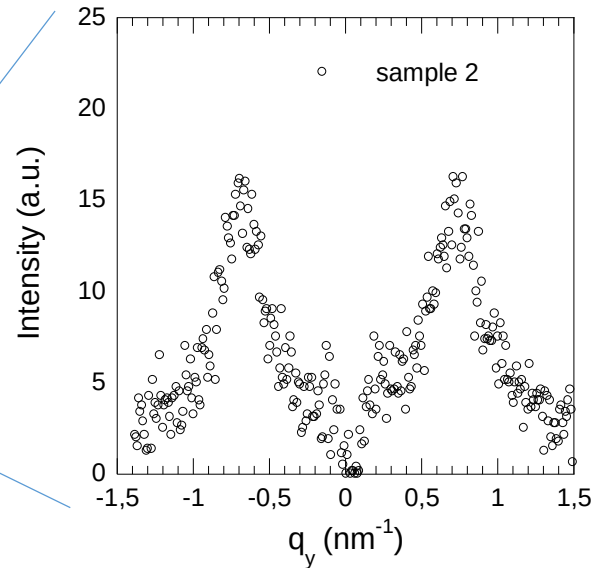




$\alpha_i \sim \alpha_c$ (substrate)

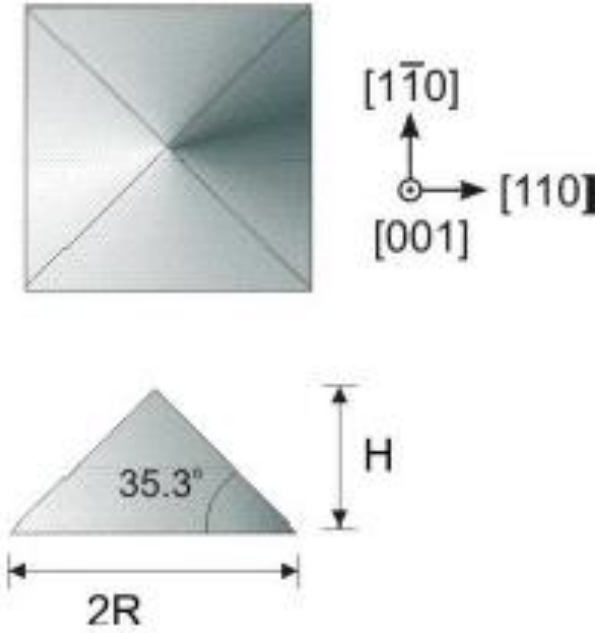


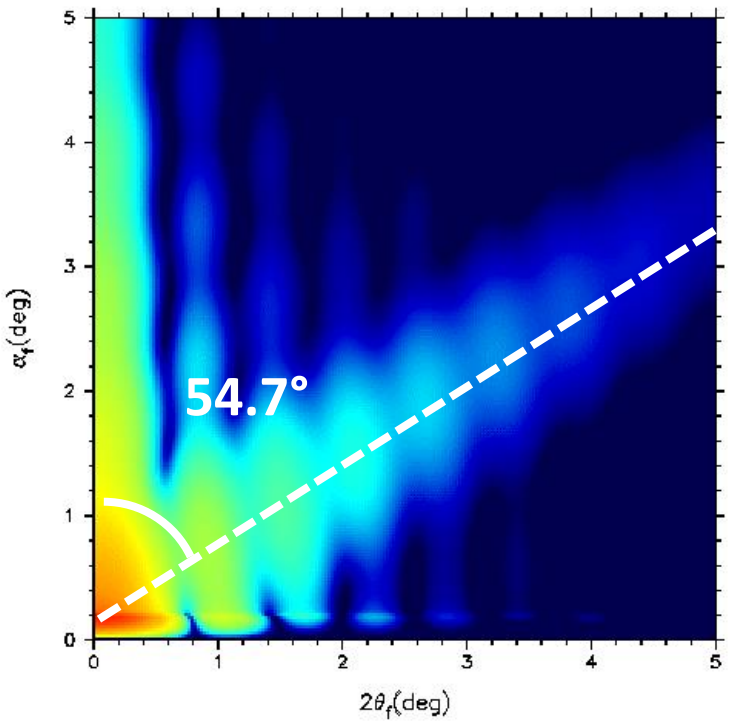
$\alpha_i >> \alpha_c$ (substrate)

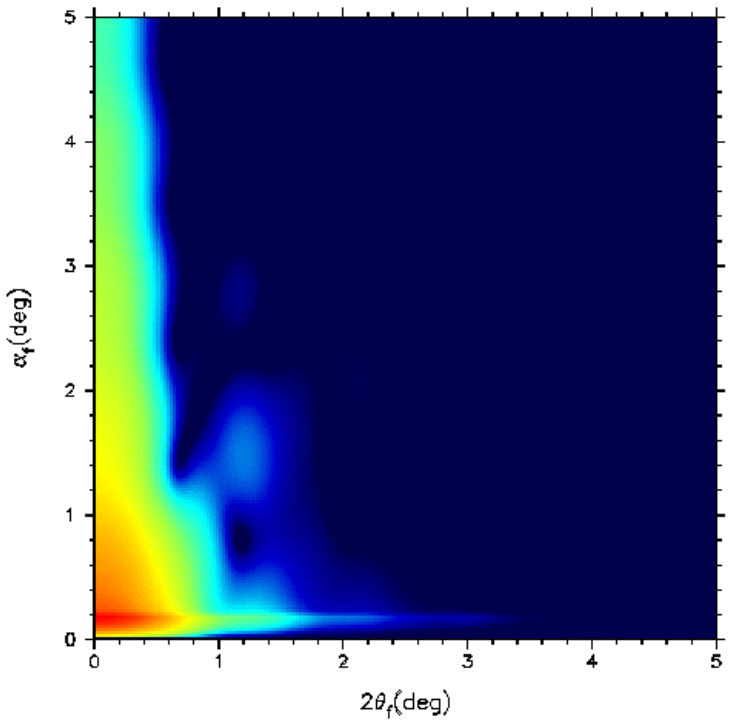


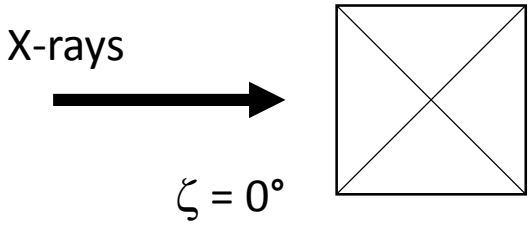
$D_{intercluster}$ = 9nm

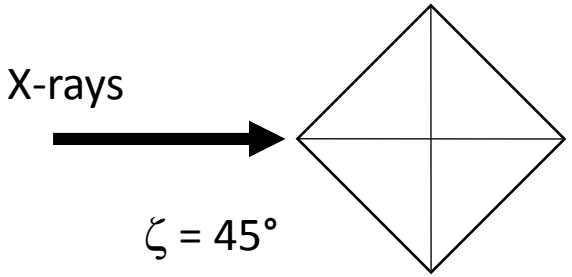
Scattering from facets: pyramid



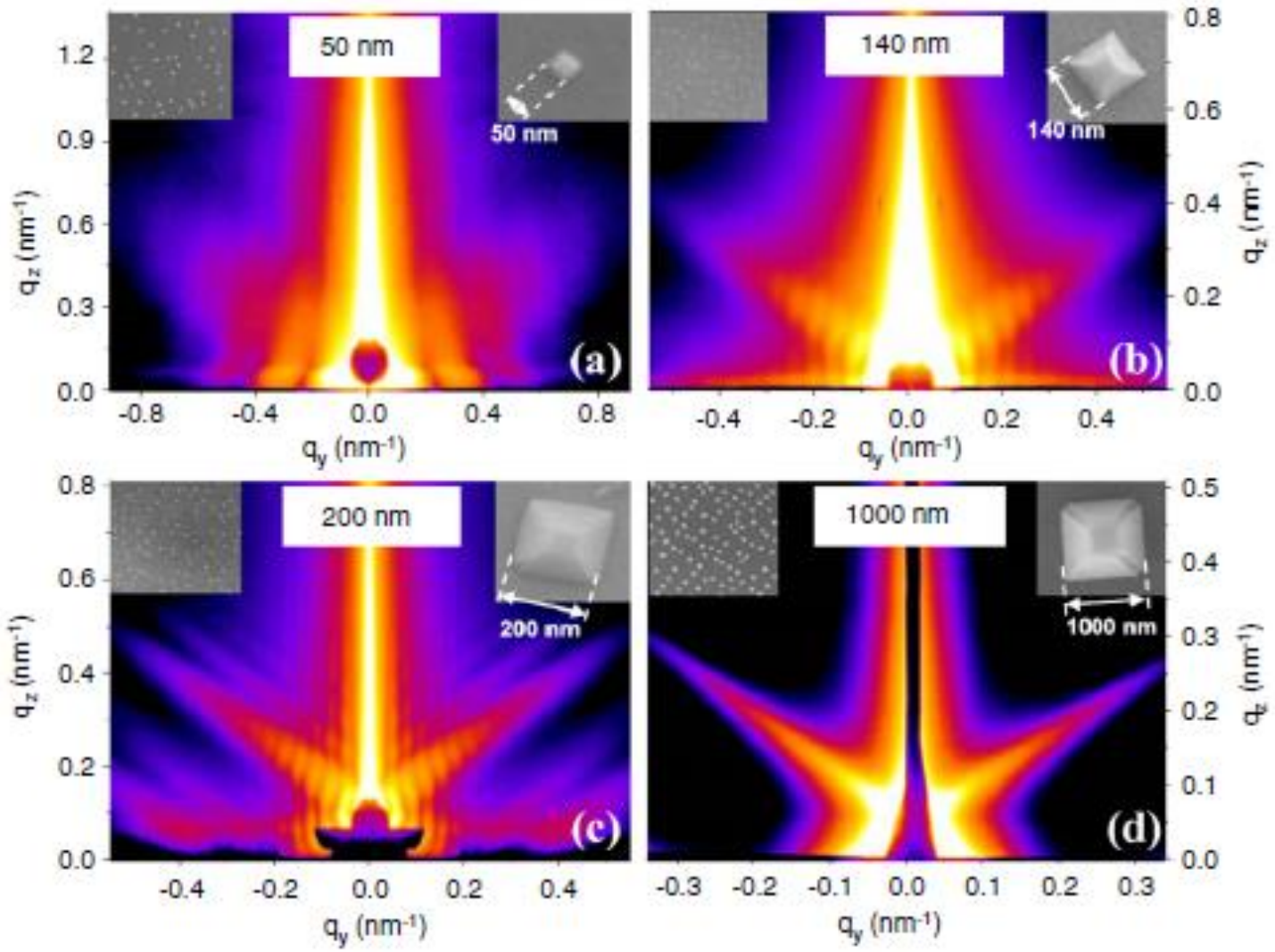








Scattering from facets: Ge/Si(001) quantum dots

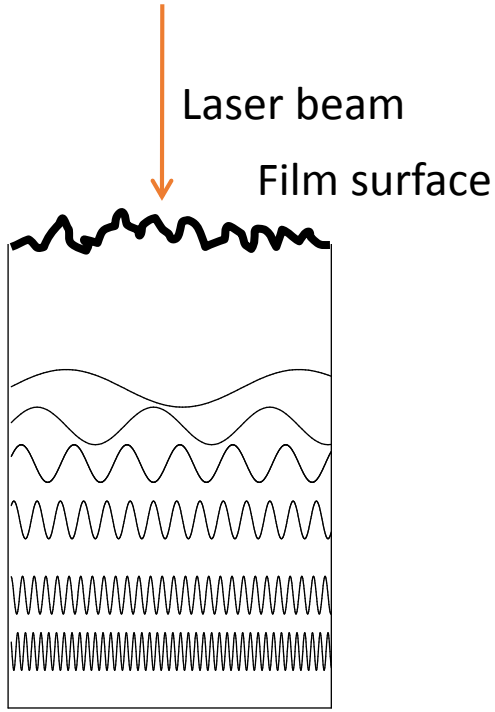


Bragg rod is proportional to the facet area

A.V. Zozulya, et al. Phys. Rev. B 78 (2008) 121304

In-situ GISAXS: study of LIPSS formation

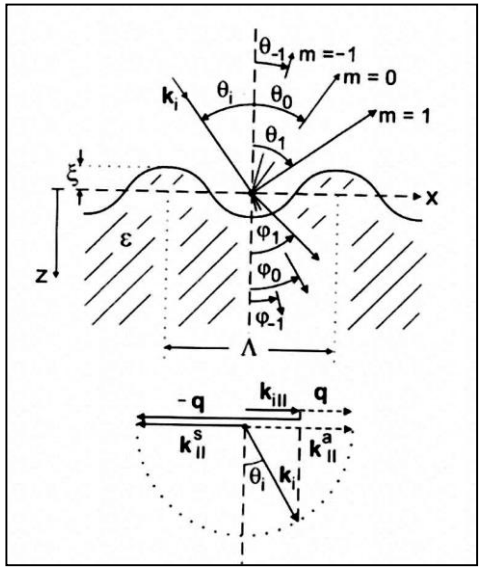
Laser Induced Periodic Surface Structures (LIPSS)



- Interference of the incident and reflected light at the interface produces Ripples with a period L :

$$\Lambda = \frac{\lambda}{n \pm \sin\Theta_i}$$

l: light wavelength
Θ: angle of incidence
n : refraction index



- Roughness :

$$\sigma = \sqrt{\sigma_0^2 + \frac{kT}{2\pi\gamma} \ln\left(\frac{\lambda_l}{\lambda_s}\right)}$$

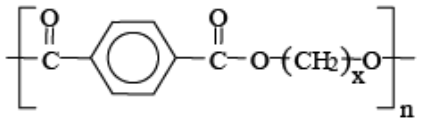
s_o : Molecular Roughness
l_l : longest wavelength
l_s : shortest wavelength

C. Bollinne, S. Cuenot, B. Nysten, and A.M. Jonas. Eur. Phys. J. E 12, 389–396 (2003).
Z. Guosheng, P.M. Fauchet, A.E. Siegman. Phys. Rev. B, 5366 (1982)

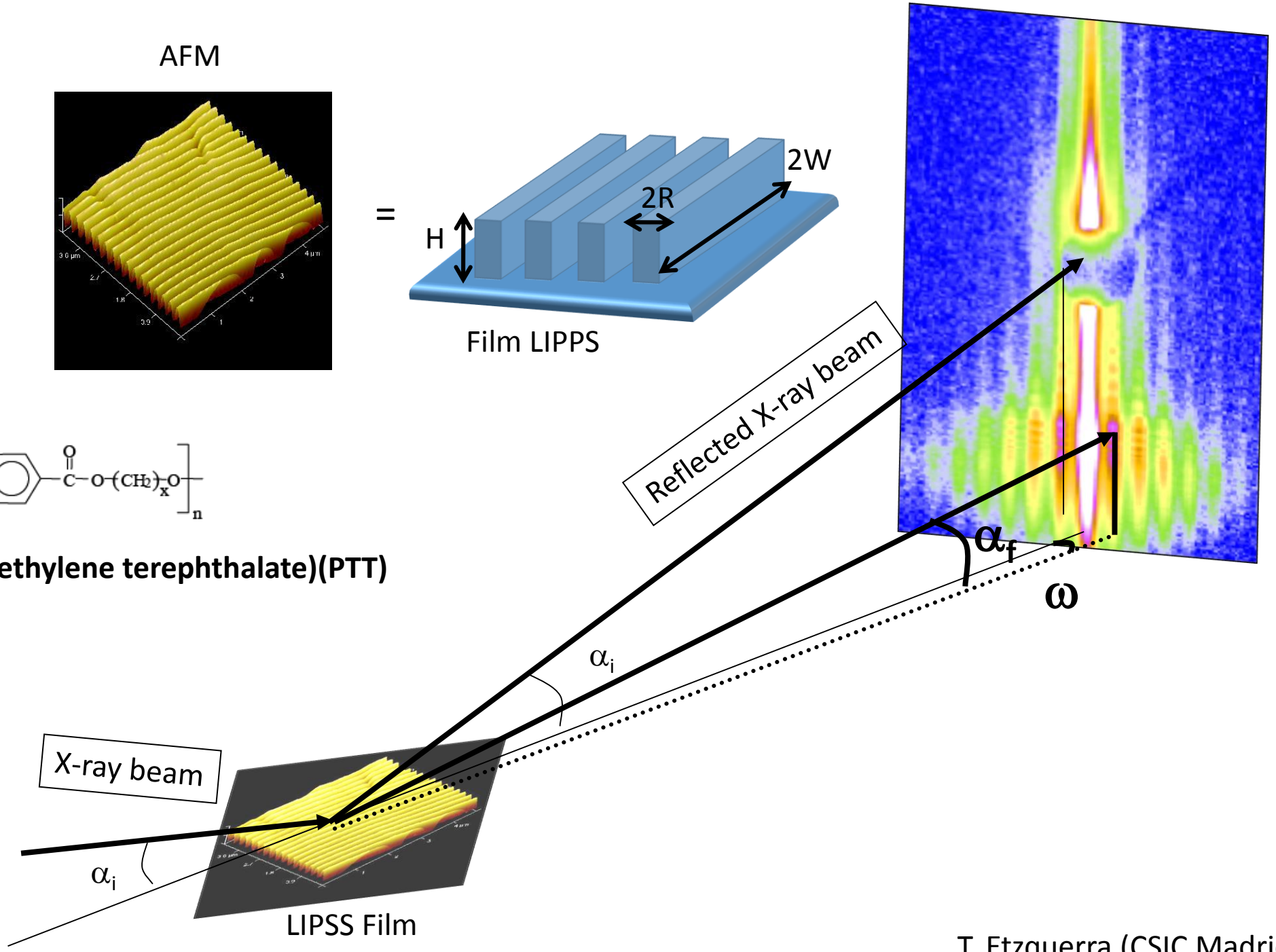
AFM

=

Film LIPPS

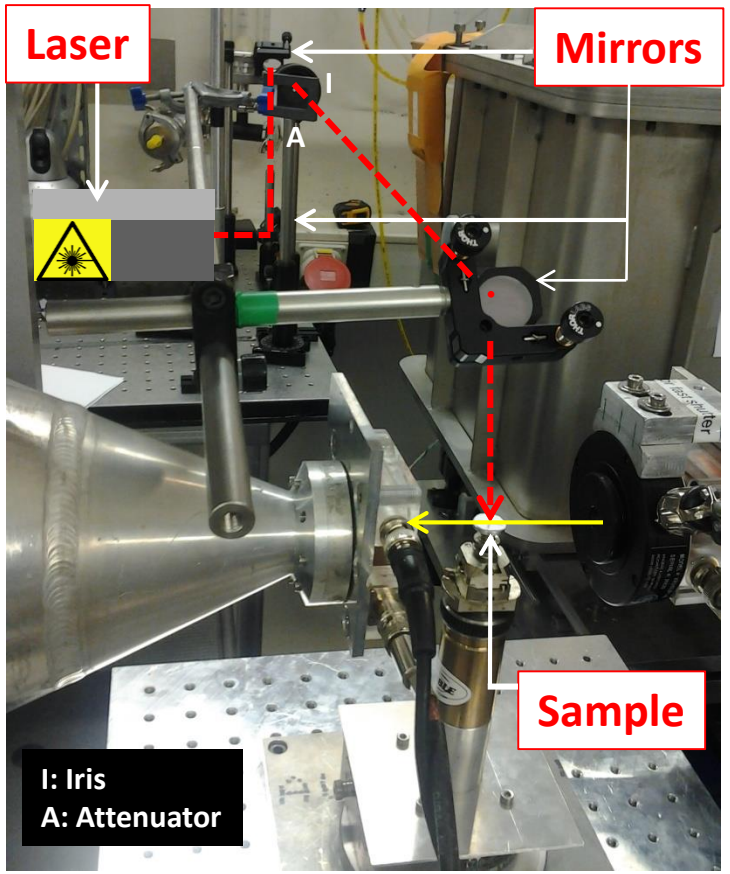


Poly(tri methylene terephthalate)(PTT)



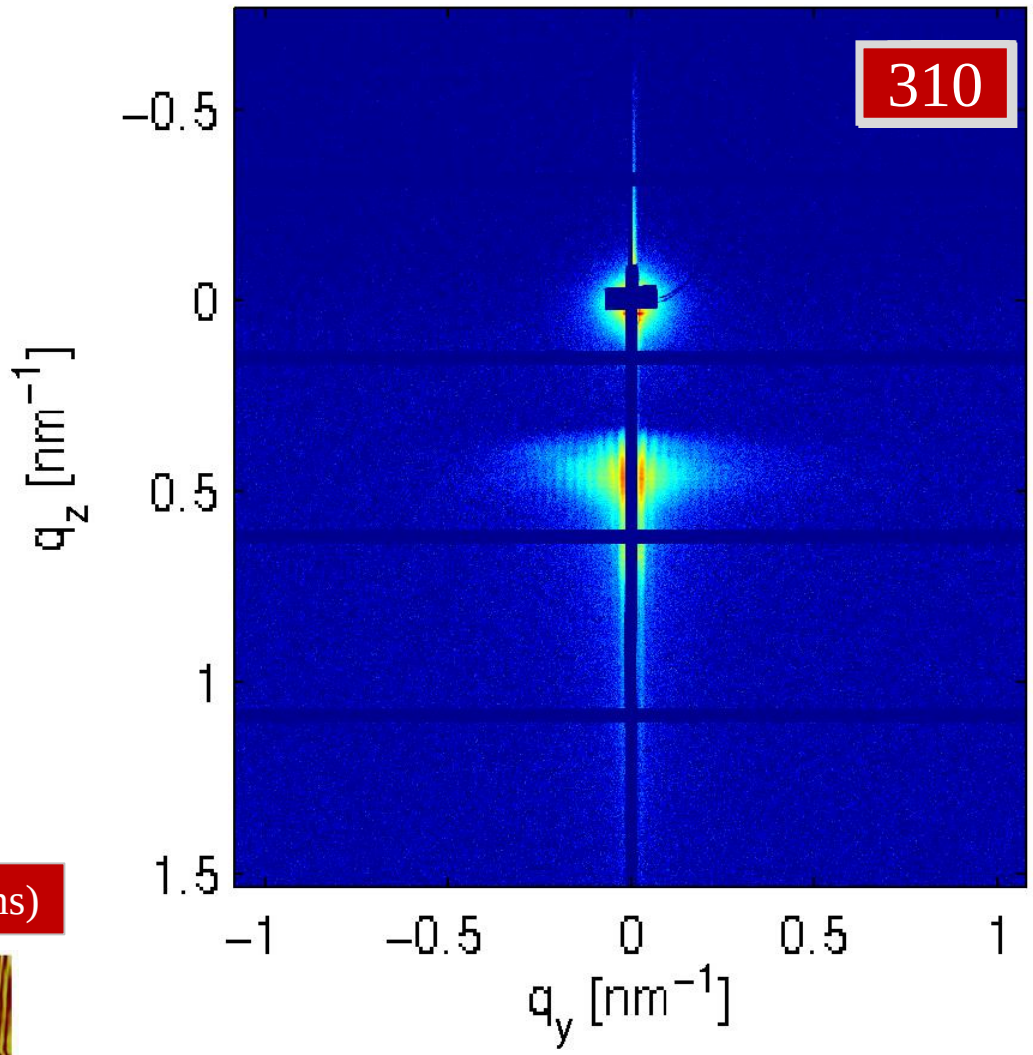
T. Etzquerra (CSIC Madrid)

Set-up @ BM26, ESRF



F=7 mJ/cm² @ N pulses (8ns)

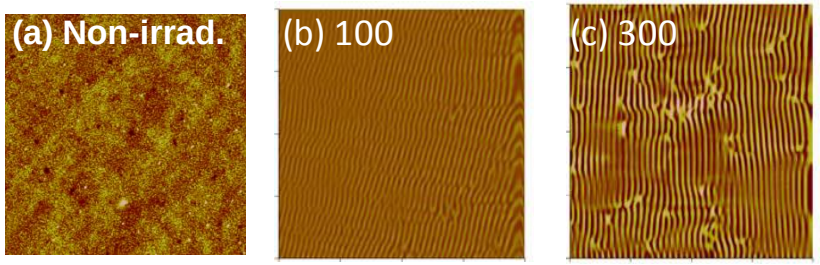
N pulses (8ns)



AFM

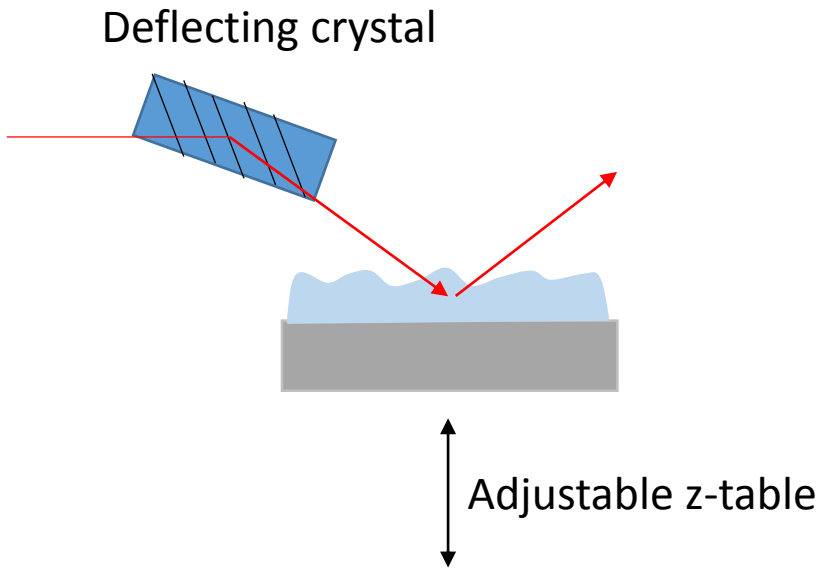
5x5 μm²

F=7 mJ/cm² @ N pulses (8ns)

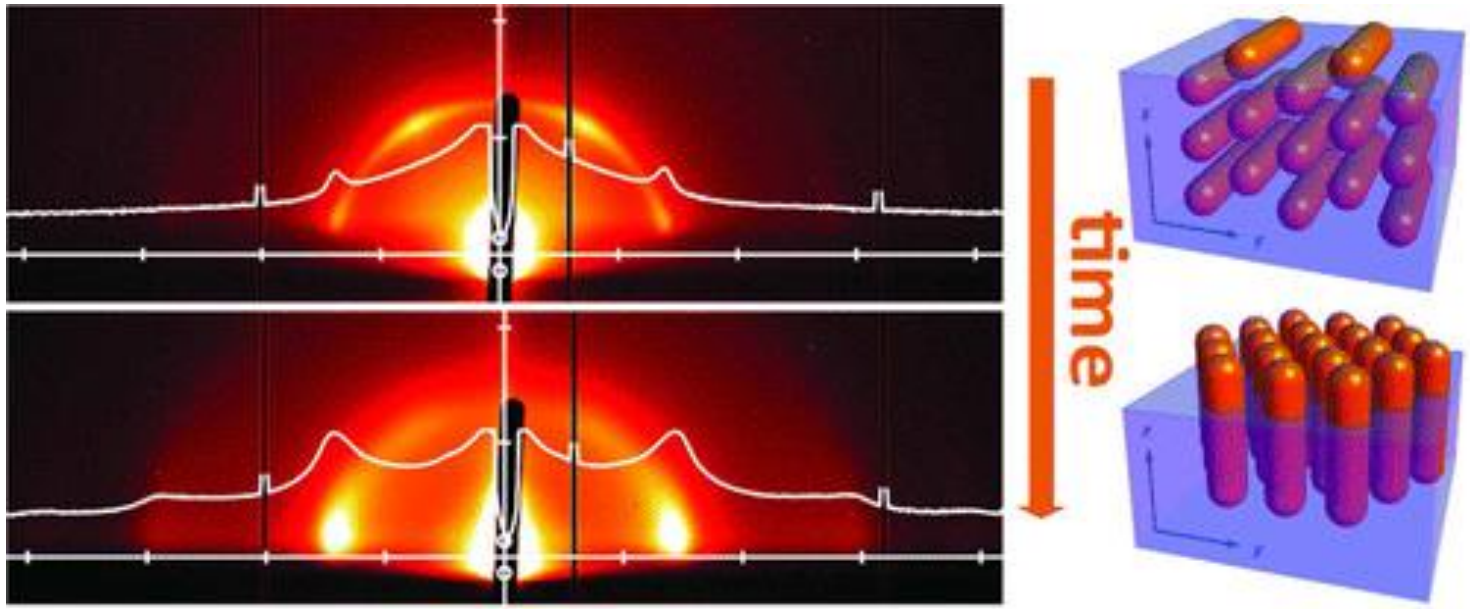


Final height about 50nm, periodicity about 200 nm

GISAXS at the liquid-air interface



Colloidal CdSe/CdS nanorods

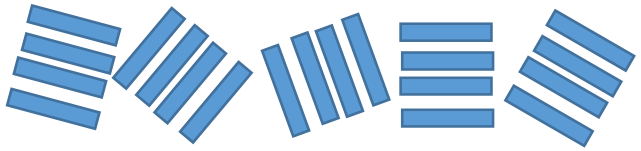


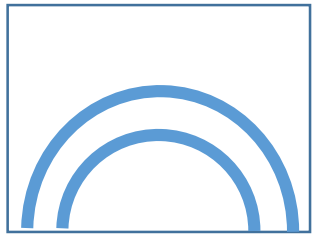
F. Pietra et al. Nano Letters 12 (2012) 5515-5523

GIWAXS – crystallinity and orientation

Detector

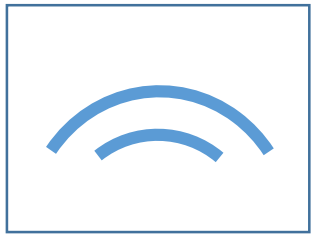
Isotropic:





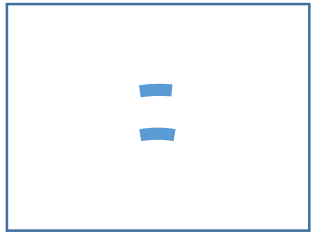
Rings

Textured – slightly oriented:



Arcs

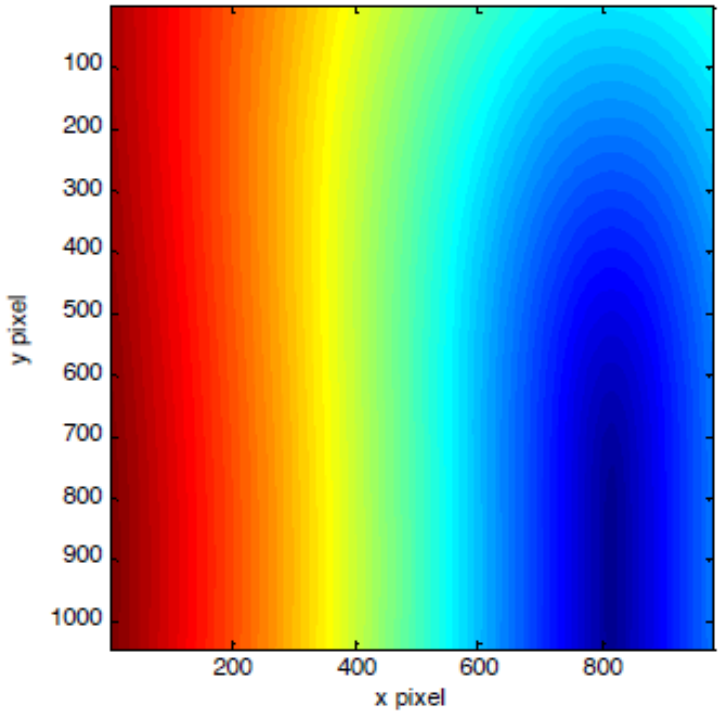
Highly oriented:

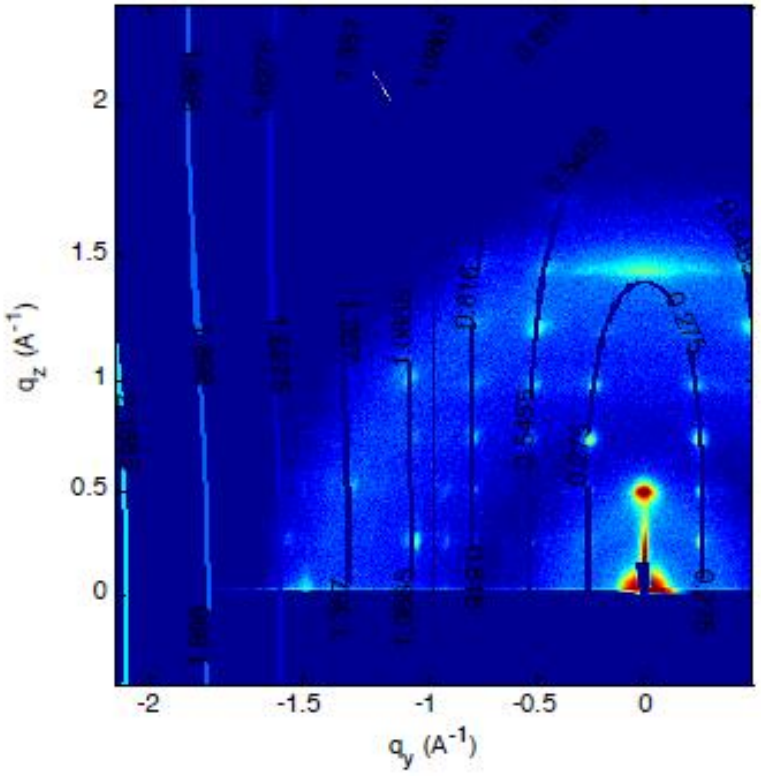


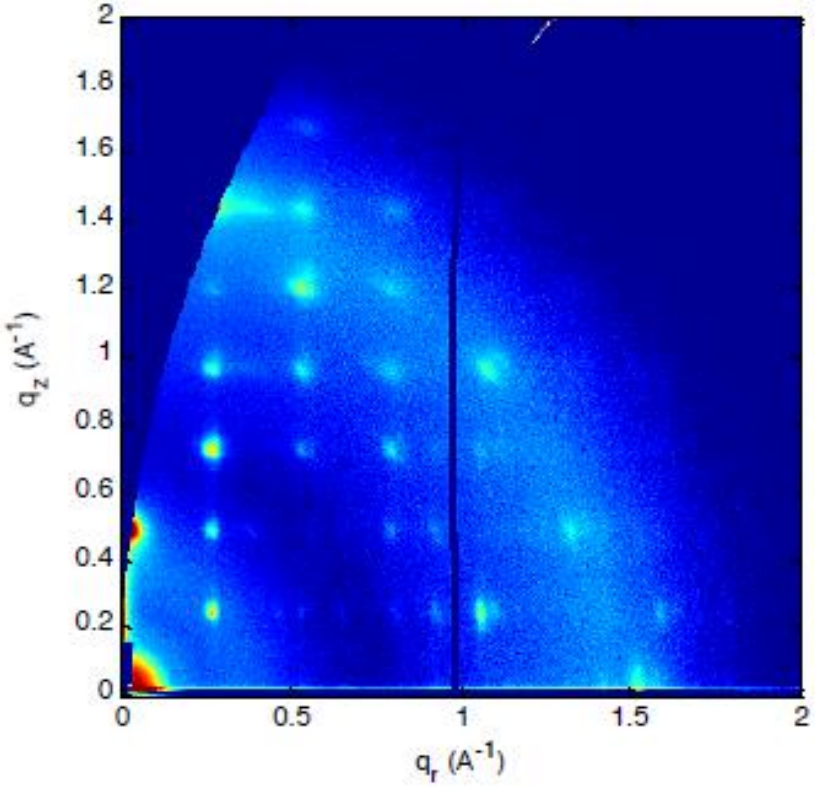
Spots

GIWAXS images

Maps of constant q_r values in pixel space





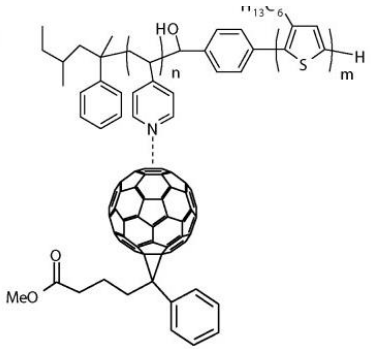


$$q_r = \sqrt{q_x^2} + \sqrt{q_y^2}$$

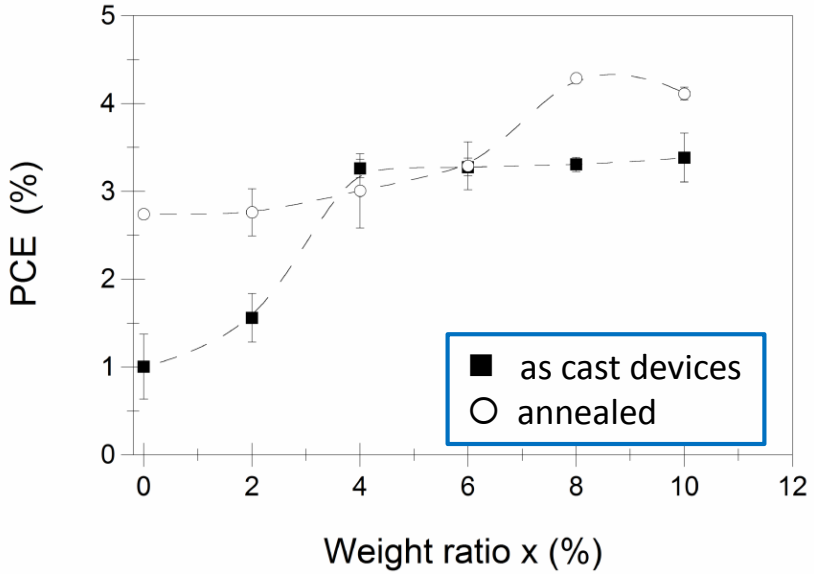
$$q = \sqrt{q_r^2} + \sqrt{q_z^2}$$

GIWAXS (1) - Block-copolymer additives in OPVs

P3HT:PCBM:P3HT-*b*-P4VP blends



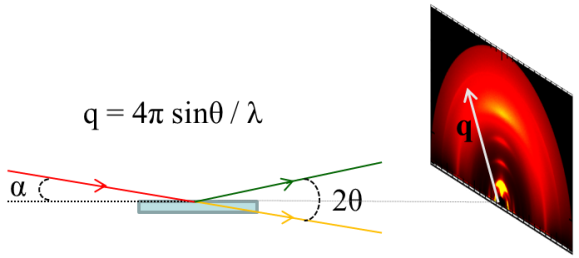
- Why P3HT- b -P4VP:
non-covalent supramolecular interactions between P4VP and
- P3HT- *b* -P4VP is blended with P3HT:PCBM
- Inverted OPV devices
  - Glass/ITO/TiOx/active layer/MoO_3/Ag
- Goal:
  - Exploit the PCBM - P4VP interactions to trigger the morphology and improve the power conversion efficiency (PCE)

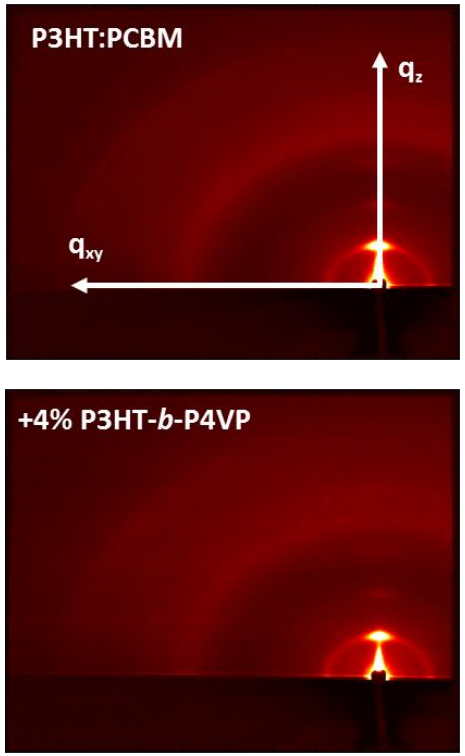


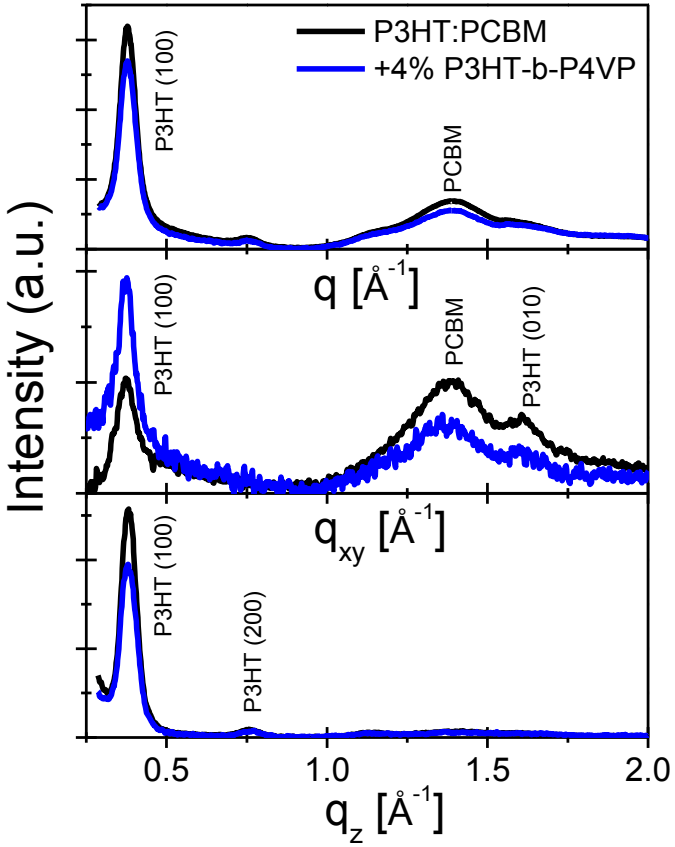
Prof. G. Hadziioannou (Uni Bordeaux)

GIWAXS (1) - Block-copolymer additives in OPVs

P3HT- b -P4VP as nanostructuring agent in the P3HT:PCBM blend*

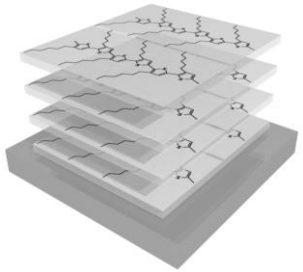


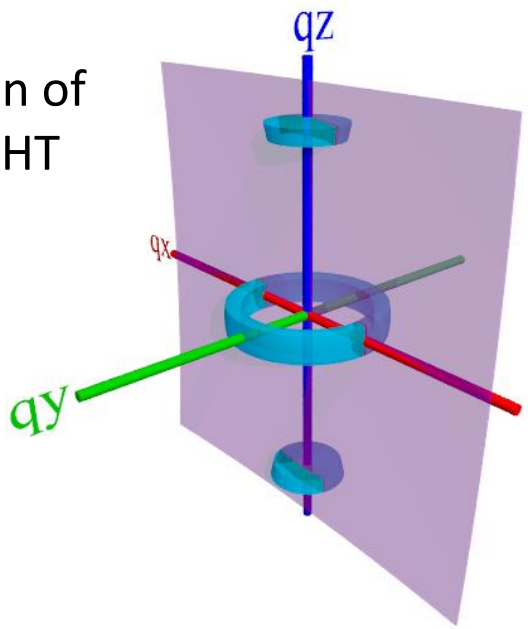




Upon P3HT- *b* -P4VP incorporation:

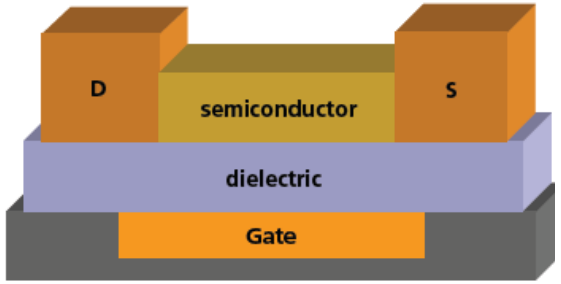
- PCBM is less aggregated → more interfaces for exciton dissociation
- Minor decrease in the crystallinity of P3HT
- Increase in the population of the face-on oriented P3HT crystallites



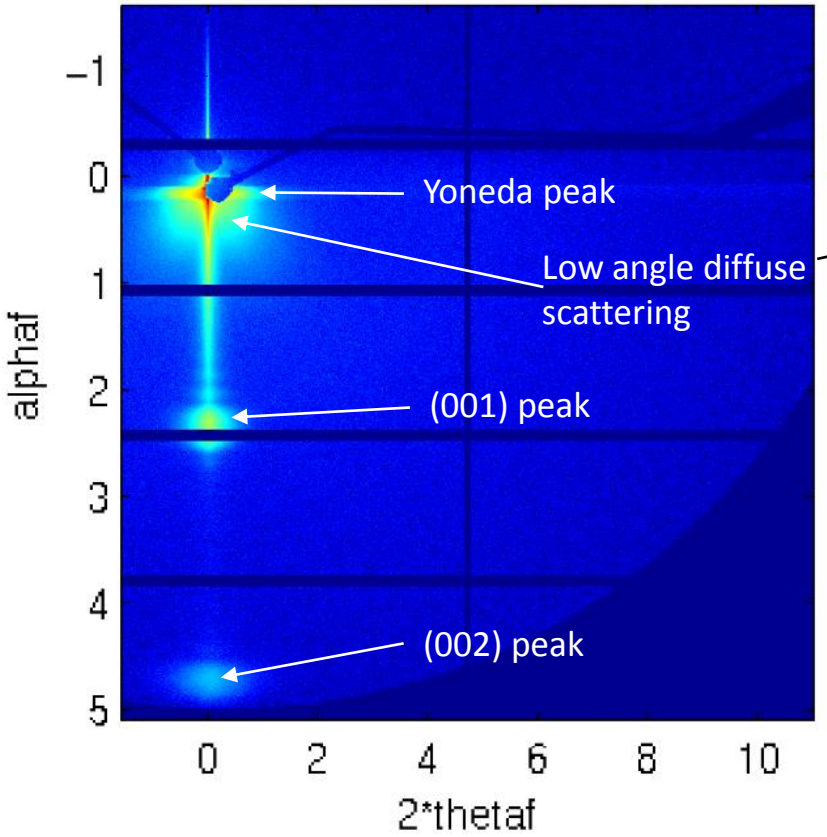


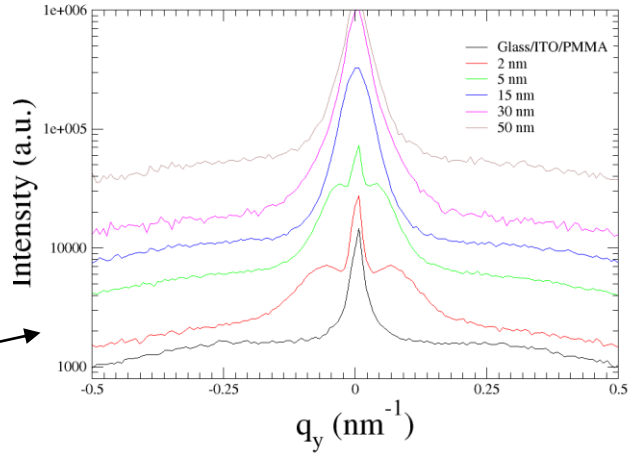
* *Adv. Mat*. 2012, **24**, 2196-2201

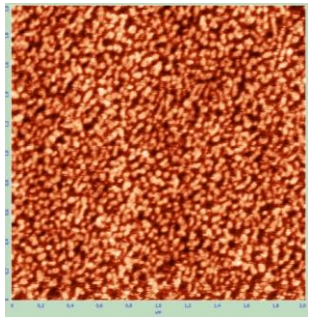
GIWAXS (2) – Ordering in organic thin film transistors



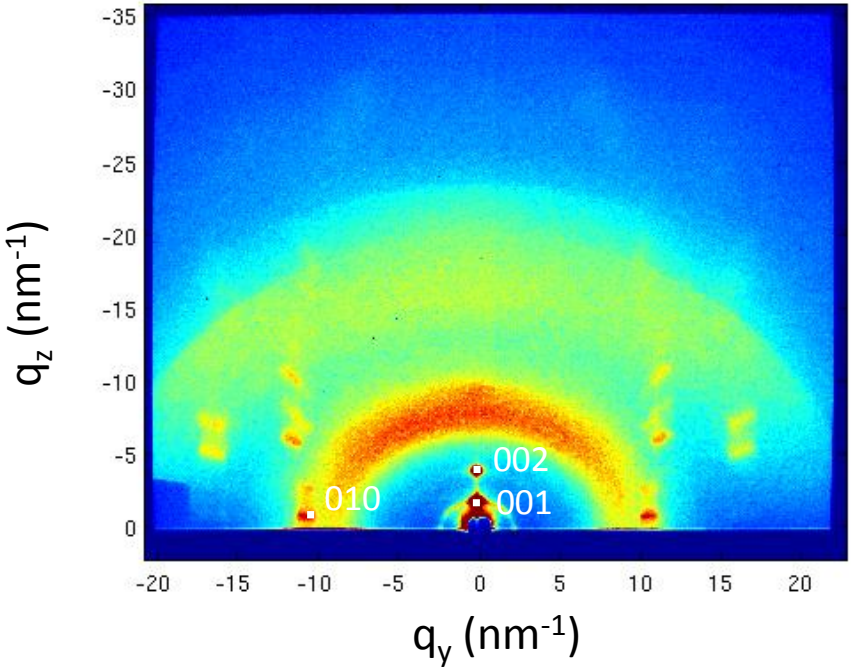
GISAXS





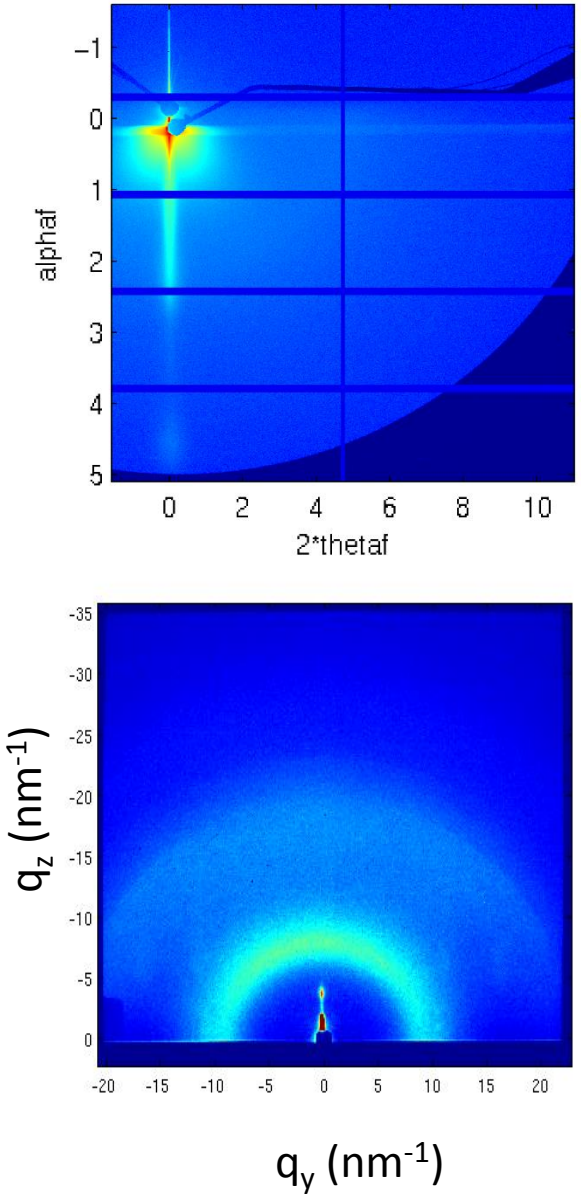


GIWAXS

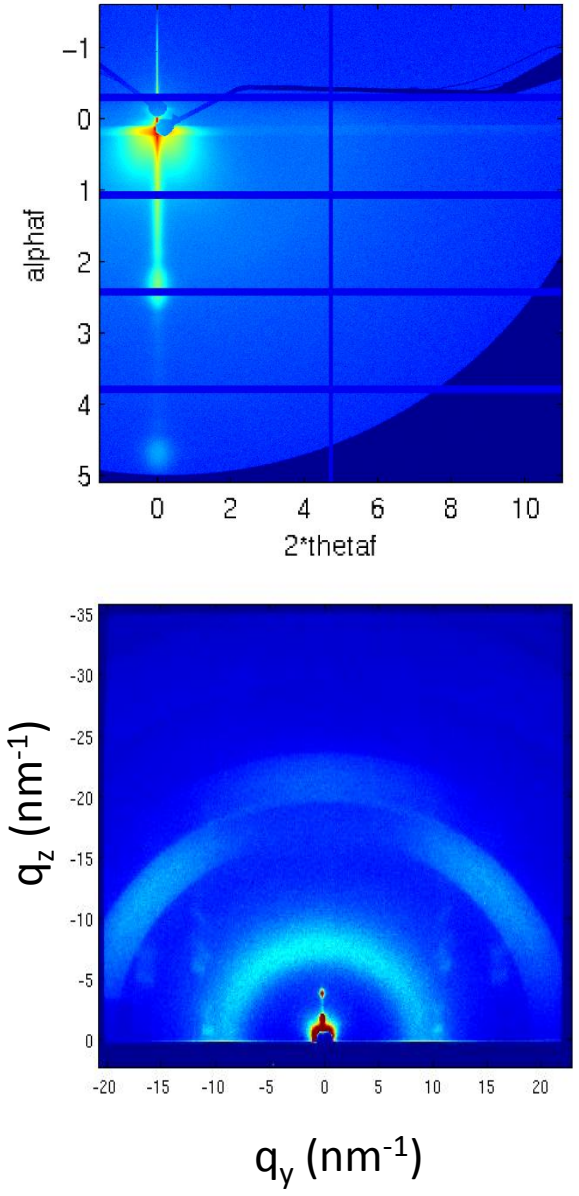


GIWAXS (2) – Ordering in organic thin film transistors

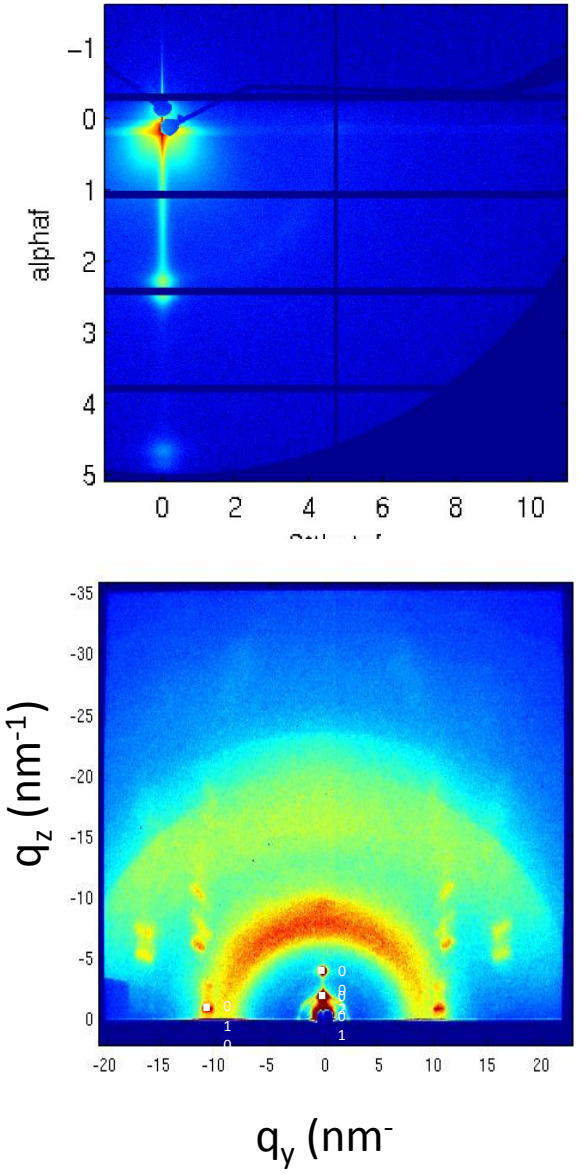
MM1320 (5 nm)



MM1322 (15 nm)



MM1325 (50 nm)



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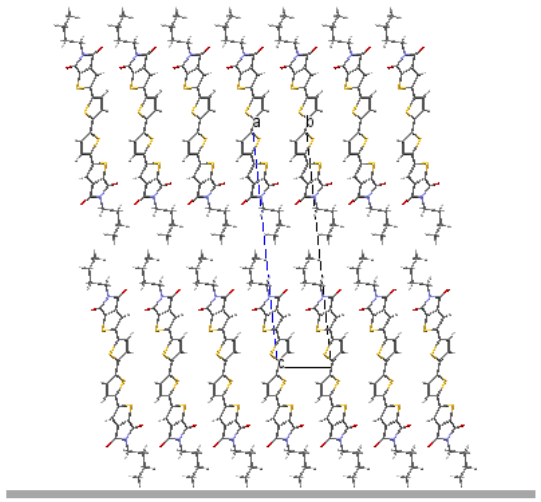


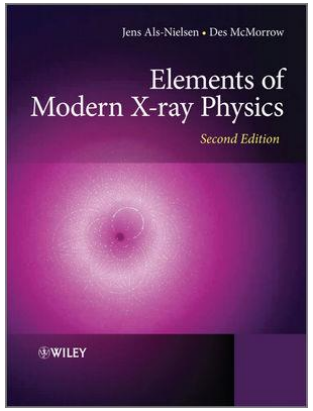
Software for DWBA

- IsGISAXS from R. Lazzary (Windows)
  R. Lazzari, (U. Curie, Paris) J. Appl. Cryst. 35:406-21 **(2002)**

- FitGISAXS from D. Babboneau (Igor Pro)
  D. Babboneau (U. Poitiers) *J. Appl. Cryst. 43 929-936* ***(2010)***

- BornAgain (Python)
  C. Durniak et al, (Juelich)

Books and references



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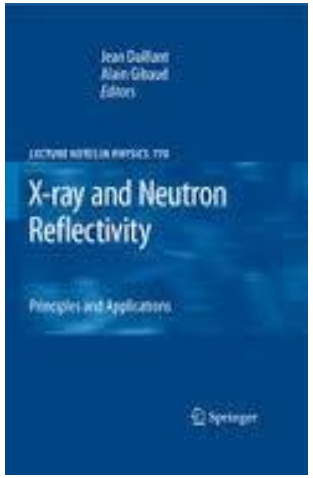

Conclusions

- GISAXS and GIWAXS are powerful tools to obtain statistical structural information on sub-monolayers, monolayers and multilayers of soft and hard condensed matter
- GISAXS → 1-100 (1000) nm
- GIWAXS → down to 0.1 nm
- Surface sensitivity
- High intensity allows for in-situ study

Thank you for your attention!

Questions?