Methoden moderner Röntgenphysik II: Struktur und Dynamik kondensierter Materie

Vorlesung zum Haupt/Masterstudiengang Physik

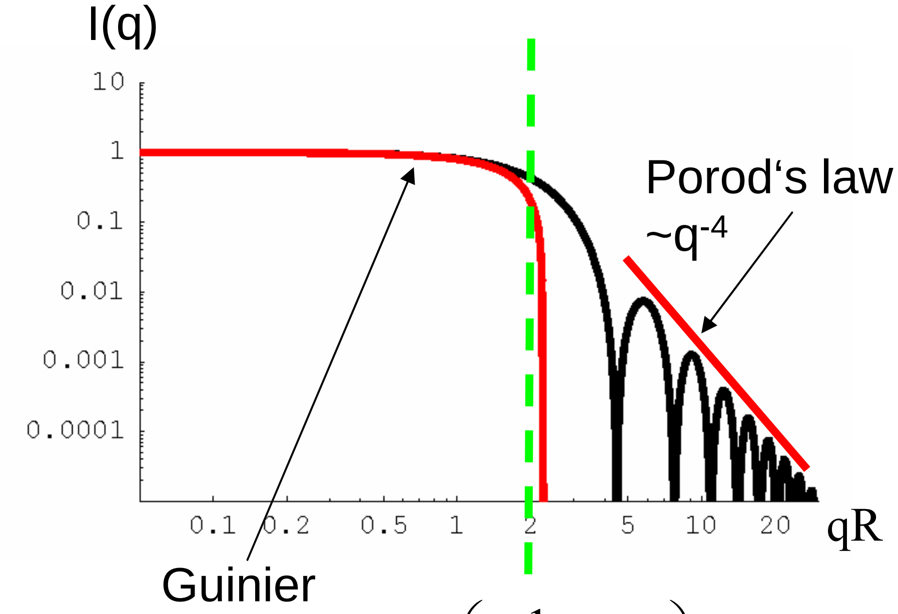
SS 2011

G. Grübel, M. Martins, E. Weckert et al.

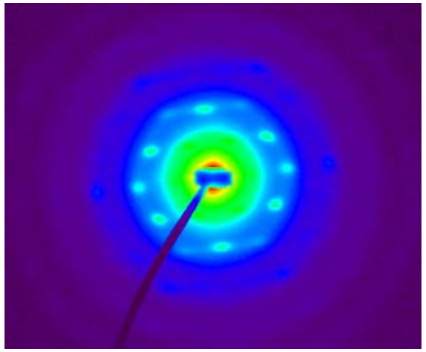
SemRm3, Physik, Jungiusstrasse
Di: 14:00-15:30
Do: 11:20-12:50
S. Roth (SR)
21.4.2011, 28.4.2011 & 3.5.2011 finden statt
26.4.2011 fällt aus

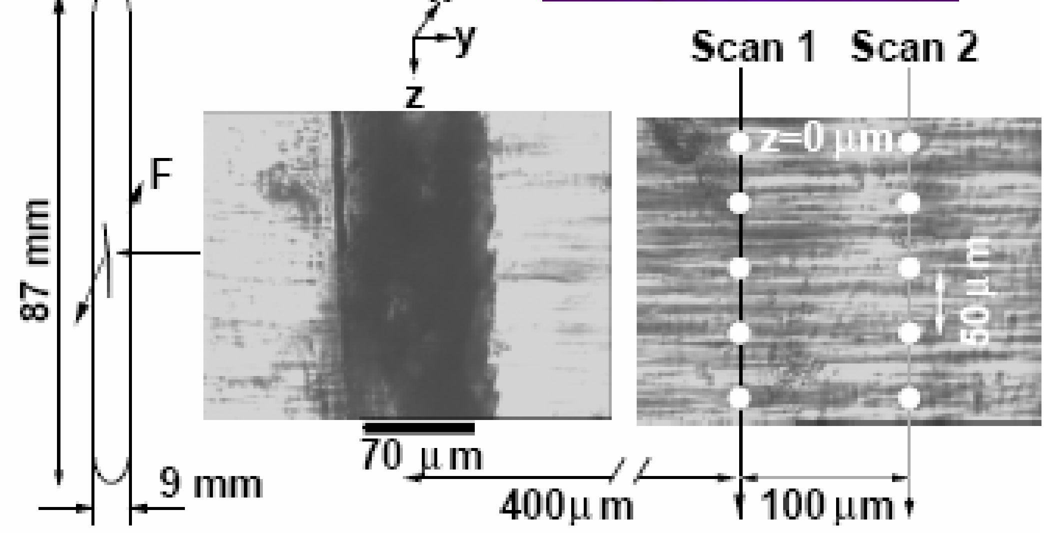
Summary last lecture

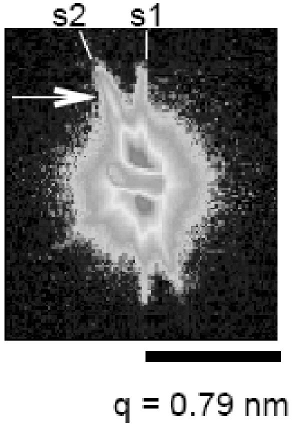
- Approximations for Form factor:
  Very useful to get first-hand information about multiple length scales
- Influence of form factor (concentrated samples)
- Examples:
  - Colloidal crystals
  - Cracks & crazes



$$I(q) = I(0)\cdot\exp\left(-\frac{1}{3}R_G^2 q^2\right)$$







Questions?

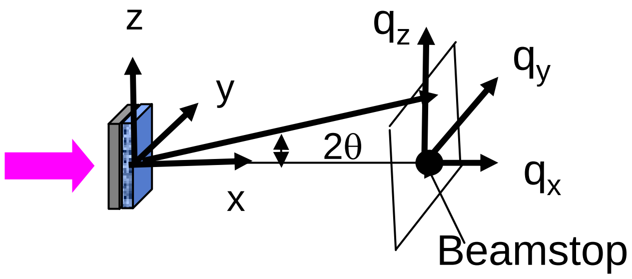
Outline

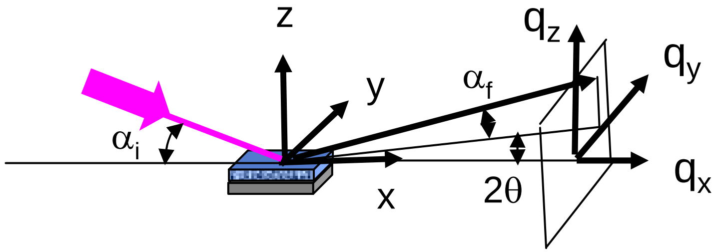
Au on glass!

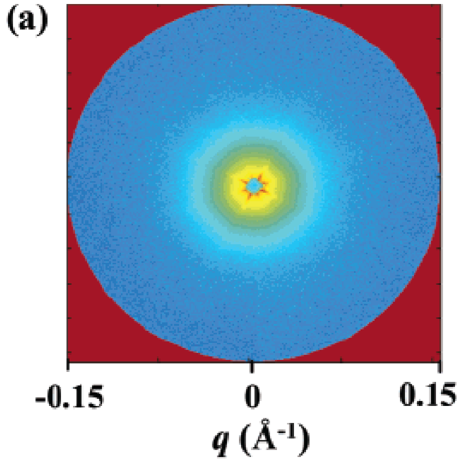
- SAXS versus GISAXS
- GISAXS – theory
- Instrumentation
- Application examples:
  - Gold on glass
  - in-situ growth of colloidal crystals
  - Polymer nanochannels

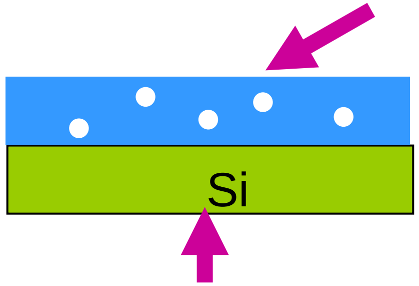
It is important to understand the basic features of the different GISAXS pattern and cuts.

T-SAXS vs. GISAXS

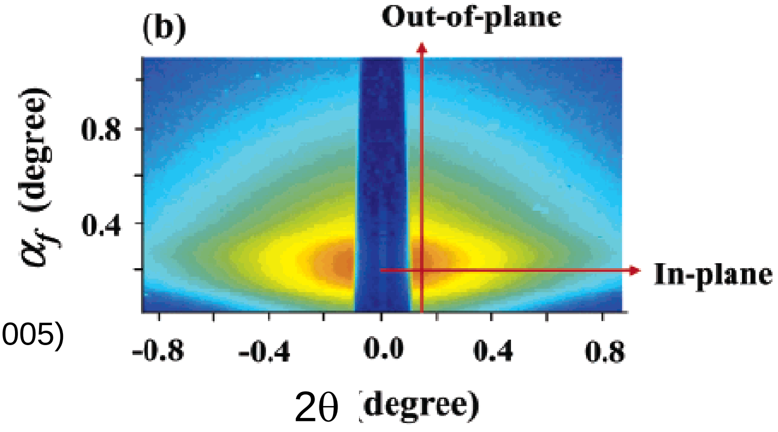








Lee et al., Macromolecules, 38, 8991 (2005)

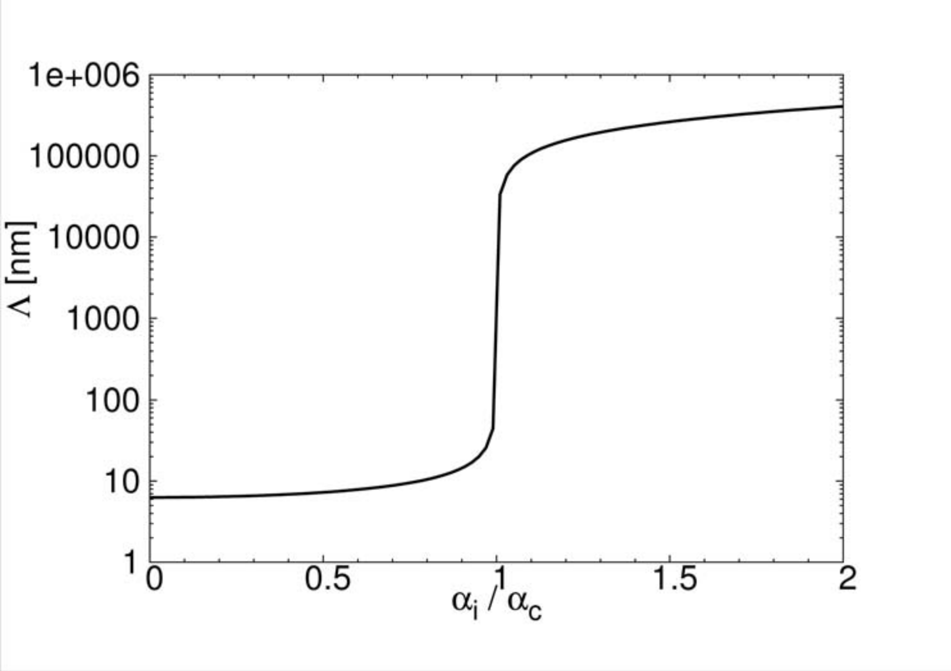


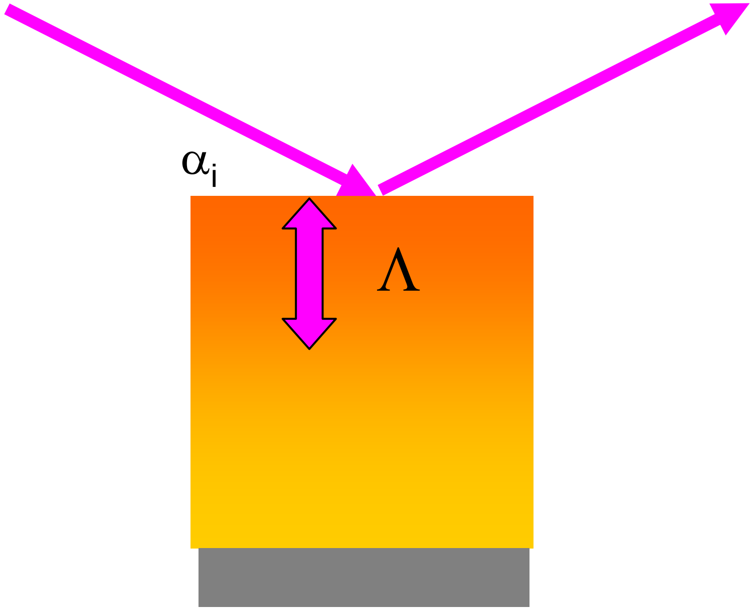
- Easy measurement
- Easy analysis
- In-plane information (q_y,q_z)
- Any possible scattering from substrate
- Transparency of substrate
- High energy

- Strong intensity
- Easy preparation of samples
- Full information (q_x,q_y,q_z)
- Scattering from surface / internal structure
- Scattering from reflected AND transmitted beam
- Refraction effects (DWBA)
- Special setup

Surface sensitivity

Scattering depth of x-rays: $\Lambda = \frac{\lambda}{\sqrt{2}\pi} \cdot \frac{1}{\sqrt{\sqrt{\left(\alpha_i^2 - \alpha_c^2\right)^2 + 4\beta^2} - \left(\alpha_i^2 - \alpha_c^2\right)}}$

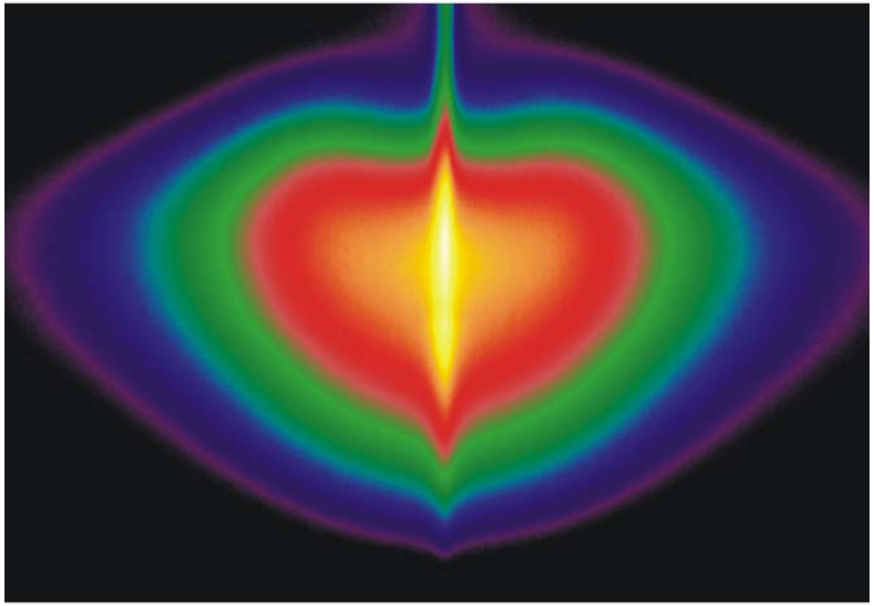




Vary incident angle $\alpha_i < \alpha_c$ to probe surface near region only or penetrate large sample volume

History

- 1963 Yoneda – anomalous Scattering below α_i
- 1988 Sinha – rough multilayers
- 1989 Levine – kinetics of gold nanoparticles on glass
- 1996 Müller-Buschbaum – mesoscopic length scales in polymer films
- 2003 Müller-Buschbaum – combination with µfocused beams
- Since 2006 „going nano“ … PETRA III



BW4, CCD
Au
d=5nm
t=3h
T=300°C

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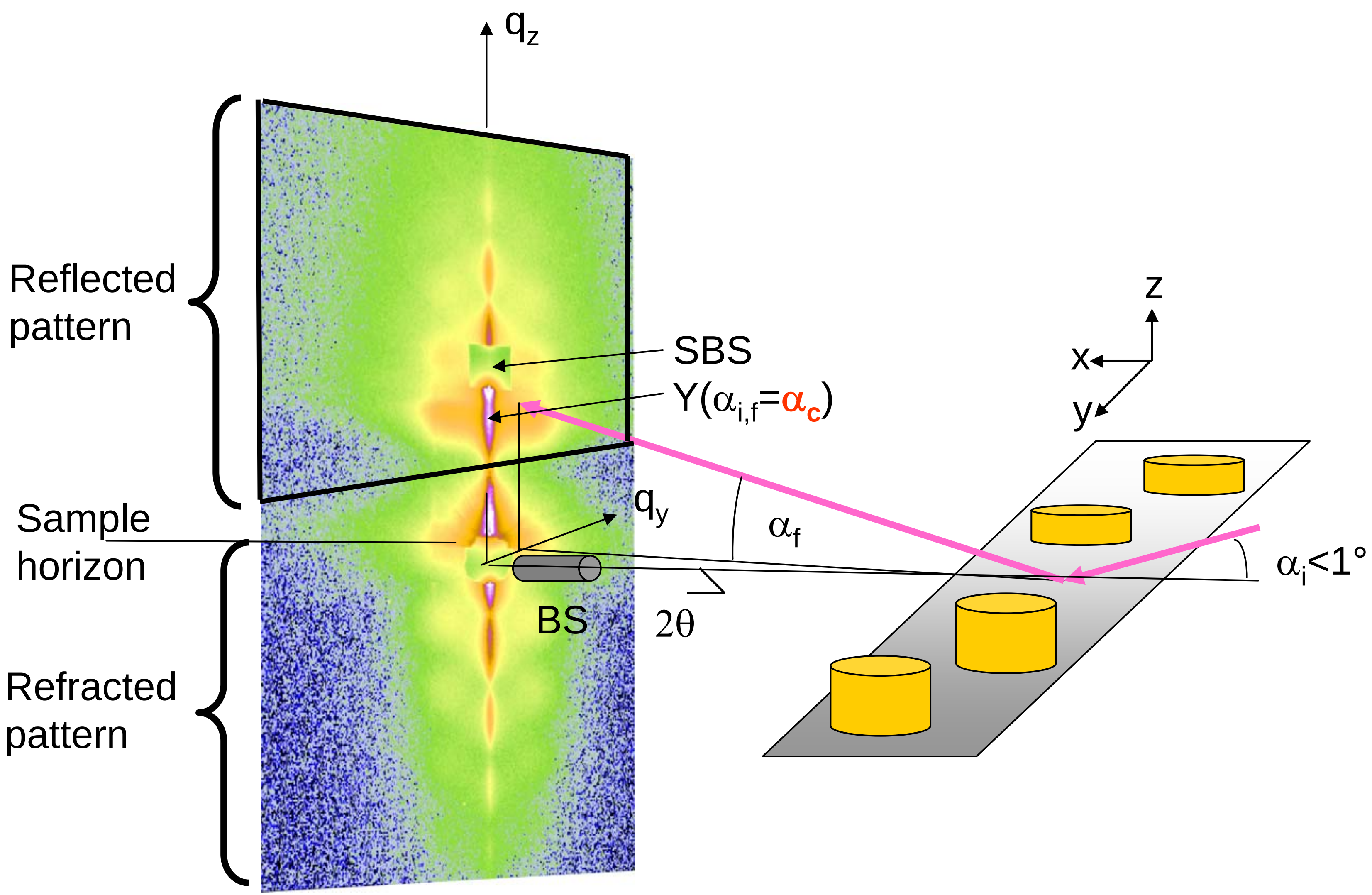
Grazing incidence small-angle x-ray scattering



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PHYSICAL REVIEW VOLUME 131, NUMBER 5 1 SEPTEMBER 1963

Anomalous Surface Reflection of X Rays

Y. Yoneda
Department of Applied Physics, Faculty of Engineering, Kyushu University, Fukuoka, Japan

(Received 9 January 1963; revised manuscript received 2 May 1963)

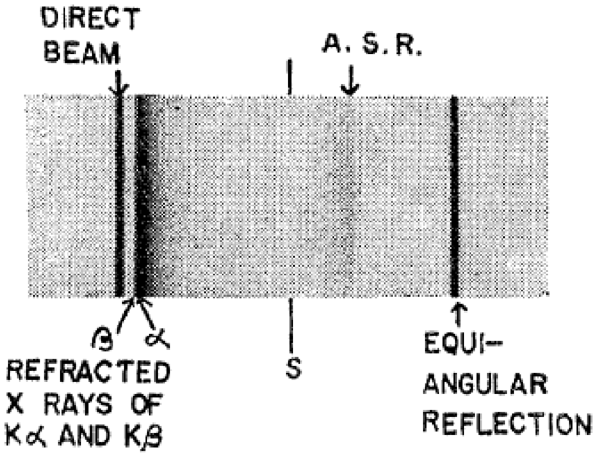


Fig. 2. Photograph of A.S.R. by a glass sample, ×2.

The first sucessful experiment

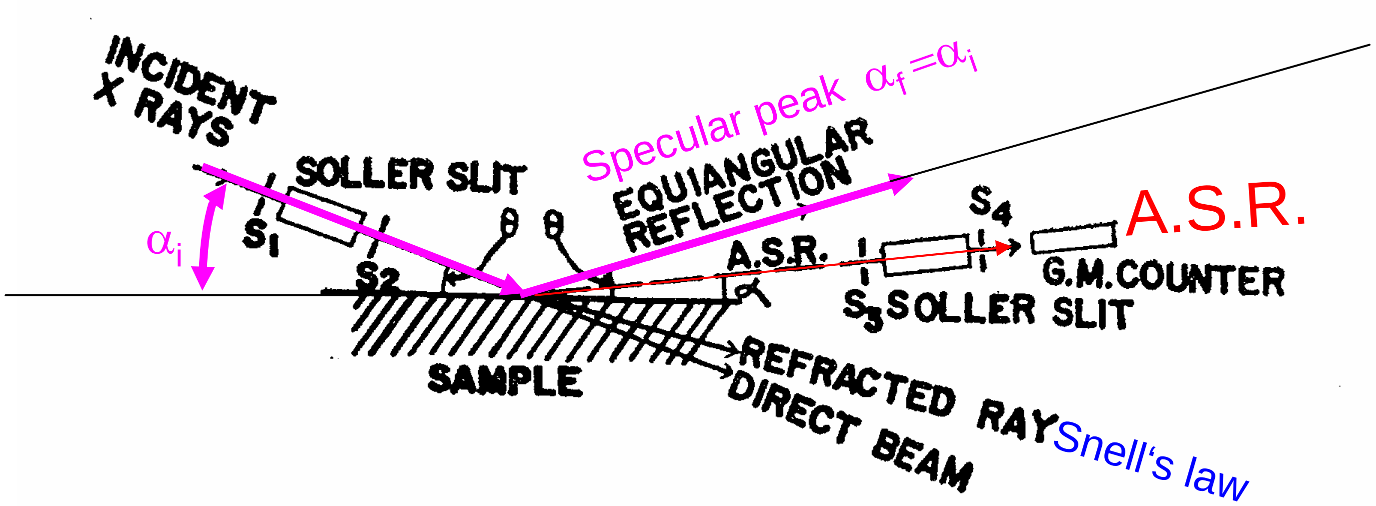


FIG. 1. Schematic view of the experimental arrangement in the incident plane.

Anomalous Surface Reflection
(diffuse scattering)

Au, 20nm-200nm
Si

Intensity between α_f=0° and α_f=α_i !!!

Why ?

Yoneda, Phys. Rev. 131, 2010 (1963)

Refractive index for x-rays

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

real part

Number density of atoms

Atomic number

$$\delta = \frac{\lambda^2}{2\pi} r_0 \underbrace{NZ}_{\rho_e}$$

imaginary part

wavelength

Absorption coefficient

$$\beta = \frac{\lambda}{4\pi}\mu$$

$$e^{-\mu x}$$

(Lambert-Beers law)

	$r_0\rho_e$ [10^{10}cm^{-2}]	μ_x [cm^{-1}]
Vacuum	0	0
PS (C8H8)n	9.5	4
Si	19.7	85
Au	131.5	4170

$$\boxed{\alpha_c = \sqrt{2\delta}}$$

Critical angle

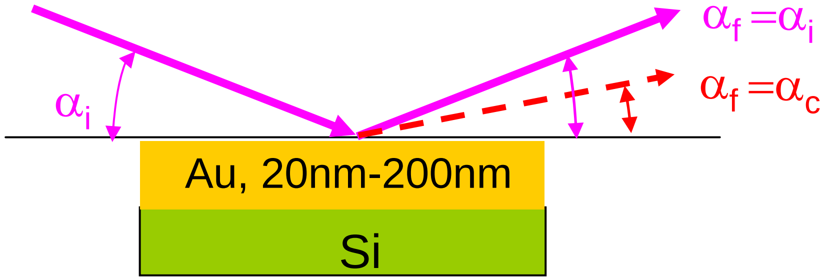
α_c(Si)=0.2°
α_c(Au)=0.5°

$$\boxed{\lambda \approx 1\text{Å} \Rightarrow \delta \sim 10^{-7}\ldots 10^{-6}}$$

Very small!

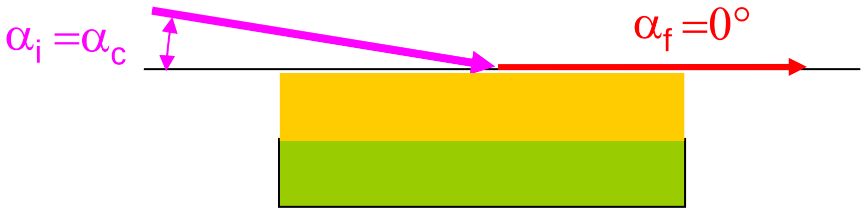
Matter: |n(X-rays)|<1 optically less dense than vacuum (remember Bragg‘s law)

Origin of intensity at α_c

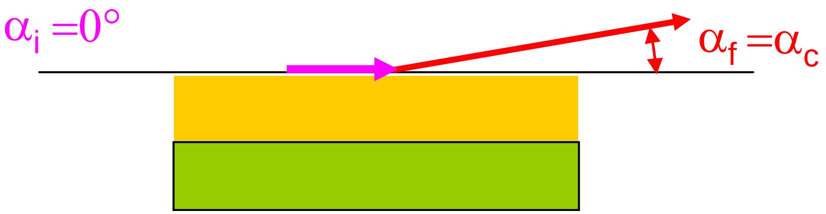


α_f(Au) = 0.56° = α_c(Au,1.8Å)

Total external reflection

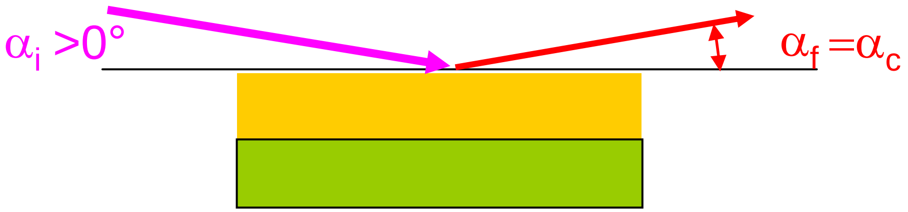


Reciprocity theorem & critical angle



must stem from wave parallel to surface

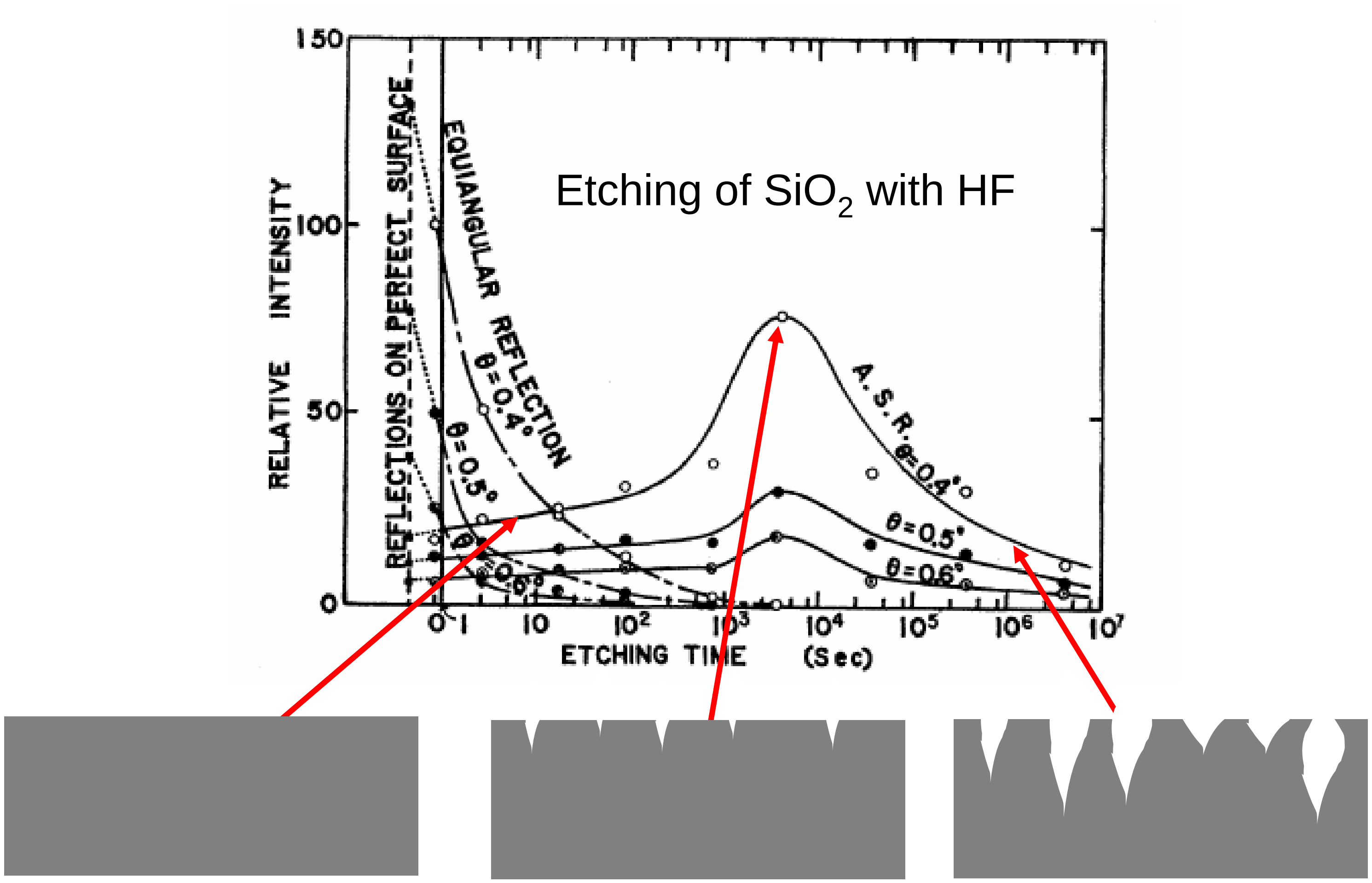
Yoneda



Yoneda, Phys. Rev. 131, 2010 (1963)

Hint: Roughness of the sample

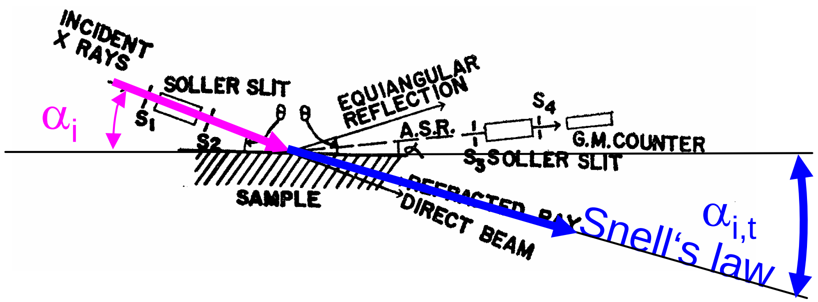
Yoneda peak = Scattering effect!

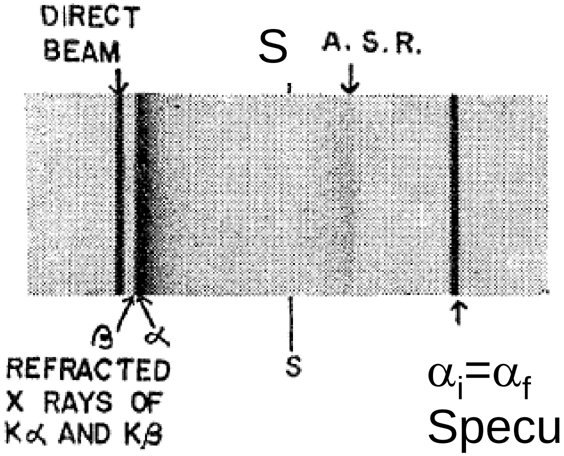


Etching of SiO_2 with HF

Basically the same

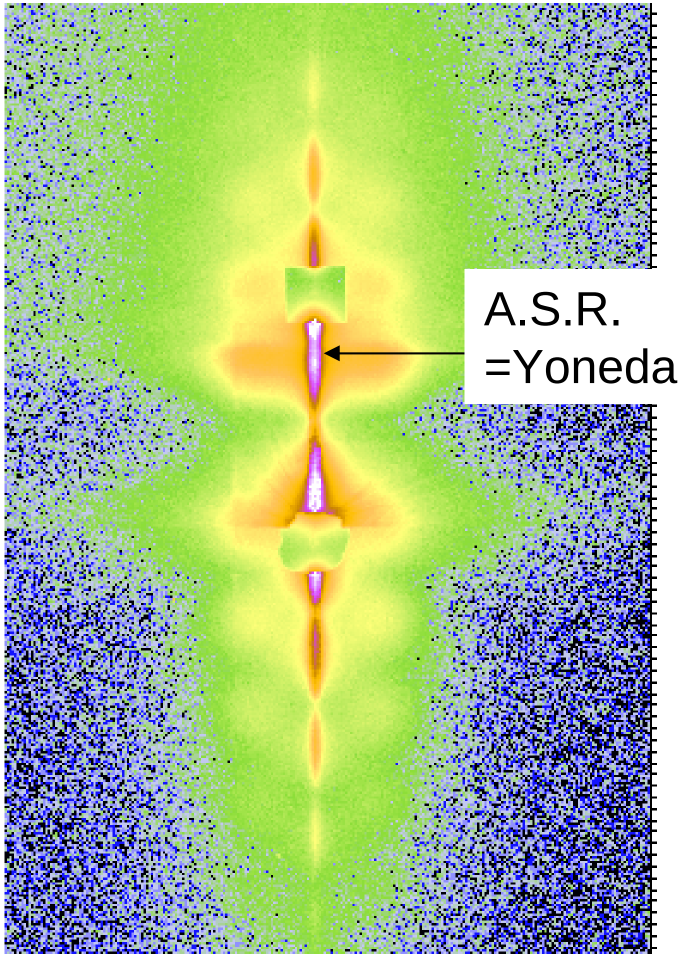
1963





$\alpha_i=\alpha_f$
Specular peak

today

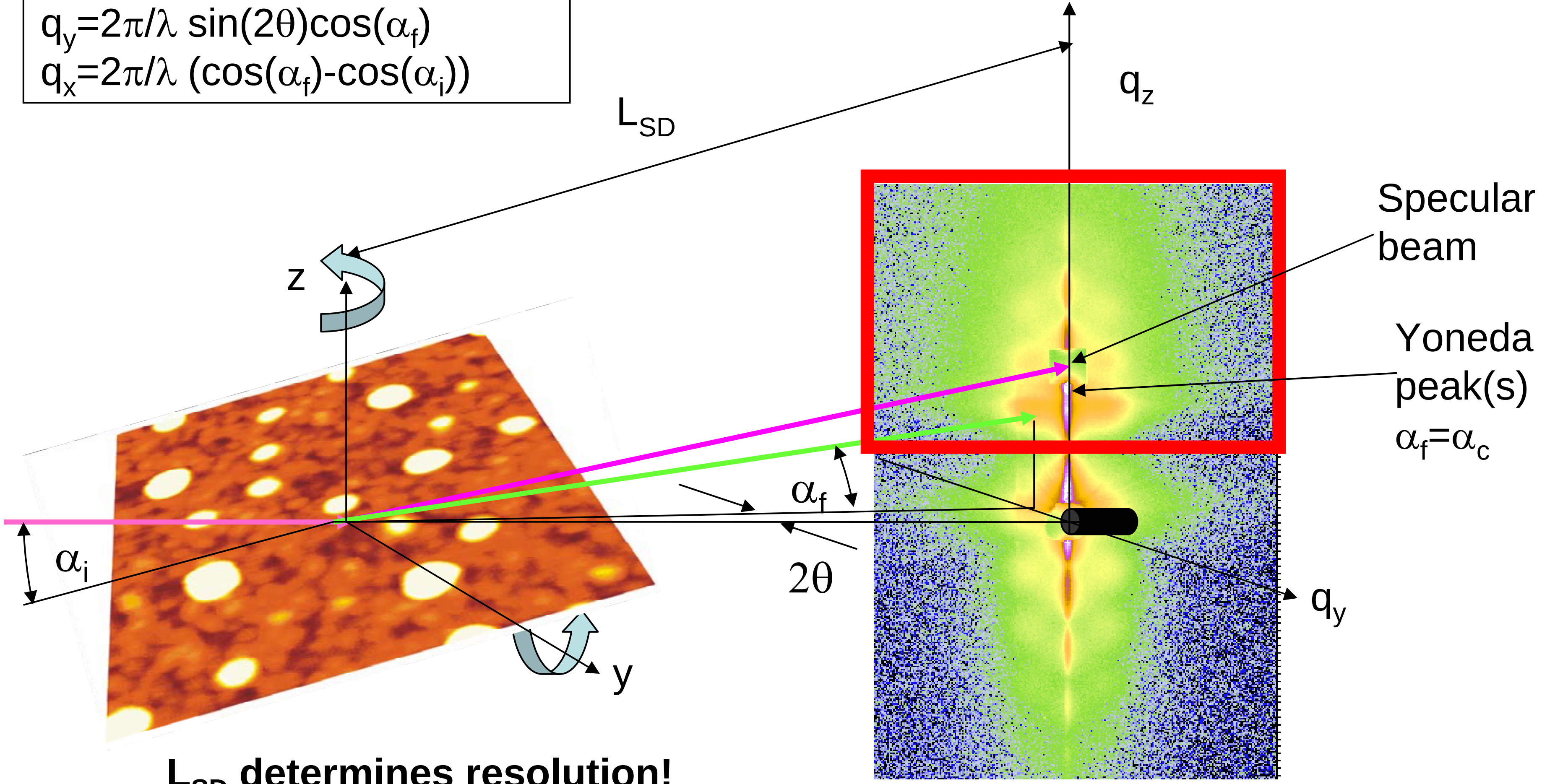


A.S.R.
=Yoneda peak

µGISAXS – more details

Grazing Incidence Small Angle X-Ray Scattering, GISAXS

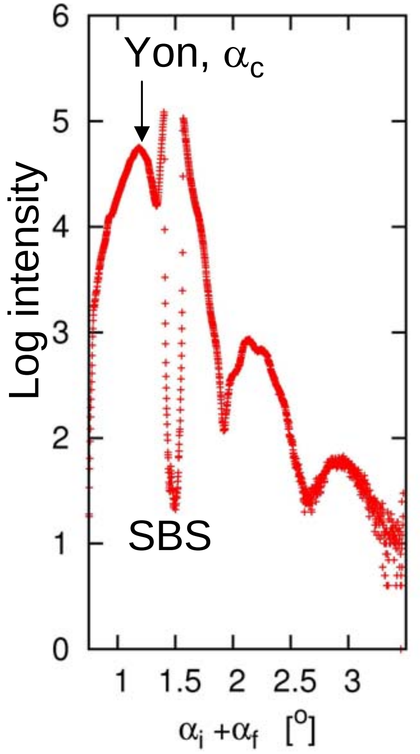
$q_z=2\pi/\lambda \sin(\alpha_i+\alpha_f)$
$q_y=2\pi/\lambda \sin(2\theta)\cos(\alpha_f)$
$q_x=2\pi/\lambda (\cos(\alpha_f)-\cos(\alpha_i))$



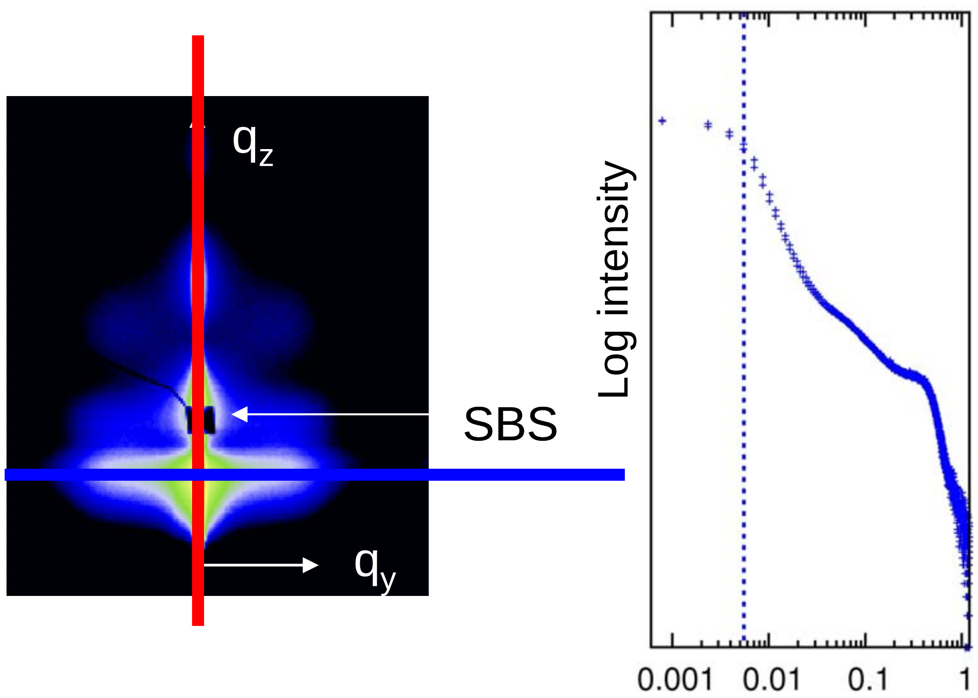
L_{SD} determines resolution!

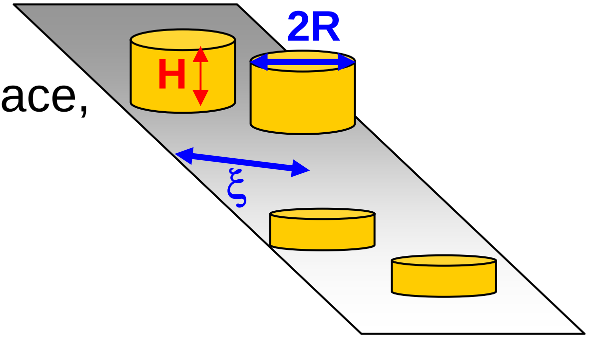
Grazing incidence small-angle x-ray scattering

cut at constant θ



cut at constant α_f





Correlation perpendicular to surface, e.g. height of nanoparticles, roughness, layer thickness

Detector-scan

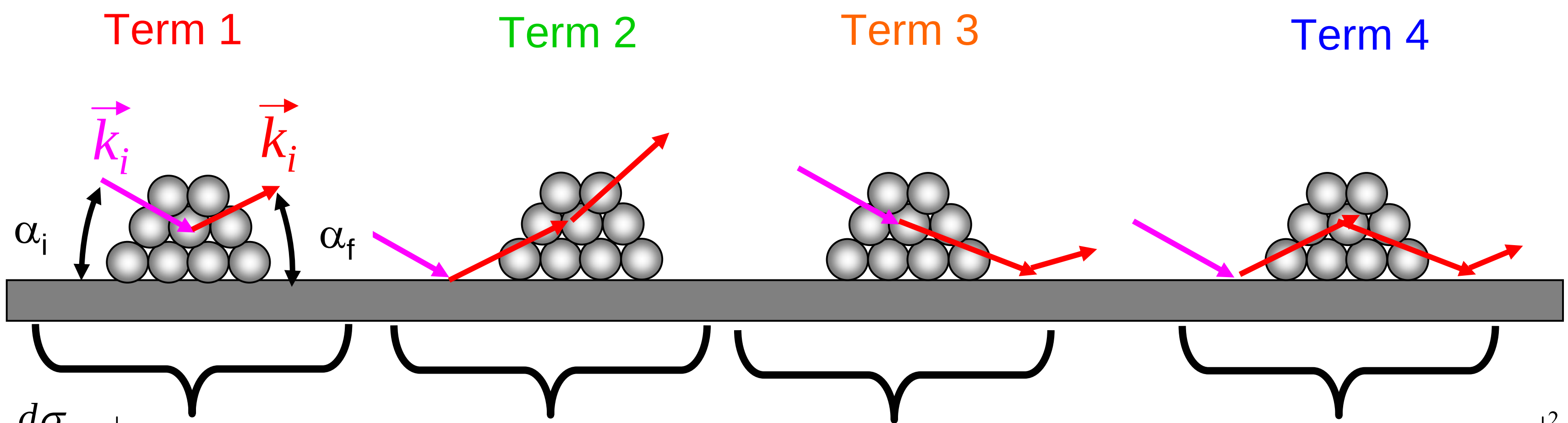
In-plane structures, e.g. distances ξ, Radius R

Out-of-plane scan

Salditt et al., Phys.Rev.B **51,** 5617 (1995)
Naudon et al., Physica B, **283**, 69 (2000)
Renaud et al., Science, **300**, 1416 (2003)
Müller-Buschbaum, Anal. Bioanal. Chem **376**, 3 (2003)

Distorted Wave Born approximation

Form factor: multiple scattering



$$\frac{d\sigma}{d\Omega} \propto \left| \underbrace{P(q_y, k_{fz} - k_{iz})}_{\text{Born term}} + R(\alpha_i)P(q_y, k_{fz} + k_{iz}) + R(\alpha_f)P(q_y, -k_{fz} - k_{iz}) + R(\alpha_i)R(\alpha_f)P(q_y, -k_{fz} + k_{iz}) \right|^2$$

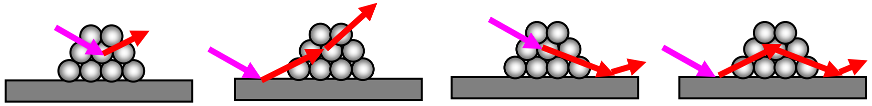
with $P(\vec{q}) = \int_V \exp(i\vec{q}\vec{r})\, d^3 r$

- Coherent interference between four waves along α_f
- Cross section depends on qy and qz
- Weighting with the reflection coefficients in incidence and emergence

Now for surfaces (nanoparticles)…

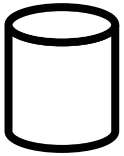
$$I(q_y,q_z)= c\,|P(q_y,q_z)|^2 \times S(q_y)$$

Form factor: multiple scattering

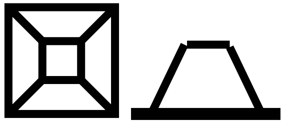


Shape, size and orientation

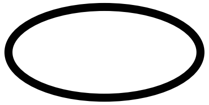
- cylinder



- pyramid



- ellipsoid



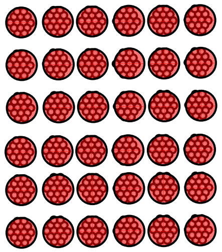
+ size distributions

Interference function

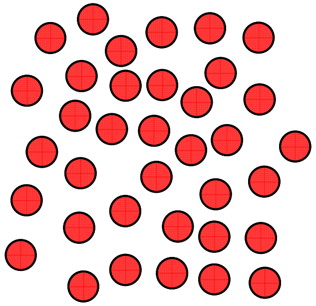
$S(q_y)$=FT(pair correlation function)

Spatial arrangement of the particles

- lattice



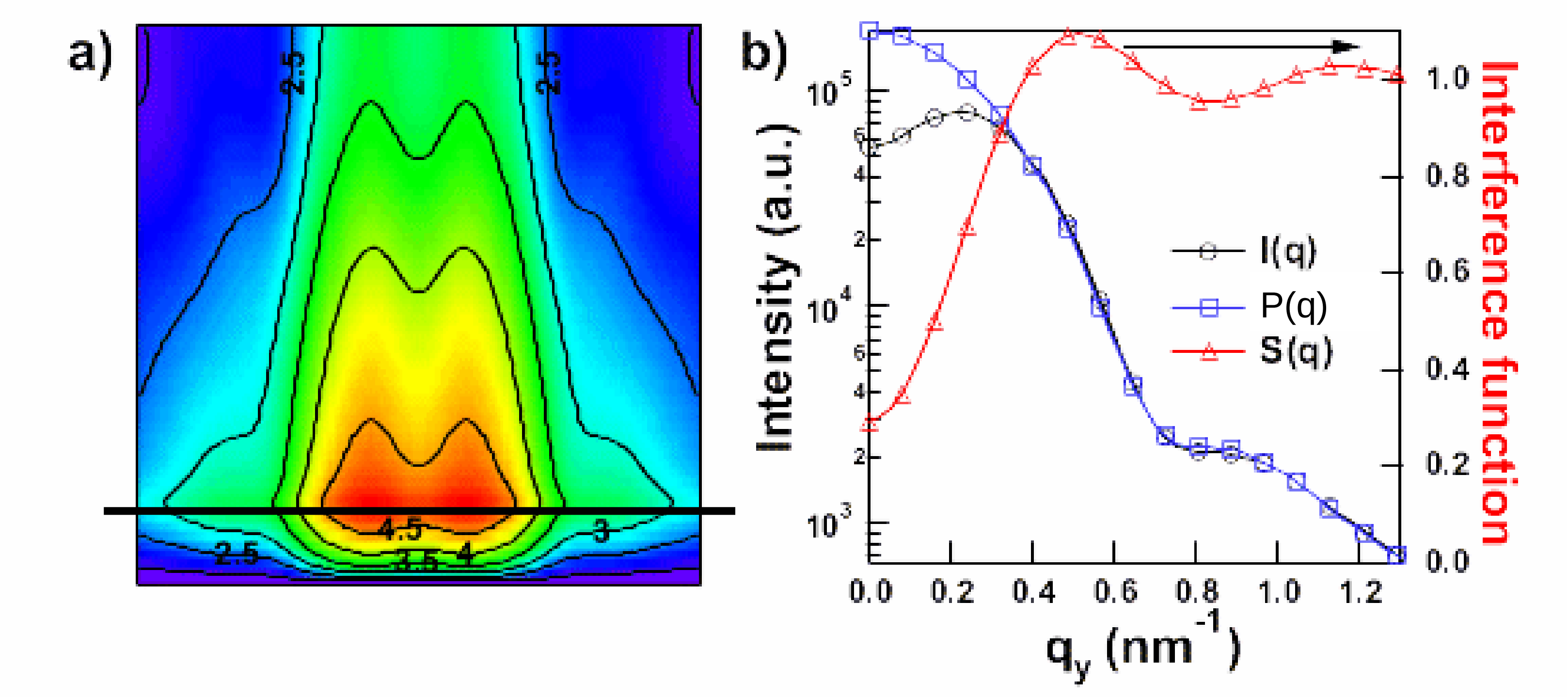
- paracrystal



+ mean distance
+ fluctuation of distances

Simulations: IsGISAXS (R. Lazzari)

$$I(q_y,q_z)= c\ |P(q_y,q_z)|^2 \times S(q_y)$$



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- SAXS versus GISAXS
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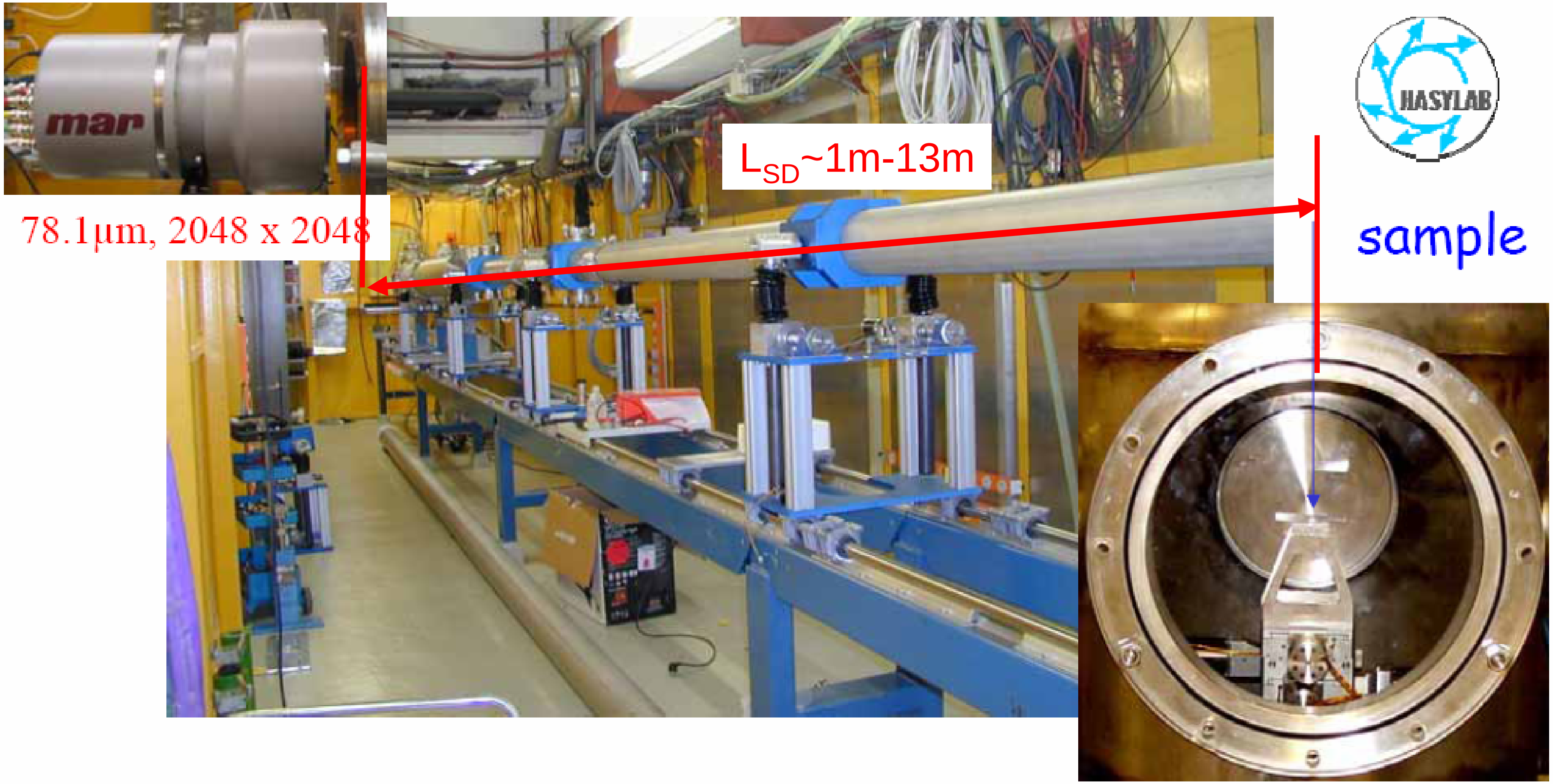
BW4 / HASYLAB (Hamburg, Germany)

for GI(U)SAXS experiments at the BW4 beamline @ HASYLAB (DESY, Hamburg)

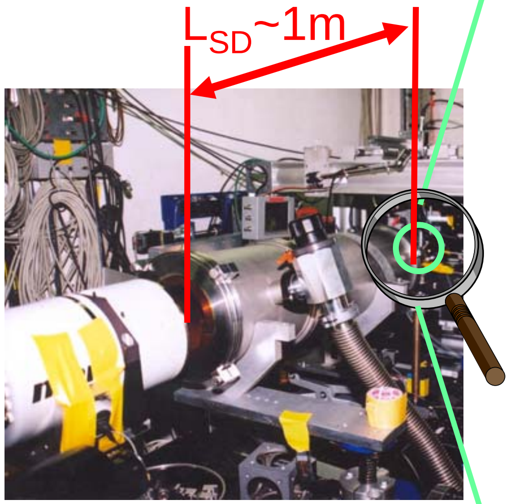


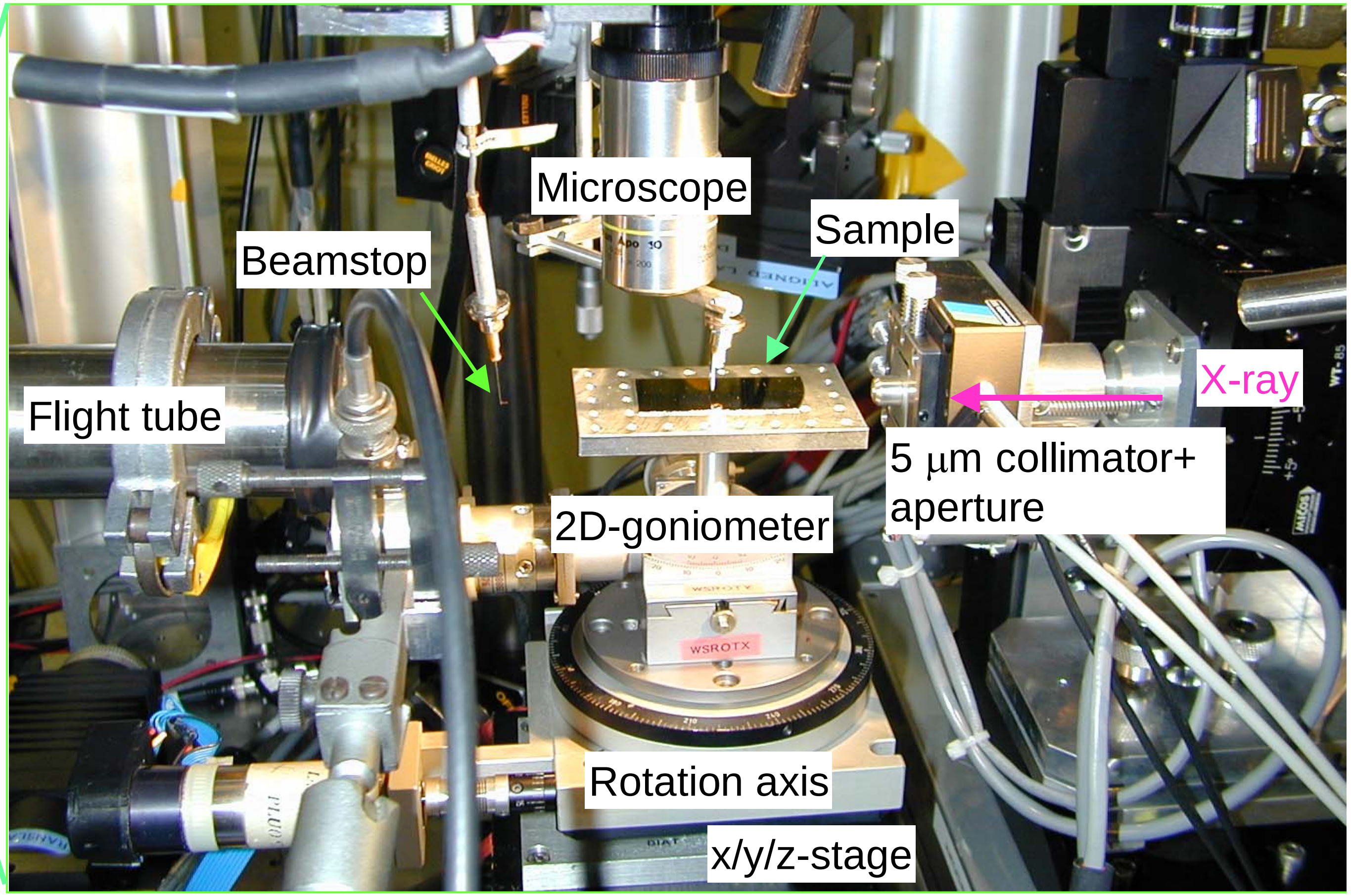
sample – detector distance up to **13 m** possible – optimized conditions for GI(U)SAXS

ID13 / ESRF (Grenoble, France)

Mean information ⇔ local information

Combination of GISAXS with micro-focus beam

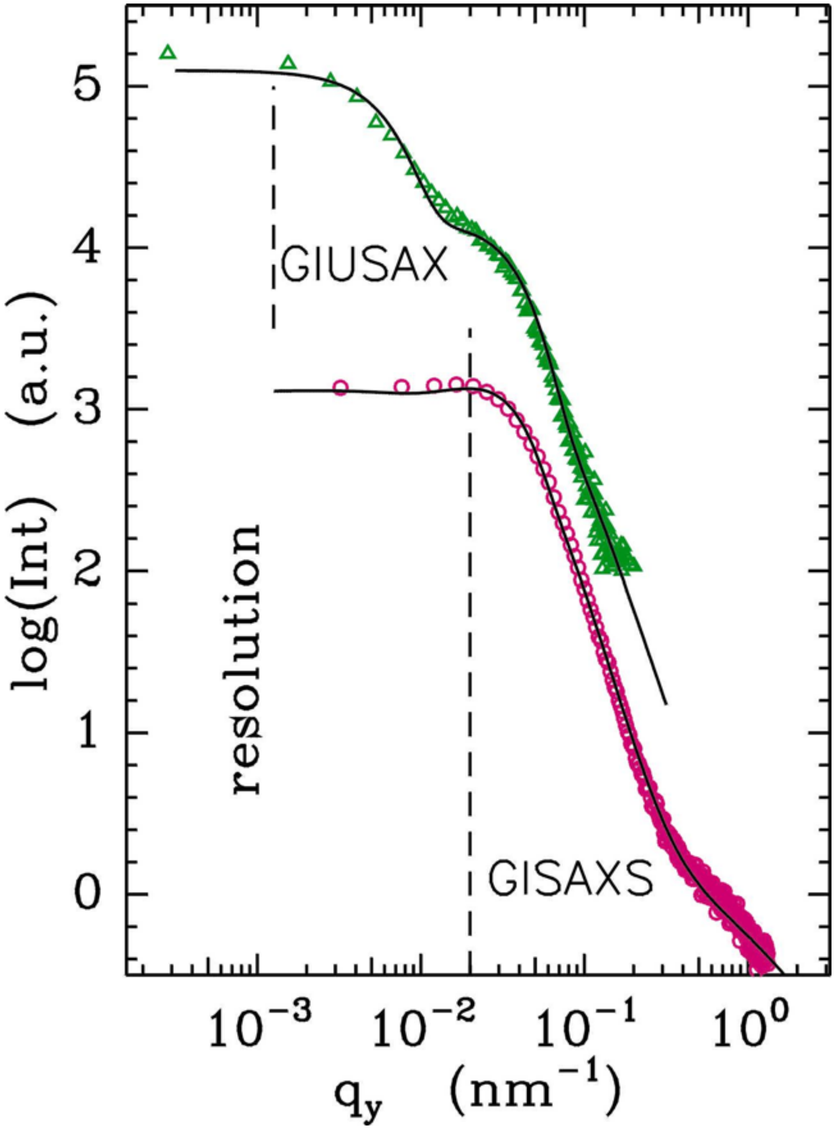




diameter of micro beam GISAXS experiment at ID13 (ESRF) 5μm

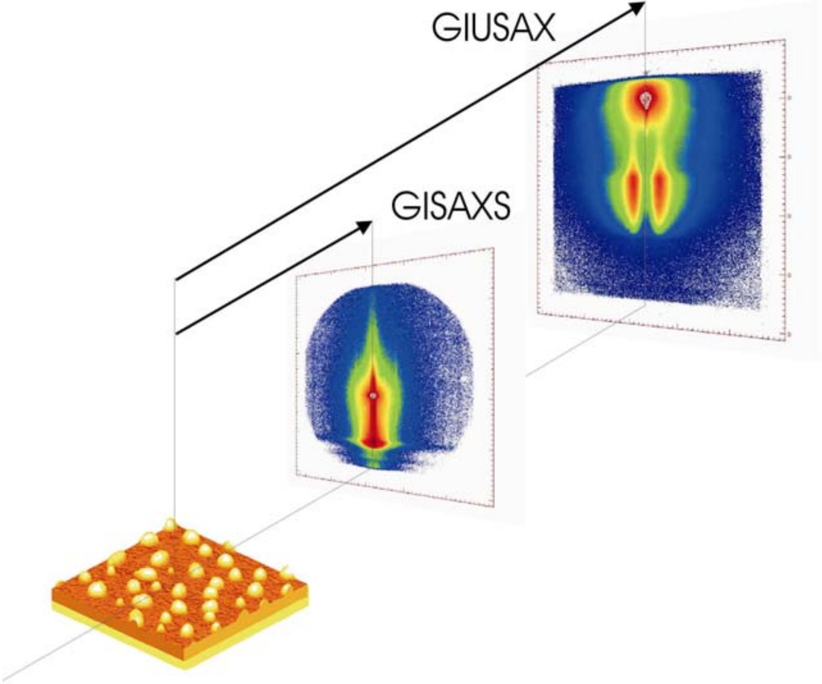
footprint (x/y) 300 x 5 μm^2 → local information

GISAXS & GIUSAXS



combination of GIUSAXS and GISAXS experiment:

GIUSAXS: sample-detector distance 12.8 m
GISAXS: 1.9 m



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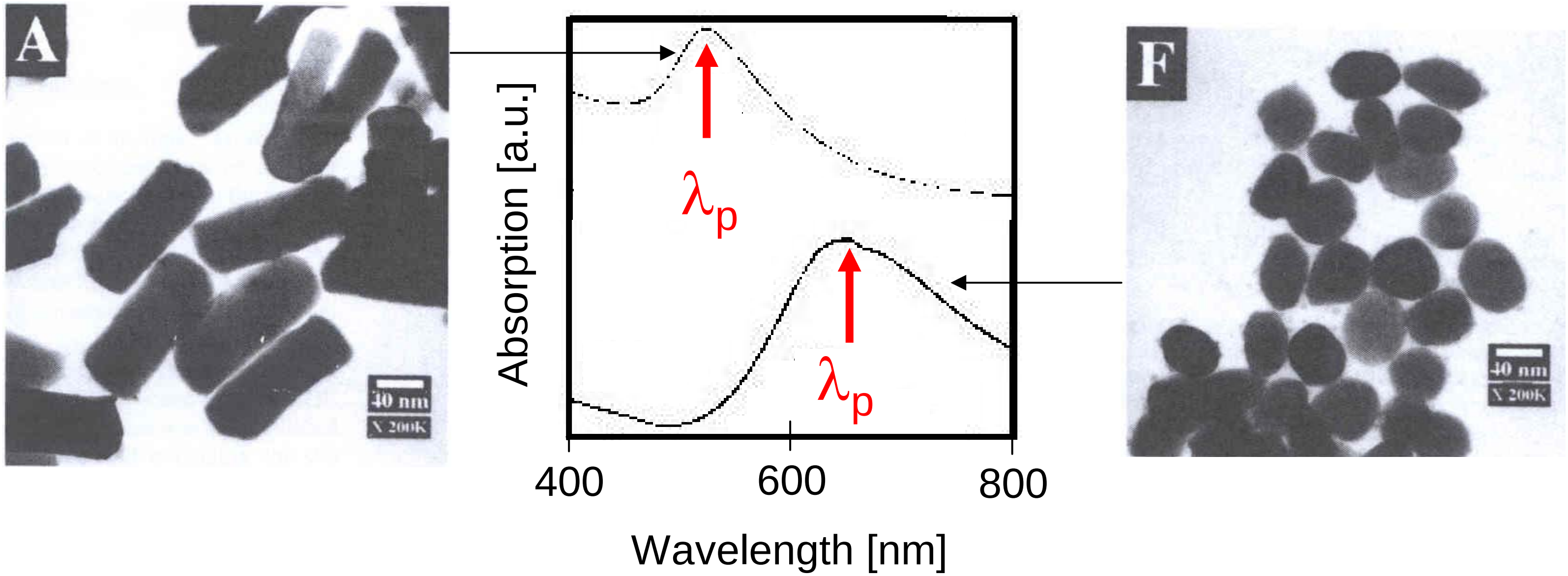
Tempering Au nanoparticles

Optical properties: sharp resonances ⟺ plasmon resonances
(visible light) cluster arrangement & shape



J.C. Hulteen et al., J Phys. Chem. B 101, 7727 (1997)

Annealing

S.V.R., H. Walter (CSEM), R. Domnick (identif) et al., (in preparation)

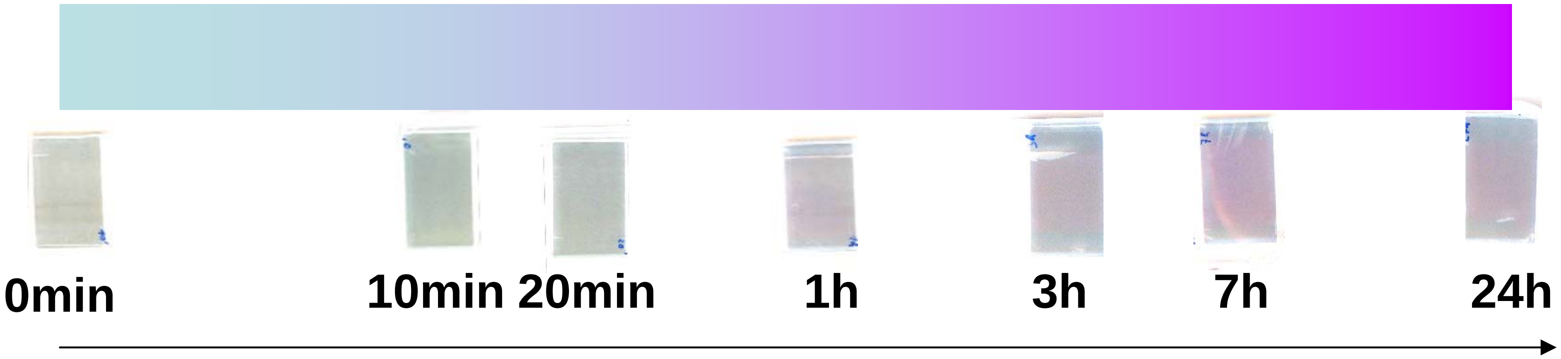
Au on glass

Parameters: Au layer mass thickness: **3nm , 5nm, 8nm**

Annealing time

approaching critical coalescence thickness

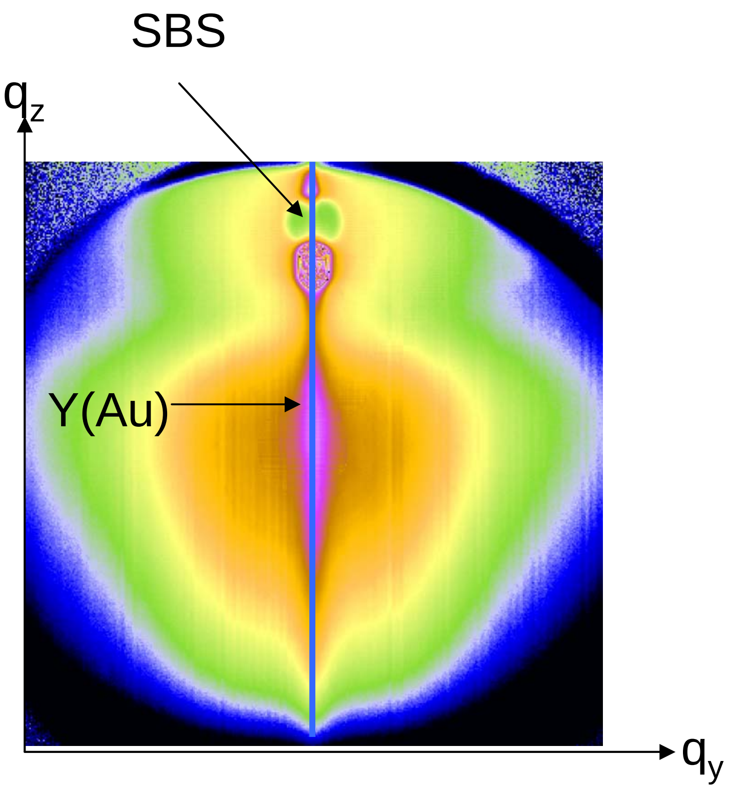
(cluster -> metal character)

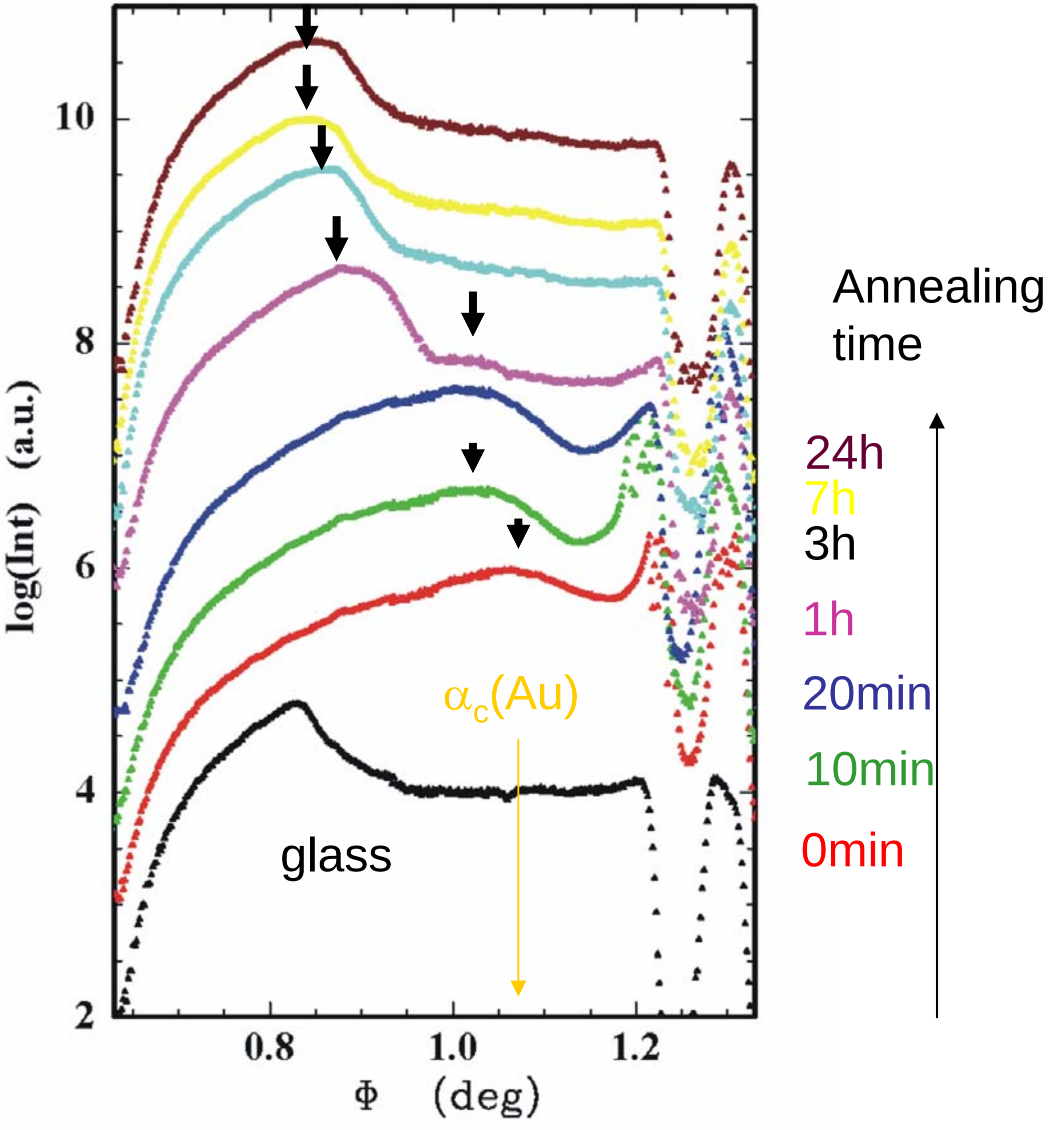


Log (Annealing time)

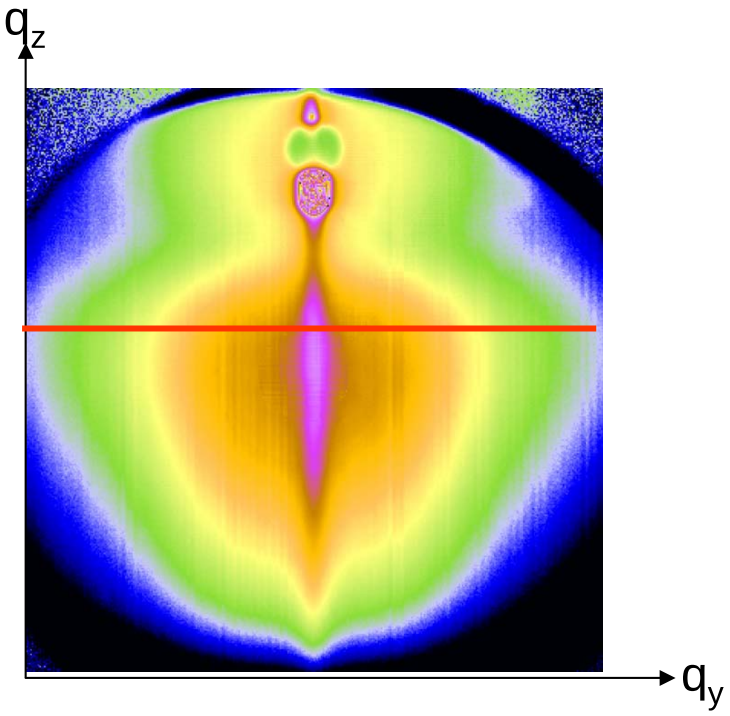
@ T_{anneal}=300°C < 1064°C (bulk melting point)

Surface coverage

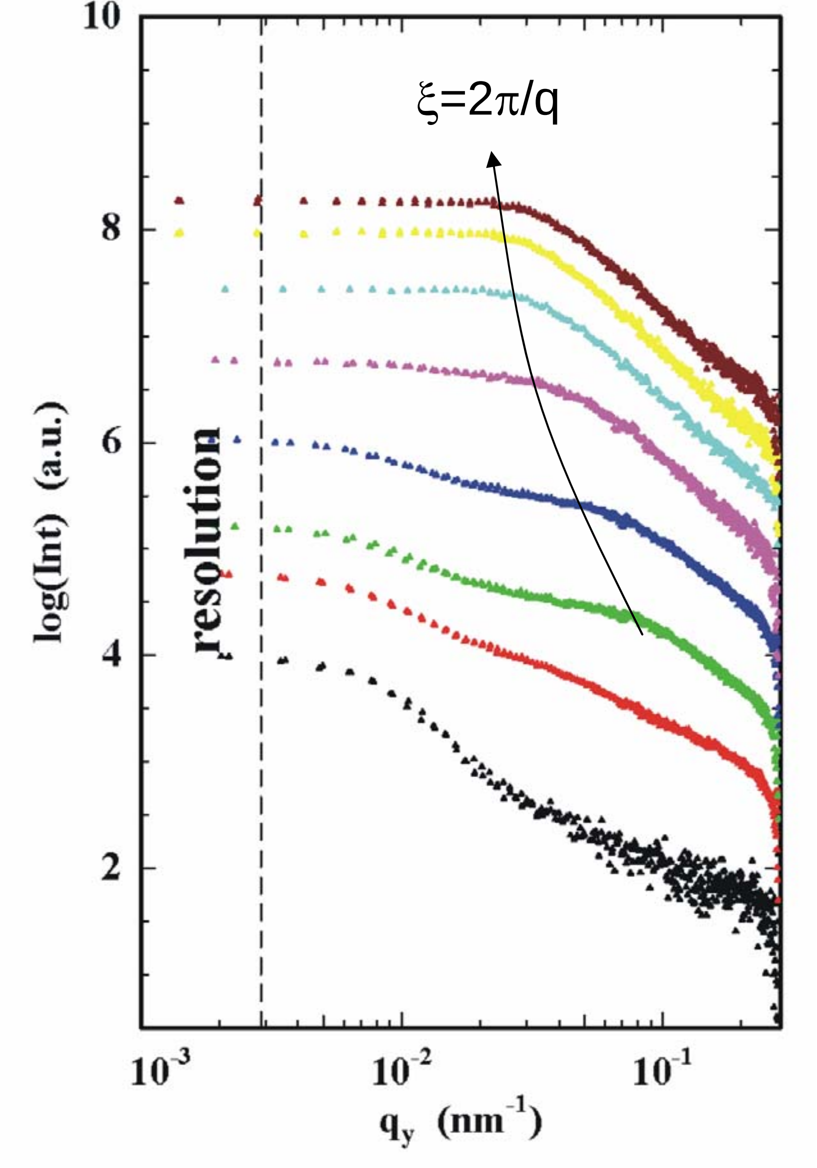



Detector scan (8nm)

In-plane ordering

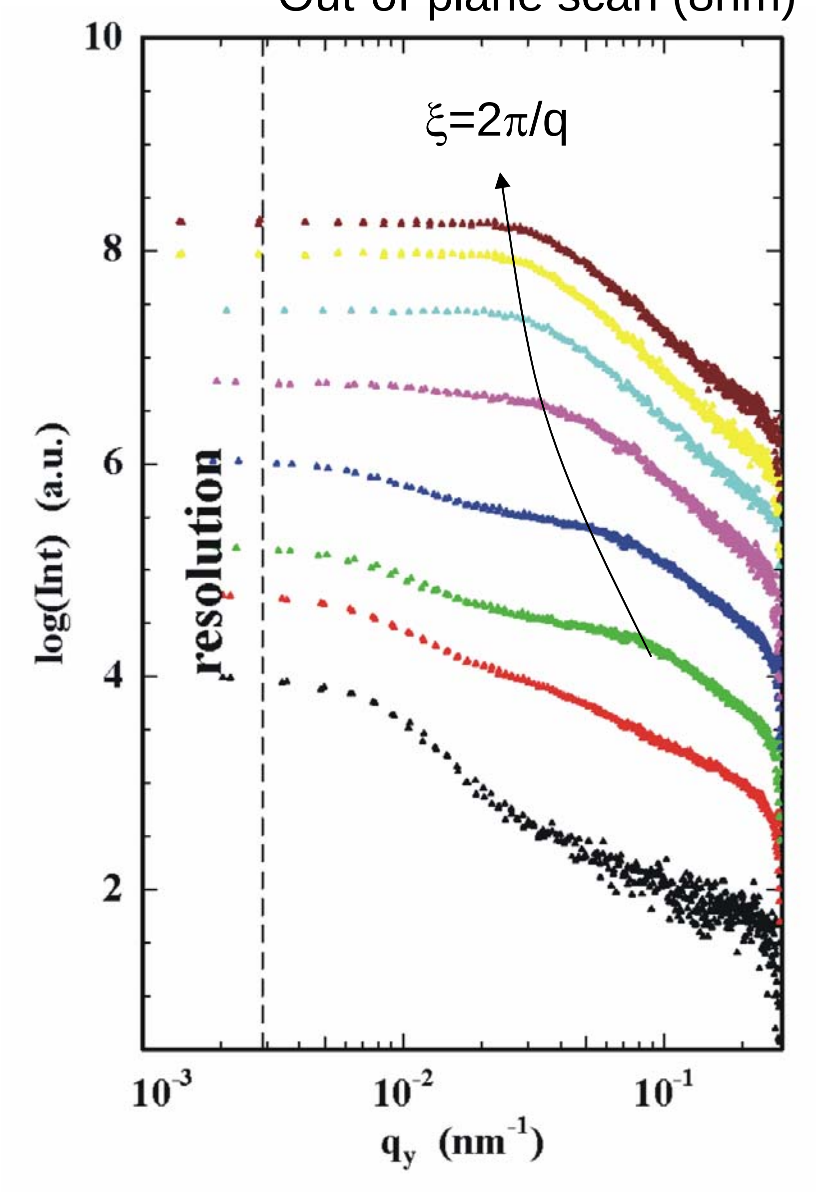


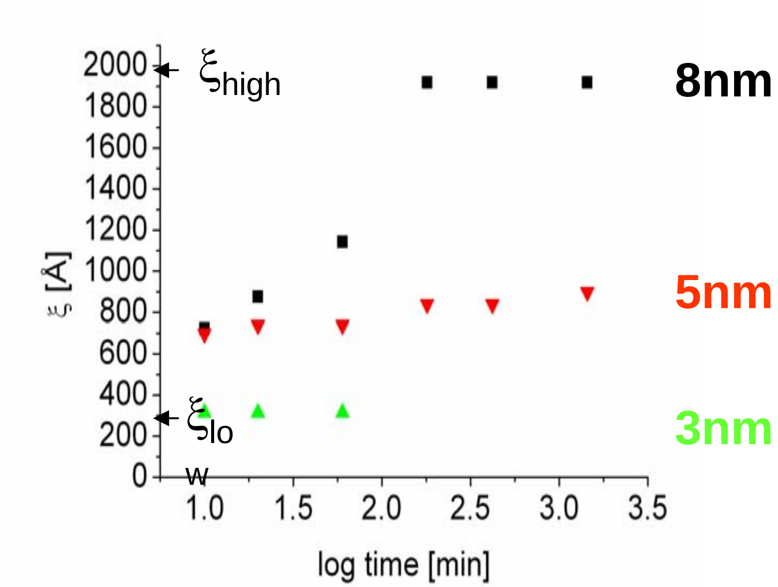
Out-of-plane scan (8nm)

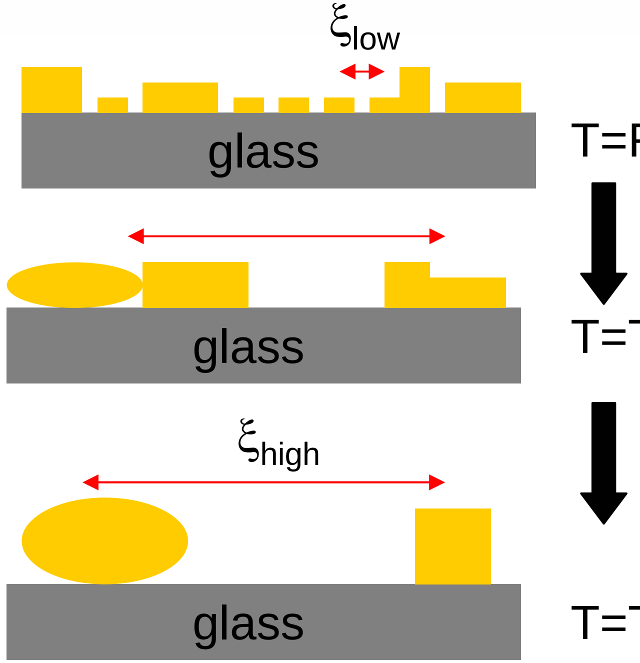


Lateral length scales

Out-of-plane scan (8nm)







T=RT, 0min

$T=T_{anneal}$, 0min < t ≤1h

$T=T_{anneal}$, t>1h

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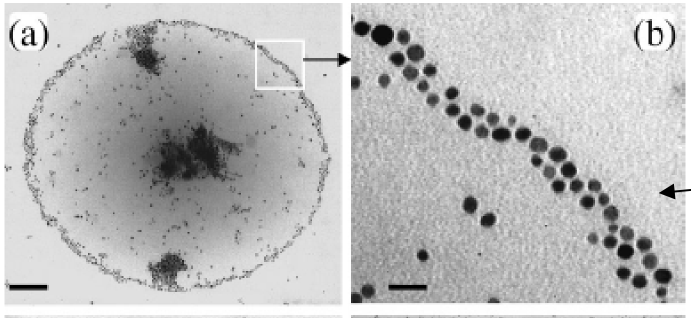
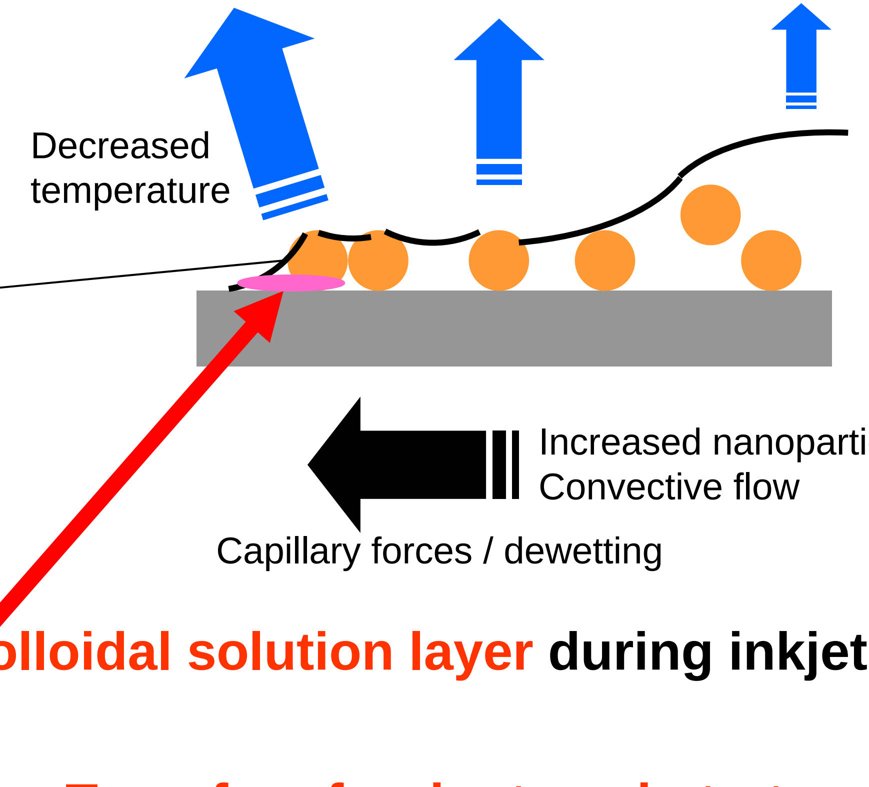
In-situ nanostructuring from solution

http://www.siliconsolar.com

Circuits, solar cells -> printing: electrodes, cost reduction



Govor et al., PRE **69**, 061609 (2004)



Evaporation of solvent

Decreased temperature

Increased nanoparticle concentration
Convective flow

Capillary forces / dewetting

Control drying-up of colloidal solution layer during inkjet printing

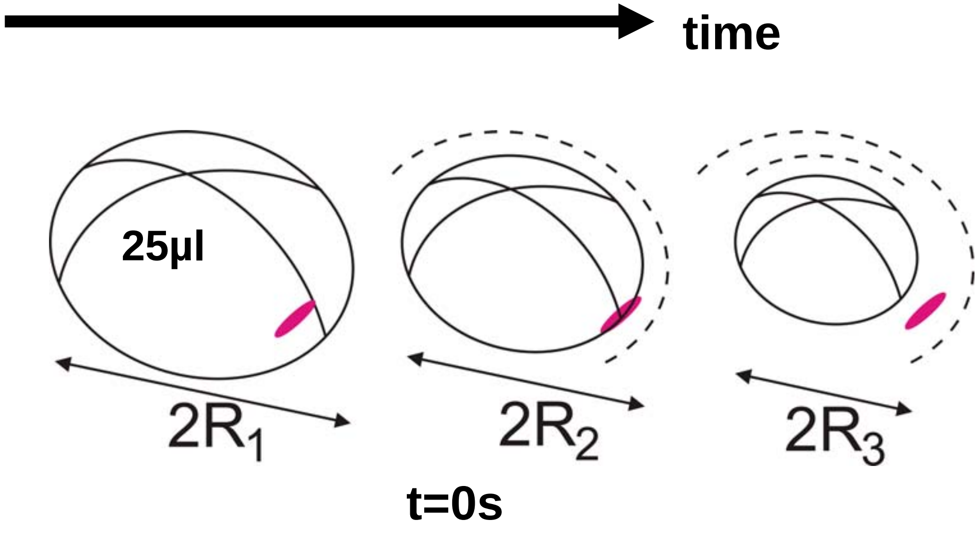
Critical step: Transfer of order to substrate

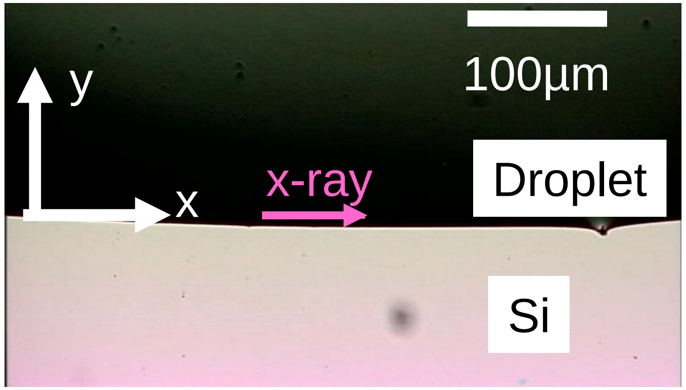
Real-time results: nanoGISAXS/ ID13 ESRF

2nm Au spheres in water
Slow evaporation time

300nm beam by Fresnel Zone plates

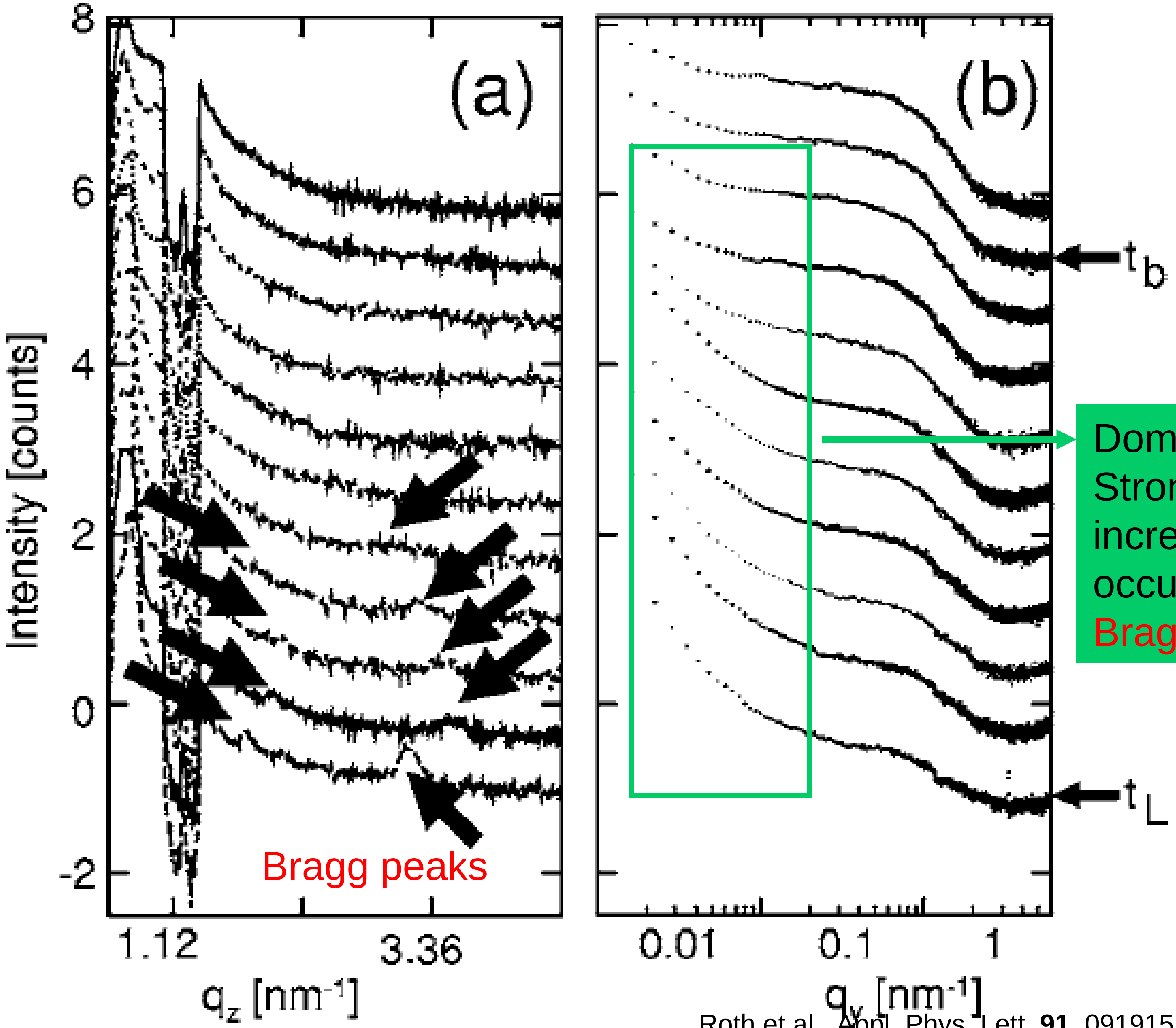
First nanobeam in-situ GISAXS





Roth et al., Appl. Phys. Lett. **91**, 091915 (2007)

Real-time results: nanoGISAXS/ ID13 ESRF

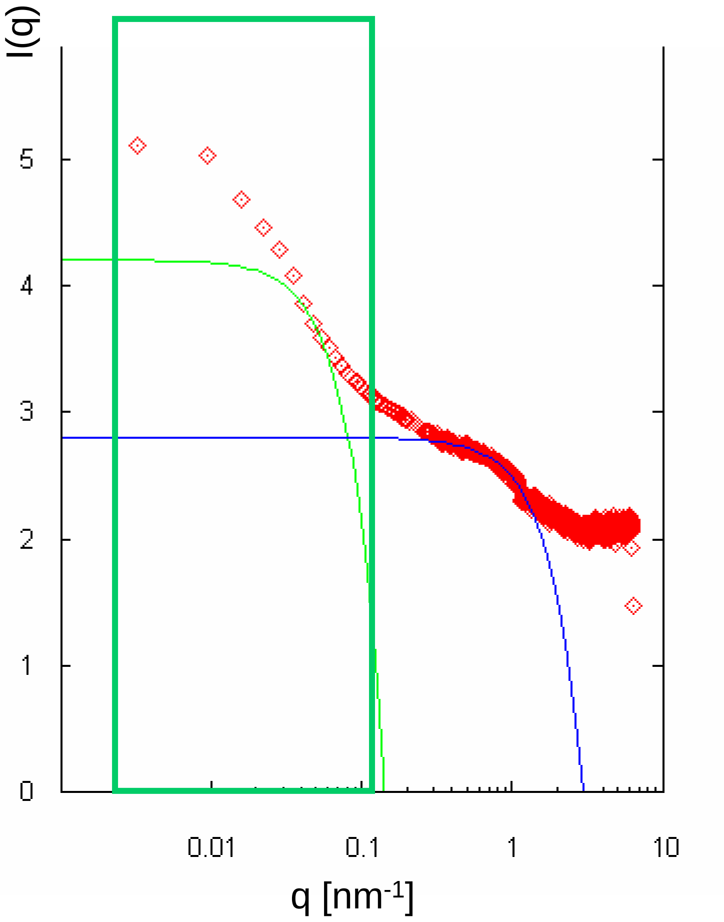


Bragg peaks

Domain building: Strong intensity increase before occurence of Bragg peaks!

Roth et al., Appl. Phys. Lett. **91**, 091915 (2007)

Guinier Approximation

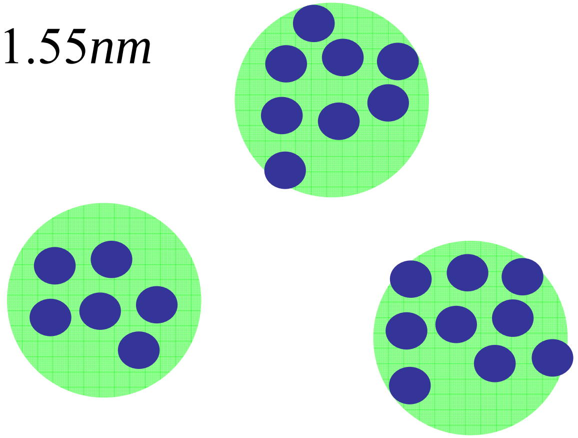


$$\lim_{q\to 0} I(q) = \Delta\rho^2 \cdot V^2 \cdot \exp(-q^2 \cdot \frac{R_g^2}{3})$$

Radius of Gyration R_g

Monodisperse spheres of radius R=2nm:

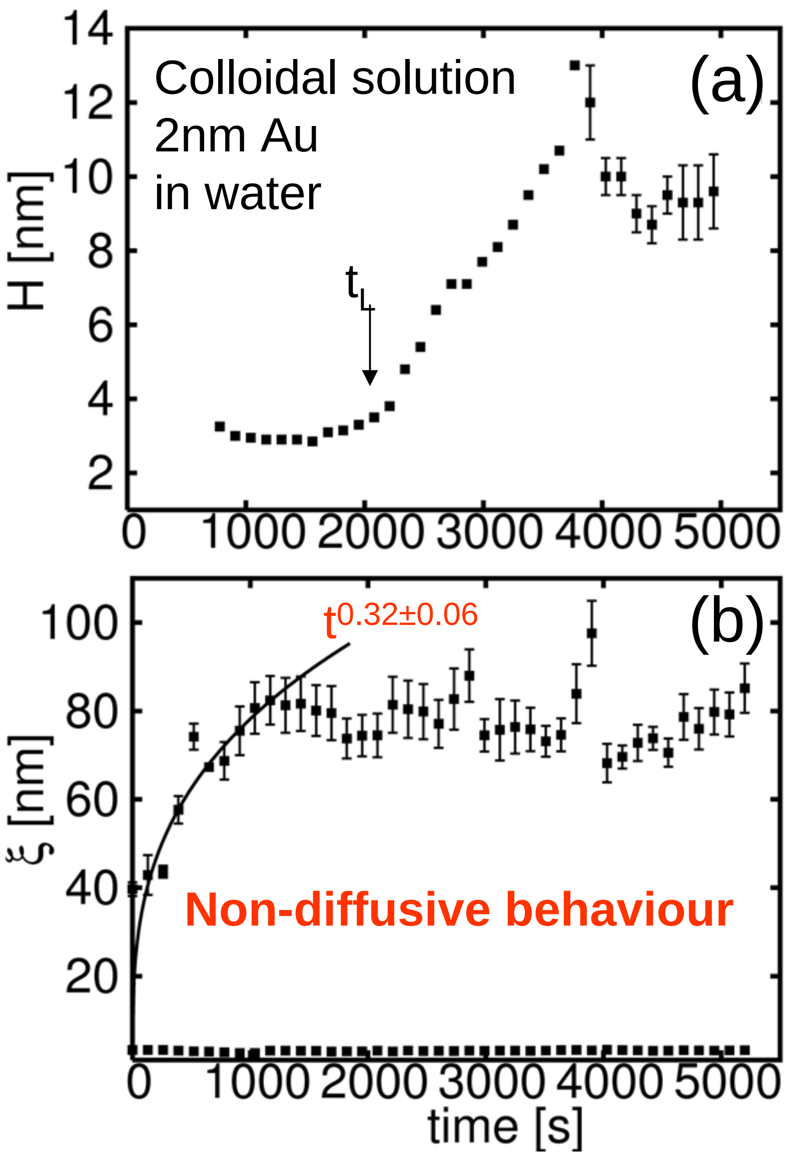
$$R_g = \sqrt{3/5} \cdot R = 1.55nm$$



2nm Colloids
domains

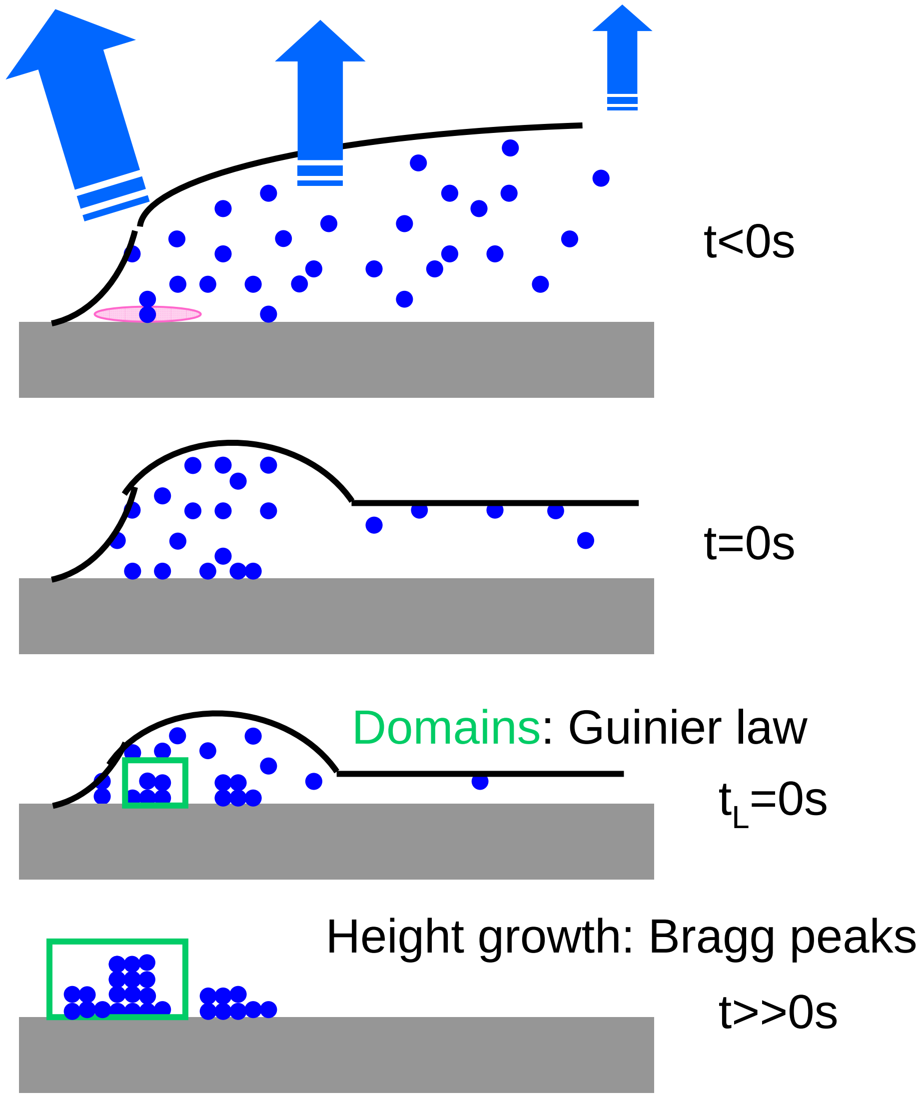
Very useful to get a hand on length scales!
Sometimes only valid in limited q-range

Real-time results: nanoGISAXS/ ID13 ESRF



Colloidal solution
2nm Au
in water

Non-diffusive behaviour



t<0s

t=0s

Domains: Guinier law

t_L=0s

Height growth: Bragg peaks

t>>0s

Roth et al., Appl. Phys. Lett. **91**, 091915 (2007)

Outline

Au on glass!

- ➢SAXS versus GISAXS
- ➢GISAXS – theory
- ➢Instrumentation
- ➢Application examples:
  - Gold on glass
  - in-situ growth of colloidal crystals
  - ➡ Polymer nanochannels

APPLIED PHYSICS LETTERS 88, 083114 (2006)

Route to create large-area ordered polymeric nanochannel arrays

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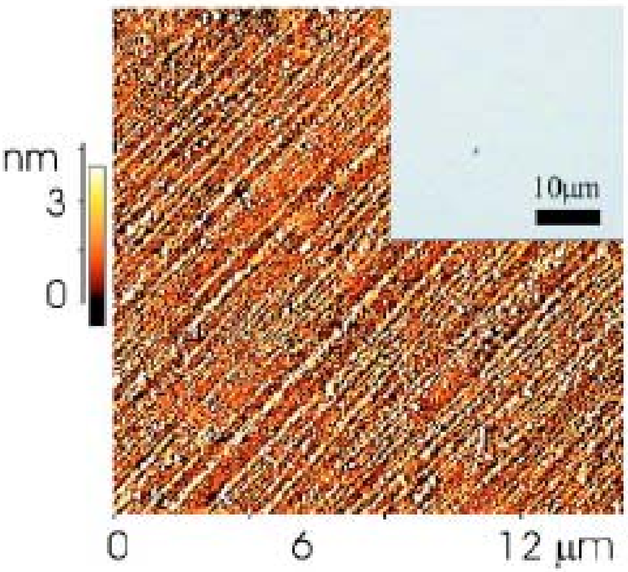
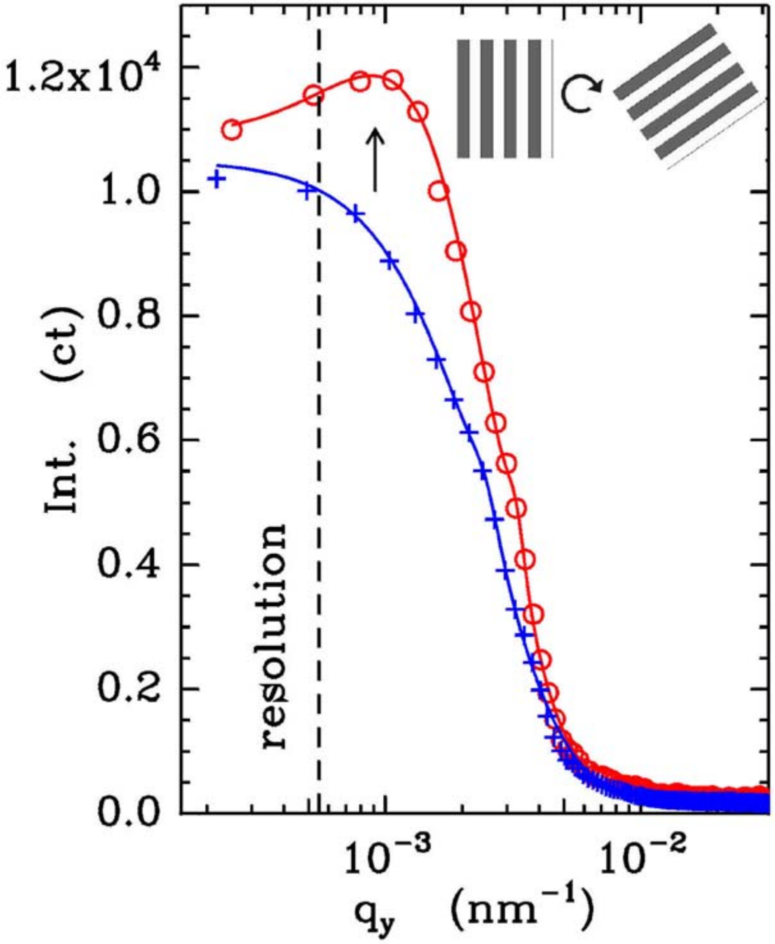
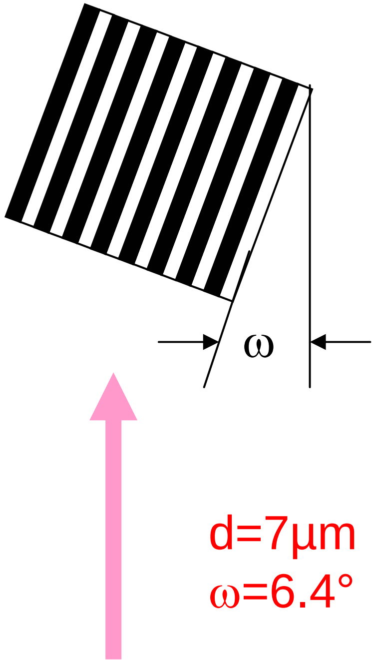
BW4, GIUSAXS 13m, α_i=0°
Polymeric nanochannels

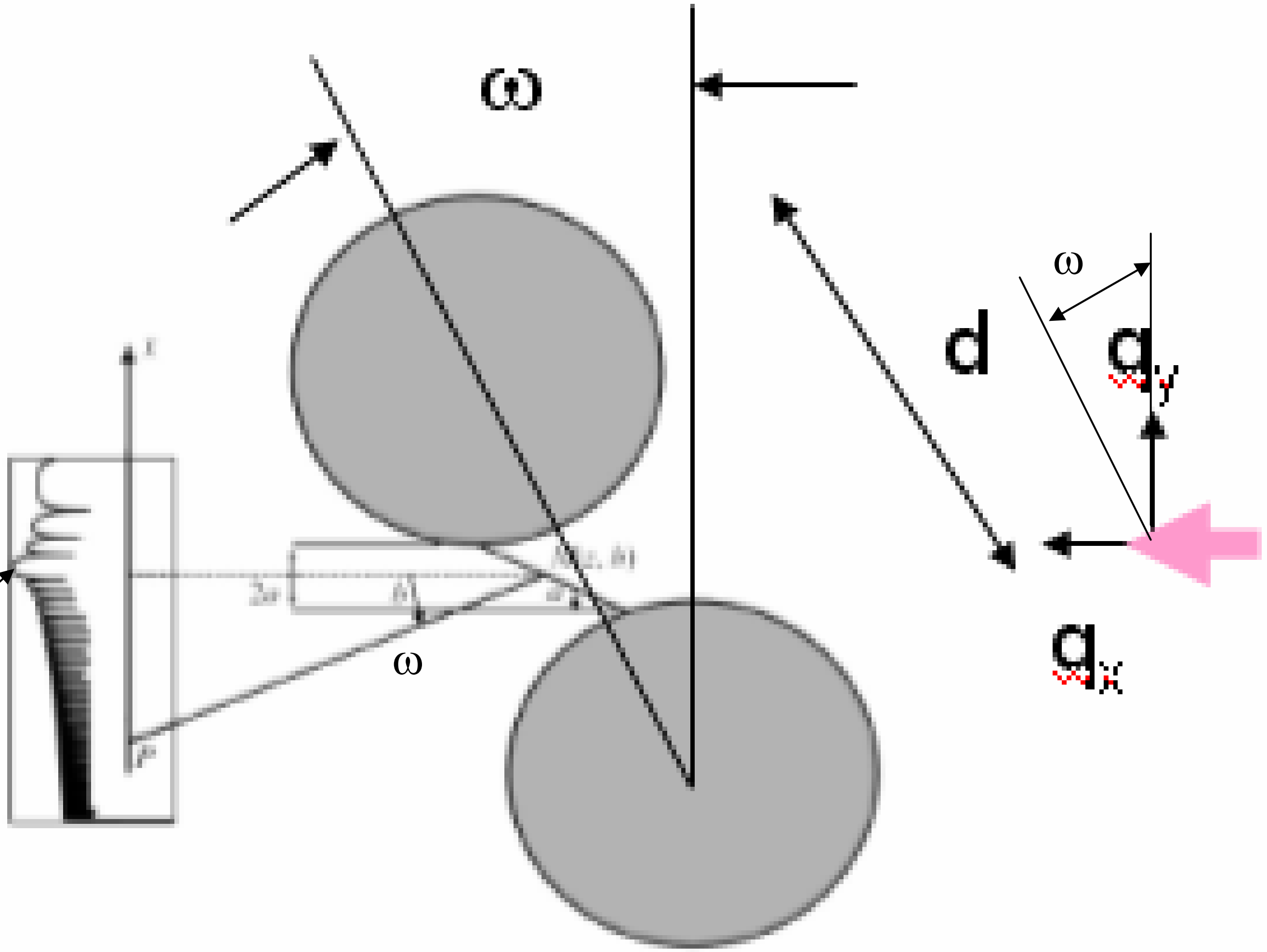






d=7µm
ω=6.4°

GIUSAXS @ α_i=0°



Zero order

$q_y \cos\omega + q_x \sin\omega = 0$

In direction of d

$q_x = 2\pi/\lambda\ (\cos(\alpha_f) - \cos(\alpha_i))$

$q_y + 2\pi/\lambda\ 1/2\ \alpha_f^2 / \omega = 0$ → Calculate tilt angle ω

The End