Methoden moderner Röntgenphysik I:
Struktur und Dynamik kondensierter Materie

Vorlesung zum Haupt/Masterstudiengang Physik

WS 2008/9

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

Location:SemRm4, Physik, Jungiusstrasse

Thursdays 10.15 –11.45

G.Grübel (GG), A.Meents (AM), C. Gutt (CG), S. Roth (SR)

Soft Matter Applications

Stephan V. Roth

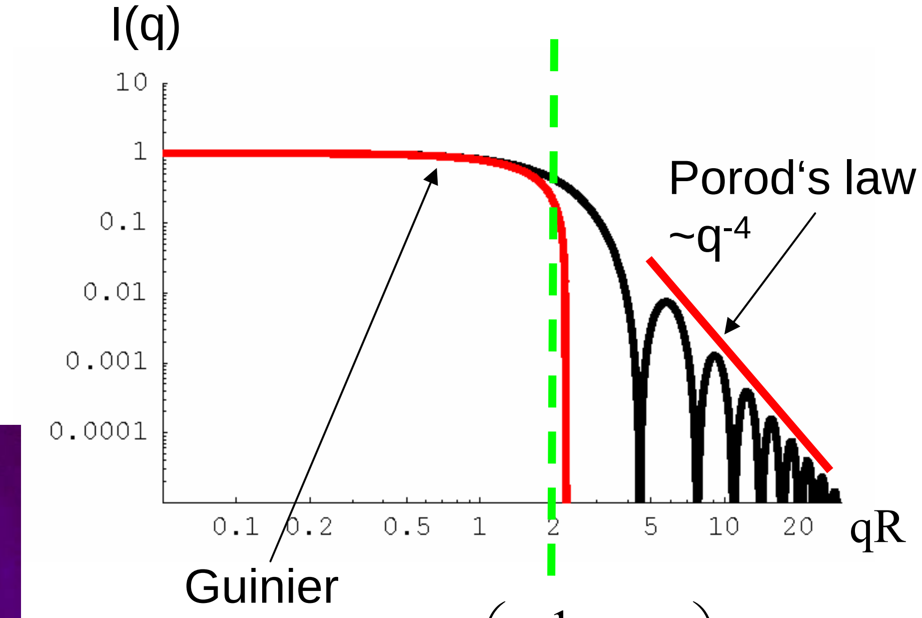
Introduction	(GG)
Modern Crystallography	(AM)
Coherence based techniques	(CG)
Soft matter applications	(SR)

22.01.2009	Basics, theory, preparation – a primer
29.01.2009	Small-angle X-ray scattering and its applications
➡ 03.02.2009	Polymer, colloidal and nanocomposite surfaces
	(Note change Thursday (5.)-> Tuesday) (3.)

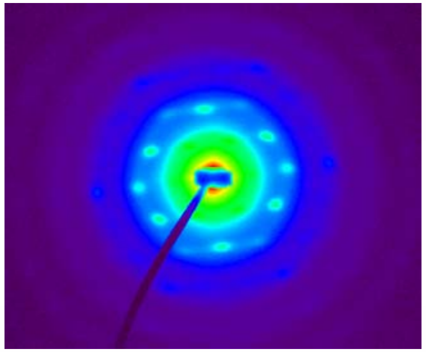
Aim: Overview over use of soft matter and x-ray scattering of soft matter

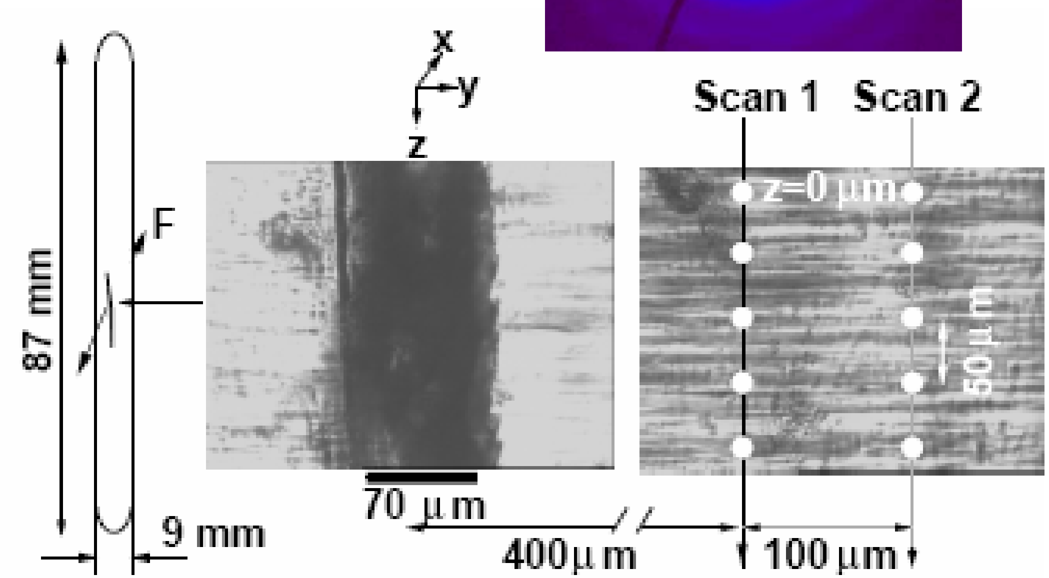
Summary last lecture

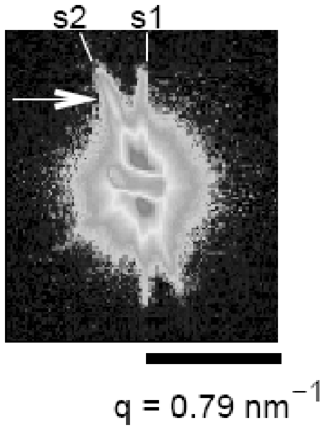
- Approximations for Form factor:
  Very useful to get first-hand information about multiple length scales
- Influence of form factor (concentrated samples)
- Examples:
  - Colloidal crystals
  - Cracks & crazes



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







Questions?

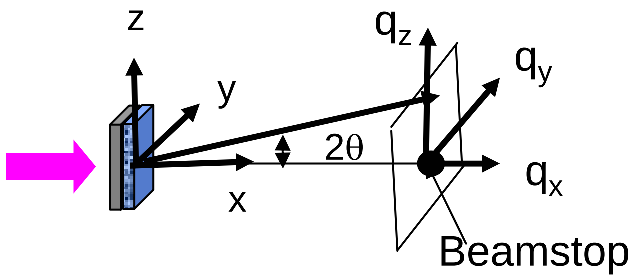
Outline

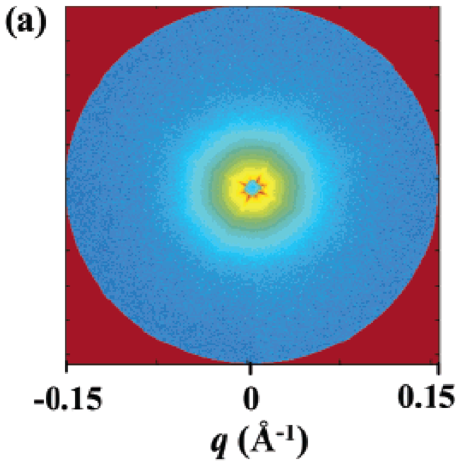
- SAXS versus GISAXS
- GISAXS – theory
- Instrumentation
- Application examples:
  - Gold on glass
  - in-situ growth of colloidal crystals
  - Polymer nanochannels

Au on glass!

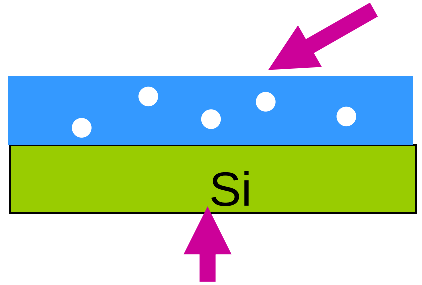
It is important to understand the basic features of the different GISAXS pattern and cuts.

T-SAXS vs. GISAXS

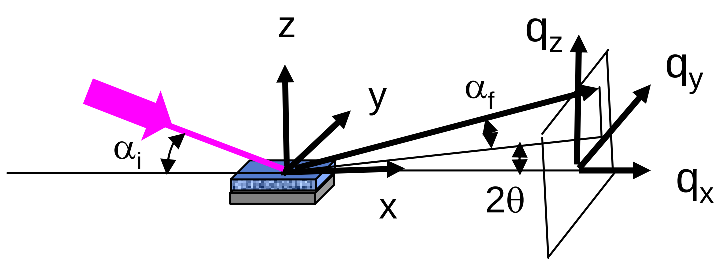


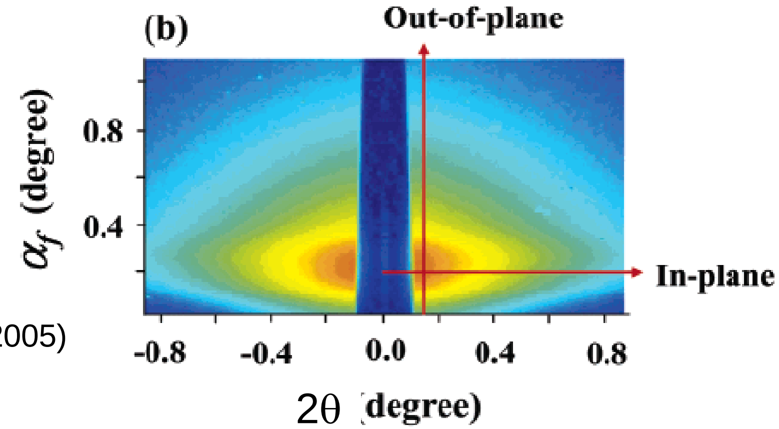


- Easy measurement
- Easy analysis
- In-plane information (q_y,q_z)
- Any possible scattering from substrate
- Transparency of substrate
- High energy



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

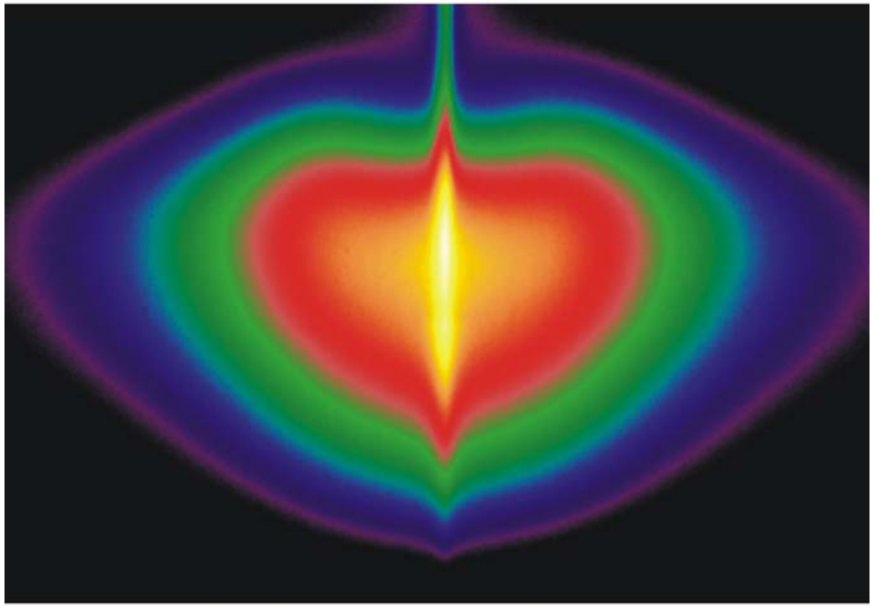




- Strong intensity
- Easy preparation of samples
- Full information (q_x,q_y,q_z)
- Scattering from surface / internal structure
- Scattering from reflected AND transmitted beam
- Refraction effects (DWBA)
- Special setup

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

Outline

Au on glass!

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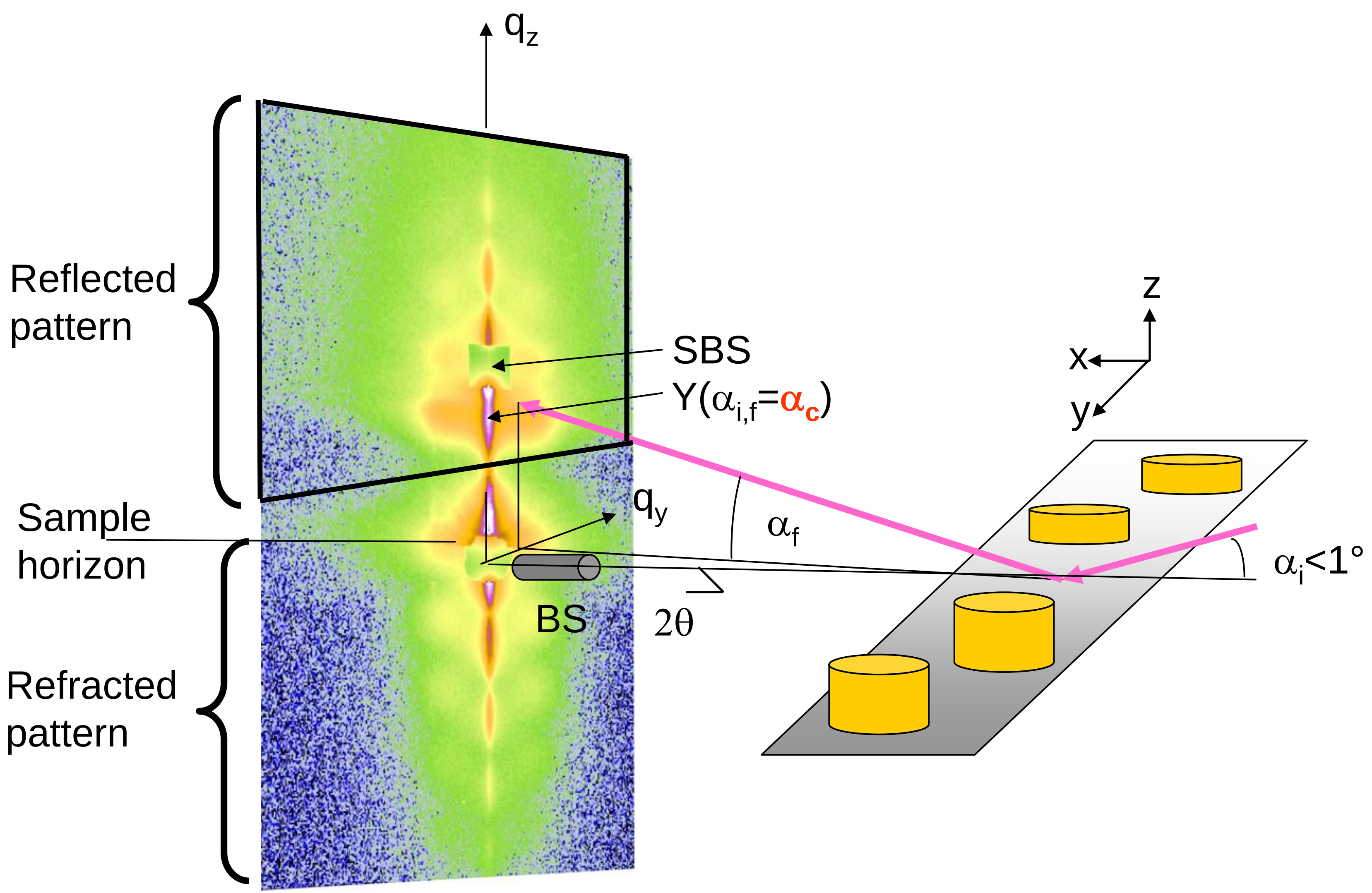
  - in-situ growth of colloidal crystals
  - Polymer nanochannels

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)

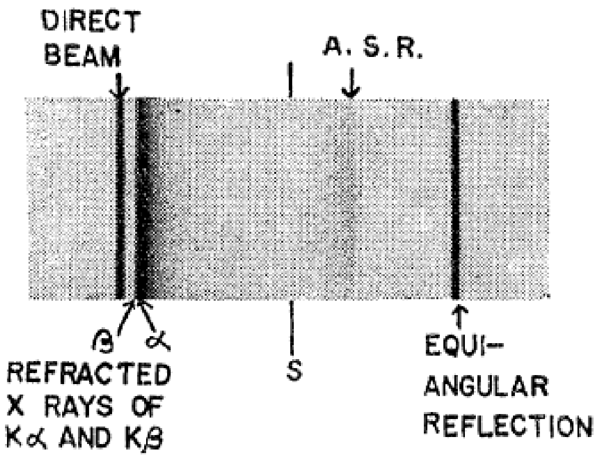


FIG. 2. Photograph of A.S.R. by a glass sample, ×2.

The first sucessful experiment

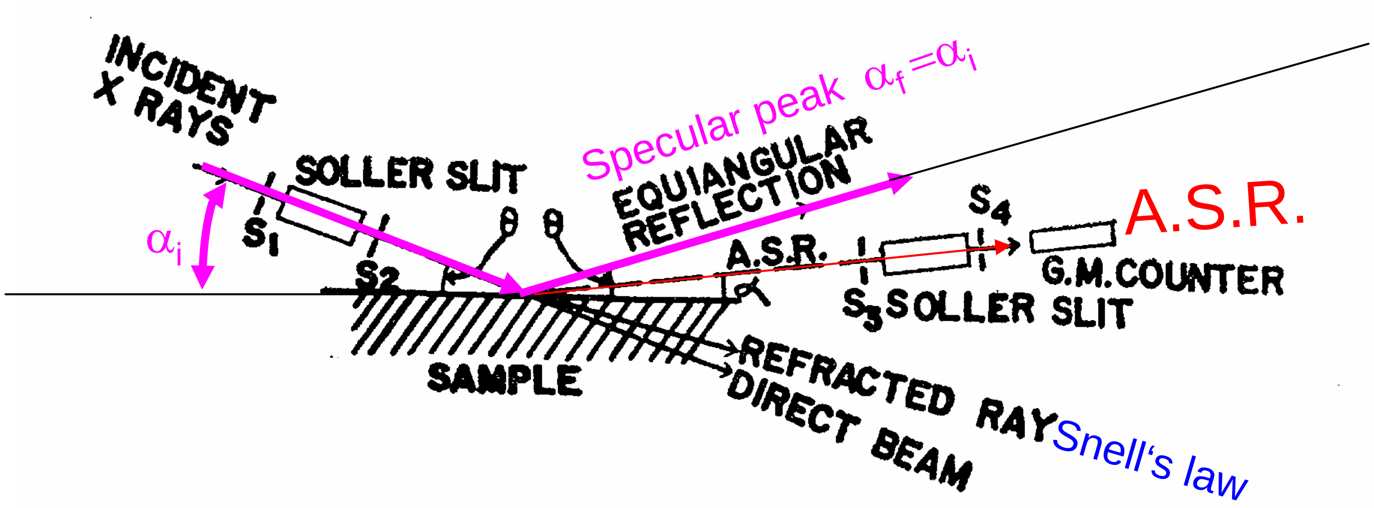


FIG. 1. Schematic view of the experimental arrangement in the incident plane.

Anomalous Surface Reflection
(diffuse scattering)

Intensity between α_f=0° and $\alpha_f=\alpha_i$!!!

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

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

Critical angle

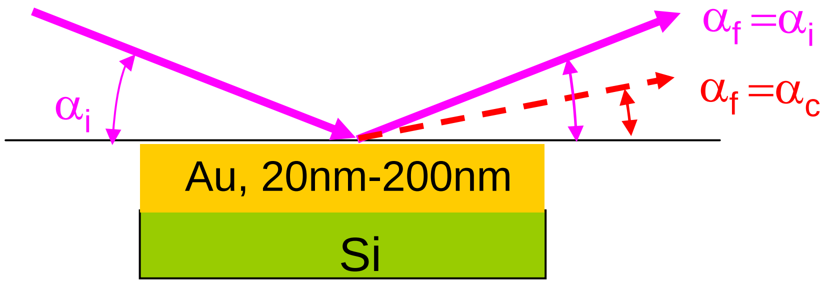
α_c(Si)=0.2°
α_c(Au)=0.5°

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

Very small!

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

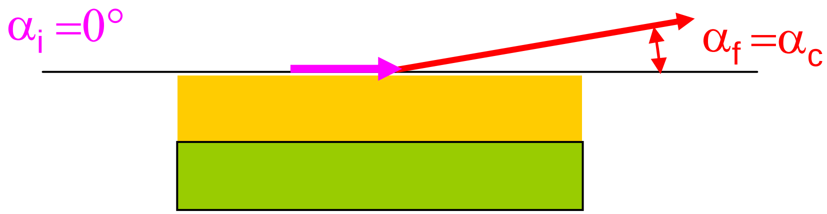
Origin of intensity at α_c



α_f(Au) = 0.56° = α_c(Au,1.8Å)

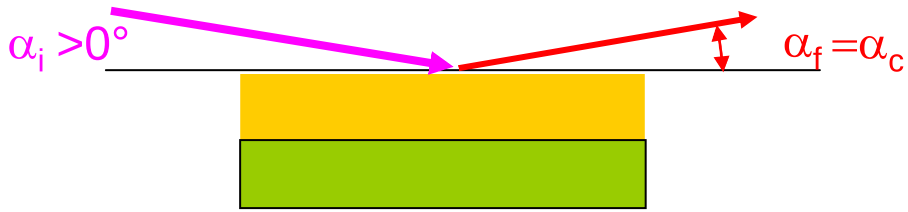
Total external reflection

Reciprocity theorem & critical angle



must stem from wave parallel to surface

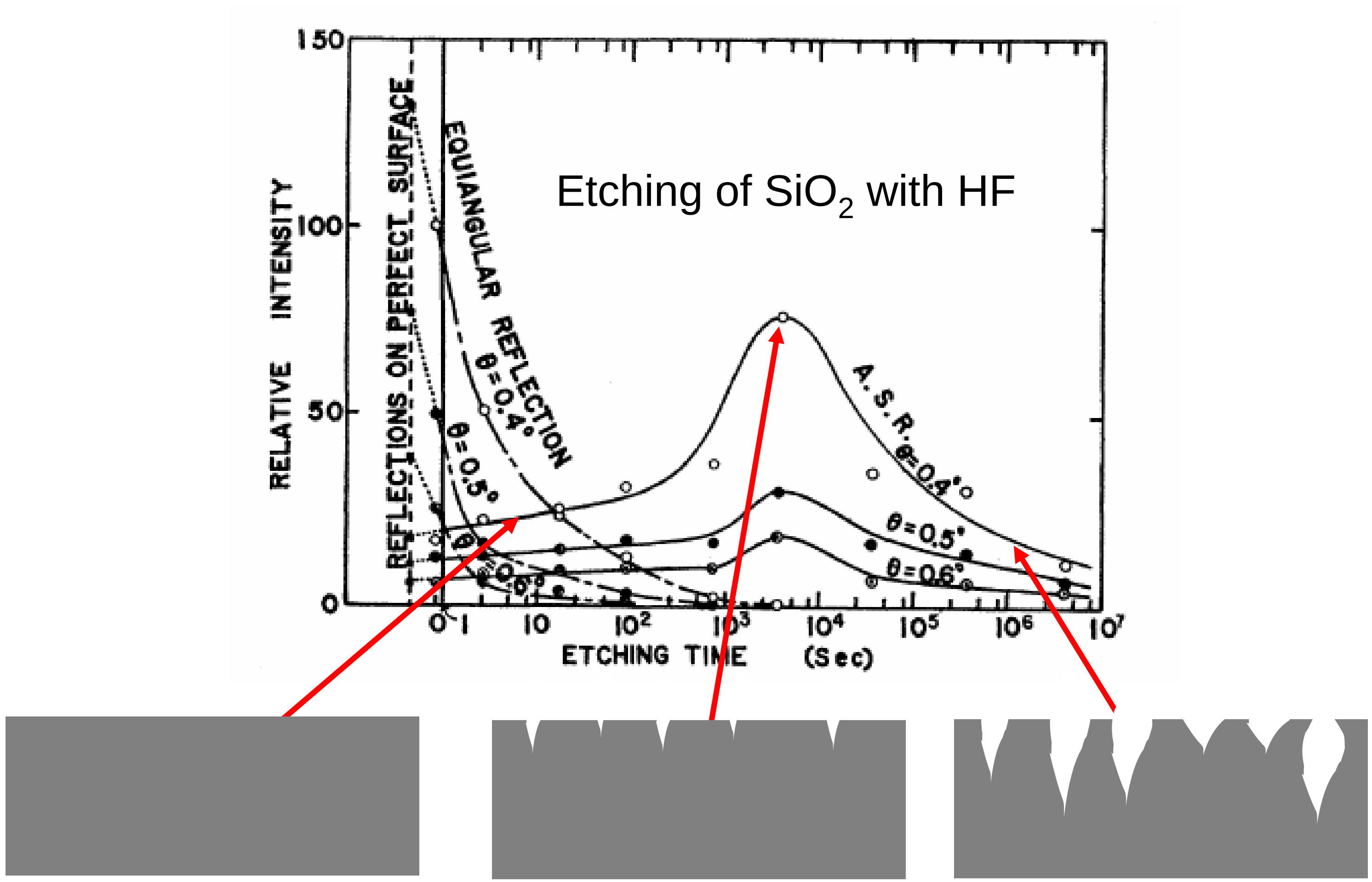
Yoneda



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

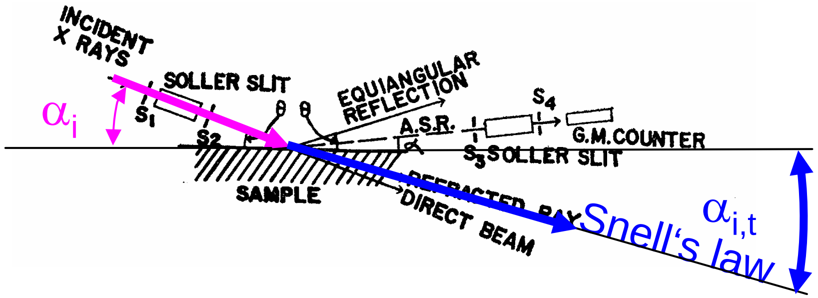
Hint: Roughness of the sample

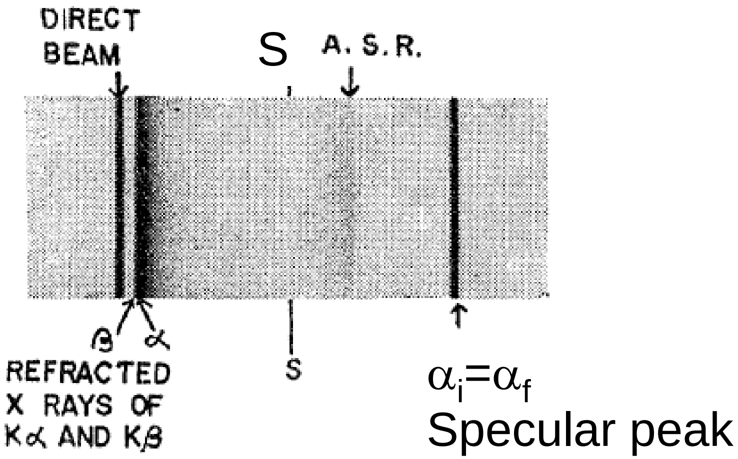
Yoneda peak = Scattering effect!



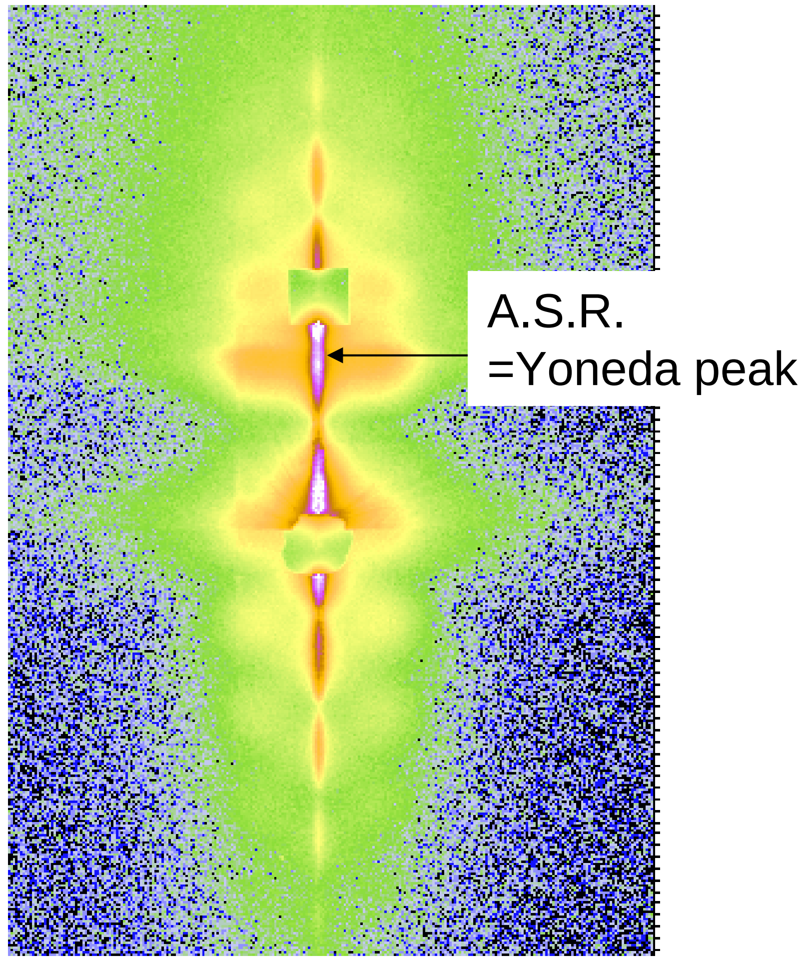
Basically the same

1963





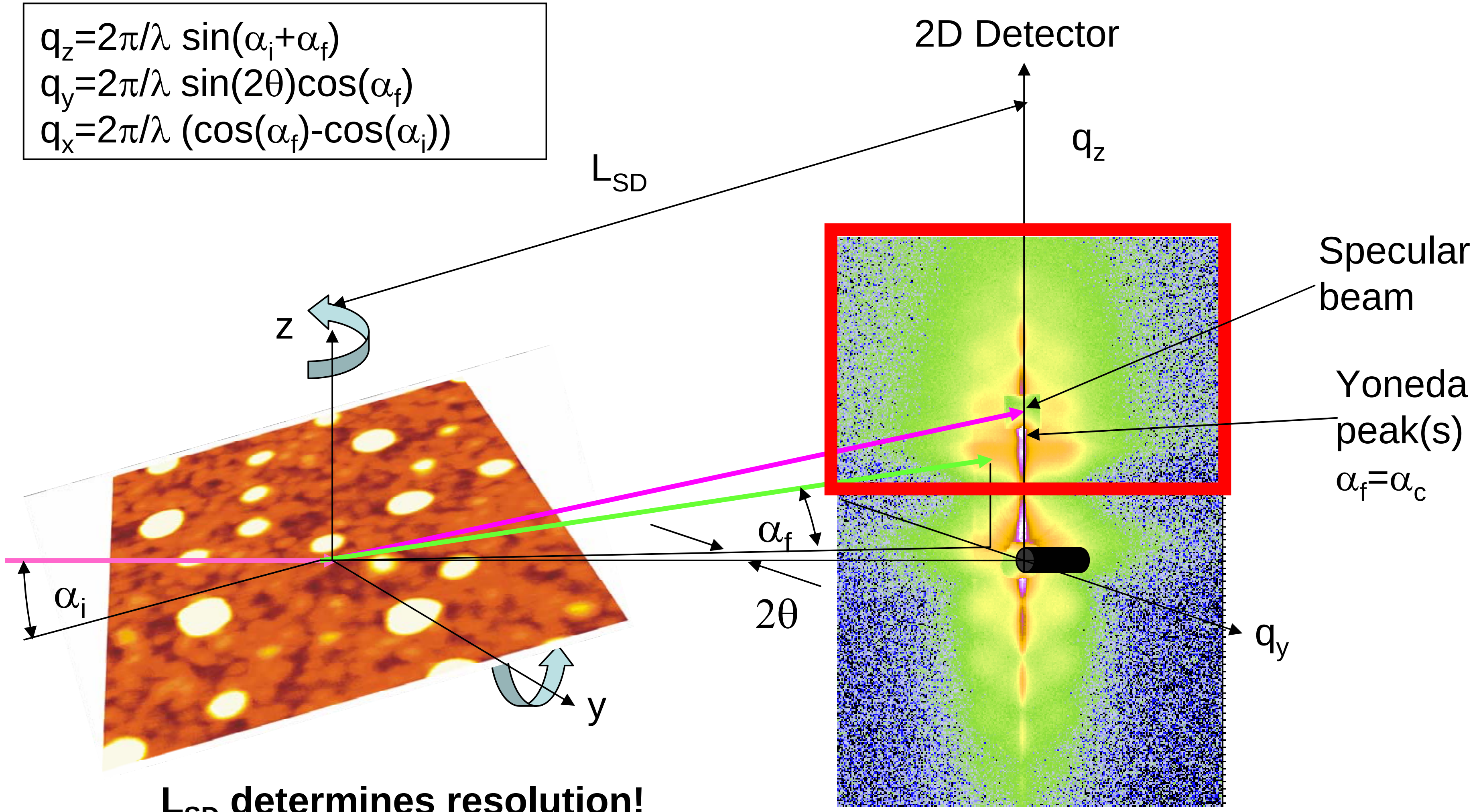
today



µGISAXS – more details

Grazing Incidence Small Angle X-Ray Scattering, GISAXS

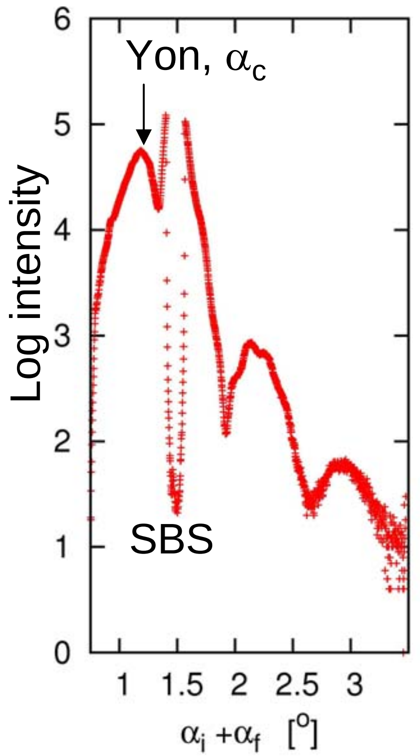
$q_z = 2\pi/\lambda \sin(\alpha_i + \alpha_f)$
$q_y = 2\pi/\lambda \sin(2\theta)\cos(\alpha_f)$
$q_x = 2\pi/\lambda (\cos(\alpha_f) - \cos(\alpha_i))$

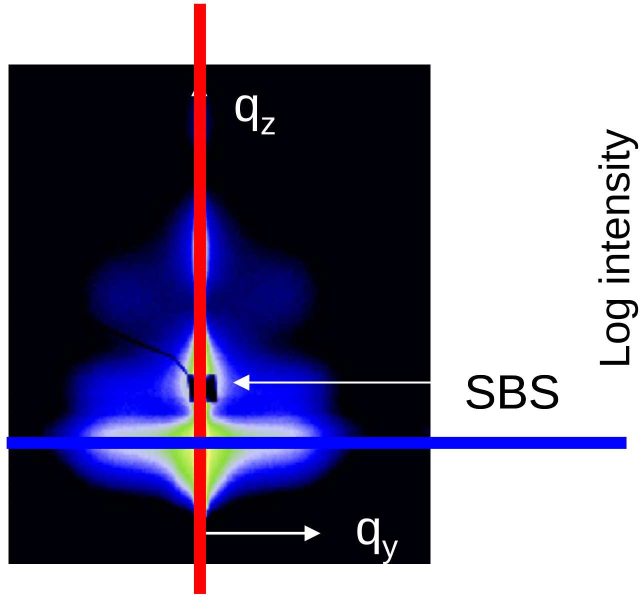


L_{SD} determines resolution!

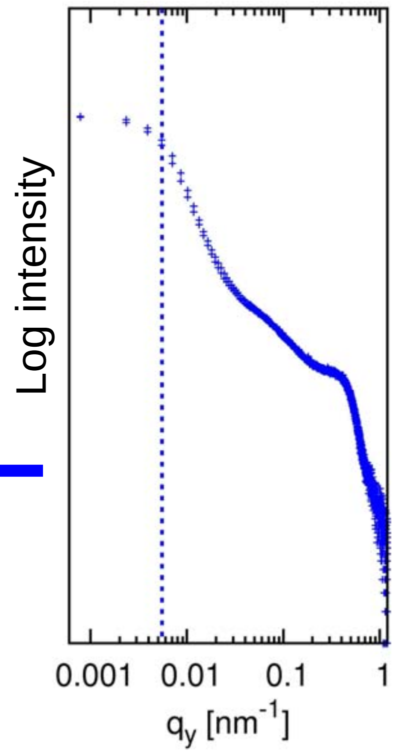
Grazing incidence small-angle x-ray scattering

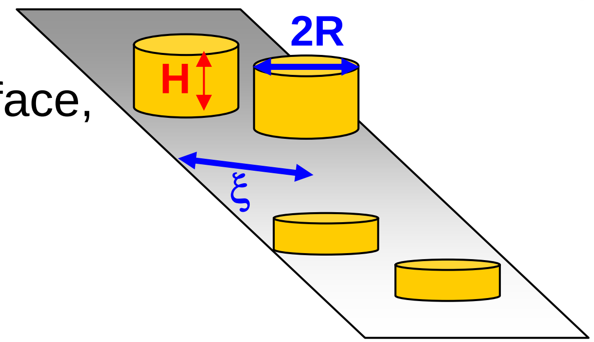
cut at constant θ





cut at constant α_f





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

Detector-scan

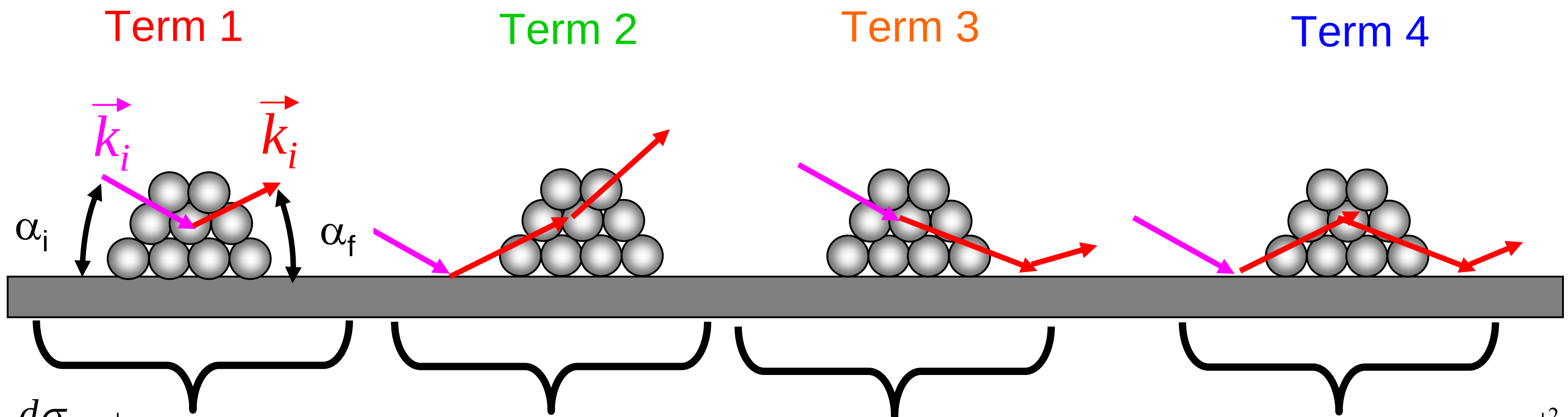
In-plane structures, e.g. distances ξ, Radius R

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



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

Born term

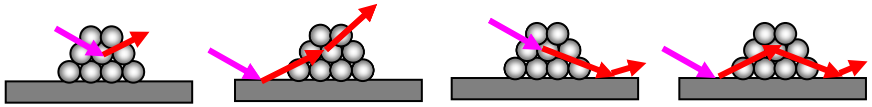
with $P(\vec{q}) = \int_V \exp(i\vec{q}\vec{r}) d^3 r$

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

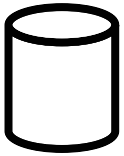
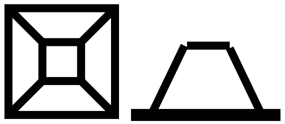
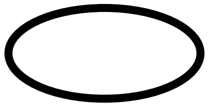
Now for surfaces (nanoparticles)…

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

Form factor: multiple scattering



Shape, size and orientation

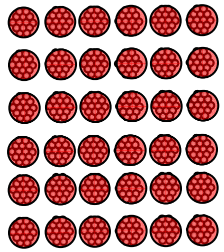
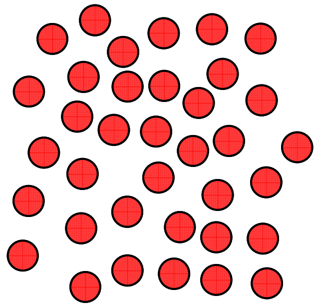
- cylinder 
- pyramid 
- ellipsoid 

+ size distributions

Interference function

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

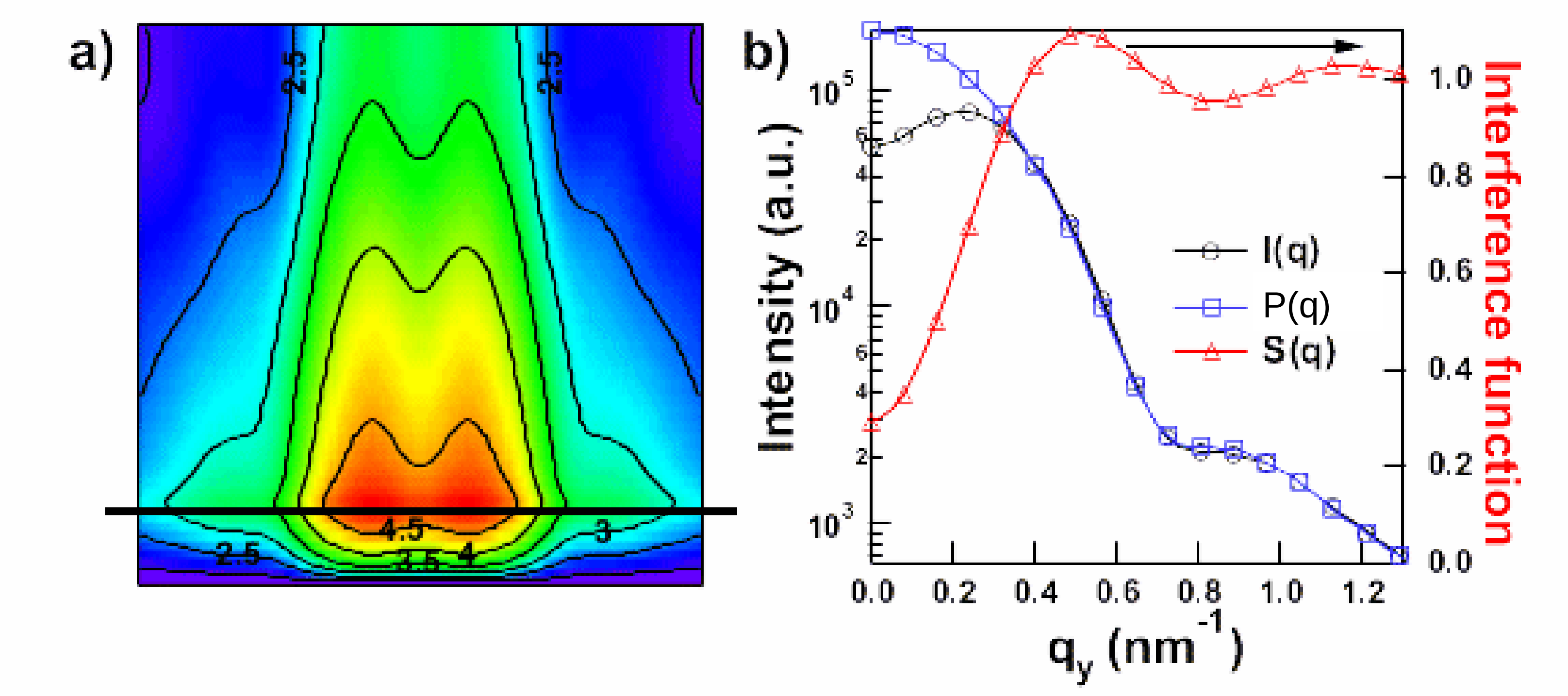
Spatial arrangement of the particles

- lattice 
- paracrystal 

+ mean distance
+ fluctuation of distances

Simulations: IsGISAXS (R. Lazzari)

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



Outline

Au on glass!

- SAXS versus GISAXS
- GISAXS – theory
- Instrumentation
- Application examples:
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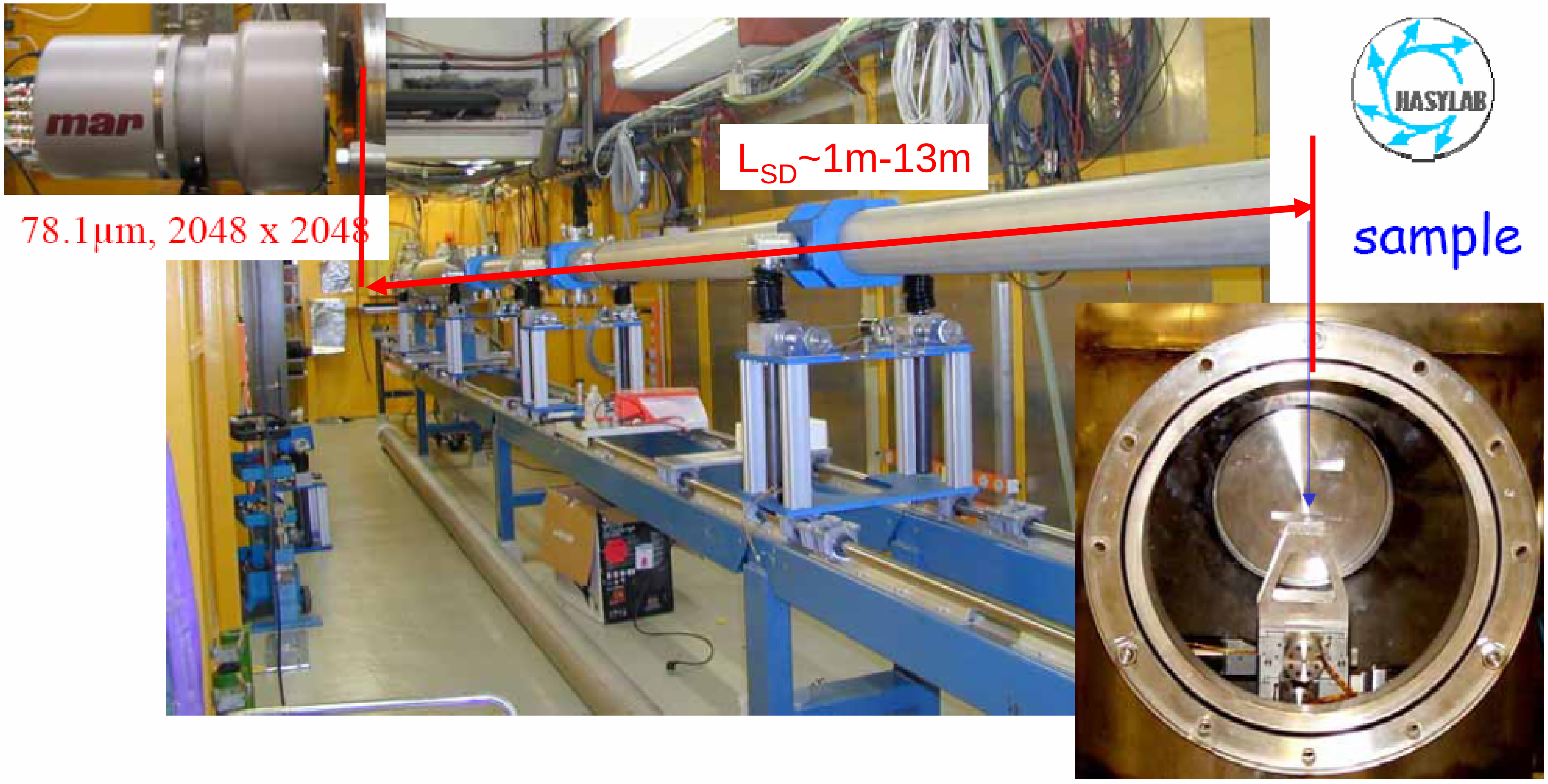
BW4 / HASYLAB (Hamburg, Germany)

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

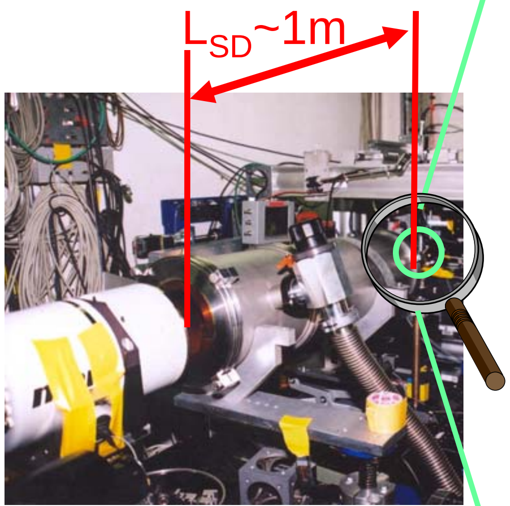


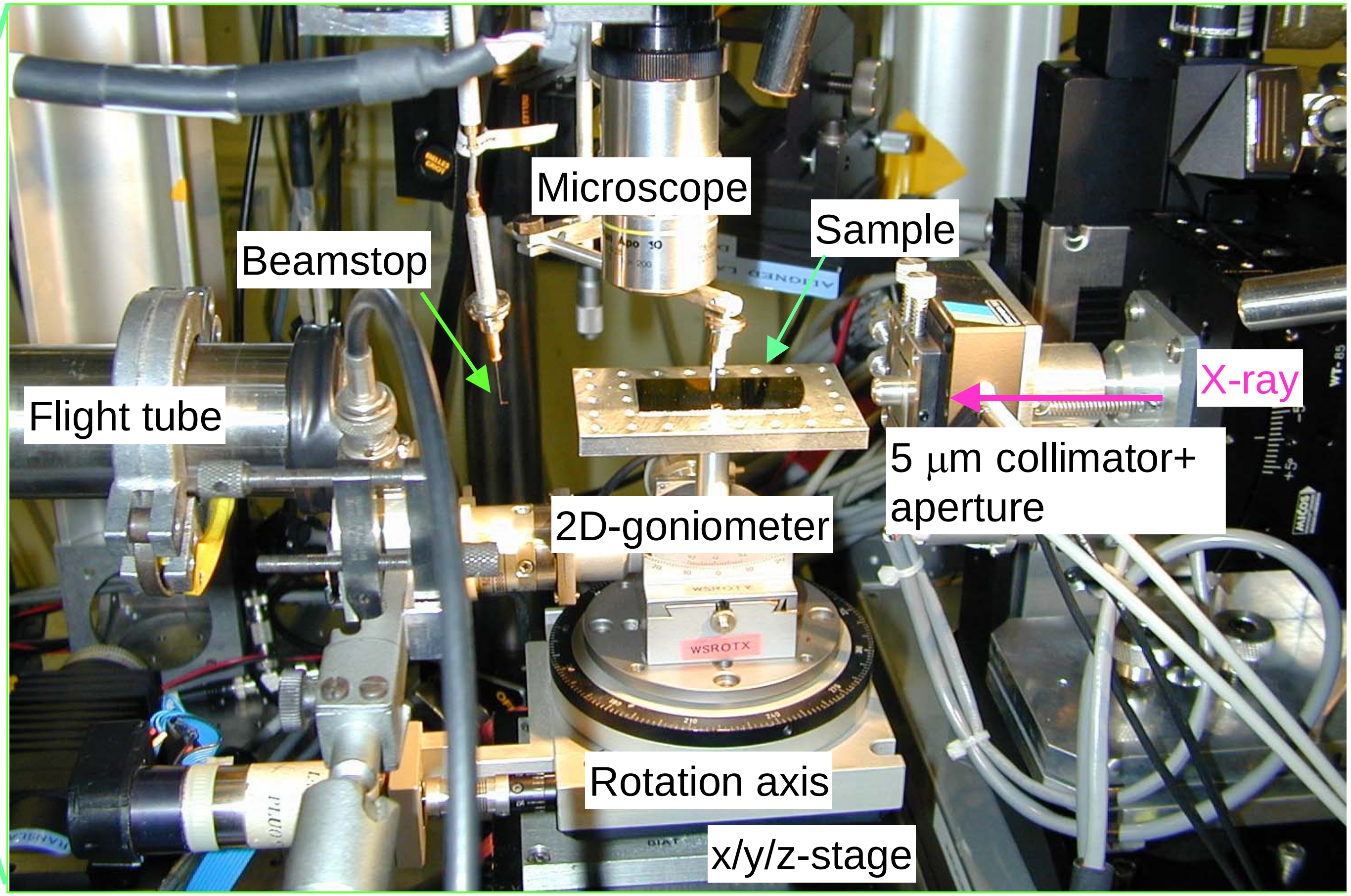
sample – detector distance up to **13 m** possible – optimized conditions for GI(U)SAXS

ID13 / ESRF (Grenoble, France)

Mean information ⇔ local information

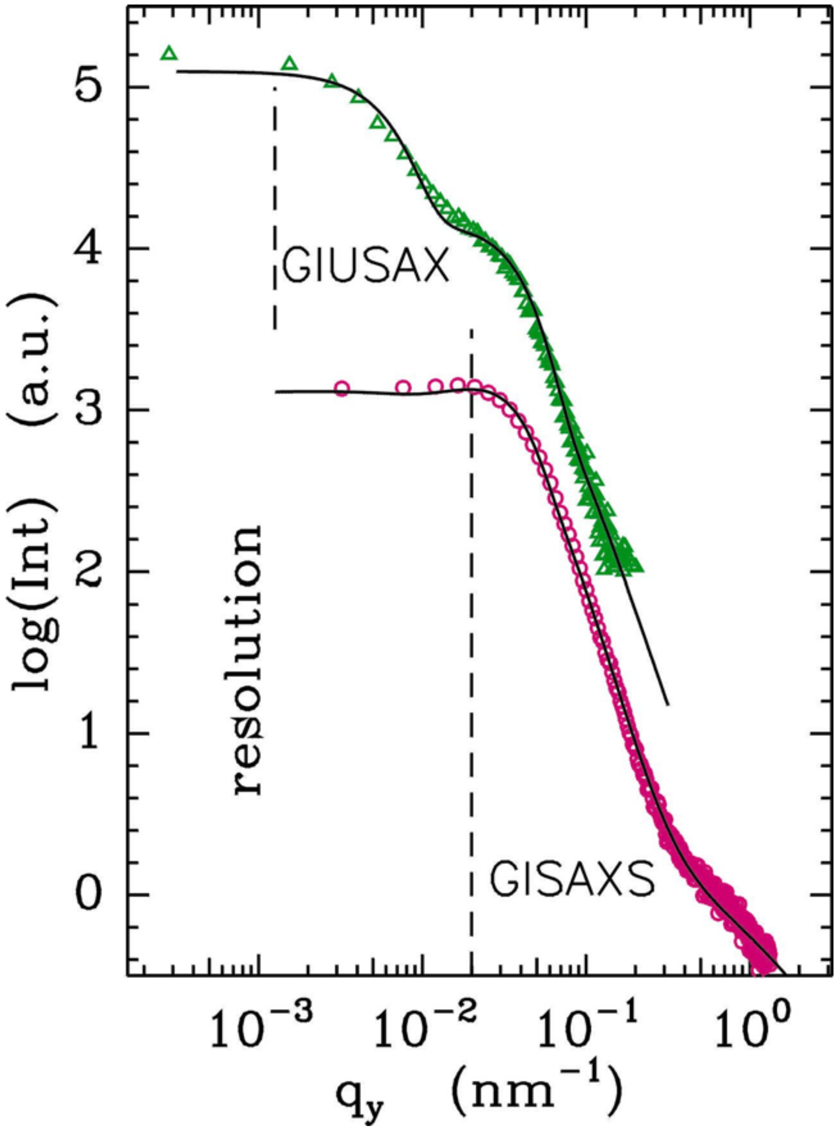
Combination of GISAXS with micro-focus beam





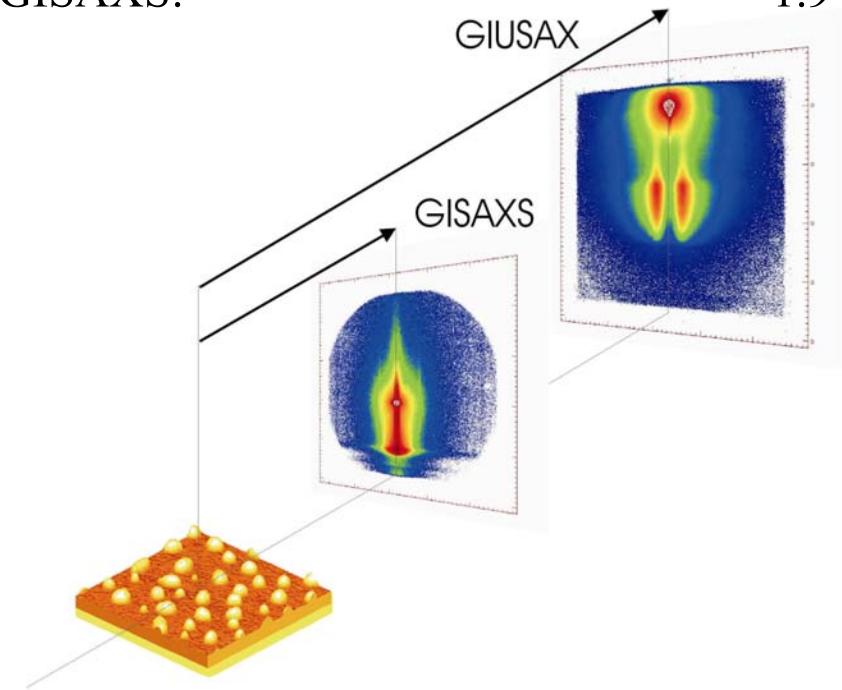
diameter of micro beam GISAXS experiment at ID13 (ESRF) 5μm
footprint (x/y) 300 x 5 μm² → local information

GISAXS & GIUSAXS



combination of GIUSAXS and GISAXS experiment:

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



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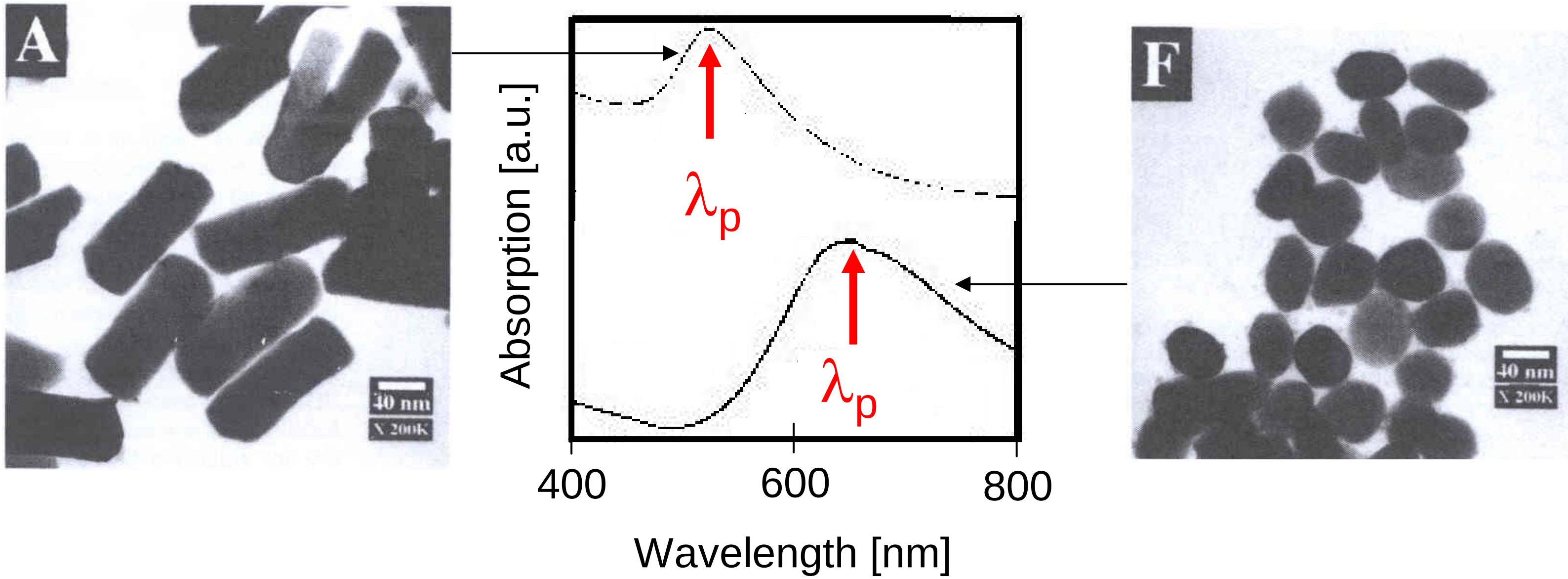
Au on glass!

Tempering Au nanoparticles

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



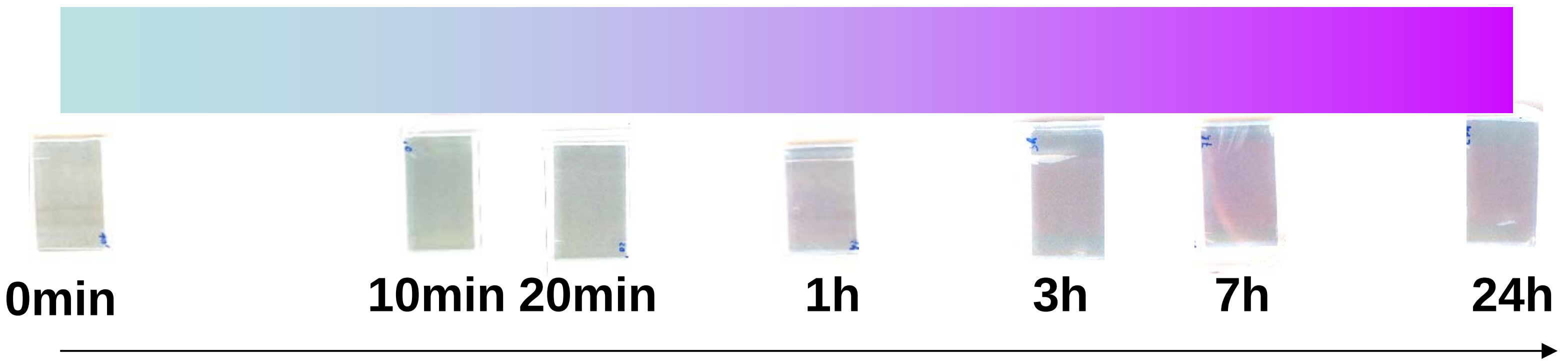
J.C. Hulteen et al., J Phys. Chem. B 101, 7727 (1997)

Annealing

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

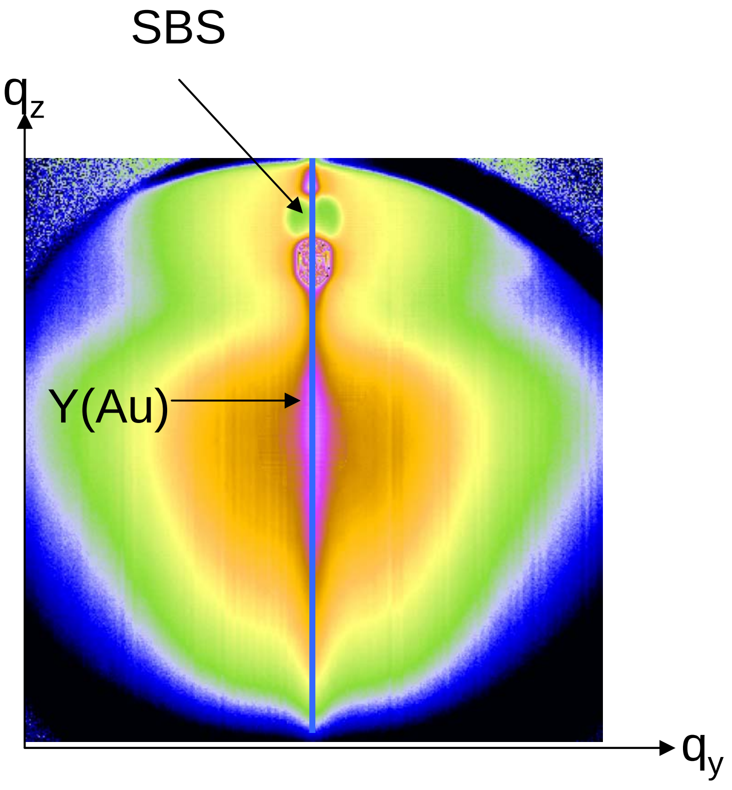
Au on glass
Parameters: Au layer mass thickness: **3nm , 5nm, 8nm**
Annealing time

approaching critical coalescence thickness
(cluster -> metal character)

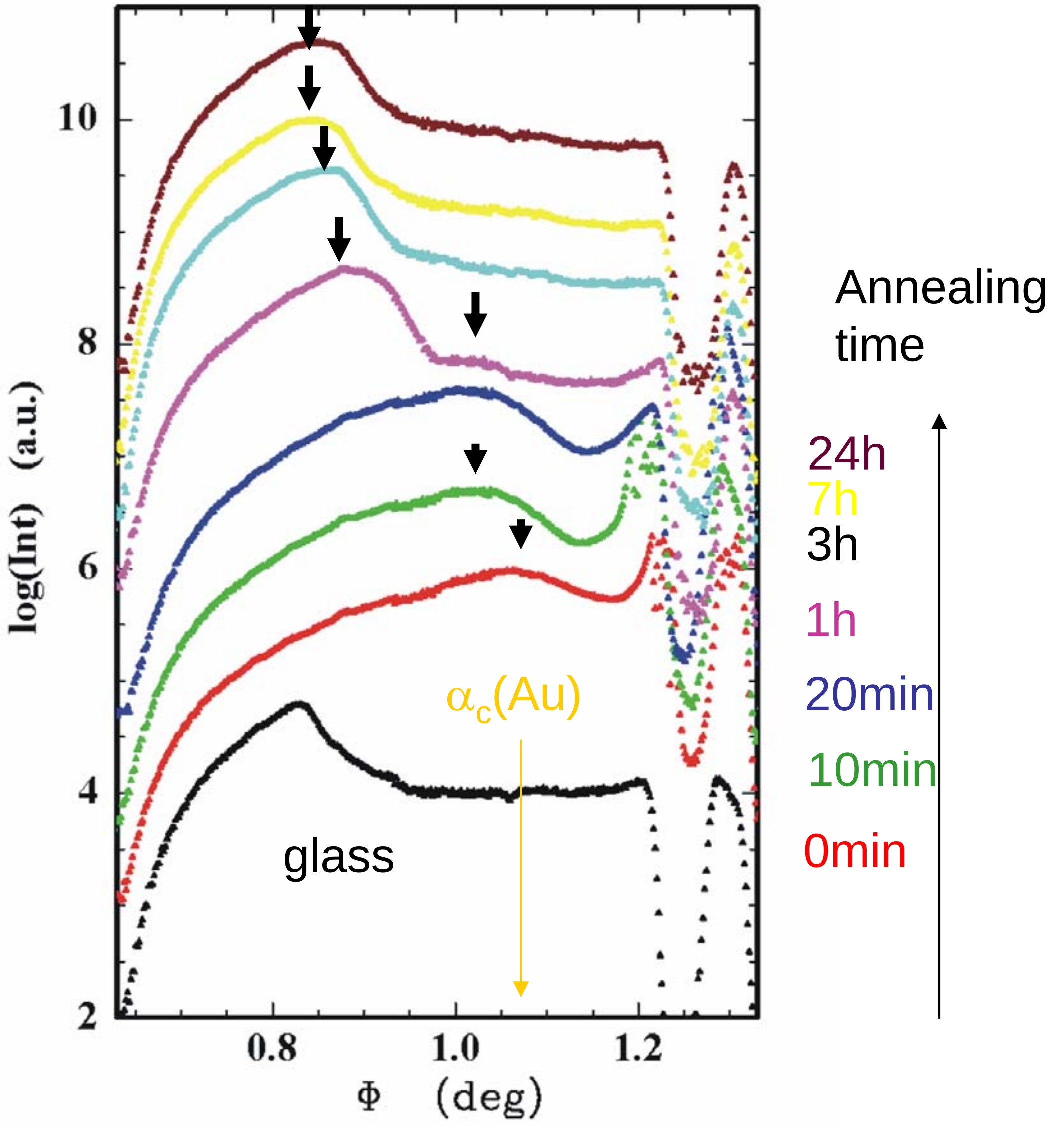


Log (Annealing time)
@ T_{anneal}=300°C < 1064°C (bulk melting point)

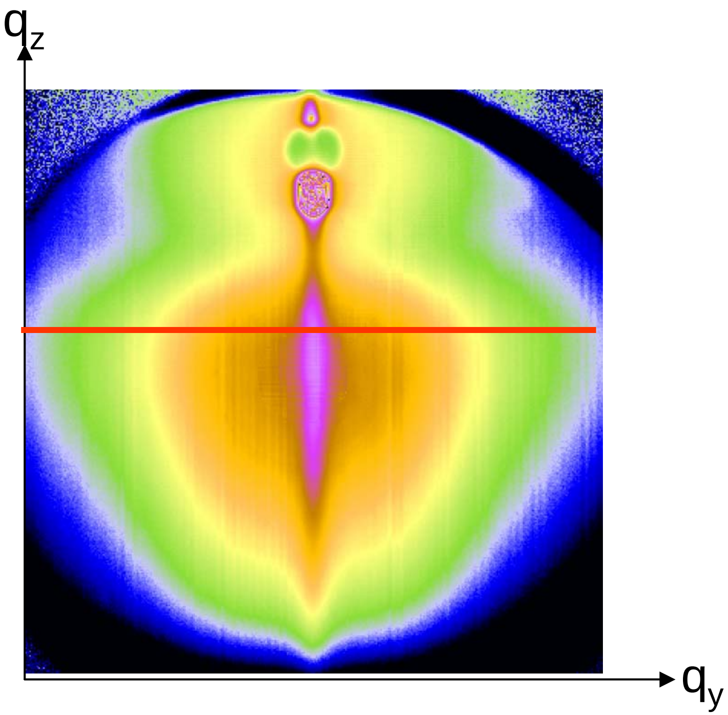
Surface coverage

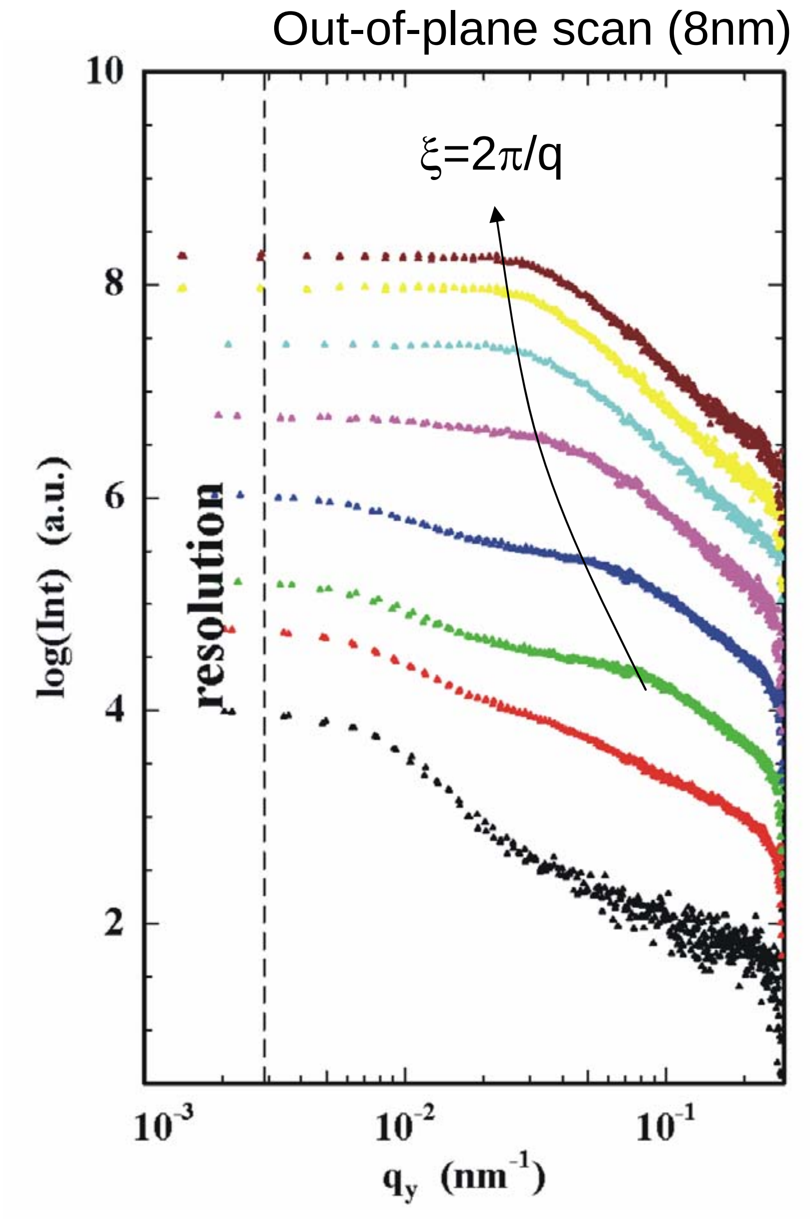


Detector scan (8nm)

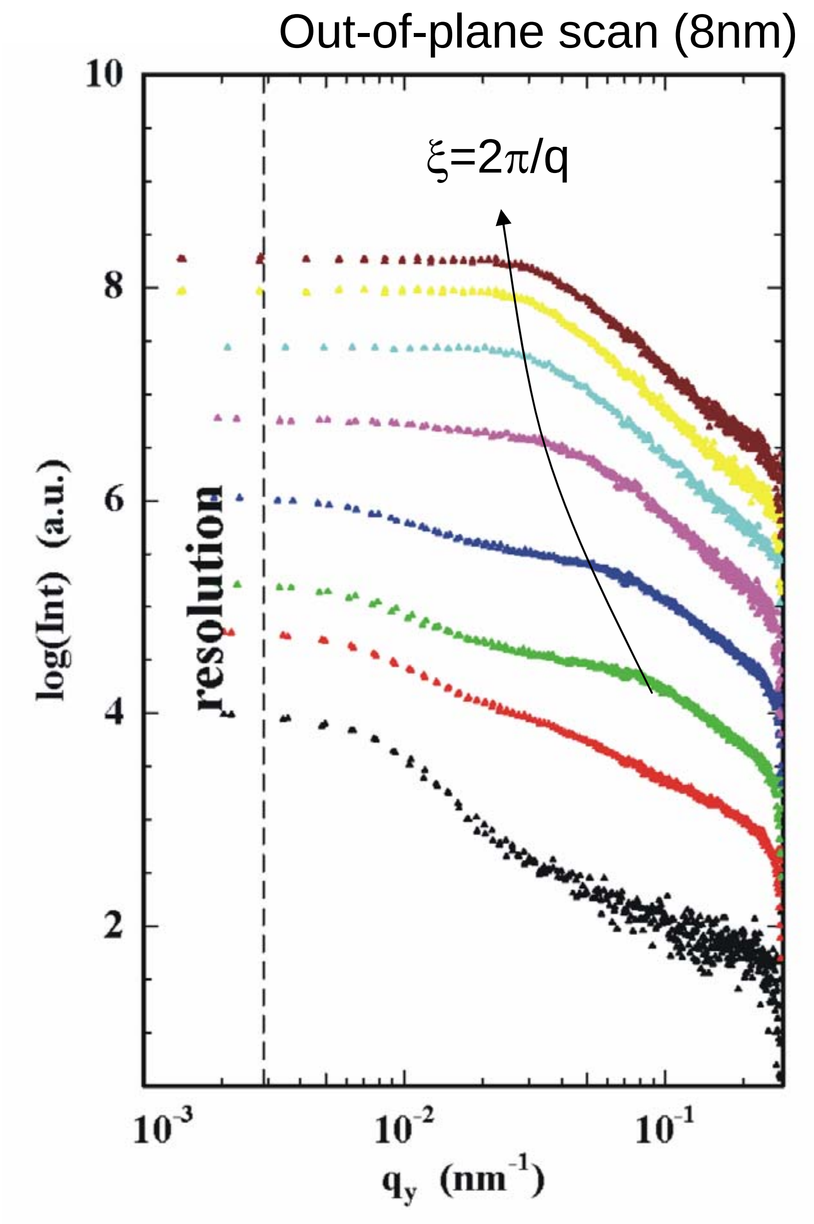


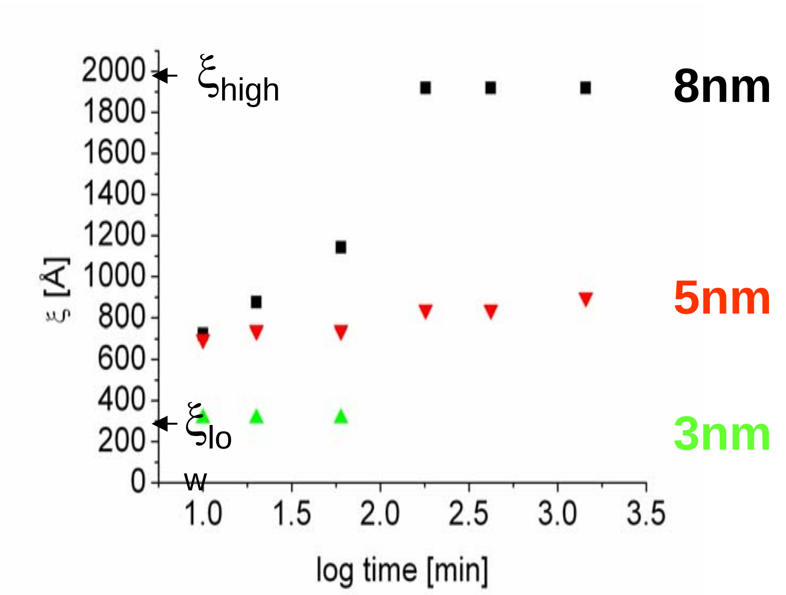
In-plane ordering

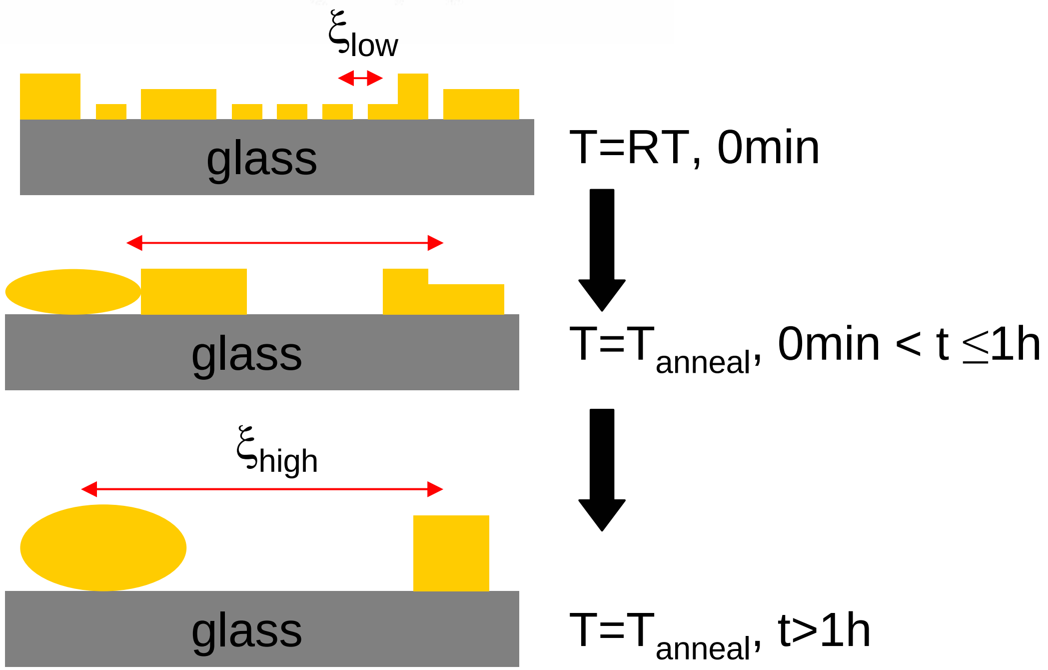




Lateral length scales







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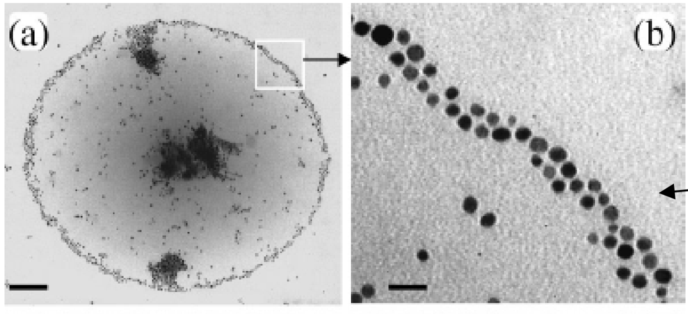
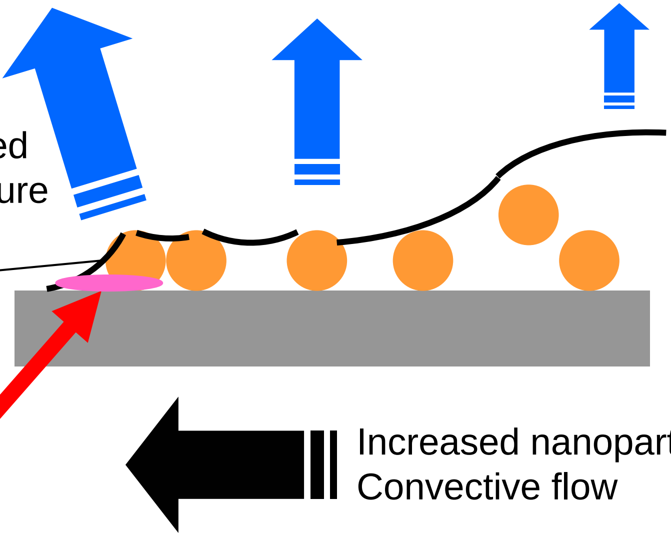
In-situ nanostructuring from solution

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

http://www.siliconsolar.com



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



Control drying-up of colloidal solution layer during inkjet printing

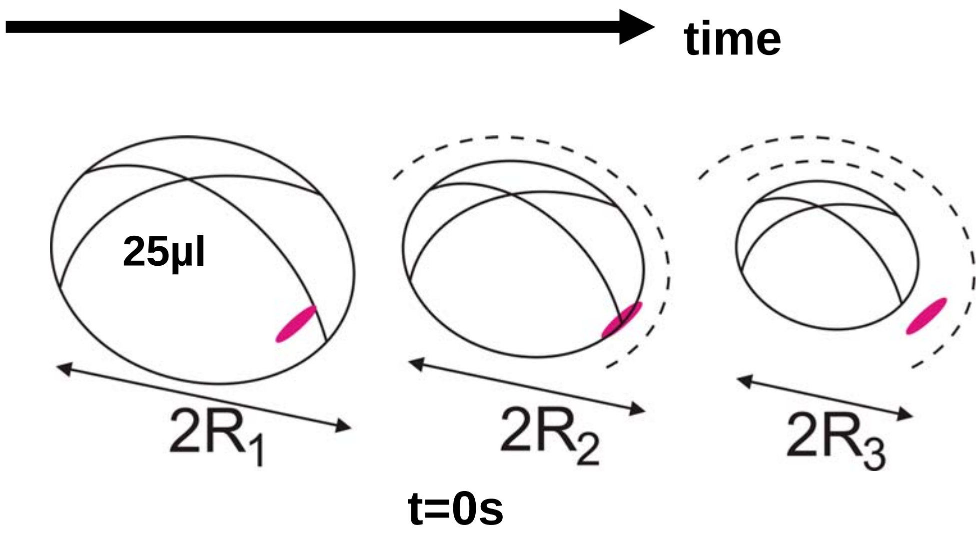
Critical step: Transfer of order to substrate

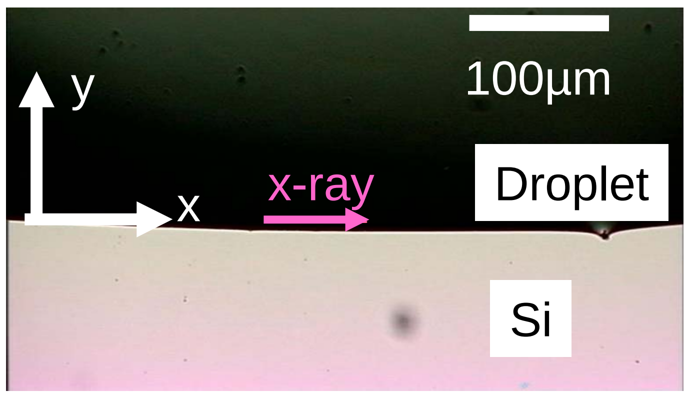
Real-time results: nanoGISAXS/ ID13 ESRF

2nm Au spheres in water
Slow evaporation time

300nm beam by Fresnel Zone plates

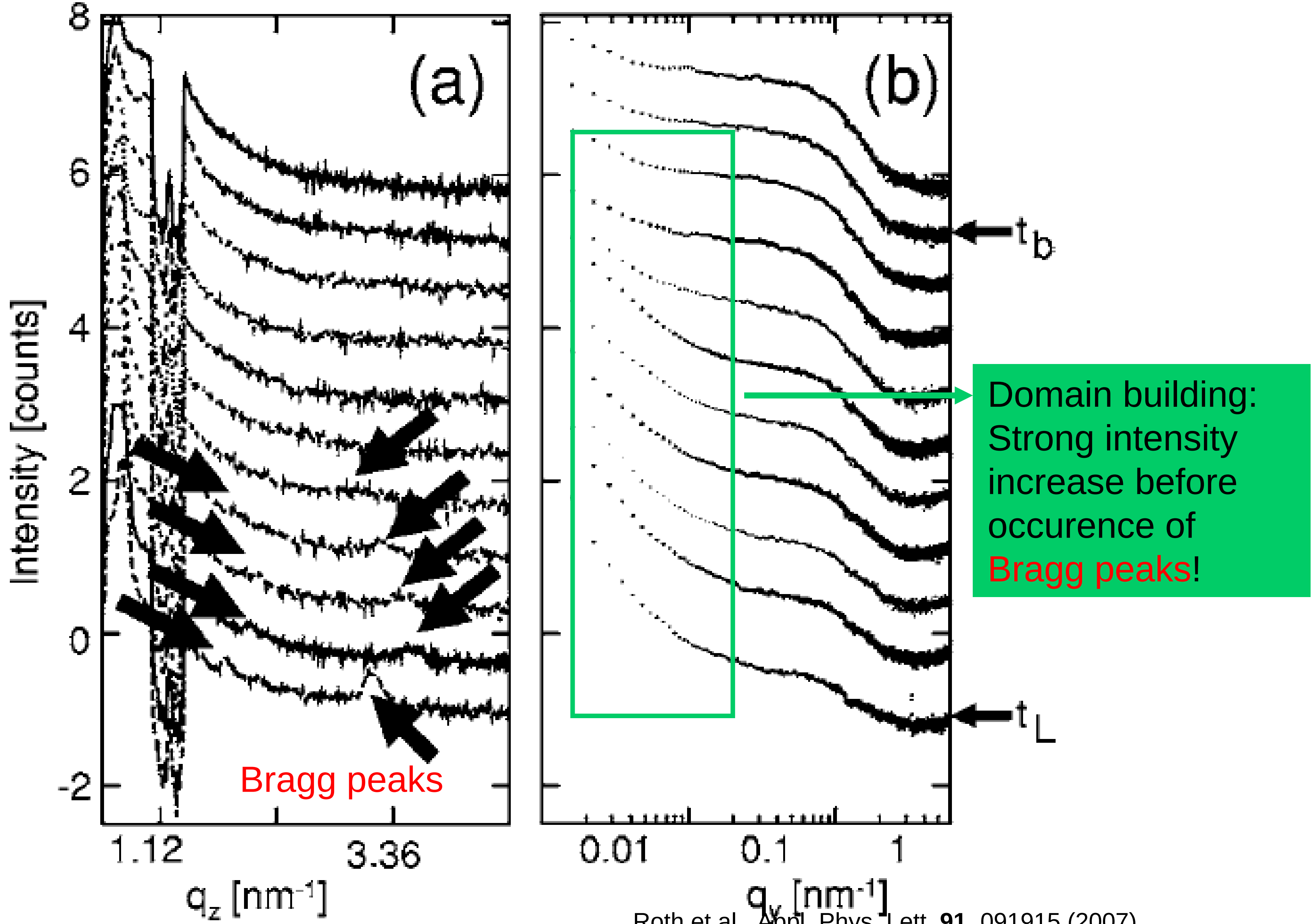
First nanobeam in-situ GISAXS





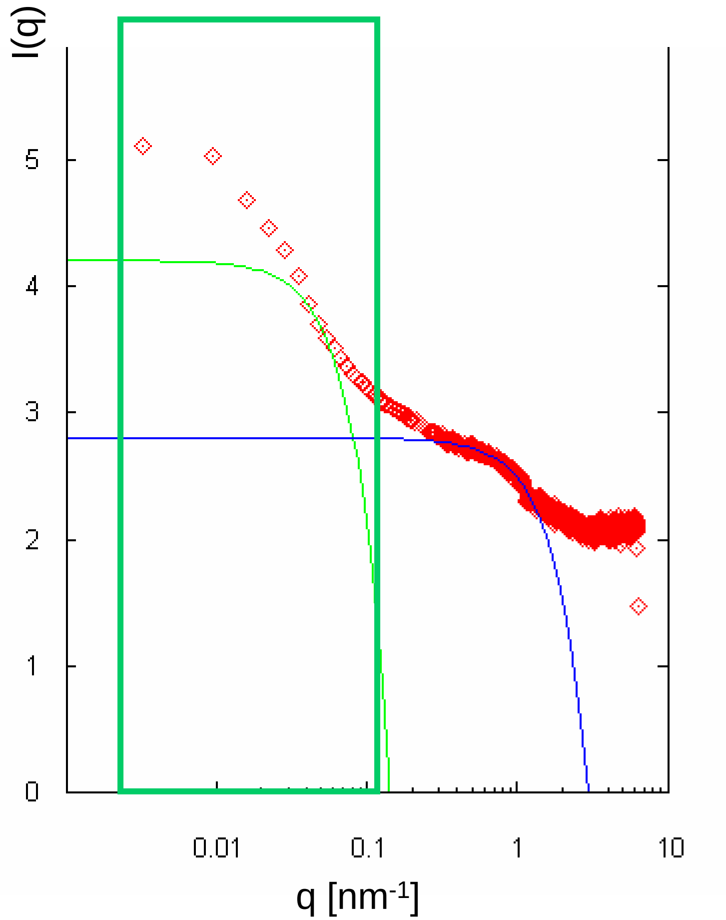
Roth et al., Appl. Phys. Lett. **91**, 091915 (2007)

Real-time results: nanoGISAXS/ ID13 ESRF



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

Guinier Approximation

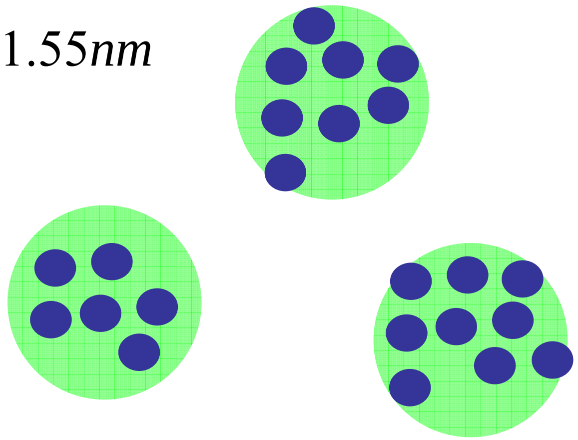


$$\lim_{q \to 0} I(q) = \Delta\rho^2 \cdot V^2 \cdot \exp(-q^2 \cdot \frac{R_g^2}{3})$$

Radius of Gyration R_g

Monodisperse spheres of radius R=2nm:

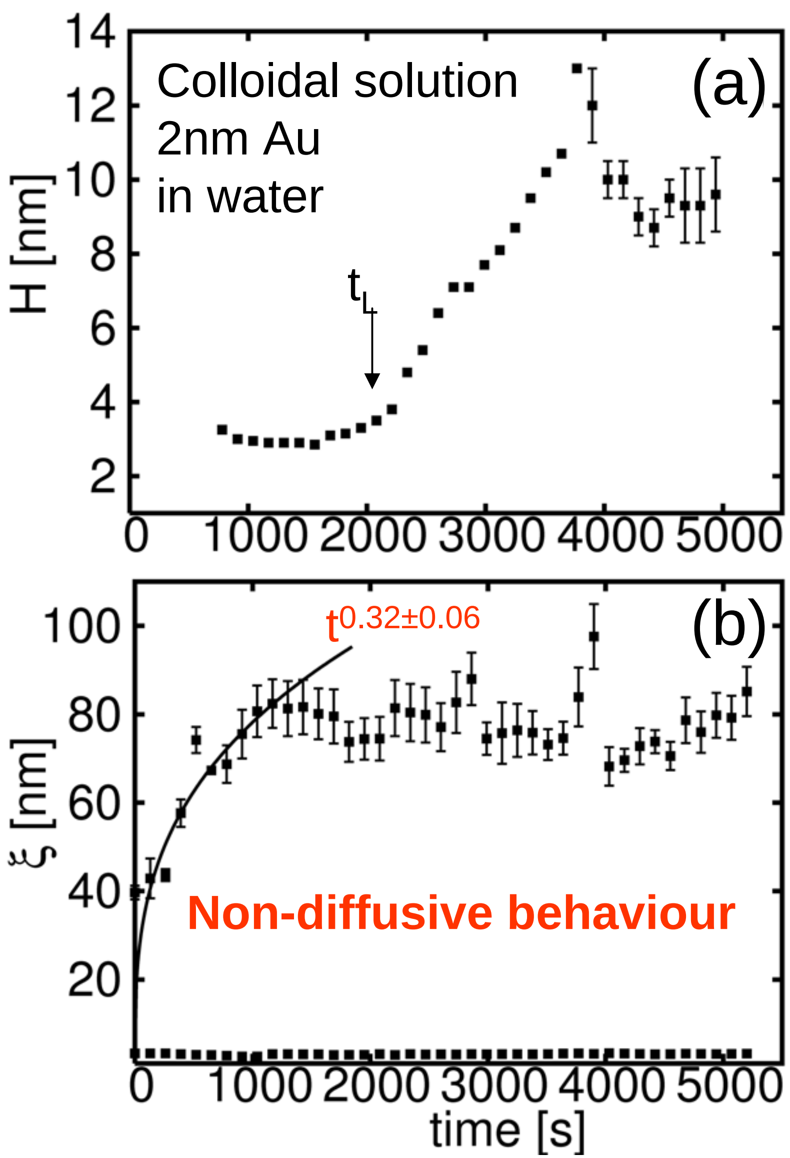
$$R_g = \sqrt{3/5} \cdot R = 1.55nm$$

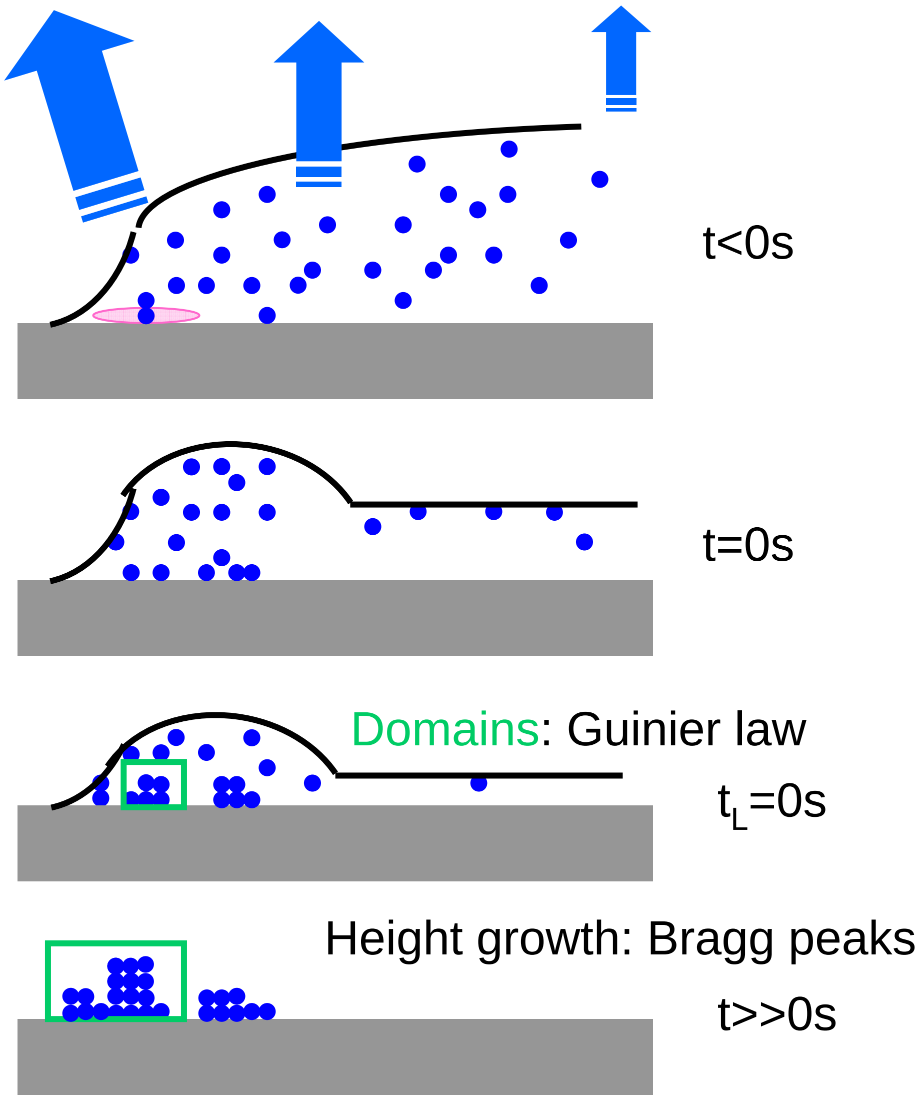


2nm Colloids
domains

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

Real-time results: nanoGISAXS/ ID13 ESRF





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

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Route to create large-area ordered polymeric nanochannel arrays

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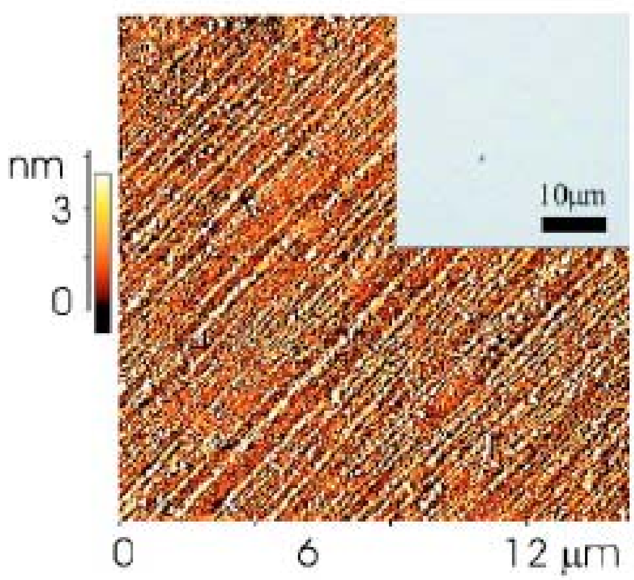
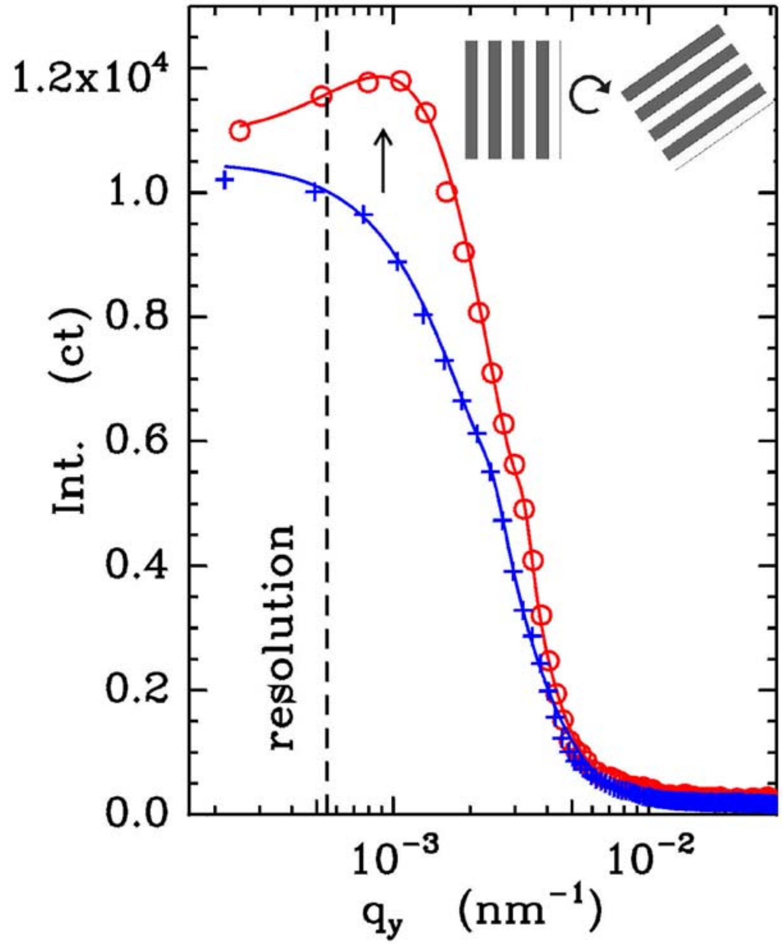
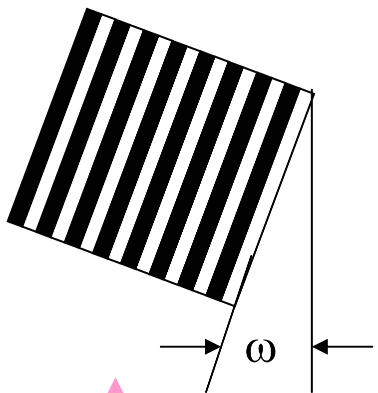
BW4, GIUSAXS 13m, α_i=0°
Polymeric nanochannels

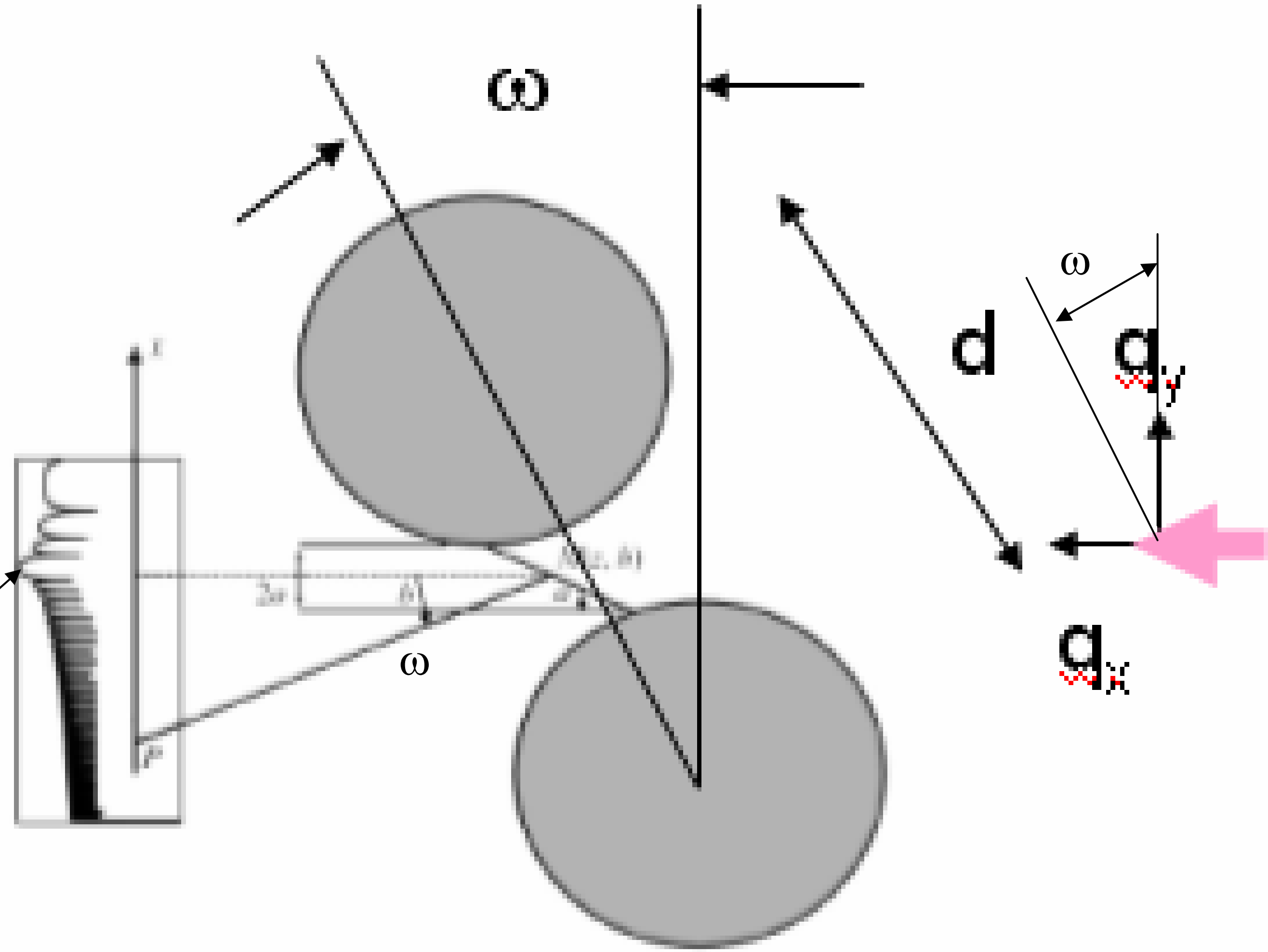






d=7µm
ω=6.4°

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