Methoden moderner Röntgenphysik II

Streuung und Abbildung

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17.06.2014

- Methoden moderner Röntgenphysik II:
  Streuung und Abbildung
- Vorlesung zum Haupt/Masterstudiengang Physik
  SS 2014 (Nr. 66-362)
- G. Grübel, M. Martins, E. Weckert
- Location:
  Hörs AP, Physik, Jungiusstrasse
  Tuesdays 12.45 – 14.15
  Thursdays 8:30 – 10.00
- Übungen: 2 SWS: Dienstag 14:30 – 16:00 (wenn vereinbart)
  (Nr. 66-363)
  SemRm 4
- **EXKURSION: 1.7.2014, ab 14:15? Bestätigung!!!**

Outline I

- 03.06 : Small-Angle X-ray Scattering (SAXS)
- 05.06 : Applications &
  A short excursion into Polymeric materials
- 17.06 : Grazing incidence SAXS (GISAXS)
- 19.06 : In-situ studies of metal layer growth (M. Schwartzkopf)
- 24.06 : The polymer-metal interface – application of GISAXS
  On the route to organic electronics

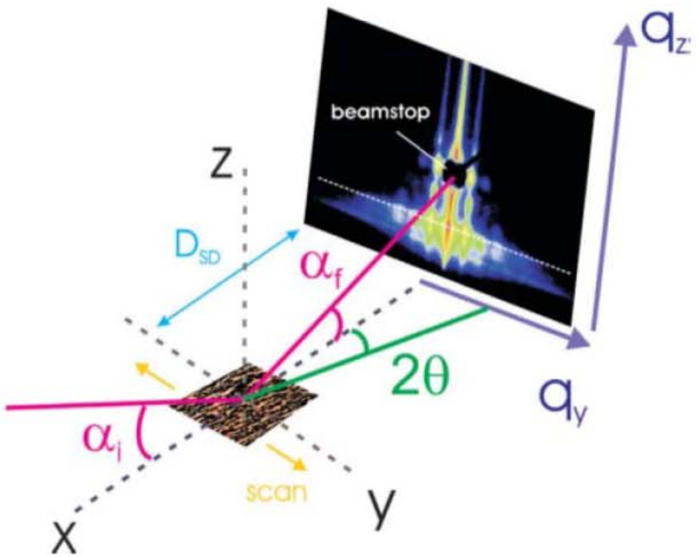
Bachelor-/Masterarbeiten

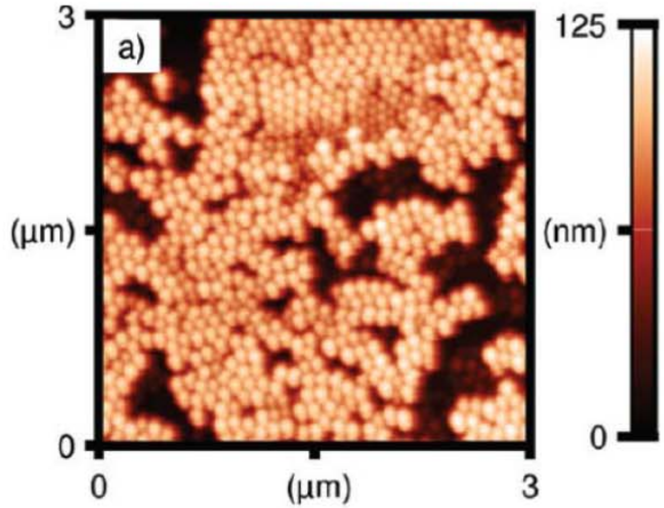
im Bereich Nanowissenschaften und Materialien für

Wenn Ihr Lust habt, in einem internationalen Team aus Physikern, Chemikern und Informatikern mitzuarbeiten, freuen wir uns auf Euch!

Themenbereiche sind:

- Sputterdeposition von organischen und metallischen Nanostrukturen
- Sprühbeschichtung und Gießtechniken (‚solution casting‘)
- Charakterisierung verschieden hergestellter Nanostrukturen, z.B. mittels Rasterkraftmikroskopie, Ellipsometrie, Kontaktwinkelmessungen und Röntgenstreuung
- Aufbau und Durchführung von Echtzeitexperimenten am Synchrotron
- Simulation und Modellierung von in-situ Streuexperimenten

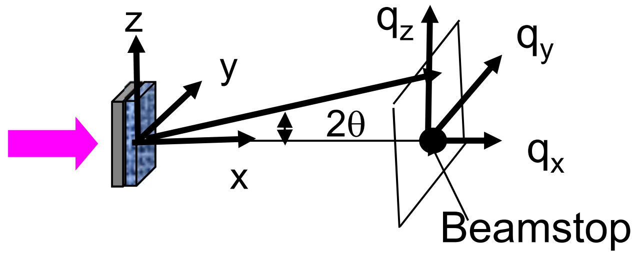


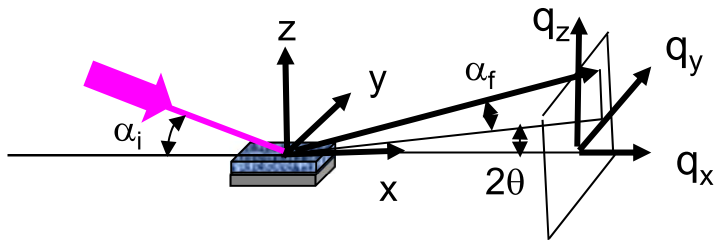


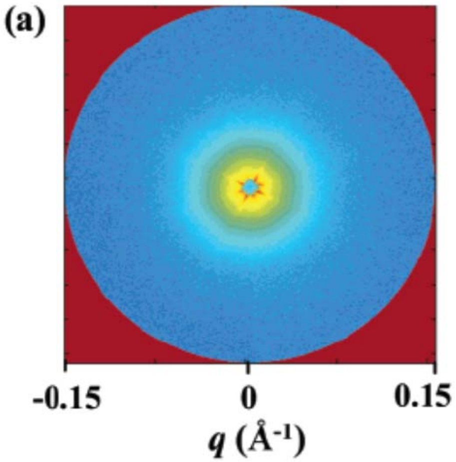
Outline

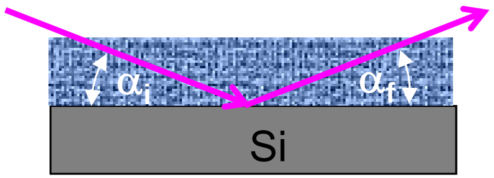
- ➔ Thin films ➔Grazing incidence SAXS : A Primer
- > Nanostructuring by annealing
- > The highest resolution

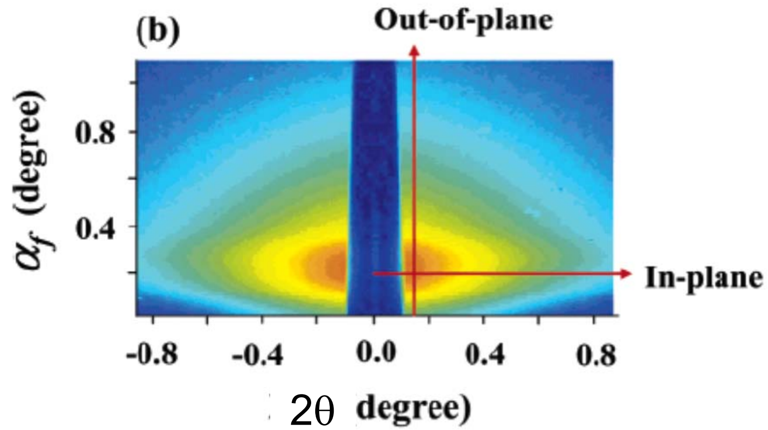
T-SAXS vs. GISAXS









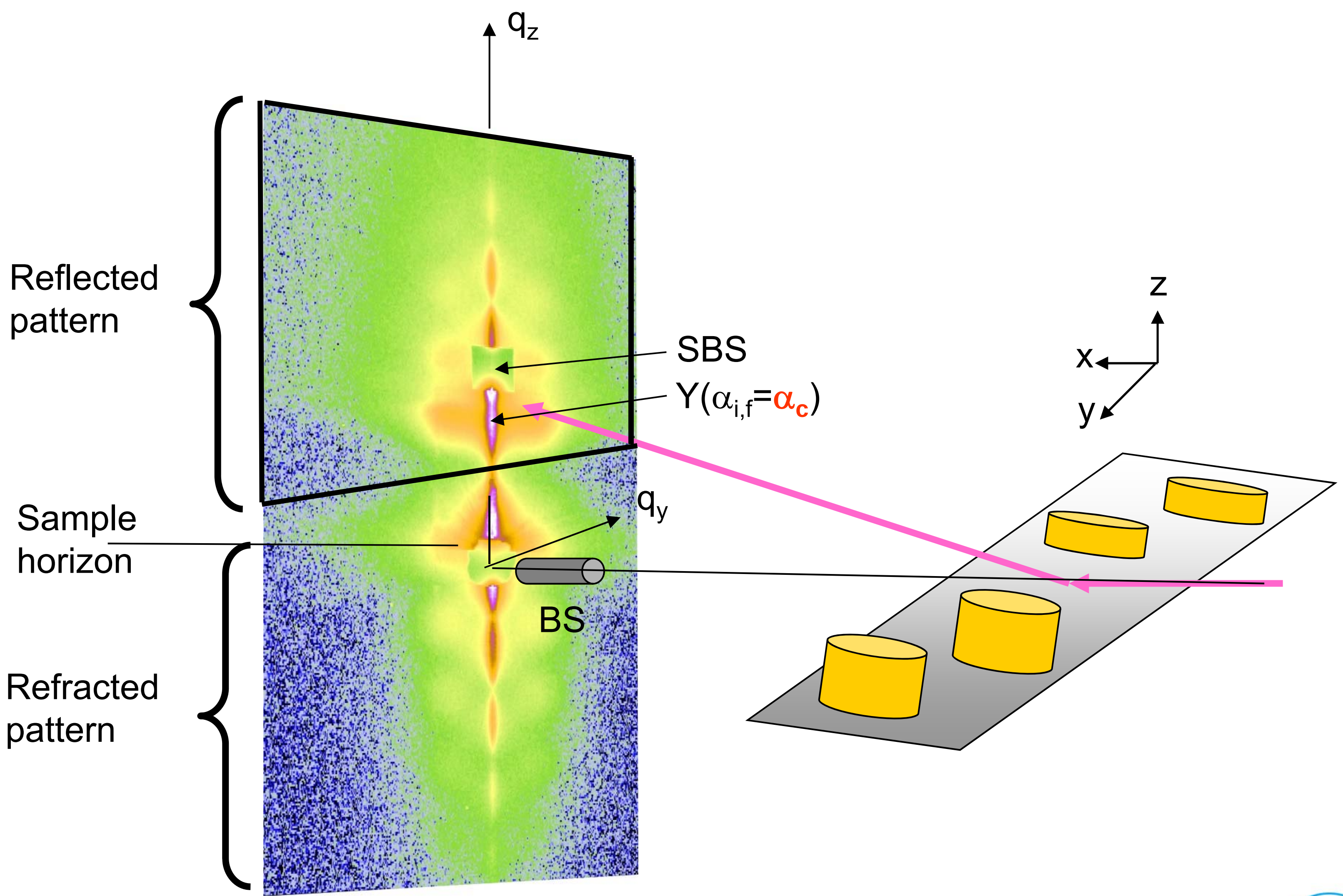


- Easy measurement
- Easy analysis
- In-plane information (q_y,q_z)
- Any possible scattering from substrate
- Transparency of substrate
- High energy

- 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)

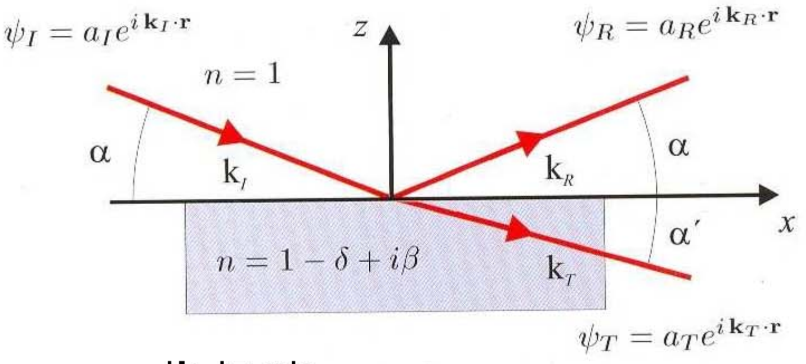
Lee et al., Macromolecules, 38, 8991 (2005)

Grazing incidence small-angle x-ray scattering



Snell's law and the Fresnel equations (1) (see 10.4.2014)

$k = |\mathbf{k}_I| = |\mathbf{k}_R|$



$|\mathbf{k}_T| = nk$

Require that the wave and its derivative is continuous at the interface:

$$a_I + a_R = a_T \quad \text{(A)}$$

$$a_I\mathbf{k}_I + a_R\mathbf{k}_R = a_T\mathbf{k}_T \quad \text{(B)}$$

||: $a_I k\cos\alpha + a_R k\cos\alpha = a_T(nk)\cos\alpha'$ (B')

⊥: $-(a_I - a_R)k\sin\alpha = -a_T(nk)\sin\alpha'$ (B'')

$$\cos\alpha = n\cos\alpha' \quad \text{(B' +A)}$$

α, α' small: ($\cos z = 1 - z^2/2$)

$$\alpha^2 = \alpha'^2 + 2\delta - 2i\beta$$
$$= \alpha'^2 + \alpha_c^2 - 2i\beta \quad \text{(C)}$$

$$a_I - a_R / a_I + a_R = n(\sin\alpha' / \sin\alpha) \approx \alpha'/\alpha \quad \text{(B''+A)}$$

Fresnel equations:

$$r = a_R/a_I = (\alpha - \alpha') / (\alpha + \alpha')$$

$$t = a_T/a_I = 2\alpha / (\alpha + \alpha')$$

r: reflectivity t: transmittivity

Snell‘s law and the Fresnel equations (2) (see 10.4.2014)

<u>Note:</u> α’ is a complex number

$\alpha' = Re(\alpha') + i\, Im(\alpha')$

<u>Consider z-component of transmitted wave:</u>

$= a_T \exp(ik \sin\alpha' z) \approx a_T \exp(ik\alpha' z)$

$= a_T \exp(ik Re(\alpha')z) \bullet \exp(-k\, Im(\alpha')z)$

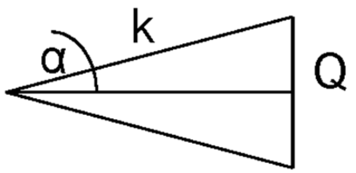
exponential damping

intensity fall-off: $\exp(-2k\, Im(\alpha')\, z))$

<u>1/e penetration depth Λ:</u> $z\, 2k\, Im(\alpha') = 1 \quad (z= \Lambda)$

$$\Lambda = 1 / 2k\, Im(\alpha')$$

use wavevector notation:



$\sin\alpha = (Q/2)/k$

$Q \equiv 2k\sin\alpha \approx 2k\alpha$

$Q_c \equiv 2k\sin\alpha_c \approx 2k\alpha_c$

<u>use dimensionless units:</u>

$q \equiv Q/Qc \approx (2k/Q_c)\alpha$

$q' \equiv Q'/Qc \approx (2k/Q_c)\alpha'$

$$q^2 = q'^2 + 1 - 2\, ib_u \qquad \text{(D)}$$

$b_u = (2k/Q_c)\beta = (4k^2/Q_c^2)\mu/2k = 2k\mu/Q_c^2$

$Q_c = 2k\alpha_c = 2k\, \mathrm{sqrt}(2\delta)$

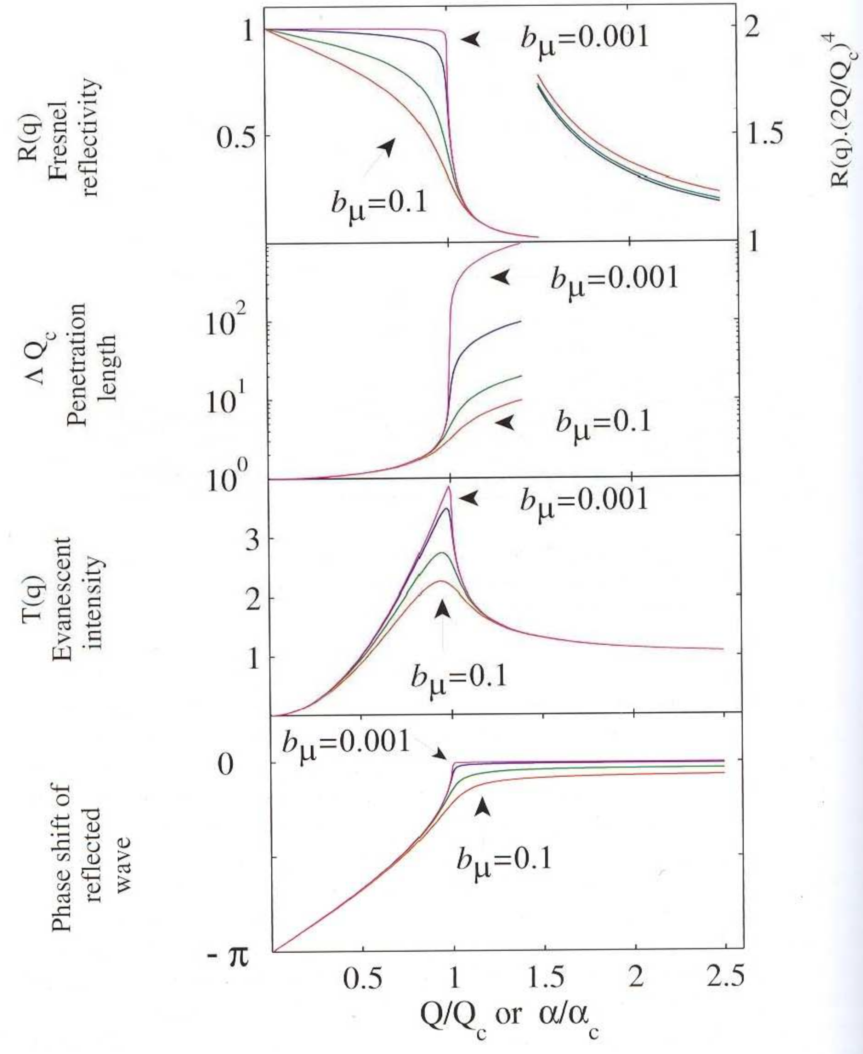
Snell's law and the Fresnel equations (4) (see 10.4.2014)

Fresnel equations:

q>>1: $R(Q) \sim 1/q^4$,
$\Lambda \approx \mu^{-1}$,
$T \approx 1$,
no phase shift

q<<1: $R \approx 1$,
$\Lambda \approx 1/q_c$ small,
T very small,
$-\pi$ phase shift

q=1: $T(q=1) \approx 4\, a_l$



(Als-Nielsen)

Total reflection – Yoneda peak

> Refractive Index for X-rays $n = 1 - \delta + i\beta$

- Real part: $1 - \delta = 1 - \frac{\lambda^2}{2\pi} r_0 \rho_e$; $\rho_e = NZ$

  N = Number density of atoms, Z = Atomic number

- Imaginary Part: $\beta = \frac{\lambda}{4\pi}\mu$

> Snell's Law / Total reflection: $\alpha_c = \sqrt{2\delta} \sim \sqrt{\rho}$

> Maximum of the Fresnel transmission function

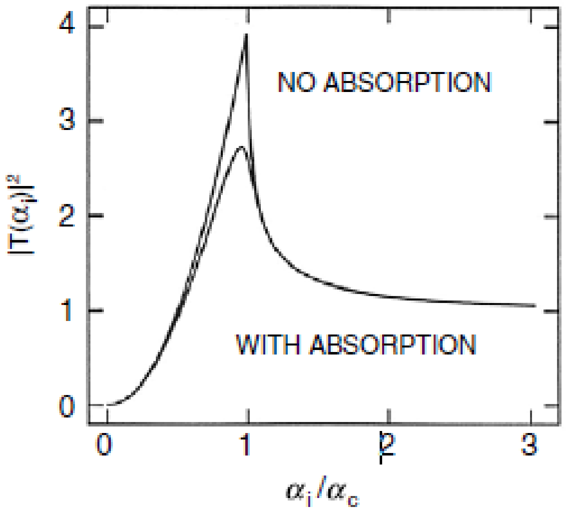
> Electrical field on surface: $2xE_i$

> Increased scattering at surface

> Yoneda peak [Yoneda, 1963]

- Occurs when $\alpha_{i,f} = \alpha_c$

> Material sensitive



Renaud et al., Surf. Sci. Rep. **6**4, 255 (2009)

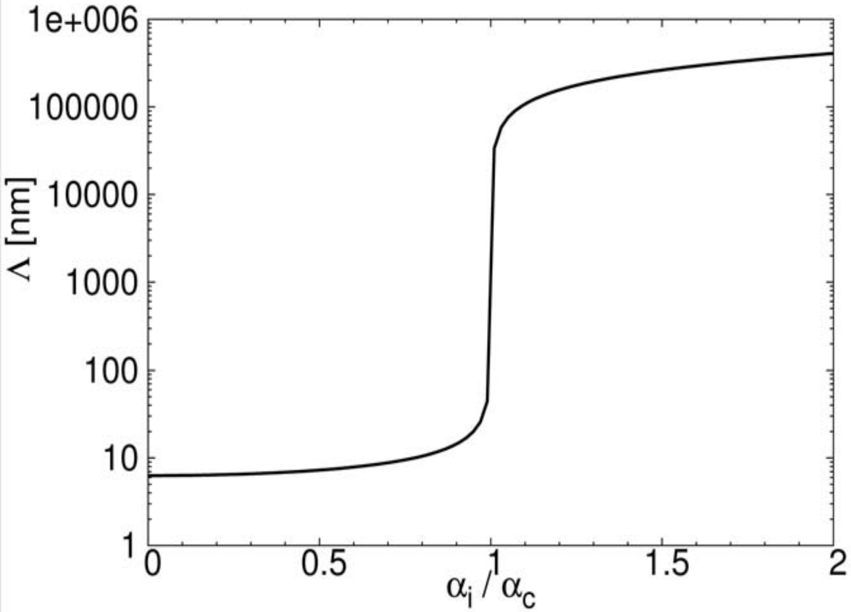
GISAXS: Tuning of penetration depth

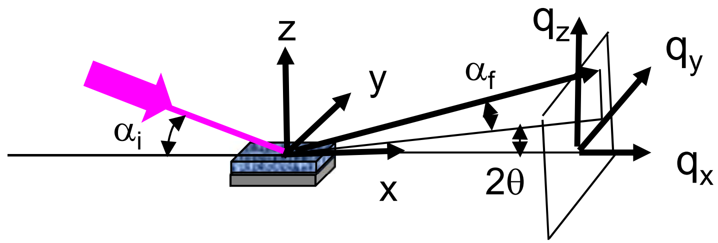
> Scattering depth:

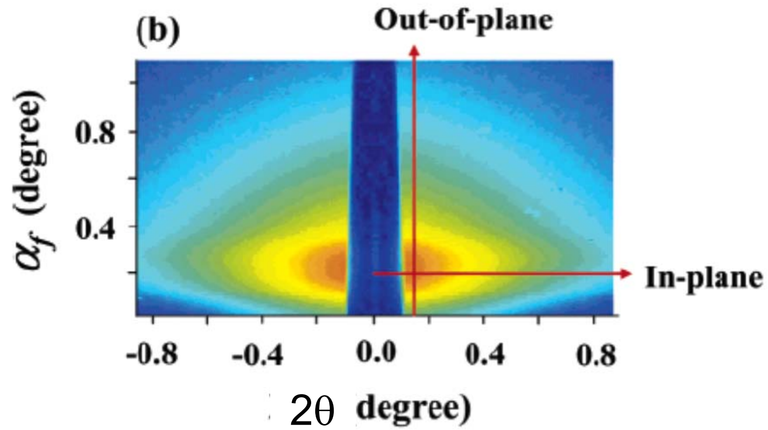
$$\Lambda = \frac{\lambda}{\sqrt{2}\pi} * \frac{1}{\sqrt{\sqrt{(\alpha_i{}^2-\alpha_c{}^2)^2+4\beta^2}-(\alpha_i{}^2-\alpha_c{}^2)}}$$

> Tune depth sensitivity

> Exercise: energy variation





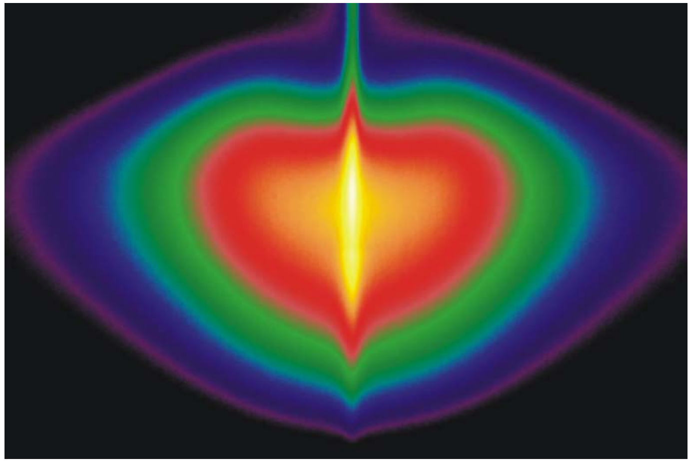


- Strong intensity
- Easy preparation of samples
- Full information (q_x,q_y,q_z)
- Scattering from surface / internal structure
- Scattering from reflected AND transmitted beam
- Refraction effects (DWBA)

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

History

>	1963	Yoneda	Anomalous Surface Reflection of X-Rays
>	1988	Sinha et al.	surface roughness
>	1989	Levine et. al.	simple qualitative analysis
>	1995	Lairson et. al.	GISAXS with a 1D-Detector
>	1995	Rauscher et. al.	Theory of GISAXS in DWBA
>	1996	Müller-Buschbaum et. al.	GIUSAXS on soft matter: **DESY**
>	1999	Kegel et. al.	GISAXS on semiconductors quantum dots
>	2002	Lazzari	IsGISAXS
>	Since 2003	Müller-B., Roth et. al.	Micro-/nanoGISAXS: **ESRF / DESY**



BW4, CCD
Au
d=5nm
t=3h
T=300°C

History

> 1963 Yoneda – anomalous Scattering below α_i

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)

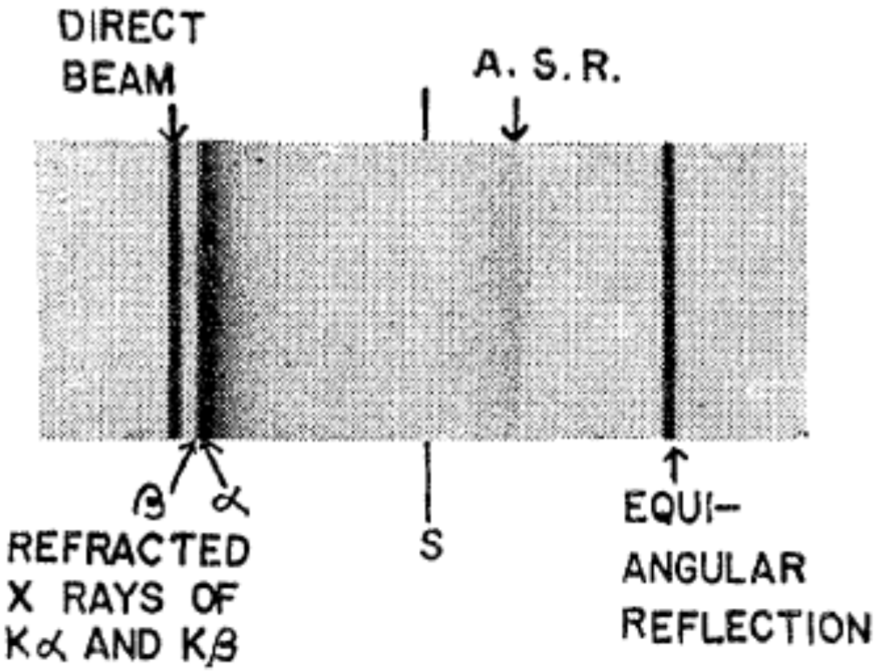


FIG. 2. Photograph of A.S.R. by a glass sample, ×2.

The first sucessful experiment

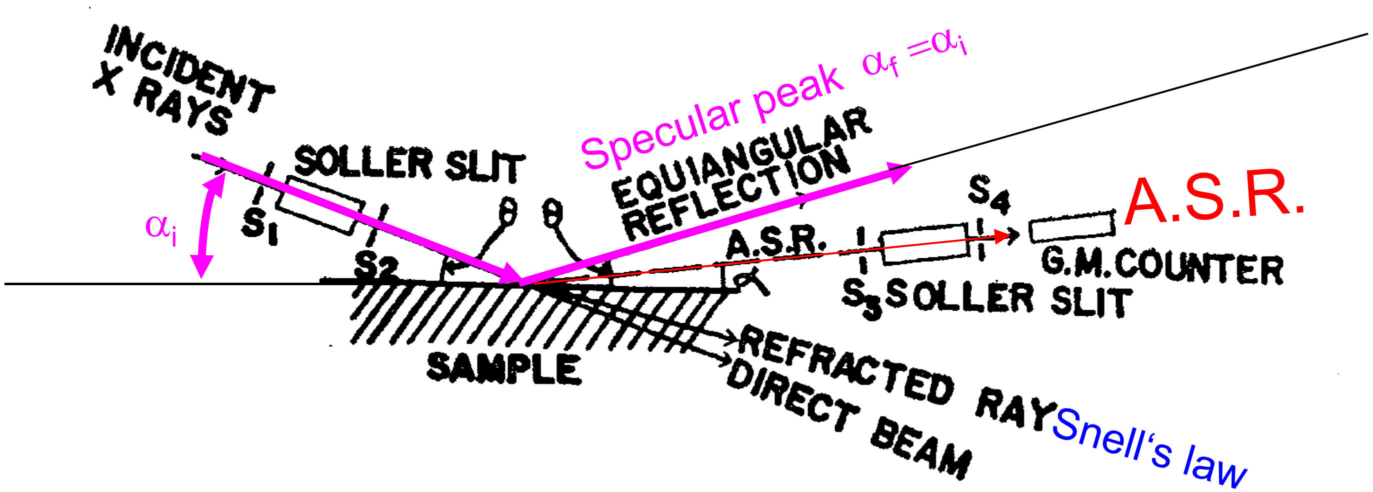


FIG. 1. Schematic view of the experimental arrangement in the incident plane.

Anomalous Surface Reflection
(diffuse scattering)

Intensity between α_f=0° and 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

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

Critical angle

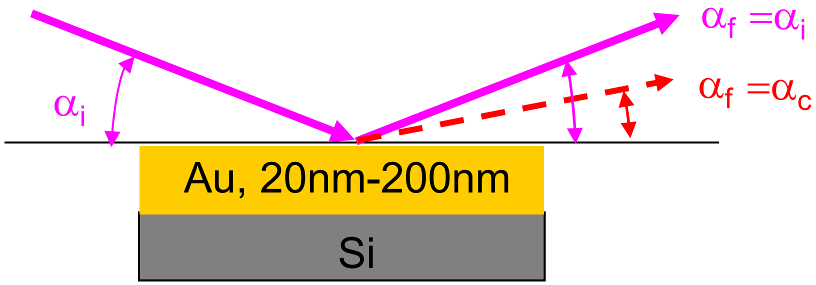
α_c(Si)=0.2°
α_c(Au)=0.5°

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

Very small!

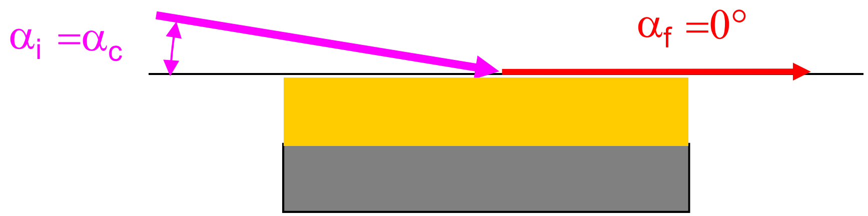
Matter: |n(X-rays)|<1 optically less dense than vacuum (remember Bragg‘s law)

Origin of intensity at α_c

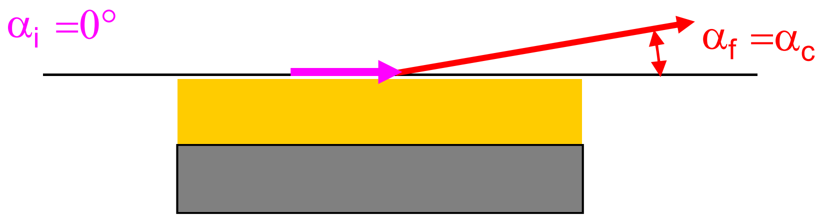


α_f(Au) = 0.56° = α_c(Au,1.8Å)

Total external reflection

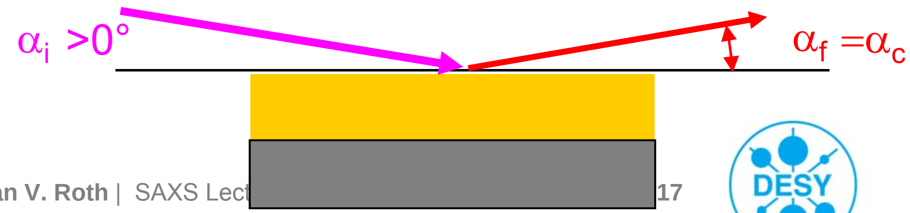


Reciprocity theorem & critical angle



must stem from wave parallel to surface

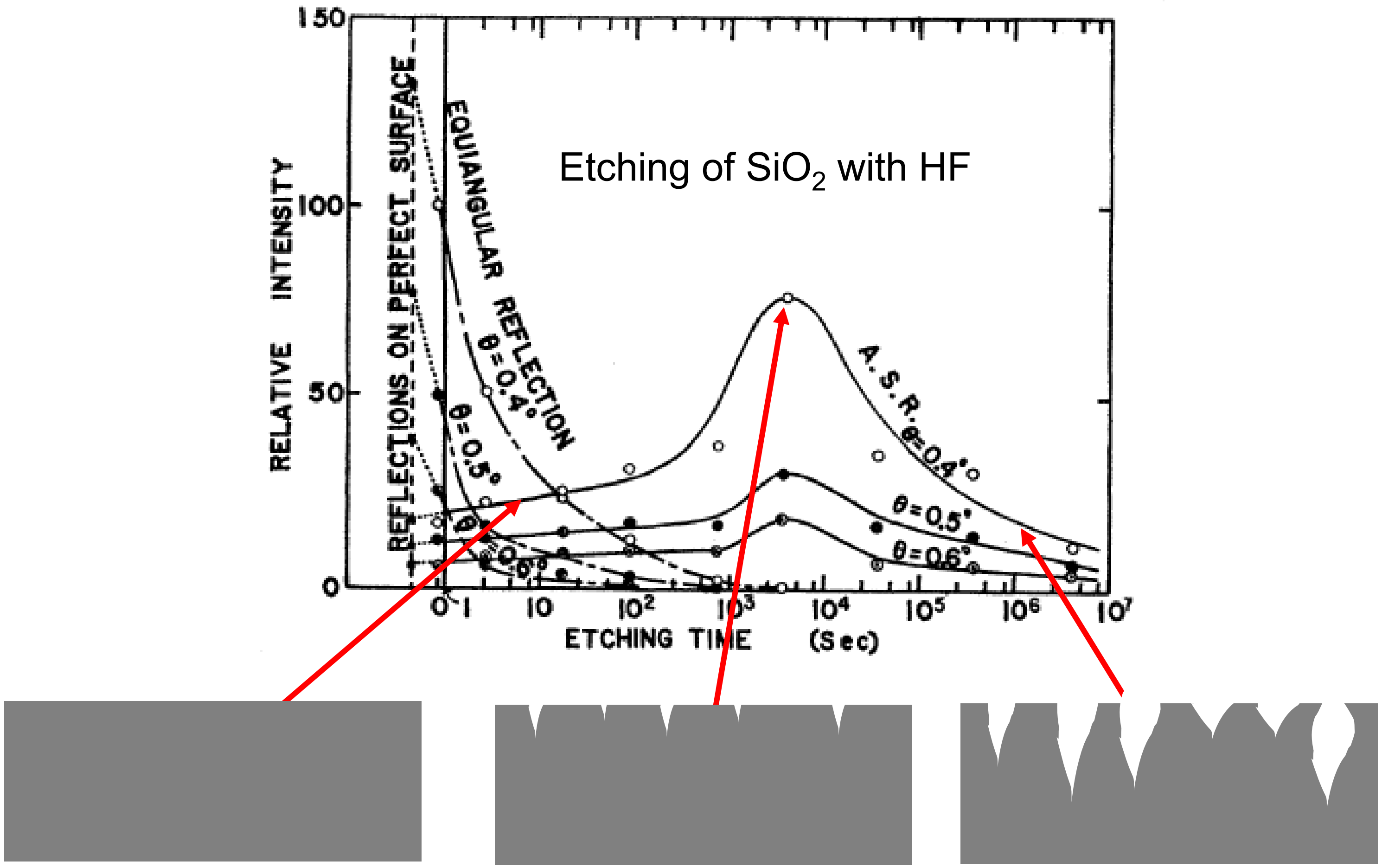
Yoneda



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

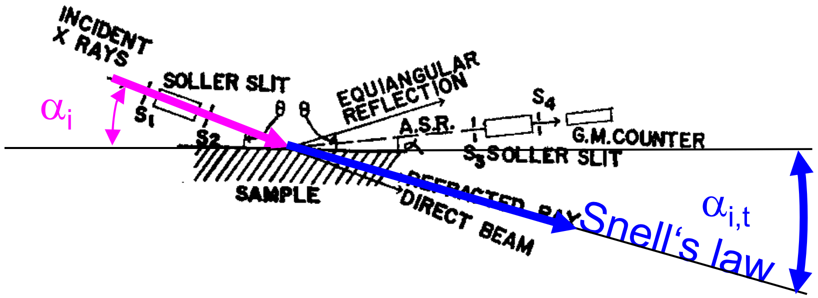
Hint: Roughness of the sample

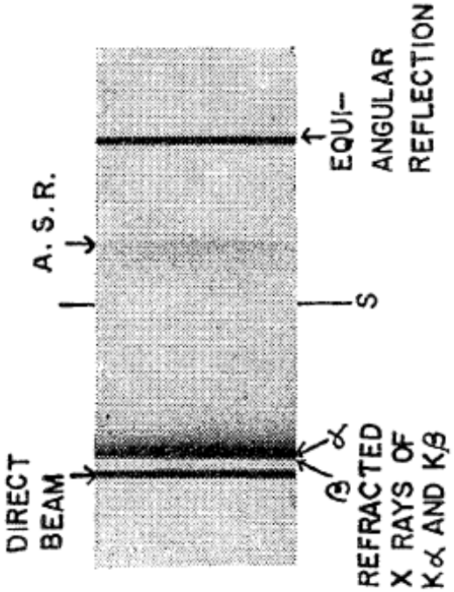
Yoneda peak = Scattering effect!



Basically the same

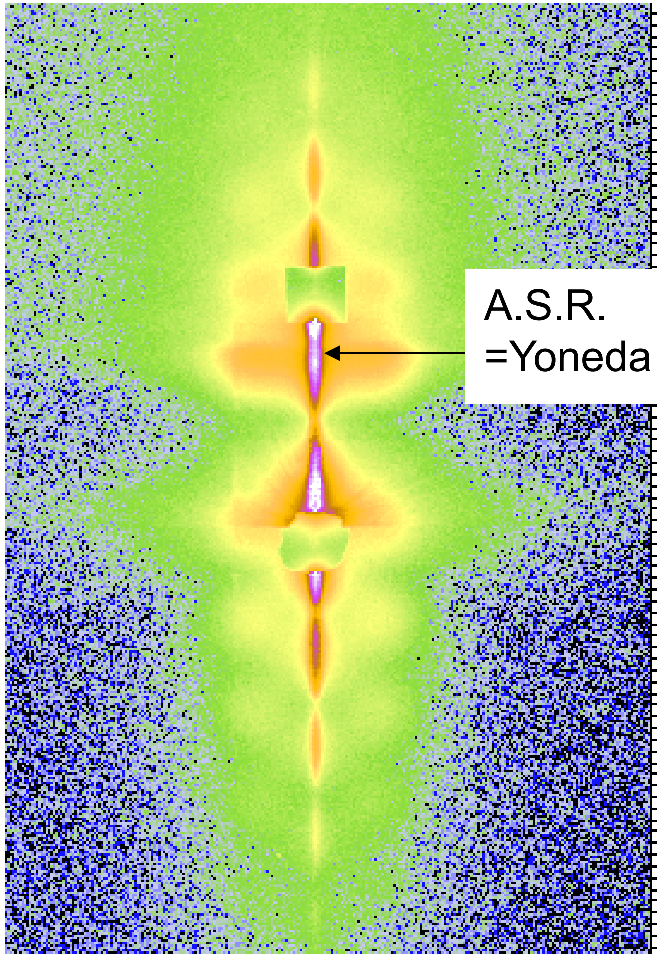
1963





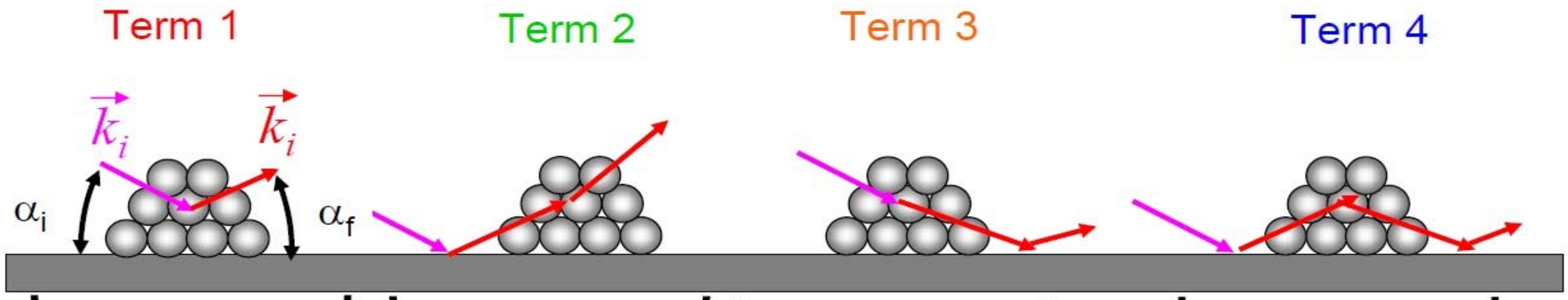
$\alpha_i=\alpha_f$
Specular peak

today



Theory

> Distorted-wave Born approximation



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

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

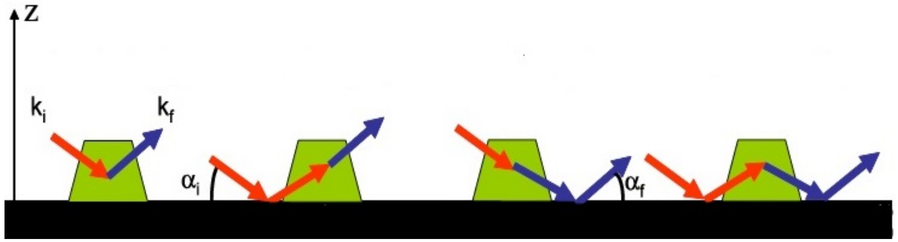
- coherent interference between four waves along $\boldsymbol{\alpha_f}$
- each term weighted with the Fresnel coefficients
- cross section just depends on $\boldsymbol{q_y}$ and $\boldsymbol{q_z}$

Courtesy: R. Lazzari (U Paris VI/VII)

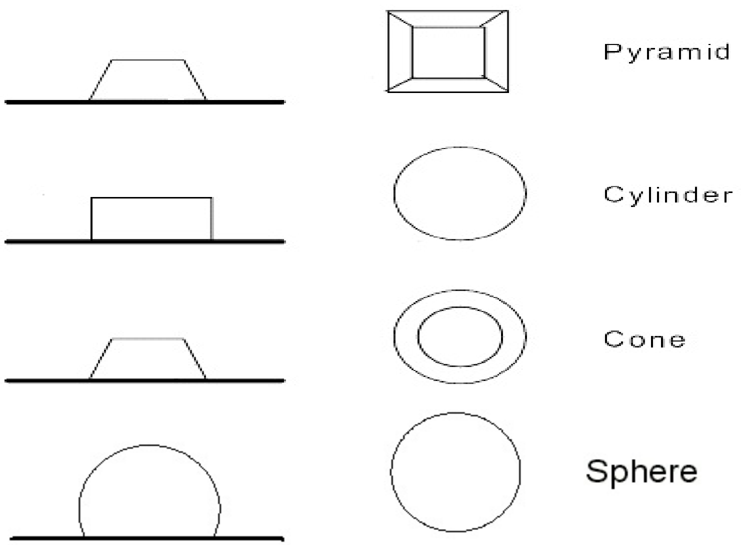
Theory - Simulation

- Cross section (particle form factor * interference function)
- $I(q_y, q_z) = c * P(q_y, q_z) * S(q_y)$

Particle form factor: multiple scattering



- Shape, Size, Orientation, Distribution

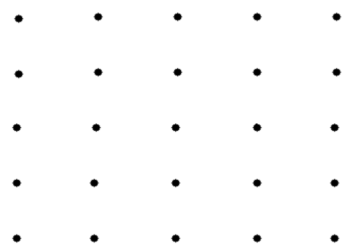


Interference function

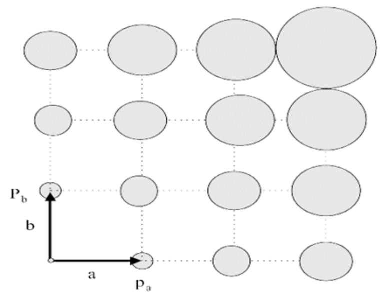
Three main cases

1) Disordered lattice
   - pair correlation function

2) Regular bidimensional lattice



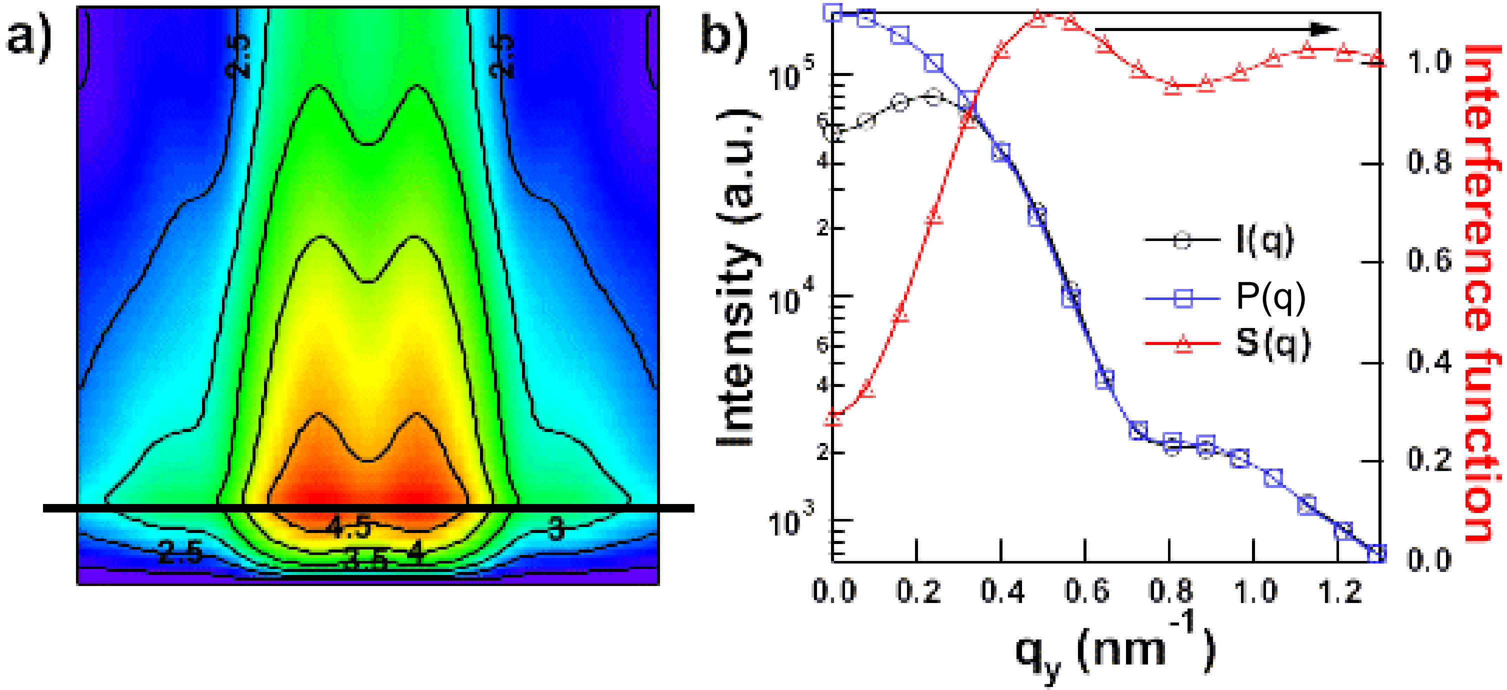
3) Bidimensional paracrystal



Courtesy: R. Lazzari (U Paris VI/VII)
Manual IsGISAXS

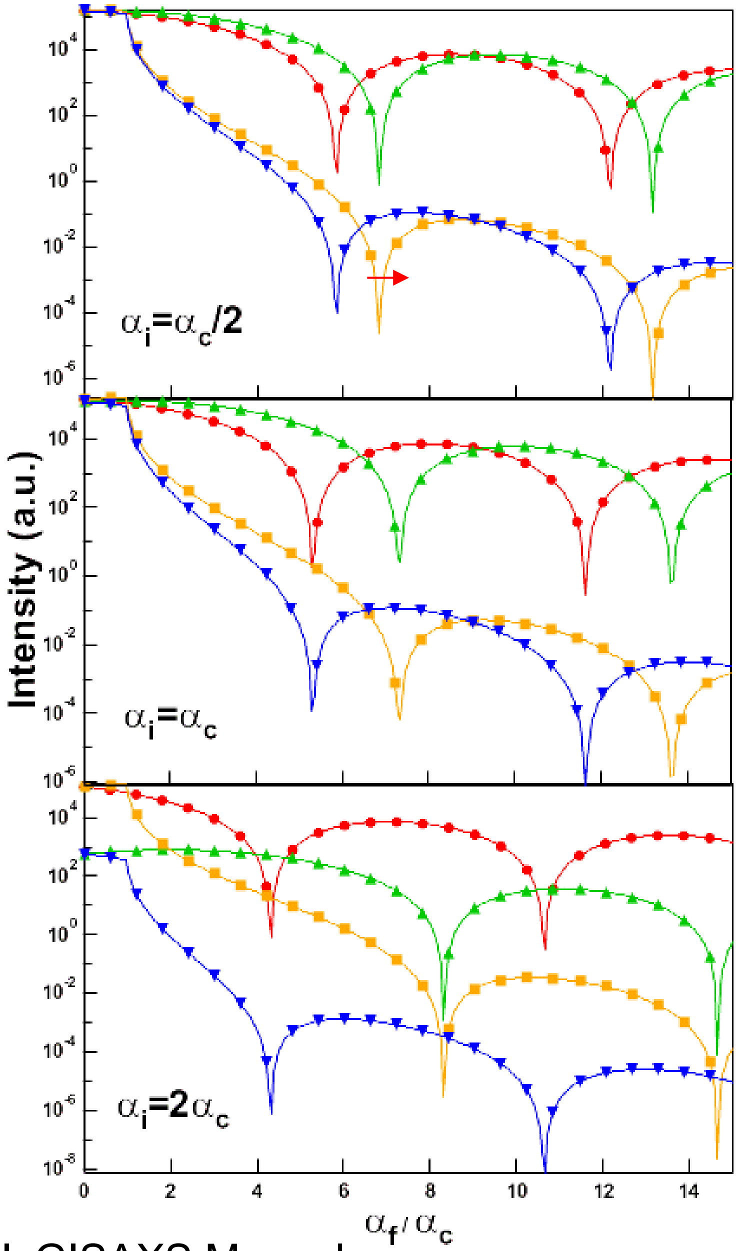
Simulations: IsGISAXS (R. Lazzari)

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



IsGISAXS Manual

DWBA – results



IsGISAXS Manual

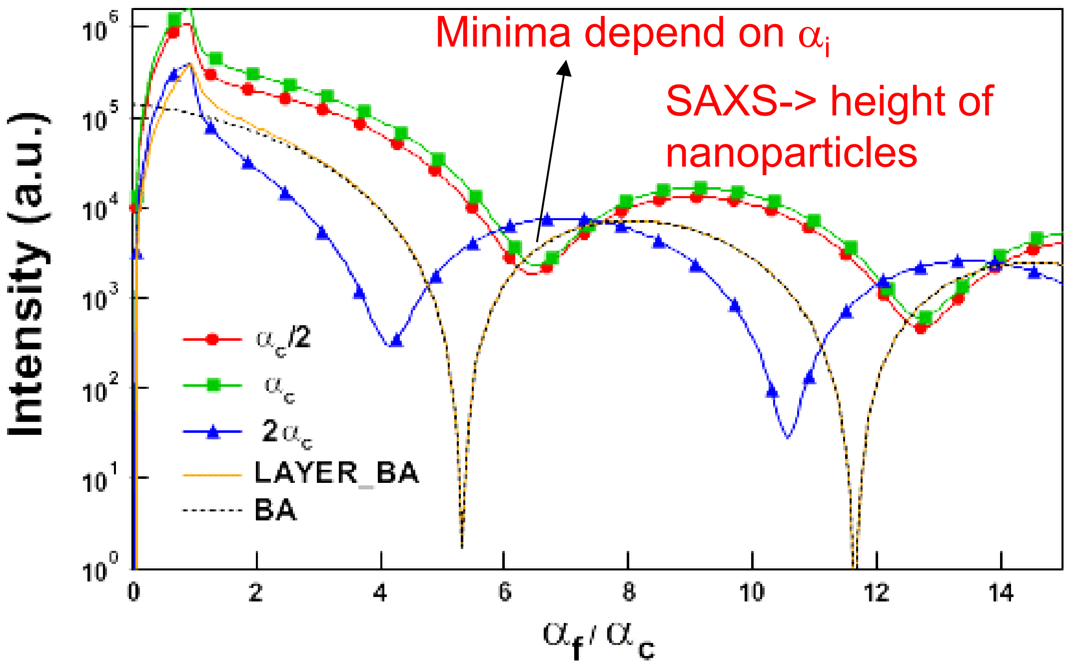
Term 1

Term 2

Term 3

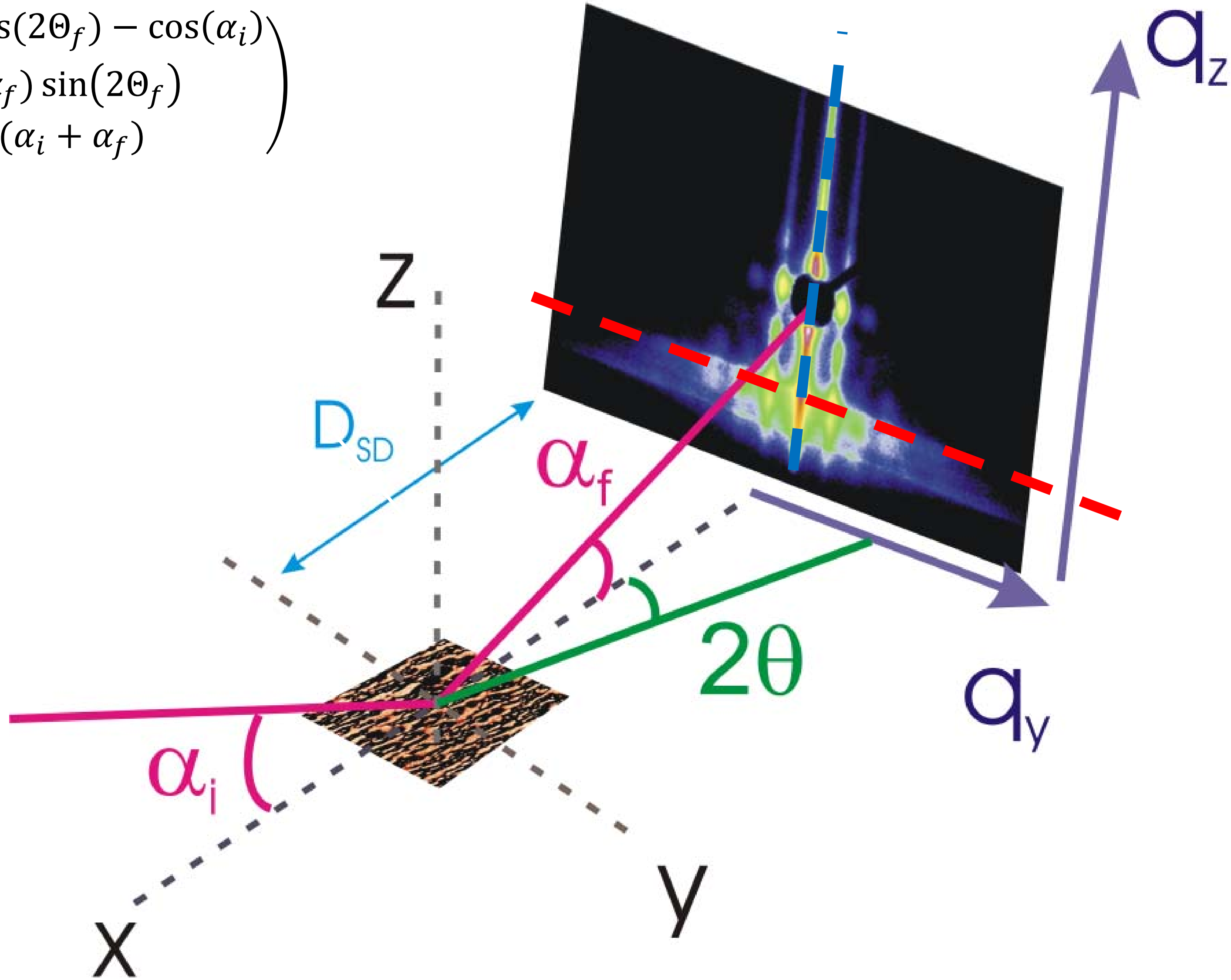
Term 4

Yoneda peak



Grazing incidence small-angle x-ray scattering

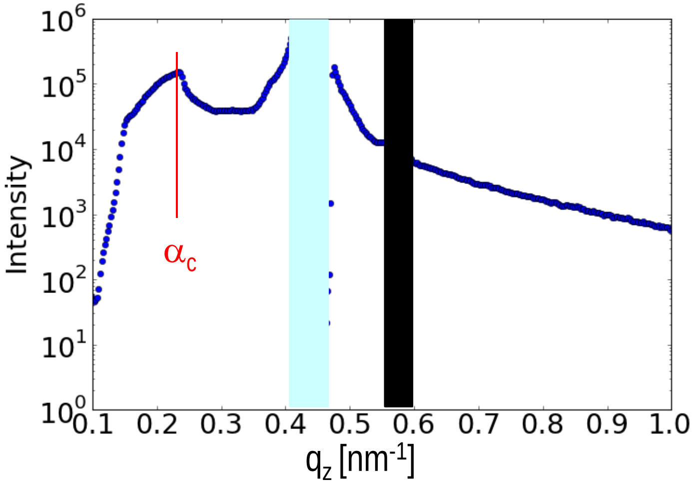
$$\vec{q} = \frac{2\pi}{\lambda}\begin{pmatrix} \cos(\alpha_f)\cos(2\Theta_f) - \cos(\alpha_i) \\ \cos(\alpha_f)\sin(2\Theta_f) \\ \sin(\alpha_i + \alpha_f) \end{pmatrix}$$

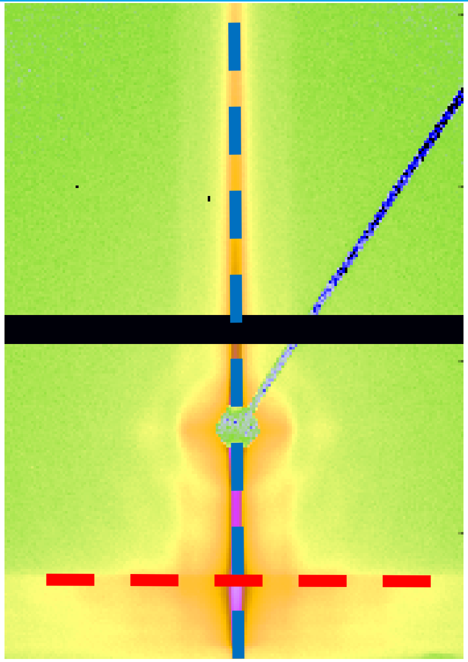


Mueller-Buschbaum, Anal. Bioanal. 376, 3 (2003)

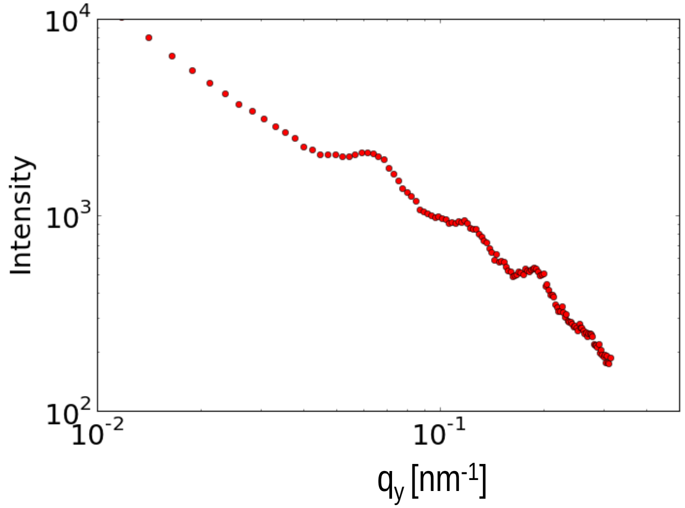
GISAXS – A Primer

cut at constant θ



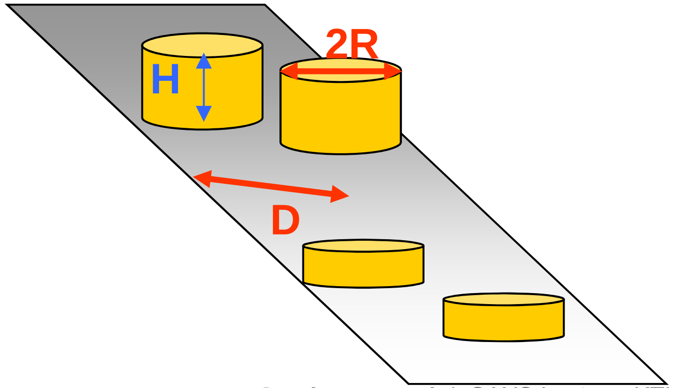


cut at constant α_f



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

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

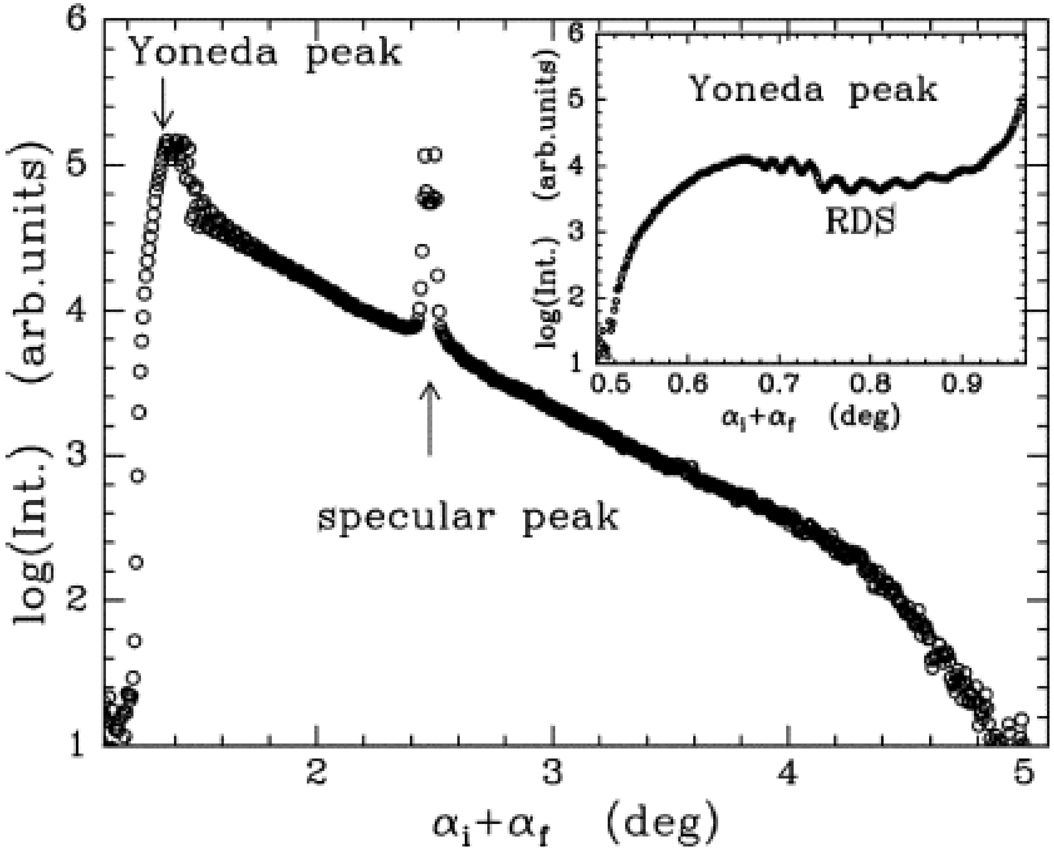


$q_z = 2\pi/\lambda \sin(\alpha_i + \alpha_f)$

$q_y = 2\pi/\lambda \sin(2\theta)\cos(\alpha_f)$

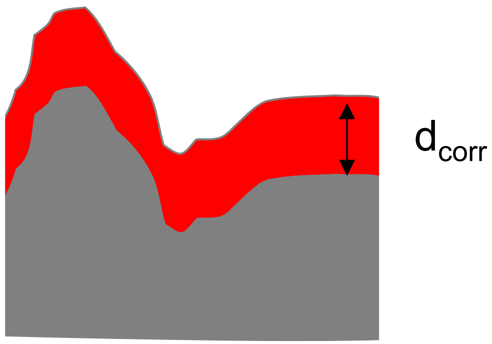
Salditt et al.; Phys.Rev.B **51,** 5617 (1995)
Naudon et al.; Physica B, **283**, 69 (2000)
Renaud et al.; Science, **300**, 1416 (2003)

Resonant diffuse scattering (RDS)

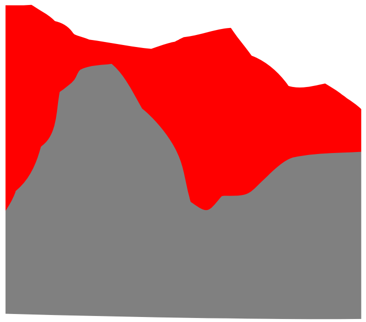


Correlated roughness

$\Delta q_z = 2\pi / d_{corr}$



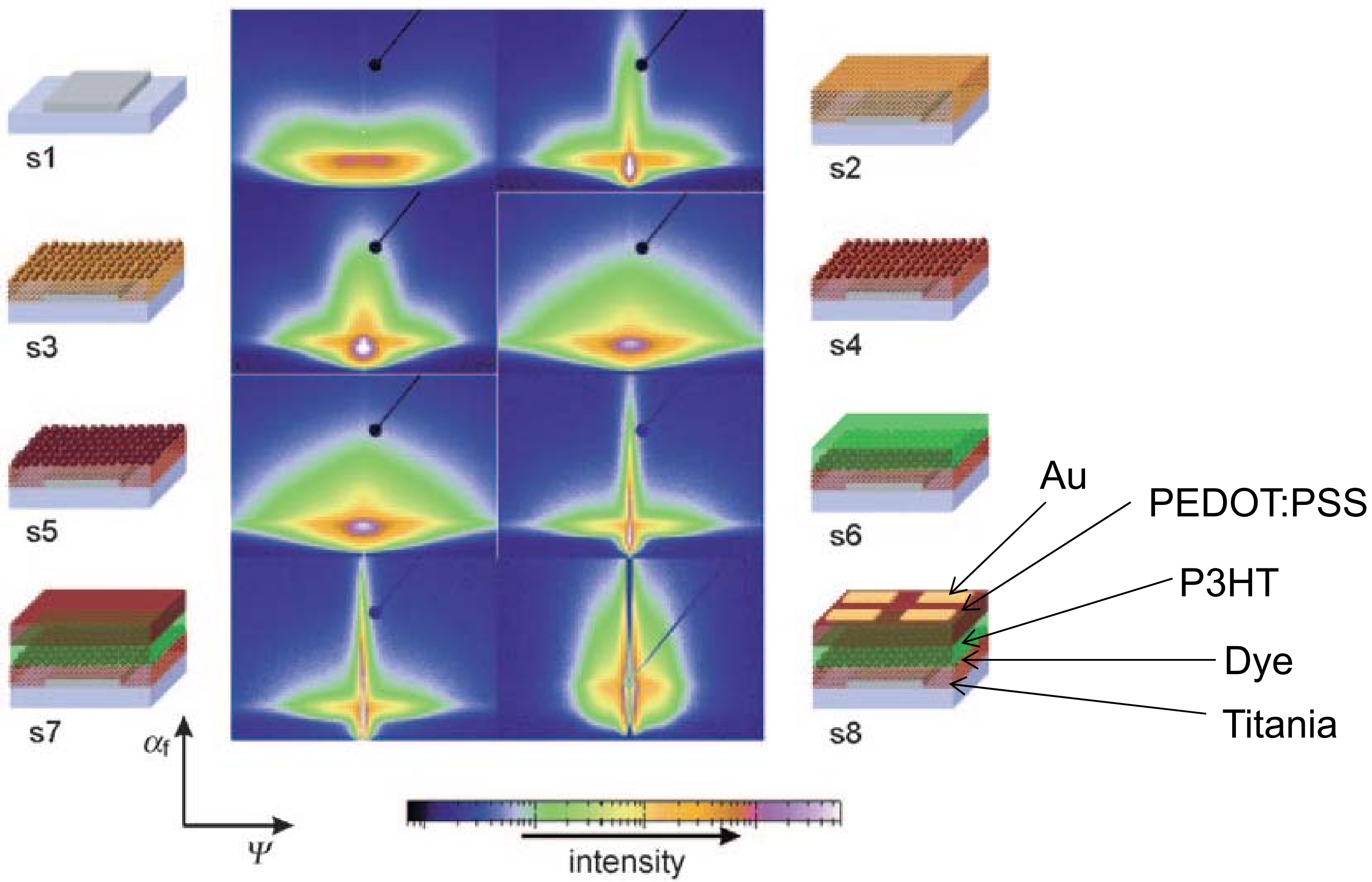
Uncorrelated interfaces



Müller-Buschbaum, Anal Bioanal (2003)

Application of penetration depth

> Preservation of morphology of a self-encapsulated thin titania film



> Self-assembly, dip-, spin-, sputter-, spray-coating, fluidic, vacuum deposition

Perlich, SVR, Müller-Buschbaum et al., ChemPhysChem **10**, 799 (2009)

Outline

- Thin films ➔Grazing incidence SAXS : A Primer
- ➔ Nanostructuring by annealing
- The highest resolution

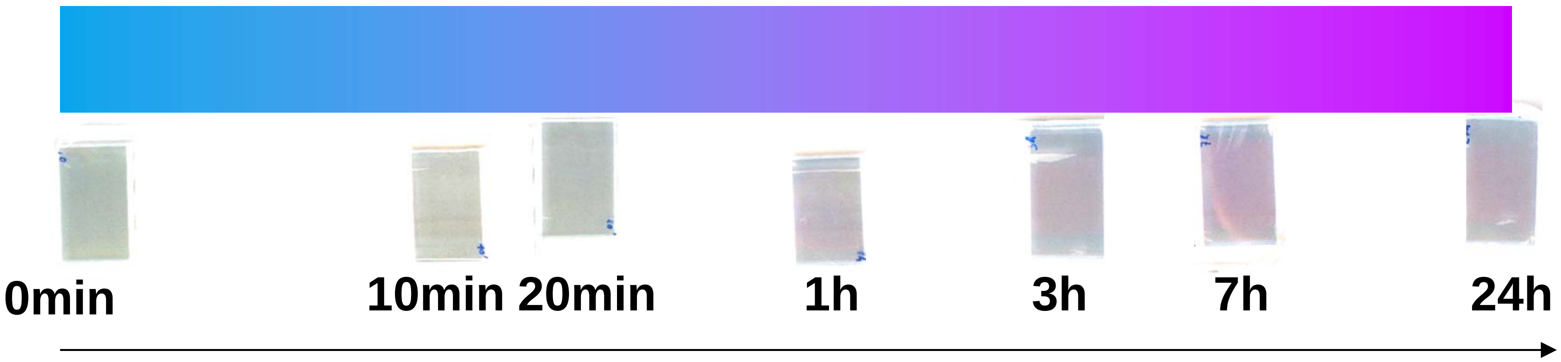
Annealing

> Au on glass

> Parameters:

- Au layer mass thickness: **3nm , 5nm, 8nm**
- **Annealing time**

approaching critical coalescence thickness
(cluster -> metal character)

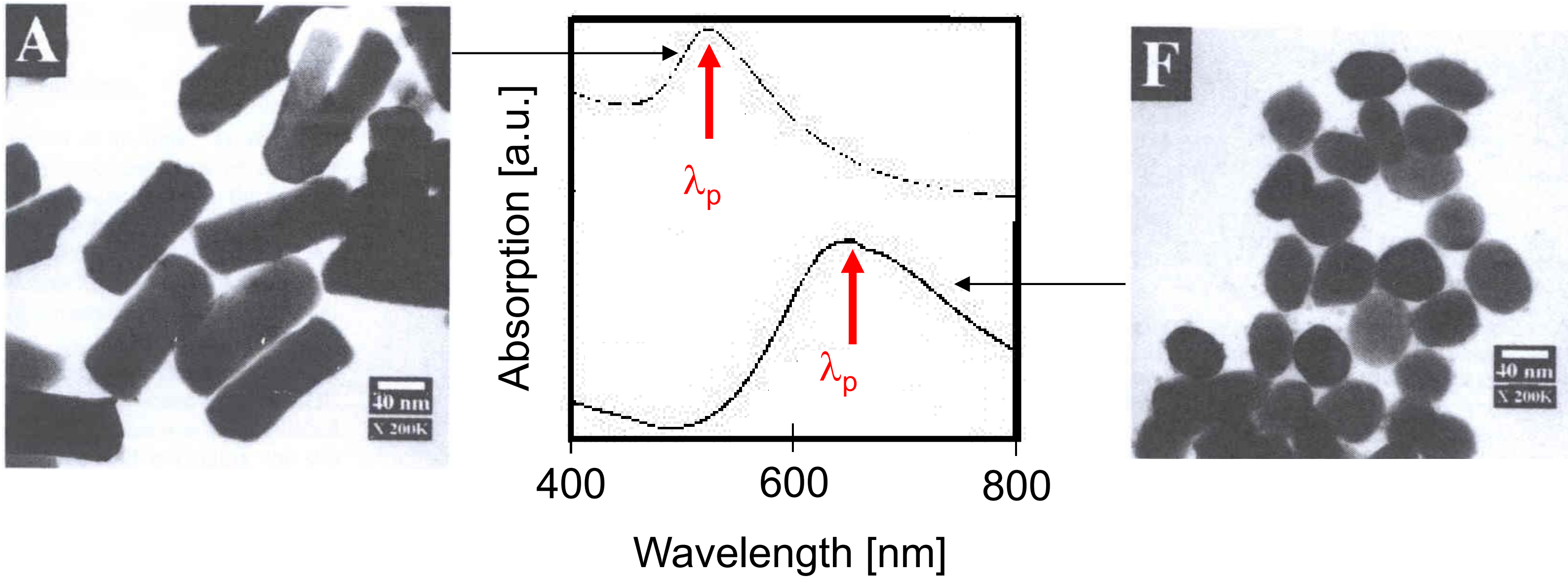


Log (Annealing time)
@ T_{anneal}=300°C < 1064°C (bulk melting point)

Plasmon resonance

Optical properties: sharp resonances ↔ plasmon resonances

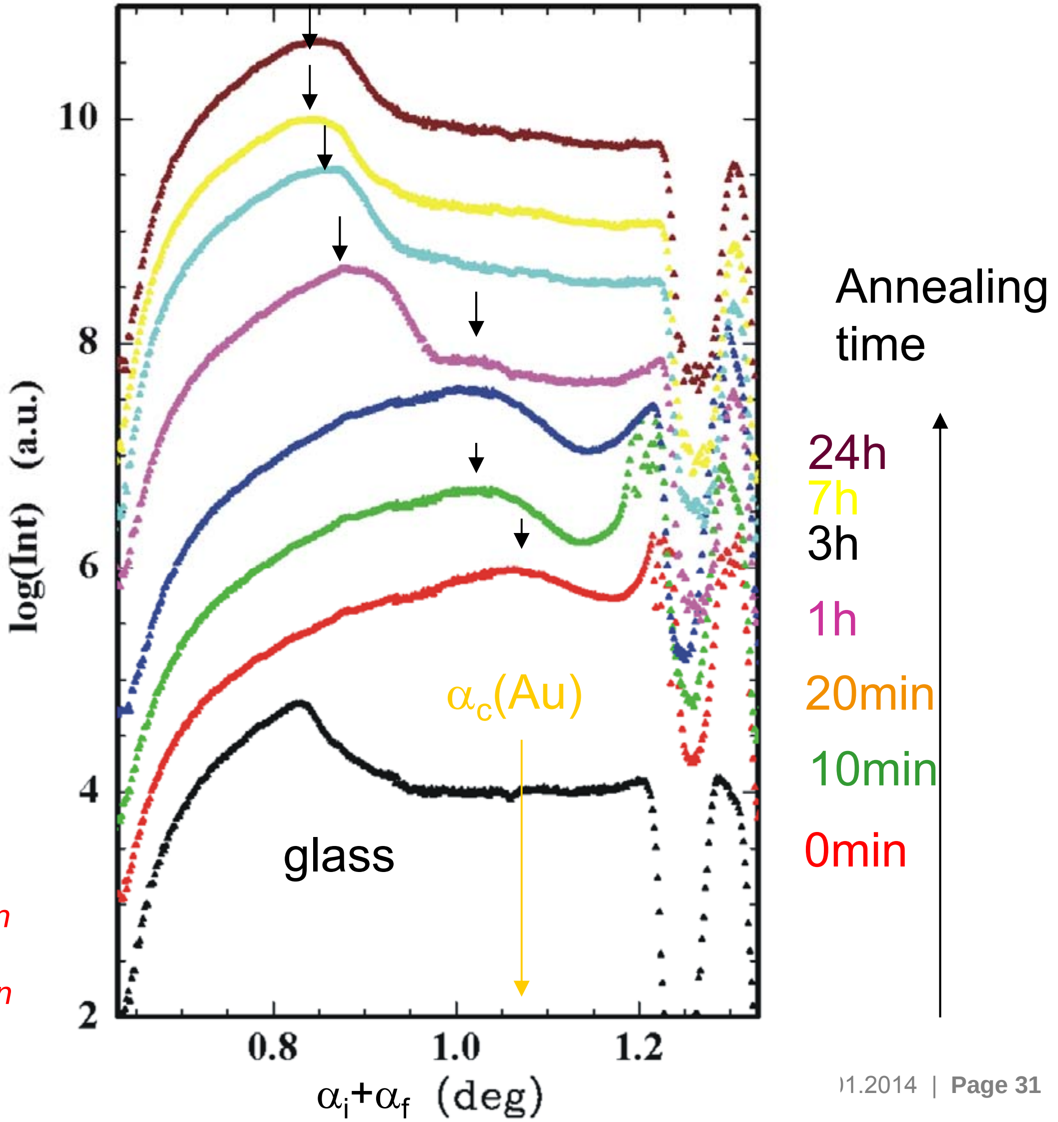
(visible light) cluster arrangement & shape



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

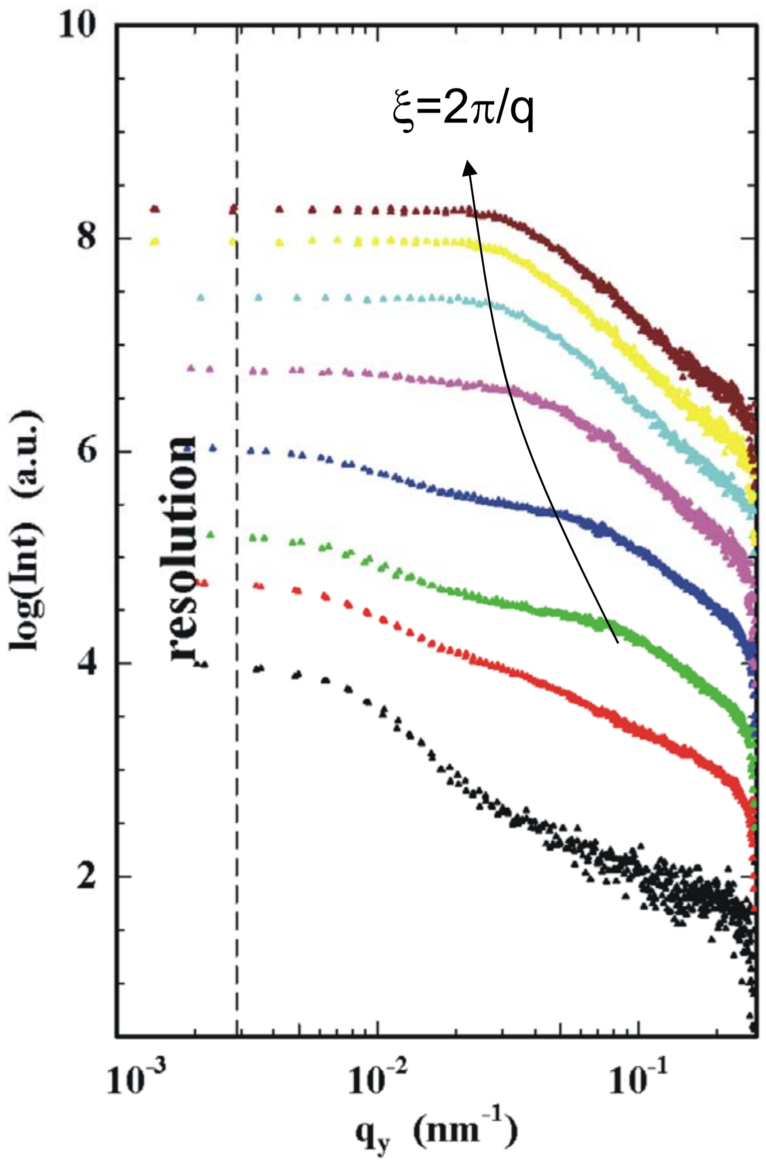
Surface coverage

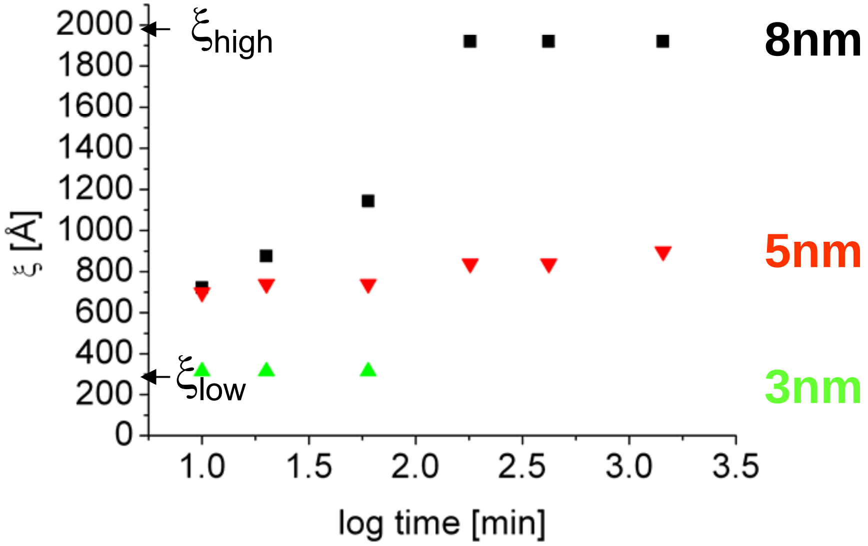
> Thickness Au 8nm

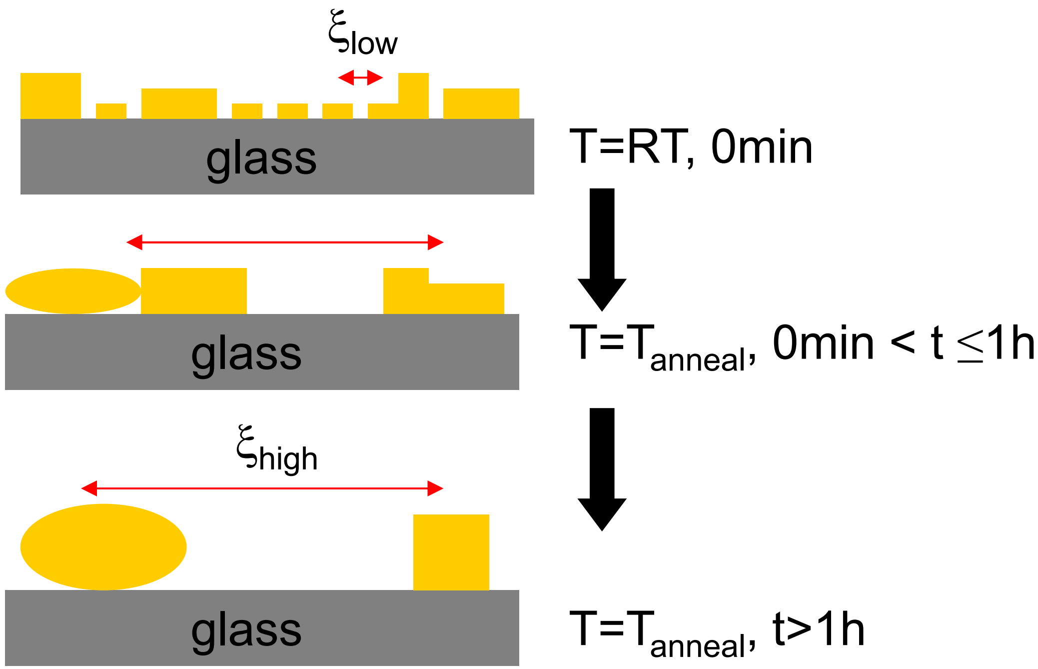


Roth et al., "*Gold nanoparticle thin films on glass: Influence of film thickness and annealing time*", in: "*Synchrotron Radiation and Structural Proteomics*", Pan Stanford Series on Nanobiotechnology - Volume 2, Eds.: E. Pechkova and C. Riekel (2010)

Cluster distance





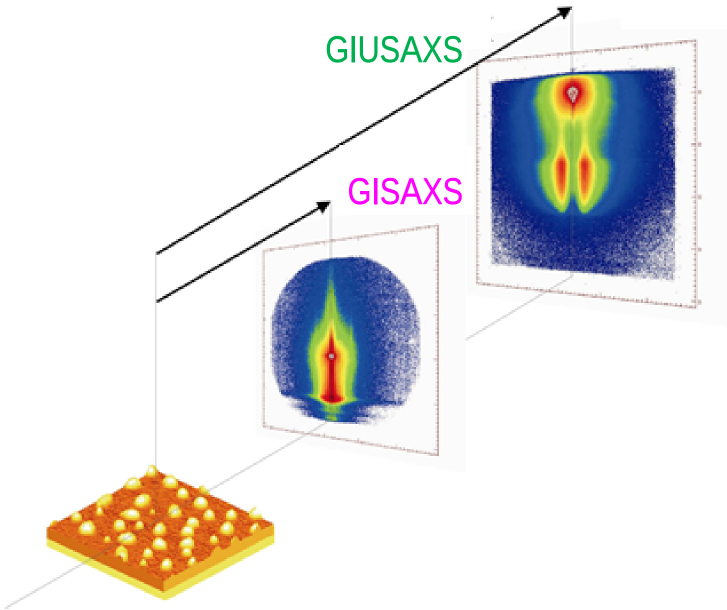


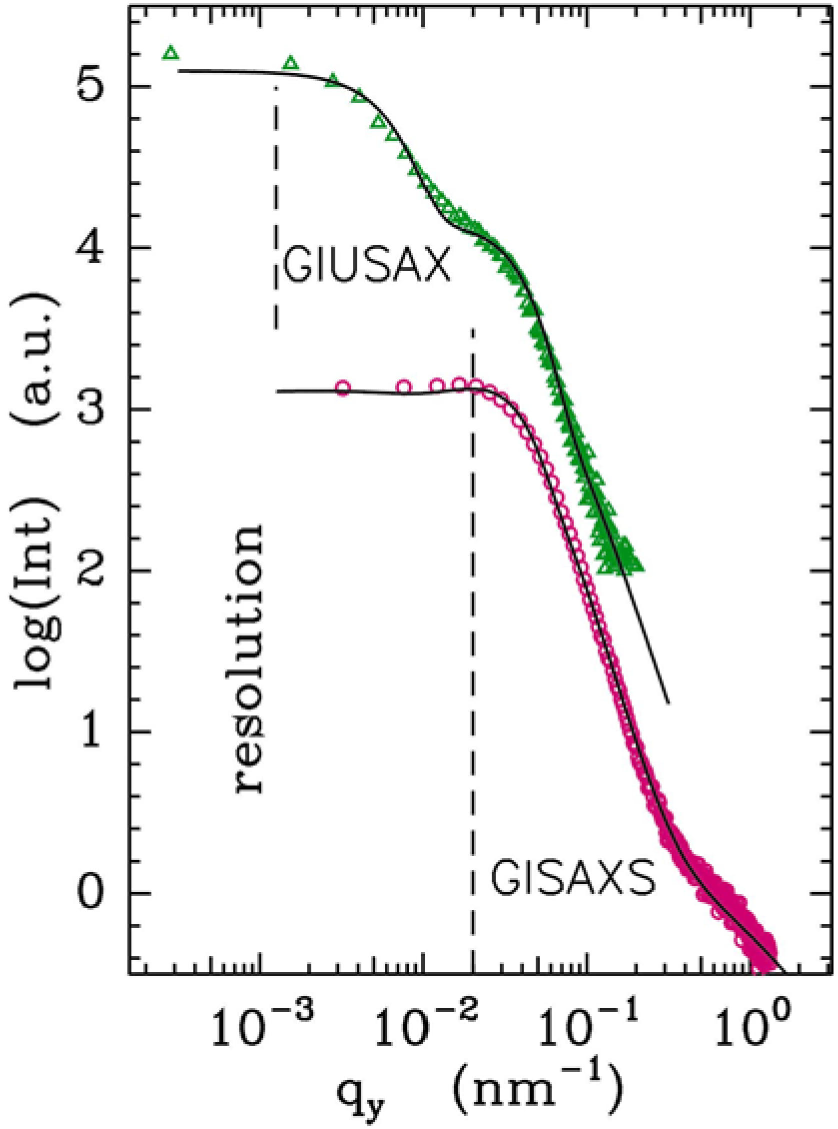
GISAXS and GIUSAXS

> Combination of GIUSAXS and GISAXS experiment at same ai

> GIUSAXS SDD = 12.8m

> GSAXS SDD=1.9m





Data: Courtesy by P. Müller-Buschbaum, TUM

Outline

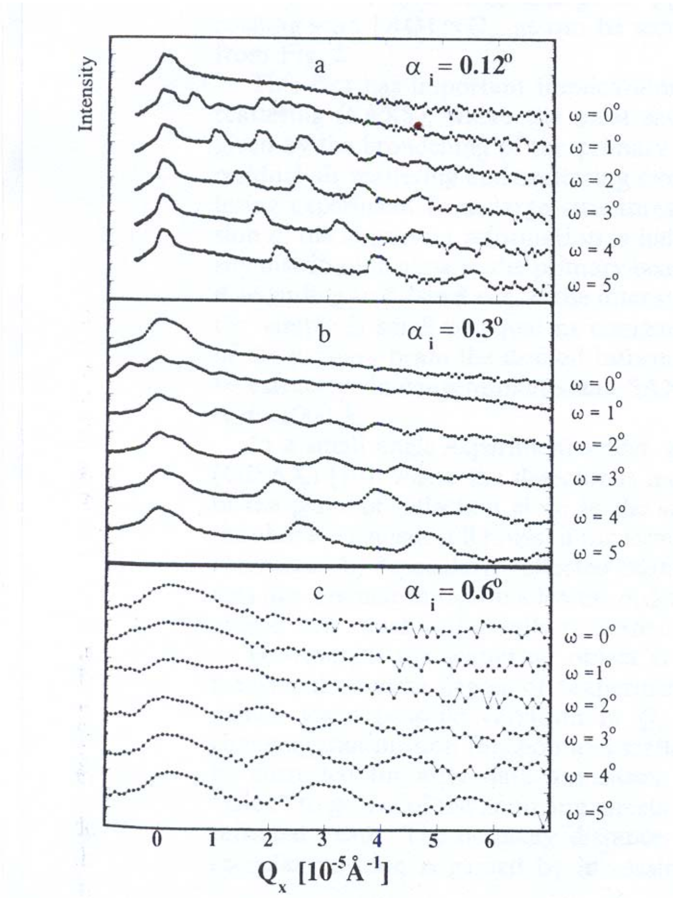
> Thin films ➔Grazing incidence SAXS : A Primer

> Nanostructuring by annealing

➡ The highest resolution

The highest resolution…

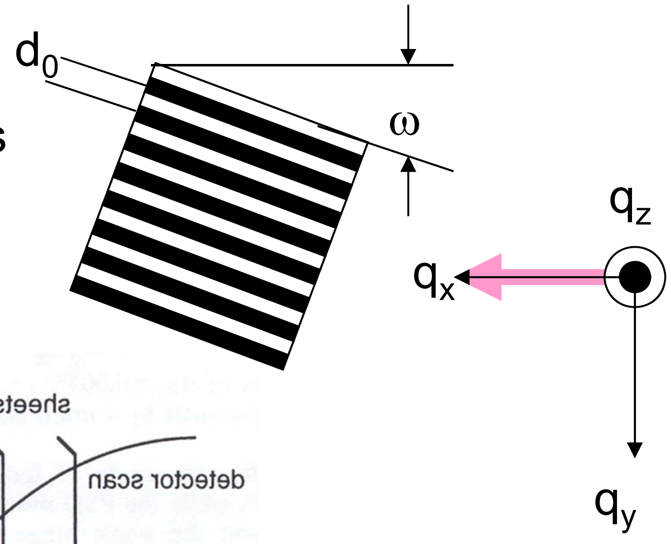
Following Salditt et al., Z. Phys. B **96** (1994) 227: Use grids!

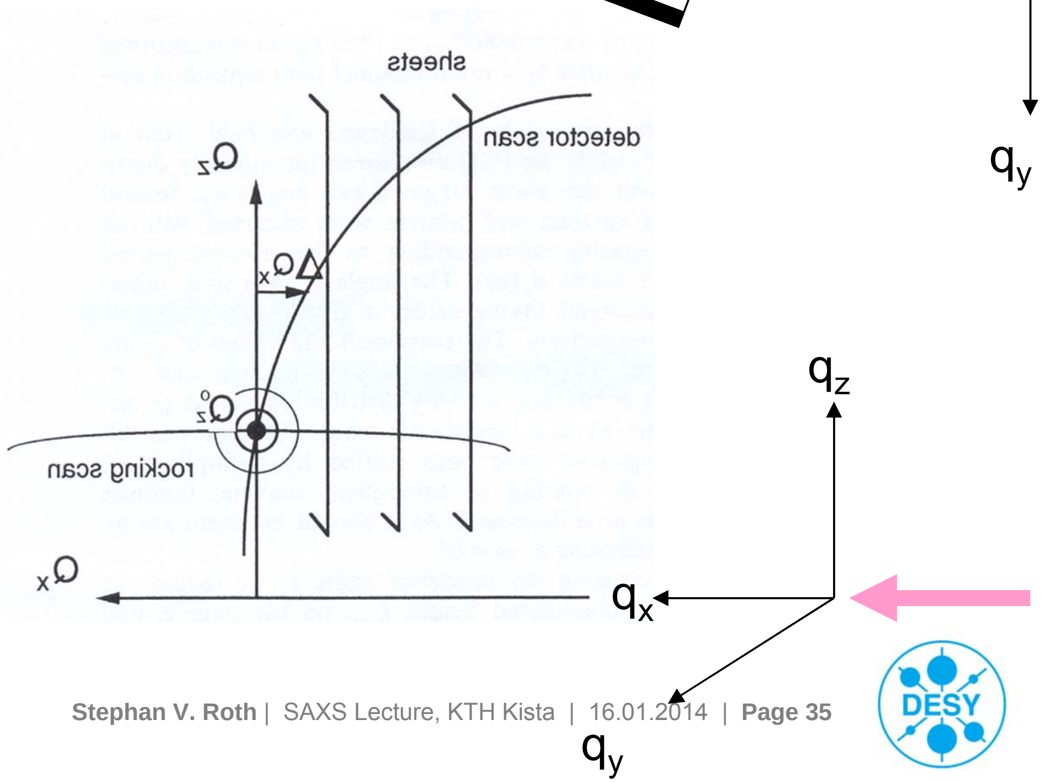


Adjacent orders

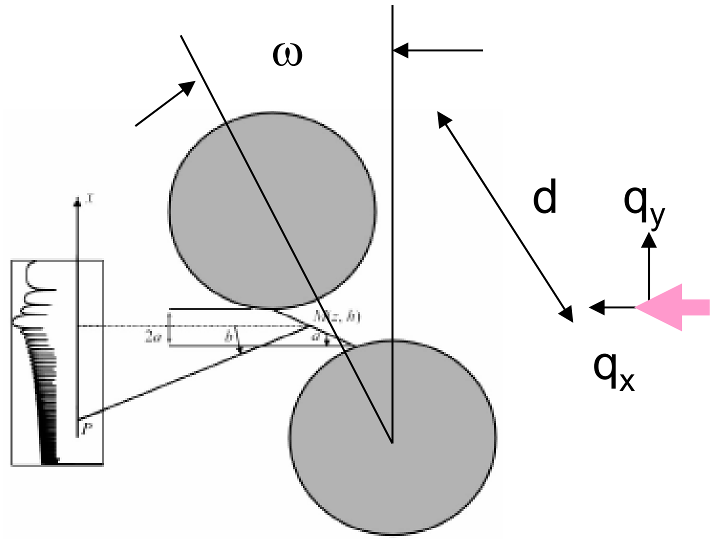
$2\pi/d = \Delta(q_x) / \omega$

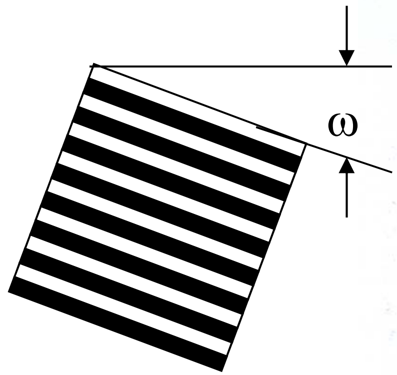
$d = d_0 / \omega$

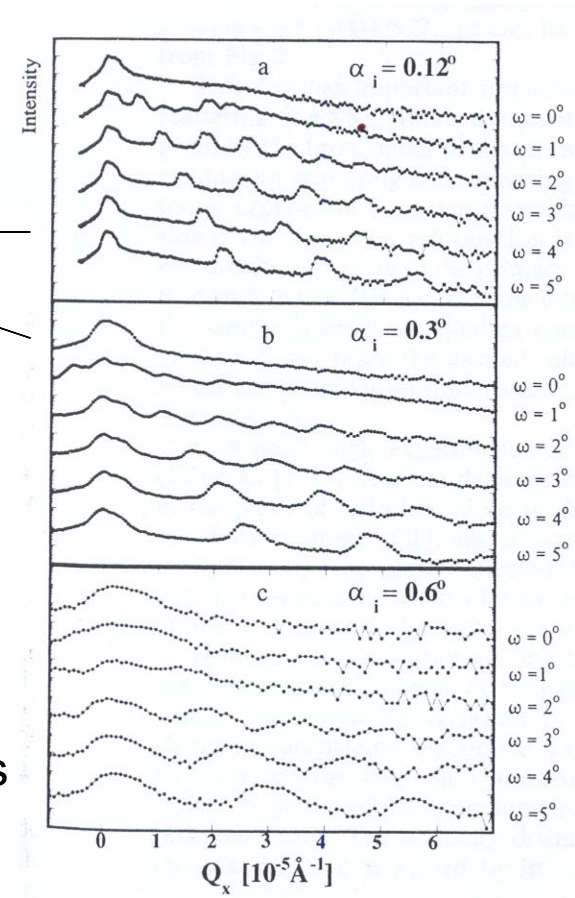




…some analogons…







Zero order

$q_y + 2\pi/\lambda\ 1/2\ \alpha_f^2\ /\ \omega = 0$

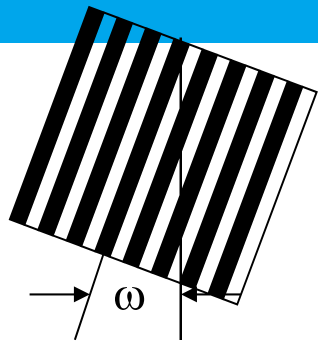
$q_x = 2\pi/\lambda\ (\cos(\alpha_f) - \cos(\alpha_i))$

Adjacent orders

$2\pi/d = \Delta(q_x)\ /\ \omega$

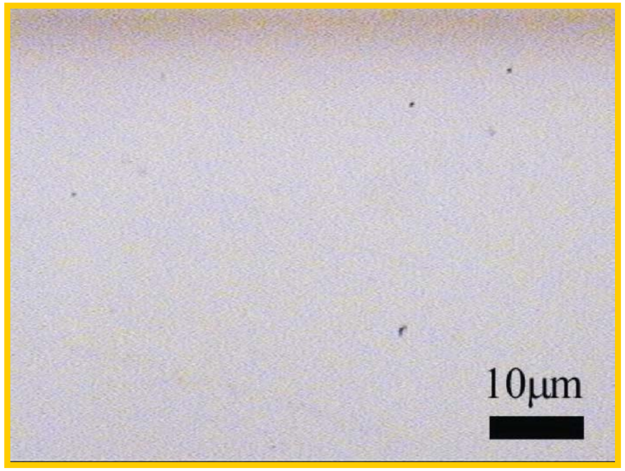
$-q_y + q_x / \tan\omega = 0$

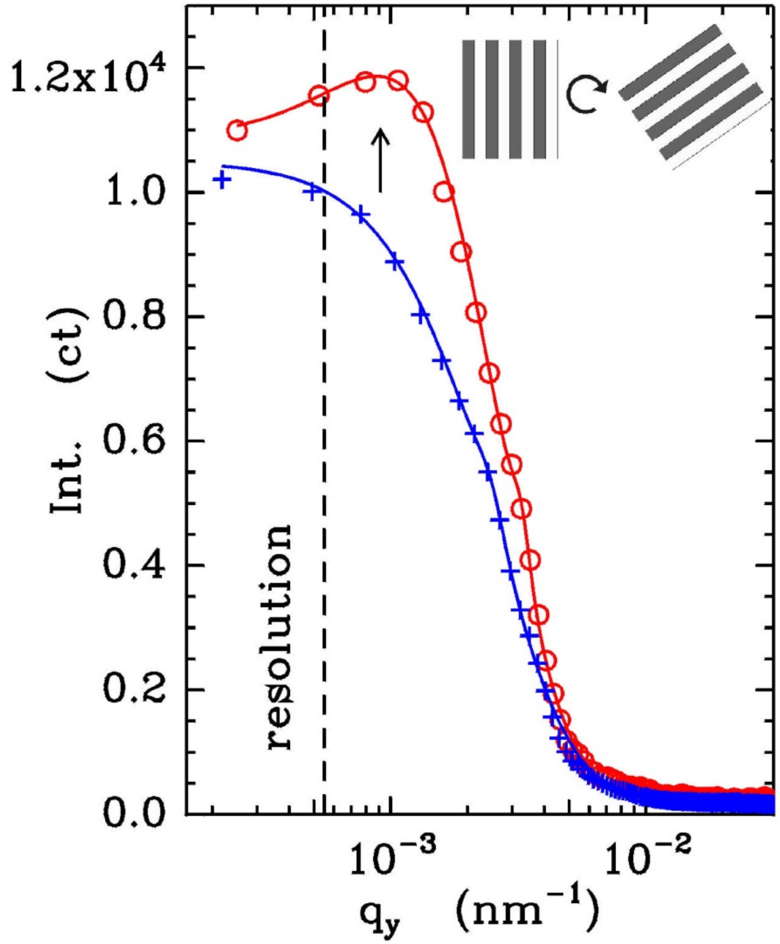
…and at BW4: Polymeric nanochannels

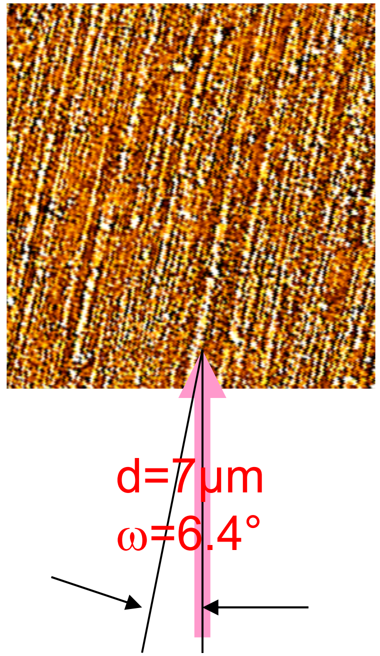


Müller-Buschbaum et al., Appl. Phys. Lett. **88**, 083114 (2006)
HASYLAB – highlight, www.hasylab.desy.de (2006/2007)

Beam size:
B=400x400µm²
λ=1.38Å
L_{SD}=13m
α_i=0°







d=7µm
ω=6.4°