Methoden moderner Röntgenphysik II

Streuung und Abbildung

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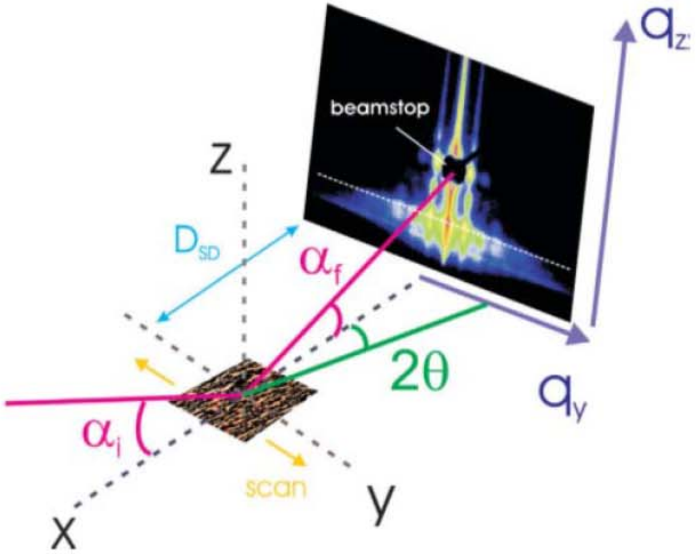
Bachelor-/Masterarbeiten

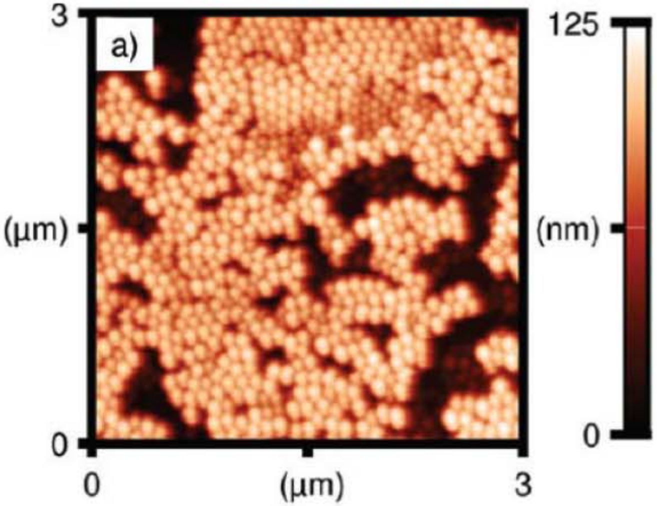
im Bereich Nanowissenschaften und Materialien für

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

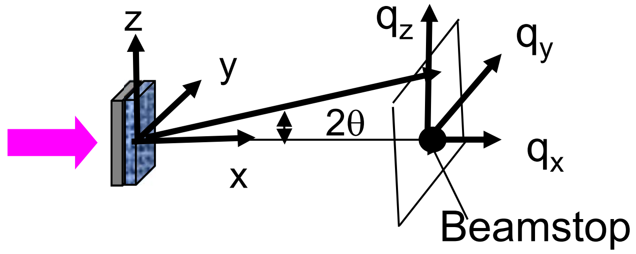


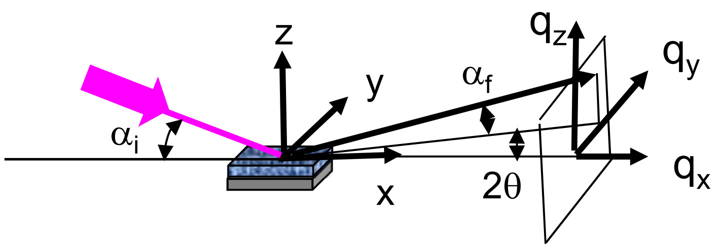


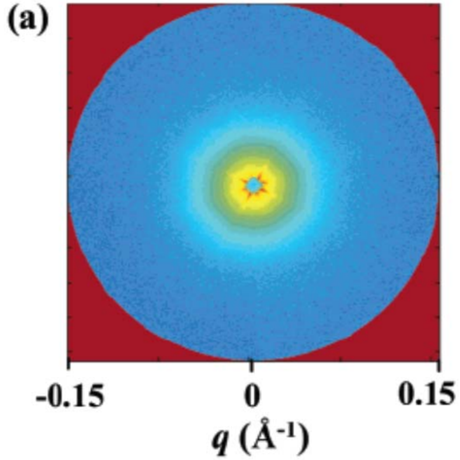
Outline

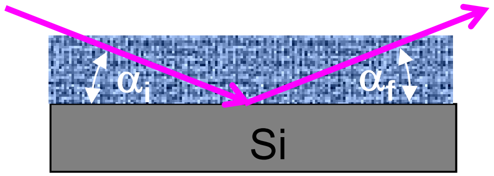
- ➔ Thin films ➔Grazing incidence SAXS : A Primer
- > Nanostructuring by annealing
- > The highest resolution

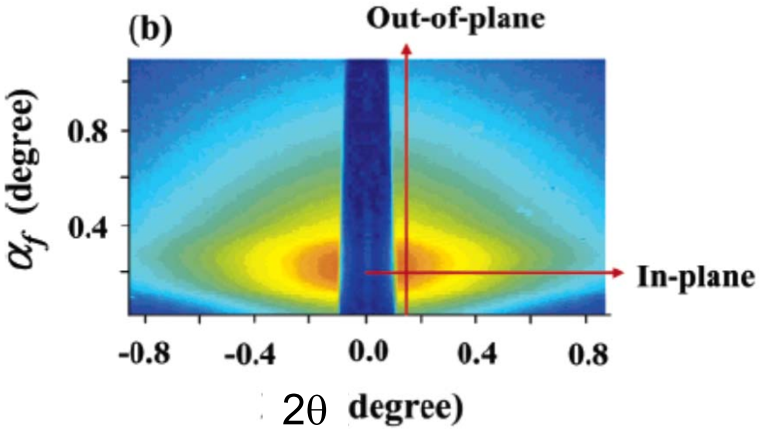
T-SAXS vs. GISAXS









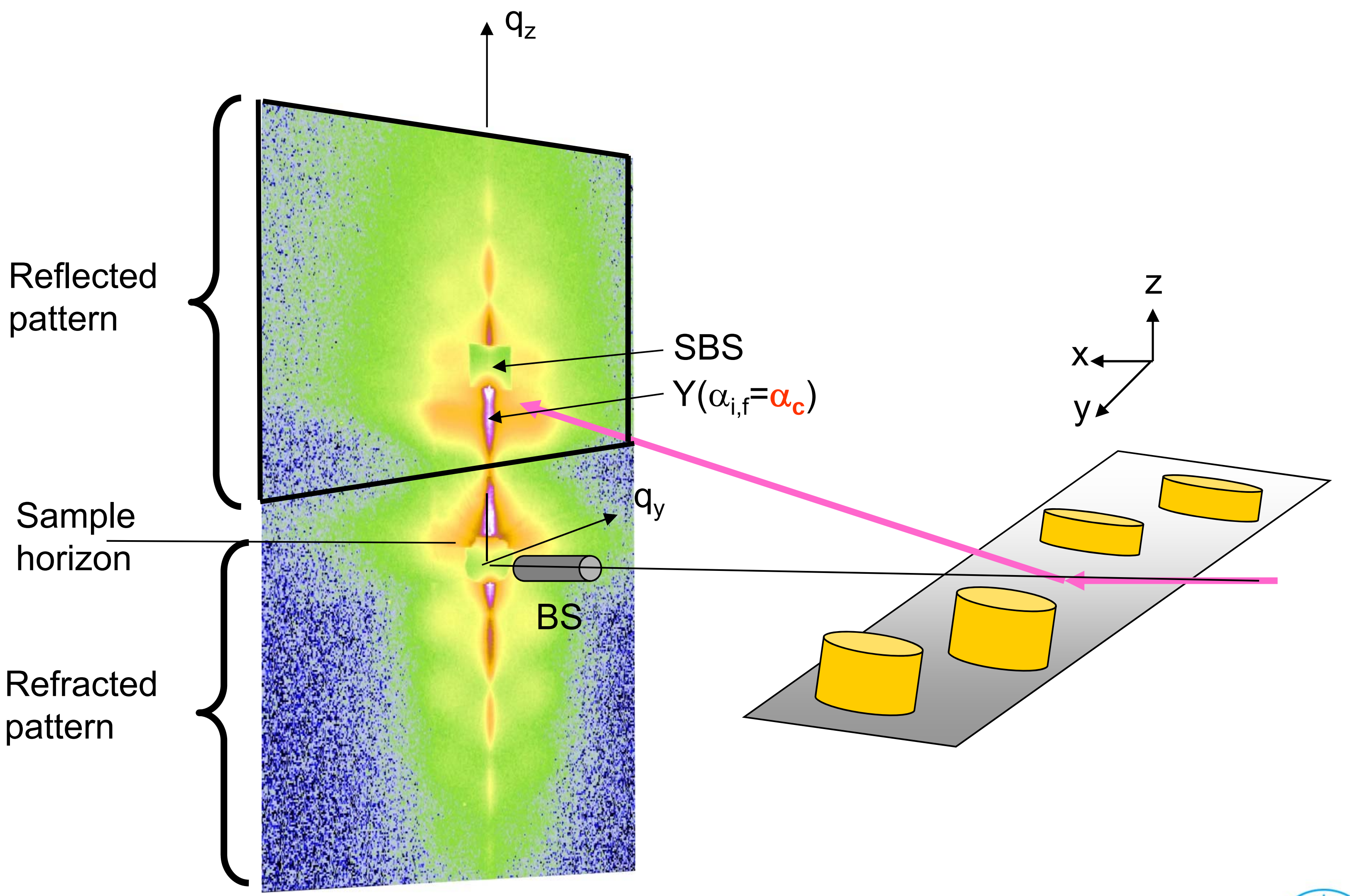


- Easy measurement
- Easy analysis
- In-plane information (q_y,q_z)
- Any possible scattering from substrate
- Transparency of substrate
- High energy

- 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)

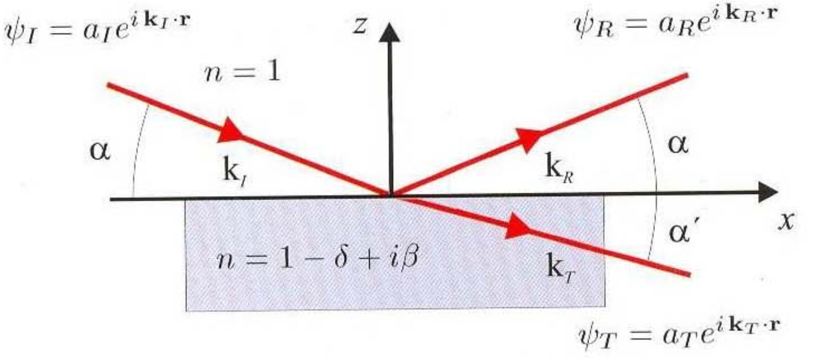
Lee et al., Macromolecules, 38, 8991 (2005)

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:

$$\boxed{\begin{aligned} a_I + a_R &= a_T && \text{(A)} \\ a_I\mathbf{k}_I + a_R\mathbf{k}_R &= a_T\mathbf{k}_T && \text{(B)} \end{aligned}}$$

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

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

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

<u>α, α' small:</u> ($\cos z=1-z^2/2$)

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

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

<u>Fresnel equations:</u>

$$\boxed{\begin{aligned} r &= a_R/a_I = (\alpha - \alpha')\,/\,(\alpha + \alpha') \\ t &= a_T/a_I = 2\alpha\,/\,(\alpha + \alpha') \end{aligned}}$$

r: reflectivity t: transmittivity

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

Note: α' is a complex number

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

Consider z-component of transmitted wave:

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

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

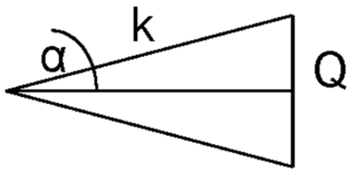
exponential damping

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

1/e penetration depth Λ: $z\,2k\,\mathrm{Im}(\alpha') = 1 \quad (z = \Lambda)$

$$\boxed{\Lambda = 1 / 2k\,\mathrm{Im}(\alpha')}$$

use wavevector notation:



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

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

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

use dimensionless units:

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

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

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

$b_u = (2k/Q_c)\text{ß} = (4k^2/Q_c^2)\mu/2k = 2k\mu/Q_c^2$

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

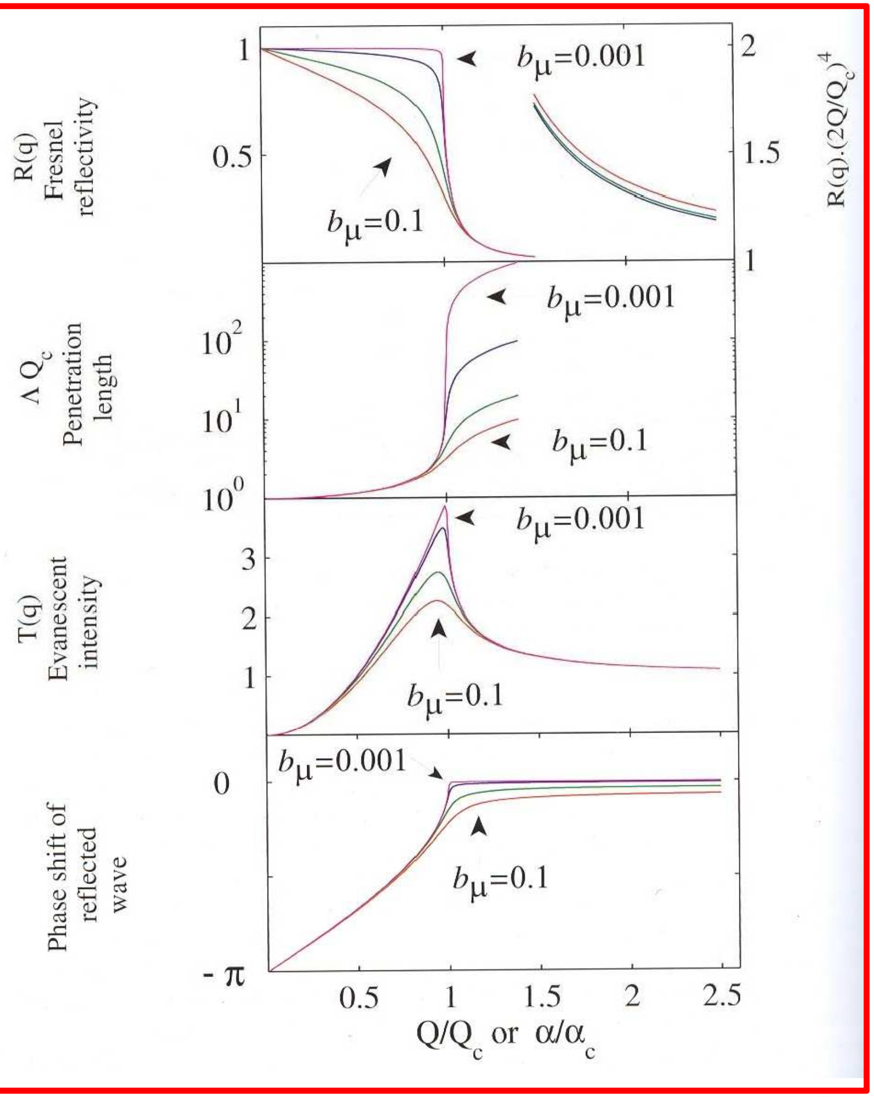
Snell‘s law and the Fresnel equations (4) (see 10.4.2014)

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

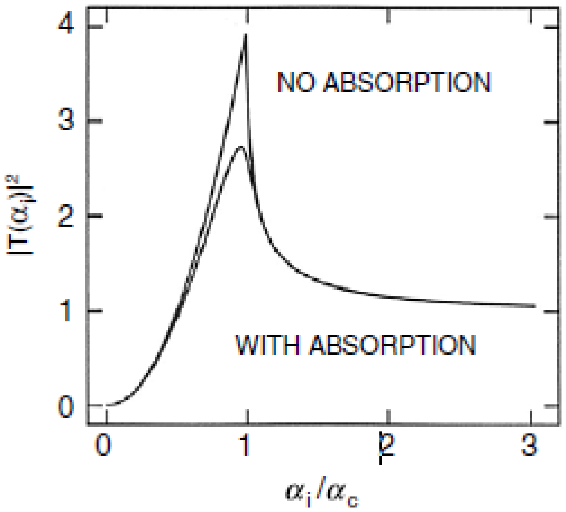


(Als-Nielsen)

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

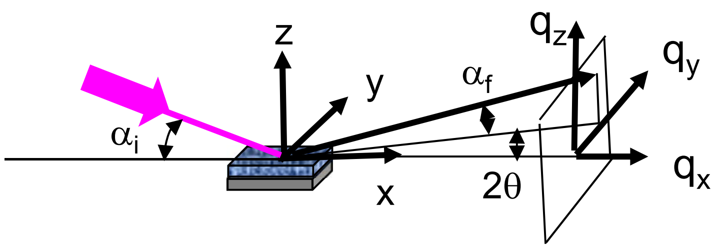


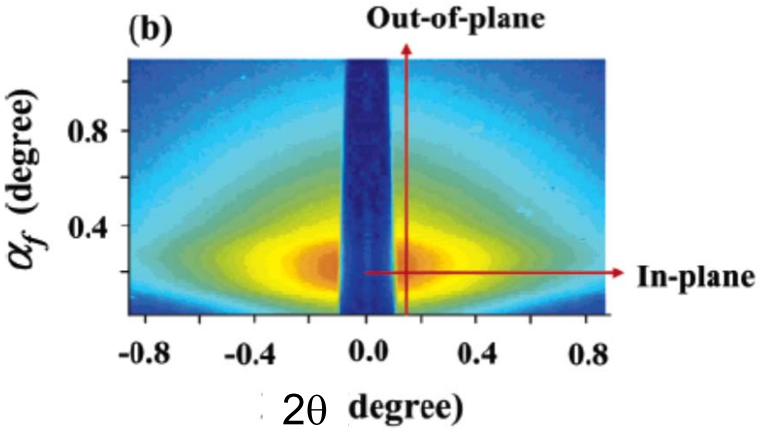
Renaud et al., Surf. Sci. Rep. **64**, 255 (2009)

GISAXS: Tuning of penetration depth

> Scattering depth:

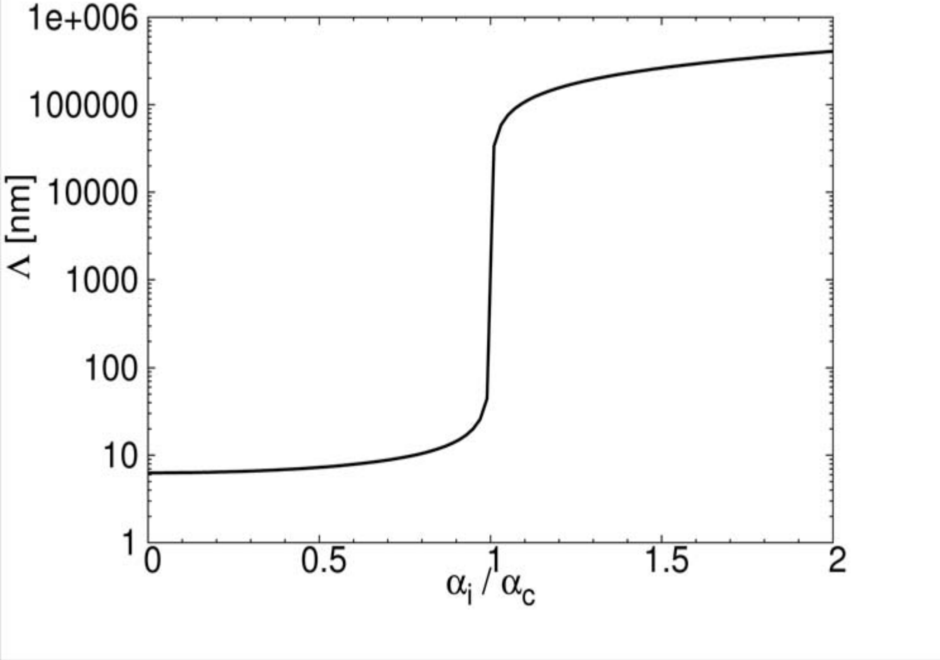
$$\Lambda = \frac{\lambda}{\sqrt{2}\pi} * \frac{1}{\sqrt{\sqrt{({\alpha_i}^2 - {\alpha_c}^2)^2 + 4\beta^2} - ({\alpha_i}^2 - {\alpha_c}^2)}}$$





> Tune depth sensitivity

> Exercise: energy variation

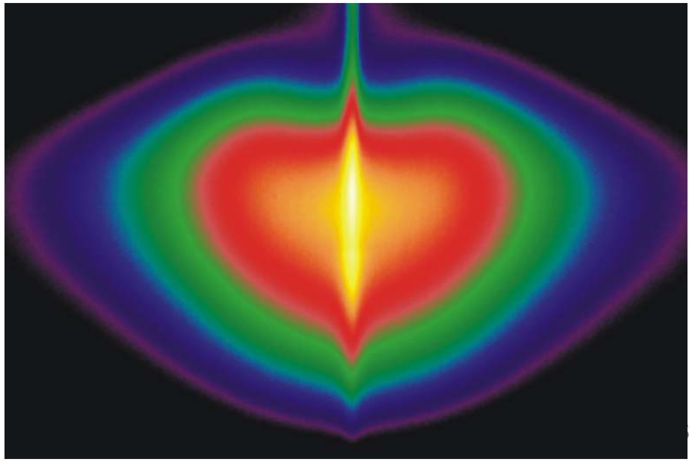


- Strong intensity
- Easy preparation of samples
- Full information (q_x,q_y,q_z)
- Scattering from surface / internal structure
- Scattering from reflected AND transmitted beam
- Refraction effects (DWBA)

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)

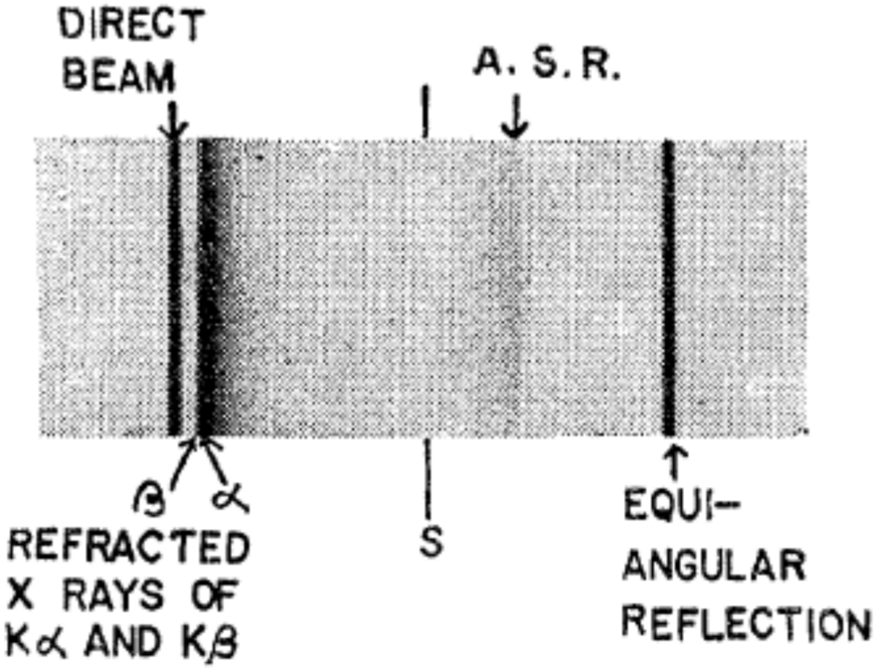


FIG. 2. Photograph of A.S.R. by a glass sample, ×2.

The first sucessful experiment

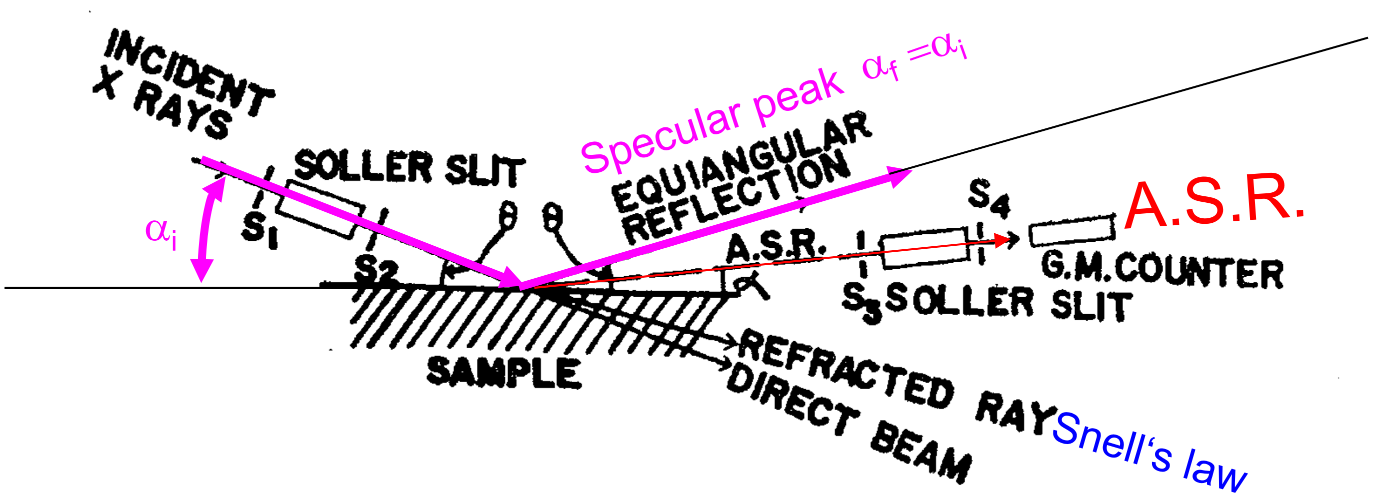


FIG. 1. Schematic view of the experimental arrangement in the incident plane.

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

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

Critical angle

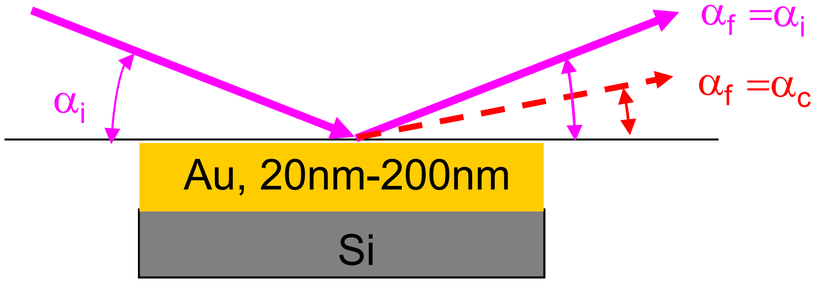
α_c(Si)=0.2°
α_c(Au)=0.5°

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

Very small!

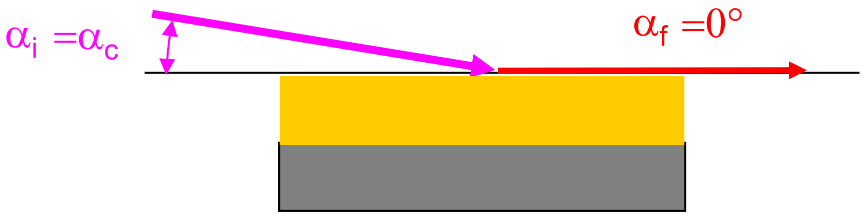
Matter: |n(X-rays)|<1 optically less dense than vacuum (remember Bragg's law)

Origin of intensity at α_c

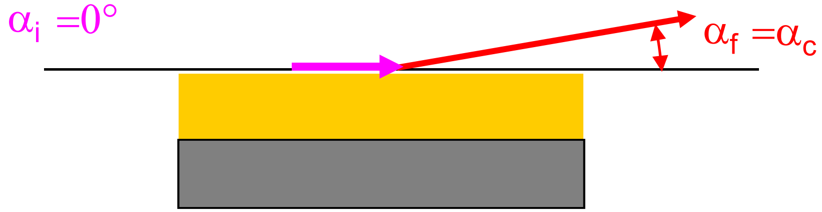


$\alpha_f(Au) = 0.56° = \alpha_c(Au,1.8Å)$

Total external reflection

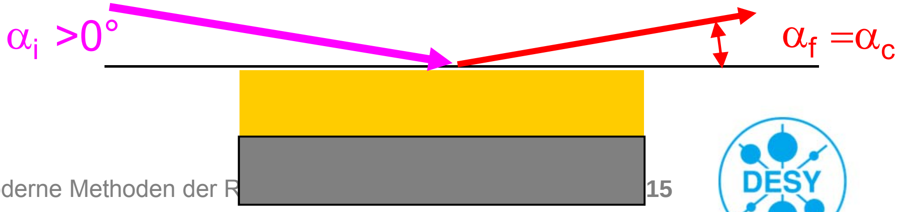


Reciprocity theorem & critical angle



must stem from wave parallel to surface

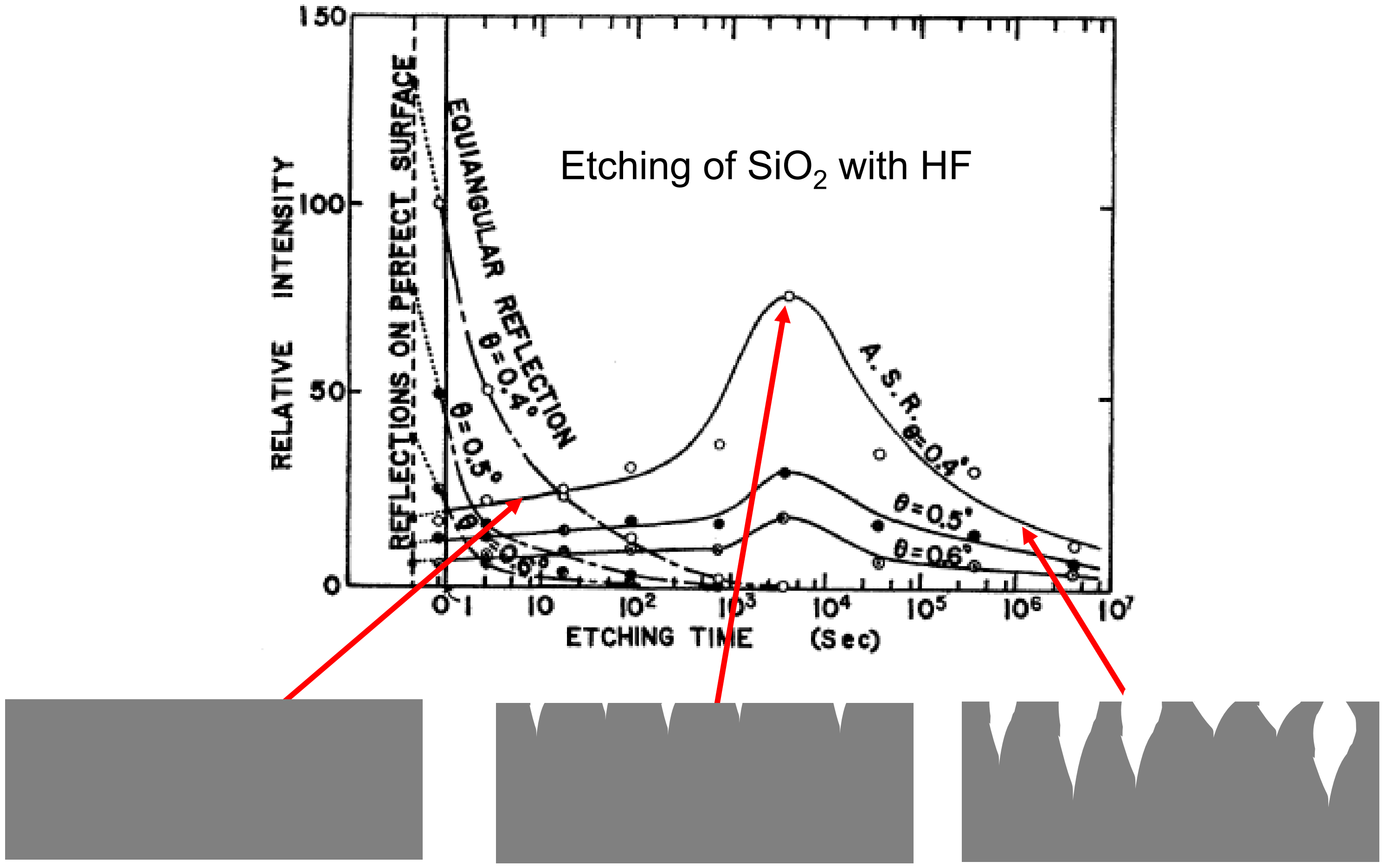
Yoneda



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

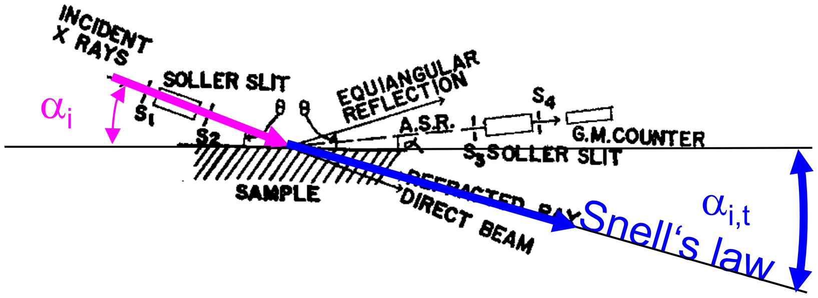
Hint: Roughness of the sample

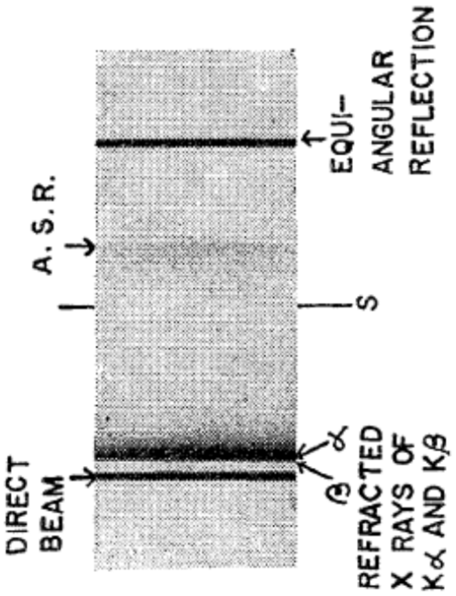
Yoneda peak = Scattering effect!


Etching of SiO_2 with HF

Basically the same

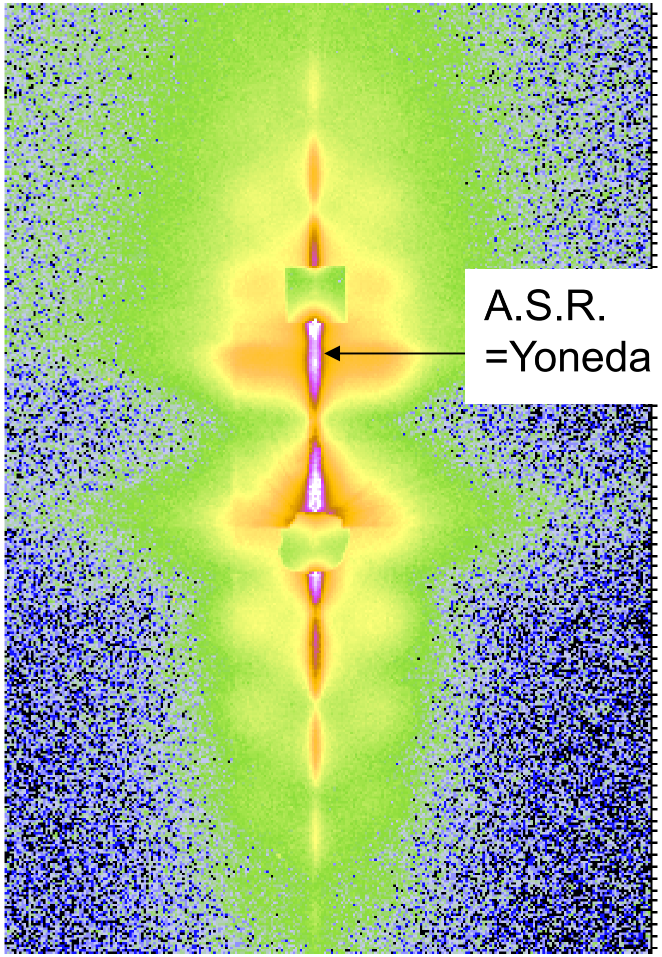
1963





$\alpha_i=\alpha_f$
Specular peak

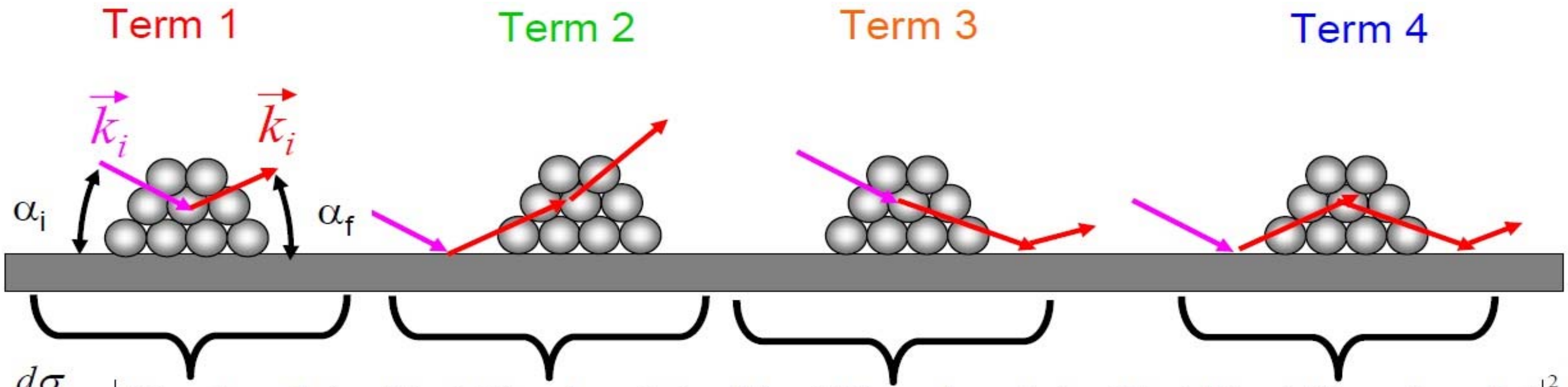
today



A.S.R.
=Yoneda peak

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

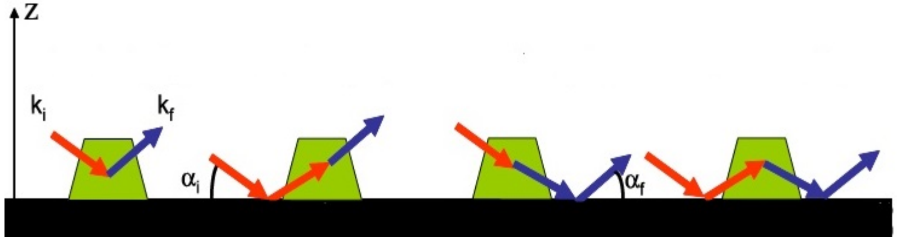
- coherent interference between four waves along $\boldsymbol{\alpha_f}$
- each term weighted with the Fresnel coefficients
- cross section just depends on $\boldsymbol{q_y}$ and $\boldsymbol{q_z}$

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

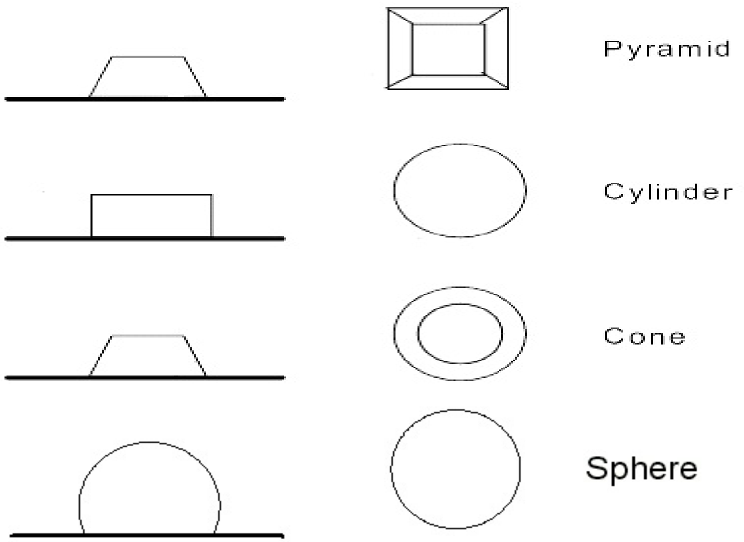
Theory - Simulation

- 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

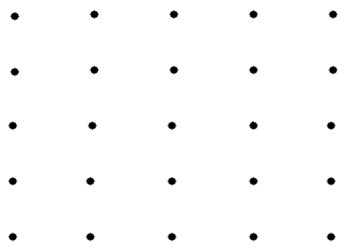


Interference function

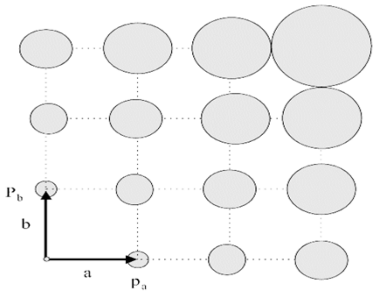
Three main cases

1) Disordered lattice
   - pair correlation function

2) Regular bidimensional lattice



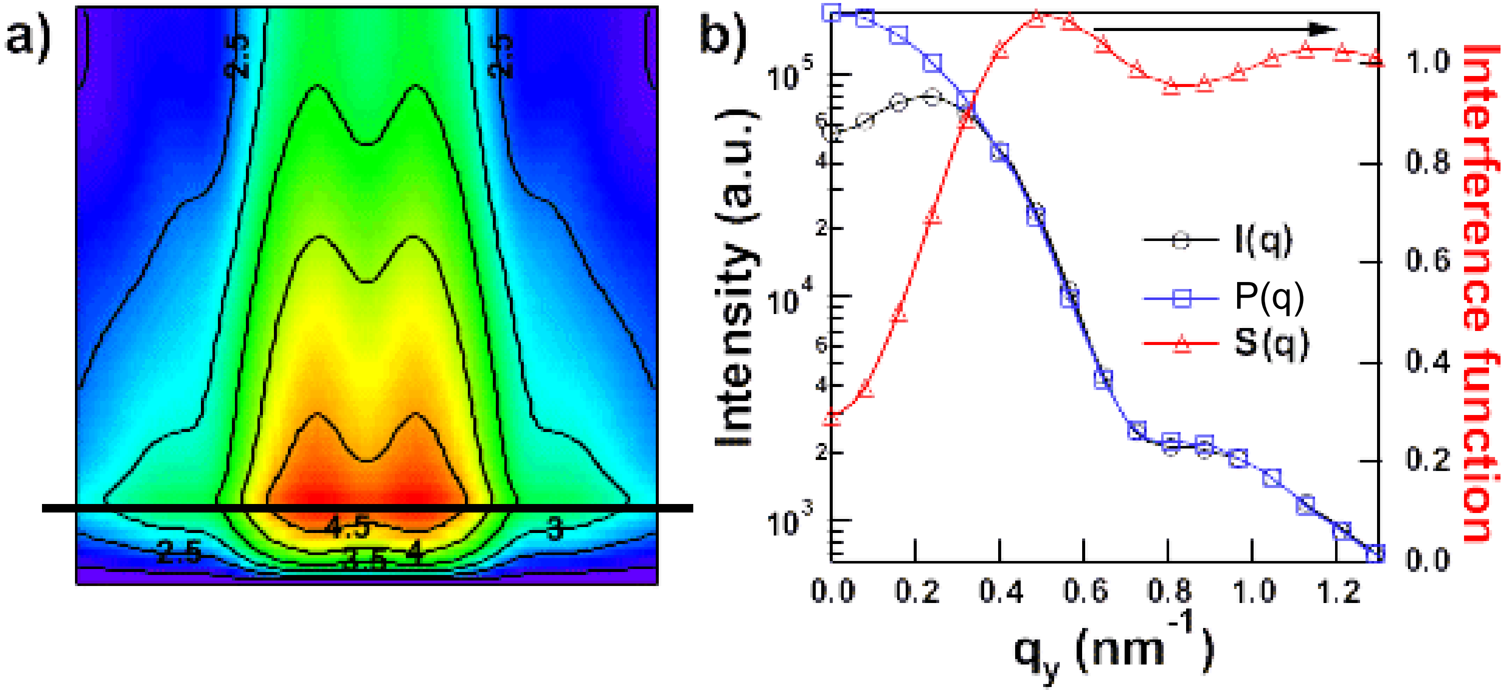
3) Bidimensional paracrystal



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

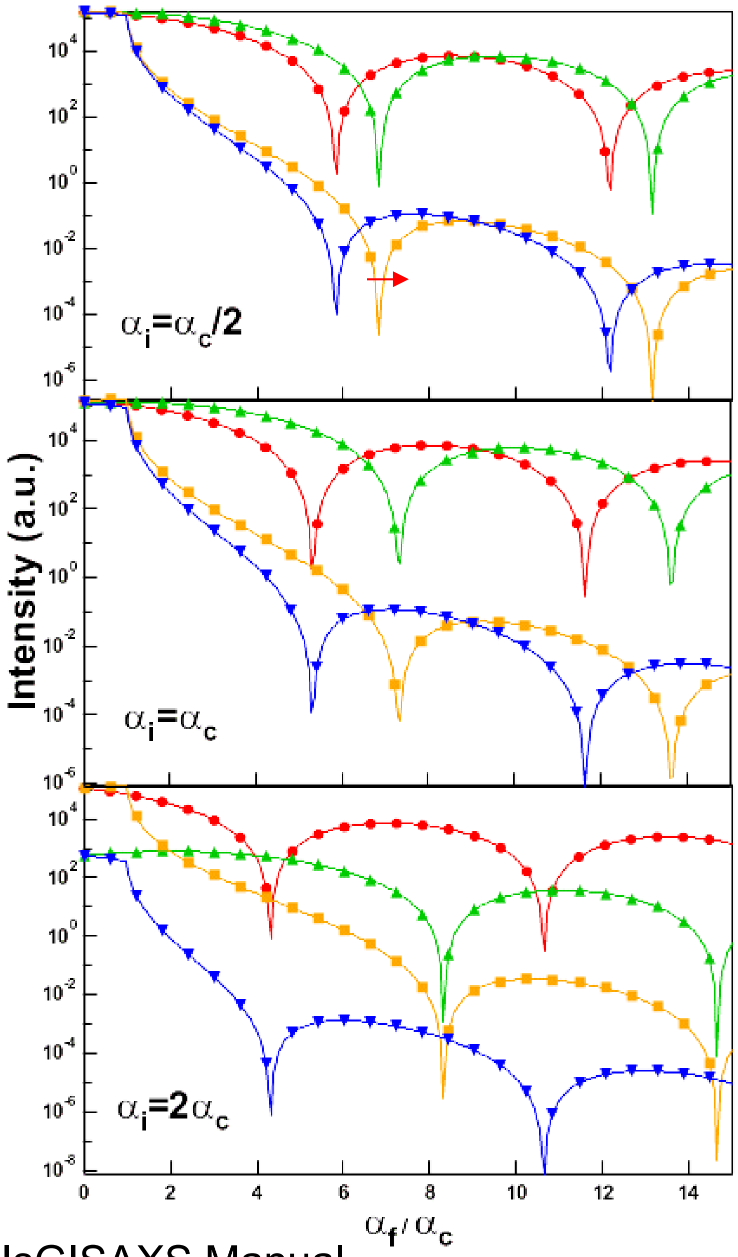
Simulations: IsGISAXS (R. Lazzari)

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



IsGISAXS Manual

DWBA – results



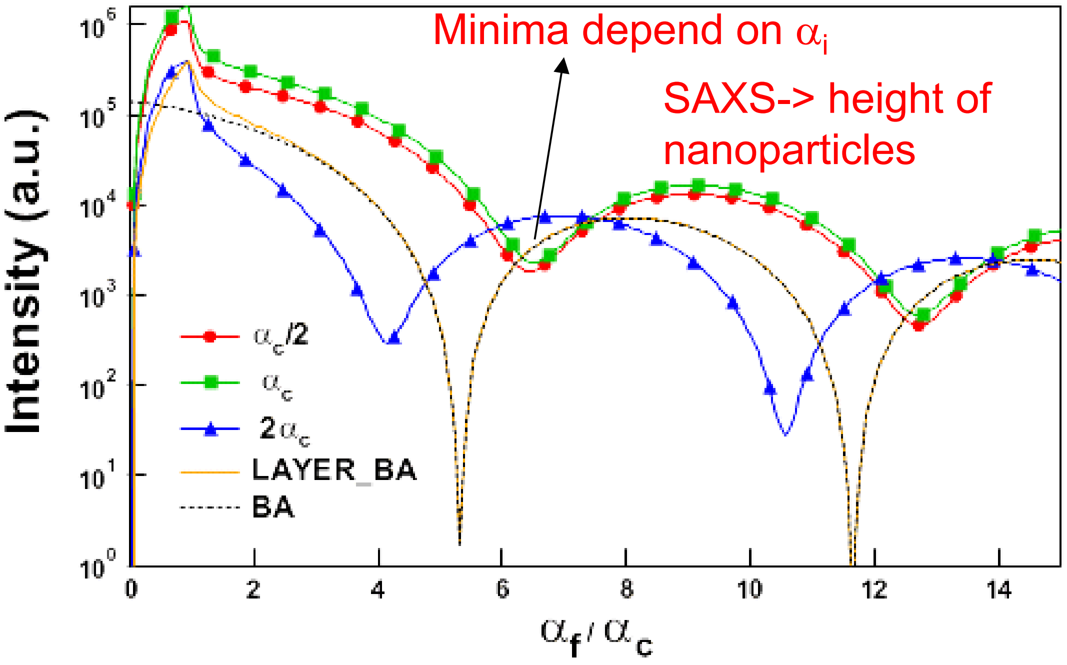
IsGISAXS Manual

Term 1

Term 2

Term 3

Term 4



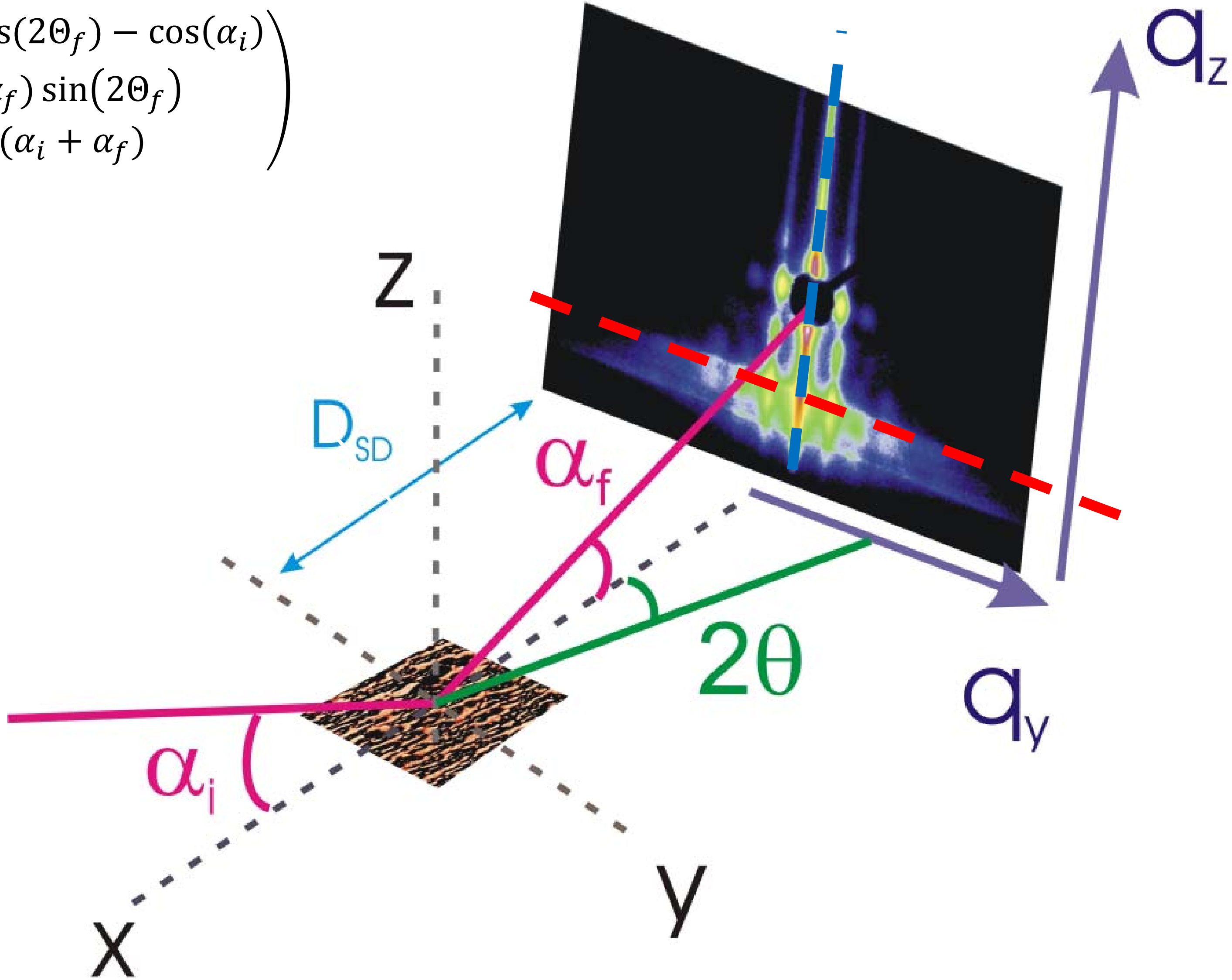
Yoneda peak

Minima depend on α_i

SAXS-> height of nanoparticles

Grazing incidence small-angle x-ray scattering

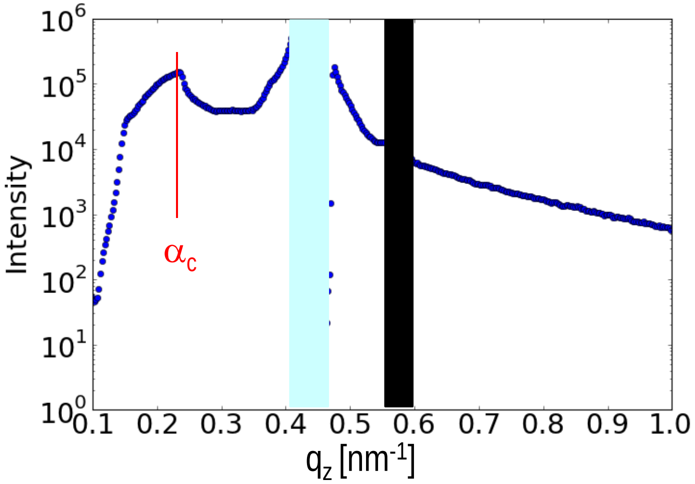
$$\vec{q} = \frac{2\pi}{\lambda}\begin{pmatrix} \cos(\alpha_f)\cos(2\Theta_f) - \cos(\alpha_i) \\ \cos(\alpha_f)\sin\left(2\Theta_f\right) \\ \sin(\alpha_i + \alpha_f) \end{pmatrix}$$

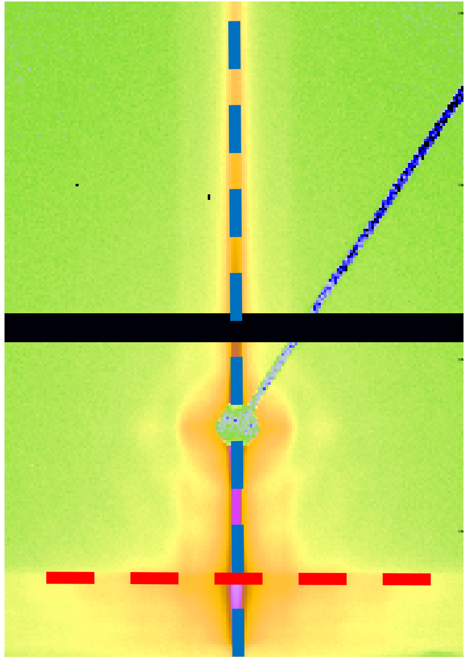


Mueller-Buschbaum, Anal. Bioanal. 376, 3 (2003)

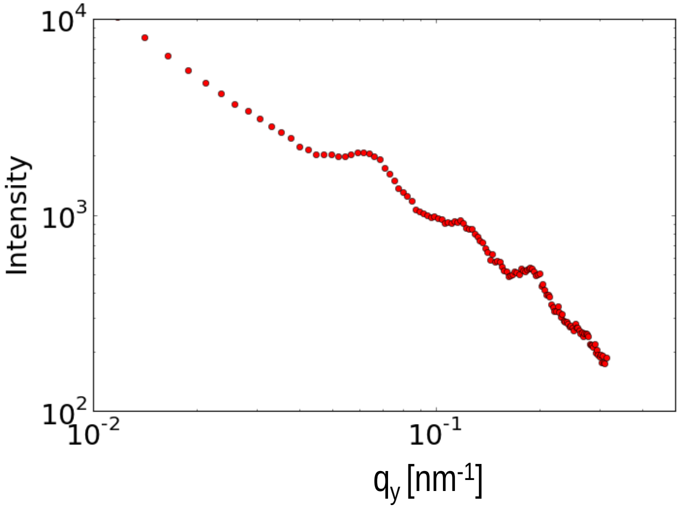
GISAXS – A Primer

cut at constant θ



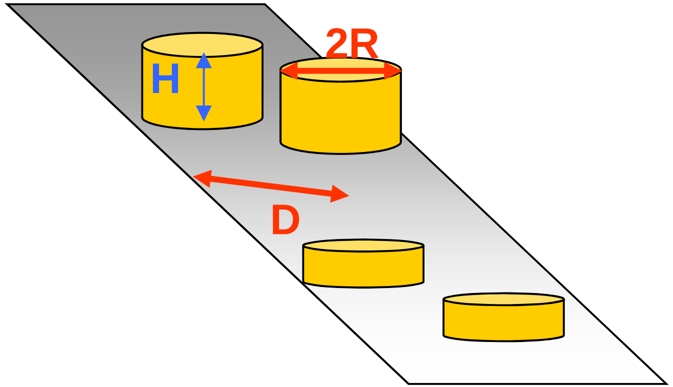


cut at constant α_f



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

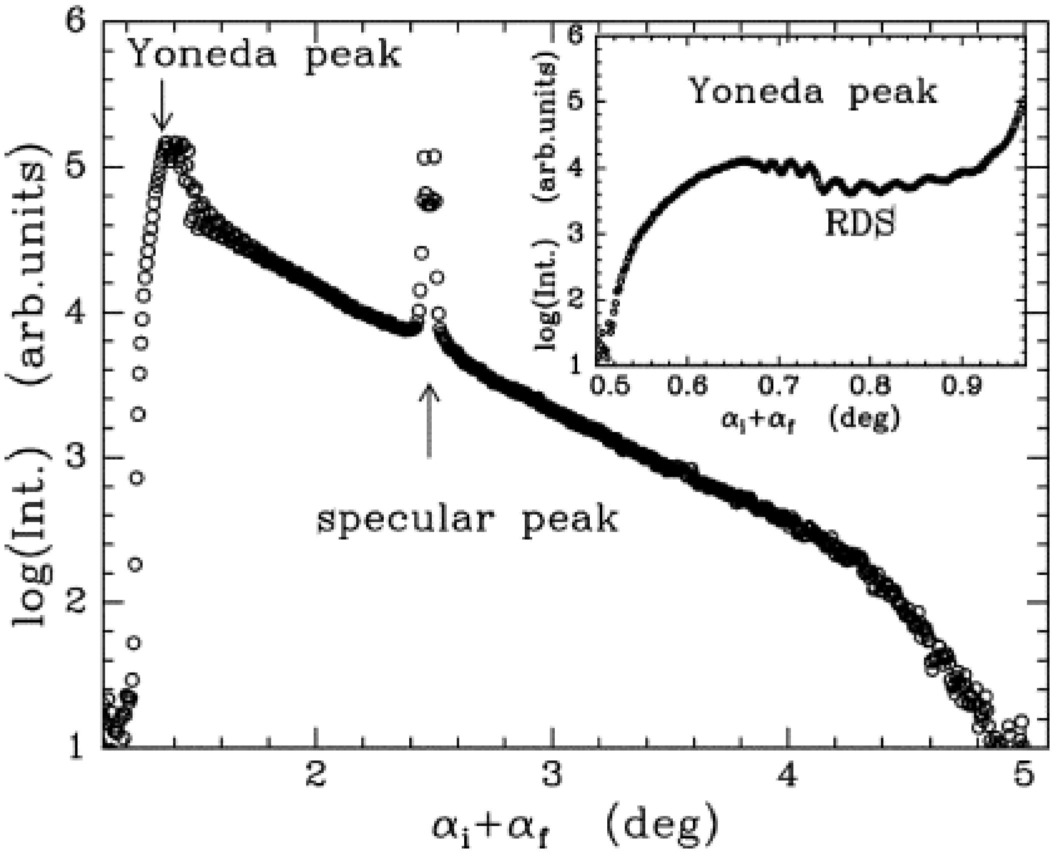
In-plane structures, e.g. distances D, Radius R



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

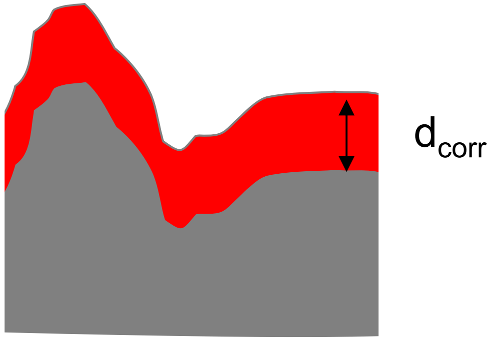
Salditt et al.; Phys.Rev.B **51,** 5617 (1995)
Naudon et al.; Physica B, **283**, 69 (2000)
Renaud et al.; Science, **300**, 1416 (2003)

Resonant diffuse scattering (RDS)

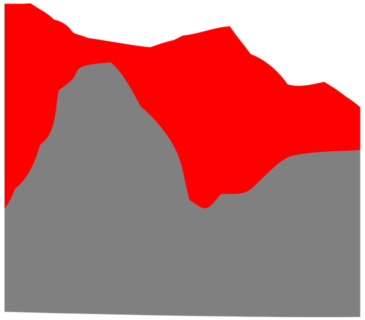


Correlated roughness

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



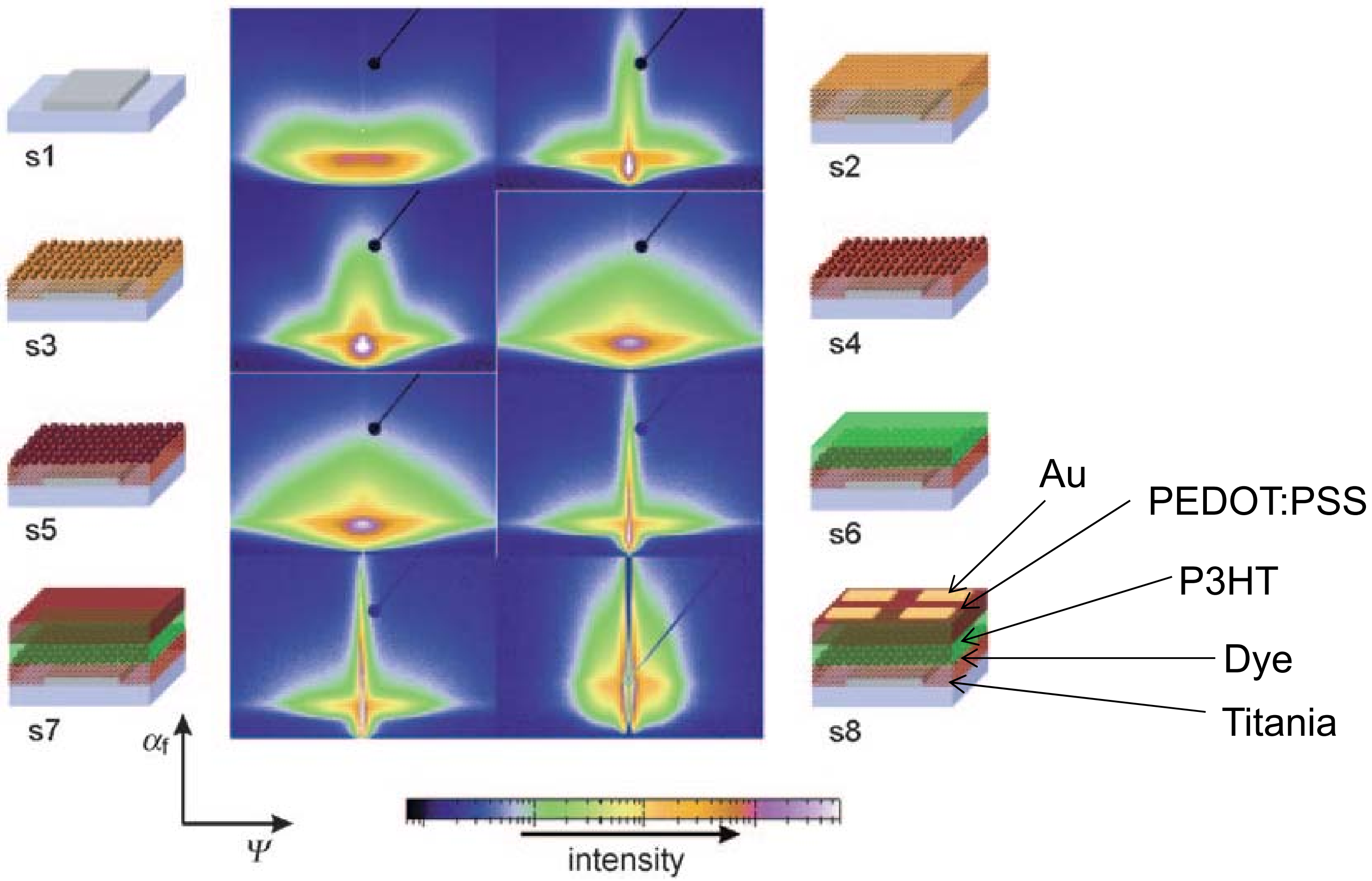
Uncorrelated interfaces



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)

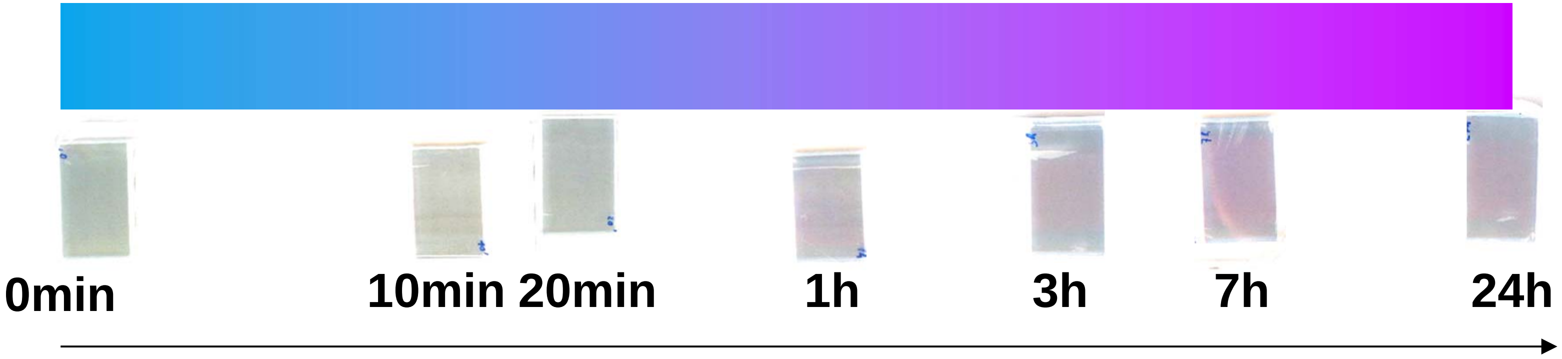
Outline

- > 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)

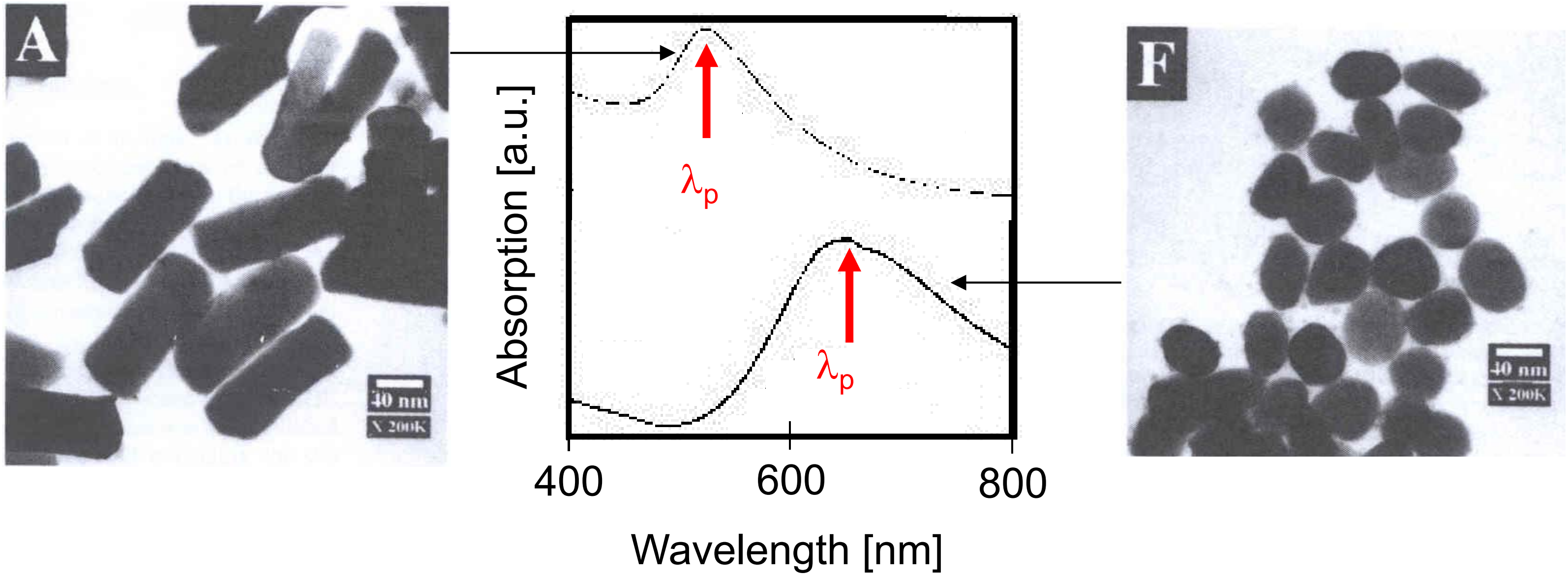


Log (Annealing time)
@ T_{anneal}=300°C < 1064°C (bulk melting point)

Plasmon resonance

Optical properties: sharp resonances ↔ plasmon resonances

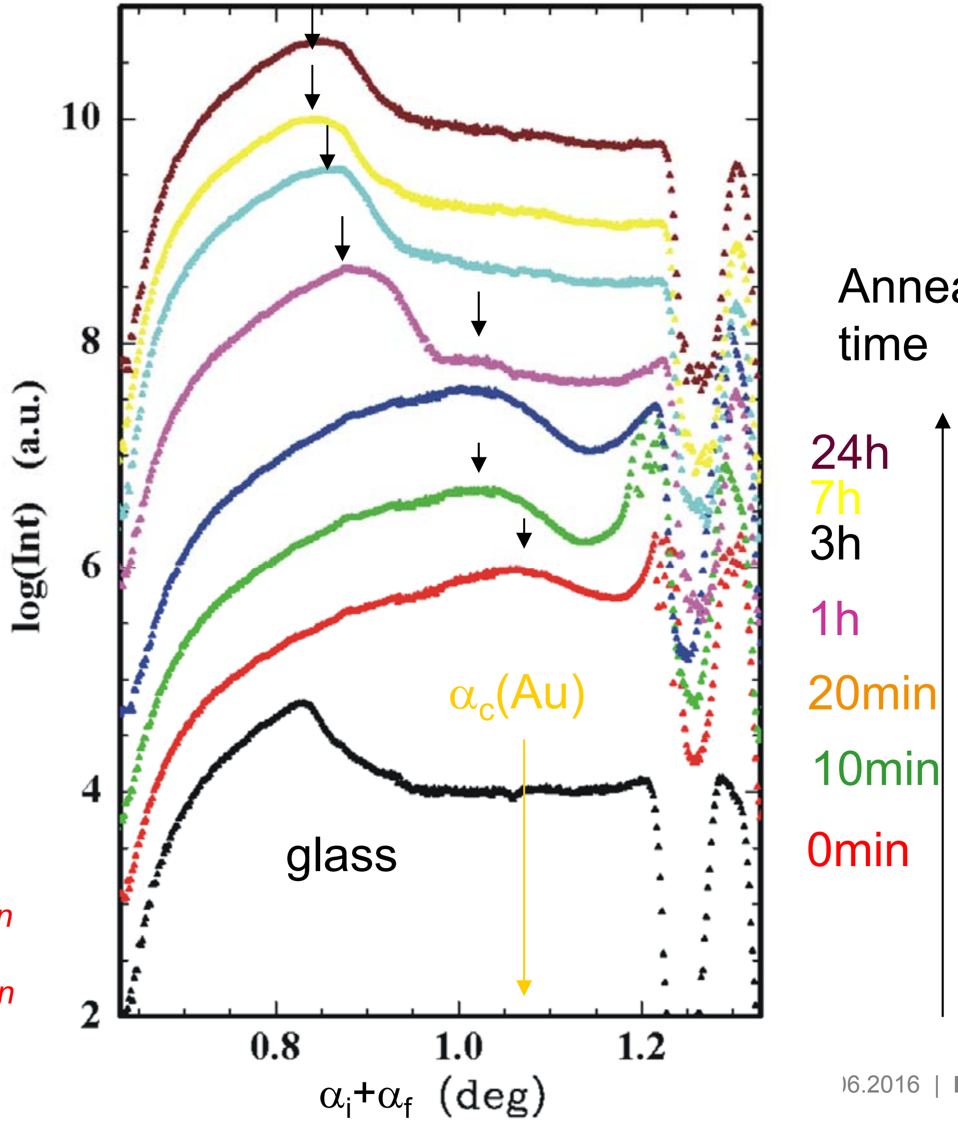
(visible light) cluster arrangement & shape



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

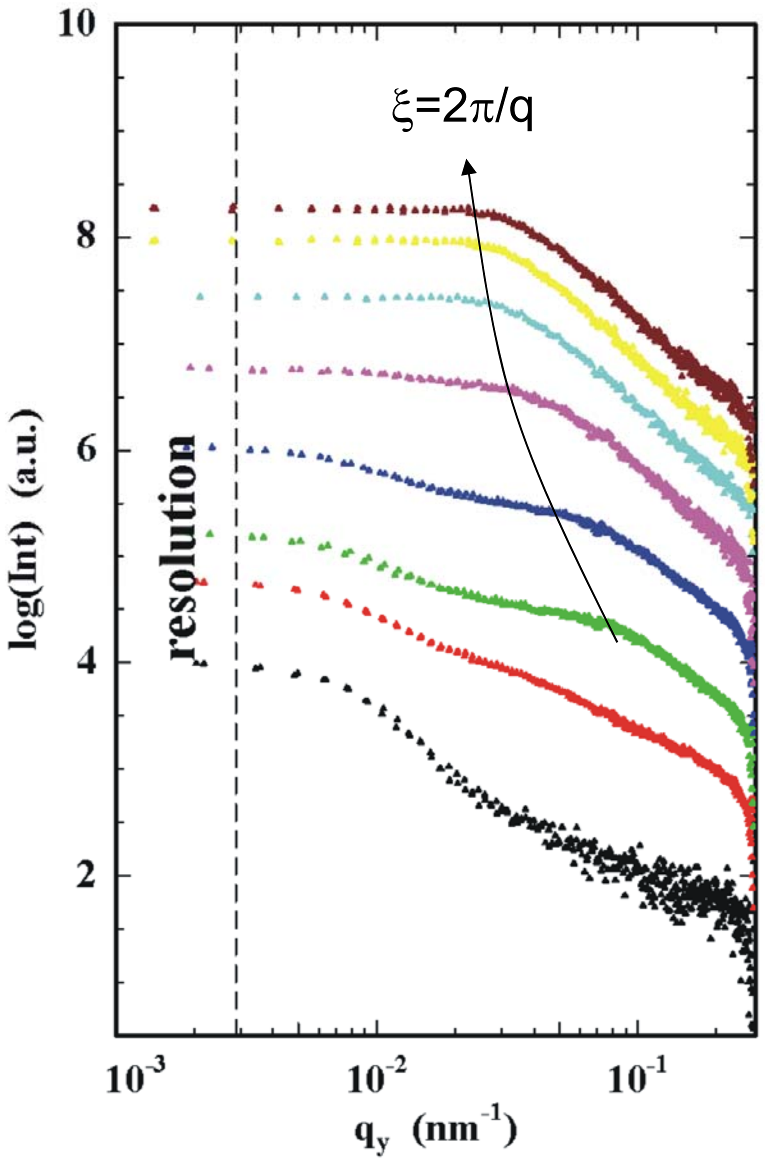
Surface coverage

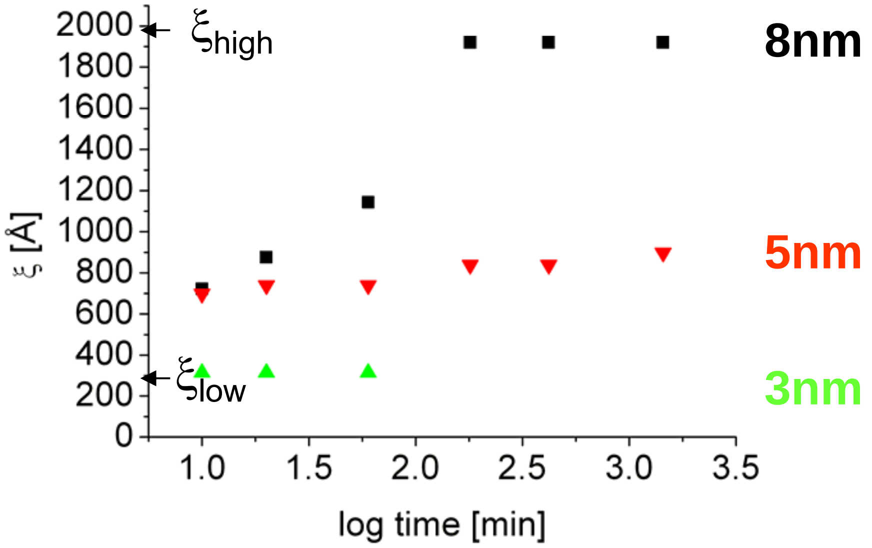
- Thickness Au 8nm

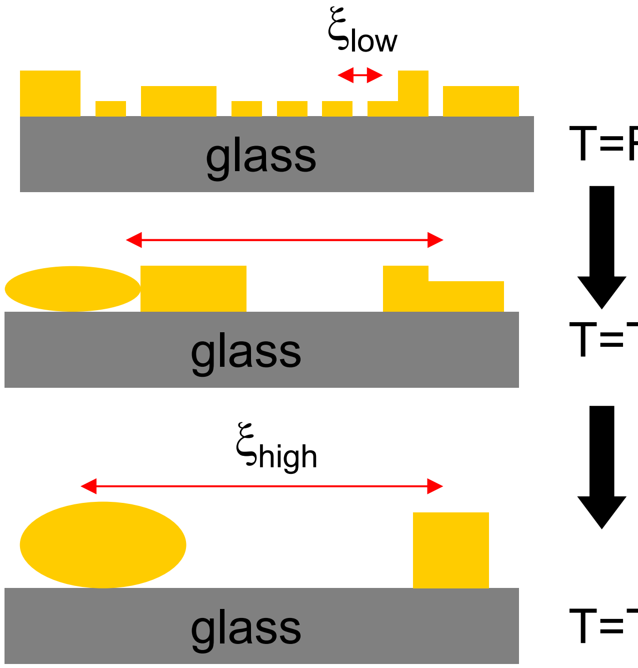


Roth et al., "*Gold nanoparticle thin films on glass: Influence of film thickness and annealing time*", in: "*Synchrotron Radiation and Structural Proteomics*", Pan Stanford Series on Nanobiotechnology - Volume 2, Eds.: E. Pechkova and C. Riekel (2010)

Cluster distance







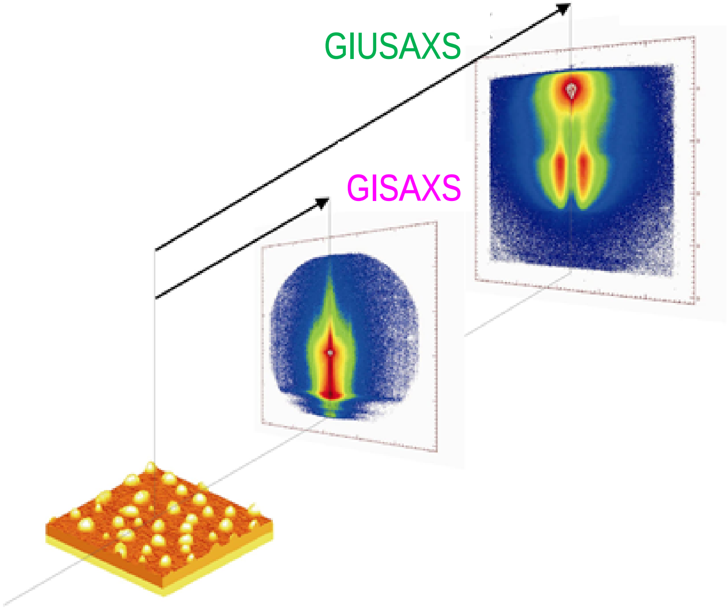
T=RT, 0min

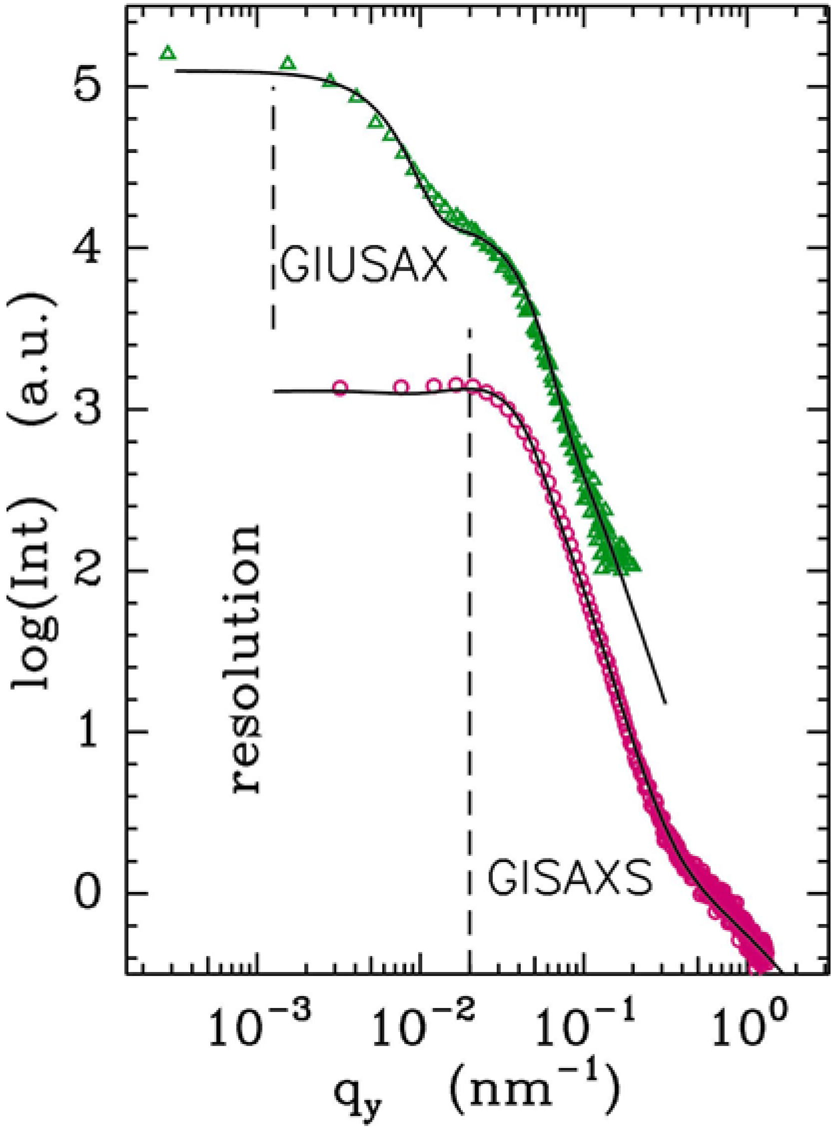
T=T_{anneal}, 0min < t ≤1h

T=T_{anneal}, t>1h

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

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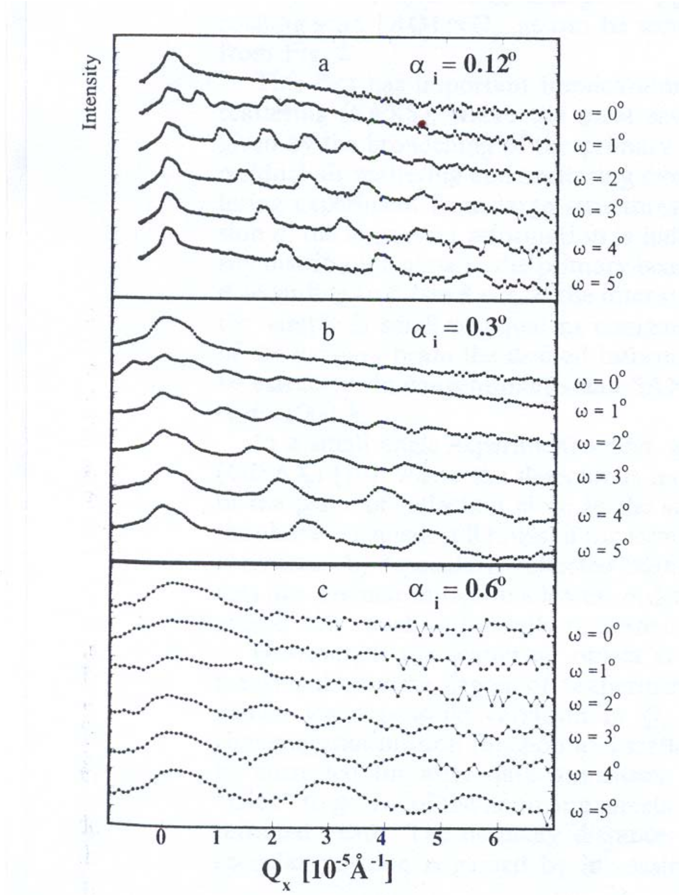
The highest resolution…

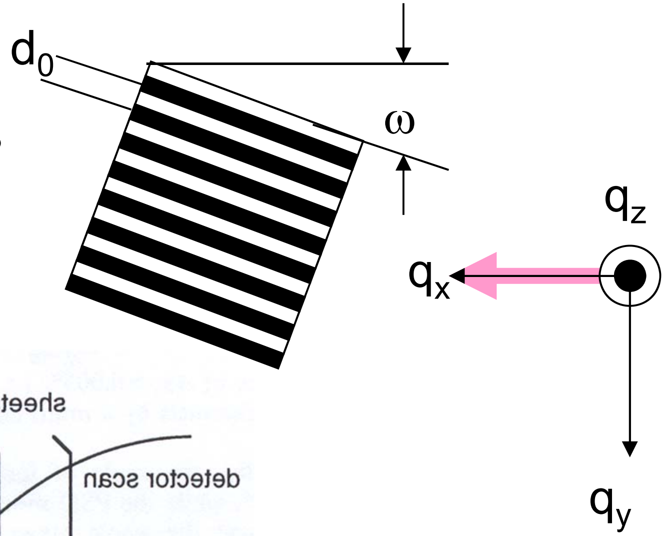
Following Salditt et al., Z. Phys. B **96** (1994) 227: Use grids!

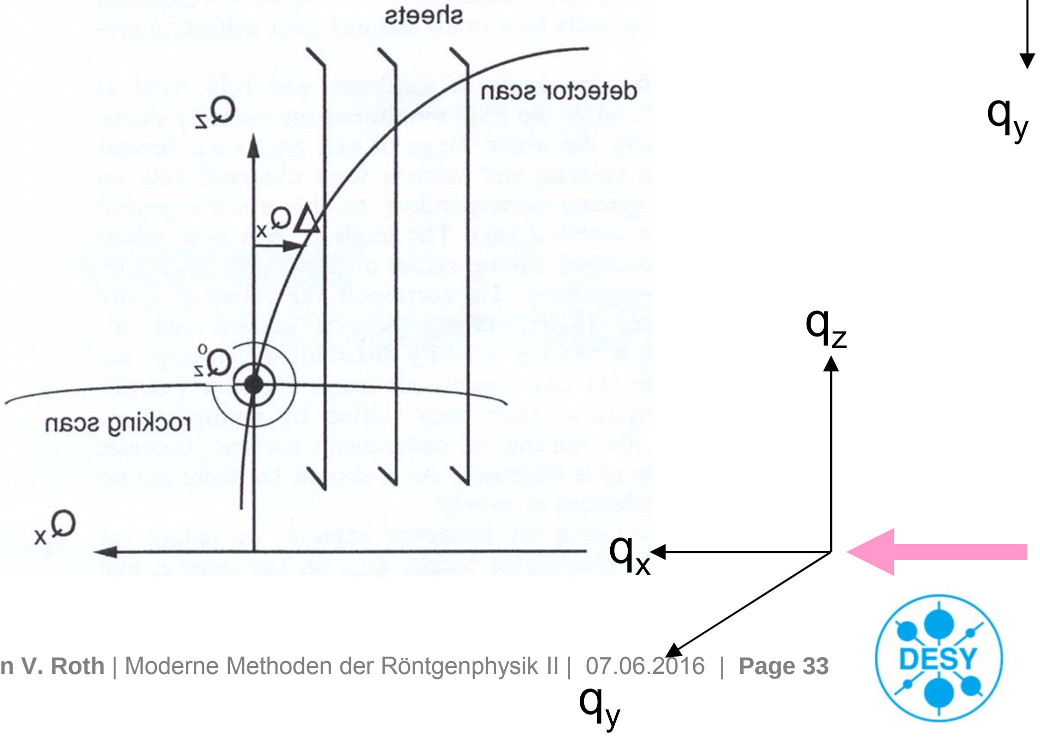


Adjacent orders

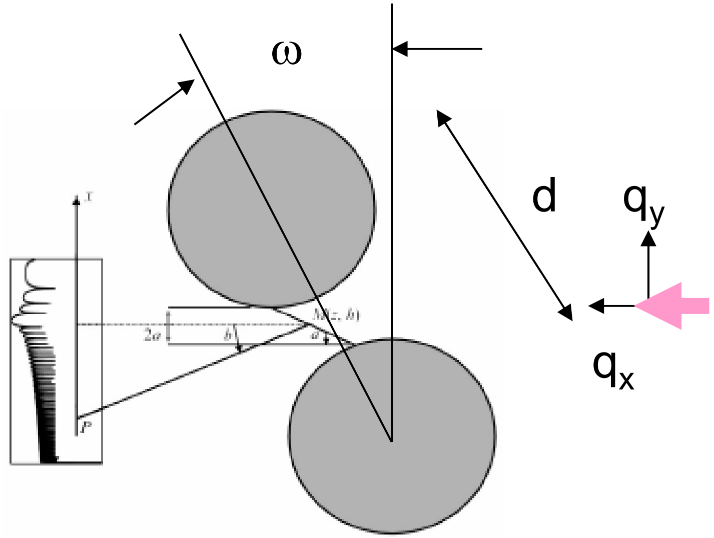
$2\pi/d = \Delta(q_x) / \omega$

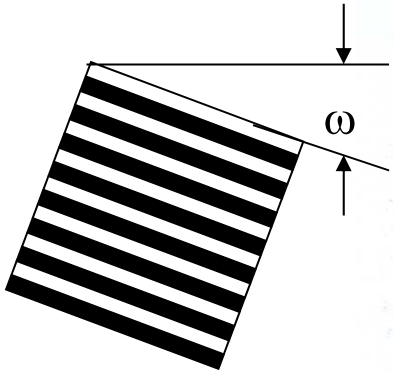
$d = d_0 / \omega$

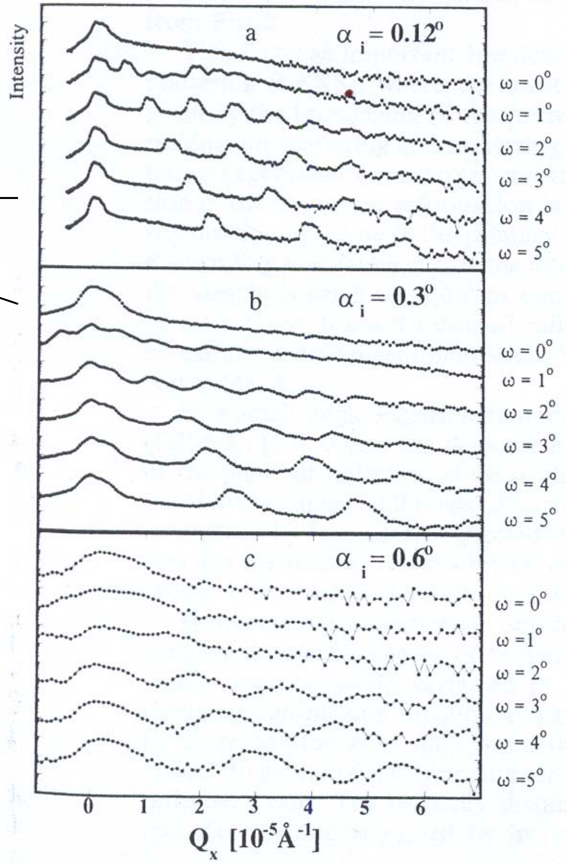




…some analogons…







Zero order

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

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

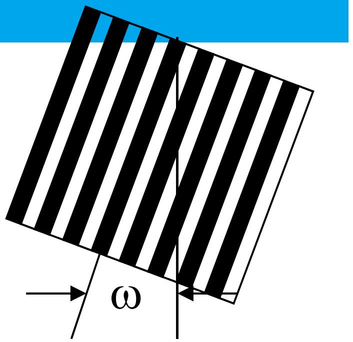
Adjacent orders

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

$$\underbrace{\hspace{10em}}$$

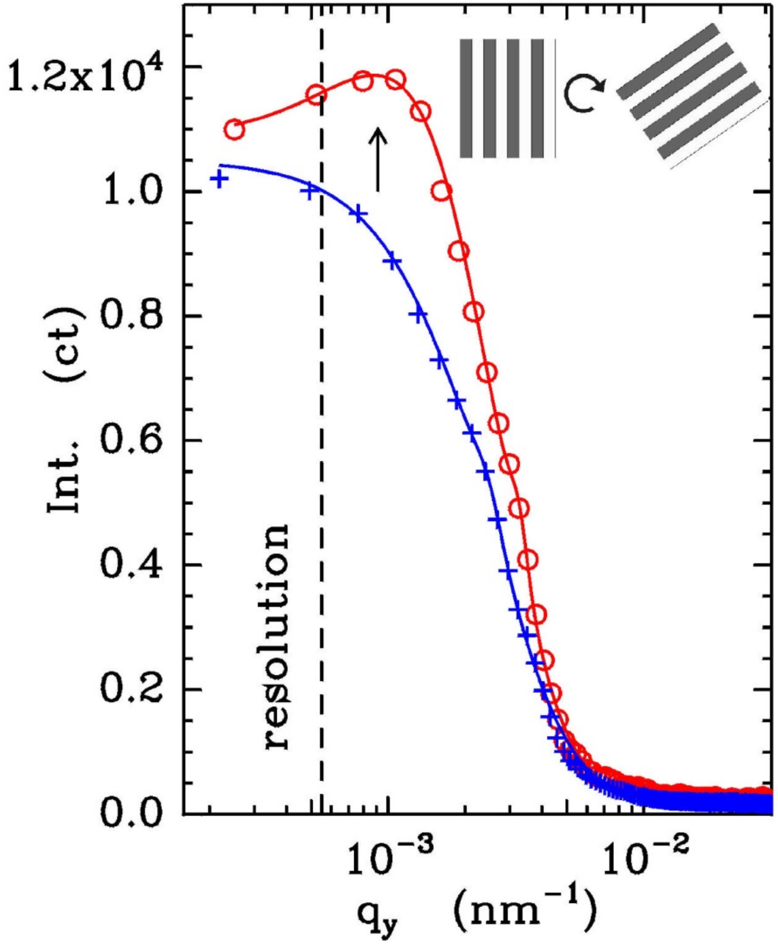
$$\boxed{-q_y + q_x / \tan\omega = 0}$$

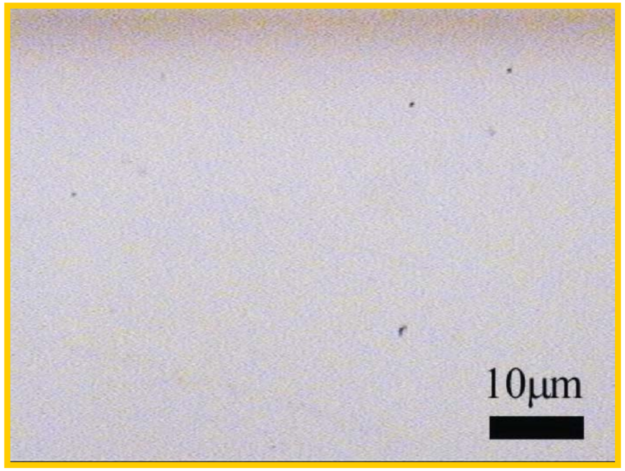
…and at BW4: Polymeric nanochannels

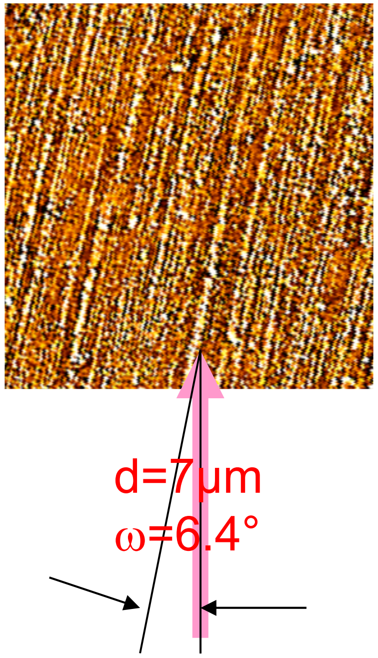


Müller-Buschbaum et al., Appl. Phys. Lett. **88**, 083114 (2006)
HASYLAB – highlight, www.hasylab.desy.de (2006/2007)

Beam size:
B=400x400µm^2
λ=1.38Å
L_{SD}=13m
α_i=0°







d=7µm
ω=6.4°

d=7µm
ω=6.4°

HELMHOLTZ
ASSOCIATION

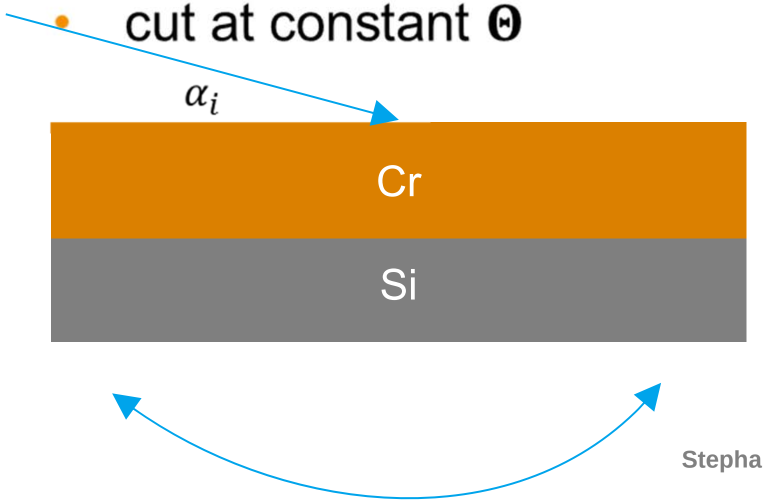
DESY

Theory

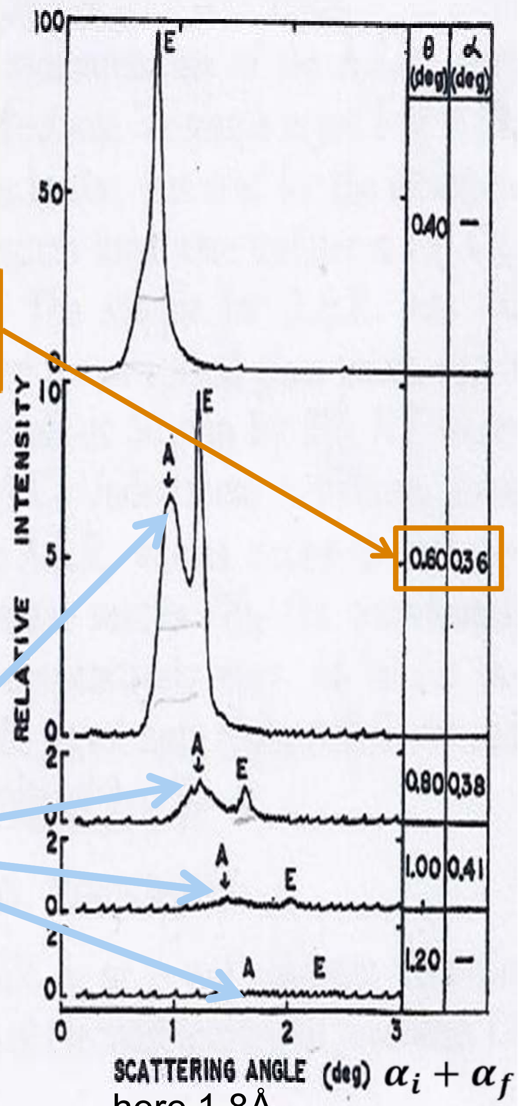
	$r_0\rho_e\,[10^{10}cm^{-2}]$	$\mu_x\,[cm^{-1}]$	$\alpha_c[°]$
vacuum	0	0	---
Si	19,9	93	0,2
Cr	56,3	1208	0,32

- $\alpha_c = \sqrt{2\delta}$ $\quad \delta = \frac{\lambda^2}{2\pi} r_0\rho_e \quad \lambda = 1{,}34$ Å
-

- dependent on material and wavelength
- reflection under α_c called Yoneda-Peak
- cut at constant **Θ**



$\alpha_i + \alpha_f = 0{,}6 + \alpha_f = 0{,}96°$
$\Rightarrow \alpha_f = 0{,}36° = \alpha_c$ (Cr,1,8Å)



$\alpha_i + \alpha_f$

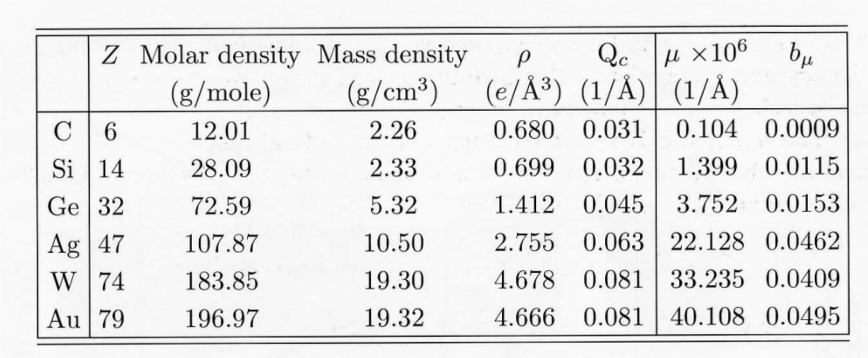
here 1,8Å

FIG. 5. A.S.R. and equiangular reflection by a Cr sample. X-ray source: Mo radiation, no filter, 35 kV, 13 mA.

Snell's law and the Fresnel equations (3) (see 10.4.2014)

use table to extract μ, ρ, f' yielding Q_c

and calculate b_u $(b_u <<1)$:



	Z	Molar density (g/mole)	Mass density (g/cm^3)	ρ (e/Å^3)	Q_c (1/Å)	$\mu \times 10^6$ (1/Å)	b_μ
C	6	12.01	2.26	0.680	0.031	0.104	0.0009
Si	14	28.09	2.33	0.699	0.032	1.399	0.0115
Ge	32	72.59	5.32	1.412	0.045	3.752	0.0153
Ag	47	107.87	10.50	2.755	0.063	22.128	0.0462
W	74	183.85	19.30	4.678	0.081	33.235	0.0409
Au	79	196.97	19.32	4.666	0.081	40.108	0.0495

$$b_u = 2k\mu / Q_c^2$$

use (D): $q^2 = q'^2 + 1 - 2\,i b_u$

get:

$$\boxed{\begin{aligned} r(q) &= (q-q') / (q+q') \\ t(q) &= 2q / (q+q') \\ \Lambda(q) &= 1 / Q_c \,\mathrm{Im}(q') \end{aligned}}$$