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JÜLICH FORSCHUNGSZENTRUM

X-ray and Neutron Scattering from Nanostructures ... on a Surface

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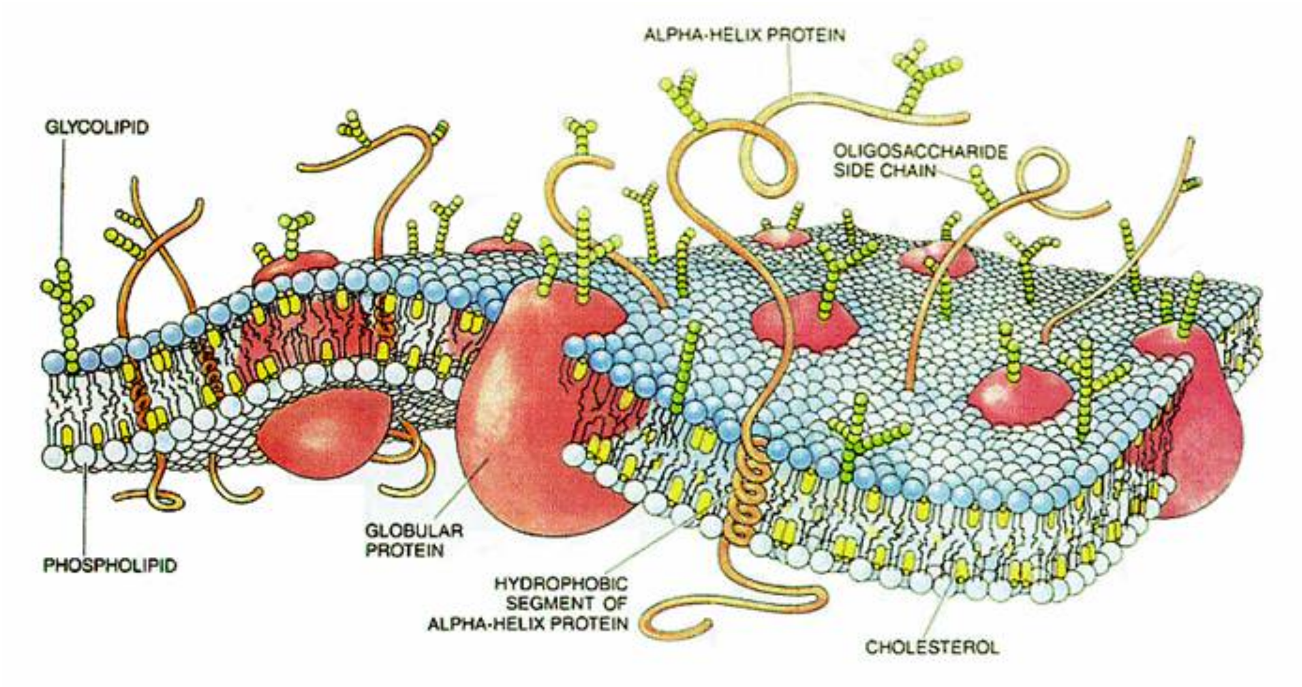
Plan

- **Introduction: Nanoscience and Nanotechnology**
- Method: Reflectivity, off-specular scattering and GISAS
- Specular reflectivity
- Measurement of neutron reflectivity
- Crystallography at mesoscopic length scales: GISAXS from a nanoparticle assembly on a surface
- Conclusion and outlook

Biological membranes:



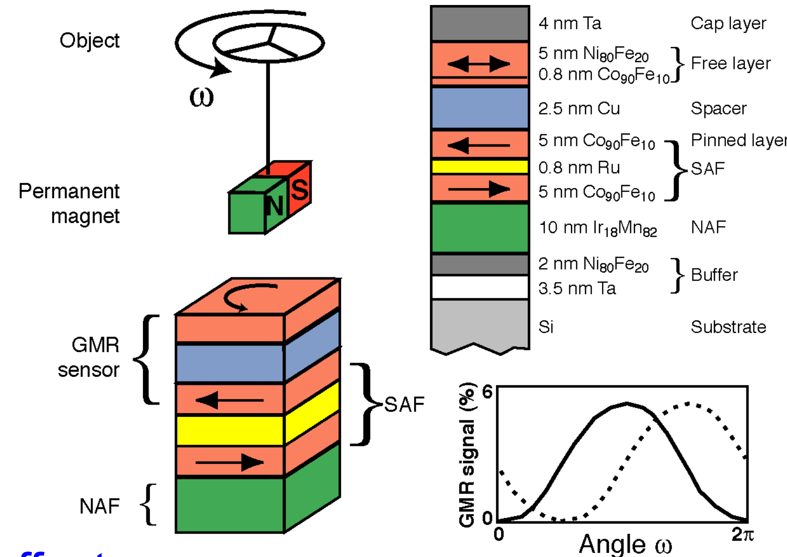
Source: http://www.ncnr.nist.gov/programs/reflect/cnbt/

- Semi-permeable phospholipid bilayer
- Hydrophobic and hydrophilic components
- Membrane proteins and other molecules in biomembranes
- Involved in cell signaling, cell adhesion, cells fusion and ion conductivity

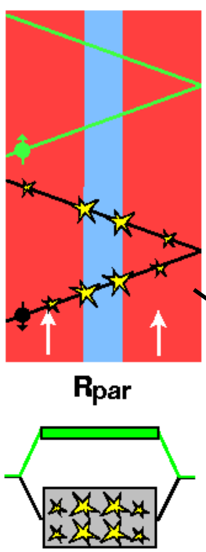
Magnetic thin films

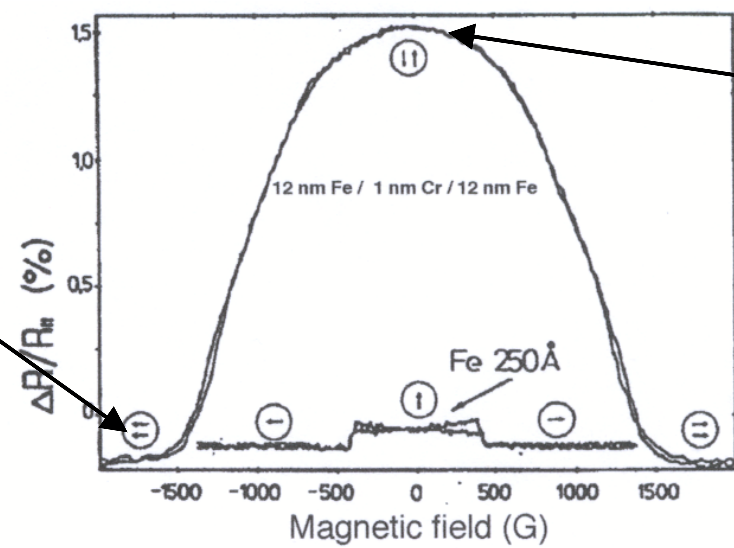
- Ultra thin films
- Anisotropies at surfaces and interfaces
- Exchange bias
- Interlayer exchange coupling
- Giant magnetoresistance
- Tunnel magnetoresistance…

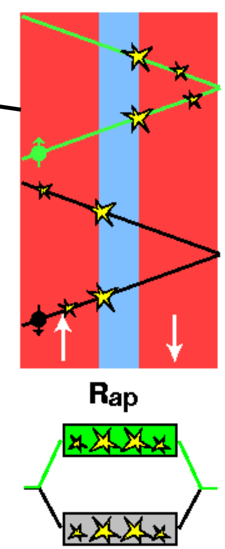
Sensor:



The Giant Magneto-Resistance effect:





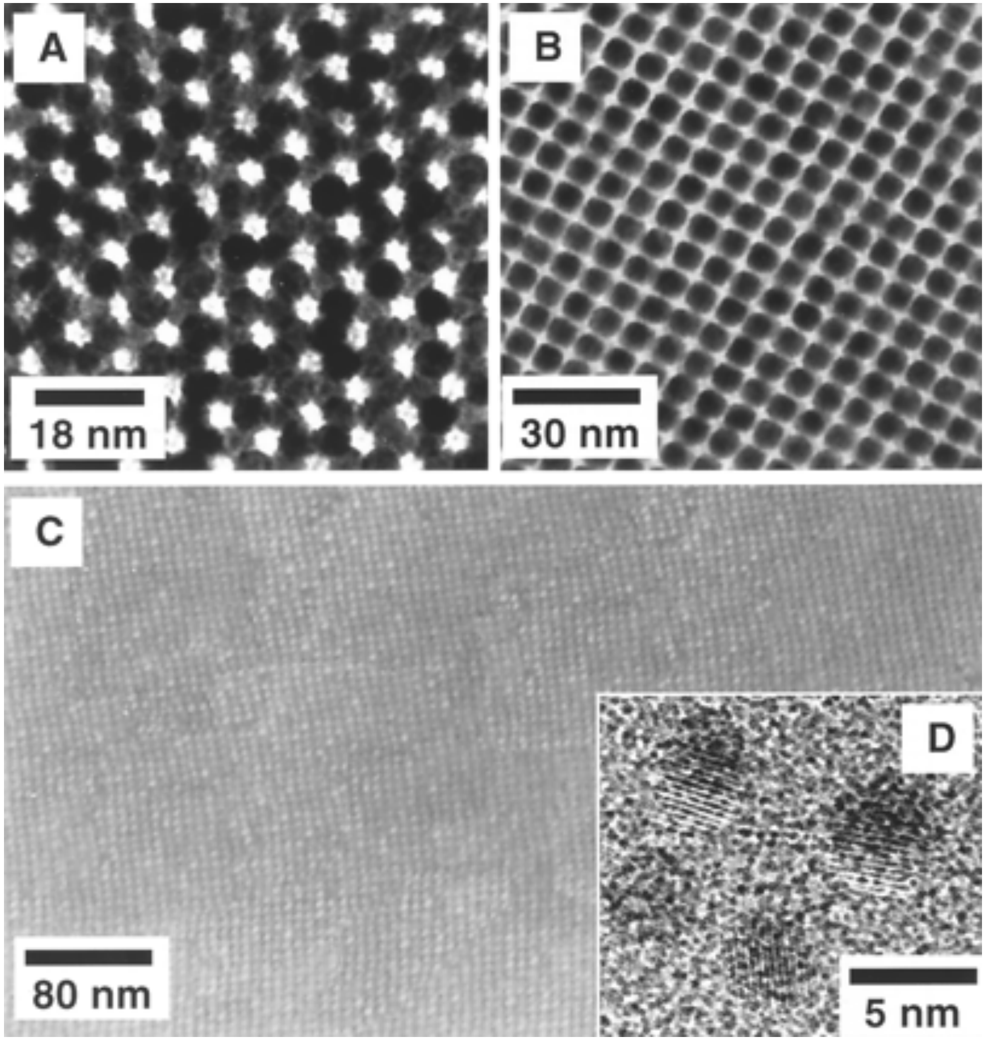


New Field of science: Spintronics

Nobel Prize 2007

A. Fert et al. (1988), P. Grünberg et al. (1989)

Self-organized magnetic nanoparticles for high density storage media



S. Sun, C. Murray, D. Weller, L. Folks, A. Moser, Science **287**, 1989 (2000)

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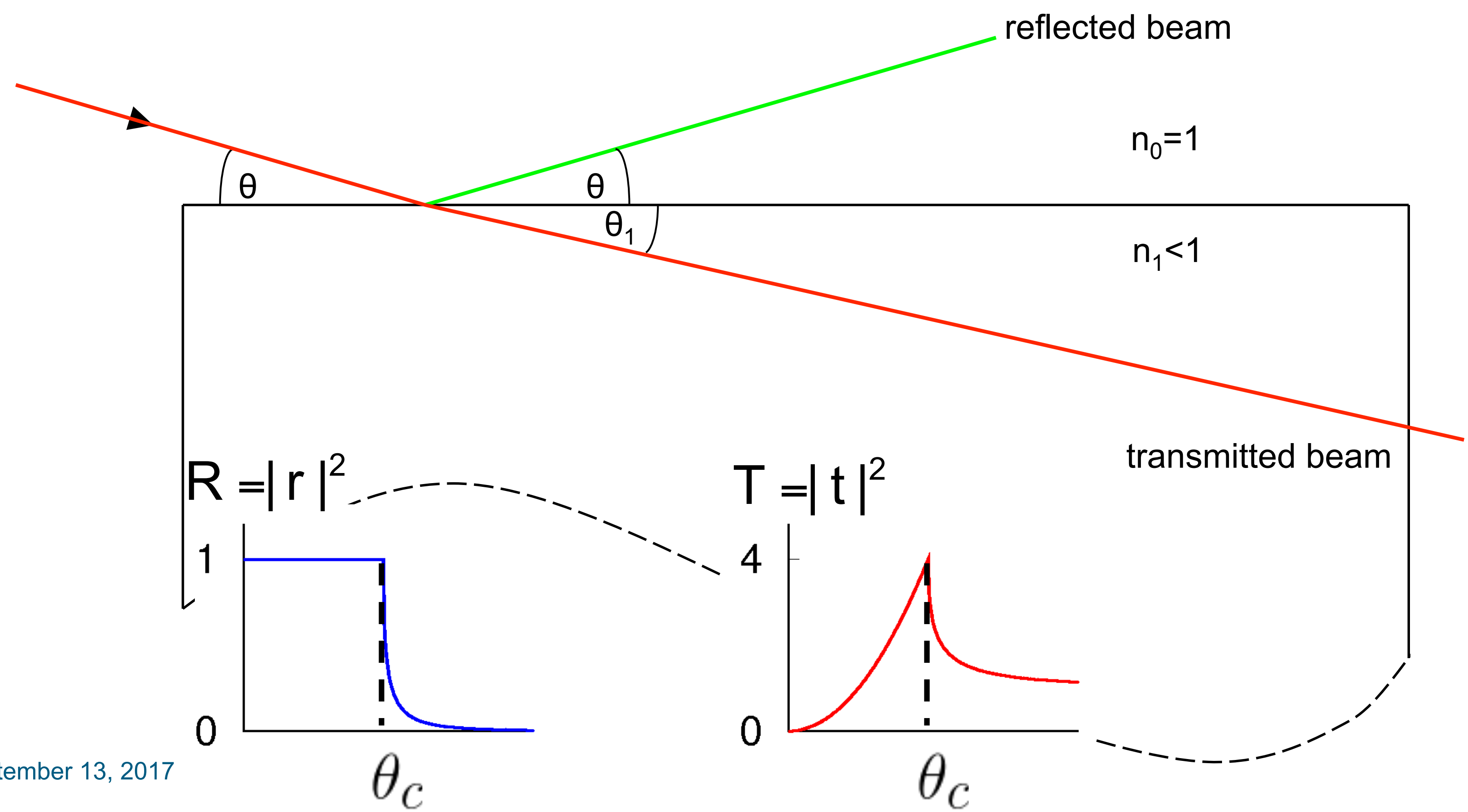
Specular reflectivity: flat surface

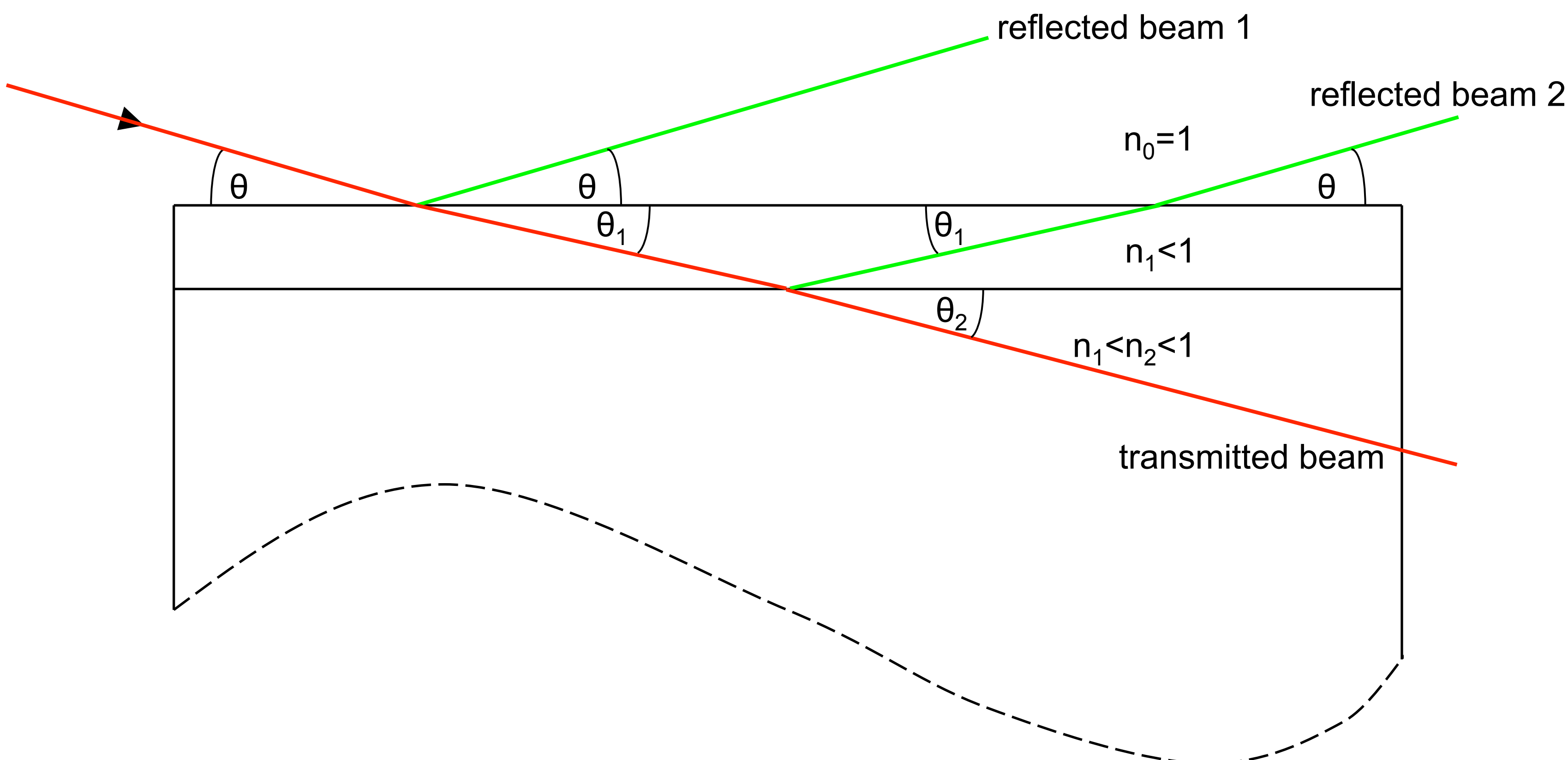
Refraction: $\theta_1 < \theta$, if $n_1 < n_0$

typically $n < 1$ for neutrons and x-rays



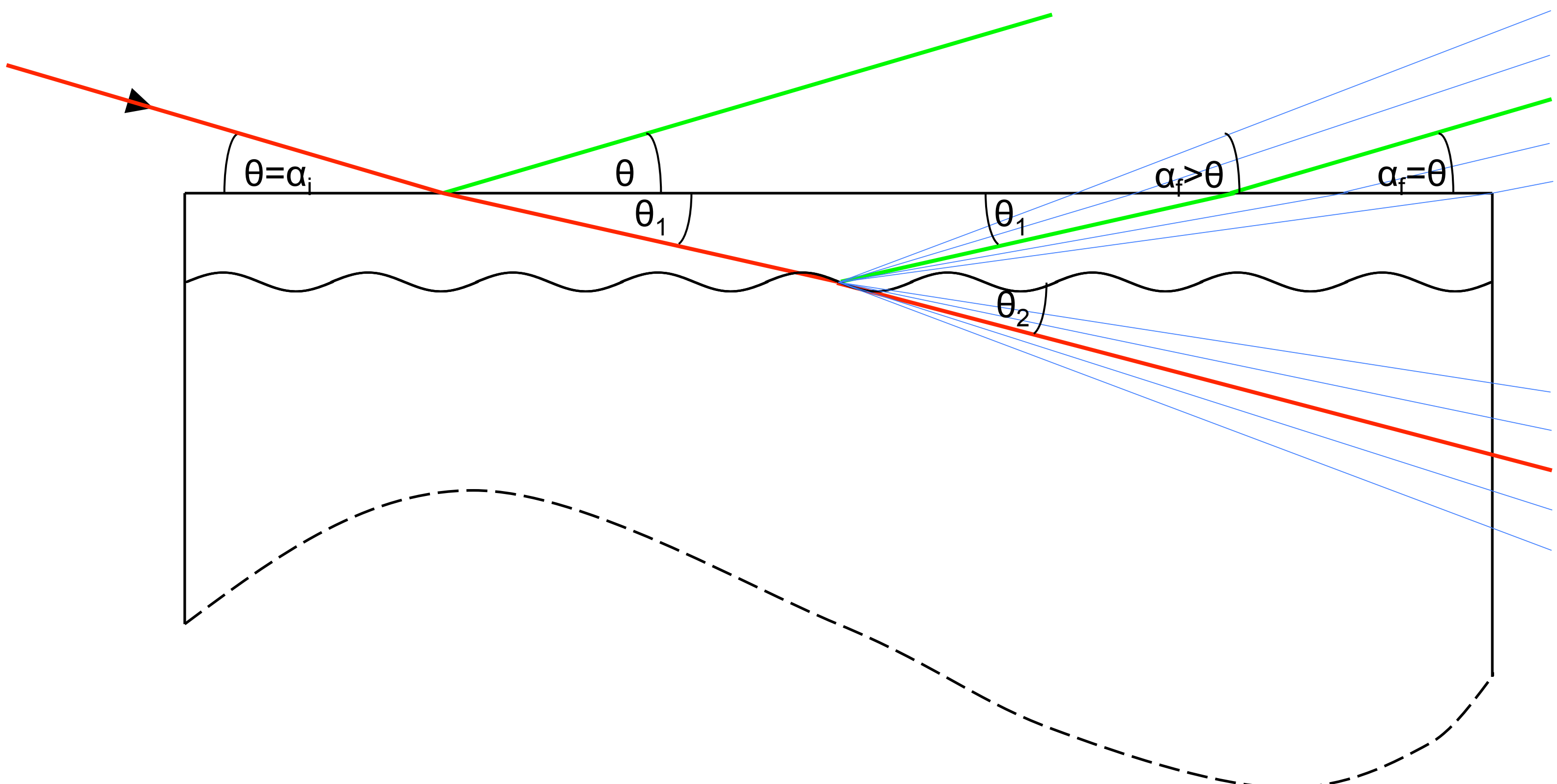
Specular reflectivity: layer on surface

Interference between reflected beams according to path length difference



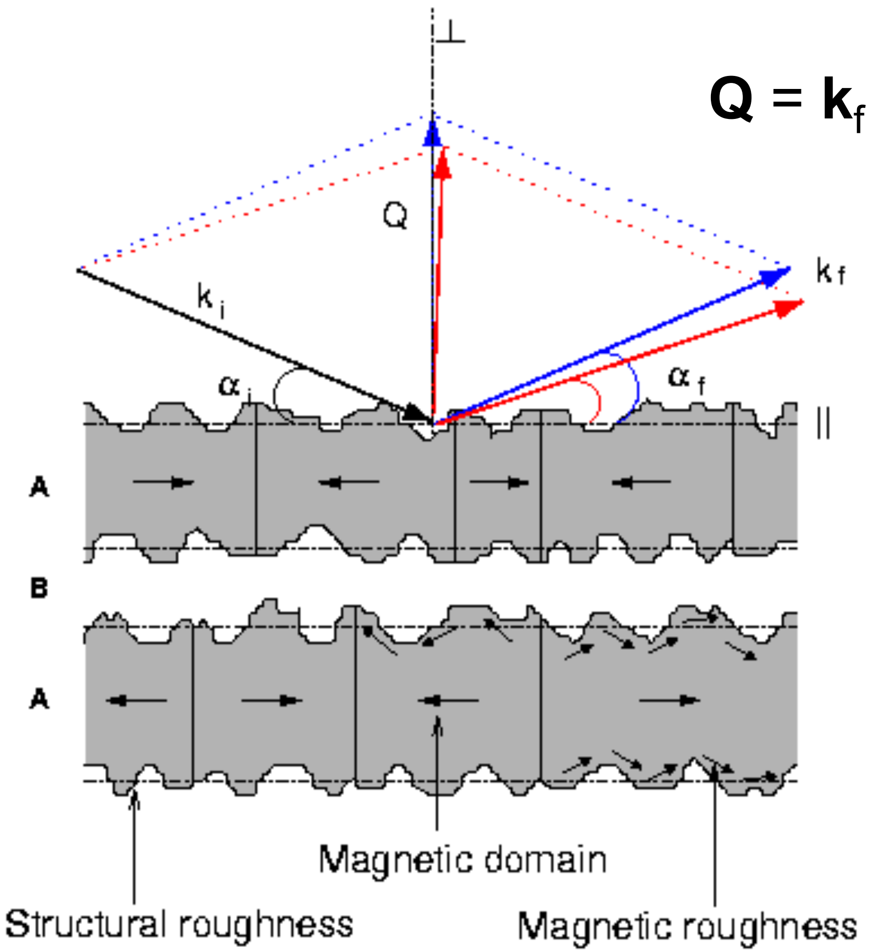
Offspecular scattering: rough interface

Broken translational invariance
→ Off-specular (diffuse) scattering



Reflectivity and off-specular scattering

• In-plane structure can be investigated by off-specular diffuse scattering:



$\mathbf{Q} = \mathbf{k}_f - \mathbf{k}_i$, $k = 2\pi / \lambda$

If $\alpha_f = \alpha_i$ then $Q_{||} = 0$:

• specular reflectivity

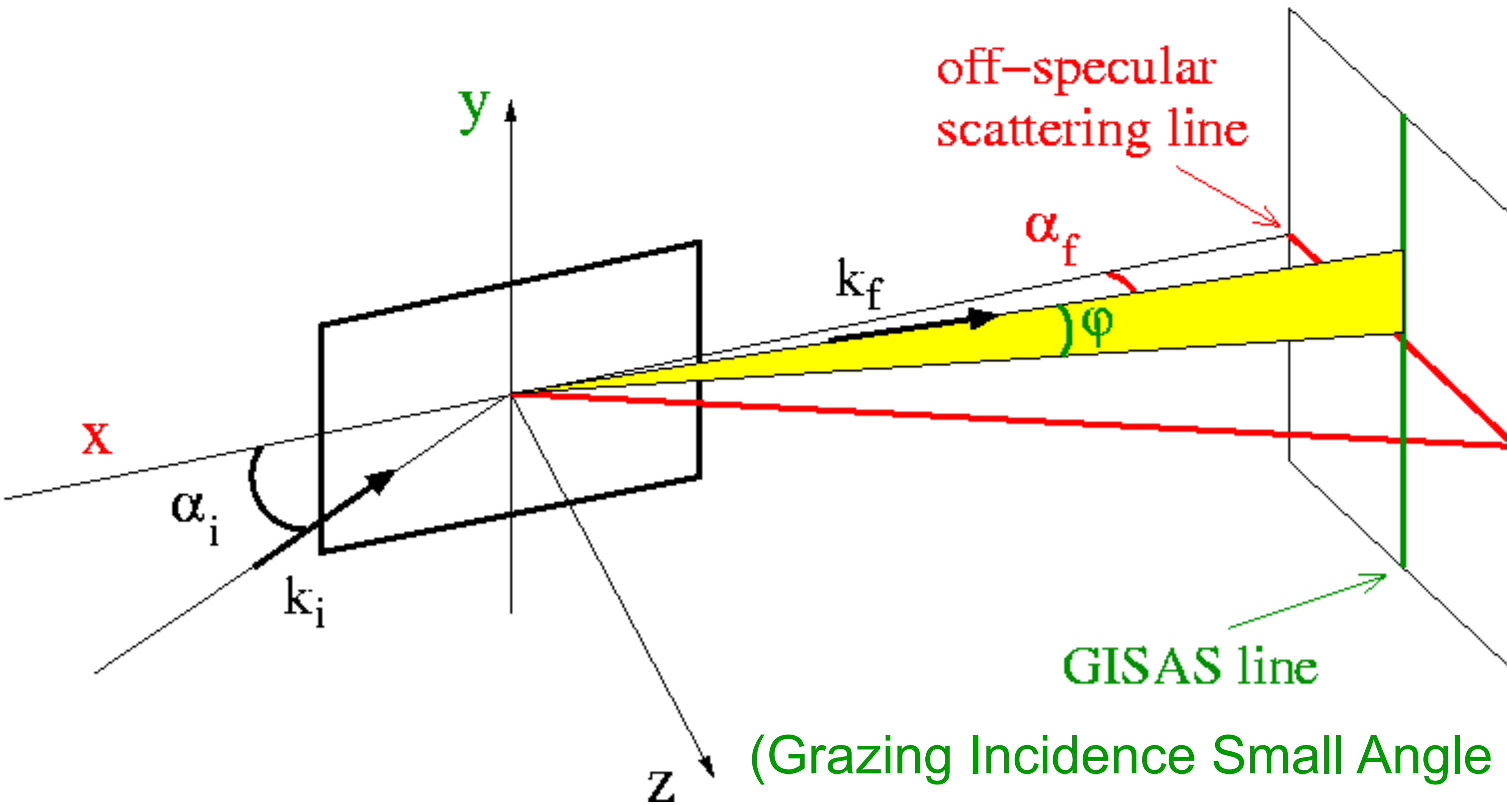
• average over lateral coordinates

If $\alpha_f \neq \alpha_i$ then $Q_{||} \neq 0$:

• off-specular scattering

• lateral correlations can be probed

The two scattering geometries



(Grazing Incidence Small Angle Scattering)

$$\mathbf{Q} = \mathbf{k_f} - \mathbf{k_i} = \begin{cases} Q_x \cong k.(\alpha_i^2 - \alpha_f^2 - \varphi^2)/2 \\ Q_y \cong k.\varphi \\ Q_z \cong k.(\alpha_i + \alpha_f) \end{cases}$$

typically: (neutrons!)

$$\begin{cases} 2\pi / Q_x \approx 1 - 20\ \mu m \\ 2\pi / Q_y \approx 1 - 300\ nm \end{cases}$$

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Wave equation in homogeneous medium.

Schrödinger equation for the neutron wave function:

$$\left[-\frac{\hbar^2}{2m}\Delta + V(\mathbf{r})\right]\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

$$E = \hbar^2 k^2/(2m)$$

$$k = 2\pi/\lambda$$

Small |**Q**| values are probed;

→ Potential of the homogeneous medium:

$$V_1 = \frac{2\pi\hbar^2}{m}\rho$$

Scattering length density: $\rho = \sum_j N_j b_j$

Optical index

We receive:

$$\left[\Delta + \left(k^2 - 4\pi\rho\right)\right]\psi(\mathbf{r}) = \left[\Delta + k^2\left(1 - \frac{\lambda^2}{\pi}\rho\right)\right]\psi(\mathbf{r}) = \left[\Delta + k_1^2\right]\psi(\mathbf{r}) = 0$$

k_1 : wave vector in medium

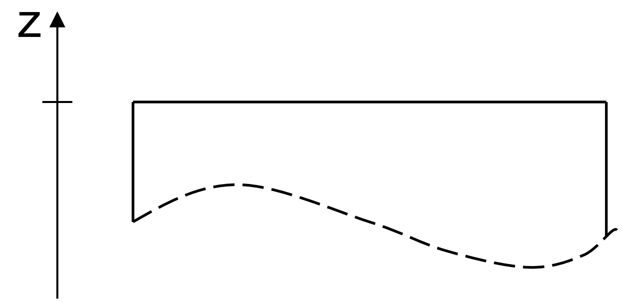
Index of refraction:

$$n = \frac{k_1}{k} \qquad\qquad n \simeq 1 - \frac{\lambda^2}{2\pi}\rho$$

$1 - n$ is positive for most materials and of the order of 10^{-6} to 10^{-5}

Solution for a sharp surface. Fresnel's formulas

$$V(z) = \begin{cases} 0 & for \quad z > 0 \\ V_1 & for \quad z \leq 0 \end{cases}$$



$$\psi(\mathbf{r}) = e^{i(k_x x + k_y y)} \psi_z(z)$$

$$\frac{d^2\psi_z(z)}{dz^2} + k_z^2(z)\psi_z(z) = 0$$

General solution:

$$\psi_{zl}(z) = t_l e^{ik_{zl}z} + r_l e^{-ik_{zl}z},$$

l=0: vac. l=1: medium

Boundary conditions:

$$t_0 = 1 \;\; ; \;\; r_1 = 0 \;\; ; \;\; \psi_{z0}(z=0) = \psi_{z1}(z=0) \;\; ; \;\; \frac{d\psi_{z0}}{dz}(z=0) = \frac{d\psi_{z1}}{dz}(z=0).$$

Solution for a sharp surface. Fresnel's formulas

We receive:

$$1 + r_0 = t_1 \quad ; \quad k_{z0}(1 - r_0) = k_{z1} t_1.$$

Reflectivity R and transmissivity T:

$$R = |r_0|^2 \quad ; \quad T = |t_1|^2$$

Fresnel's formulas:

$$\text{Reflectivity :} \qquad R = \left| \frac{k_{z0} - k_{z1}}{k_{z0} + k_{z1}} \right|^2$$

$$\text{Transmissivity :} \qquad T = \left| \frac{2k_{z0}}{k_{z0} + k_{z1}} \right|^2$$

Snell's law of refraction. Total external reflection

Continuity of the wave vector components parallel to surface:

$$k_{x0} = k_{x1} \qquad k_{y0} = k_{y1}$$

Leads to Snell's law of refraction:

$$\frac{\cos\theta}{\cos\theta_1} = \frac{k_1}{k_0} = n_1$$

Total external reflection for θ < θ_c defined by:

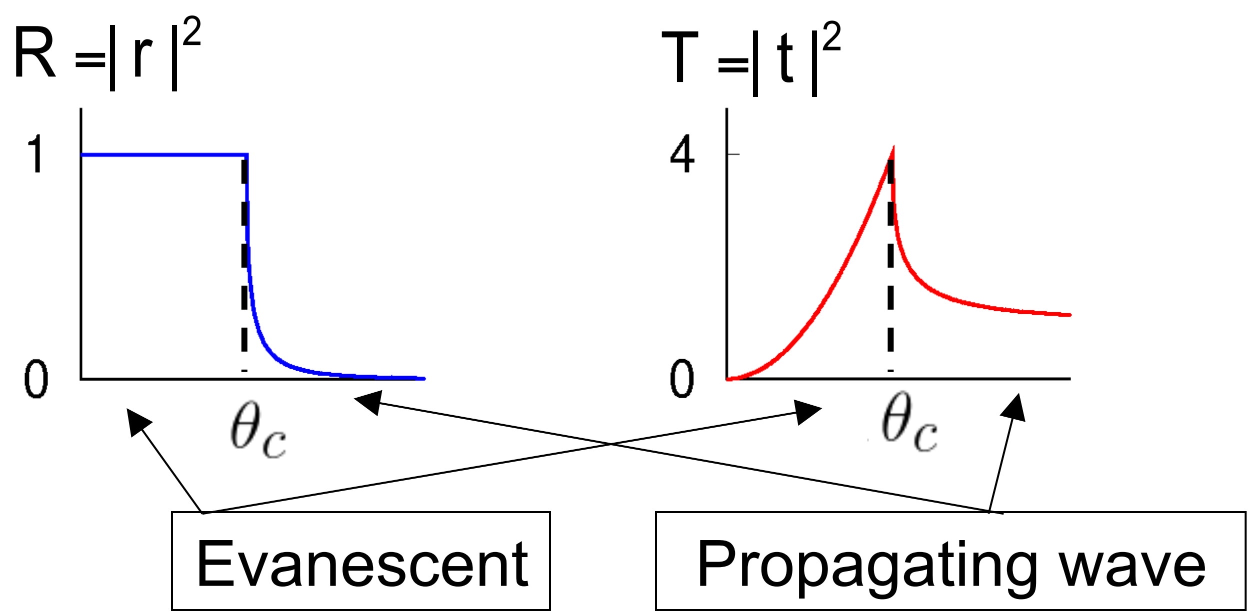
$$n_1 = \cos\theta_c \qquad \theta_c \simeq \lambda\sqrt{\frac{\rho}{\pi}}$$

Total external reflection

Normal components of the incoming and refracted wave vectors:

$$k_{z1}^2 = k_{z0}^2 - k_{z0,c}^2 \qquad \text{with} \qquad k_{z0,c} = \frac{2\pi}{\lambda}\sin\theta_c = \sqrt{4\pi\rho}.$$

Reflectivity and transmissivity:



Reflectivity from a layer on substrate

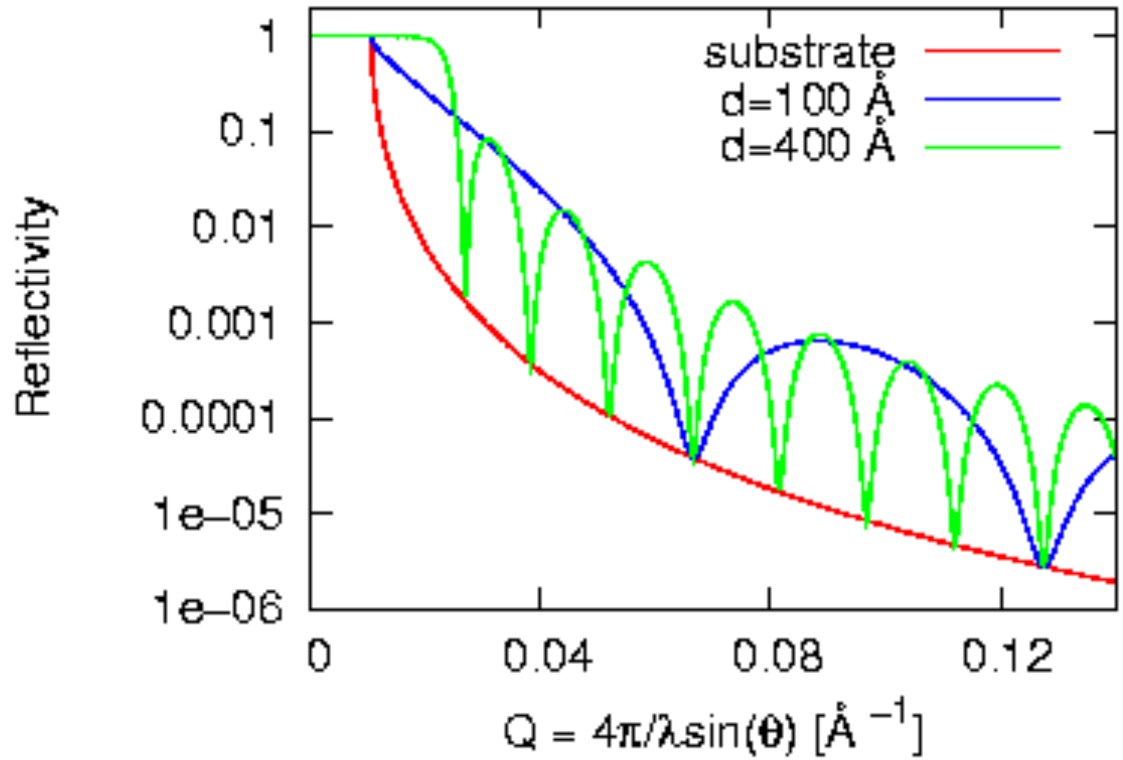
Optical path length difference between beams reflected at surface and interface:

$$\Delta = 2d \sin\theta$$

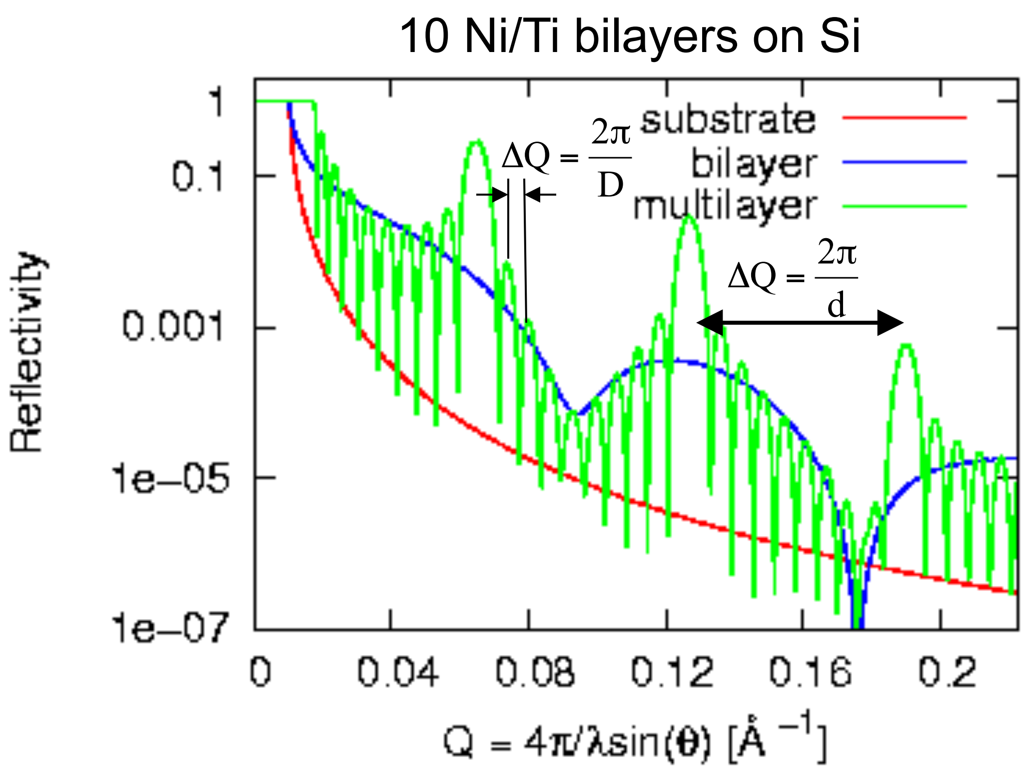
$\rightarrow$ Distance between interference maxima:

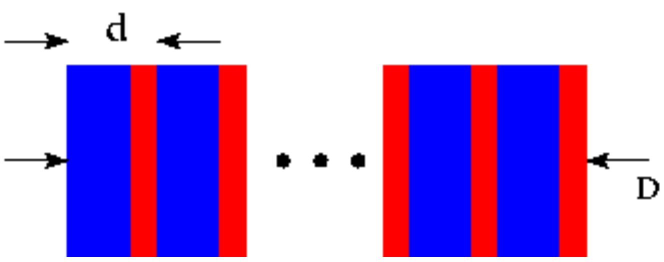
$$\delta Q \simeq \frac{2\pi}{d}$$

Ni layer on Si substrate

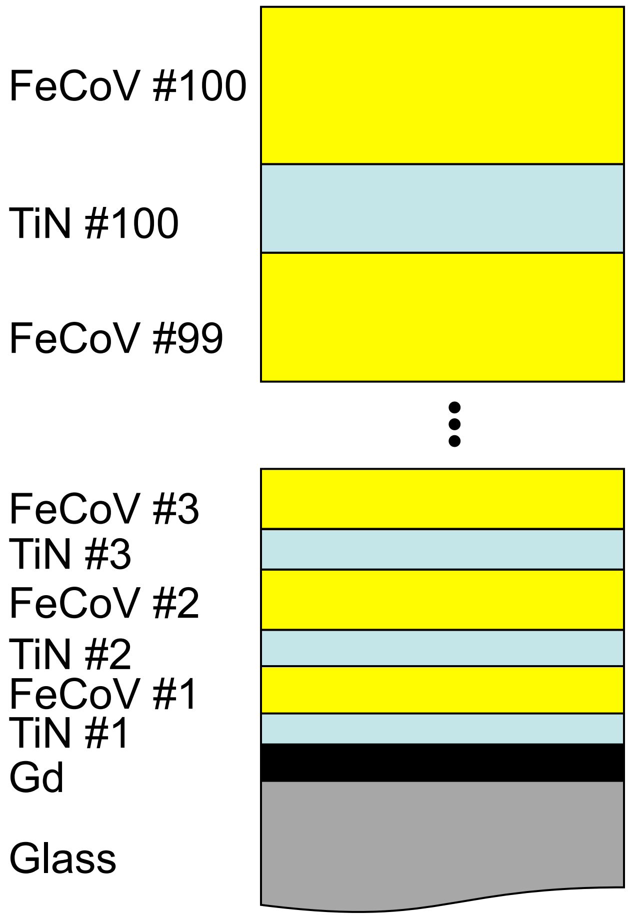


Reflectivity from a multilayer



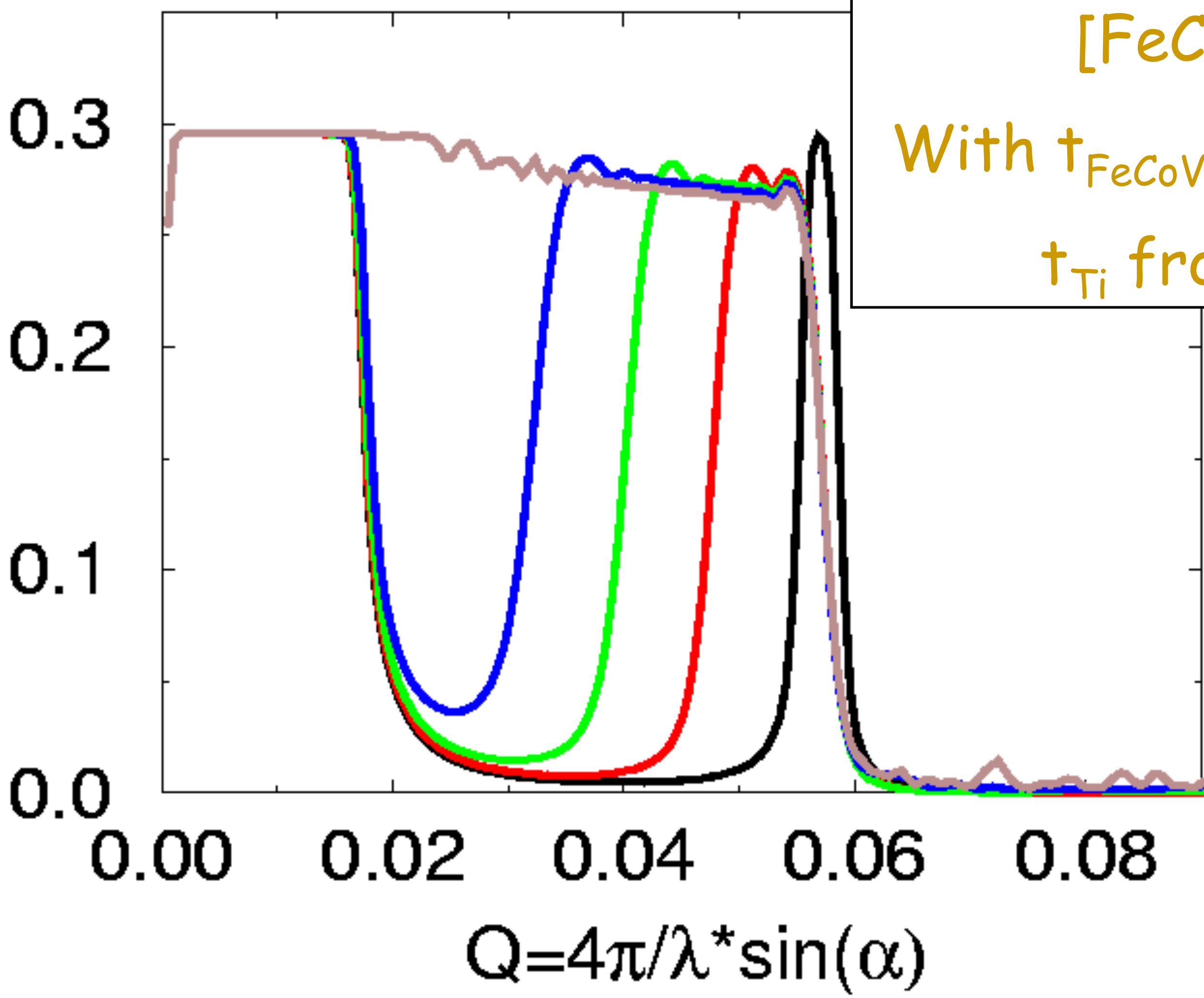


Reflectivity from a supermirror



nuclear sld.

Reflectivity from a supermirror



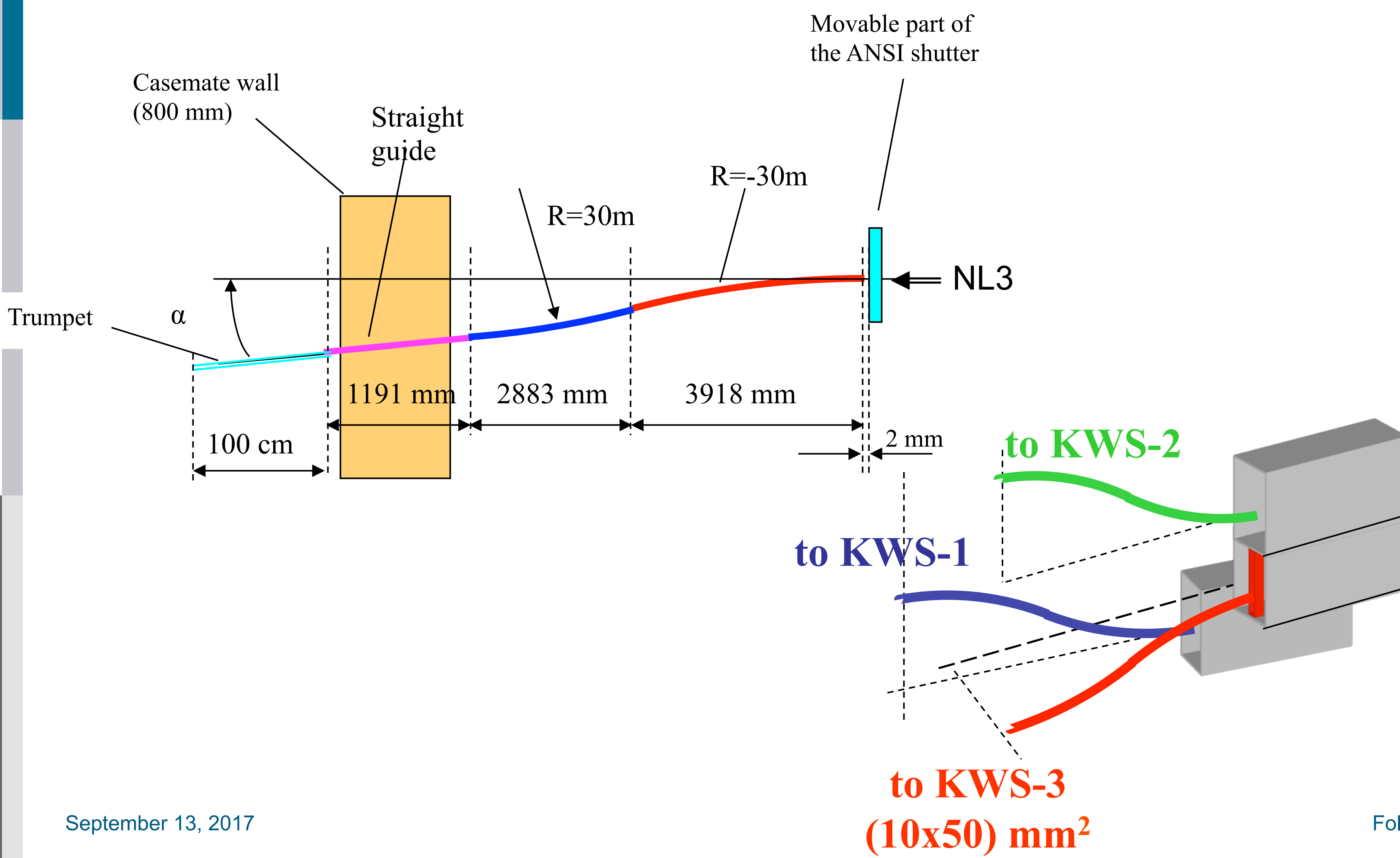
$[FeCoV/TiN]_{100}$

With t_{FeCoV} from 6 to 70 nm

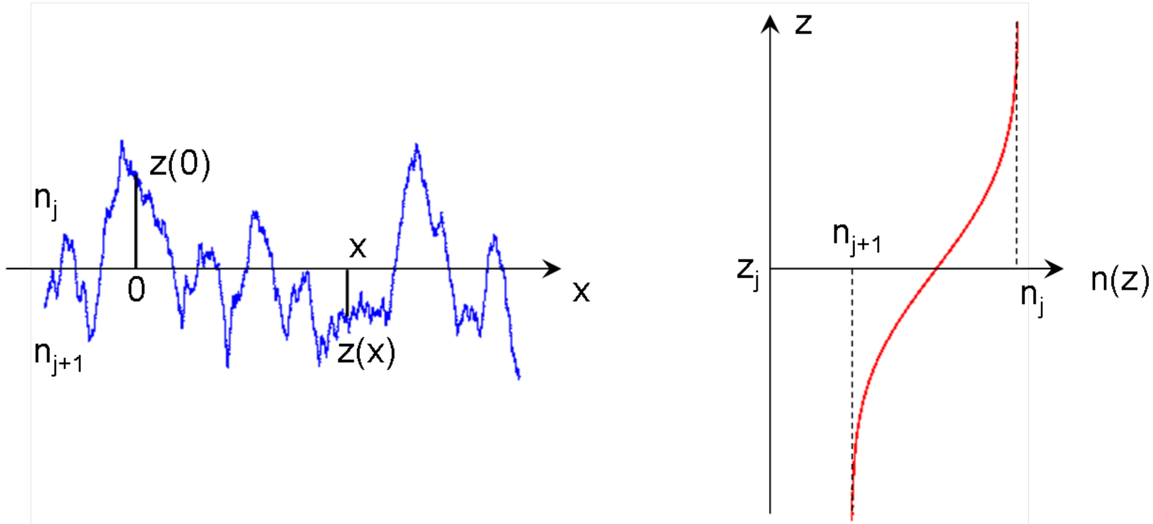
t_{Ti} from 5.5 to 12.6 nm

Reflectivity from a supermirror: Application

The S-shape supermirror-coated guide of KWS-3 @ JCNS



Roughness and interdiffusion



z is a gaussian random variable with distribution function:

$$P(z) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{z^2}{2\sigma^2}\right),$$

→ Profile of refraction index between layers j and j+1:

$$n(z) = \frac{n_j + n_{j+1}}{2} - \frac{n_j - n_{j+1}}{2} \mathrm{erf}\left(\frac{z - z_j}{\sqrt{2}\sigma_j}\right) \quad \text{with} \quad \mathrm{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-t^2} dt.$$

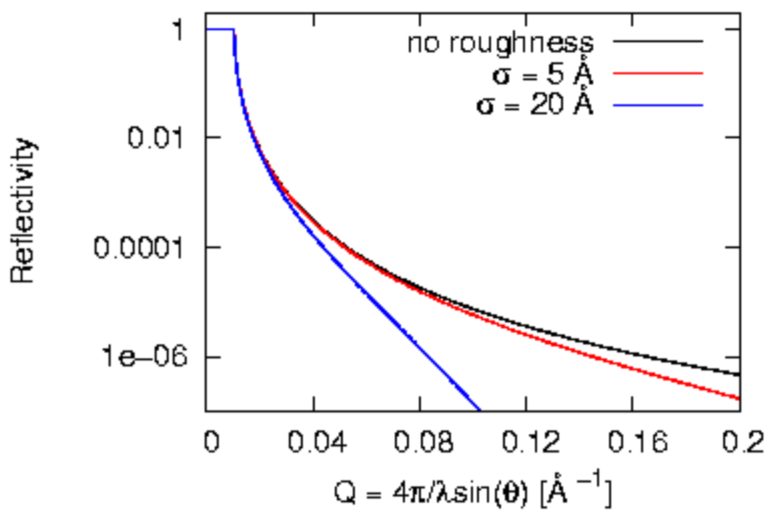
Roughness and interdiffusion

Reflectivity from such a surface obtained by averaging:

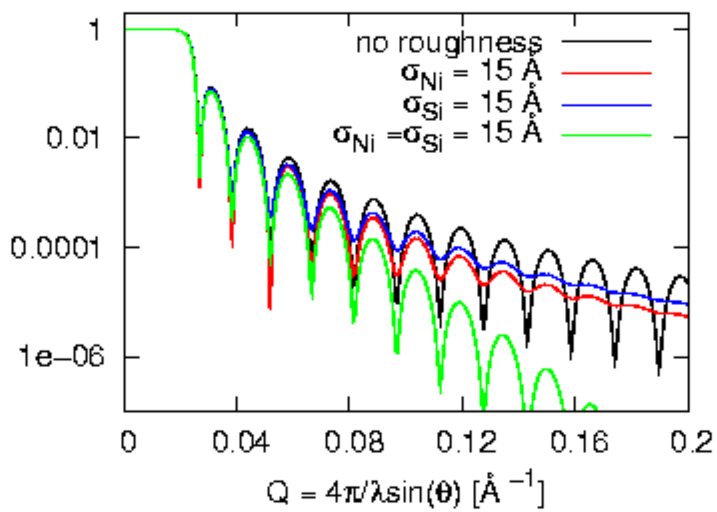
$$R_{rough} = R_{flat} \cdot \exp\left(-4\sigma_j^2 k_{zj} k_{zj+1}\right).$$

σ_j : root mean squared deviation from the nominal position of the interface

Si substrate



Ni on Si



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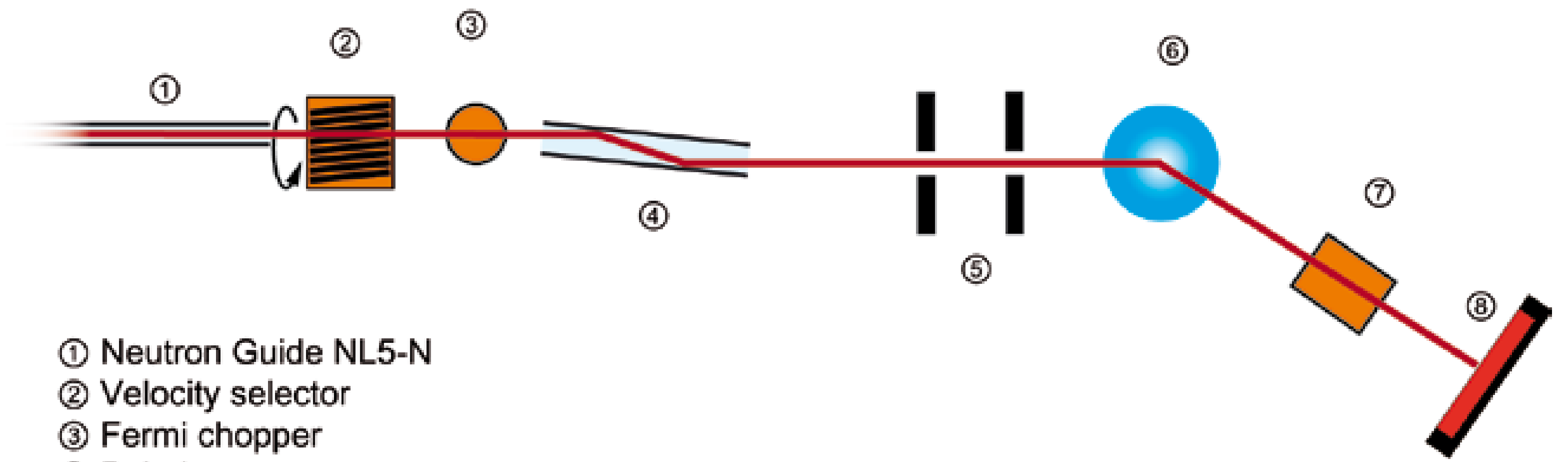
Aim : Measure R as a function of $Q = \frac{4\pi}{\lambda} \sin\theta$

in order to determine the scattering length density profile

Monochromatic instrument

- Fixed λ, varying θ



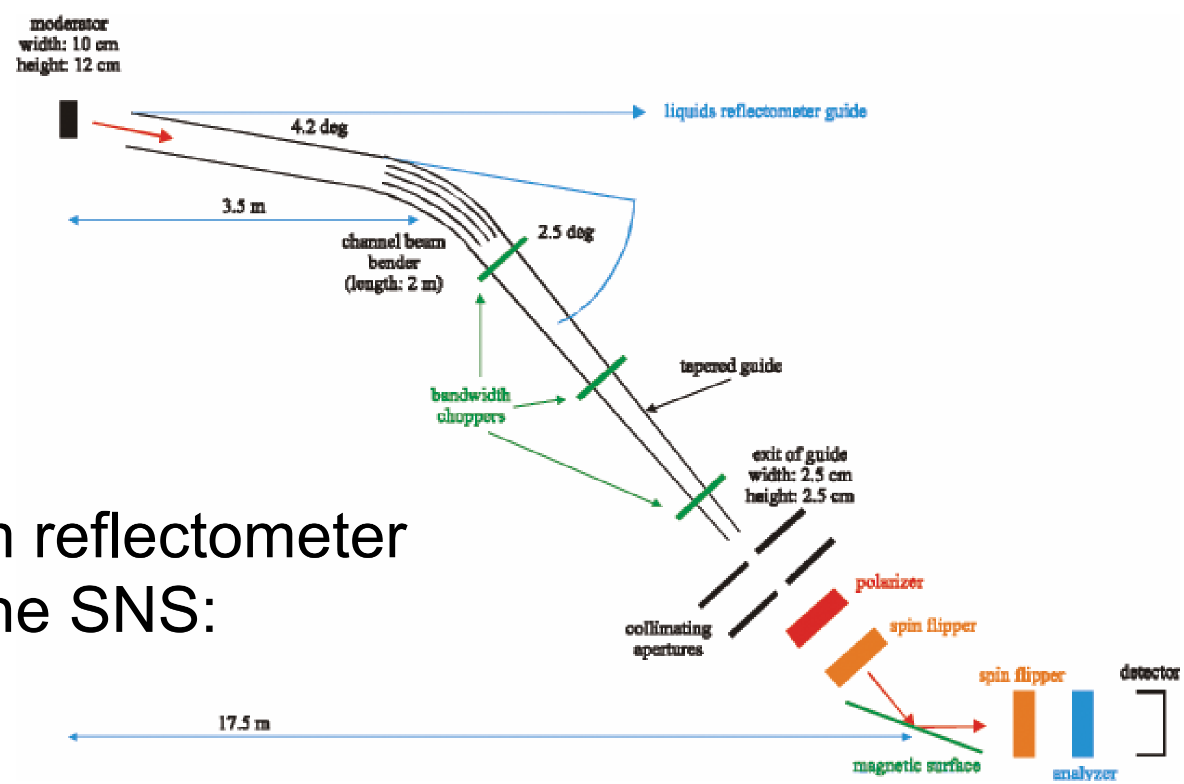
① Neutron Guide NL5-N
② Velocity selector
③ Fermi chopper
④ Polarizer
⑤ Slit pair
⑥ Hexapod sample table
⑦ Polarization analyzer (^{3}He)
⑧ Detector

MARIA of the JCNS at FRM-II

Courtesy of S. Mattauch, JCNS

Time-of-flight instrument

- Fixed θ, varying λ
- λ encoded by time of flight t over distance L: $\lambda = \frac{h}{mL} t.$



Magnetism reflectometer of the SNS:

Courtesy of V. Lauter, ORNL

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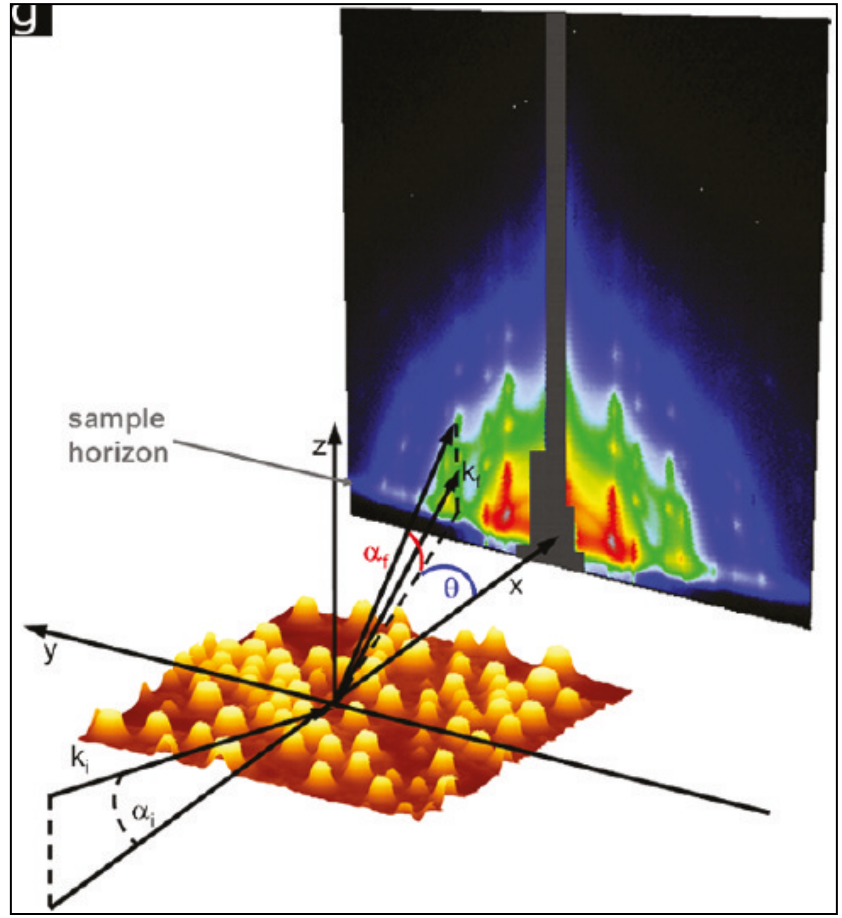
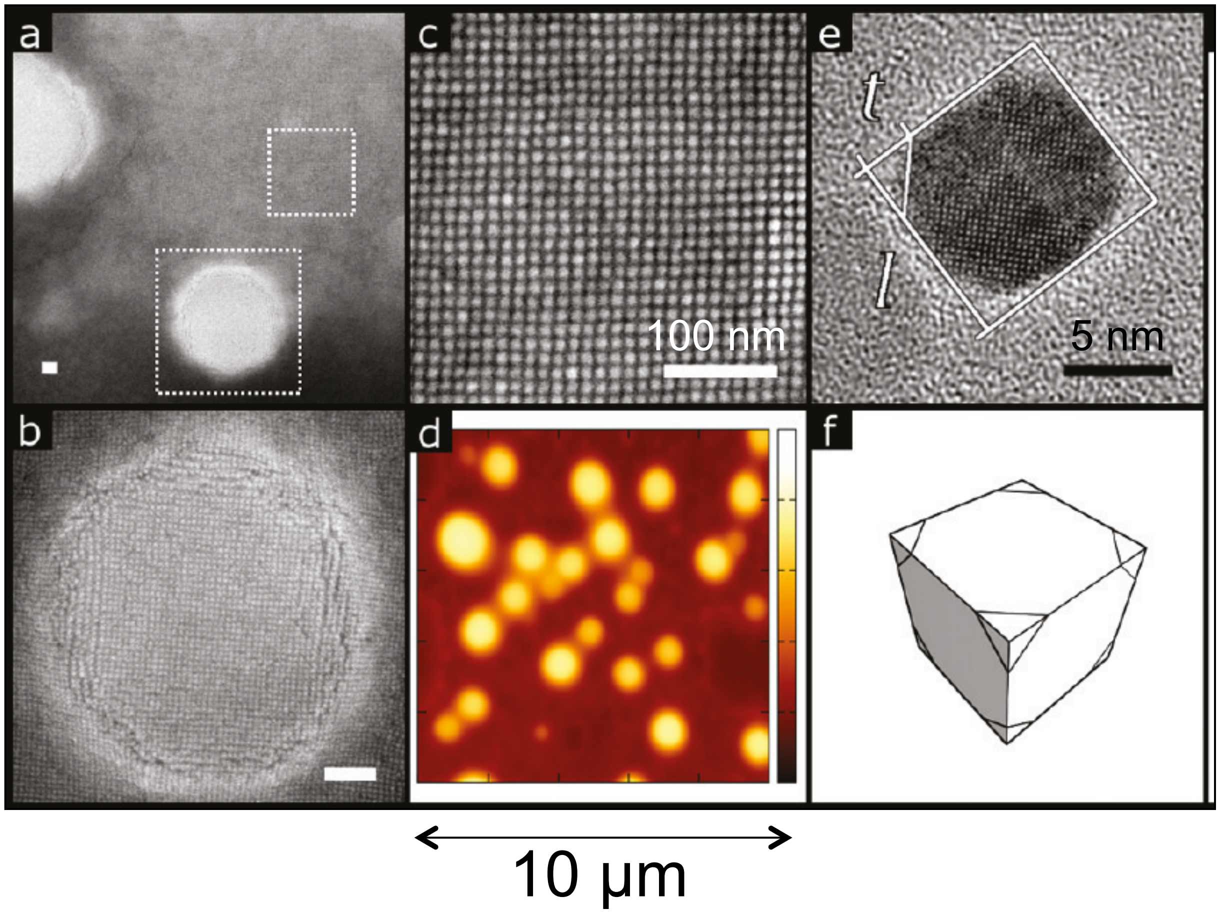
Crystallography at the nanoscale: GISAXS from nanoparticle assemblies

- Self assembled nanoparticles: materials with new functions
- In plane structure by surface sensitive techniques: SEM, AFM
- Full 3D structure by GISAXS



S. Disch, E. Wetterskog et al. Nano Letters **11**, 1651 (2011)

In-plane 2D Structure



Nanoparticles:
- Iron oxide
- Single crystalline
- Truncated cubes

Mesocrystals:
- Obtained by solvent evaporation in magnetic field
- Height: 300 nm
- Lateral: µm's

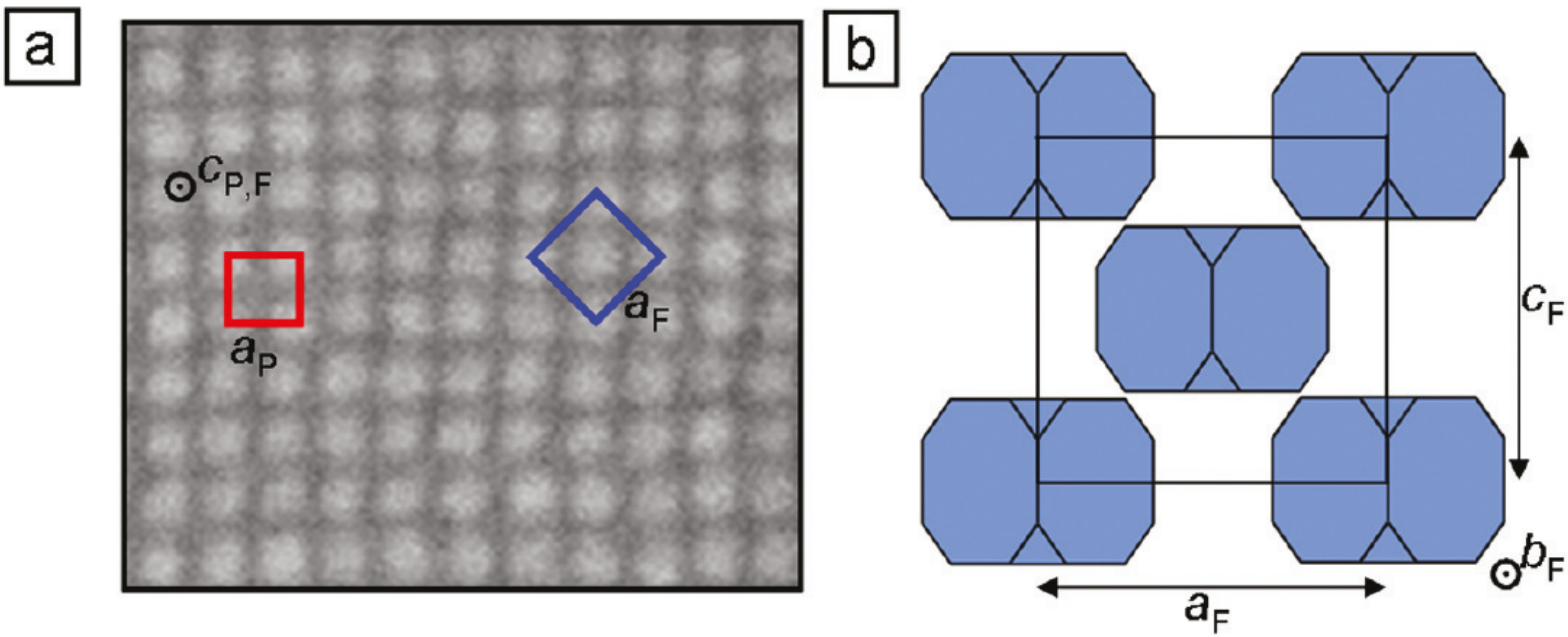
Whole sample film:
- 2D powder

Square lattice with a = 13.10(5) nm

S. Disch, E. Wetterskog et al. Nano Letters **11**, 1651 (2011)

Possible 3D structures

Five different cubic and tetragonal Bravais lattices are possible:
sc, st, bcc, bct and fcc



bcc and fcc are excluded from packing and geometrical considerations

S. Disch, E. Wetterskog et al. Nano Letters **11**, 1651 (2011)

3D structure determined by GISAXS: bct

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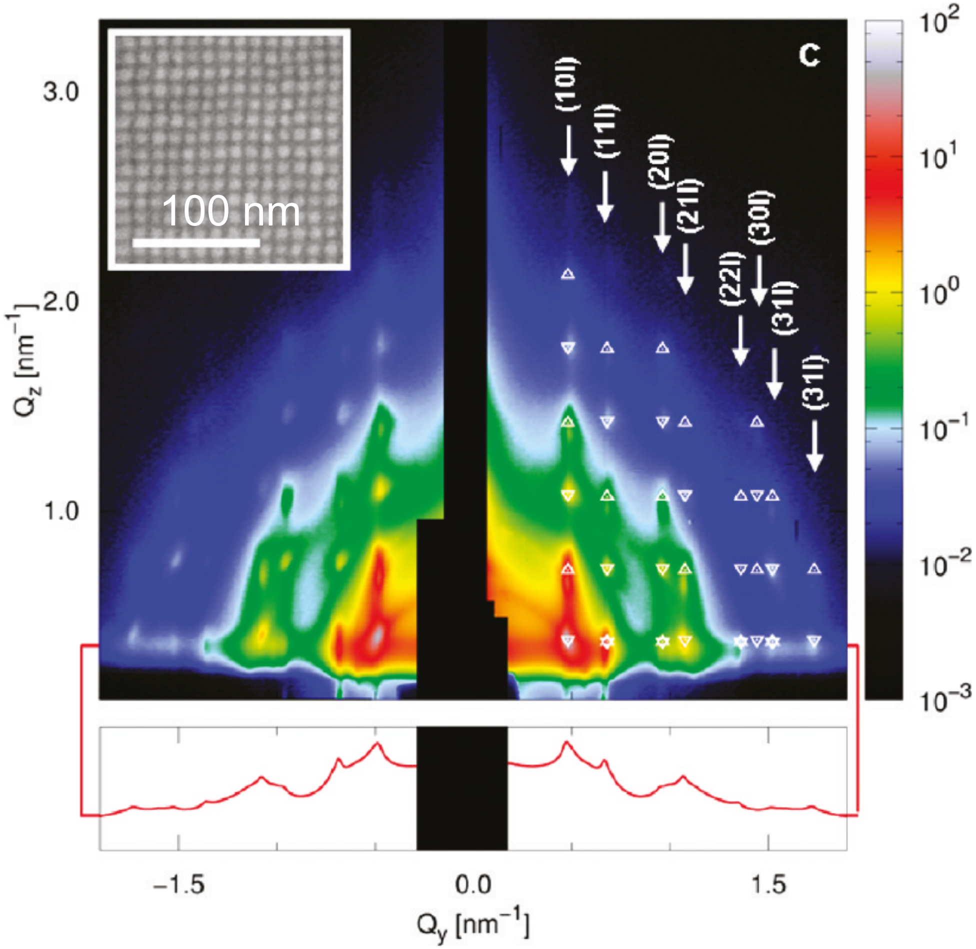
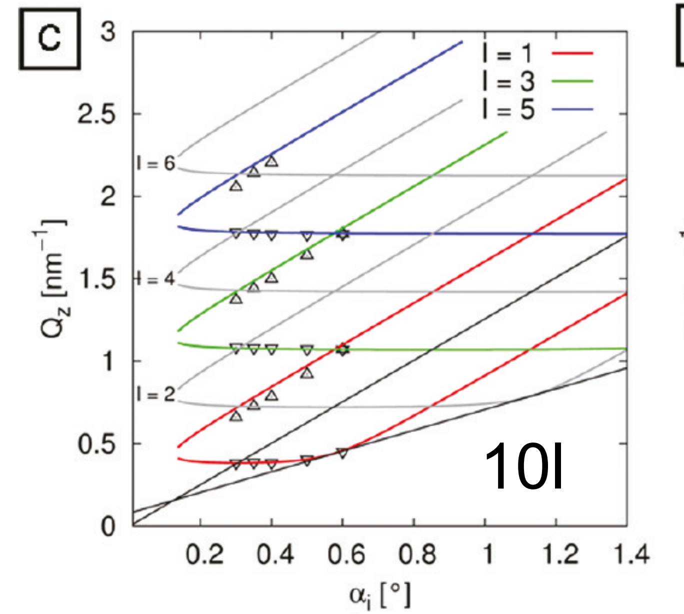
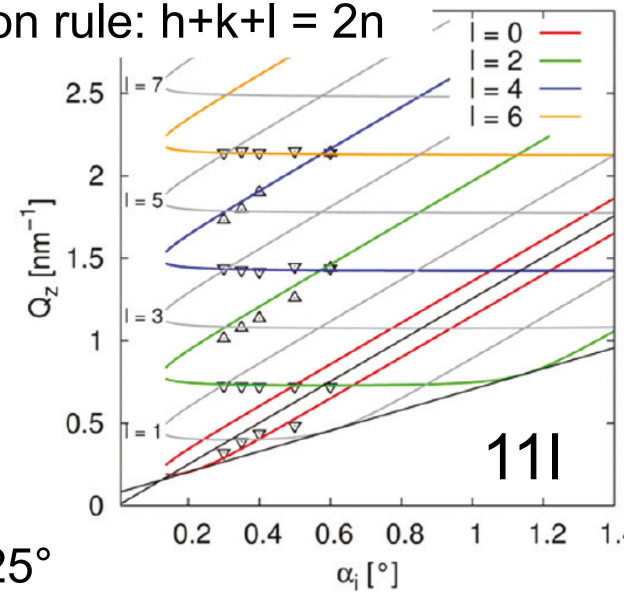




Extinction rule: h+k+l = 2n



Tetragonal lattice:

$$Q_z = k_{i,z} + \sqrt{k_{c,z}^2 + \left[\sqrt{4\pi^2\left(\frac{h^2+k^2}{a^2}+\frac{l}{c^2}\right) - Q_y^2} \pm \sqrt{k_{i,z}^2 - k_{c,z}^2}\right]^2}$$

C = 17.80(5) nm α_c = 0.125°

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Conclusion

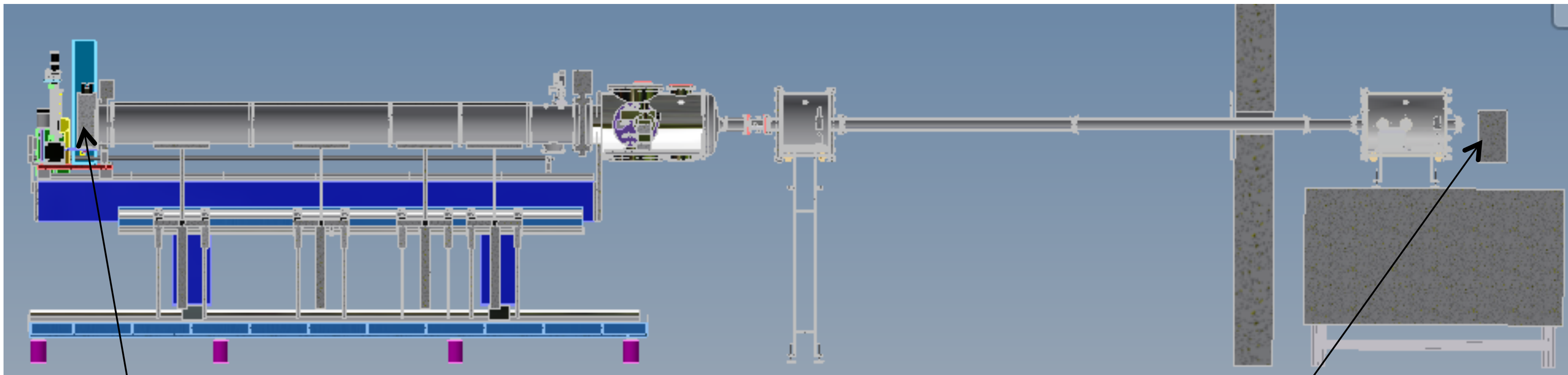
Reflectometry and grazing incidence scattering:

depth-resolved investigation of the chemical (and magnetic) order parameter(s) and its (their) in-plane fluctuations

Outlook : GALAXI@JCNS

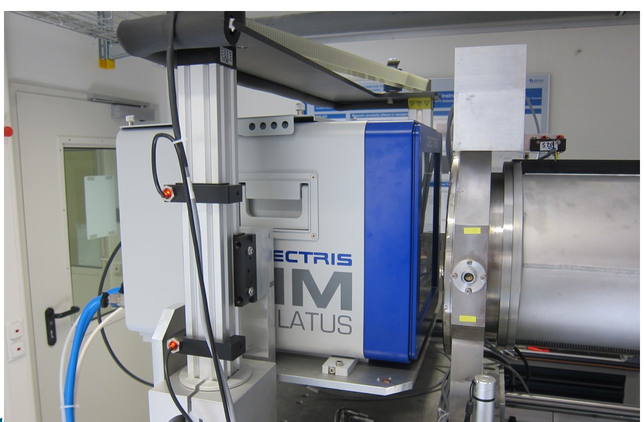
High brillance laboratory GISAXS diffractometer

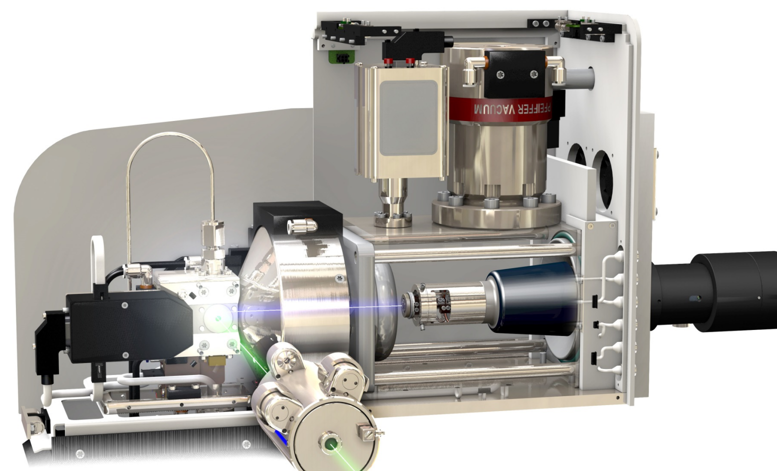
Ulrich Rücker



1M Pilatus from Dectris

Metaljet from Bruker AXS





Flux: 10^9 ph/mm^2/s

Thank you for your attention