Neutron and x-ray reflectometry
Neutron reflectometry

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10th anniversary

French-Swedish Winter School in Neutron Scattering: Applications to Soft Matter (6-9 Dec. 2016)

http://snss.se/SFN/

The Swedish Neutron Scattering Society and Société Française de Neutronique jointly organize a school on the use of neutrons for soft matter. The school will take place 6 -9 December 2016 at the Ångström Laboratory of Uppsala University, Sweden. For more information, program and registration please visit the school's webpage at: http://snss.se/SFN/

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Reflection from interfaces

Content

Recapture: Scattering problem

Scattering at small momentum transfer

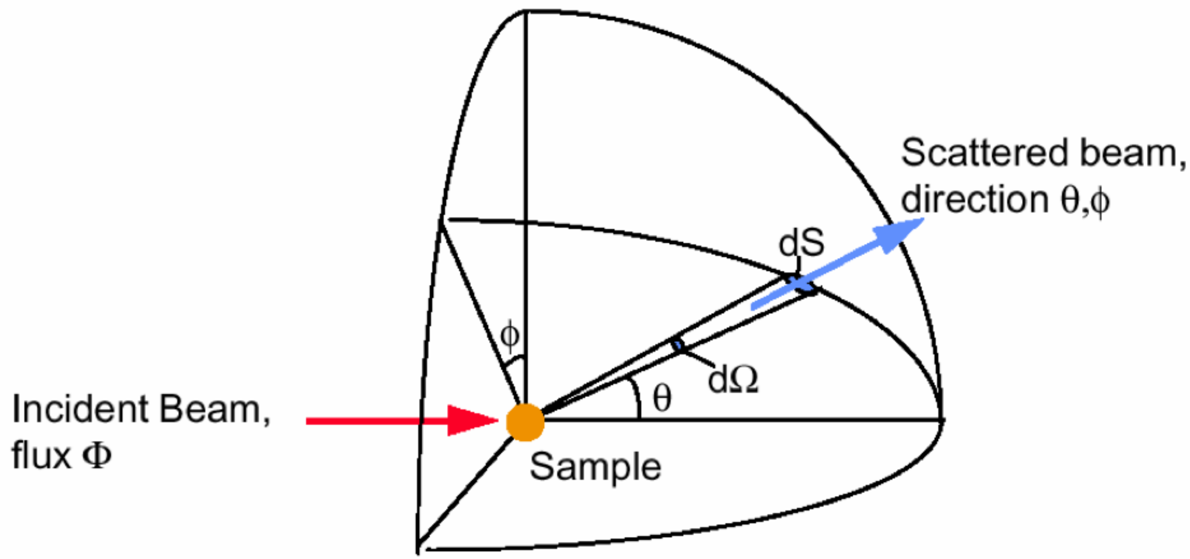
Specular reflectivity

Off-specular scattering

Gracing incidence scattering

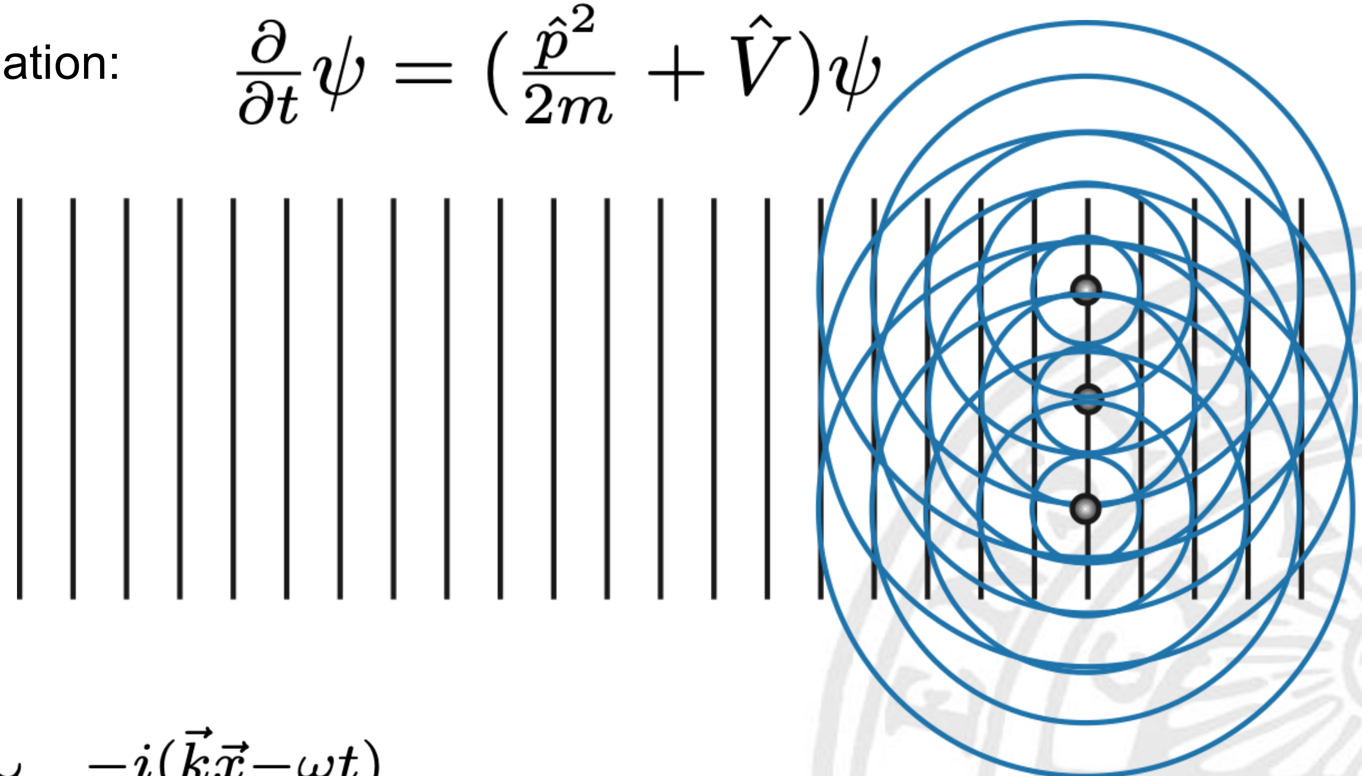
What do we measure?

Φ = number of incident particles per area and time
σ = total number of particles scattered per time and Φ
$d\sigma/d\Omega$ = number of particles scattered per time into a certain direction per area and Φ
$d^2\sigma/d\Omega dE$ = number of particles scattered per time into a certain direction per area with a certain energy per energy interval and Φ



The scattering problem

Schrödinger equation: $$\frac{\partial}{\partial t}\psi = \left(\frac{\hat{p}^2}{2m} + \hat{V}\right)\psi$$



$$\psi_i(\vec{r},\omega) \cong e^{-i(\vec{k}\vec{x}-\omega t)}$$

$$\psi_f(\vec{r},\omega) \cong e^{-i(\vec{k}\vec{x}-\omega t)} + f(\theta)\frac{e^{-i(\vec{k}\vec{r}-\omega t)}}{\vec{r}}$$

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Potential

$$S(Q,E) = \frac{4\pi}{\sigma_s}\frac{k_i}{k_f}\frac{\partial^2\sigma}{\partial\Omega\partial E_f} \cong \sum_{\alpha'\alpha}\rho(E_f)\left|\langle k_f, E_f|\hat{V}|k_i, E_i\rangle\right|^2\delta(\hbar\omega - E_{\alpha'\alpha})$$

This equation is also known as scattering law or dynamical structure factor. It **completely describes the structural and dynamic properties** of the sample.

For neutrons (scattering at the core) wave length (10^{-10} m) is much larger than the size of the scattering particle (10^{-15} m). This implies that no details of the core can be seen and the scattering potential can be described by a single constant b, the scattering length:

$$V(\vec{r}) = \frac{2\pi h}{m} b\delta(\vec{r} - \vec{R})$$

This is called the Fermi pseudo potential. b is a phenomenological constant and has to be determined experimentally.

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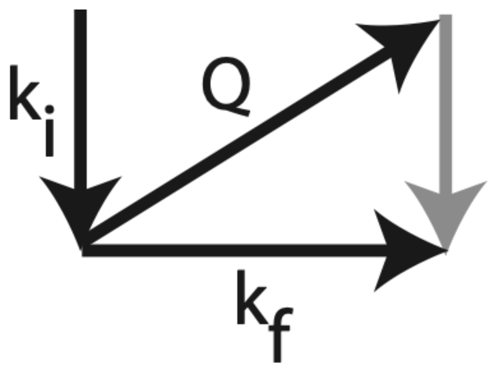
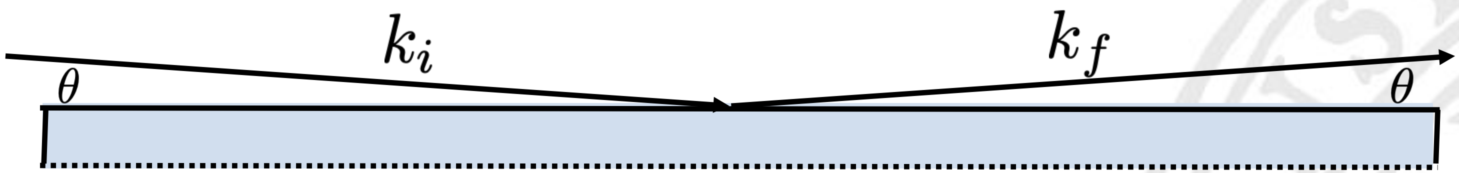
Small momentum



$$\vec{Q} = \vec{k}_f - \vec{k}_i$$

$$|Q| = \frac{2\pi}{\lambda} sin(2\theta)$$

$$\omega = \frac{\hbar k_f^2}{2m} - \frac{\hbar k_i^2}{2m}$$



Example: Wavelength 1 nm scattered at an angle of 0.6°.

Q = 0.0658 nm^{-1},
and a length scale of approx. 100 nm is probed

No details on the atomic ordering seen anymore
Continuum theory

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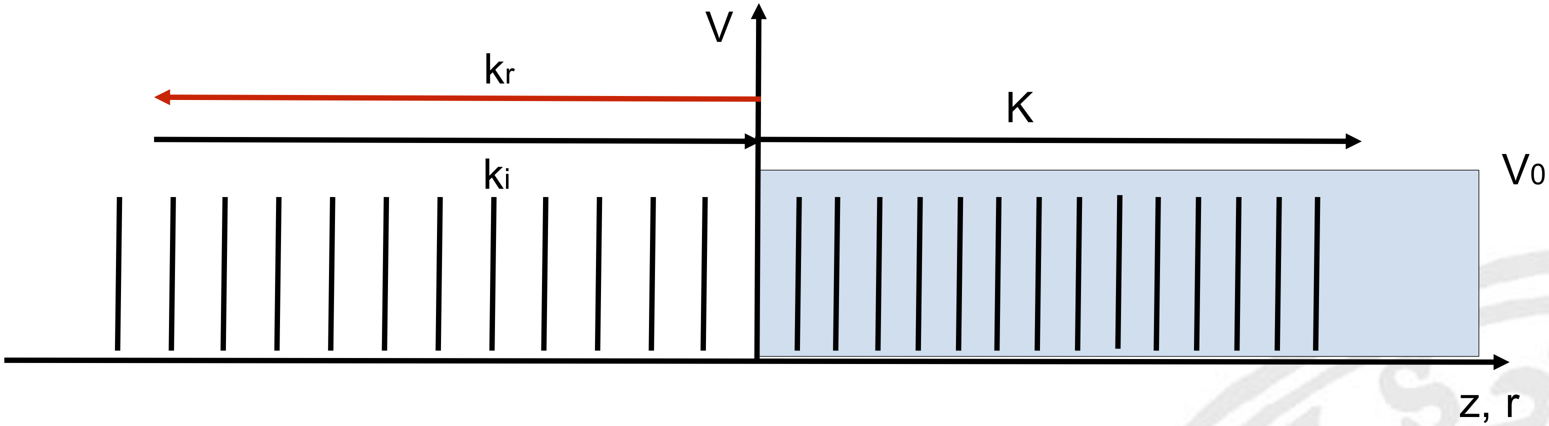
Scattering length density



$$V_0 = \frac{2\pi\hbar^2}{m_n}\sum b_{coh,i}\rho_{n,i} = \frac{2\pi\hbar^2}{m_n}SLD$$

$$\rho_n = \frac{\rho N_A}{m_a}$$

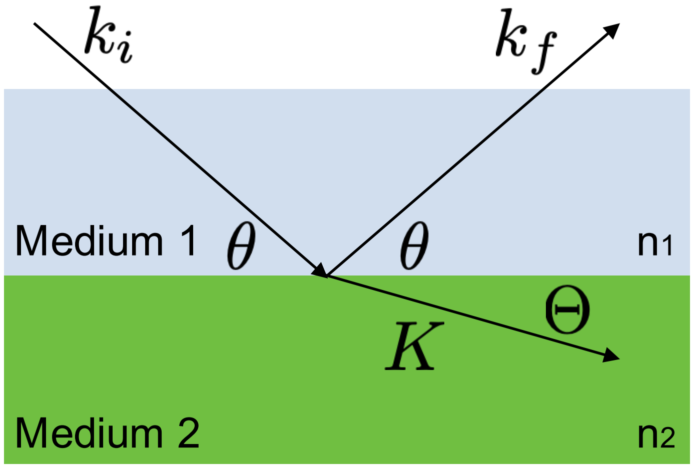
Examples:

H_2O: $\rho_n = \frac{1}{30}\frac{1}{\mathring{A}^3}$ $\sum b_i = -1.68 * 10^{-5}\mathring{A}$ $SLD = -0.56 * 10^{-6}\frac{1}{\mathring{A}^2}$

D_2O: $\rho_n = \frac{1}{30}\frac{1}{\mathring{A}^3}$ $\sum b_i = 19.15 * 10^{-5}\mathring{A}$ $SLD = 6.4 * 10^{-6}\frac{1}{\mathring{A}^2}$

Reflection and refraction

General case

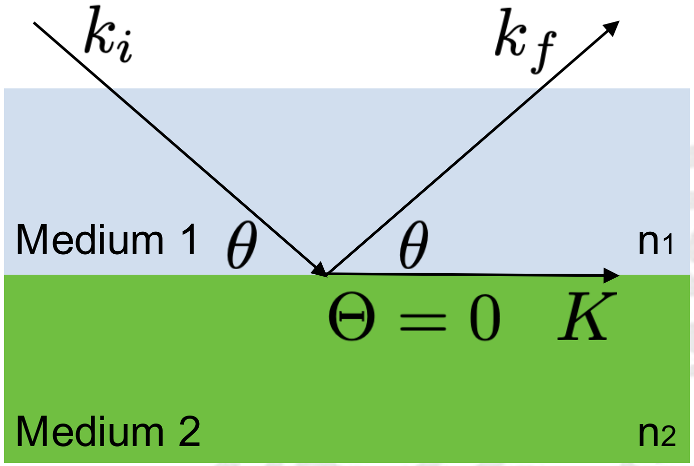


Snellius law:

$$\frac{n_2}{n_1} = \frac{\cos\theta}{\cos\Theta}$$

$$n_1 < n_2$$

Evanescent wave



$$\frac{n_2}{n_1} = \cos\theta_c$$

For $n_1 = 1$: $n = \cos\theta_c$

$$Q_c = \frac{4\pi}{\lambda}\sin\theta_c = 2k\sqrt{1 - cos^2\theta_c}$$

$$Q_c = \sqrt{4k^2(1-n^2)} = \sqrt{16\pi SLD}$$

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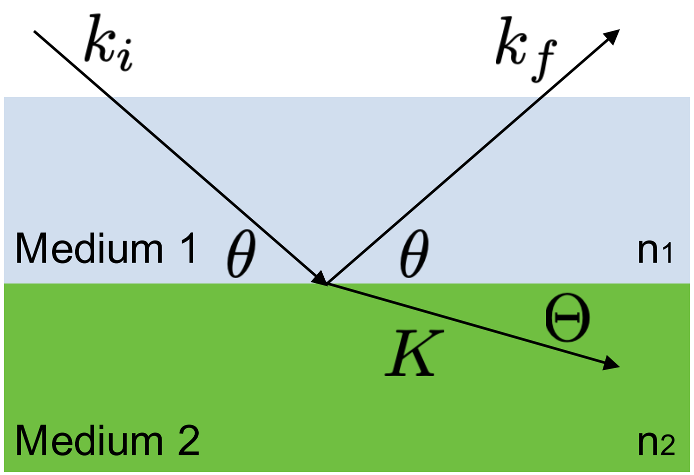
Fresnel reflectivity



Specular condition: $k_{i\perp} = k_{f\perp} = k_\perp$

Continuity of wave functions:

$$1 + r = t$$

$$k_{i\perp}(1 - r) = K_\perp t$$

Reflection coefficient:

$$r = \frac{k_\perp - K_\perp}{k_\perp + K_\perp}$$

Transmission coefficient:

$$t = \frac{2k_\perp}{k_\perp + K_\perp}$$

Above the surface:

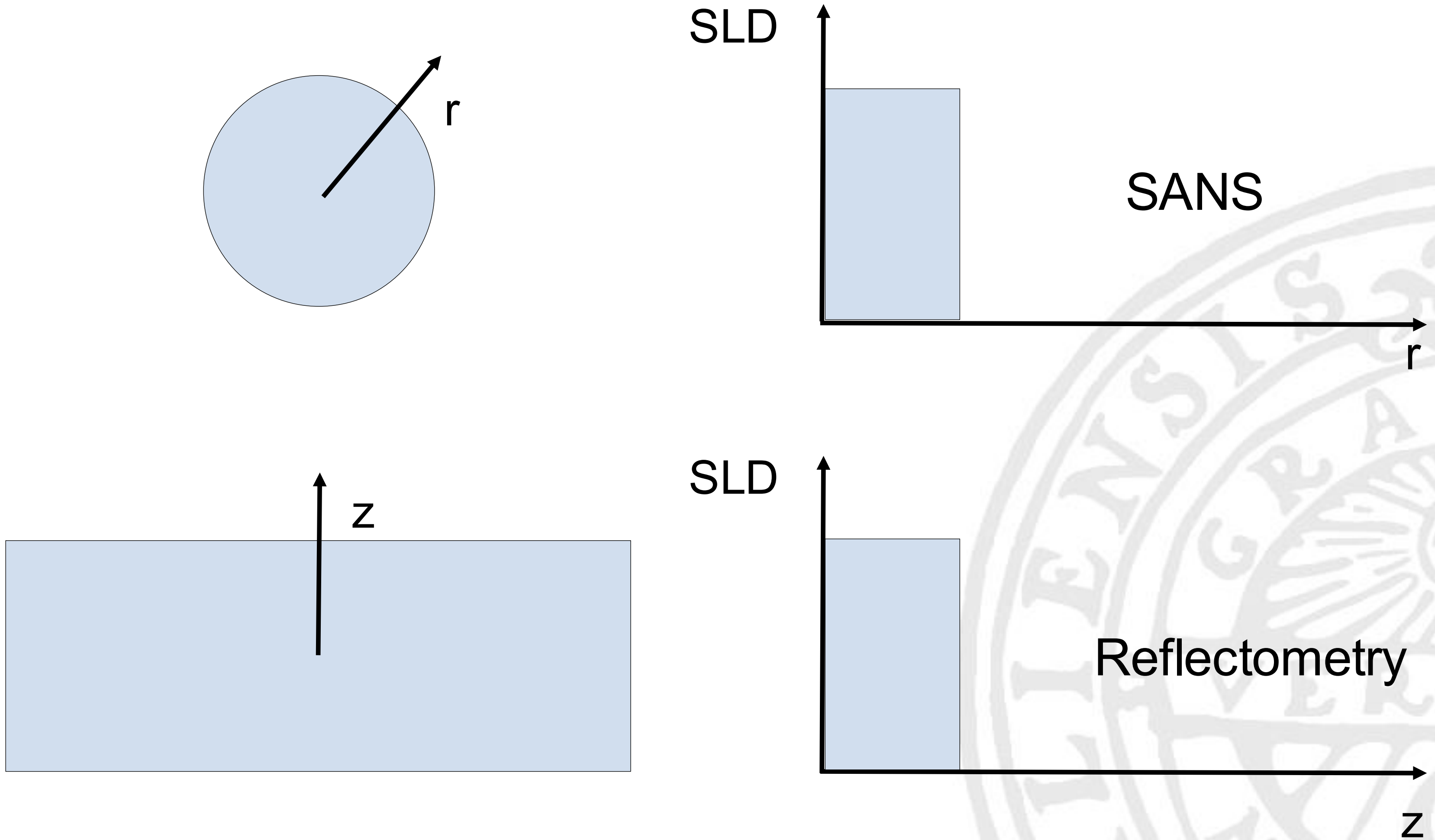
$$\Psi_z = e^{ik_{i\perp},z} + re^{ik_{f\perp},z}$$

Below the surface:

$$\Psi'_z = te^{iK_{\perp},z}$$

For $Q_z >> Q_c$: $R = r^2 \approx \frac{Q_c^2}{Q_z^4}$

Density profil



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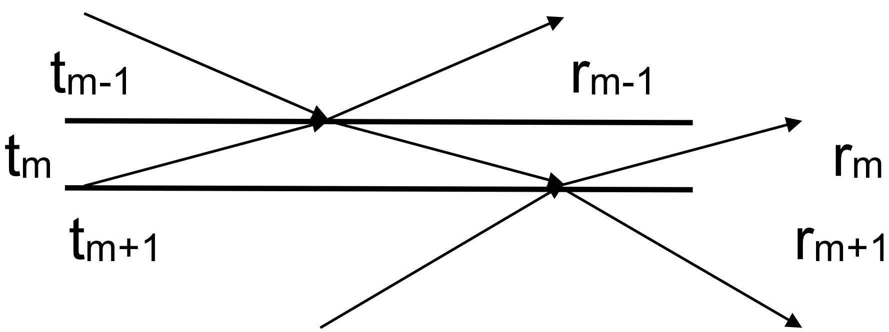
Non sharp/multiple interfaces - Layers

Non sharp interfaces (Born approximation):

$$R(Q_z) = R_F(Q_z)\frac{1}{SLD}\int \frac{\partial SLD}{\partial z} e^{iQ_z z} dz$$

Layers:



Fresnel amplitude for the interface m, m-1:

$$R_{m,m-1} = a_{m-1}^4 \left(\frac{R_{m+1,m} + F_{m-1,m}}{R_{m+1,m}F_{m-1,m} + 1} \right)$$

$$R_{m,m+1} = a_m^2 \frac{r_m}{t_m}$$

$$F_{m-1,m} = \left(\frac{Q_{m-1} - Q_m}{Q_{m-1} + Q_m} \right)$$

$$a_m = e^{\frac{iQ_m d_m}{2}} \qquad Q_m = \sqrt{Q_z^2 - Q_{c,m}^2}$$

Parratt 1954, Phys. Rev. 95, 359 (1954)

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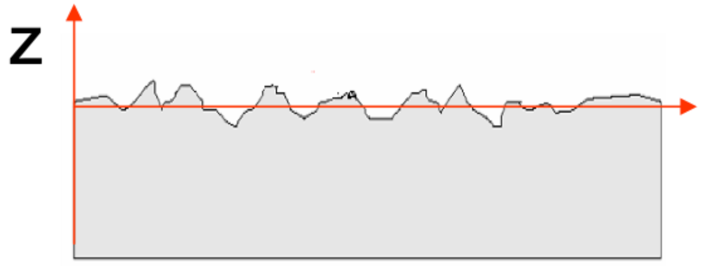
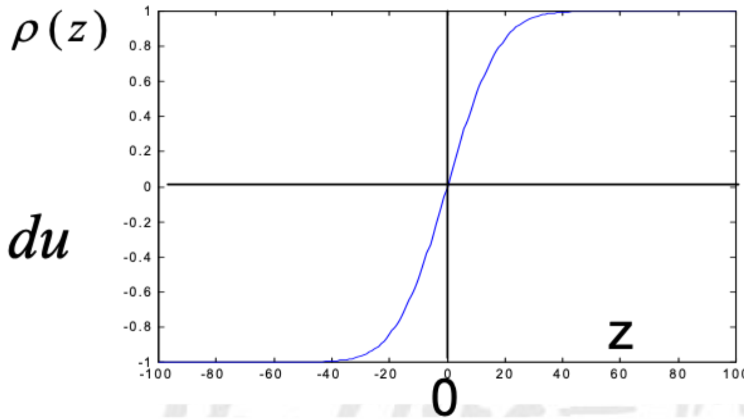
Rough surface



$$\updownarrow \sigma = \sqrt{\overline{(\Delta z)^2}}$$

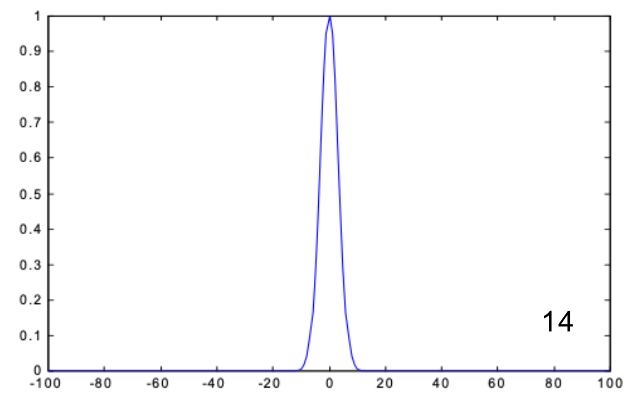


Surface profile (error function):

$$\rho(z) = \rho_0 erf(z) = \frac{\rho_0}{\sqrt{2\pi}\sigma}\int_0^z e^{-u^2/2\sigma^2}du$$

Derivative:

$$\frac{d\rho(z)}{dz} = \frac{\rho_0}{\sqrt{2\pi}\sigma}e^{-u^2/2\sigma^2}$$



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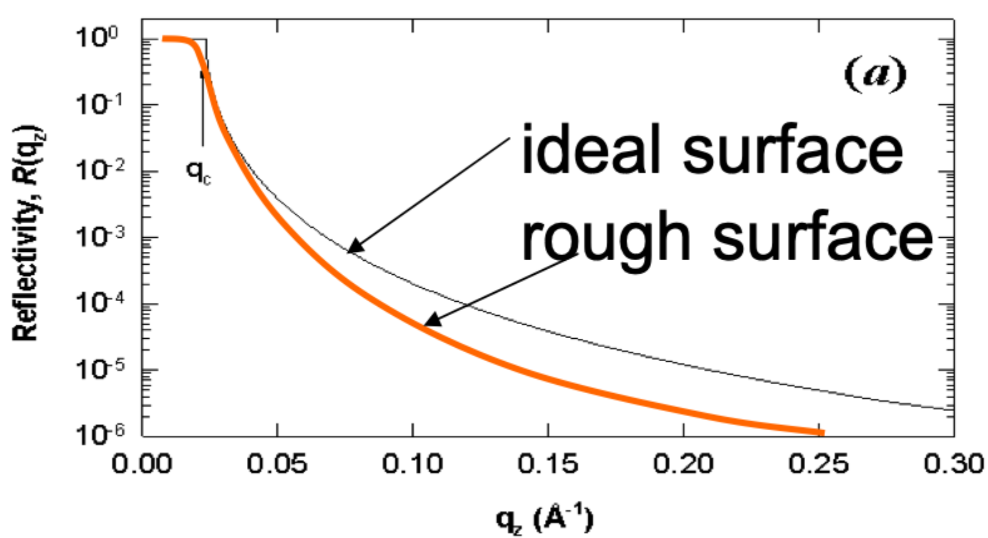
Gaussian roughness

Master formular yields for a Gaussian roughness a damped Fresnel reflectivity:

$$R(Q_z) = R_F(Q_z)\exp(-Q_z^2\sigma^2)$$

$R_F(Q_z)$ is the Fresnel reflectivity of the ideal surface. Roughness adds a damping factor, similar to the Debye-Waller factor:



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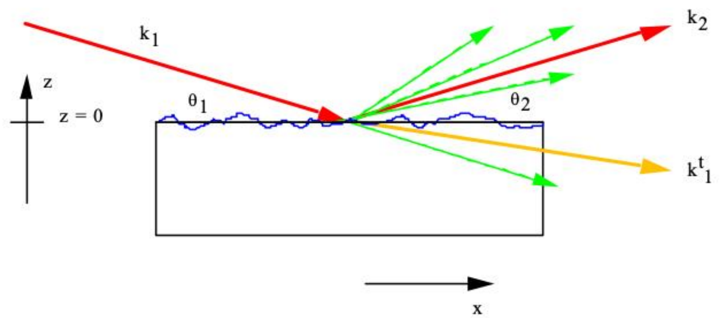
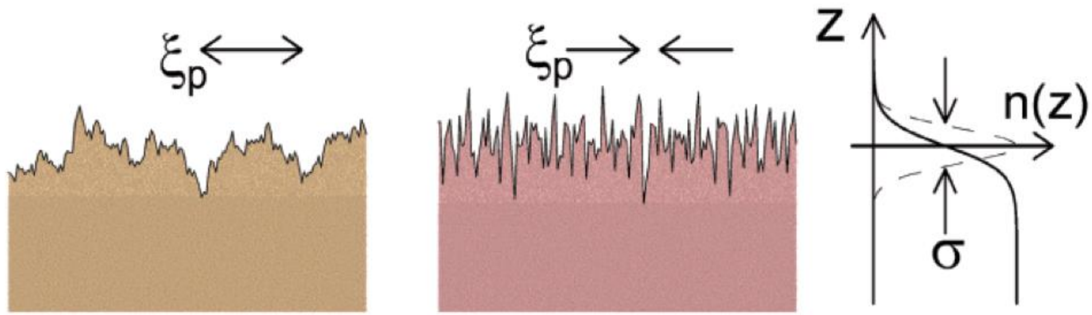
Roughness length scales

- Surface roughness causes diffuse (non-specular) scattering and so reduces the magnitude of the specular reflectivity



- The way in which the specular reflection is damped depends on the length scale of the roughness in the surface as well as on the magnitude and distribution of roughness



Note that roughness introduces a SLD profile averaged over the sample surface

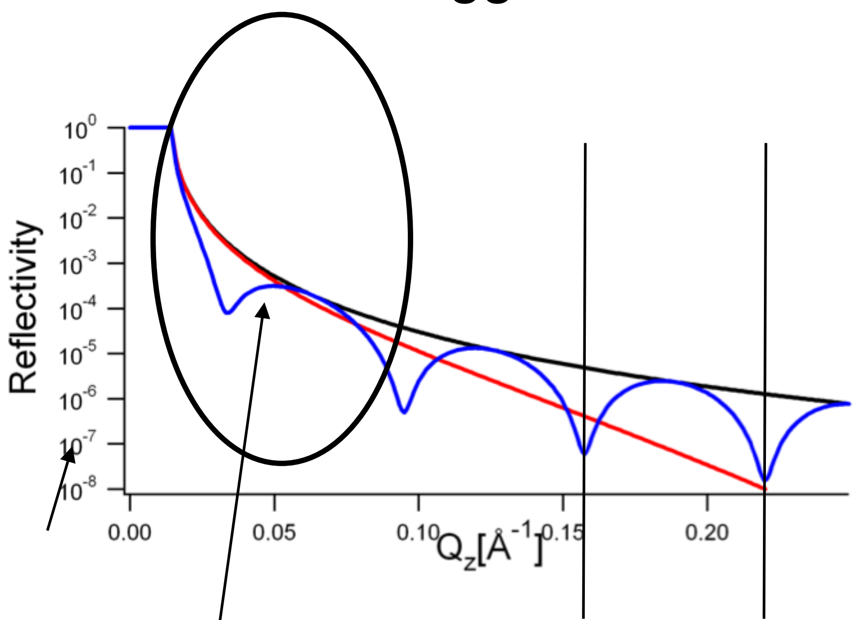
"sparkling sea"model -- specular from many facets

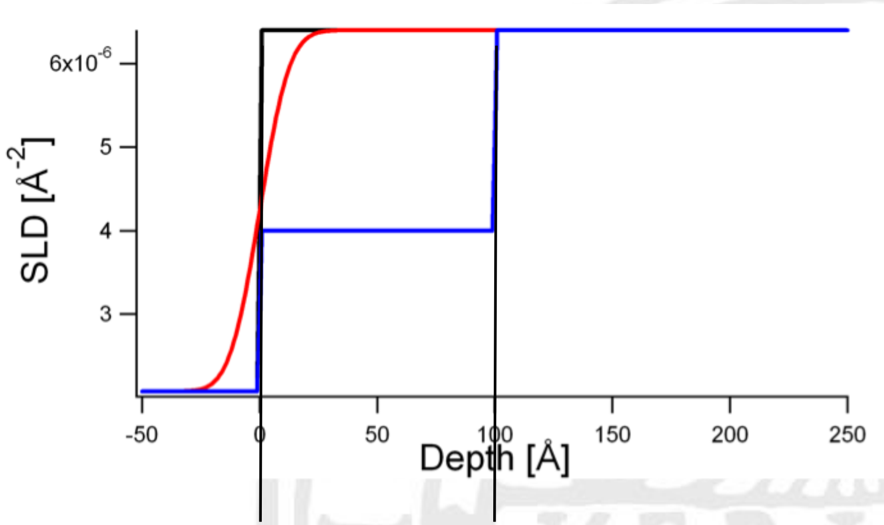
each piece of surface scatters indepedently -- Nevot Croce model

$$R = R_F e^{-2k_{Iz}k^t_{1z}\sigma^2}$$

Reflectivity

Braggs law: $n\lambda = 2d \sin\theta$





Huge dynamic range

$$\frac{2\pi}{d} = 0.63\ nm^{-1}$$

10 nm

Optical correction needed: $Q_z = \sqrt{Q_m^2 - Q_c^2}$

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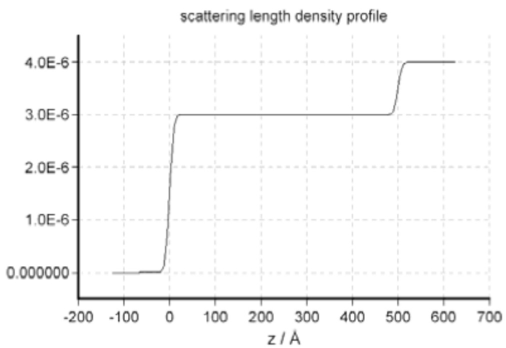
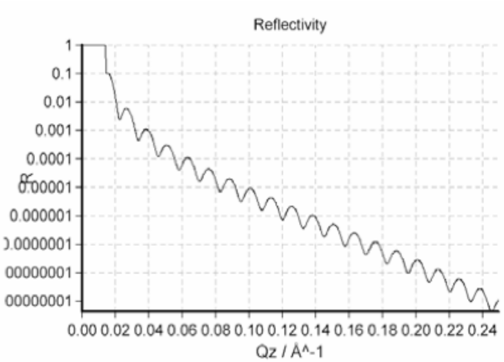
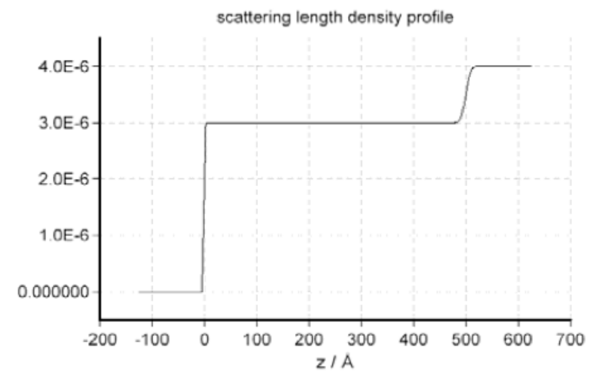
Rough surface and interface

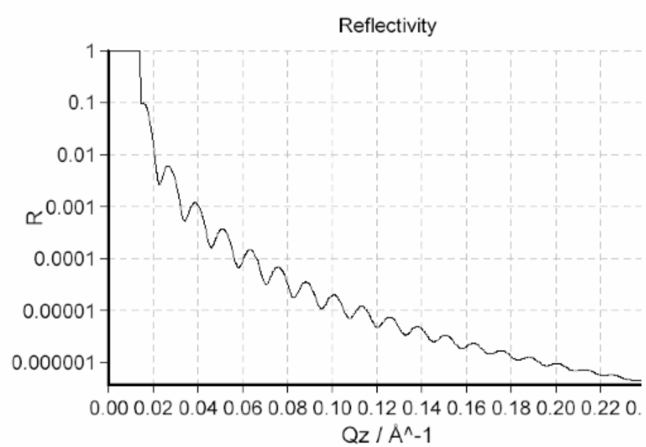
Rough surface, rough interface



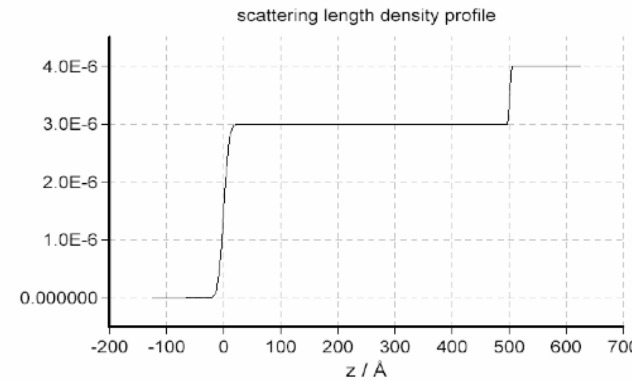


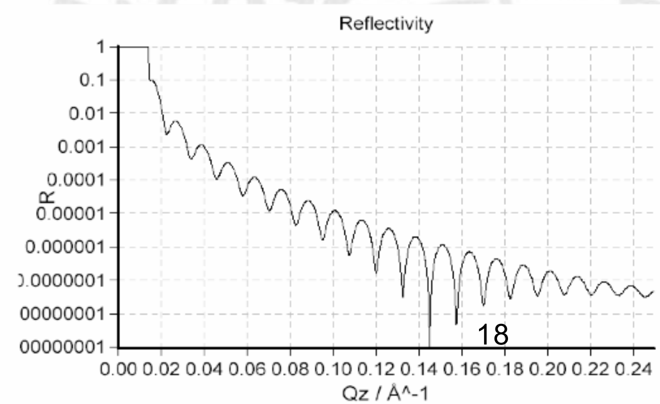
smooth surface, rough interface



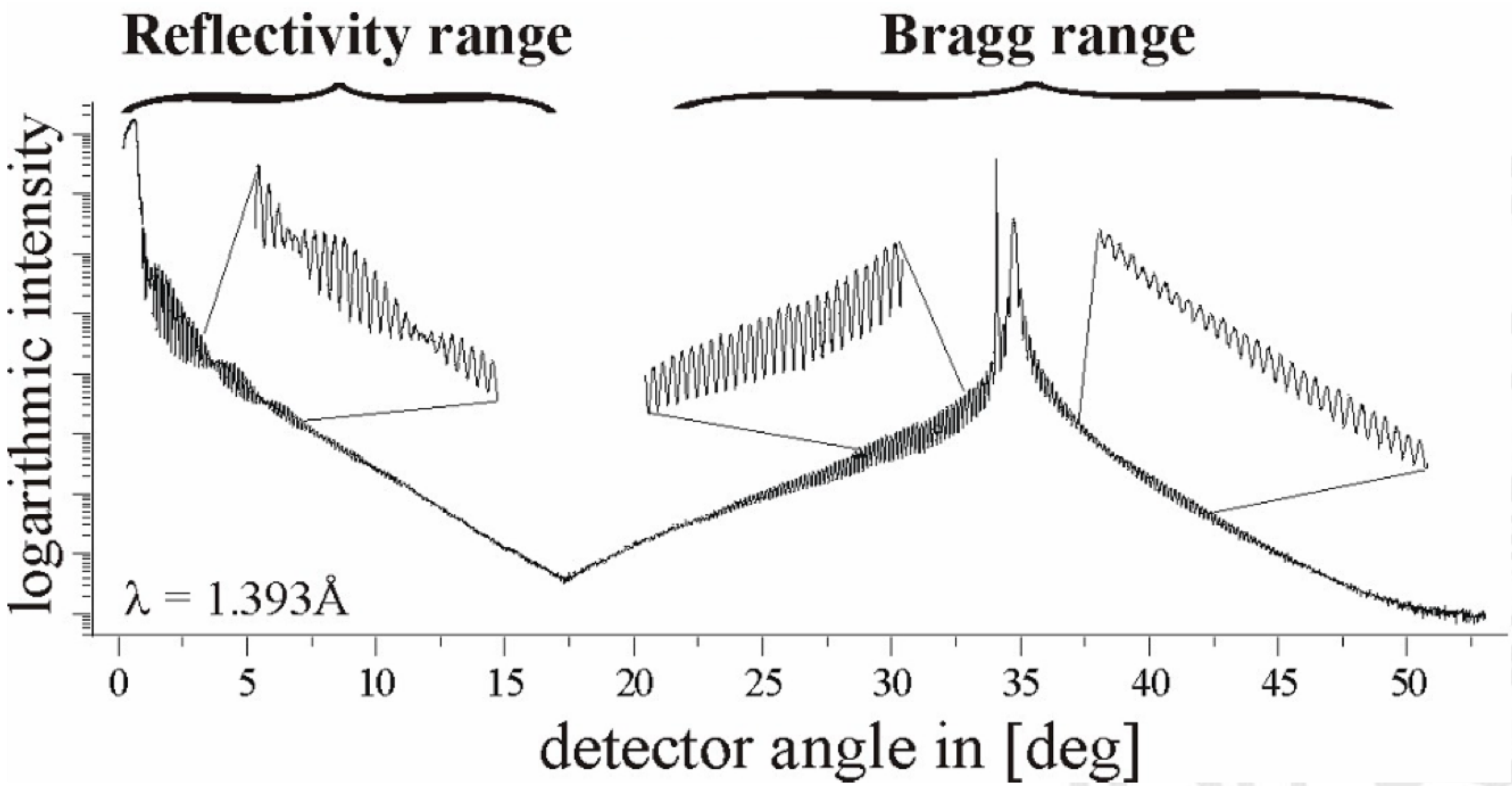


rough surface, smooth interface



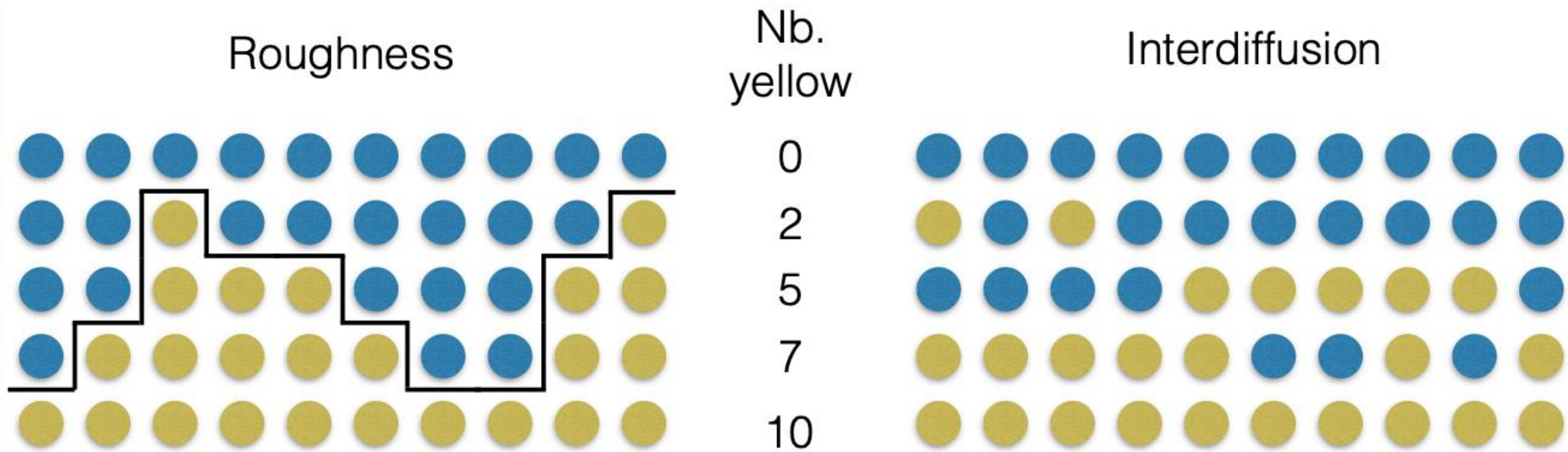


Reflectivity - Bragg range



O. Hellwig, PhD Thesis, RUB 2000

Roughness or interdiffusion



The reflectivity is the same!

Diffuse scattering

Scattering function in the Born approximation:

$$S(\vec{Q}) = \int \langle \rho(0)\rho(R) \rangle e^{i\vec{Q}\bullet\vec{R}} d^3R$$

Pair correlation function:

$$C(\vec{R}) = \langle (\rho(0) - \langle \rho(0) \rangle)(\rho(\vec{R}) - \langle \rho(\vec{R}) \rangle) \rangle$$
$$= \langle \rho(0)\rho(\vec{R}) \rangle - \langle \rho(0) \rangle \langle \rho(\vec{R}) \rangle$$
$$= \langle \rho(0)\rho(\vec{R}) \rangle - \langle \rho(0) \rangle^2$$

Inserting:

$$S_{tot}(\vec{Q}) = \underbrace{\langle \rho(0) \rangle^2 \int e^{i\vec{Q}\bullet\vec{R}} d^3R}_{\textbf{Specular Reflection}} + \underbrace{\int C(\vec{R}) e^{i\vec{Q}\bullet\vec{R}} d^3R}_{\textbf{Diffuse Scattering}}$$

$$= S_{spec}(\vec{Q}) + S_{diff}(\vec{Q})$$

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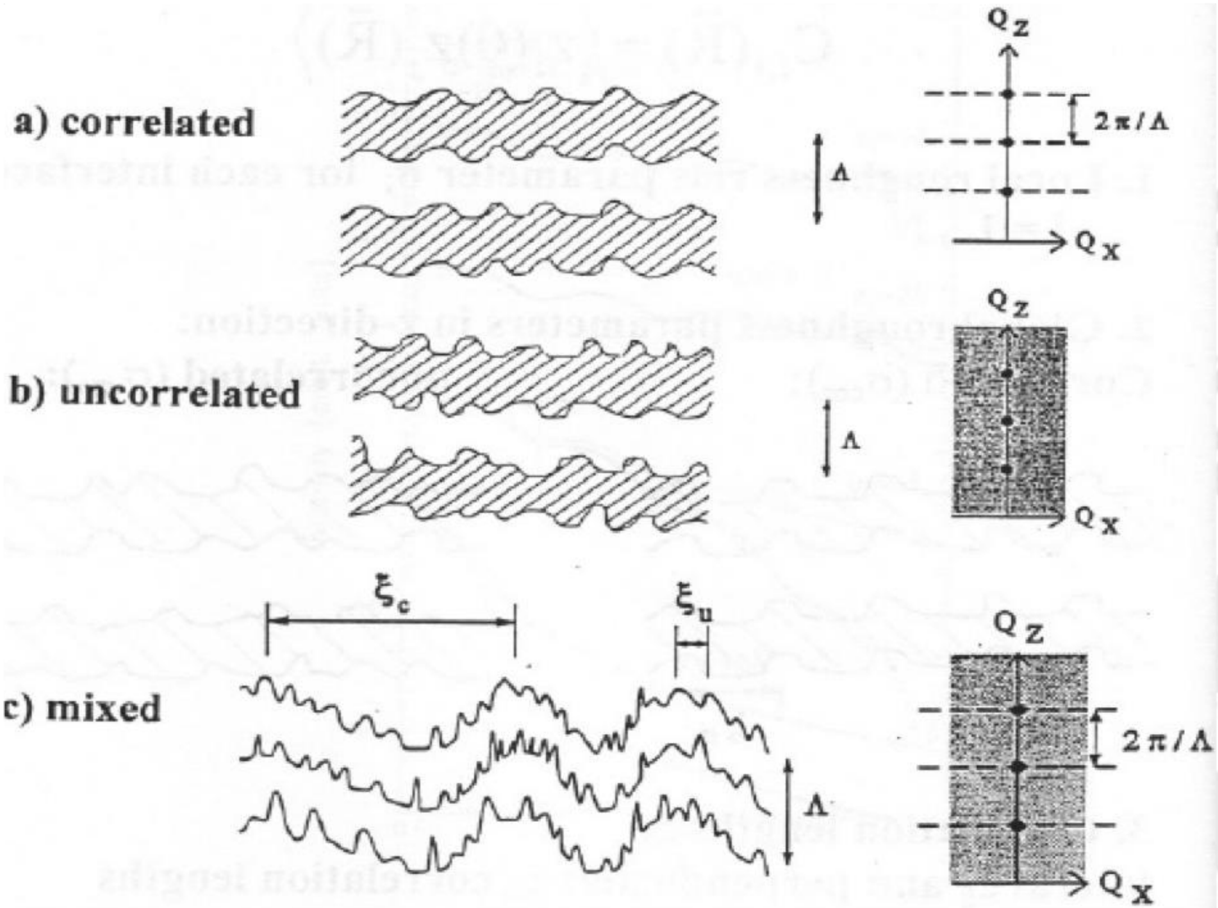
Diffuse scattering from multilayers

Real space: **Reciprocal space:**



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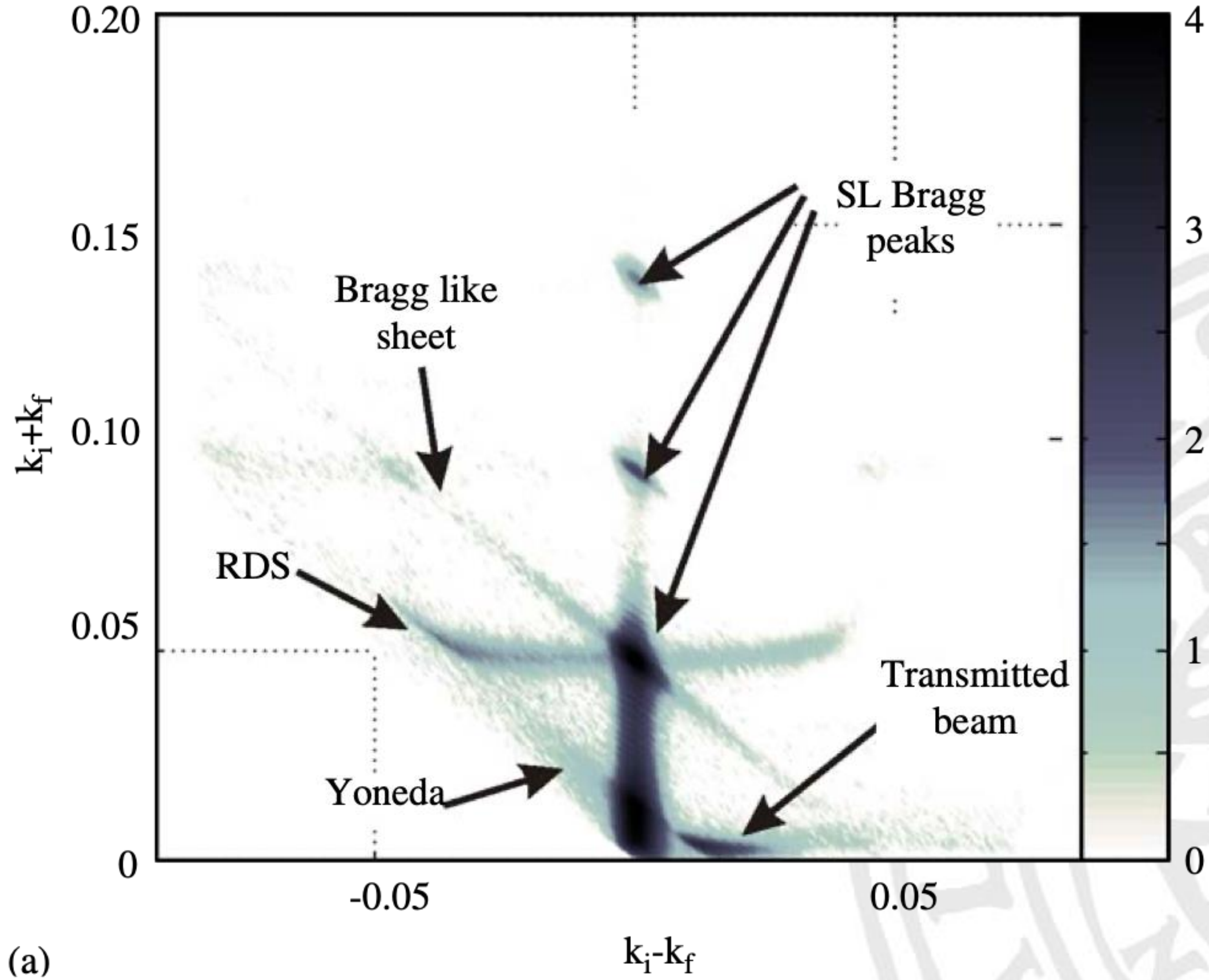
Resonant diffuse scattering



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Grazing incidence scattering

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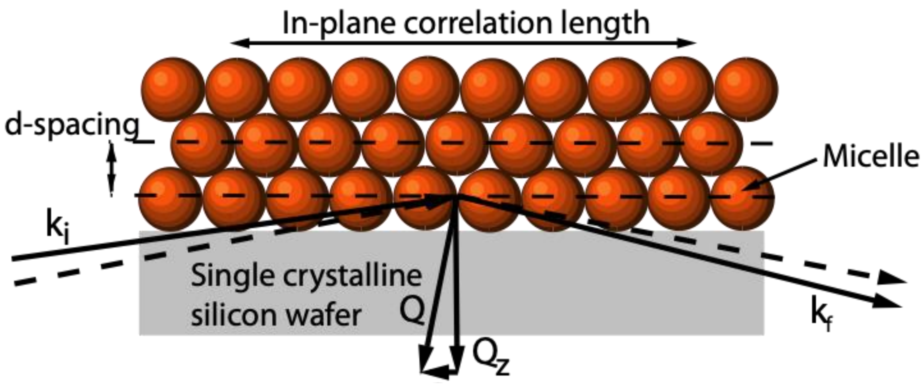
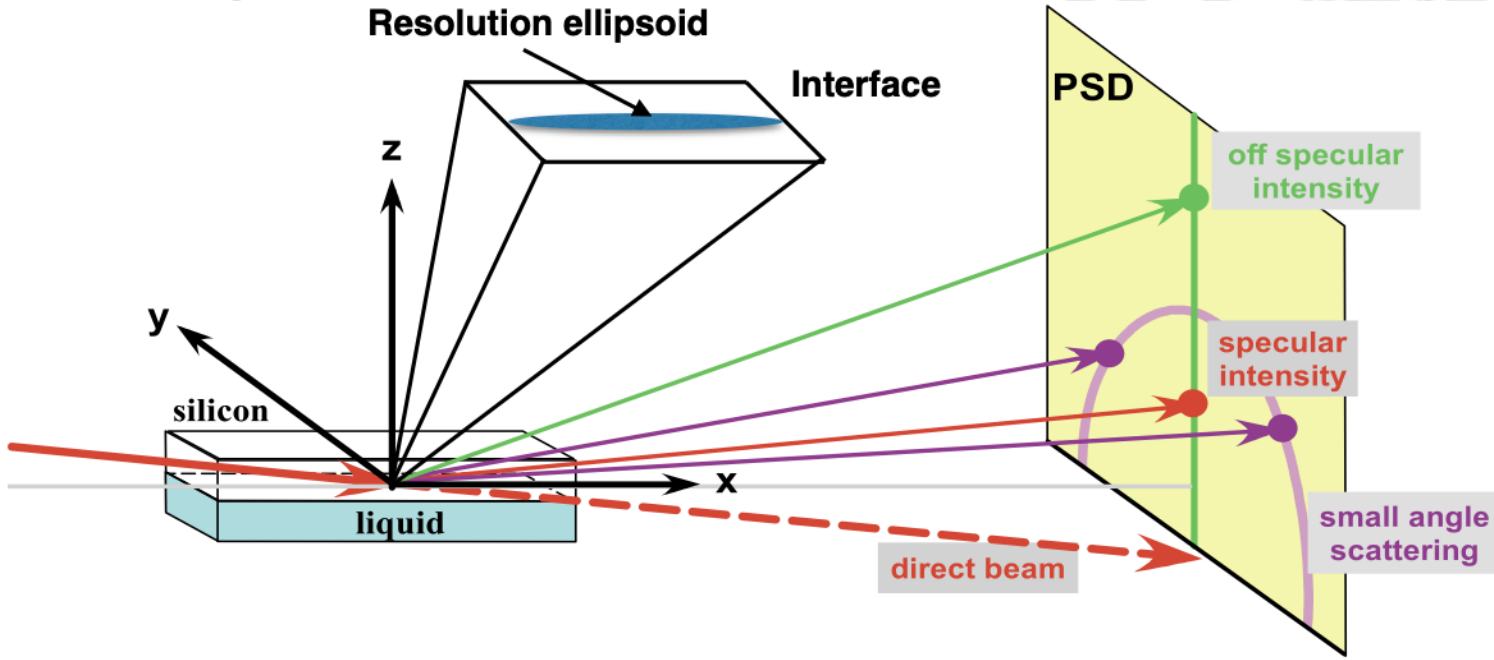


$$Q_x = \frac{2\pi}{\lambda}[cos(\alpha_i) - cos(\alpha_f)]$$

$$Q_y = \frac{2\pi}{\lambda}[sin(\phi_f) - 0]$$

$$Q_z = \frac{2\pi}{\lambda}[sin(\alpha_i) + sin(\alpha_f)]$$



Coherent and incoherent sum

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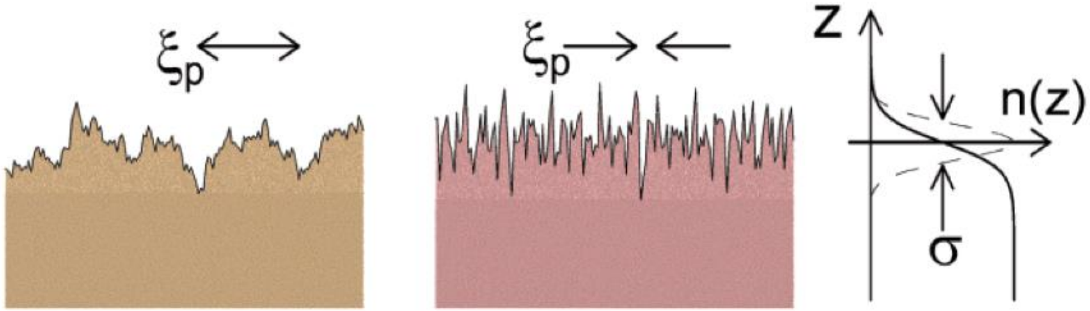
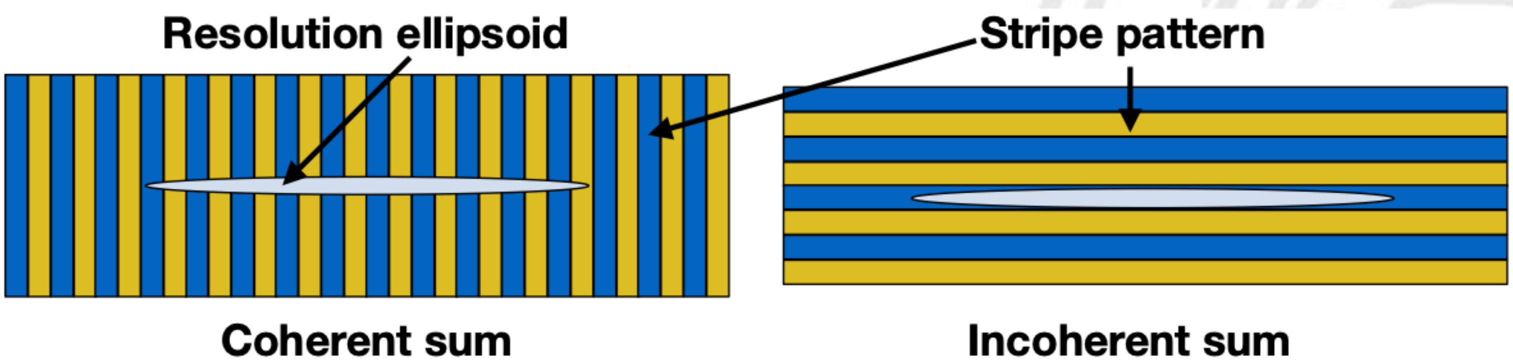


Note that roughness introduces a SLD profile averaged over the sample surface

"sparkling sea"model -- specular from many facets

each piece of surface scatters indepedently -- Nevot Croce model

$$\longrightarrow \quad R = R_F e^{-2k_{Iz}k_{1z}^{t}\sigma^2}$$



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Length scales

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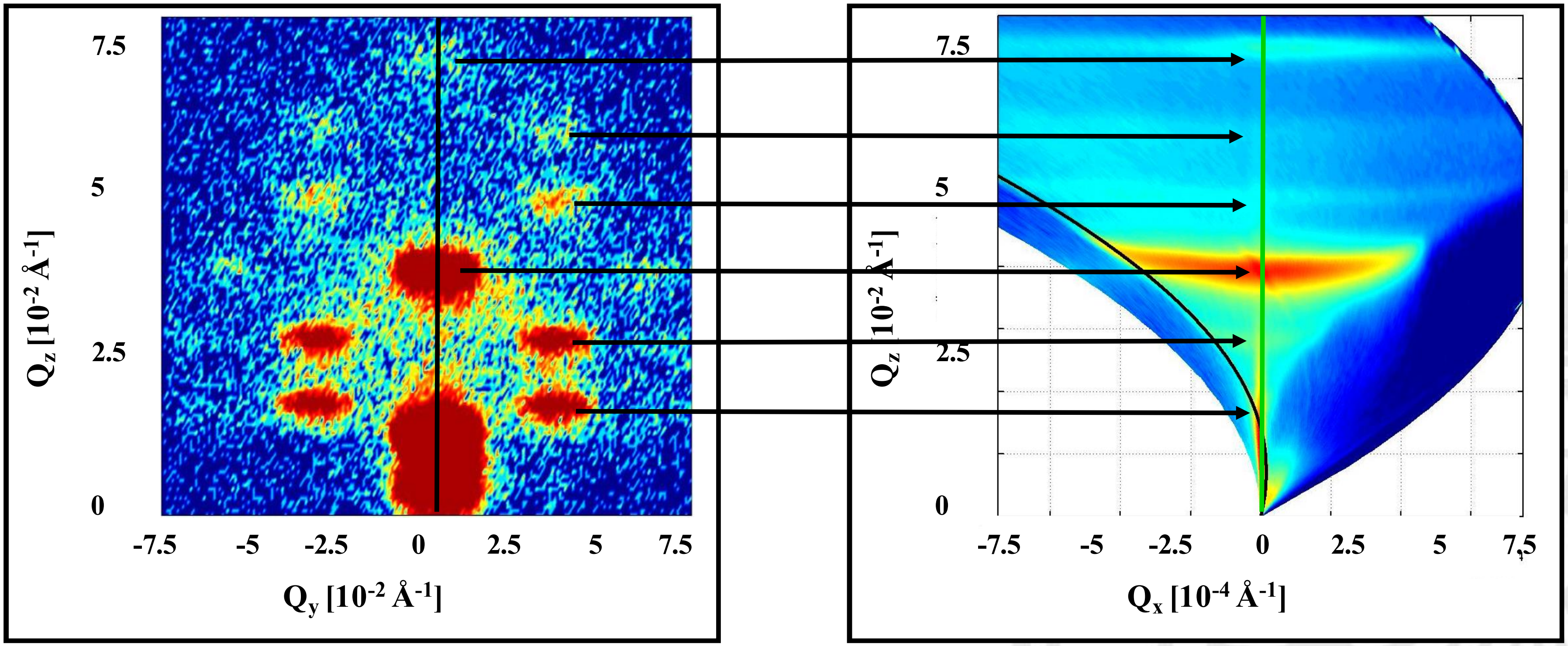

$\Delta Q_x \sim 10^{-5}$ Å^{-1} ⇔ ~ 65 µm

$\Delta Q_y \sim 4 \cdot 10^{-3}$ Å^{-1} ⇔ ~ 150 nm

$\Delta Q_z \sim 7 \cdot 10^{-4}$ Å^{-1} ⇔ ~ 850 nm

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Crystallisation

Langmuir **2009,** *25,* 64−66

Crystallization of Soft Crystals

Max Wolff,*[,†] Andreas Magerl,[‡] and Hartmut Zabel[†]

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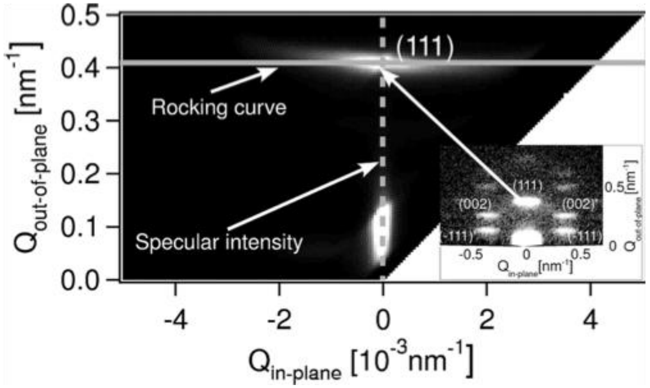

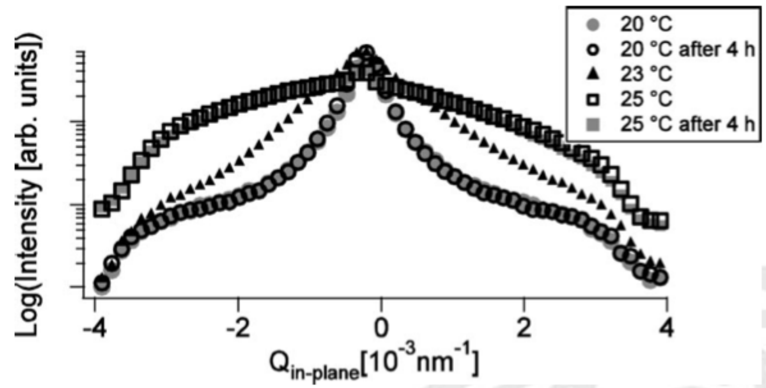

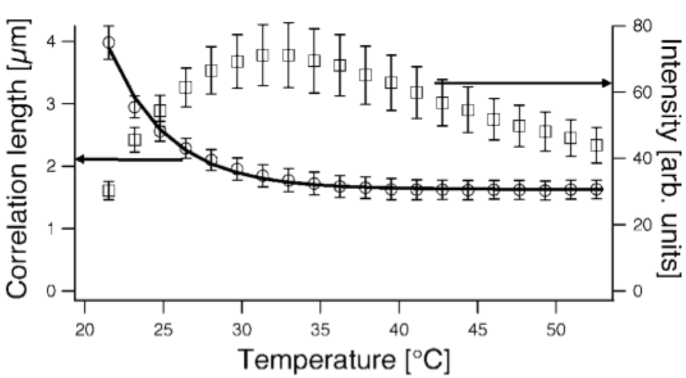

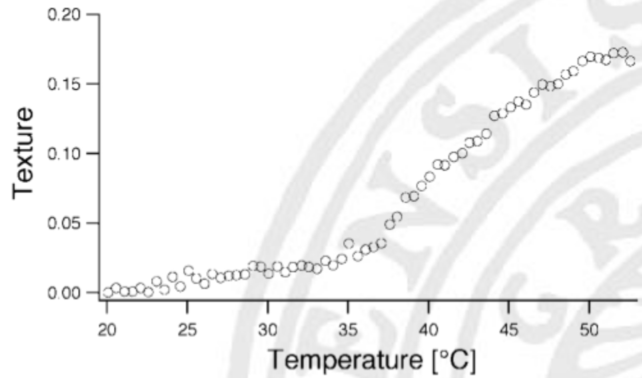

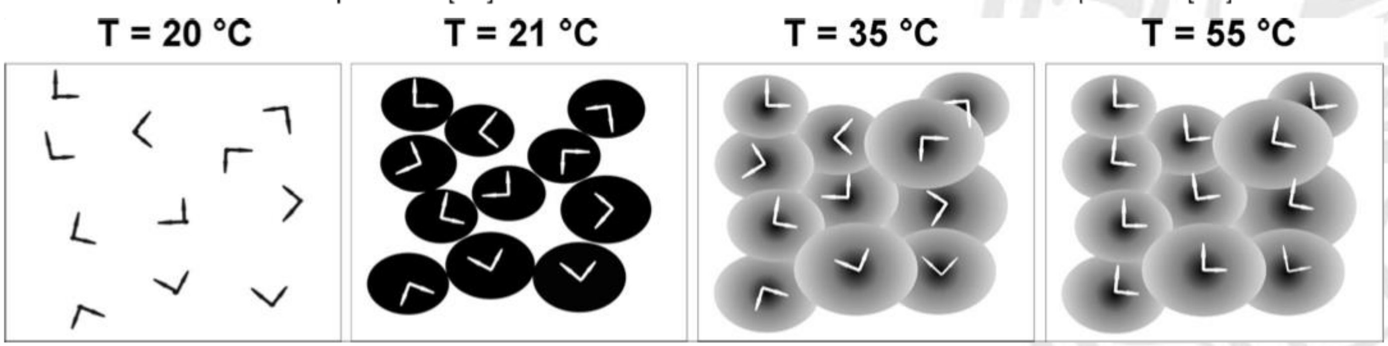

Penetration depth

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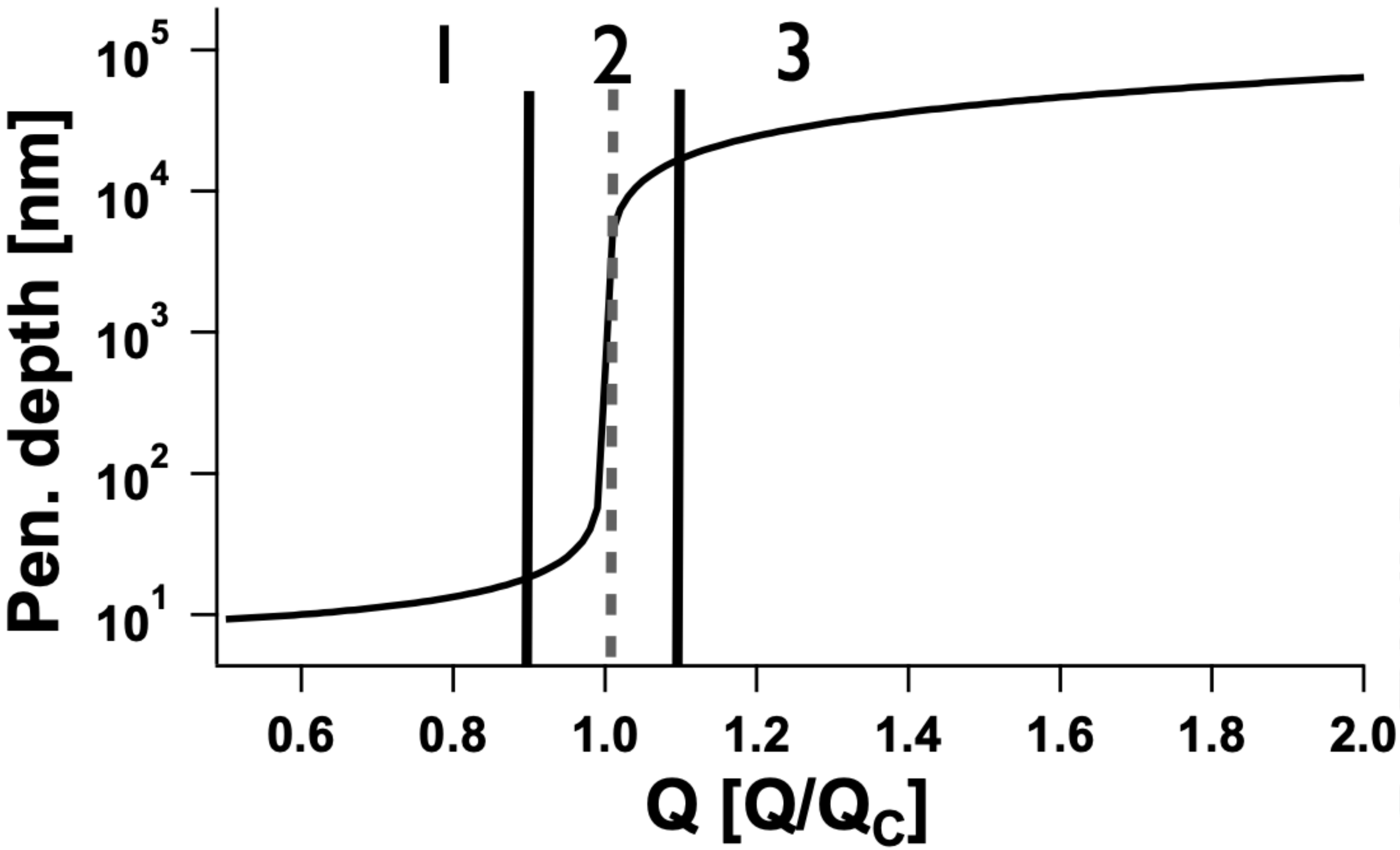

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Depth sensitive information

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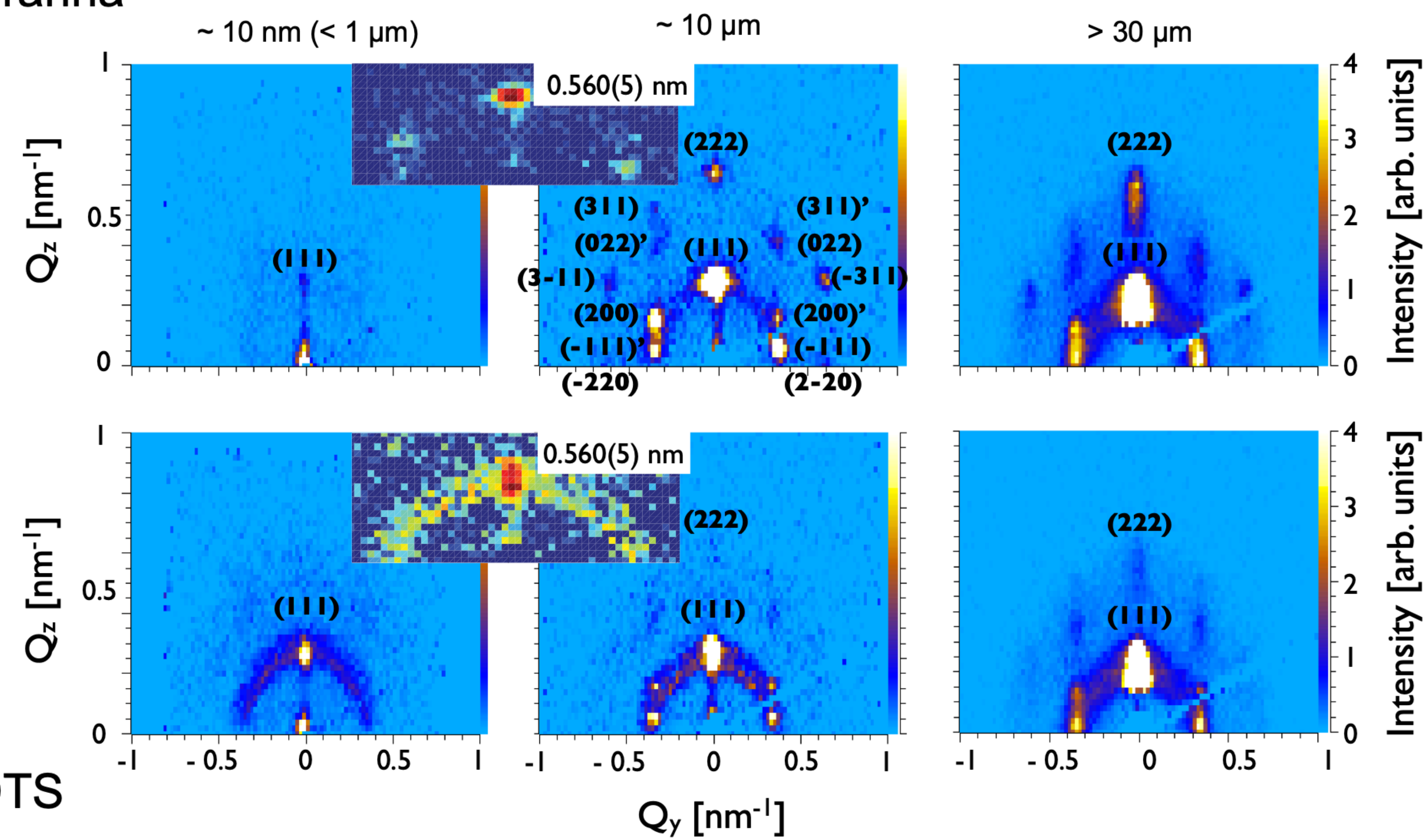
Piranha



OTS

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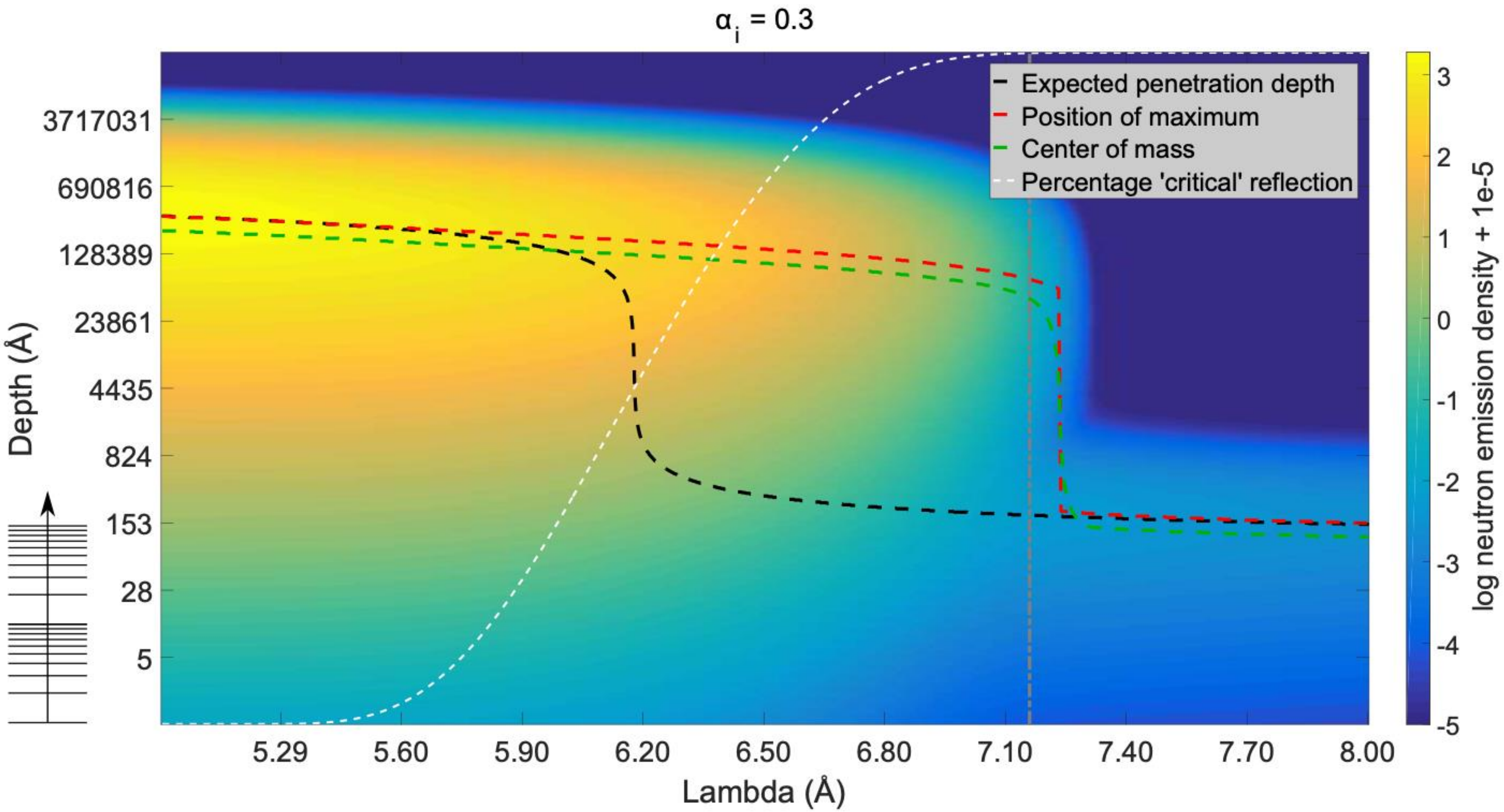
Main contribution to scattering



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Distorted wave Born approximation

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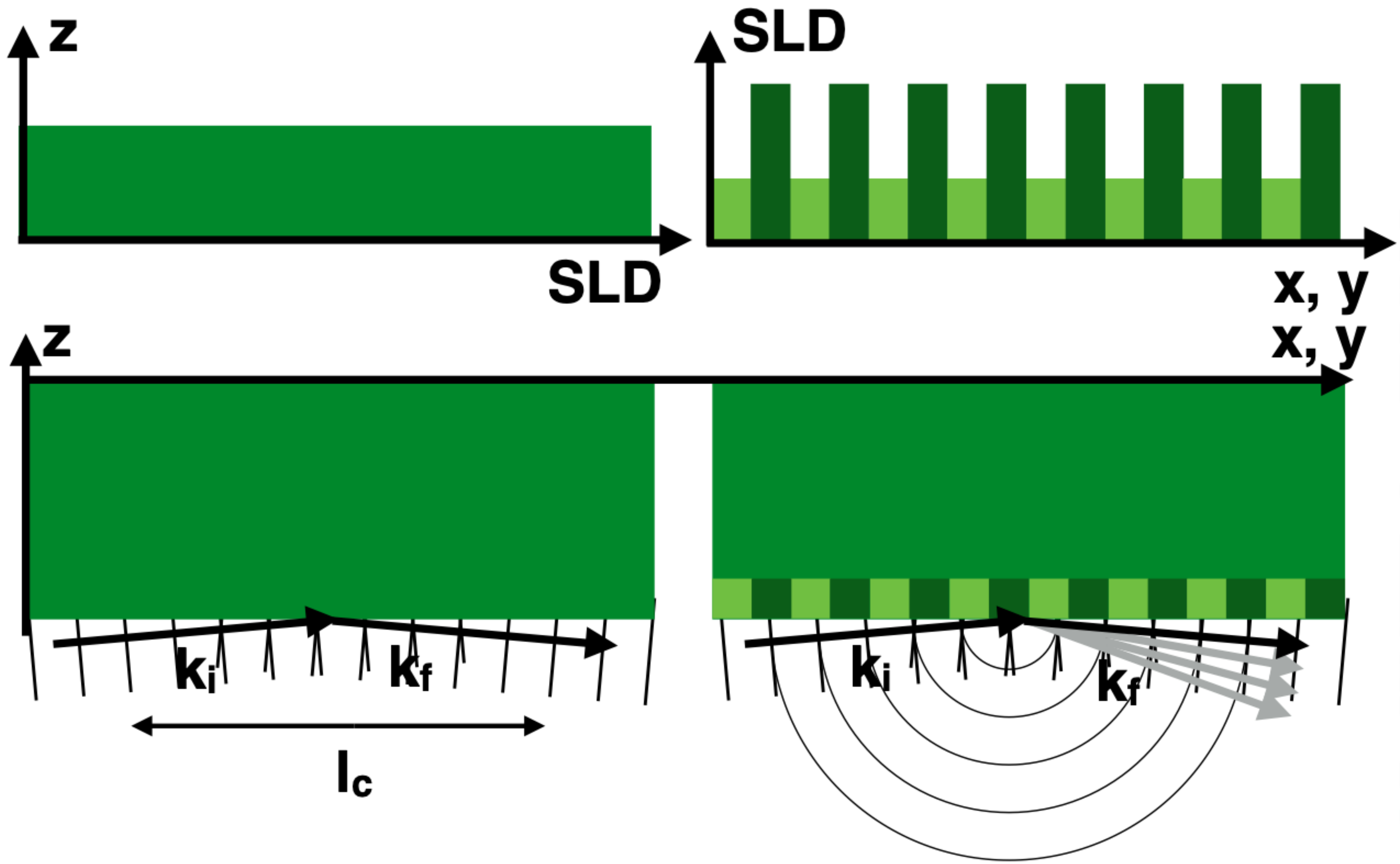

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Further reading

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S. Köhler, T. Arnold, J. Birch, M. Cardenas, S. Dorri, M. Månsson, T. Nylander, S. Rogers, S. V. Roth, Y. Sassa, M. Wolff, Recent progress in Grazing Incidence Small-Angle Neutron Scattering, Advances in Colloid and Interface Science **349**,103757 (2026).

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Summary

attering at small momentum transfer can be described by plane wav

The scattering potential become continuous

Reflectivity measurements assess the scattering length density profile

Small angle scattering can address single particles form factors

Gracing incidence scattering probes in-plane corrections at surface

Super-ADAM instrument

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The core of Super-ADAM is the instrument @ Institut Laue-Langevin (Grenoble, France):

Super-ADAM is one of the approx. 30 neutron reflectometers world wide and 1 out of 3 @ ILL, 2 @ ESS

Super-ADAM is unique in terms of resolution and polarisation analysis for science on quantum technology

Demand is twice of what Super-ADAM can accommodate

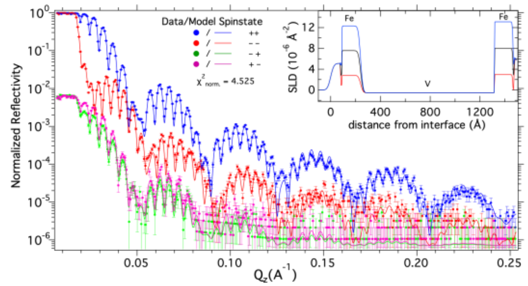
Community on surface science using neutrons is one of the fastest growing

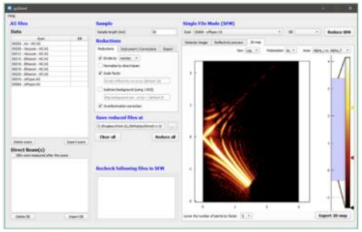
Support for users:

Beam time
User training
Design of the experiment
Conducting the experiment (24/7 support)
Data processing
Fitting
Answer to the scientific question

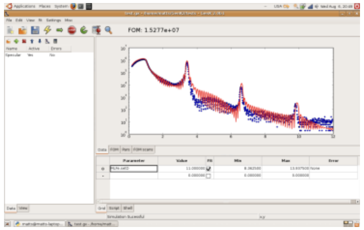
Example of high resolution measurement:

100 nm thick layer
0.2 % spin leakage



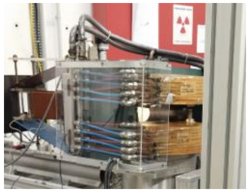


Data processing and visualisation



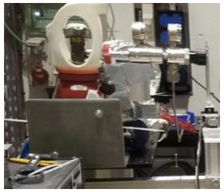
Fitting and simulations (BoTofit/Sim):
GenX: https://aglavic.github.io/genx/

Sample environment



Electromagnet: 5 T, 0.02 - 1200 K

Solid-liquid cells



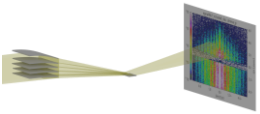
Gas loading

Projects benefiting from Super-ADAM:

SAGA

GISANS beamline for ESS

Optimisation of reflectometry /reference layers (ESS-ISIS project)



Port-GISANS (RÅC project)

Neutron optics/detectors
Characterised @ Super-ADAM