Surface Sensitive X-ray Scattering

Introduction

- Concepts of surfaces
- Scattering (Born approximation)

Crystal Truncation Rods

- The basic idea
- How to calculate
- Examples

Reflectivity

- In Born approximation
- Exact formalism (Fresnel)
- Examples

Grazing Incidence Diffraction

- The basic idea
- Penetration depth
- Example

Diffuse Scattering

- Concepts of rough surfaces
- Correlation functions
- Scattering Born-approximation
- DWBA
- Examples

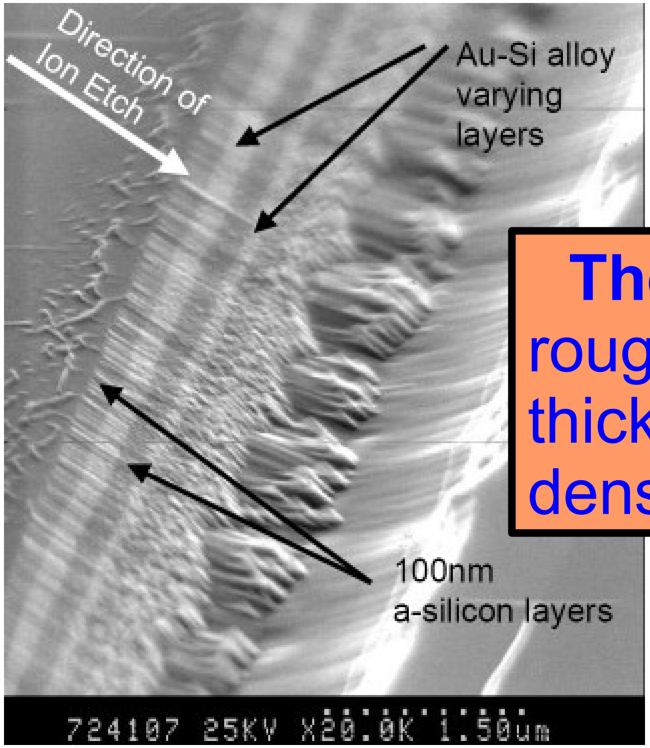
With x-ray and neutron reflectivity surfaces, buried interfaces and the properties of thin film systems can be investigated on a micro- and nanoscale.

Fundamental science, e.g.:

- layer growth
- roughness evolution

Industrial applications, e.g.:

- semiconductor devices
- storage devices / harddisks
- coatings
- lubricants
- catalysts



The layers'
roughnesses ?
thicknesses ?
densities ?

Advantages of x-ray and neutron reflectometry:

- Resolution in the Å-regime
- Gives a lot of information with just one measurement
- Usually non-destructive
- Highly element specific
- No special preparation of the sample
- (Averaged information over whole sample area)

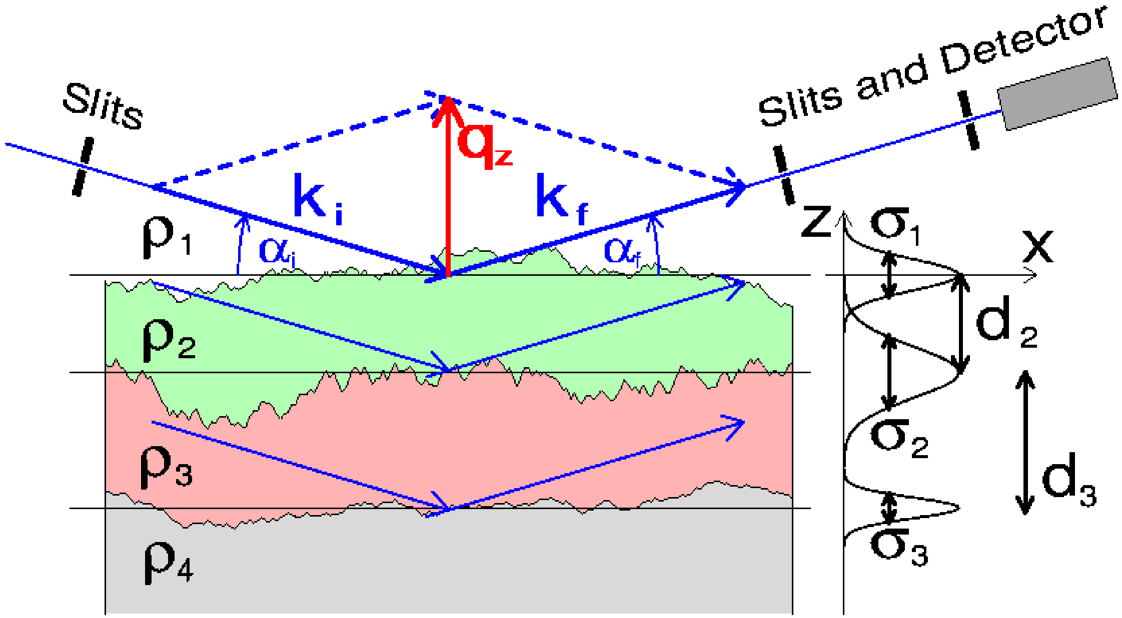
Disadvantages of x-ray and neutron reflectometry:

- No unique results without preknowledge
- No fast results
- Interpretation/analysis often not easy
- (No local information)

Theoretical Part

a) General Considerations

Photons with wavelength λ (or neutrons with $\lambda = h/\sqrt{2mE}$)
are scattered elastically (no energy change: $\lambda_i = \lambda_f$) at the surface.
The incident angle α_i equals the exit angle α_f .

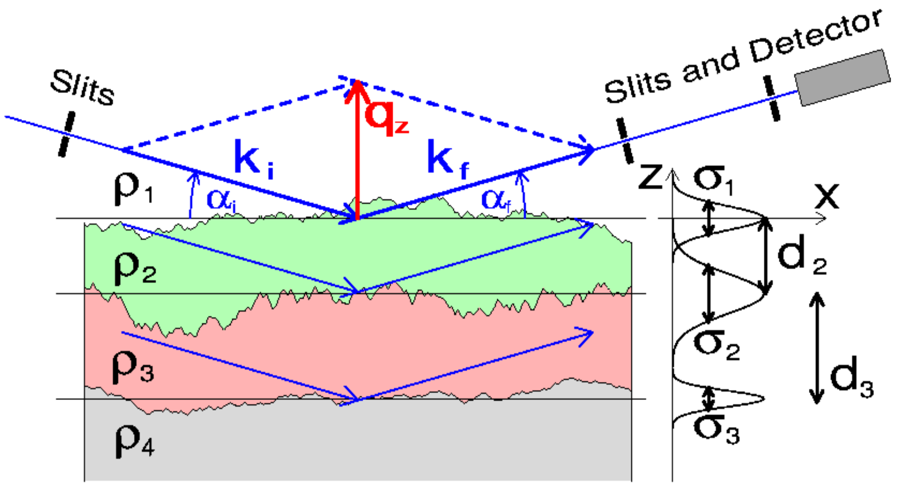


The density ρ_j means:

- Electron density for x-rays
- Scattering length density for neutrons

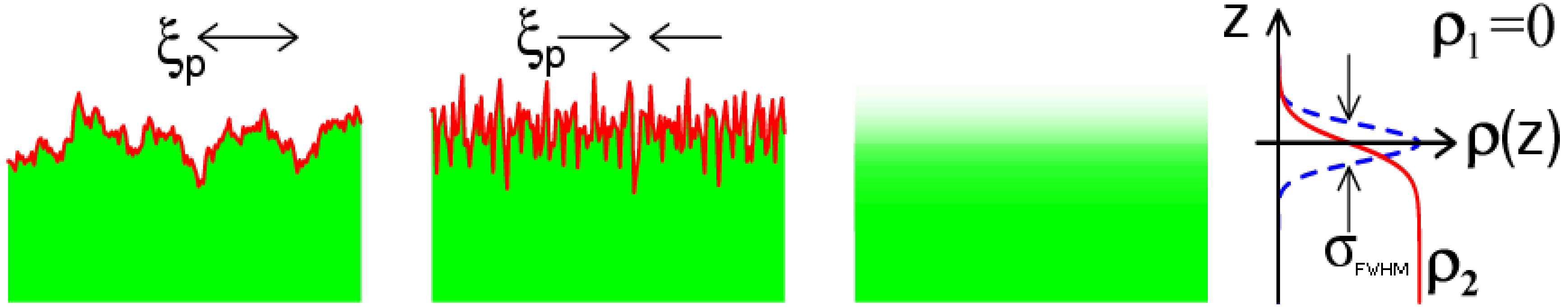
Wave vector transfer

$$q_z = \frac{4\pi}{\lambda}\sin(\alpha_f) = 2k_0\sin(\alpha_f)$$



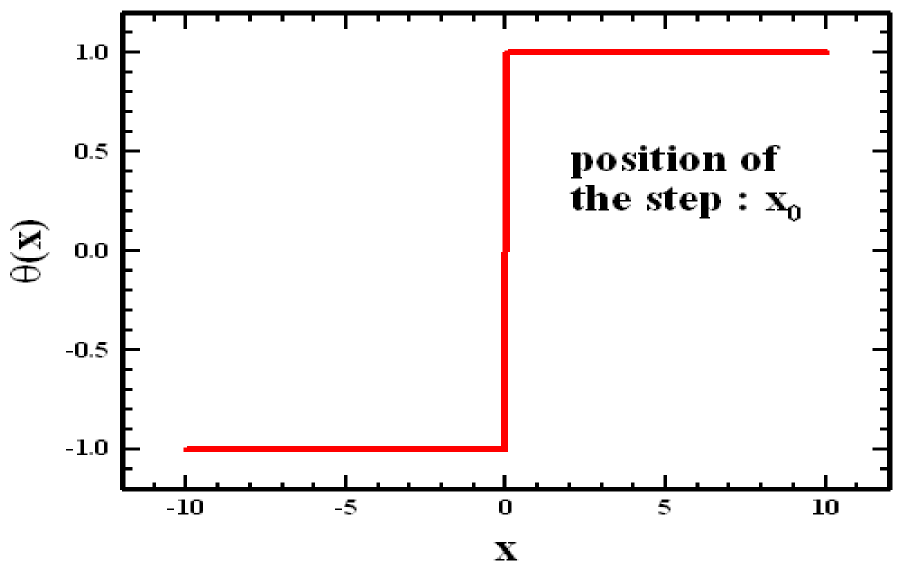
q_z **is perpendicular to the surface**
$\Rightarrow$
only sensitive to information perpendicular to the surface :
electron (scattering length) density profile $<\rho(x,y,z)>_{(x,y)} = \rho(z)$.

That means: a reflectivity cannot distinguish different in-plane structures.

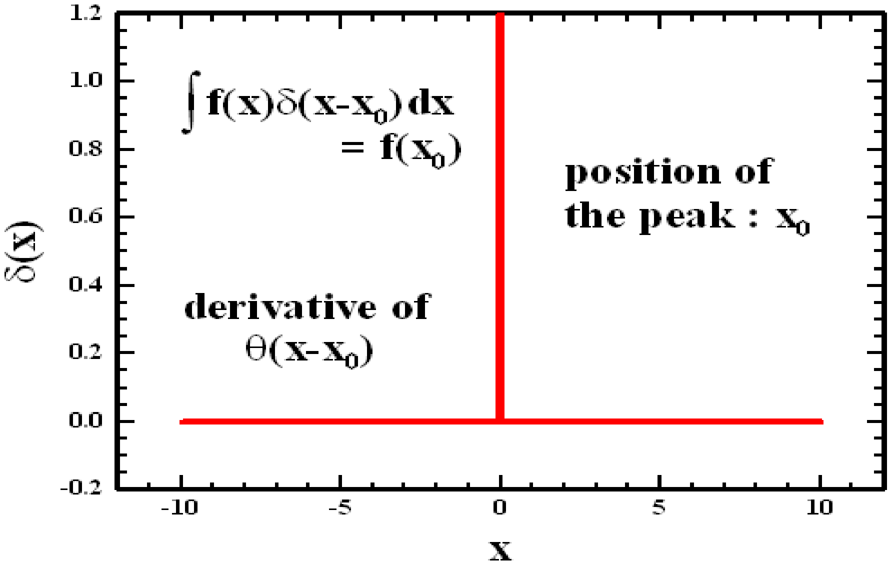


These different surfaces have the same reflectivity !

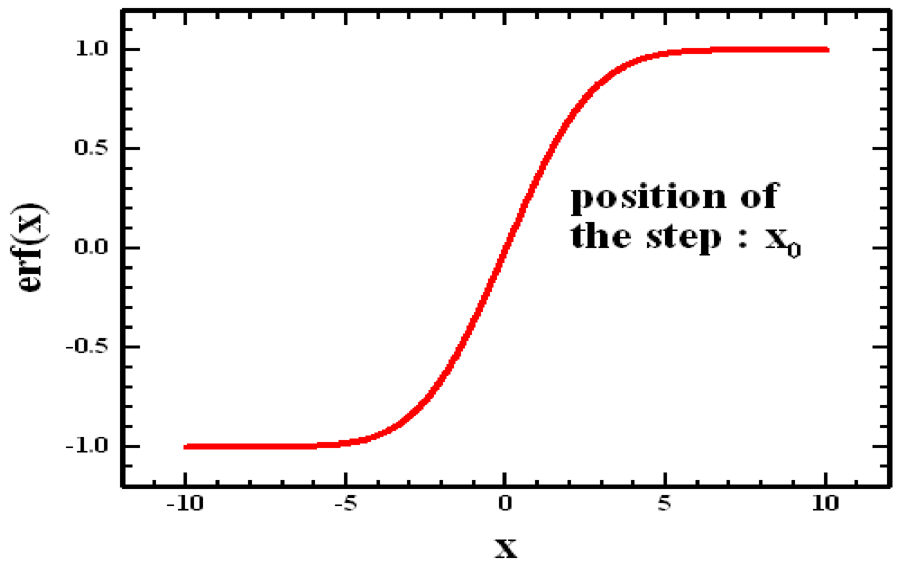
The following functions are important in the following:



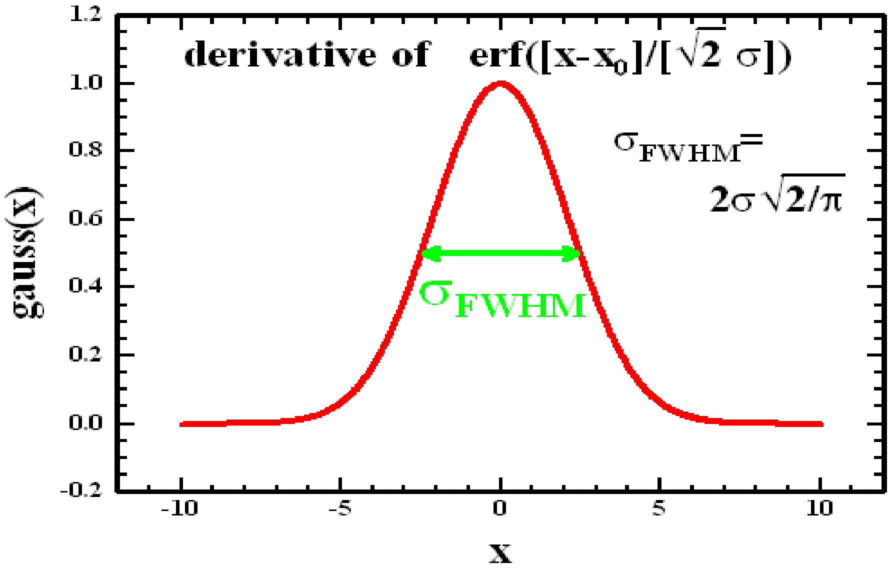
step function $\theta(x-x_0)$



delta function $\delta(x-x_0)$



error function $\mathrm{erf}([x-x_0]/[\sqrt{2}\,\sigma])$



Gaussian $\exp(-[(x-x_0)/\sigma]^2/2)$

Specularly Reflected Intensity in Born Approximation ($I_{scatt} \ll I_0$)

$$I(q_z) \propto \frac{1}{q_z^4} \left| \int \frac{d\rho(z)}{dz} \exp(iq_z z)\, dz \right|^2$$

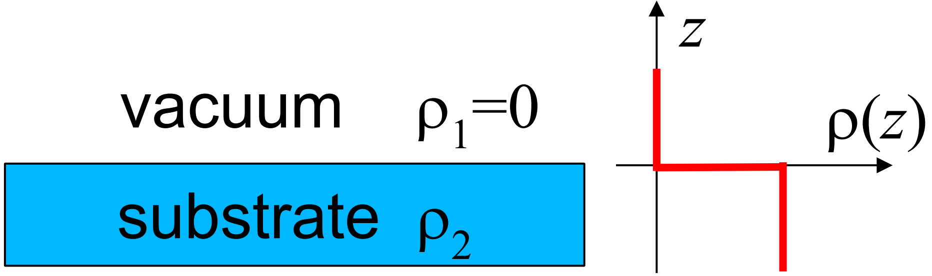
Given by the absolute square of the Fouriertransformation of the derivative of the density/(scattering length) profile and divided by q_z^4.

Consequences:

- Reflected intensity drops fast with increasing angle : $1/q_z^4$
- Only differences in density can be seen (contrast) : Derivative
- Only sensitive to density properties in z-direction : Density profile
- No direct picture visible : Fourier space
- Phase information gets lost $\Rightarrow$ no unique solution : Absolute square

Examples

1) single smooth surface at $z = 0$



vacuum $\rho_1 = 0$

substrate ρ_2

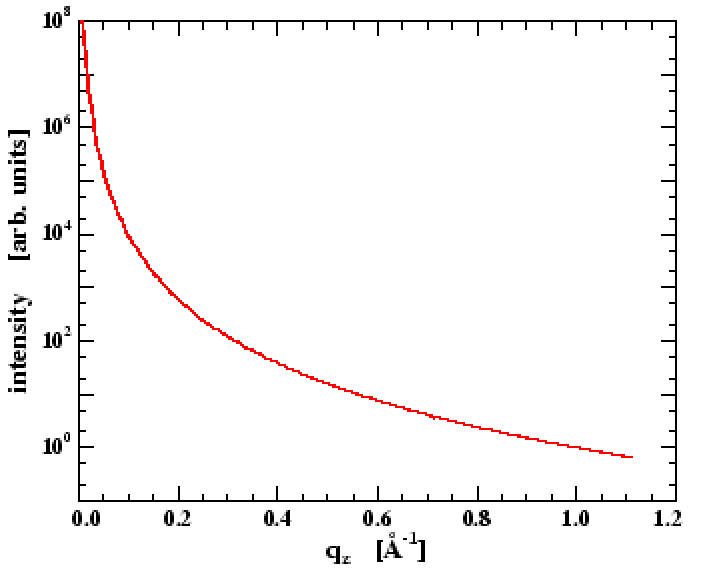
Density profile: $\rho(z) = \frac{\rho_2}{2}\left(1 - \Theta[z]\right) \quad \Rightarrow \quad \frac{d\rho}{dz} \propto \delta(z)$

$$I(q_z) \propto \frac{1}{q_z^4}\left|\int \frac{d\rho(z)}{dz}\exp(iq_z z)\,dz\right|^2$$

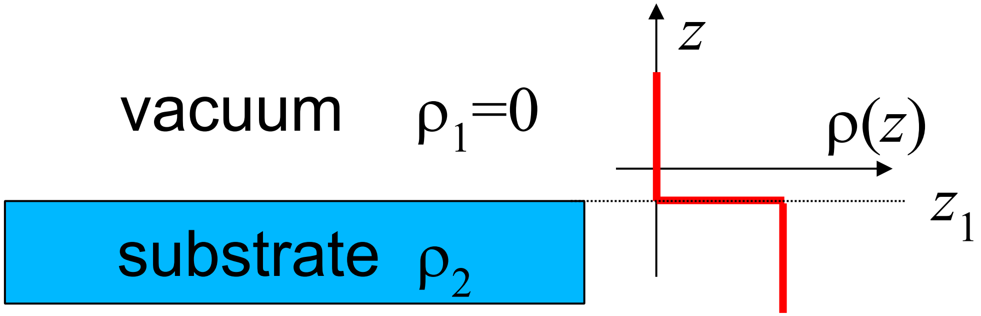
$$= \frac{1}{q_z^4}\left|\int \delta(z)\exp(iq_z z)\,dz\right|^2$$

$$= \frac{1}{q_z^4}\left|\exp(iq_z \cdot 0)\right|^2 = \boxed{\frac{1}{q_z^4}} \cdot |1|^2 = \frac{1}{q_z^4}$$

Reflectivity of a Smooth Surface in Born Approximation



2) single smooth surface at $z = z_1$ (shifted)



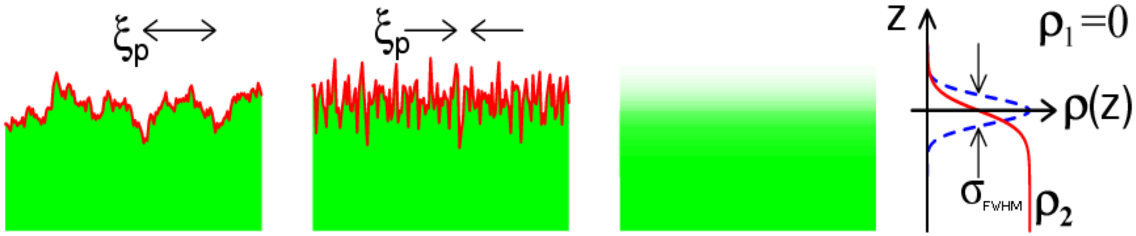
Density profile: $\rho(z) = \frac{\rho_2}{2}\left(1 - \Theta[z - z_1]\right) \Rightarrow \frac{d\rho}{dz} \propto \delta(z - z_1)$

$$I(q_z) \propto \frac{1}{q_z^4}\left|\int \frac{d\rho(z)}{dz}\exp(iq_z z)\,dz\right|^2 = \frac{1}{q_z^4}\left|\int \delta(z - z_1)\exp(iq_z z)\,dz\right|^2$$

$$= \frac{1}{q_z^4}\left|\exp(iq_z z_1)\right|^2 = \boxed{\frac{1}{q_z^4}} \cdot 1^2 = \frac{1}{q_z^4}$$

A shift of the sample does not change the reflectivity.

3) single rough surface with roughness σ



Density profile: $$\rho(z) = \frac{\rho_2}{2}\left[1 - \operatorname{erf}\left(\frac{z}{\sqrt{2}\,\sigma}\right)\right] \quad \Rightarrow \quad \frac{d\rho}{dz} \propto \exp\left(\frac{-z^2}{2\sigma^2}\right)$$

$$I(q_z) \propto \frac{1}{q_z^4}\left|\int \frac{d\rho(z)}{dz}\exp(iq_z z)\,dz\right|^2$$

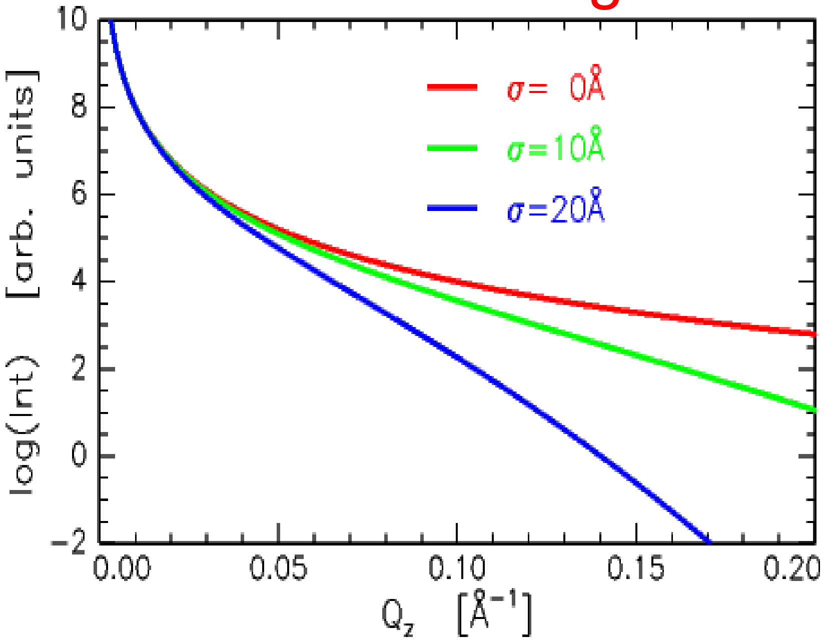
$$= \frac{1}{q_z^4}\left|\int \exp\left(\frac{-z^2}{2\sigma^2}\right)\exp(iq_z z)\,dz\right|^2$$

Fourier transformation is known!

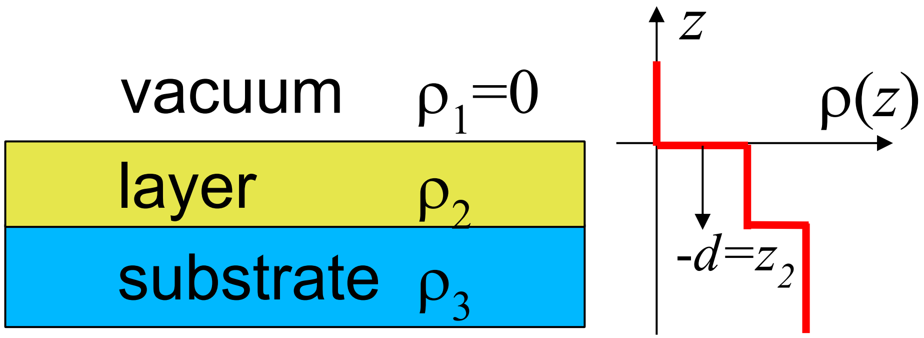
$$\propto \frac{1}{q_z^4}\left|\exp\left(\frac{-q_z^2\sigma^2}{2}\right)\right|^2 = \frac{1}{q_z^4}\boxed{\exp(-q_z^2\sigma^2)}$$

Debye-Waller factor

Effect of the roughness



4) single smooth layer with thickness *d*



Density profile:

$$\rho(z)=\frac{\Delta\rho_1}{2}[1-\Theta(z)]+\frac{\Delta\rho_2}{2}[1-\Theta(z+d)]$$

Derivative of $\rho(z)$:

$$\frac{d\rho}{dz}\propto\Delta\rho_1\,\delta(z)+\Delta\rho_2\cdot\delta(z+d)$$

with: $\Delta\rho_1=\rho_2-\rho_1$
$\Delta\rho_2=\rho_3-\rho_2$

$$I(q_z)\propto\frac{1}{q_z^4}\left|\int\frac{d\rho(z)}{dz}\exp(iq_z z)\,dz\right|^2=\frac{1}{q_z^4}\left|\int[\Delta\rho_1\,\delta(z)+\Delta\rho_2\,\delta(z+d)]\exp(iq_z z)\,dz\right|^2$$

$$=\frac{1}{q_z^4}\left|\Delta\rho_1+\Delta\rho_2\exp(-iq_z d)\right|^2=\frac{1}{q_z^4}[\Delta\rho_1+\Delta\rho_2\exp(iq_z d)]\cdot[\Delta\rho_1+\Delta\rho_2\exp(-iq_z d)]$$

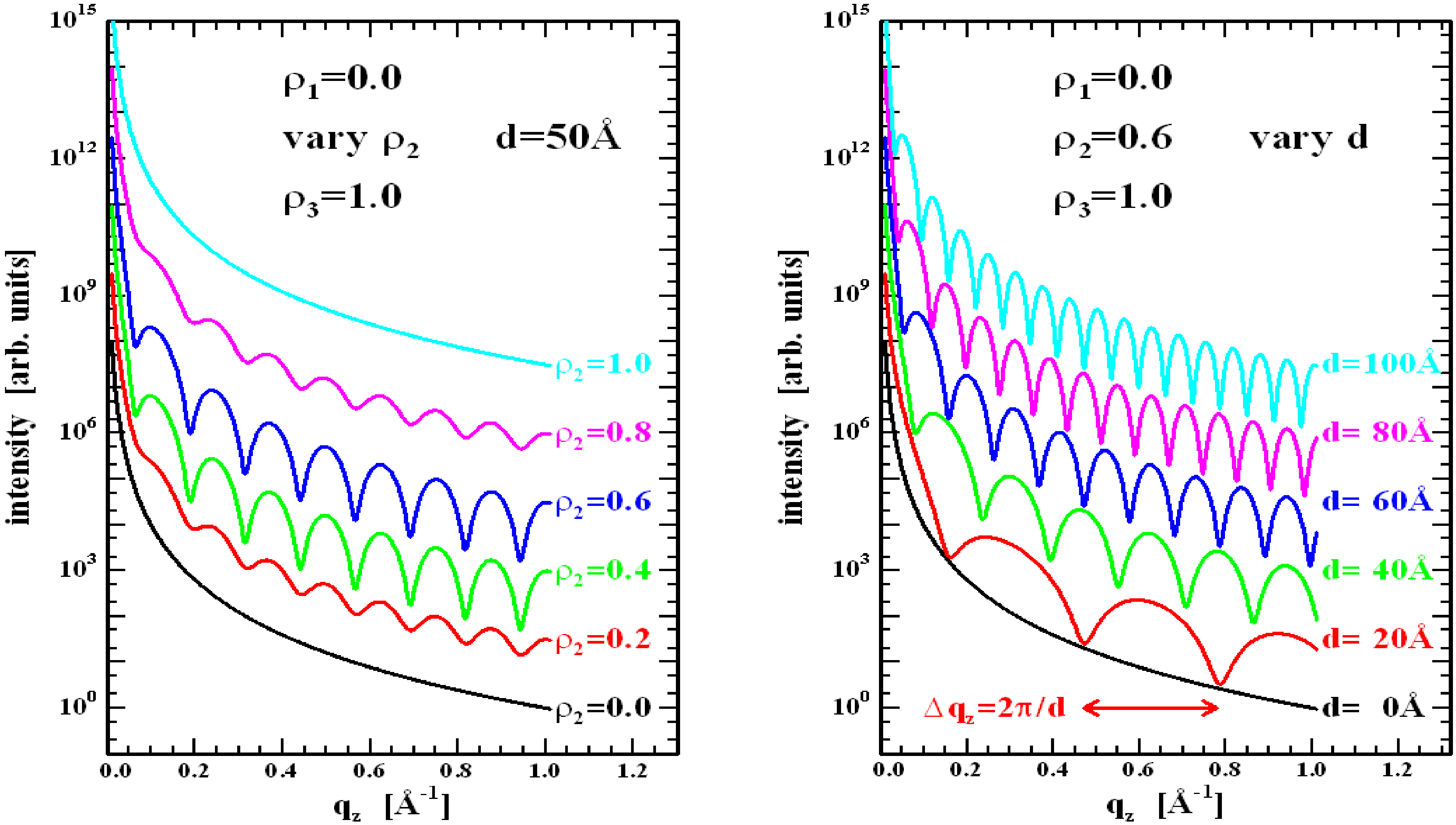
$$=\frac{1}{q_z^4}(\Delta\rho_1^2+\Delta\rho_2^2+\Delta\rho_1\Delta\rho_2[\exp(iq_z d)+\exp(-iq_z d)])$$

$$=\frac{1}{q_z^4}[\Delta\rho_1^2+\Delta\rho_2^2+2\Delta\rho_1\Delta\rho_2\cos(q_z d)]$$

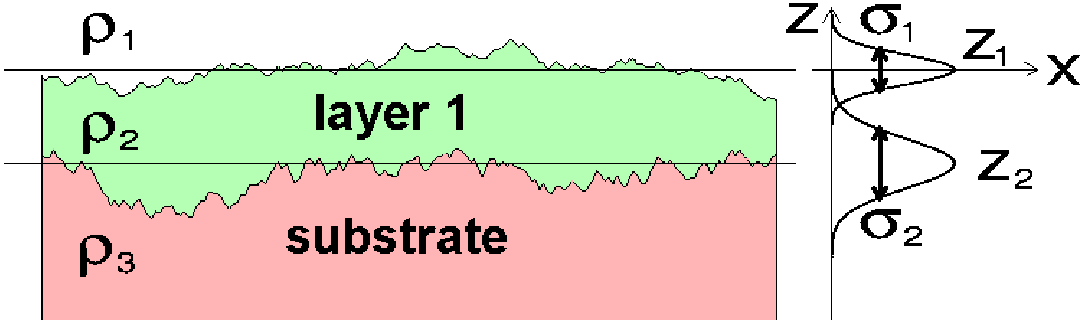
oscillating function

- Contrasts $\Delta\rho_1$ and $\Delta\rho_2$ determine the visibility of the oscillations.
- Film thickness d determines the period via $\Delta q_z = 2\pi/d$.

completely smooth one-layer system



5) single layer with rough interfaces and thickness $d = -z_2$



Density profile:

$$\rho(z) = \frac{\Delta\rho_1}{2}\left[1 - \mathrm{erf}\left(\frac{z - z_1}{\sqrt{2}\,\sigma_1}\right)\right] + \frac{\Delta\rho_2}{2}\left[1 - \mathrm{erf}\left(\frac{z - z_2}{\sqrt{2}\,\sigma_2}\right)\right]$$

Derivative of $\rho(z)$:

$$\frac{d\rho}{dz} \propto \frac{\Delta\rho_1}{\sigma_1}\exp\left(\frac{-(z - z_1)^2}{2\sigma_1^2}\right) + \frac{\Delta\rho_2}{\sigma_2}\exp\left(\frac{-(z - z_2)^2}{2\sigma_2^2}\right)$$

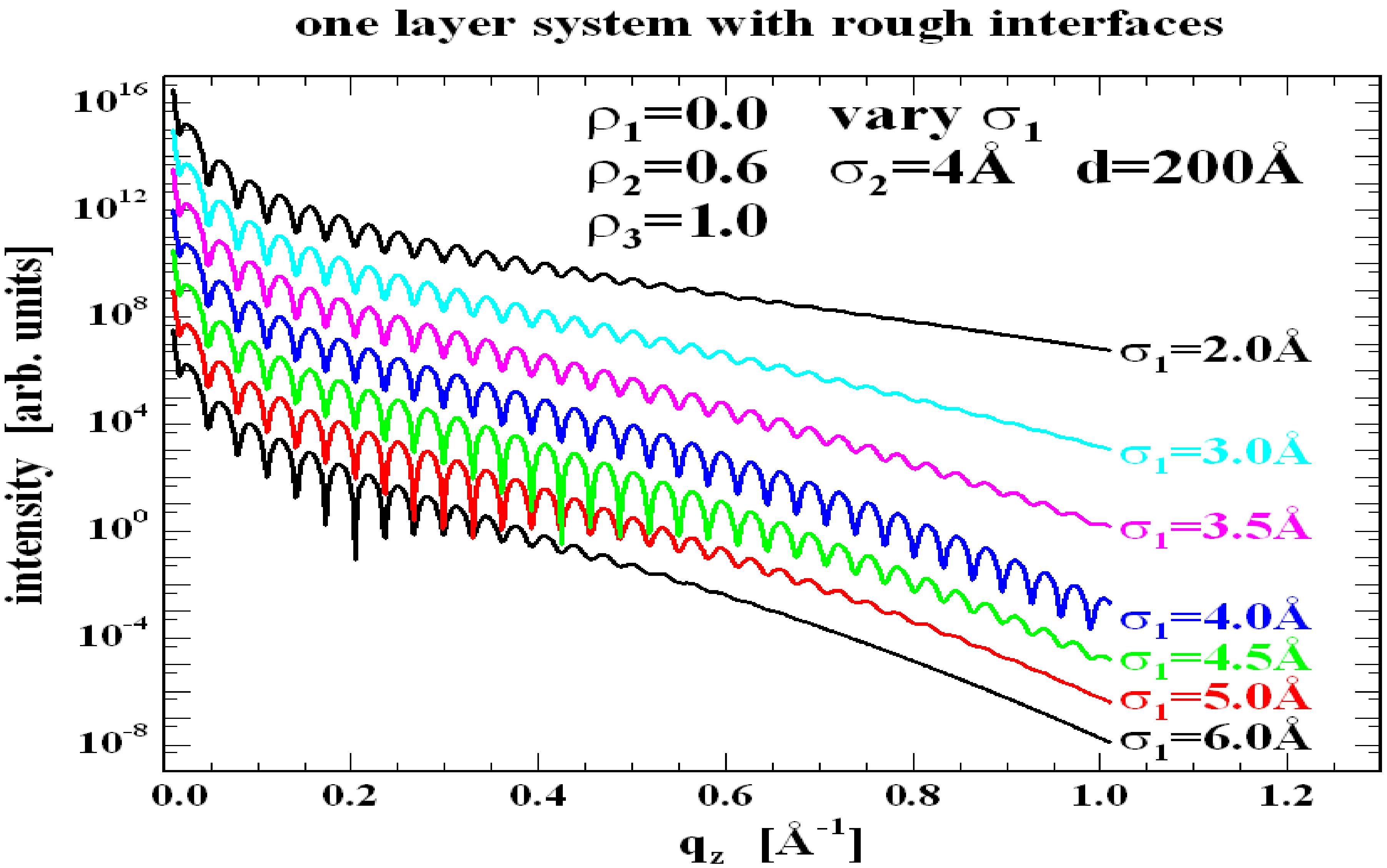
using :

$$\int \exp\left(\frac{-(z - z_1)^2}{2\sigma_1^2}\right)\exp(iq_z z)\,dz = \exp(iq_z z_1)\sqrt{2}\,\sigma_1\exp\left(\frac{q_z^2\sigma_1^2}{2}\right)$$

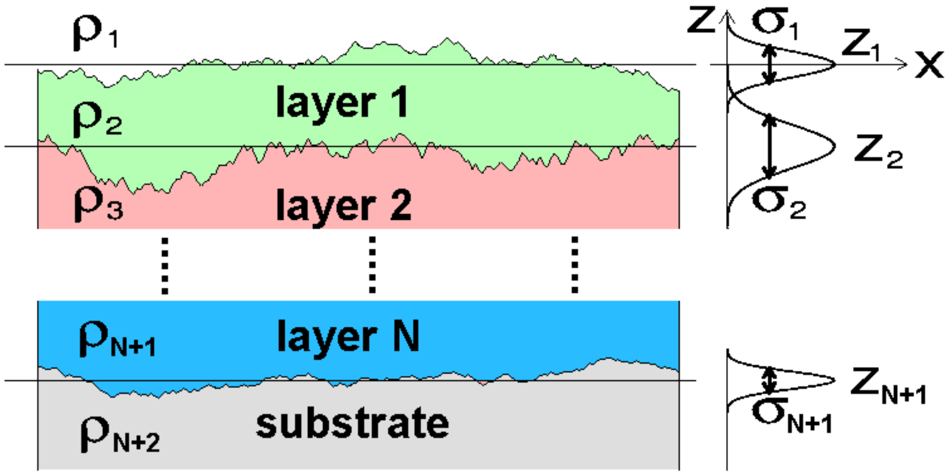
Result :

$$I(q_z) \propto \frac{1}{q_z^4}\left[\Delta\rho_1^2\exp\left(-q_z^2\sigma_1^2\right) + \Delta\rho_2^2\cdot\exp\left(-q_z^2\sigma_2^2\right) + 2\Delta\rho_1\Delta\rho_2\exp\left(-q_z^2\frac{\sigma_1^2 + \sigma_2^2}{2}\right)\cos(q_z z_2)\right]$$

- At large q_z the scattering is dominated by the smoothest interface.
- The difference between the σ's of a layer determines the “die-out” of the oscillations.


one layer system with rough interfaces

5) general case: N rough layers



Density profile:

$$\rho(z)=\frac{1}{2}\sum_{j=1}^{N+1}\Delta\rho_j\left(1-\mathrm{erf}\left[\frac{z-z_j}{\sqrt{2}\,\sigma_j}\right]\right)\quad \text{with}\quad \Delta\rho_j=\rho_{j+1}-\rho_j$$

$$I(q_z)\propto\frac{1}{q_z^4}\left(\sum_{j=1}^{N+1}\Delta\rho_j^2\exp\left(-q_z^2\sigma_j^2\right)\right.$$

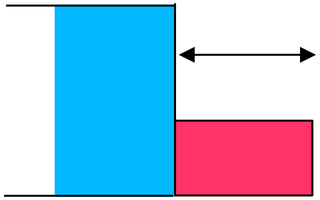
$$\left.+2\sum_{j=1}^{N}\sum_{k=j+1}^{N+1}\Delta\rho_j\Delta\rho_k\exp\left(-q_z^2\frac{\sigma_j^2+\sigma_k^2}{2}\right)\cos\left[q_z\left(z_j-z_k\right)\right]\right)$$

Scattering terms from the single interfaces

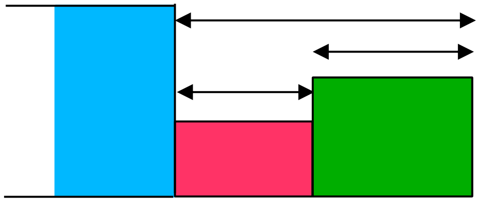
Each distance z_j-z_k gives an oscillating term, scaled with the respective Debye-Waller factor and the contrasts at the interfaces.

For a first guess on reflectivity data: Fourier backtransformation of $q_z^{\,4} \cdot I(q_z)$ will show distinct peaks for each oscillation (⇔ distance).

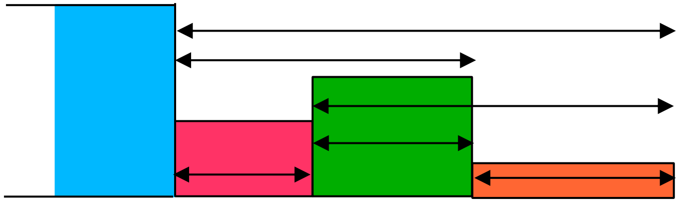
Maximum number of distances



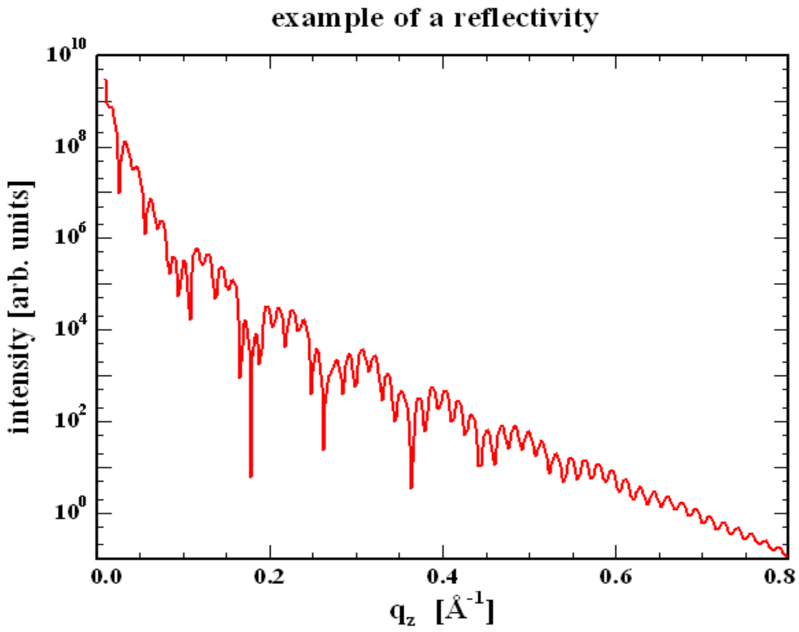
1 layer : 1



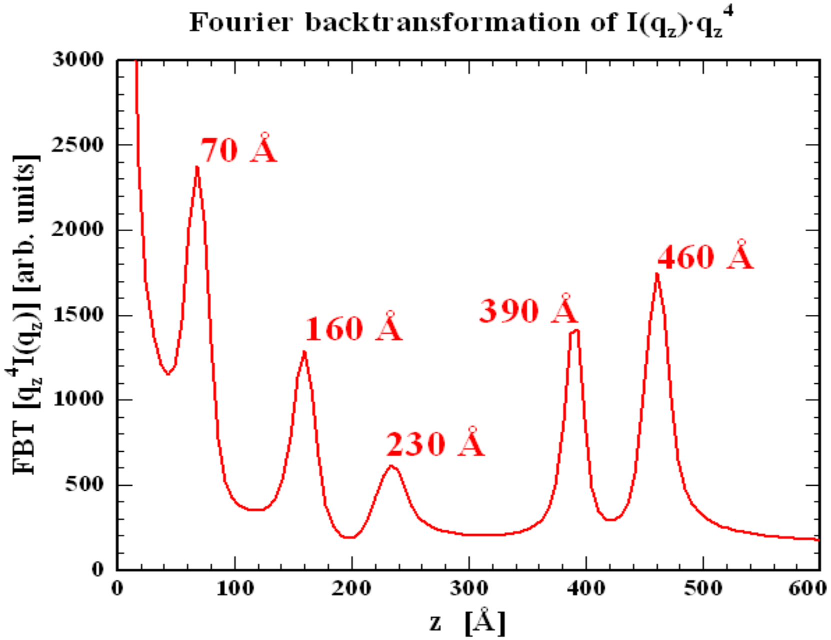
2 layers : 3

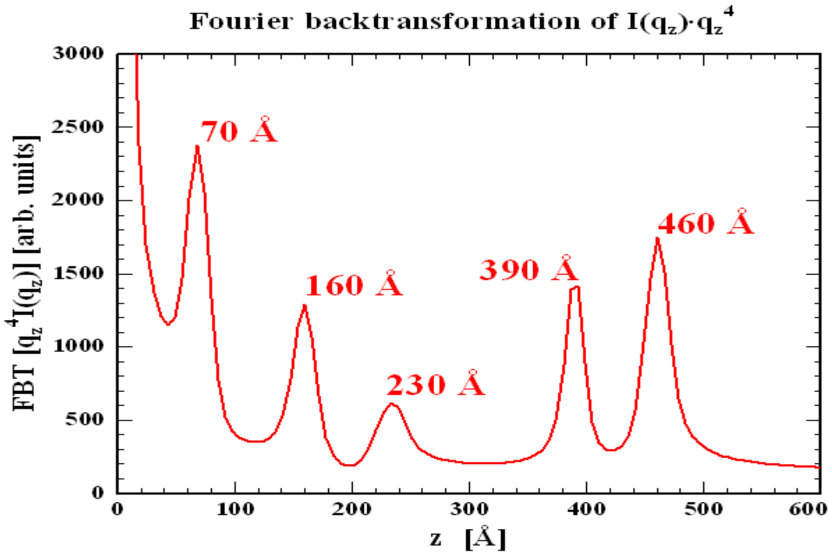


3 layers : 6



FTB →

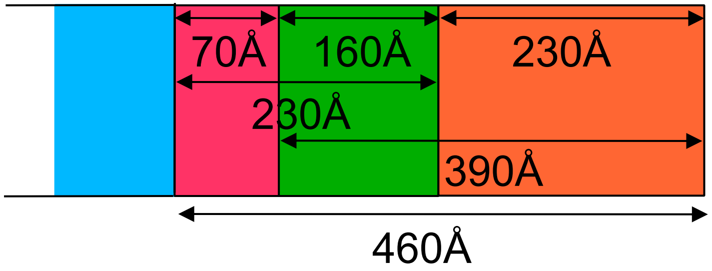




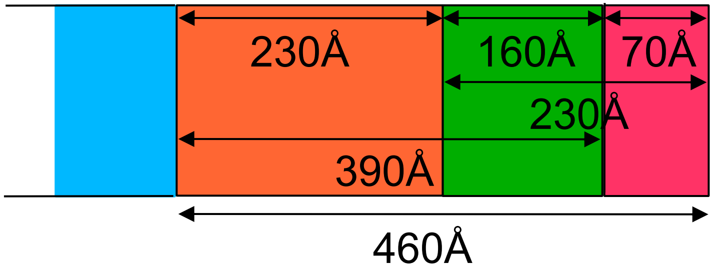
Only 5 peaks !

Likely a 3-layer system with one layer thickness matching the sum of two neighboring layers.

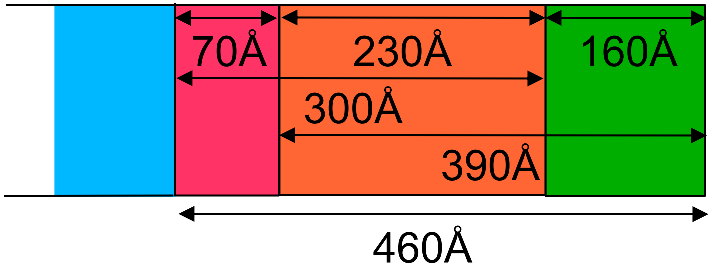
Two possibilities:

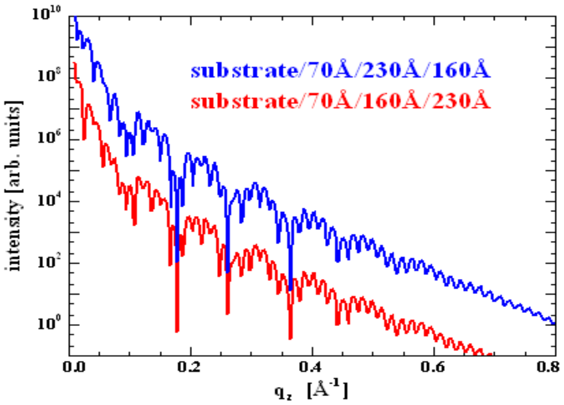


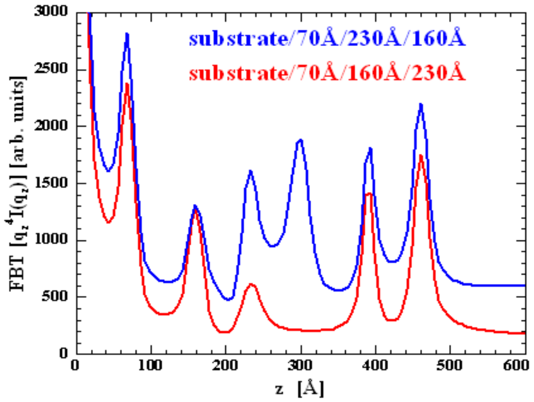
or



Result of swapping layers







c) The Exact Fresnel Formalism (Optical Treatment)

Born approximation diverges for $q_z \to 0$ $\Rightarrow$
The reflected intensity **cannot** be larger than the incident intensity.
Multiple scattering for small angles have to be taken into account.

Starting point: Helmholtz equation

(remember: neutrons can be treated as waves)

$$\nabla^2 \boldsymbol{E}(\boldsymbol{r}) + k_0^2 n^2(\boldsymbol{r}) \boldsymbol{E}(\boldsymbol{r}) = 0$$

$\boldsymbol{r}$: vector in space
$\boldsymbol{E}$: electrical field for photons / wave function for neutrons
$k_0 = 2\pi/\lambda$: modulus of the wave vector
n : refractive index

for reflectivity : $n(\boldsymbol{r}) = n(z)$

Electron density (for x-rays) or scattering length density (neutrons) translates to the refractive index :

$$n(z) = 1-\delta(z)+i\beta(z)$$

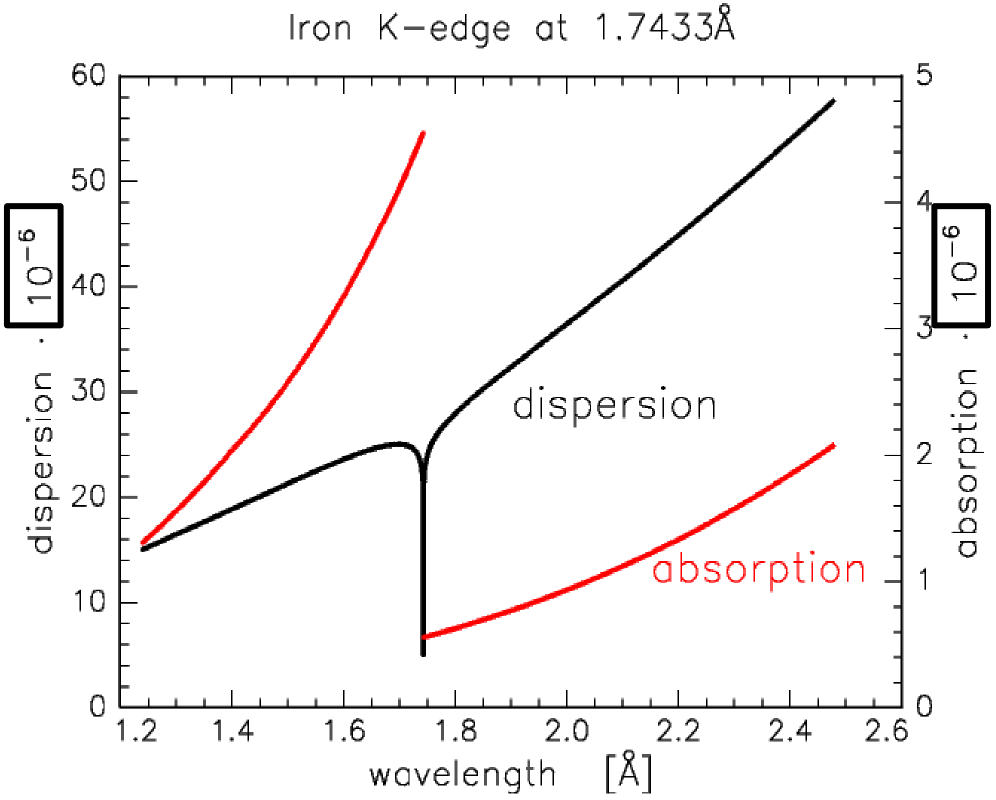
with the dispersion δ and the absorption β .

X-rays:

$$\delta(z)=\frac{\lambda^2}{2\pi} r_e \rho(z) \frac{f_0(q_z)+ f_{\Re}(\lambda)}{Z}$$

$$\beta(z)=\frac{\lambda^2}{2\pi} r_e \rho(z) \frac{f_{\Im}(\lambda)}{Z}$$

r_e : classical e⁻ radius
ρ : e⁻ density
Z : number of e⁻
f_0 : formfactor
$f_{\Re} + i f_{\Im}$: corrections to formfactor



Neutrons:

$$\delta(z)=\frac{\lambda^2}{2\pi} N(z) b$$

β is usually negligible
N : particle density
b : scattering length

Mean value of the refractive index: $n<1$

$\Rightarrow$ total external reflection

$\Rightarrow$ critical angle α_c

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

Fresnel reflection coefficient for a single smooth surface:

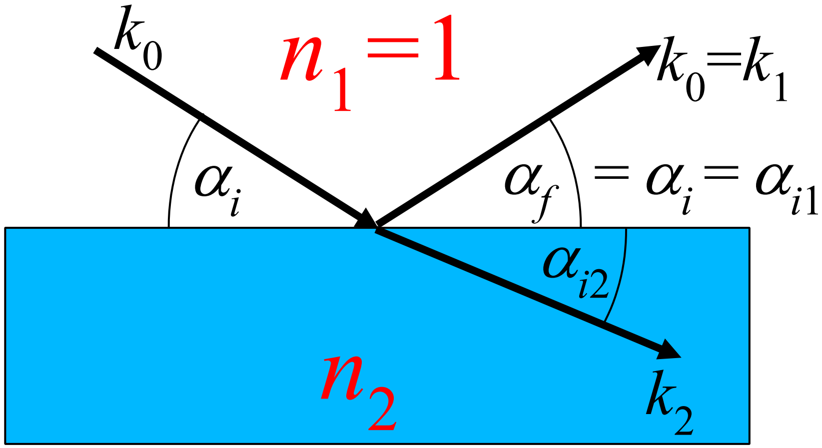
$$r_{1,2} = \frac{k_{z1} - k_{z2}}{k_{z1} + k_{z2}}$$

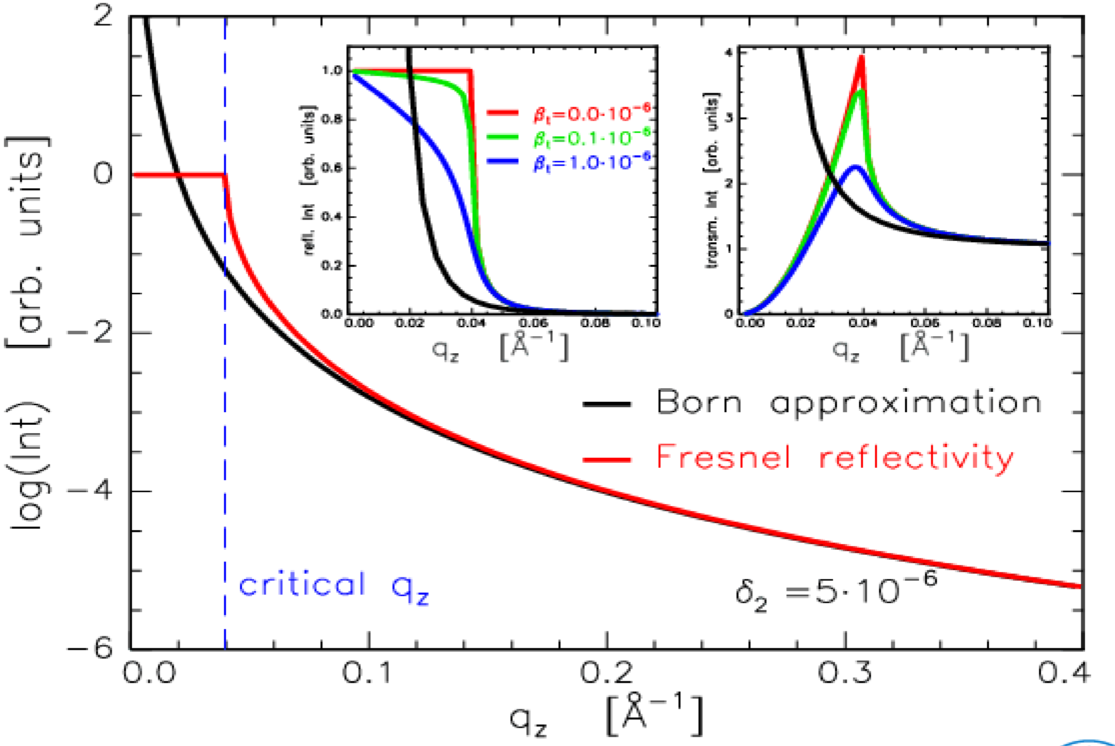
with

$$k_{z1} = k_1 \sin\alpha_{i1} = k_0 \sin\alpha_i = q_z/2$$

$$k_{z2} = k_2 \sin\alpha_{i2} = k_0 \sqrt{n_2^2 - \cos^2\alpha_i}$$

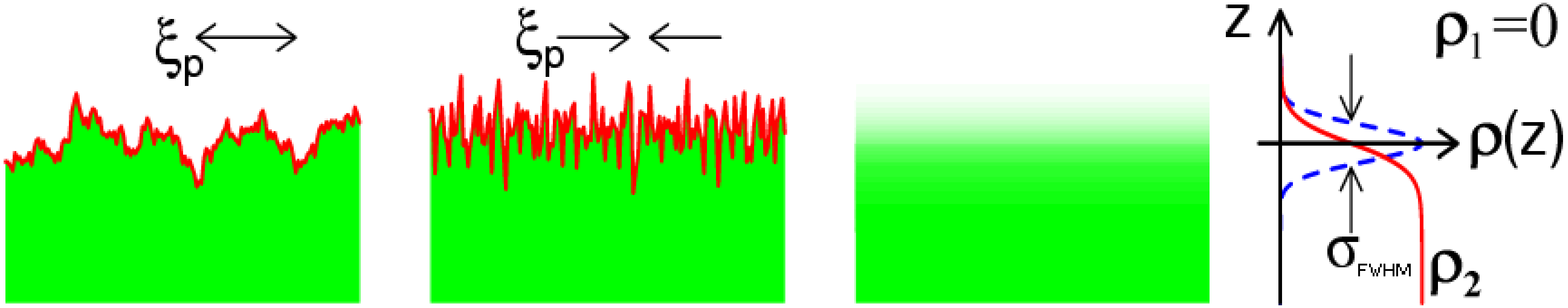
$$I(\alpha_i) = |r_{1,2}|^2$$





If a surface is rough, the Fresnel reflection coefficient can be modified.

The result depends on the exact probability function of the interface.



Solids : Error-function profile ⇒ Gaussian probability function

Polymers : tanh-function profile ⇒ $1/\cosh^2$ probability function

$$\tilde{r}_{1,2} = r_{1,2} \exp\left(-2k_{z1} k_{z2} \sigma^2\right)$$

Gaussian

$$\tilde{r}_{1,2} = \frac{\sinh\left[\sqrt{3}\,\sigma\left(k_{z1} - k_{z2}\right)\right]}{\sinh\left[\sqrt{3}\,\sigma\left(k_{z1} + k_{z2}\right)\right]}$$

$1/\cosh^2$

Smooth layer systems (recursive formalism by Parratt)

for each interface j: $r_{j,j+1} = \dfrac{k_{z,j} - k_{z,j+1}}{k_{z,j} + k_{z,j+1}}$ $\qquad k_{z,j} = k_0 \sqrt{n_j^2 - \cos^2 \alpha_i}$

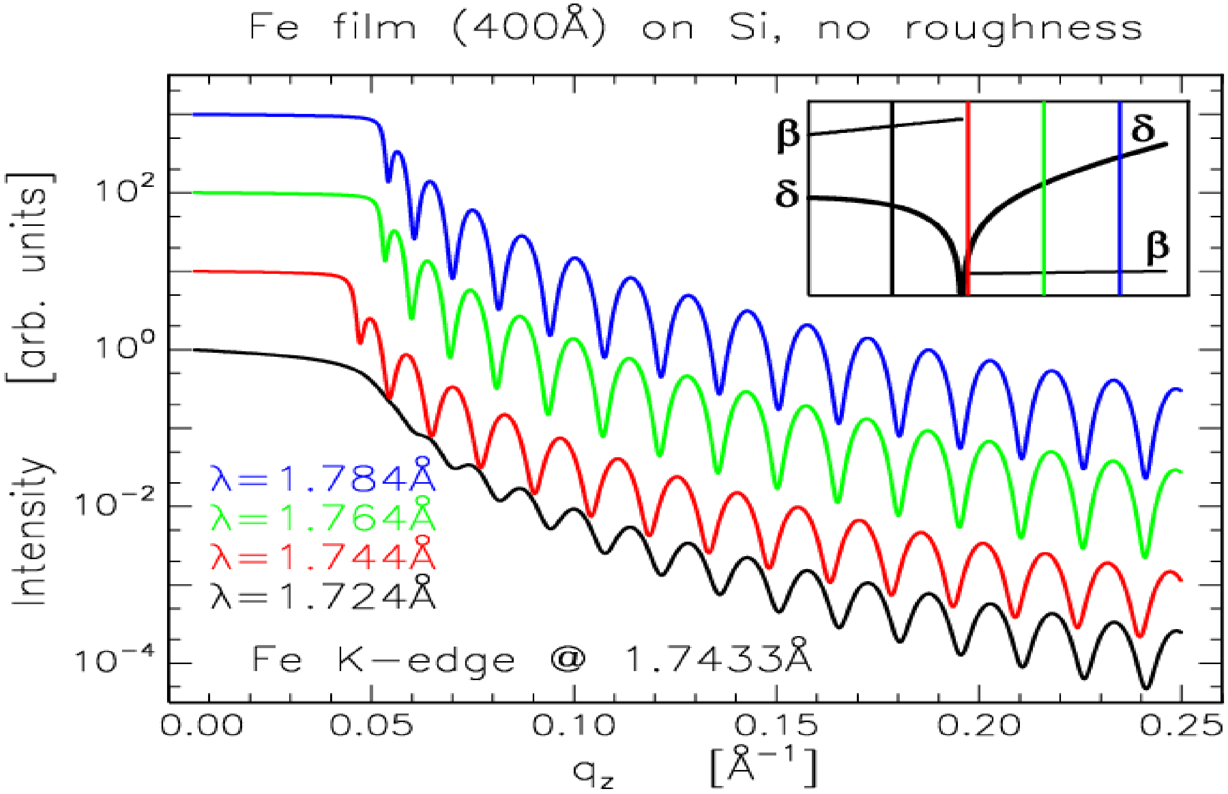
Recursion:

starting with $X_{N+1} = 0$

(N: number of layers)

end of recursion:

$$|X_1|^2 = I(q_z)$$



$$X_j = \exp\left(-2ik_{z,j} z_j\right) \frac{r_{j,j+1} + X_{j+1} \exp\left(2ik_{z,j+1} z_j\right)}{1 + r_{j,j+1} X_{j+1} \exp\left(2ik_{z,j+1} z_j\right)}$$

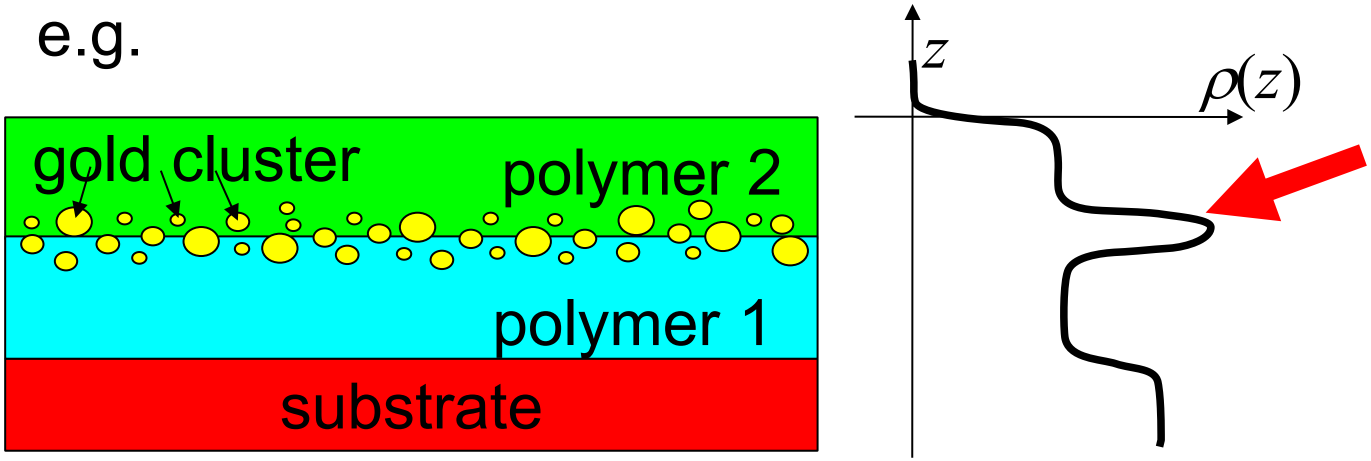
For rough layer systems the $r_{j,j+1}$ can be replaced by the $\tilde{r}_{j,j+1}$

$$\tilde{X}_j = \exp\left(-2ik_{z,j} z_j\right) \frac{\tilde{r}_{j,j+1} + X_{j+1} \exp\left(2ik_{z,j+1} z_j\right)}{1 + \tilde{r}_{j,j+1} X_{j+1} \exp\left(2ik_{z,j+1} z_j\right)}$$

However, this is only an approximation.

It fails for thin layers with large roughness.

e.g.

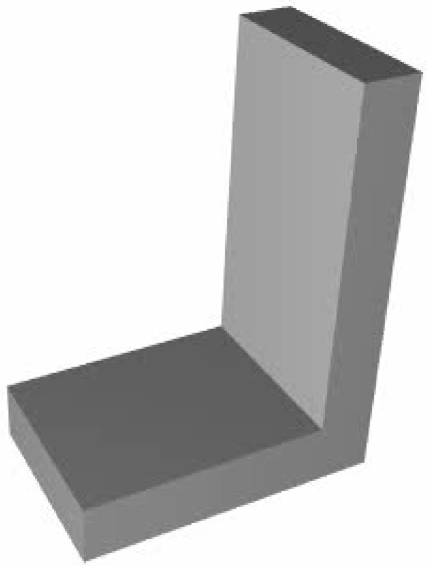


This layer can be described by a standard thin film model but the Parratt formalism may fail.

There is a way to get around this problem (see later).

Experimental part

1) The diffractometer



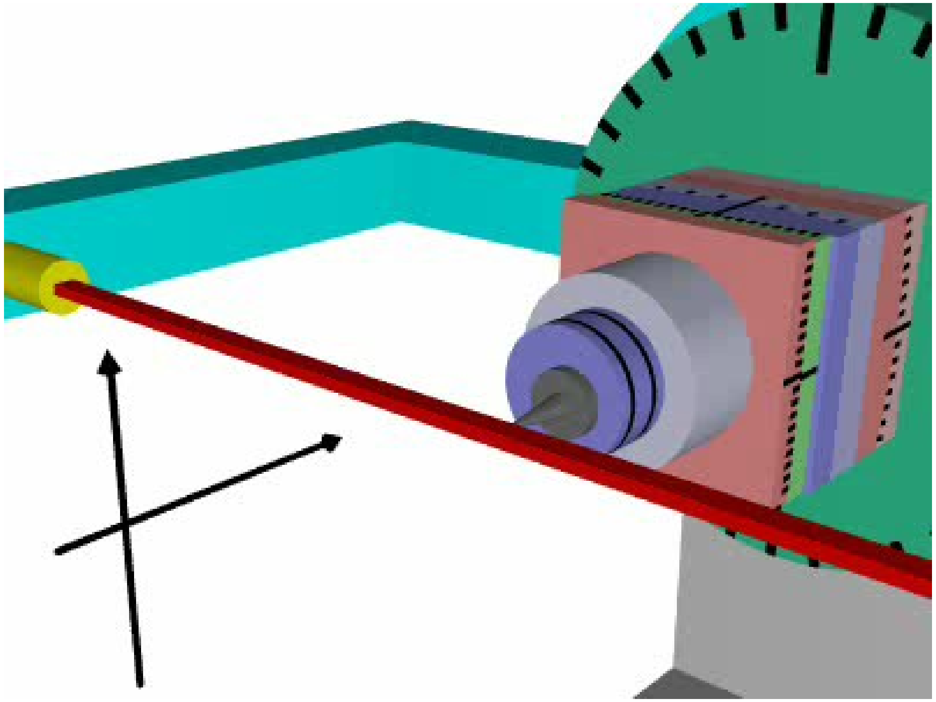
Has many degrees of freedom with high accuracy (0.001° angular resolution / 0.001mm translational resolution).

Many slits are necessary to define the beam direction (not discussed here).

Degrees of freedom

- 2θ : Detector rotation
- ω : Sample rotation (incident angle)
- χ : 1. Euler angle (align surface parallel)
- ϕ : 2. Euler angle (not used for reflectivity)
- y : Sample movement up↔down
- x : Sample movement along the beam
- z : Sample movement horizontally
- gy : Goniometer movement up↔down

2) Alignment of the sample



Goal

Put the center of the sample surface to center of rotation (marked by the beam after centering the diffractometer).

Procedure

1) Scan the primary beam without the sample. Note the intensity I_0 and the width σ and go with 2θ to the maximum. Calibrate this to 0.
2) Scan the sample in y-direction. Move y so that the sample cuts half of the beam.
3) Scan ω. Find the maximum, go there and calibrate to 0.
4) Redo step 2).
5) The ω-scan may not look symmetric. Move the sample in x-direction until it is.
6) Go to some ω–2θ value (e.g. $\omega=1°$, $2\theta=2°$), scan ω and go to the maximum. Calibrate this as $2\theta/2$. This is much more accurate than step 3).
7) If the width of 6) is **not** $\sigma/2$ the sample is bent and has to be cut in smaller pieces!
8) Scan χ widely and go to the maximum to make the surface parallel to the beam.

Techniques for refinement

1) Standard technique

- Take the data and have a qualitative look at it.
- Parametrize a density profile by film thickness, averaged film densities and interface roughnesses which may match the data. So create a model of the system.
- Take into account all external parameters (resolution of the diffractometer, background, size of the beam, size of the sample) and include them into the model.
- Take a reasonable assumption on the parameters which may match the sample conditions best (preknowledge) and calculate a reflectivity using the Parratt formalism with modified Fresnel reflection coefficients.
- Optimize χ^2 under the constraint of physical reasonability.

$$\chi^2 = \sum_{j=1}^{M} \left(I_{j,\mathrm{Data}}(q_z) - I_{j,\mathrm{Model}}(q_z) \right)^2$$

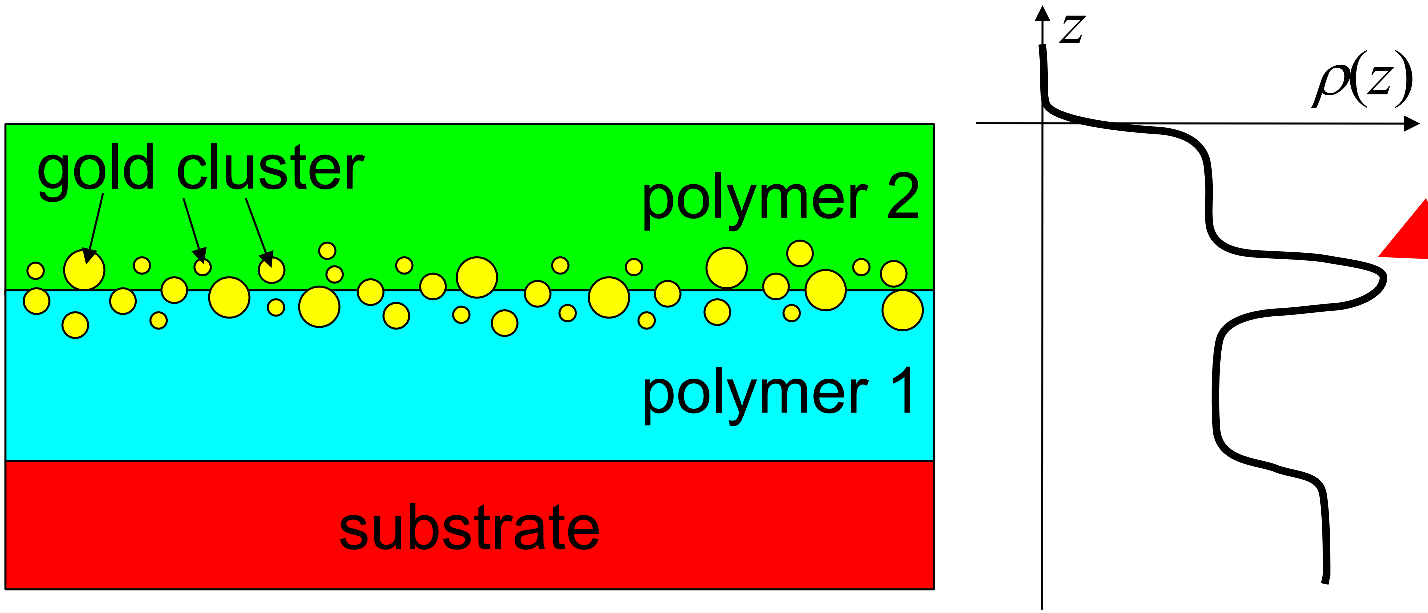
with M data points

2) Effective density model

The standard technique usually works well.
It fails if the system contains thin layers with roughnesses equal or larger than the film thickness (incomplete layers).

Reason: Interfaces cannot be treated separately any more.

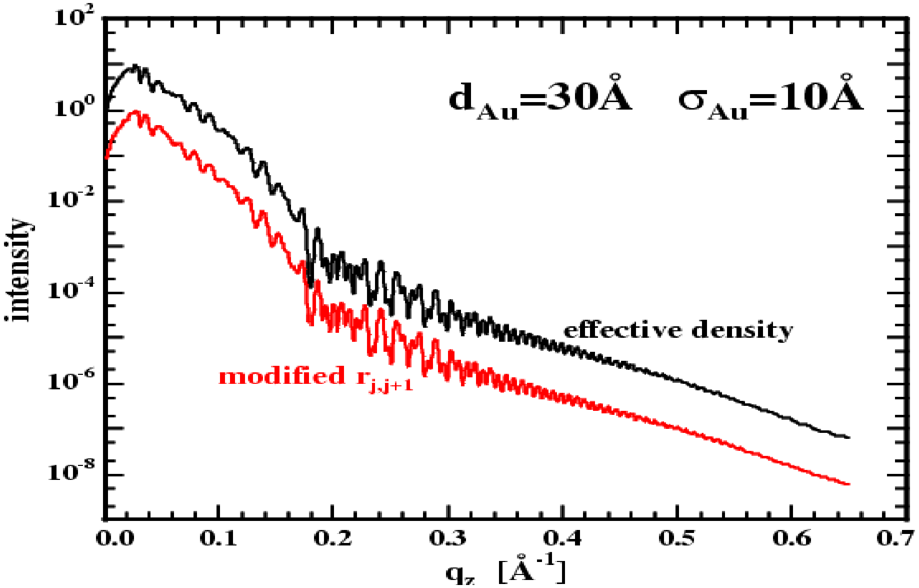
Example: Thin (30Å) gold layers embedded in polymer matrices

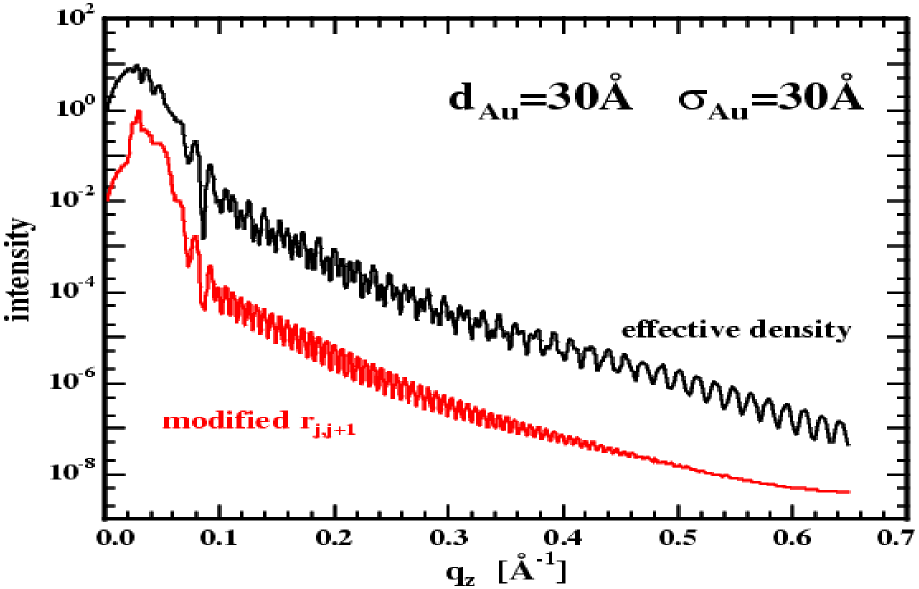


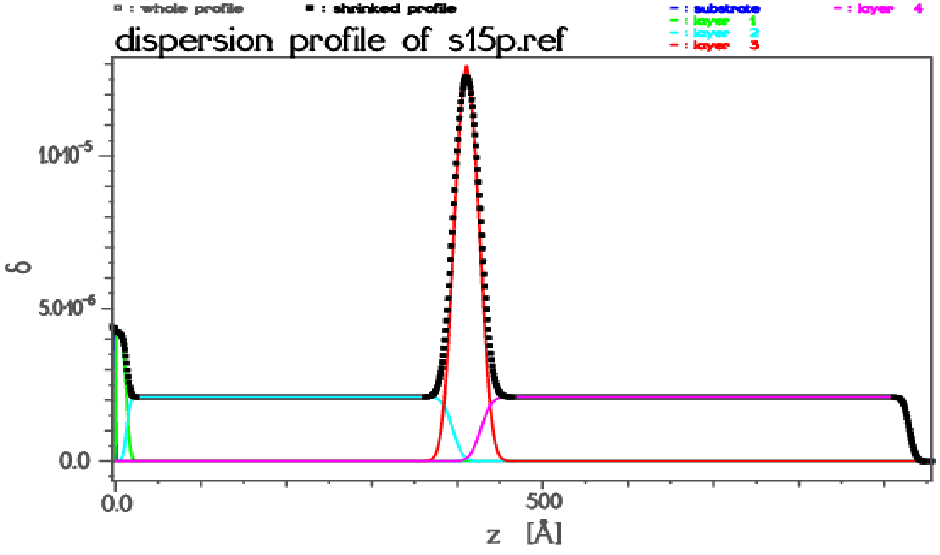
This layer can be described by a standard thin film model but the Parratt may fail.

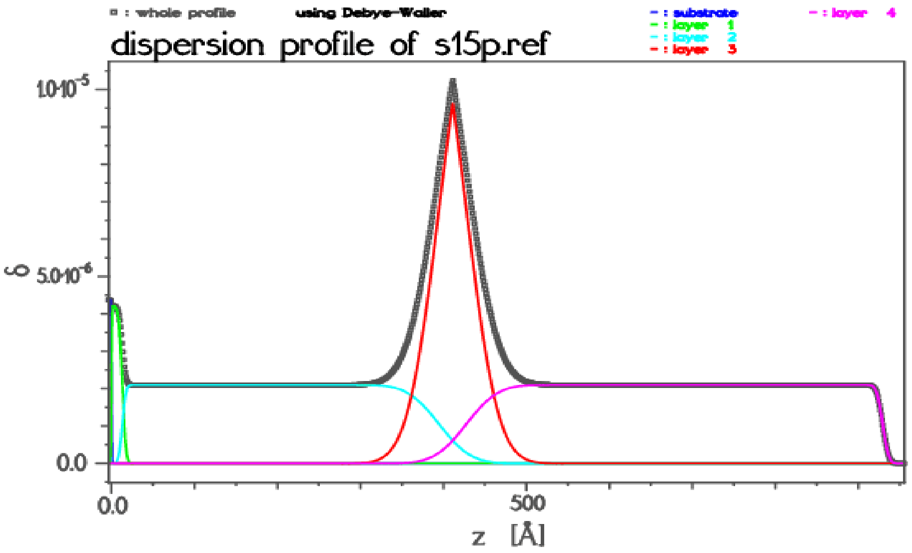
Reflectivity can be calculated by the effective density model.

1) calculating the whole density profile first
2) slicing into many very thin completely smooth sublayers
3) using this slicing for the iterative Parratt algorithm (slow!)

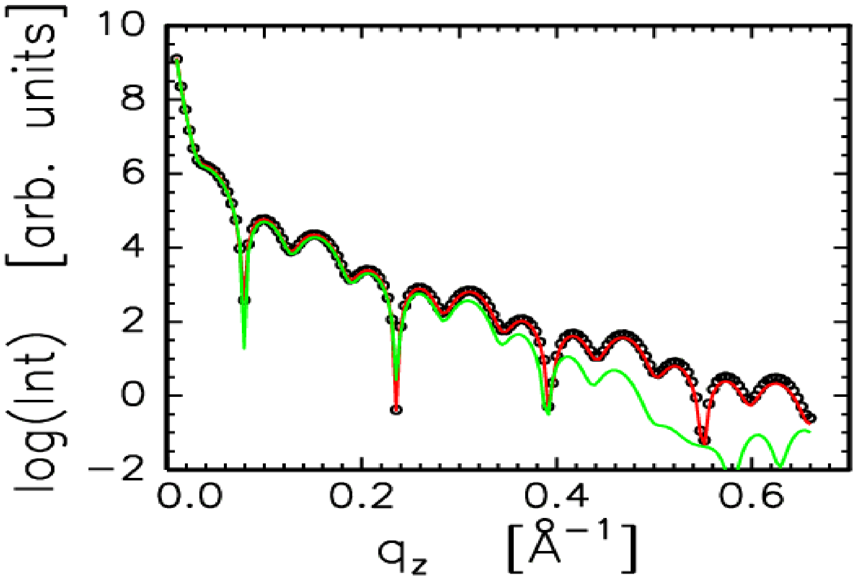


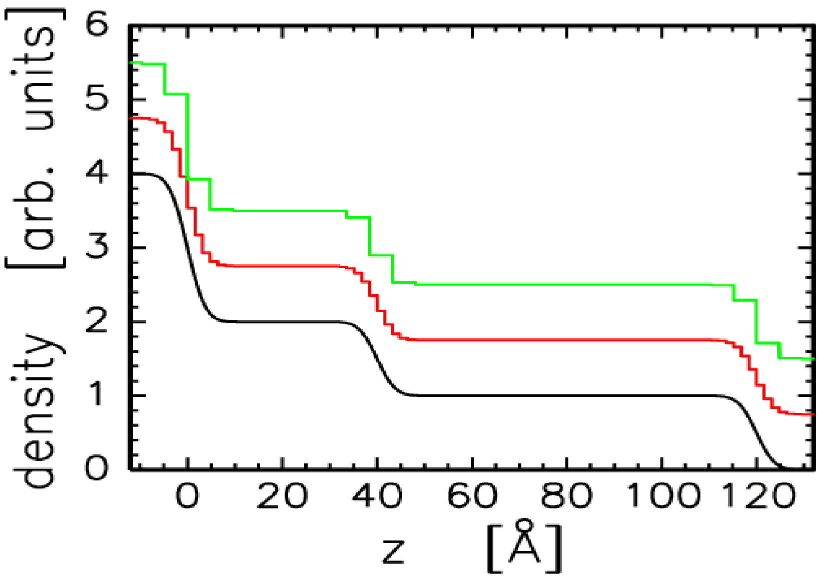


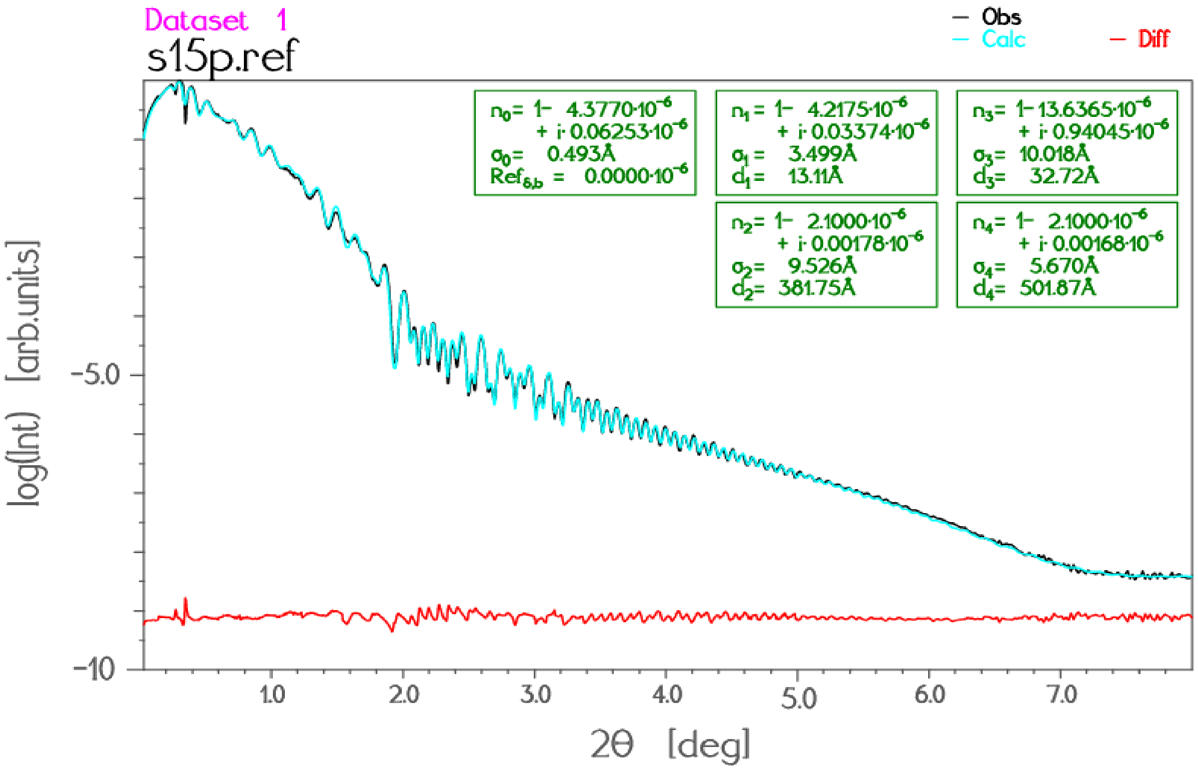




The slicing has to be adapted to th q_z-range which has been covered.







$n_0 = 1 - 4.3770 \cdot 10^{-6} + i \cdot 0.06253 \cdot 10^{-6}$
$\sigma_0 = 0.493Å$
$Ref_{6,b} = 0.0000 \cdot 10^{-6}$

$n_1 = 1 - 4.2175 \cdot 10^{-6} + i \cdot 0.03374 \cdot 10^{-6}$
$\sigma_1 = 3.499Å$
$d_1 = 13.11Å$

$n_3 = 1 - 13.6365 \cdot 10^{-6} + i \cdot 0.94045 \cdot 10^{-6}$
$\sigma_3 = 10.018Å$
$d_3 = 32.72Å$

$n_2 = 1 - 2.1000 \cdot 10^{-6} + i \cdot 0.00178 \cdot 10^{-6}$
$\sigma_2 = 9.526Å$
$d_2 = 381.75Å$

$n_4 = 1 - 2.1000 \cdot 10^{-6} + i \cdot 0.00168 \cdot 10^{-6}$
$\sigma_4 = 5.670Å$
$d_4 = 501.87Å$

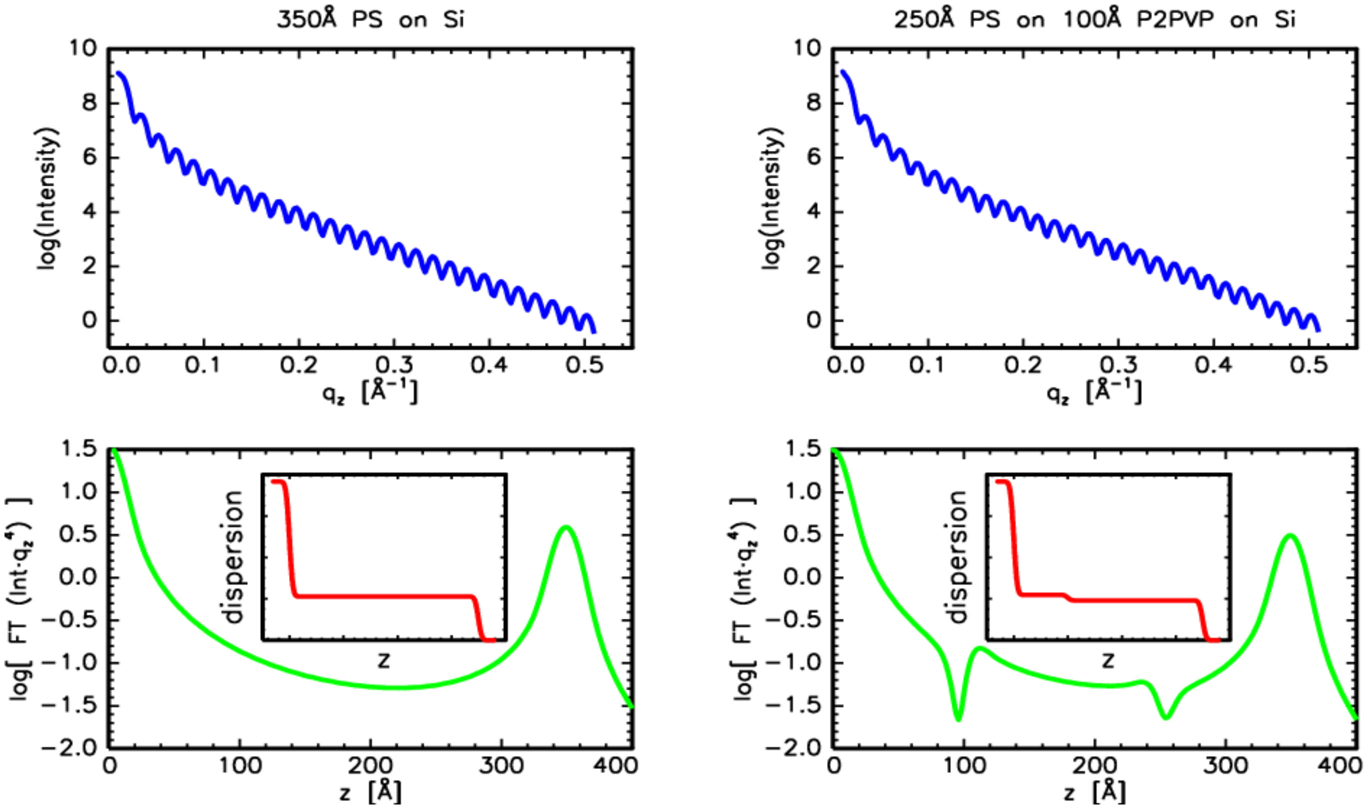
Data and fit of a
Si-PSSA(15%)-Au-PS
thin film system
(effective density model)

red curve is the difference

3) The Fourier method

To increase the sensitivity to low contrast interfaces: Include the Fourier backtransformation of $I(q_z)$ (Patterson function $P(z)$) to the refinement.

$$P(z)=\left|\int_{q_{z,low}}^{\infty} q_z^4 I(q_z)\cos(q_z z)\,dq_z\right|^2 \quad\Rightarrow\quad I(q_z)\propto\frac{1}{q_z^4}\left|\int\frac{d\rho(z)}{dz}\exp(iq_z z)\,dz\right|^2$$

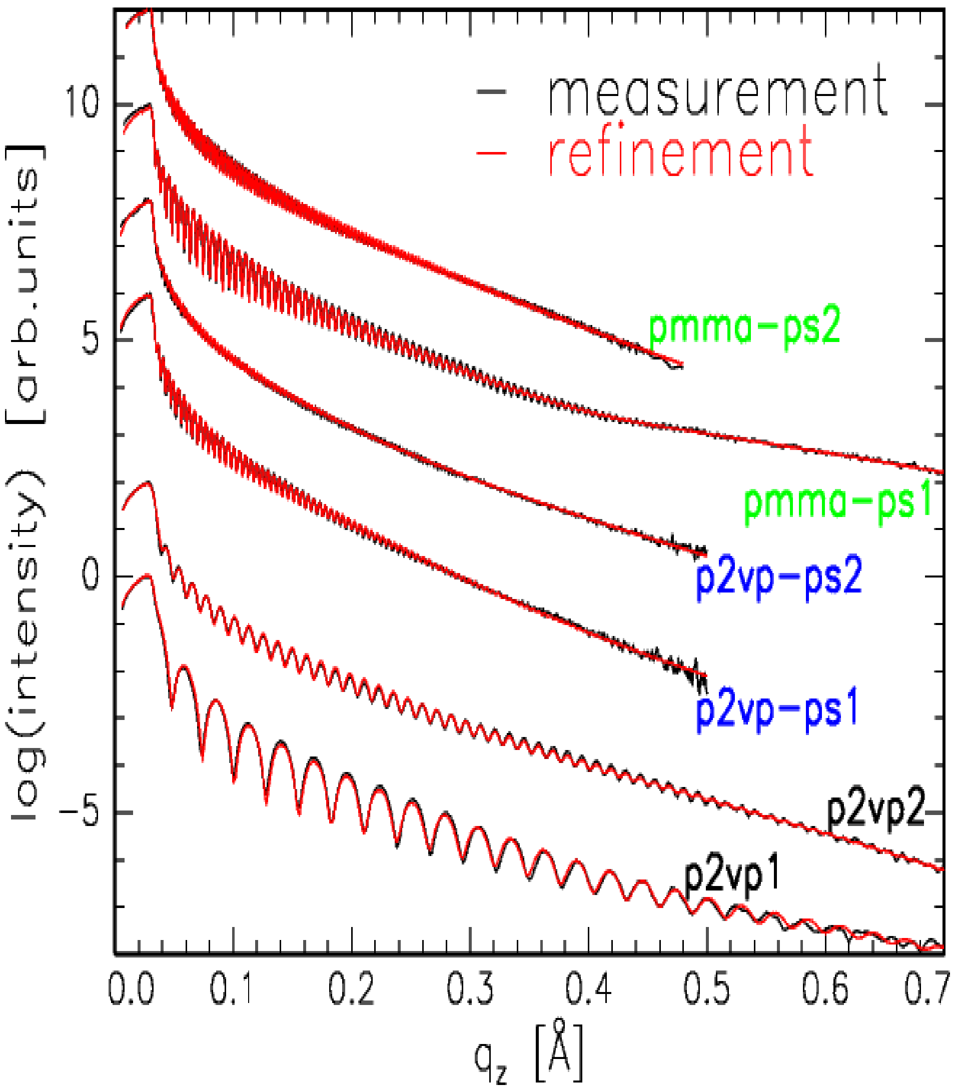


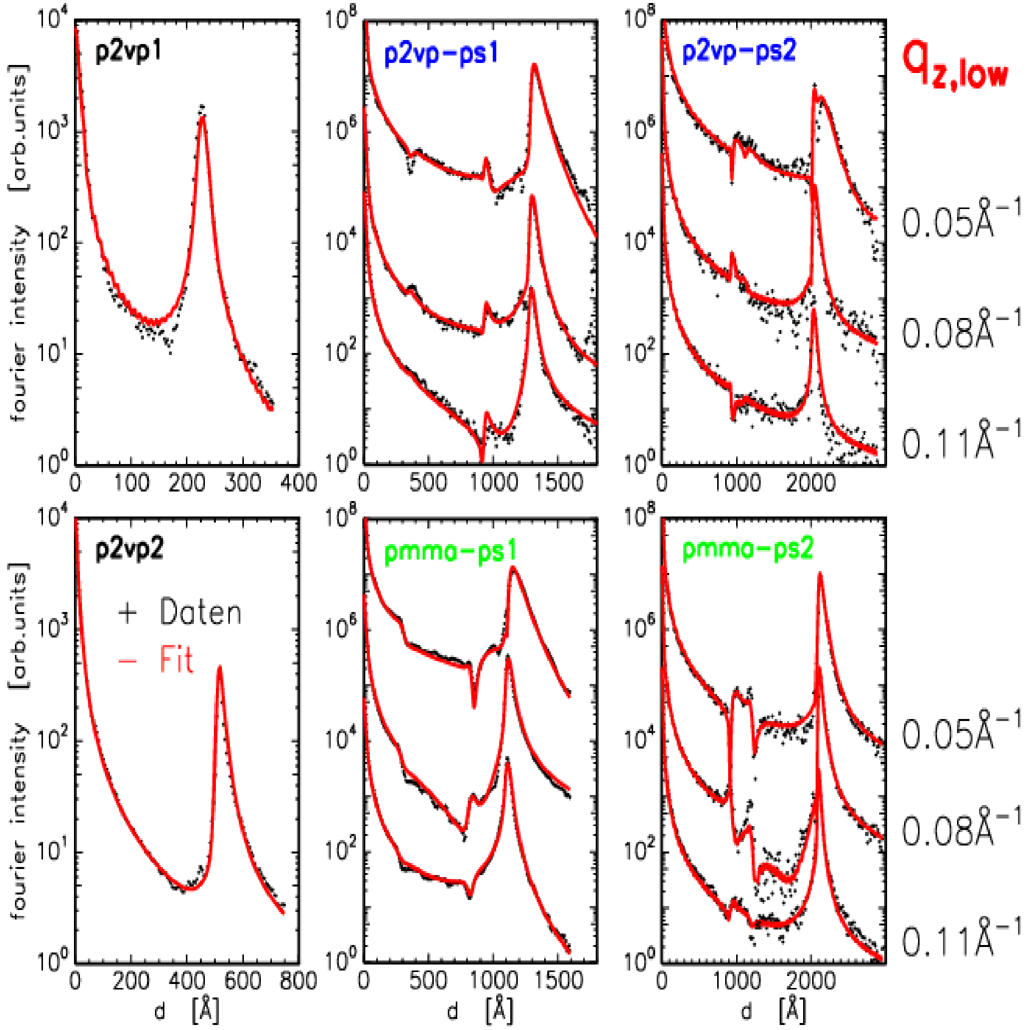
Position of the peaks/dips
⇒
Layer thickness

Shape+intensity
⇒
Probability function of the interface

Polymer Mono- and Bilayers @ 11keV

$\delta_{Si}=4.03\cdot10^{-6}$ / $\delta_{PS}=1.92\cdot10^{-6}$ / $\delta_{P2VPP}=2.00\cdot10^{-6}$ / $\delta_{PMMA}=2.17\cdot10^{-6}$





Summary

- X-ray or neutron reflectometry is a very helpful tool to investigate thin layer systems.

- The reflectivity is basically sensitive to the density profile perpendicular to the sample surface.

$$I(q_z) \propto \frac{1}{q_z^4} \left| \int \frac{d\rho}{dz} \exp(iq_z z)\, dz \right|^2$$

- Special care has to be taken when aligning the samples on a diffractometer.

- To successfully analyze the data often special tricks have to be applied.