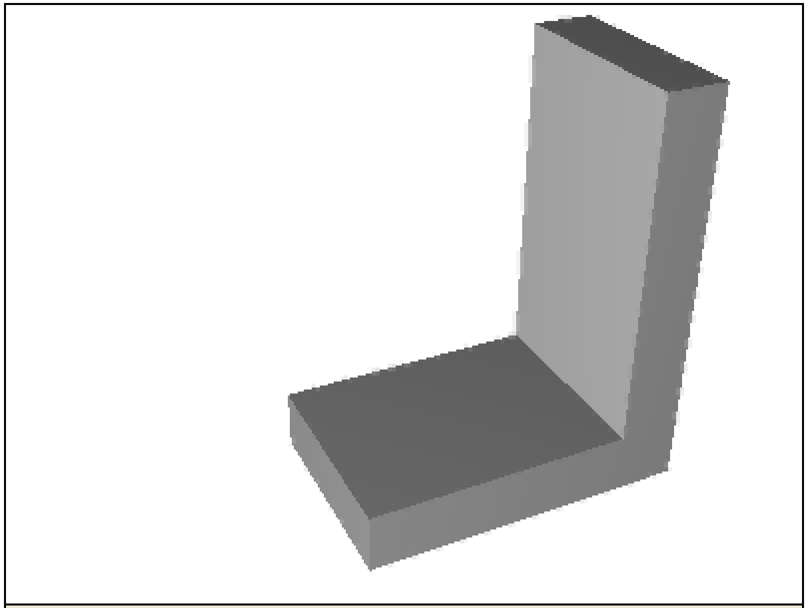
Experimental part

1) The diffractometer

Has many degrees of freedom with high accuracy (0.001° angular resolution / 0.01mm translational resolution).

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



diffractometer.avi

Degrees of freedom

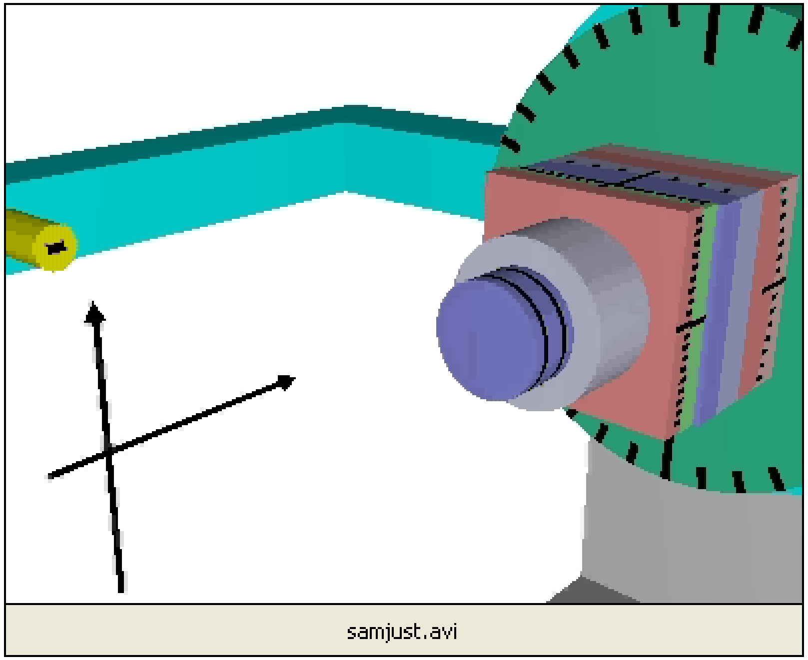
- 2θ : Detector rotation
- ω : Sample rotation (incident angle)
- χ : 1. Euler angle (align surface parallel)
- ϕ : 2. Euler angle (not used for reflectivity)

- 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).



samjust.avi

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.

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

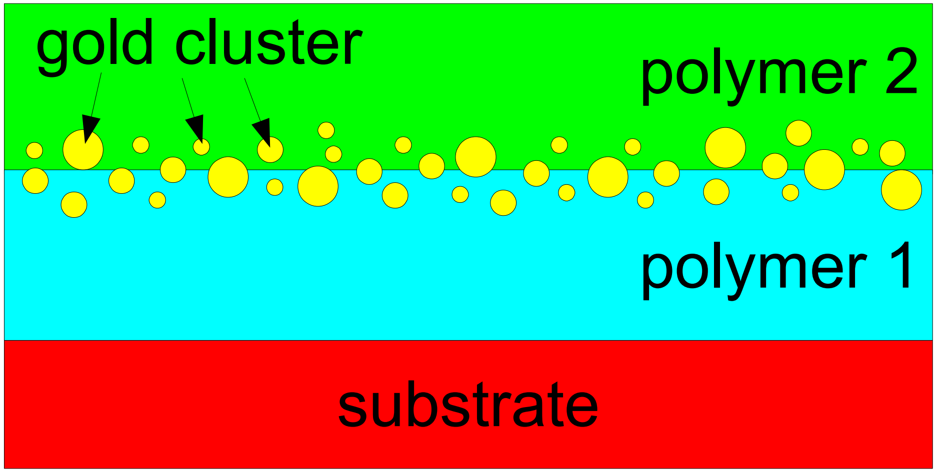
with M data points

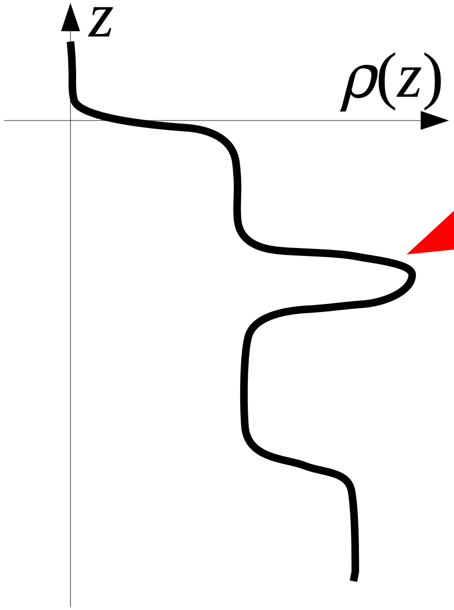
2) Effective density model

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

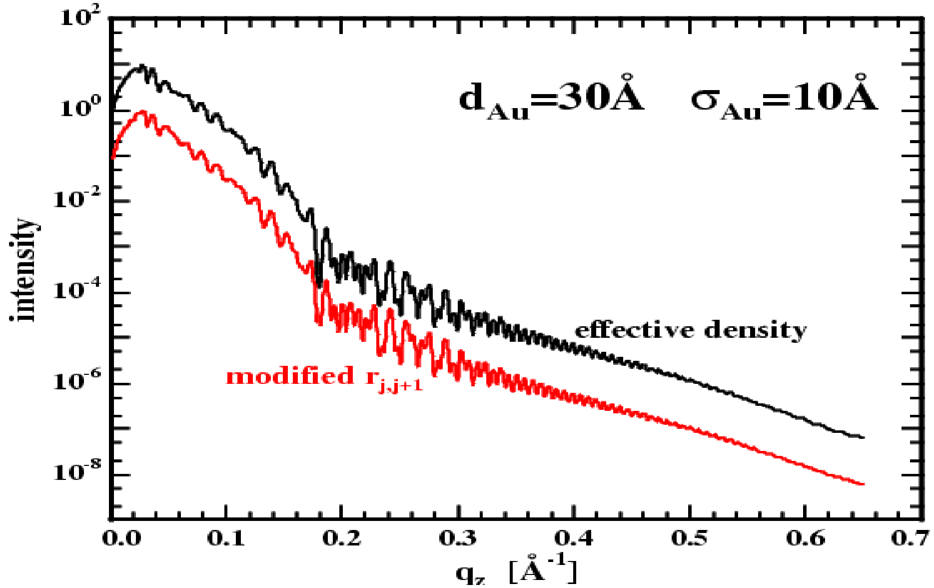


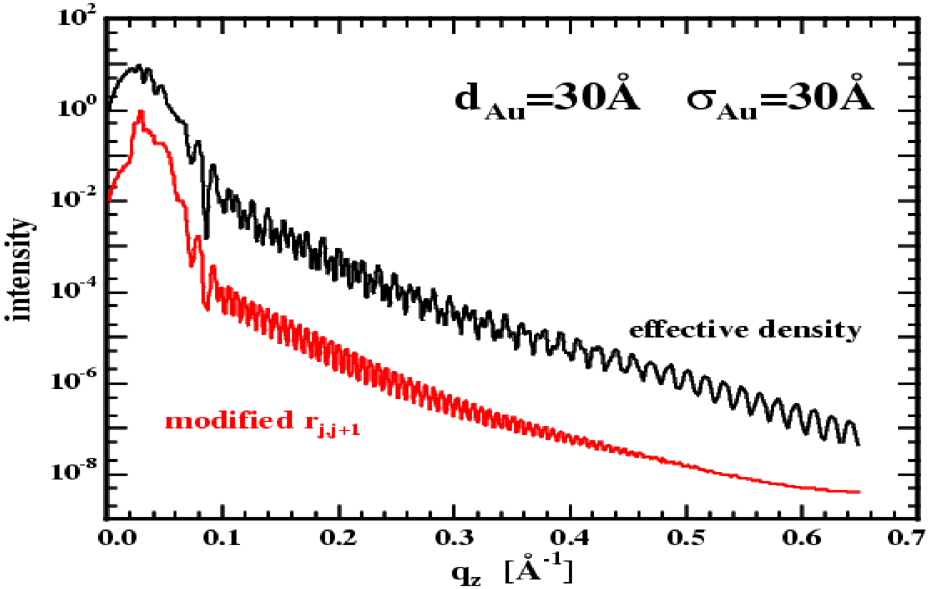


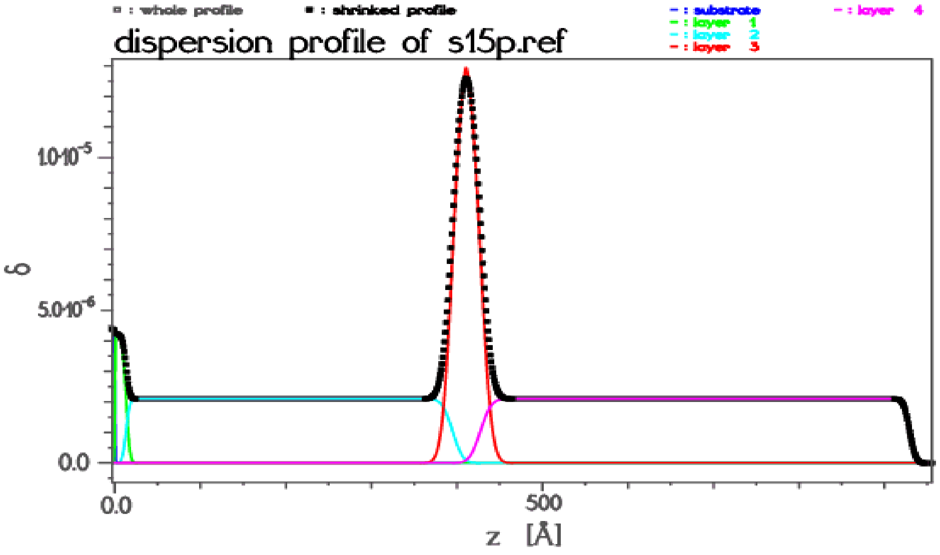
This layer can be described by a standard thin film model but the Parratt may fail.

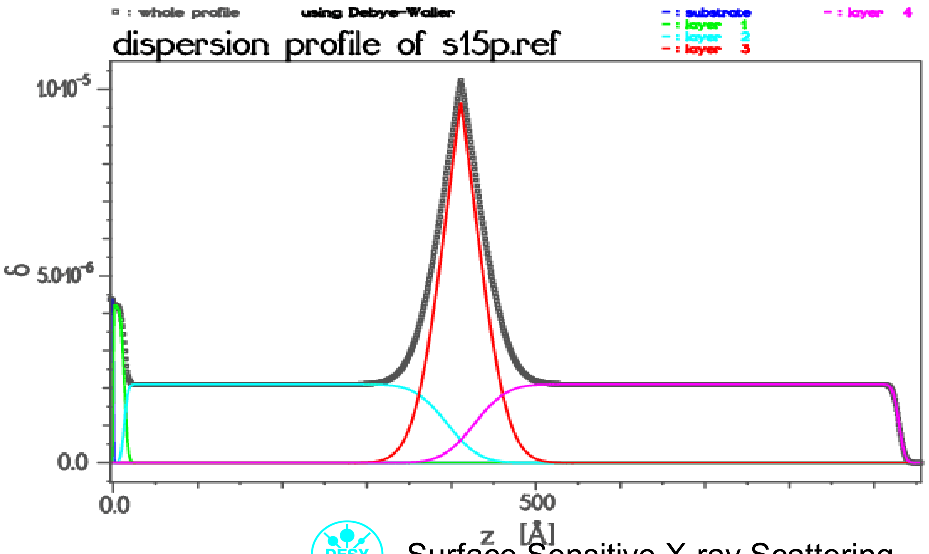
Reflectivity can be calculated by the effective density model.

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!)

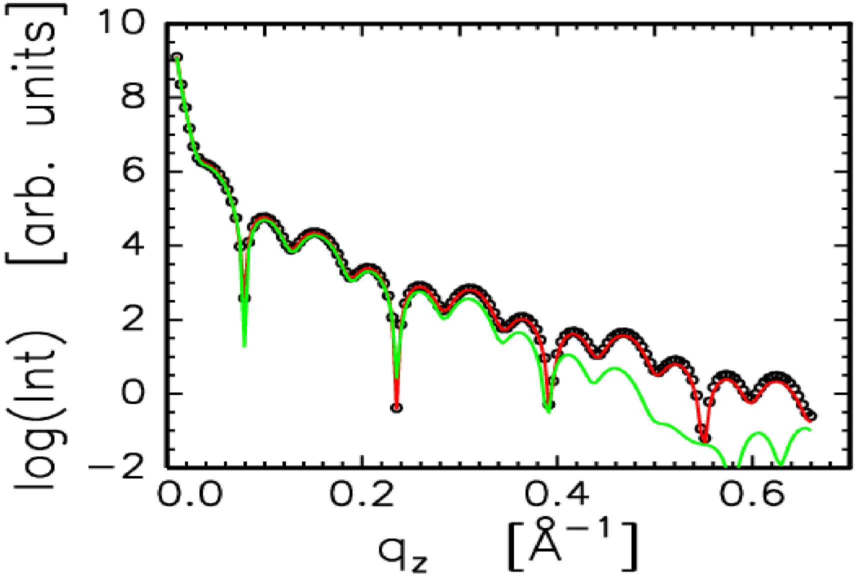


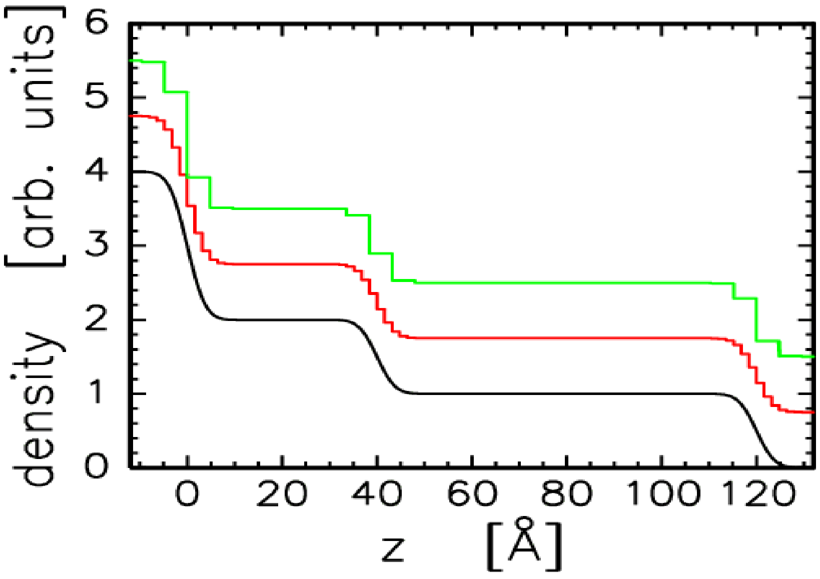


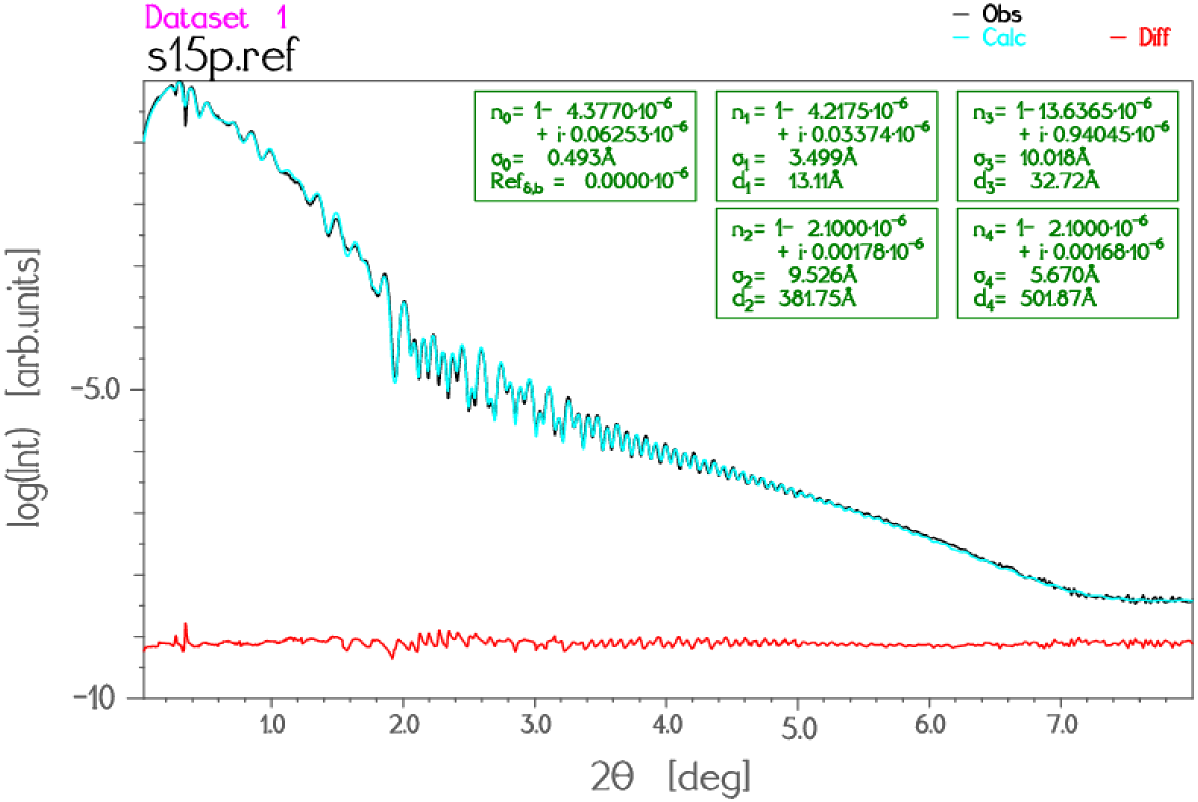




The slicing has to be adapted to th q_z-range which has been covered.







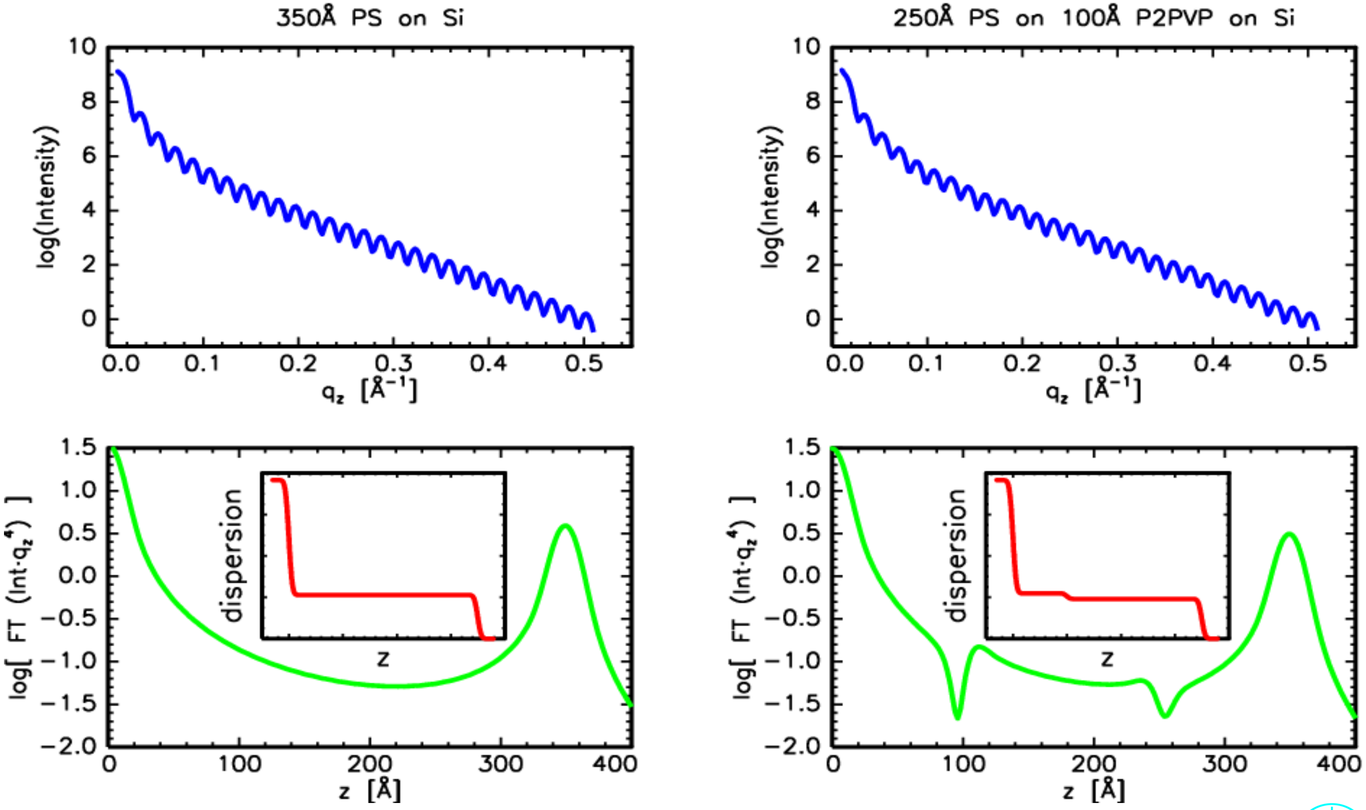
Data and fit of a Si-PSSA(15%)-Au-PS thin film system (effective density model)

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

$\Rightarrow$

Layer thickness

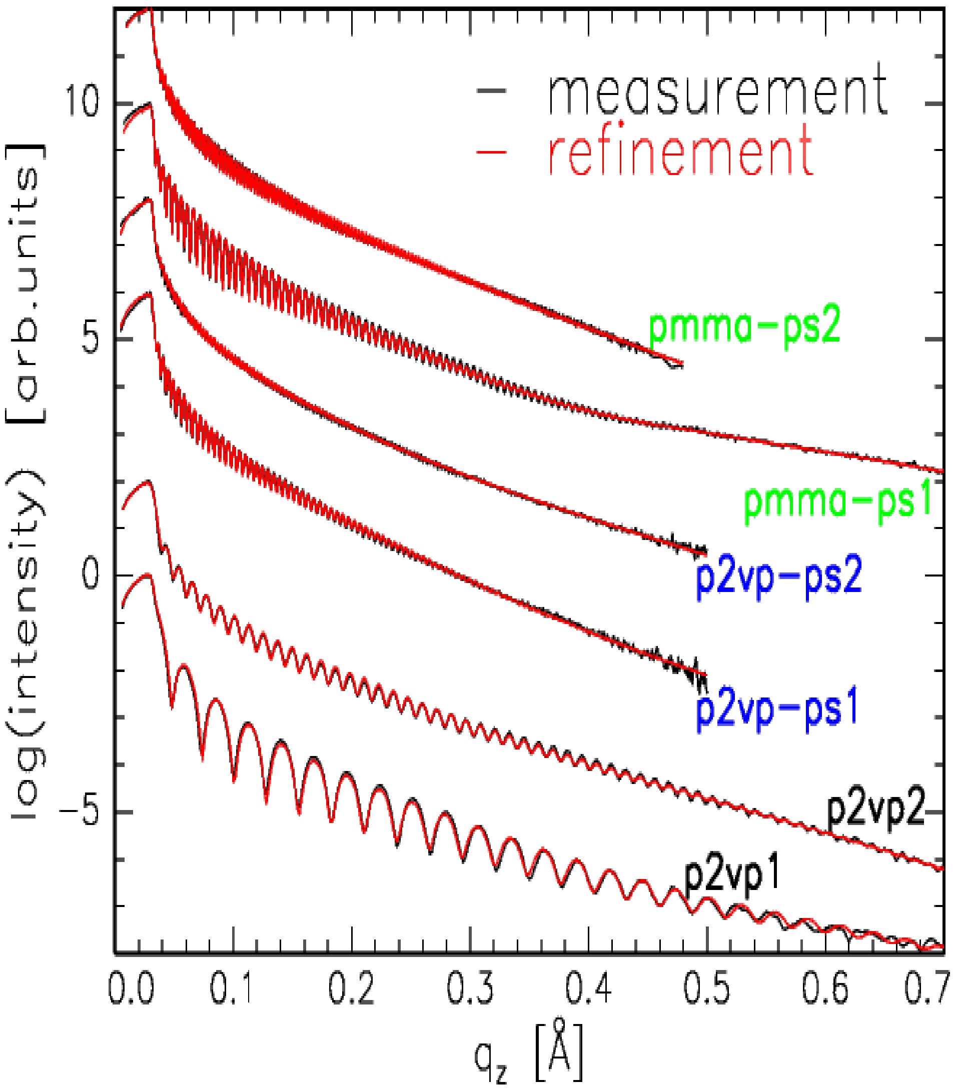
Shape+intensity

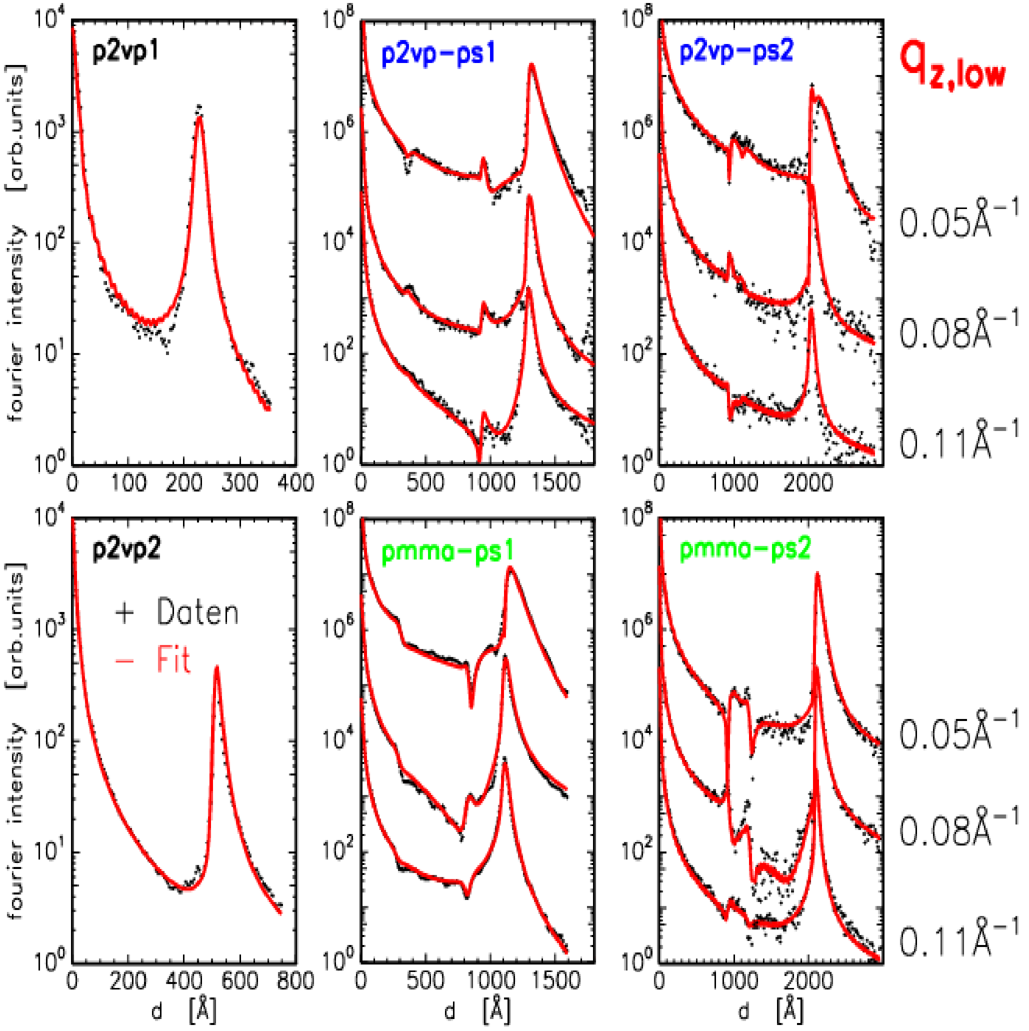
$\Rightarrow$

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.

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

- 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.