Formalisme matriciel et le programme Reflex

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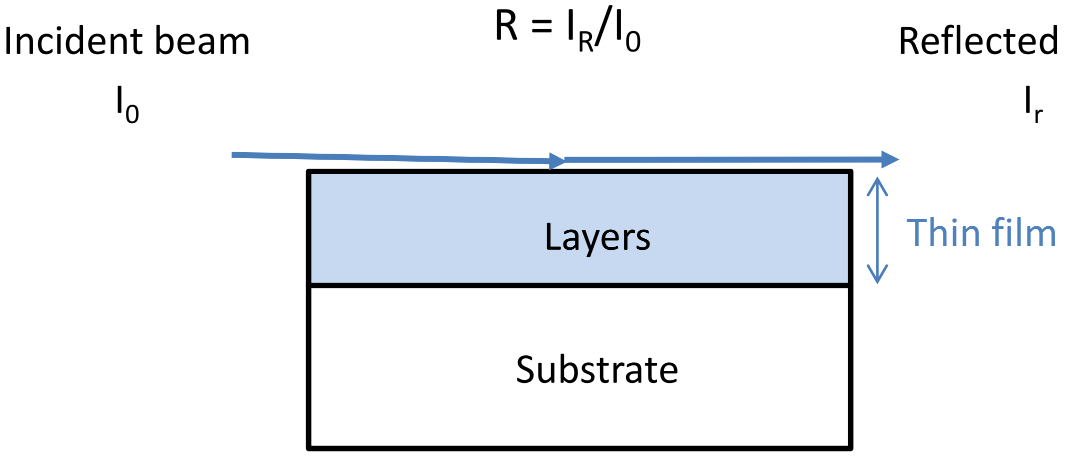
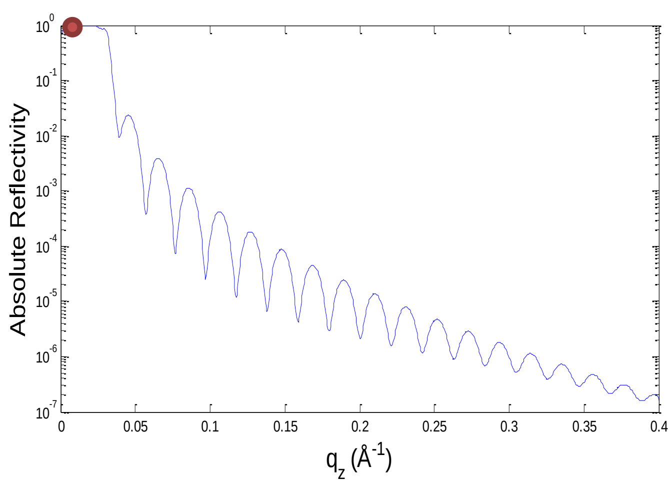
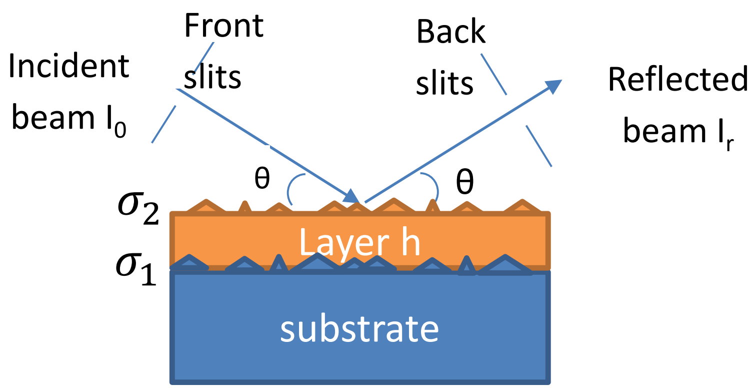
1 - Basic principles of X-ray Reflectivity

In a typical specular x-ray reflectivity experiment, a collimated beam is impinging on the surface of a flat sample at a grazing incident angle θ. The reflectivity (R) is measured as a function of the wave vector transfer q_z which for specular reflectivity is perpendicular to the surface and is given by $q_z = 4\pi \sin\theta/\lambda$. The specular reflectivity is defined as the ratio of the reflected to the incident intensity $R = I_R/I_0$ is measured as a function of increasing wave vector transfer.





Parameters influencing reflectivity



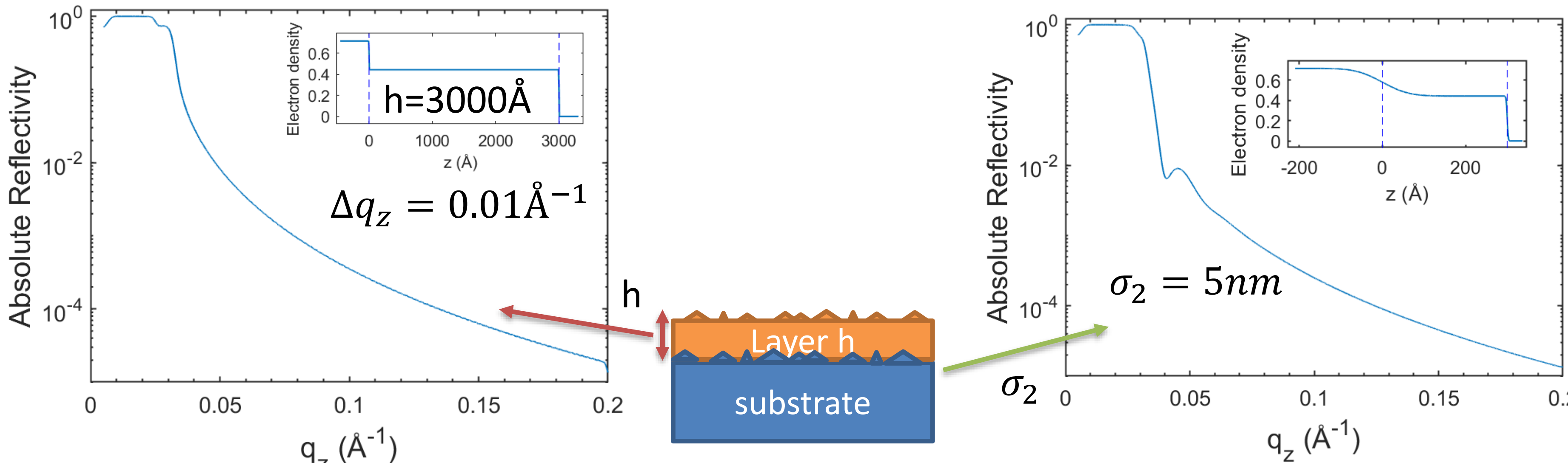
Parameters intrinsic to the nature of the sample:

- **Normal electron density profile** of the material(s)
- Layer **thickness** h: Kiessig fringes
- Surface and interface **roughness** σ_i : reduces specular reflection
- For a multilayer : the pattern and its number of repetitions

Geometric parameters that influence measurement:

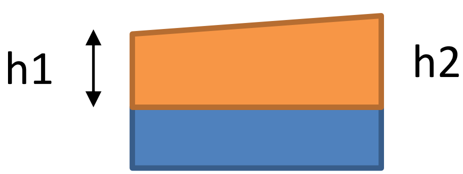
- **Angular resolution** : The angular aperture of the slits (Beam collimation), which affects the resolution of the measurement
- **Spectral resolution** : A beam that is not purely monochromatic affects the measurement
- **Sample size** influences reflected intensity.
- **Sample curvature** : an unflat surface leads to specular loss and an increase in diffuse scattering
- **coherence** of X-rays in synchrotrons

Reflectivity: limitations

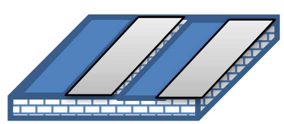


max. measurable thickness/resolution

high substrate roughness



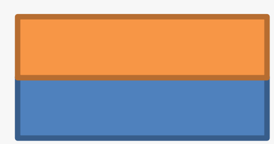
non-uniform thickness
Curved sample



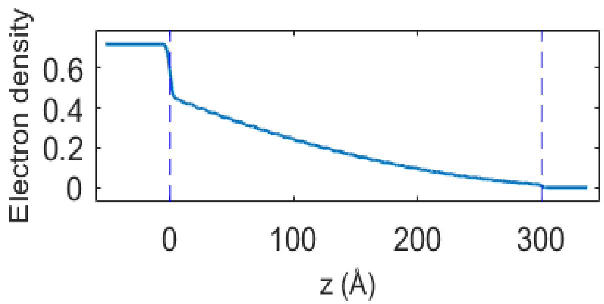
surface illuminated by the beam, inhomogeneous

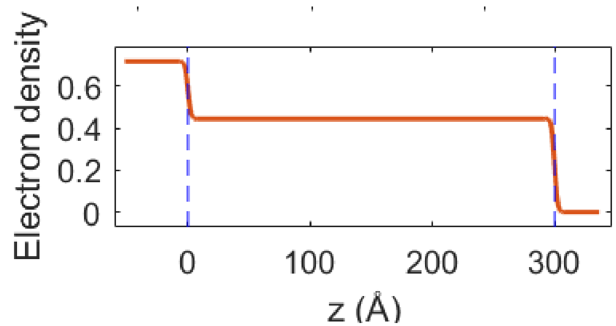
<u>**ideal sample:**</u>

Homogeneous flat surface
not very rough (σ < 1nm)
not very thick (h < 1500Å)
3 layers max



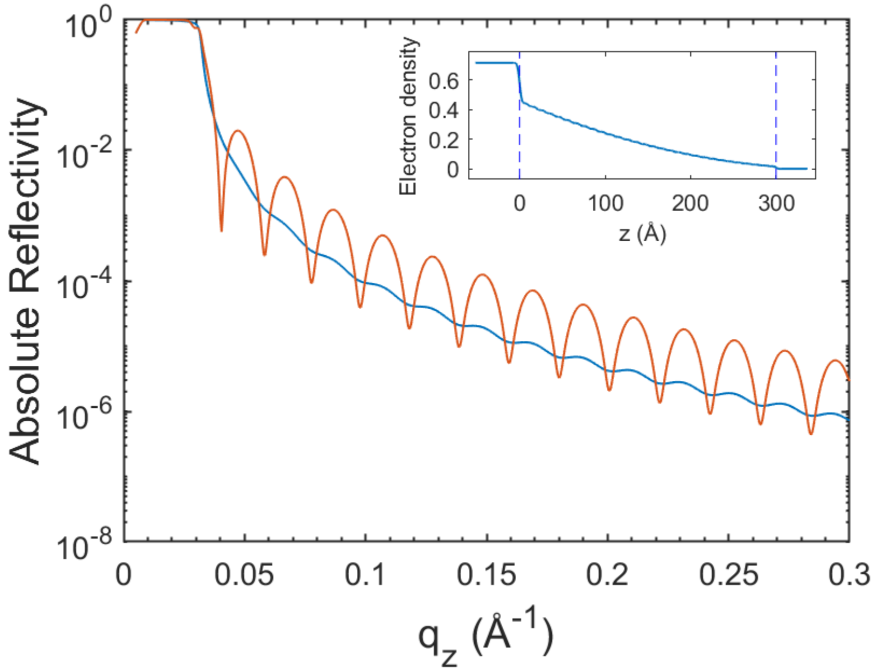
Complicated samples for reflectivity analysis





density gradient

uniform density



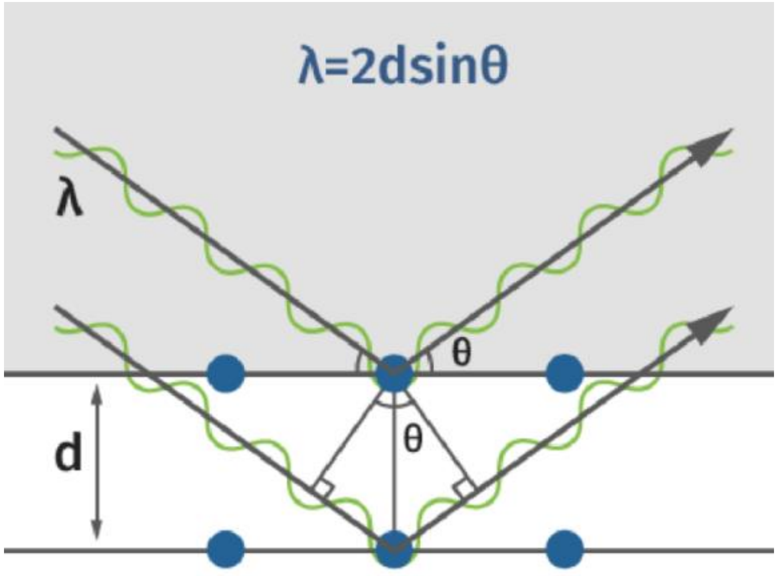
multiply characterization techniques: AFM, …

non-uniqueness of solution due to loss of phase

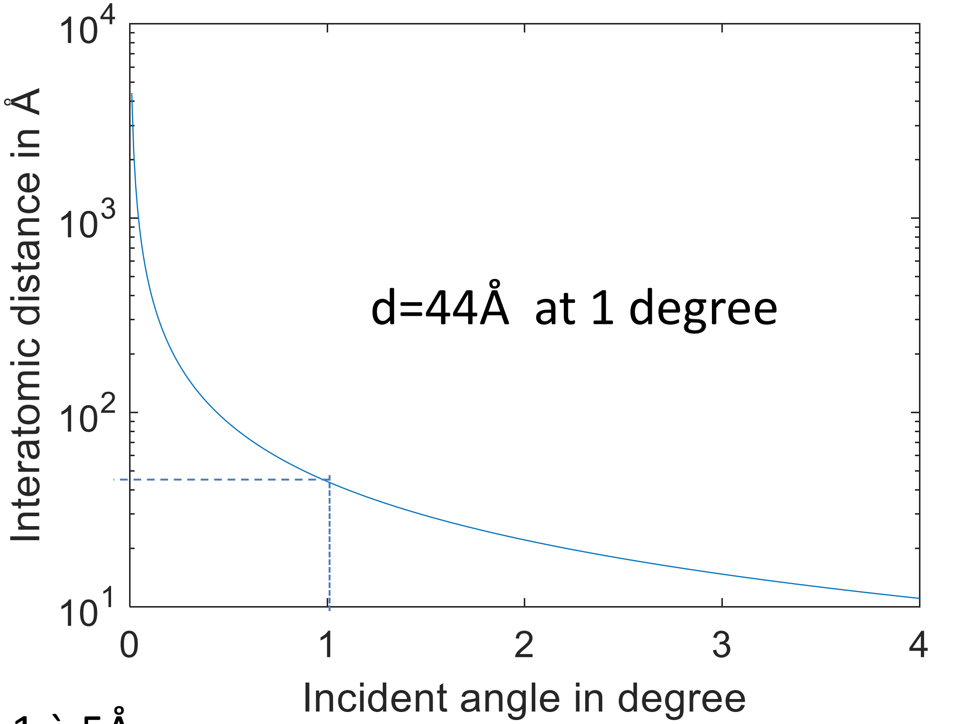
2 - THEORETICAL BACKGROUND
2.1 From optics to X-rays

► **At small angles : Approximation of continuum of electron density**

Constructive interference if:



Interatomic distance allowing constructive interference at a wavelength of 1.54Å



average distance between atomic planes : 1 à 5Å
i.e. an incident angle of about 15°.

► Reflection of an electromagnetic wave at the surface

Medium studied : **Isotropic, linear and homogeneous dielectric and non magnetic**

The calculation is based on the classical formalism of electromagnetic waves applied to X-rays

Maxwell Equations

And

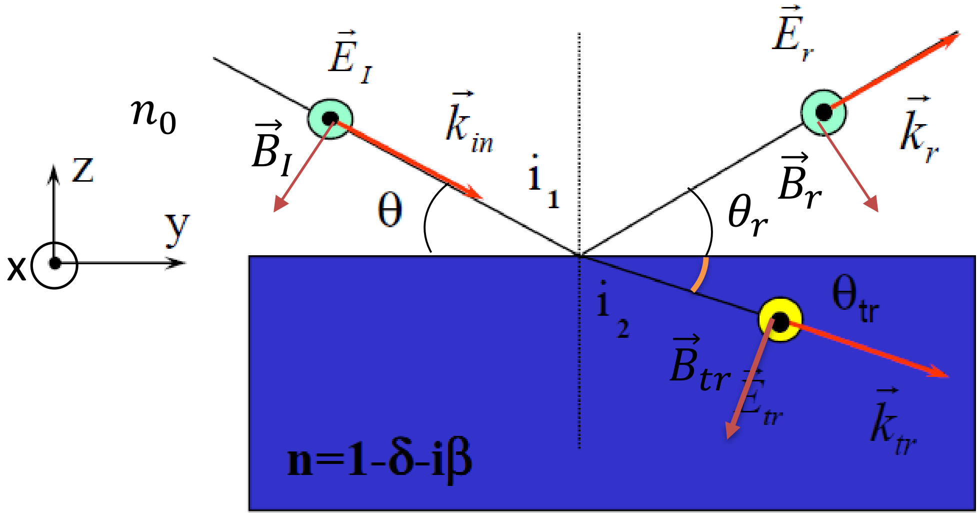
Boundary Conditions of the electric and magnetic fields at each interface

And

Fresnel coefficients of reflection (r) and transmission (t)

Reflection and transmission of an electromagnetic wave at an ideal surface

The incident wave "TE" for Transverse Electric (polarized "s") is taken according to $\vec{e}_x$.



In each medium the electric field is a solution of **Helmoltz equation:**

$$\Delta\vec{E} + k_j^2\vec{E} = 0$$

Plane waves

$$\vec{E}_j = A_j e^{i(\omega t - \vec{k}_j . \vec{r})}\, \vec{e}_x \quad \text{with j=I,T,R}$$

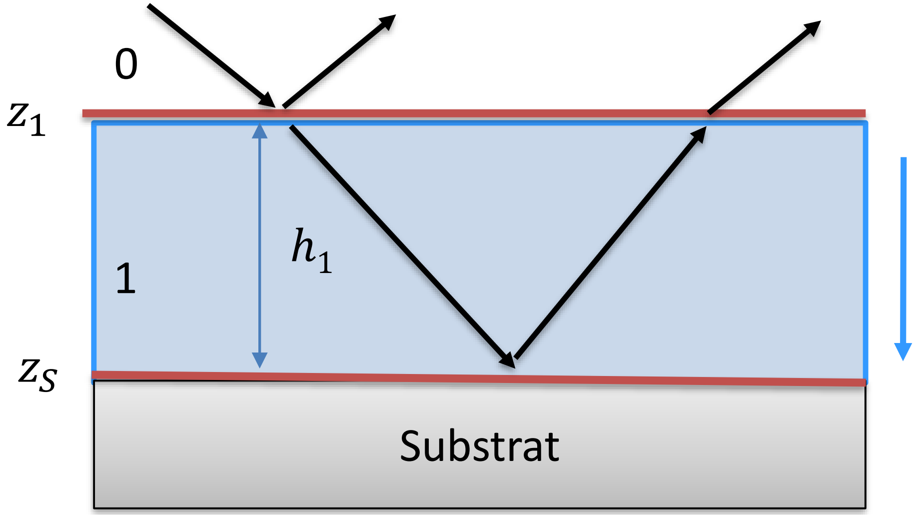
$$\vec{B}_j = \frac{\vec{k}_j \wedge \vec{E}_j}{\omega}$$

2.2 The basics of the Abeles matrix technique

The Abeles matrix calculation method is an approach used mainly to study the propagation of waves through thin films and stratified media (François Abélès 1950).

The idea is to model the propagation of electromagnetic wave in a medium made up of several stacked layers, each with different optical properties (refractive index, thickness, etc.). For each interface between two layers, part of the wave is transmitted and part is reflected.

Example : One layer one a substrate



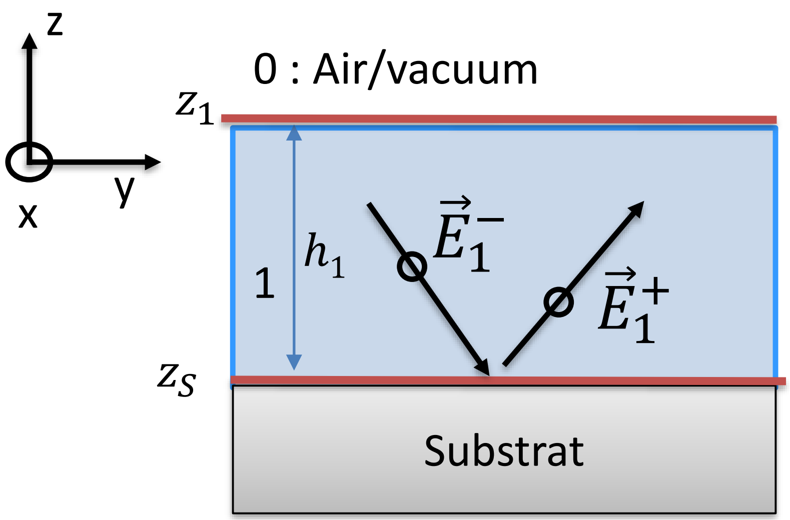
$R_{0,1}$: Interface matrix (refraction and reflection)

T_1 : Propagation matrix in medium 1 (translation)

$R_{1,S}$: Interface matrix (refraction and reflection)

Example: one layer one a substrate

The calculation is performed with the component normal to the plane of incidence



At altitude z the downwards travelling waves is defined by the electric filed in the medium 1:

$$\vec{E}_1^- = A_1^- e^{i(\omega t - k_{y,1} y + k_{z,1} z)} \vec{e}_x$$

And the upwards travelling waves is defined by:

$$\vec{E}_1^+ = A_1^+ e^{i(\omega t - k_{y,1} y - k_{z,1} z)} \vec{e}_x$$

the upward and downward travelling waves are superimposed, so that the resulting electric field in medium 1 along Ox is:

$$E_1 = \left(A_1^+ e^{-ik_{z,1} z} + A_1^- e^{+ik_{z,1} z}\right) e^{i(\omega t - k_{y,1} y)}$$

$$E_1 = \left(u_1^+(z) + u_1^-(z)\right) e^{i(\omega t - k_{y,n} y)}$$

Laws of Conservation

At altitude z the upwards and downwards travelling waves are superimposed so that the electric filed in the medium 1 is:

BOUNDARY CONDITIONS at $z = z_1$

Conservation of $\begin{cases} \text{tangential component of the elctrique field E} \\ \text{tangential component of the magnetic field} \Leftrightarrow \dfrac{\partial E}{\partial z} \end{cases}$

Conservation of

$$\begin{cases} E(z_1) & u_0^+(z_1) + u_0^-(z_1) = u_1^+(z_1) + u_1^-(z_1) \\ \dfrac{\partial E}{\partial z}(z_1) & k_{z,0}\left(u_0^+(z_1) - u_0^-(z_1)\right) = k_{z,1}\left(u_1^+(z_1) - u_1^-(z_1)\right) \end{cases}$$

$$k_{z,1} = -k_0\sqrt{n_1^2 - n_0^2 cos^2\theta}$$

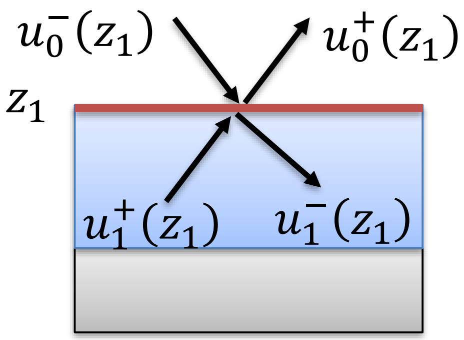
wave vector in medium 1

Definition of the **refraction matrix R** at the z_1 interface:

Example : One layer one a substrate

Using the **laws of conservation at interface z_1**, the link between the electric field in air and in medium 1 can be written in matrix form and we can define a refraction/reflection matrix $R_{0,1}$ when we go from medium 0 to medium 1:

$$\underbrace{\begin{bmatrix} u_0^+(z_1) \\ u_0^-(z_1) \end{bmatrix}}_{\text{Electric field in Vacuum at } z_1} = \underbrace{\begin{bmatrix} p_{0,1} & m_{0,1} \\ m_{0,1} & p_{0,1} \end{bmatrix}}_{R_{0,1}} \underbrace{\begin{bmatrix} u_1^+(z_1) \\ u_1^-(z_1) \end{bmatrix}}_{\text{Electric field in medium 1 at } z_1} = R_{0,1} \begin{bmatrix} u_1^+(z_1) \\ u_1^-(z_1) \end{bmatrix}$$



Electric field in Vacuum at z_1

Electric field in medium 1 at z_1

with $p_{0,1} = \frac{k_{z,0} + k_{z,1}}{2k_{z,0}}$ and $m_{0,1} = \frac{k_{z,0} - k_{z,1}}{2k_{z,1}}$

$k_{z,0}$ wave vector in vacuum

$$k_{z,1} = -k_0\sqrt{n_1^2 - n_0^2 cos^2\theta}$$

wave vector in medium 1

Definition of the **propagation matrix T** in medium 1:

Example : One layer one a substrate

The amplitude of the electric field within the medium n varies with depth z

$$z_1 \Longrightarrow z_S = z_1 + h$$

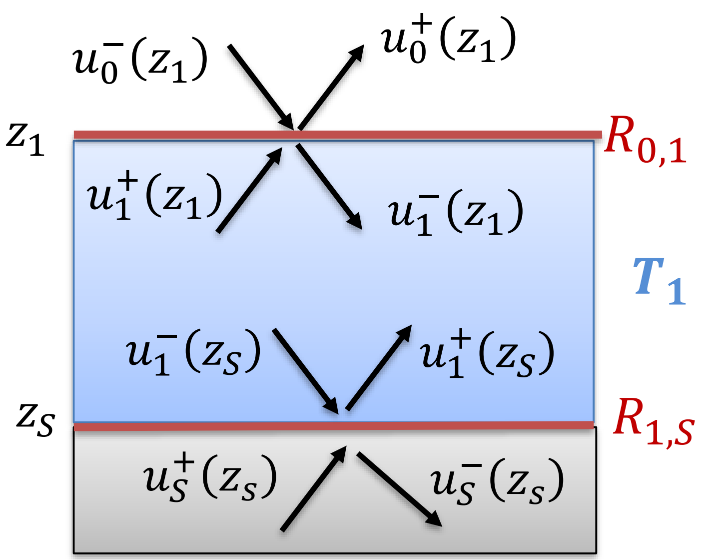
$$u_1^+(z_1) = A_1^+ e^{-ik_{z1}z_1} \Longrightarrow u_1^+(z_S) = A_1^+ e^{-ik_{z,1}(z_1+h)} = u_1^+(z_1)e^{-ik_{z,1}h}$$

$$\begin{bmatrix} u_1^+(z_1) \\ u_1^-(z_1) \end{bmatrix} = \begin{bmatrix} e^{-ik_{z,1}h} & 0 \\ 0 & e^{ik_{z,1}h} \end{bmatrix} \begin{bmatrix} u_1^+(z_S) \\ u_1^-(z_S) \end{bmatrix} = T_1 \begin{bmatrix} u_1^+(z_S) \\ u_1^-(z_S) \end{bmatrix}$$

T_1: translation matrix

$$\begin{bmatrix} u_0^+(z_1) \\ u_0^-(z_1) \end{bmatrix} = [R_{0,1} T_1 R_{1,S}] \begin{bmatrix} u_S^+(z_S) \\ u_S^-(z_S) \end{bmatrix}$$

M: transfer matrix



Example : One layer one a substrate

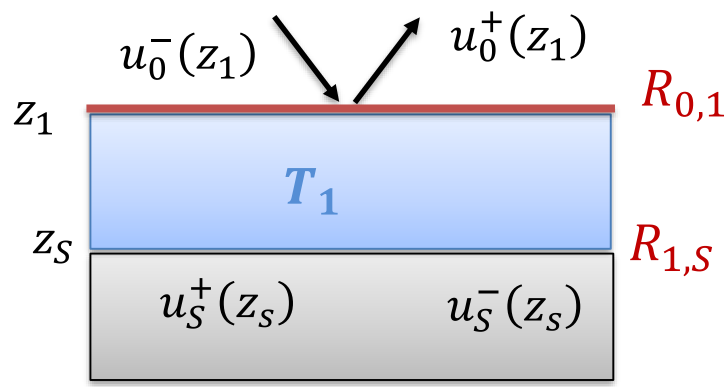
$$\begin{bmatrix} u_0^+(z_1) \\ u_0^-(z_1) \end{bmatrix} = [M] \begin{bmatrix} u_S^+(z_s) \\ u_S^-(z_s) \end{bmatrix}$$

$$M = \begin{bmatrix} p_{0,1} & m_{0,1} \\ m_{0,1} & p_{0,1} \end{bmatrix} \begin{bmatrix} e^{-ik_{z,1}h} & 0 \\ 0 & e^{ik_{z,1}h} \end{bmatrix} \begin{bmatrix} p_{1,2} & m_{1,2} \\ m_{1,2} & p_{1,2} \end{bmatrix}$$

$$M = \begin{bmatrix} p_{0,1}p_{1,2}e^{-ik_{z,1}h} + m_{0,1}m_{1,2}e^{ik_{z,1}h} & m_{1,2}p_{0,1}e^{-ik_{z,1}h} + m_{0,1}p_{1,2}e^{ik_{z,1}h} \\ m_{0,1}p_{1,2}e^{-ik_{z,1}h} + m_{1,2}p_{0,1}e^{ik_{z,1}h} & m_{0,1}m_{1,2}e^{-ik_{z,1}h} + p_{0,1}p_{1,2}e^{ik_{z,1}h} \end{bmatrix}$$

The reflection coefficient by the sample is defined as the ratio of the reflected electric field to the incident electric field at the surface of the material :

$$r = \frac{u_0^+(z_1)}{u_0^-(z_1)} = \frac{M_{11}u_S^+(z_s) + M_{12}u_S^-(z_s)}{M_{21}u_S^+(z_s) + M_{22}u_S^-(z_s)}$$

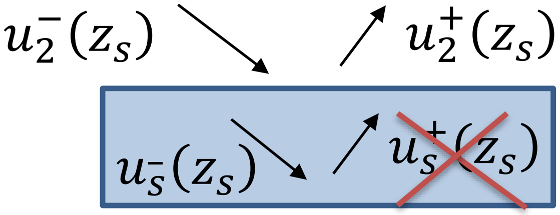


Example : One layer one a substrate

$$r = \frac{u_0^+(z_1)}{u_0^-(z_1)} = \frac{M_{11}u_s^+(z_s) + M_{12}u_s^-(z_s)}{M_{21}u_s^+(z_s) + M_{22}u_s^-(z_s)}$$

It is reasonable to assume that no wave will be reflected back from the substrate if x-rays penetrate only few microns:

thus $u_s^+(z_s) = 0$



$$r = \frac{u_0^+(z_1)}{u_0^-(z_1)} = \frac{M_{12}}{M_{22}}$$

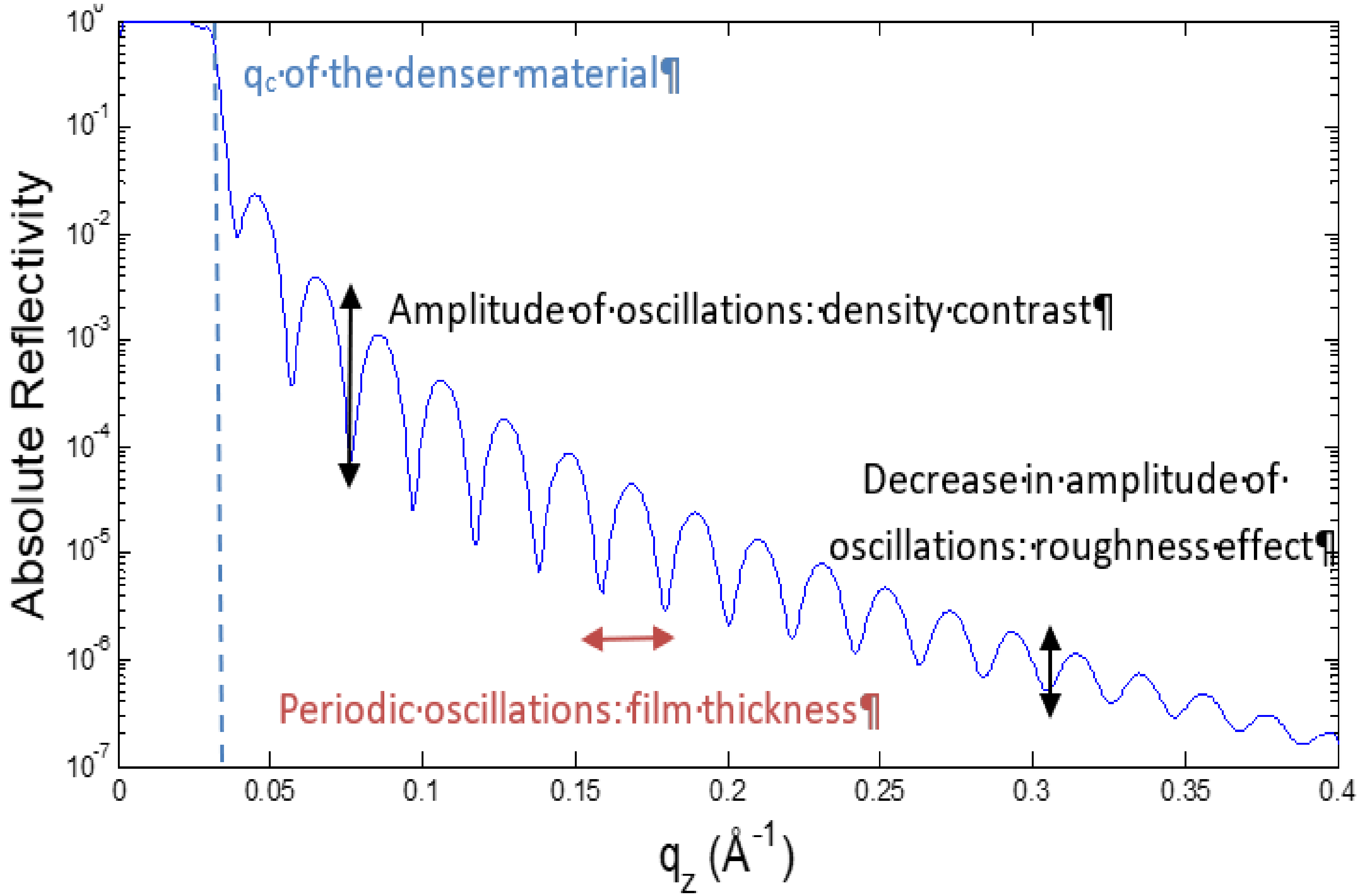
Example : One layer one a substrate

$$r = \frac{M_{12}}{M_{22}} = \frac{m_{1,2}p_{0,1}e^{-ik_{z,1}h} + m_{0,1}p_{1,2}e^{ik_{z,1}h}}{m_{0,1}m_{1,2}e^{-ik_{z,1}h} + p_{0,1}p_{1,2}e^{ik_{z,1}h}} = \frac{r_{01}e^{-ik_{z,1}h} + r_{12}e^{ik_{z,1}h}}{e^{-ik_{z,1}h} + r_{01}r_{12}e^{ik_{z,1}h}}$$

$$r = \frac{r_{01}e^{-ik_{z,1}h} + r_{12}e^{ik_{z,1}h}}{e^{-ik_{z,1}h} + r_{01}r_{12}e^{ik_{z,1}h}} = \frac{r_{01} + r_{12}e^{i2k_{z,1}h}}{1 + r_{01}r_{12}e^{i2k_{z,1}h}}$$

$$R = rr^* = \frac{r_{01}^2 + r_{12}^2 + 2r_{01}r_{12}\cos(2k_{z,1}h)}{1 + r_{01}^2 r_{12}^2 + 2r_{01}r_{12}\cos(2k_{z,1}h)}$$

Example : One layer one a substrate



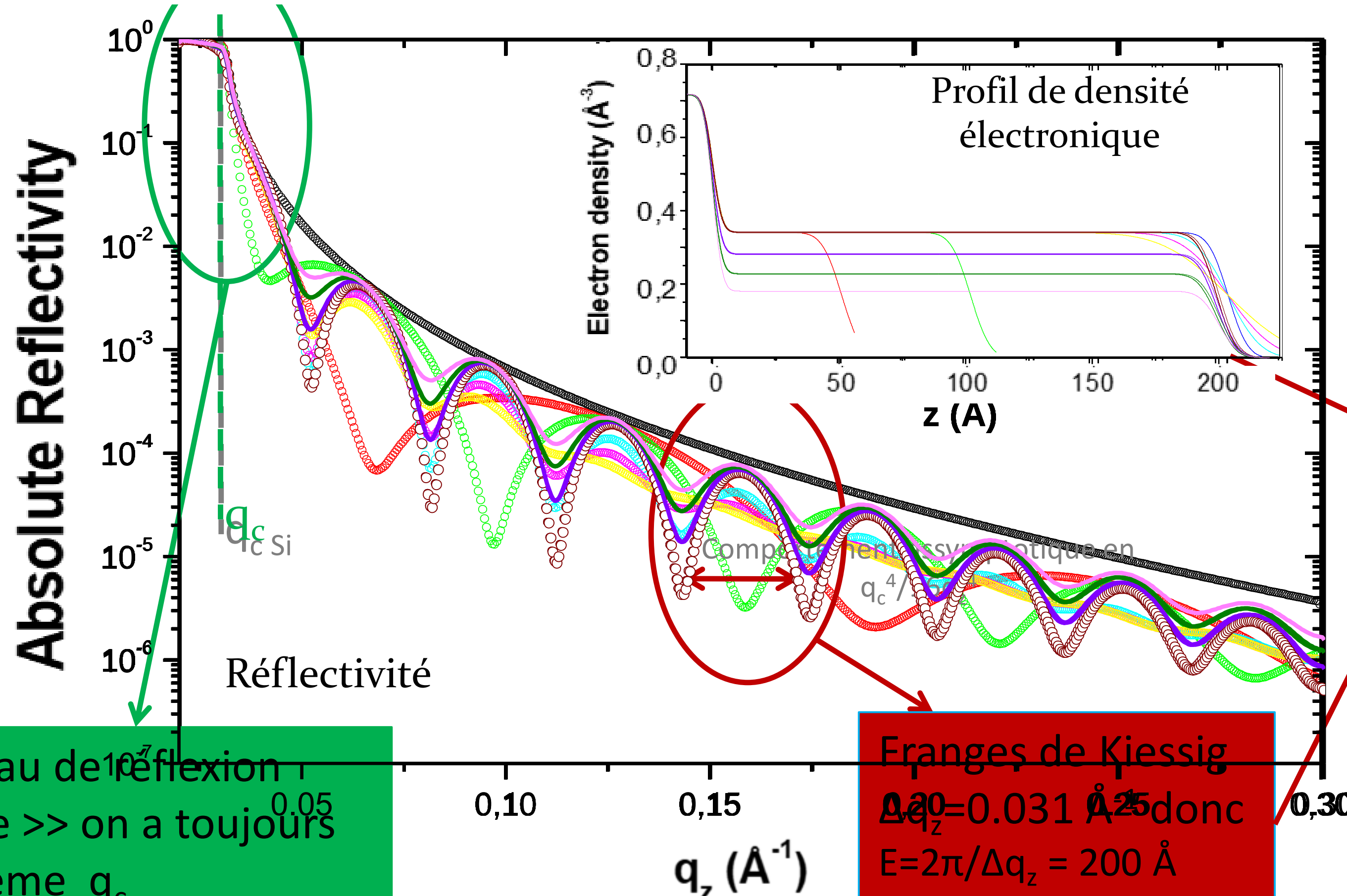
(1) X ray reflected from different interfaces interfere constructively and destructively as a function of incoming angle: Kiessig fringes

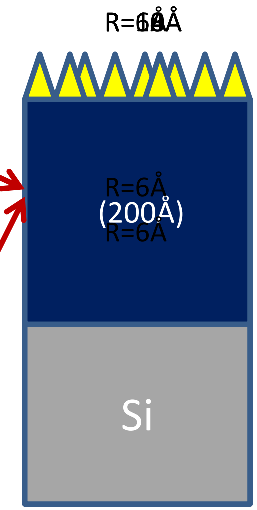
(2) Period of fringes scales inversely with **thickness** of layers: ***2π/Δq***

(3) Electron density contrast determines **amplitude** of fringes

Kiessig fringes: First observed by Heinz Kiessig in 1931 for Ni on glass

Influence of the different parameters





Plateau de réflexion totale >> on a toujours le même q_c

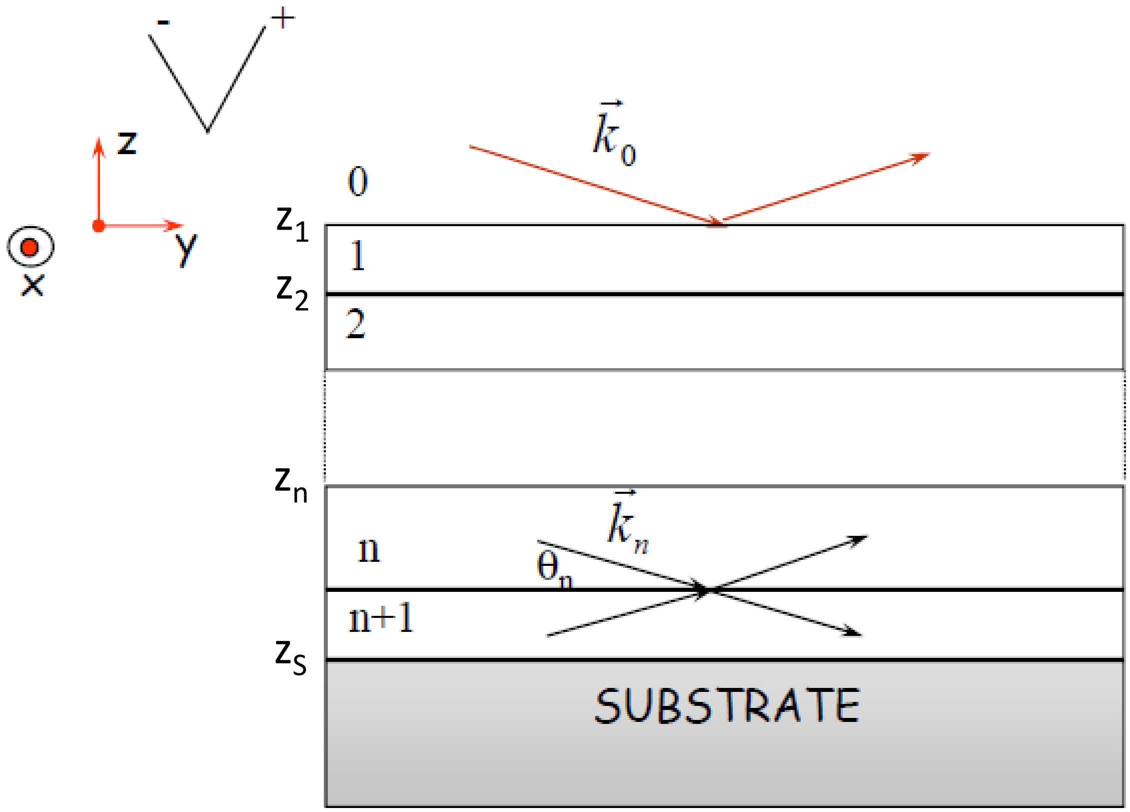
q_c du Substrat Si 0.0318 A^{-1}

Franges de Kiessig

Δq_z=0.031 Å^{-1} donc

E=$2\pi/\Delta q_z$ = 200 Å

Generalization to a multilayer (n+1 layers)



The signs – and + label the direction of propagation of the wave; air is labelled medium 0 and stratified media are identified by $1 \leq j \leq n$ layers in which upwards and downwards wave travel

$$\vec{E}^- = A_n^- e^{i(\omega t - k_{y,n} y - k_{z,n} z)} \vec{e}_1$$

Electric field in the nth layer of the downwards travelling wave

Generalization to a multilayer (n+1 layers)

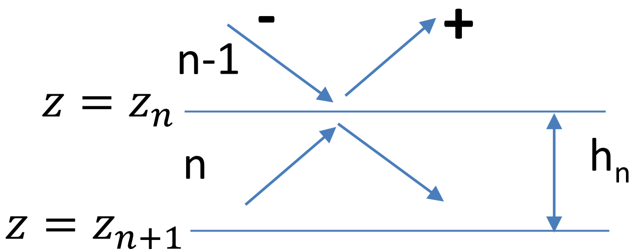
At interface z_n, the link between the electric field in medium n-1 and in medium n is defined by a refraction/reflection matrix $R_{n,n+1}$:

$$\begin{bmatrix} u_{n-1}^{+}(z_n) \\ u_{n-1}^{-}(z_n) \end{bmatrix} = \begin{bmatrix} p_{n-1,n} & m_{n-1,n} \\ m_{n-1,n} & p_{n-1,n} \end{bmatrix} \begin{bmatrix} u_n^{+}(z_n) \\ u_n^{-}(z_n) \end{bmatrix} = R_{n-1,n} \begin{bmatrix} u_n^{+}(z_n) \\ u_n^{-}(z_n) \end{bmatrix}$$

$R_{n-1,n}$: refraction matrix

$$p_{n-1,n} = \frac{k_{z,n-1} + k_{z,n}}{2k_{z,n-1}}$$

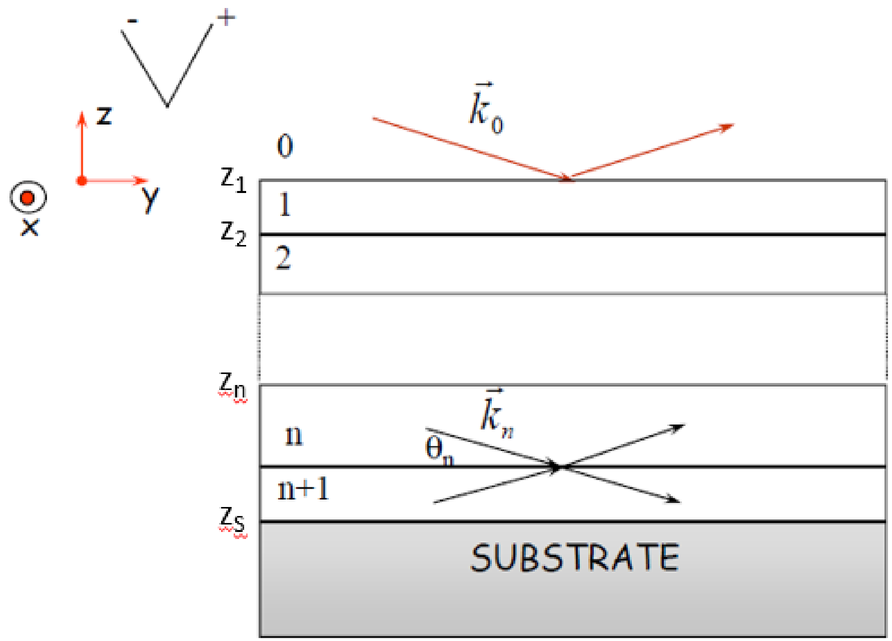
$$m_{n-1,n} = \frac{k_{z,n-1} - k_{z,n}}{2k_{z,n-1}}$$



$$\begin{bmatrix} u_n^{+}(z_n) \\ u_n^{-}(z_n) \end{bmatrix} = \begin{bmatrix} e^{-ik_{z,n}h_n} & 0 \\ 0 & e^{ik_{z,n}h_n} \end{bmatrix} \begin{bmatrix} u_n^{+}(z_{n+1}) \\ u_n^{-}(z_{n+1}) \end{bmatrix} = T_n \begin{bmatrix} u_n^{+}(z_{n+1}) \\ u_n^{-}(z_{n+1}) \end{bmatrix}$$

T_n: translation matrix

Generalization to a multilayer (n+1 layers)



$$M = \left(\prod_1^{n+1}\left(R_{i-1,i}T_i\right)\right) R_{n+1,S}$$

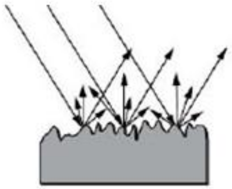
$$r = \frac{u_0^+(z_1)}{u_0^-(z_1)} = \frac{M_{12}}{M_{22}}$$

The reflected intensity is : $R = rr^*$

Roughness in matrix technique

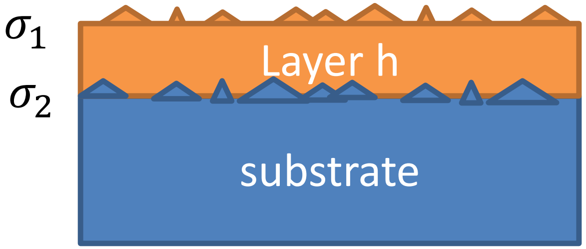
To take interfacial roughness into account in the specular reflected intensity, the amplitude coefficients $\boldsymbol{m_{n,n+1}}$ **and** $\boldsymbol{p_{n,n+1}}$ **are, respectively, reduced by the factors** $\boldsymbol{e^{-(k_{z,n}+k_{z,n+1})^2\sigma_{n+1}^2/2}}$ **and** $\boldsymbol{e^{-(k_{z,n}-k_{z,n+1})^2\sigma_{n+1}^2/2}}$

giving rise to a reduction of the Fresnel coefficient by the Debye–Waller factor:



$$r_{n,n+1}^{rough} = r_{n,n+1}^{flat} e^{-2k_{z,n}k_{z,n+1}\sigma_{n+1}^2}$$

$$r = \frac{r_{01}e^{-2k_{z,0}k_{z,1}\sigma_1^2} + r_{12}e^{-2k_{z,1}k_{z,2}\sigma_2^2}e^{i2k_{z,1}h}}{1 + r_{01}e^{-2k_{z,0}k_{z,1}\sigma_1^2}r_{12}e^{-2k_{z,1}k_{z,2}\sigma_2^2}e^{i2k_{z,1}h}}$$



$$R = \frac{r_{01}^2e^{-4k_{z,0}k_{z,1}\sigma_1^2} + r_{12}^2e^{-4k_{z,1}k_{z,2}\sigma_2^2} + 2r_{01}e^{-2k_{z,0}k_{z,1}\sigma_1^2}r_{12}e^{-2k_{z,1}k_{z,2}\sigma_2^2}\cos(2k_{z,1}h)}{1 + r_{01}^2e^{-4k_{z,0}k_{z,1}\sigma_1^2}r_{12}^2e^{-4k_{z,1}k_{z,2}\sigma_2^2} + 2r_{01}e^{-2k_{z,0}k_{z,1}\sigma_1^2}r_{12}e^{-2k_{z,1}k_{z,2}\sigma_2^2}\cos(2k_{z,1}h)}$$

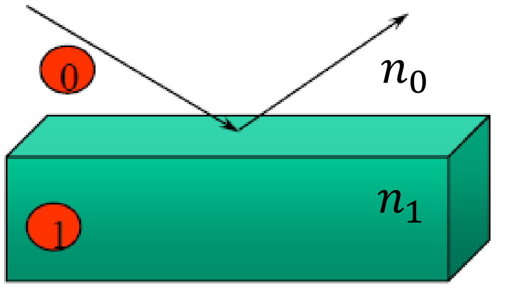
Reflexion on a substrate

transfer matrix

$$M = R_{01} = \begin{bmatrix} p_{01} & m_{01} \\ m_{01} & p_{01} \end{bmatrix}$$

$$p_{0,1} = \frac{k_{z,0} + k_{z,1}}{2k_{z,0}} \qquad m_{0,1} = \frac{k_{z,0} - k_{z,1}}{2k_{z,0}}$$

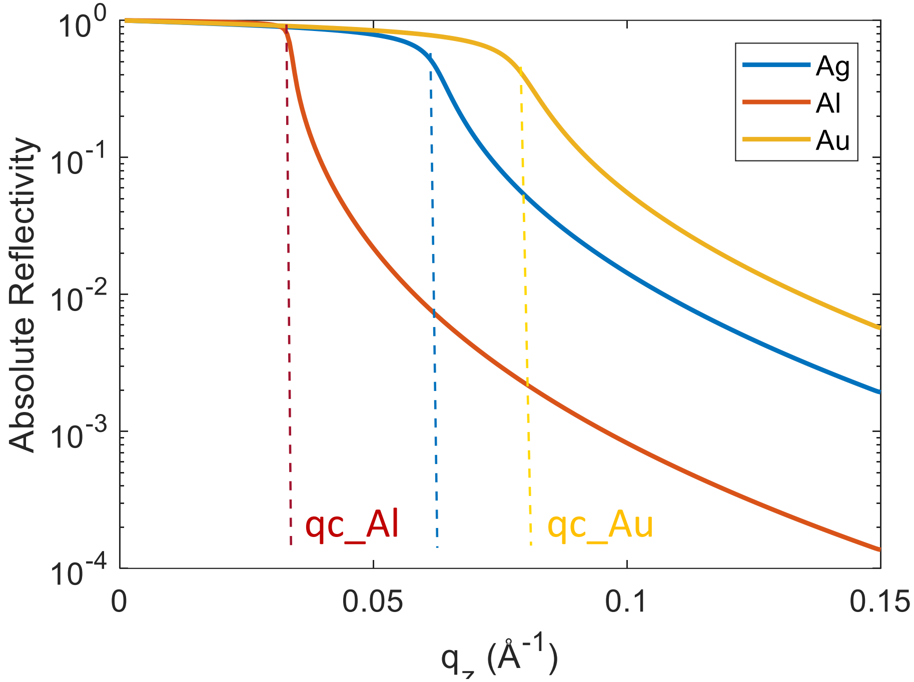
$$r_{01} = \frac{M_{12}}{M_{22}} = \frac{m_{01}}{p_{01}} = \frac{k_{z,0} - k_{z,1}}{k_{z,0} + k_{z,1}}$$



$$r_{01} = \frac{q_{z0} - \sqrt{q_{z0}^2 - q_c^2 - 32\pi^2(\beta - \beta_0)/\lambda^2}}{q_{z0} + \sqrt{q_{z0}^2 - q_c^2 - 32\pi^2(\beta - \beta_0)/\lambda^2}}$$

$$q_{z0} = 2k_0 n_0 sin\,\theta$$
$$q_c = 2k_0 sin\sqrt{2(\delta - \delta_0)}$$

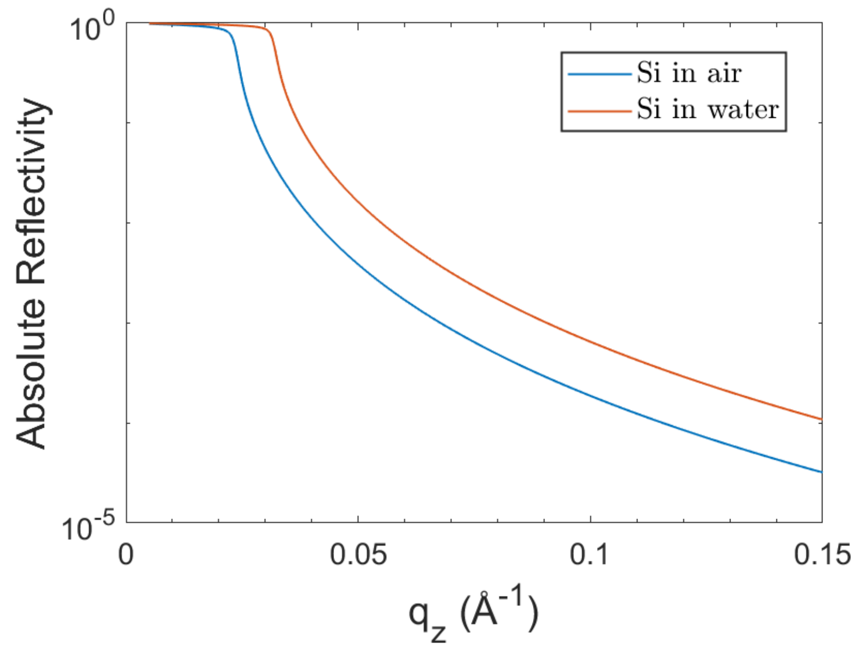
δ_0 and β_0 are negligible for air



->Link between absorption and density

Gold (Au) high electron density qc=0.079167 and non-negligible absorption effect $\beta = 48.4131\ 10^{-7}$

Aluminum (Al) classical electron density qc=0.033582 and negligible absorption effect $\beta = 1.5472\ 10^{-7}$



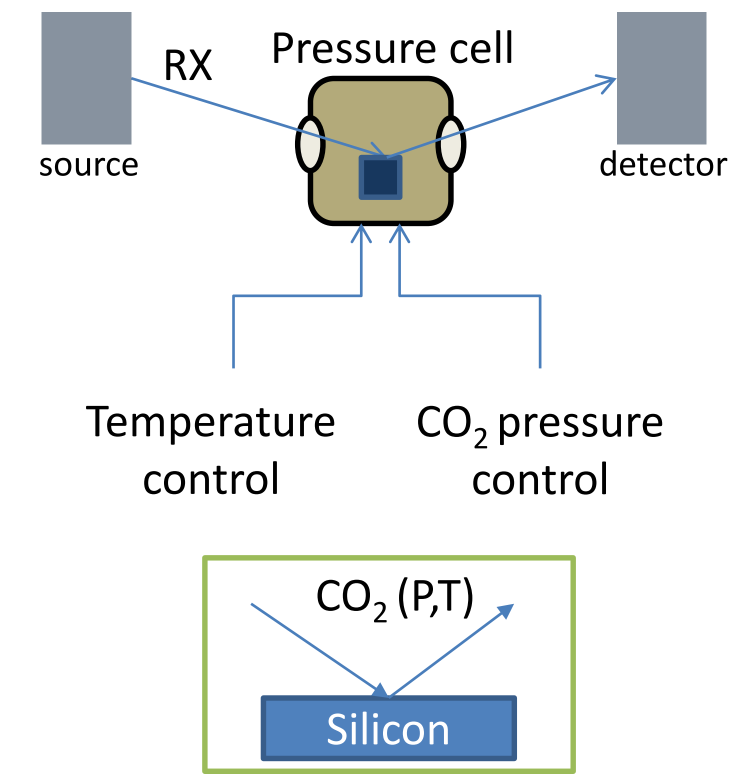
->Effect of the environment surrounding the sample

qc silicone in air : 0.0317

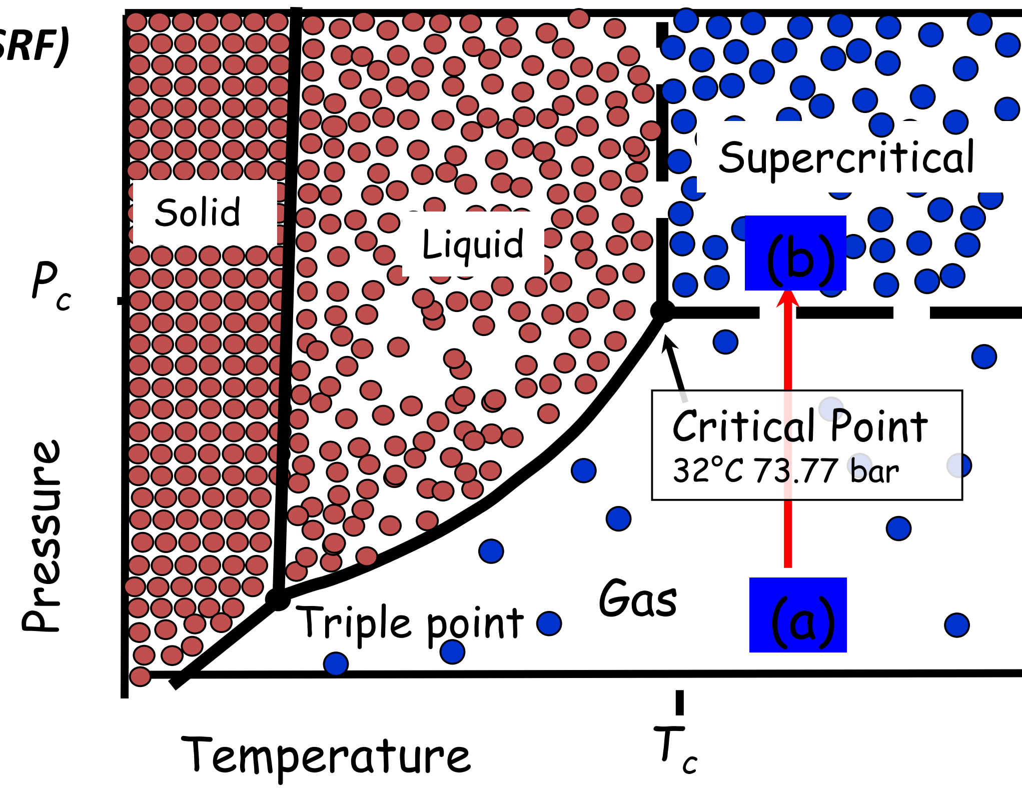
qc silicone in water : 0.0237

Example of measurement : X-ray Reflectivity Study of silicone substrate in Carbon Dioxide

Experimental device used at the ID10B(ESRF)



✓ ***Phase diagram of CO_2***



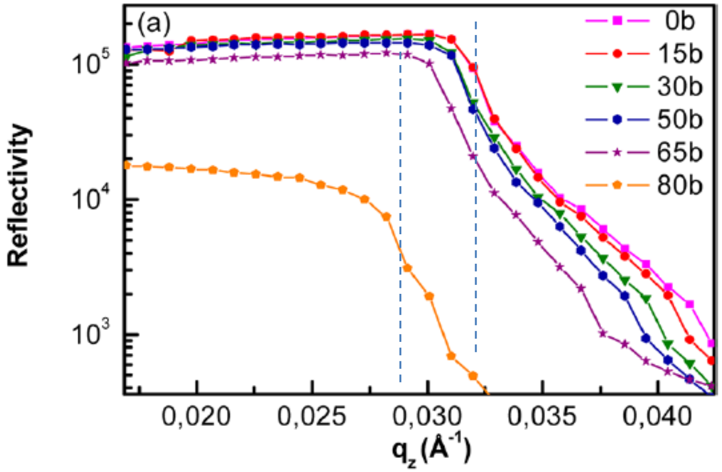
How does the reflectivity evolve when a silicon substrate is subjected to CO_2 according to the path (a) to (b) ?

X-ray Reflectivity Study of silicone substrate in Carbon Dioxide

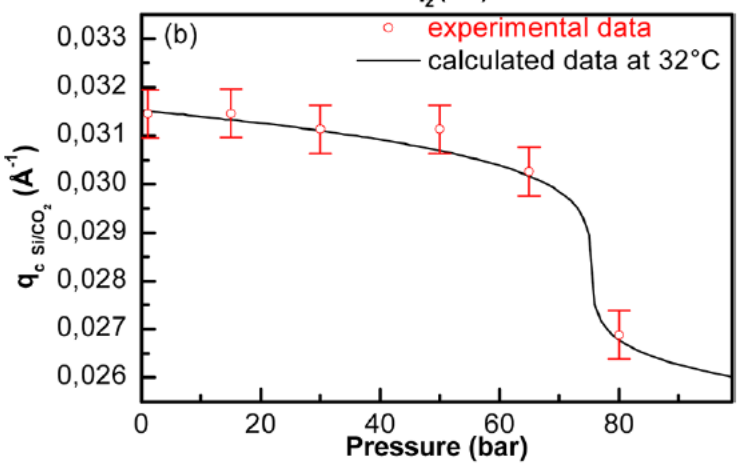
$$R_{\perp} = |r_{\perp}|^2 = \left| \frac{q_{z0} - \sqrt{q_{z0}^2 - q_c^2 - 32\pi^2(\beta - \beta_0)/\lambda^2}}{q_{z0} + \sqrt{q_{z0}^2 - q_c^2 - 32\pi^2(\beta - \beta_0)/\lambda^2}} \right|^2$$

$$q_c = 2k_0 sin\sqrt{2(\delta - \delta_0)}$$

the critical angle of the substrate itself is affected by the presence of the pressurized gas in contact with it.



loss of the reflected intensity mainly related to the fact that the incident and reflected beams are **attenuated** in the cell by the increasing pressure of the gas.

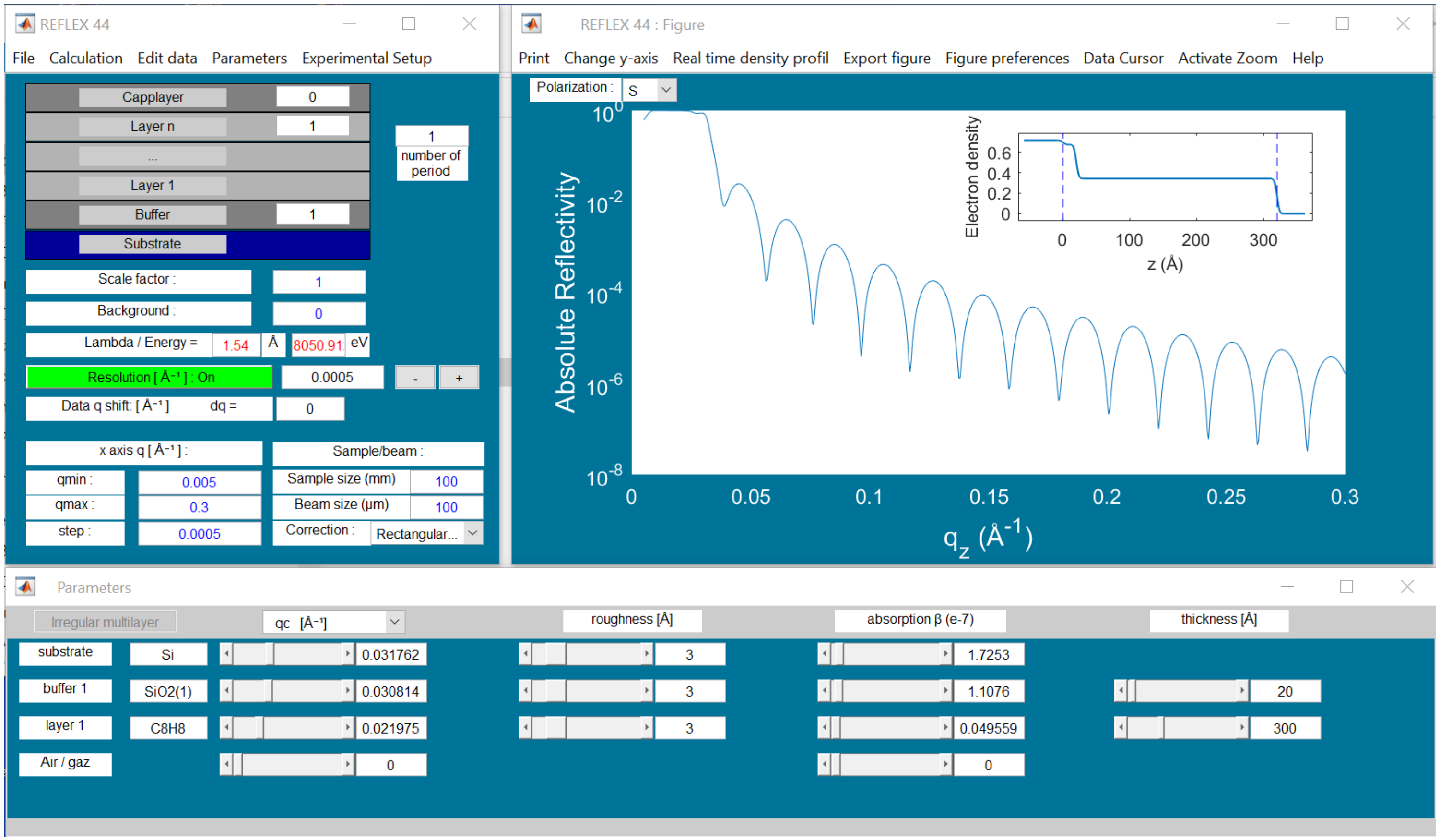


the critical angle gradually decreases when the CO_2 pressure increases

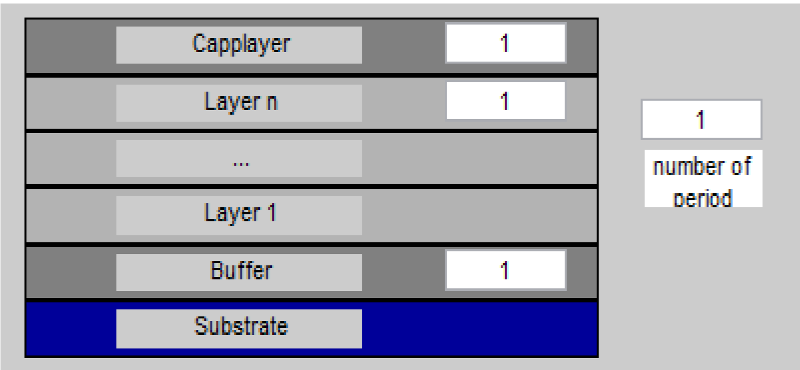
3 – REFLEX : SOFTWARE OVERVIEW

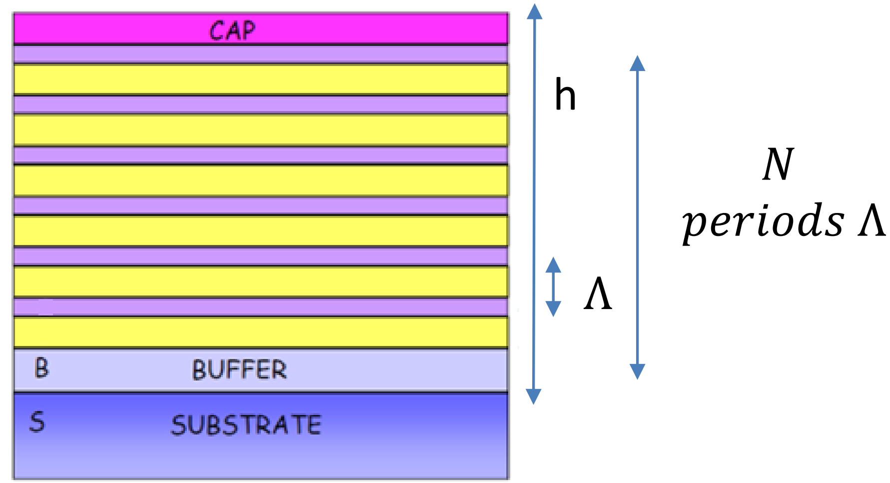
3.1 Reflectivity on a periodic multilayer

The REFLEX software is a completely integrated program for treatment of X-rays reflectivity data. REFLEX uses a slab-model approach with the matrix method taking into account the interfacial roughnesses of each layer together with their respective thickness and electron density.



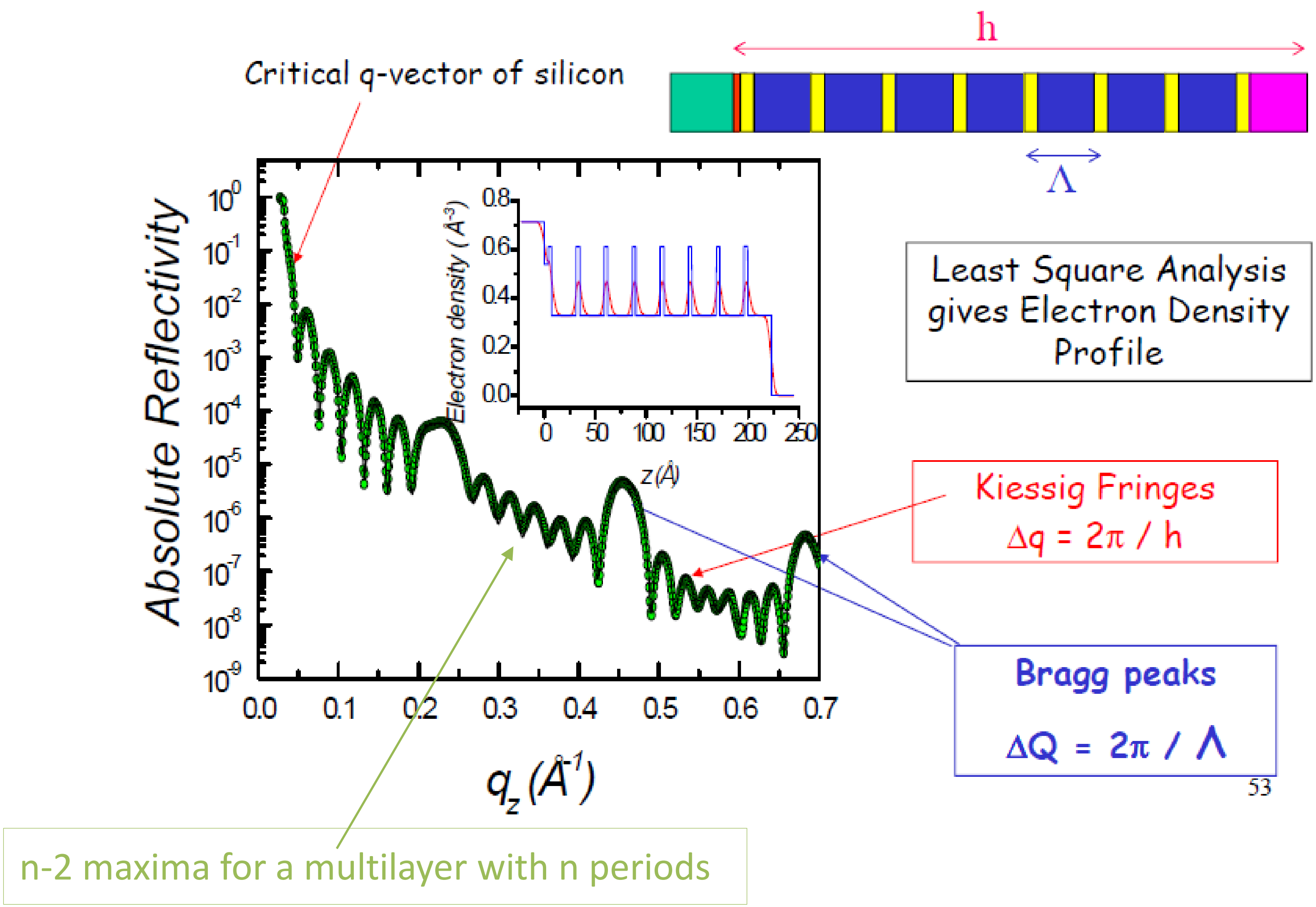
How to model the sample structure ?



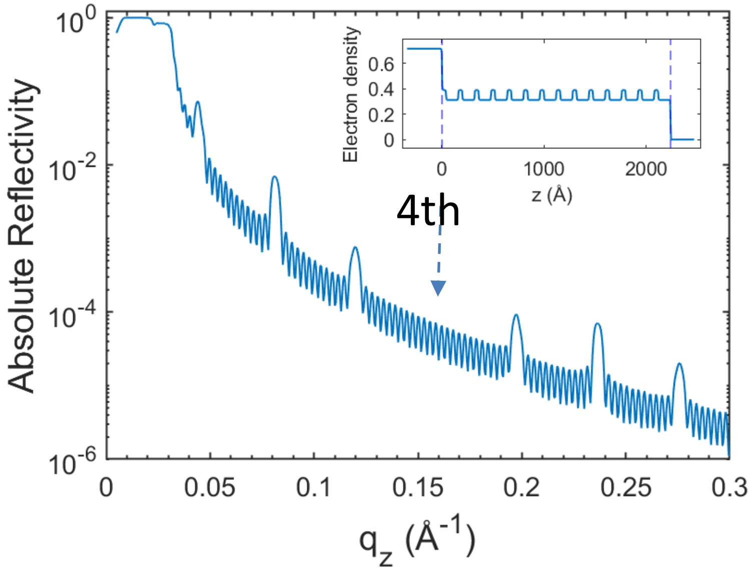


The number of “**Cap layers**” is the number of layers in contact with the fluid (air for example)
“**Layer n**” is the number of layers that are repeated as a typical motif or unit cell inside the multilayer.
Next to this box is a box labelled "**number of period**" containing the number of repeated periods of this motif (or unit cell) inside the multilayer.
The number of “**Buffer**” is the number of layers at the substrate/film interface. The buffer layer and the cap layer are not incorporated in the unit cell and hence are not repeated.

Reflectivity on a periodic multilayer



Reflectivity on a periodic multilayer

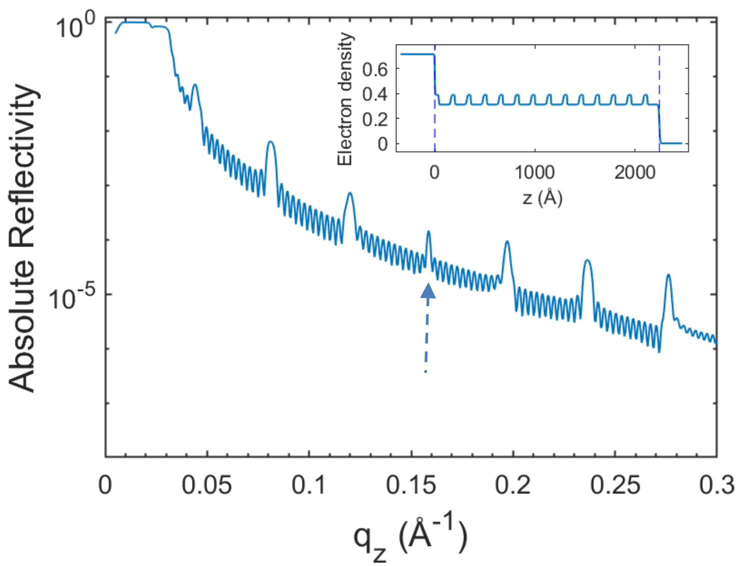


If the ratio of the thicknesses d_2/d_1 is equal to an integer p, there is extinction of the (p+1)th Bragg peak on the reflectivity curve (rule relevant if the roughness of the 2 layers are similar).

$d_2 = 120Å$ $d_1 = 40Å$ $d_2/ d_1 = 4 - 1 = 3$

$\sigma_2 = 2Å$ $\sigma_1 = 2Å$ **Same roughness**

Extinction of the 4th Bragg peak



$d_2 = 120Å$ $d_1 = 40Å$ $d_2/ d_1 = 3$

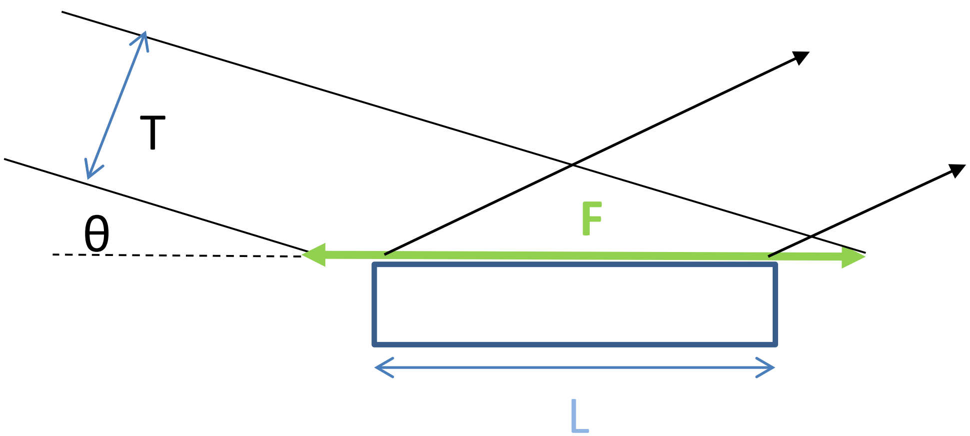
$\sigma_2 = 6Å$ $\sigma_1 = 1Å$ **Different roughness**

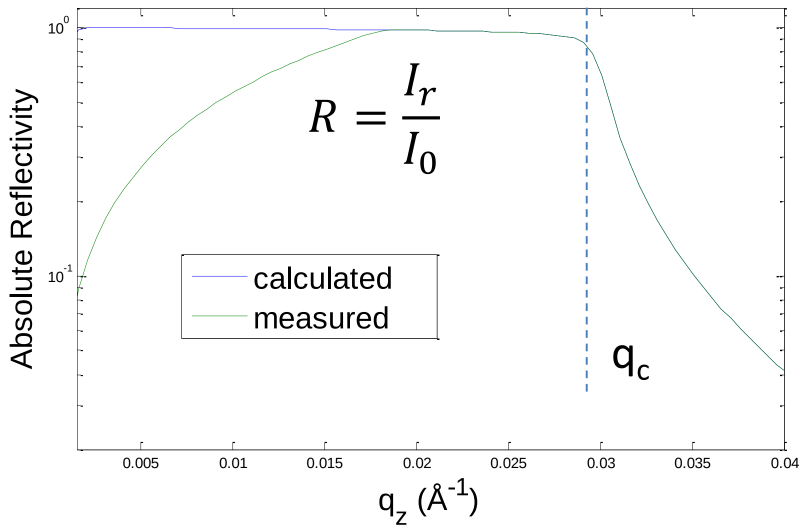
4th Bragg peak visible

3.2 Geometric parameters in relation to the measurement

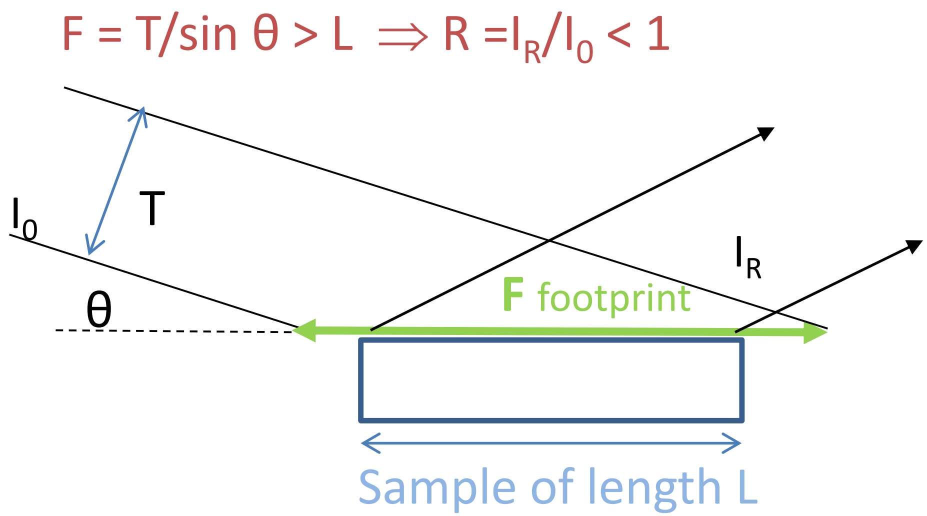
The REFLEX program allows the user to take into account many experimental parameters which may affect the theoretical reflected intensity

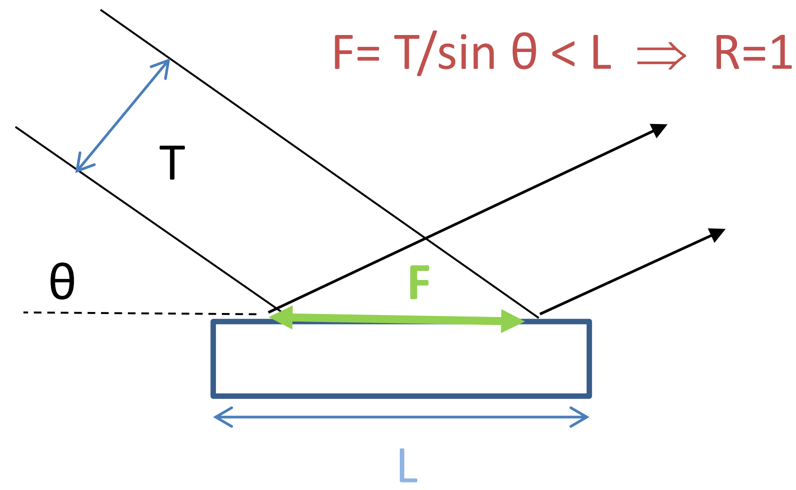
<u>Sample size/beam size</u>:
Because XRR measurements start below the critical angle of external reflection, the beam footprint (F) projected onto the sample is often larger than the length (L) of the sample in the direction of the incident beam. Therefore, even below the critical angle of external reflection, only a portion of the incident intensity is completely reflected by the sample. The reflectivity is therefore less than 1.

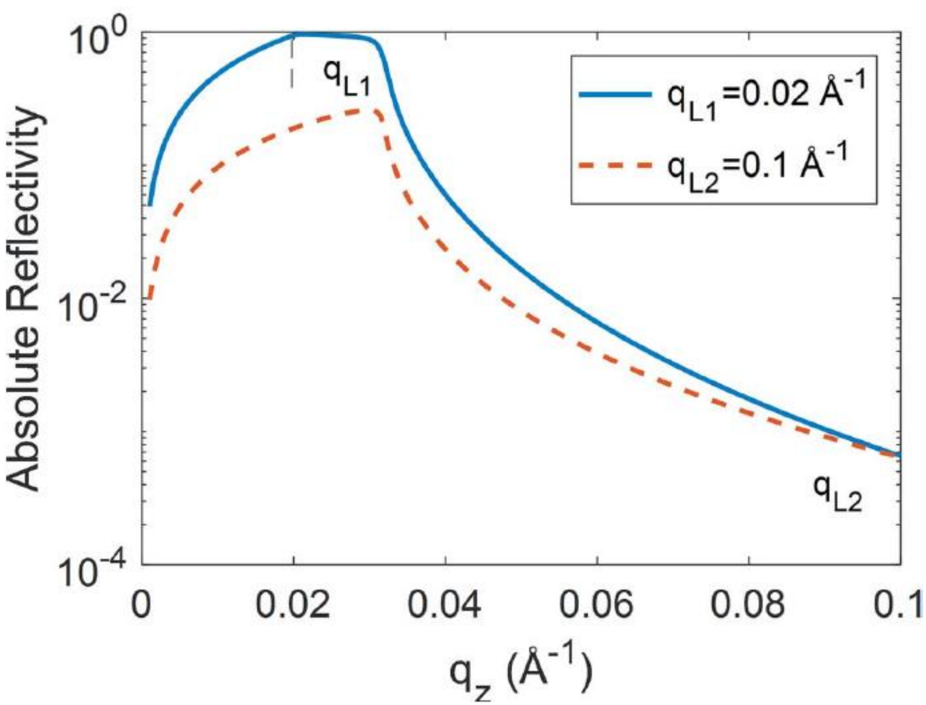




Relationship between incident angle and footprint of the beam





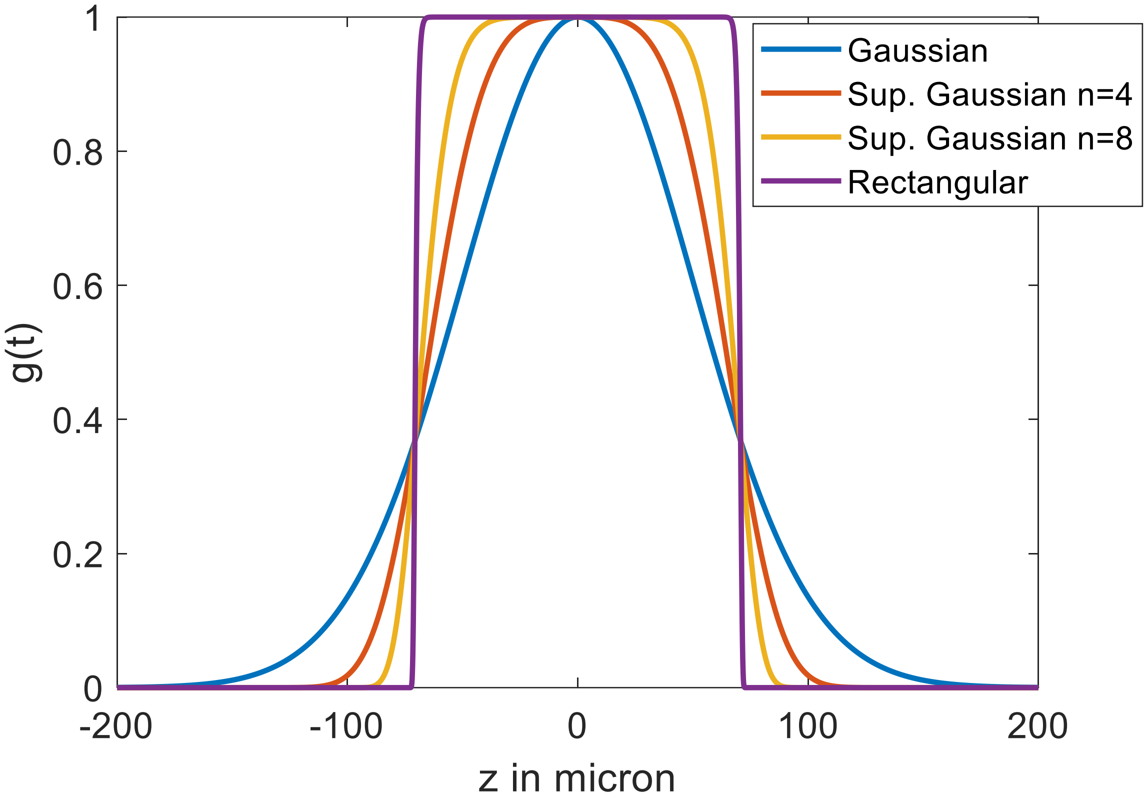


q_L is the limiting wavevector when L = F

$$q_L = \frac{4\pi}{\lambda} sin\theta_L = \frac{4\pi}{\lambda}\frac{T}{L}$$

the sample size cannot be corrected by a simple vertical translation of the reflectivity curve (the correction depends on qz). **Correction by changing the curve normalization is incorrect**

Effect of the beam profile on the reflectivity curve



Beam profile Gaussian :

$$g(t) = Ae^{-\frac{z^2}{2\sigma^2}}$$

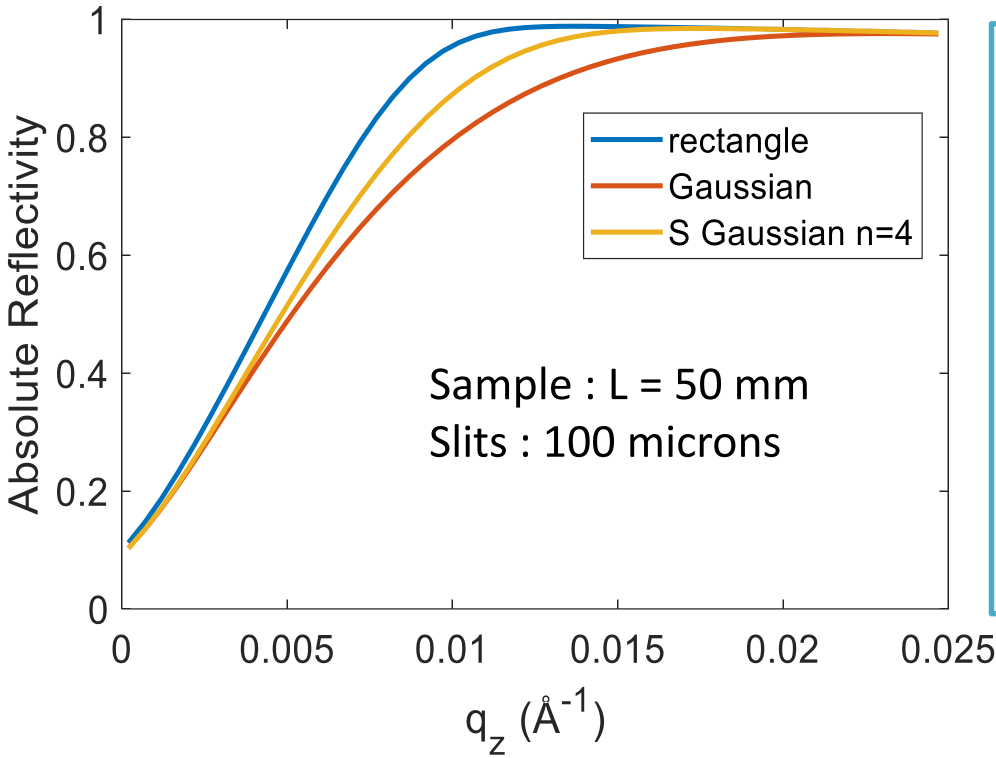
with $\sigma = \frac{T}{2}\frac{1}{\sqrt{2ln2}}$

Beam profile super Gaussian :

$$g(t) = Ae^{-\left(\frac{z}{\sqrt{2}\,\sigma}\right)^n}$$

where n =4,8, …

Effect of the beam profile on the reflectivity curve



Beam profile rectangular:

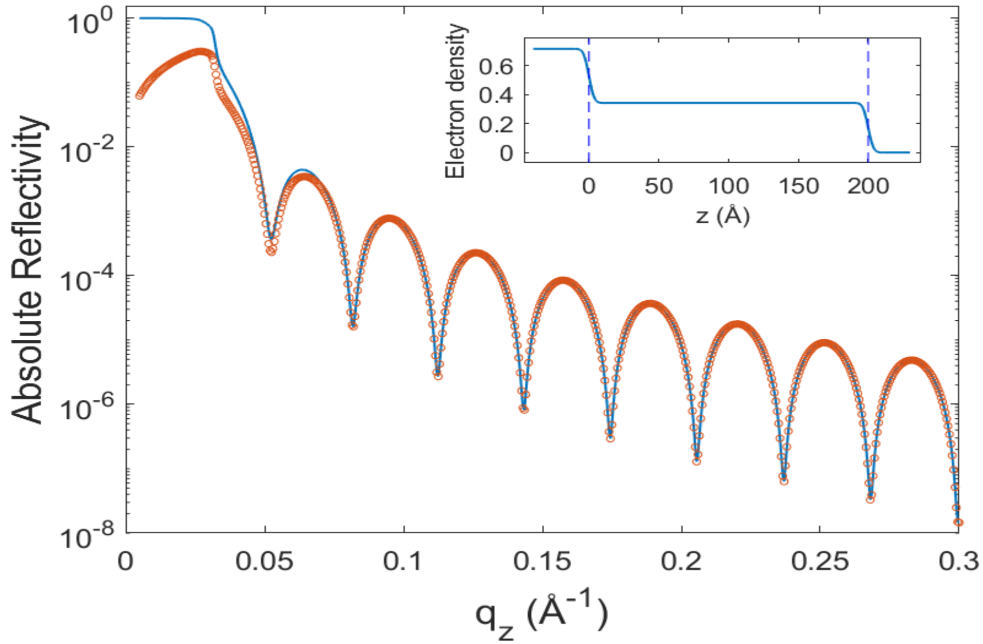
$$I_{\text{corrected}} = I_{\text{calculated}} \frac{L}{F} = I_{\text{calculated}} \frac{L\theta}{T}$$

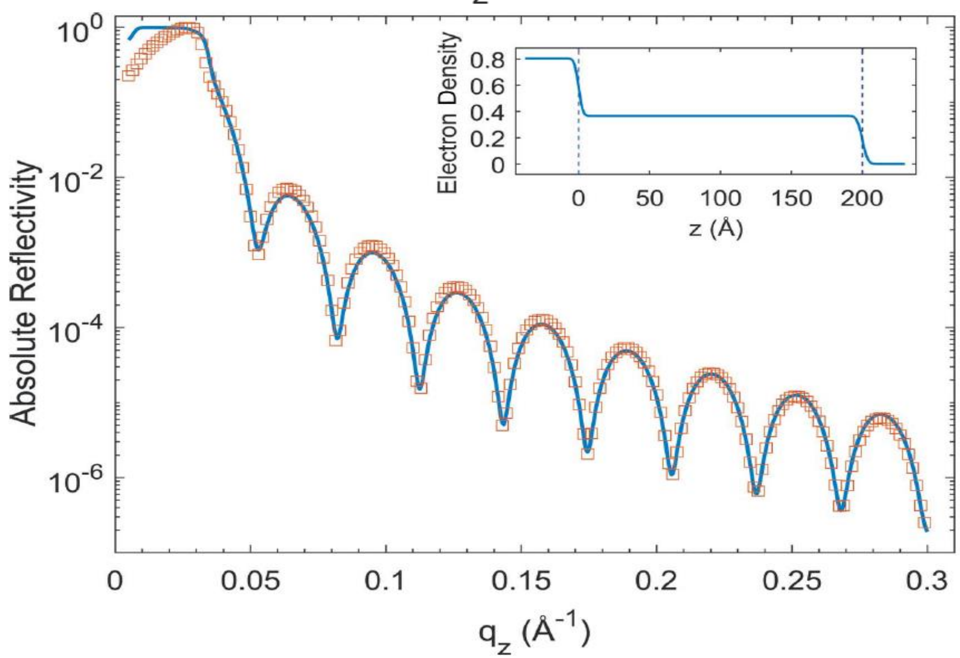
Beam profile g(t) :

$$I_{\text{corrected}} = I_{\text{calculated}} \frac{\int_0^a g(t)\,\mathrm{d}t}{\int_0^\infty g(t)\,\mathrm{d}t}, \qquad a = \frac{L}{2}\sin\theta$$

It is observed that the slopes of the foot print functions changes according to the type of beam profile. For the Gaussian beam profile the curvature of the plot is prominent and visible. It can be observed from the figure that the Gaussian beam profile shows highest limiting wave vector q_L. As the beam profile approaches the rectangular box function, q_L gradually decreases.

Relationship between incident angle and footprint of the beam





It would be a critical error to correct the intensity reduction at small q_z by a scale factor which affects the normalization of the entire curve rather than the size of the sample/beam.

PS thin film on a silicon wafer

Curve fitted with footprint correction:

PS : $q_c = 0.021975$ Å^{-1}

Si : $q_c = 0.031762$Å^{-1}

Curve normalized and fitted without footprint correction:

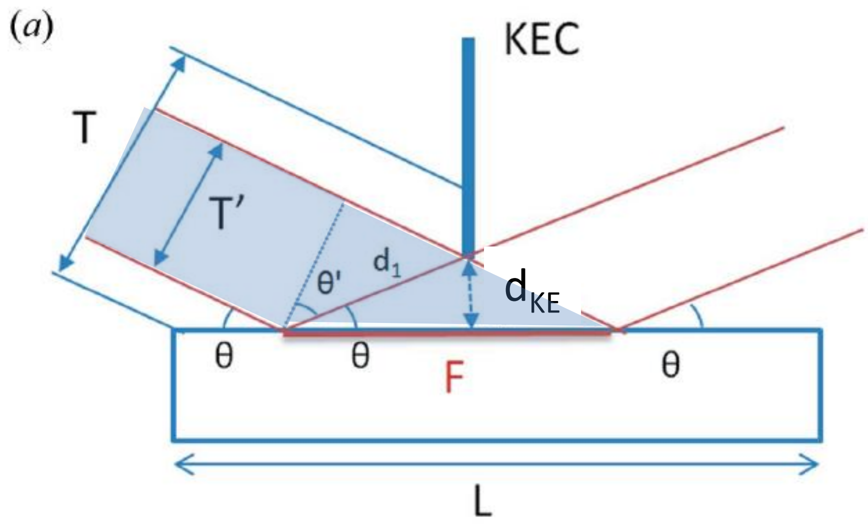
PS : $q_c = 0.022708$ Å^{-1}

Si : $q_c = 0.033645$ Å^{-1}

Significant mistakes are made in the density of the sample, which is incorrectly increased in this case.

Correction of reflectivity measured with a beam knife edge

Bruker-AXS developed the so-called knife-edge collimator (KEC) to reduce the beam footprint and reduce air scattering (improve contrast and resolution)



"knife" that is approached to the surface of the sample up to a few µm when measuring at small angles.

$$T' = 2d_{Ke}\cos(\theta) \qquad F = 2d_{Ke}/tan\theta$$

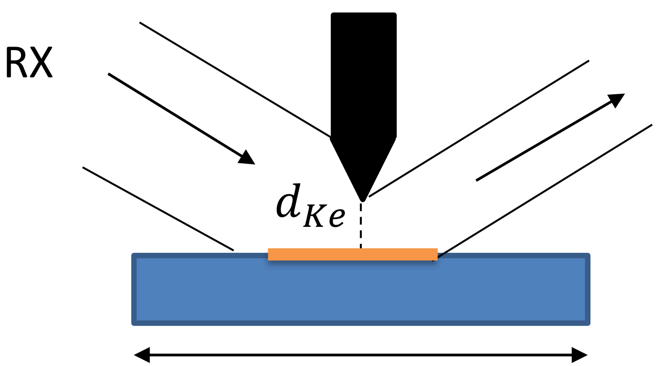
d_{Ke} ranges from 2 to 20 µm

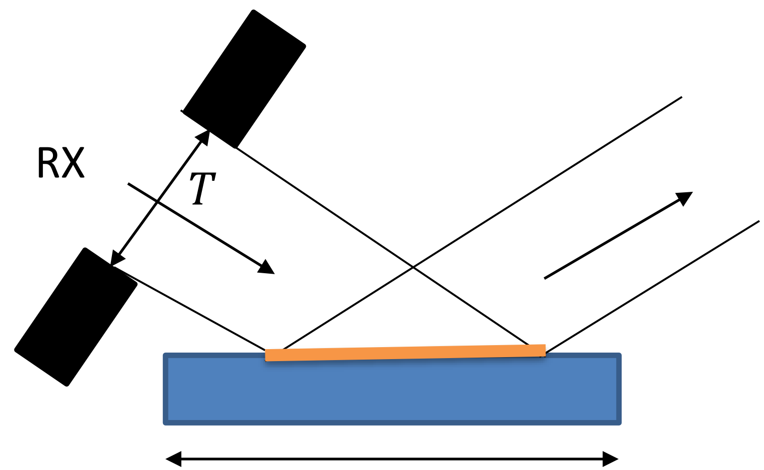
F << L with a knife

Correction of reflectivity measured with a beam knife edge

$$q_{Lke} = \frac{4\pi}{\lambda} sin\theta_L = \frac{4\pi}{\lambda} sin\frac{2d_{Ke}}{L}$$

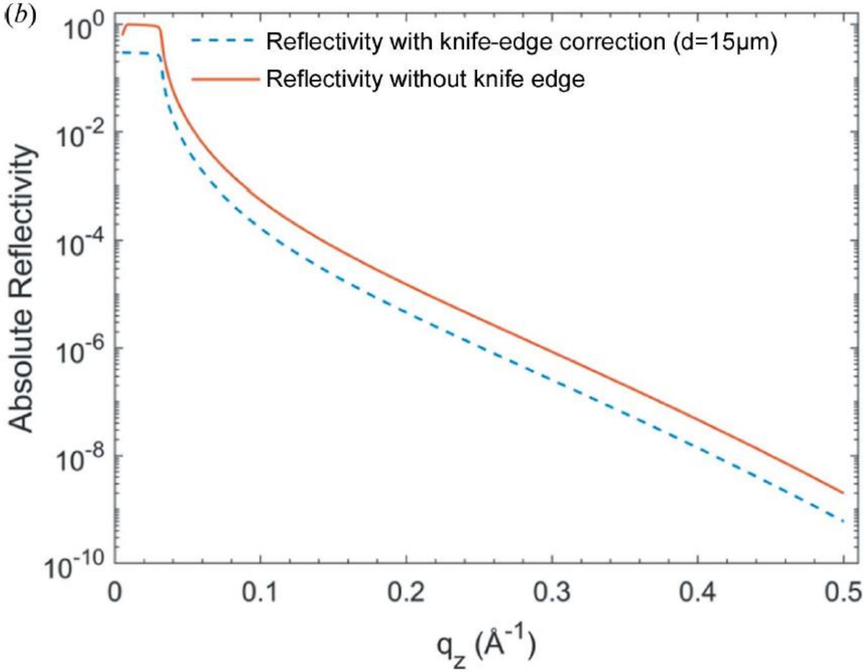
$$q_L = \frac{4\pi}{\lambda} sin\theta_L = \frac{4\pi}{\lambda} sin\frac{T}{L}$$





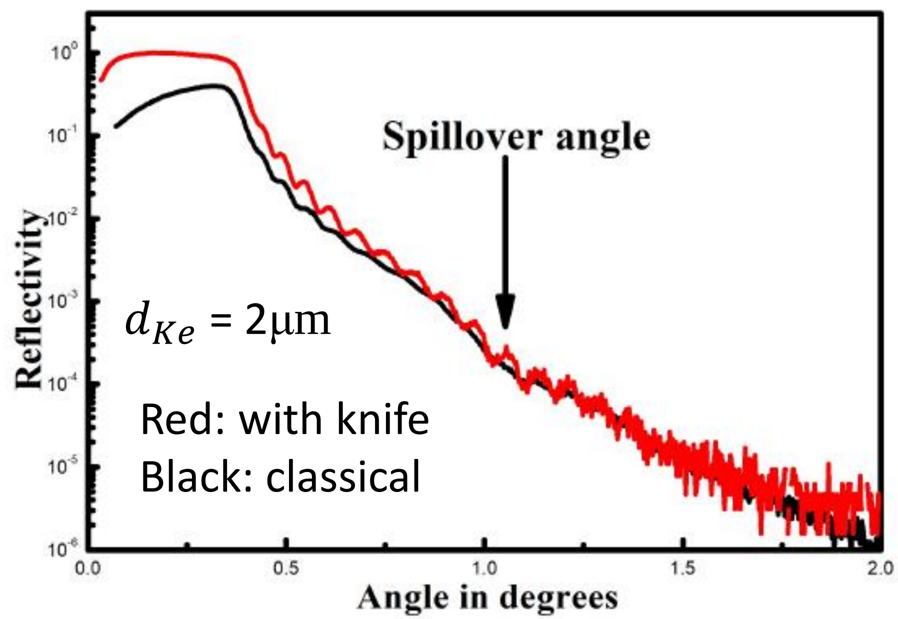
Using typical parameters for a laboratory setup, d_{Ke} = 15μm, T= 50 μm, L = 2 cm, q_L of **0.012Å^{-1}** and **0.0204Å^{-1}** for Cu radiation, are calculated for the beam-knife edge setup and the classical setup, respectively. The critical angle for silicon is **0.0317Å^{-1}**, implicating that for many organic films with critical angles in general well below that of silicon it becomes important to apply the footprint correction especially in the case of a classical setup.

$$I_{\text{corrected}} = I_{\text{calculated}} \frac{T'}{T} = I_{\text{calculated}} \frac{2d\cos\theta}{T}$$



Constant difference between the corrected and the exact Fresnel reflectivity

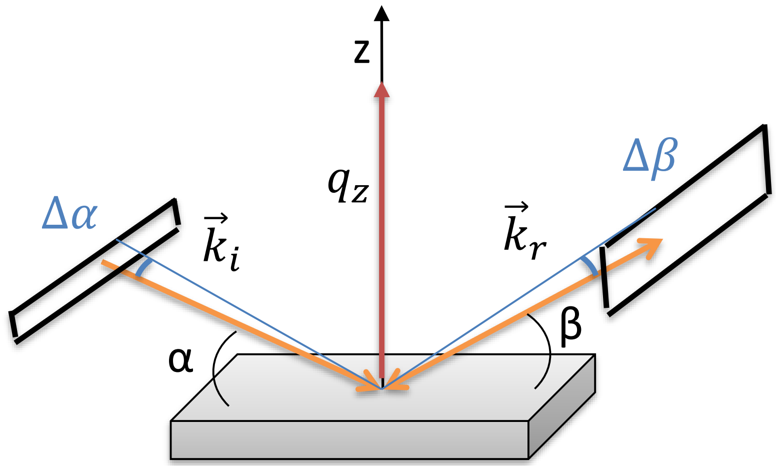
Er_2O_3 thin film samples on GaAs substrate



Increased resolution of the measurement due to reduction of beam width by the knife edge

Das, A. et al. (2018). *Journal of Applied Crystallography*, *51*(5), 1295-1303.

Instrumental resolution



$\vec{q}_z = \vec{k}_r - \vec{k}_i$
$q_z = k_0(sin\alpha + sin\beta)$
$dq_z = k_0(cos\alpha\, d\alpha + cos\beta\, d\beta) + dk_0\,(sin\alpha + sin\beta)$

dk_0 is related to the wavelength dispersion by

$$dk_0 = -k_0 \frac{d\lambda}{\lambda}$$

With the assumption that $d\alpha$ and $d\beta$ are randomly distributed, the uncertainty in q_z is given by

$$\Delta q_z^2 = k_0^2(cos^2\alpha\,\Delta\alpha^2 + cos^2\beta\,\Delta\beta^2) + \Delta k_0^2(sin\alpha + sin\beta)^2$$

Instrumental resolution

For specular reflectivity, the incoming and outgoing angles α and β are equal to θ so that the resolution-function along z is:

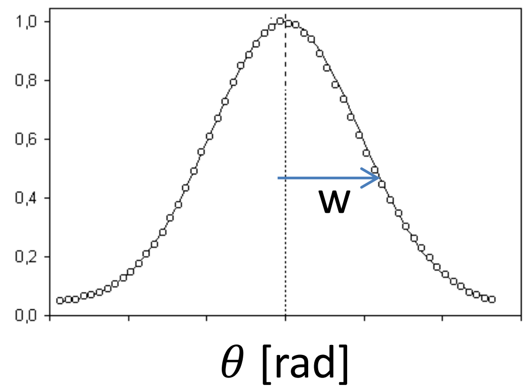
$$\Delta q_z = \sqrt{k_0^2 cos^2\theta(\Delta\alpha^2 + \Delta\beta^2) + 4\Delta k_0^2 sin^2\theta}$$

For specular reflectivity measurements, θ is always very small and $\Delta k_0 sin\theta$ is negligible:

$$\Delta q_z = \frac{2\pi}{\lambda} w \cos(\theta) \text{ with } w = \sqrt{\Delta\alpha^2 + \Delta\beta^2}$$

Resolution: Instrumental resolution is handled by convolving the calculated reflectivity curve with a Gaussian. The half width at half maximum(HWHM) of which is related to the instrument resolution by:

$$\Delta q_z = \frac{2\pi}{\lambda} w \cos(\theta)$$

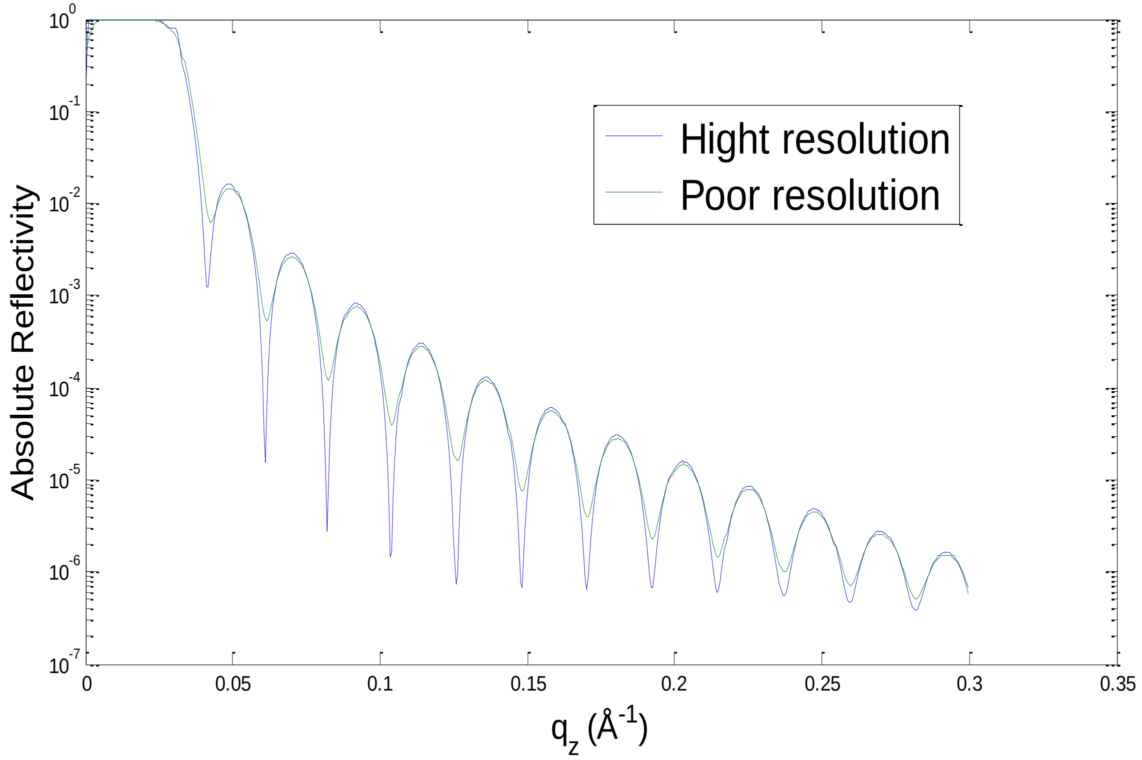


w is measured through direct beam (without sample)

where $w = \sqrt{\Delta\alpha^2 + \Delta\beta^2}$ is the HWHM of the direct through beam. The lower is this value the better the resolution.

Instrumental resolution

the high resolution gives a better estimation of some typical features like the Kiessig fringes minima and the critical angle.



In practice, the better the resolution the more difficult it is to track the reflectivity curve over a wide range of wave-vector transfers.

3.2 Autocorrelation function of the first derivative of the electron density

In the first order Born approximation, the reflectivity is proportional to the Fourier transform of the electron density scattering with respect to the vertical position z:

$$R(q_z) = R_F(q_z) \left| \frac{1}{\rho_S} \int_{-\infty}^{+\infty} \frac{\partial \langle \rho(z) \rangle}{\partial z} e^{iq_z z} dz \right|^2$$

Master formula

where $R_F(q_z)$ is the Fresnel reflectivity of the substrate with an average density ρ_S

Born approximation valid for $q_z \gg q_c$

(1) No multiple reflections at the interfaces

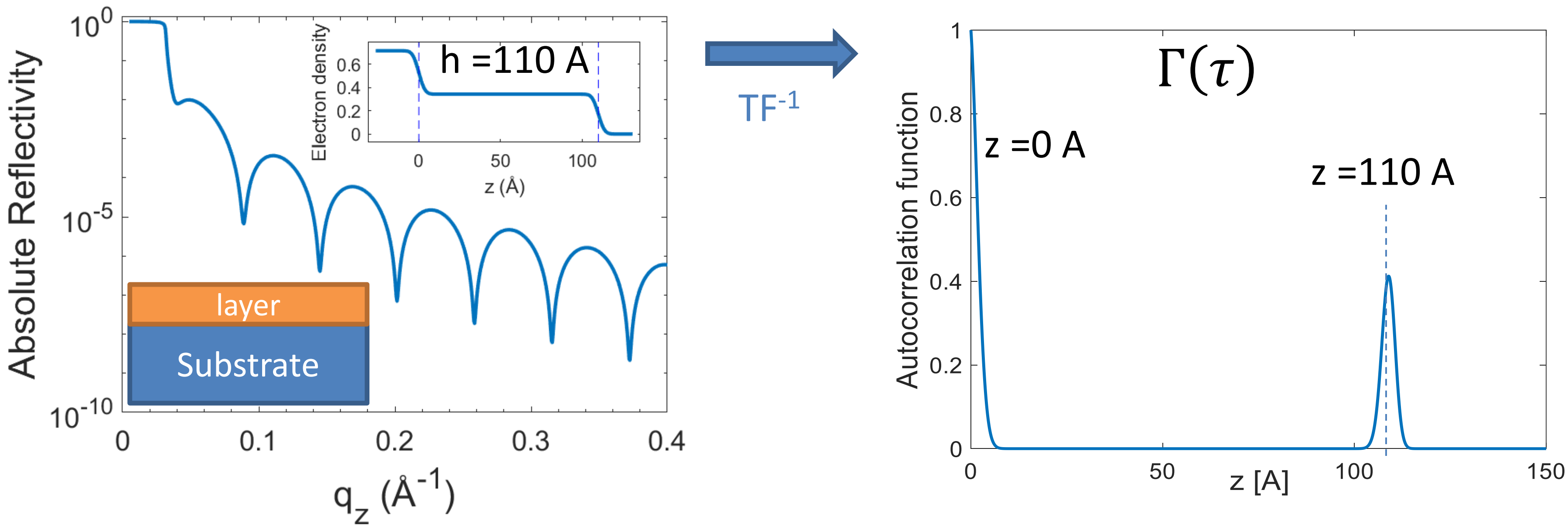
(2) The effects of refraction can be neglected

(3) No absorption. The reflection coefficient at each interface is proportional to the contrast of electron density

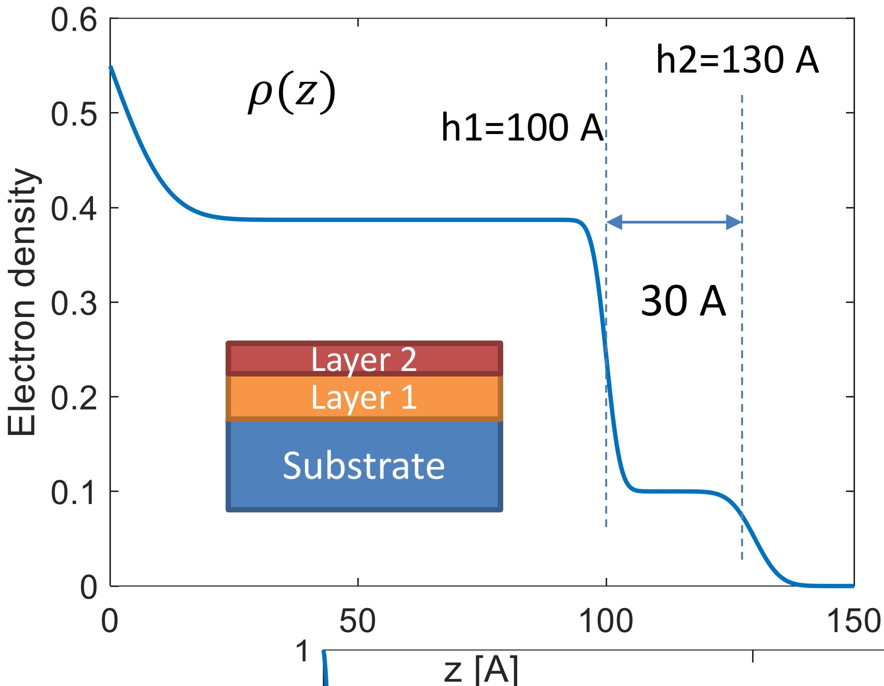
$$\frac{R(q_z)}{R_F(q_z)} = \frac{1}{\rho_S^2} \iint \frac{\partial \rho(z)}{\partial z} \frac{\partial \rho(z')}{\partial z} e^{iq_z(z-z')} dz dz' = \frac{1}{\rho_S^2} TF[\rho'(z) \otimes \rho'(z)]$$

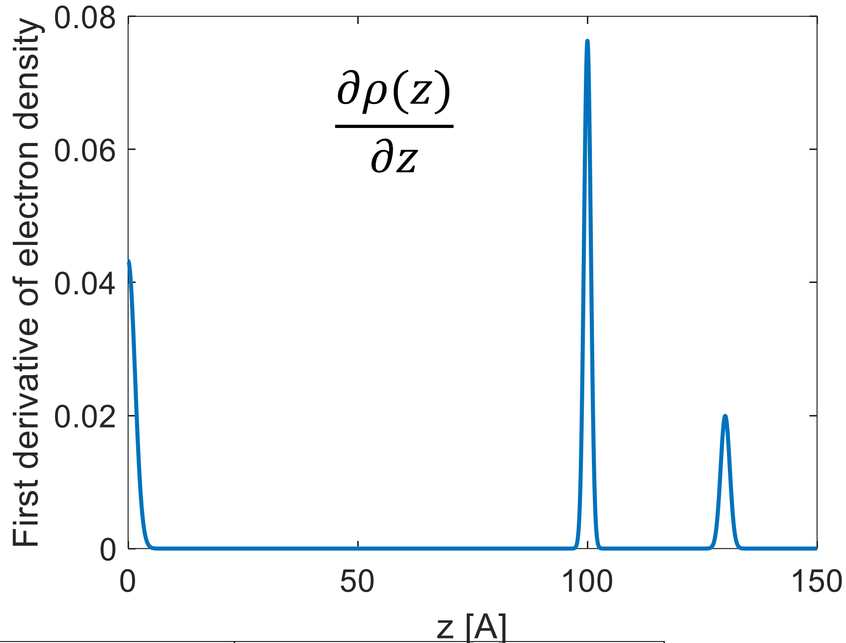
so that a data inversion gives the autocorrelation function of the first derivative of the electron density

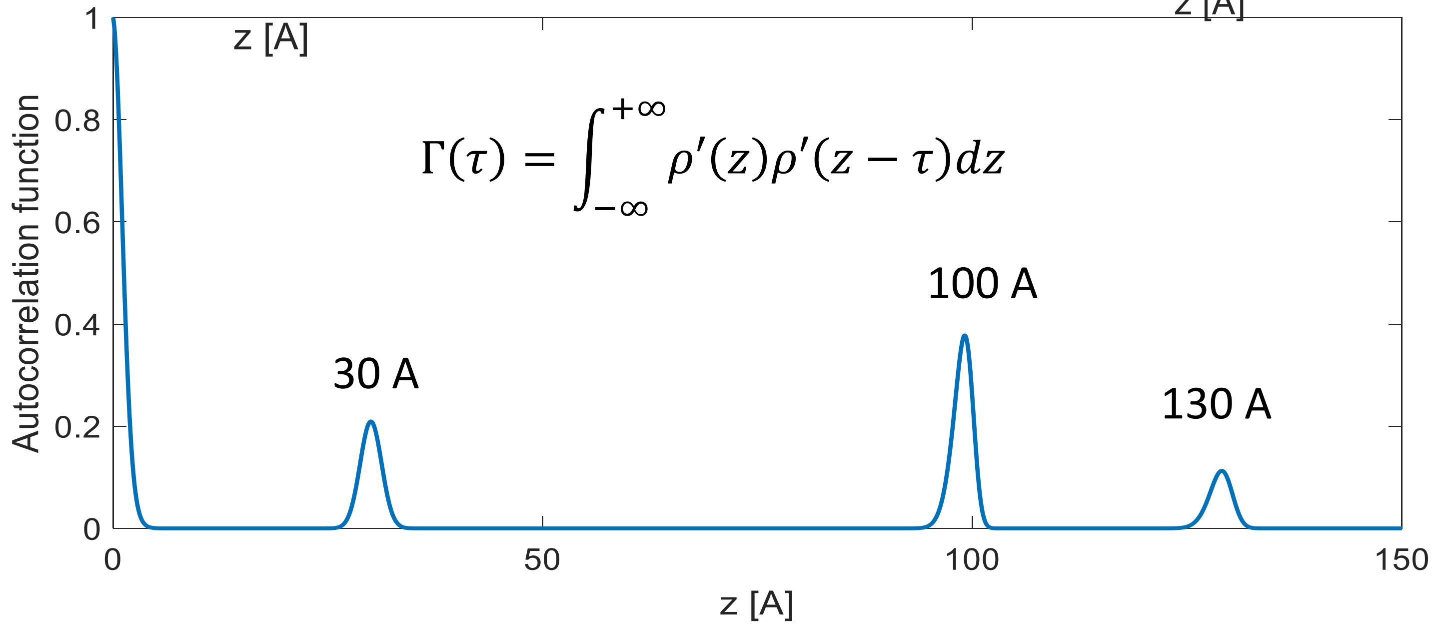
$$\Gamma(\tau) = \rho'(z) \otimes \rho'(z) = \int_{-\infty}^{+\infty} \rho'^{(z)} \rho'^{(z-\tau)} dz = TF^{-1}\left[\rho_S^2 \frac{R(q_z)}{R_F(q_z)}\right]$$



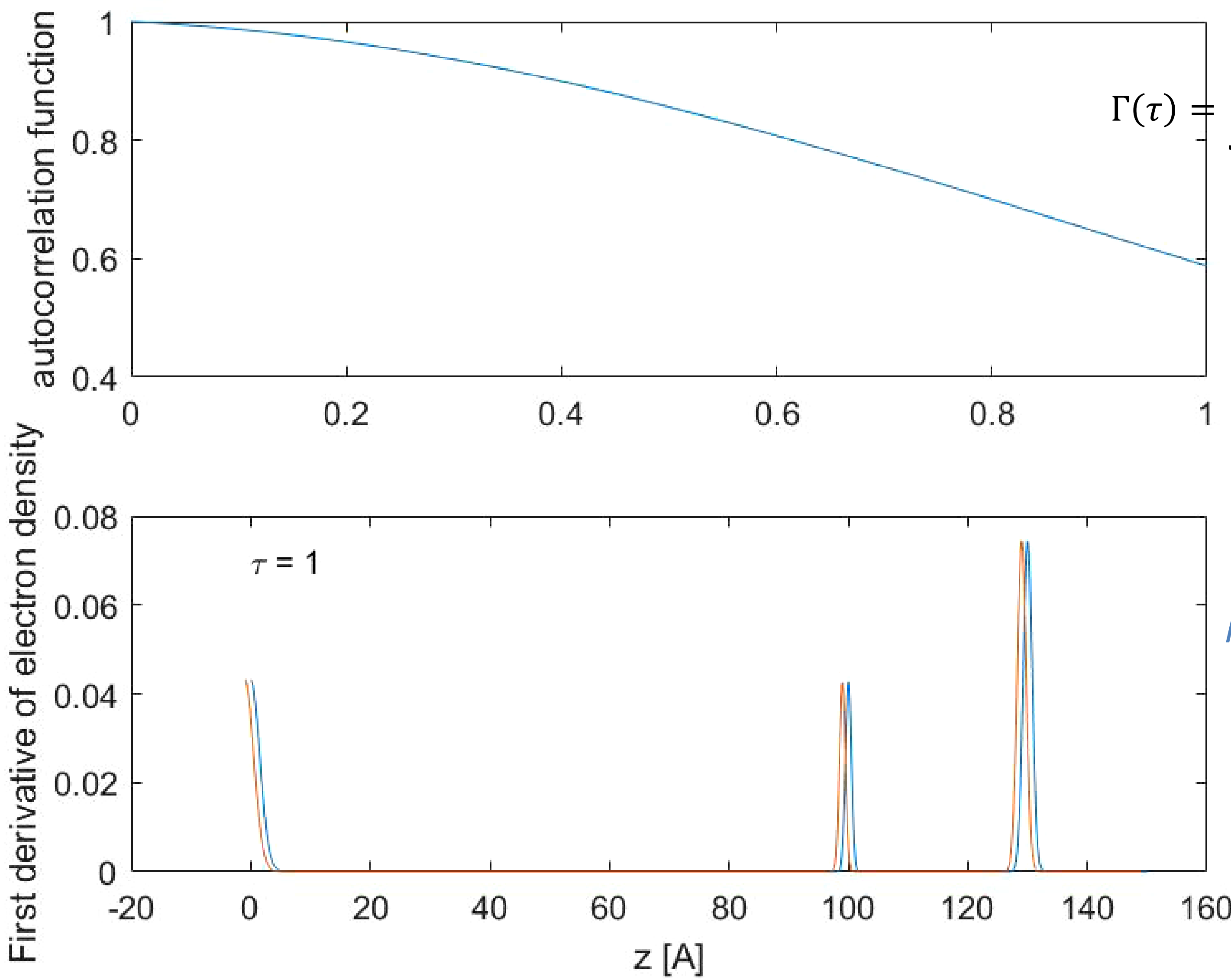
Example : two layers on a substrate







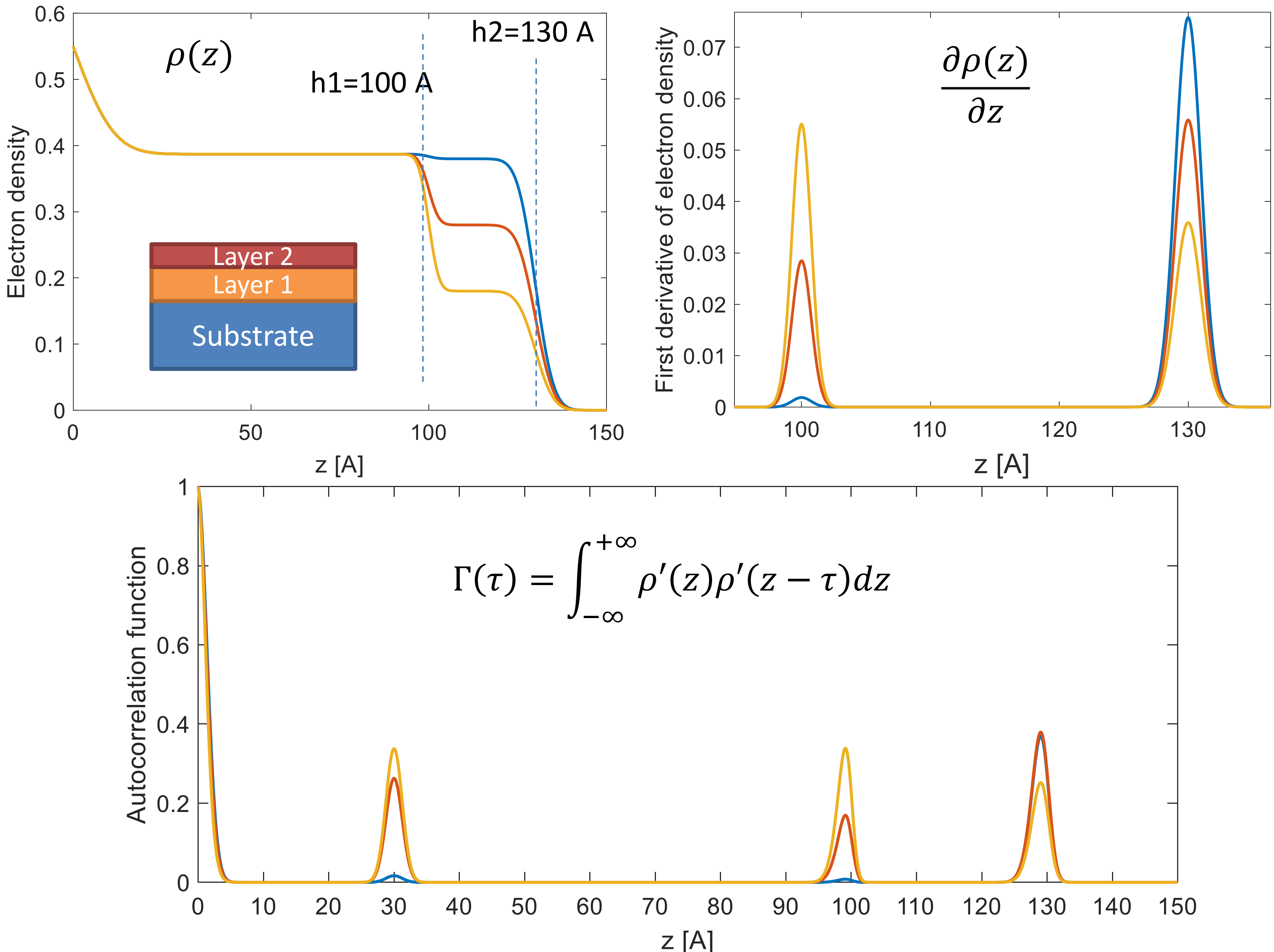
Example : two layers on a substrate



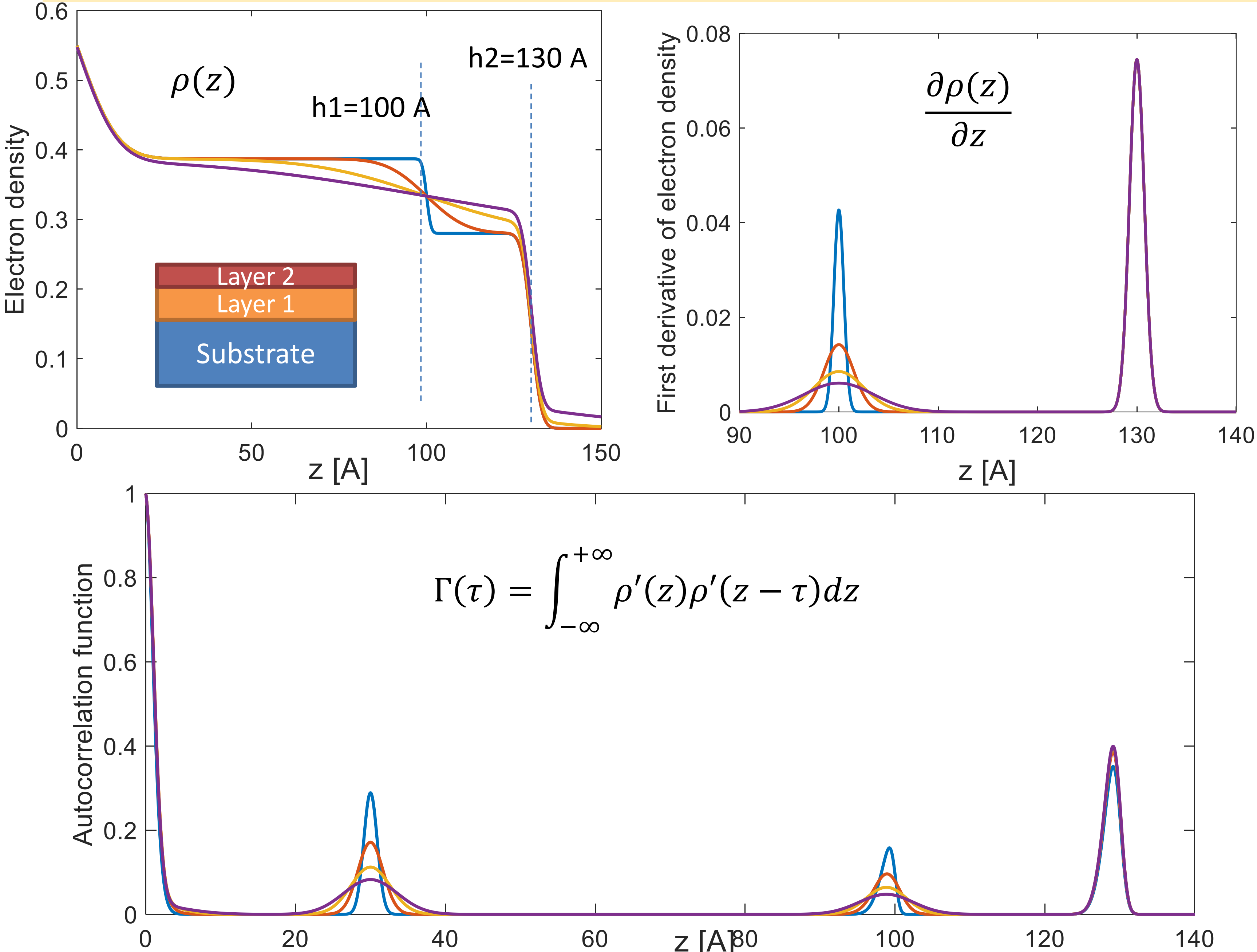
$$\Gamma(\tau) = \int_{-\infty}^{+\infty} \rho'(z)\rho'(z-\tau)dz$$

$$\rho'(z)\rho'(z-\tau)$$

Example : two layers on a substrate (effect of density contrast)

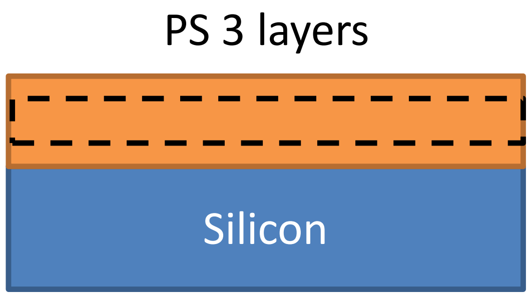


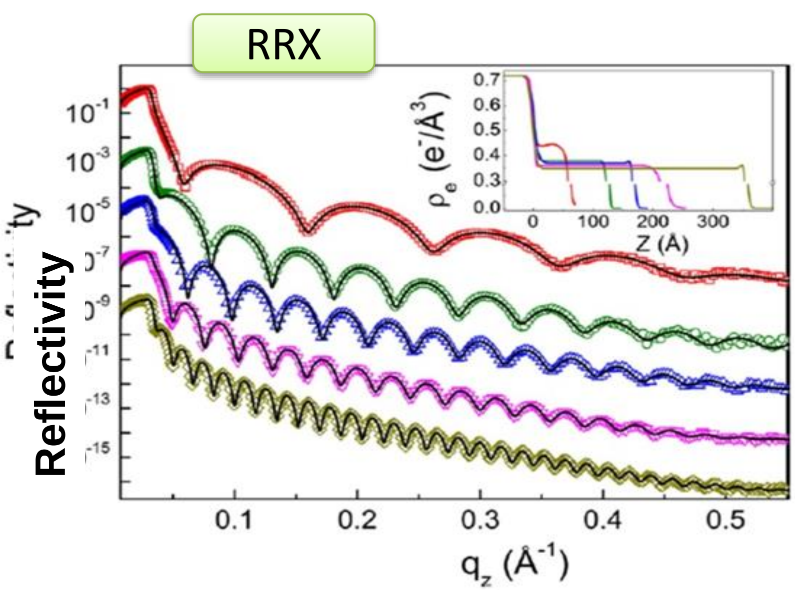
Example : two layers on a substrate (effect of roughness)



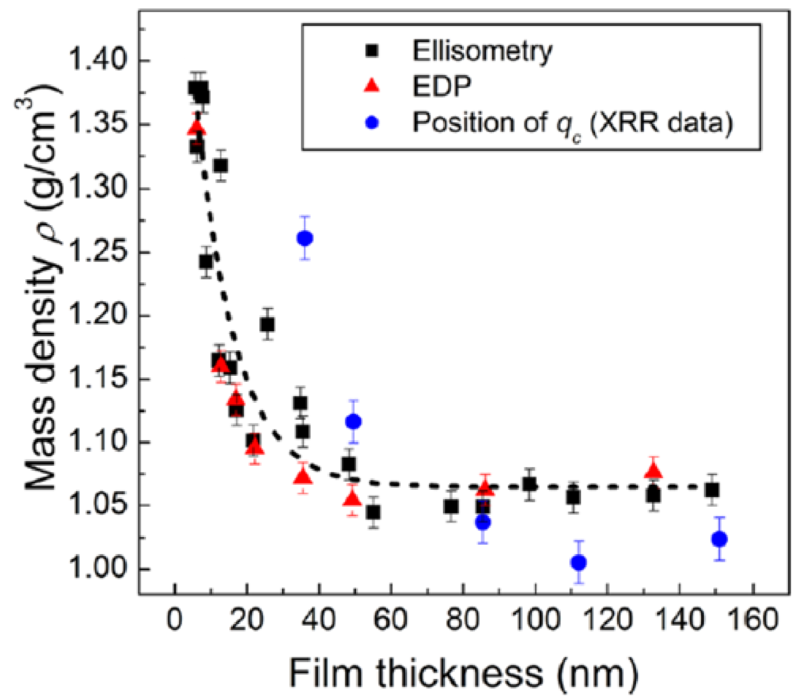
4 – Examples of XRR data analyzed with REFLEX

4.1 X-ray reflectivity study of the density of polystyrene thin films





Vignaud et al Langmuir (2014)

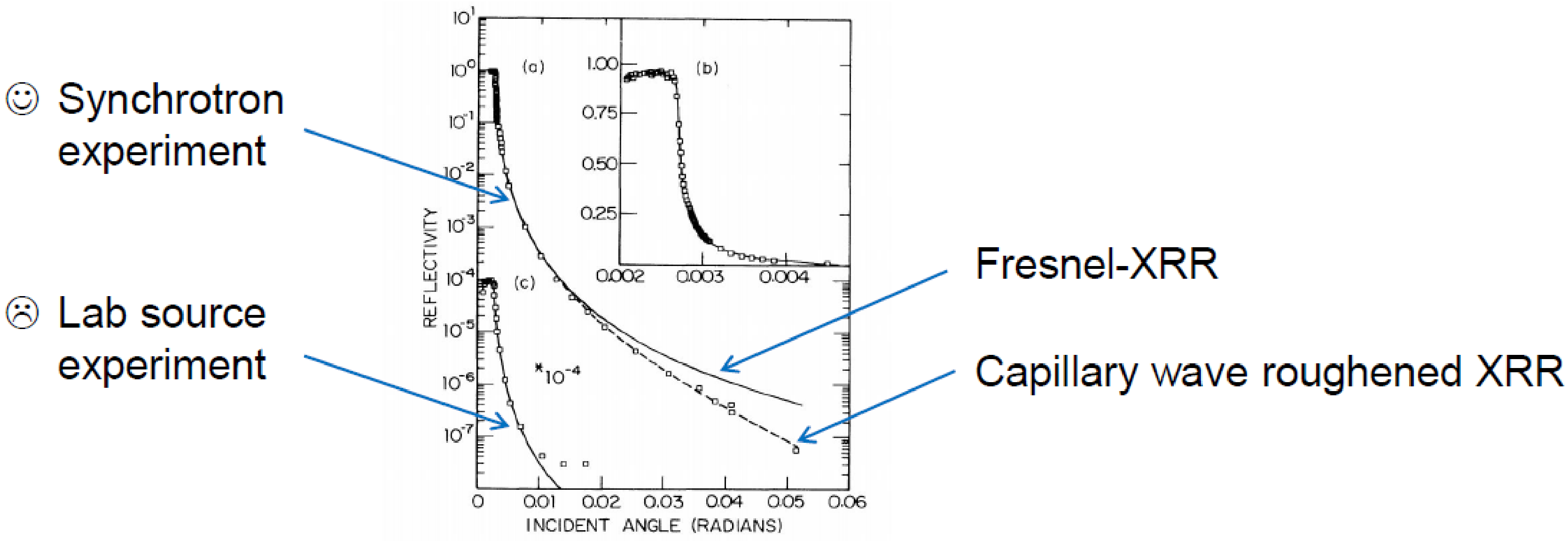


- **Films of less than 50 nm show a strong increase in their densities**

4.2 Surface Roughness of Water Measured by X Ray Reflectivity

Surface Roughness of Water Measured by X-Ray Reflectivity

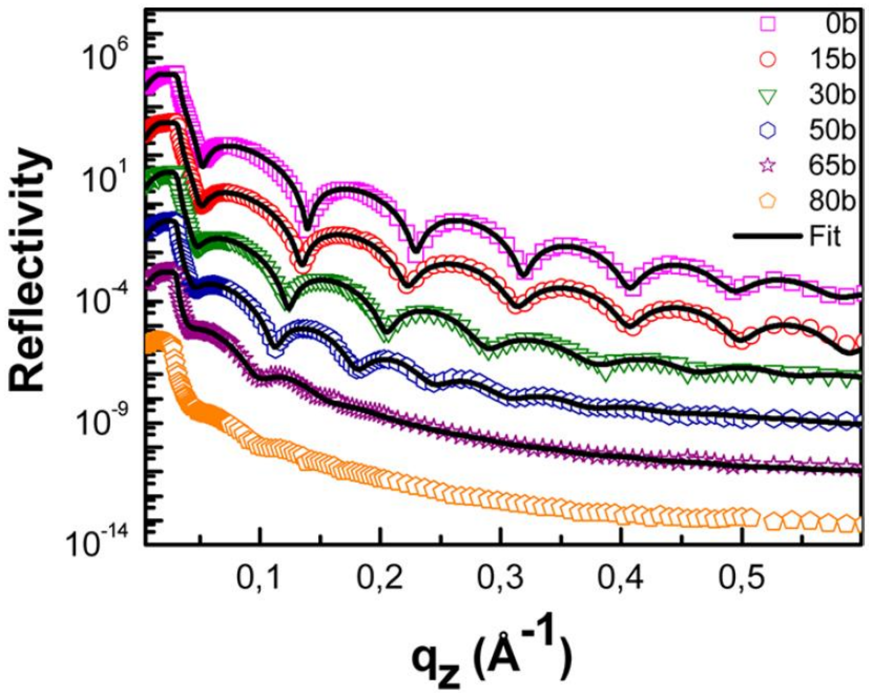
A. Braslau et al., Phys. Rev. Lett. 54, 114 (1985).

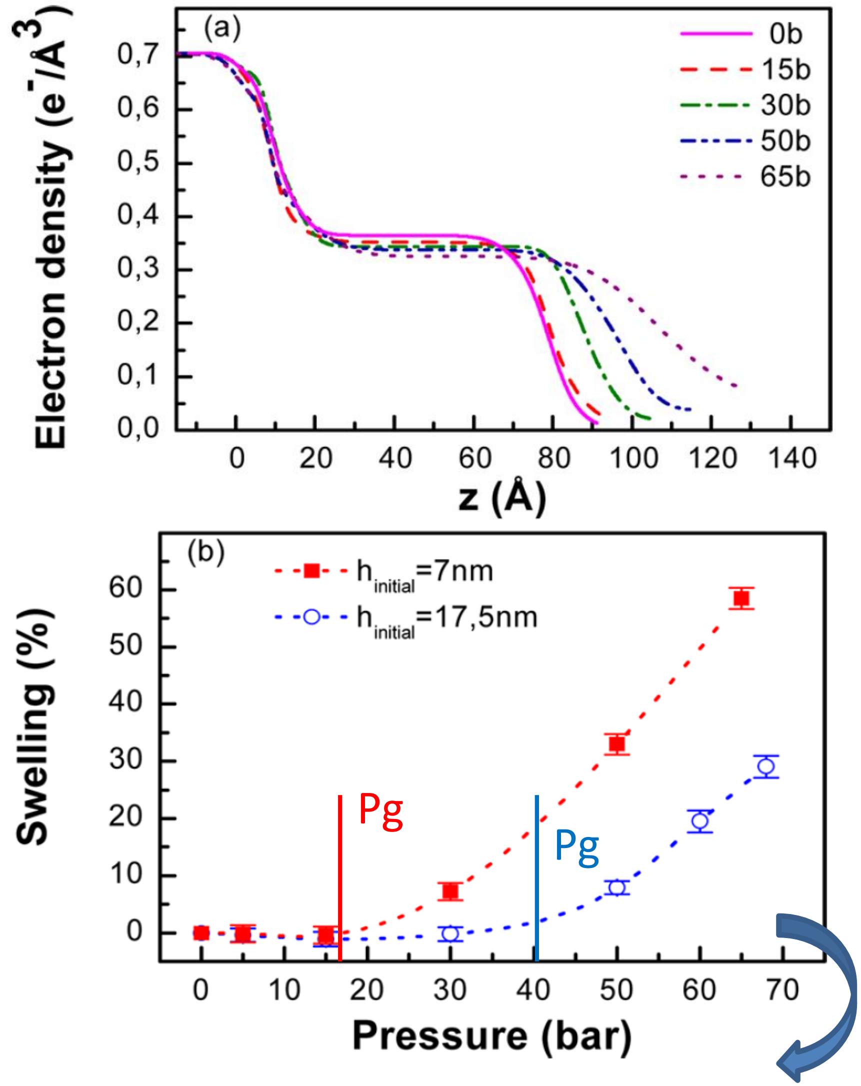


- Roughness of 3.24 Å
- Very close to what is expected from thermally excited capillary waves
- First such measurement of surface roughness of any liquid
- Synchrotron radiation necessary

4.3 In-situ study of the swelling of PS thin films under CO2 pressure

Evolution of the film thickness during the in-situ pressurization of the CO_2



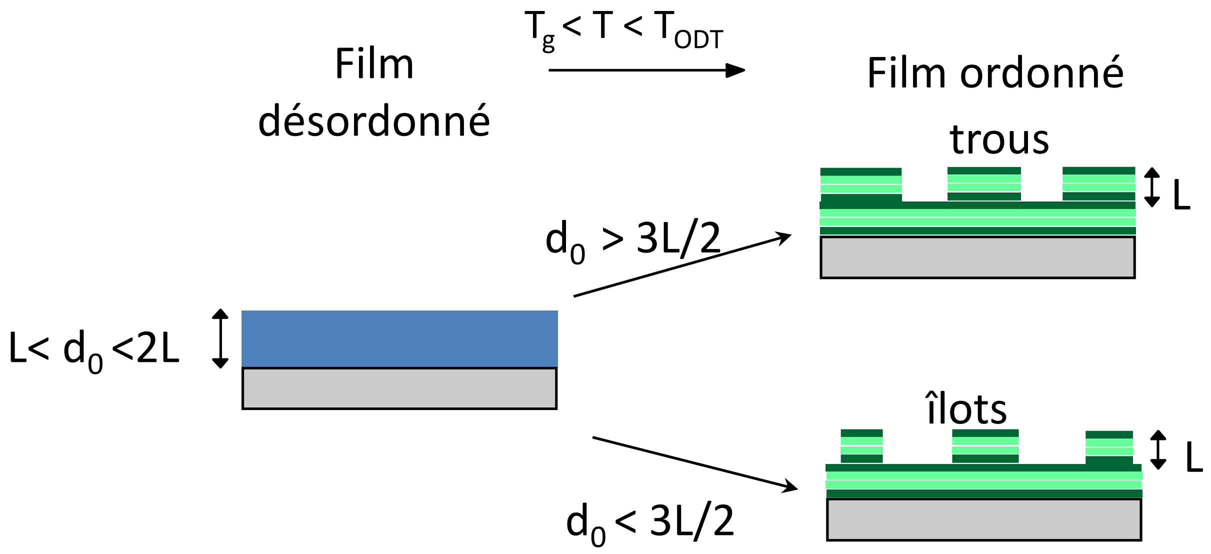


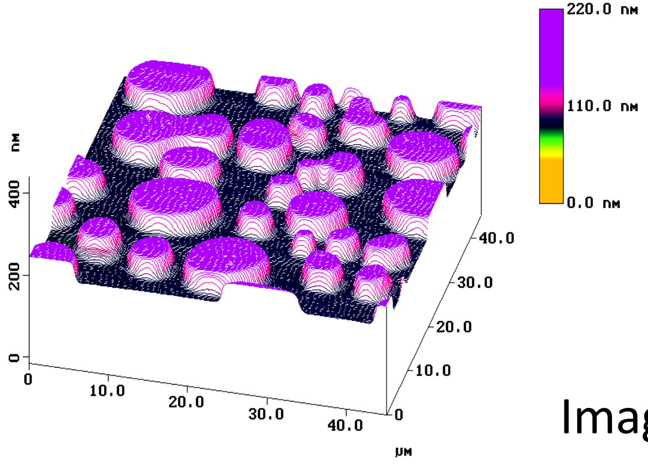
- The films are swollen
- Their electronic density decreases
- The roughness increases

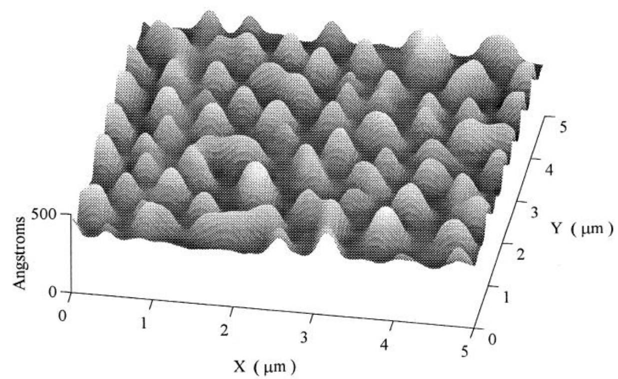
Existence of a pressure from which the film is free to swell: Pg by analogy with Tg

Chebil, Vignaud, Grohens, Beuvier, Konovalov, Sanyal and Gibaud, Macromolecules (2012)

4.4 *Mise en ordre d'un film de copolymère diblock symétrique*

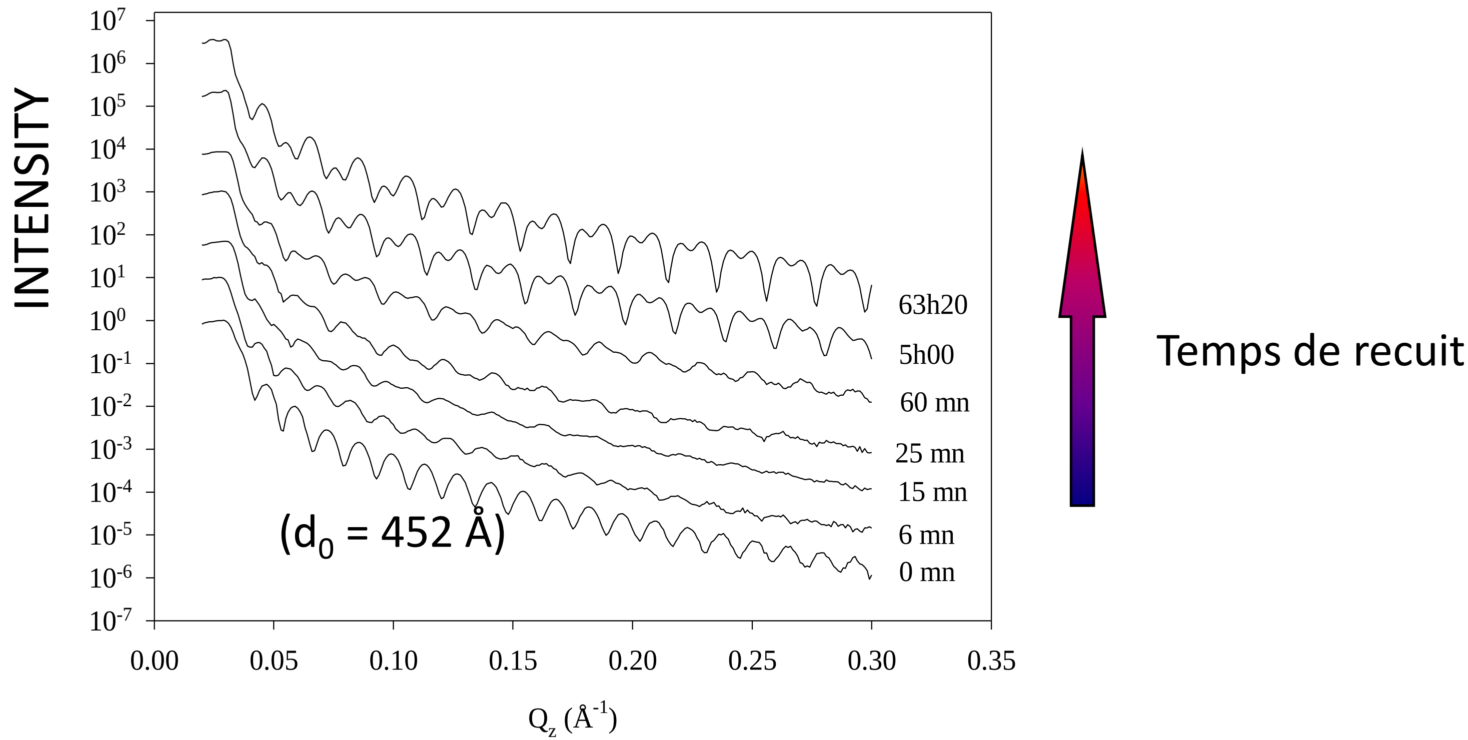




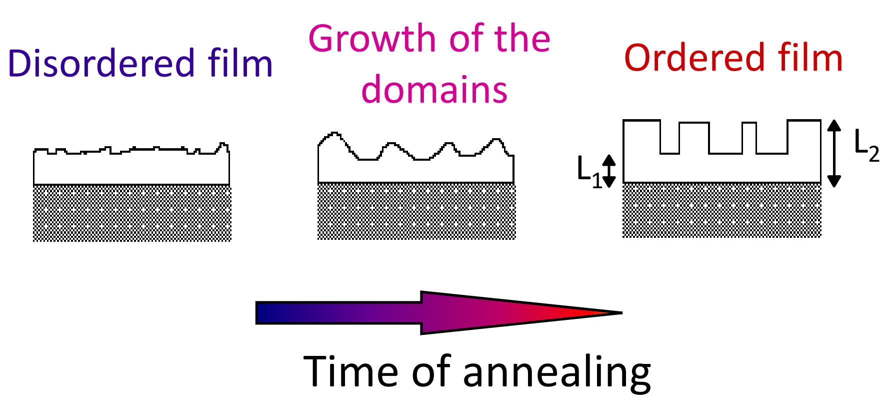


Images AFM : PS-PBMA

4.3 *Mise en ordre d'un film de copolymère diblock symétrique*



3 régimes



• Dés le début du recuit, le film se scinde en 2 épaisseurs et évolue vers un nouvel état d'équilibre indiquant un processus de décomposition spinodale


That's all Folks!

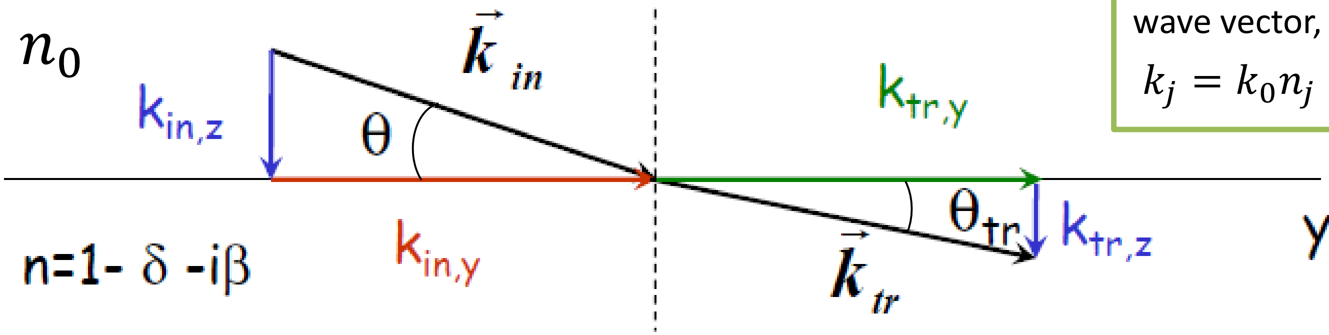
APPENDIX 1 : Calculation of Fresnel coefficients

Conservation of the tangential component k_y of the wave vectors

$$k_{in,y} = k_{tr,y} = k_{r,y}$$

the modulus of the wave vector in medium j is related to the wave vector, k_0, in air as:

$$k_j = k_0 n_j \qquad k_0 = \frac{2\pi}{\lambda}$$



y axis : $k_{in,y} = k_{in} cos\ \theta = n_0 k_0 cos\ \theta$ $\qquad k_{tr,y} = k_{tr} cos\ \theta_{tr} = n k_0 cos\ \theta_{tr}$

$$n_0 cos\ \theta = n\ cos\ \theta_{tr}$$

Snell – Descartes Law

z axis : $k_{in,z} = -\ k_{in}\ sin\ \theta = -n_0 k_0\ sin\ \theta$ $\qquad k_{tr,z} = -k_{tr}\ sin\ \theta_{tr} = -\ n k_0\ sin\ \theta_{tr}$

$$k_{tr,z} = -\left(k_{tr}^2 - k_{tr,y}^2\right)^{\frac{1}{2}} = -(n^2 k_0^2 - n_0^2 k_0^2 cos^2\theta)^{1/2}$$

$$k_{tr,z} = -k_0 (n^2 - n_0^2 cos^2\theta)^{1/2}$$

APPENDIX 1 : Calculation of Fresnel coefficients

Continuity of the tangential electric field at the surface of separation of the two media (z = 0)

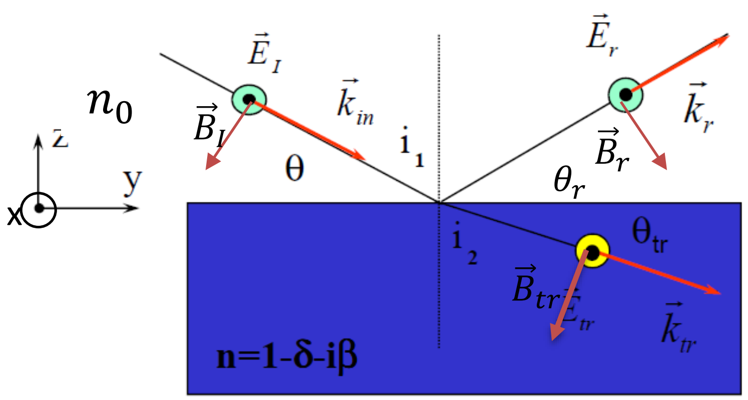
$$A_{in}e^{i(\omega t-k_{in,y}y)}+A_{r}e^{i(\omega t-k_{r,y}y)} = A_{t}e^{i(\omega t-k_{tr,y}y)}$$

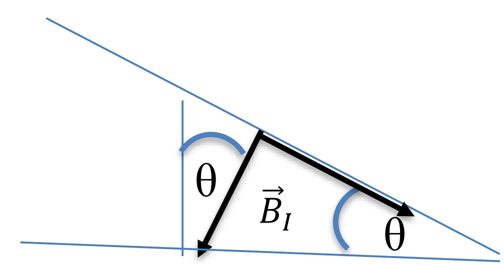
Continuity of the tangential magnetic field (z =0)

$$-\frac{k_{in}}{\omega}sin\theta A_{in}e^{i(\omega t-k_{in,y}y)}+\frac{k_{r}}{\omega}sin\theta A_{r}e^{i(\omega t-k_{r,y}y)} = -\frac{k_{tr}}{\omega}sin\theta_{tr}A_{t}e^{i(\omega t-k_{tr,y}y)}$$

$$k_{in,z} = -\,k_{in}\,sin\,\theta = -k_{r,z} \qquad k_{tr,z} = -k_{tr}\,sin\,\theta_{tr}$$

$$k_{in,z}A_{in}e^{i(\omega t-k_{in,y}y)}+k_{r,z}A_{r}e^{i(\omega t-k_{r,y}y)} = k_{tr,z}A_{t}e^{i(\omega t-k_{tr,y}y)}$$





APPENDIX 1 : Calculation of Fresnel coefficients

$$\begin{cases} A_{in} e^{i(\omega t - k_{in,y} y)} + A_r e^{i(\omega t - k_{r,y} y)} = A_t e^{i(\omega t - k_{tr,y} y)} \\ k_{in,z} A_{in} e^{i(\omega t - k_{in,y} y)} + k_{r,z} A_r e^{i(\omega t - k_{r,y} y)} = k_{tr,z} A_t e^{i(\omega t - k_{tr,y} y)} \end{cases}$$

Equations are valid $\forall y$, $\forall t$ and $k_{in,y} = k_{tr,y} = k_{r,y}$

Writing the reflected amplitude $r_\perp = A_r / A_{in}$ for the electric field perpendicular to the plane of incidence and the transmitted one $t_\perp = A_t / A_{in}$

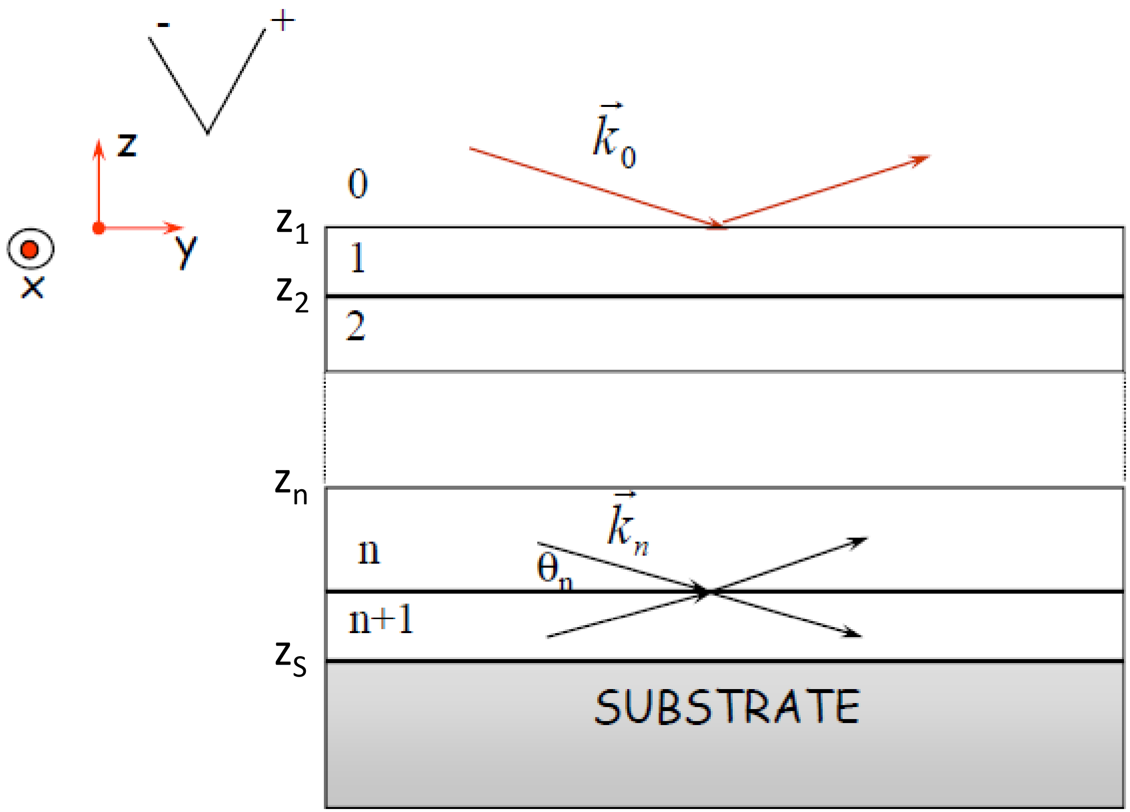
At grazing angle of incidence for x-rays : $\boldsymbol{r_\perp \simeq r_\parallel \simeq r}$

$$\begin{cases} A_{in} + A_r = A_t \\ k_{in,z} A_{in} + k_{r,z} A_r = k_{tr,z} A_t \end{cases} \qquad \begin{cases} 1 + r_\perp = t_\perp \\ k_{in,z} + k_{r,z} r_\perp = k_{tr,z} t_\perp \end{cases}$$

$$\begin{cases} 1 + r_\perp = t_\perp \\ k_{in,z}(1 - r_\perp) = k_{tr,z} t_\perp \end{cases} \Rightarrow \frac{1 + r_\perp}{1 - r_\perp} = \frac{k_{in,z}}{k_{tr,z}}$$

$$\boxed{r_\perp = \frac{k_{in,z} - k_{tr,z}}{k_{in,z} + k_{tr,z}}}$$

APPENDIX 2: Calculating the components of the transfer matrix



The signs – and + label the direction of propagation of the wave; air is labelled medium 0 and stratified media are identified by $1 \leq j \leq n$ layers in which upwards and downwards wave travel

$$\vec{E}^{-} = A_n^{-} e^{i(\omega t - k_{y,n} y - k_{z,n} z)} \vec{e}_1$$

Electric field in the nth layer of the downwards travelling wave

APPENDIX 2: Calculating the components of the transfer matrix

Laws of Conservation

$$k_{y,n} = k_n \cos\theta_n = k_0 \cos\theta$$

$$k_{z,n} = -k_n \sin\theta_n = -\sqrt{k_n^2 - k_{n,y}^2}$$

At altitude z the upwards and downwards travelling waves are superimposed so that the electric filed in the medium n is:

$$E_n = \left(A_n^+ e^{ik_{z,n}z} + A_n^- e^{-ik_{z,n}z}\right) e^{i(\omega t - k_{y,n}y)}$$

$$E_n = \left(u_n^+(z) + u_n^-(z)\right) e^{i(\omega t - k_{y,n}y)}$$

BOUNDARY CONDITIONS at $z = z_{n+1}$

Conservation of

$$\begin{cases} \text{tangential component of the elctrique field E} \\ \text{tangential component of the magnetic field} \Leftrightarrow \dfrac{\partial E}{\partial z} \end{cases}$$

APPENDIX 2 : Calculating the components of the transfer matrix

Conservation of

$$\begin{cases} E(z_{n+1}) & u_n^+(z_{n+1}) + u_n^-(z_{n+1}) = u_{n+1}^+(z_{n+1}) + u_{n+1}^-(z_{n+1}) \\ \dfrac{\partial E}{\partial z}(z_{n+1}) & k_{z,n}\left(u_n^+(z_{n+1}) - u_n^-(z_{n+1})\right) = k_{z,n+1}\left(u_{n+1}^+(z_{n+1}) - u_{n+1}^-(z_{n+1})\right) \end{cases}$$

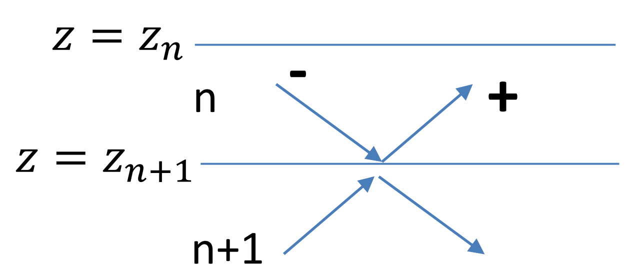
The combination of these two equations can be written in a matrix form and we can define a refraction matrix $R_{n,n+1}$ when travelling from medium n to medium n + 1:

$$\begin{bmatrix} u_n^+(z_{n+1}) \\ u_n^-(z_{n+1}) \end{bmatrix} = \begin{bmatrix} p_{n,n+1} & m_{n,n+1} \\ m_{n,n+1} & p_{n,n+1} \end{bmatrix} \begin{bmatrix} u_{n+1}^+(z_{n+1}) \\ u_{n+1}^-(z_{n+1}) \end{bmatrix} = R_{n,n+1} \begin{bmatrix} u_{n+1}^+(z_{n+1}) \\ u_{n+1}^-(z_{n+1}) \end{bmatrix}$$

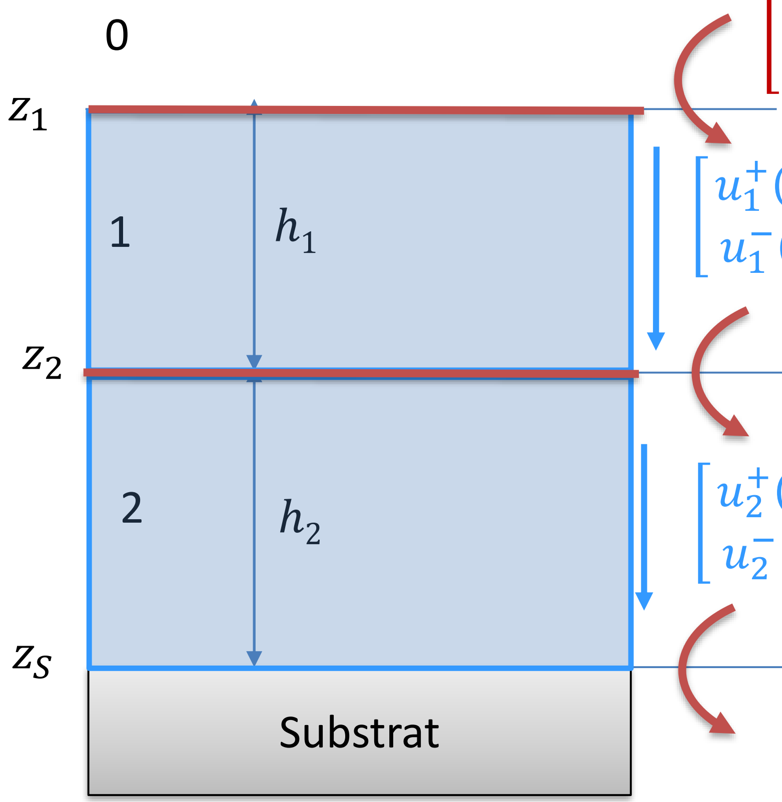
$R_{n,n+1}$: refraction matrix

$$p_{n,n+1} = \frac{k_{z,n} + k_{z,n+1}}{2k_{z,n}}$$

$$m_{n,n+1} = \frac{k_{z,n} - k_{z,n+1}}{2k_{z,n}}$$



APPENDIX 2 - Example : 2 layers on a substrate



$$\begin{bmatrix} u_0^+(z_1) \\ u_0^-(z_1) \end{bmatrix} = R_{0,1} \begin{bmatrix} u_1^+(z_1) \\ u_1^-(z_1) \end{bmatrix}$$

$$\begin{bmatrix} u_1^+(z_1) \\ u_1^-(z_1) \end{bmatrix} = T_1 \begin{bmatrix} u_1^+(z_2) \\ u_1^-(z_2) \end{bmatrix}$$

$$\begin{bmatrix} u_1^+(z_2) \\ u_1^-(z_2) \end{bmatrix} = R_{1,2} \begin{bmatrix} u_2^+(z_2) \\ u_2^-(z_2) \end{bmatrix}$$

$$\begin{bmatrix} u_2^+(z_2) \\ u_2^-(z_2) \end{bmatrix} = T_2 \begin{bmatrix} u_2^+(z_s) \\ u_2^-(z_s) \end{bmatrix}$$

$$\begin{bmatrix} u_2^+(z_s) \\ u_2^-(z_s) \end{bmatrix} = R_{2,s} \begin{bmatrix} u_s^+(z_s) \\ u_s^-(z_s) \end{bmatrix}$$

$$\begin{bmatrix} u_0^+(z_1) \\ u_0^-(z_1) \end{bmatrix} = \left[R_{0,1} T_1 R_{1,2} T_2 R_{2,s} \right] \begin{bmatrix} u_s^+(z_s) \\ u_s^-(z_s) \end{bmatrix}$$

M: transfer matrix

APPENDIX 2 - Example : 2 layers on a substrate

$$\begin{bmatrix} u_0^+(z_1) \\ u_0^-(z_1) \end{bmatrix} = \left[R_{0,1} T_1 R_{1,2} T_2 R_{2,s}\right] \begin{bmatrix} u_s^+(z_s) \\ u_s^-(z_s) \end{bmatrix} = \begin{bmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{bmatrix} \begin{bmatrix} u_s^+(z_s) \\ u_s^-(z_s) \end{bmatrix}$$

M: transfer matrix

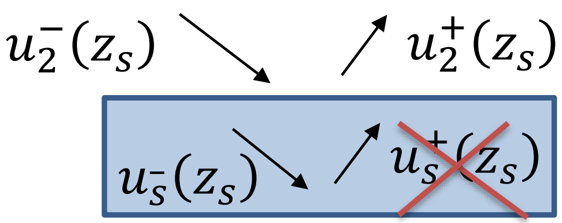
The reflection coefficient by the sample is defined as the ratio of the reflected electric field to the incident electric field at the surface of the material :

$$r = \frac{u_0^+(z_1)}{u_0^-(z_1)} = \frac{M_{11} u_s^+(z_s) + M_{12} u_s^-(z_s)}{M_{21} u_s^+(z_s) + M_{22} u_s^-(z_s)}$$

It is reasonable to assume that no wave will be reflected back from the substrate if x-rays penetrate only few microns:

thus $u_s^+(z_s) = 0$ $\Rightarrow$

$$\mathrm{r} = \frac{M_{12}}{M_{22}}$$



$$r = \frac{r_{0,1} + r_{1,2} e^{-2ik_{z,1}h_1} + r_{2,s} e^{-2i(k_{z,2}h_2 + k_{z,1}h_1)} + r_{0,1} r_{1,2} r_{2,s} e^{-2ik_{z,2}h_2}}{1 + r_{0,1} r_{1,2} e^{-2ik_{z,1}h_1} + r_{1,2} r_{2,s} e^{-2ik_{z,2}h_2} + r_{2,s} r_{0,1} e^{-2i(k_{z,1}h_1 + k_{z,2}h_2)}}$$

To fit reflectivity data, please follow the steps below:

1- Load your data (menu **File** $\Rightarrow$ **import data**).

2- Fill the fields related to the reflectometer: the instrumental resolution Δq_z and the wavelength (or energy) of the incident beam.

3- Fill the field related to the structure of the sample: the number of layer and enter the nature of the different material if it exists in the database.

4- Complete parameters relating to the size of the sample and the beam dimension in order to adjust the beginning of the reflectivity curve.

Manual adjustment of parameters: Before automatically performing the fitting process, it is important to manually adjust the parameters in order to minimize the difference between the calculated and measured reflectivity curves. Otherwise the optimization program will not converge to a good solution. It is thus important to know how the parameters influence the reflectivity curve.

Automatic adjustment of parameters

When calculated reflectivity curve is close to the data, user can fit by using the menu **Calculus ⇒ Fit**. The user has the option of using three different methods to minimize the χ^2 value (define below): Levenberg–Marquardt , Simplex search and Trust Region methods. χ^2 parameter is used to describe how close the calculated data matches the experimental ones and is given by:

$$\chi^2 = \frac{1}{n}\sum_{i=1}^{n}\left(\frac{ydata_i - ycalc_i}{ydata_i}\right)^2$$

where there are a total of n measured data points, $ydata_i$ each of which has a corresponding theoretical value, $ycalc_i$.

The most popular method for curve-fitting is Levenberg-Marquardt. With Trust Region Method, it is possible to constrain the solution into a range. If a variable starts at an initial estimate x_0, a variation percentage, v%, of x_0 is authorized so that the solution x is always in the range:

$$x_0 - x_0{*}v/100 \le x \le x0 + x_0{*}v/100$$

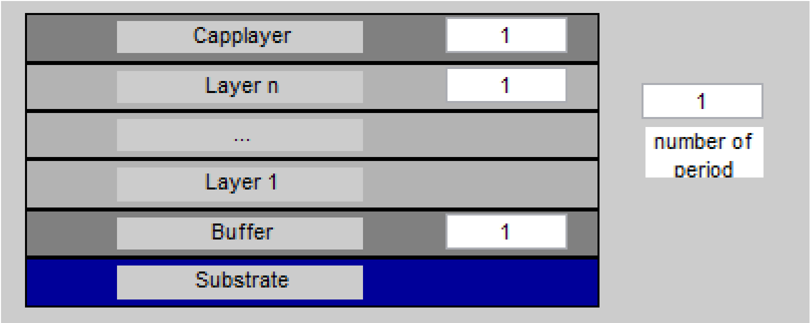
These constraints may be used to limit a parameter to within a physically reasonable range.

Installing Reflex

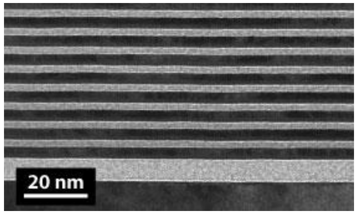
1- Extract the reflex53.zip file to the user PC desktop.
2- In the reflex53 directory, double-click on the MCRInstaller.exe file in order to install it.
3- Double-click on the reflex53.exe to start the program

REFLEX can be working as an executable file under windows XP/seven/11

How to model the sample structure ?



Reflex allows analyzing reflectivity data measured on a multilayer film



The number of “Cap layers” is the number of layers in contact with the fluid (air for example)

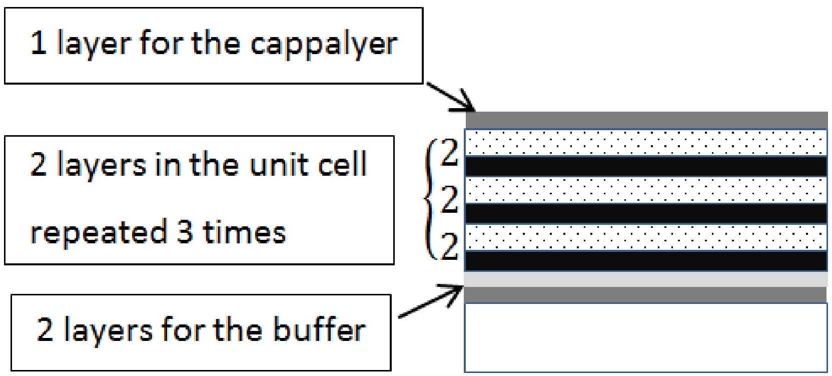
“Layer n” is the number of layers that are repeated as a typical motif or unit cell inside the multilayer.

Next to this box is a box labelled "number of period" containing the number of repeated periods of this motif (or unit cell) inside the multilayer.

The number of “Buffer” is the number of layers at the substrate/film interface. The buffer layer and the cap layer are not incorporated in the unit cell and hence are not repeated.

How to model the sample structure ?

Example 1: a multilayer consisting of 3 repeating unit cells made of a bilayer with 2 buffer layers and a single cap layer



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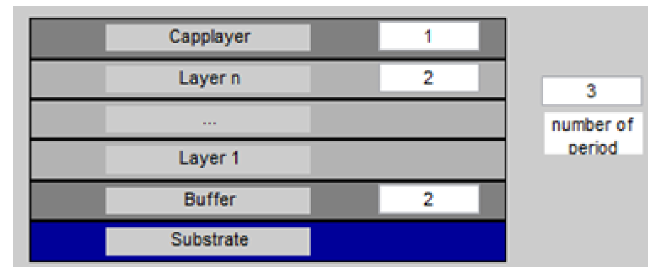
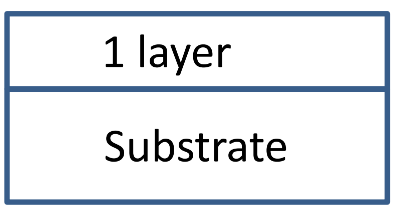


Example 2: single layer on substrate



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Caplayer	Layer n	Buffer 1	Number of period
0	1	0	1

=> Care must be taken to ensure that the model is physically representative of the system being studied