Structural analysis of thin films by reflectometry

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July 2009, updates: September 2014, October 2021
English version September 2024

What is (specular) X-ray and neutron reflectometry for thin films ?

Definition : *specular* means that the incident angle equals the reflection angle relative to the surface normal of the thin film.

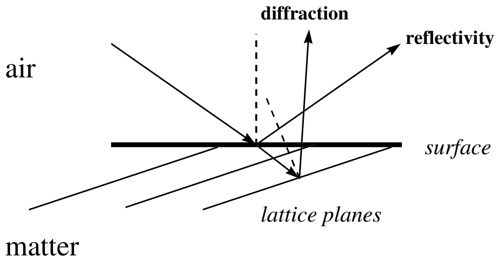
Key points

- measure the intensity of the reflected beam as a function of incident angle to deduce the properties of the material
- it works because there is 'density' contrast → refraction
- depth profiling → layer thicknesses, roughnesses, and densities (gradients)
- *in situ* measurements : growth, adsorption, annealing, ···
- research fields : thin films for semiconductor devices, optical and other coatings, magnetic layers, biological membranes, ···

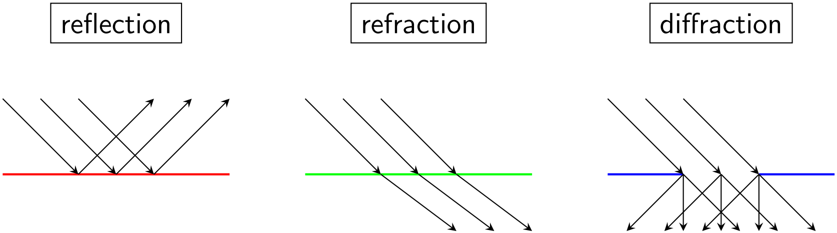
Reflectivity versus diffraction

Diffraction : *interference* induced by long-range order, very often 3D
diffraction plane : fictious diffraction planes

Réflectivité : *interference* by electronic density contrast, always 1D
diffusion plane : surface or physical interface



Reflection, refraction and diffraction



Personal thoughts

X-ray *reflectivity* : emphasizes the reflection of X-rays, measured by reflectometry
X-ray *reflectometry* : focusses on the technique to measure the reflectivity

A reflectometry experiment always combines the reflection and refraction of X-rays and may include diffraction (or rather interference) effects.

X-ray *reflectivity* should actually be called X-ray *refractivity* in view of the importance of refraction at very low angles.

X-ray reflectometry is a diffusion technique which permits to determine the electronic density across a stratified medium

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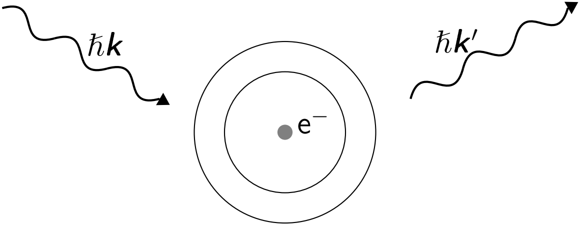


Units and magnitudes

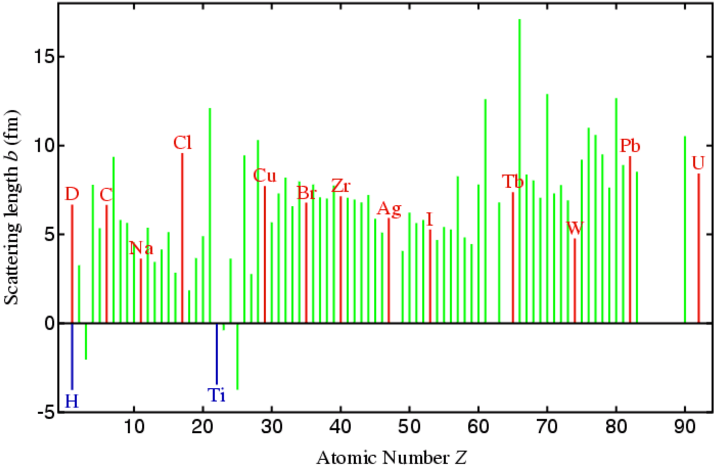
$$A_{\text{sc}} = -A_{\text{in}} b \frac{e^{-ikr}}{r}$$

- b is the **scattering power** or **scattering length** ; it is expressed in length units.
  - electron : $b = r_0$ Thomson scattering length ($= 2.82.10^{-5}$ Å)
  - nucleus : $b = b_c$ coherent scattering length

For a multi-element compound a scattering length density (SLD ou ρ) is defined by :

$$\rho = \frac{\sum_{i=1}^{N} b_i}{V_m} = \frac{\sum_{i=1}^{N} Z_i r_0}{V_m}$$

Coherent scattering length (neutrons)



Units and magnitudes

The scattering length density is expressed in $[\text{area}]^{-2}$and can be linked to the electronic density ρ_{e} and mass density ρ_{m} by :

$$\rho = r_0 \rho_{\mathrm{e}}$$

and

$$\rho = N_{\mathrm{A}} r_0 \rho_{\mathrm{m}} \frac{\sum c_i Z_i}{\sum c_i A_i}$$

The goal of a reflectometry experiment is to determine ρ (or ρ_{e} or ρ_{m}).

X-ray reflectometry is a diffusion technique which permits to determine the electronic density across a stratified medium

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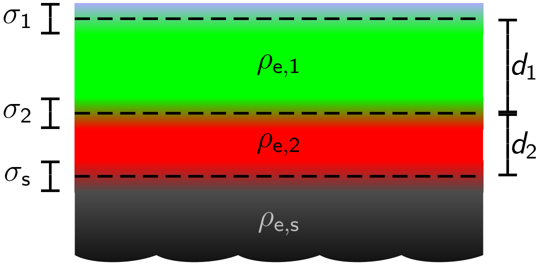

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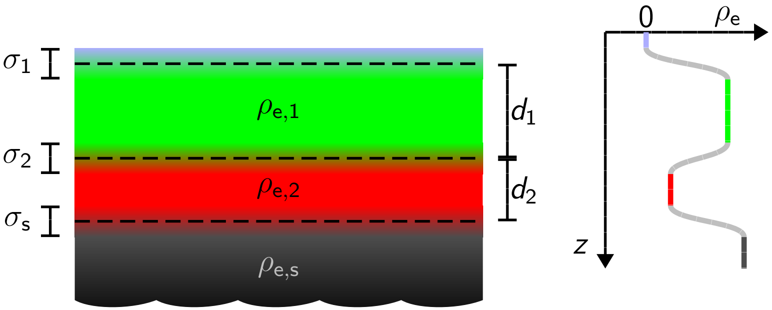

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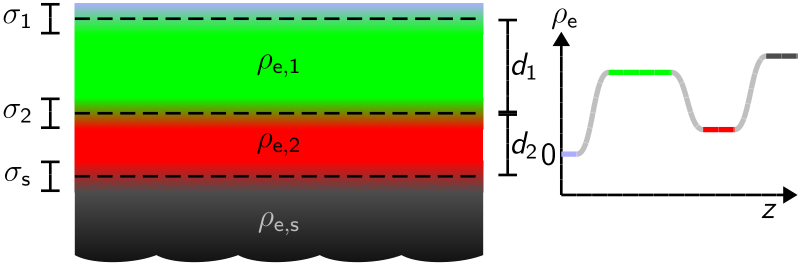
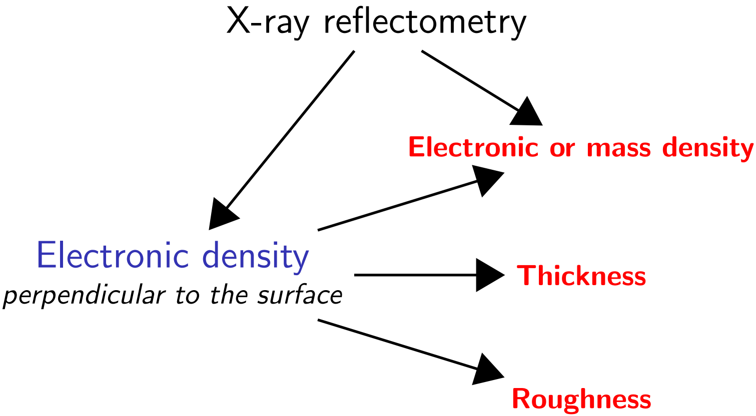


X-ray reflectometry

↓

Electronic density

perpendicular to the surface


X-ray reflectometry
Electronic or mass density
Electronic density
perpendicular to the surface
Thickness
Roughness

X-ray reflectometry

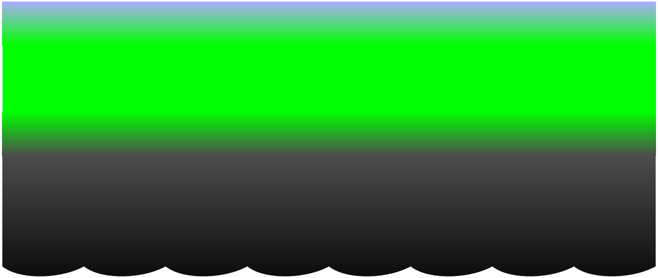
Electronic or mass density

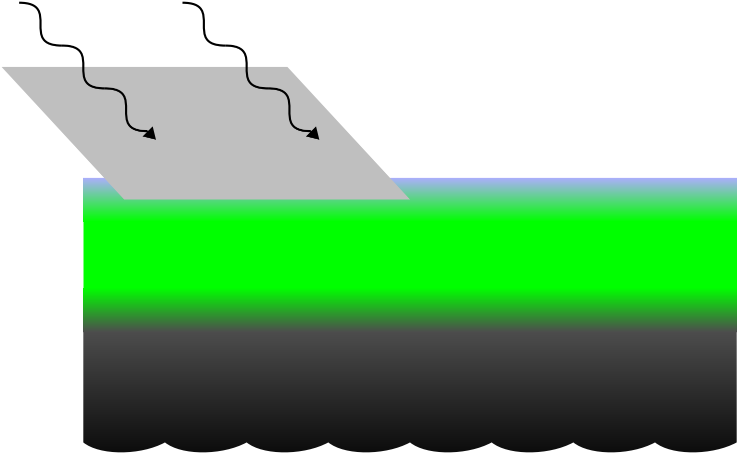
Electronic density
perpendicular to the surface

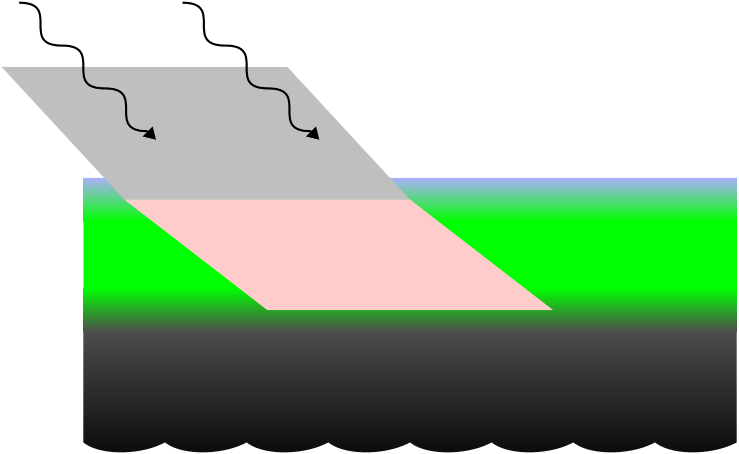
Thickness

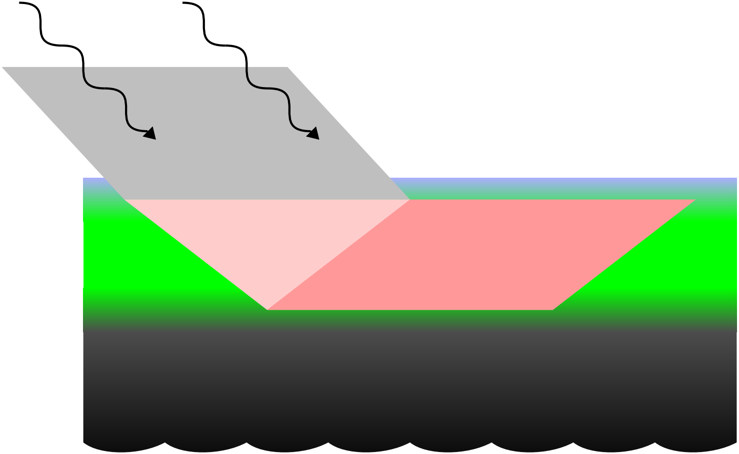
Roughness

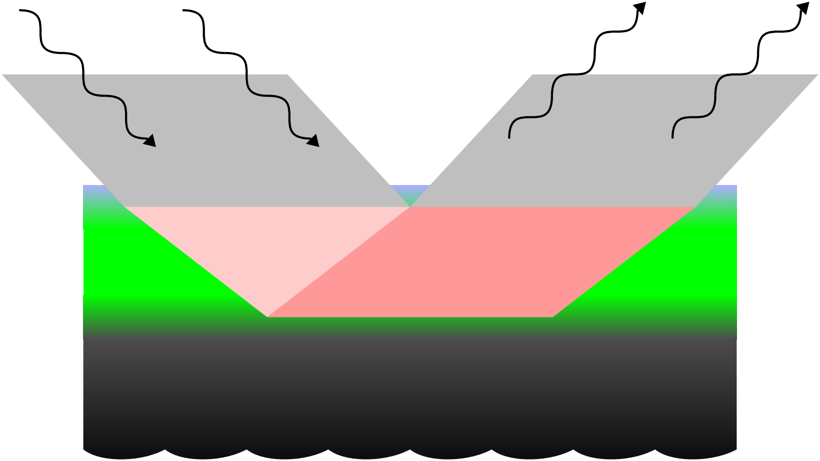
Maximum 3 layers

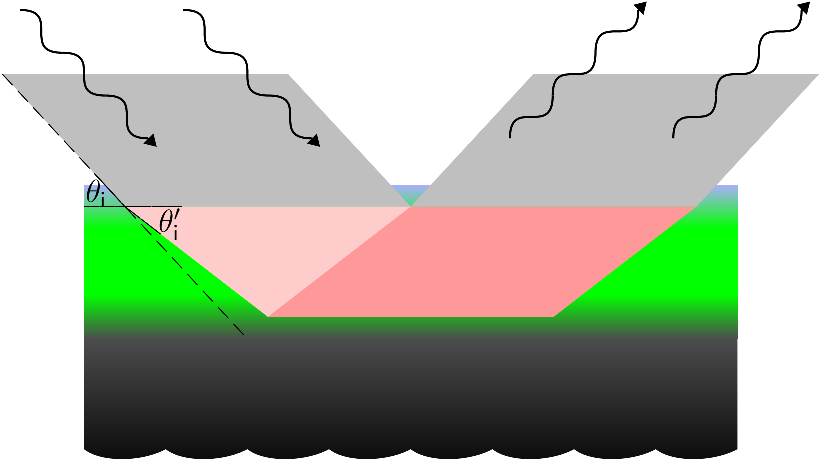




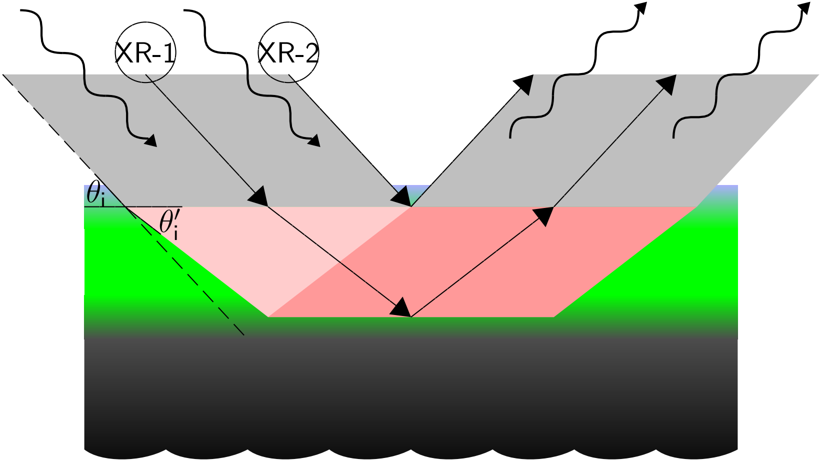








Loi de Snell-Descartes : $\cos\theta_i = n_f \cos\theta_i{}'$



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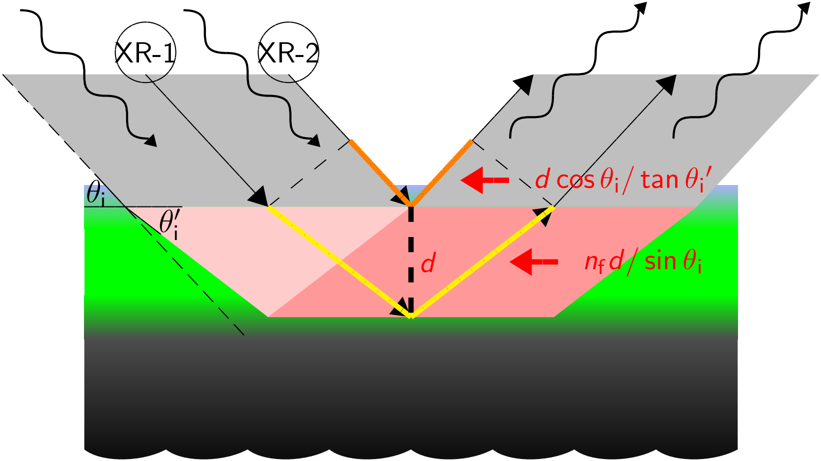


Loi de Snell-Descartes : $\cos\theta_i = n_f \cos\theta_i'$

Calculation of the refracted angle

$$\cos\theta_i = n_f \cos\theta_i{}'$$

$$\cos\theta_i{}' = \frac{\cos\theta_i}{n_f}$$

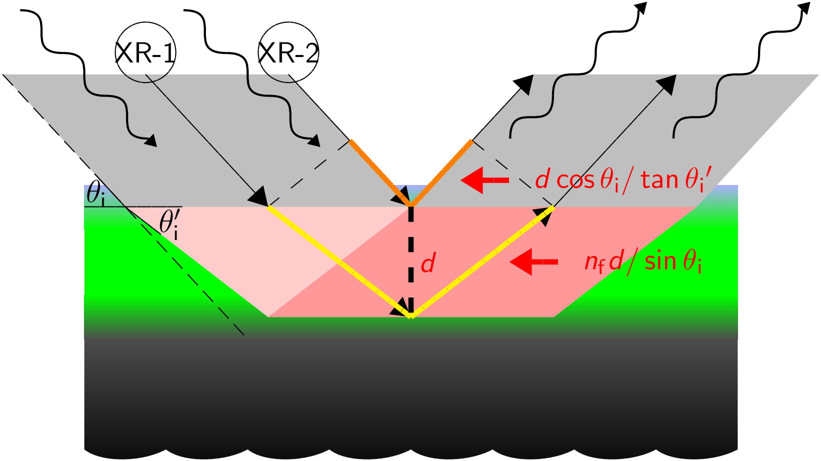
$$n_f = 1.0 - \frac{r_0\lambda^2}{4\pi^2}\rho_e$$

$$\cos\theta_i{}' > 1.00 \text{ if } \theta_i \text{ very small} \cdots$$

$$\boxed{\cos\theta_c = n_f = 1.0 - \frac{r_0\lambda^2}{4\pi^2}\rho_e}$$

Some critical angles ($\lambda = 1.5405$Å)

compound	Mass density (gcm^{-3})	electronic density ($eÅ^{-3}$)	critical angle ($^\circ$)
Si	2.333	0.701	0.224
Al_2O_3	3.998	1.181	0.287
Ge	5.893	1.588	0.333
ZnO	5.653	1.589	0.334
InN	6.921	1.811	0.356
Au	19.283	4.656	0.571



Snell-Descartes law : $\cos\theta_i = n_f \cos\theta_i'$

In order to have constructive interference the difference in optical path lengths should be :

$$m\lambda = 2d\left(\frac{n_{\mathrm{f}}}{\sin\theta'} - \frac{\cos\theta}{\tan\theta'}\right)$$

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The Bragg's law that follows is :

$$\sin^2\theta = \frac{m^2\lambda^2}{4d^2} + \sin^2\theta_\mathrm{c} = \frac{m^2\lambda^2}{4d^2} + \frac{\lambda^2 r_0 \rho_\mathrm{e}}{\pi}$$

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For $\theta \gg \theta_c$:

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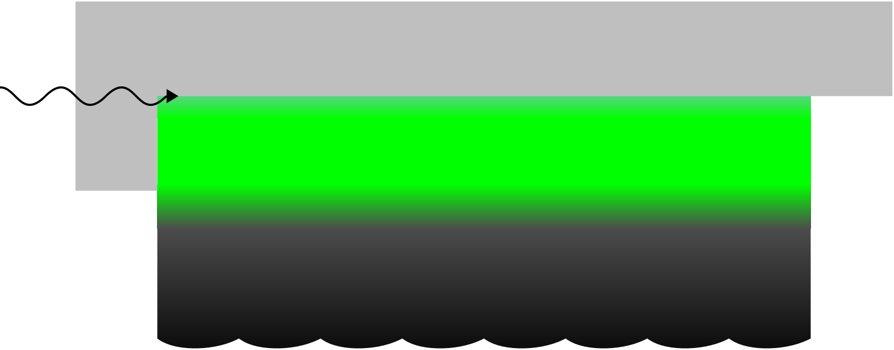
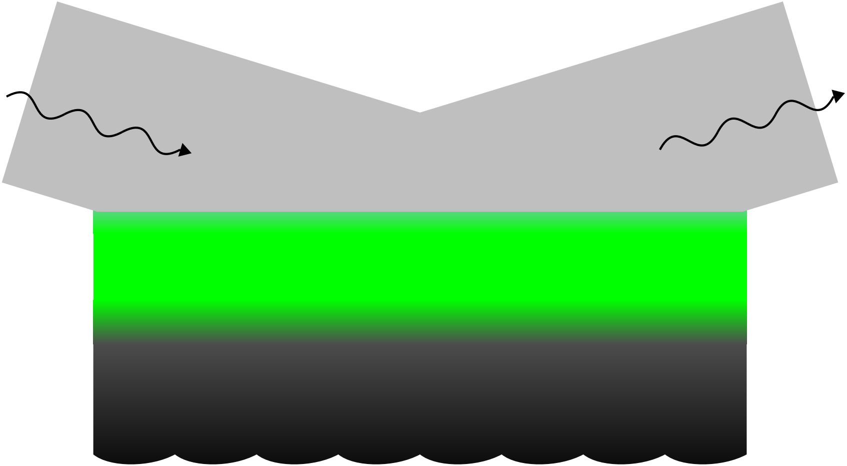
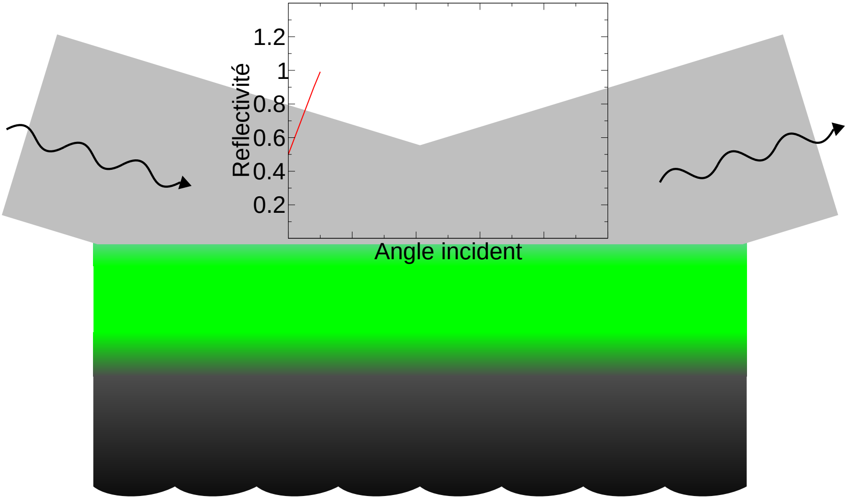
For $\theta \gg \theta_\mathrm{c}$:

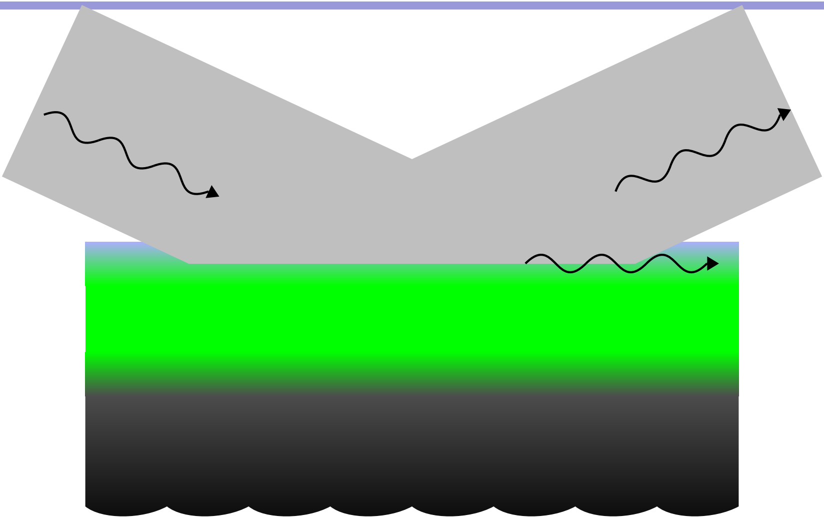
$$\sin^2\theta = \frac{m^2\lambda^2}{4d^2} + \cancel{\sin^2\theta_\mathrm{c}} = \frac{m^2\lambda^2}{4d^2} + \cancel{\frac{\lambda^2 r_0\rho_\mathrm{e}}{\pi}} \Longrightarrow \sin\theta = \frac{m\lambda}{2d} \Longrightarrow \boxed{m\lambda = 2d\sin\theta}$$

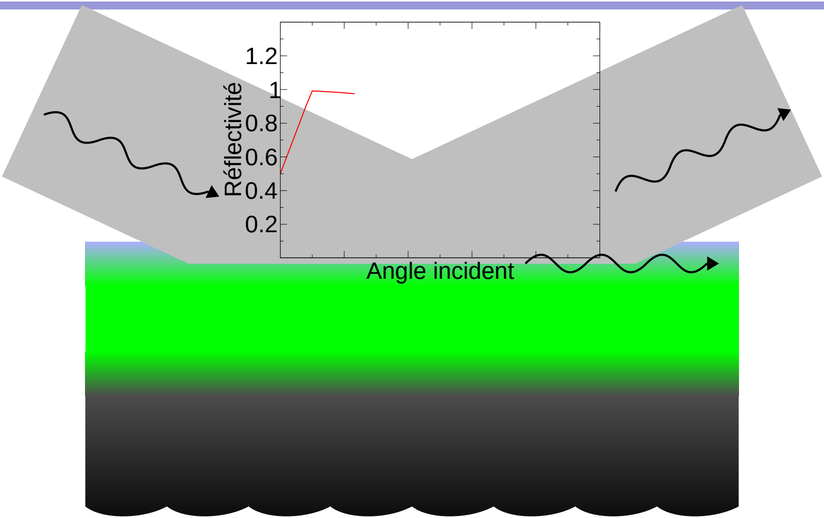
$$\Phi_{\mathrm{i}} = N_0 \qquad R = \frac{\Phi_{\mathrm{i}}}{\Phi_{\mathrm{e}}} = \frac{1}{2} \qquad \Phi_{\mathrm{e}} = N_0/2$$

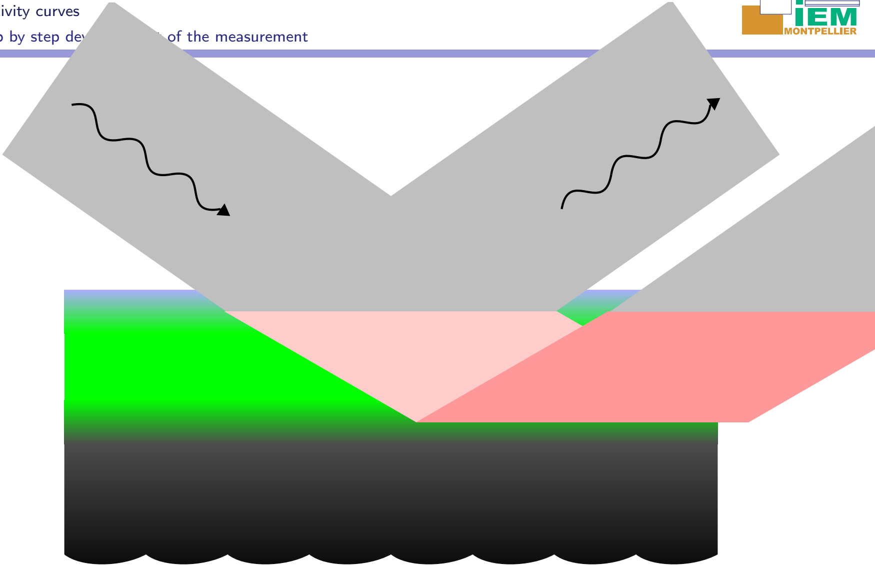


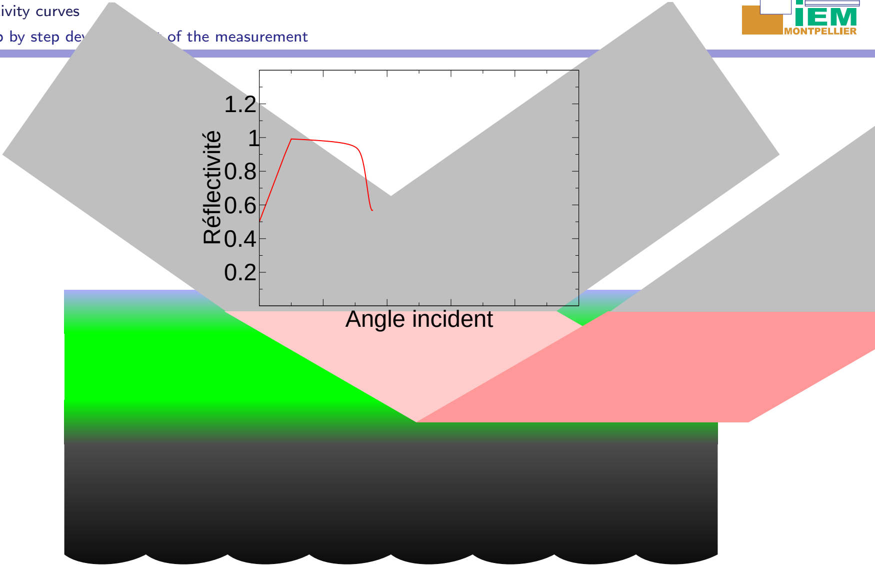


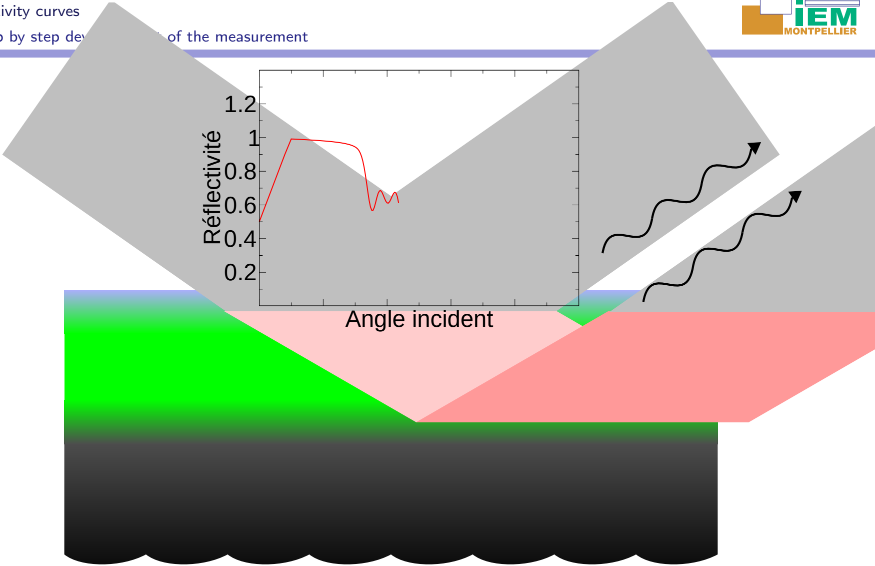

1.2
1
0.8
0.6
0.4
0.2
Reflectivité
Angle incident

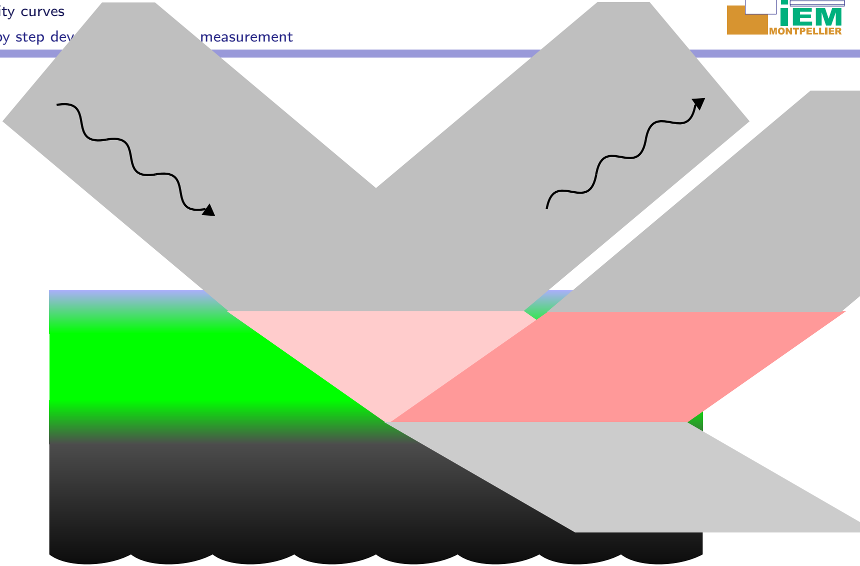


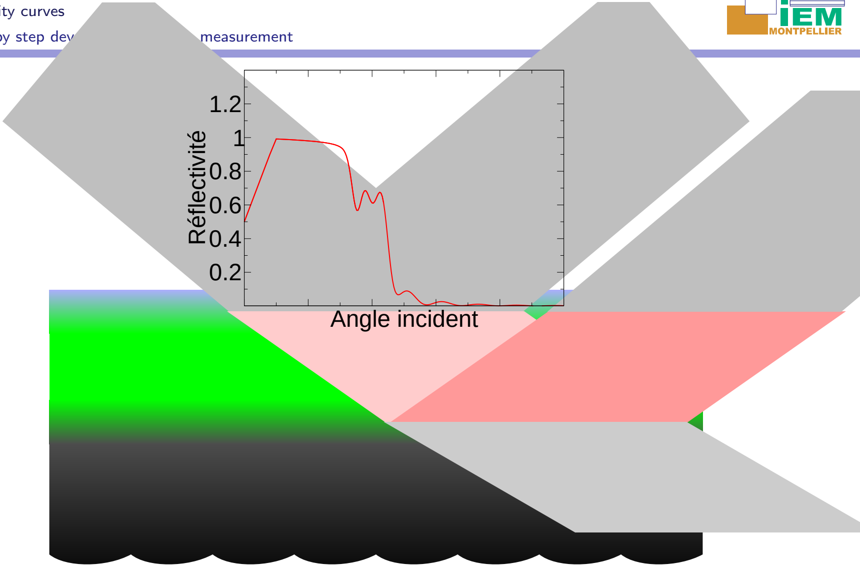

1.2
1
0.8
0.6
0.4
0.2
Réflectivité
Angle incident

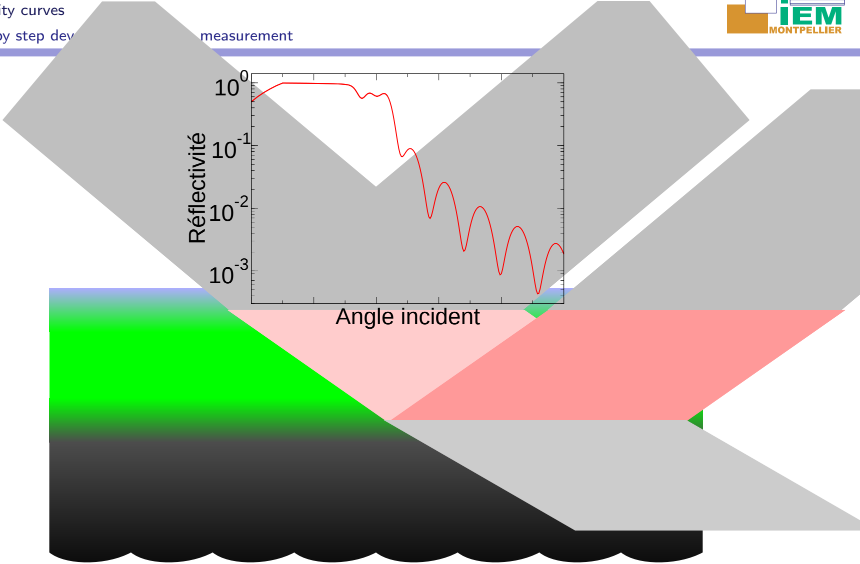


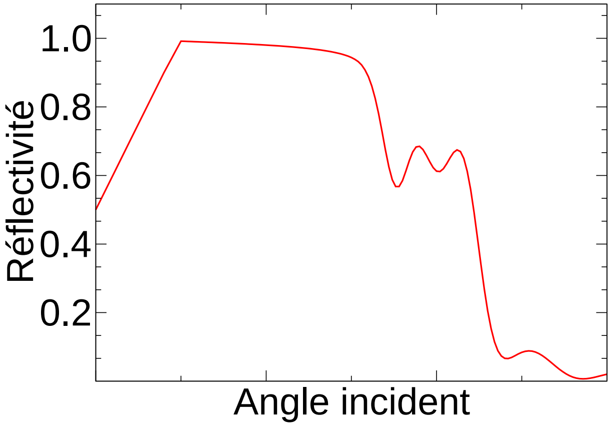

Réflectivité
1.2
1
0.8
0.6
0.4
0.2
Angle incident

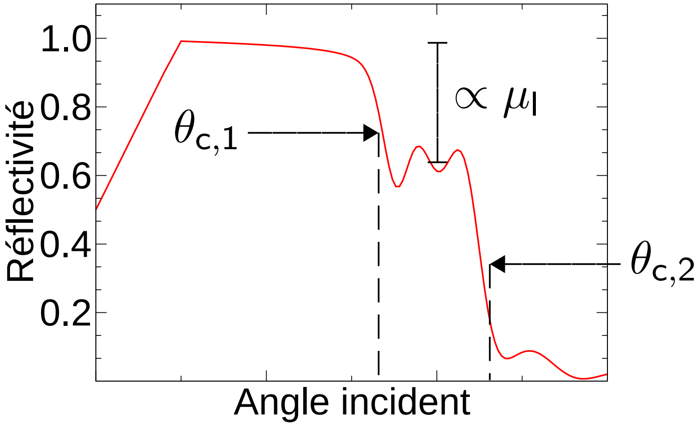

Réflectivité
1.2
1
0.8
0.6
0.4
0.2
Angle incident

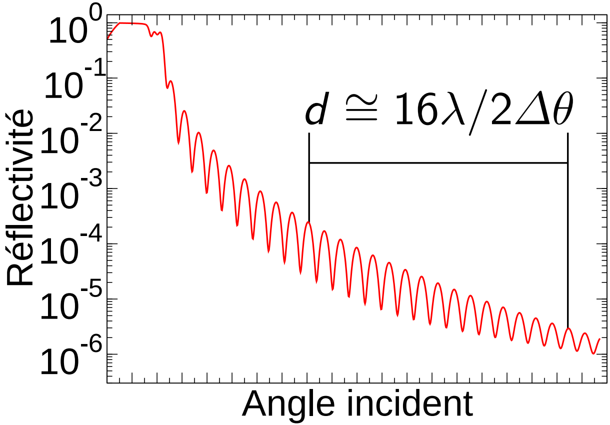


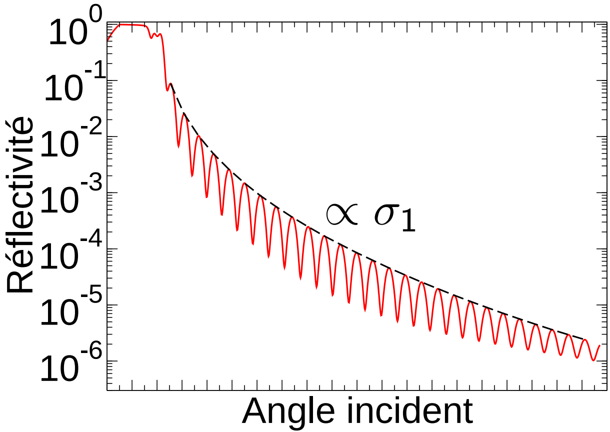

1.2
1
0.8
0.6
0.4
0.2
Réflectivité
Angle incident

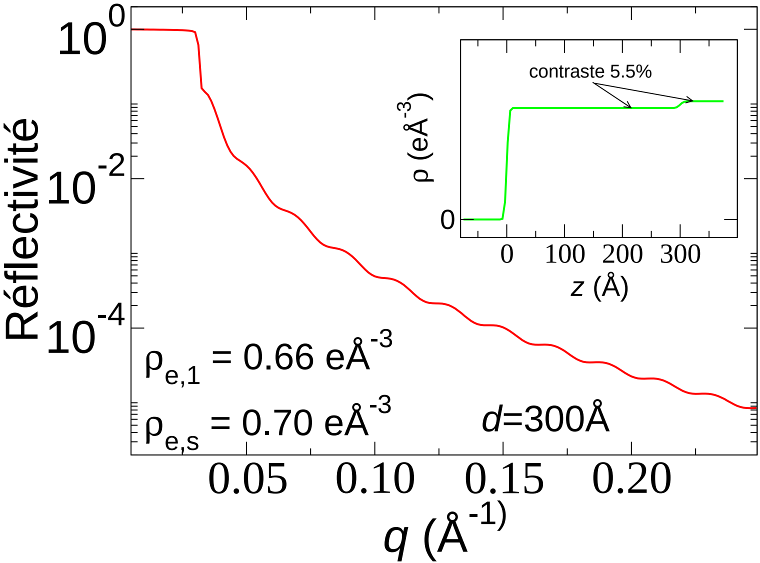

10^{0}
10^{-1}
10^{-2}
10^{-3}
Réflectivité
Angle incident

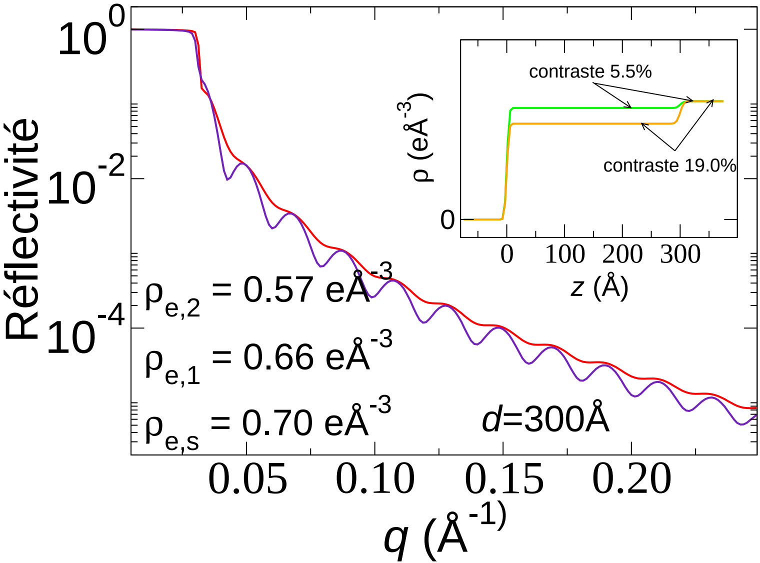

1.0
0.8
0.6
0.4
0.2
Réflectivité
Angle incident

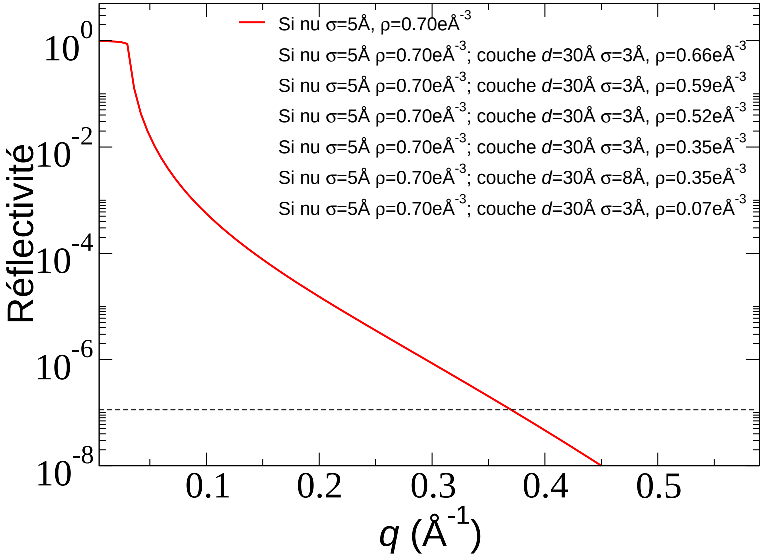

1.0
0.8
0.6
0.4
0.2
Réflectivité
Angle incident
$\theta_{c,1}$
$\theta_{c,2}$
$\propto \mu_l$

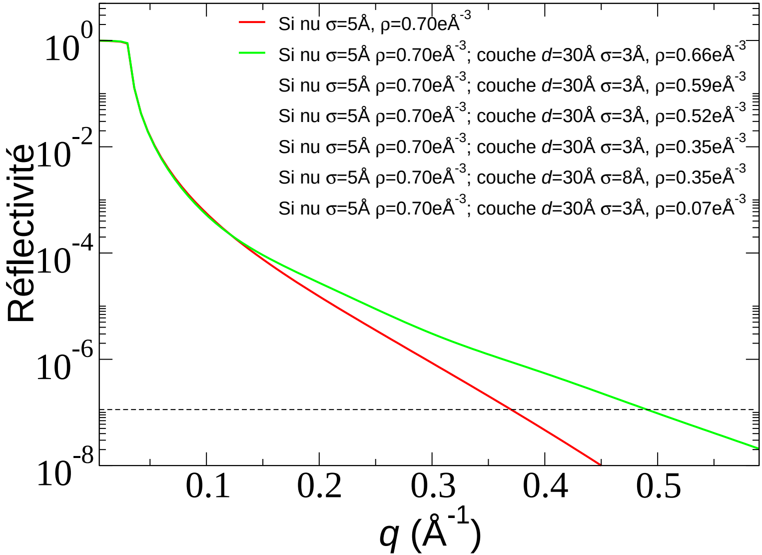

Réflectivité
10^0
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
$d \cong 16\lambda/2\Delta\theta$
Angle incident


Réflectivité
10^0
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
$\propto \sigma_1$
Angle incident


Réflectivité
10^0
10^{-2}
10^{-4}
0.05
0.10
0.15
0.20
q (Å^{-1})
$\rho_{e,1}$ = 0.66 eÅ^{-3}
$\rho_{e,s}$ = 0.70 eÅ^{-3}
d=300Å
contraste 5.5%
ρ (eÅ^{-3})
0
0
100
200
300
z (Å)


Réflectivité
10^0
10^{-2}
10^{-4}
0.05
0.10
0.15
0.20
q (Å^{-1})
$\rho_{e,2}$ = 0.57 eÅ^{-3}
$\rho_{e,1}$ = 0.66 eÅ^{-3}
$\rho_{e,s}$ = 0.70 eÅ^{-3}
d=300Å
contraste 5.5%
contraste 19.0%
ρ (eÅ^{-3})
0
0
100
200
300
z (Å)


Si nu σ=5Å, ρ=0.70eÅ-3
Si nu σ=5Å ρ=0.70eÅ-3; couche d=30Å σ=3Å, ρ=0.66eÅ-3
Si nu σ=5Å ρ=0.70eÅ-3; couche d=30Å σ=3Å, ρ=0.59eÅ-3
Si nu σ=5Å ρ=0.70eÅ-3; couche d=30Å σ=3Å, ρ=0.52eÅ-3
Si nu σ=5Å ρ=0.70eÅ-3; couche d=30Å σ=3Å, ρ=0.35eÅ-3
Si nu σ=5Å ρ=0.70eÅ-3; couche d=30Å σ=8Å, ρ=0.35eÅ-3
Si nu σ=5Å ρ=0.70eÅ-3; couche d=30Å σ=3Å, ρ=0.07eÅ-3
Réflectivité
10^0
10^-2
10^-4
10^-6
10^-8
0.1
0.2
0.3
0.4
0.5
q (Å-1)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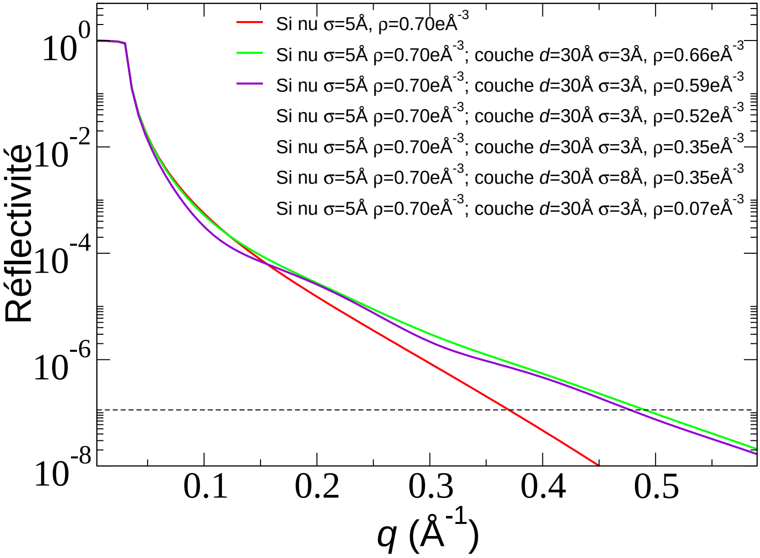
Réflectivité
10^0
10^-2
10^-4
10^-6
10^-8
0.1
0.2
0.3
0.4
0.5
q (Å-1)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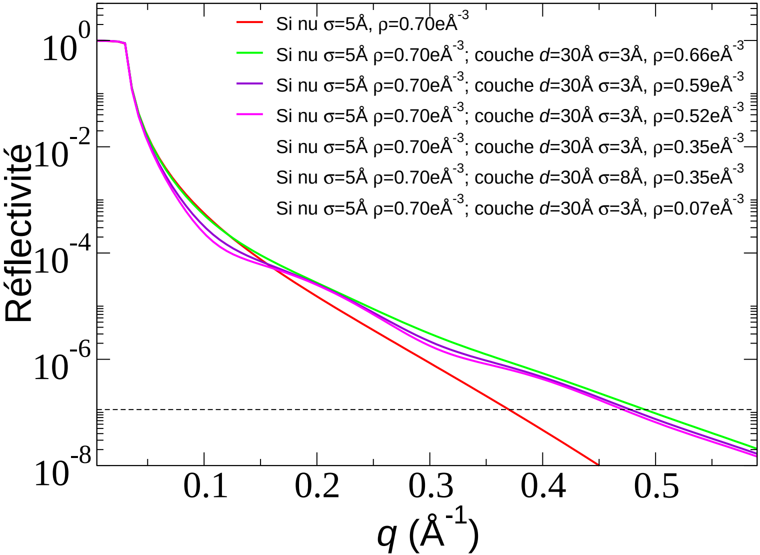
10^0
10^-2
10^-4
10^-6
10^-8
0.1
0.2
0.3
0.4
0.5
q (Å-1)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Si nu σ=5Å ρ=0.70eÅ-3; couche d=30Å σ=3Å, ρ=0.66eÅ-3
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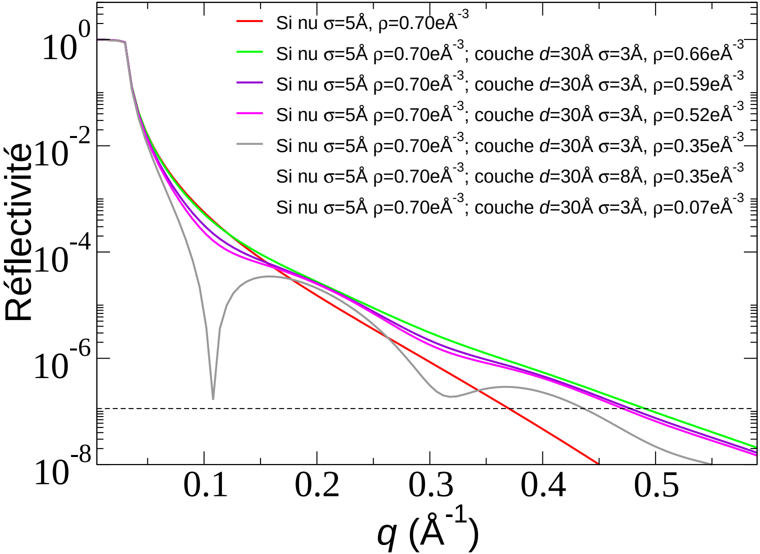
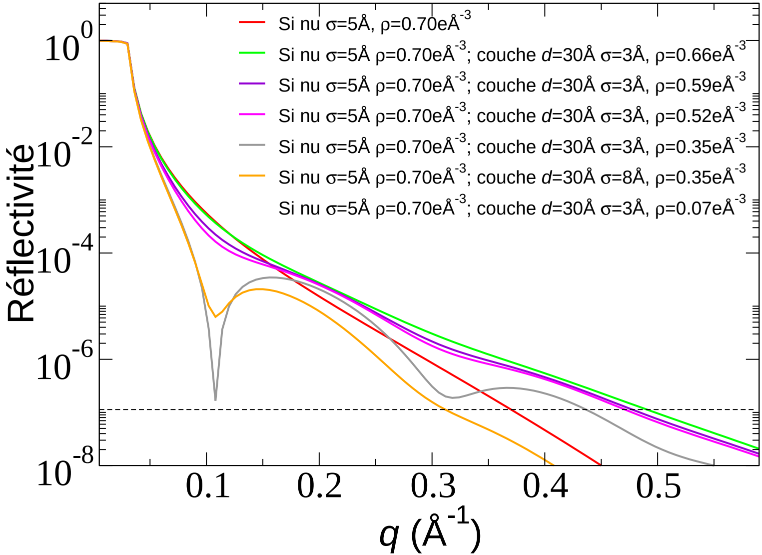
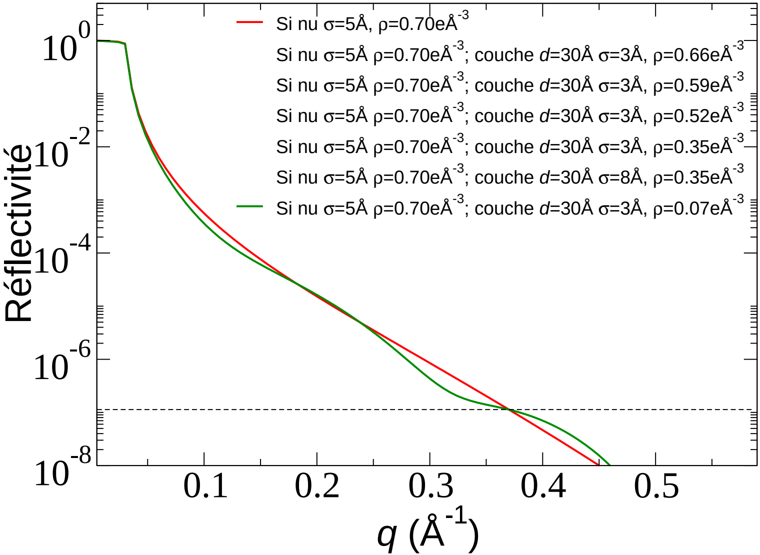
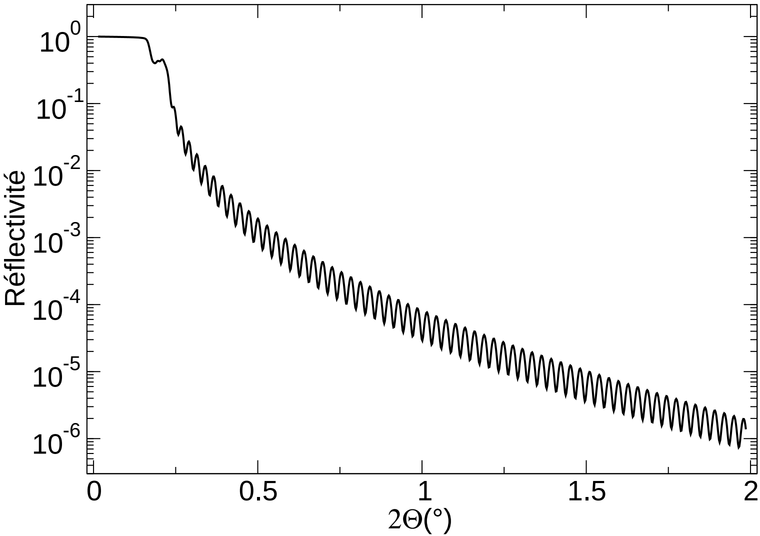
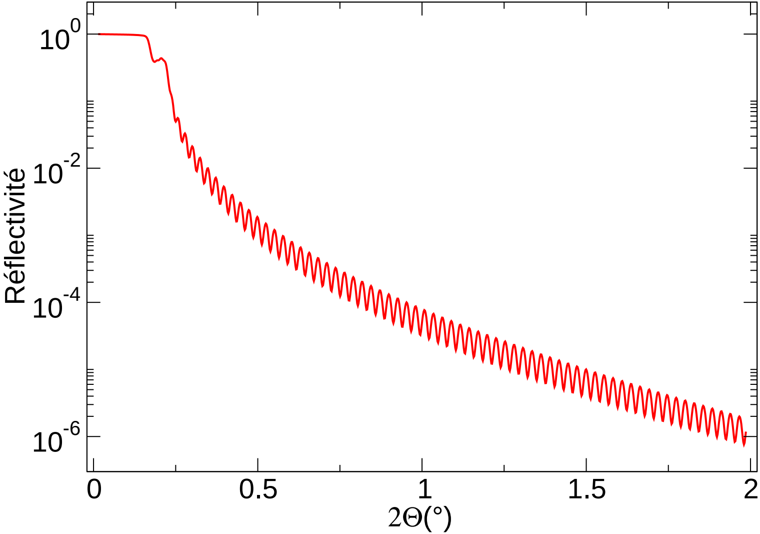
Si nu σ=5Å ρ=0.70eÅ-3; couche d=30Å σ=3Å, ρ=0.52eÅ-3
Si nu σ=5Å ρ=0.70eÅ-3; couche d=30Å σ=3Å, ρ=0.35eÅ-3
Si nu σ=5Å ρ=0.70eÅ-3; couche d=30Å σ=8Å, ρ=0.35eÅ-3
Si nu σ=5Å ρ=0.70eÅ-3; couche d=30Å σ=3Å, ρ=0.07eÅ-3
Réflectivité
10^0
10^-2
10^-4
10^-6
10^-8
0.1
0.2
0.3
0.4
0.5
q (Å-1)

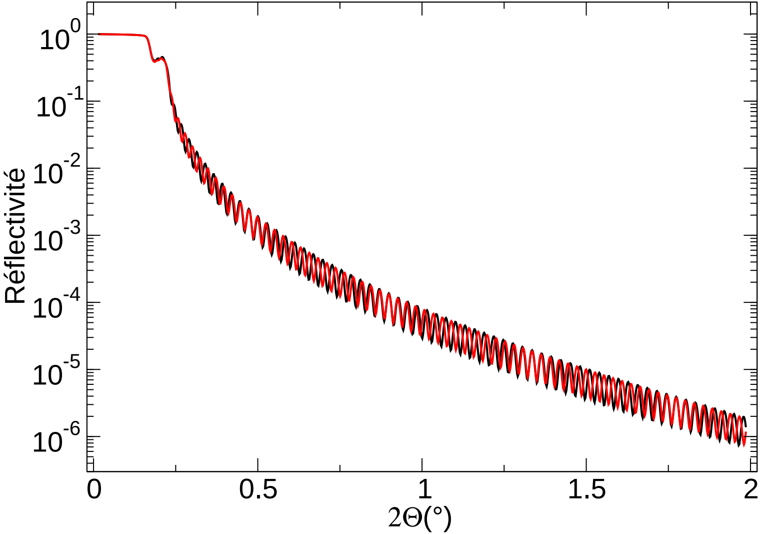

Si nu σ=5Å, ρ=0.70eÅ^-3
Si nu σ=5Å ρ=0.70eÅ^-3; couche d=30Å σ=3Å, ρ=0.66eÅ^-3
Si nu σ=5Å ρ=0.70eÅ^-3; couche d=30Å σ=3Å, ρ=0.59eÅ^-3
Si nu σ=5Å ρ=0.70eÅ^-3; couche d=30Å σ=3Å, ρ=0.52eÅ^-3
Si nu σ=5Å ρ=0.70eÅ^-3; couche d=30Å σ=3Å, ρ=0.35eÅ^-3
Si nu σ=5Å ρ=0.70eÅ^-3; couche d=30Å σ=8Å, ρ=0.35eÅ^-3
Si nu σ=5Å ρ=0.70eÅ^-3; couche d=30Å σ=3Å, ρ=0.07eÅ^-3
Réflectivité
10^0
10^-2
10^-4
10^-6
10^-8
0.1
0.2
0.3
0.4
0.5
q (Å^-1)

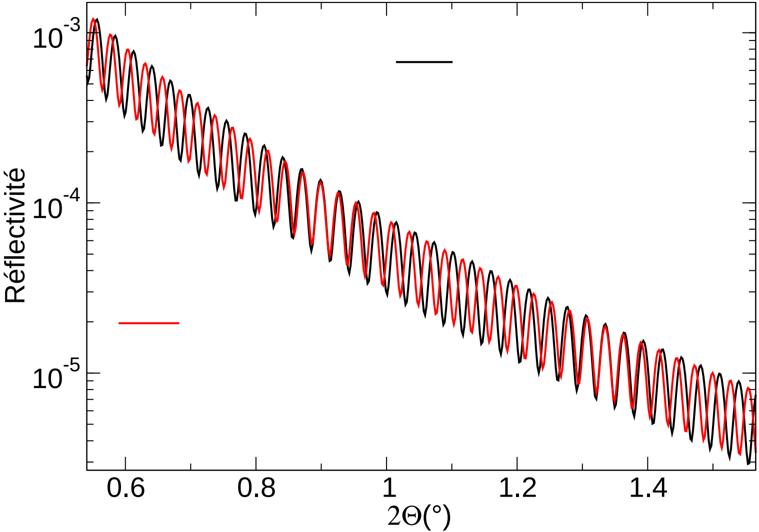

Si nu σ=5Å, ρ=0.70eÅ-3
Si nu σ=5Å ρ=0.70eÅ-3; couche d=30Å σ=3Å, ρ=0.66eÅ-3
Si nu σ=5Å ρ=0.70eÅ-3; couche d=30Å σ=3Å, ρ=0.59eÅ-3
Si nu σ=5Å ρ=0.70eÅ-3; couche d=30Å σ=3Å, ρ=0.52eÅ-3
Si nu σ=5Å ρ=0.70eÅ-3; couche d=30Å σ=3Å, ρ=0.35eÅ-3
Si nu σ=5Å ρ=0.70eÅ-3; couche d=30Å σ=8Å, ρ=0.35eÅ-3
Si nu σ=5Å ρ=0.70eÅ-3; couche d=30Å σ=3Å, ρ=0.07eÅ-3
Réflectivité
10^0
10^-2
10^-4
10^-6
10^-8
0.1
0.2
0.3
0.4
0.5
q (Å-1)

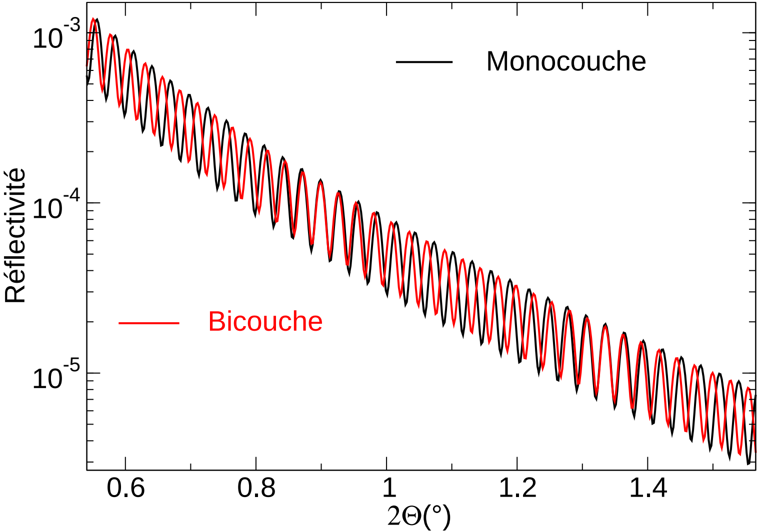

Si nu σ=5Å, ρ=0.70eÅ-3
Si nu σ=5Å ρ=0.70eÅ-3; couche d=30Å σ=3Å, ρ=0.66eÅ-3
Si nu σ=5Å ρ=0.70eÅ-3; couche d=30Å σ=3Å, ρ=0.59eÅ-3
Si nu σ=5Å ρ=0.70eÅ-3; couche d=30Å σ=3Å, ρ=0.52eÅ-3
Si nu σ=5Å ρ=0.70eÅ-3; couche d=30Å σ=3Å, ρ=0.35eÅ-3
Si nu σ=5Å ρ=0.70eÅ-3; couche d=30Å σ=8Å, ρ=0.35eÅ-3
Si nu σ=5Å ρ=0.70eÅ-3; couche d=30Å σ=3Å, ρ=0.07eÅ-3
Réflectivité
10^0
10^-2
10^-4
10^-6
10^-8
0.1
0.2
0.3
0.4
0.5
q (Å-1)

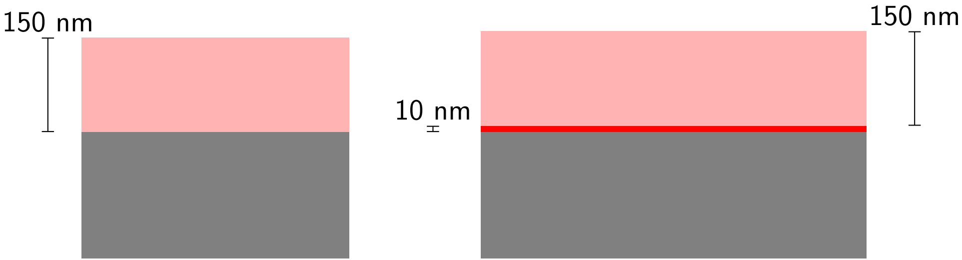

Réflectivité
10^{0}
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
0
0.5
1
1.5
2
$2\Theta(°)$


Réflectivité
10^0
10^{-2}
10^{-4}
10^{-6}
0
0.5
1
1.5
2
2Θ(°)


Réflectivité
10^{0}
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
0
0.5
1
1.5
2
2Θ(°)


Réflectivité
10^{-3}
10^{-4}
10^{-5}
0.6
0.8
1
1.2
1.4
2Θ(°)


Monocouche
Bicouche
Réflectivité
10^{-3}
10^{-4}
10^{-5}
0.6
0.8
1
1.2
1.4
$2\Theta(°)$



Single layer

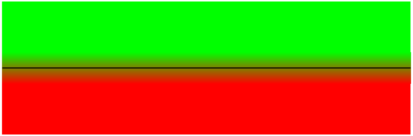
- $\rho_m = 1.36$ gcm^{-3}
- $d = 150$ nm
- $\sigma_1 = 0.5$ nm ; $\sigma_2 = 0.3$ nm
- substrat silicium

Bilayer

- $\rho_{m,1} = 1.36$ gcm^{-3} ; $\rho_{m,2} = 1.80$ gcm^{-3}
- $d_1 = 150$ nm ; $d_2 = 10$ nm
- $\sigma_1 = 0.5$ nm ; $\sigma_2 = 0.4$ nm ; $\sigma_3 = 0.3$ nm
- Silicon substrate

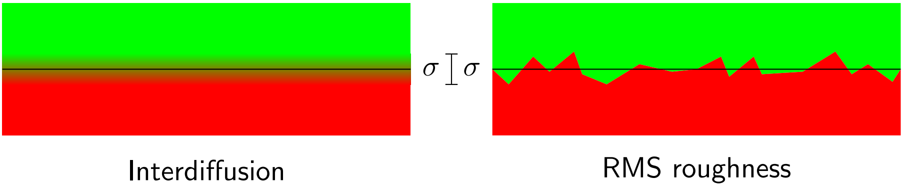
- Sample size : 20 mm x 20 mm
- Sample sould be 'flat' on a macroscopic scale
- A lab diffractometer with point detector is usually sufficient
- Multi-interval measurement with variable step and counting time recommended
- Thin films need not to be crystalline
- Time of the measurement : 5 min $< t_{\text{measurement}} <$ 24h
- Analysis time : 5 min $< t_{\text{analysis}} <$ 1 week

- thickness between 2 and 450 nm
- density contrast larger than 3%
- roughness lower than 4 nm
- layer should be 'homogeneous'
- difficult (but not impossible) to make difference between 'interdiffusion' and 'true roughness'



Interdiffusion

- thickness between 2 and 450 nm
- density contrast larger than 3%
- roughness lower than 4 nm
- layer should be 'homogeneous'
- difficult (but not impossible) to make difference between 'interdiffusion' and 'true roughness'



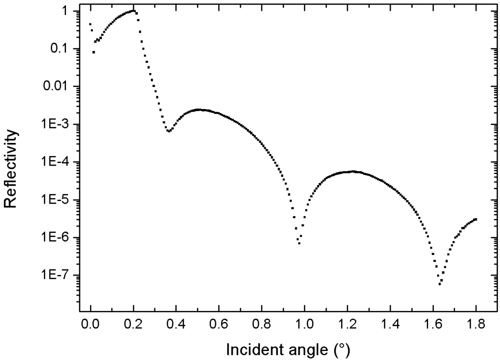
$$\boxed{\rho_{\mathrm{e}} = N_{\mathrm{A}}\rho_{\mathrm{m}}\frac{\sum c_{\mathrm{j}} Z_{\mathrm{j}}}{\sum c_{\mathrm{j}} A_{\mathrm{j}}}}$$

$$\boxed{\rho_e = N_A \rho_m \frac{\sum c_j Z_j}{\sum c_j A_j}}$$

Pour $2 < Z < 18 \Rightarrow A_j \approx 2Z_j$
et par conséquent :

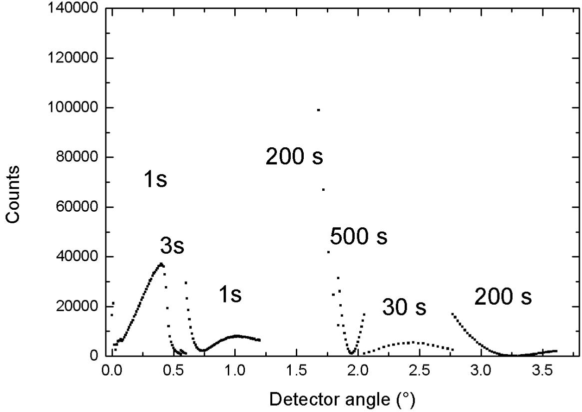
$$\boxed{\frac{2\rho_e}{N_A} \approx \rho_m}$$

A typical measurement of an organic layer of 68 Å



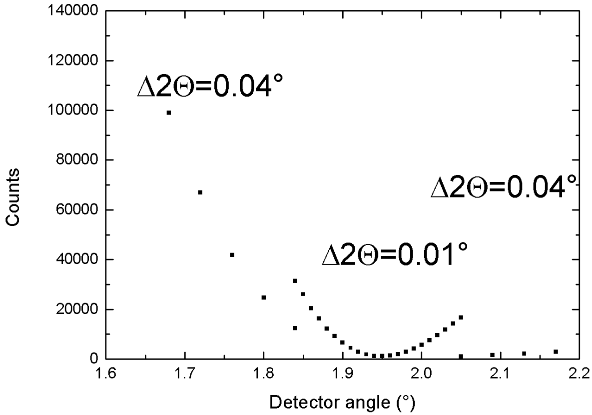
It concerns a measurement for which the data are 'reduced'

Raw data of the preceding curve



Counting time for the different intervals

Raw data of the preceding curve



Differents steps for different intervals

Some basic rules

Because of its large dynamic intensity range (6-7 orders of magnitude) a reflectometry measurement is often multi-interval. For each interval one defines a counting time and optimal step size.

Step size and counting time - I

- steps
  - determine the width Δ of a typical fringe
  - the optimal step size is given by $\Delta(2\Theta) \approx \Delta/10$
  - you could take a smaller step size around the critical angle and close to the minima of very large fringes

Some basic rules

Because of its large dynamic intensity range (6-7 orders of magnitude) a reflectometry measurement is often multi-interval. For each interval one defines a counting time and optimal step size.

Step size and counting time - II

- counting time
  - standard deviation of the counting of N photons (Poisson statistics) : $\sqrt{N}$
  - relative error σ for 1000 photons : $\frac{\sqrt{N}}{N} \approx 0.03$
  - for each measurement point $>$ 1000 counts $\rightarrow$ $\sigma < 0.03$ everywhere
  - example (pre-measurement) : $\mathrm{I}(2\theta) = 50$ cps $\rightarrow T = 20$ s