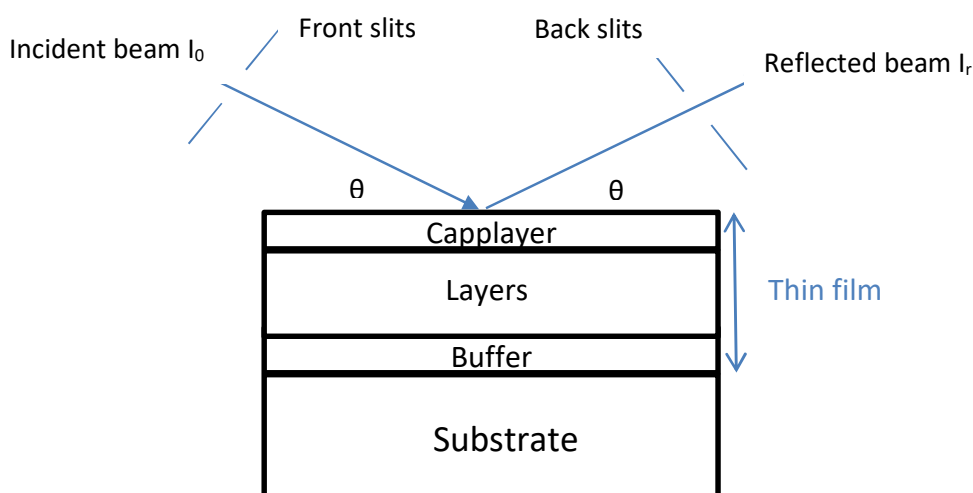


REFLEX : a program for X-ray reflectivity data analysis

Vignaud, G., & Gibaud, A. (2019). REFLEX: a program for the analysis of specular X-ray and neutron reflectivity data. *Journal of Applied Crystallography*, 52(1), 201-213.

In a typical specular x-ray reflectivity experiment, a collimated beam is impinging on the surface of a flat sample at an 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.



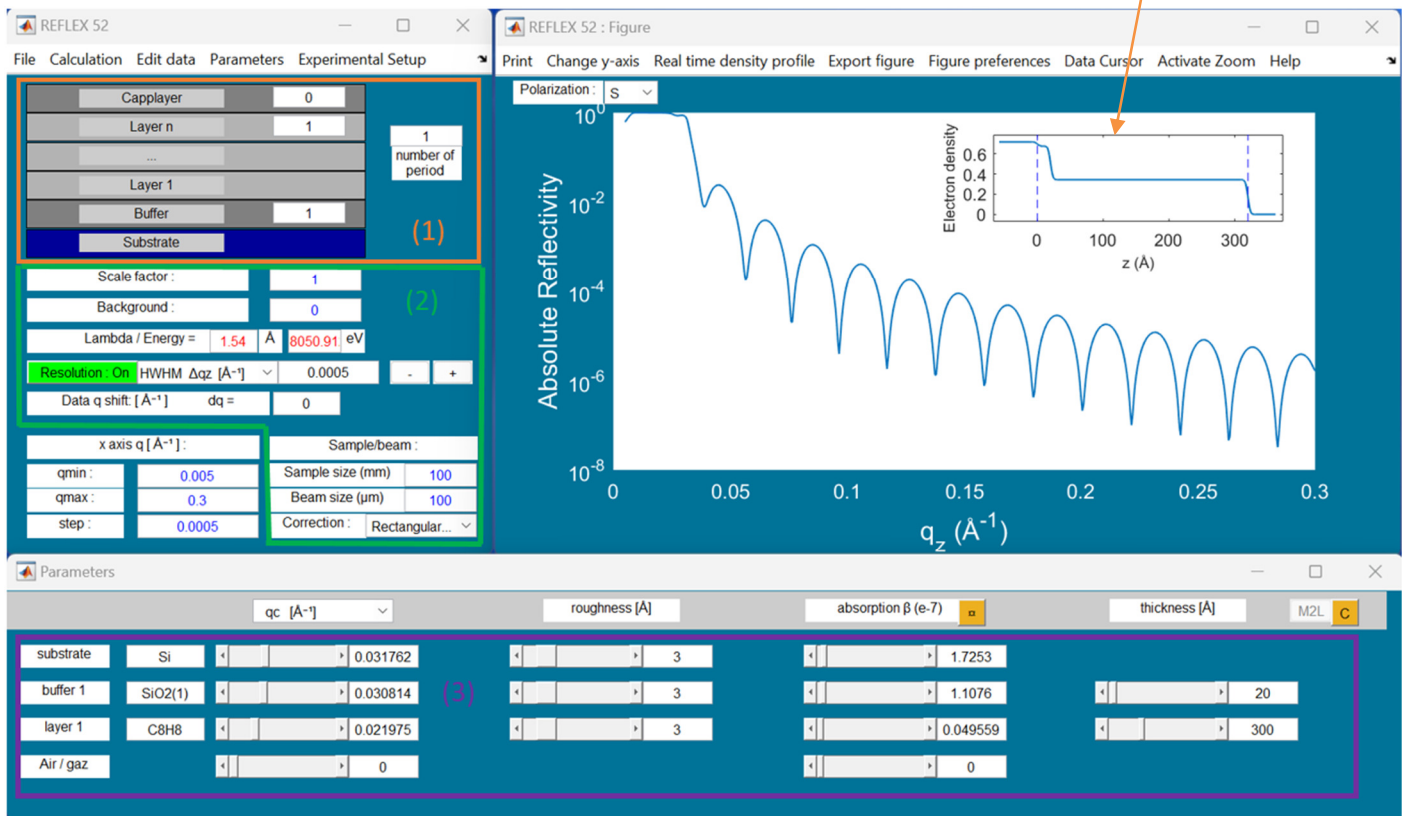
Specular reflectivity from a stratified medium

REFLEX uses a slab-model approach with the Abeles matrix method taking into account the interfacial roughnesses of each layer together with their respective thickness and electron density [1]. The calculus for the specular reflection of neutrons is limited to non-polarized reflectivity.

REFLEX can be working as an executable file under windows. When running the program, three windows will be displayed on the screen. The top right window shows the measured and calculated reflectivity, the top left window provides essential information about the sample itself together with information about the energy of incident radiation and instrumental parameters. Finally the bottom window depends on the parameters put in the top left window and is basically providing information about the slabs constituting the stacking on the substrate. Note that the sequence always starts with the substrate and ends up with air or a fluid in contact with the sample.

We first start with the explanation of the content of each window starting with the one in the top left window.

The density profile can be moved with the mouse



TOP LEFT WINDOW:

In this window there are two areas that are labelled (1) and (2). Let us first start with the information contained in area (1)

(1): Modeling the sample structure:

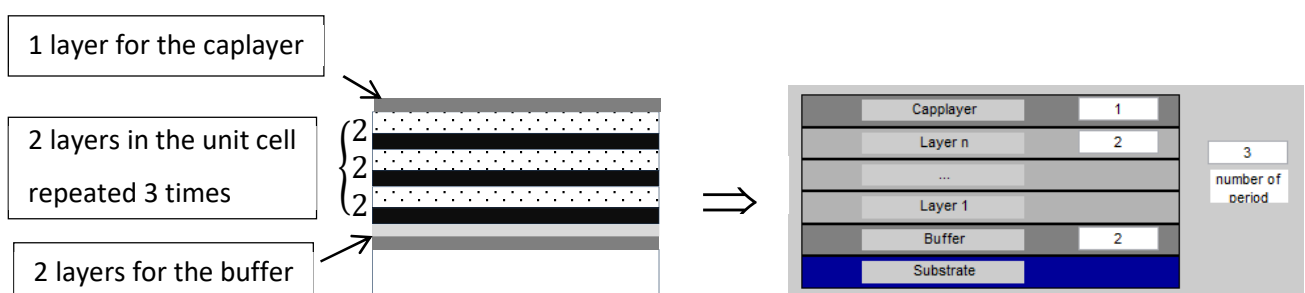
In a general case, i.e. for a multilayer stacking, four parameters can be provided in the labelled 1 part of the left box on the above image. Starting from the top:

- The number of "Cap layers" is the number of layers in contact with the fluid (air for example)
- The number displayed in the field "Layer n" is the number of layers that are repeated as a typical motif or unit cell inside the multilayer (for instance if $n=2$ we have a bilayer).
- 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 (for instance 10 will mean 10 repetitions of n layers).
- 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.

In order to show how to use this window we provide in the following two examples

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



Example n°2: a single layer on a substrate

For just a single layer on substrate, the table below gives all the possibilities you can enter:

| Capplayer | Layer n | Buffer | Number of period |
|-----------|---------|--------|------------------|
| 1 | 0 | 0 | 1 |
| 0 | 1 | 0 | 1 |
| 0 | 0 | 1 | 1 |

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

We now describe the content of area labelled (2).

(2): Parameters in a relation to the measurement:

In the top left window frame, you can change:

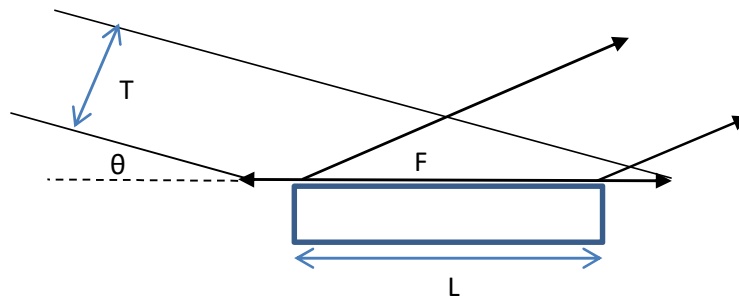
- **The scale factor:** This parameter allows adjusting the normalization of the data. To extract the normalized reflectivity from the data, usually the reflected intensity is divided by the intensity of the direct beam. The intensity of the direct beam is obtained by scanning the detector into the direct beam after having carefully attenuated the direct beam to avoid detector saturation. The direct beam depends of the experimental setup (front slit, back slit,...). Due to different causes (bending of the sample, divergence of the beam, ?...) the normalized data may need to be corrected by setting the scale factor. However we recommend to maintain it to 1 unless you know the reason for which it differs from unity.
- **The background:** The background adds a constant value at all q_z values. The background can be estimated from an off specular reflectivity measurement.
- **Lambda/Energy:** here is the wavelength (or the energy) of the incident beam in angstrom (or in electron volt)
- **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:

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

where w is the HWHM of the direct through beam. The lower is this value the better the resolution giving rise to a better estimation of some critical features like the Kiessig fringes minima or the critical angle. Please also note that *Reflex* allows to choose a Lorentzian profile or to download the measured direct beam in order to take in account an eventual asymmetry of the beam (to download the direct beam, intensity as a function of 2θ is expected). Conventional X-ray optics use narrow slits to collimate the incident X-ray beam. The divergences of the incident beam $\Delta\alpha$ and the reflected beam $\Delta\beta$ need to be small enough to precisely define the angular width of the direct beam, $w = \sqrt{\Delta\alpha^2 + \Delta\beta^2}$. For more information consult the paper by Gibaud et al [2].

As the flux of neutron beams is quite low compared to the one of x-rays, the neutron reflectivity measurements are not made with a constant resolution in space but with $\frac{\Delta q_z}{q_z} = cst$ enabling a constant footprint. The instrumental resolution for neutrons is implemented such as aforementioned in *Reflex*.

- **Data q shift:** this allows correcting a possible misalignment of the zero of the detector. In such a case the scattering angle set to θ is a little bit shifted and becomes $\theta + \Delta\theta$. Usually, you should not have to use this parameter.
- **Sample/beam:** These parameters provide information about the geometry of the sample and of the incident beam. As XRR measurements usually start below the critical angle of external reflection, the footprint of the beam (F) on the sample is frequently larger than the length (L) of the sample along the direction of the incident beam. As a consequence, even below the critical angle for external reflection, only a part of the incident intensity is totally reflected by the sample. The reflectivity is thus less than 1. It is straightforward to show that if the direct beam makes an incident angle θ with the surface of the sample and has a thickness T (which depends on the aperture of the front slits) then the footprint of the beam on the sample is: $F = T / \sin \theta$



When $F > L$, the corrected intensity is reduced to the following simple expression, which is linear in θ :

$$I_{\text{corr}} = I_{\text{calculated}} L/F = I_{\text{calculated}} L \theta / T$$

⇒ Data reduction procedures in X ray reflectivity necessitates to have a perfect knowledge of the sample and beam geometry.

In the next section, we describe how the parameters used to calculate XRR curves are put in the bottom window labelled "Parameters".

(3) Parameters used to calculate XRR curves:

The measured X-rays reflectivity depends on the electron density profile, perpendicular to the surface. Although the electron density profile is normally a continuously varying function, the interfacial structure can often be well approximated by a slab model in which layers of thickness, electron density and roughness are defined. Since neutron reflectometry is sensitive to contrast arising from different nuclei (as compared to electron density, which is measured in x-ray scattering), q_c is replaced by the neutron scattering length density (SLD) in *reflex* software. To take roughness into account in specular reflectivity, the reflection coefficient of a flat surface (Fresnel coefficient) is corrected by the Croce-Névot factor [3].

For example, below are the parameters used to calculate the reflectivity curve of a sample in ambient air, made of a polystyrene layer of 300 Å thick, deposited on silicon substrate. The surface roughness of silicon and of the polymer film are 3 Å and 5 Å respectively.

The screenshot shows the 'Parameters' window in the Reflex software. It contains several input fields and dropdown menus for defining material properties. Labels (a) through (e) are placed over the interface to highlight specific features:

- (a) Points to the material selection dropdown for the substrate, which currently shows 'Si'.
- (b) Points to the q_c [Å⁻¹] input field, which currently shows 0.031762.
- (c) Points to the absorption β (e⁻⁷) input field, which currently shows 1.7253.
- (d) Points to the absorption β (e⁻⁷) dropdown menu, which currently shows 'a'.
- (e) Points to the M2L button in the top right corner.

- (a) There are two different methods available to the user to designate materials in Reflex. In the first method, the user enters manually the value of the critical wave vector q_c in the 'popup' menu labelled (b) (or the scattering length density SLD for neutron) and can adjust the value by mean of slider button. In the second method, which is applicable only for energies between 10 eV and 30 keV for X-ray and soft X-ray reflectivity, the material is specified by its chemical formula and the optical constants are computed directly from the atomic scattering factors. A 'popup' menu labelled (a) is attached to each layer which enables the user to enter the chemical formula of the element which constitutes the selected layer. The corresponding q_c and β for X-rays are then automatically copied into the " q_c " and "absorption" fields of the selected layer. For example, if Si for silicon or H₂O for water are entered in the pop-up region in place of the question mark, the program will search in the database (provided by the Center for X-Ray Optics at Lawrence Berkeley National Laboratory (LBL) [4]) the anomalous atomic form factor (real f' and imaginary f'' part) of these elements at the working energy.

The Reflex optical-constants database contains data for over 110 materials. The optical-constants database is a directory of ASCII files, in which each optical-constants file contains three columns of optical data (Energy, f' , and f'') associated with a single material. In order to create an additional optical constant, a user need only fill in a menu (Parameters \Rightarrow **Database** \Rightarrow **Add/Replace material**) with its chemical formula and equally important its density.

The screenshot shows the 'Add a new compound in the Database' dialog box. It contains the following fields and buttons:

- A text area for the chemical formula, with the example 'Polystyrene' entered.
- A text field for the name of the compound (Silicon), with 'C8-H8' entered.
- A text field for the density of the compound in g/cm³ (Si 2.33 g/cm³), with '1.05' entered.
- An 'Add' button at the bottom.

Example which shows how to fill the fields for enter PS in the database

The program automatically extracts the anomalous atomic form factor (real f' and imaginary f'' part) from the database and creates a new ASCII file containing the optical constants for the desired material in accord with the existing format.

In the particular case of soft X-rays, it should be noted that δ and β issued from the database may not be right when the energy is closed to an X-ray absorption edge. Indeed δ and β can have abrupt variations (including negative values of δ) at the edge of an absorption threshold [5, 6]. However, since version 52, interpolation has been greatly improved near an absorption threshold (thanks to Jacopo Remondina).

Regarding the neutron reflectivity, there is also a database of the bound coherent scattering lengths extracted from the Atomic Institute for Austrian Universities [7]. The bound coherent neutron scattering lengths database is centralized in an Excel file which contains two columns: the first column, Z-Symb-A, gives the nuclides charge number Z, the element symbol and the mass number A. The second column gives the bound coherent scattering lengths. As an example, by entering 8-O-17 for the oxygen in the pop-up region in place of the question mark, Reflex automatically fills in the corresponding scattering length density (SLD).

- (b) and (c)** Here are the critical wave vector q_c (can choose between q_c , the Scattering Length Density (SLD) and the δ parameter) and the coefficient of absorption β of the layer. The index of refraction of a material can be obtained by application of the elastically bounded electron model. Such a model yields $n = 1 - \delta - i\beta$ in which δ and β are given by:

$$\delta = \frac{r_e \lambda^2}{2\pi} \rho_e = \frac{r_e \lambda^2}{2\pi} \mathcal{N} \rho \frac{\sum_p x_p (Z_p + f'_p)}{\sum_p x_p M_p}$$

$$\beta = \frac{r_e \lambda^2}{2\pi} \mathcal{N} \rho \frac{\sum_p x_p (f''_p)}{\sum_p x_p M_p}$$

Where $r_e = 2.810^{-15}\text{m}$ is the classical radius of the electron, λ is the wavelength, ρ_e the electron density, \mathcal{N} the Avogadro number, f' and f'' the real and imaginary part of the anomalous atomic form factor, M_p the molar mass of element p and Z_p its atomic number, ρ the mass density. The value of the parameter δ is ranging from 10^{-5} to 10^{-6} for X-rays with wavelength approximately 1 Å. The parameter β is related to the X-Rays absorption, expressed by the linear absorption coefficient μ as shown in the following formula:

$$\beta = \frac{\lambda \mu}{4\pi}$$

Unlike the parameter δ , the critical wave vector q_c does not depend on the wavelength, but is directly linked to the electron density in the material by:

$$q_c = \frac{4\pi}{\lambda} \sqrt{2\delta} = 3.75 \cdot 10^{-2} \sqrt{\rho_e} = 7.088 \sqrt{\rho}$$

where the units of the electron density is $\text{e}/\text{\AA}^3$.


SLD(\AA^{-2}) can be computed from material densities:


$$SLD = \frac{\rho \mathcal{N} r_e \sum_p x_p (Z_p + f'_p)}{\sum_p x_p M_p}$$

The neutron refractive index is very different from x-rays index and is determined from the Schrödinger equation to obtain: $n = 1 - \frac{\lambda^2}{2\pi} \rho b$ where ρ is the number of atoms per unit volume and b the scattering length.


$$SLD = \frac{\rho \mathcal{N} \sum_p x_p b_p}{\sum_p x_p M_p}$$

where b_p is the scattering length contributions from the atom (p).

(d) there is a button near the absorption . By pressing it, it becomes green and a link between $q_c/\Delta SLD$ and absorption is made via the mass density ρ . Idea proposed by A. Van der Lee arie.van-der-lee@umontpellier.fr which assumes that a variation of electron density is related to a variation of mass density and thus also leads to a variation of the absorption β

(e) There are two buttons in this space. The first, , converts a multi-layer pattern into a series of layers. For example, if in a multilayer, a pattern of 2 layers is repeated 8 times, pressing this button will result in 16 layers. **The advantage of this is that, once a multilayer has been fit, a new fit can be made, cancelling out the constraint of repeating the same pattern.** Moreover, with the ability to correlate layers (function described below), it is possible to fit these layers, keeping, for example, their electron densities equal and leaving their roughnesses or thicknesses... free to vary from one layer to another....



The second button, , is used to correlate/link parameters between different layers. This opens a new window in which several matrices can be used to correlate parameters.

| | | qc1 | qc2 | qc3 | qc4 | qc5 | | sig1 | sig2 | sig3 | sig4 | s | | abs1 | abs2 | abs3 | abs4 | a | | h1 | h2 | h3 | h4 | h5 | | | |
|--------|---------|------|-----|-----|-----|-----|---|------|-------|------|------|---|---|---------|-------|------|------|---|---|-----|-----|----|----|----|---|---|-----------|
| C8H8 | 0.02197 | qc1 | 1 | 0 | 0 | 0 | 0 | 3 | sig1 | 1 | 0 | 0 | 0 | 0.04955 | abs1 | 1 | 0 | 0 | 0 | 300 | h1 | 1 | 0 | 0 | 0 | 0 | Clear all |
| C5H8O2 | 0.02344 | qc2 | 0 | 1 | 0 | 0 | 0 | 3 | sig2 | 0 | 1 | 0 | 0 | 0.08780 | abs2 | 0 | 1 | 0 | 0 | 150 | h2 | 0 | 1 | 0 | 0 | 0 | Clear qc |
| C8H8 | 0.02197 | qc3 | 0 | 0 | 1 | 0 | 0 | 3 | sig3 | 0 | 0 | 1 | 0 | 0.04955 | abs3 | 0 | 0 | 1 | 0 | 300 | h3 | 0 | 0 | 1 | 0 | 0 | Clear sig |
| C5H8O2 | 0.02344 | qc4 | 0 | 0 | 0 | 1 | 0 | 3 | sig4 | 0 | 0 | 0 | 1 | 0.08780 | abs4 | 0 | 0 | 0 | 1 | 150 | h4 | 0 | 0 | 0 | 1 | 0 | Clear h |
| C8H8 | 0.02197 | qc5 | 0 | 0 | 0 | 0 | 1 | 3 | sig5 | 0 | 0 | 0 | 0 | 0.04955 | abs5 | 0 | 0 | 0 | 0 | 300 | h5 | 0 | 0 | 0 | 0 | 1 | Detect |
| C5H8O2 | 0.02344 | qc6 | 0 | 0 | 0 | 0 | 0 | 3 | sig6 | 0 | 0 | 0 | 0 | 0.08780 | abs6 | 0 | 0 | 0 | 0 | 150 | h6 | 0 | 0 | 0 | 0 | 0 | Validate |
| C8H8 | 0.02197 | qc7 | 0 | 0 | 0 | 0 | 0 | 3 | sig7 | 0 | 0 | 0 | 0 | 0.04955 | abs7 | 0 | 0 | 0 | 0 | 300 | h7 | 0 | 0 | 0 | 0 | 0 | |
| C5H8O2 | 0.02344 | qc8 | 0 | 0 | 0 | 0 | 0 | 3 | sig8 | 0 | 0 | 0 | 0 | 0.08780 | abs8 | 0 | 0 | 0 | 0 | 150 | h8 | 0 | 0 | 0 | 0 | 0 | |
| C8H8 | 0.02197 | qc9 | 0 | 0 | 0 | 0 | 0 | 3 | sig9 | 0 | 0 | 0 | 0 | 0.04955 | abs9 | 0 | 0 | 0 | 0 | 300 | h9 | 0 | 0 | 0 | 0 | 0 | Help |
| C5H8O2 | 0.02344 | qc10 | 0 | 0 | 0 | 0 | 0 | 3 | sig10 | 0 | 0 | 0 | 0 | 0.08780 | abs10 | 0 | 0 | 0 | 0 | 150 | h10 | 0 | 0 | 0 | 0 | 0 | |
| C8H8 | 0.02197 | qc11 | 0 | 0 | 0 | 0 | 0 | 3 | sig11 | 0 | 0 | 0 | 0 | 0.04955 | abs11 | 0 | 0 | 0 | 0 | 300 | h11 | 0 | 0 | 0 | 0 | 0 | |

If you want to link all the qc in the C8H8 layers, for example, in the qc1 column, you need to enter 1 in front of C8H8. This means that $qc1=qc3=qc5=qc7$... You can do the same with C5H8O2 in the qc2 column resulting in: $qc2=qc4=qc6=qc8$ As it can be tedious to fill in all these matrices, there's a **detect** button that automatically searches for identical layers (so it's best to correlate layers before fitting).

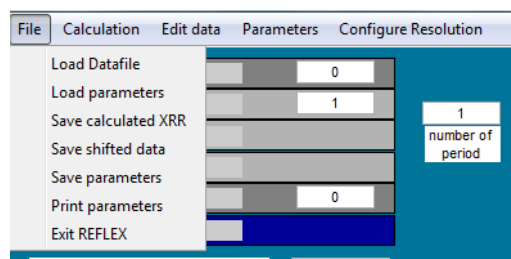
| | | | qc1 | qc2 | qc3 | qc4 | qc5 |
|--------|---------|------|-----|-----|-----|-----|-----|
| C8H8 | 0.02197 | qc1 | 1 | 0 | 0 | 0 | 0 |
| C5H8O2 | 0.02344 | qc2 | 0 | 1 | 0 | 0 | 0 |
| C8H8 | 0.02197 | qc3 | 1 | 0 | 1 | 0 | 0 |
| C5H8O2 | 0.02344 | qc4 | 0 | 1 | 0 | 1 | 0 |
| C8H8 | 0.02197 | qc5 | 1 | 0 | 0 | 0 | 1 |
| C5H8O2 | 0.02344 | qc6 | 0 | 1 | 0 | 0 | 0 |
| C8H8 | 0.02197 | qc7 | 1 | 0 | 0 | 0 | 0 |
| C5H8O2 | 0.02344 | qc8 | 0 | 1 | 0 | 0 | 0 |
| C8H8 | 0.02197 | qc9 | 1 | 0 | 0 | 0 | 0 |
| C5H8O2 | 0.02344 | qc10 | 0 | 1 | 0 | 0 | 0 |
| C8H8 | 0.02197 | qc11 | 1 | 0 | 0 | 0 | 0 |

Matrix automatically filled with "Detect"

Remarks:

- (1) Only the lower triangular part of each matrix can be filled (below the diagonal of 1).
- (2) The configuration of the matrix on qc generates the same matrix on absorption (the two are not independent).
- (3) If, for example, $qc3=qc1$, by putting 1 in column qc1 opposite row qc3, then qc3 cannot also be equal to qc2 by putting 1 in column qc2 opposite row qc3. You might as well put 1 in column qc1 opposite qc2 and qc3.

We now describe the menu bar "File":



Load Datafile: this menu loads the data. The data format has to be ASCII (text format). It consists of two columns: one for q_z or $\theta/2\theta$ and the other for the normalized intensity. The file extension is usually .dat



Avoid any duplication in the data if you want to fit them!

| q_z | R |
|----------------|----------------|
| 2.0000000e-002 | 8.8649878e-001 |
| 2.0500000e-002 | 9.3600872e-001 |
| 2.1000000e-002 | 9.3868109e-001 |
| 2.1500000e-002 | 9.3728660e-001 |
| 2.2000000e-002 | 9.3576110e-001 |
| 2.2500000e-002 | 9.3422799e-001 |
| 2.2000000e-002 | 9.3268845e-001 |
| 2.2500000e-002 | 9.3114222e-001 |
| 2.3000000e-002 | 9.2958904e-001 |
| 2.3500000e-002 | 9.2802867e-001 |

Duplication

Load parameters: the user can load all the saved parameters corresponding to a calculated curve with *Reflex*. The file extension is .par

Save calculated XRR: allows saving the calculated curve. The saved file contains two columns one for q_z and the other for the calculated intensity.

Save shifted data: when the measured data have an offset due to a misalignment of the zero of the detector, it is possible to correct it with the menu **Data q shift**. Then the corrected data can be saved with this menu.

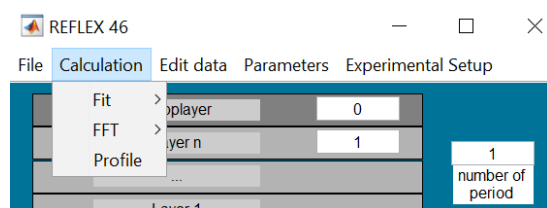
Save parameters: This shortcut menu enables you to save all the parameters (density, roughness, resolution, background, scale factor, size of the sample...) in a file with extension .par and to reload the parameters in *Reflex* later.

Print parameter: allows printing the parameters in a text file

| RESUME du FIT : 17-Jan-2018 | | | | | |
|------------------------------------|--------|-------------|----------|------------|-----------|
| Nombre total de couches | : | 62 | | | |
| Nombre de couches du buffer | : | 1 | | | |
| Nombre de couches dans une periode | : | 2 | | | |
| Nombre de périodes | : | 30 | | | |
| Nombre de couches en surface | : | 1 | | | |
| | qc | Rho | rugosité | absorption | epaisseur |
| Subtrat | 0.0318 | 0.7193 | 3.0 | 1.73 | |
| Buffer1 | 0.0100 | 0.0711 | 2.0 | 0.92 | 15.0 |
| Couche1 | 0.0350 | 0.8710 | 2.0 | 0.09 | 50.0 |
| Couche2 | 0.0200 | 0.2844 | 2.0 | 0.05 | 100.0 |
| Caplayer1 | 0.0400 | 1.1376 | 1.0 | 1.00 | 10.0 |
| Air | 0.0000 | 0.0000 | 0.0 | 0.00 | 0.0 |
| | | | | | |
| Lambda | : | 1.540 | | | |
| Bruit de fond | : | 0 | | | |
| Coefficient de normalisation | : | 1.000 | | | |
| Résolution | : | 0.0005 | | | |
| Taille échantillon | : | 100.0 mm | | | |
| Taille faisceau | : | 100 μ m | | | |

Exit reflex: to quit *Reflex* software

Menu bar "Calculation":



Fit reflectivity: opens a calculation window to fit the data

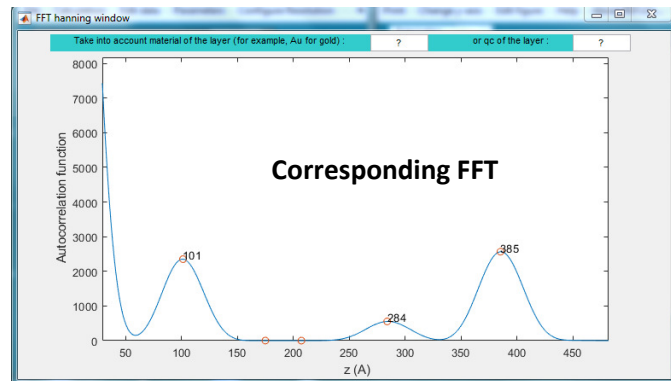
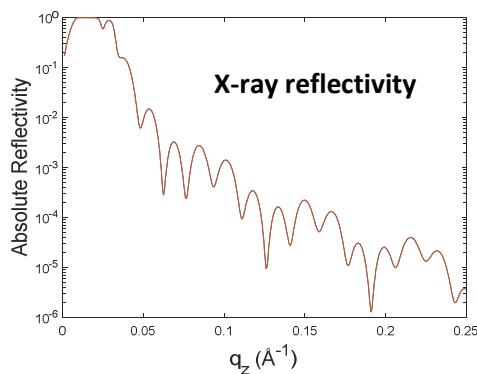


See below to have more details about the fitting process

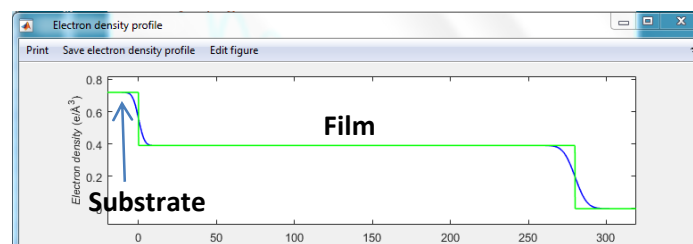
Fit reflectivity+autocorelation function (Patterson functions) [8]: as above but in addition to the reflectivity curve, the autocorrelation function is fitted. The simultaneous refinement of the reflectivity in real-space and reciprocal-space does not only improve the sensitivity to certain parameters but may also prevent the usually applied local

optimization techniques from getting stuck in local minima. As an example, polymer bilayers x-ray reflectivity measurements, with large q_z -range and high resolution, yield very accurate results of polymer–polymer interfaces if the FT method is used to analyze the data [9]. It can be applied to any reflectivity data from low-contrast layer systems.

FFT: gives the Fourier transform of the reflectivity curve normalized by the Fresnel reflectivity of the substrate. This data inversion gives the autocorrelation function of the first derivative of the electron density.

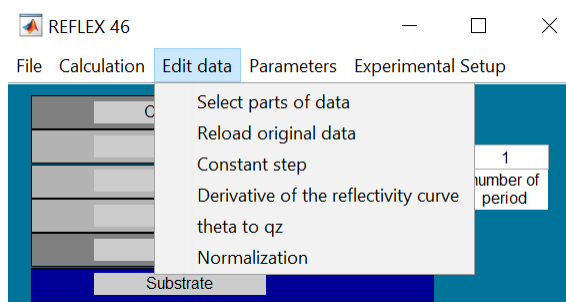


Profile: calculates the Electron density profile from the fit to the data. Note that the text (Film, Substrate,...) can be directly moved with the mouse.



Electron density profile of a PS thin film (28 nm) on a silicon substrate

Menu bar "Edit data":

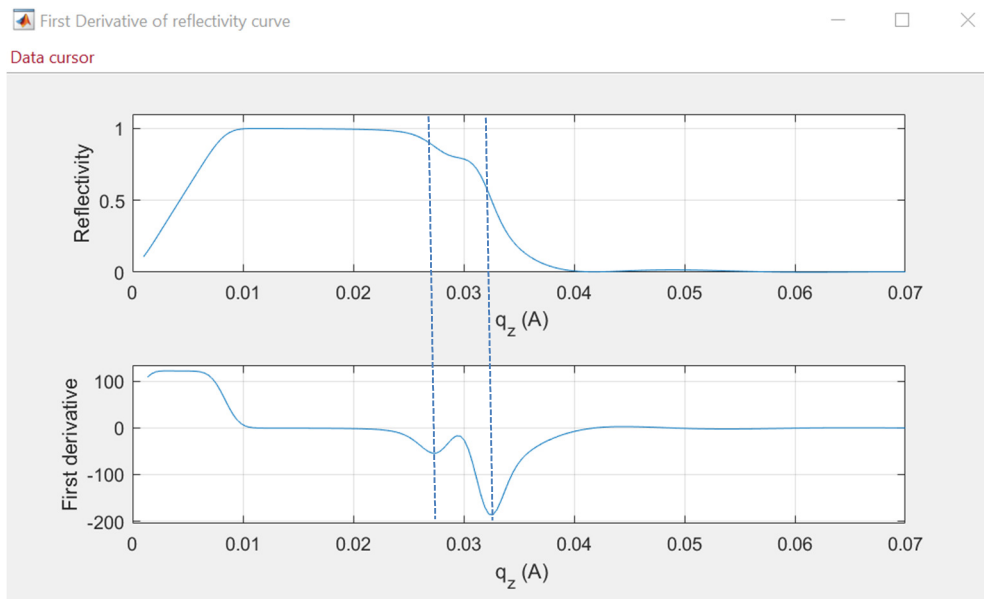


Select parts of data: the user can select manually and easily a part of the reflectivity curve.

Reload original data: Reload the original data (not modified).

Constant step: this shortcut menu is useful to calculate the data with a constant step. Indeed, to make the data adjustment, calculated curve takes the same step that the data. If the step is not constant, this presents a problem for the convolution of the calculated reflectivity curve with the resolution function. This is no longer useful on the latest versions of reflex.

Derivative of the reflex curve: this menu allows to derive the reflectivity curve to locate the position of the q_c .

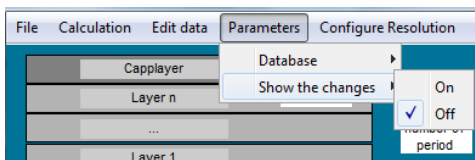


It is necessary to be careful because if the film is of a thickness lower than 100nm, the q_c determined in this way can be erroneous.

Theta to q_z : allows to convert the data measured in theta to q_z data; this last format is necessary in reflex.

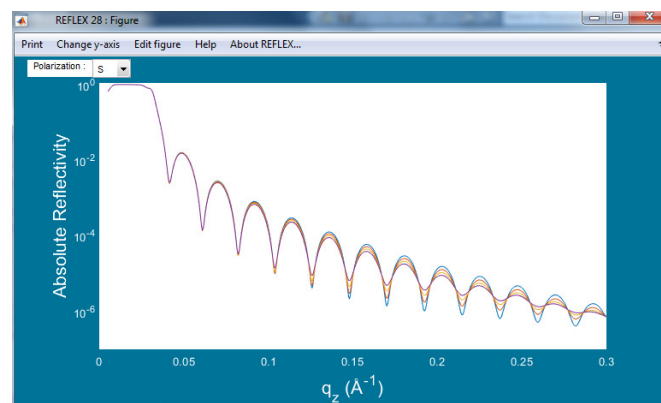
Normalization: to normalize the measured data by the intensity of the direct beam.

Menu bar "Parameters":

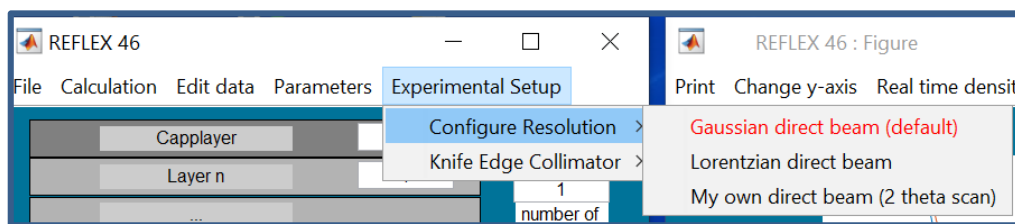


Database: allows to consult the compounds present in the database and to add new compounds.

Show the changes: when is **On**, it makes possible to follow the evolution of the calculated reflectivity curve when some parameters are modified.



Menu bar "Experimental Setup":



Configuration Resolution: the user can choose the kind of resolution applied to the calculated reflectivity curve.

Knife Edge Collimator: if the reflectivity measurements were made with a knife, this menu allows to correct the effect of the knife on the reflectivity curve. Knife-edge collimator (KEC) is used to reduce the influence of the finite sample size on the measured reflectivity and to obtain a proper area of total external reflection. The KEC consists of a "knife" that is approached to the surface of the sample up to a few μm when measuring at small angles.

Reflectivity analysis method:

A refinement procedure is then used to minimize the differences between the theoretical and measured reflectivity curves, by adjusting and determining the parameters that describe the studied sample. Please follow the steps below:

- 1- Load your data (**File \Rightarrow Load Datafile**). The data file must be a text format. It consists of two columns: one for q_z and the other for the normalized intensity. As the instrumental resolution is handled by convolving the theoretical reflectivity curve with a Gaussian, the step in q_z must be constant. If it is not the case, a menu (**Edit data \Rightarrow Constant step**) allows calculating the data with a constant step.
- 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 layers and enter the nature of the different materials if they exist in the database. Sometimes, even though you expect only one layer on a substrate, if its electron density is not homogenous, it is needed to model it with several layers of different electron density to correctly describe the evolution of the density. Note that the general procedure is to fit the data using the minimum number of layers required for a satisfactory fit (in order to limit the number of parameters and correlations between them).
- 4- Fill the parameters related to the size of the sample and the beam dimension in order to adjust the beginning of the reflectivity curve.
- 5- **Manual adjustment of parameters:** this step depends on which sample you wish to analyze. Before automatically performing a fit to the data, 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.

a) Reflection on a homogeneous material:

In the simplest case of a unique substrate, reflectivity curve is modelled by a minimum of three variables: q_c , absorption β and surface roughness σ . Normally starting values for q_c and β are given by the database.

Figure 1 shows the calculated reflectivity curves for a Si substrate with two different values of surface roughness. It can be seen that the reflectivity curve consists of two different regimes:

- $q_z < q_c$: because the refractive index of materials for X-rays is slightly less than 1, when q_z is less than q_c the total external reflection occurs and the normalized reflected intensity is equal to $R=1$ whatever the surface roughness.
- $q_z > q_c$: the incident beam is split into a reflected and refracted beam into the substrate leading to a strong drop of the total reflected intensity. For a flat surface (not rough, $\sigma = 0$), the reflectivity curve decays with a power law $1/q_z^4$. Roughness gives rise to diffuse scattering, resulting to a less intensity in the specular reflected beam. The reflect curve decreases more rapidly with a larger surface roughness ($\sigma = 5 \text{ \AA}$). In others words, the larger the roughness of a substrate, the faster the decay rate of X-ray reflectivity curve.

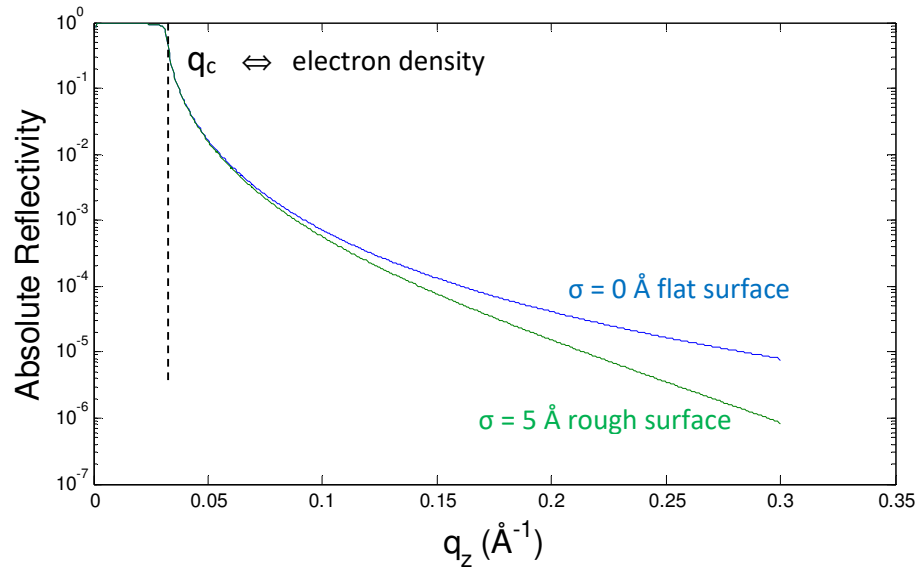


Figure 1

b) Reflection on a single layer on substrate:

If the sample is made of a single layer on a substrate: in addition to the parameters of the substrate, q_c , β , interfacial roughness and thickness of the layer are necessary. Figure 2 shows the calculated reflectivity of a PS thin film deposited onto a silicon substrate.

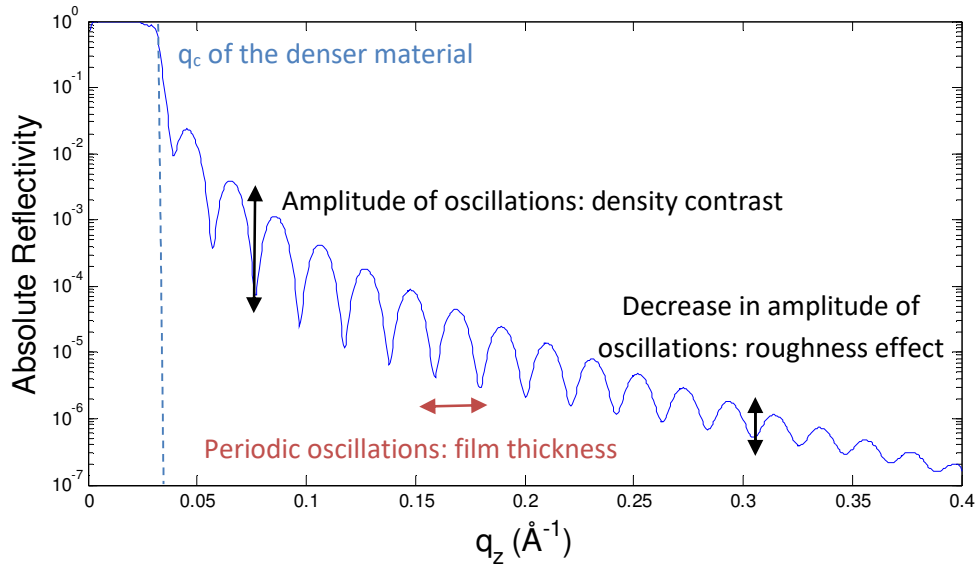


Figure 2

Periodic oscillations: Periodic oscillations in intensity labelled as Kiessig fringes related to the thickness of the thin layer appear in the reflectivity curve. For $q_z > q_c$, the x-ray beam penetrates inside the film. Reflection therefore occurs at the free surface and at PS/substrate interface of the film. The interferences between the rays reflected from the top and the bottom of the film surfaces result in interference fringes. The Kiessig fringes appear as a consequence of these interferences. A rough estimate of the thickness can be done from $h \approx 2\pi/\Delta q_z$ where Δq_z is the difference between $q_{z\min}$ of two consecutive minima in the reflectivity curve (at $q_z \gg q_c$).

The thickness of a thin film can be obtained with a pretty good precision by a Fourier transform of the reflectivity curve normalized by the Fresnel reflectivity of the substrate. This data inversion gives the autocorrelation function of the first derivative of the electron density (see Figure 3) allowing a quick indication (in angstrom) of the layer thicknesses present. A menu (**Calculation** \Rightarrow **FFT**) is available to perform this FFT. *Reflex* offers the possibility to choose a function (also known as an apodization function) to operate the FFT. “No window” means a rectangular window which involves simply truncating (sudden changes) the dataset before and after the window. This implies spectral leakage, i.e Fourier transform develops non-zero values at several frequencies other than the main frequency associated to the periodic oscillations of the reflectivity curve. Other windows like Hann, Blackman windows, ... are available to moderate these sudden changes because discontinuities have undesirable effects on the discrete Fourier transform (DFT) and/or the algorithms that produce samples of the DFT. Please see documentation about Digital Signal Processing/Windowing [10] to have more details.

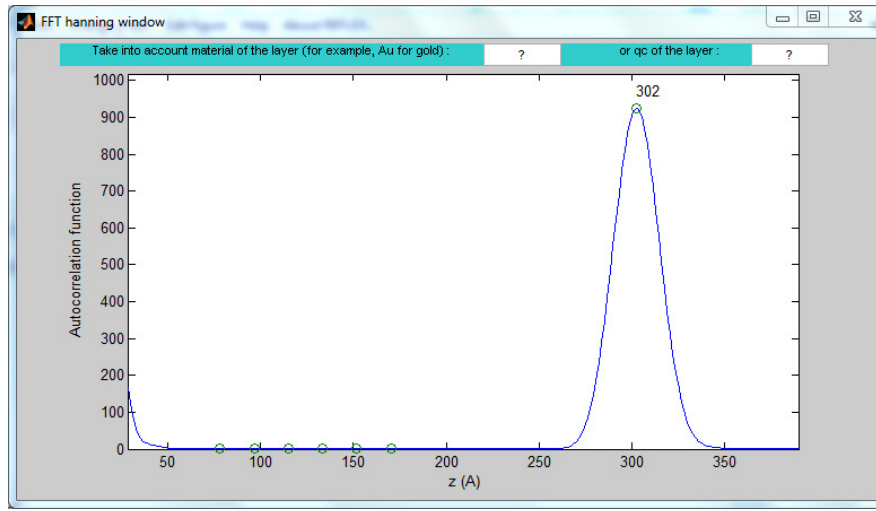


Figure 3

Amplitudes of oscillations: the amplitude of the oscillations depends on the difference between the densities of the film and its substrate. The smaller the difference between the two densities, the smaller the amplitude of the oscillations. The best contrast yielding a large amplitude for the Kiessig fringes is obtained when the electron density of the film is half the one of the substrate.

Note that poor instrumental resolution also affects the amplitude of the oscillations due to a smearing of the data.

Decrease in amplitude of oscillations: the amplitude of the oscillations is reduced by increasing q_z (at high wave vector transfer) due to the interface roughness. In addition, the larger the roughness of the substrate, the faster the reflectivity curves falls with increasing q_z .

5) Automatic adjustment of parameters

When the calculated reflectivity curve is close to observed one, user can fit the model to the data by using the menu **Calculation** \Rightarrow **Fit**. The user has the option of using five different methods to minimize the χ^2 value (define below): Levenberg –Marquardt [11], Simplex search [12], interior-point algorithm [13], Sequential quadratic programming (SQP) which is described in Chapter 18 of Nocedal and Wright [14] and the genetic algorithm (GA) [15, 16]. χ^2 parameter is used to describe how close the calculated data matches the experimental ones and is given by:

$$\chi^2 = \frac{1}{n} \sum_{i=1}^n \left(\frac{y_{data_i} - y_{calc_i}}{y_{data_i}} \right)^2$$

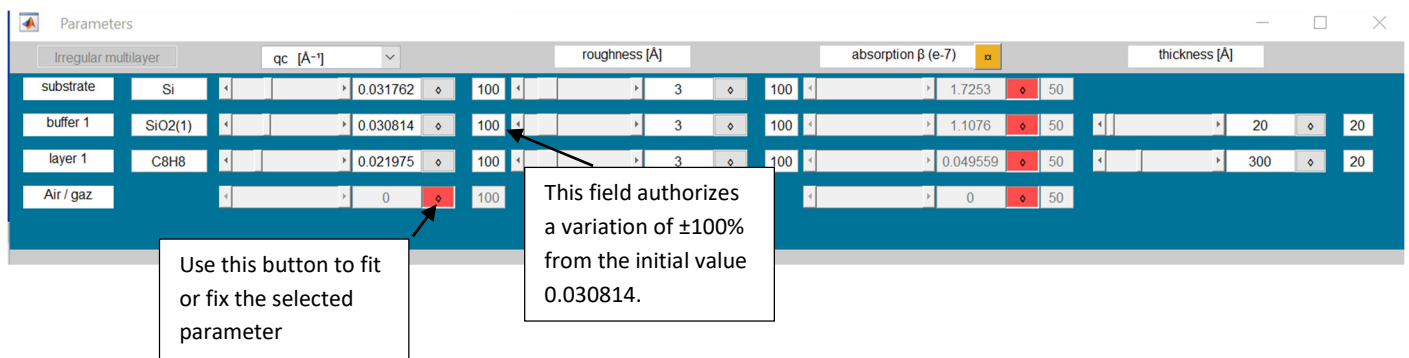
where there are a total of n measured data points, y_{data_i} each of which has a corresponding theoretical value, y_{calc_i} .

The most popular method is *Levenberg-Marquardt* algorithm (LMA) which is used in many software applications for solving generic curve-fitting problems. Levenberg Marquardt is a fast method and after few iterations converges on an accurate solution. It is more reliable when there are few initial values. The main problem is that *LMA* may get stuck in local minima not necessarily corresponding to the global minimum. The *Simplex* search method differs from the *Levenberg-Marquardt* in that it does not use derivatives, which confers safer convergence properties to the Simplex method since it is much less prone to finding false minima. *Interior-point* methods are a certain class of algorithms that solve linear and nonlinear convex optimization problems. It handles large, sparse problems, as well as small dense problems. The algorithm satisfies bounds at all iterations,

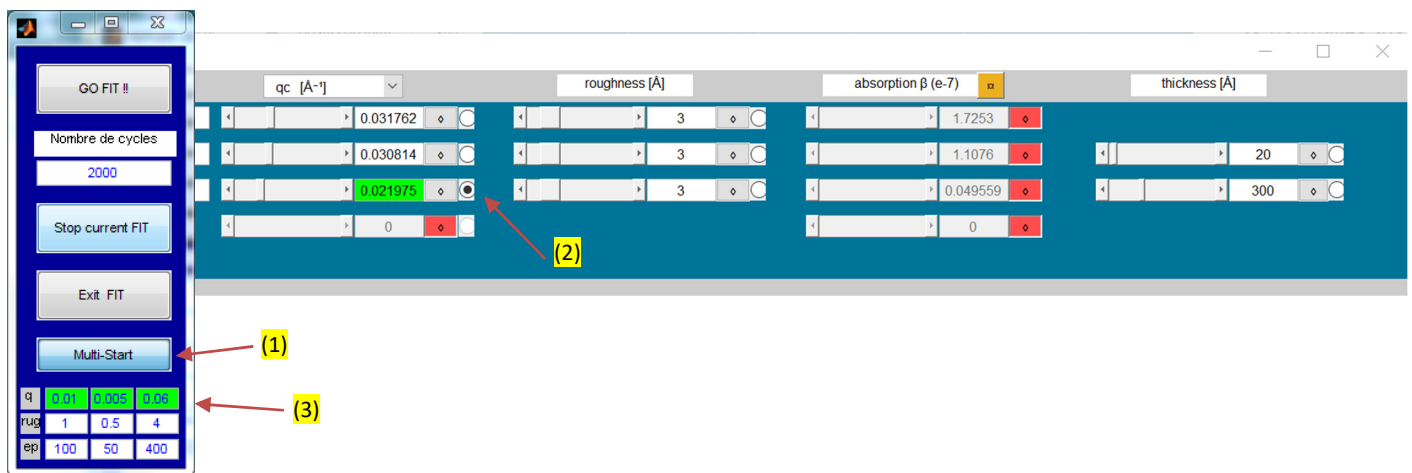
and can recover from NaN or Inf results. It is a large-scale algorithm. *SQP* is an iterative method for constrained nonlinear optimization. It is not a large-scale algorithm. With Trust Region Method and *SQP* algorithm, it is possible to constrain the solution into a range. These constraints may be used to limit a parameter to within a physically reasonable range. Constraints are especially important in cases where fits are relatively insensitive to some parameters, which may lead to significant cross correlation. In such a situation, the parameter can oscillate or diverge during the fitting process and constraints can limit this behaviour. This effect often arises with roughness parameters, as their effects are mainly noticed in the high-Q area, where data statistics (especially neutron) are poorer. 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:

$$x_0 - x_0 \cdot v / 100 \leq x \leq x_0 + x_0 \cdot v / 100$$

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



As a fit can stop because it may get stuck in local minima, a Multi-start menu allows the user to perform a fitting process with different initial starting values of the selected parameter (q_c , roughness or thickness). The retained fit is directly related to the better χ^2 .

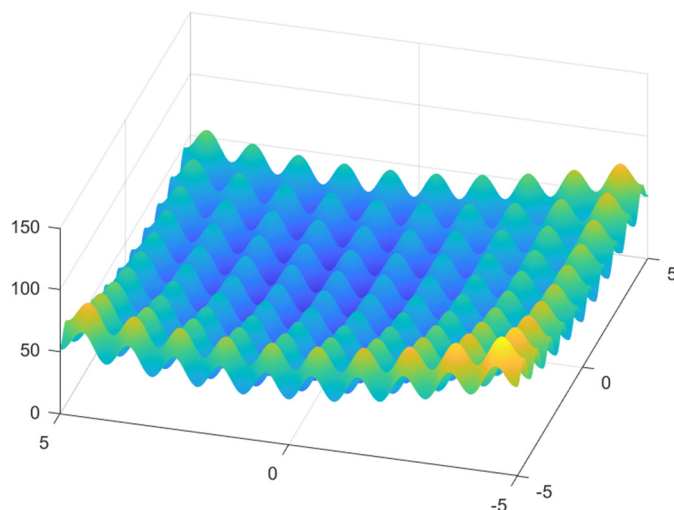


- (1) Push the Multi-Start button to allow a fitting process with different starting values
- (2) Select the concerned parameter
- (3) Complete the range: first value, step and last value.

Classical optimization procedures, such as gradient-based search (Levenberg Marquardt...), have good performance, but may tend to be trapped in local minima. The **genetic algorithms** developed during the recent decade combine the advantages of stochastic search with intelligent strategy of solution finding. These algorithms mimic the main features of the Darwinian theory of evolution operating on the basis of “struggle for life” and “survival of fittest” principles. The genetic algorithm repeatedly modifies a population of individual solutions. At each step, the genetic

algorithm selects individuals at random from the current population to be parents and uses them to produce the children for the next generation. Over successive generations, the population "evolves" toward an optimal solution. The advantage of genetic algorithms is that they are able to find multiple global minima, whereas simulated annealing provides only one solution at a time. It is a reliable method for finding global best fits, even if the starting guesses for the fit are far from the solution. For more details, see for example the following references [17, 18].

For example, with a genetic algorithm, it is possible to find the global minimum on the Rastrigin function as shown on the figure below (the global minimum is at (1,1), and its value is 0). It is challenging because it has infinite local extrema.



References

1. Gibaud, A. and G. Vignaud, *Specular Reflectivity from smooth and rough surfaces*, in *X-ray and Neutron Reflectivity*. 2009, Springer. p. 85-131.
2. Gibaud, A., G. Vignaud, and S.K. Sinha, *The correction of geometrical factors in the analysis of x-ray reflectivity*. *Acta Crystallographica Section A: Foundations of Crystallography*, 1993. **49**(4): p. 642-648.
3. Nevot, L. and P. Croce, *Caractérisation des surfaces par réflexion rasante de rayons X. Application à l'étude du polissage de quelques verres silicates*. *Revue de Physique appliquée*, 1980. **15**(3): p. 761-779.
4. Henke, B.L., E.M. Gullikson, and J.C. Davis, *X-ray interactions: photoabsorption, scattering, transmission, and reflection at E= 50-30,000 eV, Z= 1-92*. *Atomic data and nuclear data tables*, 1993. **54**(2): p. 181-342.
5. Mezger, M., et al., *Molecular orientation in soft matter thin films studied by resonant soft X-ray reflectivity*. *Physical Review B*, 2011. **83**(15): p. 155406.
6. Yan, H., et al., *Accurate and Facile Determination of the Index of Refraction of Organic Thin Films Near the Carbon 1 s Absorption Edge*. *Physical review letters*, 2013. **110**(17): p. 177401.
7. Rauch, H. and W. Waschkowski, *Neutron Scattering Lengths in ILL Neutron Data Booklet*, edited by A.-J. Dianox & G. Lander. 2003, Philadelphia, PA, USA: Old City Publishing.
8. Vignaud, G., et al., *Ordering of diblock PS-PBMA thin films: An X-ray reflectivity study*. *Physica B: Condensed Matter*, 1998. **248**(1-4): p. 250-257.
9. Seeck, O., et al., *Analysis of x-ray reflectivity data from low-contrast polymer bilayer systems using a Fourier method*. *Applied Physics Letters*, 2000. **76**(19): p. 2713-2715.
10. Oppenheim, A.V., *Discrete-time signal processing*. 1999: Pearson Education India.

11. Moré, J.J., *The Levenberg-Marquardt algorithm: implementation and theory*, in *Numerical analysis*. 1978, Springer. p. 105-116.
12. Lagarias, J.C., et al., *Convergence properties of the Nelder--Mead simplex method in low dimensions*. SIAM Journal on optimization, 1998. **9**(1): p. 112-147.
13. Byrd, R.H., J.C. Gilbert, and J. Nocedal, *A trust region method based on interior point techniques for nonlinear programming*. Mathematical Programming, 2000. **89**(1): p. 149-185.
14. Nocedal, J. and S.J. Wright, *Sequential quadratic programming*. 2006: Springer.
15. blasco, X., *Basic Genetic Algorithm* (<https://www.mathworks.com/matlabcentral/fileexchange/39021-basic-genetic-algorithm>), MATLAB Central File Exchange. Retrieved January 10, 2022. . 2022.
16. Goldberg, D.E., *Genetic algorithms*. 2006: Pearson Education India.
17. Ulyanenko, A., K. Omote, and J. Harada, *The genetic algorithm: refinement of X-ray reflectivity data from multilayers and thin films*. Physica B: Condensed Matter, 2000. **283**(1-3): p. 237-241.
18. Van der Lee, A., F. Salah, and B. Harzallah, *A comparison of modern data analysis methods for X-ray and neutron specular reflectivity data*. Journal of Applied Crystallography, 2007. **40**(5): p. 820-833.