In a typical specular x-ray reflectivity experiment, a collimated beam is impinging on the surface of a flat sample at an incident angle $\theta$. 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 $q_z = \frac{4\pi \sin \theta}{\lambda}$. The specular reflectivity is defined as the ratio of the reflected to the incident intensity $R = \frac{I_r}{I_0}$ is measured as a function of increasing wave vector transfer.

*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.
TOP LEFT WINDOW:

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

1 layer for the caplayer

2 layers in the unit cell repeated 3 times

2 layers for the buffer

\[\text{Layer 1} \rightarrow \text{Layer 2} \rightarrow \text{Layer 1} \rightarrow \text{Layer 2} \rightarrow \text{Layer 1} \rightarrow \text{Layer 2} \rightarrow \text{Layer 1} \rightarrow \text{Layer 2} \rightarrow \text{Layer 1} \rightarrow \text{Layer 2} \rightarrow \text{Caplayer}\]
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:

<table>
<thead>
<tr>
<th>Caplayer</th>
<th>Layer n</th>
<th>Buffer</th>
<th>Number of period</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

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

We now describe the content of region 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 on 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. Reflex also allows choosing a Lorentzian profile for the direct beam. Besides one can also download a measurement of the direct beam (intensity as a function of 2\(\theta\)) and use this profile for the convolution with the calculated curve. The advantage is that it is not necessary to fill in the HWHM for the Gaussian profile. In addition, sometimes the intensity profiles of beams cannot be exactly modeled with Gaussian profiles or any mathematical equation because beam sources for X-ray reflectivity are collimated with several optical mirror systems. In some cases, the intensity profiles of beams are asymmetrical with respect to the vertical center of the beam because of the collimating geometry or the slit system. See for example Figure 1 of the work of Ahn et al.[2]. Besides when measurements are performed in high resolution at synchrotron and the incident beam is coherent, the shape of the direct beam is not Gaussian due to diffraction by the slits [3]. The fact that on can directly introduce in the calculation the shape of the measured direct beam can be thus of interest if the direct beam is not really Gaussian. 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 [4].

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 \( \frac{\Delta q_z}{q_z} = \text{cst} \) that measure with 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 \( \theta \) is a little bit shifted and becomes \( \theta + \Delta \theta \).

- **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 assuming that the profile of the beam is rectangular, if the direct beam makes an incident angle \( \theta \) 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: \( F = \frac{T}{\sin \theta} \)

![Footprint Diagram](image)

When \( F > L \), the corrected intensity is reduced to the following simple expression, which is linear in \( \theta \):

\[
I_{\text{corr}} = \frac{I_{\text{calculated}}}{F} \cdot L = I_{\text{calculated}} \cdot \frac{L}{\theta/T}
\]

The user can also choose a Gaussian profile for this correction. In that case, the corrected reflected intensity of the detector is given by:

\[
I_{\text{corrected}} = I_{\text{calculated}} \cdot \frac{\int_0^a g(t) \, dt}{\int_0^\infty g(t) \, dt} \quad a = \frac{L}{2} \sin \theta
\]

where \( g(t) = Ae^{-\frac{t^2}{(\theta^2/4)}} \) is the Gaussian function which describe the direct beam. The Gaussian correction may improve or modify a little bit the shape of the reflectivity curve when reflectivity is less than 1.

![Gaussian Profile](image)
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 [5].

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 3Å and 5Å respectively.

(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 $\beta$ 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) [6]) 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 ⇒ Database ⇒ Add new material) with its chemical formula and equally important its density.

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

The program automatically extract from the database the anomalous atomic form factor (real $f'$ and imaginary $f''$ part) and create 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-ray, you should be noted that $\delta$ and $\beta$ automatically copied from the database may be not right when the energy is closed to an X-ray absorption threshold. Indeed $\delta$ and $\beta$ can have abrupt variations (including negative values of $\delta$) at the edge of an absorption threshold [7, 8].

Regarding the neutron reflectivity, there is also a database of the bound coherent scattering lengths extracted from the Atomic Institute for Austrian Universities [9]. 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 $q_c$ and the coefficient of absorption $\beta$ 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 $\delta$ and $\beta$ are given by:

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

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

Where $r_e = 2.810^{-15}$ m is the classical radius of the electron, $\lambda$ is the wavelength, $\rho_e$ the electron density, $N$ 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, $\rho$ the mass density. The value of the parameter $\delta$ is ranging from $10^{-5}$ to $10^{-6}$ for X-rays with wavelength approximately 1 Å. The parameter $\beta$ is related to the X-Rays absorption, expressed by the linear absorption coefficient $\mu$ as shown in the following formula:
Unlike the parameter $\delta$, the critical wave vector $q_c$ does not depend on the wavelength, but is directly linked to the electron density in the material by:

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

where the units of the electron density is $e^- / \lambda^3$.

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

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/2theta 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!**

<table>
<thead>
<tr>
<th>$q_z$</th>
<th>$R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0000000</td>
<td>8.8649878e-001</td>
</tr>
<tr>
<td>2.0500000</td>
<td>9.3600872e-001</td>
</tr>
<tr>
<td>2.1000000</td>
<td>9.8681090e-001</td>
</tr>
<tr>
<td>2.1500000</td>
<td>1.0574660e-001</td>
</tr>
<tr>
<td>2.2000000</td>
<td>9.5576110e-001</td>
</tr>
<tr>
<td>2.2300000</td>
<td>9.9427999e-001</td>
</tr>
<tr>
<td>2.2600000</td>
<td>9.3268613e-001</td>
</tr>
<tr>
<td>2.3000000</td>
<td>9.3116222e-001</td>
</tr>
<tr>
<td>2.3300000</td>
<td>9.2806694e-001</td>
</tr>
<tr>
<td>2.3500000</td>
<td>9.280867b-001</td>
</tr>
</tbody>
</table>

**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

![Parameter Table]

**Exit reflex:** to quit Reflex software

**Menu bar "Calculation":**

![Calculation Menu]

**Fit:** opens a calculation window to fit the data

![Fit Window]

**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.

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, it can be interesting to calculate the data curve with the same step that the calculated curve.

**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.

![Reflectivity Curve](image)

**Menu bar "Configure Resolution":**

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

**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 ⇒ 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.

2. Fill the fields related to the reflectometer: the instrumental resolution \( \Delta q_z \) 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.
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 $\beta$ and surface roughness $\sigma$. Normally starting values for $q_c$ and $\beta$ 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:

- $q_i < q_c$: because the refractive index of materials for X-rays is slightly less than 1, when $q_i$ is less than $q_c$ the total external reflection occurs and the normalized reflected intensity is equal to $R=1$ whatever the surface roughness.

- $q_i > q_c$: 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 $1/q_i^2$. 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 ($\sigma = 5$ Å). In others words, the larger the roughness of a substrate, the faster the decay rate of X-ray reflectivity curve.

![Figure 1](image)

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, $q_c$, $\beta$, 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.
**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
\[
h \approx \frac{2\pi}{\Delta q_z} \frac{1}{q_{z-min}}
\]
where \( \Delta q_z \) 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 (Calculus \( \Rightarrow \) 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.
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 Calculus ⇒ Fit. The user has the option of using four different methods to minimize the $\chi^2$ value (define below): Levenberg –Marquardt [11], Simplex search [12], interior-point algorithm [13] and the Sequential quadratic programming (SQP) algorithm which is described in Chapter 18 of Nocedal and Wright [14]. $\chi^2$ parameter is used to describe how close the calculated data matches the experimental ones and is given by:

$$\chi^2 = \frac{1}{n} \sum_{i=1}^{n} \left( \frac{y_{\text{data}i} - y_{\text{calc}i}}{y_{\text{data}i}} \right)^2$$

where there are a total of $n$ measured data points, $y_{\text{data}}$, each of which has a corresponding theoretical value, $y_{\text{calc}}$.

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 fast method and after few iterations converge on an accurate solution. It is more reliable when there are few initial values. The main problem is that the LMA may get stuck in local minima which is not necessarily 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 region, 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 \( \chi^2 \).

References


