Reflectivity Workshop

Getting started with *MOTOFIT*, *LEPTOS*, *STOCHFIT*, *IMD*, and *REFLEX*

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Contents

1   Introduction

This document gives a fast introduction to the X-ray reflectivity programs *MOTOFIT* (http://motofit.sourceforge.net/wiki/index.php/Main_Page), *LEPTOS* (http://www.bruker-axs.de/leptos.html), *STOCHFIT* (http://stochfit.sourceforge.net/), *IMD* (http://rxollc.com/idl/index.html), and *REFLEX* (http://reflex.irdl.fr/Reflex/reflex.html). It is by no means intended to replace the official documentation, but it serves uniquely to get rapidly started using a simple example, and it provides as well some exercises.

As additional programs two helper programs are provided. *REFLECTOOLS* (Windows) is a program to convert mass density values to scattering length density valeus and vice-versa, when the chemical composition is known or supposed. The conversion can be done for a large X-ray energy interval. You can download *REFLECTOOLS* here: https://www.afc.asso.fr/htdocs/images/reflecto2021/reflectools2021.zpp. Rename the file *reflectools.zpp* to *reflectools.zip* and extract the files into a folder of your choice. The executable file is *reflectools2021.exe*.

REFCONVERT (Windows) is a GUI program to convert files in different formats to other formats. Download *REFCONVERT* here: https://www.afc.asso.fr/htdocs/images/reflecto2021/refconvert.xx Rename *RefConvert.xx* to *Refconvert.exe* and place ir in a folder of your choice.

2   *IMD*

*IMD* uses the ESRF program *XOP* (http://www.esrf.eu/Instrumentation/software/data-analysis/xop2.3). Please follow the detailed installation instructions on the *IMD* pages. In order to start the program double-click on the dos-batch file $\cdots$\xop2.3\imd4xop.bat.

If not already done, select the 'Reflectance, Phase, Psi, Delta' checkbox (see Fig. 1). Then go to the 'Independent Variables' tab and change if neccesary the definition of 'Incident Angle' to grazing and also the Wavelength to that of Cu radiation (1.5405 Å). (Fig. 2). You may want as well change the 'precision', the number of decimal numbers in e.g. the wavelength tab in order to be the wavelength to 1.5405 Å and not to 1.541 Å. The present version of IMD does not seem to 'remember' these settings, so of you do not want to redo these settings every time you start *IMD*, you could save a 'master file'. For that, once you have done the basic settings, go to File → Save and save a 'master.imd' file on an appropriate place. Next time when you start *IMD*, you should first load this file by 'File → Open'.

Now you can read in the data. You need to have a .txt file containing two colums. The first column is θ (grazing), if not, this should be specified in the 'incidence angle' tab. The second column is the reflectivity, usually normalized. With *IMD* it is, however, also possible to give a y-scale factor. The columns are separated by one or more spaces. First you should change the working
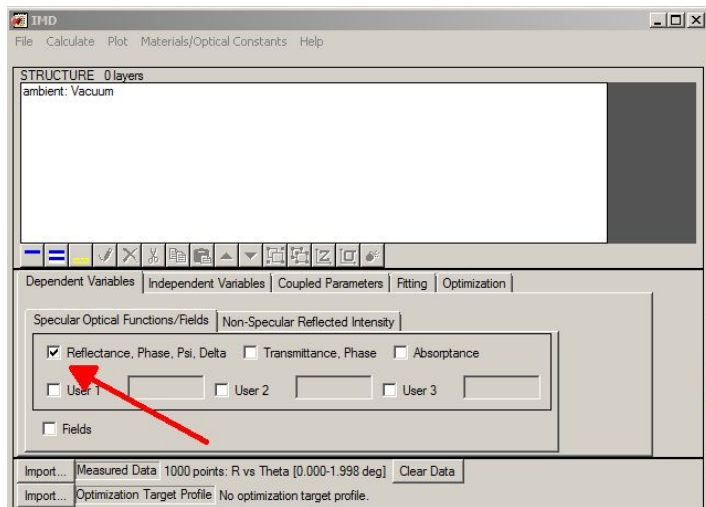
Figure 1: Opening screen *IMD*.
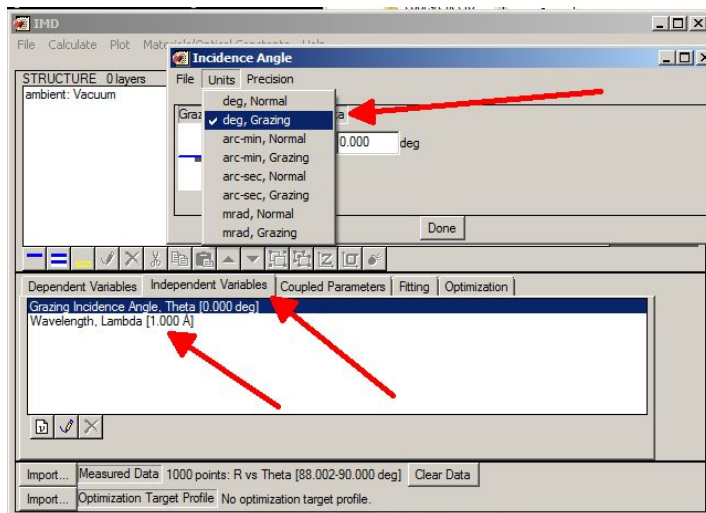
Figure 2: Setting the grazing incident angle in *IMD*.

directory. Go in the main *IMD* window to File → Change working directory and

choose your working directory. Then, to read in the data, go to File → Import Measured Data. You will get the screen in Fig. 3. If your data do not contain standard uncertainties, you should remove sig_m from the IDL command to read the data (see 1 in Fig. 3). If you want to apply some scale factor you can do it on the place indicated by arrow 3. Now you really read the data by choosing 'Read Data File' (in 2). Choose the file 'bico.txt'.
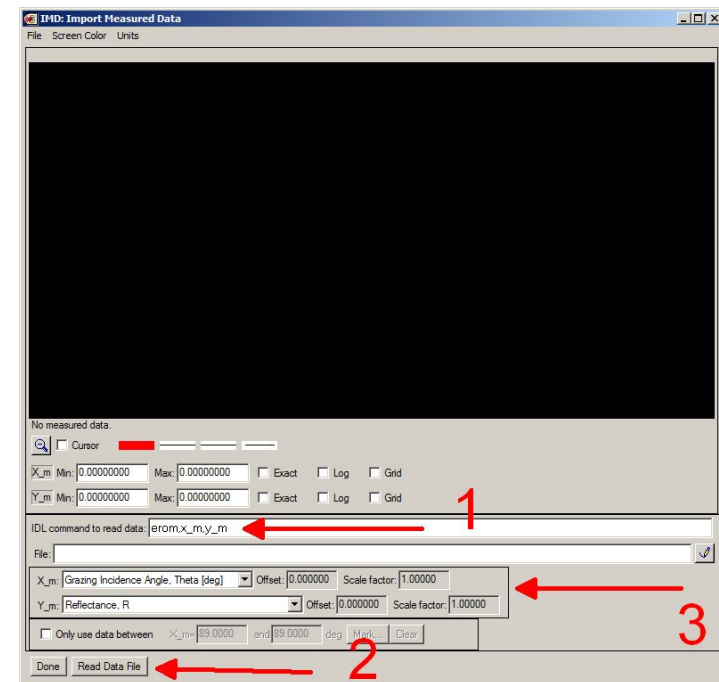
Figure 3: Configuring the 'Import Measured Data' screen in *IMD*.

You should now have the reflectivity curve displayed as in Fig. 4 when you set the y-axis to log-scale (see arrow).

Go back to the main *IMD* screen and define the starting model. Only the 'ambient' is defined. Note that this has to be changed for special X-ray or neutron experiments where the 'ambient' can be a liquid or a solid. Choose the left-most button right under the STRUCTURE window to add a layer. You can now use the material data base to select a material, *i.e.* silica (SiO2_llnl_cxro.nk). This file contains the optical constants for silica for a wide range of wavelengths. Define

Figure 4: Having the first data set on log-scale in *IMD*.
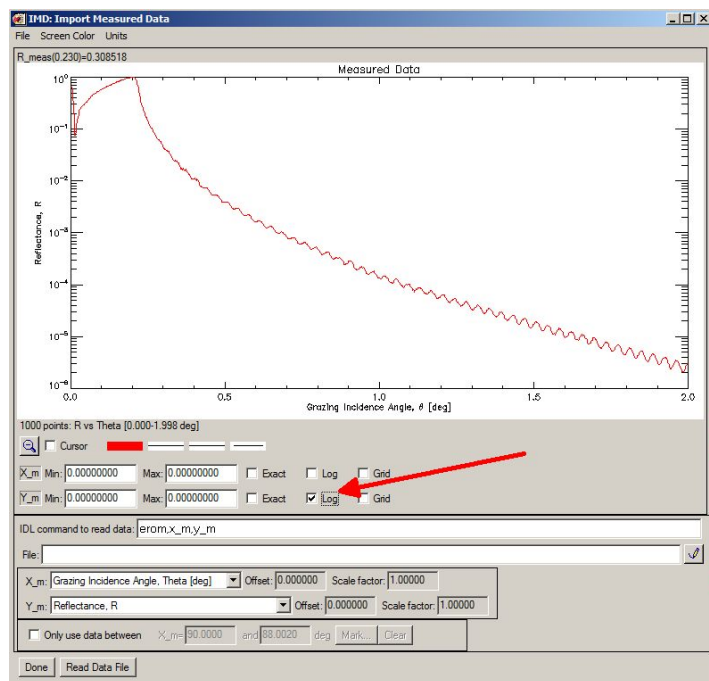

Figure 5: Adding layers in *IMD*.

as well the thickness and a starting roughness, *e.g.* 1000 Å for the thickness and 5.0 Å for the roughness (see Fig. 5). Note that quite often you have to confirm the value in the box by giving a <return>. Add also a silicon substrate (third button from the left) with 5 Å roughness. You can also specify a layer by giving its mass density and chemical composition. Select for this the radio button 'Composition and Density' in the layer or substrate screen. When this has been done you should go back to the 'Independent Variables' on the main *IMD* screen and choose the angular interval for which the reflectivity has to be calculated from the model parameters. Double-click on 'Grazing Incidence Angle' and select 1000 values between 0.000 and 1.998 degrees, the same number as in the experimental file. You are not obliged to do this, but it seems reasonable to do so. You are asked as well to fill in the 'Instrumental Angular Resolution, delta(Theta)' (Fig. 6). This is basically the width of the incident beam on the sample. It is used to convolve (or 'smear') the calculated data with a gaussian
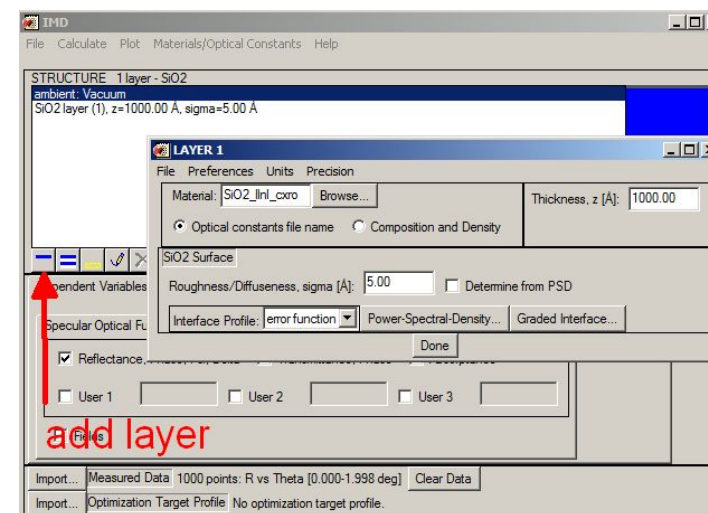
function in order to have a more realistic calculation close to the experimental curve. Give here as value 0.008 degrees. In order to do a calculation just go to 'Calculate' in the uopper toolbar in the main *IMD* screen and do 'Specular Optical Functions/Fields and you should get a screen as in Fig. **??**. Go to logscale by displaying the supplementary options which you can get when pressing the most-left button just under the graph (indicated by an arrow in the Figure). Now you should try to improve your model in order to get the calculated reflectivity closer to the experimental reflectivity. This can be done in two different ways, either by manually changing the model parameters until the calculated reflectivity agrees well with the experimental reflectivity. Or you can use some kind of fit procedure, *i.e.* a non-linear least-squares procedure to optimize the model parameters. We will try first the manual procedure. This gives at the same time a way to see how the reflectivity changes if you change one or more model parameters. In order to see how the reflectivity changes if you change the thickness, go to the main *IMD* screen - after having closed the screen with experimental and calculated reflectivity - and add as new independent parameter the 'SiO2 Layer (layer1), Thickness, z' parameter (Fig. **??**). Double-click on the newly created independent thickness parameter and change the number of values to 100 between 900 and 1100 Å. Do a calculation via the 'Calculate' op-
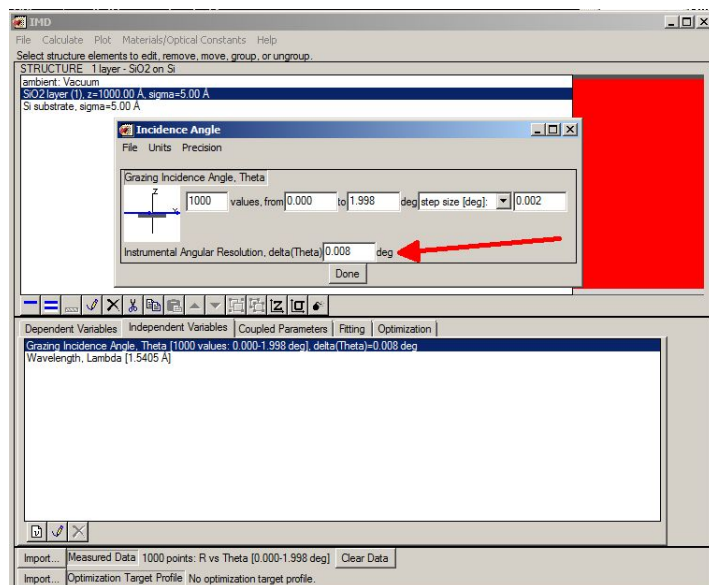
Figure 6: Specifying the angular interval for which the reflectivity is calculated in *IMD*.

Figure 7: Displaying the experimental and calculated reflectivity in *IMD*.

tion of the upper toolbar in the main *IMD* screen, choose log-scale via the 'Axis' tab and deselect z[SiO2(1)] as continuous variable. The screen should look like as in Fig. 9. Change the thickness slider smoothly in order to see the calculated reflectivity change. Try to find an optimal value and try then to fit the curve close to the critical angle. You see that the critical angle of the green calculated curve is at a higher value than that of the experimental red curve, meaning that the model density is too high. Since we use the optical constants database we need to fit on the optical refractive index. From the formula that relates the mass density to the optical index, we know that a higher density gives a lower refractive index. Thus the refractive index needs to be lowered. The changes are however subtle. Put the thickness at the optimal value in the structure tab and add the 'SiO2 Layers(layer 1) Refractive index 1' independent parameter. The variation is specified as a percentage of the nominal value. A reasonable change would be to vary the index between 100.0000% and 100.0010% of the nominal value. Change also the precision of the optical index to 8 numbers. You should get the curve as shown in Fig. 10. Leave the y-scale in linear mode,
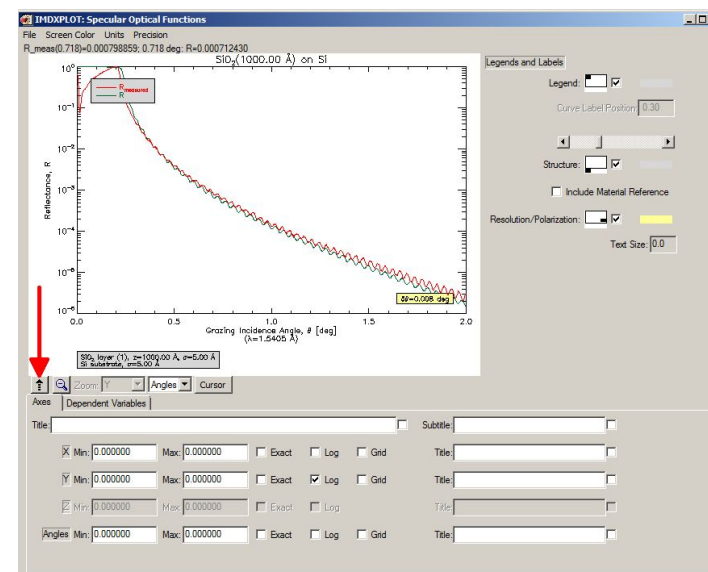
which is much more sensitive than logarithmic around the critical angle. We can observe in Fig. 10 that the normalisation was probably not correct. This can be corrected by re-importing the data with the proper multiplication factor for the reflectivity data. Alternatively, you can try to fit the data using one of the fitmodules implemented in *IMD*. Open the fit and then the optimization tabs in the main *IMD* screen (Fig. 11, 1). In the 'Fitting' tab you can add the parameters you want to optimize using the add button (2). If you open the optimization tab (1) the you can add other non-model related parameters such as scale factors. In the 'Optimization Settings' you can choose the 'Optimization Algorithm' (4). Try different ones to see what it gives. The weights are important to choose (3). We choose here 'Equal', *i.e.*, the same weight for each data point. This can be a good strategy if the experiment has been set up to have an approximately identical number of counts for each data point, *i.e.* longer counting times at higher angles.
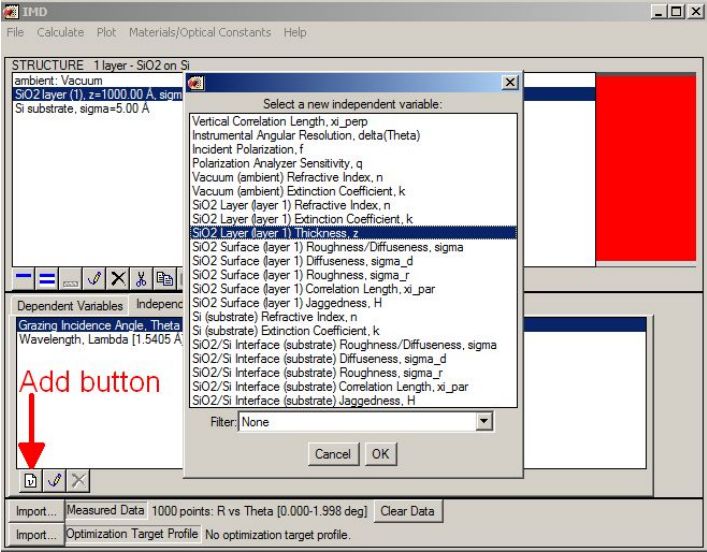
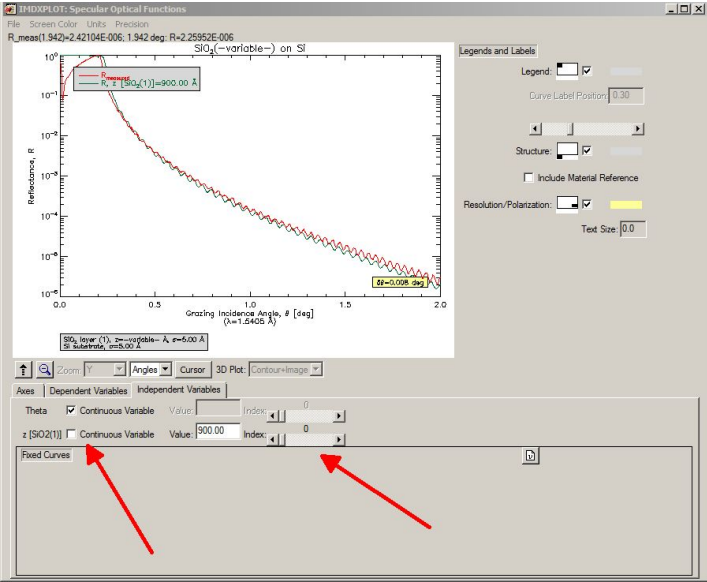Figure 8: Adding a new thickness independent parameter in *IMD*.
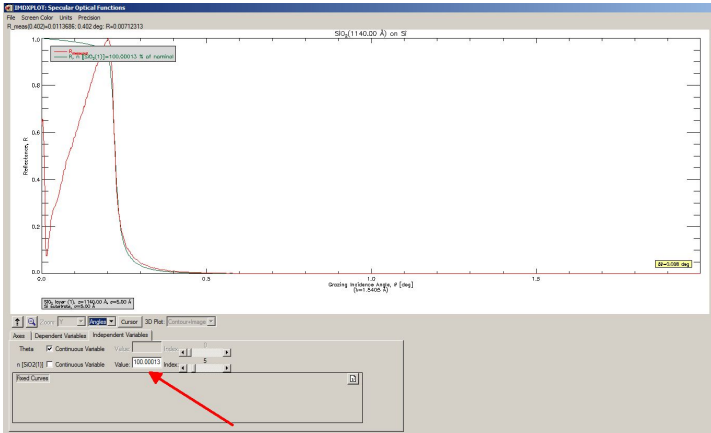

Figure 10: Manually adjusting the optical index in *IMD*.

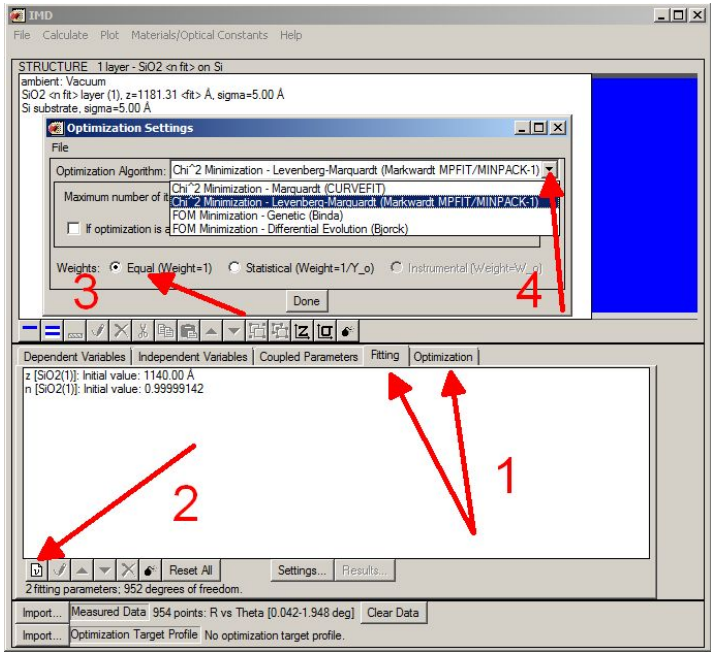Figure 9: Manually adjusting the thickness in *IMD*.

Figure 11: Fitting in *IMD*.

3   *MOTOFIT*

MOTOFIT is build on *IGOR*, see the *MOTOFIT* wiki (http://motofit.sourceforge.net/wiki/index.php/Main_Page) how to install *IGOR* and *MOTOFIT* as extension. Start *IGOR* and if *MOTOFIT* has been correctly installed, then it should appear as the second menu item from the right (Fig. 12). In order to start the reflectivity module, first select 'Load Motofit' and when that is done select 'Fit Reflectivity data' and only that one. 'Load experimental data' does not load the reflectivity module.
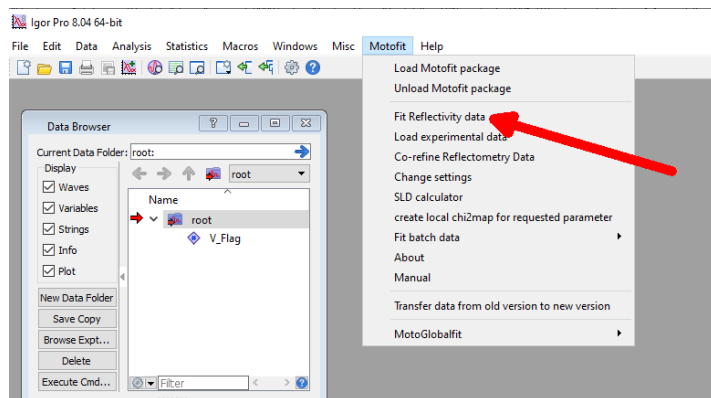

Figure 12: Starting *IGOR* and *MOTOFIT*.

If done, a screen pops up (Fig. 13) in which the user is asked to give the number of model points, the maximum model data resolution and the experimental resolution. It is not strictly necessary that the number of model data points or the model data resolution coincide with those in the experimental data file, but it is only advised to do so. This information can be found by opening the experimental data file with a text editor (take a simple one, Notepad or so, and not Word, since the latter may destroy the formatting of the file), or if the file has been obtained by the file-converter *REFCONVERT*, then this information is given upon conversion (Fig. 14). You can follow the instructions in this section with the data file lpvd1corrc2.txt, but you can also use another data file. Choose 'complex SLD' in 'which mode' (Fig. 13).

Leave the minimum data resolution as it is, since setting at 0.00 as you may have in your data file may give problems with a finite experimental resolution
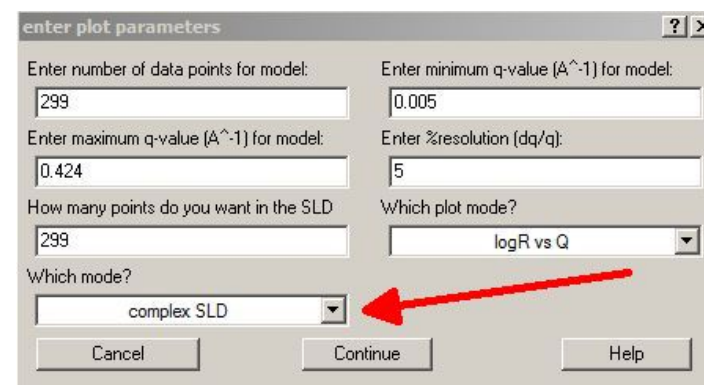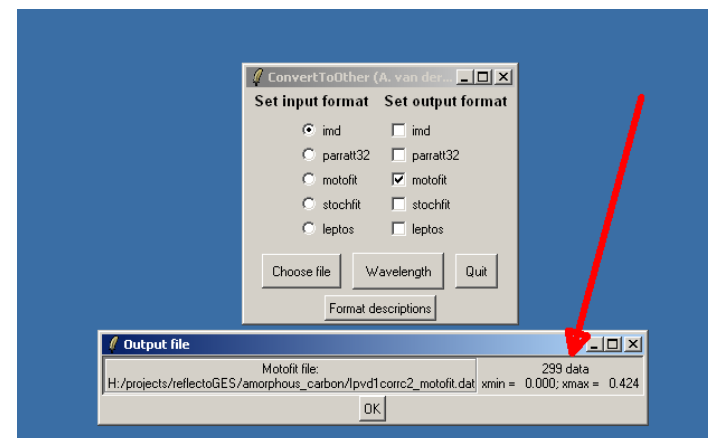

Figure 13: Entering simulation parameters.

Figure 14: Getting information from *REFCONVERT*.

($\delta q/q$), since the convolution of the instrumental resolution function should be done for negative q values as well if the data set starts at q=0.00.

Click on "Continue" and the main window of the *MOTOFIT* reflectivity fit module pops up. In first instance three different panes can be distinguished (Fig. 15). In **1** the SLD calculator is shown, this can be started from the upper *IGOR* toolbar, motofit, SLD calculator. The calculator calculates the scattering length density (SLD) as a function of the chemical formula and the mass density of the

molecular volume. Note that both the Neutron and the X-ray SLD are calculated. Especially the X-ray SLD could be slightly dependent of the wavelength, which cannot be entered here. For practical cases, and for having a good starting point for the optimisation, the calculated values should be sufficient.
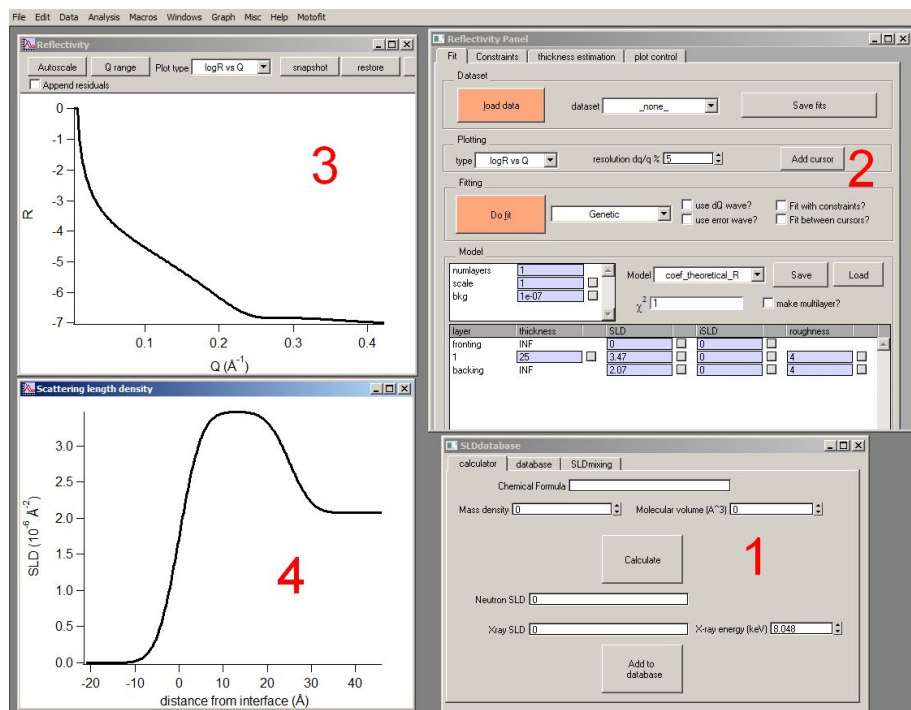

Figure 15: Presentation of the model panels of *MOTOFIT*.

In **2** the main model panel is given. Here the thin film model can be defined, the data imported and exported, and the fit started. In **3** the reflectivity based on the current model in **2** is given. As soon as a value changes in the model, **3** is updated (Fig. 16). In **4** the density profile of **2** is given. This one is updated as well, as soon as the values in **2** change. The fast fourier transform of the model (or experimental data) can be calculated using the tab 'thickness estimation' on panel **2**. This can give useful information about the thicknes(ses) present in the layer system. Note that the SLD is to be given in 10^{-6} Å^{-2}, and the absorption part just in Å^{-2}. Thickness and roughness are to be given in Å.

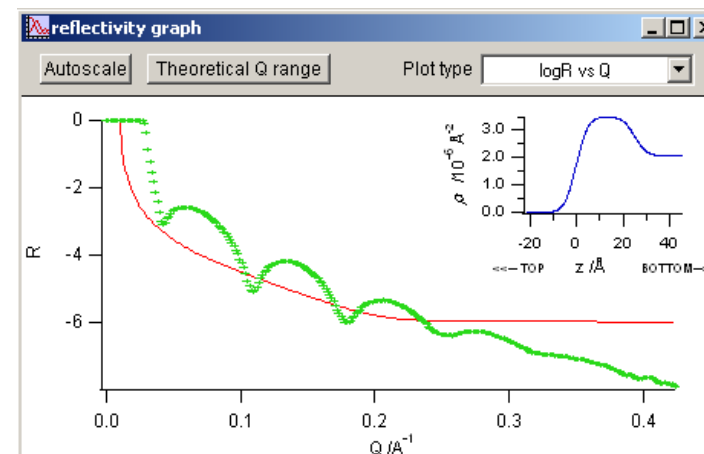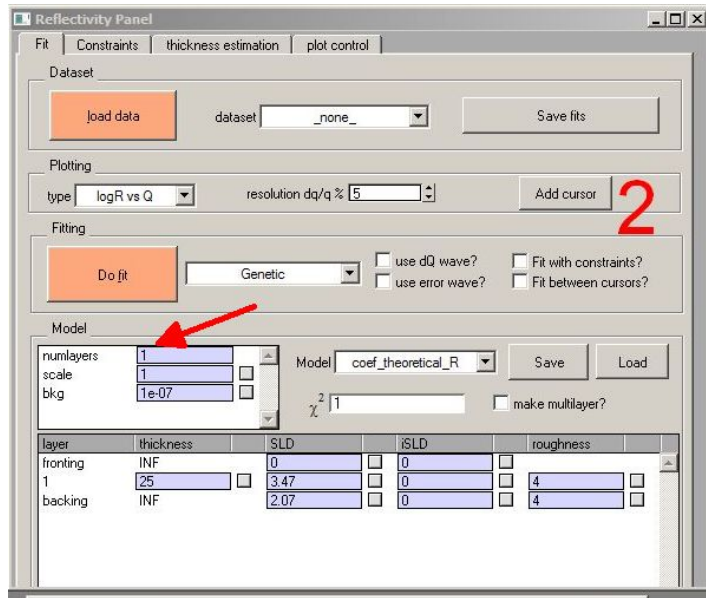In the upper left part of **2** the number of layers can be specified and equally

Figure 16: Calculated and simulated reflectivity in *MOTOFIT*.

well a scalefactor for non-normalized data (Fig. 17). 'Fronting' represents the SLD of the 'fronting' medium, very often vacuum or air, but it can be also water or, in the case of neutrons, Si or a mixture of normal and deuterated water. You should specify here the real part (SLD) and the imaginary part (iSLD). 'Backing' represents the SLD of the 'backing' medium or substrate.

In the middle part experimental data can be loaded ('Load data'). Navigate to your file and import the data. *IGOR* wants to know whether the experimental data should be displayed in the reflectivity panel **3**. Answer 'yes' and the experimental curve is displayed (Fig. 18). Since the initial model has SLD values for a typical neutron reflectivity experiment, the calculated (red) critical angle is much too far too the left compared to that of the (green) experimental curve.

Use the 'thickness estimation' tab to get a first estimate of the thickness of the film. Change the high Q value for FFT to the experimental one and press <enter>. Use the SLD calculator to get initial values for the SLD's of the film and the substrate. Try to fit by hand the experimental to the theoretical curve by adjusting the values in the model panel **2**. Note that in the present case the background value 1e-6 should absolutely be removed. The parameters shown below should give a reasonable starting point for an optimisation. In order to fit the checkboxes behind each parameter should be checked if the parameter is *not* to be refined.
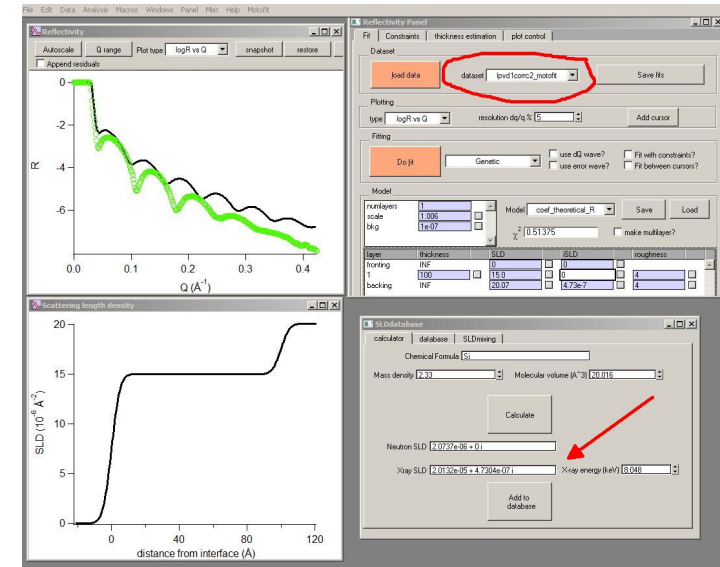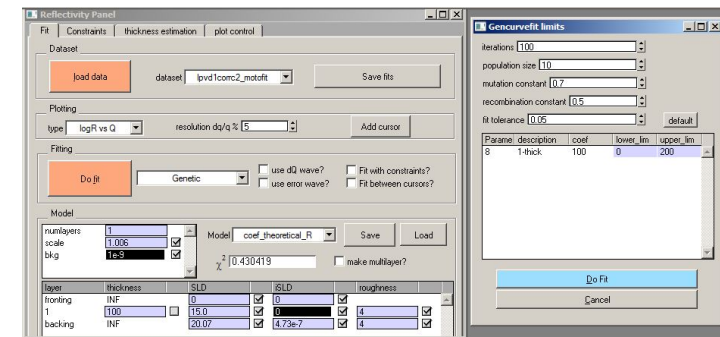
In addition the proper dataset should be selected in the upper part of the

Figure 17: Entering thin film parameters in *MOTOFIT*.

Figure 18: Importing and using experimental data in *MOTOFIT*.

Figure 19: Specifying fit limitations in *MOTOFIT*.

panel nearly at the right - even if the experimental file has already been loaded (Fig. 18).

Now the optimisation can be started: there is a choice between a Genetic Optimization, a Levenberg-Marquardt non-linear least-squares minimization, and an genetic optimisation followed by a Levenberg-Marquardt minimization. The last should be the best, but for the moment let's try simply the Genetic Optimization. Click on 'Do fit' and click subsequently 'continue' in the Set-up panel for the genetic optimization. You should check at beforehand all parameters that should *not* be optimized. So if you want to optimize only the thickness, leave this parameter unchecked. Unless you are an expert in the genetic algorithm, you should not touch the default values given in the 'Gencurve limits' window. In the next panel you give the lower and upper limits in between the algorithm is allowed to vary the refinable parameter (Fig. 19). This can be very useful: restrict the parameters to reasonable/meaningful values. Restrict the thickness to a valeur between 50 and 150 nm.

Check in the fitting part of the main panel 'Use dQ wave?'. Click on 'continue' to start the genetic calculation. During the calculation a color table for each

parameter shows the evolution of each parameter. Each color should be as uniform as possible. Below the calculated curve is updated each time a lower χ^2 is reached (Fig. 20).
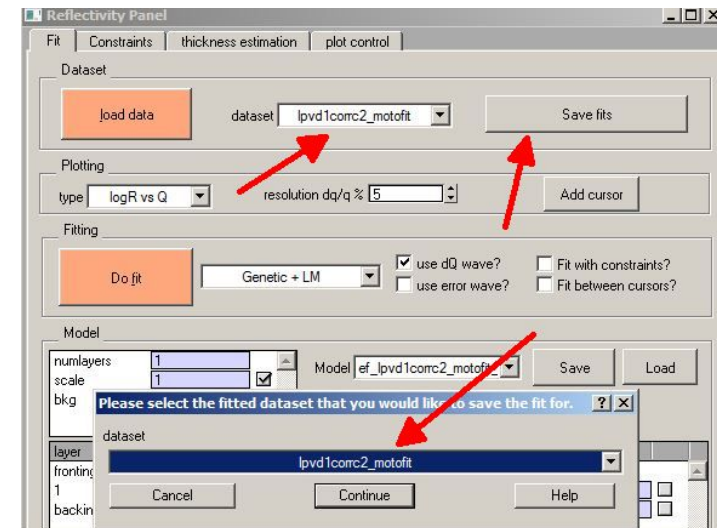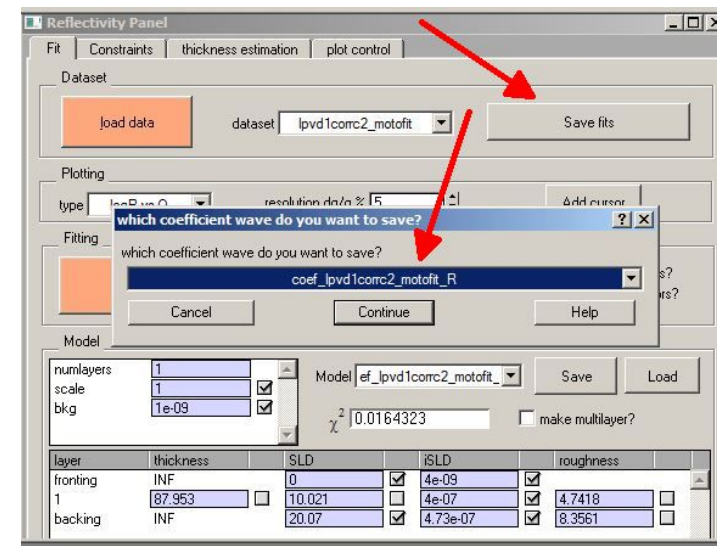
If you are satisfied with the fit - you can try to fit other parameters such as the scale or the absorption parameters, or try to do a Levenberg-Marquardt
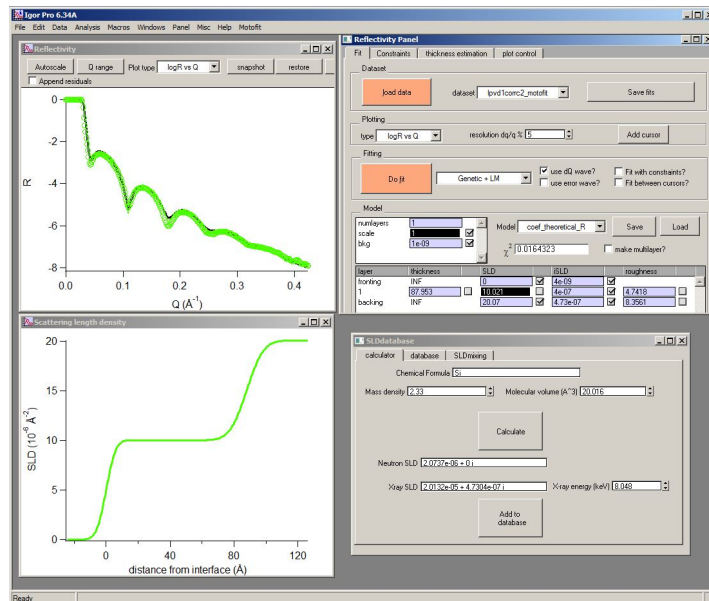
Figure 20: Final results of fit in *MOTOFIT*.

Figure 21: Saving calculated reflectivity data in *MOTOFIT*.

Figure 22: Saving film parameters in *MOTOFIT*.

minimization - you should save the best fit, *i.e.* the simulated reflectivity data and the best fit parameters. To save the simulated reflectivity data, click on 'Save fits' , and select the reflectivity data calculated from the best fit parameters (fit_name) in the window that pops up now ('Please select the fitted dataset that you would like to save the fit for?', Fig. 21).

In order to save the model parameters click on 'Save model' and in the window that pops up ('which coefficient wave do you want to save?', Fig. 22), select the coefficient wave belonging to the present fit. This is in general not Coef_theoretical but the next one in the list where also the name of the experimental dataset appears.

The program proposes to save the model parameters in *IGOR*'s proprietary format with extension .itx. This is advisable, since in this format the model parameters can be imported again using 'Load model', or even by double clicking on the .itx file if *IGOR* is not yet up. In the latter case, *IGOR* is automatically started and you should enter the number of data points etc. Note that the experimental data file is not automatically loaded, but it should be imported using 'Load data'. Also, make sure that the proper model wave is selected, because
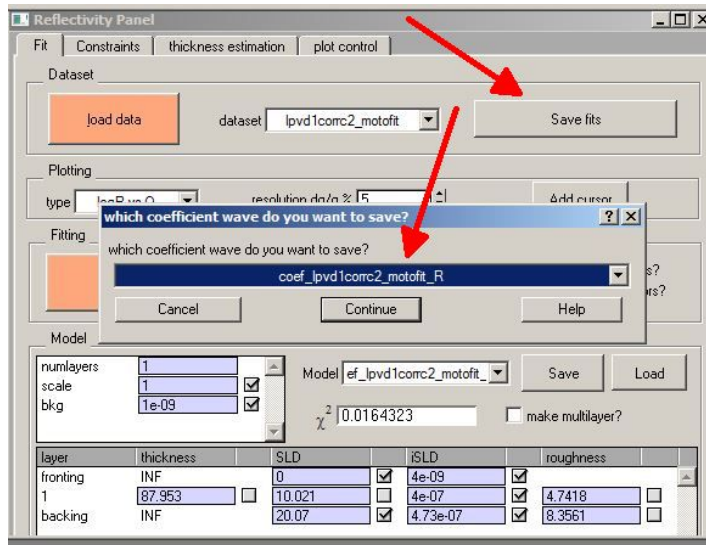
Figure 23: Re-using old film parameters in *MOTOFIT*.

IGOR starts always up with the default model parameters (Fig. 23). Load the old model parameters with 'Load', select the file end import the parameters. The screen will not automatically update, since you have to choose in 'Model' the right set of model parameters.

4 *LEPTOS*

Start *LEPTOS*: the screen is divided into 5 at first sight different panels (Fig. 24). Number **1-4** are, however, basically the same, but they can display four different tasks belonging to the same *project*. A *project* comprises all meta-data belonging to a measurement on a particular sample, *i.e.* the experimental set-up, the data itself, the model, and the data fit. In the most-left pane, **1**, you can switch between different projects. The four different tasks of the default project are 'Merged plots, Maps, Estimation and Transformation. In the smallest panel in the lower left corner, some technical information about the current calculation/process are displayed. It is a good idea to look from time to time in this panel whenever the program does not do what you want it to do, since the information of what goes wrong is displayed here, and not in a pop-up window.
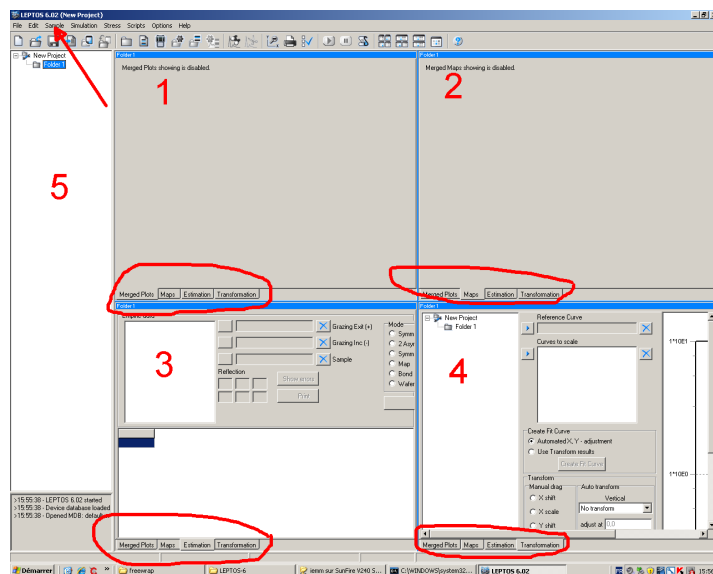

Figure 24: Presentation of work panels in *LEPTOS*.

Start now setting up a new project: go to 'Sample' in the upper task bar and select 'New Sample'. In the project panel (most-left panel) the sample identification 'Sample1' appears and the four central panels change as well and you can change between a 'Sample', a 'Simulation Parameters', 'Depth Profile'

and 'Diffractometer' sub-panel (Fig. 25). In the 'Sample' panel a substrate 'SUB' must be defined. Click on 'Material' and select 'Si'. In order to define a layer, click on 'Insert layer', and then on 'Material'. If you select 'C' in the list, you will notice that the substrate that was before present in the 'Depth Profile' panel just underneath, has disappeared. Even if you give now a finite layer in the 'Sample Pane', the depth profile will not appear. You can look now in the message panel in the lower left corner and you see the message 'Zero stiffness tensor components'.
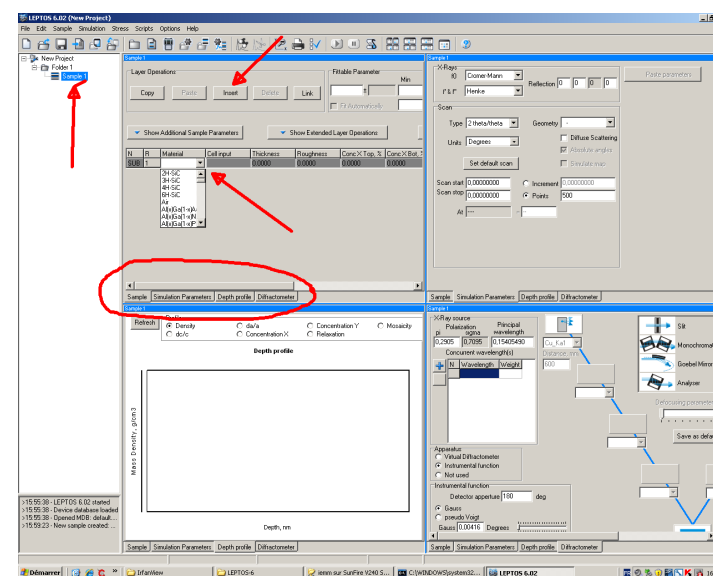

Figure 25: Specifying film parameters in *LEPTOS*.

This means that the material 'C' has not been correctly defined in the database. You can try to correct/complete this entry of the database by selecting 'File' $\rightarrow$ 'Open MDB', but of course you need to know the stiffness tensor components of crystalline carbon ('graphite'). Better is to add a new entry 'Amorphous carbon' to the data base (Fig. 26), because then less information is required which is anyhow not of importance for a reflectivity fit.

Click on 'New' in the 'Materials' part of the MDB panel (**1**), and select then 'Amorphous' (**2**) (Fig. 26). Fill in a suitable name 'Amorphous carbon' and give then the chemical composition of the material (Fig. 27) - in the asymmetric unit,
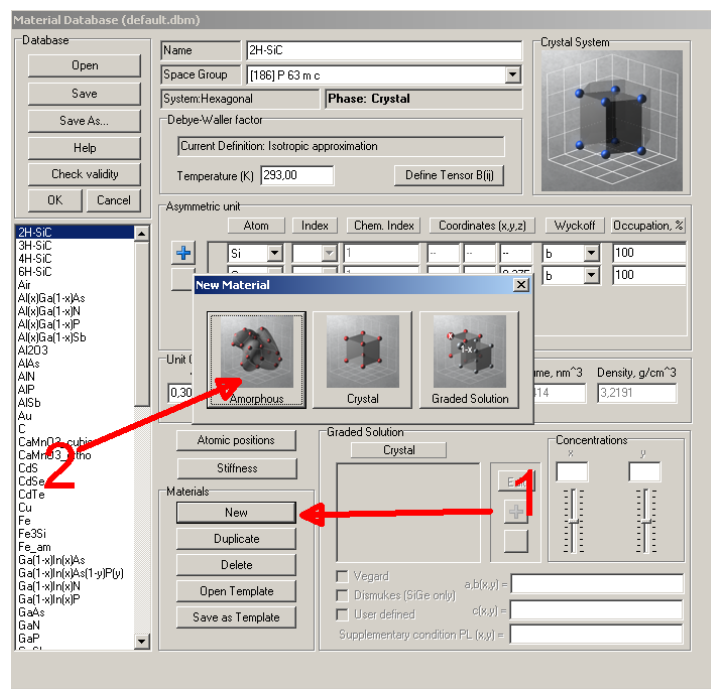
Figure 26: Adding a new (amorphous) material to the database in *LEPTOS*.

Figure 27: Specifying the chemical nature of a new material in the database of *LEPTOS*.

which is of course not relevant for an amorphous material, but you should set it up in this way. Click on 'OK' and select then 'Amorphous carbon' instead of (crystalline) carbon as thin layer.

If you fill now in a thickness, *e.g.* 100, in the thickness box of the layer, then you will see just below the depth profile of this silicon/carbon system. Fill in now two reasonable values for the substrate/film and film/air interface, e.g. 0.5, and you see also appearing these roughnesses in the depth profile. It is noted that these values are in nm.

Go now to the 'Simulation Parameters' tab, and fill in the 'Scan start' and 'Scan stop' values (Fig. 28). For *LEPTOS* it is a good idea to set the instrumental function FWHM of a Gaussian function to its proper value (in the 'Diffractometer' tab) or to at least the step size:

Now you are ready to do a simulation: go to either 'Sample' → 'Simulate' or press F6 and the simulated curve appears on the screen (Fig. 29) and also as
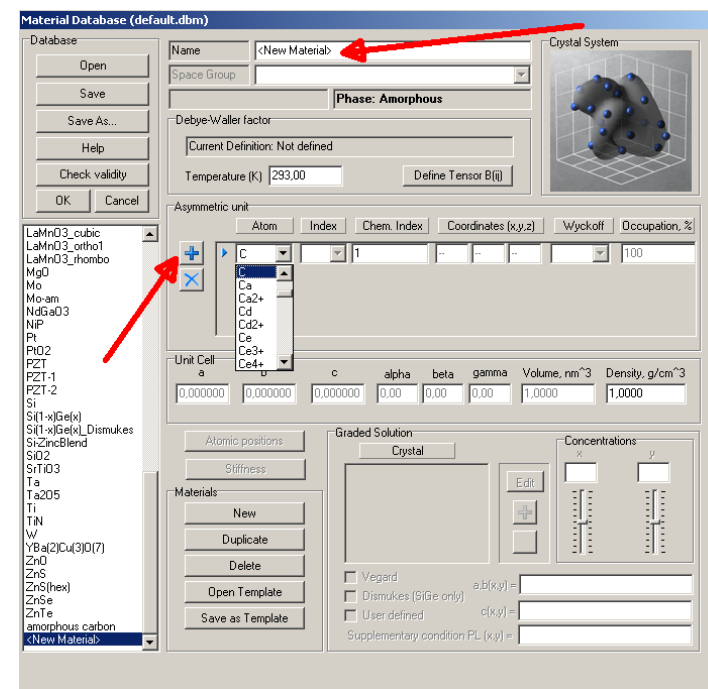
a new entry in the left-most project panel.

Select now in one of the other panels the 'Sample' tab and check for e.g. the thickness of the carbon film the 'Fit automatically' box. There is ofcourse not yet a fit to do, but this gives a means to calculate the simulated reflectivity as a function of the thickness by just changing the slider between the defined Min and Max values (Fig. 30). This can be done as well for the roughness and the density.

Now the experimental data should be imported. Go to 'File' → 'Import Data', select 'ASCII-Files' and pick up your data file. You see now your experimental data on the screen and a new entry in the project panel - the name of your experimental data file. In order to associate the experimental data file to the model you need to create a 'Fit Curve' object by selecting simultaneously the simulation and the experimental data objects in the project panel. Click right
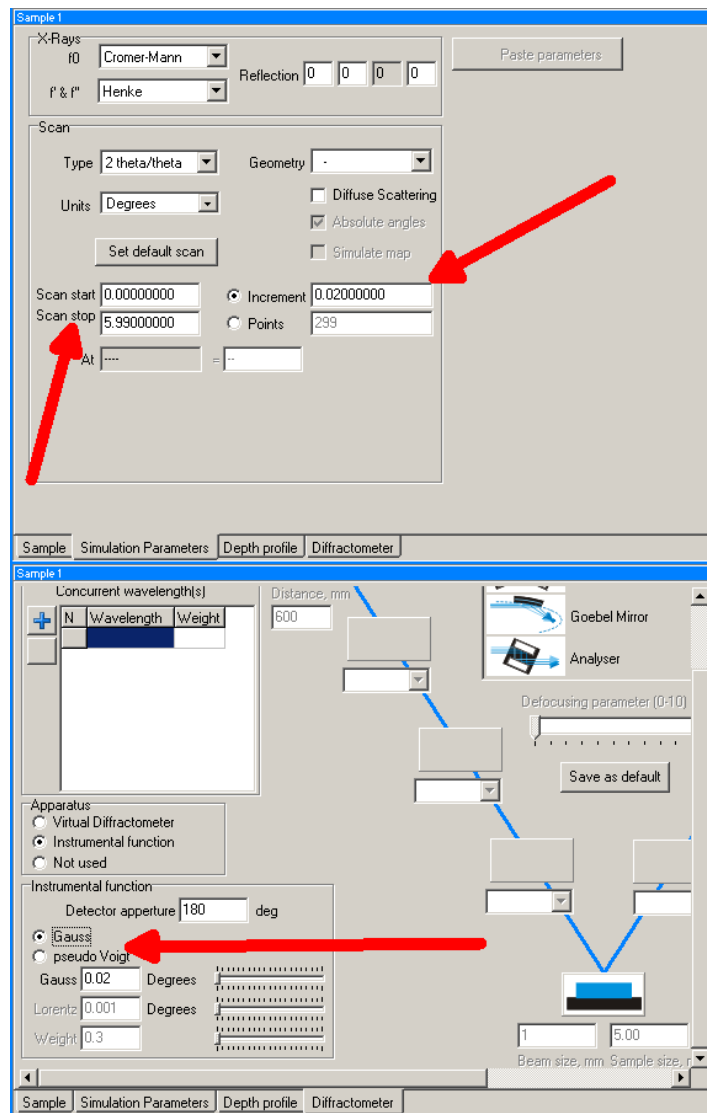
Figure 28: Specifying simulation parameters in *LEPTOS*.

and select/create the fit curve object (Fig. 31).

Now the plot in the 'Fit Curve' object contains both the experimental as the
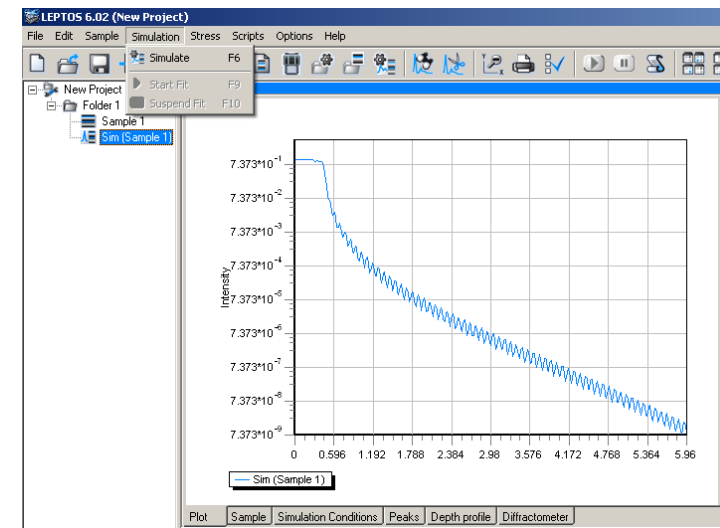
Figure 29: Performing a simulation in *LEPTOS*.

simulated data. Note that there is a 'Options & Cost functions' tab as well, in which the fit method can be specified. In order to do a data fit you can proceed by a manual adjustment using the sliders of the different parameters in the 'Sample' tab or by trying an automatic adjustment using the fit methods in the 'Options & Cost functions' tab. In both cases the fittable parameters need to be specified in the 'Sample' tab. If the automatic mode is specified, then the intensity scale and the background parameter can be specified to be fitted as well in the 'Options & Cost functions' tab.
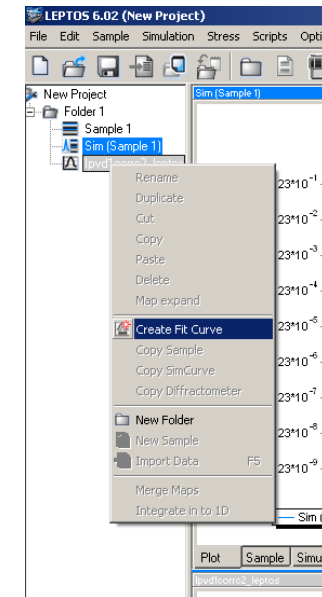
The 'Options & Cost functions' tab gives the value of the cost-function being mimimized as well. Perform the fit by selecting 'Simulation' in the upper menu bar and then 'Start Fits' or by pressing F9, or by clicking on the start icon in the upper horizontal tool bar (Fig. 32).
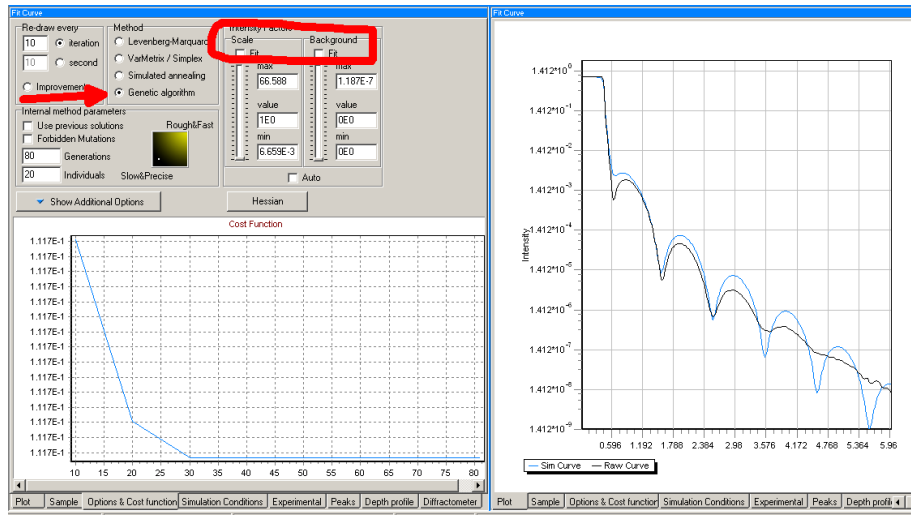
Another interesting tool is the 'Transformation tool', which can be used as well to create the 'Fit Curve' object and to apply scaling factors and offsets before the fit. Focus the cursor on 'Folder' in the project panel and select the 'Transformation' tab (Fig. 33). Select the simulated curve as the 'Reference Curve' and the experimental curve as 'Curves to scale'. With the different tools in the 'Transformation' tab you can now try to scale and/or apply offsets the experimental data. Be prudent to do automatic adjustments if the simulation is
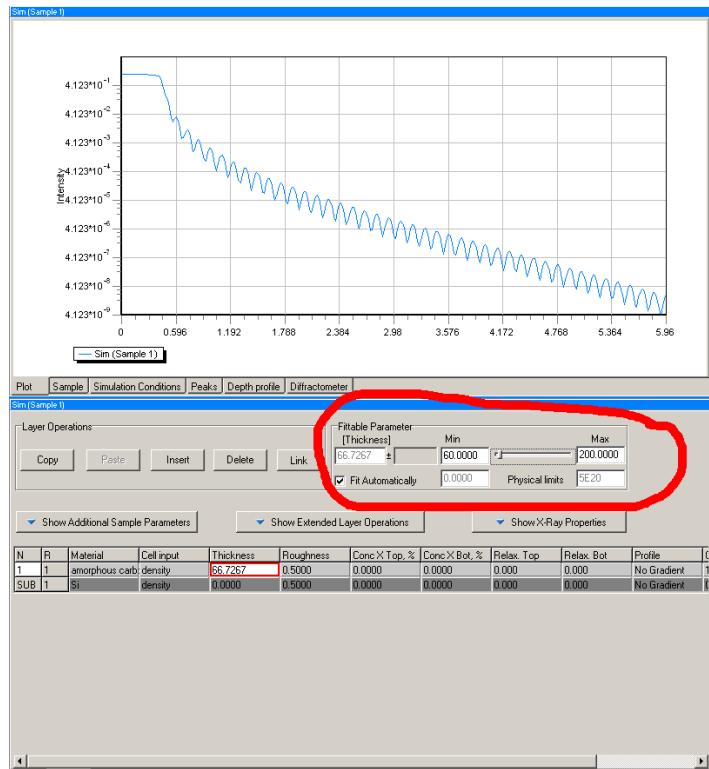
Figure 30: Using the sliders to change the reflectivity in *LEPTOS*.

Figure 31: Creating a 'Fit object' in *LEPTOS*.

not already very close to the experimental curve. If you are satisfied click on 'Create Fit Curve' and the 'Fit Curve' object is created in the same folder as the current project.

It is also possible to change the x-scale from θ to 2θ and vice versa using the Horizontal transform of the 'Transformation' tab. It is noted that *LEPTOS* uses by default 2θ for the x-scale. More complicated x-scale transformations, such as $q \rightarrow 2\theta$ can be done in the 'Experimental' tab of the 'experimental file' object (Fig. 34).

Figure 32: Performing a fit in *LEPTOS*.

Figure 33: Adjusting scales and offsets in *LEPTOS*.

Figure 34: Transforming the x-axis in *LEPTOS*.

5   Practical exercise *MOTOFIT*

In this part you are going to try to fit a real system: a nominal 300 Å thick Fe layer capped by a nominal 25 Å Au layer on a MgO substrate. Obtain first the nominal mass density values of MgO, Fe, and Au, by e.g. a search on Internet or by consulting a database. Start *MOTOFIT* and load the reflectivity module. The experimental data are in *LEPTOS* format, file mgo_fe_au_010.dat, convert them to *MOTOFIT* format with *REFCONVERT* as to obtain mgo_mgo_fe_au_010_motofit.dat. Calculate with the internal SLD calculator of *MOTOFIT* start values for the SLD and iSLD of the substrate and the two layers. Since you do not know anything about the roughness values, put them at arbitrary values between 2 and 8 Å. In the reflectivity panel, in order to have a better viewable experimental curve, double-click on the experimental curve and switch off the drawing of the error bars. Set de drawing mode to 'Lines between points'. If you have done all of this you should have a reflectivity graph panel and a reflectivity data panel as shown below (Fig. 35 and Fig. 36).

It is clear that the reflectivity calculated using the actual model parameters does not correspond at all to the experimental reflectivity. In order to have a first estimate for the thickness of the Fe layer, zoom into the FFT graph in the lower part of the model panel. Take care that you have selected as dataset your experimental file. If not you will see the FFT of the model parameters. If you do so, you find that the actual Fe layer is closer to 380 Å than to 300 Å. Note that this can be as well the sum of the capping Au layer and the actual Fe layer.

It is clear that the reflectivity calculated using the actual model parameters does not correspond at all to the experimental reflectivity. In order to have a first estimate for the thickness of the Fe layer, zoom into the FFT graph in the lower part of the model panel. Take care that you have selected as dataset your experimental file. If not you will see the FFT of the model parameters. If you do so, you find that the actual Fe layer is closer to 380 Å than to 300 Å. Note that this can be as well the sum of the capping Au layer and the actual Fe layer.

Now you can start fitting. First you need to decide which parameters you need to fit. The substrate parameters, except the roughness at the substrate/film interface can be left fixed. The thicknesses and the roughnesses of the two films need to be adjusted as well as the SLD's of the film. Is it necessary to adjust the absorption parameters iSLD? Start fitting while keeping in an external file your starting point. If the fit is not done correctly then the values may float away very easily. See what happens if you fit all fittable parameters at once, of if you try to
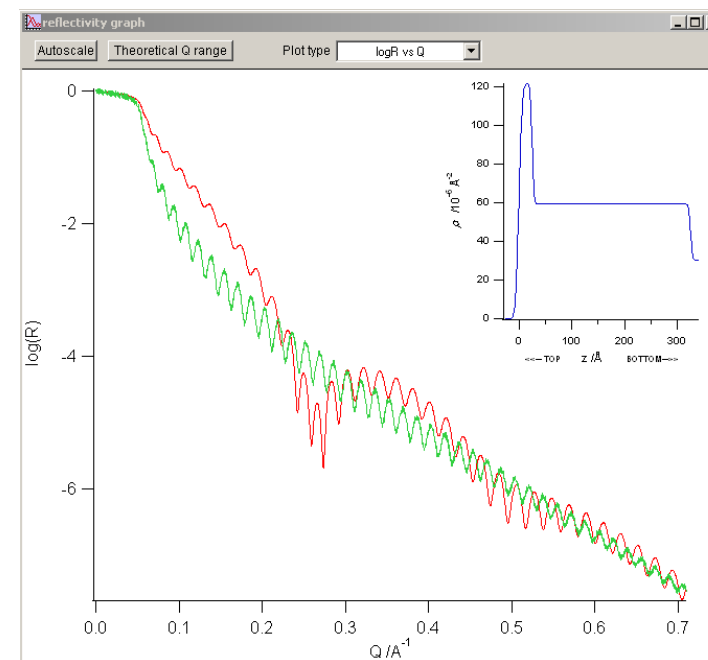

Figure 35: Reflectivity graph panel after defining the model parameters.

fit parameter by parameter. Take care to determine proper fit boundaries. You can finish by a Levenberg-Marquardt optimisation. Sometimes the log-screen says that the tolerance is reached, but the program seems to continue fitting. Click in that case on 'abort' and the optimisation will certainly stop. Make notes (final parameters/ χ^2) on what happens if you use different fit strategies - *i.e.* start fitting with parameters x instead of y, etc. One important parameter to inspect is the layer thickness of Au, which has tendancy to refine at much too low values. How can this be avoided? Here below is what you should find approximately if you have performed a good fit (Fig. 38).
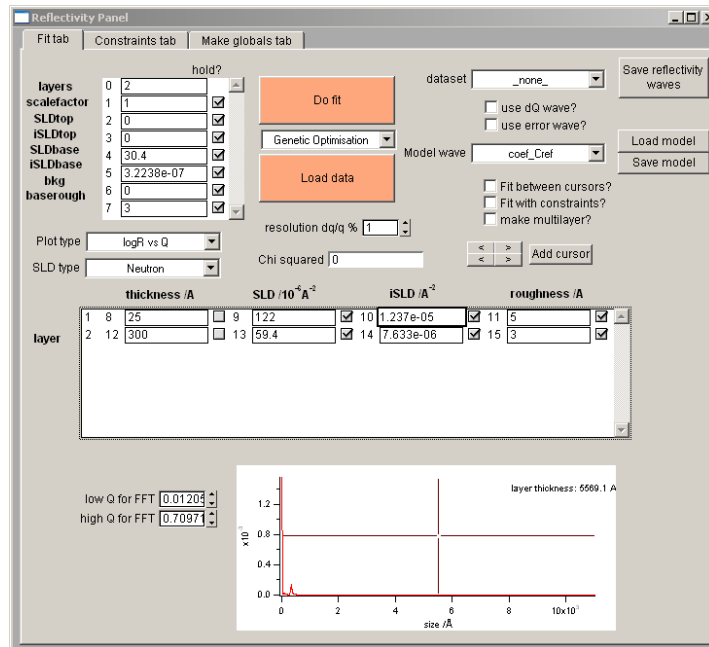
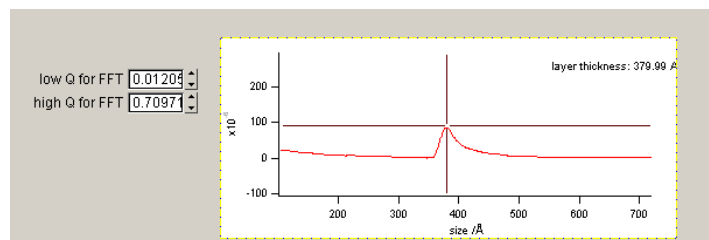Figure 36: Reflectivity data panel after defining the model parameters.

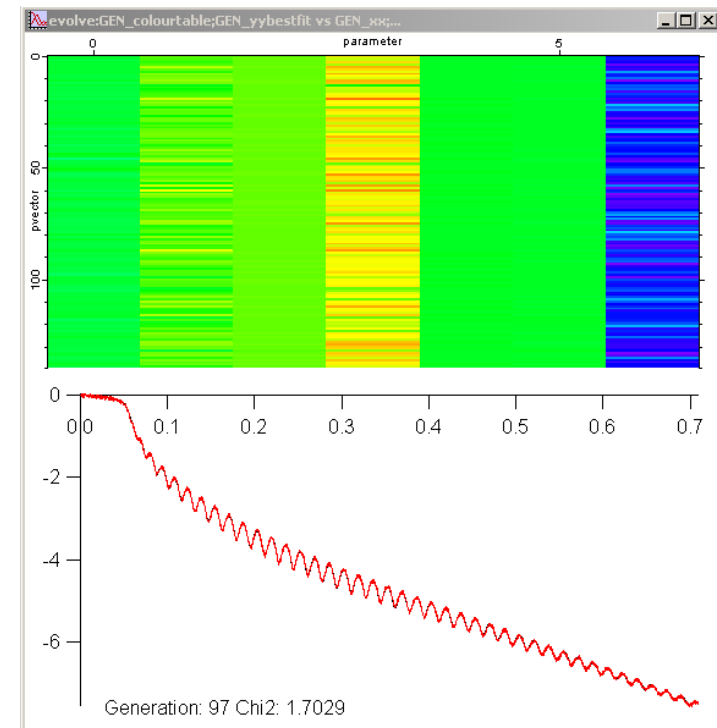Figure 37: FFT (Patterson) of experimental data.

Figure 38: Final fit result; in red the experimental data, and in black the best fit.

6   Practical exercise *LEPTOS*

in this section a very thin layer of ZnO on top of Si will be fitted. The data, zno_si_leptos.dat, are already in *LEPTOS* format, so the file can immediately imported into *LEPTOS*. Define a thin ZnO layer on top of the Si substrate, and take 349 data points between 0.00 and 3.50 (Gaussian FWHM parameter in the 'diffractometer' tab set at 0.01). Create a 'Fit Curve' object that comprises the simulation and the experimental data. Try first to adjust the model by hand in order to find a suitable starting point for the fit. Your starting point should be approximately like this (Fig. 39):

You will find that it is very difficult to find a good starting point. Try now fitting with a suitable optimisation algorithm. What results do you get with the different algorithms? The final fit should look like here below (Fig. 40):

The second exercise concerns the determination of the mass density of an approximately 400 nm thick organo-silicon layer on a wafer of Si. The difficult point is that the interference fringes due to the thickness are not visible. The data are in *IMD* format (ech390.txt) and should therefore be transformed into *LEPTOS* format with *REFCONVERT*. Create a new folder in *LEPTOS* and load the experimental file. Create a new amorphous material SiOCH in the MDB database and set up the thin layer system with Si as substrate.

Fig. 41 gives the reflectivity calculated for a 400 nm thick organo-silicon film on silicon where the initial density is $\rho = 1$ gcm^{-3}, and the substrate/film and film/air roughness 0.7 and 0.5 nm, respectively. It is shown clearly that there are fringes which are absent in the experimental reflectivity curve. It is noted that a gaussian FWHM of 0.006 was used to convolve the simulated data. In order to get rid of the fringes, you can either increase the gaussian FWHM, or you can artificially increase the thickness. The thickness is not interesting, since it cannot be determined from the fringes in the experimental curve. Try both approaches, and conclude that increasing the gaussian FWHM is the best method. Why? A value of 0.012 should be sufficient. Create now a Fit Curve object and try to find the density and eventually the thickness of the thin film. Why is it possible to find a thickness (there are no fringes)? You see in Fig. 42 that the experimental curve was not normalized to 1 in the angular region below the first critical angle. Try to fit the data while excluding this part and see if it makes a difference.

Make a zoom around the critical angles. Are you satisfied? In the plot below (Fig. 43) you can see that the first calculated cristical angle is too much to the
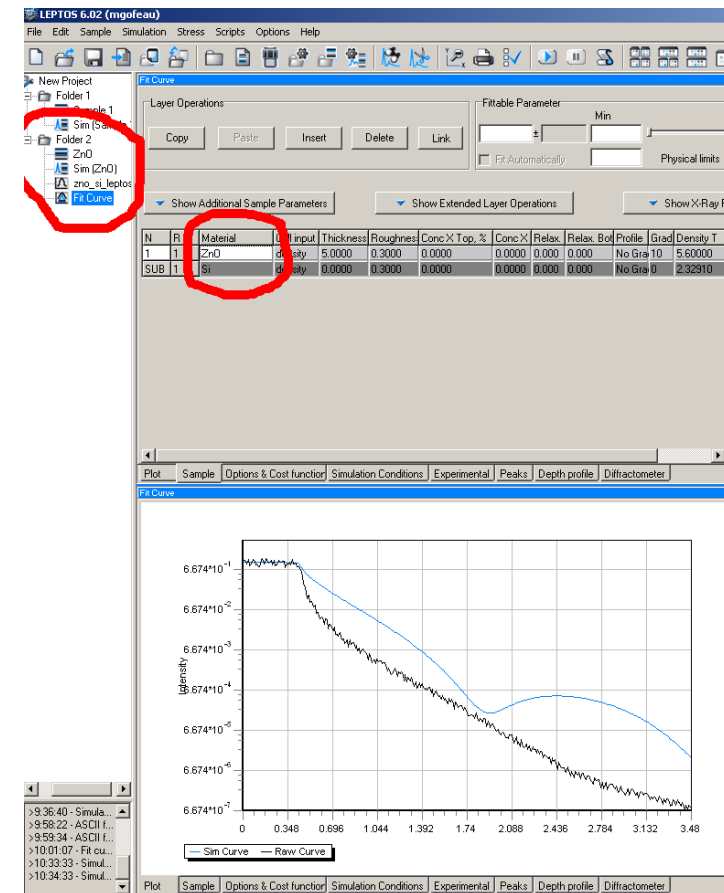

Figure 39: Starting point in *LEPTOS* for the fit of the thin ZnO layer on Si

right and the second too much to the left. The second concerns the critical angle of the silicon film which should in principle not shift, so it could be that there is small misalignement of the sample - probably a height problem. You can, with *LEPTOS*, correct for this misalignement by creating a new Fit Curve object, but now by hand.

Click for that on the folder belonging to this experiment and go then to the Transformation tab. Choose as reference curve the simulation with the proper values and as curves to scale the experimental data. The best is to do a manual
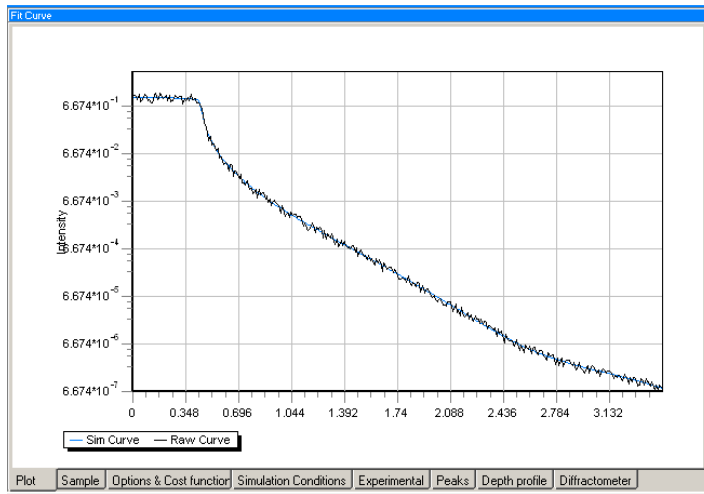
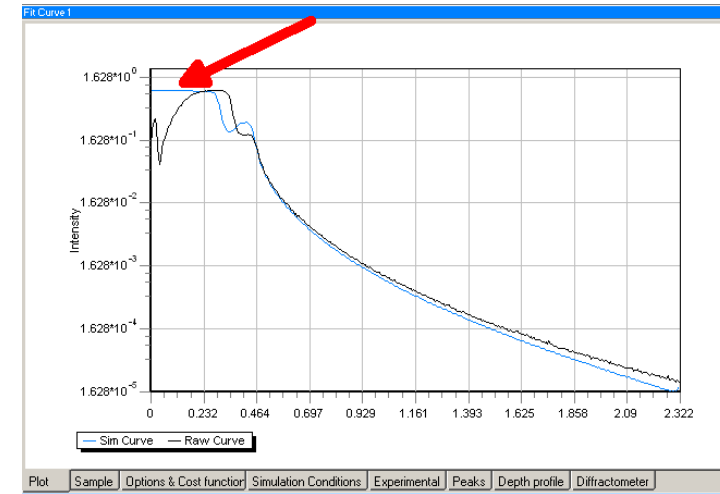Figure 40: Final fit results in *LEPTOS* for the fit of the thin ZnO layer on Si
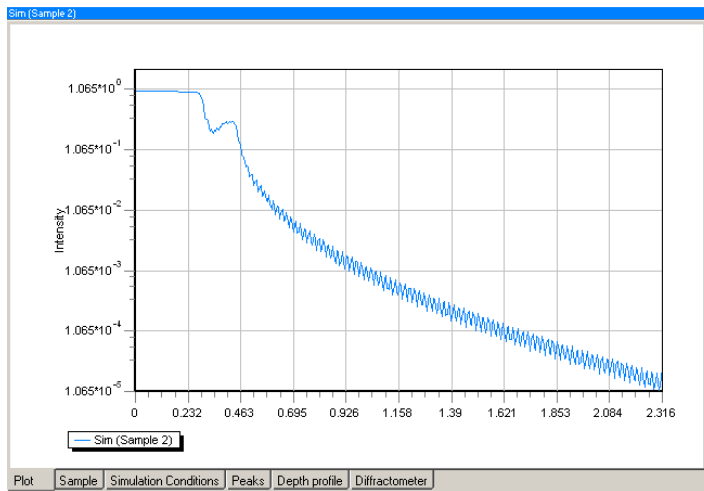

Figure 41: Preliminary simulation of a 400 nm thick organo-silicon film ($\rho = 1$ gcm^{-3}) on silicon.

Figure 42: Experimental data and preliminary data simulation of the organo-silicon film.
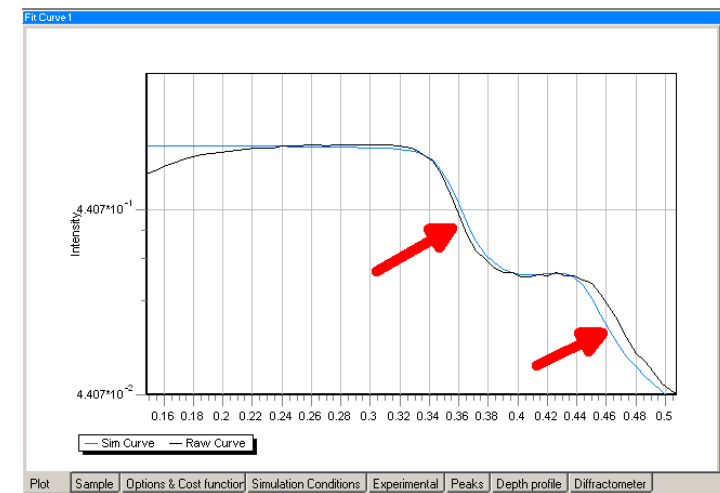

Figure 43: Organo-silicon film fit of the experimental data around the critical angles

drag in the x-direction (Fig. 44). Select 'Use Transform' and click on 'Create Fit
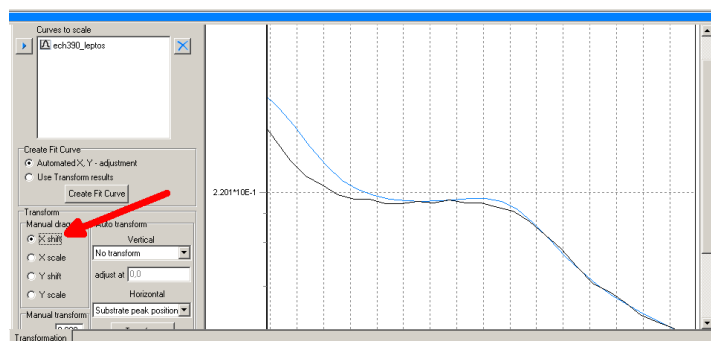
Curve'. Try now to fit again.

Figure 44: Manual correction of a theta displacement.

WIth the genetic algorithm it is now pretty easy to find a very good fit (Fig. 45). Note that this has a very important influence on the final thickness and density which were 350 nm and 1.41 gcm^{-3}, respectively, before the manual adjustment and 391 nm and 1.34 gcm^{-3} after that adjustment. It is to be noted as well that the exact value of the density depends on the exact chemical composition, which was taken here as SiOCH. If another chemical composition had been taken then the thickness could have changed as well. Try for example to fit with a composition of SiO$_{0.5}$C$_2$H$_6$ and compare with the earlier results. You can also compare the results with a fit done with *MOTOFIT*.
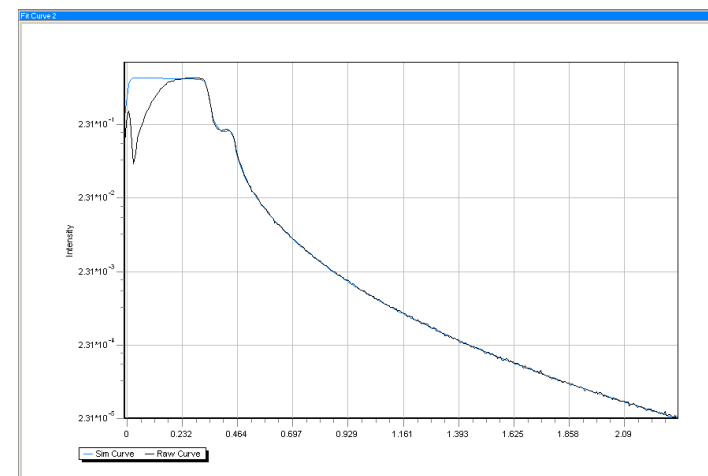

Figure 45: Final fit of the x-ray reflectivity data of the organo-silicon film

7   *STOCHFIT*

In this section we will see how *STOCHFIT* can be used to detect the existance of a second layer which will not be detected automatically by *LEPTOS* or *MOTOFIT*. Details will be found which can not be found using the classical methods, but eventually we may return back to the classical methods with the results found with *STOCHFIT*. We use the same data as before, *i.e.* lpvd1corrc2.txt (amorphous carbon film on silicon) properly converted to *STOCHFIT* format using *REFCONVERT*. Start *STOCHFIT* and load the experimental data. The substrate SLD is called 'Subphase SLD' in *STOCHFIT* language and the unities are in 10^{-6} Å^{-2}. A fronting medium can be defined ('Superphase SLD'), e.g. water, but here it should be at 0.00, since air is the fronting medium. The absorption values are in Å^{-2}, but using this fitting method, they can be neglected - possibly not if heavier elements are involved. The X-ray wavelength should be set at 1.5405 Å. Set the subphase SLD at 20, the film SLD at 11.0, and the film thickness at 83 Å in accordance with what was found with the other two programs. The number of boxes should be set at 2-3 times the thickness of the layer, take 200. If done, the screen should look as in Fig. 46. Note that the standard way of representation of the reflectivity in *STOCHFIT* is to divide the true reflectivity by the Fresnel reflectivity of the substrate. This gives an enhanced
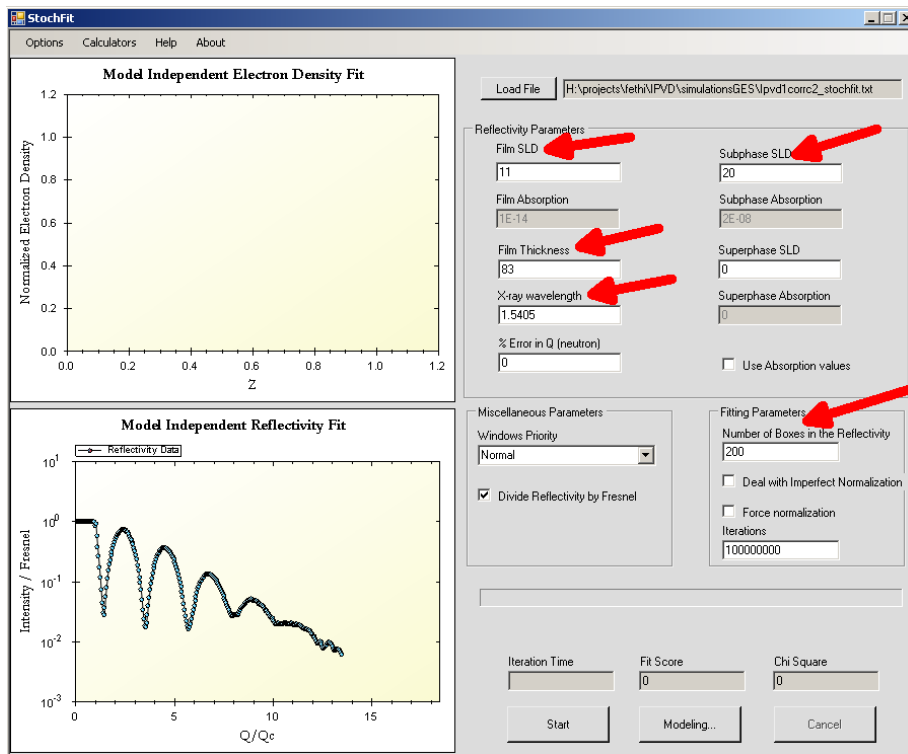
view of the Kiessig fringes.

Figure 46: *STOCHFIT* screen at the start of the optimization.

Figure 47: *STOCHFIT* screen at the end of the optimization.

Click on 'Start', sit back and see how the iteration evolves. This may take several minutes or more, depending on the speed of the processor. A 'Chi Square' of about 7145 is sufficient in this case. Click now on 'Cancel' and confirm upon the question if you are really sure. The screen should look like this (Fig. 47):

Click now on 'Modeling' and a new screen pops up, in which you can model the electron density profile. You should decide for the number of layers to take and if you want to model each tiny detail. In this particular case, it seems judicious to neglect the waviness in the thin film plateau of the density profile. On the other hand, it seems that at the substrate/film interface there is more density than usual and that this cannot be modeled correctly by a large substrate/film roughness. Set now the values of the normalized rho and the thickness at val-
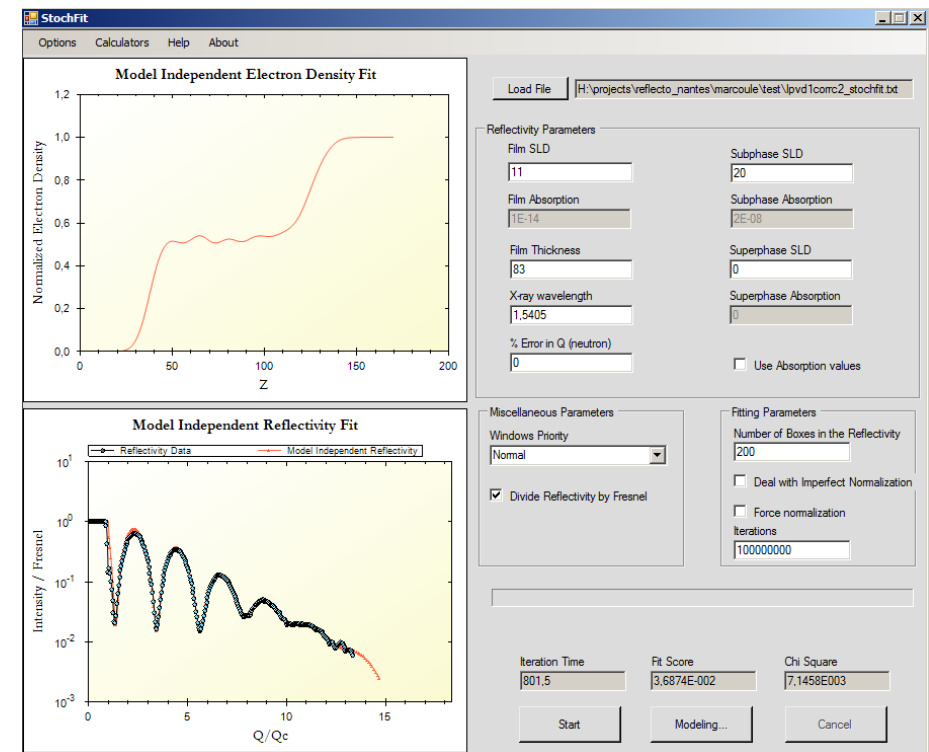
ues as to make coinciding the blue line with the black line (Fig. 48).

Clicking on 'Fit' should give now two layers with normalized rho's of 0.52 and 0.69, respectively, thicknesses of 79 and 12 Å, respectively. You can now continue by doing a classical reflectivity fit by using these two pre-defined slabs. For that, click on 'Reflectivity Fit' in the 'Profile Modeling' panel and you will get the 'Reflectivity Modeling' panel (Fig. 49):

You can decide here which parameters you do not want to vary by clicking on the 'Hold' tick boxes. Try to refine everything at once by clicking on 'Fit'. Click on 'Fit' and you will end up with a nearly perfect fit shown in Fig. 50. You can try to reproduce these fit results in *MOTOFIT* or in *LEPTOS* by introducing a second layer in these programs, and by converting the film parameters in Fig. 50 to *MOTOFIT* or in *LEPTOS* parameters. Note that the electron density
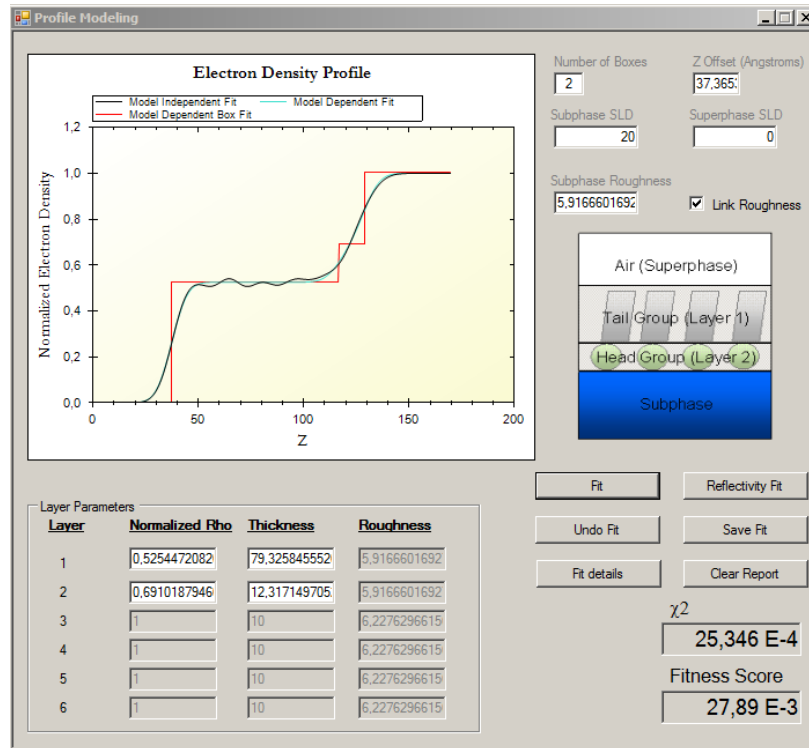
Figure 48: Profile modeling in *STOCHFIT*.

Figure 49: Classical reflectivity modeling in *STOCHFIT*.

normalization in *STOCHFIT* is done with respect to the substrate ('Subphase') SLD.

Alternatively you can try 'stochasting fitting'. This is a stochastic random search within user specified limits and can take much more time than the classical fit, and you will end up with a couple of solutions that are not all very physical, *e.g.* a very large roughness combined with a rather small layer thickness. This should be used with care. Fig. 51 gives the results of stochasting fitting for the present data set. You can see that rather different electron density profiles yield nearly identical reflectivity profiles.

It should be noted that *STOCHFIT* is probably only a good choice for relatively thin layers, *i.e.* for total layers less than 20 or 30 nm thick. Calculations become very long for thicker layers.
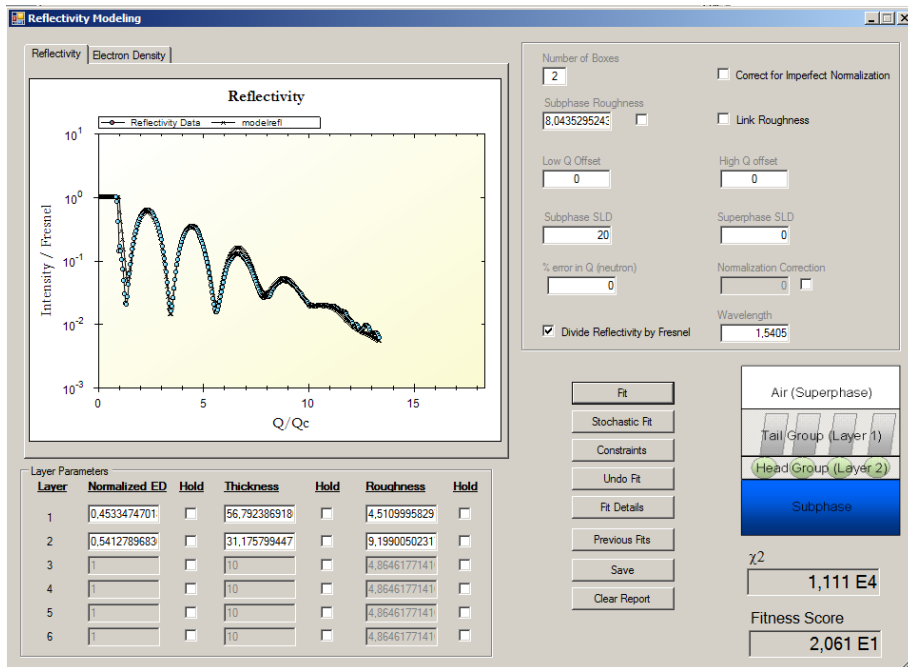
Figure 50: Final fit results for the amorphous carbon layer system using the classical reflectivity modeling in *STOCHFIT*.
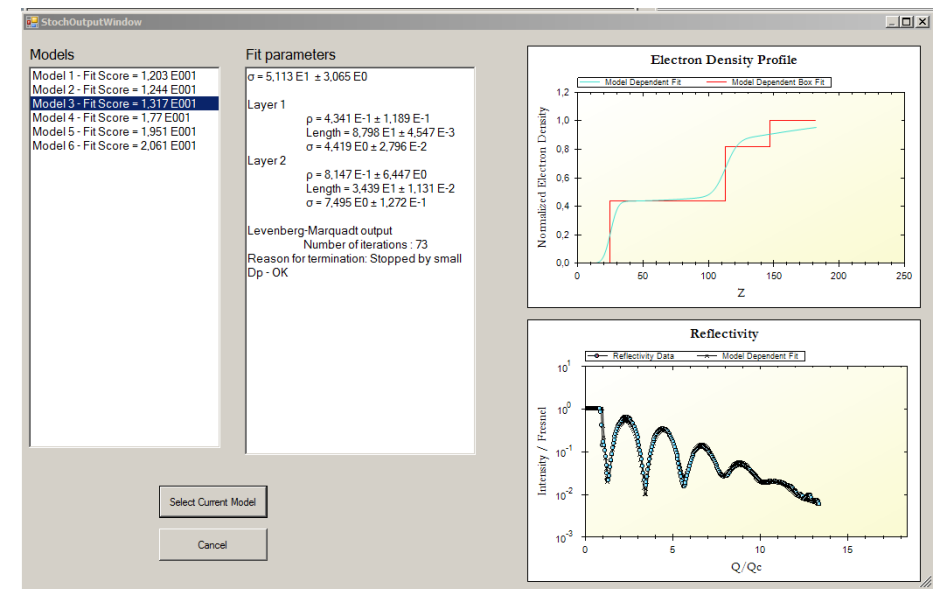

Figure 51: Final fit results for the amorphous carbon layer system using the stochastic fit module in *STOCHFIT*.

8   *REFLEX*

REFLEX has been developped by Alain Gibaud and Guillaume Vignaud and uses the MATLAB library for the calculations. The MATLAB runtime library can be downloaded for free and needs to be installed for running *REFLEX*. The installation instructions can be found on the *REFLEX* website (see the introductory chapter of this document; do not forget to download the manual). The reflectivity data need to be in q-units and should not contain the $q = 0$ data point. Alternatively θ or 2θ can be read in the program and should then be converted to q data using the predefined wavelength. The 'density' data are defined in q_c units (Å^{-1}) and can be obtained from the more normal scattering length density ρ (units (Å^{-2})) by the following formula: $q_c = 7.088\sqrt{\rho}$. In versions of *REFLEX* starting from 31 (*dd* October 2nd, 2018) 'density' values can also be defined in terms of the scattering length density ρ and δ. *REFLEX* contains a database and a calculator for the conversion between mass density ρ_m using the chemical formula to q_c and the absorption coefficient β. A number of materials can be called by their name, other materials can be defined and added to the database. Optical constants between 10 eV and 30 keV are available. Note also that the program can be used for neutron reflectivity and more specifically for soft X-ray reflectivity where reflectivity changes become visible between *s*-polarized and *p*-polarized beams. We will not treat the latter aspects in this tutorial.

The *REFLEX* program interface is divided into three panels, a panel with general parameters, a panel with the reflectivity graph, and a panel with the layer parameters. *REFLEX* uses by default a three-layer model on top of a substrate and with the possibility to define a fronting medium (air/gaz; in the layer panel). The three-layer model consists of a top-layer (capplayer), a multi-layer (layer 1···layer n) and a buffer layer between the multilayer and the substrate (Fig. 52). In order to create a true multilayer the periodicity can be defined. For a simple layer on top of a substrate either the number of capplayers, the number of layers, or the number of buffer-layers should be set to 1 and the other two to zero. Other panels can pop up for certain tasks: *e.g.* a new panel for fitting, a panel for the calculation of the auto-correlation function (FFT), or the calculation of the density profile.

We start with some simulations. Define a Si substrate, and for the 'capplayer 1' set $q_{c,film}$ at 0.02 Å^{-1} with a thickness of 10 Å and $\beta_{film} = 10^{-7}$. Set q_{max} at 0.05 Å^{-1}. Set the sample length at 100 mm. Leave the other instrumental and sample parameters as they are. What is the value of $q_{c,film}$ that you can
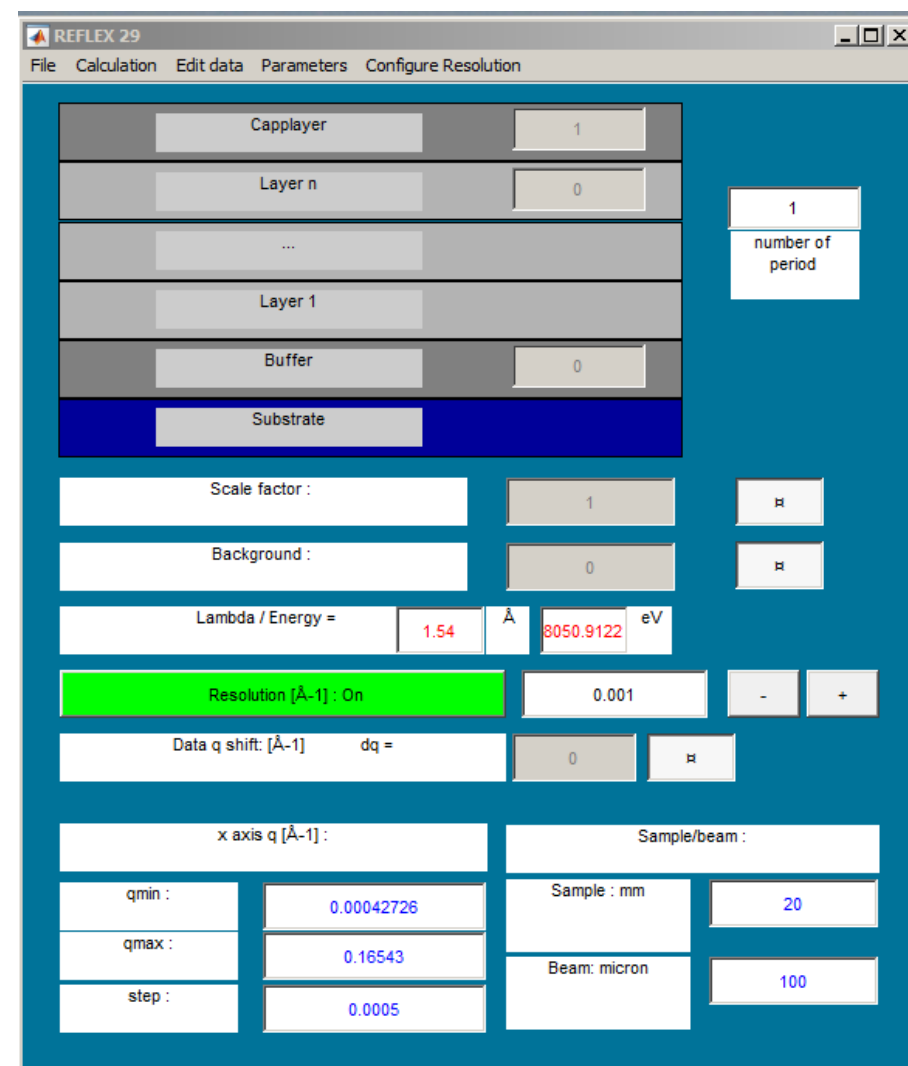

Figure 52: General parameters panel of *REFLEX*.

read in the figure? Now change the thickness using the slider to approximately 100 Å and then to 1000 Å. How does the experimental $q_{c,film}$ change? At 1000 Å the experimental $q_{c,film}$ is very close to the theoretical $q_{c,film}$ (Fig. 53) and only now the mass density can be determined directly from the experimental $q_{c,film}$.

For lower thicknesses a fitting of the complete curve need to be done in order to determine a value for $q_{c,film}$ that can be used to derive a value for the SLD (Scattering Length Density) or mass density - if the chemical composition is known - of the film. Note also that only for relatively thick layers Kiessig fringes can be observed.
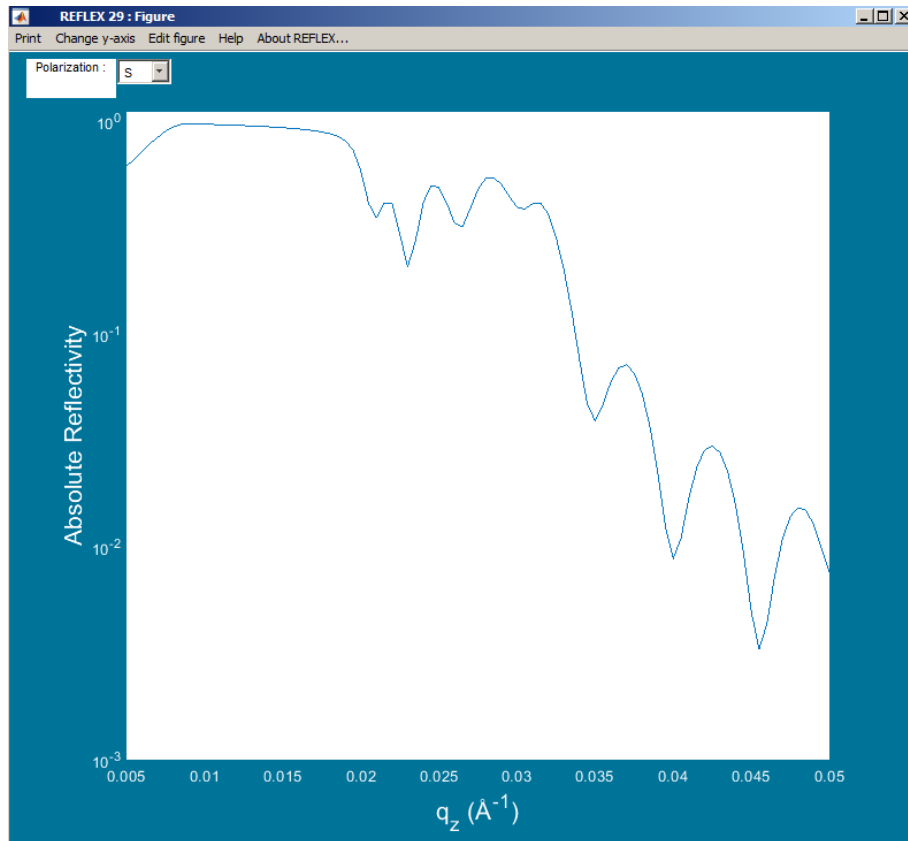

Figure 53: Reflectivity of a low-density capplayer of 1000 Å on a silicon substrate).

Now change the value of β_{film} to lower and higer values. What do you observe? Does $q_{c,film}$ change? Note that you can get the screen coordinates as reflectivity coordinates by using the 'Data Cursor' option of the upper horizontal menu of the 'Figure' panel. Since the value of β_{film} is highly chemical sensitive,

this effect can be used to extract chemical information from a reflectivity curve. What happens more if β_{film} is really high, *e.g.* 3.10^{-7}? Answer: the plateau of external reflection is not flat anymore, which makes it harder to do a direct extraction of $q_{c,film}$. Change now the sample and beam parameters in the general parameters panel. A specificity of *REFLEX* is that it takes into account sample and beam parameters in order to correct for the 'spill-over' effect. This affects only very low angles (Fig. 54; *T* is the thickness of the beam, *L* is the length of the sample and *F* is the footprint of the beam on the sample):
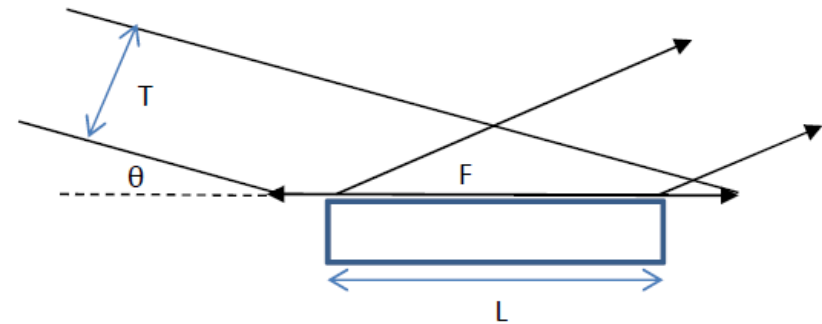

Figure 54: Spill-over effect (picture taken from the *REFLEX* manual).

Beam sizes of 100 μ and sample lengths larger of equal than 50 mm give mostly satisfactorily results. Verify what happens when you change the sample size from 100 to 20 mm. You should absolutely avoid that the spill-over angle is larger than the critical angle, although if you are really sure about these parameters *REFLEX* will be able to sort you out of these problems, unlike other reflectivity programs. Note also that *REFLEX* has the possibility to use a measured direct beam for the correction of these effects, *i.e.* it can take into account the non-rectangular shape of the direct beam (that has normally a shape that is in between a gaussian and a lorentzian). For this go to 'Configure Resolution in the 'General Parameters' panel.

Define now a capplayer that is denser than silicon (*e.g.* 0.06 Å^{-1} and $\beta_{film} = 3.10^{-7}$) and change the thickness of the layer between 10 Å and 1000 Å. Set q_{max} at 0.2 Å^{-1} and leave beam size and sample length at 100 μ and 20 mm, respectively. At what thickness the experimental $q_{c,film}$ becomes equal to the theoretical $q_{c,film}$? At what thickness the Kiessig fringes become visible?

Maybe it helps if you set q_{max} temporarily to larger values. Investigate the effect of surface roughness and substrate/film roughness on the appearance of the Kiessig Fringes and thus the possibility to determine very low thicknesses from X-ray reflectivity curves. With a proper data collection strategy and a well aligned diffractometer it should be possible to measure reflectivities down to 10^{-7}. Set the background at half this value. You will find out that with a substrate/film roughness of 10 Å, an excellent surface roughness of only 3 Å it becomes nearly impossible to determine the thickness of a nominal 30 Å thick layer (Fig. 55). With the roughness values of substrate and surface exchanged it is hardly better.

What is the upper thickness limit you can determine with X-ray reflectivity? This depends in the first place on the beam size perpendicular to the goniometer axis, in the second place on the minimum step size of the goniometer, and in the third place on sample parameters such as density contrast and surfacial and interfacial roughnesses. The half width at half maximum of a good diffractometer can be as low as $\Delta\theta = 0.008^0$. In order to convert to q units apply the following formula: $\Delta q_z = 2\pi\Delta\theta/\lambda$ with $\Delta\theta$ in radians, giving $\Delta q_z = 0.0006$ Å. Using very modern diffractometers with optimal optical elements one can half this resolution. The minimum step size on older diffractometers is usually $\Delta\theta = 0.001^0$, but step size on very modern diffractometers can be $\Delta\theta = 0.0001^0$. Do an investigation with different instrumental and sample parameters to determine what thicknesses can be determined using X-ray reflectometry. Remember that, in order to do a correct fit of the reflectivity curve, one should have approximately 8 points between two subsequent Kiessig maxima.

In the first example we try to fit the reflectivity of an organic layer on top of a silicon substrate (file *orga1.dat*). The nominal thickness is 1000 Å, the sample length was 20 mm, the beam thickness 100 μ and the resolution 0.001 Å^{-1}. Load the data and define a proper model for a one-layer system. Do not forget to set the correct resolution. Using the default values, the reflectivity panel should look as in Fig. 56. for the moment no density no absorption and no thickness is defined for the layer. Try to get an idea about approximate values for q_c and the absorption coefficient β by using the on-line SLD calculator or the build-in *REFLEX* calculator. For the latter option, go to the 'parameters' menu in the general parameters panel, then to 'Database', and then to 'Add new Material'. A typical organic compound could have a density between 0.9 and 1.4 gcm^{-3} and as chemical elements C, H, N, and O. The name that has been given for the compound can be used in the 'parameters' panel for setting initial values
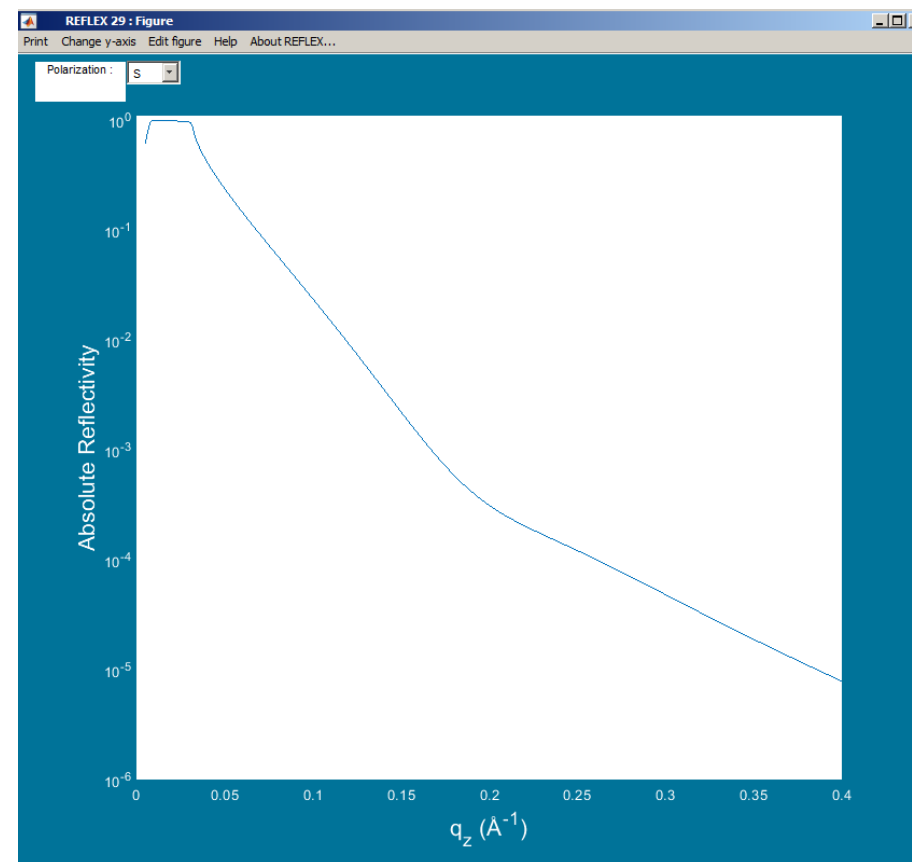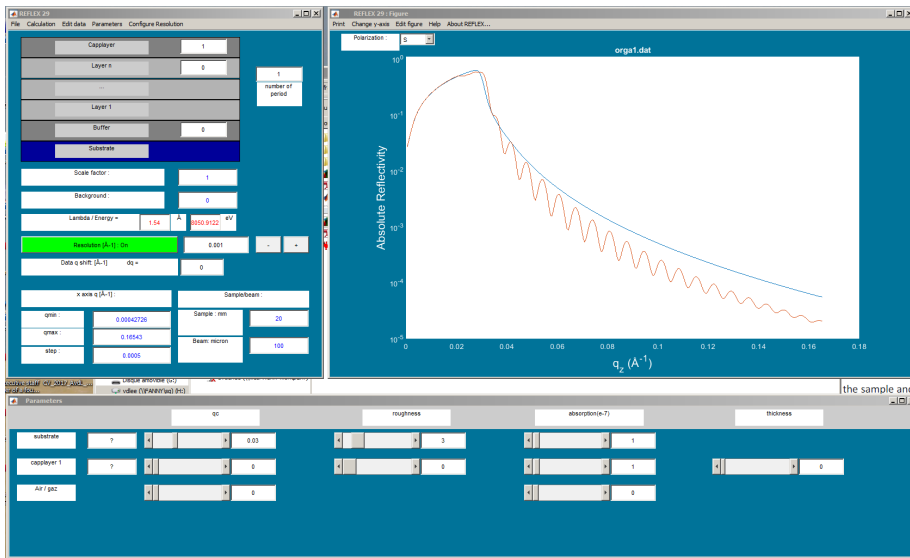

Figure 55: Simulation of the reflectivity of a very thin dense layer on silicon with *REFLEX* manual).

for q_c and β. An initial value for the thickness can be the nominal value of the value obtained by calculating the auto-correlation function. For the latter go to 'Calculation' and 'FFT' and choose one of the algorithms (Fig. 57). Check the differences and set a value for the thickness of the organic layer.

You can now adjust the calculated curve by adjusting the sliders. There is no reason to adjust other parameters than the substrate/film roughness parameter, because the substrate is known and its bulk parameters should remain fixed. Try to get an ajustment manually. What are the final parameters? Now you

Figure 56: *REFLEX* panels after loading the *orga1.dat* file.

Figure 57: FFT calculation without window.
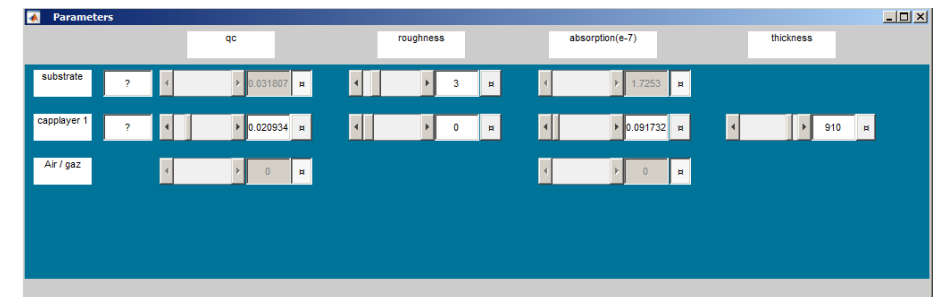
Figure 58: Parameter panel after having fixed some of the parameters.

can also try to adjust the calculated curve by a fitting procedure. For that go to 'Calculate' and 'Fit' and a Fit panel should open. You should now fix the parameters that you do not want to refine, *i.e.* the substrate density and the substrate absorption. Parameters can be fixed by pressing the button right after the parameter value. The parameter value becomes then greyed-out (Fig. 58) and the refinement button blue. Choose the Levenberg-Marquardt algorithm. Try to run the fit and check the results. The match should be perfect since the 'experimental' data have been simulated. If the match is not perfect, try to adjust manually or do a multi-start (Fig. 59). What values for q_c and β do you obtain?

Calculate now using *REFLECTOOLS* the mass density from q_c and also from β. *REFTOOLS* needs the real and imaginary part of the scattering length density ρ, as well as the correct formula. The formula's that relate q_c and β to the real and imaginary part of the scattering length density are $\rho' = (q_c/7.088)^2$ and $\rho'' = 2\pi\beta/\lambda^2$, respectively. The nominal composition of the thin film is $C_{12}H_5O_2N_3$.

In the second example we fit the experimental reflectivity of a nominally 100 nm thick thermal silica on a silicon substrate. Quit *REFLEX* and start it again. The half width at half maximum of the direct beam is $\Delta\theta = 0.008^0$ and the length
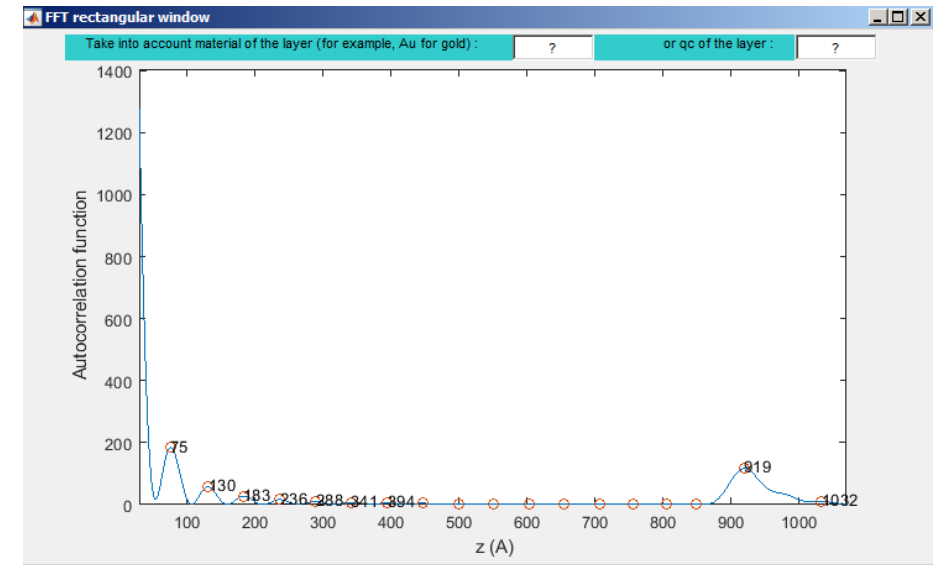
of the sample 20 mm. In order to convert to q units apply the following formula: $\Delta q_z = 2\pi\Delta\theta/\lambda$ with $\Delta\theta$ in radians. Import the file *bic0-reflex.txt* (note that in *REFLEX* the first point can not be at $q = 0.000$). After having imported the data, you should convert the θ data to q by selecting in the 'Edit data' menu the 'theta to qz' option. Now create a thermal silica in the database. Thermal silica has usually a density of about 2.20 gcm^{-3}. Make an estimation of the
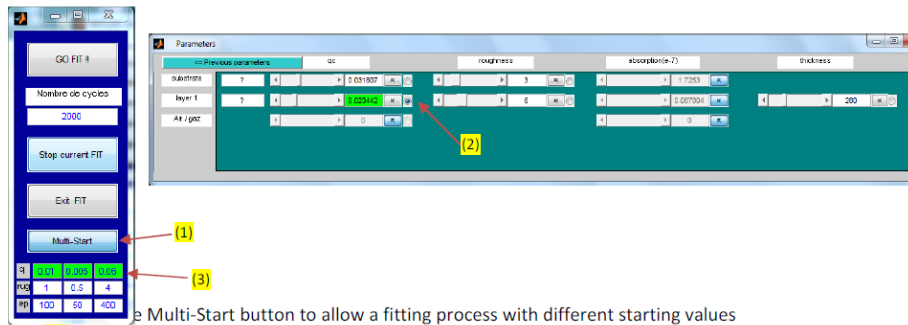
Figure 59: Multi-start possibility in *REFLEX*; picture taken from the *REFLEX* manual.

Figure 60: Importing and converting a θ-scan in *REFLEX*.

thickness by FFT or by adjusting the thickness slider. Fit the roughnesses. Note that you should probably adjust the scale factor, either by fitting or by manual adjustment. Note that the roughness between substrate seems to very difficult to fit and it should probably be fixed at a relatively low value. It is interesting to see that fitting this roughness diverges to a very large value and that the calculated reflectivity does not show up any fringes anymore while the χ^2 is lower (Fig. 61) than the best result with fringes (Fig. 62). If the adjustment completely diverges you can go back to the previous parameters by pressing the button 'Previous parameters' in the 'Parameters' panel. It is in general difficult to fit all parameters at once. What are your final results? Are the experimental and theoretical Kiessig fringes exactly overlapping? It appears that they are overlapping at some points, then for a certain interval not, and then start to overlap again. This is an indication of a 'beating' phenomenon, caused by a very thin layer either in between the substrate and the film or at the surface. Because this layer is very thin, it does not show up in the FFT autocorrelation function. You can try to model it by adding a very thin layer either at the surface or at the interface between the substrate and the layer.

A trial calculation using *STOCHFIT* seems to indicate that there is a 10% denser top layer at the surface of approximately 30 Å (Fig. 64). This model-independent fit gives a perfect overlap between the experimental and calculated Kiessig fringes. Do this fit and wait until it converges to $\chi^2 = 28210$ - this will
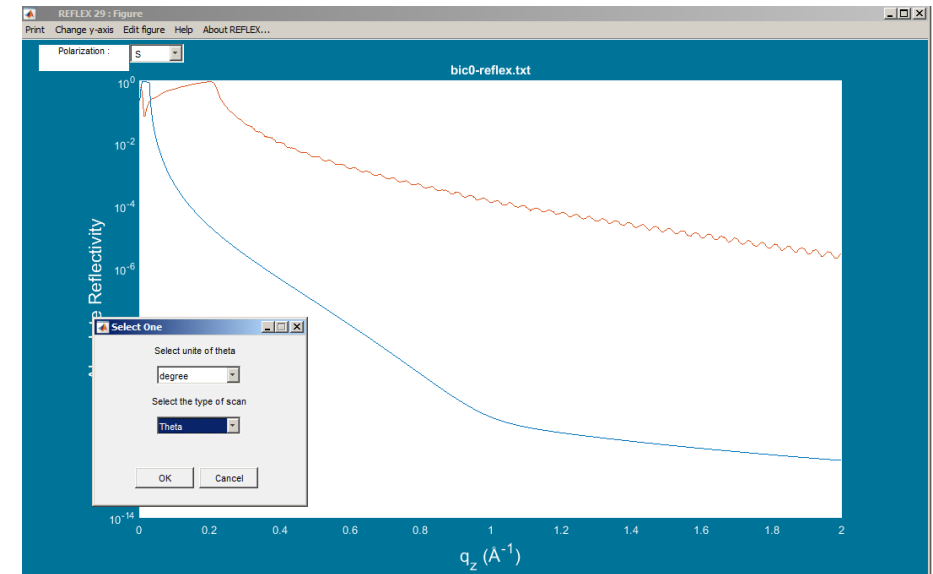
take quite a long time. Then try to model the system by a two slab-model either in *STOCHFIT* or *REFLEX*.

In the third example we want to study the reflectivity curve of a bilayer. Examples of this kind are encountered in metallic thin film which tend to oxidize when placed in air. The reflectivity curve of an oxidized niobium thin film deposited on a sapphire substrate is shown in Fig. 65. The upper layer obviously corresponds to the niobium oxide. The oxide layer grows as a function of time of exposure to air and reaches a maximum thickness after a few hours. Load the file *Sapphire_Nb.dat*.

The reflectivity curve displays a very characteristic shape which includes the following features:

- Short wavelength oscillations which can be identified with interferences within the (thick) nobium layer.

- A beating of the oscillations with a longer wavelength in qz which comes from the presence of the oxide (Nb_2O_5) on top of the niobium layer, this
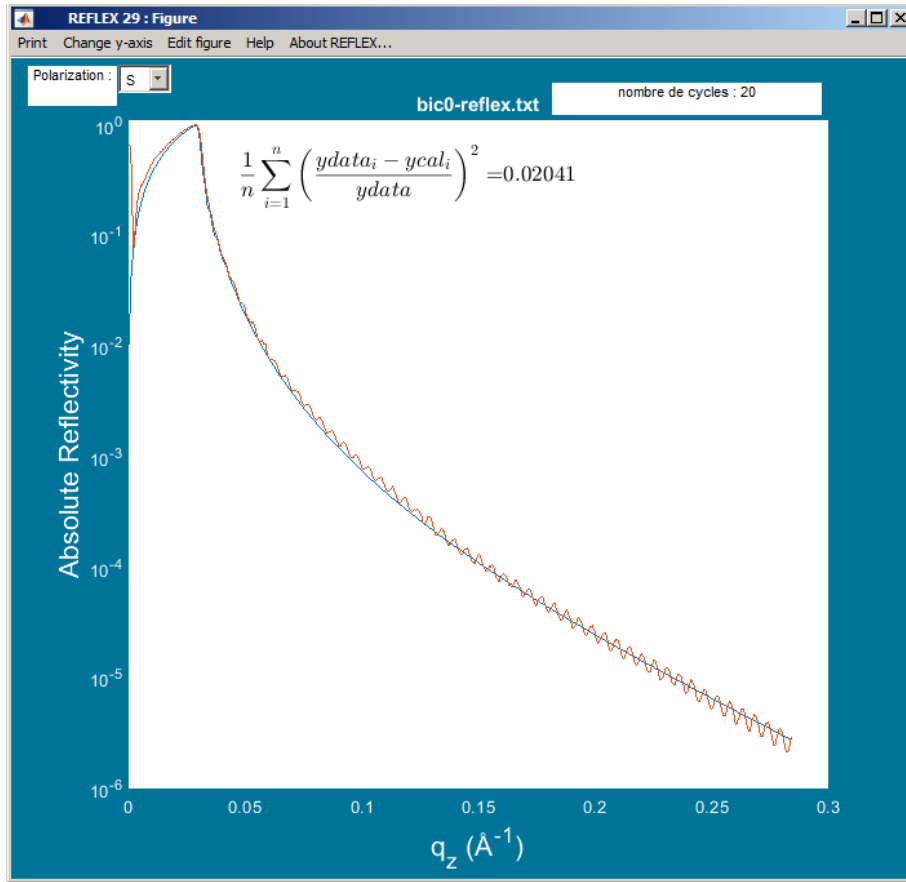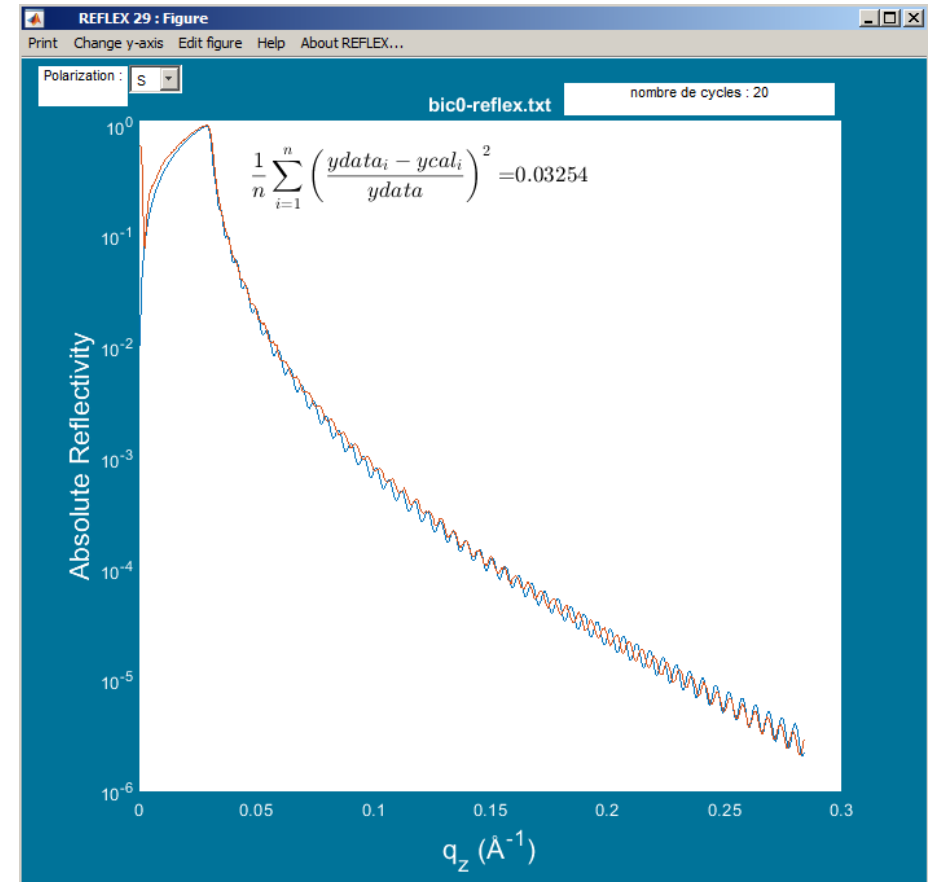
Figure 61: Over-fitting of data for *bic0* with low χ^2.

Figure 62: More the less correct fitting for *bic0*, but with a higher χ^2.

leads to two interfaces at nearly the same altitude from the surface of the sapphire substrate.

Start by checking which elements are present in the database (Sapphire Al_2O_3 ?, Niobium Nb? Niobium oxide Nb_2O_5?). For the latter option, go to the 'parameters' menu in the general parameters panel, then to 'Database', and then to 'Look at the database'. Create the missing ones ('Add new Material' menu). You can find on the internet that the density of Nb_2O_5 is 4.6 gcm^{-3}. Define a proper model for a two-layer system: Nb_2O_5 on thick Nb deposited on a sapphire substrate. A 'popup' menu 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 'qc' and 'absorption' fields of the selected layer. Make an estimation of the thicknesses by FFT. There are two peaks related to the thick layer of Nb and another associated with the total thickness of Nb+Nb2O5. The latter thickness is not reliable because the oxide is too thin. Enter the thickness of Nb and search for Nb2O5 by adjusting the thickness slider.
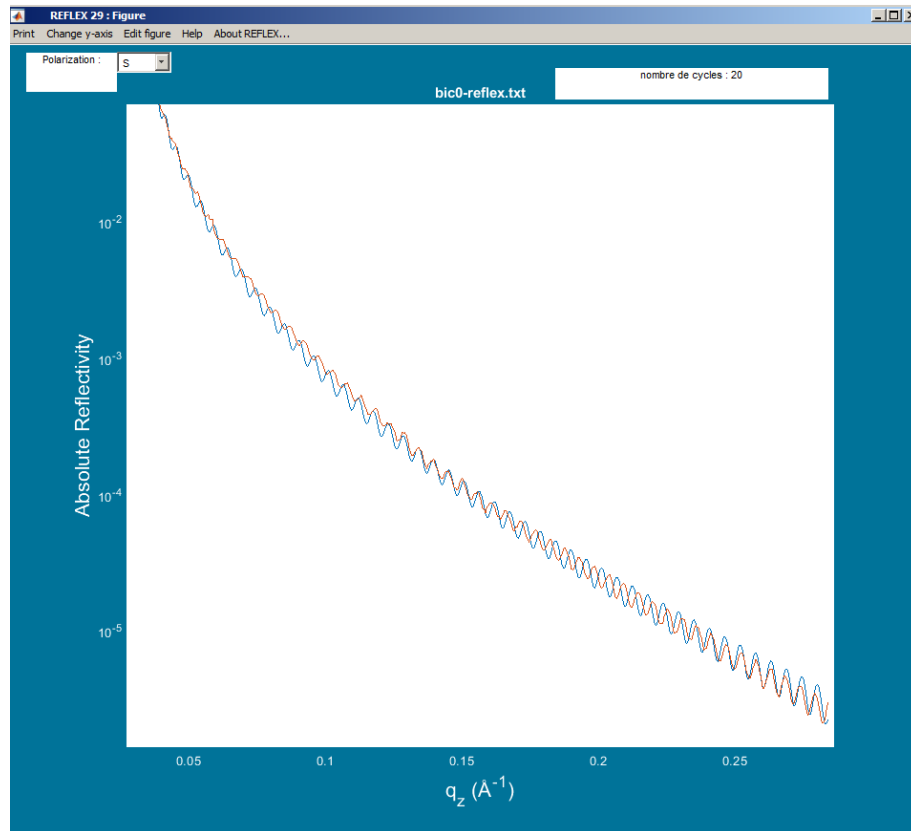
Figure 63: Signature of the presence of a second layer in *bic0*.

Figure 64: *STOCHFIT* model independent fit of the reflectivity data of *bic0*.

In the fourth example we want to fit the reflectivity of an ideal periodic multi-layer W/Si on a silicon substrate (free of natural oxide, Fig. 66). Import the file *multilyer.dat* which consists of two colons: one for q_z and the other for the normalized reflected intensity. Set the resolution to $\Delta q_z = 0.0005$ Å^{-1}, the sample length to 20 mm and the beam thickness to 100 μm. X-ray reflectivity loaded curve exhibits a maximum at very low wave vector transfer q_z related to total external reflection of the X-ray beam, Kiessig fringes and Bragg reflections related to the total thickness of the film and to the internal repetition of a well-organized motif, respectively. We can ve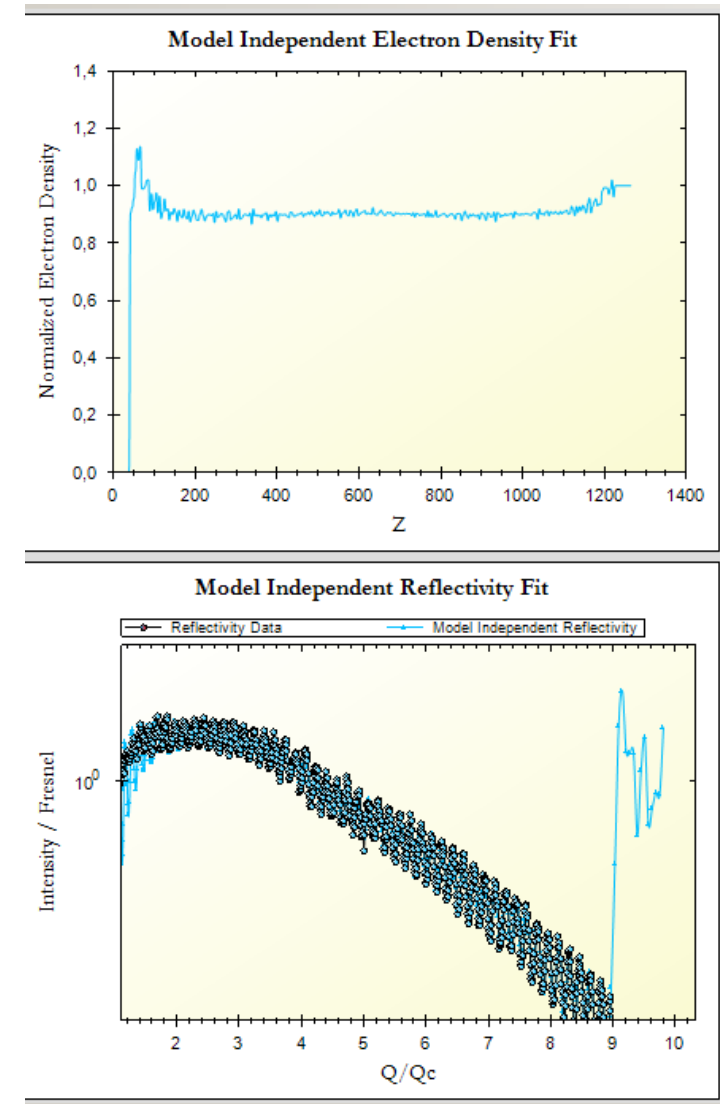rify that it is not obvious to get information from the FFT autocorrelation function which does not give any information on the total thickness of the multilayer and not either the number of periods. We know
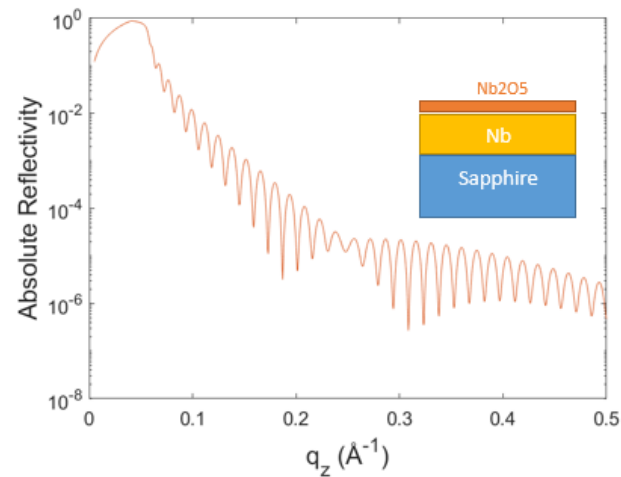
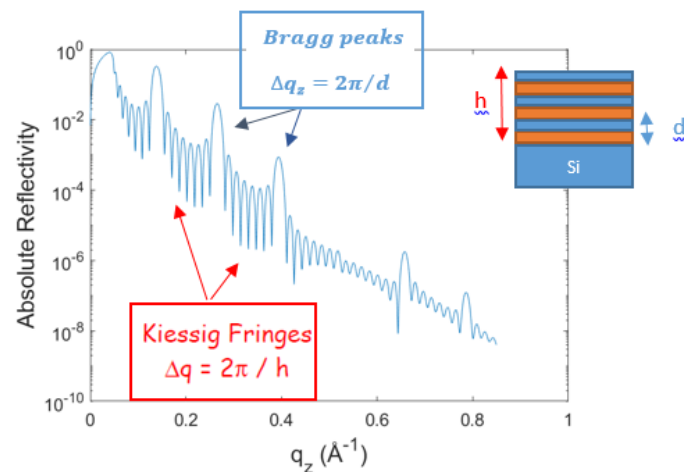Figure 65: *REFLEX* bilayer model and reflectivity for the third example.

Figure 66: *REFLEX* multilayerlayer model and reflectivity for the fourth example.

that the multilayer consists of a motif (tungsten/silicon bilayer) that is repeated several times. To configure the sample parameters (thickness of the bilayer,

number of period,...), it is possible to get information directly from the reflectivity curve according to the following rules:

1. The thickness of the bilayer (pattern) can be estimated from the following relationship: $d = 2\pi\Delta q_z$, where Δq_z is the spacing between 2 consecutive Bragg peaks.

2. The total multilayer thickness gives rise to Kiessig fringes between the Bragg peaks. There are $n - 2$ maxima in between two consecutive Bragg peaks for a flat multilayer with n periods.

3. Let d_1 and d_2 be the thicknesses which constitute the bilayer (with $d_1 > d_2$). If the ratio of the thicknesses d_1/d_2 is equal to an integer p, there is extinction of the $(p+1)$th Bragg peak on the reflectivity curve. Caution, this rule is only relevant if the roughness of the 2 layers are similar. It means that if there is no extinction of a Bragg peak, roughnesses are different.

4. Interfacial roughness between the layers leads to a progressive damping of the Bragg peaks with q_z, whereas the roughness of the sample surface reduces the intensity of the whole curve.

Determine the thickness of the bilayer, its number of repetitions and the ratio of thicknesses d_1/d_2. For the roughness, start by setting a roughness of 3 at all interfaces. Search for the best combination of d_1 and d_2 that makes up the bilayer. You can now adjust the calculated curve by adjusting the sliders and finally try to adjust the calculated curve by a fitting procedure.