EUROPEAN SPALLATION SOURCE

Reflectometry Concepts

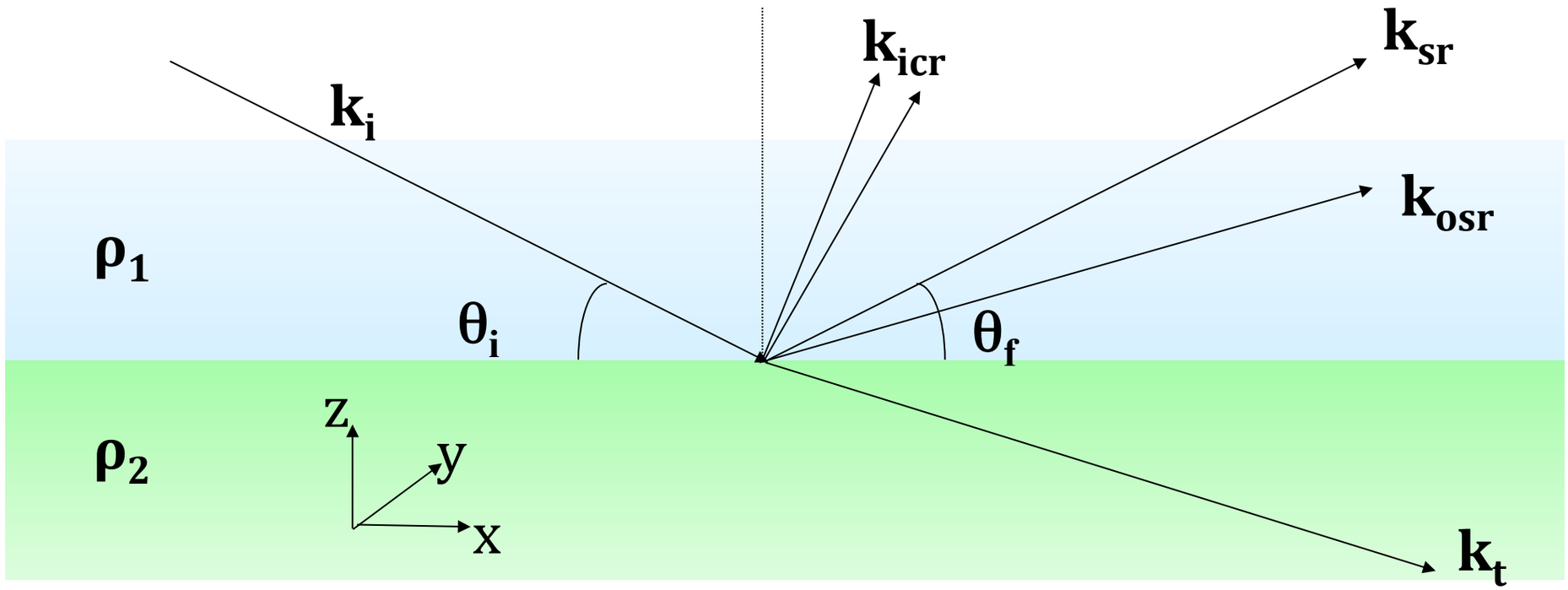
- Reflection from a planar interface
- Reflection from thin films
- Experiment
- Data Analysis in Motofit

Reflection from a Planar Interface

Reflection and transmission of neutrons:

$k = 2\pi/\lambda$

$\rho_1 \neq \rho_2$



The initial neutron with wave vector k_i may undergo specular reclection (sr), off-specular reflection (osr), incoherent reflection (icr) or transmission (t), which change its wavevector but not its energy (elastic scattering).

In specular reflection, the reflection angle θ_f equals the incident angle θ_i.

For a homogeneous material the potential is the same all over the x,y-plane – consider only z-component of k. (largest application today is disordered surfaces)

Neutron wavefunction

Schrödinger equation for an elastically scattered neutron:

$$\frac{\mathrm{h}^2}{2m}\nabla^2\psi(r)+V(r)\psi(r)=E\psi(r) \qquad (1)$$

Ψ(r) is the neutron wavefunction

E is the neutron energy – does not change in elastic scattering

V(r) is the nuclear potential of the material which the neutron travels through:

$$V(r)=\frac{h^2}{2\pi m}\left\langle\sum_j b_j\delta\left(\vec{R}-\vec{r}_j\right)\right\rangle \qquad (2)$$

V(r) = is only non-zero when neutron position R = r_j (nuclear radius ~10^{-15}m)

-> nuclei scatter like point objects (have no form factor)

Scattering length density in a homogeneous material:

$$\rho_n(z)=\sum_j n_j b_j \longrightarrow V(r)=\frac{h^2\rho}{2\pi m} \qquad (3)$$

constant potential

Neutron wavefunction

The neutron wavefunction is a complex plane wave:

(averaging over y) $$\psi(x,z) = e^{ik_x}\psi(z) \qquad (4)$$

k_x is the wavevector that describes the neutron motion parallel to the interface – does not change in elastic scattering

Combining (1) and (4): $$\frac{\partial^2\psi}{\partial z^2} + q^2\psi = 0 \qquad (5)$$

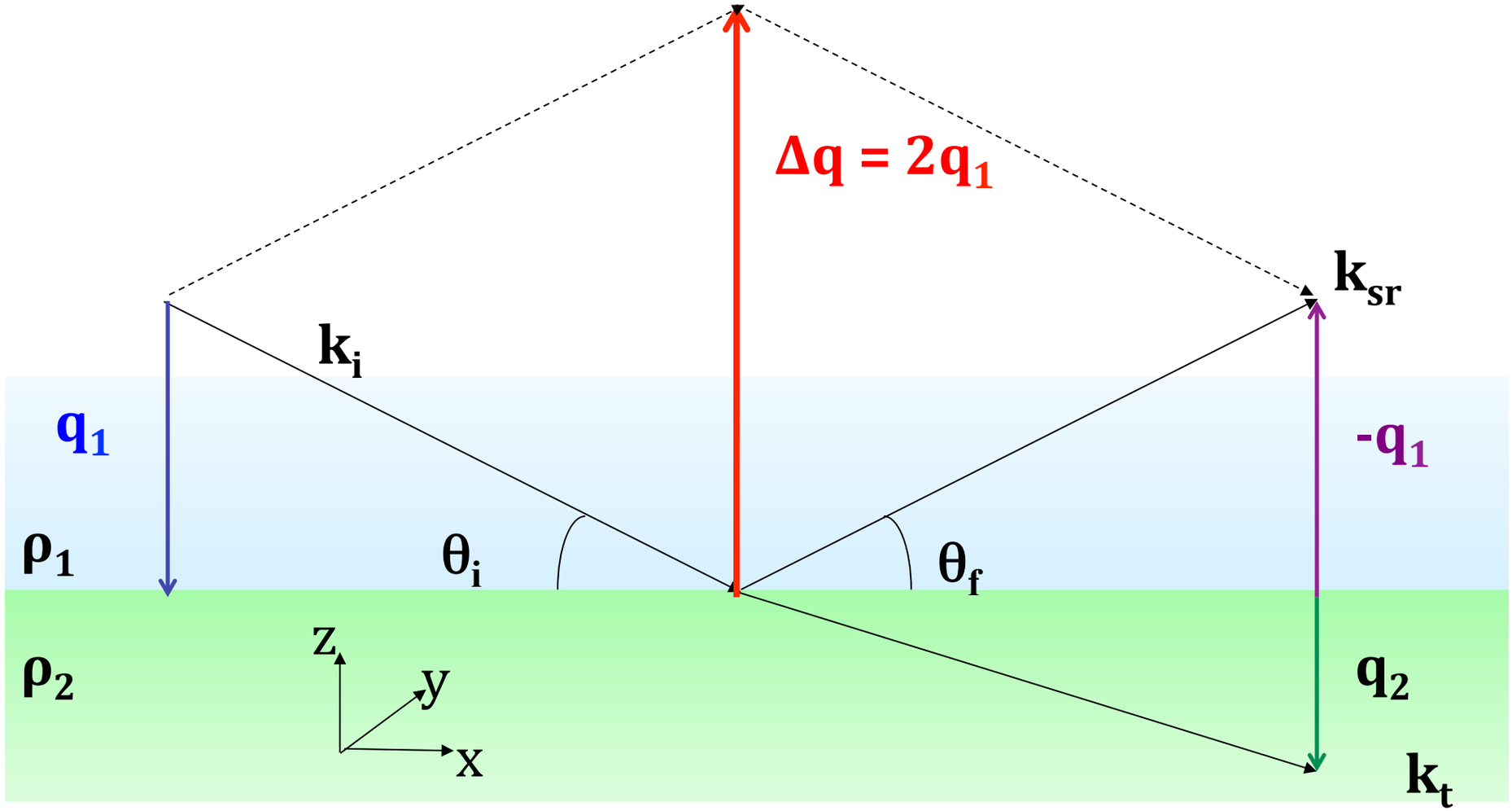
where $$q^2(z) = \frac{8\pi^2 m}{h^2}\left[E - V(z)\right] - k_x^2 \qquad (6)$$

is the momentum transfer or scattering vector normal to the interface.

Reflection from a Planar Interface

$k = 2\pi/\lambda$

$\rho_1 \neq \rho_2$



In specular reflection, the reflection angle θ_f equals the incident angle θ_i.

For a homogeneous material the potential is the same all over the x,y-plane – consider only z-component of k.

Reflection and Transmission coefficients

The neutrons are partially reflected and transmitted:

$$\psi(z) = \begin{cases} e^{(iq_1 z)} + re^{(-iq_1 z)} & z \geq 0 \\ te^{(iq_2 z)} & z \leq 0 \end{cases} \qquad (7)$$

Where r and t are the reflection and transmission coefficients. The boundary condition is that Ψ(z) and its derivatives are continuous at z=0:

$$1 + r = t \qquad \text{and} \qquad q_1 - q_1 r = q_2 t \qquad (8)$$

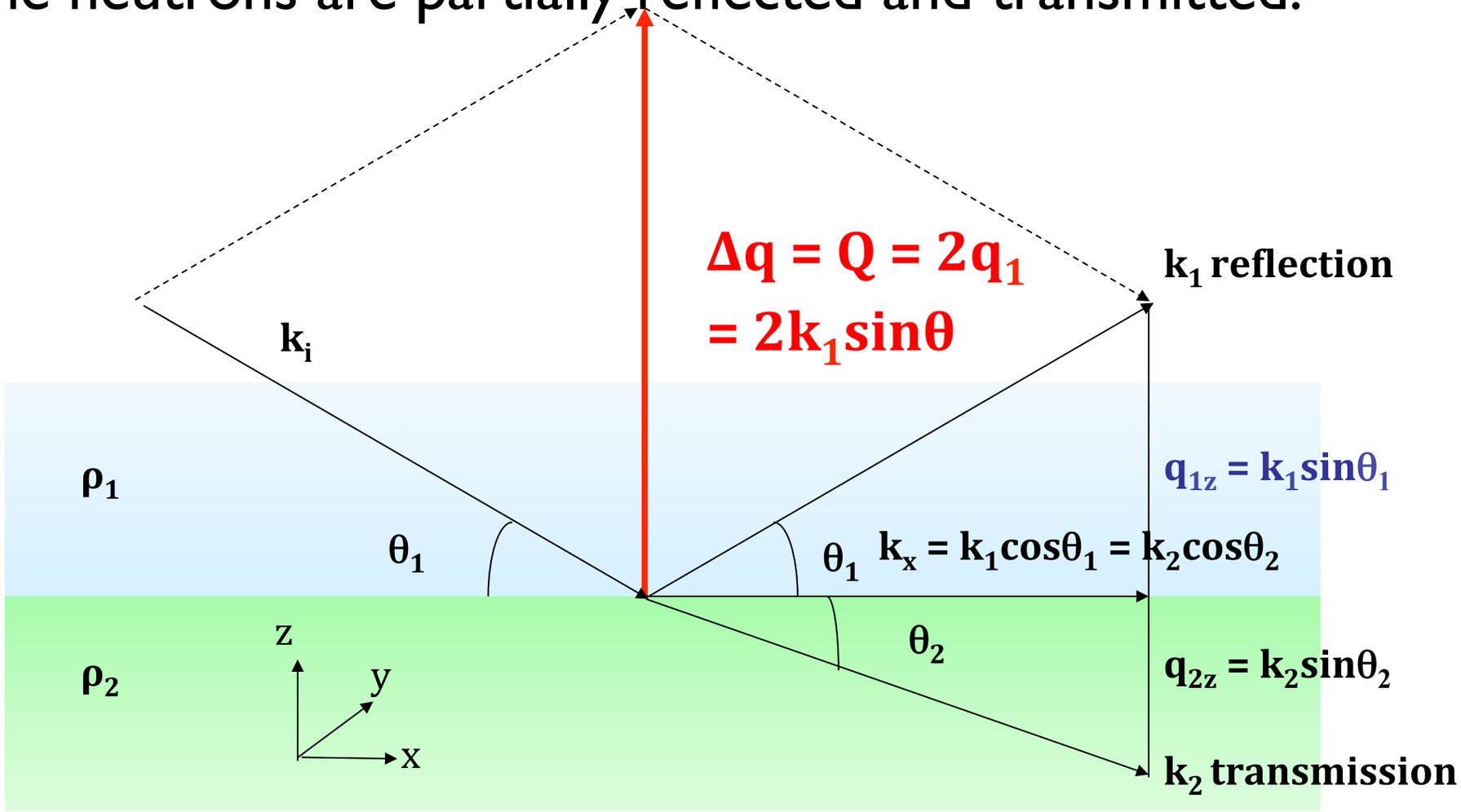
q_1 and q_2 are the scattering vectors above and below the interface. This gives:

$$r = \frac{q_1 - q_2}{q_1 + q_2} \qquad \text{and} \qquad t = \frac{2q_1}{q_1 + q_2} \qquad (9)$$

These are the Fresnel reflection and transmission coefficients.

Q and Scattering length density

The neutrons are partially reflected and transmitted:



For elastic scattering:

$$k_i^2 = k_x^2 + q_i^2 \qquad (10)$$

Using (6) :

$$k_i^2 = \frac{8\pi^2 m}{h^2}\left(E - V_i\right) \qquad (11)$$

Q and Scattering length density

The refractive index is the ratio between the wavevectors in 2 media:

$$n_{12} = \frac{k_2}{k_1} \quad \text{or} \quad n_{12} = \frac{\cos\theta_1}{\cos\theta_2} \quad \text{Snell's Law} \qquad (12)$$

Using (3), (11) and the de Broglie relation for the neutron energy ($h^2/2m\lambda^2$) gives the neutron refractive index and its relation to the scattering length densities of the two media.

$$n_{12} = 1 - \frac{\lambda^2}{2\pi}(\rho_2 - \rho_1) \qquad (13)$$

Total reflection occurs when $\theta_2 = 0$ for transmission and the critical reflection angle is

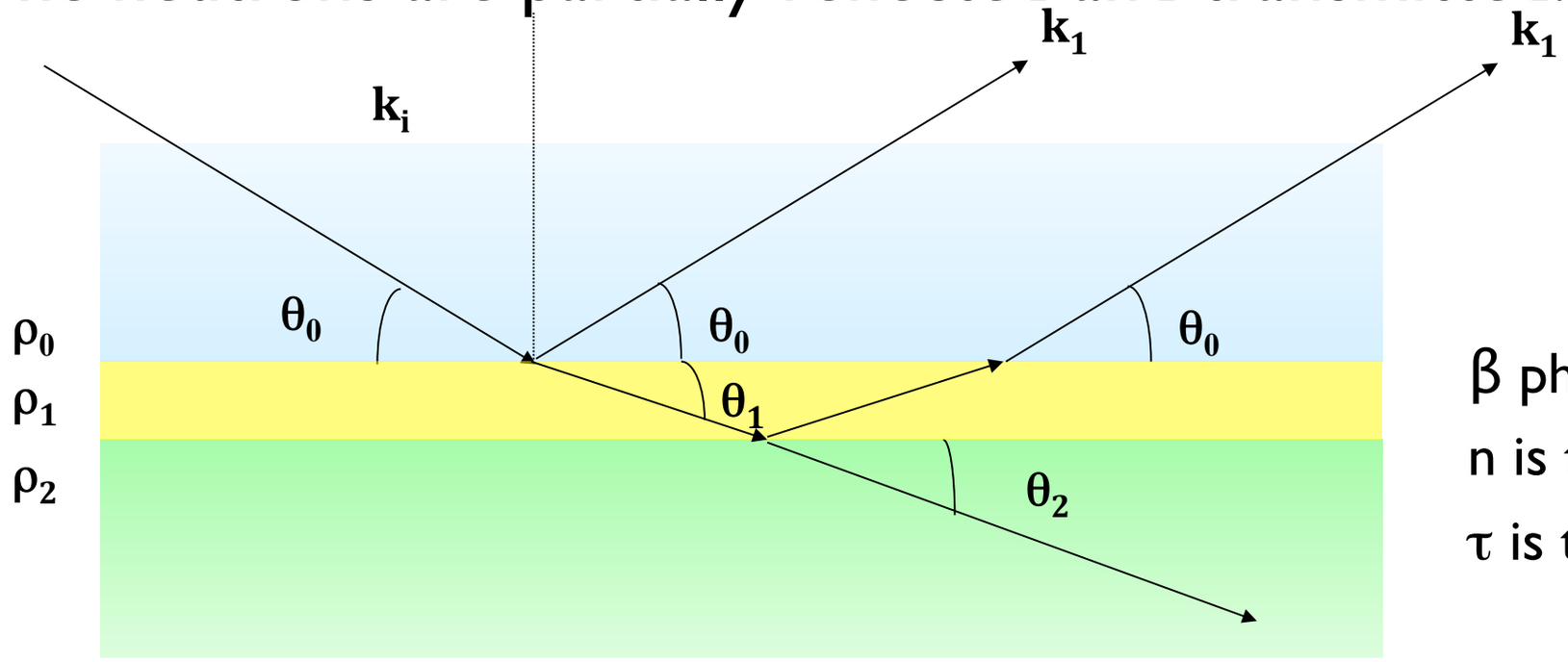
$$\cos\theta_c = 1 - \frac{\lambda^2}{2\pi}(\rho_2 - \rho_1) \qquad (14)$$

$$Q_c = \frac{4\pi \sin\theta_c}{\lambda} \qquad (15)$$

The critical momentum transfer vector q_c depends on ρ_1 and ρ_2 for any λ.

Reflection from a homogeneous thin film

The neutrons are partially reflected and transmitted:



$$\beta_i = \frac{2\pi}{\lambda} n_i \tau_i \sin\theta_i$$

β phase thickness of the film

n is the neutron refractive index

τ is the film thickness

The reflection amplitude and intensity are given by:

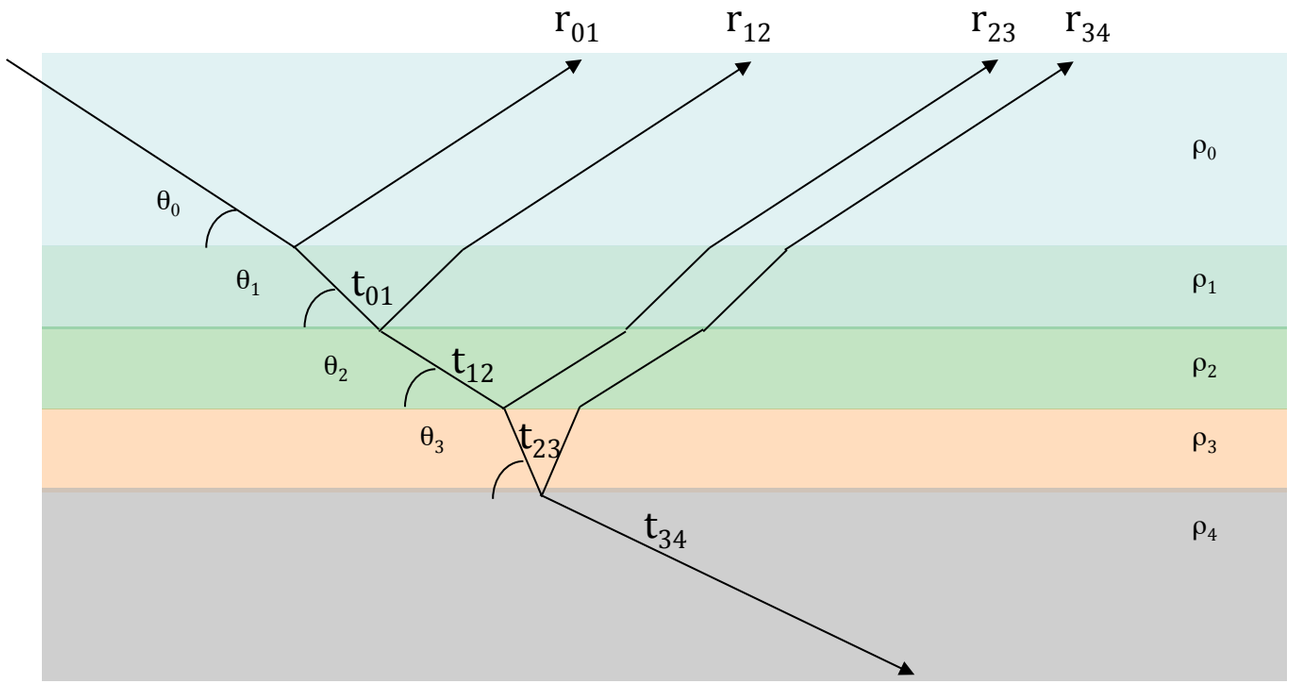
$$\underline{R} = \frac{r_{12} + r_{23}e^{2i\beta}}{1 + r_{12}r_{23}e^{2i\beta}} \qquad R = \left|\underline{R}\right|^2 = \frac{r_{12}^2 + r_{23}^2 + 2r_{12}r_{23}\cos 2\beta}{1 + (r_{12}r_{23})^2 + 2r_{12}r_{23}\cos 2\beta} \qquad (16)$$

The intensity maxima and minima occur at cos2β=±1, which allows the film thickness to be estimated from the separation of minima in q:

$$\tau = \frac{2\pi}{\Delta Q} \qquad (17)$$

Reflection from a multilayer film

For a multilayer film with several sublayers with different scattering length density:



The Fresnel reflection coefficient r can be modified to include the effects of interfacial roughness:

$$r_j^+ = r_j e^{-\frac{1}{2}\kappa^2\sigma^2} \qquad (18)$$

For each layer the reflected amplitude is described by a characteristic Abeles matrix:

$$\left[M_j\right] = \begin{bmatrix} e^{i\beta_{(j-1)}} & r_j^+ e^{i\beta_{(j-1)}} \\ r_j^+ e^{-i\beta_{(j-1)}} & e^{-i\beta_{(j-1)}} \end{bmatrix} \qquad (19)$$

The total reflection amplitude is given by the product of all the layers

$$\left[M\right] = \prod_{i=1}^{n} M_i \qquad (20)$$

The reflection intensity from a layer is given by:

$$R_j = \frac{m_{12}m_{21}}{m_{11}m_{22}} = \left|r_j^+\right|^2 \qquad (21)$$

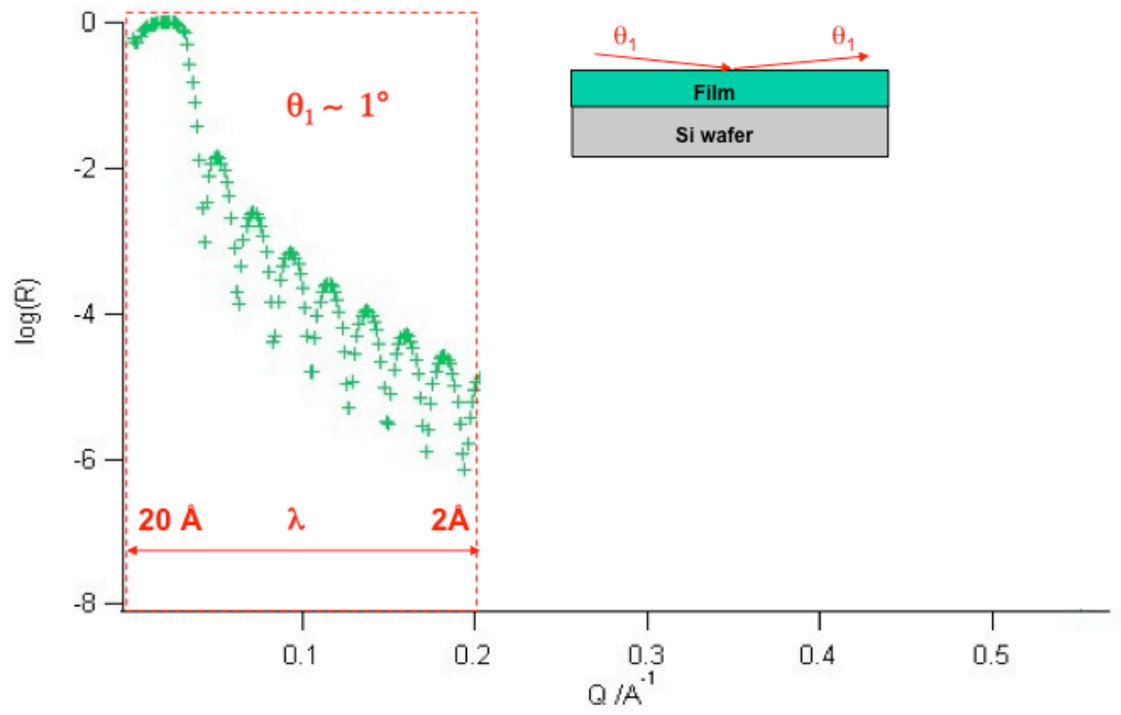
The Experiment

Since $q = 4\pi\sin\theta/\lambda$, reflectivity R(q) can be measured in two ways:

1) using a monochromatic beam and scanning the angle of incidence θ

2) using a polychromatic beam covering a range of q-values at any given θ

In method 2 the range of q is measured simultaneously, which allows structural changes to be monitored as a function of time.



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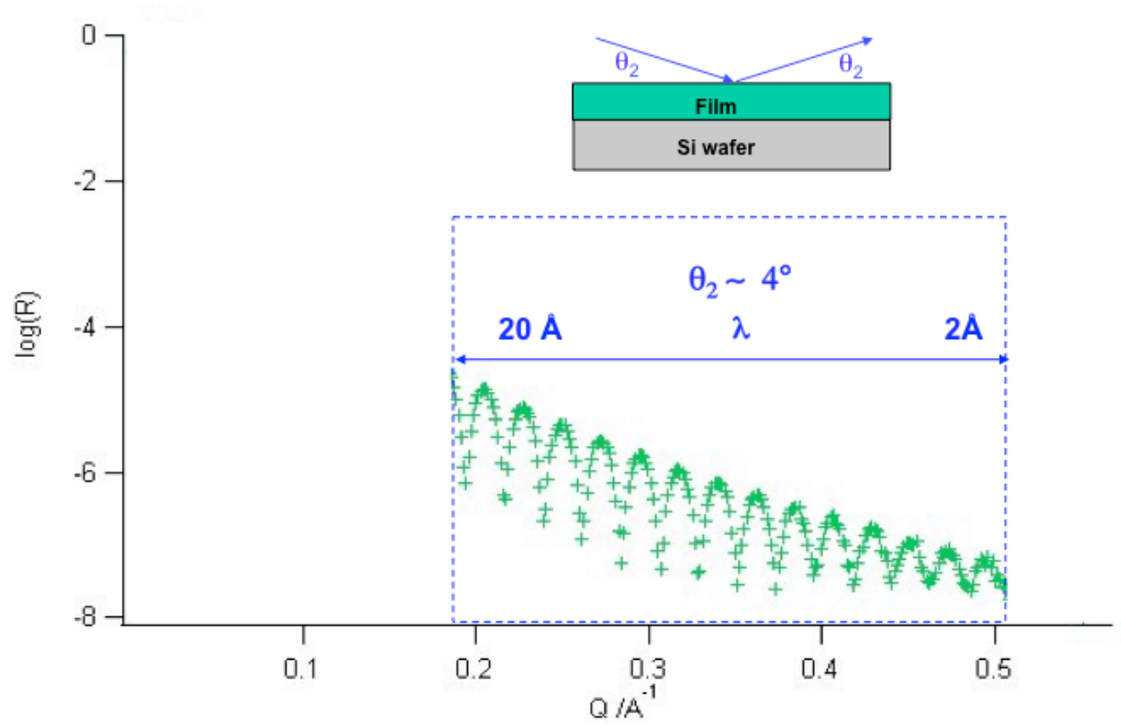

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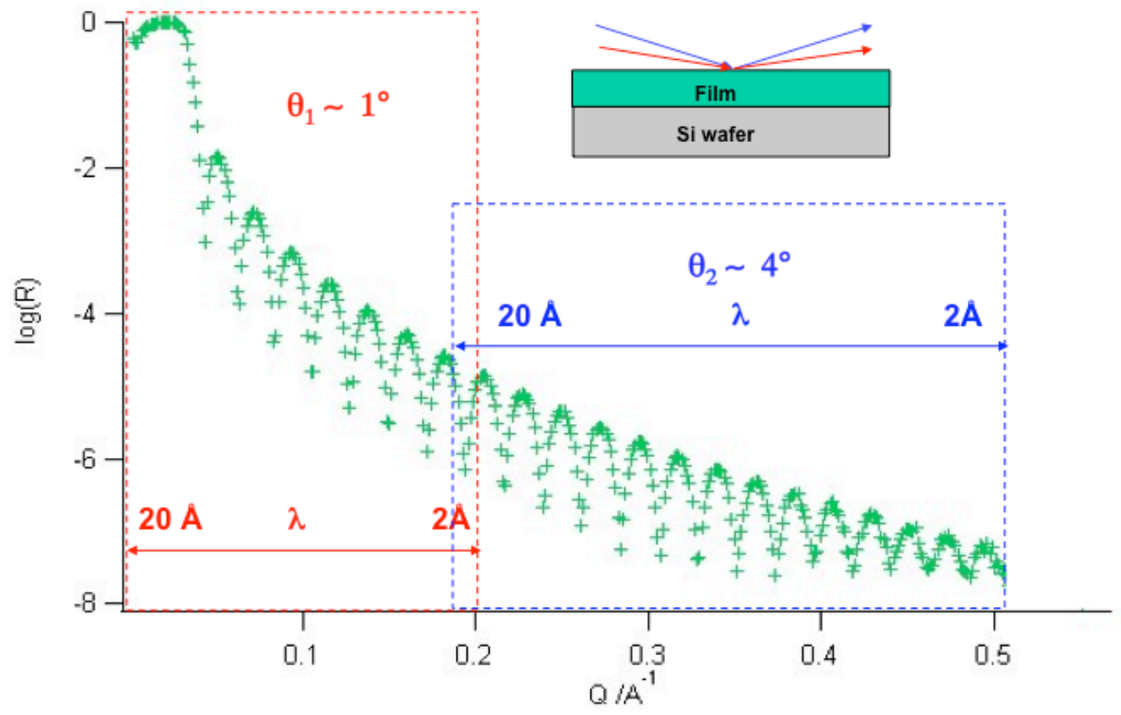


The Experiment

Since $q = 4\pi\sin\theta/\lambda$, reflectivity R(q) can be measured in two ways:

1) using a monochromatic beam and scanning the angle of incidence θ (x−rays)

2) using a polychromatic beam covering a range of q-values at any given θ (neutrons)

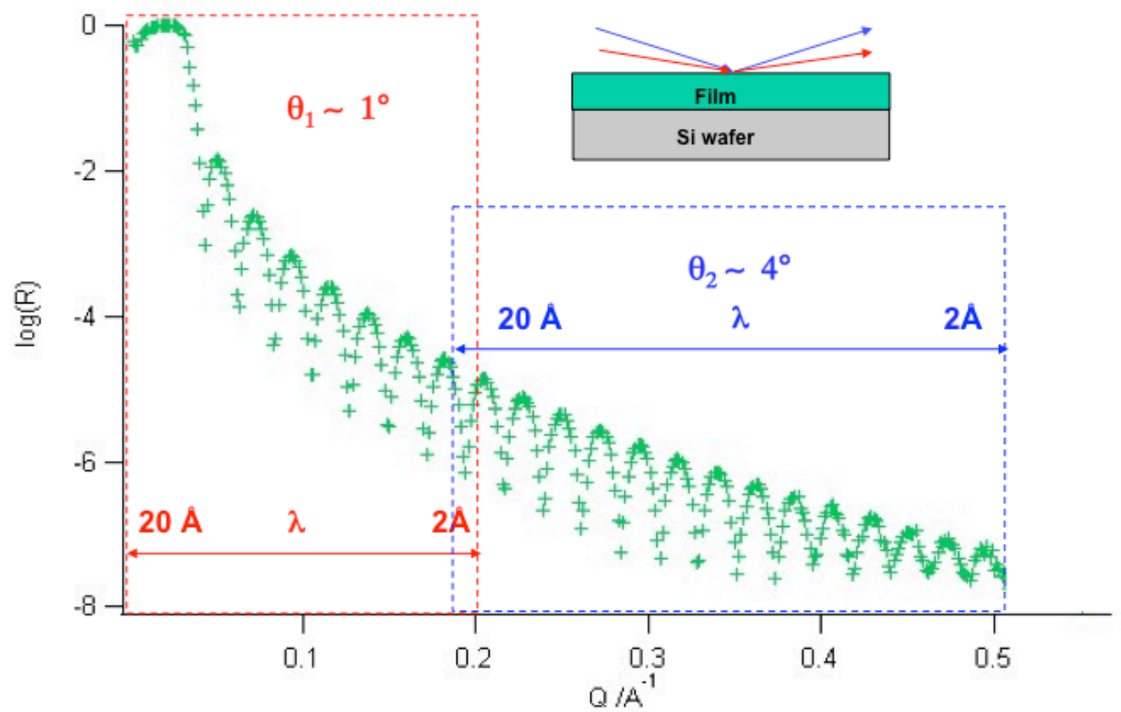
In method 2 the range of q is measured simultaneously, which allows structural changes to be monitored as a function of time.

When using polychromatic beam, the neutron wavelength distribution is determined from their *time-of-flight*, since the neutron velocity depends on their wavelength:

$$v = \frac{h}{m\lambda}$$ neutron velocity

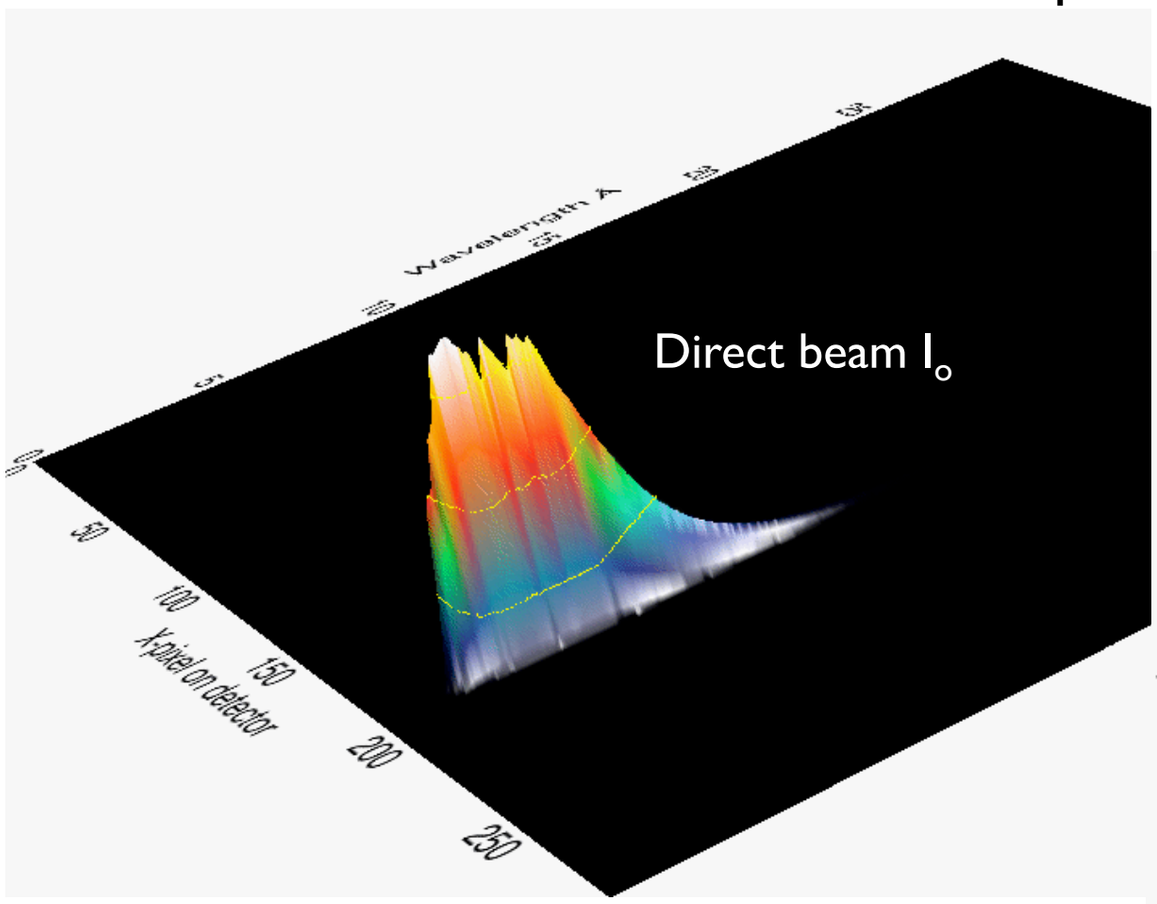
$$v * tof = D$$ time-of-flight distance

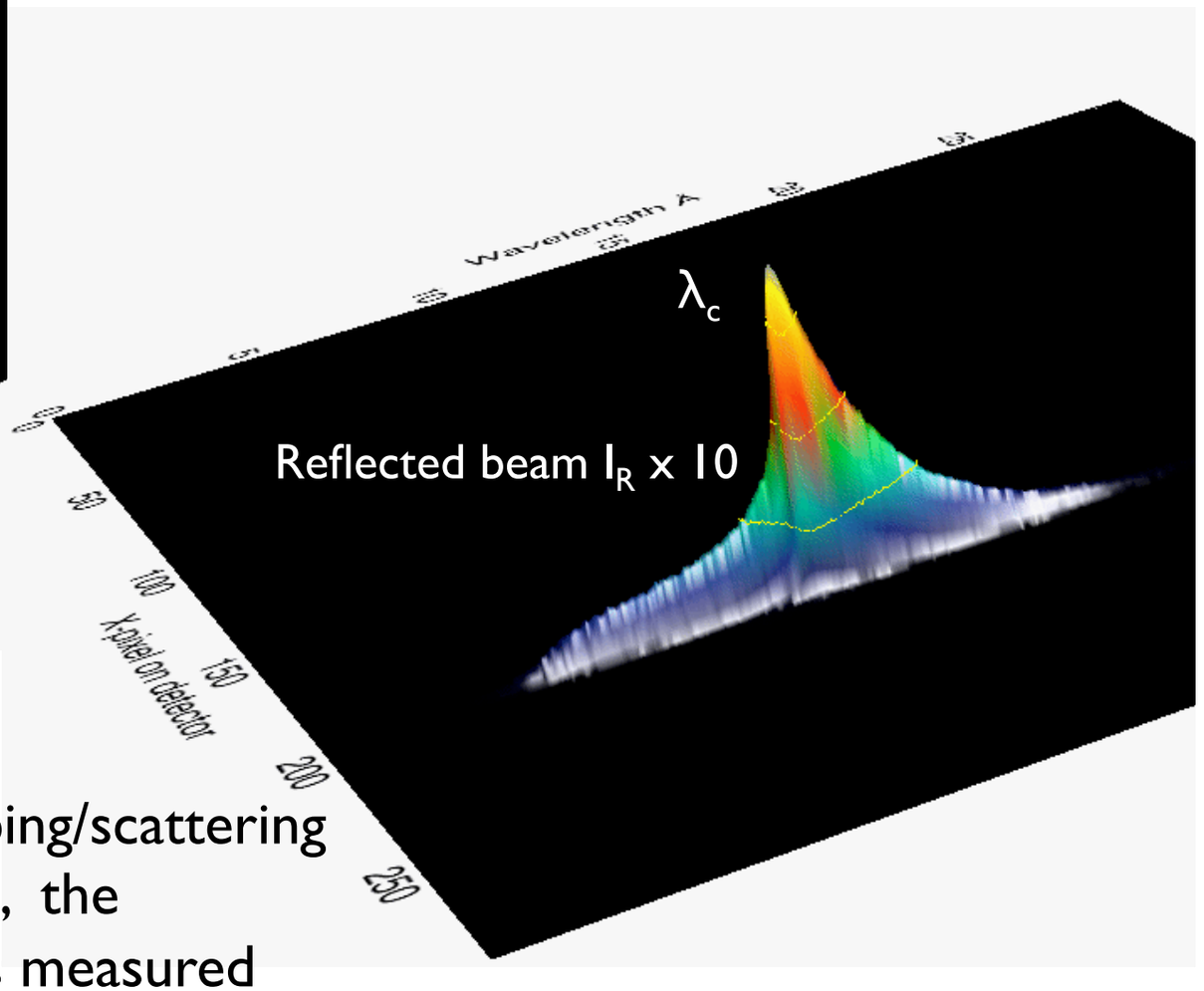
$$\lambda = \frac{h}{mD} tof$$ neutron wavelength



The Experiment

Reflectivity R is the ratio of reflected intensity over the incident beam intensity I_R/I_0 - when both are measured with the same beam parameters (slits) this also normalises data.



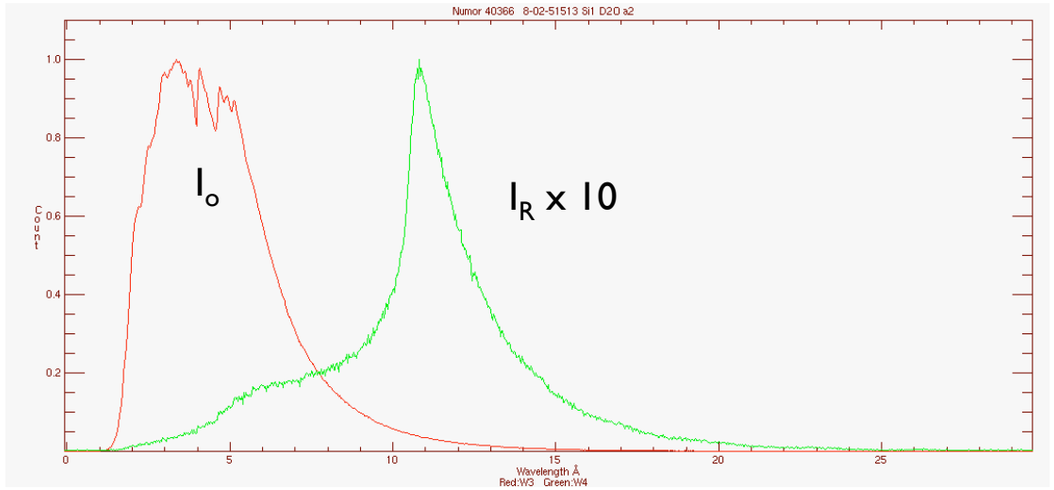


If the incident beam travels through an absorbing/scattering medium (such as a silicon wafer or a window), the incident intensity or a transmission function is measured through this.

The Experiment

Reflectivity R is the ratio of reflected intensity over the incident beam intensity I_R/I_0:

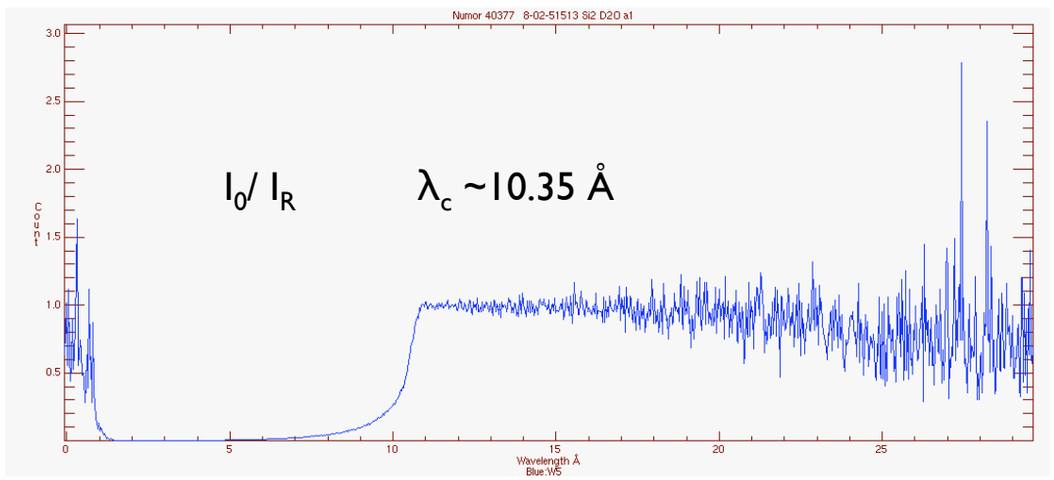
1) below the critical Q, R= 1
2) for a time-of-flight experiment, only ~10% of the incident beam is reflected as above the critical angle the intensity falls with ~Q^{-4}

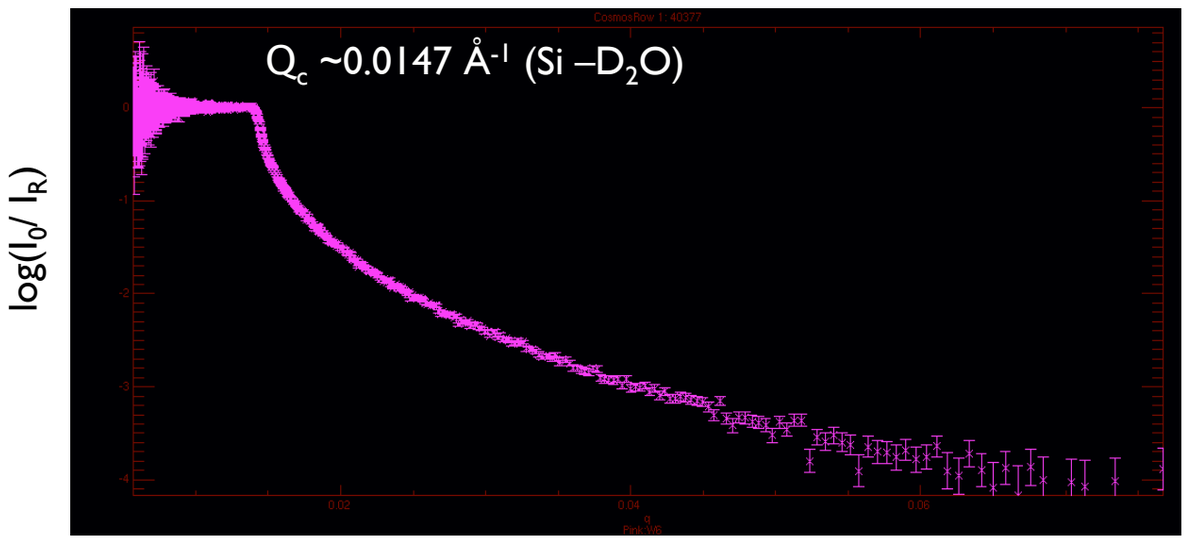


The critical q value is a property of the materials:
for silicon $\rho_1 = 2.07 \times 10^{-6}$ Å^{-2}
for D_2O $\rho_2 = 6.35 \times 10^{-6}$ Å^{-2}

Q_c (Si–D_2O) = 0.0147 Å^{-1}

$\rho_2 > \rho_1$ → total *external* reflection (Q: why?)





$$Q_c = \frac{4\pi \sin\theta_c}{\lambda}$$

The Experiment

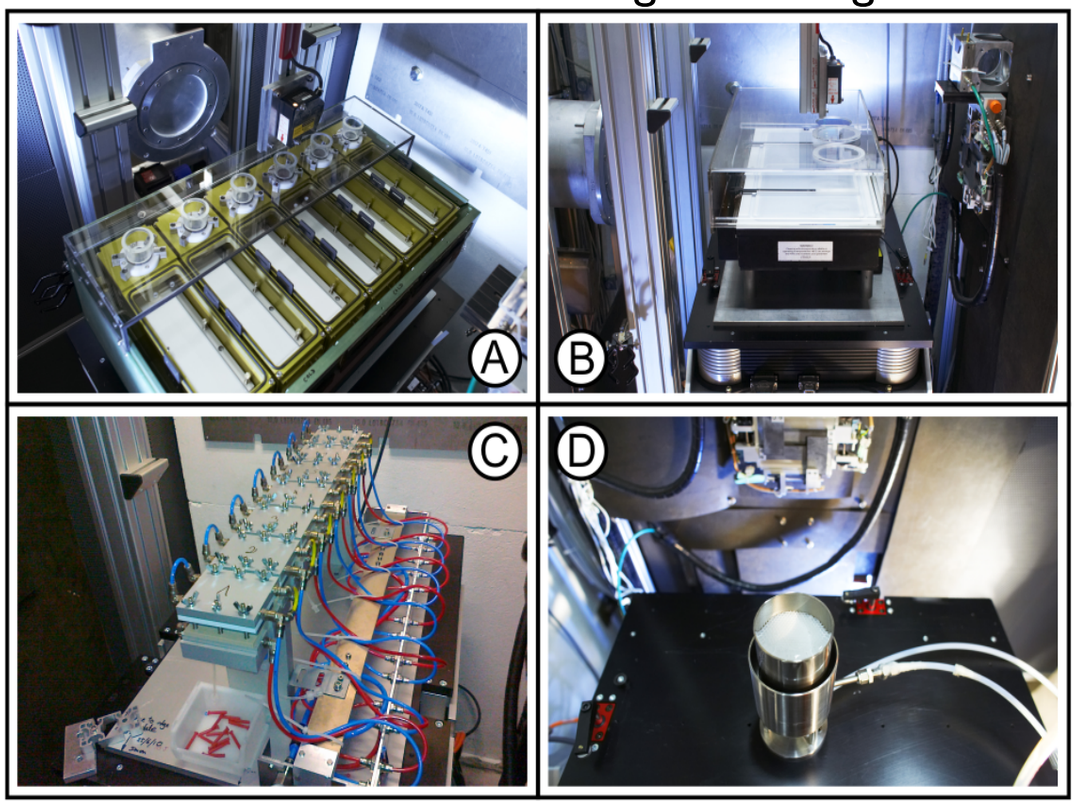
Neutrons penetrate many materials easily, but…they are strongly scattered by liquids (incoherent scattering), and also absorbed by some materials.

Many solid materials are almost transparent to neutrons and can be used to deliver the beam to buried interfaces, e.g. the solid-liquid interface

many kinds of sample cells and environments are used for liquid surfaces, e.g.

air-liquid troughs

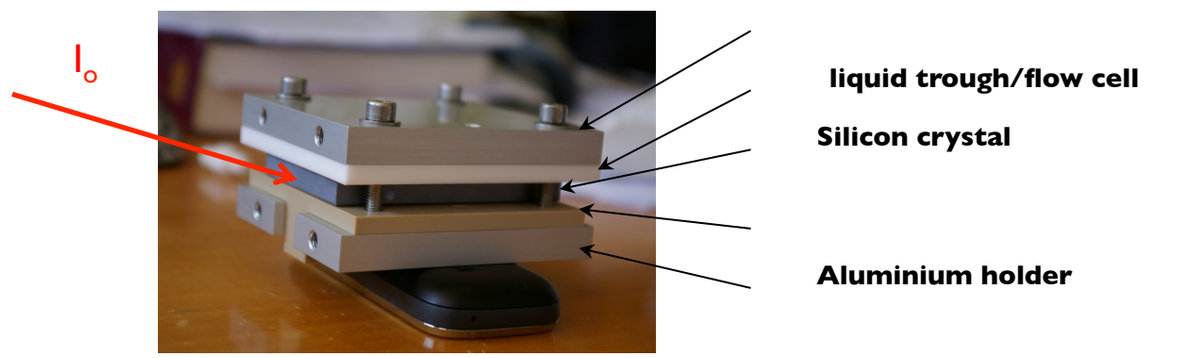
Langmuir troughs

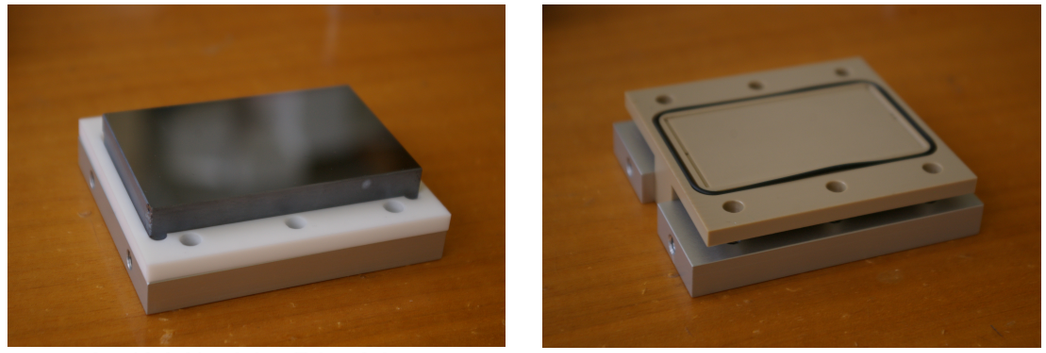


multi-rack for S/L cells

overflowing cylinder

A typical solid-liquid flow cell:





Si (111): 80×50×10 mm

Reflection data analysis

Building model structures to represent the system

Optical matrix calculation to fit theoretical reflectivity to experimental data

Parameters: film thickness, scattering length density, roughness

From these is is possible to work out the volume fraction ϕ or the water fraction (1- ϕ)

$$\rho_{layer} = \phi\rho_s + (1-\phi)\rho_w$$

Contrast variation: simultaneous fits to several data sets are used to obtain

- the fraction of a component in a multicomponent film
- the location of components in a multicomponent film
- deuterium labeling to create contrast between components

Reflection data – what does it reveal?

Neutrons reflection measures the film thickness and scattering length density.

From these is is possible to work out:

- the area per molecule A and the surface coverage Γ per unit area.

$$A = \frac{n \cdot V_w}{t_{layer} \cdot (1-\phi)}$$

volume of water

$$\Gamma = \frac{10^{26}}{A \cdot N_A}$$

- number of molecules per unit area
- the density of a material
- orientation of a molecule from thickness

EUROPEAN SPALLATION SOURCE

Data analysis

Installation and Introduction to Motofit

Building models and fitting data in Motofit:

Manual vs fitting algorithms

Using constraints

Co-refining multiple contrasts

Introduction to projects

Igor Pro graphing/fitting package

http://www.wavemetrics.com/

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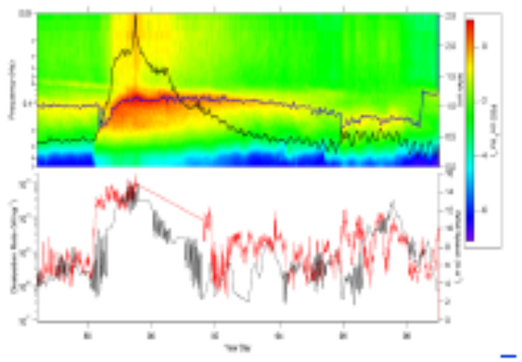
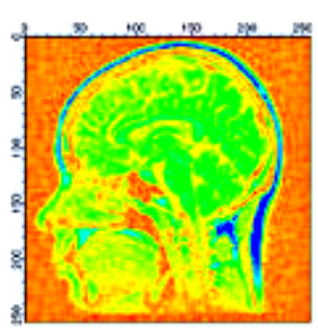
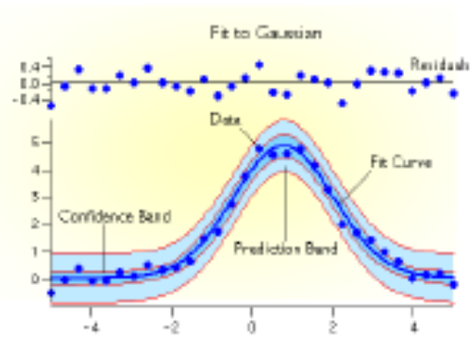
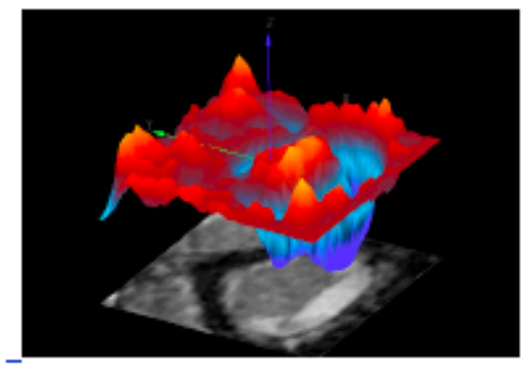








IGOR Pro 6.2 New Features

IGOR Pro 6 Brochure (PDF, 4.4MB)

Product Updates

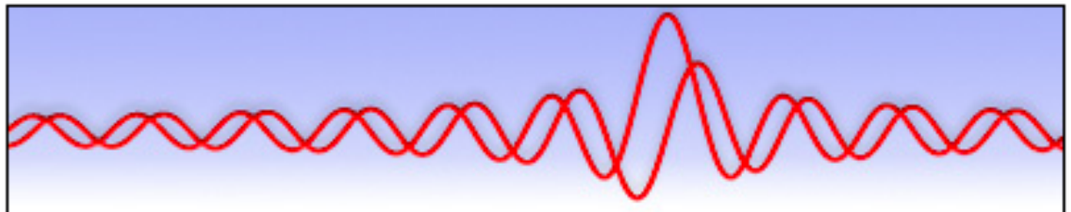
The latest release of IGOR Pro is version 6.22A.

The latest release of the Japanese version of IGOR Pro is 6.22J.

The latest release of the XOP Tookit is version 6.02.

IGOR NIDAQ Tools MX 1.05 now available.

The latest release of



IGOR Pro 6 is an extraordinarily powerful and extensible scientific graphing, data analysis, image processing and programming software tool for scientists and engineers.

See Details **Try Now** **Buy Now**

- Macintosh and Windows Platforms
- Journal-quality scientific graphs
- 3D and volume visualization
- Flexible image display
- Handles large data sets very quickly
- Extensive scientific and engineering data analysis
- Curve fitting, peak fitting

IGOR XOP Toolkit
Allows a C programmer to extend IGOR Pro. Add operations, functions, menus, dialogs, and windows for data analysis, data acquisition or other purposes.

IGOR NIDAQ Tools MX
Acquire data directly into IGOR Pro. Supports data acquisition devices made by National Instruments.

IGOR Filter Design Laboratory
Design FIR (Finite Impulse Response) and IIR (Infinite Impulse Response) filters and to apply

Igor Pro graphing/fitting package

Install Igor 6 using one of the installers:

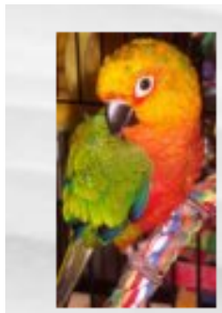
setupIgor6.exe - for Windows PC

Igor6-2.dmg - for Mac

- general scientific graphing, progamming, instrument control and peak/curve fitting.
- Demo version runs Motofit analysis for NR – can save text files but not experiment files

Motofit by Andrew Nelson

http://motofit.sourceforge.net/wiki/index.php/Main_Page



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Main Page

Motofit and Reflectometry(scattering) resources Wiki.

This Wiki describes the use of Motofit to analyse X-ray and neutron reflectometry data, although there is some information on other scattering techniques.

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search

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Contents [hide]

Optical matrix modeling of reflectivity

- neutrons and X-rays
- Genetic curve fitting algorithm
- simultaneous fitting of multiple contrasts (incl. pol neutrons/X-rays)

Download address for Motofit

http://sourceforge.net/projects/motofit/

Download

motofit_installers4.zip contains:

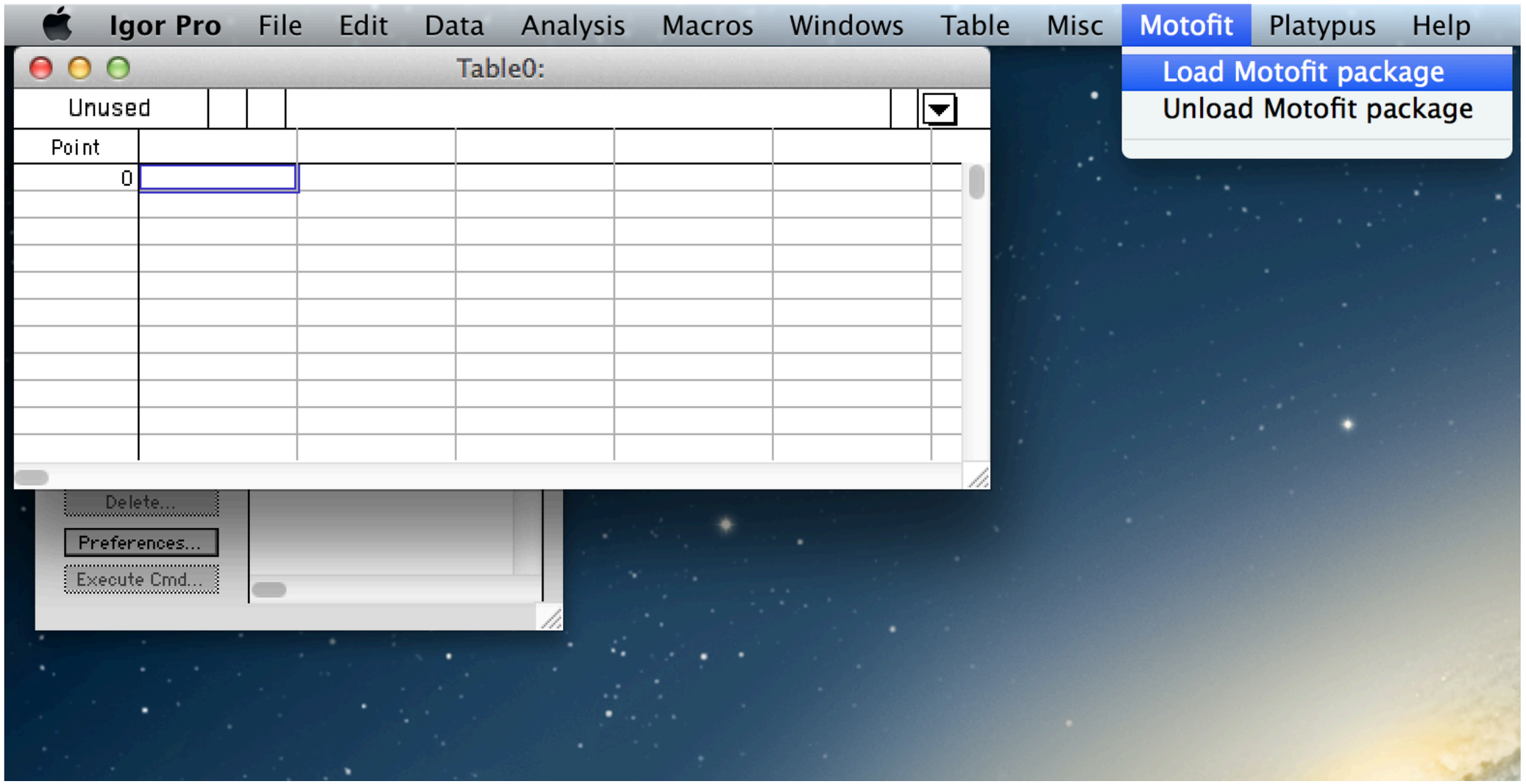
motofitInstaller.exe - for Windows PC

motofitInstaller.dmg - for Mac

(also contains Platypus data reduction software)

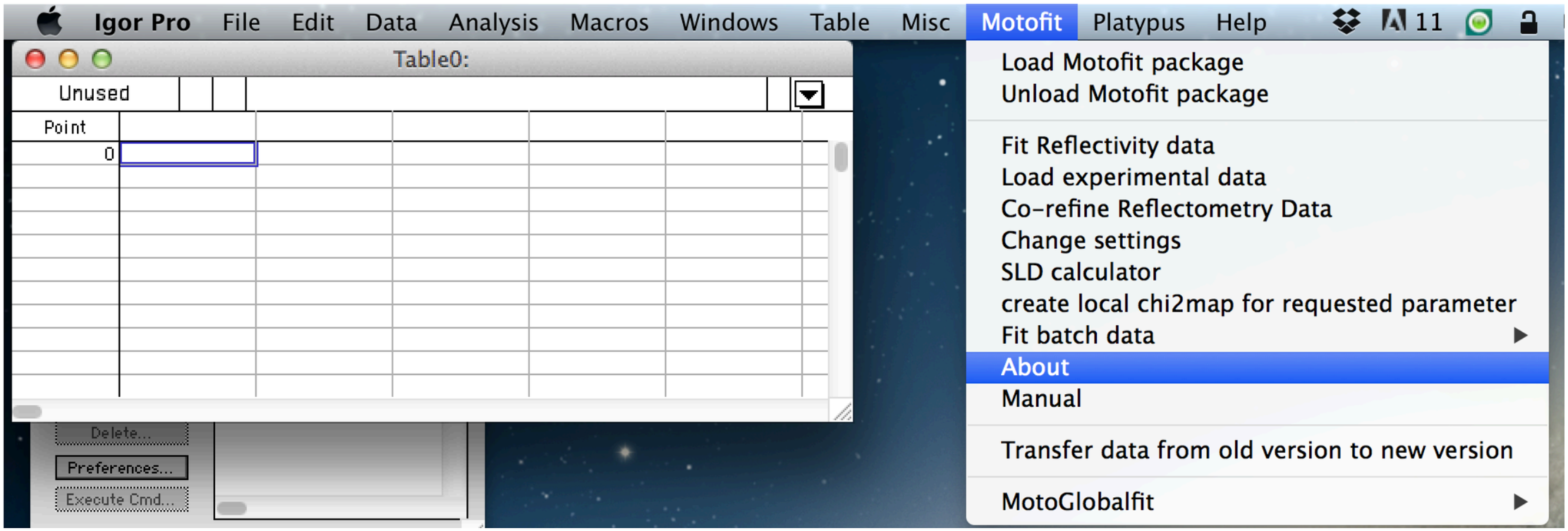
Instructions to fit data in Motofit

1. start Igor
2. from the Motofit menu – “load Motofit”



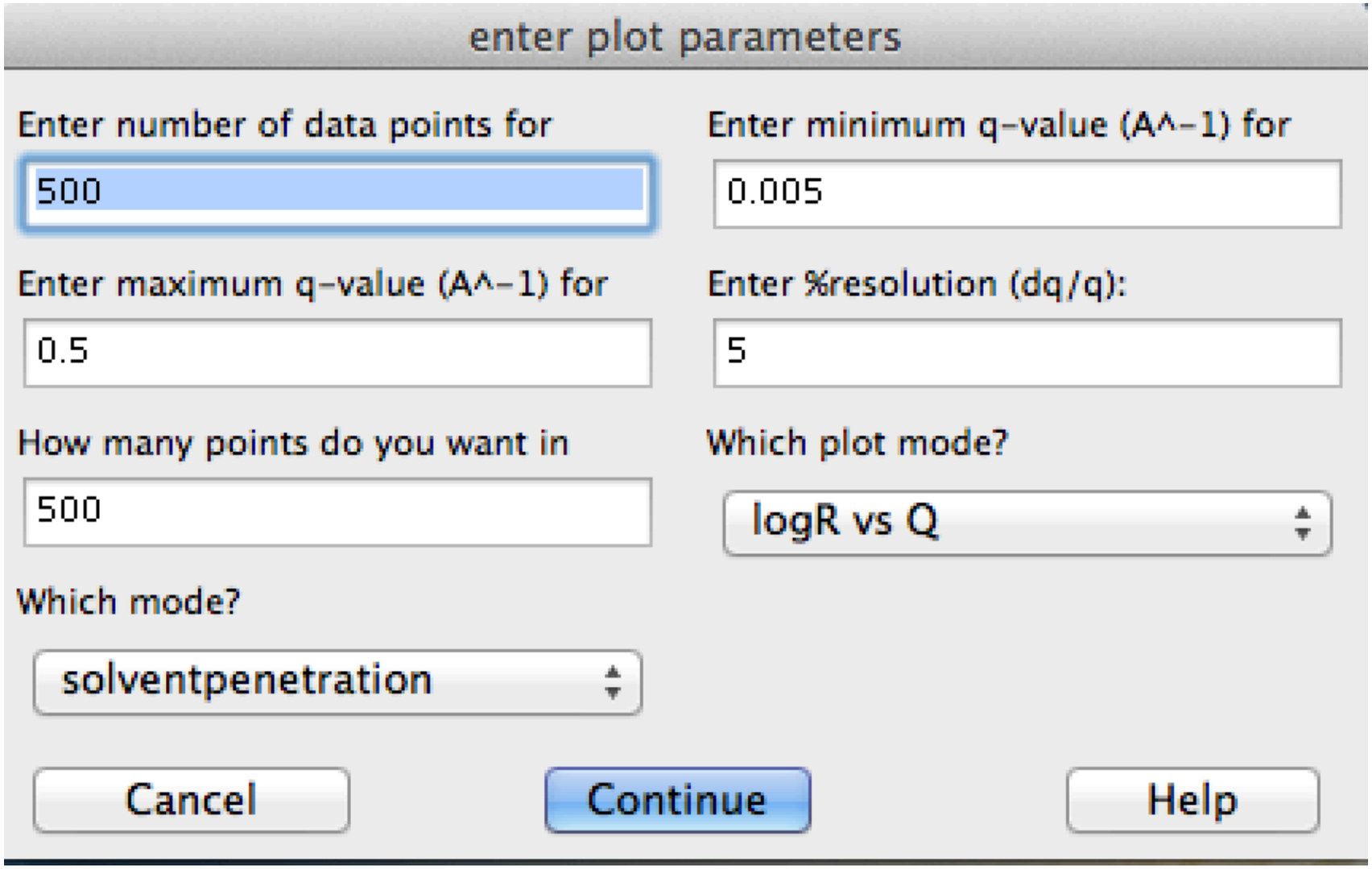
Instructions to fit data in Motofit

3. Motofit menu – “Fit reflectivity data”

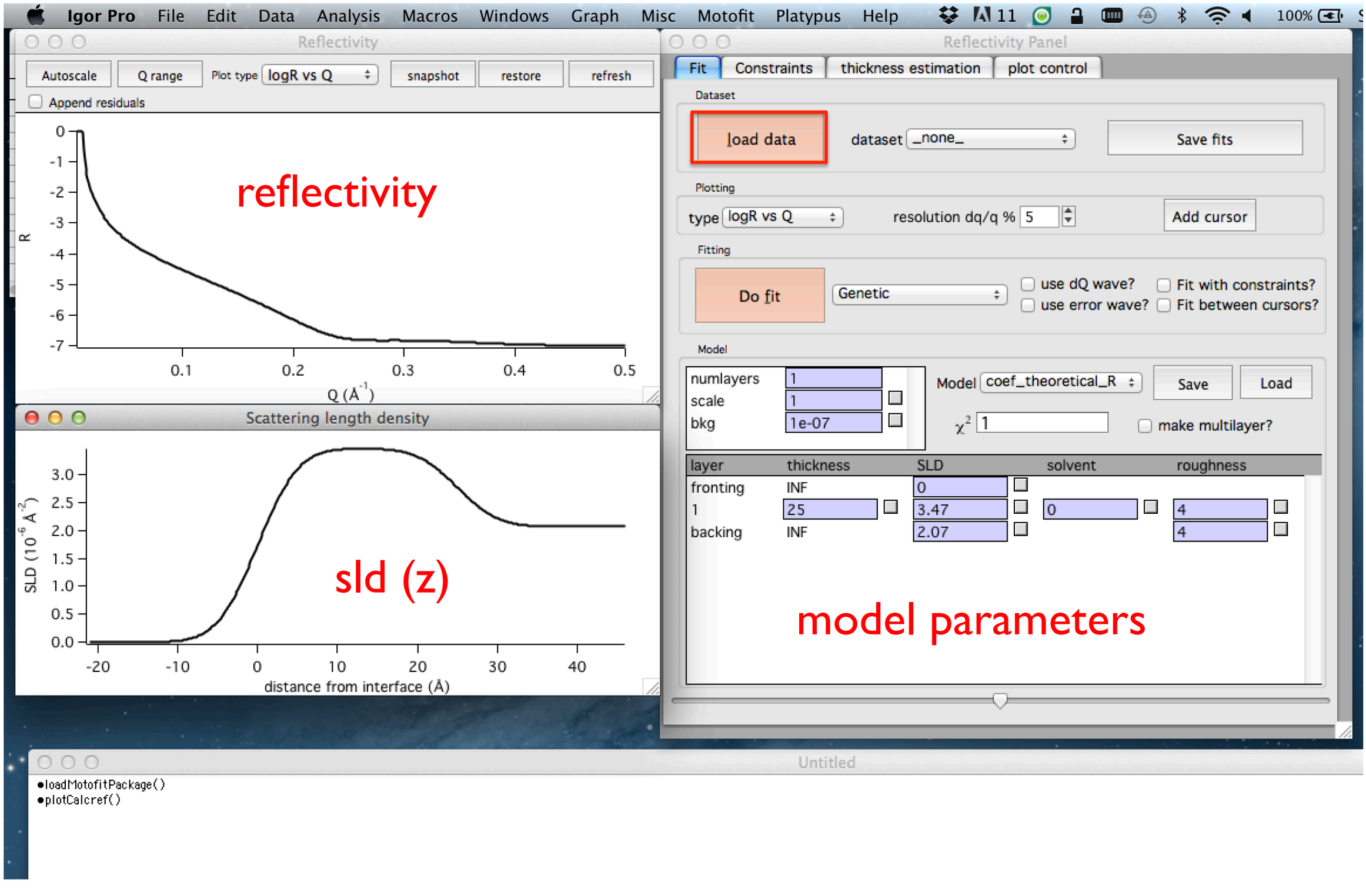


Instructions to fit data in Motofit

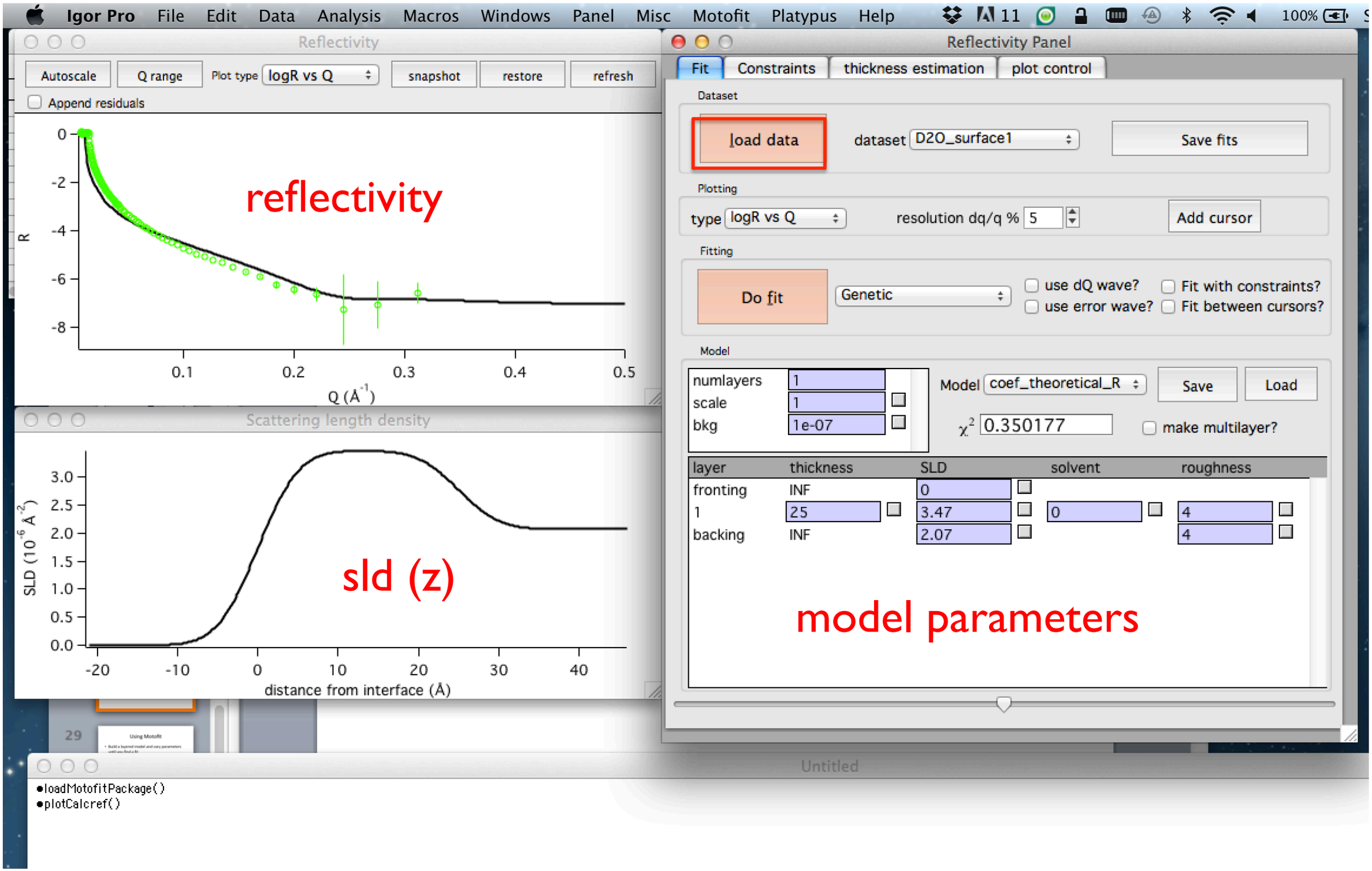
4. choose q-range, no. of points contrast etc.



Instructions to fit data in Motofit

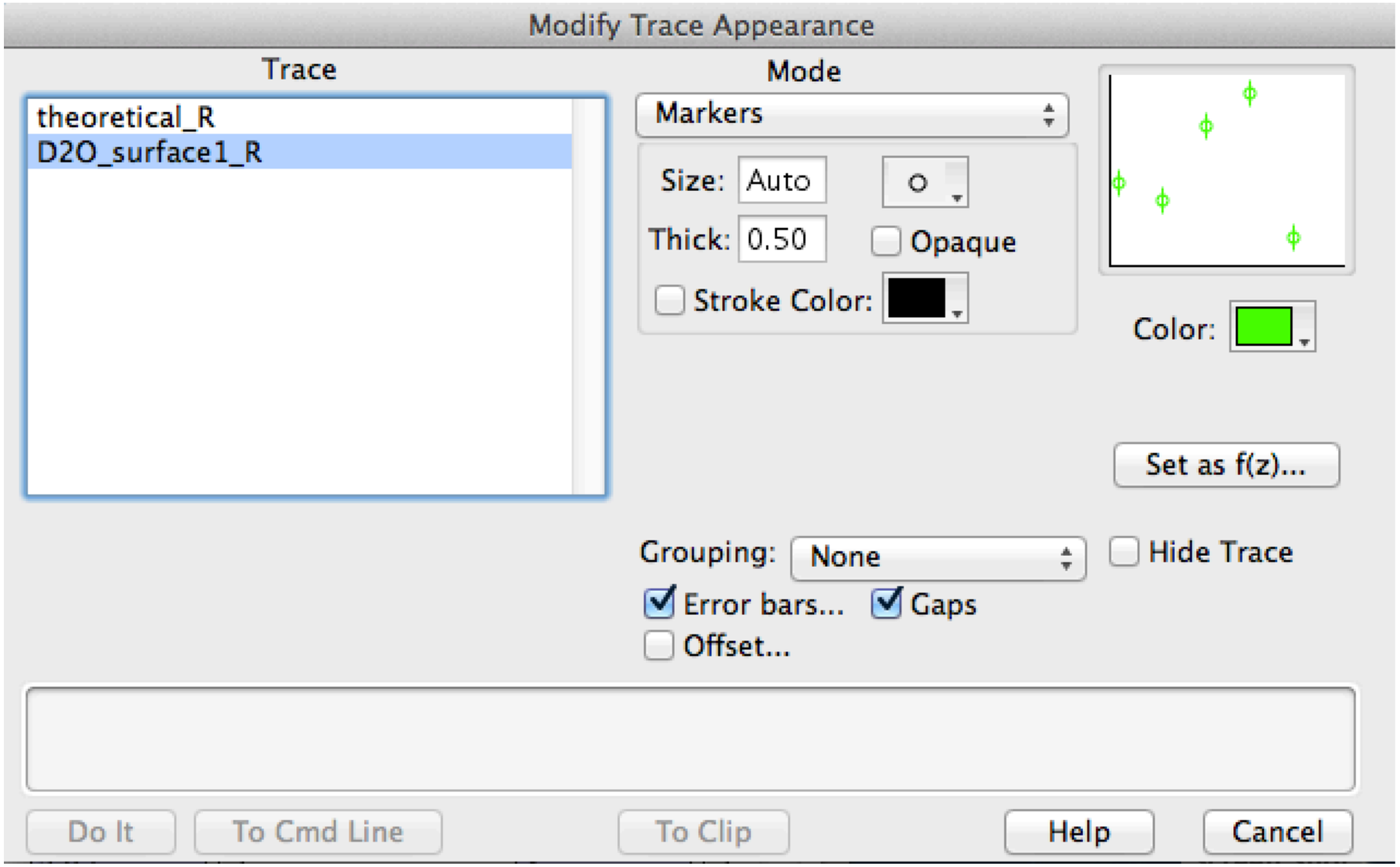


Instructions to fit data in Motofit



Instructions to fit data in Motofit

To modify the appearance of the graphs , double click on e.g. the data



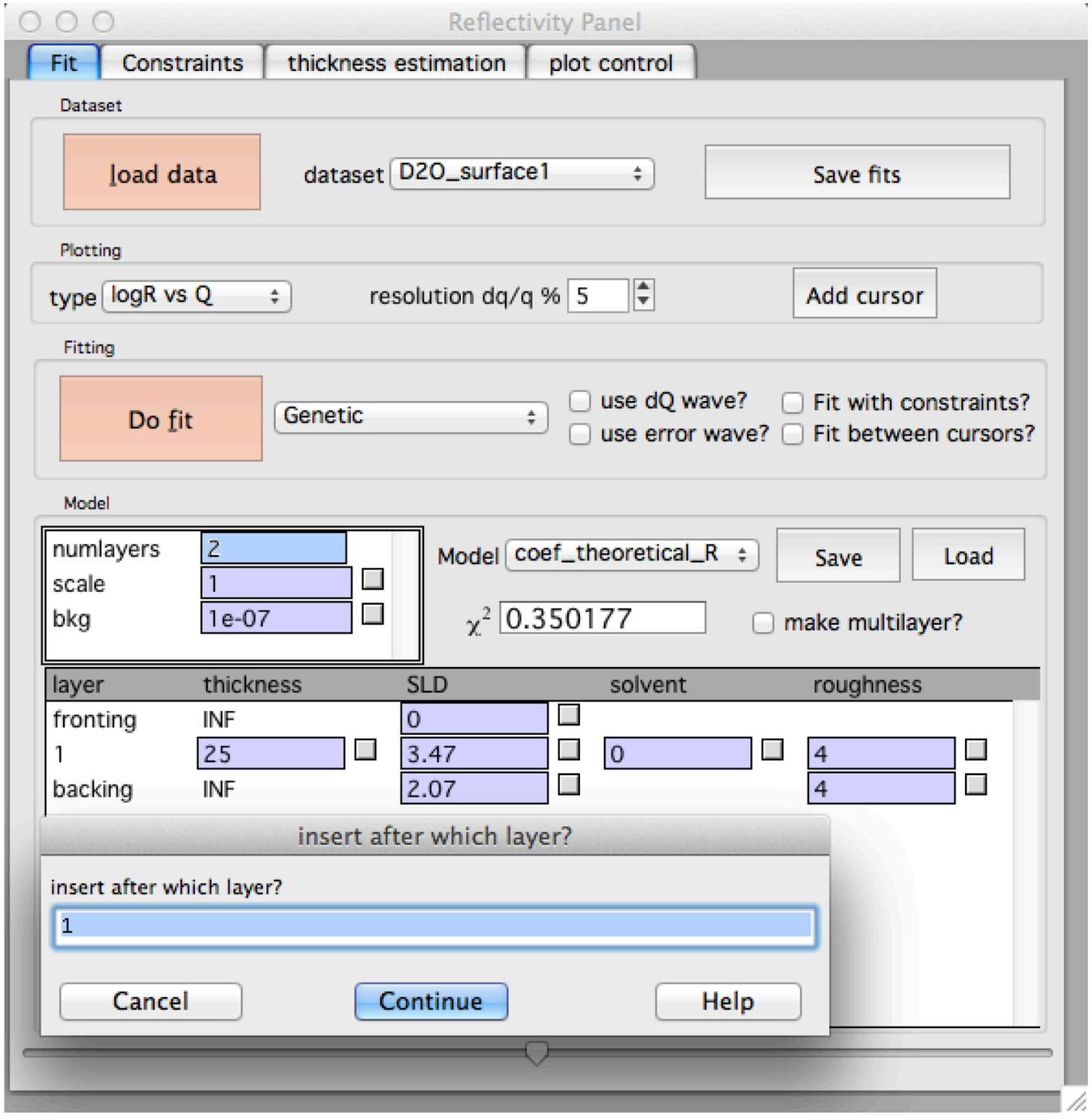
Instructions to fit data in Motofit

To start building a model structure, add the number of layers you think you will need

Then put in starting points for the parameters

Fronting:
the material through which the beam enters

Backing:
the material behind the interface



Instructions to fit data in Motofit

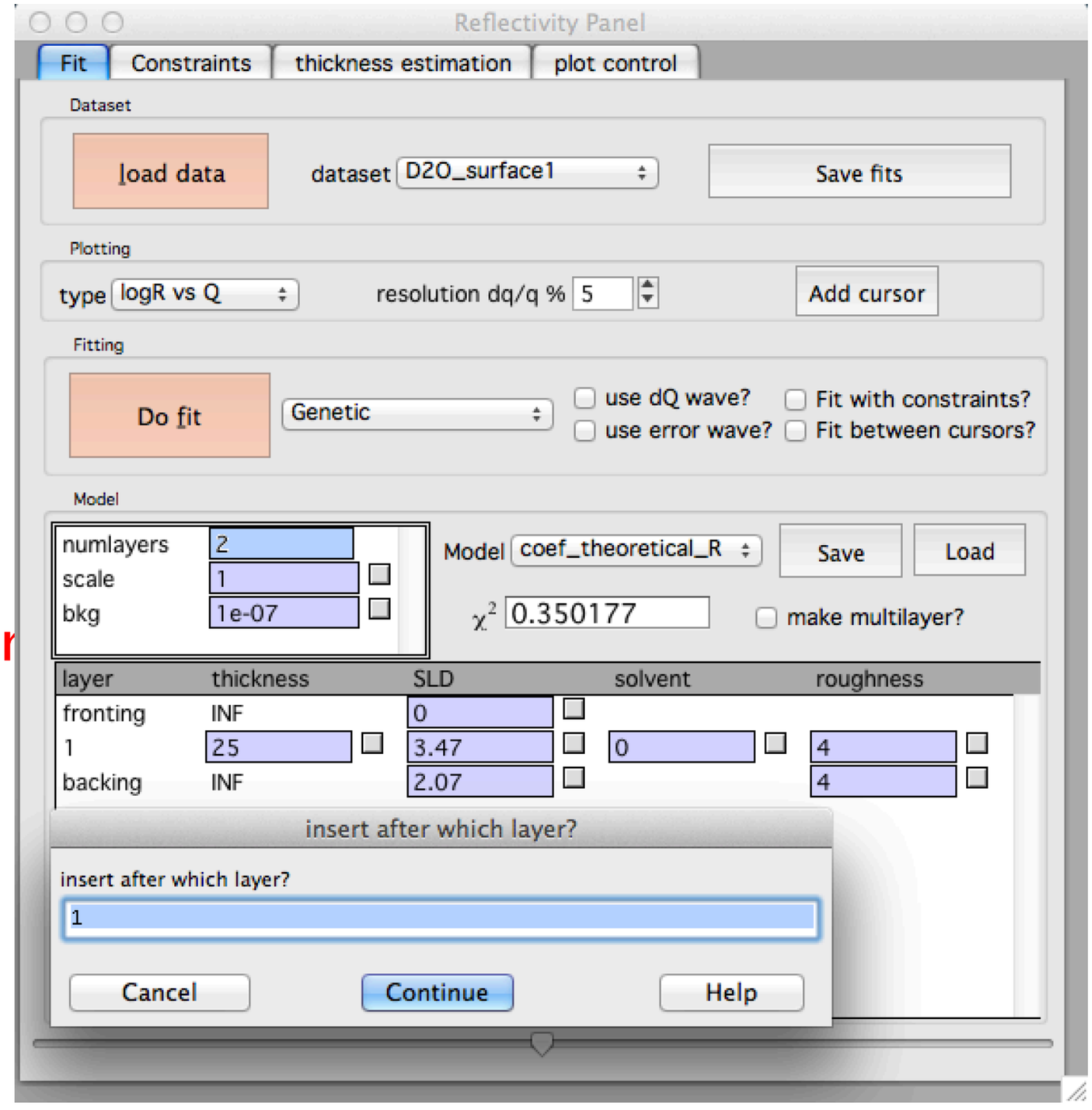
The parameter table creates a coefficient wave which is used to calculate the theoretical reflectivity

resolution: experimental

Background: fitted, can have been subtracted or not.

roughnesses are for the interface to the previous layer i.e. the first box is for the fronting material surface

Fit curves and coefficients can be saved and re-loaded as text file.



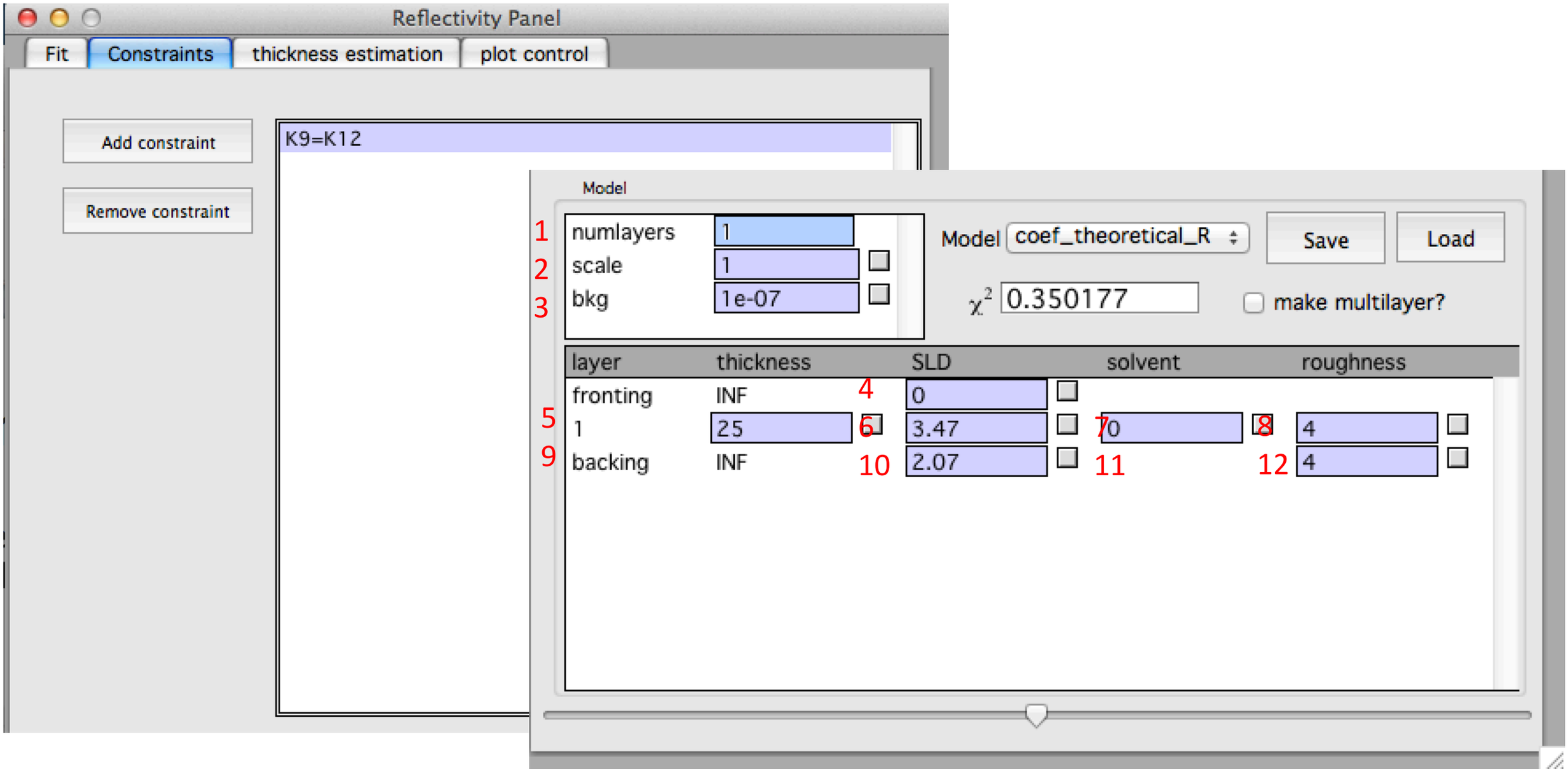
Two ways of using Motofit

1. Build a layered model and vary parameters until you find a fit
2. Fitting with either Levenberg-Marquart or Genetic algorithm does the variation automatically

To get familiar with the fitting, best to start with the manual option.

Using Constraints

- linear constraints: e.g. two roughnesses must be the same
- Fit parameters numbered in sequence from the top



Fitting

- To hold a parameter constant, tick the box next to it. For example, hold the sld of D2O, because you know what it is.
- If you found a good fit manually, tick all parameters to hold them, then choose the data set you want to fit, and do a Levenberg-Marquart fit – this saves the fit curve, model and sld curve.

Fitting

- To do a Genetic fit, choose which variables to hold, then click on Do Fit. This gives a table in which you give the limits within which the algorithm varies each parameter in turn. Try to be realistic and only use this when relatively close to a fit – won't work from a mile away.

Fitting Multiple contrasts

- From the Motofit main menu, choose “Co-refine Reflectometry data”
- This gives you a panel into which you can add two or more data sets (e.g. the same surface in H2O and D2O)
- You can link parameters in the two contrasts that you want to have the same value – e.g. the thickness of a layer.

Saving, exporting, graphics

- you can save your work in an Igor experiment file (.exp) – this keeps all your data, fits and models in one package.
- you can write notes about the experiment by selecting in the Windows menu “new…” – Notebook.
- you can export data as a text file – either the reflectivity, sld or each x and y wave separately.
- save your plots as image files by “save graphics”

Projects

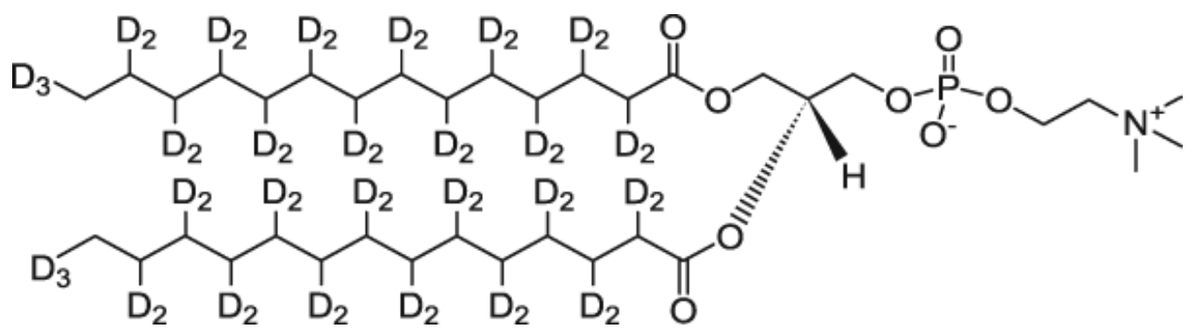
1. A lipid bilayer multiple contrasts
2. A two-component membrane + protein
3. A multilayer substrate + SAM + lipid monolayer

Download data + resources from:

https://www.dropbox.com/s/775jja8b657uml5/Reflection_tutorial_data.zip?dl=0

1.Lipid bilayer

- Lipid bilayer on a silicon wafer
- Lipid = DMPC
- Contrasts:



a) DMPC in D2O/H2O

b) chain-deuterated DMPC in D2O/H2O

- on individual substrates

1.Lipid bilayer

Task 1: calculate the sld for

Silicon, Silicon dioxide, H2O and D2O

The headgroup and chains of DMPC and dDMPC

Task 2: calculate the expected critical Q

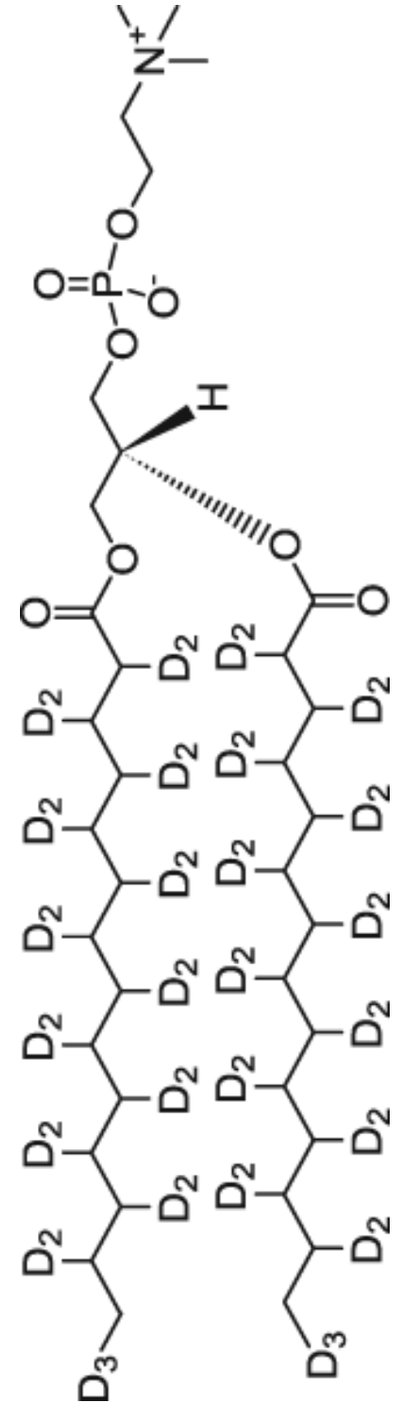
for Si-D2O and Si-H2O

Task 3: How would you build a model structure of this sample? What parameters do you need?

Resource: HERCULES_Neutron reflectivity.doc

Molecular volumes and sld

d54-Dimyristoyl phosphatidylcholine: $C_{36}H_{18}D_{54}NO_8P$ – MW 732.265



Group	*V (DPPC)/ Å³*	*V (DOPC)/ Å³*	*V (POPC)/ Å³*
CH_3	53.57±0.91	52.79±0.4	50.41±0.77
CH_2	27.93±0.1	28.13±0.09	28.24±0.17
C=C		45.91±0.69	42.1±2.31
COO Carbonyl	43.58±1.05	37.4±1.28	38.43±1.47
C_3H_5 Glycerol backbone	65.47±2.11	81.62±2.96	72.48±2.28
PO_4 Phosphate	66.36±2.95	51.05±6.31	52.12±2.23
$C_5H_{13}N$ Choline	107.62±2.49	129.68±5.25	120.68±2.98
H_2O	29.5±0.5	29.5±0.5	29.5±0.5
Total	1215.79±14.27	1322.19±20.52	1255.78±17.12
Experimental [7-10]	1232	1295	1267

1.Lipid bilayer

Data (DMPC_datafiles.zip):

Silicon surface 1:

- D2O_surface1.dat
- H2O_surface1.dat
- d54DMPC_D2O_surface1.dat
- d54DMPC_H2O_surface1.dat

Silicon surface 2:

- D2O_surface2.dat
- H2O_surface2.dat
- DMPC_D2O_surface2.dat
- DMPC_H2O_surface2.dat

Load files into Motofit

Fit structure of each Si-SiO2 surface first

Fit each bilayer data in both contrasts

Compare structure of DMPC and d54DMPC

1.Lipid bilayer

Q 1: Can you fit DMPC and d54DMPC to the same structure?

Q2: What is the area per molecule for DMPC and d54DMPC?

Q3: How would you estimate the error in determining the area per molecule from this data?

2.Two-component bilayer + protein

- Lipid bilayer on a silicon wafer
- Lipids = chain deuterated DMPC and egg sphingomyelin (SM)
- Contrasts: D2O/H2O
- Protein: equinatoxin II

2.Two-component bilayer + protein

Task 1: calculate the sld for SM

Task 2: Build a model structure that allows you to find out what mol fraction of SM the bilayer contains.

Task 3: Estimate the scattering length density of the protein equinatoxin in H2O and D2O – use

Equinatoxin_sequence.docx

Protein_volume&sld_calculation.xlsx

2.Two-component bilayer + protein

Data (DMPC_SM_datafiles.zip):

- Silicon_D2O.dat
- Silicon_H2Oe.dat
- d54DMPC_SM_D2O_1.dat
- d54DMPC_SM_H2O_1.dat
- hEquinatoxin_D2O_1.dat
- d54DMPC_SM_D2O_2.dat
- d54DMPC_SM_H2O_2.dat
- hEquinatoxin_H2O_2.dat

Fit structure of Si-SiO2 surface first

Fit both sets of bilayer data in both contrasts

Fit effect of protein

2.Two-component bilayer + protein

Q 1: What is the fraction of SM in the bilayer?

Q2: What is the error in determining this?

Q3: What effect does the protein equinatoxin have on the bilayer structure?

3.Multilayer + SAM + monolayer

- A multilayer substrate on a silicon wafer
- Self-assembled octadecyl monolayer
- Lipid monolayer = DMPC + DOGS-NTA
- Contrasts: D2O + CMSi (matched to Si)

3.Multilayer + SAM + monolayer

Task 1: Calculate sld and D2O content of CmSi?

Task 2: Build a model structure that allows you to fit the multilayer substrate + SAM

- Si – SiO2 – Cr – Au – octadecyl monolayer
- how thick is the SAM?

Task 3: Based on the first fit – find the structure of the lipid monolayer

Q: what would make fitting these structures easier?