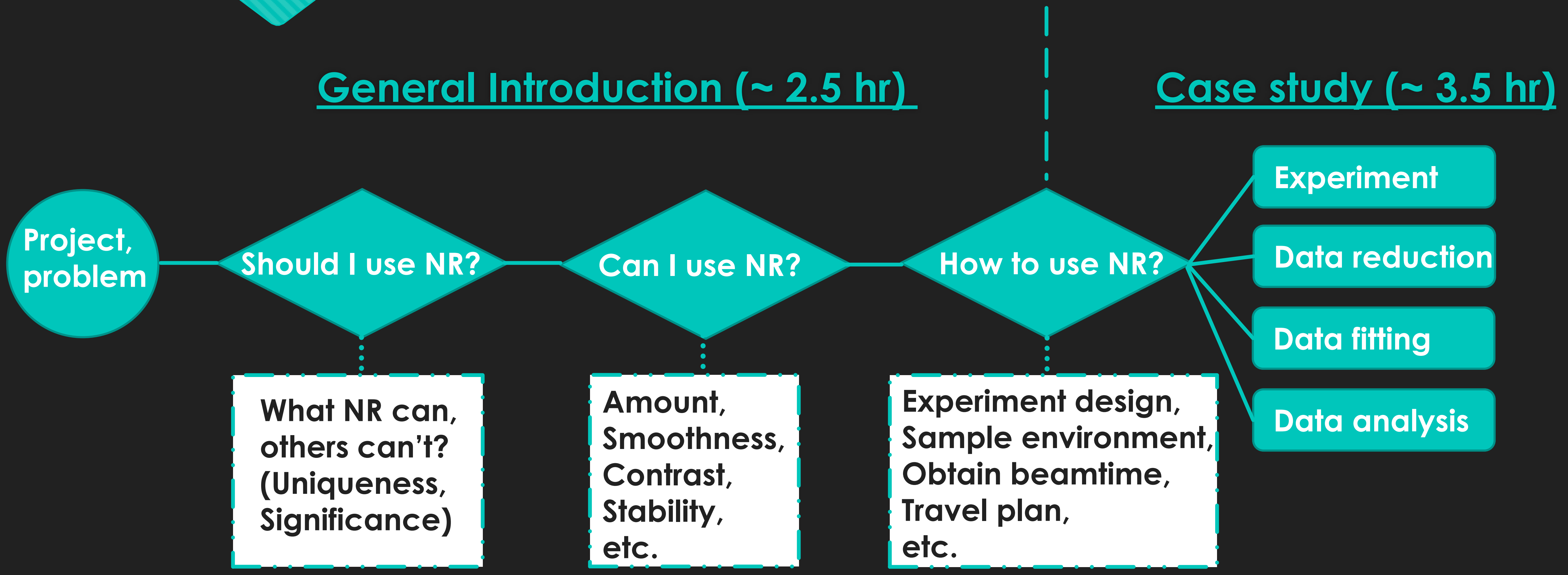
Neutron Reflectivity Investigation of the Propagation of Melt Polymers across a Glassy Interface

CHRNS School on Methods and Applications of SANS and NR

NIST Center for Neutron Research

July 2024

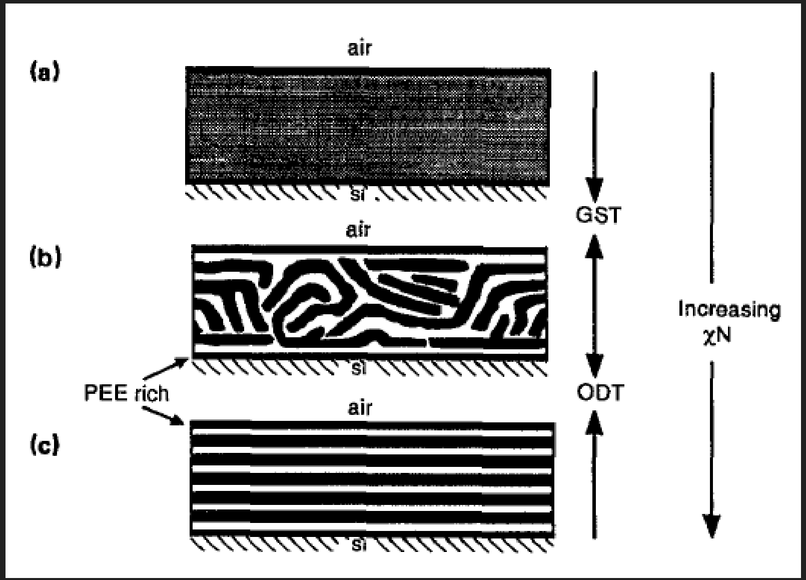
Schedule & Content



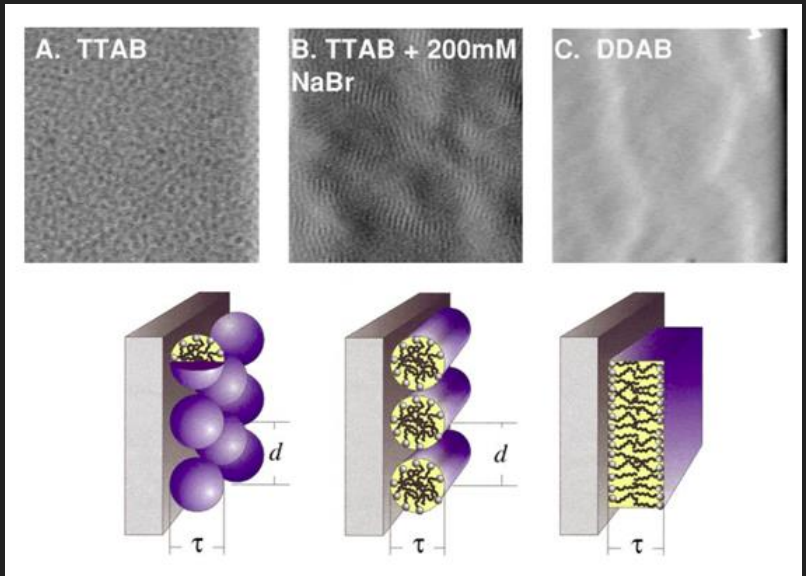
What NR is for?

Neutron reflectometry is a technique for investigating the thickness and the chemical composition of one or several thin layers at a surface or an interface of many materials.

- Application examples (air-solid interface)



J. Chem. Phys., Vol. 96, No. 11, 1992

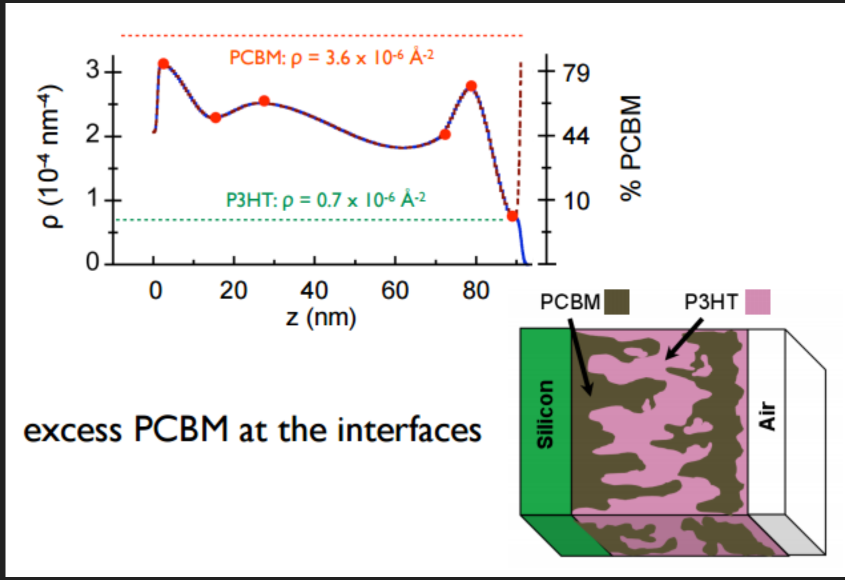


PHYSICAL REVIEW E, VOL 63, 041604

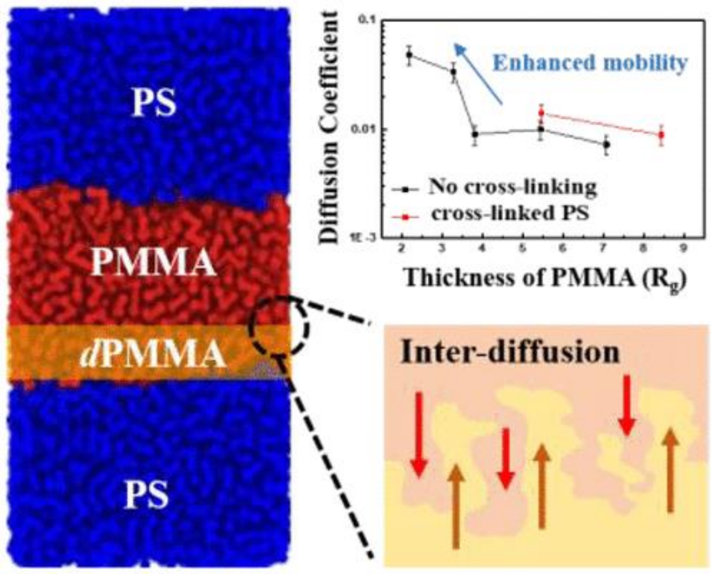
What NR is for?

Neutron reflectometry is a technique for investigating the thickness and the chemical composition of one or several **thin layers** at a **surface** or an **interface** of **many materials**.

○ Application examples (solid-solid interface)



Soft Matter, 2010, 6, 641–646

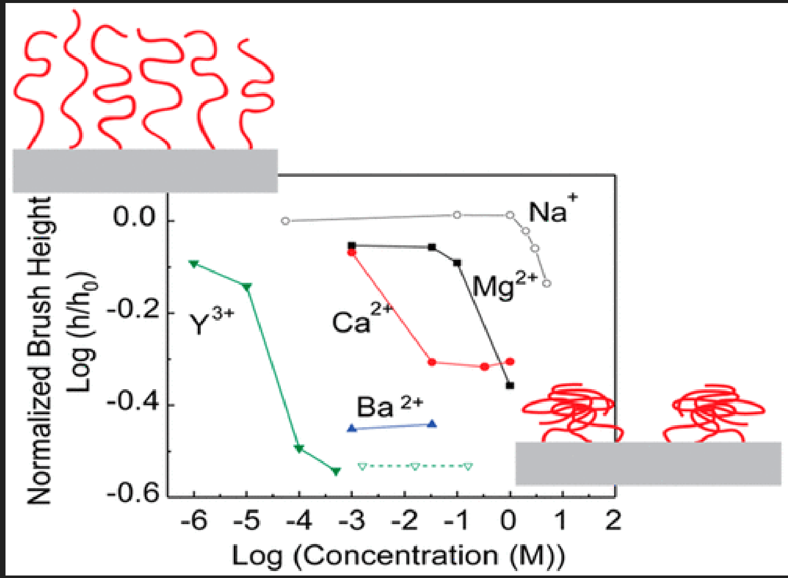


ACS Macro Lett. 2020, 9, 10, 1483–1488

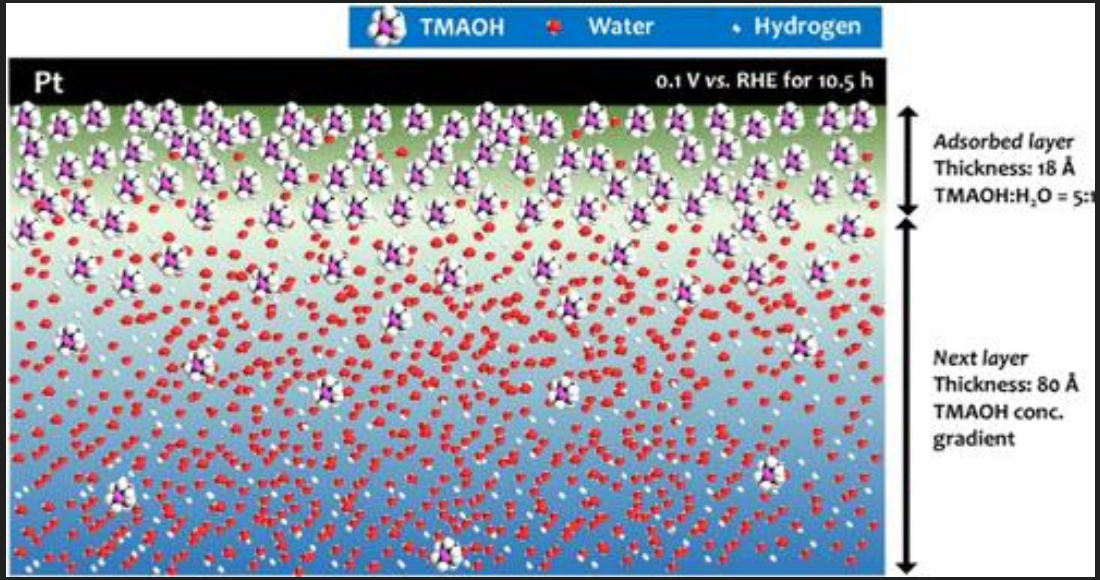
What NR is for?

Neutron reflectometry is a technique for investigating the thickness and the chemical composition of one or several thin layers at a surface or an interface of many materials.

- Application examples (liquid-solid interface)



Macromolecules 2016, 49, 15, 5609–5617

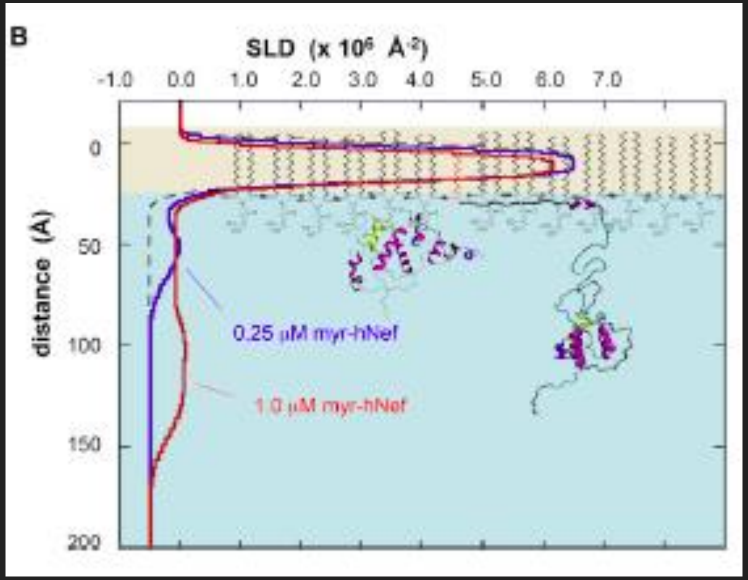


ACS Appl. Mater. Interfaces 2020, 12, 1825−1831

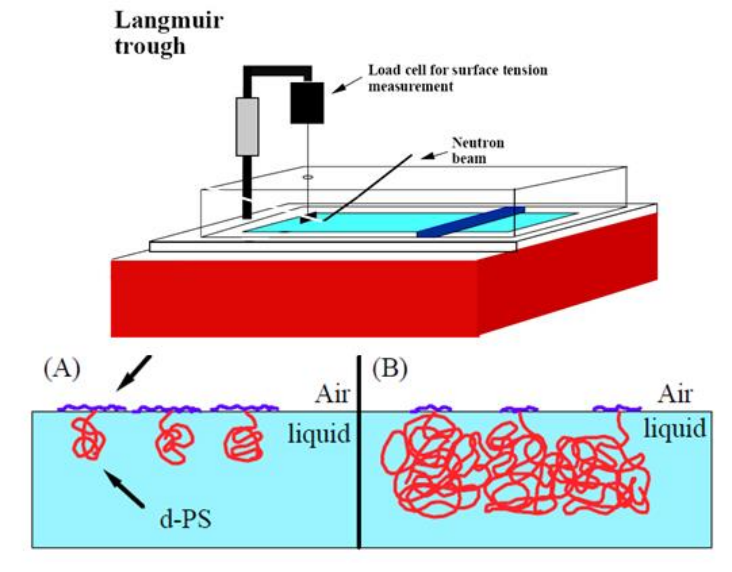
What NR is for?

Neutron reflectometry is a technique for investigating the thickness and the chemical composition of one or several **thin layers** at a **surface** or an **interface** of **many materials**.

- Application examples (air-liquid interface)



Structure 21, 1822–1833, October 8, 2013



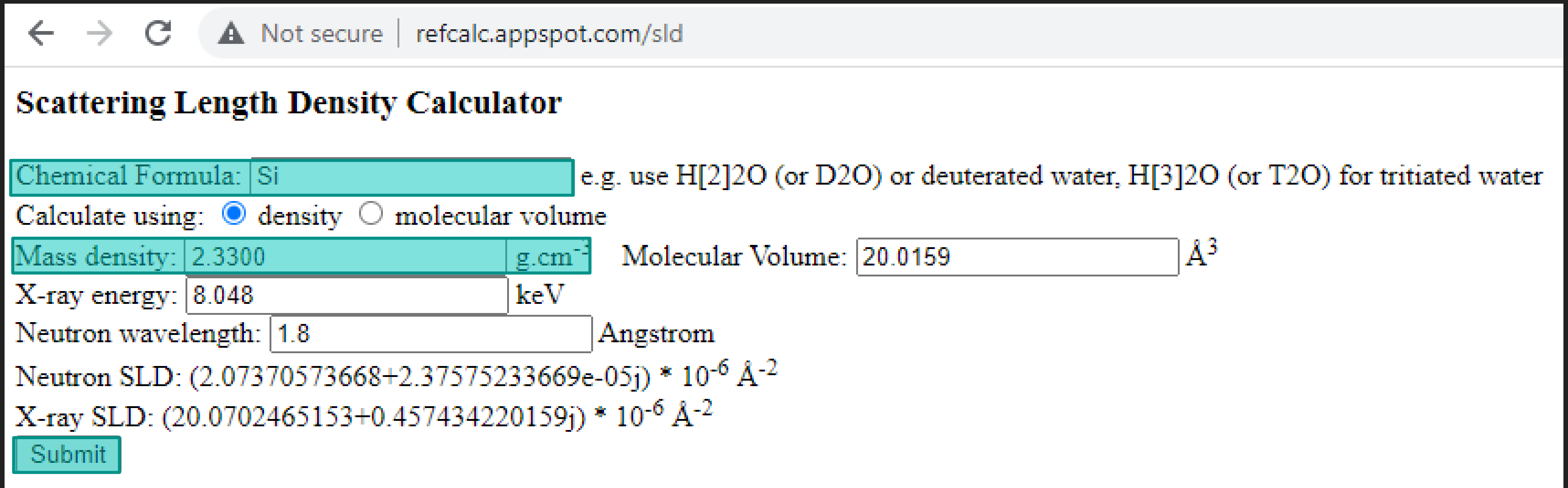
Macromol. Rapid Commun. ***21*, 243–270 (2000)**

What information NR provides?

- Scattering length density (SLD) vs. depth profile

  (composition vs. depth profile; concentration vs. depth profile; etc.)

  SLD calculator: http://www.refcalc.appspot.com/sld



What is a SLD vs. depth profile?

Example

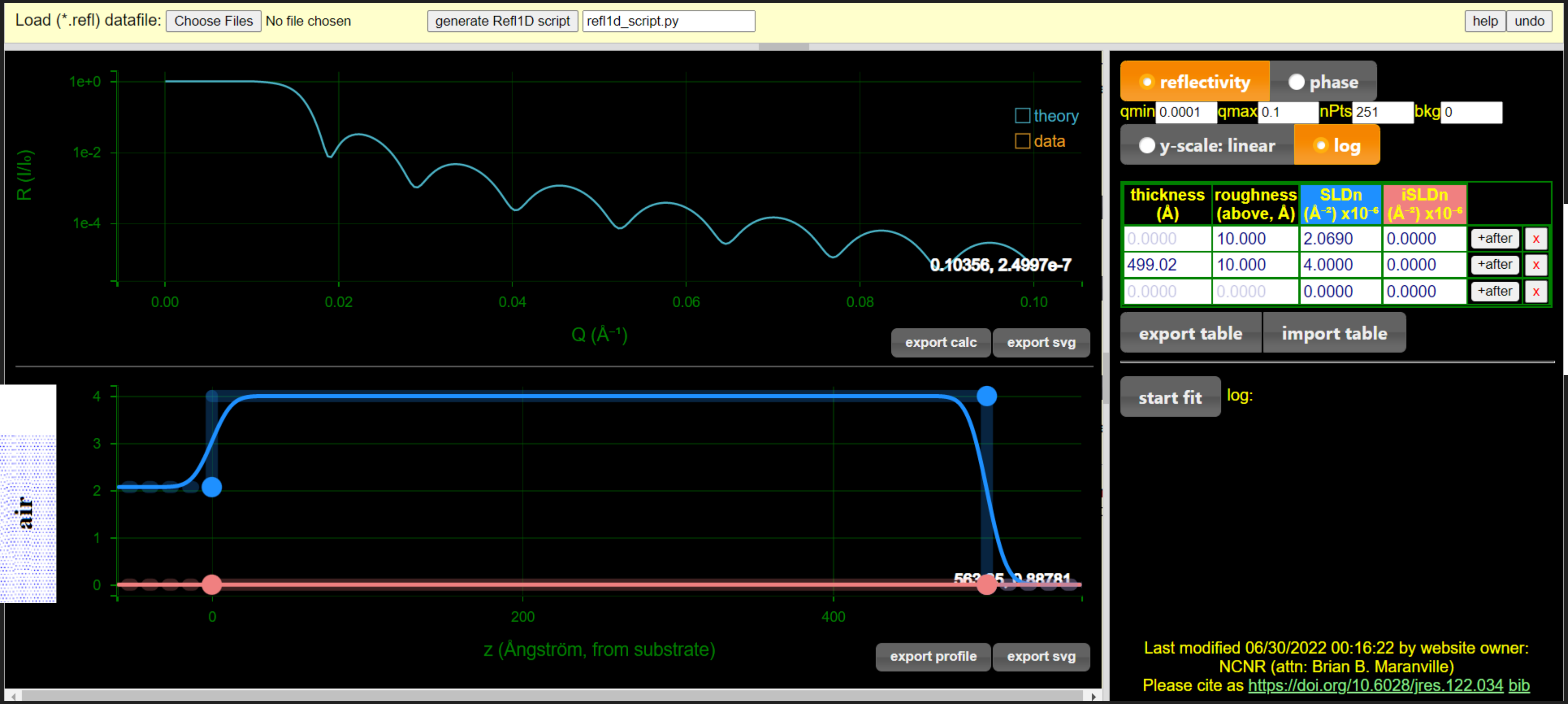
- H2O **Density**: 0.997 g/cm³
  SLD (neutron) = -0.56×10^{-6} Å^{-2}
  SLD (X-ray) = 9.44×10^{-6} Å^{-2}
- D2O **Density**: 1.10 g/cm³
  SLD (neutron) = 6.37×10^{-6} Å^{-2}
  SLD (X-ray) = 9.43×10^{-6} Å^{-2}
- H2O:D2O = 91.9: 8.1 **Density**: 1.0 g/cm³
  SLD (neutron) = 0.00×10^{-6} Å^{-2}
  SLD (X-ray) = 9.43×10^{-6} Å^{-2}
- BSA protein
  Density: 2.32 g/cm³

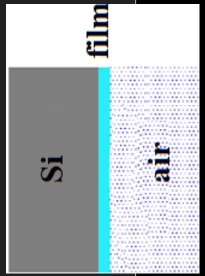
practice

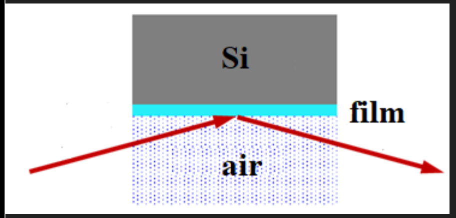
- PMMA
  Formula: $(C_5O_2H_8)_n$
  Density: 1.18 g/cm³
  SLD = 1.06×10^{-6} Å^{-2}
- dPC
  Formula: $(C_{16}O_4H_{12}D_6)_n$
  Density: 1.22 g/cm³
  SLD = 3.27×10^{-6} Å^{-2}
- Si
  Formula: Si
  Density: 2.32 g/cm³
  SLD = 2.07×10^{-6} Å^{-2}

Data fitting (R ⟶ SLD profile)

https://ncnr.nist.gov/instruments/magik/calculators/reflectivity-calculator.html





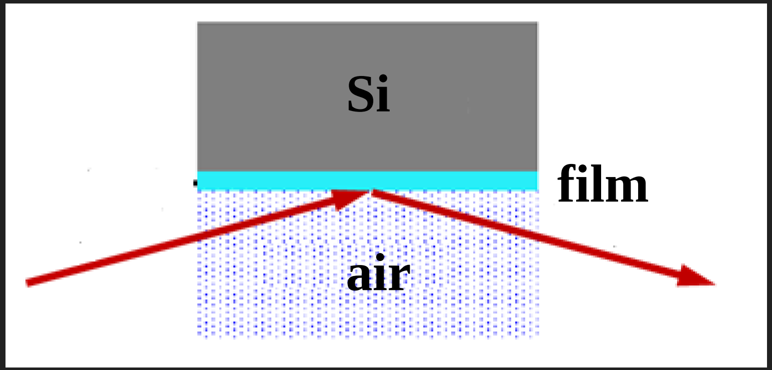


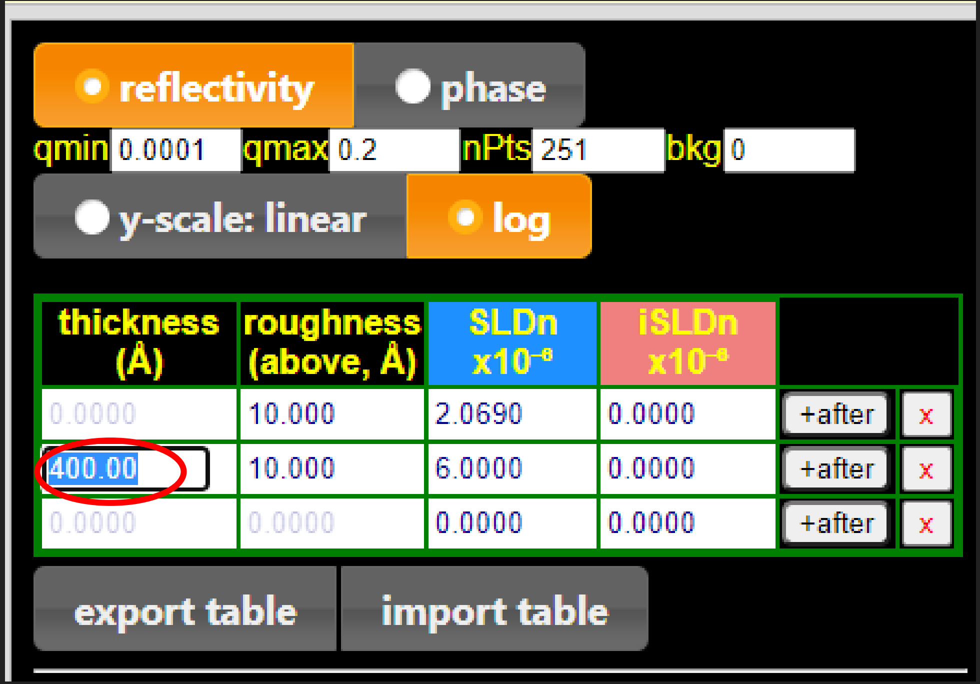
Thickness & Reflectivity

https://ncnr.nist.gov/instruments/magik/calculators/reflectivity-calculator.html

- practice
  - Single layer film on Si substrate

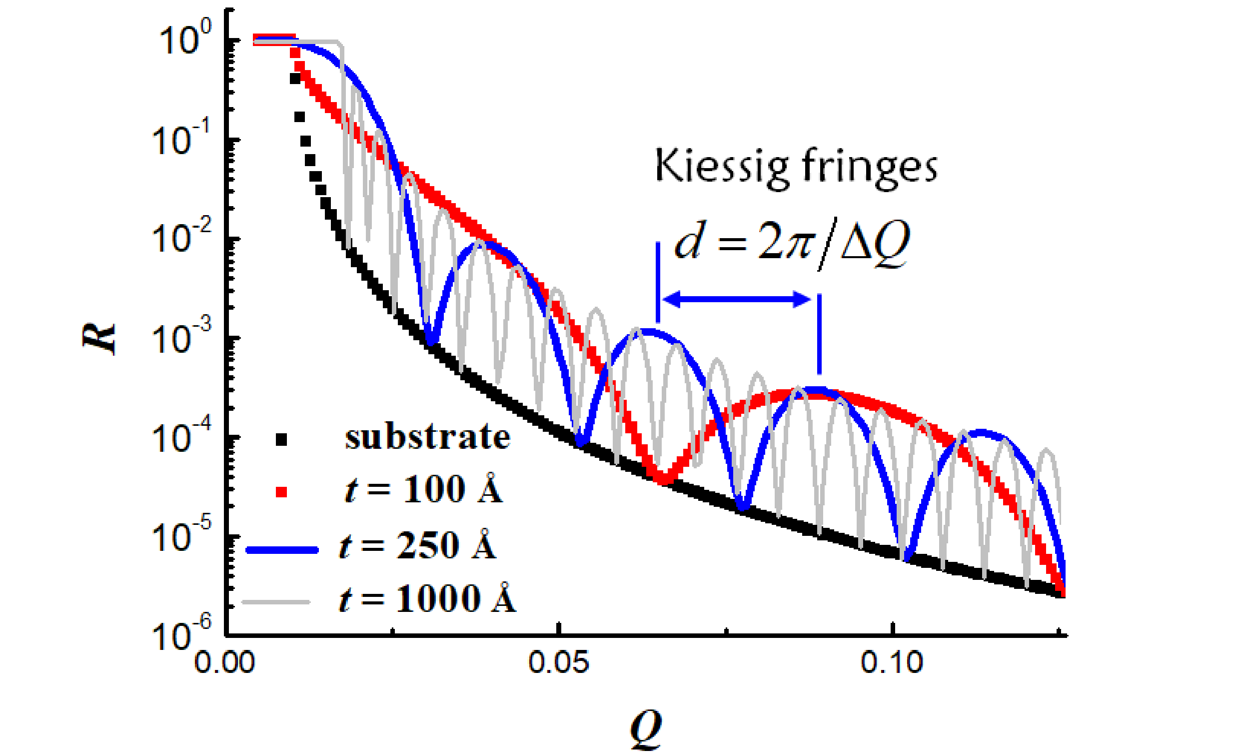
    Vary film thickness
    (100, 250, 1000)





Thickness & Reflectivity

thickness period



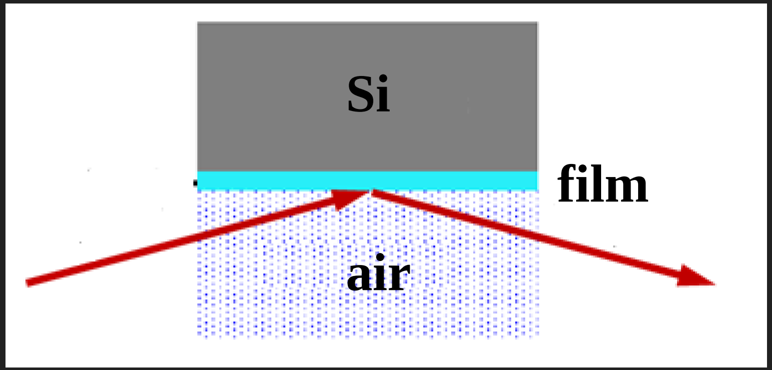
at large Q, $\mathrm{R} \approx (16\pi^2/Q^4)[\rho^2 + (\rho_s - \rho)^2 + 2\rho(\rho_s - \rho)\cos(Qd)]$

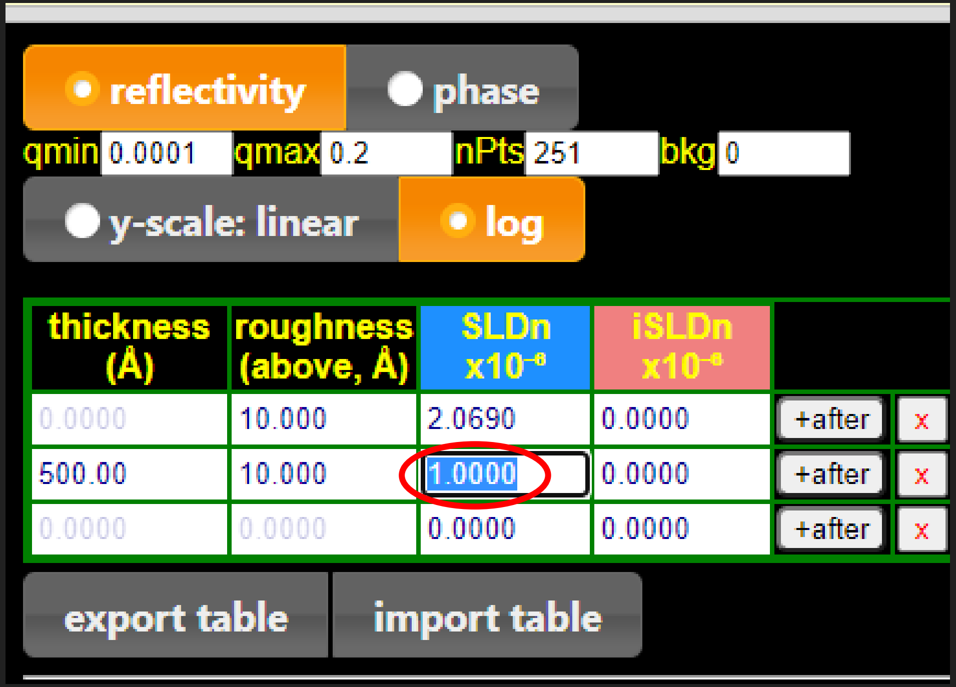
SLD & Reflectivity

https://ncnr.nist.gov/instruments/magik/calculators/reflectivity-calculator.html

- practice
  - Single layer film on Si substrate

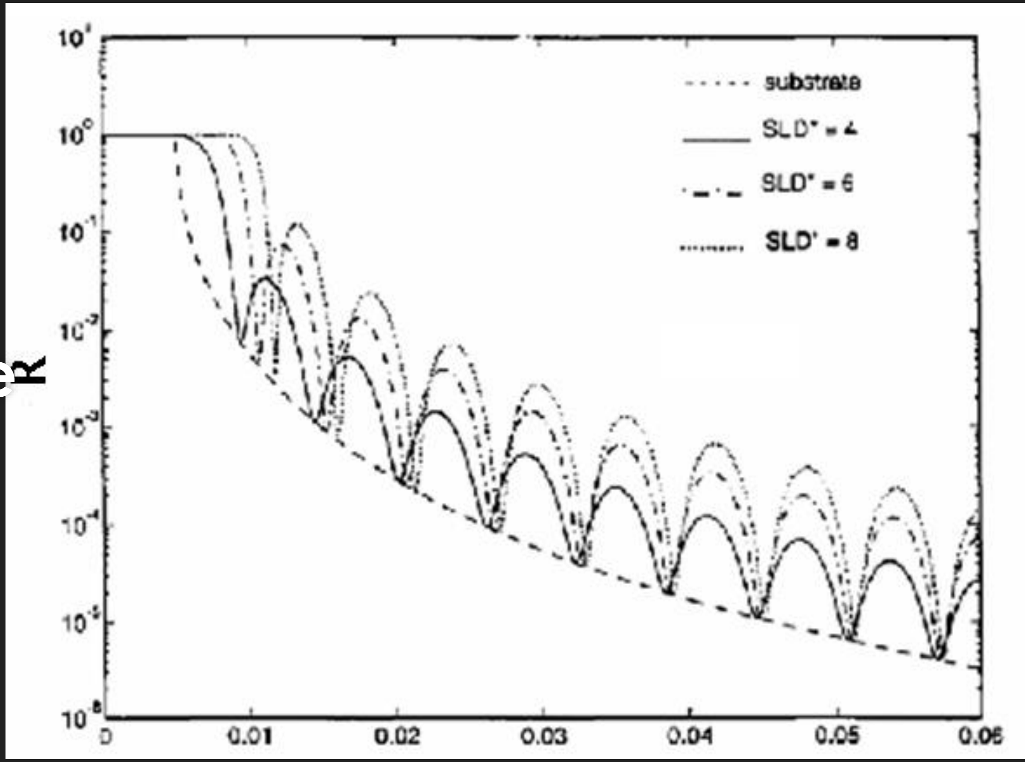
    Vary film SLD
    (1.0, 2.07, 3.0, 6.0)





SLD & Reflectivity

composition (SLD) amplitude



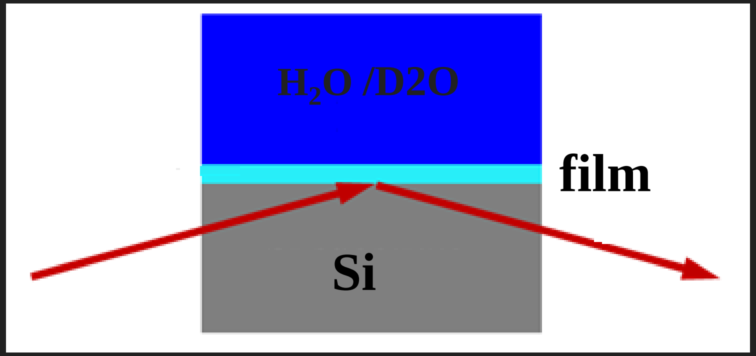
$$\text{at large } Q, \quad \mathrm{R} \approx (16\pi^2/Q^4)[\rho^2 + (\rho_s - \rho)^2 + 2\rho(\rho_s - \rho)\cos(Qd)]$$

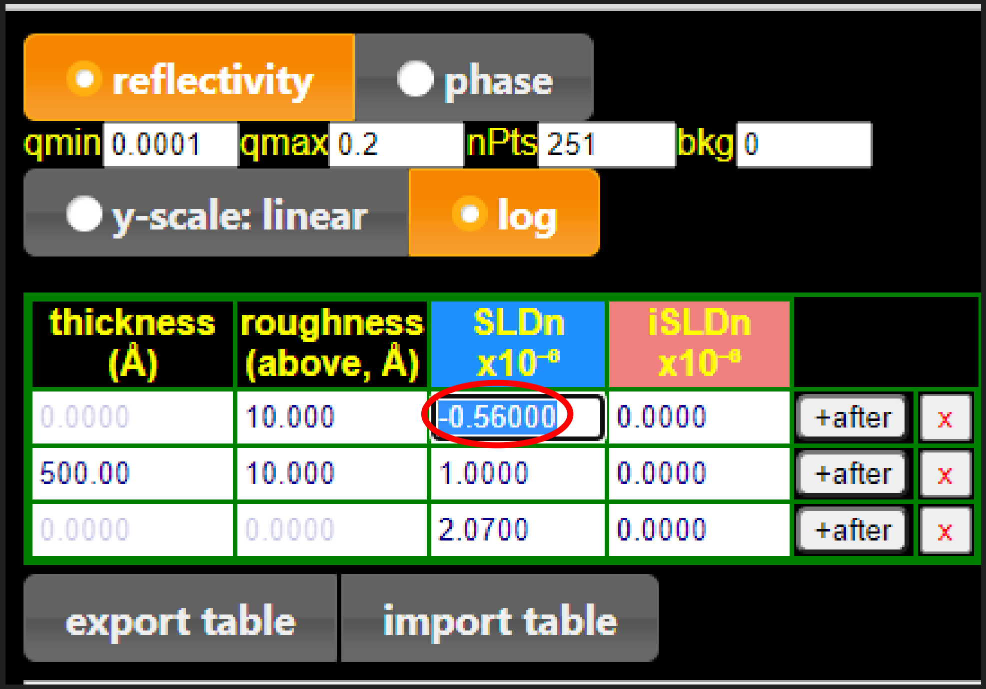
SLD & Reflectivity

https://ncnr.nist.gov/instruments/magik/calculators/reflectivity-calculator.html

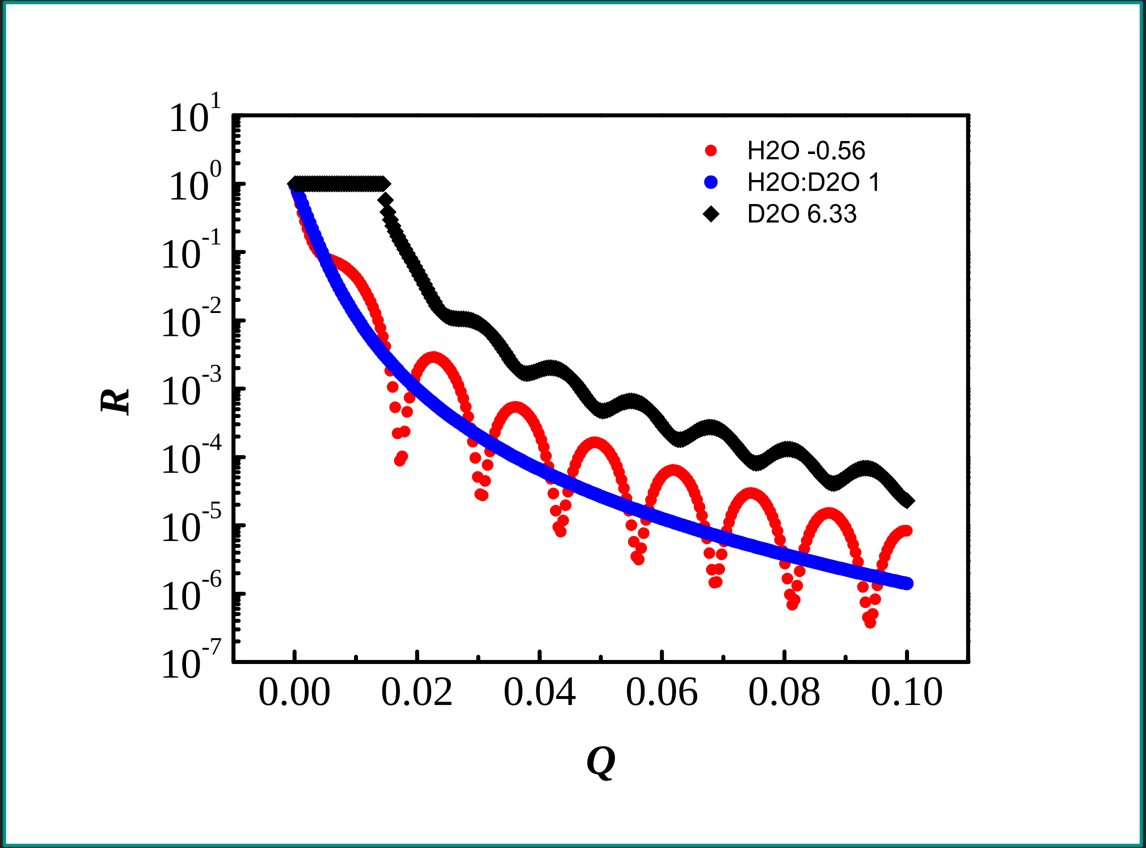
- practice

  Vary substrate SLD (-0.56; 1; 6.33)





SLD & Reflectivity

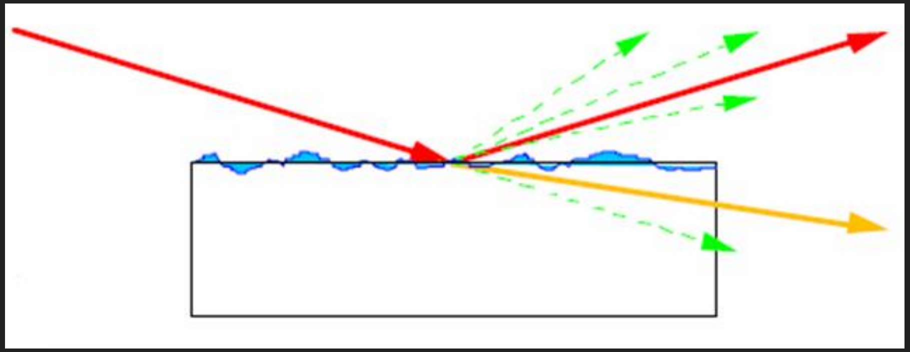


Roughness & Reflectivity

https://ncnr.nist.gov/instruments/magik/calculators/reflectivity-calculator.html

- practice
  - Single layer film on Si substrate

    Vary film roughness
    (0, 10, 50, 100)



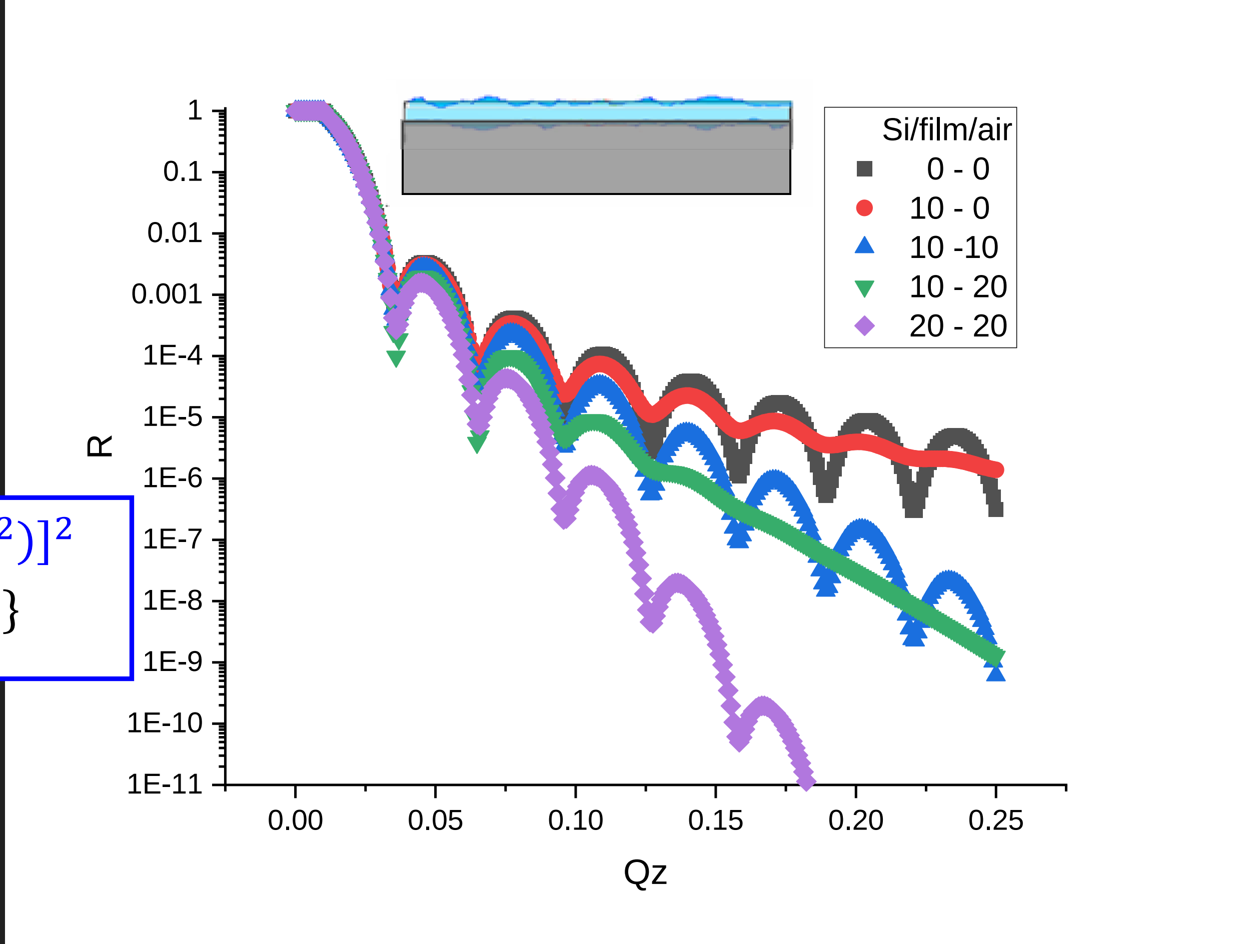
Roughness & Reflectivity

at large Q, for flat surface and interface,

$$R \approx (16\pi^2/Q^4)[\rho^2 + (\rho_s - \rho)^2 + 2\rho(\rho_s - \rho)\cos(Qd)]$$

at large Q, for diffuse surface and interface,

$$R \approx (16\pi^2/Q^4)\{\rho^2[\exp(-\sigma_1{}^2Q^2)]^2 + (\rho_s - \rho)^2[\exp(-\sigma_2{}^2Q^2)]^2 + 2\rho(\rho_s - \rho)\exp(-\sigma_1{}^2Q^2)\exp(-\sigma_2{}^2Q^2)\cos(Qd)\}$$



roughness (interfacial width) decay

NR summary

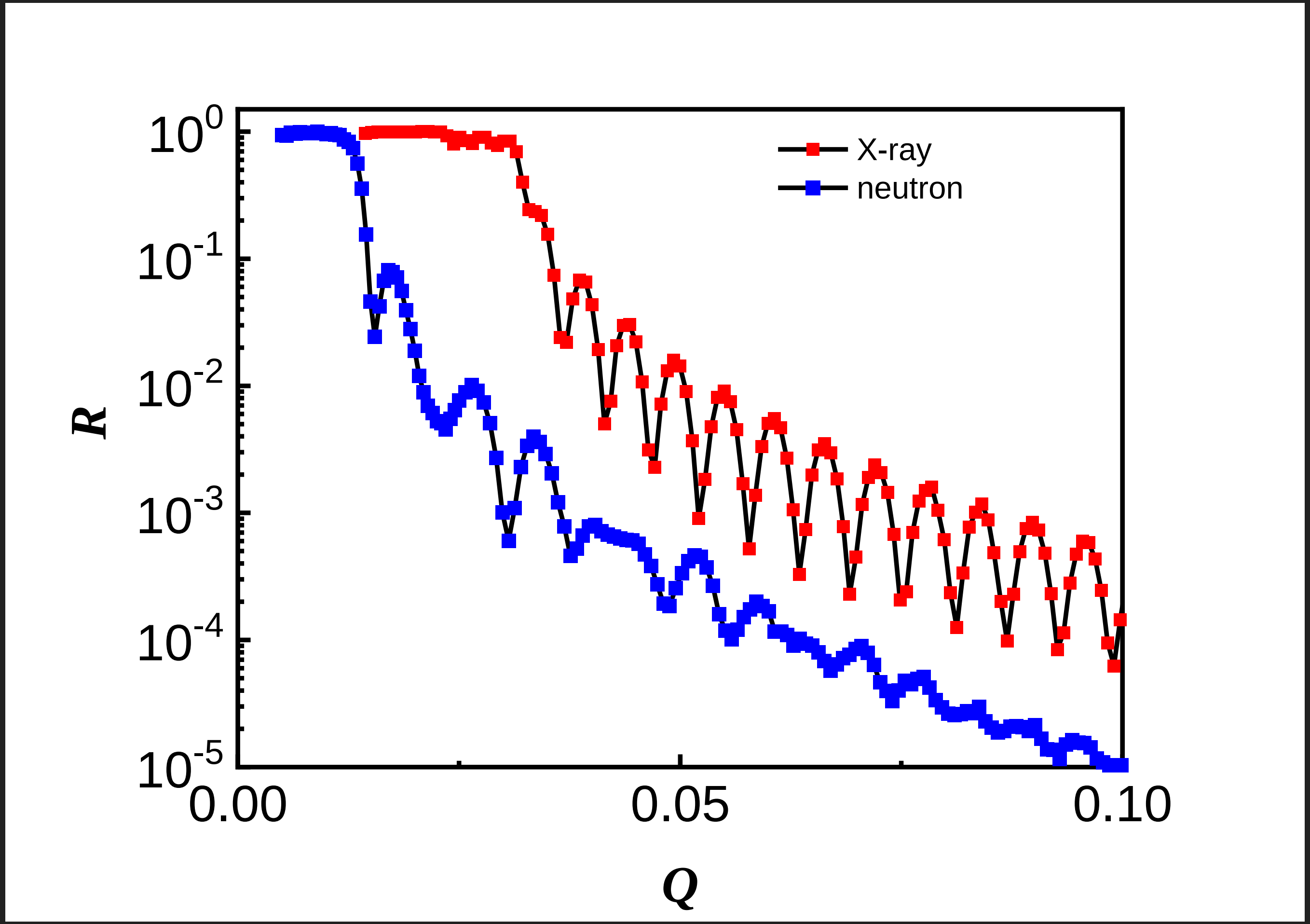
$$R = \frac{I_{\text{reflection}}}{I_{\text{incident}}} = f(Q, \rho, n, d, \sigma \ldots)$$

Substrate: Si, quartz, sapphire

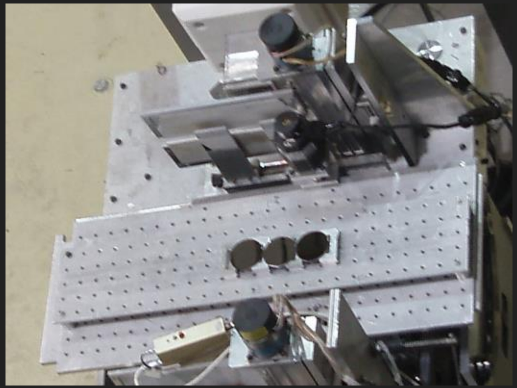
Sample Size: 2 ~ 4 inches

Typical Cases: diffusion, corrosion, adsorption, segregation, deposition…

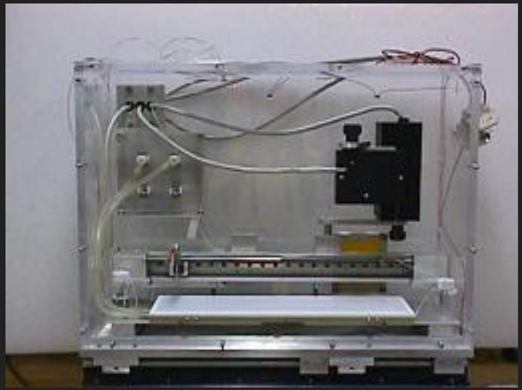
X-ray & Neutron Comparison



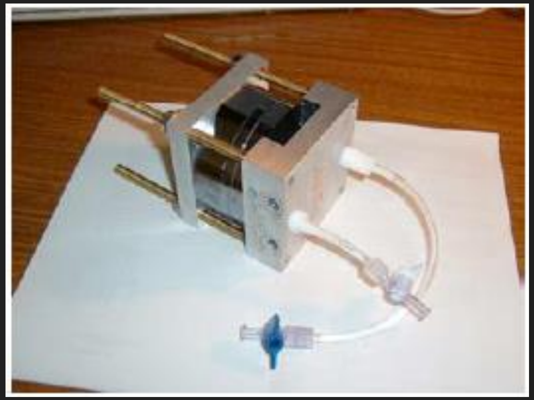
Sample environments



solid/air



liquid/air

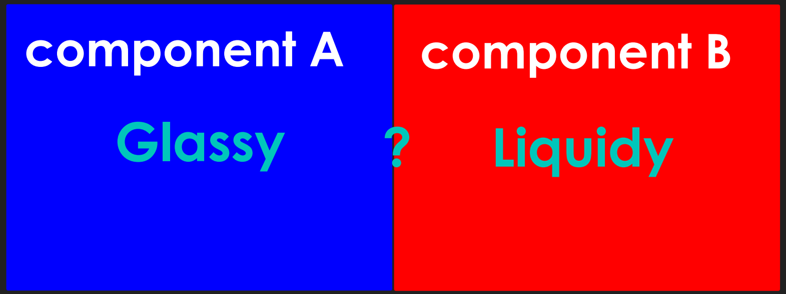


solid/liquid

vacuum, humidity, pressure …

Experiment

Neutron Reflectivity Investigation of the **Propagation** (transportation, diffusion, sorption, etc.) of a **Melt Polymer** across a **Glassy polymer** Interface



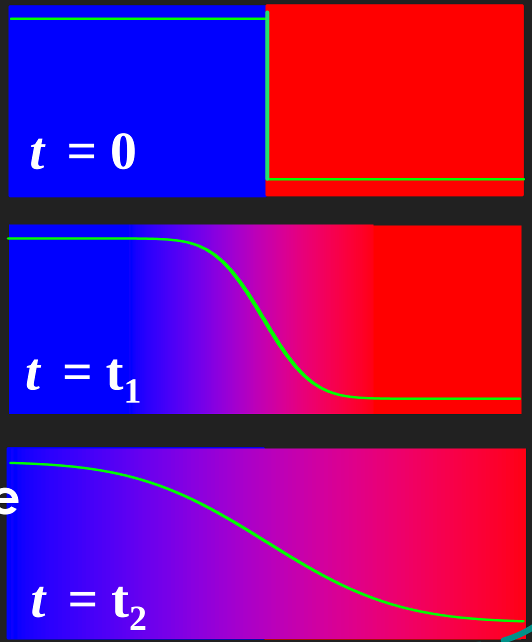
Background: types of diffusion

Fick's law of diffusion: $J = -D\nabla\varphi$ (Adolf Fick in 1855)

Fickian diffusion

(i.e. Case I diffusion)

No clear boundaries



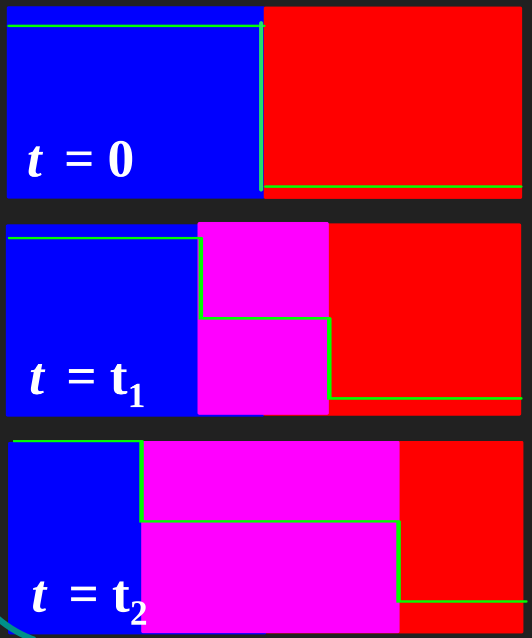
mass uptake
$M \propto t^{1/2}$

Non-Fickian diffusion

Anomalous diffusion

A combination of Case I and Case II diffusion to different extents

Case II diffusion



Sharp front

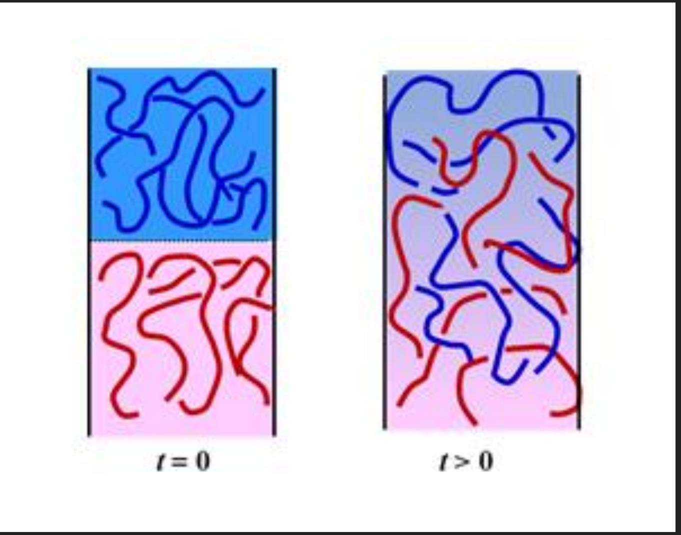
mass uptake
$M \propto t$

What causes different types of diffusion?

Case I diffusion

(e.g. PS/dPS, PMMA/dPMMA)

$T > T_{gA}, T_{gB}$



diffusion control

(relaxation negligible)

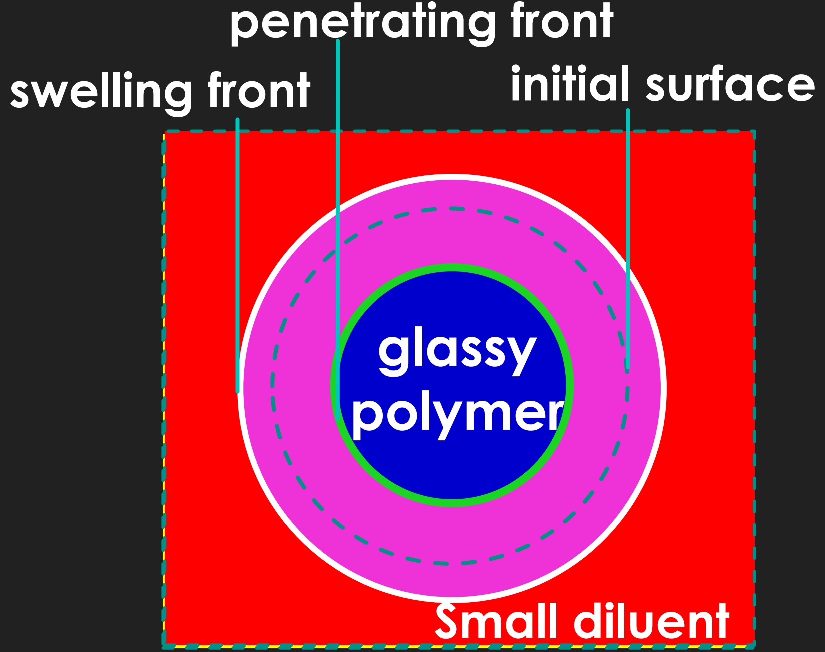
Anomalous diffusion

Comparable diffusion and relaxation effects

Case II diffusion

(e.g. PMMA rod/methanol)

$T < T_{gA}, T >> T_{gB}$

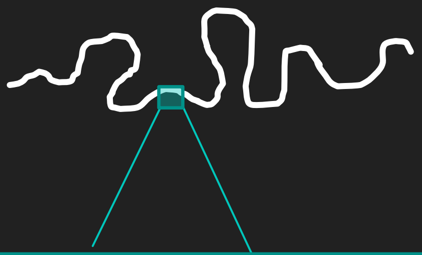


relaxation control

Polymer basics

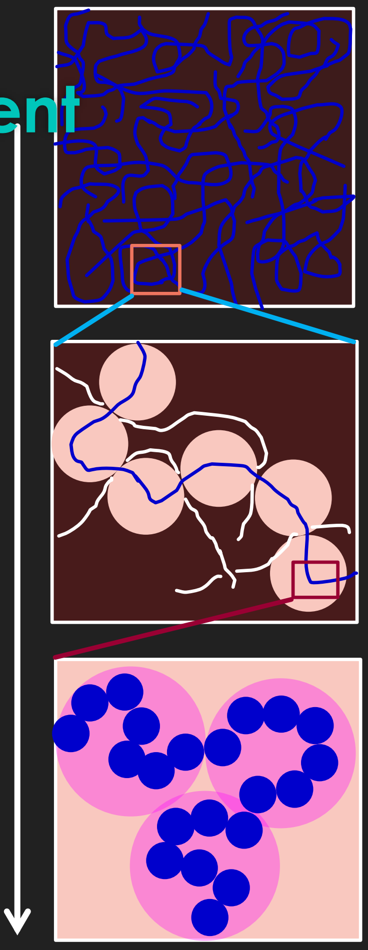
- chain-like structure
  Mn, Mw

  ➜ Repeat units



$– CH_2 – CH_2 – CH_2 – CH_2 – CH_2 –$

- Entanglement
  Me



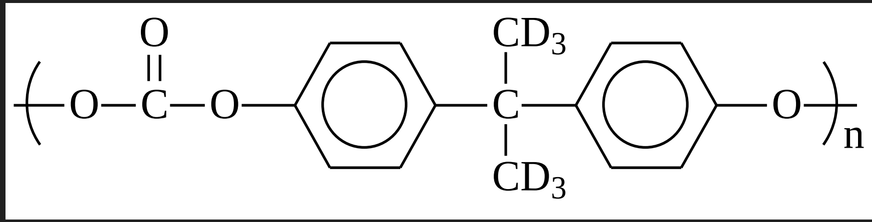
- Glass transition
  T_g

System investigated

component A

- deuterated polycarbonate

dPC



$T_g \approx 151$ °C

$M_n = 8.4\times10^4$ g/mol

$R_g = 11.0$ nm

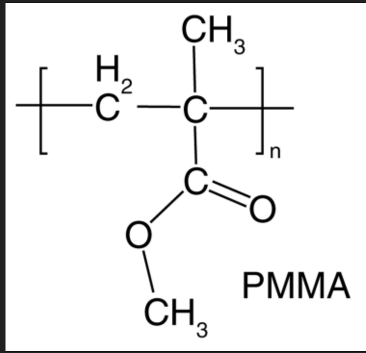
$M_e = 11{,}60$ g/mol

highly entangled

component B

- poly(methyl methacrylate)

PMMA



$T_g \approx 88$ °C

$M_n = 4.0\times10^3$ g/mol

$R_g = 1.6$ nm

non-entangled

(M_e: average molecular weight between entanglement points)

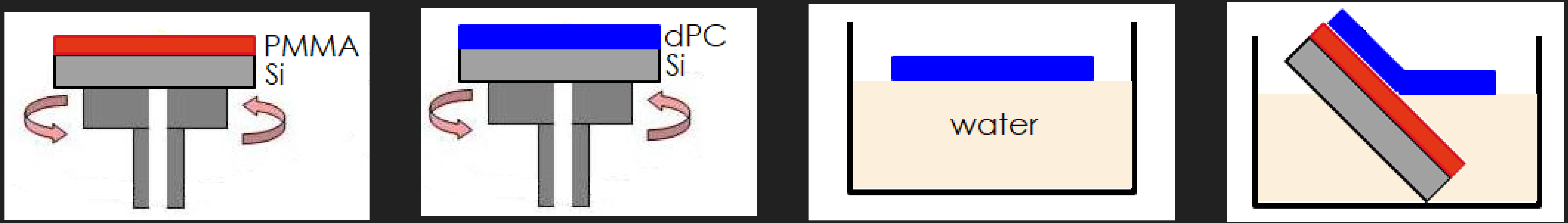
Objective

- To learn reflectivity measurements on bilayer polymer thin films.
- To determine the time evolution of interfacial profile.
- To play with the chain-like feature of polymers and understand its effect on interdiffusion.

Sample preparation

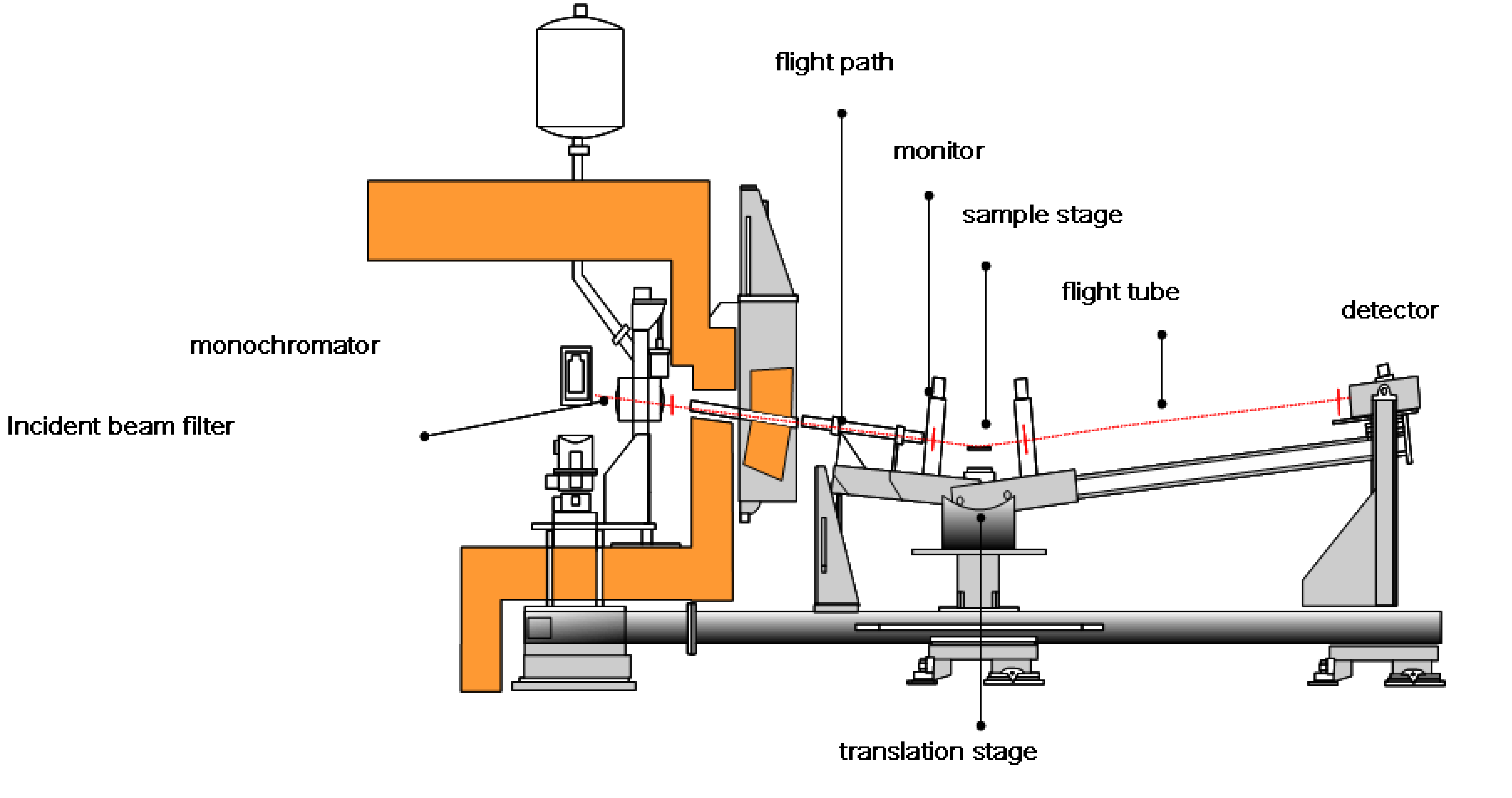
○ dPC/PMMA/Si

- Step 1 Remove the silicon oxide layer from the Si substrate
  (First “piranha” solution (70/30 v/v H_2SO_4 (50%)/ H_2O_2 (30%)) and then 5 % HF solution)
- Step 2 Spin coat a PMMA layer on the cleaned Si wafer
- Step 3 Spin coat a dPC layer on another Si wafer
- Step 4 Float the dPC film on the water surface then pick it up on the wafer with PMMA layer



NR measurement

- instrument



Data reduction

- https://reductus.nist.gov/
- Template _ unpolarized
- ncnrdata/ng7/201608/22440/data/1-4E3

Specular

7204 (as-cast)

7419 (20 min at 135 °C)

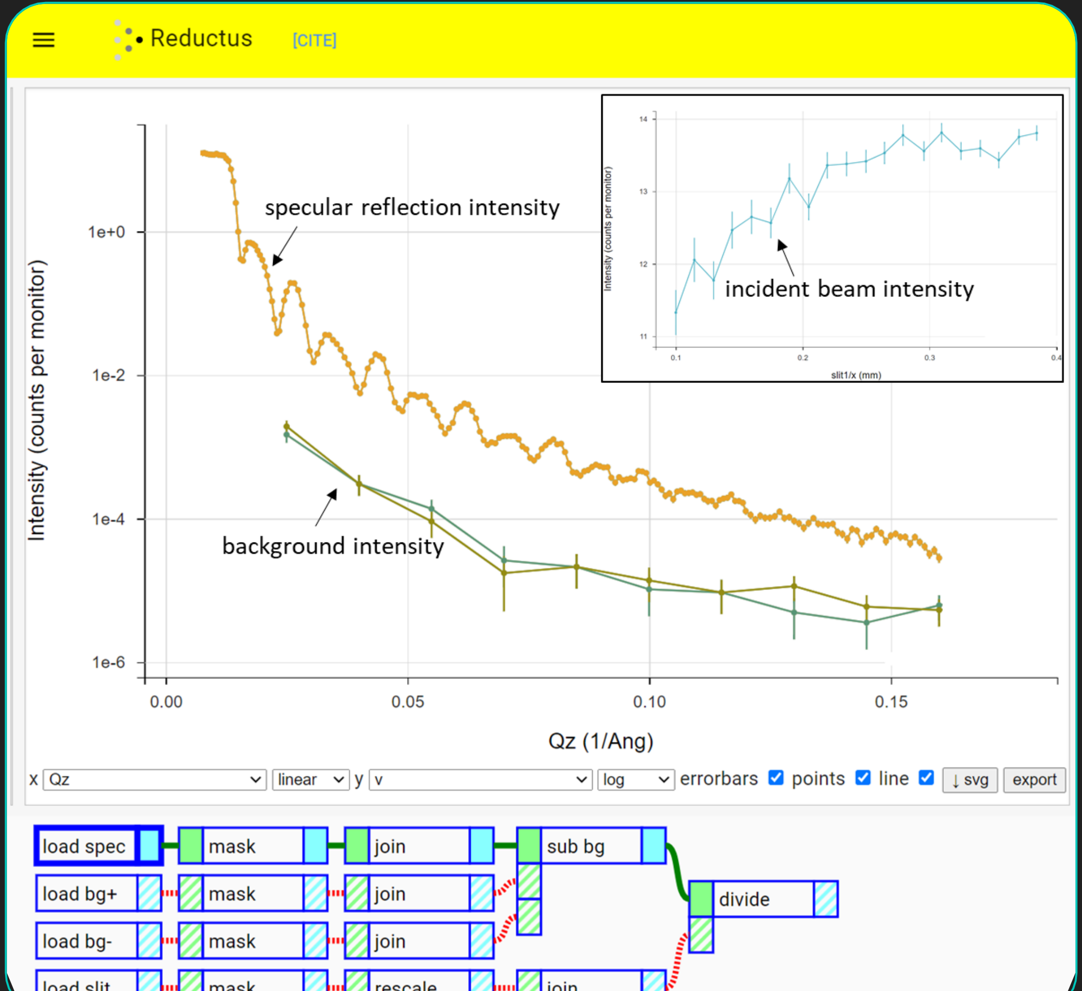
7619 (65 min at 135 °C)

Background

7205, 7206 (+, -)

Slits

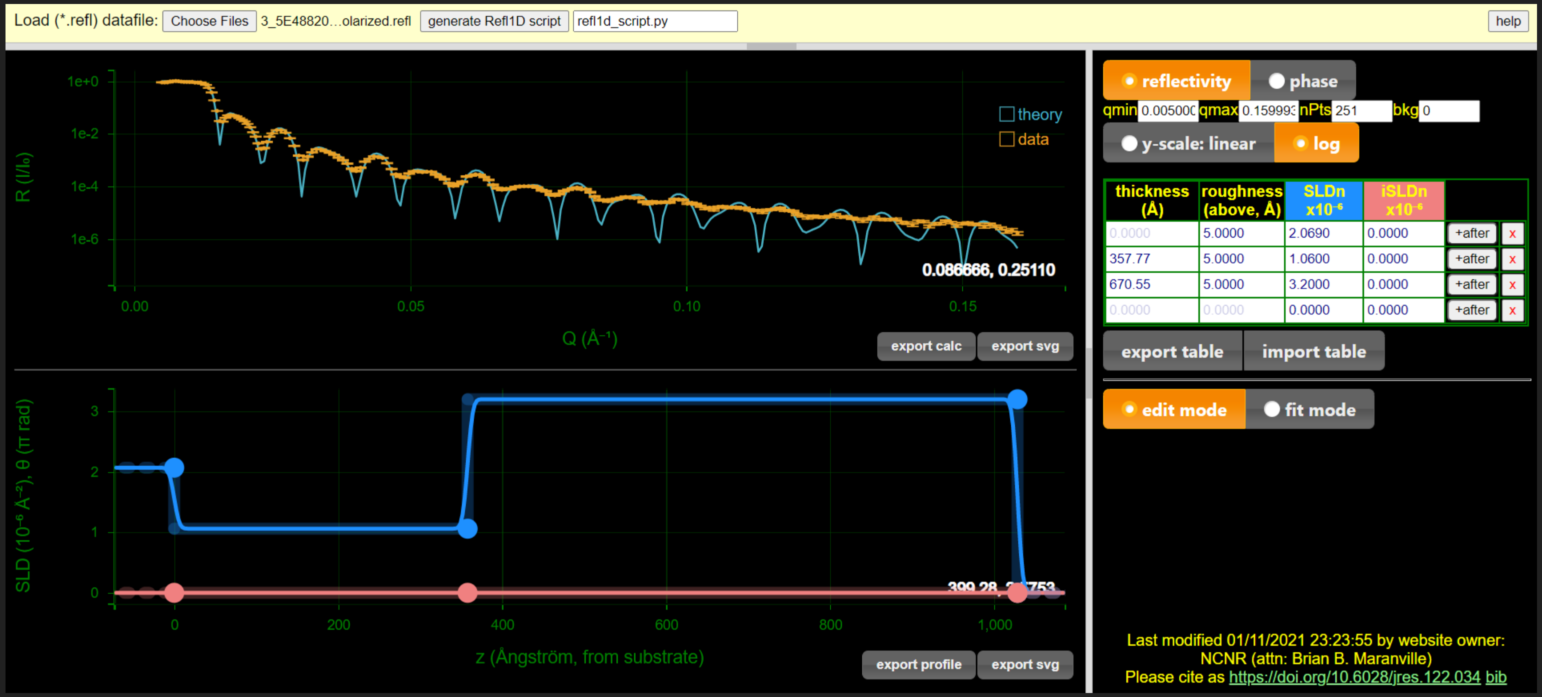
7127 (35 mm beam through air)



Data fitting

- Generate refl1D script

https://ncnr.nist.gov/instruments/magik/calculators/reflectivity-calculator.html



Data fitting

- Edit refl1D script
  - Load data
  - Stack layers
  - Set constraints
  - Fit parameters

refl1d_script (2).py

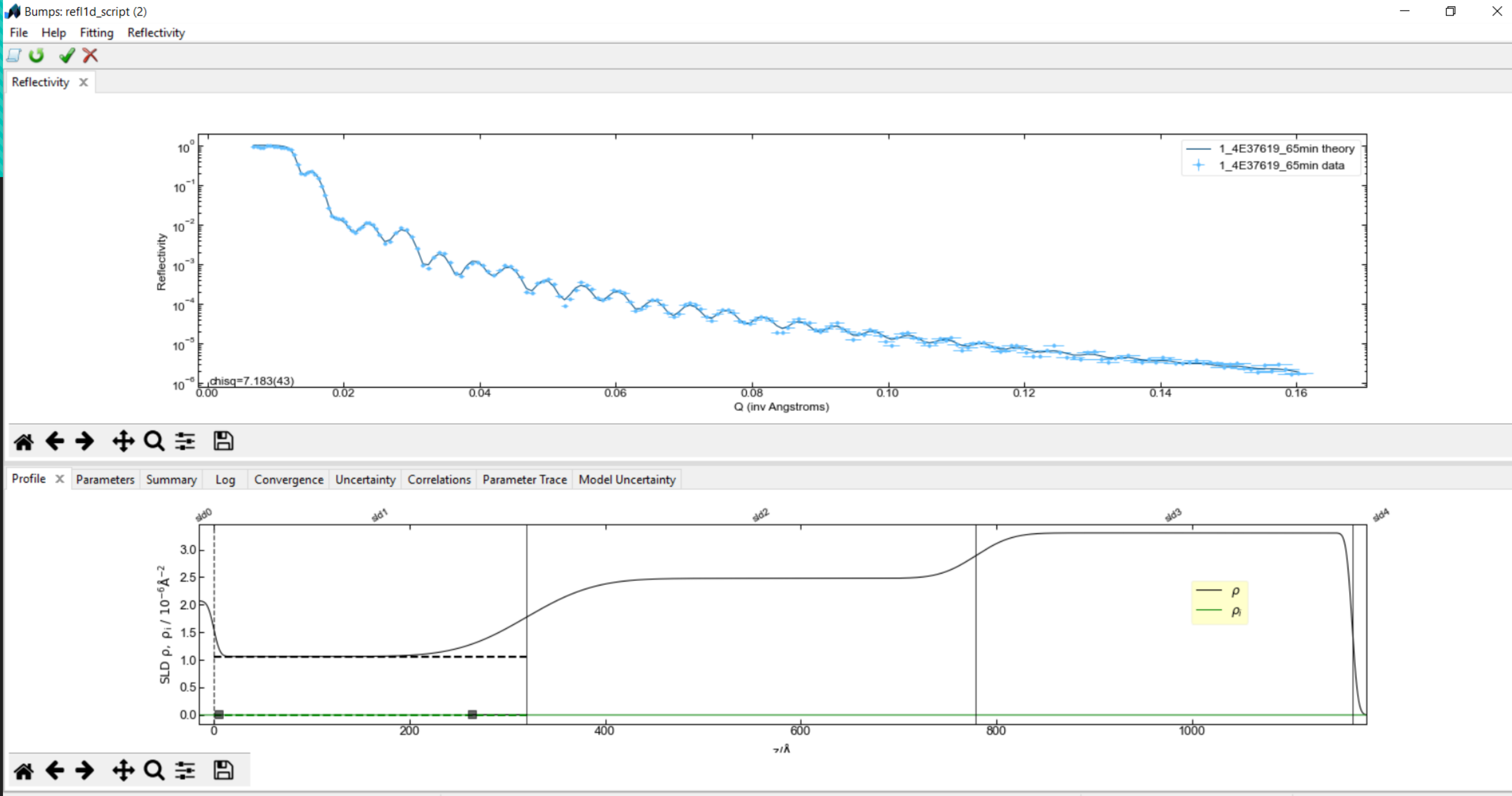
```python
from refl1d.names import *
from copy import copy
## === Data files ===
probe = load4('1_4E37619_65min.refl', back_reflectivity=False)
#probe = Probe(T=numpy.linspace(0.14829, 3.6500, 251), L=5.0000)

# Background parameter
probe.background.value = 0.0000
# probe.background.range(1e-9, 1e-5)

## === Stack ===
##
## First, we create a 'material' for each layer, which has an real and imaginary
## scattering length density, stored in a Refl1d object called 'SLD'
sld0 = SLD(name='Si', rho=2.0690, irho=0.0000)
sld1 = SLD(name='PMMA', rho=1.0600, irho=0.0000)
sld2 = SLD(name='Mix', rho=2.4500, irho=0.0000)
sld3 = SLD(name='dPC', rho=3.2800, irho=0.0000)
sld4 = SLD(name='Air', rho=0.0000, irho=0.0000)

## Then layers are created, each with its own 'material'.  If you want to force
## two layers to always match SLD you can use the same material in multiple layers.
## The roughnesses of each layer are set to zero to begin with:
layer0 = Slab(material=sld0, thickness=0.0000, interface=5.0000)
layer1 = Slab(material=sld1, thickness=319.15, interface=55.000)
layer2 = Slab(material=sld2, thickness=459.75, interface=30.000)
layer3 = Slab(material=sld3, thickness=384.36, interface=5.000)
layer4 = Slab(material=sld4, thickness=0.0000, interface=0.0000)

sample = Stack()
sample.add(layer0)
sample.add(layer1)
sample.add(layer2)
sample.add(layer3)
sample.add(layer4)
```


Bumps: refl1d_script (2)
File
Help
Fitting
Reflectivity
Reflectivity
1_4E37619_65min theory
1_4E37619_65min data
Reflectivity
chisq=7.183(43)
Q (inv Angstroms)
0.00
0.02
0.04
0.06
0.08
0.10
0.12
0.14
0.16
Profile
Parameters
Summary
Log
Convergence
Uncertainty
Correlations
Parameter Trace
Model Uncertainty
sld0
sld1
sld2
sld3
sld4
SLD ρ, ρi / 10⁻⁶Å⁻²
ρ
ρi
0
200
400
600
800
1000
z/Å

Conclusion