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Reflectivity: An Introduction.

Dr Stephen A. Holt
Bragg Institute, ANSTO

Specular Reflectivity ?

- Planar Interfacial Structure
  - < 1 nm – 100's nm
- Applied to following interfaces
  - Air/Liquid
  - Air/Solid
  - Solid/Solid (buried interfaces)
  - Solid/Liquid
  - Liquid/Liquid

The Plan

- Introduction to Reflectometry
  - Some background theory
  - Provide a framework
- Important Parameters
  - SLD
  - Thickness
  - Roughness
- Data Treatment.

Will Not Address

1. In Plane Structure
2. Instrumentation
3. Sample quality
4. Sample environment

Introduction

- Basic Concepts
  - Geometry
  - Scope of Method
  - Contrast Variation

- Experimental Considerations

Specular Reflectivity

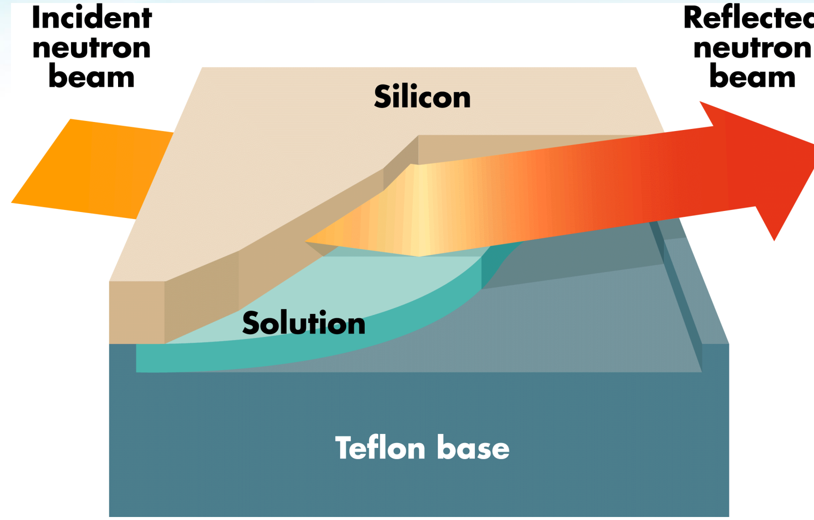
- Effective for studying ***Structure Perpendicular*** to the interface
- Applies to layers with thicknesses from Å to sub-micron
- Does *NOT* rely upon order within the plane - therefore suitable for disordered interfaces
- Resolution typically on the sub-molecular scale

“Wet” Interfaces

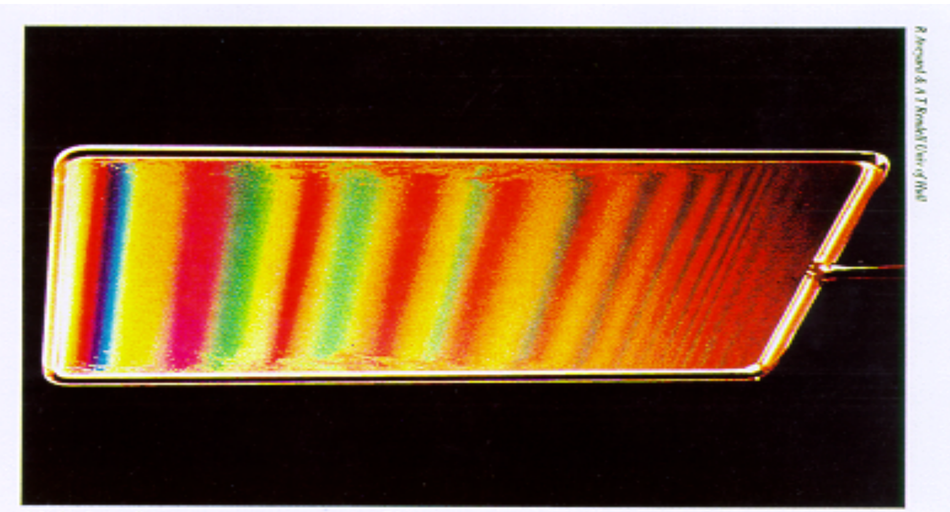
- Restrictions mentioned earlier are particularly severe for wet interfaces

- Very few methods can be applied to the *in situ* study of structure at liquid interfaces at molecular resolution or better.

Analagous to optical interference, ellipsometry



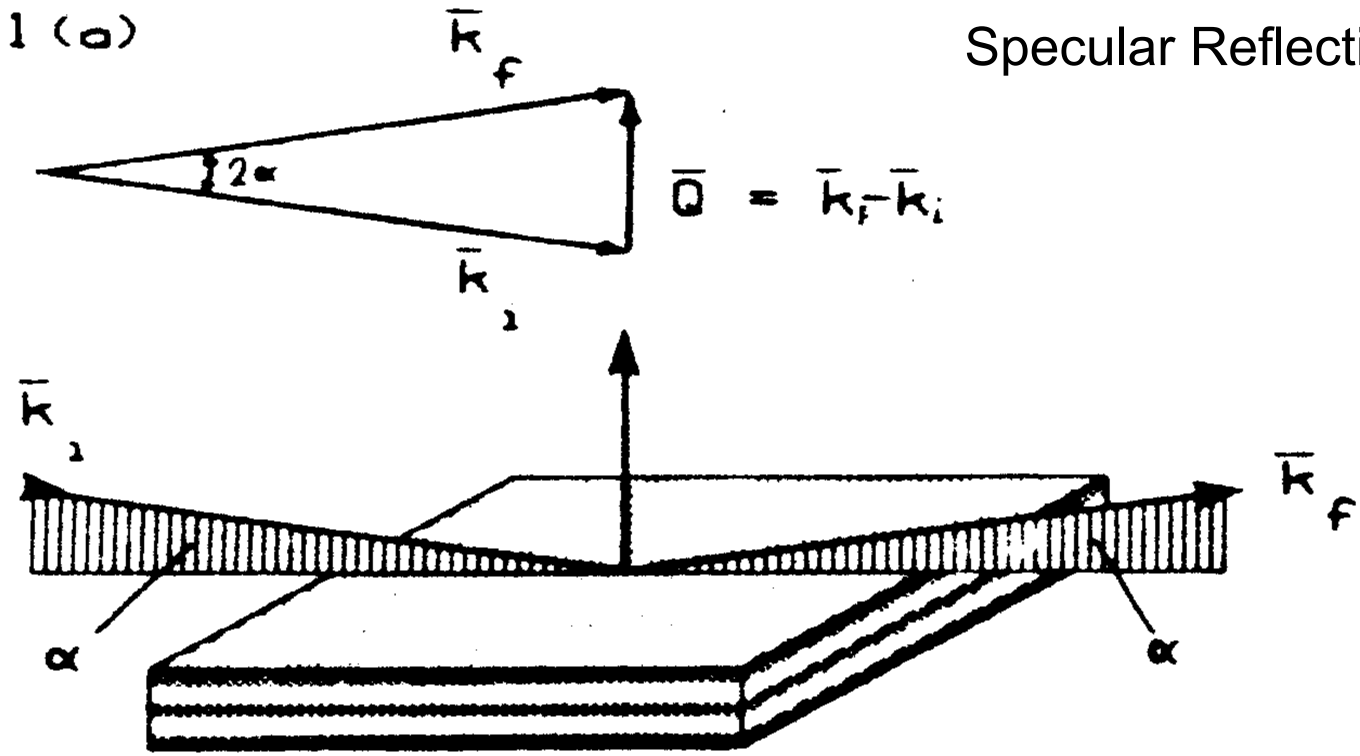
Equivalent to electromagnetic radiation with the electric vector perpendicular to the plane of incidence



Light interference pattern on soap film

Depth Profiling : **provides information on concentration or composition profile perpendicular to the surface or interface**

Geometry



Specular Reflection

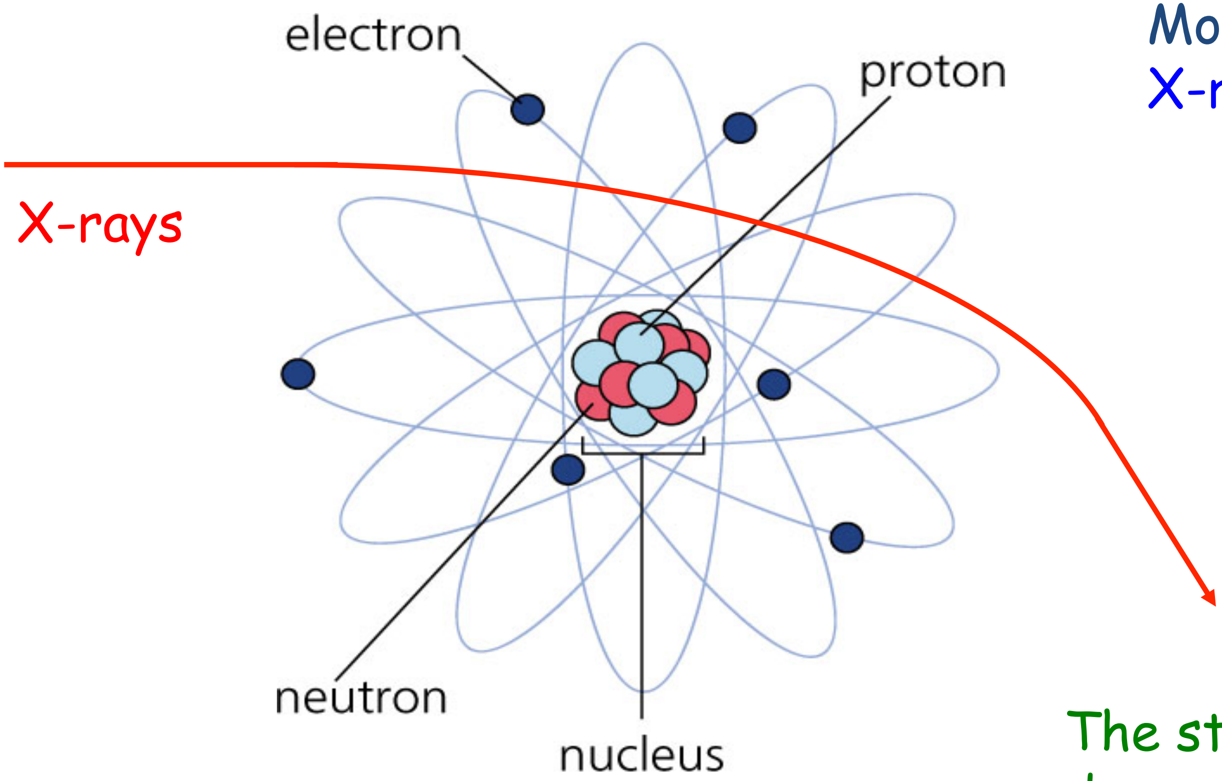
Probe change in refractive index

- Could be for any radiation.

Kjaer *et al*, J. Phys. Chem. **1989**, 93, 3200 - 3206

X-ray Scattering

X-rays scatter from the electron cloud of atoms

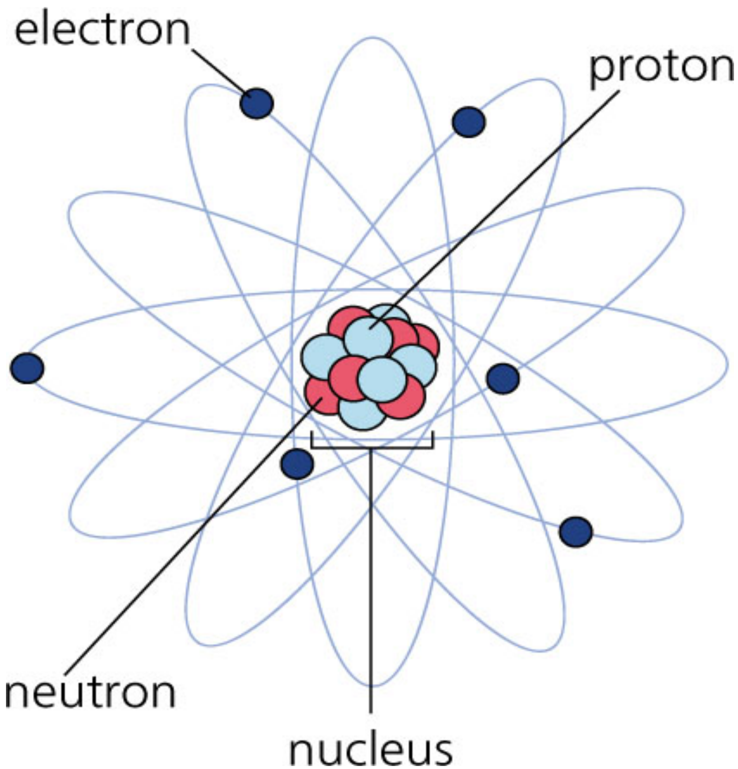


Most of matter is electrons
X-rays are weakly penetrating

The strength of the scattering depends on atomic number (Z).

How do Neutrons Scatter?

Neutrons scatter from the nucleus, not the electron cloud…



On this scale:

The nucleus is ~$^1/_5$th the size of the atom…

Why let a good picture get in the way of reality?

According to neutrons ~99.9999999% of matter is "empty space"

Refractive Index and Scattering Length Density

n = 1 for air, and slightly <1 for other materials

$$n = 1 - (\delta + i\beta)$$

Scattering Length Density

$$\delta = \frac{\lambda^2}{2\pi} r_e N_A \frac{\Sigma_i \rho_i Z_i}{\Sigma_i M_i}$$

r_e = Bohr electron radius
$= e^2 / 4\pi\varepsilon_o mc^2$
$= 2.818 \times 10^{-15}$ m

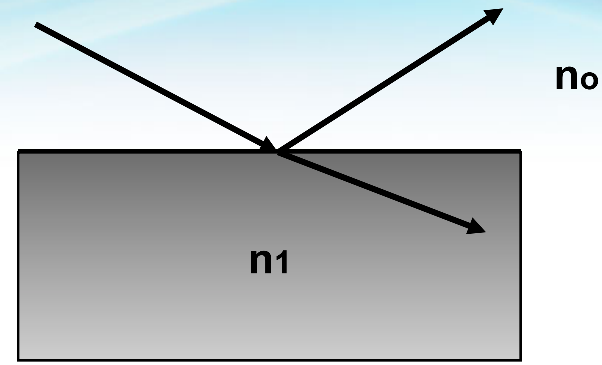
ρ_i mass density
Z_i atomic number of i^{th} atom
M_i molar mass of i^{th} atom

About silicon and higher Z, need to account for β

$$\beta = \frac{\lambda^2}{2\pi} r_e N_A \frac{\Sigma_i \rho_i f''_i}{\Sigma_i M_i}$$

f'' is the imaginary component of the X-ray atomic form factor that describes the absorption in a material

Specular reflection of neutrons



Refractive index defined using the usual convention in optics:

$$n = k_1 / k_0$$

$$n = 1 - \delta + i\beta$$

$$\delta = \frac{\lambda^2}{2\pi} N_b = \frac{\lambda^2}{2\pi} N_A \sum_i \frac{\rho_i}{A_i}\left(b_{0,i} + b_i^{'}\right)$$

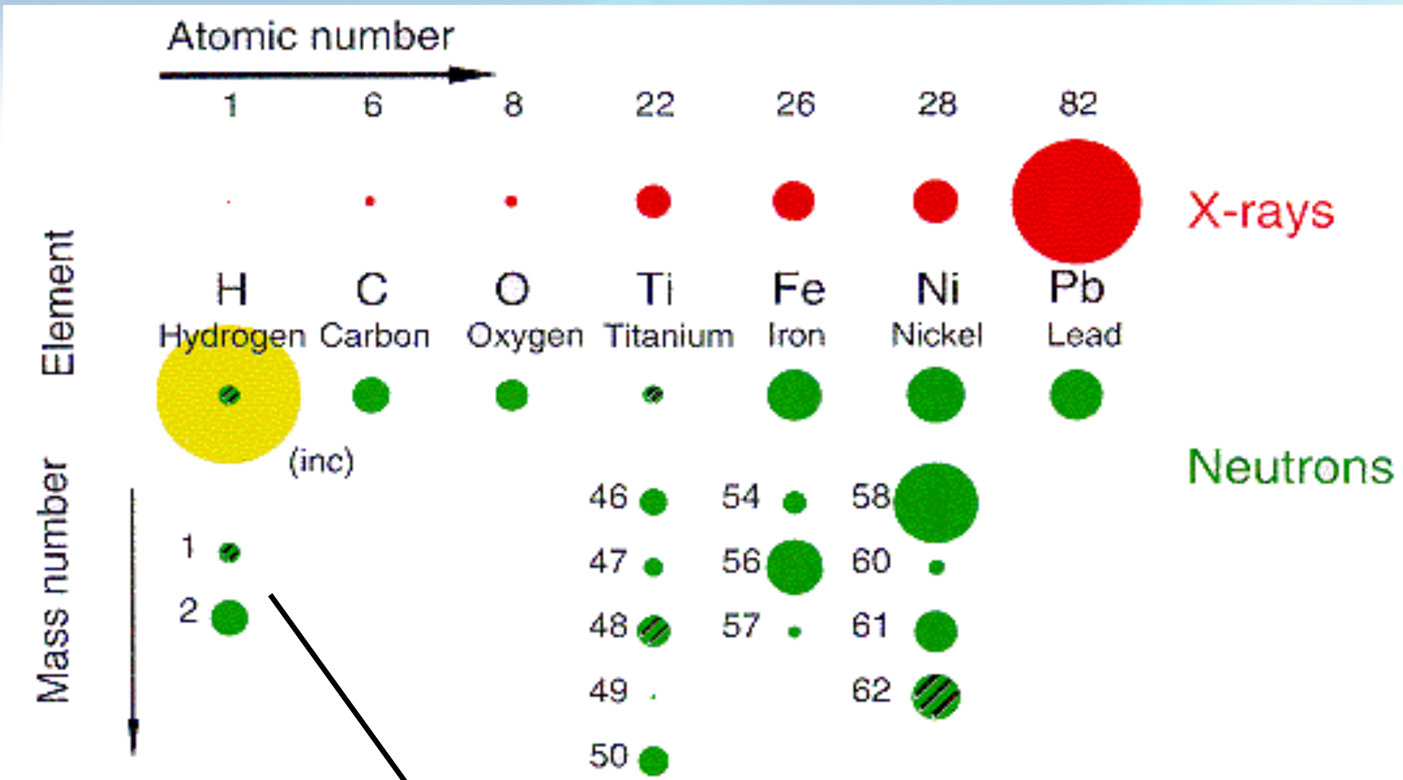
Scattering Length Density

$$\beta = \frac{\lambda^2 \mu_N}{4\pi}$$

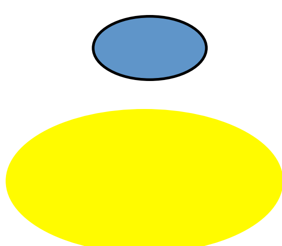
Can usually ignore β (especially for soft matter)

δ is typically of order $10^{-5} – 10^{-6}$

Refractive Index for neutrons



The diameters of the circles shown scale with the scattering amplitude f_x (sinΘ= 0) for x-rays, and b_{coh} * 10 for neutrons. Hatching indicates negative scattering amplitudes.



H -3.74 fm (-3.74 x 10^{-5} Å)

D 6.67 fm (6.67 x 10^{-5} Å)

Extensively use H/D isotopic substitution to manipulate " contrast " or refractive index

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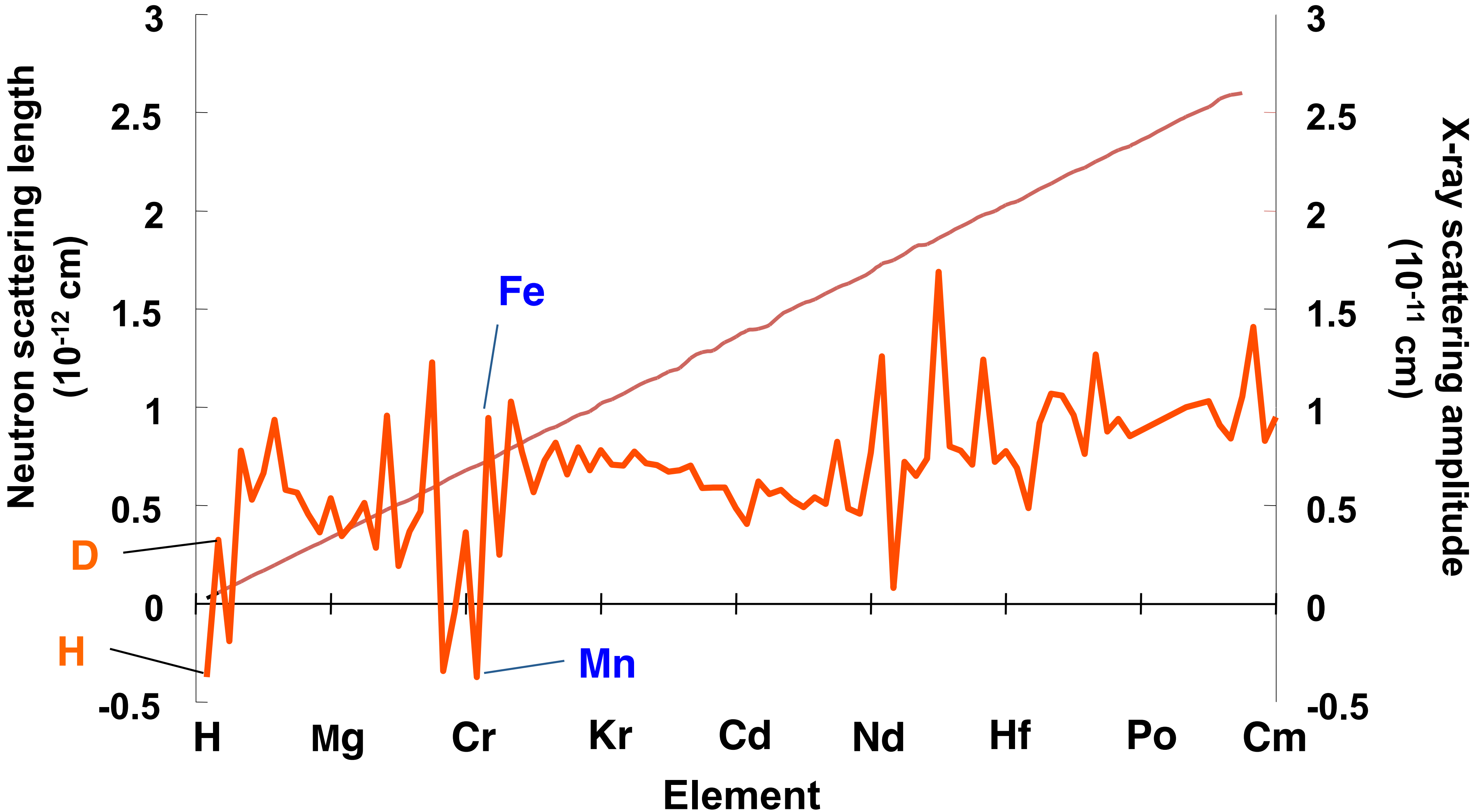
Scattering 'Power'



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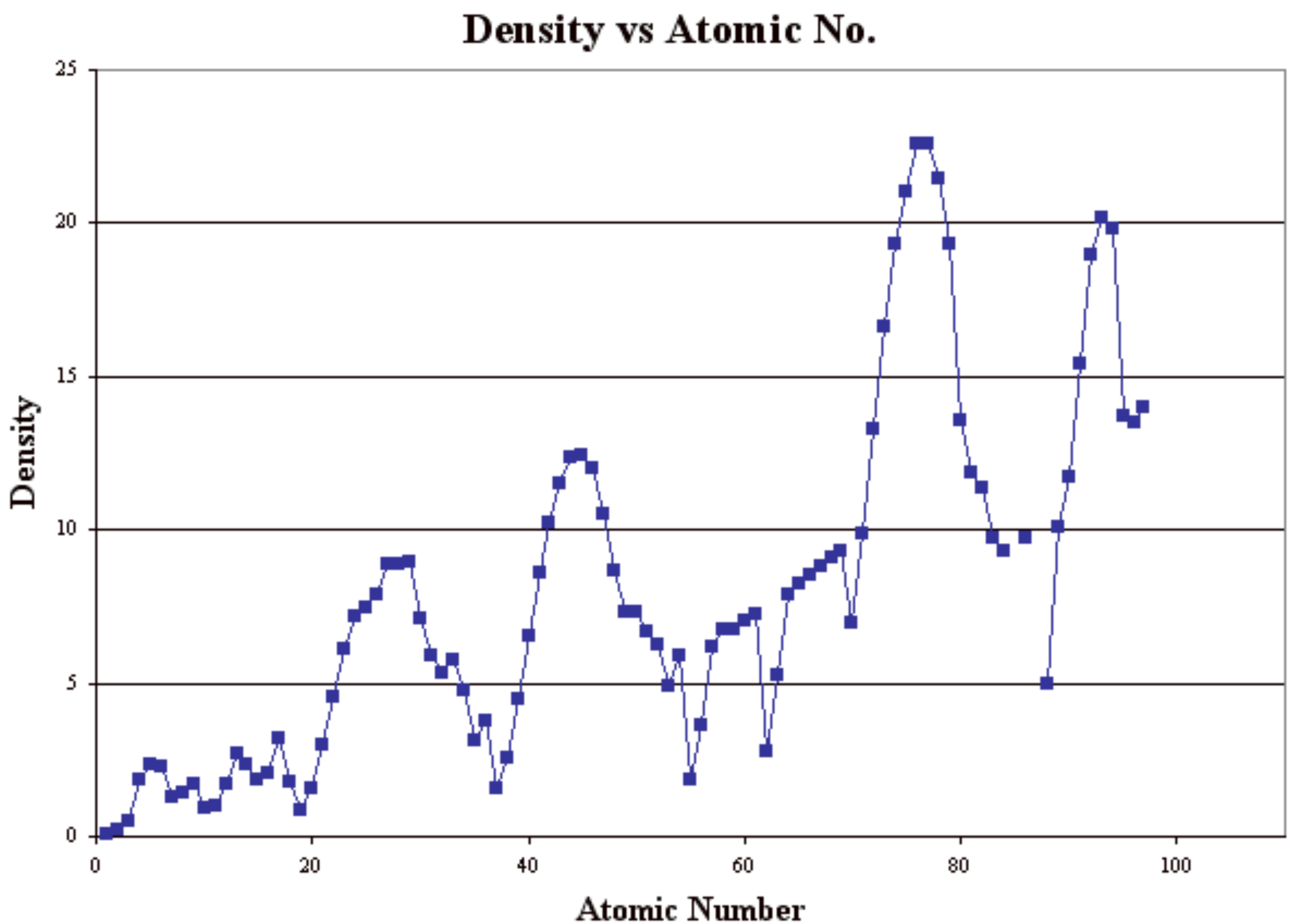
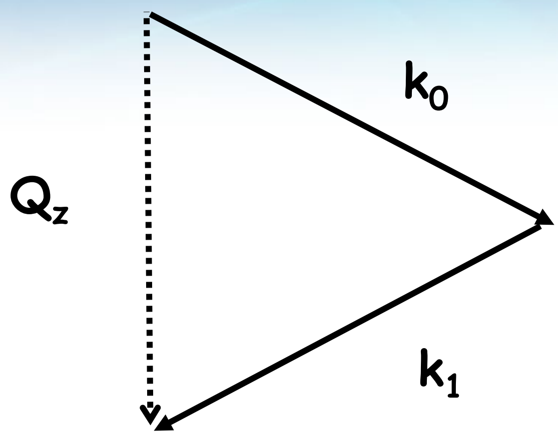


http://cationsanddogions.blogspot.com.au/2011/05/periodic-table-trends.html

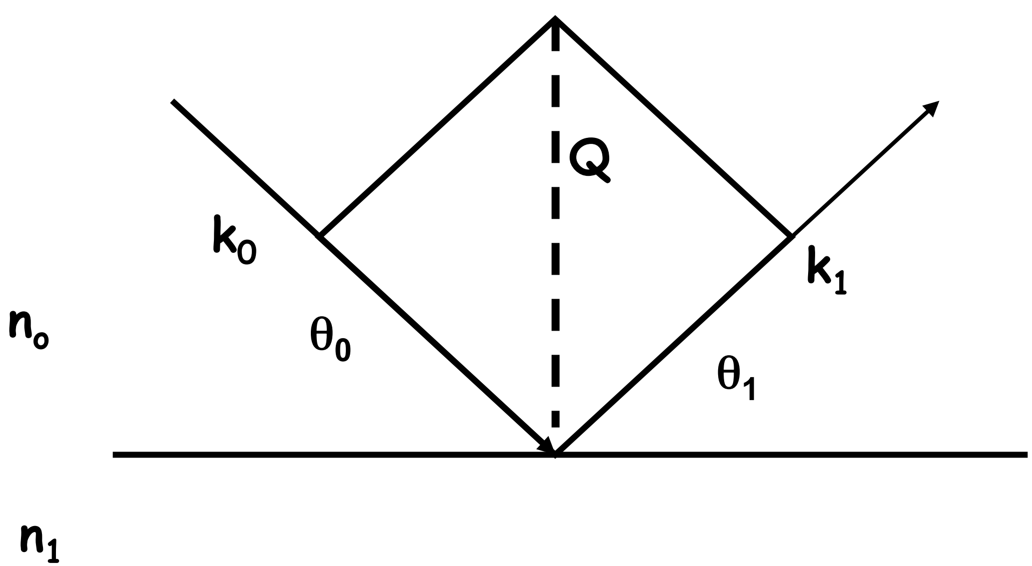
Refractive index, Q, Q_c in terms of wave-vectors :



$$Q = k_0 - k_1$$

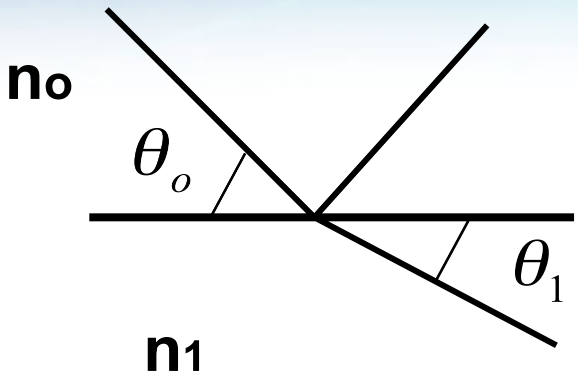
$$Q_z = 2k\sin\theta$$

$$Q_z = \frac{4\pi}{\lambda}\sin\theta$$



Specular reflection of neutrons

(some basic optics)



From Snell's Law, $n = \frac{n_1}{n_0} = \frac{\cos\theta_0}{\cos\theta_1}$

At total reflection $\theta_0 = \theta_c \quad \theta_1 = 0.0 \quad \cos\theta_1 = 1.0$

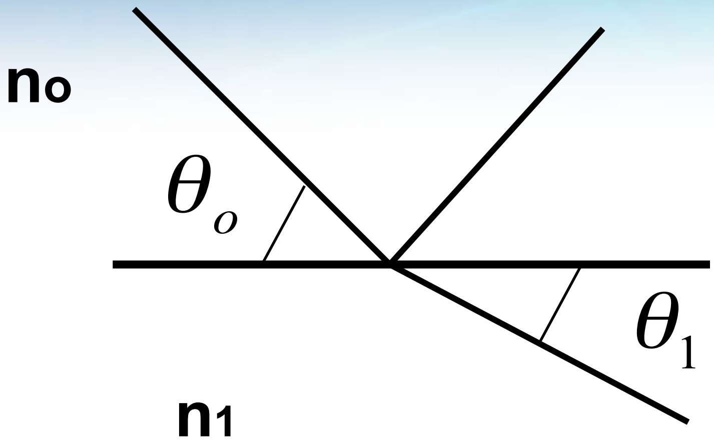
Critical angle

$$\theta_c = \sqrt{16\pi\left(\Delta SLD\right)}$$

Total reflection (R=1.0) for $\theta < \theta_c$

Specular reflection of neutrons

(some basic optics)



Total reflection (R=1.0) for $\theta < \theta_c$

For $\theta > \theta_c$ Fresnel's Law

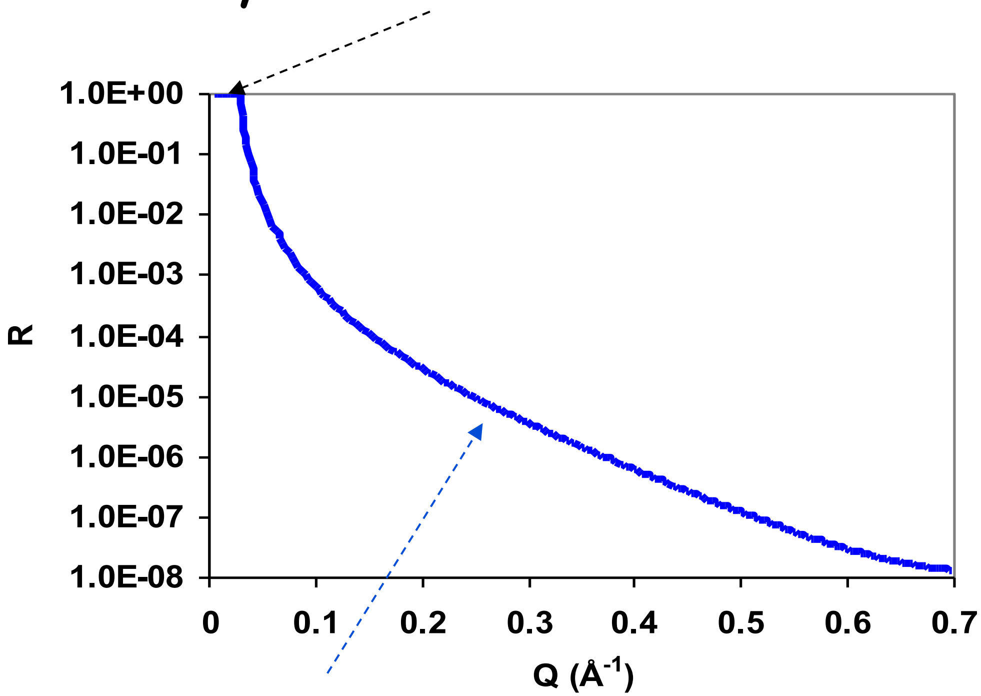
$$R = \left| \frac{n_0 \sin\theta_0 - n_1 \sin\theta_1}{n_0 \sin\theta_0 + n_1 \sin\theta_1} \right|^2$$

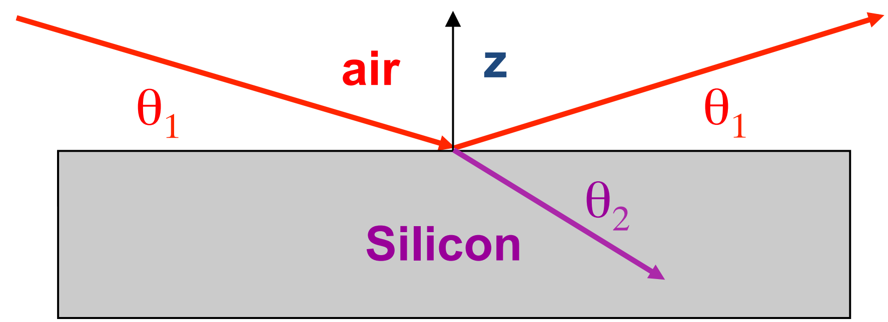
$\theta < \theta_c$ $n_1 \sin\theta_1$ is imaginary (Evanescent wave)

$\theta > \theta_c$ $n_1 \sin\theta_1$ Is real, and zero at $\theta = \theta_c$

Fresnel Reflectivity

At low angles (below the critical angle: θ_c) all radiation is totally reflected – *total external reflection*





Reflectivity falls as Q_z^{-4}

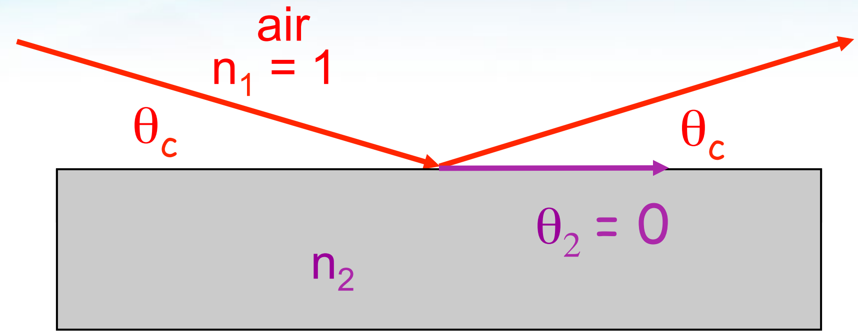
$$R(Q) = \frac{16\pi^2 (\Delta SLD)^2}{Q_z^4}$$

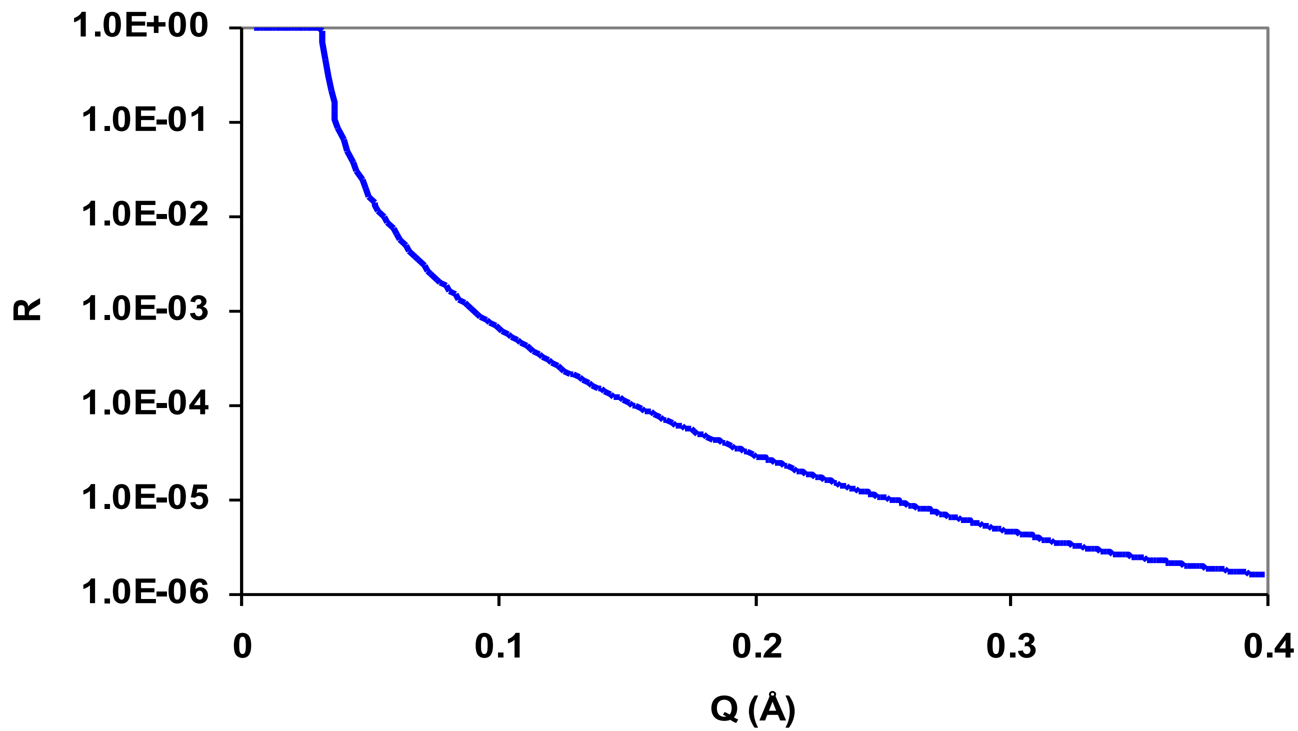
ΔSLD = Change in Scattering Length Density

$Q_z = 4\pi \sin\theta / \lambda$

The Critical Angle (θ_c)

$$\theta_c = \sqrt{16\pi\left(\Delta SLD\right)}$$



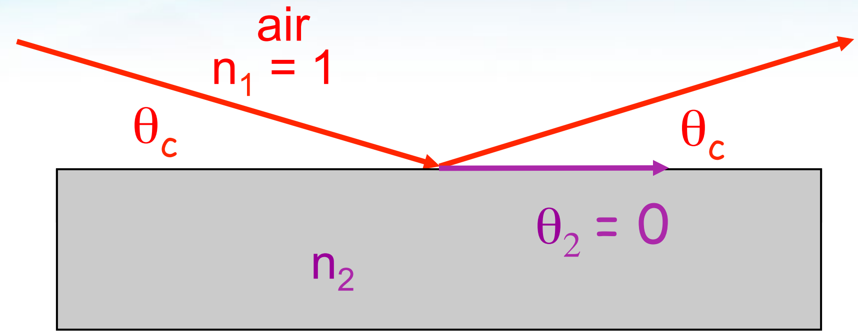


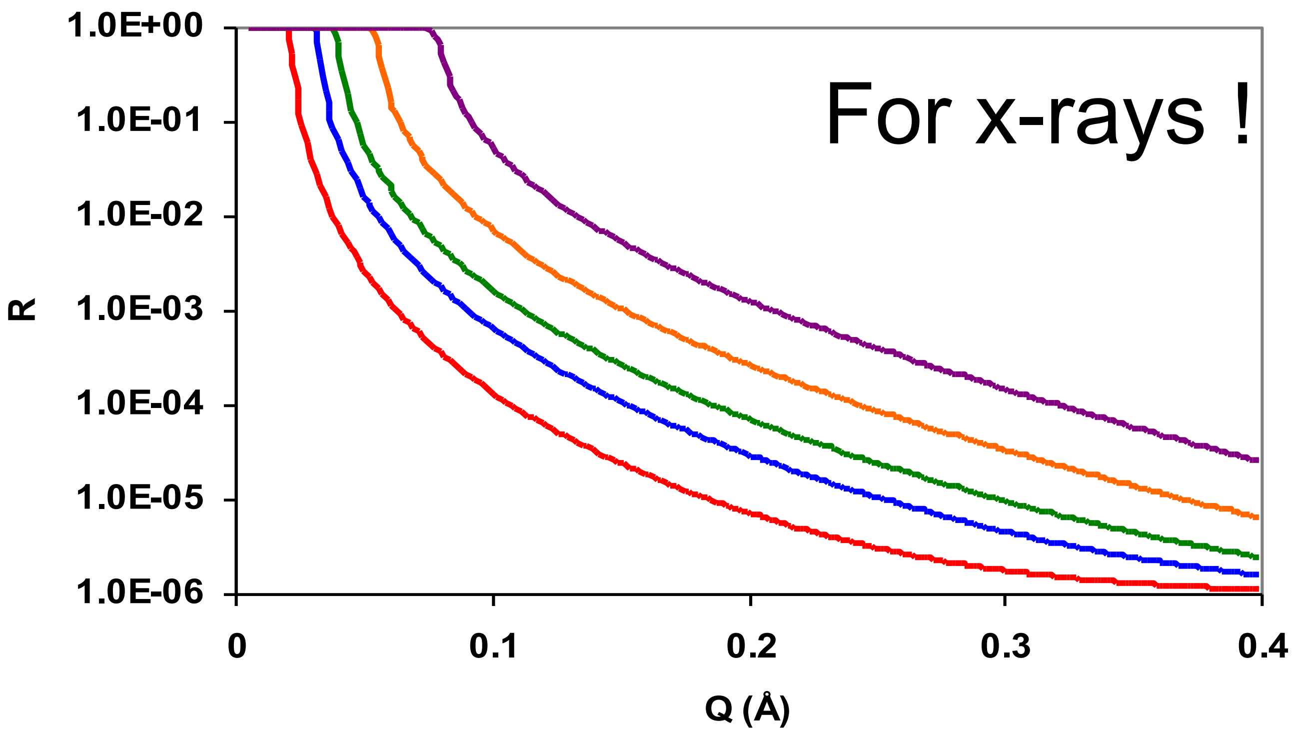
	Qc
Si	0.032

The Critical Angle (θ_c)

$$\theta_c = \sqrt{16\pi(\Delta SLD)}$$

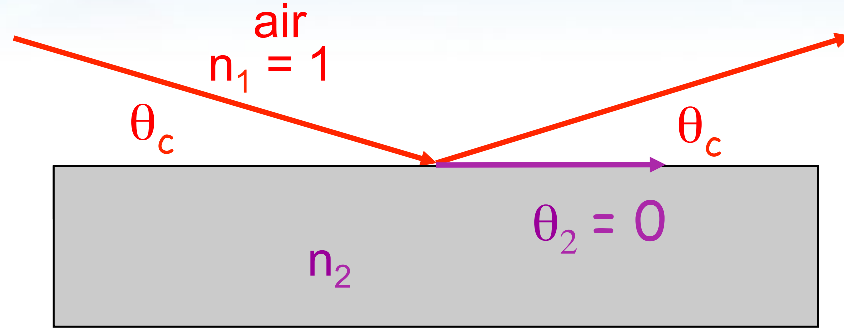
For x-rays contrast comes from change in electron density (p_e)



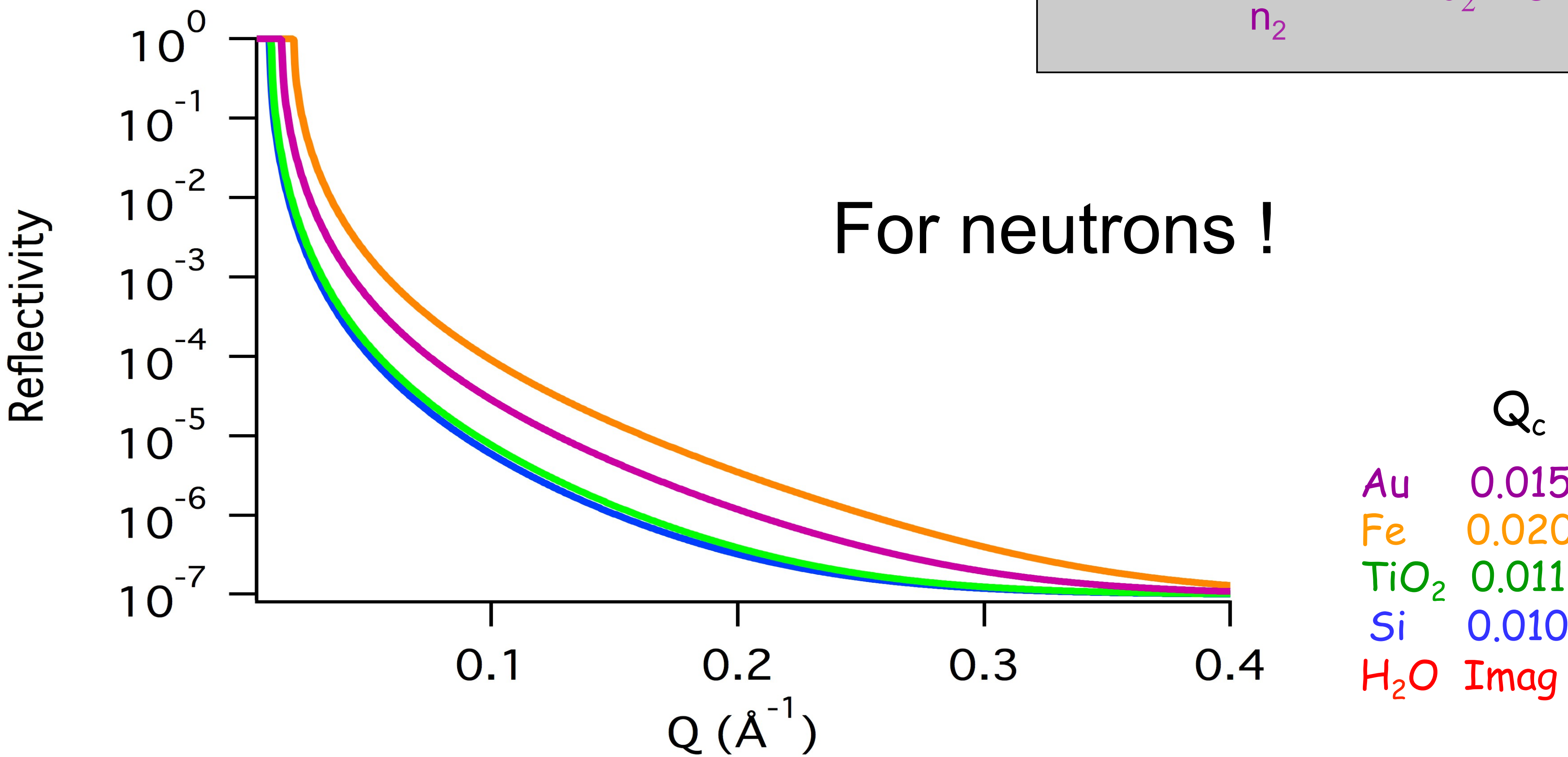


	Q_c
Au	0.079
Fe	0.056
TiO_2	0.040
Si	0.032
H_2O	0.022

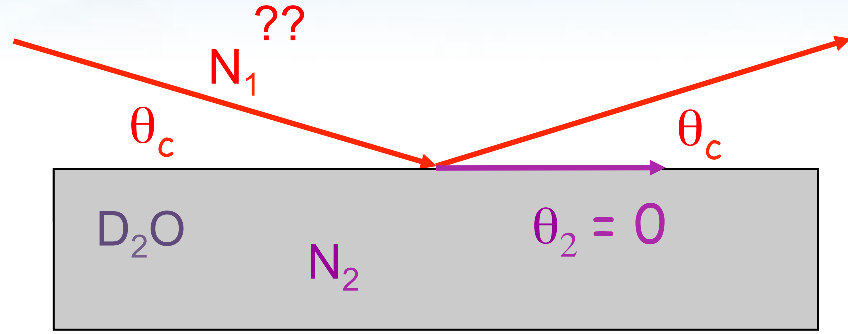
The Critical Angle (θ_c)



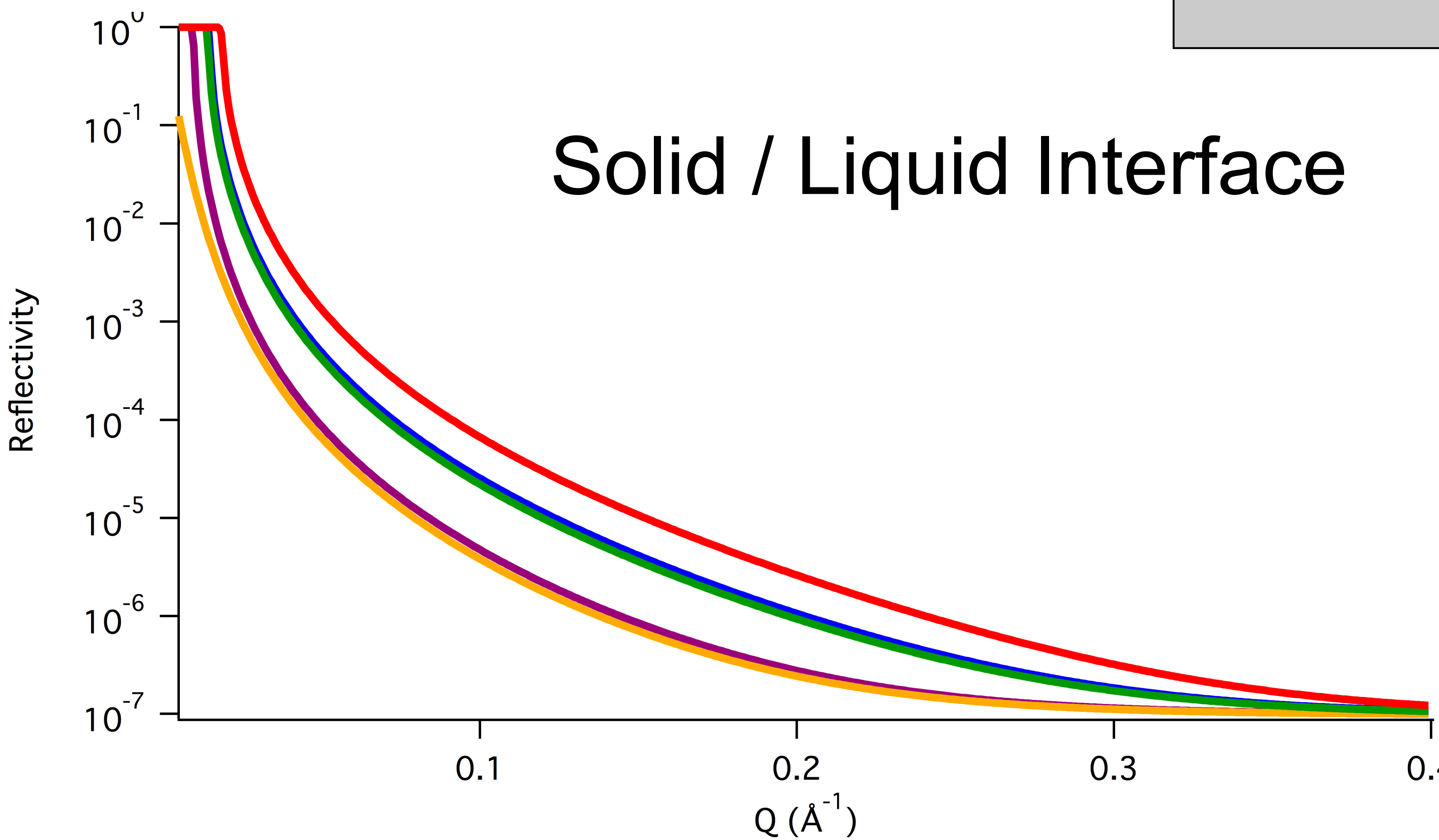
For neutrons !



The Critical Angle (θ_c)



Solid / Liquid Interface

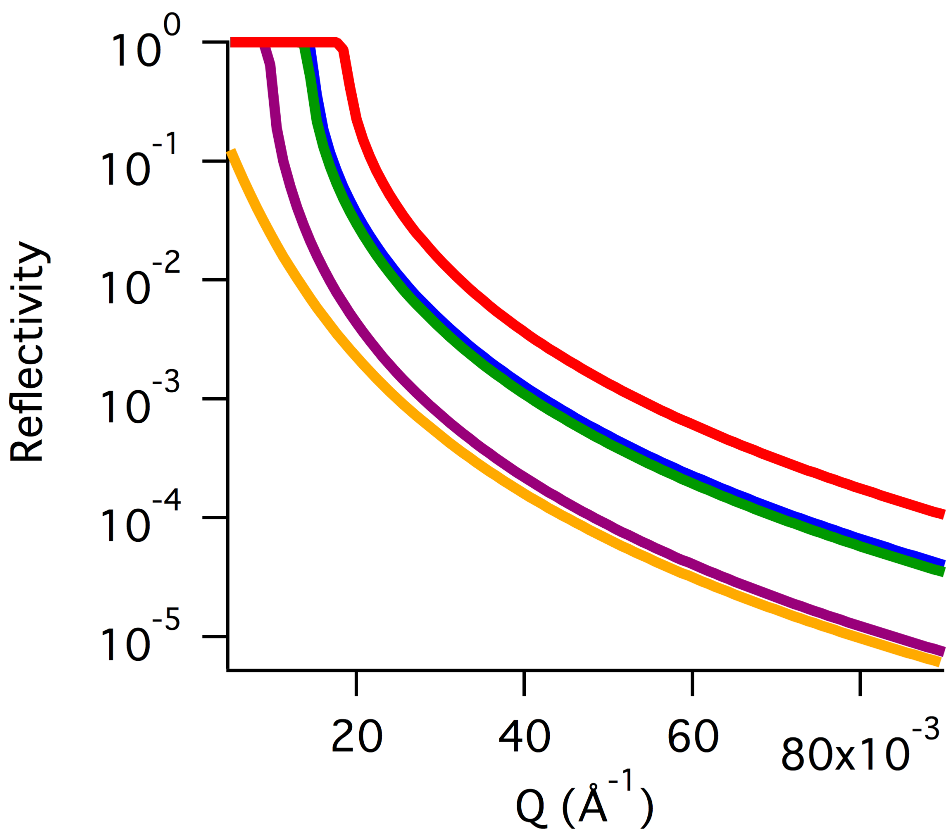


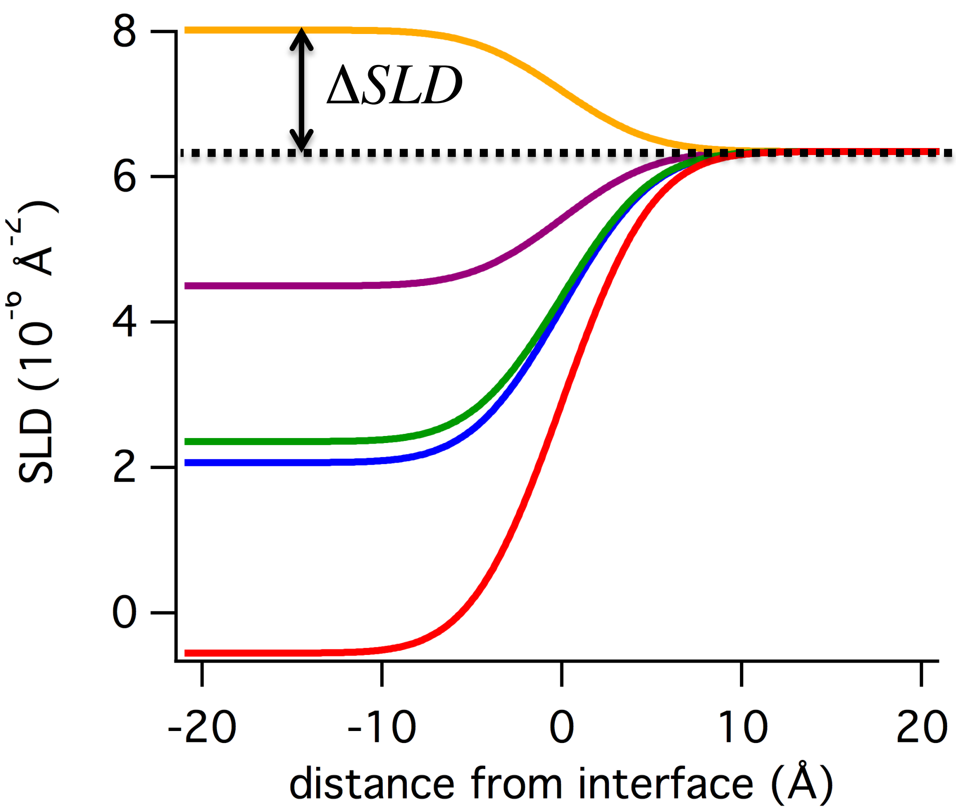
	Q_c
Au	0.0095
Fe	Imag
TiO_2	0.014
Si	0.015
H_2O	0.019

The Critical Angle (θ_c)

$$\theta_c = \sqrt{16\pi(\Delta SLD)}$$

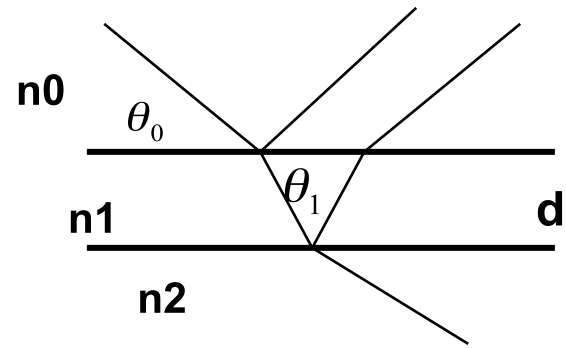
	Q_c
Au	0.0095
Fe	Imag
TiO_2	0.014
Si	0.015
H_2O	0.019





Specular Reflection

What about more than just a simple interface between two media ?

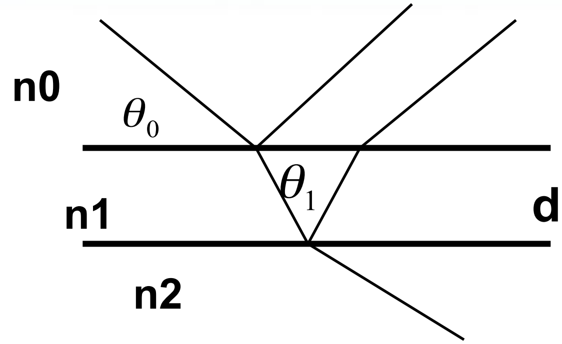


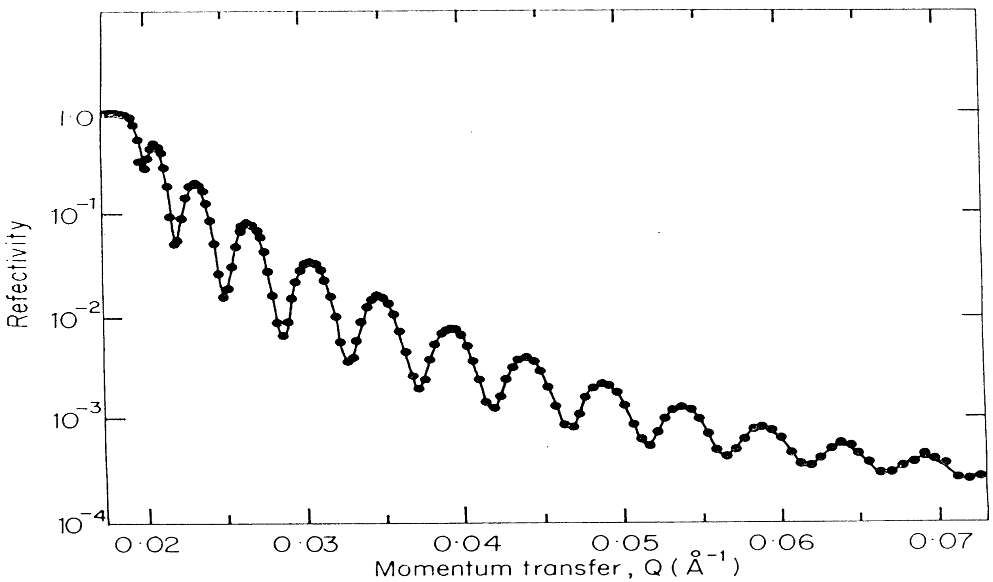
Interference effects can be observed from thin films with x-rays or neutrons and can be described using standard thin film optical methods

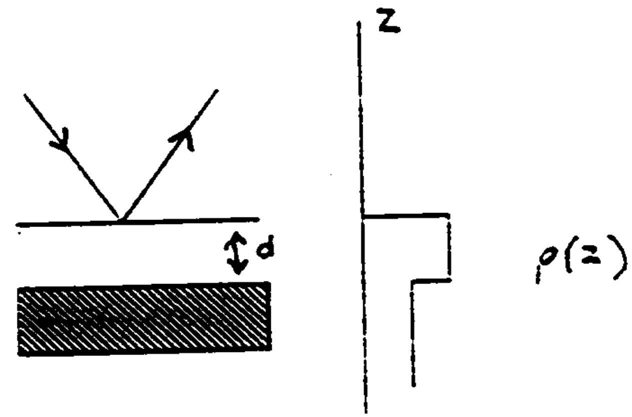
Specular Neutron Reflection

For a single thin film at an interface

$$R(Q) = \left| \frac{r_{01} + r_{12} e^{-2i\beta}}{1 + r_{01} r_{12} e^{-2i\beta}} \right|^2$$



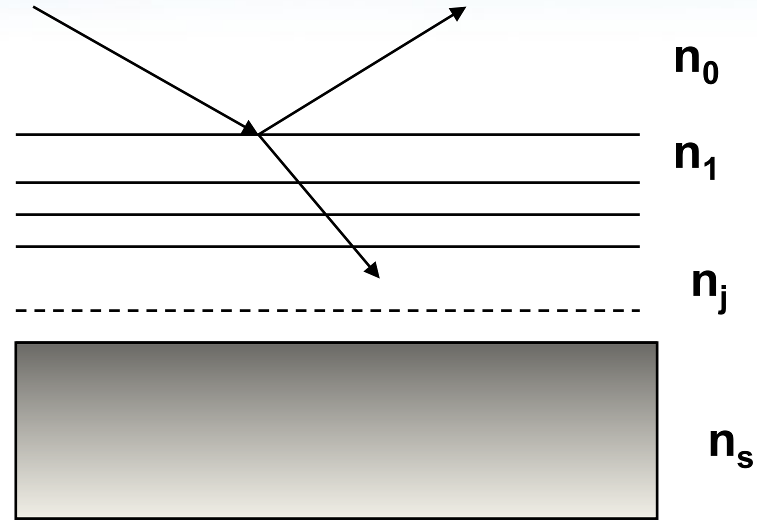




Reflection from multiple layers

Born and Wolf matrix formulism

Applying conditions that wave functions and their gradients are continuous at each boundary gives rise to a **Characteristic matrix** per layer,



$$Mj = \begin{bmatrix} \cos\beta_j & -(i/p_j)\sin\beta_j \\ -ip_j\sin\beta_j & \cos\beta_j \end{bmatrix}$$

$$p_j = n_j \sin\theta_j$$

$$\beta_j = (2\pi/\lambda) n_j d_j \sin\theta_j$$

$$M_R = [M_1].[M_2]----[M_n]$$

The resultant reflectivity is

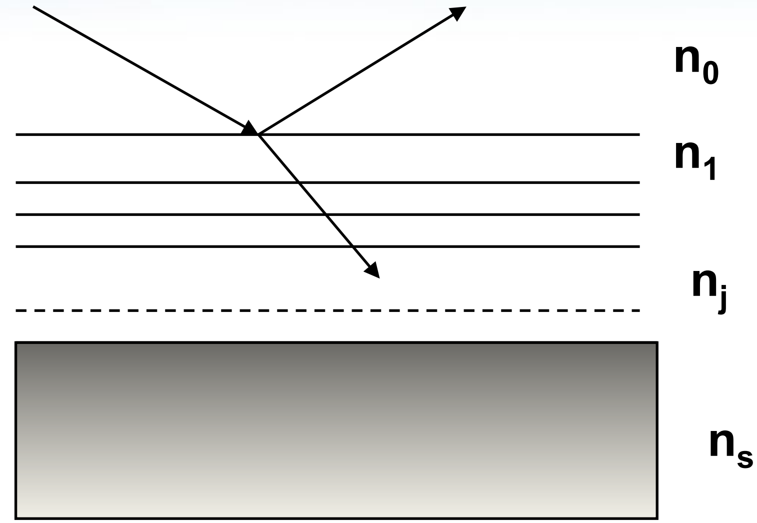
$$R = \left[\frac{(M_{11} + M_{12}p_s)p_a - (M_{21} + M_{22})p_s}{(M_{11} + M_{12}p_s)p_a + (M_{21} + M_{22})p_s} \right]^2$$

(Born & Wolf, 'Principles in Optics', 6th Ed, Pergammon, Oxford, 1980)

Reflection from multiple layers

Optical Transfer Matrix Method

Applying conditions that wave functions and their gradients are continuous at each boundary gives rise to a **Characteristic matrix** per layer,



$$Mj = \begin{bmatrix} \exp(i\beta_{m-1}) & r_m \exp(i\beta_{m-1}) \\ r_m \exp(-i\beta_{m-1}) & \exp(-i\beta_{m-1}) \end{bmatrix}$$

$$p_j = n_j \sin\theta_j$$

$$\beta_j = (2\pi/\lambda) n_j d_j \sin\theta_j$$

$$r_j = \left(\frac{p_{j-1} - p_j}{p_{j-1} + p_j}\right) \exp\left(-\frac{1}{2} Q_{j-1} Q_j \langle\sigma\rangle^2\right)$$

$$M_R = M_1 M_2 M_3 \ldots M_{n+1} = \begin{bmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{bmatrix}$$

$$R = \frac{M_{21} M_{21}^*}{M_{11} M_{11}^*}$$

Calculation involves *n, d,* σ

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Calculating SLDs – X-rays

$$SLD = r_0 \rho_e$$

$$SLD = r_0 N_A \frac{\sum_i Z_i}{\sum_i A_i} \rho_i$$

r_0 - electron radius

ρ_e - electron density

N_A - Avogadro's Number

A - Atomic mass

Z - Atomic number

ρ - physical density

Calculating SLDs - neutrons

$$\mathrm{SLD} = \sum_i b_i \frac{\rho_i \times \mathrm{N_A}}{A_i}$$

b_i - scattering length of the component

ρ_ι - physical density of the component

N_A - Avogadro's Number

A_i - Atomic mass

$$SLD = \frac{\sum b}{Vol}$$

www.molinspiration.com

https://www.ncnr.nist.gov/resources/activation/

Motofit. https://sourceforge.net/projects/motofit/

Home Instruments

Material

H2O

Neutron Activation

For rabbit system [Calculate]

Thermal flux	Cd ratio	Thermal/fast ratio
1e8	0	0
Mass	**Time on beam**	**Time off beam**
1	10	1 y

Absorption and Scattering

[Calculate]

Density	Thickness
1	1
Source neutrons	**Source X-rays**
1 Ang	Cu Ka

Chemical formula

The chemical formula parser allows y

simple formula

A basic formula consists of element
Example: ***CaCO3*** represents the ch

multi-part formula

Formulas can be built from parts by
unit.
Example: ***CaCO3+6H2O***, ***CaCO3 6***

isotopes

Isotopes are represented by element
water.
Example: ***O[18]*** represents the ^{18}O

density

H2O at 1.00 g/cm^3

Source neutrons: 1.000 Å = 81.80 meV = 3956 m/s
Source X-rays: 1.542 Å = 8.042 keV

1/e penetration depth (cm)		Scattering length density (10^{-6}/Å^2)		Scattering cross section (1/cm)		X-ray SLD (10^{-6}/Å^2)	
abs	80.836	**real**	-0.561	**coh**	0.004	**real**	9.469
abs+incoh	0.186	**imag**	-0.000	**abs**	0.012	**imag**	-0.032
abs+incoh+coh	0.177	**incoh**	20.693	**incoh**	5.366		

Neutron transmission is 0.462% for 1 cm of sample (after absorption and incoherent scattering).
Transmitted flux is 4.616e+5 n/cm^2/s for a 1e8 n/cm^2/s beam.

https://www.ncnr.nist.gov/resources/activation/

H_2O at 1.00 g/cm^3

Source neutrons: 1.000 Å = 81.80 meV = 3956 m/s
Source X-rays: 1.542 Å = 8.042 keV

1/e penetration depth (cm)		Scattering length density ($10^{-6}/Å^2$)		Scattering cross section (1/cm)		X-ray SLD ($10^{-6}/Å^2$)	
abs	80.836	real	-0.561	coh	0.004	real	9.469
abs+incoh	0.186	imag	-0.000	abs	0.012	imag	-0.032
abs+incoh+coh	0.177	incoh	20.693	incoh	5.366		

Neutron transmission is 0.462% for 1 cm of sample (after absorption and incoherent scattering).
Transmitted flux is 4.616e+5 n/cm^2/s for a 1e8 n/cm^2/s beam.

D_2O at 1.10 g/cm^3

Source neutrons: 1.000 Å = 81.80 meV = 3956 m/s
Source X-rays: 1.542 Å = 8.042 keV

1/e penetration depth (cm)		Scattering length density ($10^{-6}/Å^2$)		Scattering cross section (1/cm)		X-ray SLD ($10^{-6}/Å^2$)	
abs	44266.649	real	6.335	coh	0.508	real	9.369
abs+incoh	7.373	imag	-0.000	abs	0.000	imag	-0.031
abs+incoh+coh	1.549	incoh	3.272	incoh	0.136		

Neutron transmission is 87.32% for 1 cm of sample (after absorption and incoherent scattering).
Transmitted flux is 8.732e+7 n/cm^2/s for a 1e8 n/cm^2/s beam.

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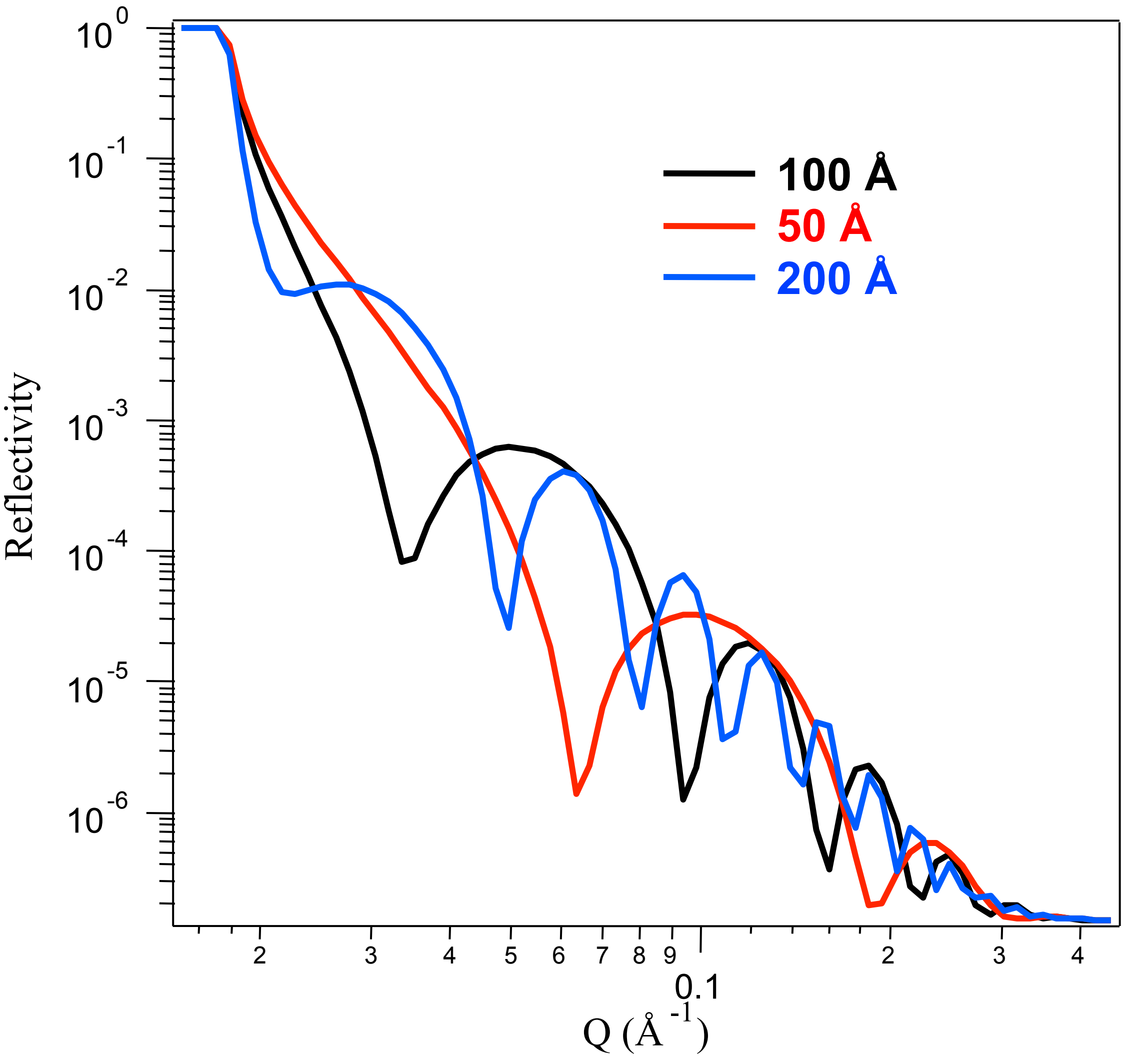
https://www.ncnr.nist.gov/resources/activation/

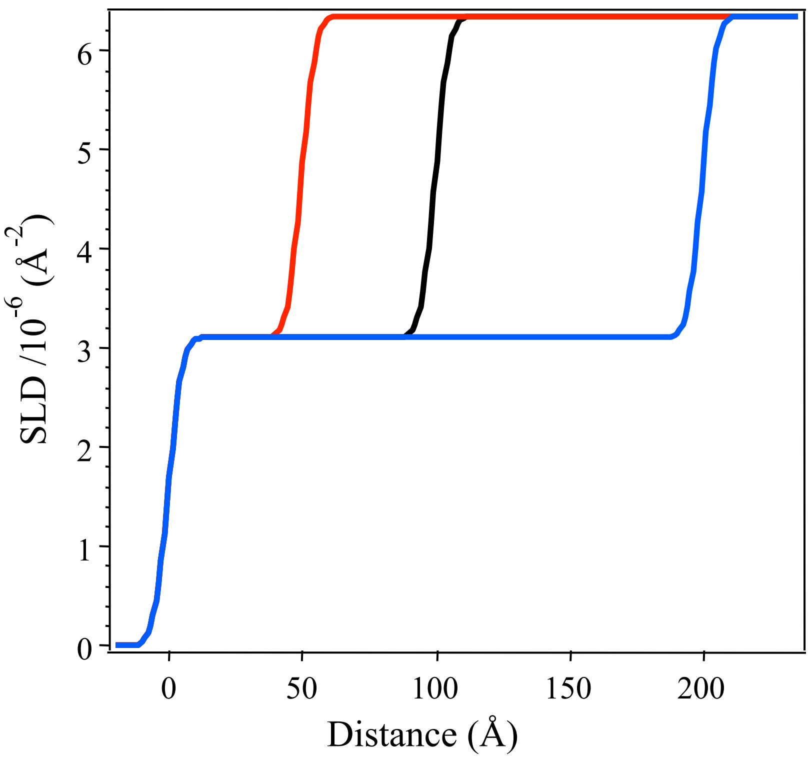
Typical SLDs

Material	SLD
H_2O	-0.55×10^{-6} Å^{-2}
D_2O	6.35×10^{-6} Å^{-2}
Si	2.07×10^{-6} Å^{-2}
Quartz	3.47×10^{-6} Å^{-2}
Poly ethylene	-0.33×10^{-6} Å^{-2}
d – poly ethylene	8.24×10^{-6} Å^{-2}

Thickness

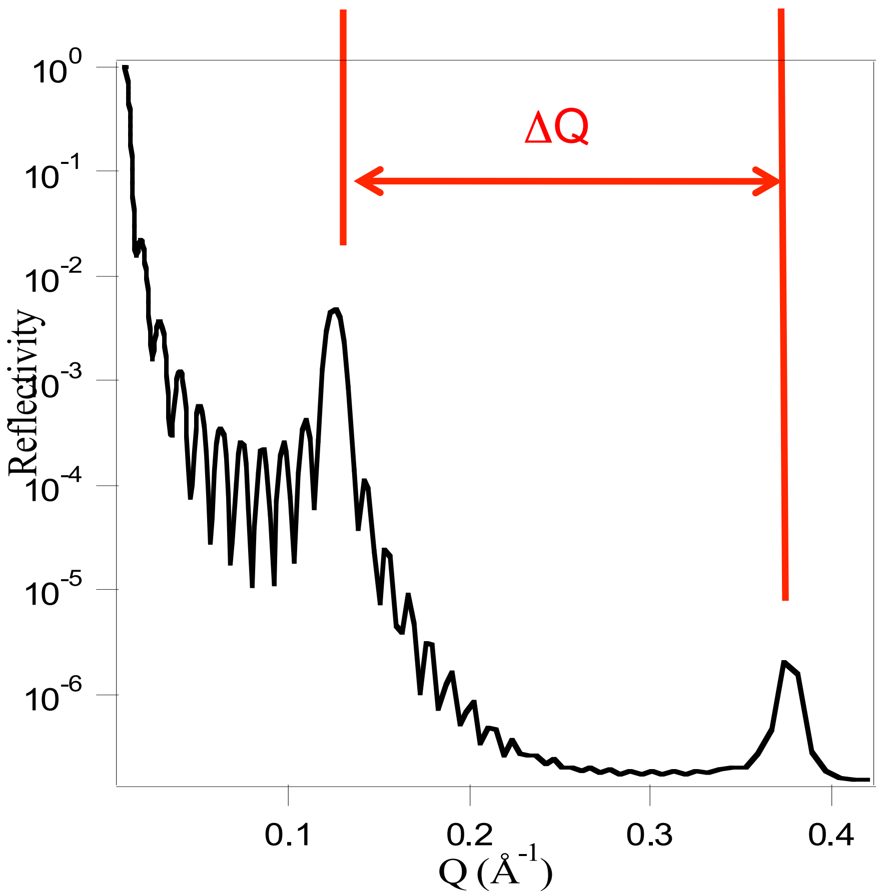
$$D = \frac{2\pi}{\Delta Q}$$

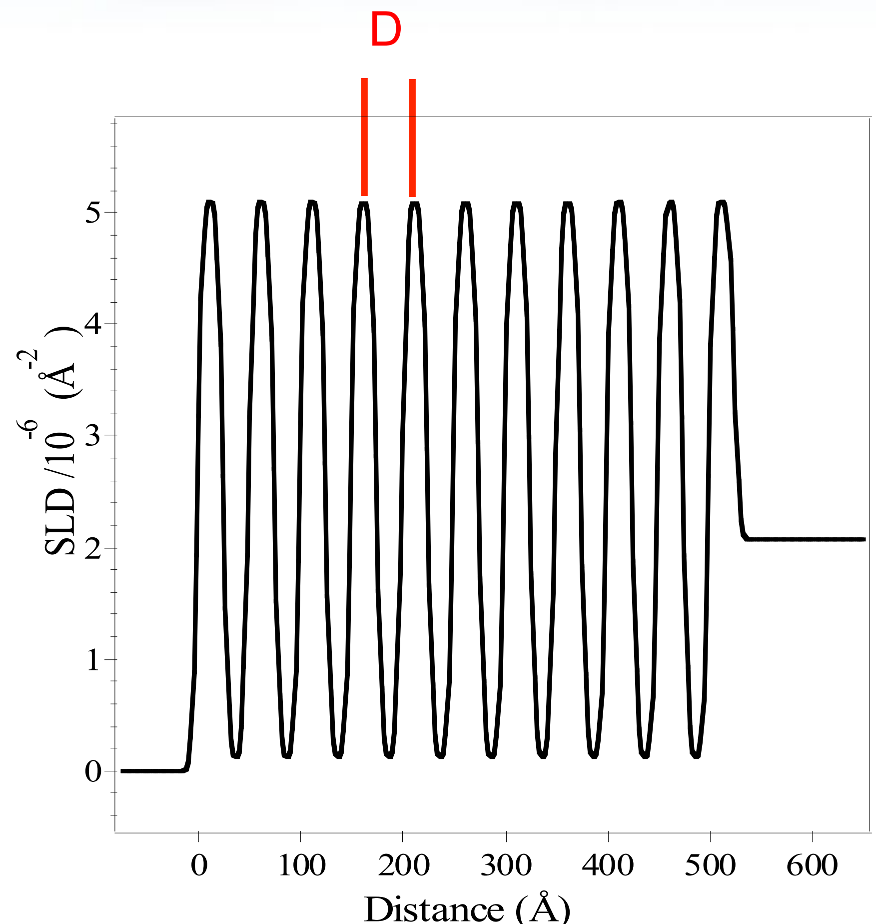




Thickness

15 Bilayers, Silicon substrate.

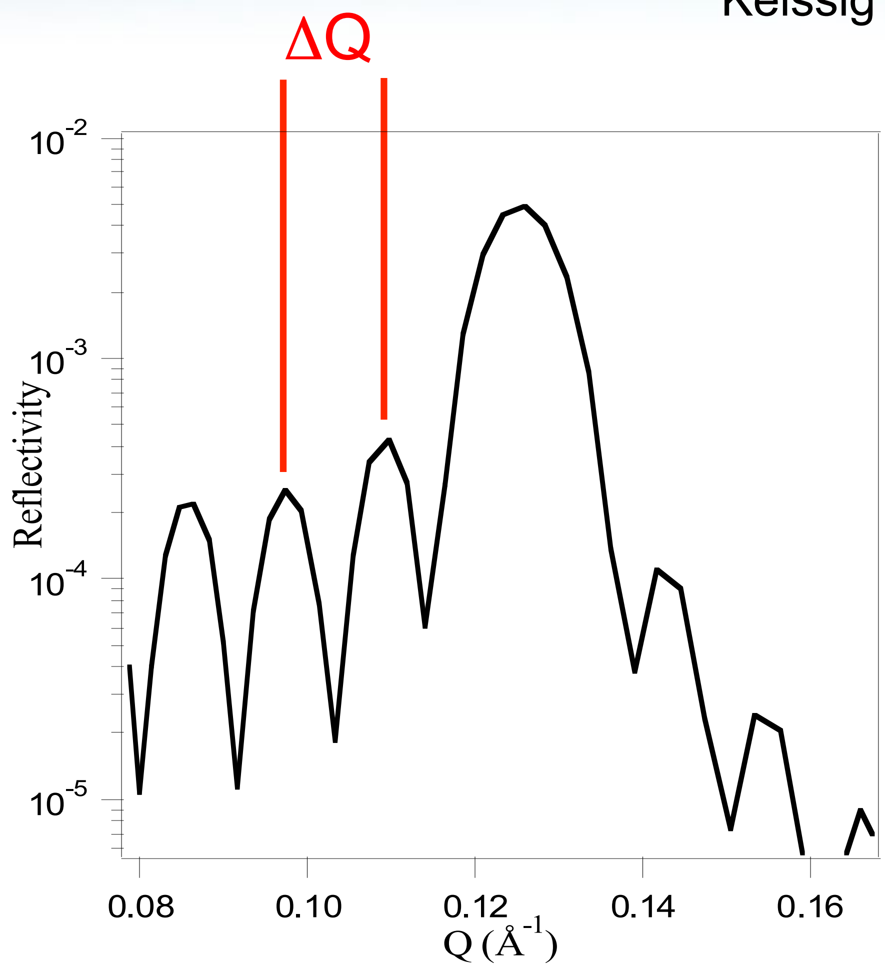


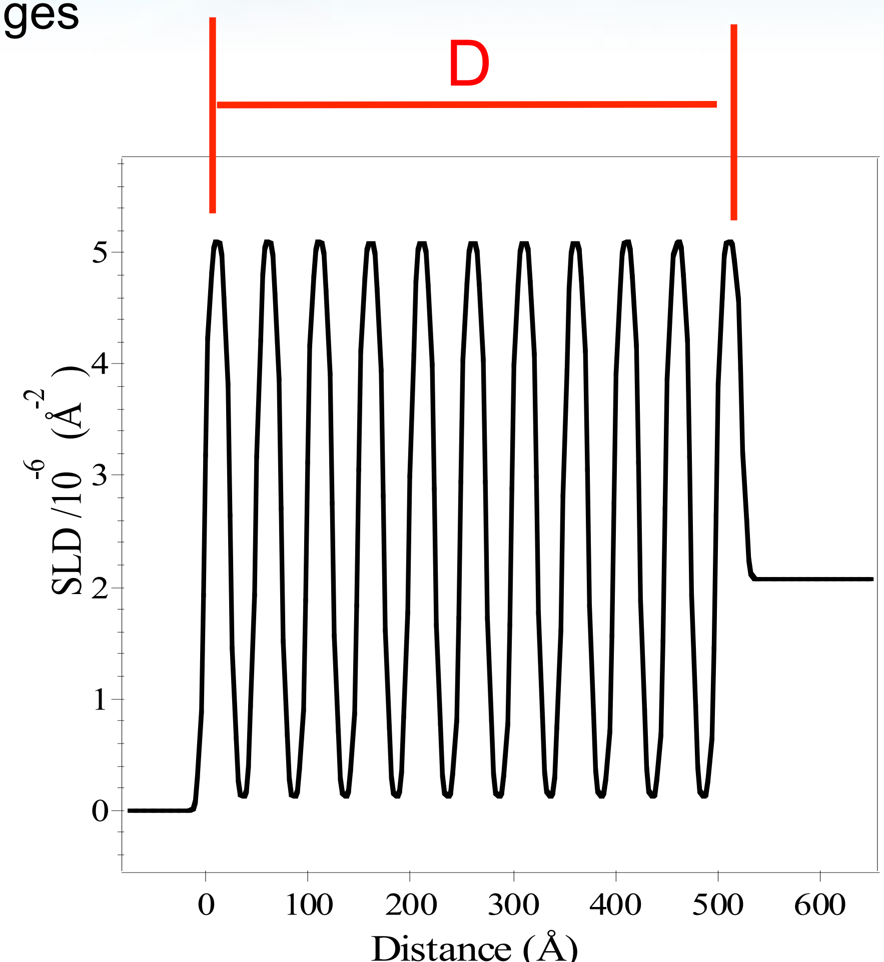


$$D = \frac{2\pi}{\Delta Q}$$

Thickness

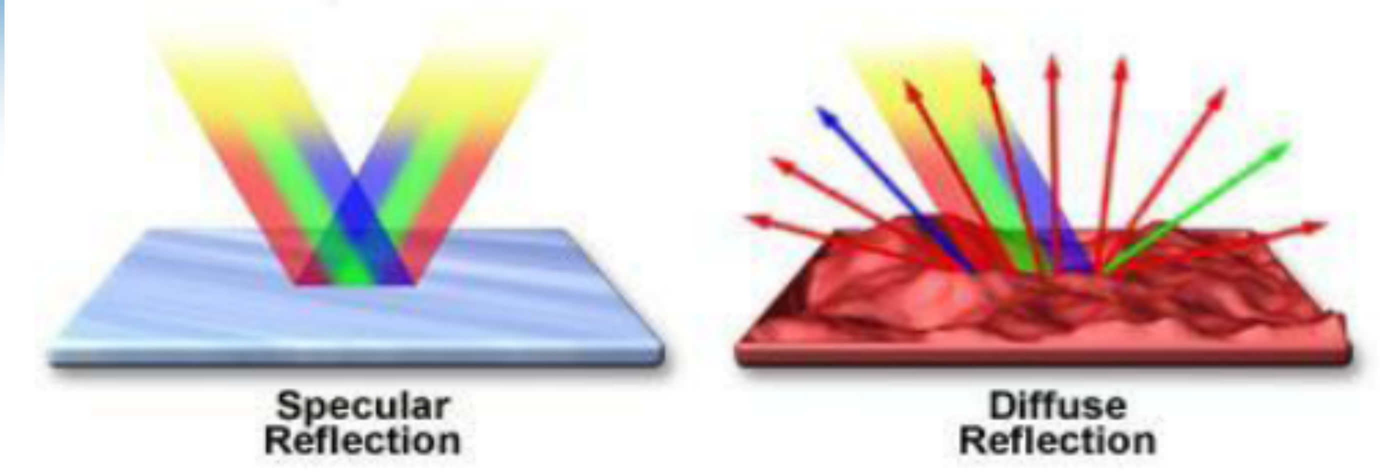
Keissig Fringes

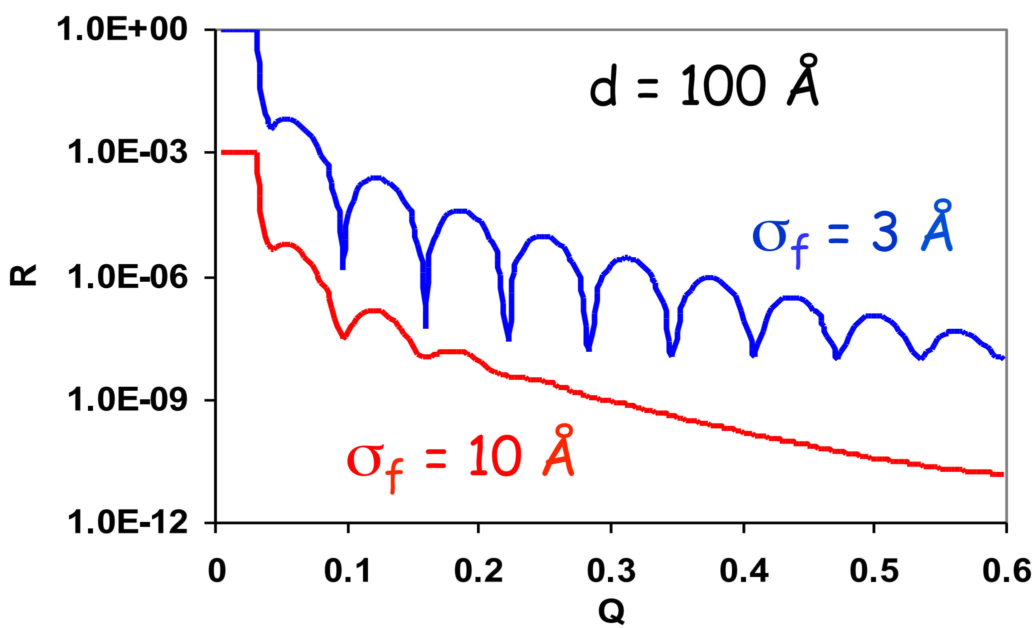




$$D = \frac{2\pi}{\Delta Q}$$

Interfacial Roughness (σ)



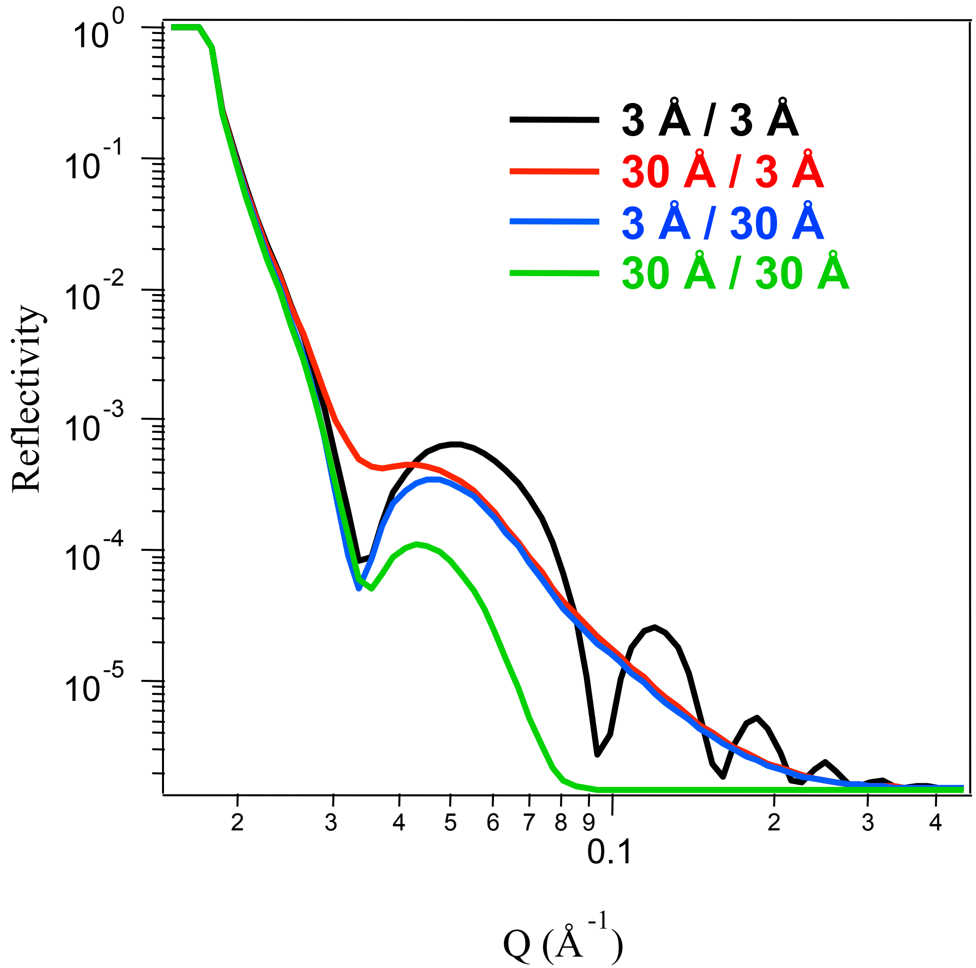


Local variation in incident angle leads to diffuse scattering

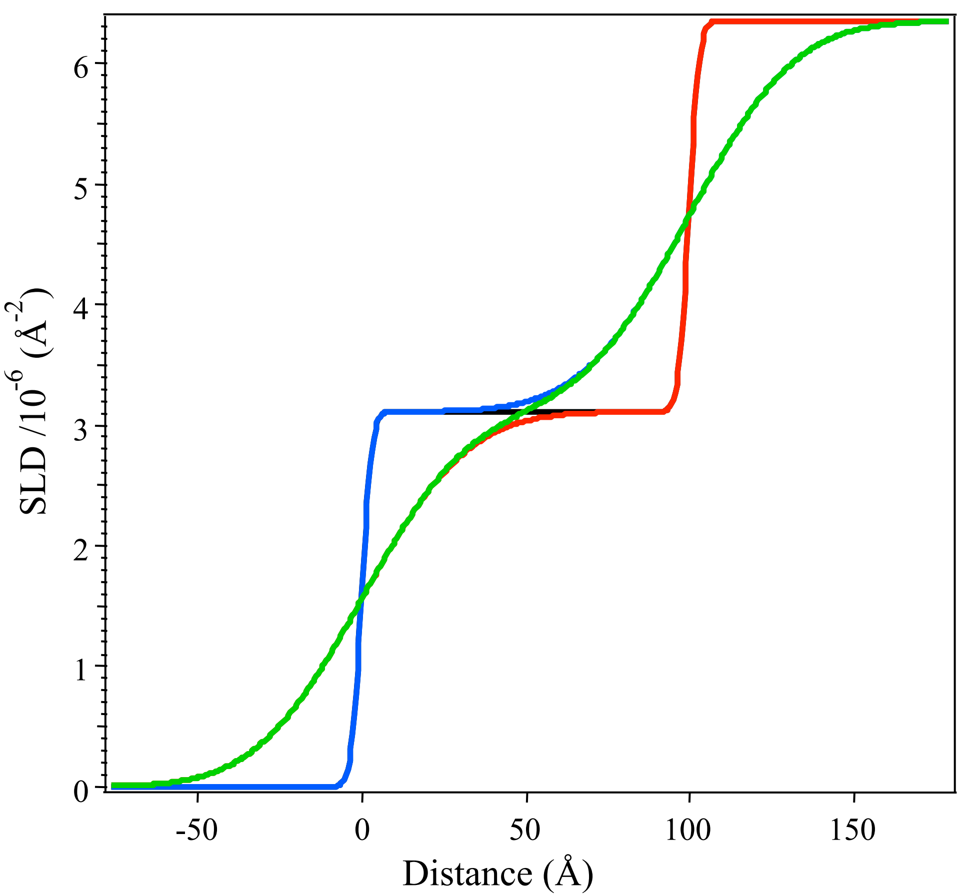
Increasing roughness:
- dampens Kiessig fringes

R falls faster than Q_z^4
- background is increased

Roughness



Reflectivity
10^{0}
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
3 Å / 3 Å
30 Å / 3 Å
3 Å / 30 Å
30 Å / 30 Å
2 3 4 5 6 7 8 9 0.1 2 3 4
Q (Å^{-1})

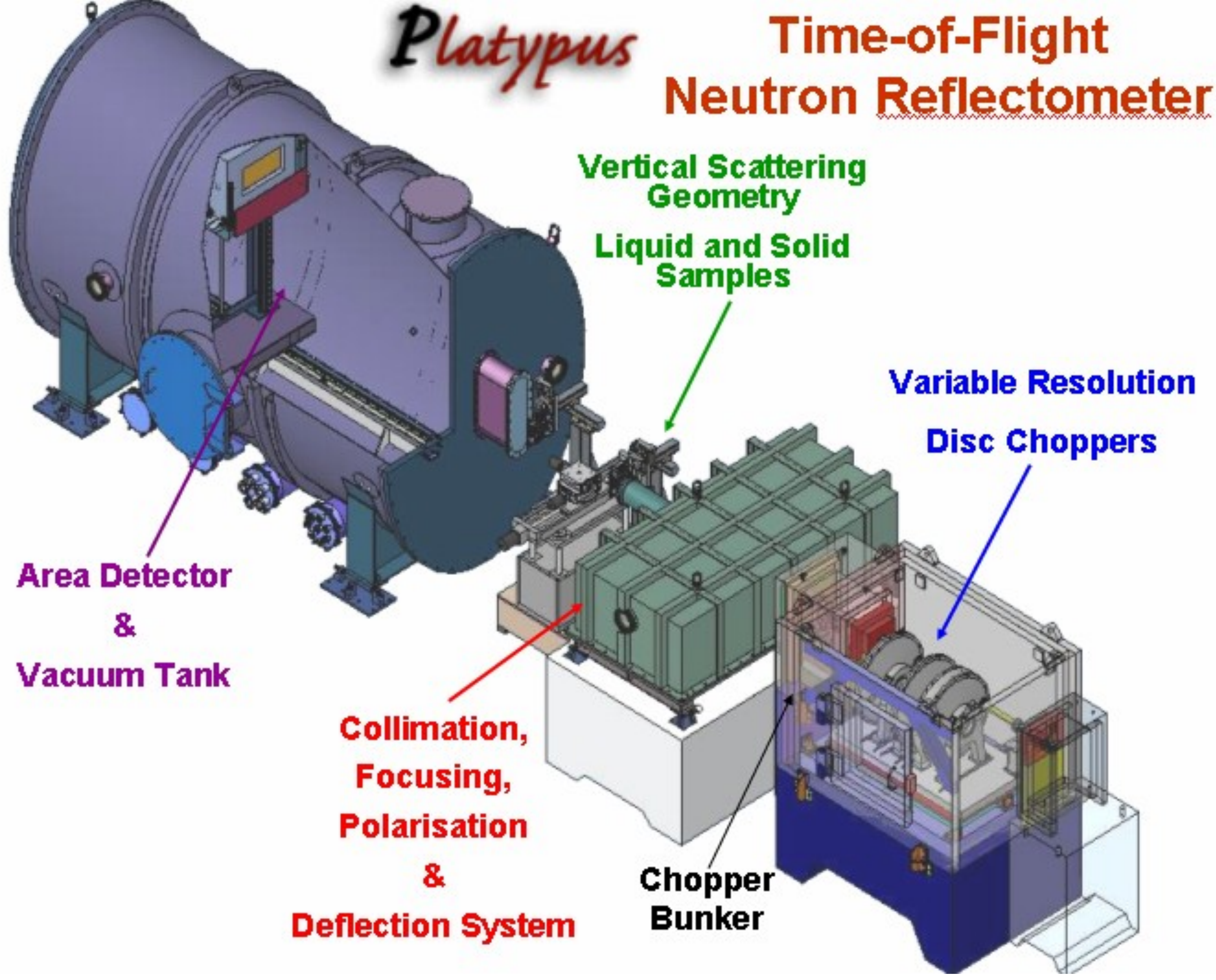


SLD /10^{-6} (Å^{-2})
0 1 2 3 4 5 6
-50 0 50 100 150
Distance (Å)

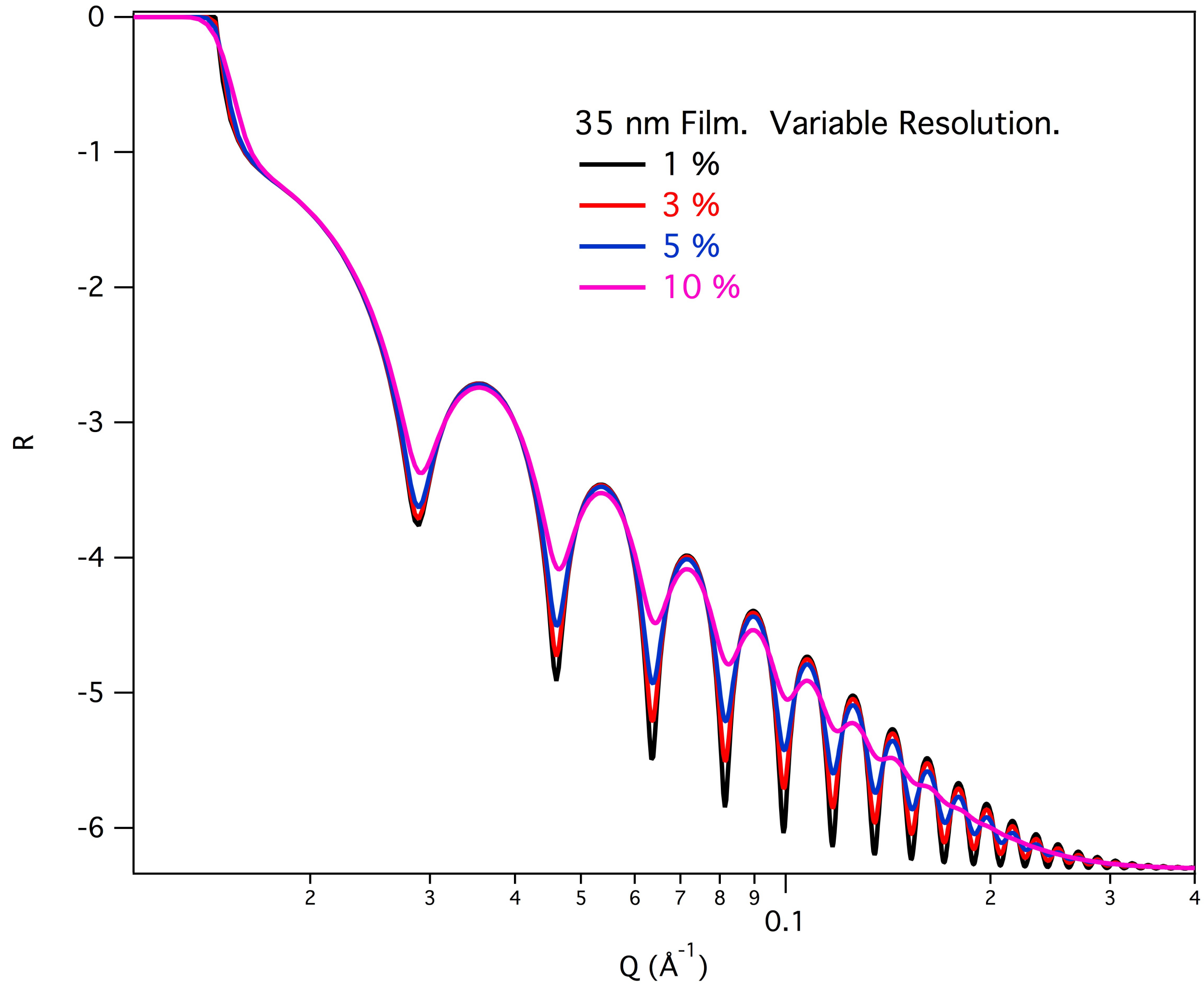
Resolution

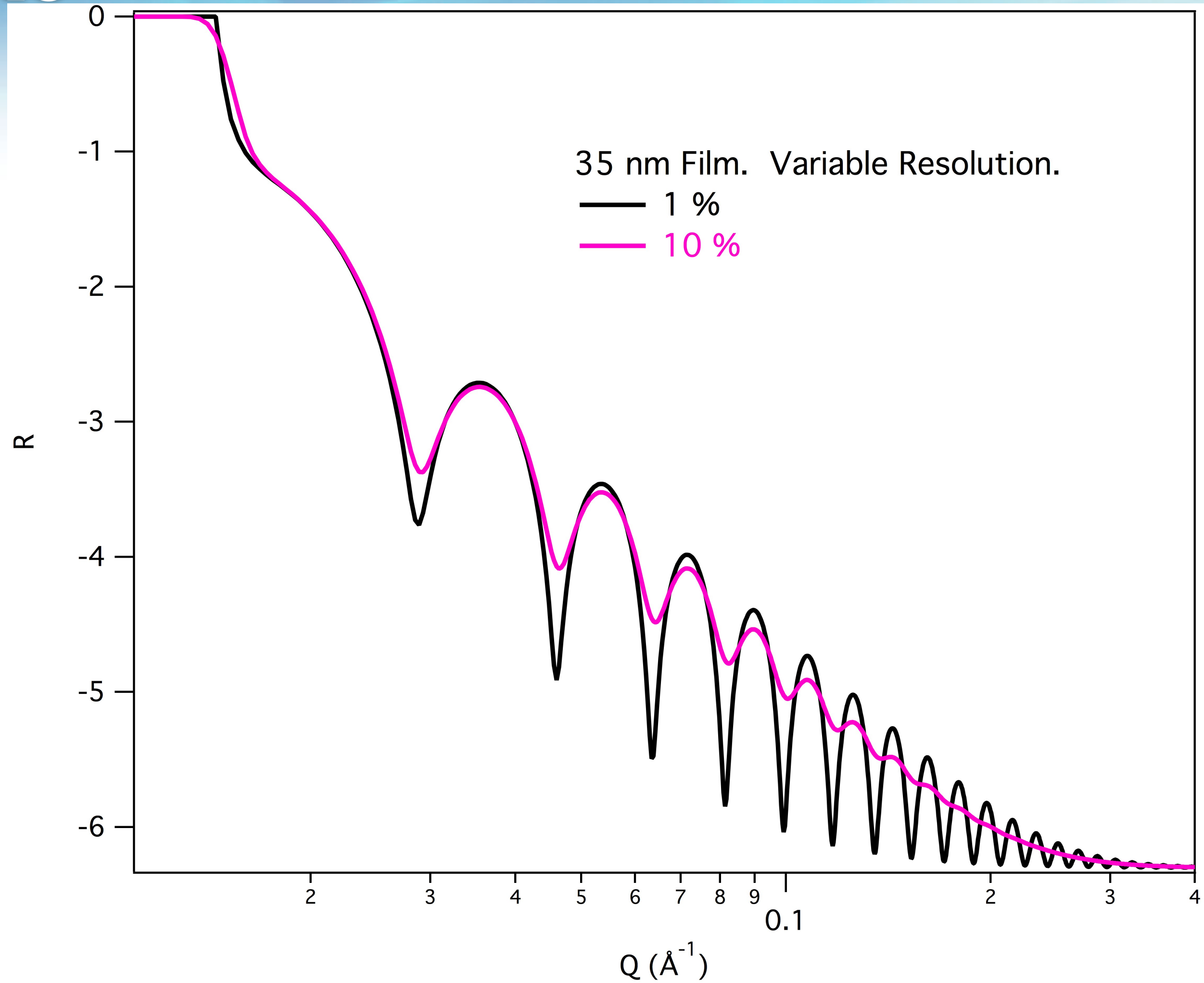
- Sample to Detector Distance fixed (usually)
- Adjust resolution
  - Angular resolution of incident beam
  - Time (wavelength) resolution of beam.
    - For time of flight measurements.
- Instrument Resolution
  - Convolution of two terms.

Platypus Time-of-Flight Neutron Reflectometer



Effect of Resolution.

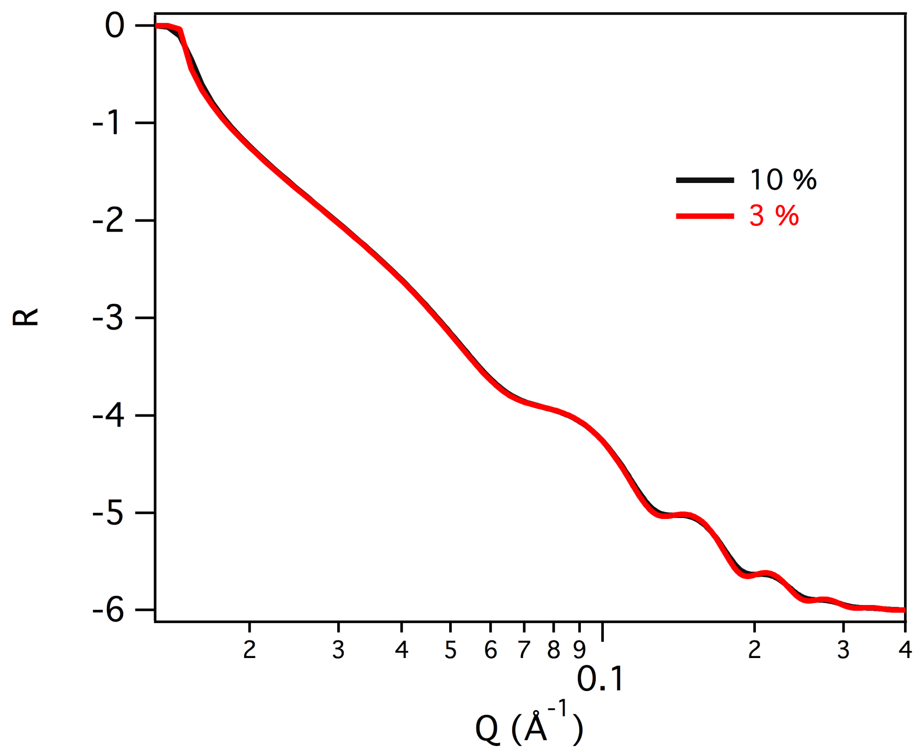


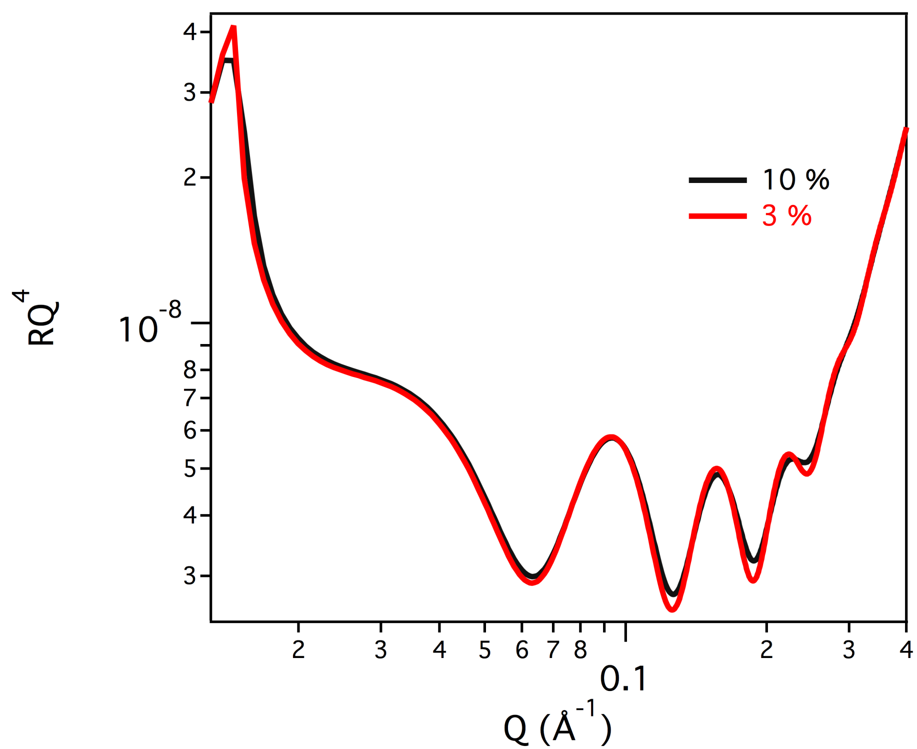


But higher resolution will mean less flux. Know your sample and decide upon the tradeoffs.

Resolution – Thinner films lower is better

100 Å Polymer film at Si / D_2O Interface

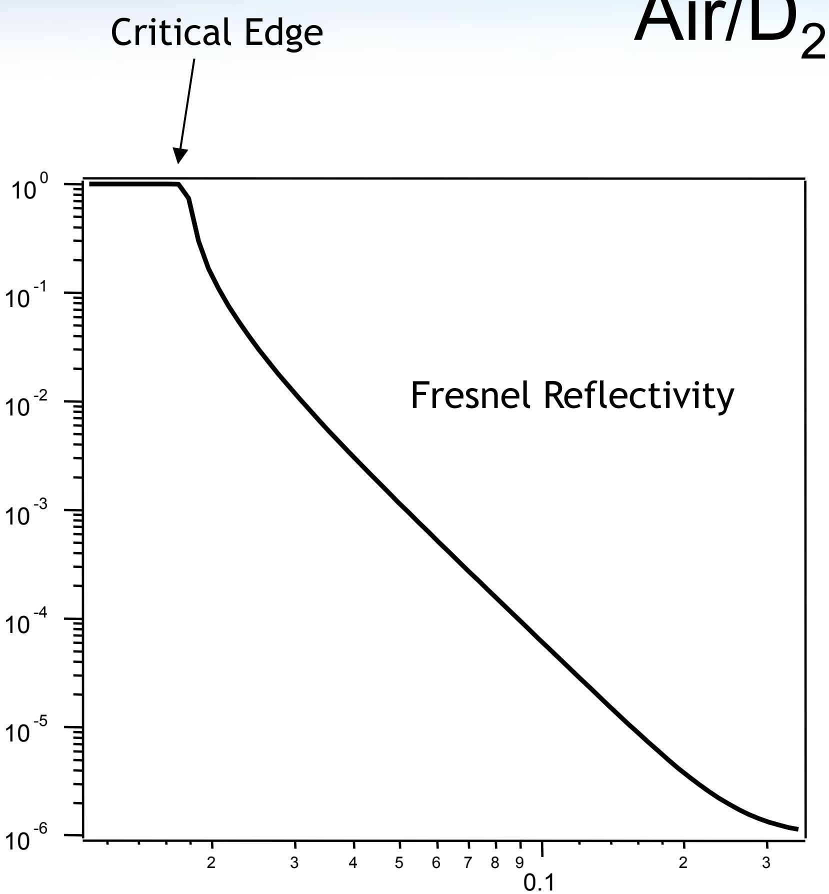


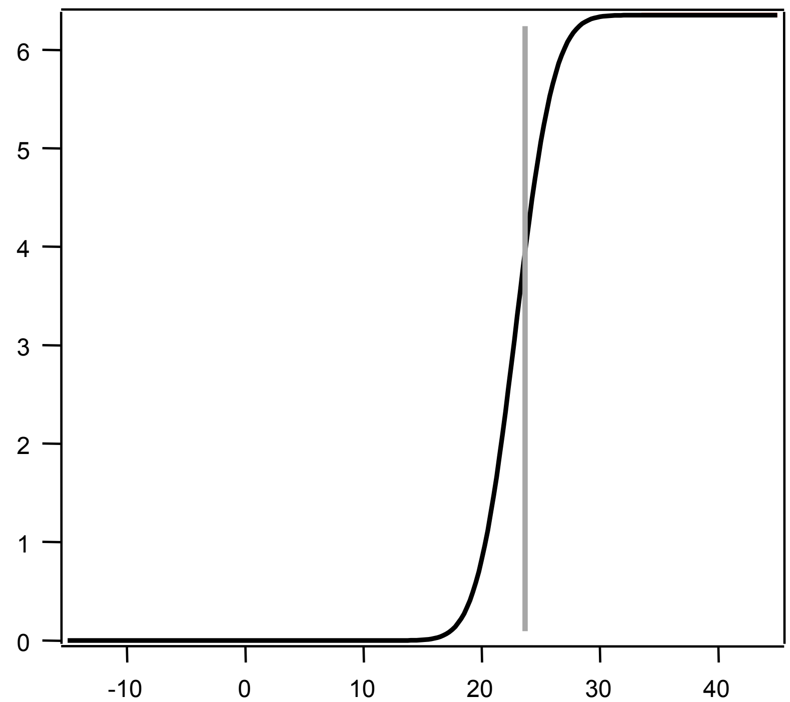


Basic Example

- Air/Water interface
- Add a monolayer.
- Calculate Neutron Reflectivity

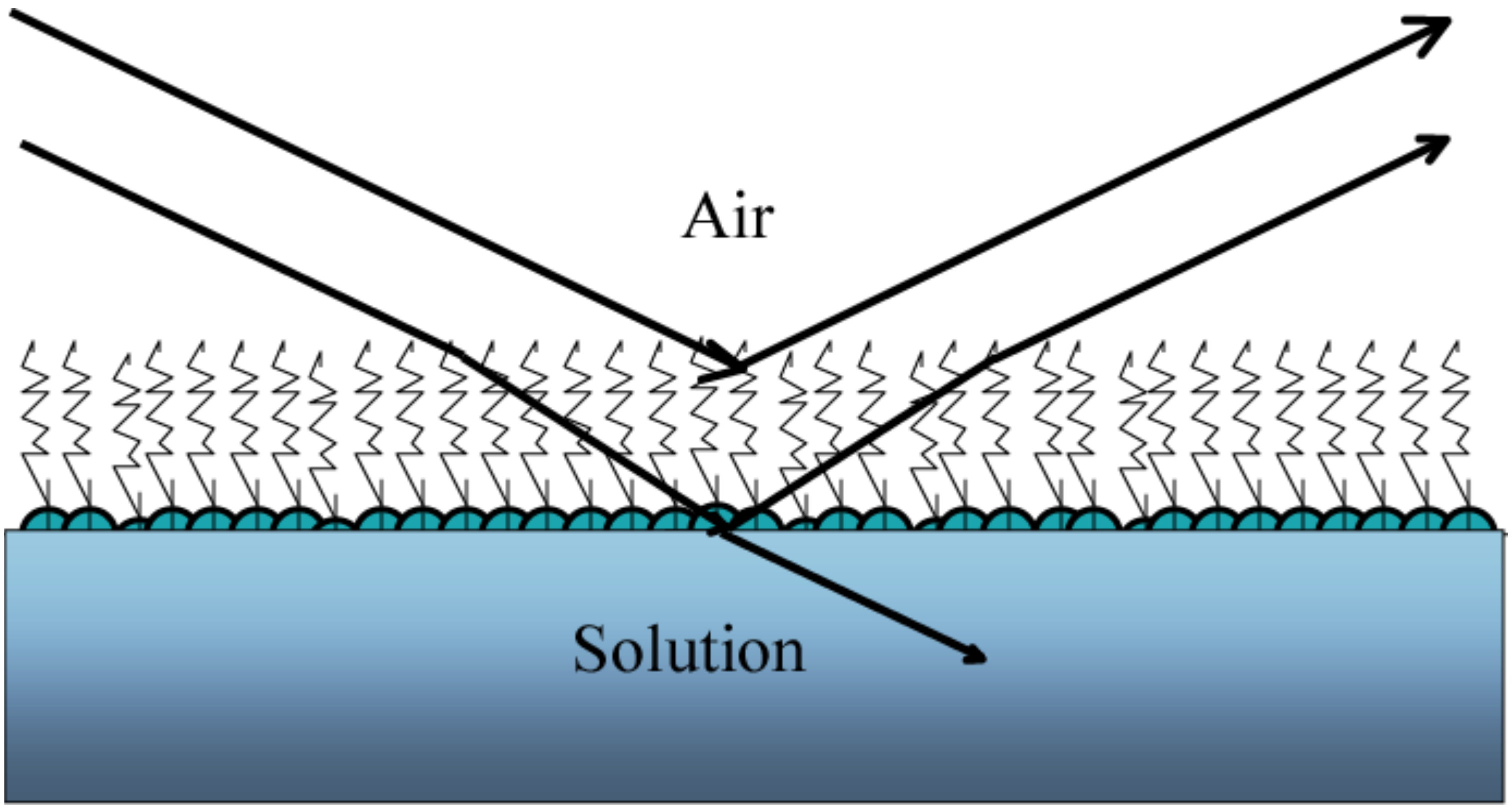
Air/D_2O Interface

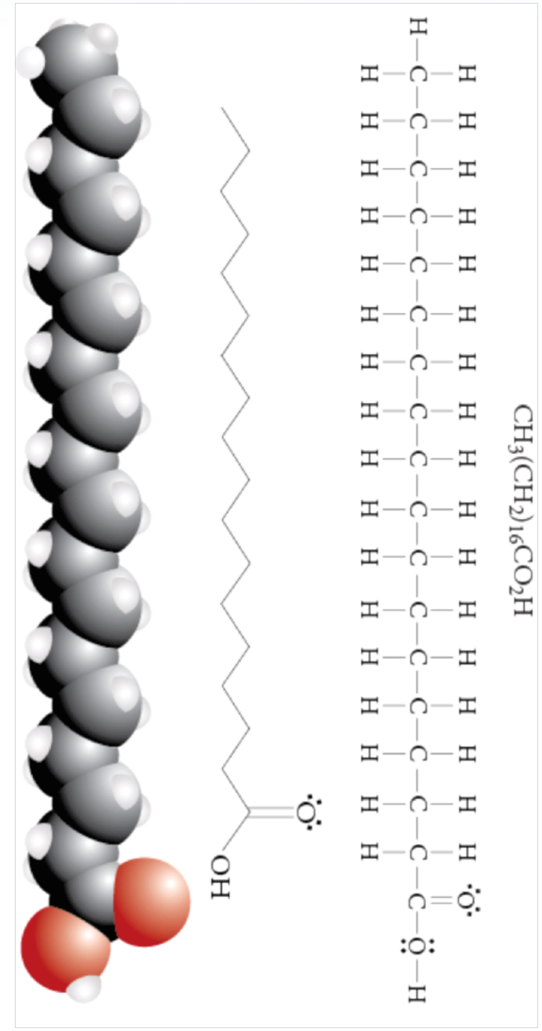




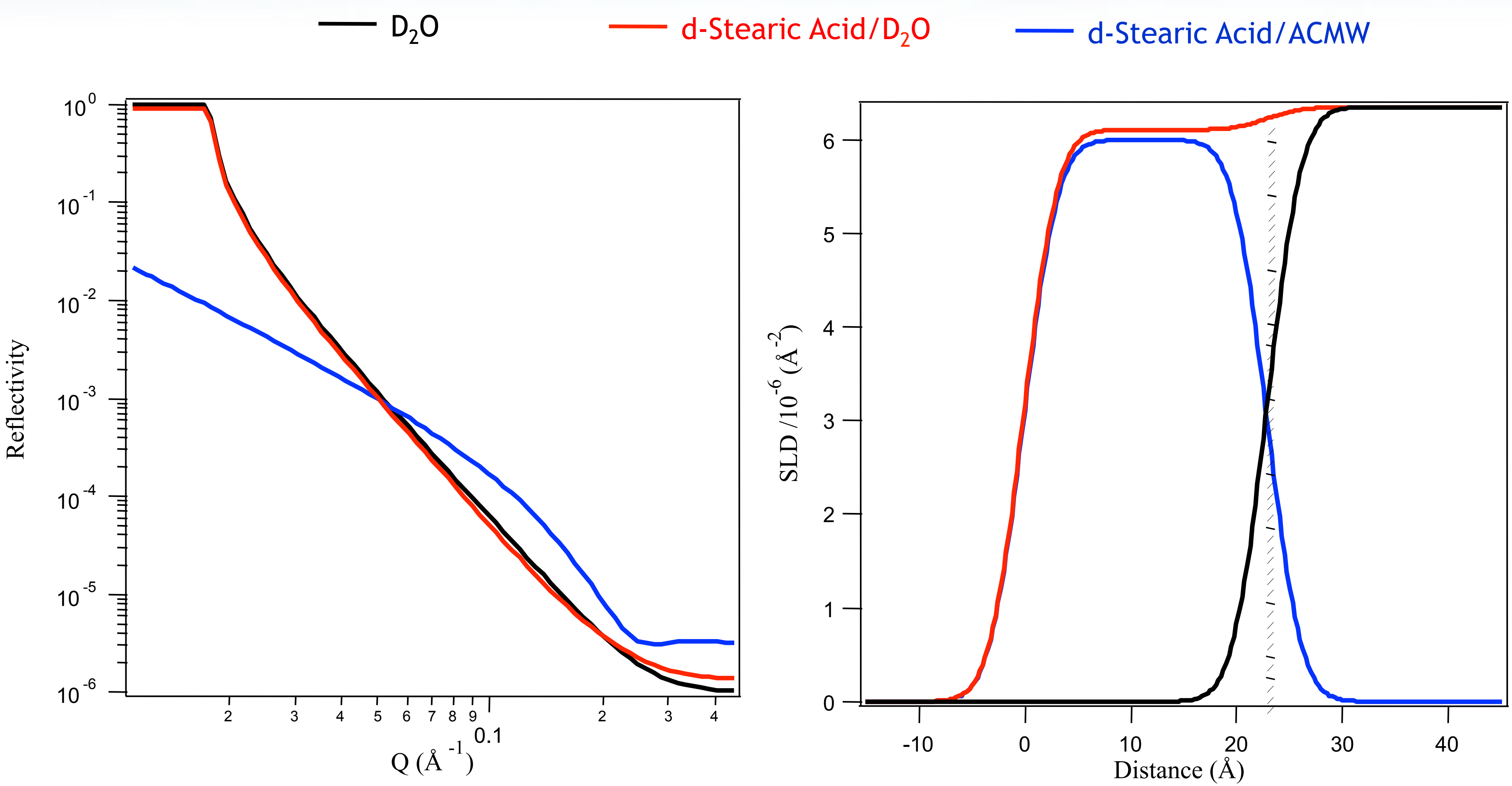
Australian Government | ansto

Langmuir Films

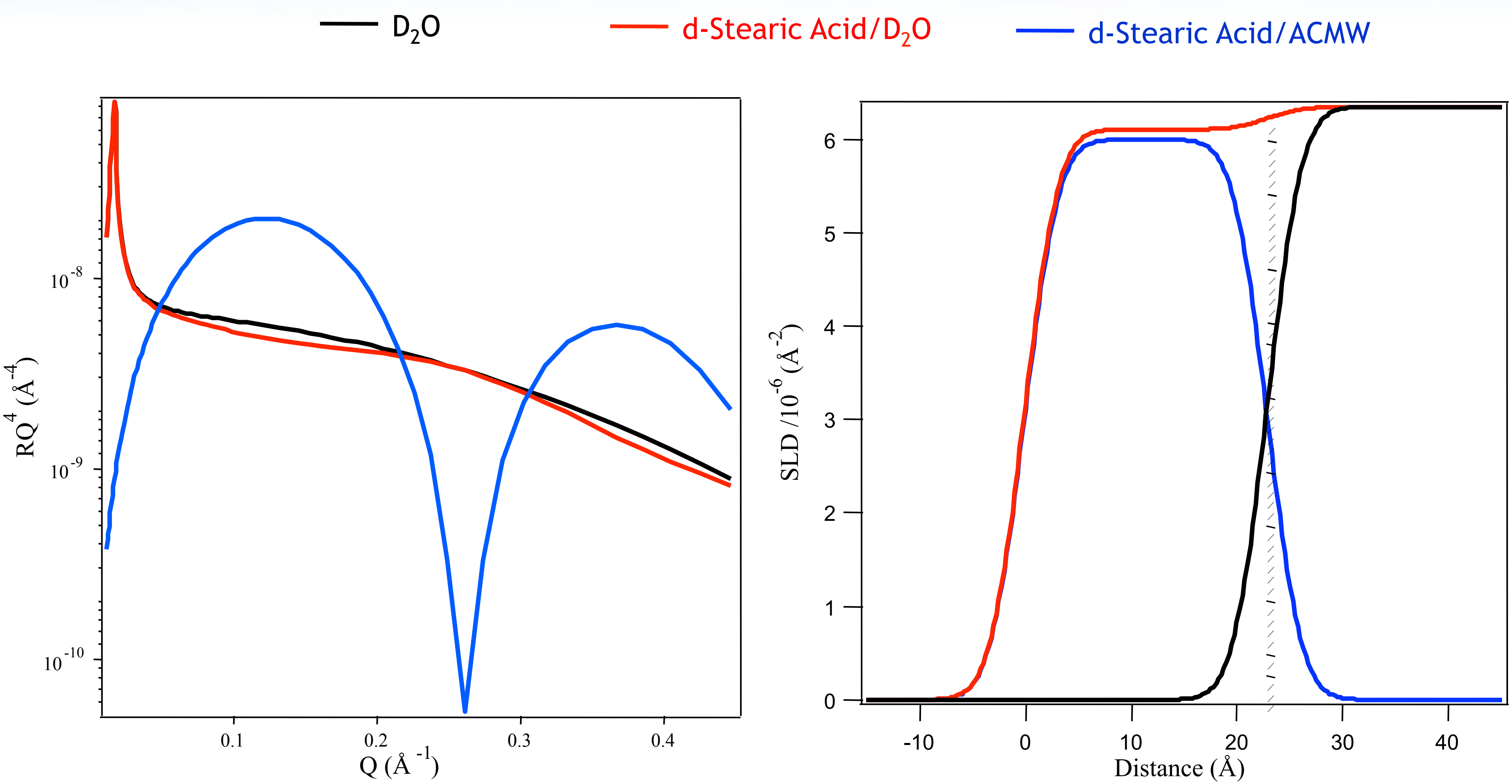




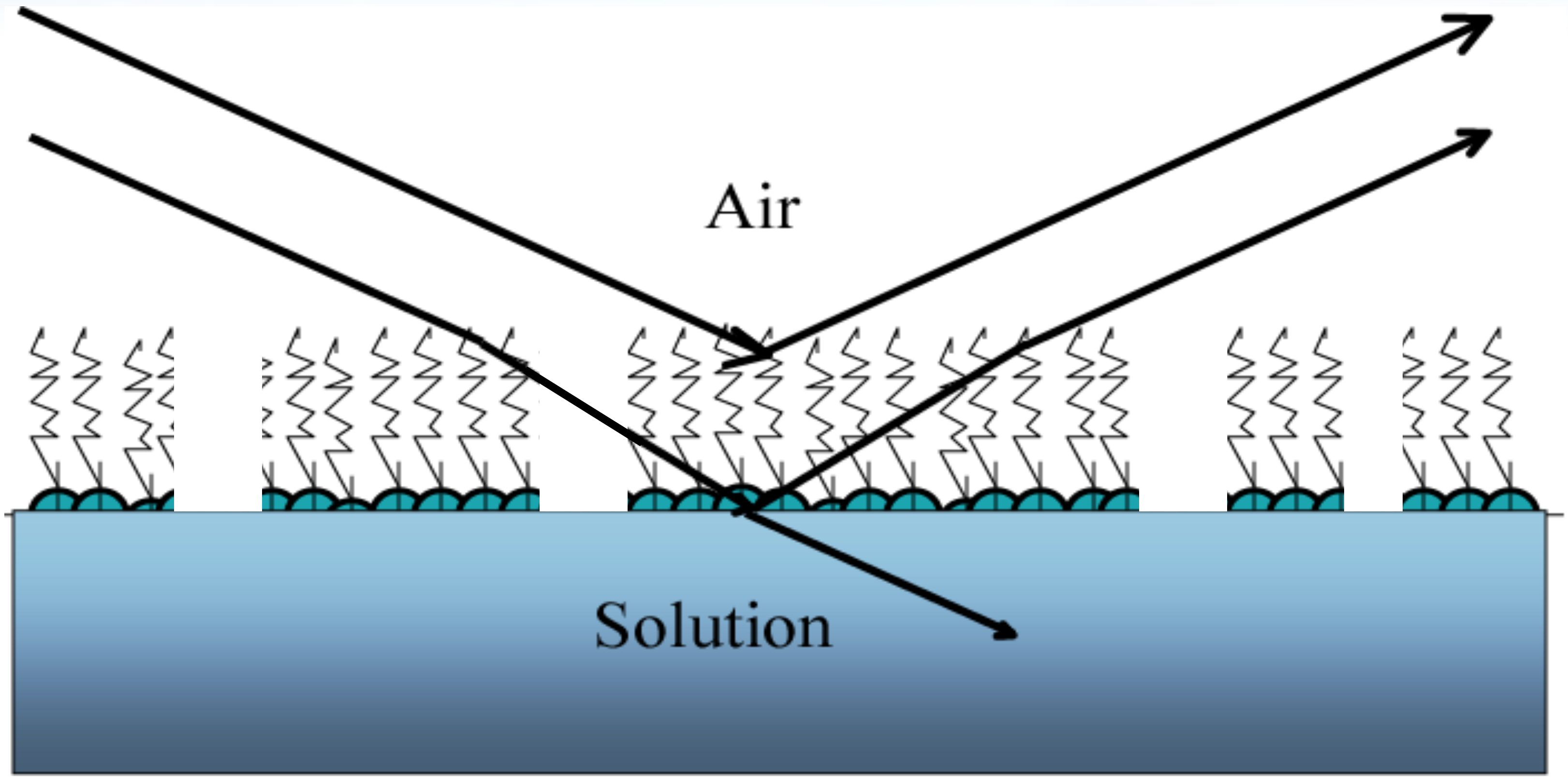
Stearic Acid at the Air/Water Interface



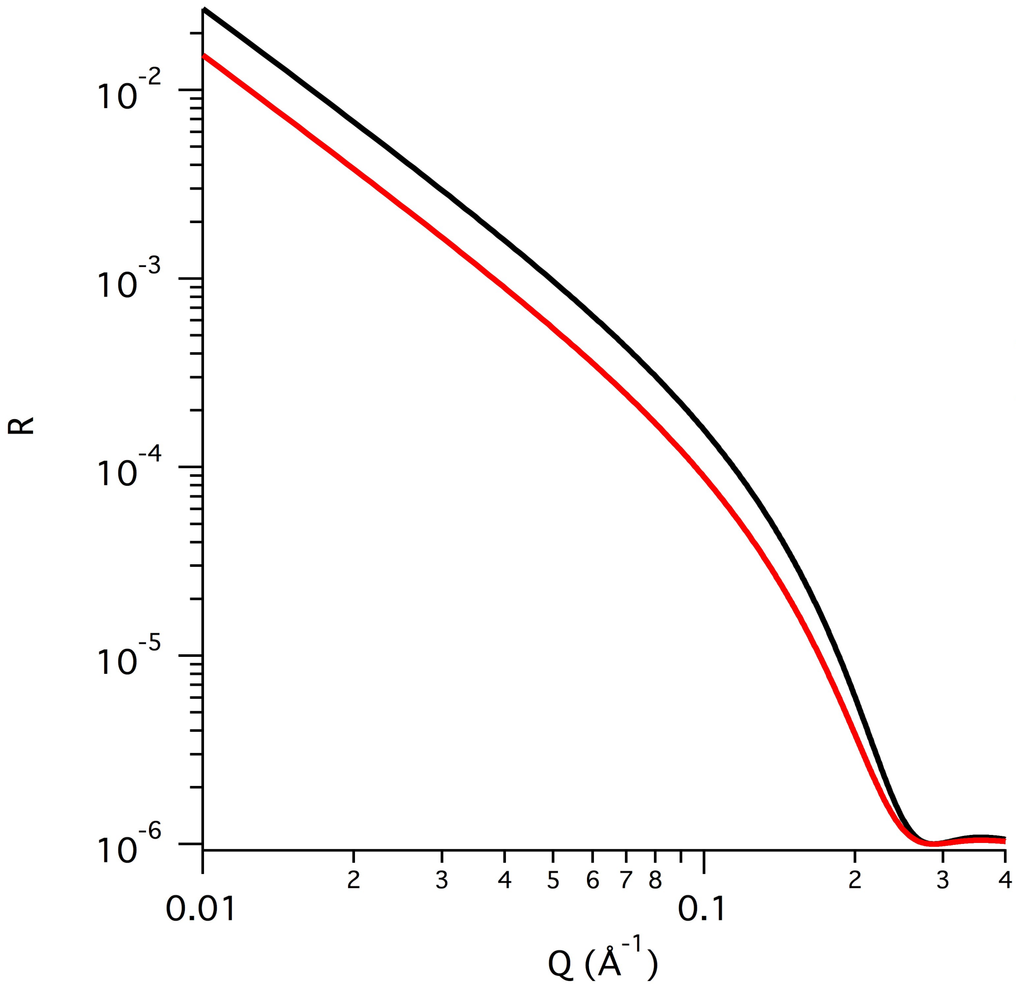
Stearic Acid at the Air/Water Interface

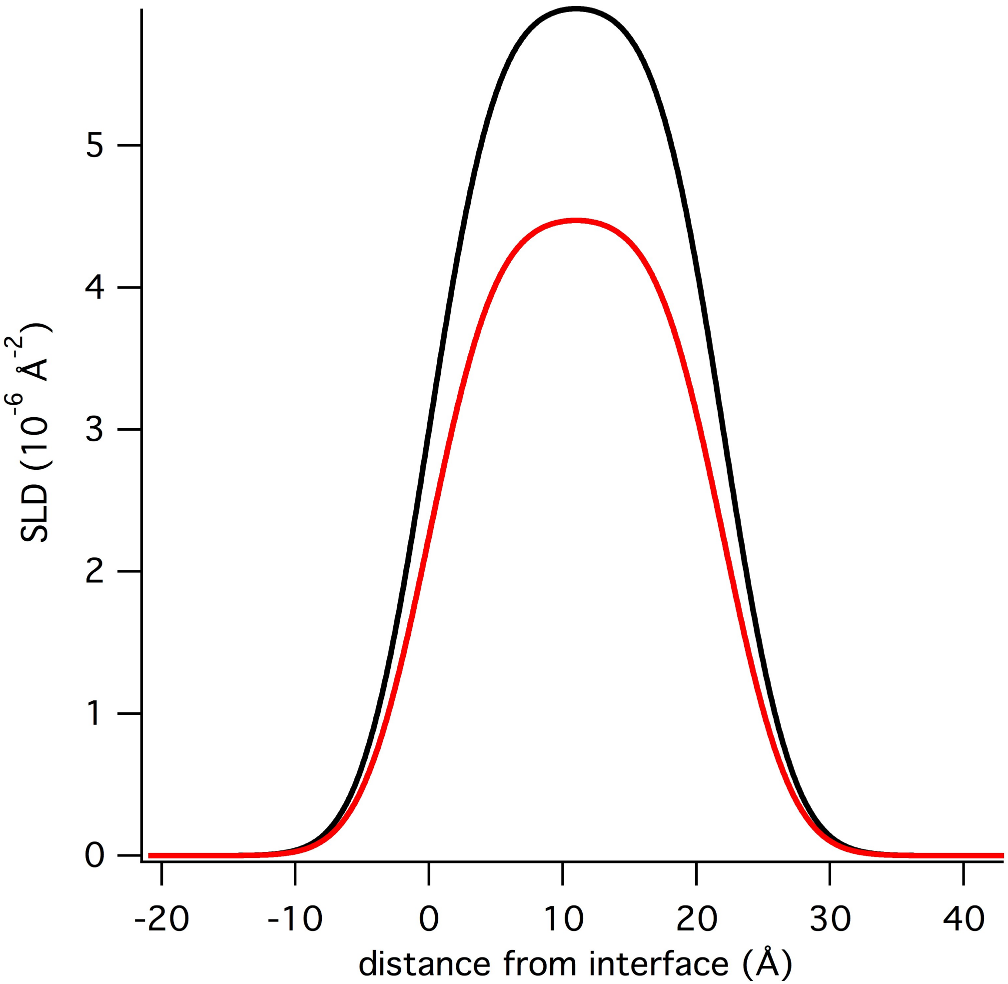


Langmuir Films



Stearic Acid. Partial Coverage





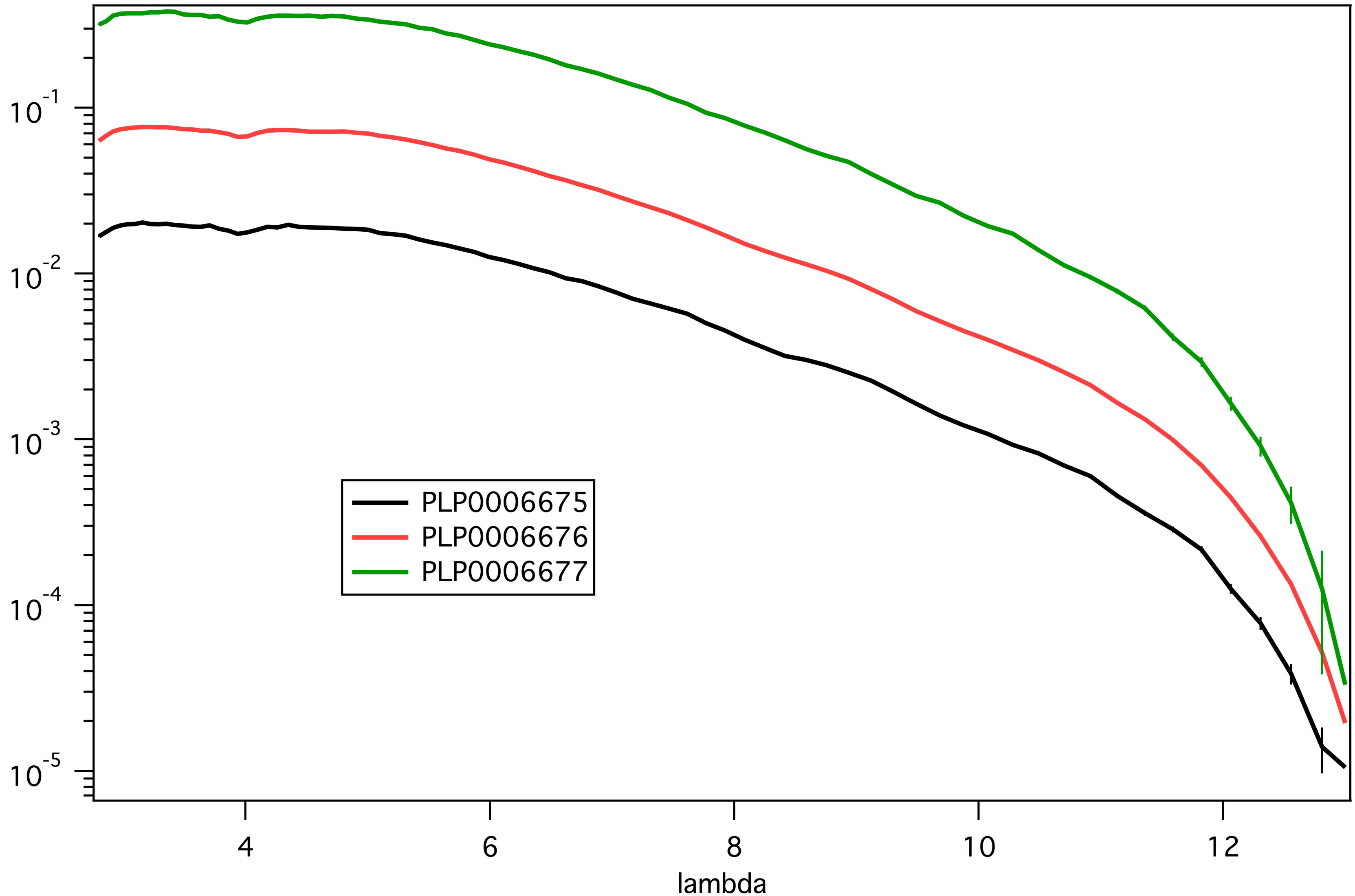
Qualitative Analysis

- Need to be able to do something with the data.
- Can usually do some qualitative or semi quantitative data analysis while on the instrument.
  - Depends on complexity of system.
- Ultimately need data which is absolutely scaled for quantitative analysis.

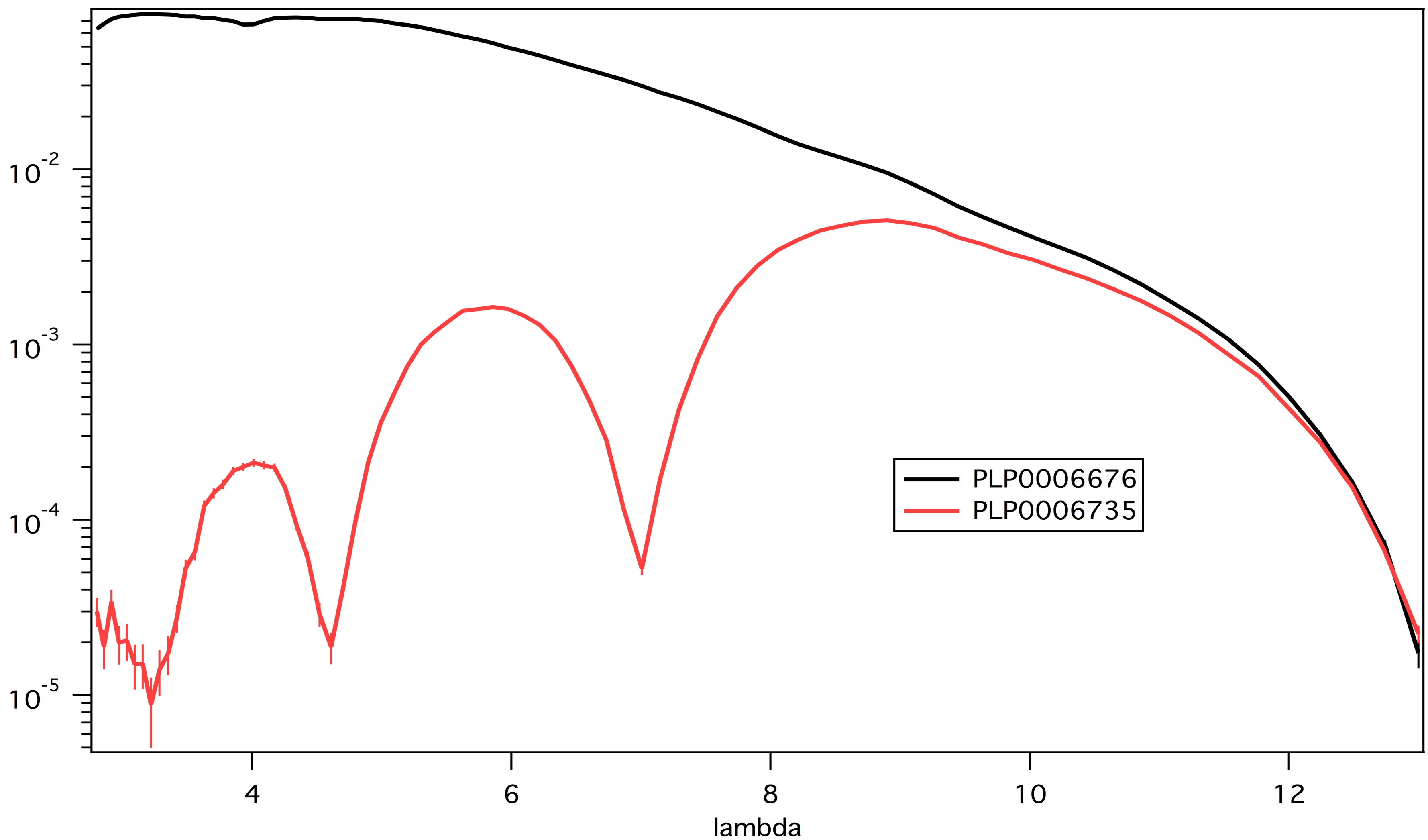
Data Reduction.

- Reflectivity
  - I_R / I_I
- Measure reflected intensity.
- What about incident intensity.
- Time of Flight Experiment.
  - Measure Direct Beam for expt conditions.
- Normalise all measurements via DB.

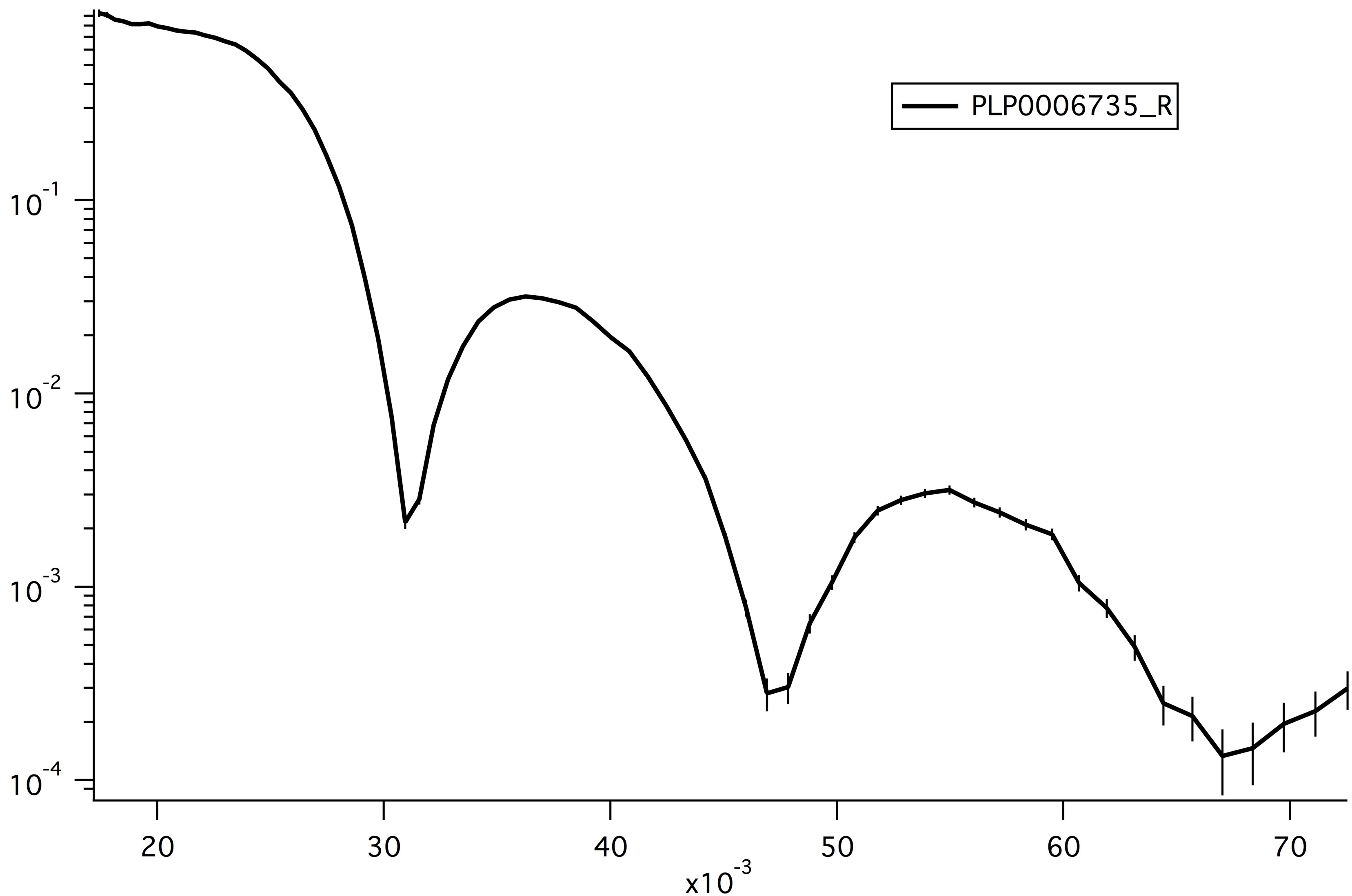
Direct Beams



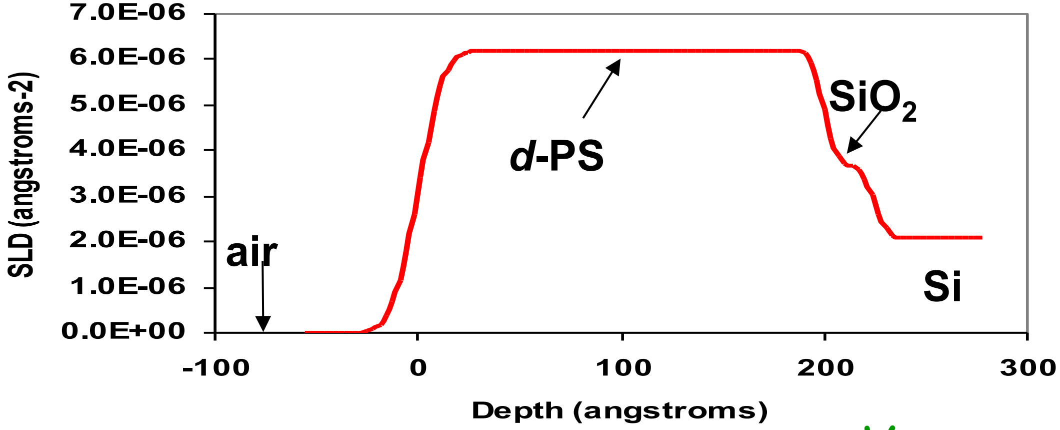
Direct Beam & Data



Reduced Data



Solving a Structure: Data Modelling



Reflectometry is an *indirect* method

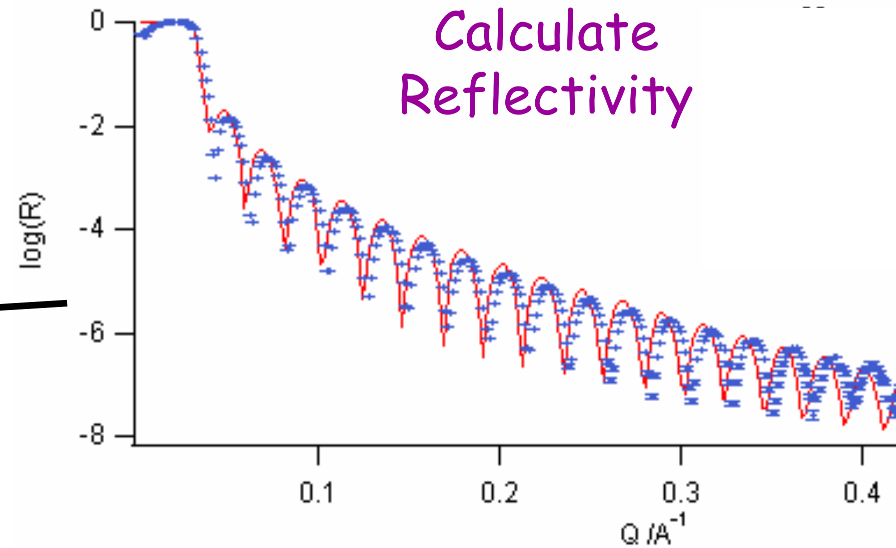
Structural Model

Vary thickness, SLD & roughness

Calculate Reflectivity

Least-Squares Regression

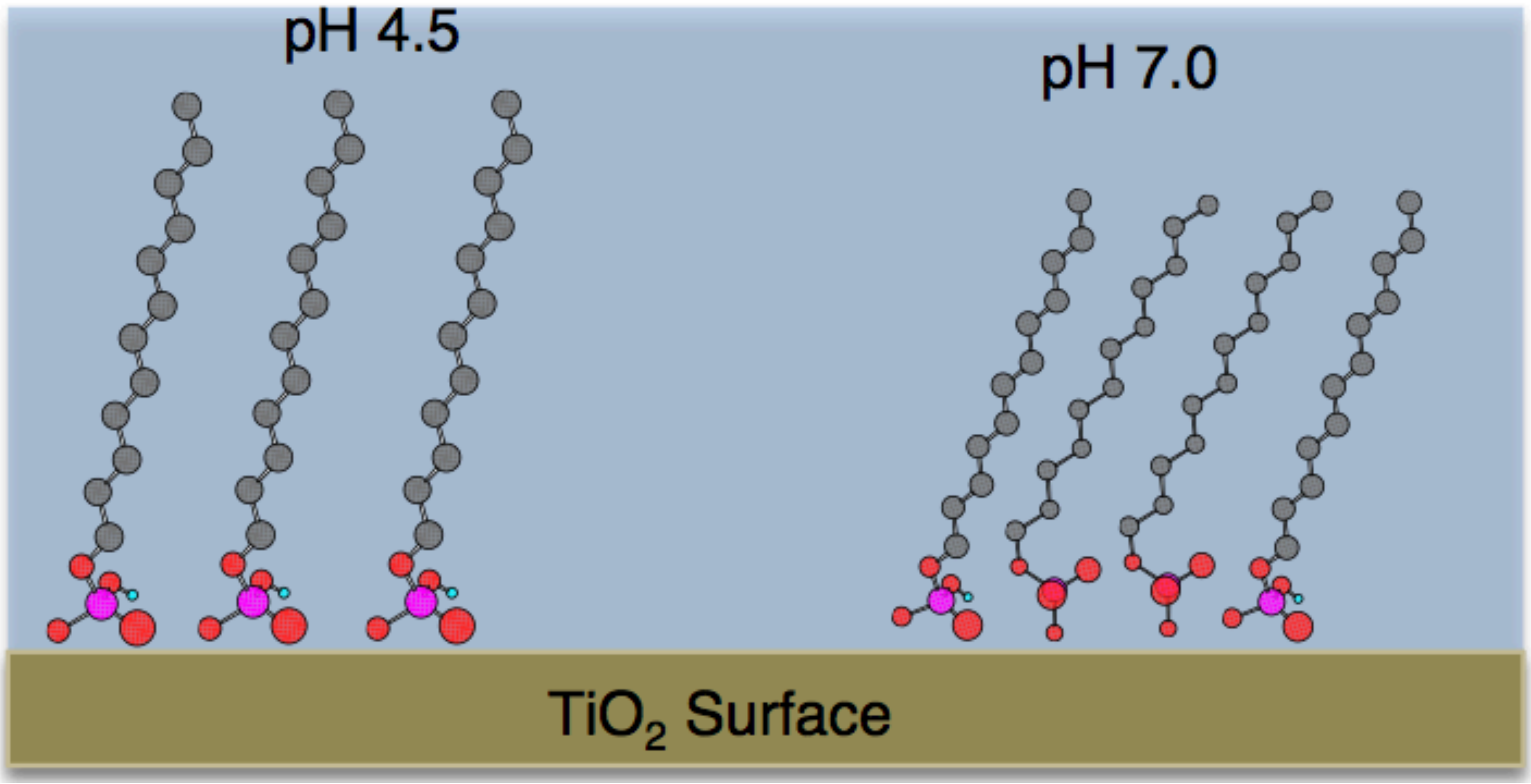
Compare with Experimental R Vs Q



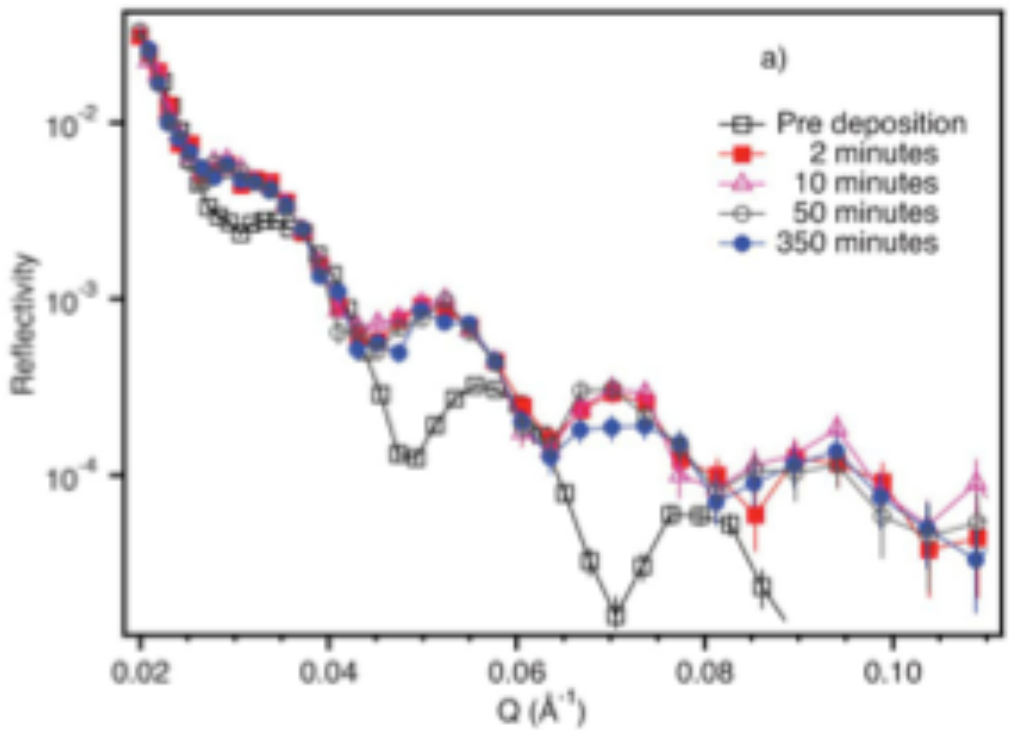
Data fitting software.

- A number of programs available
  - Motofit
  - Rascal
  - ….
- Virtually all use Optical Transfer Model approach

Dodecylamine on TiO_2



Dodecylamine on TiO_2



Holt et al. *RSC Advances*, 2013, 3, 2581-2589

Constrained Fit

- Alkane layer on TiO2. Phosphate headgroup.
- Two datasets
  - D_2O subphase
  - TiO_2 matched subphase.

Other Fitting Options

- For Example
  - Fit area per molecule.

$$SLD = \frac{b}{d \times APM} + \left(1 - \frac{V}{d \times APM}\right) \times b_{soln}$$

  - With multiple contrasts

Any Questions ?