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Introduction to neutron reflection

Adrian Rennie

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Outline

Inteference of waves

Refractive index

Critical angle, total reflection

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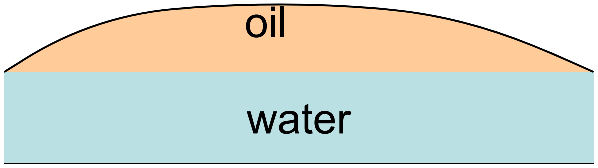
Reflection

Light



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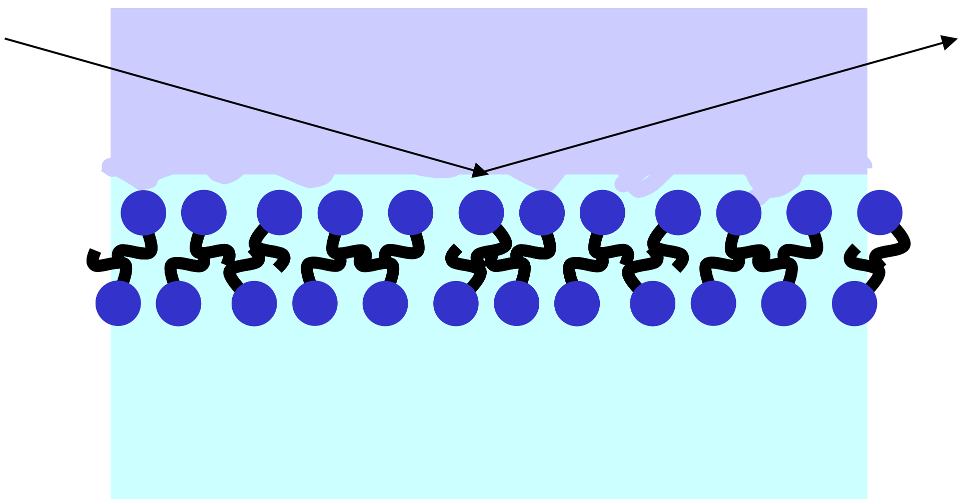
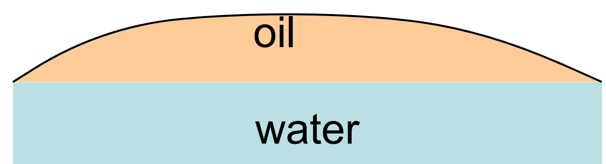
Reflection



Light



Reflection and Refraction: Snell's Law

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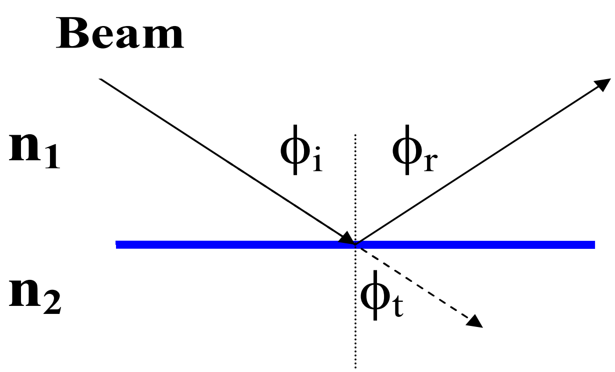
Optical Notation



For specular reflection:

$\phi_i = \phi_r$

Transmitted beam is refracted:

$n_2 \sin \phi_t = n_1 \sin \phi_i$

n is refractive index

Reflection and Refraction: Snell's Law

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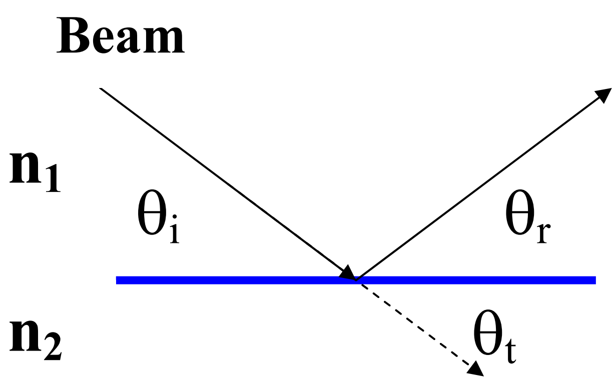
Neutron Reflection Notation



For specular reflection:

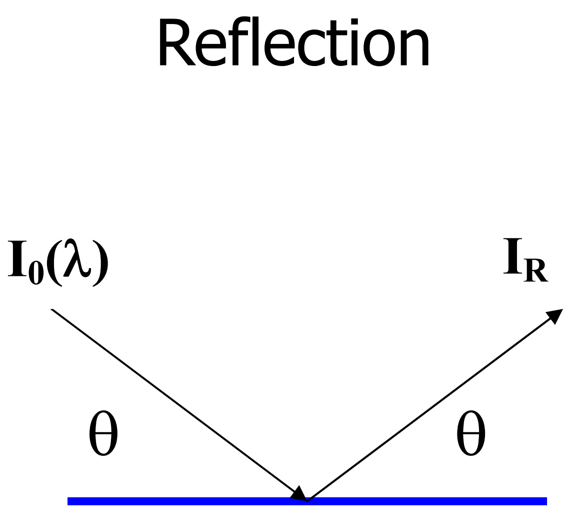
$$\theta_i = \theta_r$$

Transmitted beam is refracted:

$$n_2 \cos \theta_t = n_1 \cos \theta_i$$

n is refractive index

Reflection – measured quantities



Reflected beam deflected: $2\,\theta$

Reflectivity

$R(Q) = I_R/I_0(\lambda)$

Momentum transfer

$Q = (4\pi/\lambda) \sin\theta$

Demonstration Calculations

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

www.ncnr.nist.gov/instruments/magik/calculators/magnetic-reflectivity-calculator.html

Critical Angle and Below (critical wavelength and above)

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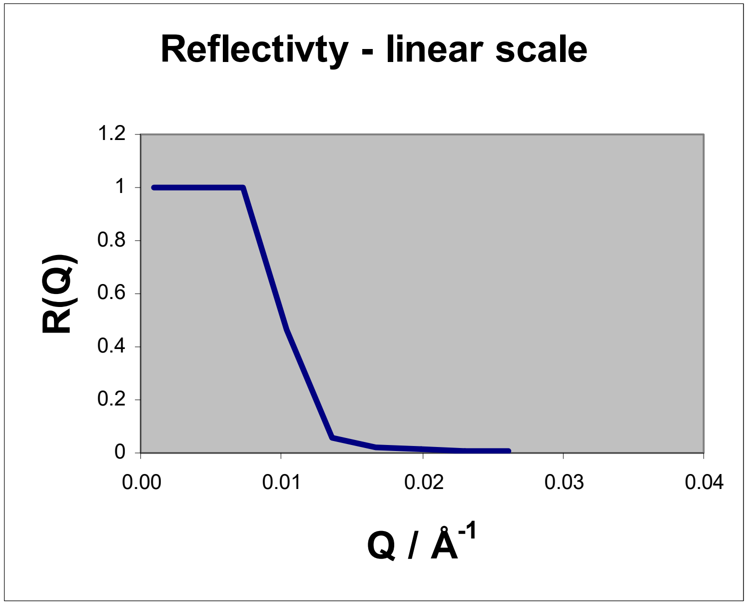
Density difference between two bulk phases determines the critical momentum transfer/angle, Q_c or θ_c



Any variation in intensity below critical angle is probably telling you about the experiment rather than the interface

R (Q) = 1 for $\theta < \theta_c$ is often used as a calibrant

$R(Q) \sim 1/Q^4$ for sharp interface

Total reflection below critical angle θ

$\cos\theta = n_2/n_1$

Calculating Refractive Index

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Neutrons

$$n = 1 - (\lambda^2 \Sigma_i b_i/V / 2\pi)$$

λ is the wavelength

$\Sigma_i b_i$ is the sum of scattering lengths in volume V

b is known for most stable nuclei

$\rho = \Sigma_i b_i/V$

Scattering Lengths of Nuclei

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Nucleus	Scattering Length / fm
^{1}H	-3.741
^{2}H (or D)	6.675
C	6.648
O	5.805
Si	4.151
Cl	9.579

Source: H. Rauch & W. Waschkowski

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Properties of Common Materials

Material	Scatt. Length Density / 10^{-6} Å^{-2}	Refractive index at 10 Å
H_2O	-0.56	1.000009
D_2O	6.35	0.999899
Si	2.07	0.999967
Air	0	1.000000
Polystyrene	1.4	0.999971

Contrast in a Thin Film

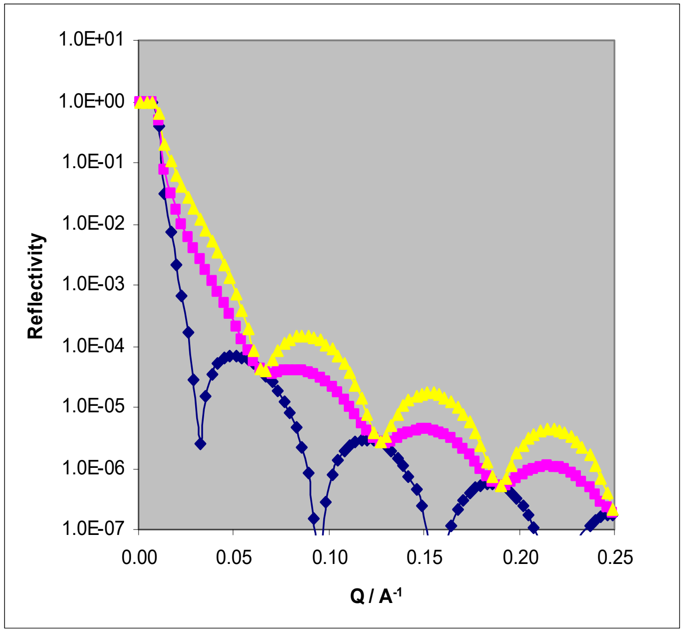
Calculation for Neutrons

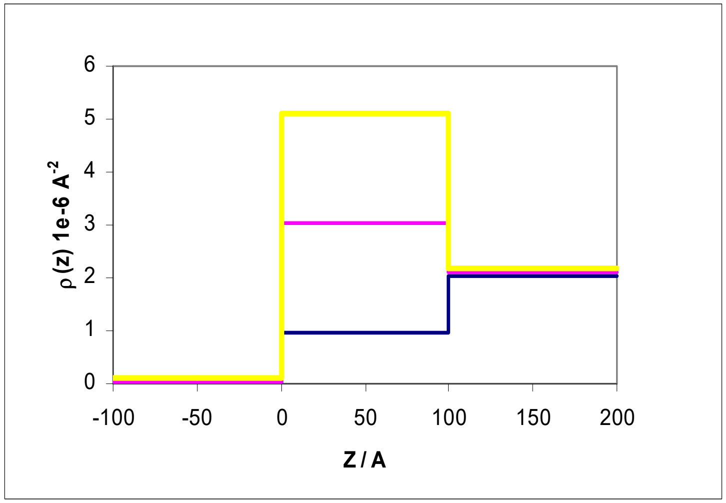
100 Å layer with ρ=1, 3 & 5 x 10^{-6} Å^{-2} on Si (ρ=2.07 x 10^{-6} Å^{-2})

Increasing contrast changes visibility of fringes

Phase change makes large difference

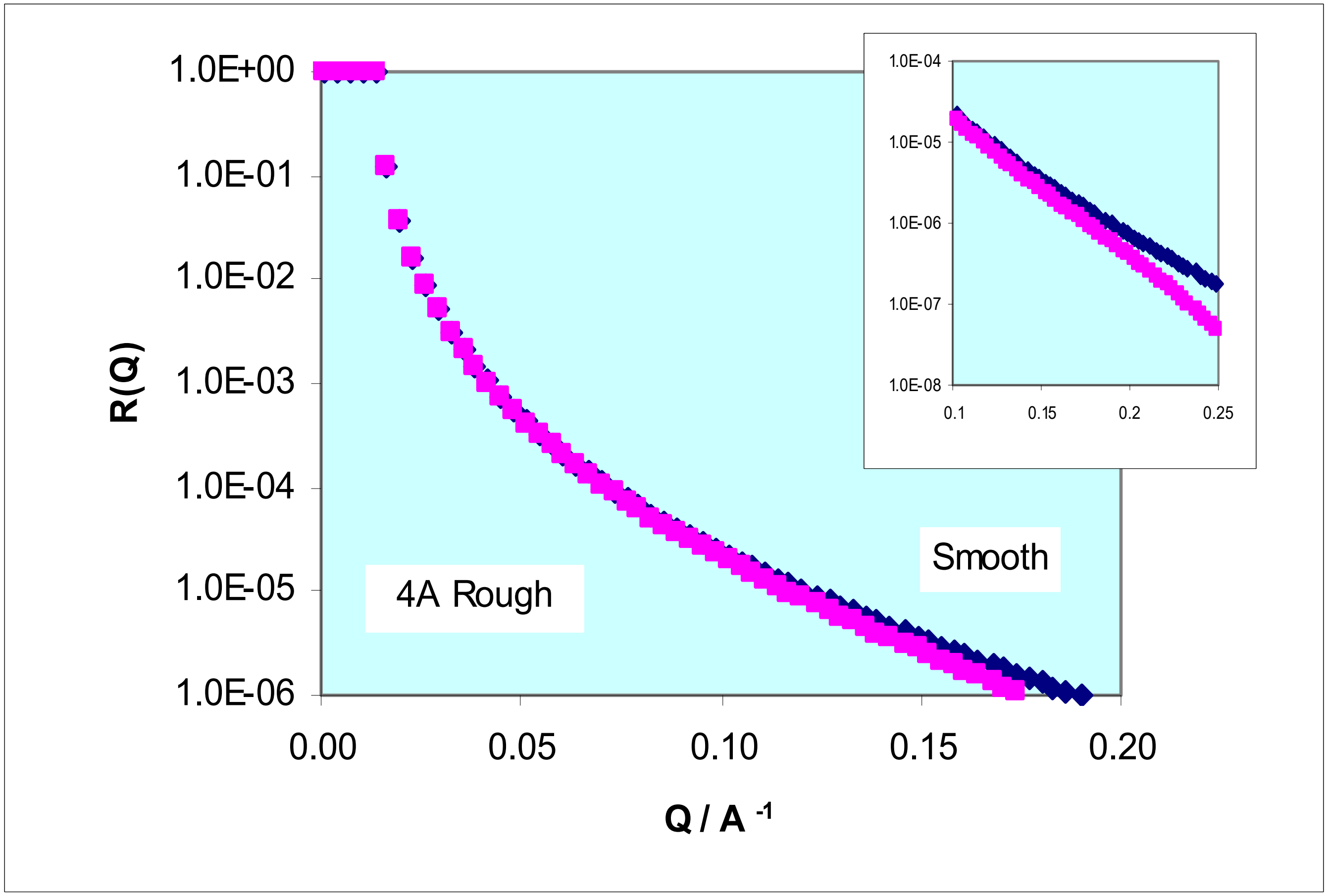
Fringes (Kiessig fringes) – spacing indicates film thickness for a single layer.





Roughness

Reflectivity from rough surfaces is decreased.



L. Nevot, P. Crocé *J. Phys. Appl.* **15**, T61 (1980)

Intensity of Reflected Signal

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Waves interfere constructively for

$$2\ d \sin\theta = \lambda,\ 2\lambda,\ 3\lambda\ \ldots \text{ (Bragg's law)}$$

Measured reflectivity will depend on angle and wavelength.

Total reflection for angles less than critical angle, $\theta_c = \arccos(n_1/n_2)$

Useful Physical Ideas

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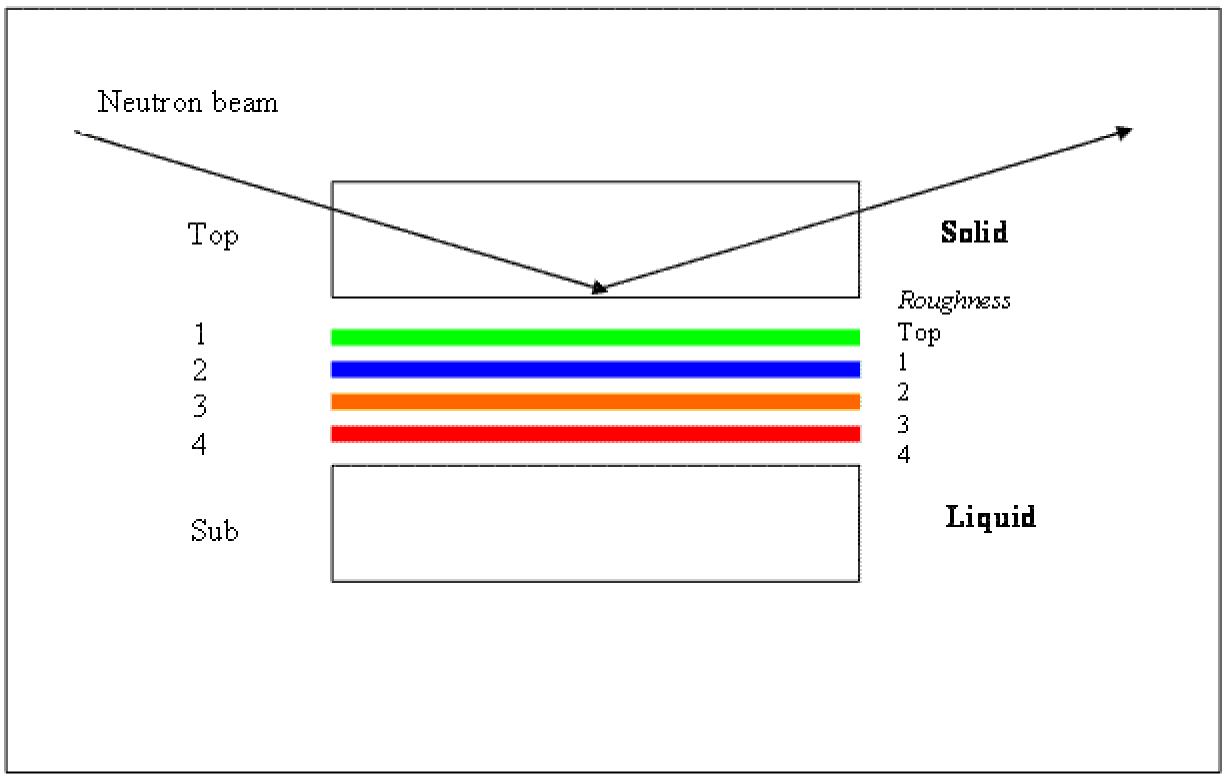
Models for complex interfaces can be constructed from multiple thin layers of different refractive index, n or scattering length density, ρ.



Useful Physical Ideas

Isotopes (e.g. D/H substitution) can be used to label particular species or alter contrast

Neutrons have spin – effectively a field dependent contribution to scattering length

Abeles Optical Matrix Method

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$$r_j = \begin{bmatrix} e^{i\beta_{j-1}} & r_{j-1}e^{i\beta_{j-1}} \\ r_{j-1}e^{-i\beta_{j-1}} & e^{-i\beta_{j-1}} \end{bmatrix}$$

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

$$p_j = n_j \sin\theta_j$$

$$r_j = (p_{j-1} - p_j)/(p_{j-1} + p_j)$$

$$M_R = [M_1][M_2]...[M_{n-1}]$$

$$R(Q) = M_{21}M_{21}^* / M_{11}M_{11}^*$$

Magnetic Contrast

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$b_m = \mu_0\, e^2\, S\, \gamma\, /\, 4\pi\, m_e$

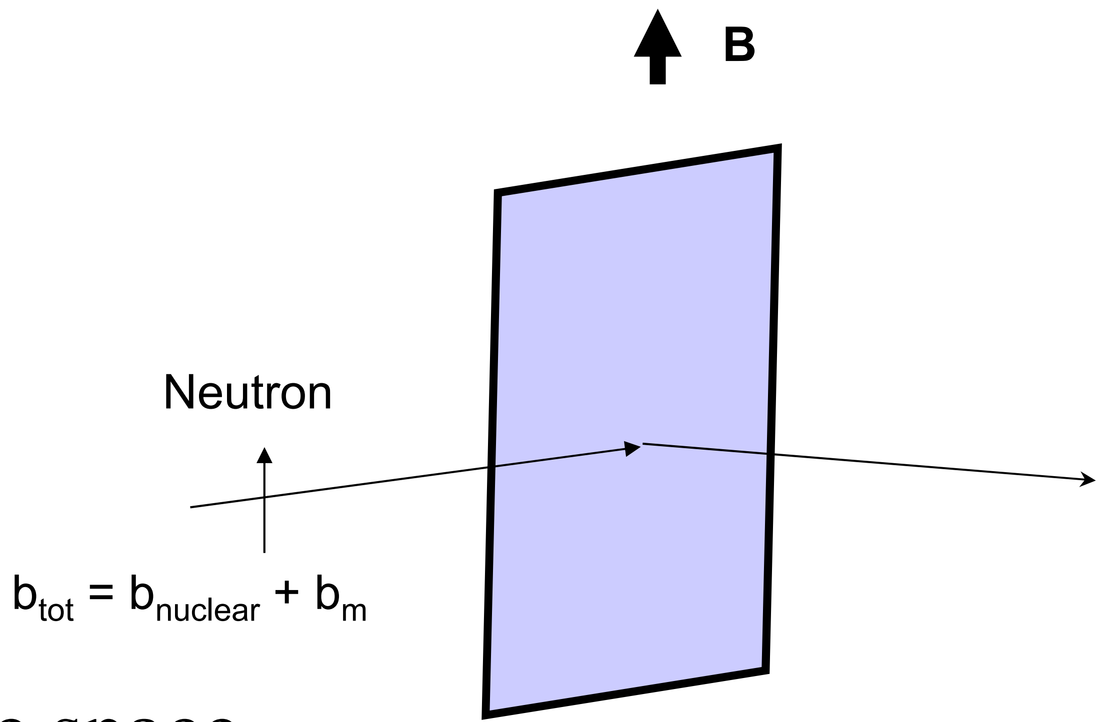
e, electronic charge

m_e, electron mass

S, spin

μ_0, Permeability of free space

γ, gyromagnetic ratio, 1.913



$b_{tot} = b_{nuclear} \pm b_m$

Magnetic Contrast

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$b_m = \mu_0\, e^2\, S\, \gamma \,/\, 4\pi\, m_e$

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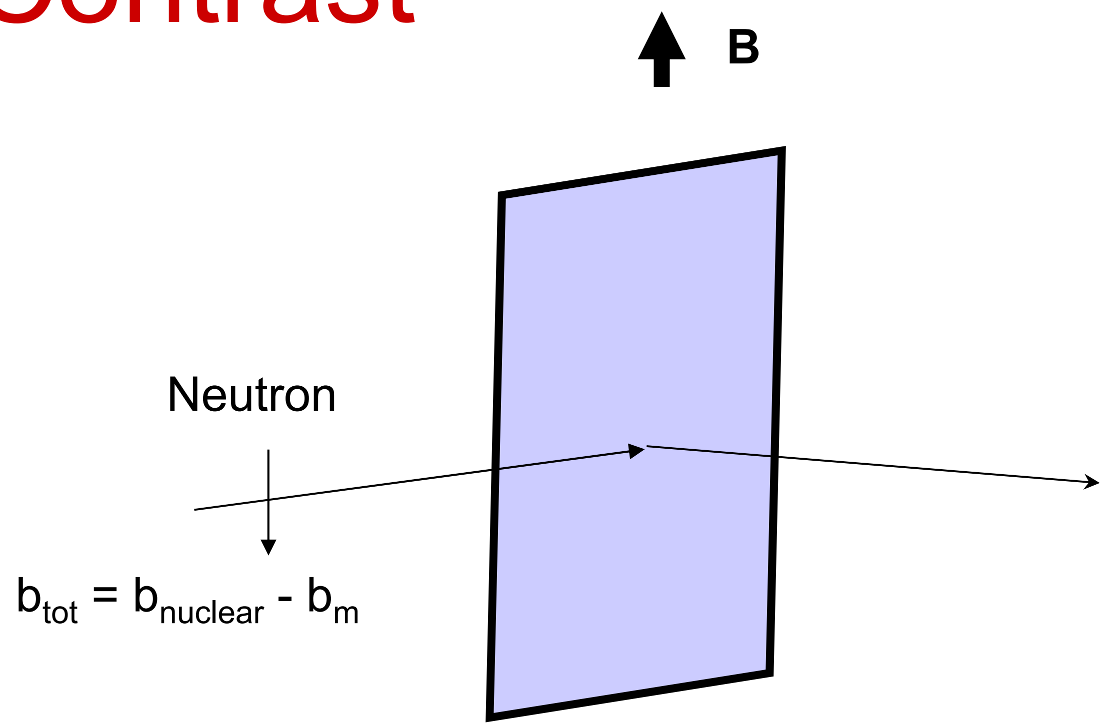

$b_{tot} = b_{nuclear} \pm b_m$

Scattering and Reflection

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ρ(Q) is Fourier transform of the scattering length density distribution normal to the interface, ρ(z)

$$R(Q) = \frac{16\pi^2}{Q^2}\left|\rho(Q)\right|^2$$

$$\rho(Q) = \int_{-\infty}^{\infty} \rho(z) e^{-iQz} dz$$

For sharp interface:

$R(Q) \sim 1/Q^4$

Partial Structure Factors

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Interface consists of distinct components: *1, 2, 3*

$$R(Q) = \frac{16\pi^2}{Q^2} \left| \int \rho(z) e^{iQz} dz \right|^2$$

$$\rho(z) = b_1 n_1(z) + b_2 n_2(z) + b_3 n_3(z)$$

$$R(Q) = \frac{16\pi^2}{Q^2} (b_1^2 h_{11} + 2b_1 b_2 h_{12} + b_2^2 h_{22} + 2b_2 b_3 h_{23} + b_3^2 h_{33} + 2b_3 b_1 h_{31})$$

h_{ij} are transforms of $n_i n_j$ – pair correlation functions

Lu, J. R.; Thomas, R. K.; Penfold, J. *Adv. Coll. Inter. Sci.* **2000**, 84, 143-304.

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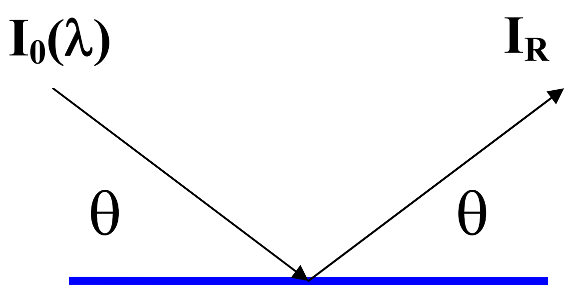
Practical Aspects of Neutron Reflection
How to Collect Data

Adrian R. Rennie

Reflection – measured quantities

Reflection



Reflected beam deflected:

$2\,\theta$

Reflectivity

$R(\theta, \lambda) = I_R/I_0(\lambda)$

Momentum transfer

$Q = (4\pi/\lambda) \sin \theta$

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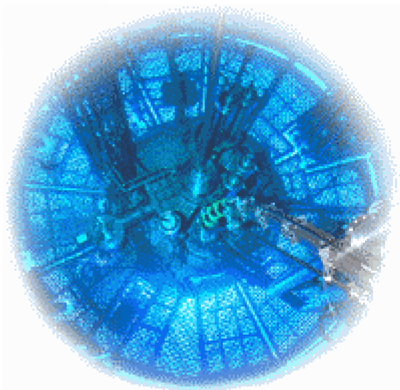
Best Sources of Neutrons



ILL reactor continuous

Thermal Flux 1.5×10^{15} n cm^{-2} s^{-1}

SNS, ORNL

60 Hz, 300 μs

5×10^{17} n cm^{-2} s^{-1} (Peak)

Neutrons: Speed & Wavelength

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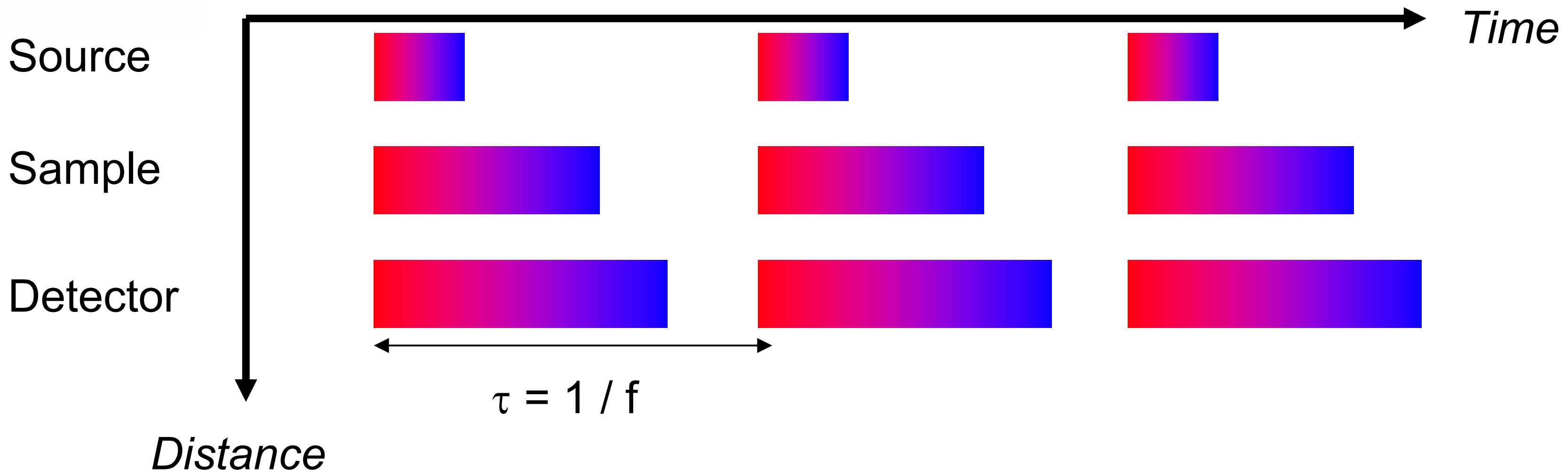
Velocity, v, from de Broglie relation

$$v\,\lambda = 3956 \text{ m s}^{-1} \text{ Å}$$

i.e. 10 Å has 400 m s^{-1}

Gravity is significant, separate wavelengths mechanically

Using a Pulsed Source



Detection time (after source pulse) gives wavelength

Choppers can select a wavelength

D17 Reflectometer

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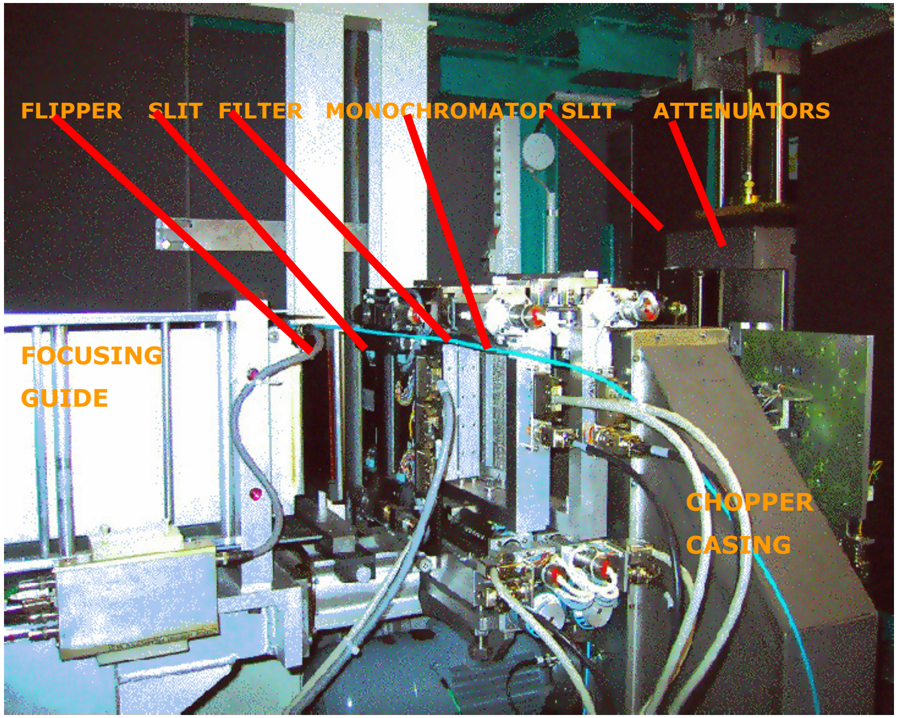

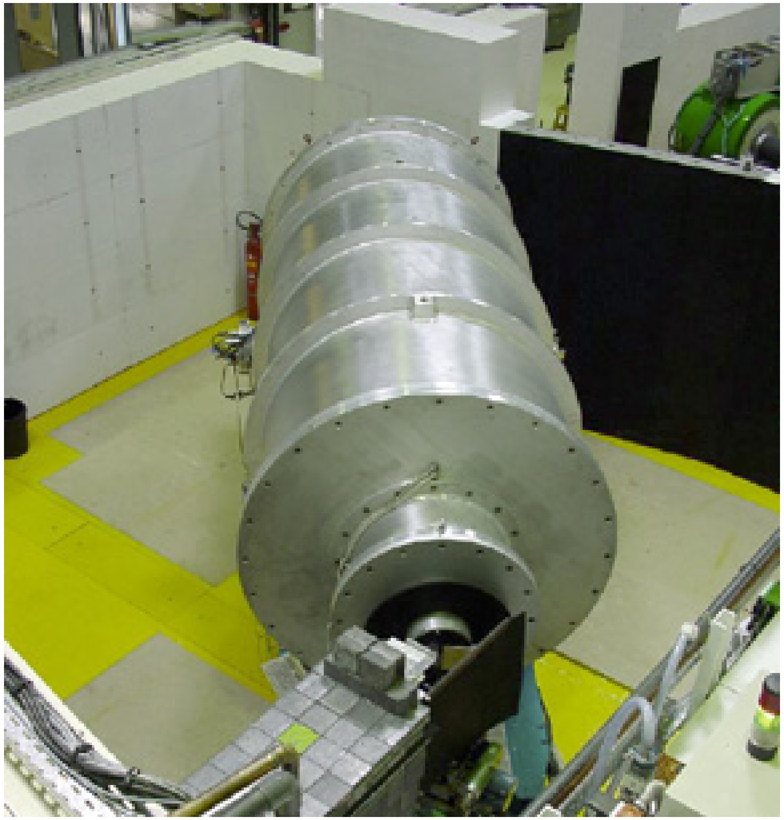

Practical Issues

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Reflectivity drops quickly with increasing Q (or angle). Signal is easily 'lost' in background.

To observe fringes it will be necessary to measure over an appropriate range of Q and to have sufficient resolution (ΔQ small enough).

Reflection from a Thin Film

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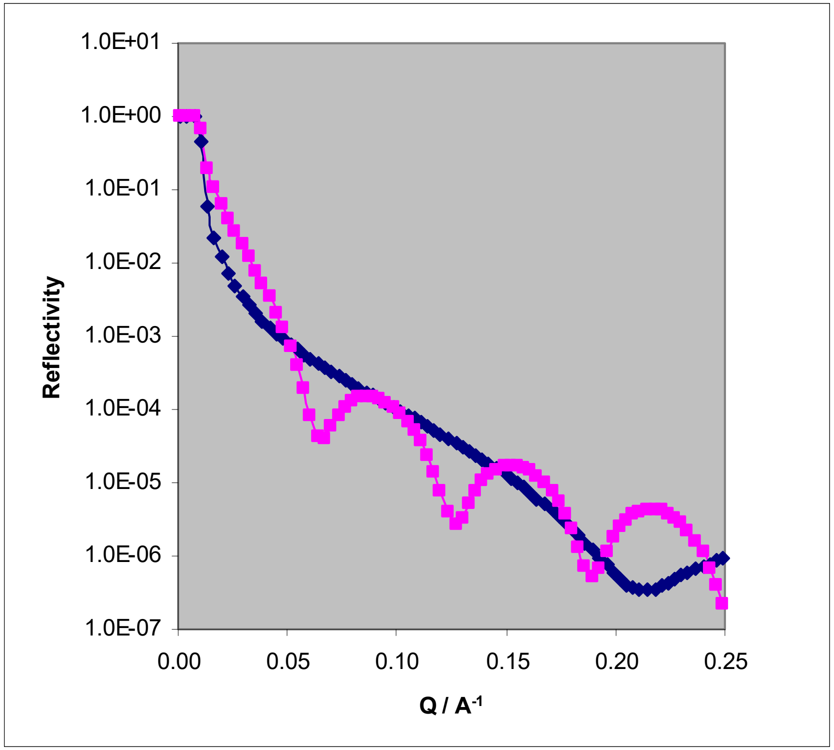
Model calculation on smooth surface.

Fringe spacing depends on thickness

Fringe spacing ~ $2\pi/d$



Model layer with $\rho = 5 \times 10^{-6}$ Å^2 on Si (2.07×10^{-6} Å^{-2}) Blue 30 Å, Pink 100 Å. No roughness.

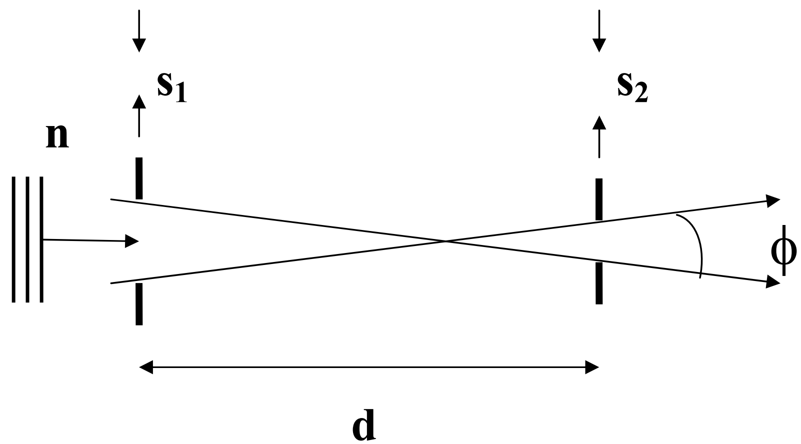
Resolution in Q

$Q = (4\pi/\lambda) \sin \theta$

Depends on $\Delta\lambda$ and $\Delta\theta$

Angle resolution, $\Delta\theta$, depends on collimation (slits)

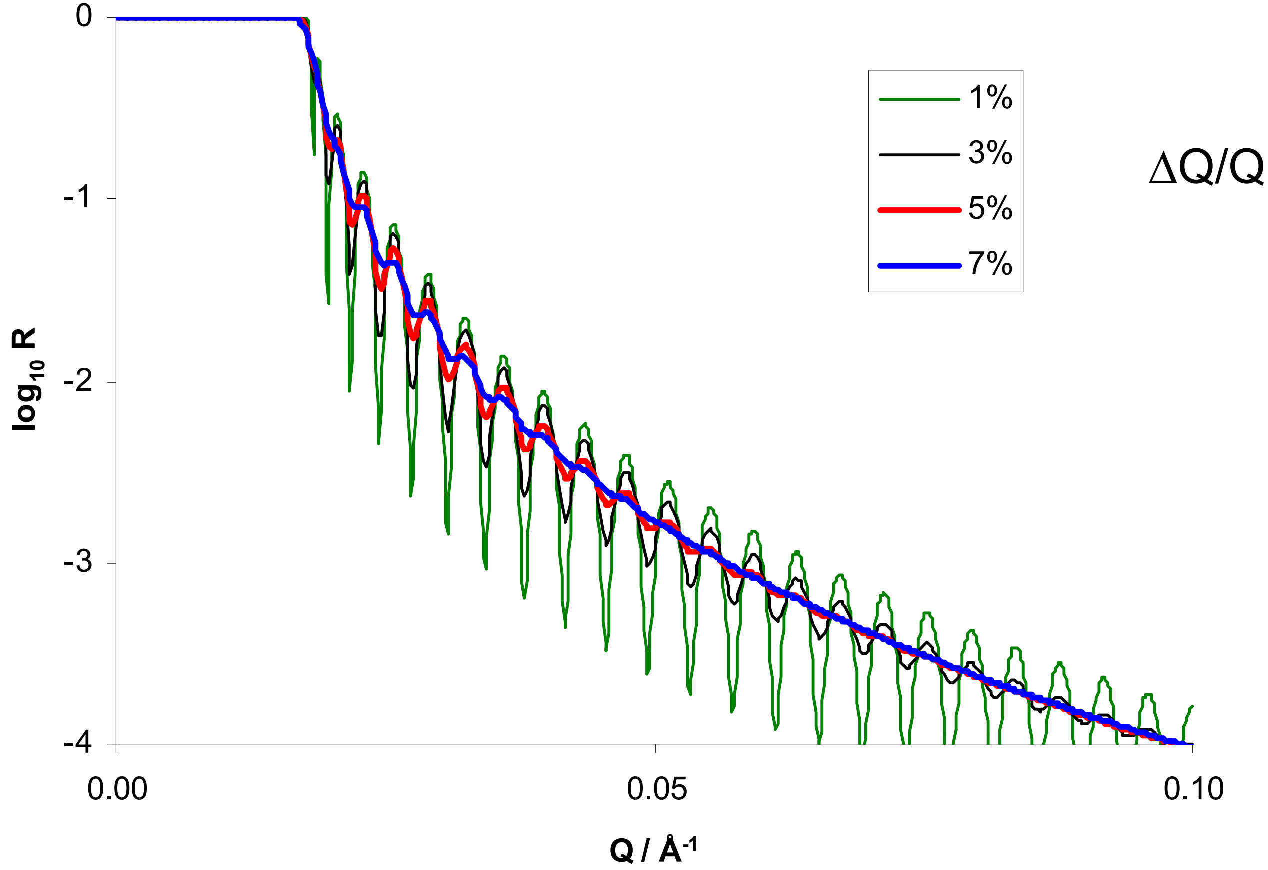
Wavelength resolution depends on monochromator or time resolution in measuring neutron pulse



Higher Resolution = Lower Flux

$$(\Delta Q/Q)^2 = (\Delta\lambda/\lambda)^2 + (\Delta\theta/\theta)^2$$

Effects of Resolution



Silicon substrate: film thickness 1500 Å (150 nm)
scattering length density 6.3×10^{-6} Å^{-2}

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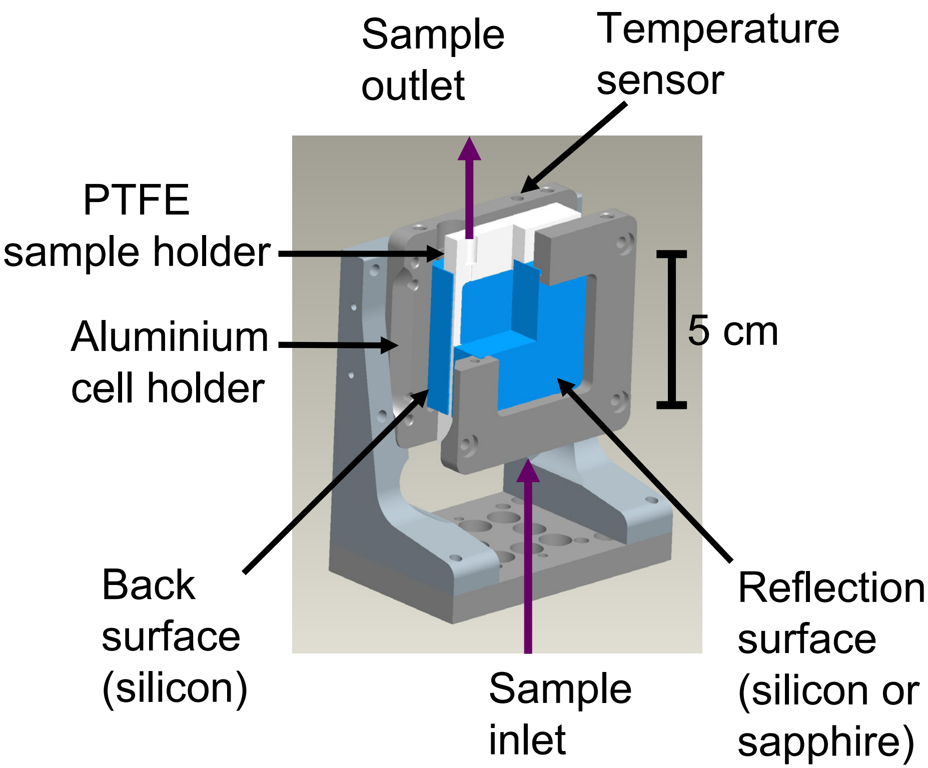
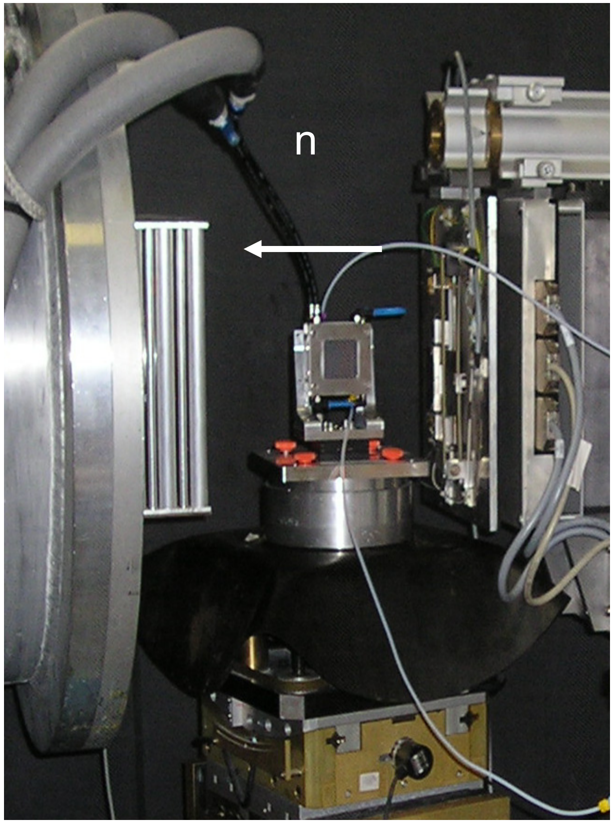
Sample Holder

D17 reflectometer
ILL, France





Alignment

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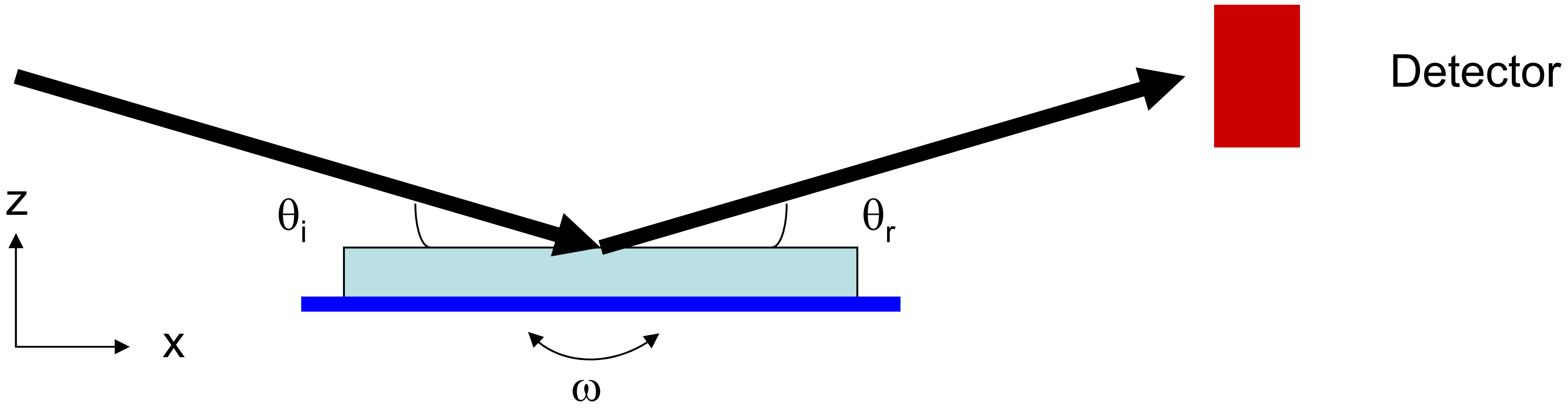
Rotation table must have centre on beam axis

Sample must be centred on rotation (half obscure the direct beam) – eucentric mount

Determine θ from the position of beam on a detector

Aligning a Sample



Design mount with surface at centre of rotation of ω. Eucentric mount.

Put centre of surface on the line through axis of rotation (x direction)

The rotation ω stage must be centred on the incident beam.

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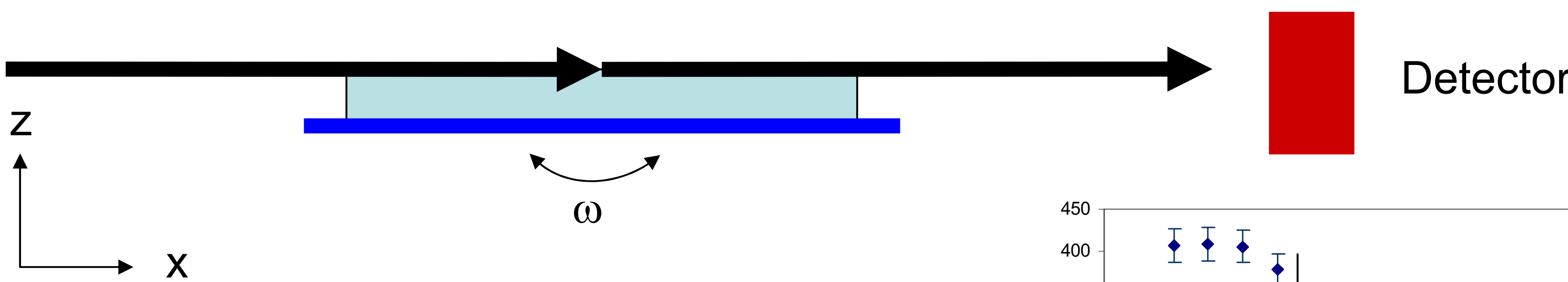
Aligning a Sample

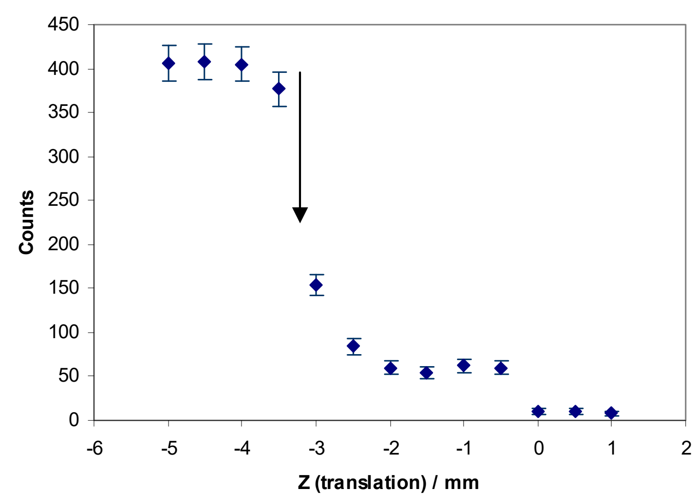
Set sample and detector to nominal zero

Choose fine slits to give collimated beam



Scan z

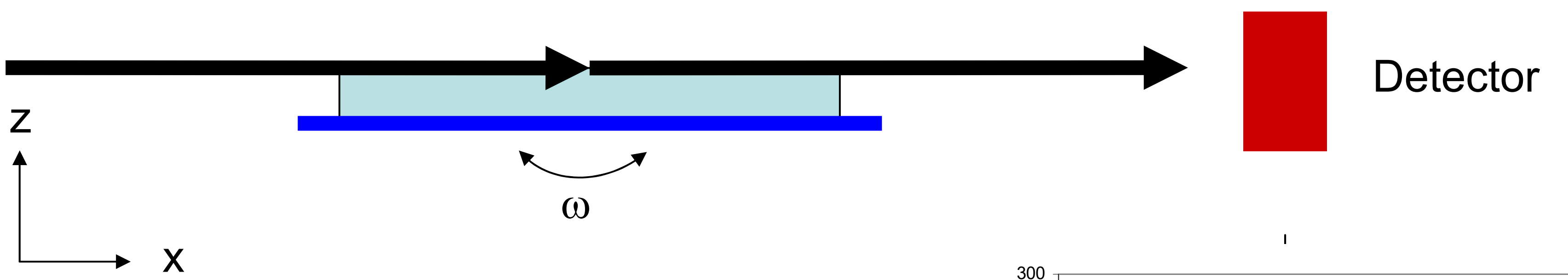
Look at intensity on detector



Identify z = -3.2 (~230 cts) as position interface intersects direct beam

Aligning a Sample

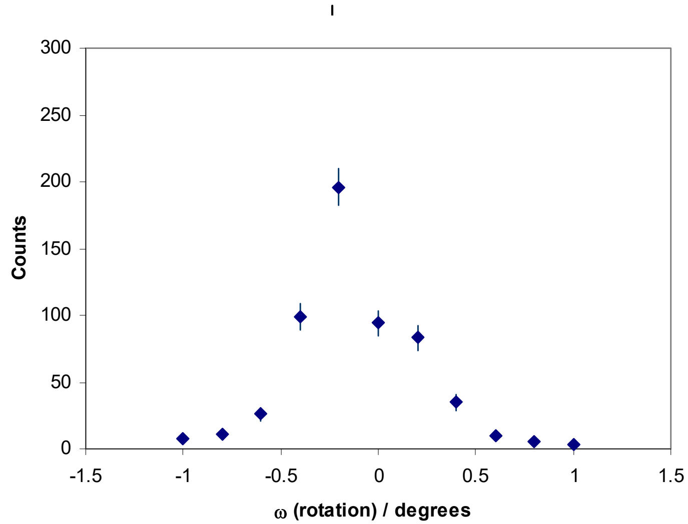
Move z to approximate sample in beam position



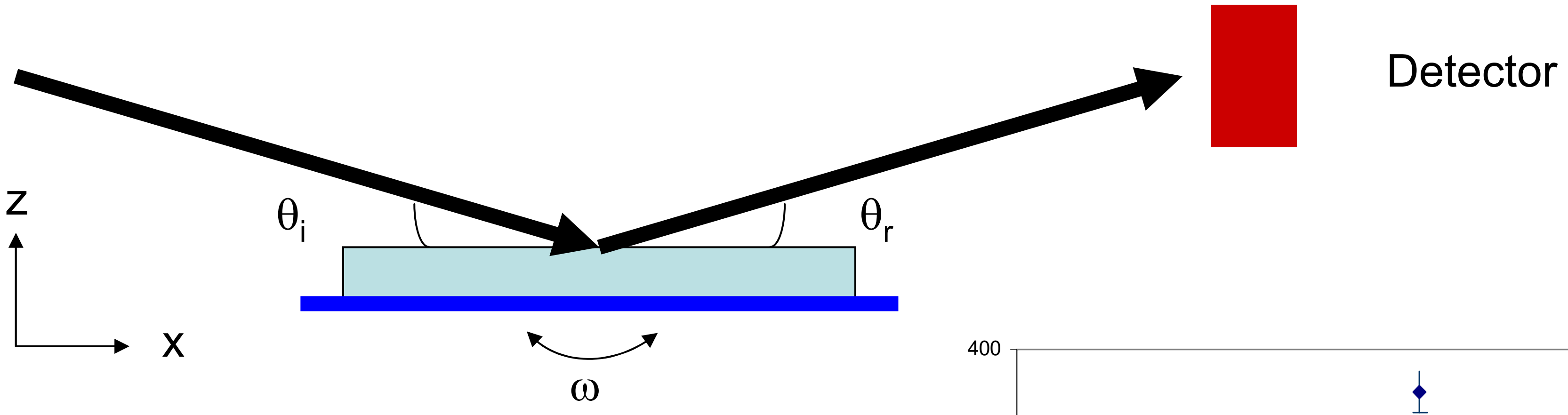
Scan ω

Look at intensity on detector

Identify ω = -0.22 (~190 cts) as approximate sample offset angle



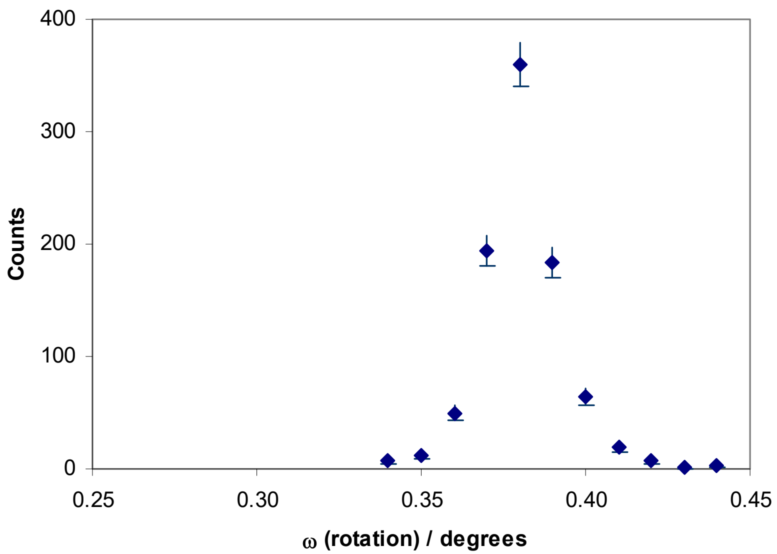
Aligning a Sample



Use approximate ω and z offset from alignment on direct beam

Set detector to small angle of reflection (e.g. 0.5°) and align more precisely.

Scan ω and look for peak. Position is 0.378° and so offset is -0.122°.



Aligning a Sample

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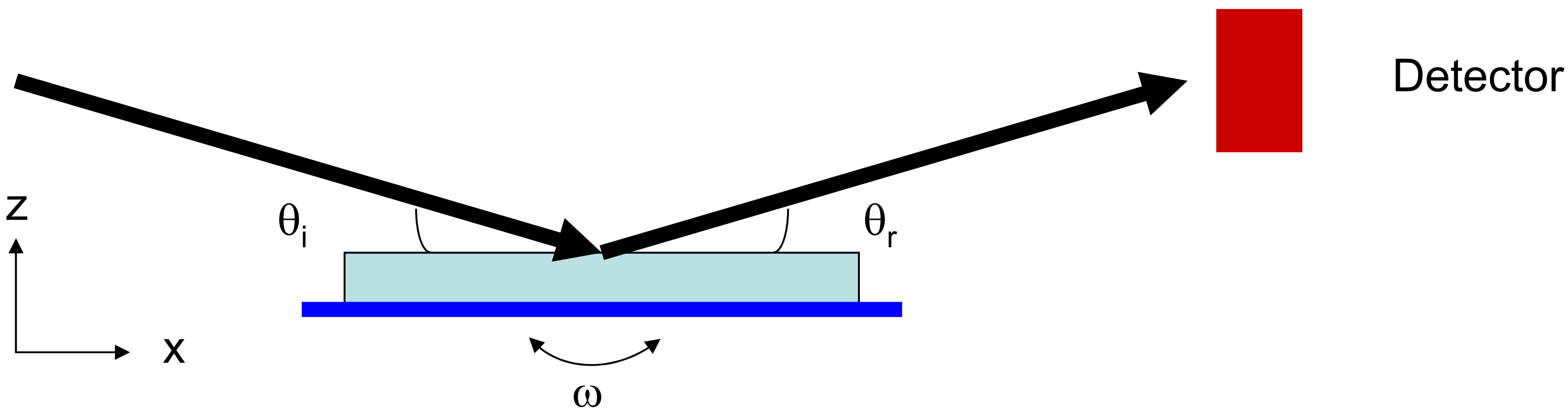
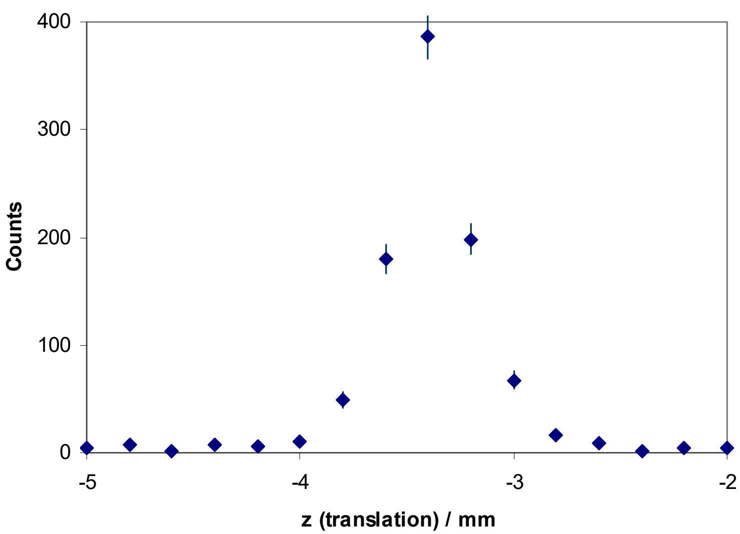


Use new ω offset and z offset from alignment on direct beam

Check translation (z) offset in reflection mode.

Scan z and look for peak. Position is -3.38 mm.



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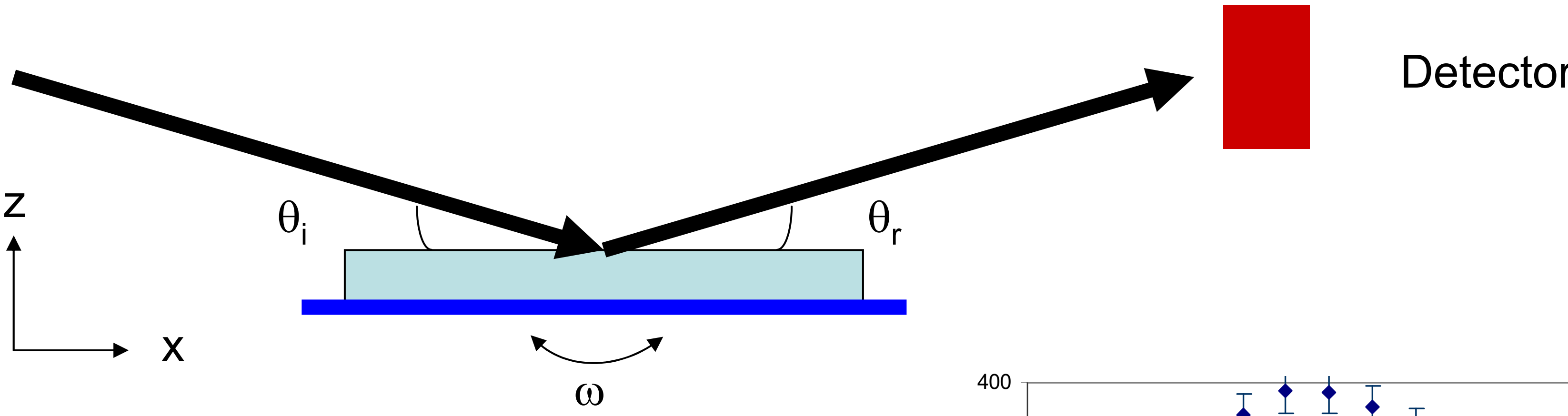
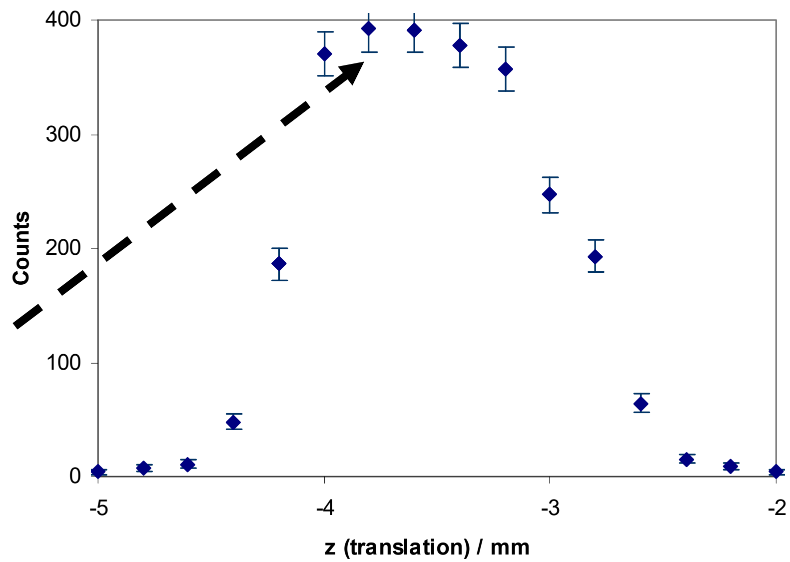
Comments on Alignment



Angular (ω) width can depend on flatness of sample as well as resolution from slits and wavelength spread

If sample is very under-illuminated, translation (z) scan will have a flat top



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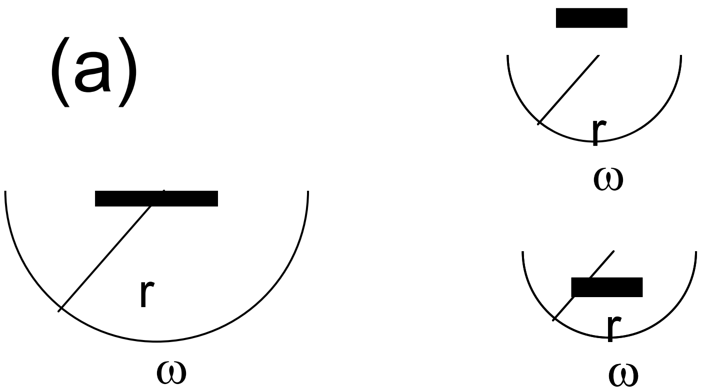
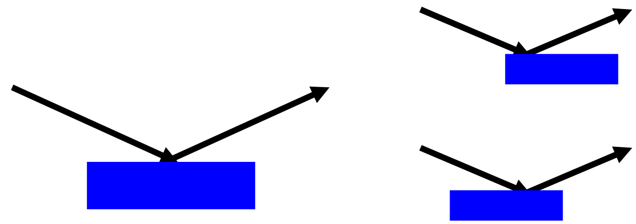
Summary - Mounting and Alignment

(a)



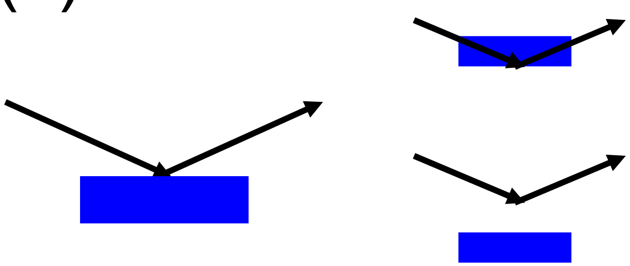
Eucentric mount

(b)



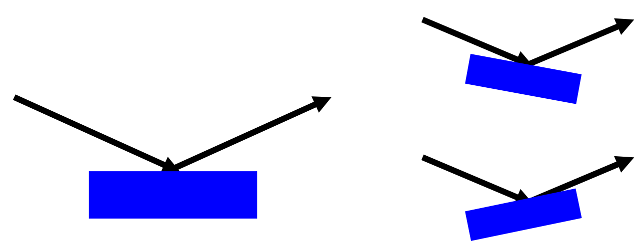
Centred on beam

(c)



z position correct

(d)



ω offset correct

Comments on Alignment

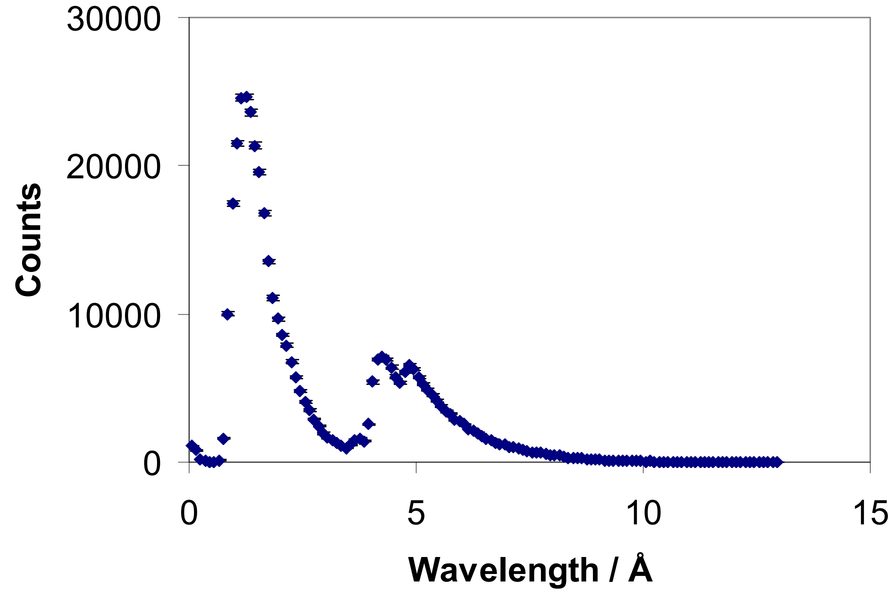
Using the results of alignment scans needs offsets or new zero positions to be set on the instrument. Warning: there is no general convention of signs on different instruments

Linear thermal expansion can be ~2 x 10^{-5} K^{-1}. 4 cm of aluminium changed by 50 C gives a shift of 0.04 mm.

Calibrations

Scan angle, measure different λ or a combination of λ and angle

Measure direct beam (through sample environment if needed)



Incident beam spectrum, LARMOR

Samples

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Low incident angle requires large uniform surface area. Footprint ~ s / tan θ.

Areas often several cm^2.

Smooth surface. 10 Å roughness will reduce the reflectivity at q=0.1 $Å^{-1}$ by 2.7. 15 Å reduces reflectivity by a factor of 10.

Liquids will have surface oscillations (capillary waves). Need to avoid other, induced waves.

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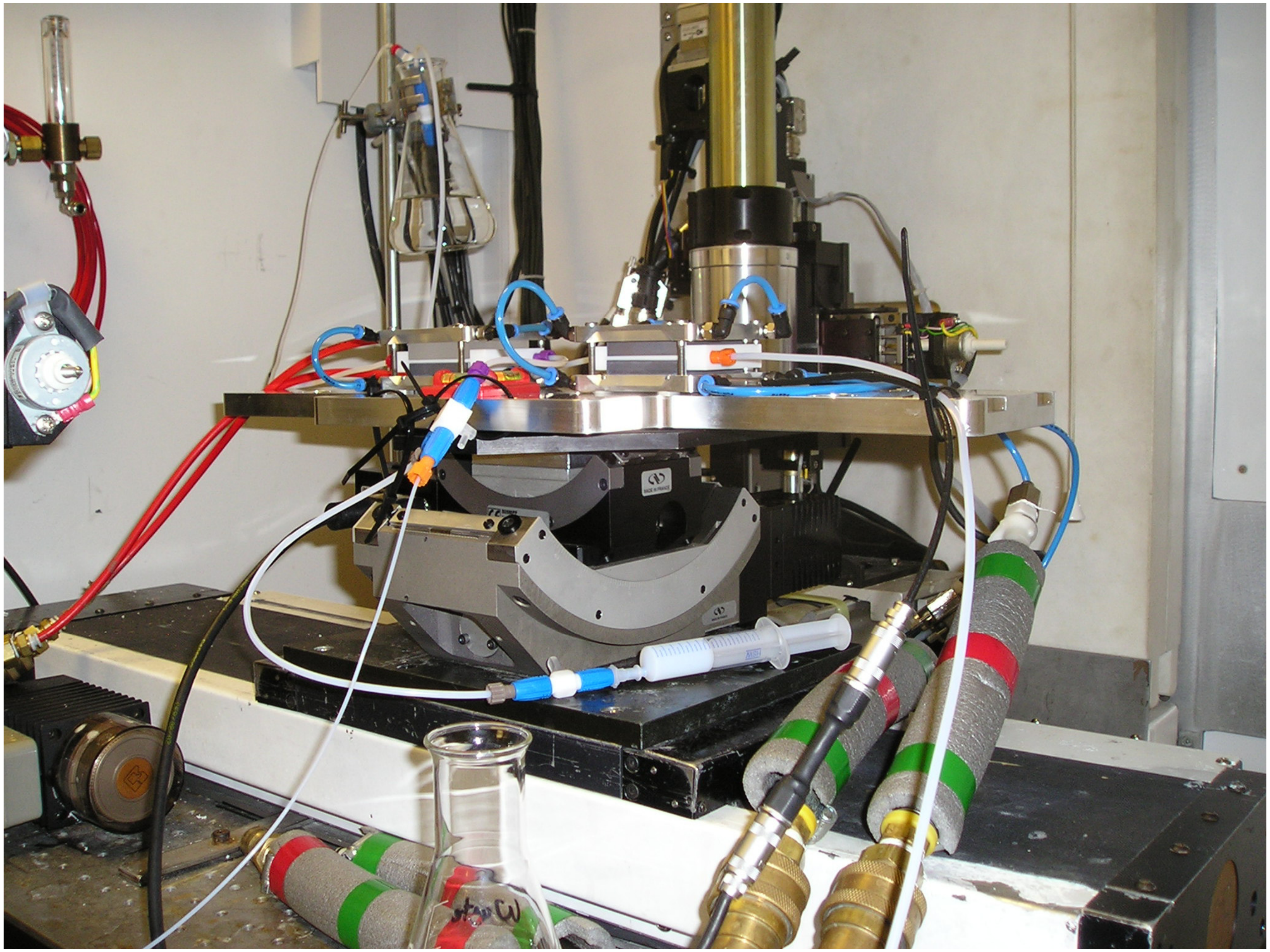
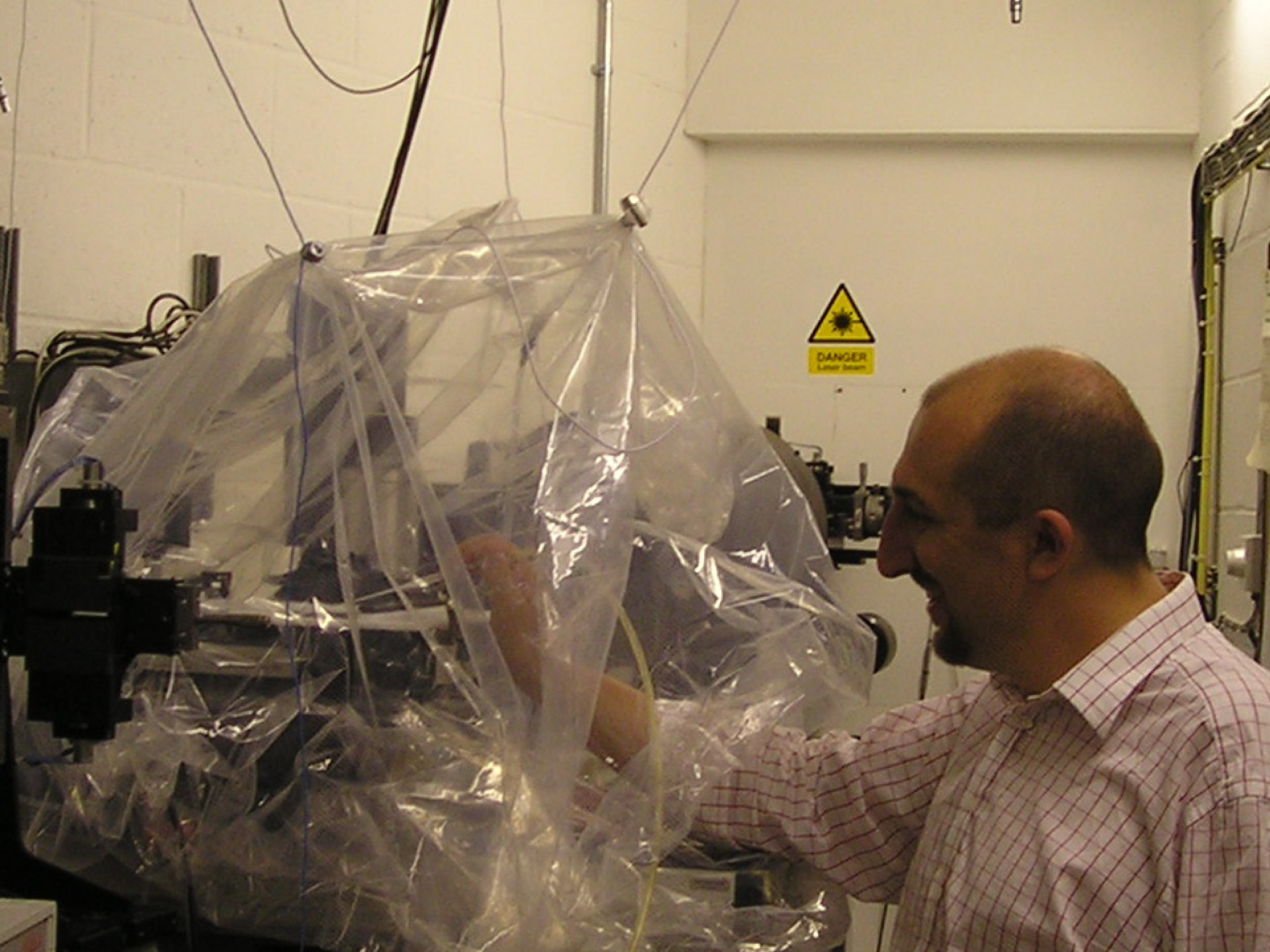
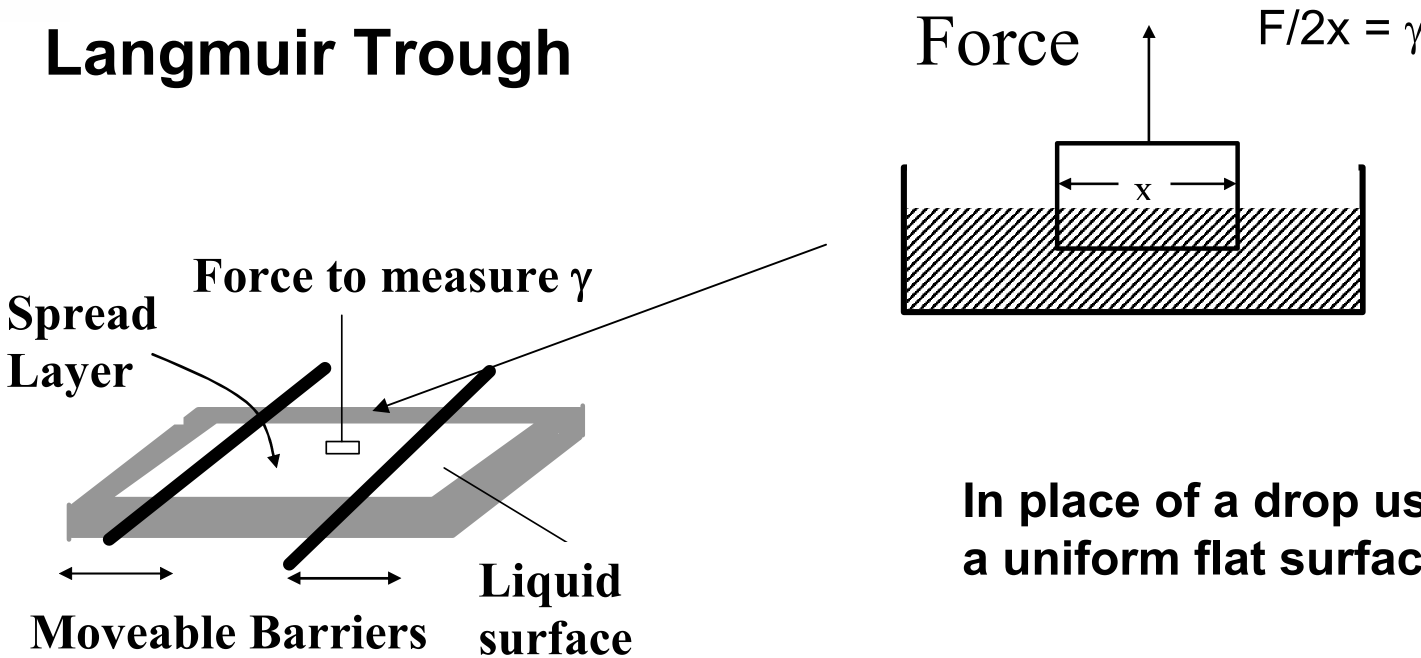
Sample Cell




DANGER
Laser beam

Chemistry on a Liquid Surface

Langmuir Trough



In place of a drop use, a uniform flat surface

What is measured?

Reflected signal may have a large background

For hydrogenous substrate ~ 5 x 10^{-6} incident beam

Attenuation by reduced transmission (caused by scattering or absorption) may be significant

Critical Angle and Below (critical wavelength and above)

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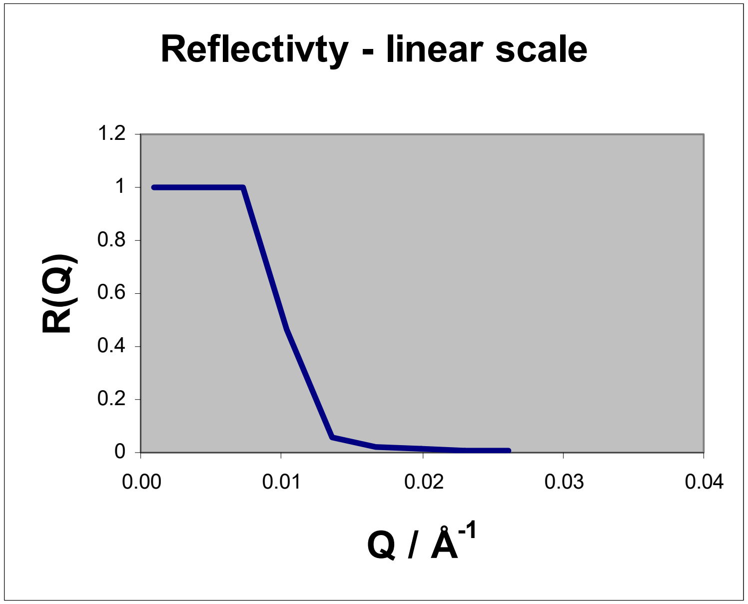
Density difference between two bulk phases determines the critical momentum transfer/angle, Q_c or θ_c

Any variation in intensity below critical angle is probably telling you about the experiment rather than the interface

$R = 1$ for $\theta < \theta_c$ is often used as a calibrant

Total reflection below critical angle θ

$\cos\theta = n_2/n_1$



Intensity of Reflected Signal

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- Waves interfere constructively for

$$2\, d \sin \theta = \lambda, 2\lambda, 3\lambda \ldots$$

- Measured reflectivity will depend on angle and wavelength. Add wave amplitudes with allowance for phase and calculate intensity as square of amplitude.
- Total reflection for angles less than critical angle, $\theta_c = \arccos(n_1/n_2)$

Fresnel Formula

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Reflection from an interface between two media with $\Delta\rho = \rho_1 - \rho_2$ is for $Q >> Q_c$:

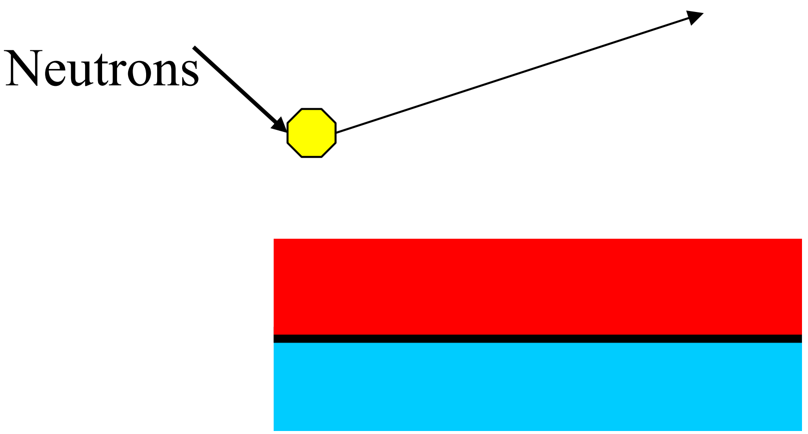
$$R(Q) = 16\,\pi^2\,(\Delta\rho)^2 / Q^4$$

Note

This does not depend on sign of $\Delta\rho$.

Fate of a Neutron at an Interface

- Reflected
- Scattered/Diffracted from surface
- Absorbed
- Scattered from bulk (either side of surface)
- Other accidents



What does background look like?

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X-ray scattering – glass

Sinha et al., *Phys. Rev. B.* **38**, 2297, 1988.

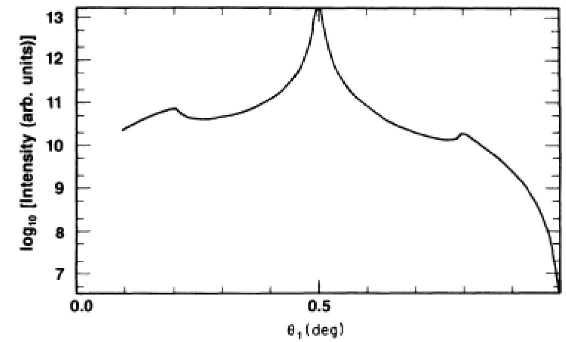
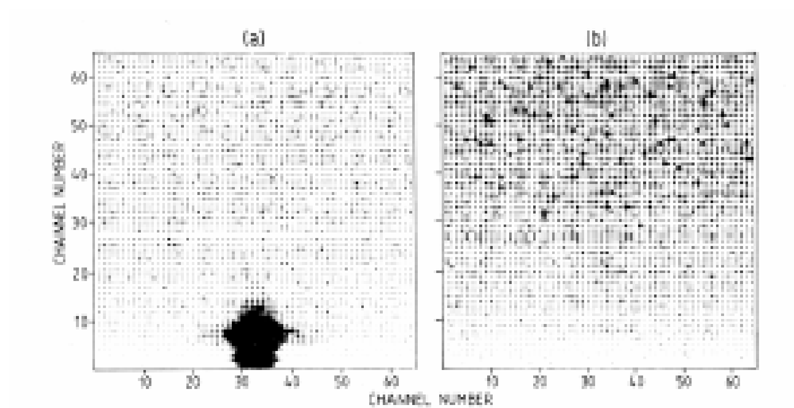


FIG. 6. Calculation of diffuse scattering in the distorted-wave Born approximation for rocking curve where θ_1 and θ_2 are varied such that 2θ is fixed at 1°. The asymmetry is due to the area of the illuminated surface decreasing as θ_1 is increased. The q_y direction has been integrated over. Parameters are $\sigma=7$ Å, $h=0.2$, $\xi=7000$ Å, and the optical constants for Pyrex are given in Sec. V.

Neutron scattering from D_2O and from null reflecting water

Rennie et al., *Macromolecules* **22**, 3466-3475 (1989).



Contrast Matching

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H_2O $\rho = -0.56 \times 10^{-6}$ Å^{-2}

D_2O $\rho = +6.35 \times 10^{-6}$ Å^{-2}

$y \times 6.35 + (1-y) \times (-0.56) = 0$

$6.91\ y = 0.56$ or $y = 0.56 / 6.91 = 0.081$

i.e. 8% by volume of D_2O in H_2O has $n = 1$

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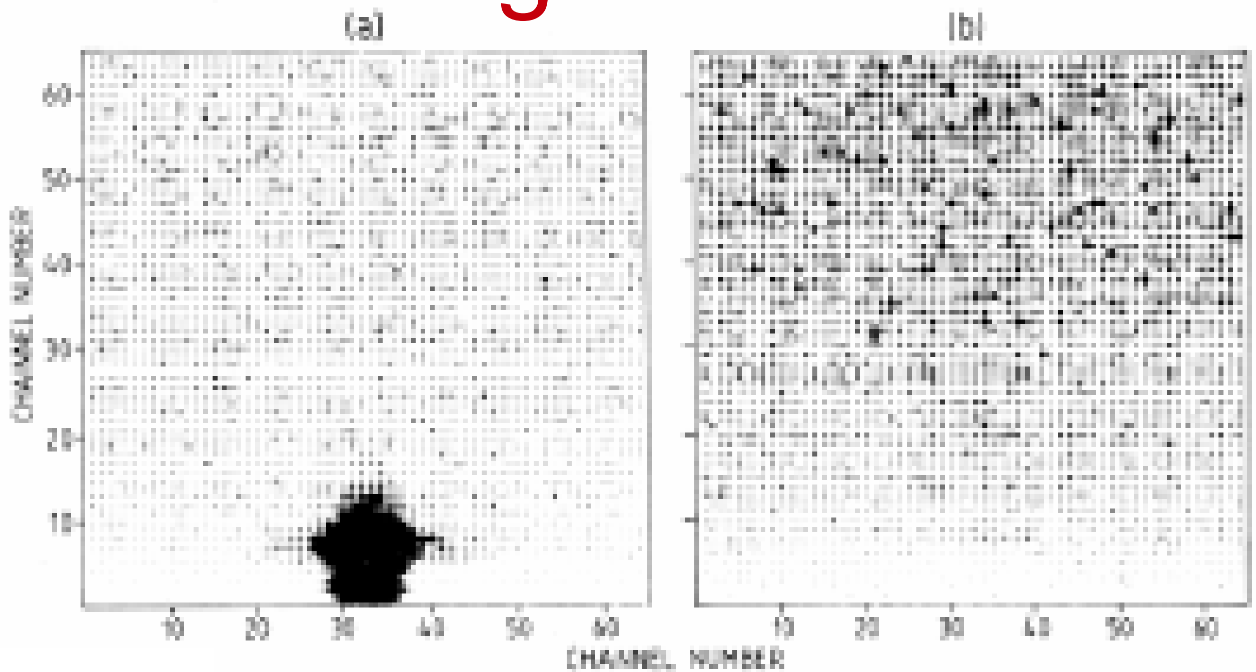
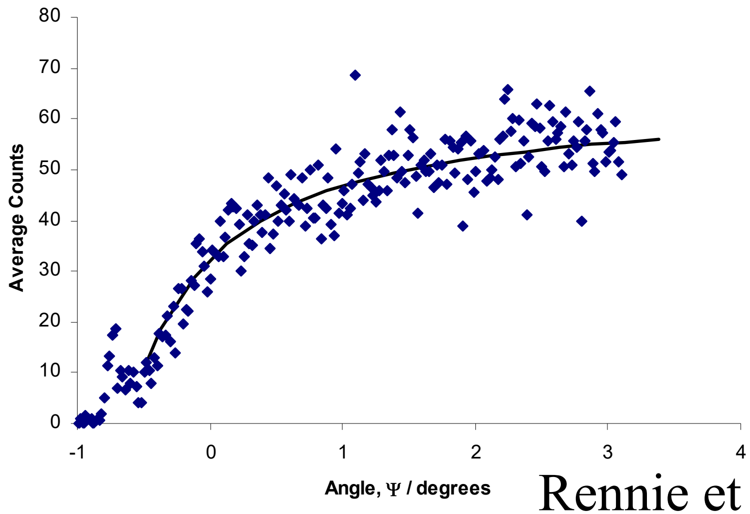
What does background look like?





Scattering from D_2O

and from null reflecting water

($8\%\ D_2O$)

Rennie et al., *Macromolecules* **22**, (1989), 3466-3475.

Comments on Calculations

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Programs that lose data

It is common to use logaritmic scales but background subtraction can give negative data points. $R\ Q^4$ is useful.

Experimental issues

Resolution – often needs to be included

Illumination

Small samples are often not able to reflect all the beam and a geometrical correction is applied.

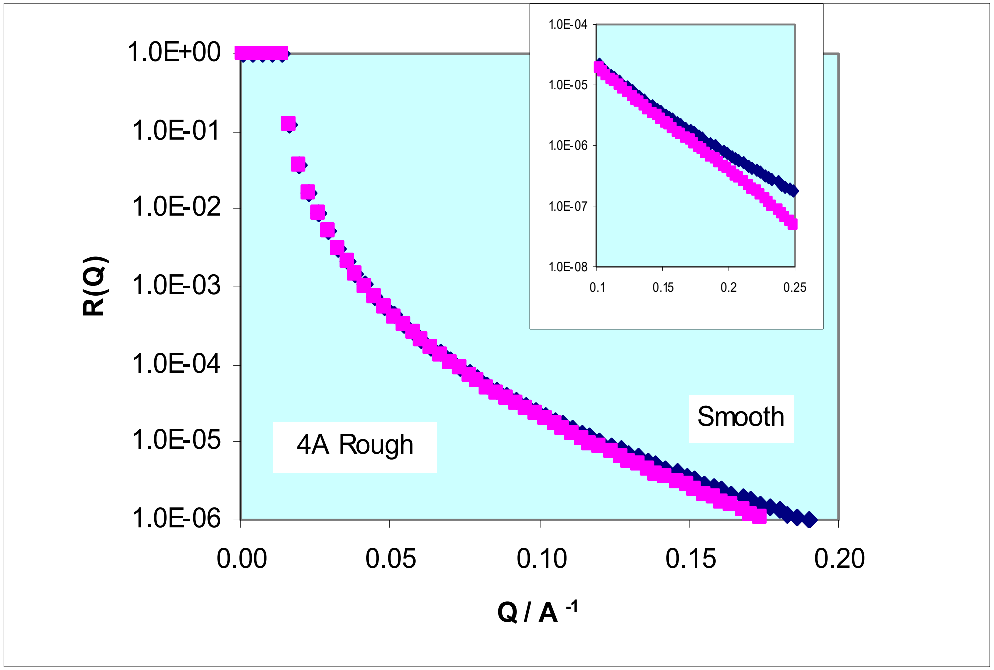
Absolute reflectivity

Data is constrained if it is on an an absolute scale

Roughness

Reflectivity from rough surfaces is decreased.

'Gaussian' roughness' – intensity decreases by $\exp(-Q^2\xi^2/2)$ for scattering vector, Q and amplitude of roughness, ξ.



L. Nevot, P. Crocé *J. Phys. Appl.* **15**, T61 (1980)

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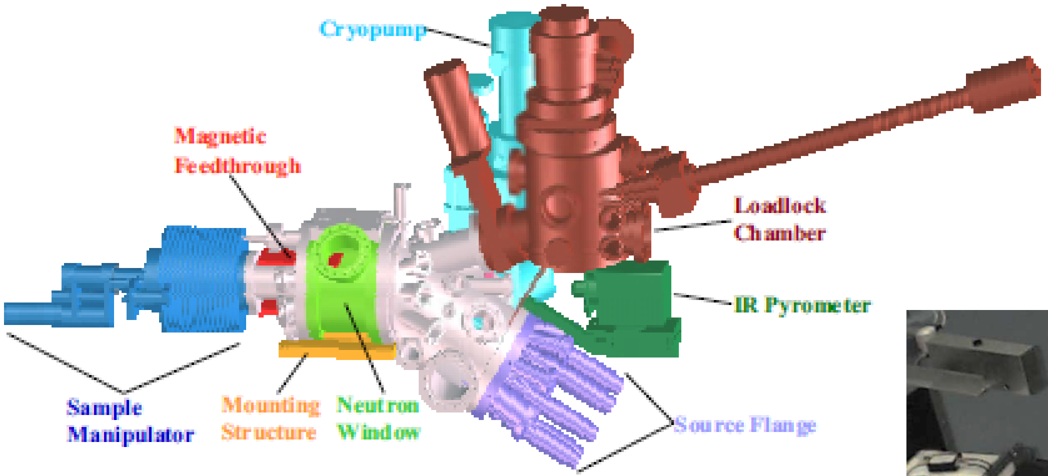
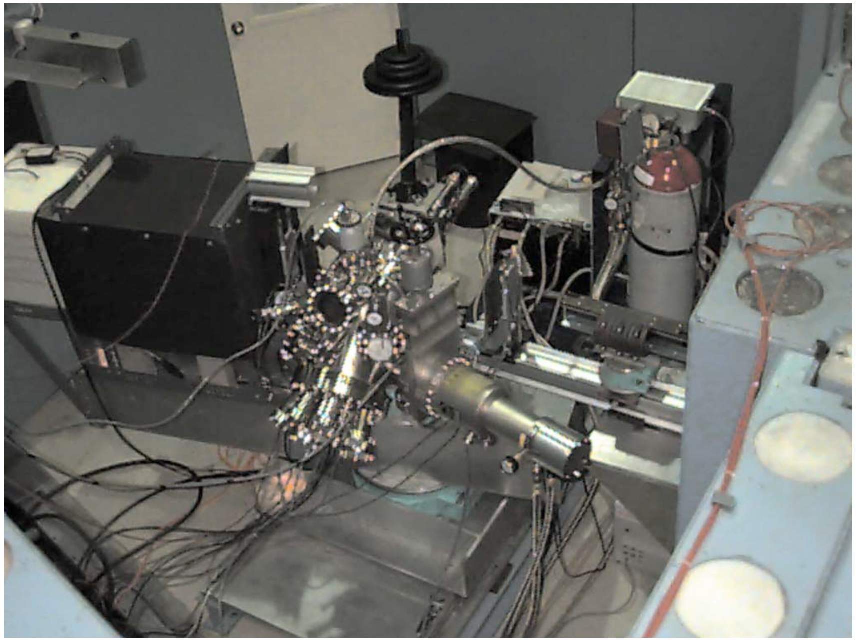
Do’s and Don’ts

- Do not bend samples – care with mounts
- Use anti-vibration mounts for liquids – air borne noise causes vibrations
- Capillary waves cause scattering

Thin Film Growth



J. A. Dura, J. LaRock 'A molecular beam epitaxy facility for in situ neutron scattering' *Rev. Sci. Instrum*. **80**, (2009), 073906.



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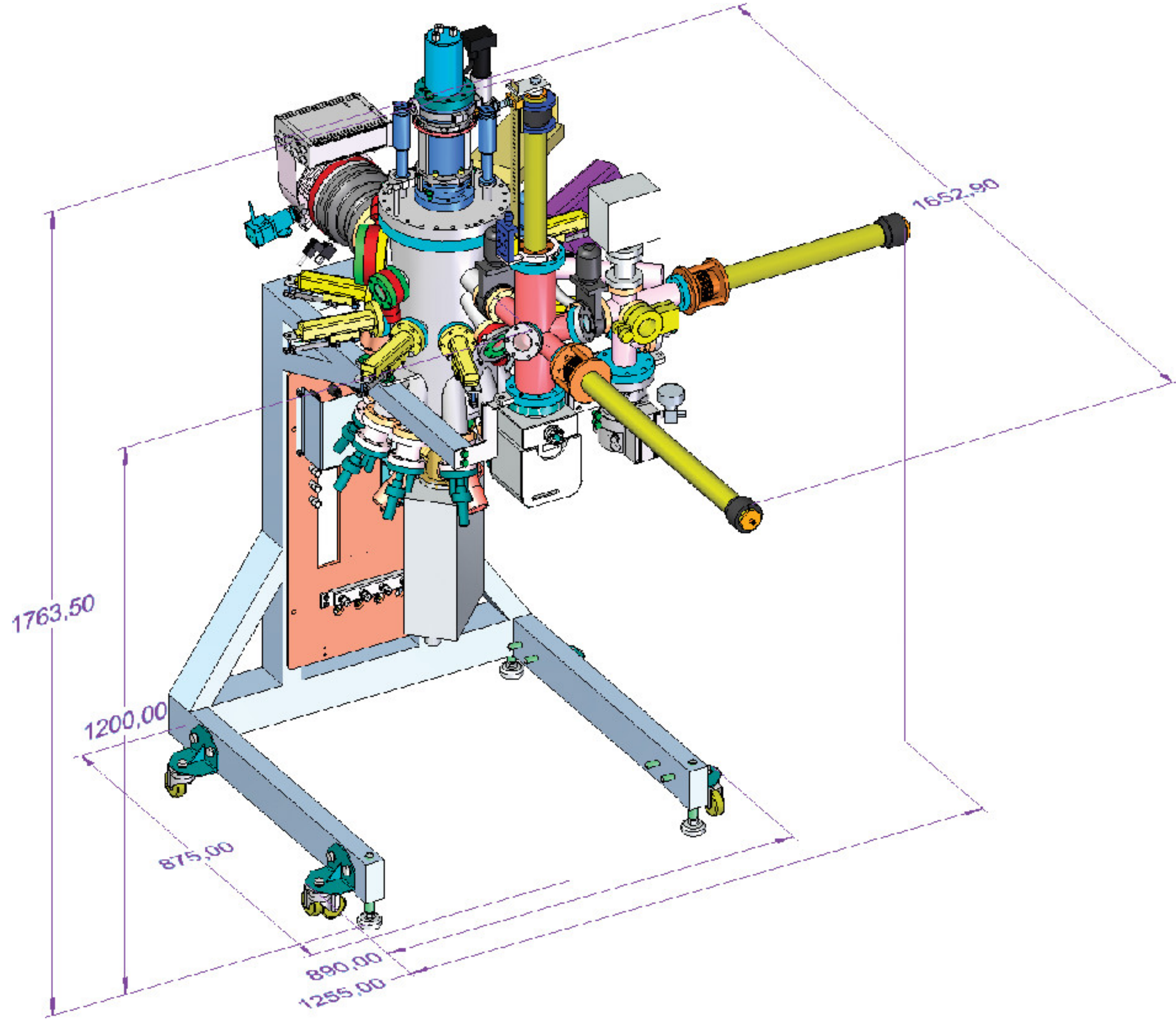
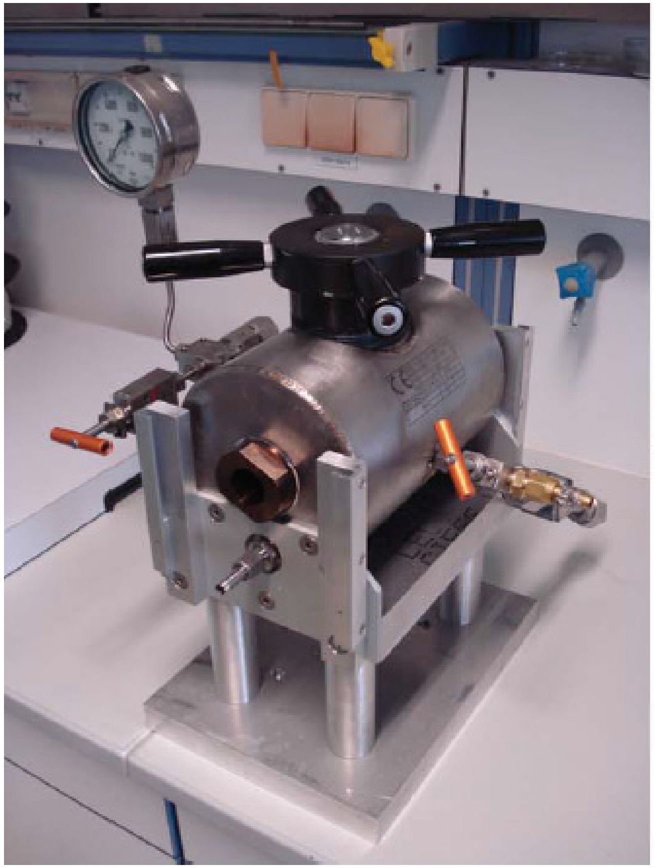
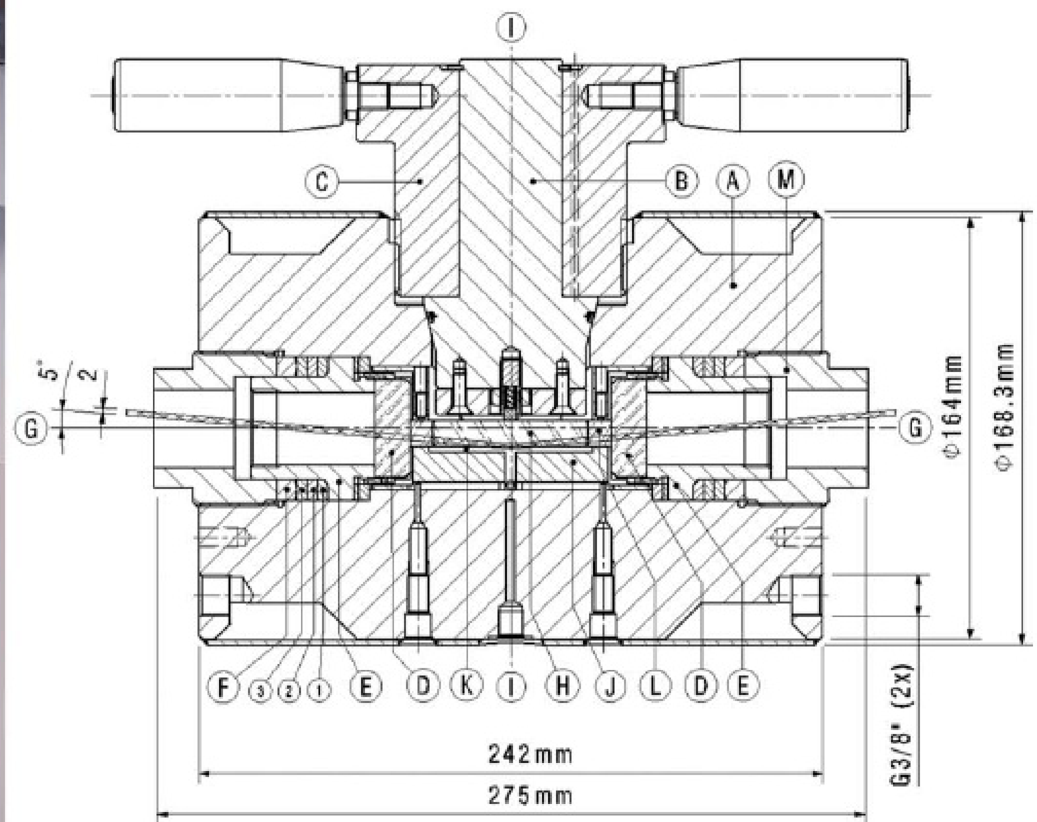


A. A. Baker, W. Braun, G. Gassler, S. Rembold, A. Fischer, T. Hesjedal 'An ultra-compact, high-throughput molecular beam epitaxy growth system' *Review of Scientific Instruments* **86**, (2015), 043901.

High Pressure

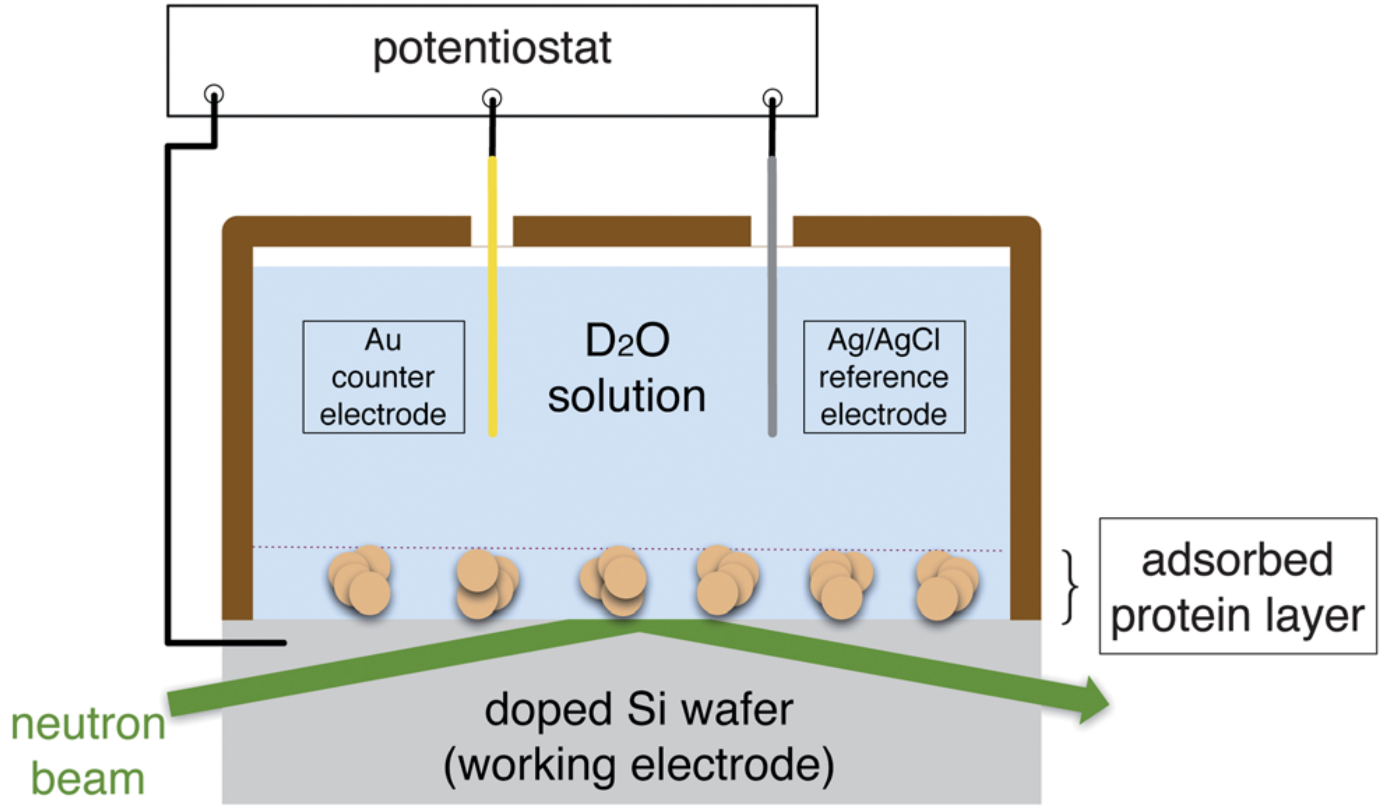
U





Martin Kreuzer, Thomas Kaltofen, Roland Steitz, Beat H. Zehnder, Reiner Dahint ‘Pressure cell for investigations of solid–liquid interfaces by neutron reflectivity’ *Rev. Sci. Instrum*. **82**, (2011), 023902.

Electric Potential and Electric Currents



Alexandros Koutsioubas, Didier Lairez, Gilbert Zalczer, Fabrice Cousin 'Slow and remanent electric polarization of adsorbed BSA layer evidenced by neutron reflection' *Soft Matter*, **8**, (2012), 2638-2643.

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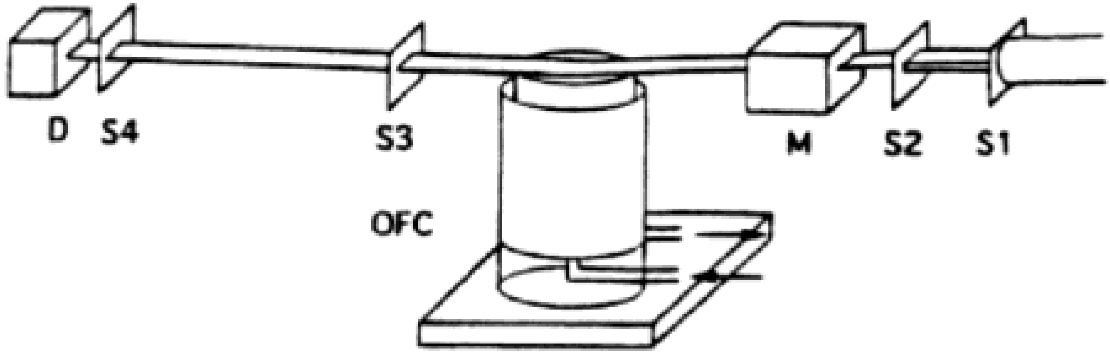
Continuously Generated Fresh Liquid Surface



Julian Eastoe, Alex Rankin, Ray Wat, Colin D. Bain, Dmitrii Styrkas, Jeff Penfold 'Dynamic Surface Excesses of Fluorocarbon Surfactants' *Langmuir*, **19**, (2003), 7734-7739.

Battery Electrodes

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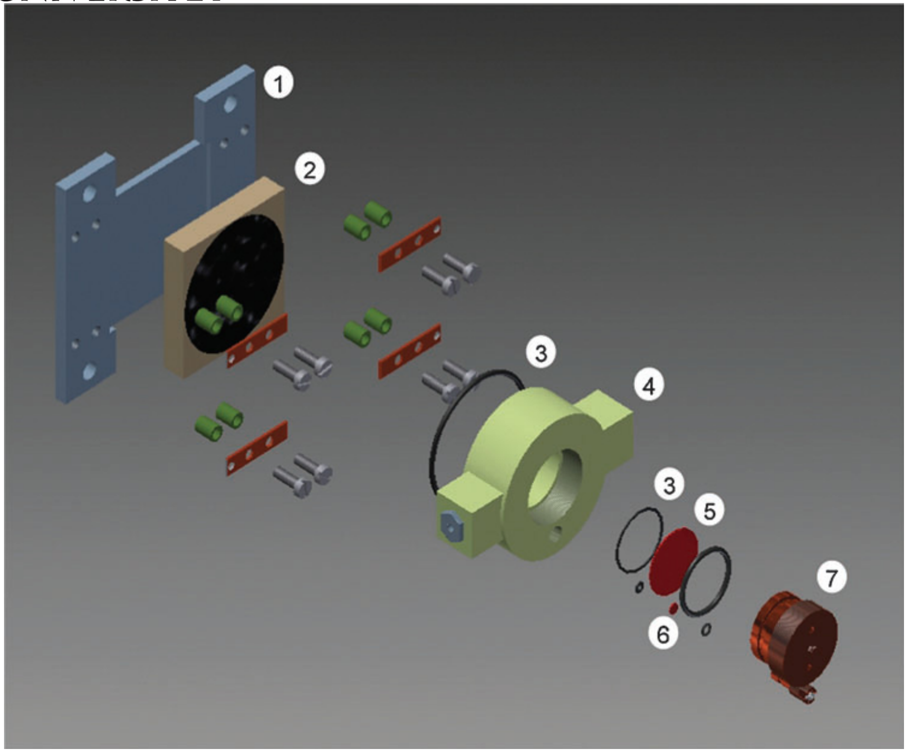

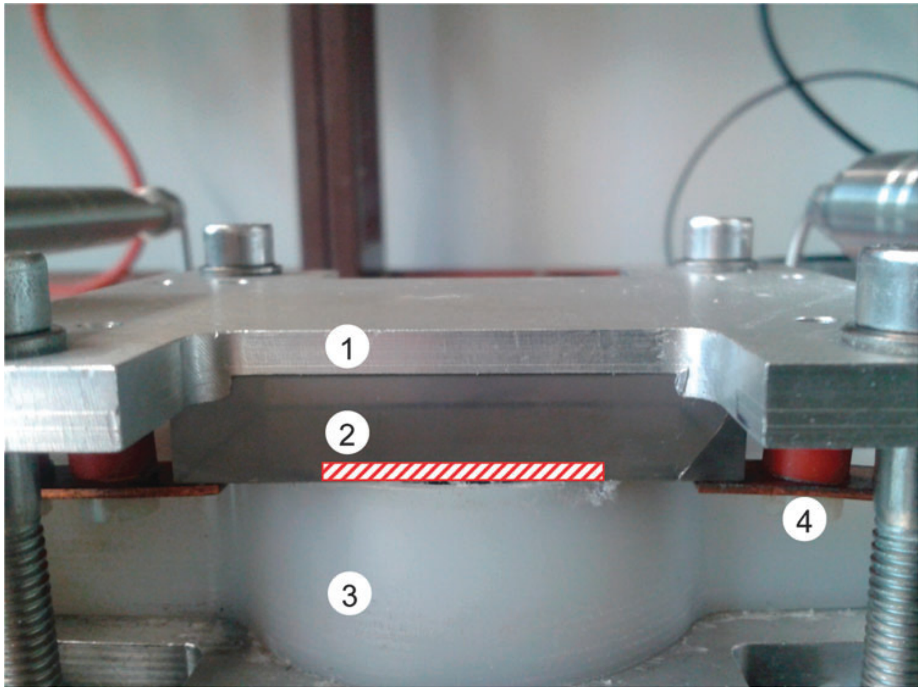

B. Jerliu, L. Dörrer, E. Hüger, G. Borchardt, R. Steitz, U. Geckle, V. Oberst, M. Bruns, O. Schneider, H. Schmidt 'Neutron reflectometry studies on the lithiation of amorphous silicon electrodes in lithium-ion batteries' *Phys. Chem. Chem. Phys.*, **15**, (2013), 7777-7784.

Liquid / Liquid Interfaces

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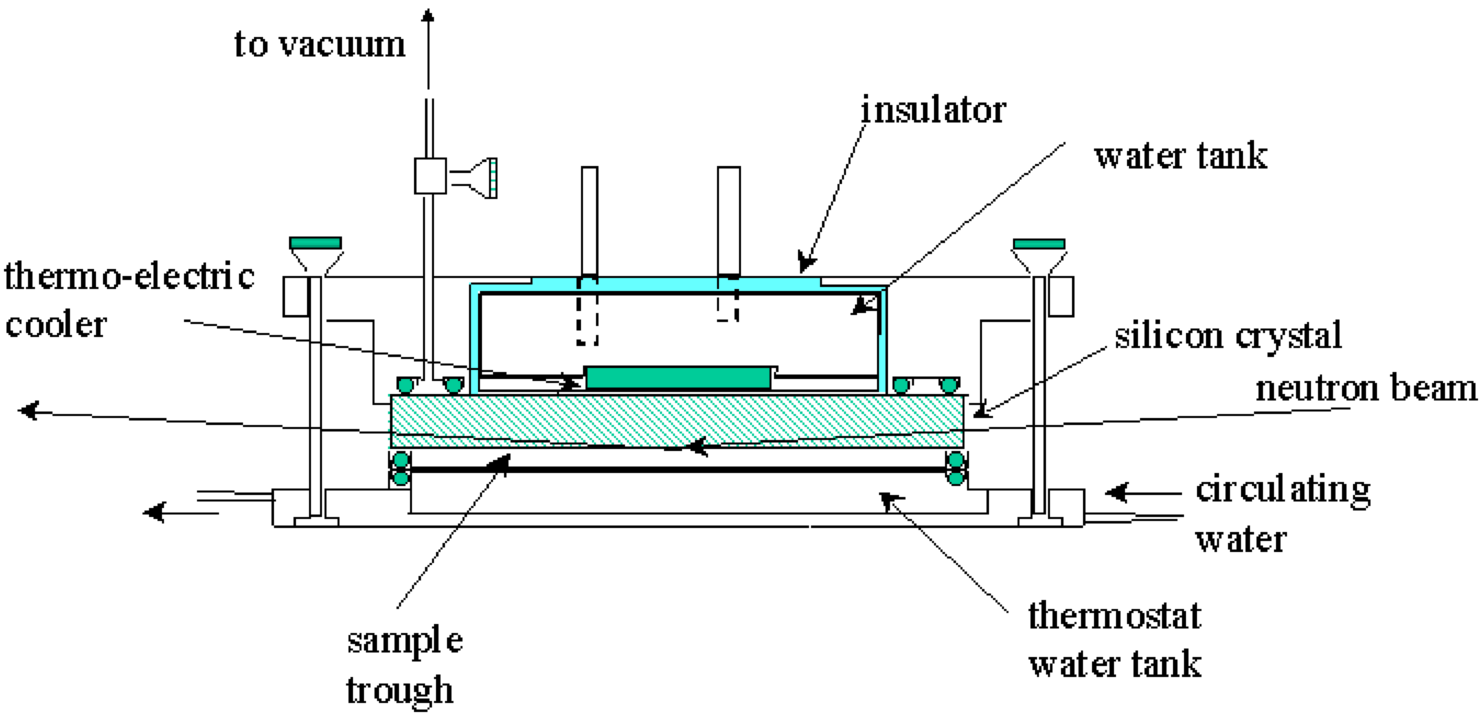

A. Zarbakhsh, J. Bowers, J. R. P. Webster, 'A new approach for measuring neutron reflection from a liquid/liquid interface' *Meas. Sci. Technol*. **10**, (1999), 738-743.

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What has not (yet) been covered?

Ellipsometry and X-rays

Needs more calculations for *s* and *p* waves

How to write a minimisation routine?

How to install your favourite program?

Specific examples of real samples etc.