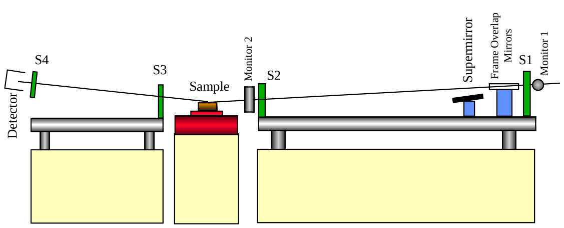
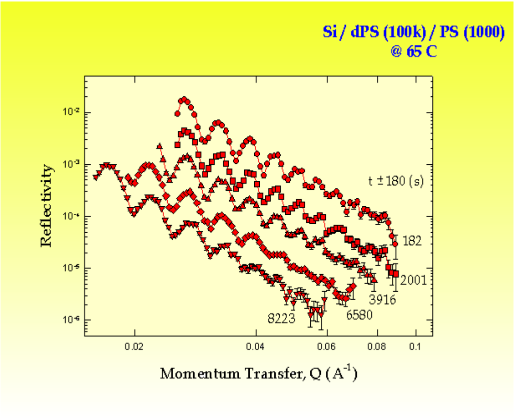
ISIS Neutron Scattering Training Course : Large Scale Structures Module : May 2010

Introduction to Neutron Reflectivity

J.R.P.Webster

ISIS Facility, Rutherford Appleton Laboratory





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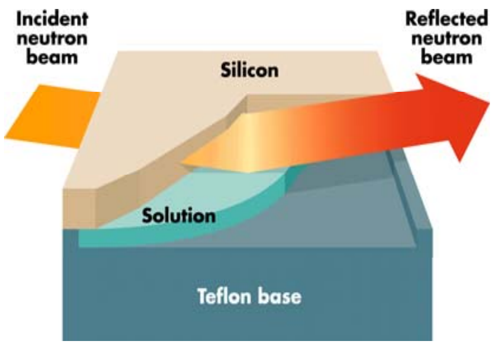
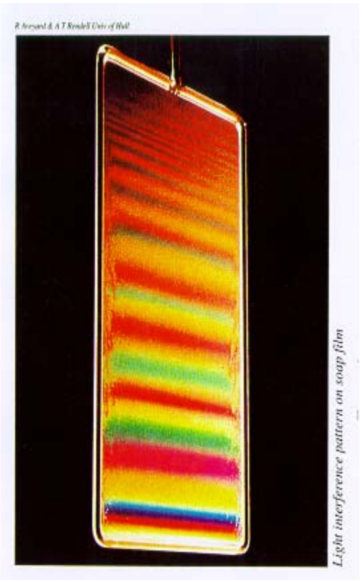
Specular reflection of neutrons from surfaces and interfaces

Analagous to optical interference, ellipsometry



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



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

(Penfold, Thomas, J Phys Condens Matt, 2 (1990)1369,
T P Russell, Mat Sci Rep 5 (1990) 171)

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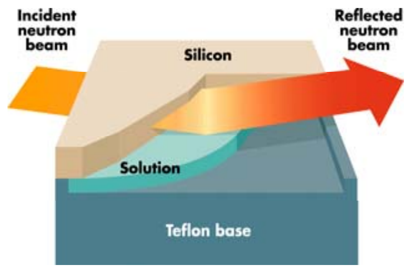
Reflectometry

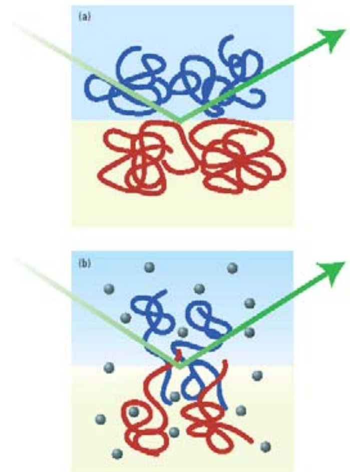
Kinetics

- Polymer Diffusion
- Critical exponents in SCF
- Protein unfolding
- Non equilibrium surfactant films
- Temporal resolution of
  - Ion transfers
  - Solvent transfers
  - Polymer structure



Model Devices

- Thin polymer films (finite size effects)
- Spin coating

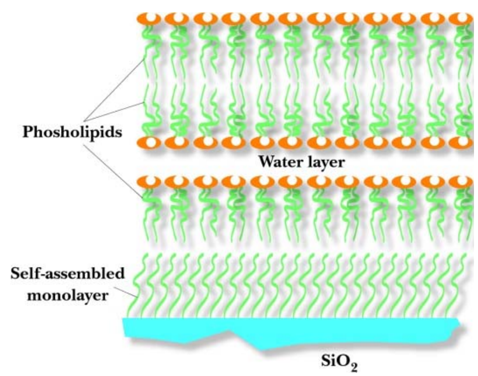


Surfactants

- Parametric Studies
- Liquid/Liquid Interface
- Reduce Label size in Structural Studies
- Self Assembly
- Foams

Electrochemistry

- Electrodeposition and Surface nucleation
- Self Assembly of systems
  - Metal Hydroxide electroprecipitation (batteries)
  - Novel templating mechanisms



Biology

•Protein adsorption

•Biocompatible polymers

•Drug transport

•Anaesthesia mechanisms

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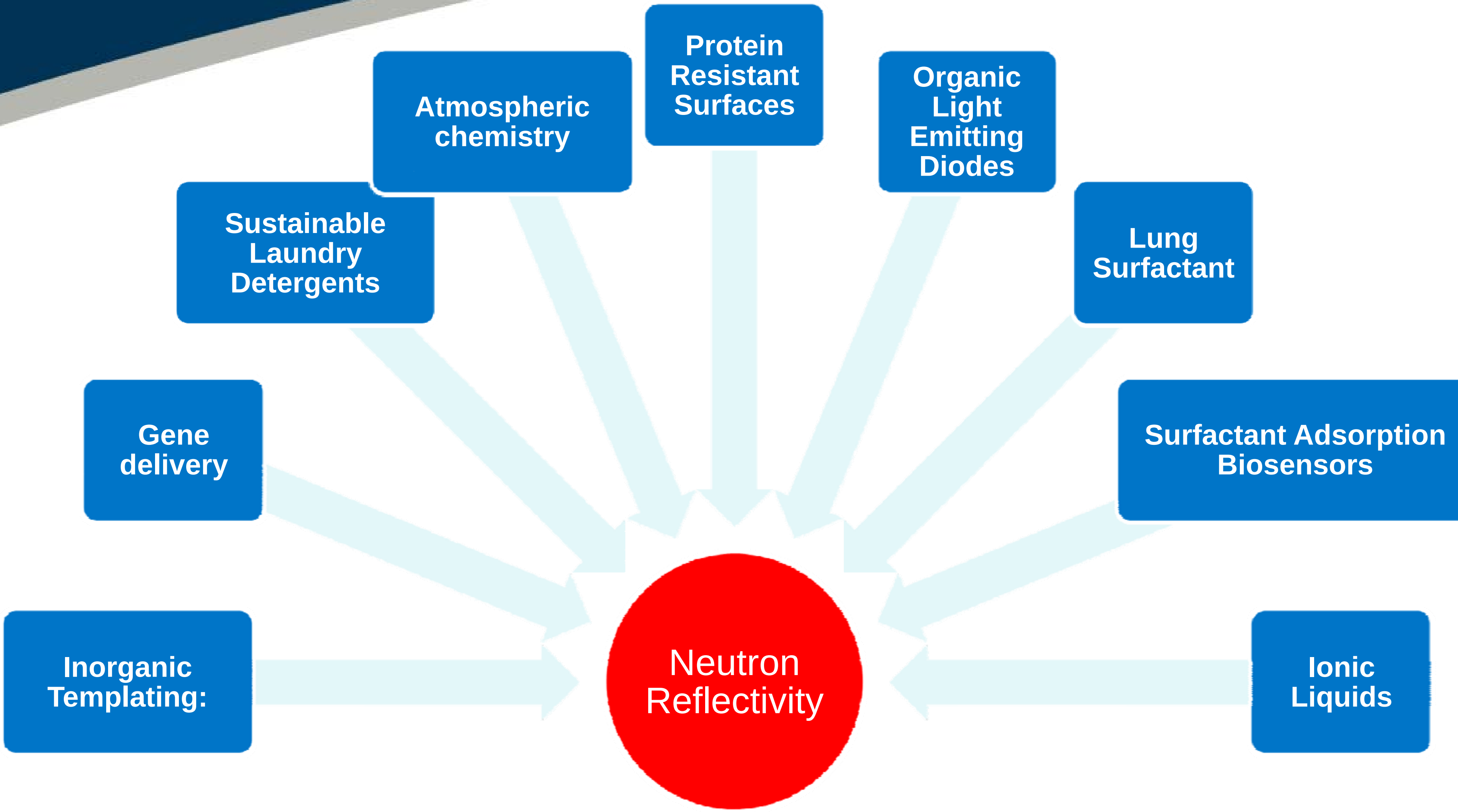
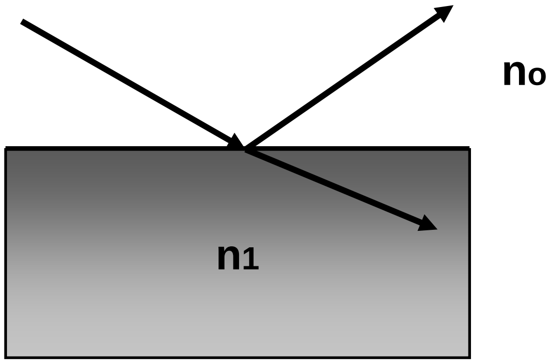


Specular reflection of neutrons



Refractive index defined using the usual convention in optics:

$$n = k_1 / k_0$$

$$n = 1 - \lambda^2 A - i \lambda B$$

$$A = Nb / 2\pi$$

$$B = N(\sigma_a + \sigma_i) / 4\pi$$

X-rays

$$n = 1 - \alpha - i\beta$$

$$\alpha = N\lambda^2 Z\, re / 2\pi$$

$$\beta = \lambda \mu / 4\pi$$

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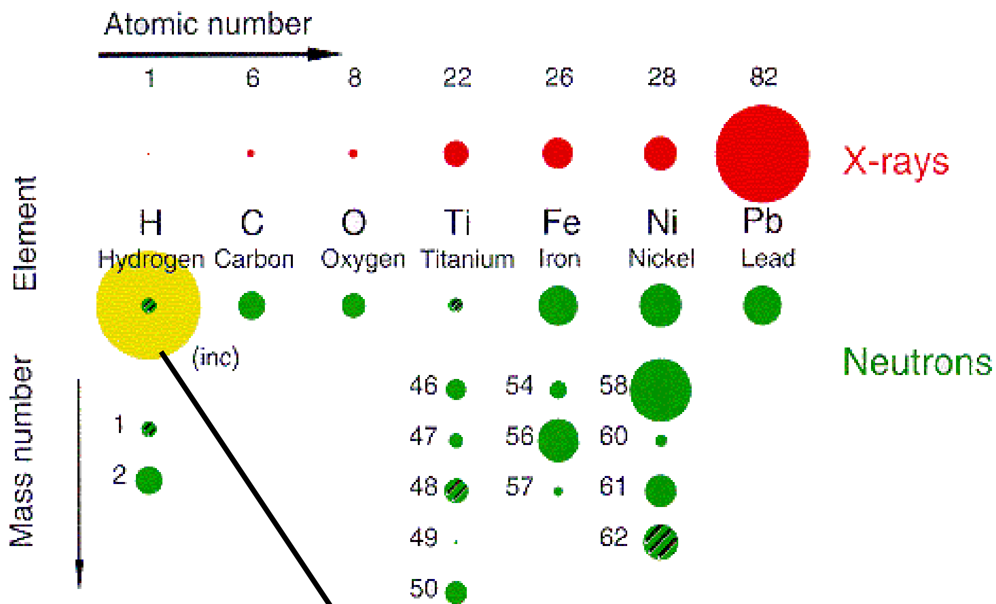
Refractive Index for neutrons



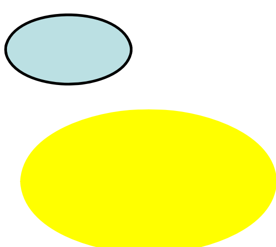
The diameters of the circles shown scale with the scattering amplitude f_x (sinΘ= 0) for x-rays, and b_{coh} * 10 for neutrons. Hatching indicates negative scattering amplitudes.

$$n = k_1 / k_0$$

$$n = 1 - \lambda^2 A - i\lambda B$$

$$A = N b / 2\pi$$

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

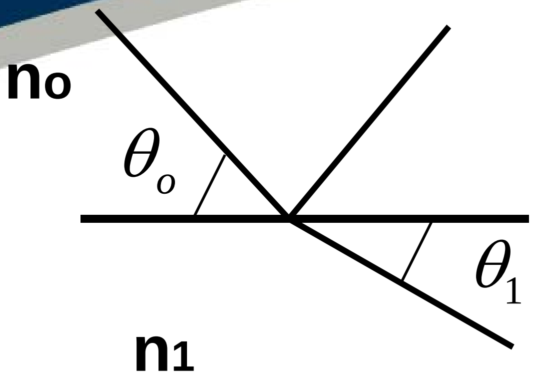


H -0.374 x 10-12 cm

D 0.667 x 10-12

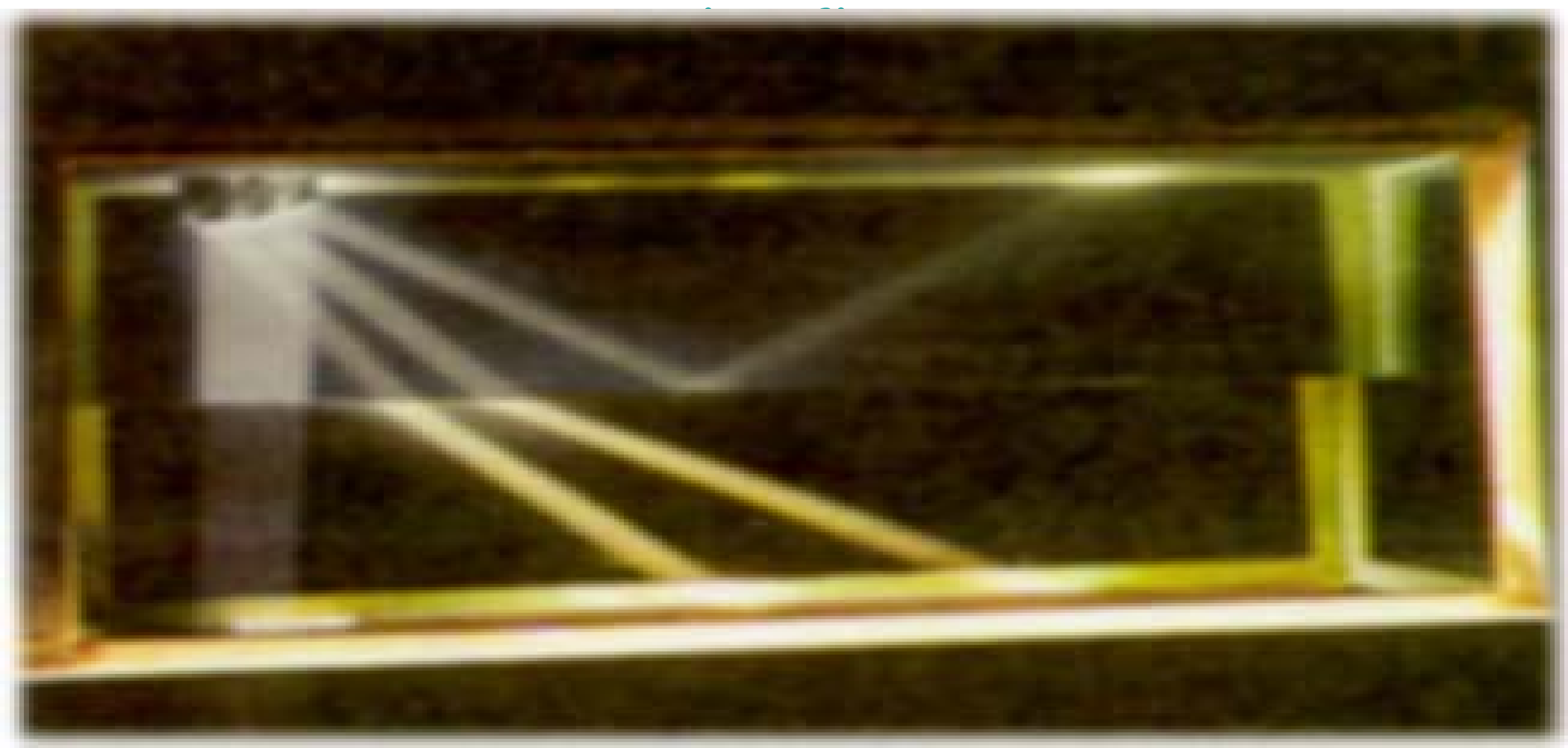
n < 1.0 hence **TOTAL EXTERNAL REFLECTION**

Specular reflection of neutrons
(some basic optics)

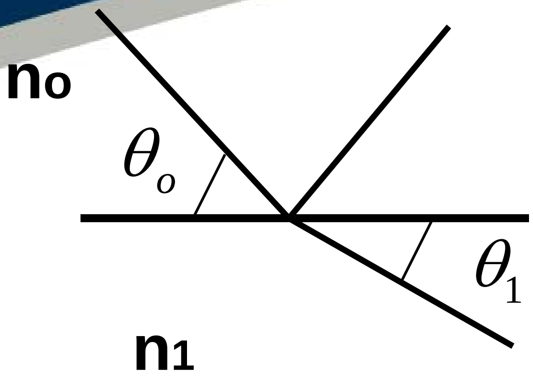


From Snell's Law, $$n = \frac{n_1}{n_0} = \frac{\cos\theta_0}{\cos\theta_1}$$

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



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 $\theta_0 = \theta_c$

$\theta_1 = 0.0$ $\qquad \cos\theta_1 = 1.0$

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

Critical angle

$$\cos\theta_c = 1 - Nb\frac{\lambda^2}{2\pi}$$

$$\theta_c = \lambda\sqrt{\frac{Nb}{\pi}}$$

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

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

$$n_1 \sin\theta_1 = \left(n_1^2 - n_0^2 \cos\theta_0^2\right)^{1/2}$$

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

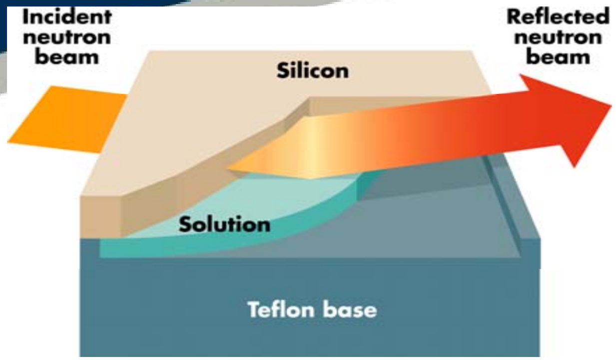
$\theta > \theta_c$ $n_1 \sin\theta_1$ Is real, and zero at $\theta = \theta_c$

Some typical values for θ_c and σ_a

Material	θ_c (deg / Å)
Ni	0.1
Si	0.047
Cu	0.083
Al	0.047
D_2O	0.082

Material	σ_a(barns)
Si	0.17
Cu	3.78
Co	37.2
Cd	2520
Gd	29400

Specular Neutron Reflection (simple interface)

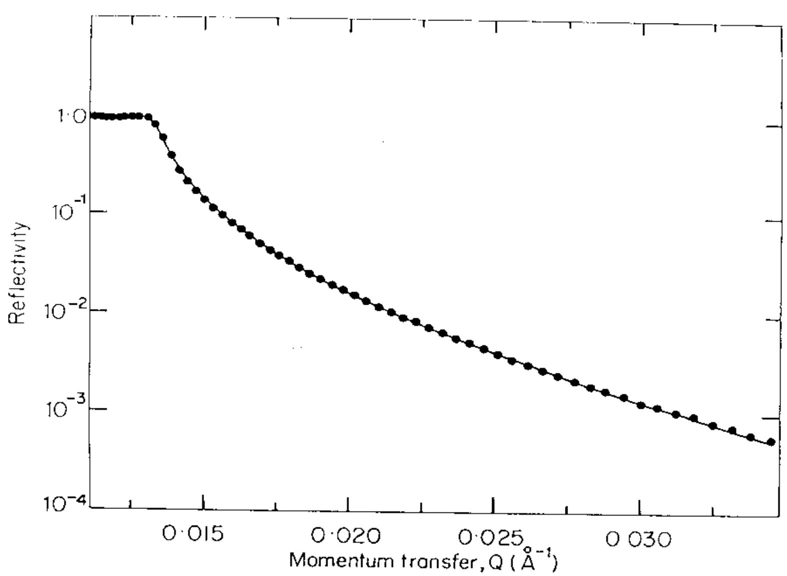


Within **Born Approximation** the Reflectivity is given as,

$$R(Q) = \frac{16\pi^2}{Q^4} \left| \int \rho'(z) e^{-iQz} dz \right|^2$$

$$Q = k_1 - k_2 = 4\pi \sin\theta / \lambda$$

Reflectivity from a simple single interface is then given by **Fresnels Law**



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

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

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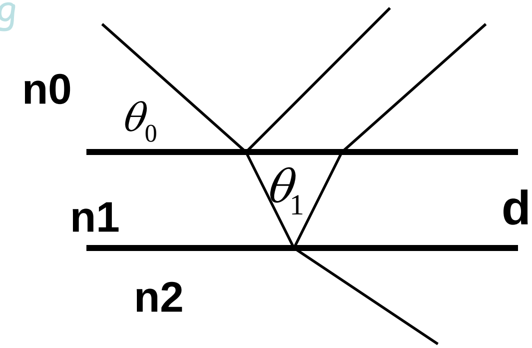
Specular Neutron Reflection

For thin films see interference effects that can be described using standard thin film optical methods



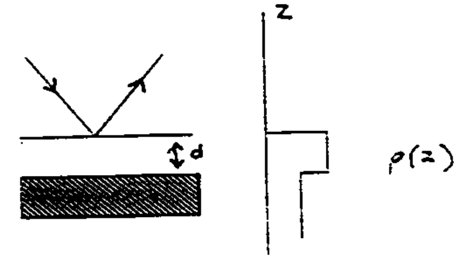
For a single thin film at an interface

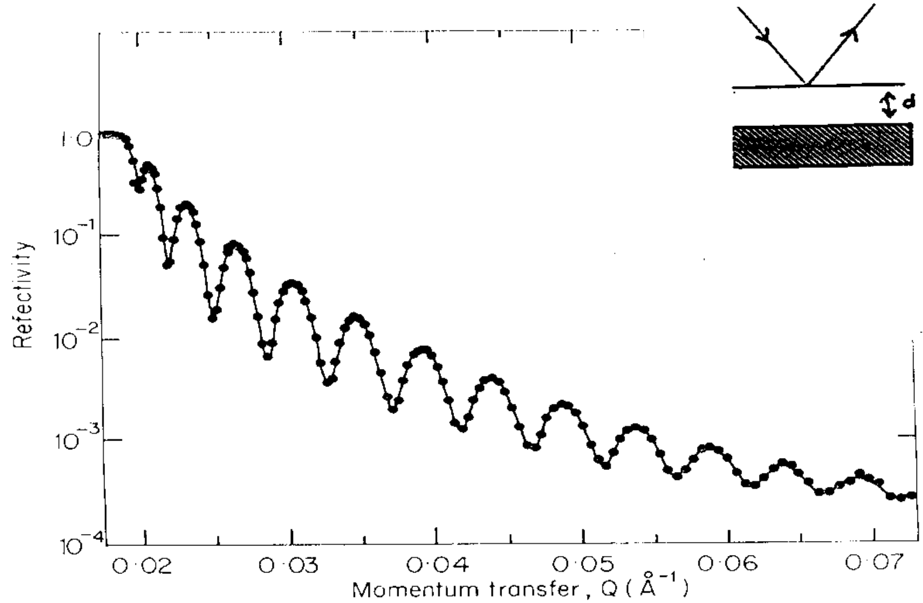
$$R(Q) = \left| \frac{r_{01} + r_{12} e^{-2i\beta}}{1 + r_{01} r_{12} e^{-2i\beta}} \right|^2$$

$$r_{ij} = \frac{(p_i - p_j)}{(p_i + p_j)}$$

$$p_i = n_i \sin \vartheta$$

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





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For a single thin film :

$$R(Q)=\frac{r_{01}^2+r_{12}^2+2r_{01}r_{12}\cos 2n_1k_1d_1}{1+r_{01}^2r_{12}^2+2r_{01}r_{12}\cos 2n_1k_1d_1}$$

For Q>>Q_c :

$$R(Q)\sim\frac{16\pi^2}{Q^4}\left[(\rho_1-\rho_0)^2+(\rho_2-\rho_1)^2+2(\rho_1-\rho_0)(\rho_2-\rho_1)\cos(Qd)\right]$$

Fourier transform of 2 delta functions (young's slits)

FRINGE SPACING :

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

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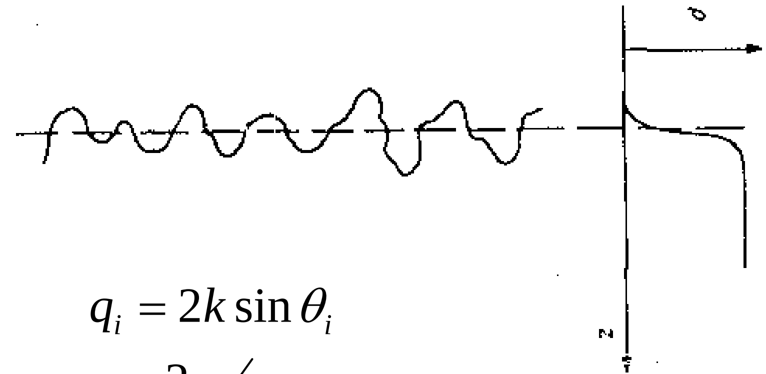
Rough or Diffuse Interface



For a simple interface reflectivity modified by,

$$R = R_0 \exp\left(-q_0 q_1 \sigma^2\right)$$

$$q_i = 2k \sin\theta_i$$

$$k = 2\pi/\lambda$$

σ **is rms Gaussian roughness**

Gaussian factor (like Debye-Waller factor) results in larger that q^{-4} dependence in the reflectivity.

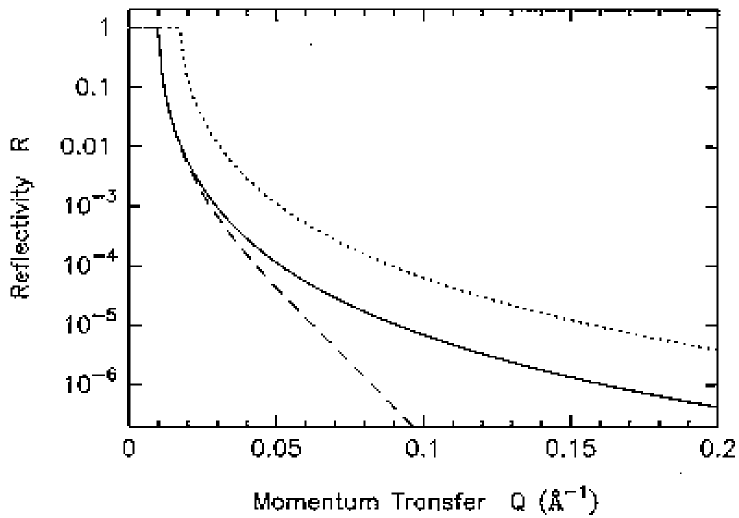
(Nevot, Croce, Rev Phys Appl 15 (1980) 125, Sinha, Sirota, Garoff, Stanley, Phys Rev B 38 (1988) 2297)

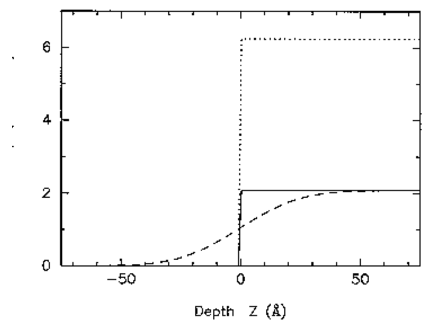
Can be also applied to reflection coefficents in formulism for thin films,

$$r_{ij} = \frac{\left(p_i - p_j\right)}{\left(p_i - p_j\right)} \exp\left(-0.5\left(q_i q_j \sigma^2\right)\right)$$

From specular reflectivity cannot distinquish between roughness and diffuse interface

Reflectivity from a simple interface





Effect of roughness and sld

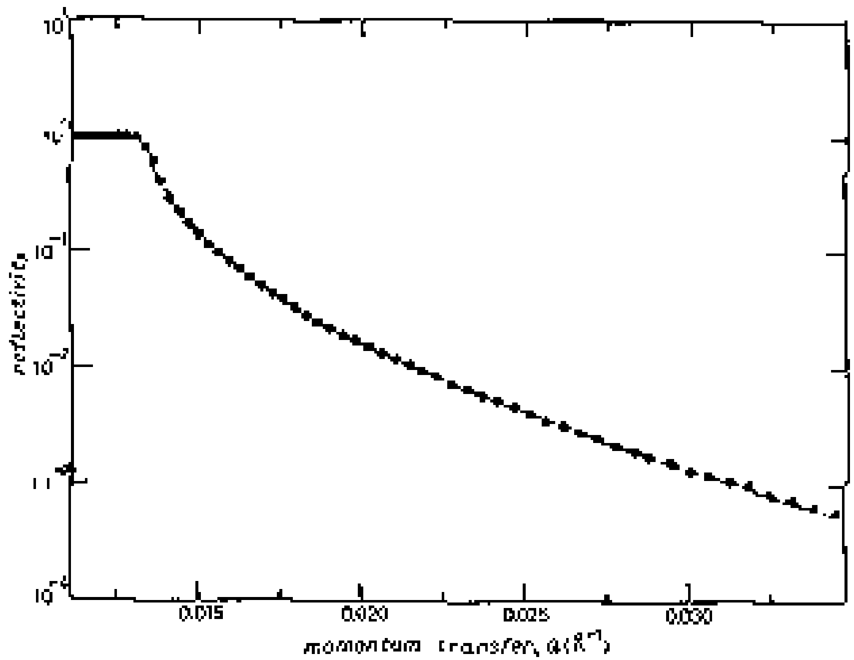
Glass optical flat

$$\theta = 0.35$$

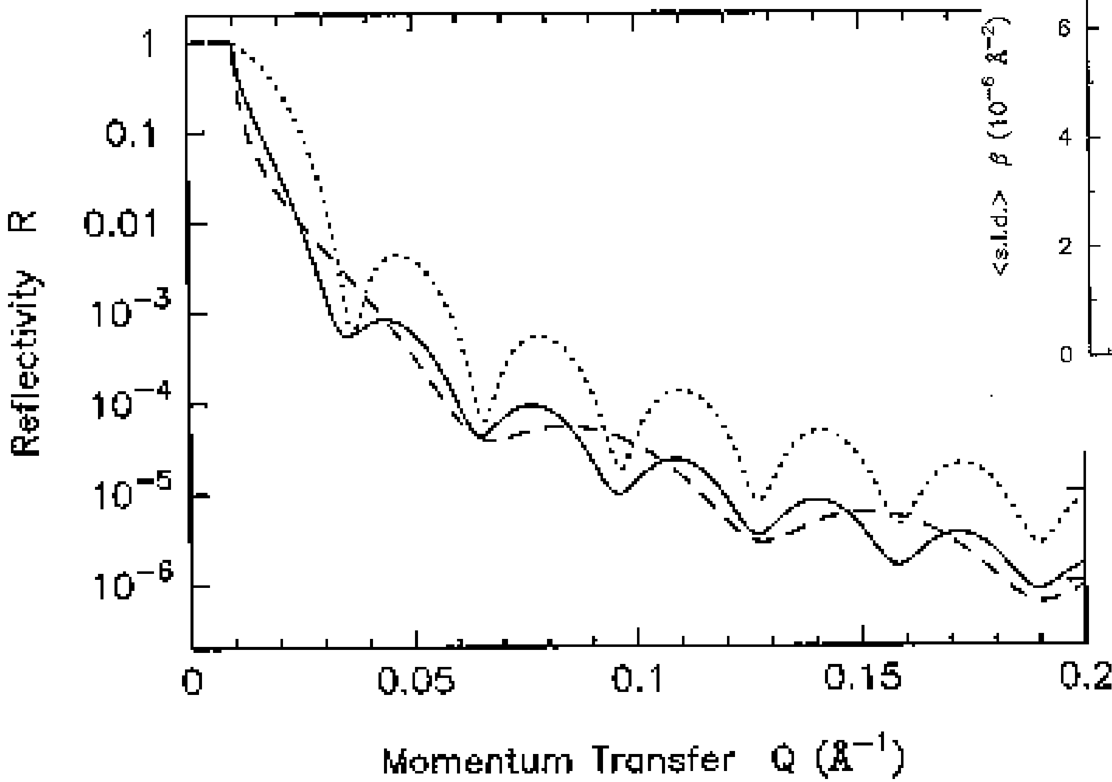
$$Nb = 0.35x10^{-5}\,\mathrm{A}^{-2}$$

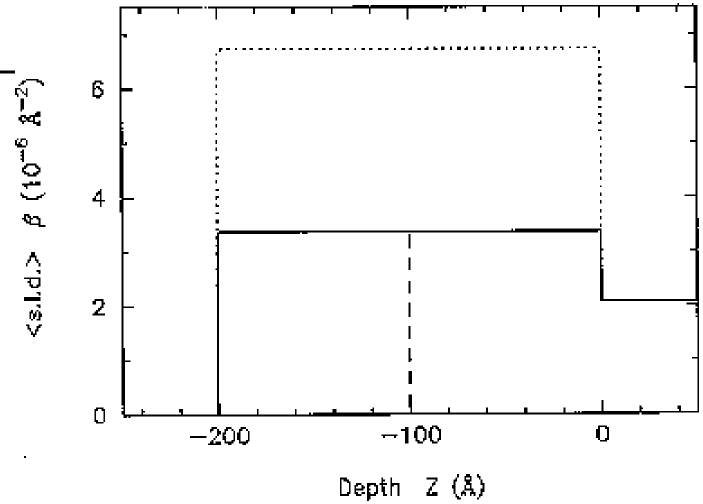
$$\sigma = 33\mathrm{A}$$

$$\Delta\theta = 5\%$$



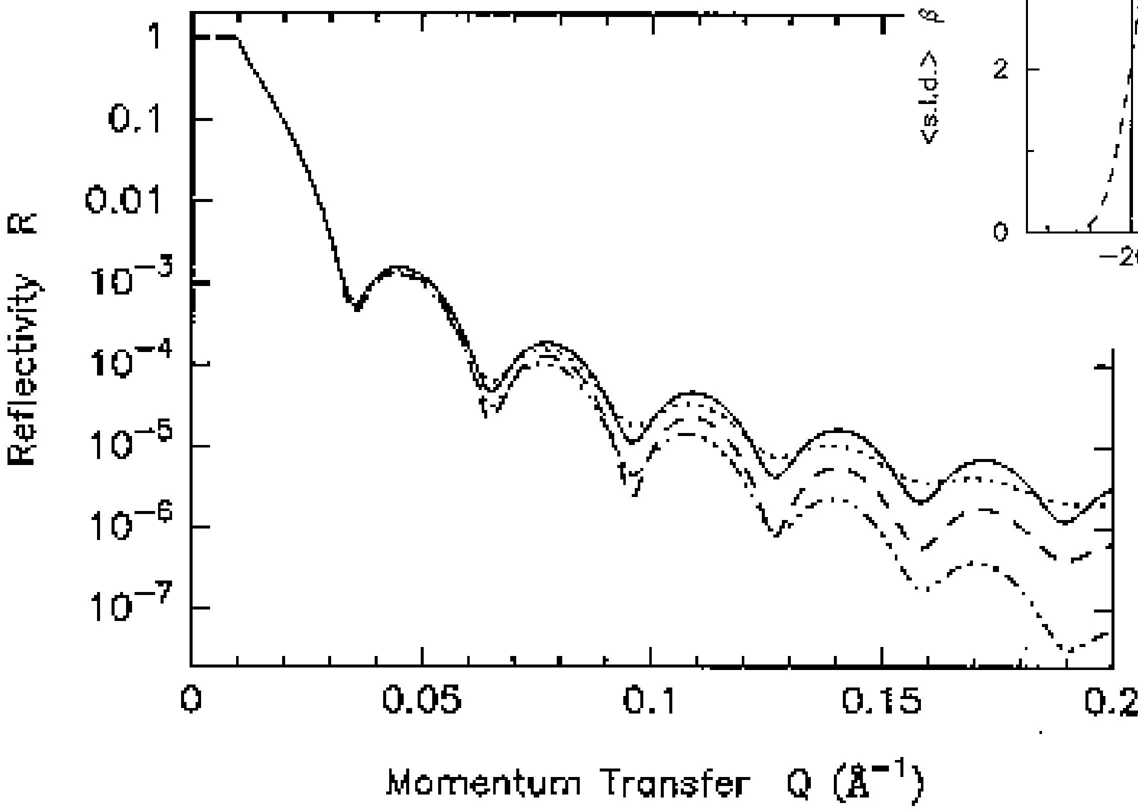
Reflectivity from thin films

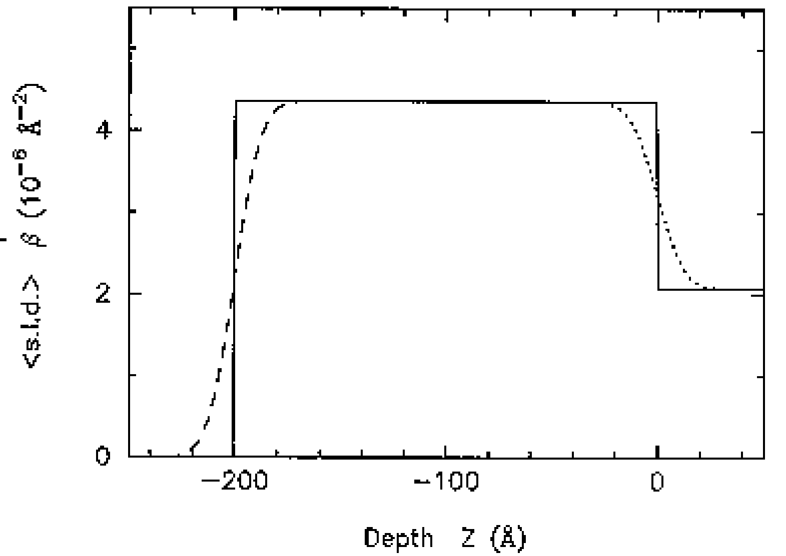




Effect of film thickness and refractive index

Reflectivity from thin films





Effect of interfacial roughness

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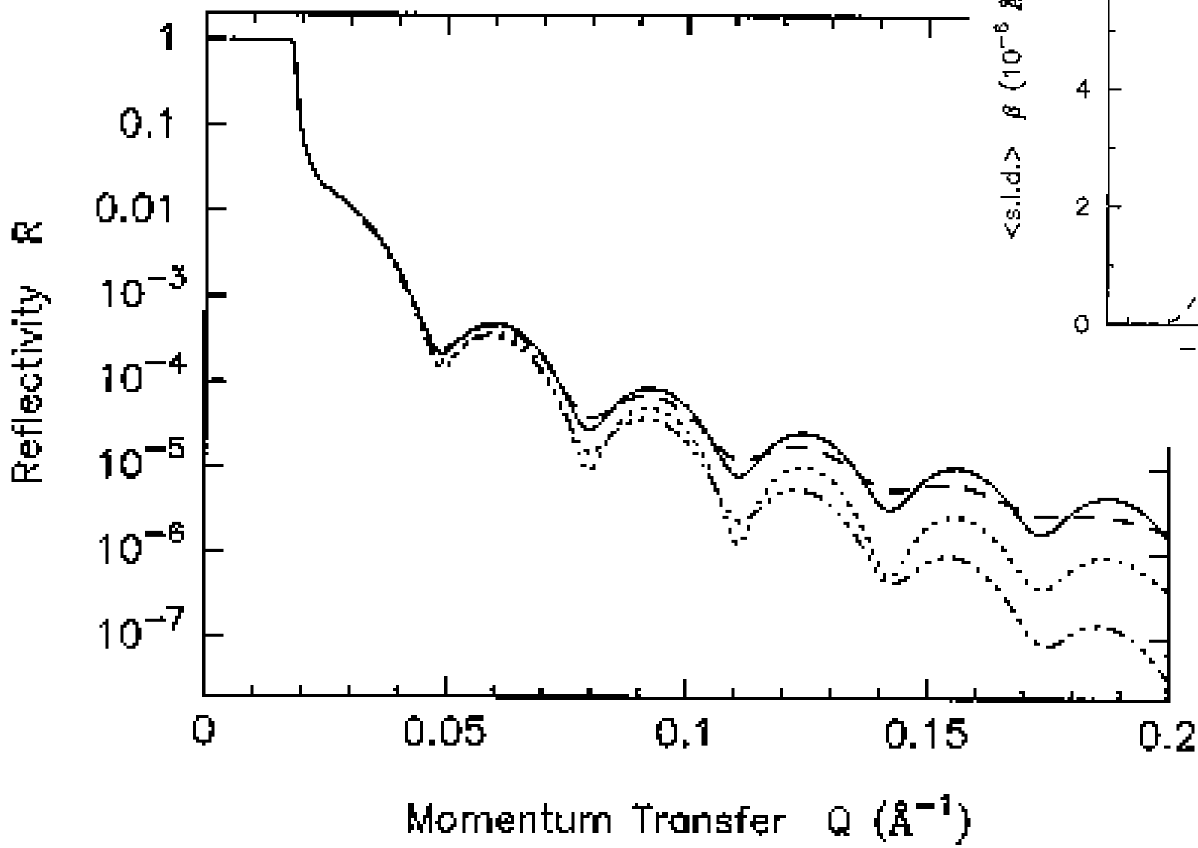
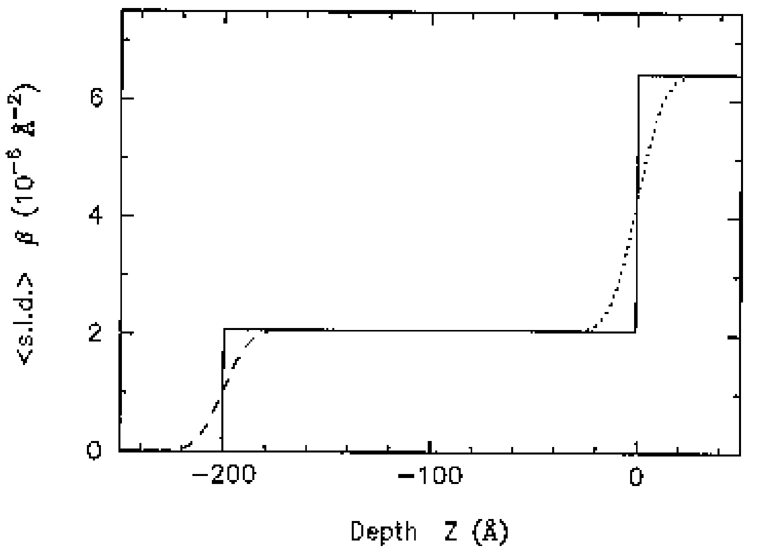
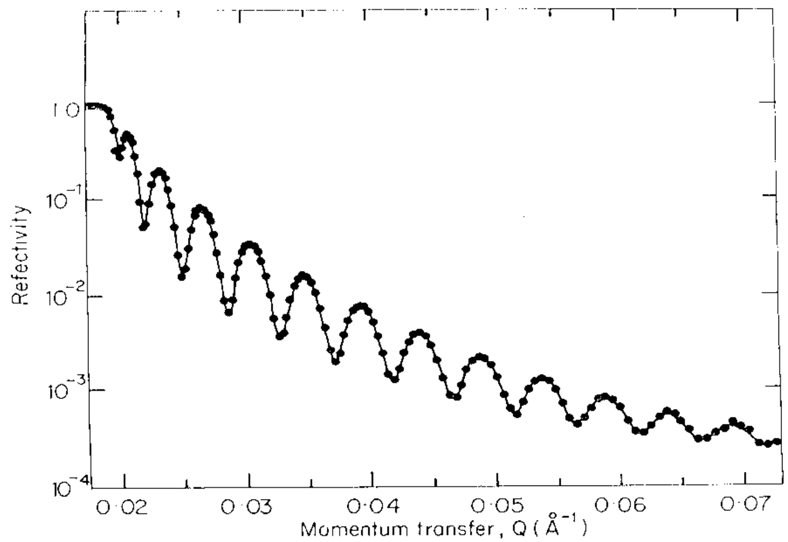
Reflectivity from thin films





Effect of interfacial roughness

Reflectivity from a thin film



Deuterated L-B film on silicon

$$d = 1198\text{A}$$

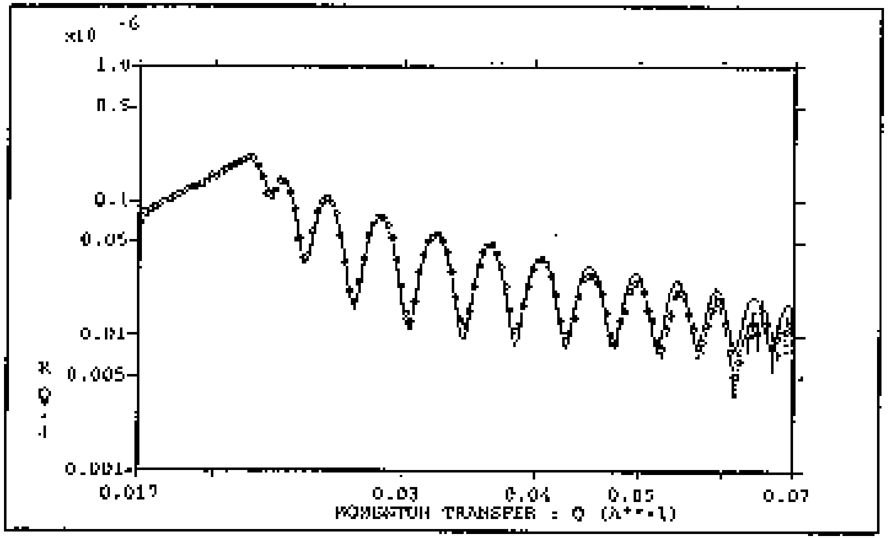
$$Nb = 0.74x10^{-5}\,\text{A}^{-2}$$

$$\theta = 0.5, \Delta\theta = 4\%, \sigma = 20\text{A}$$

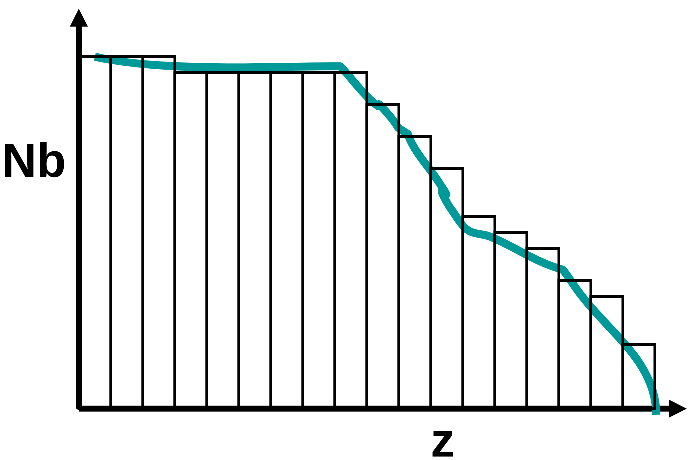
NiC film on silicon

$$d = 1194\text{A}, Nb = 0.94x10^{-5}\,\text{A}^{-2}$$

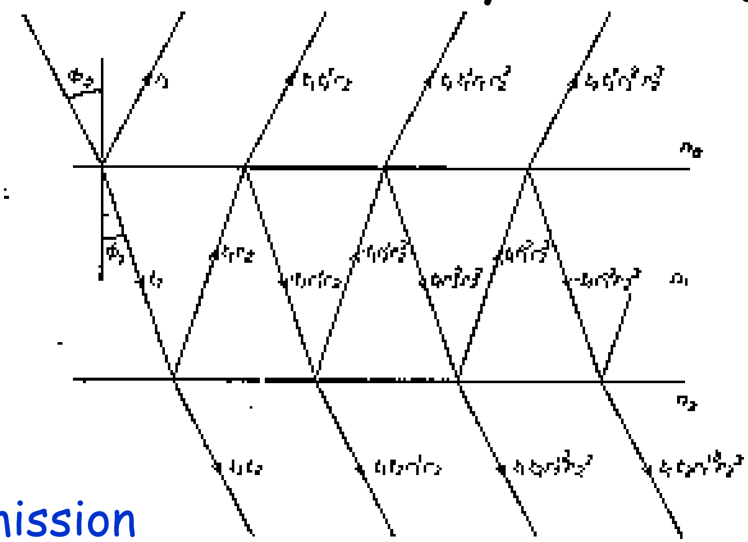
$$\theta = 0.5, \Delta\theta = 4\%, \sigma_1 = 10, \sigma_2 = 15\text{A}$$



Reflection from more complex interfaces (multiple layers)



Airy's fomula (Parratt)



Combination of reflection and transmission coefficients give amplitude of successive beams reflected,

$$r_1, t_1 t_1' r_2, -t_1 t_1' r_1 r_2^2, t_1 t_1' r_1^2 r_2^3$$ and so on

(Parratt, Phys Rev 95 91954) 359
G B Airy, Phil Mag 2 (1833) 20)

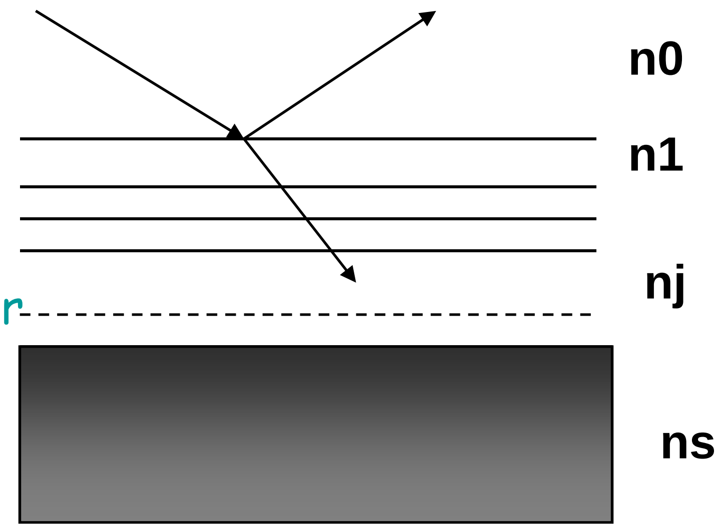
Phase change on traversing film, $\delta_1 = \frac{2\pi}{\lambda} n_1 d_1 \sin\theta_1$

$$R = r_1 + t_1 t_2' r_2 e^{-2i\delta_1} - t_1 t_1' r_1 r_2^2 e^{-4i\delta_1} + \ldots$$

More general matrix formulisms (Born & Wolf, Abeles) available

Reflection from multiple layers

Born and Wolf matrix formulism



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

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

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

$$p_j = n_j \sin\theta_j$$

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

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

The resultant reflectivity is

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

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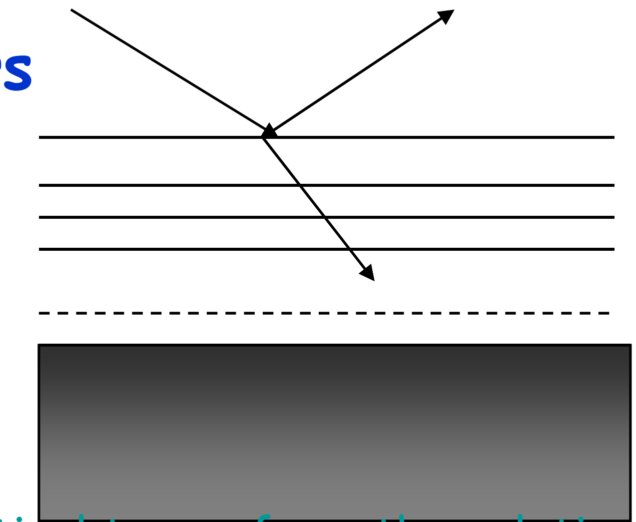
Reflection from multiple layers



In Born and Wolf approach can only include roughness / diffusiveness at interfaces by further sub-division in small layers.

Abeles method, using reflection coefficients overcomes this limitation

Define characteristic matrix per layer, in optical terms from the relationship between electric vectors in successive layers,

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

$$[C_1].[C_2]----[C_{n+1}] = \begin{bmatrix} a & b \\ c & d \end{bmatrix}$$

To include roughness,

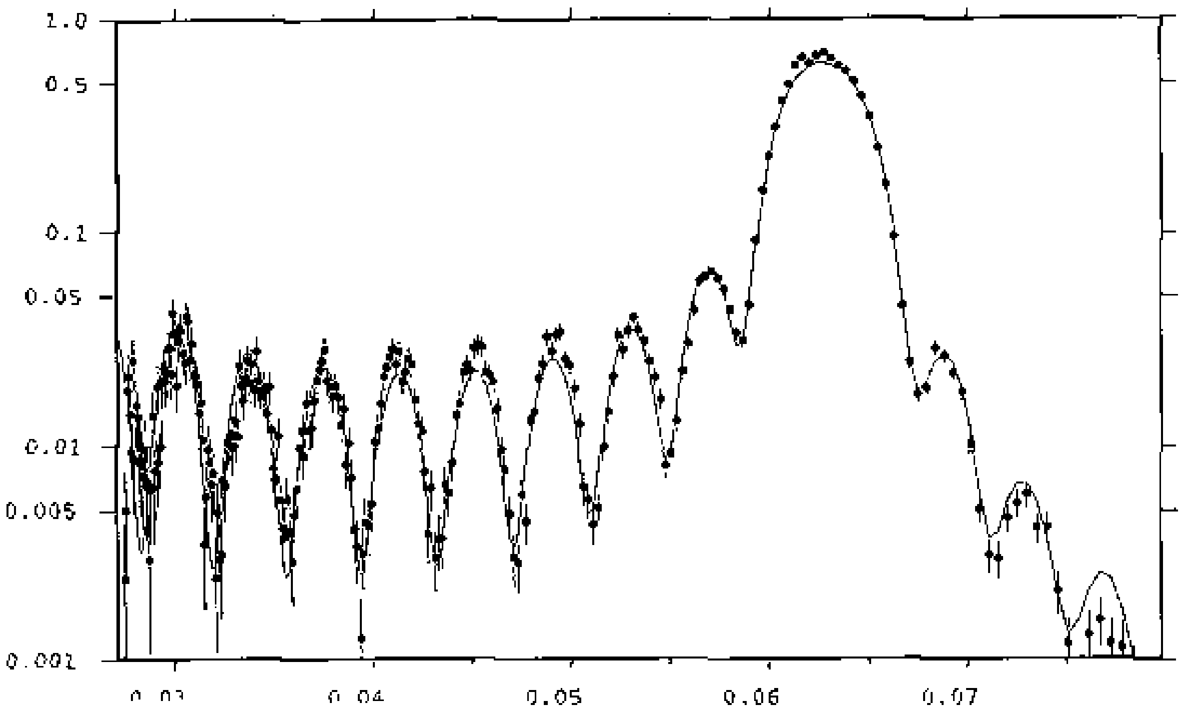
$$r_j = \frac{(p_{j-1} - p_j)}{(p_{j-1} + p_j)} \exp - 0.5 q_j q_{j-1} \sigma^2$$

(Heavens, 'Optical properties of solid thin films', Butterworths, London, 1955, F Abeles, Annale de Phys 5 (1950) 596)

The resultant Reflectivity is then,

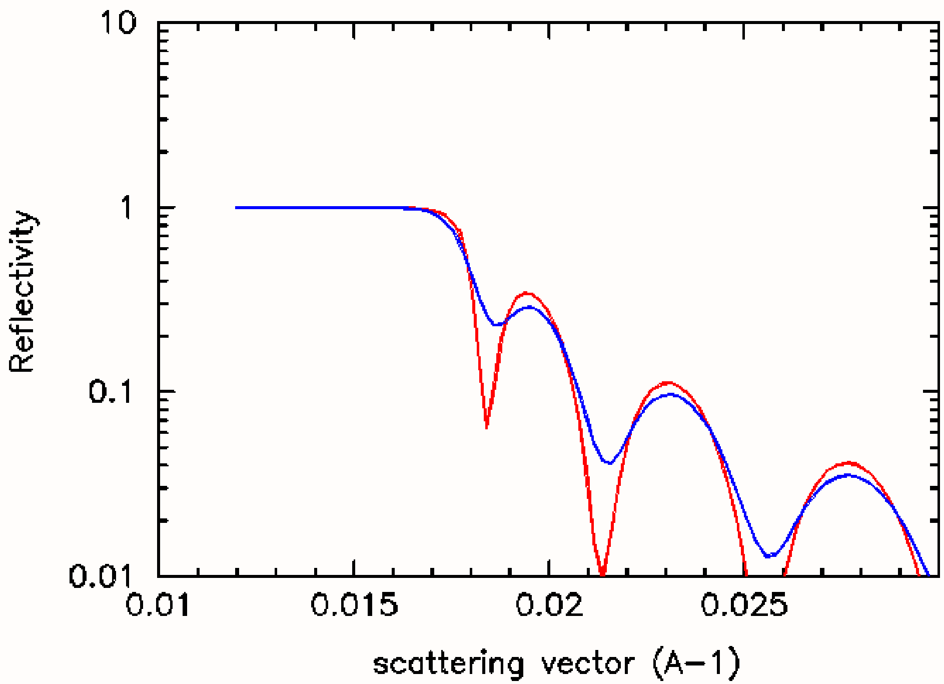
$$R = CC^* / AA^*$$

Multiple Layer films



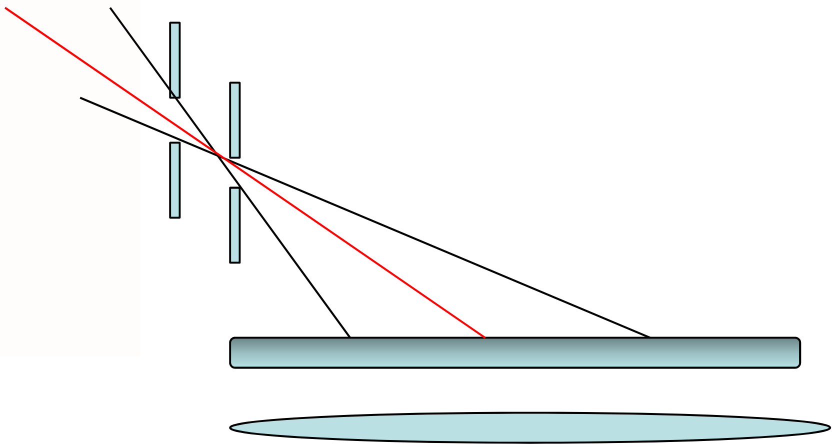
Region around 1st order Bragg peak for Ni/Ti multilayer
15 bilayers (46.7, 1.0 x 10-5 / 55.7,-0.13x10-5)

Effects of resolution



$$\Delta Q^2 / Q^2 = \Delta t^2 / t^2 + \Delta\theta^2 / \theta^2$$

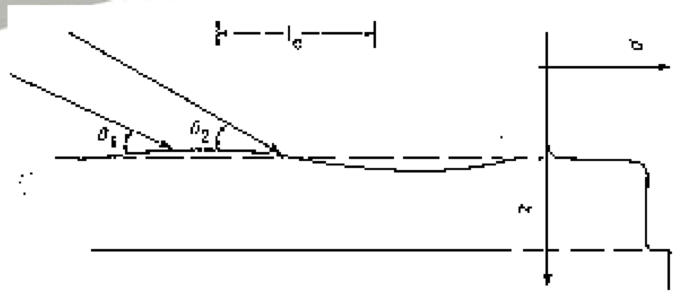
On SURF and CRISP resolution is dominated by collimation

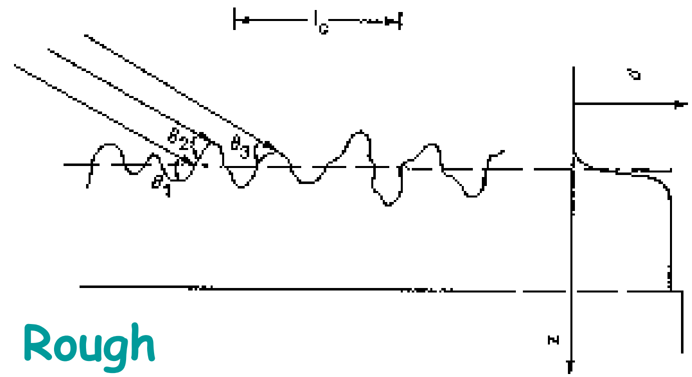


1000 Å film on Si , ΔQ/Q 2%, 6%

Damps interference fringes, rounds critical edge

Surface roughness and Waviness





Curvature >> coherence length → **Rough**

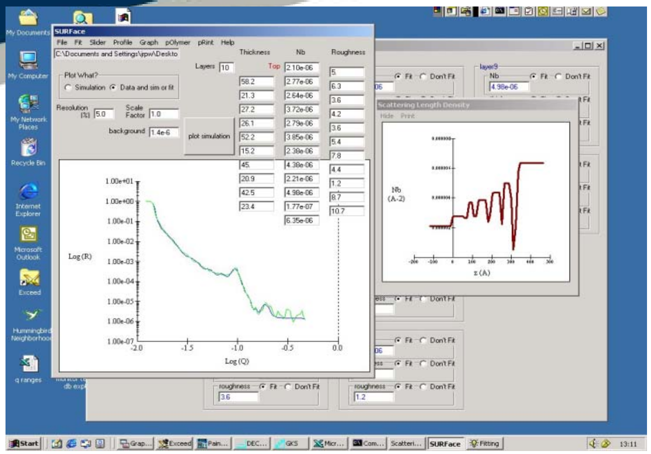
Curvature << coherence length → **Waviness**

This initially has an effect similar to resolution, and in the extreme can be treated by geometrical optics.

Incoherent reflectivity from 2 surfaces, separated by an adsorbing media:

$$R_{tot}(Q) = R_1(Q) + \frac{(1 - R_1(Q))^2 R_2(Q) A(Q)}{1 - R_1(Q) R_2(Q) A(Q)}$$

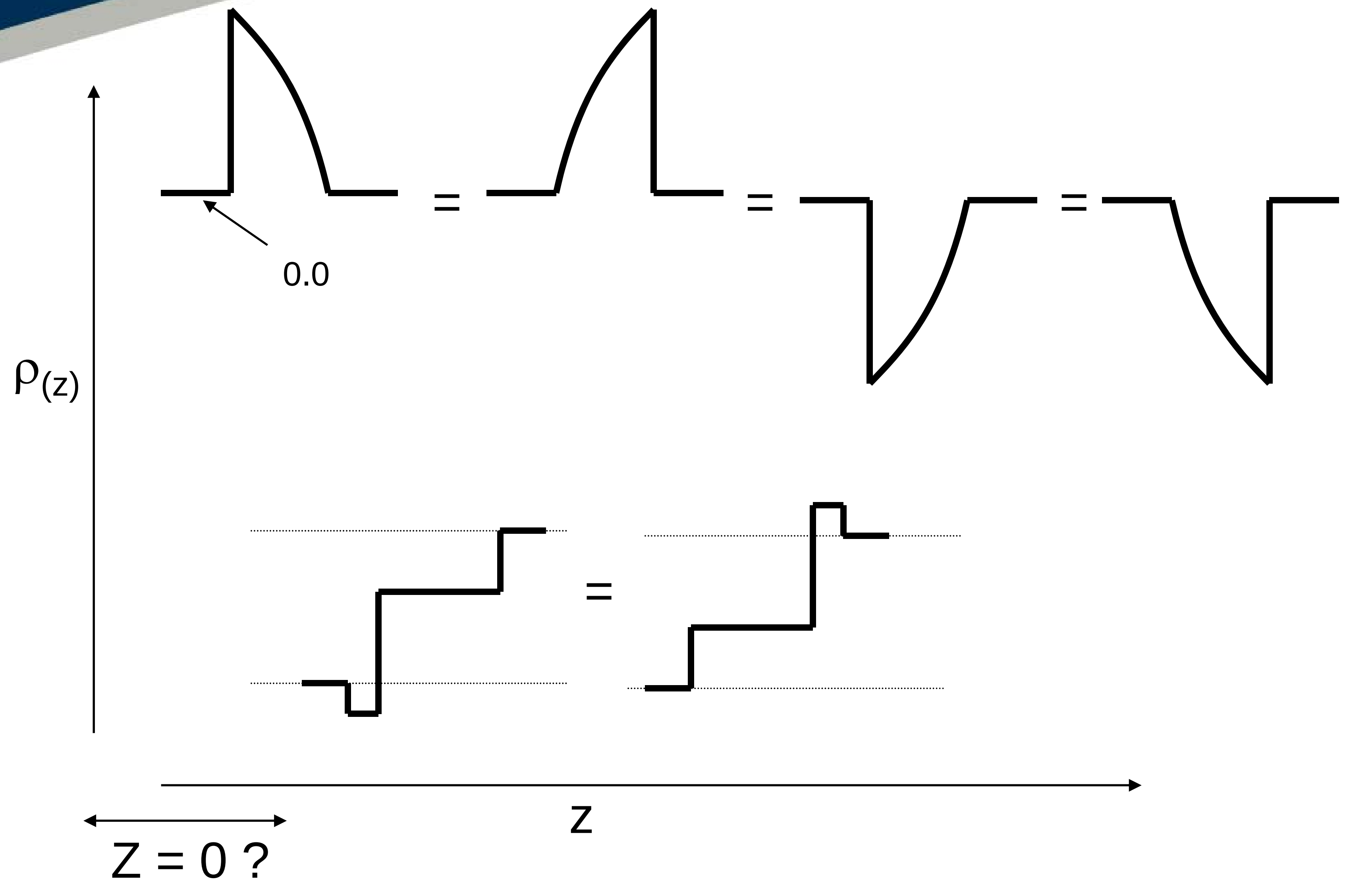
Model fitting Reflectivity data



reflectivity → Scattering length density

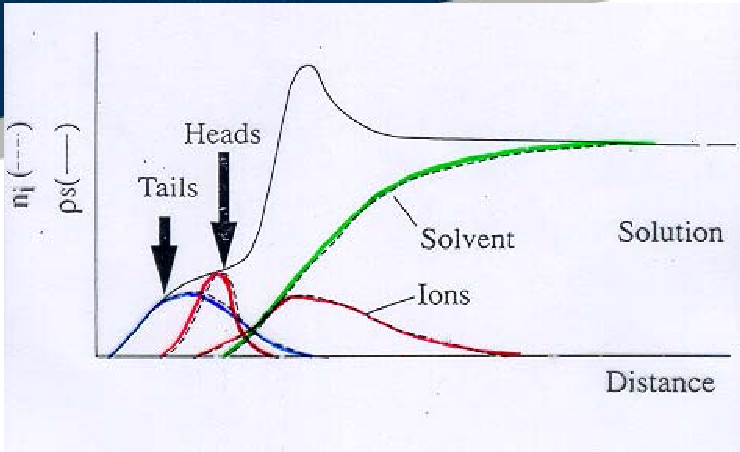
- Uniqueness ?
- Resolution ?
- Model dependent / overinterpretation of data ?
- Does the scattering length density profile give access to the necessary physical parameters (Intra molecular) ?

Steepest decent, simplex, simulated annealing, genetic, cubic spline + fft, etc etc } Lateral (z) and rotational invariance



ρ(z)
0.0
=
=
=
=
z
Z = 0 ?

Partial Structure Factors



$$R(\kappa)=\frac{16\pi^2}{\kappa^2}\left|\int_{-\infty}^{+\infty}\rho(z)e^{-i\kappa z}dz\right|^2$$

$$\rho(z)=b_c n_c(z)+b_h n_h(z)+b_s n_s(z)$$

$$R(\kappa)=\frac{16\pi^2}{\kappa^2}\left[b_c^2 h_{cc}+b_h^2 h_{hh}+b_s^2 h_{ss}+2b_c b_h h_{ch}+2b_c b_s h_{cs}+2b_h b_s h_{hs}\right]$$

Self Partial Structure Factors : $$h_{ii}=\left|\hat{n}_i\right|^2$$

$\hat{n}_i$ is a one dimensional Fourier transform of $n_i(z)$

Cross partial structure factors: $$h_{ij}=\mathrm{Re}\left\{\hat{n}_i\hat{n}_j\right\}$$

(Crowley, Lee, Simister, Thomas, Penfold, Rennie, Coll Surf 52 (1990) 85)

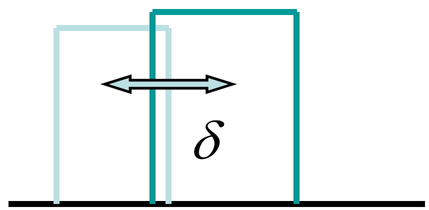
Cross Partial Structure Factors

If one distribution is shifted by δ Fourier transform is changed by phase factor $\exp(i\kappa\delta)$

$$\hat{n}_i'(z) = n_i(z-\delta)$$
$$\hat{n}_i'(\kappa) = n_i(\kappa)\exp(i\kappa\delta)$$

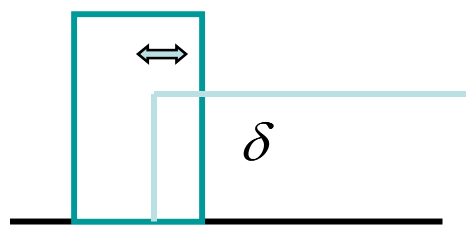
$$h_{ij} = \mathrm{Re}\{\hat{n}_i \hat{n}_j\}\exp(i\kappa\delta_{ij})$$

If both even functions



$$h_{ij} = \pm[h_{ii}h_{jj}]^{1/2}\cos i\kappa\delta$$

If even + odd functions

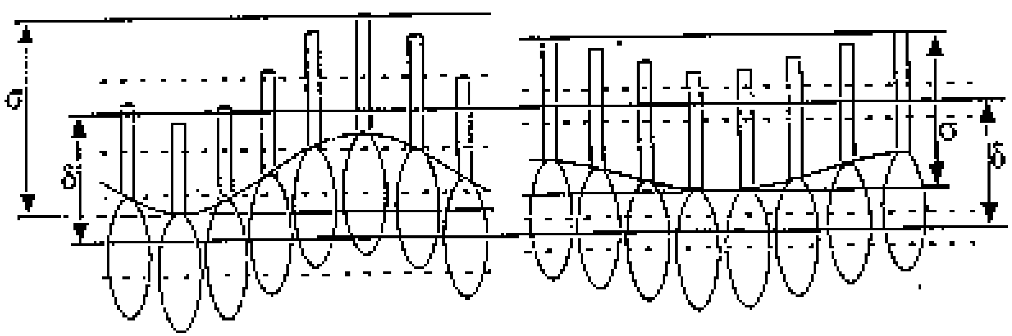


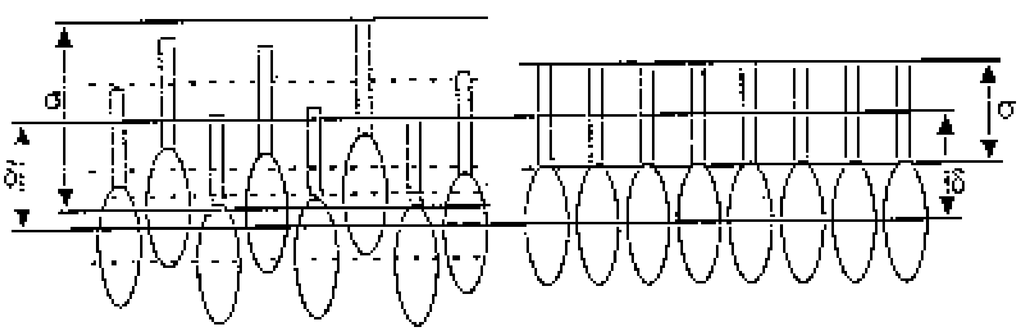
$$h_{ij} = \pm[h_{ii}h_{jj}]^{1/2}\sin i\kappa\delta$$

$\pm$ because of phase uncertainty

Model Self-terms as Gaussian (solvent as tanh)

Effect of capillary wave and structural roughness on cross-terms

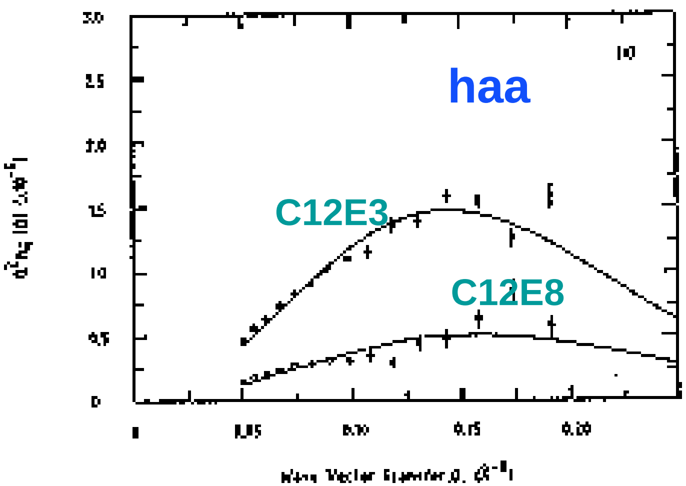


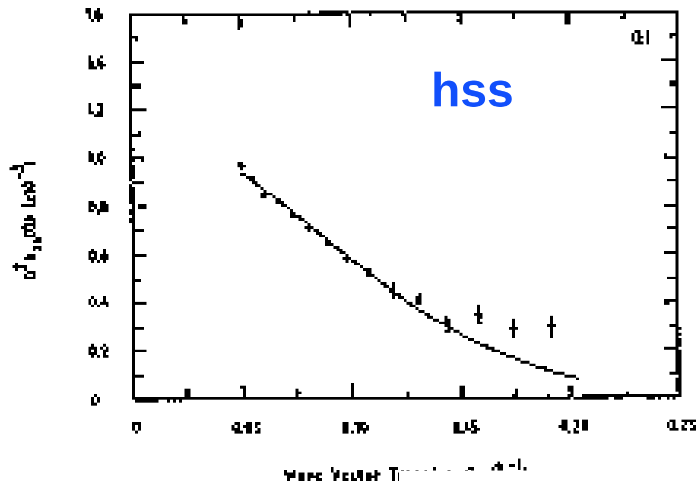


Widths of individual distributions affected by roughness,

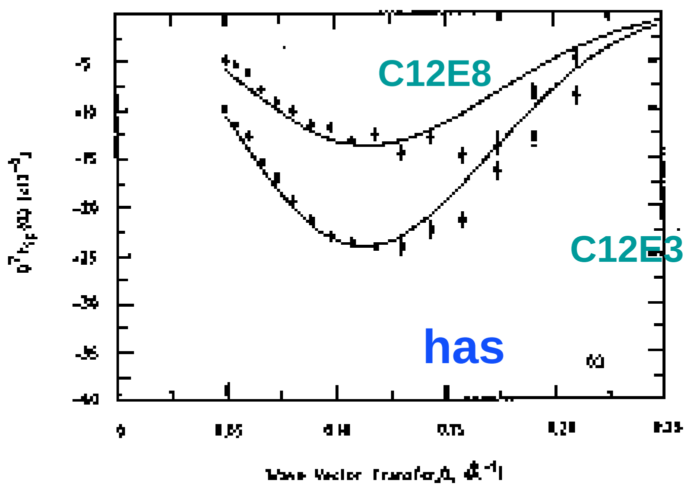
but separations are NOT

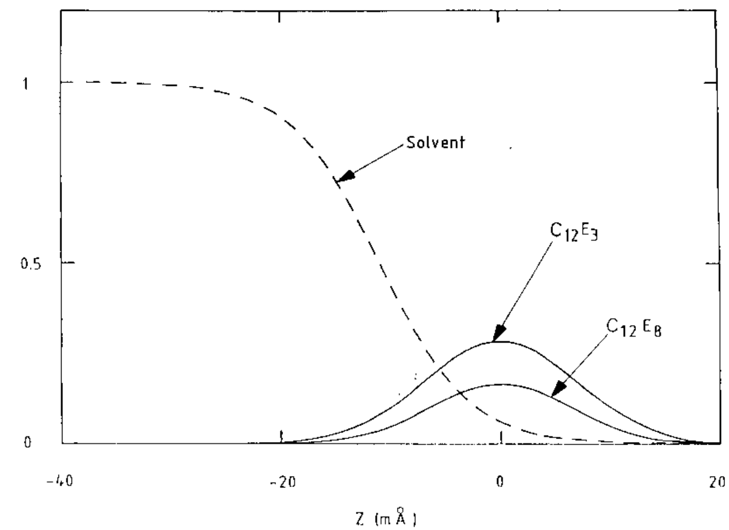
Partial Structure Factor Analysis





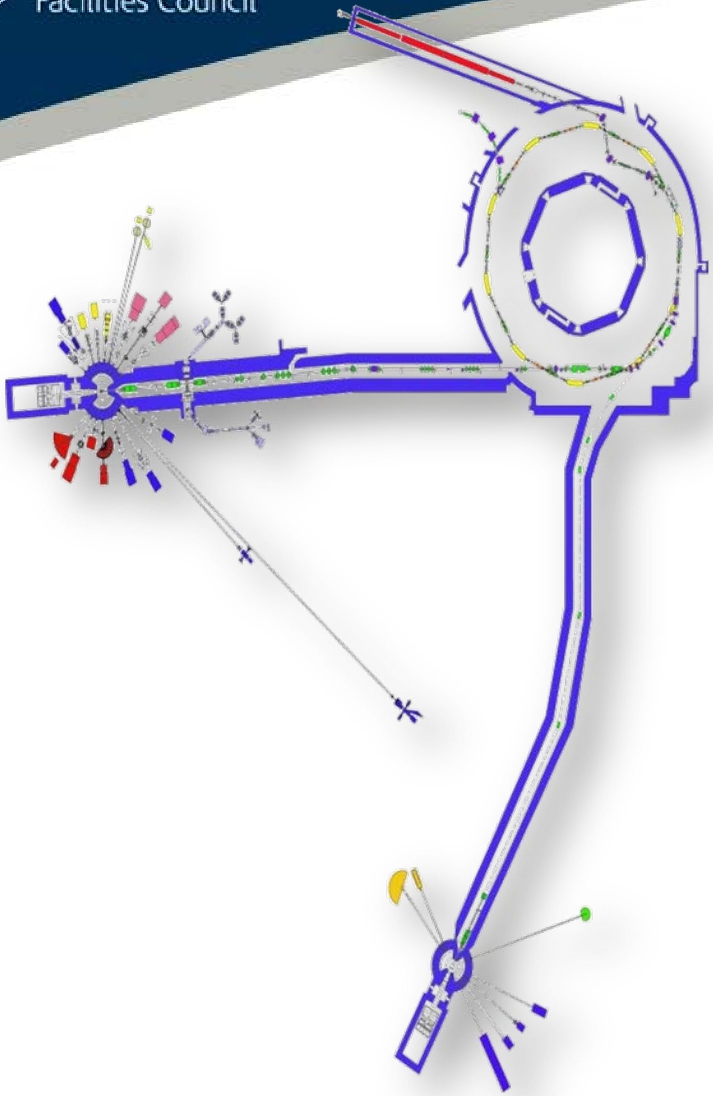
Structure of binary non-ionic mixtures
5 x10^{-5} M 30/70 C12E3 / C12E8





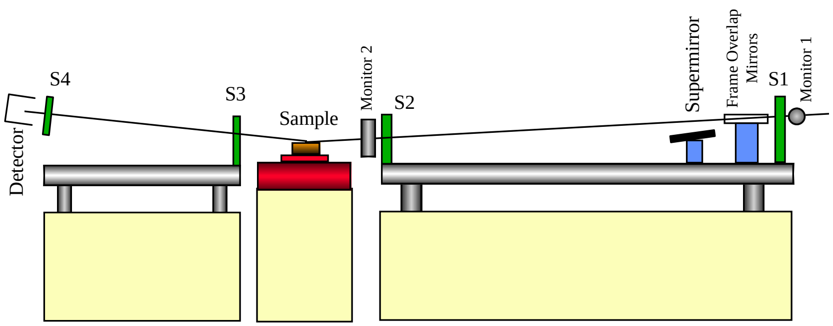
Example of simplest labelling scheme : solvent, alkyl chain of each surfactant

Neutron Reflectivity at ISIS



Measure variation of reflectivity with scattering vector, Qz, perpendicular to the interface

Using 'white beam' TOF method with fixed angle and range of wavelengths



INTER, POLREF, OFFSPEC, SURF, CRISP reflectometers

(Penfold, Williams, Ward, J Phys E 20 91987) 1411; J Penfold et al, J Chem Soc, Faraday Trans, 94 (1998) 955

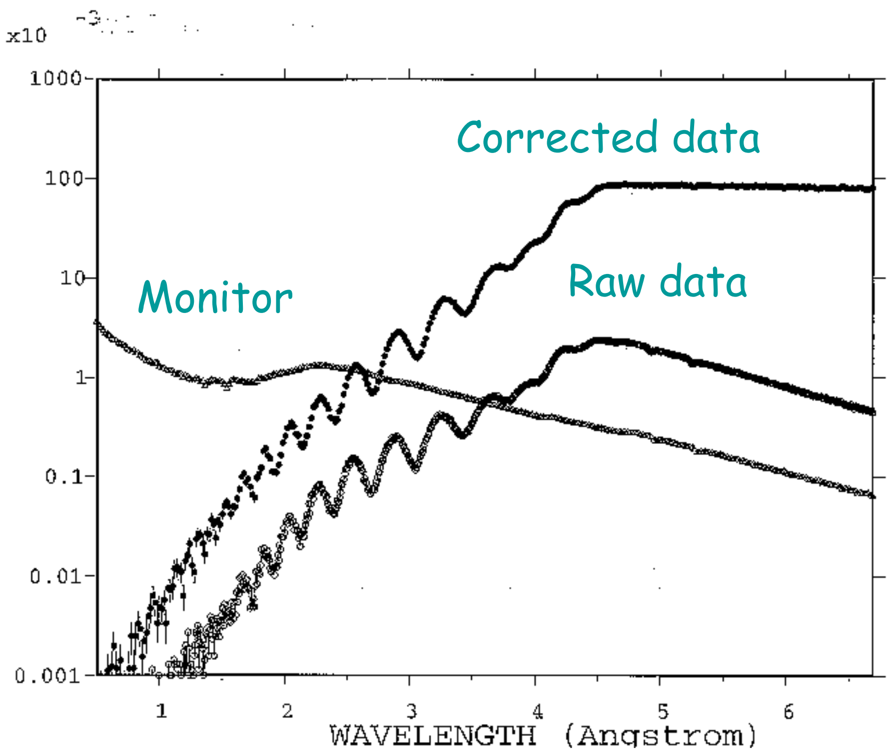
Science & Technology Facilities Council

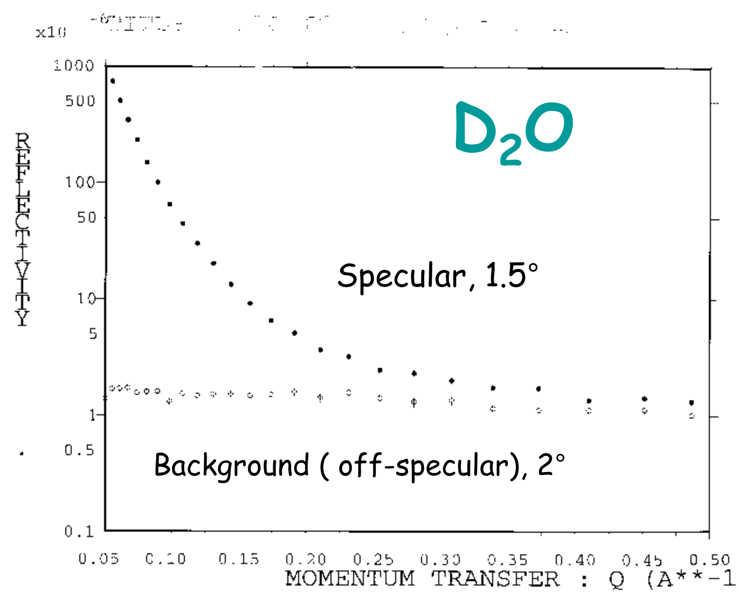
Instrumentation

Correct for detector efficiency, spectral shape, background

$$R\left(Q\left(\lambda_i,\theta\right)\right) = f\,\frac{\left[I_d(\lambda_i) - b_d(\lambda_i)\right]}{\left[I_m(\lambda_i) - b_m(\lambda_i)\right]}\,\frac{\varepsilon_m(\lambda_i)}{\varepsilon_d(\lambda_i)}$$

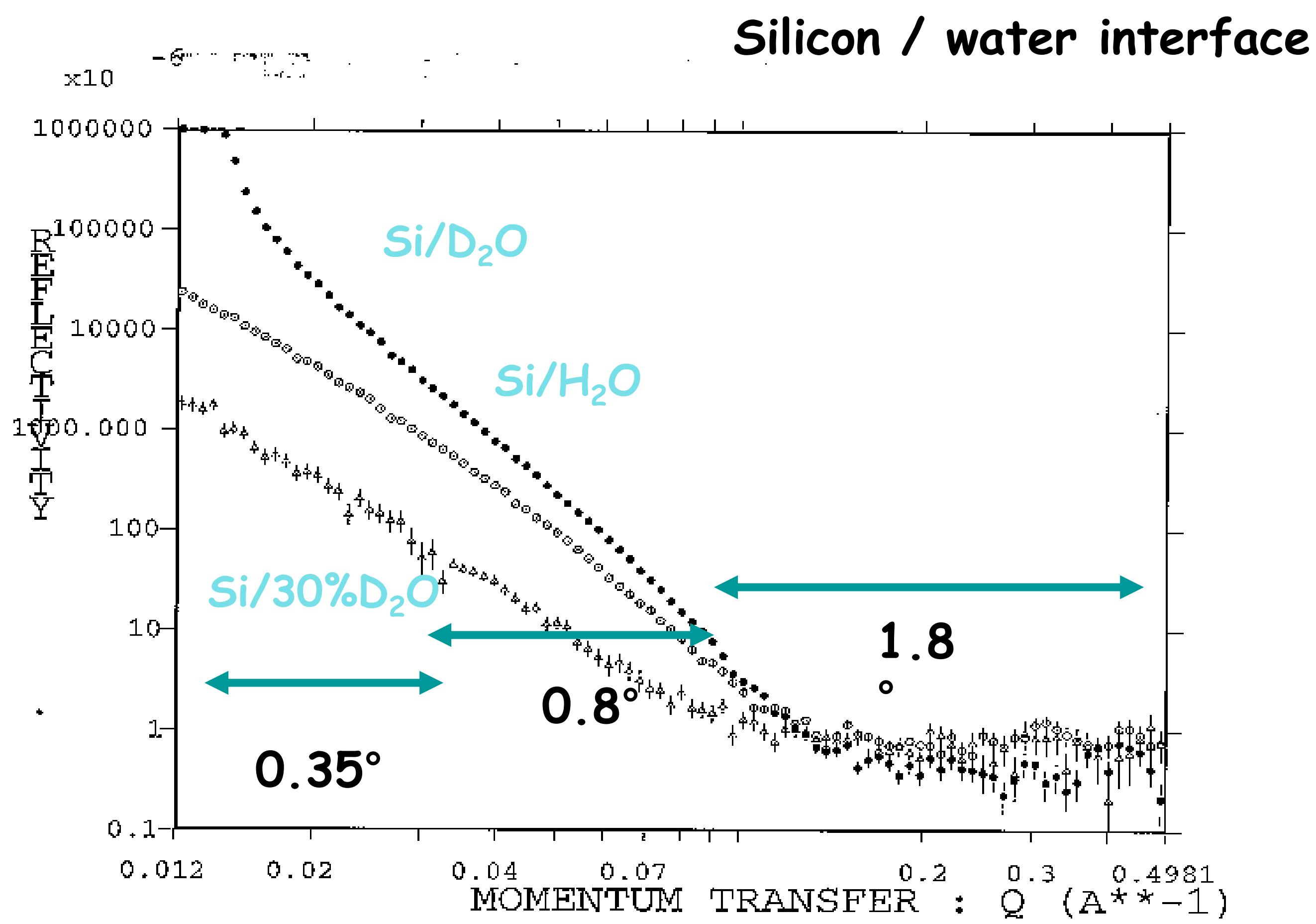
d,m refer to the detector and monitor

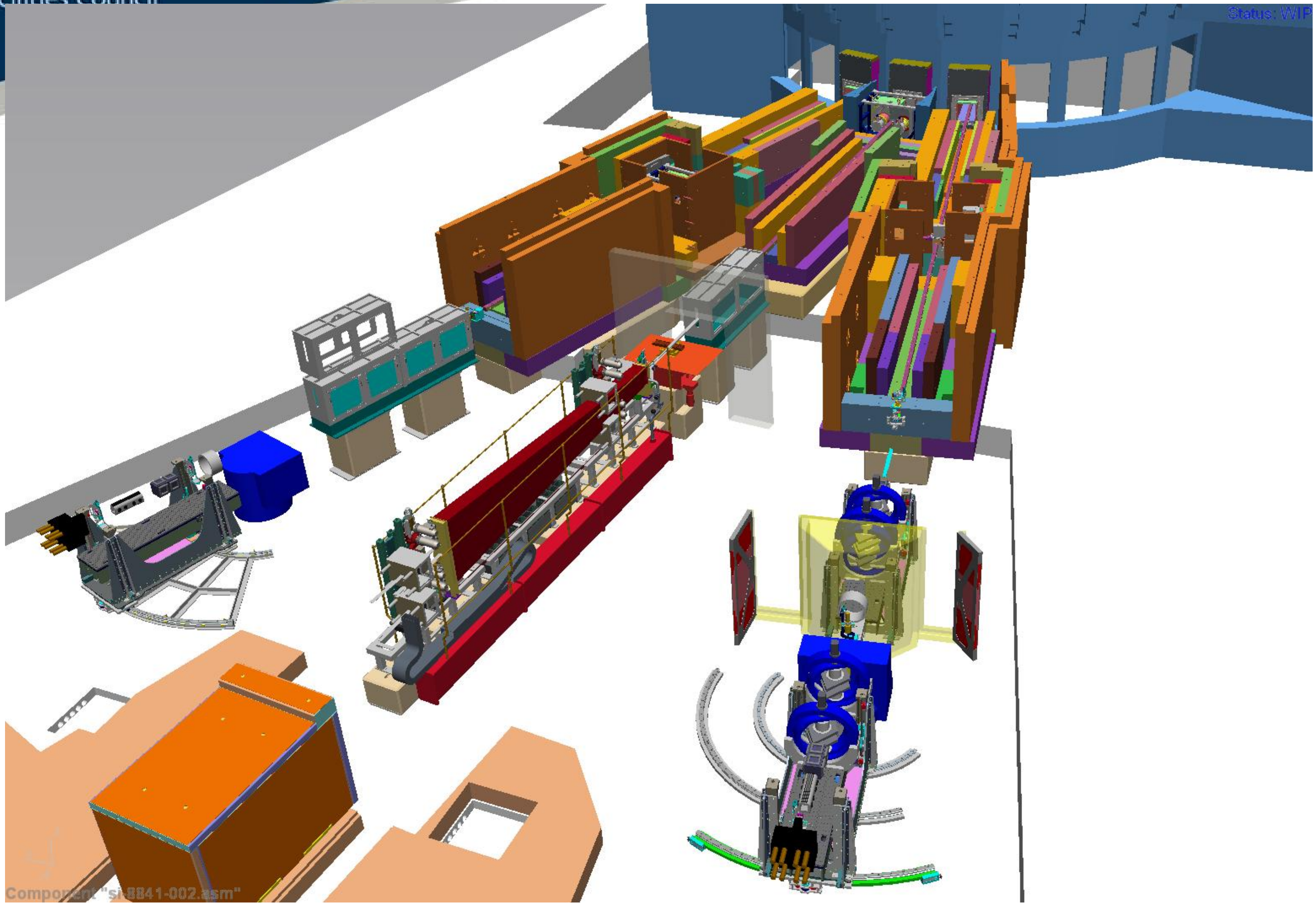




Science & Technology Facilities Council

Instrumentation




Status: WIP
Component "si-8841-002.asm"

Reflectometry Village

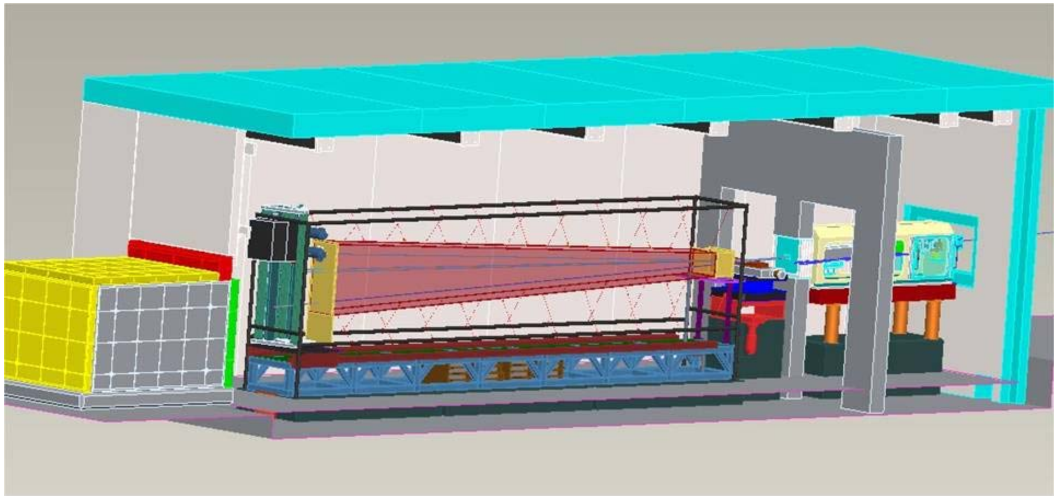
Inter

Designed for the study of chemical interfaces, with a particular emphasis on the air-water interface

>10 times the flux of SURF

Much wider dynamic range

Tuneable resolution



Scientific Opportunities

- **Biology**
  - Cell adhesion using synthetic polymer analogues
  - Kinetics of action of interfacial enzymes
  - Interfacial structure of designed peptides (folding)
  - Biofouling and adsorption kinetics
  - Interlayer forces in polymer and biological systems
  - Supported bilayers
- **Polymer diffusion**

wavelength range	1 – 16 (22) Å
Moderator	Coupled s-CH_4 grooved – 26K
Primary flight path	19m (m=3 supermirror guides)
Secondary flight path	3-8 m
Beam size	60(h) x 30(v) mm
Flux at sample	~10^7 n/s/cm^2

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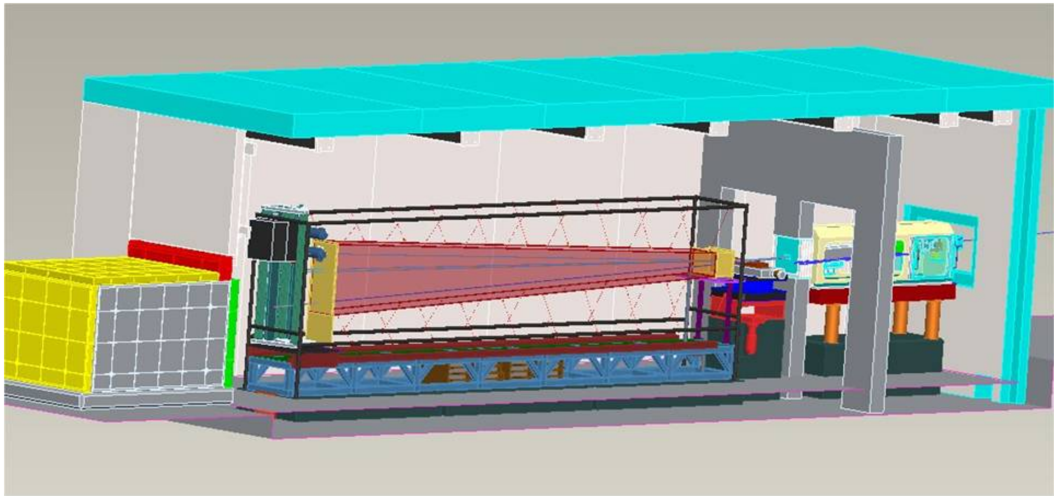

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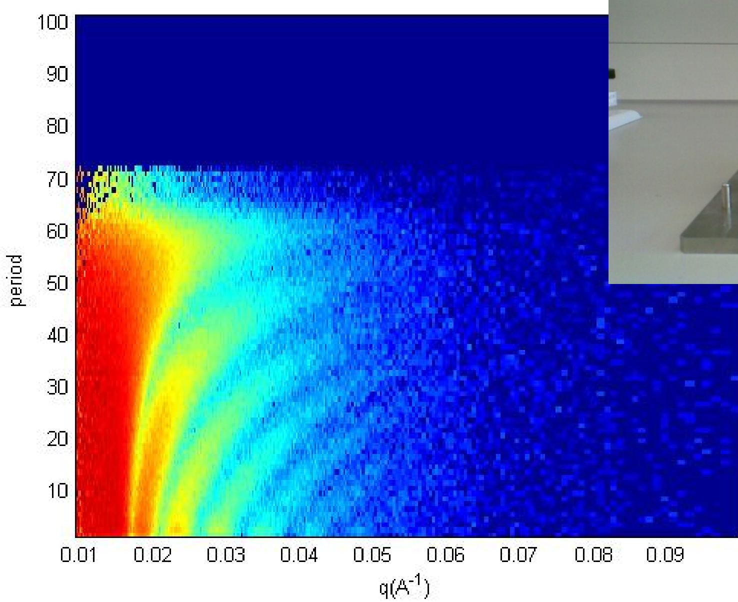
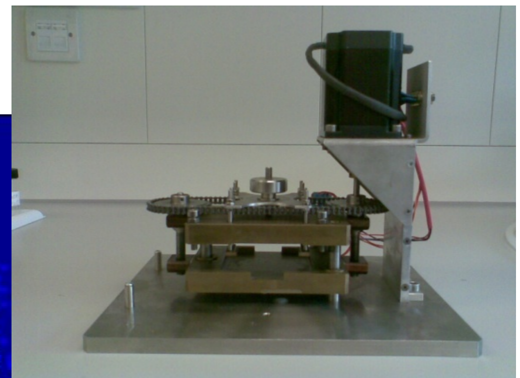
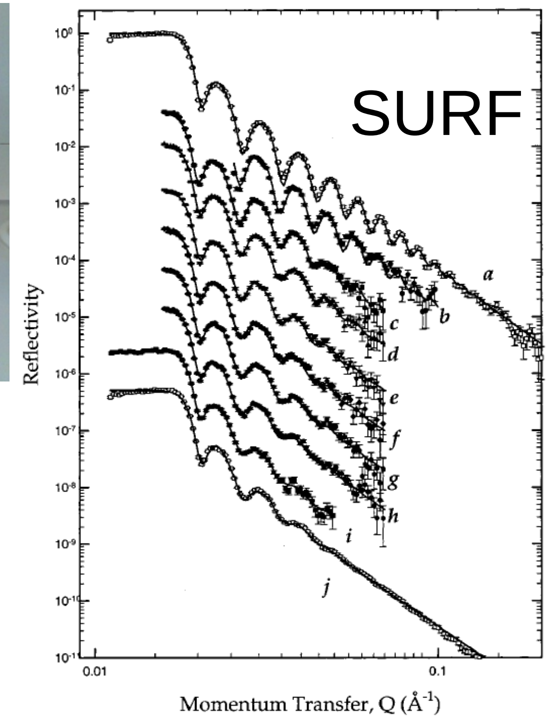
Kinetic data from INTER







Science & Technology

PolRef

Uses polarised neutrons to study the inter an intra-layer magnetic ordering in thin films and surfaces

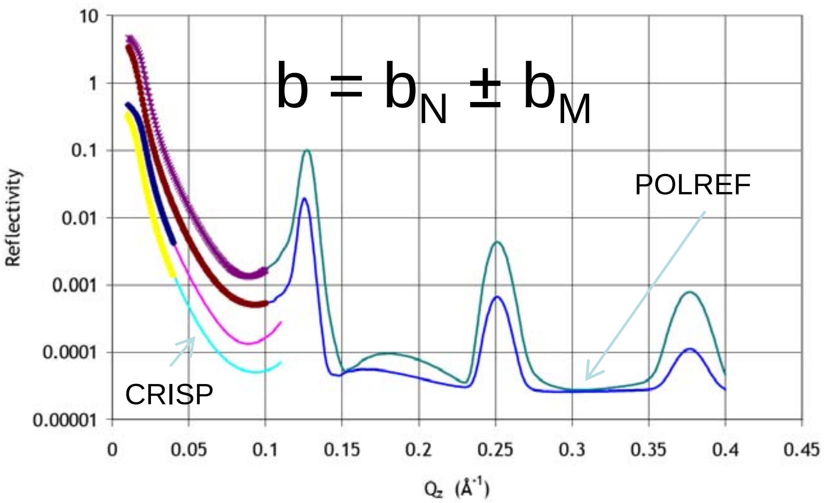
>20 times the flux of CRISP

Much wider dynamic range

Flexible polarisation

Dual Geometry

High precision sample stage



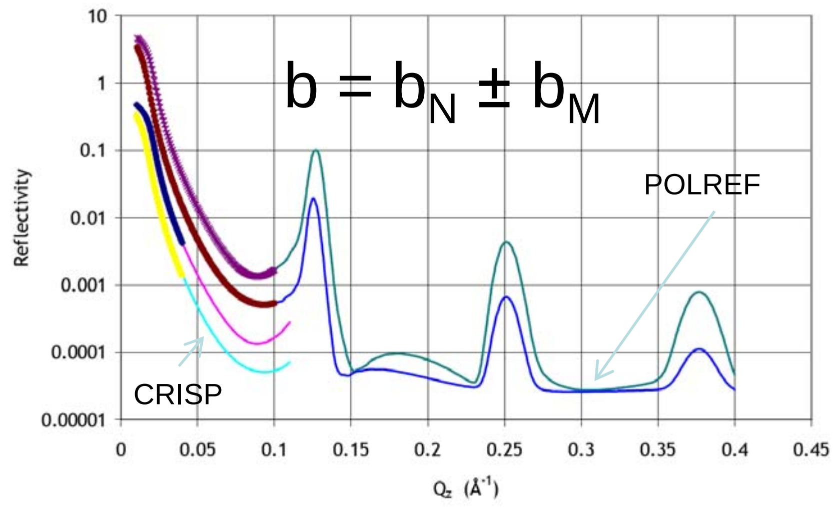
wavelength range	0.9 – 16 Å
Moderator	Coupled s-CH_4 grooved – 26K
Primary flight path	23m
Secondary flight path	3 m
Beam size	60(h) x 30(v) mm
Flux at sample	~10^7 n/s/cm^2

Scientific Opportunities

- **Spin Electronics**
  - Spin-Injection
  - Spin Torque
  - Dilute magnetic semiconductors
  - Giant/Tunnelling magneto-resistance
- **Model Magnetic Systems**
  - Ultrathin films (finite size effects)
  - Exchange springs (domain walls, surface magnetic phase transitions)
  - Stabilise new single-crystal phases (Ce, Mn,..)

PolRef

- Uses polarised neutrons to study the inter an intra-layer magnetic ordering in thin films and surfaces
- >20 times the flux of CRISP
- Much wider dynamic range
- Flexible polarisation
- Dual Geometry
- High precision sample stage



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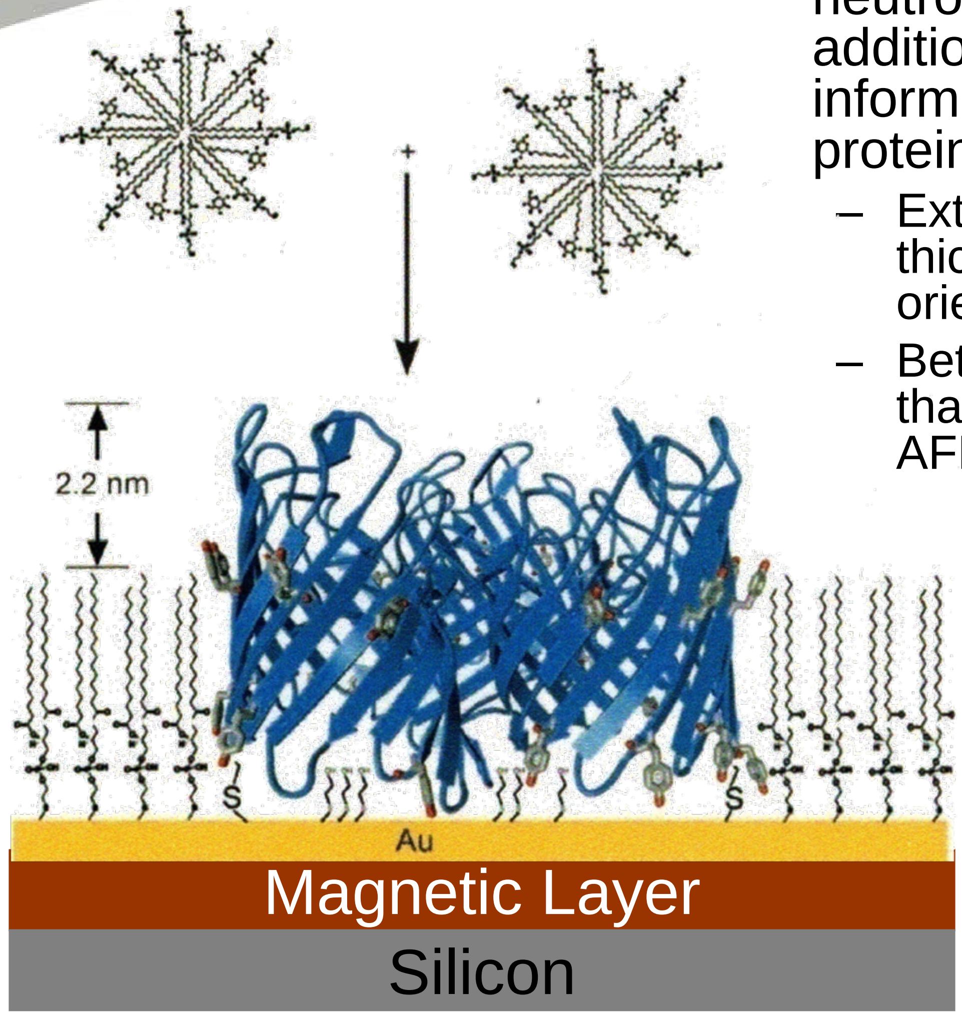
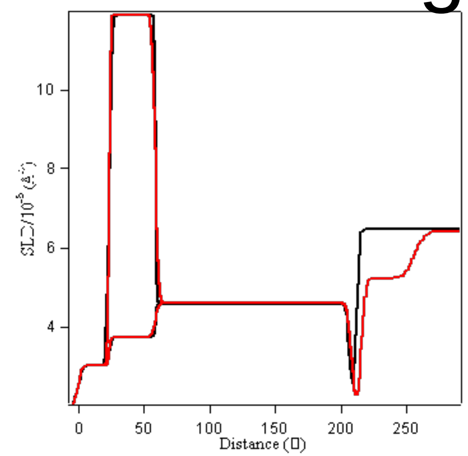
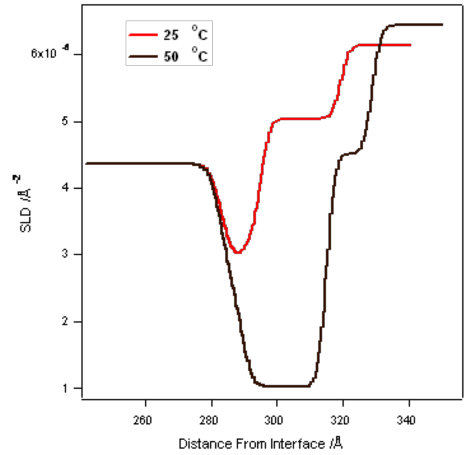
Polarised Neutrons for Biology

- Use polarised neutrons to provide additional information for protein absorption
  - Extract protein thickness and orientation
  - Better resolution than conventional AFM studies





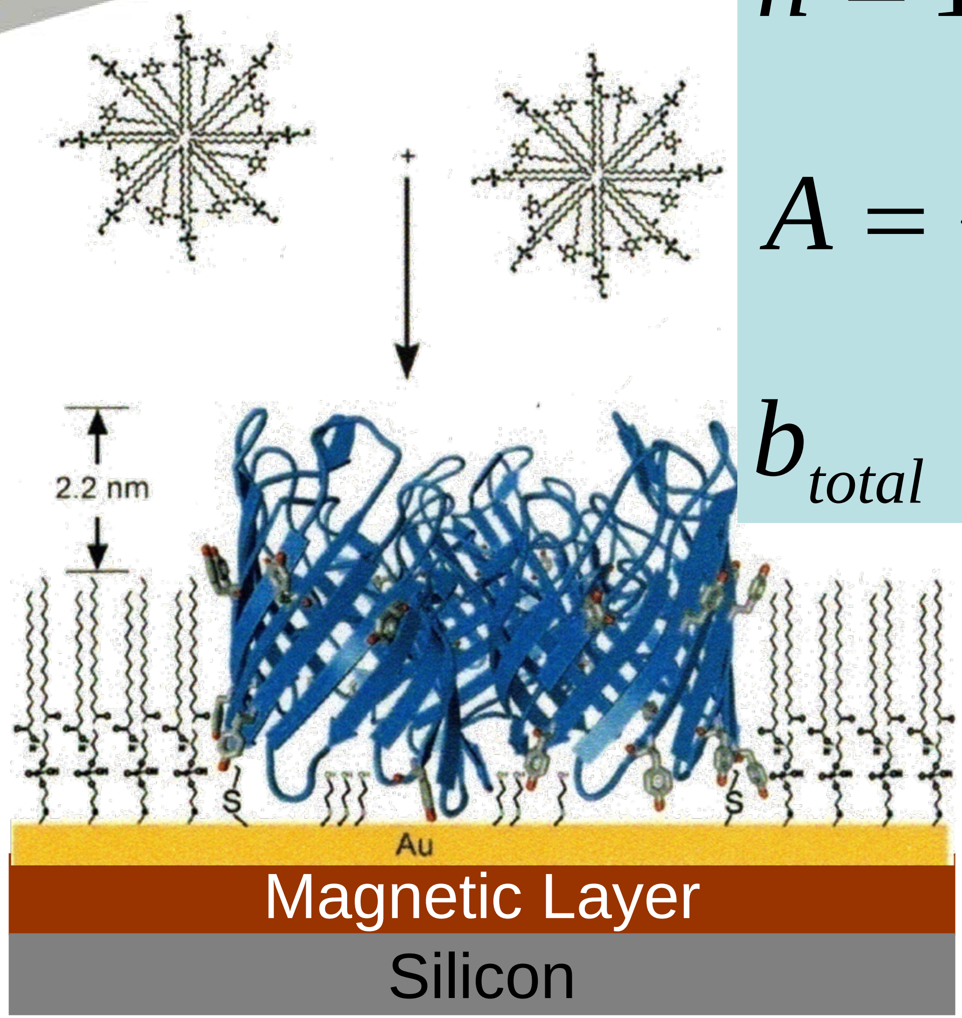


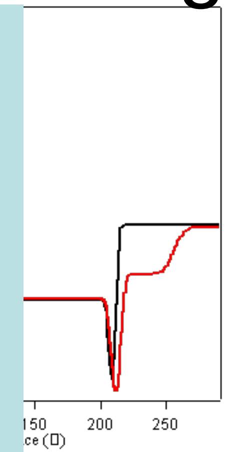
Polarised Neutrons for Biology

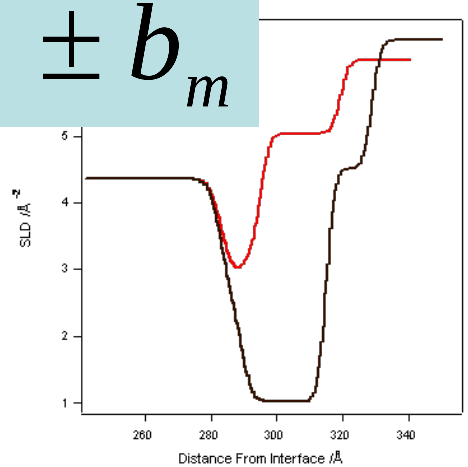
$$n = 1 - \lambda^2 A - i\lambda B$$

$$A = \frac{Nb}{2\pi}$$

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

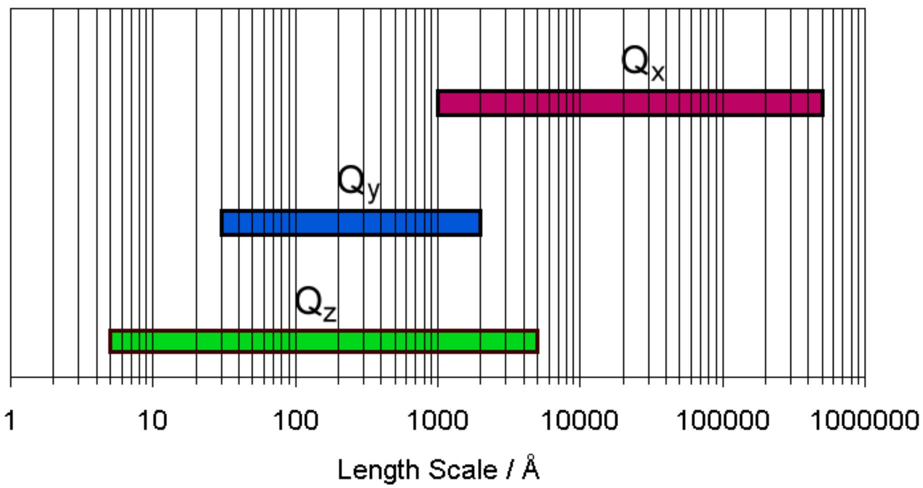






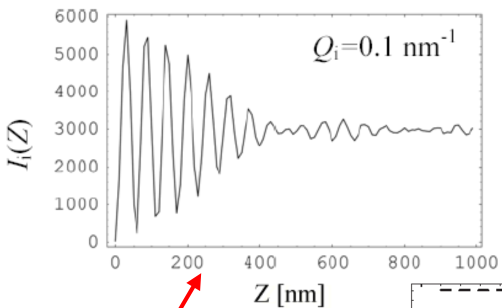
Neutron Spin-Echo

In-plane dynamic range of 50Å-42μm

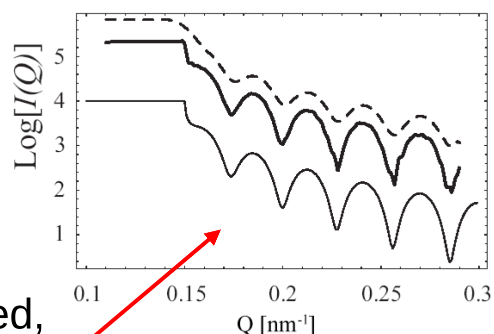


Scientific Opportunities

- **In-plane Structures**
  - Patterned Storage Media
  - Mesoporous films
  - Polymers
  - Biological membranes
  - Surfactants
- **Grazing Incidence Diffraction**
  - Surface crystalline structure
  - Surface phase transitions
  - Magnetic surface structure

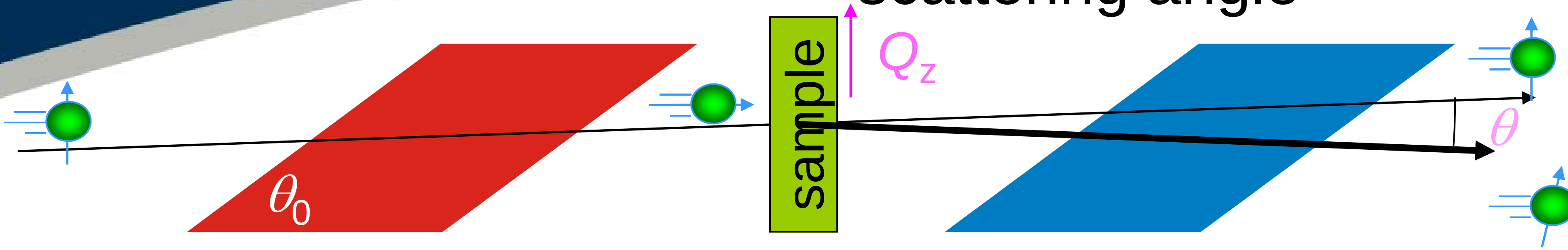


Simulated, measured signal.



Simulated, measured reflectivity.

Larmor precession codes scattering angle



Unscattered beam gives spin echo (net precession) Independent of height and angle

$$\phi = 0$$

Scattering by sample over angle *q* results in a net precession

$$\phi = c\lambda BL\cot(\theta_0)\,\theta \approx zQ_z$$

Proportional to the **spin echo length** ***z***

$$z = c\lambda^2 BL\cot(\theta_0)/2p$$

Measure polarisation

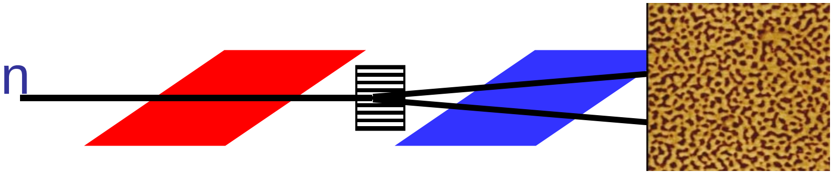
$$\frac{P}{P_0} = \int d\Omega \cos\phi f(\phi) \approx \int dQ_x dQ_y dQ_z \cos(zQ_z) S(Q)$$

Keller *et al.* Neutron News **6**, (1995) 16

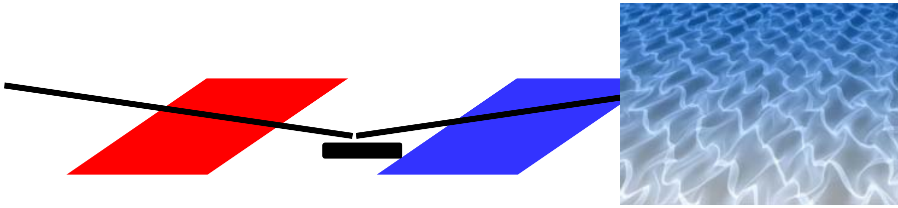
Rekveldt, NIMB **114**, 366 (1996)

5 modes of operation

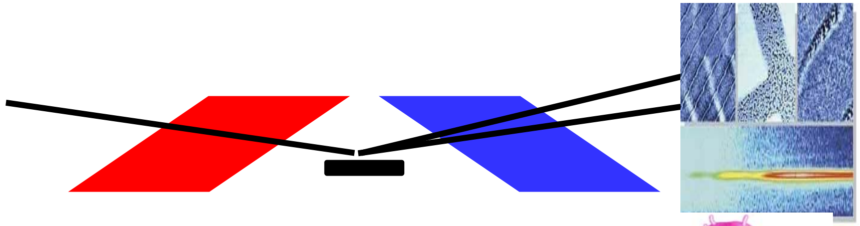
SE reflection measurements to probe in plane structure



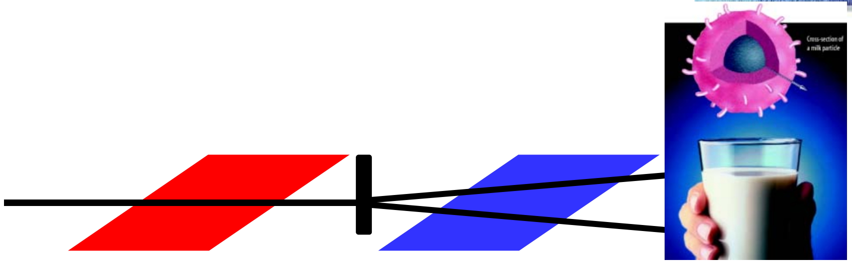
SE reflectivity with “high resolution” at low q and “wavy surface”



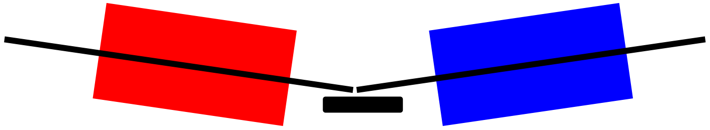
Spin-echo reflection “separation” of specular and off-specular reflection



Spin echo small angle scattering in transmission (SESANS)



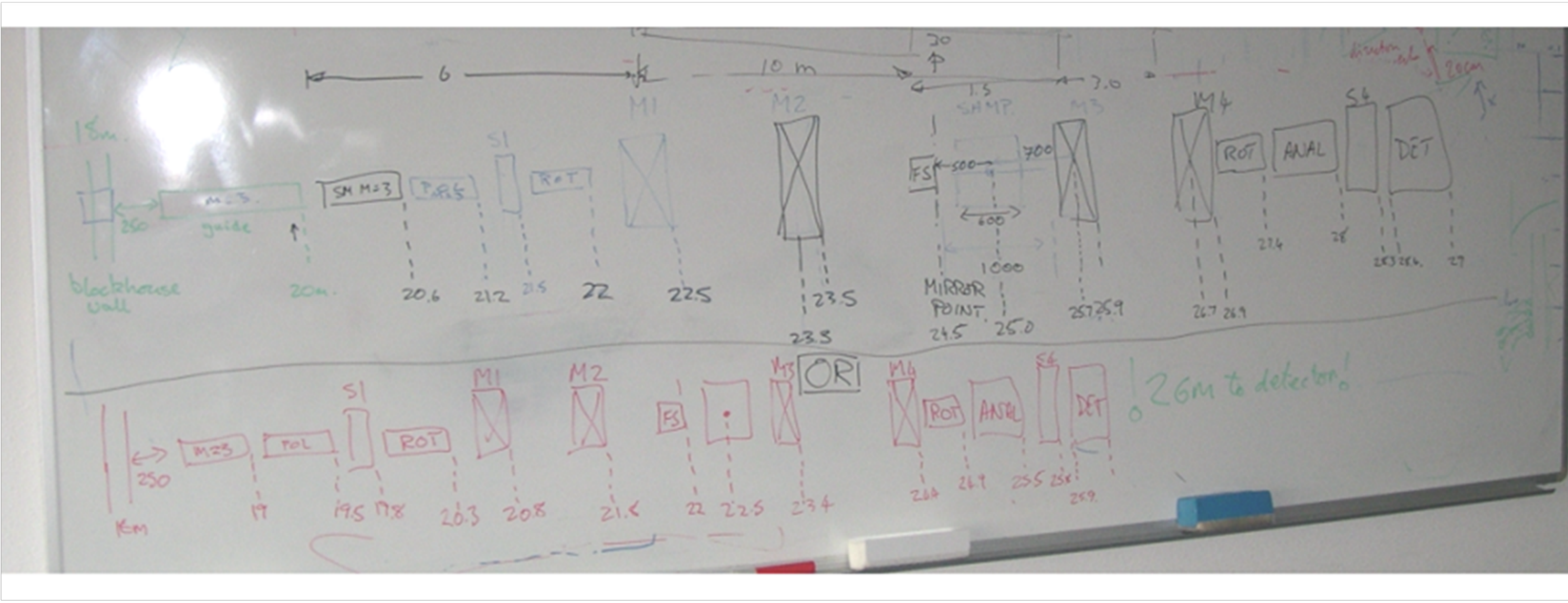
Classical Spin echo in transmission or reflection of inelastic samples



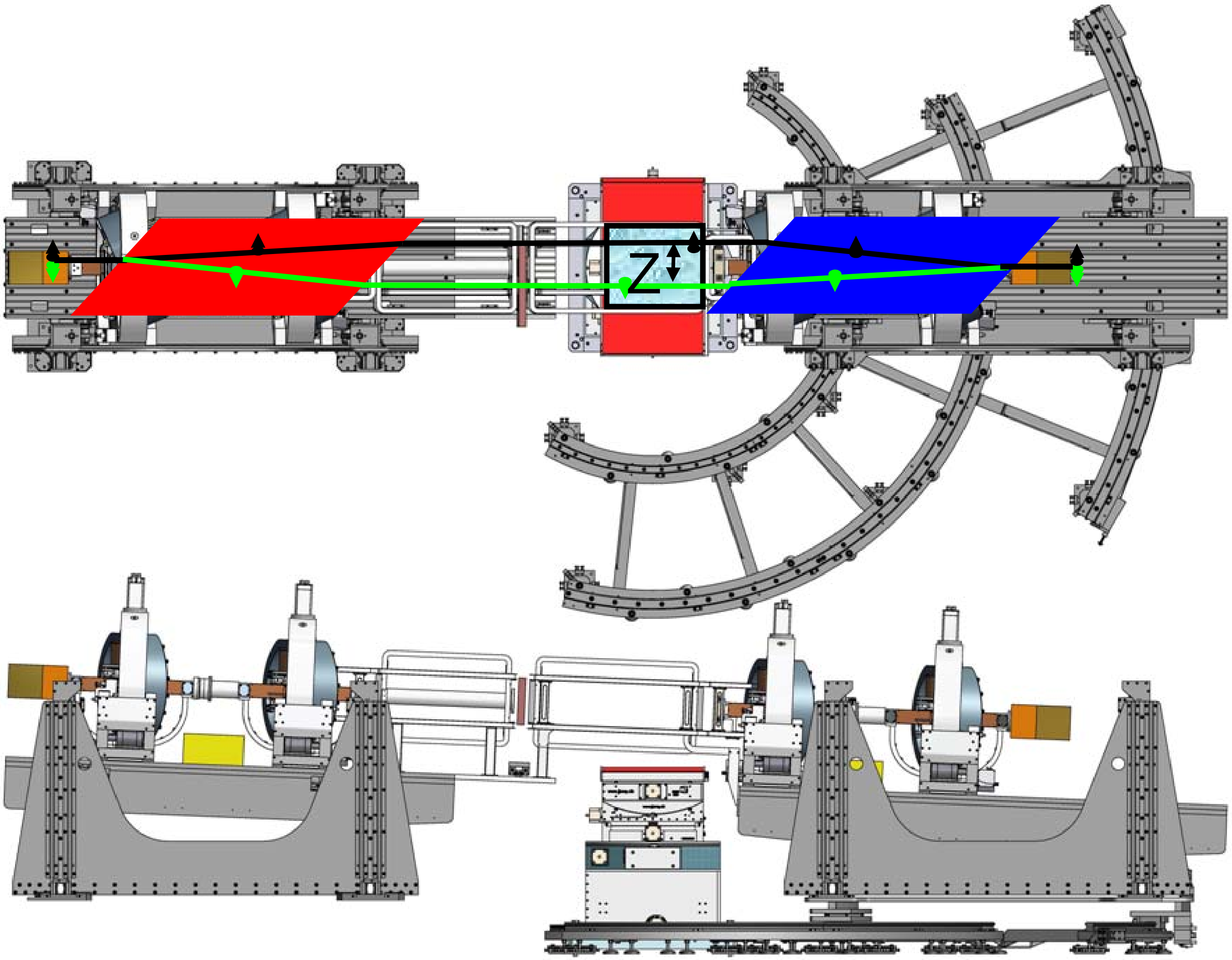
Science & Technology Facilities Council

Realisation/Design

Nov 05



Realisation/Design



Aug 08

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Realisation/Design

May 09