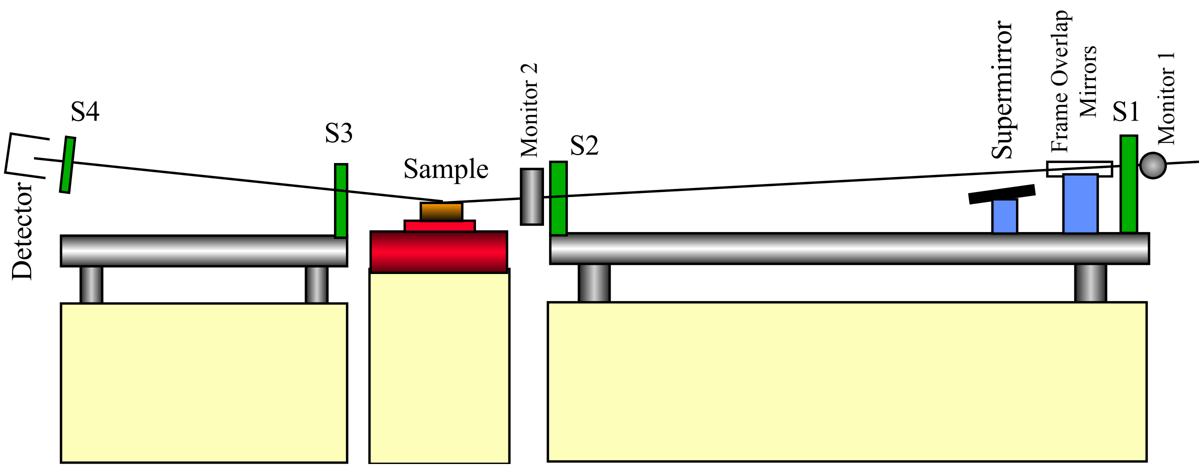
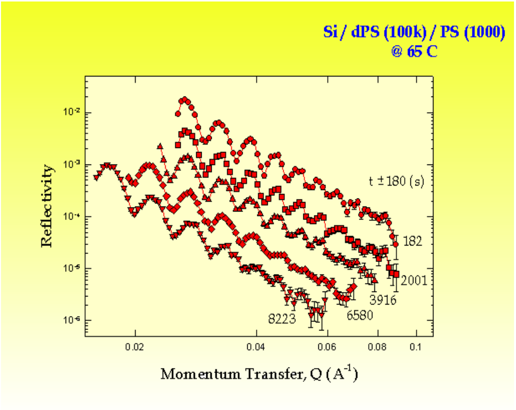
Introduction to Neutron Reflectivity

J.R.P.Webster

ISIS Facility, Rutherford Appleton Laboratory





Reflectometry

TS1

CRISP

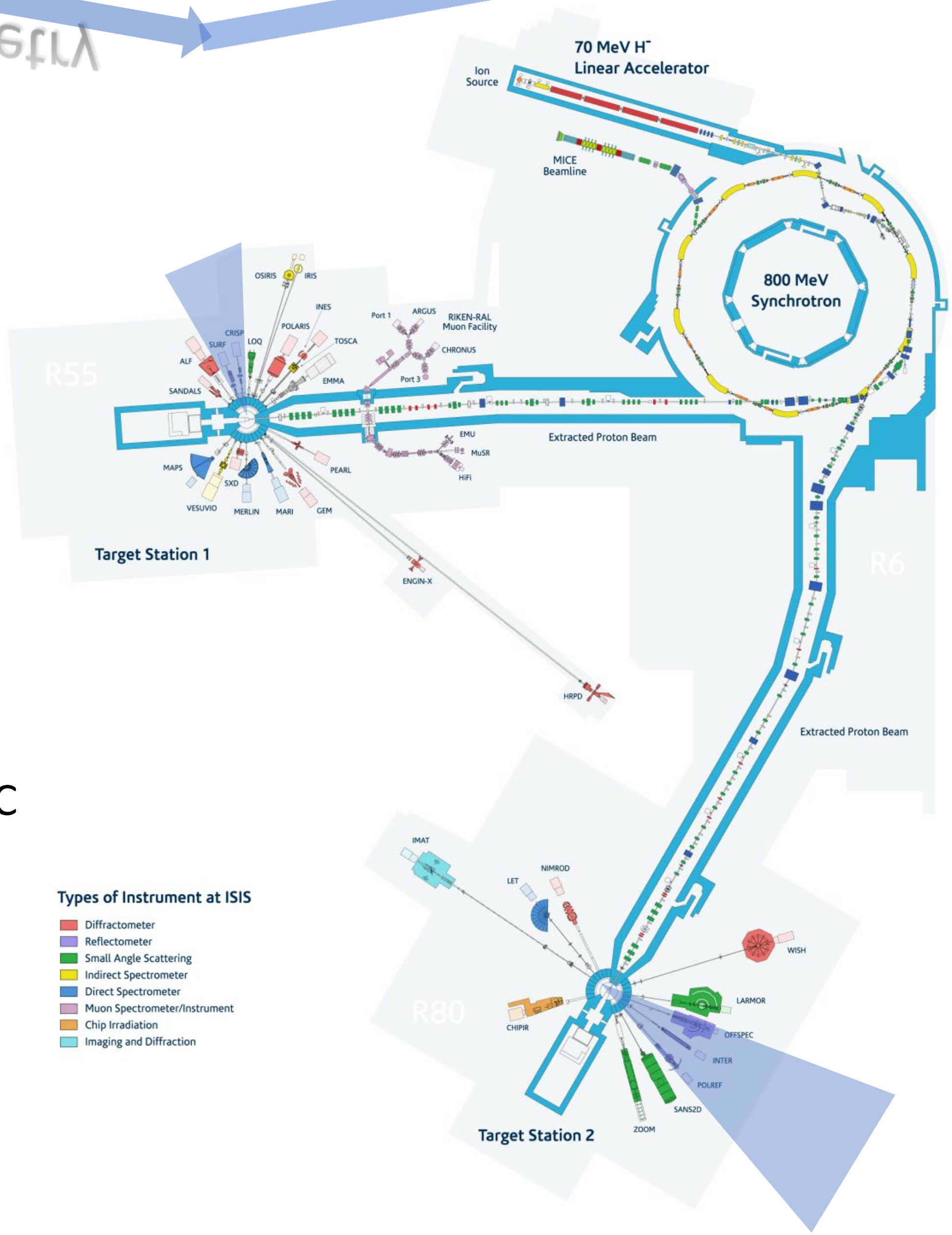
SURF

TS2

OFFSPEC

INTER

POLREF













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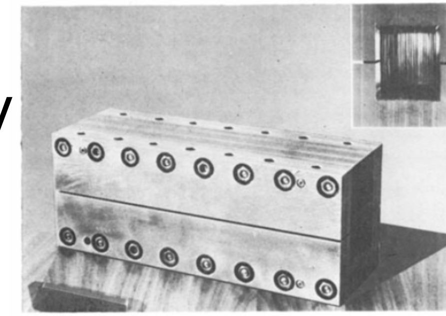
Neutrons – a tailor-made probe

- **Neutron wavelength and energy 'just right' for condensed matter** *- structure and dynamics*
- **Neutron cross-section** *- isotopic dependence*
- **H / D contrast** *- nuclear form factor*
- **Magnetic Moment** *- magnetic order*
- **Weak probe** *- theoretical interpretation*
- **Highly penetrating** *- bulk probe - complex SE*
- **Non Destructive**

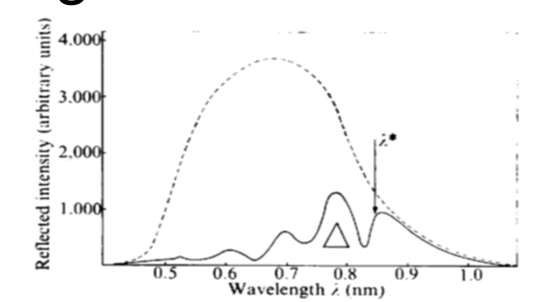
Evolution of Neutron Reflectivity (ISIS centric)



Polarising Soller Guide

1965 Koester: gravity mirror
determination of scattering lengths

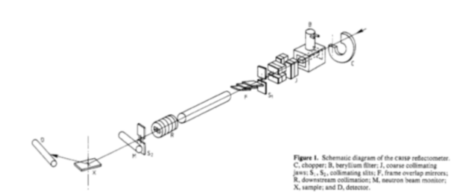
1976 Hayter, Penfold, Williams
first interference fringes



Fe/Co thin film: Nature, 262, 1976, 569

1981 Application of NR to chemical
surfaces and interfaces
(Faraday Trans, D17)

1986 Argonne IPNS polarised
reflectometer (Gian Felcher)
CRISP 1st spectrum (august)



1988 Spread monolayers (Richardson)

1998 Adsorption at the Liquid Surface
(Penfold, Thomas)

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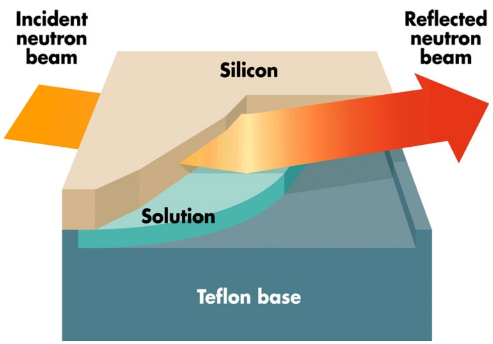
Specular reflection of neutrons from surfaces and interfaces

Analagous to optical interference, ellipsometry



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

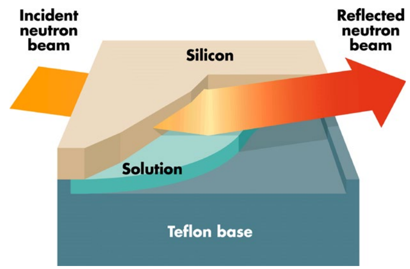
Depth Profiling : **provides information on concentration or composition profile perpendicular to the surface or interface**

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

Reflectometry

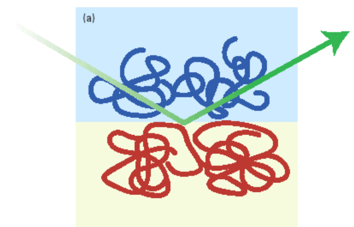
Kinetics

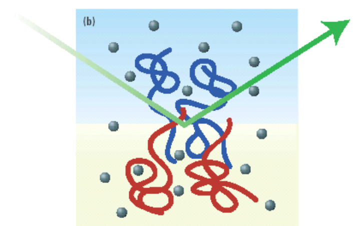
- Polymer Diffusion
- Critical exponents in SCF
- Protein unfolding
- Non equilibrium surfactant films
- Temporal resolution of
  - Ion transfers
  - Solvent transfers
  - Polymer structure



Model Devices

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



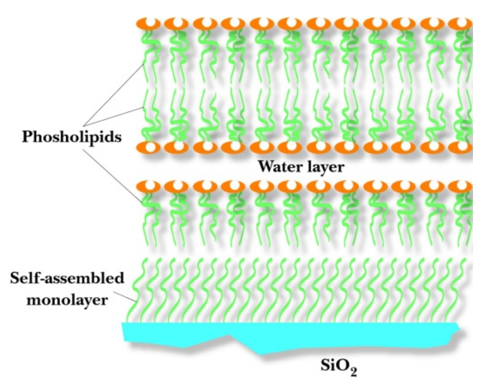


Surfactants

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

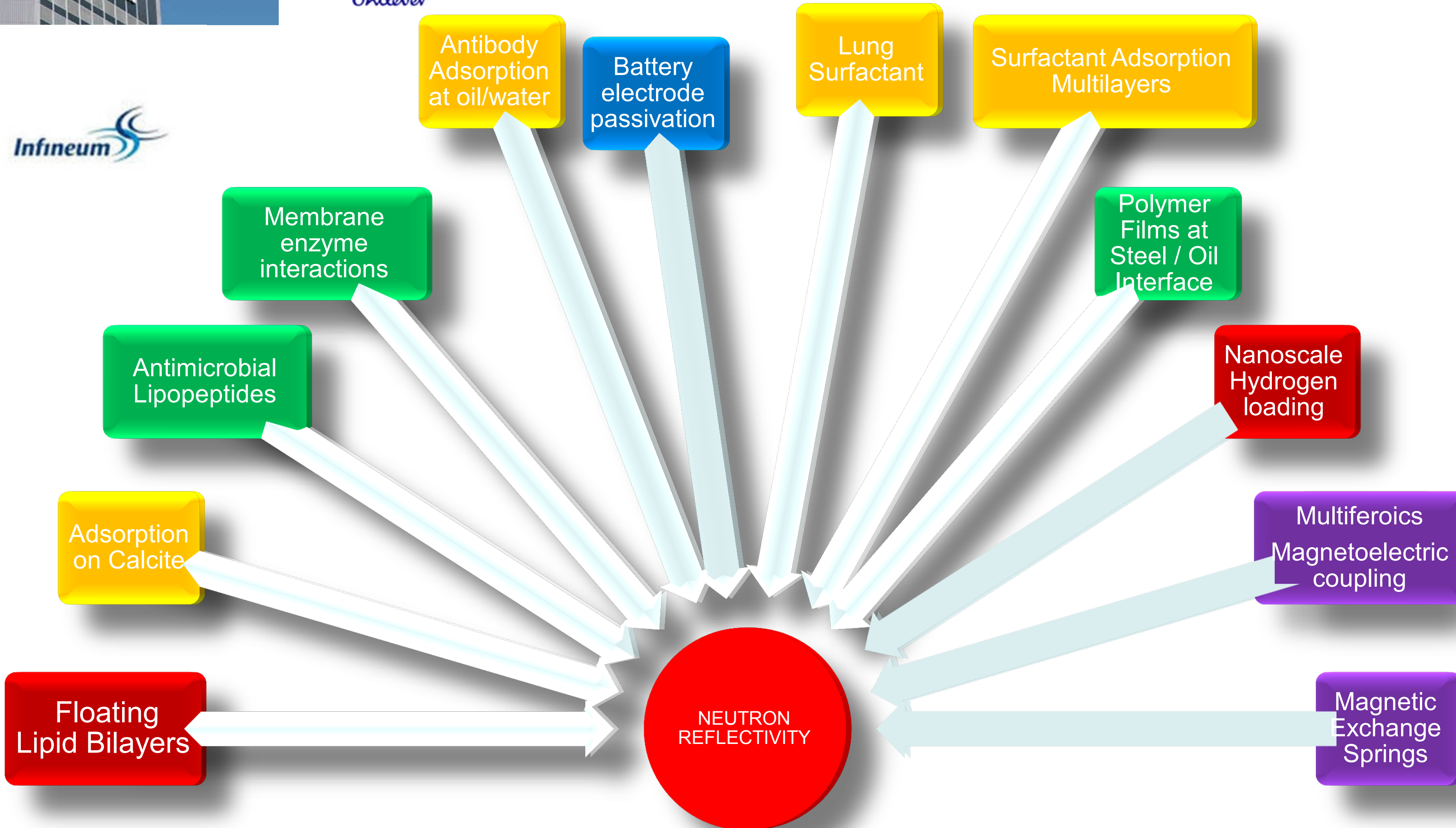
Electrochemistry

- 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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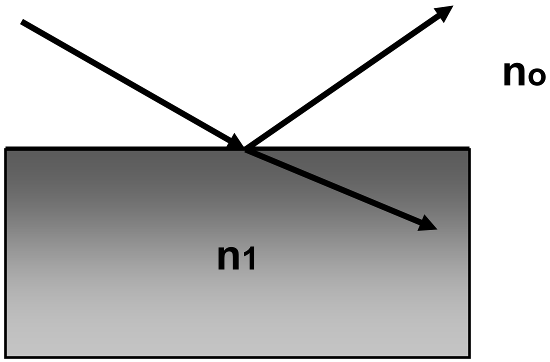
Specular reflection of neutrons



Refractive index defined using the usual convention in optics:

$$n = {k_1}/{k_o}$$

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

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

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

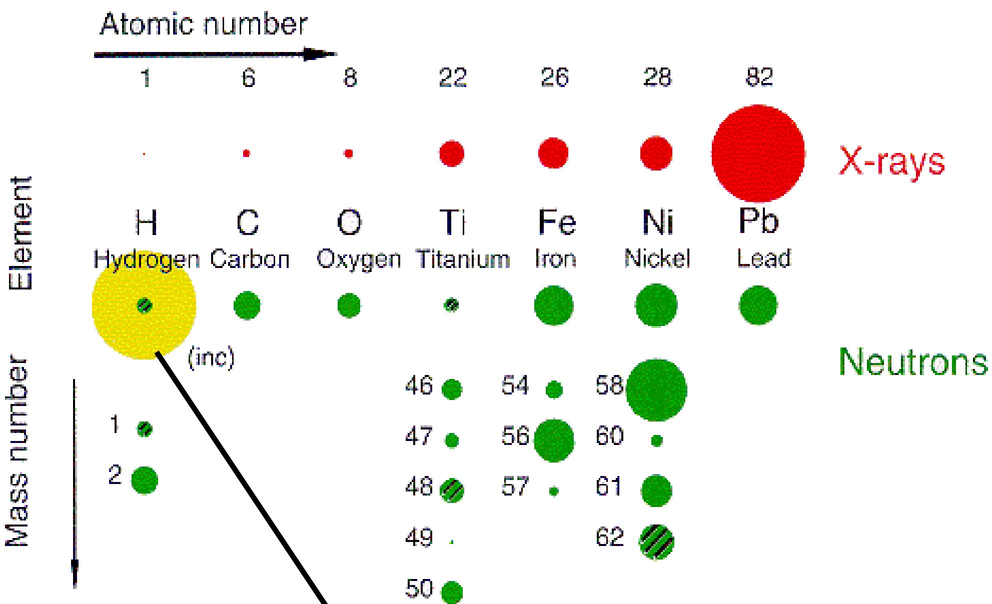
X-rays

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

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

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

Refractive Index for neutrons



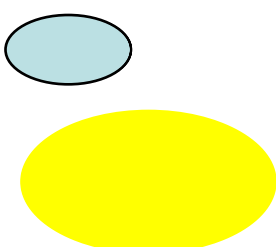
The diameters of the circles shown scale with the scattering amplitude f_x (sin Θ= 0) for x-rays, and b_{coh} * 10 for neutrons. Hatching indicates negative scattering amplitudes.

$$n = {k_1}/{k_0}$$

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

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

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

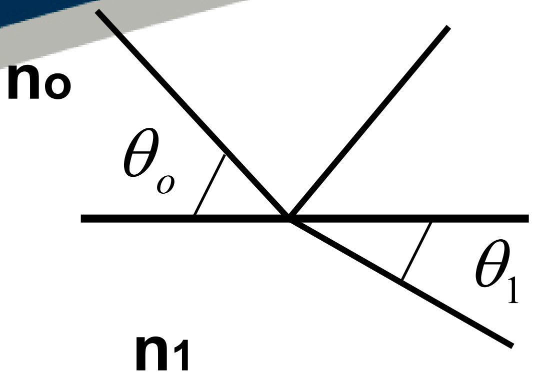


H -0.374 x 10^{-12} cm

D 0.667 x 10^{-12} cm

n < 1.0 hence TOTAL EXTERNAL REFLECTION

Specular reflection of neutrons
(some basic optics)



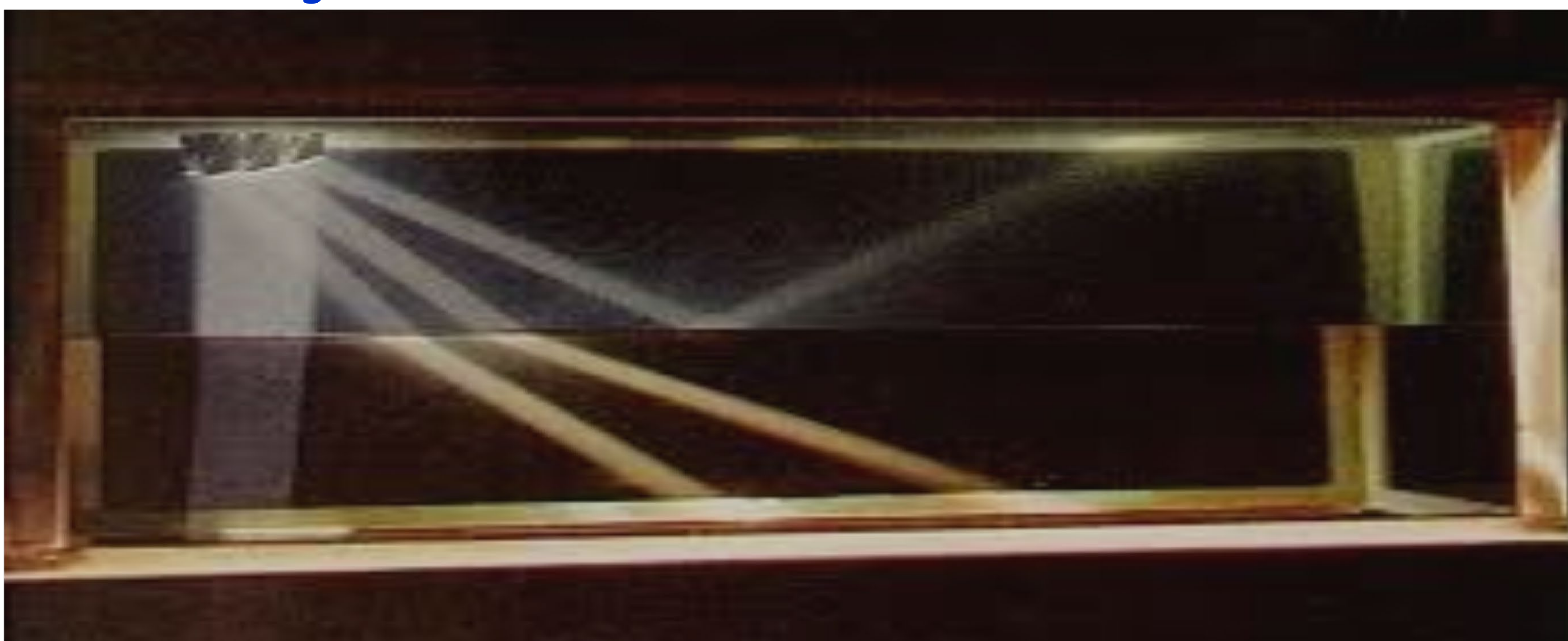
From Snell's Law, $n = \frac{n_1}{n_0} = \frac{\cos\theta_0}{\cos\theta_1}$

At total reflection $\theta_0 = \theta_c$

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

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

Critical angle



Specular reflection of neutrons
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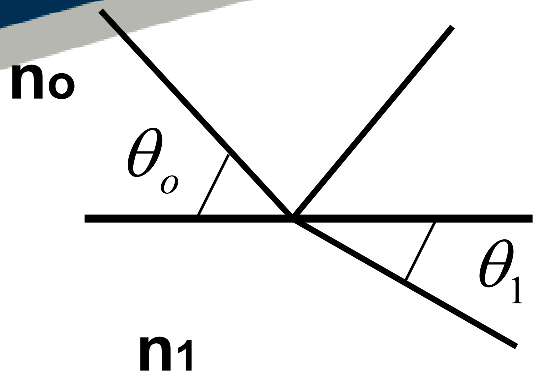

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Critical angle

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

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

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 $\theta = \theta_c$

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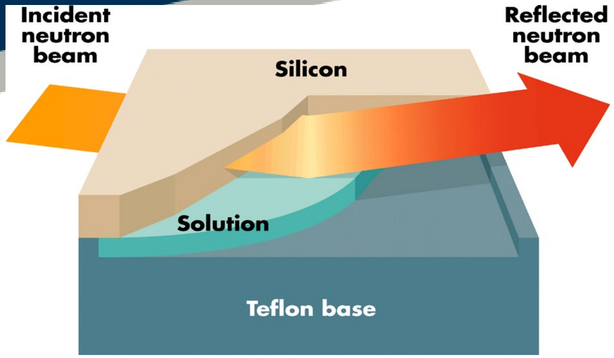
Some typical values for θ_c and σ_a

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
Al	0.231

Specular Neutron Reflection (simple interface)

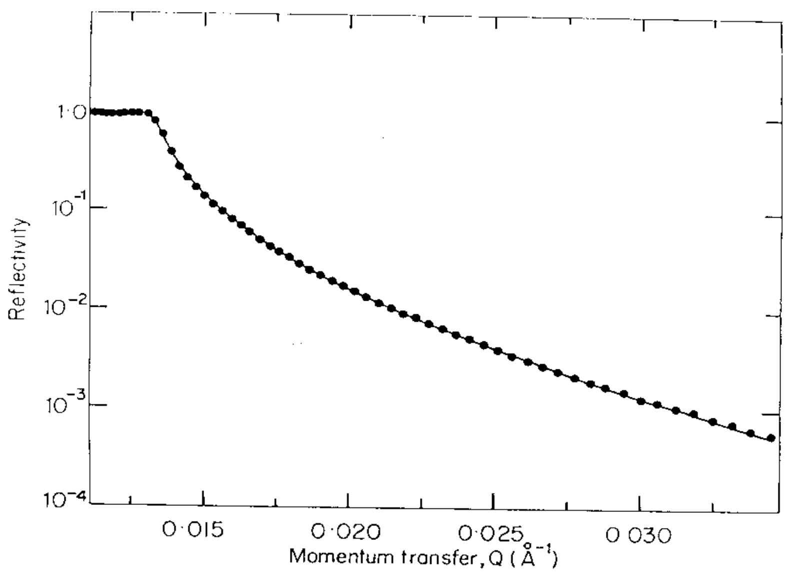


Within **Born Approximation** the Reflectivity is given as,

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

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

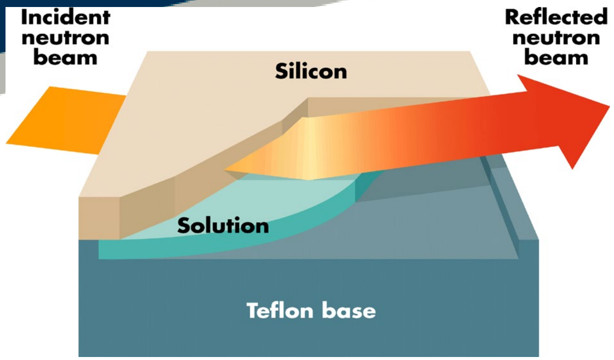
Reflectivity from a simple single interface is then given by **Fresnels Law**



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

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

Specular Neutron Reflection (simple interface)



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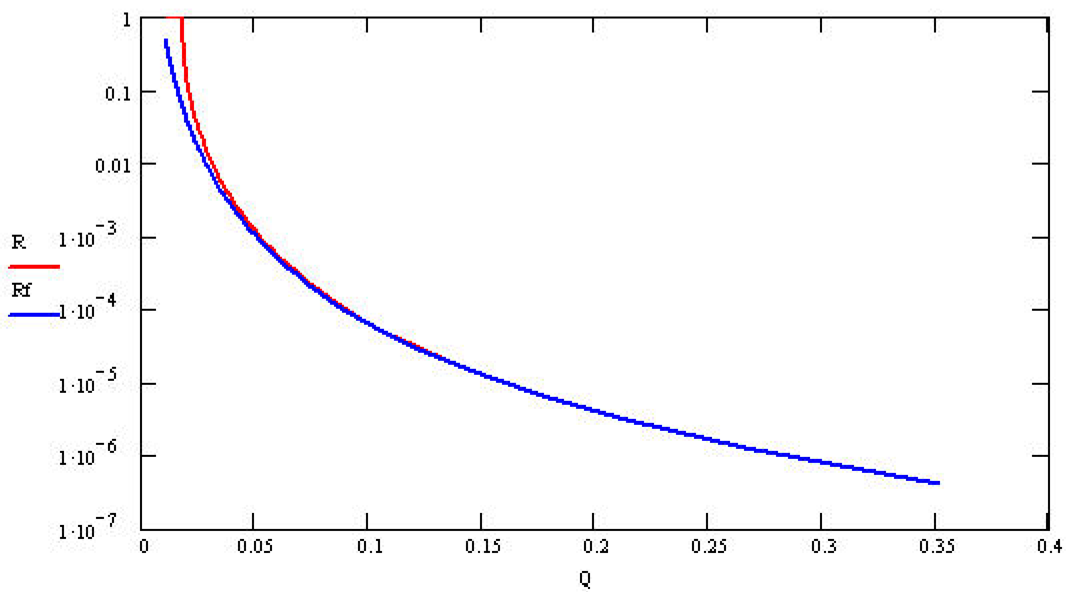

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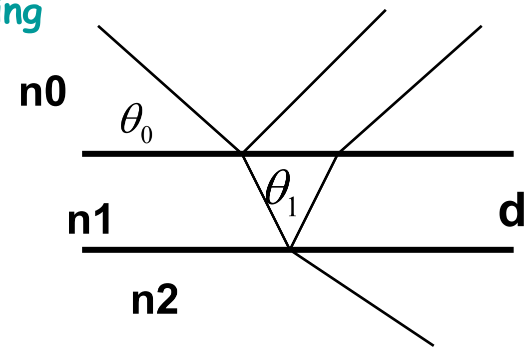
Specular Neutron Reflection

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



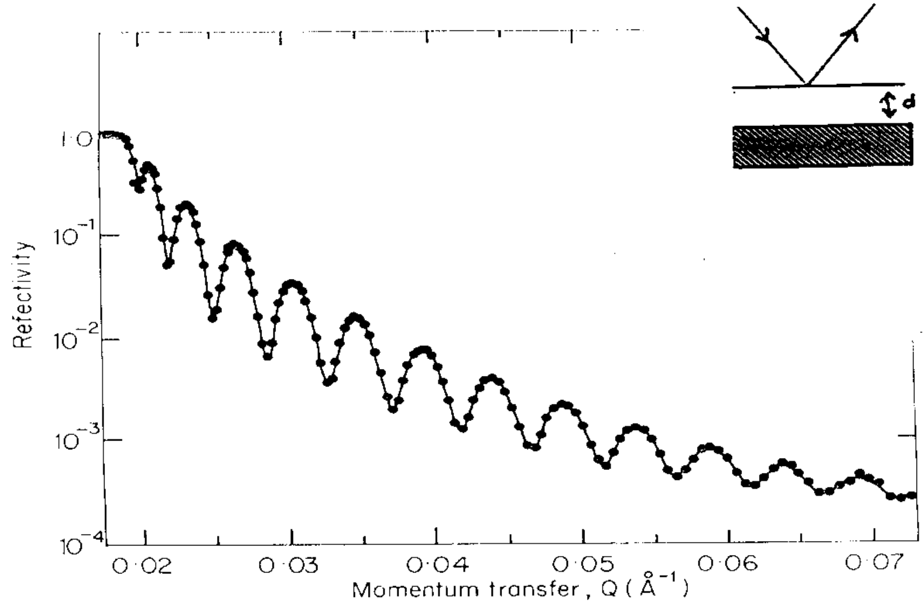
For a single thin film at an interface

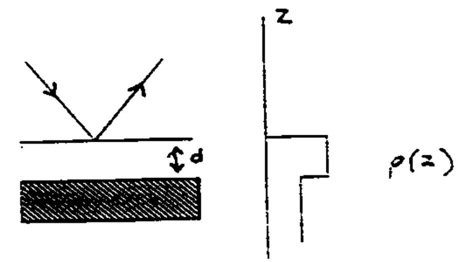
$$R(Q) = \left| \frac{r_{01} + r_{12} e^{-2i\beta}}{1 + r_{01} r_{12} e^{-2i\beta}} \right|^2$$

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

$$p_i = n_i \sin\theta$$

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





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For a single thin film :

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

For Q>>Q_c :

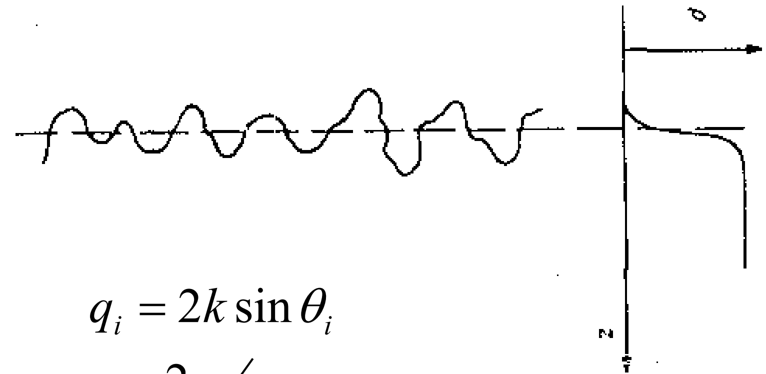
$$R(Q) \sim \frac{16\pi^2}{Q^4}\left[(\rho_1 - \rho_0)^2 + (\rho_2 - \rho_1)^2 + 2(\rho_1 - \rho_0)(\rho_2 - \rho_1)\cos(Qd)\right]$$

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

FRINGE SPACING :

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

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.

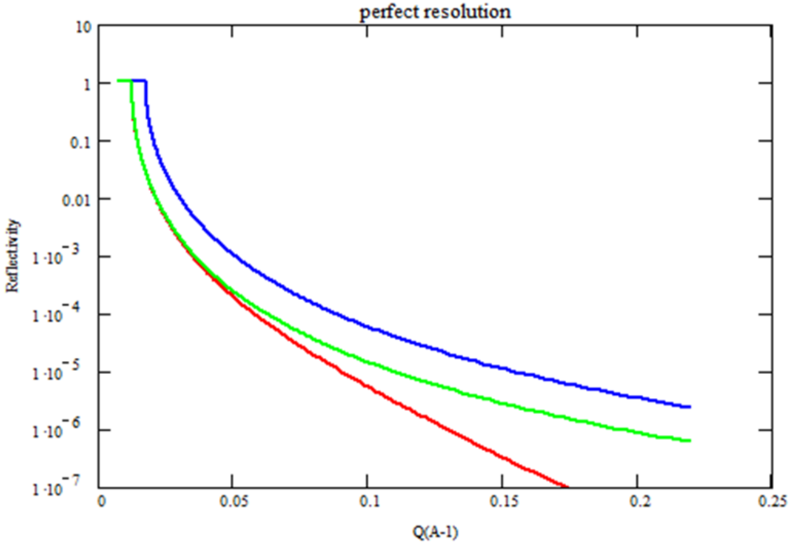
(Nevot, Croce, Rev Phys Appl 15 (1980) 125, Sinha, Sirota, Garoff, Stanley, Phys Rev B 38 (1988) 2297)

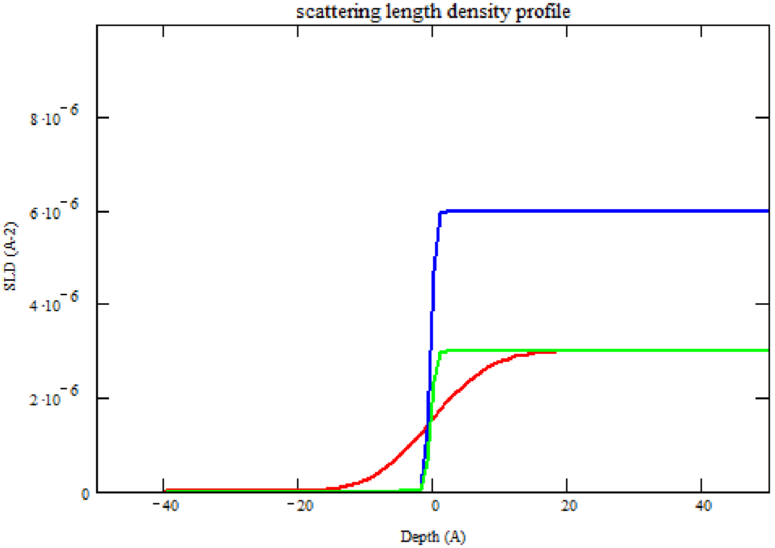
Can be also applied to reflection coefficents in formulism for thin films,

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

From specular reflectivity cannot distinquish between roughness and diffuse interface

Reflectivity from a simple interface





Effect of roughness and sld

Glass optical flat

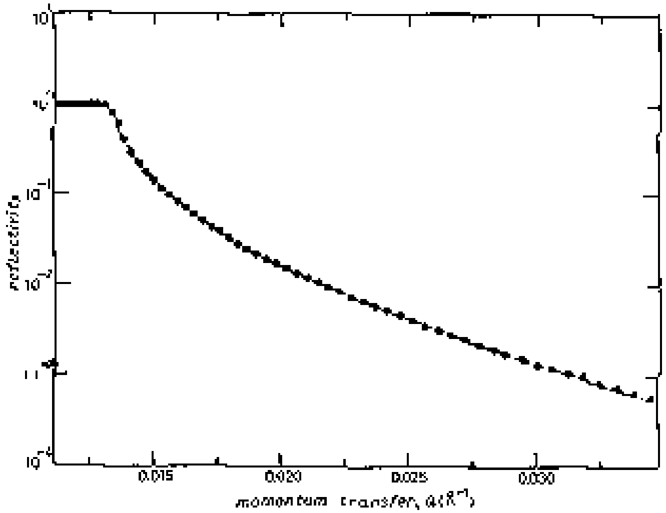
$$\theta = 0.35$$

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

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

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

Penfold & Thomas 1990



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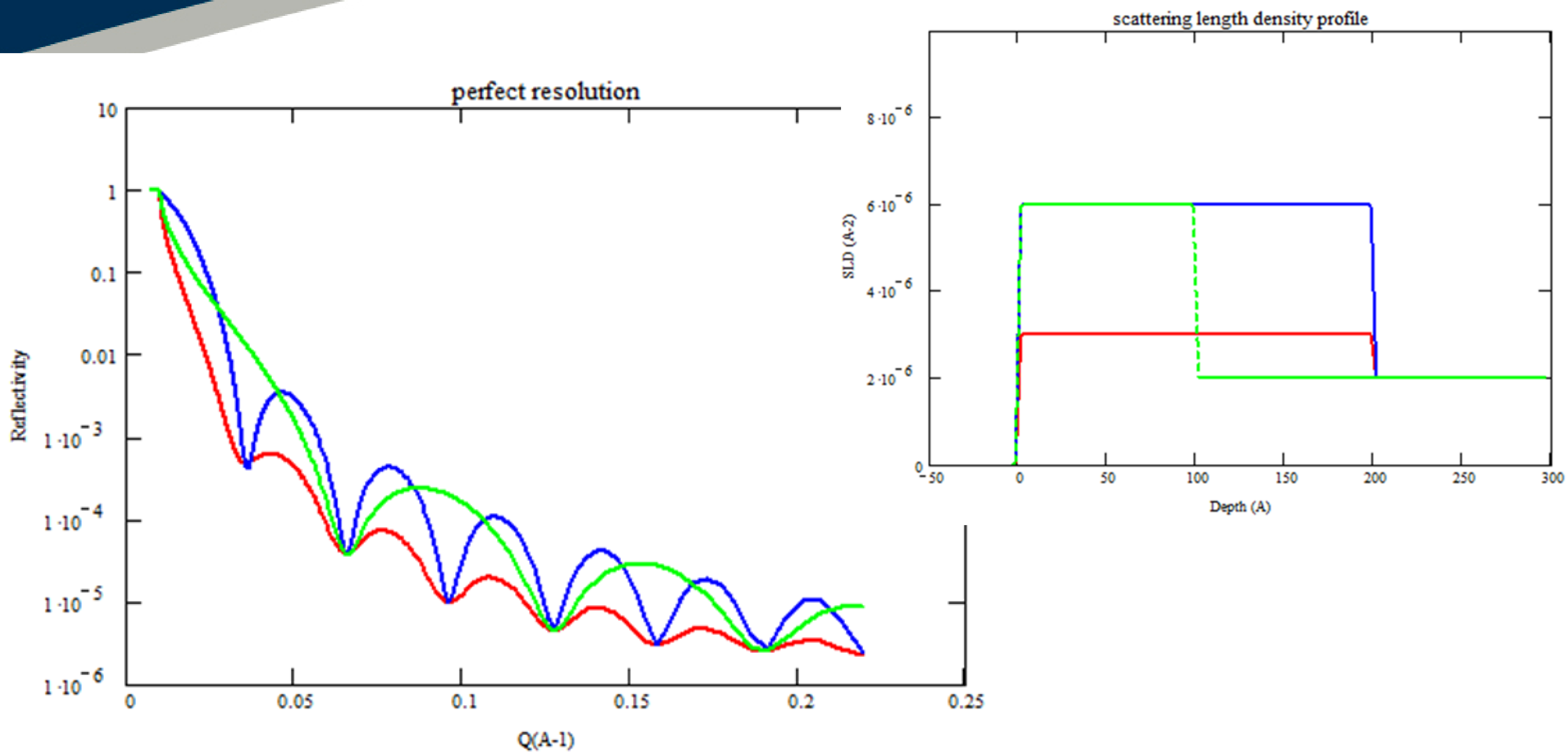
Reflectivity from thin films



Effect of film thickness and refractive index

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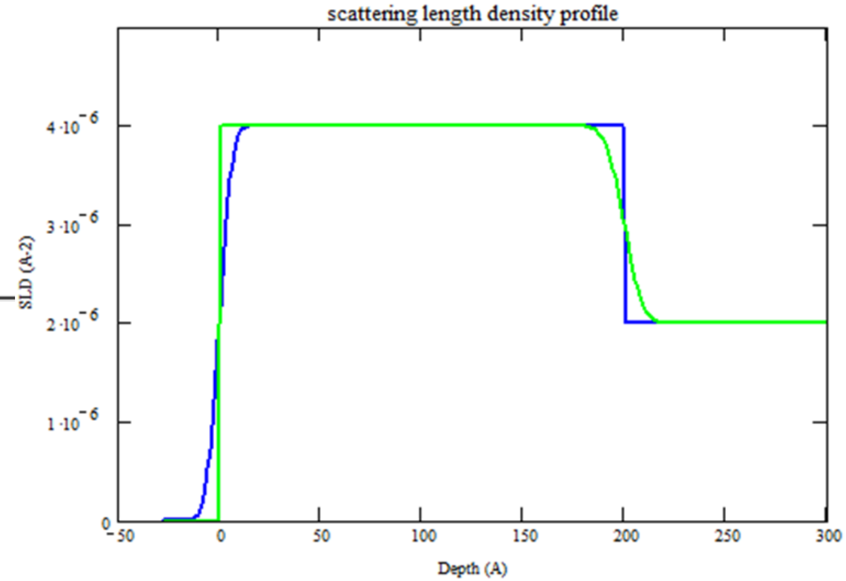
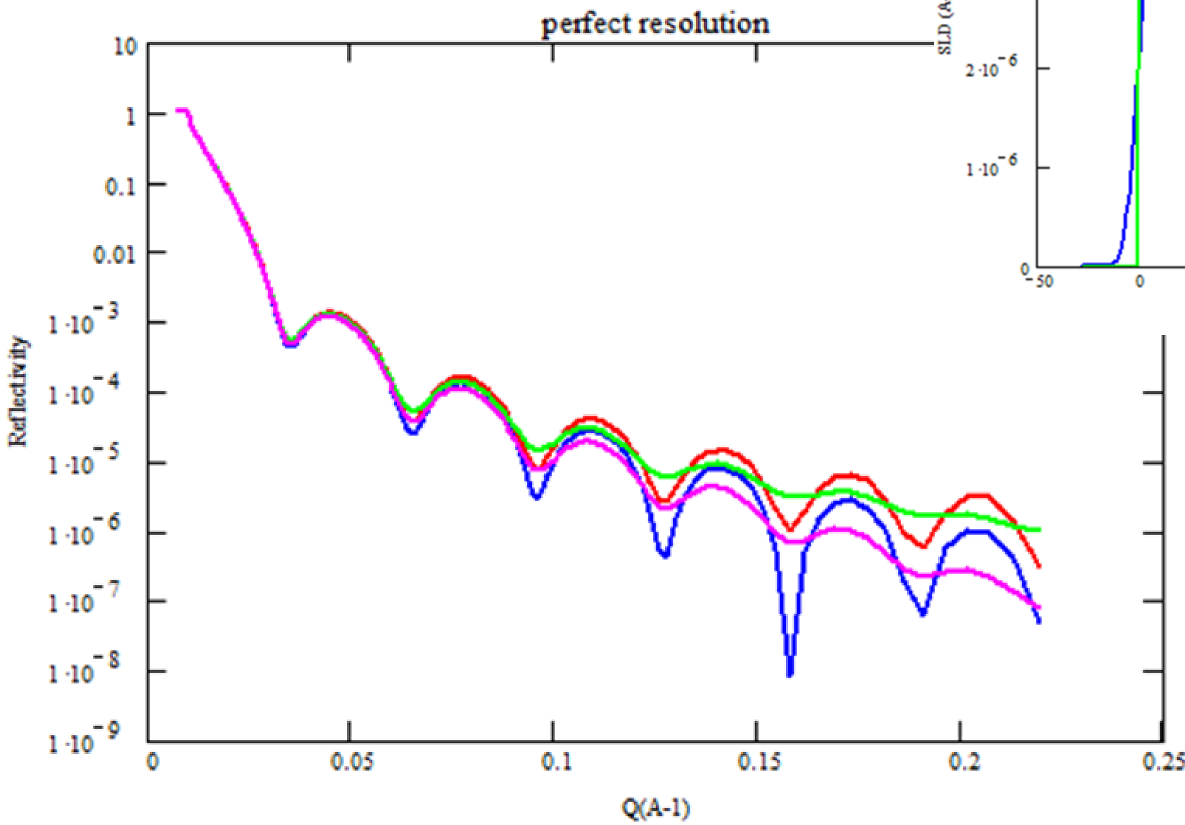
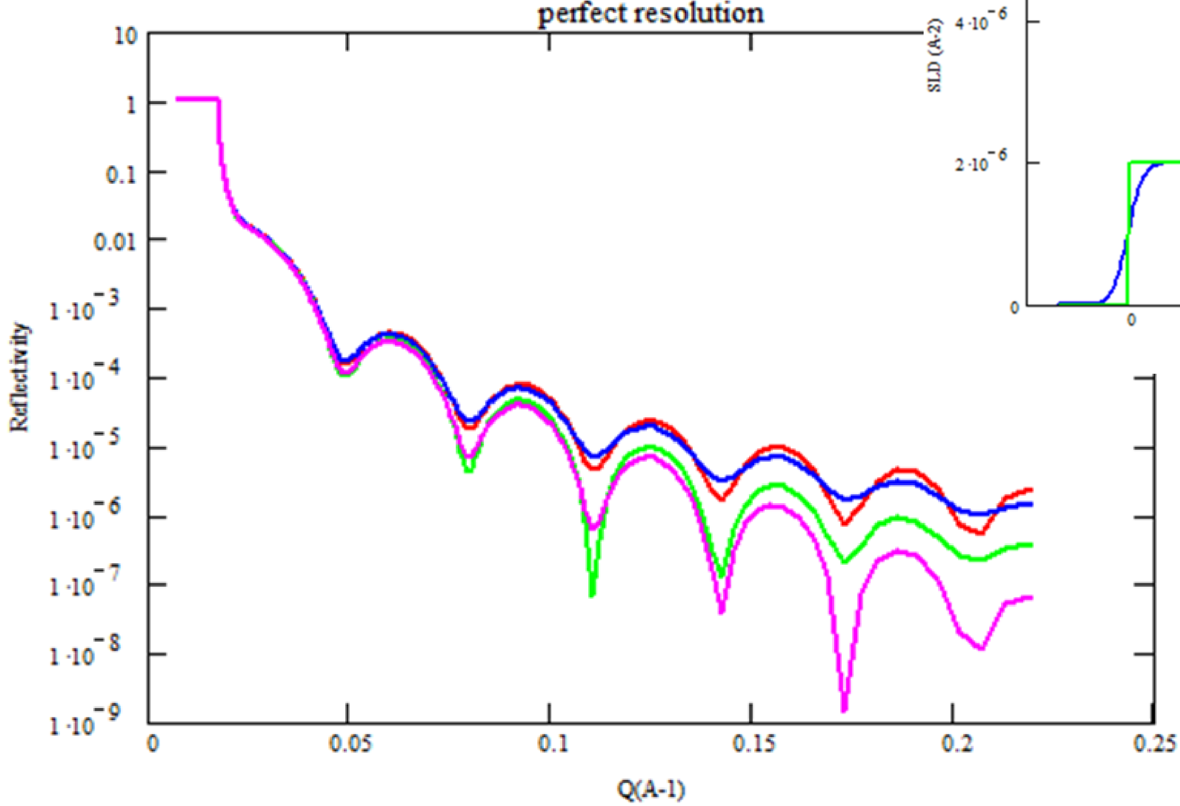
Reflectivity from thin films

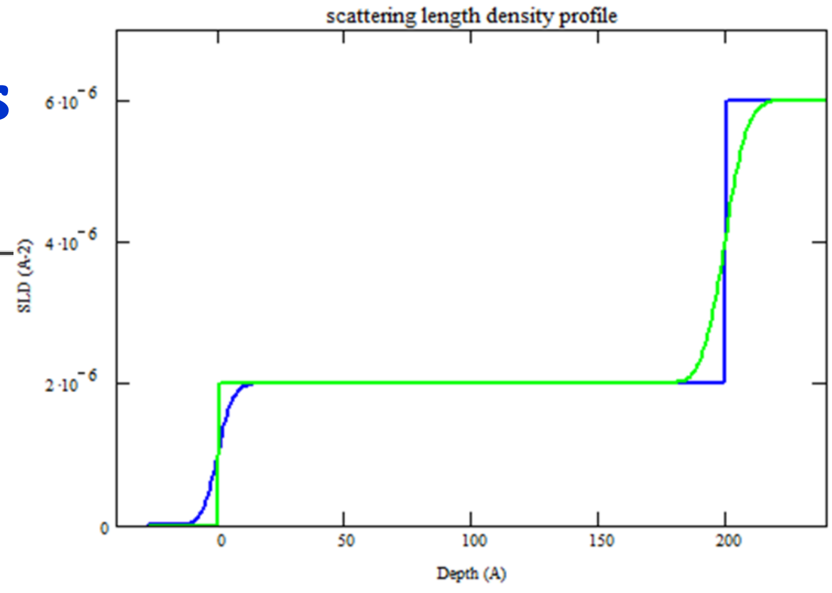




Effect of interfacial roughness

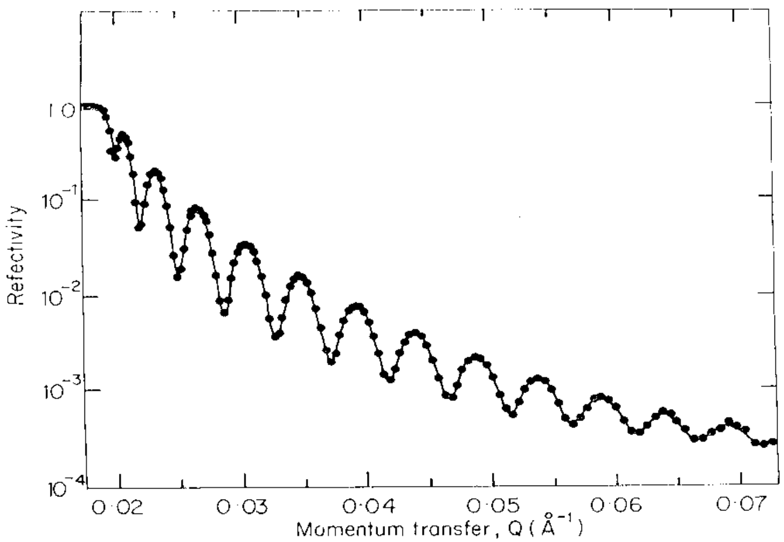
Reflectivity from thin films





Effect of interfacial roughness

Reflectivity from a thin film



Deuterated L-B film on silicon

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

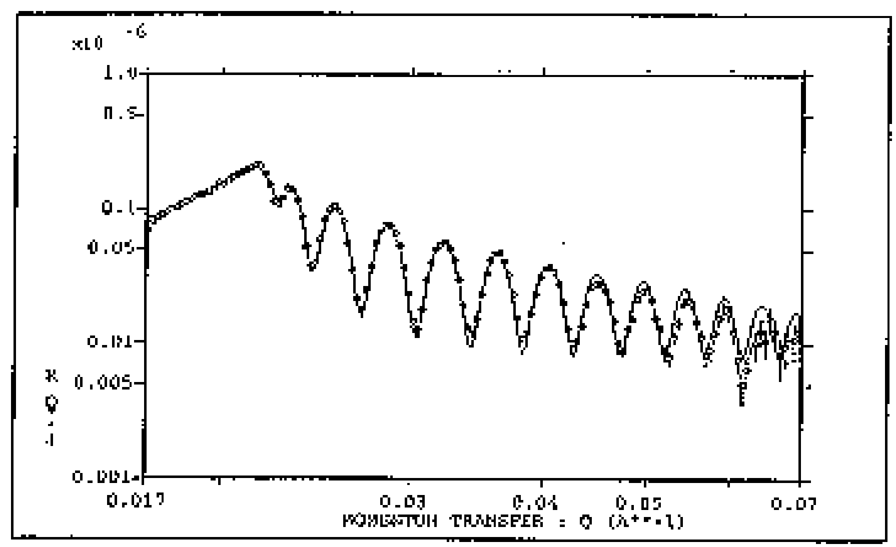
$$Nb = 0.74x10^{-5}\,\text{A}^{-2}$$

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

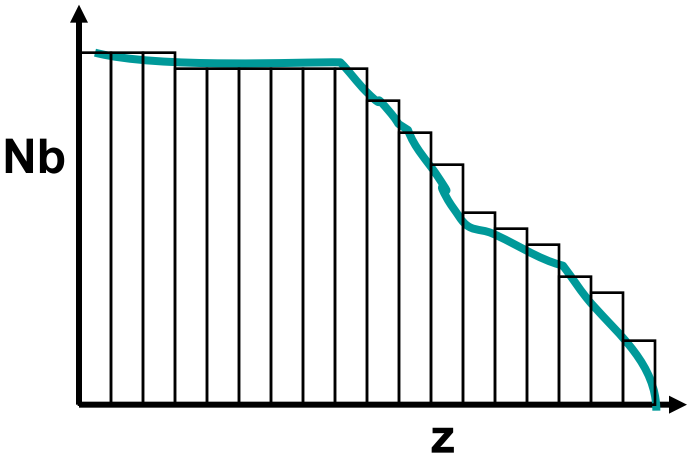
NiC film on silicon

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

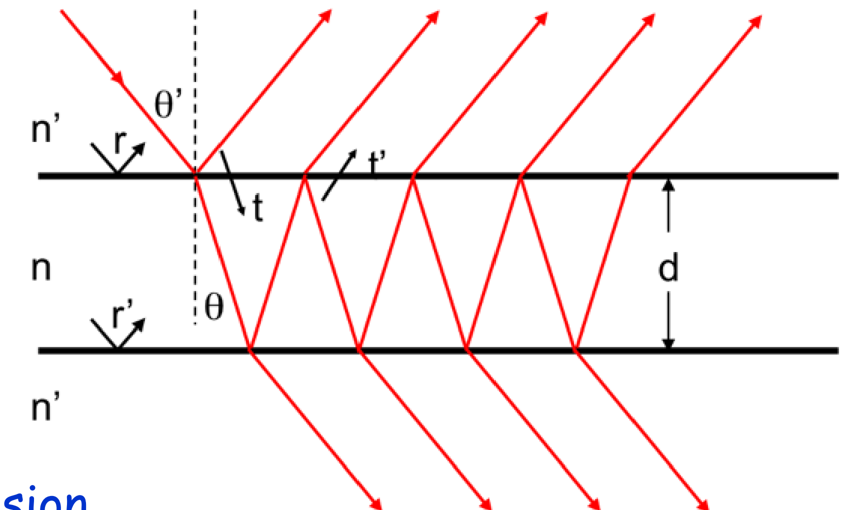
$$\theta = 0.5, \Delta\theta = 4\%, \sigma_1 = 10, \sigma_2 = 15\text{A}$$



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)

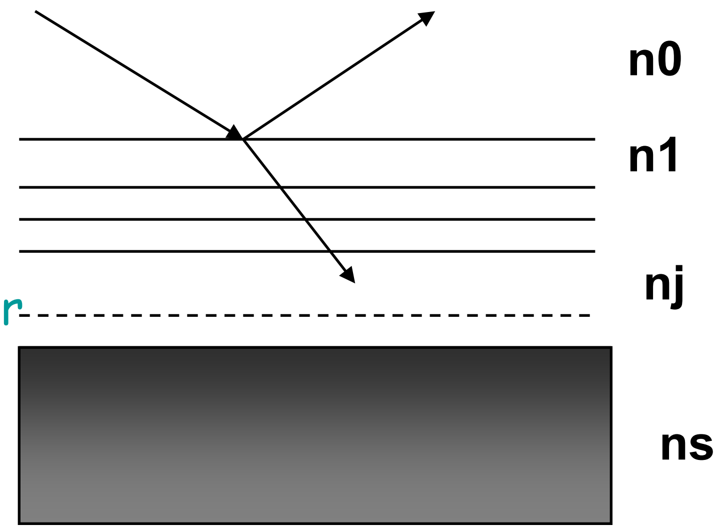
Phase change on traversing film, $\delta_1 = \frac{2\pi}{\lambda} n_1 d_1 \sin\theta_1$

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

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)

$$p_j = n_j \sin\theta_j$$

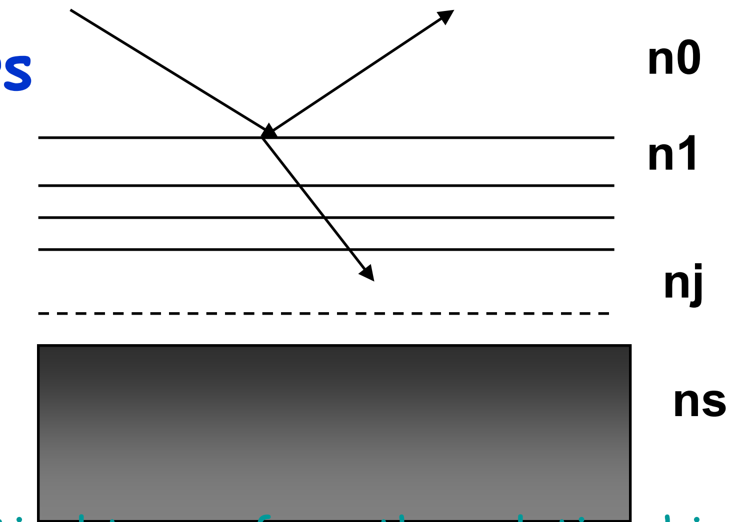
$$\beta_j = (2\pi/\lambda) n_j d_j \sin\theta_j$$

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

The resultant reflectivity is

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

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,

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

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

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

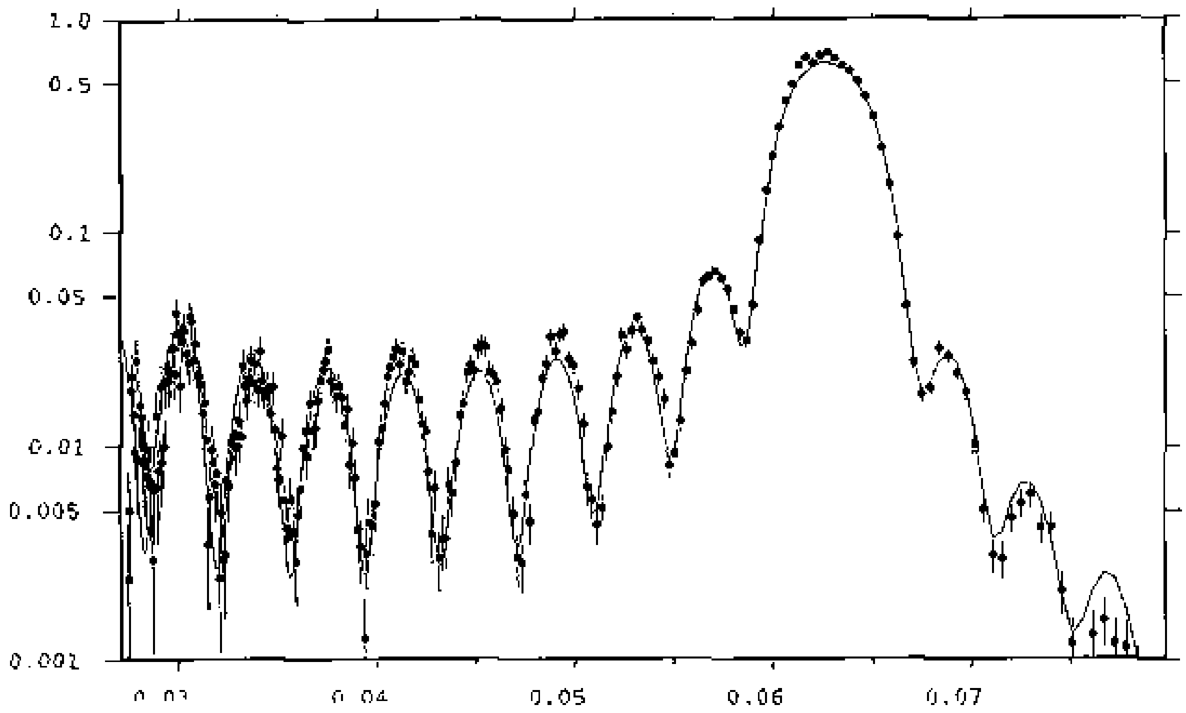
To include roughness,

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

The resultant Reflectivity is then,

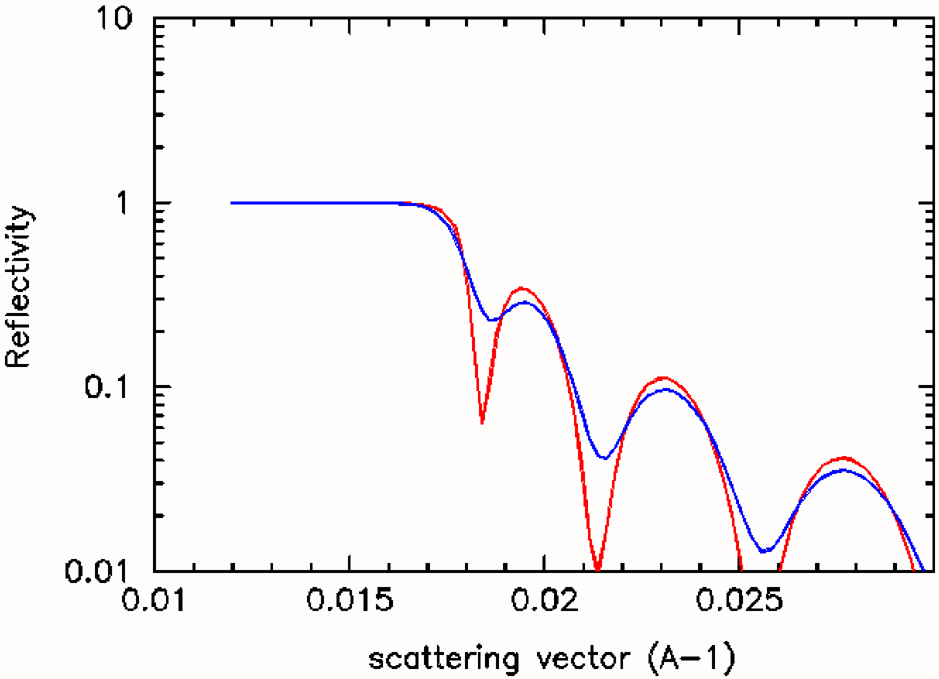
$$R = CC^* / AA^*$$

Multiple Layer films



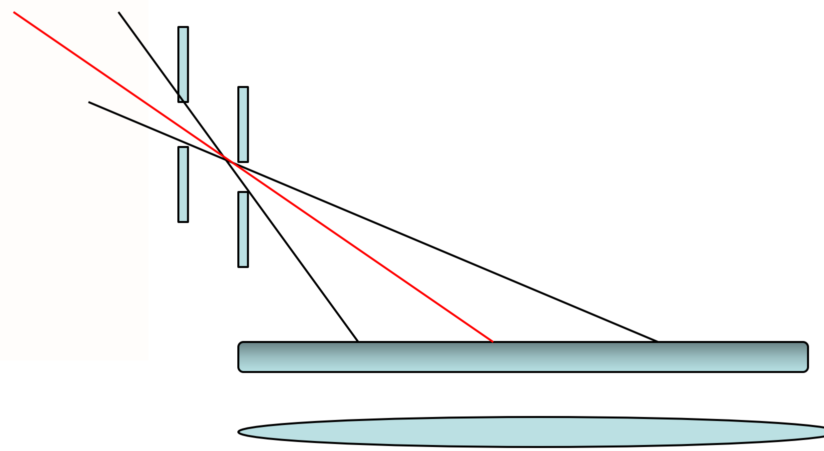
Region around 1st order Bragg peak for Ni/Ti multilayer
15 bilayers (46.7, 1.0 x 10-5 / 55.7,-0.13x10-5)

Effects of resolution



$$\frac{\Delta Q^2}{Q^2} = \frac{\Delta t^2}{t^2} + \frac{\Delta \theta^2}{\theta^2}$$

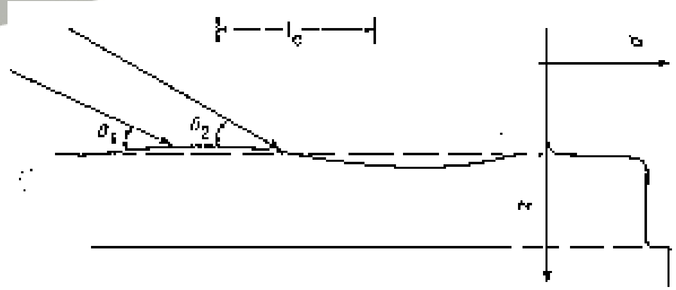
On ISIS reflectometers resolution is dominated by collimation

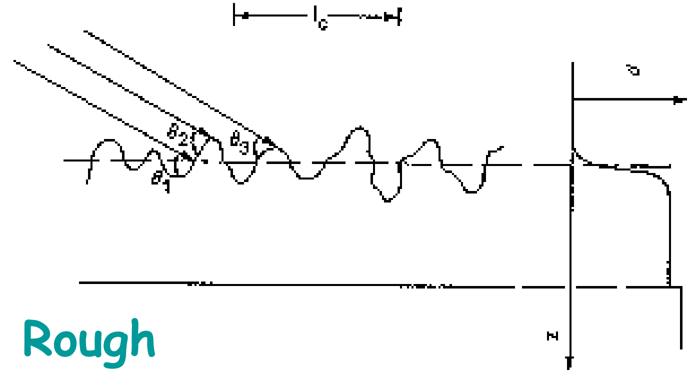


1000 Å film on Si , ΔQ/Q 2%, 6%

Damps interference fringes, rounds critical edge

Surface roughness and Waviness





Curvature > coherence length ⇒ Rough

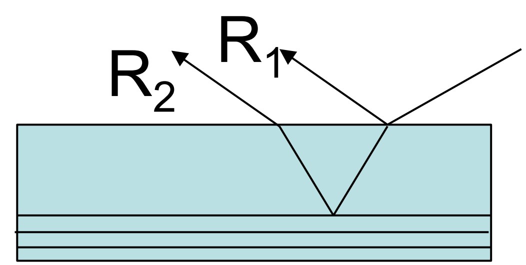
Curvature < coherence length ⇒ Waviness

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

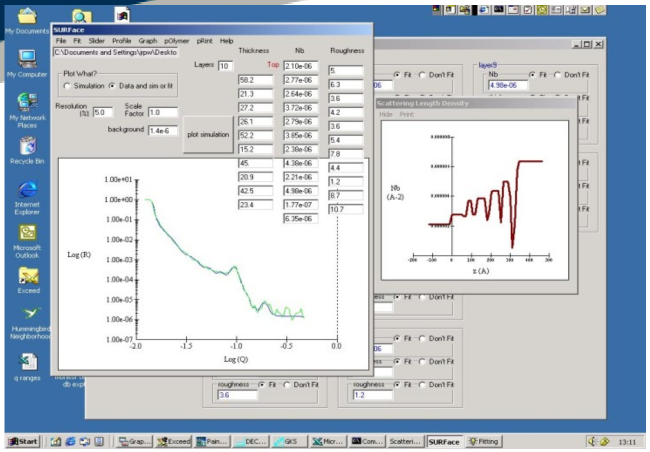
Incoherent reflectivity from 2 surfaces, separated by an adsorbing media:

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

Thickness > coherence length
A(Q) ~ Beer-Lambert



Model fitting Reflectivity data

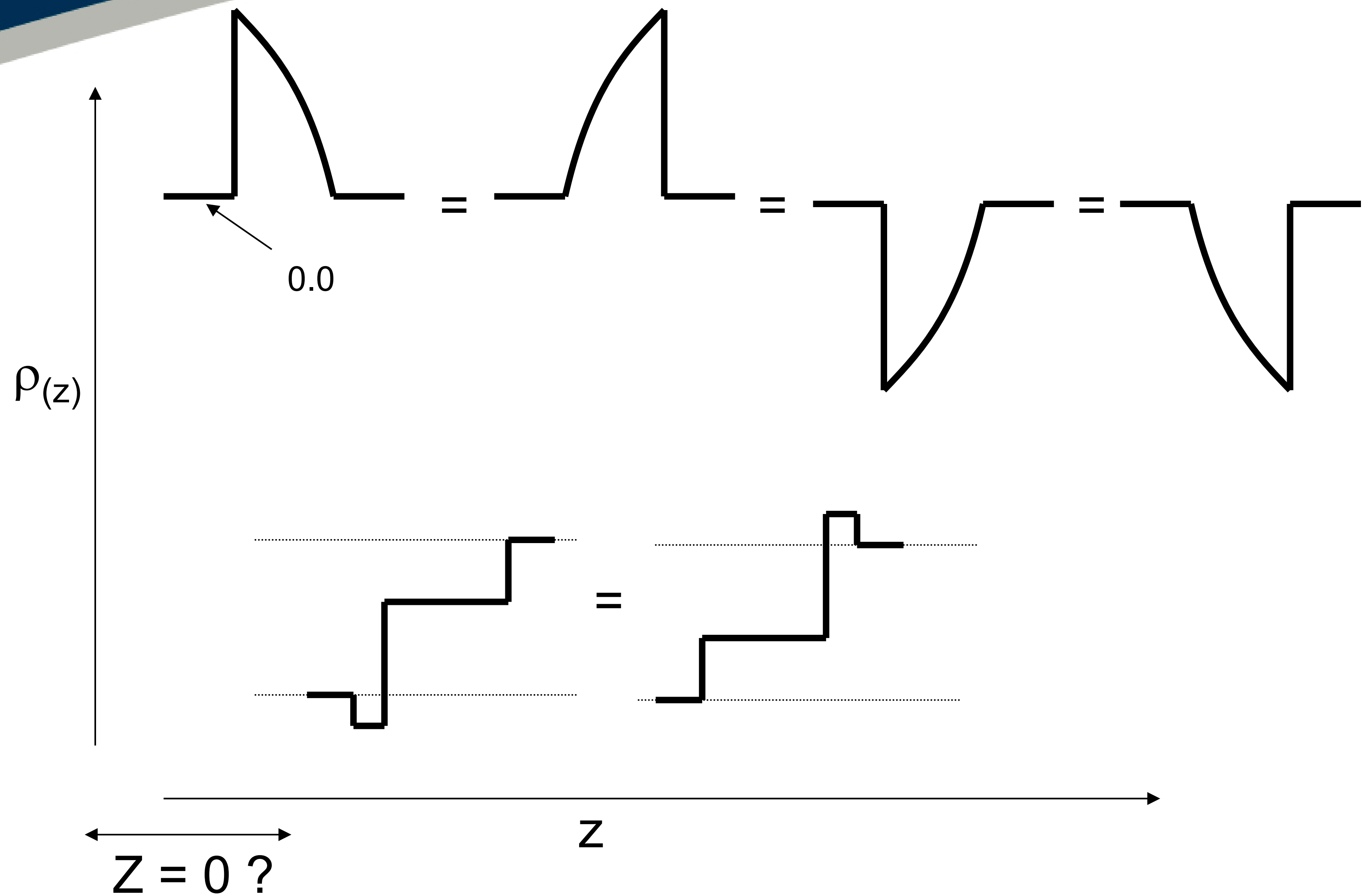


reflectivity → Scattering length density

- Uniqueness ?
- Resolution ?
- Model dependent / over interpretation 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

D. Sivia et al., J. Appl. Phys 70, 732 (1991)



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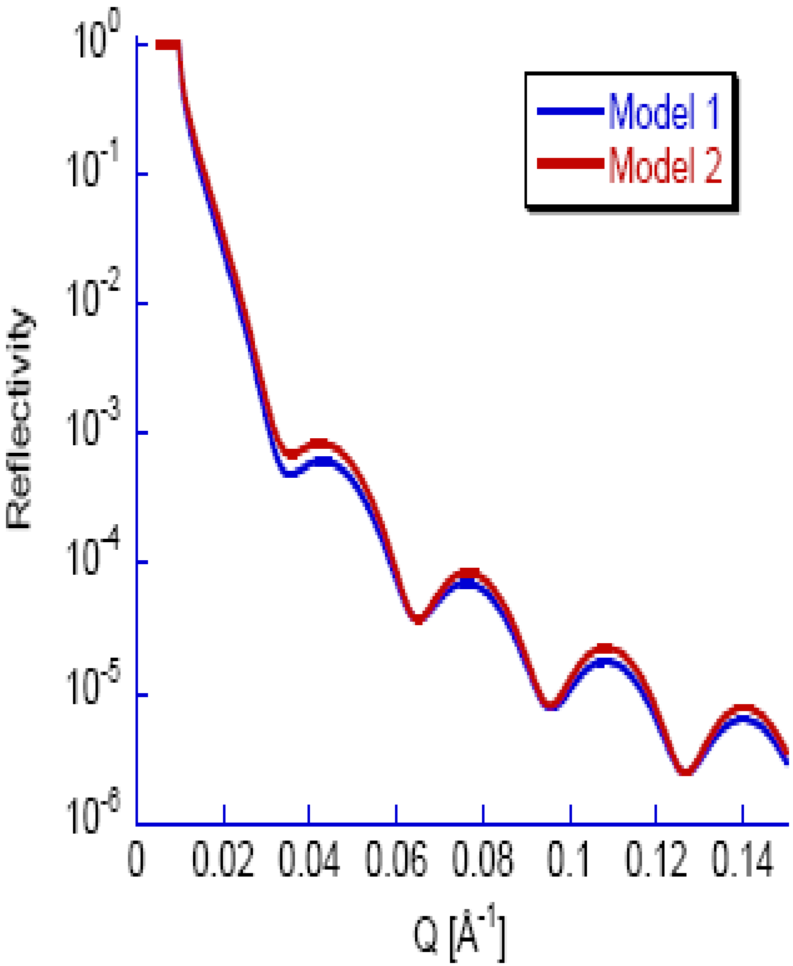
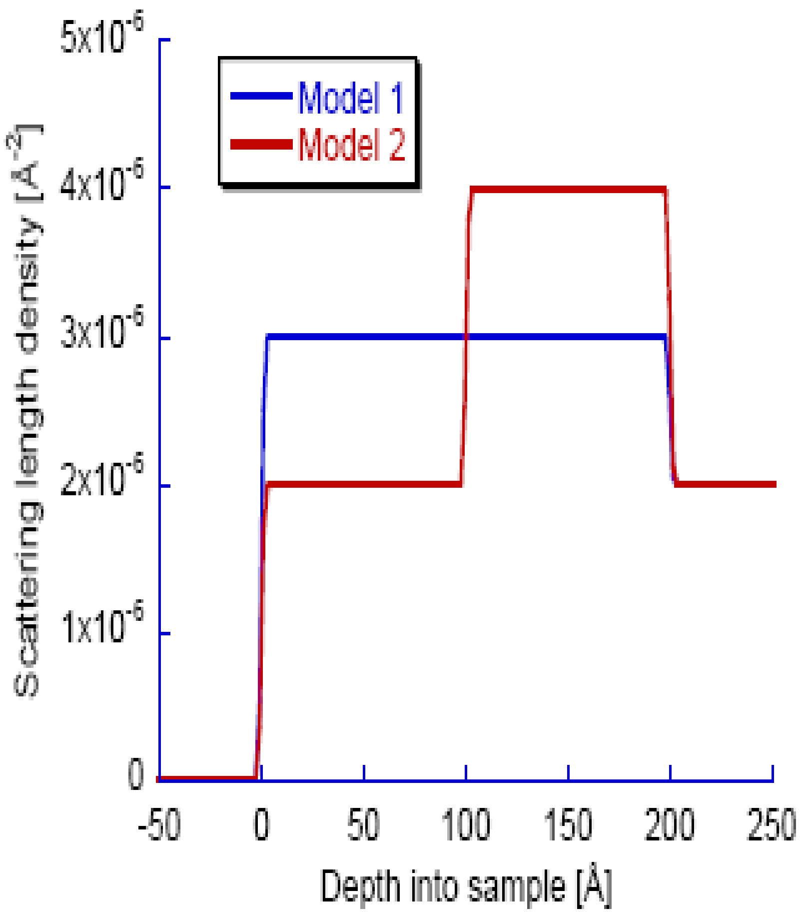
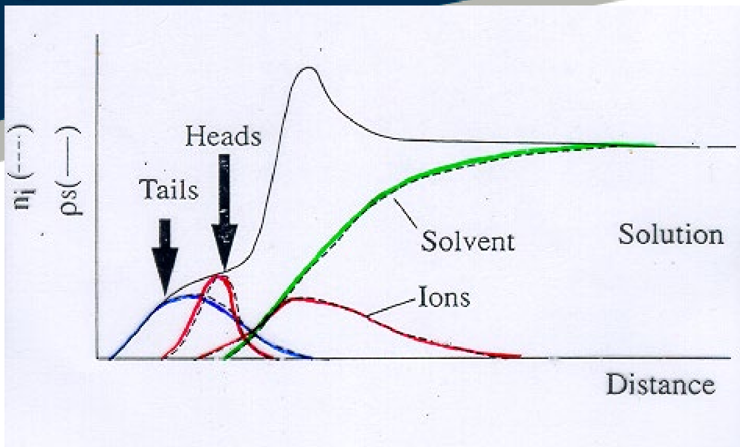
D. Sivia et al., J. Appl. Phys 70, 732 (1991)

Perils of fitting





Partial Structure Factors

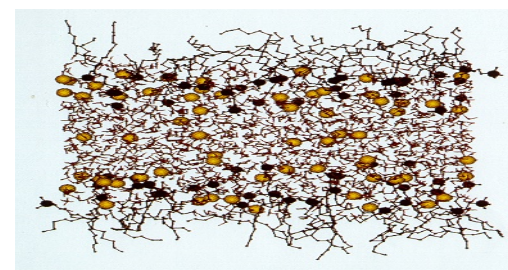


$$R(Q) = \frac{16\pi^2}{Q^2}\left|\int_{-\infty}^{+\infty}\rho(z)e^{-iQz}dz\right|^2$$

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

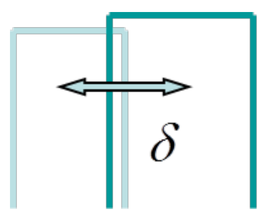
$$R(Q) = \frac{16\pi^2}{Q^2}\left[b_c^2 h_{cc} + b_h^2 h_{hh} + b_s^2 h_{ss} + 2b_c b_h h_{ch} + 2b_c b_s h_{cs} + 2b_h b_s h_{hs}\right]$$

Self Partial Structure Factors : $h_{ii} = |\widehat{n_i}|^2$



$\widehat{n_i}$ is a one dimensional Fourier transform of $n_i(z)$

Cross partial structure factors:



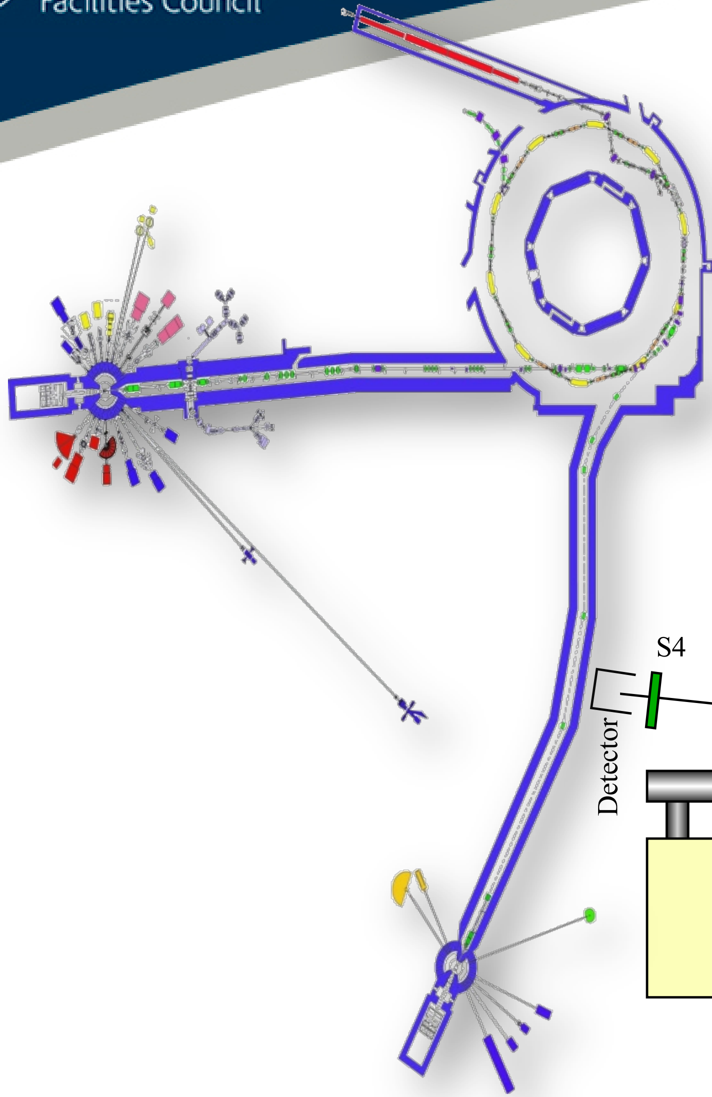
$$h_{ij} = \pm\left[h_{ii}h_{jj}\right]^{1/2}\cos iQ\delta$$

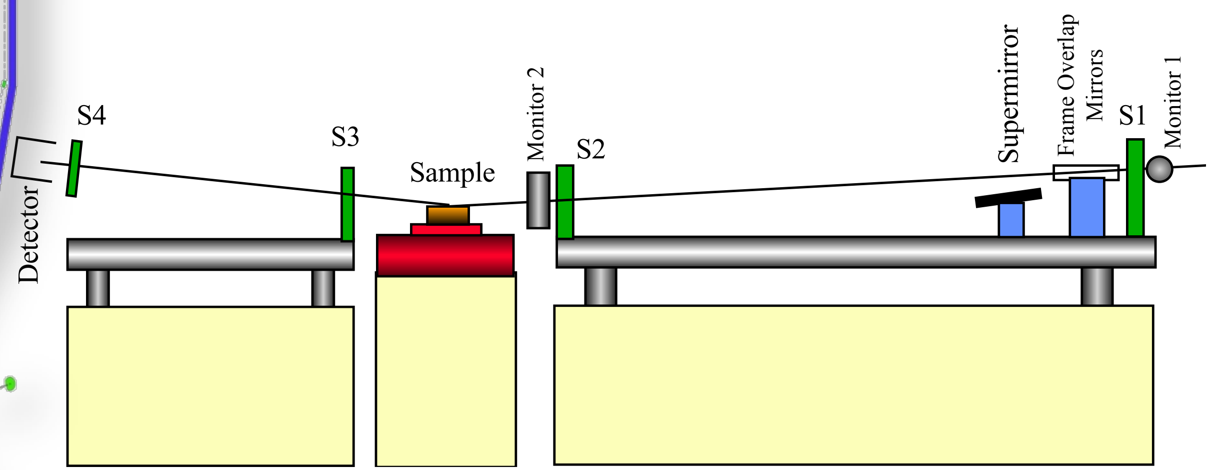
(Crowley, Lee, Simister, Thomas, Penfold, Rennie, Coll Surf 52 (1990) 85)

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



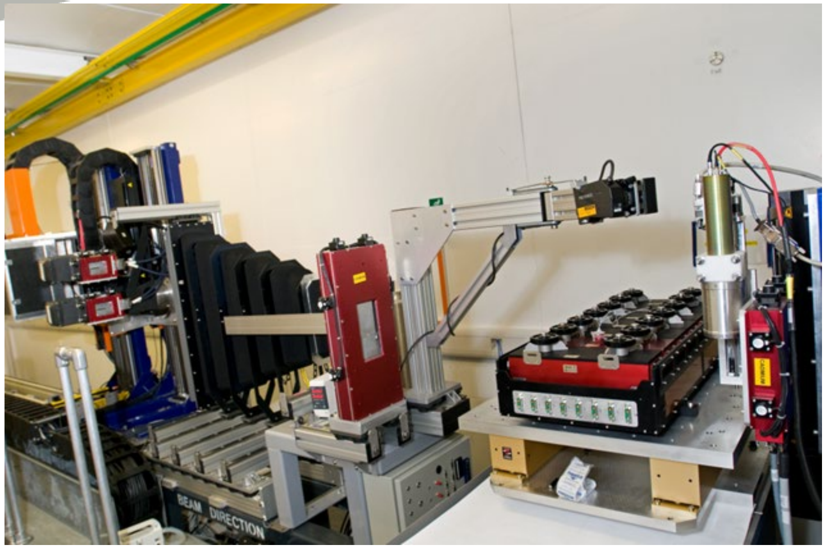


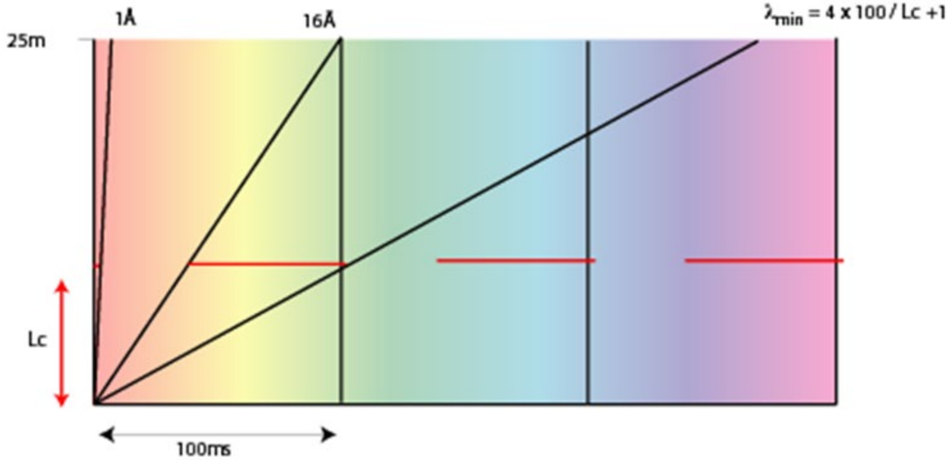
INTER, POLREF, OFFSPEC, SURF, CRISP reflectometers

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

reflectometers at ISIS

Instrumentation





White beam time of flight, fixed geometry: Wavelength range 1-7(16)Å

Q range 3 x10^{-3} to 0.5 $Å^{-1}$

Q_{max} (d_{min}) limited by background:

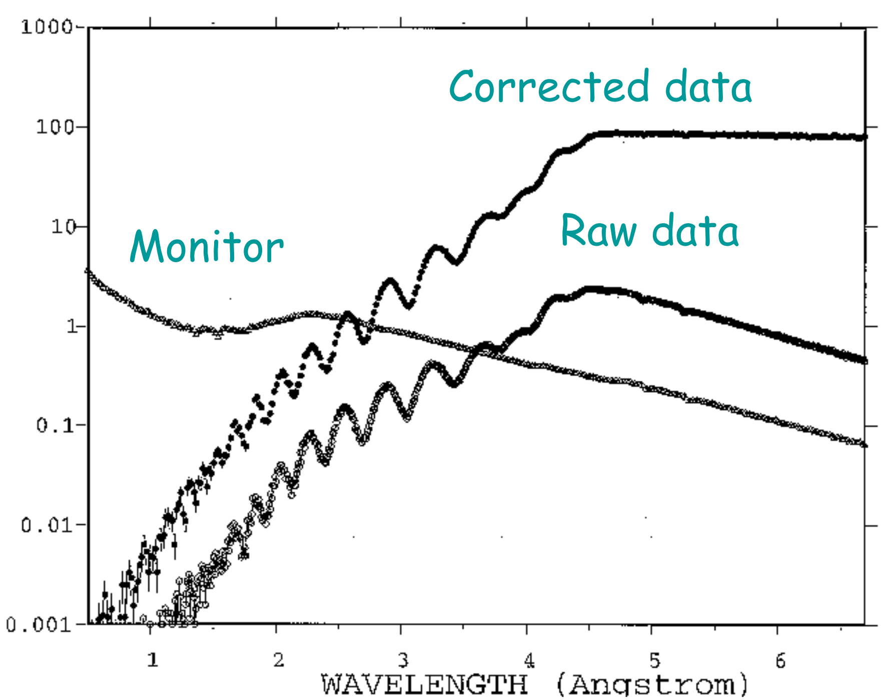
incoherent scattering in sample
1.5 x 10^{-6} for D_2O, 4x10^{-6} for H_2O
<10^{-6} for silicon

d_{max} determined by $\Delta Q/Q$

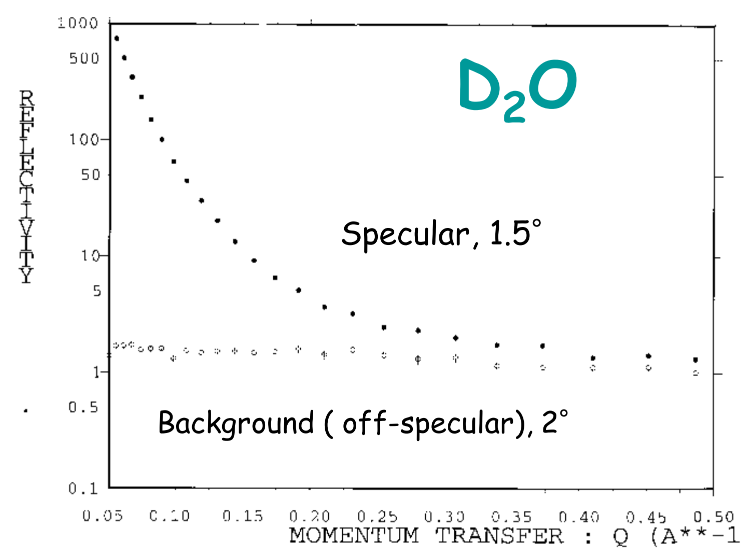
Instrumentation

Correct for detector efficiency, spectral shape, background

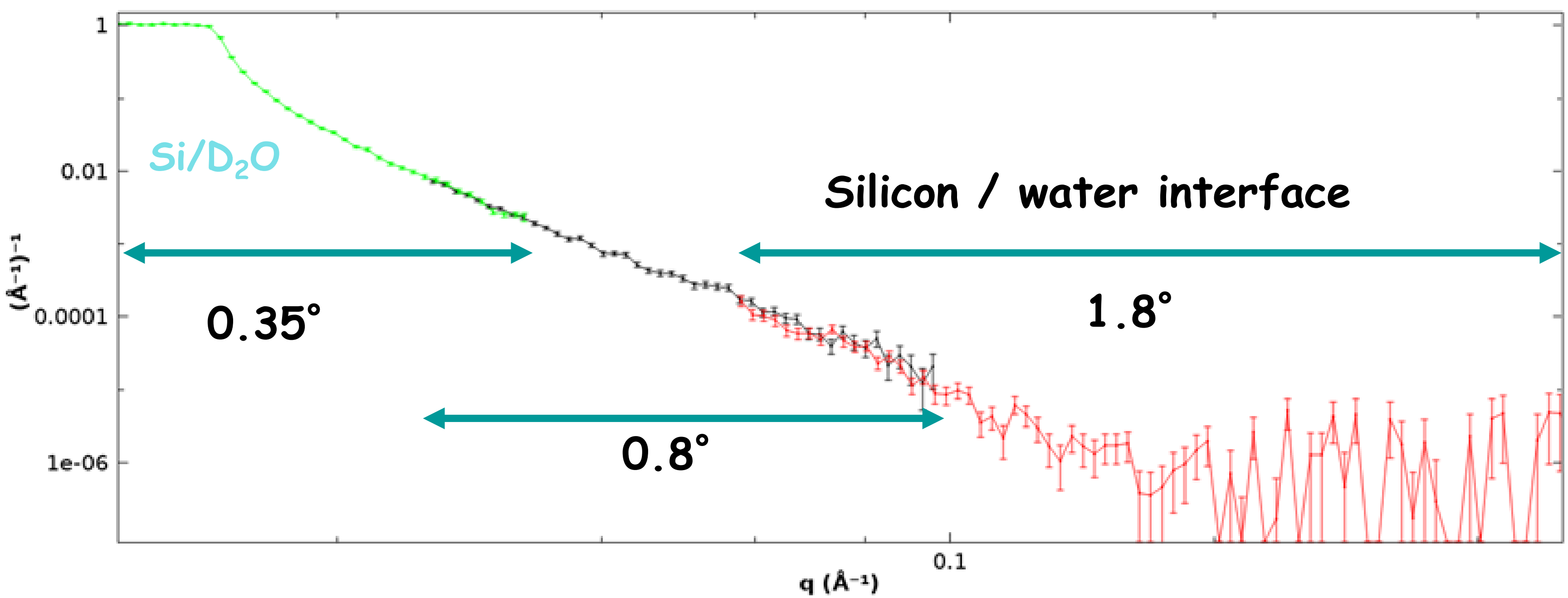
$$R(Q(\lambda_i,\theta)) = f\,\frac{[I_d(\lambda_i)-b_d(\lambda_i)]}{[I_m(\lambda_i)-b_m(\lambda_i)]}\,\frac{\varepsilon_m(\lambda_i)}{\varepsilon_d(\lambda_i)}$$



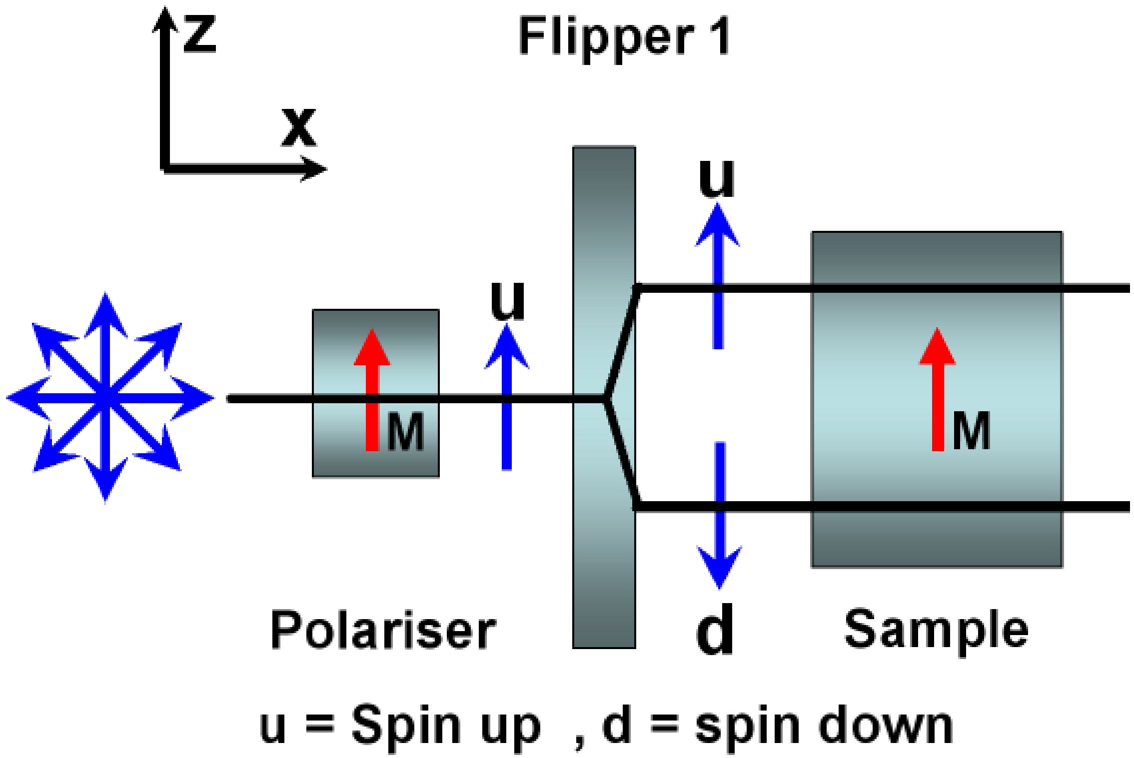
d,m refer to the detector and monitor
m can also be a direct beam



Instrumentation



Polarised neutrons



Now measure to reflectivity curves spin up and spin down.

Experiments now takes 4 times as long to get similar statistics!

There several ways of polarising and flipping neutrons, but that is beyond scope of this talk.

W. Gavin Williams Polarized neutrons Oxford Science
A.-J. Dianoux et al, Neutron Data Booklet (Institut Laue-Langevin, 2002), 1st ed.

Polarised Neutron Reflectivity (PNR)

It is assumed that the polarisation vector and magnetisation are parallel

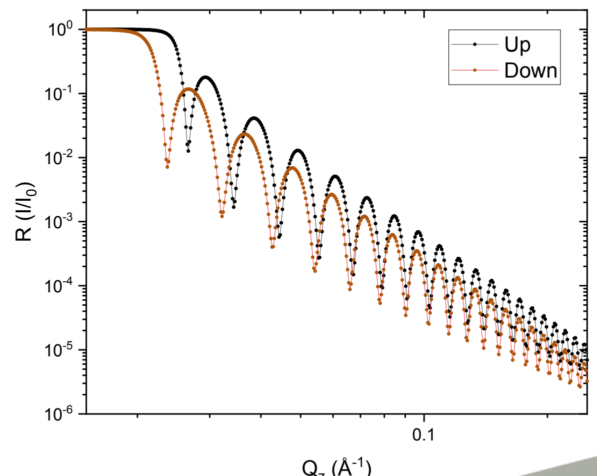
$$V = V_n \pm V_m$$

where $V_n = \frac{2\pi\hbar^2}{m} Nb$ and $V_m = \frac{2\pi\hbar^2}{m} Np = \pm\mu_n B$

With $p = (2.695 \times 10^{-4}/\mu_B)|\boldsymbol{\mu_i}|$

For a single magnetic layer $V = \frac{\hbar}{2\pi m} N(b_N \pm b_m)$

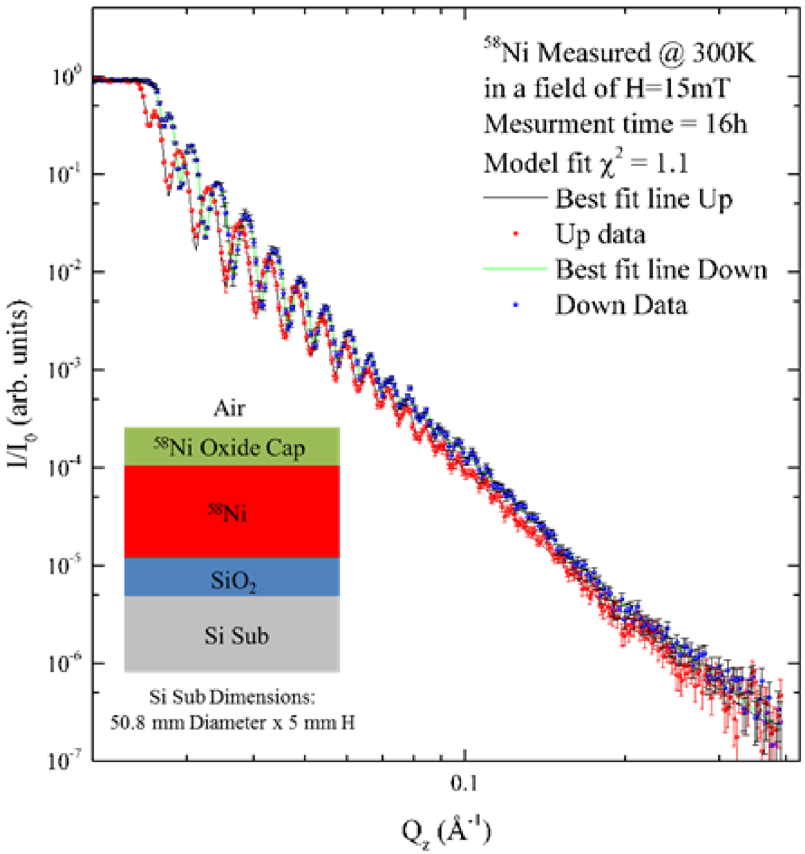
This essential means you get two reflectivity curves as the magnetic layer has two different values for its SLD depending it M is Parallel or anti-parallel to the Polarisation P direction

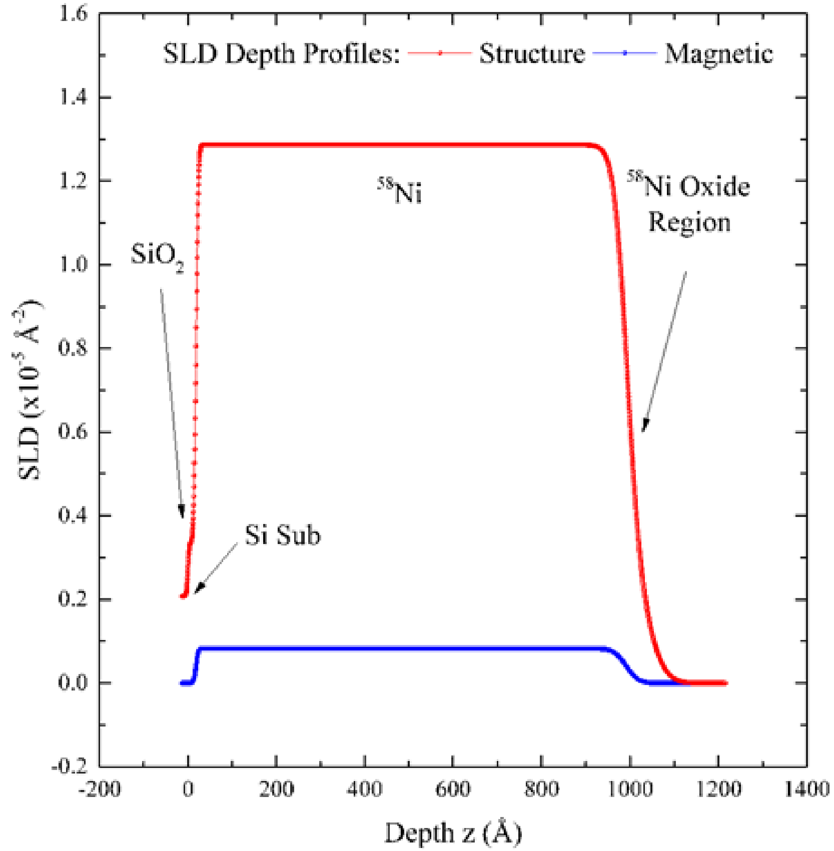


A 500 Å Ni layer on Si substrate

- Bland et al, Phys Rev B, 46, 3391 (**1992**)
- Zabel et al Physica B 276-278, 17 (**2000**)
- R. M. Moon et al Phys Rev, **1969**, 181, 920-931
- S. Blundell et al, JMMM, **1993**, 121, 185-188
- Bland et al, Phys Rev B, 46, 3391 (**1992**)
- G. L. Squires introduction to the Theory of Thermal neutron scattering

Example of Polarised Neutron Reflectivity (PNR)





PNR provides both the Nuclear (structural) and magnetic SLD depth profile.

Effectively functions as a depth dependent magnetometer

But takes longer than NR by a factor 4 for similar statistics

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Simple determination of surface excess (how much stuck to surface/interface)

Air Contrast Matched Water

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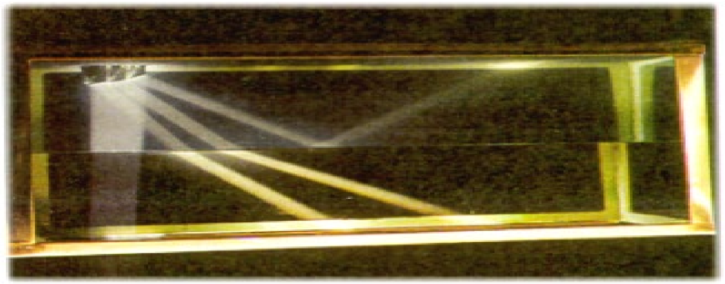
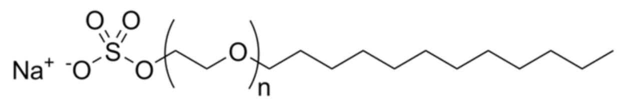
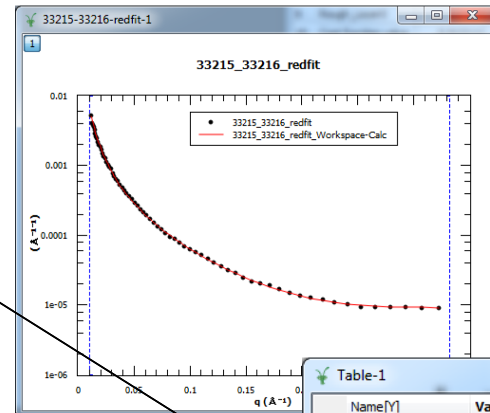
Deuteration Facility



$C_wH_xD_yO_zS$



$$A = \sum b \, / \, d\rho$$



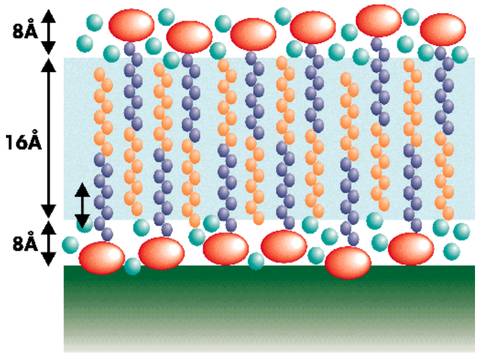
$$\Gamma = 1 \, / \, A.N_{av}$$

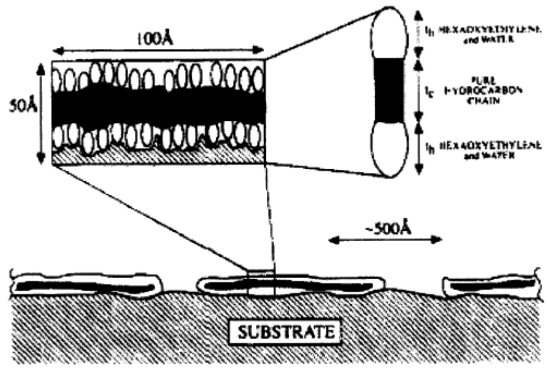
Table-1

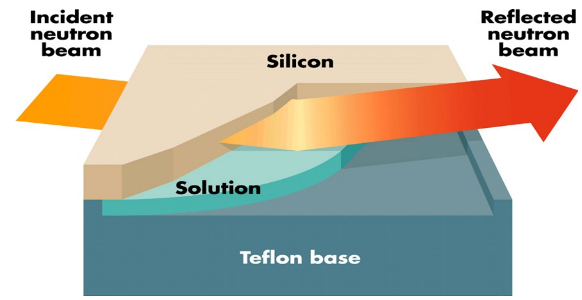
	Name[Y]	Value[Y]	Error[Y]
0	Theta	2.3	0
1	ScaleFactor	1	0
2	AirSLD	0	0
3	BulkSLD	0	0
4	Roughness	0	0
5	BackGround	9.09315e-06	2.69601e-07
6	Resolution	5	0
7	SLD_Layer0	3.51781e-06	4.94563e-08
8	d_Layer0	19.6907	0.303912
9	Rough_Layer0	0	0
10	Cost function value	0.912111	0

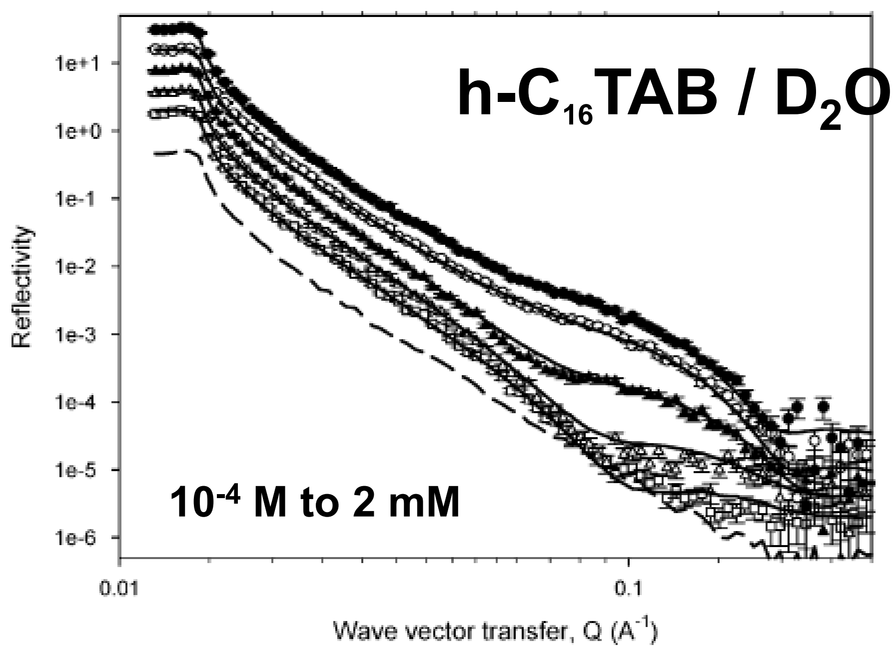
$$d\rho = \sum b_1 / A_1 + \sum b_2 / A_2$$

Surfactant adsorption at the solid-solution interface

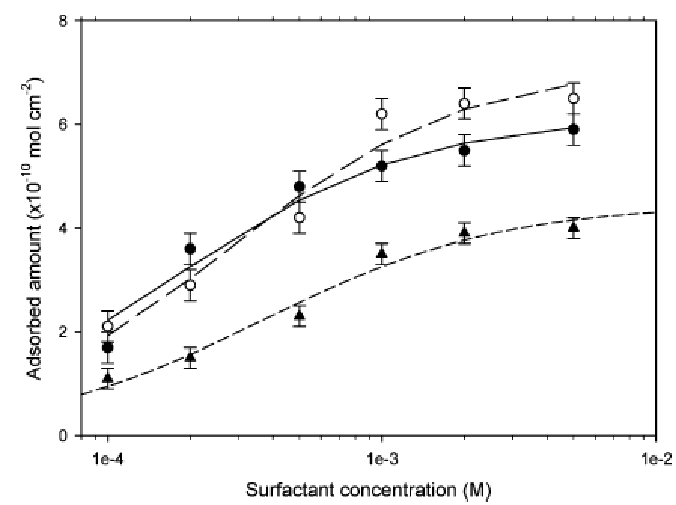








(●) silica, (o) philic cellulose, (Δ) phobic cellulose



Penfold et al, Langmuir 25 (2007) 8357

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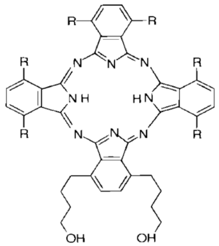
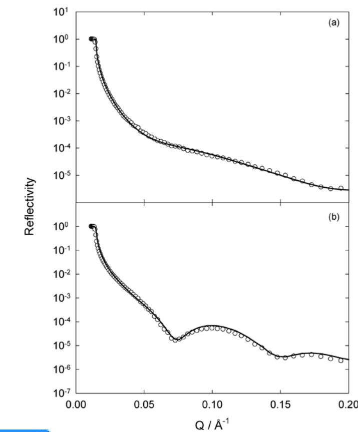
Optical biosensors

Principle: contaminants in water degrade lipid layer allowing release of trapped NO_2 causing colour change in pigment.

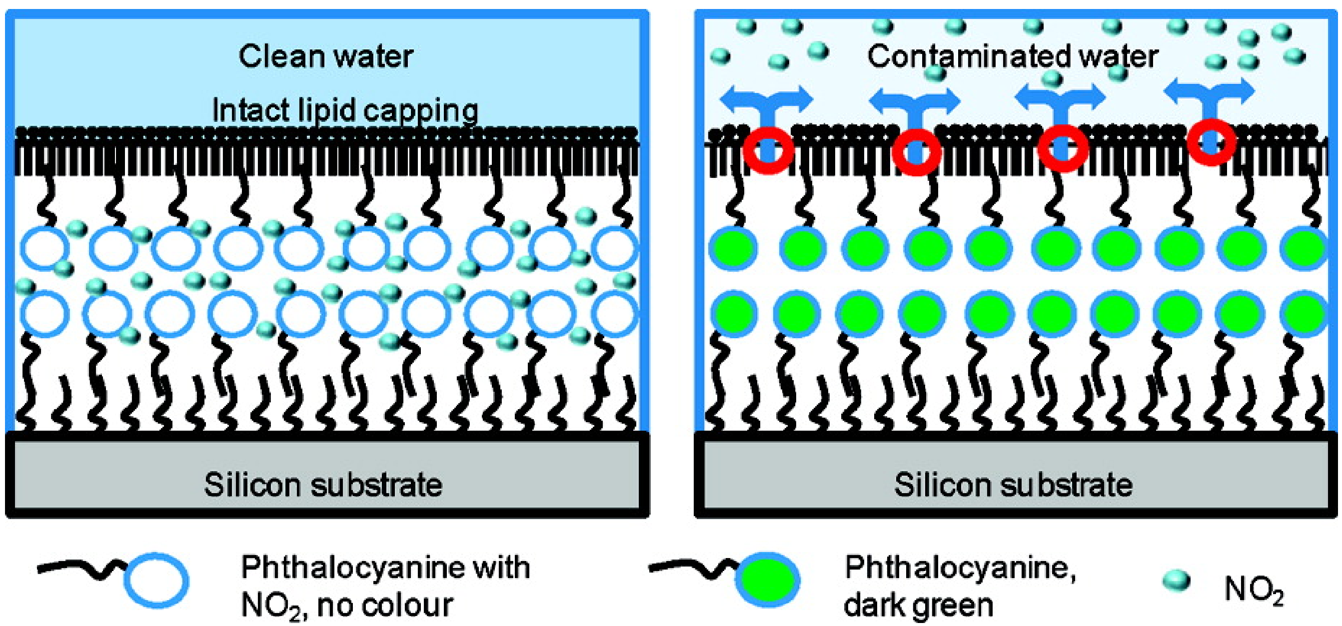


Chemical structure of the phthalocyanine ligand. The six R groups are C10H21.

(a) Reflectivity profiles for DPPC-DPPE+PEG layer and (b) 2 layers of phthalocyanine covered by DPPC-DPPE+PEG at the silicon−D2O interface. The best fits to the data are shown by solid lines.

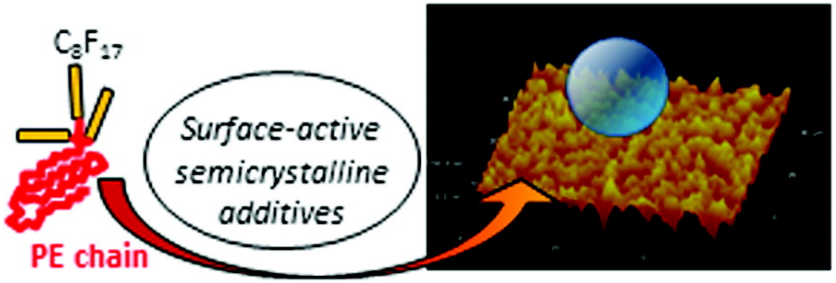


Reflectivity demonstrates effectiveness of the lipid layer in partitioning (sealing) the deposited phthalocyanine layers from the bulk water.



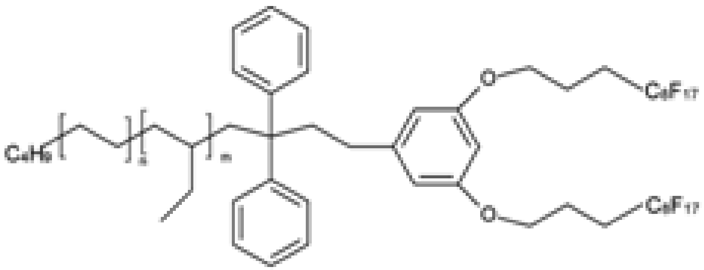
Langmuir 2010, 26(19), 15383–15387

Surface Modification of Polyethylene with Multi-End-Functional Polyethylene Additives



- “New” surface properties for polymer films
- Polymer hydrophobicity greatly enhanced by end addition of fluorine
- Multi-end-fluorinated chain additives spontaneously surface enrich
- Suitable for one step batch process
- Marked increase in both hydrophobicity and lipophilicity
- PTFE like surface properties

Hardman et al, *Langmuir* 2012 ,28,5125-5137

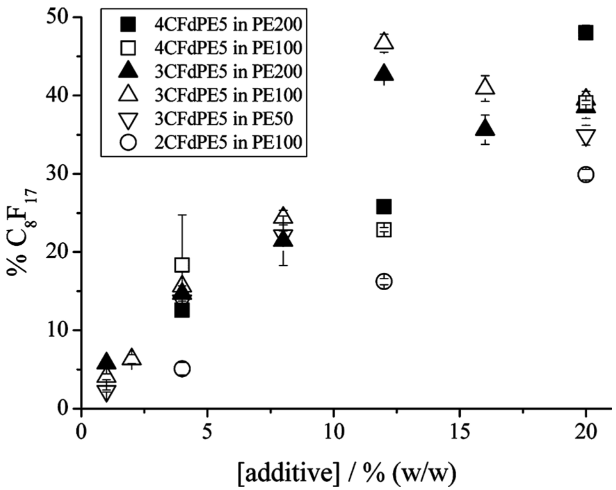


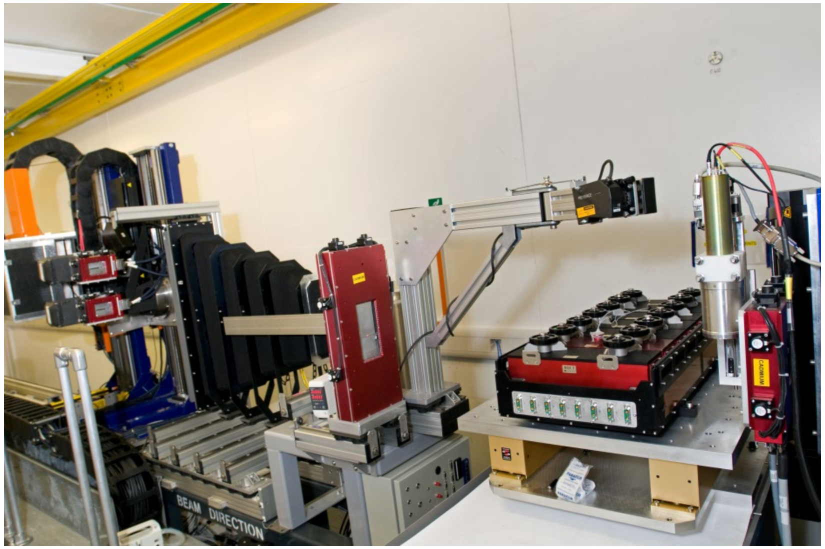
Additives made from polymerised 1,3 butadiene end capped with diphenyl ethylene and terminated with fluorinated aryl ether bromide followed by saturation with D_2 at 500 psi

sample code	target M_n/kg mol^{-1}	measured M_n/kg mol^{-1}	M_w/M_n	% end-capping	f (= [D]/[H + D])	T_m/˚C
2CFdPE5	5	7.1	1.05	84	0.43	96
PE50	50	56.6	1.04			106

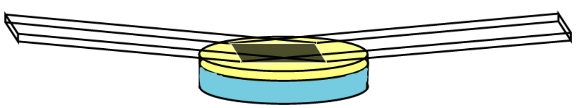
- Samples prepared by spin coating 1% polymer + additive in warm toluene at 2000 rpm onto silicon
- Resultant films ~1000Å thick

- XPS data confirm fluorocarbon present at film surface





- NR on INTER at ISIS
- Samples heated to 120° C Tm~109°
- Data taken at 2 angles of incidence (0.6, 1.8°) with constant q resolution
- ~40 minutes per sample
- Blended films neutron refractive index close to that of air



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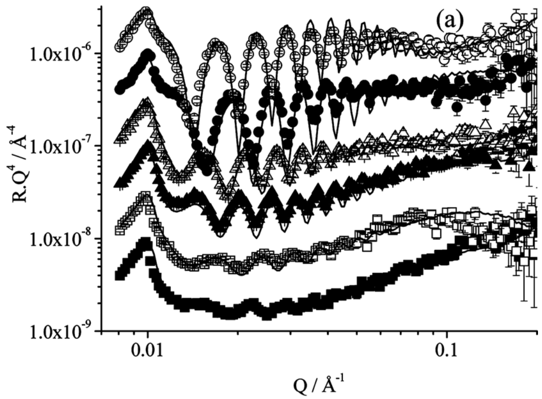
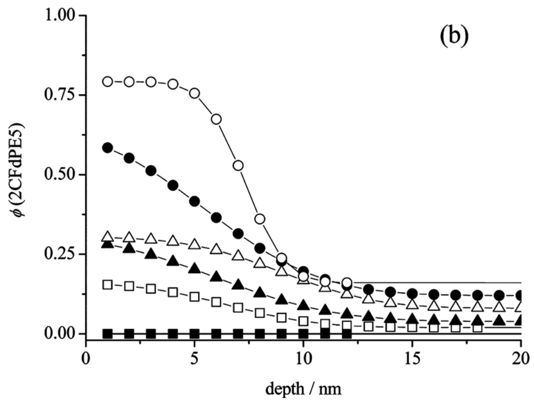
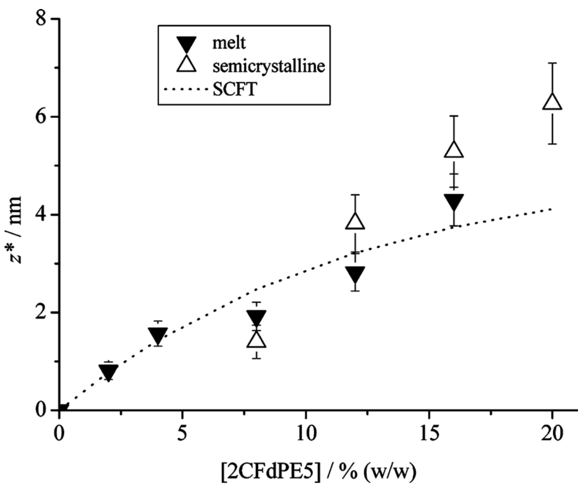


Kiessig fringes from film thickness: visibility proportional to additive surface excess



Data fitted to an error function profile 0,2,4,8,12,16% additive



Comparison of adsorbed amount determined by NR (melt), Nuclear Reaction Analysis and simulated by SCF theory (χ_b-χ_s =3.0k_BT)

Conclusions

- Poly(ethylene) materials with well defined multi fluorocarbon functional groups produced
- As additives in blends generate films with enhanced hydrophobicity and lipophilicity
- At room temperature films are inherently crystalline but not sufficiently rough to give rise to super hydrophobicity (Wenzel wetting)
- Melting transition does not cause gross changes in self-organisation (NR Vs NRA data)

Acknowledgements

- Richard Thompson
- Sarah Hardman
- Lian Hutchings
- Nigel Clarke
- Soloman Kimani
- Laura Mears

Durham (synthesis, NRA, Contact angle, AFM, SCF calculations)

- Emily Smith

Nottingham(XPS)

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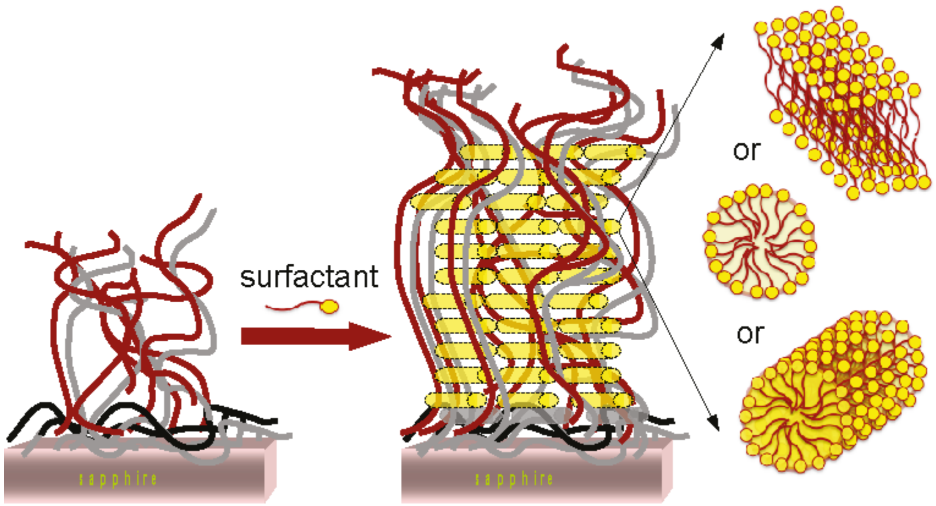
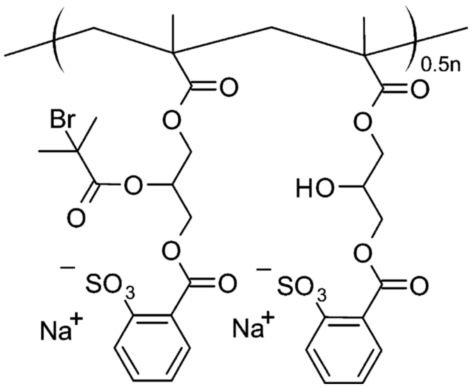
A Neutron Reflectivity Study of Surfactant Self-Assembly in Weak Polyelectrolyte Brushes at the Sapphire-Water Interface



- Poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) Brushes and oppositely charged surfactant sodium dodecyl sulfate (SDS)
- PDMAEMA neutral at pH9 and cationic at pH3

Moglianetti et al, *Langmuir* 2011 ,27,4489-4496



- Polymer brushes grown by SI-ATRP onto sapphire substrate using a macroinitiator
- Characterised by ellipsometry, X-ray reflectivity, and neutron reflectivity measurements (Moglianetti et al. *Langmuir* 2010, 26, 12684–12689.)

sample	dry thickness (nm)	γ (Å)	Γ_{DMAEMA} (10^{-25} mol $Å^{-2}$)	σ (nm^{-2})	*N*	M_w (kg/mol)
a	5	47	3.5 ± 0.3	0.13 ± 0.02	155	24 ± 5
b	11	100	7.4 ± 0.7	0.12 ± 0.02	443	70 ± 16
c	17	142	10.4 ± 1.0	0.14 ± 0.02	430	68 ± 15
d	17	167	12.4 ± 1.2	0.18 ± 0.03	434	68 ± 15

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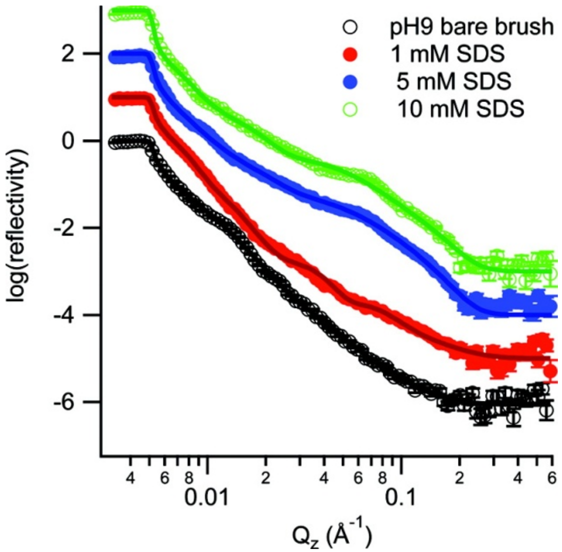
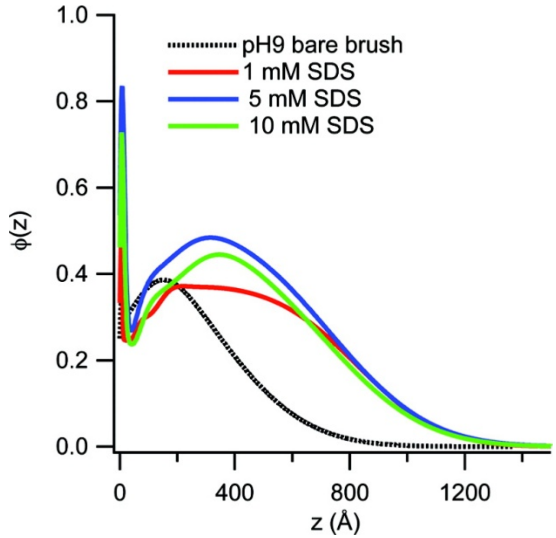
- NR data collected on the SURF reflectometer at ISIS
- Sapphire-D_2O qc ~0.0048 $Å^{-1}$
- 4 angles of incidence 0.1, 0.25, 0.7, 1.5° data combined to cover 0.0033<q<0.6$Å^{-1}$
- Reflectivity modelled as three to five layers each characterised by a thickness, scattering length density and Gaussian roughness.
- SLD of segments and surfactant similar- determine VFP of SDS+DMAEMA
- Polymer adsorbed amount known and constant (grafted, no free polymer)

$$\varphi(z) = \frac{\rho_{D_2O} - \rho(z)}{\rho_{D_2O} - \rho_{DMAEMA}}$$

pH 9 uncharged polymer (brush "d" dry thickness 17nm)



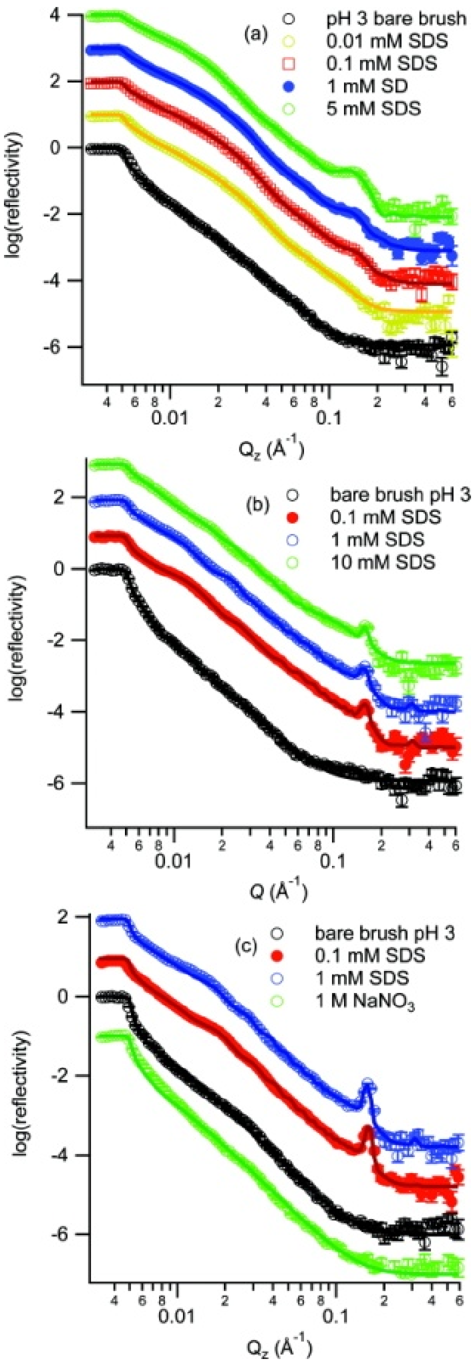


- No change in reflectivity up to 1mM SDS
- Development of fringe corresponds to swelling of adsorbed layer

[SDS] (mM)	Γ_{SDS} (10^{-25} mol Å^{-2})	n_{SDS}/n_{DMAEMA}
1	4.6 ± 0.5	0.37
5	6.7 ± 0.7	0.55
10	5.3 ± 0.5	0.43

Onset of SDS adsorption analogous to CMC in bulk
Lowering of chemical potential in brush estimated from cac /cmc ~$1.4k_BT$

pH 3 cationic polymer



- Brushes a-c (5,11,17 nm dry brush) with increasing SDS concentration and with addition of salt
- No change in R when rinse with D2O
- Presence of Bragg peak indicates multilayers formed
- Addition of salt results in loss of Bragg peak
- As brush thickness increases onset of change in R at higher concentration (0.01 – 0.1mM) with sharper Bragg peak
- Bragg peak position suggests spacing of ~40Å typical of an SDS micelle or bilayer

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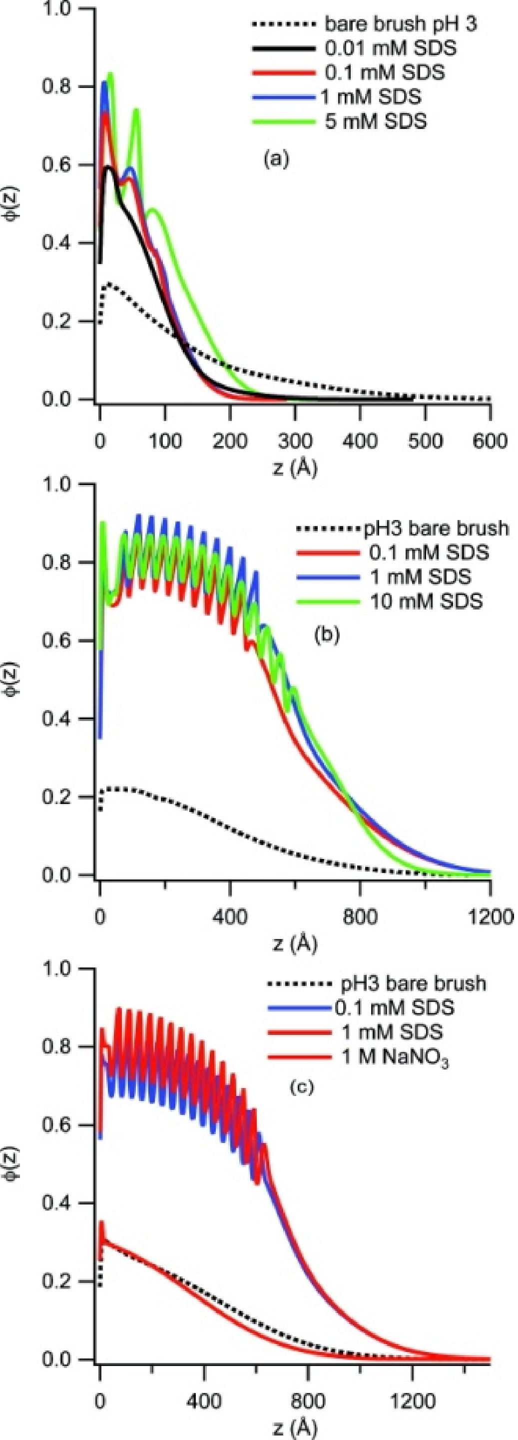


Interfacial volume fraction profiles SDS+DMAEMA

- 5nm brush 1-3 bilayers. Exchange of ions (OH^-, DS^-) ~17.5% at .01mM results in deswelling (loss of mobile counter-ions). Up to 0.35 SDS/DMAEMA
- 11nm brush 10-14 bilayers. Onset of uptake 0.1mM. Up to 2 SDS/DMEAMA. Excess DS^- over charged segments brings in Na^+ resulting in osmotic swelling
- 17nm brush 15 bilayers. Onset of uptake 0.1mM corresponding to 4.4 k_BT relative to SDS micelle. ~3k_BT from screening of headgroup repulsions
- Addition of salt returns bare brush surface excess. Brush thickness ~15% less. Osmotic → salted regime

Conclusions

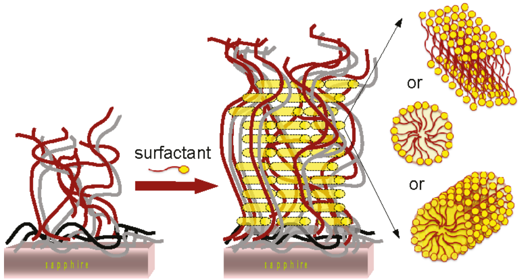
- Polymer brushes provide a convenient method of systematically exploring the interactions between strongly interacting polyelectrolytes and surfactants

- PDMAEMA brushes of moderate grafting density exhibit significant uptake of the anionic surfactant SDS

- In the absence of PDMAEMA 89% of a single bilayer is formed at the sapphire-water interface at a SDS concentration of 7 mM

- At pH 3, multilayered surfactant aggregates form within the brushes, with a periodic repeat that is consistent with lamellae of SDS bilayers or a hexagonal phase of cylindrical SDS micelles

- At pH 9 electrostatic screening is absent but hydrophobic effect sufficient driving force for adsorption.



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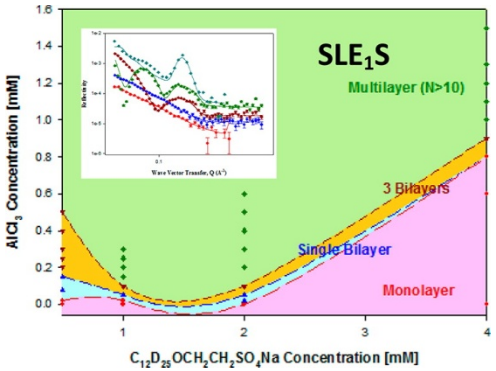
Acknowledgements

• Simon Titmuss	Edinburgh
• Mauro Moglianetti	EPFL
• Steve Armes	Sheffield
• Steve Edmondson	Loughborough

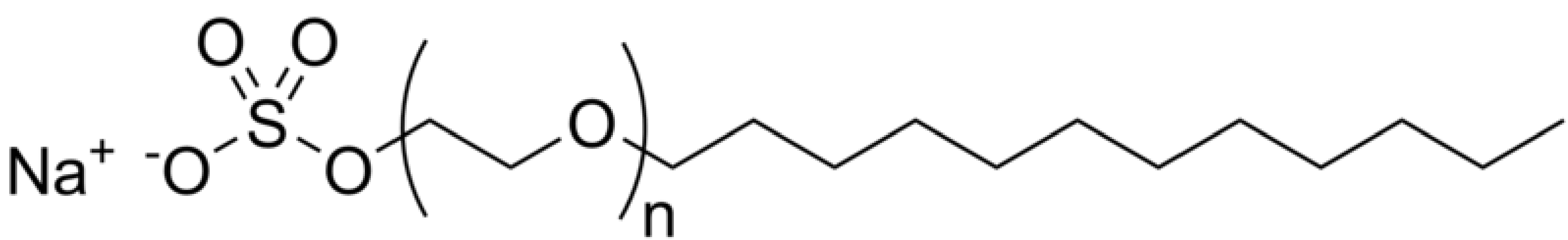
Surface Multilayers at the Air-Water Interface

Surface Multilayers at the Air-Water Interface in Dilute Surfactant Solutions



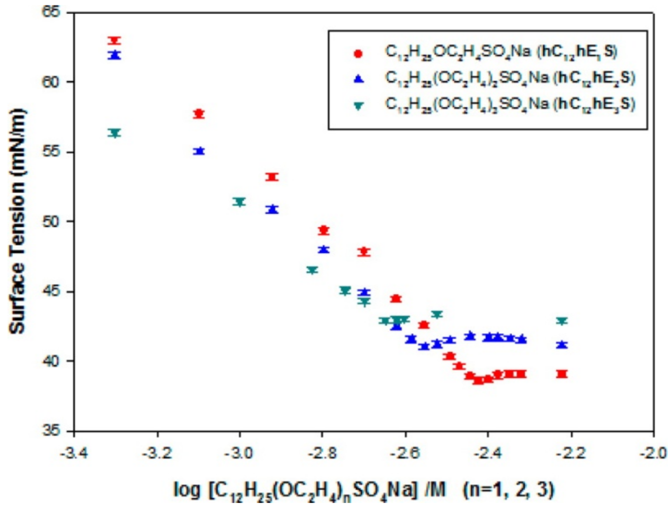
- sodium lauryl ether sulfate, SLES + Al^{3+}
- NR and ST used to study Surface Adsorption

Anionic detergent found in many personal care products (soaps, shampoos, toothpaste…) often in mixtures with non-ionics



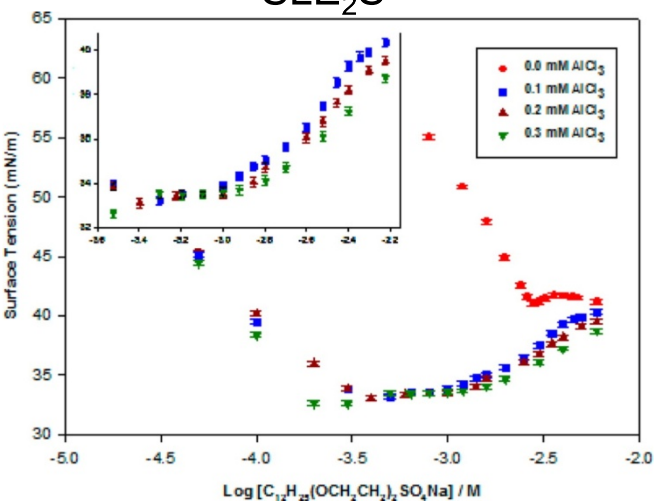
Xu, Penfold, Thomas, Petkov, Tucker, Webster, *Langmuir* 2013, 29, 11656-11666

Surface Tension Without Al^{3+}



- Small minimum -> low level of impurity, ≤ 0.01%.
- plateau region increases as eo length increases but CMC decreases
- ~greater tendency for micelle formation

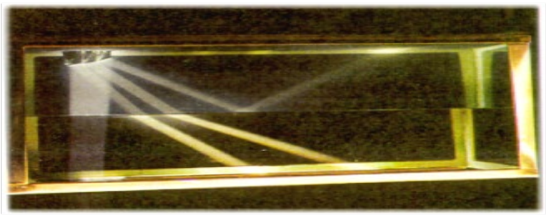
SLE$_2$S



Surface Tension With Al^{3+}

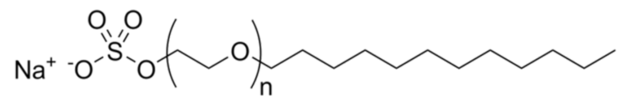
- Surface tension curve shifted to lower cmc in presence of Al^{3+}
- As SLES in excess ST converges

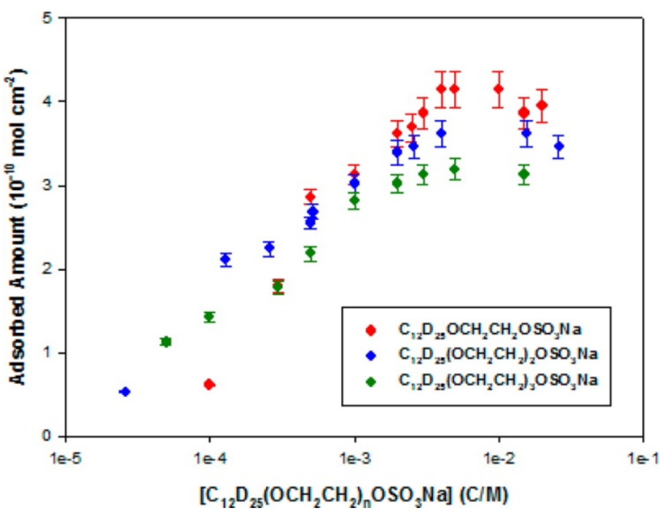
NR Without Al^{3+}



$A = \sum b / d.Nb$

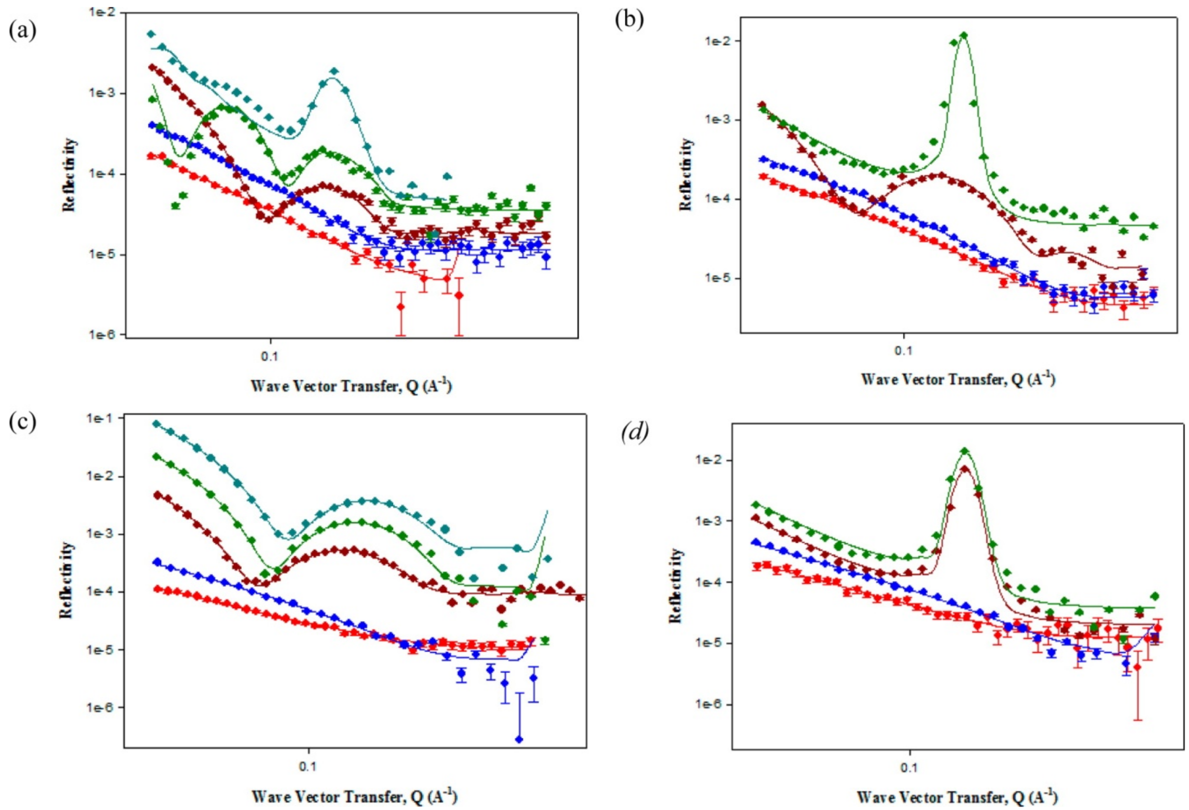
$\Gamma = 1/A.N_{av}$





- alkyl chain d labelled SLES, dC12hE1S, dC12hE2S, and dC12hE3S.
- thin monolayer, ~17 ± 2 Å, of uniform composition

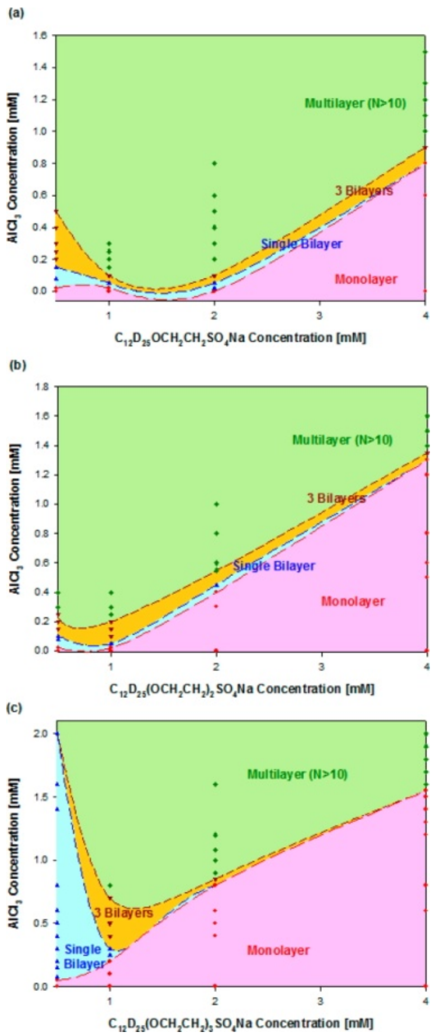
NR With Al^{3+}

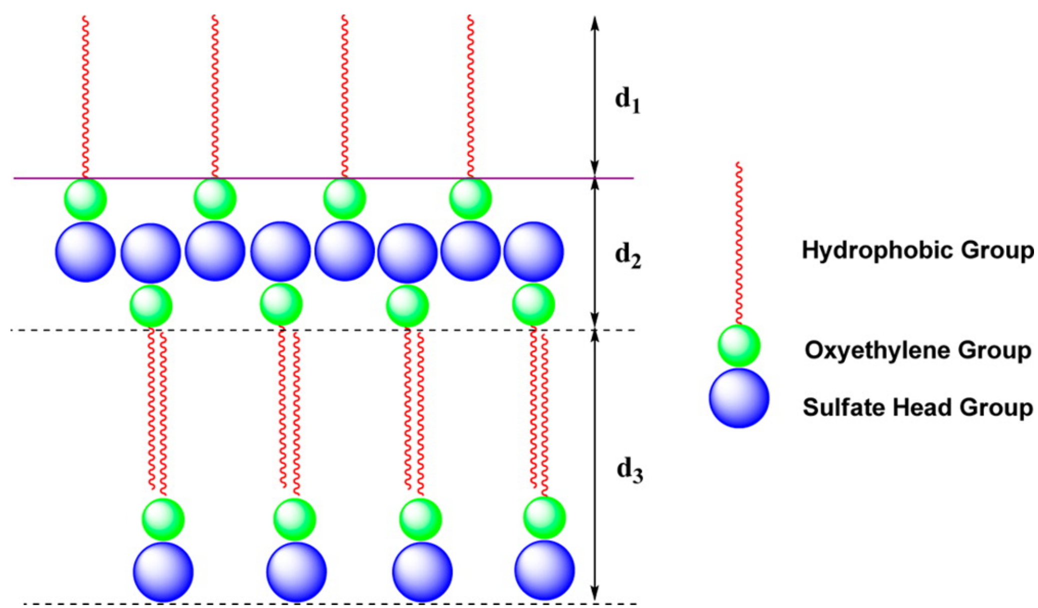


(a) 1 mM SLE1S, 0.0 mM (red), 0.02 mM (blue), 0.05 mM (dark red), 0.1 mM (dark green), 0.2 mM AlCl3 (dark cyan)
(b) 2 mM SLE2S, 0.0 mM (red), 0.4 mM (blue), 0.5 mM (dark red), 0.6 mM AlCl3 (dark green)
(c) 0.5 mM SLE3S, 0.0 mM (red), 0.05 mM (blue), 0.15 mM (dark red), 0.5 mM AlCl3 (dark green), 0.8 mM AlCl3 (dark cyan)
(d) 4 mM SLE3S, 0.0 mM (red), 1.5 mM (blue), 1.6 mM (dark red), and 1.8 mM AlCl3 (dark green).

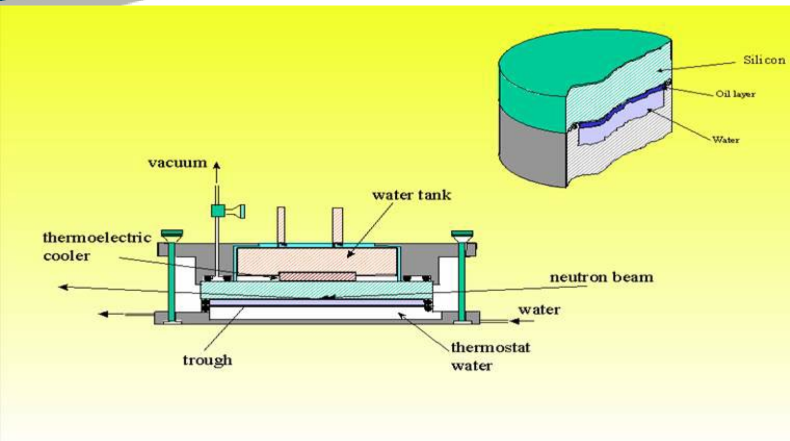
Approximate Surface Phase Diagrams For SLES / Al^{3+}

- strong complexation between SLES and Al^{3+}, transition from monolayer to surface multilayer structures
- EO1 – EO3 increase monolayer region - require more Al^{3+} to drive multilayers
- Increasing EO size disrupts complexation and multilayer formation





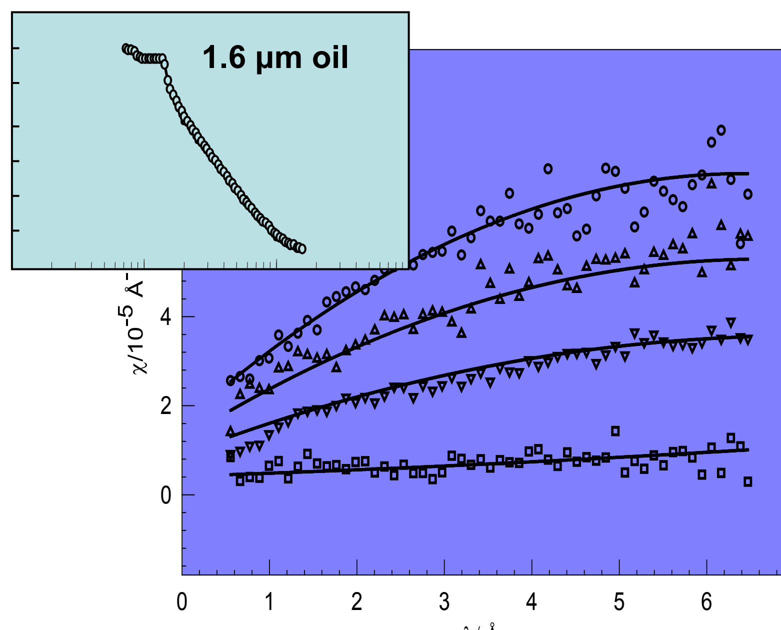
Neutron Reflectivity at the Liquid/Liquid Interface



$$n(\lambda) \approx 1 - \frac{\lambda^2}{2\pi} Nb + i \frac{\lambda}{4\pi} N\sigma$$

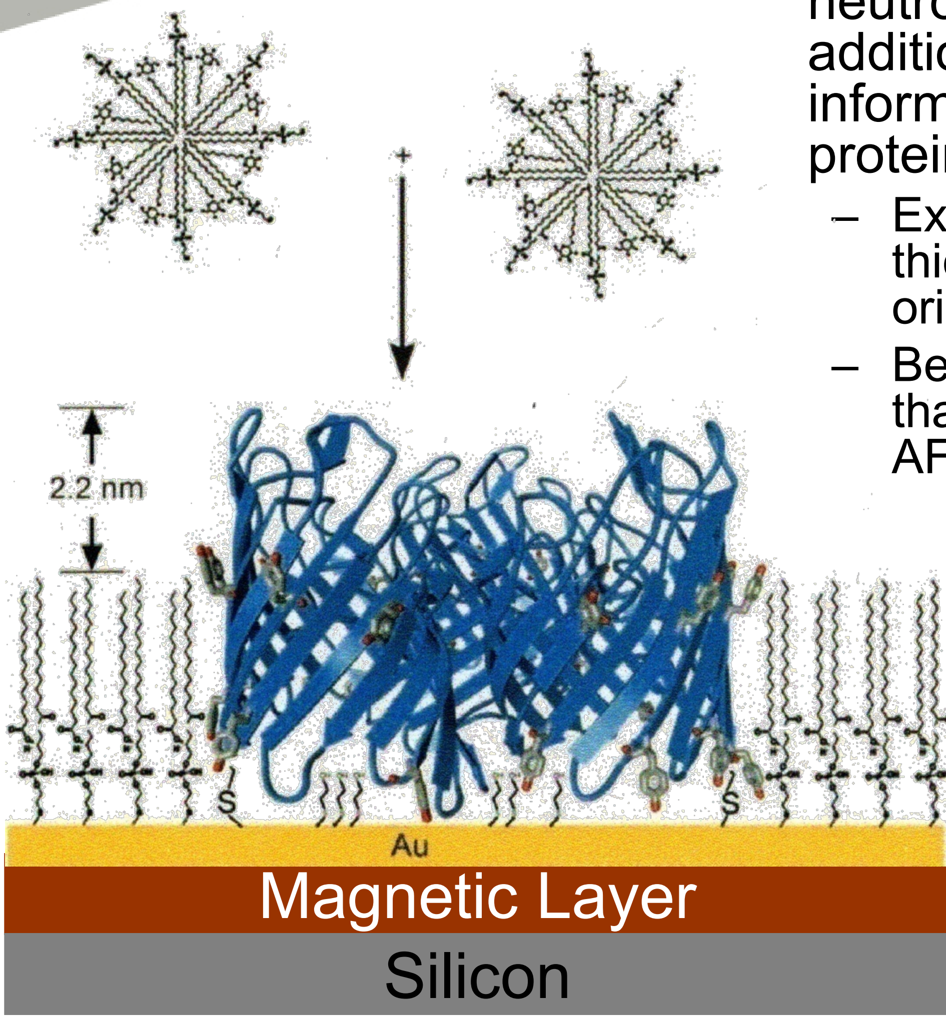
$$R_{tot} = R_1 + \frac{AR_2(1-R_1)^2}{1-AR_1R_2} \qquad A = \exp\left(\frac{-2\chi d_{oil}}{\sin\theta_{oil}}\right)$$

- spin coat oil onto hydrophobed block
- freeze oil and assemble cell, introduce aqueous phase
- Film stable/reproducible
- Use a super mirror to change θ_i
- reflection from silicon/oil and oil/water phase decoupled
- with increasing sld get direct measure of oil thickness

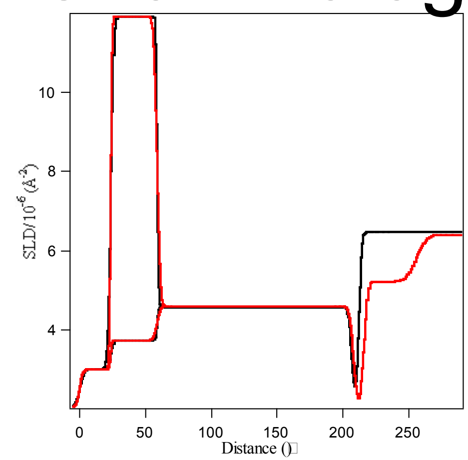


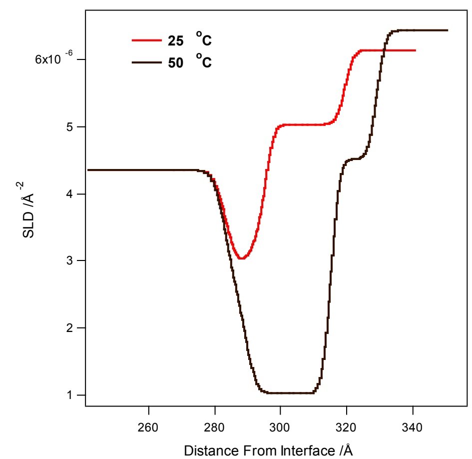
Meas. Sci. Tech. (1999)

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



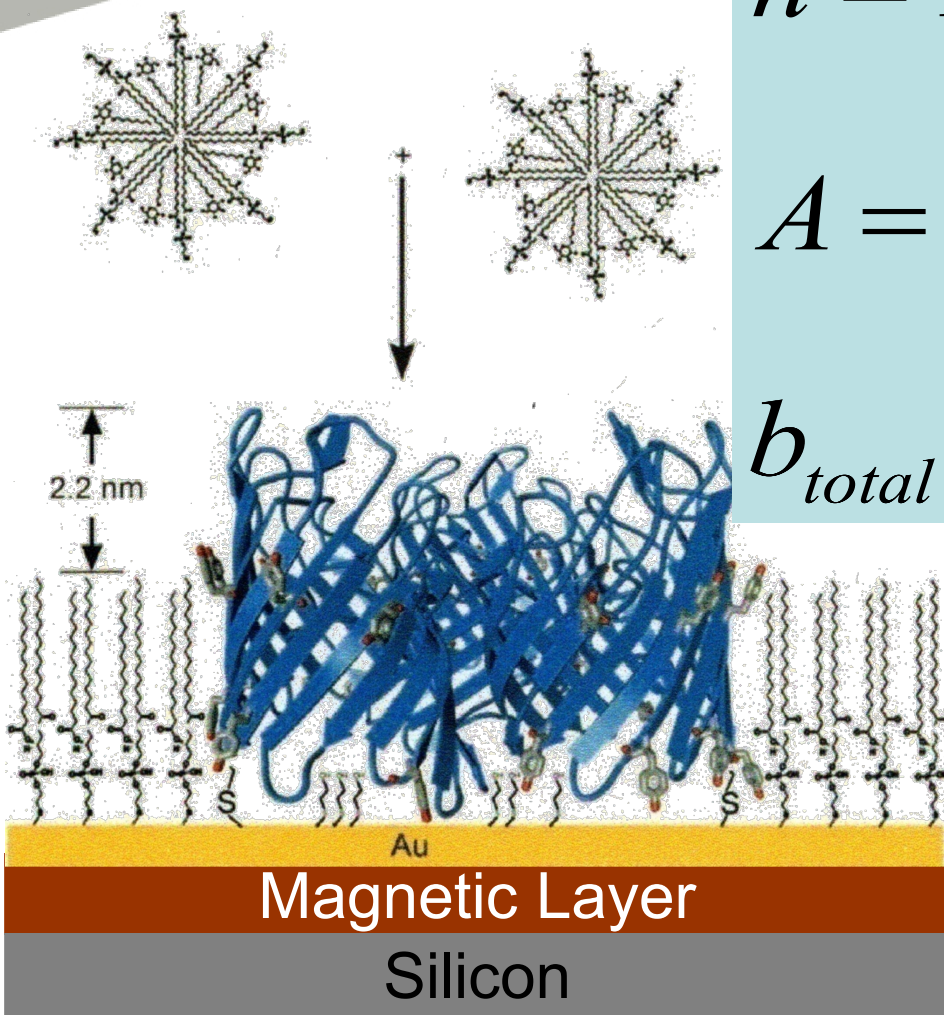


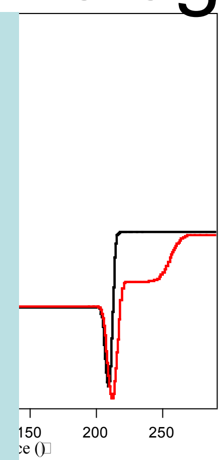
Polarised Neutrons for Biology

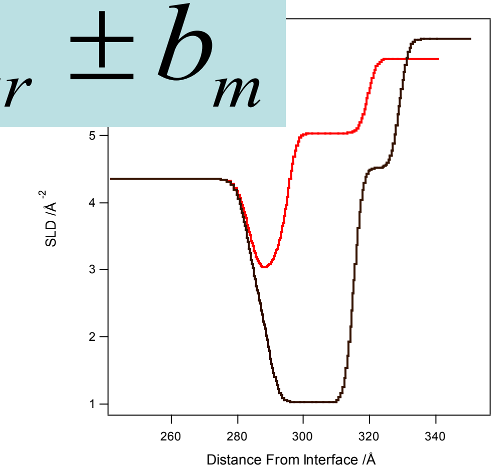
$$n = 1 - \lambda^2 A - i\lambda B$$

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

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







Reflectometry Summary

- Depth profile sensitive to number and type of atom
- ~10Å resolution
- Interface thickness ~ 5Å to 5000Å
- ‘buried’ interfaces
- Contrast variation
  - invisible substrate
  - Pick out components in complex mixtures
  - unique structure determination

Background material

The following review articles, book chapter, and book provide a useful background to Neutron Reflectivity. The articles and book chapter are readily available on line and the book is available form most on-line outlets, such as Amazon.

(a) Basic Reviews on Neutron and x-ray reflectivity

(1) J Penfold, RK Thomas, J Phys: Condens Matt 2 (1990) 1369
(2) TP Russell, Mat Sci Rep 5 (1990) 171

(b) Applications of neutron reflectivity in surfactants and polymer-surfactant

(1) JR Lu, RK Thomas, J Penfold, Adv Coll Int Sci 84 (2000) 143
(2) DJF Taylor, RK Thomas, J Penfold, Adv Coll Int Sci 132 (2007) 69
(3) J Penfold, RK Thomas, Int Sci and Technol, Adv Chem of Monolayers and Interfaces, Vol 14, Chapt 4, 87-115, Ed I Imae, Elsevier, 2007.

(c) Basic scattering theory

(1) Elementary Scattering Theory for x-ray and neutron users, DS Sivia, OUP, 2011, ISBN 978-0-19-922868-3