Introduction to Neutron Reflectivity

J.R.P. Webster
ISIS Facility, Rutherford Appleton Laboratory
Reflectometry

TS1
CRISP
SURF

TS2
OFFSPEC
INTER
POLREF

Types of Instrument at ISIS:
- Diffractometer
- Reflectometer
- Small Angle Scattering
- Indirect Spectrometer
- Direct Spectrometer
- Muon Spectrometer/Instrument
- Chip Irradiation
- Imaging and Diffraction
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)

1965 Koester: gravity mirror determination of scattering lengths
1976 Hayter, Penfold, Williams first interference fringes
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)
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,
Reflectometry

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

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

**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

**Biology**
- Protein adsorption
- Biocompatible polymers
- Drug transport
- Anaesthesia mechanisms
Specular reflection of neutrons

Refractive index defined using the usual convention in optics:

\[
n = \frac{k_1}{k_0}
\]

\[
n = 1 - \lambda^2 A - i \lambda B
\]

\[
A = \frac{Nb}{2\pi}
\]

\[
B = \frac{N(\sigma_a + \sigma_i)}{4\pi}
\]

X-rays

\[
n = 1 - \alpha - i \beta
\]

\[
\alpha = N\lambda^2 Z re/2\pi
\]

\[
\beta = \lambda \mu / 4\pi
\]
Refractive Index for neutrons

\[ n = \frac{k_1}{k_0} \]

\[ n = 1 - \lambda^2 A - i\lambda B \]

\[ A = \frac{Nb}{2\pi} \]

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

H: \(-0.374 \times 10^{-12}\) cm

D: \(0.667 \times 10^{-12}\) 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
\[ \theta_0 = \theta_c \]
\[ \theta_1 = 0.0 \quad \cos \theta_1 = 1.0 \]

Total reflection (R=1.0) for \( \theta < \theta_c \)
Specular reflection of neutrons
(some basic optics)

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\[ \theta_0 = \theta_c \]
\[ \theta_1 = 0.0 \]
\[ \cos \theta_1 = 1.0 \]

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

For \( \theta > \theta_c \) Fresnel’s Law

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

\[ \theta < \theta_c \quad n_1 \sin \theta_1 \quad \text{is imaginary (Evanescent wave)} \]

\[ \theta > \theta_c \quad n_1 \sin \theta_1 \quad \text{is real, and zero at } \theta = \theta_c \]
### Some typical values for $\theta_c$ and $\sigma_a$

<table>
<thead>
<tr>
<th>Material</th>
<th>$\theta_c$ (deg / Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>0.1</td>
</tr>
<tr>
<td>Si</td>
<td>0.047</td>
</tr>
<tr>
<td>Cu</td>
<td>0.083</td>
</tr>
<tr>
<td>Al</td>
<td>0.047</td>
</tr>
<tr>
<td>D$_2$O</td>
<td>0.082</td>
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<table>
<thead>
<tr>
<th>Material</th>
<th>$\sigma_a$ (barns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>0.17</td>
</tr>
<tr>
<td>Cu</td>
<td>3.78</td>
</tr>
<tr>
<td>Co</td>
<td>37.2</td>
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<tr>
<td>Cd</td>
<td>2520</td>
</tr>
<tr>
<td>Gd</td>
<td>29400</td>
</tr>
<tr>
<td>Al</td>
<td>0.231</td>
</tr>
</tbody>
</table>
Specular Neutron Reflection (simple interface)

Within Born Approximation the Reflectivity is given as,

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

\[ Q = k_1 - k_2 = 4\pi \sin \frac{\theta}{\lambda} \]

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

\[ R = \frac{|n_0 \sin \theta_0 - n_1 \sin \theta_1|^2}{|n_0 \sin \theta_0 + n_1 \sin \theta_1|} \]

\[ R(Q) = \frac{16\pi^2}{Q^4} \Delta \rho^2 \]
**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 **Fresnel's Law**

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

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

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

\[ r_{ij} = \frac{p_i - p_j}{p_i + p_j} \]

\[ p_i = n_i \sin \theta \]

\[ \beta_i = \frac{2\pi}{\lambda} n_i d_i \sin \theta_i \]
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 \( Q \gg Q_c \):

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

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

FRINGE SPACING:

\[
\Delta Q = \frac{2\pi}{d}
\]
For a simple interface reflectivity modified by,

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

\( \sigma \) is rms Gaussian roughness

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

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

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

From specular reflectivity cannot distinguish between roughness and diffuse interface

Reflectivity from a simple interface

Glass optical flat

\[ \theta = 0.35 \]

\[ Nb = 0.35 \times 10^{-5} \text{ A}^{-2} \]

\[ \sigma = 33\text{Å} \]

\[ \Delta \theta = 5\% \]

Penfold & Thomas
1990
Reflectivity from thin films

Effect of film thickness and refractive index
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

\[ d = 1198 \text{Å} \]
\[ N_b = 0.74 \times 10^{-5} \text{Å}^{-2} \]
\[ \theta = 0.5, \Delta \theta = 4\%, \sigma = 20 \text{Å} \]

NiC film on silicon

\[ d = 1194 \text{Å}, N_b = 0.94 \times 10^{-5} \text{Å}^{-2} \]
\[ \theta = 0.5, \Delta \theta = 4\%, \sigma_1 = 10, \sigma_2 = 15 \text{Å} \]
Reflection from more complex interfaces (multiple layers)

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

\[ r_1, t_1 t_2 r_2, -t_1 t_1 r_1^2 r_2^2, t_1 t_1 r_1^2 r_2^3 \quad \text{and so on} \]

Phase change on traversing film,

\[ \delta_1 = \frac{2\pi}{\lambda} n_1 d_1 \sin \theta_1 \]

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

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

Airy's formula (Parratt)

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\[ \text{G B Airy, Phil Mag 2 (1833) 20} \]

(\text{Parratt, Phys Rev 95 91954}) 359

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

\[ r_1, t_1 t_2 r_2, -t_1 t_1 r_1^2 r_2^2, t_1 t_1 r_1^2 r_2^3 \quad \text{and so on} \]

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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 continuous at each boundary gives rise to a Characteristic matrix per layer,

\[
M_j = \begin{bmatrix}
\cos \beta_j & -(i/p_j) \sin \beta_j \\
-ip_j \sin \beta_j & \cos \beta_j
\end{bmatrix}
\]

\[
p_j = n_j \sin \theta_j
\]

\[
\beta_j = \left(\frac{2\pi}{\lambda}\right)n_j d_j \sin \theta_j
\]

\[
M_R = [M_1][M_2] \ldots [M_n]
\]

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,

\[
C_j = \begin{bmatrix}
    e^{i\beta_{j-1}} & r_je^{i\beta_{j-1}} \\
    r_je^{-i\beta_{j-1}} & e^{-i\beta_{j-1}}
\end{bmatrix}
\]

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

To include roughness,

\[
r_j = \frac{(p_{j-1} - p_j)}{(p_{j-1} + p_j)} \exp(-0.5q_jq_{j-1}\sigma^2)
\]

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, \( \Delta Q/Q \) 2%, 6%

Damps interference fringes, rounds critical edge
Surface roughness and Waviness

Curvature > coherence length \[\rightarrow\] Rough

Curvature < coherence length \[\rightarrow\] 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

\[A(Q) \sim\text{Beer-Lambert}\]
Model fitting Reflectivity data

• 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
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: \[ h_{ii} = |\hat{n}_i|^2 \]

\( \hat{n}_i \) 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, $Q_z$, perpendicular to the interface

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

INTER, POLREF, OFFSPEC, SURF, CRISP reflectometers

Instrumentation

White beam time of flight, fixed geometry: Wavelength range 1-7(16)Å
Q range $3 \times 10^{-3}$ to 0.5 Å$^{-1}$

$Q_{\text{max}}$ (d$_{\text{min}}$) limited by background:

$\Delta Q/Q$

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

incoherent scattering in sample
1.5 x 10$^{-6}$ for D2O, 4x10$^{-6}$ for H2O
<10$^{-6}$ for silicon
Instrumentation

Correct for detector efficiency, spectral shape, background

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

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

Monitor

Corrected data

Raw data

D\textsubscript{2}O

Specular, 1.5°

Background (off-specular), 2°
Instrumentation
There several ways of polarising and flipping neutrons, but that is beyond scope of this talk.
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 \( p = (2.695 \times 10^{-4}/\mu_B)|\mu_i| \)

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

\[ R(I/I_0) \]

\[ Q_z (\text{Å}^{-1}) \]

A 500 Å Ni layer on Si substrate

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

Air Contrast Matched Water

\[ A = \sum b / d \rho \]

\[ \Gamma = 1 / A.N_{av} \]

\[ d \rho = \sum b_1 / A_1 + \sum b_2 / A_2 \]

\[ C_{wHxDyOzS} \]
Surfactant adsorption at the solid-solution interface

$h\text{-C}_{16}\text{TAB} / D_2O$

$10^{-4}$ M to 2 mM

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

Optical biosensors

Principle: contaminants in water degrade lipid layer allowing release of trapped NO₂ causing colour change in pigment.

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

(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.

Chemical structure of the phthalocyanine ligand. The six R groups are C₁₀H₂₁.
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
Additives made from polymerised 1,3 butadiene end capped with diphenyl ethylene and terminated with fluorinated aryl ether bromide followed by saturation with D₂ at 500 psi.

<table>
<thead>
<tr>
<th>sample code</th>
<th>target $M_n$/kg mol⁻¹</th>
<th>measured $M_n$/kg mol⁻¹</th>
<th>$M_w/M_n$</th>
<th>% end-capping</th>
<th>$f (= [D]/[H + D])$</th>
<th>$T_m$/°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>2CFdPE5</td>
<td>5</td>
<td>7.1</td>
<td>1.05</td>
<td>84</td>
<td>0.43</td>
<td>96</td>
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<tr>
<td>PE50</td>
<td>50</td>
<td>56.6</td>
<td>1.04</td>
<td></td>
<td></td>
<td>106</td>
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</tbody>
</table>

- 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
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 ($\chi_b - \chi_s = 3.0k_B T$)
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
  • Durham (synthesis, NRA, Contact angle, AFM, SCF calculations)
• Nigel Clarke
• Soloman Kimani
• Laura Mears
• Emily Smith
  • Nottingham(XPS)
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
• 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.)

<table>
<thead>
<tr>
<th>sample</th>
<th>dry thickness (nm)</th>
<th>γ (Å)</th>
<th>$\Gamma_{\text{DMAEMA}}$ (10$^{-25}$ mol Å$^{-2}$)</th>
<th>$\sigma$ (nm$^{-2}$)</th>
<th>$N$</th>
<th>$M_w$ (kg/mol)</th>
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</thead>
<tbody>
<tr>
<td>a</td>
<td>5</td>
<td>47</td>
<td>$3.5 \pm 0.3$</td>
<td>$0.13 \pm 0.02$</td>
<td>155</td>
<td>$24 \pm 5$</td>
</tr>
<tr>
<td>b</td>
<td>11</td>
<td>100</td>
<td>$7.4 \pm 0.7$</td>
<td>$0.12 \pm 0.02$</td>
<td>443</td>
<td>$70 \pm 16$</td>
</tr>
<tr>
<td>c</td>
<td>17</td>
<td>142</td>
<td>$10.4 \pm 1.0$</td>
<td>$0.14 \pm 0.02$</td>
<td>430</td>
<td>$68 \pm 15$</td>
</tr>
<tr>
<td>d</td>
<td>17</td>
<td>167</td>
<td>$12.4 \pm 1.2$</td>
<td>$0.18 \pm 0.03$</td>
<td>434</td>
<td>$68 \pm 15$</td>
</tr>
</tbody>
</table>
• NR data collected on the SURF reflectometer at ISIS

• Sapphire-D$_2$O qc $\sim$0.0048 Å$^{-1}$

• 4 angles of incidence 0.1, 0.25, 0.7, 1.5° data combined to cover 0.0033<q<0.6Å$^{-1}$

• 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

<table>
<thead>
<tr>
<th>[SDS] (mM)</th>
<th>$\Gamma_{SDS} \left(10^{-25} \text{ mol} \ \text{Å}^{-2}\right)$</th>
<th>$n_{SDS}/n_{DMAEMA}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$4.6 \pm 0.5$</td>
<td>0.37</td>
</tr>
<tr>
<td>5</td>
<td>$6.7 \pm 0.7$</td>
<td>0.55</td>
</tr>
<tr>
<td>10</td>
<td>$5.3 \pm 0.5$</td>
<td>0.43</td>
</tr>
</tbody>
</table>

Onset of SDS adsorption analogous to CMC in bulk
Lowering of chemical potential in brush estimated from cac /cmc $\sim 1.4k_B T$
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 ~40 Å typical of an SDS micelle or bilayer
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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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

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

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$^{3+}$

\[ A = \sum \frac{b}{d} \cdot Nb \]

\[ \Gamma = \frac{1}{A \cdot N_{av}} \]

- alkyl chain d labelled SLES, dC12hE1S, dC12hE2S, and dC12hE3S.
- thin monolayer, $\sim 17 \pm 2$ Å, of uniform composition
(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

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

\[ R_{tot} = R_1 + \frac{AR_2(1 - R_1)^2}{1 - AR_1R_2} \]

\[ A = \exp\left(\frac{-2\chi_d_{oil}}{\sin \theta_{oil}}\right) \]

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

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

\[ n = 1 - \lambda^2 A - i\lambda B \]

\[ A = \frac{Nb}{2\pi} \]

\[ b_{\text{total}} = b_{\text{nuclear}} \pm b_m \]
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

(2) TP Russell, Mat Sci Rep 5 (1990) 171

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


(c) Basic scattering theory