Modelling Data – Better Approaches
How to get useful information?

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Define $g_s(Q_z)$ in terms of measured reflectivity and $R_F(Q_z)$ (the Fresnel reflectivity for perfectly sharp interface):

$$g_s(Q) = Q^2 \frac{(R - R_F)}{(1 - R)}$$

$$\ln g_s(Q) \approx -t^2 Q^2 / 12$$

Roughly $\ln (Q^2 R) \approx -t^2 Q^2 / 12$

Contrast match of two bulk phases $R_F(Q) = 0$
Real Interfaces are not just layers

Slab models are easy to calculate but people are not very interested in just thickness and scattering length density
Surface Excess and Area per Molecule

Volume per molecule: \( V_m \)
Scattering length: \( b_m \)
Scattering length density: \( \rho = \frac{b_m}{V_m} \)

Thickness of layer: \( t \)
Scattering length density \( \rho \)
Area per molecule: \( A_m \)
\( V_m = t A_m \)
Scattering length density:
\( \rho = \frac{(b_m / V_m)}{t A_m} = \frac{b_m}{t A_m} \)

Area per molecule: \( A_m = \frac{b_m}{t \rho} \)
Adsorption of Surfactant

Surface active molecules
Amphiphilic
Bind to surface – how?
What are properties?

Hexadecyl trimethyl ammonium bromide
C_{16}H_{33}N(CH_3)_3^+ Br^-
Some Possible Structures

- Monolayer
- Bilayer
Cationic Surfactant

CTAB at 27° C on amorphous SiO$_2$

(a) D$_2$O  (b) cmSiO$_2$

at 6 $\times$ 10$^{-4}$ M

Models

Solid line – Bilayer

Dashed line - Monolayer
Cationic Surfactant

- CTAB 27 C on SiO₂
- Label heads & tails

  Head 6 +/- 2 Å
  Tail 28 +/- 4 Å
  Roughness ~ 8 Å
  Fractional Coverage
  35% at 3 \times 10^{-4} \text{ M}
  80% at 6 \times 10^{-4} \text{ M}

Different representation is helpful
How to Look at Data?

\[ \log_{10} R \text{ vs } Q \]

\[ RQ^4 \text{ vs } Q \]
Effects of Resolution

Silicon substrate: film thickness 1500 Å
scattering length density $6.3 \times 10^{-6}\,\text{Å}^{-2}$
Non-Uniform Surfaces

If you have patches of different layers at an interface do you average the density or average the reflectivity?

What is the coherence length of a neutron?
Describing Polymers

• Interdiffusion – is this roughness?
• Brushes – parabolic density profile
  (E. P. K. Currie et al *Physica* B, 283 17 – 21)
• Other scaling laws e.g. O. Guiselin *J. Phys.* **50**, 3407-3425 (1989).

We expect smooth profiles!
Fig. 6  Experimental reflectivity profiles obtained at ILL (circles) and fitted reflectivity profiles using a polymer layer model (dashed curves) and a lattice mean-field theory (solid curves) for polymers grafted on a Si/SiO$_2$/initiator surface at 328 K (top) and 293 K (bottom) in D$_2$O (left) and cmSi (right). Reflectivity profiles using a polymer layer model with zero roughness are also shown (dotted curves). The top right panel contains an inset displaying $q^4R(q)$ versus $q$ for small $q$.

Repeating Layers

A one dimensional crystal

Bragg’s law

Intensity of peaks may Depend on size and disorder
Calculate reflectivity for a profile
Using Multiple Contrasts

Simultaneous fits for multiple data sets
Off-specular Scattering, GISANS, Near-surface SANS

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Interfaces are 3-dimensional

Understanding rheology – shear flow

Fate of a Neutron at an Interface

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

Below $k_c$ no travelling wave enters the sample.

Amplitude decays with depth in sample.

Decay length depends on $(\theta_c - \theta)$.

Evanescent wave can cause scattering.
Looking at Materials

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Off-specular & Reflection

\[
Q_z \approx (2\pi/\lambda) (\theta_i + \theta_f)
\]

\[
Q_x \approx (2\pi/\lambda) (\theta_i + \theta_f) (\theta_i - \theta_f)
\]

Peter Müller-Buschbaum ‘GISAXS and GISANS as metrology technique for understanding the 3D morphology of block copolymer thin films’ European Polymer Journal 81, (2016), 470-493.
10% vol. dispersion, Radius ~350 Å. Sapphire substrate, $\theta_i = 0.35$ deg

PS latex in D$_2$O Liquid/Sapphire

Strong Off-specular Scattering
PS latex in D$_2$O Liquid/Sapphire

Transform to map of $Q_z Q_x$

10% vol. dispersion, Radius $\sim$350 Å, sapphire substrate, $\theta_i = 0.35$ deg
Some Scattering at Interfaces

X-ray scattering –
glass


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**FIG. 6.** Calculation of diffuse scattering in the distorted-wave Born approximation for rocking curve where $\theta_1$ and $\theta_2$ are varied such that $2\theta$ is fixed at $1^\circ$. The asymmetry is due to the area of the illuminated surface decreasing as $\theta_1$ is increased. The $q_y$ direction has been integrated over. Parameters are $\sigma = 7$ Å, $h = 0.2$, $\xi = 7000$ Å, and the optical constants for Pyrex are given in Sec. V.
Scattering from D$_2$O and from null reflecting water (8% D$_2$O)

Interfacial structure: GISANS

Calculating Scattering

Distorted Wave Born Approximation (DWBA)

Simply allow for sequential events e.g.

Reflection then Scattering
Refraction then Scattering
Scattering then Reflection

(a) Optical Matrix Calculation
(b) Weak Scattering (Born approximation)
How deep is the evanescent wave?

Silicon/D$_2$O Interface
Copolymer films

Changes with Depth

Horizontal cuts

- Used wavelength to probe different depths
- Longer wavelength looks nearer the surface

Diffraction from Surface Layers

Penetration depth

\[ z_{1/e} = \sqrt{2\lambda} / 4\pi \left[ \sqrt{(\theta_i^2 - \theta_c^2)^2 + \left( \frac{\lambda}{2\pi \mu} \right)^2 - (\theta_i^2 - \theta_c^2)} \right]^{1/2} \]

A depth sensitive technique:

Wavelength

Incident angle
Data at different angles
Data at different angles

- $z_1/e$
- $\langle z_{1/e} \rangle$
- $Z_{1/e}$

Graph showing intensity and $\log(z_{1/e})$ vs. $\theta_l/\theta_c$ for different values of $a$ and $z_g$.
QCM-D data: structure forms with a separation from the interface [Hellsing et al. 2017, manuscript]
Scattering at Interfaces

- Off-specular scattering
- Near Surface SANS
- GISANS

What is the difference?
PS latex in D$_2$O Liquid/Sapphire

Transform to map of $Q_z Q_x$

$10\%$ vol. dispersion, Radius $\sim$350 Å, sapphire substrate, $\theta_i = 0.35$ deg
PS latex in D$_2$O – sapphire surface

Sum along $Q_x$

10% vol dispersion, 0.35
Assign Bragg peaks (index)

\[ Q_1 = 0.00282 \text{ Å}^{-1} \]
\[ d = 2230 \text{ Å} \]

3 first peaks outside range

10% vol dispersion, 0.35, 0.8 and 1.5 deg

\[ y = 0.002820x - 0.000360 \]
PS latex in D$_2$O – sapphire surface

Sum along $Q_x$

$R(Q)$

10% vol dispersion, 0.35
Compare Qx and Qz