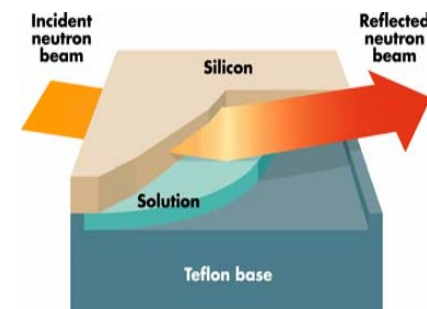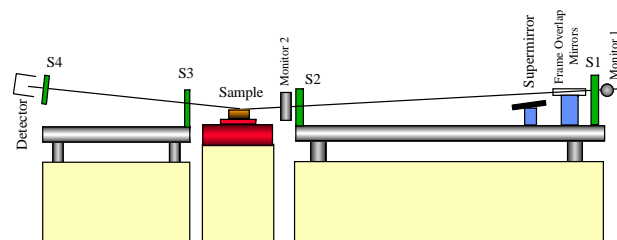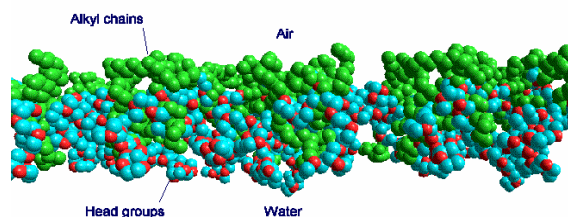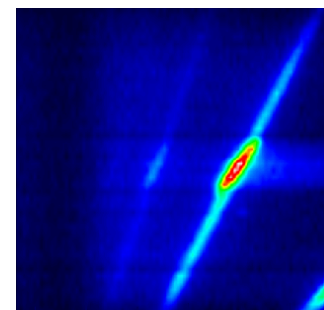Oxford Summer School. September 2007

Soft Condensed Matter 1

The study of surfaces and interfaces using Neutron Reflectometry (adsorption, polymer films, bio-interfaces)
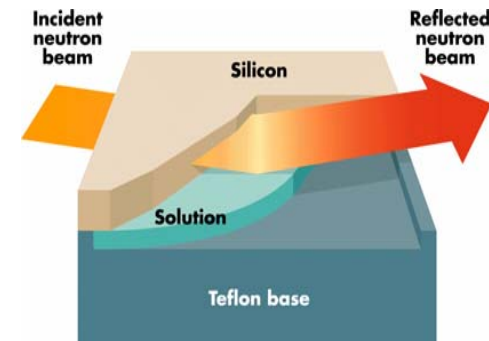
Jeff Penfold
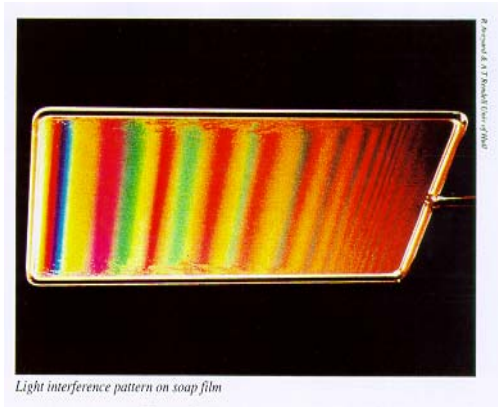**ISIS Facility, Rutherford Appleton Lab**

Specular reflection from surfaces and interfaces

DEPTH PROFILING : provides information about concentration / composition profiles normal to the interface
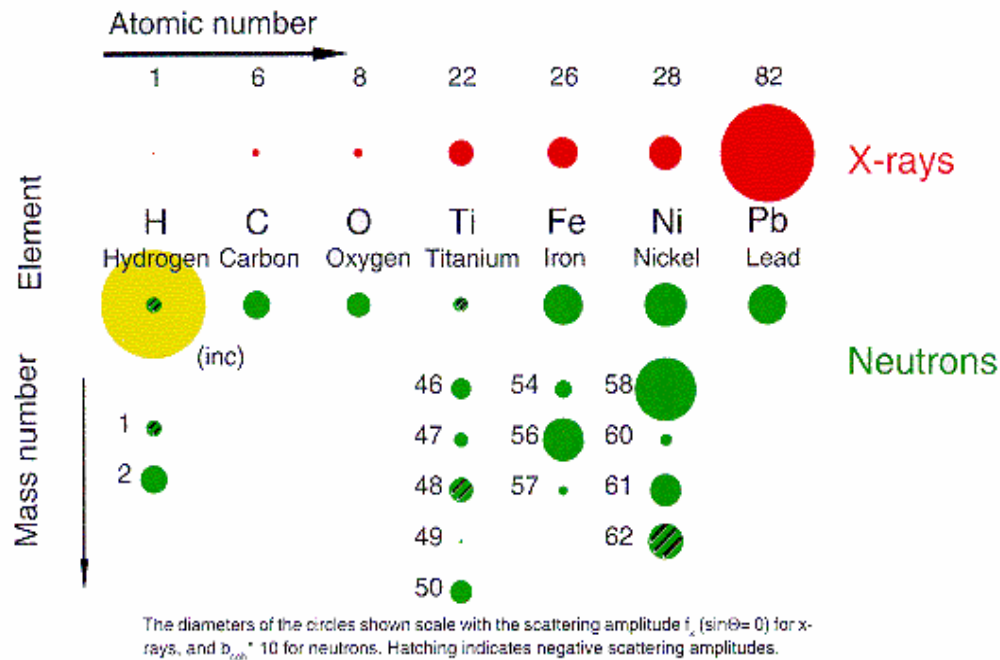

Incident neutron beam | Reflected neutron beam | Silicon | Solution | Teflon base

Analagous to optical interference, ellipsometry

Light interference pattern on soap film

- **Manipulate Refractive Index**
- **Penetrating probe**
- **Magnetic Interaction**
- **In-situ, non-destructive**
- **Require optical quality surfaces**

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

Refractive Index for Neutrons

Atomic number

1   6   8   22   26   28   82

X-rays

H   C   O   Ti   Fe   Ni   Pb
Hydrogen Carbon Oxygen Titanium Iron Nickel Lead

Element

(inc)

Mass number

1

2

46   54   58
47   56   60
48   57   61
49   62
50

Neutrons

The diameters of the circles shown scale with the scattering amplitude f_x ($\sin\Theta = 0$) for x-rays, and b_{coh} * 10 for neutrons. Hatching indicates negative scattering amplitudes.
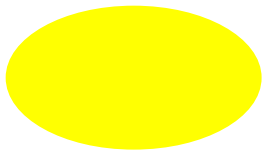
$$n = \frac{k_1}{k_0}$$

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

$$A = \frac{N b}{2\pi}$$

Extensively use H/D isotopic substitution to manipulate " contrast " or refractive index
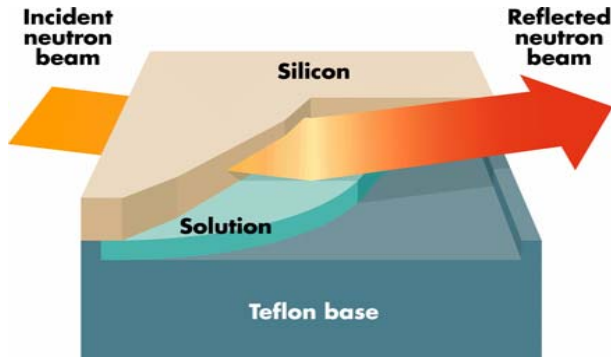
H -0.374×10^{-12} cm

D 0.667×10^{-12}

n < 1.0 hence

TOTAL EXTERNAL REFLECTION

Typically $\theta_c \sim 0.1° / \text{Å}$

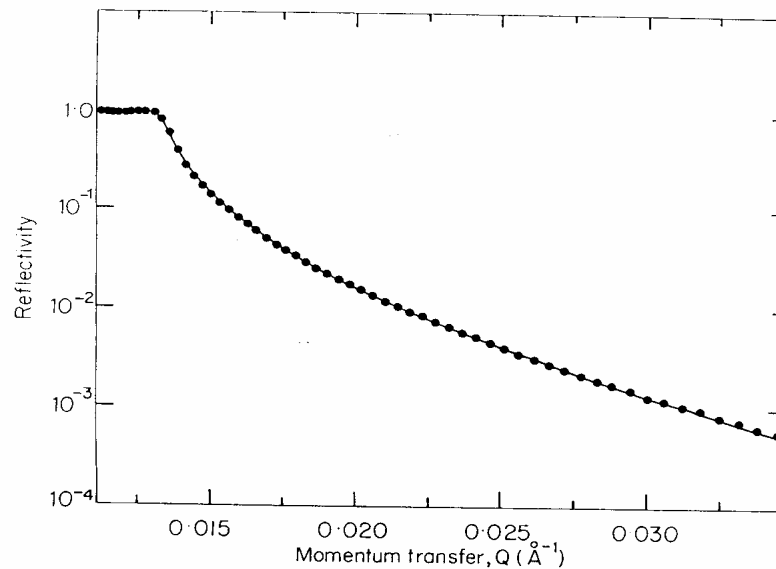# Specular Neutron Reflection
(simple interface)

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**

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

Specular Neutron Reflection

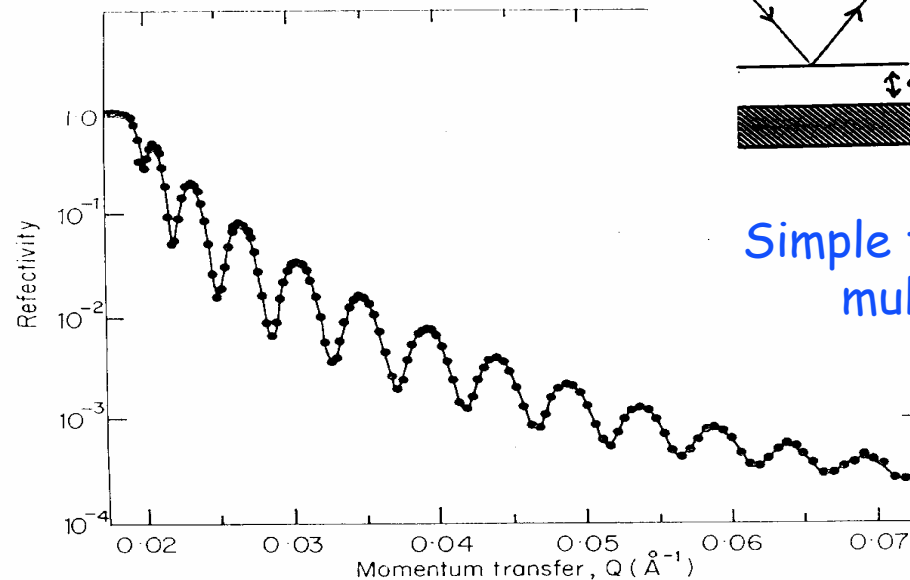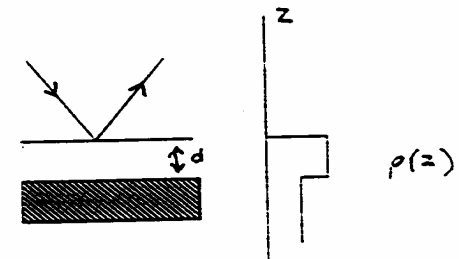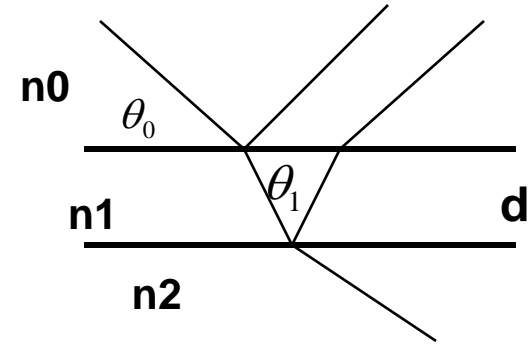For thin films see interference effects that can be described using standard thin film optical methods

For a single thin film at an interface

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

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

$$p_i = n_i \sin \vartheta$$

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

n0

θ_0

n1   d

θ_1

n2

z

$\rho(z)$

d

Simple to extend to multilayers

Reflectivity

10^0

10^{-1}

10^{-2}

10^{-3}

10^{-4}

0·02   0·03   0·04   0·05   0·06   0·07

Momentum transfer, Q (Å⁻¹)

Visibility of fringes affected by resolution, contrast, sample quality

CLRC

ISIS

Off-Specular Scattering
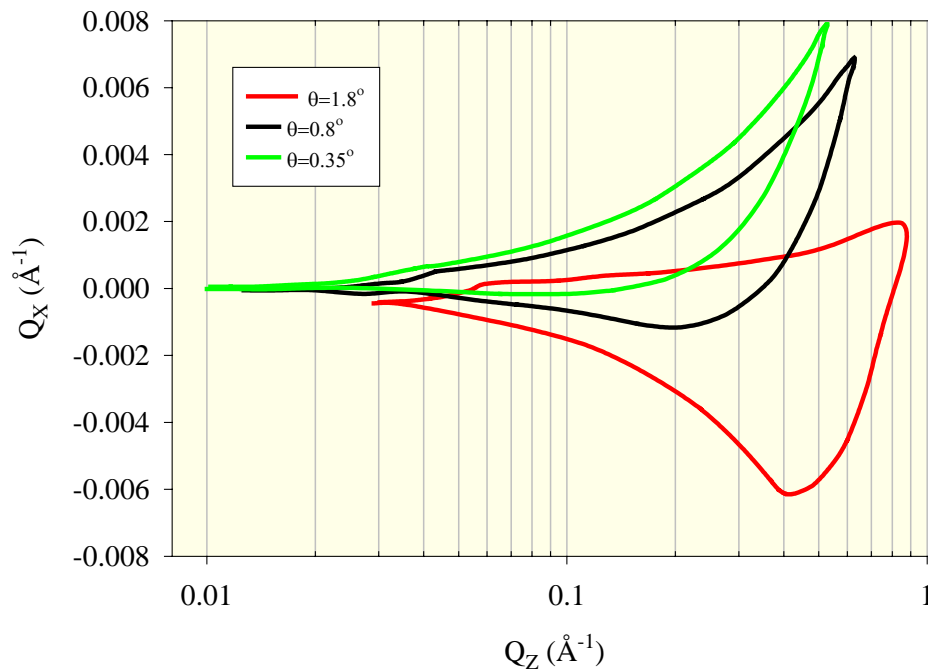
Figure 1. The accessible wave-vector range for a series of incident angles for the current SURF geometry.
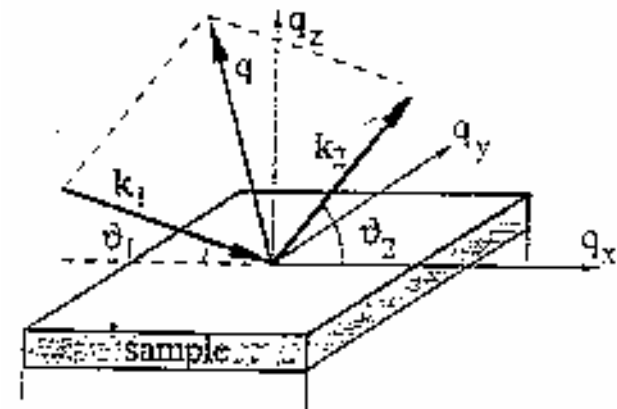
$$q=k_1-k_2$$
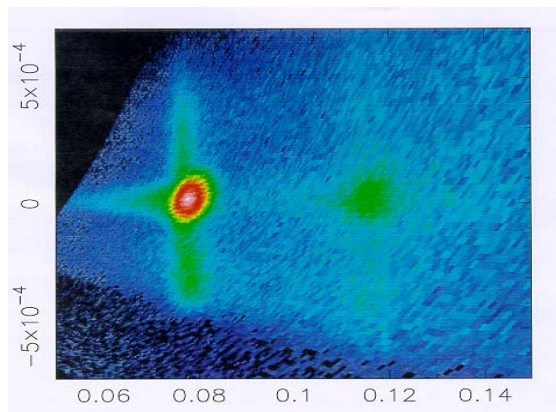$$q_z=2k\sin\theta$$
$$q_x=k(\cos\theta_1-\cos\theta_2\cos\psi)$$
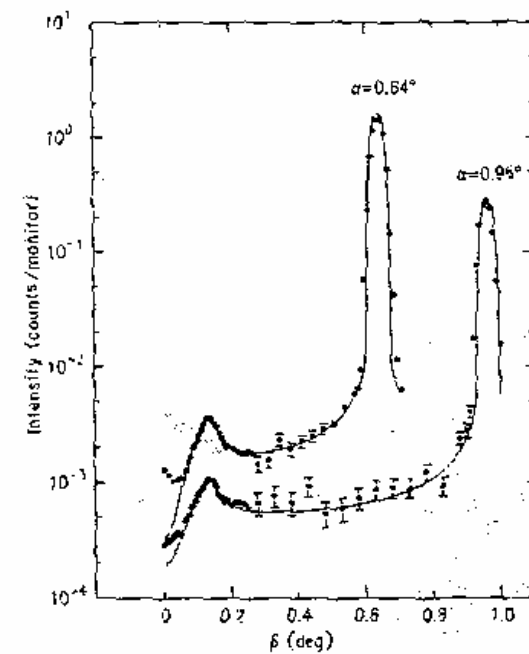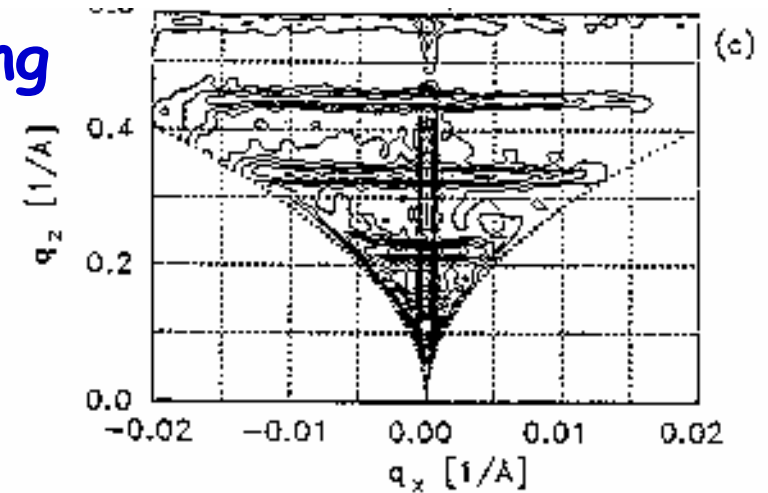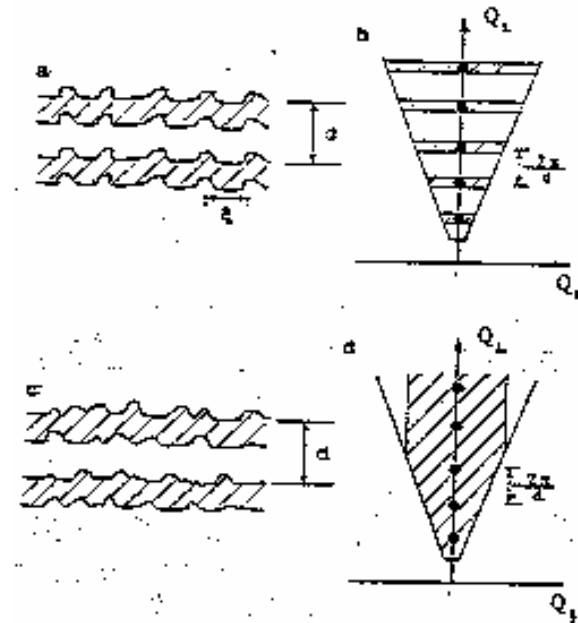$$q_y=k\cos\theta_1\sin\psi$$

ψ is angle out of plane

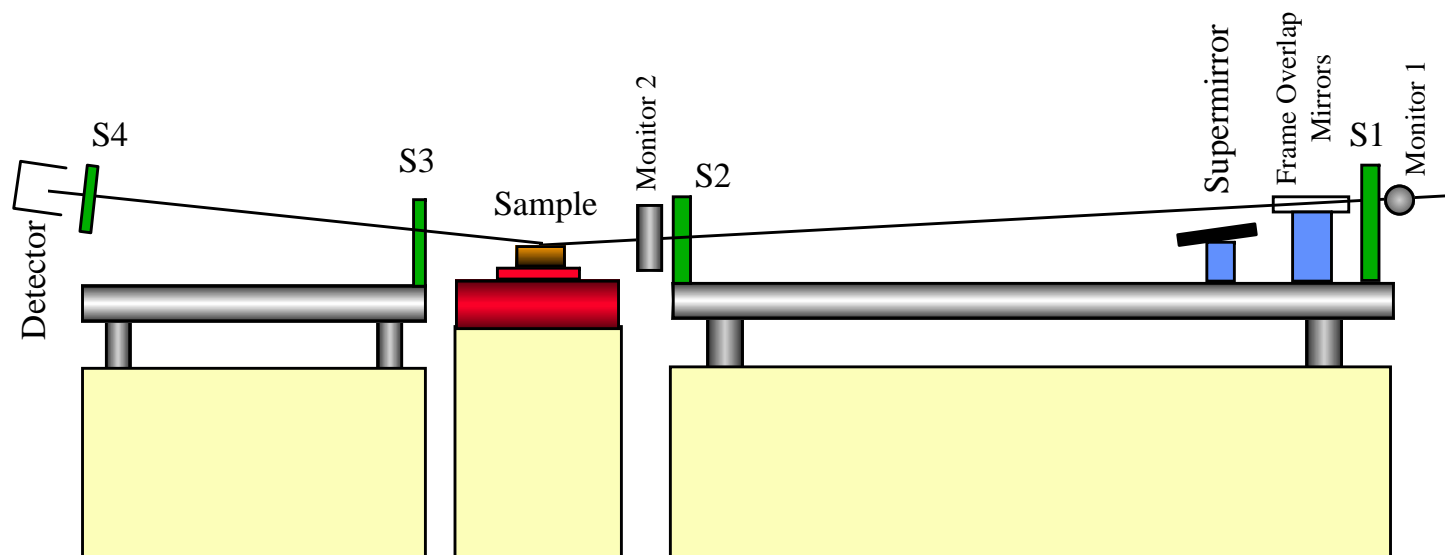(Sinha et al, Phys Rev B 38 (1988) 2297)

Off-specular or diffuse scattering

In Distorted Wave Born Approximation, DWBA

$$\left.\frac{d\sigma}{d\Omega}\right)_{diff} = N^2 b^2 L_x L_y \left|T_i(k_i)\right|^2 \left|T_r(k_r)\right|^2 S(q)$$

$$S(q) = \frac{1}{|\alpha|^2} e^{-(\alpha^2 - \alpha^{*2})\sigma^2/2} \int dx \int dy \, e^{iq.\rho} \left(e^{|\alpha|^2 C(x,y)} - 1\right)$$

Experimental Considerations

SURF, CRISP reflectometers at ISIS

White beam time of flight, fixed geometry: Wavelength range 1–7Å

Q range 5×10^{-3} to 0.5 Å^{-1}

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

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

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

(Penfold et al, J Chem Soc, Faraday Trans, 93 (1997) 3899)

Reactor based Instruments   D17 (ILL)
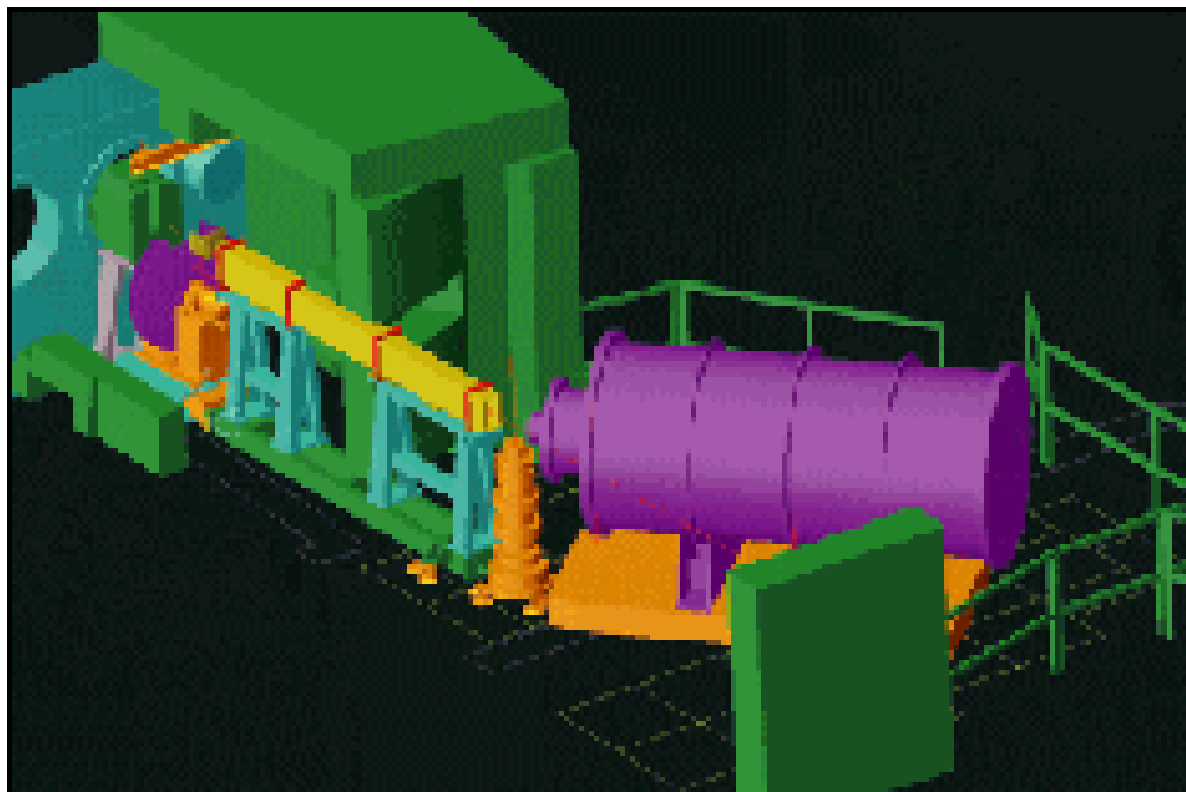
Monochro mode

Ni/Ti multilayer 5Å, 4%

Polarised mode

Fe/Si multilayer 5.5Å

0.005 to 1.5 Å-1

TOF mode

0.002 to 4 Å-1
Δλ 0.1 to 20%

Situated on a cold guide, H18
Vertical Surfaces
TOF / monochromatic /polarised modes

Experimental Considerations

Resolution

Accessible Q range

Si/D2O

Si/H2O

Si/cmSi
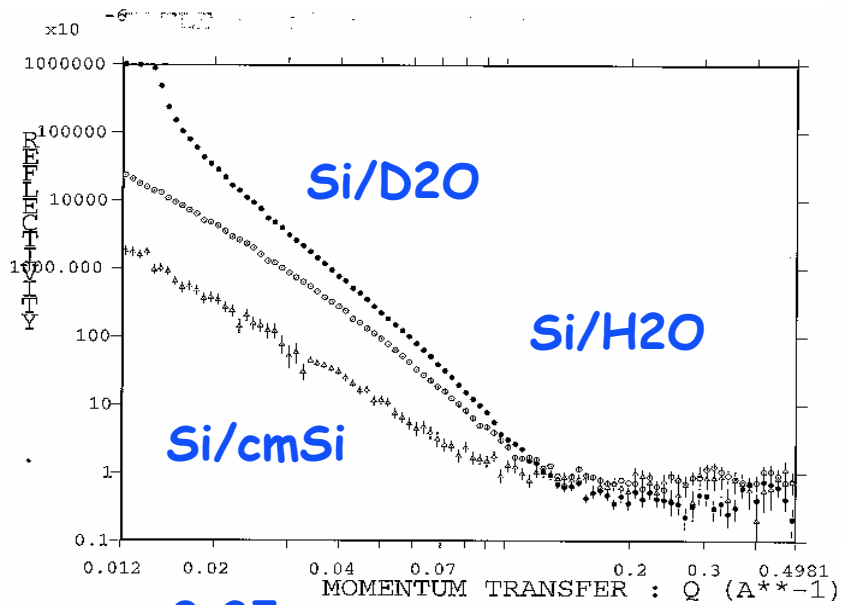
0.35

0.8

1.8

Silicon / water interface
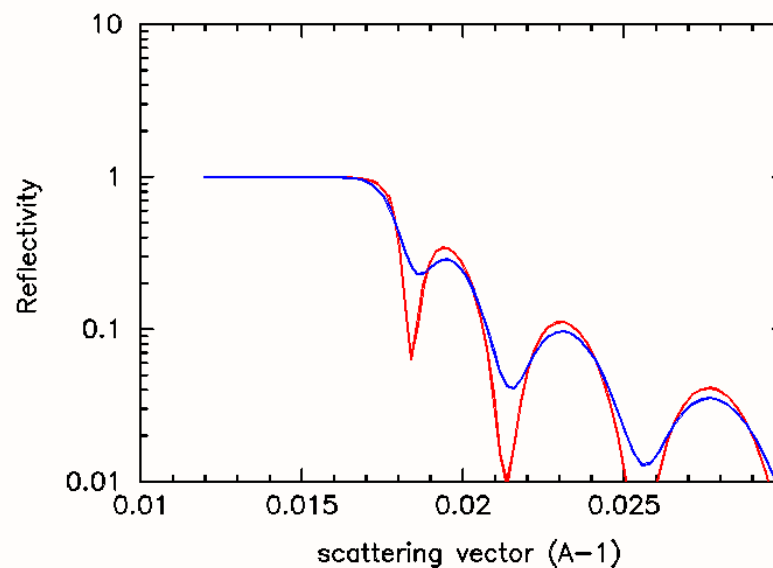
1000 Å film on Silicon
$\Delta\theta \sim 2\%,\ 6\%$

$$\Delta Q^2 \Big/ Q^2 = \Delta t^2 \Big/ t^2 + \Delta\theta^2 \Big/ \theta^2$$
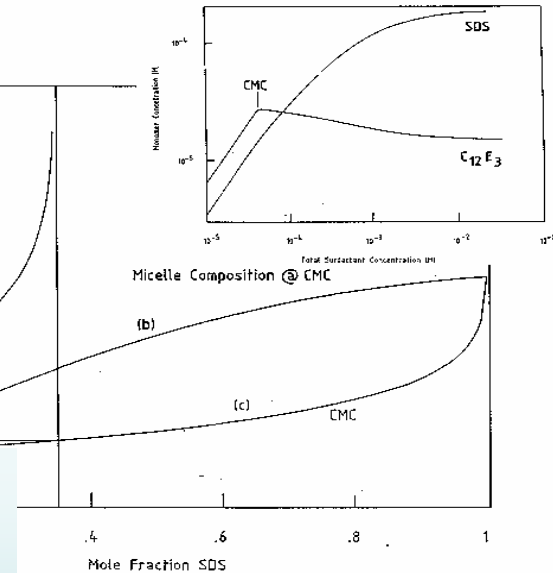
Surface Roughness / Surface Waviness

Curvature << coherence length

Surface is WAVY

Additional resolution term
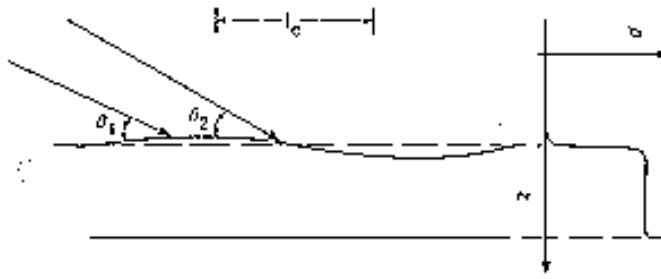
Geometrical optics

$$r_j = \frac{\left(p_{j-1} - p_j\right)}{\left(p_{j-1} + p_j\right)} \exp - 0.5 q_j q_{j-1} \sigma^2$$
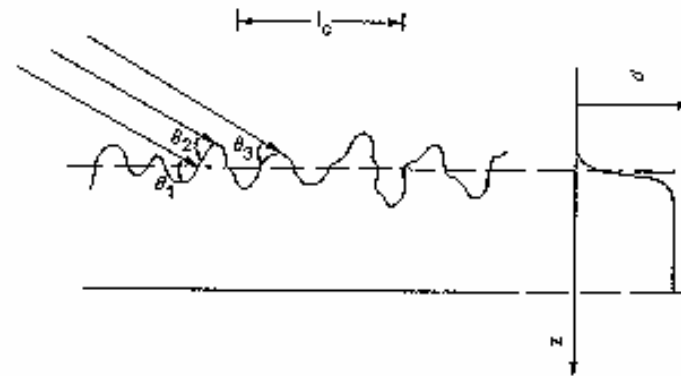
Curvature >> coherence length

Surface is ROUGH

(Nevot and Croce, Rev Phys Appl 15 (1980) 125)

Adsorption at Interfaces
(surfactants, polymer/surfactants)

Lu, Thomas, Penfold,
Adv Coll Int Sci 84
(2000) 143-304
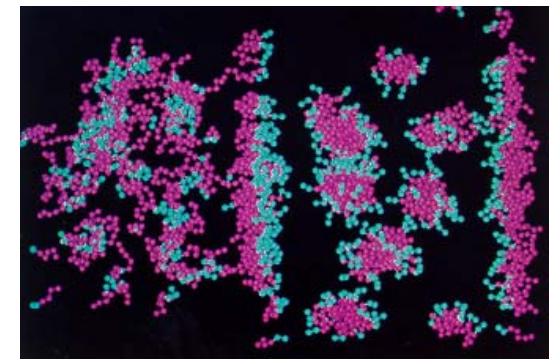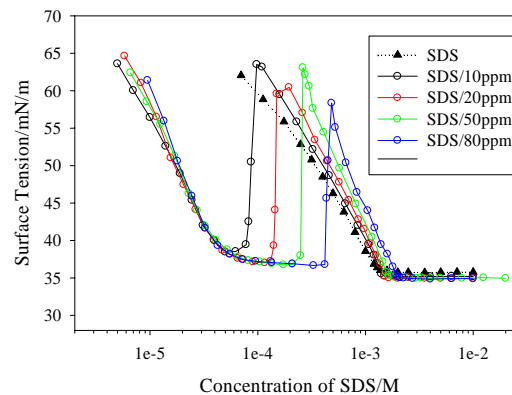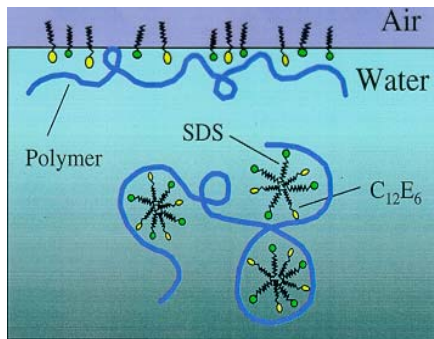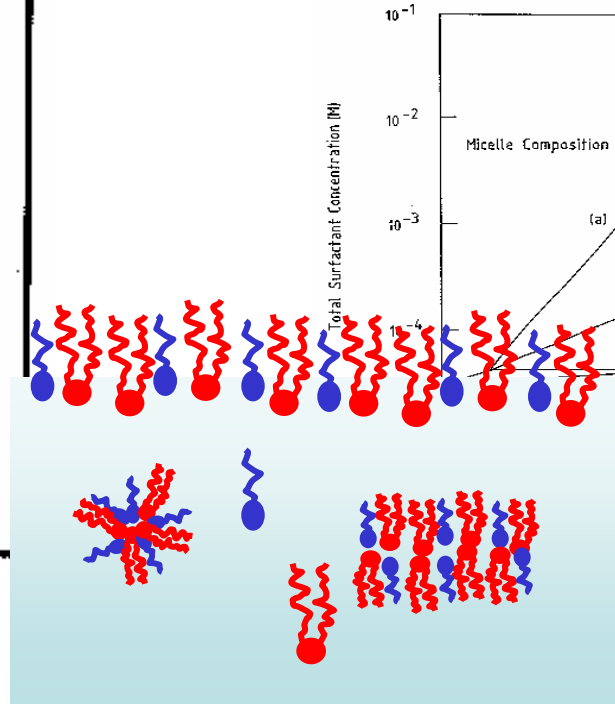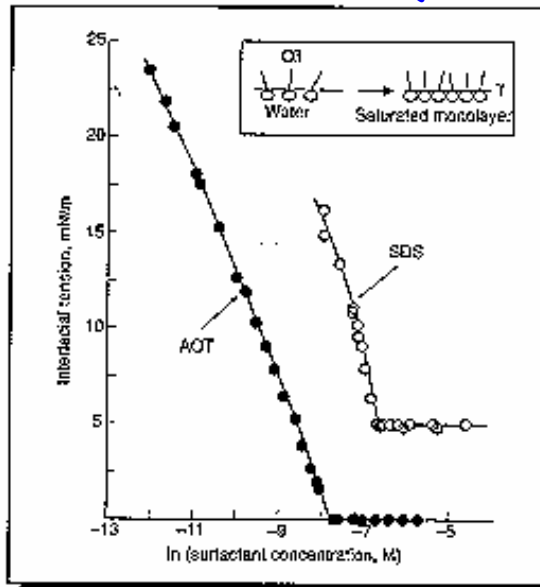
Thin Monolayers

Surfactant Adsorption at the air-water interface

d-C12h-E8 / nrw

9 x 10-5M (22.0)

9 x 10-6M (15.0)
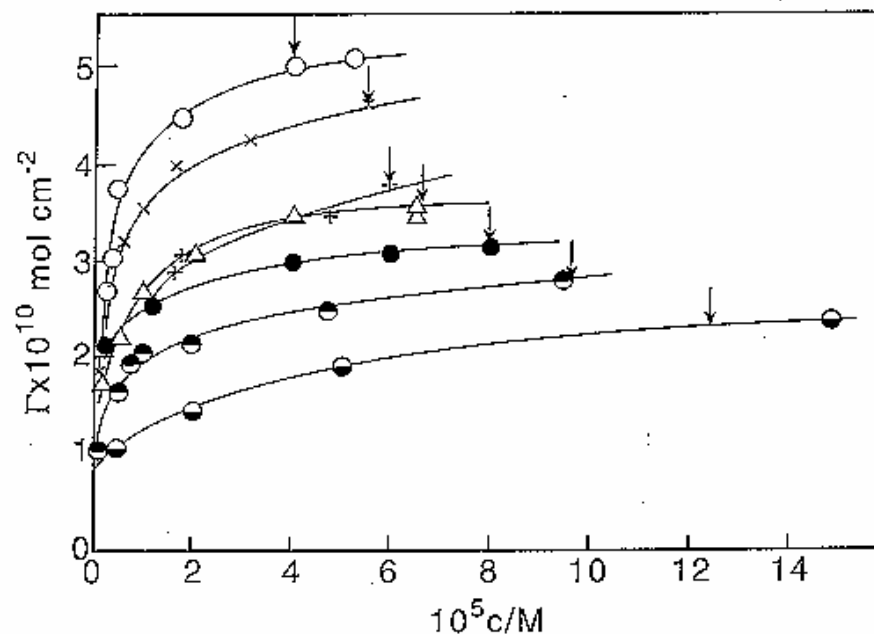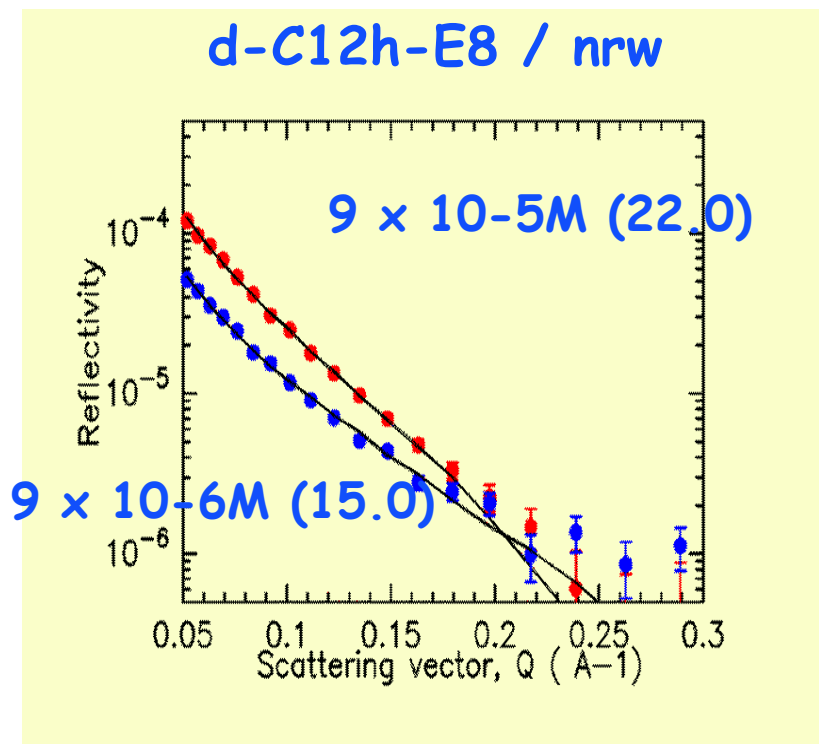
$$A = \frac{\sum b}{\tau\rho}$$

Non-ionic adsorption
C12E2 to C12E12
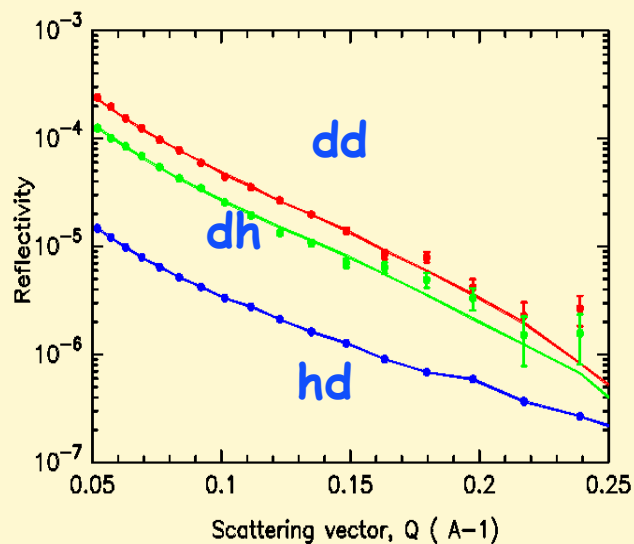
(Lu, Thomas, Penfold, Adv Coll Int Sci, 84 (2000) 143)

Thin Monolayers

dd

dh

hd

5 x 10-4M C12E3 / C12E8

Total
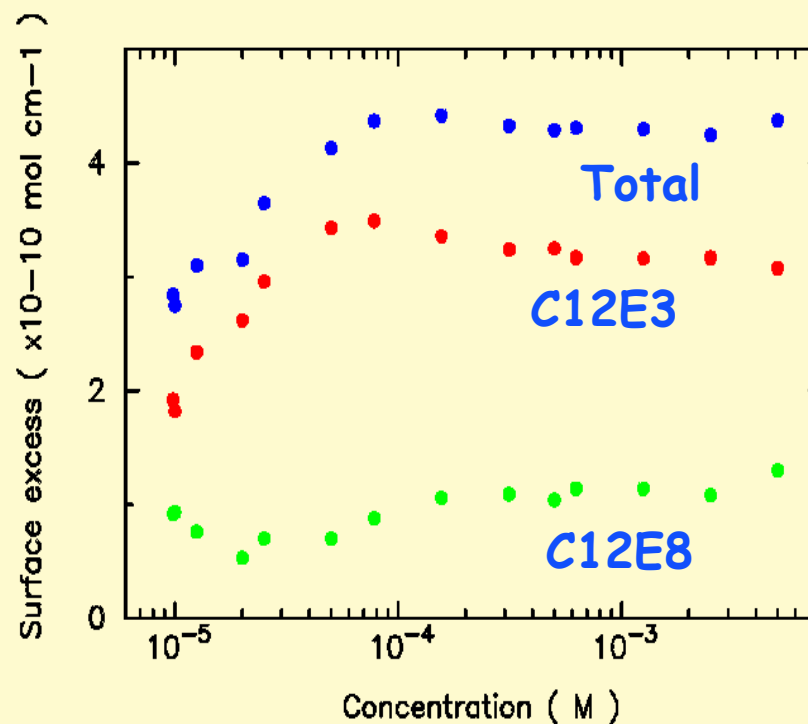
C12E3

C12E8

50/50 C12E3 / C12E8

$$d\rho = \frac{\sum b_1}{A_1} + \frac{\sum b_2}{A_2}$$

CLRC

ISIS

DHDAB / C12En surface composition (solution conc)
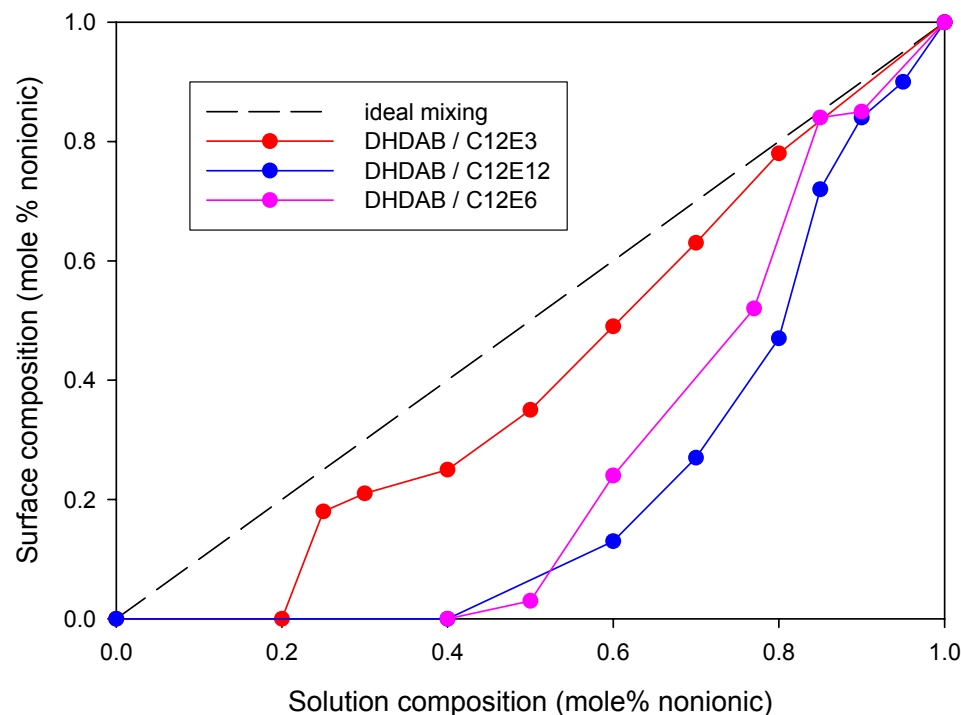
See extreme departure from ideality which cannot be accounted for by existing theories or structural changes in surface layer on mixing

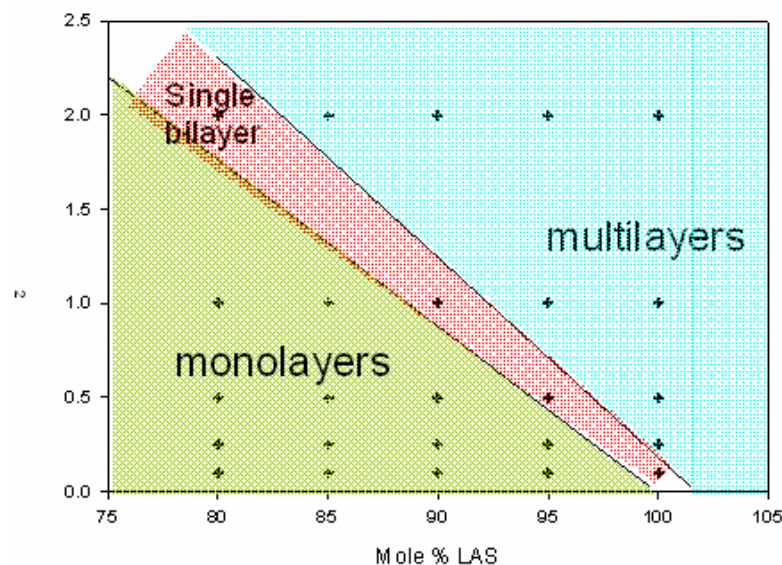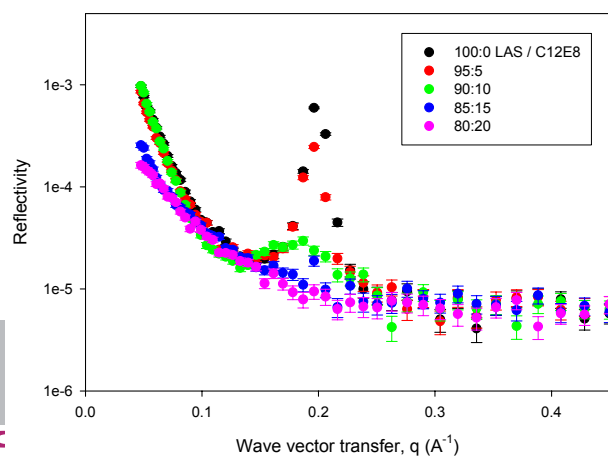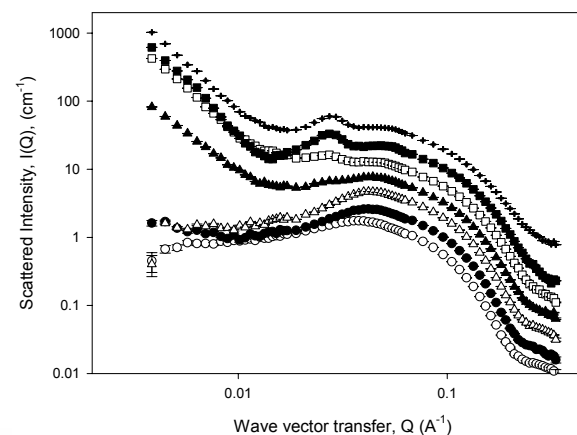Changes in bulk phase behaviour mediating changes in monomer conc
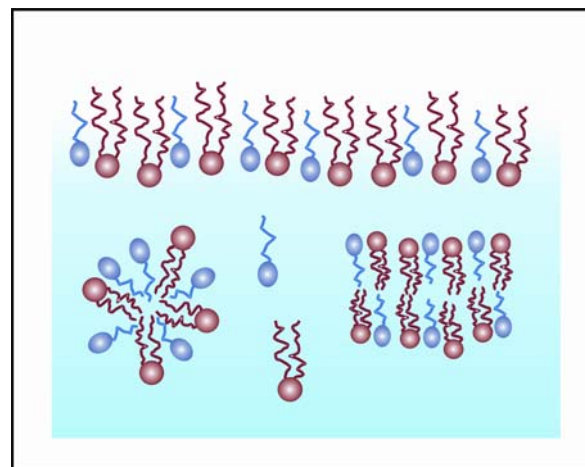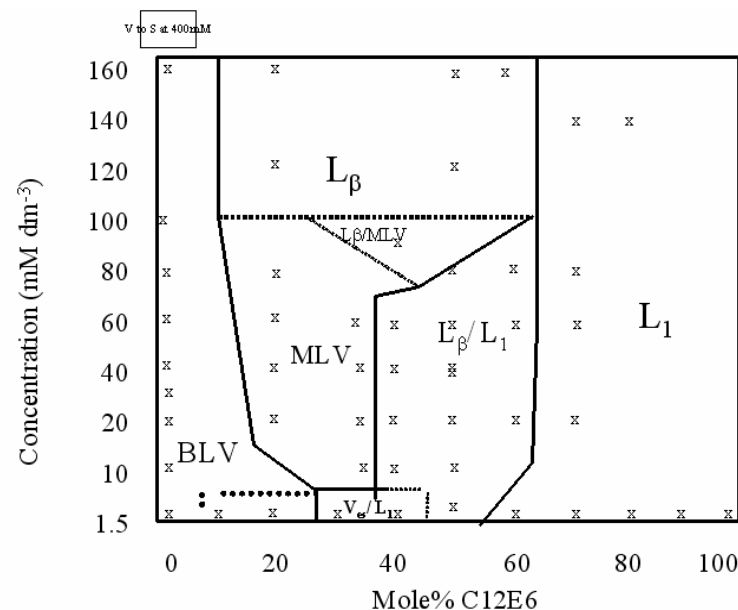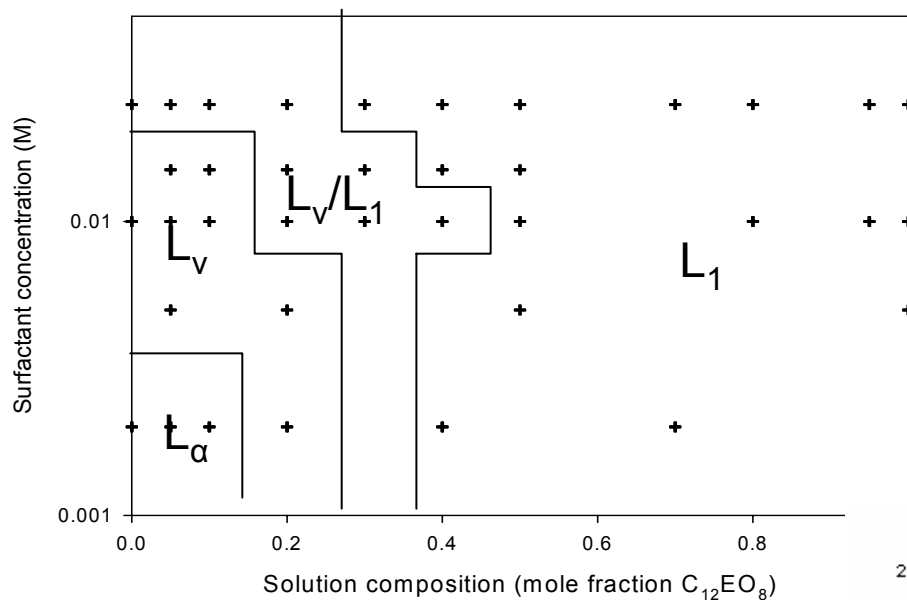
Penfold, Tucker, Thomas, Langmuir 20 (2004) 1269; 2265

LAS / $C_{12}E_8$ (in presence of Ca^{2+}) in solution and at a/w interface

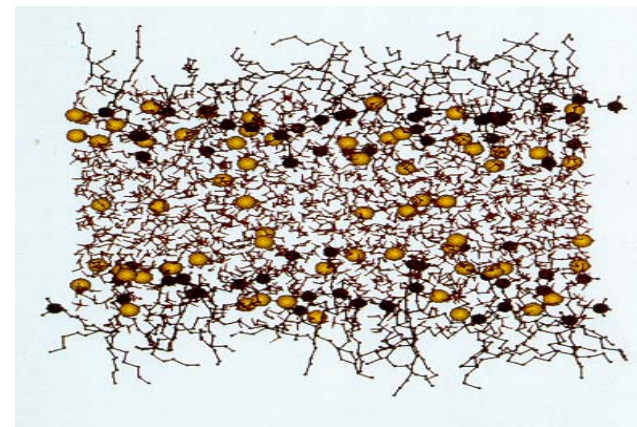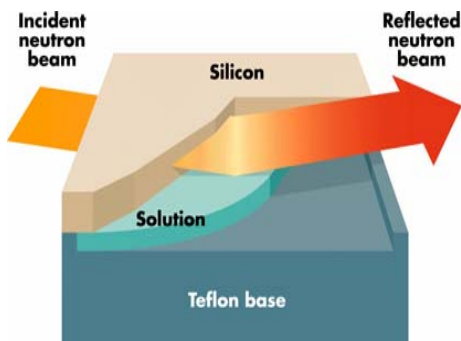# Structure of C$_{16}$TAB adsorbed layer

From simple labelling scheme (hg, chain, solvent)
compare distributions with computer simulations of
Klein (Pennsylvannia) and Brinckmann (Aachen)
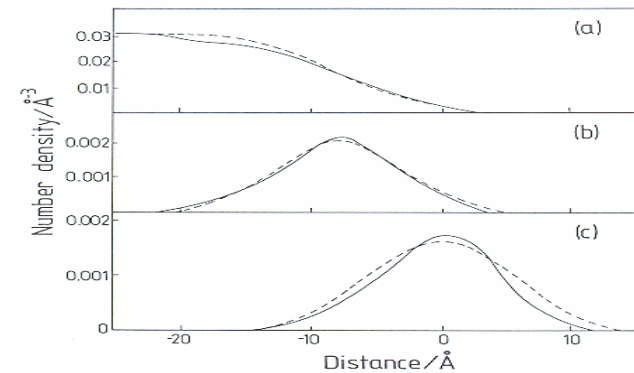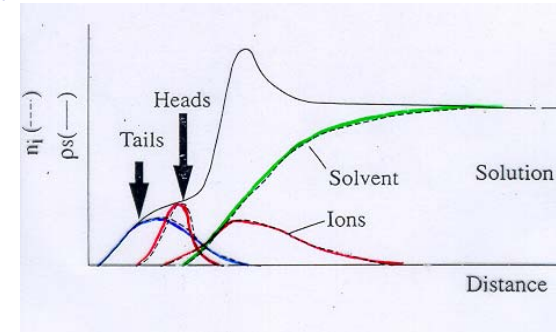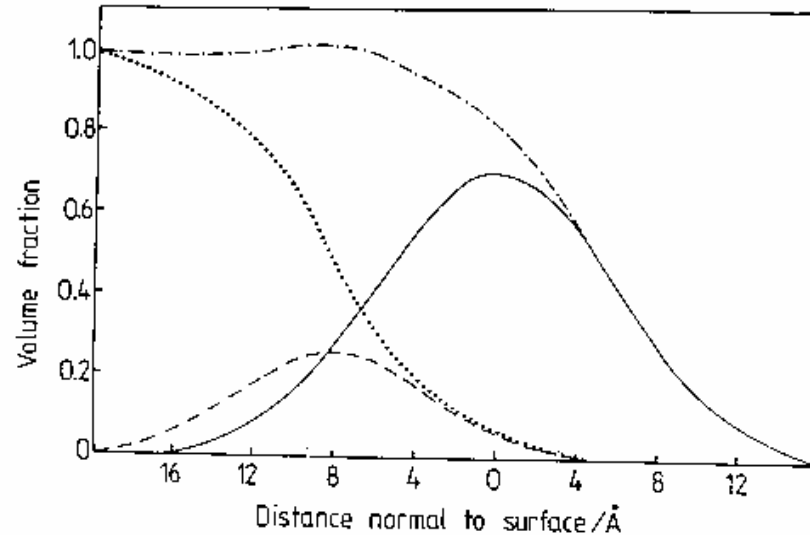
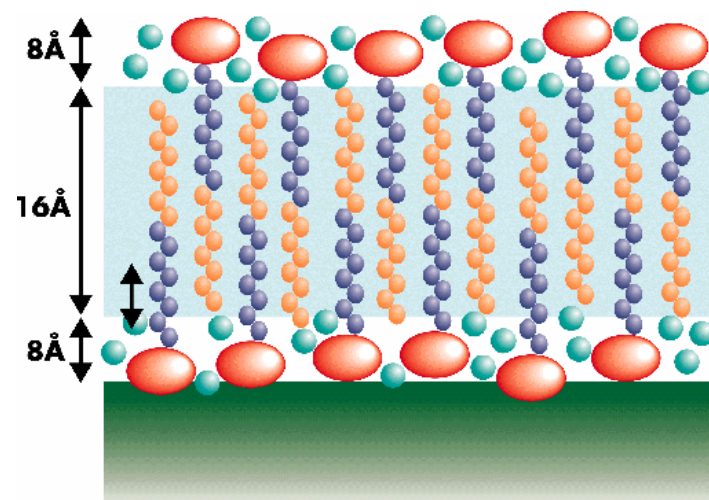$$\rho(z) = b_c n_c(z) + b_h n_h(z) + b_s n_s(z)$$

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

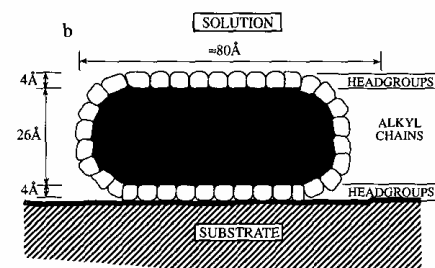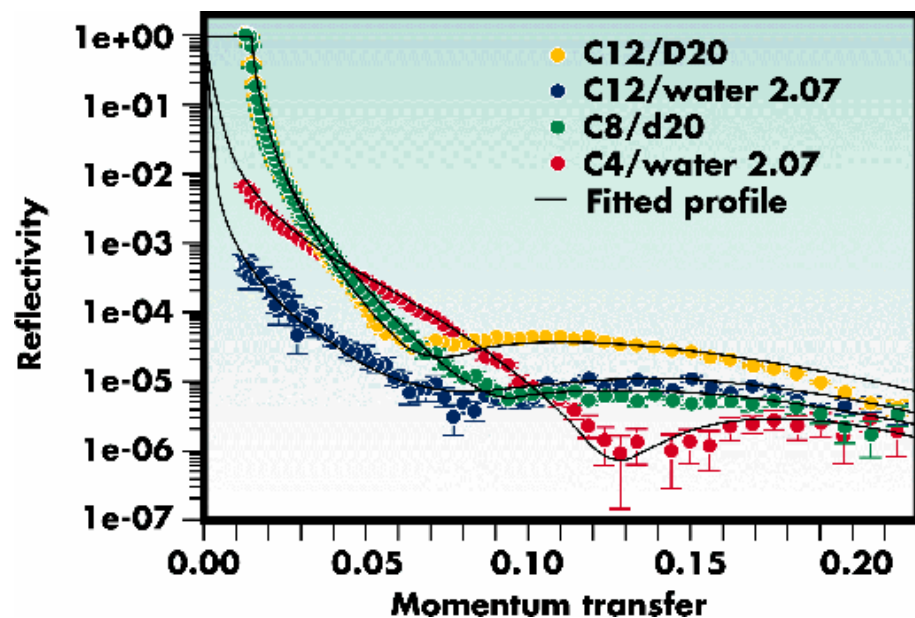*Lu, Hromadova, Simister, Thomas, Penfold,*
J Phys Chem 99 (1995) 8233

Surfactants at the solution-solid interface

Detailed surface structure from labelling

8Å

16Å

8Å

Fragmented bilayer or flattened micellar structure
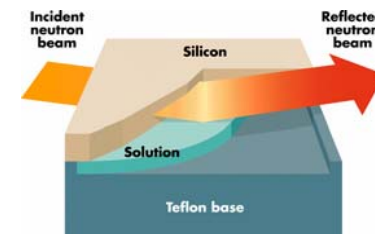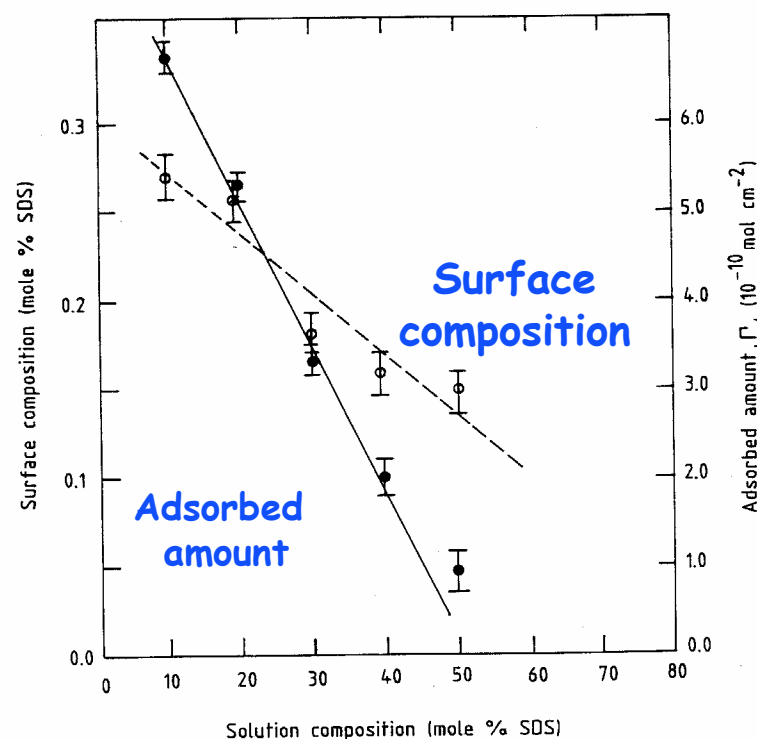

Reflectivity

- C12/D20
- C12/water 2.07
- C8/d20
- C4/water 2.07
- — Fitted profile

Momentum transfer

SOLUTION
≈80Å
HEADGROUPS
ALKYL CHAINS
HEADGROUPS
SUBSTRATE
4Å
26Å
4Å
b

(Fragneto, Thomas, Rennie, Penfold, Langmuir 12 (1996) 6036)

Only indirect information about in-plane structure

CLRC

ISIS

10⁻³M 20/80 SDS / C12E6
at hydrophilic silica / solution interface

In D2O

Green : hh
Red : dh

In H2O

No adsorption for solutions compositions > 50/50

Surface composition

Adsorbed amount
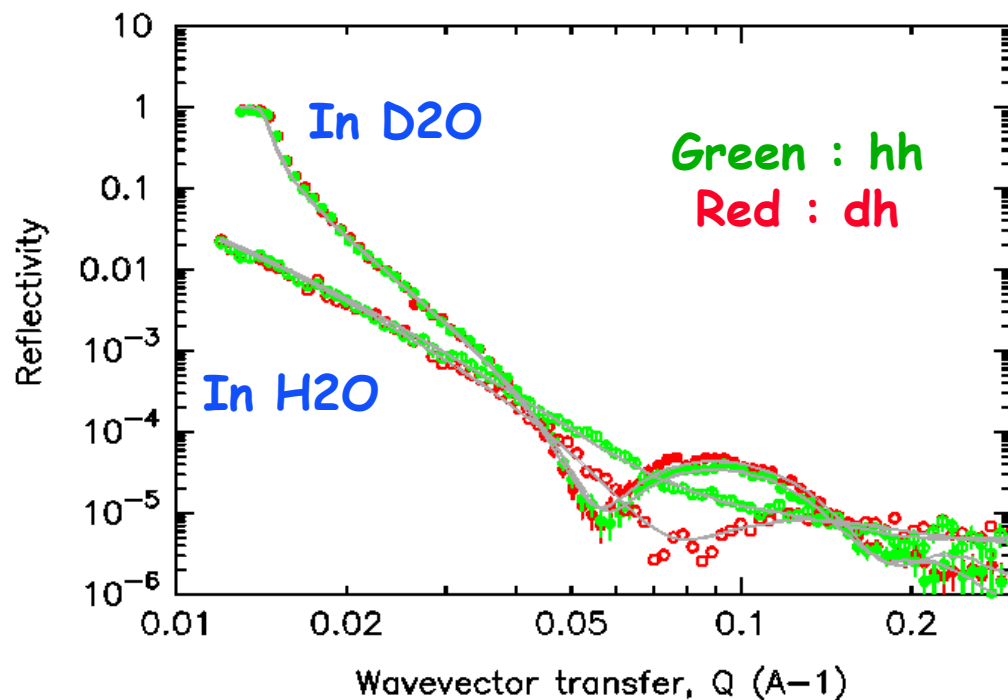
Adsorption markedly modified by relative affinity of the two different surfactants for the surface

Penfold, Staples, Tucker, Thomas, Langmuir 18 (2002) 5755

SDS adsorption onto poly-dmdaac coated surface

10-4 to 10-2M SDS

Red : 10-4M in 0.1M NaCl
Blue : 5 x 10-4M
Green : 10-3M
Pink : 5 x 10-3M
Yellow : 10-2M

Si / D20

Reflectivity (y-axis)
Wave vector transfer (x-axis)

SDS Isotherm

Adsorbed amount (x 10-10 mol cm-2) (y-axis)
SDS Concentration (M) (x-axis)
1e-4   5e-5   10-3   5e-3   0.01
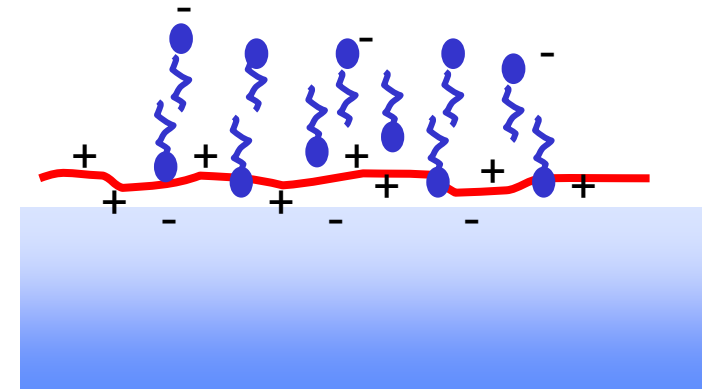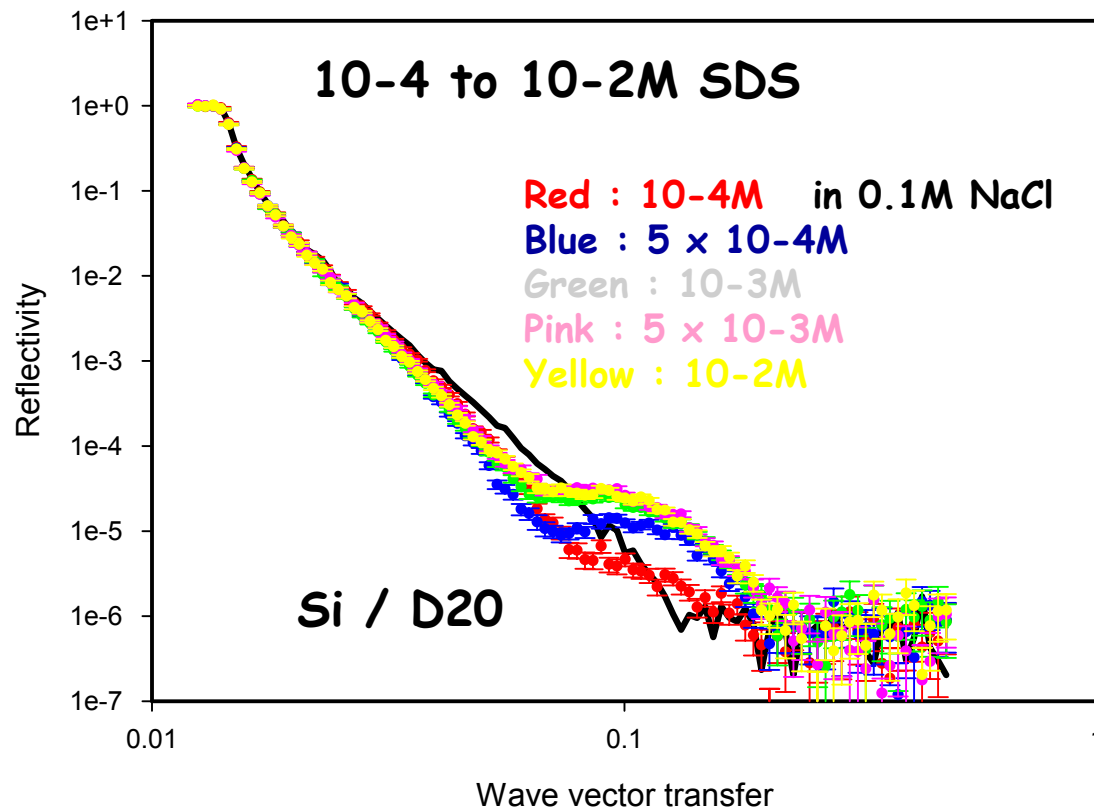
- **Polymer remains intact**
- **Strong SDS adsorption layer ~ 36 to 40 angstroms**
- **Surface charge reversal**

$$\Gamma = \frac{d}{NV}\left(\frac{\rho_s - \rho_f}{\rho_s}\right)$$
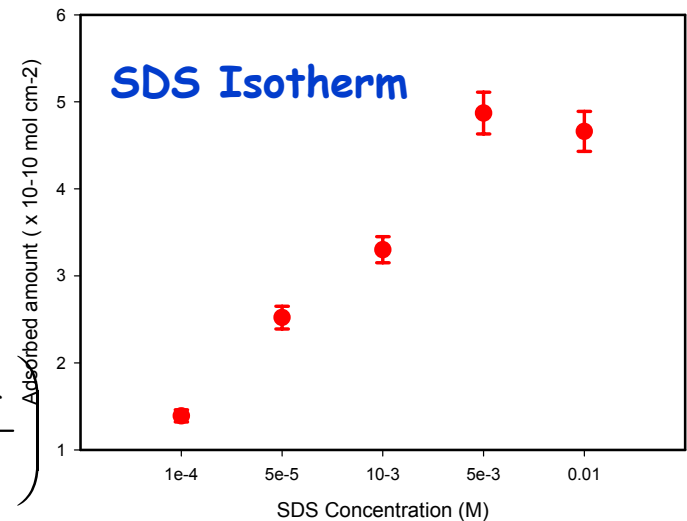
Adsorption at plateaux similar to that at A/W interface
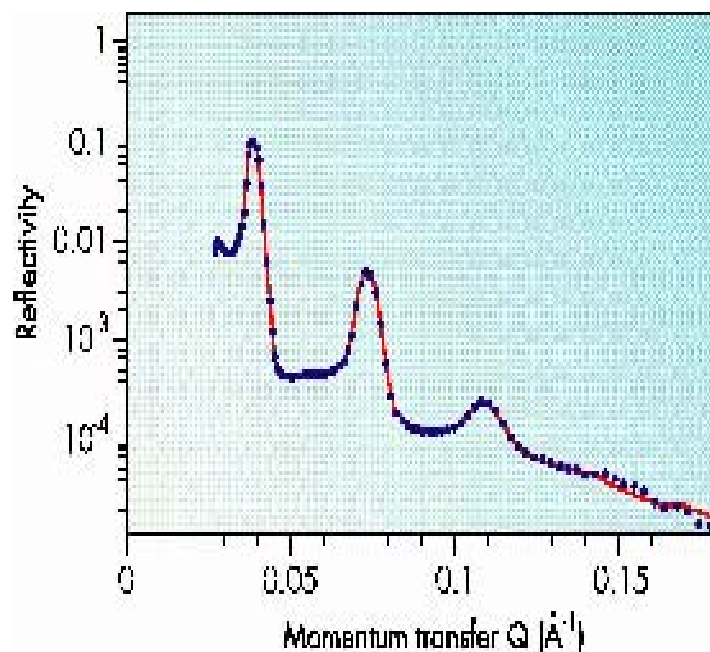
Penfold, Staples, Tucker, Thomas, Langmuir 20 (2004) 7177

CLRC

ISIS

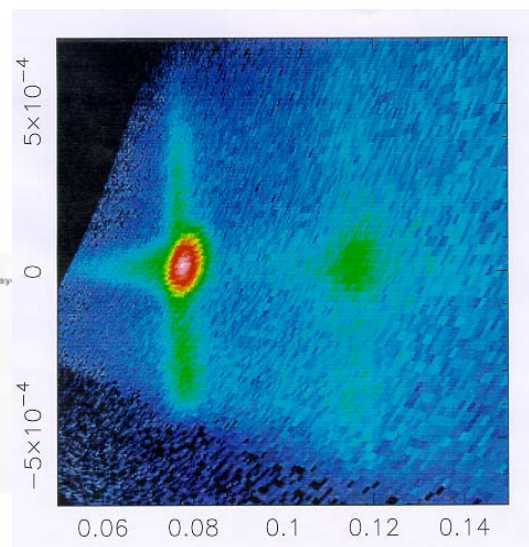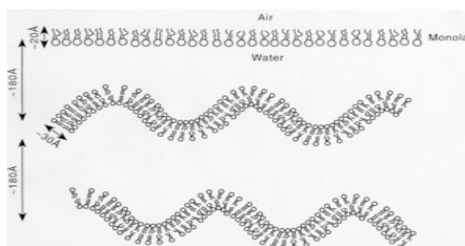# Surface ordering in Surfactant systems

(Li, Weller, Thomas, Rennie, Webster, Penfold, Heenan, Cubitt, J Phys Chem 103 (1999) 10800)
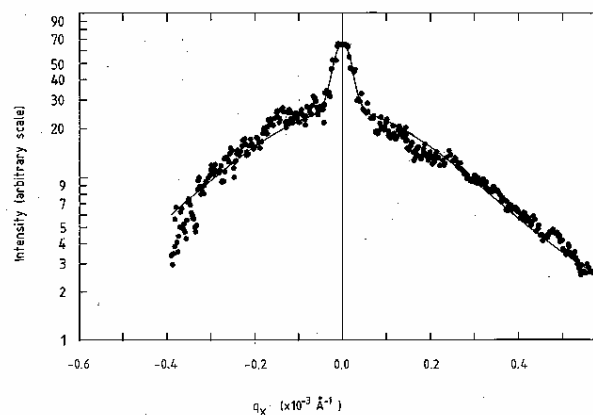
2% AOT / D2O

See well-defined 'Bragg peaks' associated with surface lamellar ordering, extending ~1 micron into the bulk solution
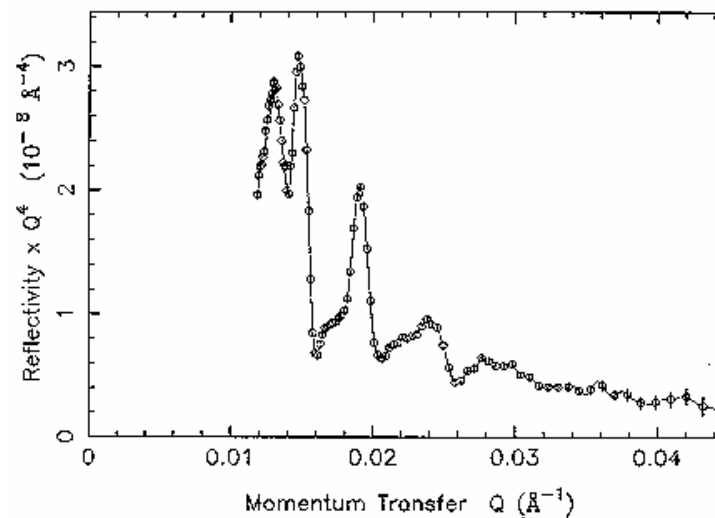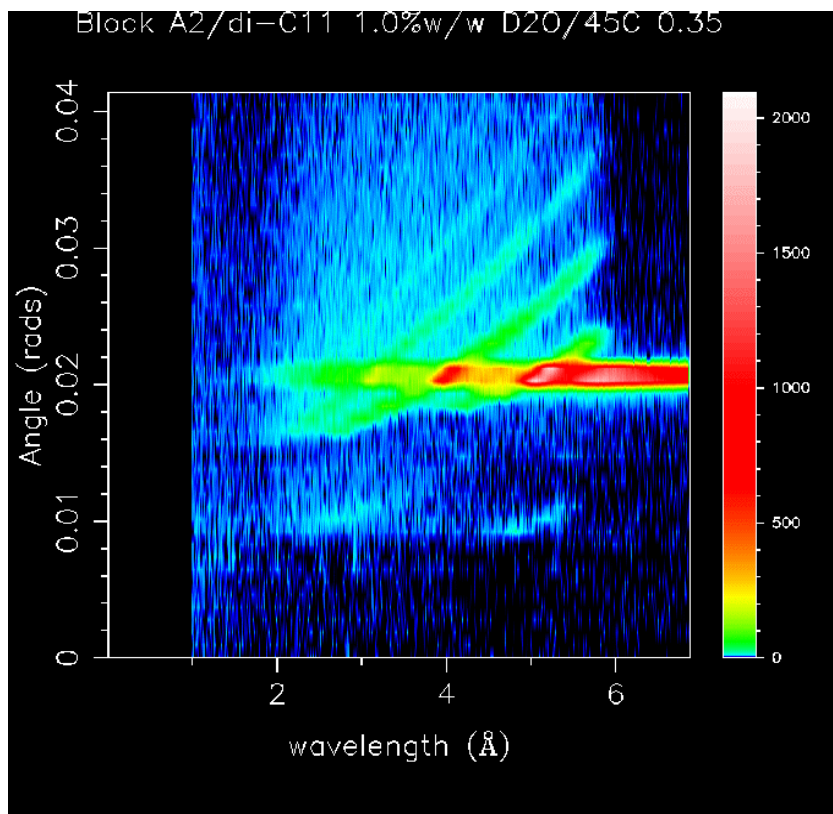
Observe strong 'off-specular' scattering at constant Qz.

With increasing temp see increased order, decrease in spacing, and increasing in-plane correlation length

di-C11 at L/S interface

Block A2/di-C11 1.0%w/w D2O/45C 0.35

**Regular repeating main diffraction
peak + subsiduary peaks
(n-1) peaks ⇨ n repeating units**
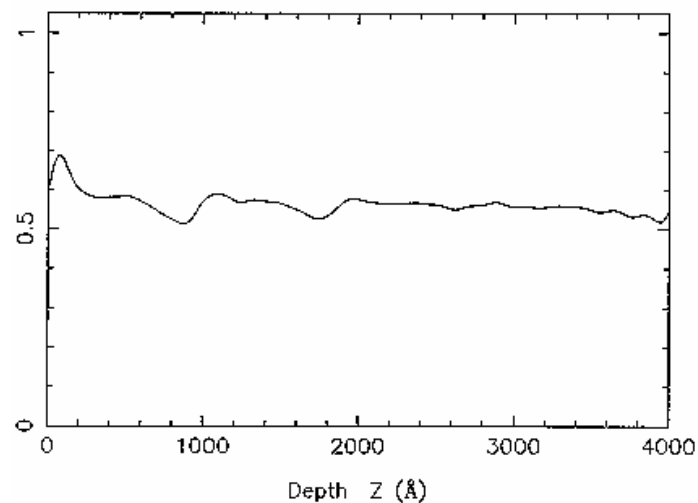
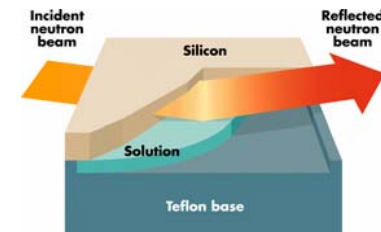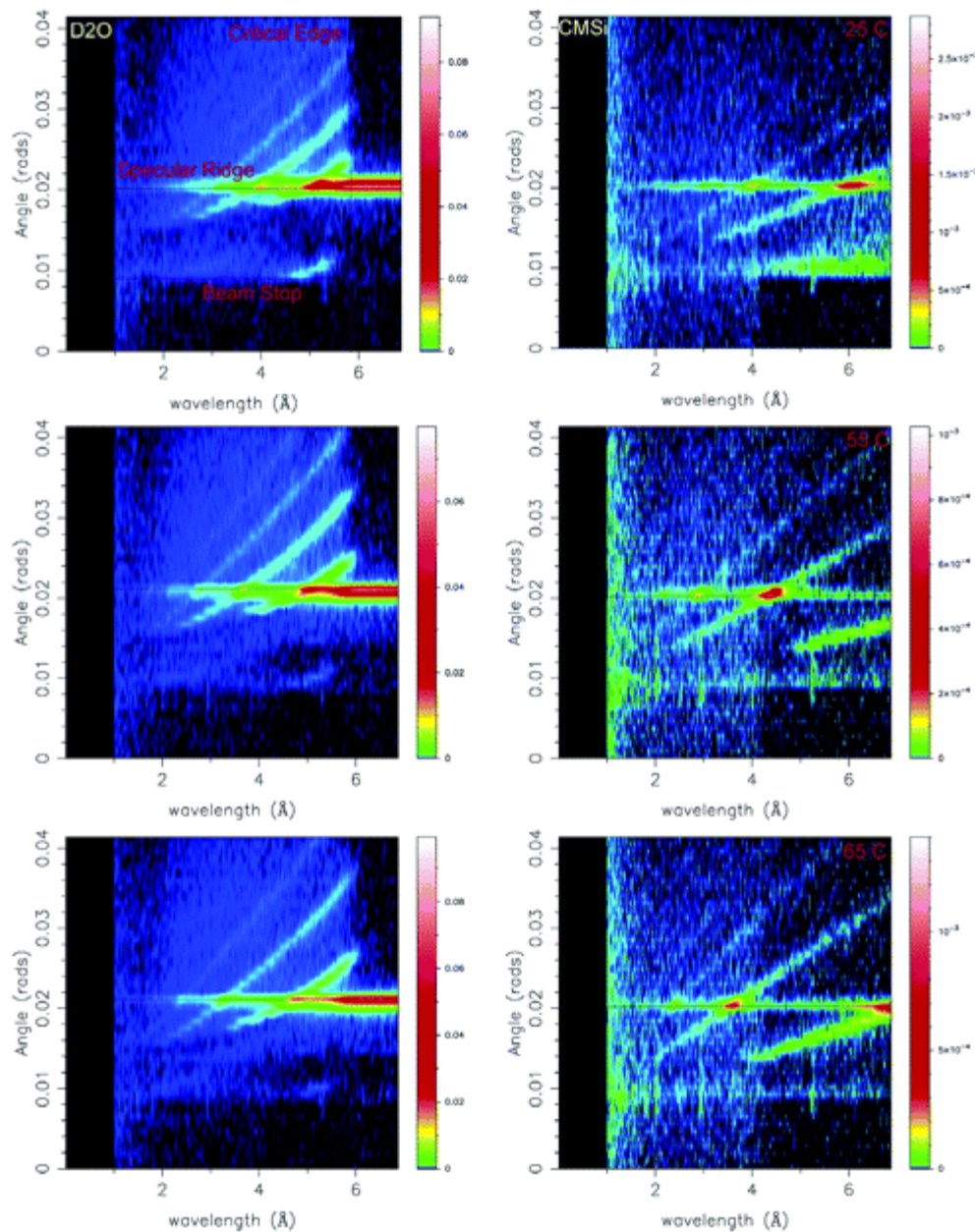**Evidence for adsorption
of vesicles at the interface**

**Structure is 2 equally spaced layers
separated by ~ 900Å**

1% di-C_{12}TAB in D_2O and CmSi

At 25, 55 65c

Polymer-Surfactant Adsorption

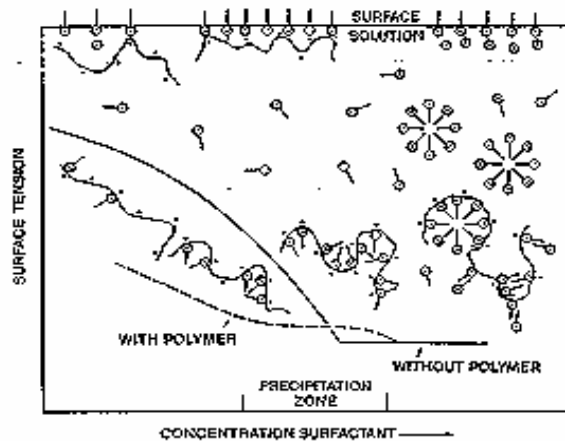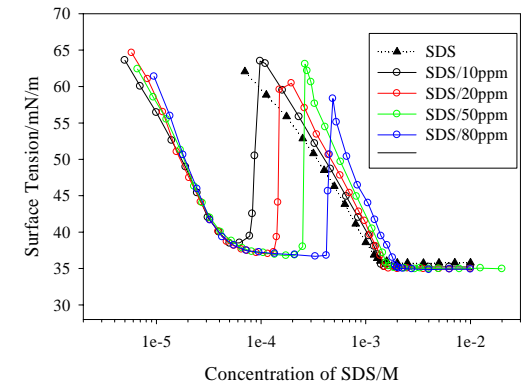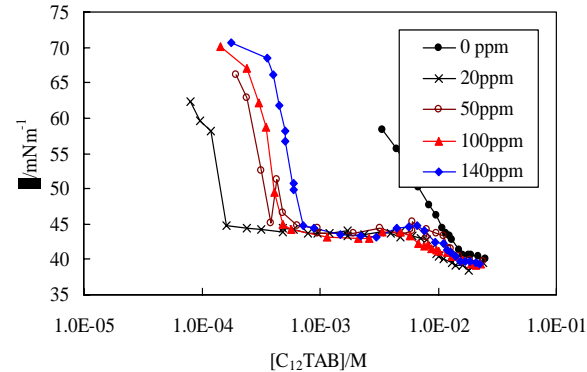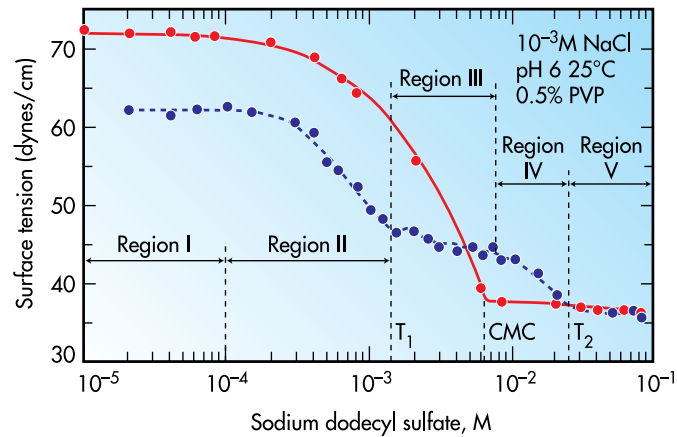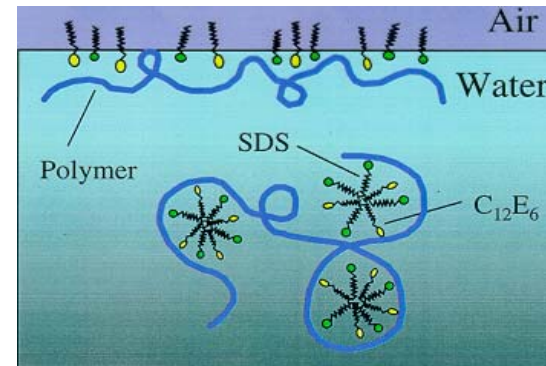Strong surface poly-electrolyte / surfactant interaction results in more complex behaviour

SDS / PEO
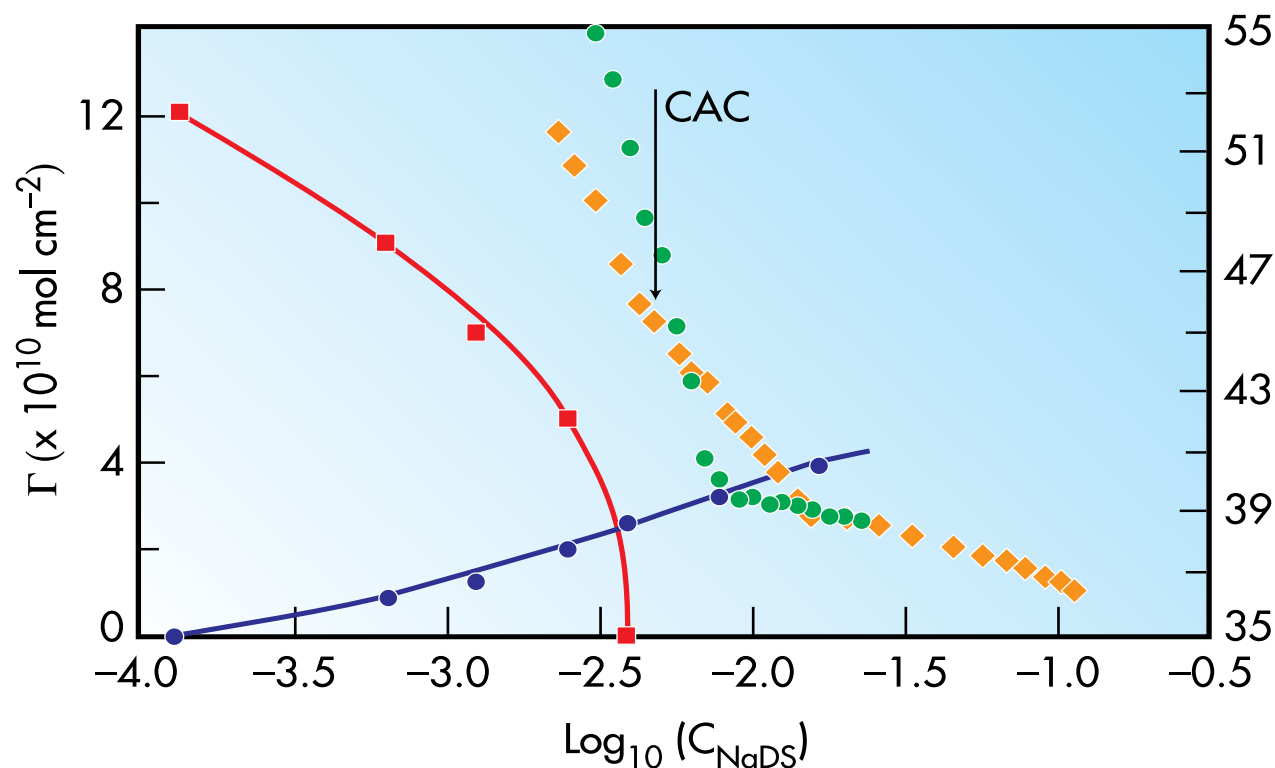
With increasing surfactant conc, progressive displacement of polymer from surface up to CAC

Some evidence for polymer / surfactant interaction at surface

Thomas 2

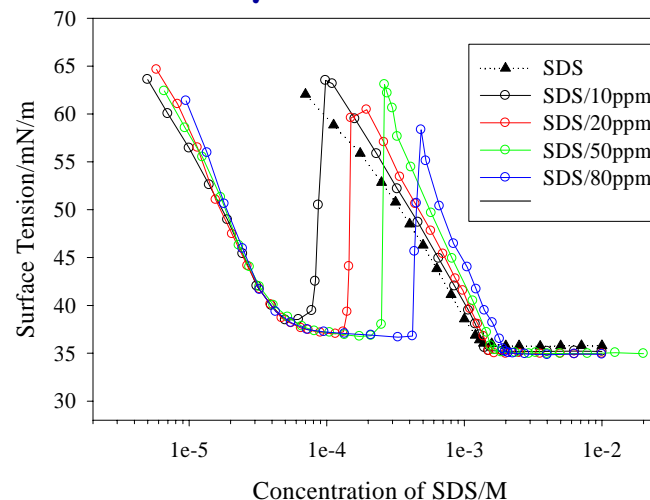(Adsorbed amounts red : PEO, blue:SDS, Surface tension Green : SDS, Yellow : PEO-SDS)

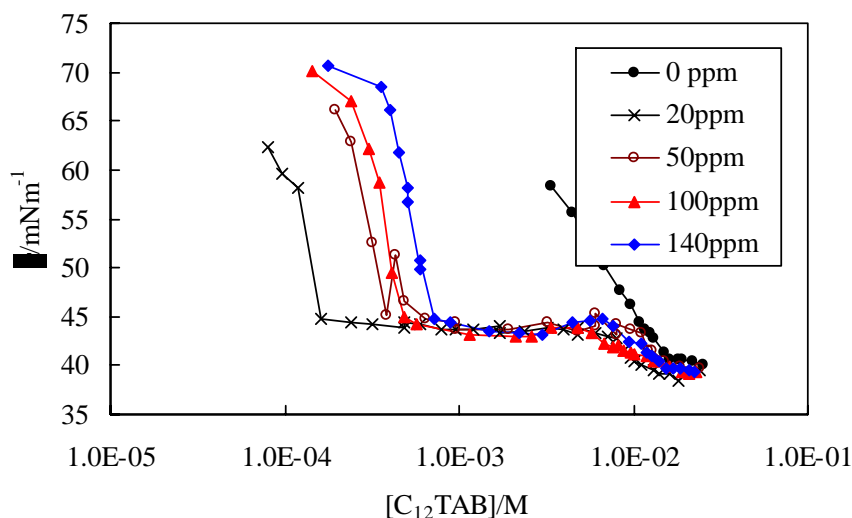# Strongly interacting polymer / surfactant mixtures

- Poly-electrolyte / charged surfactant, strong interaction, more complex behaviour

- See range of different surface tension and neutron reflectivity behaviour for

  NaPSS / CnTAB
  poly-dmdaac / SDS
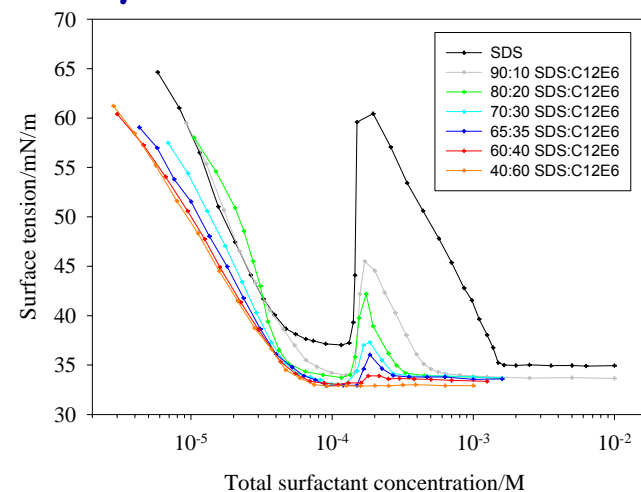 poly-dmdaac / SDS / C12E6
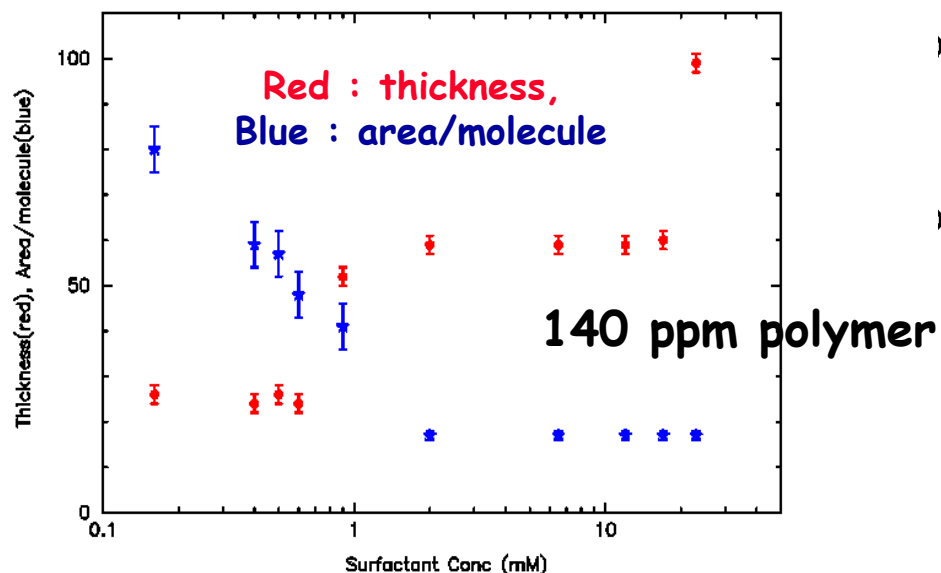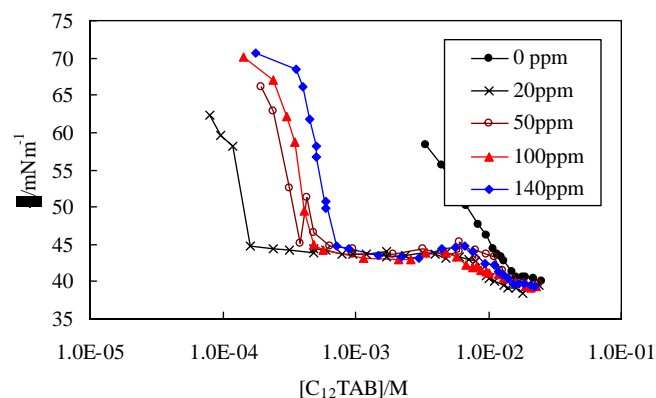 PVPmCl / SDS
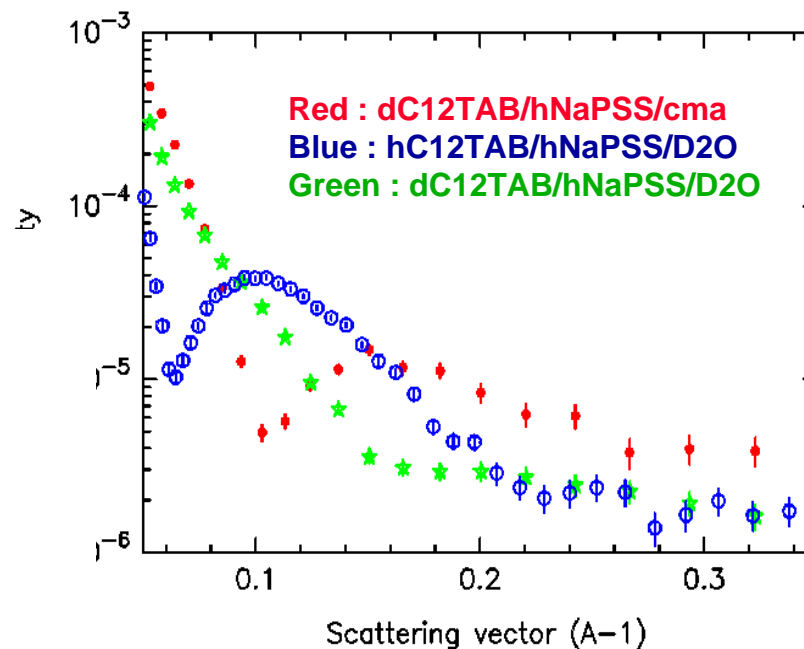
Poly-dmdaac / SDS

NaPSS / C12TAB

Poly-dmdaac / SDS / C12E6

NaPSS(140ppm)/C12TAB

Red : dC12TAB/hNaPSS/cma
Blue : hC12TAB/hNaPSS/D2O
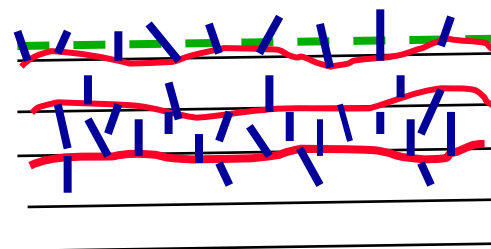Green : dC12TAB/hNaPSS/D2O

Red : thickness,
Blue : area/molecule

140 ppm polymer

At low surf concs, monolayer ~20Å
20% vol fraction polymer
At higher surf concs see more
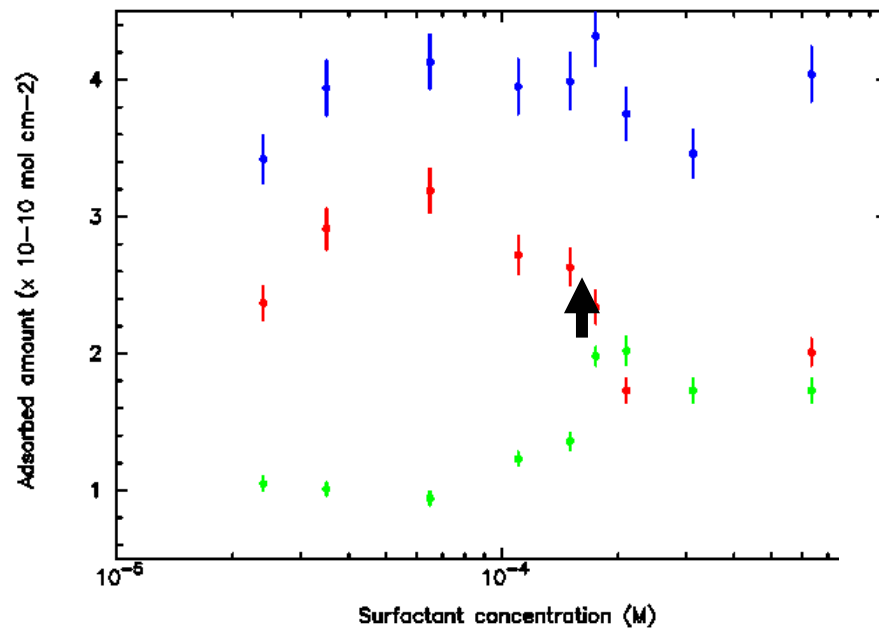ordered structure, 'layering' of
polymer/surfactant complexes
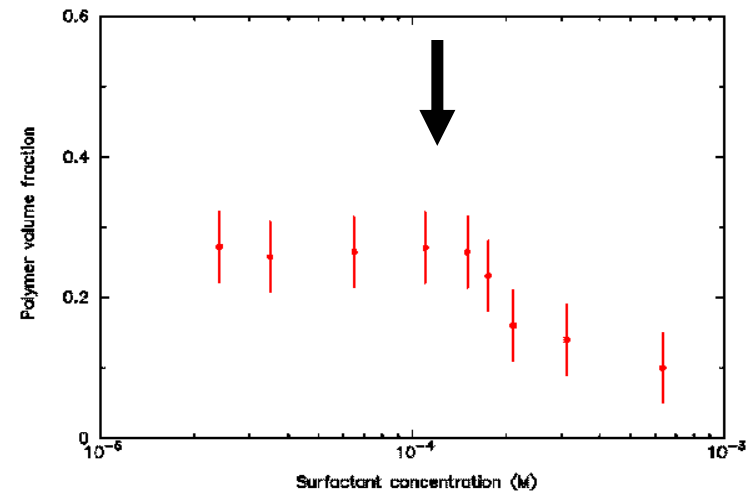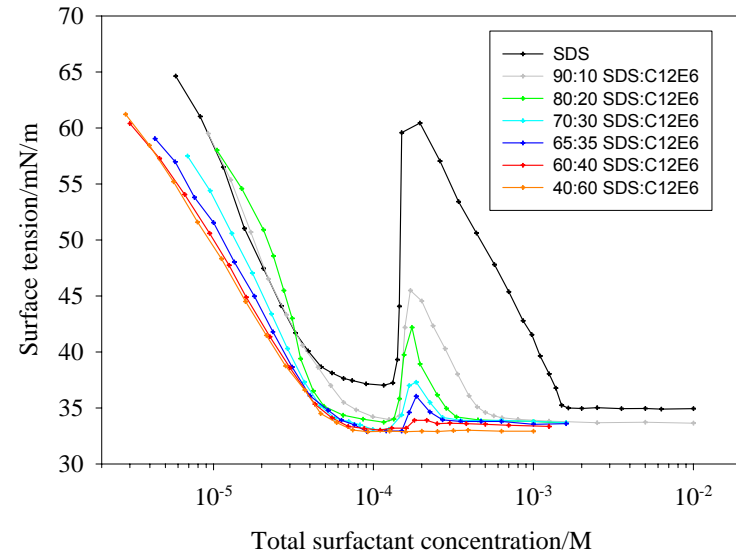
1.2 x 10-2M C12TAB

Taylor et al, Langmuir 19 (2003) 3172;
7740;18 (2003) 9783

80/20 SDS / C12E6
/ 20 ppm poly-dmdaac
/ 0.1 M NaCl

Adsorbed amount of surfactant
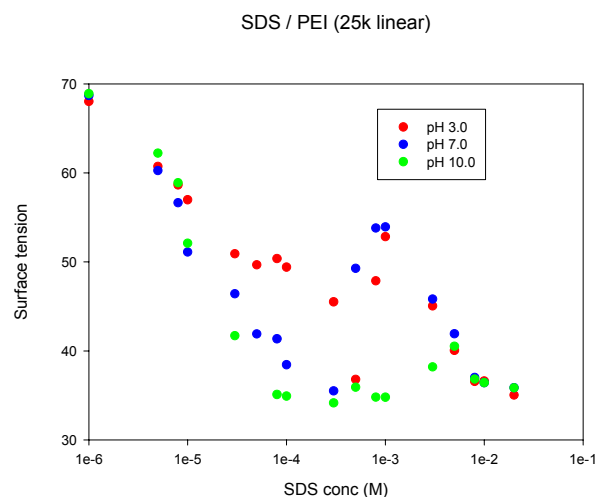Blue : total, red : SDS,
green : C12E6

Polymer volume fraction

Polyelectrolyte – surfactant mixtures (PEI / SDS)

25k linear PEI

SDS / PEI (25k linear)

25k branched PEI

PEI (25k branched)

Legend for top-right plot:
- SDS
- SDS /PEO
- SDS / poly-dmdaac
- SDS / PEI

Legend (surface tension plots):
- pH 3.0
- pH 7.0
- pH 10.0

Axis labels: Surface tension, SDS conc (M), Adsorbed amount (x 10-10 mol cm-1), Adsorbed amount

Diagram labels: C$_{12}$TAB, air, solution, NaPAA
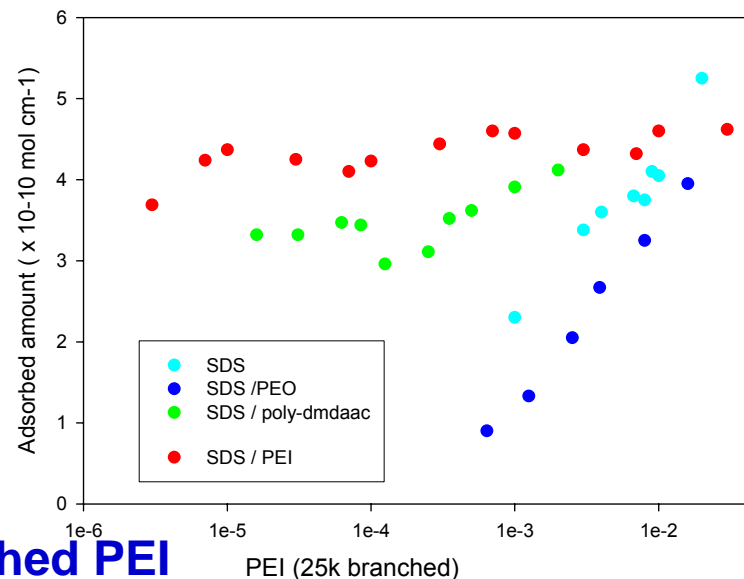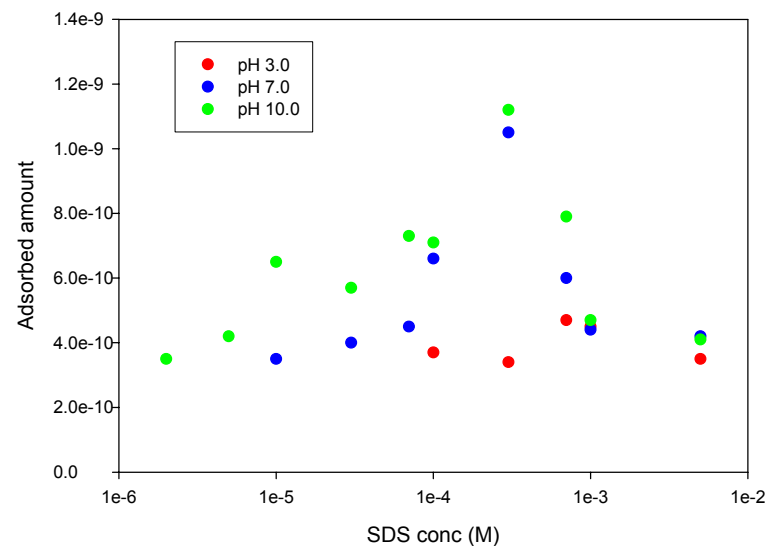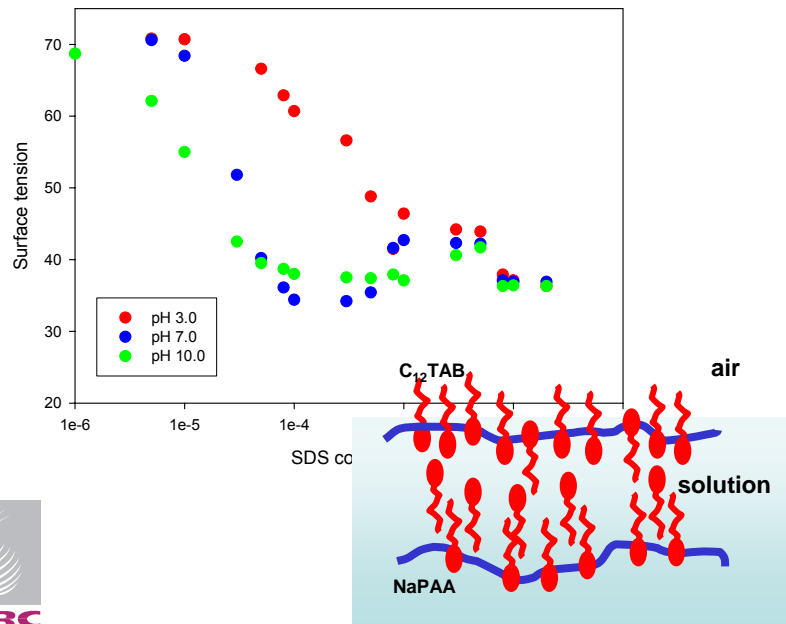
Penfold et al, Langmuir 21 (2005) 10061

Polymer thin films and interfaces
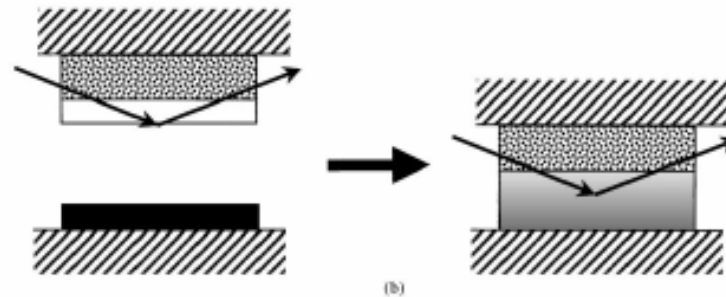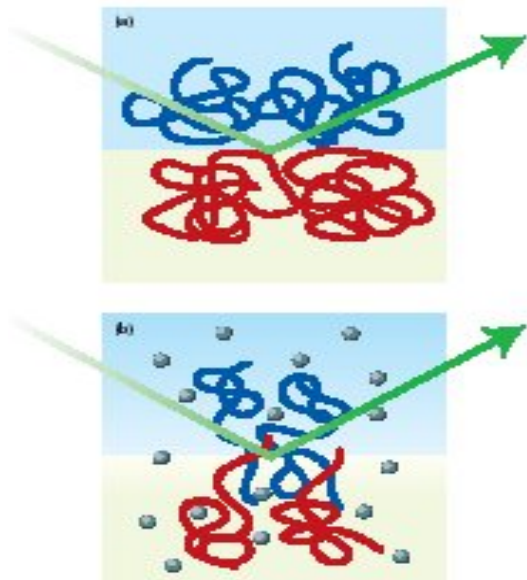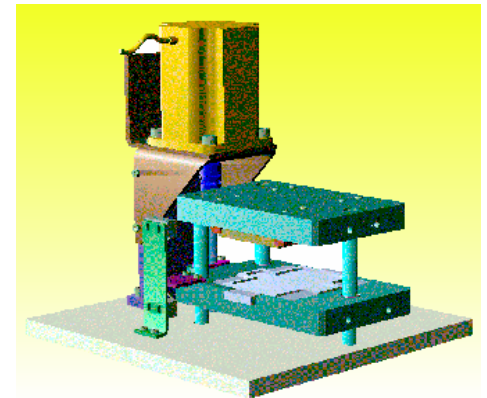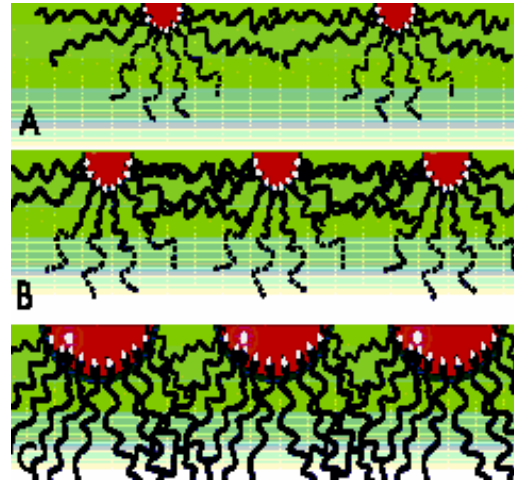
Effect of CO2 sorption on thin polymer films

(R Gupta, K Lavery, T Russell, J Watkins, MRSEC, Massachusetts, Amherst
J Webster, ISIS)

h-PS(217K)/d-PS(209K)/Si
62C & 82 bar CO_2

0 min

30 min

60 min

90 min

120 min

140 min

5 mins per profile
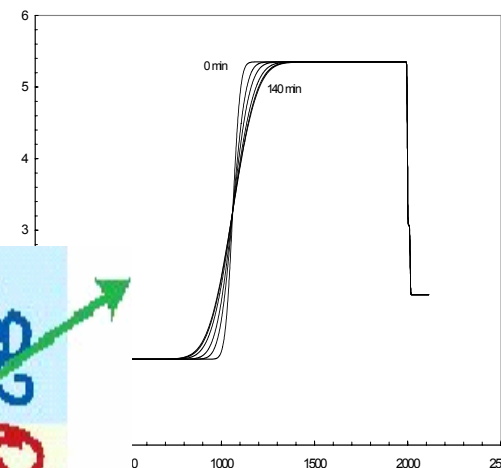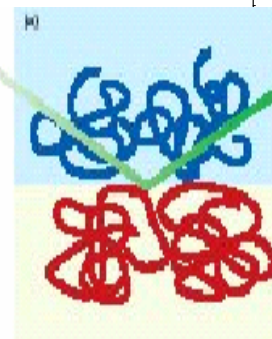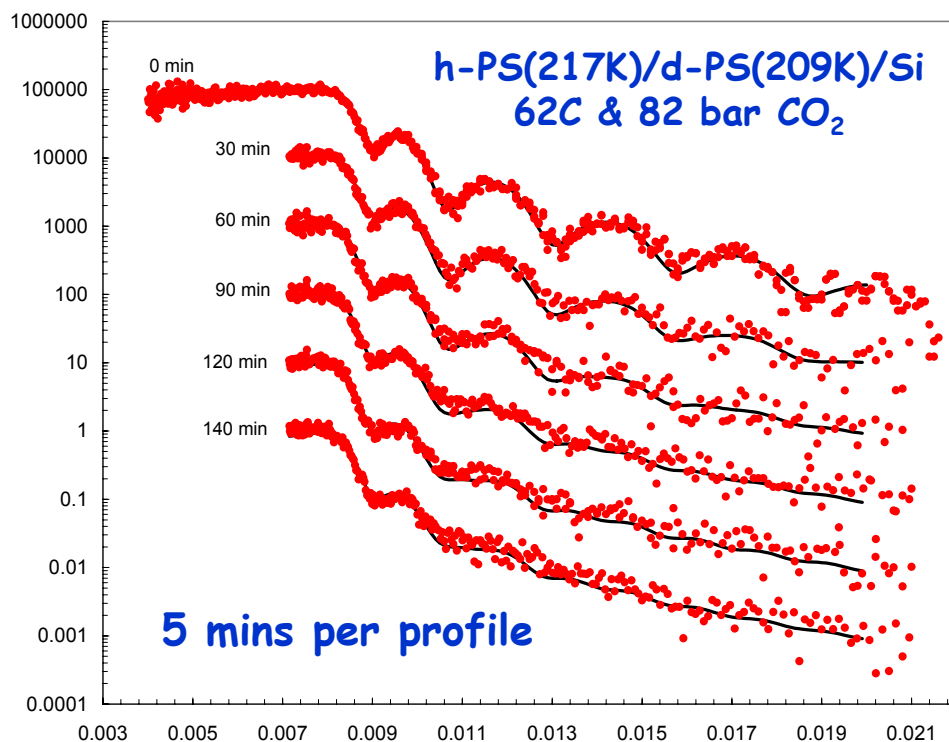
Inter-diffusion modelled using an error function
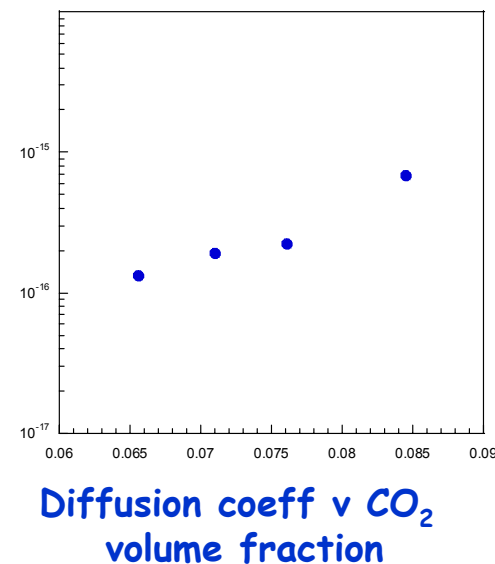
Diffusivity of PS chains in CO_2 dilated PS shows marked increase in mobility with increasing CO_2 volume

Diffusion coeff v CO_2 volume fraction

Early stages of oligomer-polymer inter-diffusion

d-PMMA (115k) / MMA oligomer (510, 1020 MW)

(Bucknall et al, Chem Eng Sci 56 (2001) 1)
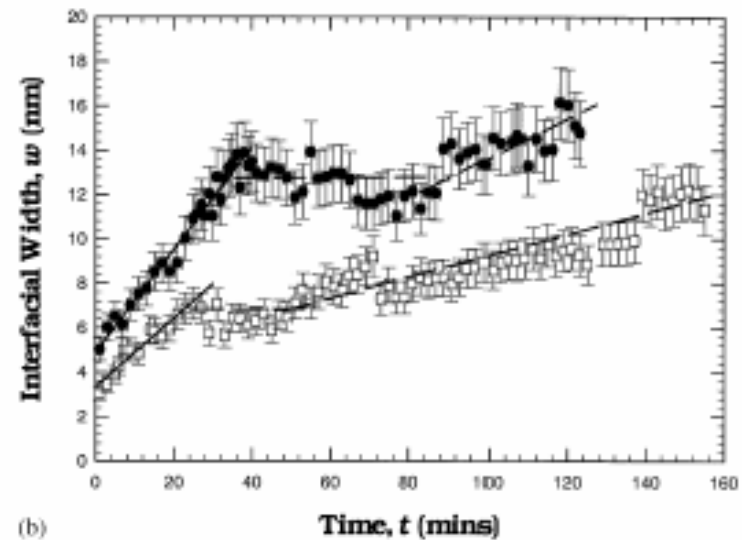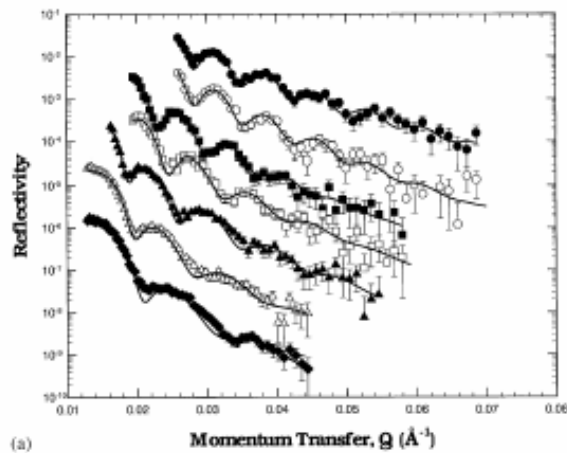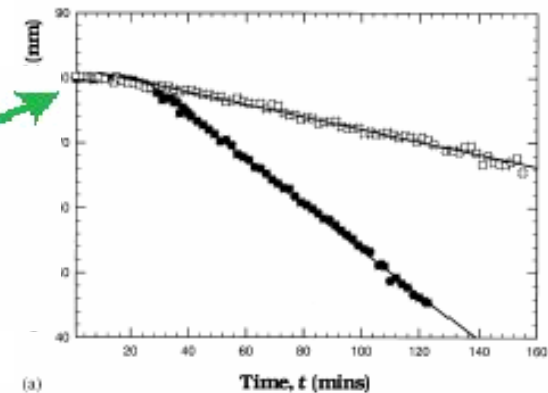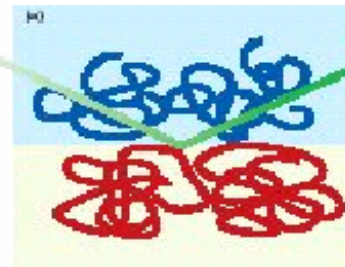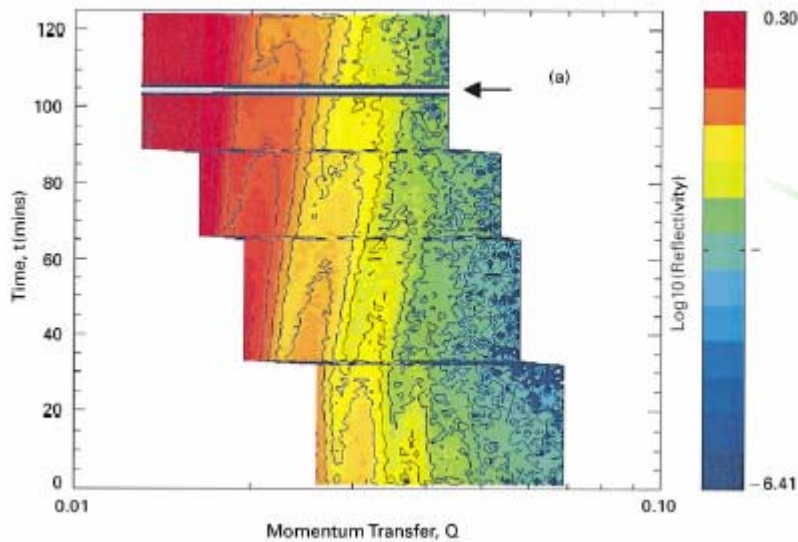
d-PMMA thickness decreases with time
Interfacial width increase with time
Induction period observed in d

$$w \propto t^{1.0}$$

Class II,
Class 1 (Fickian if n=0.5))

Polymer-Plasticiser Diffusion

(Higgins, Butler, Bucknall, Chem Eng Sci, 56 (2001) 5473)
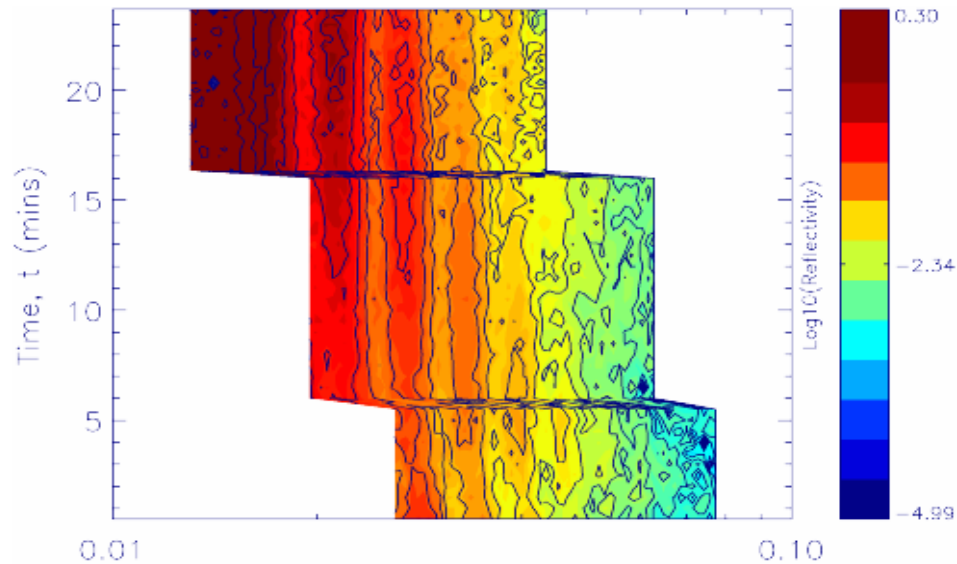
d-PMMA (200K) / DOP (dioctyl phthtalate)

DOP
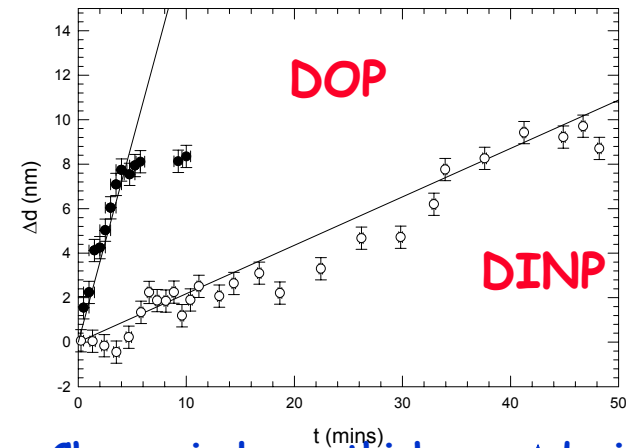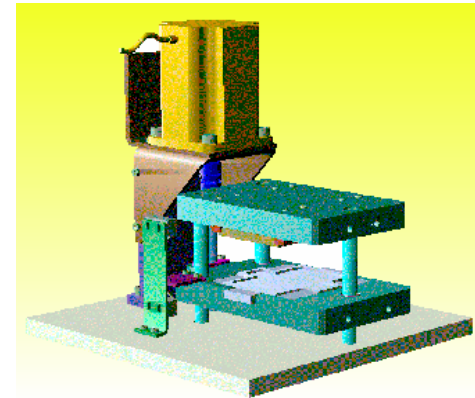
DINP

Change in layer thickness Δd with time

20 sec runs
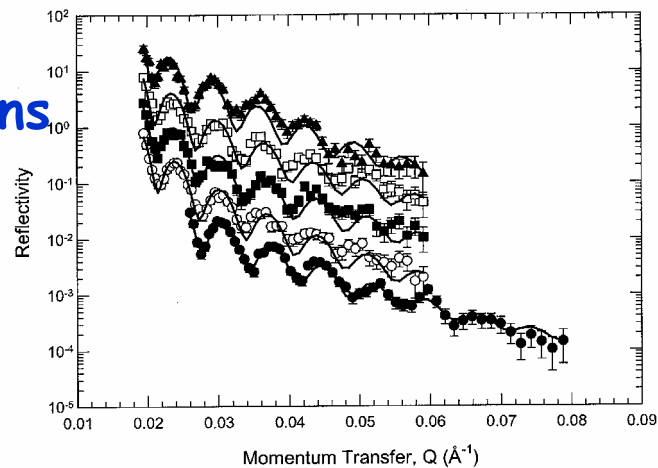
d-PMMA (200K) / DINP (diisononyl phthtalate)

Increase in thickness due to ingress of plasticiser

Evidence for Capillary Waves at Immiscible Polymer/Polymer Interfaces

(Sferrazza, Xiao, Jones, Bucknall, Webster, Penfold
Phys. Rev. Let. 78, (1997), 3693)

Interfacial widths measured by NR 70% thicker than predictions of mean field theory

Due to capillary wave contribution.

$$\Delta^2 = \Delta_0^2 + \left\langle \Delta \zeta^2 \right\rangle$$

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ISIS
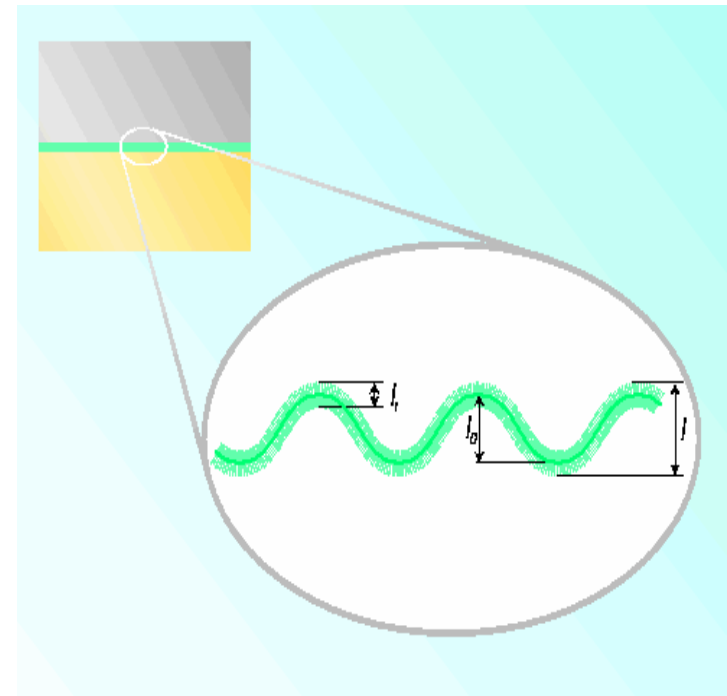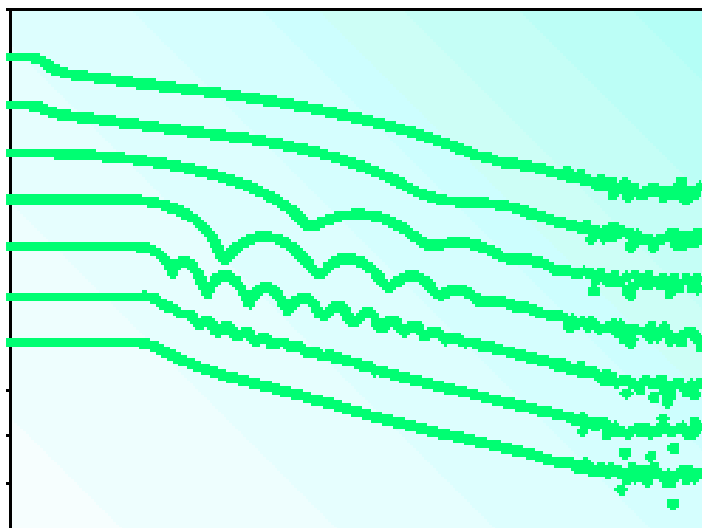
Bilayers of deuterated PS (60 to 4800Å) on PMMA

$$\lambda_{coeh} \approx 20 \mu m$$

Gravitational cut-off too long to contribute, ~ 2mm

$$\Delta^2 = \Delta_0^2 + \left\langle \Delta\zeta^2 \right\rangle$$

$$\left\langle \Delta\zeta^2 \right\rangle = \frac{k_B T}{4\pi\sigma_0} \ln \frac{(2\pi/\Delta_0)^2}{(2\pi/\lambda_{coeh})^2 + (2\pi/a_{dis})^2}$$

Short wave-vector cut-off due to dispersion forces acting across the film
Log dependence for d<1000, which levels off when dispersion capillary length > neutron coherence length
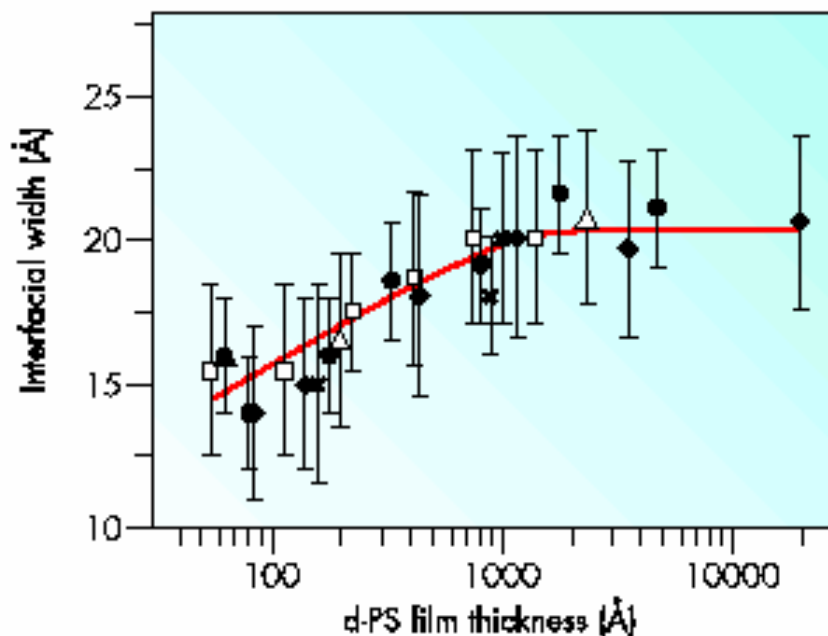
Measured width ~20, fitted intrinsic width = 9.3
(predicted width =11.8)

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Bio-interfaces

Fibers of extracellular matrix (ECM)
Glycoprotein
Carbohydrate
EXTRACELLULAR FLUID
Glycolipid
Filaments of cytoskeleton
Cholesterol
Peripheral protein
Integral protein
CYTOPLASM

7 Å
7 Å
6 Å
28 Å
7 Å
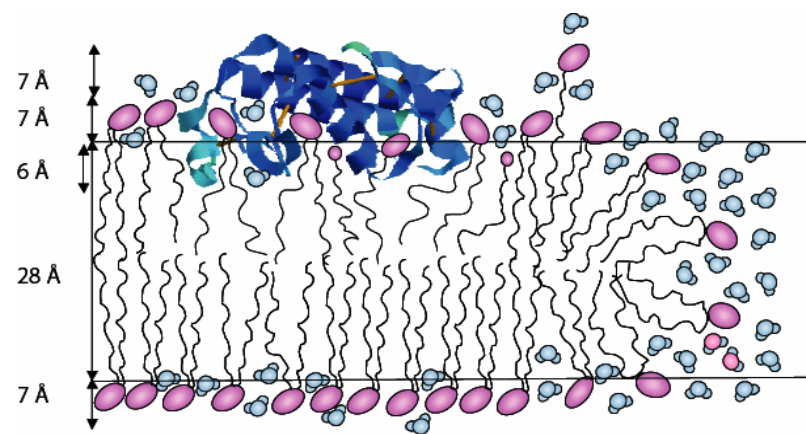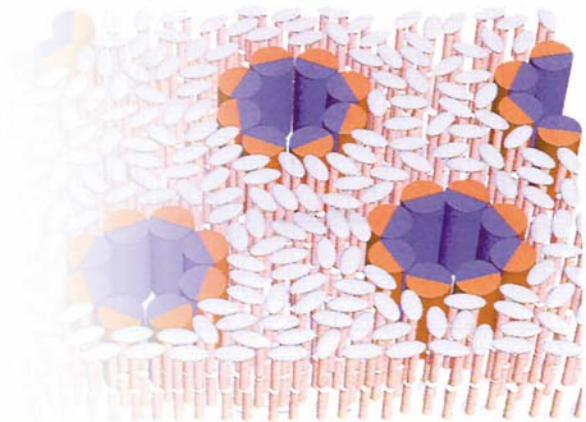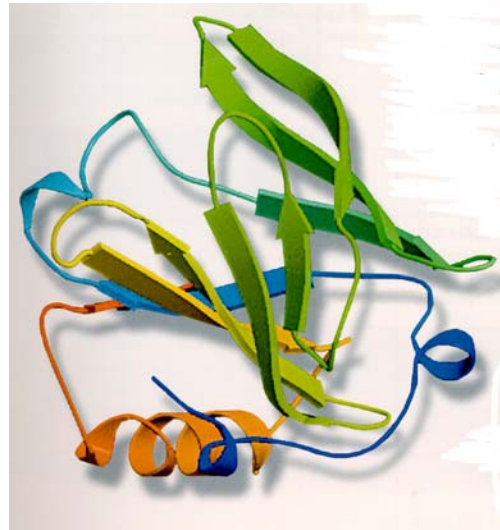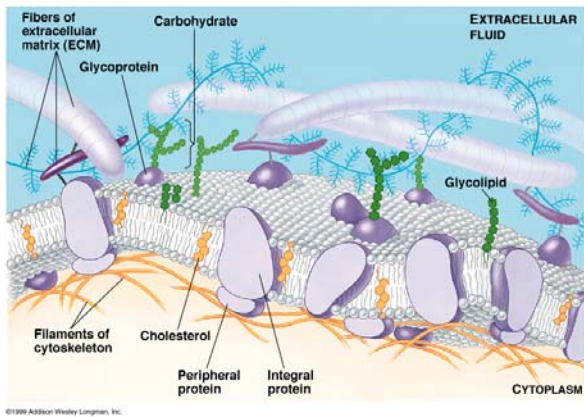
Adsorption of Proteins at Interfaces
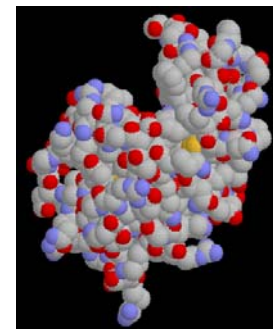
**Structural conformation
of Lysozyme at the air-water
interface**

**In H2O/D2O mixtures measure
extent of protein / solvent overlap**

**Adopts structure to minimise
charged group/air contact**
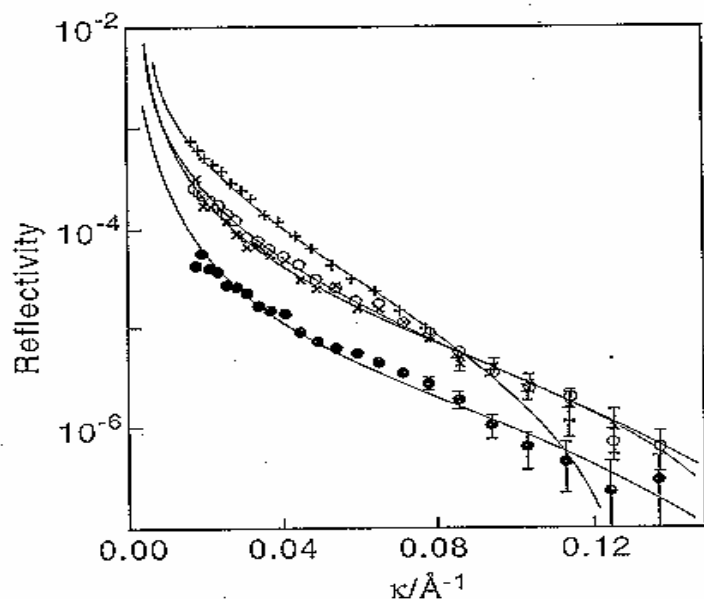
In nrw obtain adsorbed amounts

**At low concs d~30 sideways-on config
At high concs d~47 longways-on**

**Retains globular structure,
no significant denaturation**
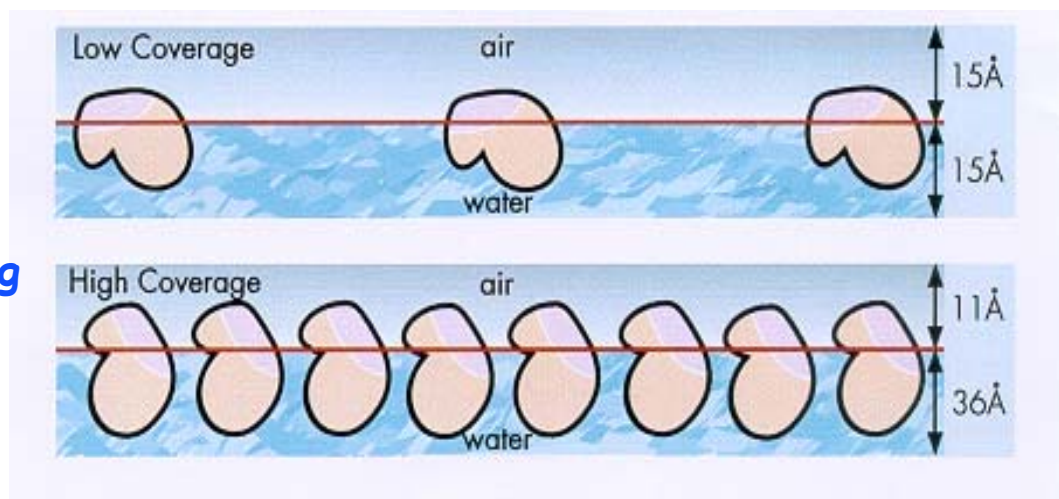
(Lu, Su, Thomas, Penfold, Webster, J Chem Soc, Faraday Trans 94 (1998) 3279)

Structure of Lysozyme layer at the hydrophilic silica / water interface

(Su, Lu, Thomas, Cui, Penfold, J Coll Int Sci 203 (1998) 419)

1 g dm-3 in D2O

pH 7.0

pH 4.0

0.03 g dm-3

1.0 g dm-3
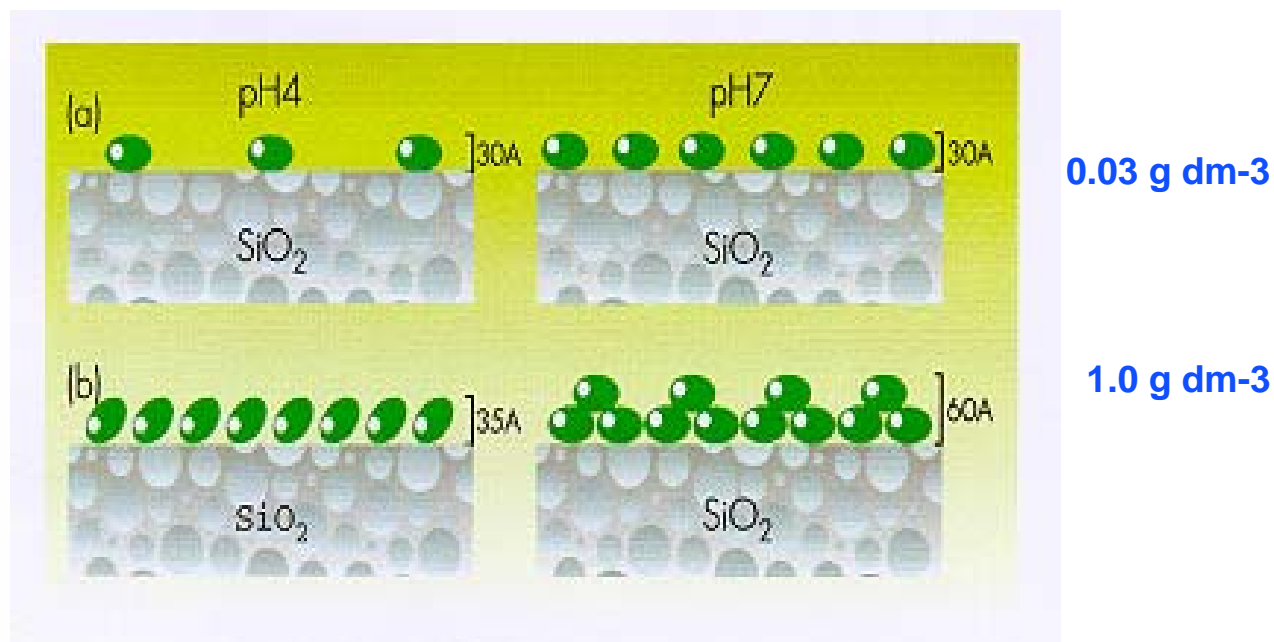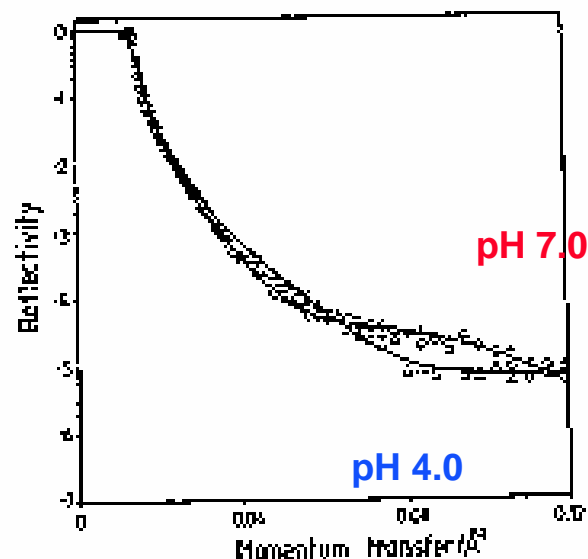
Effect of pH reversible

**Structure and adsorbed amount dominated by
electrostatic interactions between molecules
in the layer and not with the interface**

**Measurements suggest that Lysozyme retains its tertiary structure
on adsorption and that no significant denaturation takes place**

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Thermal denaturation of interfacial protein layers

B-lactaglobulin at air-solution interface
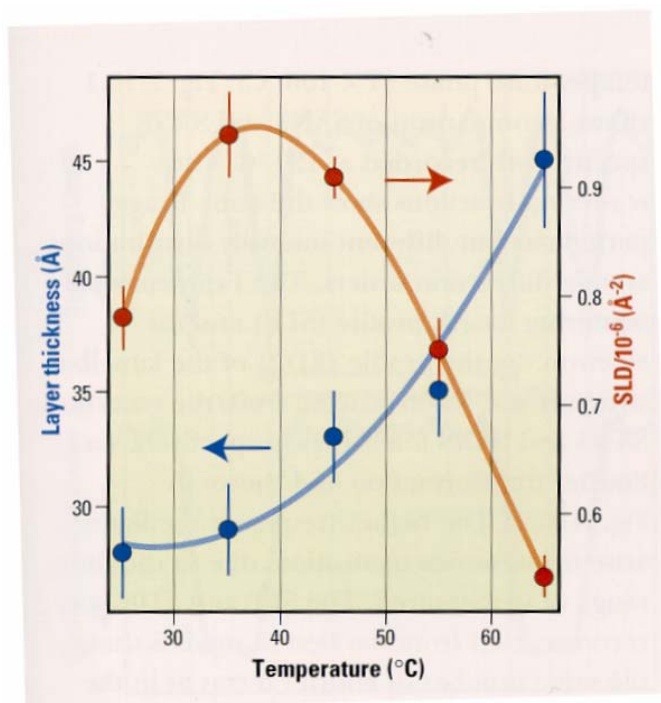
pH 7.0, 1 mg/ml

Thickness and density changes with temp due to thermal denaturation

Initial thickness just less than protein dimension (28 cf 35Å)

Extract fraction of unfolded protein as function of temp.

$\Delta H \sim 50$ kcal / mol
$Tm \sim 52°C$

Lower than observed in bulk

(J W White, S Holt et al, ANU)

Model Membranes
(Membrane / Protein interactions)
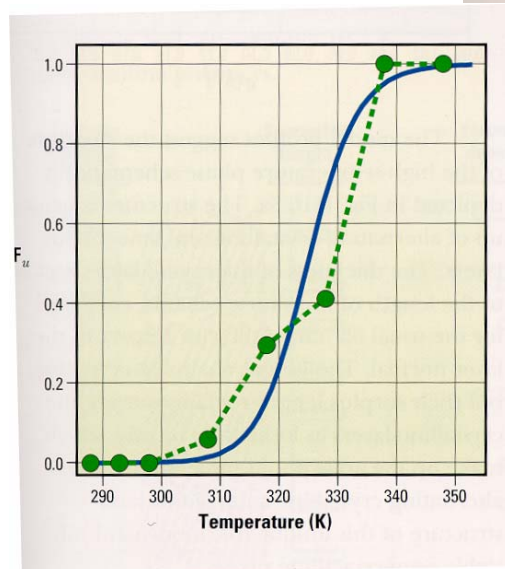
Combination of Langmuir-Blodgett, Langmuir-Schaeffer and self-assembly techniques, assemble free-standing bi-layers adjacent to an OTS coated surface
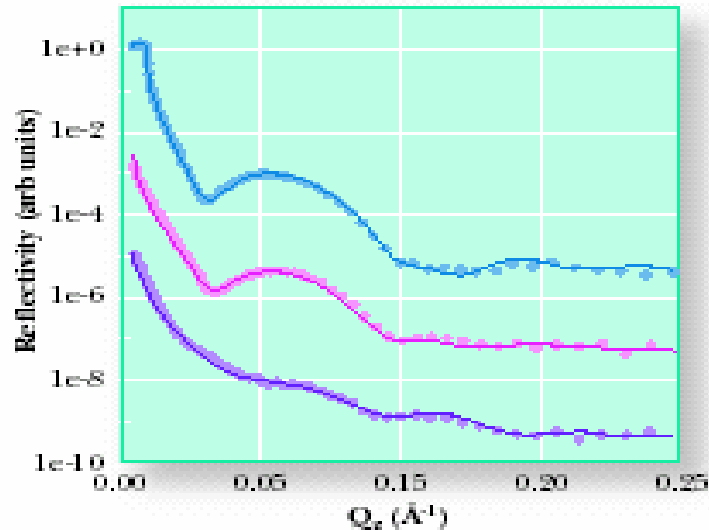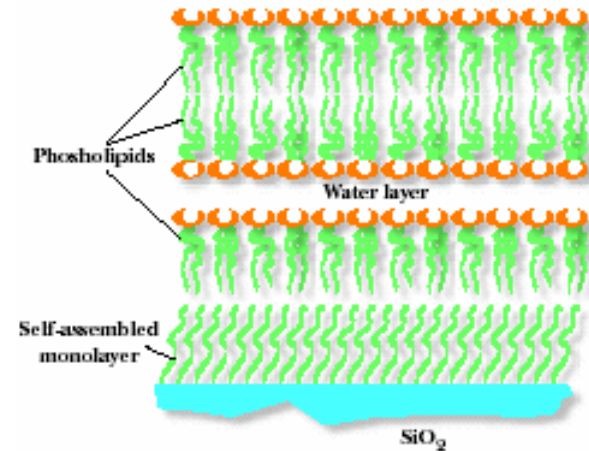
DMPC bi-layer at 15c in D2O, H2O and 50:50 H2O/D2O

Observe transition from low temp crystalline gel phase to high temp fluid phase

(Roser, Hughes, University of Bath)

Phospholipase A$_2$ hydrolysis of model membranes

PLA$_2$ enzymes catalyse hydrolysis of phopholipids (from own immune system to snake venom) to maintain membrane composition, signal transduction and inflamatory response.
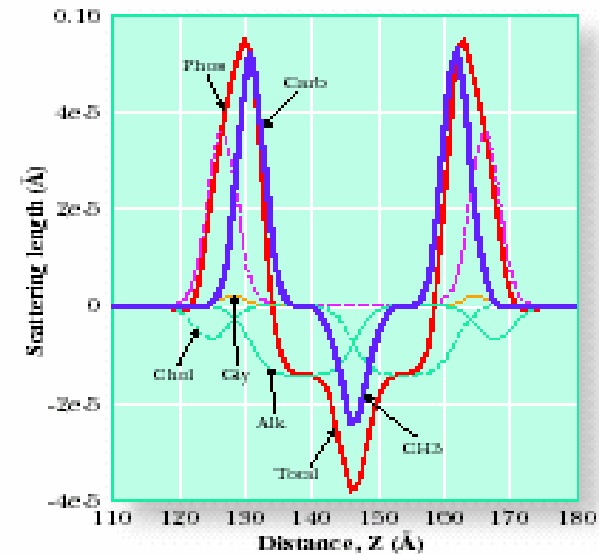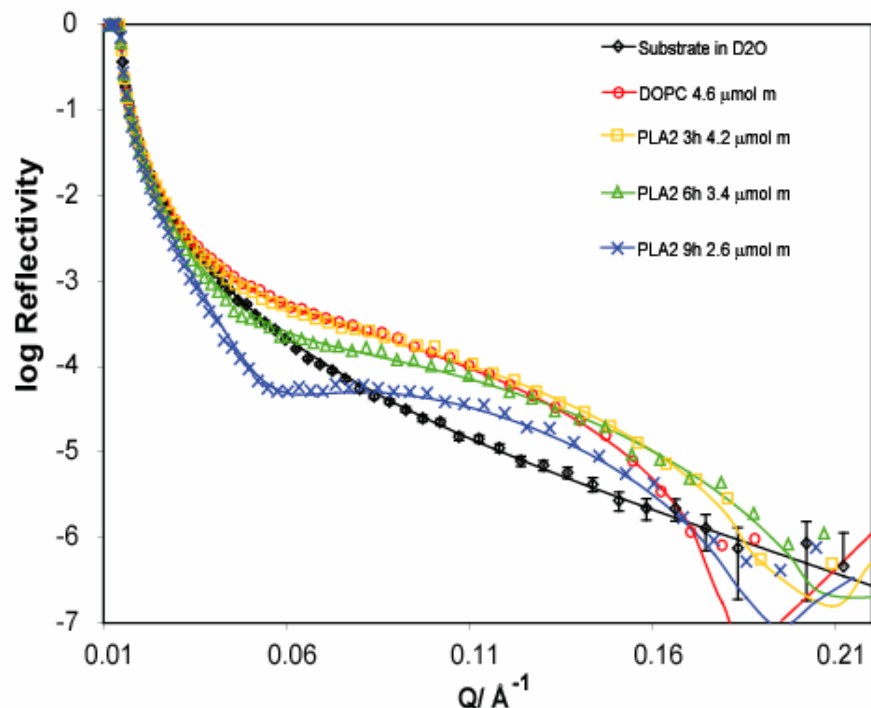Converts di-acyl phospholipid into acyl lyso phospholipid and fatty acid

DOPC supported membrane
Porcine pancreatic PLA$_2$

PLA$_2$ water soluble, but only active at membrane surface
Heterogeneous catalysis

See initially adsorption of PLA2 dormant for ~ 3 hours, then see progressive reduction in phospholipid coverage
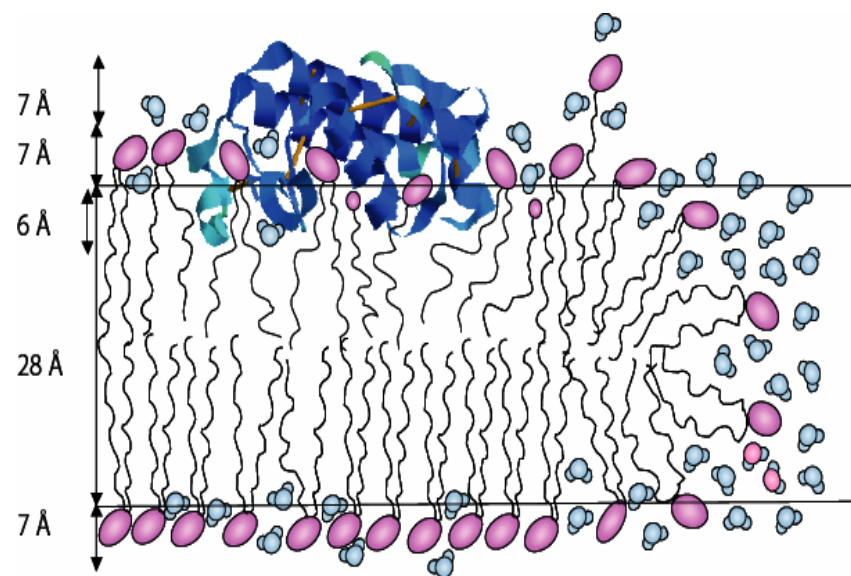
Determine location of enzyme in catalytic environment and follow kinetics of hydrolysis

(H P Vacklin, F Tiberg, R K Thomas, Biophys J 84(2) 177A-178A (2003))

Summary

Basics of technique introduced

The scope of the application of reflectometry
to the study of surfaces and interfaces, illustrated
over a broad range of applications which include

- Surfactant adsorption
- Ordered structures
- Complex mixtures (polymer-surfactants)
- Polymer thin films and interfaces
- Bio-membranes, surfaces

Presented work from a number of collaborations and groups:

Thomas (Oxford), Unilever, Bucknall (Georgia Tech), Jones (Sheffield),
Russel (USA), White (Australia), Lu (Manchester), Roser (Bath)

CLRC

ISIS