Neutron Reflectivity study of interfaces

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Action D43
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COST Action D43
Colloid and Interface Science for Nanotechnology

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A

- Neutron Reflectivity
- application of neutron reflectometery in resolving these buried interfaces
- Fluid-Fluid interface and why and how ?
- Application of neutron reflectometery in resolving these buried interfaces
- Typical results

B

Conformation of alkylated azacrown ether at;

Air - water interface,
Oil - water interface.
& the role of fatty acid,

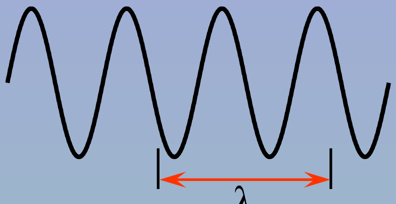
Structure studies of lipids at the oil-water interface

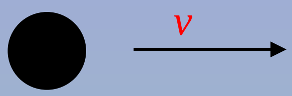
C

Concluding remarks and future work.

The Neutron | Wave-particle duality

de Broglie (1924)





$m_n = 1.674 \times 10^{-27}$ kg

$$\lambda = \frac{h}{m_n v}$$

Thus:

$\lambda \sim 10^{-10}$ m

$E \sim k_B T$

Neutrons scattered by nucleus

isotopic substitution - labelling

$b_H = -3.74 \times 10^{-15}$ m

$b_D = +6.67 \times 10^{-15}$ m

complex sample environment

repetitive measurements

nuclear reactors or spallation sources

The *Spallation Neutron*

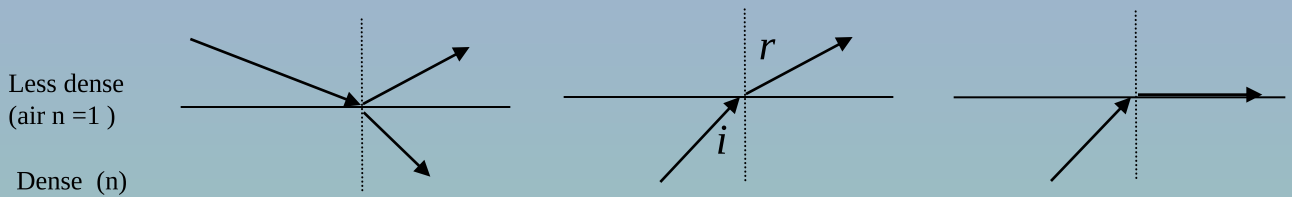
Reactor Source

Reflectivity

Theory

A newer version of well known phenomenon

Refraction of light



$$n = \frac{\sin r}{\sin i}$$

In French, Snell's Law is called "la loi de Descartes"

In case of neutron for most materials n <<1

1. *Principle of Optics*

2. *Quantum approach*

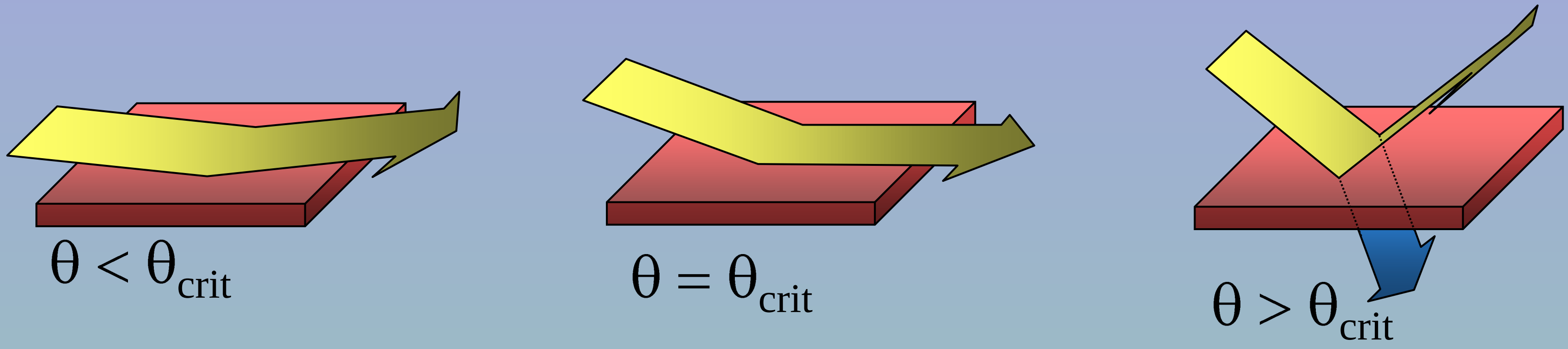
$$n = 1 - \lambda^2 A + i\lambda C$$

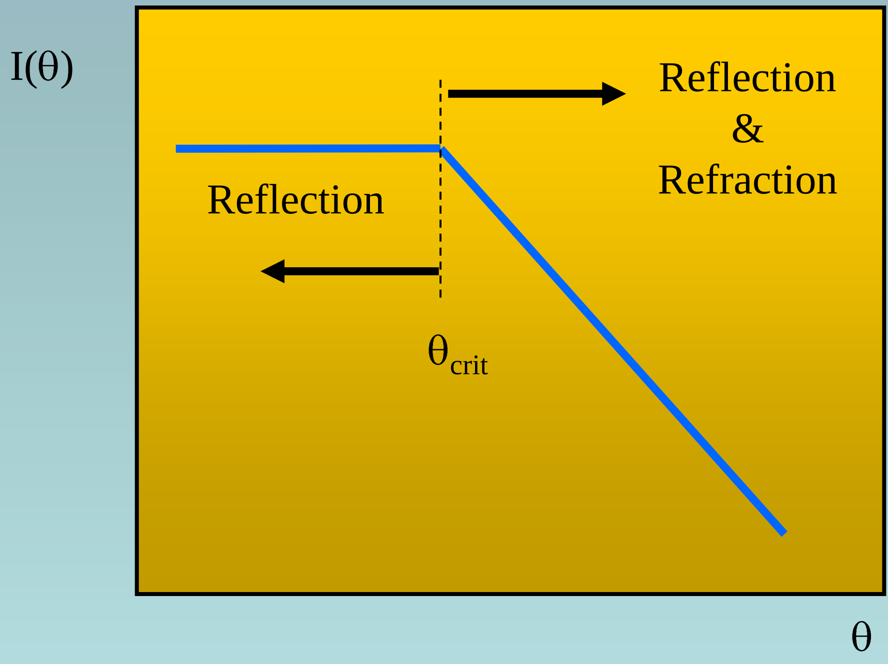
$$A = Nb/(2\pi)$$

$$C = N\sigma_A/(4\pi)$$

Where N is the atomic number density of medium
B is the bound atom coherent scattering length.
The term σ_A is the absorption cross-section
For polymeric species and solvents of low relative molecular mass Nb
can be replaced by the scattering length density of the polymer segment or solvent molecule, ρ.

The neutron | Reflectivity





$$Q = \frac{4\pi \sin\theta}{\lambda}$$

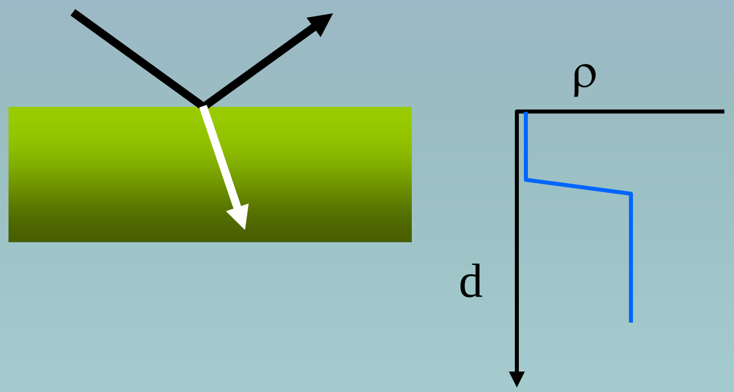
The Neutron

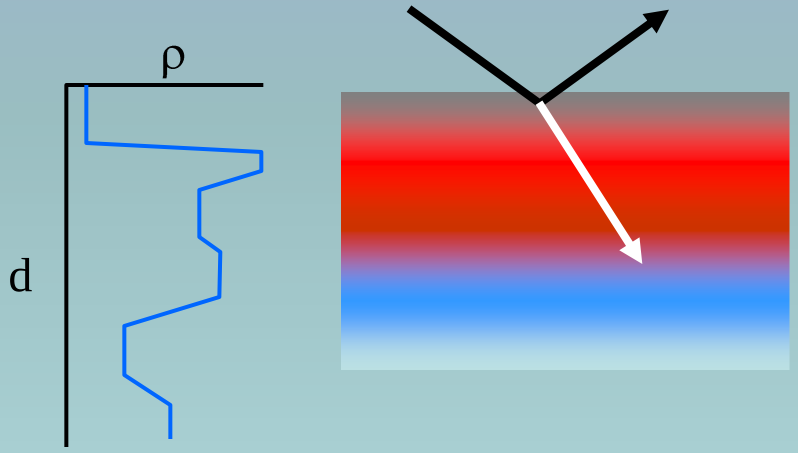
Reflectivity

Structural information $\perp r$ to the surface

Simplest Case

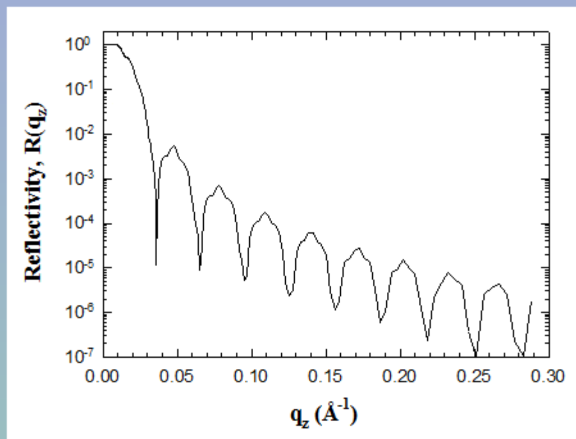
Complex Case



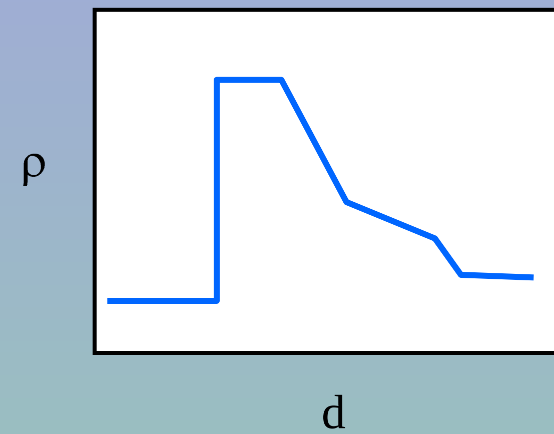


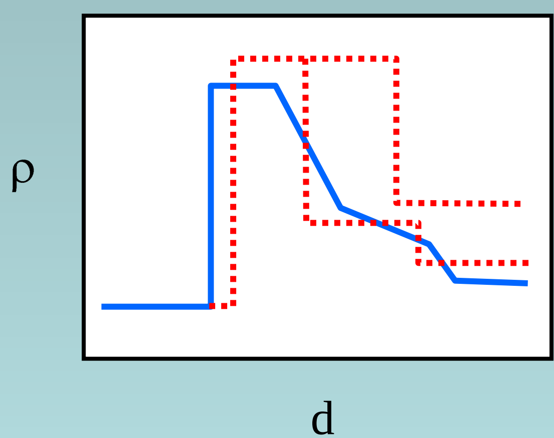
Lateral structure give rise to Off - Specular

The Reflectivity | Data Analysis



Ideal world





Optical matrix method

The transmission and reflection from one layer to the next is described as a matrix multiplication product.

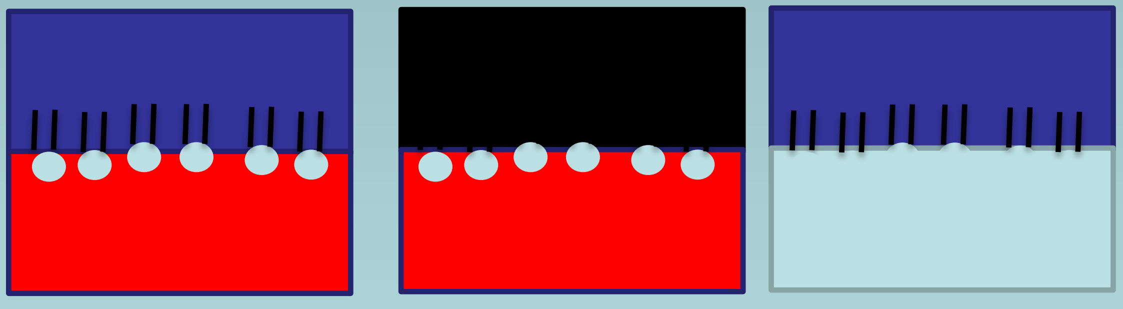
Proposed a model and compare with the data

Scattering length density A^2

Critical angle

$$\rho = \frac{N_A d \sum_i b_i}{m} \qquad \rho^{\pm} = N \times (b \pm C \cdot \mu_b) \qquad \theta_c = \left(\frac{\lambda^2}{\pi} \rho \right)^{1/2}$$

Contrast variation



The neutron Reflectivity | Applications

Surface Chemistry	Surfacatnts, Polymers, Protein, Lipids at air –water solid –liquid and liquid –liquid interfaces
Solid surfaces	Thin films, multilayers, polymers
Magnetic sample	Magnetic multilayers, superconductors and thin films

A

The Liquid/Liquid Interface Why and How?

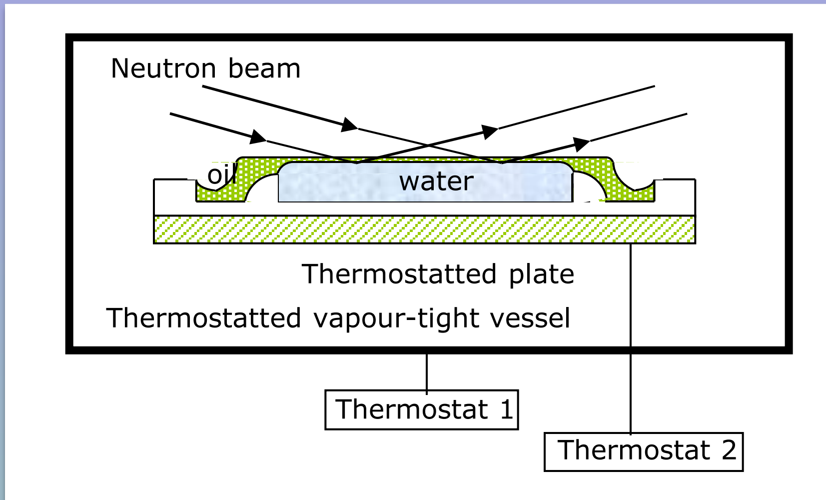
Why

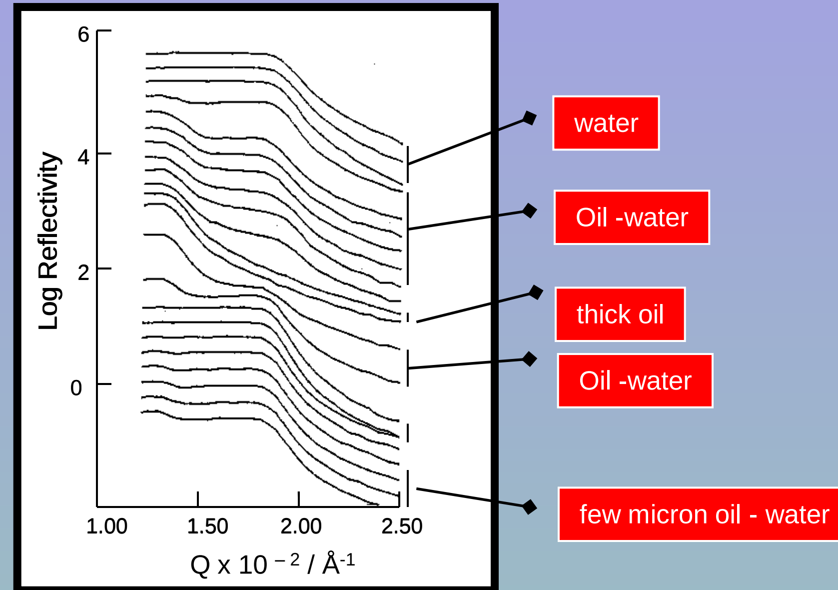
Transport properties of cell membrane
Stabilisation of emulsion
Mixed surfactants and cold water cleaning
Proteins (and surfactants) at Oil / Water: Important in biological & food systems
Proteins stabilise a diverse range of colloids including: blood, ice-cream, milk

How

Sum Frequency Spectroscopy
x-ray reflectivity
Neutron reflectivity

Condensation Method

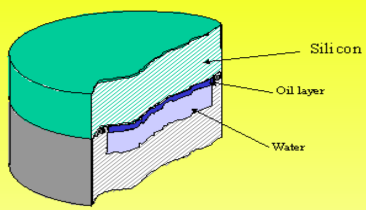


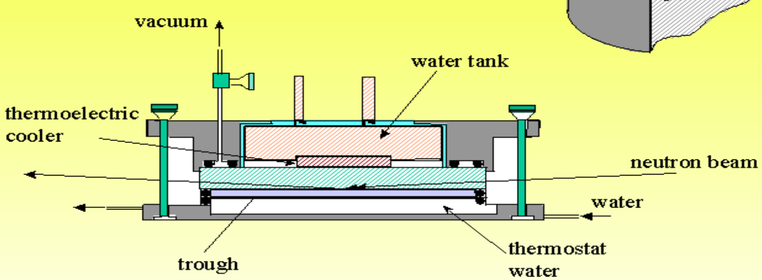


Method: Relies on balancing the condensation and drainage rates of the oil film

Limitation: the maintenance of a uniform condensed oil layer is a non-trivial and very time-consuming task. the technique is restricted to the study of volatile oils limited contrast can be used.

Spin-Freeze method





Hydrophobe silicon surface: Chemically modify using trichlorosilane from chloroform Spread oil using a spinner. Freeze rapidly, assemble cell and introduce aqueous phase.

- **Hydrophobic silicon surface**
- **Spread hexadecane**
- **Spin (2000 rpm for 20 s)**
- **Cool block to *T* < 18 ºC**

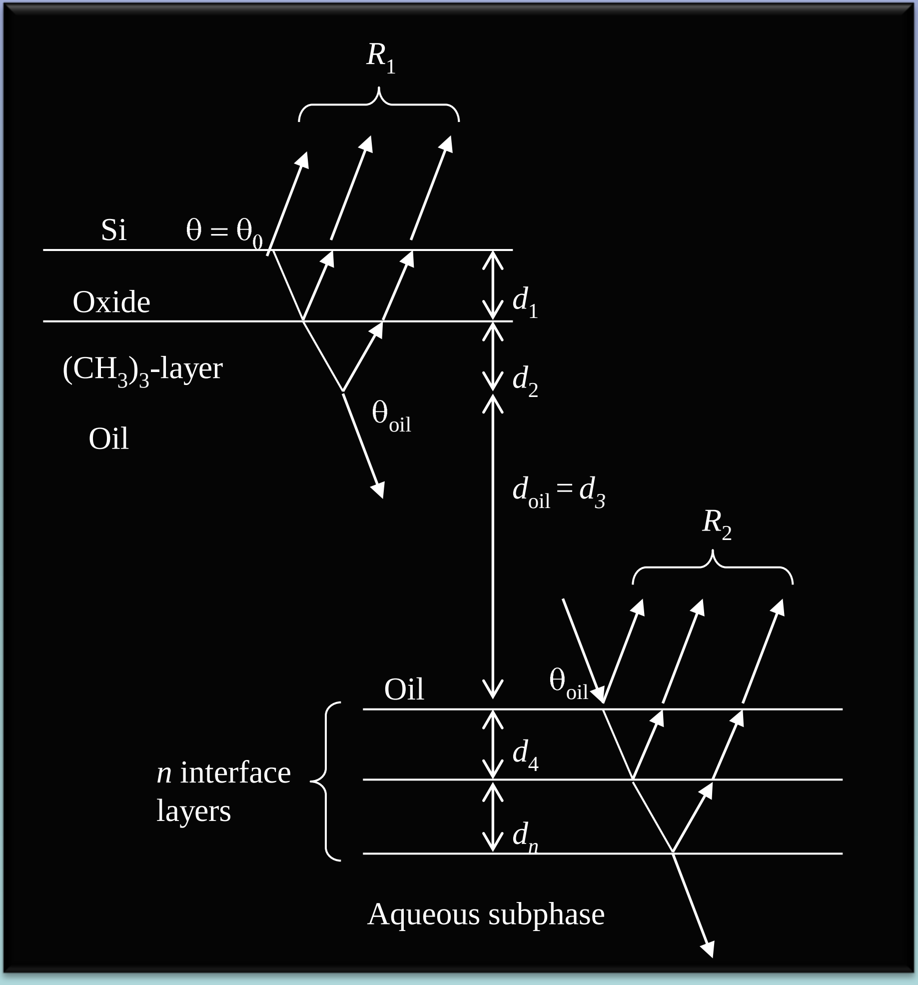
- Assemble cell
- Warm block to *T* >18 ºC
- Measure **reflectivity**

“A new approach to measuring neutron reflection from a liquid/liquid interface” A, Zarbakhsh, J. Bowers and J.R.P.Webster. M. Sci. Technol, 10, 738-743 **1999**.

Thickness of oil film is determined by mass of oil added and spinning speed

Experimental & analysis

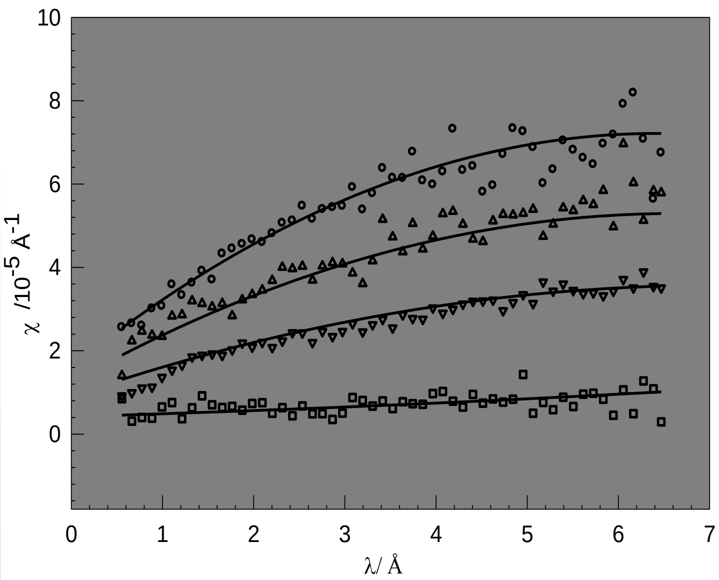
- Use a supermirror to change Q
- Film stable/reproducible



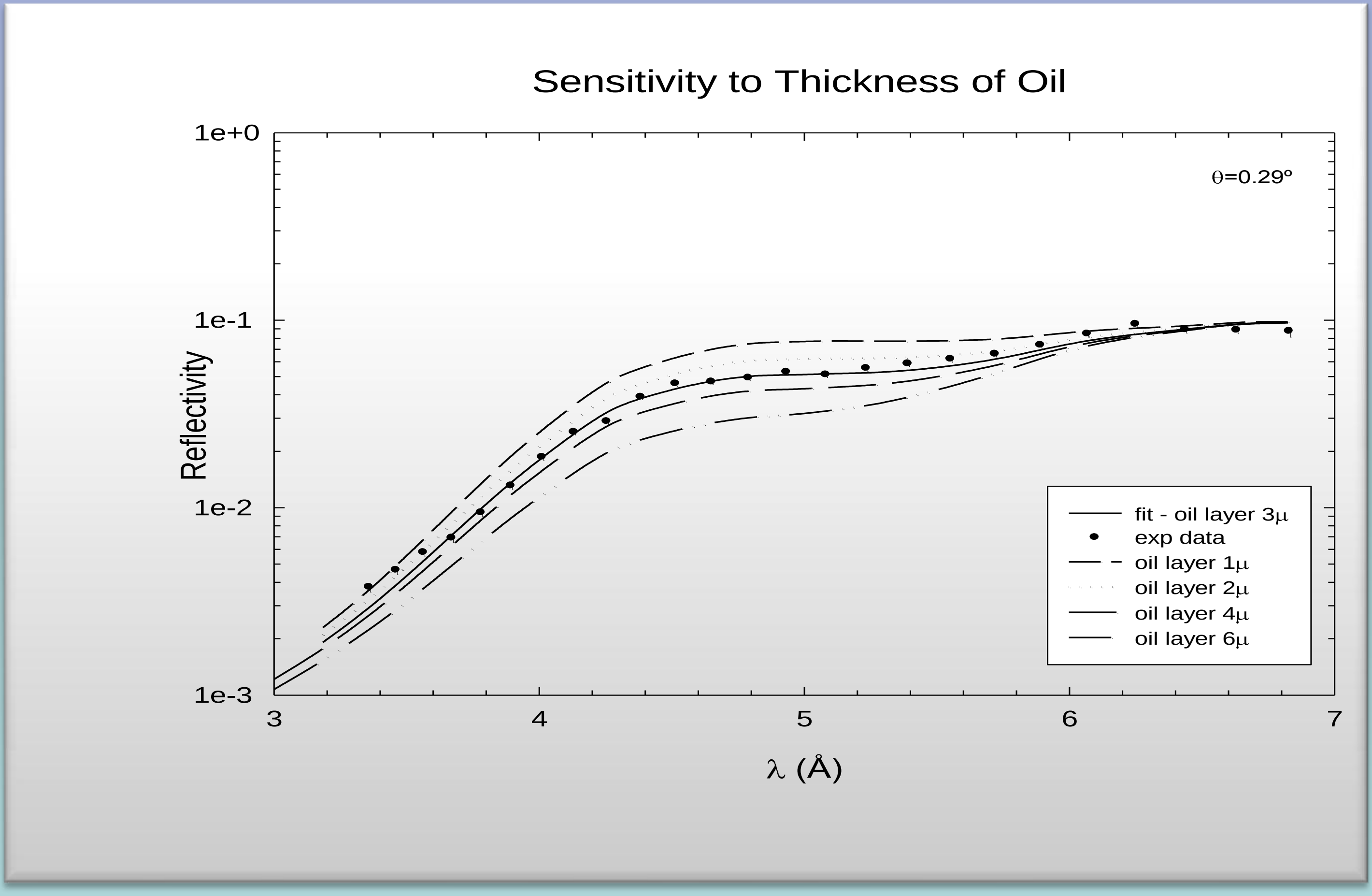
$$n(\lambda) \approx 1 - \frac{\lambda^2}{2\pi} Nb + i \frac{\lambda}{4\pi} N\sigma$$

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

$$A = \exp\left(\frac{-2\chi d_{oil}}{\sin\theta_{oil}}\right)$$



$T = \exp(-\chi l)$



Sensitivity to Thickness of Oil
θ=0.29°
Reflectivity
1e+0
1e-1
1e-2
1e-3
3
4
5
6
7
λ (Å)
fit - oil layer 3μ
exp data
oil layer 1μ
oil layer 2μ
oil layer 4μ
oil layer 6μ

Interfacial width at bare hexadecane-water interface

The reflectivity can be written

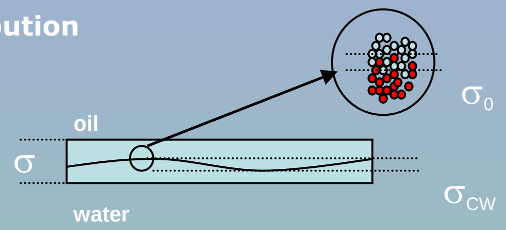
$$\mathrm{Ln}(R/R_F) = -Q_z Q_T \sigma^2$$

- The **interfacial width, σ**

$$\sigma^2 = \sigma_0^2 + \sigma_{CW}^2$$

σ_0 **including the intrinsic**

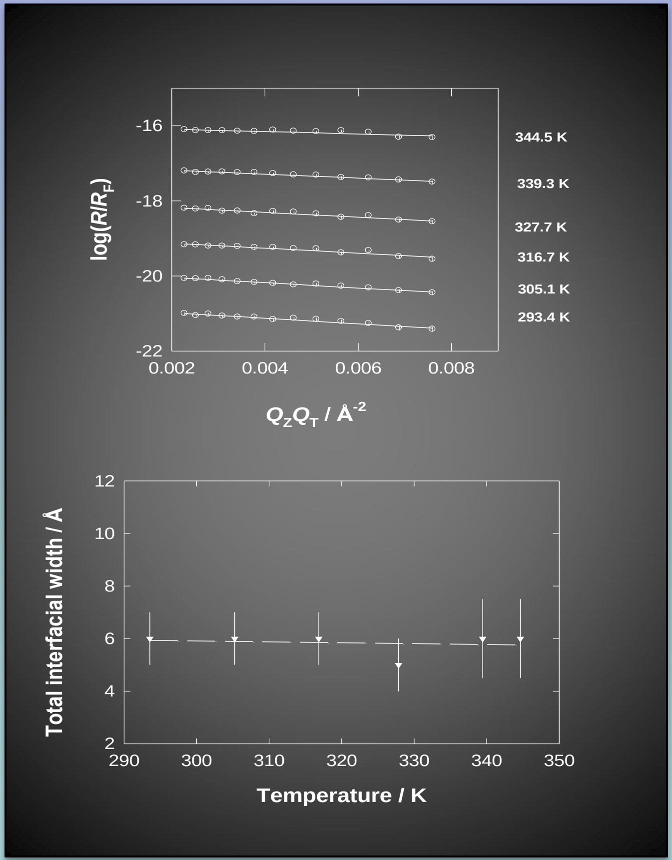
σ_{CW} **capillary-wave contribution**



$$\sigma_{CW}^2 = \left[kT/(2\pi\gamma)\right] \ln\left(Q_{max}/Q_{min}\right)$$

$$Q_{min} = \left(2\pi/\lambda\right)\Delta\beta \sin\theta$$

$$Q_{max} \approx \left(2\pi/a\right)$$



interfacial tension varies as

$$\gamma\,/\,\mathrm{mN\ m^{-1}} = 54.5 - 0.076(T/\mathrm{K} - 298)$$

NR	σ_0 **= 6.0 ± 1.0 Å**
XR	σ_0 **= 6.0 ± 0.2 Å***
Expected	σ_0 **= 5.55 Å**

"Width of the hexadecane–water interface: A discrepancy resolved"
Ali Zarbakhsh*, James Bowers, and John Webster.
Langmuir, **21** (25), 11596 -11598, **2005**.

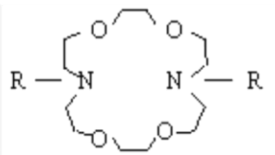
B

Macrocyclic ligands at the air-water and the oil-water interface

- Cationic transport carriers in different extraction base techniques

- The Langmuir films of these azacrown ether have potential in chemical sensing and molecular electronics applications

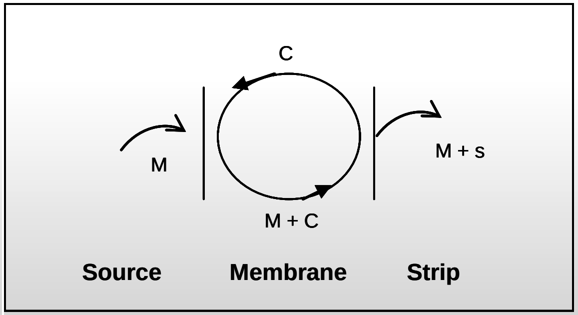
- They can act as a good representative of biological transport systems



$R = C_{16}H_{33}$

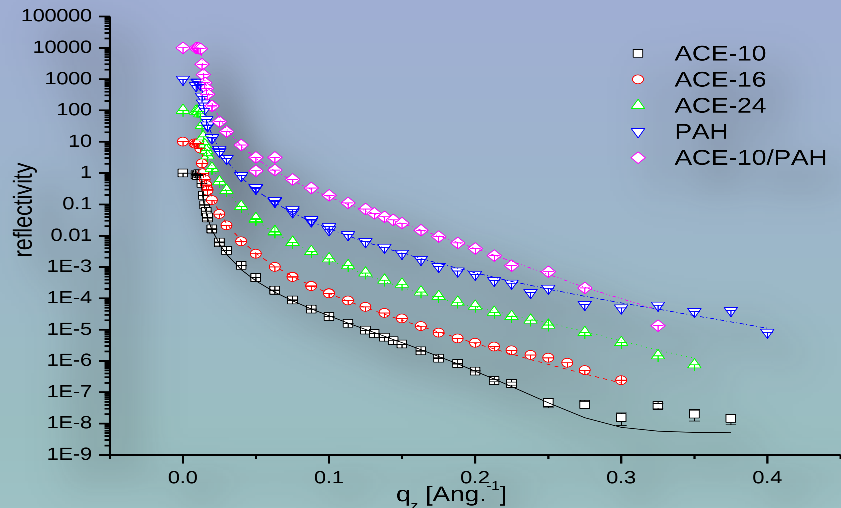
Stabilization of alkylated azacrown ether by fatty acid at the air-water interface.
Zarbakhsh A, Campana M, Webster JR, Wojciechowski K
Langmuir 26(19):15383-15387 05 Oct 2010

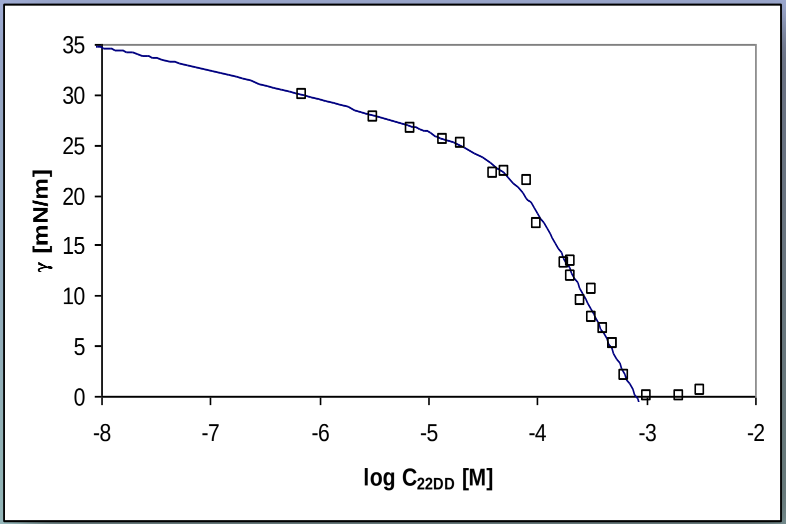
Buffle et al. used the alkylated azacrown ethers in conjunction with fatty acids for transporting heavy metal ions (Cu(II), Cd(II), Pb(II)) against their concentration gradient in so called Permeation Liquid Membrane (PLM) devices. A typical PLM device consists of a hydrophobic membrane separating two aqueous compartments between which the transport of metal ions takes place. The process involves thus two extraction steps - one at each aqueous-membrane interface. The membrane could be either unsupported (bulk organic phase), or supported in the pores of a thin inert polymer support. In either case the membrane consists of a solution of the carrier (e.g. a mixture of azacrown ether and fatty acid) in a nonpolar solvent.



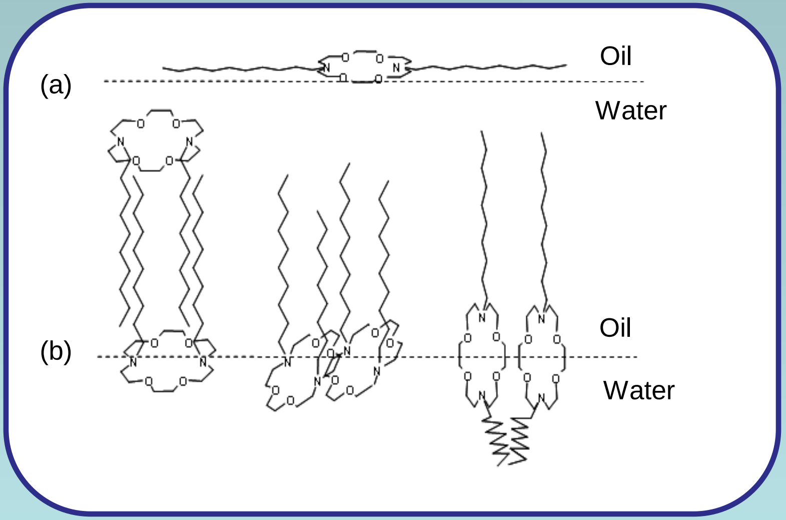
Source	*Membrane*	Strip
(aqueous medium + metal species (M))	*(organic medium + carriers (**C**))*	(aqueous medium + Complexing agent (**S**))

X-ray reflectivity : toluene -water interface





Surface tension isotherm can not be understood using a simple Langmuir or Frumkin model

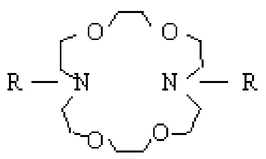


ACE10

(a) A possible expanded model
(b) Reoriented model

X-ray data could not distinguish between these Possible models.

Air –water interface experiment

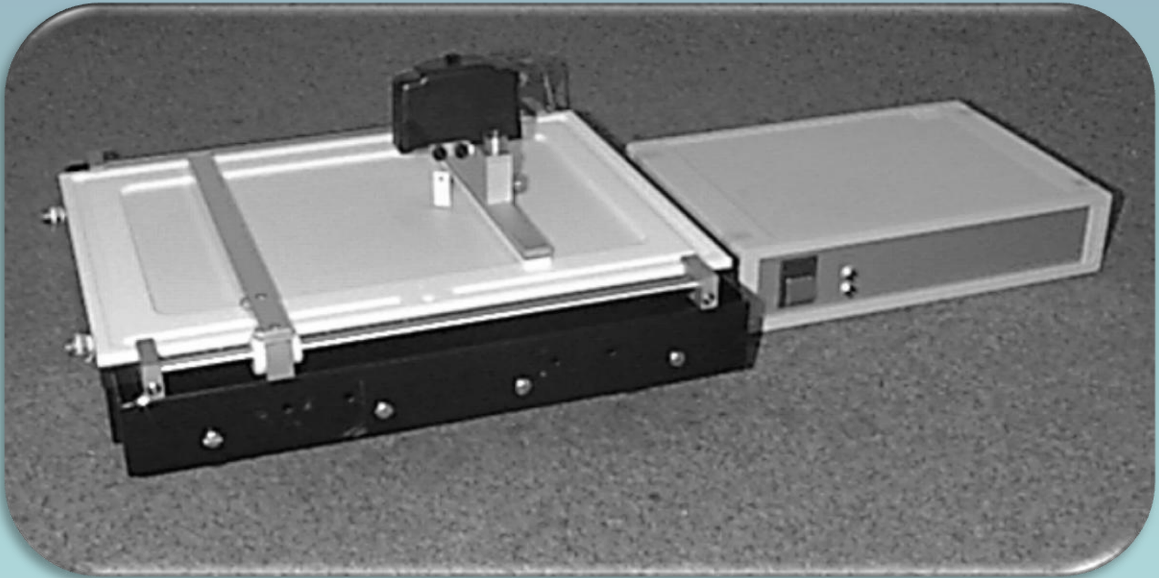


R = $C_{16}D_{33}$

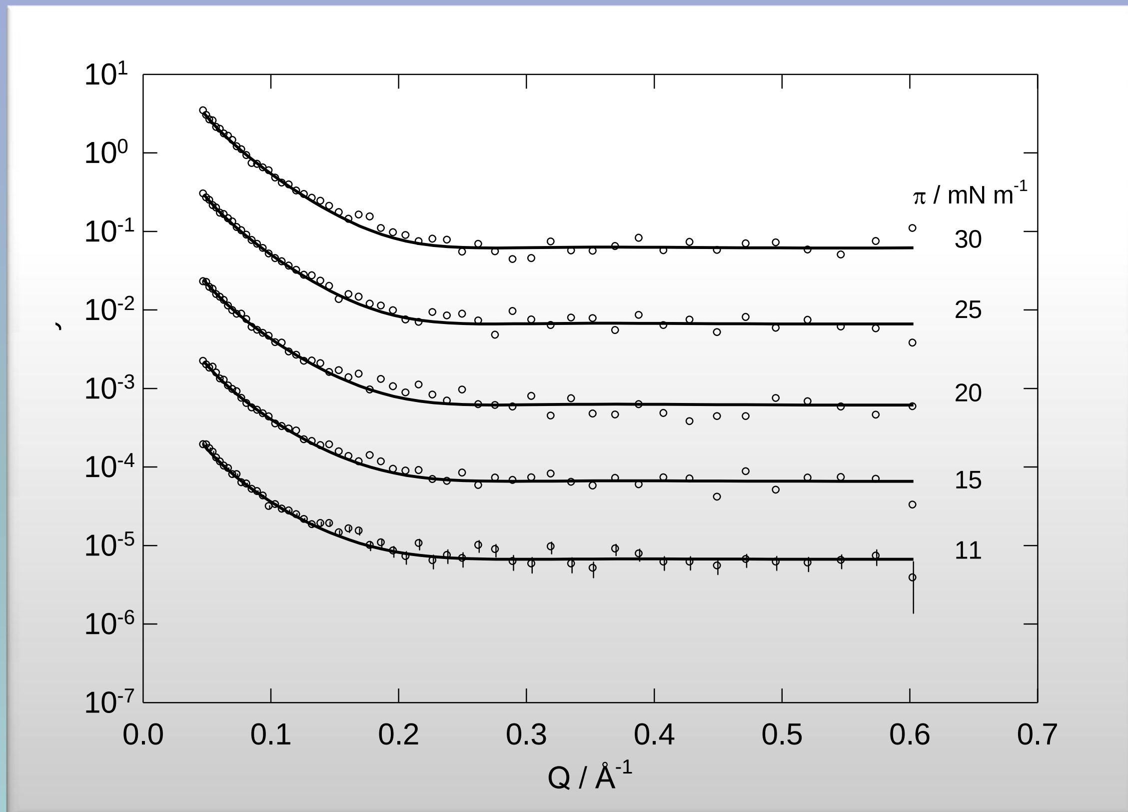
Two contrasts

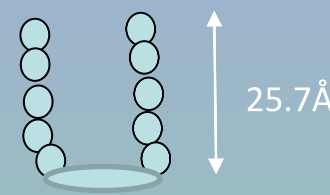
1. Air – null reflecting water

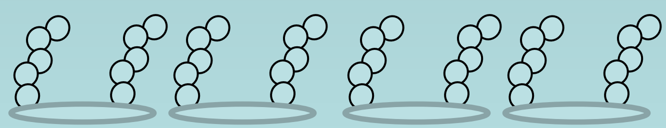
2. Air – D_2O



Reflectivity data for contrast 1 (air-null reflecting water) interface for a solution of d-ACE-16 measured at 1.5°. The solid lines correspond to a single layer model with film thickness 21.5 ± 0.5 Å.

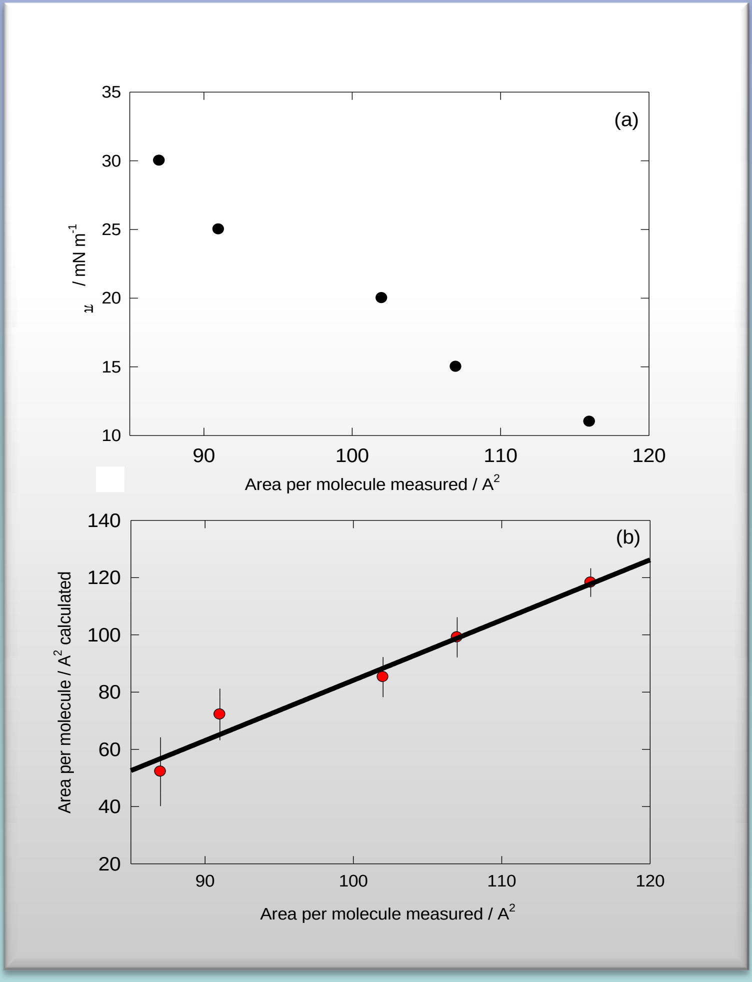




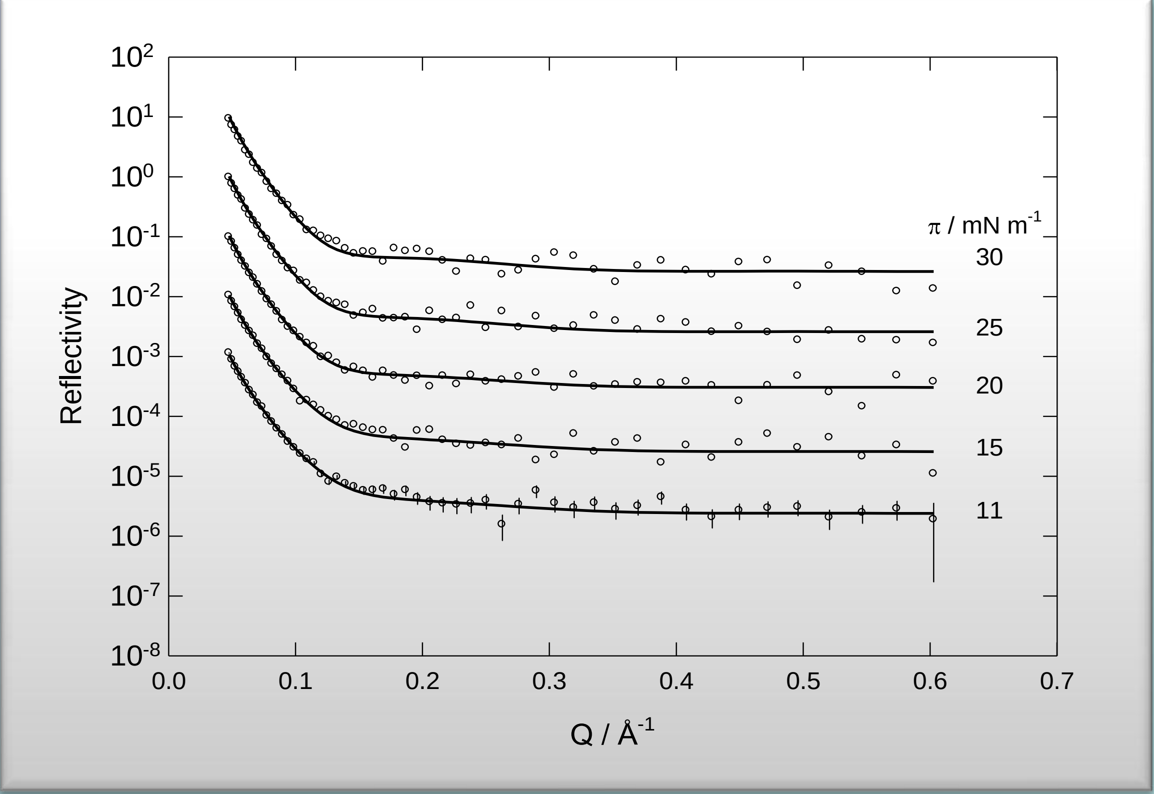


21.5 ± 0.5 Å

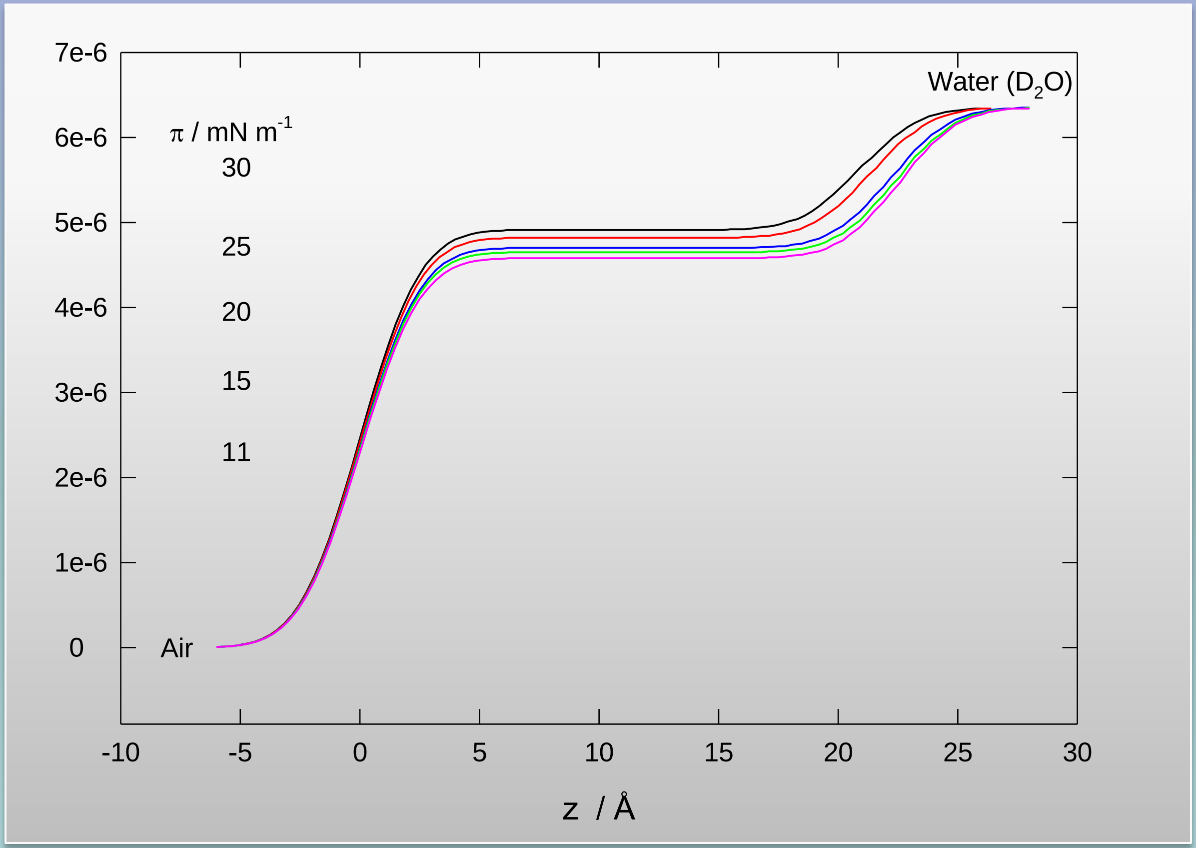
Analyses of reflectivity data measured for contrast 1: (a) π vs area per molecule for d-ACE-16 estimated from the area of the trough (b) the area per estimated from the area of the trough as a function of the area per molecule obtained from the fits to the neutron profiles.



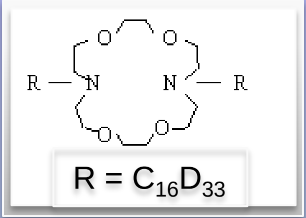
Reflectivity data for contrast 2 (air-D_2O) interface for a solution of d-ACE-16 measured at 1.5°. The solid lines correspond to a single layer model with film thickness 21.5 ± 0.5 Å.



Scattering length density profiles used to model the contrast 2 (for d-ACE-16 at the air-D_2O)



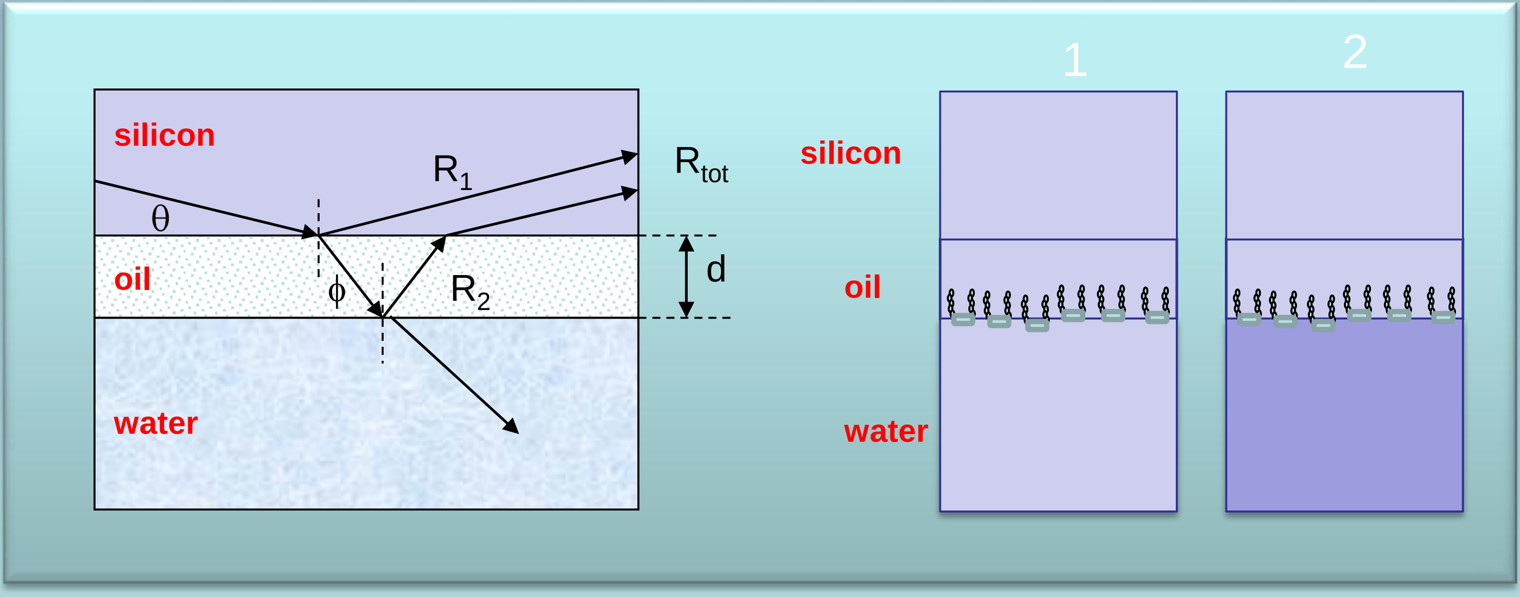
Oil –water interface experiment



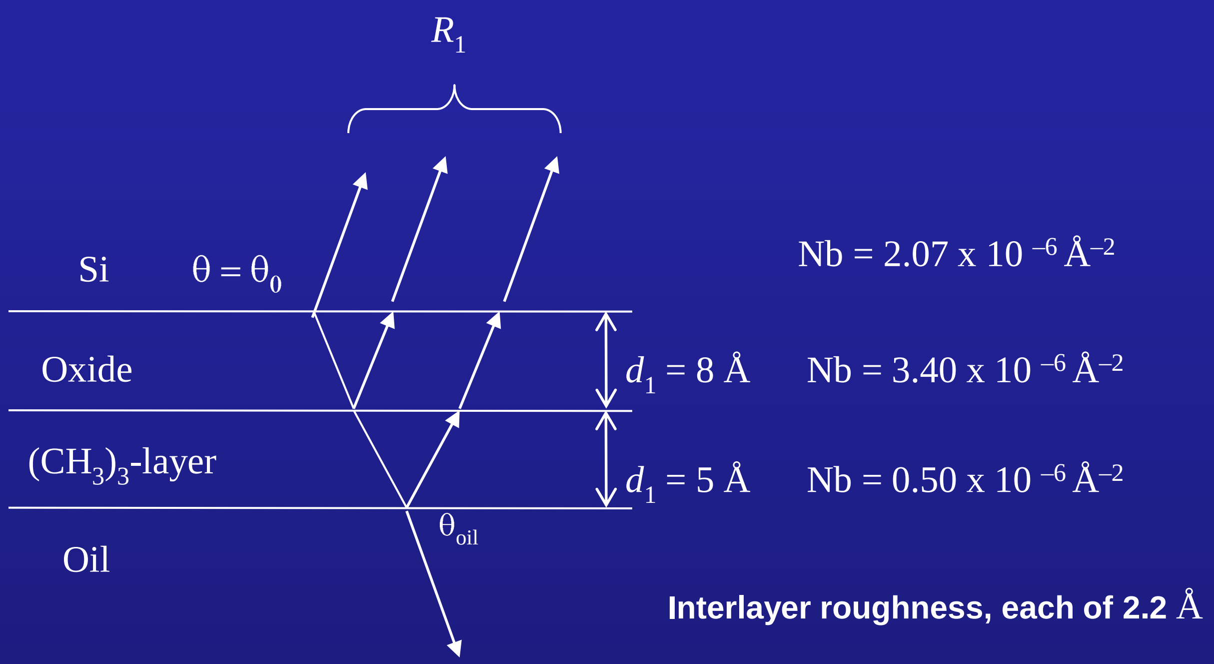
Two contrasts

1. Si contrast matched oil – Si contrast matched water

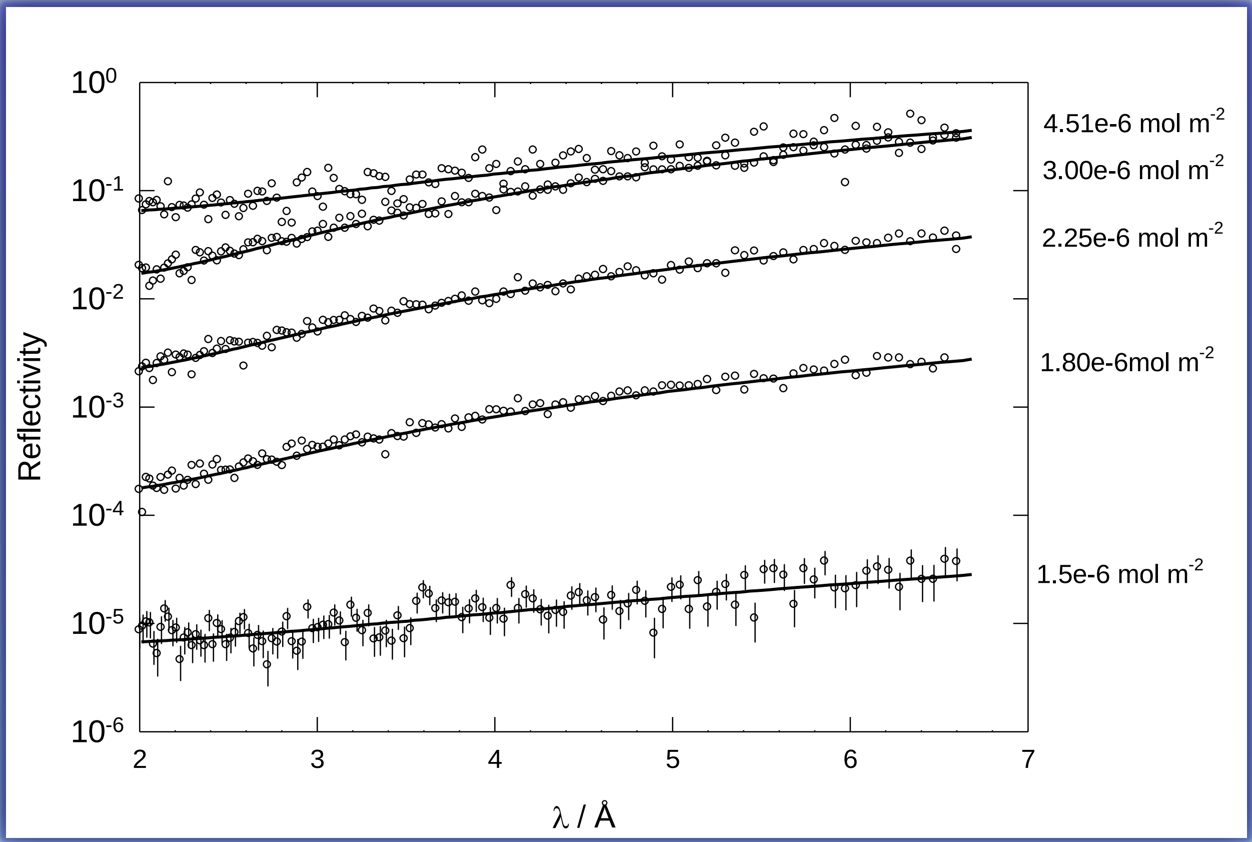
2. Si contrast matched oil –D_2O



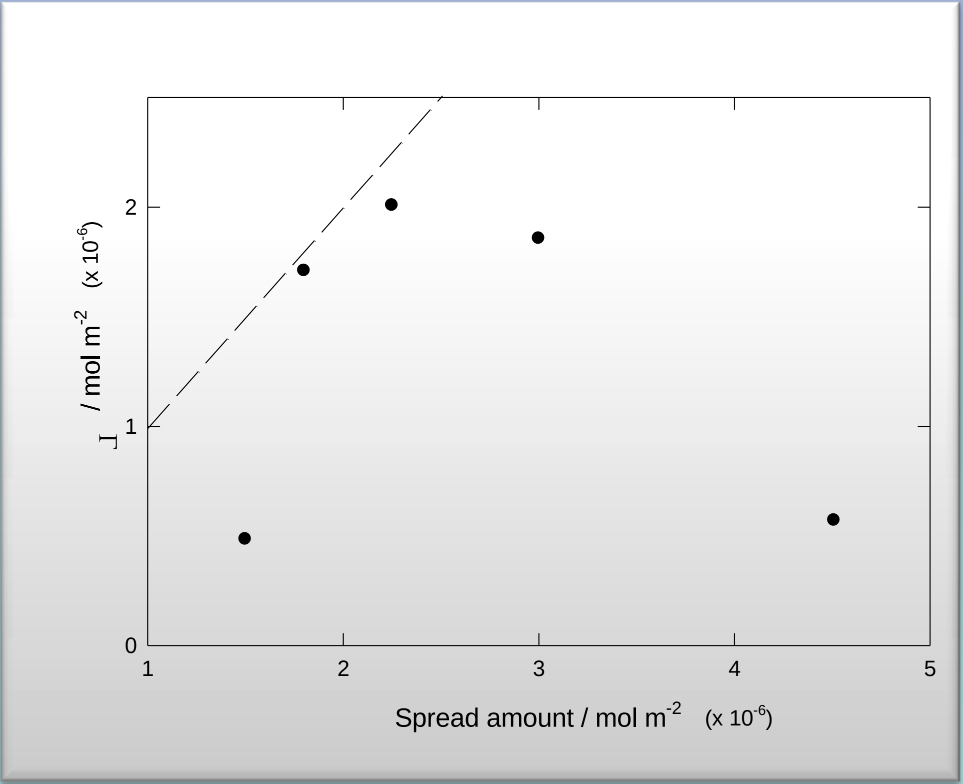
R_1 Part of reflectivity



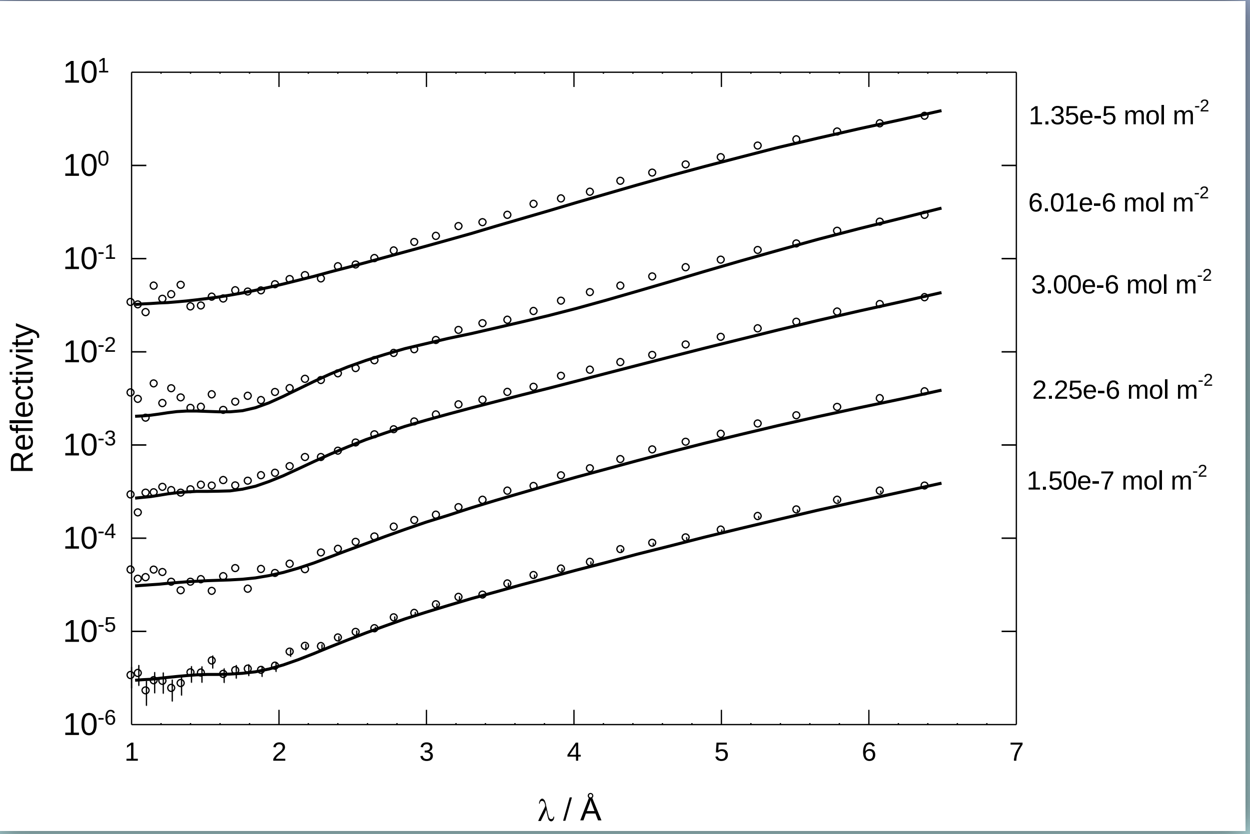
Reflectivity data measured at 1.4°, for contrast 3 (Si - hexadecane scattering length density matched to the Si - aqueous solution with scattering length density matched to Si), for a series of spread amounts for the d-ACE-16. The solid lines correspond to a single layer model with film thickness 29.0 ± 2.0 Å.



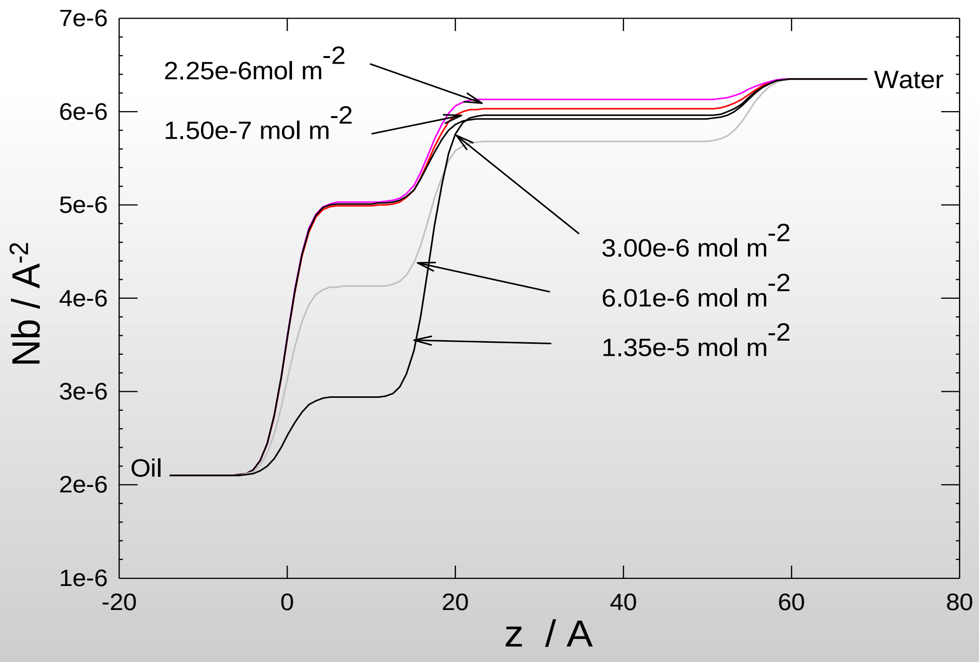
The fitted adsorbed amount deduced from contrast 3 for the d-ACE-16 at the oil-water interface is plotted as a function of spread amount. The dash line shows the idealised line.

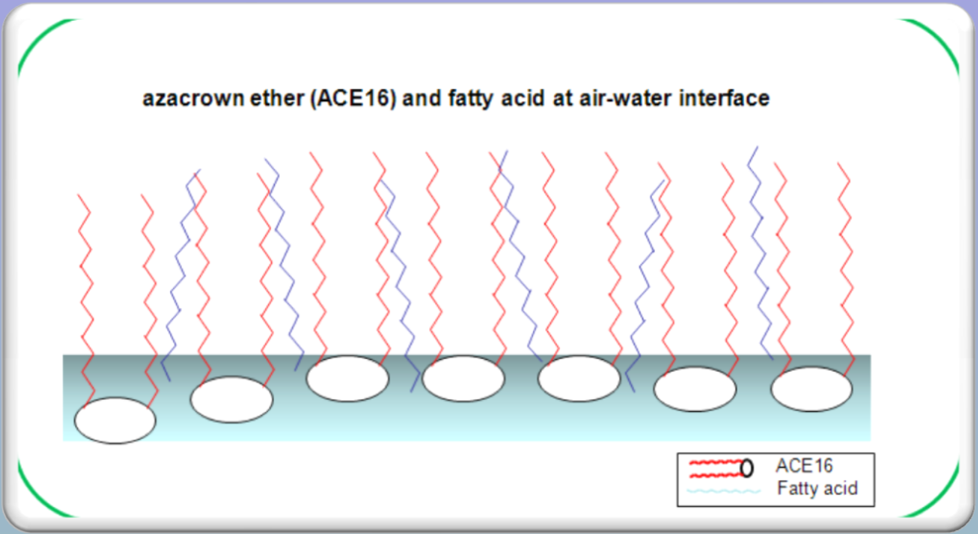


Reflectivity data for the contrast 4 (Si - hexadecane scattering length density matched to the Si - D_2O) for a series of d-ACE-16 spread amounts measured at 1.4°. The solid lines correspond to a two-layer model (17 Å at the hexadecane side of the interface and 38 Å at solution side of the interface.

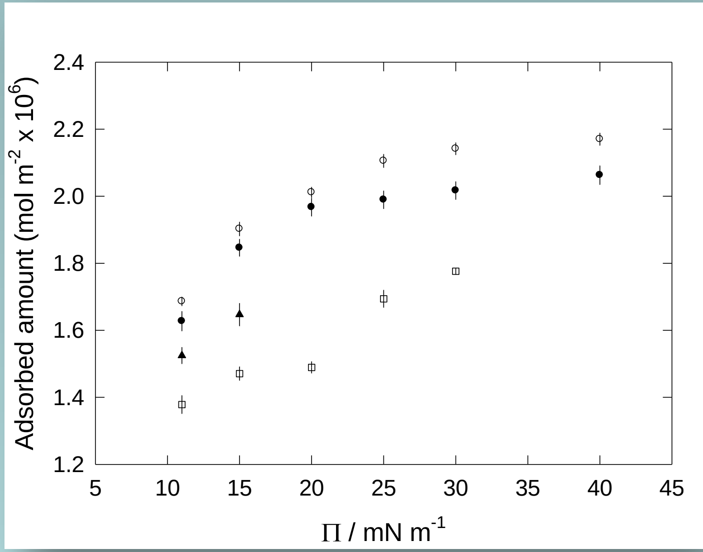


Scattering length density profiles used to model the contrast 4 data

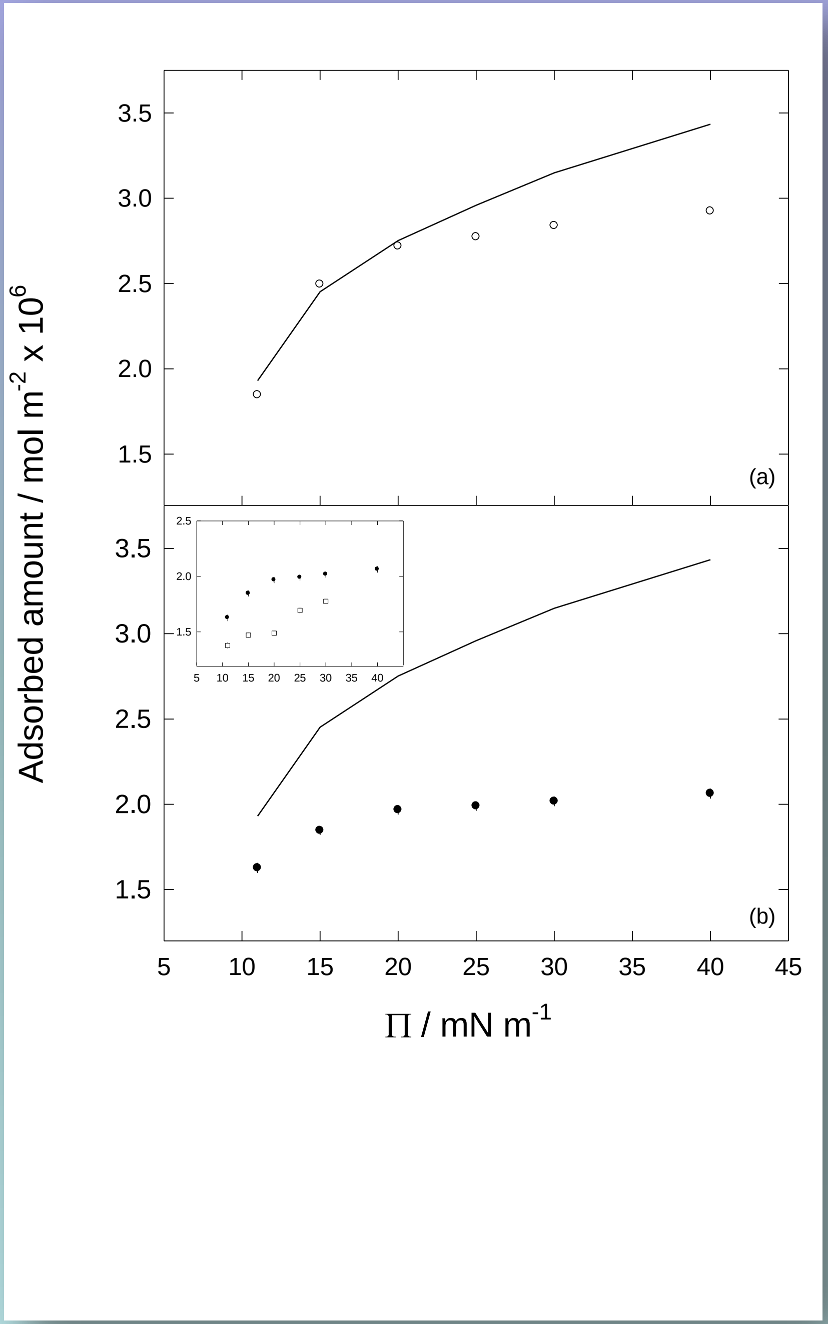




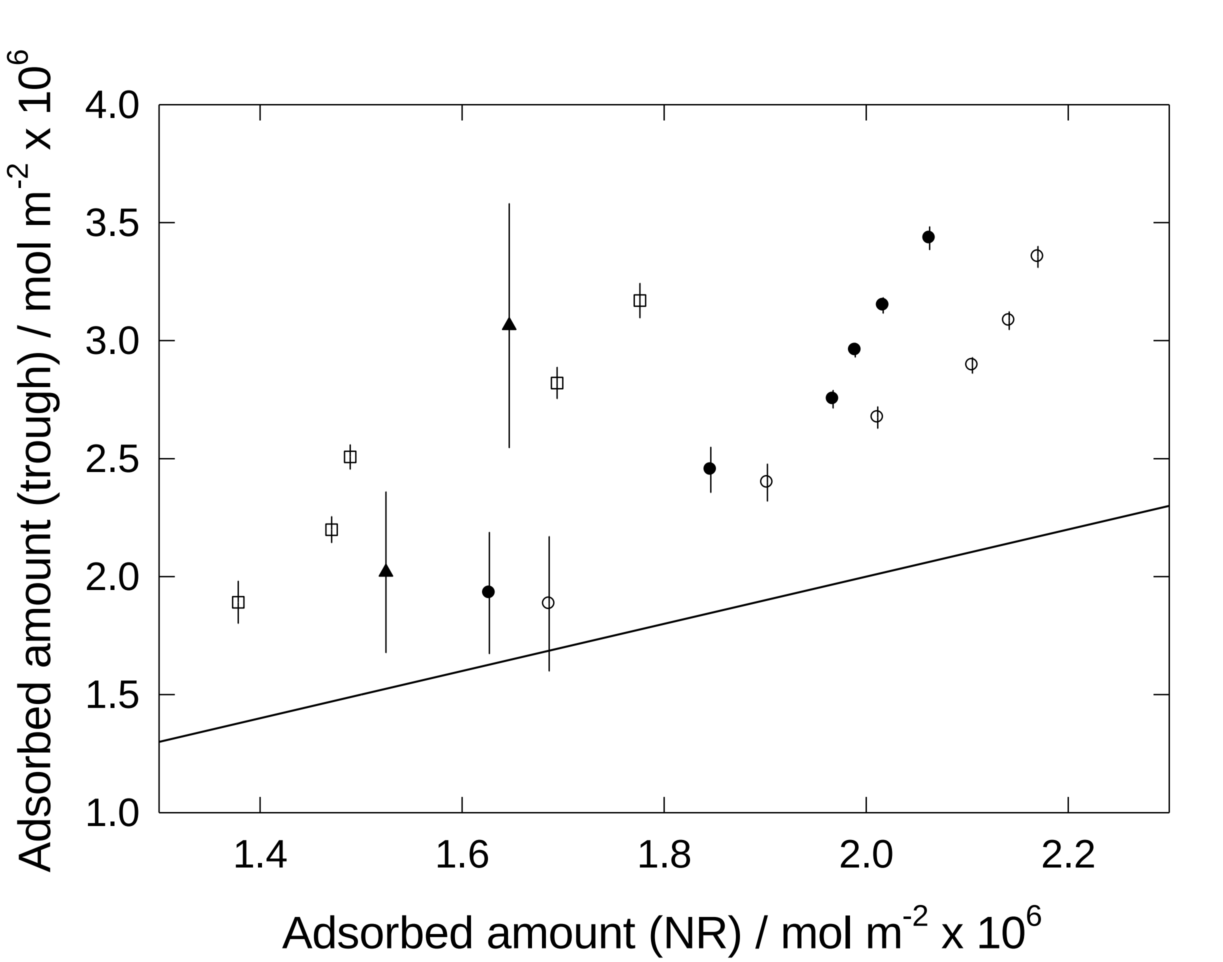
azacrown ether (ACE16) and fatty acid at air-water interface
ACE16
Fatty acid



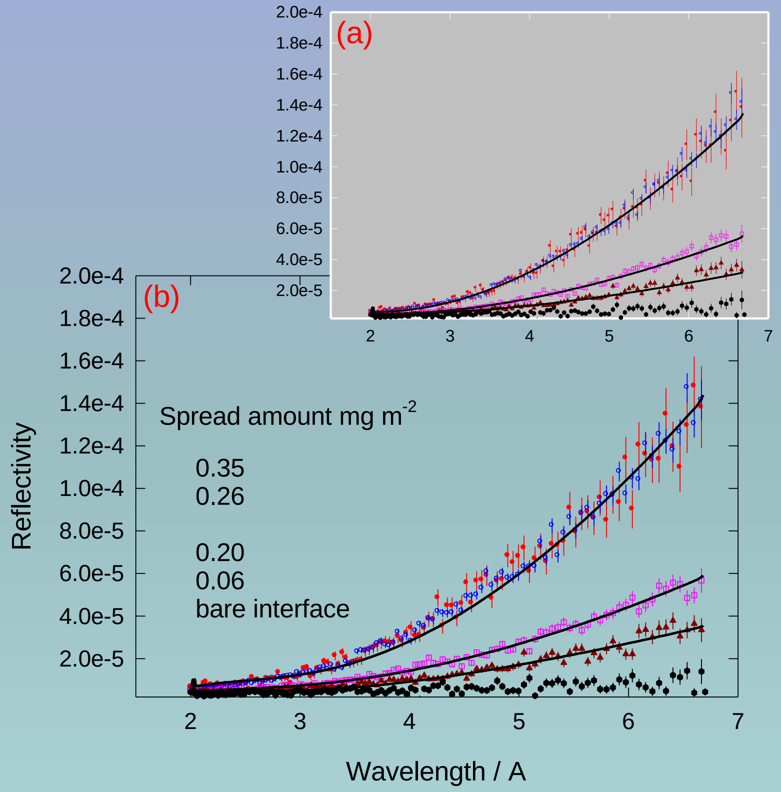
Adsorbed amount (mol m-2 x 106)
Π / mN m-1

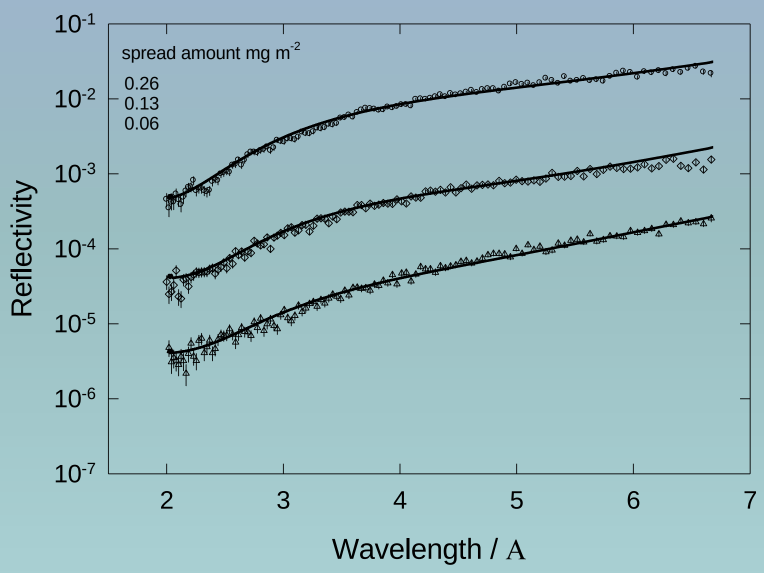


Adsorbed amount / mol m-2 x 106
Π / mN m-1
(a)
(b)

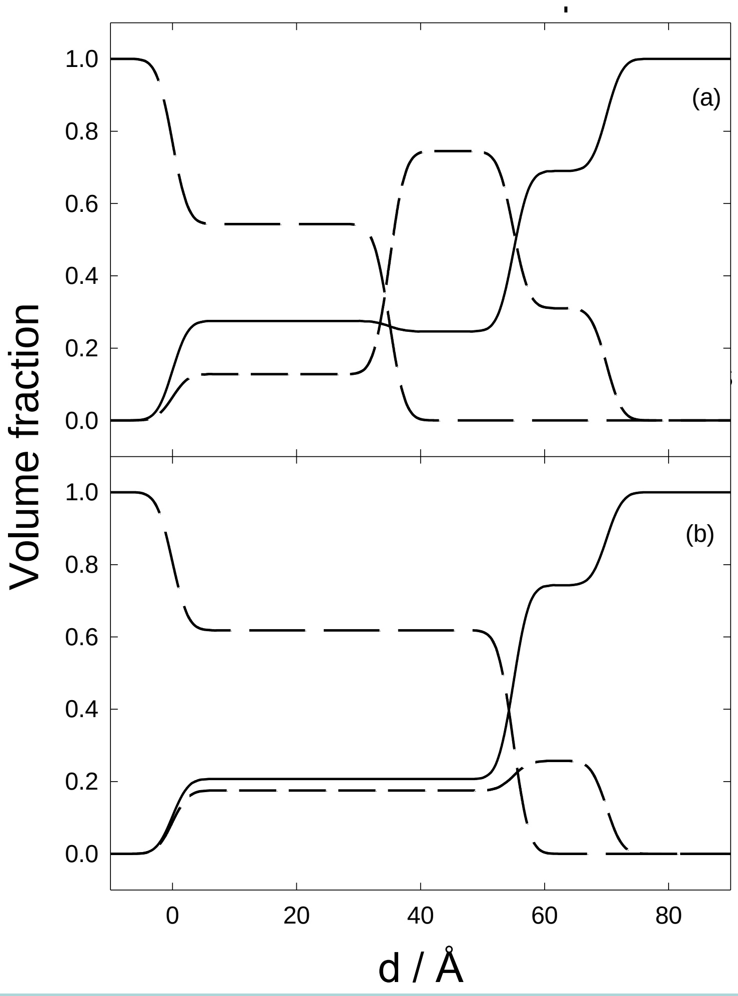

Adsorbed amount (trough) / mol m-2 x 10^6
4.0
3.5
3.0
2.5
2.0
1.5
1.0
1.4
1.6
1.8
2.0
2.2
Adsorbed amount (NR) / mol m-2 x 10^6

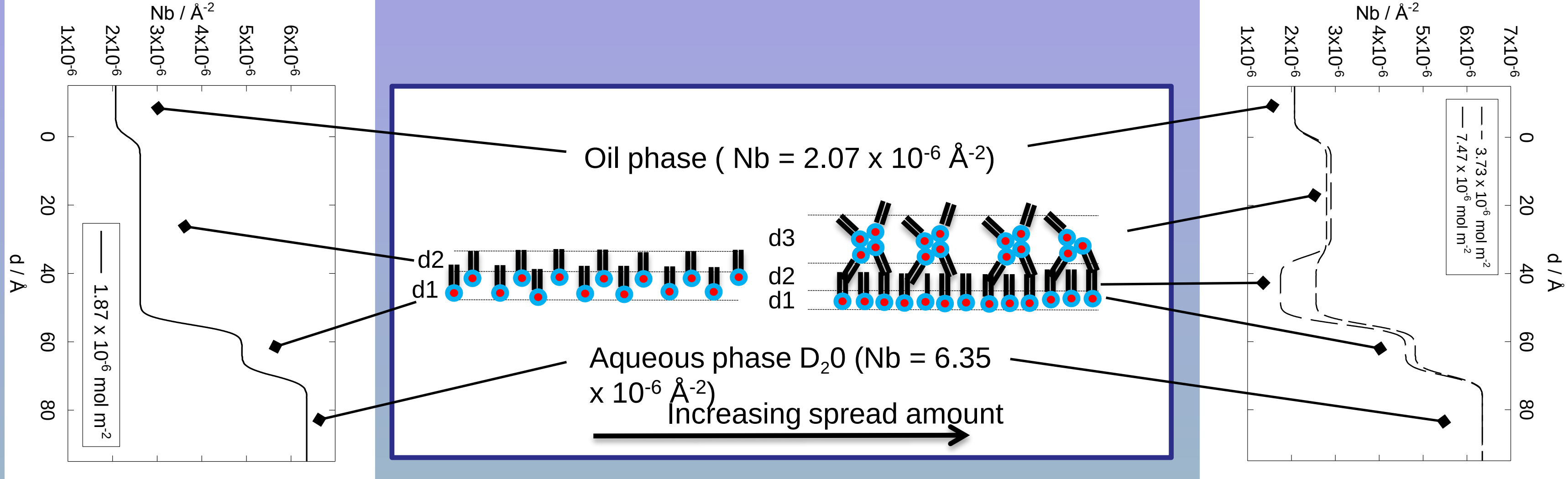
Structural study of lipids at the oil-water interface

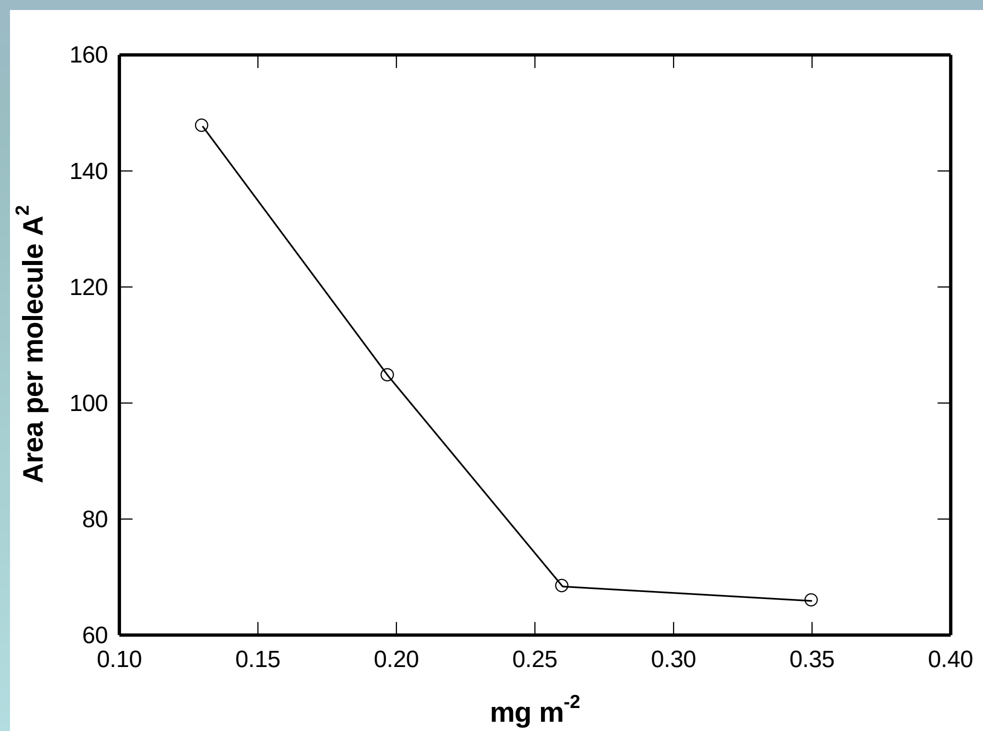




Volume fraction profiles 0.26 & 0.06 mg m^{-2}




Nb / Å^-2
1x10^-6
2x10^-6
3x10^-6
4x10^-6
5x10^-6
6x10^-6
7x10^-6
d / Å
0
20
40
60
80
1.87 x 10^-6 mol m^-2
3.73 x 10^-6 mol m^-2
7.47 x 10^-6 mol m^-2
Oil phase (Nb = 2.07 x 10^-6 Å^-2)
d1
d2
d3
Aqueous phase D20 (Nb = 6.35 x 10^-6 Å^-2)
Increasing spread amount


Area per molecule A^2
160
140
120
100
80
60
0.10
0.15
0.20
0.25
0.30
0.35
0.40
mg m^-2

C

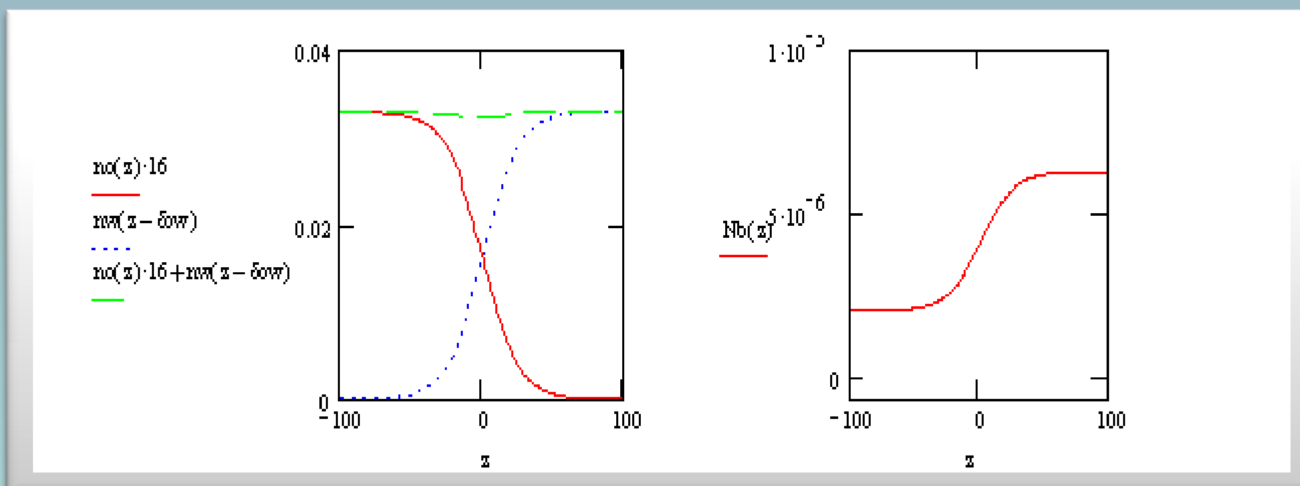
Final Remarks

Application and refinement of a method for structural studies at a liquid-liquid interface using neutron reflectometery.

- Absorption isotherms and molecular conformations have been deduced.
- We have recently extend these studies to lipids conformations and interactions at Liquid – Liquid interfaces.
- We have also working on application of series of isotopic substitutions to resolve the distribution of oil and water at these important interfaces.

Partial structural study at the oil-water interface

Contrast	hexadecane	water
1	4e-6 $Å^{-2}$	D_2O
2	4e-6 $Å^{-2}$	H_2O
3	4e-6 $Å^{-2}$	3e-6 $Å^{-2}$
4	CMSi	D_2O
5	CMSi	H_2O
6	CMSi	3e-6 $Å^{-2}$



a) Possible number density profiles of water (nw) and oil (no). The oil number density is per methylene unit. b) Corresponding scattering length density profile. The width of the scattering length density profile is ~5Å which agrees with theory and our previous neutron experiment.