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Applying Neutron and X-ray methods to Soft Matter II: thin films

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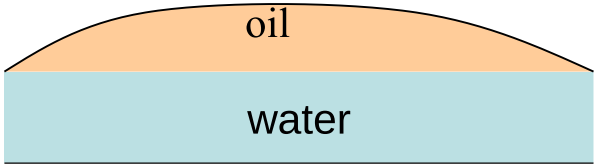
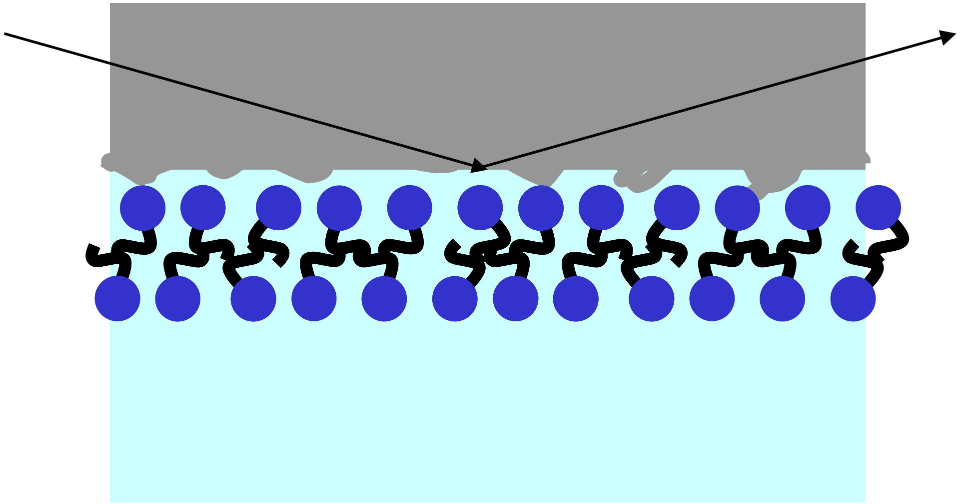
Uppsala University, Sweden

Reflection

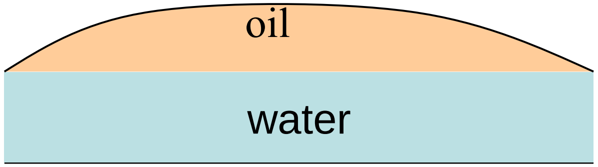
Light



Reflection

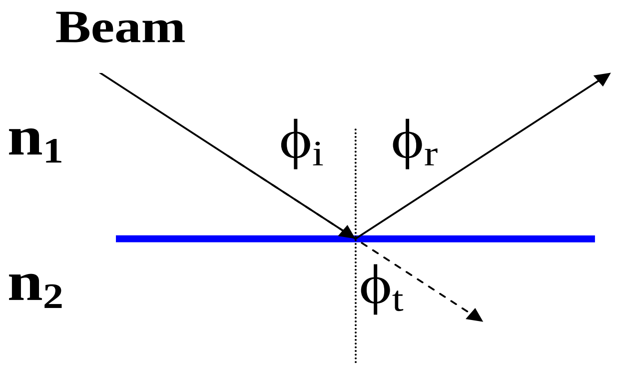


Light



Reflection and Refraction: Snell's Law

Optical Notation



For specular reflection:

$\phi_i = \phi_r$

Transmitted beam is refracted:

$n_2 \sin \phi_t = n_1 \sin \phi_i$

n is refractive index

Reflection and Refraction: Snell's Law

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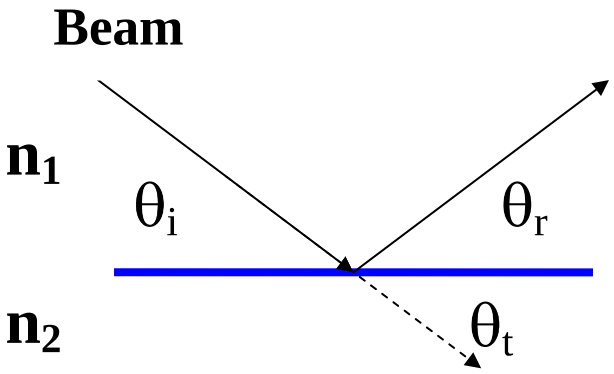
Neutron Reflection Notation



For specular reflection:

$$\theta_i = \theta_r$$

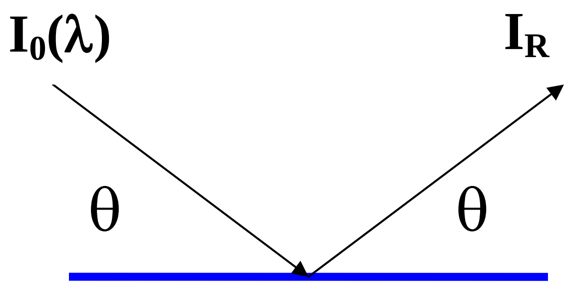
Transmitted beam is refracted:

$$n_2 \cos \theta_t = n_1 \cos \theta_i$$

n is refractive index

Reflection – measured quantities

Reflection



Reflected beam
deflected: $2\,\theta$

Reflectivity
$R(Q) = I_R/I_0(\lambda)$

Momentum transfer
$Q = (4\pi/\lambda)\sin\theta$

Contrast in a Thin Film

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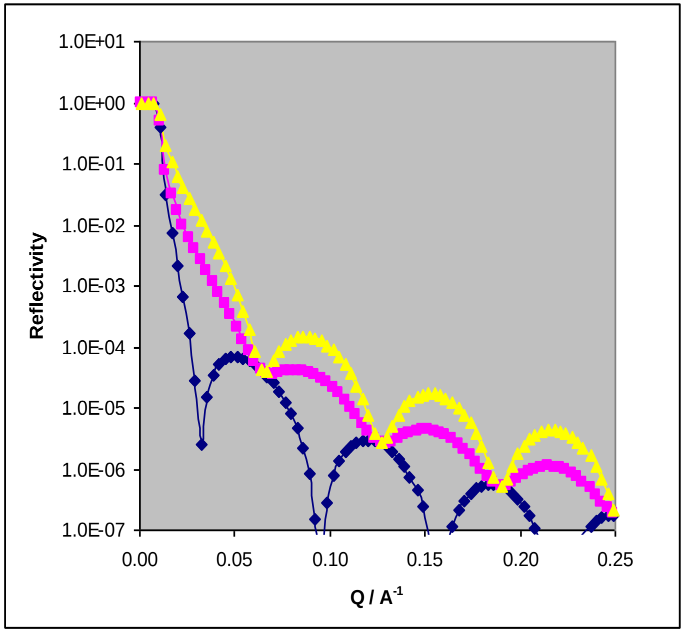
Calculation for Neutrons

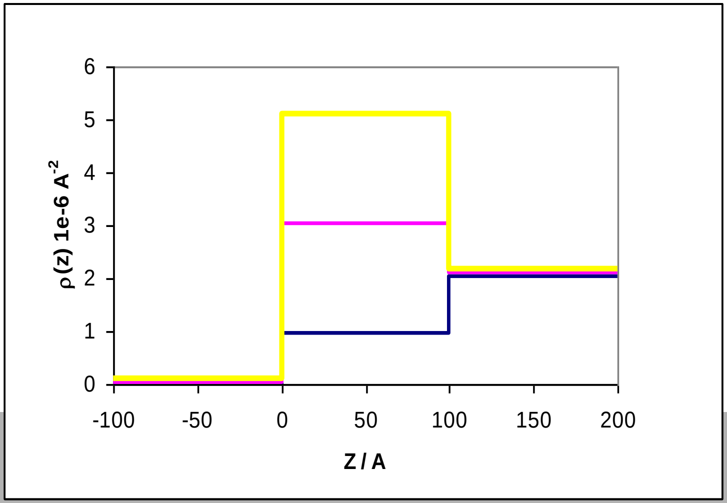
100 Å layer with ρ=1, 3 & 5 x 10^{-6} Å^{-2} on Si (ρ=2.07 x 10^{-6} Å^{-2})

Increasing contrast changes visibility of fringes

Phase change makes large difference

Fringes (Kiessig fringes) – spacing indicates film thickness for a single layer.





Roughness

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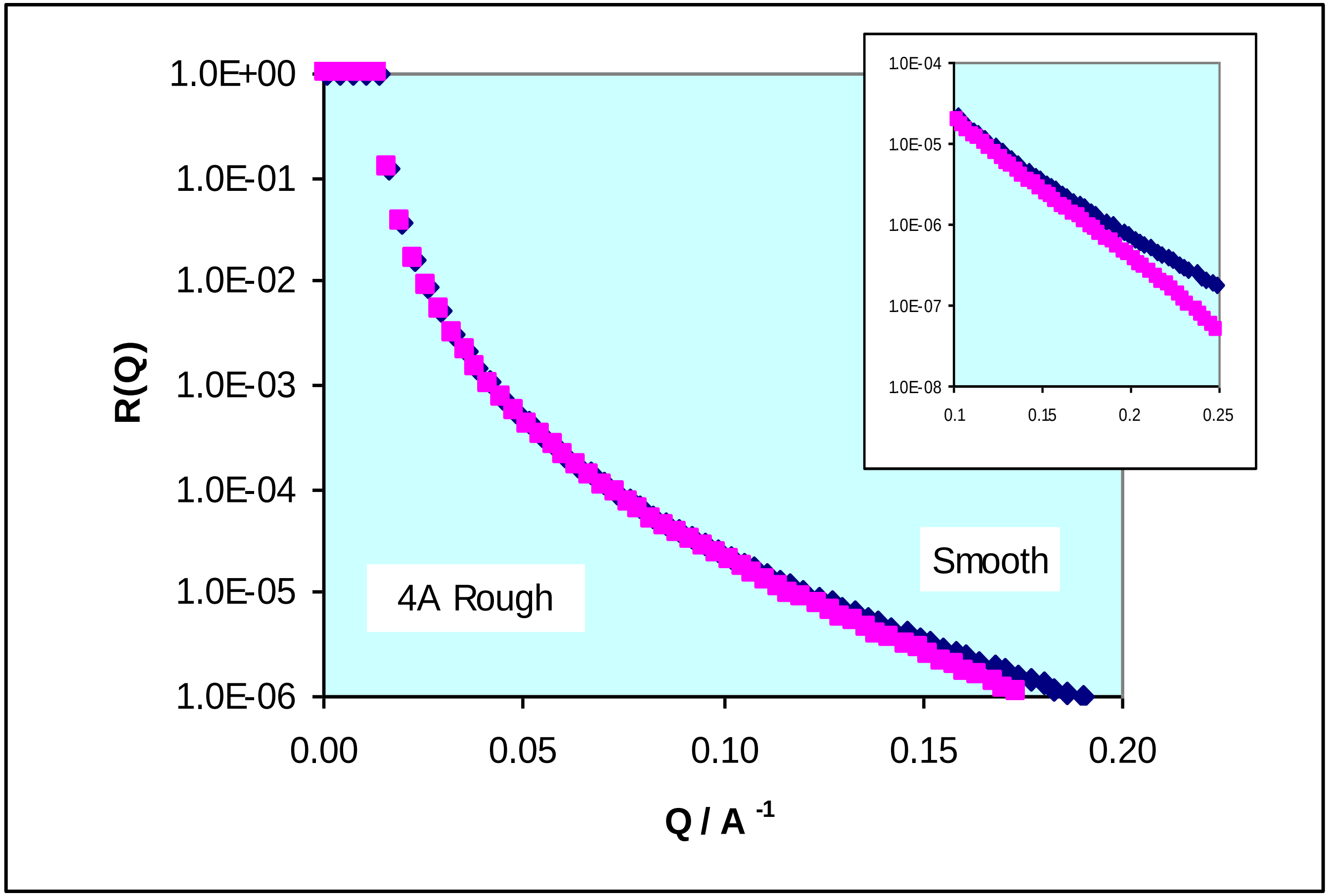
Reflectivity from rough surfaces is decreased.



L. Nevot, P. Crocé *J. Phys. Appl.* **15**, T61 (1980

Intensity of Reflected Signal

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Waves interfere constructively for

$$2\, d \sin \theta = \lambda,\ 2\lambda,\ 3\lambda\ \ldots \text{ (Bragg's law)}$$

Measured reflectivity will depend on angle and wavelength.

Total reflection for angles less than critical angle,

$$\theta_c = \arccos(n_1/n_2)$$

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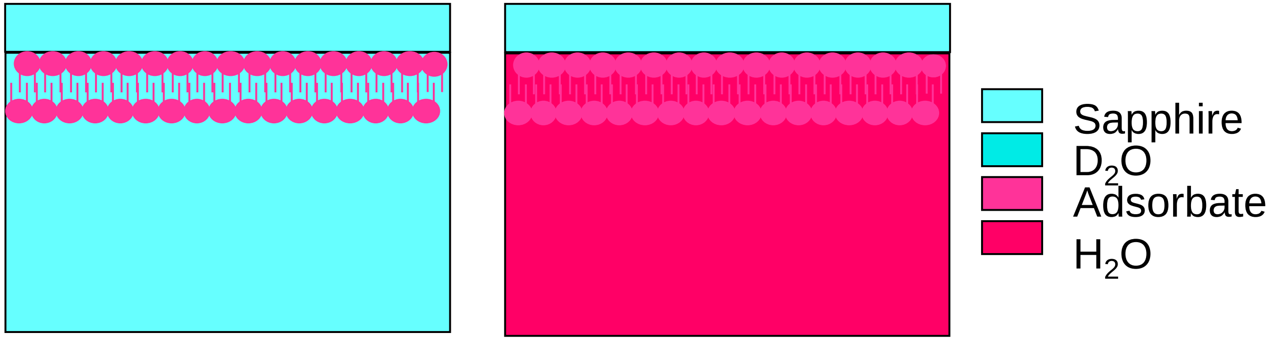
Useful Physical Ideas

Isotopes (e.g. D/H substitution) can be used to label particular species or alter contrast



Useful Physical Ideas

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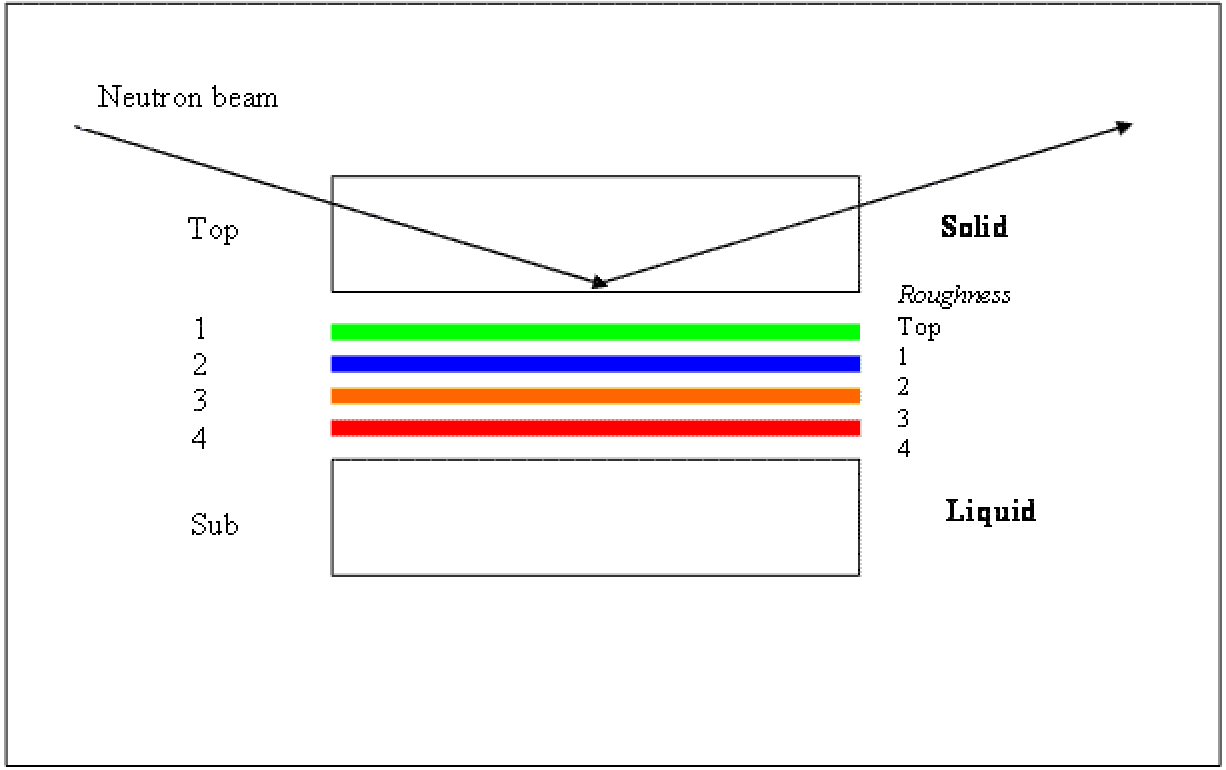
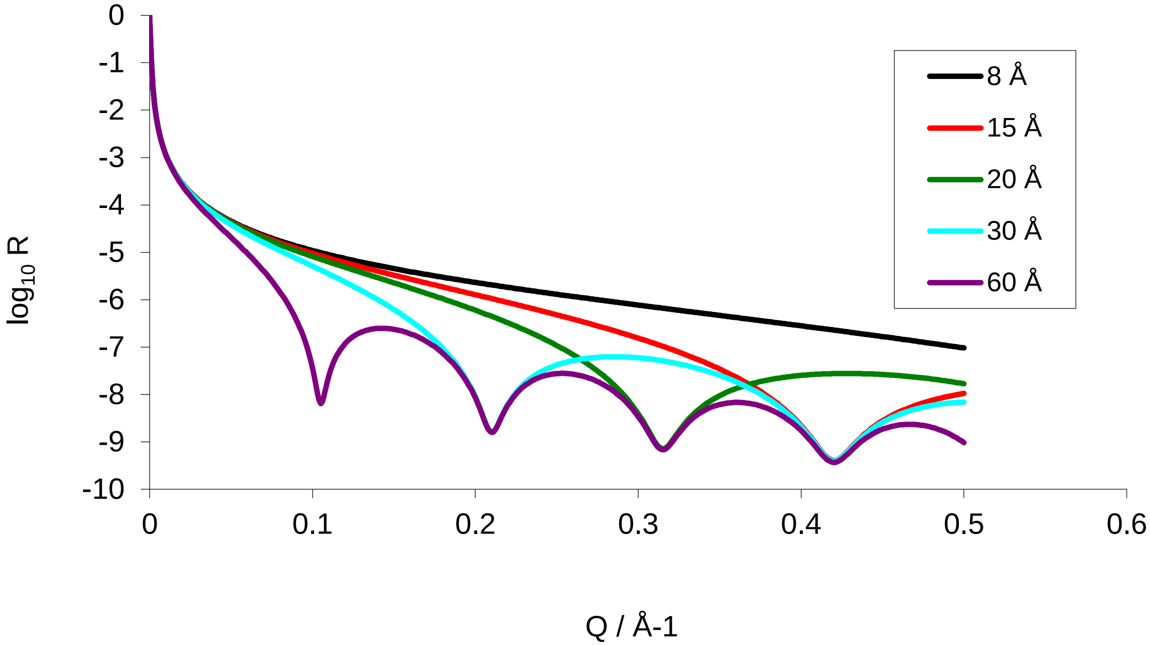
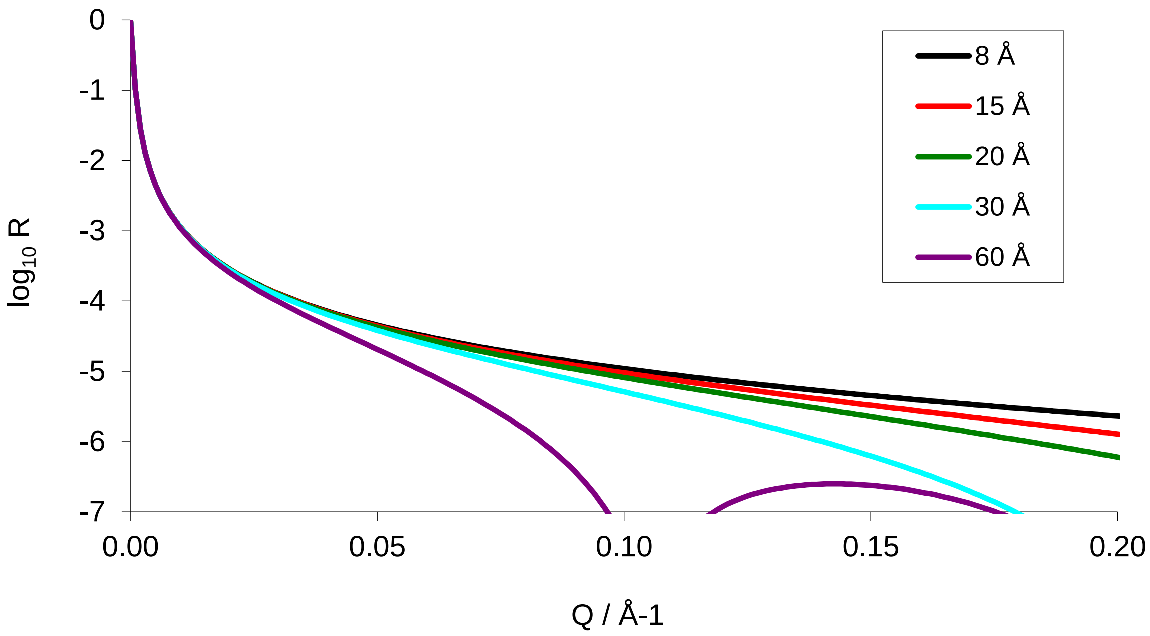
Models for complex interfaces:
multiple thin layers of different refractive index, n



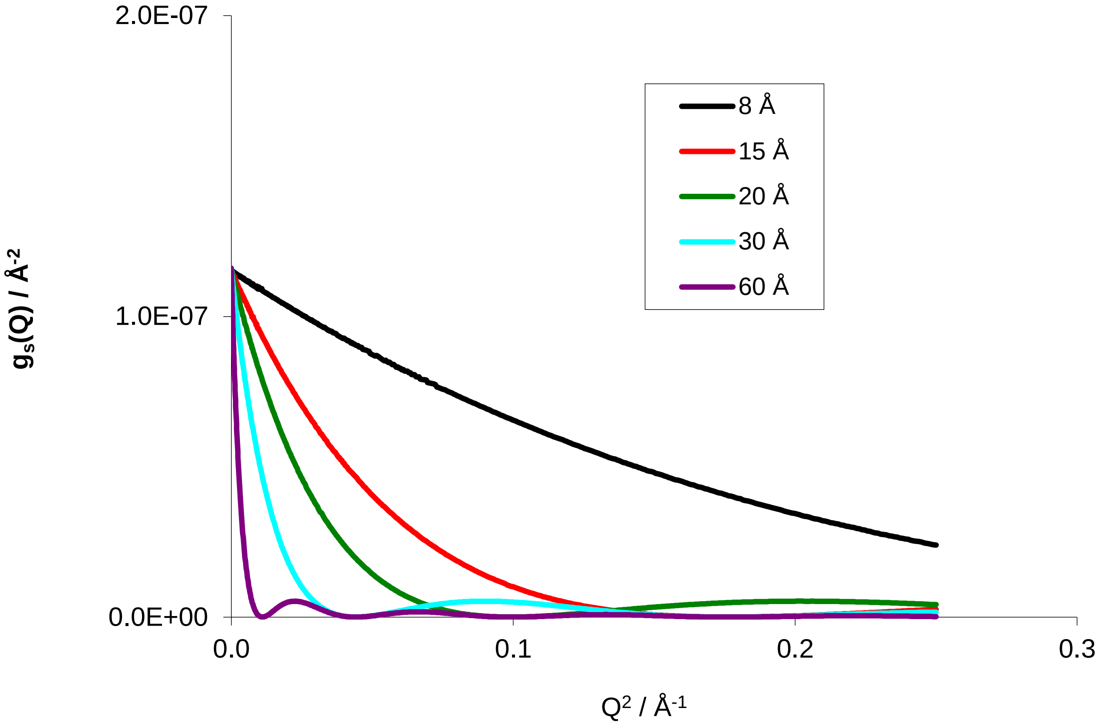
Understanding Reflection - Monolayers



Understanding Reflection - Monolayers



Understanding Reflection - Monolayers



$$g_s(Q) = Q^2\,(R - R_F) / (1 - R)$$

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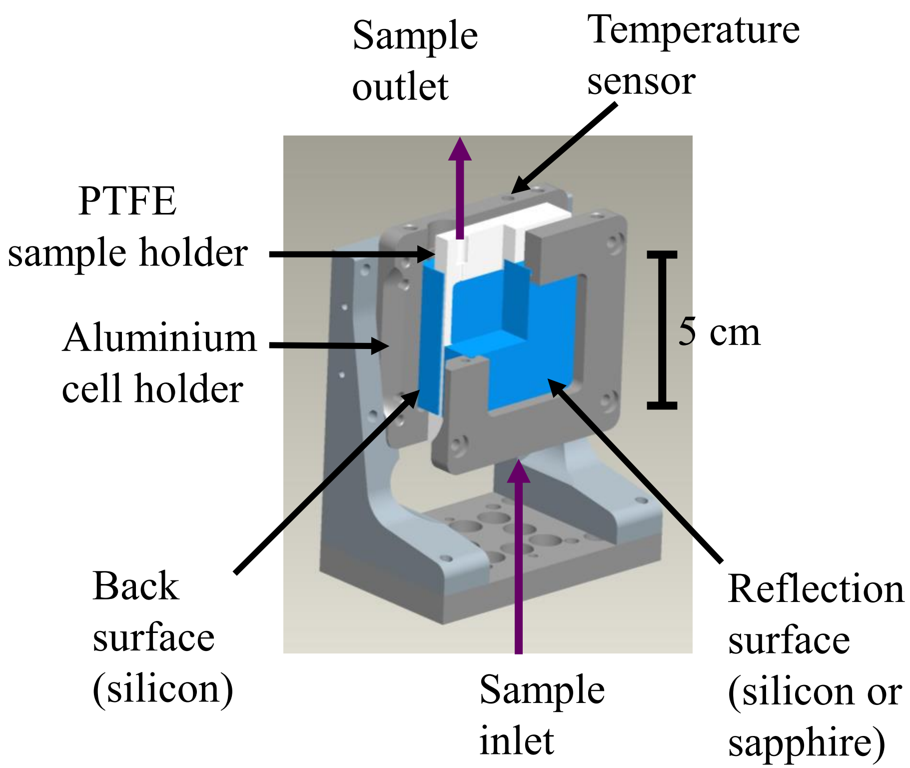
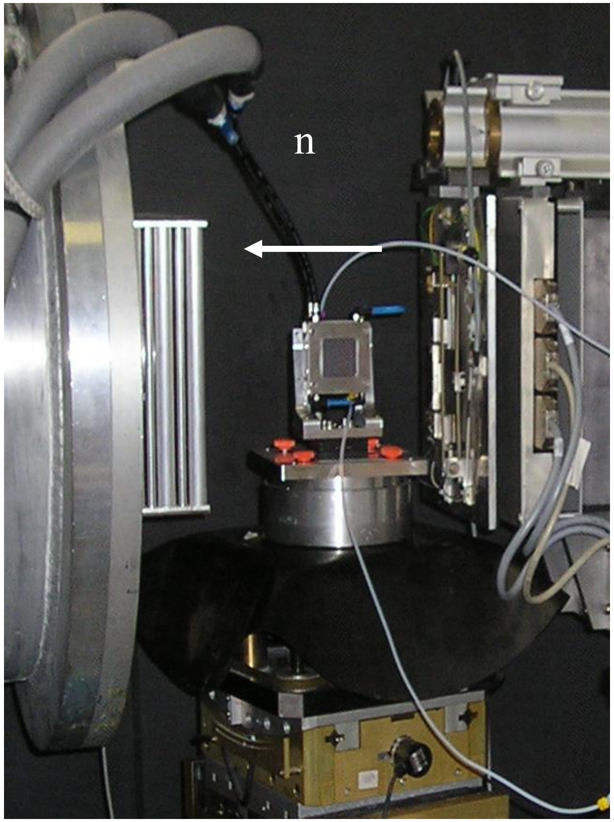
Solid/liquid Sample Cell



D17 reflectometer
ILL, France

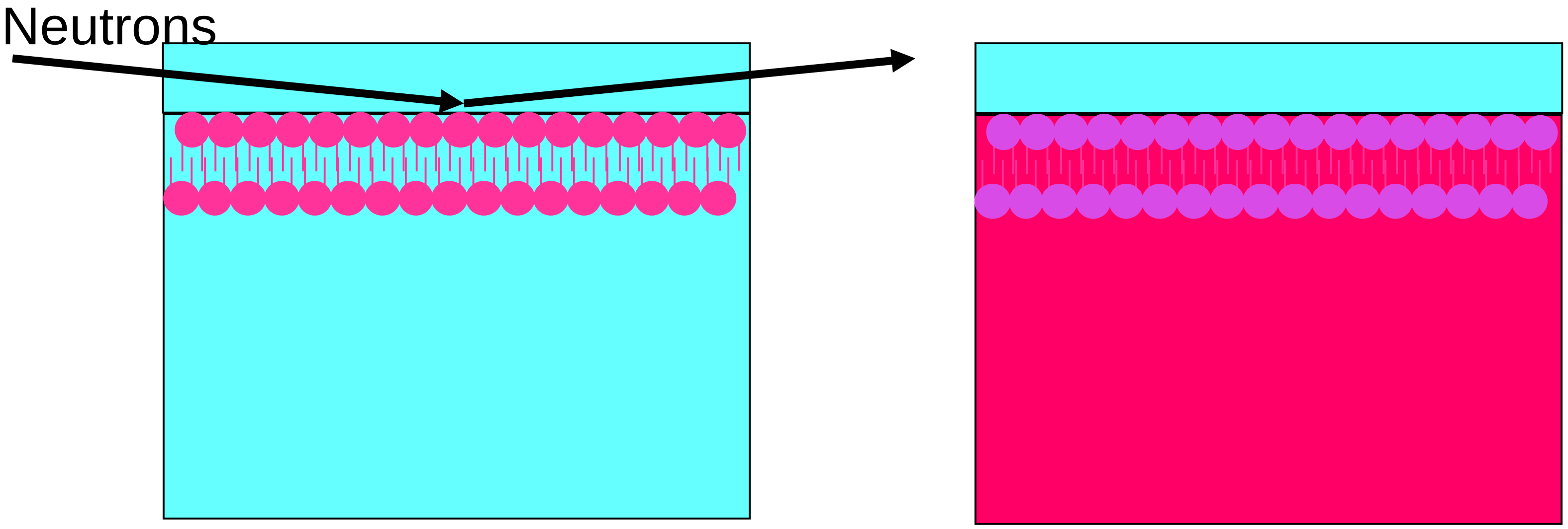


A. R. Rennie *et al. Rev. Sci. Instrum*. **86**, (2015), 016115.

Neutron reflection

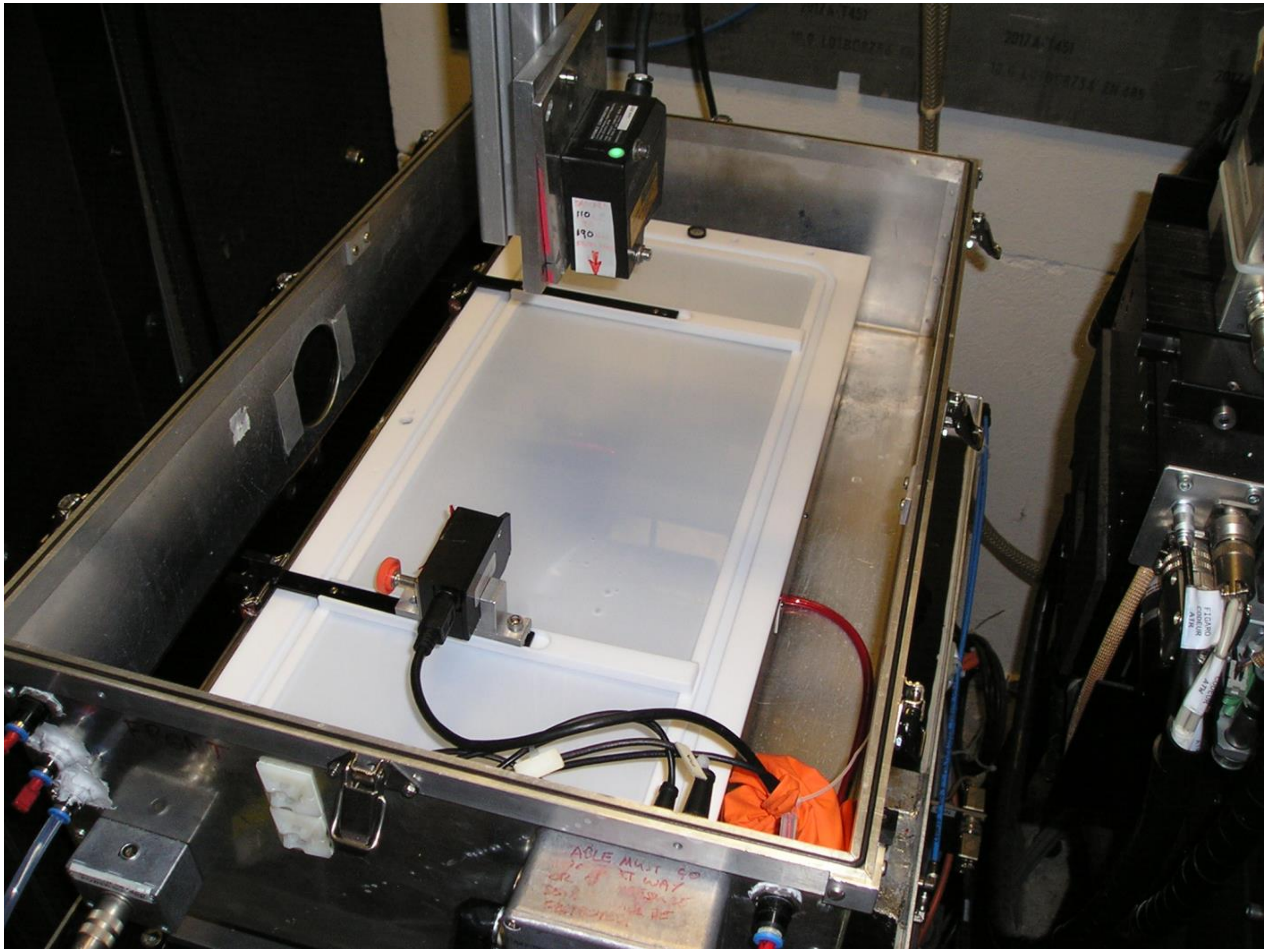
Contrast matching

Solvent hydrogen/deuterium composition



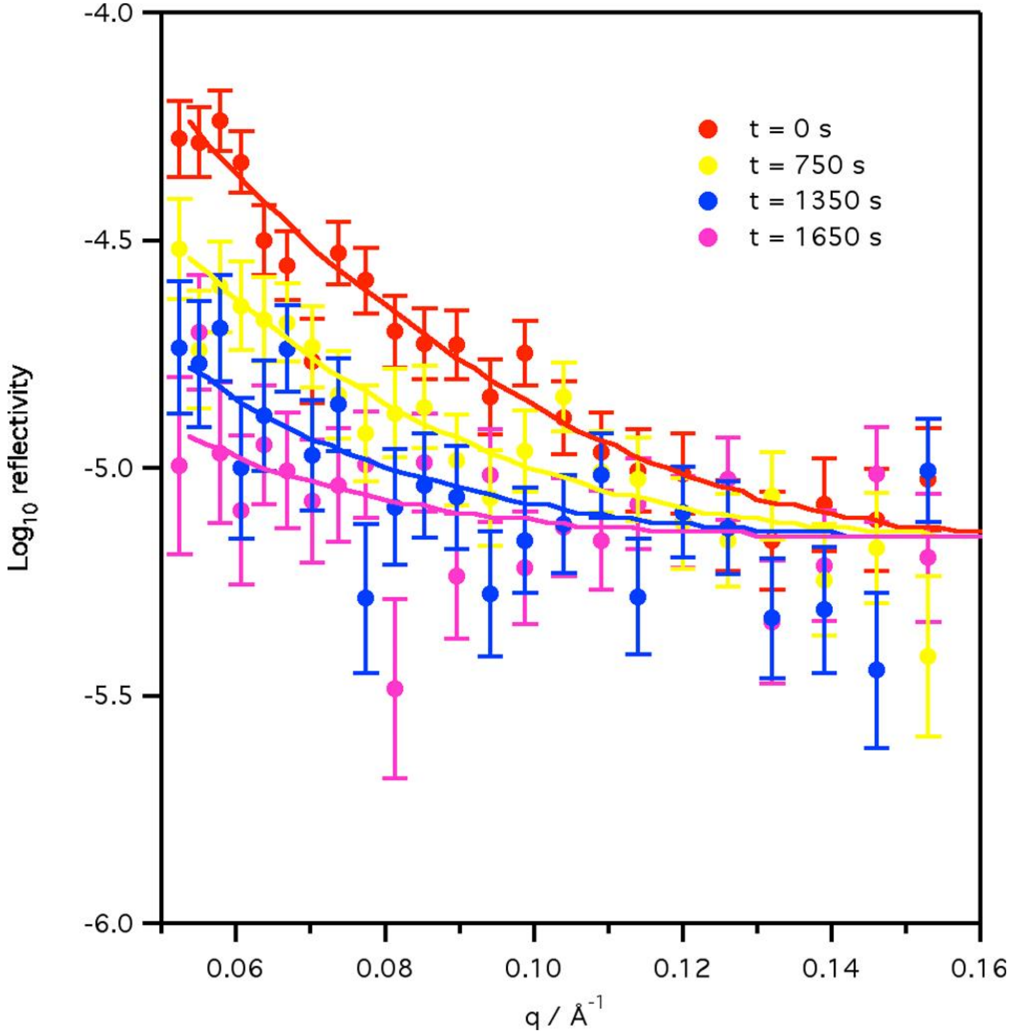
Liqid surfaces / Model Lung Surfactants

Spread films of lipids and proteins on a Langmuir trough



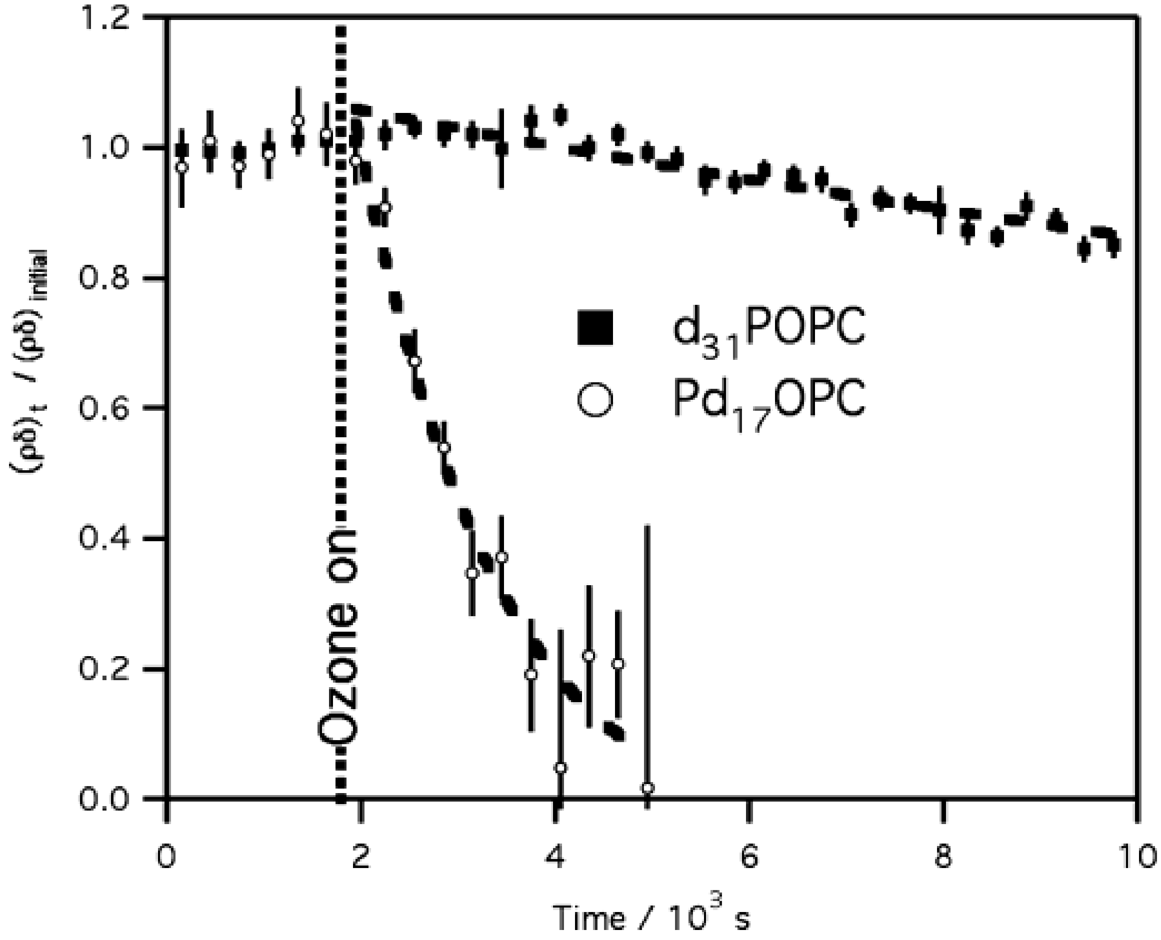
Observe Reflectivity changes during a reaction

$Pd_{17}OPC$ with O_3



Langmuir, **29**, (2013), 4594-4602.

Observe Reflectivity changes during a reaction



Langmuir, **29**, (2013), 4594-4602.

Lung Surfactant – a simple model

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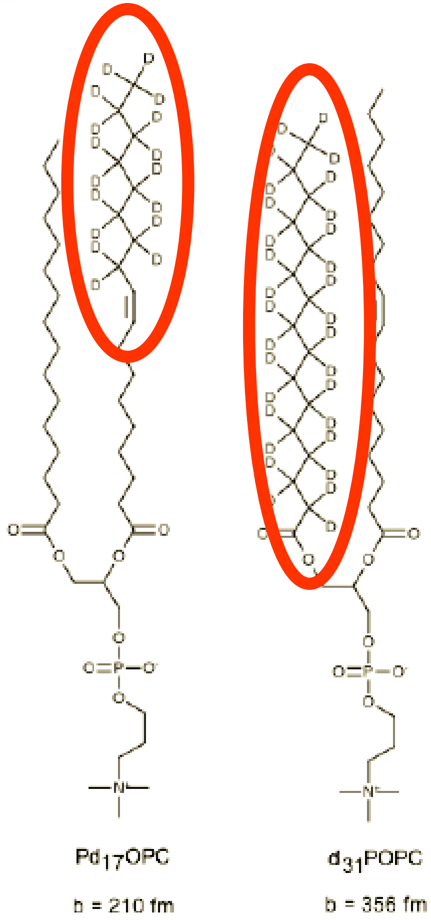

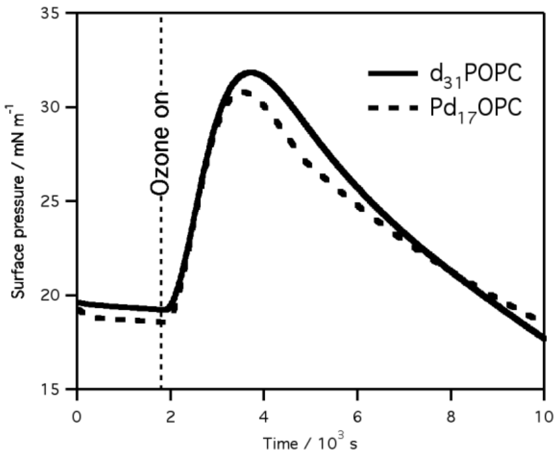

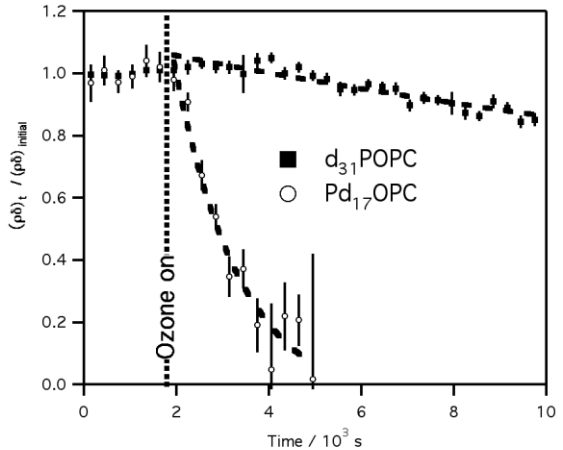

Deuterium labelling clarifies ozone damage mechanism

Compare deuterated palmitic chain and oleic chain

Research: Uppsala, Birkbeck, ISIS

Saturated Lipid

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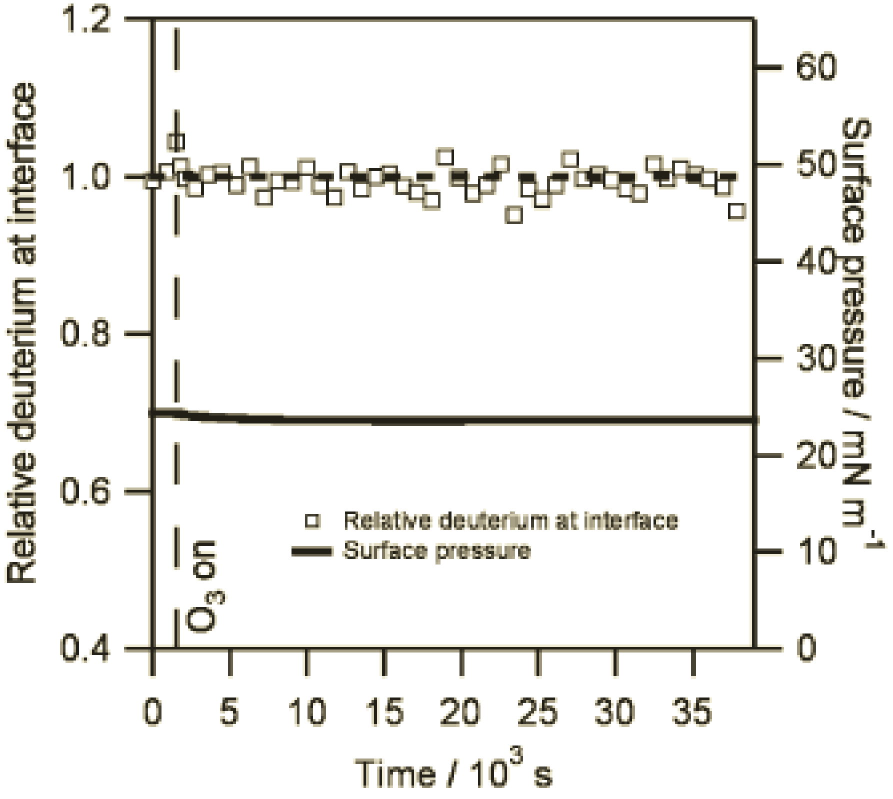
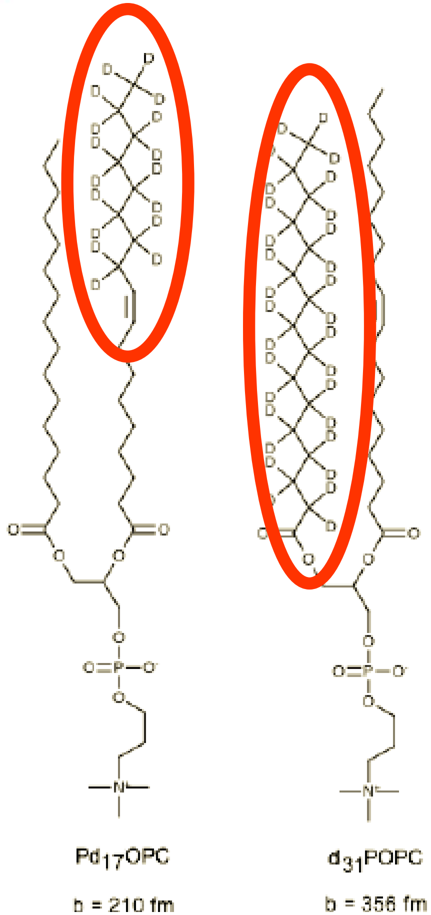
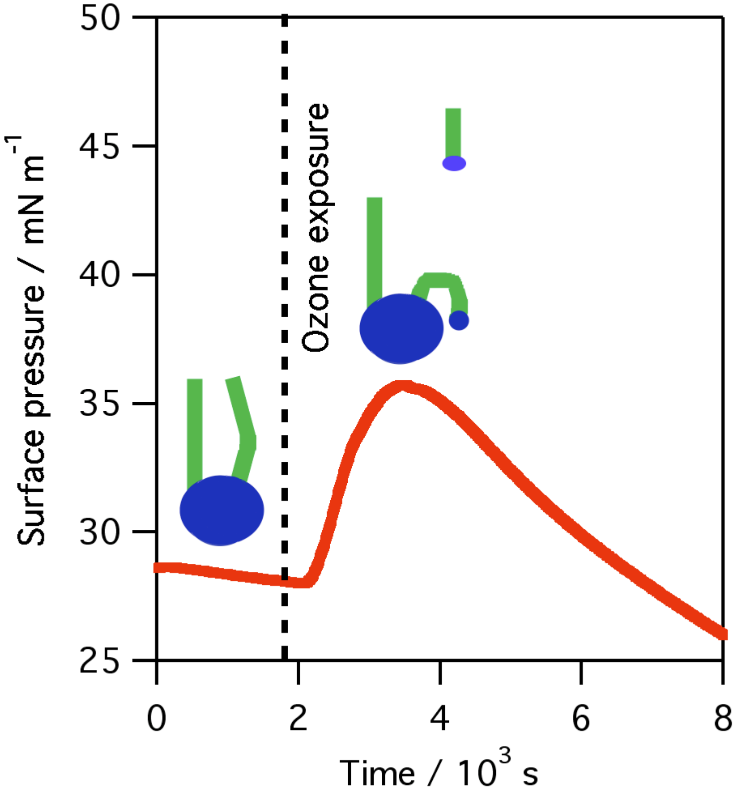
DPPC – saturated lipid



Langmuir, **29**, (2013), 4594-4602.

'Model' Lung Surfactant





End of one chain is lost and gives transient surface pressure increase

Langmuir, **29**, (2013), 4594-4602.

Perennial Rivers in Africa

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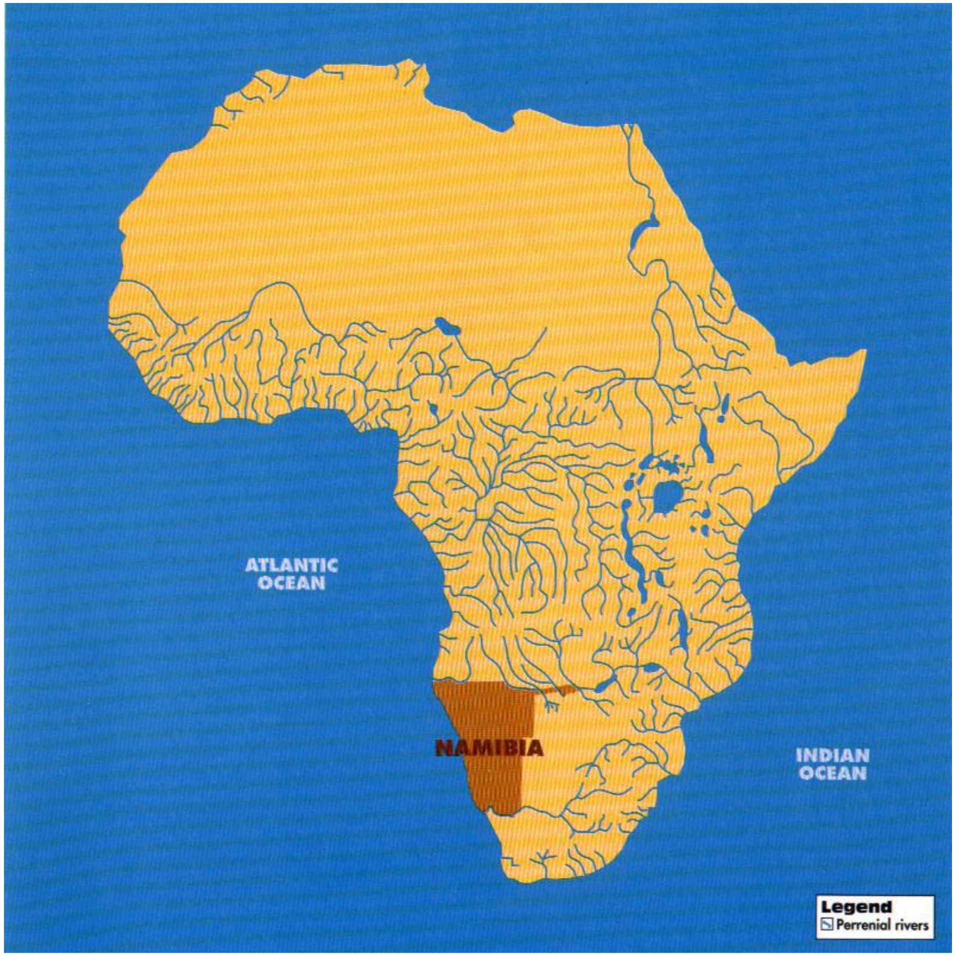

Supply Technology

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Village Scale

Major Steps in Purification

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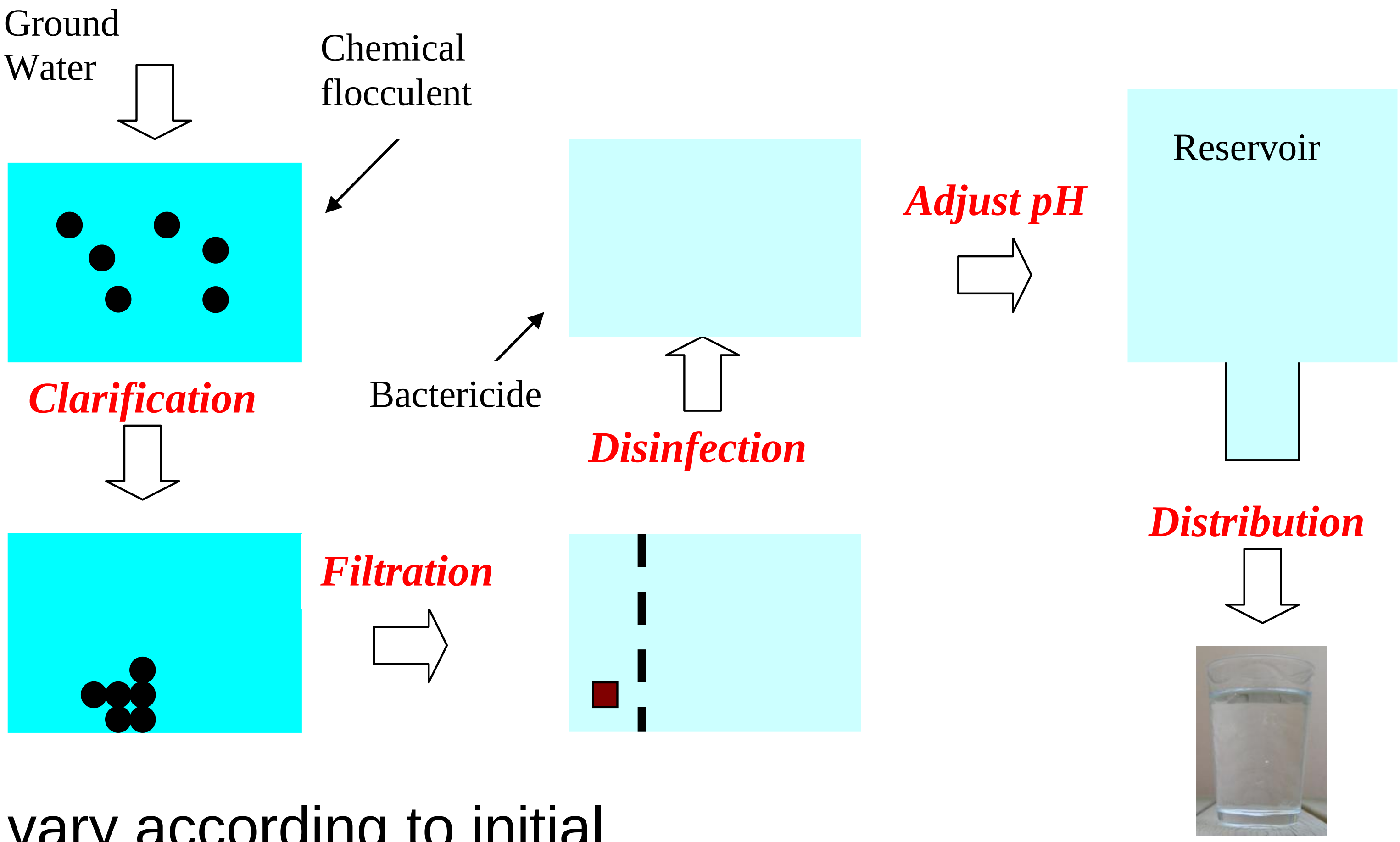

Details vary according to initial water source and requirements

Muddy Water treated with crushed *Moringa oleifera* seeds

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Comparative tests

Effect of concentration

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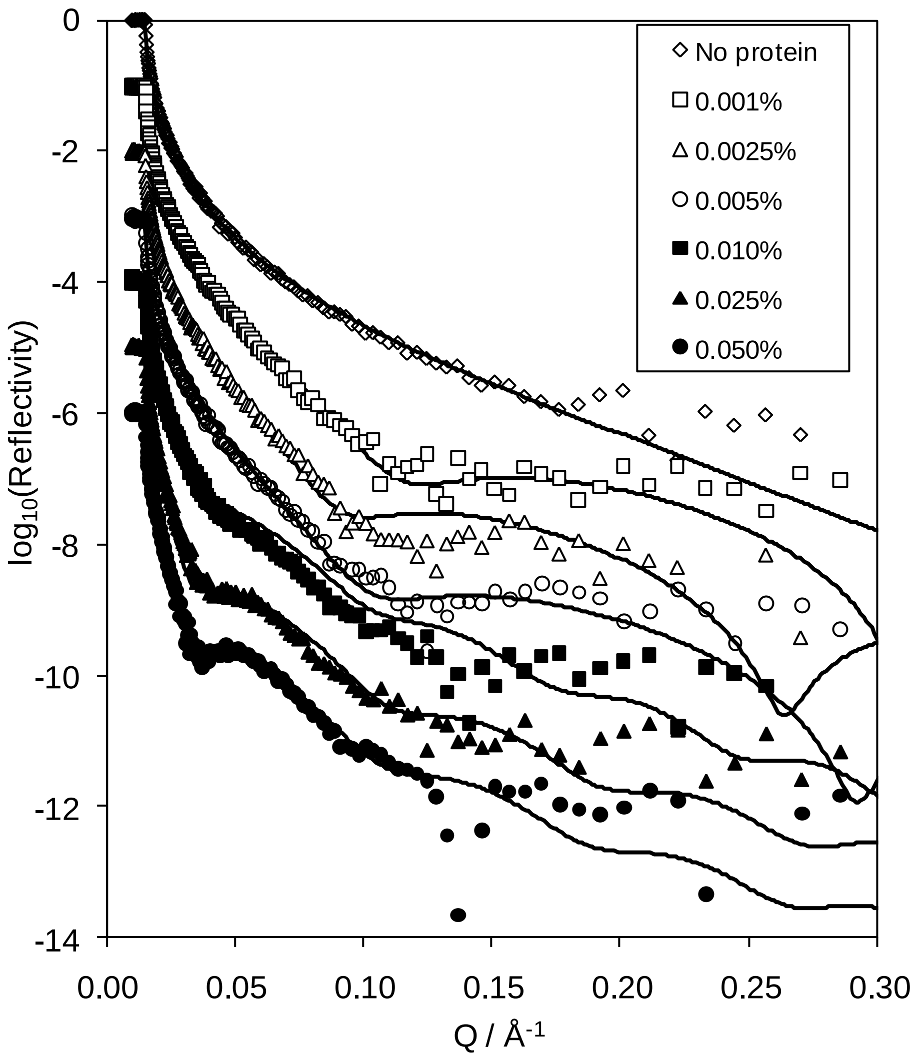
Moringa oleifera protein in D_2O at silica surface as model for mineral



MO Protein Adsorbed Layer on SiO_2

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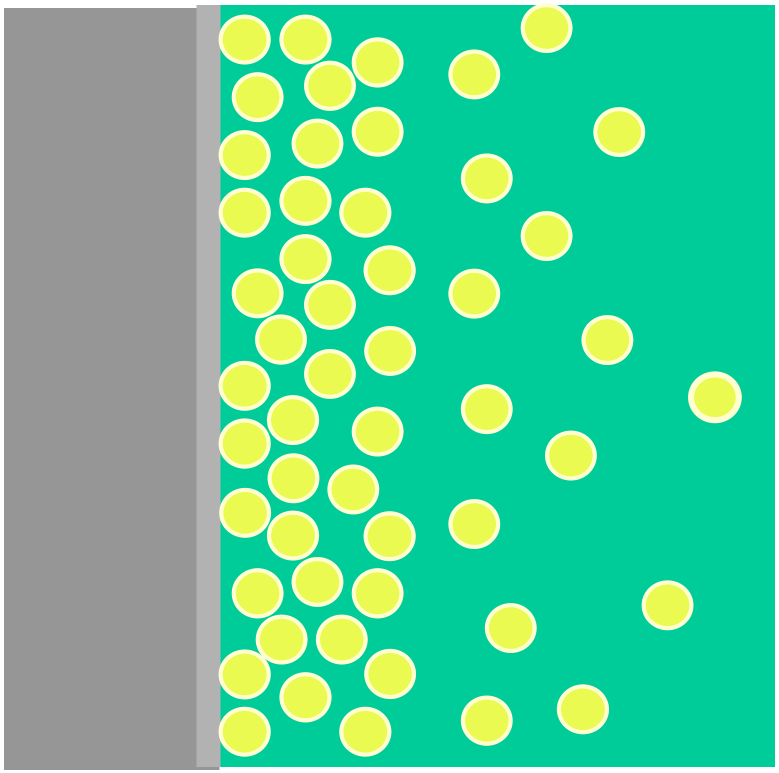

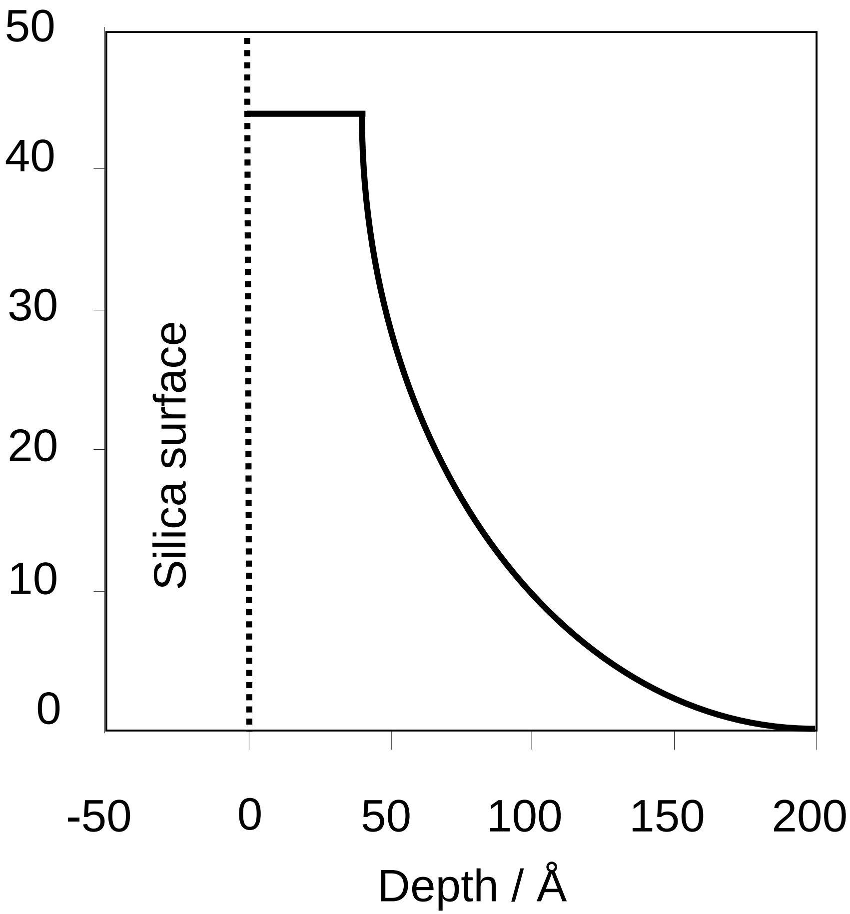

H. M. Kwaambwa *et al*., *Langmuir* **26**, 3902-3910 (2010).

Adsorption to PS Latex Particles

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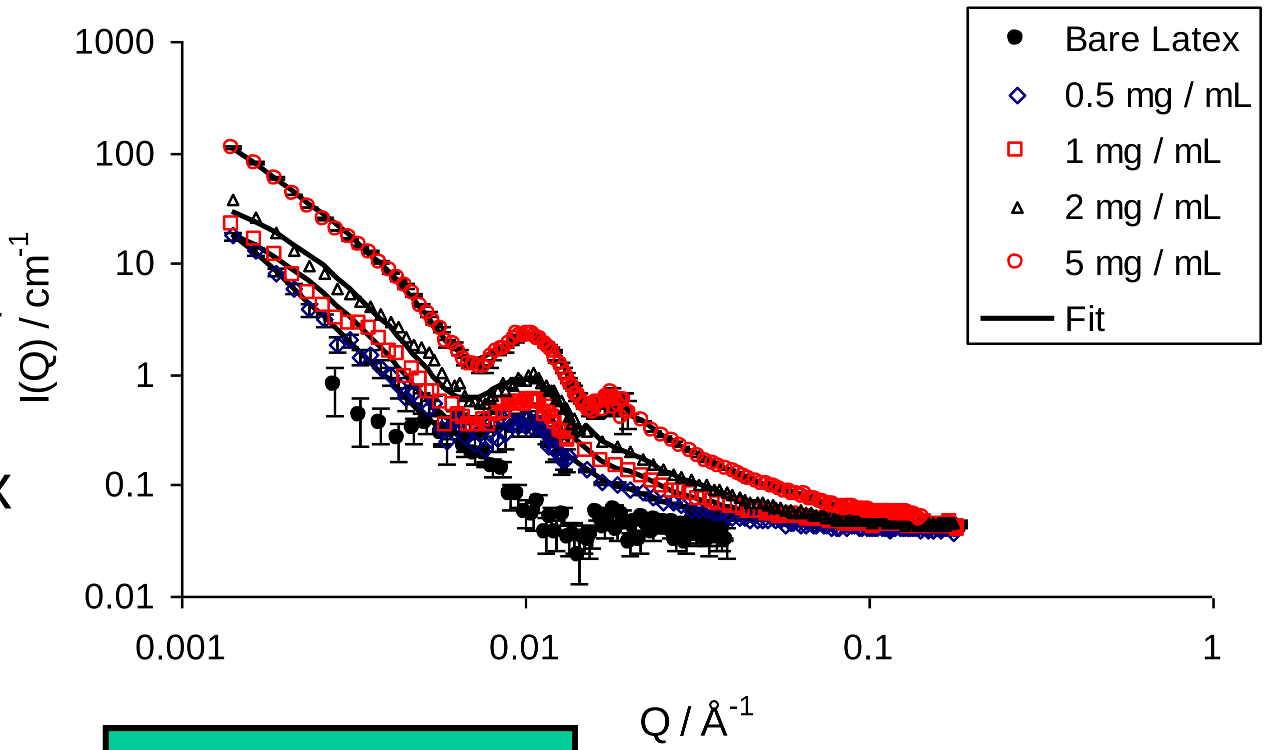
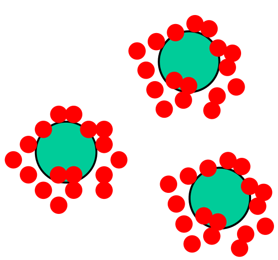
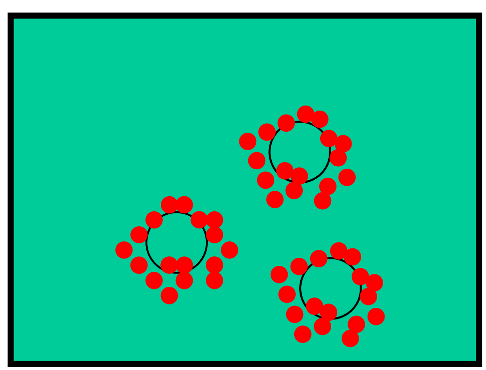


Moringa oleifera protein.

Deuterated latex in D_2O





SANS Data – D22 ILL

Use 'contrast matching' with D_2O

Hellsing et al *Coll. Surf. A*, **460**, (2014), 460–467.

Adsorption Different Surfaces

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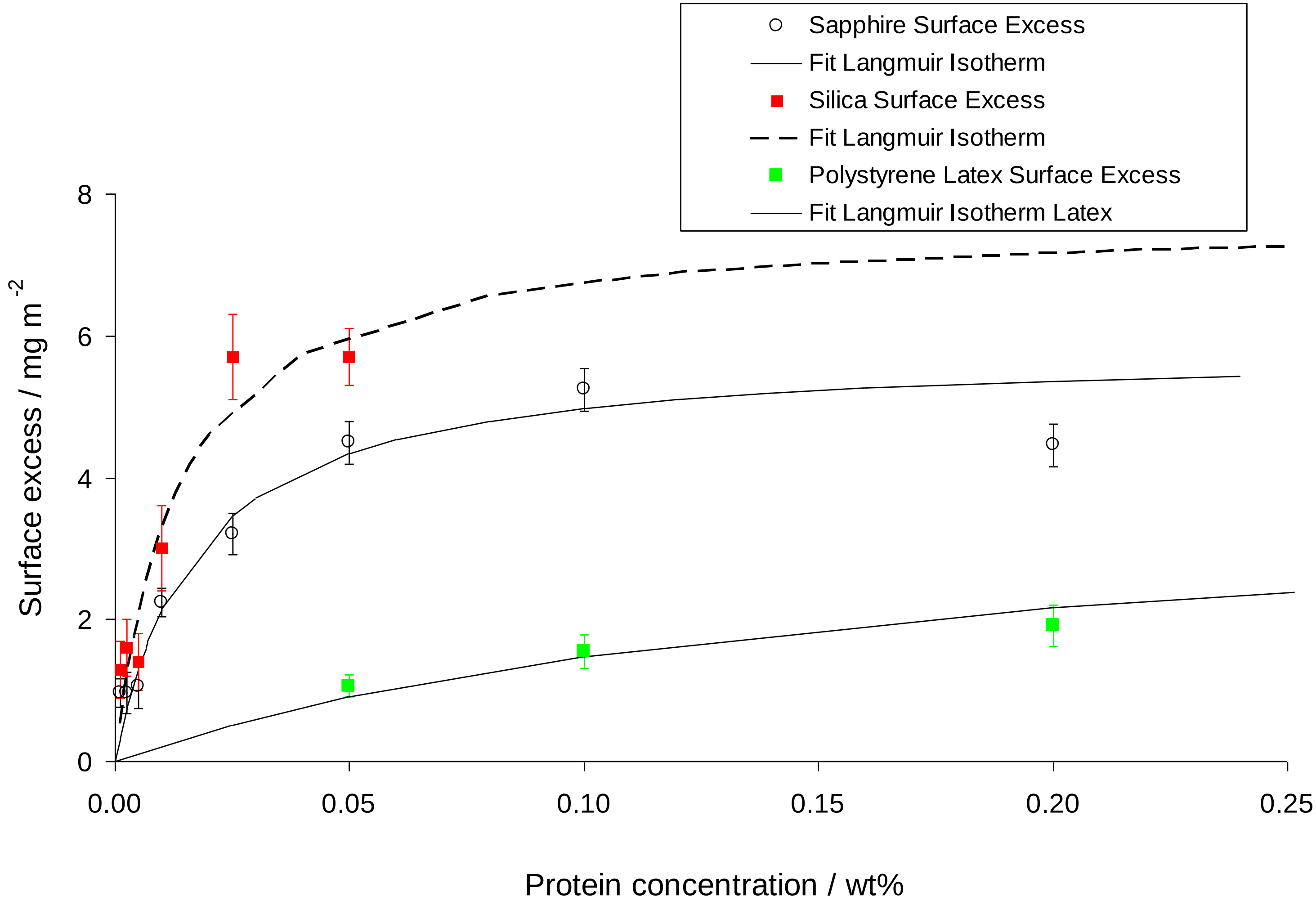

Describing Flocs - Fractal Aggregates

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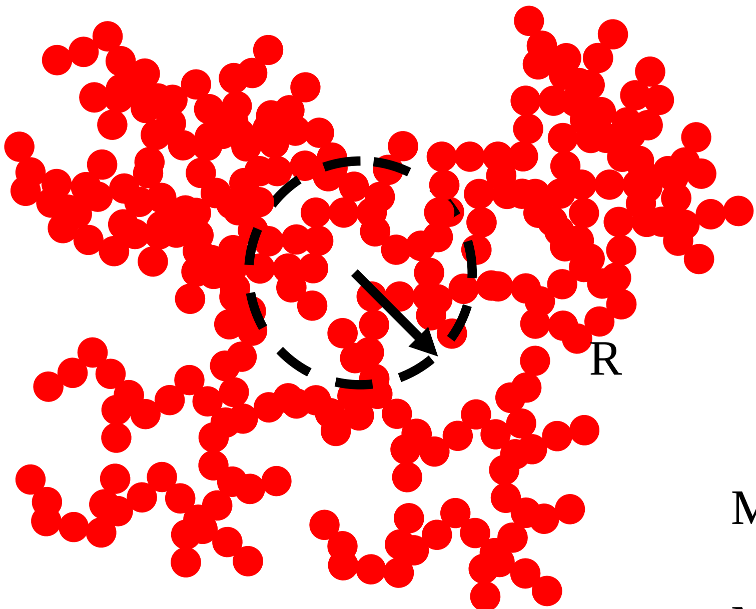
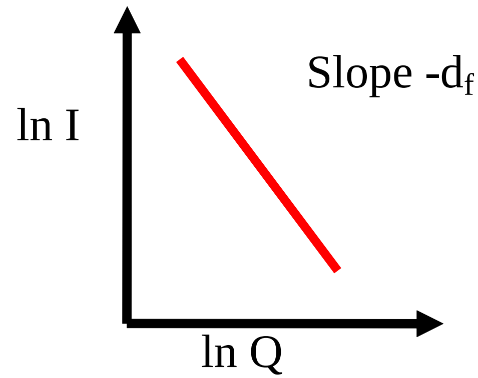


Mass fractal

$M \sim R^d$



Scattered Intensity

$Q = (4\pi/\lambda) \sin(\theta/2)$

Diffusion limited $d_f \sim 1.75$

Reaction limited $d_f \sim 2.3$

Weitz, Meakin et al.

USANS – hydrogenous latex

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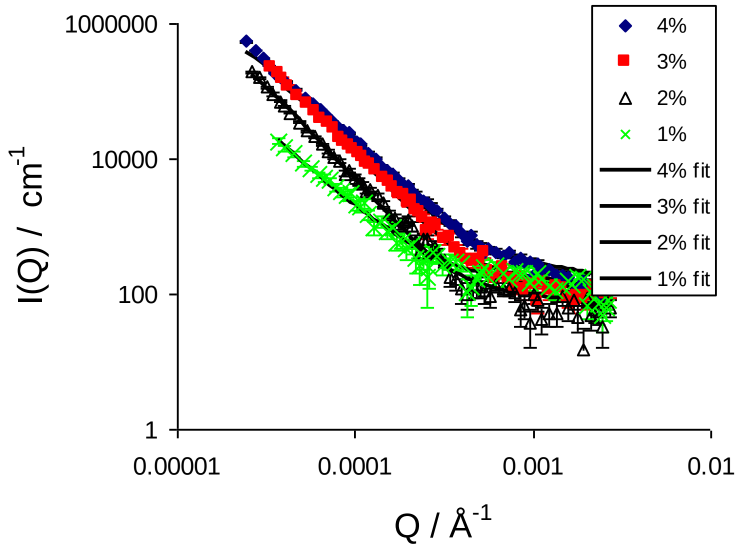

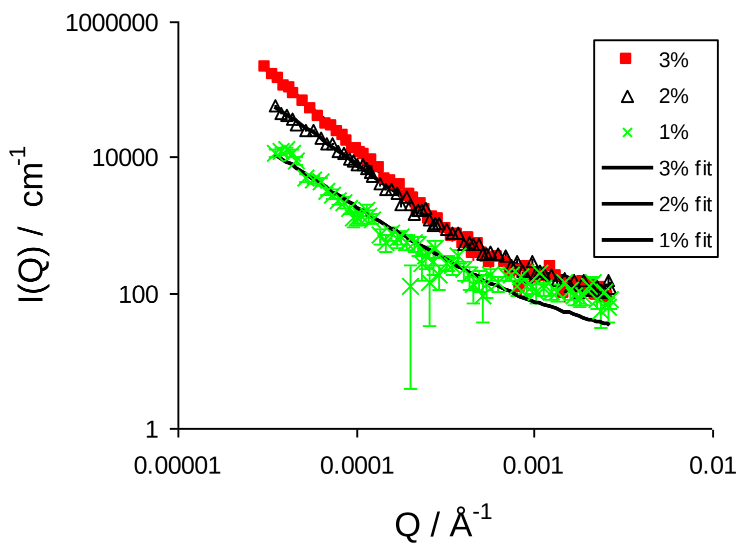

0.2% *Moringa Oleifera* protein   0.2% *Moringa Stenopetala* protein

Flocs – change with particle concentration

Model: J. Teixeira (1988) 'Small-Angle Scattering by Fractal Systems' *J. Appl. Cryst*. **21**, 781-785.

Fractal Dimensions

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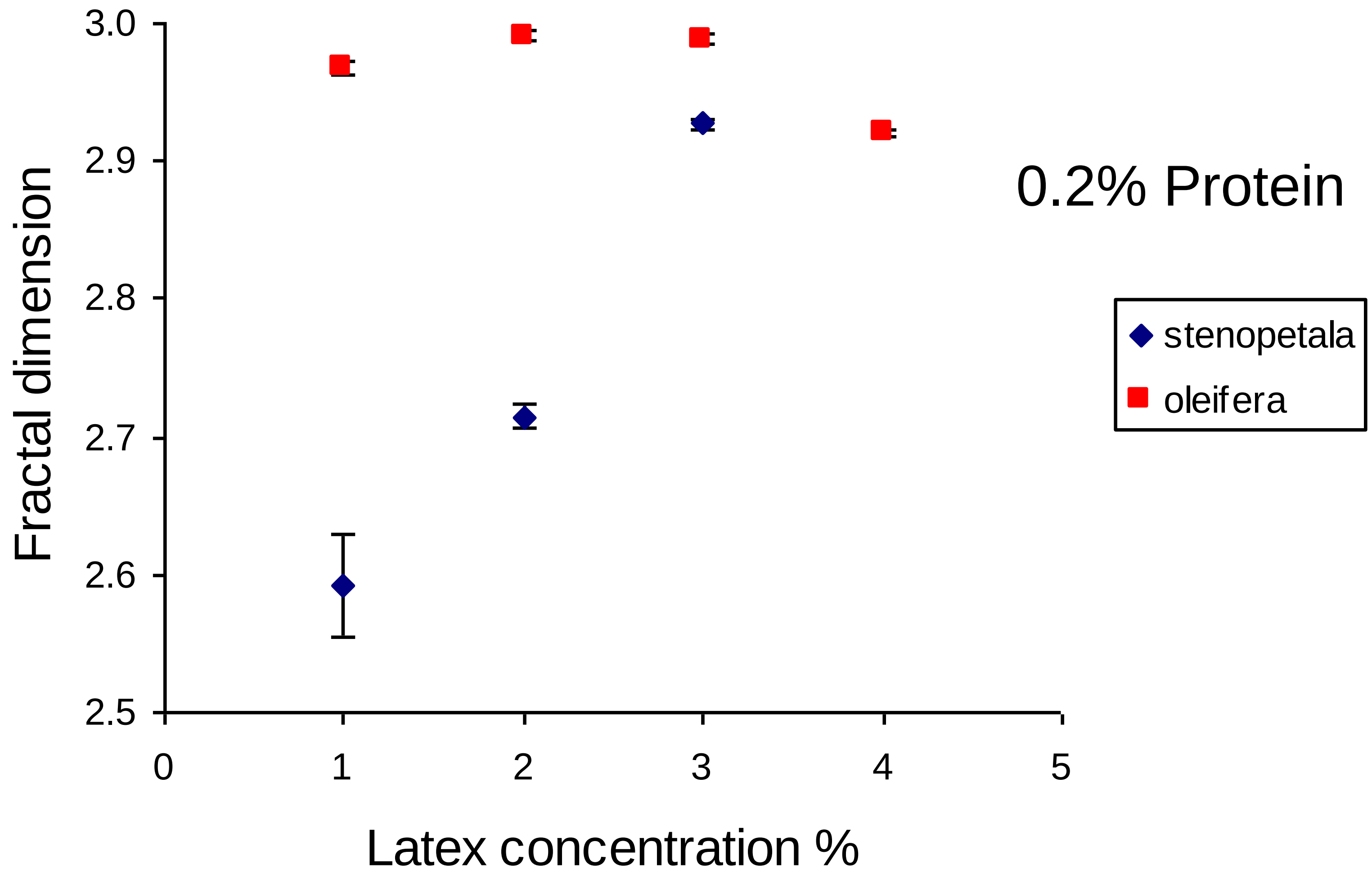

Hellsing *et al Coll. Surf. A* **460**, (2014), 460-467.

How does MO protein work?

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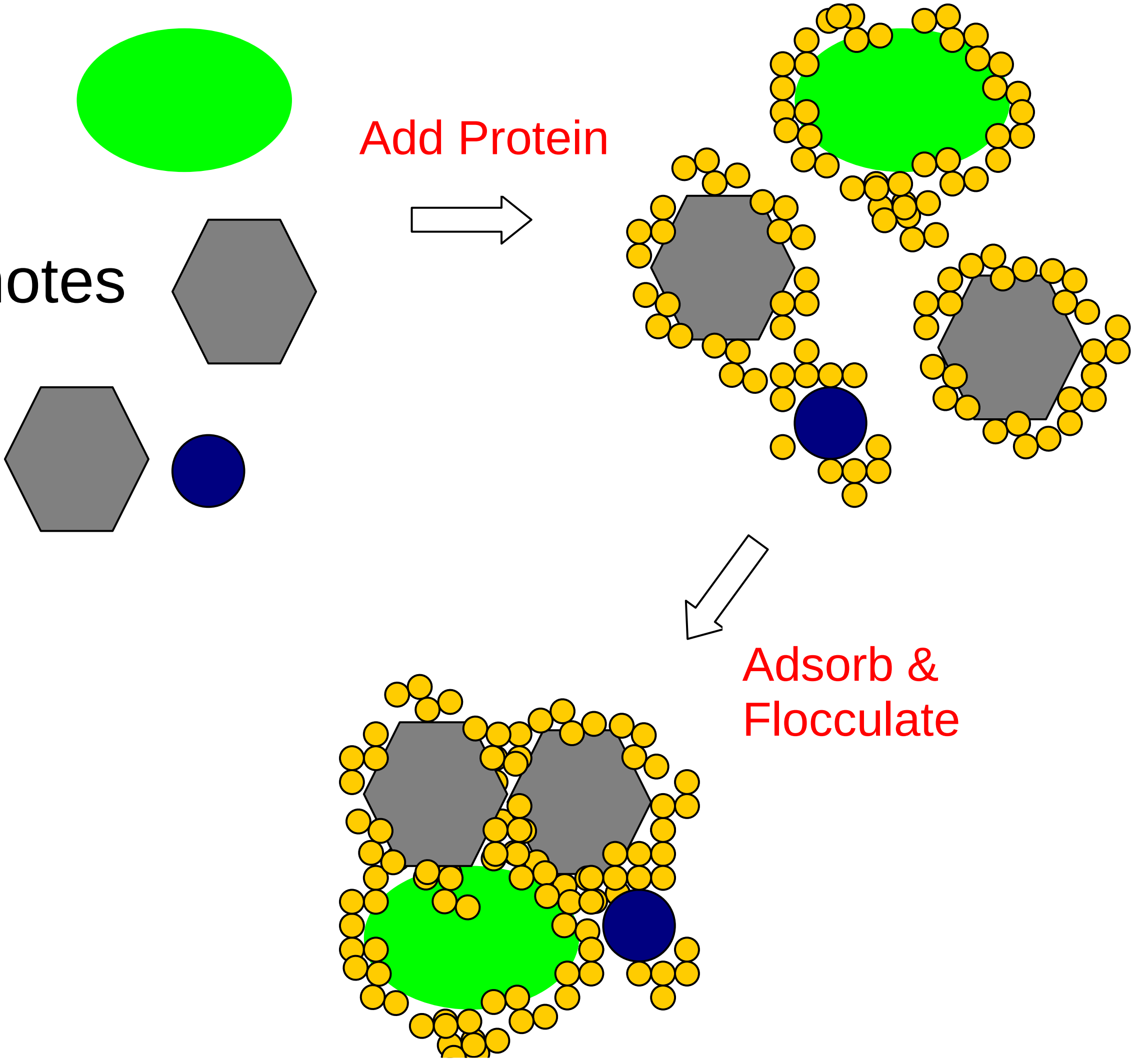
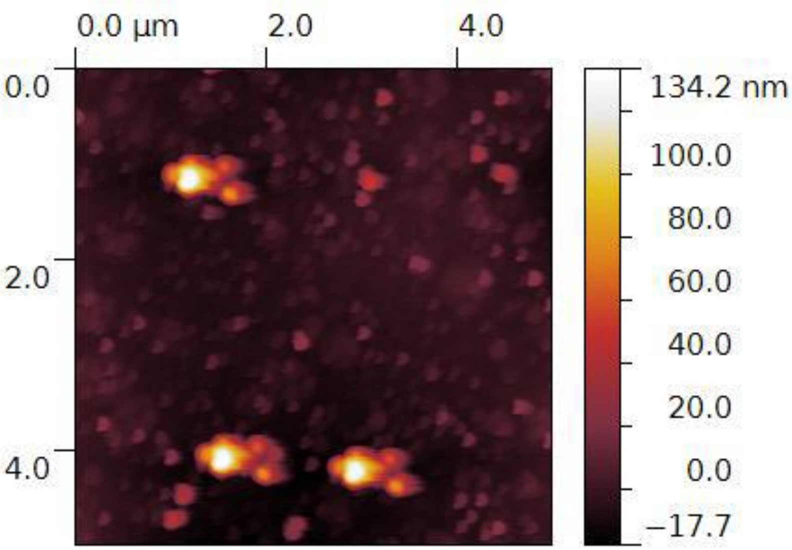
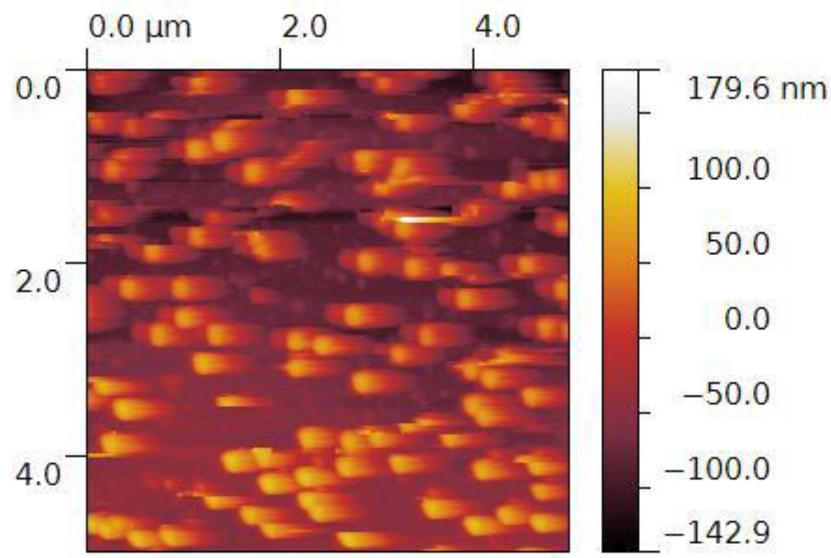
Adsorption to range of different particles promotes heterocoagulation



Can we stick particles at a surface?



Acid cleaned glass



Glass rinsed with *Moringa oleifera* seed protein

Coll. Surf. B: Biointerfaces **168**, (2018), 68-75.

Controlled Binding

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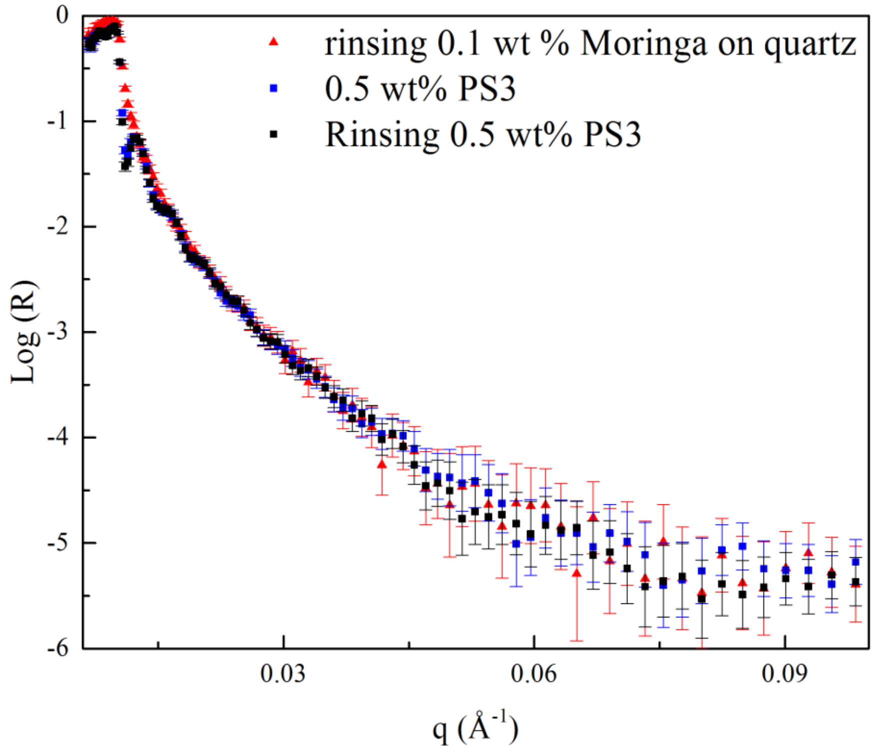
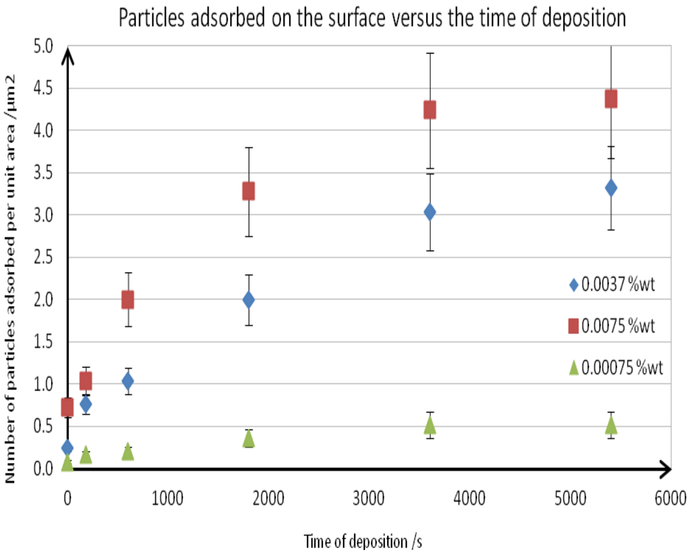


Depends:

Square root of time

Concentration



Interfacial structure: GISANS

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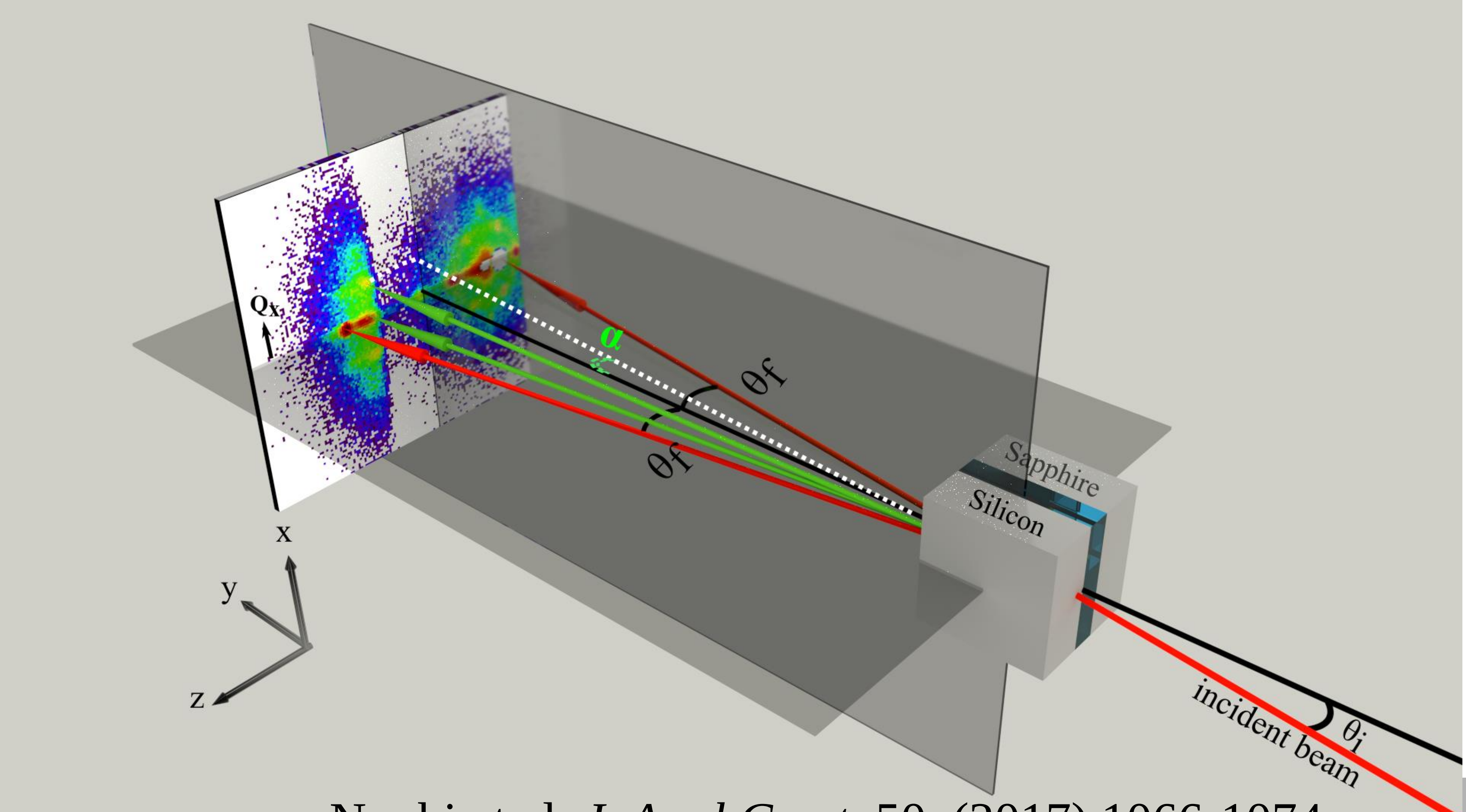

Nouhi et al. *J. Appl.Cryst.* 50, (2017) 1066-1074.

Penetration depth

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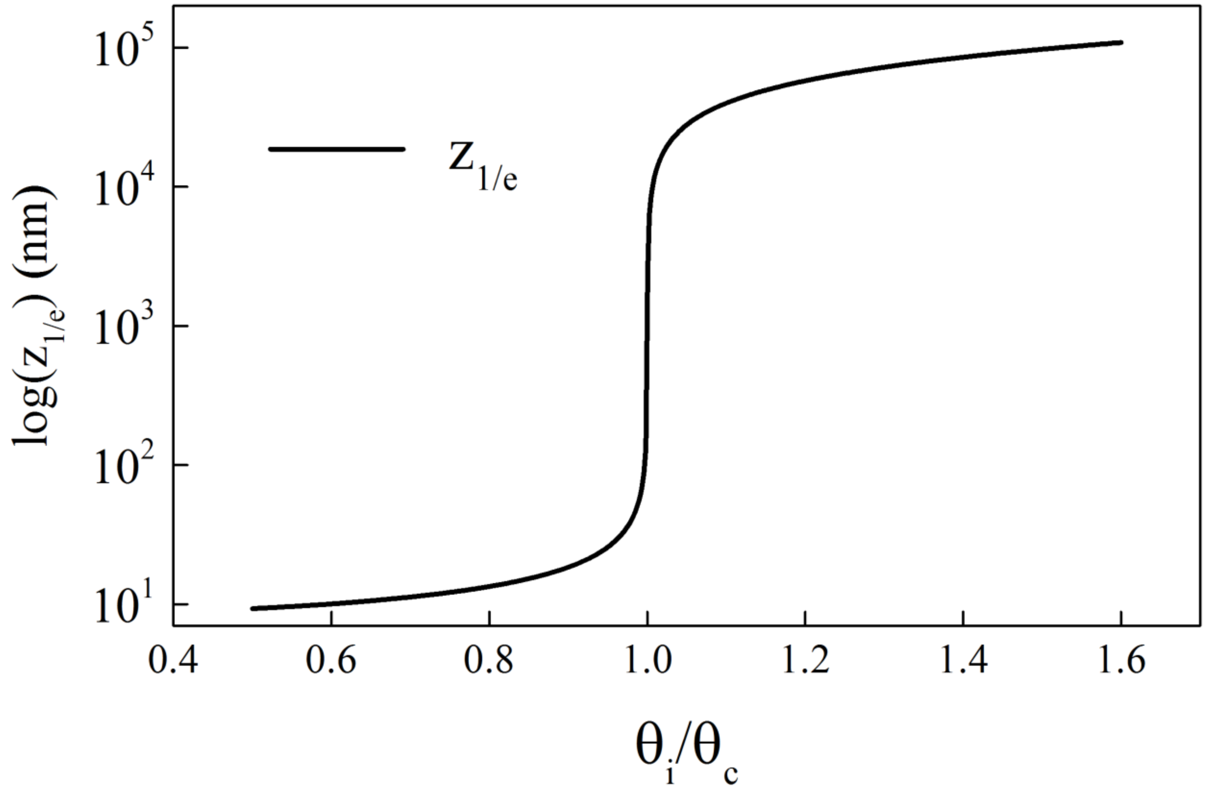
$$z_{1/e} = \sqrt{2}\lambda \Big/ 4\pi \left[\sqrt{(\theta_i^2 - \theta_c^2)^2 + (\frac{\lambda}{2\pi}\mu)^2} - (\theta_i^2 - \theta_c^2) \right]^{1/2}$$

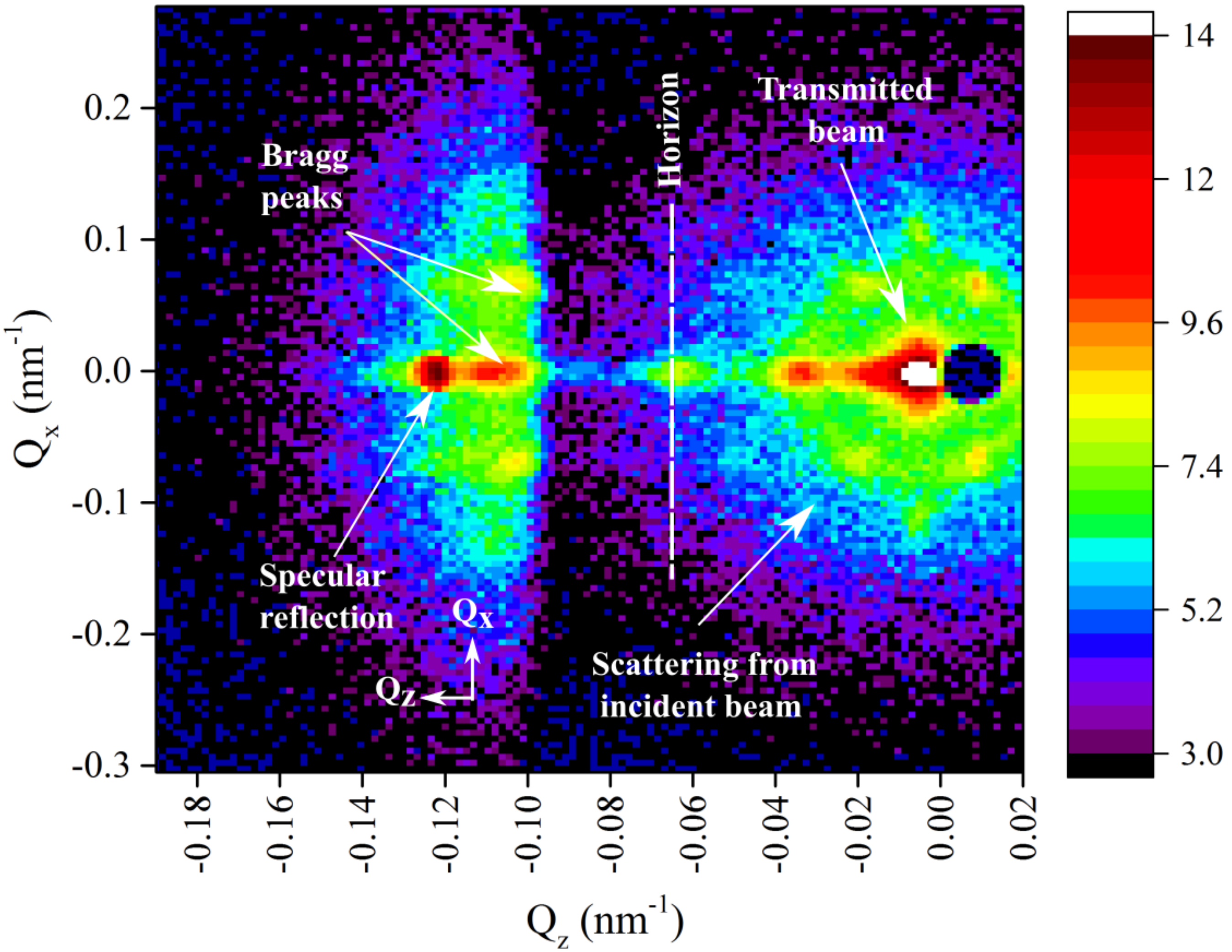
A depth sensitive technique:

- Wavelength
- Incident angle



Nouhi et al. *J. Appl.Cryst.* 50, (2017) 1066-1074.

Diffraction from Surface Layers



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Thank you for your attention

Questions?