Neutron Reflectometry for Formulations

Becky Welbourn
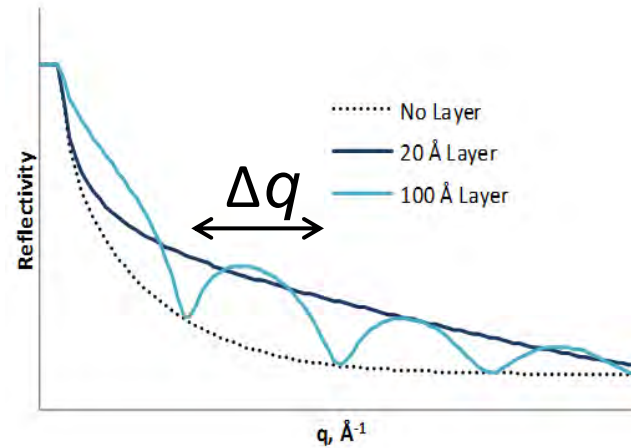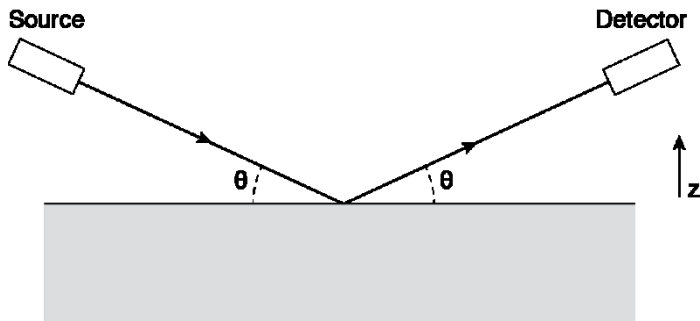
(becky.welbourn@stfc.ac.uk)

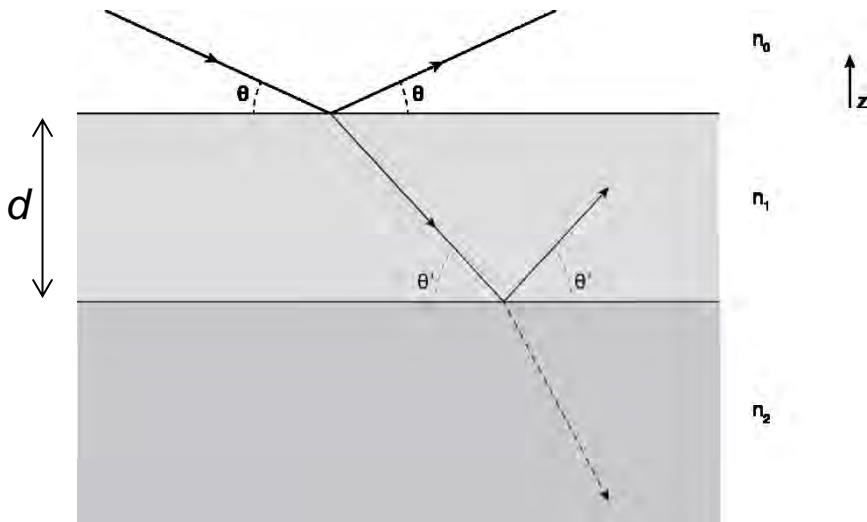# Why Use Neutron Reflection?

- Probes buried interfaces in-situ
    - H/D exchange allows focus on different parts of the system
    - Elemental sensitivity is not mass related

- Example systems measured:
    - Biological membranes
    - Solar cells
    - Detergents
    - Corrosion inhibitors
    - Magnetic thin-film
    - …

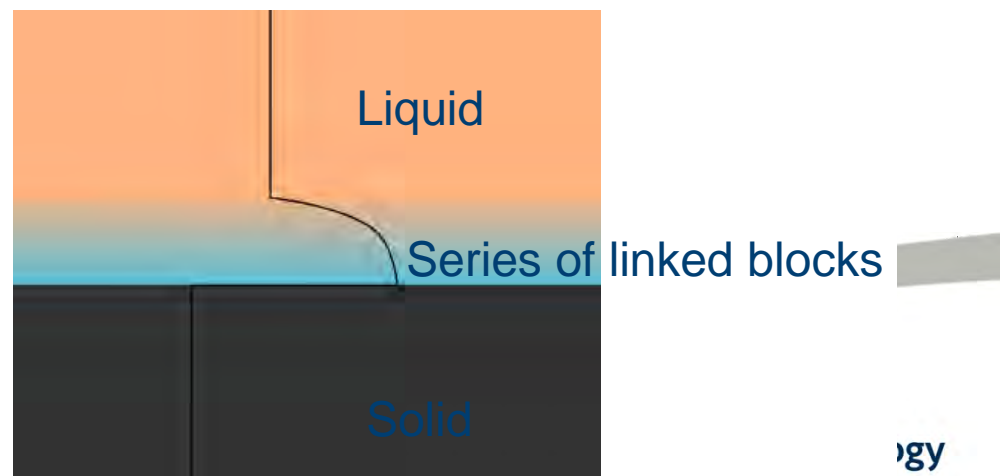# Experimental Geometry
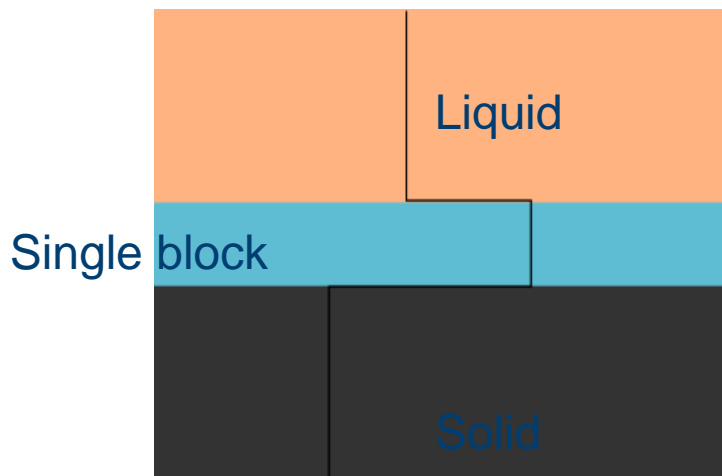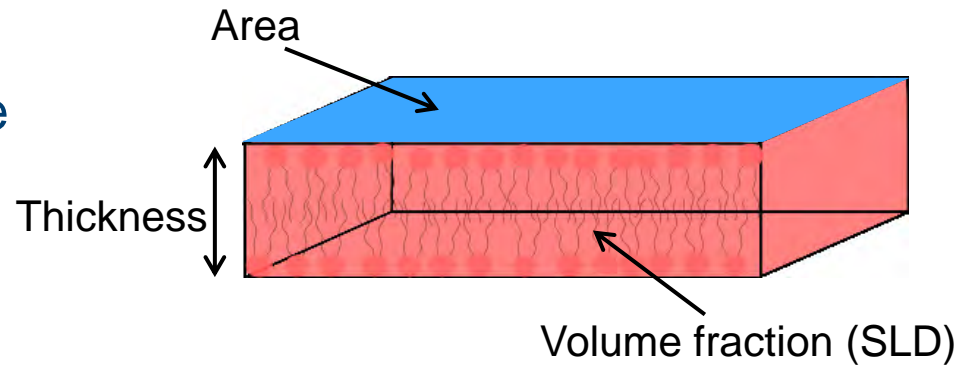

$$\Delta q = \frac{2\pi}{d}$$

- Solid-liquid
- Air-liquid
- Air-solid

Science & Technology
Facilities Council

Extracting Sample Information

- Consider the system as a series of "blocks" at the surface:

  - Thickness
  - SLD (hydration)

  } Amount on the surface

  - Roughness

Area

Thickness

Volume fraction (SLD)

Liquid

Single block

Solid

Liquid

Series of linked blocks

Solid

Sample Environment – e.g.

- Solid liquid
  - HPLC pump/syringe pump
  - Water baths
  - Potentiostat

- Air-liquid
  - Langmuir troughs
  - humidity, temperature, gas
  - FTIR

- Air-solid
  - Active heating/cooling
  - Vacuum or N_2 atmosphere
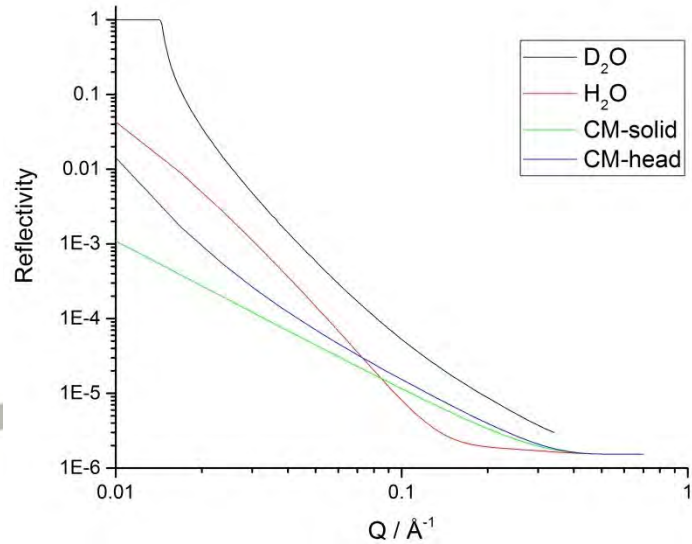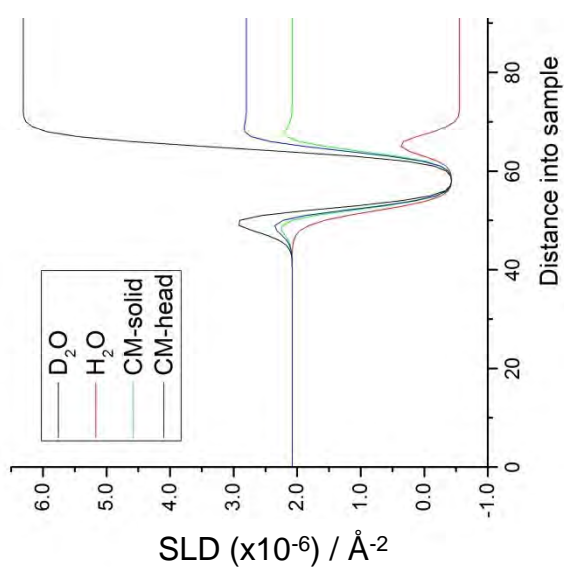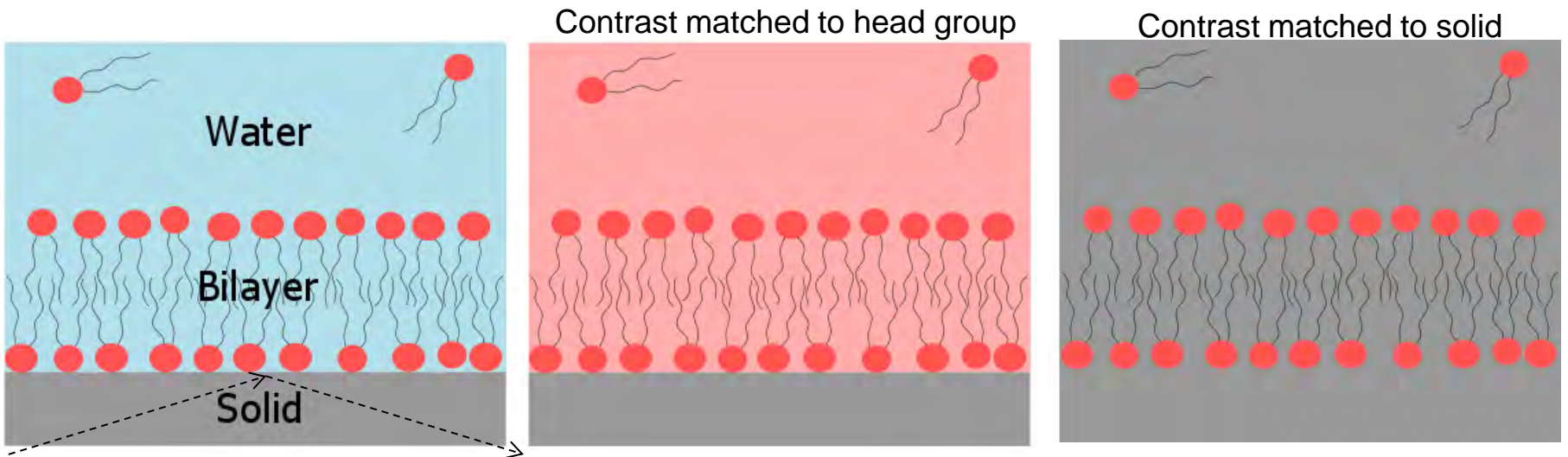 - Magnets/cryostats for magnetic samples
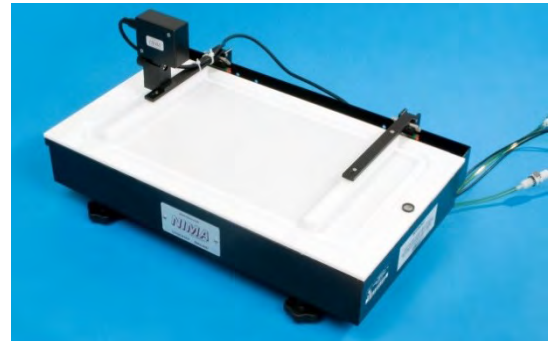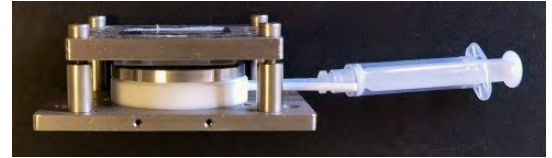
NR beamlines

- We have 4 reflectometers here at ISIS:
  - SURF and INTER
    - NR, incl. liquid surfaces
  - POLREF
    - Also capable of PNR and vertical samples
  - OFFSPEC
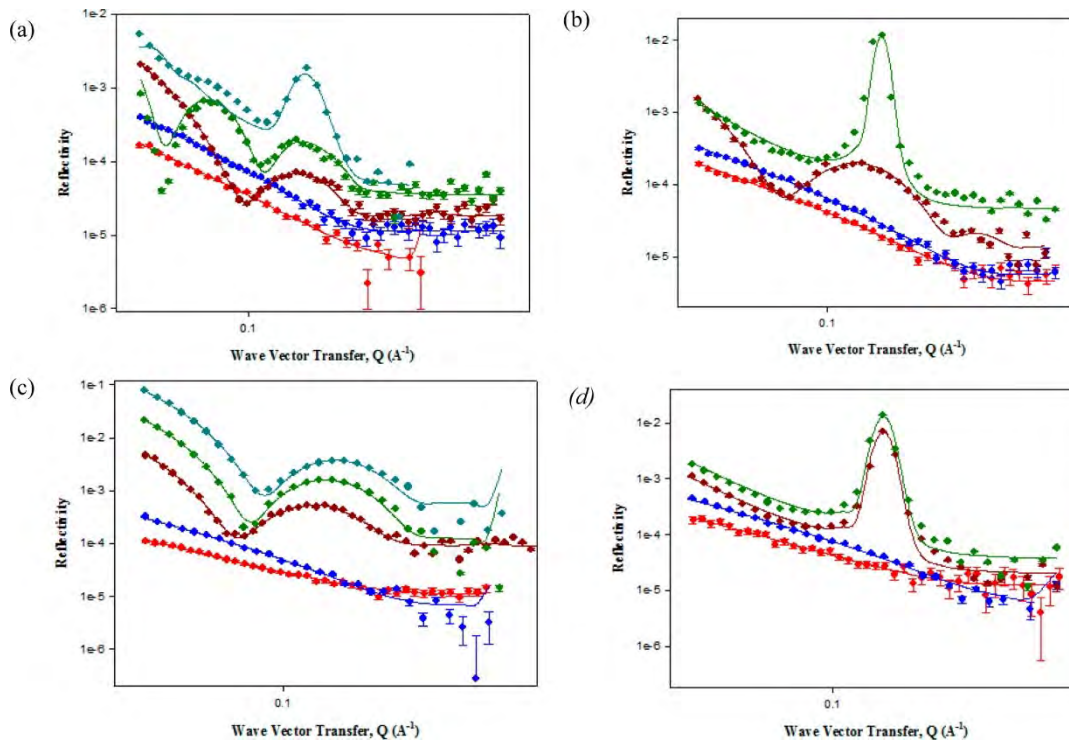   - PNR, with focus on off-specular and spin-echo

Contrast Matching

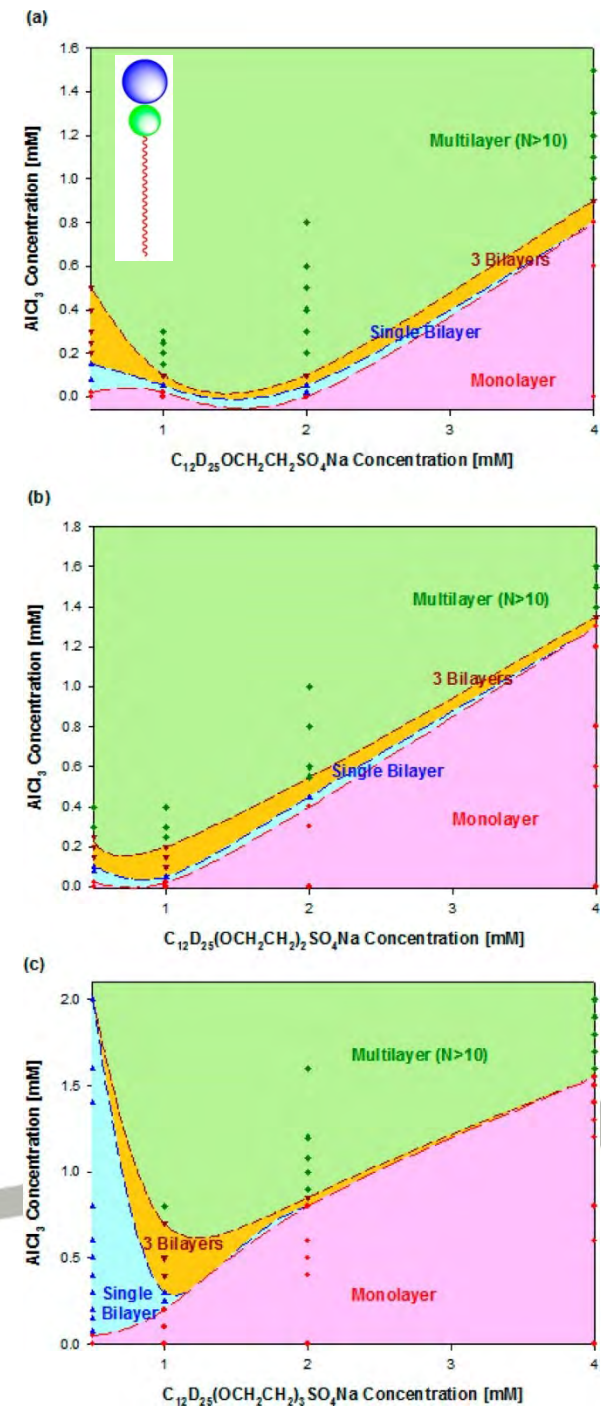Contrast matched to head group

Contrast matched to solid
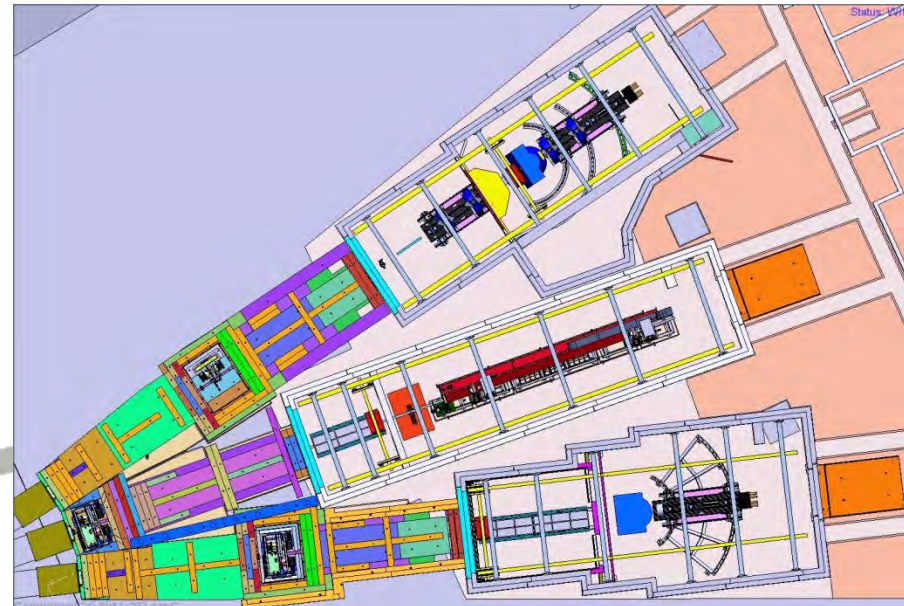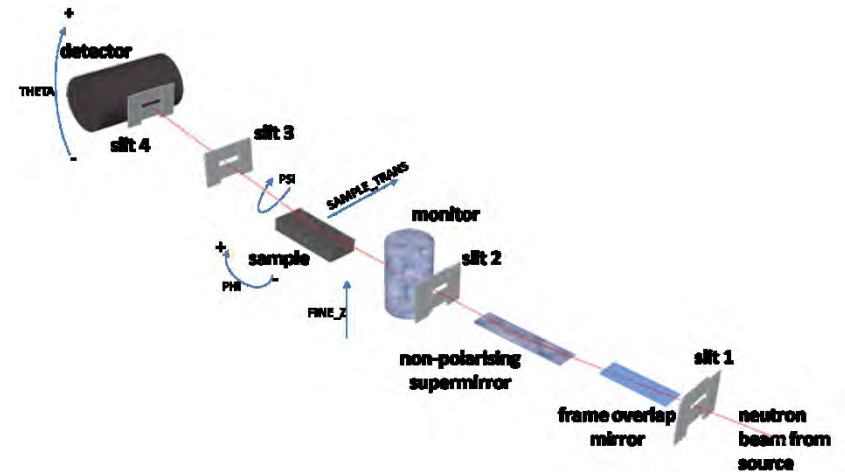
Some Examples

Anionic Surfactant Multilayers

Xu et al. 2013, *Langmuir*, 29

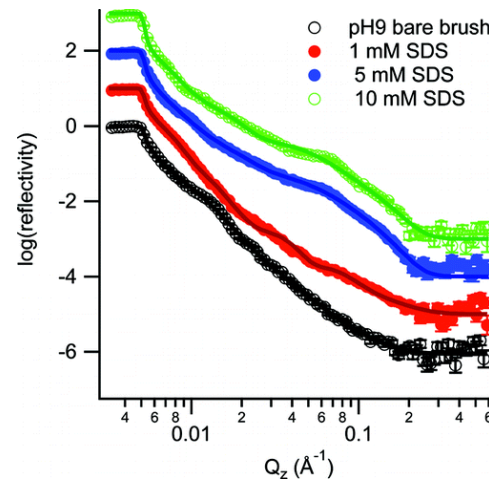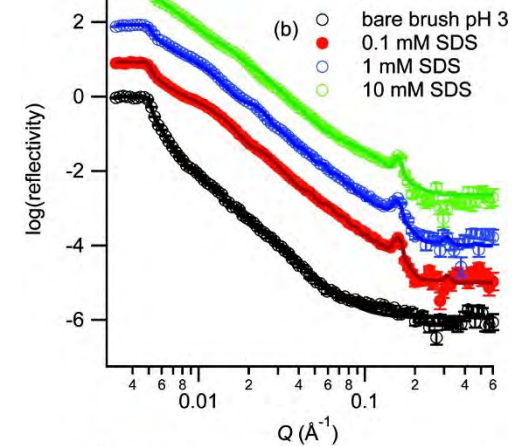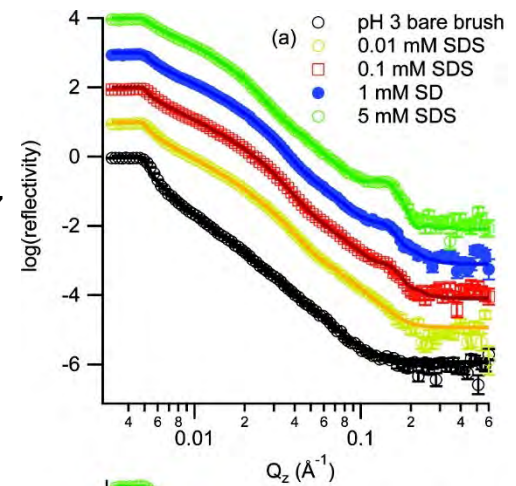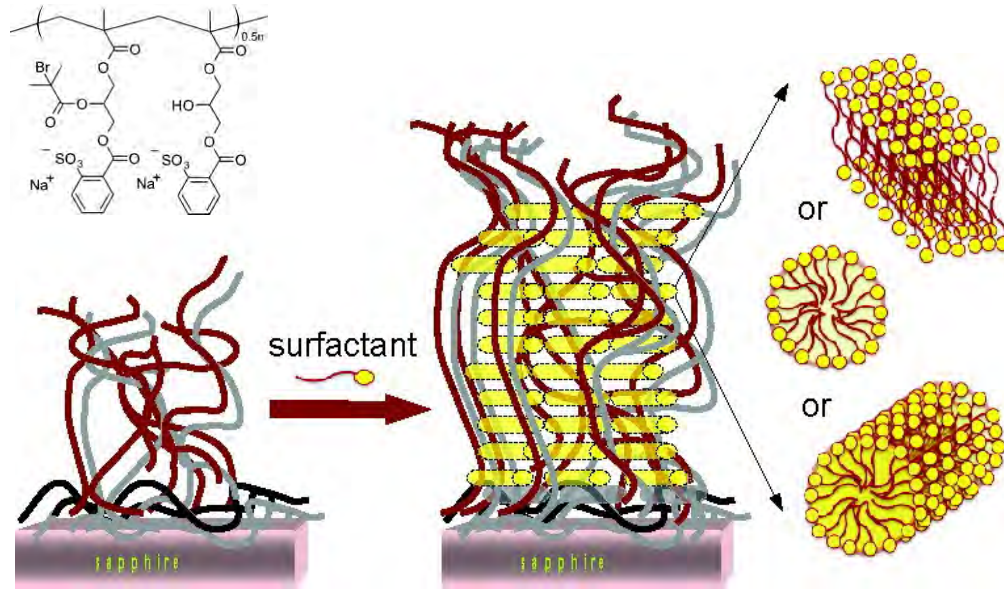- Surfactant single and multi-layer formation at air-liquid interface
  - Including inter-layer spacing
- Variation with chain length and added Al^{3+}

Mixed Surfactants and Polymers

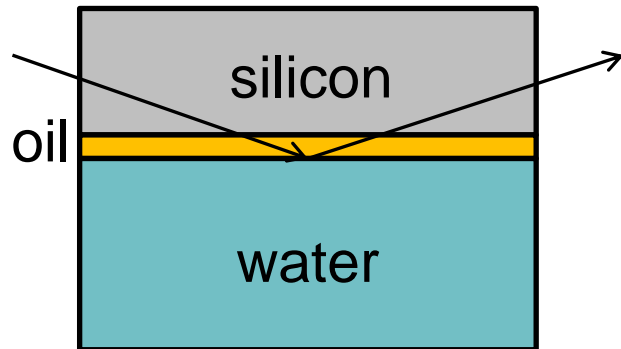Moglianetti et al. 2011, *Langmuir*, 27
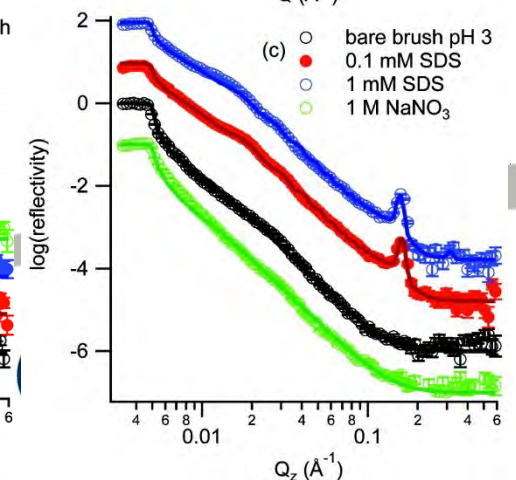
- Various polymer brushes are characterised with varying:
  - added surfactant (SDS)
  - pH
  - salt
- Partial deuteration could be used

Surfactants at the Oil-Water Interface

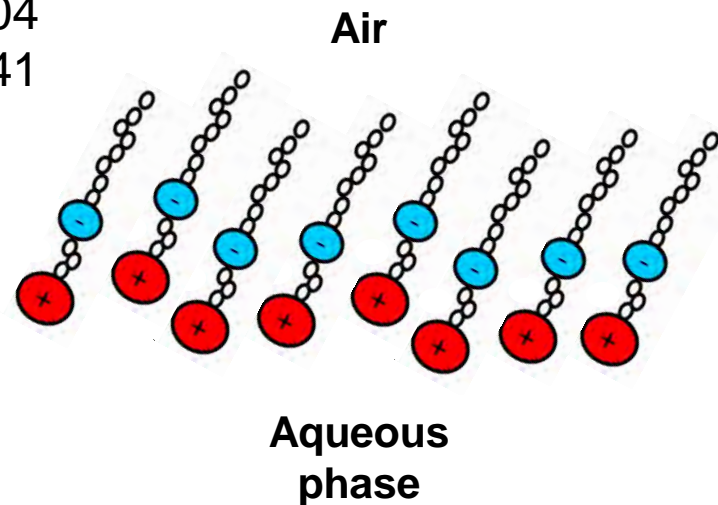Zarbakhsh et al. 2005, *Langmuir*, 21, 11704
Campana et al. 2014, *Langmuir*, 30, 10241

Air

Spin-freeze method:

silicon

oil

water

- Hydrophobic silicon surface
- Spread hexadecane
- Spin (2000 rpm for 20 s)
- Cool block to $T < 18\ °C$

- Assemble cell
- Warm block to $T > 18\ °C$
- Measure reflectivity

Aqueous phase
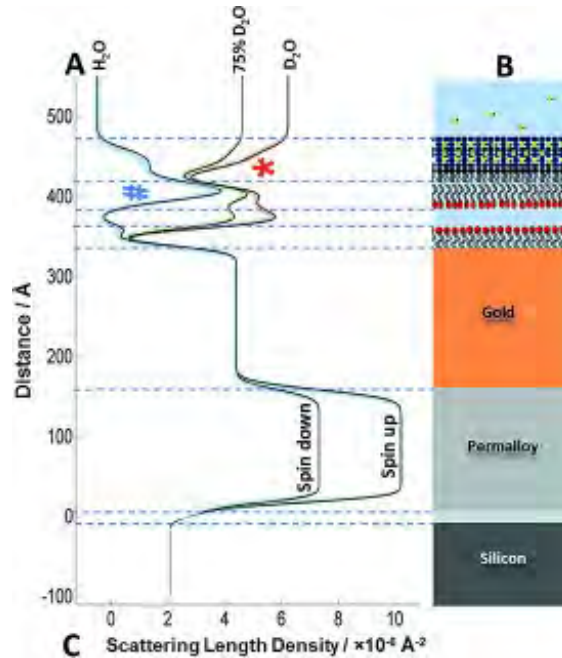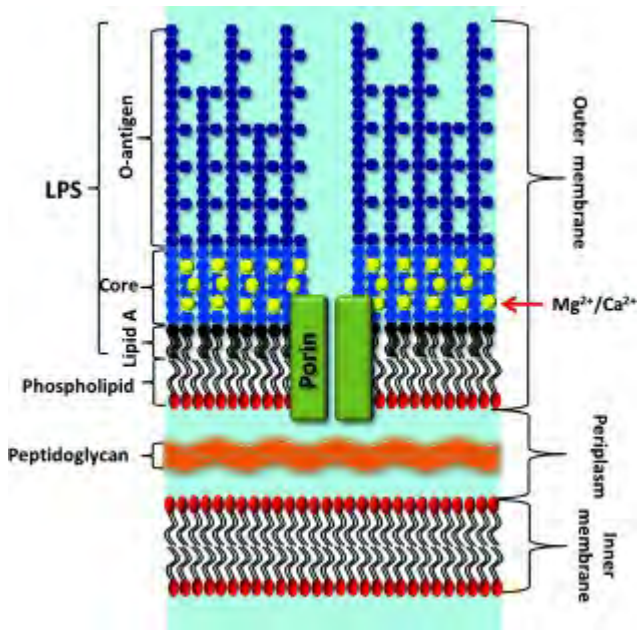
- Use careful contrast variation to "see" different parts
- See broader interface, with staggered conformation (both zwitterionic and non-ionic)

Oil

CM Si-oil

D_2O

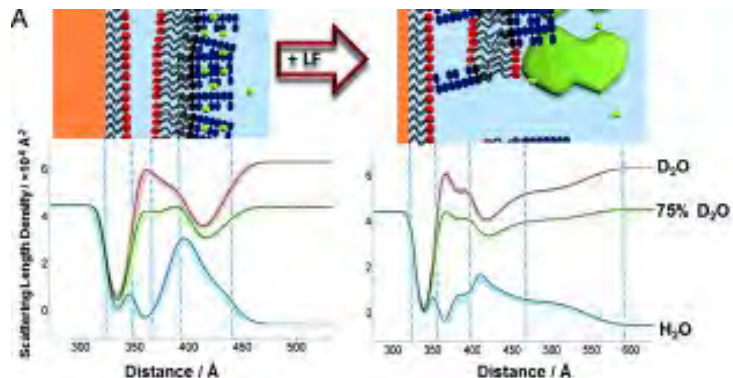Oil

Aqueous phase

Aqueous phase
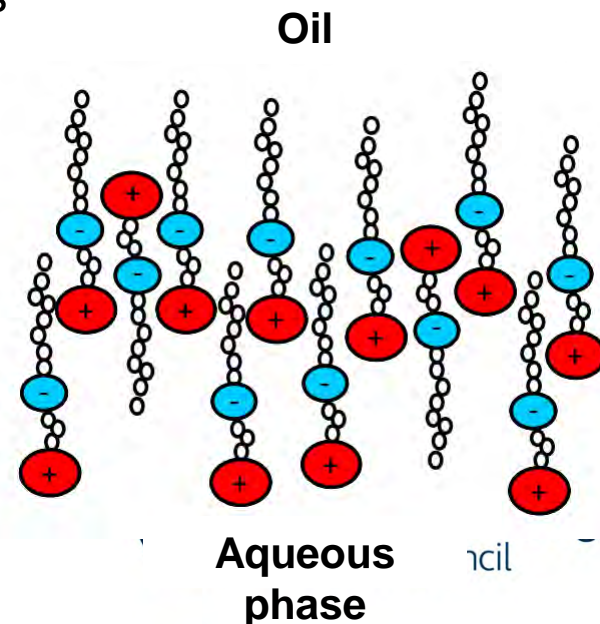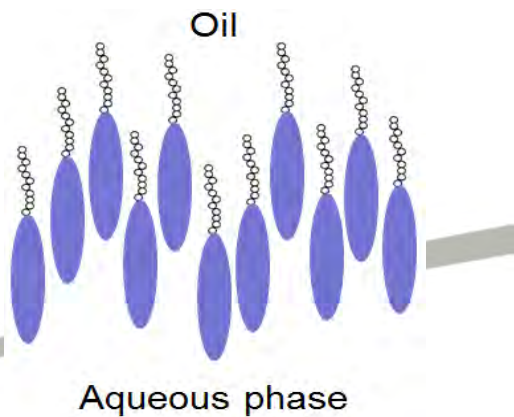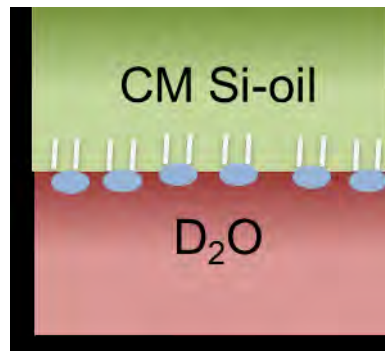
Studying Asymmetric Membranes *in vitro*

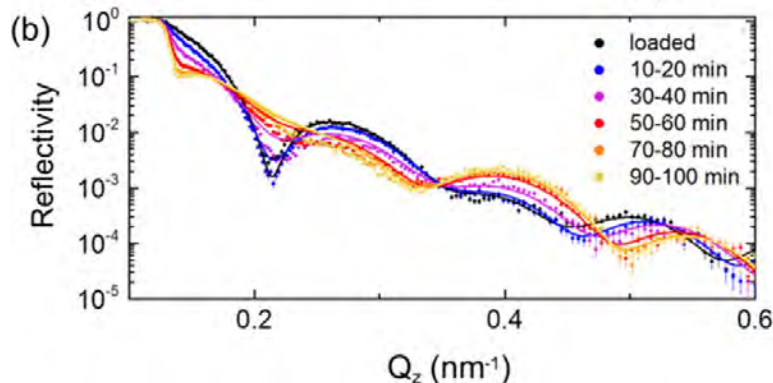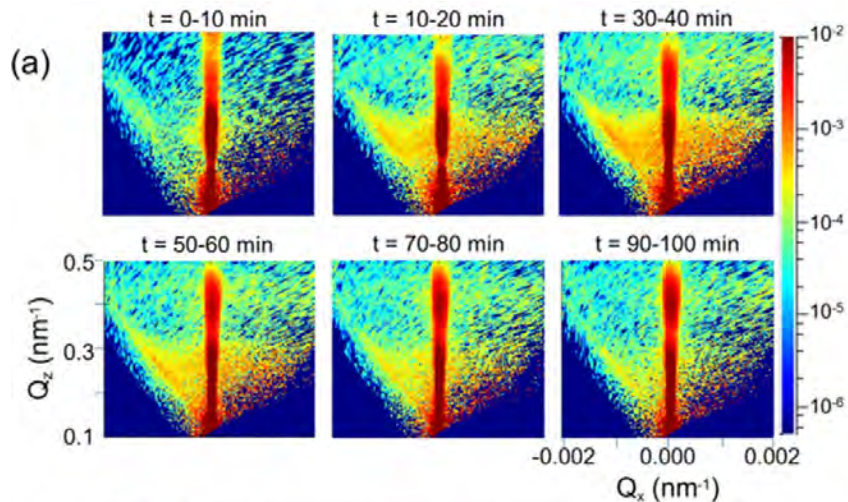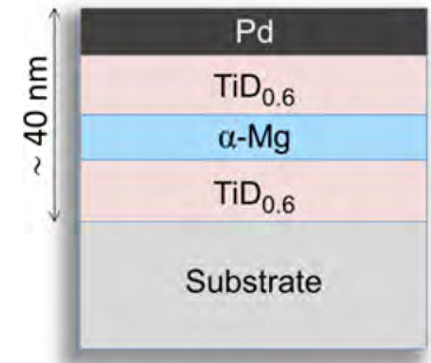Clifton et al. 2015, *Angew. Chem. Int. Ed.*

- Mimic outer membrane using a floating bilayer model

- Use PNR for extra contrast

- See disruption of the layer on addition of 2 different proteins

Hydrogen Storage: Kinetic Studies

Bannenberg et al. 2016, *J Phys Chem C*, 120

- Hydrogen (deuterium) loading and unloading into the Mg layer was measured with time
  - kinetic slices of 1min and 10min
- Both off-specular and specular were measured