Chemical Applications of Neutron Scattering:
Coherent Scattering and Adsorbed Layers
EXAMPLES

ISIS Neutron School 2017

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Talk Outline

- **Neutron scattering**
  - **Coherent scattering - structure**
  - Incoherent scattering - dynamics
- Examples of surfaces / neutron applications:

Adsorbed layers:

In-plane structure – 2D diffraction (D20)

Out-of-plane structure – reflection (SURF, CRISP, INTER, POLREF, OFFSPEC)

What's adsorbed? (IQNS - dynamics) IRIS

Colloidal dispersions (dominated by surfaces)

What's on the surface? SANS (LOQ)

What arrangement ? SE- SANS

Liquid structure PDF (SANDALS, NIMROD)

- **Conclusions**

We use LOTS of different techniques to answer complex problems
Too much to cover…. See how far we get..

Conclusions

Neutrons

Very powerful tool(s) for Structure (Dynamics)

- Contrast between H and D very useful: highlight
- Can ‘see’ Hydrogen: Highlight
- Excellent transmission (extreme/commerical conditions)

BUT.

- Tricky to get hold of/limited access

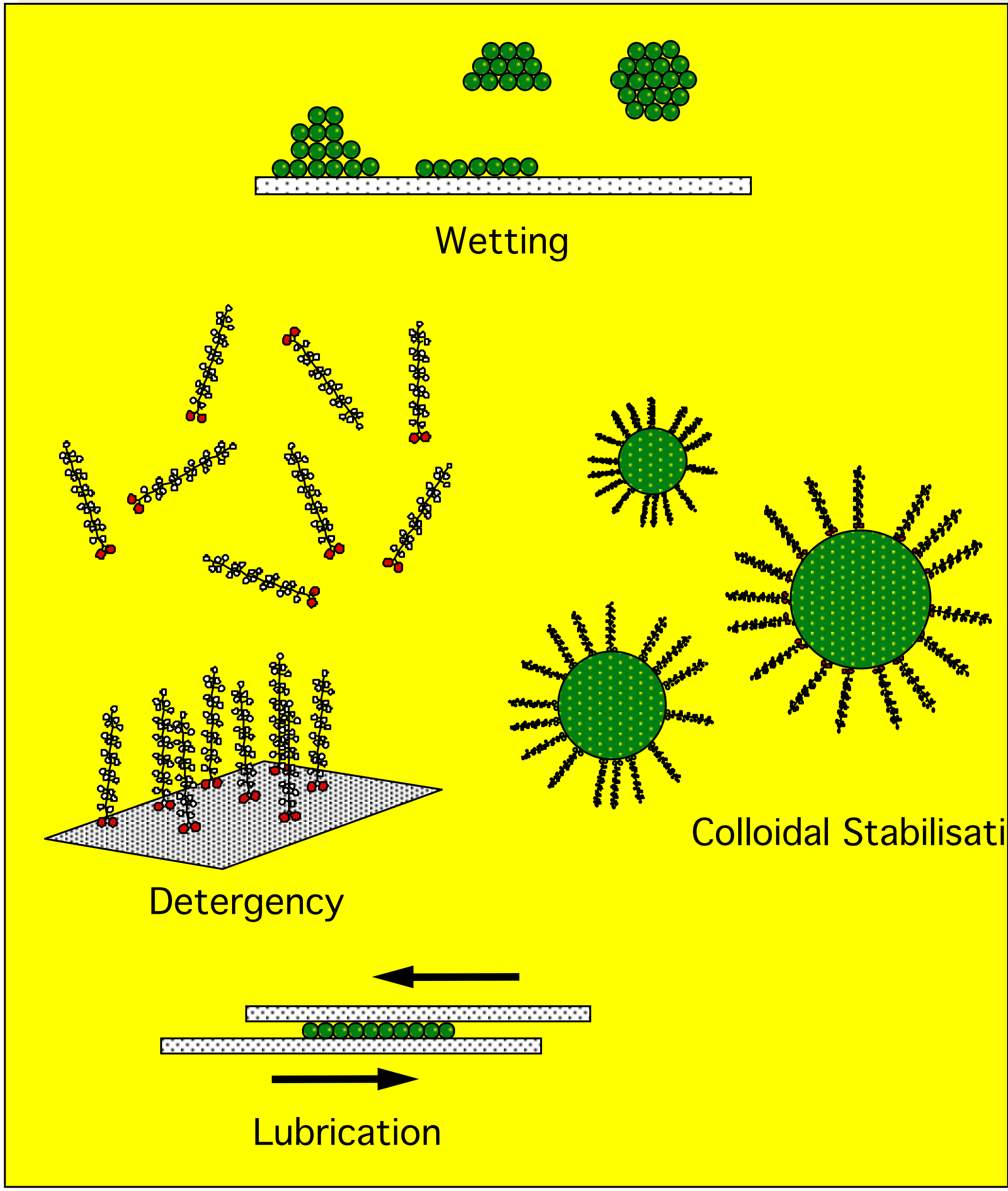
(complement with other methods)

Examples of Monolayers

- Academic and industrial issues:
  Colloidal stablisation, wetting behaviour, Slip agents, molecular patterning, detergency, liquid crystals.
  Solid monolayers

- Mixtures / Multicomponent:
  Cheaper …

- 'Buried' monolayers inaccessible to study:
  Need to get through bulk phase
  -neutrons have great transmission
  Unusual experimental approaches



Talk Outline

- Examples of surfaces / neutron applications:

Adsorbed layers:

In-plane structure – 2D diffraction

Out-of-plane structure – reflection

What's adsorbed? (IQNS - dynamics)

Colloidal dispersions (dominated by surfaces)

What's on the surface? SANS

What arrangement ? SE- SANS

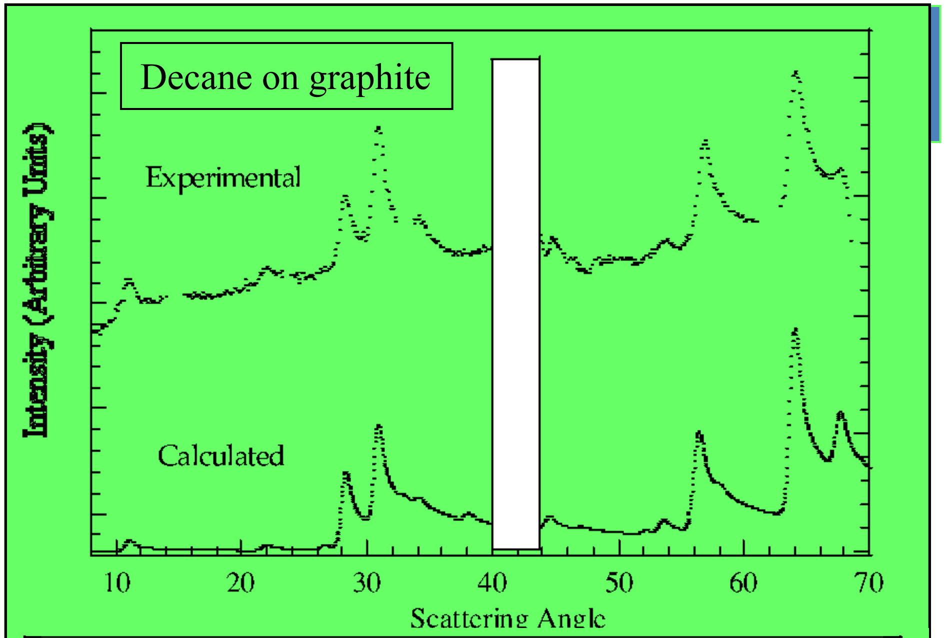
Liquid structure PDF (NIMROD)

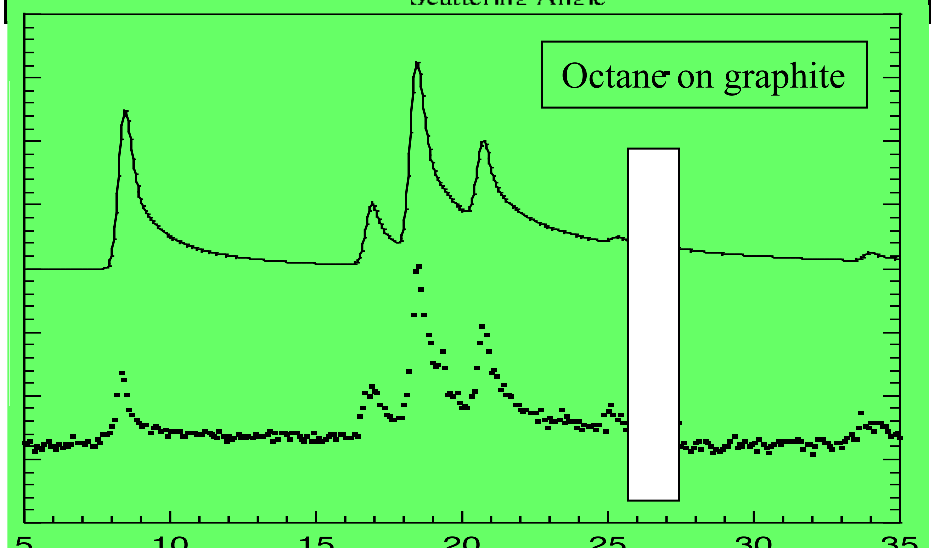
3D diffraction:crystallography

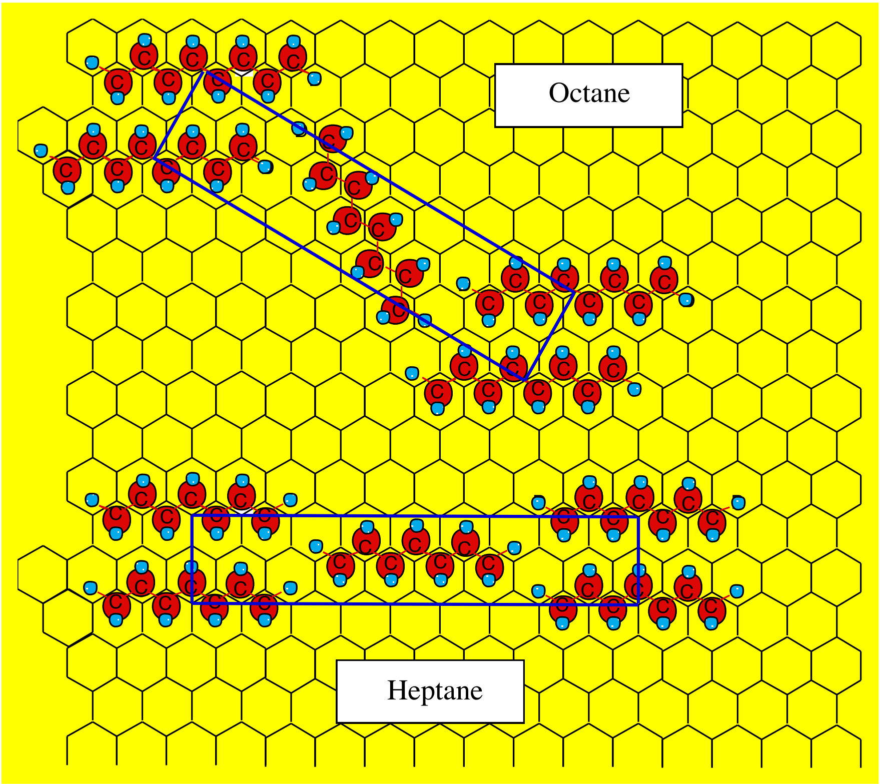
- ‘work horse’ of chemical community
- Crystal structures of minerals, materials, organic molecular structure determination.
- Neutrons very good at hydrogen (xrays no so good)
- Adjacent elements (look the same to xrays)

TODAY: 3D ➔ 2D diffraction

In-plane 2D Structure: X-ray and Neutron diffraction





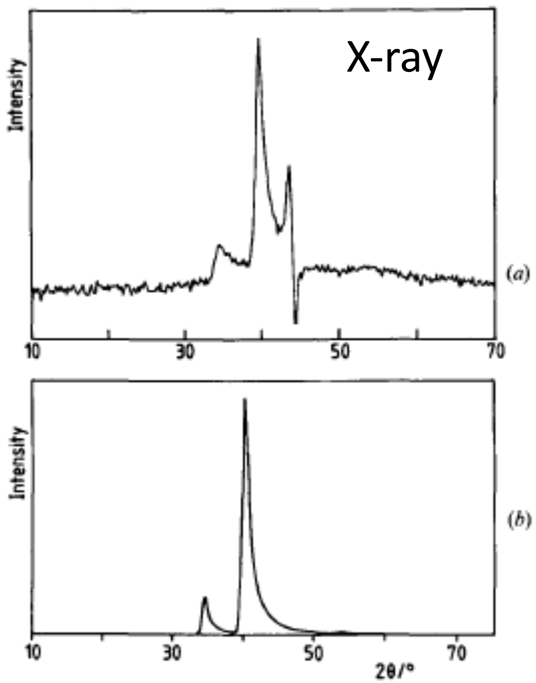


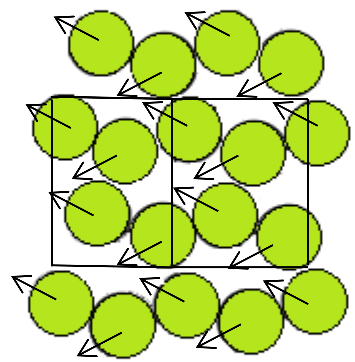
Neutrons: sensitive to hydrogen
X-rays: greater precision
Independent information
Combination is often essential

Why Xrays AND neutrons are important.

Low coverage

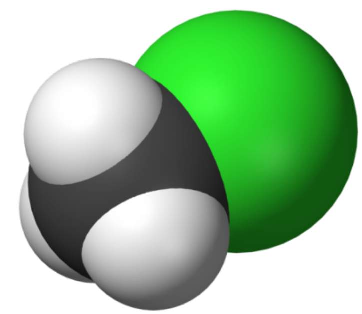
Chloromethane monolayer: X-rays

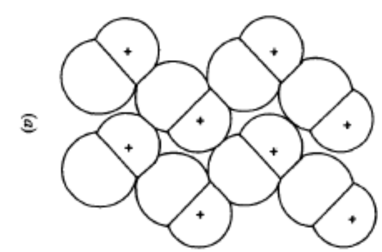




Chlorine atoms

Where are CH_3 groups?
Guessed:
Ferro electric ordering?
Like bulk crystal plane…



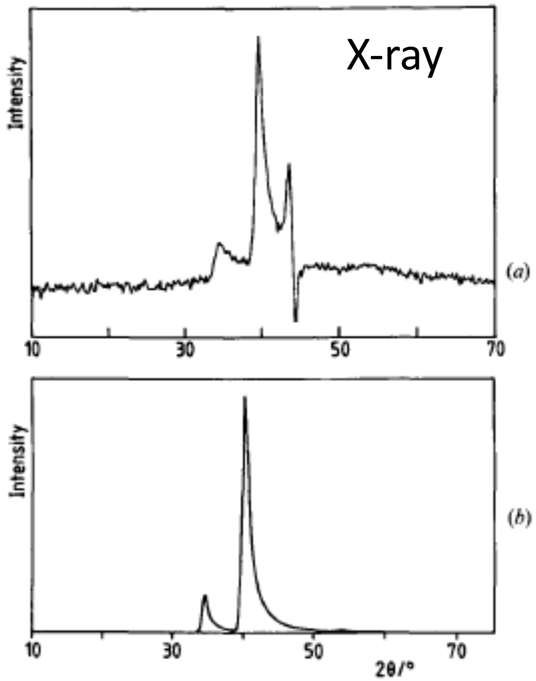


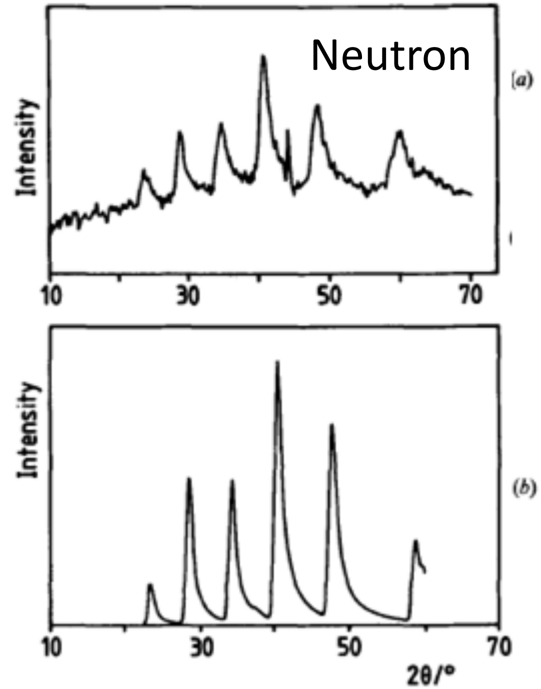
Bulk Plane

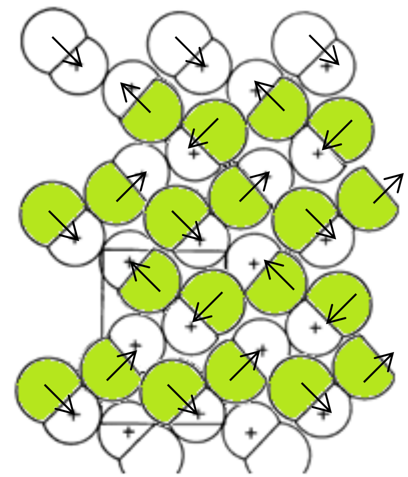
Morishige, et al., *Mol Phys* , **72** 395-411 (1991). 'The Structure of Chloromethane Monolayers Adsorbed on Graphite'.

Chloromethane

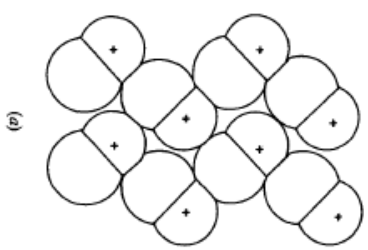
Low coverage



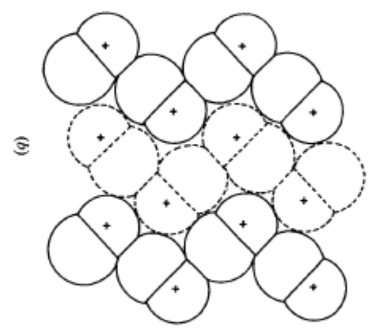




Monolayer

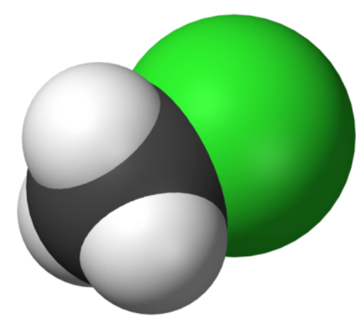


Bulk Plane



Monolayer

With neutrons:
Anti ferroelectric
Alternating chains



Morishige, et al., *Mol Phys* , **72** 395-411 (1991). 'The Structure of Chloromethane Monolayers Adsorbed on Graphite'.

Need neutrons to see CH_3 groups and full symmetry

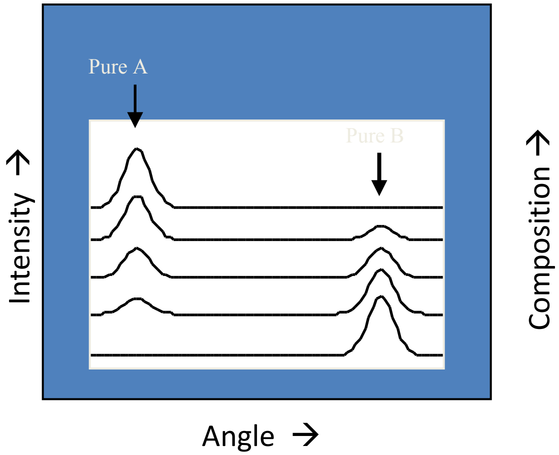
Mixing:
How do you tell if two species like each other?

1) They avoid each other ➔ phase separation:

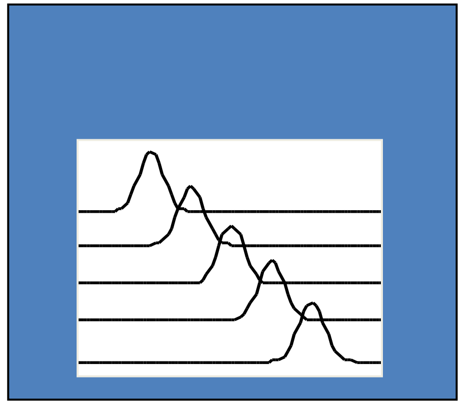
Mixing ideally

Special relationship; stoichiometric complex Molecular compound

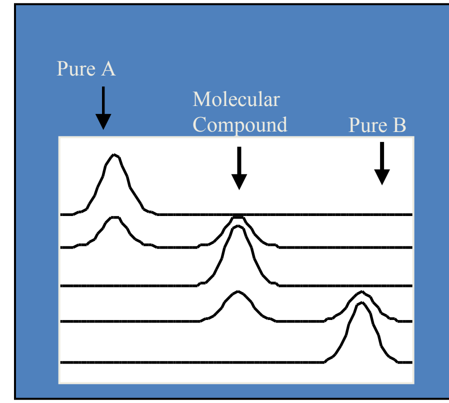
Structure: Diffraction from Mixed Monolayers
How do molecules mix on a surface?



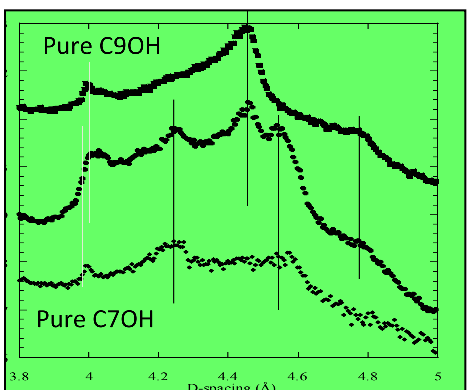
(a) Phase sep.



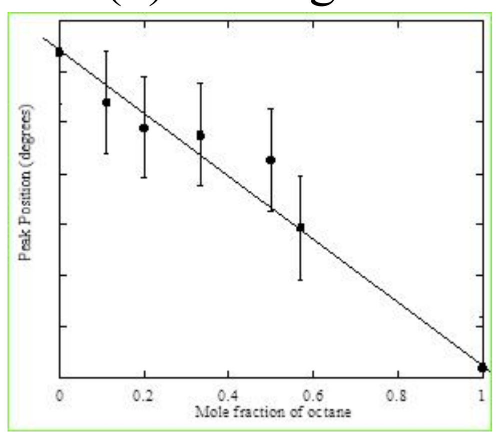
(b) Mixing



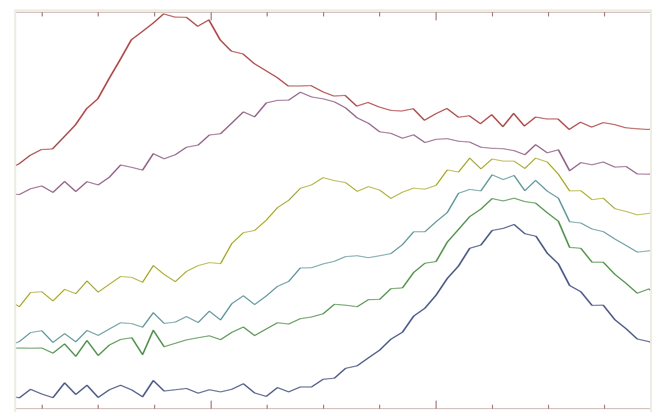
(c) Molecular compound



Heptanol/nonanol

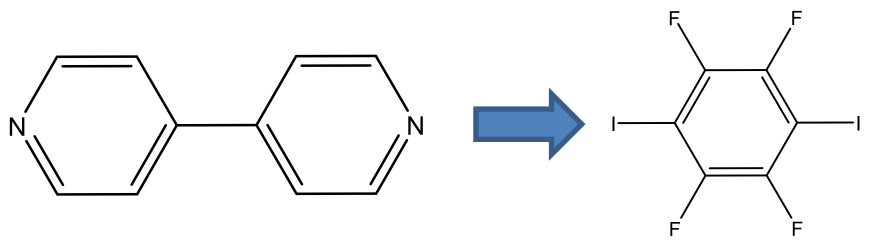


Heptanol/octanol



Hexanol/heptanol

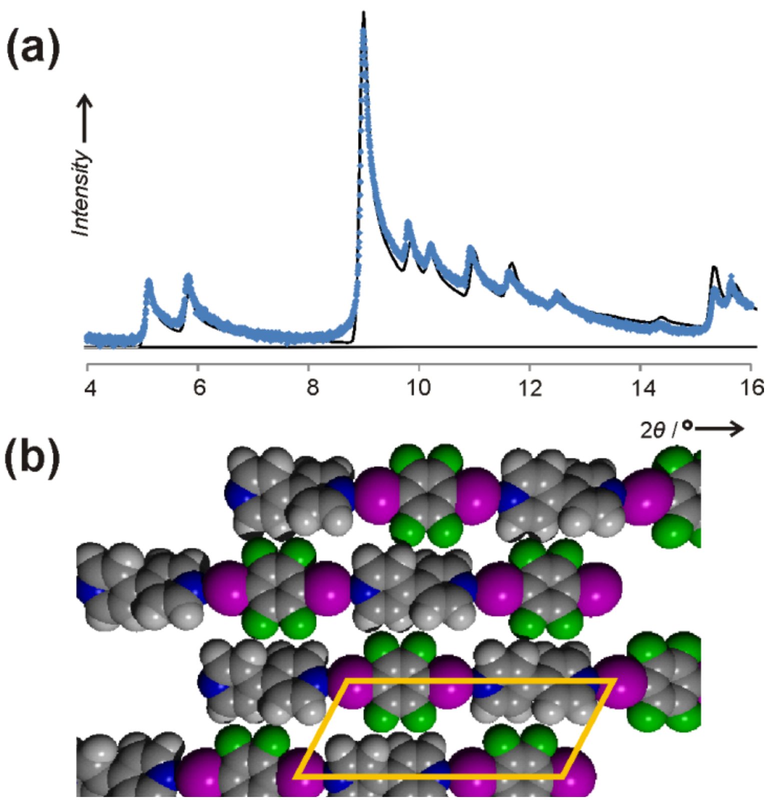
‘Special, non-covalent bonding between molecules’
Big topic of supramolecular self assembly

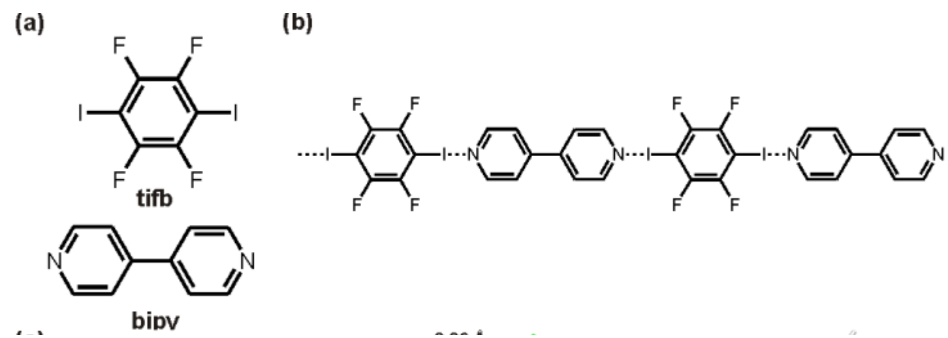


Donation of lone pair from nitrogen to Iodine ataom

Novel Chemical interactions: Halogen Bonded co-crystal

N….I-C





Monolayer

'New hydrogen bonds'
Very stable layers
$^{2D}T \gg {}^{3D}T$
Directional
Strong
'Controls' strength and orientation

2D –diffraction: summary

- Can see in-plane molecular structure.
  (non-invasive)
- X - ray and neutrons can be essential :
  Neutrons ‘see’ H
- Determine surface phase behaviour
- Characterise inter molecular bonding

Talk Outline

- Examples of surfaces / neutron applications:

Adsorbed layers:

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What's adsorbed? (IQNS - dynamics)

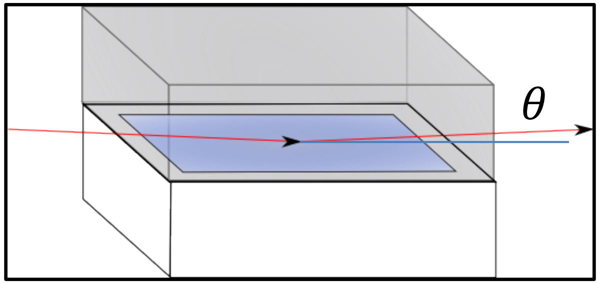
Colloidal dispersions (dominated by surfaces)

What's on the surface? SANS

What arrangement ? SE- SANS

Liquid structure PDF (NIMROD)

Neutron Reflection: how does it work?



- Extend to new solid/liquid Interfaces: iron oxides, stainless, alumina, Ti oxides, Ni, Cu …

(previously: silica, Al_2O_3)

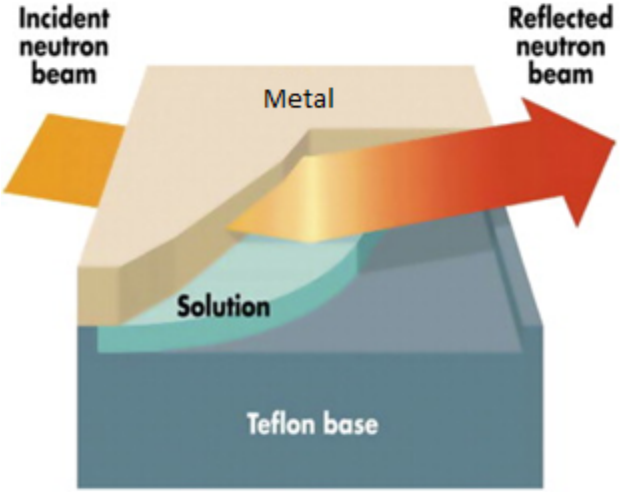
- New conditions:

applied shear

…nction of 'angle' (q)..

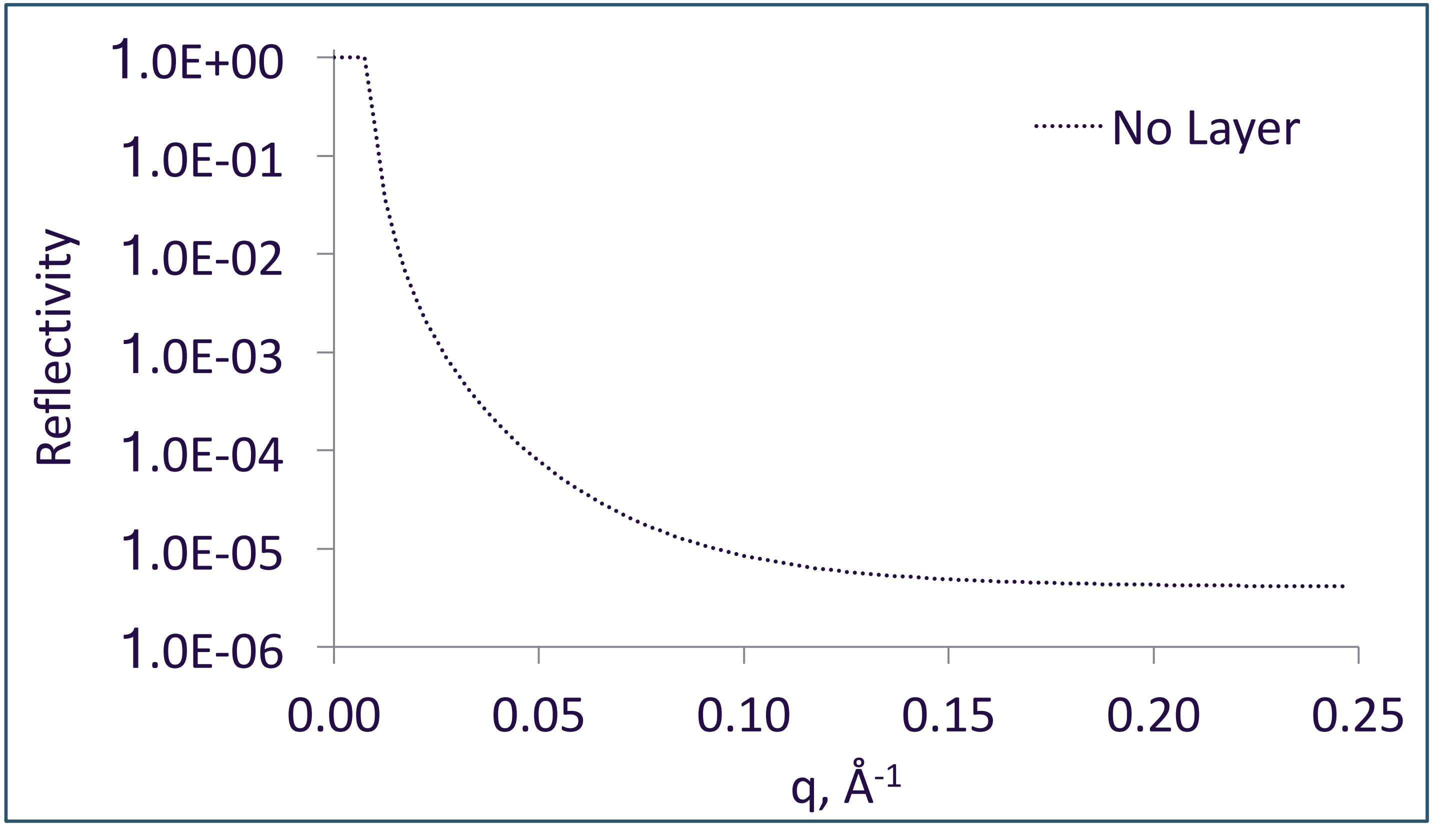
…aces

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

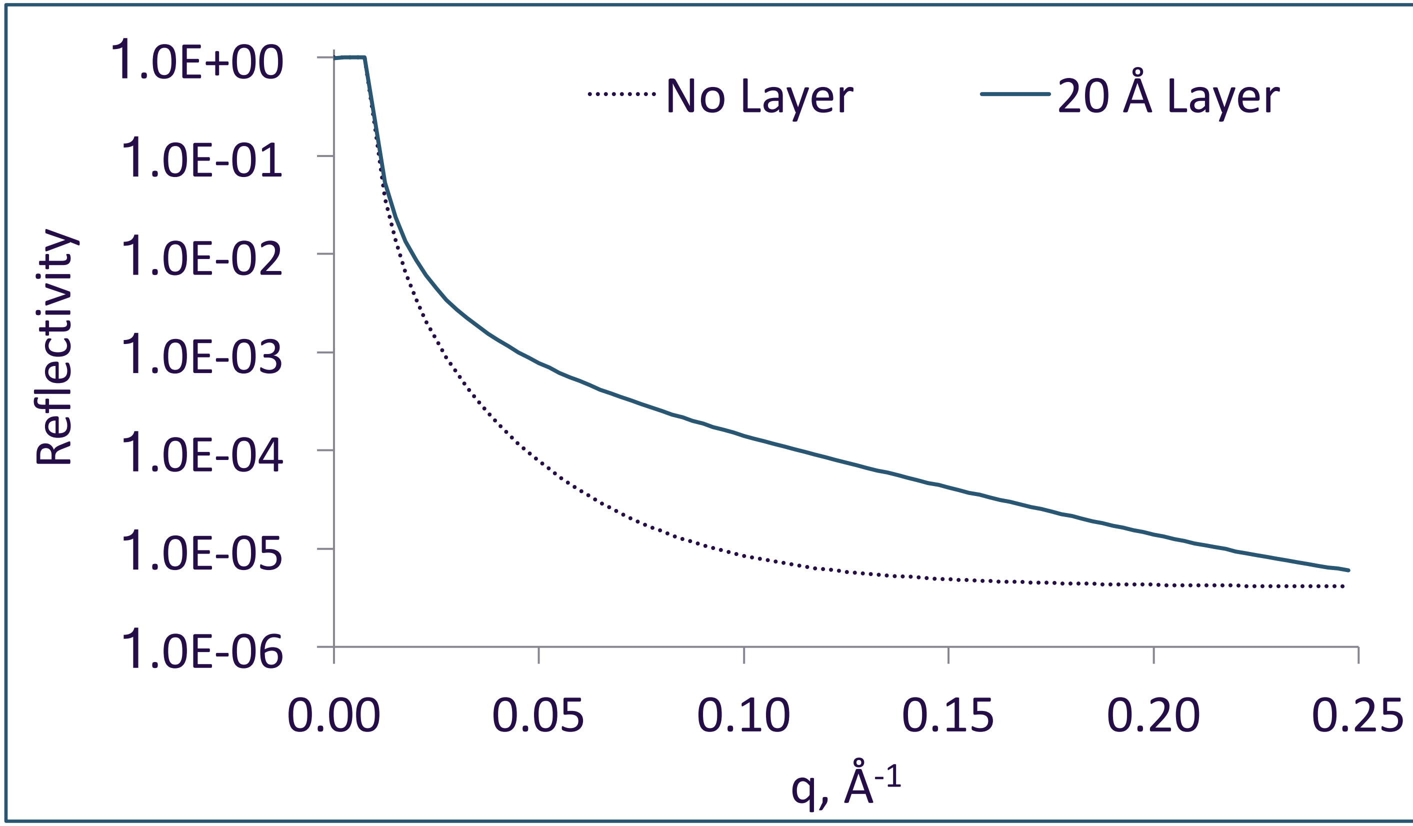


Solid/liquid cell

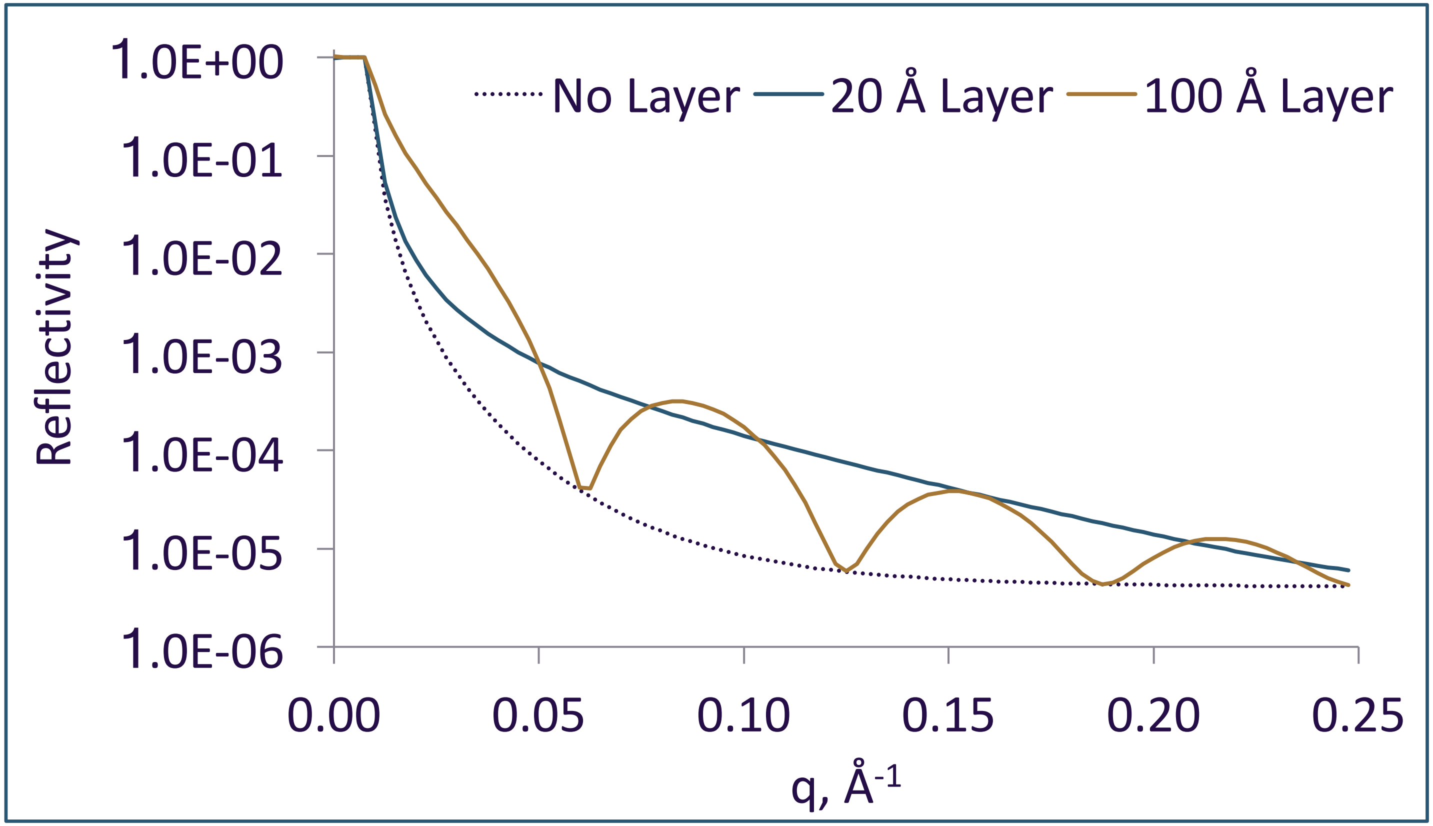
Neutron Reflection Theory



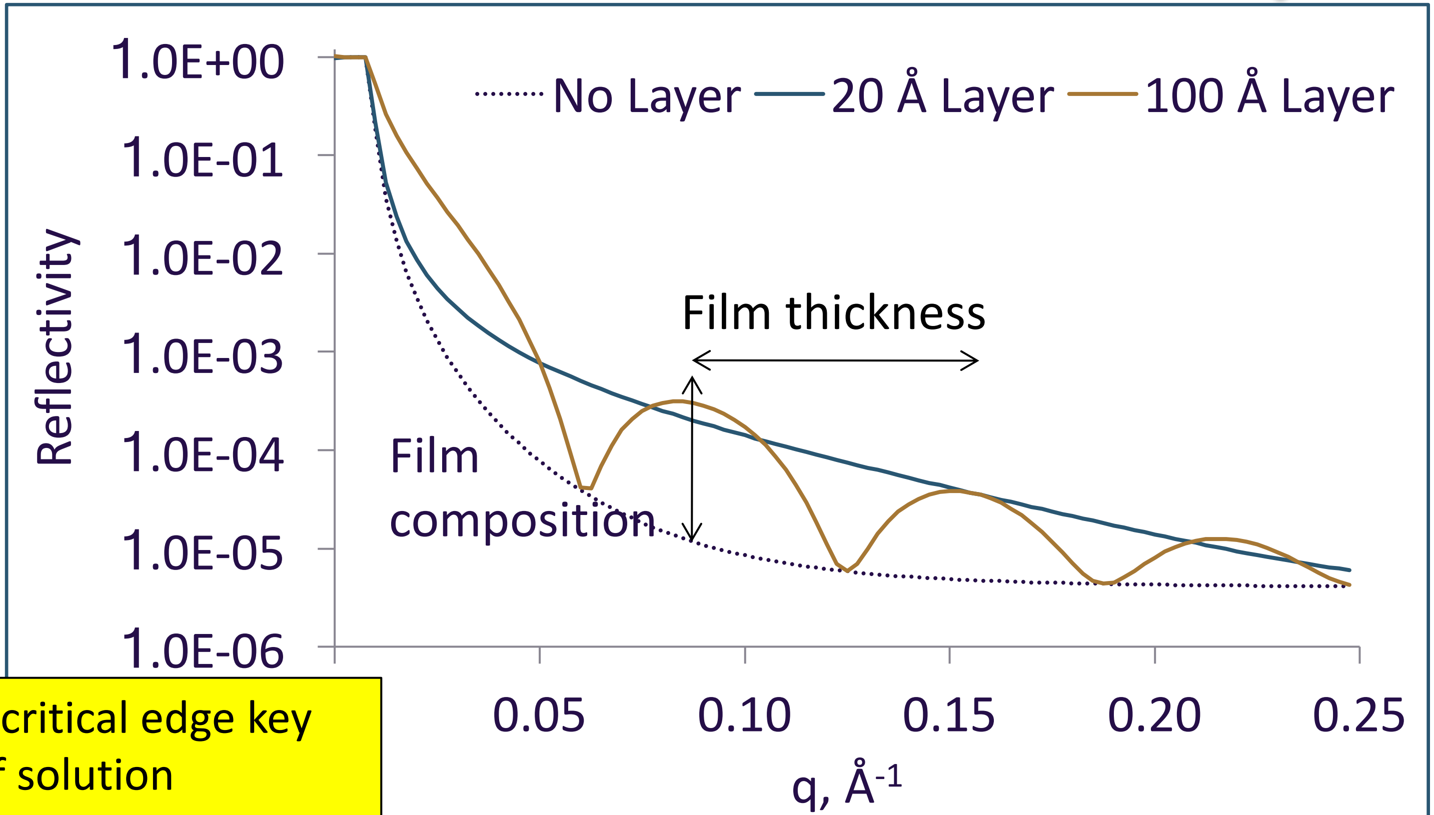
Neutron Reflection Theory



Neutron Reflection Theory

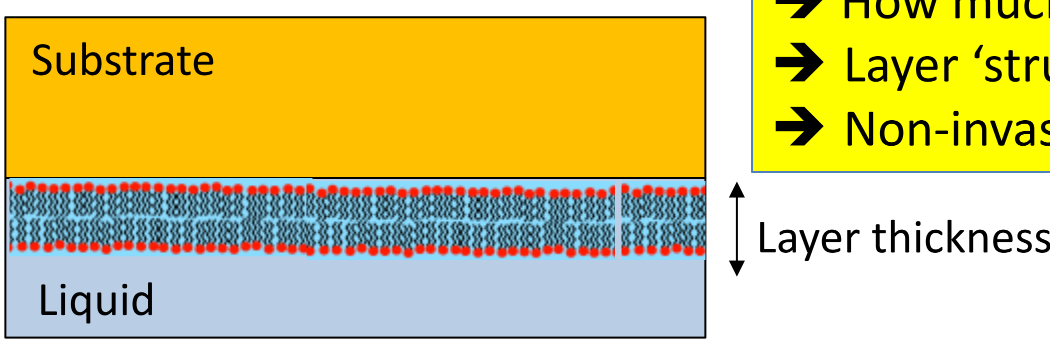


Neutron Reflection Theory



Position of critical edge key indicator of solution composition
(Tutorial problem)

‘Fit’ experimental data to model.
➔ How much material at the surface
➔ Layer ‘structure’
➔ Non-invasive/in-situ



Neutron: ‘Magic’

- Contrast matching..
- Making things disappear!
- Unique structural solution.

➔ BIG advantage of neutrons

- Need to make sure complete exchange of solutions.. Not always easy..
- Ask me about ‘baby oil’?

Reflection Example #1

- Calcite ($CaCO_3$)

Very important mineral

Scale in your kettle

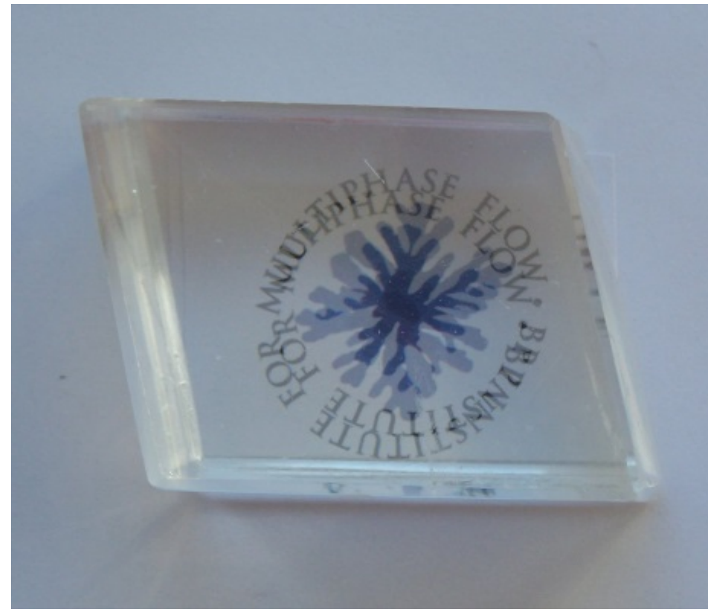
Oil reservoirs

Overbasing agent in engines

What adsorbs and how?

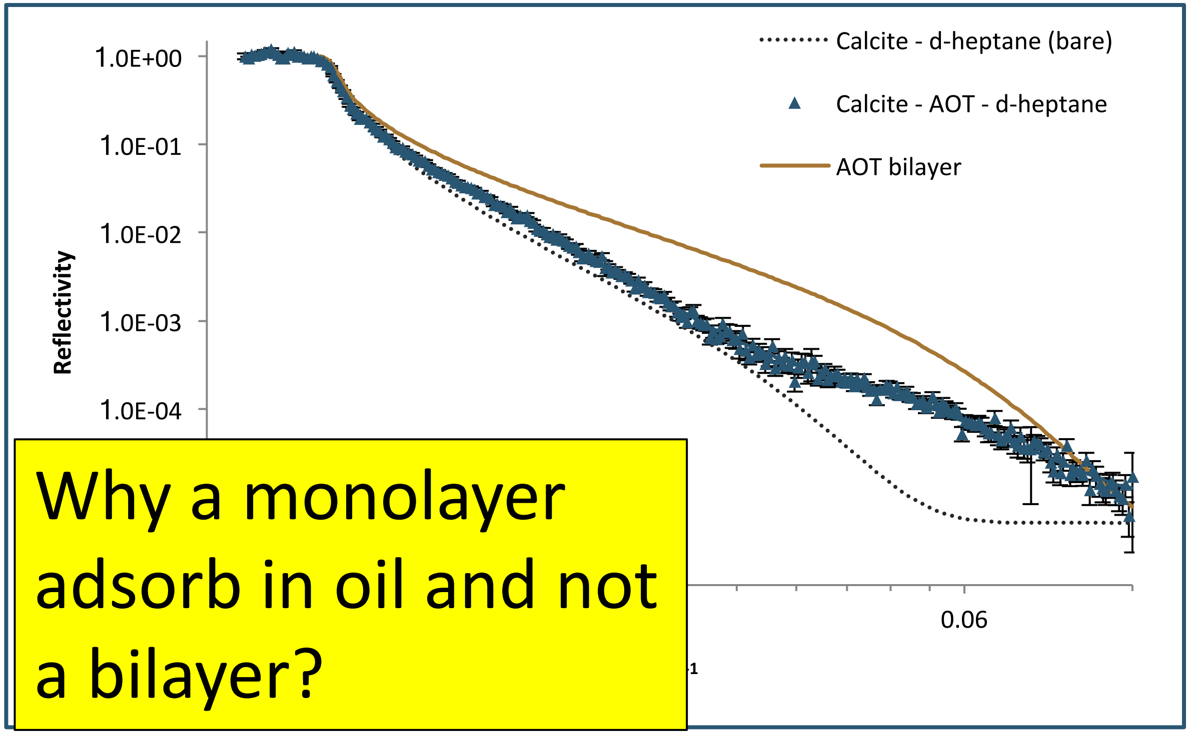
In oil? In water?

Polymers? Surfactants?

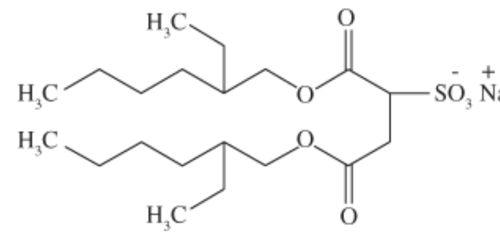


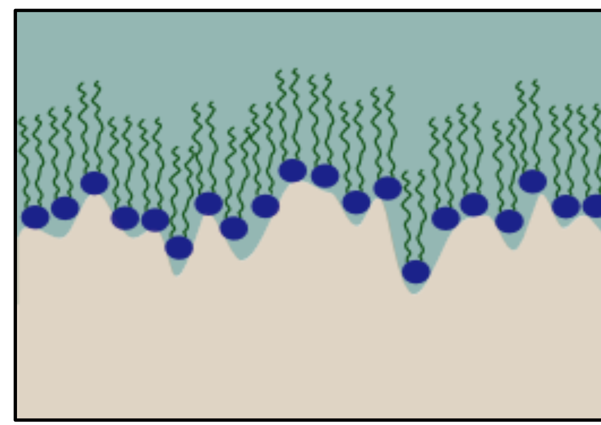
(Birefringent…! Double refraction)

Neutron reflection: Example #1
Surfactant, AOT, on Calcite (CaCO3) in oil



Why a monolayer adsorb in oil and not a bilayer?

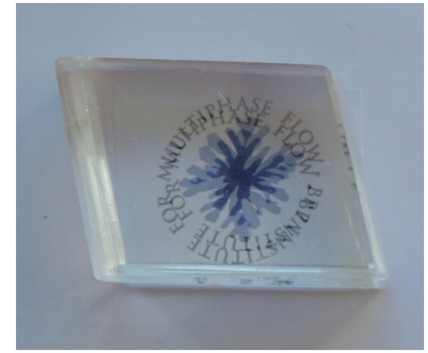


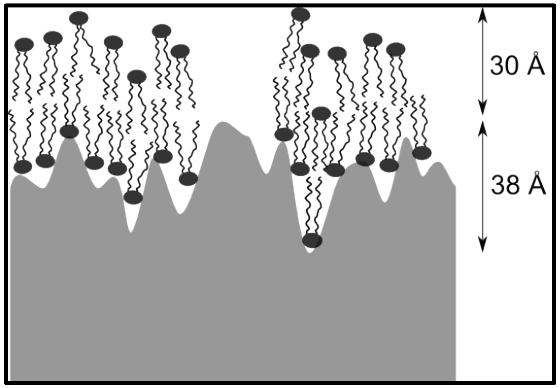


Adsorption of a monolayer on a surface:

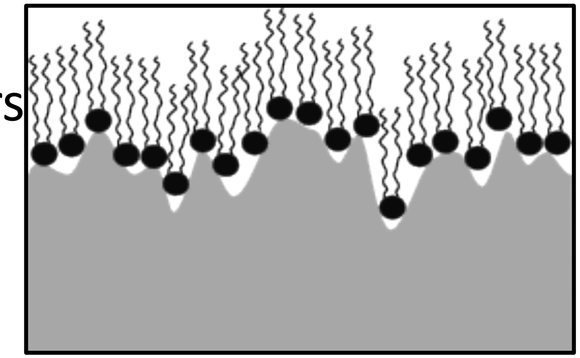
(The bare surface, monolayer and bilayer calculations)

Reflection Example : Additives on calcite..

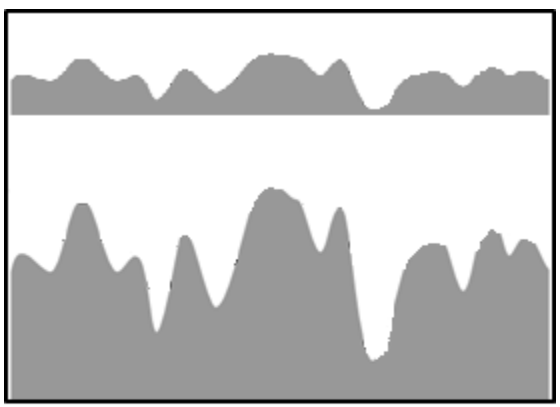




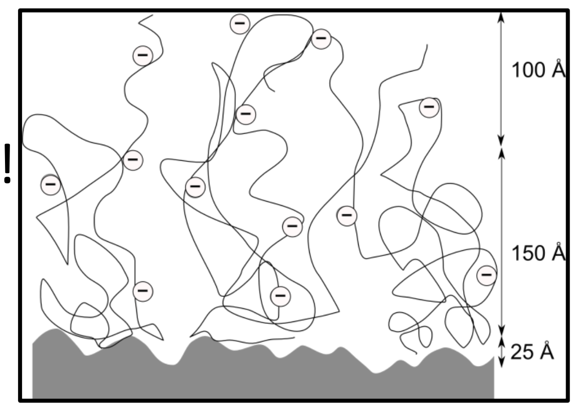
Monolayers, Bilayers multilayers and adsorbed polymers

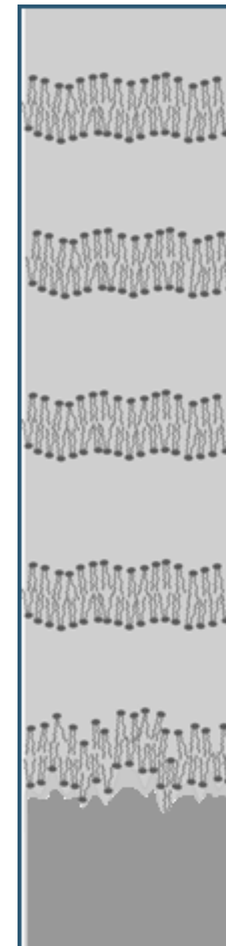


Surface corrosion



Molecular precision!



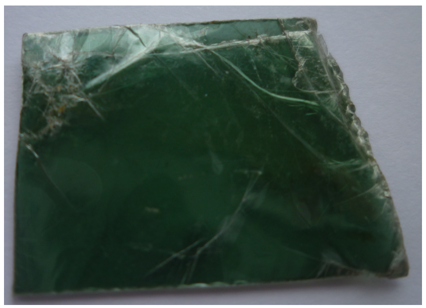


Why a bilayer adsorbs in water?

Reflection Example : Mineral Surfaces - mica

(Kate Miller)

Layered silicate: mineral books



Mica:

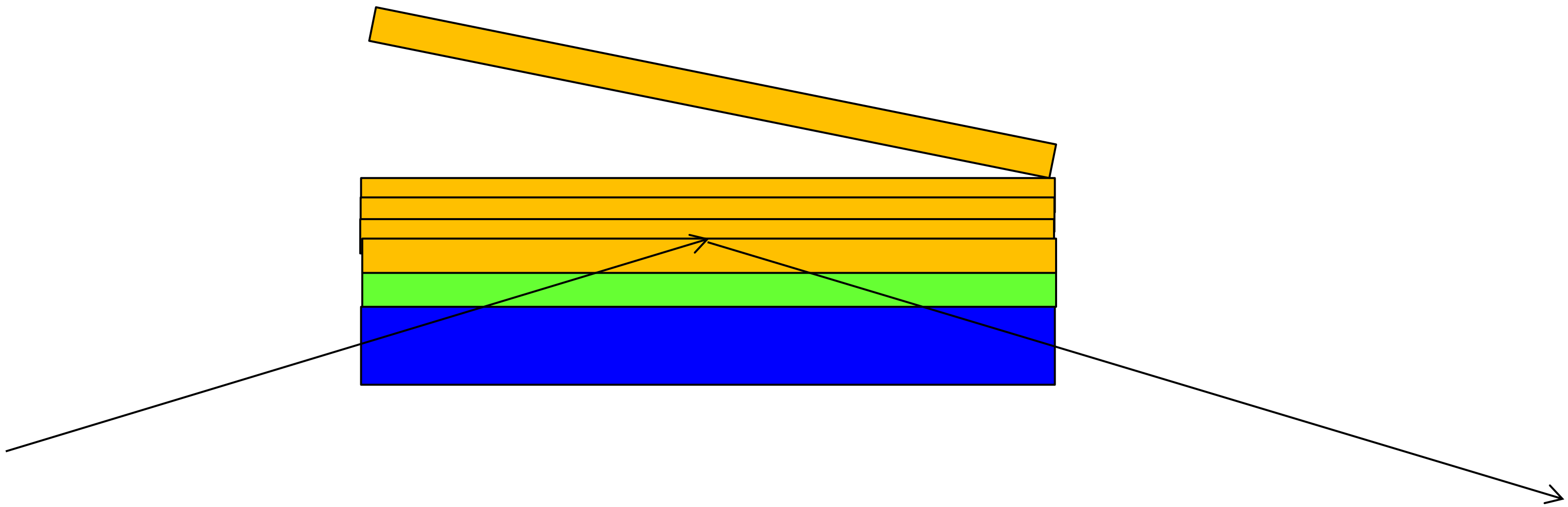
Clays are key component of many oil reserviors

Very common in AFM/SFA studies

Many attempts to study with neutron reflection failed

- ➔ **To hard to get a beam through**
- ➔ **Can’t deposit through vapour**
- ➔ **Thin sheets too flexible/break.. So..?**

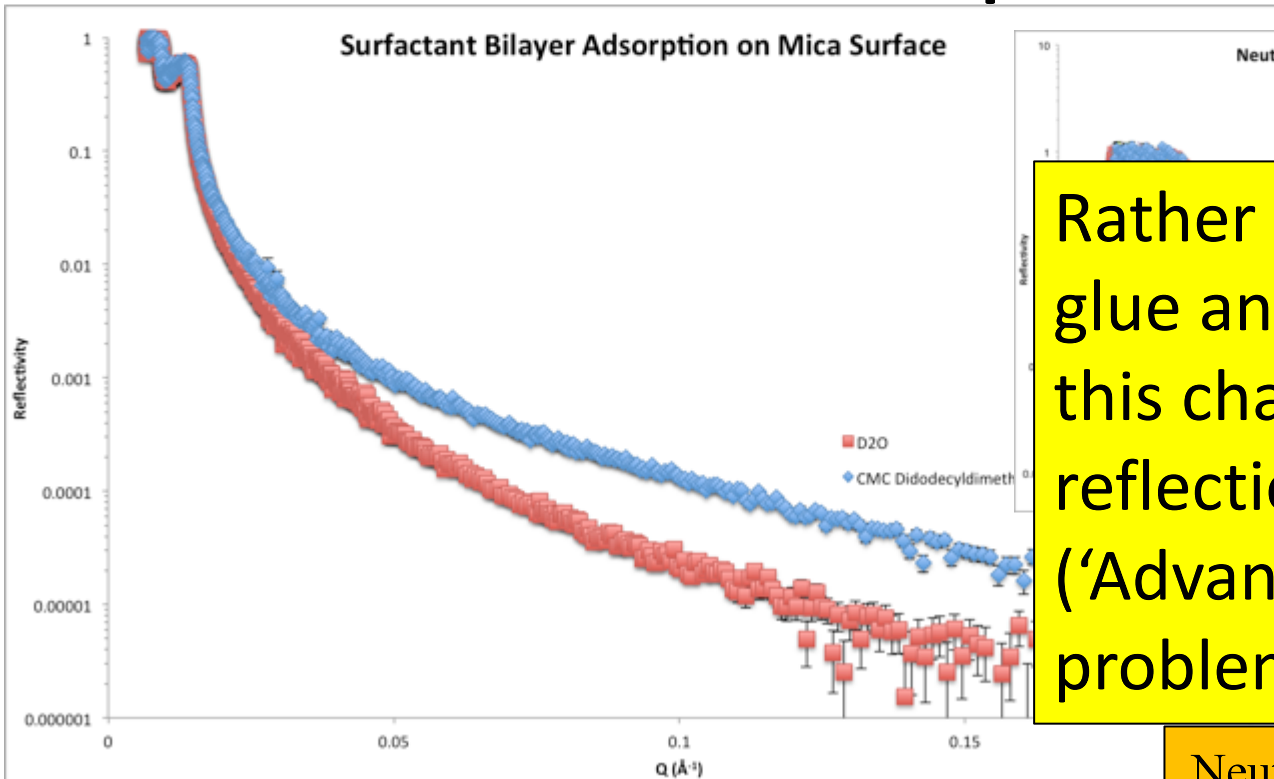
‘Peeling’ Mica

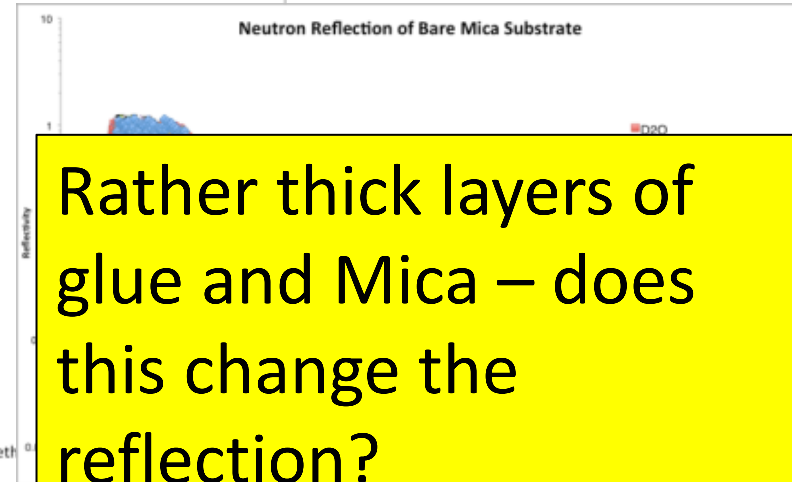


Support very thin layers on solid substrate and ‘peel’

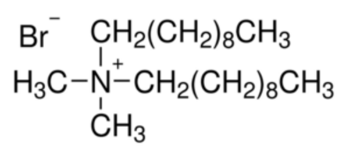
Does it work?.......
Can we see adsorption on mica in solution?…

Surfactant adsorption on mica





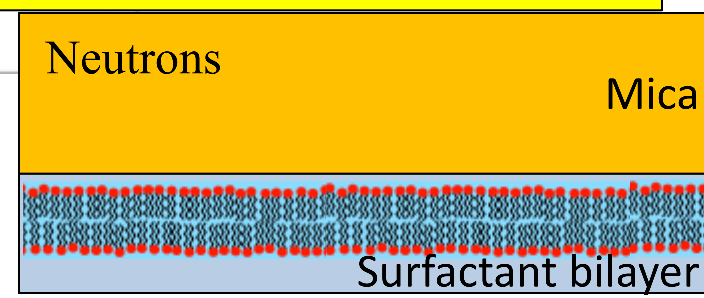
Rather thick layers of glue and Mica – does this change the reflection? ('Advanced' tutorial problem)

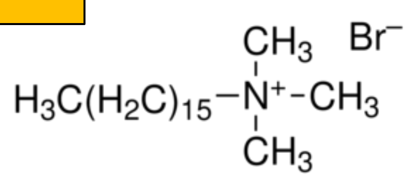


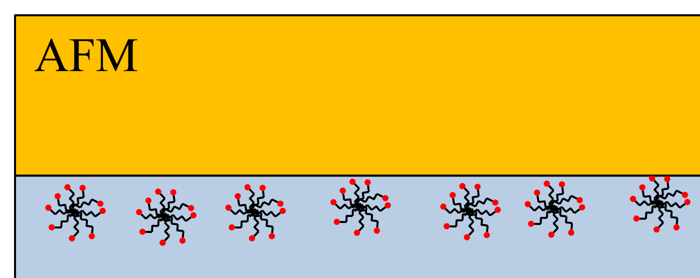
Non-invasive:

(a) DiDoDAB: Complete bilayer (same result as AFM)

Neutrons non-invasive



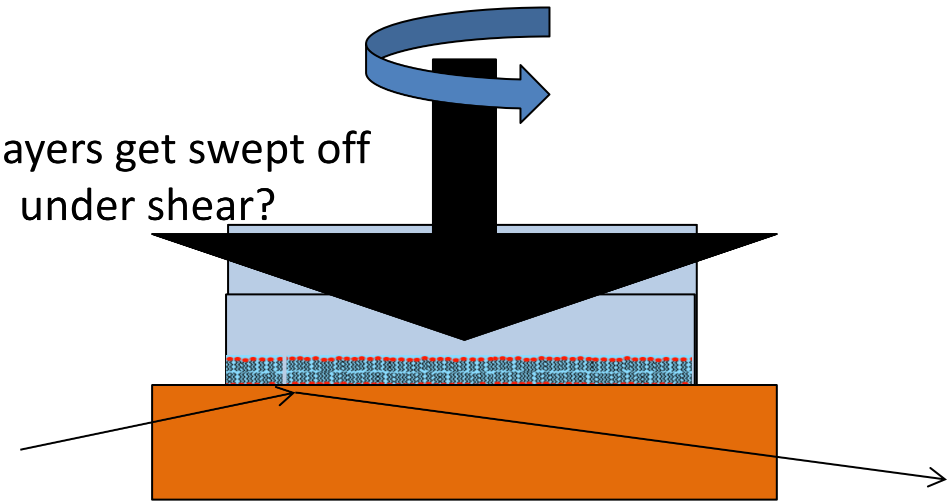


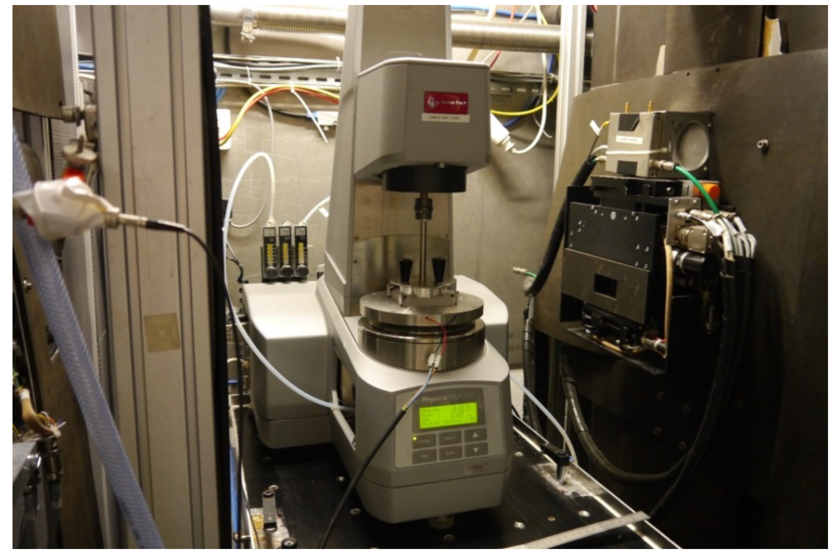


(b) CTAB: NOT same as AFM

Example: Layers under Shear

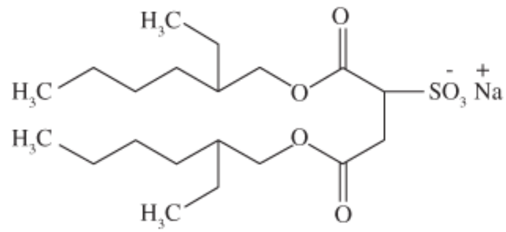
Do layers get swept off under shear?



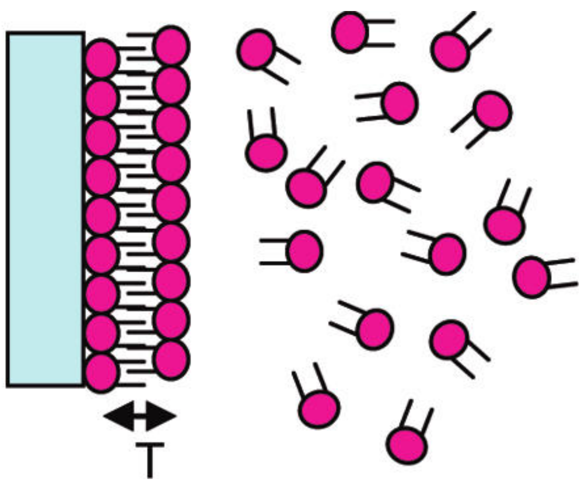


(steady and oscillatory shear)
Modest shear rates < $500 s^{-1}$
(pipe flow, or flow over rock-beds)

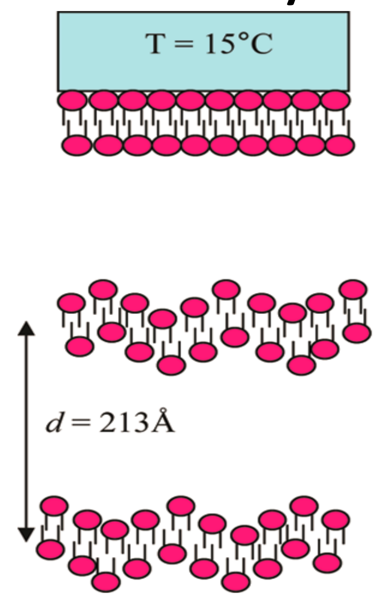
Shear/Flow:
AOT on Alumina/water



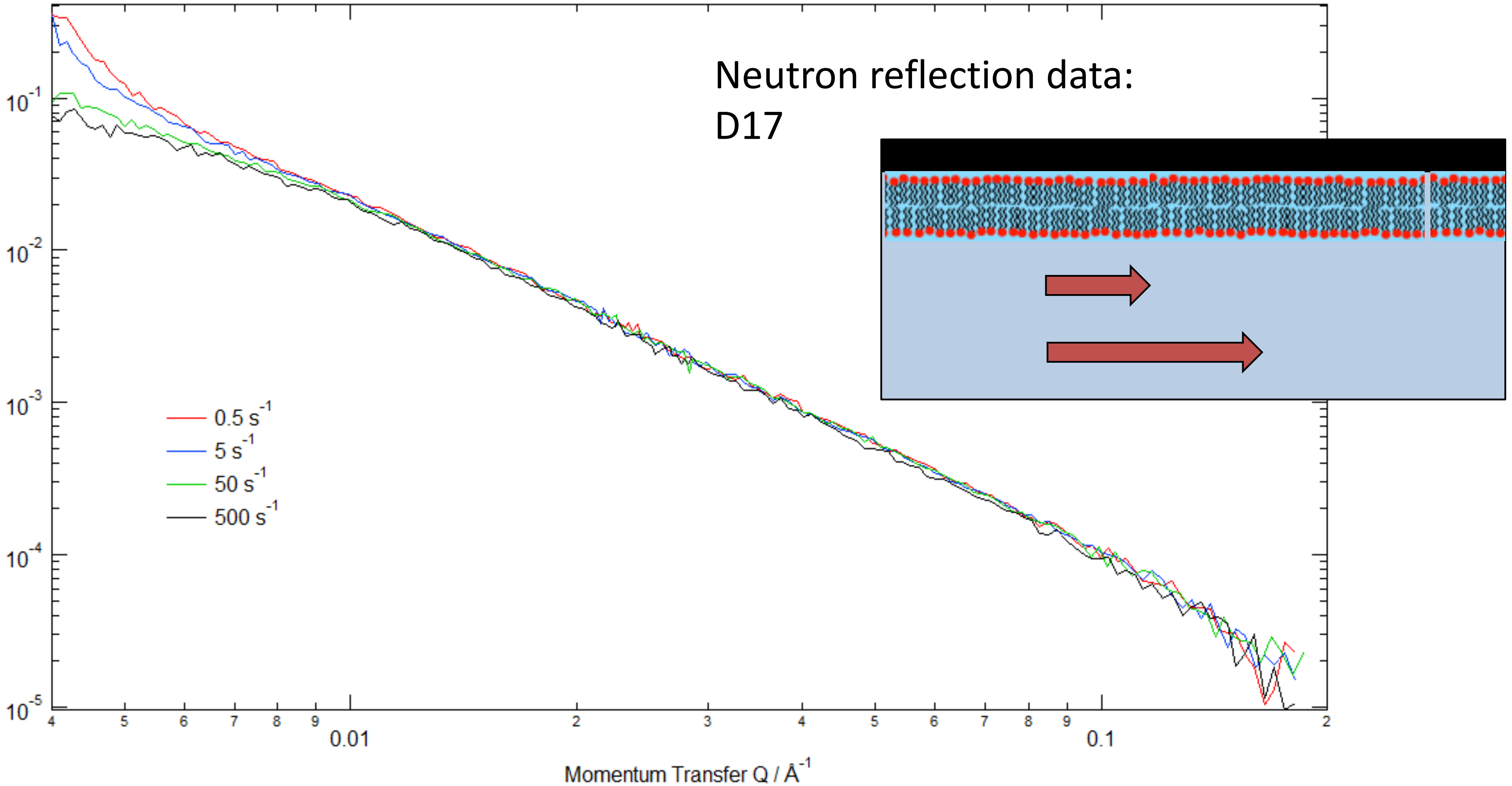
Thin layers



Thick layers



Effects of Shear: neutron reflection: Thin layer

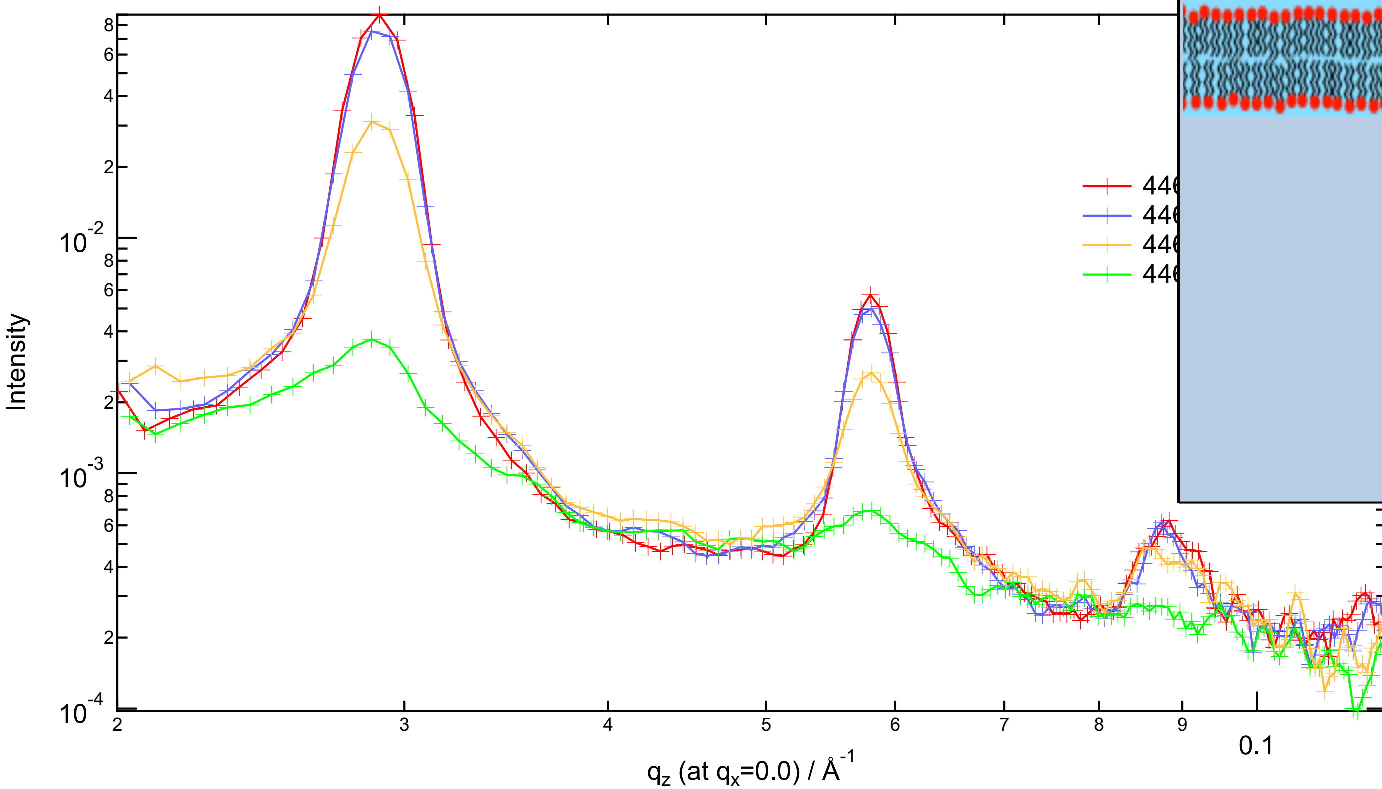


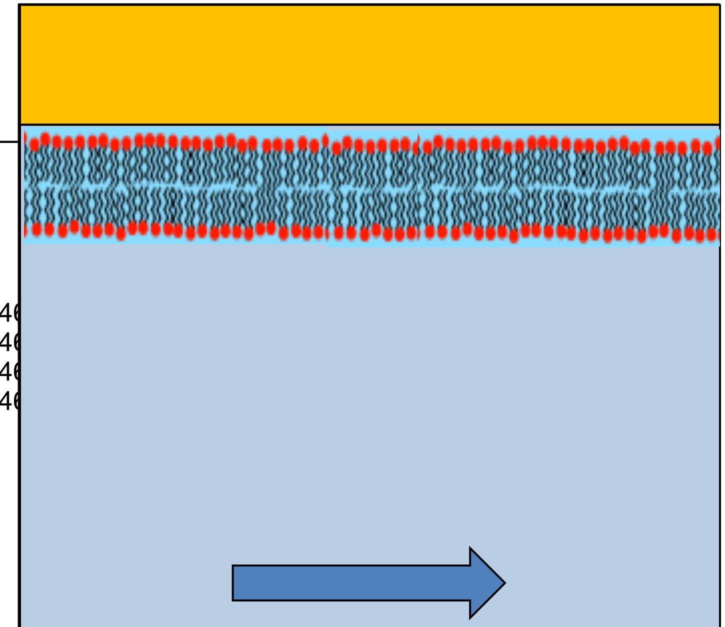
SURFACTANT BILAYER (thin layer approx. 30A thick)
Data: under steady shear increasing to approx 1000s^{-1}:

Shear has no effect on thin layer

Very thin layer - too thin for significant shear effects.
(Same result under oscillatory shear).

Effects of Shear: neutron reflection: Thick layer





Shear has big effect on thick layers

Higher shear rates planned

Adsorbed multi layer

Thick layer!!

Under steady and oscillatory shear: ➔ BIG effects

Critical shear rate that delaminate the layers

Talk Outline

- Examples of surfaces / neutron applications:

Adsorbed layers:

In-plane structure – 2D diffraction

Out-of-plane structure – reflection

What's adsorbed? (IQNS - dynamics)

Colloidal dispersions (dominated by surfaces)

What's on the surface? SANS

What arrangement ? SE- SANS

Liquid structure PDF (NIMROD)

Quasi-elastic neutron scattering

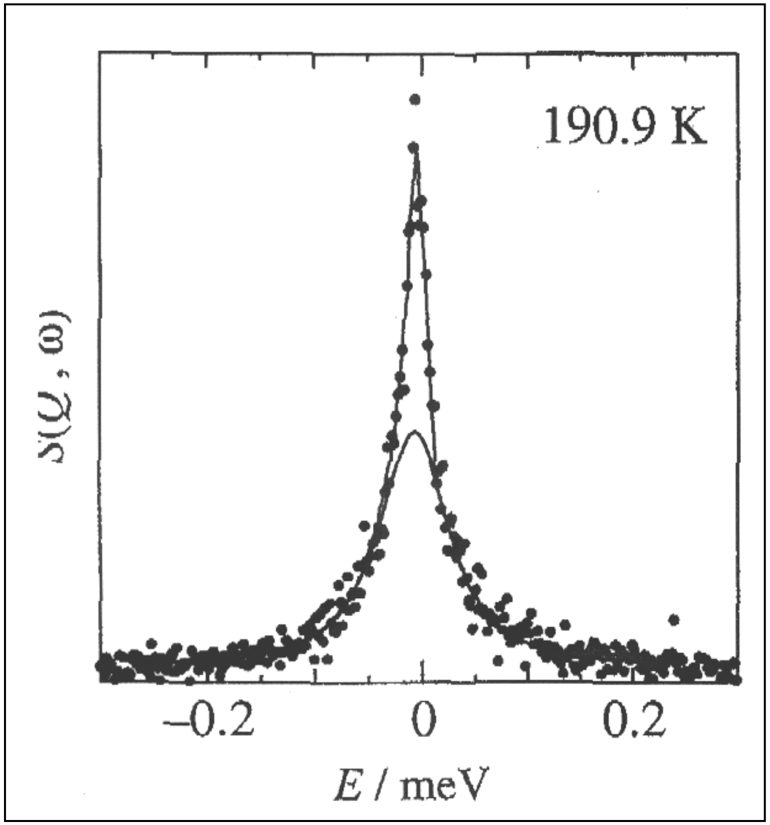
- Diffusive motions
- How long to move out of your ‘box’

Incoherent Neutron Scattering

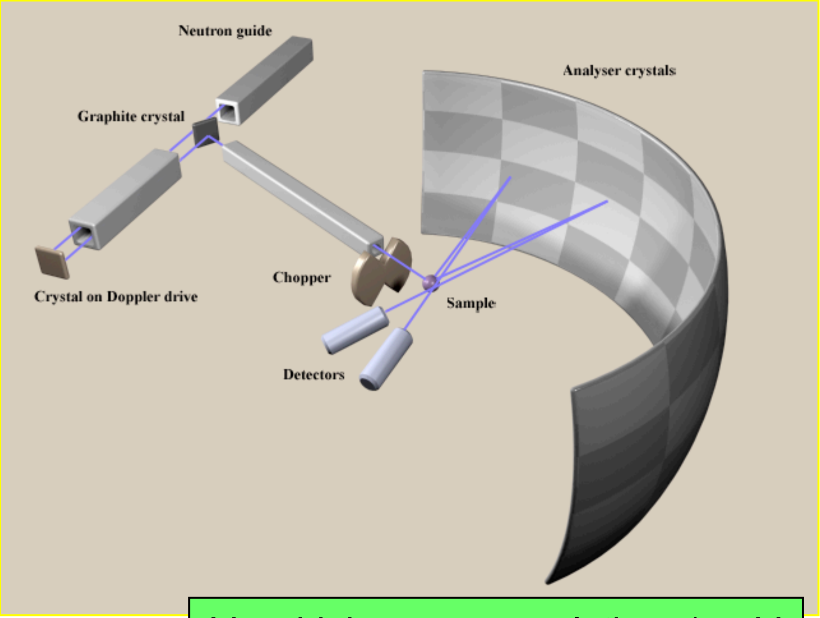
- Actually get a distribution of scattered neutron energies:

Details of the angular dependence of the scattering can inform us about molecular motions

Intensity

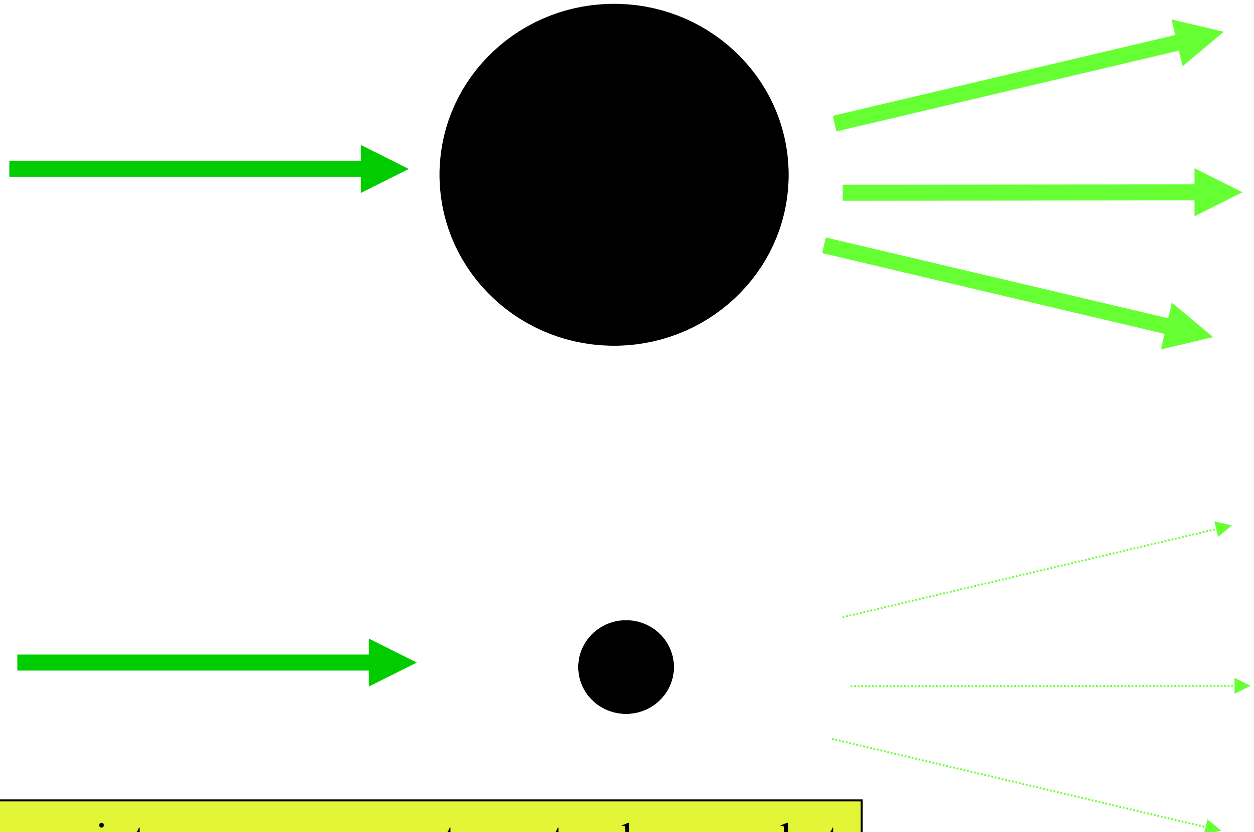


ΔE



Very high energy resolution, 1 μeV
IN10/IN16/IRIS

Hydrogen and Deuterium are different



Hydrogen – very strong scatterer

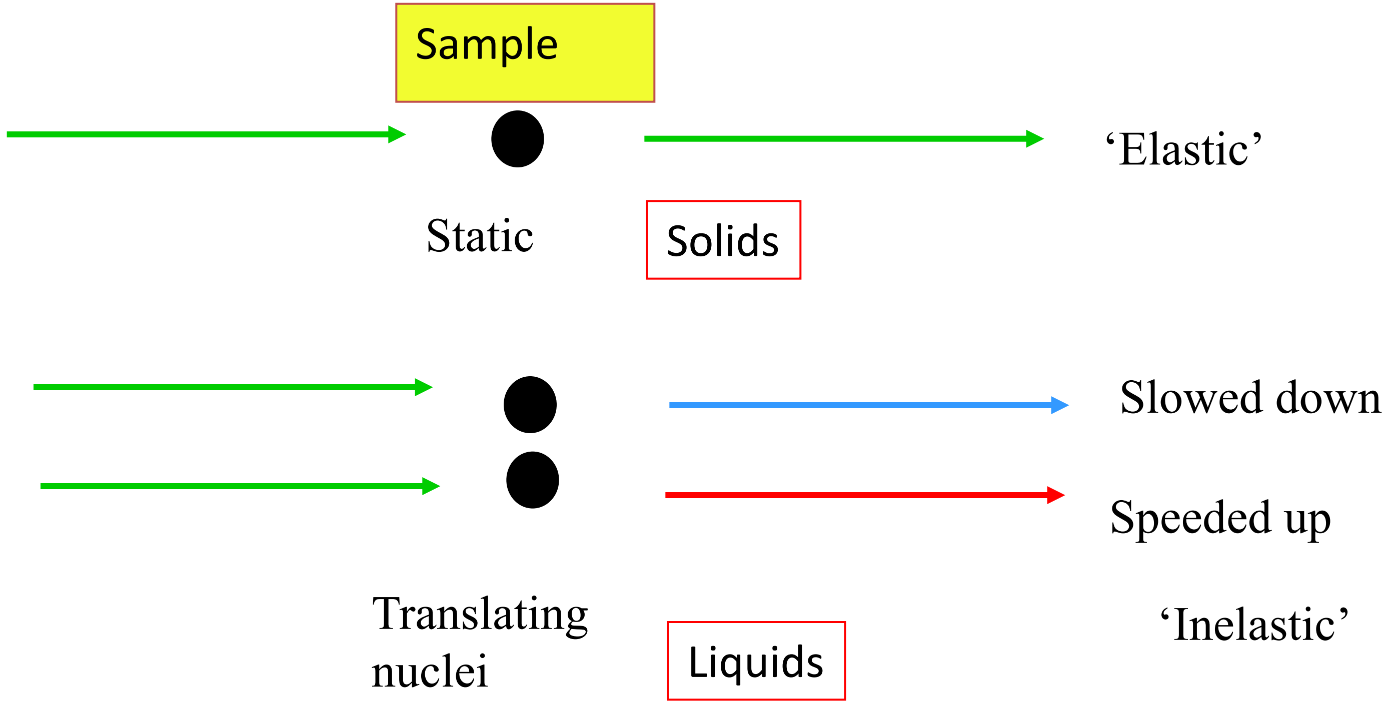
Deuterium – weak scatterer

In a mixture can use neutrons to choose what we ‘see’

Quasi-elastic Incoherent Neutron Scattering (IQNS) – ‘Dynamics’

- Isotopic substitution to distinguish components (H>>D)
- Dynamics to differentiate adsorbed from non-adsorbed materials

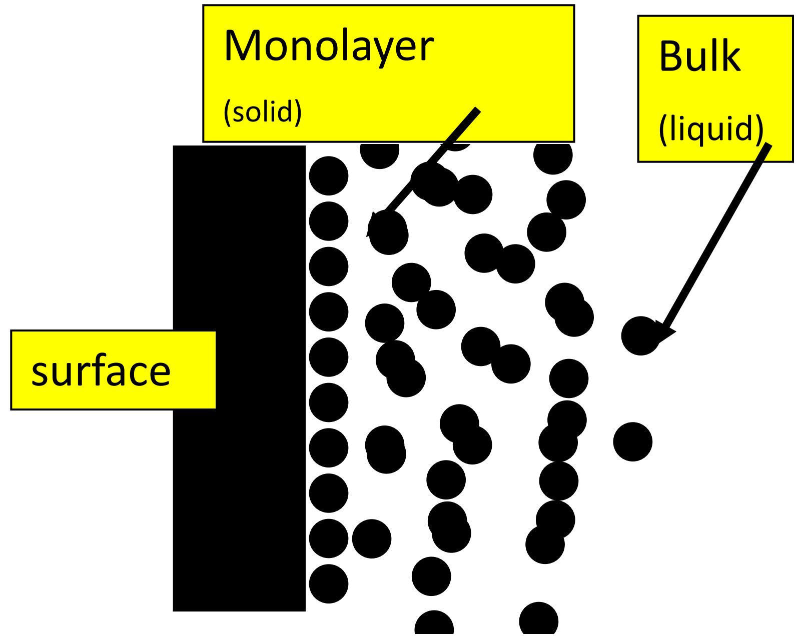
- Neutrons can exchange energy with sample nuclei:



Intensity of elastic scattering → Amount of adsorbed material

Adsorbed Molecules are different

Adsorbed layers are 'static'

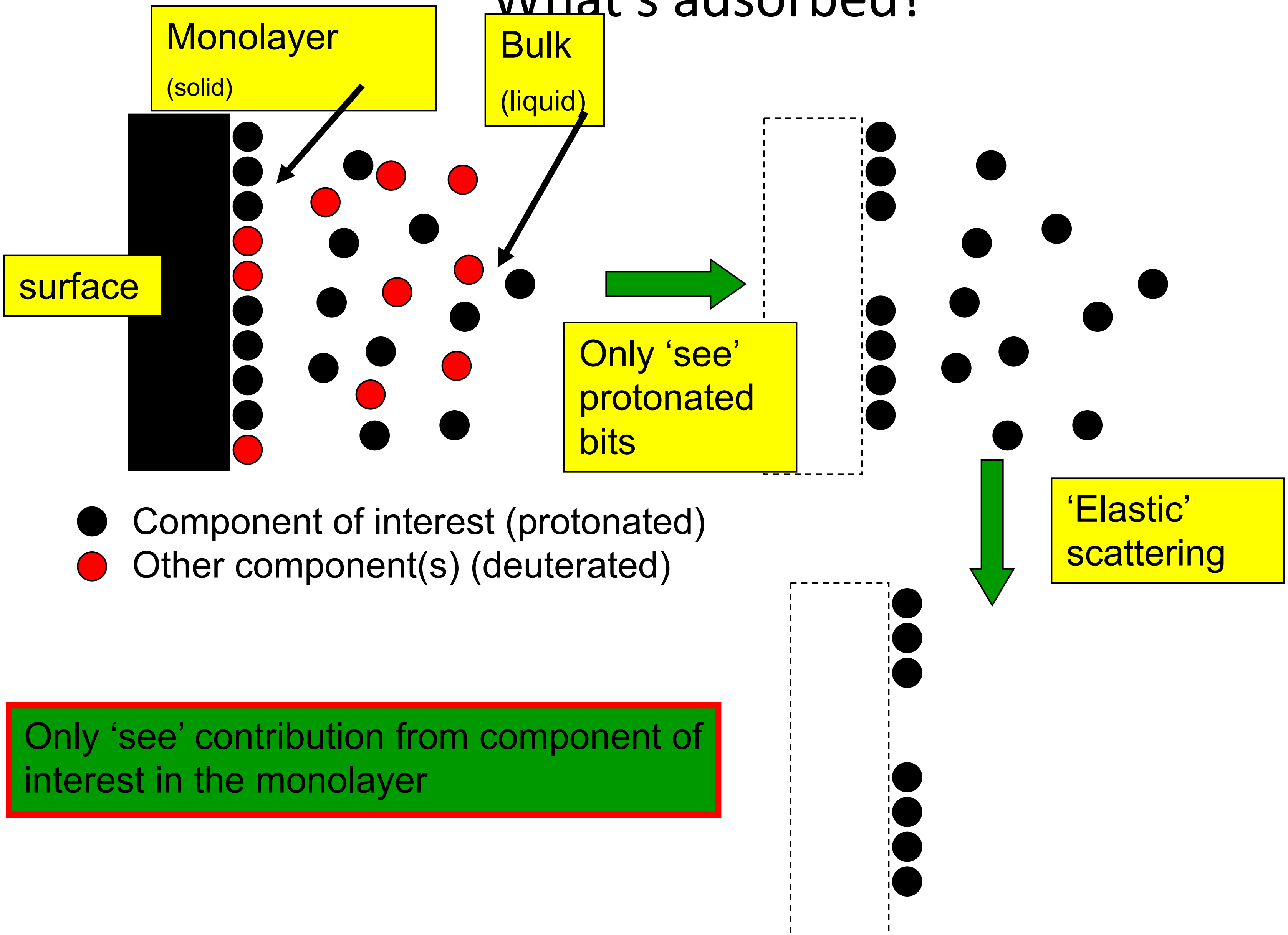


Liquids are 'dynamic'

Use mobility to distinguish adsorbed layers

‘IQNS’

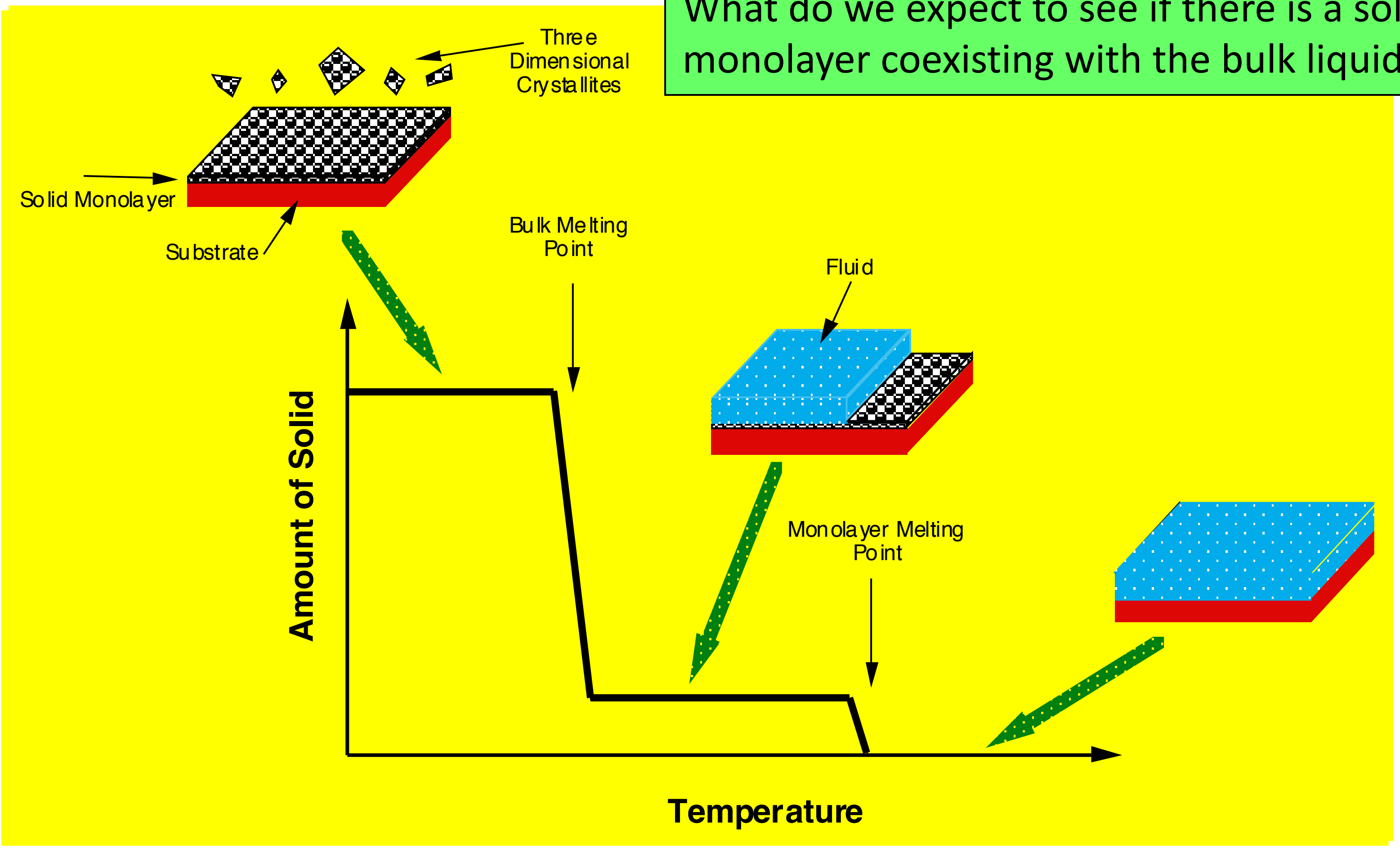
What’s adsorbed?



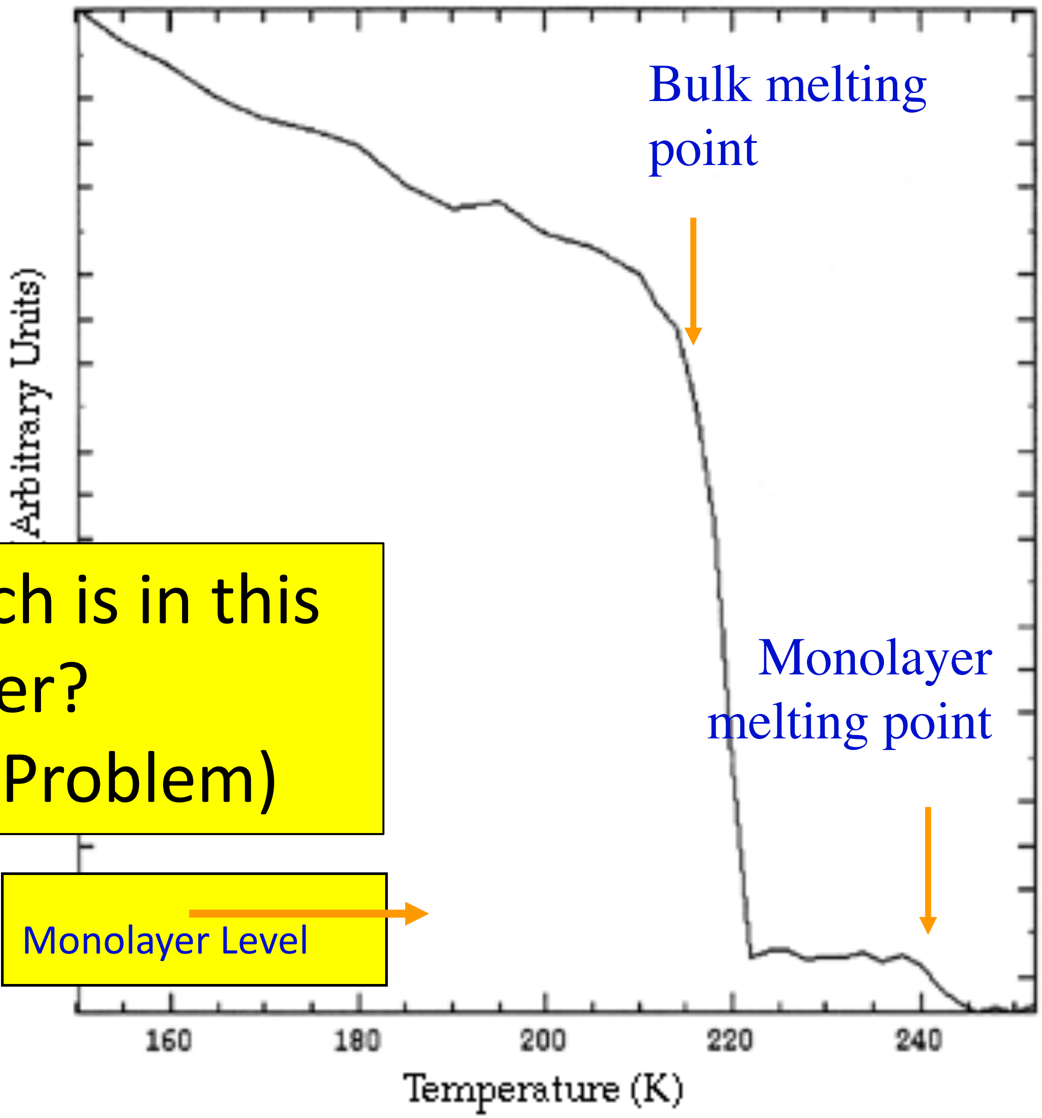
Only ‘see’ contribution from component of interest in the monolayer

Incoherent quasi-elastic neutron scattering (IQNS)

What do we expect to see if there is a solid monolayer coexisting with the bulk liquid?



IQNS Results: Octane on Graphite

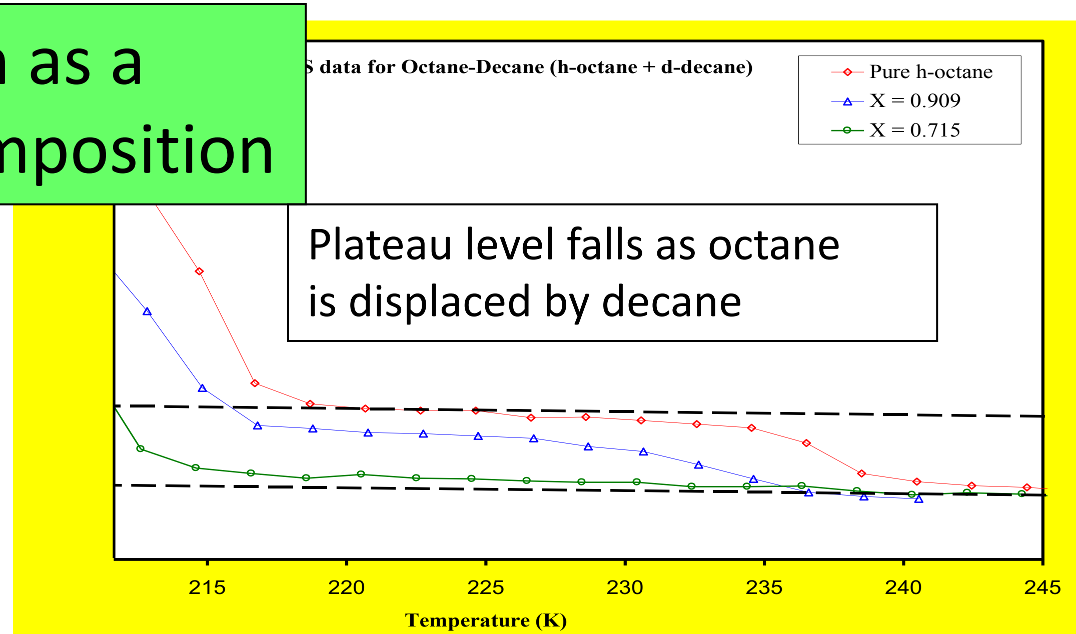


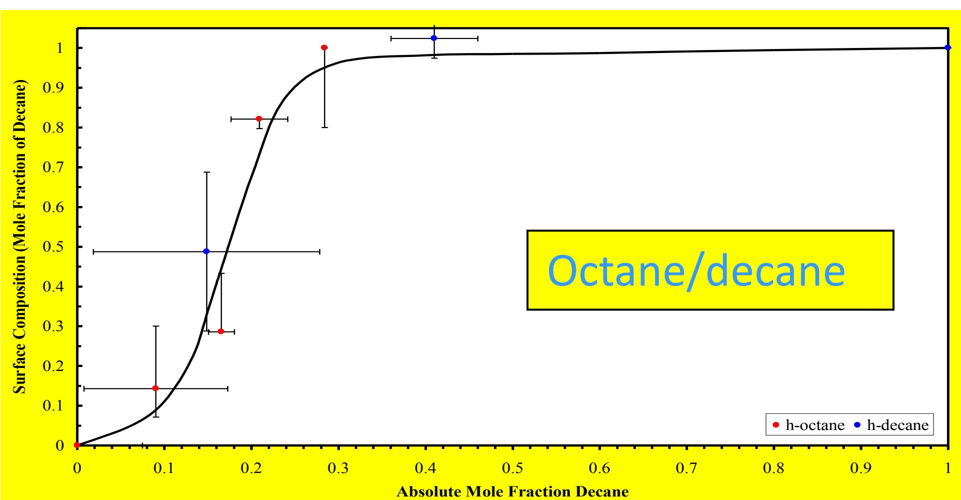
How much is in this monolayer?
(Tutorial Problem)

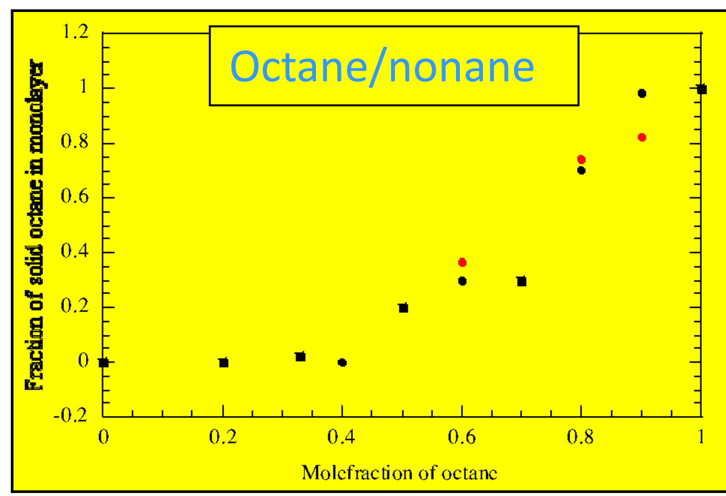
Monolayer Level

What’s adsorbed: (IQNS) Results from mixtures

Monolayer composition as a function of solution composition

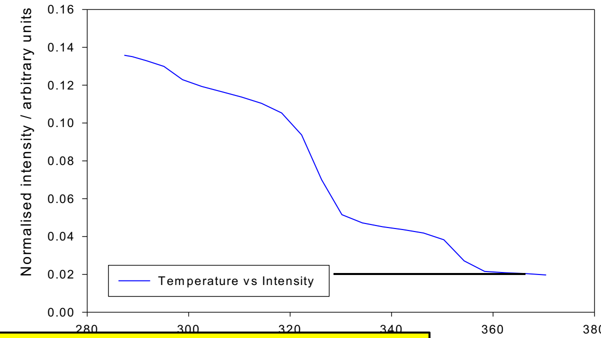






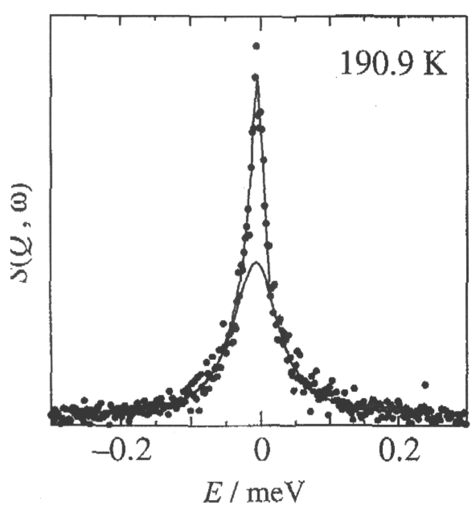
Dynamics of Adsorbed Layers

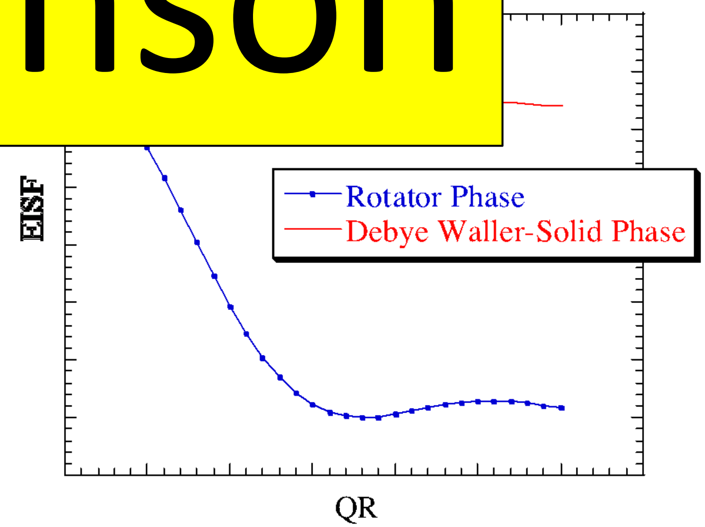
- Distinguish solid from liquid
  – elastic scattering
- Diffusion coefficient of liquid layers
  – Width of the quasi-elastic peak



Mark Johnson

- Rotati
  – q-dependence of the elastic scattering





Talk Outline

- Examples of surfaces / neutron applications:

Adsorbed layers:

In-plane structure – 2D diffraction

Out-of-plane structure – reflection

What's adsorbed? (IQNS - dynamics)

Colloidal dispersions (dominated by surfaces)

What's on the surface? SANS

What arrangement ? SE- SANS

Liquid structure PDF (NIMROD)

What are Colloids?

• T

• D

Exampl

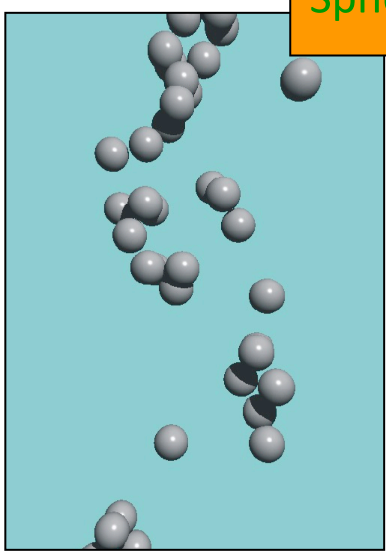
Want to know

What shape are the separate colloids

What orientation

What arrangement

Spheres



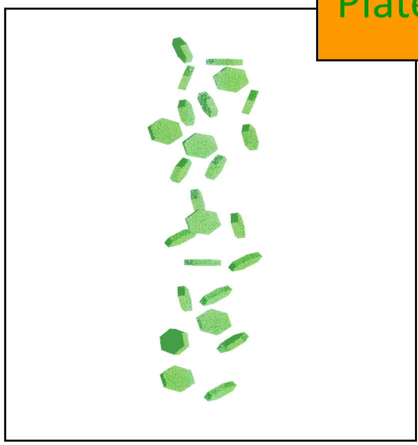
Important flow properties

Need to 'look' through metal cells

Opaque samples

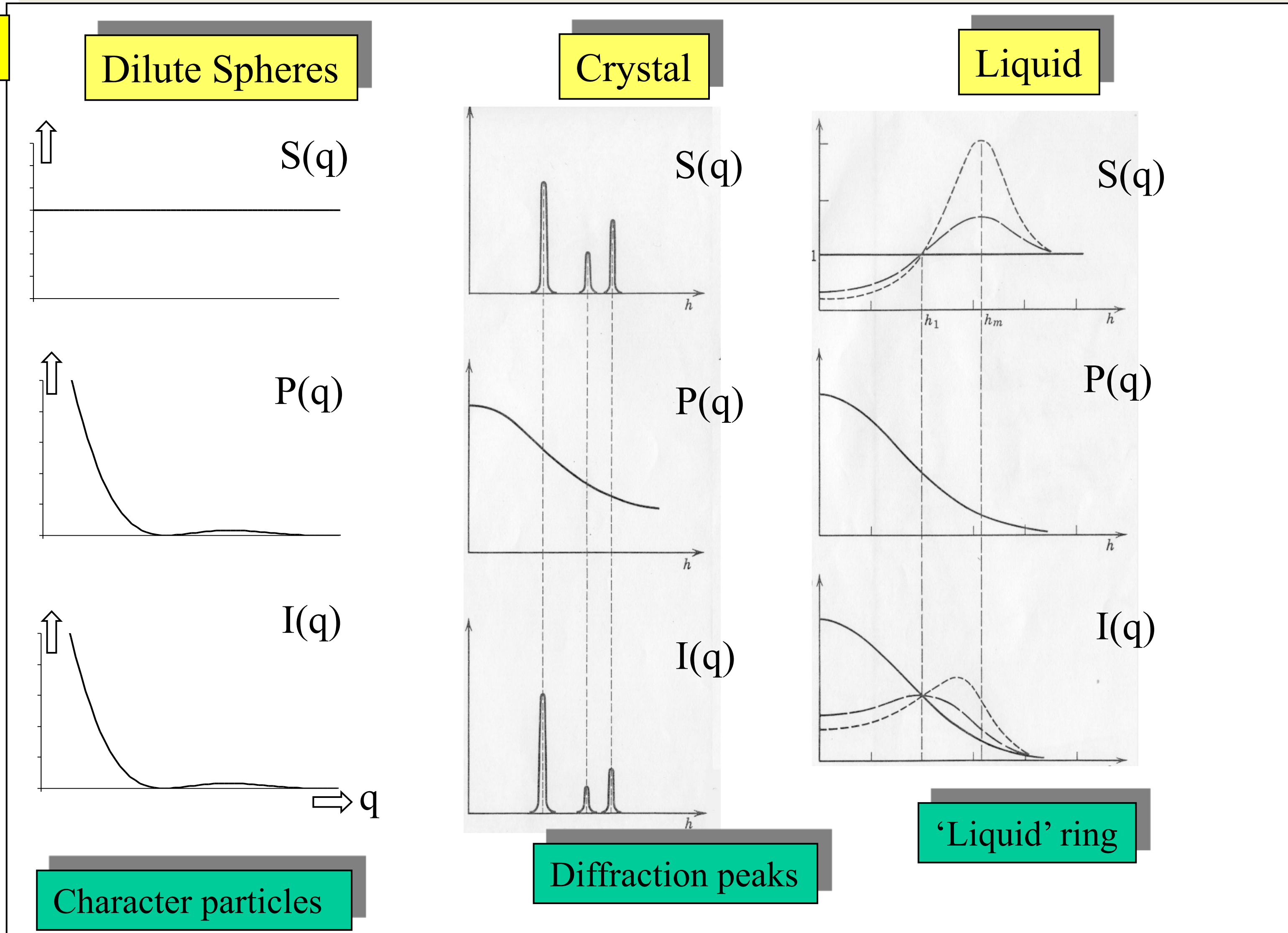
Neutron Transmission

Plates



Form and Structure Factors

$I(Q)=P(Q)S(Q)$

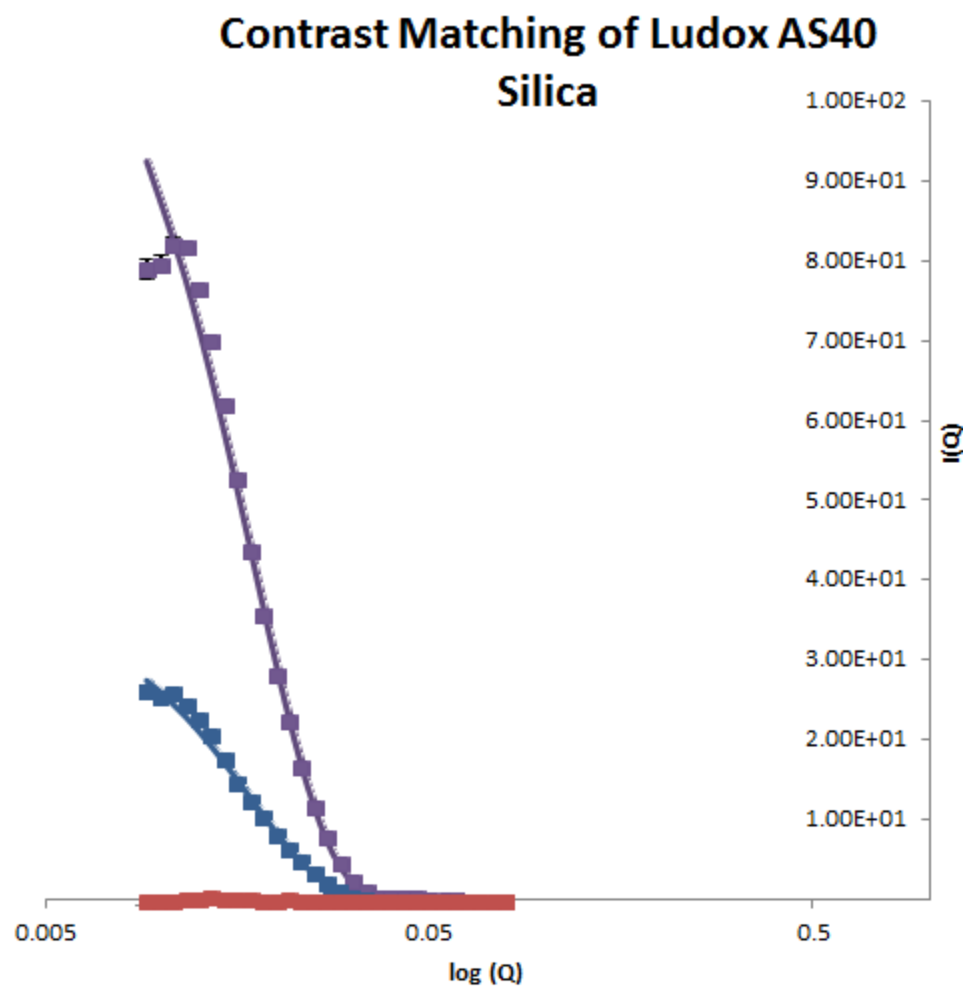


SANS: single colloid scattering (Dilute) What’s on the surface

Mixtures: **Contrast matching**: ‘magic’

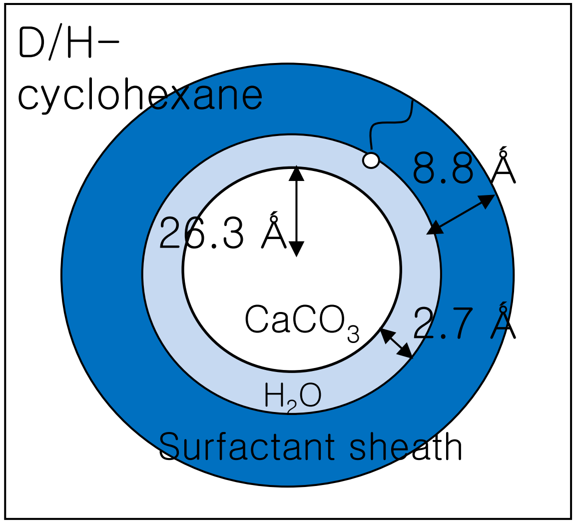
- Scattering from silica in water: Mixtures of H_2O and D_2O

Change scattering of water (refractive index = ‘colour’): silica –disappears



‘See’ each component of a mixture separately
Simplify complex systems

Small Angle Scattering: - P(Q)
Dilute core-shell particles
Thin water layer on calcite colloids in oil



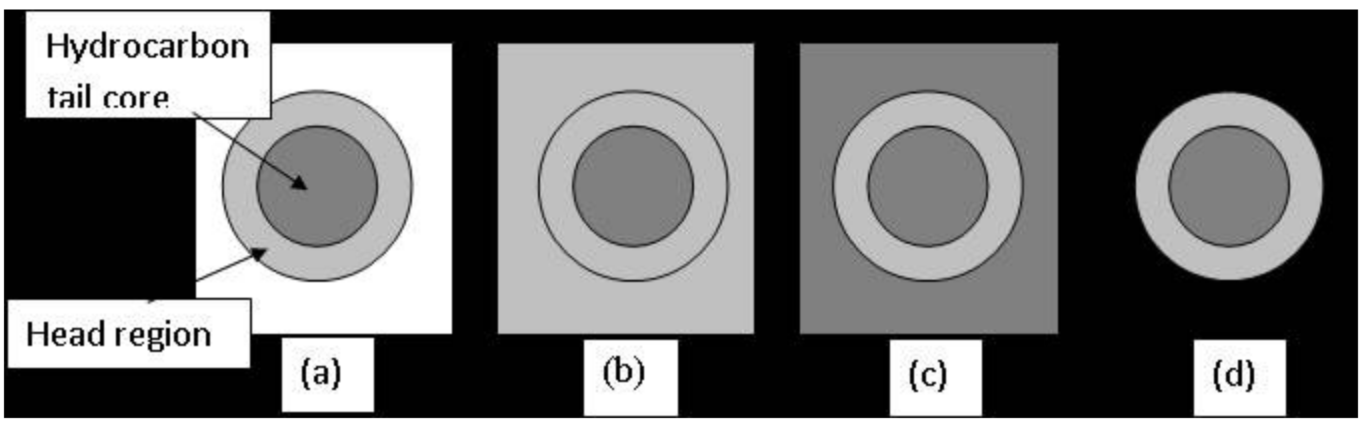
P(Q) form factor for core-shell more complex
Structure: core/water/surfactant/oil

'Contrast variation'
H_2O and D_2O mixtures
change 'colour' of different bits

Thanks to Richard Heenen and co

Contrast variation:

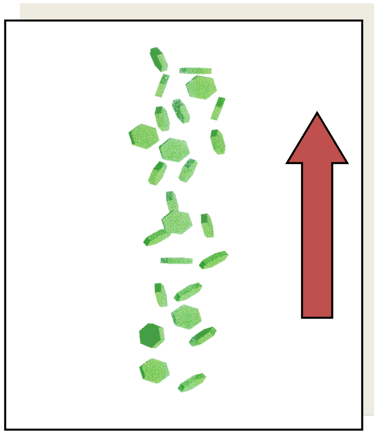
- Enhance sensitivity to each bit by selective deuteration



IF TIME
SANS: Single particle orientation

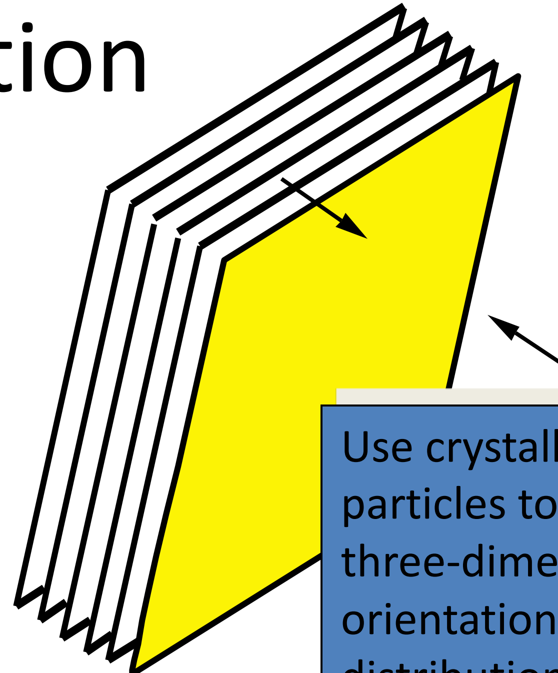
- SANS of plate-like particles

SANS: single particles - orientation



Flow
Direction

When is the extent of orientational order?
Under flow?
With particle size?
Aspect ratio?
Concentration?



Use crystalline nature of particles to obtain full three-dimensional orientational distribution function

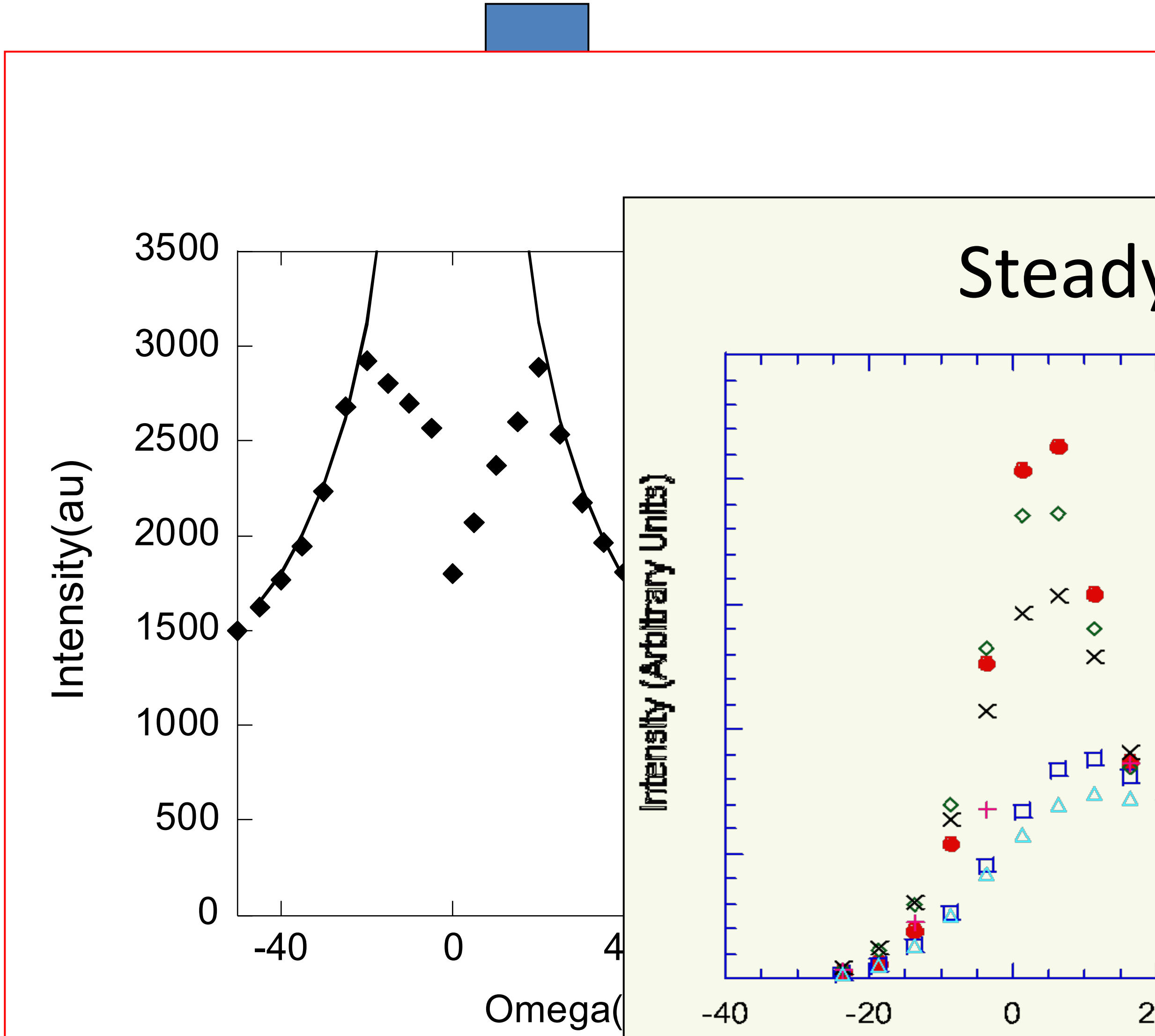
Anisotropic Particles

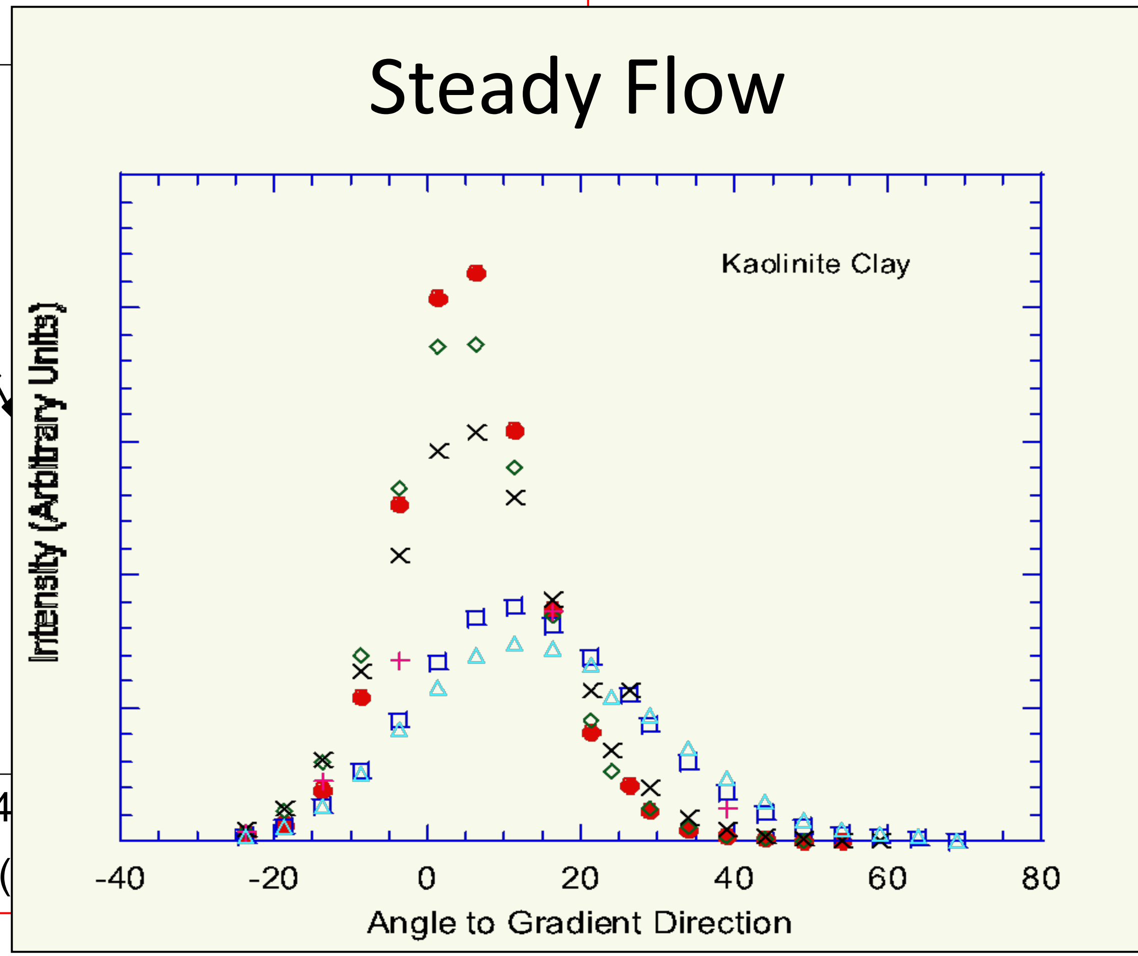
Completely random particle distribution => ‘powder’ ring

Perfectly aligned => single ‘spot’

Preferred orientation => ‘arc’ of intensity

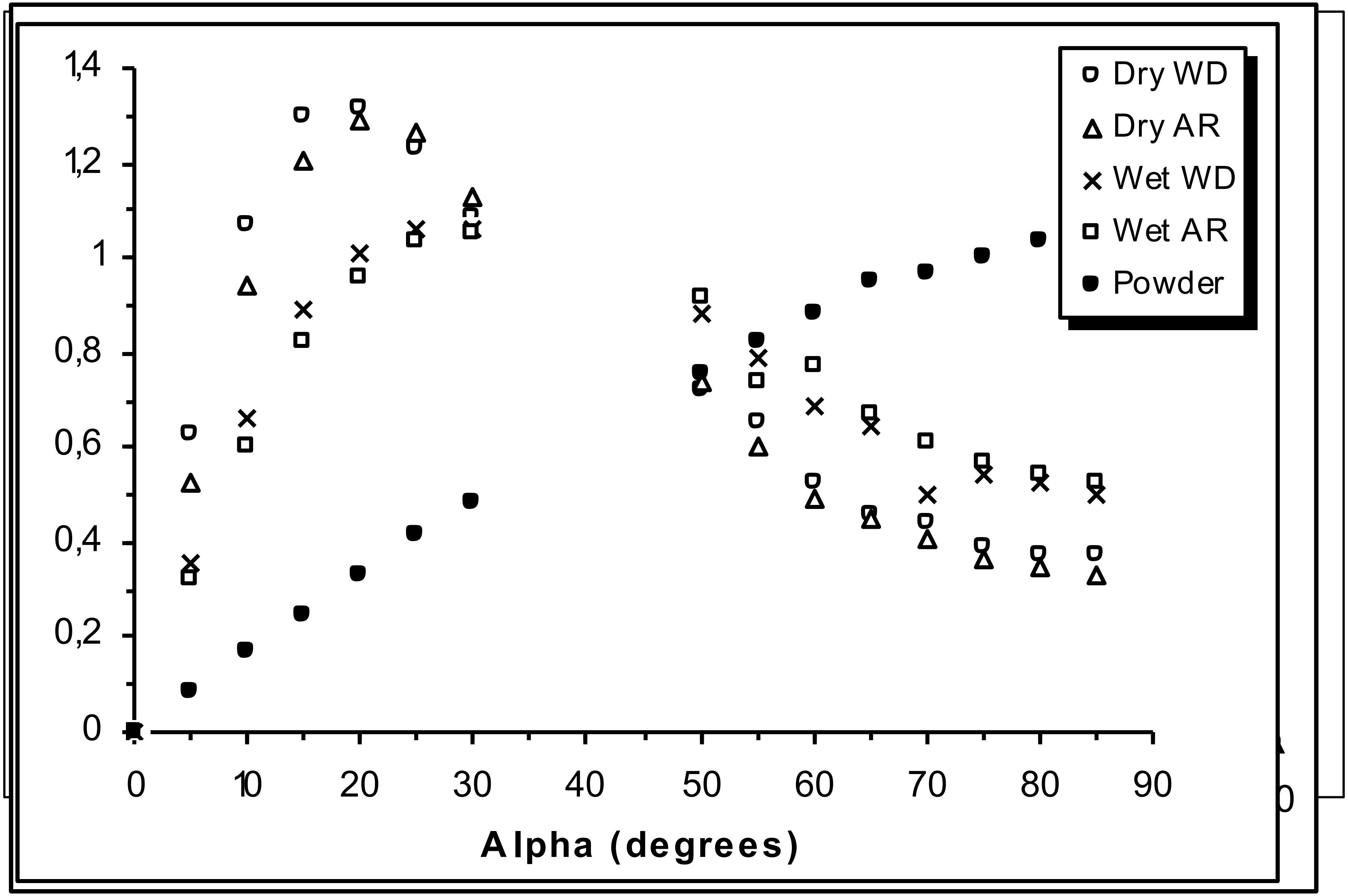
Measuring orientational order of plates





Orientational order of the plates in flow

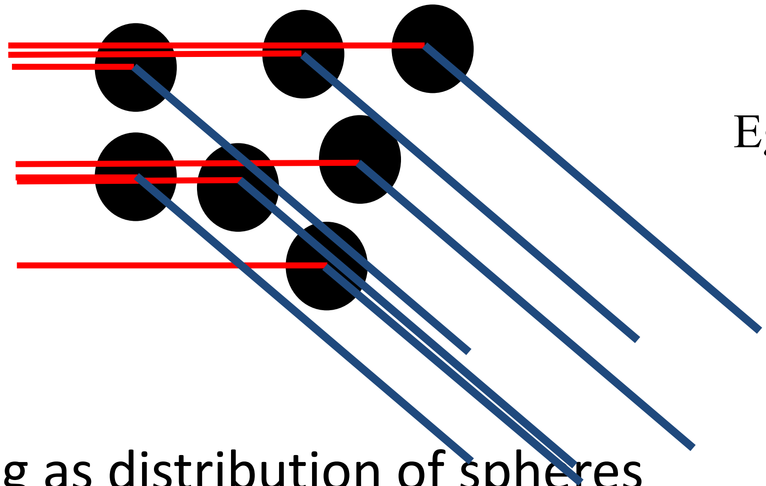
Dense Clay pastes under static and cross-flow conditions



Two colour cars

END of EXTRA BIT

SANS: Interference Between Objects



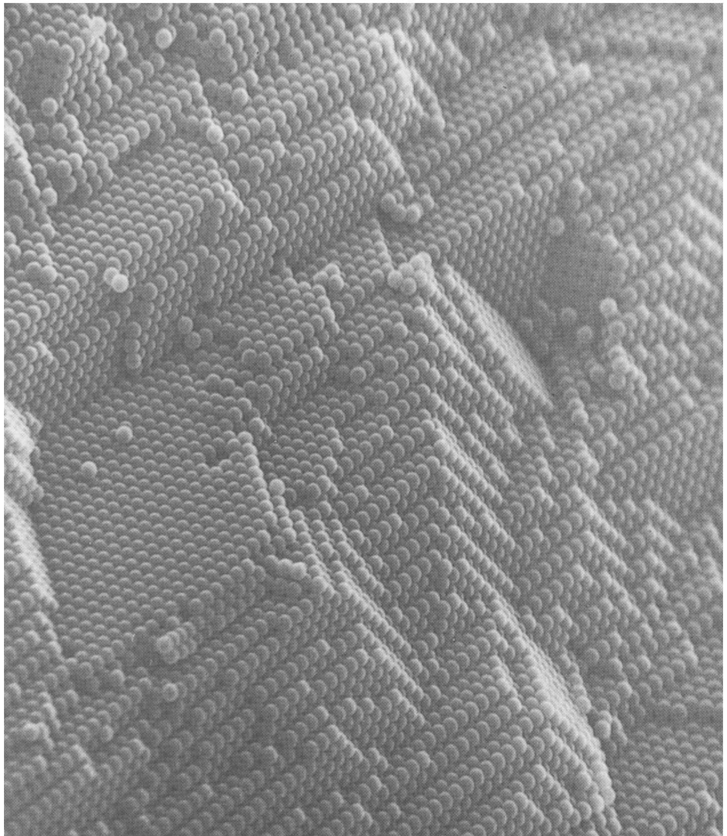
Eg Colloidal dispersion

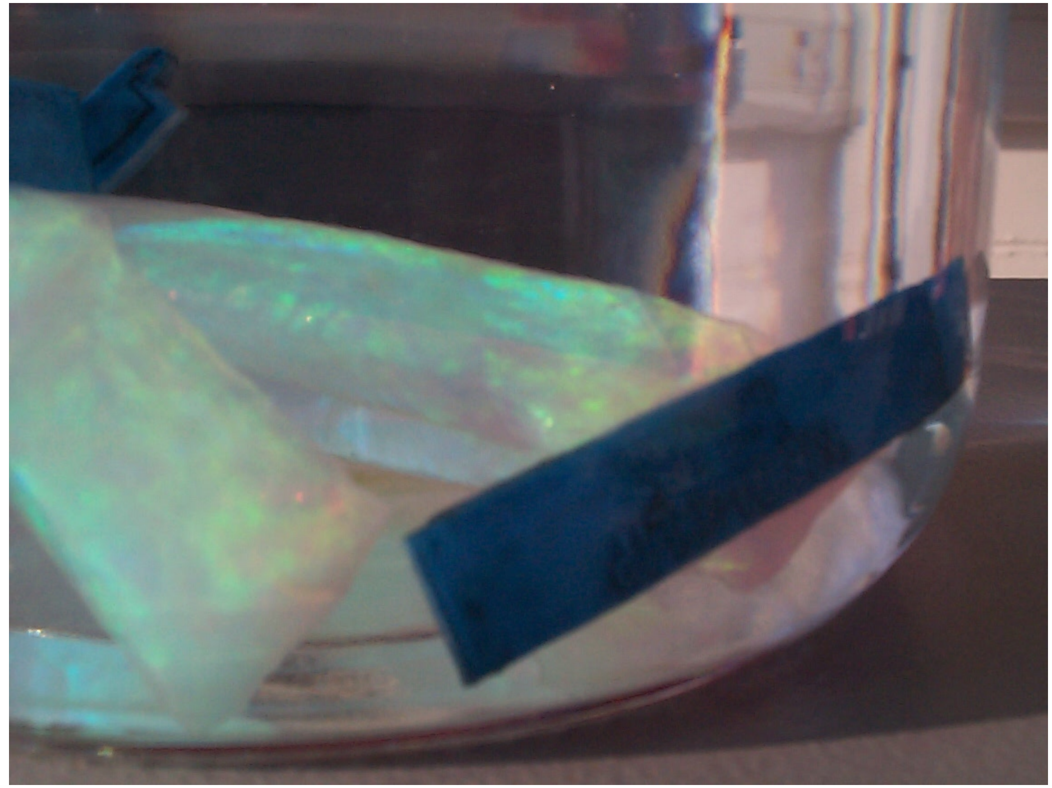
- Consider scattering as distribution of spheres
  - we know scattering for isolated object, e.g. spheres (P(Q))
  - S(Q) is called the interference or ‘structure factor’ arising from interference of scattering from different colloids.
  - Measured intensity is:

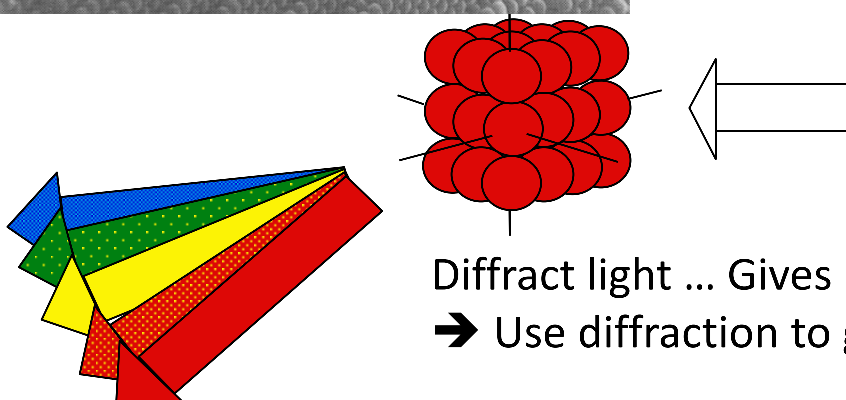
$$I(Q)=P(Q)xS(Q)$$

- Other systems:
  - Crystal - unit cells repeat on a regular lattice

Colloidal crystals of spheres



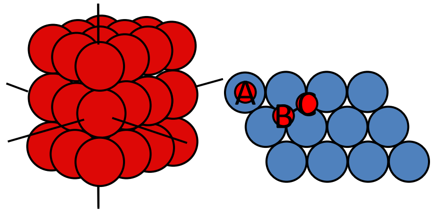


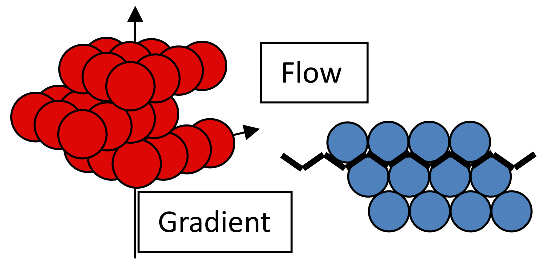


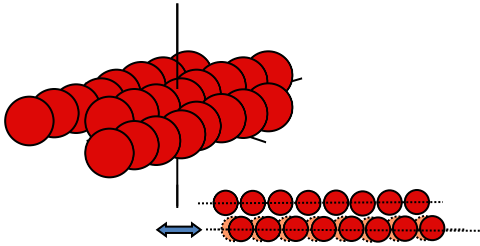
Diffract light … Gives 'diffraction patterns'

➔ Use diffraction to give structure

Colloidal Spheres under flow





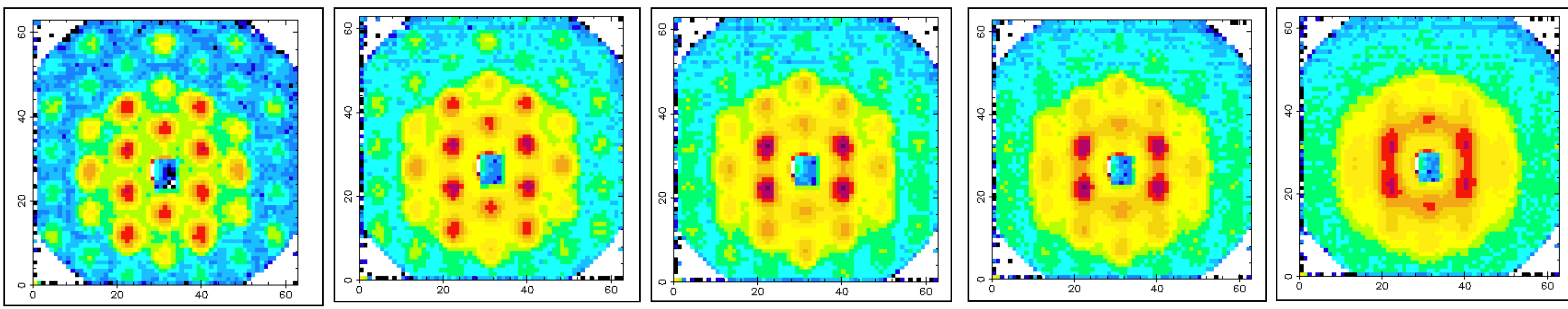


Crystal
Perfectly ordered sequence
of perfect hexagonally ordered layers

'Layers'
Perfect hexagonally ordered layers
Sliding over each other with many different positions

'Strings'
Particles in lines

Increasing Shear Rate



'Crystal'

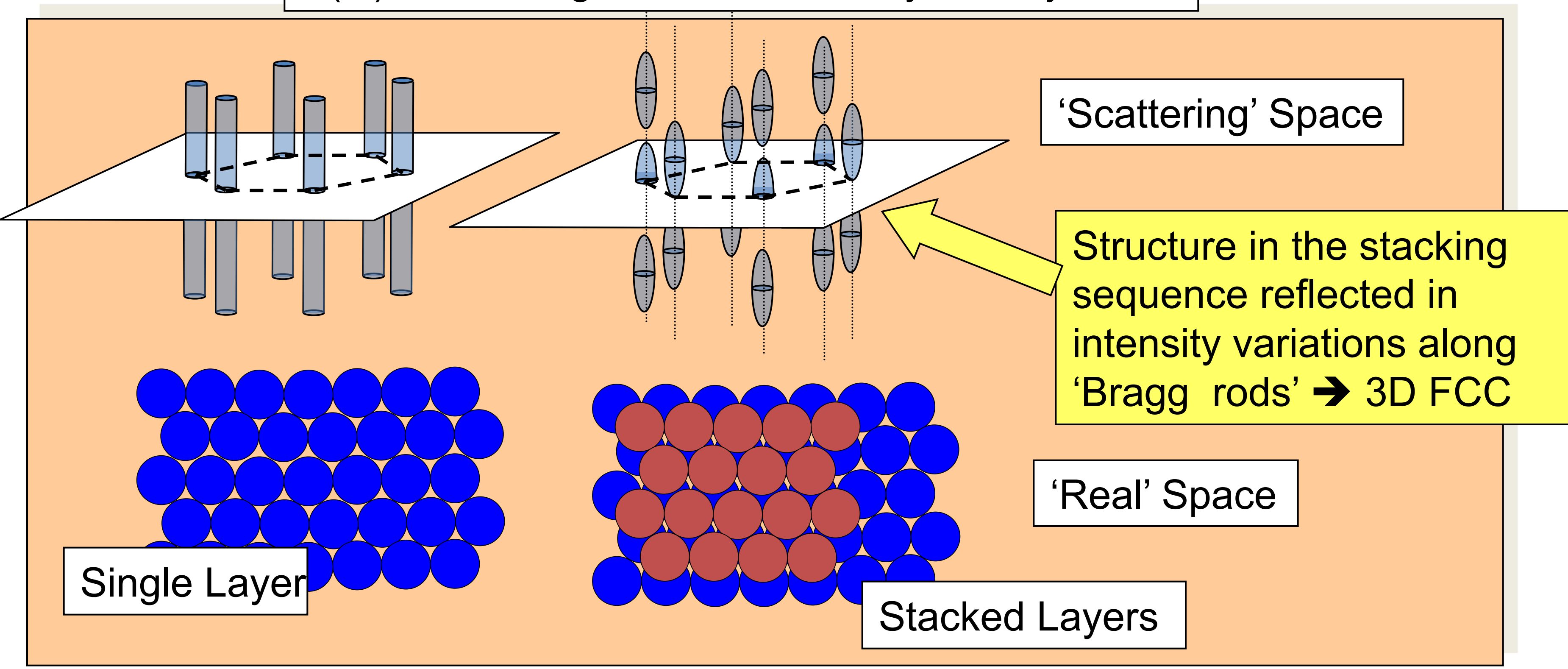
'Sliding layers'

'Strings'

Charged stabilised latex spheres 8%

Behaviour like 'atoms' only much larger scales and slower

S(Q): Scattering Patterns from Layered Systems



IF – TIME

EXTRA BIT SE- SANS

TRICKY!!!!

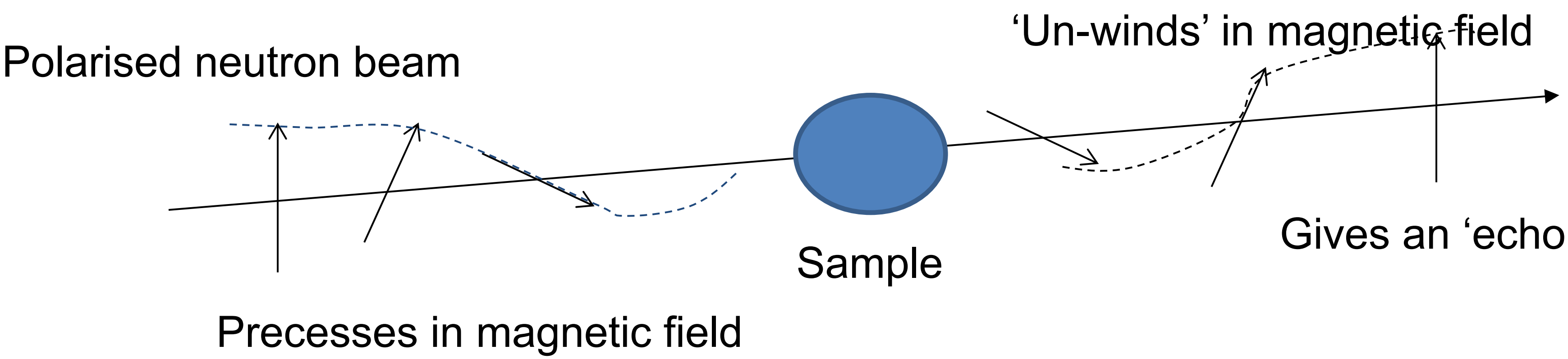
SANS ➔ SE-SANS VERY BIG objects

Big objects are seen at **small** scattering angles (‘Reciprocal space’)
To see scattering by SANS at small angles need VERY tightly collimated beam: BUT THEN NO FLUX!!

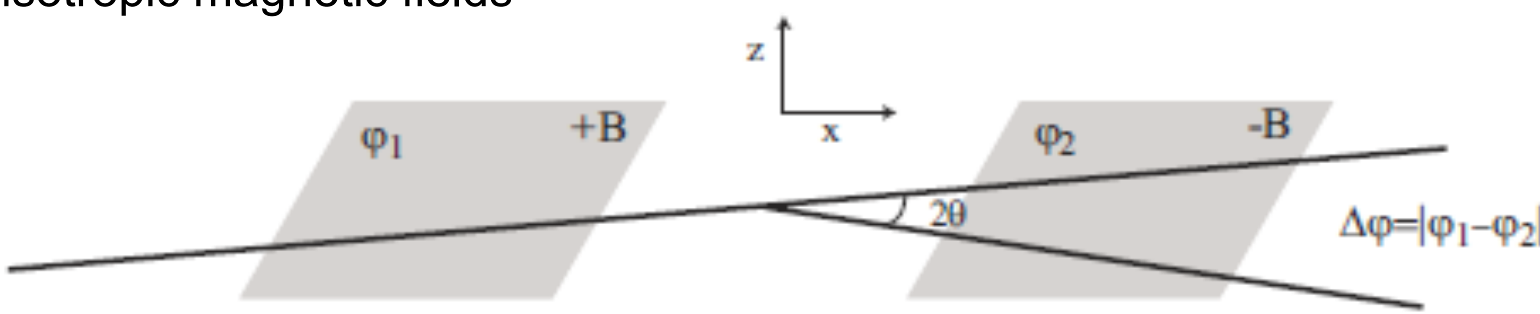
Spin echo SANS ➔ Keep wide open beam and Encode the scattering angle in the neutron spin!!

(VERY CLEVER IDEA THIS!!)

Spin Echo -SANS
Encode scattering angle in the neutron polarisation



Anisotropic magnetic fields



Collect intensity as a function of 'z' (combination of field angle, wavelength etc)
(Precession usually in horizontal plane)

Andersson 2008

SE SANS technique: Basic approach

- Beam polarised in and out
- Polarisation rotates one way and then back
- Depends upon time in the magnetic fields
- If neutrons don’t change direction ➔ big echo
- If neutrons change direction (funny shaped field) ➔ Weaker ‘echo’ or depolarised.
- Spin echo to encodes the angle (q’)

➔ Actually Measure:

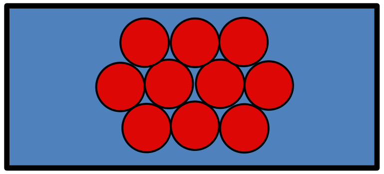
Real space, density-density correlation function, G(z)

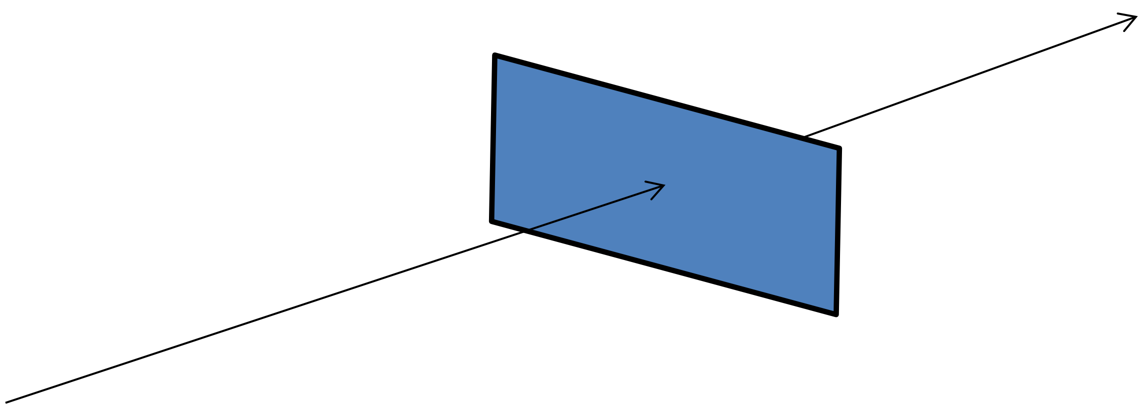
Example: Silica particles in polymer matrix
Colloidal Crystal

- J. Baumberg Samples:

Hexagonal layers of 200nm silica in polymer matrix, 0.47 volume fraction.

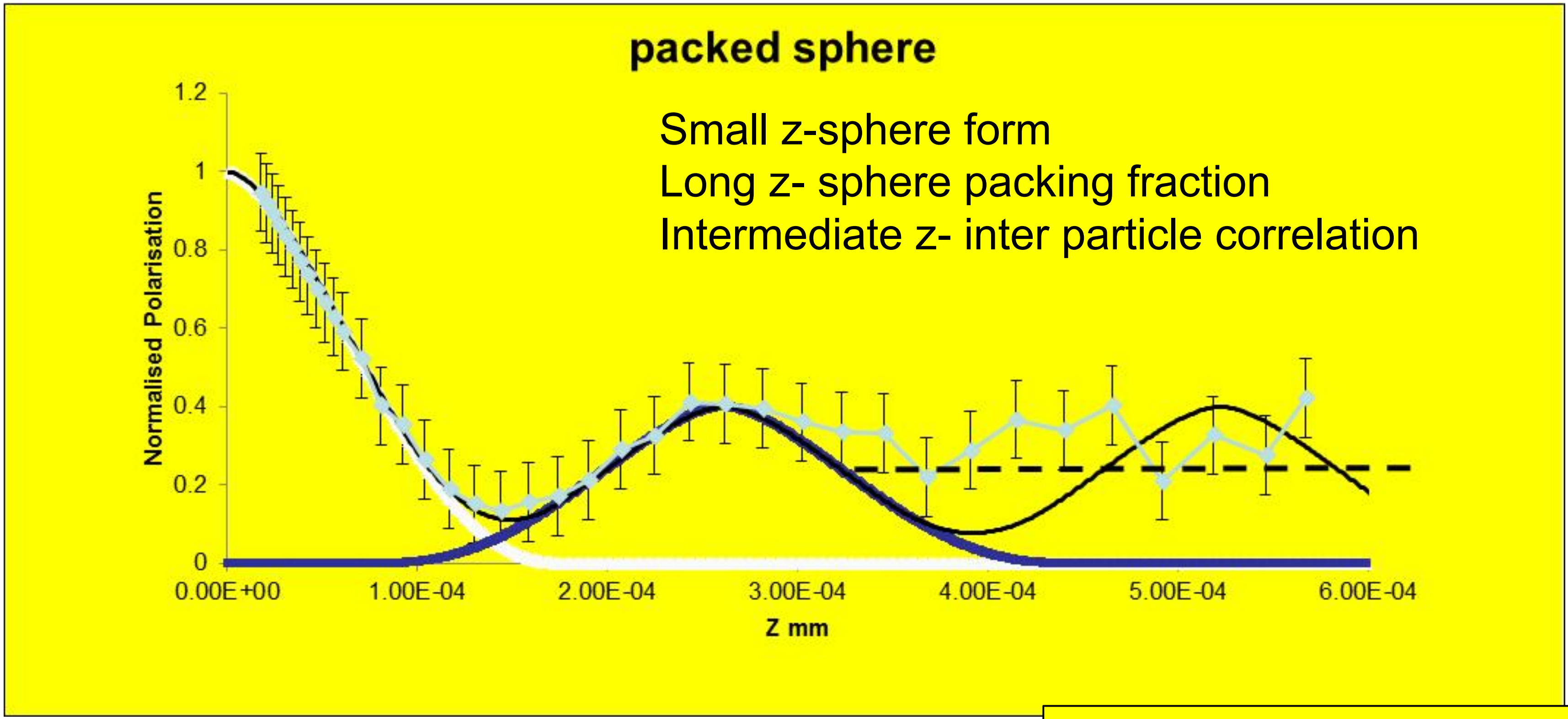
Layers oriented and regularly stacked





Volume fraction 0.47 silica spheres
Ordered by 'bending' process
Stacked in layers.

• 'Ordered' array of spheres: SE-SANS



Larmor ➔ NEW INSTRUMENT

(i) Core radius (big!): 90nm (good agreement)

(ii) Vol fract as z➔ ∞, 0.22 in reasonable agreement.

(iii) First correlation peak is less ordered than expected.

(iv) Higher order correlations of a true crystal are lost.

Clearly indicates significant positional disorder in the 'crystal'.

End SE-SANS extra bit

Talk Outline

- Examples of surfaces / neutron applications:

Adsorbed layers:

In-plane structure – 2D diffraction

Out-of-plane structure – reflection

What's adsorbed? (IQNS - dynamics)

Colloidal dispersions (dominated by surfaces)

What's on the surface? SANS

What arrangement ? SE- SANS

Liquid structure PDF (NIMROD)

Can we 'understand' liquid structure?

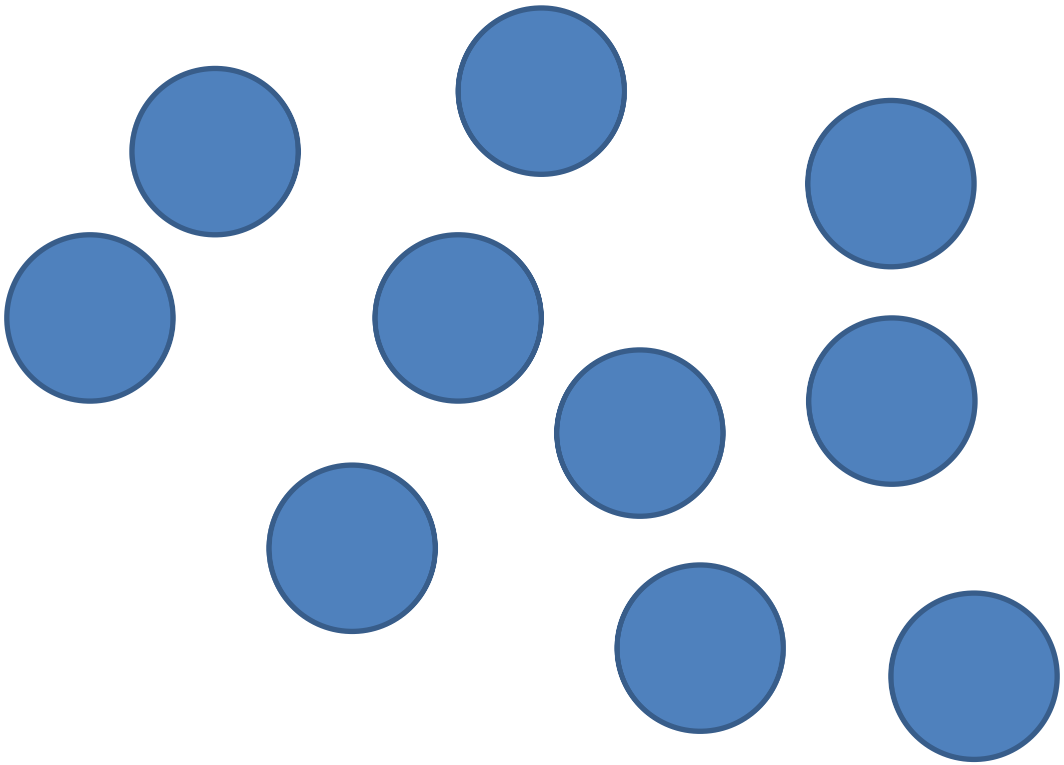
- No long range order: NO diffraction??

Oh dear!!

But still a lot of structure..

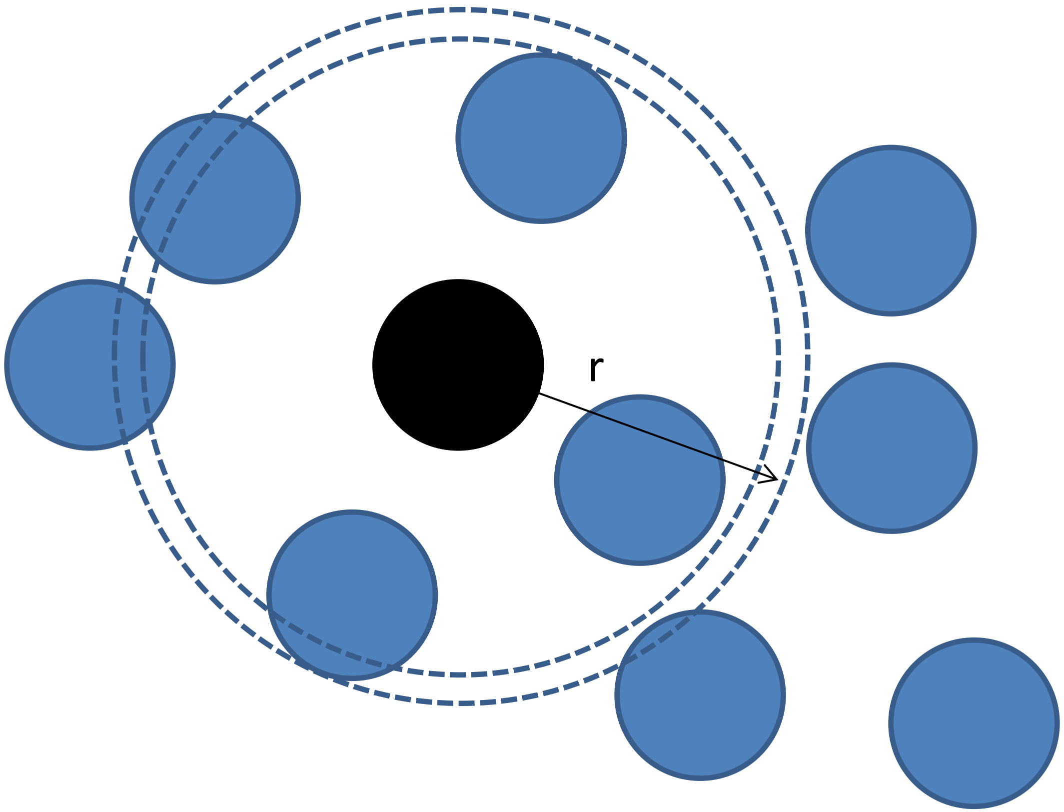
Radial distribution function

Liquid species



Radial distribution function

Liquid species

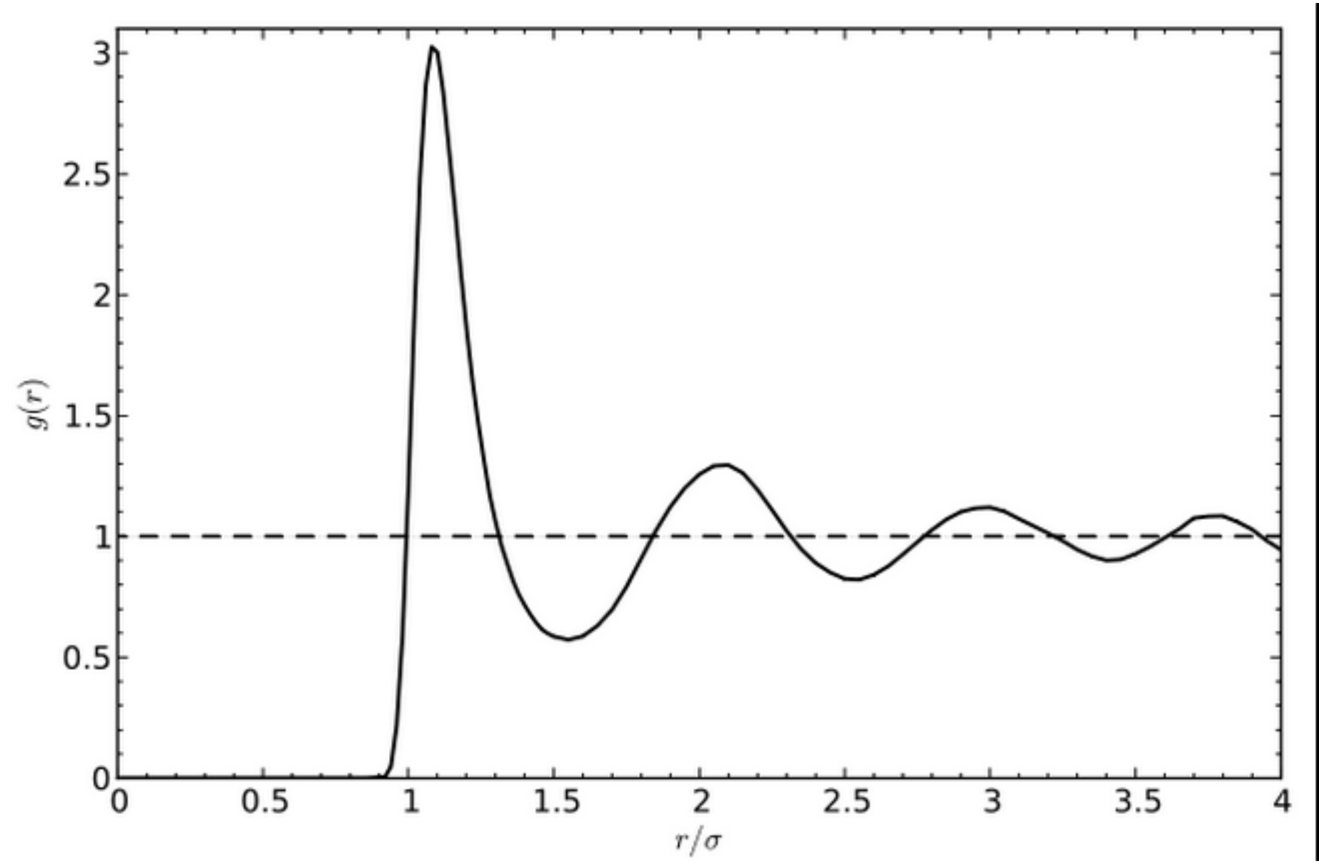


How many species in this shell at distance r from the central one: g(r)

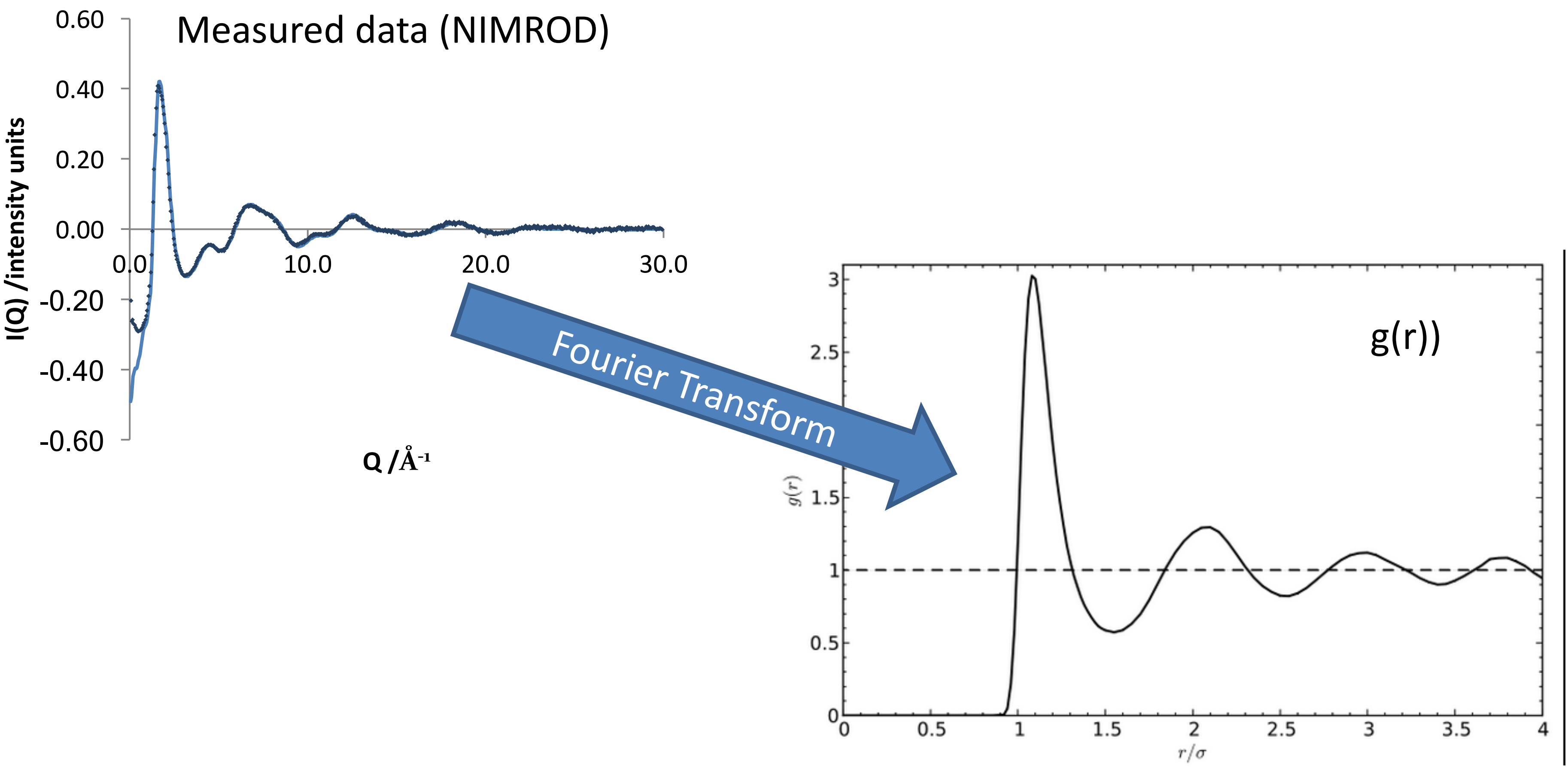
Pair distribution function: g(r)

(normalised)

- ‘Hard’ core…
- Nearest neighbour shells..
- …



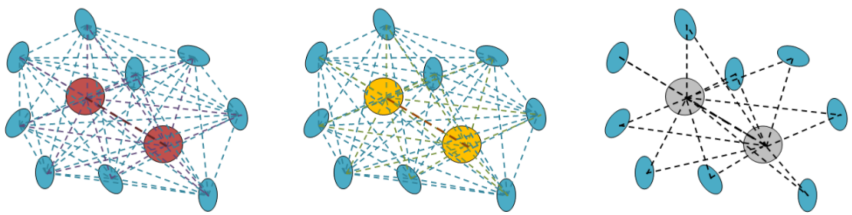
Pair distribution function: g(r), FT of scattering data



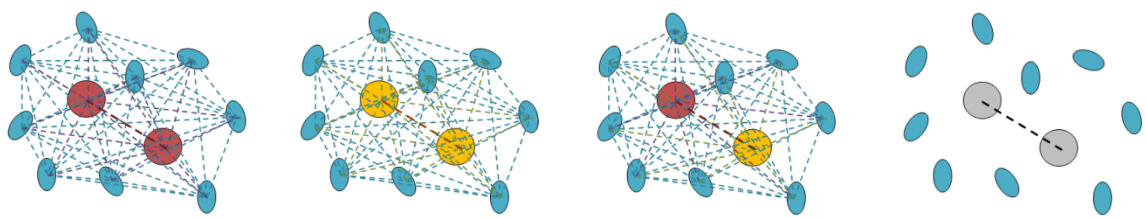
Can we ‘understand’ liquid structure? See all Atom-Atom distances

- Separate different atom contributions by isotopic exchange (H and D):

a) First difference (big circles exchanged):



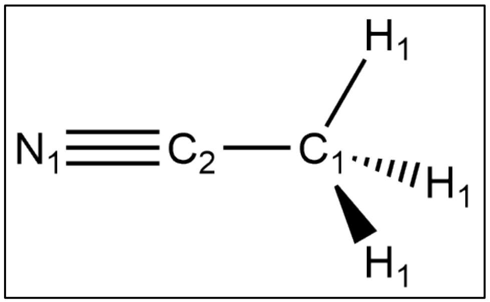
b) Second difference:

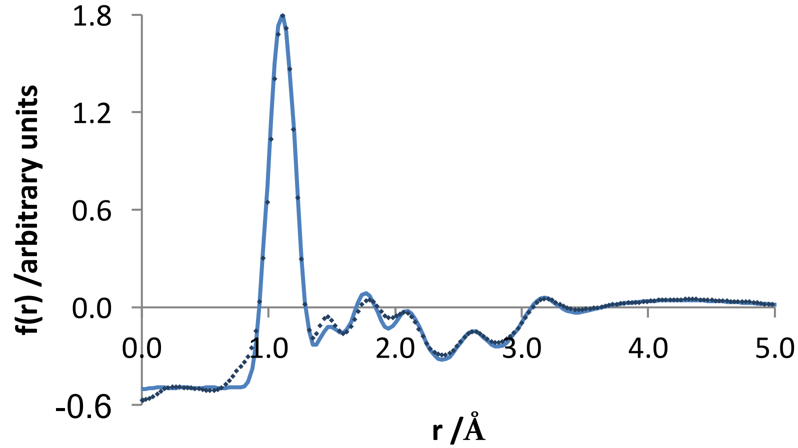


➔ ONLY solute-solute distances!!

PDF example: Acetonitrile

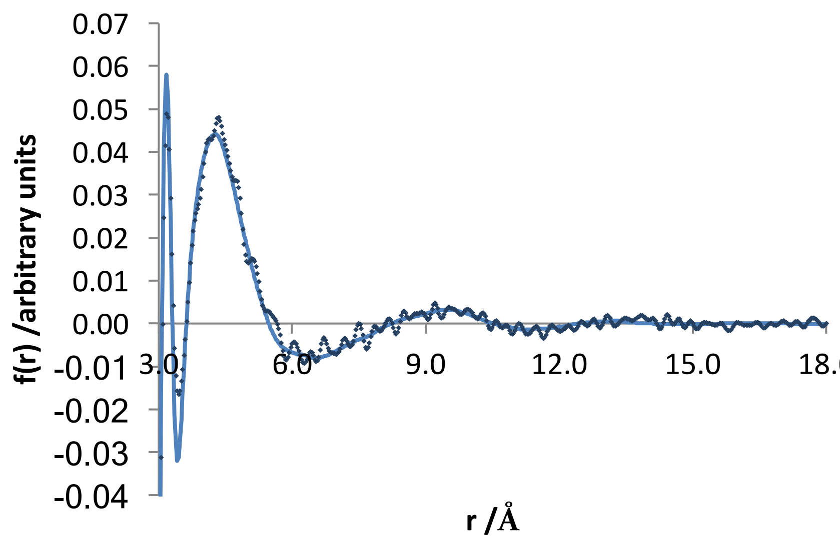
- See correct molecular structure at short distances





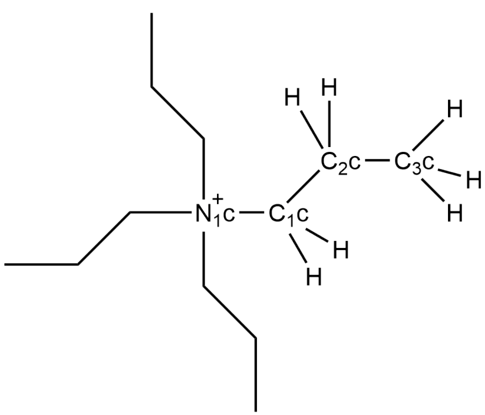
- Solvent shells at

Longer distances

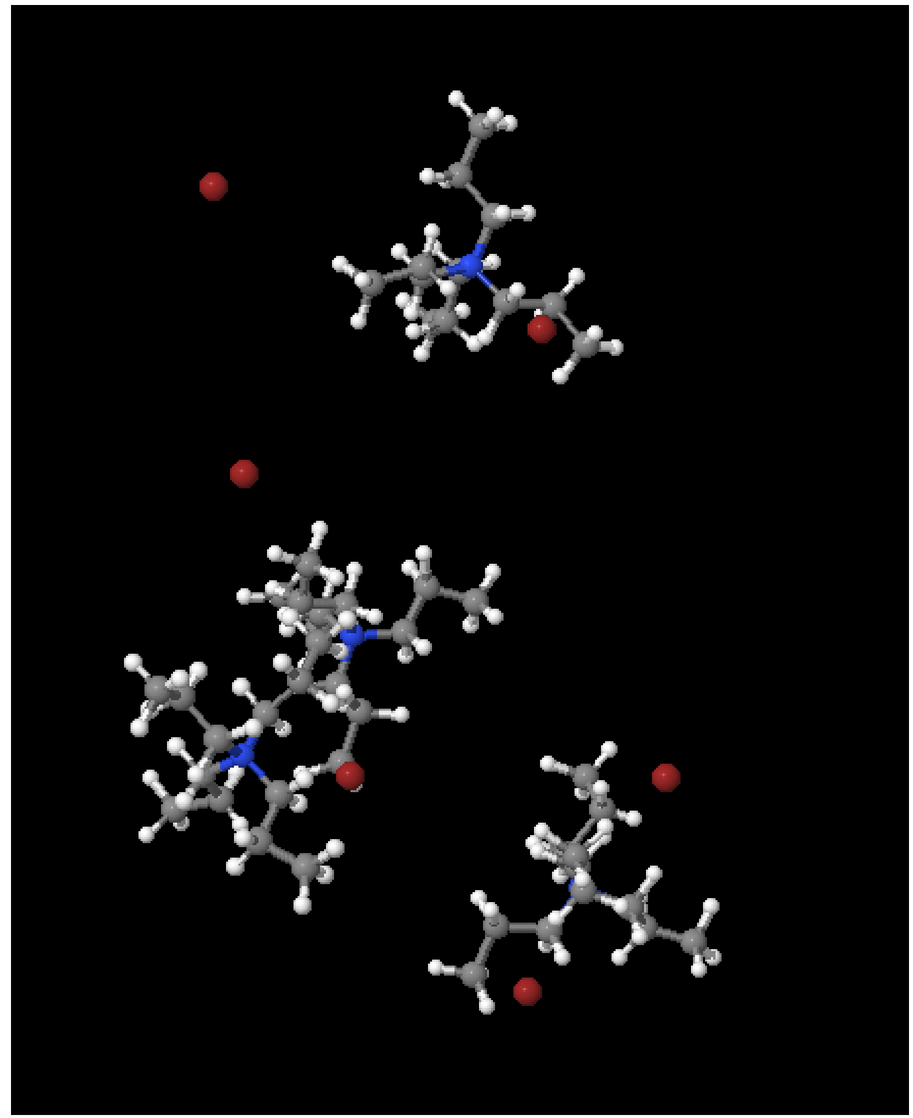


Supercapacitors: Ions in acetonitrile

- TPA Br in acetonitrile:
- See ‘ion pairs’



Br-



Talk Outline

- Neutron sources
  - **Coherent scattering - structure**
  - Incoherent scattering - dynamics
- Examples of surfaces / neutron applications:

Adsorbed layers:

In-plane structure – 2D diffraction

Out-of-plane structure – reflection

What's adsorbed? (IQNS - dynamics)

Colloidal dispersions (dominated by surfaces)

What's on the surface? SANS

What arrangement ? SE- SANS

Liquid structure PDF (NIMROD)

- Conclusions

Thanks..

- Adam Brewer Halogen bonding:
- Kate Miller/Lucy Griffin/Seung Lee: Calcite and Mica
- Beth Howe/ Becky Welbourne (Phoebe Allen): PDF
- Tom Arnold (DIAMOND): Alkane diffraction

ILL/ISIS / KEK/ LLB/ Berlin..etc.
– neutron Time
DIAMOND/SLS – SAXS time
All the (Long suffering) beamline scientists

Thank YOU !

UNIVERSITY OF CAMBRIDGE

BP INSTITUTE FOR MULTIPHASE FLOW