



UNIVERSITY OF
CAMBRIDGE

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

ISIS Neutron School 2019
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University of Cambridge, UK*

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)

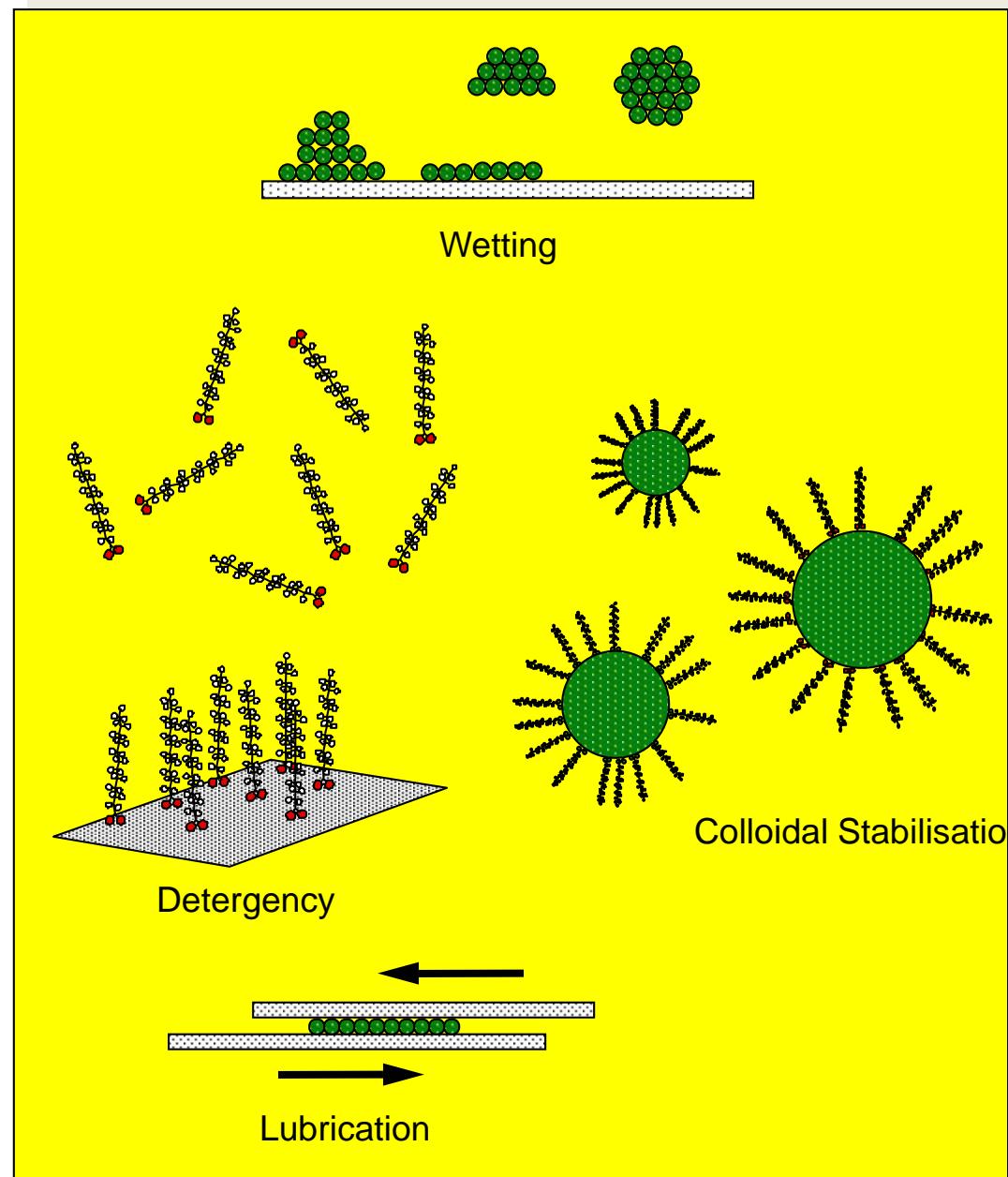
- Contrast between H and D very useful: highlight
- Can ‘see’ Hydrogen: Highlight
- Excellent transmission (extreme/commerical conditions)

BUT.

- Tricky to get hold of/limited access
(complement with other methods)

Examples of Monolayers

- Academic and industrial issues:
Colloidal stabilisation, molecular patterning,
wetting behaviour, detergency,
Slip agents, liquid crystals.
Corrosion,
- 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

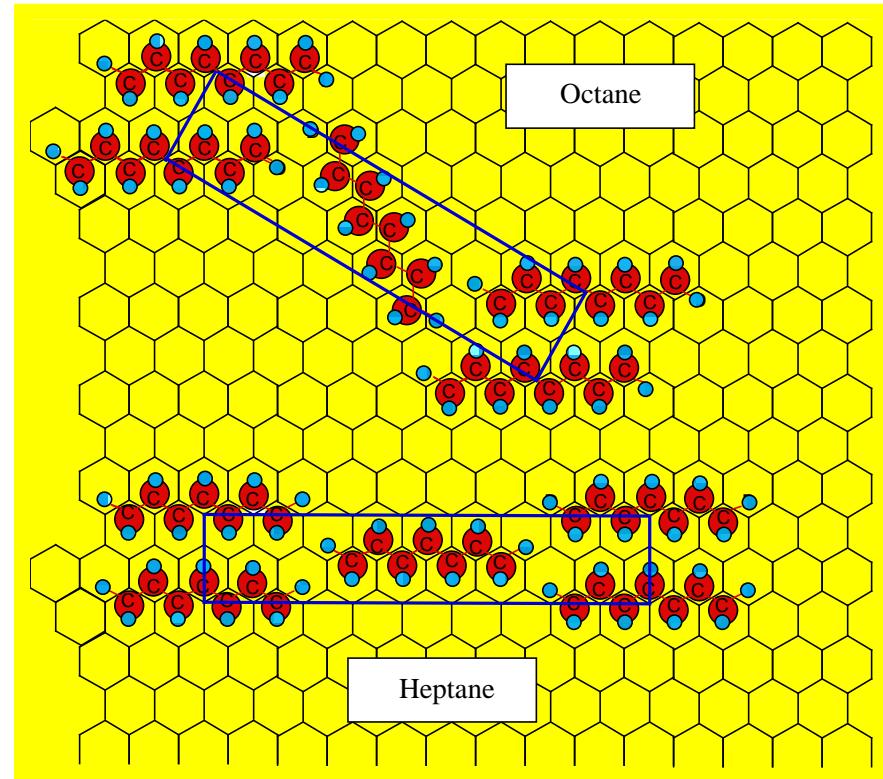
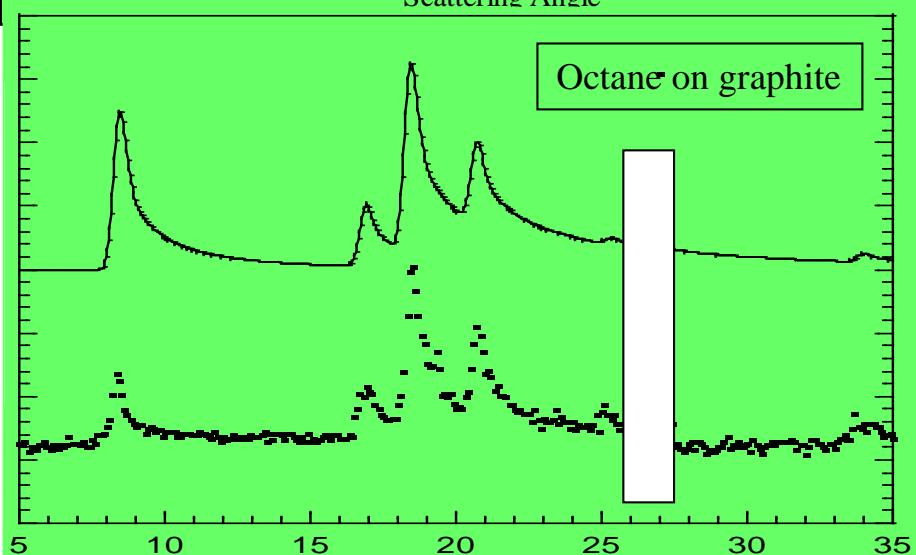
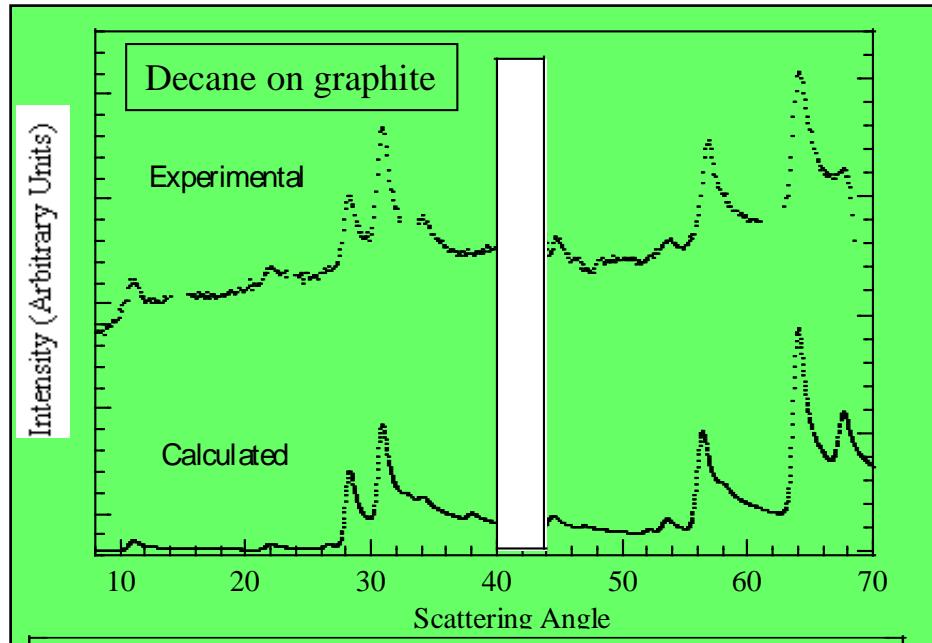
Liquid structure PDF (NIMROD)

3D diffraction: crystallography

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

TODAY: 3D → 2D diffraction

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



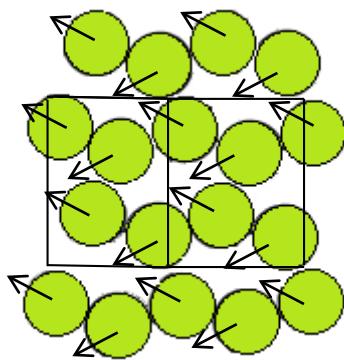
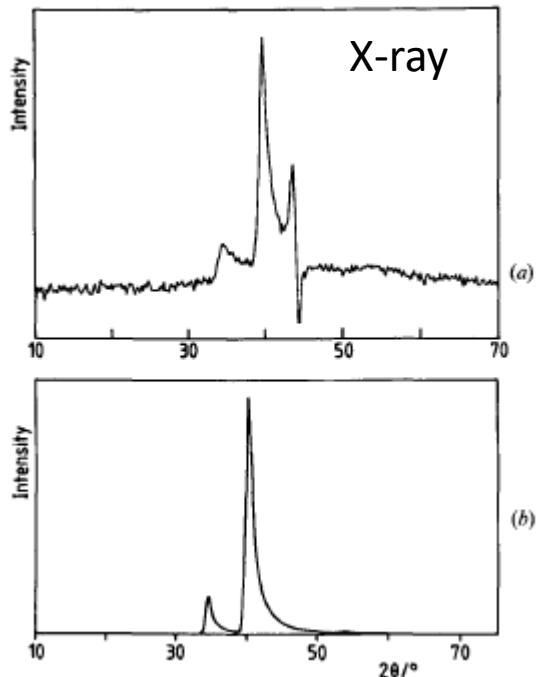
Neutrons: sensitive to hydrogen
X-rays: greater precision
Independent information
Combination is often essential

Why Xrays AND neutrons are important.

Low coverage

Chloromethane monolayer:

X-rays



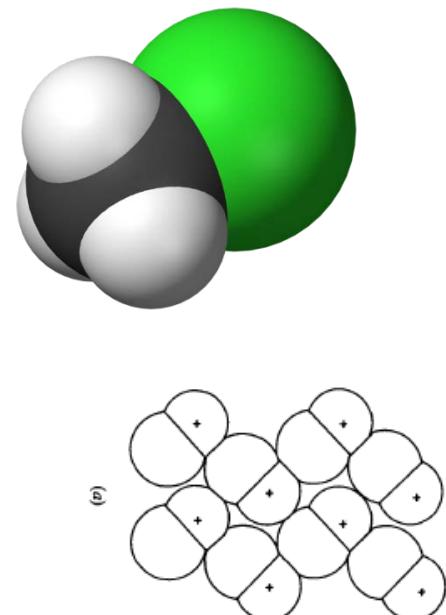
Chlorine atoms

Where are CH_3 groups?

Guessed:

Ferro electric ordering?

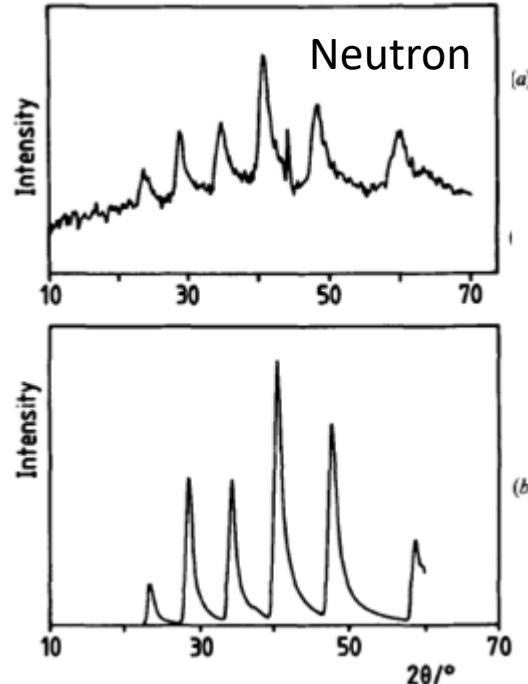
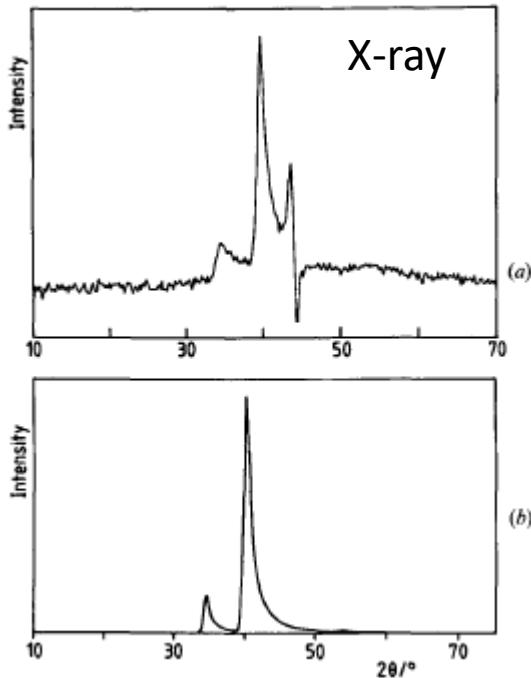
Like bulk crystal plane...



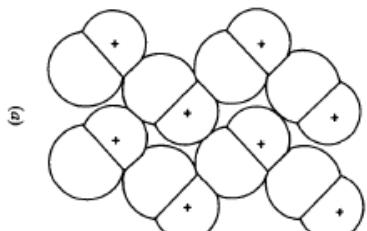
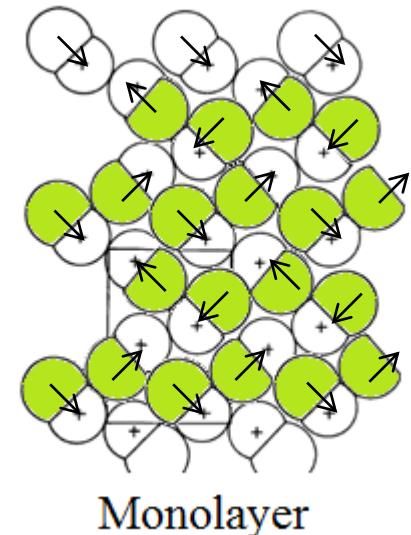
Bulk Plane

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

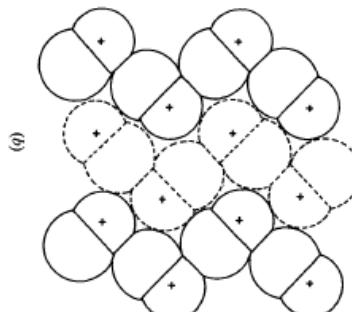
Chloromethane



Low coverage

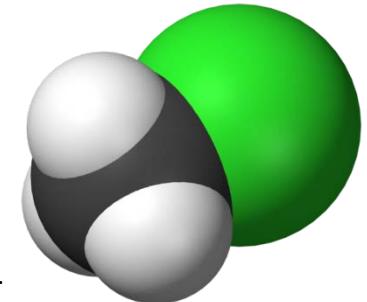


Bulk Plane



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

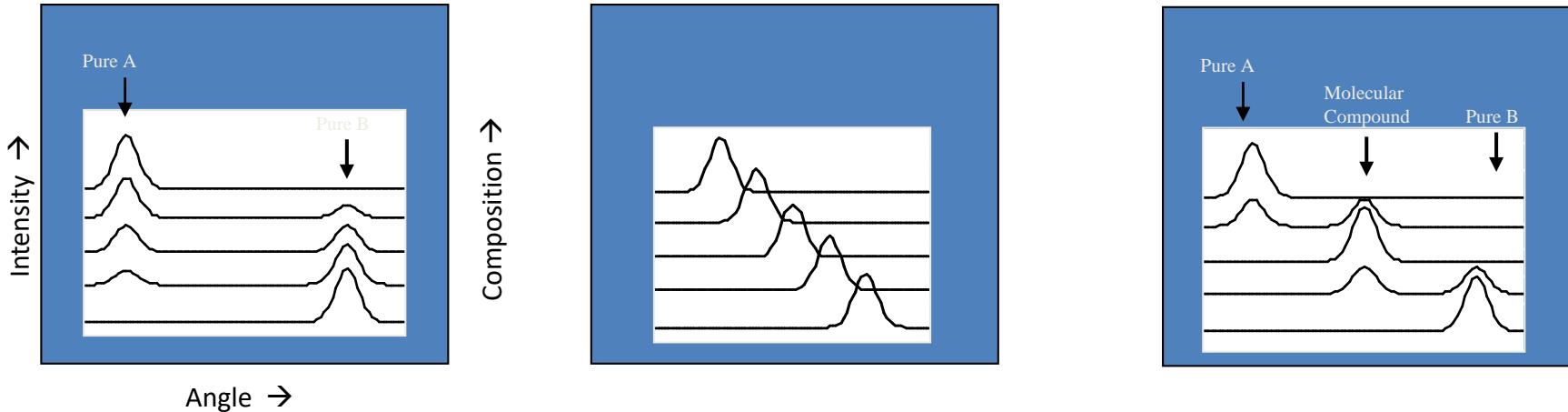


Special relationship; stoichiometric complex Molecular compound



Structure: Diffraction from Mixed Monolayers

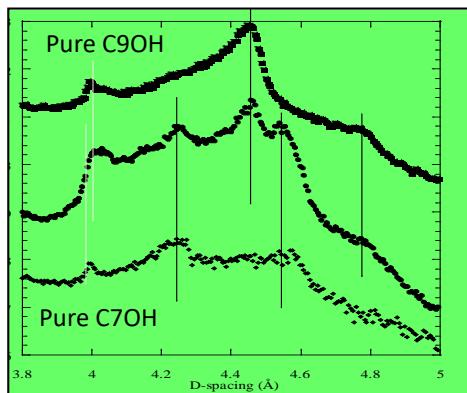
How do molecules mix on a surface?



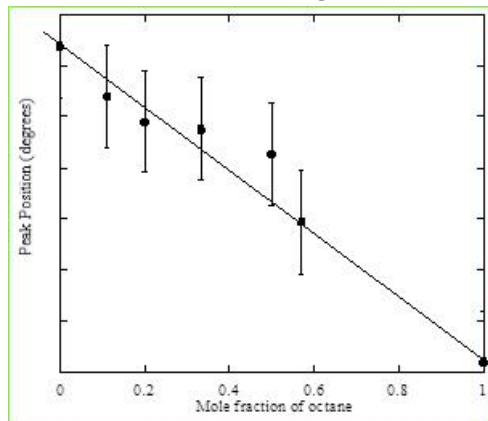
(a) Phase sep.

(b) Mixing

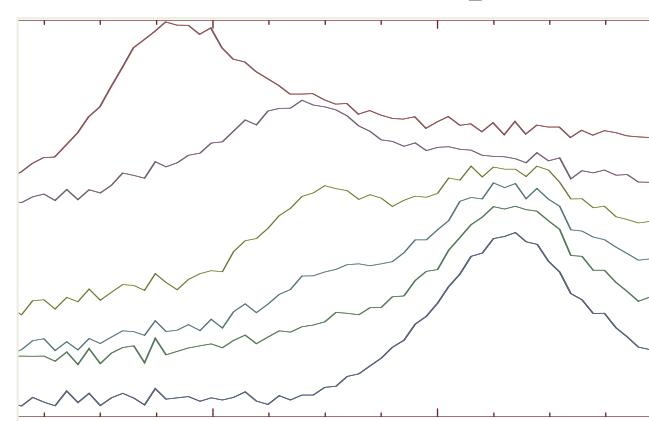
(c) Molecular compound



Heptanol/nonanol

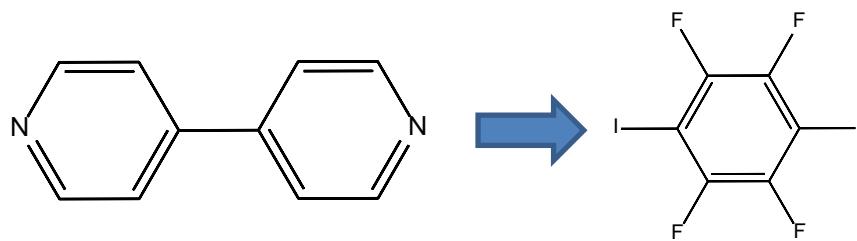


Heptanol/octanol



Hexanol/heptanol

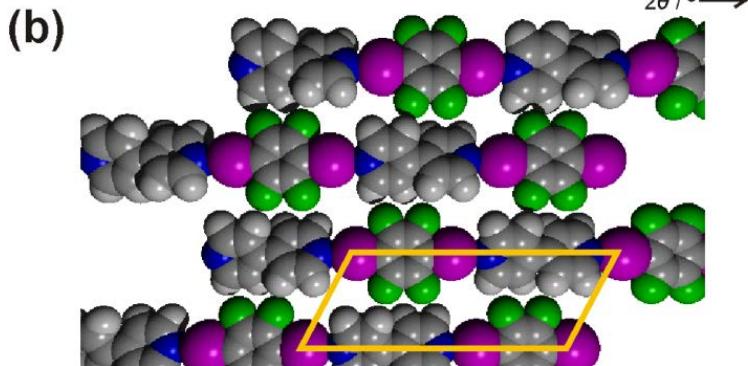
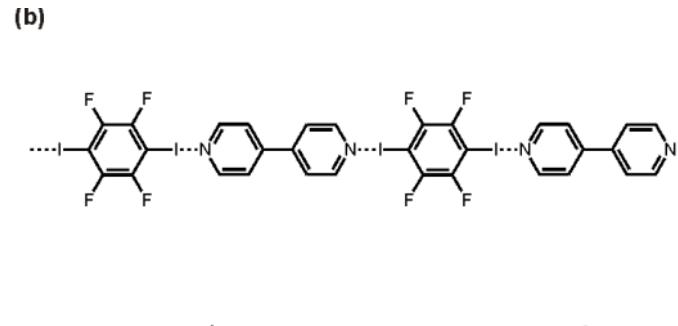
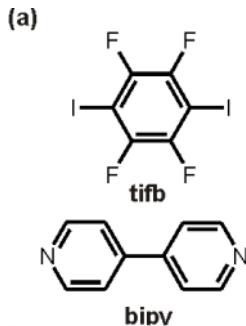
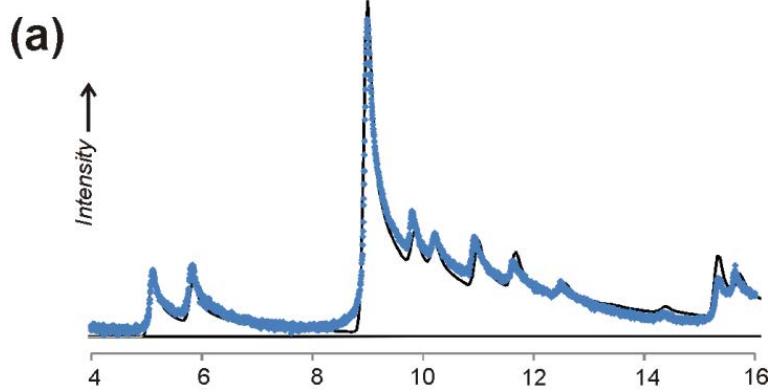
‘Special, non-covalent bonding between molecules’
Big topic of supramolecular self assembly



Donation of lone pair from nitrogen to Iodine atom

Novel Chemical interactions: Halogen Bonded co-crystal

N....I-C



Monolayer

'New hydrogen bonds'
Very stable layers
 $2DT \gg 3DT$
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:

In-plane structure – 2D diffraction

Out-of-plane structure – reflection

What's adsorbed? (IQNS - dynamics)

Colloidal dispersions (dominated by surfaces)

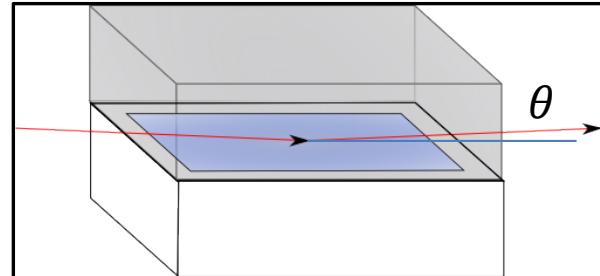
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What arrangement ? SE- SANS

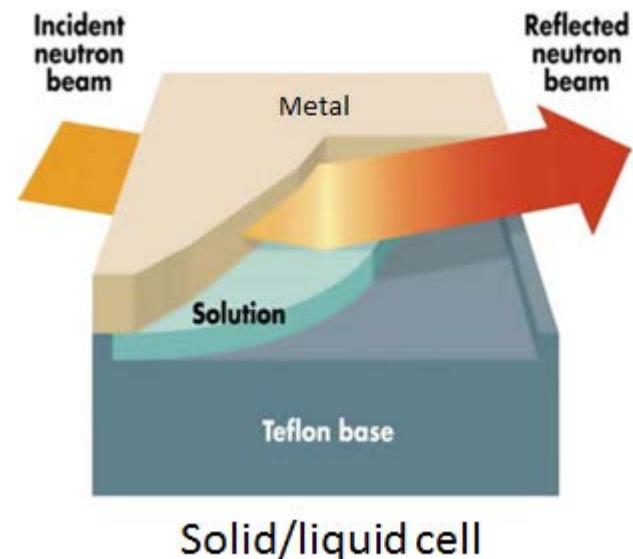
Liquid structure PDF (NIMROD)

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

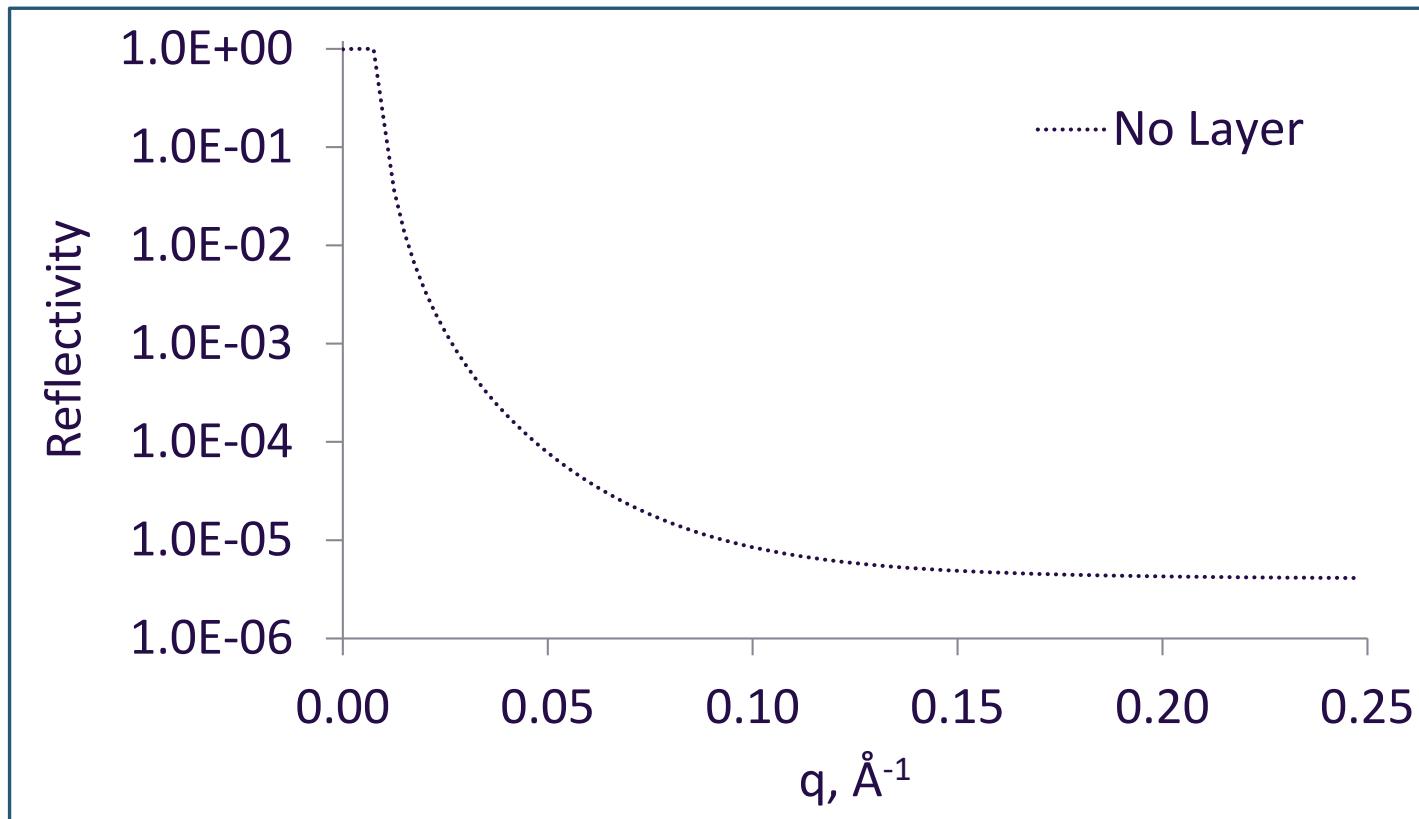


function of 'angle' (q)..
aces

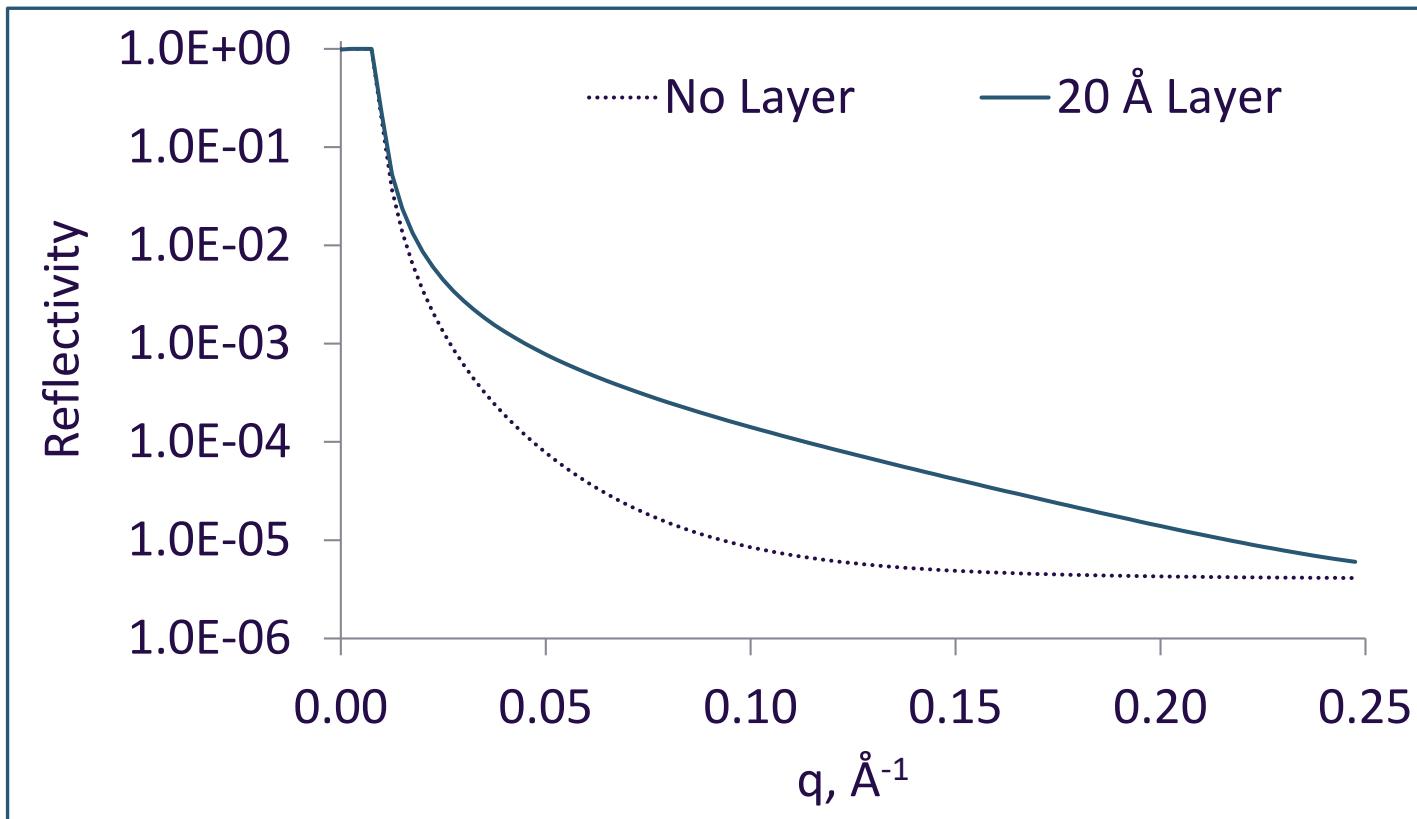


$$q = \frac{4\pi \sin \theta}{\lambda}$$

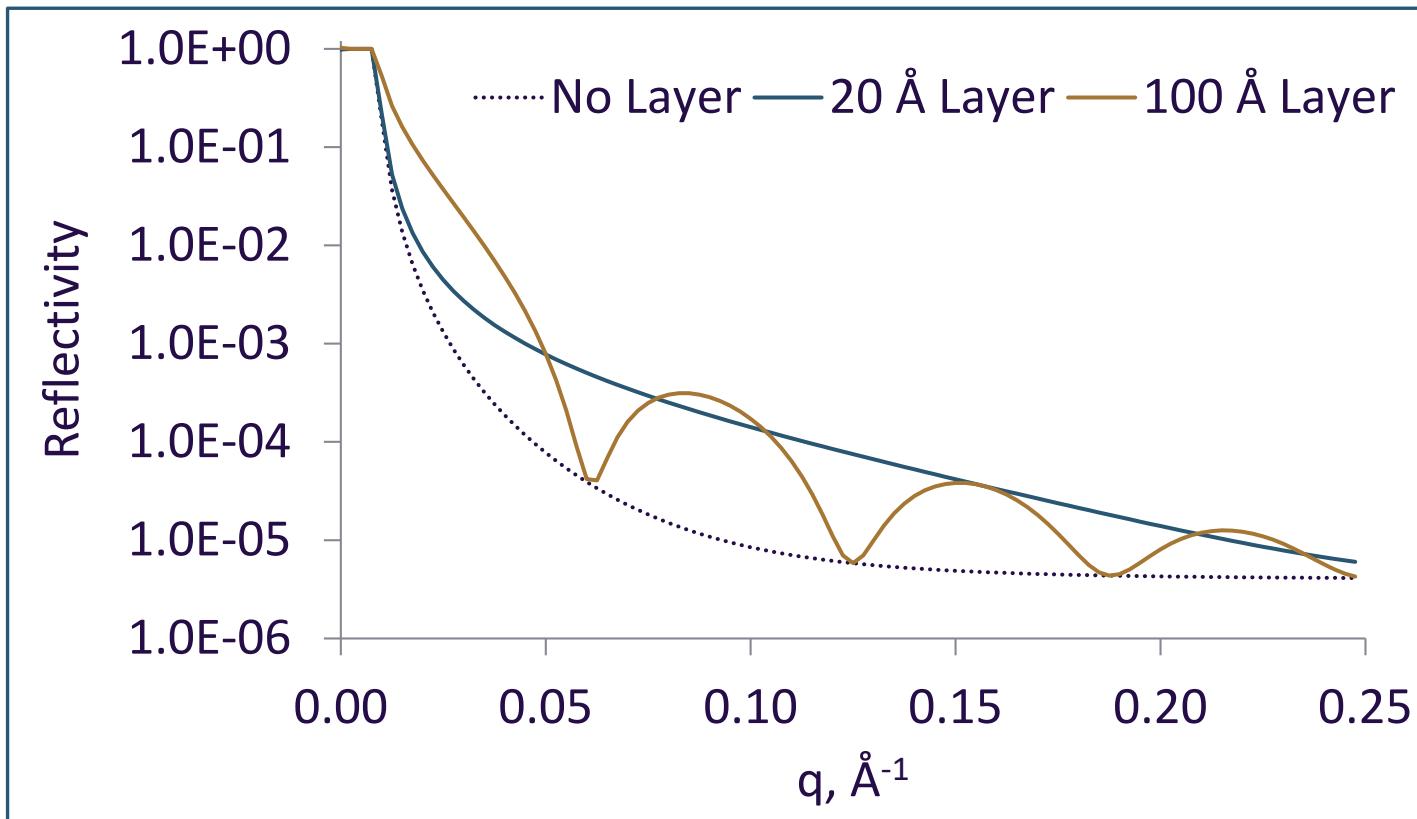
Neutron Reflection Theory



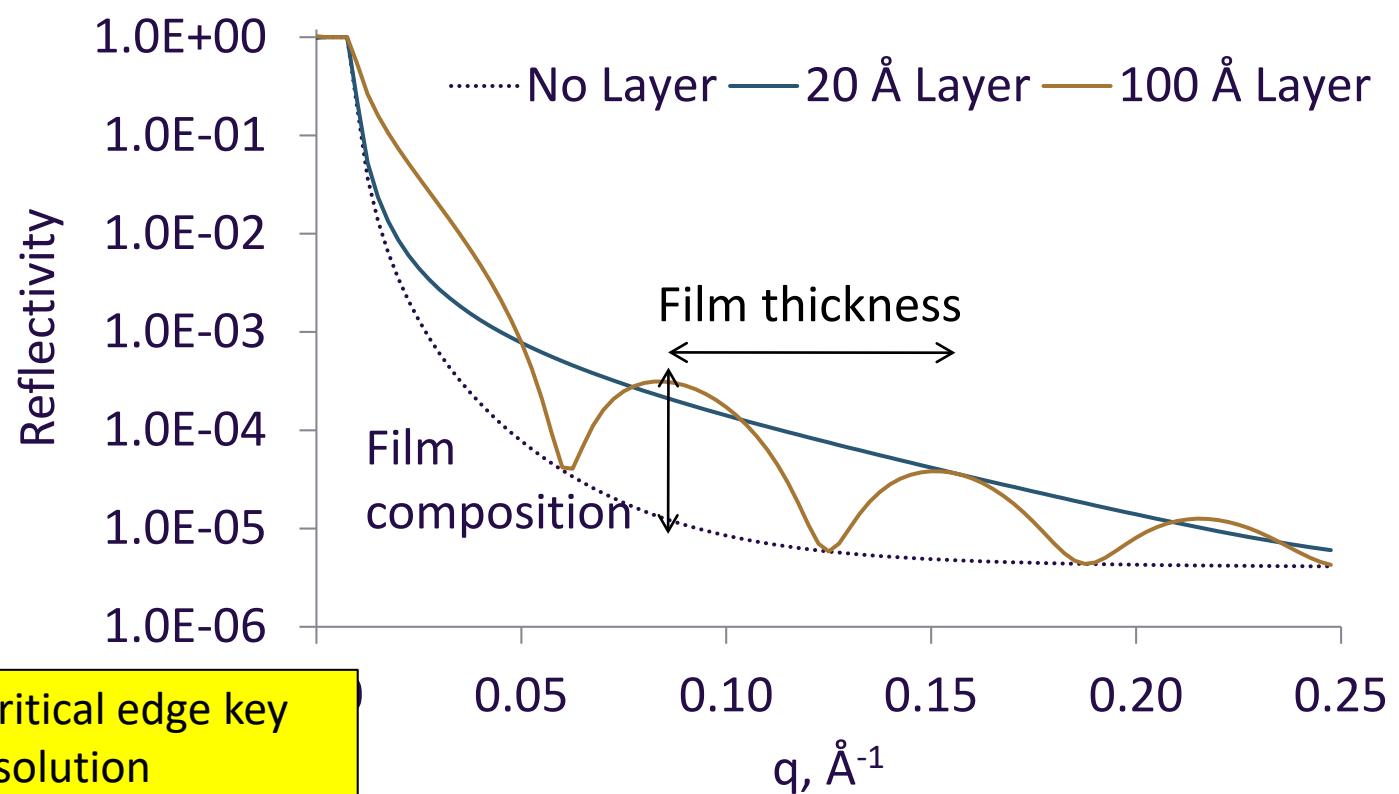
Neutron Reflection Theory



Neutron Reflection Theory



Neutron Reflection Theory



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

Substrate

Liquid

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

Layer thickness

Thin layer reflection: Add amplitudes

$$\frac{n_1}{n_0} = \frac{\cos\theta_0}{\cos\theta_1}$$

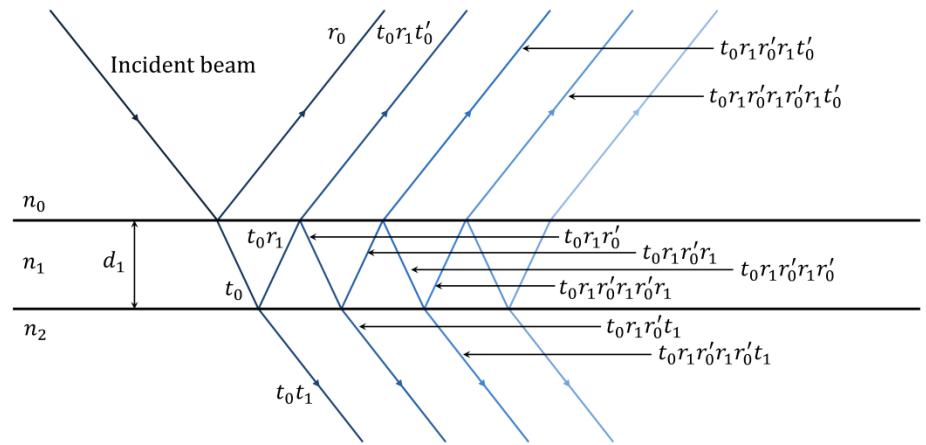
$$\frac{n_1}{n_0} = \cos\theta_c$$

$$r_{ij} = \frac{n_i \sin\theta_i - n_j \sin\theta_j}{n_i \sin\theta_i + n_j \sin\theta_j} \quad t_{ij} = 1 - r_{ij}$$

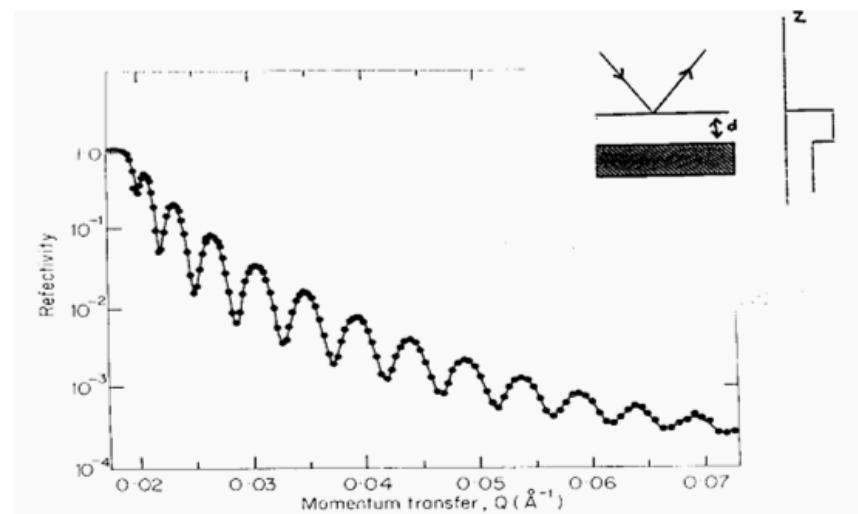
$$R(Q) = \left| \frac{r_{01} + r_{12}e^{-2i\beta}}{1 + r_{01}r_{12}e^{-2i\beta}} \right|^2$$

$$n_i = 1 - \frac{\lambda^2}{2\pi} \rho_i$$

$$\beta_i = (2\pi/\lambda)n_i d \cos\theta_i$$



Tutorial problem: geometric series



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’?

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

Reflection Example #1

- Calcite (CaCO_3)

Very important mineral

Scale in your kettle

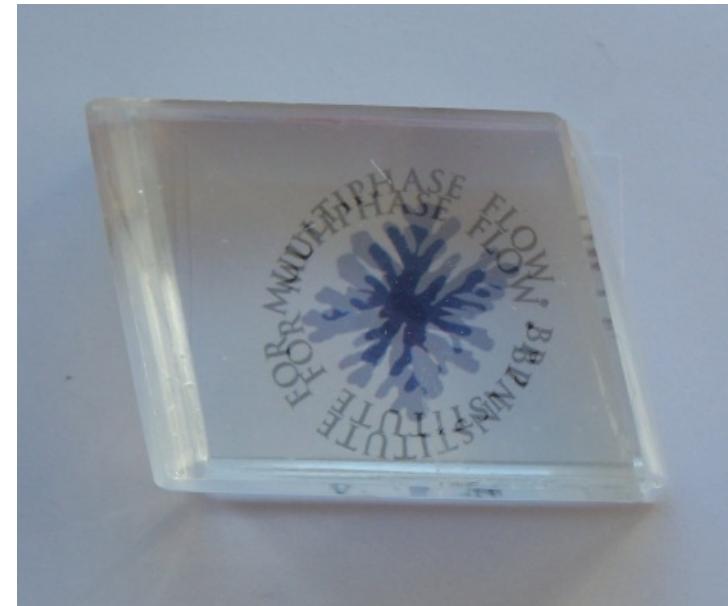
Oil reservoirs

Overbasing agent in engines

What adsorbs and how?

In oil? In water?

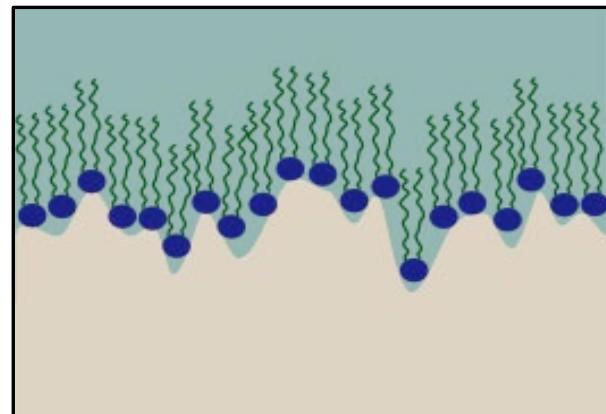
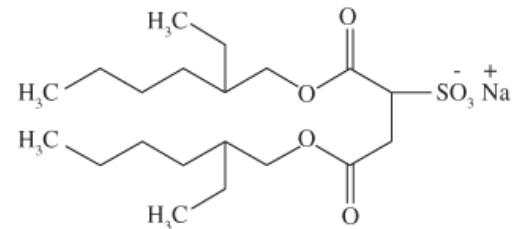
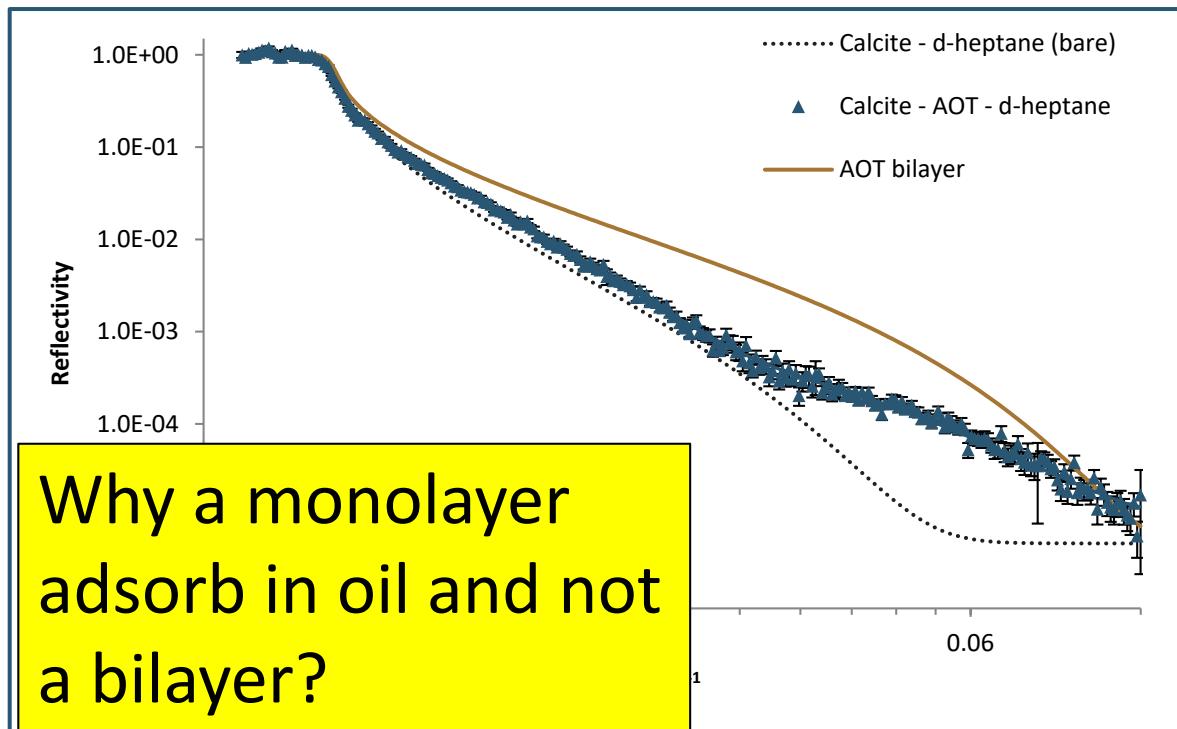
Polymers? Surfactants?



(Birefringent...! Double refraction)

Neutron reflection: Example #1

Surfactant, AOT, on Calcite (CaCO_3) in oil

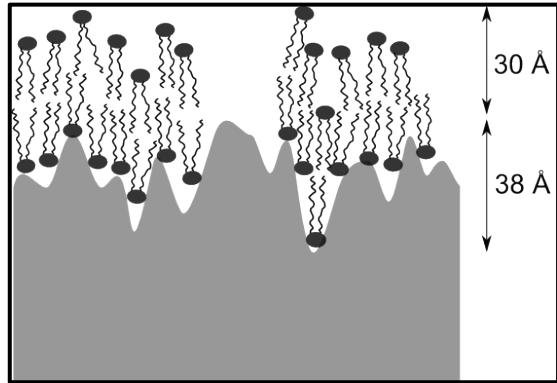
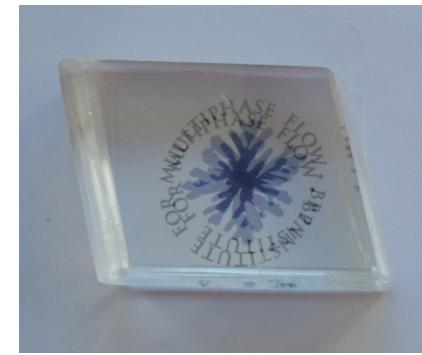


Adsorption of a monolayer on a surface:

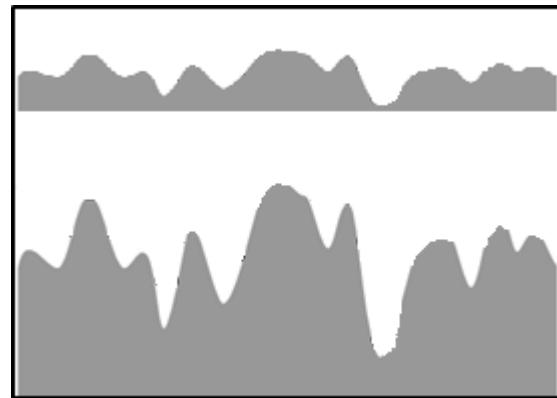
(The bare surface, monolayer and bilayer)

What adsorbs in water.....?

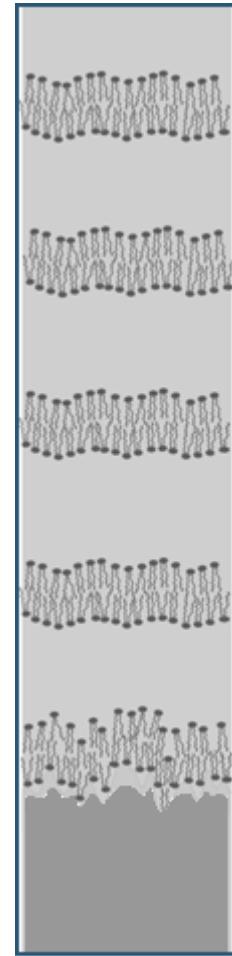
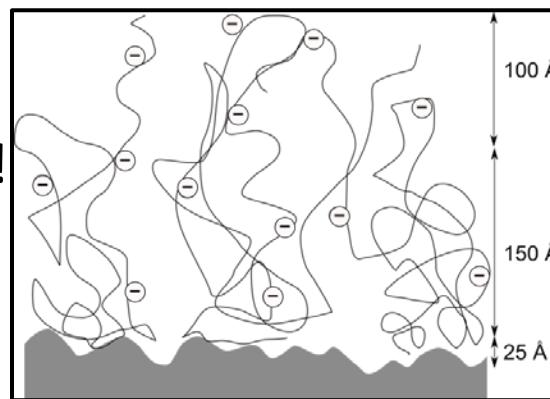
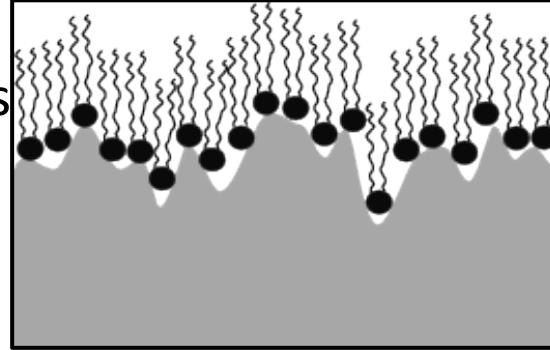
Reflection Example : Additives on calcite..



Monolayers, Bilayers,
multilayers and
adsorbed polymers



Molecular precision!



Reflection Example : Mineral Surfaces - mica

(Kate Miller)

Layered silicate: mineral books



Mica:

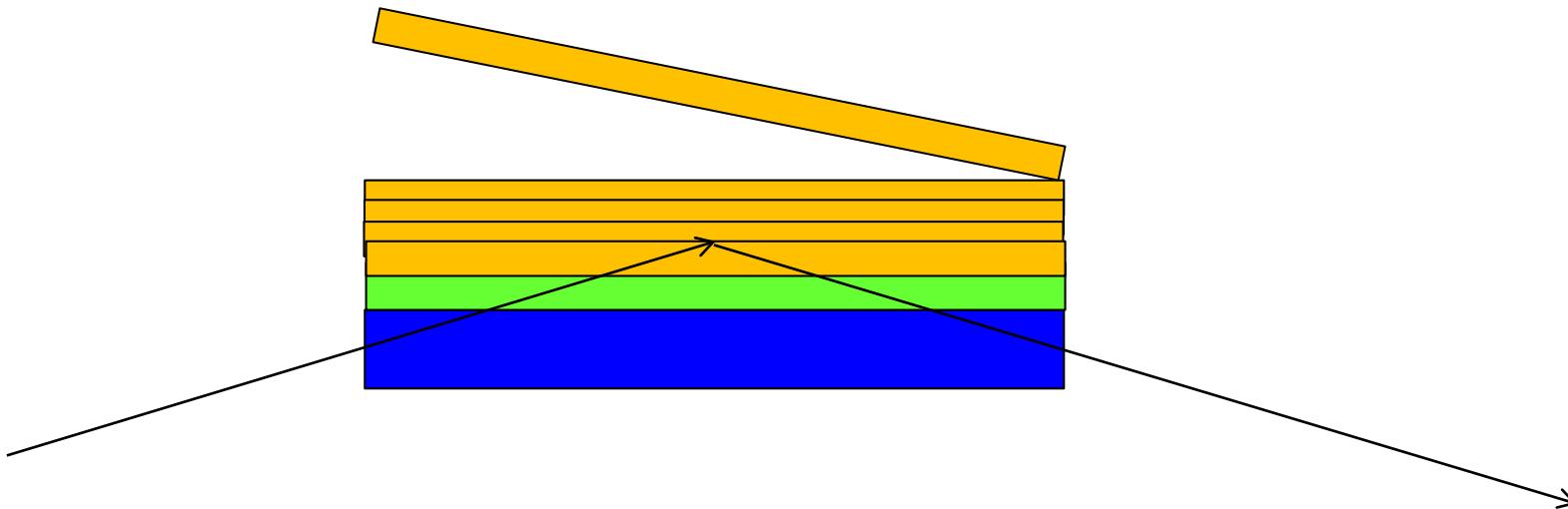
Clays are key component of many oil reservoirs

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

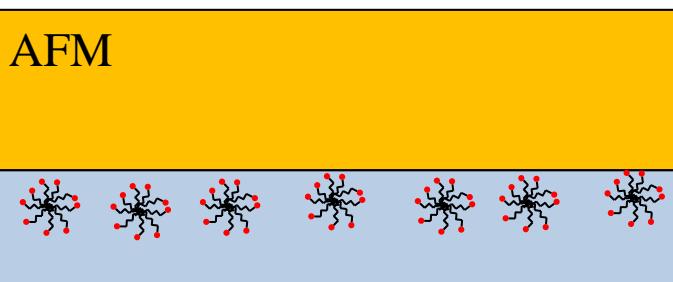
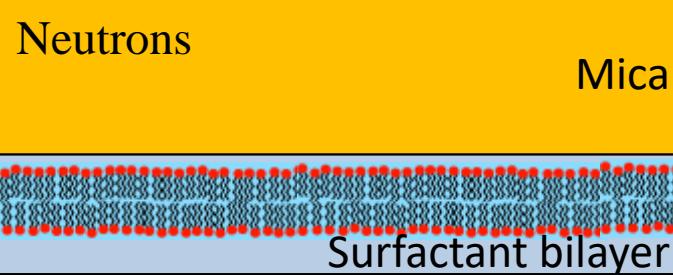
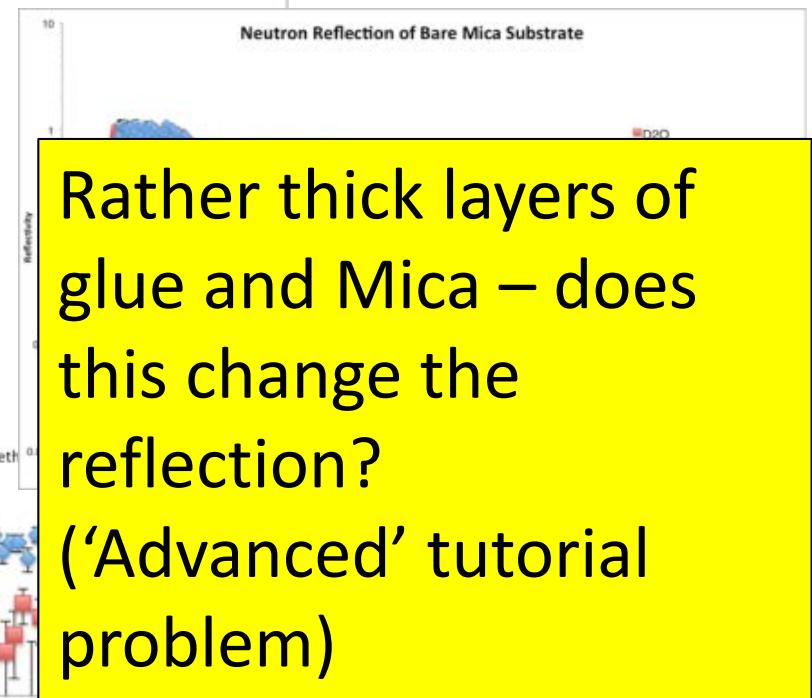
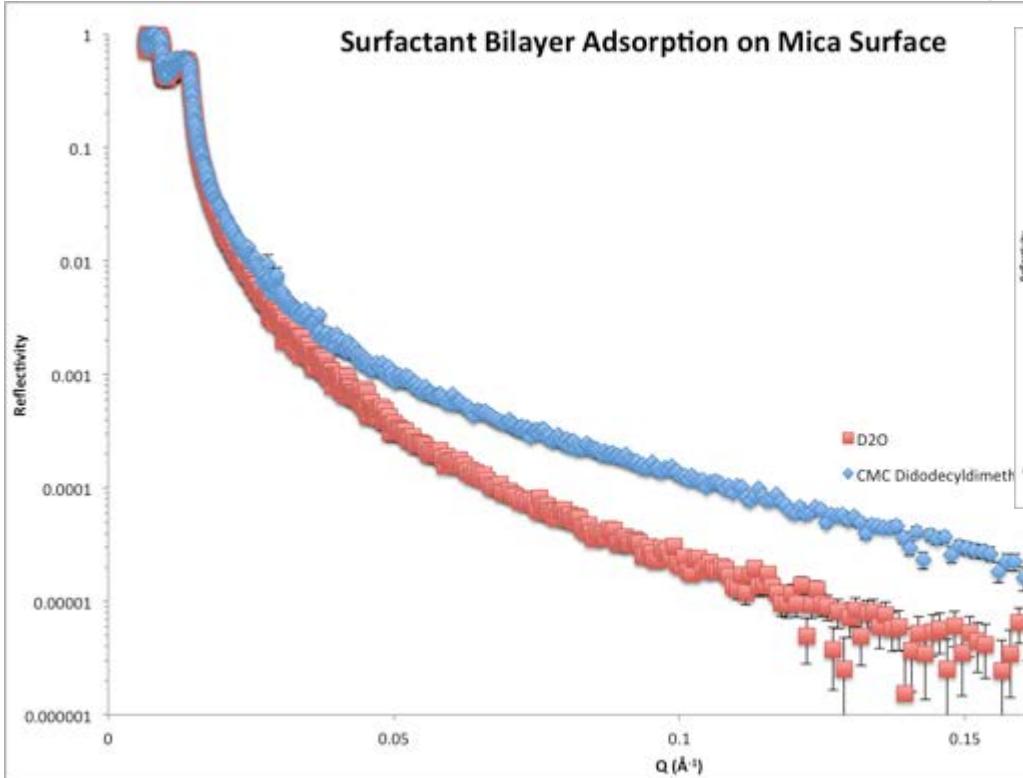


Support very thin layers on solid substrate and ‘peel’

Does it work?.....

Can we see adsorption on mica in solution?...

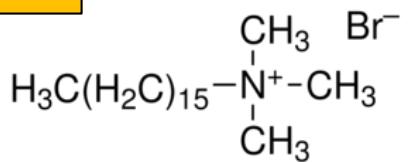
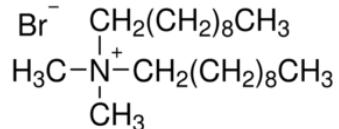
Surfactant adsorption on mica



Non-invasive:

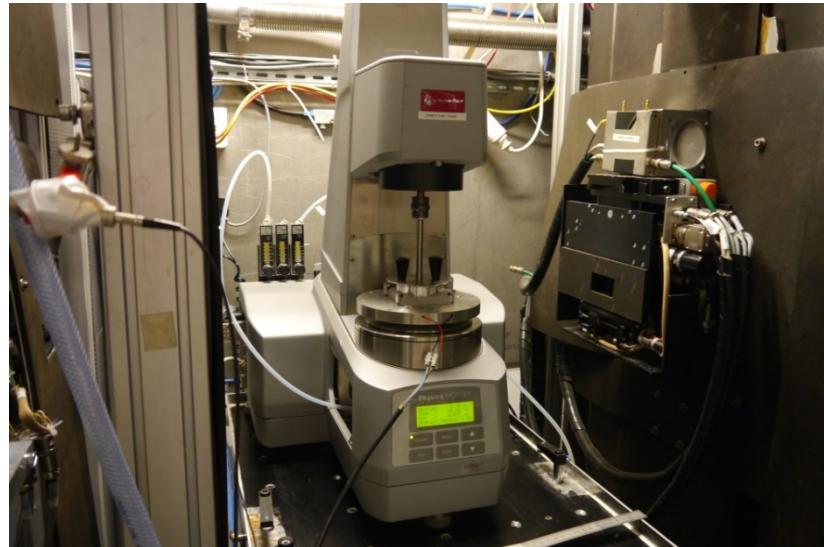
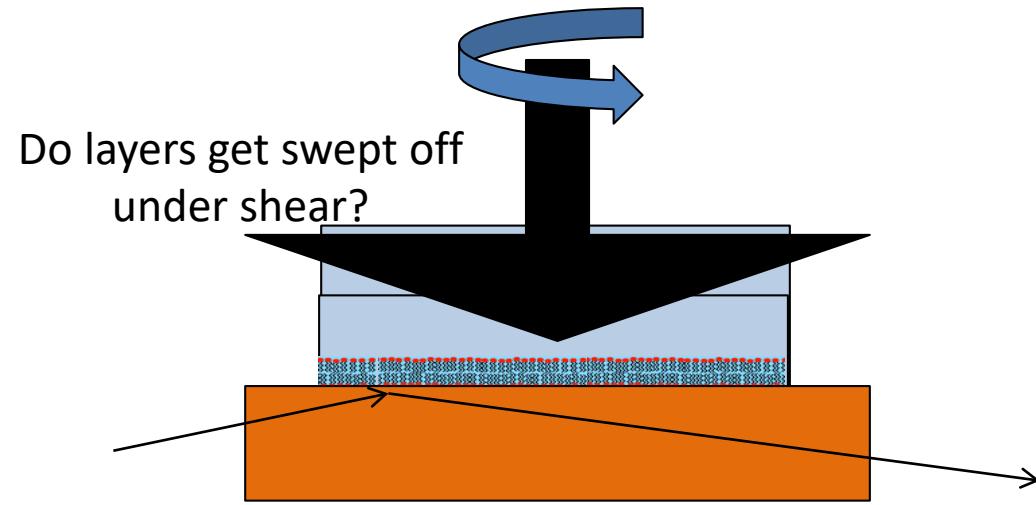
(a) D₂O: same result as AFM

Neutrons non-invasive
(same result as AFM)



(b) CTAB: NOT same as AFM

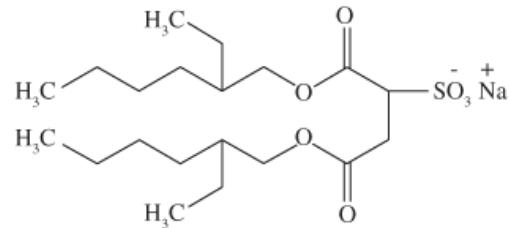
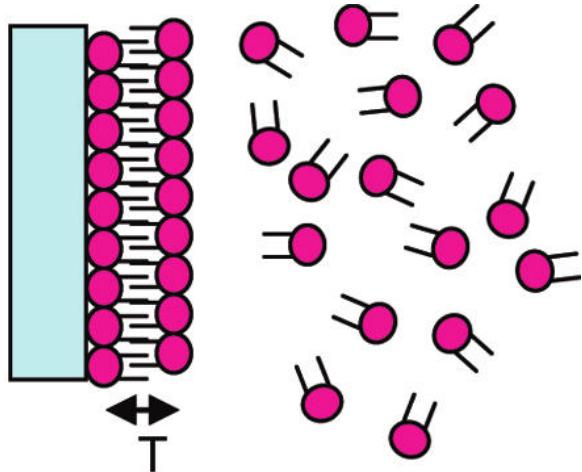
Example: Layers under Shear



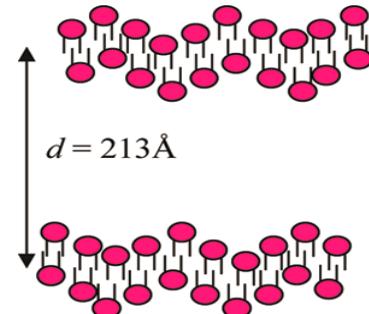
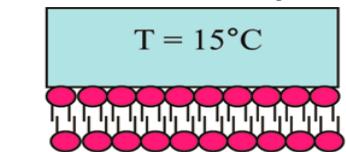
(steady and oscillatory shear)
Modest shear rates $< 500\text{s}^{-1}$
(pipe flow, or flow over rock-beds)

Shear/Flow: AOT on Alumina/water

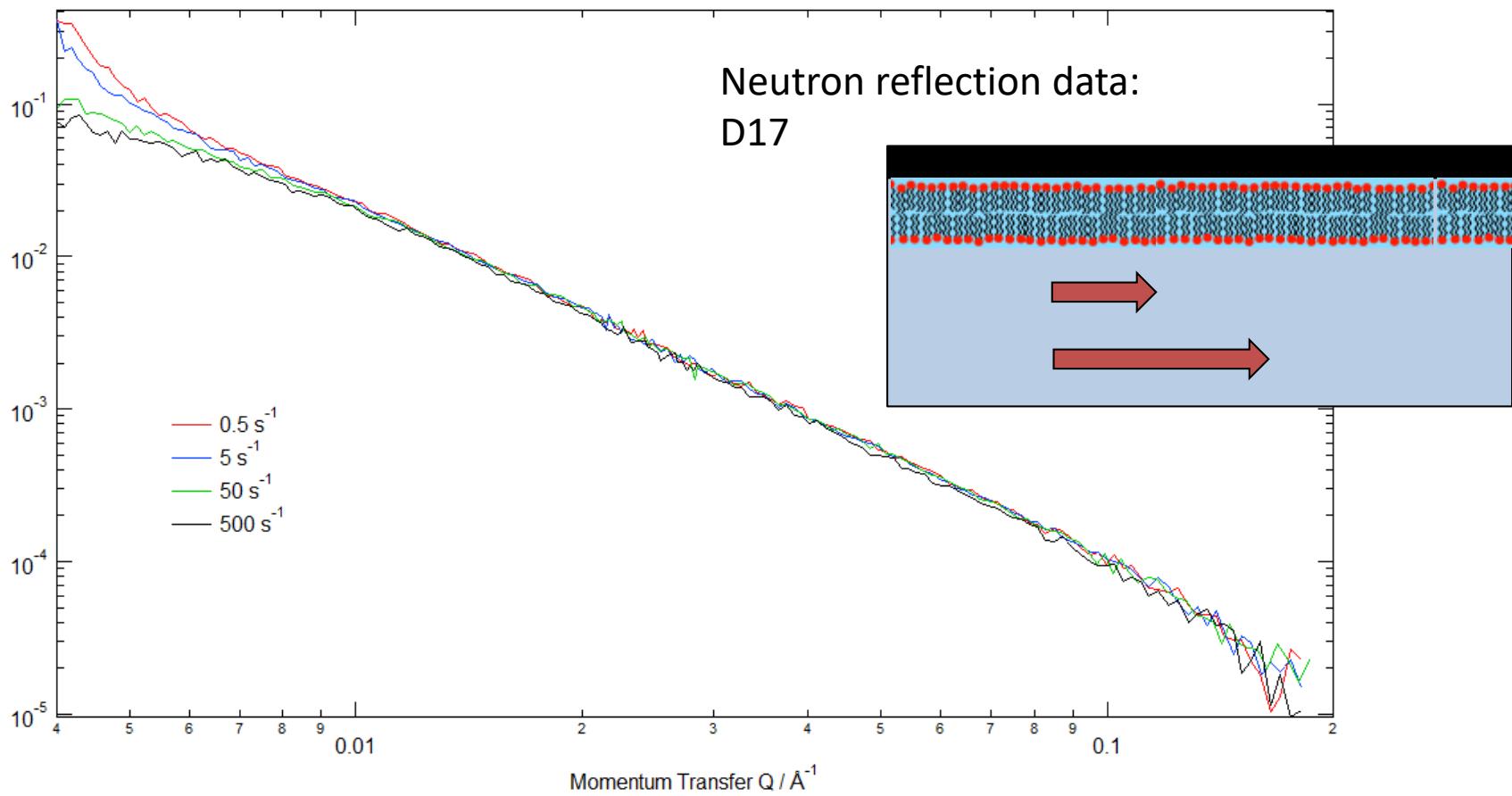
Thin layers



Thick layers



Effects of Shear: neutron reflection: Thin layer



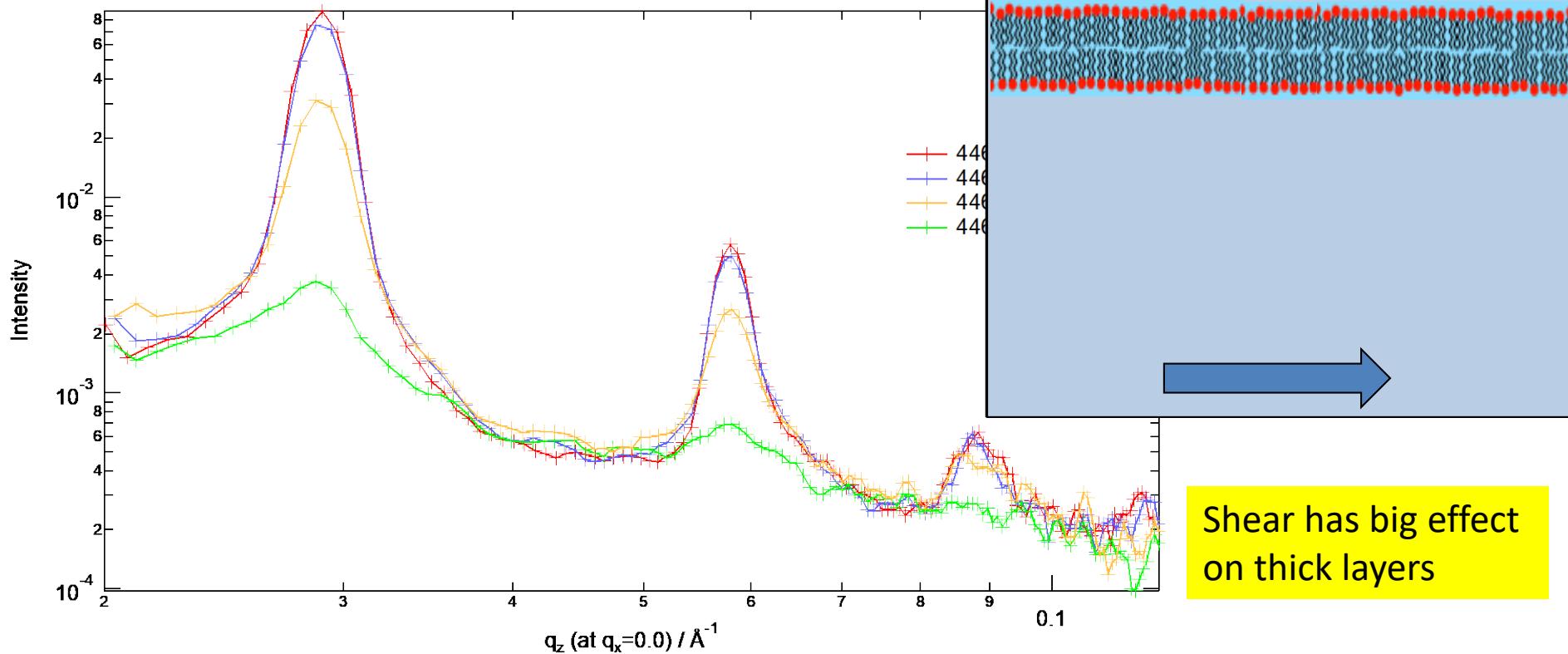
SURFACTANT BILAYER (thin layer approx. 30 \AA thick)

Data: under steady shear increasing to approx 1000 s^{-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

Adsorbed multi layer

Thick layer!!

Under steady and oscillatory shear: → BIG effects

Higher shear rates
planned

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

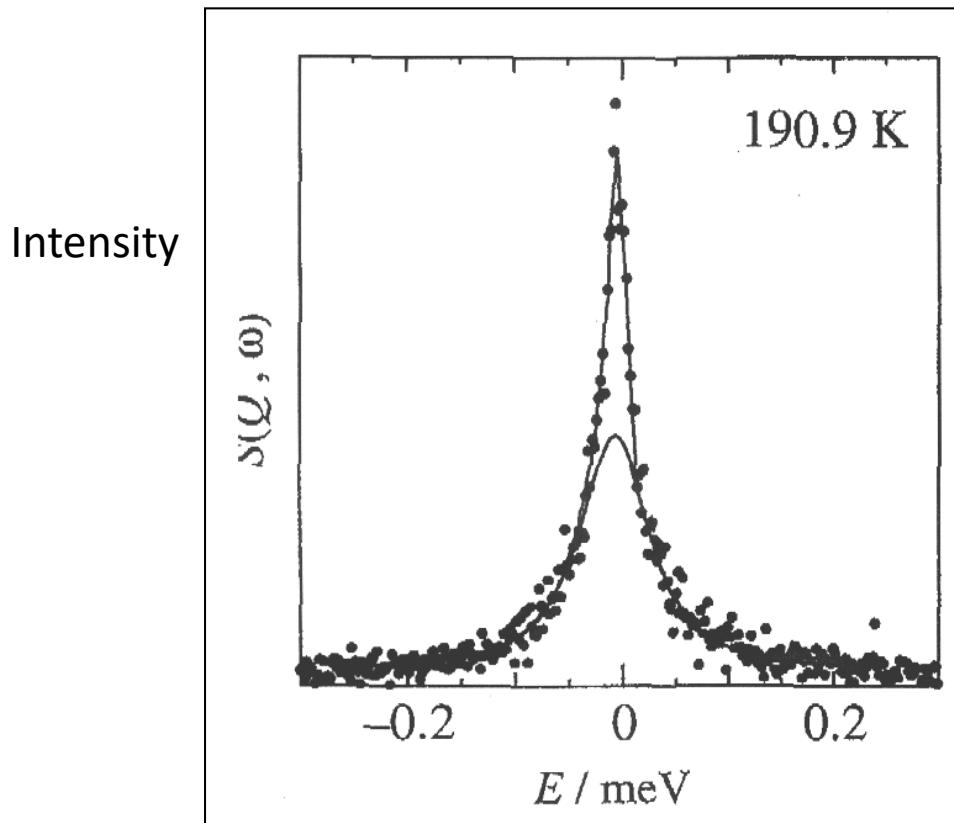
Liquid structure PDF (NIMROD)

Quasi-elastic neutron scattering

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

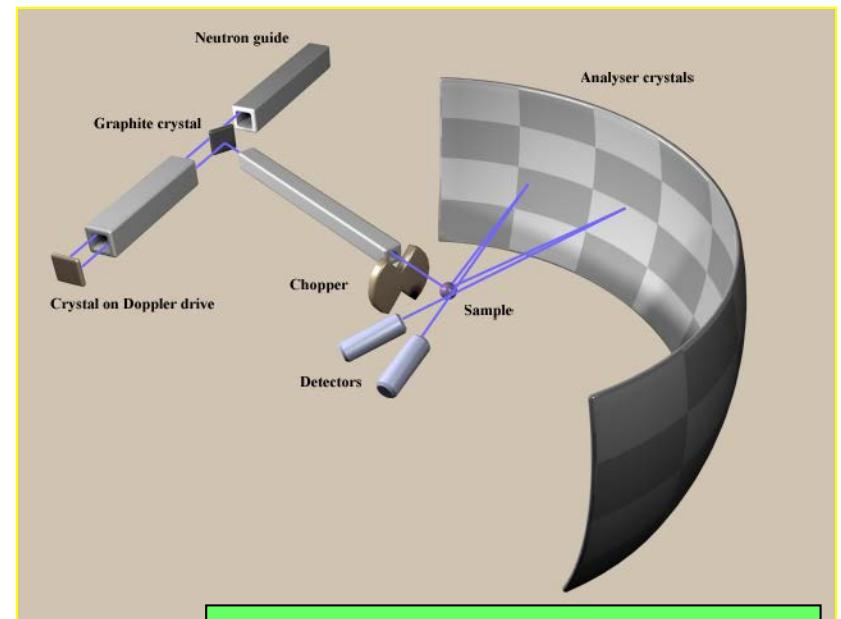
Incoherent Neutron Scattering

- Actually get a distribution of scattered neutron energies:



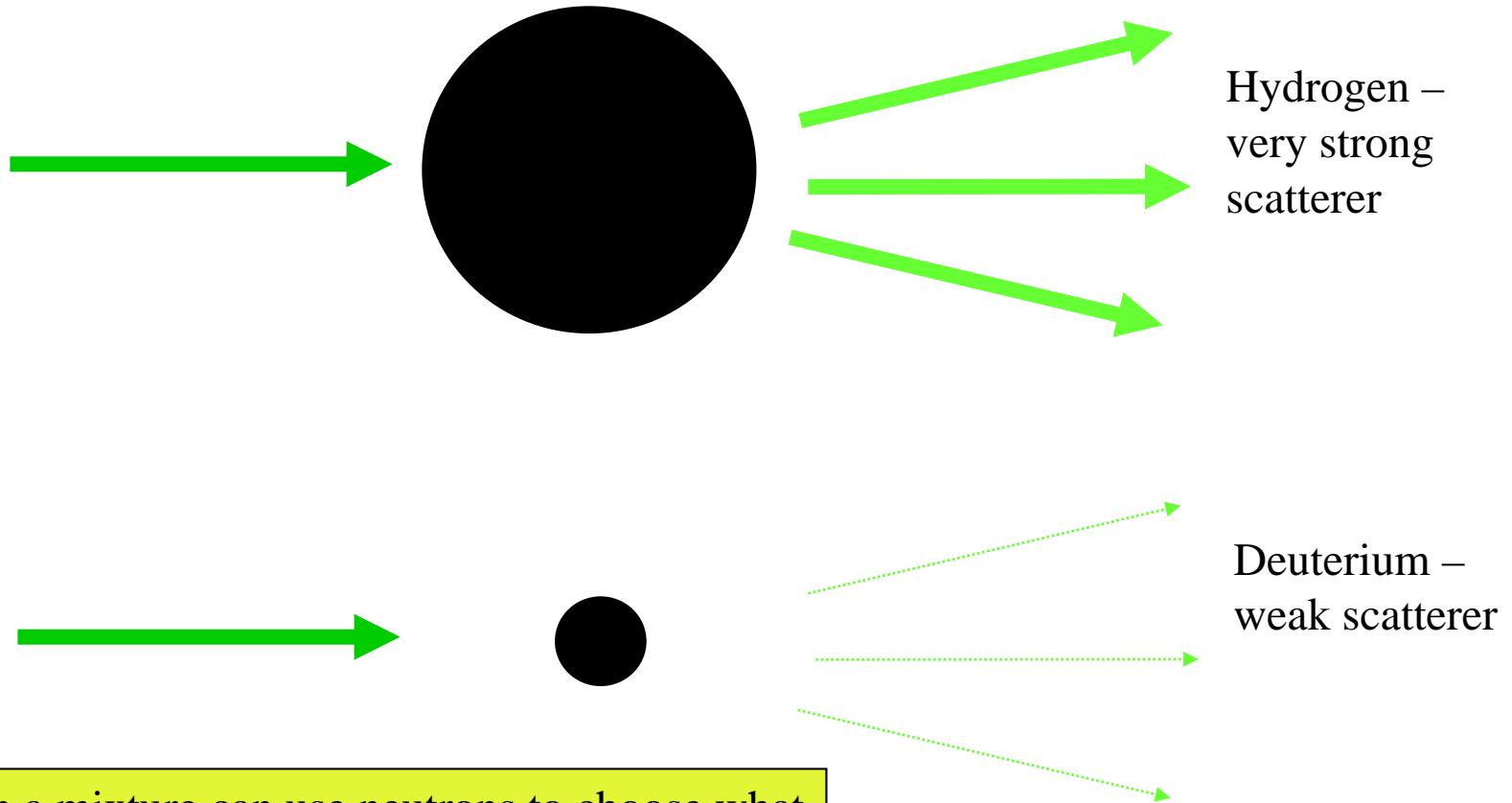
ΔE

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



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

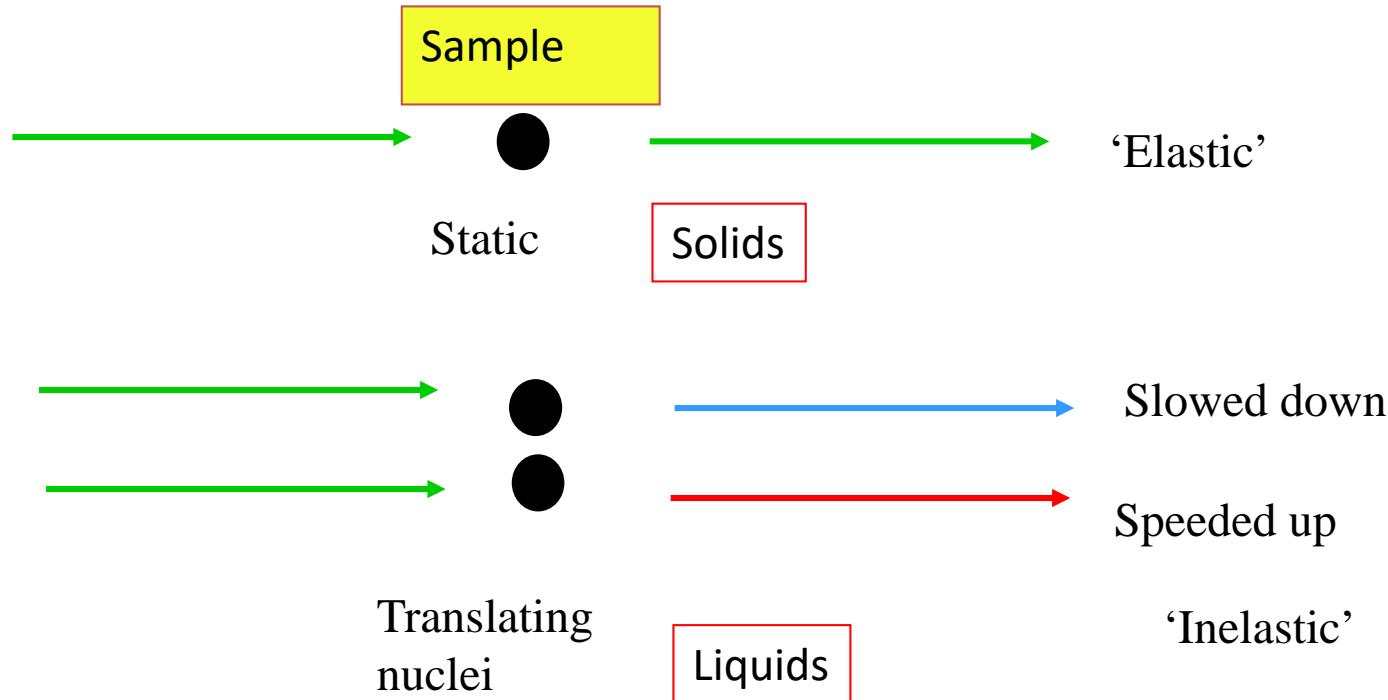
Hydrogen and Deuterium are different



In a mixture can use neutrons to choose what we 'see'

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

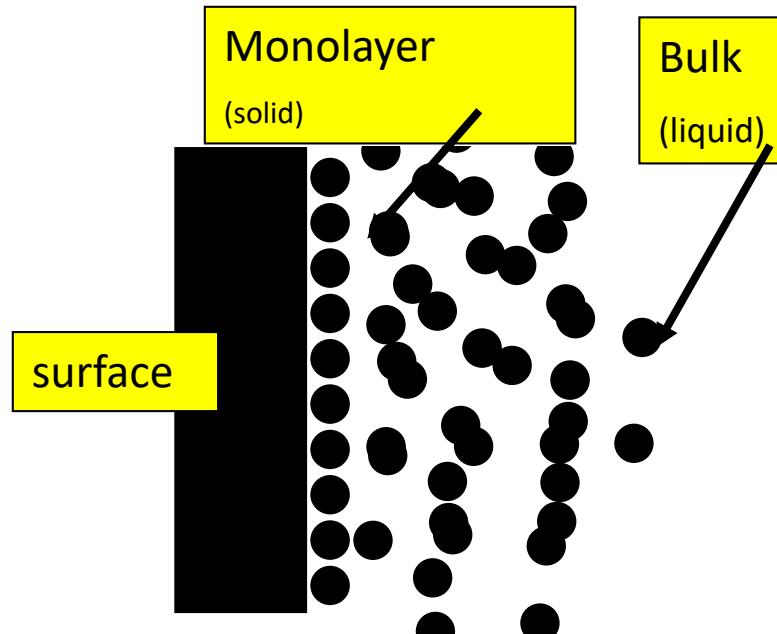
- Isotopic substitution to distinguish components ($H \gg D$)
 - Dynamics to differentiate adsorbed from non-adsorbed materials
- Neutrons can exchange energy with sample nuclei:



Intensity of elastic scattering → Amount of adsorbed material

Adsorbed Molecules are different

Adsorbed layers are 'static'

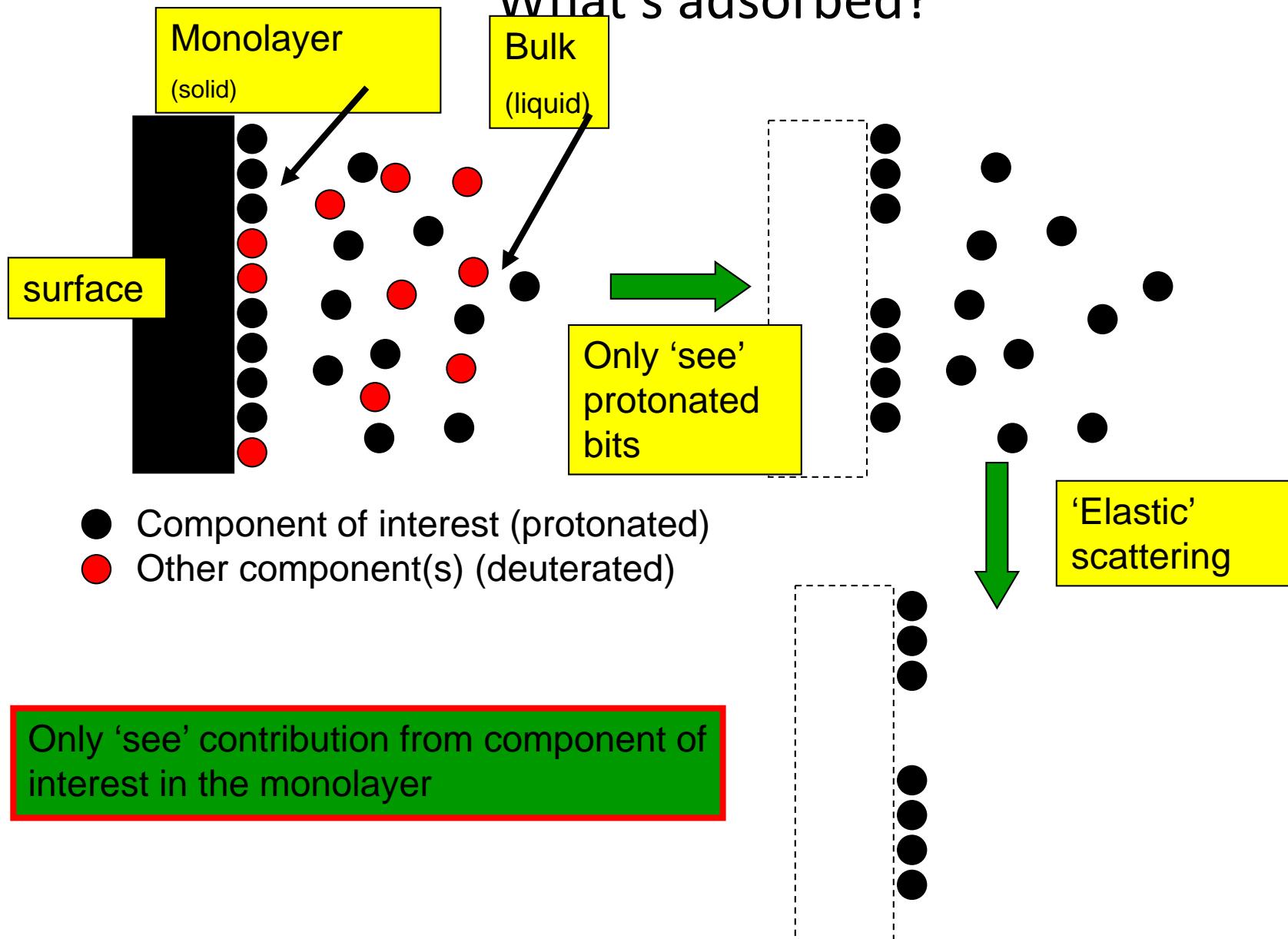


Liquids are 'dynamic'

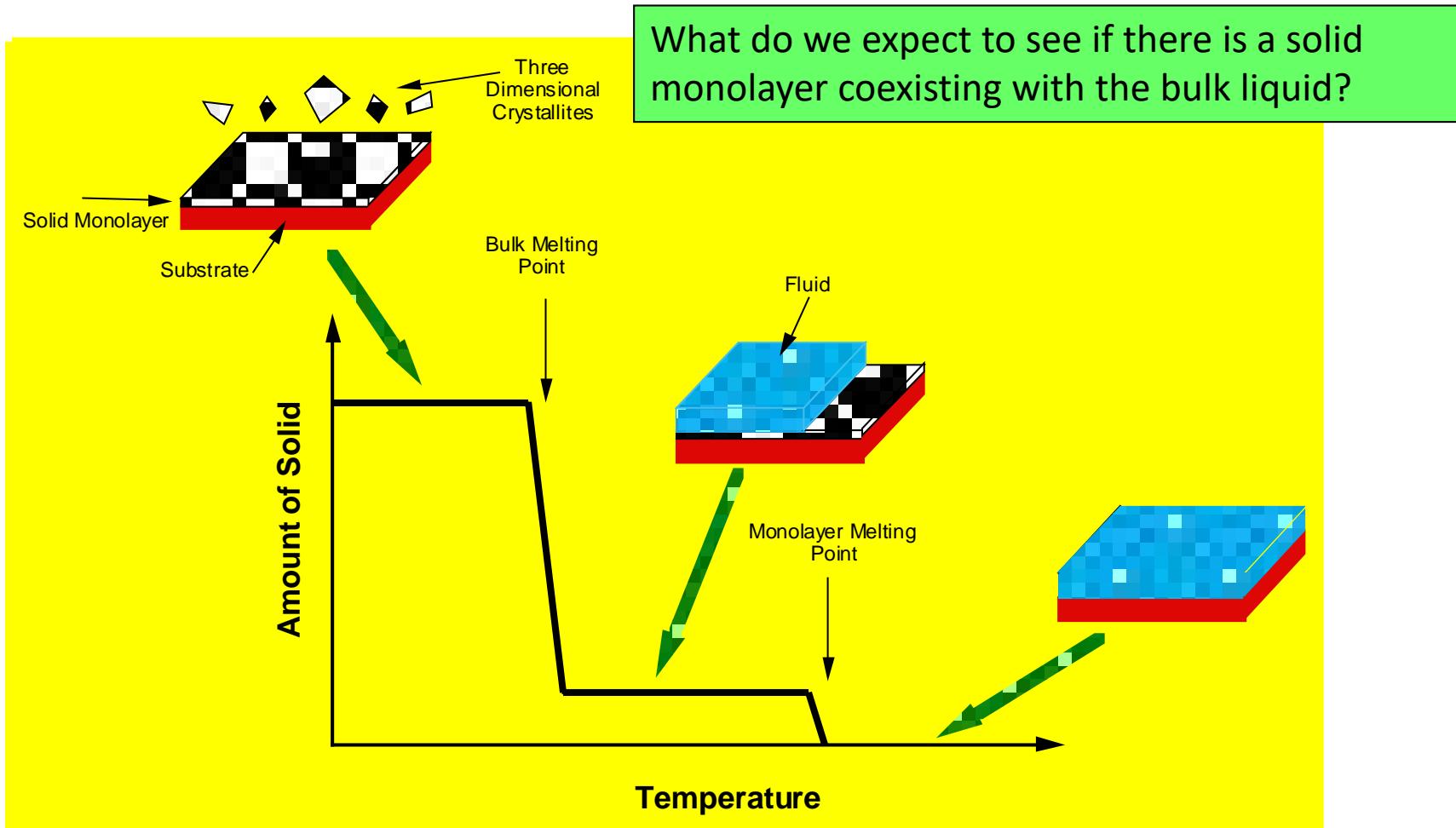
Use mobility to distinguish adsorbed layers

'IQNS'

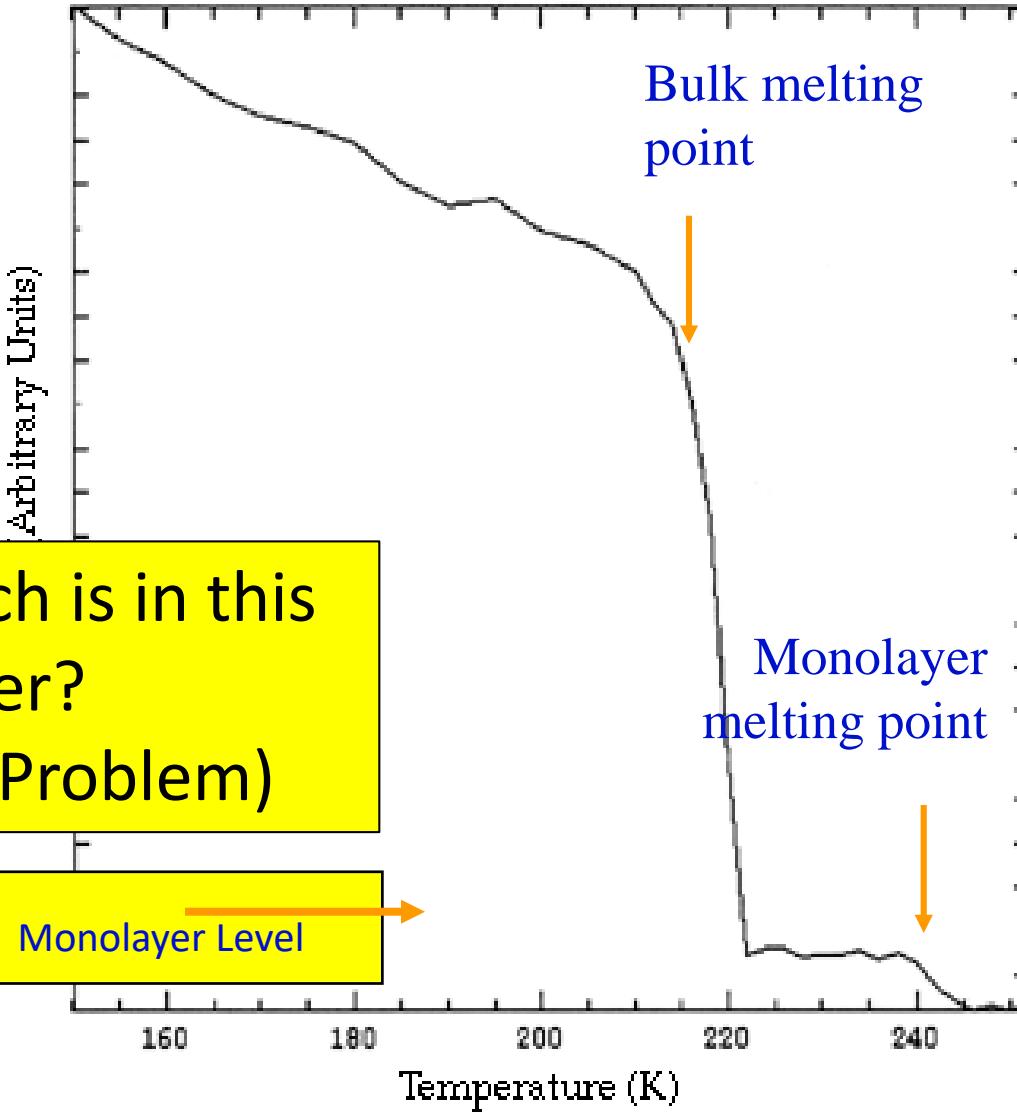
What's adsorbed?



Incoherent quasi-elastic neutron scattering (IQNS)



IQNS Results: Octane on Graphite



What's adsorbed: (IQNS) Results from mixtures

Monolayer composition as a function of solution composition

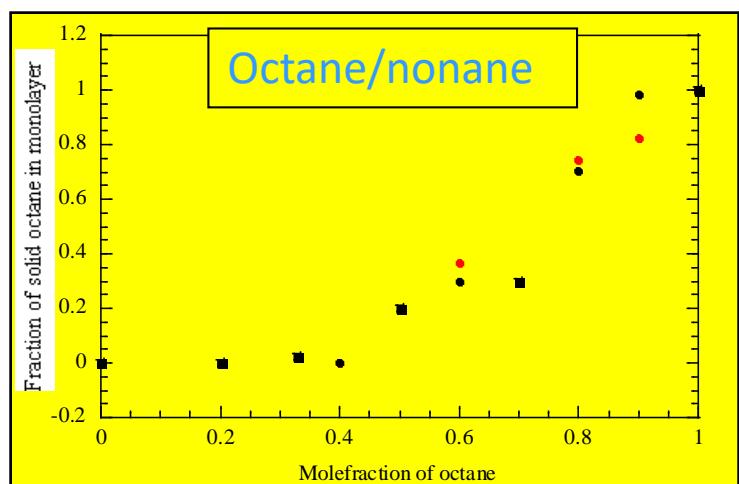
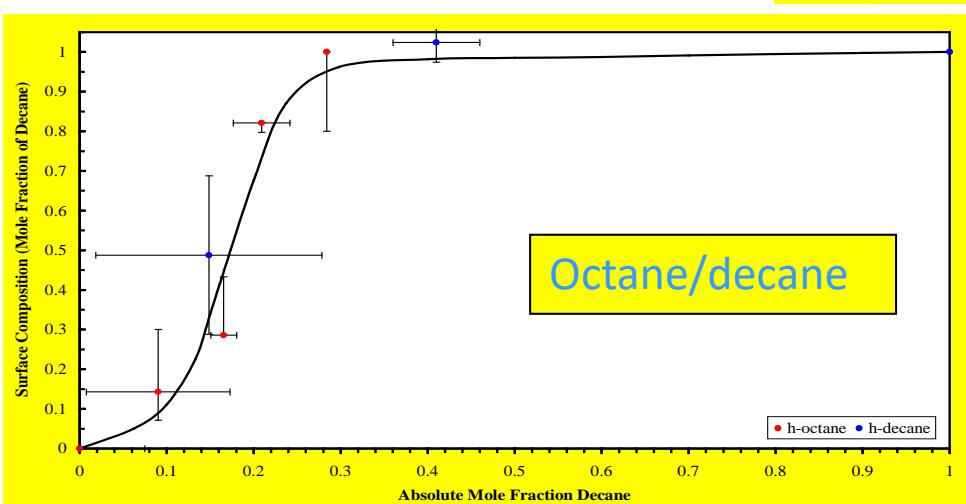
S data for Octane-Decane (h-octane + d-decane)

● Pure h-octane
△ X = 0.909
○ X = 0.715

Plateau level falls as octane is displaced by decane

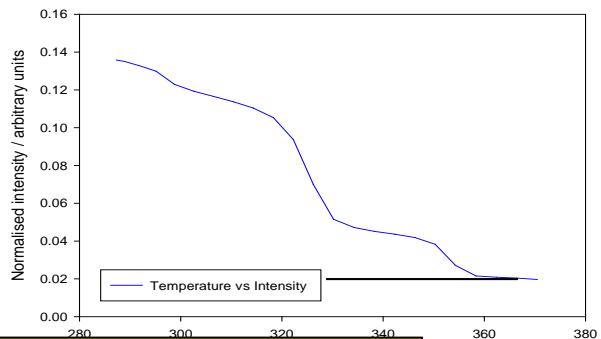
215 220 225 230 235 240 245

Temperature (K)



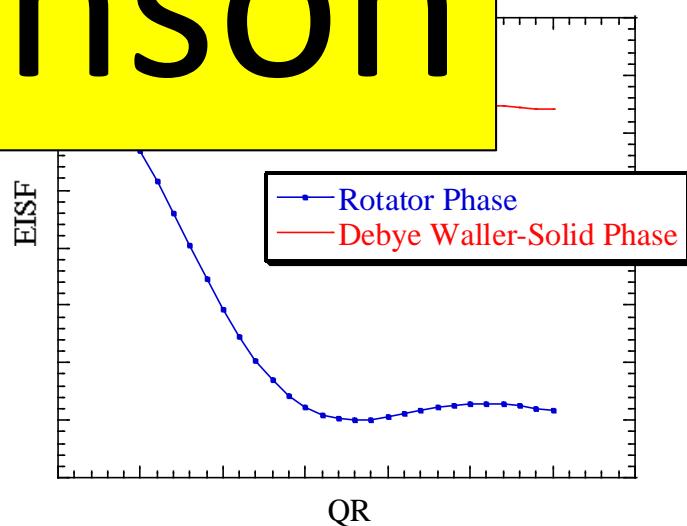
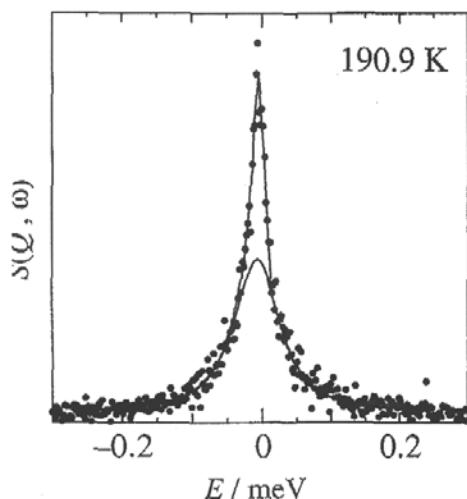
Dynamics of Adsorbed Layers

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



Mark Johnson

- Rotations
 - 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)

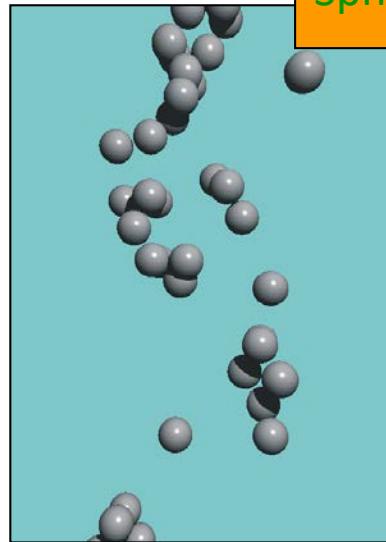
What are Colloids?

'nanoparticles'

- To know
- What shape are the separate colloids
- What orientation
- What arrangement

Example

Spheres



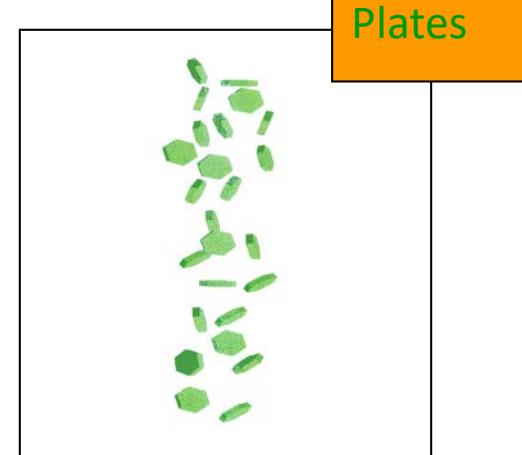
Important flow properties

Need to 'look' through metal cells

Opaque samples

Neutron Transmission

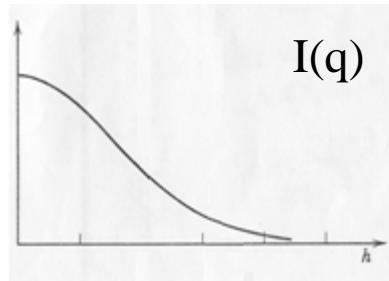
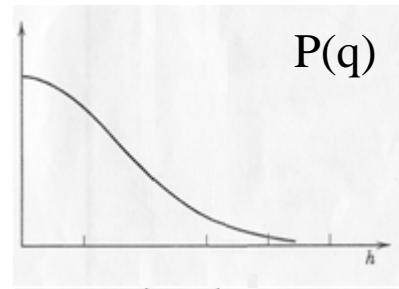
Plates



Form and Structure Factors

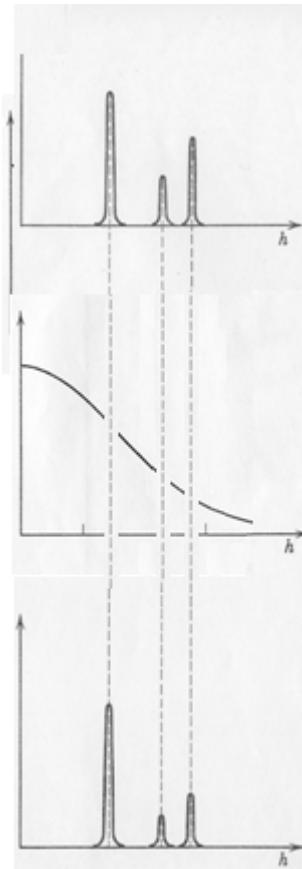
$$I(Q) = P(Q)S(Q)$$

Dilute Spheres



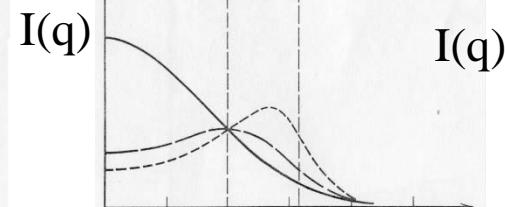
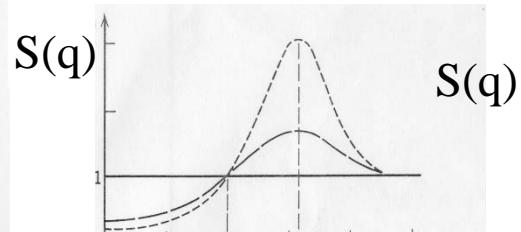
Characterise particles

Crystal



Diffraction peaks

Liquid



'Liquid' ring

SANS: single colloid scattering (Dilute)

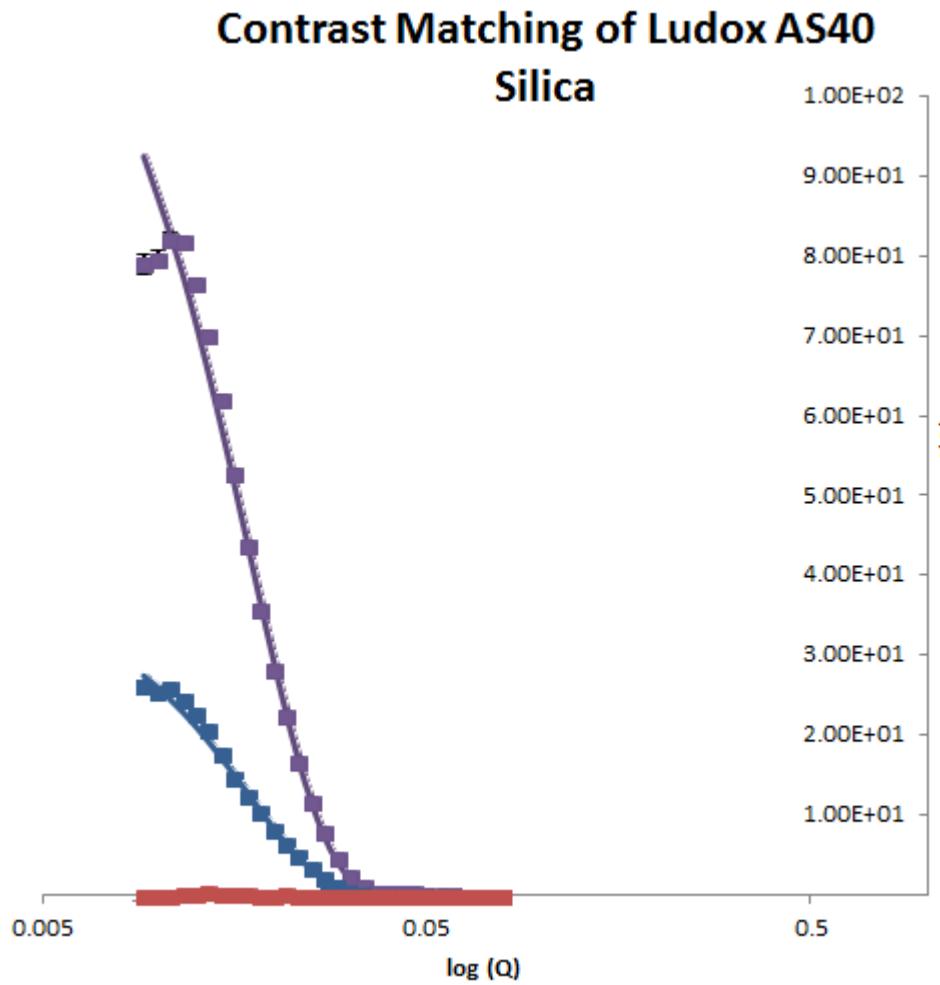
What's on the surface

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



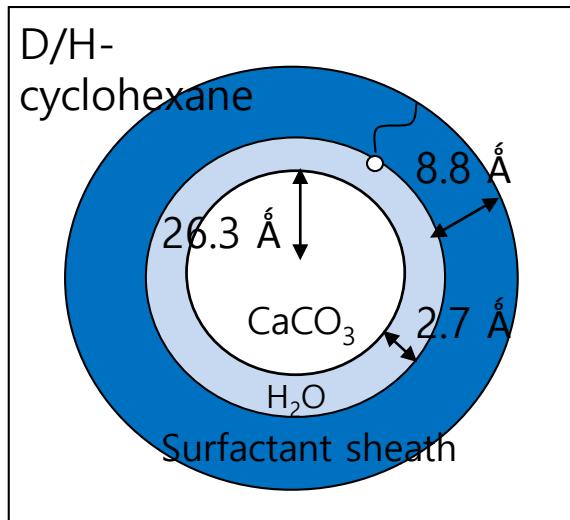
‘See’ each component of a mixture separately
Simplify complex systems

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

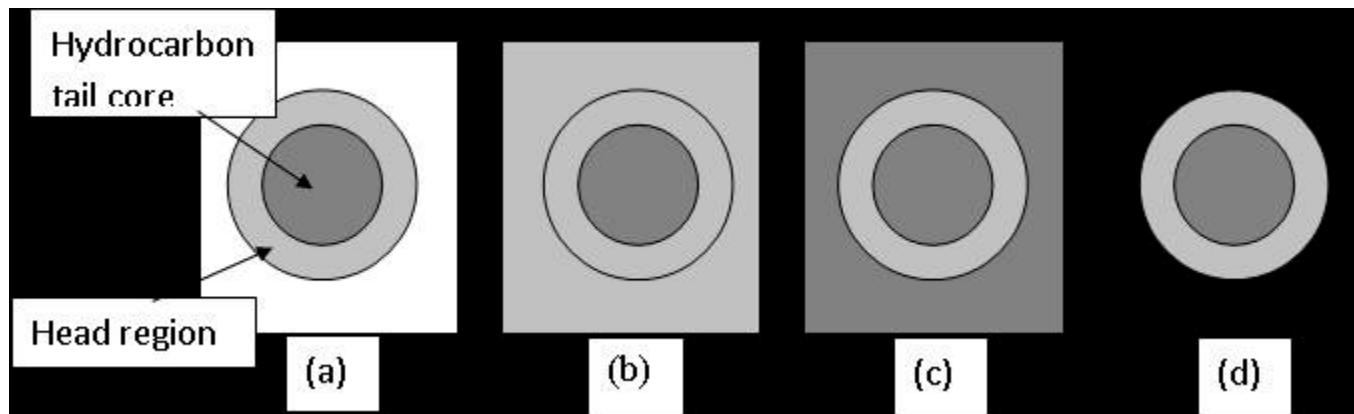


Structure: core/water/surfactant/oil

'Contrast variation'
H₂O and D₂O mixtures
change 'colour' of different bits

Contrast variation:

- Enhance sensitivity to each bit by selective deuteration

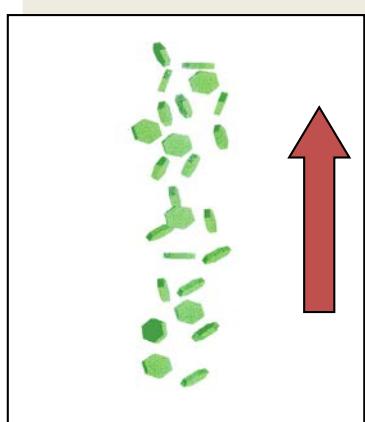


IF TIME

SANS: Single particle orientation

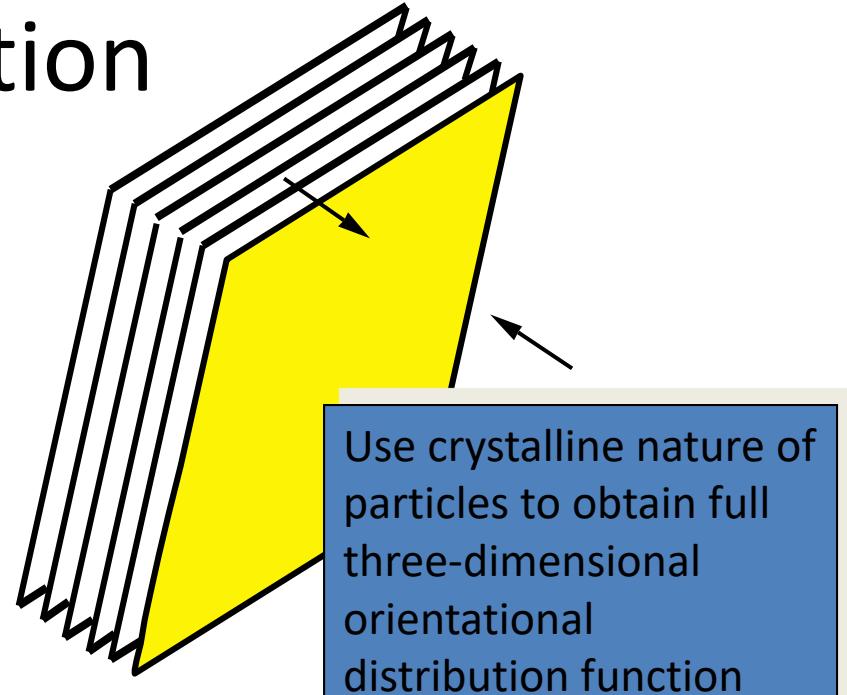
- SANS of plate-like particles

SANS: single particles - orientation



Flow
Direction

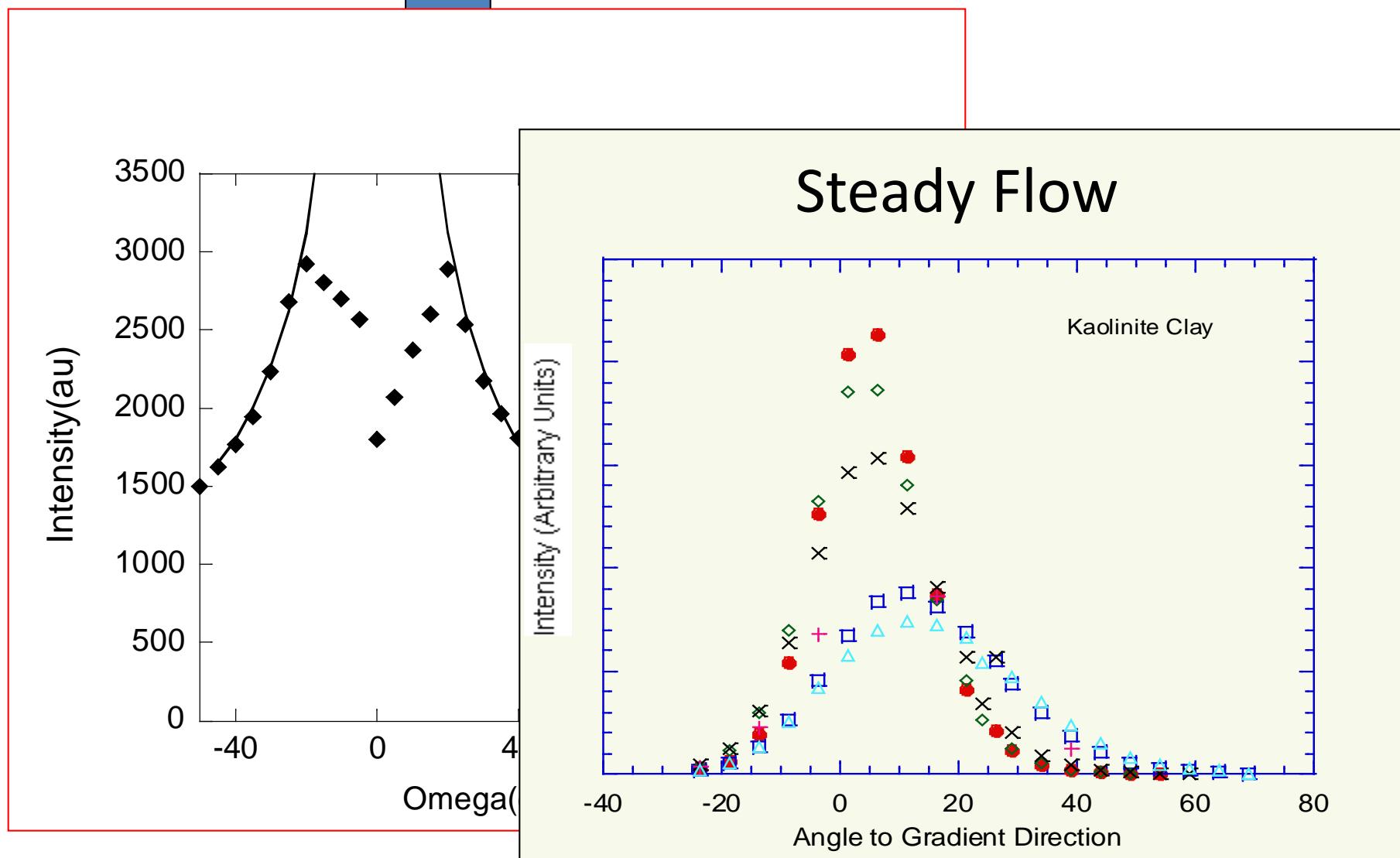
When is the extent of orientational order?
Under flow?
With particle size?
Aspect ratio?
Concentration?



Anisotropic Particles

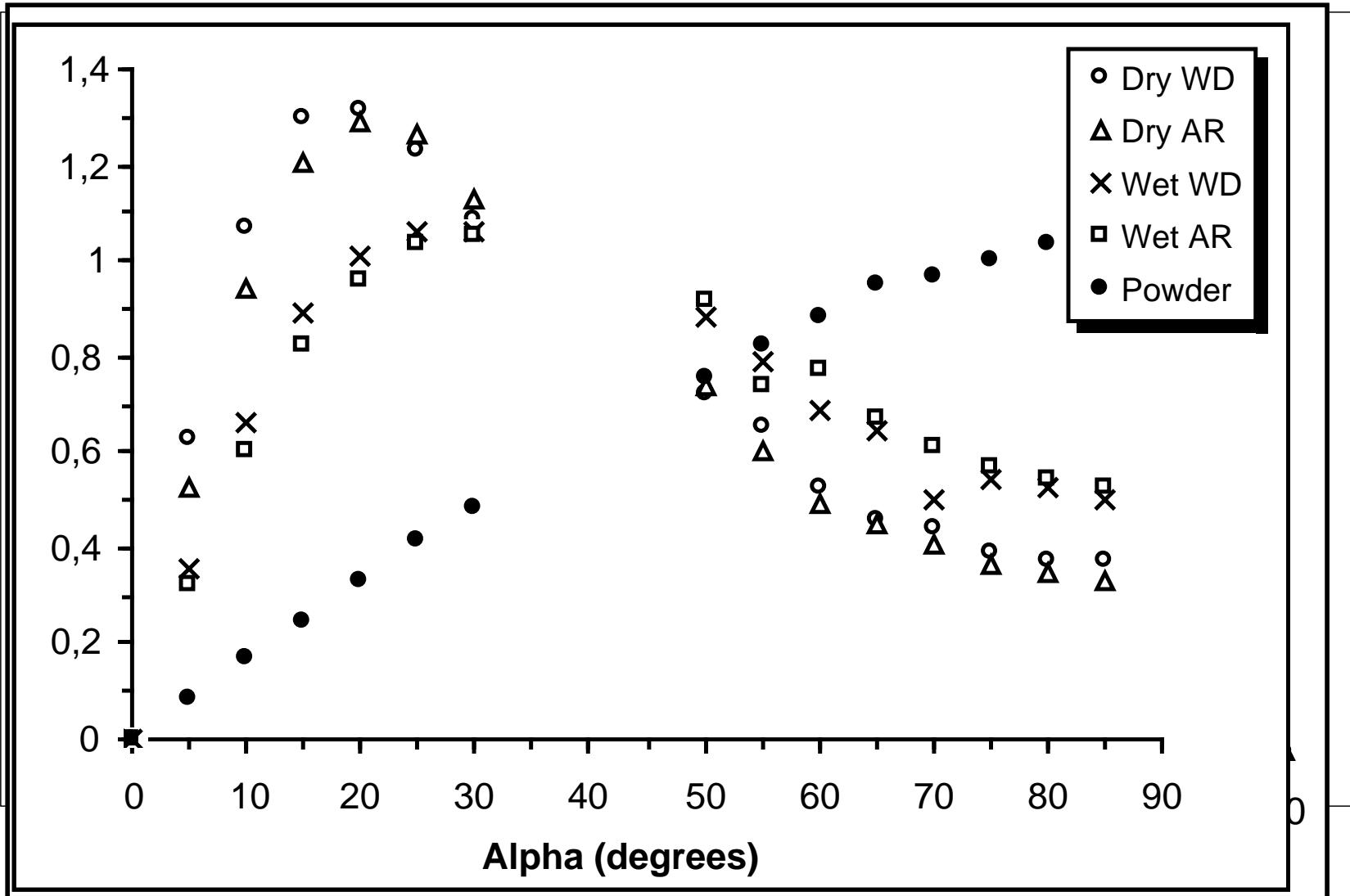
Completely random particle distribution => 'powder' ring
Perfectly aligned => single 'spot'
Preferred orientation => 'arc' of intensity

Measuring orientational order of plates



Orientational order of the plates in flow

Dense Clay pastes under static and cross-flow conditions

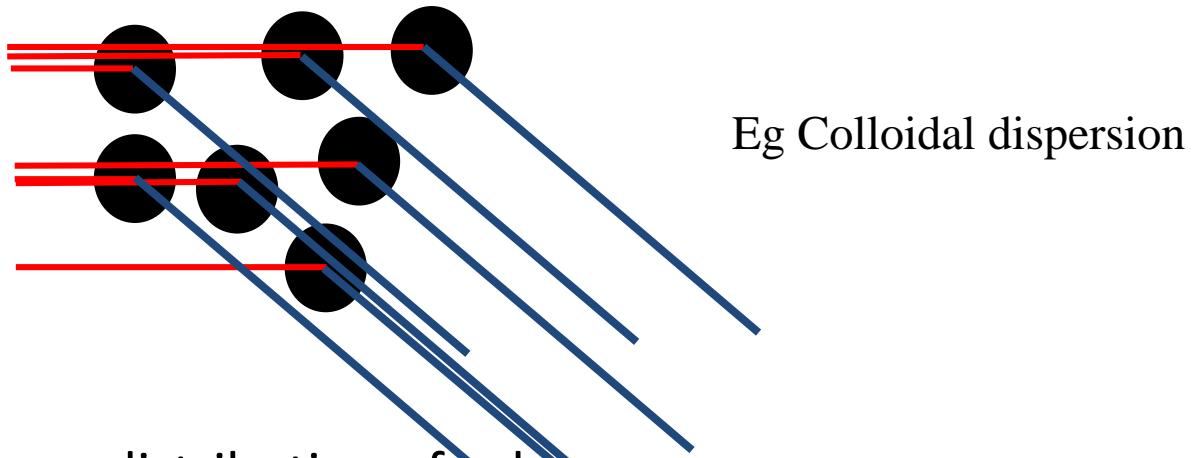


Two colour cars



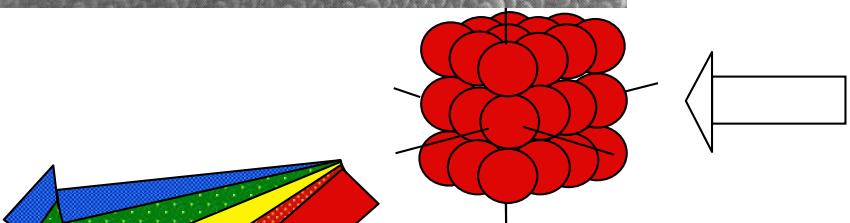
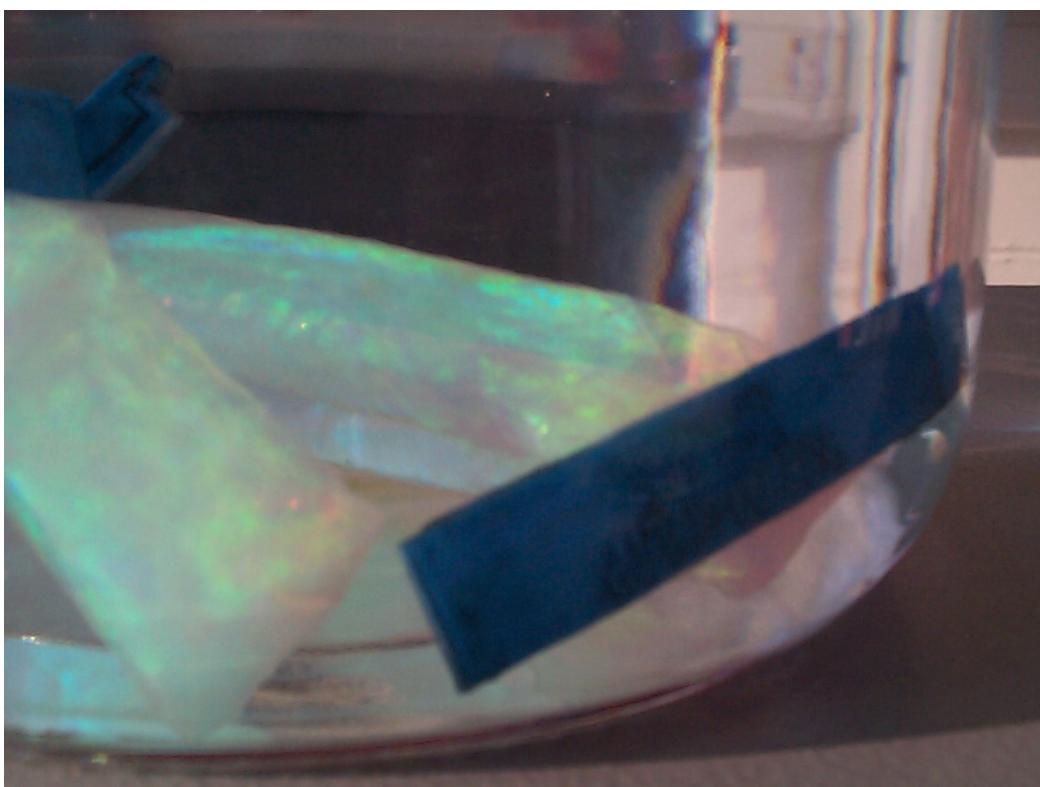
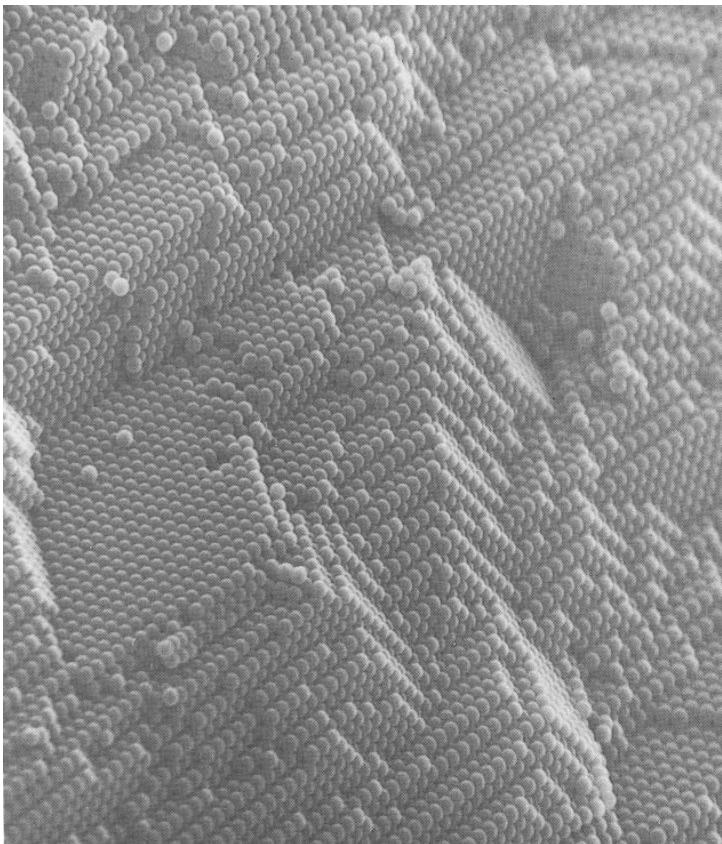
END of EXTRA BIT

SANS: Interference Between Objects



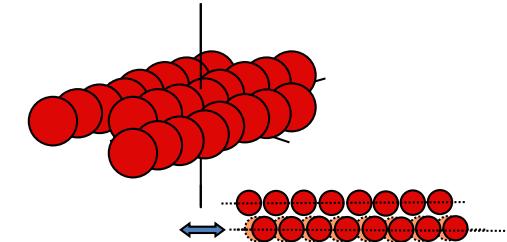
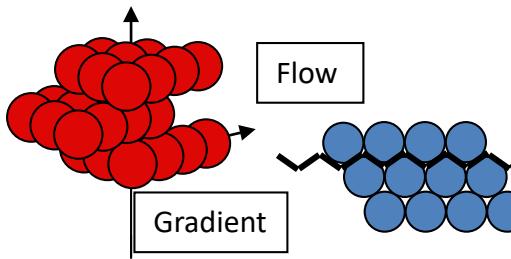
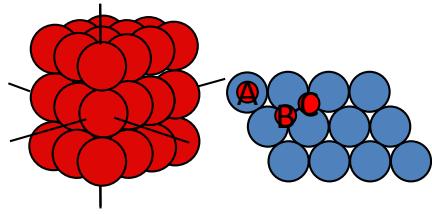
- Consider scattering as distribution of spheres
 - Isolated object, e.g. spheres ($P(Q)$)
 - $S(Q)$ is called the interference or ‘structure factor’: interference from different colloids.
 - Measured intensity is:
$$I(Q)=P(Q) \times S(Q)$$
- Other systems:
 - Crystal - unit cells repeat on a regular 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

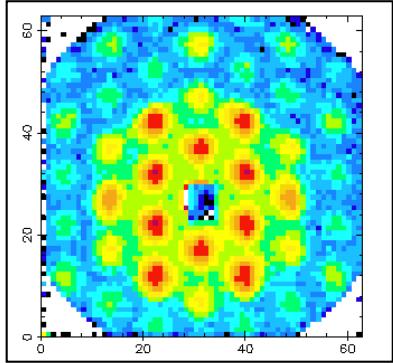
'Layers'

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

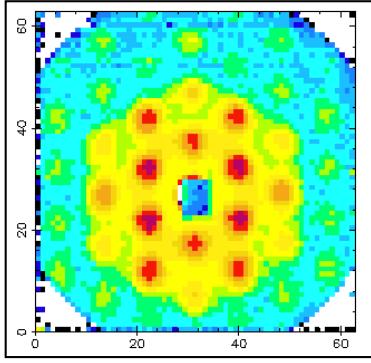
'Strings'

Particles in lines

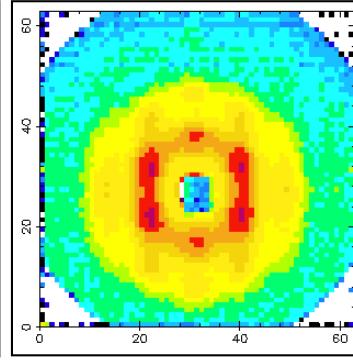
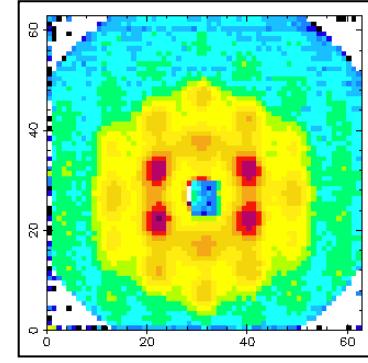
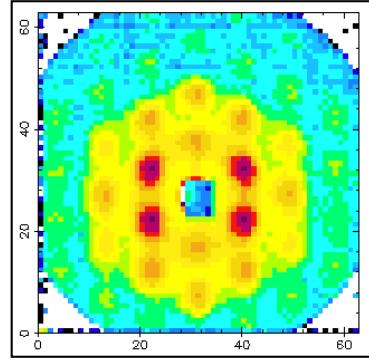
Increasing Shear Rate



'Crystal'



'Sliding layers'

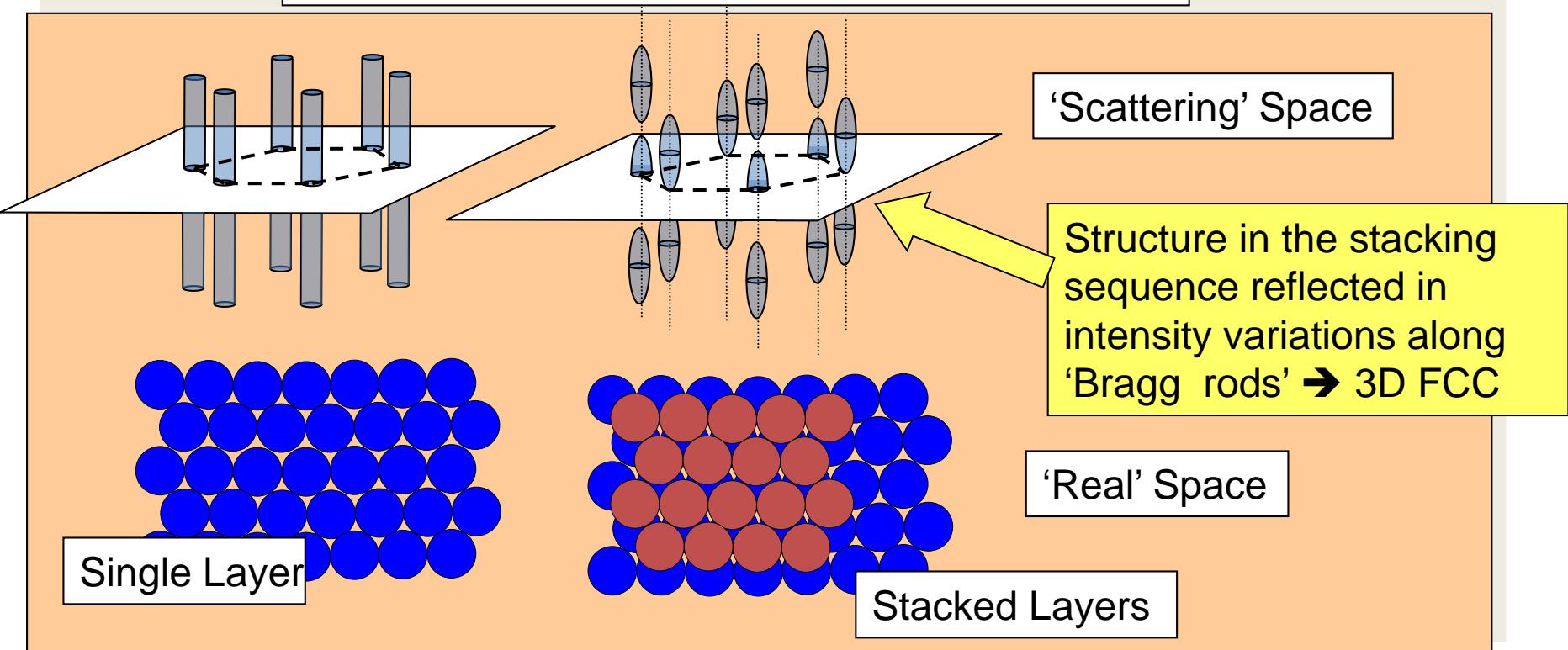


'Strings'

Behaviour like 'atoms' only much larger scales and slower

Charged stabilised
latex spheres 8%

$S(Q)$: 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’)

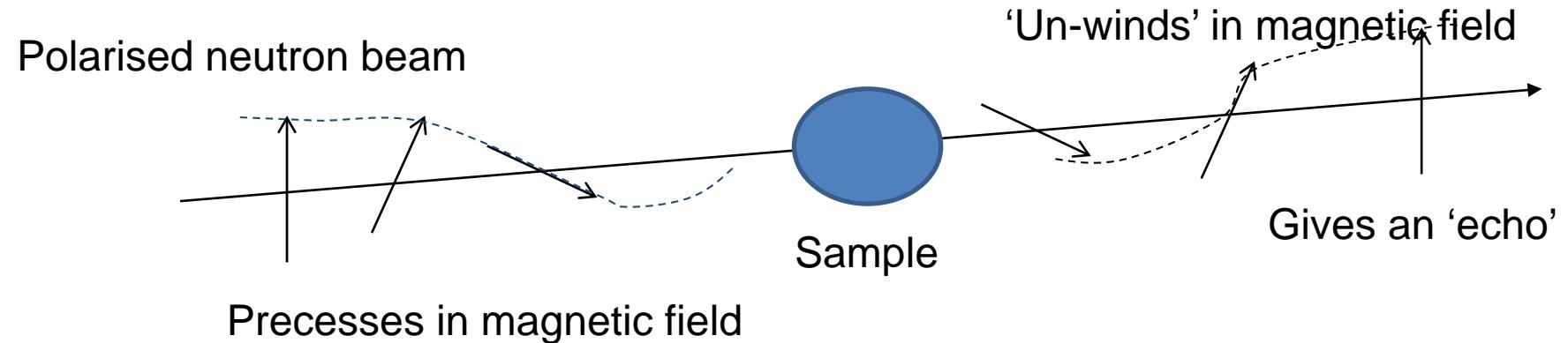
To see scattering by SANS at small angles need **VERY**
tightly collimated beam: BUT THEN NO FLUX!!

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

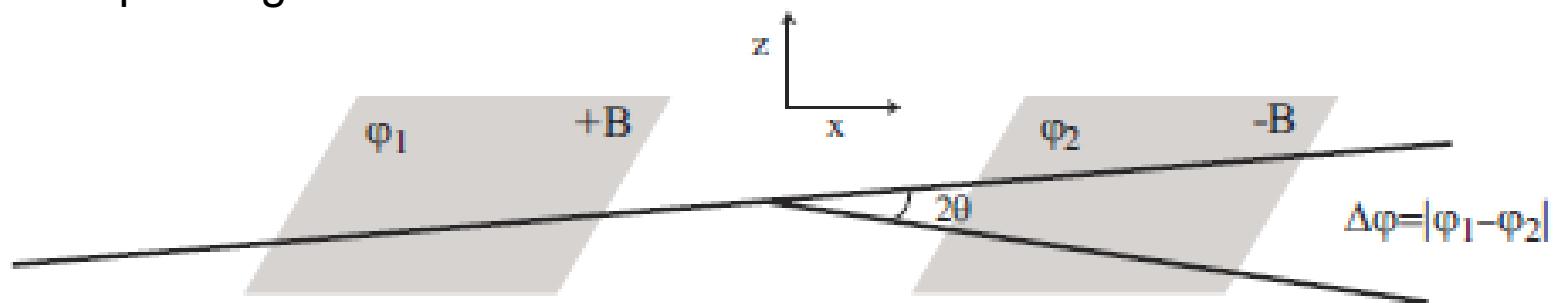
(**VERY CLEVER IDEA THIS!!**)

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, $G(z)$

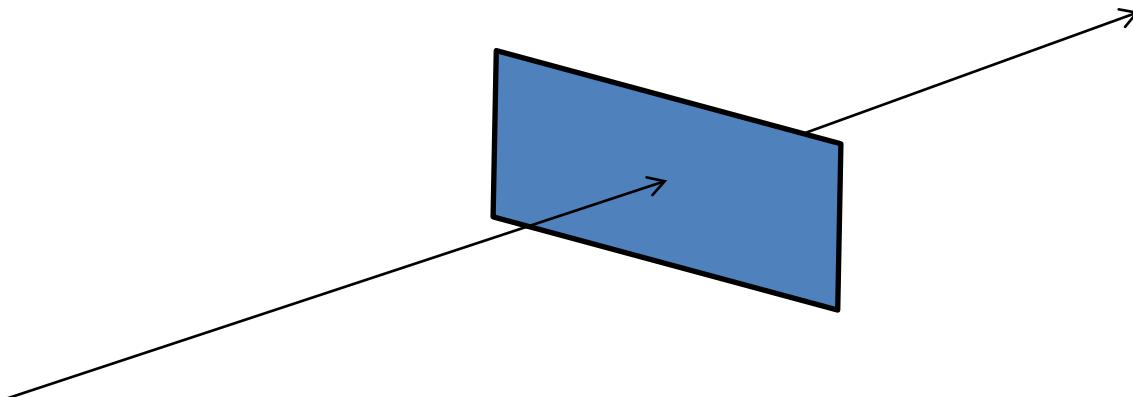
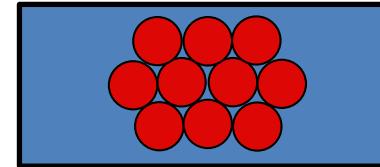
Example: Silica particles in polymer matrix

Colloidal Crystal

- J. Baumberg Samples:

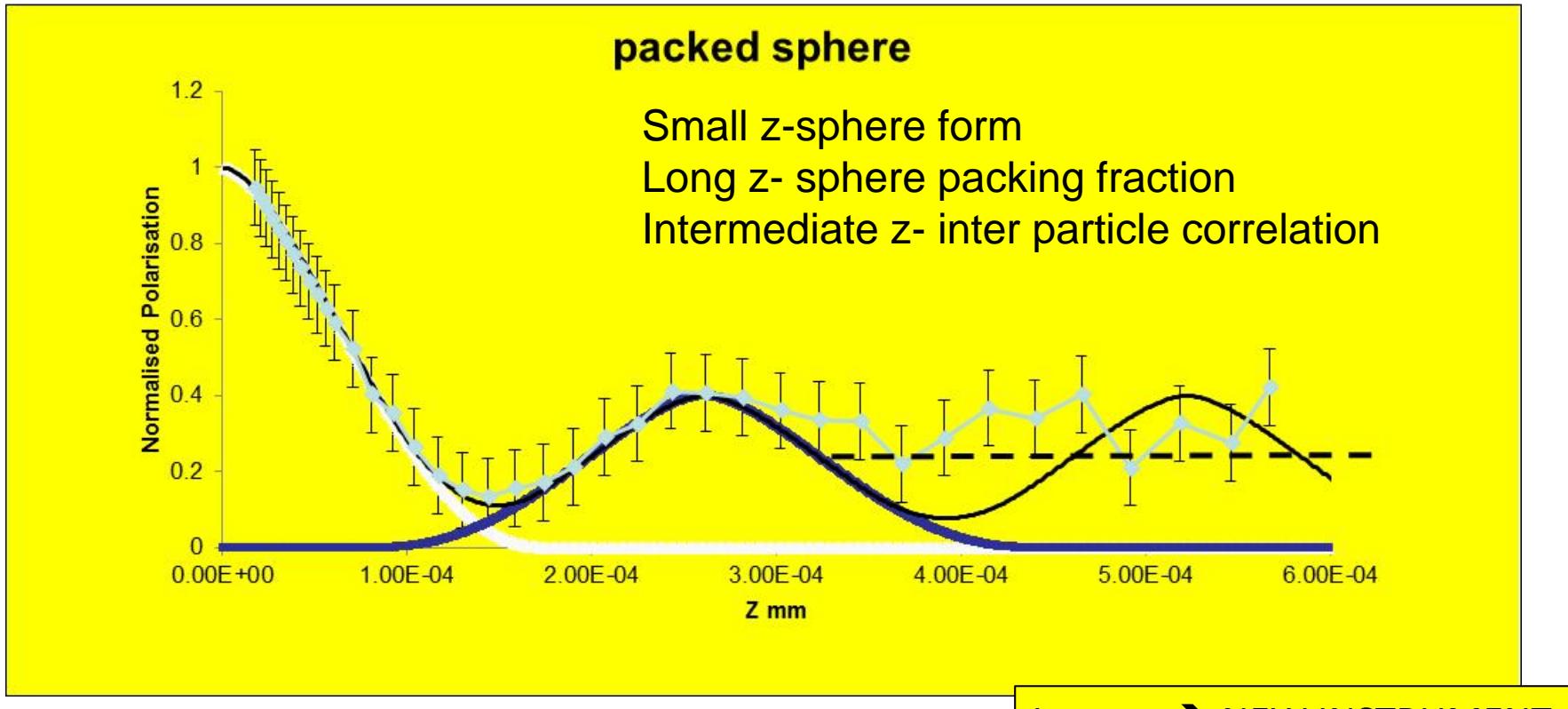
Hexagonal layers of 200nm silica in polymer matrix, 0.47 volume fraction.

Layers oriented and regularly stacked



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

- ‘Ordered’ array of spheres: SE-SANS



- (i) Core radius (big!): 90nm (good agreement)
- (ii) Vol fract as $z \rightarrow \infty$, 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?

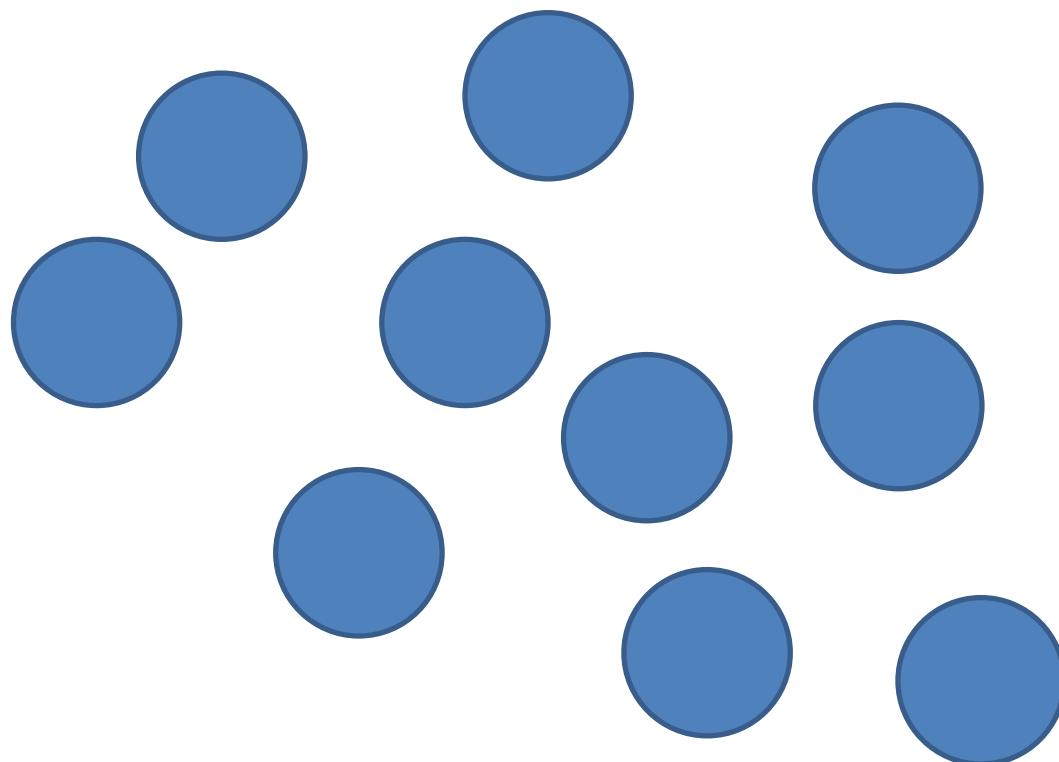
- No long range order: NO diffraction??

Oh dear!!

But still a lot of structure..

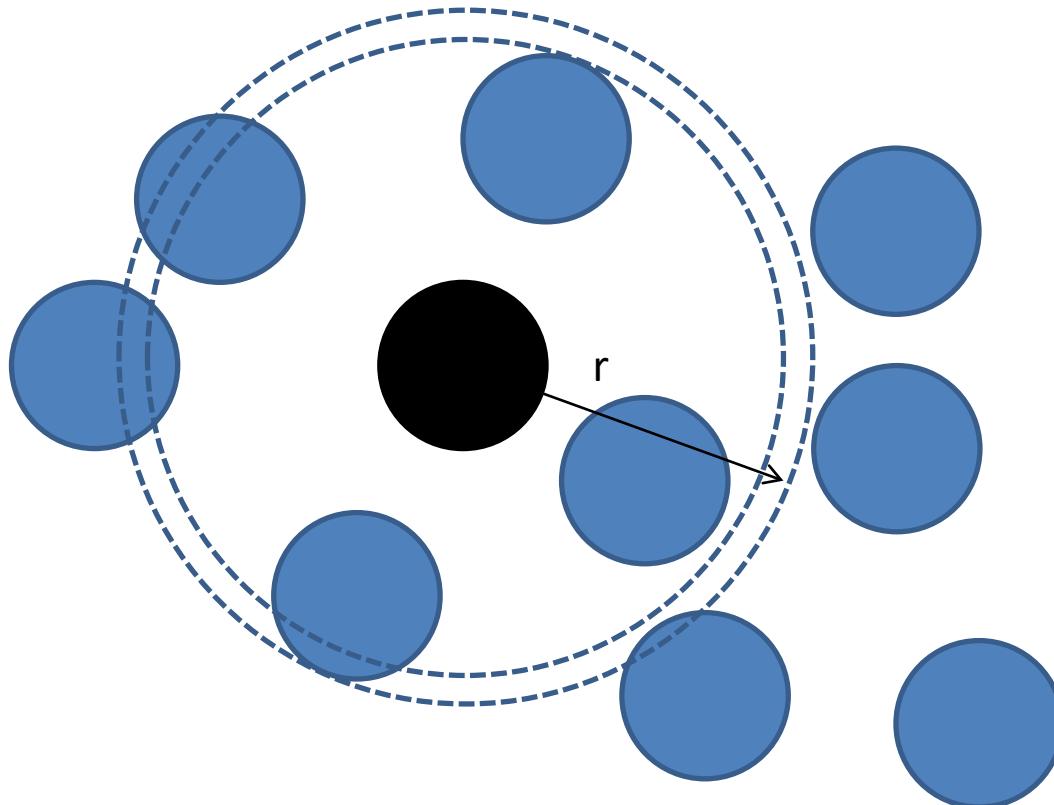
Radial distribution function

Liquid species



Radial distribution function

Liquid species

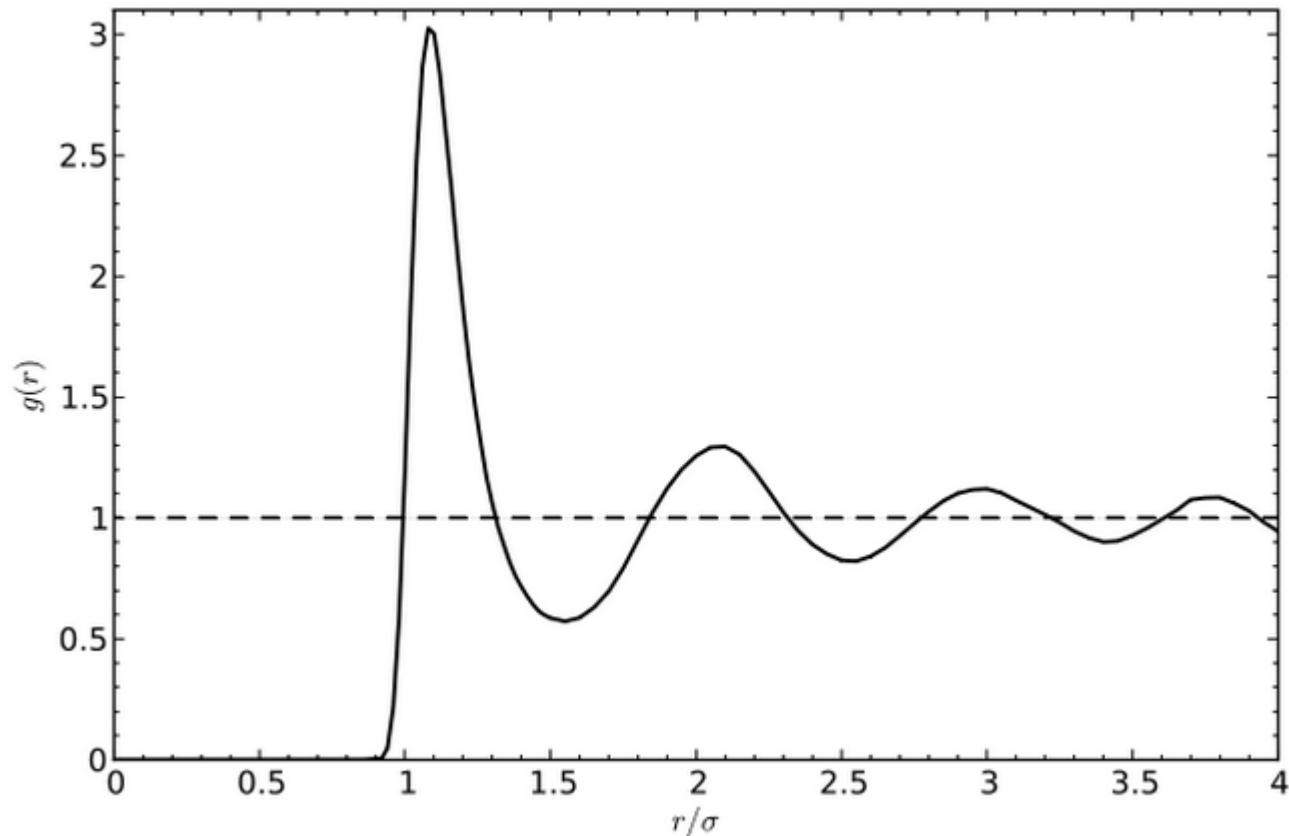


How many species in this shell at distance r from the central one: $g(r)$

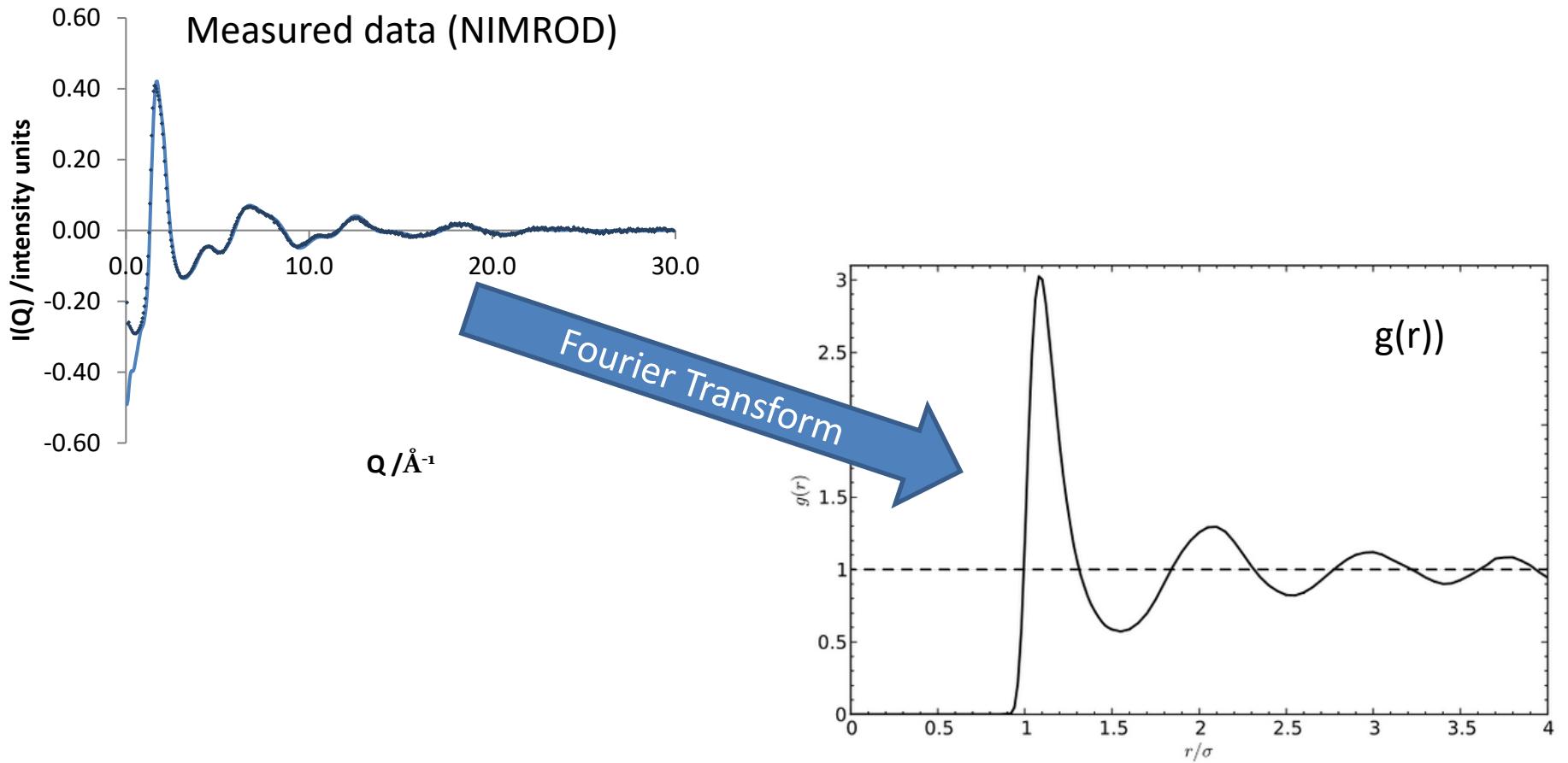
Pair distribution function: $g(r)$

(normalised)

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



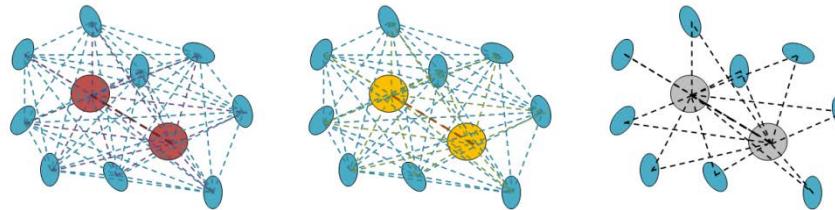
Pair distribution function: $g(r)$, FT of scattering data



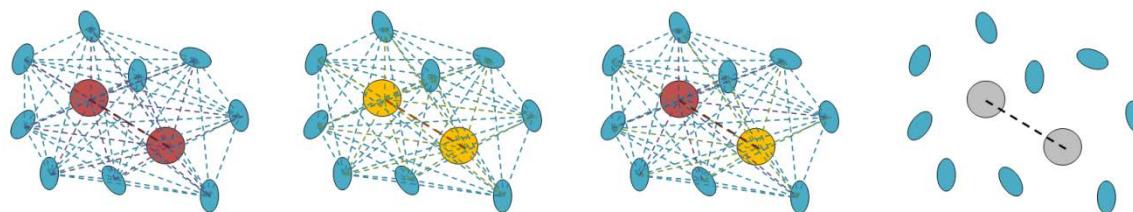
Can we ‘understand’ liquid structure?

See all Atom-Atom distances

- Separate different atom contributions by isotopic exchange (H and D):
 - a) First difference (big circles exchanged):



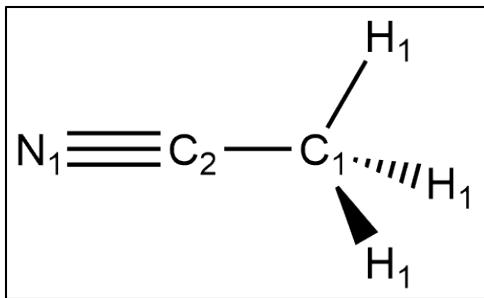
- b) Second difference:



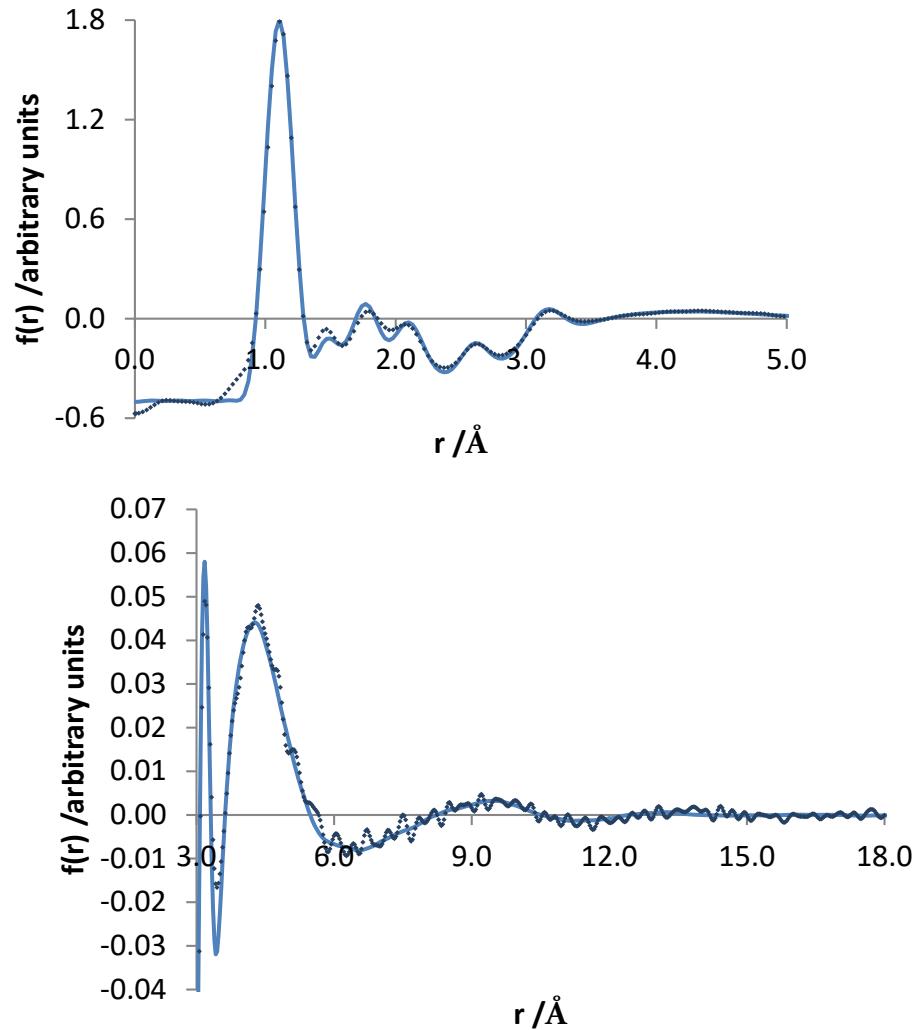
→ ONLY solute-solute distances!!

PDF example: Acetonitrile

- See correct molecular structure at short distances

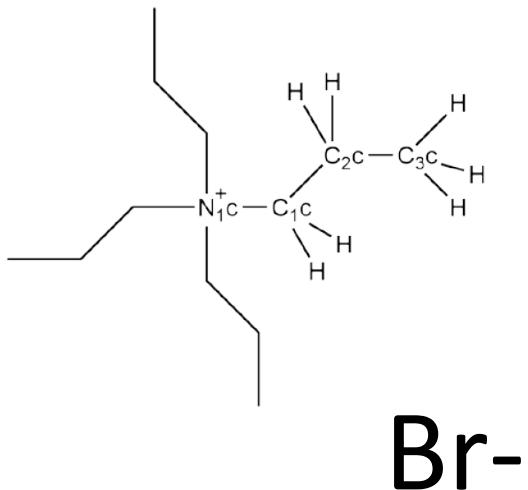


- Solvent shells at Longer distances



Supercapacitors: Ions in acetonitrile

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



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



