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

## ISIS Neutron School 2015


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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

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**

# 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, molecular patterning,
  wetting behaviour, detergency,
  Slip agents, liquid crystals.

  Solid monolayers

- Mixtures / Multicomponent:

  Cheaper …

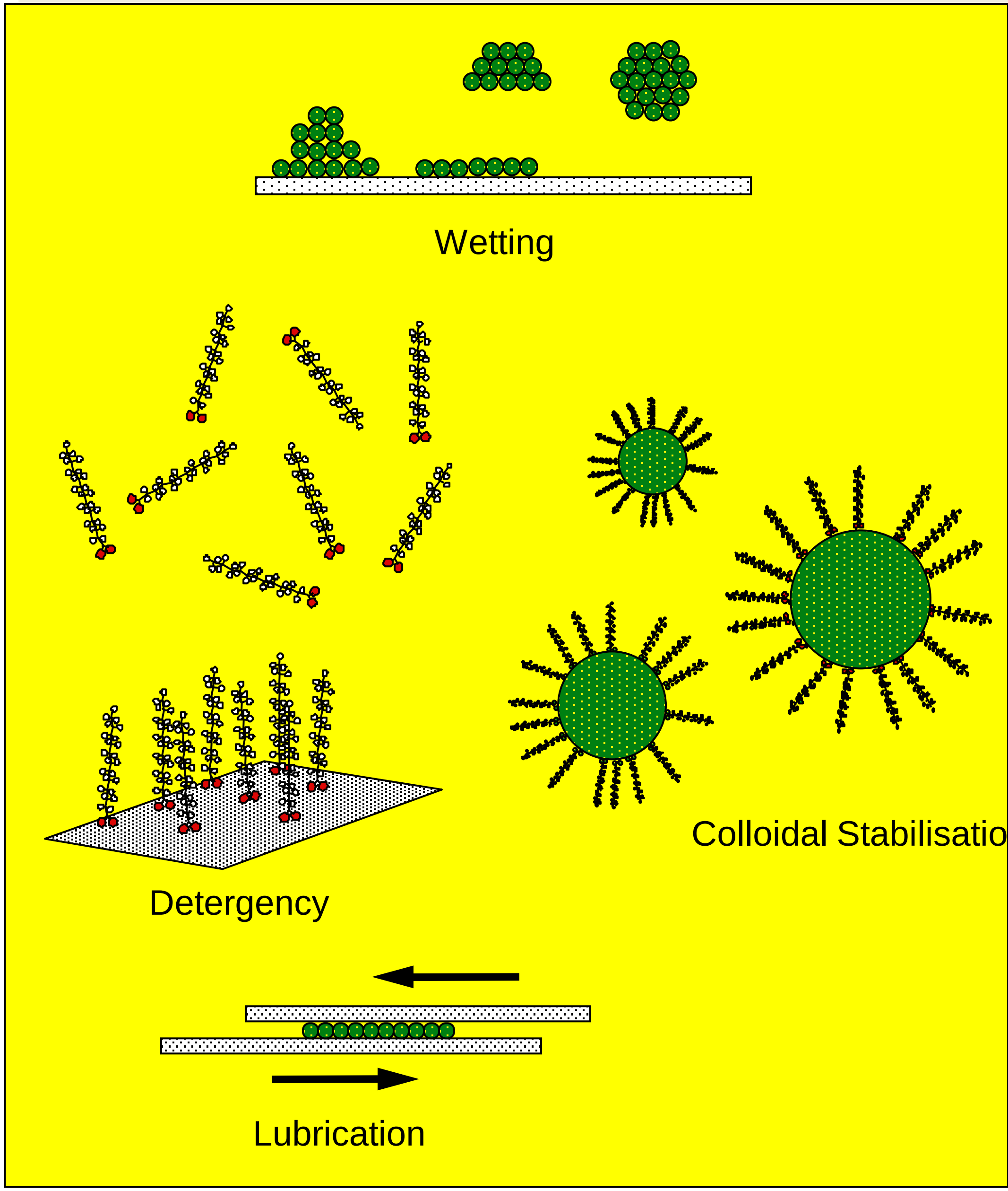
- ‘Buried’ monolayers

  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

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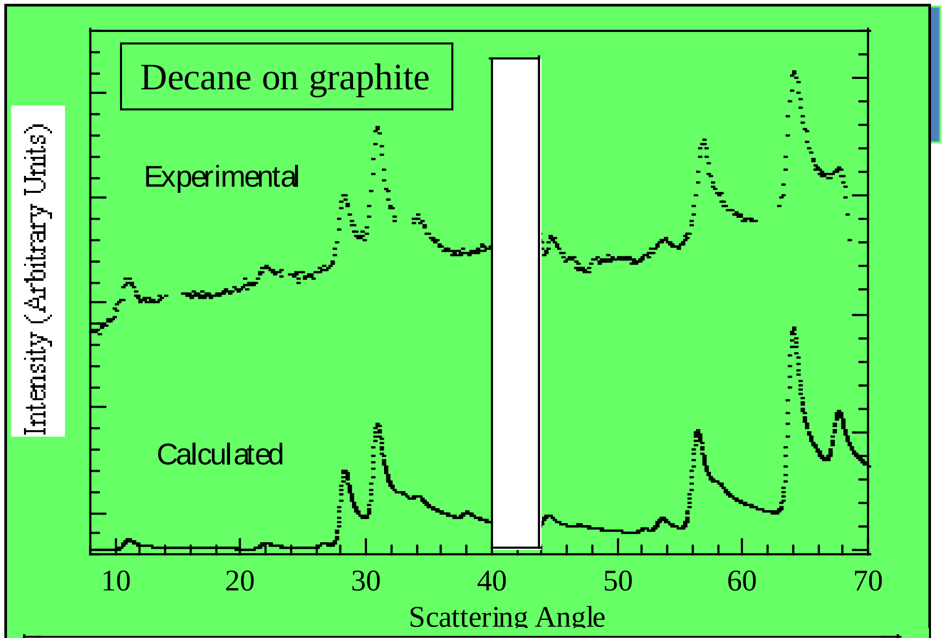
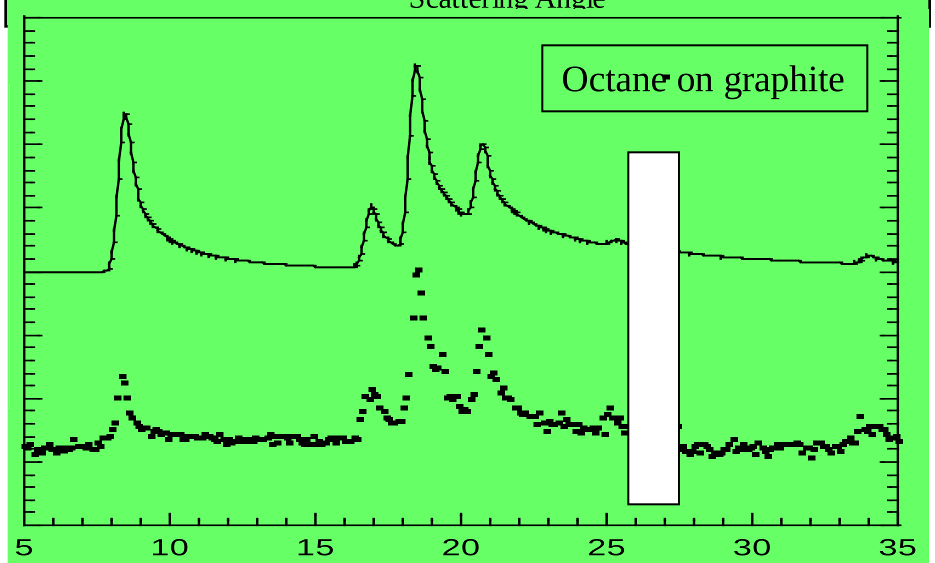
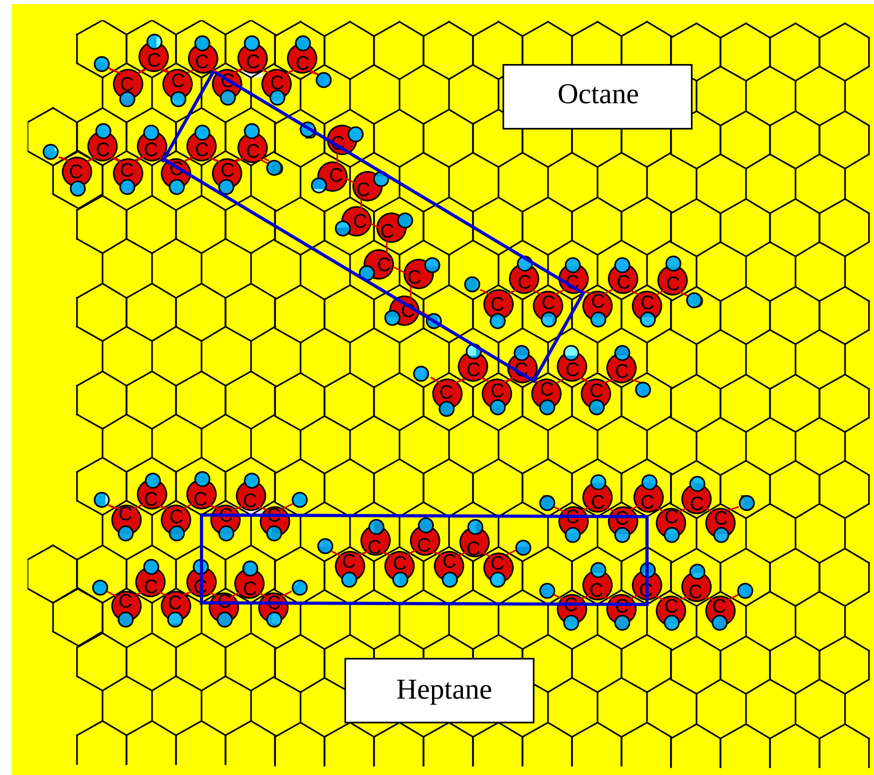
# In-plane 2D Structure:
# X-ray and Neutron diffraction



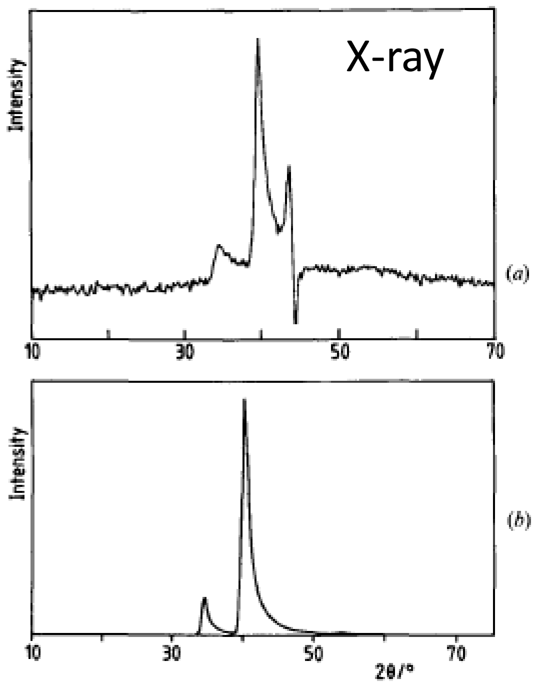



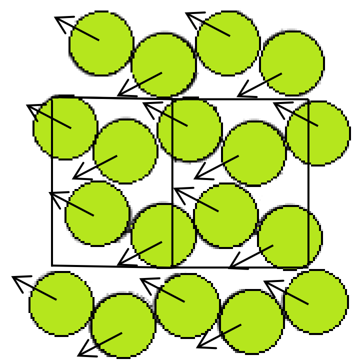




Neutrons: sensitive to hydrogen
X-rays: greater precision
Independent information
Combination is often essential

Low coverage

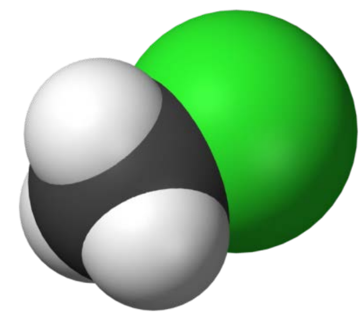
# Chloromethane: X-rays

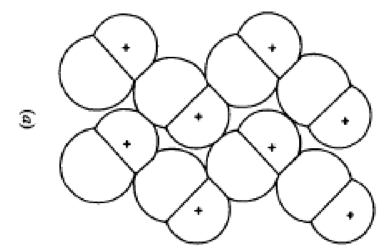


Chlorine atoms

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



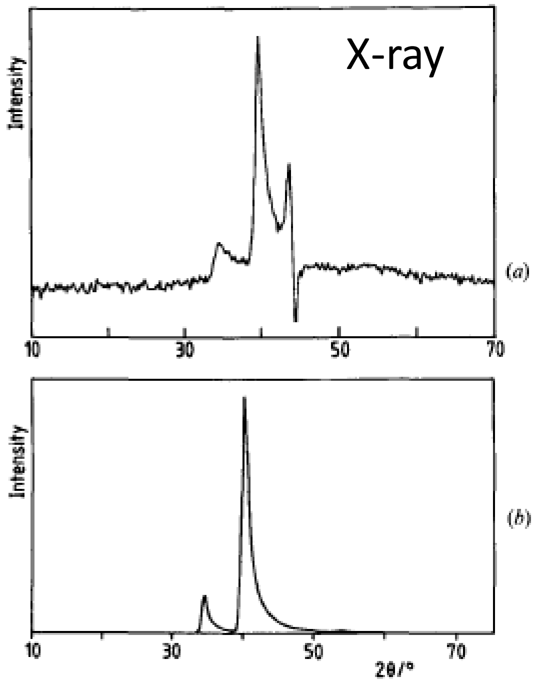


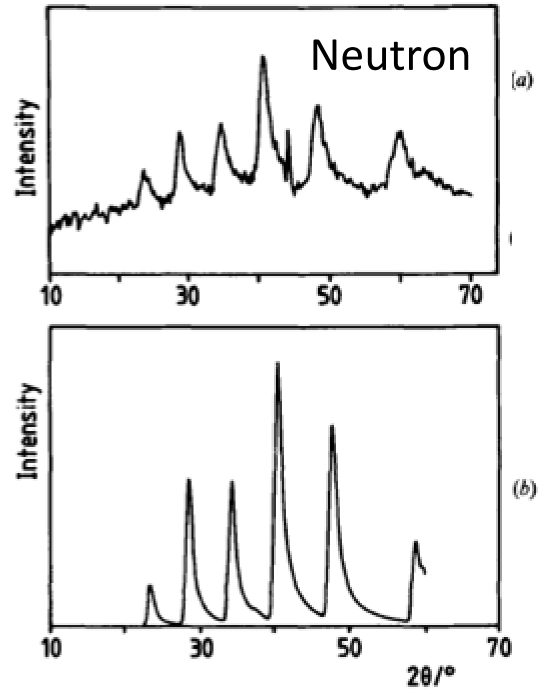
Bulk Plane

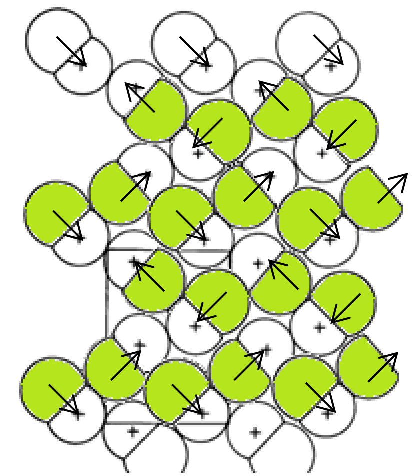
Morishige, et al., *Mol Phys* , **72** 395-411 (1991). 'The Structure of Chloromethane Monolayers Adsorbed on Graphite'.

# Chloromethane

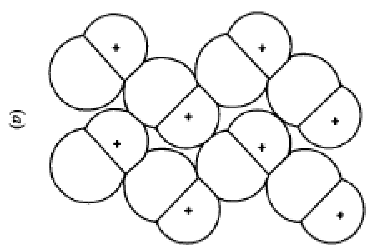
Low coverage



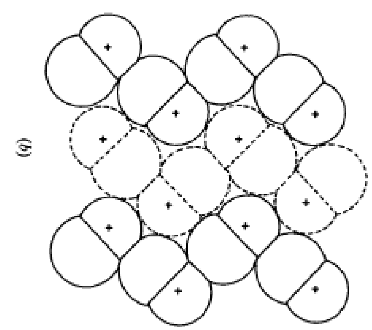



Monolayer

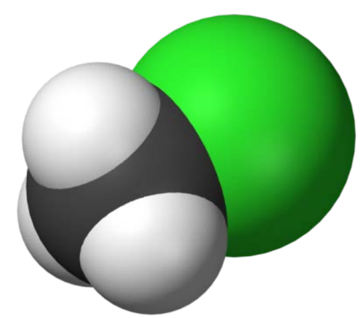


Bulk Plane



Monolayer

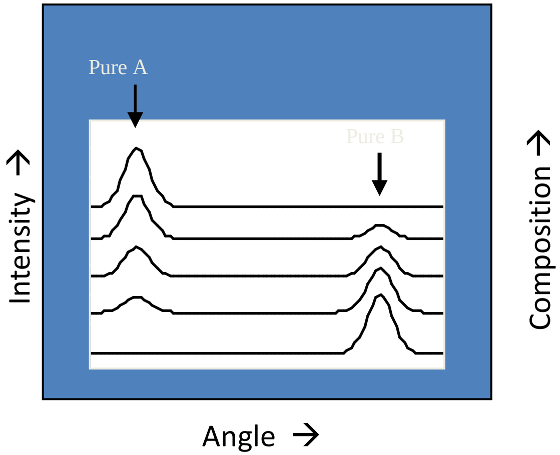
**With neutrons:**
Anti ferroelectric
Alternating chains



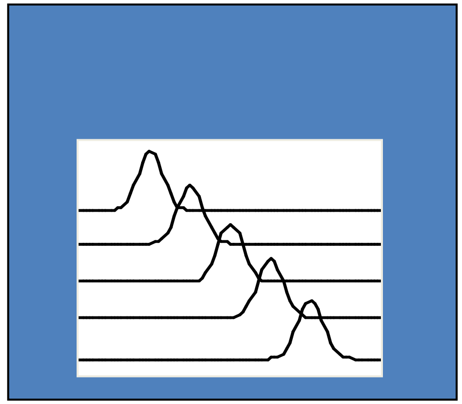
Morishige, et al., *Mol Phys* , **72** 395-411 (1991). 'The Structure of Chloromethane Monolayers Adsorbed on Graphite'.

**Need neutrons to see $CH_3$ groups and full symmetry**

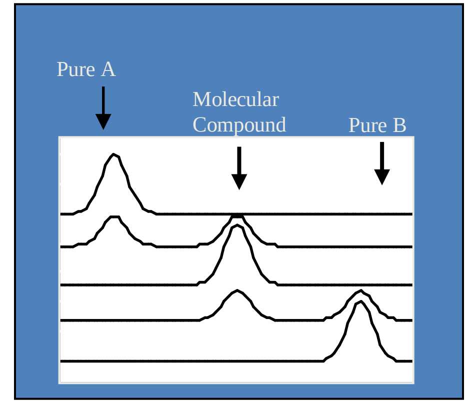
# Structure: Diffraction from Mixed Monolayers



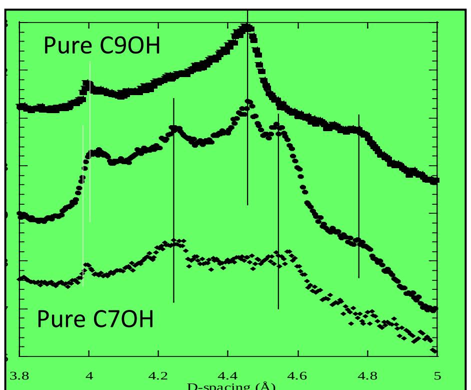

(a) Phase sep.



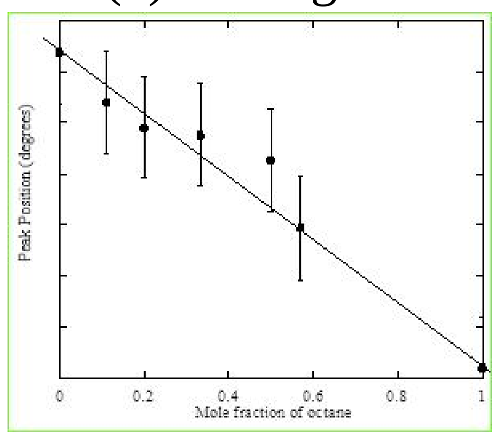
(b) Mixing



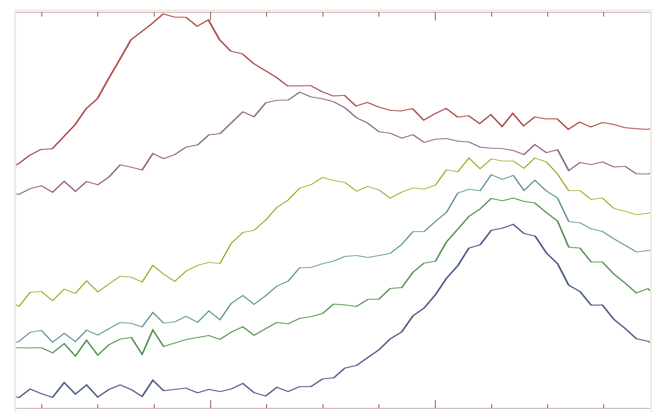

(c) Molecular compound




Heptanol/nonanol



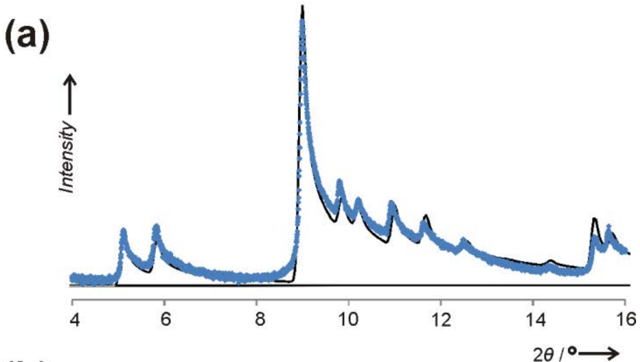

Heptanol/octanol

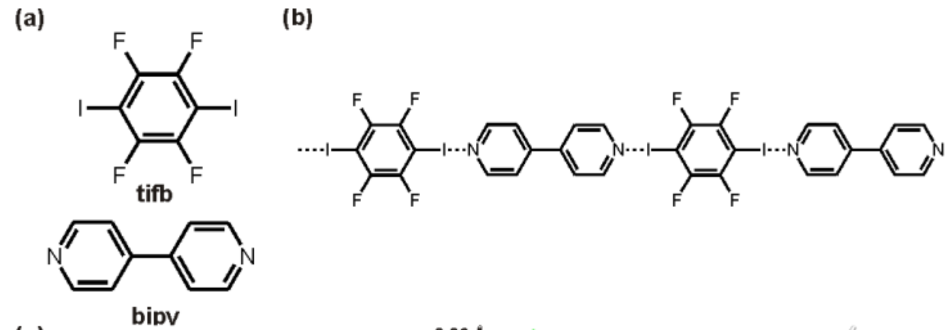


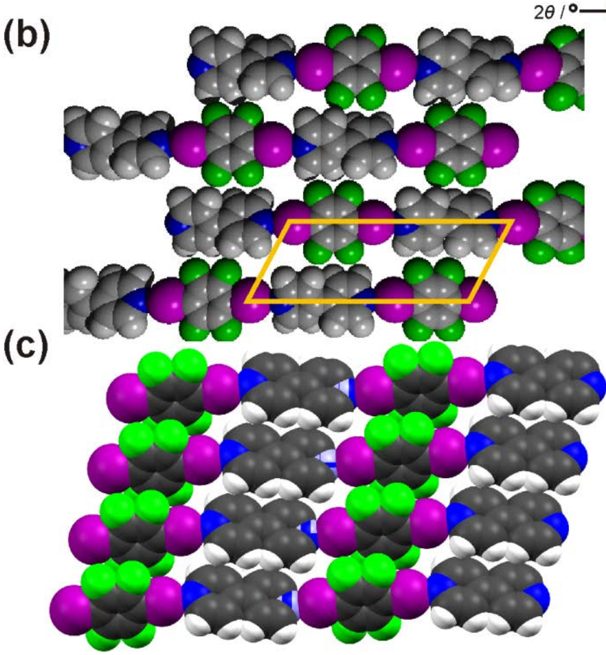

Hexanol/heptanol

# Novel Chemical interactions: Halogen Bonded co-crystal

N….I-C




Monolayer

Bulk plane

Very stable layers
$^{2D}T >> {}^{3D}T$
Directional
Strong
'Controls' strength and orientation

# 2D –diffraction: summary

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

# 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)

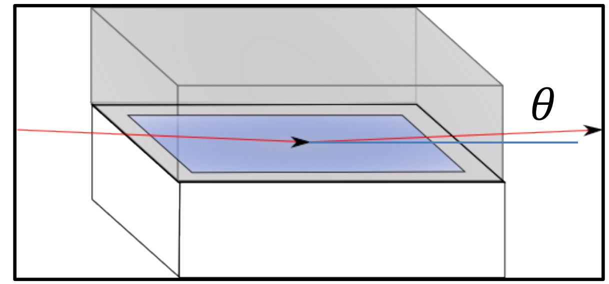
# Neutron Reflection: how does it work?

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

(previously: silica, $Al_2O_3$)

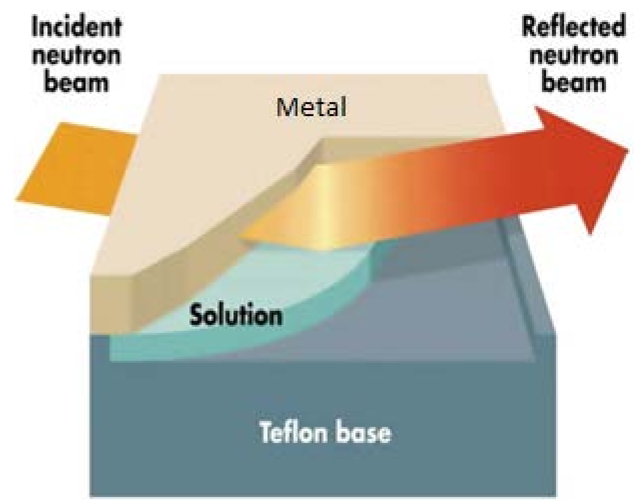
- New conditions:

  applied shear




nction of 'angle' (q)..

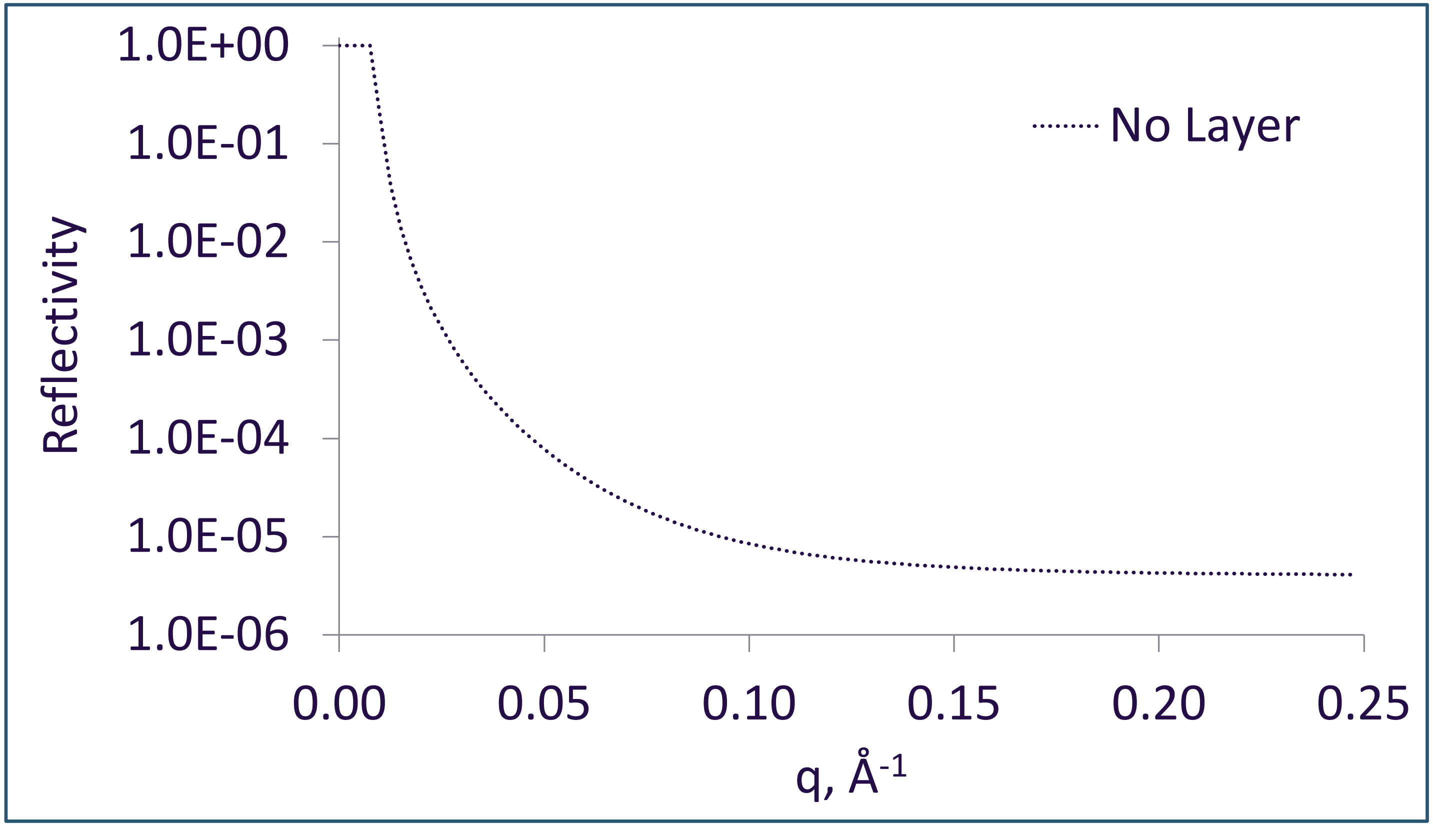
ces




Solid/liquid cell

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

# Neutron Reflection Theory



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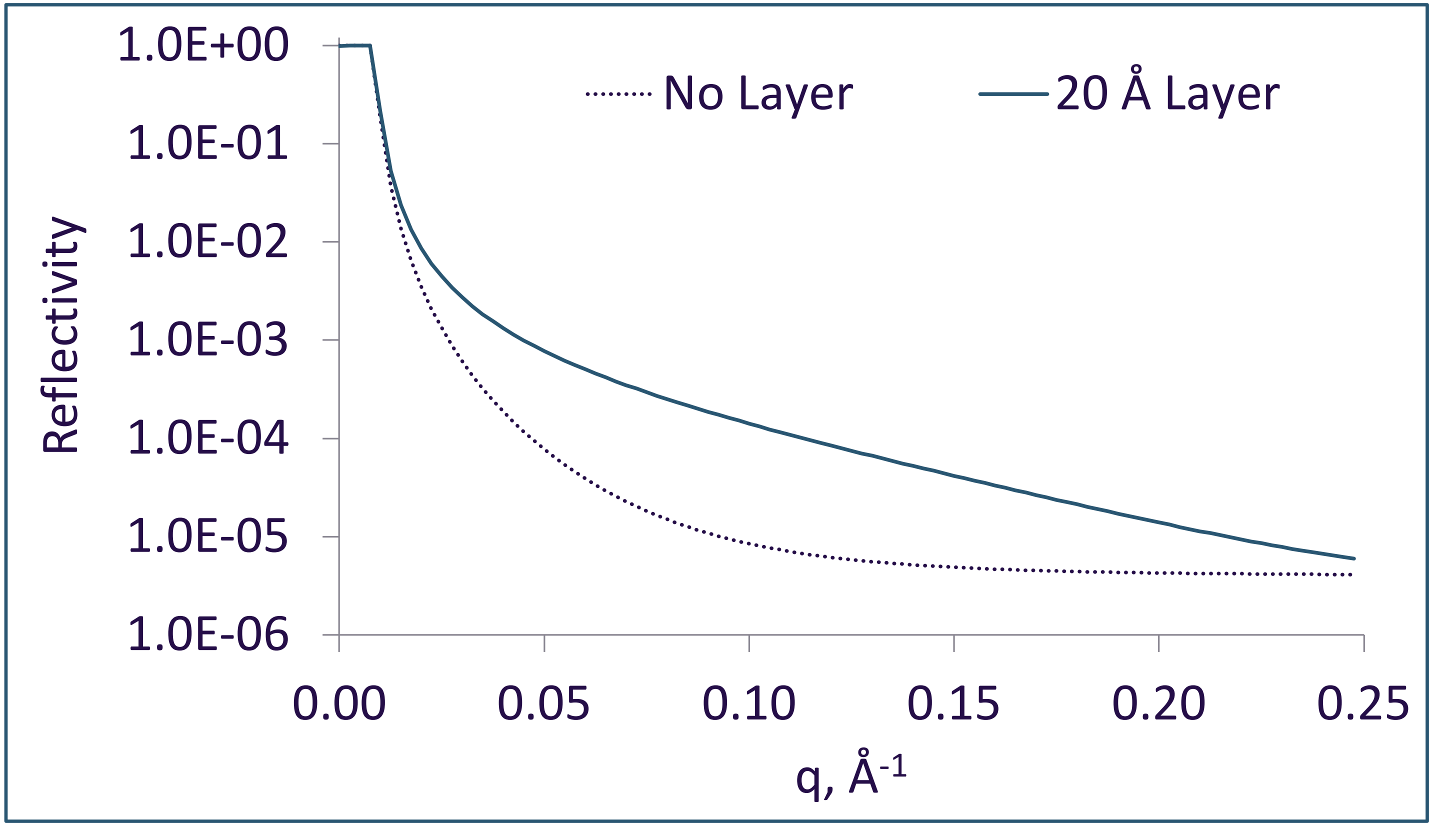

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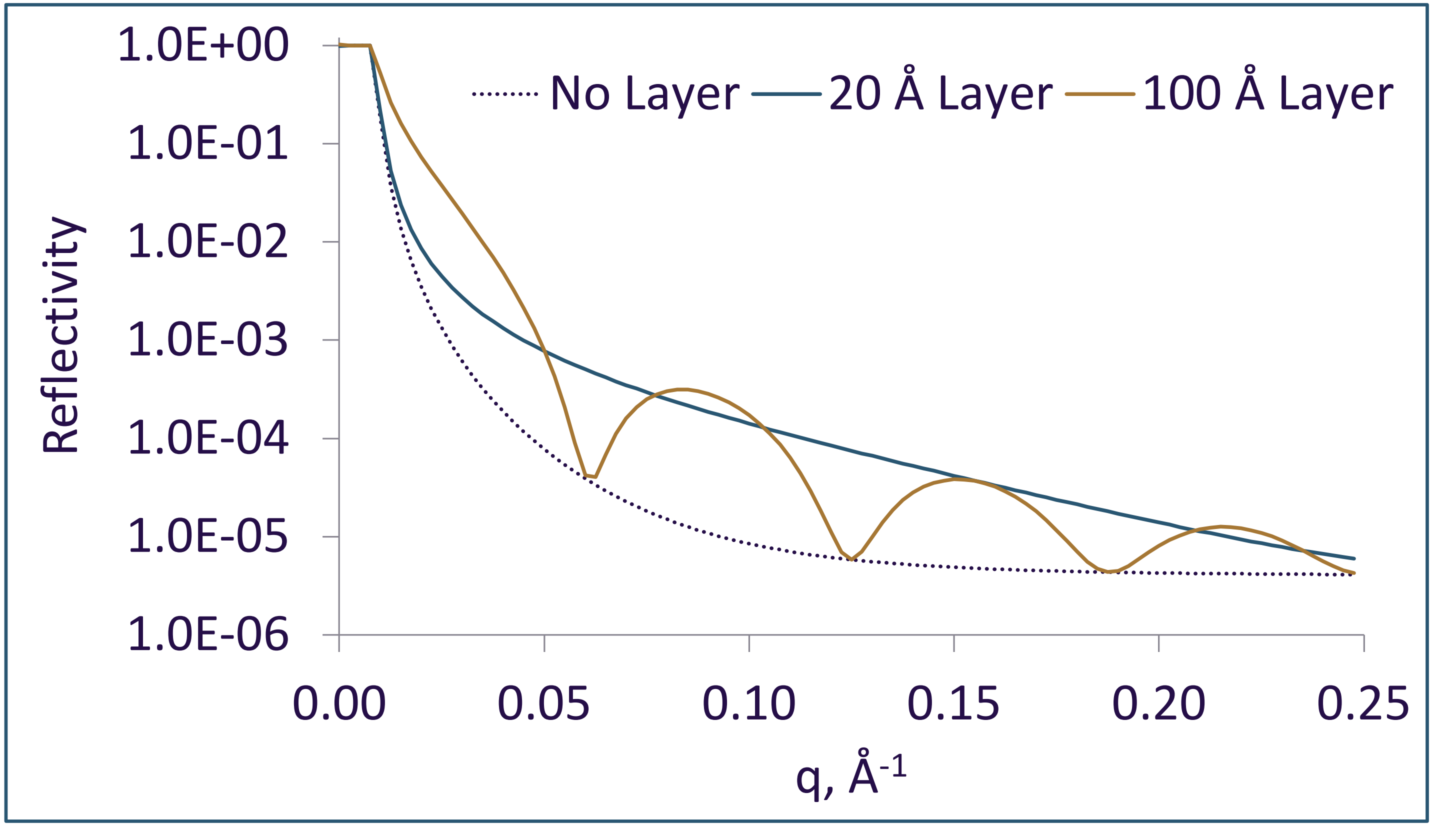

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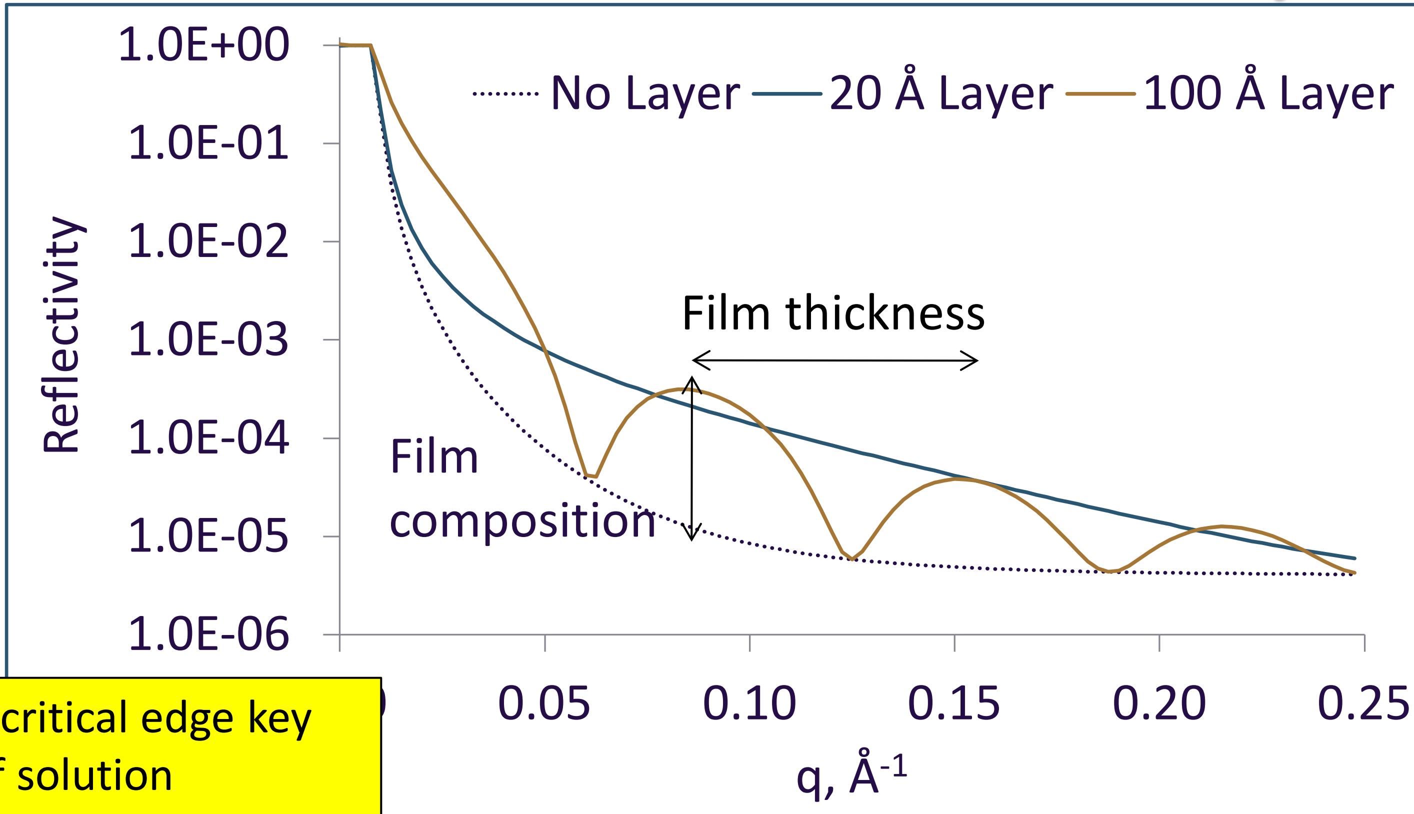
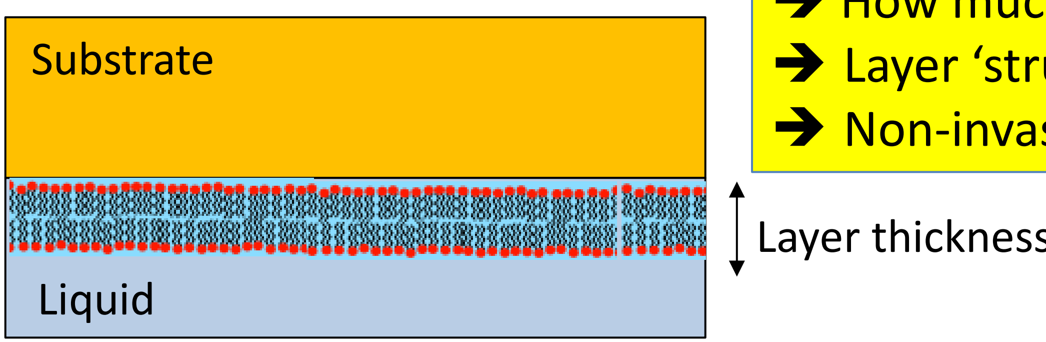



Position of critical edge key indicator of solution composition
(Tutorial problem)

‘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..

# Reflection Example #1

- Calcite ($CaCO_3$)

Very important mineral

Scale in your kettle

Oil reservoirs

Overbasing agent in engines

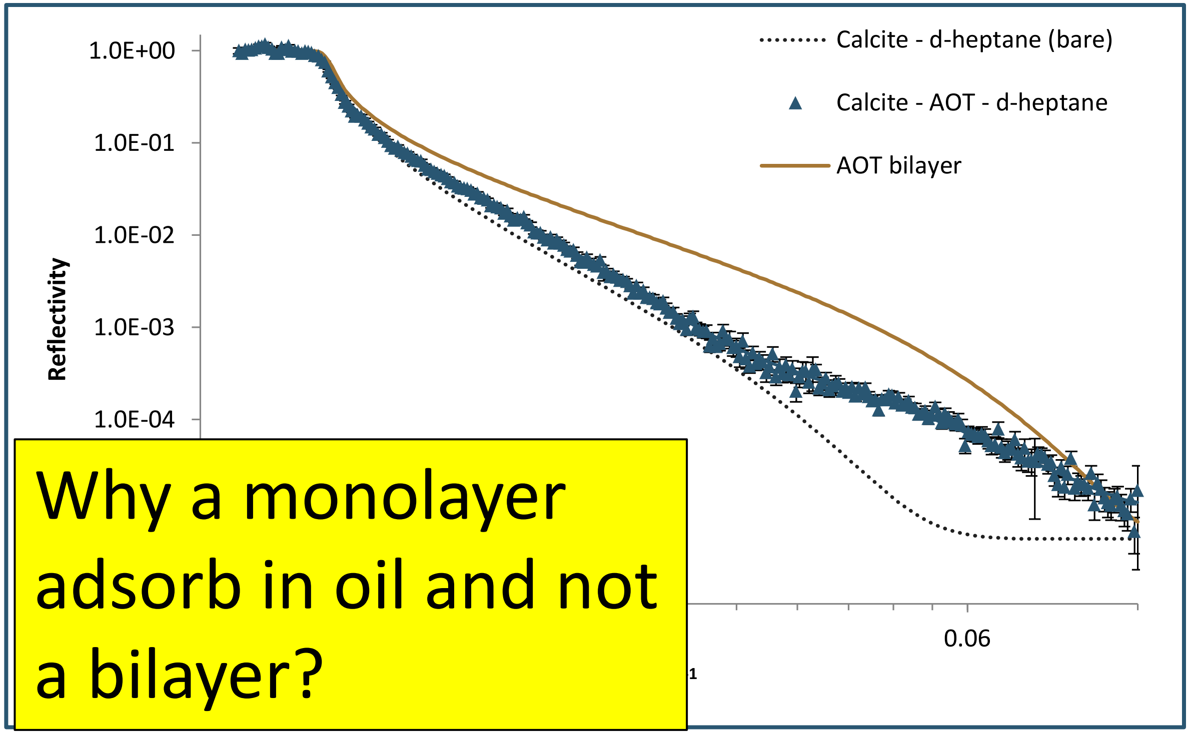
What adsorbs and how?

In oil? In water?

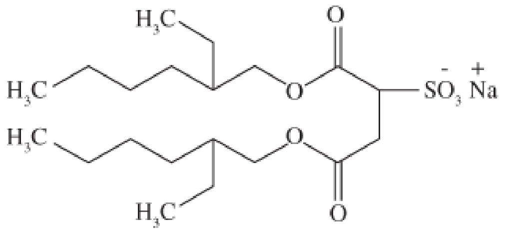
Polymers? Surfactants?

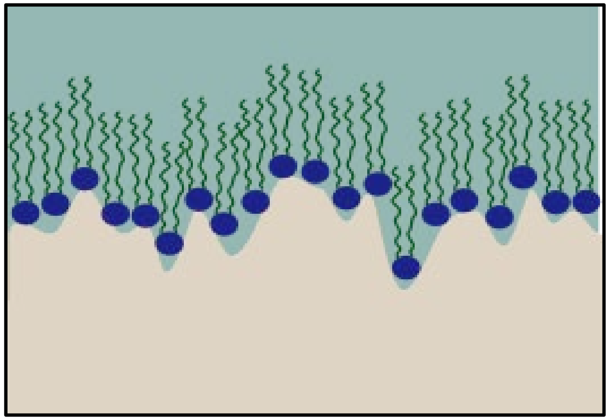
(Birefringent…! Double refraction)

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




Why a monolayer adsorb in oil and not a bilayer?

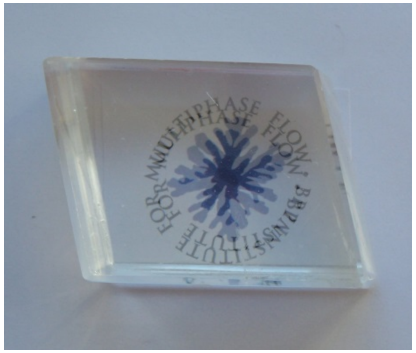


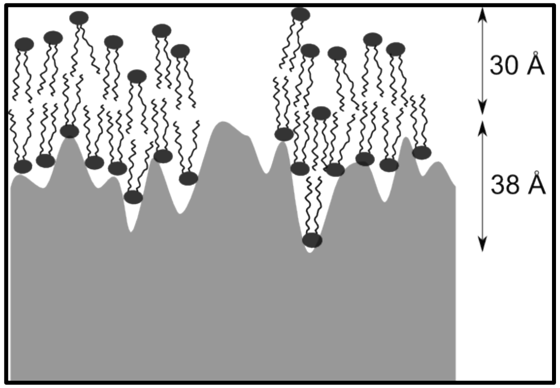



Adsorption of a monolayer on a surface:

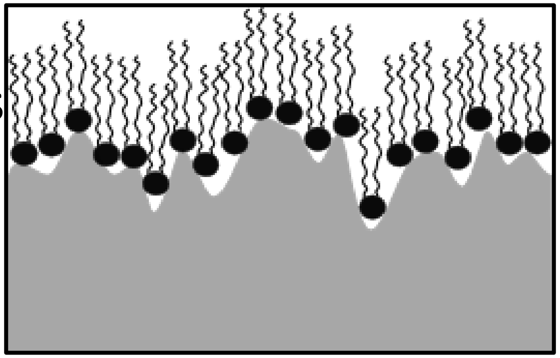
(The bare surface, monolayer and bilayer calculations)

# Reflection Example #1: Additives on calcite..

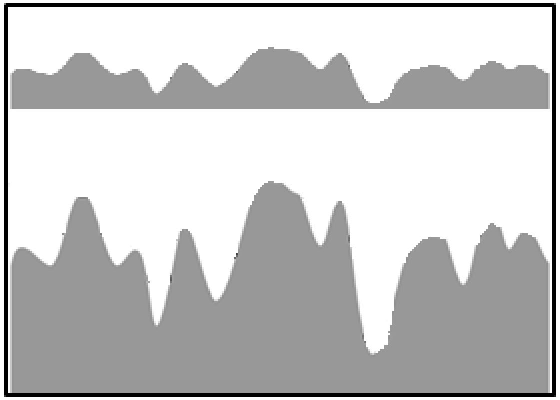




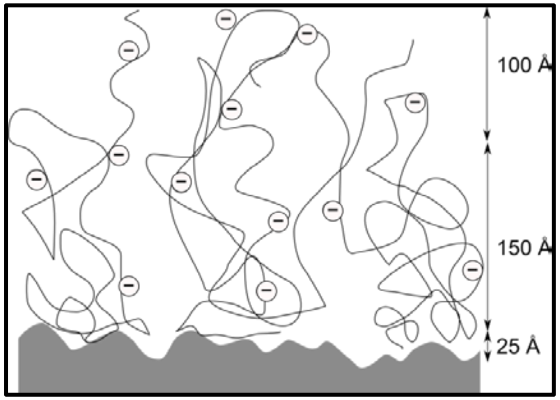

Monolayers, Bilayers multilayers and adsorbed polymers

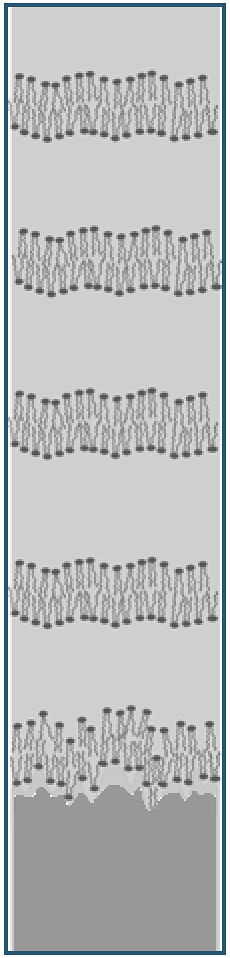


Surface corrosion



Molecular precision!



Why a bilayer adsorbs in water?

# Reflection Example #2: Mineral Surfaces - mica

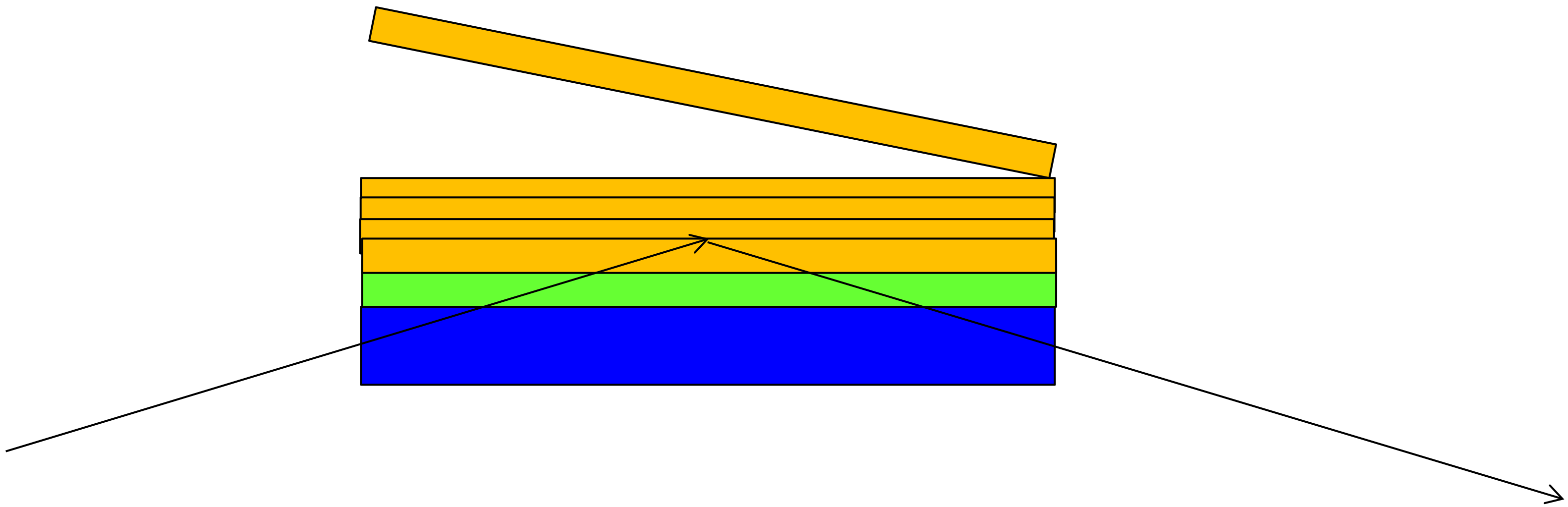
(Kate Miller)

Layered silicate: mineral books

**Mica:**
**Clays are key component of many oil reserviors**

**Very common in AFM 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..?**

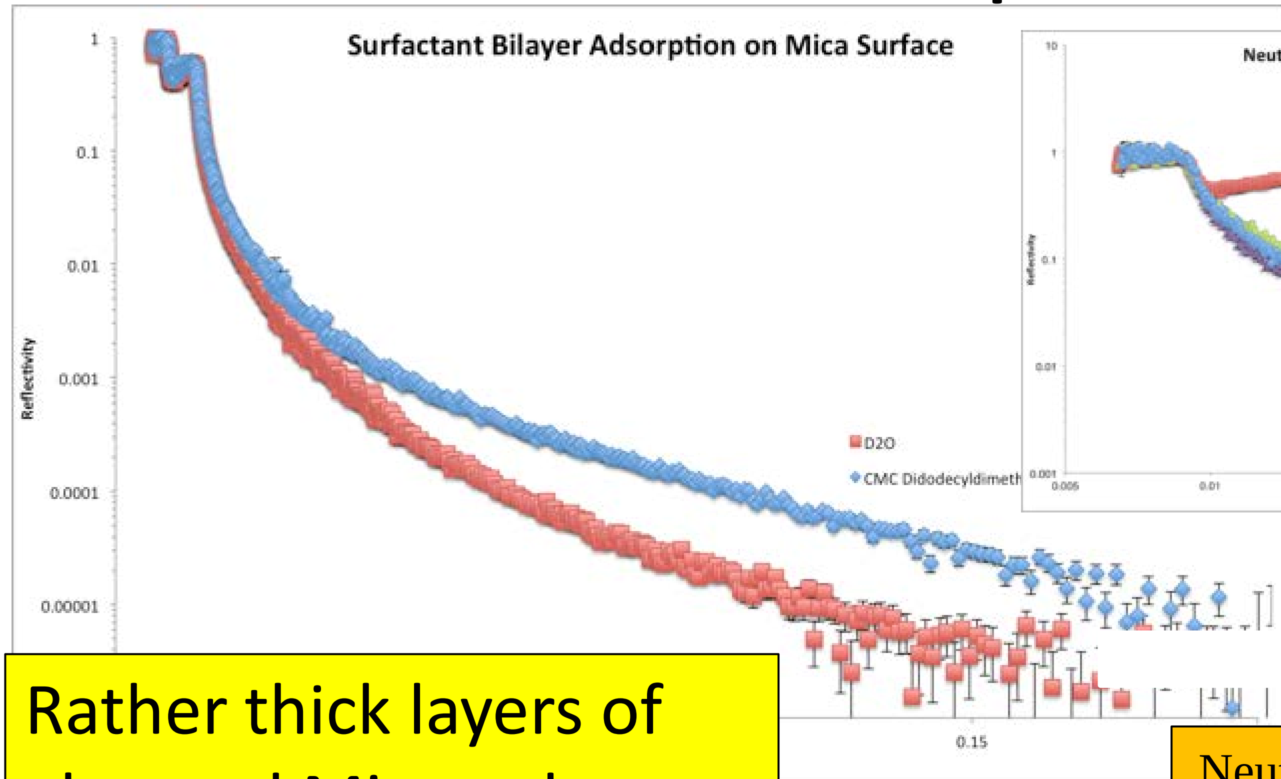
# ‘Peeling’ Mica

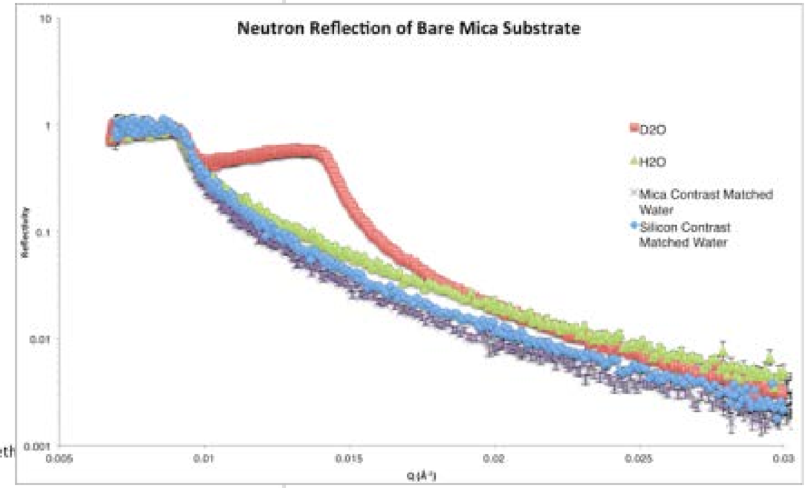


Support very thin layers on solid substrate and ‘peel’

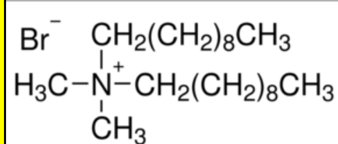
Does it work?.......
Can we see adsorption on mica in solution?...

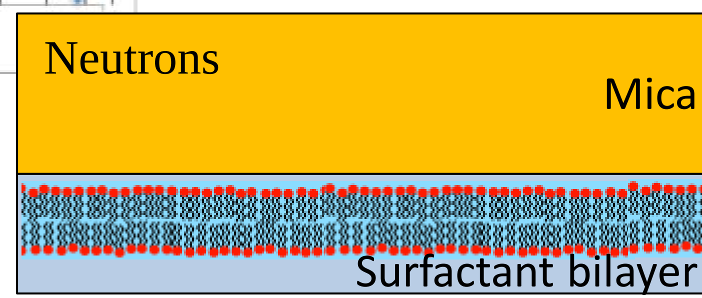
# Surfactant adsorption on mica




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



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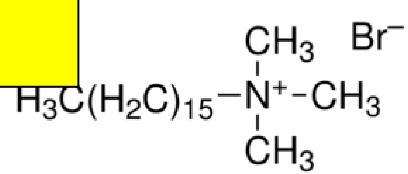
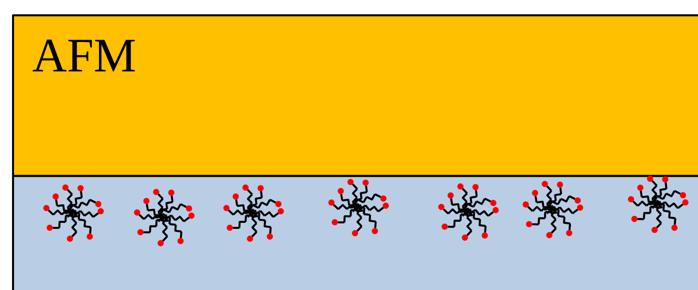
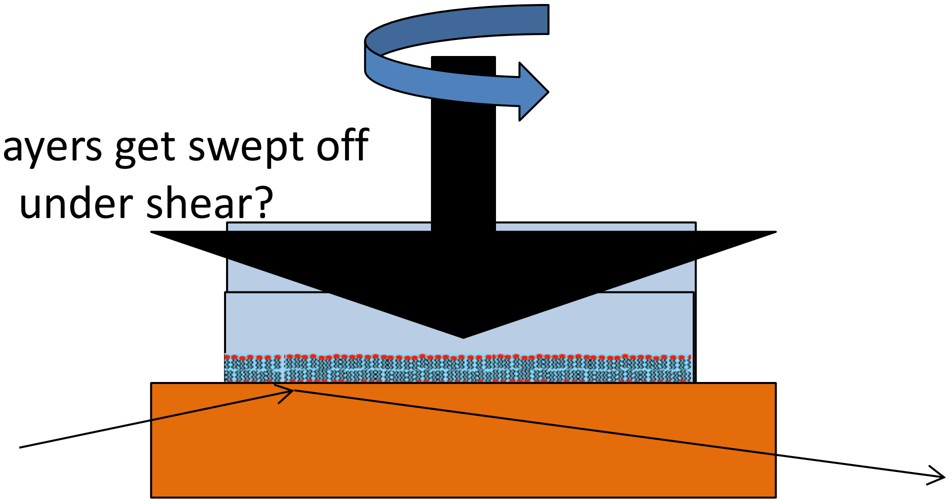


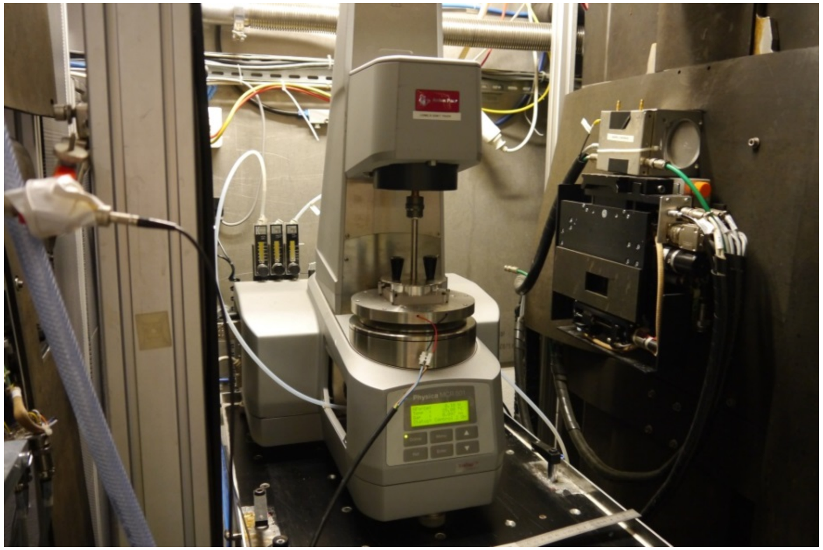
(b) CTAB: NOT same as AFM



# Example #3: Layers under Shear

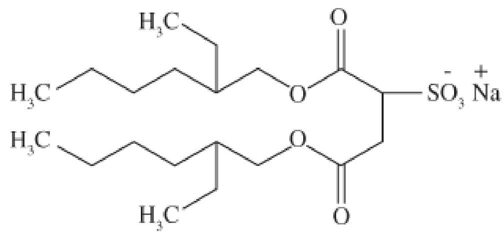
Do layers get swept off under shear?



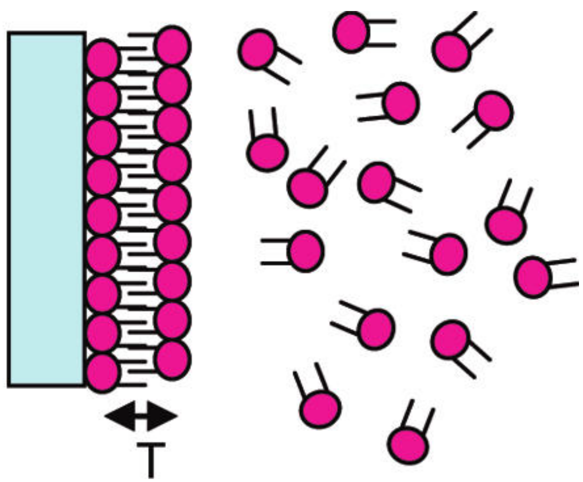


(steady and oscillatory shear)
Modest shear rates < $500 s^{-1}$
(pipe flow, or flow over rock-beds)

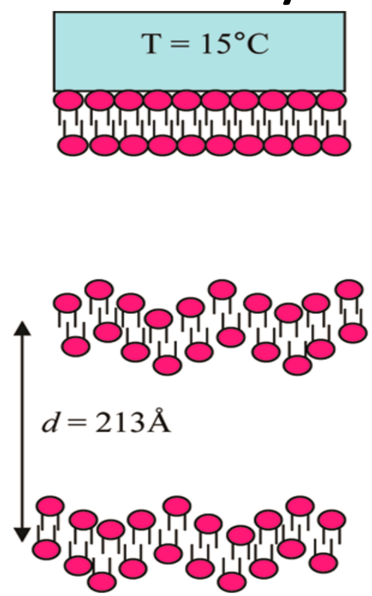
# Shear/Flow:
# AOT on Alumina/water



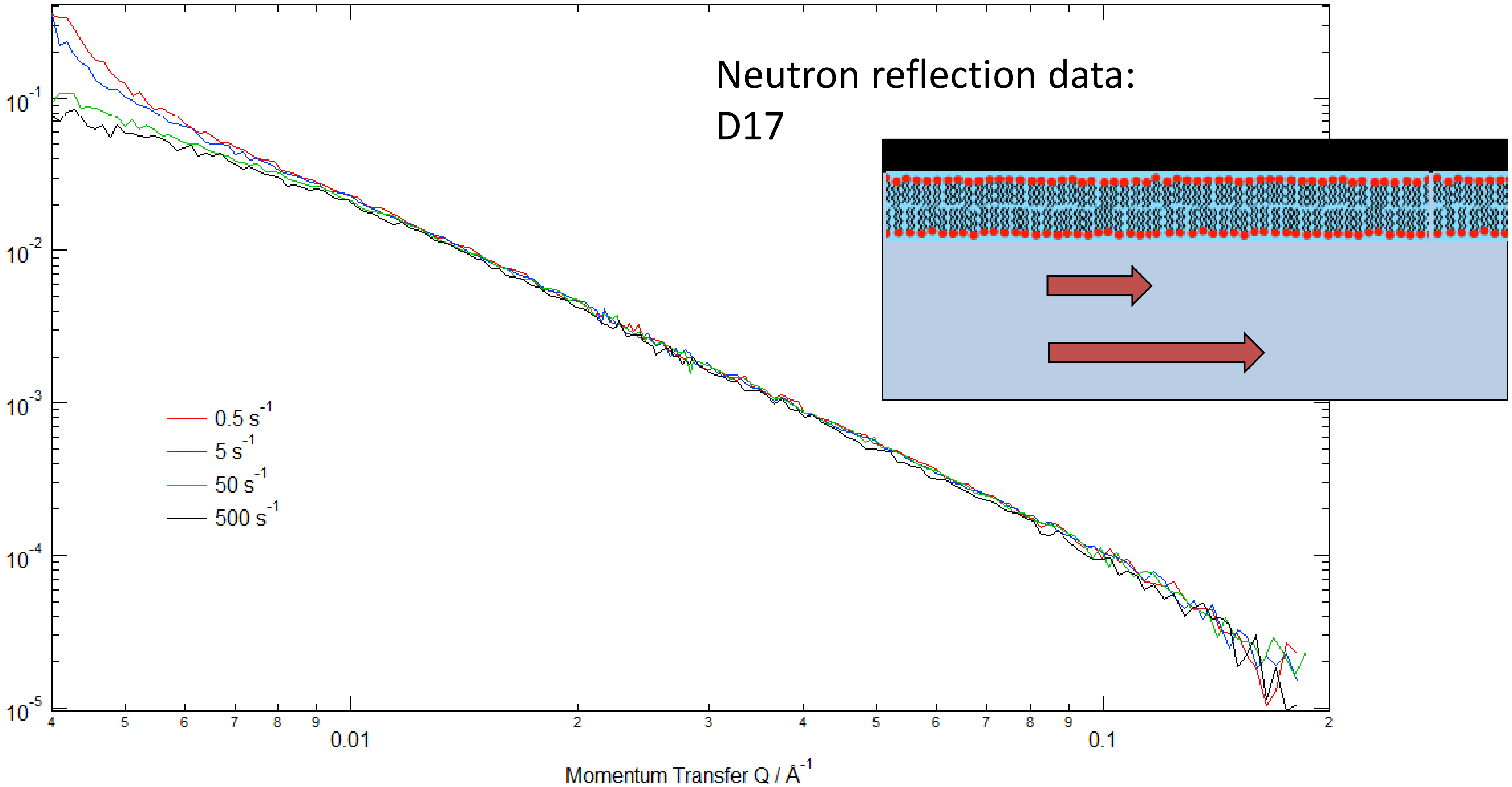

Thin layers




Thick layers



# Effects of Shear: neutron reflection: Thin layer



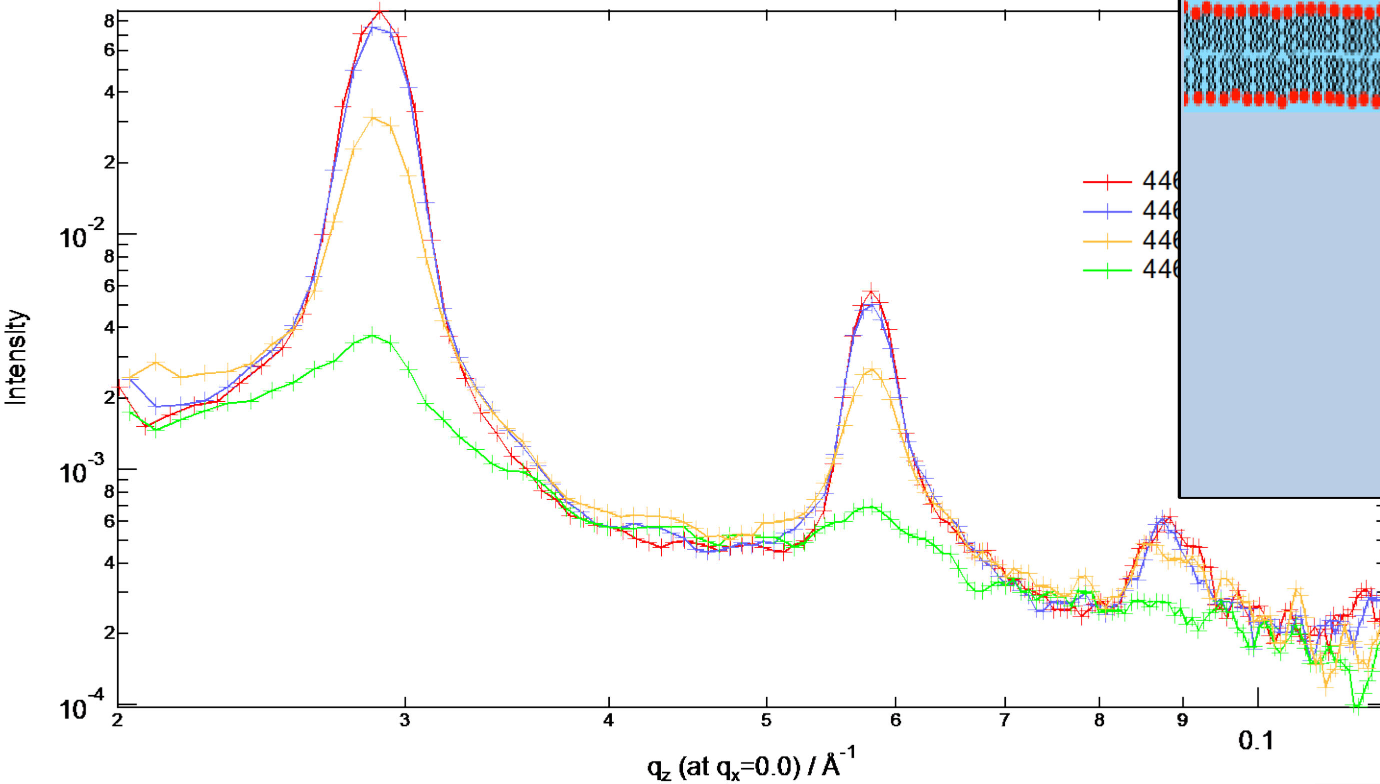

**SURFACTANT BILAYER (thin layer approx. 30A thick)**

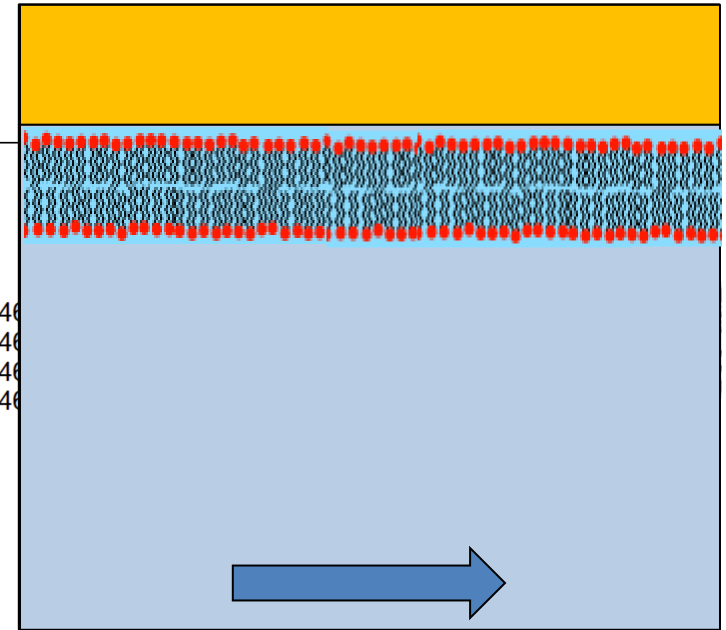
Data: under steady shear increasing to approx 1000s$^{-1}$:

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

**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

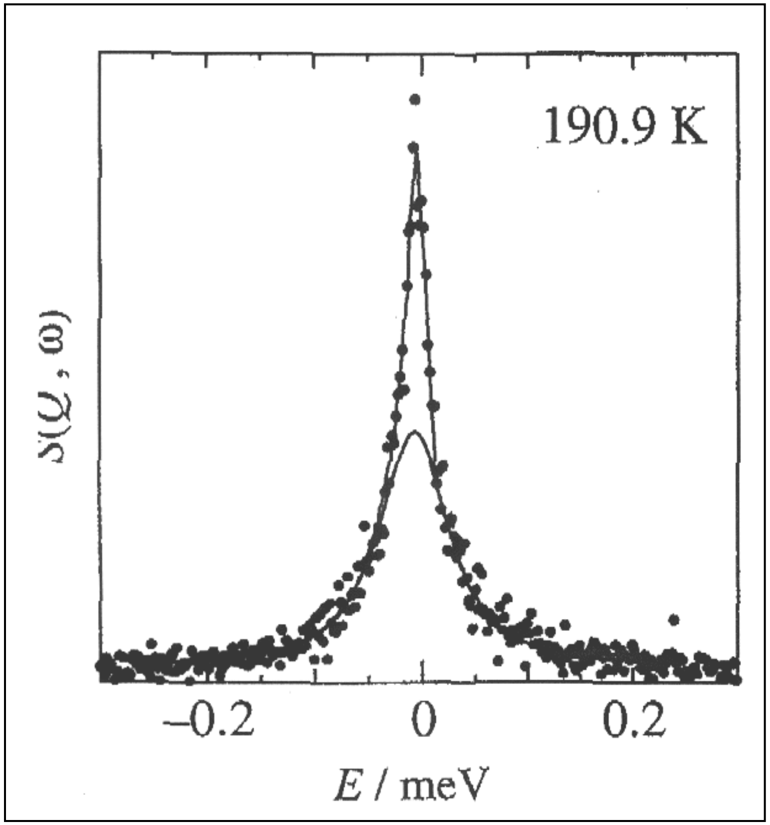
- Diffusive motions
- How long to move out of your ‘box’

# Incoherent Neutron Scattering

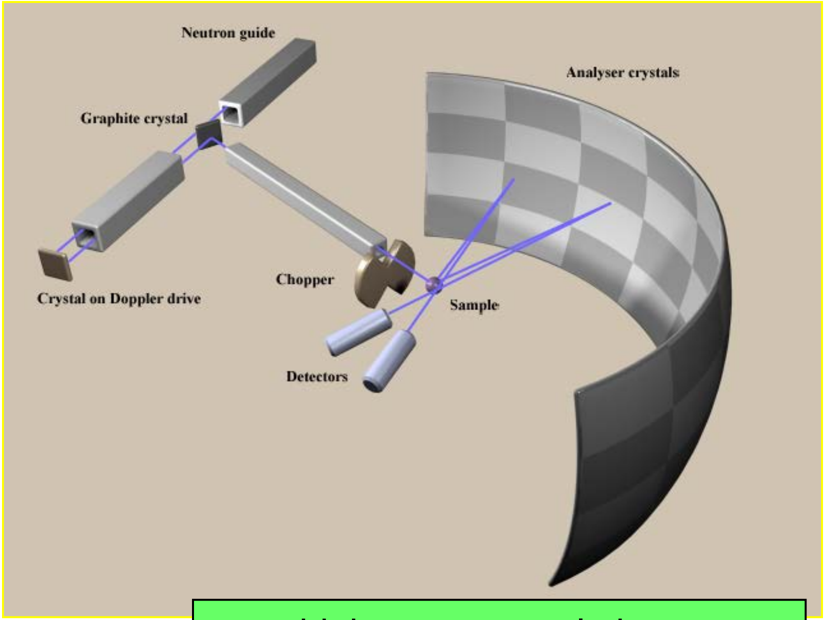
- Actually get a distribution of scattered neutron energies:

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

Intensity

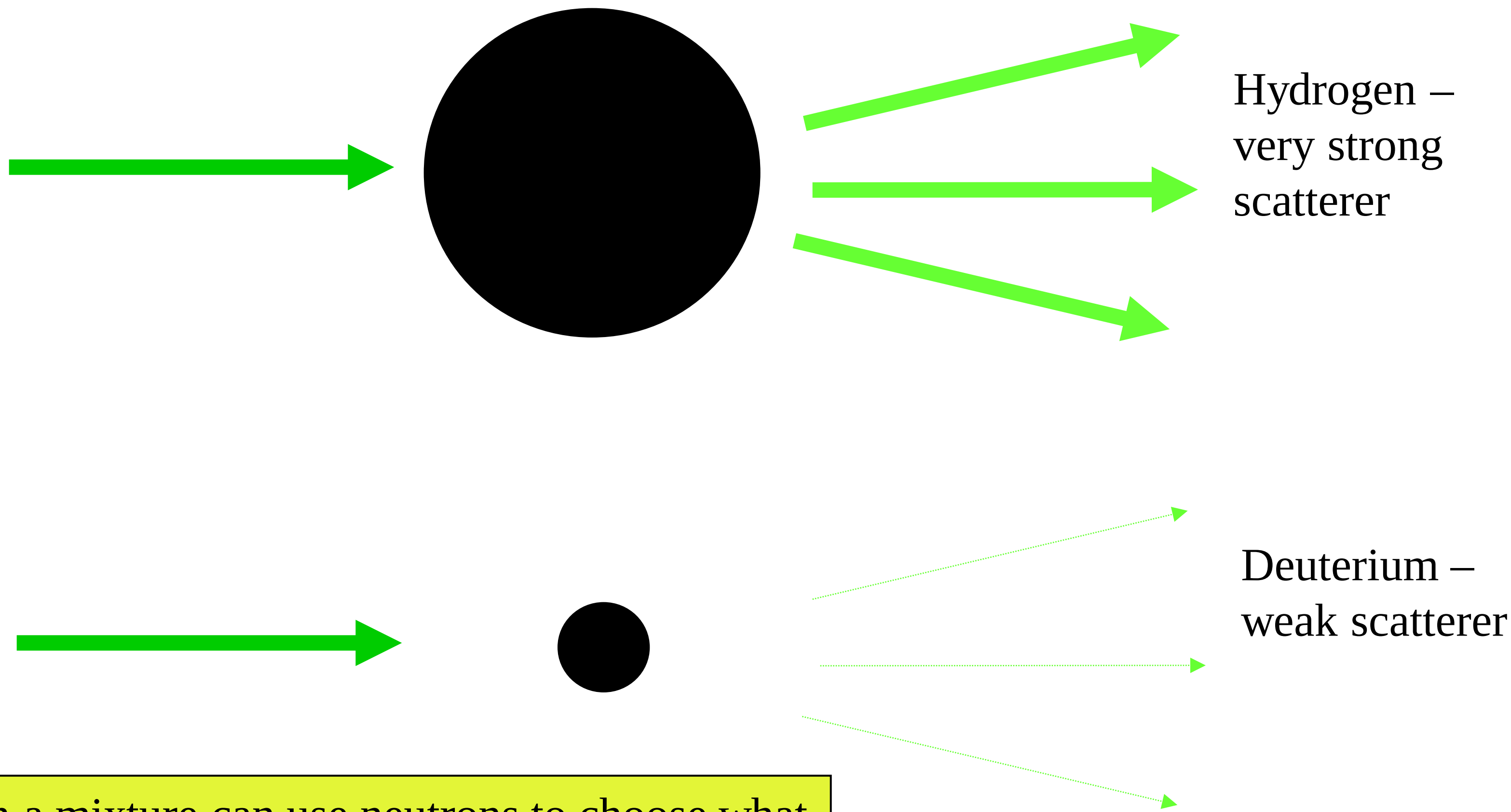



ΔE




Very high energy resolution, 1 μeV

# Hydrogen and Deuterium are different

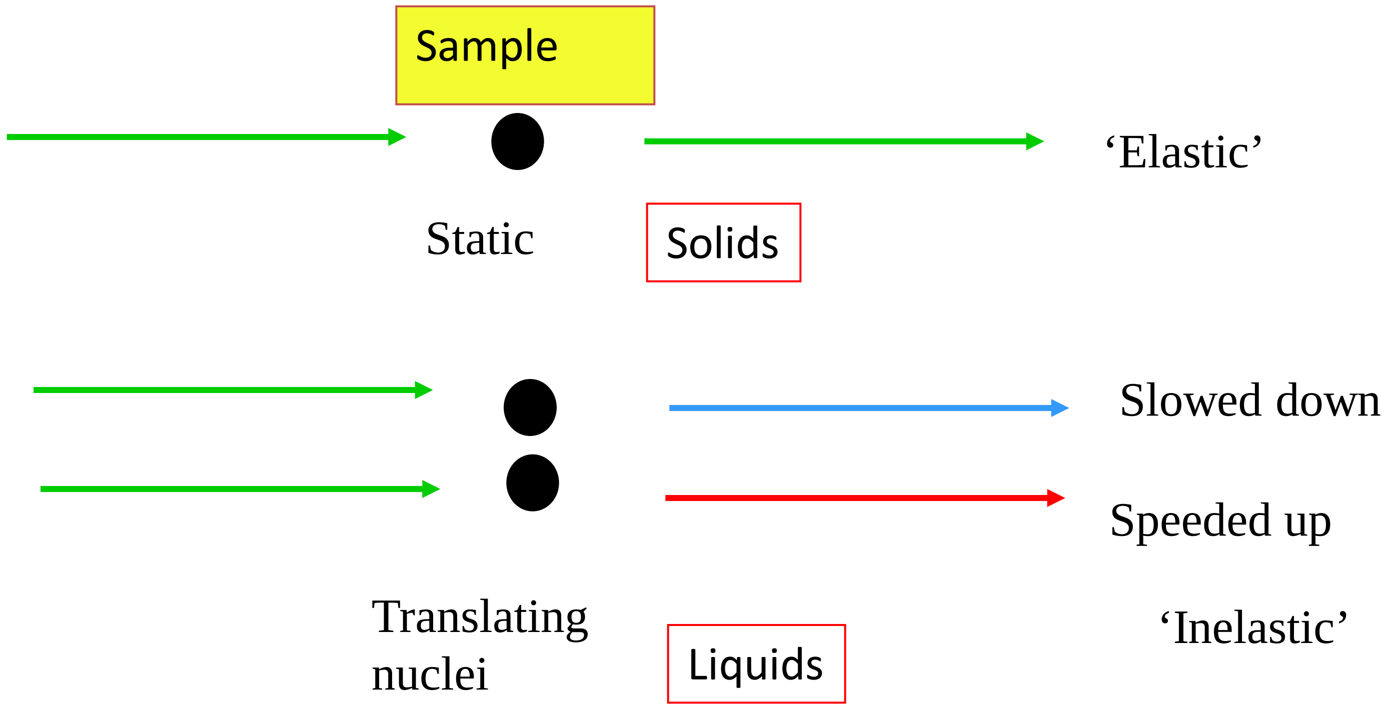



In a mixture can use neutrons to choose what we ‘see’

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

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

- Neutrons can exchange energy with sample nuclei:

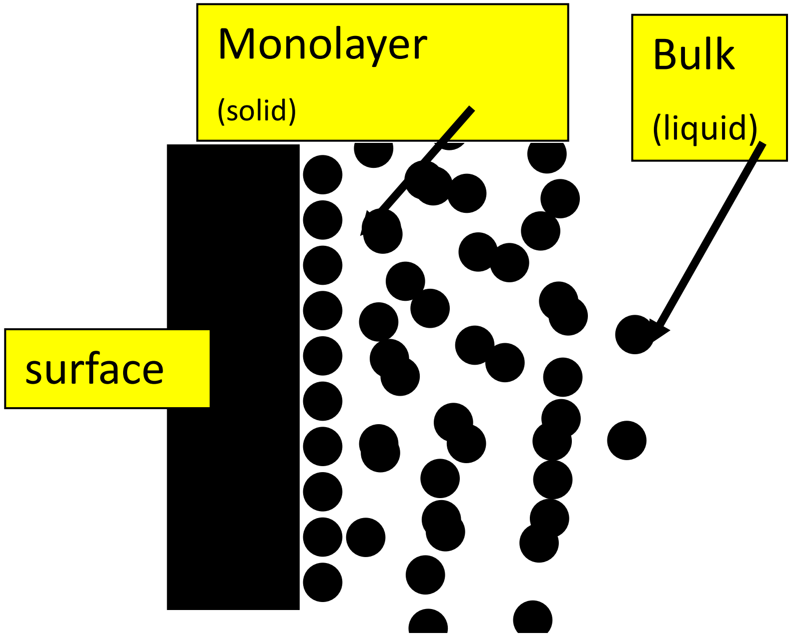



Intensity of elastic scattering ➔ Amount of adsorbed material

# Adsorbed Molecules are different

Adsorbed layers are 'static'

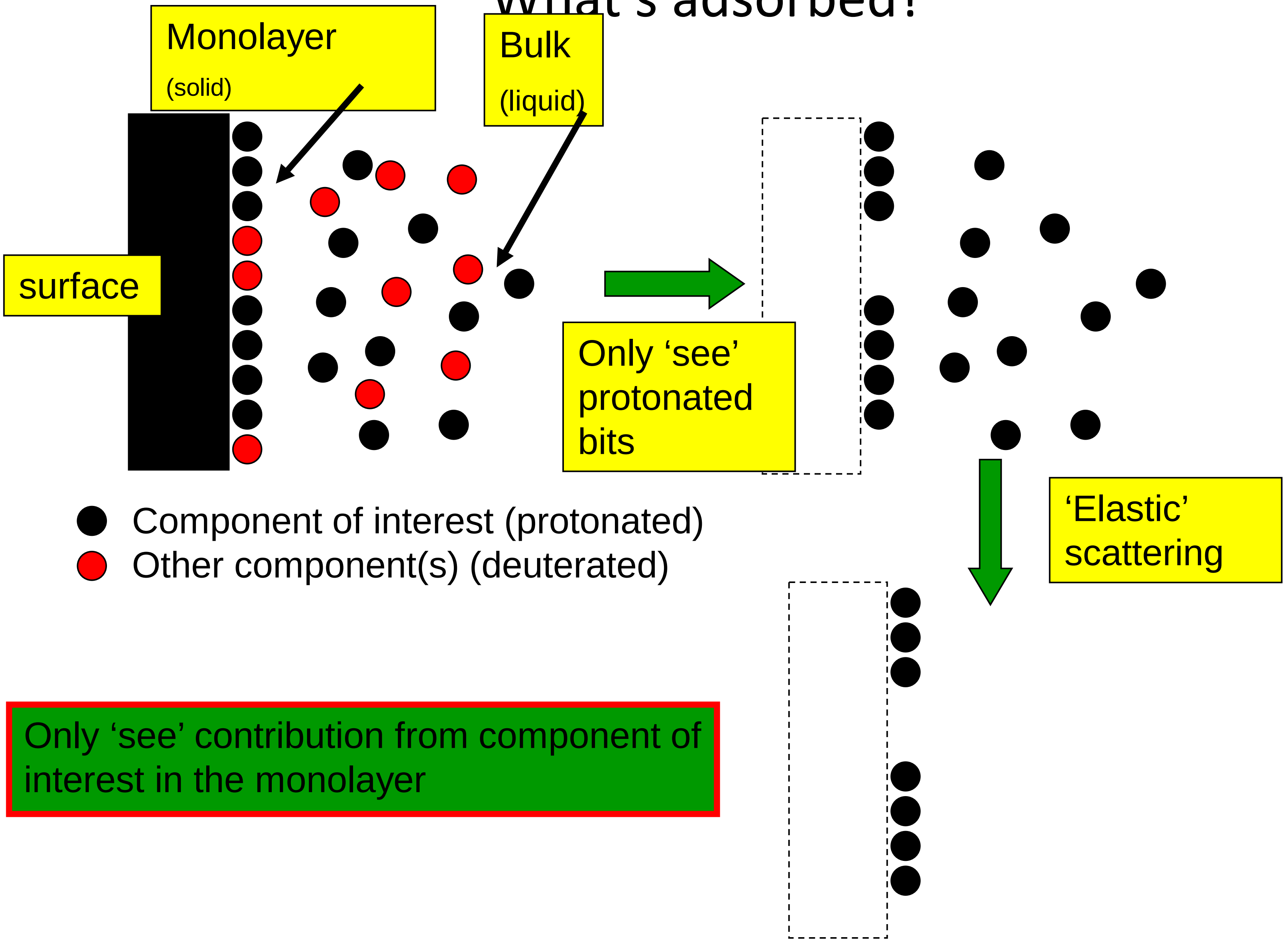
Liquids are 'dynamic'




Use mobility to distinguish adsorbed layers

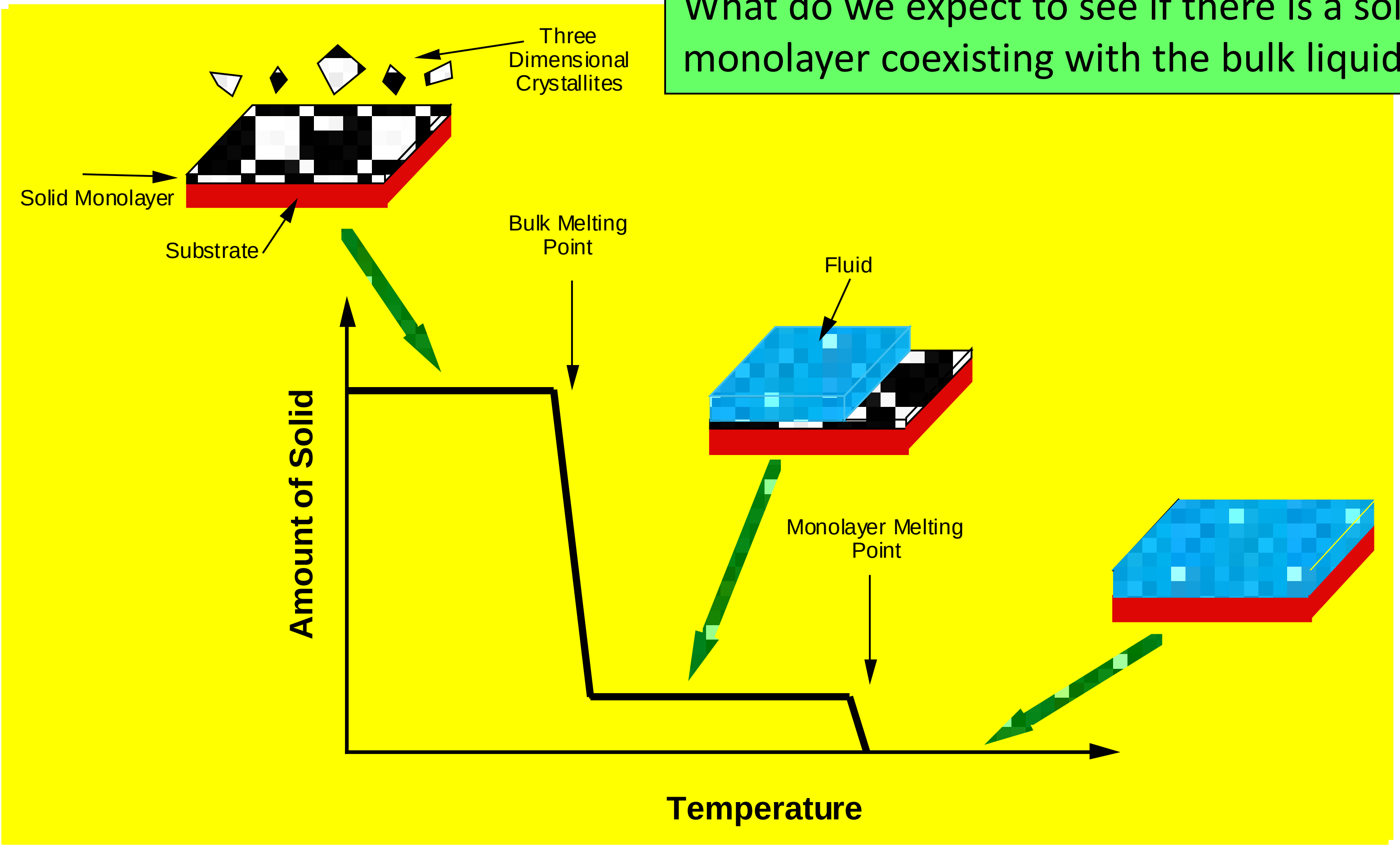
# ‘IQNS’

# What’s adsorbed?

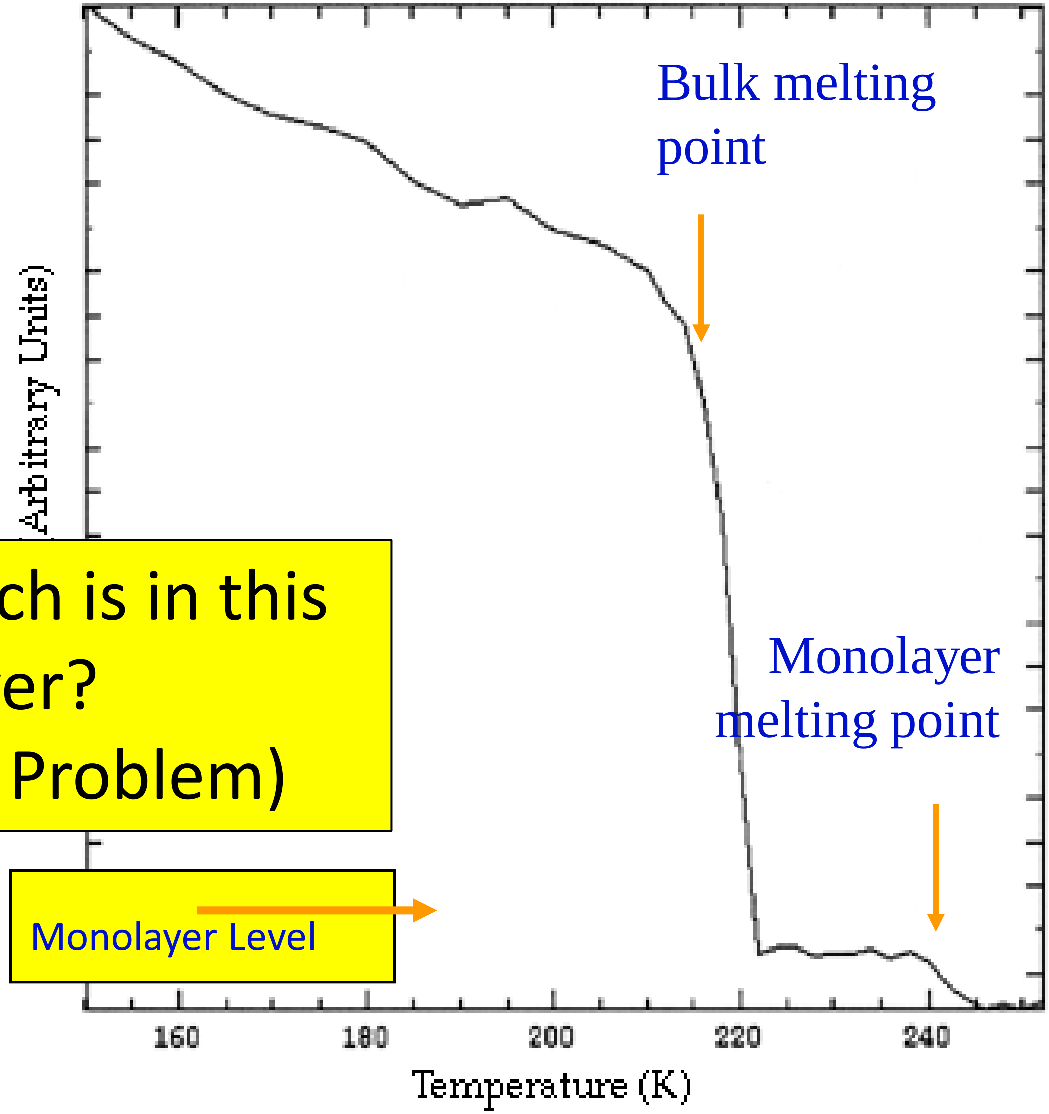


# Incoherent quasi-elastic neutron scattering (IQNS)

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



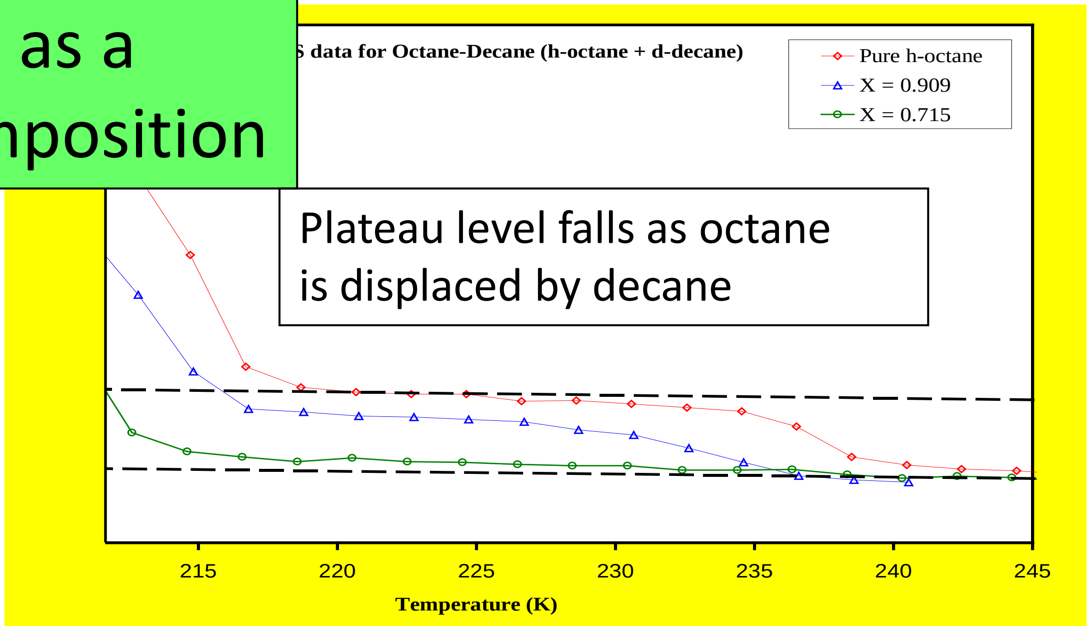
# IQNS Results: Octane on Graphite

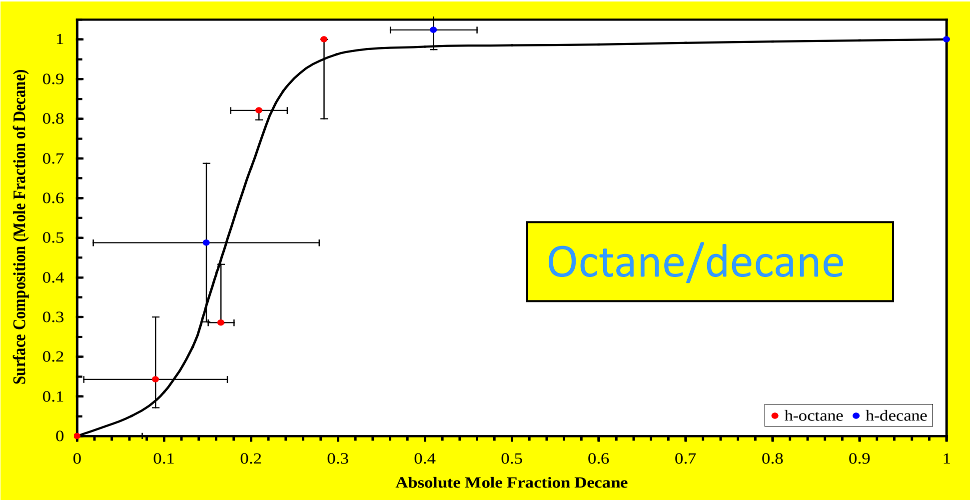


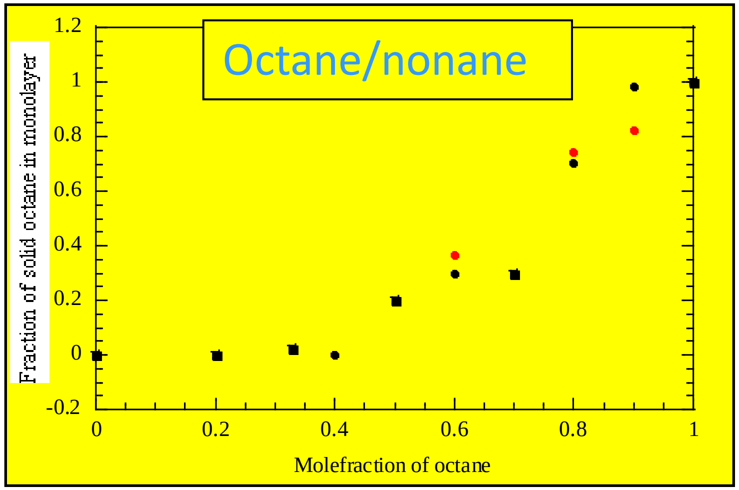

How much is in this monolayer?
(Tutorial Problem)

# What’s adsorbed: (IQNS) Results from mixtures

Monolayer composition as a function of solution composition

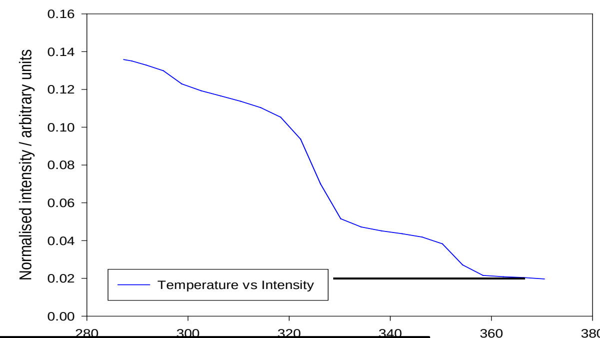


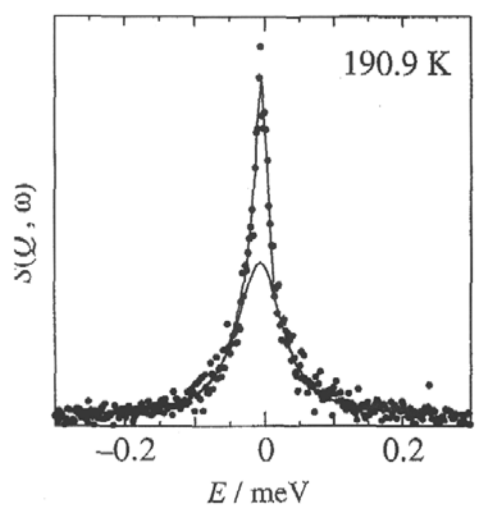
# Dynamics of Adsorbed Layers

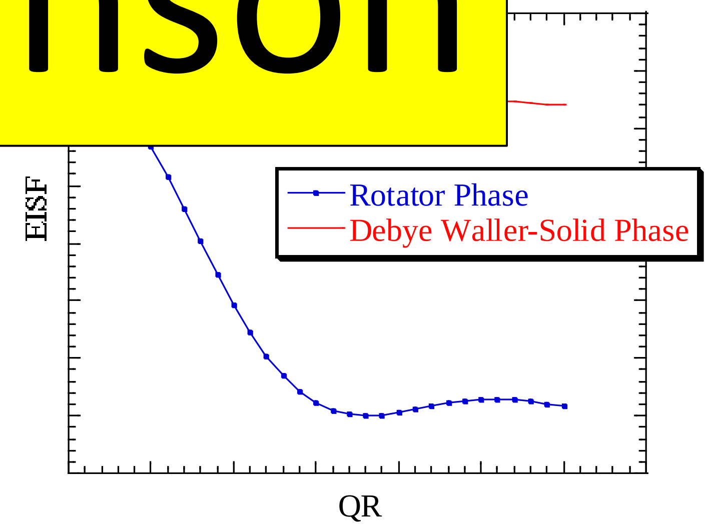
- Distinguish solid from liquid
  - elastic scattering
- Diffusion coefficient of liquid layers
  - Width of the quasi-elastic peak




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

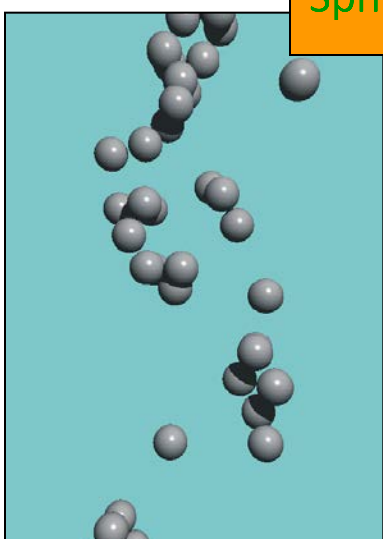
## Want to know

What shape are the separate colloids

What orientation

What arrangement

Spheres



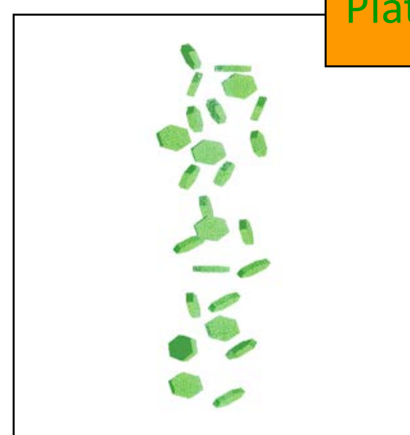
Important flow properties

Need to ‘look’ through metal cells

Opaque samples

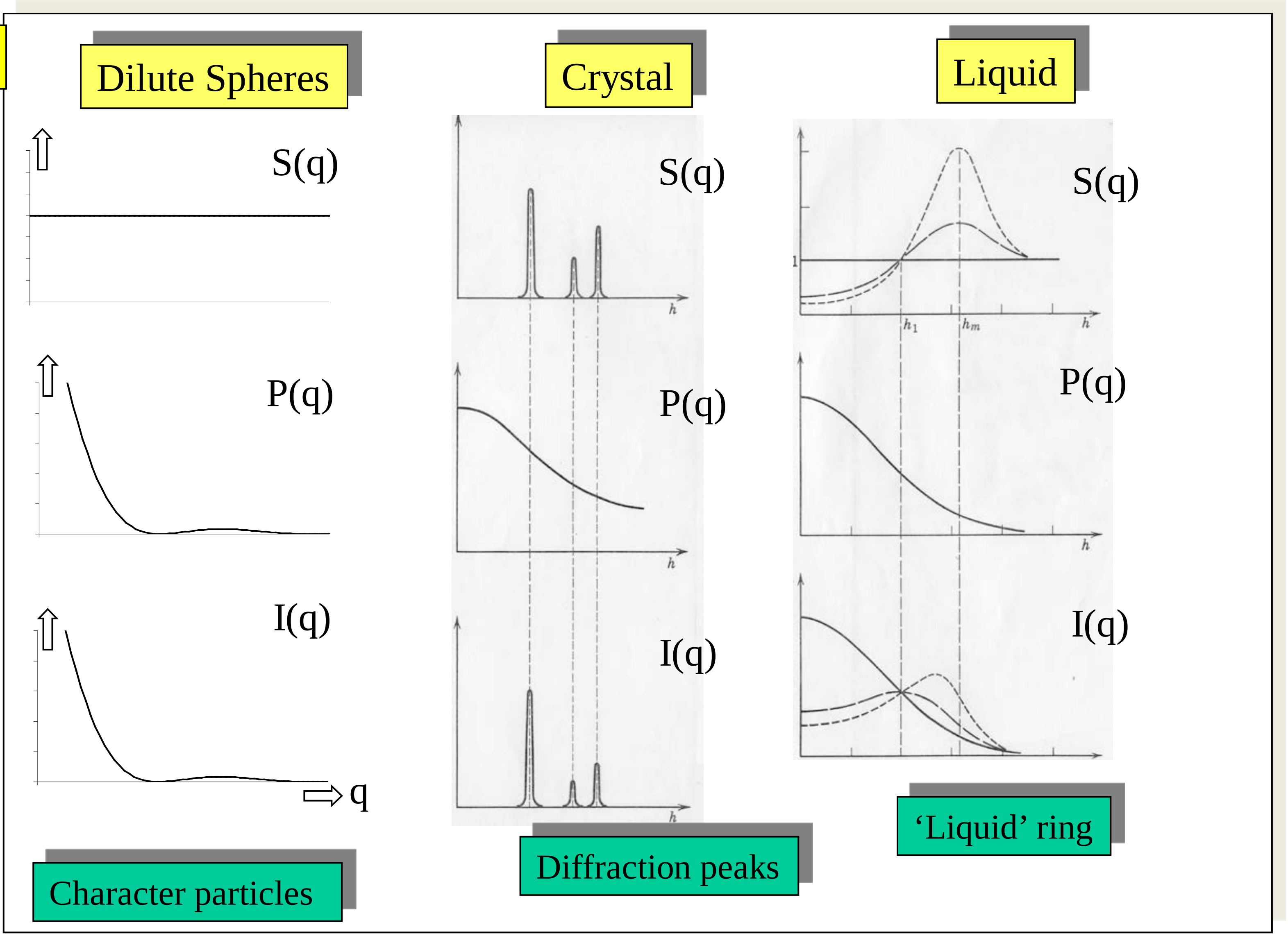
Neutron Transmission

Plates



# Form and Structure Factors

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

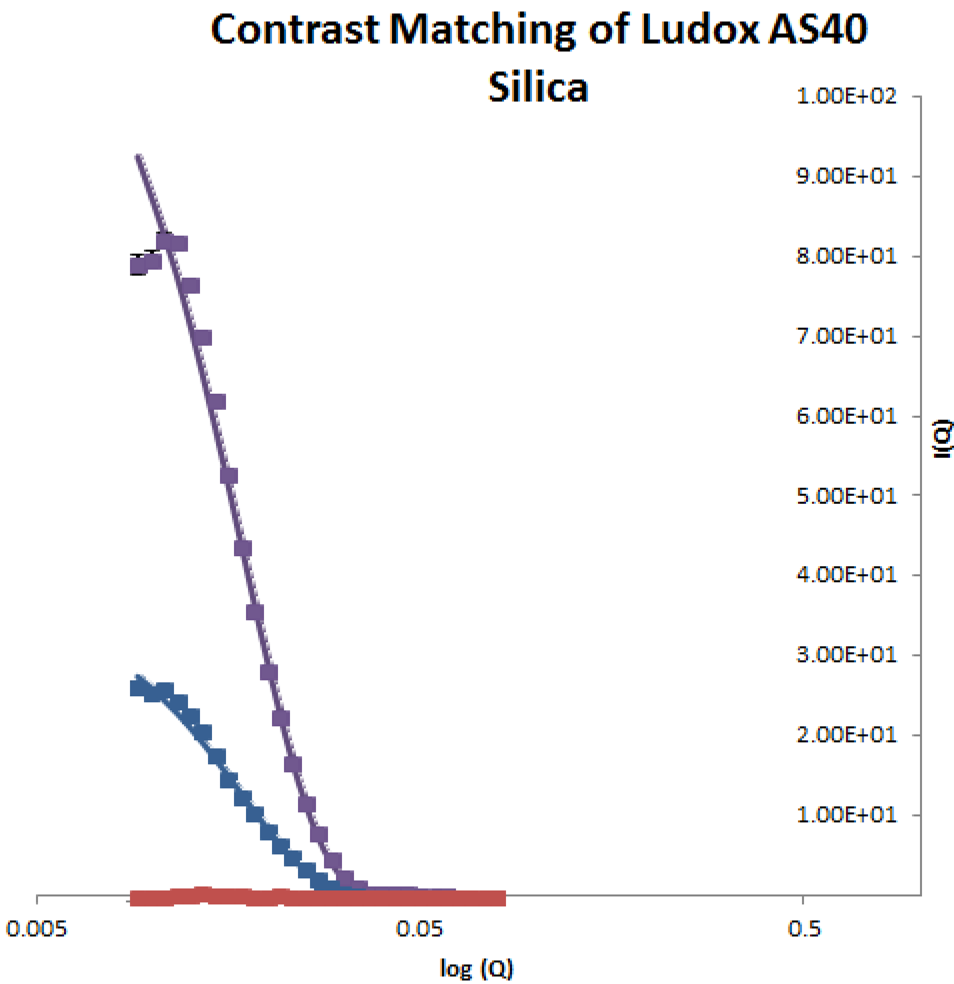


# SANS: single colloid scattering (Dilute) What’s on the surface

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

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

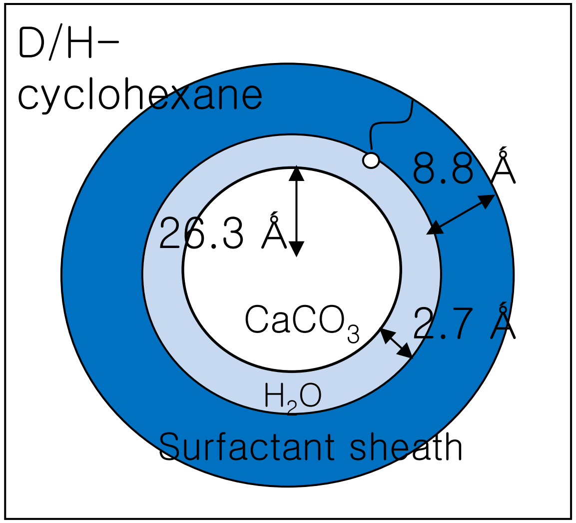
Change scattering of water (refractive index = ‘colour’): silica –disappears




‘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



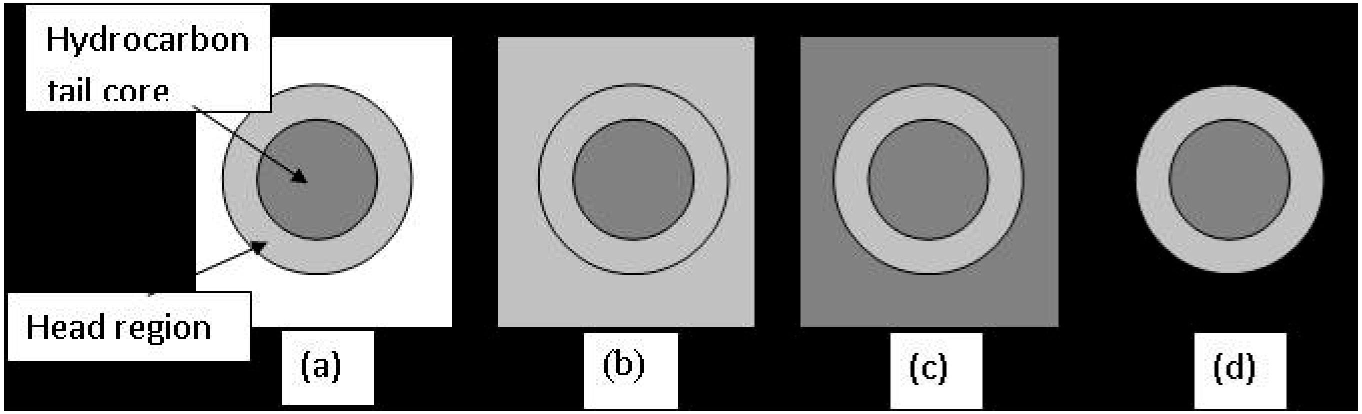

P(Q) form factor for core-shell more complex
Structure: core/water/surfactant/oil

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

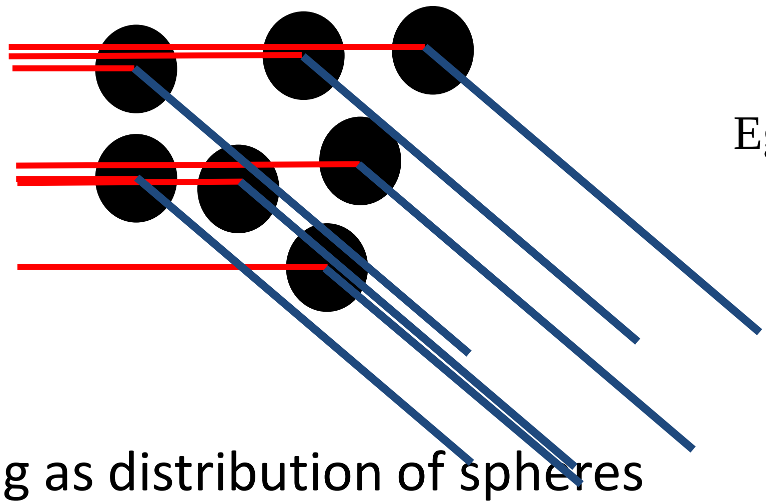
*Thanks to Richard Heenen and co*

# Contrast variation:

- Enhance sensitivity to each bit by selective deuteration



# SANS: Interference Between Objects



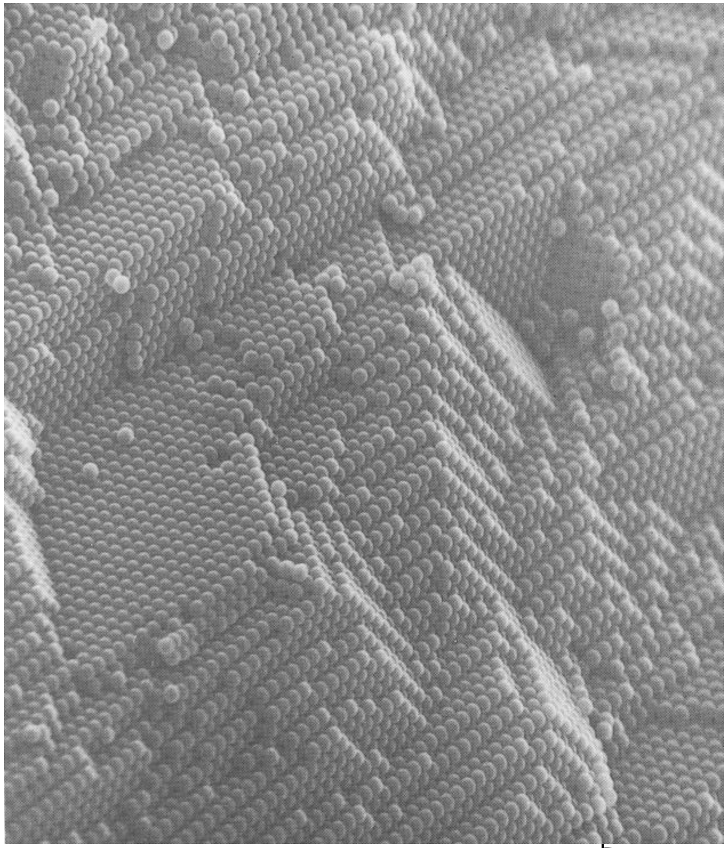
Eg Colloidal dispersion

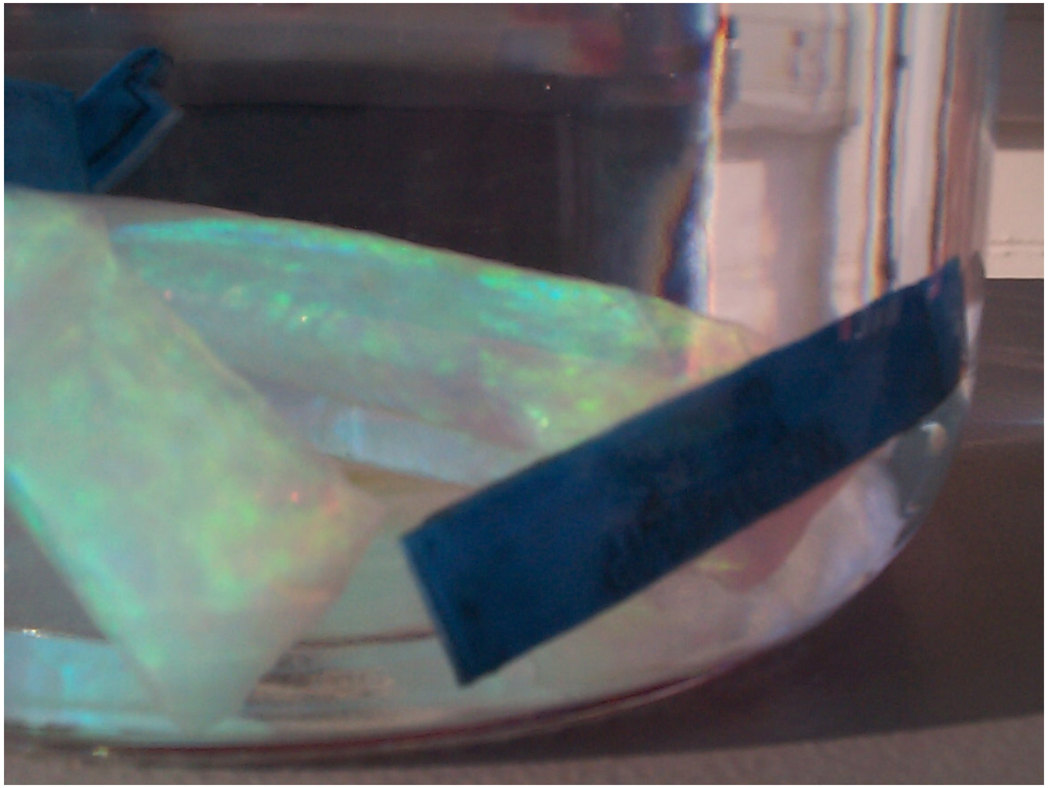
- Consider scattering as distribution of spheres
  - we know scattering for isolated object, e.g. spheres (P(Q))
  - S(Q) is called the interference or 'structure factor' arising from interference of scattering from different colloids.
  - Measured intensity is:

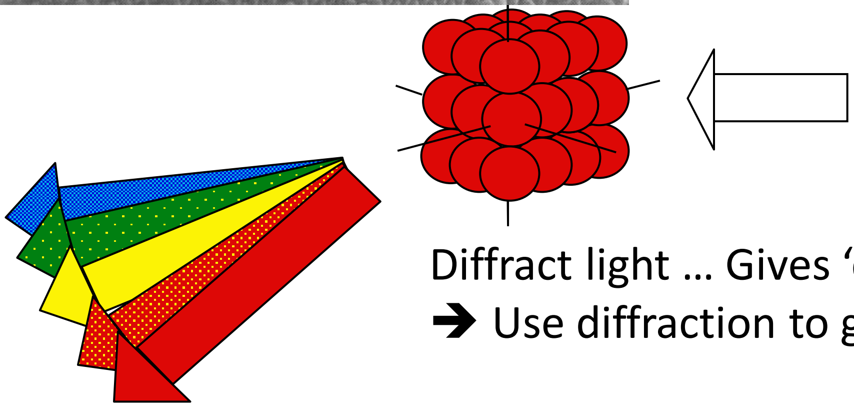
$$I(Q)=P(Q)xS(Q)$$

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

# Colloidal crystals of spheres



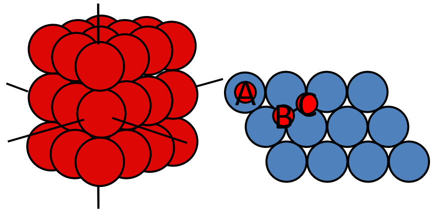


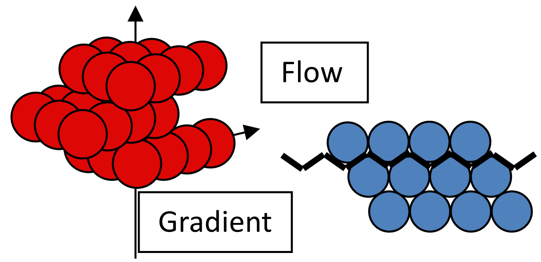


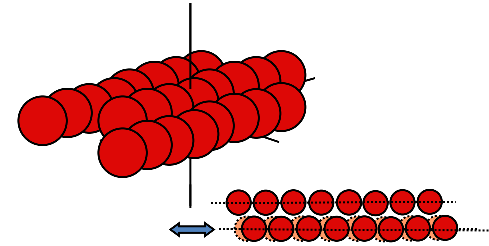
Diffract light … Gives ‘diffraction patterns’

➔ Use diffraction to give structure

# Colloidal Spheres under flow



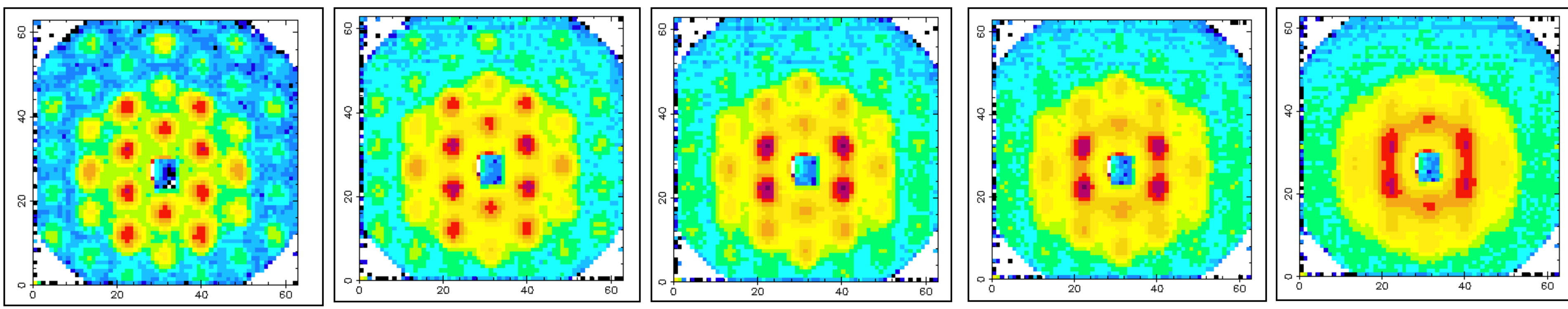



**Crystal**
Perfectly ordered sequence
of perfect hexagonally ordered layers

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

**'Strings'**
Particles in lines

Increasing Shear Rate



'Crystal'

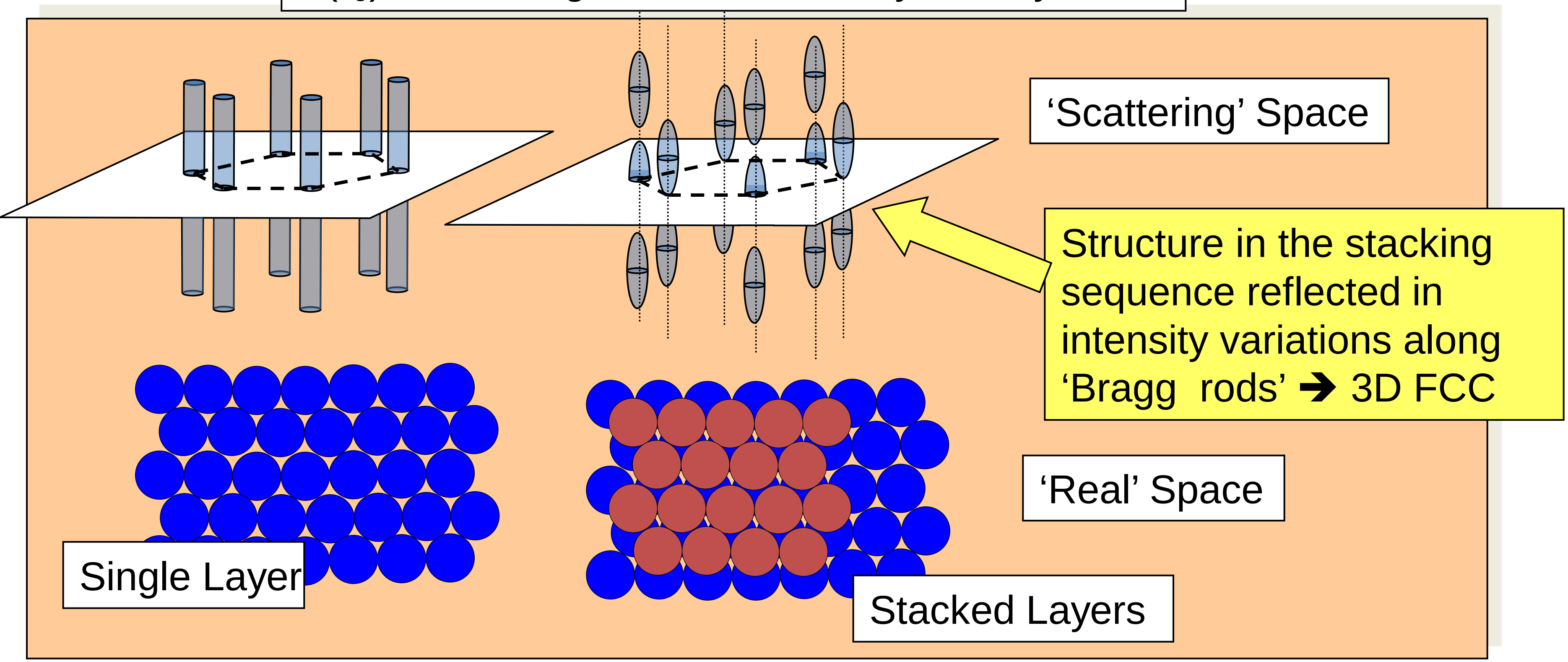
'Sliding layers'

'Strings'

Charged stabilised latex spheres 8%

Behaviour like 'atoms' only much larger scales and slower

# S(Q): Scattering Patterns from Layered Systems



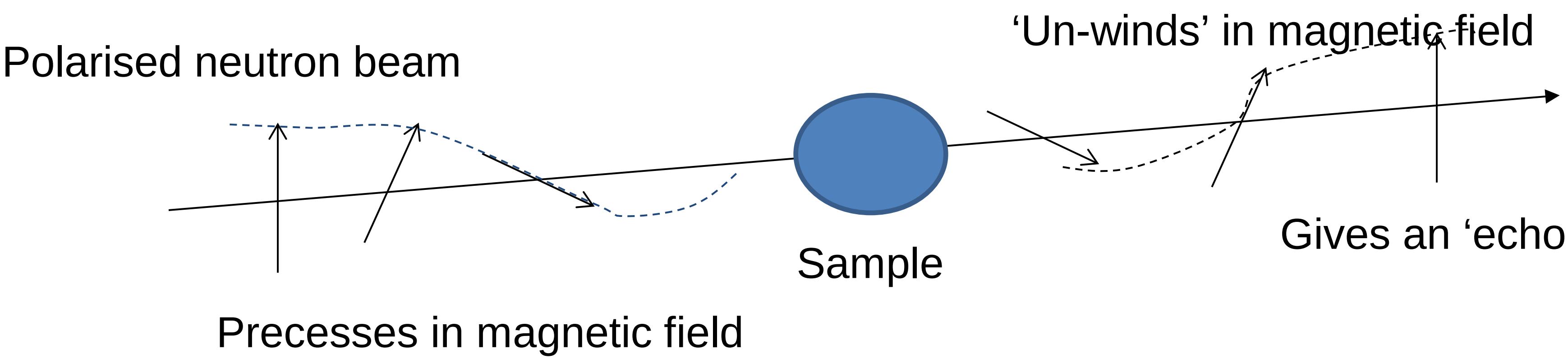
# SANS → SE-SANS VERY BIG objects

**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!!

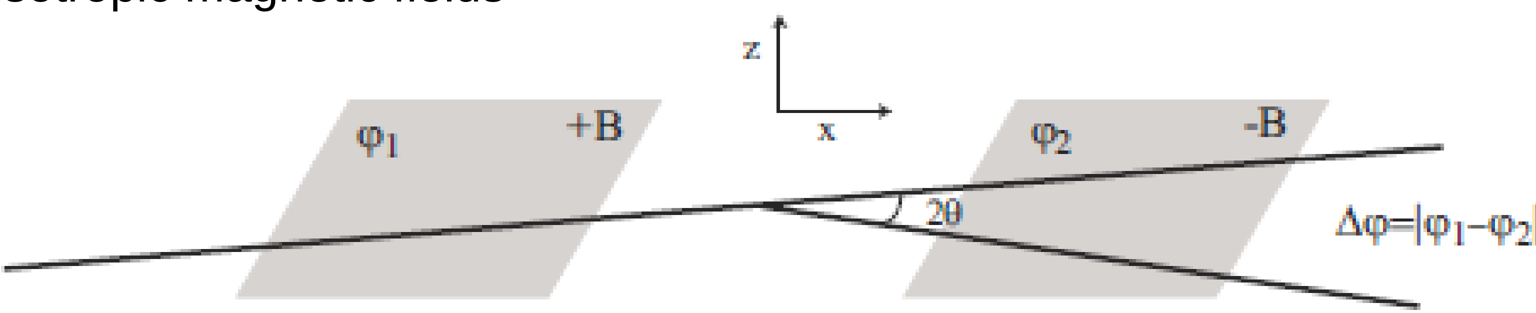
Spin echo SANS → Keep wide open beam and Encode the scattering angle in the neutron spin!!

(VERY CLEVER IDEA THIS!!)

# SE-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:

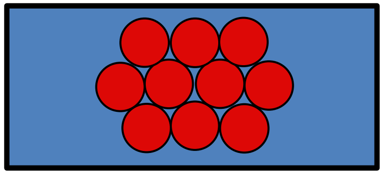
Real space, density-density correlation function, G(z)

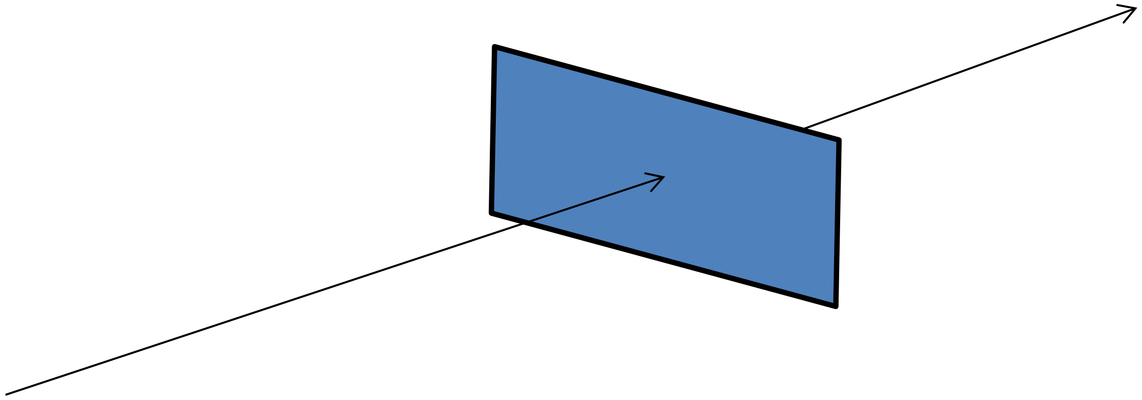
# Silica particles in polymer matrix Colloidal Crystal

- J. Baumberg Samples:

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

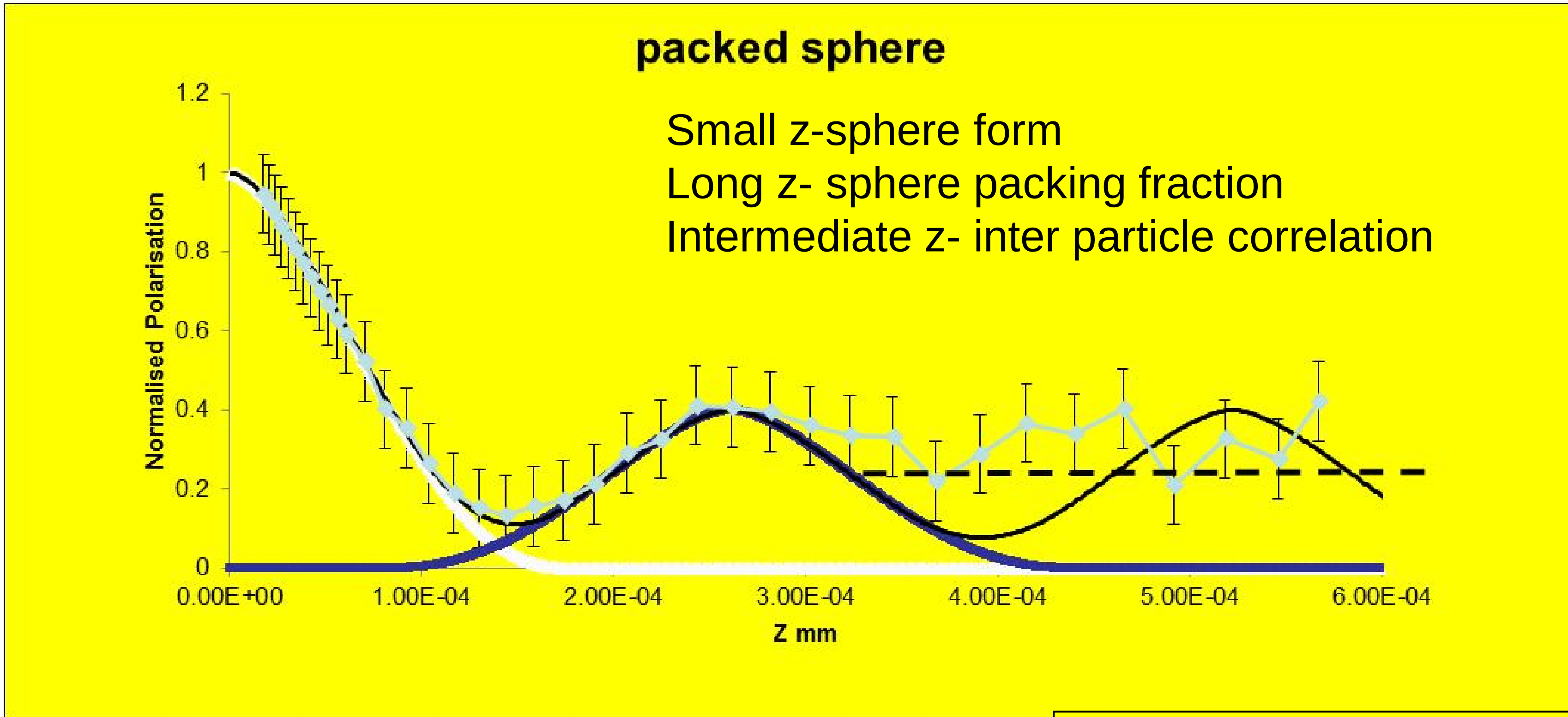
Layers oriented and regularly stacked





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’.

# 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?

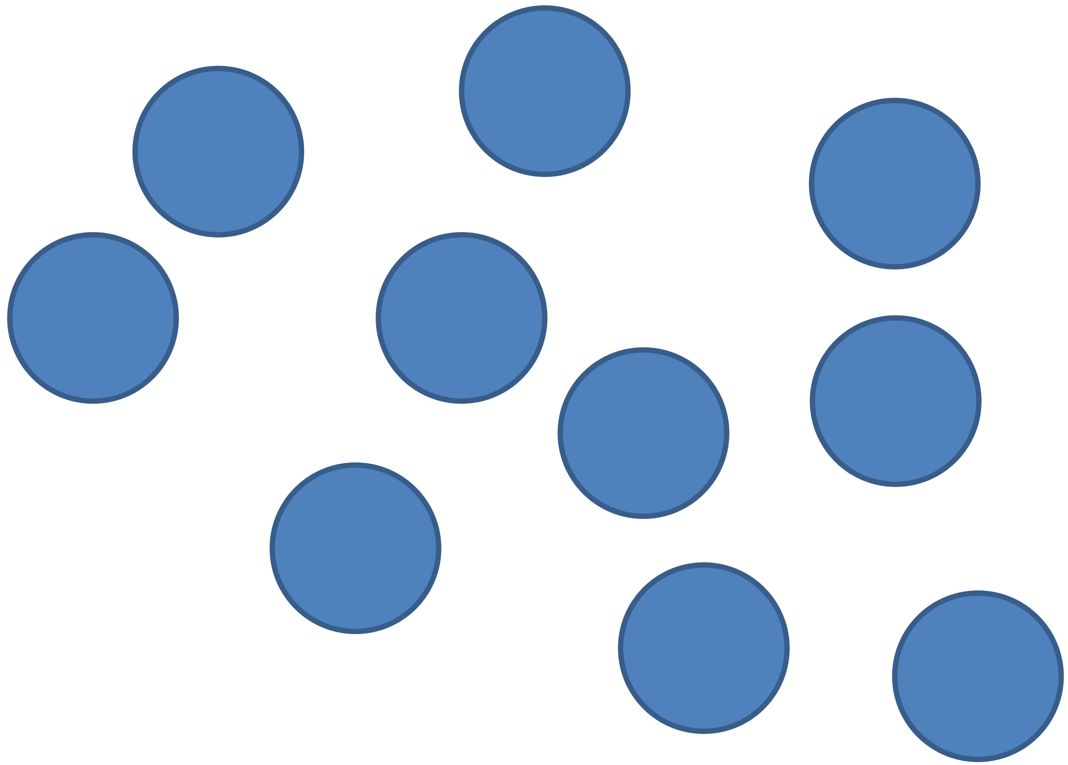
- No long range order: NO diffraction??

Oh dear!!

But still a lot of structure..

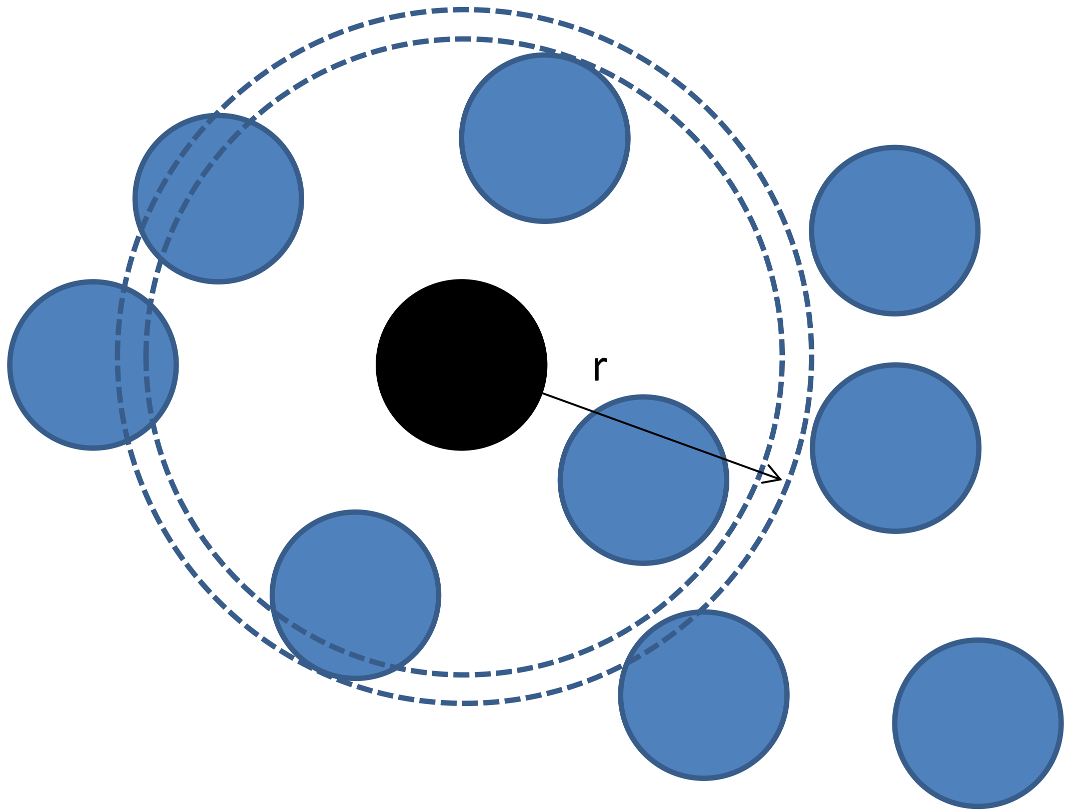
# Radial distribution function

Liquid species



# Radial distribution function

Liquid species

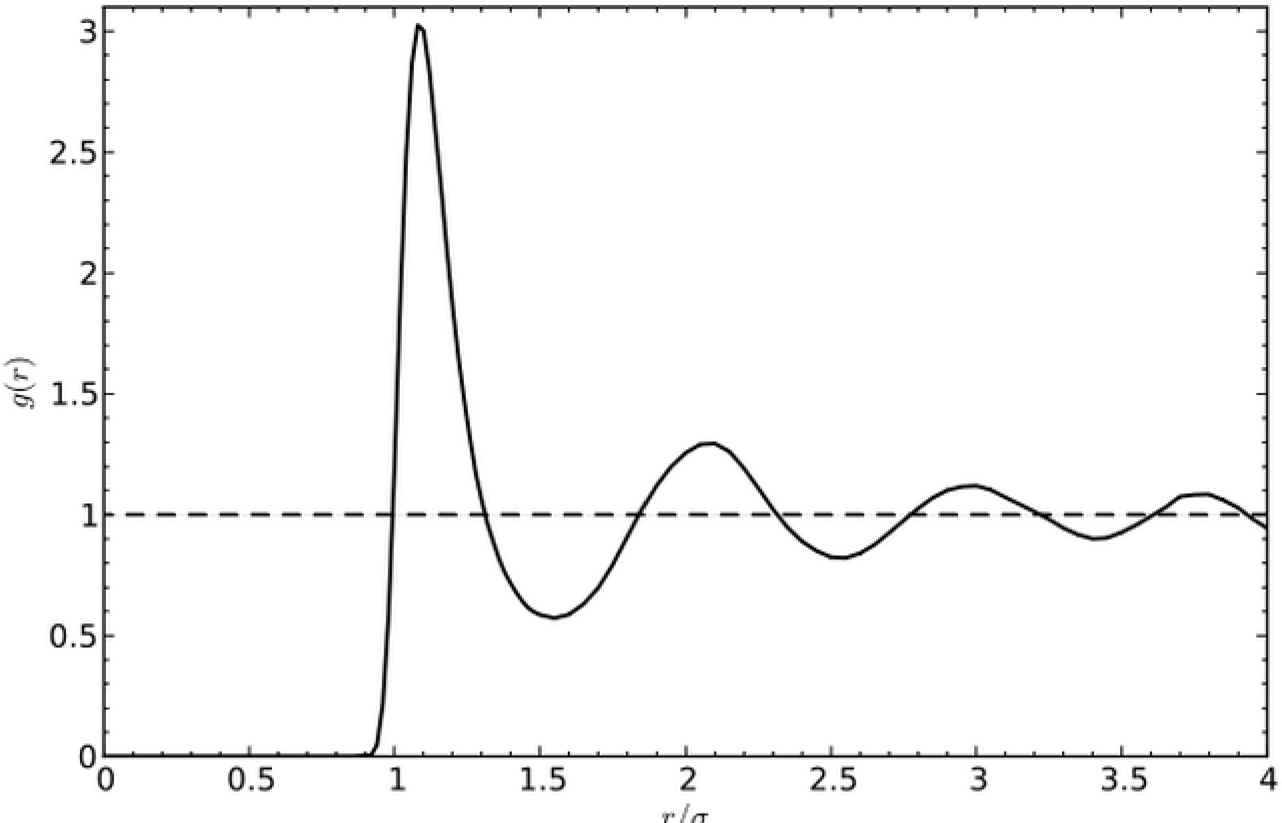



How many species in this shell at distance r from the central one: g(r)

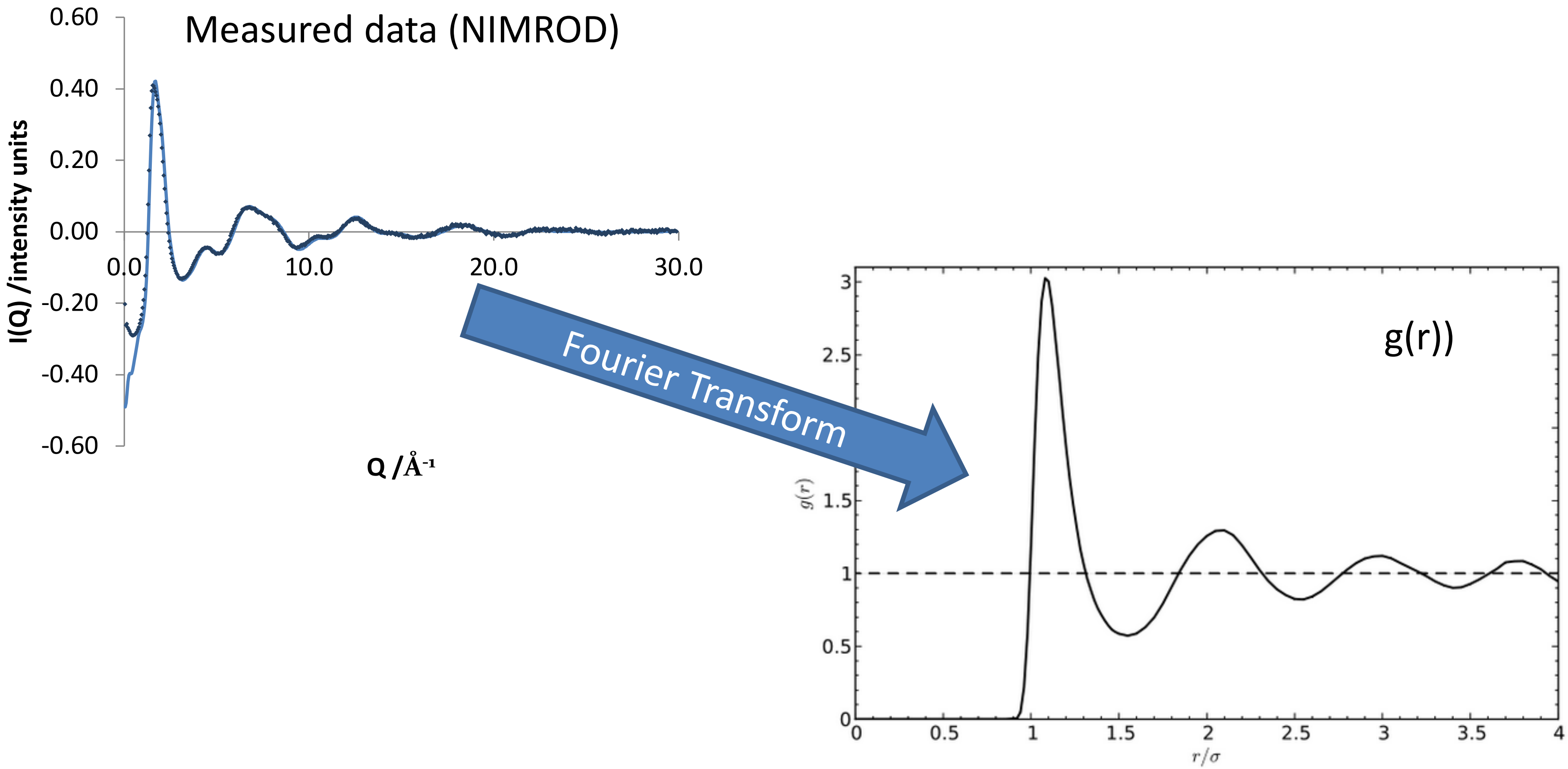
# Pair distribution function: g(r)

(normalised)

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



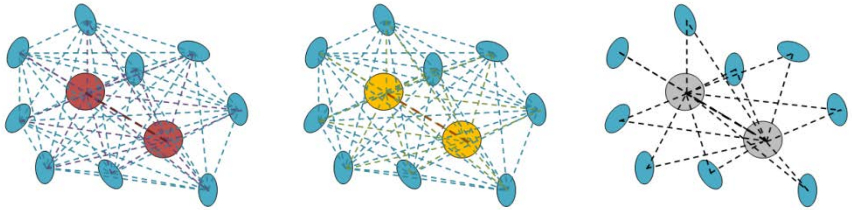
# Pair distribution function: g(r), FT of scattering data



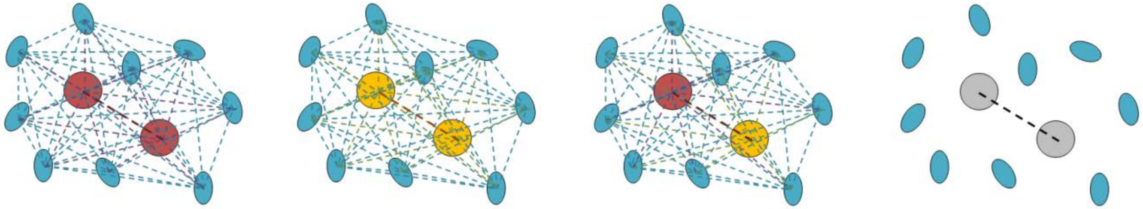
# Can we ‘understand’ liquid structure? See all Atom-Atom distances

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

a) First difference (big circles exchanged):



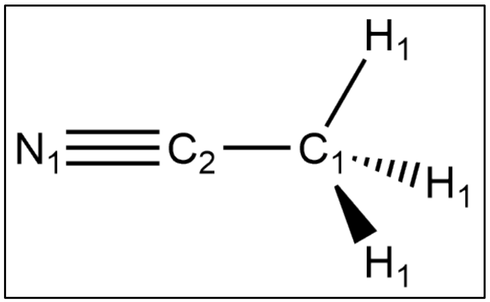
b) Second difference:

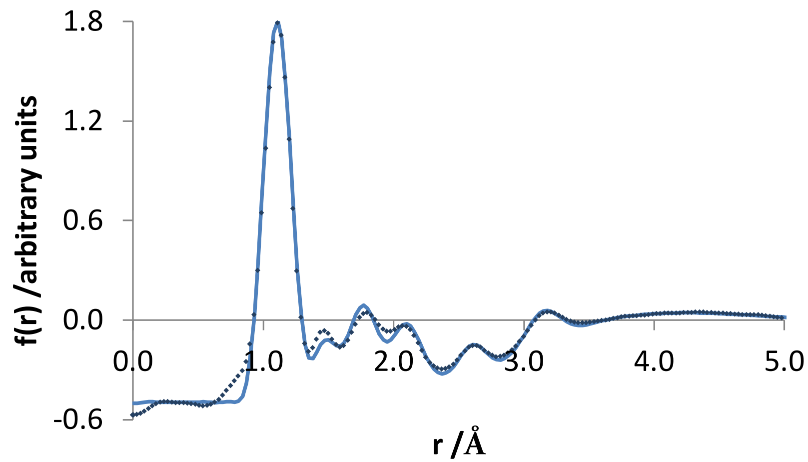


➔ ONLY solute-solute distances!!

# PDF example: Acetonitrile

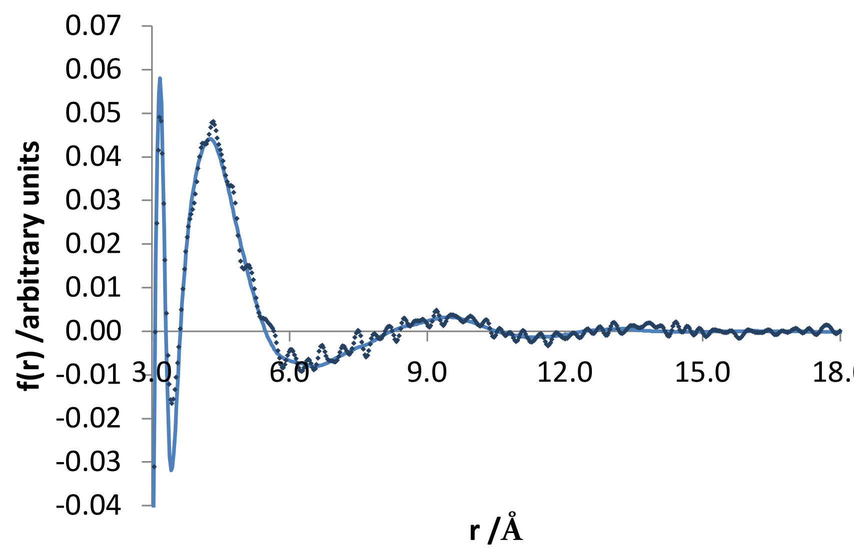
- See correct molecular structure at short distances



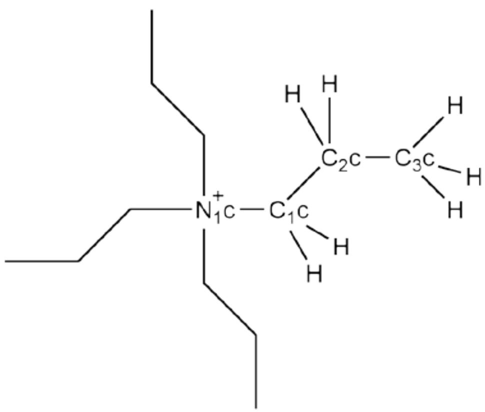

- Solvent shells at

Longer distances

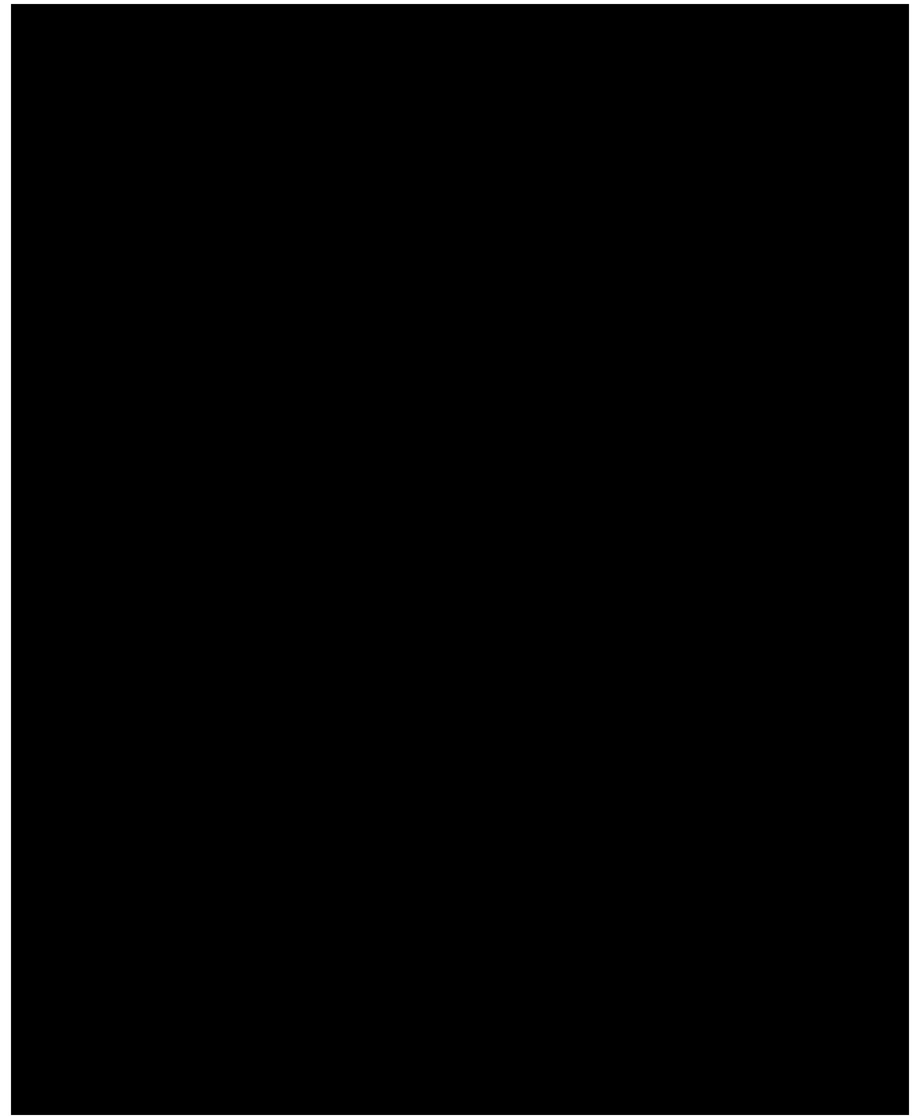


# Supercapacitors: Ions in acetonitrile

- 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