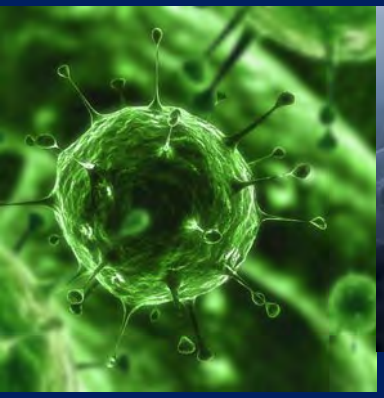
Small-Angle Neutron Scattering: Applications to Multi-Component Systems

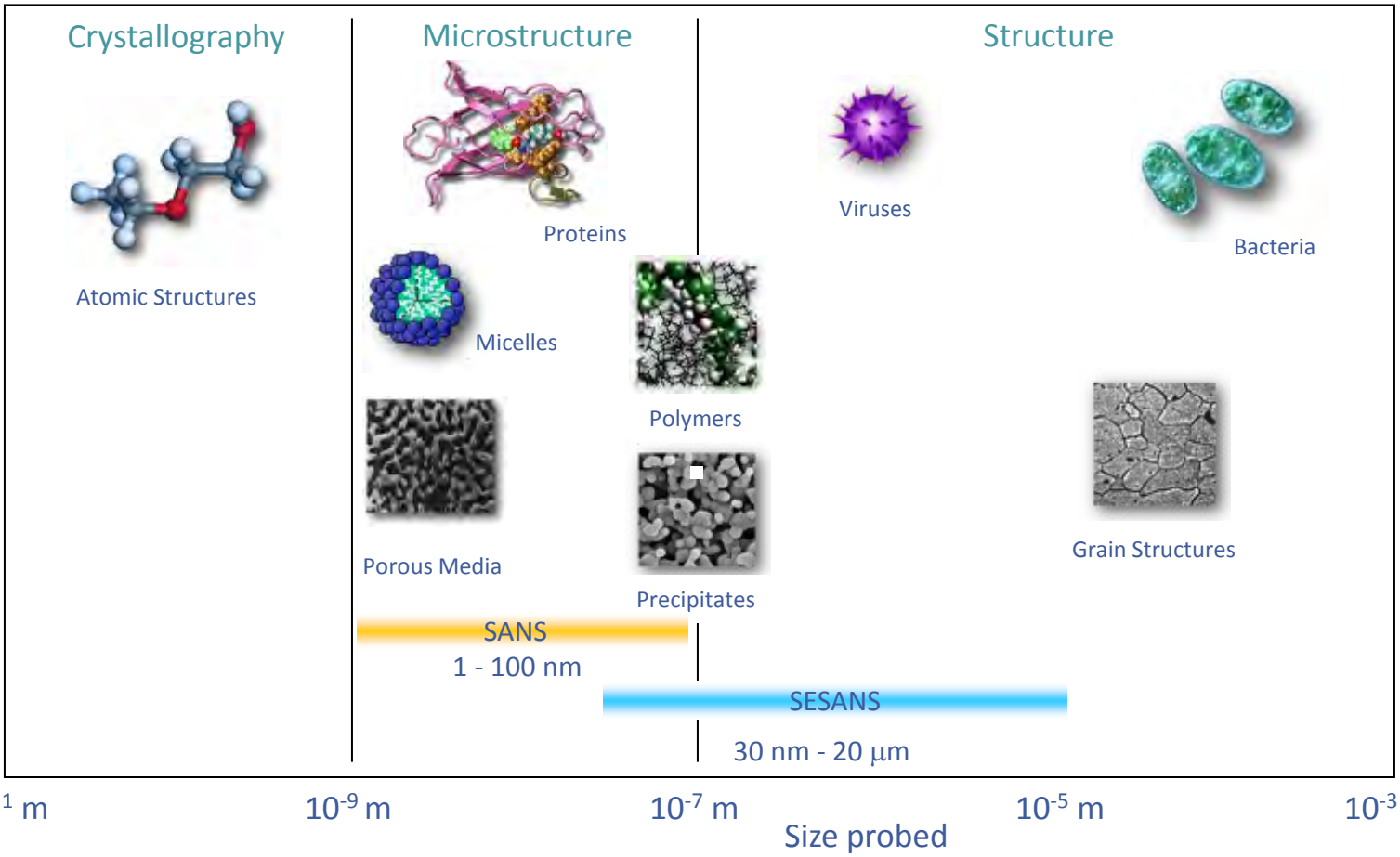




Sarah Rogers

ISIS Facility, Rutherford Appleton Laboratory, UK

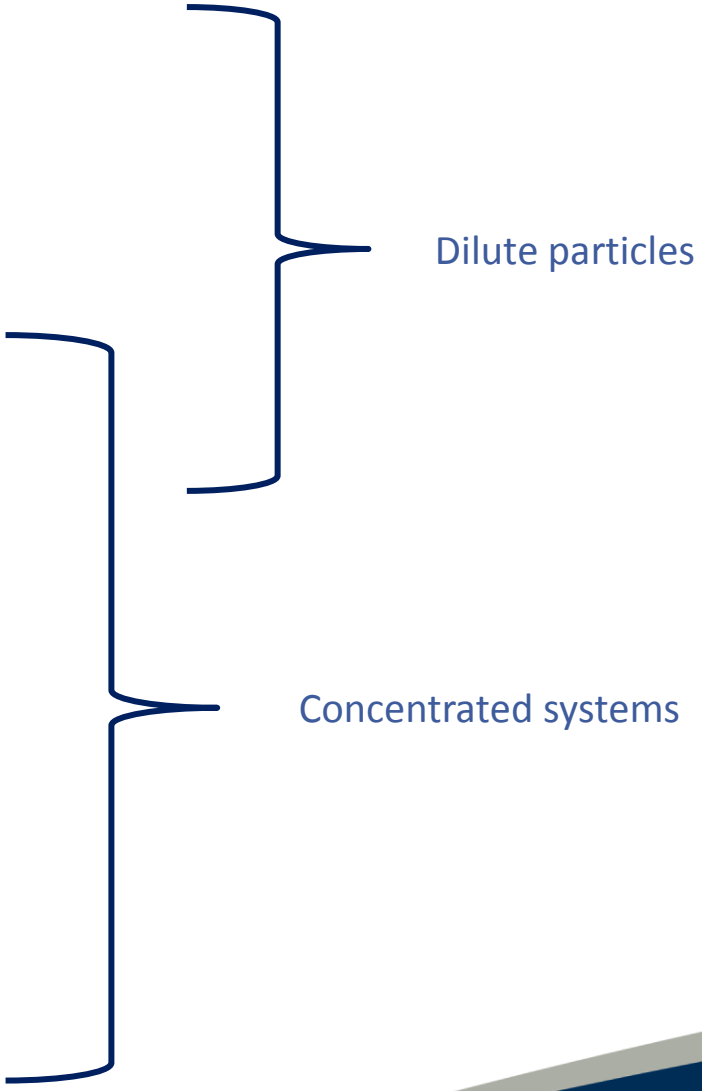
What is S_{mall}-A_{ngle} N_{eutron} $S_{cattering}$?

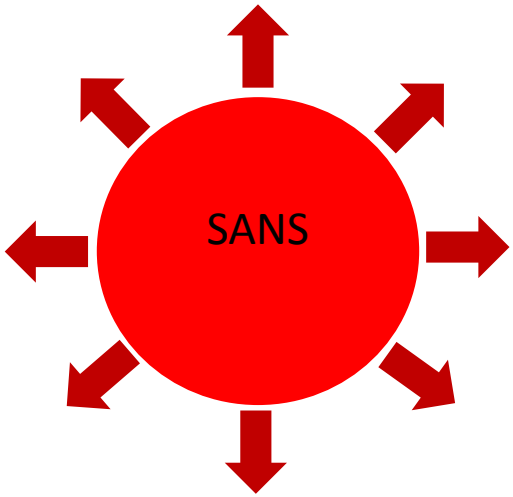


- Can determine the size, polydispersity , structure and interactions within a wide range of disordered materials
- Materials studied include surfactants, polymers, liquid crystals, nanoparticles, lipids & fibres
- Lengthscales probed range from 1s to 100s nm for SANS

What SANS (and SAXS) Tells Us

- Nanostructure
  - size
  - shape
- Internal features
  - contrast variation
- Molecular weight – aggregation number
- Surface/volume (Porod)
- Interactions
  - hard
  - soft
  - charged
- Location of components
  - contrast variation
  - interfaces
- Relation to microstructure
  - porous solids etc.





Polymers in solution for drug coatings

Solution scattering

Templating of nanoparticles with micelles and microemulsions

Ionic liquid mixtures

Flux line lattices

Colloidal crystals

Growth of fibrils

Defects in metals

Surfactant stabilised carbon nanotubes

Foams

Interfacial structures of polymers at various interfaces

Nanoparticles in metal alloys

Exchange in nanoemulsions

Organic Light Emitting Diodes (OLEDS)

Interaction of perfume with micelles

Interaction of polymers with DNA

Carbon nanotubes

Movement of drugs through and into vesicle bilayers

Orientation of peptide fibrils

Micellization in CO_2

Anomalous relaxation behaviour in alcohol-water mixtures

Hydrogen loading

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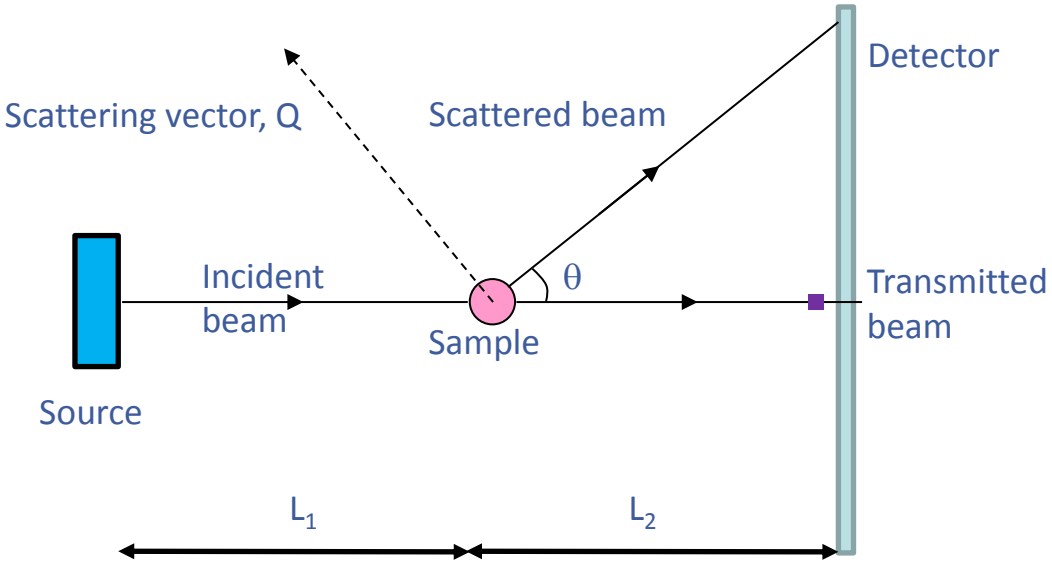
SANS Transmission Geometry

Lengthscales are explored in reciprocal space by detecting the number of scattered neutrons as a function of the scattering vector, *Q*. *Q* is inversely proportional to distance, *D*, by the approximation:

$$Q = \frac{2\pi}{D}$$



Units are either $Å^{-1}$ or nm^{-1} i.e. the smaller the value of *Q* the bigger the object

Q is also related to wavelength and the scattering angle by:

$$Q = \frac{4\pi \sin\left(\frac{\theta}{2}\right)}{\lambda}$$

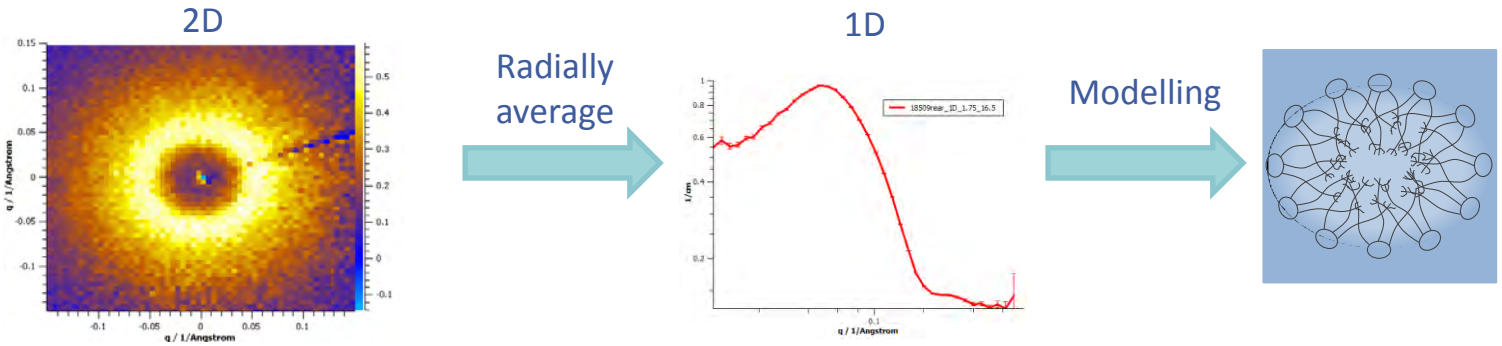
$L_1 = L_2$ for optimal *Q* resolution

To reach the smallest *Q* values the incident flux is always lower in conventional 'pinhole collimation' SANS as a long incident collimation is needed

Q (size) range is varied by altering θ or λ

‘Typical’ Experiment

The 2D SANS patterns obtained are often radially averaged to given an ‘intensity’, I(*Q*), vs. *Q* plot



I(*Q*) contains the information on size, shape and interactions between the scattering centres in the sample. For monodisperse spheres I(*Q*) can be defined as:

$$I(Q) = (\rho_p - \rho_m)^2 N_p V_p^2 P(Q) S(Q) + \mathrm{B}$$

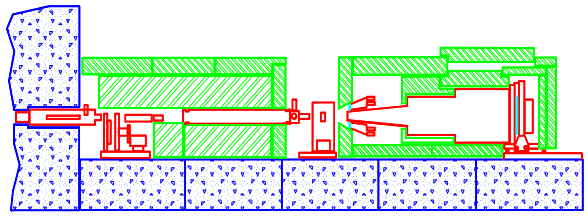
Form factor: intra-particle information
- size and shape of particle

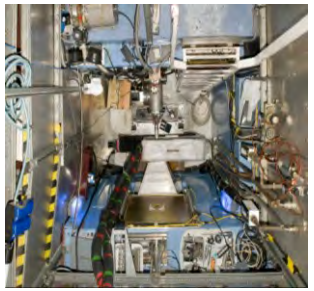
Structure factor: inter-particle information. Depends on the type of interactions in the system. S(*Q*) = 1 for dilute dispersions

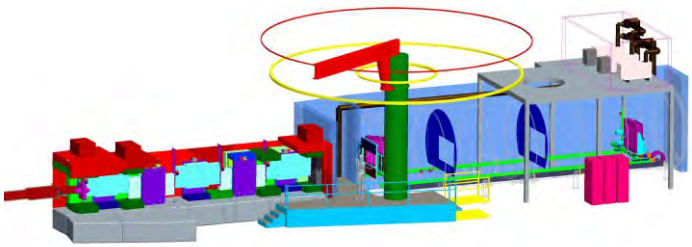
‘Flat background’. Generally regarded as due to ‘incoherent’ scattering, often due to hydrogen

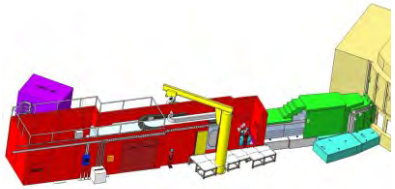
Beamlines

- There are four to choose from
- LOQ was the 1st ISIS SANS instrument and is positioned on the 50 Hz first target station, TS-1
- Sans2d is the first SANS instrument to be built on the optimized TS-2
- Larmor SANS set up is available. The spin-echo setup is being developed with the NWO and TU-Delft over the next year
- Zoom is currently under construction. Shutter will be open later this year
- Various different capabilities on the different beamlines
- Talk to the SANS team!







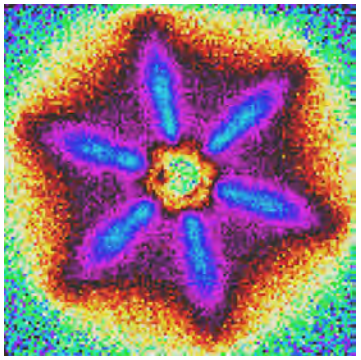


The Sample Environment

Extensive available sample environments allow a broad range of science to be studied via SANS at ISIS.

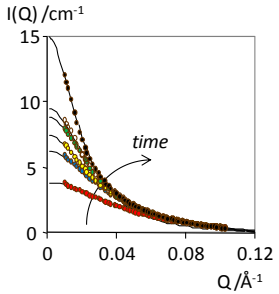
Sample environment includes:

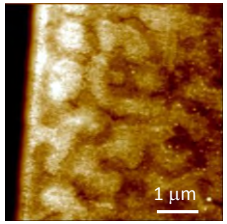
- Standard ISIS cryostats, furnaces and magnets
- Sample changer with temperature control
- Linkham stages for advanced temperature control
- Rheometer and shear cells
- Pressure cell – 600 bar with stirring. Predominantly used with CO_2
- T-jump cell – study non-equilibrium phases
- *In-situ* DLS and UV-vis
- Grazing Incidence SANS (GISANS)
  - ➢ Study of in-plane structure on the nm lengthscale
- Stopped-flow – mixing kinetics
- Well equipped offline labs allow for further characterization
  - ➢ X-ray sets, AFM, BAM, spectrometers

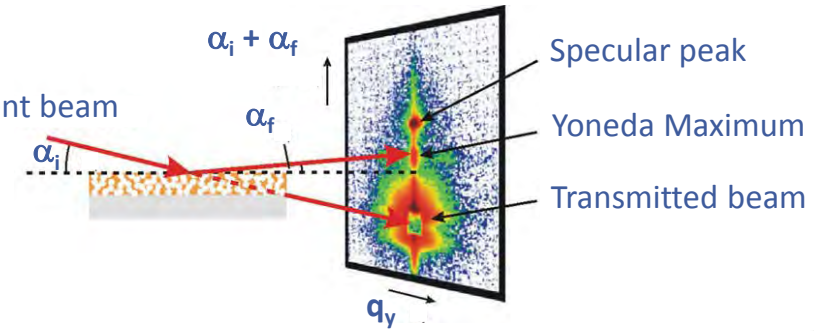


(a)

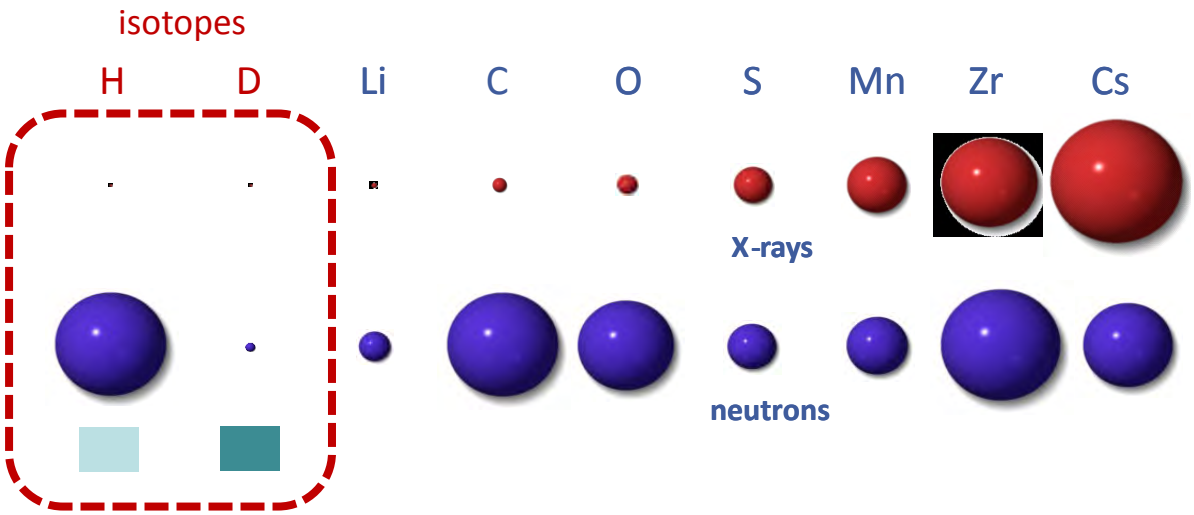
(b)

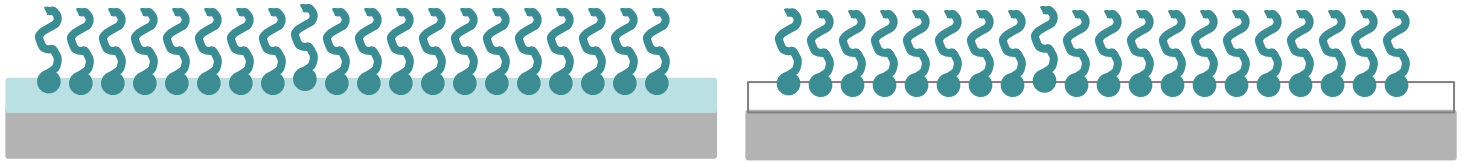


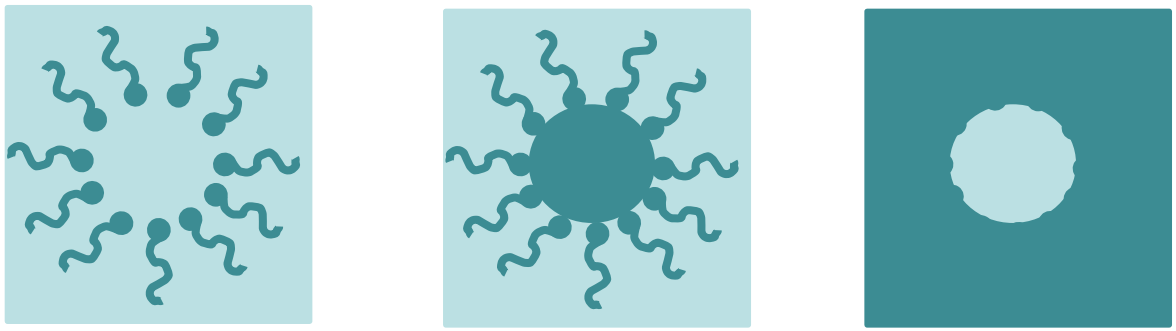




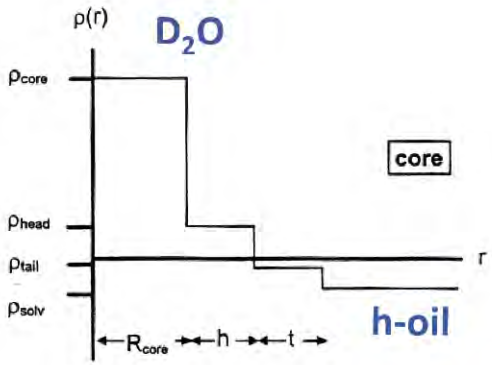
Nuclear Interaction Changes

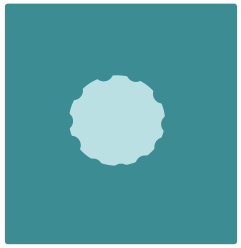


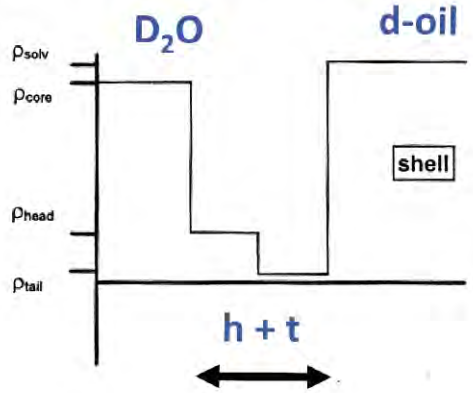


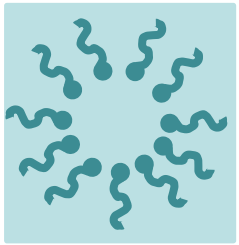


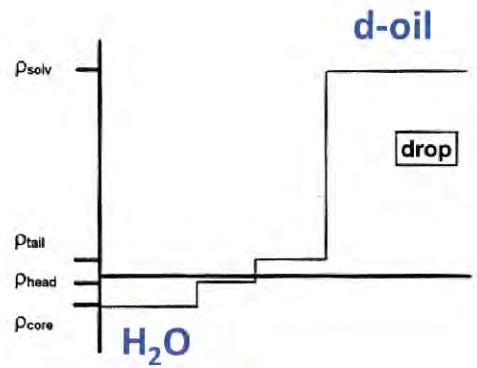
Example of Contrast Variation

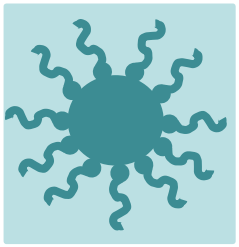




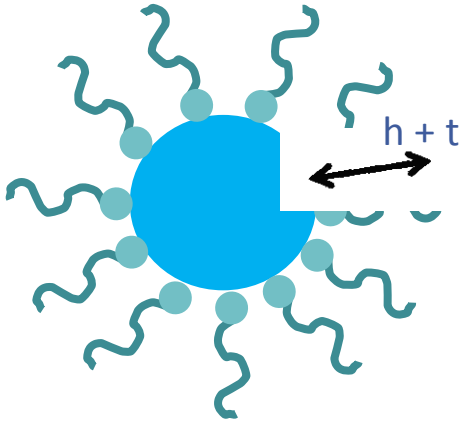






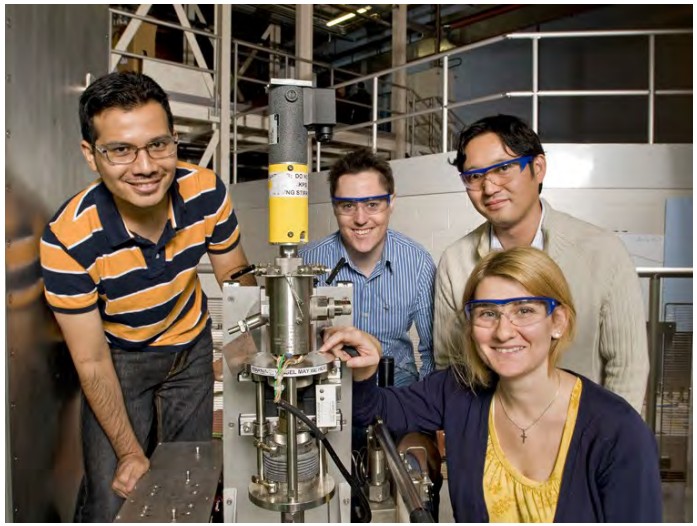


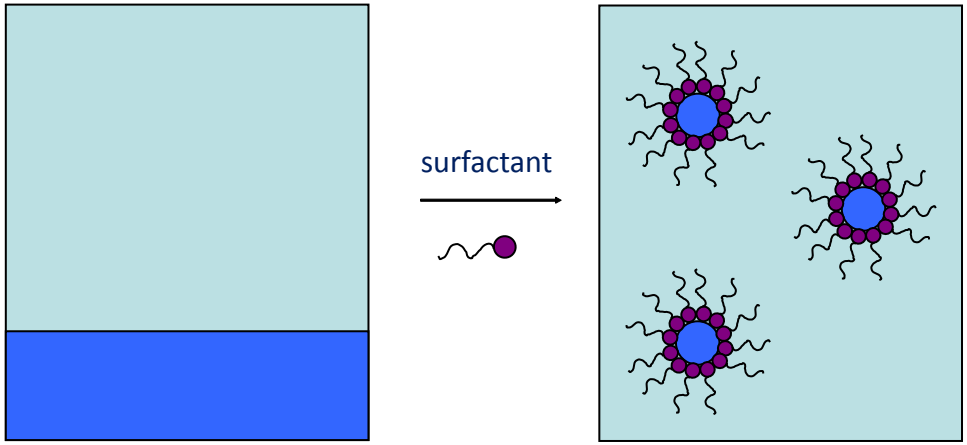
- Neutron scattering powers vary erratically with atomic number.
- In particular D and H are very different (see previous table).
- Using deuterated materials we can make parts of a system 'disappear.



Collaboration between University of Bristol and the ISIS SANS team studying the modification of the physico-chemical properties of sc-CO_2 with surfactants for use in enhanced oil recovery. Low viscosity of CO_2 promotes fingering through porous media rather than a uniform sweep.

Modifiers commonly used in oily solvents are incompatible with CO_2. Can self assembled custom-made surfactants be used?



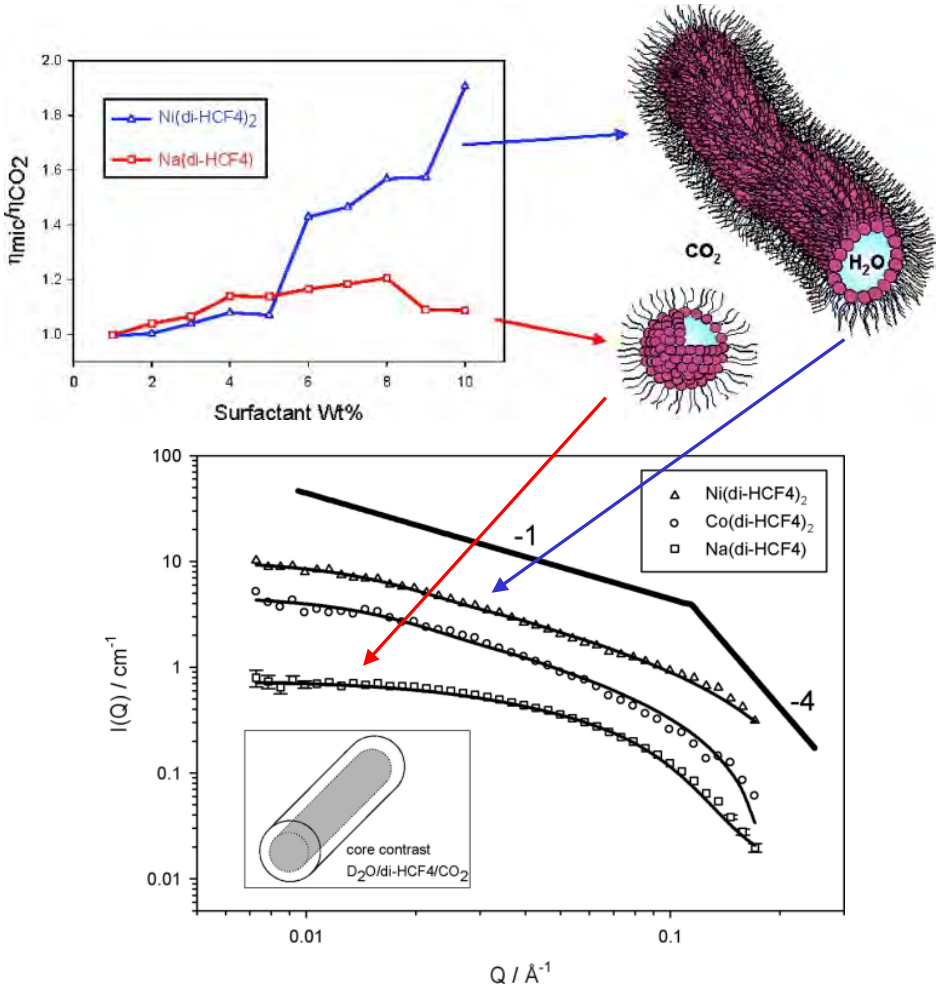


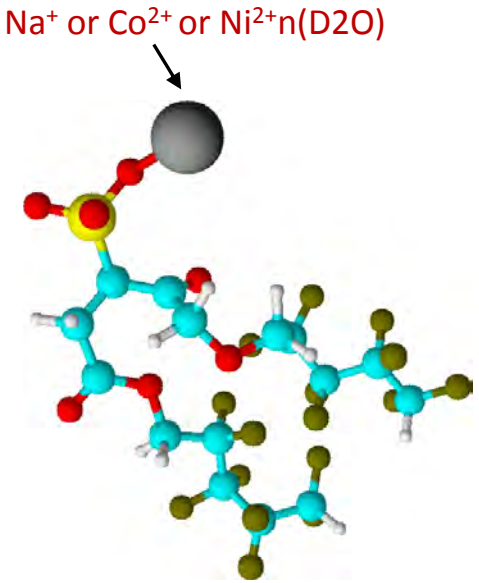
Why Neutron and Small Angle Scattering?

High penetrating power of neutrons allows a p-cell with thick windows to be employed

Using D_2O allows us to see 'nanopools' of water in the CO_2

Length-scales being probed are ideal for SANS





Results

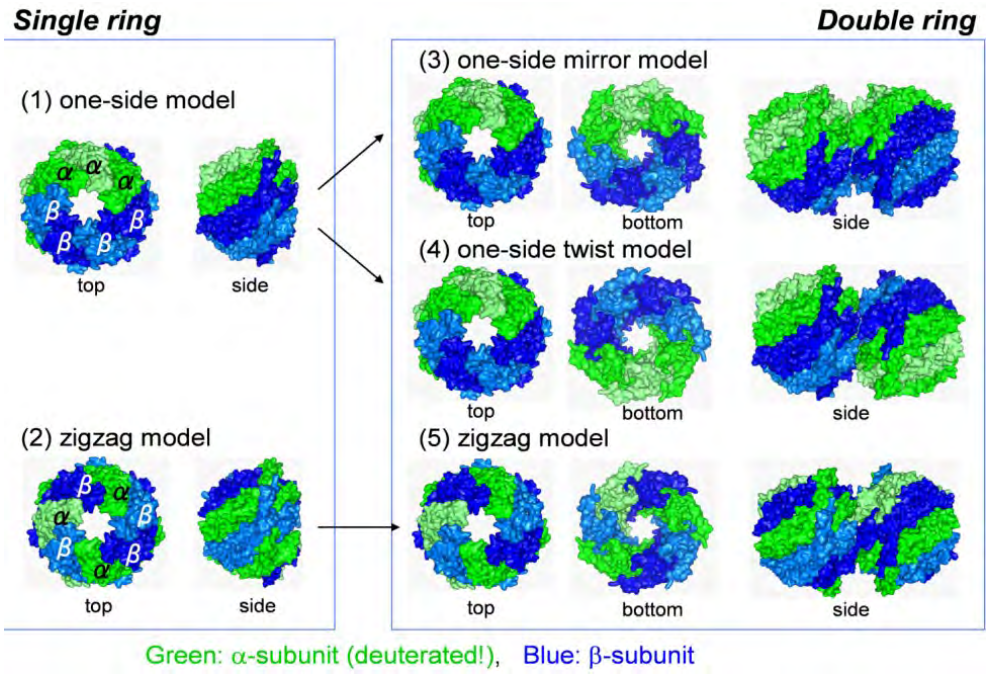
Altering the counterion of the CO_2 active surfactant DHCF4 from Na to Ni or Co causes a viscosity enhancement of up to 90% compared to pure CO_2

Why? Neutrons have the answer! Micelle shape changes from spherical to wormlike as counterion changes from Na^+ to Co^{2+} or Ni^{2+}

Langmuir 2010, 26(1), 83-88

Study by Kyoto University of the solution structure of proteasome activators (PA) which regulate the breakdown or damaged or unneeded proteins for recycling into new ones.

PA28 is comprised of a seven-membered ring containing two very similar subunits, named α and β.



Why SAS?

Neutrons are non-destructive so samples are not altered by beam damage

Contrast variation can be used to highlight specific parts of the system

Length-scales being probed are ideal for SAS

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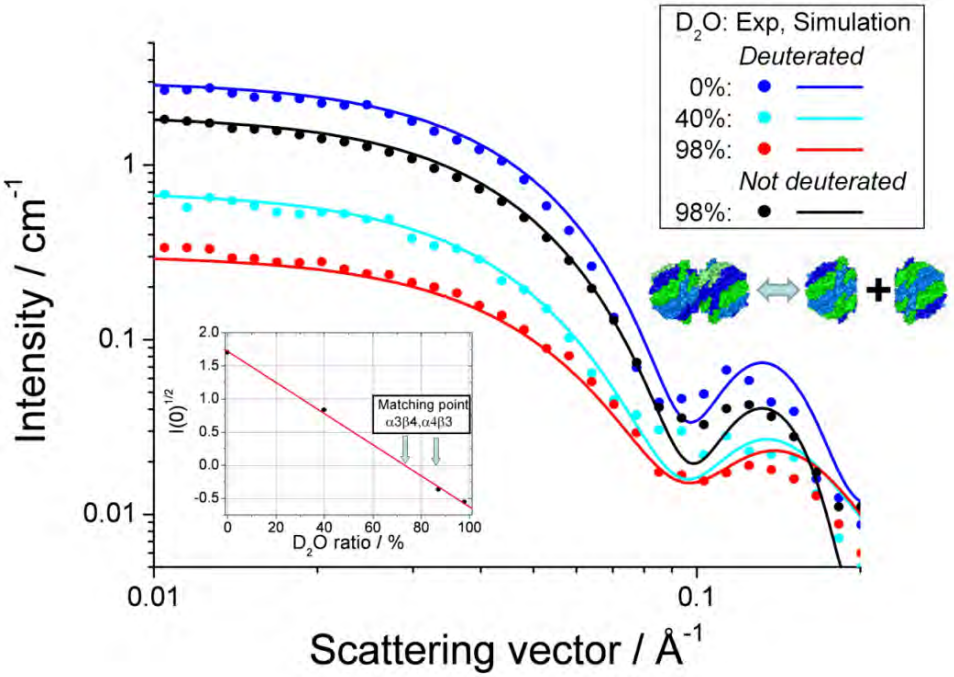
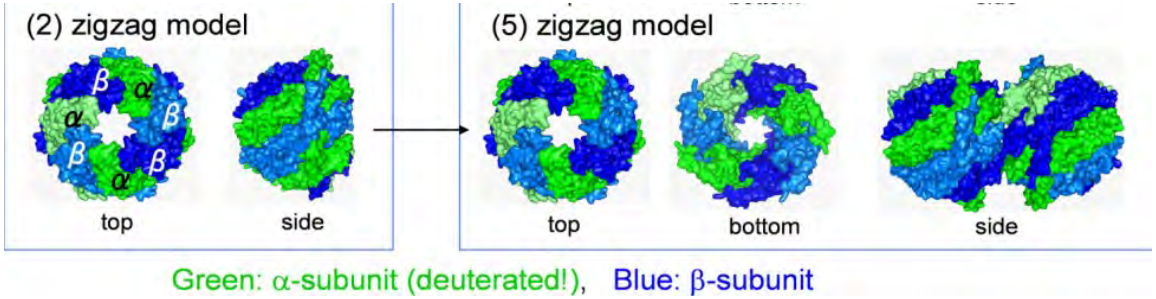
Results

CV-SANS shows that the PA28 heptamer rings are made up of three α and four β subunits in an alternating zig-zag.

SANS intensities also reveal that there is a well defined solution equilibrium between heptamer and it's double-ring dimer.





Green: α-subunit (deuterated!), Blue: β-subunit

BBRC 2013, 432(1), 141

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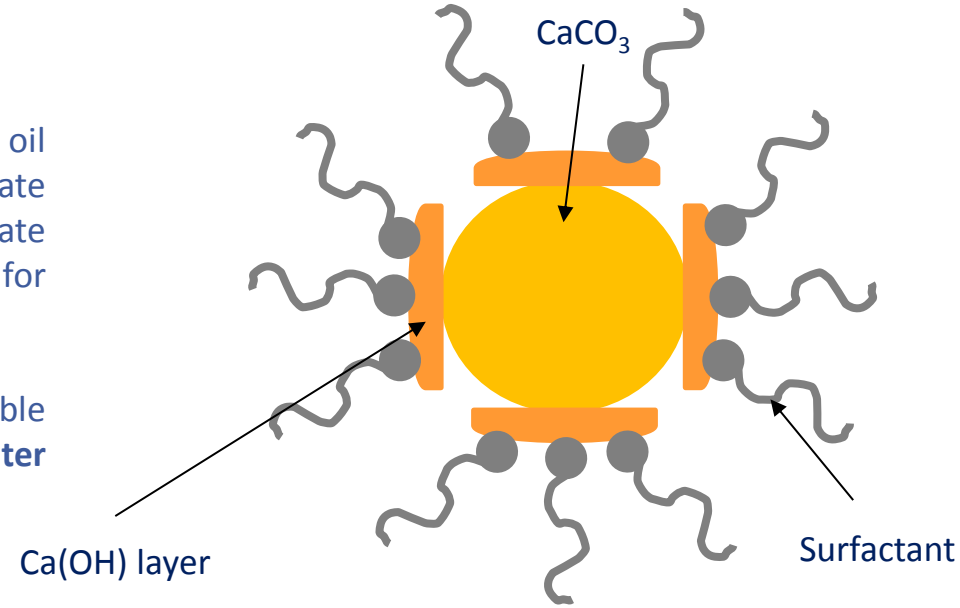
Work carried out by Infineum studying engine oil additives which consist of calcium carbonate nanoparticles – $CaCO_3$ - stabilized by a sulfonate surfactant. The stability of these particles is crucial for their correct performance.

The combustion process can produce a considerable amount of water: **how does the presence of water effect these particles?**



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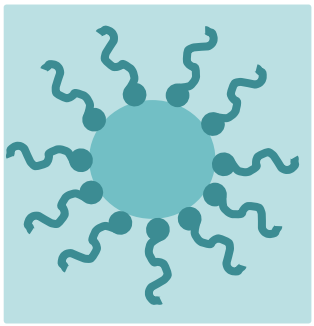

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Why Neutron and Small Angle Scattering?

H/D Contrast provides direct view of water

Length-scales being probes are ideal for SANS

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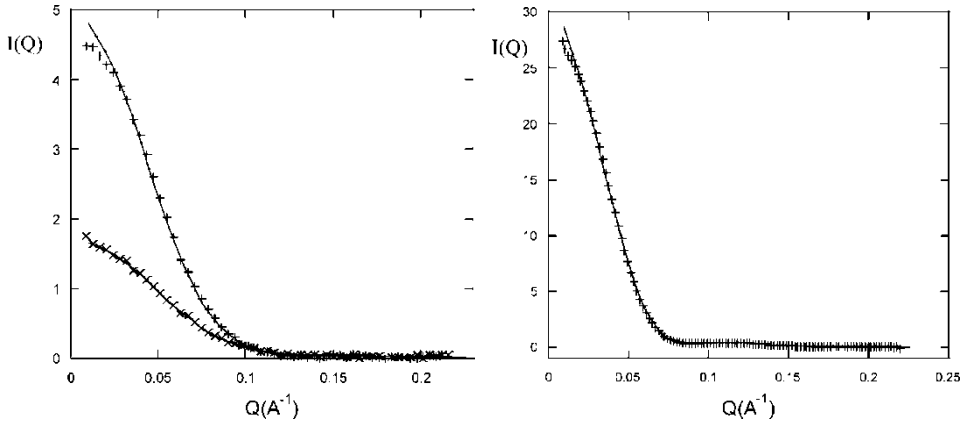
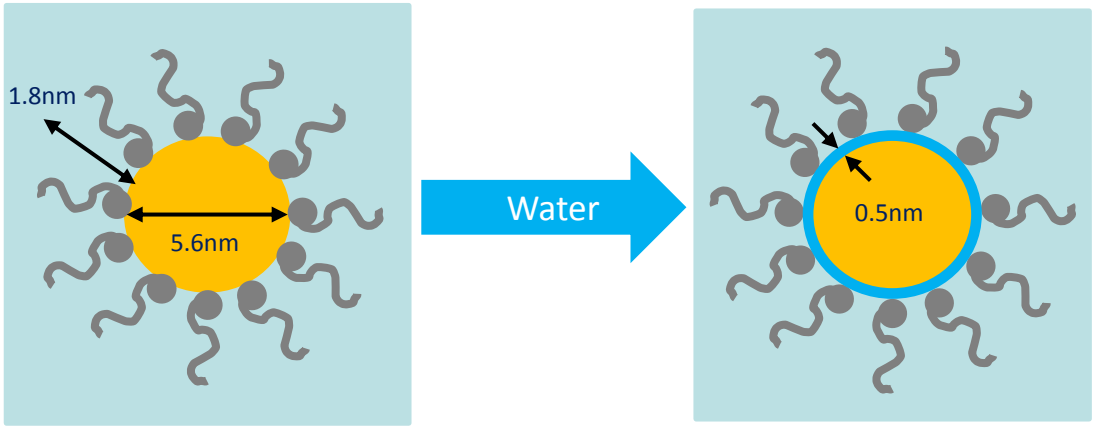
Results

$CaCO_3$ particles are spherical with dia. ~5.6nm

Surfactant monolayer is of thickness ~1.8nm

Water layer inserts between the calcium cation at the surface of the particle and the sufonate anion





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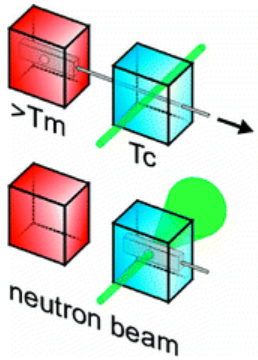
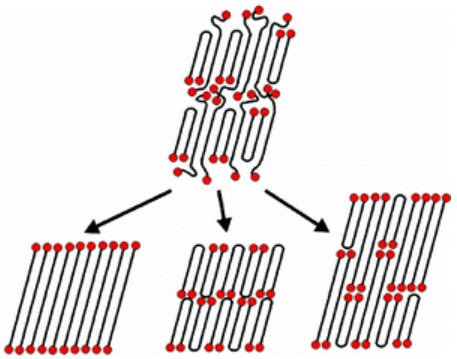
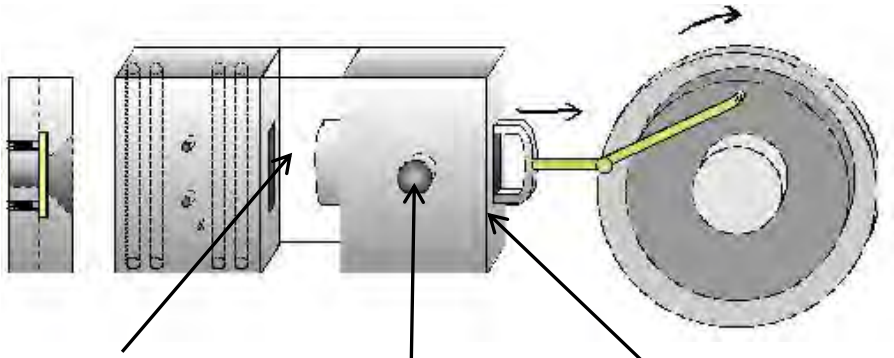
Langmuir 2008, 24, 3807 - 3813

Collaboration between University of Sheffield and the ISIS SANS Team studying transient phases in polymer crystallisation using a temperature jump (T-jump) cell designed for SAS beamlines.

Polymer crystallisation is a highly non-equilibrium process and several different lamellar structures are possible







Sample sits here for ambient conditions

Neutrons

Sample is moved to the heated block for the SANS measurement

Why SANS?

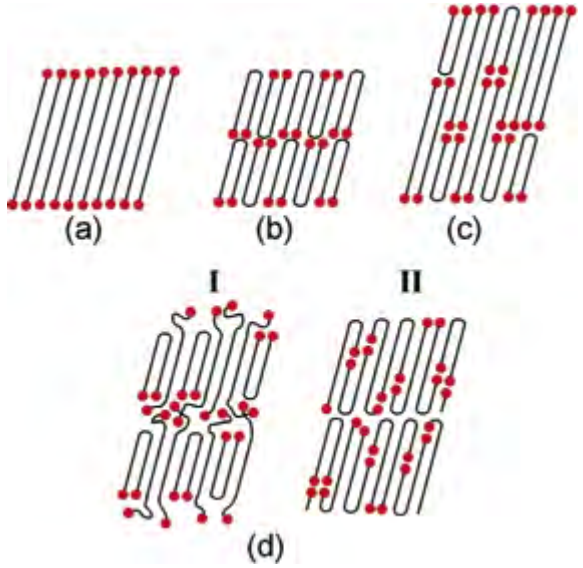
SAS is a powerful technique for studying lamellar structures

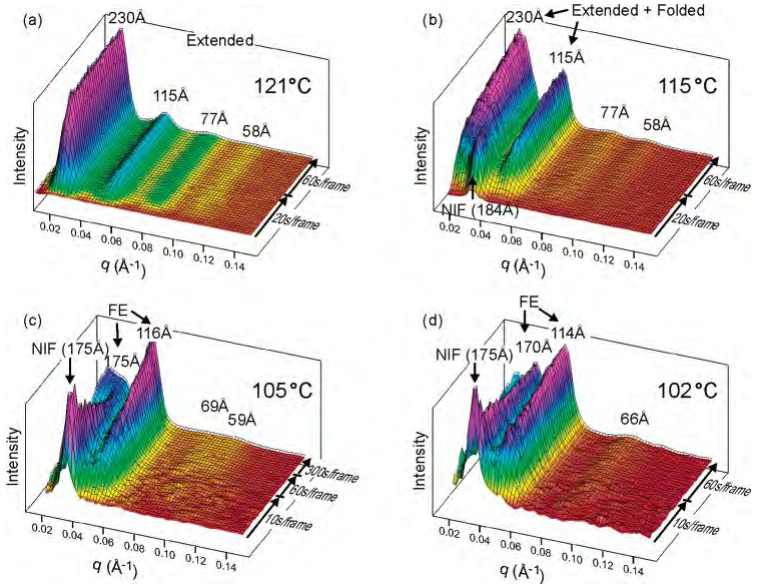
Using selectively deuterated segments, SANS can provide information on the location and state of order of such segments

Results

Material $C_{12}D_{25}C_{192}H_{384}CHDC_{11}D_{23}$ used

Lamellar structures possible are (a) extended chain form, (b) once-folded chain forn, (c) triple-layer mixed folded-extended (FE) form and (d) alternative models for the noninteger folded (NIF) form





Results

NIF form has a lifetime of ~ 1minute – time resolution achievable via SANS

Real-time SANS ‘snap shots’ reveal structural changes with time and temperature

Macromolecules 2005, 38, 7201 - 7204

GISANS – theory and system

Performed TOF GISANS on Sans2d

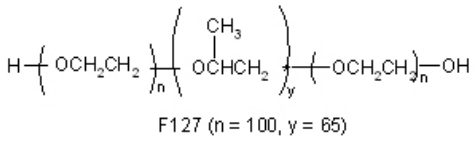
Nanoscale density correlation and/or shape of nanosized objects at surfaces, at buried interfaces or in thin films

α chosen between about half α_c and several α_c of the film material:

$\alpha < \alpha_c$ surface >> internal

$\alpha \geq \alpha_c$ surface and internal

$\alpha > \alpha_c$ surface << internal

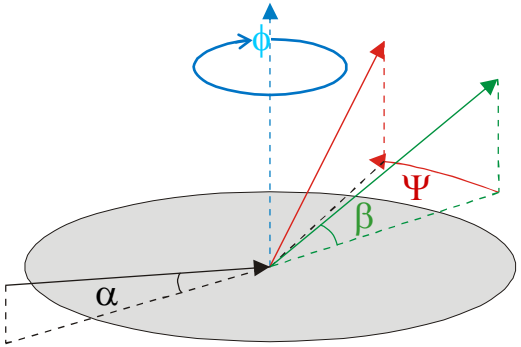


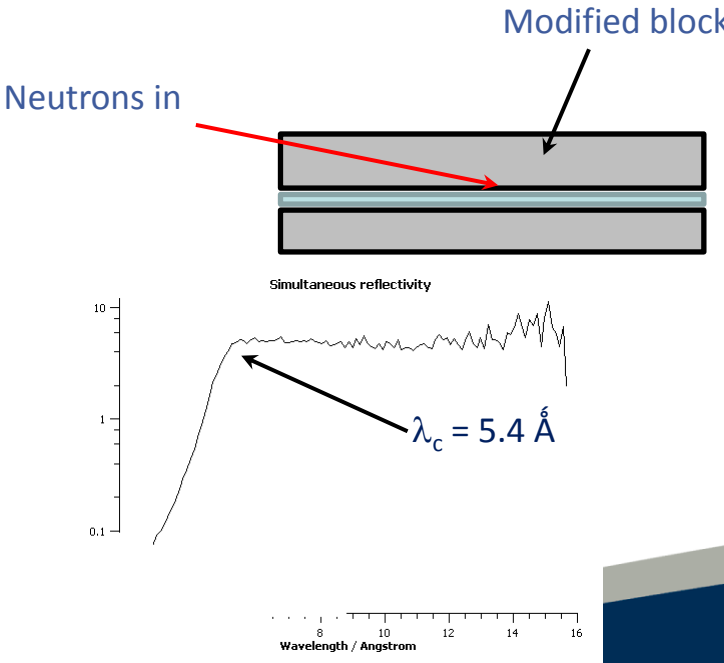
F127 (n = 100, y = 65)

With TOF we capture GISANS simultaneously with bulk and surface scatter. "Near surface" SANS happens close to "critical wavelength" λ_c.

Sample is 20% F127 solution between modified Si blocks

Beam stop detector records simultaneous NR profile





Crystallization of 20wt% F127 in D_2O via GISANS, M Wolff (Uppsala)

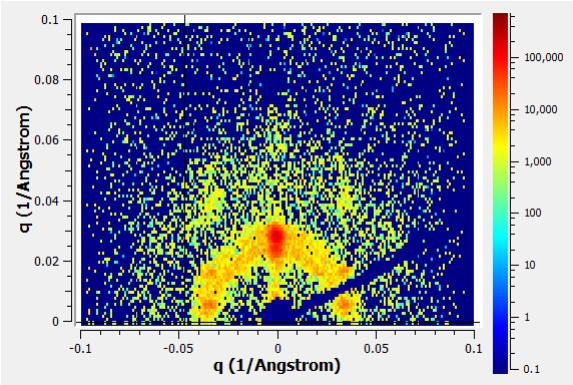
GISANS allows in-plane structure on the nm lengthscale to be studied

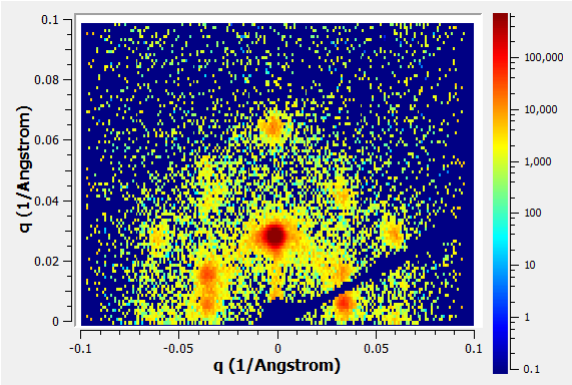
- Above and below critical temperature (T_c)
  - below T_c = micelles
  - above T_c = crystallization
- Studying the D_2O/Si interface. Two different Si surfaces
  - one hydrophobic (OTS)
  - one hydrophilic (piranha cleaned)
- Critical wavelength = 5.4 Å
  - Anything below 5.4 Å = bulk > surface
  - Anything above 5.4 Å = surface > bulk
  - **TOF gives you all the above conditions simultaneously**

Hydrophobic

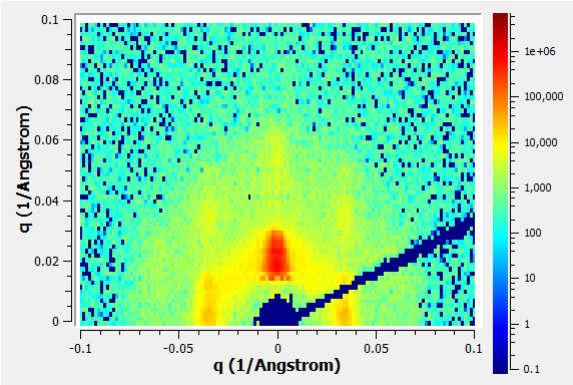
Hydrophilic

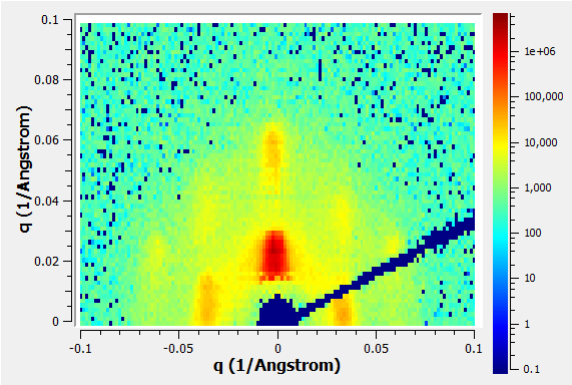
At λ_c GISANS shows different crystallization at surface





Below λ_c bulk structure is dominant and structures are the same





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THANKS to…..

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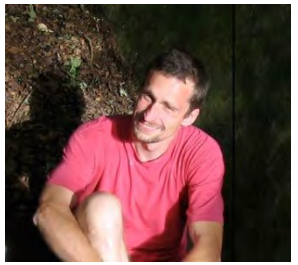

The University Of Sheffield.

And you for listening!

Any questions?

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