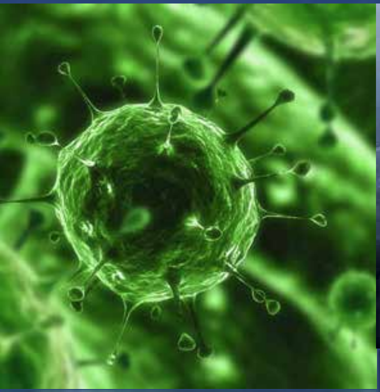
# Small-Angle Neutron Scattering: Applications to Multi-Component Systems

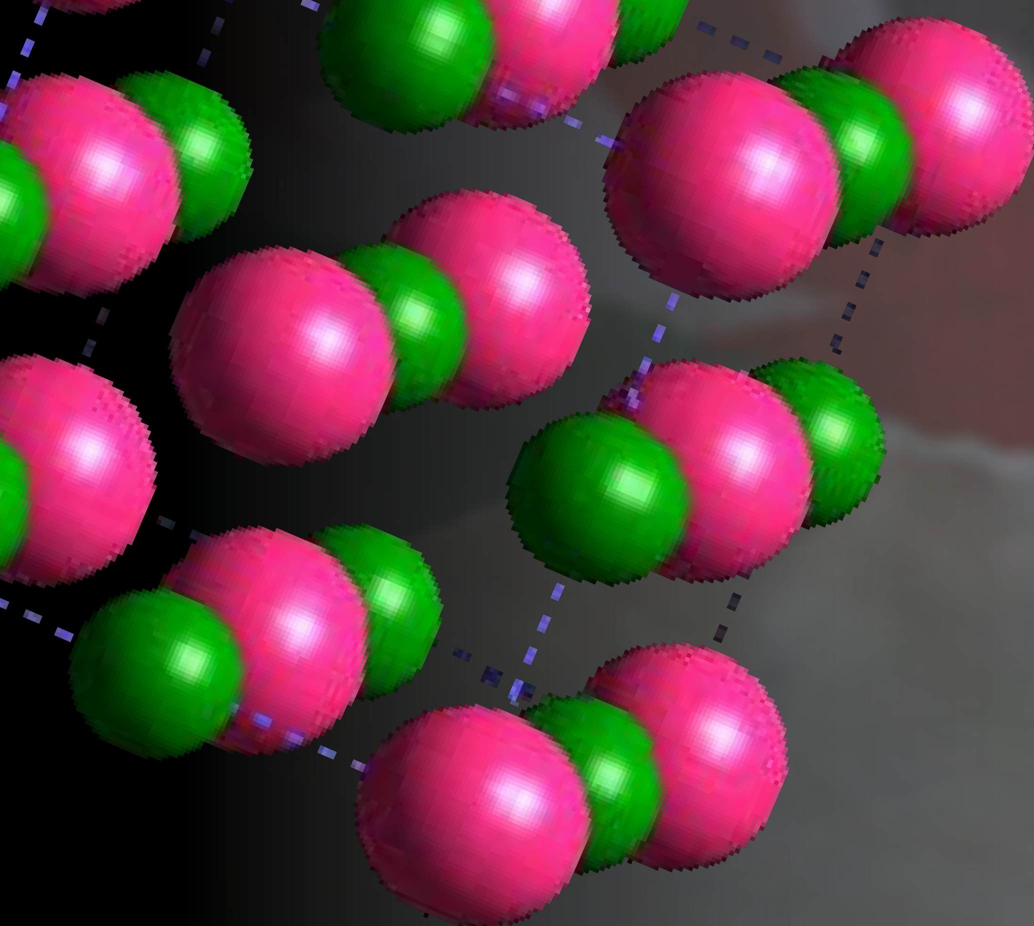




Sarah Rogers
ISIS Facility, Rutherford Appleton Laboratory, UK

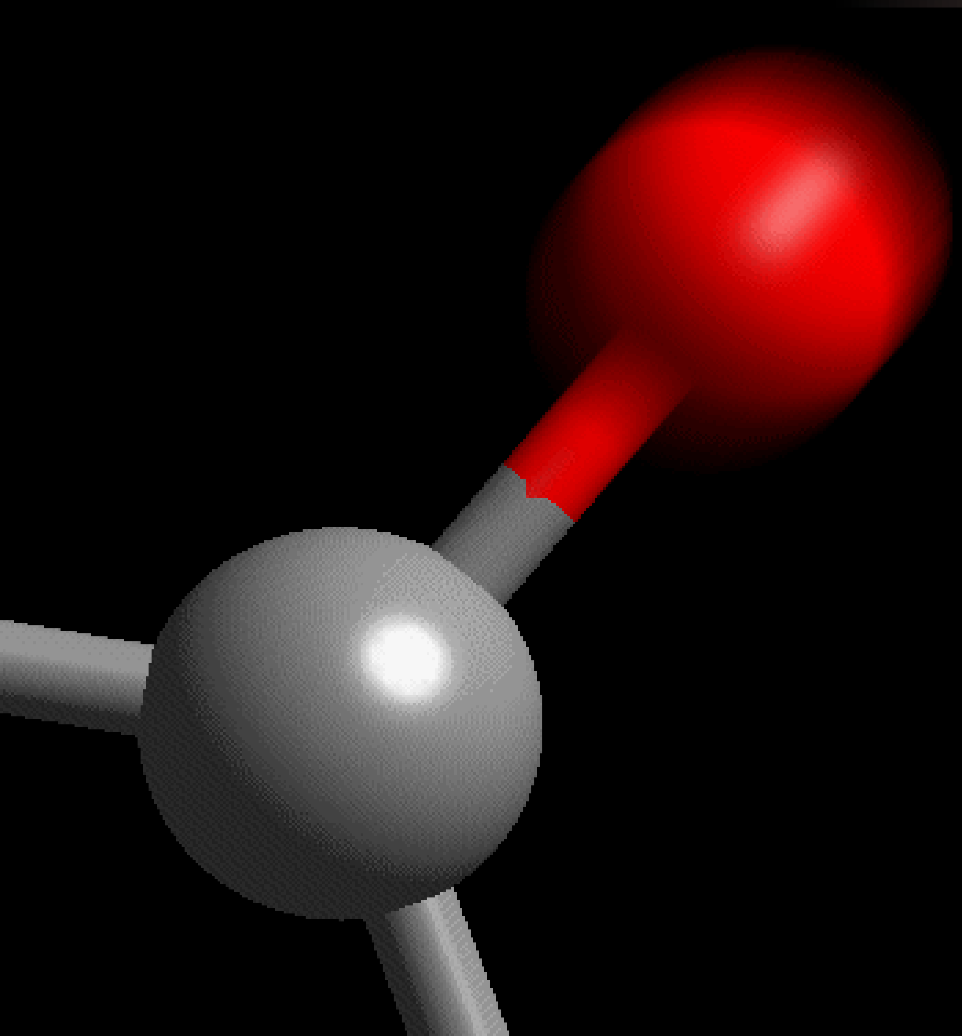

Neutrons for Science

# Neutrons



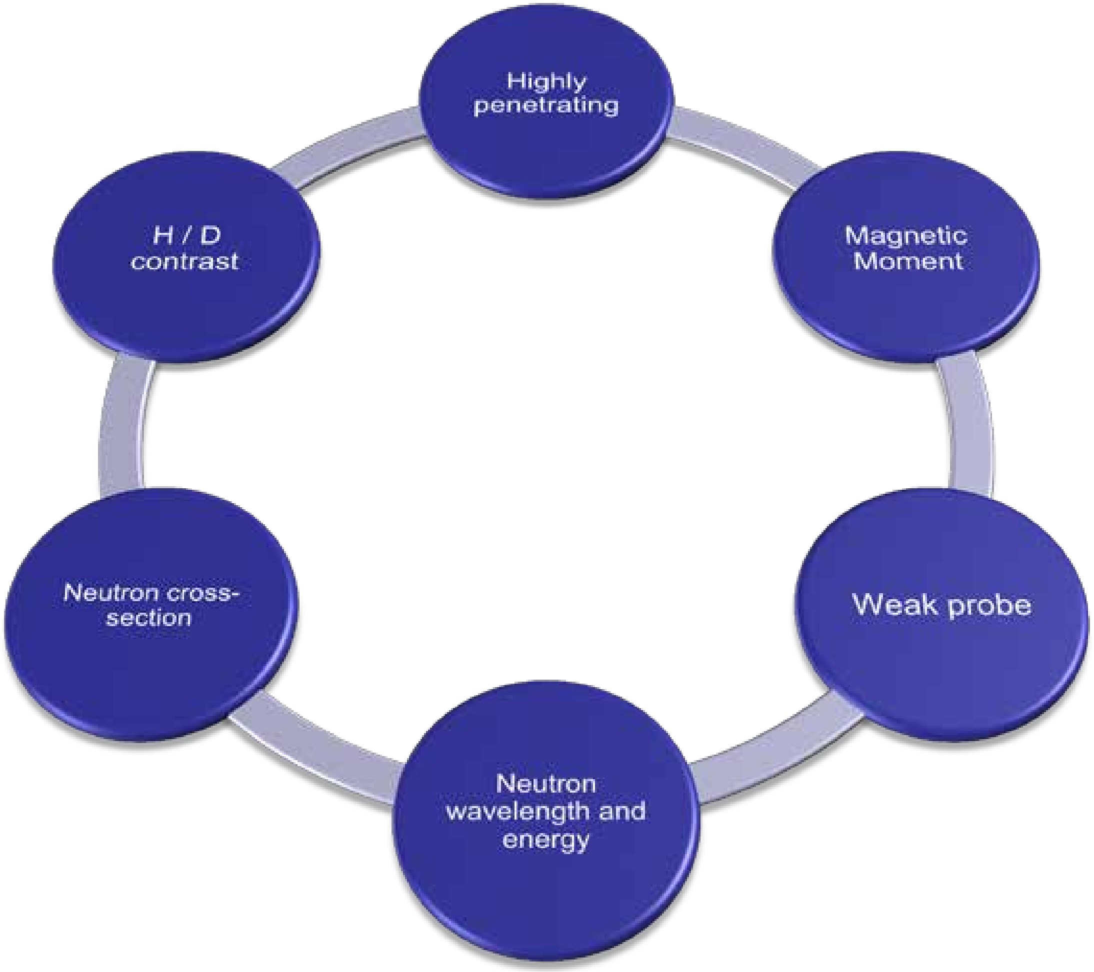
Where atoms are...

# Neutrons

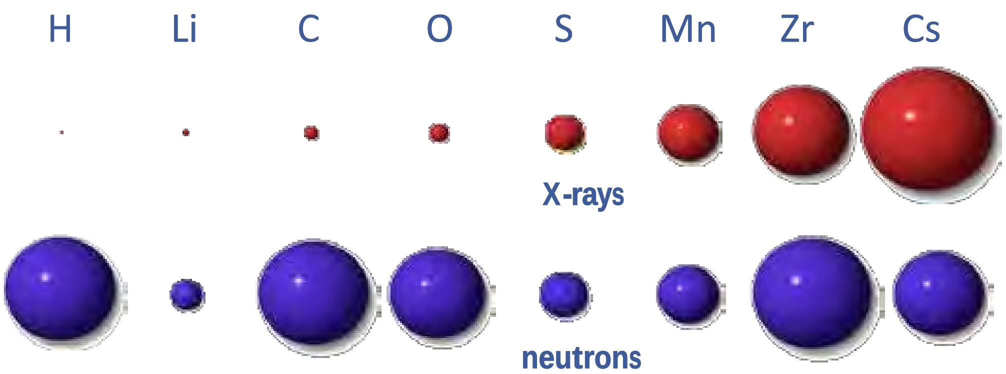


...and what they do

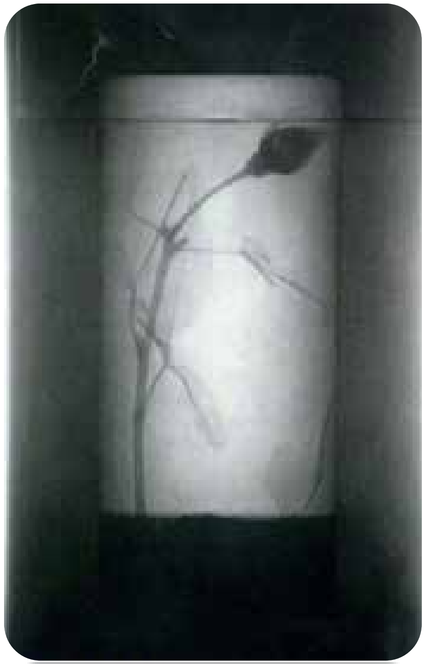
# Neutron
## Properties

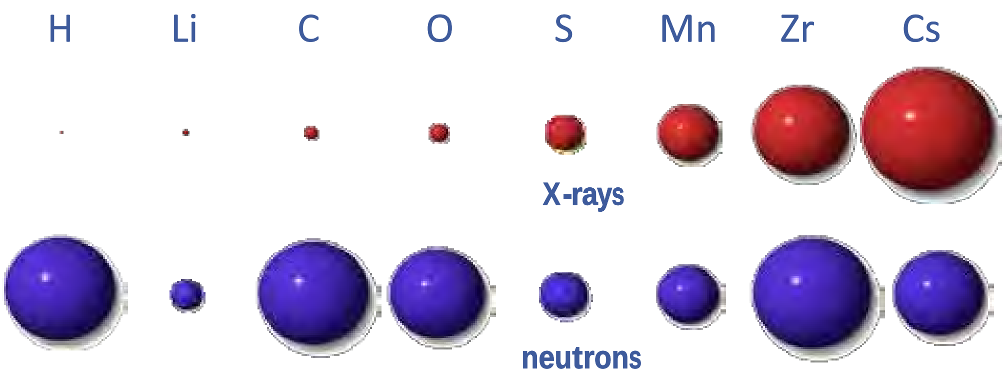


# Neutron
## Properties

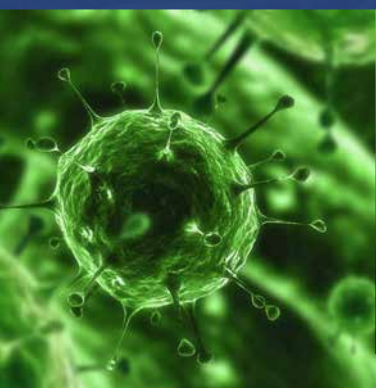
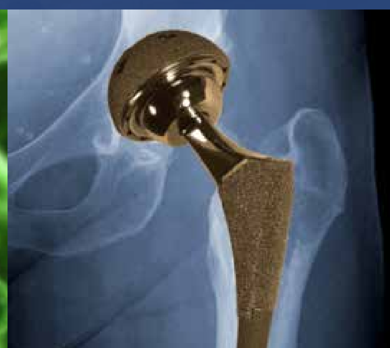


# Neutron
## Properties





# Spallation Neutrons



Accelerator Driven Neutron Source (Spallation)

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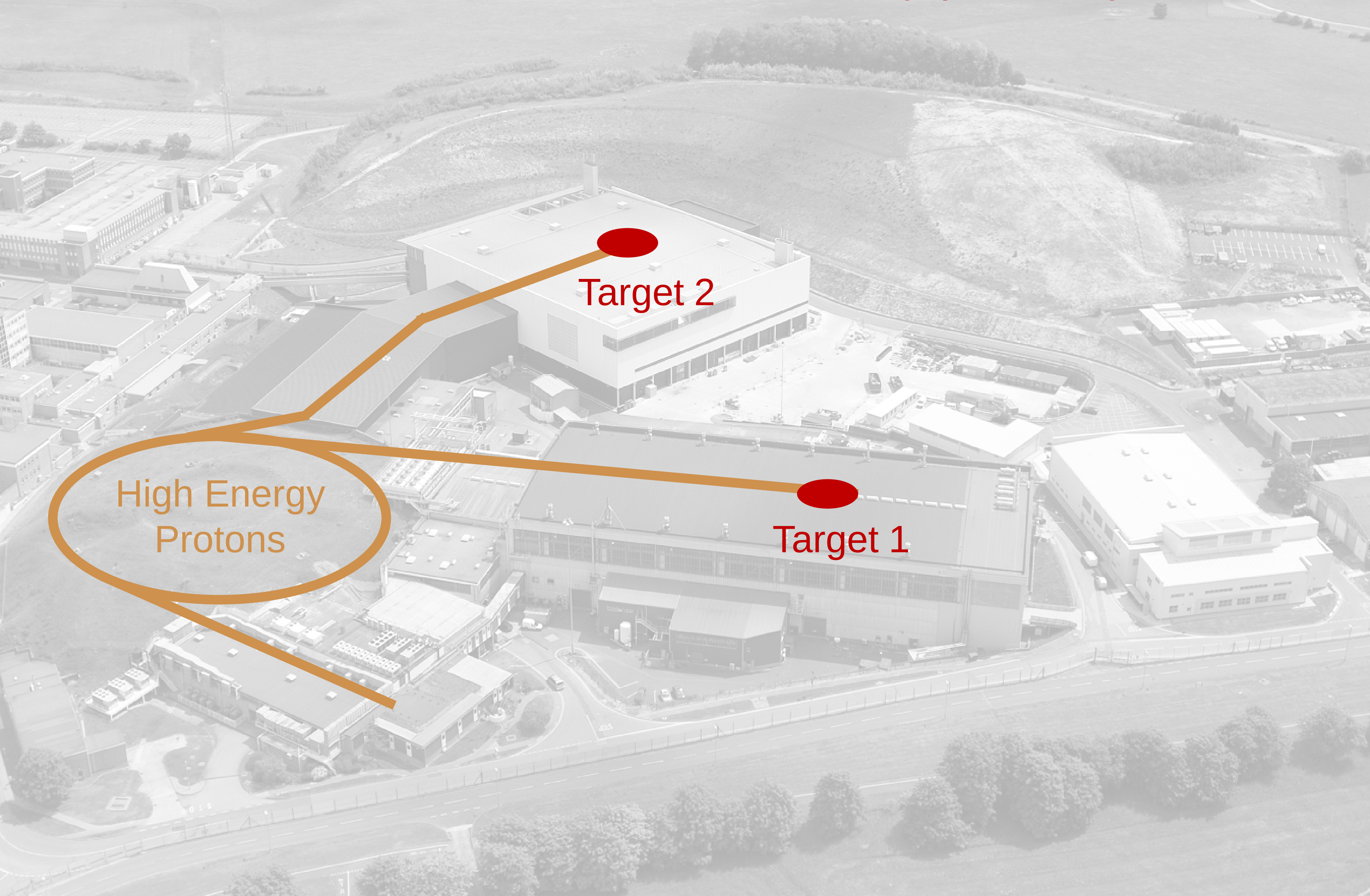
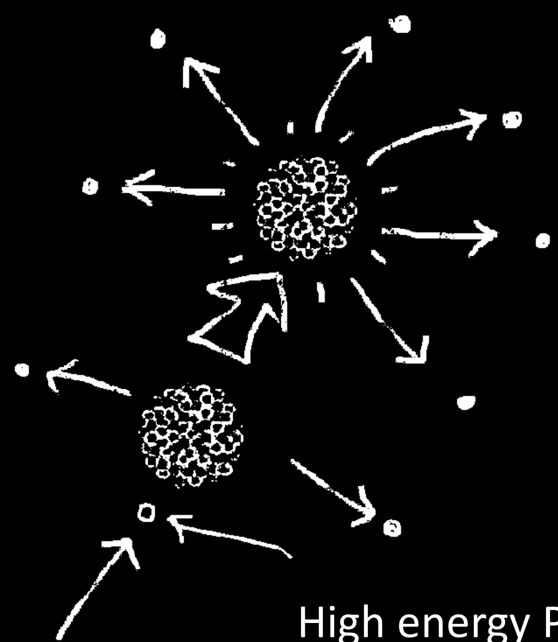
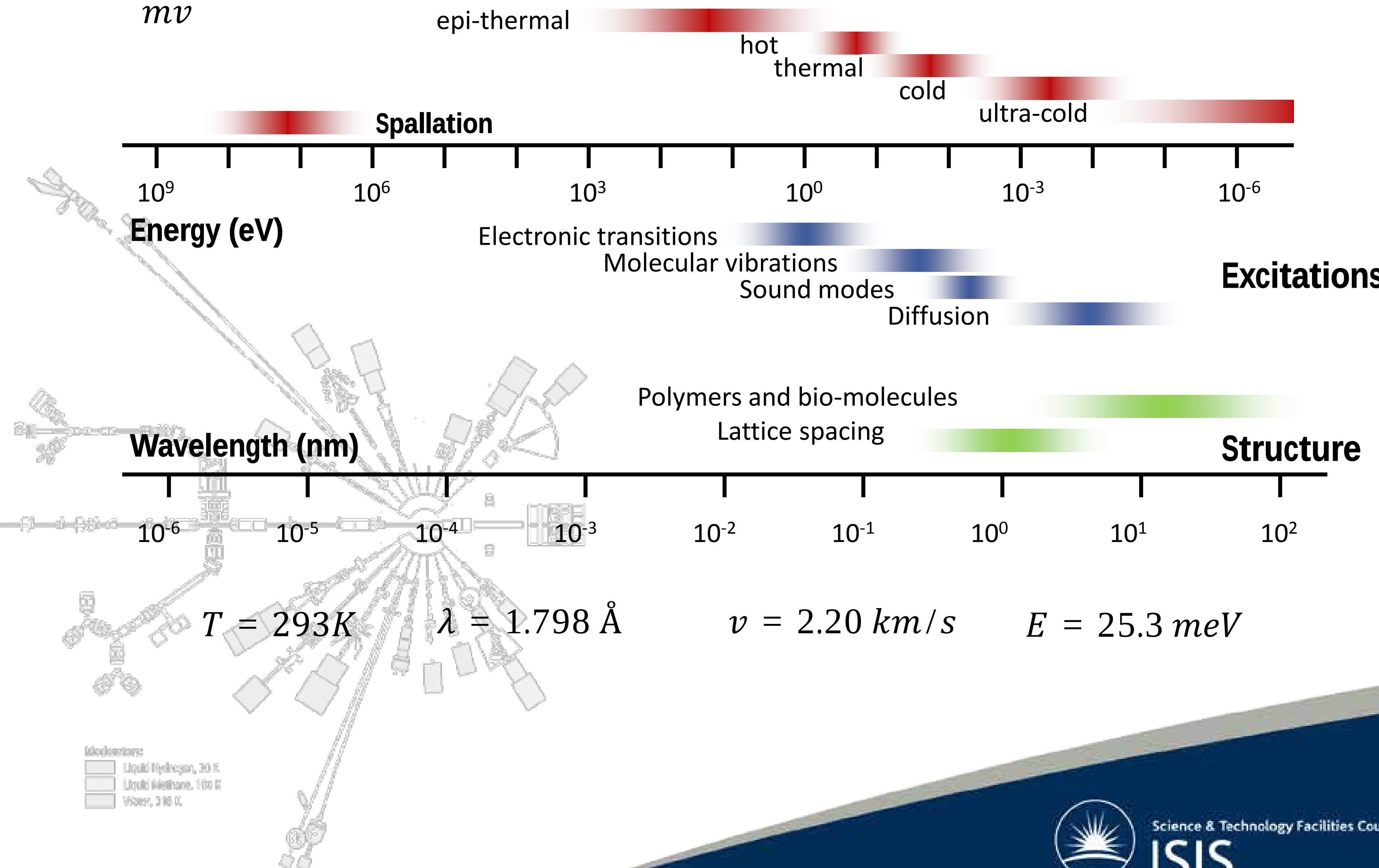





The collision of high energy protons with the tungsten nuclei releases neutrons

# Moderators

$$\lambda = \frac{h}{mv}$$




$T = 293K \quad \lambda = 1.798\ \text{Å} \quad v = 2.20\ km/s \quad E = 25.3\ meV$

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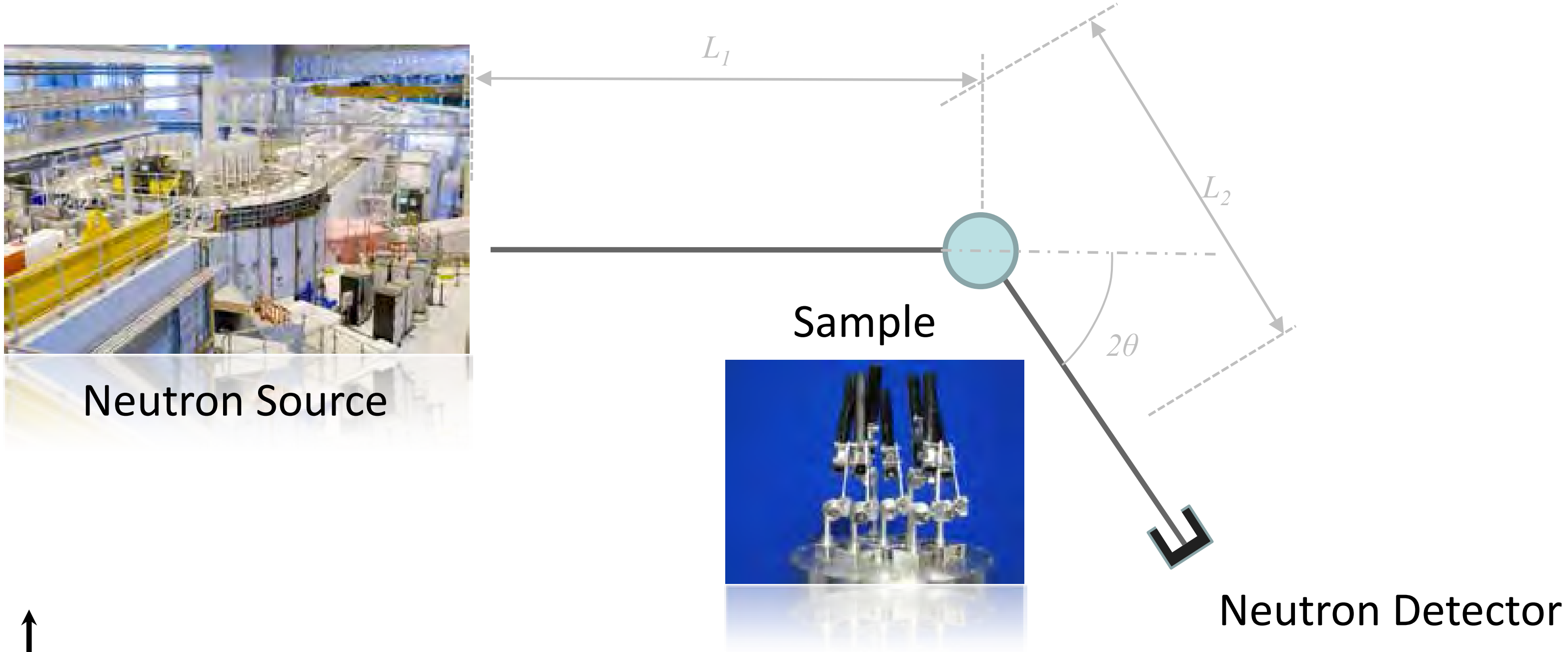


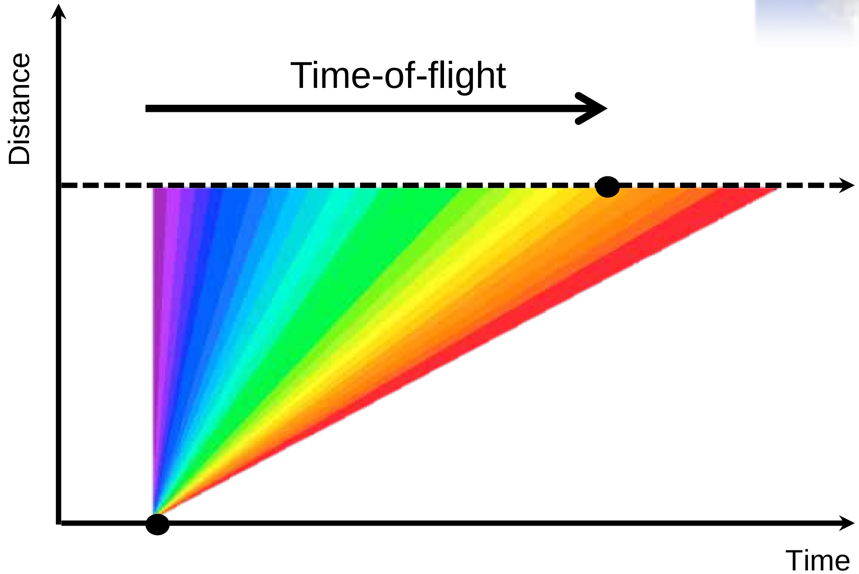


$$v = (L_1 + L_2)/t$$

$$E = \frac{1}{2}mv^2 \qquad \lambda = \frac{h}{mv} \qquad n\lambda = 2d\sin\theta$$

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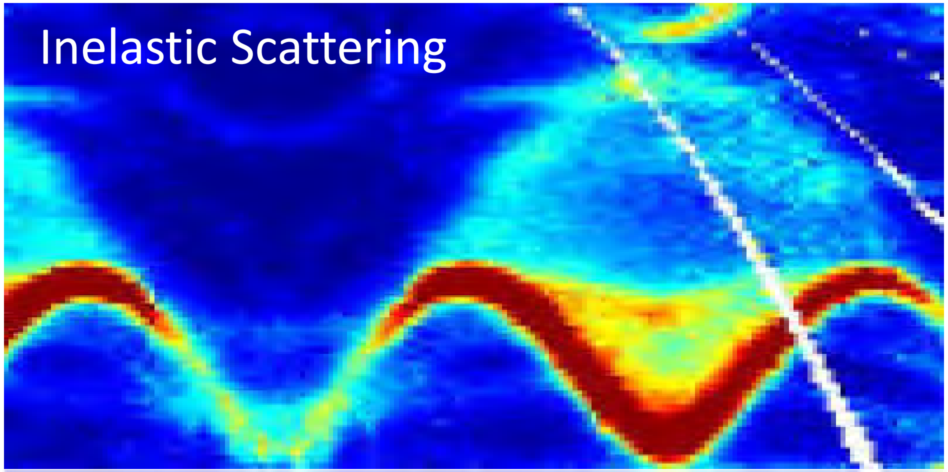
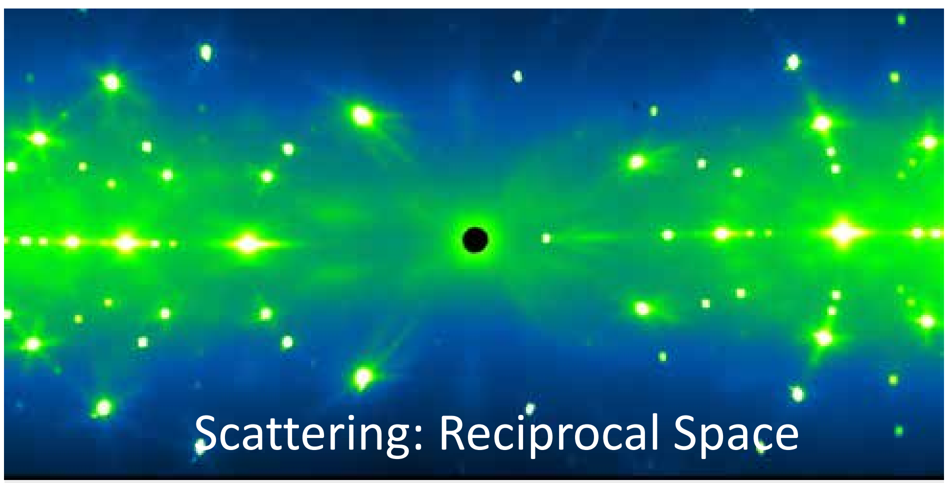
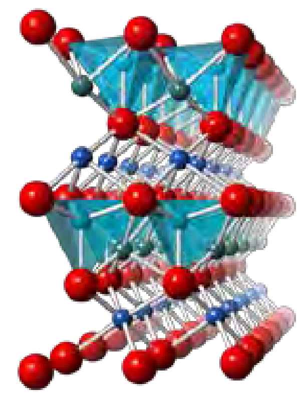

Inelastic Scattering


Dynamical Behaviour


Scattering: Reciprocal Space


Structure: Real Space

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## Spectroscopy
MAPS
LET
MARI
MERLIN
HET

## Molecular Spectroscopy
IRIS
OSIRIS
TOSCA
VESUVIO

## Engineering
ENGIN-X

## Large Scale Structures
SANS2D
OFFSPEC
POLREF
INTER
CRISP
SURF
LOQ

## Diffraction
HRPD
SXD
POLARIS
GEM
WISH
PEARL
INES

**30**

**Neutron and Muons Instruments**

## Muons
EMU
MuSR
HIFI
ARGUS

## Disordered Materials
SANDALS
NIMROD

## Target Station 2 – Phase 2 Instruments
IMAT
ZOOM
LARMOR
CHIPIR

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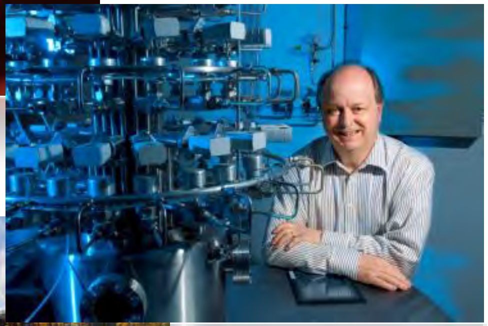
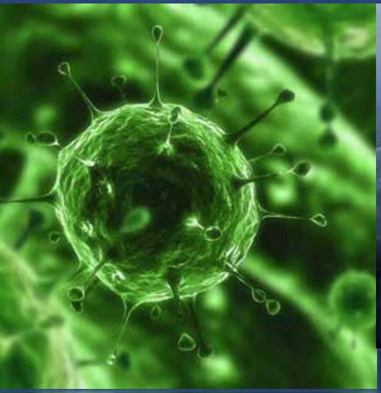
World leading expertise and instrumentation in the application of neutrons to condensed matter science

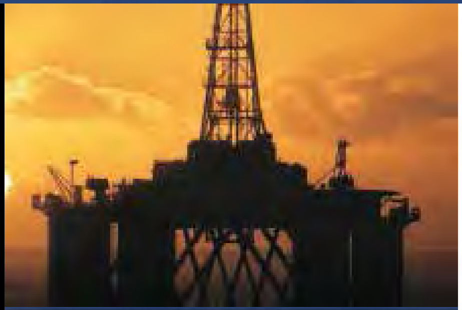



~ 2000 users/yr
~450 publications/yr
~ 800 experiments/yr
90% of UK Users 5/5* Departments

**Access Mechanisms**
- Direct access
- Rapid access
- Xpress
- Programme access
- Commercial
- ICRD scheme

# Neutron & Nanometers

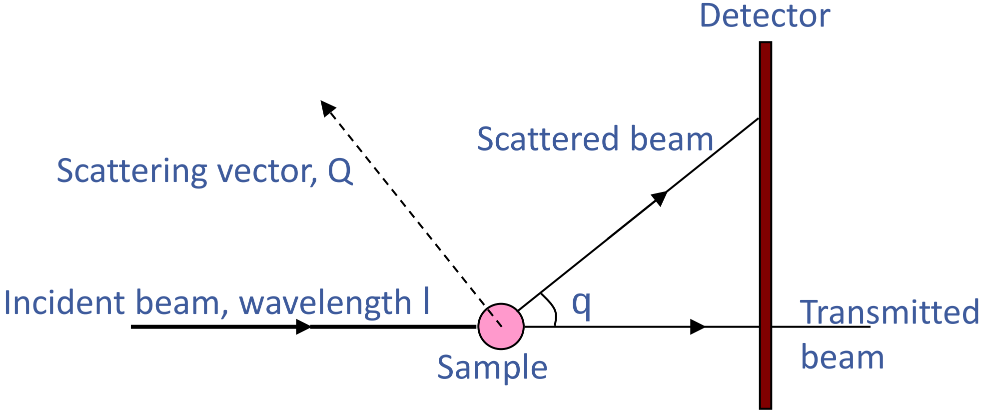




# Small-Angle Neutron Scattering (SANS)

Lengthscales probed range from 10s to 100s nm. They 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:

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

*Q* (size) range is varied by altering *q* or *l*

Allows the bulk properties of a material:

- Size
- Polydispersity
- Structure
- Particle Interaction

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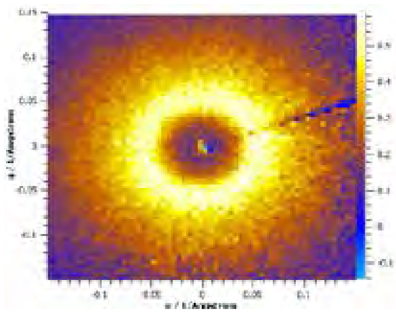
# ‘Typical’ Experiment

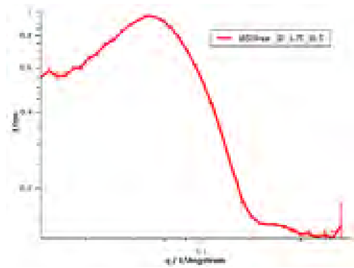
The 2D SANS patterns obtained are often radially averaged to given an ‘intensity’, I(*Q*), vs. *Q* plot

2D

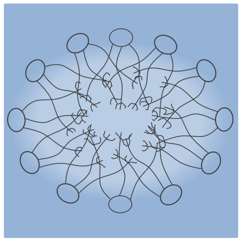


Radially average

1D



Modelling



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:

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

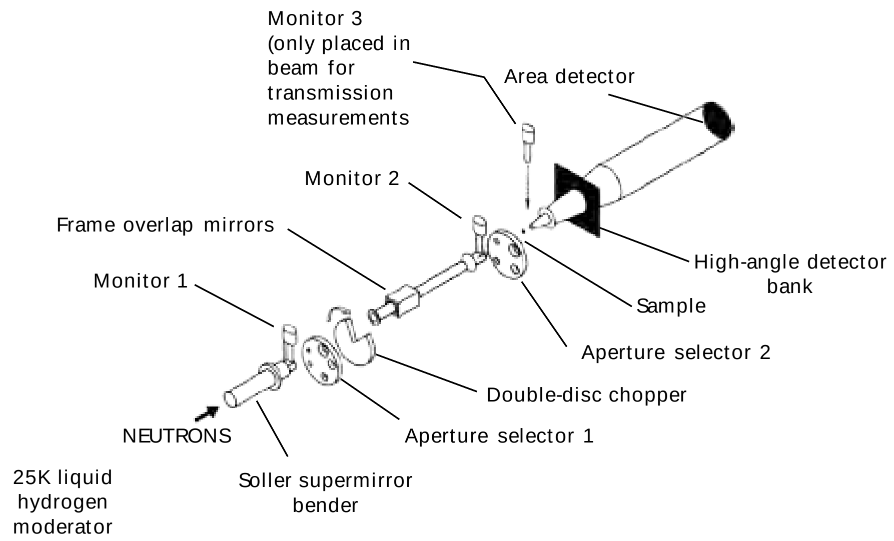
Form factor: intra-particle information
- size and shape of particle

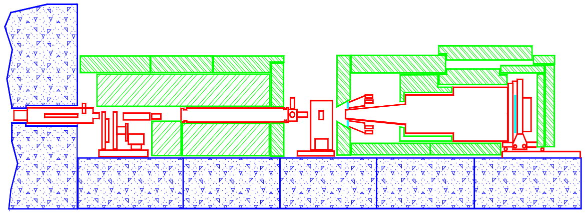
Structure factor: inter-particle information. Depends on the type of interactions in the system. S(*Q*) = 1 for dilute dispersions

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

# The 1st - Loq

- LOQ was the 1st ISIS SANS instrument and is positioned on the 50 Hz first target station, TS-1
- This instrument has demonstrated the power of SANS at a pulsed source
- Using a fixed sample - main detector distance of 4 m and neutron wavelengths of 2 to 10 Å at 25 Hz a Q-range of 0.007 – 0.3 $Å^{-1}$ is accessible
- This Q-range can be extended to 1.4 $Å^{-1}$ by employing the wide-angle detector bank
- Extensive sample environments available
- Sample area is the 'pit' which is accessible via a ladder
- Crane available

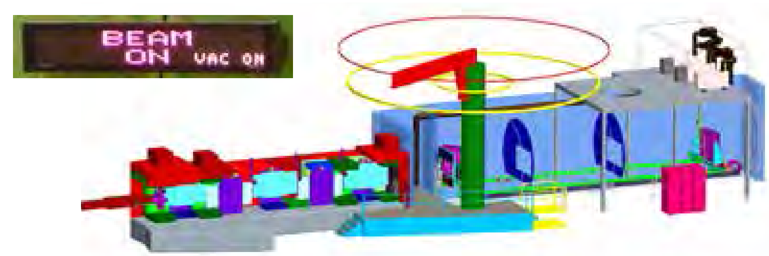


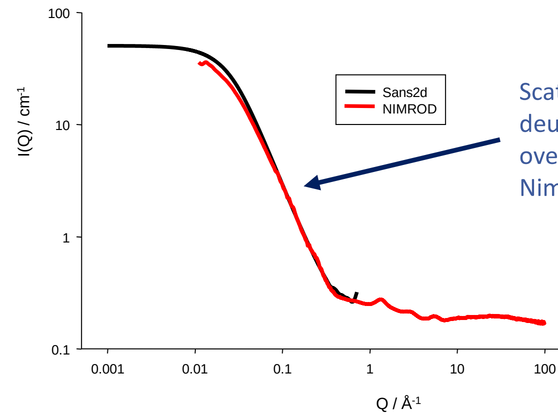



For further info contact Steve King: stephen.king@stfc.ac.uk

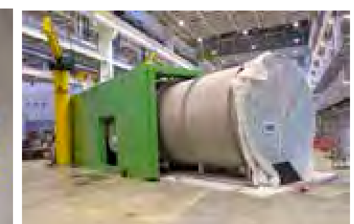
# The present - Sans2d

- Sans2d is the first SANS instrument to be built on the optimized TS-2
- Operational since 2009
- 2 x $1m^2$ movable detectors provide a uniquely wide simultaneous Q range at good resolution: Q = 0.001 to 3 $Å^{-1}$, $\lambda$ = 1.75 to 17 Å
- Detector 1 moves +/- 0.3 m sideways, to 12 m from sample. Detector 2 may be offset to 1.4 m sideways in 3.25 m diam vacuum tank and rotates to face sample
- Combining the low background and high flux of Sans2d has allowed weakly scattering samples to be studied more efficiently
- Crane available – shared with Zoom




Scattering from partially deuterated polymer shows good overlap between Sans2d and Nimrod



For further info contact Sarah Rogers: sarah.rogers@stfc.ac.uk

# Larmor: Flexible Spin-Echo for Larmor Precession

- Shutter opened on 20th March 2014
- SANS is available now. The spin-echo setup is being developed with the NWO and TU-Delft over the next year
- Polarized Beam with Analysis
- Wavelengths 0.5 – 13 Å gives SANS Q range of 0.004 - 1.6 $Å^{-1}$
- Length scales of ~20 nm to 20 mm can be studied using SESANS
- Large block house but detector can move 90° on air pads
- Huber sample stack allows for accurate sample alignment
- Crane available

TU Delft Delft University of Technology

For further info contact Rob Dalgliesh: robert.dalgliesh@stfc.ac.uk

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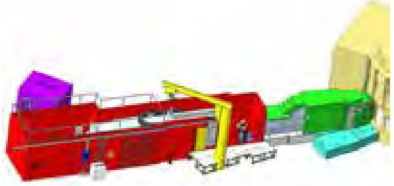
# Future 2 - Zoom

- Currently under construction
- Planned open shutter date is November 2016
- SANS will be available from day 1. Polarized and focusing SANS will be delivered later
- Detector can move to 6 or 9 m from sample
- Vacuum tank can also move 3 m for focusing optics installation
- Wavelengths 1.75 – 16.5 Å gives Q range of 0.002 - 1 $Å^{-1}$
- Focusing will allow ultra low Q of 0.0003 $Å^{-1}$ ~ 2 mm
- Huber sample stack allows for accurate sample alignment
- Crane available – shared with Sans2d



For further information contact Ann Terry: ann.terry@stfc.ac.uk

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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

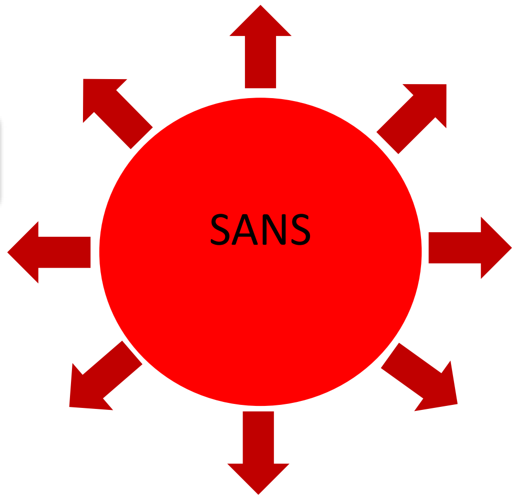
Defects in metals

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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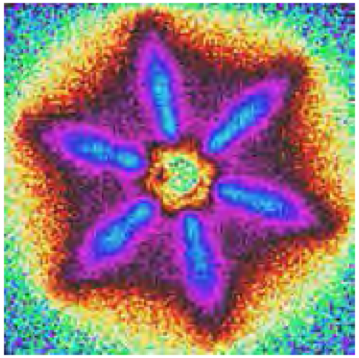
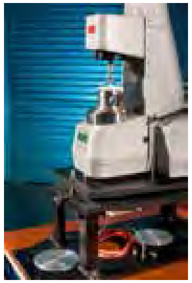
# The Sample Environment

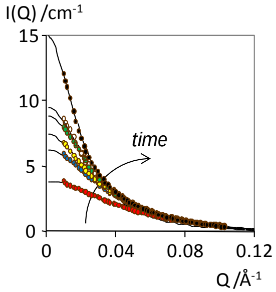
Extensive available sample environments allow a broad range of science to be studied via SANS at ISIS.

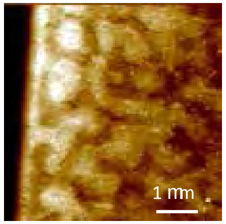




(a)

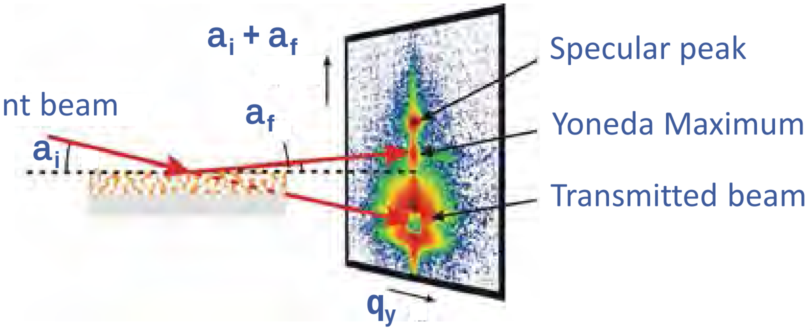
(b)



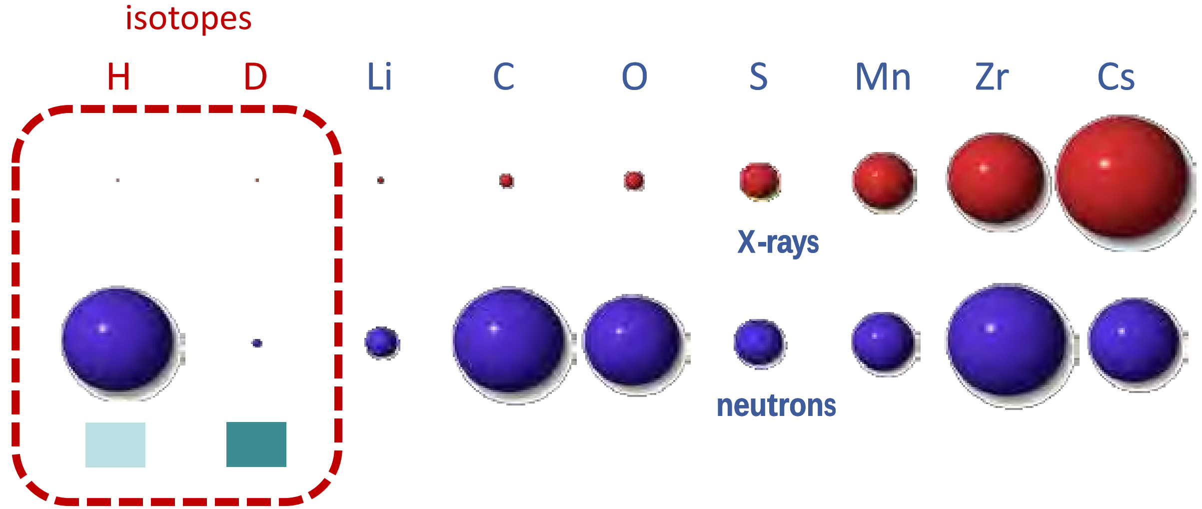



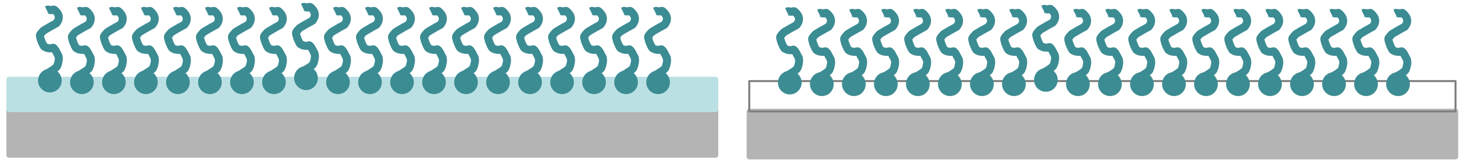

Sample environment includes:

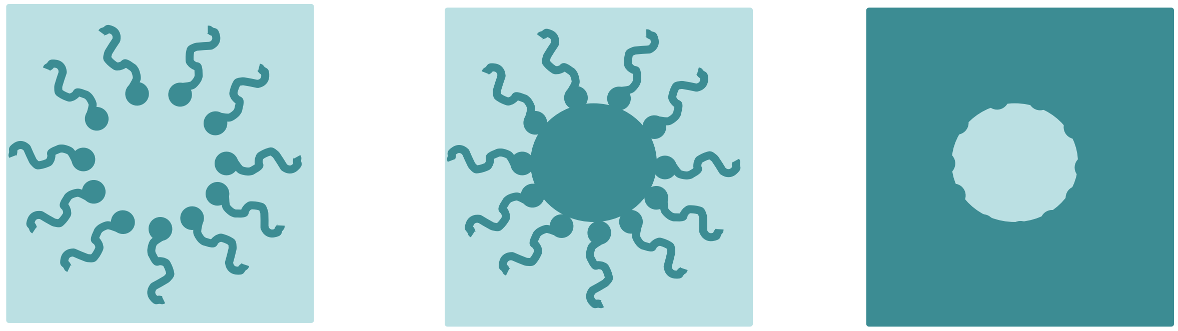
- Standard ISIS cryostats, furnaces and magnets
- Sample changer with temperature control
- Linkham stages for advanced temperature control
- Rheometer and shear cells
- Pressure cell – 600 bar with stirring.  Predominantly used with $CO_2$
- T-jump cell – study non-equilibrium phases
- *In-situ* DLS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



Nuclear Interaction Changes

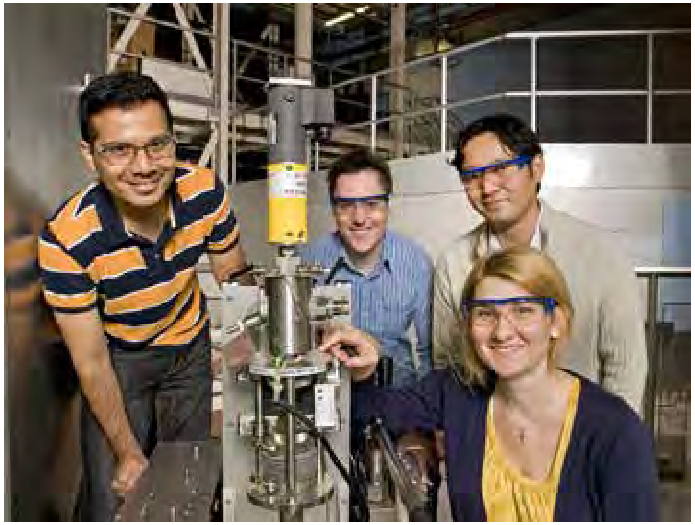


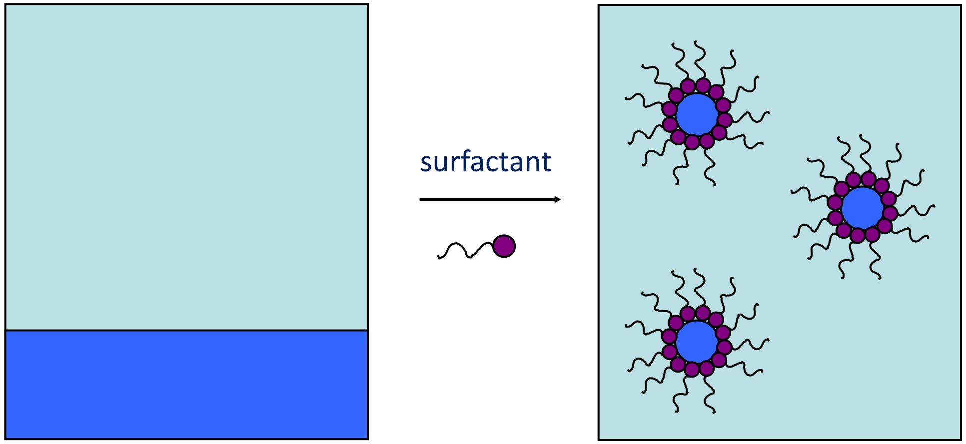





Collaboration between University of Bristol and the ISIS SANS team studying the modification of the physico-chemical properties of sc-$CO_2$ with surfactants for use in enhanced oil recovery. Low viscosity of $CO_2$ promotes fingering through porous media rather than a uniform sweep.

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



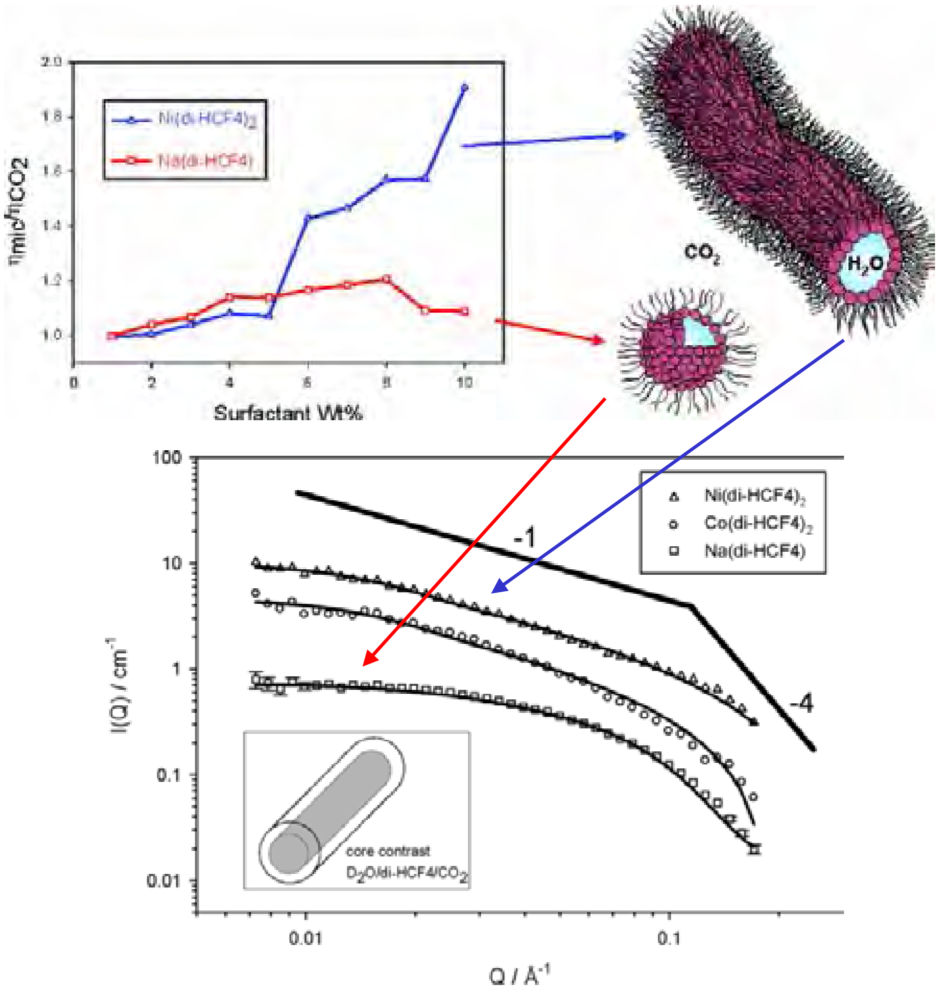


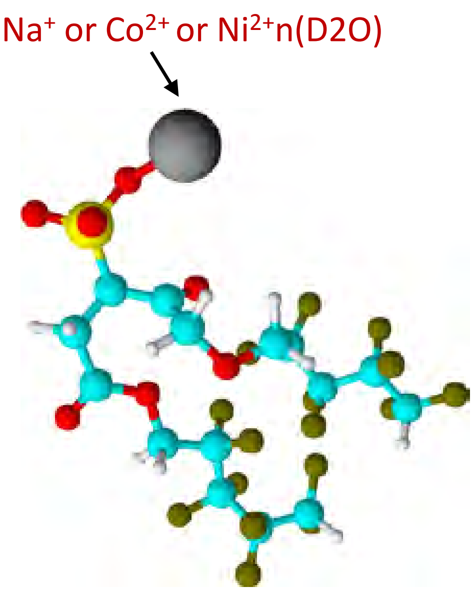

## Why Neutron and Small Angle Scattering?

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 $CO_2$

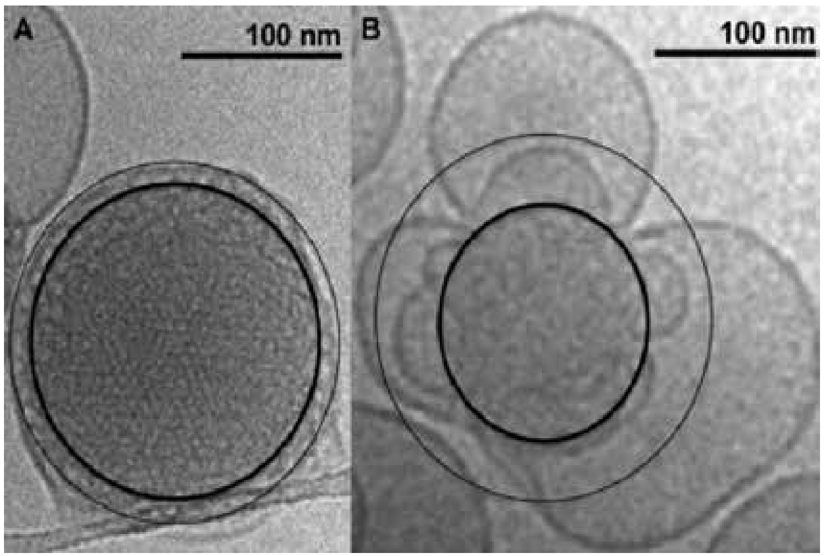
Why? Neutrons have the answer! Micelle shape changes from spherical to wormlike as counterion changes from $Na^+$ to $Co^{2+}$ or $Ni^{2+}$

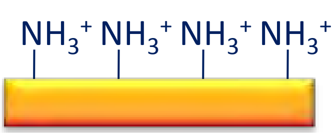
Langmuir 2010, 26(1), 83-88

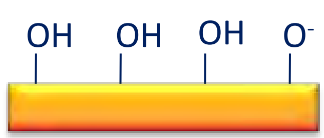
Science & Technology Facilities Council ISIS

Collaboration between Lund University and the ISIS LSS team studying reversed lipid liquid crystalline nanoparticles as drug delivery vehicles

These systems are stabilised by low fractions of the surfactant P80. Location of the P80 within the particle largely control their function




**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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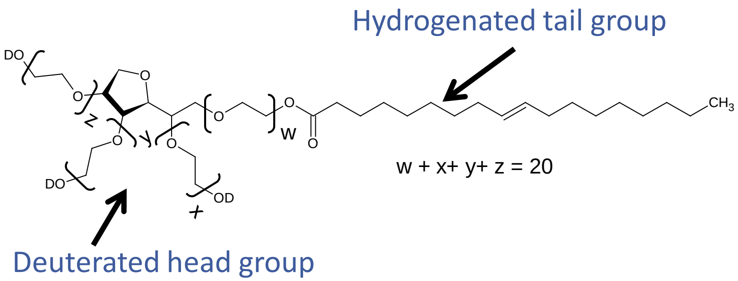
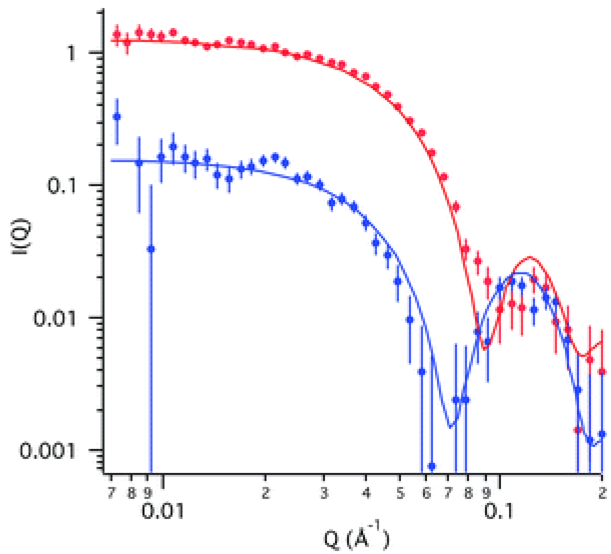
## Results

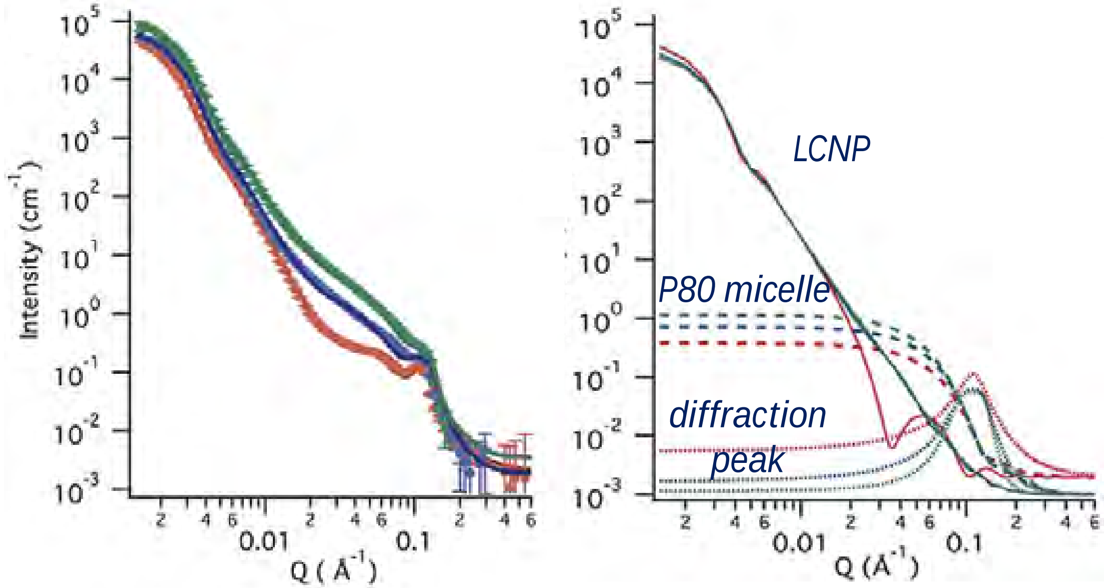
SANS reveals the core-shell structure of the d-P80 micelles




SANS profiles in P80 micelles in $H_2O$ (red) and 1:1 $H_2O$:$D_2O$ (blue)

SANS profiles with modelled contributions shown




## Results

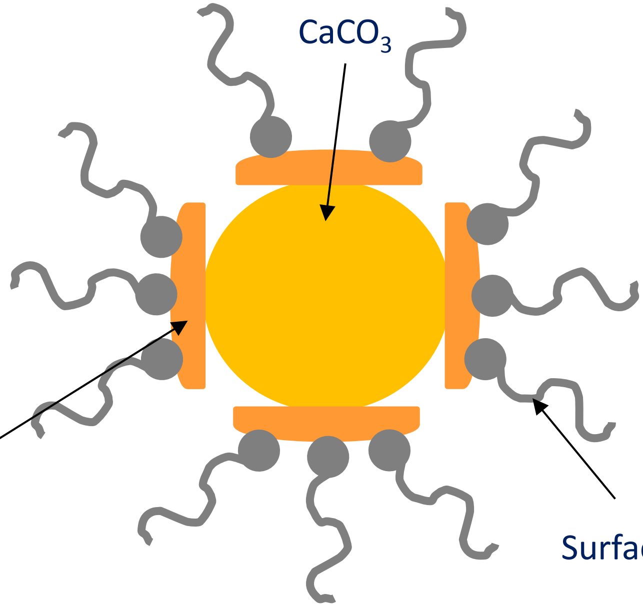
CV-SANS, CV-NR and SAXS have been used to determine a detailed picture of the internal structure of the LCNPs, where the P80 is located within these structures and how the particles are stabilised

Soft Matter 2015, 11, 1140

Science & Technology Facilities Council ISIS

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?**




**Why Neutron and Small Angle Scattering?**

H/D Contrast provides direct view of water

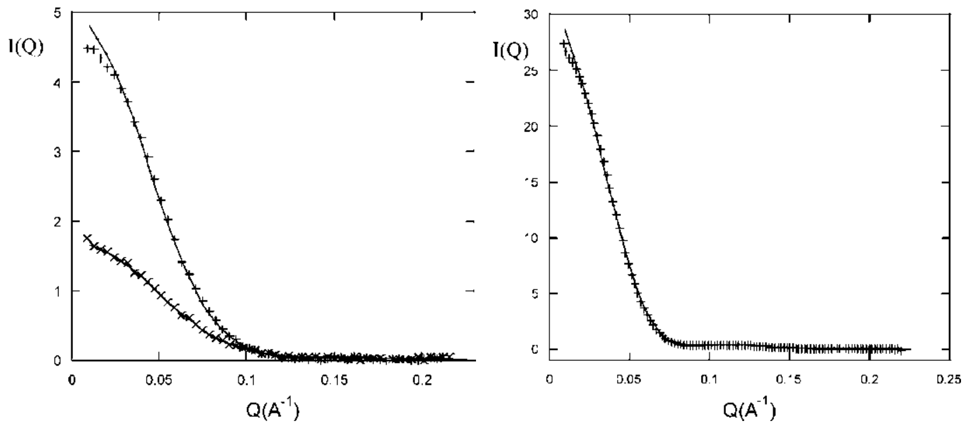
Length-scales being probes are ideal for SANS

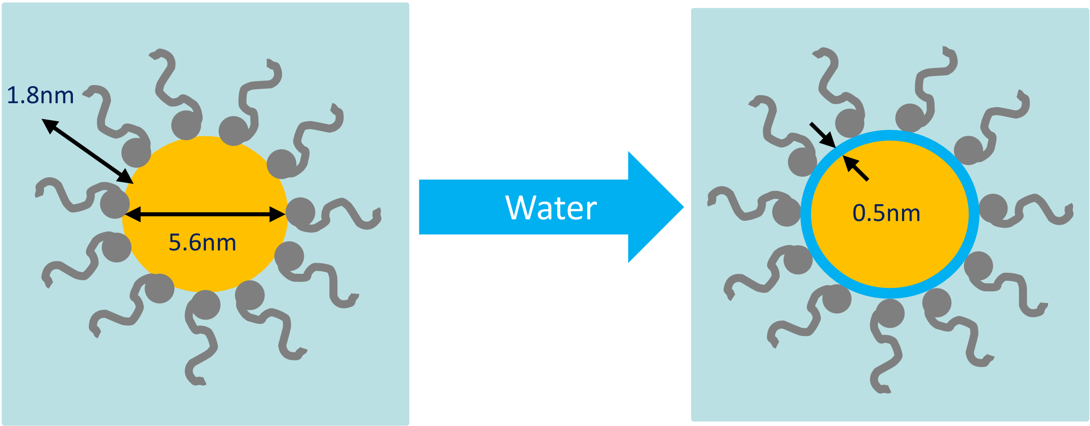
## Results

$CaCO_3$ 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

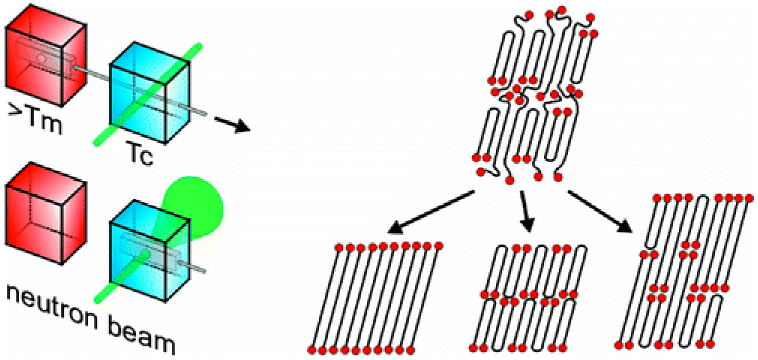


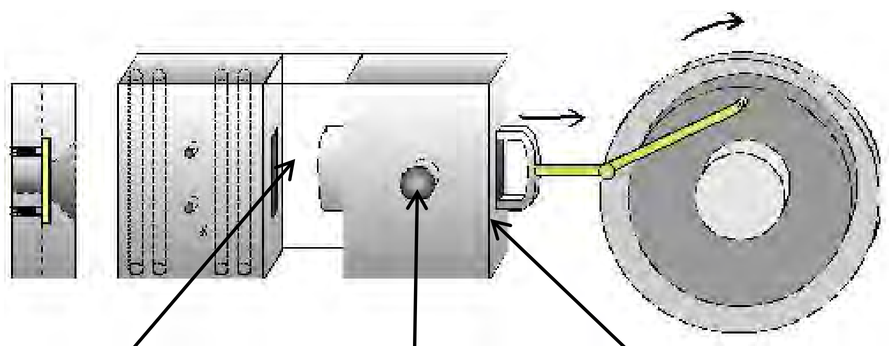




Langmuir 2008, 24, 3807 - 3813

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?

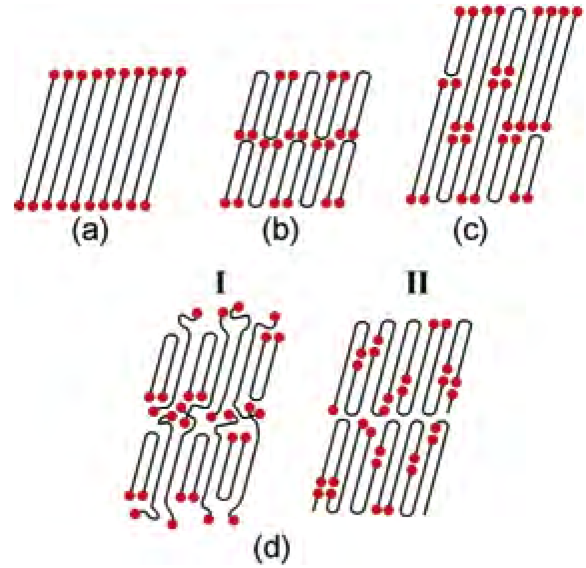
SAS is a powerful technique for studying lamellar structures

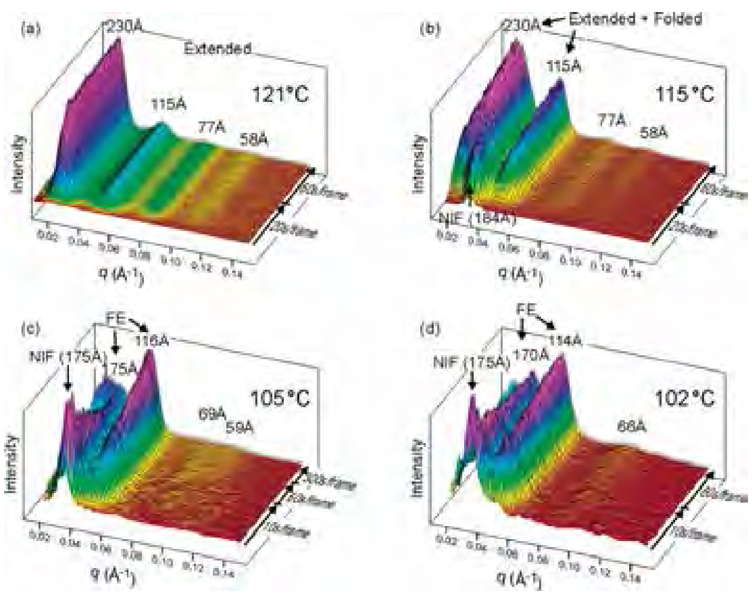
Using selectively deuterated segments, SANS can provide information on the location and state of order of such segments

## 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

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Thanks for listening!

Questions?

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