Small-angle and ultra-small-angle neutron scattering

An introduction

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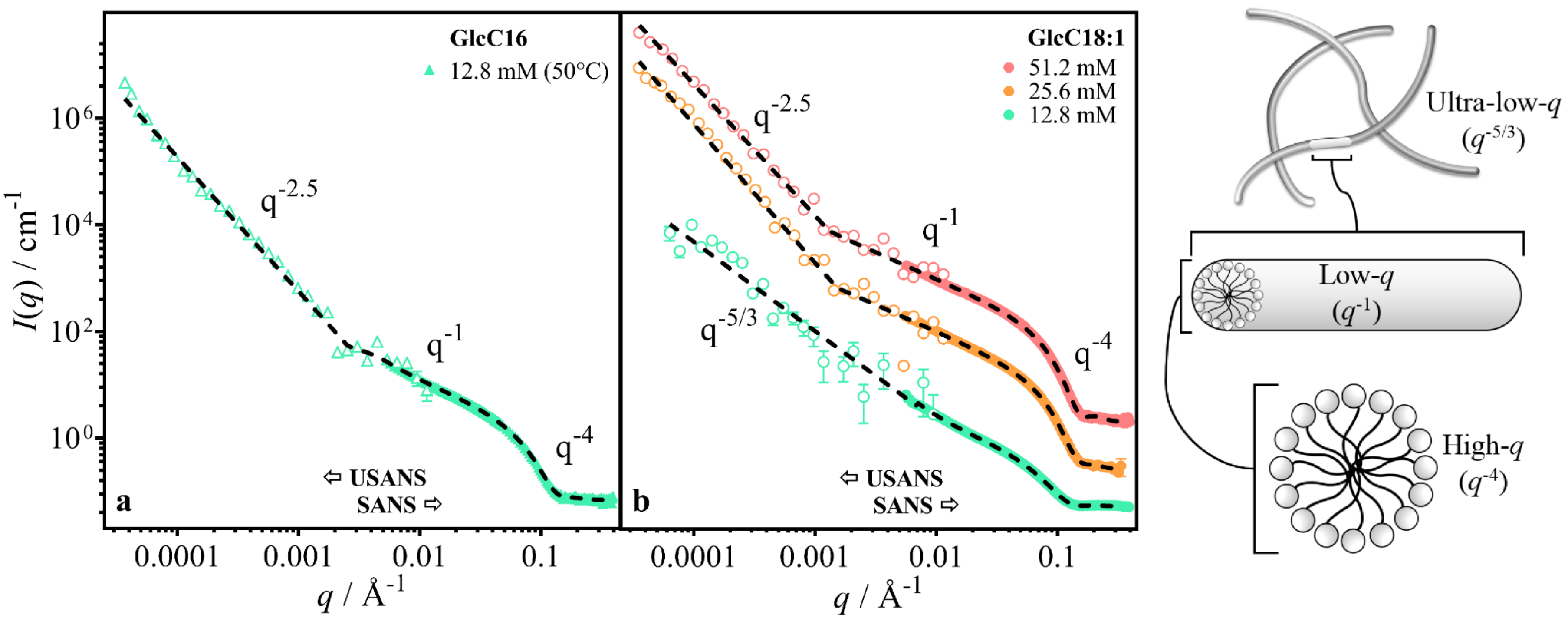
Advanced Scattering and Microscopy School

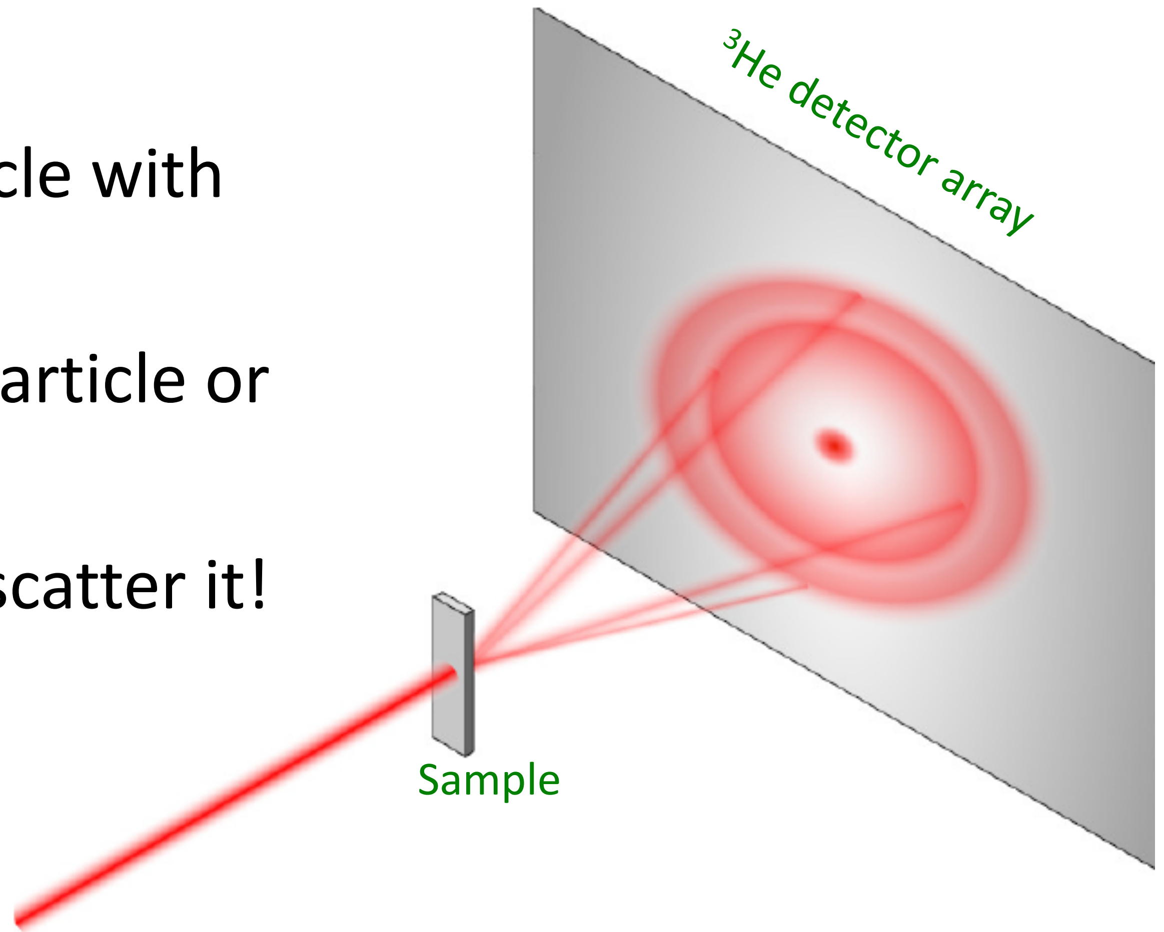
SM2 Meeting, Monash University,
13th July 2022

Part 1 - What does it do?



Part 2 - neutrons

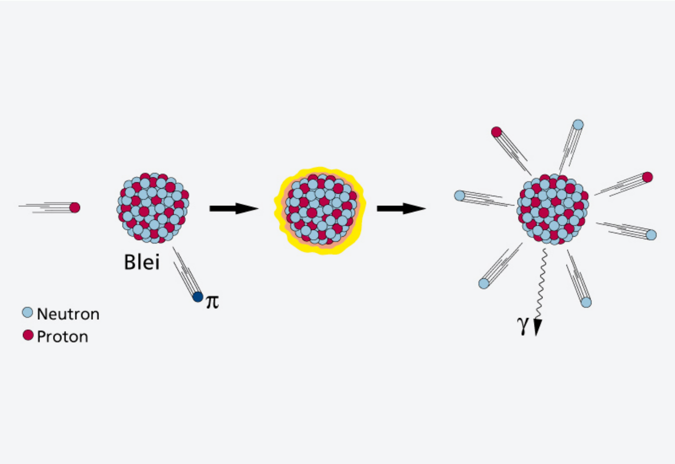
- Subatomic particle with no charge
- Can behave as particle or wave (duality)
- Therefore I can scatter it!

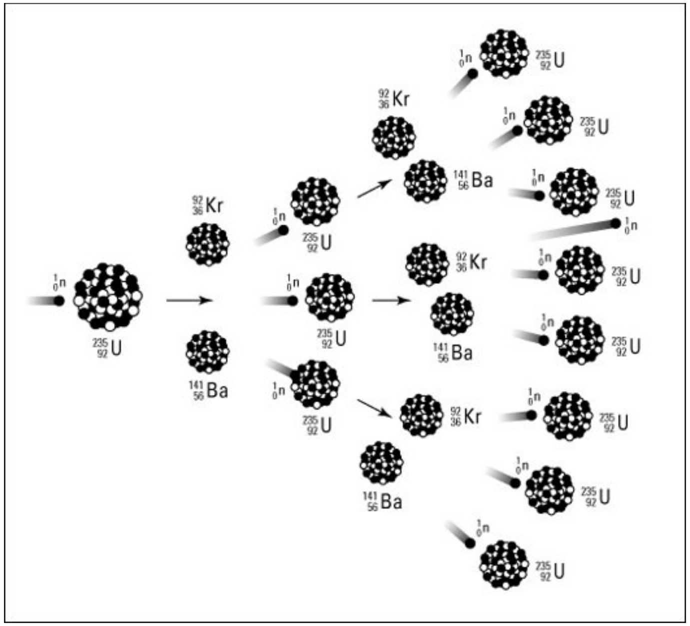


Part 2 - neutrons

- How to make neutrons (in large enough quantities to be useful):
- 1) Spallation
  Proton beam is accelerated and fired at heavy metal target in pulses, dislodging neutrons
- 2) Nuclear fission
  Neutrons released during decay of unstable heavy nucleus, causing chain reaction within radioactive sample

  Both are used in research to generate neutrons for scattering experiments





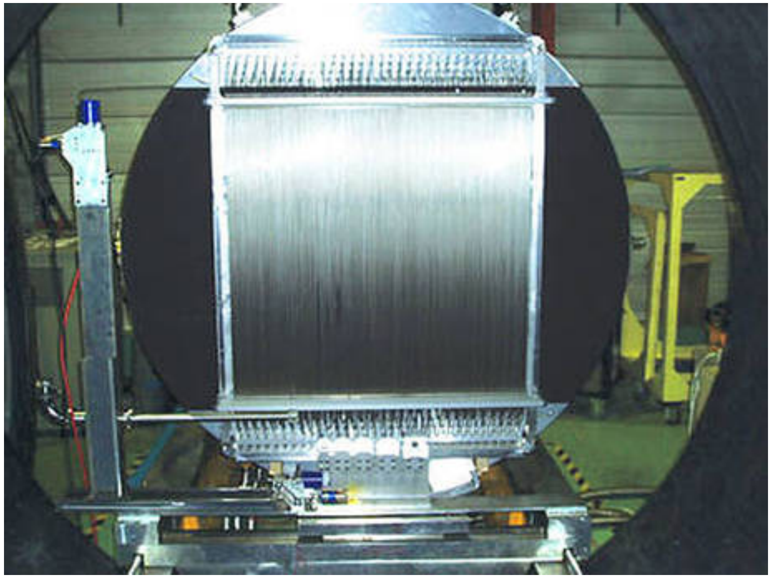
Part 2 - neutrons

The 2 after ^{3}He refers to the proton number, not the number of nuclei!!

- How to detect scattered neutrons?
- Current best technology is the $^{3}He_{2}$ element detector
- Array of tubes filled with $^{3}He_{2}$ and CF_{3} gases
- Incident neutron causes the reaction:

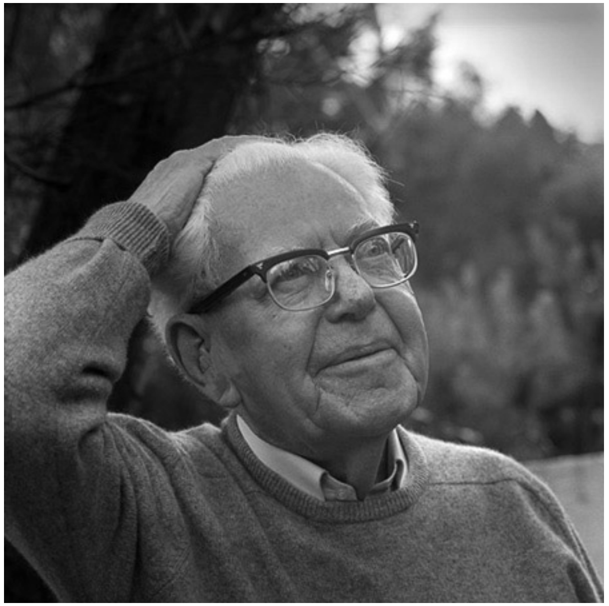
$$^{1}n_{0} + {}^{3}He_{2} \rightarrow {}^{1}H_{1} + {}^{3}H_{1} + 765\text{ keV}$$

- The proton and triton are released with high kinetic energy, and ionise the CF_{3} gas. These CF_{3}^{+} ions are detected capacitively and thus turned to a current.



Part 2 - neutrons

- **Sir Marcus Laurence Elwin Oliphant**
- Born in 1901 in Adelaide
- Eminent nuclear physicist and humanitarian
- **Discovered ^{3}He** whilst bombarding deuterons with more deuterons
- This also happened to be **the first demonstration of nuclear fusion**
- Worked on Manhattan project in WW2
- Founding Professor of ANU
- Died in 2000 (age 98) in Canberra



Part 2 - neutrons

- ISIS, near Oxford, UK
- Spallation source
- LOQ – ToF instrument

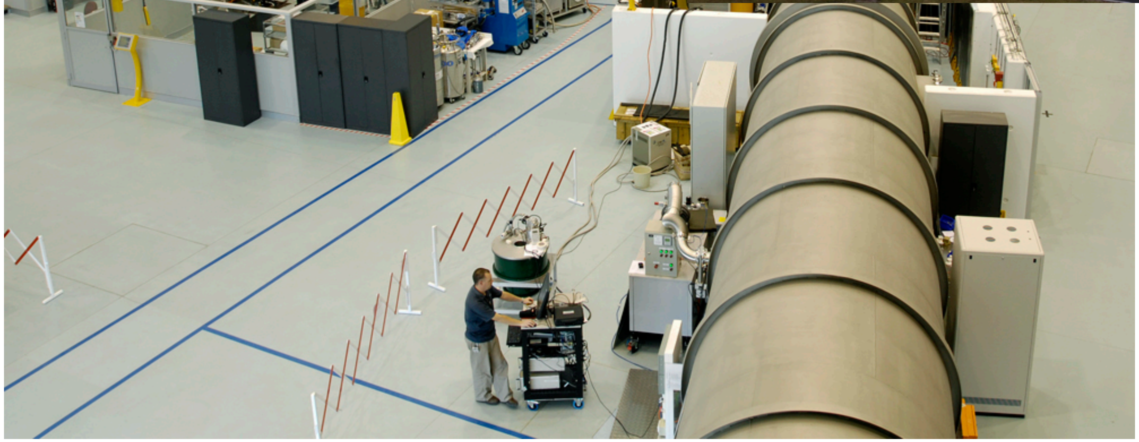
Part 2 - neutrons

NEUTRONS FOR SCIENCE®
Institut Laue-Langevin

- ILL, Grenoble, France
- Reactor source
- D22 – small-angle diffractometer

Part 2 - neutrons

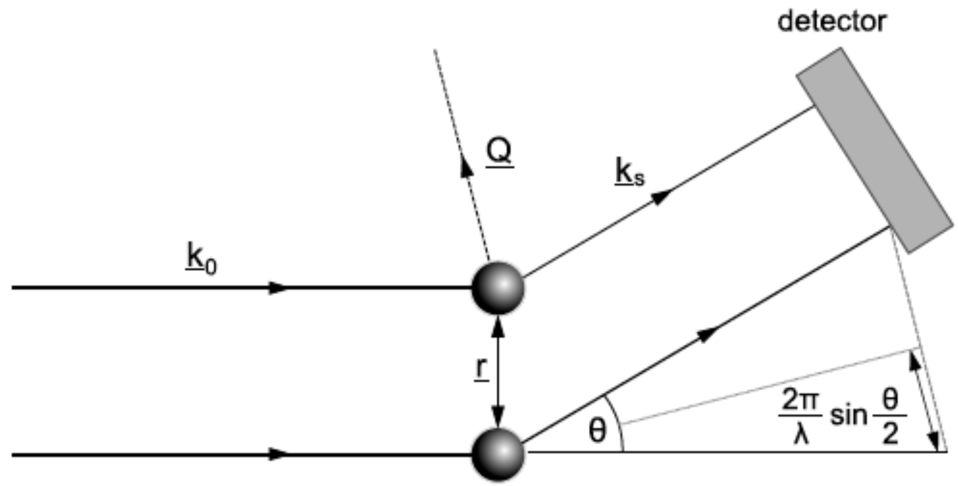
- Bragg Institute (Lucas Heights, nr Sydney)



- Reactor source
- Neutron science and medical isotope production

Part 2 - neutrons

- Neutrons are scattered by nuclei of atoms
- Scattered intensity as a function of angle gives information on spatial arrangement and interactions between scatterers
- Size range probed 1-100 nm

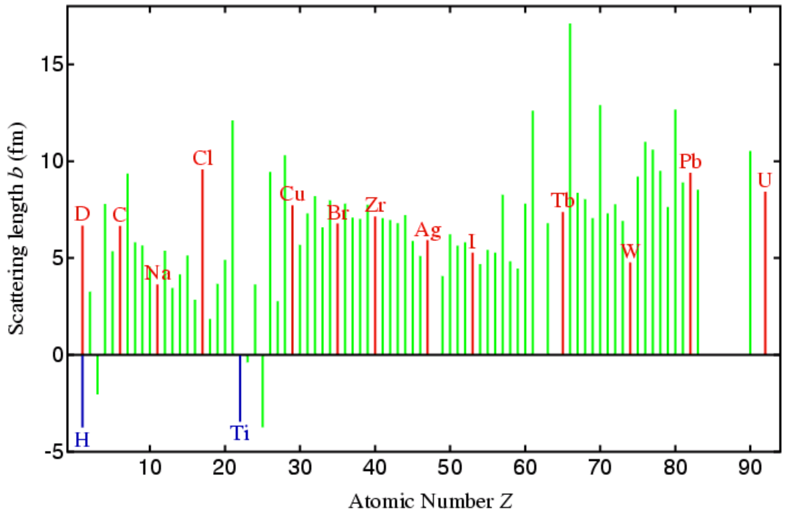


$$Q = \frac{4\pi}{\lambda} sin\frac{\theta}{2}$$

- Key quantities are scattered intensity *I*, and scattering vector, *Q*
- Think of *Q* as inversely proportional to size: small *Q* = big stuff, big *Q* = small stuff.

Part 2 - neutrons

- Q: If neutrons are scattered by nuclei of atoms, where does the contrast come from? (c.f. refractive index for light)
- A: Different nuclei scatter differently, because of a property called scattering length
- This varies randomly with atomic number:



Nucleus	$b/(10^{-12}$ cm)	Compound	$\rho/(10^{10}$ cm^{-2})
^{1}H	-0.374	H_2O	-0.560
^{2}H (D)	0.667	^2H_2O (D_2O)	6.356
^{12}C	0.665	toluene	0.941
^{16}O	0.580	D-toluene	5.662
^{14}N	0.936	TX-100	0.519
^{32}S	0.285	AOT	0.542

- Most important point: H and D scatter really differently, so deuteration provides contrast.

Part 2 - neutrons

- In general, a contrast (difference in scattering length density) of less than $1.5\text{x}10^{10}$ cm^{-2} is poor contrast.

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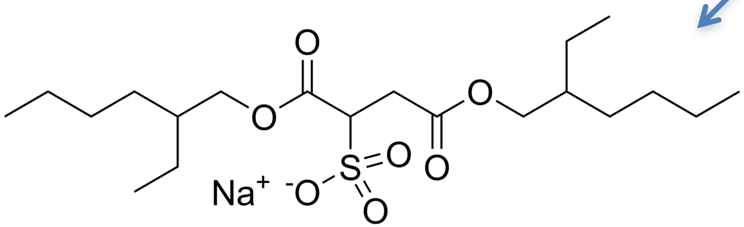
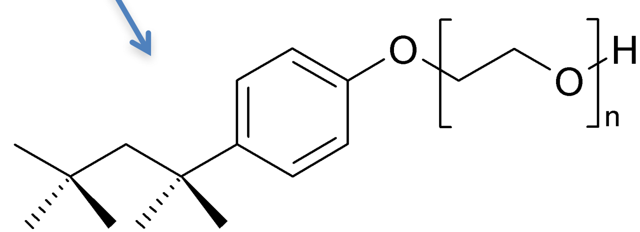
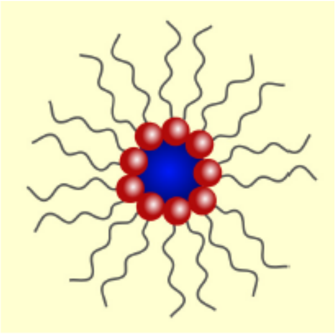




Part 2 - neutrons

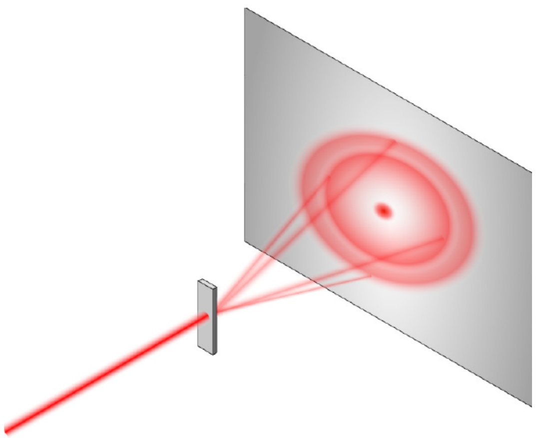
- Take an emulsion droplet (water, surrounded by stabiliser in oil)
- Or a (nano)particle with a shell of polymer

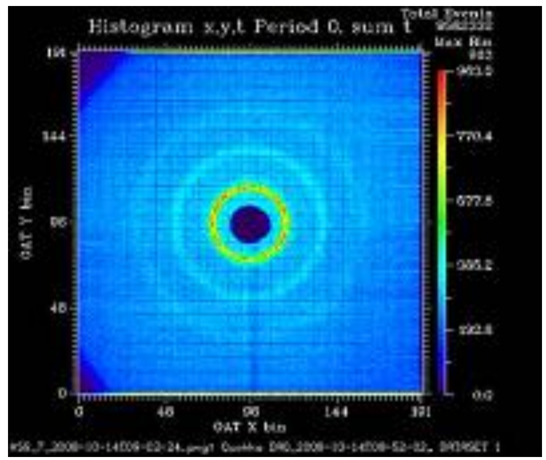


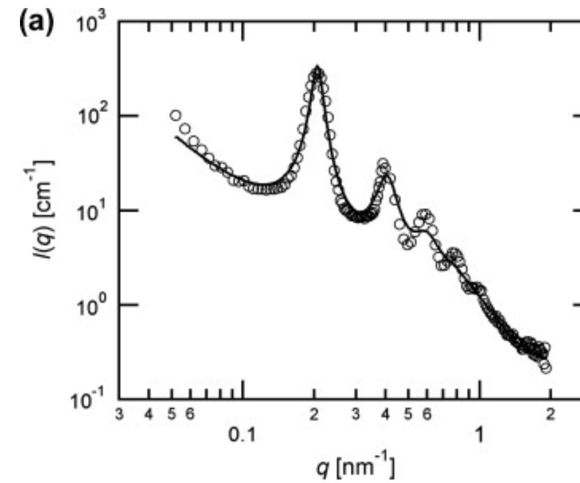
core contrast: $\rho_1 \neq \rho_2 = \rho_3$ shell contrast: $\rho_1 = \rho_3 \neq \rho_2$ drop contrast: $\rho_1 = \rho_2 \neq \rho_3$

Part 2 - neutrons

- Rationalising detector patterns: radial averaging
- Angle on detector calculated by trig.



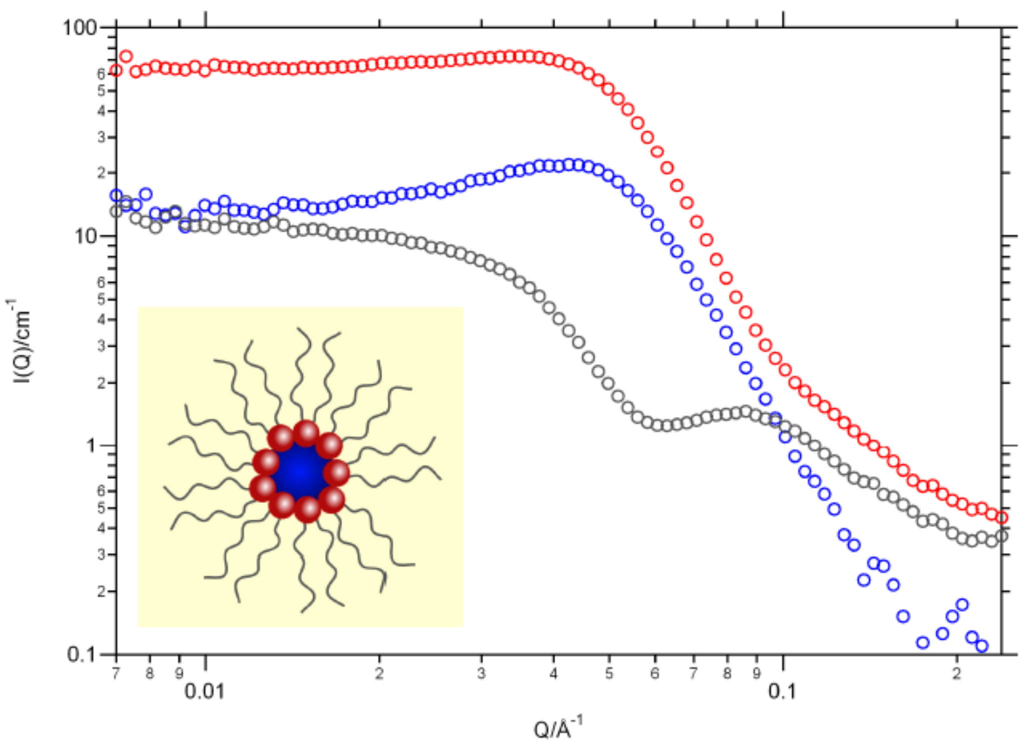


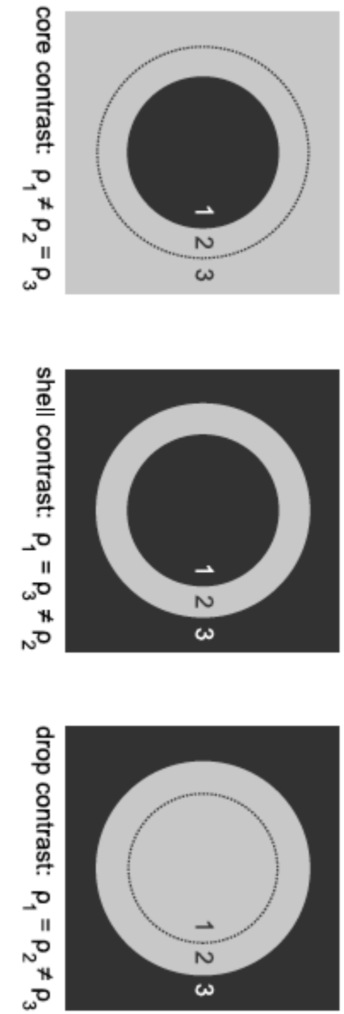


- Angle then converted to *q*, and intensity *I* plotted against *q*.
- Usually use log/log scales to make things easier to see.

Part 2 - neutrons

- Take an emulsion droplet (water, surrounded by stabiliser in oil)





core **shell** **drop**

Part 2 - neutrons

- Nice data! But what does it tell us?
- Need to apply a quantitative model

- Global expression $$I(Q) = \phi_p \cdot (\rho_p - \rho_s)^2 \cdot V_p \cdot P(Q,R) \cdot S(Q) + B_{inc}$$
- Form of a sphere $$P(Q,R) = \left[\frac{3(\sin(QR) - QR \cdot \cos(QR))}{(QR)^3}\right]^2$$
- Form of a core-shell sphere $$P(Q,r) = \frac{16\pi^2}{9}\left[(\rho_h - \rho_s)3r_d^3\left(\frac{\sin(Qr_d) - Qr_d\cos(Qr_d)}{(Qr_d)^3}\right) - 3r_c^3\left(\frac{\sin(Qr_c) - Qr_c\cos(Qr_c)}{(Qr_c)^3}\right)\right]^2 + \left[(\rho_c - \rho_s)3r_c^3\left(\frac{\sin(Qr_c) - Qr_c\cos(Qr_c)}{(Qr_c)^3}\right)\right]^2$$
- Structure factor $$S(Q) = 1 + \left[\frac{N_p k_B T \chi}{1 + Q^2\xi^2}\right] \qquad S(Q) = \frac{1}{[1 - N_p] \cdot f(r_d, \phi_p)}$$

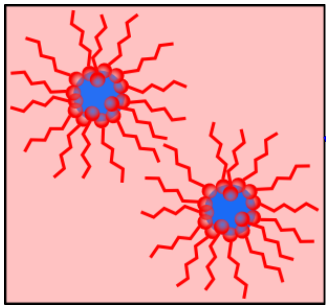
Part 2 - neutrons

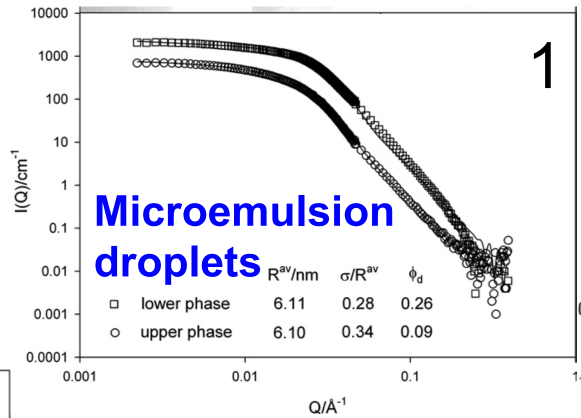
- Things I can learn from neutron scattering:
  - Size of objects
  - Shape (sphere, ellipsoid, rod, fractal, worm, sheet…)
  - Charge
  - Volume fraction
  - Interaction potential/pair potential
  - Porosity
  - Large scale structuring
  - Etc…..

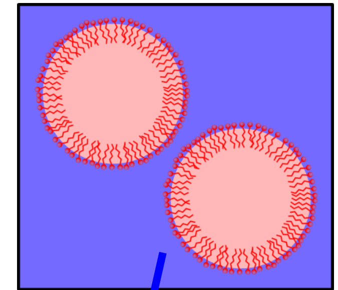
  - With careful experimental design, I can learn almost anything I want about hard and soft structures from 1-100(00) nm!

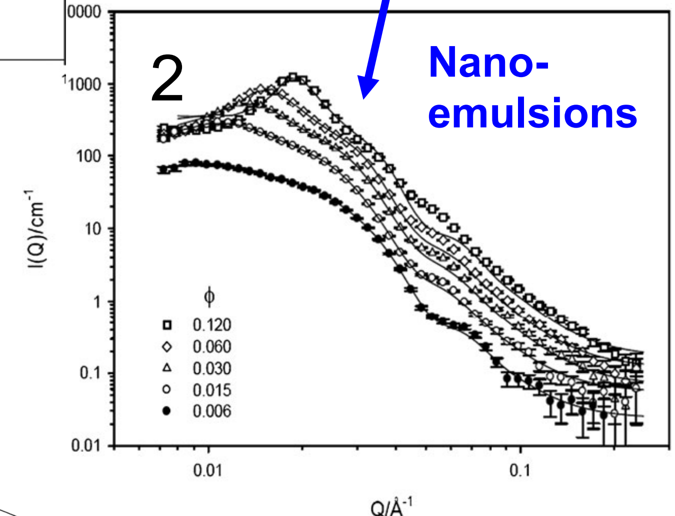
MANY YEARS AGO…

1. *Soft Matter* **5** (2009) 78
2. *PCCP* **11** (2009) 9772
3. *Soft Matter* **5** (2009) 2125
4. *JCIS* **344** (2010) 447

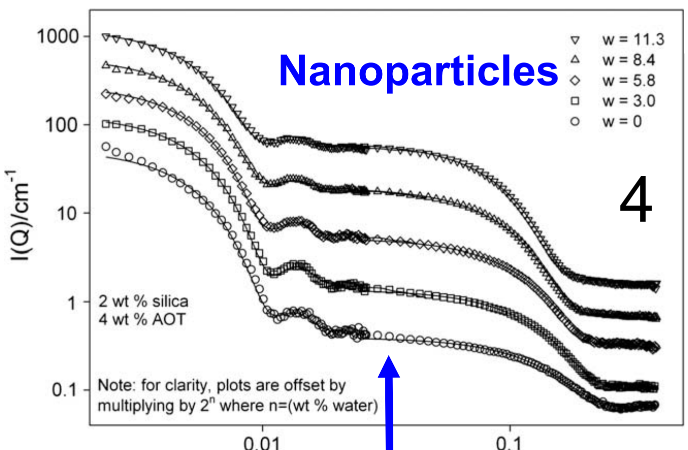


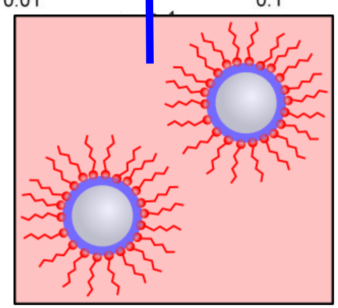


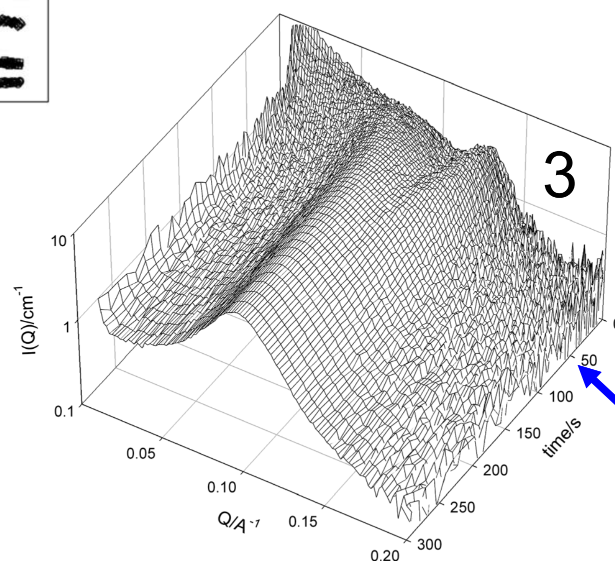


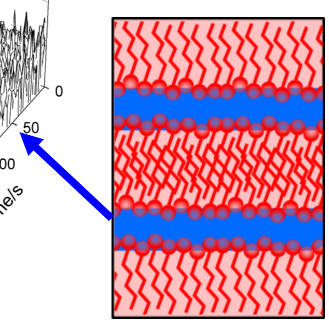


SANS on soft matter

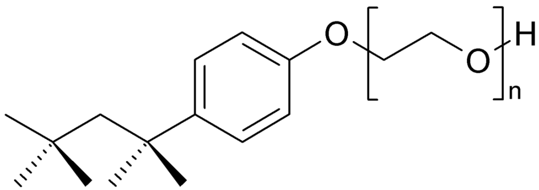


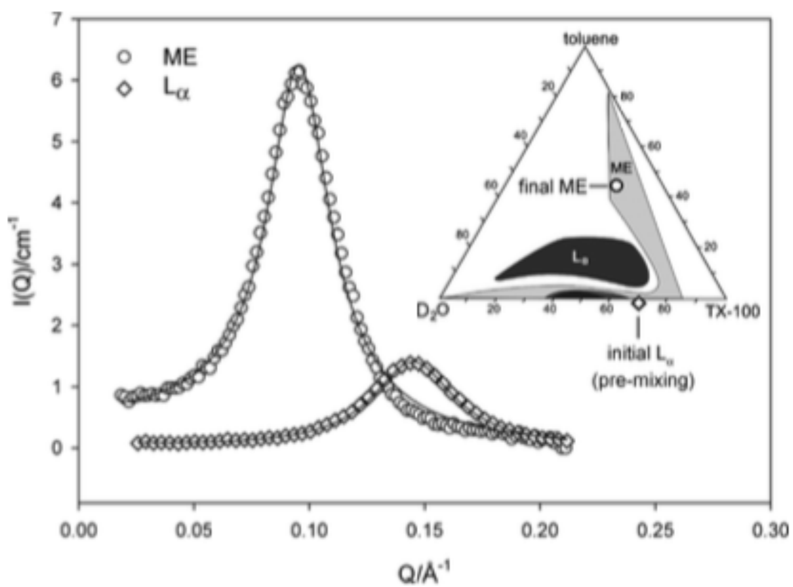


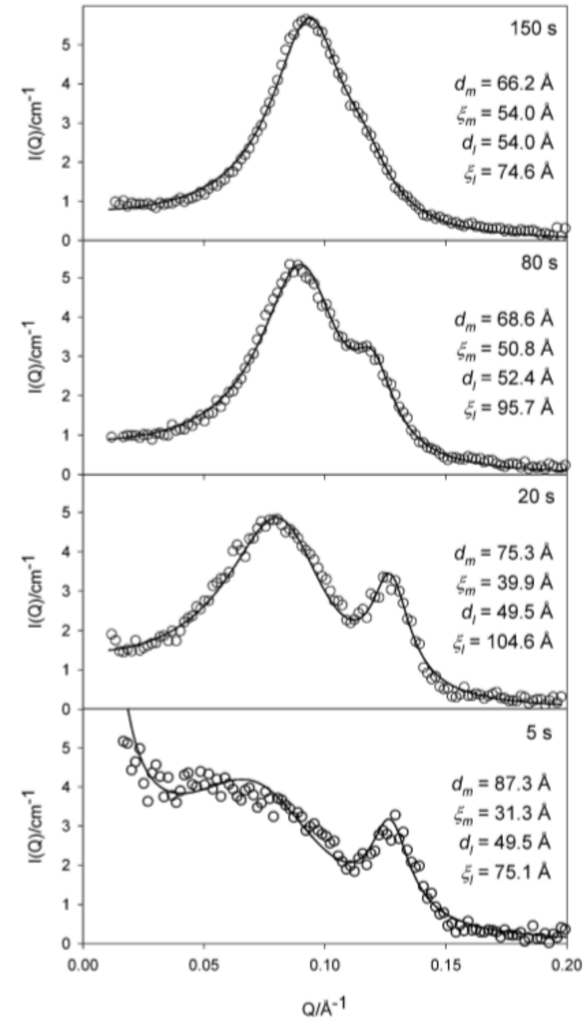




ISN'T NEUTRON SCATTERING SLOW?



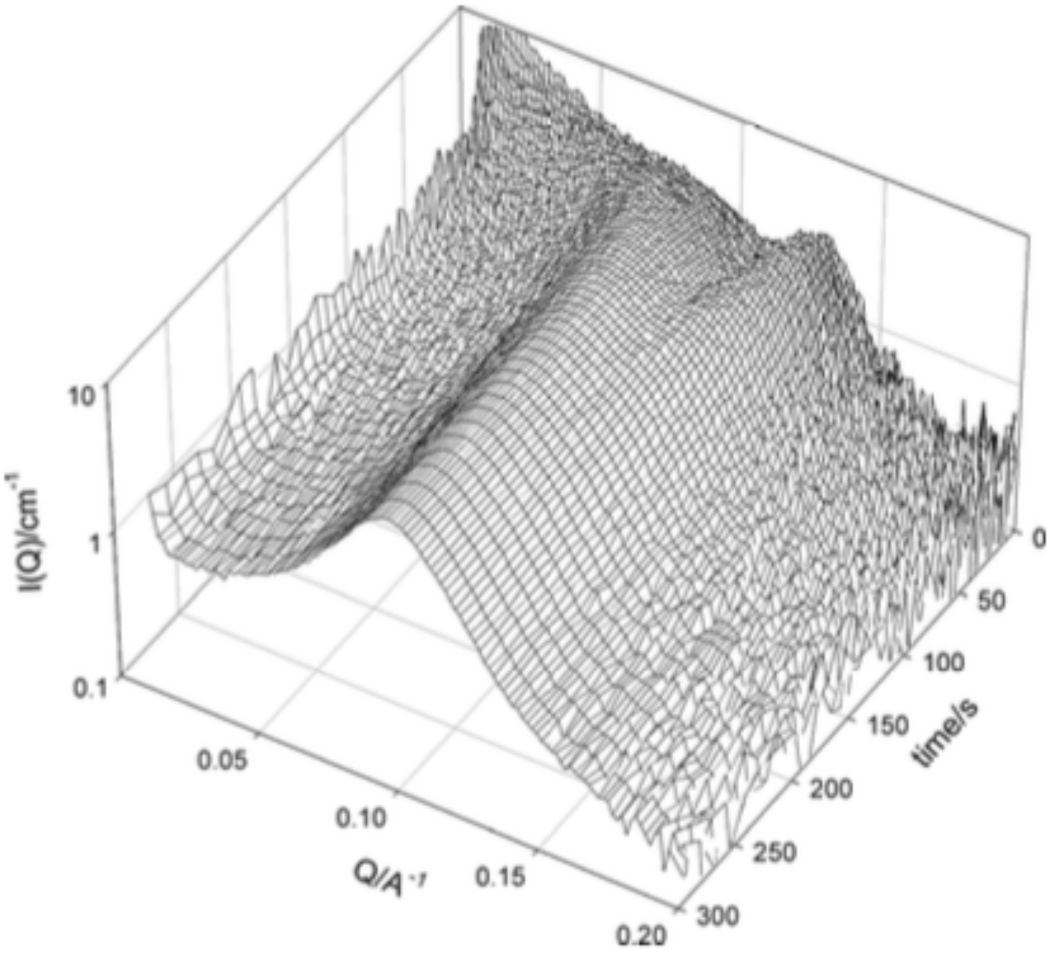




ISN'T NEUTRON SCATTERING SLOW?

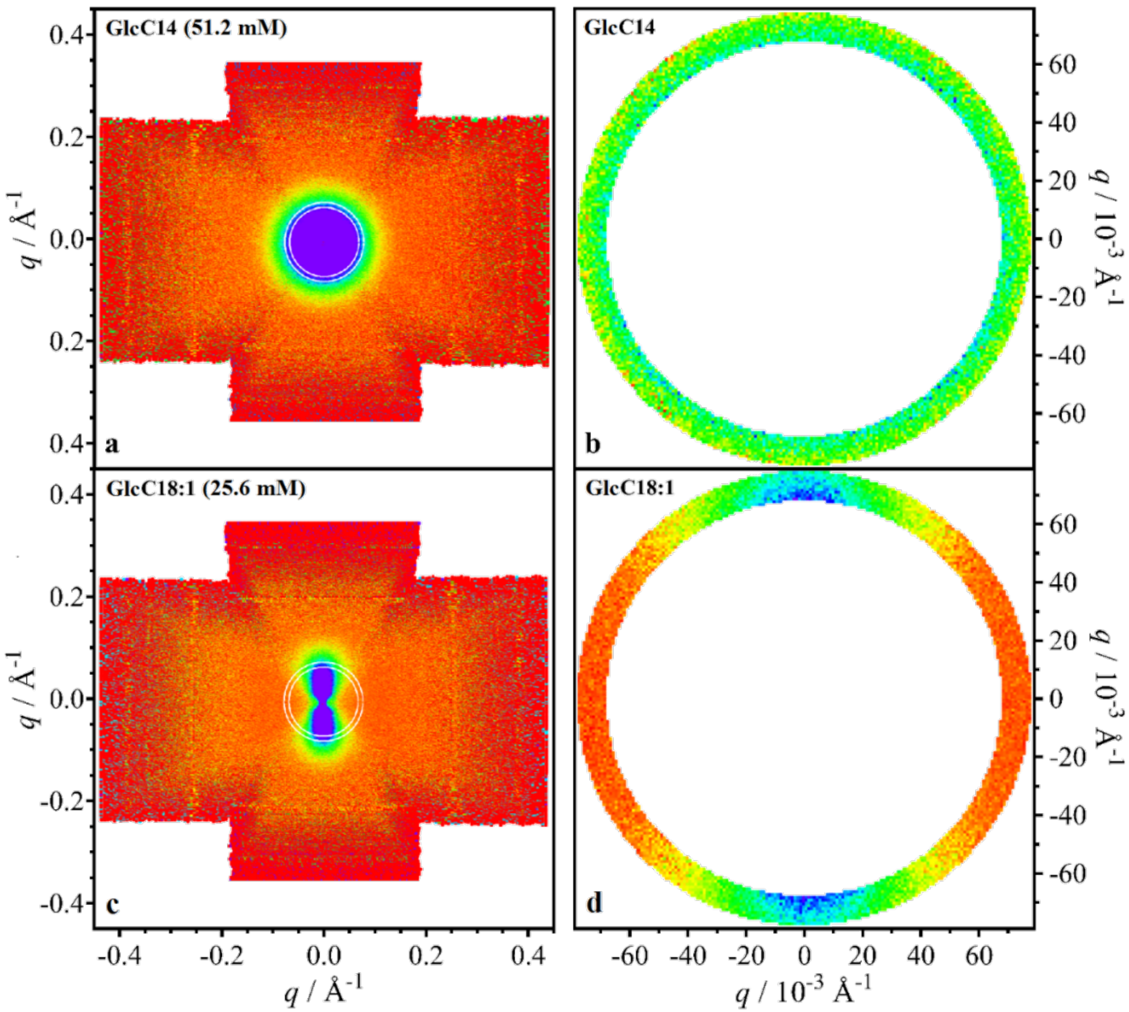
- Time-slices start with 20 ms duration!
- Binning 2–3 runs together to improve signal:noise
- Watch soft matter evolution in real time!

- Fast can be very useful, but sometimes slow is good…

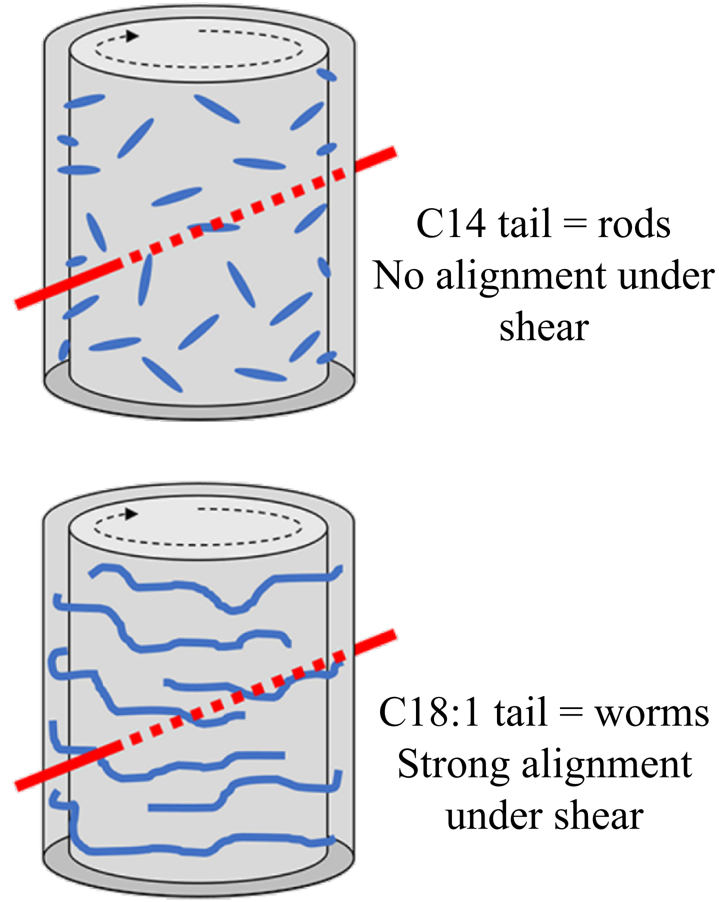


SMaCLab Soft Materials and Colloids

RHEO-SANS



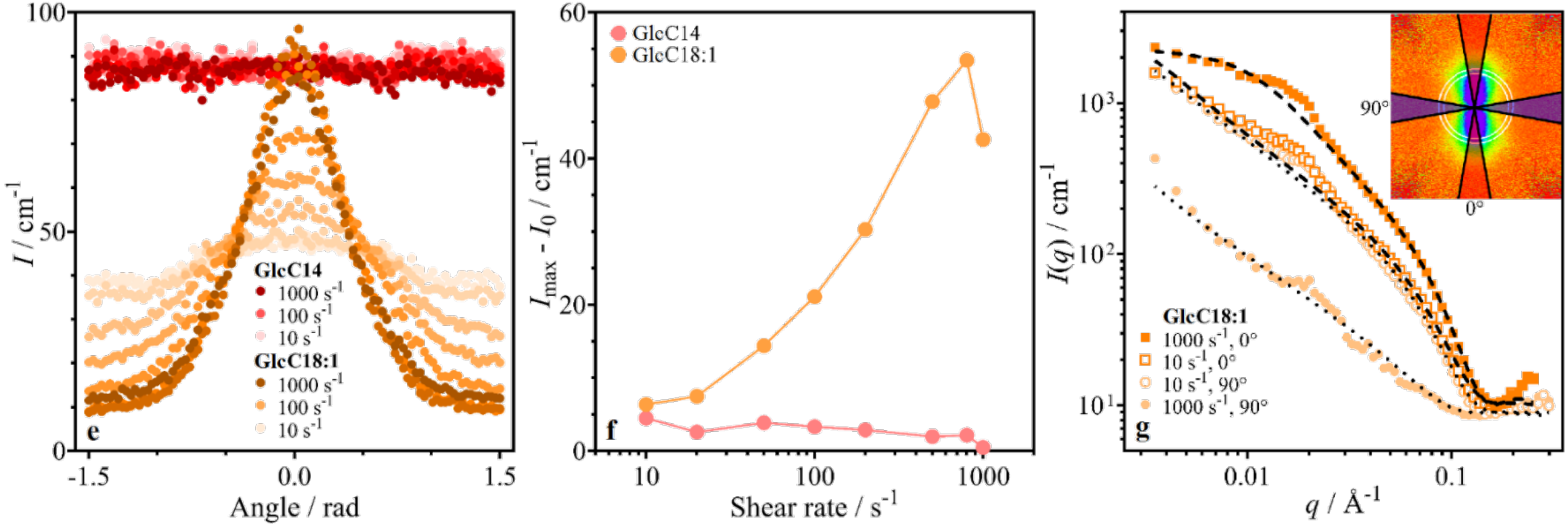
GlcC14 (51.2 mM)
GlcC14
GlcC18:1 (25.6 mM)
GlcC18:1
a
b
c
d
q / Å-1
q / 10-3 Å-1
0.4
0.2
0.0
-0.2
-0.4
60
40
20
0
-20
-40
-60



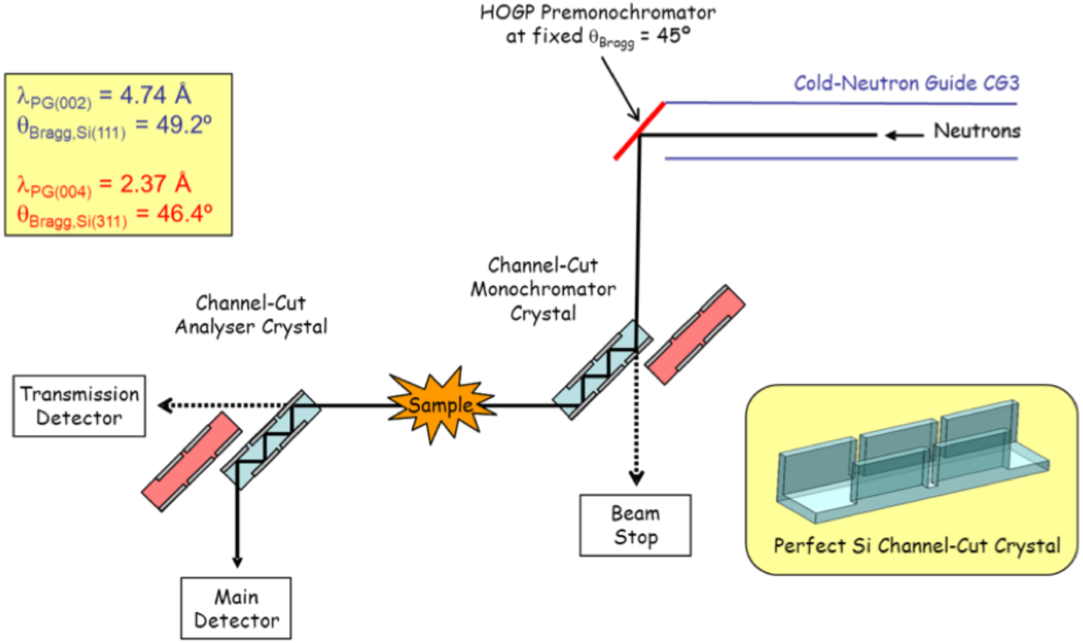
C14 tail = rods
No alignment under shear
C18:1 tail = worms
Strong alignment under shear

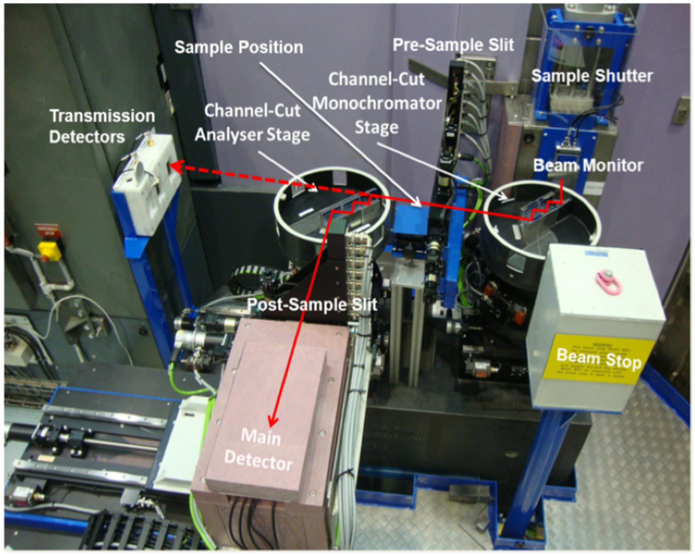
RHEO-SANS

- Strong level of alignment for C18:1 worms
- Quantify using annular and sector analysis
- Annulus shows degree of alignment with shear field as a function of shear rate
- Sector analysis shows effective form factor parallel and perpendicular to shear field



USANS (Kookaburra)

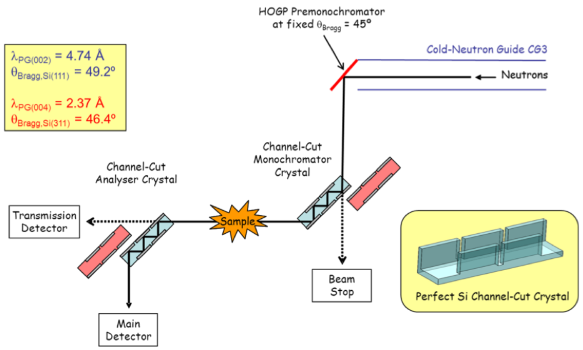




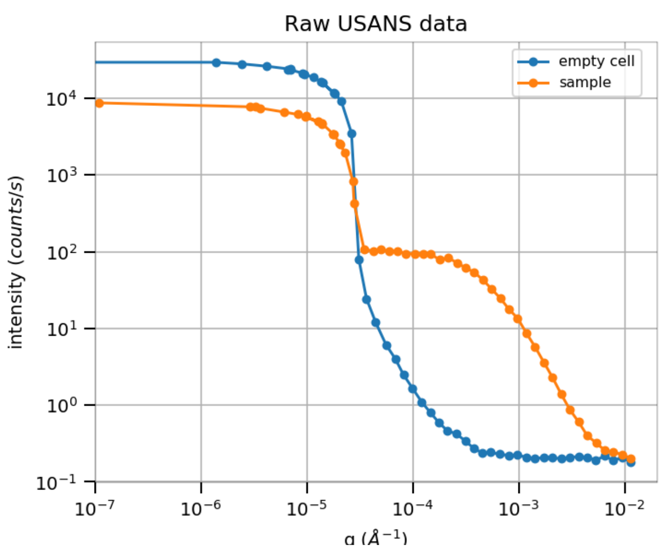
Reference: Rehm, C.; de Campo, L.; Brûlé, A.; Darmann, F.; Bartsch, F.; Berry, A., Design and performance of the variable-wavelength Bonse–Hart ultra-small-angle neutron scattering diffractometer KOOKABURRA at ANSTO. Journal of Applied Crystallography 2018, 51 (1), 1-8.

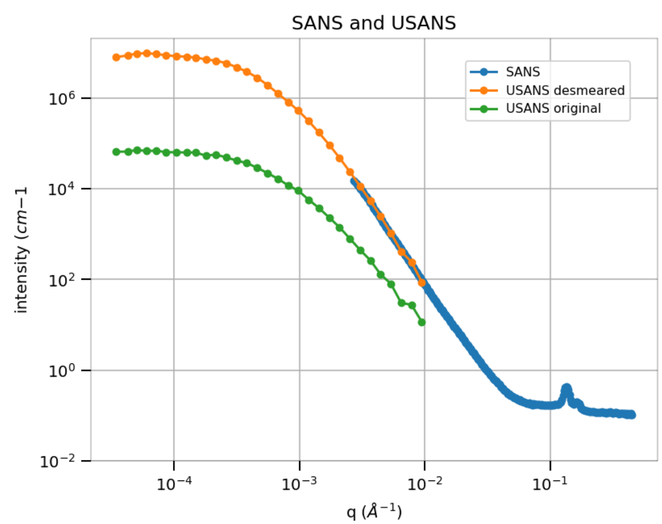
*Many thanks to Dr Liliana de Campo and Dr Jitendra Mata (ANSTO) for the slides and information!

USANS Measurements



Sample optimisation:
Scattering Strength, Measurement time, Large cells
Sample must be stable during USANS scan





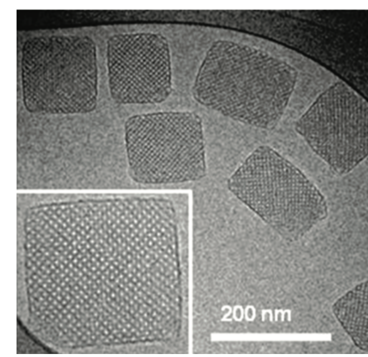
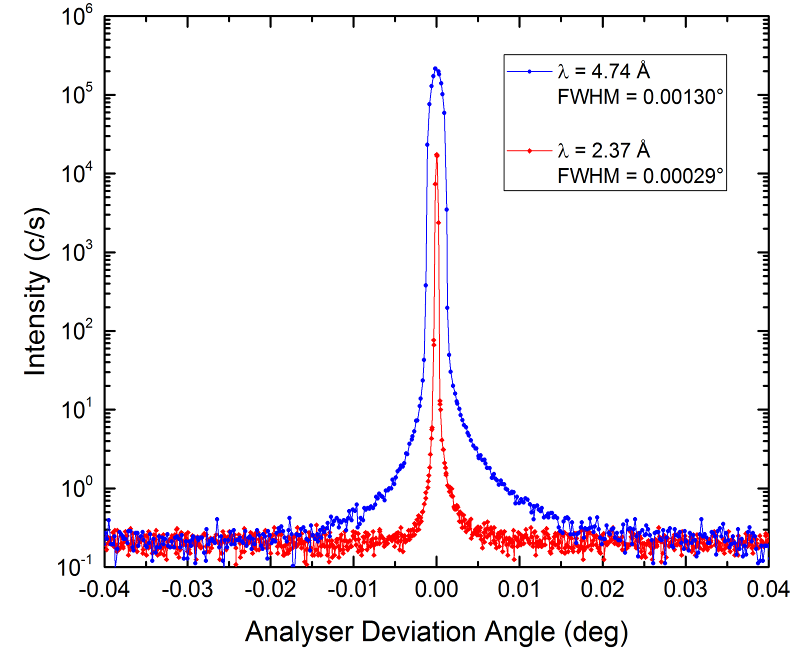


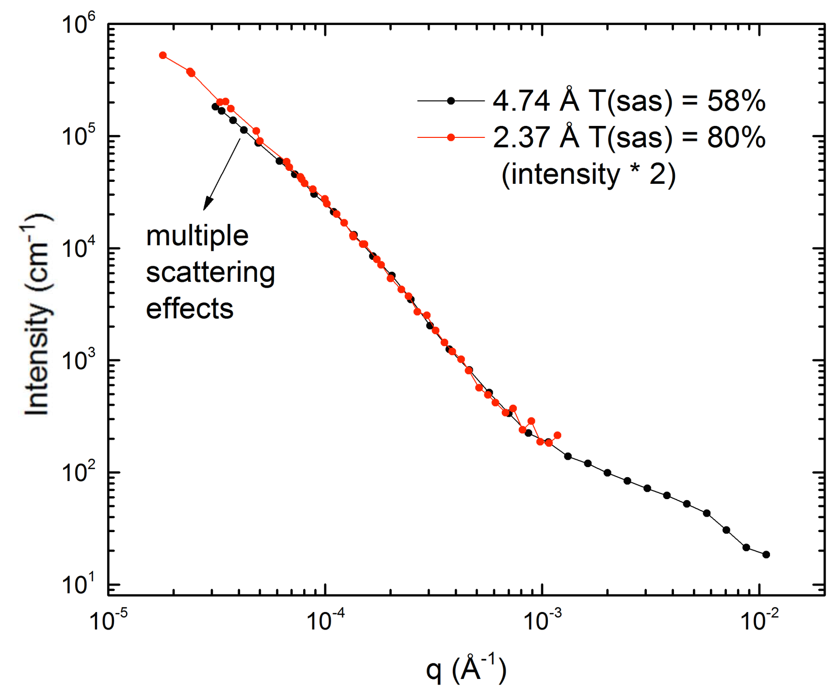
Image from Muir et al.,
Phys. Chem. B 2012, 116.3551-3556

Point–by–point method

USANS Instrument Characteristics: operates in 2 wavelengths

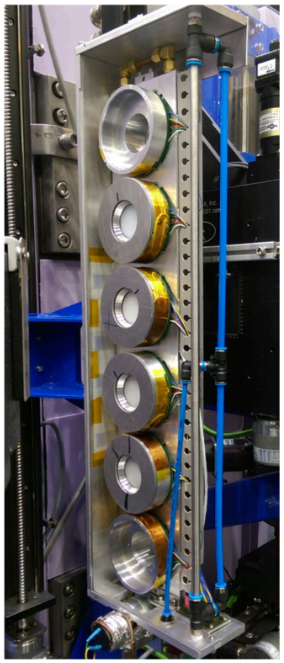
Instrument characteristics	High-Intensity Mode	High-Resolution Mode
Wavelength λ	4.74 Å	2.37 Å
Premonochromator	HOPG(002) at $\theta_B = 45°$	HOPG(004) at $\theta_B = 45°$
Channel-cut crystals	Si(111) at $\theta_B = 49.2°$	Si(311) at $\theta_B = 46.4°$
Full Darwin width, $2\Delta\theta_D$	21 μrad	5.04 μrad
Minimum momentum transfer, q_{min}	3×10^{-5} Å	1.5×10^{-5} Å
Vertical q resolution, Δq_{ver}	0.0586 Å	0.117 Å
Wavelength resolution, $\Delta\lambda/\lambda$	3.5%	2.0%
Neutron flux (beam 5 cm $\times$ 5 cm)	215000 cm^{-2} s^{-1}	17500 cm^{-2} s^{-1}
Noise-to-signal ratio (empty beam)	1.1×10^{-6}	1.3×10^{-5}



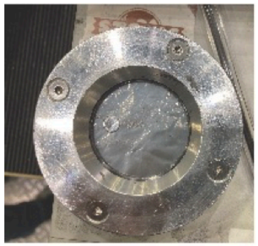


From: Yang et al., RSC Adv., 2015, 5, 107916-107926.

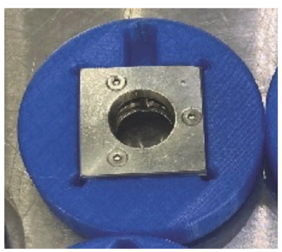
USANS Sample Environments



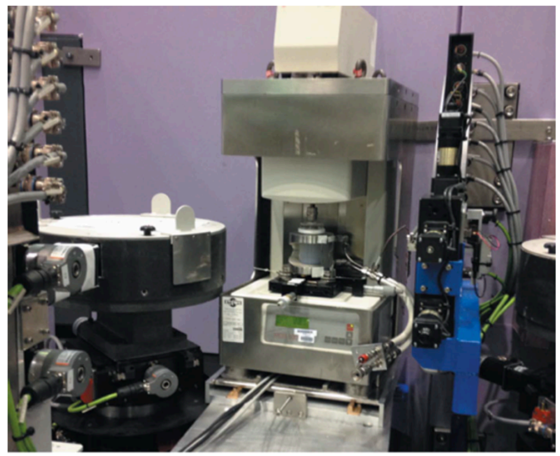
Temperature controlled sample tumbler



USANS cell
Standard: 1.5ml



SANS cell:
Standard: 0.35ml



Rheometer

High field magnet with cryostat

ANSTO