

## ISIS Neutron Training Course Introduction to SANS

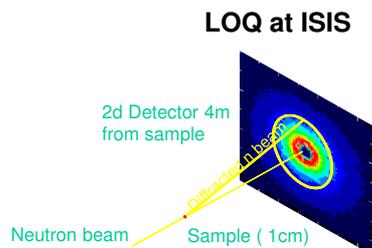
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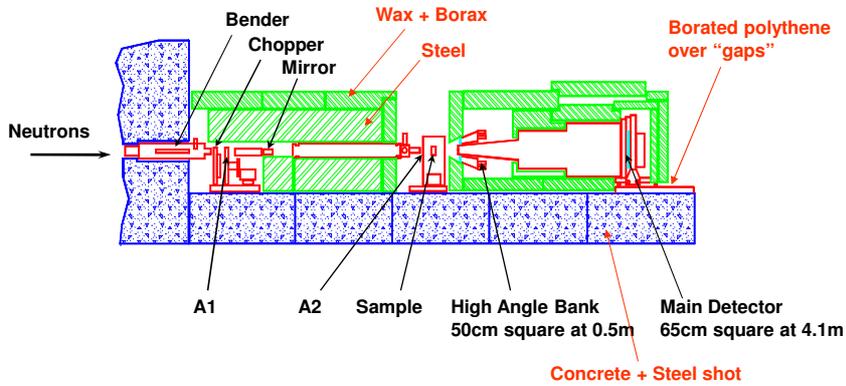


### Small angle diffraction

- Scattering (or diffraction) of X-rays, light, or neutrons at **small angles** is used to examine objects that are **large** compared to the wavelength  $\lambda$  of the radiation used.
- A **diffraction pattern** is obtained (not a direct image)
- Rather than use scattering angle  $\theta$  to show the diffraction pattern we use the **scattering vector** (in “reciprocal space”):
- $Q = k = (4\pi/\lambda) \cdot \sin(\theta/2)$
- where  $\lambda$  is the wavelength.
- Neutron “contrast variation” provides powerful and often unique insights.
- Carefully designed experiments provide information on much more than “structure” alone.
- Most of the concepts here apply also to Neutron Reflection.



### A SANS beam line - LOQ at ISIS



Simple beam line, with fixed  $L_1 \sim L_2 \sim 4\text{m}$ .  
Circular apertures A1 and A2,  
usually 20 & 10 mm diameter, collimate the  
beam.

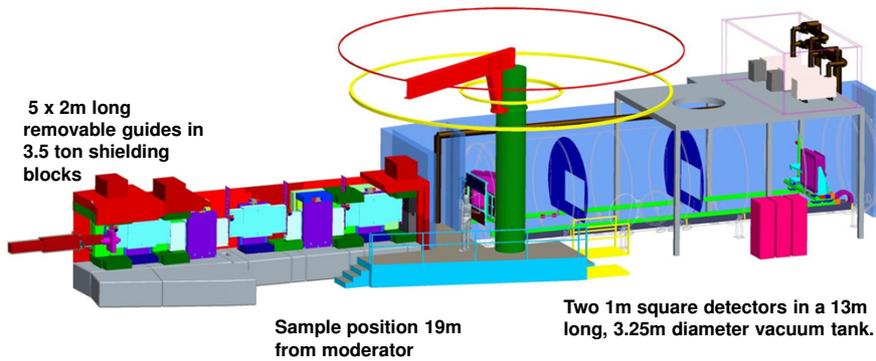
Note the large amount of shielding.

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



### SANS2d on ISIS TS-2

Uses neutron guides and movable  
detectors to have a choice of Q ranges.



At  $L_1 = L_2 = 4\text{m}$   $\sim 7$  to  $3$  to  $> 50$  (with Q)  
times count rate of LOQ.

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





SANS2d with end of 3.25m diameter vacuum tank open.

SANS2d two 1m square detectors.

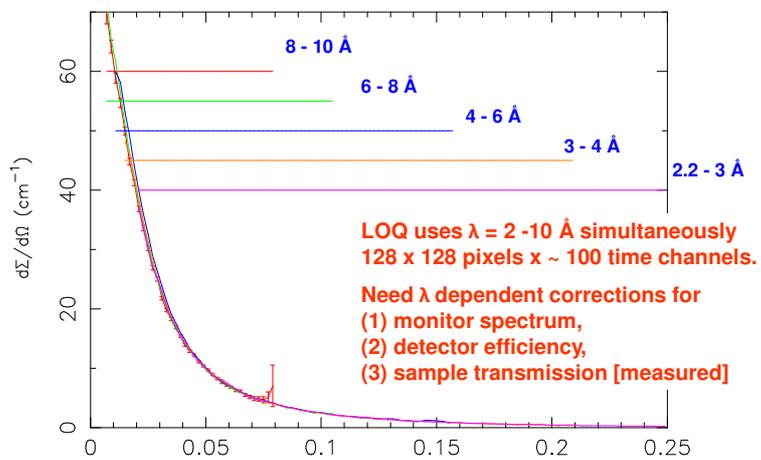


### Small angle diffraction

- $Q = k = \frac{4\pi}{\lambda} \sin(\theta/2)$       units  $\text{\AA}^{-1}$  or  $\text{nm}^{-1}$ ,  
1 $\text{\AA}$  = 0.1nm, 1nm =  $10^{-9}$ m
- Note Bragg diffraction peak for plane spacing  $d$  is at  $Q = 2\pi/d$
- Small  $Q$  probes **long** distances in the sample
- Large  $Q$  probes **short** distances.
- LOQ at ISIS uses wavelengths  $\lambda$  of 2 to 10  $\text{\AA}$ , with a 64 cm square detector at 4.1 m from the sample.
- $Q = 0.006$  to  $0.28 \text{\AA}^{-1}$  probes distances of about 10 to 1000  $\text{\AA}$  ( 1 to 100 nm ).
- SANS2d uses 2 to 16.5  $\text{\AA}$  and larger detectors which be slid off sideways and up to 12m away, so has huge  $Q$  ranges.
- At ISIS we use **time of flight** to record say 100 diffraction patterns at different wavelengths in each run, then we combine the patterns to a single  $Q$  scale.

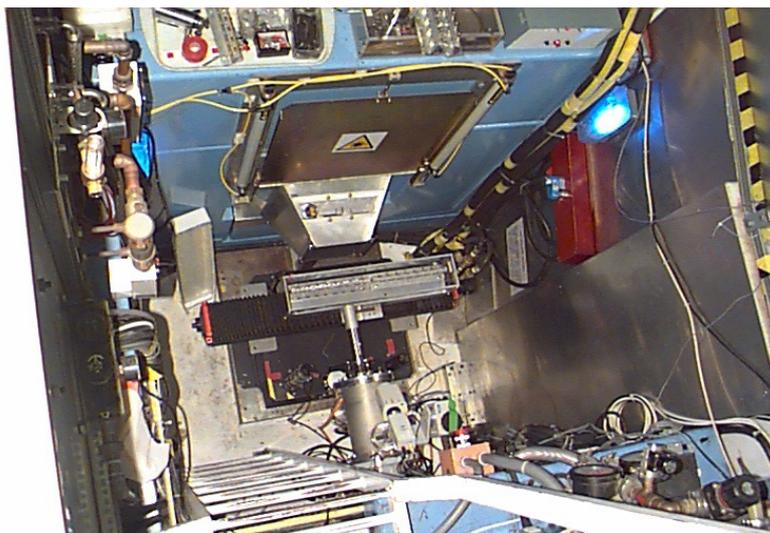


Time-of-flight SANS has **WIDE Q range in single measurement**  
 IF can combine data from different  $\lambda$   
 E.g. here polymer "Gaussian coil" for 49% d-PS in h-PS



R.K.Heenan, J.Penfold & S.M.King, J.Appl.Cryst. 30(1997)1140-1147

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



LOQ Sample area





SANS2d Sample area



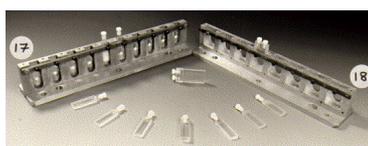
Double deck sample changer , cell racks with plasma sprayed gadolinium oxide.



### Small Angle Samples

#### Neutrons –

- 8-12 mm diameter beam
- 1mm thick ( 2mm in D<sub>2</sub>O)
- Quartz glass cells  
(as for UV spectroscopy, no Boron which adsorbs neutrons, as does Cadmium)
- Pressure, shear cells, cryostat, furnace etc, fairly easy

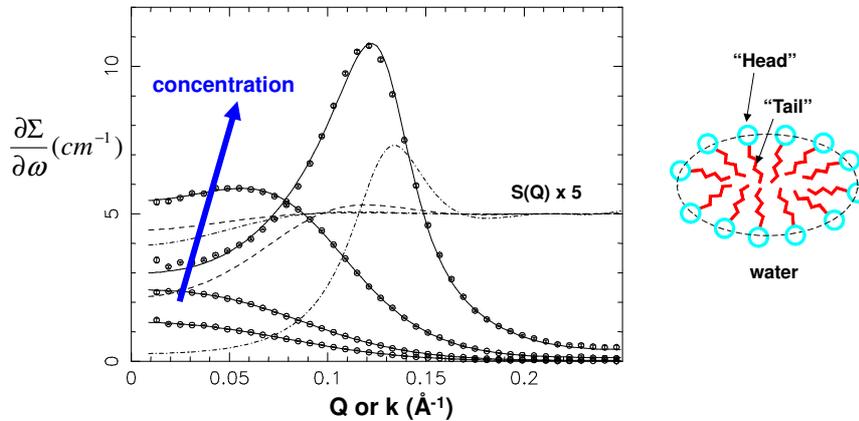


#### X-Rays –

- << 1mm beam
- Thin samples
- Radiation damage and/or heating ?
- Powerful synchrotron X-ray beams do now allow more complex sample environment  
– can still fry samples!



Size, shape and interaction of particles in solution from SANS.  
 Data and fits for 0.9, 1.8, 7 and 29 % volume



Diffraction pattern from small particles, DDAO micelles,  $C_{12}H_{25}NO(CH_3)_2$  in  $D_2O$   
 On increasing concentration SANS may be “pushed down” at small  $Q$ , until we get a “Bragg” peak from  $D \sim 2\pi/Q$  spacing between neighbouring particles.  
 Core  $R \sim 16.5 \text{ \AA}$ , shell  $\sim 2 \text{ \AA}$  ( or  $3.8 \text{ \AA}$  if add 4 water per head),  
 axial ratio  $X \sim 1.7$ , aggregation number  $\sim 103$ , “charge” per head in  $S(Q) \sim 0.7$

D.J.Barlow, M.J.Lawrence, T.Zuberi, S.Zuberi & R.K.Heenan, Langmuir 16(2000)10398-10403.



What SANS ( & 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.)
- } Dilute particles
- } Concentrated systems

We always learn something ....



## SANS science includes:

- Surfactant micelles, structure & interaction potentials
- Microemulsion droplets - contrast variation for structure & composition
- Block copolymer micelle - size & density profile.
- Polymer solutions
- Polymer/surfactant interaction.
- Bulk (melt or solid) polymers, using H-D contrast
- Polymer density profile (interfaces large droplets)
- Biomolecular solutions - protein conformation
- Membranes, vesicles
- Porous materials, voids in metals
- Phase separation
- Liquid crystals
- Magnetic scattering
- Alloy structure
- Fractal dimensions
- Nature of surfaces



## SANS definitions:

Instead of plotting against  $\theta$  we use ( $Q$  for neutrons,  $k$  for X-rays):

$$Q = k = \frac{4\pi}{\lambda} \sin(\theta/2) \quad \text{Units } \text{\AA}^{-1} \text{ or } \text{nm}^{-1},$$

scattering angle  $\theta = \text{atan}(R/L)$

[CARE sometimes called  $2\theta$ ]

"Intensity", often called  $I(Q)$ , is properly the absolute scattering cross section  $\partial\Sigma(Q)/\partial\omega$  in units of  $\text{cm}^{-1}$ . It is the probability of a neutron of wavelength  $\lambda$  being scattered, per unit solid angle, at that  $Q$ .

Counts in a detector of area  $A$ , at radius  $R$  and distance  $L$  from sample are:

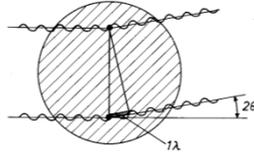
$$I(R, \lambda) = I_0(\lambda) \cdot \frac{\partial \Sigma(Q)}{\partial \Omega} \cdot \Delta \Omega(R) \cdot t \cdot T(\lambda) \cdot \eta(\lambda),$$

Solid angle  $\Delta\Omega = A/L^2$ ,  $t$  = sample thickness,  $T$  = sample transmission and  $\eta$  = detector efficiency, and  $\tan(\theta) = R/L$ .



**Simple diffraction theory for SAS:**  
**SNOOZE here if you are not good at maths ....**

For a rotationally averaged or centro-symmetric particle:



Scattered waves from pairs of points in the sample interfere with each other.

Whole number of wavelengths “constructive interference” = Bragg condition.

Mathematically we sum the amplitudes and phases of the interfering waves over all possible “pairs of points”.

( “Points” could be individual atoms, but in SANS we do not usually know where the atoms are, so we average them out into continuous regions.)

This can be done to get F(Q) for all sorts of particle shapes, polymer coils etc, though often involves a numerical integration of some complicated equations.



**SAS theory:**

**Dilute particles** – subtract uniform solvent & sum over one particle:

$$P(Q) = NV^2 (\Delta\rho)^2 F^2(Q) \quad \text{Note } NV = \phi \text{ volume fraction}$$

Randomly oriented or centro-symmetric particle, ONLY gives information on average radial density distribution  $\rho(r)$  or  $g(r)$  :

$$F(Q) = \int 4\pi r^2 \rho(r) \frac{\sin(Qr)}{Qr} dr$$

[ This is a Fourier transform: small Q is for large r, high Q for small r ]

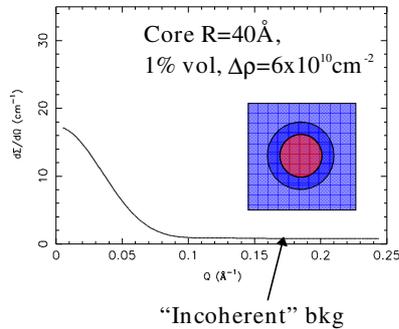
For X-rays  $\rho(r)$  is in electrons per unit volume, (times the probability of scattering for one electron).

For neutrons  $\rho(r)$  is in “neutron scattering per unit volume”

= “Scattering length density” (more later about this).



**Example: dilute uniform spheres:**



$$\frac{\partial \Sigma}{\partial \omega} = I(Q) = NV^2 (\Delta\rho)^2 P(Q) + BKG$$

$$P(Q) = F^2(Q, r) \rightarrow 1 \text{ as } Q \rightarrow 0$$

$\Delta\rho$  = neutron scattering length density difference, (particle - solvent), can be +ve or -ve but give same signal.

For sphere:

$$F(Q, r) = \frac{3(\sin(Qr) - Qr \cos(Qr))}{(Qr)^3}$$

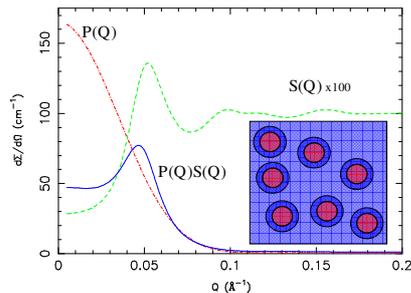
Diffraction pattern  $I(Q)$  falls off faster when particle size increases.

$I(Q=0)$  intensity increases (linearly if dilute) with concentration  $\phi = NV$

and with “contrast”  $(\Delta\rho)^2$  [note SQUARED ]



**Example: interacting spheres:**



10%  $R=40 \text{ \AA}$  radius spheres, in “core” contrast, (polydispersity  $\sigma/R_{bar} = 0.15$ ,  $\Delta\rho=6 \times 10^{10} \text{ cm}^{-2}$ ). plus another 16% in invisible 15  $\text{\AA}$  coating gives hard sphere  $S(Q)$  of 26 % vol &  $R = 55 \text{ \AA}$   $S(Q) \rightarrow 1$  at high  $Q$

At higher volume fractions we start to see interference from waves scattered by adjacent particles ( it was there all along, but at smaller  $Q$ , inside the beam stop!).  $I(Q=0)$  is now pushed lower!

First approximation multiply  $P(Q)$  by “inter-particle structure factor”  $S(Q)$  - depends on “long range” interparticle interactions.

$S(Q)$  from Fourier transform of interparticle  $g(r)$  & hence interaction potential for colloids or Bragg  $d = 2\pi/Q_{peak}$  in “liquid crystal”.

$$\frac{\partial \Sigma}{\partial \omega} = I(Q) = NV^2 (\Delta\rho)^2 P(Q)S(Q) + BKG$$



Neutron scattering length densities for contrast ( $\Delta\rho$ )<sup>2</sup>

Average atomic scattering lengths  $b$  over any suitable volume  $V$ , such as one molecule or one scattering particle:

$$\rho = \frac{\sum n_i b_i}{V} \qquad V_{MOLAR} = \frac{M}{\rho_{BULK} N_A}$$

e.g. water  $V = \frac{18.0152 \text{ g.mol}^{-1}}{1.0 \text{ g.cm}^{-3} \cdot 6.023 \times 10^{23}} = 29.915 \times 10^{-24} \text{ cm}^3 = 29.915 \text{ \AA}^3$

H<sub>2</sub>O  $\rho = \frac{(2 \times (-0.3739) + 0.580) \times 10^{-12} \text{ cm}}{29.915 \times 10^{-24} \text{ cm}^3} = -0.56 \times 10^{10} \text{ cm}^{-2}$

D<sub>2</sub>O  $\rho = \frac{(2 \times 0.667 + 0.580) \times 10^{-12} \text{ cm}}{29.915 \times 10^{-24} \text{ cm}^3} = 6.40 \times 10^{10} \text{ cm}^{-2}$

**NOTE** units of length per unit volume!

$\times 10^{10} \text{ cm}^{-2}$  is the same as  $\times 10^{-6} \text{ \AA}^{-2}$ ,  $1 \text{ \AA} = 10^{-8} \text{ cm} = 0.1 \text{ nm}$   
<sup>1</sup>H (<sup>7</sup>Li, <sup>62</sup>Ni, <sup>48</sup>Ti etc) have a **negative  $b$**  due to phase shift via neutron spin interaction.



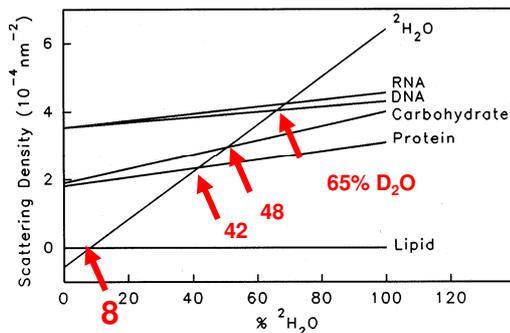
Neutron sld's - useful tips 1.

- **NOTE** D- molecules more dense, can assume same molar volume as H- form, better to work in %vol not %w to get same systems.
- Deuterated molecules are at best ~ 99% D, and often only 97 - 98% D  
 e.g. sld of "99% D<sub>2</sub>O"  $0.01 \times (-0.56) + 0.99 \times (6.40) = 6.33 \times 10^{10} \text{ cm}^{-2}$
- D-toluene is cheap but D/H mixtures span a smaller range of sld's.
- sld (d-polystyrene) > sld(D<sub>2</sub>O), need mix h-PS to match water.
- Sld of most inorganic substrates is conveniently between h- and d-solvent. Some high bulk densities have higher sld ( e.g. Al<sub>2</sub>O<sub>3</sub>). TiO<sub>2</sub> has a low sld due to the negative scattering length of Ti.
- "Hydration water" in surfactant head, especially large nonionics like (EO)<sub>n</sub> makes sld vary with water contrast.
- **IMPORTANT** to measure the bulk density of systems.



### Neutron sld's - Biology.

- In biology D<sub>2</sub>O/H<sub>2</sub>O mixtures can match out the protein, lipid, nucleic acid, etc. after allowing for D – H exchange



Molecule	Bulk density (g.cm <sup>-3</sup> )	Molecular weight (g.mol <sup>-1</sup> )	Molar volume (Å <sup>3</sup> )	Scattering length density (10 <sup>10</sup> cm <sup>-2</sup> )
H <sub>2</sub> O	1.0	18.015	29.915	-0.560
D <sub>2</sub> O	1.112	20.0314	29.915	6.400
toluene C <sub>7</sub> H <sub>8</sub>	0.865	92.140	176.884	0.939
C <sub>7</sub> D <sub>8</sub>	0.9407	100.205	176.884	5.647
heptane C <sub>7</sub> H <sub>16</sub>	0.684	100.20	243.267	-0.547
C <sub>7</sub> D <sub>16</sub>	0.794	116.33	243.267	6.300
cyclohexane C <sub>6</sub> H <sub>12</sub>	0.779	84.161	179.403	-0.278
C <sub>6</sub> D <sub>12</sub>	0.891	96.258	179.406	6.685
silicon	2.329	28.0855	20.025	2.074
SiO <sub>2</sub> vitreous	2.2	60.0843	45.352	3.475
SiO <sub>2</sub> α quartz	2.648	"	37.679	4.183
TiO <sub>2</sub>	4.23	79.899	31.366	2.604
Al <sub>2</sub> O <sub>3</sub>	3.97	101.961	42.648	5.699
poly(ethylene)-CH <sub>2</sub> -	0.92	14.027	25.318	-0.329
poly(styrene) - C <sub>8</sub> H <sub>8</sub> -	1.05	104.151	164.71	1.412
d-poly(styrene) - C <sub>8</sub> D <sub>8</sub> -	1.131	112.216	164.71	6.468



“Contrast” - example

e.g.  $(\Delta\rho)^2$  for SiO<sub>2</sub> in toluene – see table on previous page

H-toluene  $(3.5 - 0.9)^2 \sim 6.8$

D-toluene  $(3.5 - 5.6)^2 \sim 4.4$

i.e. scatters 50% more in H-toluene, but d-toluene may be better as can use 2mm not 1mm thick sample, and there is much less incoherent background from H.

Q resolution

SANS is smeared out by Q resolution function - depends on detector pixel size, detector spatial resolution, sample size and properties of the neutron source.

*Fits to sharp features, particularly at small Q, will ideally need resolution smearing.*

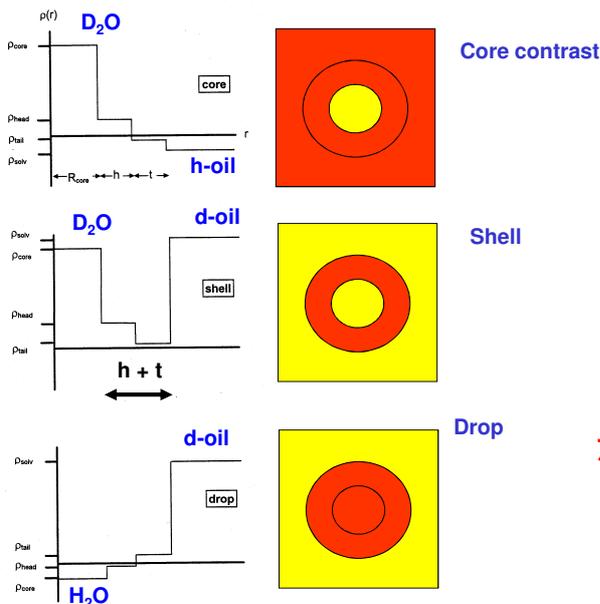
For further information:

D.F.R.Mildner & J.M.Carpenter, J.Appl.Cryst. 17(1984)249-256.

J.S.Pedersen, D.Posselt & K.Mortensen, J.Appl.Cryst. 23(1990)321-333.



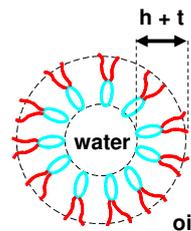
Contrast variation



Neutron scattering powers vary erratically with atomic number.

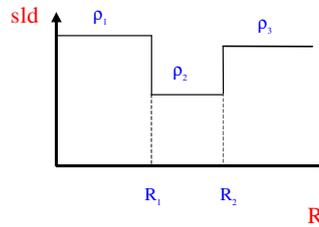
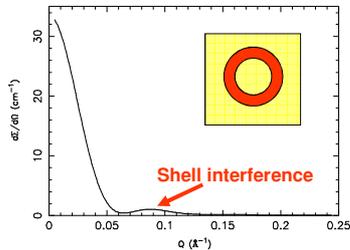
In particular D and H are very different, large positive and small negative (due to a phase shift).

Using deuterated materials we can make parts of a sample “disappear”.



For core plus shell spherical particle

e.g. Spherical Shell  $R_1 = 40 \text{ \AA}$  ( $R_2 - R_1 = 15 \text{ \AA}$  (with 15% polydispersity))



$$I(Q) = N \left\{ (\rho_1 - \rho_2) V_1 F(Q, R_1) + (\rho_2 - \rho_3) V_2 F(Q, R_2) \right\}^2$$

$$F(Q, r) = \frac{3(\sin(Qr) - Qr \cos(Qr))}{(Qr)^3}$$

At “contrast match”  $\rho_1 = \rho_3$ , then we see “hollow shell” with oscillation in  $I(Q)$  which is very sensitive to the details and composition of the structure.

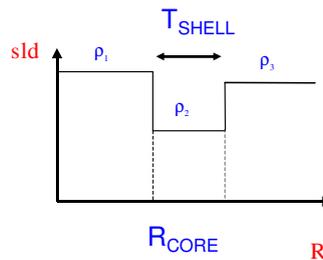
$$I(Q) = N(\rho_1 - \rho_2)^2 \left\{ V_1 F(Q, R_1) - V_2 F(Q, R_2) \right\}^2$$



### Practical computations

**NOTE – the way equations are presented in scientific papers may not be the best way to use them in a computer program and vice-versa!**

There are many ways to re-arrange the equations, e.g. the core/shell sphere on the previous slide can become:



$$I(Q) = \frac{16\pi^2 N}{Q^6} \left\{ (\rho_1 - \rho_2) f(Q, R_{CORE}) + (\rho_2 - \rho_3) f(Q, R_{CORE} + T_{SHELL}) \right\}^2$$

$$f(Q, r) = (\sin(Qr) - Qr \cos(Qr))$$

Where there are  $N$  particles per unit volume (usually per  $\text{cm}^3$ ).

Note that we may need to include a factor  $10^{48}$  to convert  $Q(\text{\AA}^{-1})^6$  to  $\text{cm}^{-6}$ .



## Incoherent & Inelastic scattering

Hydrogen (and to a lesser extent some other atoms, e.g. Cl) has “incoherent” scatter which gives a “flat background”,

e.g. 1mm H<sub>2</sub>O gives ~ 1cm<sup>-1</sup> which may be large compared to a SANS signal, especially at high Q.

Actually around half of this is **multiple inelastic scattering**. “Cold” neutrons are thermalised in “warm” H<sub>2</sub>O, neutrons are accelerated to shorter wavelengths. Signal detected depends on detector efficiency (lower at shorter λ) and at a pulsed source on the sample-detector distance.

The inelastic spectrum is quite different for other hydrogenous materials.

This can make background subtraction and matching of main and high angle detectors quite difficult and sometimes almost impossible!

**Always allow a flat background in any fitting** to allow for errors in initial background subtraction - then ask is it reasonable? – then try fixing its value.



## GUINIER APPROXIMATION

For ANY shape dilute particle as Q tends to zero

$$I(Q \rightarrow 0) = NV^2(\Delta\rho)^2 \exp\left\{\frac{-Q^2 R_g^2}{3}\right\}$$

radius of gyration  $R_g$  = mean square from centre of mass  
( weighted by neutron scattering lengths !).

Sphere  $R_g = \sqrt{\frac{3}{5}}R$       Cylinder  $R_g^2 = \frac{R^2}{2} + \frac{L^2}{12}$

Guinier plot:  $\log_e(I(Q))$  against  $Q^2$     gradient =  $-R_g^2/3$ ,  
intercept =  $\log_e(I_0)$  gives M or aggregation number,  
good to  $QR \sim 1$  or sometimes more.

**Interparticle S(Q) may suppress (or increase) intensity at small Q**, so may need to extrapolate to zero concentration.

**Model fits over wide Q range are better !**



POROD'S LAW - surface to volume ratio from high Q limit

Well defined, sharp interface

$$I(Q) \rightarrow \frac{2\pi(\Delta\rho)^2 S}{Q^4}$$

If a plot of  $Q^4 I(Q)$  will has a plateau value  $y$  [units  $\text{\AA}^4 \text{ cm}^{-1}$ ] then

$$S(\text{cm}^2 / \text{cm}^3) = \frac{10^{32} y}{2\pi(\Delta\rho)^2} \quad \Delta\rho \text{ in cm}^{-2}$$

A good "incoherent" background subtraction is vital !

Can try FIT to  $Q^{-4}$  and additional flat background.

[ Other "power laws" may (or may not) relate to "fractal" materials or rough surfaces, thin sheets, thin rods etc. ]



## Other shaped particles

Remember that for a rotationally averaged or centrosymmetric particle,  $I(Q)$  is proportional to the square of the Fourier transform of  $r^2\rho(r)$ .

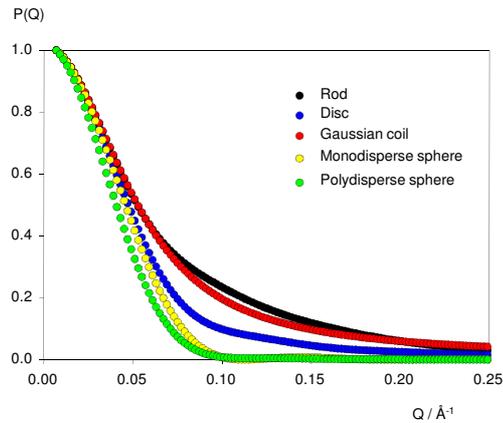
Large distances give more diffraction signal at small Q

Small distances give more diffraction signal at high Q

So what happens if we change the shape of the particle ....



**DILUTE PARTICLE SHAPE**



$R_G = 31 \text{ \AA}$  (i.e. are same at small Q)

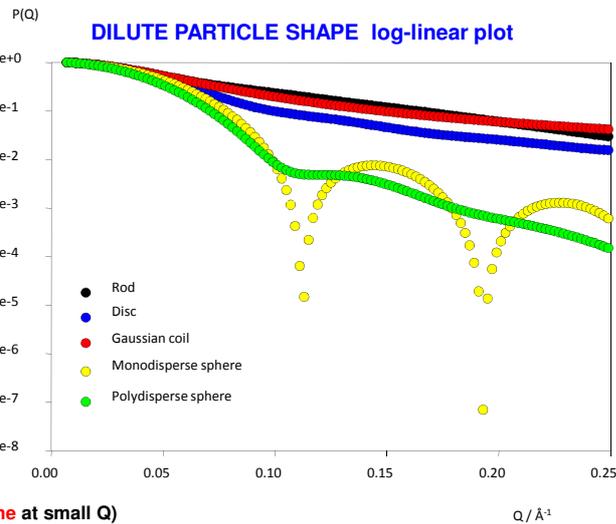
Rod  $R = 10 \text{ \AA}$ ,  $L = 104.5 \text{ \AA}$

Disc  $R = 43.6$ ,  $L = 10 \text{ \AA}$

Gaussian coil  $R_G = 31 \text{ \AA}$

Monodisperse sphere  $R = 40 \text{ \AA}$  has  $R_G = 40 \times \sqrt{3/5} = 31 \text{ \AA}$

Polydisperse (Schultz)  $R_{bar} = 40 \text{ \AA}$ ,  $\sigma/R_{bar} = 0.15$ , is steeper at small Q



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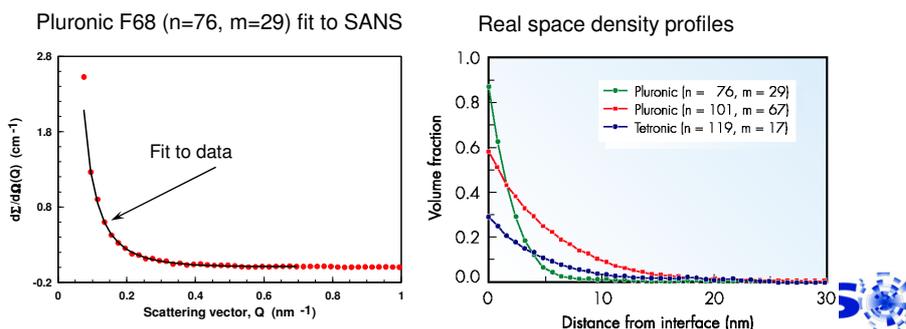
Interfacial structure ?

SANS provides information about density or composition profiles, especially if we can contrast match the core or substrate.

This is very useful for thicker layers of polymers – this is a whole subject in itself. It is possible, after carefully matching solvent to the substrate to either fit or use Fourier transform methods to obtain polymer density profiles.

You may have to EXPERIMENTALLY find accurate “match point” for core particle – bulk density/composition of core may not be accurately known.

TRIAL CALCULATIONS of “shell” contrast are useful as signal does not scale uniformly with core radius or shell thickness!



Thin sheets - lamellae

SANS of infinite flat sheet of thickness  $\ell$  is in the directions normal to the sheet

$$I(Q) \propto \frac{\sin^2(Q\ell/2)}{(Q\ell/2)^2}$$

Small Q “Sheets Guinier”, gradient of  $\log_e(Q^2I(Q))$  against  $Q^2$  is  $-\ell^2/12$ .

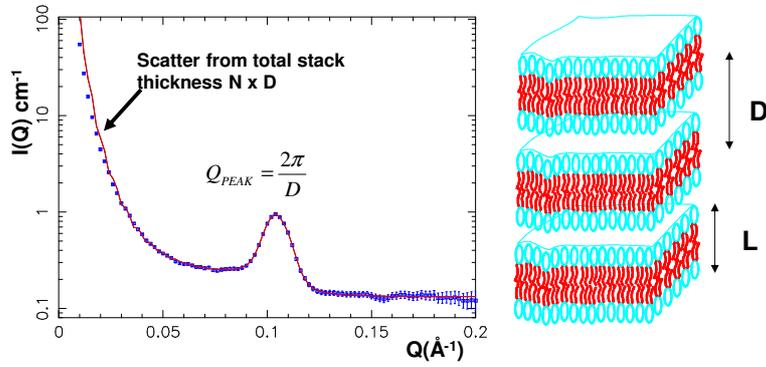
Multiply by a one dimensional S(Q) for a “paracrystalline lattice” attempt to fit lamellar peaks etc.

Useful for a FINITE NUMBER of layers, with strong scatter at small Q from the total thickness of the stack (compare: Fourier transform method or Caille peak fit for an infinite stack or neutron reflection from multi-layers).

P(Q) for sheets is easily modified for shell/core/shell with various shell types.

( see e.g. N.T.Skipper, A.K.Soper & J.D.C.McConnell, J.Chem.Phys. 94(1991)5751-5760 )

**Example: 3% DPPC lipid in D2O, multi-lamellar stack, fit by randomly oriented paracrystal model.**

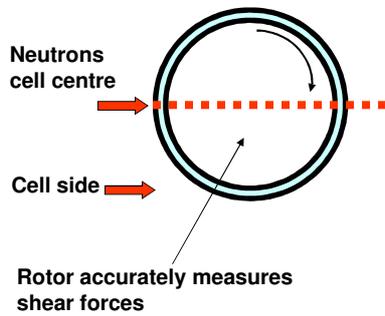


Fit has 18 layers of (L = 4.64nm lipid + 1.32nm water) D = 5.96 nm  
 $\sigma_D/D = 7\%$ ,  $\sigma_L/L = 10\%$  (fixed)



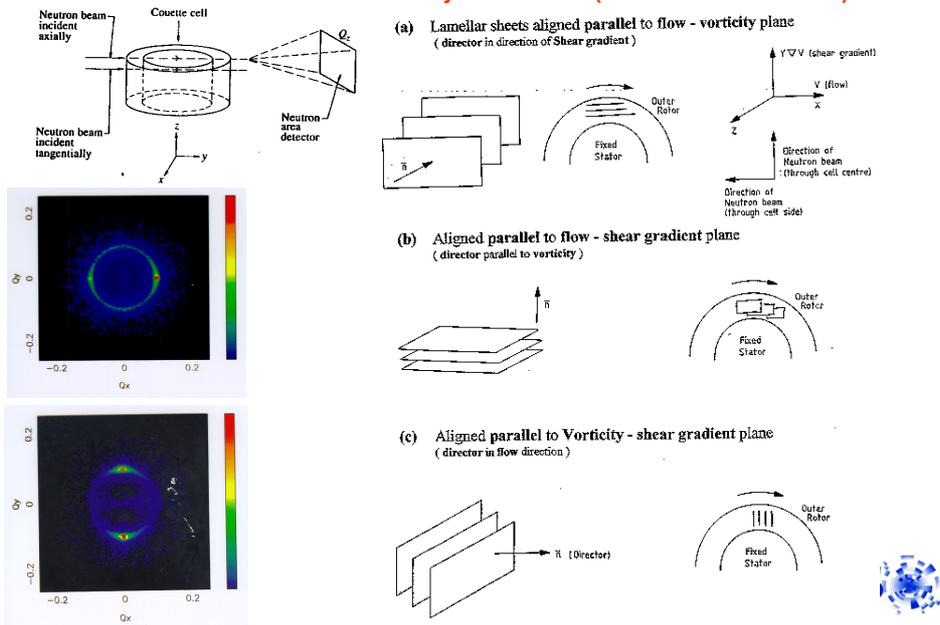
**Example – Oriented lamellae Anton-Paar rheometer.**

Constant and Oscillatory flow. Shear gradient  
 G is speed/gap distance ~ 1 to 20000 sec<sup>-1</sup>,  
 (gap is 0.5mm, radius 25mm)



Shear orientation of lamellar phases

At least 3 ways to orient ! (sometimes mixtures)



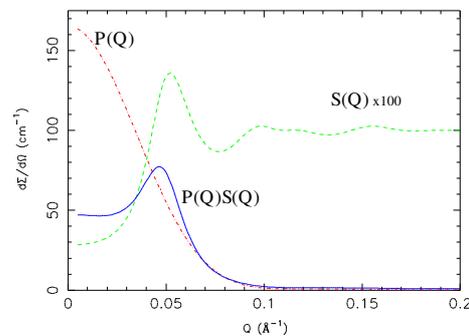
Interacting particles – S(Q) in more detail

$I(Q) = P(Q) \times S(Q) = \text{Form Factor} \times \text{Structure Factor} + \text{BKG}$

where S(Q) can be calculated for hard spheres, charged spheres etc.

As volume fraction increases I(Q) is pushed down at small Q until it becomes a “Bragg” peak at  $d = 2\pi / Q$

e.g. 26 % vol hard sphere S(Q) of  $R = (40 \text{ \AA} \text{ core} + \text{matched } 15 \text{ \AA} \text{ shell})$  with polydispersity  $\sigma/R_{\text{bar}} = 0.15$  ( $\Delta\rho = 6 \times 10^{10} \text{ cm}^{-2}$ )



### S(Q) for interacting particles in solution

“Measure S(Q)”, assuming P(Q) constant using a series of concentrations, “divide by most dilute P(Q)”.

But P(Q) for micelles, polymers etc. often changes ! Better to fit SANS data (over a wide Q range), which shows where S(Q) → 1 and P(Q) can be trusted.

Monodisperse **Hard Sphere S(Q)** - analytic equation, depends on Diameter  $\sigma$  and Volume fraction  $\eta$ . “Works” for (slightly) anisotropic particles. [more examples later]

Modifications to hard sphere can add attractive or repulsive square well potential ( e.g. Sharma & Sharma square well).

Full maths for **polydisperse hard spheres** solved by van Beurten & Vrij.

**Charged particle S(Q) can be VERY strong, even at low volume fractions. Important to know about this (if only because we will measure some examples this week !)**

e.g. “**Hayter & Penfold model**” needs diameter  $\sigma$ , volume  $\eta$ , the charge on the particle (surface potential) and  $\kappa = 1/r_D$  the “inverse Debye length”.



### Aside - Debye Length – for charged particle interactions

**Debye length** is such that the effective strength of the charge falls off by  $1/e = 1/2.718$ .

Adding more ions (salt) makes the Debye length shorter, weakens S(Q) and makes it more like “hard sphere”.

For simple solutions Debye length may be calculated:

$$r_D^2 = \frac{\epsilon_0 K_r RT}{2\rho N_A^2 e^2 I} \quad \text{Ionic strength} \quad I = \frac{1}{2} \sum (m_+ z_+^2 + m_- z_-^2)$$

e.g. 1:1 electrolyte, at 0.1 molal in water at 25°C (e.g. approx 0.1M NaCl)

$$r_D^2 = \frac{(8.85 \times 10^{-12} \text{C}^2 \text{N}^{-1} \text{m}^{-2}) 78 (8.31 \text{JK}^{-1} \text{mol}^{-1}) (298 \text{K}) (10^{20} \text{\AA}^2 \text{m}^{-2})}{2(1000 \text{kg} \cdot \text{m}^{-3}) (6.02 \times 10^{23} \text{mol}^{-1})^2 (1.6 \times 10^{-19} \text{C})^2 (0.1 \text{mol} \cdot \text{kg}^{-1})}$$

$$r_D = 9.6 \text{\AA}, \quad 1/r_D = 0.10 \text{\AA}^{-1}$$

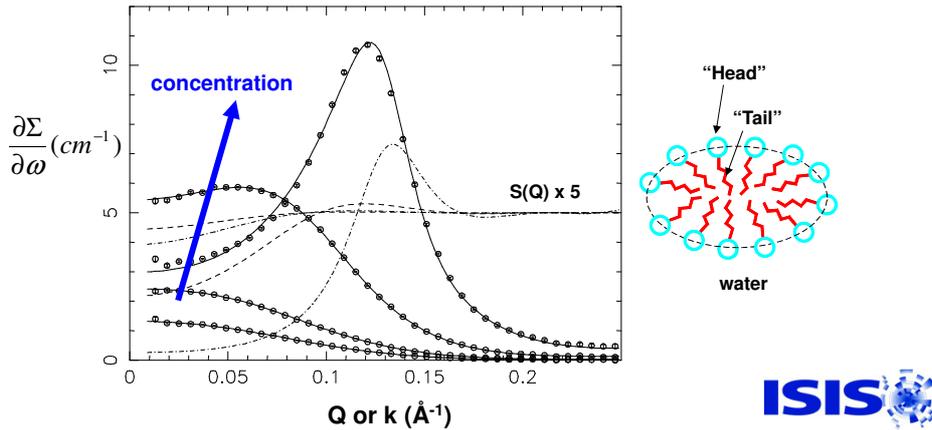


**Example: DDAO Micelles - size, shape & interactions**

*N,N*-dimethyldodecylamine-*N*-oxide (DDAO) or lauryldimethylamineoxide (LDAO) or  $C_{12}AO$  is  $C_{12}H_{25}NO(CH_3)_2$

Data and fits at 29, 7, 1.8 & 0.9 % vol. “non-ionic” needs “charged sphere”  $S(Q)$  !  
 Core radius  $\sim 16.5 \text{ \AA}$ , head group shell  $\sim 2 \text{ \AA}$  ( or  $3.8 \text{ \AA}$  if add 4 water per head),  
 axial ratio  $X \sim 1.7$ , aggregation number  $\sim 103$ , “charge” per head  $\sim 0.7$

D.J.Barlow, M.J.Lawrence, T.Zuberi, S.Zuberi & R.K.Heenan, *Langmuir* **16**(2000)10398-10403.



**$S(Q)$  for Fractal aggregates or pores ?**

$I(Q)$  from “Fractals” give straight line regions on log-log plot (but so do some other scattering laws !)

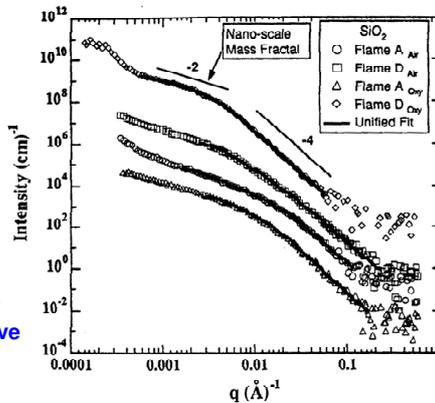
Lots of examples – rocks, coal, cement, zeolites, silicas etc.

Volume or Mass Fractals give  $Q^{-d}$  where  $d$  ranges:

- $d = 1$  – thin rods,
- $d \sim 1.8$  diffusion limited aggregation ( particles stick on first contact )
- $d \sim 2.1$  reaction limited aggregation ( some relaxation after sticking)
- $d = 3$  perfectly rough,

Surface fractals give  $Q^{-(6-d)}$  where  $d = 2$  - smooth i.e.  $Q^{-4}$  Porod law up to  $d = 3$  - perfectly rough.

Other scattering laws also give power laws in  $Q$  !!! Diffuse interfaces can give steeper than  $Q^{-4}$ , to  $Q^{-6}$

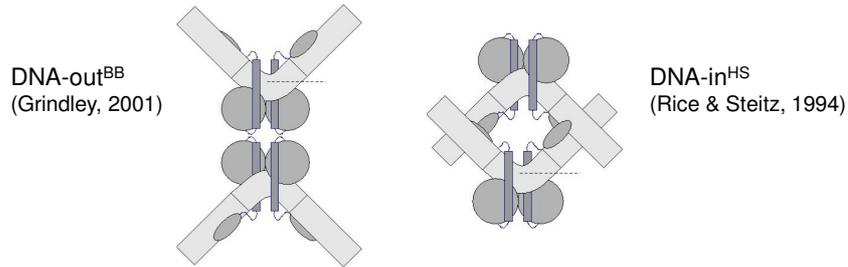


Example: fumed silica aggregates  
 J.Hyeon-Lee, G.Beaucage, S.E.Pratsinis & S.Vemury, *Langmuir* **14**(1998)5751-5756  
 SAXS & USAXS of flame generated silica aggregates. Isolated aggregates (can be diluted in solution) of large primary particles  $R \sim 100 \text{ \AA}$ , which can also be imaged by electron microscopy. Small “mass fractal” region, surface fractal at higher  $Q$  for some samples.



**Example - Contrast variation in Biology:  
Tn3 resolvase – DNA complex**

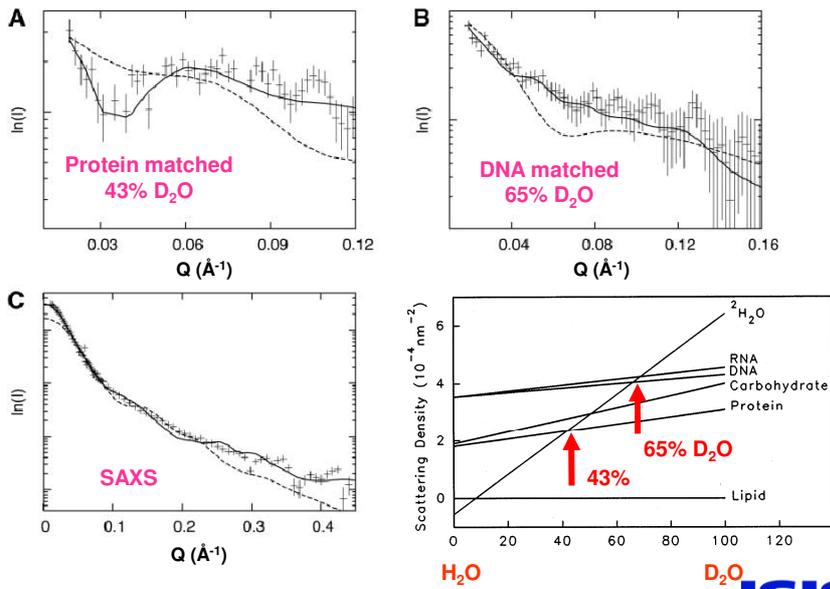
- Tn3 resolvase breaks and re-join DNA strands.
- Is DNA “outside” or “inside” the complex ?
- Used synthetic DNA of known size. SAXS for best overall shape, contrast match protein & DNA with H<sub>2</sub>O/D<sub>2</sub>O for SANS..
- Atomic coordinates available for 3d model.



M.Nöllmann, Jiuya He, O.Byron, & W.M.Stark, Mol. Cell 16 (2004) 127-137



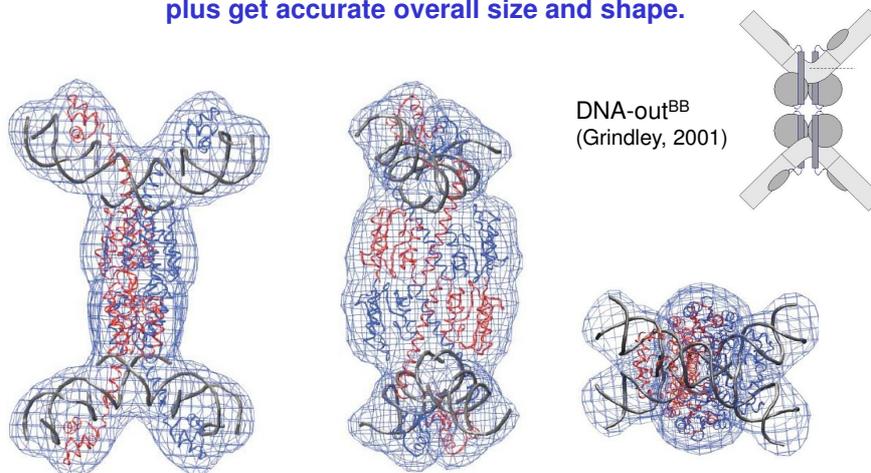
**I(Q) Data: SAXS (2.1 DL), SANS (LOQ),  
best fits: lines DNA-out, dashed DNA-in**



Nöllmann et al. (2004) Mol. Cell 16 127-137



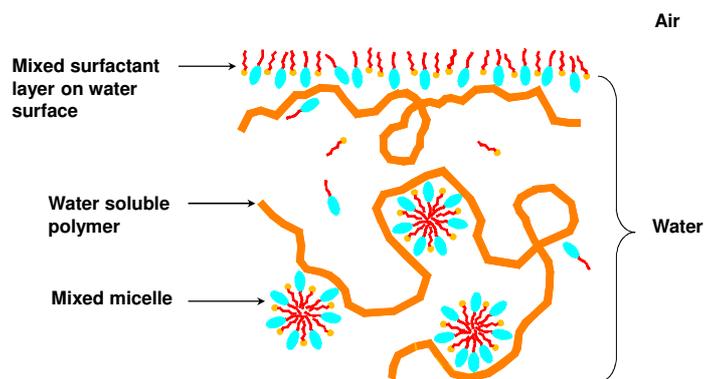
**Answer: DNA is “outside”, plus get accurate overall size and shape.**



Nöllmann et al. (2004) Mol. Cell 16 127-137



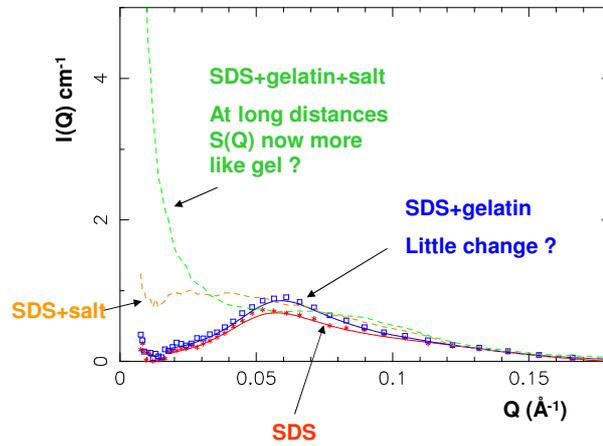
**Example: Polymer/surfactant interactions**



**Neutron contrast variation is the key !**  
**Look at the surface with neutron reflection, the bulk solution with SANS**



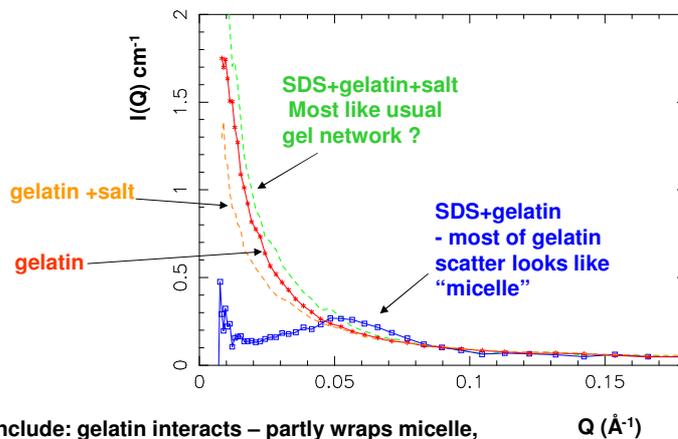
**CONTRAST VARIATION - 2%w SDS, surfactant micelles + 5%w gelatin, polymer gel:**  
**only d-SDS visible, gelatin matched to 40% D<sub>2</sub>O**



R.K.Heenan, S.J.White, T.Cosgrove, A.Zarbaksh, A.M.Howe & T.D.Blake, *Progress in Colloid & Polymer Science* **97**(1994)316-320,  
 T.Cosgrove, S.J.White, A.Zarbaksh, R.K.Heenan & A.M.Howe, *Langmuir* **11**(1995)744-749,  
 T.Cosgrove, S.J.White, A.Zarbaksh, R.K.Heenan & A.M.Howe, *J.Chem.Soc. Faraday Trans.* **92**(1996)595-599.



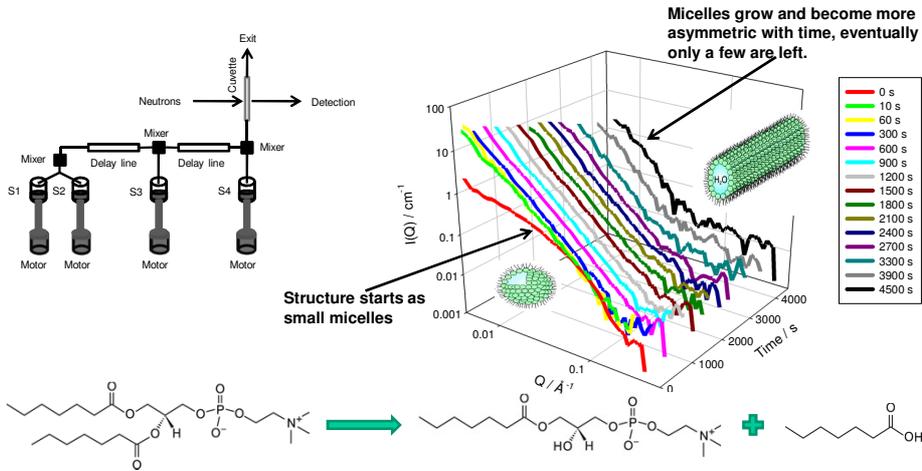
**CONTRAST VARIATION - SDS, surfactant micelles + gelatin, polymer gel:**  
**d-SDS matched to D<sub>2</sub>O, only gelatin visible**



**Conclude: gelatin interacts – partly wraps micelle, long range structure dominated by charged micelle S(Q) until add salt when gelatin network dominates.**



Stopped-Flow (in Event Mode) DHCP + enzyme, J.Lawrence et.al. (Kings College, London)



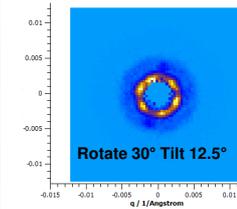
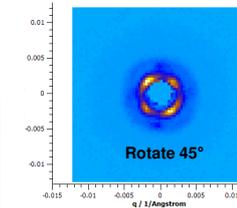
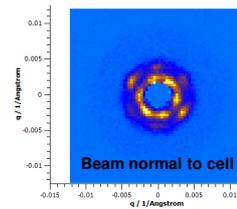
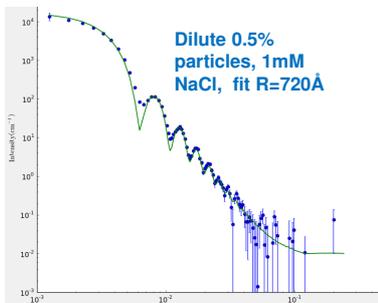
- Lipid DHCP is a model for cell membranes. Enzyme cuts one tail off DHCP to give lysolecithin, which dissolves, and heptanoic acid which remains in the micelle but causes a shape change.
- Here cycled 6 times, showing 10sec time slices from event mode data. Other systems have achieved 0.5sec in single shot.
- Event mode allows time binning choice after the expt.



Sans2d – crystallography with 1.4 micron “atoms”. A.Rennie & M.Helsing (Uppsala)

- Understanding the physics of flowing colloidal particles is important for many industrial processes.
- Here near monodisperse 1.4 micron diameter polystyrene particles at 8% in water crystallise into domains a few mm in size.
- By rotating and rocking the colloidal crystal in the neutron beam the nature of the packing (fcc, hcp, bcc) and stacking faults can be revealed.
- Data was collected to very small Q at 12m sample to detector on Sans2d with neutrons of wavelength 1.75 to 12.5Å.

SANS from 8% particles



## Useful references

NOTE many text books and lecture courses focus on deriving all the equations – we have not done that here

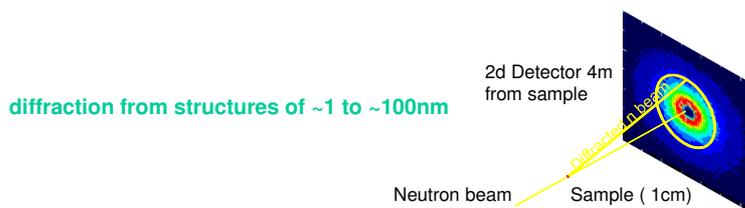
Always look in research papers for a better understanding (though some authors may not be as good as others ...).

[www.isis.stfc.ac.uk](http://www.isis.stfc.ac.uk) , then “groups”, connects to Large Scale Structures group page etc.

[www.smallangle.org](http://www.smallangle.org) has links to FISH, SASVIEW, fibre diffraction software, plus a “useful links” to many other places, particularly the NIST “SANS tutorials”. Further talk to come on “Fitting”.



## Introduction to SANS - Conclusions



- **Dilute particles** - polymers, colloids, proteins etc. - size and shape.
- **Concentrated particles** - interparticle spacings & interaction potential (hard, charged repulsive, soft attractive )
- **Contrast variation** - selective deuteration or swapping H<sub>2</sub>O for D<sub>2</sub>O is a powerful method to highlight parts of a structure - “shell” thickness, composition, density profile, structural relationships in mixed system.
- **SANS** works best on well characterised model systems but “real” materials are also possible!

