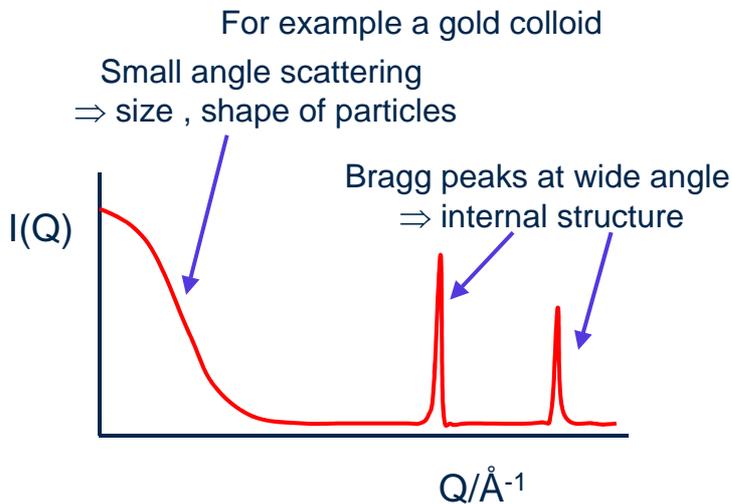


Scattering . 5

SANS and SAXS

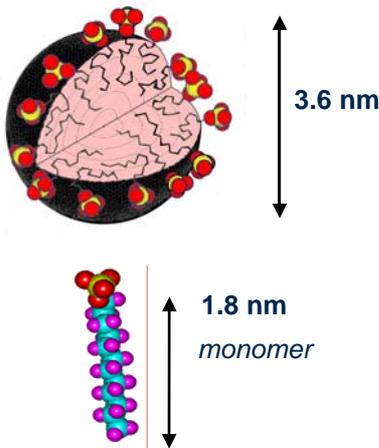
Introduction



Small angle X-ray and neutron scattering have numerous applications in colloid and material science with a spatial resolution from 5 to 50000Å (with USANS).

Typically in a dispersion we may see different structures over different Q regimes. We shall focus on the small-angle regime but in contrast to light scattering we can now visualise much smaller objects at the extreme of the colloidal range.

Micelles



Typically surfactant micelles are ~ 30 to 50Å whereas polymeric micelles can be considerably larger typically 100 to 200Å. Both these size ranges are well within the range of both SAXS and SANS. Contrast however is an important factor. The table below shows the approximate values for sodium dodecyl sulphate and water:

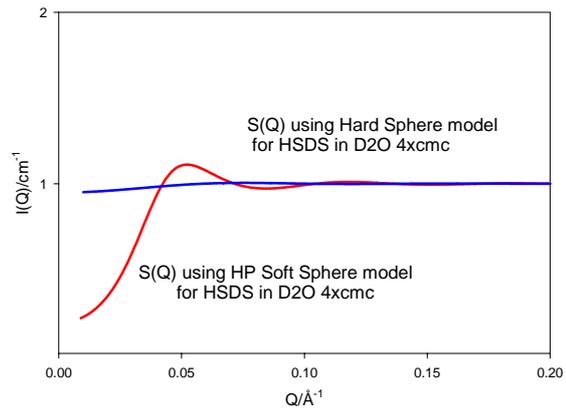
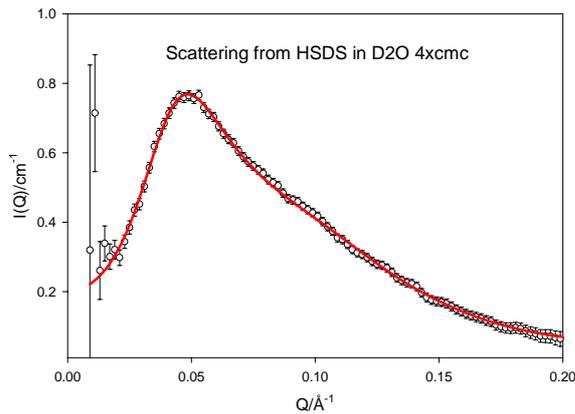
	$\rho_N / 10^{-6} \text{ Å}^{-2}$	$\rho_X / 10^{-6} \text{ Å}^{-2}$
H ₂ O	-0.5	9.4
D ₂ O	6.4	9.4
SDS (H)	0.37	12*
SDS(D)	6.72	12

* not density corrected

From the table it is clear that both X-rays and Neutrons can be used to measure the scattering from SDS micelles. For neutrons HSDS in D₂O is best (why??).

The typical scattering from SDS micelles (the monomers are too small and too dilute to be seen in this experiment) is shown below. The first thing of real note is that the scattering has a maximum even though the micelle volume fraction is ~0.006. A simple hard sphere structure factor would not predict this. The second figure shows the S(Q) from the Lekner hard sphere model we calculated earlier.

The oscillations are very damped and on this scale almost invisible. This tells us that the hard sphere interaction is not strong enough to give an appreciable structure at these dilutions. We clearly need a much more slowly decaying potential. For micelles which are charged the obvious potential is an electrostatic one. This model was developed by Hayter and Penfold. [*Mol Phys* **42** p109-119 1981]



The repulsive potential between the micelles is just an exponential as in the theory of colloid stabilisation.

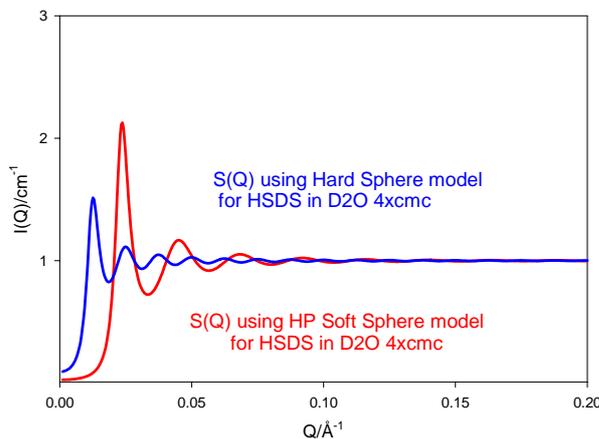
$$U(r) = \pi \epsilon_0 \epsilon \sigma^2 \psi_0^2 \exp(-\kappa(r - \sigma)) / r \text{ for } r > \sigma \quad [5.1]$$

where $\epsilon_0 \epsilon$ is the permittivity of free space x the dielectric constant, σ is the particle diameter. κ is the Debye screening length (the longer κ the more screened the charges are and the faster the potential falls to zero) κ depends directly on the ionic strength of the solution and $1/\kappa$ can be thought of as the 'thickness' of the

electrostatic double layer. $\kappa = \left[\frac{e^2 \sum c_i z_i^2}{\epsilon k_B T} \right]^{1/2}$ [5.2]. NB the ionic strength is defined

as $\frac{1}{2} \sum c_i z_i^2$. [5.3] ψ_0 is the surface potential and can be approximated by

$$\psi_0 = \frac{z_m}{\pi \epsilon_0 \epsilon \sigma (2 + \kappa \sigma)} \quad [5.4] \text{ Essentially we have the potential and if we use the mean}$$



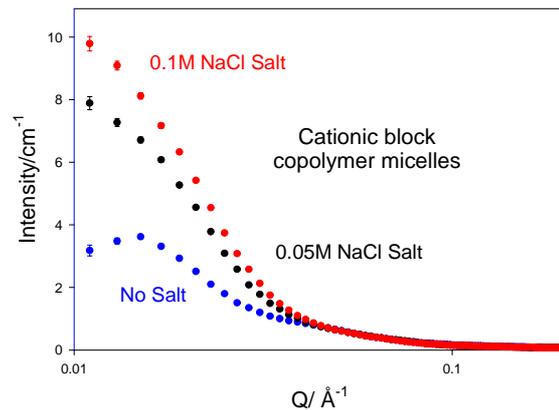
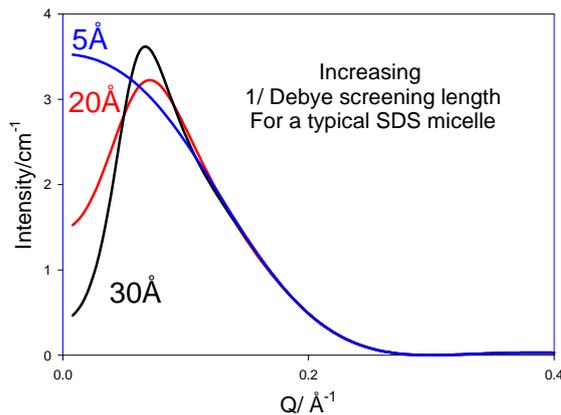
spherical approximation we can find the radial distribution function $g(r)$ This it turns out isn't so easy as we have to solve a many body problem. One approach due to Ornstein and Zernike (See R. Hunter Foundation of Colloid Science Vol 2 p 703)

is to write the correlation function between two particles as the sum of a direct term $c(r)$ between two particles and an indirect contribution that is transmitted via a third

{cf Eqn 3.3 and the paragraph that follows beneath it). The function $c(r)$ is

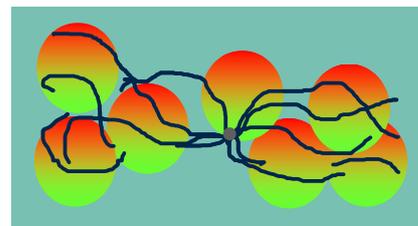
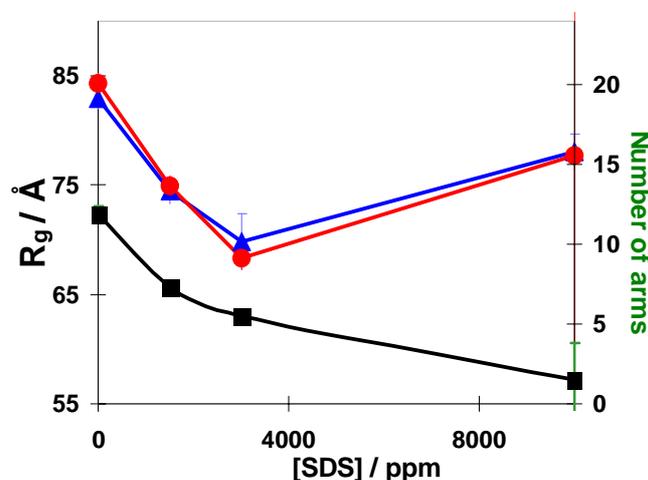
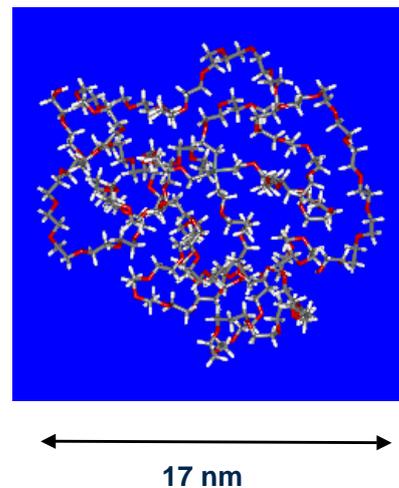
not a closed function but it can be expressed by 'omitting' some unmanageable terms. The mean spherical approximations (MSA) is one of these approaches. The figure above (RHS) shows the $S(Q)$ calculated from the MSA approach, The major feature is that at this dilution the hard sphere interaction is negligible but the longer range exponential function is not. In the figure we compare these two function for a

concentrated dispersion and they clearly approach each other though the soft-sphere approach still decay more slowly. In the experimental data we show a fit to the MSA approximation or SDS at 4 times its cmc. The fit parameters give us the size (38Å) and hence the aggregation number (how?) and an idea of the surface charge. Increasing the ionic strength causes the potential to collapse and the figure below shows the effect on the total scattering. At a high enough ionic strengths the structure factor collapses to unity and the scattering just gives the $P(Q)$ form factor. The experimental data on the RHS shows this effect for a block copolymer micelle.



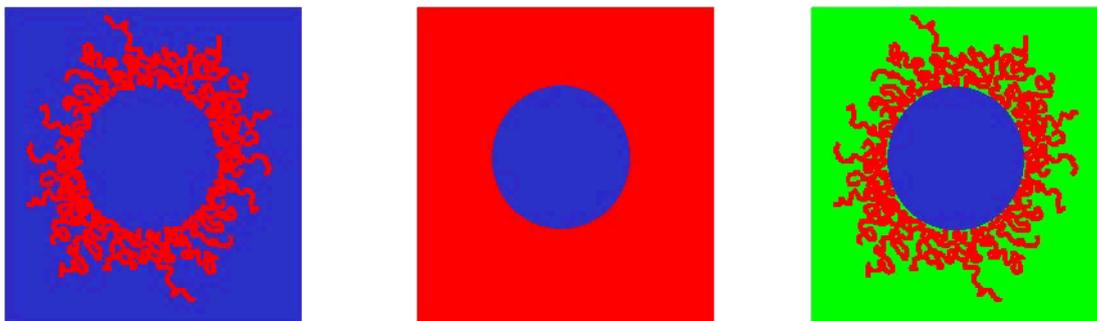
Stars

All shapes have characteristic form factors and for star polymers the two main parameters are the number of arms and the radius of gyration. [Ref Langmuir (1999), 15(24), p8376 1999] The arms of the star can be decorated by micelles of SDS. So we can follow the change in shape of the star as it is decorated. At first it contracts and then it expands as a charged rod! The number of arms decreases from 12 to 2. [See figure below]. The micelles though are invisible (see next section).



Adsorbed polymers

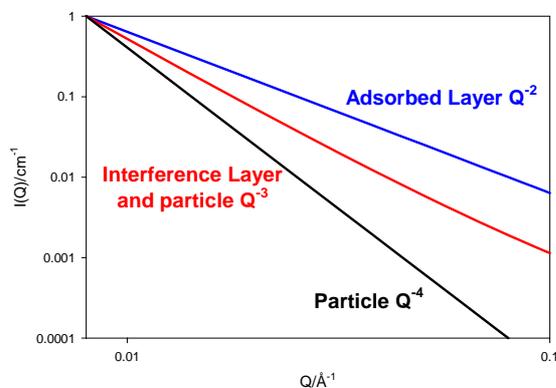
The structure of polymer at interfaces is a very important area of study as polymers are used in a widely to modify the properties of surfaces and dispersions. These applications range from modifying surfaces to prevent protein deposition [for



implants] to controlling the flow of oil in underground wells. These systems are more complex as there are two distinct scattering regimes: the particle (p) and the layer (ℓ). The basic equation for the form factor was given in lecture 2 as [2.11]

$$P(Q) = \sum_I \sum_J \left\langle \frac{\sin(Qr_{IJ})}{Qr_{IJ}} \right\rangle_{\text{orientations}} \quad [2.11]$$

An alternative strategy is to use the so-called scattering amplitudes $A(Q)$ where $P(Q) = A(Q)^2$ [5.5]. (Remember we always measure the intensity not the amplitude). For the system above we have an added complication in that we can get interference



between the particle and the adsorbed layer and so Equation [5.5] is now very important and leads to three terms for the scattering:

$$I(Q) = I_{pp}(Q) + I_{p\ell}(Q) + I_{\ell\ell}(Q) \quad [5.6].$$

Each of these terms must be considered if we wish to learn about the adsorbed layer. The first term is just due to the particle and the third is due to the layer. The middle term is a cross-interference term. Because the scattering length densities for the layer

and particle are different the three terms contain different contrast factors *i.e.*.

$$I_{pp}(Q) = (\rho_p - \rho_s)^2 \phi_p V_p P_{particle}(Q) \quad [5.7] \quad I_{\ell\ell}(Q) = (\rho_\ell - \rho_s)^2 \phi_\ell V_\ell P_{layer}(Q) \quad [5.8]$$

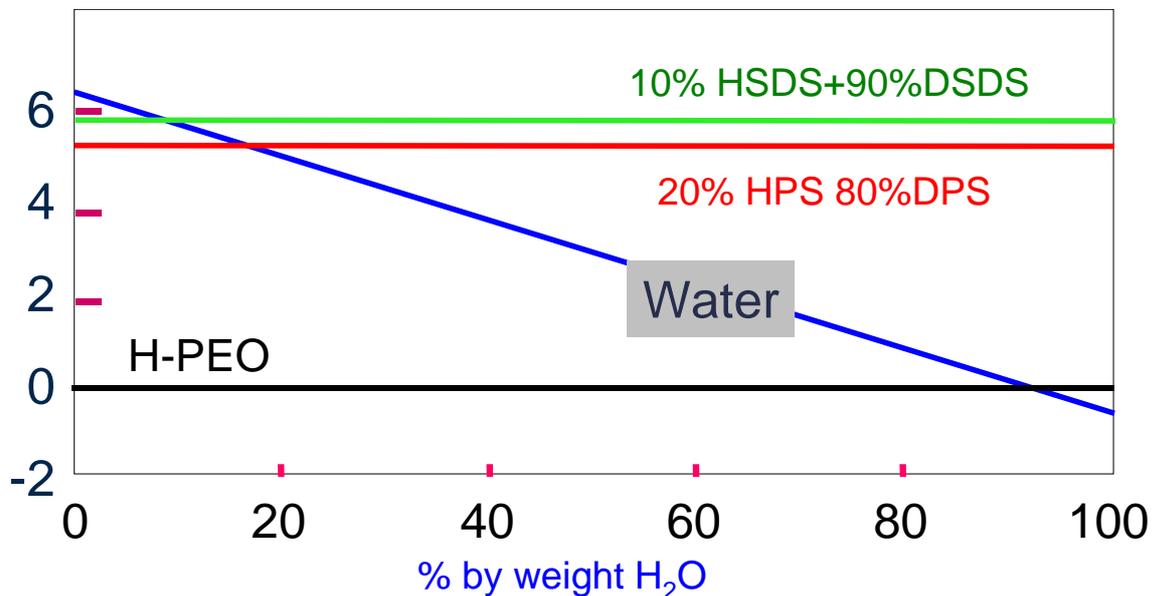
$$\text{and } I_{\ell\ell}(Q) = (\rho_\ell - \rho_s)(\rho_p - \rho_s) \phi_p V_p P_{particle/layer}(Q) \quad [5.9].$$

The basic forms of the three terms are quite complex but have the following basic Q dependencies at low Q as shown in the figure. The shape of the adsorbed layer is manifest in deviations from this basic dependence.

Contrast matching

As can be seen from the above example the scattering is very complex and will contain all three of the functions [5.7], [5.8],[5.9]. In order to simplify this we can use the method of contrast variation.

For neutrons the SLD is strongly isotope dependent. For example as shown in the table =on p 5.1 H₂O and D₂O are very different. This means we can make up water mixtures such that the effective SLD anywhere within this range.



So we can effectively reduce the scattering to either just the particle or just the layer. If we then measure the total scattering at another contrast so they are both visible we can also extract the interference term.

This allows us to make some observations on the structure of the adsorbed layer. One nice example is a polymer brush, where one end of the chain is irreversibly attached to an interface. The volume fraction profile normal to the interface can be obtained directly from the form factor for the layer. [Langmuir (1994), 10(10), 3500-6.

