Diffusion of Surfactant Micelles

An experiment using the Neutron Spin-Echo Spectrometer

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Objectives

1) To understand what is measured by a Neutron Spin-Echo Spectrometer.
2) To understand what are the required measurements and corrections in a complete NSE experiment.
3) To understand the process of reducing the measured "echoes" to obtain the intermediate scattering function.
4) To understand the link between structure and dynamics in colloidal fluids through analysis of experimental data for a system of charged surfactant micelles.

1. Introduction

Surfactants are amphiphilic molecules in which part of the molecule is hydrophilic (likes water) and part is hydrophobic (fears water). In aqueous solution, surfactants aggregate into structures called micelles, where the hydrophobic portions of the molecules are protected from contact with water. Depending on the particular molecular architecture of the surfactant molecule, a variety of microstructures can form. Possible aggregate structures are spherical micelles, worm-like micelles, spherical vesicles, lamellar sheets, or a variety of other topologies. The surfactant aggregates form in order to minimize the free energy of the solution. As a result, they are dynamic (but equilibrium) structures, able to rearrange in response to changing environmental conditions. They also undergo thermal fluctuations and Brownian motion. This experiment will focus on this dynamic behavior of the simplest aggregate microstructure, spherical micelles.

Small-angle neutron scattering (among other techniques) provides a "static" or time-averaged view of the structure of a spherical micelle, which is typically on the order of 5 nm in diameter. SANS measures:

$$I(Q) = n \cdot P(Q) \cdot S(Q)$$

where n is the number density of aggregates and the form factor, P(Q), describes the aggregate's size, shape, and scattering properties. S(Q) is the structure factor for the micelles, which is a Fourier transform of the radial distribution function. The radial distribution function describes the probability of finding the center of another micelle at a particular distance from another micelle. For dilute or non-interacting micelles, S(Q) = 1 (a uniform probability). If there are repulsive interactions between micelles, each micelle will tend to have nearest neighbors in a somewhat well defined location. This results in S(Q) having a peaked shape, indicating liquid-like ordering of the micelles. For stronger interactions, quasi-crystalline order may be seen. As will be seen in the NSE experiment, the presence of interactions between neighboring micelles can have significant impact on the diffusion of individual micelles.

Note that this SANS definition of S(Q) is NOT the same as S(Q,ω) seen in other handouts. The similarity is an unfortunate coincidence between naming conventions of different fields of study. In this handout, S(Q) will always refer to the SANS convention. A general description of SANS and scattering from micelles is given elsewhere [1].

Questions:

• Micelles undergo shape fluctuations on a time scale of microseconds or longer. What effect would these fluctuations have on NSE measurements?

• If your scattering objects are not spherically symmetric, what motions might you be able to measure?

• Undulations and bending or flexing motions can also be measured (surfactant films, polymers etc.). How does the time scale of the motions correspond to the mechanical properties of the material and the physical properties of the solution?

2. Experimental System

This experiment will focus on the anionic surfactant sodium dodecyl sulfate (SDS). In aqueous solution, this surfactant aggregates into spherical micelles comprised of approximately 100 SDS molecules. A small fraction of the sodium ions at the micelle-water interface are free to dissociate from the interface, resulting in a net negative charge on each micelle. Figure 1 shows the structure of the SDS molecule and Figure 2 shows a schematic of the micellar organization. The micelle can be well described by a core-shell structure where the core is comprised of the hydrophobic dodecyl tails of the surfactant. The micelle core is then separated from water by the hydrophilic (charged) headgroups, arranged at the surface of the micelle. The static scattering of the 10 % by weight SDS solution is shown in Figure 3. The most obvious feature of the data is the large interaction peak arising from the screened Coulomb interactions. We will use NSE to investigate the influence of these long-range interactions of the diffusional behavior of the spherical micelles of SDS.

Useful Physical Data for SDS

Formula	$C_{12}H_{25}SO_4Na$
MW	288 g/mol
Density	~ 1 g/ml
SLD core	-0.37×10^{-6} Å^{-2}
SLD shell *	3.2×10^{-6} Å^{-2}
R core	17 Å
R total	27 Å
Concentration	10 wt % in D_2O(= 0.38M)
SLD D_2O	6.35×10^{-6} Å^{-2}
Density D_2O	1.10 g/ml

* The SLD of the shell is highly dependent on the arbitrary division between core and shell, and also on the level of hydration of the ionic groups

Questions:

• Why are we unconcerned with the exact positions of each individual atom, but rather the scattering length density of the aggregate as a whole?

• If the SDS were fully deuterated, and H_2O used as the solvent, would I(Q,0) be the same? Would I(Q,t) / I(Q,0) be the same? Would D_{eff} be the same?

• If H_2O were used as the solvent, what might you change (compared to using D_2O as the solvent) to obtain a more "optimal" detector count rate?

3. Required Measurements

The following sections describe the measurements necessary to obtain the (normalized) intermediate scattering function I(Q,t) / I(Q,0) from a neutron spin-echo measurement.

3.1 Sample scattering

Clearly, the first required measurement is the actual sample of interest. If this doesn't provide sufficient signal, then there's not much point in continuing. Note that "sufficient" has a very liberal interpretation that depends most strongly on what question you hope to answer with your measurement.

Standard sample cells for powders, melts, or liquids (such as a micellar solution) are available. These are constructed of titanium, quartz, and a compatible o-ring material. They have an inside diameter of 40 mm and thickness of 1 mm, 2 mm, or 4 mm. Many other types of sample holders and geometries are possible, provided they are constructed out of non-magnetic materials.

3.2 Instrument resolution

Instrumental resolution must be measured at each of the (Q,t) points where you have measured your sample. This measurement corrects for the imperfections and inhomogeneities in the magnetic fields that can cause a reduction in the measured polarization. Unlike other spectrometers, the instrumental resolution effects in NSE spectroscopy may be simply divided out by measuring the response of a purely elastic scattering sample. It is always advisable to measure the resolution first, rather than run out of time at the end of your experiment.

3.3 Solvent or empty cell scattering

The sample holder (including the pure solvent, if any) must then be measured. This is necessary to insure that the dynamic scattering from everything that's not your sample can be subtracted. This should be measured under identical conditions as your sample scattering.

3.4 Transmissions

Transmissions of both the sample and the solvent (with respect to an empty beam) must be measured, so that the correct fraction of solvent scattering can be subtracted.

3.5 Background

The background count rate on the detector must be measured by blocking the beam at the sample position with a neutron absorbing material. This count rate is due to stray neutrons and electronic noise on the detector. This, in general, is independent of Q and t.

<u>Questions:</u>

• How do you know if your sample scatters "well" or "good enough"?

• Does the non-uniformity of the detector need to be accounted for?

4. Data Analysis

After the data reduction, the intermediate scattering function shows a smooth decay as a function of time. A model must be fitted to the data to obtain the characteristic decay constant. In our experiment, this decay constant corresponds physically to the diffusion of the SDS micelles. The intermediate scattering function I(Q,t) / I(Q,0) may be expanded into cumulants [2,3].

$$\frac{I(Q,t)}{I(Q,0)} = \exp\left\{-\left[c_1(Q)\,t + c_2(Q)\,t^2/2! + \mathbf{K}\right]\right\}$$

For simple diffusion in a non-interacting system, the second-order and higher cumulants are zero, and the well-known result is:

$$c_1(Q) = D_o Q^2$$

In this non-interaction limit, the diffusion coefficient, D_o, can be simply related to the hydrodynamic radius, R_H, of the spherical particle through the Stokes-Einstein relation:

$$D_o = \frac{(1-\phi)k_B T}{6\pi\eta R_H}$$

Where η is the solvent viscosity and $k_B T$ is the thermal energy, and ϕ is the volume fraction of spheres. For a smooth sphere, the hydrodynamic radius is equal to the true radius of the sphere.

At high concentrations, the motion of a single particle initiates motion of the surrounding fluid and neighboring particles. Therefore the dynamics of the particles are coupled over larger distances and the measured diffusion coefficient is not the true value. This measured, or effective diffusion coefficient can be analogously defined:

$$c_1(Q) = D_{eff}(Q)\,Q^2$$

where $D_{eff}(Q)$ is now Q-dependent. Note that a dependency of Q^2 has been explicitly factored out. Through some laborious math and neglecting hydrodynamic interactions, we have the result [4]:

$$D_{eff}(Q) = \frac{D_o}{S(Q)}$$

Using this deceptively simple result, data at each individual Q-value can now be fitted to the simple functional form:

$$\frac{I(Q,t)}{I(Q,0)} = \exp(-D_{eff}\,Q^2\,t)$$

to extract $D_{eff}(Q)$. Plot D_{eff} as a function of Q and compare your result to the model calculation of S(Q) in Figure 4.

Questions:

• What does non-linear data on a plot of ln{I(Q,t) / I(Q,0)} versus time tell you about the higher order cumulants?

• Why can't you measure the diffusion coefficient of individual micelles (in a 10 % solution) by using dynamic light scattering?

• What effect would size polydispersity have on the measured I(q,t)?

5. Conclusion

This experiment involving SDS micelles is not a new study, but rather repeats some of the first measurements ever performed on a spin-echo spectrometer [5]. These experiments were quite significant, however, providing the first (and only) independent measure of S(Q) for a colloidal system. This is significant since SANS can only measure P(Q) or the product P(Q)S(Q). Today it is accepted that the structure of interacting colloidal "liquids" can be treated and calculated as an extension of the statistical mechanical framework for simple atomic fluids. When the NSE experiments were originally performed (approximately 1980), this issue was under serious debate. In fact, there was not even agreement about the structure of a simple spherical micelle. Although NSE measurements do not elucidate the average structure of a micelle, they showed that the mapping of colloidal fluids to simple atomic fluids is appropriate.

6. References

[1] S-H. Chen and T-L. Lin, "Colloidal Solutions", in *Methods of Experimental Physics*, **23B** (1987) pp.489-543.

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[5] J. B. Hayter and J. Penfold, *J. Chem. Soc., Faraday Trans. I*, **77**, (1981) 1851.

[6] J-P. Hansen and J. B. Hayter, *Molecular Physics*, **46** (1982) 651.

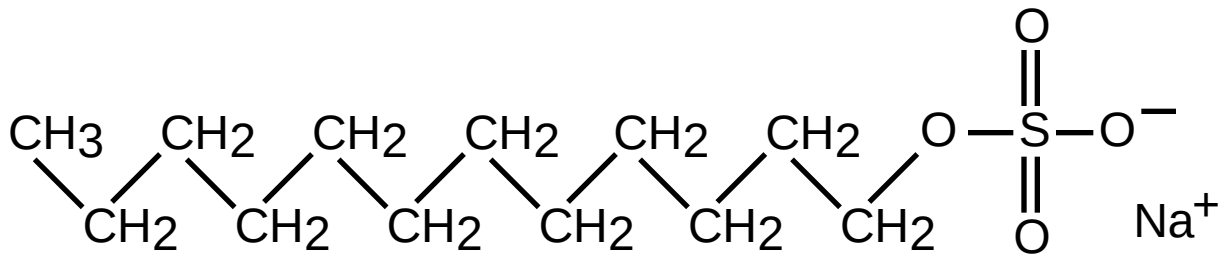

Figure 1: Molecular structure of the anionic surfactant sodium dodecyl sulfate.

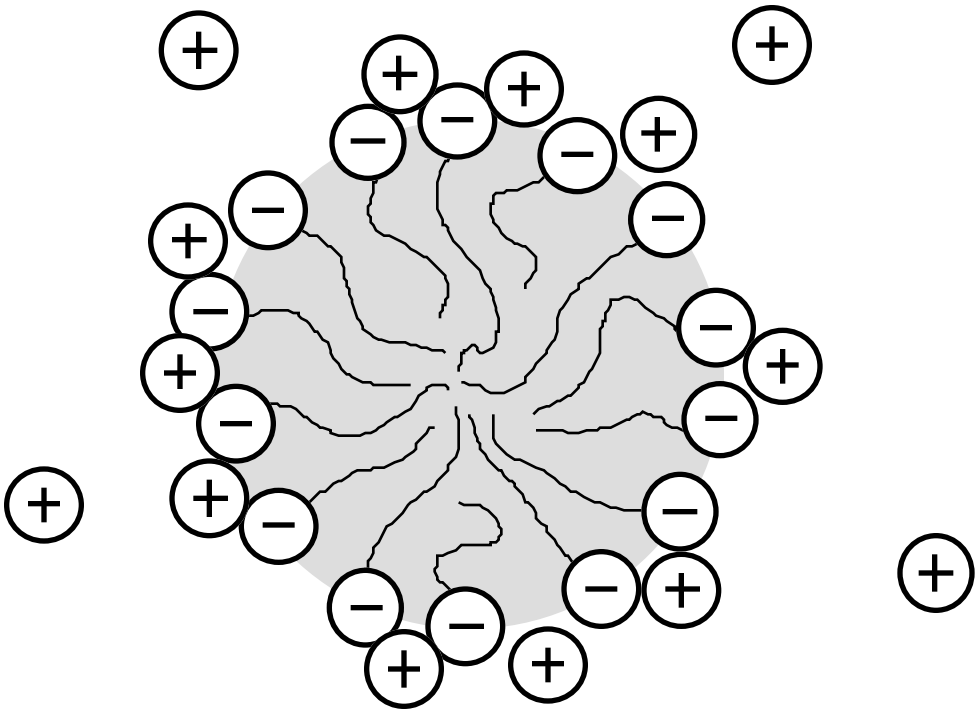

Figure 2: Schematic structure of an SDS micelle, as a slice through the center. The surfactant tails aggregate to form a hydrophobic (oily) core that has minimal surface exposed to the aqueous environment. Approximately 80% of the sodium ions are closely associated with the surface of the micelle, giving the surface a net negative charge. The diameter of the micelle is approximately 50 Å.

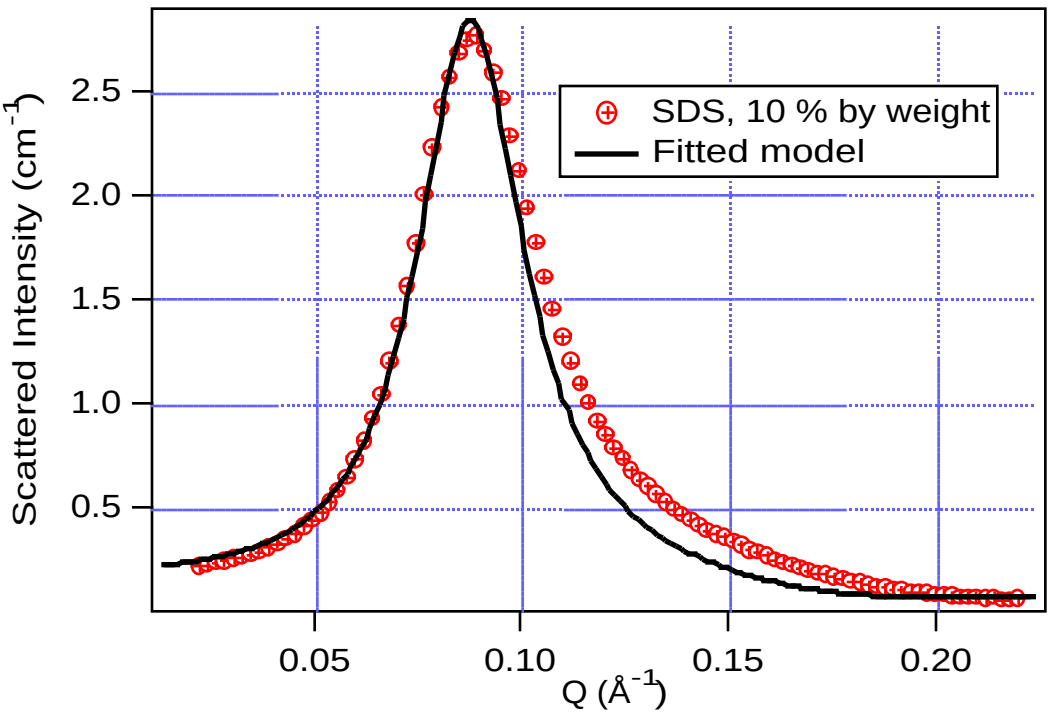

Figure 3: Small-angle neutron scattering data for 10 % by weight SDS micelles in D_2O (= 0.38 mol/l). The open circles are the experimental data, and the solid line is a fitted model using a core-shell structure for P(Q) and screened Coulomb interactions in the model for S(Q) [6]. The mismatch at intermediate Q-values is a consequence of applying a monodisperse model to SDS micelles, which have a size polydispersity of approximately 30 %.

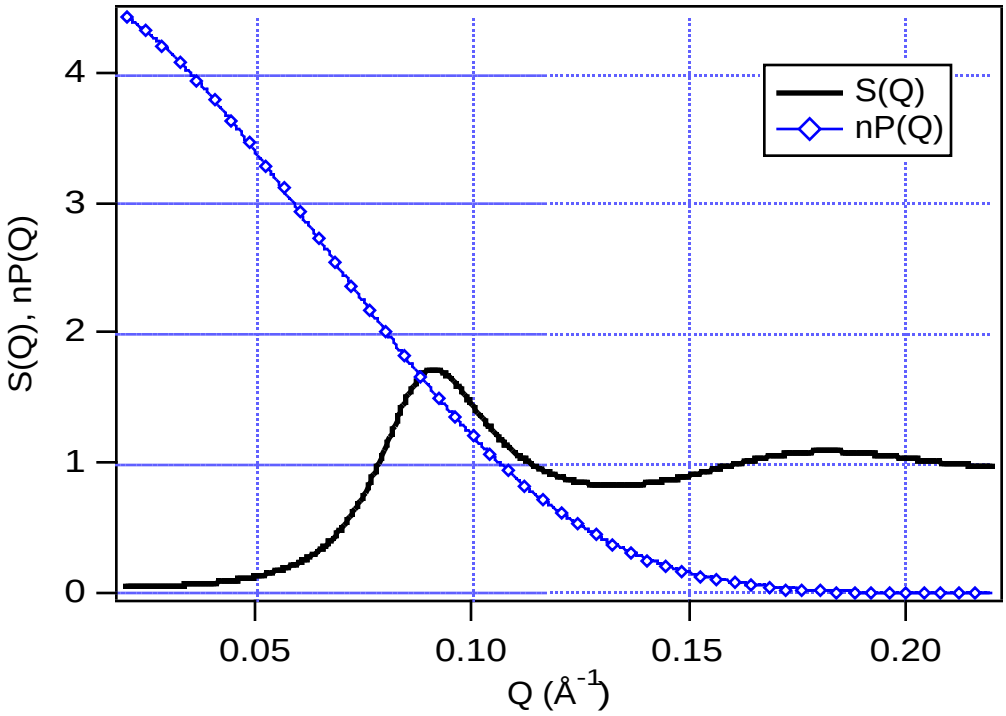

Figure 4: A plot of the separate contributions, nP(Q) (points), and S(Q) (solid line) to the model intensity I(Q) = nP(Q)S(Q).