Diffusion of Surfactant Micelles and Shape Fluctuations of Microemulsion Studied by Neutron Spin Echo

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 surfactant micelles and a ternary microemulsion

1. Introduction

Surfactants are amphiphilic molecules in which part of the molecule is hydrophilic (likes water) and part is hydrophobic (fears water); see Fig. 1. In aqueous solution, surfactants aggregate into structures called micelles. Micelles are closed shape structures where the hydrophilic portions of the molecule are exposed to the surrounding water while the hydrophobic portions are protected from contact with water, as seen in Fig. 1. When dissolved in non-polar organic solvents (hereafter referred simply as oils), surfactants form reversed micelles where the hydrophilic portions are shielded from contact with the surrounding solvent in the interior of the micelles; see Fig. 1. Depending on the particular molecular architecture of the surfactant molecule, a variety of microstructures may be formed. Possible aggregate structures are spherical, cylindrical and 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. An interesting property of the micelles is their ability to solubilize certain amount of solute in their interior which otherwise is not soluble in the solvent. For example, if micelles are formed in *n*-decane, their interior is hydrophilic (because the hydrophilic portions of the surfactant molecules are oriented inward) and small amount of water can be accommodated in the micellar core. As a result the micelles will swell and their size will increase. If we increase the amount of solubilized phase the micelles will evolve into a

microemulsion (it is called microemulsion although the droplet size is below 100 nm) – a thermodynamically stable, isotropic, and optically transparent solution.

Micelles and microemulsions undergo thermal fluctuations and Brownian motion. In the first part of this experiment we will focus on this dynamic behavior of the simplest aggregate microstructure, reverse spherical micelles. Because micelles are very small aggregates, typically in the order of 4 nm in diameter, the motion that we will observe is diffusion. In the second part of this experiment, we will investigate a reverse microemulsion that is prepared with the same surfactant and oil. In addition to the diffusion we will observe shape fluctuations of the microemulsion droplets. To provide strong scattering that originates solely from the surfactant film of our interest we will use deuterated oil and deuterated water, called film contrast. By doing this we will demonstrate the unique abilities of the Neutron Spin Echo (NSE) to probe correlations and dynamics in specifically labeled regions of a larger structure.

During the data analysis we will use some results obtained from small-angle neutron scattering (SANS) that provides a "static" or time-averaged view of the structure of a spherical micelle. SANS measures:

$$I(Q) = n\, P(Q)\, S(Q) \qquad\qquad (1)$$

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 scattering particles, which is a Fourier transform of the radial distribution function. The radial distribution function describes the probability of finding the center of a particle at a particular distance from another particle. For dilute or non-interacting particles, $S(Q) = 1$ (a uniform probability). If there are interactions between particles $S(Q)$ will having a peaked shape, indicating liquid-like ordering. For stronger interactions, quasi-crystalline order may be seen.

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?
> Intramolecular bending or flexing motions of single molecules can be measured (polymers, proteins 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

The surfactant used here as an example of diffusion of reverse micelles and shape fluctuation of microemulsion droplets is sodium bis(2-ethylhexyl)-sulfosuccinate (AOT) dissolved in deuterated n-decane (d-decane, $C_{10}D_{22}$). Figure 2 shows the structure of the AOT molecule. In decane, AOT aggregates into nearly spherical micelles of approximate radius of 2 nm. A concentration of $\phi = 10\,\%$ by volume will be used for this experiment. Deuterated water, D_2O, that has a scattering length density very similar to that of d-decane, will be dissolved in the AOT

micelles to provide film contrast of the microemulsion droplets. These ingredients are mixed at 5.4 % by volume of AOT, 4.6 % by volume of D_2O and 90 % by volume of $C_{10}D_{22}$ so that the volume fraction of the droplets is again $\phi = 0.10$. The microemulsion can be well described by a core-shell structure where the core is comprised of D_2O and the shell is formed by the AOT film.

Table 1. Some important parameters needed for the data analysis

Property @ 25 C	AOT	Deuterated n-decane	Deuterated water
Formula	$C_{20}H_{37}O_7SNa$	$C_{10}D_{22}$	D_2O
MW/ g mol^{-1}	444.6	164.4	20.0
Density/ g ml^{-1}	1.13	0.845	1.1
SLD/ Å^{-2}	~1×10^{-7}	6.54×10^{-6}	6.35×10^{-6}
Viscosity/ cP	-	~0.94	1.096

For AOT/D_2O/$C_{10}D_{22}$ microemulsion: $R_0 = 32$ Å, polydispersity $p = 16$ %

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 AOT were fully deuterated, and $C_{10}H_{22}$ and H_2O used as a solvent and solubilizate, respectively, would $I(Q,0)$ be the same? Would $I(Q,t)/I(Q,0)$ be the same? Would D_{eff} be the same?

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 NSE 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 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 early in the experiment, 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 at the respective wavelength, so that the correct fraction of solvent scattering (echo amplitude) 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.

Questions:

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

Each pixel of the 2-D detector counts neutrons with a slightly different efficiency ($\pm$ 10 %). 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. The intermediate scattering function $I(Q,t)/I(Q,0)$ may be expanded into cumulants [2,3]:

$$\frac{I(Q,t)}{I(Q,0)} = \exp\left[-\left(c_1(Q)t + \frac{c_2(Q)t^2}{2!} + \frac{c_3(Q)t^3}{3!}...K\right)\right] \qquad (2)$$

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

$$c_1(Q) = D_{eff}Q^2 \qquad (3)$$

where $D_{eff}(Q)$ is the effective diffusion coefficient. Hence

$$\frac{I(Q,t)}{I(Q,0)} = \exp\left[-D_{eff}(Q)Q^2t\right] \qquad (4)$$

In the case of diffusion and shape fluctuations, D_{eff} can be written as:

$$D_{eff}(Q) = D_{tr} + D_{def}(Q) \qquad (5)$$

where $D_{tr} = D_{eff}(0)$ is the translational diffusion coefficient, $D_{def}(Q)$ is a diffusion coefficient representative of the droplet shape deformations. $D_{eff}(Q)$ is derived from an expansion of the shape fluctuations into spherical harmonics[4], and will be defined later.

Experiment I. Diffusion of AOT micelles in $C_{10}D_{22}$

In this case we may neglect the shape deformations of the AOT micelles. (why can we do this?) The diffusion coefficient $D_{eff}(Q) = D_{tr} = D_{eff}(0)$ can be related to the hydrodynamic radius R_H of the spherical particle through the Stokes-Einstein relation:

$$D_0 = \frac{(1 - \phi)k_B T}{6\pi\eta R_H} \qquad (6)$$

where η is the solvent viscosity, $k_B T$ is the thermal energy, and ϕ is the volume fraction of micelles. 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: Through some laborious math and neglecting hydrodynamic interactions, we have the result [5]:

$$D_{eff}(Q) = \frac{D_0}{S(Q)} \qquad (7)$$

where D_{eff} is now Q-dependent. We will fit the $I(Q,t)/I(Q,0)$ data from the micelles to a single exponential decay, Equation 4, to determine a single parameter, D_{eff}. Does D_{eff} have any q-dependence?

Experiment II. Shape fluctuations in AOT/D_2O/$C_{10}D_{22}$ microemulsion

For the microemulsion case, only the surfactant shell has scattering contrast. The motions that are visible are the translation of the shell, and undulations of the shell. According to [6,7] $D_{eff}(Q)$ is given by:

$$D_{def}(Q) = \frac{5\lambda_2 f_2(QR_0)\langle|a_2|^2\rangle}{Q^2\left[4\pi\left[j_0(QR_0)\right]^2 + 5f_2(QR_0)\langle|a_2|^2\rangle\right]} \qquad (8)$$

$$f_2(QR_0) = 5\left[4j_2(QR_0) - QR_0 j_3(QR_0)\right]^2 \qquad (9)$$

where λ_2 is the damping frequency of the droplet deformation, $j_n(x)$ is the n-th order spherical Bessel function, $<|a_2|^2>$ is the mean square displacement of the 2nd-mode spherical harmonic ($n=2$) and R_0 is the mean droplet radius. Further λ_2 is given by [8]:

$$\lambda_2 = \frac{k}{\eta R_0^3} \left[4\frac{R_0}{R_s} - 3\frac{\overline{k}}{k} - \frac{3k_B T}{4\pi k} f(\phi) \right] \frac{24\eta}{23\eta' + 32\eta} \tag{10}$$

where k is the bending modulus of elasticity of the AOT film, $\overline{k}$ is the saddle-splay modulus of the AOT film, R_s is the spontaneous curvature of the AOT film, $f(\phi)$ is the mixing entropy per droplet as a function of the volume fraction ϕ, η is the bulk viscosity of deuterated n-decane (outside the droplets), and η' is the bulk viscosity of deuterated water (inside the droplets). Eq. 10 must be combined with Eq. 11:

$$p^2 = \frac{k_B T}{4\pi} \left[6(2k + \overline{k}) - 8k\frac{R_0}{R_s} + \frac{3k_B T}{2\pi} f(\phi) \right]^{-1} \tag{11}$$

where p is the polydispersity of the microemulsion droplets:

$$p^2 = \sqrt{\frac{\langle R^2 \rangle}{\langle R \rangle^2} - 1}, \qquad R_0 = \langle R \rangle \tag{12}$$

Finally, for the bending modulus of elasticity of the AOT film we obtain:

$$k = \frac{1}{48} \left[\frac{k_B T}{\pi p^2} + \lambda_2 \eta R_0^3 \frac{23\eta' + 32\eta}{3\eta} \right] \tag{13}$$

After fitting $I(Q,t)/I(Q,0)$ to a Q-dependent single exponential to determine $D_{eff}(Q)$, using Eq. 8 we can fit $D_{eff}(Q)$ to obtain λ_2 and $<|a_2|^2>$ as a fitting parameters. Then using the polydispersity found from the SANS measurements, the bending modulus of elasticity of the AOT film, k, can be calculated.

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 and the shape fluctuations of microemulsion droplets by using dynamic light scattering?
   What effect would size polydispersity have on the measured $I(Q,t)$?
   Explain the Q-dependence (or lack of Q-dependence) of D_{eff} of the AOT micelles.
   Can you see rotational motions of the spherical shell of the AOT microemulsion?
   Does the value of k make any sense?

5. Conclusion
This experiment involving AOT micelles and microemulsion is similar to one of the first measurements ever performed on an NSE spectrometer using surfactants [9]. These early experiments were quite significant, however, to demonstrate that the behavior of colloidal fluids

could be treated as an extension of 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. Today, NSE can measure the dynamics in surfactant and membrane systems, and other complex fluids, over time and length scales that are inaccessible to other techniques.

6. References

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Surfactant molecule

Hydrophobic tail   Hydrophilic head

Spherical micelle   **Inverse spherical micelle**

Microemulsion droplet   **Inverse microemulsion droplet**

Solubilized
water

Water

Surfactant   Solubilized organic   Surfactant   Organic
                           molecules (oil)   solvent (oil)

Figure 1. Illustration of micelles and microemulsions

Figure 2. Molecular structure of AOT and n-decane