RAPID COMMUNICATIONS

PHYSICAL REVIEW E VOLUME 52, NUMBER 1 JULY 1995

Bulk and surface correlations in a microemulsion

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(Received 22 February 1995)

Small angle neutron scattering and neutron reflectivity are used to study the bulk and surface structure of water–octane–tetraethylene glycol monodecyl ether ($C_{10}E_4$) bicontinuous microemulsions. When the hydrophilicity and hydrophobicity of the surfactant monolayers in the microemulsion are balanced, the surface correlation length is found to be significantly larger than its bulk analog. Varying the spontaneous curvature of the monolayers greatly influences the surface structure of the microemulsion while having a relatively slight effect on the bulk correlation function. These observations are explained using a Ginzburg-Landau theory.

PACS number(s): 68.45.−v, 61.12.Ex

Surfactants frequently self-assemble in solutions of water and oil to form monolayers which exhibit some remarkable interfacial properties [1]. The two-dimensional spreading pressure of the surfactant molecules reduces the effective interfacial tension to nearly zero so that the statistical fluctuations of the monolayer are controlled by curvature energies [2]. An expansion of the surface free energy to leading order in the curvature tensor leads to a phenomenological description of the monolayer in terms of bending rigidities and a spontaneous curvature [3]. Under conditions when these parameters are small enough, an optically isotropic phase known as the bicontinuous microemulsion may form. In this phase, surfactant monolayers separate randomly interpenetrating water and oil domains as evidenced by freeze-fracture electron microscopy and scattering experiments [4–6].

The addition of excess water and oil to a microemulsion can result in a three-phase equilibrium with the microemulsion situated between a lower water-rich phase and an upper oil-rich phase. The interfacial tension between the lower and upper phases is ultralow and is typically smaller than the sum of the water-microemulsion and oil-microemulsion interfacial tensions so that the microemulsion does not wet the water-oil interface [7]. Reducing the amphiphilicity of the surfactant by adding another component or by approaching a critical end point induces a transition where the middle phase spreads and wets the water-oil interface [8]. The relationship between amphiphilic strength of the surfactant and the wetting behavior of the microemulsion has been explored theoretically using lattice models, Ginzburg-Landau expansions, and Monte Carlo simulations [9,10]. A common feature of these theories is the oscillatory order parameter profile in the microemulsion near interfaces and the important role it plays in determining the wetting properties of the microemulsion.

Recent scattering experiments have systematically measured the bulk correlations in microemulsions as functions of surfactant chain lengths, concentration, and temperature [11,12]. By mapping the location of the macroscopic wetting transition with respect to the measured amphiphilicity of the surfactant, it was found that wetting takes place well on the structured side of the disorder line in accordance with theory. Implicit in these and other studies is the assumption that the interfacial structure of a microemulsion can be quantitatively related to its bulk correlation function. In this Rapid Communication, we use neutron scattering techniques to measure both the bulk and surface structure of bicontinuous microemulsions and demonstrate that they need not be equivalent to each other. We also show how varying the spontaneous curvature of the surfactant monolayers in the microemulsion affects the bulk and surface correlations quite differently.

Shown in Fig. 1 is the bulk small angle neutron scattering (SANS) intensity plotted as a function of the wave vector transfer Q for a microemulsion composed of water, octane, and tetraethylene glycol monodecyl ether ($C_{10}E_4$). The inset displays the phase diagram for this system as a function of surfactant concentration and temperature. Deuterium oxide, n-octane and $C_{10}E_4$ were weighed and mixed to yield a solution with water volume fraction $\phi_w=43.4\%$, oil volume fraction $\phi_o=43.4\%$, and surfactant volume fraction $\phi_s=13.2\%$. The measurement was taken at temperature $T=23$ °C on the 30 m NG7 SANS instrument at the National

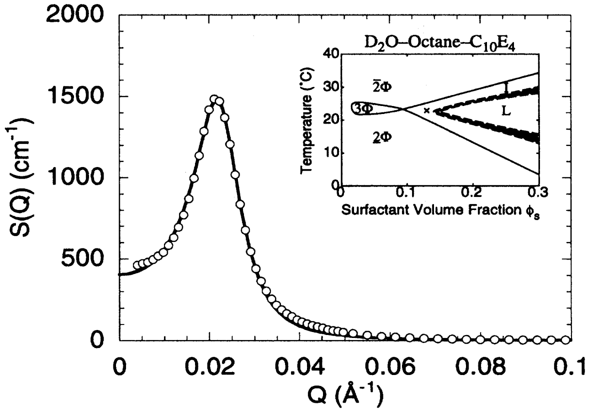

FIG. 1. Bulk small angle neutron scattering (circles) from a microemulsion and the fit (line) corresponding to $d_b=278$ Å and $\xi_b=168$ Å. The inset shows the location of this sample within the $\phi_w=\phi_o$ phase diagram for this system.

Institute of Standards and Technology (NIST) with wavelength $\lambda=5.0$ Å and wavelength spread $\Delta\lambda/\lambda=14\%$. The efficiency of the detector was determined using the incoherent scattering of H_2O and the experimental data were corrected for empty cell and background scattering and normalized to an absolute scale using the supplied calibration standards.

The difference in scattering length density between D_2O and the oil and surfactant was chosen to highlight the correlations between water domains in the microemulsion. The resulting measured scattering pattern can then be interpreted using a simple Ginzburg-Landau theory [13]. Letting the scalar field $\psi(\vec{r})$ denote the local concentration difference between water and oil in the microemulsion, the Hamiltonian can be written as

$$\mathcal{H}_0\{\psi(\vec{r})\}=\int [a_0\psi^2+a_2(\nabla\psi)^2+a_4(\nabla^2\psi)^2]\, d^3\vec{r}. \tag{1}$$

The large internal area of surfactant monolayers separating distinct water and oil regions in the microemulsion translates into favorable gradient interactions ($a_2<0$) and gives rise to the prominent peak displayed in the scattering at $Q\approx 0.02$ Å^{-1}. Since Eq. (1) is harmonic, the bulk correlation function is easily calculated analytically:

$$\langle \psi(0)\psi(r)\rangle = \exp(-r/\xi_b)\,\frac{\sin(2\pi\, r/d_b)}{(2\pi\, r/d_b)}, \tag{2}$$

where $d_b=2\pi[\frac{1}{2}\sqrt{a_0/a_4}-\frac{1}{4}a_2/a_4]^{-1/2}$ is the characteristic size of the water and oil domains in the microemulsion and $\xi_b=[\frac{1}{2}\sqrt{a_0/a_4}+\frac{1}{4}a_2/a_4]^{-1/2}$ is the length scale over which these domains are correlated. Equations (1) and (2) give a simple prediction for the theoretical scattering intensity from the microemulsion which is then convolved with the instrumental resolution function and fit to the experimental data in the vicinity of the scattering peak in Fig. 1. For this particular microemulsion, the bulk parameters are found to be $d_b=278\pm 2$ Å and $\xi_b=168\pm 7$ Å. The uncertainty in these parameters can mostly be attributed to smearing effects due to relaxed collimation and wavelength spread of the neutron beam [14].

Ginzburg-Landau theory has also been used to predict the structure of microemulsions near interfaces [10]. The presence of a planar interface at $z=0$ can be described by additional surface fields in the Hamiltonian which give rise to interfacial structure in the microemulsion:

$$\mathcal{H}_s=\int\left[s_1\psi(x,y,0)+s_1'\frac{\partial\psi}{\partial z}(x,y,0)+s_2\psi^2(x,y,0)\right]dx\,dy. \tag{3}$$

Taking these surface effects into account produces an oscillatory one-dimensional order parameter profile in the microemulsion of the following form:

$$\langle\psi(z)\rangle\sim\exp(-z/\xi_s)\cos\left(\frac{2\pi z}{d_s}+\varphi\right). \tag{4}$$

According to this theory, the surface correlation length ξ_s and domain size d_s should be identical to the corresponding parameters in the bulk correlation function, ξ_b and d_b. The phase factor φ is needed to accommodate different surface field strengths s_1, s_1', and s_2.

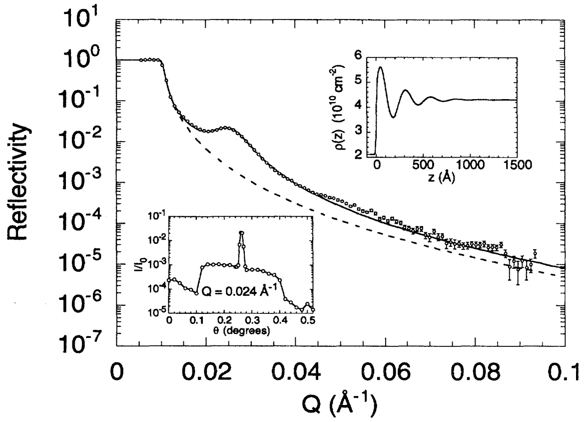

FIG. 2. Neutron reflectivity (circles) from the microemulsion at a hydrophobic silicon interface. The lower inset shows a rocking curve taken at $Q=0.024$ Å^{-1}. The dashed line is the calculated reflectivity if the microemulsion were structureless and the solid line displays the fit corresponding to the scattering length density profile shown in the upper inset ($d_s=270$ Å and $\xi_s=217$ Å).

The BT7 neutron reflectometer at NIST was used to experimentally determine the structure of the microemulsion near a solid-liquid interface. Reflectivity has proven to be a highly sensitive probe of surface structure in complex fluid systems [15]. The liquid microemulsion sample was sandwiched between a Teflon holder and a single crystalline silicon block which was treated with 1,1,1,3,3,3–hexamethyldisilizane in order to make its surface very hydrophobic and induce strong surface ordering fields in the microemulsion. Monochromated neutrons ($\lambda=2.37$ Å, $\Delta\lambda/\lambda=1\%$) were then sent through the silicon block, reflected off of the silicon-microemulsion interface, and subsequently counted with a He^3 detector. The advantage of this experimental setup is that it eliminates problems with sample evaporation that were present in an earlier vapor-liquid study [16].

Figure 2 displays the neutron reflectivity data from a microemulsion with the same component concentrations and at the same temperature as the bulk sample in Fig. 1. In order to obtain a measurable critical reflection edge, D_2O and a mixture of hydrogenous and perdeuterated octane were used so that the solution had an average neutron scattering length density of $\rho=4.3\times 10^{10}$ cm^{-2}. A rocking curve taken at $Q=0.024$ Å^{-1} shows the measured specular signal in addition to background small angle scattering from the bulk microemulsion. The dashed line in Fig. 2 illustrates the expected reflectivity if the microemulsion had not exhibited any structure at the silicon interface. In order to model the experimental data, we use the functional form in Eq. (4) and an effective interfacial roughness of 7 Å due to an adsorbed surfactant monolayer at the hydrophobic silicon surface. The theoretical reflectivity curve is then calculated from this surface profile using a recursion relation [17]. After resolution effects are taken into account, the resulting fit is shown as the

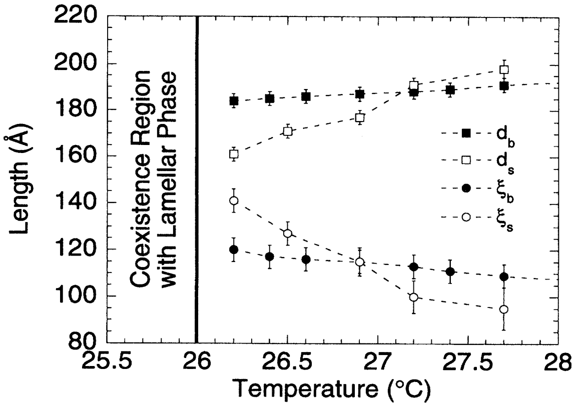

FIG. 3. Bulk and surface domain sizes and correlation lengths as a function of temperature for microemulsions with concentrations $\phi_s=20\%$ and $\phi_w=\phi_o=40\%$.

solid line in Fig. 2 and the corresponding scattering length density profile is plotted in the upper inset.

The fit to the measured neutron reflectivity in Fig. 2 corresponds to a surface domain size $d_s=270\pm2$ Å and correlation length $\xi_s=217\pm6$ Å. The slight discrepancies between the experimental data and the theoretical fit at $Q\approx0.05$ Å^{-1} are due to higher-order Fourier modes in the scattering length density profile and do not significantly affect the determination of the surface domain size and correlation length. Compared with the bulk parameters found from Fig. 1, d_s is slightly smaller than d_b while ξ_s is quite a bit larger than its respective bulk value ξ_b. These results are surprising and demonstrate that the interfacial structure of a microemulsion cannot be quantitatively inferred from its bulk correlation function. This could indicate the importance of van der Waals forces between the surface and the microemulsion as seen in wetting studies of these systems [12]. Long range interactions would then need to be added to the surface Hamiltonian in Eq. (3). However, another possibility is that the harmonic description in Eq. (1) is inadequate as evidenced by the fluctuation-driven first-order lamellar phase transition [18]. Since the water and oil domains in this microemulsion are strongly segregated, the order parameter $\psi(\vec{r})$ and its variations are not small and the effects of higher-order terms need to be seriously considered.

These particular samples were measured at a temperature where the microemulsion is almost exactly balanced between its hydrophilic and hydrophobic tendencies. The symmetry at this temperature is evidenced by the phase diagram in Fig. 1 and also by a direct measurement of the near-zero mean curvature of the surfactant monolayers [19]. We now consider the effects of spontaneous curvature on the bulk and surface structure of these microemulsions. Raising the temperature causes the surfactant monolayers to become more hydrophobic and preferentially curve toward the water domains. Figure 3 shows the results of similar bulk and surface measurements for microemulsions with concentrations $\phi_s=20\%$ and $\phi_w=\phi_o=40\%$ in the temperature range $26<T<28$ °C. The bulk and surface lengths show the same general trends as the first-order lamellar transition is approached with decreasing temperature: both domain sizes decrease while the correlations lengths increase. However, it is apparent that spontaneous curvature modifies the surface lengths to a far greater extent than it affects the bulk parameters.

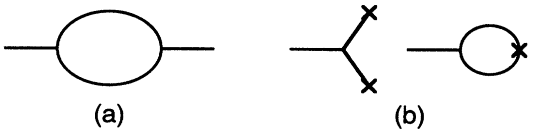

FIG. 4. (a) Second-order curvature corrections to the bulk correlation function. (b) Curvature terms can couple to linear order with various surface fields in the calculation of the microemulsion surface structure.

To understand this phenomenon, it should be noted that the Hamiltonian in Eq. (1) contains only terms that display $\psi\rightarrow-\psi$ symmetry. Since microemulsions can break water-oil symmetry through the presence of spontaneous curvature, additional terms of odd order will be needed. Because the overall volume fractions of water and oil in these microemulsions are the same, the Ginzburg-Landau expansion should continue to exhibit a minimum at $\psi=0$ which precludes the term linear in ψ. The Laplacian term $\nabla^2\psi$ is completely integrable and is equivalent to the surface field associated with s_1'. Thus, the lowest-order terms that need to be considered are cubic ones:

$$\mathcal{H}_c=\int [c\psi^3+c'\psi^2(\vec{\nabla}^2\psi)]\, d^3\vec{r}. \tag{5}$$

Since the microemulsions of Fig. 3 exhibit small mean curvatures that are less than the inverse domain size [19], the effects of these terms can be treated perturbatively. In the calculation of the bulk correlation function and $\langle\psi(\vec{q})\psi(-\vec{q})\rangle$, the most important terms diagrammatically are of the form shown in Fig. 4(a) [20]. These corrections are quadratic in c and c', and for small spontaneous curvatures they will have only a slight effect on the bulk correlation function. On the other hand, terms due to spontaneous curvature can enter the surface profile calculation for $\langle\psi(q_z)\rangle$ to linear order as illustrated in Fig. 4(b). The cubic terms in Eq. (5) couple with surface field terms denoted with ×'s to yield corrections on the order of cs_1^2, $c's_2$, etc. These diagrams explain the significant influence spontaneous curvature has on renormalizing the surface domain size and correlation length in the microemulsion while at the same time only weakly perturbing the parameters in the bulk correlation function.

To make this analysis of curvature corrections more quantitative, additional measurements of the bulk and surface structure in microemulsions will have to be made. Neutron reflectivity allows us to easily probe solid-liquid interfaces and opens up the possibility of systematically modifying the treatment of the silicon surface and studying the effects varying surface fields have on the surface structure of the microemulsion. The present study has established that the interfacial structure of a microemulsion is not directly related to its bulk correlation function. Spontaneous curvature affects the bulk and surface correlation lengths quite differently and illustrates the necessity of considering higher-order terms in the Ginzburg-Landau Hamiltonian. Work is currently underway to better understand the nature of these terms and exactly how they influence the bulk and interfacial properties of these complex liquids.

We gratefully acknowledge support from the DOE (DE–FG02–90ER45429) and the NSF (DMR–9122444). We would also like thank J. Barker at NIST for help with the SANS experiments and M. Kardar and B. Carvalho at MIT for useful suggestions and comments.

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