Direct Measurement of Structural Forces in a Supermolecular Fluid

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The force as a function of separation between two mica surfaces immersed in a reversed micellar system sodium bis(2-ethyl hexyl) sulfosuccinate (AOT)/water/heptane was measured for a range of concentrations with size and polydispersity of the micelles constant. A piezoelectric bimorph force sensor was used which produces a charge proportional to the load. At low micellar volume fractions the force is a purely attractive van der Waals interaction, while at higher concentrations, the force-distance profile oscillates with a period equal to the size expected for the micelles. The measured interaction is lower in magnitude than theoretical values for a monodisperse hard-sphere fluid between hard walls.

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The interactions between aggregates of amphiphilic molecules are of fundamental importance in governing the macroscopic properties of microemulsions. A great deal of effort has been directed at the elucidation of the structure and the dynamic behavior of reversed micelles in water-in-oil (W/O) microemulsions [1-7], but the only information about the nature of the interactions between micelles has been inferred from scattering experiments [8]. The direct measurement of the force acting between two macroscopic surfaces immersed in the system using a surface apparatus [9,10] can provide some clues as to the nature of the interaggregate interactions [11]. Moreover, the influence of the macroscopic surface on the behavior of the system can also be obtained from the force profile, and is of importance in understanding the behavior of fluids close to a wall and in thin films confined between two walls.

We report here measurements of the forces between two molecularly smooth mica surfaces immersed in the W/O microemulsion of AOT/water/heptane. In this system reversed micelles consist of spherical water cores, each coated by a monolayer of AOT, immersed in a continuous oil phase [12-16]. A large single-phase region in the phase diagram exists [17] and the micelles are spherical with a polydispersity between 20% and 35% up to quite high micellar volume fractions. The mean radius of the droplets is known to depend only on the water-to-surfactant ratio [13,14,18] $X=[\mathrm{H_2O}]/[\mathrm{AOT}]$ and so the amount of oil can be varied without changing the size or the polydispersity of the micelles. At a fixed molar ratio $X=20$ the effect of varying micellar volume fraction was studied.

All solvents were freshly distilled prior to use and water was doubly distilled. AOT (Fluka AG purum) was purified [19] by dissolving in methanol, washed with petroleum spirit several times, filtered through a Nucleopore 0.2-μm filter and dried to constant weight. For each volume fraction studied the solutions were prepared simply by adding water to a weighed solution of AOT in heptane. An optically clear solution was formed after shaking for less than 1 min.

Force measurements were carried out with the latest version of the surface force apparatus [10]. Two partly silvered mica sheets are glued, silvered side down, onto the surface of two silica cylinders (radius $R\approx 2$ cm), aligned at right angles, one mounted on a piezoelectric tube, the other on a new type of force sensor [20]. The silvered surfaces form an optical cavity into which white light is directed and the surface separation determined to ± 0.2 nm from the wavelengths emerging [21]. When the slope of the force between the surfaces is higher than the spring constant a mechanical instability occurs and parts of the force profile become inaccessible [9]. A new force measurement technique [20] which offers increased resolution with a spring constant 5 times higher than the spring normally used in the apparatus was used so as to be able to cover the entire force-distance curve. A piezo ceramic element (bimorph) is used as the force measuring spring. When the device is strained a charge develops and this is detected and amplified by custom-made electronics. With this technique the spring deflection (to within 0.03 nm corresponding to a force resolution of better than 10^{-8} N) and surface separation can be measured independently. All parameters of the surface force apparatus are controlled or measured with a computer system. The technique provides the surface separation calculated from the voltage which depends linearly on the spring deflection (i.e., the bimorph signal), and the displacement of the driving piezoelectric tube as a function of the time. From this set of data a continuous measurement of force as a function of surface separation becomes available [20] and both repulsive and attractive parts of the force profile are measurable with great accuracy.

The measurements presented are conducted using the dynamic method [22], the upper surface being driven toward the other at constant speed. The force-distance profile measured is the sum of both the hydrodynamic force and the static surface force [22]. By recording this profile at a large number of driving speeds, and assuming that the static surface force is the same at a given separation for each speed, then the static and hydrodynamic components can be extracted [23]. This procedure has been carried out for all the measurements; a full discussion is beyond the scope of this Letter and will be presented elsewhere [23].

Force-distance curves for the range of micellar volume fractions 0.6% to 29% have been studied, but only the lowest and highest micellar volume fractions are presented here (Fig. 1). For all volume fractions a steep repulsive force barrier is encountered at 4.1 nm. At low volume fraction ($\Phi < 3\%$) the force between the surfaces is monotonically attractive up to this hard wall and the attraction follows the power law expected for a van der Waals interaction. As Φ is increased the force begins to oscillate, the strength of the oscillations increasing with the micellar volume fraction—this is most clearly seen at $\Phi = 29\%$. The periodicity of the oscillations (≈ 8 nm) is close to the expected diameter of the micelles [13,18]. The hard wall encountered at 4.1 nm can be disrupted under sufficient loads (400–500 mN/m); the strength increases with the micellar volume fraction. Analysis of the refractive index obtained from the fringes of equal chromatic order [21] at separations less than 4.1 nm indicates that the hard wall is composed of a thin water film (1.5 nm thick) coating each mica surface, and a layer of AOT molecules (1.2 nm thick) separating the water film from the oil environment.

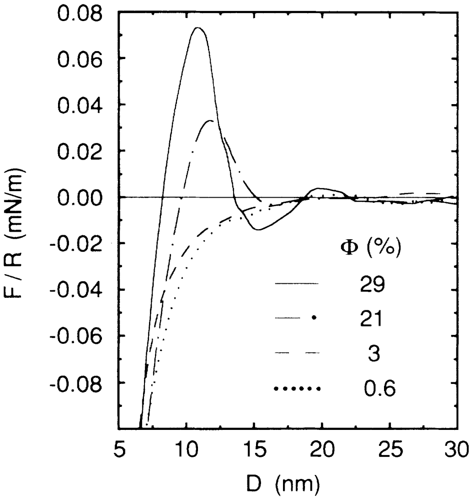

FIG. 1. Measured force F (normalized by the mean radius of curvature R of the surfaces) as a function of surface separation D between crossed mica cylinders immersed in an AOT/water/heptane reversed micellar microemulsion. The molar ratio of water to AOT is fixed at 20 for all the volume fractions studied. As the micellar volume fraction is increased, the oscillations of the force-distance profile are more pronounced. The periodicity is equal to the expected size of the micelle diameter (≈ 8 nm) [13,18]. The final contact between the surfaces is shifted out from bare mica contact in air (≈ 4.1 nm) due to a thin water film (1.5 nm thick) coating each mica surface and a layer of AOT molecules.

The oscillations observed are due to the presence of micelles between the surfaces. A phase change induced by the presence of the hard walls is ruled out. It is difficult to imagine another phase which would give rise to a linear increase in the peak amplitude of the oscillations with increasing micellar volume fraction where the periodicity remains constant (see Fig. 1). For instance, if one supposes that the profile is due to the formation of a layered structure then a decrease in periodicity would be expected with increasing volume fraction since the ratio of surfactant to water is kept constant. X-ray reflectivity has revealed an electron-density profile consistent with one or two layers of micelles away from an isolated interface [24].

Oscillatory force profiles have been observed in many fluids [25,26]. In simple fluids, the force varies between attraction and repulsion with a periodicity equal to the mean diameter of the liquid molecules and can extend up to ten molecular diameters in range [25]. The oscillatory force profile reflects the free energy of packing of the molecules between the surfaces. At separations equal to an integral number of molecular diameters the molecules can pack with a density which exceeds bulk. At nonintegral spacings the molecules cannot pack without the presence of voids and the density is lowered. The force between the walls is a consequence of this density variation [27]. The same situation exists for the packing of micelles between two hard walls.

The net pressure between two plates immersed in a bulk solution is proportional [28] to $n(0,D) - n(0,\infty)$, the difference between the contact number density of particles next to the walls when the surfaces are separated by D and when they are at infinite separation. By using a kind of superposition approximation [29] for the density profiles, the density $n(z,D)$ at a distance z from one of the walls and $D-z$ from the other wall in a slit of width D can be obtained:

$$n(z,D) = n(z,\infty)n(D-z,\infty)/n_{\mathrm{bulk}}\,, \tag{1}$$

where $n(z,\infty)$ is the density at z away from a single wall and n_{bulk} is the bulk density of the fluid in equilibrium with the inhomogeneous fluid in the slit. It follows from the contact value theorem [28] that

$$\begin{aligned} P(D) &= k_B T[n(0,D) - n(0,\infty)] \\ &= k_B T\left[\frac{n(0,\infty)n(D,\infty)}{n_{\mathrm{bulk}}} - n(0,\infty)\right]. \end{aligned} \tag{2}$$

The superposition approximation allows the pressure between two plates to be calculated from the density profile away from one isolated plate. The most general way to obtain such a profile is to perform a simulation; however, this is very cumbersome. A much simplier way is to use the Percus shielding approximation instead [30]. It has been shown that this procedure gives fairly accurate pressure-distance relationships at least up to a volume fraction of 30% and for slit widths larger than 1.1 hard-sphere diameters [30].

The measured force between the two curved mica surfaces can be converted into pressure by taking the derivative of the interaction free energy E with respect to the distance ($E=2\pi F/R$ from the Derjaguin approximation [31]). To compare the measurements with theory the van der Waals contribution must be removed. This was done simply by subtracting the force obtained at low volume fractions. Although dispersion and structural forces are not strictly additive, in this case due to the changing composition of the thin film as the surface separation varies, this approximation is reasonable as the van der Waals contribution is small compared with the total force at separations beyond 6.8 nm (the peak of the first oscillation). A comparison of the data treated in this way and the hard-sphere calculation is shown in Fig. 2. At 29% volume fraction the hard-sphere calculation gives an oscillatory pressure profile which is much larger than the measured one but much better agreement can be obtained with a volume fraction of 18%–21%. This discrepancy could be due to either error in the estimation of the volume fraction or the fact that the micelles are not interacting as true hard spheres.

Calculation of the micellar volume fraction is open to some ambiguity. The volume fraction of 29% was obtained from the density of the components and the weight fraction of the mixture. A volume fraction of about 25% can be estimated from the aggregation number and the measured size [13,18] of the micelles and assuming that all the surfactant molecules aggregate to form micelles. This is probably an upper bound because some surfactant is likely to be dissolved in the oil or water medium. Hard-sphere calculation at this volume fraction still overestimates the measured interaction pressure. This difference may be due to the polydispersity in size or the fact that micelles are not interacting as true hard spheres. The effect of polydispersity has been investigated for simple fluids. A mixture of two fluids, with different molecular diameters (equivalent to increasing the polydispersity of a single-component fluid), shows oscillations which are very much reduced in comparison with those in the pure fluid [32]. Because the AOT micellar system is polydisperse ($\approx 25\%$) the oscillations are expected [33] to be smaller in magnitude and range when compared with a monodisperse hard-sphere fluid. Nevertheless, the measured pressure profile shows considerable hard-sphere character. At first sight this result is quite surprising, as micelles are dynamic structures which are constantly rearranging with only a very short lifetime. The measurements are performed with macroscopic surfaces; as a result the force is an average across a large surface area and so, even though the micelles are transitory in nature, they give rise to a force-distance profile which is dominated by hard-sphere interactions.

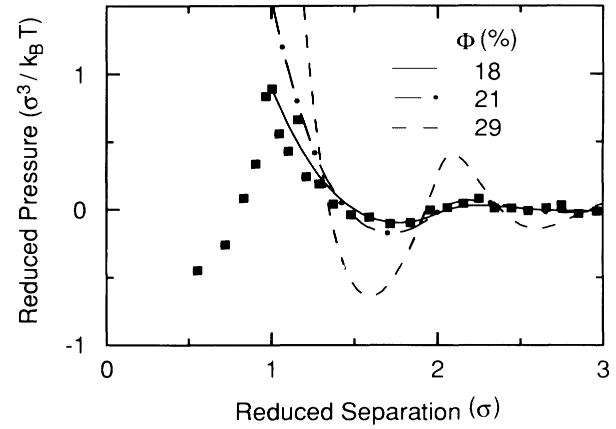

FIG. 2. Pressure profile for a hard-sphere fluid (in inequilibrium with a bulk fluid of hard spheres, diameter $\sigma=7.8$ nm) confined between two flat hard walls as a function of their separation. The experimental pressure for the highest volume fraction (squares, 1 data point in 10) was calculated by taking the derivative with respect to the distance of the force-distance profile in Fig. 1 and by using the Derjaguin approximation [31] which relates the normalized force to the interaction free energy between flat plates of unit area. The theoretical profiles (lines) were obtained from the density profile away from an isolated wall calculated using the Percus shielding approximation [30] and the superposition approximation to calculate the pressure between two plates [29]. The slit width and the pressure are expressed in a reduced scale.

Of particular interest is the force in the region where the micelles are completely depleted from the region between the surfaces. In this regime an attractive interaction exists due to the imbalance in osmotic pressure. Quantification of this effect from the data is, however, impossible because of the strong van der Waals contribution and the uncertainty in the measurements due to hydrodynamics at these small separations. Structural forces have recently been observed in a charged micellar systems both with the surface force apparatus [34] and in soap film thinning experiments [35]. In the direct force measurement experiments the effect of depletion of the micelles from between the surfaces have been accurately quantified [34]. These results open the way for a great deal of further work, as many interesting phase transitions and percolation phenomena in AOT systems can be studied.

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