Letter to the Editor

# Forces between two oil drops in aqueous solution measured by AFM

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## Abstract

The surface and hydrodynamic forces between individual oil droplets in solution can provide insight into both emulsion stability and processes such as drop coalescence in liquid–liquid extraction. We present the first measurements of the interaction forces between alkane droplets in aqueous solution using atomic force microscopy. The radii of the droplets were well below the capillary lengths for the system, thus gravity effects are negligible, and interfacial tension and interaction forces governed the system behavior. The effects of modulating electrostatic double-layer interactions and interfacial tension through the presence of an anionic surfactant are demonstrated. Challenges in interpretation of the force data due to drop deformation are also discussed. A range of drop approach and retract speeds was used to determine the regime where hydrodynamic drainage effects had significant impact on the measurement.
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## 1. Introduction

The uses of emulsions are commonplace in a variety of domestic and industrial applications. For example, the formulation, stability, and rheological properties of emulsions (dispersions of immiscible liquid drops in another liquid) are of great concern in the food processing industry for products ranging from ice cream and milk to salad dressings. However, there has been little direct study of interparticle forces within these systems. An understanding of the interaction forces between liquid–liquid interfaces, where attraction between droplets can lead to kinetic instability and coalescence in emulsions, is vital in order to predict and model emulsion stability in processing and storage situations.

Measurements of colloidal forces at deformable interfaces are complicated by the deformation of the interfaces making both measurement and interpretation more difficult than for rigid systems. Some research has been undertaken on the interaction between liquid interfaces using other techniques, notably the liquid surface force apparatus (LSFA) [1–3] and a novel approach using magnetic particles dispersed inside an emulsion droplet [4–8]. These tech-

niques have their strengths and weaknesses. The LSFA has some limitations with respect to distance resolution, and the droplet sizes employed in the magnetic particle method result in such high Laplace pressures that they behave as nearly rigid particles.

There is a growing body of experimental studies utilizing atomic force microscopy (AFM) measurements between a rigid probe and a liquid–liquid interface and theoretical analyses to interpret the measurements in light of the interfacial deformation [9–19]. This measurement technique has now been extended, for the first time, to measure the interaction of two oil drops. This is a situation more relevant to emulsion stability, where the effects of a variety of amphiphilic species on emulsion stability can be examined. The drop size employed in the AFM experiments is below the capillary length of the system, but large enough to encounter deformation. The capillary length, $\lambda$, is defined as

$$\lambda = \left( \frac{\gamma}{\Delta \rho g} \right)^{1/2}, \tag{1}$$

where $g$ is gravity, $\gamma$ is surface tension of the fluid interface, and $\Delta \rho$ is the difference in density between the fluid phases [13]. The AFM can be considered as a dynamic measurement technique, allowing one to probe not only static, but hydrodynamic effects in drop–drop interactions as well.

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In the work presented here we examine the interactions between two droplets with AFM as well as the effects of hydrodynamic forces as two drops approach and retract from each other.

## 2. Experimental method

A Digital Instruments multimode AFM and Nanoscope IIIa AFM controller were used for all experiments. Park Scientific cantilevers were sputter-coated with chromium and then gold and then hydrophobized according to [20]. Cantilever spring constants were measured according to the method of [21]. The bottom drop (in Fig. 1) was immobilized on a Melinex polymer film (semicrystalline PET film with no additives) via the procedure outlined in [18]. The second oil drop was attached to a gold-coated cantilever in aqueous solutions of sodium dodecyl sulfate (BDH Laboratory Supplies, SDS) using a step-motor-controlled syringe (World Precision Instruments, Inc.) injecting nanoliter volumes of $n$-decane (Aldrich Chemical) through a glass capillary (inner diameter $\sim 10$ μm). All solutions contained a background electrolyte of 1 mM sodium nitrate. Each solution was given 30 min to thermally equilibrate before any data were taken. The oil drops were positioned first using the coarse stepping motor, and then using the piezo tube fine control. The force curves (an approach and retract force–distance cycle) were taken at a series of scan rates with approach speeds varying from 80 nm/s to 7 μm/s. Force curves were measured between the drop and the underlying rigid Melinex film at the 10 mM SDS concentration as well. At the end of the experiments, the drops were flushed from the system and force curves between the PET substrate and cantilever were

recorded to determine the detector sensitivity of the AFM photodiode. The undistorted radii of the drops on the cantilever and the substrate were estimated from CCD camera measurements to be 35 and 50 μm, respectively.

The AFM photodiode voltage was converted to cantilever deflection using the detector sensitivity determined at the end of the experiment and then converted to force via $F = k_c \Delta d$, where $k_c$ is the spring constant of the cantilever. A simple distance balance of the AFM measurement shows that the piezo motion, $\Delta l$, is equal to the changes in deflection, $\Delta d$, separation, $\Delta D$, and deformation, $\Delta z$, of the system [11,13,19]. Using this distance balance, the deflection was subtracted from the piezo motion, leading to

$$\Delta X = \Delta l - \Delta d, \tag{2}$$

where $\Delta X$ is the change in separation distance and deformation. Defined in Fig. 1, $X$ is the distance from the bases of both drops. The definition of $X$ is somewhat arbitrary because only changes in $\Delta X$ are measured and an absolute measure of the distance $X$ is not known. It is standard practice to set an origin for $X$ and display $F(\Delta X)$ relative to this origin [13,19]. In this respect, the curves have been shifted for convenience to clearly show specific features.

The measured force is commonly normalized by the system curvature; for rigid interfaces this is the radius of the probe, but the choice of the system curvature for this measurement is not obvious because both the interfacial curvatures change with separation. The undistorted cantilever drop radius is not the correct measure of the curvature of the system, but it provides an approximate value to scale the force for this type of measurement.

## 3. Results and discussion

The interaction between two droplets at approach speeds of 80 nm/s is shown in Fig. 1 at below and above the CMC of SDS at 1 and 10 mM. The decrease in slope with concentration is most likely caused by the decrease in interfacial tension (33.4 to 8.6 mN/m [17]) which is consistent with the behavior of a single oil drop interacting with a rigid probe particle [10,11,13,16,22]. The repulsion between the drops is expected from the adsorption of the SDS onto the decane–water interfaces, while the range of the repulsion decreases with increasing ionic strength, as expected with electrostatic double-layer repulsions. The logarithm of the forces is also plotted in Fig. 1 as well, and it is clear that there is no single linear region due to the deformation of the interfaces. Previous work with a rigid particle and an oil drop has shown that for sufficiently small drops with high enough Laplace pressures, there may exist a region where the deformation is small and the limiting Debye length can be obtained [12,18]. The regressed limiting Debye lengths for the 1 and 10 mM curves in Fig. 1 are 22 and 15 nm; the expected values based on the solution ionic strengths (from the SDS and sodium nitrate concentrations) are 6.8 and 2.9 nm, respectively. This
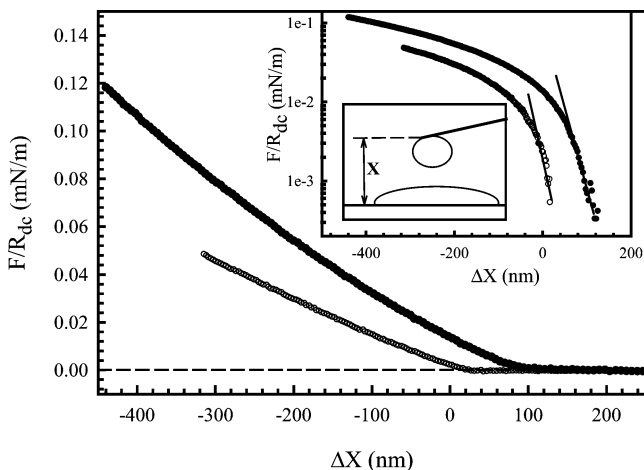


Fig. 1. The interaction force between two decane drops measured using AFM at 1 (open circles, bottom) and 10 mM (filled circles, top) SDS and 1 mM NaNO₃ background electrolyte in both cases. The force is scaled by the undistorted radius of the drop on the cantilever. The inset shows the geometry of the measurements where $X$ is the distance from the bases of both drops. The lines on the logarithm plot show the limiting Debye lengths for the force measurements, which are 22 and 15 nm for the 1 and 10 mM SDS concentration, respectively.
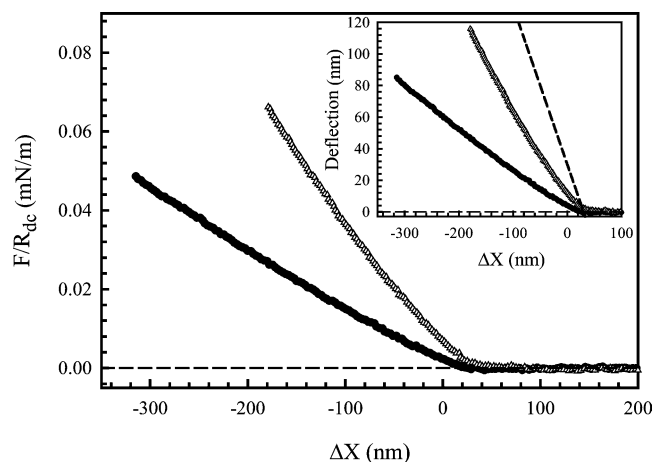
Fig. 2. The interaction force between a decane drop at 10 mM SDS with a drop on the rigid substrate (solid circles) and the rigid substrate (open triangles) measured with AFM. The inset is a plot of the deflection versus piezo motion of the large plot, with a dashed line to represent the slope of the force curve if the two surface were rigid substrates.

indicates that the deformations at the oil–water interfaces are significant even at low forces measured with the AFM. Further analysis to interpret the data and separate the effects of interfacial deformation from changes in surface forces requires a theoretical framework which we are in the processing of developing, based on previous work [11–14,17–19].

Figure 2 shows the interaction of the same oil drop at 10 mM SDS with an anchored oil drop and also the rigid substrate. In both cases the interaction is repulsive from SDS adsorption on all of the interfaces. The adsorption of SDS onto the decane interface has been well characterized by [23]. Force measurements (not shown here) between an AFM tip and the Melinex film in SDS have shown the existence of an adsorbed layer of SDS. The increase in slope for the drop–substrate interaction is a result of having less deformation in the system. The inset in Fig. 2 demonstrates this point by plotting the deflection versus piezo motion of the two force curves and a dashed line with a slope of one, which corresponds to two rigid surfaces in contact. As the interaction approaches a rigid surface interaction (i.e., one drop instead of two), the slope approaches constant compliance.

The above results can be discussed in terms of equilibrium force behavior. The typical assumption is that the AFM measurements are recorded at slow enough approach velocities so that any dynamic effects can be neglected. This approximation can be tested by tracking the force response as a function of approach speed, presented in Fig. 3 between two drops in the 10 mM SDS solution. The two slowest velocities superimpose on each other, indicating that data taken at approach velocities of 80 and 120 nm/s do not manifest any obvious hydrodynamic effects on the interaction. Strictly these measurements should be referred to as pseudo-static, since the AFM is still a dynamic measure even when hydrodynamic forces are not significant. However, hydrody-
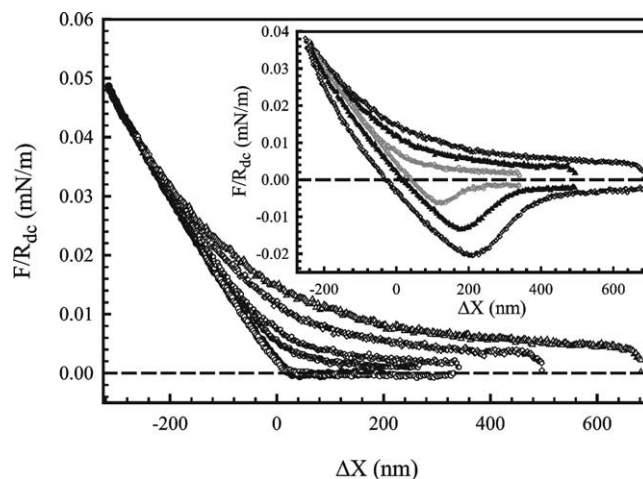


Fig. 3. The interaction of two decane drops in 10 mM SDS measured with AFM as a function of approach velocities, where the two superimposed plots at 80 and 120 nm/s. The incremental increase in force corresponds to a sequential increase of approach velocities (0.54, 1.2, 3.5, and 6.6 µm/s). The inset shows the approaching and retracting forces for scan speeds of 1.2, 3.5, and 6.6 µm/s, where the increase in speed corresponds to an increase in the magnitude of the force.

namic effects are increasingly significant at higher approach velocities (>500 nm/s).

The inset in Fig. 3 shows both the approach and retracting curves for higher velocities. The approach curves show a hydrodynamic repulsion due to film drainage between the surfaces with a dynamic behavior slower than the time scale of the measurement. The magnitude of the attractive well in the retracting curve is a function of velocity, caused by the thinned film between the oil interfaces resorting itself, again with a time scale longer than the measurement. Thus, the formation of the smoothly changing well indicates some drop elongation with the retracting behavior. AFM experiments between a rigid probe particle and one oil drop have not always shown hydrodynamic effects, where [15] observed this behavior, but [17] could not produce this behavior at any approach velocity. In this work, the relatively large drop sizes (~35 µm and 50 mm), coupled with possible interfacial flattening, produce significant hydrodynamic effects with increasing approach velocities.

## 4. Conclusions

This is the first study to demonstrate the effectiveness of the AFM to probe both pseudo-static (as discussed above) and dynamic interactions between oil droplets in aqueous solutions; further analysis is required. Qualitative trends in the force behavior between oil droplets in the presence of a variety of amphiphilic species can be obtained with the above method, but a quantitative and fundamental understanding of the measurement still requires a comprehensive modeling effort. Extracting an interaction force on a per unit area basis from the AFM data would remove the convolution of the deformation and provide quantitative insight into the force

behavior. For the pseudo-static case, the initial approach will be similar to the numerical approaches of [11] and [19] and the semianalytic results of [13,14,17] and [12,22], where the disjoining pressure may be inferred by modeling both the drop shape and the disjoining pressure. The previous models were for a rigid probe particle and a single oil drop, and this will be expanded to two oil drops where the deformation of each interface is coupled. To this end, the semianalytic approach of [13,14] will be used and a result similar to [18] may be feasible, where a planar interaction energy was extracted from the AFM measurement without inferring a form for the disjoining pressure. The hydrodynamic force is a more complicated situation, most likely requiring numerical solutions to the well-known film drainage equations.

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