Structural Forces in Soft Matter Systems

Rico F. Tabor,[†,‡] Derek Y. C. Chan,[‡,§] Franz Grieser,[⊥,‡] and Raymond R. Dagastine*[,†,‡]

[†]Department of Chemical and Biomolecular Engineering, [‡]Particulate Fluids Processing Centre,
[§]Department of Mathematics and Statistics, and [⊥]School of Chemistry, University of Melbourne, Parkville 3010, Australia

S *Supporting Information*

ABSTRACT: Oscillating structural forces arise when nanoscale colloids are confined at high concentration between two approaching surfaces. As layers of colloid are squeezed out, changes in osmotic pressure cause alternating regions of repulsion and attraction. Here, we provide direct measurements of such oscillatory structural forces between the soft interfaces of two emulsion droplets. Quantitative comparison indicates that the deformable nature of droplets allows them to act as far more sensitive probes than solid spheres. In addition, the responsive nature of soft surfaces can give rise to unexpected behaviors not encountered in rigid systems including reversible aggregation/flocculation for emulsion droplets and, potentially, spatial ordering within concentrated emulsion phases.

SECTION: Macromolecules, Soft Matter
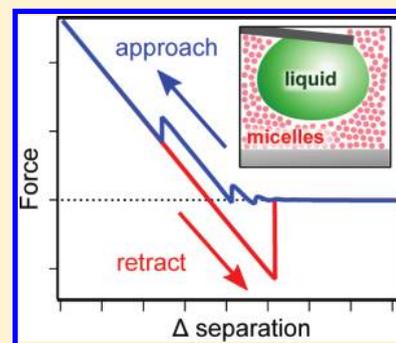
Structural forces in complex fluids can arise when high concentrations of nanoscale colloidal objects such as micelles, nanoparticles, polymer coils, or microemulsion droplets are trapped between two approaching surfaces. A somewhat simplified picture is that the confinement causes a structuring of the colloids into layers that are increasingly ordered in proximity with the surfaces when the separation reaches a few colloid diameters or less.[1] During the approach of the surfaces, layers of the colloid are "squeezed out" (Figure 1B), and the resulting fluctuations in osmotic pressure manifest as a force which alternates between attraction and repulsion. The well-known depletion interaction[2] has an analogous origin, where the presence of small particles or similar causes a net attraction between two much larger objects due to an osmotic imbalance. The depletion interaction has been extensively studied and is responsible for many flocculation processes in particulate and polymer-containing systems.[3] Structural forces can be seen as the high-concentration limit of this phenomenon. The existence and magnitude of oscillating structural forces have previously been demonstrated between solid surfaces using dispersions of micelles,[4−6] particles,[7,8] polymer coils,[9−12] and even large solvent molecules[13] as the structuring phase. Between soft surfaces, analysis has been limited to film drainage,[1] and attempts to incorporate a simpler, purely attractive depletion-type component into the force between two oil droplets[14] or solid surfaces[9] have not resulted in correct prediction of the forces seen. These structural interactions are not only relevant to soft-matter formulations such as foods and pharmaceuticals but also in the interactions of soft biological components, such as cells and tissues, and hence, a full understanding of their magnitude and effect is of great importance.

In this work, we present direct measurements of structural forces between the deformable interfaces of emulsion droplets,

caused by the presence of high concentrations of micelles or microemulsion droplets. Using the measured structural forces between solid surfaces in the same solutions as an input, we are able to predict quantitatively the measured oscillatory forces between deformable droplets (Figure 1C). This demonstrates that the force-separation behavior seen upon approach and retraction is due to the effect of the structural force component and suggests a potential flocculation pathway for droplets. A ~100 μm droplet of the fluorinated oil perfluorooctane (PFO) was captured on an atomic force microscope (AFM) cantilever under water (Figure 1A), and concentrated surfactant solution (sodium dodecyl sulfate, SDS) or microemulsion was added. After equilibration, the droplet was slowly brought toward another droplet or mica surface, and the force during close approach and separation was measured. PFO was used as the droplet phase because it cannot be solubilized by hydrocarbon surfactant micelles.[15]

The interaction between a droplet and solid surface in concentrated micellar solution (Figure 2) shows a significant difference between the forces experienced by the droplet during approach toward and retraction from the surface. Upon approach, characteristic "jump-ins" are seen, which occur when the gradient of the force acting on the cantilever exceeds the cantilever spring constant. Upon retraction, the droplet appears to be captured in an attractive "well", from which it jumps out at some critical separation. This jump-out behavior has previously been suggested by theoretical modeling of a system which incorporates a short-range attractive force well.[18] It is important to note that these interactions are measured at very low speeds
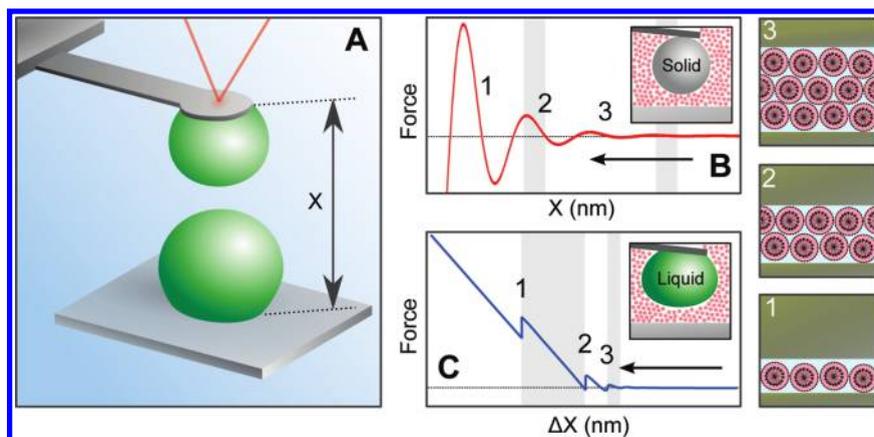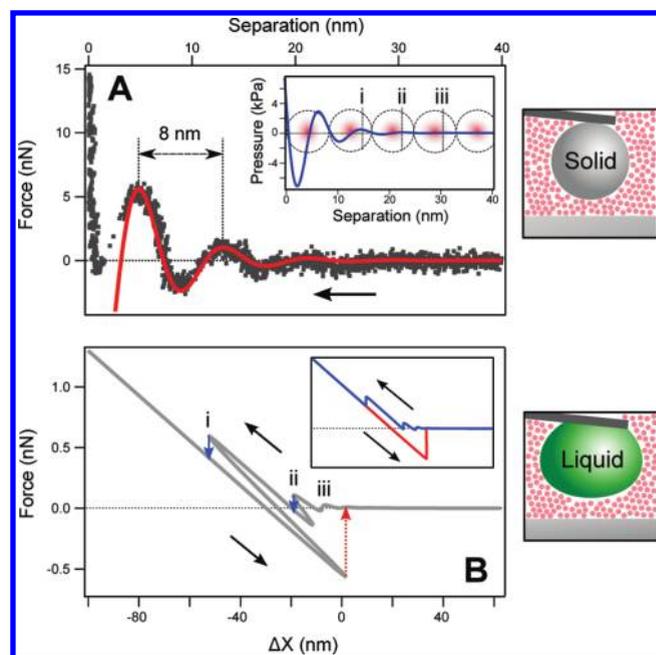
Figure 1. (A) Schematic of the AFM setup, showing an oil droplet captured on the cantilever approaching a surface-immobilized droplet. (B) Schematic showing variation of an oscillatory force with separation between a solid probe and mica surface in concentrated micellar solution. (C) Schematic of a typical oscillatory force between an emulsion drop and a mica surface. For B and C, numbers show the layers which are squeezed out during the approach cycle, and the gray shaded regions represent the force increase during elimination of layers 2 and 4 for each system, demonstrating the distorting effect of the deformable interface on the characteristic periodicity.
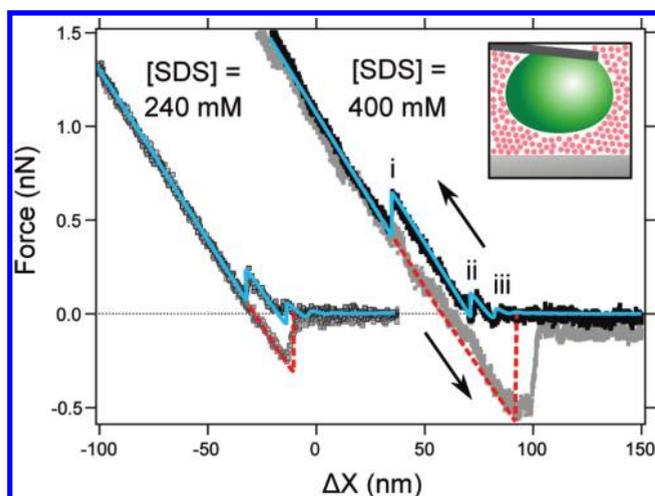
Figure 2. Measured force between a drop of perfluorooctane and a flat mica surface in 400 and 240 mM SDS solutions, showing approach (black symbols) and retraction (gray symbols) data. Lines are predictions for approach (solid) and retraction (dashed), generated as described in the paper. The points labeled i–iii correspond to points in the pressure profile between two planar interfaces (inset to Figure 3A). In the 400 and 240 mM SDS solutions, micelle radii have been reported as 23 Å,[16] and aggregation numbers were estimated to be 77 and 70, respectively.[17] Hence, number concentrations of micellar aggregates were calculated as 5.0 and 3.3 mM, respectively, corresponding to volume fractions of 0.15 and 0.09.

Figure 3. (A) Measured force between a silica sphere (radius 10 μm) and a flat mica surface in 400 mM SDS solution. Gray symbols are experimental data, and the solid line is a best fit to the data. The inset shows the corresponding effective pressure between two flat surfaces derived from these experimental data. (B) The calculated interaction force between a PFO drop (radius 45 μm) and a mica surface, accounting for pressure contributions in the film region from the structural pressure derived in part A, electrical double-layer interactions, van der Waals forces, and deformation of the drop. Diagonal arrows show the direction of cantilever travel (approach or retraction), and vertical arrows mark expected jumps.

$(20-100 \text{ nm/s})$ so that the behavior observed is in no part due to hydrodynamics.[19] As expected, the magnitude of the features seen in the force curve was significantly greater in the more concentrated surfactant solution, representing larger differences in osmotic pressure, as has been previously shown with structural forces in solid systems.[4,5]

In order to understand the force-separation behavior of the deformable systems, measurements were made in the same solutions but between a silica sphere and mica surface (Figure 3A). In this case, there is no deformation, and hence, the absolute separation is known at all points by calibrating the

distance gauge reading of the AFM, a linear variable differential transformer, with the point of sphere–surface contact. The oscillations in the force profile show a characteristic periodicity of 8 nm, consistent with the size of a SDS micelle and its associated electrical double layer.[5] By measuring the force in this case, the Derjaguin approximation can be used to provide the

effective pressure from the structural forces between parallel plates, and this is incorporated into the Chan–Dagastine–White model,[20,21] which calculates the force for a deformable interface by accounting for surface forces and deformation (Figure 3B). Because the "soft" oil–solution interface is able to deform due to the forces that it experiences, it effectively adapts to the disjoining pressure within the film generated between the droplet and the surface. It is this property that causes the distortion of the characteristic periodicity in the force behavior when compared to the solid–solid case of a silica sphere and mica surface. For the droplet–surface case, modeling predicts that the force can take one of multiple equilibrium values at certain separations[18] due to the effect of the oscillating pressure on the deformable interface. In reality however, the droplet is always being moved toward or away from the surface monotonically, and hence, only one of these force values is sampled for a given point, although this value may be different between approach and retraction. By assuming that the cantilever and drop must respond by producing an effective jump-in, when the gradient of the predicted force experienced by the cantilever exceeds the cantilever spring constant or the deformability of the drop, a net force curve is obtained (inset to Figure 3B) that shows the characteristic hysteresis between approach and retraction, which is seen in experimental data. Spring constants for the cantilevers used in these experiments were measured to be 0.10–0.15 N/m.

By modeling the thickness of the solution film between the droplet and mica interfaces as the droplet approaches the surface, it is possible to locate the points in the oscillating pressure profile where the jumps occur (labeled i–iii in Figures 2 and 3). Interestingly, this shows that the jumps appear to represent the expulsion of layers of micelles that are 2–4 layers from the surface. The final layer of micelles cannot be expelled as the droplet is unable to exert the required force to do so; the droplet will deform and flatten rather than decreasing the film thickness when the disjoining pressure in the film becomes equal to the Laplace pressure of the droplet.[20] Flattening of the droplet results in an increase in the effective area of interaction and a corresponding increase in sensitivity. This behavior clearly depends on the interfacial tension of the droplet and hence may be different in other liquid droplet systems. Hence, the deformable probe has the potential to be more sensitive to these interactions at greater separation than solid probes and also to be tunable through its interfacial tension. Significantly, the final layer of colloid offers an insurmountable steric barrier to coalescence of the droplets; hence, flocculation caused as the droplets are caught in the attractive well generated by the depletion of the second layer will be reversible. At high concentrations of both droplet and colloid, it is conceivable that such behavior could result in secondary structuring within the emulsion.

Additionally, by controlling the two parameters which determine the Laplace pressure, and hence the pressure at which flattening will occur, namely, the interfacial tension and size of the droplet, the sensitivity of the droplet as a probe for structural forces can be tailored. Hence, different regions of the bulk structure can be accessed, also suggesting that these same parameters could be used in emulsion formulations in order to tailor the effect of structural forces. This is a unique property suggested in the literature as the key attribute required to better quantify these systems.[1]

A similar interaction to the droplet–mica case is seen when measuring the force between two droplets (Figure 4), demonstrating
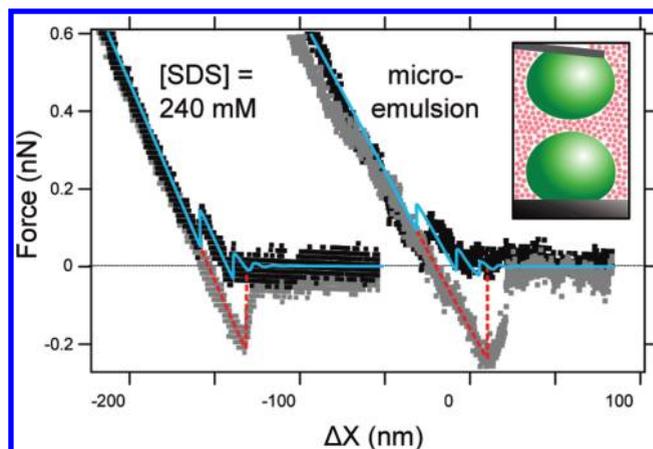
Figure 4. Measured force between two drops of perfluorooctane in 240 mM SDS solution and in an oil-in-water microemulsion, showing approach (black symbols) and retraction (gray symbols) data. Lines are predicted data for approach (solid) and retraction (dashed), generated as described in the paper. The microemulsion was formulated with tetradecane (2 wt %) as the oil phase, SDS (5.5 wt %) as the surfactant, and pentanol (5.5 wt %) as a cosurfactant in water. The microemulsion droplet number concentration and droplet radius were estimated to be 1.9 mM and 32 Å using the method of Almgren et al.,[22] giving a droplet volume fraction of 0.16.

the same hysteresis between force behavior upon approach and retraction, reflective of the complex force behavior within the system. The data in Figure 4 also demonstrate that the same structural interactions occur when the micelles are swollen to microemulsion droplets, suggesting that this phenomenon is relevant to a wide range of formulations. Interestingly, the magnitude of the interaction is similar for the two systems presented in Figure 4, despite the different sizes and volume fractions of the structuring objects, which demonstrates that the observed forces are dependent on a complex system of variables including the size, number density, and charge of objects. For the case of two oil droplets interacting, both of the droplet–solution interfaces are able to deform in response to pressure changes in the film, and hence, the apparent magnitude of the force at which layer squeeze-out events occur is lower. However, crucially, the droplets are still captured in an attractive well upon retraction. It is still energetically improbable for the droplets to eliminate the last layer of micelles or microemulsion droplets as the force required is greater than that which causes the droplets to deform. Although structural forces tend to be weaker than electrical double-layer or van der Waals interactions in rigid systems, for deformable systems, their role may be more significant due to amplification of the oscillatory structural disjoining pressure by the deformability of the interfaces. This behavior may provide a novel mechanism for higher-order structuring within concentrated soft-matter phases, where a nanoscale colloid can act as both a stabilizer and a flocculant. This can occur if the final layer provides a steric barrier which stops irreversible coalescence, but the penultimate layer generates an attractive well which causes aggregation. In contrast, the traditional case of the depletion interaction often results in irreversible phase separations. The data presented here demonstrate that complex fluids experience significant structural interactions, even when soft objects such as emulsion droplets are considered, and that highly concentrated soft-matter phases may experience unexpected phase behavior due to their internal structure.

■ ASSOCIATED CONTENT

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: rrd@unimelb.edu.au.

■ ACKNOWLEDGMENT

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