

Interactions Between Oil Droplets Probed by Force Spectroscopy with the MFP-3D™ AFM

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Understanding the interactions between the colloidal particles found in emulsions is important to a range of applications from the food and pharmaceutical industries through to oil recovery and mineral flotation. The interactions which occur between emulsion droplets are of huge importance in determining the functional properties of such systems. These interactions can be modified by the adsorption at the oil-water interface of surface-active species such as small molecule surfactants, proteins or polymers. However, the physical interactions which occur between emulsified oil droplets have traditionally been a difficult area to study, with work historically being carried out on model rigid colloidal particles¹. This has changed recently following the development of methods to attach oil droplets to atomic force microscope (AFM) cantilevers. These methods have demonstrated that the measurements are sensitive to the nature of the interfacial film² and have allowed detailed study of the force interactions between single pairs of droplets³, including recent mathematical modeling⁴. In this application note we will illustrate the advantages of studying a real fluid droplet system, capturing effects in the AFM data which are unique to deformable particles with a mobile interfacial layer. All work for this note was performed with an MFP-3D-BIO™ AFM from Asylum Research.

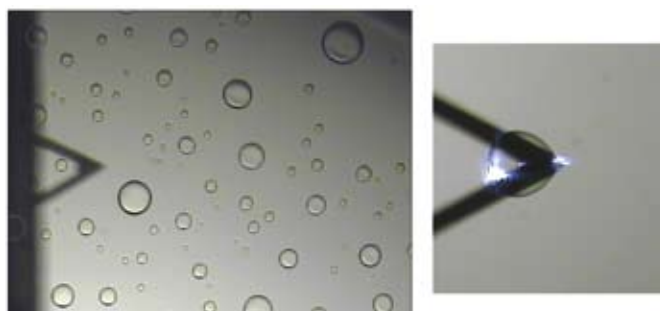


Figure 1: Oil droplets attached to glass under water (left), and attached to the AFM cantilever (right).

Methods

To attach droplets to the AFM cantilever, they first need to be sprayed onto a glass slide (which has to be thoroughly pre-cleaned). Using an ad-hoc sprayer, the oil is sprayed fleetingly over the slide to leave a close smattering of droplets on the surface (but preferably not a continuous film). Next, the slide is placed onto the sample stage of the AFM and a 100 μ L drop of water is deposited on its surface. Although most of the oil drops are displaced by the addition of water, some remain attached to the glass slide (Figure 1).

The MFP-3D AFM head containing a pre-wetted V-shaped cantilever ($k \sim 0.04 \text{ N.m}^{-1}$) is placed onto the sample so that it sandwiches the water on the slide. Then, the AFM head is positioned so that the cantilever tip is just over a droplet. Attachment of the droplet is done by simply lowering the AFM head using the thumbwheel so that the cantilever pushes into the target drop until a jump-to-contact is observed. When this occurs the

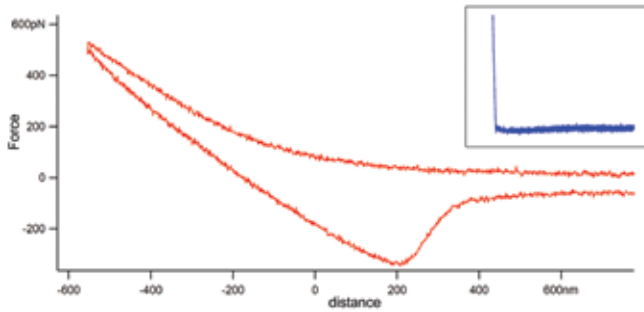


Figure 2: Force distance data for two oil drops, inset data for the bare cantilever against glass.

thumbwheel is reversed to pull the tip and droplet away from the glass (Figure 1). The lever/droplet assembly can now be positioned over a second droplet and the experiment begun. Tip engagement is carried out in the normal manner under feedback control in dc mode, with a moderate set point of $\sim 200\text{mV}$ greater than the null-point for the lever. Note that addition of surfactants, salts, polymers etc. should be done after droplet capture onto the tip.

Results

Figure 2 shows comparative force versus distance data obtained between a bare cantilever and glass (inset) and data for the interaction between two tetradecane oil droplets. The droplet data shows several interesting features. The first and most obvious is that the measurement is sensitive to the deformability of the droplets, since the slope in the contact region is clearly much less than that obtained when the bare lever was pressed against a rigid surface. The second is that there is notable adhesion upon retraction. The smooth shape of this adhesive event reveals that it originates predominantly from the hydrodynamic interaction

between the droplets and the liquid medium in which they sit. As they are forced together a water film becomes trapped between the approaching droplets. This can only drain out at a finite rate, causing repulsion if the approach speed between the droplets is too great. When they are pulled apart again the opposite occurs and water has to rush back into the newly thinned film. As before, this can only happen at a finite rate, leading to an attractive force between the droplets if they are pulled apart faster than the water can refill the gap. Both of these effects can be modified by adding material to the medium in which the droplets are bathed (in emulsions this is usually referred to as the continuous phase) – the following section discusses the effect of adding surface-active and non surface-active polymers.

Sugar beet pectin (SBP) is a plant derived protein-polysaccharide complex capable of coating oil droplets to form highly stable emulsions^{5,6,7}. We have used the MFP-3D to probe the mechanisms occurring between tetradecane droplets in the presence of SBP. Figure 3 compares the force interaction between a pair of oil droplets in the presence of a relatively low concentration of SBP (left) and the interaction between the same pair of droplets after removal of the SBP by rinsing (right). In the presence of the SBP the curves exhibit a small repulsive term appearing upon approach, followed immediately by a small attractive term (this is seen on both the approach [red] and retract [blue] data – the data sets overlay almost perfectly at this speed). After rinsing, the curves simply show monotonic repulsion with separation. This extra feature seen in the presence of the pectin is the characteristic hallmark of an effect known as “depletion.”

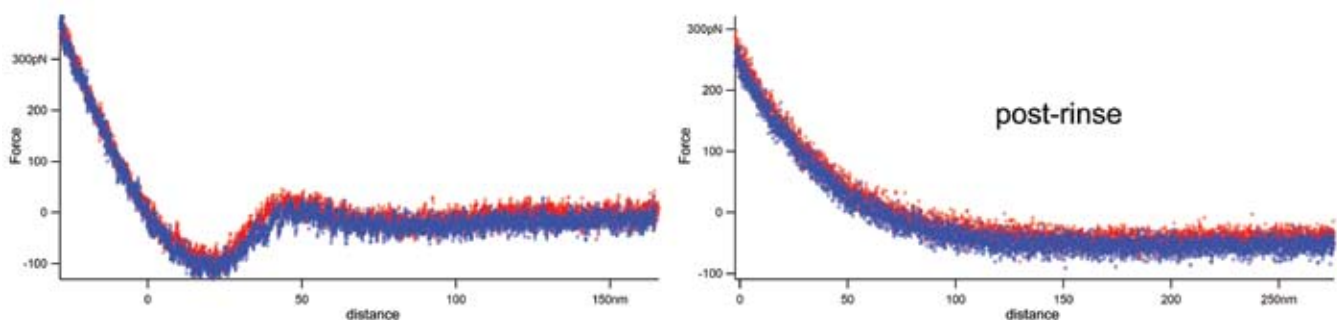


Figure 3: Droplet interaction data obtained in the presence (left) and absence (right) of SBP.

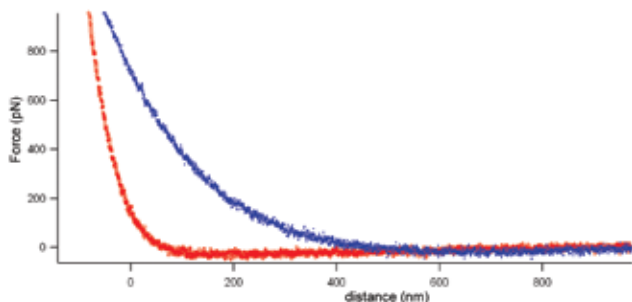


Figure 4: Approach curves for bare droplets (red) and SBP coated droplets (blue).

Depletion is caused by the osmotic pressure exerted when non-adsorbing polymers are squeezed out of the thin aqueous film that exists between two close-packed colloidal particles⁸. Work is required to exclude the solute polymer from a region of the solution due to the entropic cost of de-mixing which gives rise to the initial repulsive term seen in Figure 3 (left panel). Once the droplets are separated by pure solvent the converse is true, the particles are now held together by an effective force generated by the energy required to pull solute polymers out of the bulk solution and back into the depleted aqueous film. This gives rise to the adhesive term observed at close separation in the AFM data in Figure 3. Note that in order to observe this effect, which is very small in magnitude (typically ~ 70 pN), the droplets have to be driven together at relatively low speeds to minimize the (potentially much larger) hydrodynamic term discussed above. Thus the data shown in Figure 3 reveals that at low speeds and polymer concentration, the dominant effect on droplet behavior in the presence of SBP comes from the non-adsorbed fraction present in solution rather than the adsorbed fraction coating the droplet surfaces. Indeed we know from AFM imaging that at low concentration the polymer chains lay flat on the droplet surfaces⁹. If we increase the concentration of SBP on the droplet interface by incubating at higher SBP concentration (followed by rinsing to remove non-adsorbed polymer), the force data look quite different; the interaction is purely repulsive and the range of interaction extends much further (Figure 4 blue curve) than if the droplets are uncoated (Figure 4 red curve).

At elevated interfacial concentration, the polymeric part of the SBP coating has no room to lay flat and sticks out away from the droplet surface

into the aqueous phase. Additionally, at high bulk concentration, the SBP can form aggregates in solution which can adsorb at the interface – the repulsion observed could also be due to steric repulsion between such aggregates. Whichever of these two predominates, the force data shown in Figure 4 nevertheless reflect the steric exclusion that the extended pectin chains cause as the droplets are pushed together. Such long-range steric exclusion explains why SBP is such a good stabilizer. We know that these long range effects are due to polymer and not simple electrostatic repulsion because they remain even in the presence of salt. However, by manipulating the experimental conditions it is possible to promote inter-chain association of the pectin (Figure 5). In the presence of calcium ions, events characteristic of single molecule polymer stretching are observed in the retraction data at points well beyond droplet separation (upper panel). Samples where the pectin chains have been chemically stripped of their charged ester groups by alkali treatment show even greater inter-chain association. When droplets coated with alkali treated SBP are studied, the retract data (Figure 5 lower panel) reveal multiple polymer stretching events following droplet separation.

Finally, we explore the depletion effects between droplets further using a non-adsorbing polyelectrolyte polymer, polystyrene sulphonate (PSS).

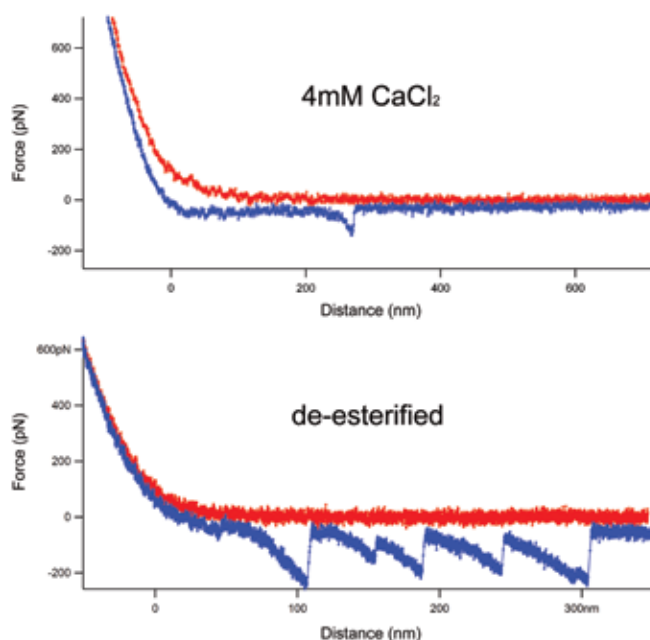


Figure 5: Association of pectin chains upon retraction of coated droplets.

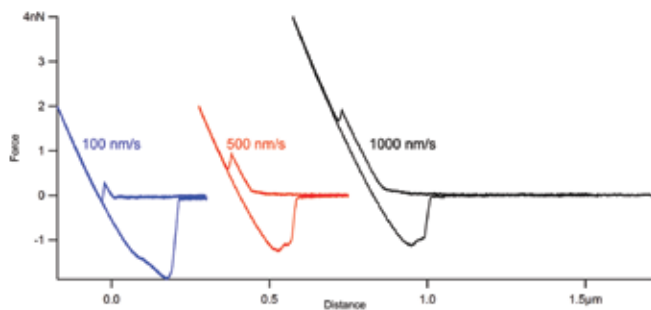


Figure 6: Droplet interaction data in presence of 2% polystyrene sulphonate. Note an arbitrary distance offset has been added to separate the data sets for clarity.

This allows us to work at higher polymer concentrations without the concern of masking depletion effects with the steric repulsion seen for SBP. Furthermore, the relatively low molecular weight and random coil nature of PSS means that it does not affect the viscosity of the continuous phase as much as the SBP. At low concentration of PSS, the force data obtained exhibited almost identical behaviour to the SBP data, namely a small repulsive peak followed by an attractive peak upon approach. At higher PSS concentration, a jump-in feature appears on the approach part of the force curves (Figure 6) and an adhesive peak upon droplet separation can be seen in the retract curves. Two interesting effects are seen in these data. The position of the jump-in moves progressively up the approach curve with increasing approach

speed whilst at the same time the magnitude of the adhesion peak reduces. This is contrary to the normally expected hydrodynamic behaviour of colloidal particles, as discussed earlier, where faster velocity produces greater adhesion upon retraction.

When the PSS concentration is increased still further the effect becomes more pronounced (Figure 7) and the jump-in moves all the way onto the retract portion of the data. This seems counter-intuitive but can be explained when one considers that the particles being pushed together are deformable. If you think of the droplets as a pair of balloons, one in each hand, the effect will be easier to conceptualize: As you push them together the balloons will deform and store elastic energy. Now imagine slowly pulling them apart; the force you feel against your hands immediately reduces (this represents the approach-retract turning point in our force data) but the region where the balloons are touching continues to be squeezed until the point at which the balloons have relaxed back to their un-deformed shape. In just the same way the thin aqueous liquid film trapped at the point of contact between the droplets will continue to be squeezed, and therefore thin-out for some time as they are pulled apart, explaining how jump-in events can occur even during the retraction part of the force-distance cycle. This effect is of course unique to deformable particles and has been

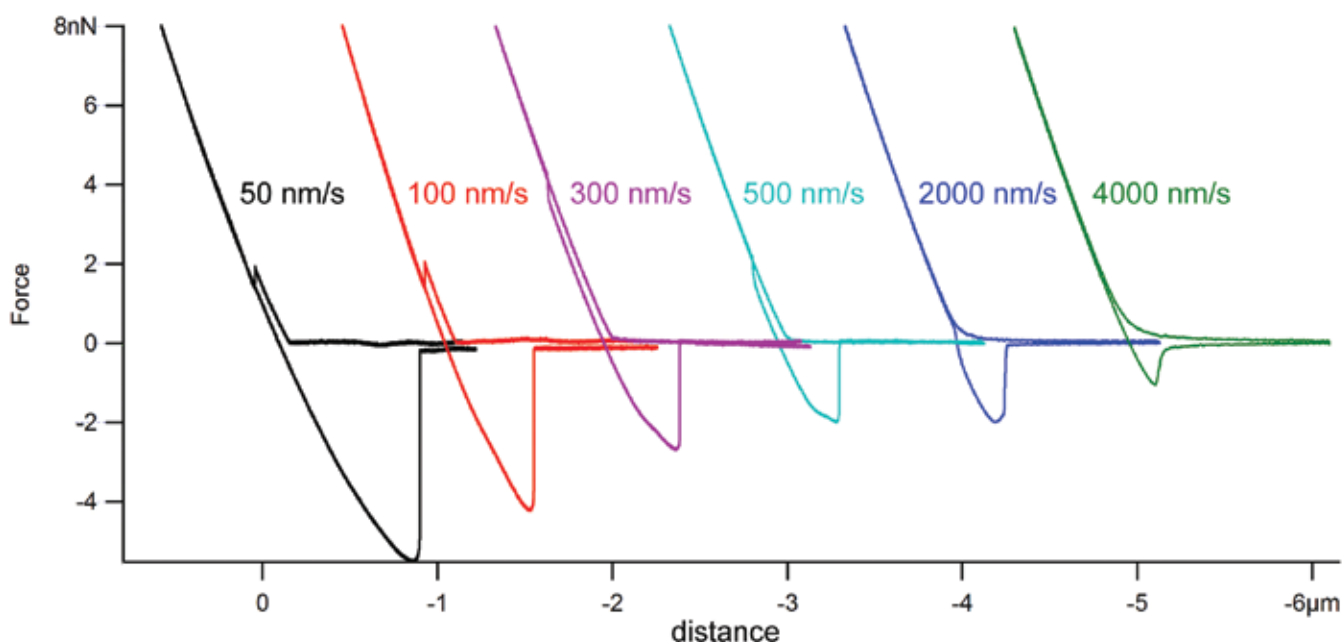


Figure 7: Droplet interaction data in presence of 3% polystyrene sulphonate. Note an arbitrary distance offset has been added to separate the data sets for clarity.

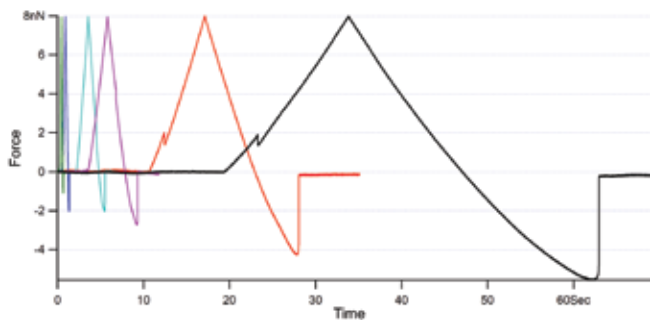


Figure 8: Chronology of droplet interaction data in presence of 3% polystyrene sulphonate.

confirmed by theoretical modelling⁹. Interestingly, careful examination of the data reveals that there is a correlation between the position of the jump-in and the magnitude of the adhesion when the droplets are finally pulled apart. If we plot the force data against time, this correlation becomes more obvious.

Figure 8 shows that the longer the time duration following jump-in, the larger is the subsequent pull-off required to separate the droplets. Our interpretation for these effects is that they result from the formation of a region devoid of polymers in the thin liquid film between the drops (an analogue of this effect is the formation of so-called 'black films' between the lamellae of draining soap films). Neutron scattering studies have provided experimental evidence that such 'black films' can also occur between adhesive emulsion droplets¹⁰.

Figure 9 summarizes the different steps of the process. As the droplets are forced together in the polymer solution (position 1), the liquid film between them is thinned (position 2), leaving less room for the polymer molecules, which require a finite volume of solvent to remain hydrated. At a certain point polymer molecules are forced out of the closing gap creating a very thin region between the droplets (position 3). At this point the droplet surfaces spontaneously jump closer together causing the jump-in events seen in the force curves. Once created this thin region quickly expands with time (position 4) pushing out polymer solute as it does so. This expansion of the very thin region can continue even whilst the drops are being pulled apart since, for a while at least, the region is still being subjected to a squeezing force by the deformed droplets. The work required to separate the droplets now becomes dominated by the area

of this very thin film, because the hydrodynamic suction created by this capillary-like film is very large. This explains the correlation between the jump-in point and the magnitude of the final pull-off adhesion seen in the force data; i.e. a slower approach speed allows the polymer to escape from the closing gap between the droplets earlier in the cycle, and subsequent expansion of this polymer-depleted region is given more time to proceed, resulting in a greater force being required to finally separate the droplets.

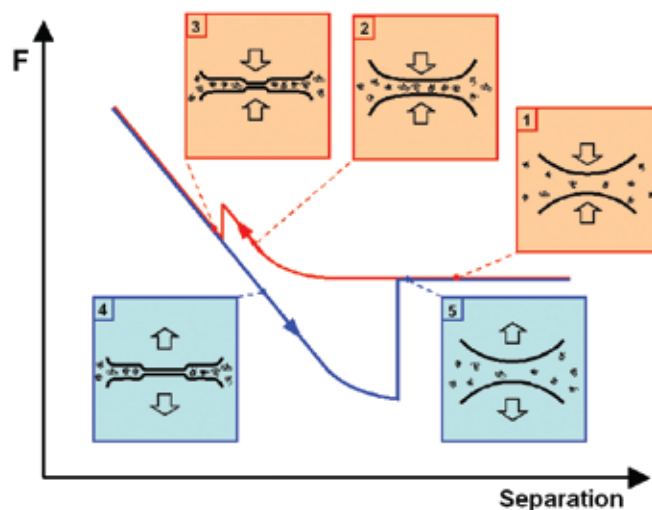


Figure 9: Interpretation of the hysteresis effect observed in the interaction between oil droplets inside a polymer solution. 1. When the droplet surfaces are far apart they don't interact. 2. As the droplet surfaces come sufficiently close together, they start to deform; polymers remain in the thin liquid film between them. 3. As the polymers diffuse away from a region of the film, a 'jump in' effect occurs which corresponds to the formation of a black spot; i.e. the local lamella thickness has reached the dimension of common black films. 4. The black spot expands with time and it keeps expanding even as the droplets are pulled apart, until a 'snap out' is observed which corresponds to the droplets being suddenly disconnected. 5. After the droplets have been separated, the droplet surfaces recover their initial shape.

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