Liquid–Liquid Interfaces

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Particle-Stabilized Water Droplets that Sprout Millimeter-Scale Tubes**

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Abstract: *Millimeter-scale tubes are observed to sprout from water droplets injected into a bath of toluene containing ethanol and silica colloids. This phenomenon requires that first a membrane is formed by the colloids which self-assemble at the droplet interface, and second, that the ethanol preferentially partitions into the aqueous phase leading to an internal overpressure. Tube growth, eruption, and shuffling droplets are subsequently observed, depending on the concentration of ethanol and colloids selected. This work opens many possibilities in the field of biomimetic droplets for fundamental studies of artificial growth at the microscale and for emulsion-related applications.*

A layer of colloidal particles will become irreversibly trapped at a fluid–fluid interface if they exhibit partial wettability with both fluid phases.[1,2] This effect has been exploited to create Pickering emulsions,[3] armored bubbles,[4] and new materials of various kinds.[5–7] When the interfaces are densely coated with particles, they behave like rigid elastic sheets[8] with moduli that are proportional to the underlying interfacial tension.[9] Such interfaces can combine variations in mean curvature with non-negligible interfacial tension.[4,10] The degree of permeability of the particle layer is a crucial characteristic when investigating Ostwald ripening in emulsions and foams[2] and compositional ripening.[11] The loss of molecules from a droplet or bubble leads to a loss of volume; this can be hindered by the rigidity of the interface. For small losses of volume, faceting has been observed,[12] whereas larger losses can lead to crumpling.[11] To date, little has been done to make use of the permeable interfaces to create droplets which expand in a controlled manner.

Transport of a minority constituent from one liquid phase into another can occur as a three-component-system equilibrates.[13–15] In the experiments described herein, we make use of water–toluene–ethanol mixtures,[16] a popular system for investigations of interfacial phenomena (Figure 1 a).[18,19] Solvent mixtures with compositions below the solid line demix, whereas above this line the ethanol makes the water and toluene miscible. The interfacial tension between demixed phases changes with the concentration of ethanol,[20] vanishing as the tie line closes in on the critical point (Figure 1 a). The behavior of such ternary systems far from equilibrium, under conditions where molecular transport occurs by diffusion, has been considered by Ruschak and

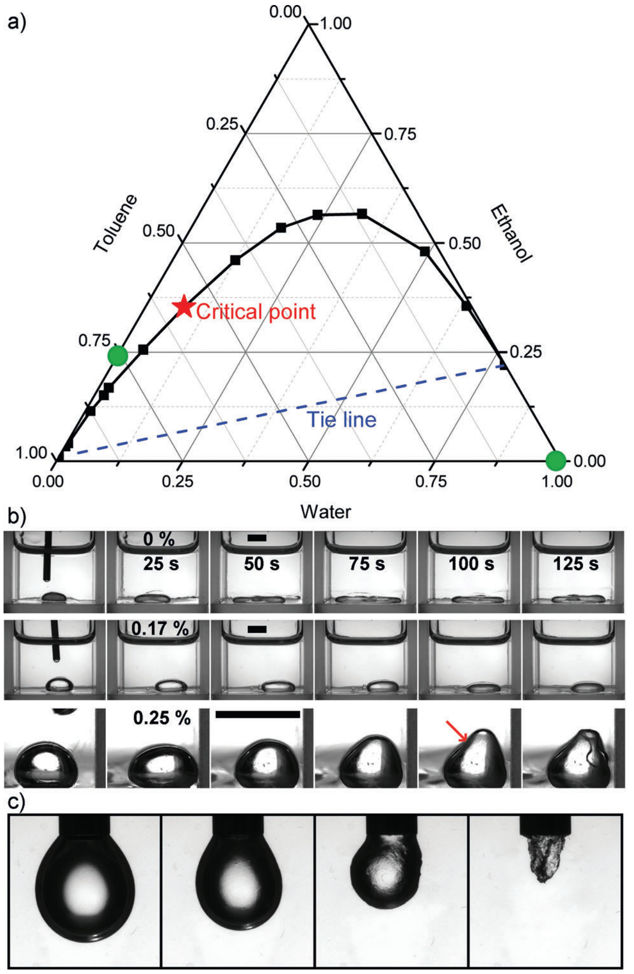

Figure 1. a) Three-fluid phase diagram for the water–toluene–ethanol system.[16] Below the solid black line the two fluid phases demix. The critical point is indicated by a red star and a representative tie line is shown as a blue dashed line. b) A series of synchronized frames following the injection of a water droplet into a bath of toluene containing ethanol (25 vol %). The top row contains no particles, the middle row contains 0.17 vol % silica particles, and the bottom row (expanded view) contains 0.25 vol % silica particles. The addition of particles turns the dynamic dissolution process into vertical growth followed by an eruption of the droplet. The red arrow indicates an inflection in the shape of the interface. Scale bars = 5 mm. c) A series of frames showing water being withdrawn from a pendant droplet coated with silica particles (see Supporting Information). The interface crumples because it cannot eject the particles (as in ref. [17]).

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Miller.[19] It has been shown that to maintain continuity across the droplet interface, the subsurface compositions (i.e. the thin layer abutting the interface) must quickly become those of the equilibrium phases joined by a tie line. Diffusion achieves this within approximately 0.1 s for subsurface layers of thickness 10 μm.[20] Using this model, the process by which the composition of two phases changes on approach to equilibrium (the diffusion pathway) can be calculated. The water–toluene–ethanol mixtures have also been used to study the Marangoni instability:[18,21] a pendant drop of water moves ("dances") in response to ethanol partitioning in from a surrounding toluene phase (see movies given in the Supporting Information). This motion occurs because the ethanol lowers the interfacial tension as it crosses the interface. Local variations in the interfacial tension induce fluid motion and thus "dancing".

As a baseline study, we first investigated what happens to a water droplet in the absence of colloidal particles. Figure 1 b (top line) shows a sequence of frames as a 50 μL water droplet is injected into a bath of toluene containing ethanol (25 vol %). The droplet is initially observed to adopt an oblate shape. This is a consequence of the balance between gravity and interfacial tension. Almost immediately, the droplet starts to expand indicating that ethanol is partitioning into the aqueous phase. Substantial fluid motion and rapid droplet expansion can be seen from 50 s onwards. We associate this dynamic behavior with the variations in interfacial tension which occur as the ethanol crosses the interface (the Marangoni instability). After 55 min, the three components shown in Figure 1 b (top line) are fully mixed.

By adding colloidal particles to the system, the dynamics of the water droplet can be modified. Figure 1 b (middle line) shows a series of frames (synchronized with those in the line above containing no particles) as a water droplet is injected into a bath of toluene containing ethanol (25 vol %) and silica particles (0.17 vol %). During droplet formation, the colloidal particles are adsorbed onto the interface (see below and Figure 1 c). The droplet is initially slightly taller than that without particles and changes shape and volume much more slowly. After about 1 min, the droplet becomes more oblate (flatter), consistent with a decrease in the interfacial tension. Evidently, the interfacial layer of particles is sufficient to suppress the large-scale flow associate with the Marangoni instability. Additionally, we assume that fresh interface, which is exposed as the droplet expands, becomes covered with further particles from the bath. The initial compositions of the two phases in this experiment are shown as green dots in Figure 1 a. For these two phases, the diffusion pathway description predicts that the boundary-layer compositions are those of the blue tie line, that is, almost all of the ethanol outside the droplet rapidly partitions into the boundary layer inside the droplet.[19,20] This description is consistent with our observations: changes to the boundary-layer composition decrease the interfacial tension. This softens the interface and thus the droplet is flattened by gravity (see Figure 1 b; middle line).

As the concentration of particles is increased there is a qualitative change in behavior. Figure 1 b (bottom line) is a series of frames (synchronized with those in the lines above) showing a water droplet injected into a bath of toluene containing ethanol (25 vol %) and silica particles (0.25 vol %). Expanded images are shown to highlight the changes. The droplet, following injection, is now considerably taller than those with no or fewer particles. Evidently, the layer of interfacial particles makes the droplet better able to withstand the effect of gravity. Droplet expansion is again observed, associated with the diffusion of components and progress towards equilibrium. However, the behavior of the expanding droplet changes markedly after 25 s with growth occurring predominantly in an upwards direction. Furthermore, an inflection is noticeable in the shape of the droplet surface (shown by the red arrow) after 100 s as it begins to form a quite different shape. Vertical growth is focused on one region at the apex of the droplet. Subsequently, the aqueous phase begins to grow and overspill (i.e. erupt) from the top of the droplet and to flow down the side (final frame). As water and ethanol are both considerably more dense than toluene, it is surprising to find the internal phase spilling over (erupting) from the top of the droplet, although it is unsurprising that it flows downwards once released.

We performed a range of experiments to identify the location of the particles and to establish their role. Considering first the location of the particles, Figure 1 c shows a series of frames as a pendant water droplet in a bath of toluene and ethanol (5 vol %) containing silica particles (0.2 vol %) is retracted. As the volume of water is decreased the droplet is observed to change shape and then to crumple. This sequence of events reflects the fact that the particles are irreversibly adsorbed at the interface, meaning that the surface area can only decrease until the particles are pushed into contact with one another (become jammed). A more complete layer of particles on the droplet surface can be formed by increasing the silica concentration in the toluene/ethanol mixture (see Supporting Information). Next, the role of the particles was evidenced through the development of a shear modulus of the interfacial layer (Figure 2 a). Thus, we conclude that increasing the concentration of silica particles, as occurs between the middle and bottom lines of Figure 1 b, modifies the mechanical properties of the liquid–liquid interface. Finally we demonstrate that the presence of silica does not change the availability of ethanol in the water–toluene–ethanol system. In this experiment, increasing concentrations of particles are dispersed in a mixture of toluene and ethanol and then the particles are centrifuged to the base of the vial; a collapsed colloid layer could be seen and liquid from the supernatant was drawn off for characterization. By examining the refractive index it can be seen that the quantity of ethanol in the supernatant is unmodified by increasing quantities of particles (see Supporting Information, Figure S3 a and S3 b).

We hypothesized that droplet growth is driven by the partitioning of the ethanol into the water and that growth is possible in the vertical direction because of the properties of the particle-coated interface. We anticipated that the droplet would be better able to resist gravity if the interfacial tension was higher. This theory was tested experimentally by choosing a lower concentration of ethanol in the toluene. In a typical experiment (see Figure 2 b), we inject a droplet of water

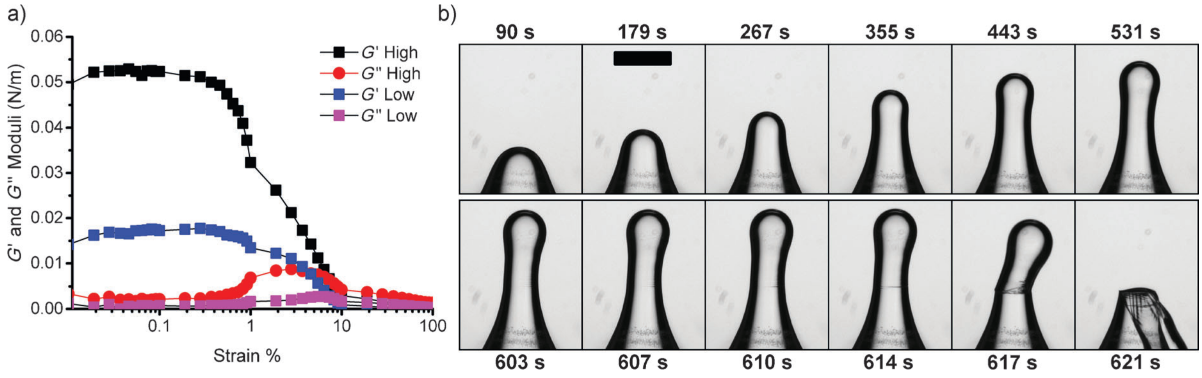

Figure 2. a) Changes in the interfacial storage (G') and loss (G'') moduli in response to oscillatory shear for interfaces formed from high (0.58 vol%) and low (0.08 vol%) concentrations of silica particles (with 5 vol% ethanol in toluene). Increasing the particle concentration results in a marked increase in the storage modulus. Values presented are an average of six measurements. The variation between G' measurement runs is substantial, giving a standard deviation of ±20%. b) Series of images with increasing time showing the sprouting of a tube from a water droplet (top line) and the process of tube buckling under its own weight (bottom line). The droplet starts as 50 µL of water, the surrounding liquid is 0.19 vol% silica particles in toluene containing 15 vol% ethanol. Scale bar 5 mm.

(50 µL) into a bath of toluene containing ethanol (15 vol%) and silica particles (0.19 vol%). The droplet again expands, but now more slowly than for the higher ethanol concentrations used in the experiments in Figure 1b. Additionally, the inflection in the shape of the interface and the vertical growth are much more pronounced (see also Figure 3a, and movies contained in the Supporting Information). The vertical growth has the form of a tube which extends to a significant height (several millimeters). Subsequently, the tube buckles and topples over (see Figure 2b). Crumpling of the interfacial layer of particles can be seen during and after the toppling process. This process is local or Brazier buckling: it is associated with a change in the cross-section of the tube and/or with local defects.[22] A new tube is sometimes observed to grow upwards from a toppled forebear. We take this to indicate that toppling is not due to a loss of interfacial tension resulting from the change in composition of the internal phase. Instead, we suggest that toppling occurs because the tube buckles under its own weight. The enhanced growth and lack of eruption at this lower ethanol concentration confirm the role of interfacial tension in the growth process.

Figure 3. a) Image sequences showing the behavior of 50 µL water droplets in toluene containing ethanol (15 vol%) as the concentration of silica particles is varied. With increasing concentration of silica particles the growth behavior slows down but passes through an optimum for tube growth (see also movies in the Supporting Information). b) Preformed water droplets (frame 1) are doused in a bath of toluene containing ethanol (15 vol%) and silica particles (0.14 vol%; before frame 2). Droplet growth is still observed (frames 2–5) in the case of a population of droplets. Times are taken starting from when the toluene–ethanol–silica mixtures were added (see also movies in the Supporting Information). c) A series of frames showing a droplet shuffling sideways across the base of the sample cell. The droplet began as 50 µL water and the continuous phase began as toluene with ethanol (15 vol%) and silica particles (0.04 vol%). Scale bars = 5 mm.

To further investigate this process, the time evolution of a series of water droplets in a bath of toluene and ethanol (15 vol%) containing sequentially higher concentrations of particles was measured (Figure 3a). As the particle concentration increases the droplet behavior changes significantly but also the rate of change of droplet behavior becomes slower. For low concentrations of particles (i.e. < 0.1 vol%) the droplets expand upwards somewhat but ultimately collapse back to give an elongated oblate droplet. At high concentration (0.42 vol%), modest expansion occurs. However, at an intermediate concentration (0.19 vol%), the droplet is observed to grow vertically in the form of a tube for several minutes before buckling. Figure 4 presents our results for a range of ethanol and particle concentrations.

By varying the sample compositions (Figures 1 and 2), we have shown that droplet growth is driven by the internal overpressure inside the droplet created by the influx of ethanol. The resulting ethanol-rich boundary layer is much less dense than the water. This gives rise to upward flow of the internal boundary layer and thus a composition gradient inside the droplet. The enhanced ethanol concentration at the top of the droplet lowers the interfacial tension locally[20] which softens the interface[19] and thus directs growth. Without the layer of trapped particles the interface loses its rigidity and cannot support growth. Figure 4 presents a non-equilibrium phase diagram showing changes in droplet growth with changing ethanol and particle concentrations. These experiments show that droplets erupt at higher ethanol concentrations (in the purple zone) and expand at lower ethanol concentrations (in the blue zone). Between these two zones, the higher moduli associated with systems having approximately 15 vol% ethanol (green zone) give dramatic tubular growth. The progress from droplet growth to eruption with increasing ethanol concentration demonstrates the interface softening at the apex of the droplet because of the internal concentration gradient. We suggest that at low concentrations of particles (orange zone), dramatic tube growth does not occur because the walls are too soft. This dependence of dilational modulus on particle concentration presumably reflects particle–particle attractions in the interfacial coating.

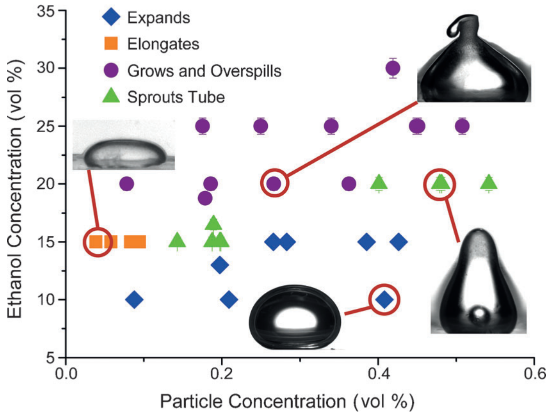

Figure 4. A non-equilibrium phase diagram showing the droplet growth behavior as the ethanol concentration and particle concentration are varied. The different growth modes are illustrated by inset images corresponding to the circled compositions.

The same physical processes can be observed for multiple droplets simultaneously (see Figure 3b and movies contained in the Supporting Information), suggesting that these results could be applicable to real-world emulsions combining water, an oil, and ethanol. Note, however, that the processes only occur simultaneously in multiple droplets when the ethanol and silica particle concentration are appropriately controlled. We further observe that the wettability of the sample cell becomes important at very low particle concentrations, leading to droplets that can be seen to “shuffle”, as shown in Figure 3c. By “shuffling” we mean that the droplet stays oblate and moves across the base of the vessel, reminiscent of Figure 1b (top line). Evidently, the yield stress of this particle-coated interface can only support a very limited amount of vertical growth.

In conclusion, we have demonstrated a new range of growth modes for water droplets stabilized by interfacial particles in multi-component liquid systems. The behavior is controlled by the concentration of ethanol and of silica particles. These parameters provide the elastic interfaces, expanding volume, and local softening required for growth. We have shown that, surprisingly, vertical growth occurs in spite of the internal phase being more dense than the surrounding solvent. This work can pave the way for future studies of droplet growth because the liquid droplets and the interfacial properties can be independently studied. Furthermore, the interactions between colloidal particles in the membrane can be tuned from strongly repulsive to strongly attractive which we believe will open new regimes of behavior.

Experimental Section

Sample preparation and imaging: The solvents toluene (Analytical Reagent grade, Fischer) and absolute ethanol (AnalaR NORMAPUR, VWR) were used as received. Distilled water was filtered and deionized with a Milli-Q system to a resistivity of 18.2 MΩcm. Fumed silica particles (HDK H30), size ≈100 nm,[3] were a gift from Wacker-Chemie (Burghausen); the proportion of silanol groups converted into methyl groups on the surface (area 250 m^2g^{-1}) is approximately 50%. The particles were dispersed in toluene using an ultrasound probe (Sonics Vibra Cell VCX-500, 500 W, 20 kHz). The oscillation amplitude was set at 30% of maximum, 10 s on, 10 s off, for a total dispersal time of 2 min. Ethanol was added afterwards to give the required composition. From this reservoir, a total volume of 5 mL of toluene–ethanol–silica mixture, measured by volume, was used in each imaging study. Movies were filmed using the Kruss Easy Drop apparatus and accompanying software. Large field of view imaging was carried out with an Aico auto 3× converter lens.

Interfacial rheology: Interfacial shear moduli were measured using a TA Instruments DHR-2 rheometer, equipped with a Pt/Ir DWR interfacial geometry and a Delrin trough with stepwise edges that pin the fluid–fluid interface (described elsewhere[23]). The ring was rinsed and flame-treated using a butane burner between uses. Two compositions were studied, containing high (0.58 vol%) and low (0.08 vol%) volume fractions of silica particles. The ethanol content for these samples was 5 vol%. A subphase of 20.15 mL of water was placed in the rheometer trough. The geometry (internal diameter 69 mm, thickness 2 mm) was then lowered into contact with the air/water interface, and the toluene–ethanol–silica dispersion (6 mL) was added on top. Values of G' and G'' were measured as the oscillating (1 Hz) shear strain was ramped from 0.01–100%.

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