

## Stability Criteria for Emulsions

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The coalescence of monodisperse silicone oil-in-water emulsions stabilized with sodium dodecyl sulfate has been studied. We report the existence of a sharp destabilization threshold, controlled by surfactant chemical potential, osmotic pressure, and droplet diameter, at which the rate of coalescence increases dramatically. We present evidence that the stability of the emulsions can be characterized by two microscopic parameters: a minimum stable value of the surfactant chemical potential and a maximum value of the pressure exerted upon a droplet-droplet interface.

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Emulsions are oil-water mixtures stabilized by a surfactant, consisting of either oil droplets dispersed in water or water droplets dispersed in oil. Emulsions are metastable, so that the average droplet size in an emulsion tends to increase with time. They thus belong to a broad class of nonequilibrium systems, including air-liquid foams and spinodally decomposing mixtures, that coarsen with time. The characteristic time scales for coarsening of emulsions can, however, span a remarkably wide range, from seconds to several years. Emulsions are extremely important for a variety of industrial applications, including oil recovery, a variety of coating processes, food processing, and cosmetology [1]. Their stability is a critical property for all applications, making an understanding of the coarsening process a subject of practical as well as fundamental importance. Unfortunately, the stability of an emulsion apparently depends on such a diverse array of experimental parameters that there exists almost no fundamental understanding of the basic principles involved. As a result, the control of emulsion stability has remained essentially an art based on empirical approaches and recipes.

In this Letter, we demonstrate that the stability of an emulsion can, under favorable conditions, be understood in simple terms. We use emulsions comprised of initially monodisperse droplets, enabling us to monitor the progress of coalescence quite precisely. Moreover, by choosing an oil (silicone) that has extremely low diffusivity in water, we completely eliminate one class of destabilization phenomena, that of Ostwald ripening. Ostwald ripening is the preferential diffusion of the dispersed fluid out of smaller droplets and into larger ones, driven by the higher Laplace pressure in small droplets. We can thus focus exclusively on the second class of destabilization phenomena, that of coalescence. Coalescence entails the rupture of a thin film formed between droplets in close contact.

We use an osmotic stress technique [2] to control both the surfactant chemical potential and the osmotic pressure of the emulsions. The surfactant chemical potential

determines the density of surfactant molecules at the oil-water interface. The applied osmotic pressure presses the oil droplets together by squeezing water out of the system, much like a piston exerting mechanical pressure on the droplets. By varying both these parameters and the droplet diameter, a simple set of stability criteria for emulsions is determined. We show that the stability of our emulsions is controlled by two microscopic parameters: the surfactant chemical potential and the pressure exerted between droplets in close contact.

The emulsions are formed from silicone oil, sodium dodecyl sulfate (SDS), and water [3]. A crude emulsion is first separated by droplet size using a fractionated crystallization scheme [4] to obtain monodisperse emulsions with several droplet diameters  $\sigma$  between 0.34 and 3.3  $\mu\text{m}$ . After separation, the droplets are sufficiently monodisperse that they form ordered crystallites [5]. Each emulsion is placed in a dialysis bag, which is immersed in a larger reservoir containing water, SDS, and a hydrophilic polymer, Dextran, with a molecular weight (MW) of 500 000. Dextran was chosen for this purpose because the osmotic pressure  $\Pi$  and surfactant chemical potential  $\mu_s$  can be independently controlled in SDS-Dextran-water mixtures [6] by varying, respectively, the polymer concentration  $C_p$  and surfactant concentration  $C_s$ . The bags are made of a cellulosic membrane with a MW cutoff of 50 000, which is permeable to water and the surfactant, but impermeable to the oil droplets and polymer.

The stability of a set of emulsions with a single droplet diameter,  $\sigma = 1.6 \mu\text{m}$ , but varying osmotic pressures and surfactant chemical potentials is summarized in Fig. 1. Because the emulsions are initially monodisperse, the onset of coalescence is easily observed with a microscope. The monodispersity of these emulsions also allows us to confirm the absence of Ostwald ripening, since we never observe droplets smaller than the initial droplet volume. The rate of coalescence, rather than being a smooth function of  $\Pi$  and  $\mu_s$ , exhibits a sharp stability threshold where it increases dramatically, as shown by the solid line in Fig. 1. Near the stability threshold, a change of a few

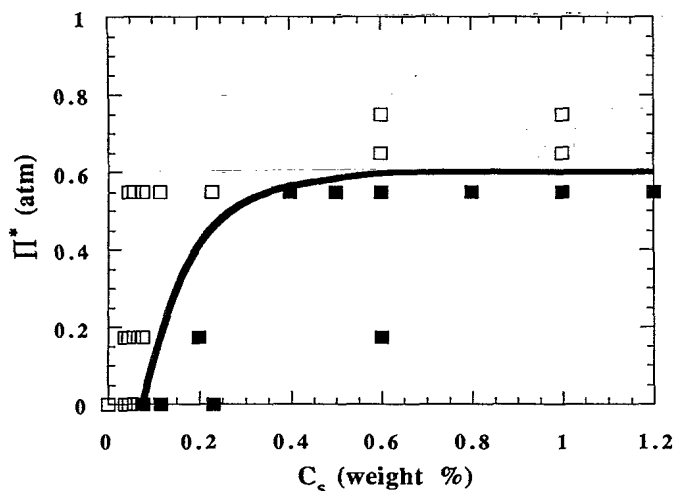


FIG. 1. Stability diagram— $C_s$  is the reservoir concentration of SDS and  $\Pi$  is the osmotic pressure. Stable emulsions are indicated by solid squares and unstable ones by open squares. The solid line represents the stability threshold.

percent in either the surfactant concentration or osmotic pressure can change the characteristic time scale for coalescence from a few days to months or years. Our operational definition of a stable emulsion is one in which no coalescence is visible fifteen days after immersion in the reservoir. As shown in Fig. 1, the emulsions are always unstable below a critical value  $\mu_s^*$  of the surfactant chemical potential, corresponding to a reservoir SDS concentration  $C_s$  of about  $2.7 \times 10^{-3}$  mol/l (0.08% by weight). This is about one third the critical micellar concentration (CMC) of SDS. Similar results are suggested in a previous light-scattering study [7] of coarsening in a polydisperse emulsion stabilized with SDS. At values of  $\mu_s$  above  $\mu_s^*$ , the emulsion becomes unstable only if the osmotic pressure is raised above a critical value  $\Pi^*$ . The value of  $\Pi^*$  becomes quite insensitive to  $\mu_s$  when  $C_s$  is raised above the CMC.

This stability diagram demonstrates the existence of two different regimes of surfactant chemical potential: In the surfactant-poor regime  $\mu_s < \mu_s^*$ , the emulsions are always unstable, suggesting that the oil-water interfaces are not sufficiently covered with surfactant molecules to prevent coalescence. In the surfactant-rich regime  $\mu_s > \mu_s^*$ , the interfaces apparently become saturated with surfactant, since their stability becomes insensitive to  $\mu_s$ , and stability is instead controlled by osmotic pressure.

In the surfactant-rich regime, the  $\sigma = 1.6 \mu\text{m}$  emulsions undergo coalescence only when most of the water is squeezed out, forming a "biliquid foam" with an oil volume fraction near 95%. In this state, the droplet surfaces contain large facets [8], along which droplets press against each other across thin films of water. At  $\Pi$  slightly above  $\Pi^*$ , coalescence proceeds by growth of a relatively small number of large droplets, as shown in Fig. 2. The emulsion shown was kept for fifteen days at

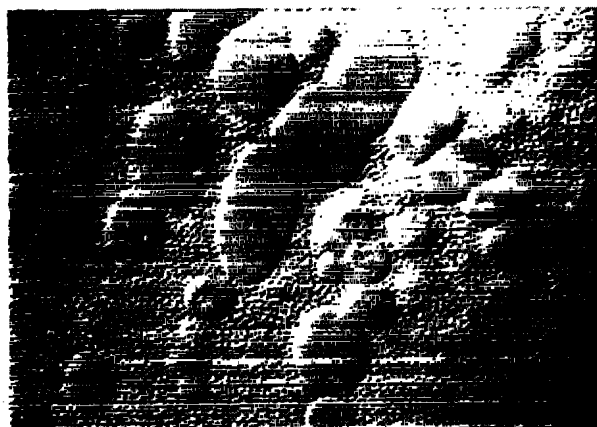


FIG. 2. Photograph of a compressed emulsion undergoing coalescence. See text for discussion.

an osmotic pressure  $\Pi = 0.7$  atm, about 15% above  $\Pi^*$ . These larger droplets are formed at randomly located nucleation centers, and grow by coalescence with their smaller neighbors. These large droplets continue to grow until they meet each other, and then (somewhat surprisingly) stop. The resulting state of the emulsion is again a biliquid foam, but is now comprised of much larger, polydisperse droplets separated by stable thin films. The stability of these large-scale foams suggests that emulsion stability may depend not only on osmotic pressure but also on droplet size.

What is the microscopic mechanism controlling stability in the surfactant-rich regime? We hypothesize that a thin film between droplets becomes unstable at a critical value  $\Pi_i^*$  of the microscopic pressure exerted on the film. This inward pressure, called the disjoining pressure, is opposed by repulsive interactions between the oil-water interfaces, and determines the film thickness. Our hypothesis is suggested by recent work done on the rupture of single soap films [9]. For a flat film, such as is produced between droplets of equal internal pressure, the disjoining pressure is equal to the pressure difference  $\Pi_i$  between the oil pressure in either droplet and the ambient water pressure. This pressure difference also determines the mean radius of curvature  $R$  on the remaining curved sections of the droplet surfaces: By Laplace's equation

$$\Pi_i = 2\gamma/R, \quad (1)$$

where  $\gamma$  is the surface tension of an oil-water interface and  $R^{-1} = (R_1^{-1} + R_2^{-1})/2$  is an average of the two principal curvatures. In a monodisperse emulsion, where the pressures in different droplets are all essentially equal, the existence of a critical pressure thus implies the existence of a critical radius of curvature  $R^* = 2\gamma/\Pi_i^*$ . The macroscopic osmotic pressure at which the droplets reach this critical pressure (or critical curvature) clearly depends upon the diameter of the undeformed droplets. In droplets of diameter  $\sigma < 2R^*$ , the Laplace pressure is above  $\Pi_i^*$  even before the droplets are deformed, so that a thin

film between such droplets is expected to be unstable as soon as it is formed. In the limit  $\sigma \gg 2R^*$ , however, the droplets must be compressed until they are essentially polyhedral before reaching the critical pressure, and in this limit  $\Pi_i \approx \Pi$ . We therefore expect that the critical osmotic pressure should show a marked drop with decreasing droplet diameter, and, at least in this simple picture, should vanish below a critical diameter.

To test these ideas, we take advantage of our ability to make monodisperse emulsions and examine the dependence of  $\Pi^*$  on  $\sigma$ . For each value of  $\sigma$ , the emulsions can be characterized by a stability diagram similar to Fig. 1. As expected,  $\mu_s^*$  is found to be quite insensitive to the value of  $\sigma$  whereas  $\Pi^*$  depends strongly on it. We show our results for  $\Pi^*$  at various droplet diameters, at fixed surfactant concentration  $C_s = 1\%$ , in Fig. 3. In the inset, we show the corresponding volume fractions of oil  $\phi^*$  measured at  $\Pi = \Pi^*$ . To facilitate comparison of the data with our expectations,  $\Pi^*$  and  $\phi^*$  are plotted here as a function of the Laplace pressure  $\Pi_0 \equiv 4\gamma/\sigma$  of the undeformed droplets. We have used a measured value of  $\gamma = 10 \pm 1$  ergs/cm<sup>2</sup> [10] to calculate  $\Pi_0$ . In the limit of small  $\Pi_0$  (or large diameter),  $\Pi^*$  approaches an extrapolated maximum of 1.0–1.2 atm.  $\Pi^*$  then decreases with increasing  $\Pi_0$ , as expected, dropping fairly rapidly until  $\Pi \approx \Pi_0 \approx 0.4$  atm, and more slowly thereafter. We note that the overall scale of  $\Pi_0$  over which  $\Pi^*$  drops by an order of magnitude is about 1 atm, roughly equal to the extrapolated maximum value of  $\Pi^*$ , and consistent with the idea that the stability threshold is associated with a single microscopic pressure  $\Pi_i^*$ .

These results also provide an explanation of the surprising stability of the large droplets observed in Fig.

2. The stable structures were created at osmotic pressures slightly above the critical pressure  $\Pi^*$  for the initial, smaller droplets, but below the large-diameter limiting value of  $\Pi^*$ , as determined from Fig. 3. Consequently, we expect films between the much larger droplets to be stable, consistent with our observations. Moreover, when the osmotic pressure on the large droplets is raised above this limiting value, the interfaces between them also become unstable, and coalescence continues until the foam is destroyed.

Our results suggest a simple model for the stability and thermodynamics of a compressed emulsion, in which (i) thin film rupture always occurs at a critical disjoining pressure  $\Pi_i^*$ , and (ii) the only relevant interaction between droplets is an essentially hard-core repulsion between oil-water interfaces. This second assumption is suggested by earlier work on interface interactions in thin water films [9], which found strong repulsive interactions that fall off rapidly at distances above about 100 Å, distances which are small compared to the critical radius  $R^* \approx 2000$  Å. This assumption is also suggested by the experiment, since only a small pressure,  $\Pi \approx 0.01$ – $0.05$  atm, is needed to raise the volume fraction of oil to roughly 0.74, the volume fraction of close-packed spheres. Furthermore, no adhesion, which would produce nonzero contact angles between droplets, is observed in the experiments.

The surface of a droplet in this picture contains several flat facet regions where the droplets press against each other, and a curved surface region of constant curvature  $R = 2\gamma/\Pi_i$ . All forces between droplets are transmitted across the facets, and the total force across a facet of area  $a$  is just  $a\Pi_i$ . The facets of each droplet's surface can be mentally extended into planes to define the faces of a polyhedral cage surrounding the droplet. The total force which must be transmitted across a particular face in an emulsion with osmotic pressure  $\Pi$  is  $\Pi a_p$ , where  $a_p$  is the area of the polyhedral face, implying that [11]

$$a/a_p \equiv \Pi/\Pi_i. \quad (2)$$

Because the interactions are purely hard core, the energy  $\Pi dV$  done in compressing the emulsion by a change of volume  $dV$  is stored entirely as an increase  $\gamma dA$  in the surface energy, where  $dA$  is a corresponding increase in the total surface area of the droplets.

The degree of deformation of the droplets is determined by the ratio  $\Pi\sigma/\gamma \propto \Pi/\Pi_0$ , which is the only dimensionless combination of parameters in the model. In the limit  $\Pi \ll \Pi_0$ , the droplets are weakly deformed spheres, and press against each other across small, nearly circular facets. Here,  $\Pi_i$  approaches  $\Pi_0$  as  $\Pi$  vanishes, and the area  $a$  of each facet grows roughly linearly with  $\Pi$ . In the limit  $\Pi \gg \Pi_0$ , the droplets become nearly polyhedral, and  $a$  approaches  $a_p$  for each facet. By Eq. (2),  $\Pi_i$  thus approaches  $\Pi$ , giving  $\Pi^* = \Pi_i^*$  when  $\Pi_0$  vanishes.

In between these limits,  $\Pi^*$  can be expressed in the

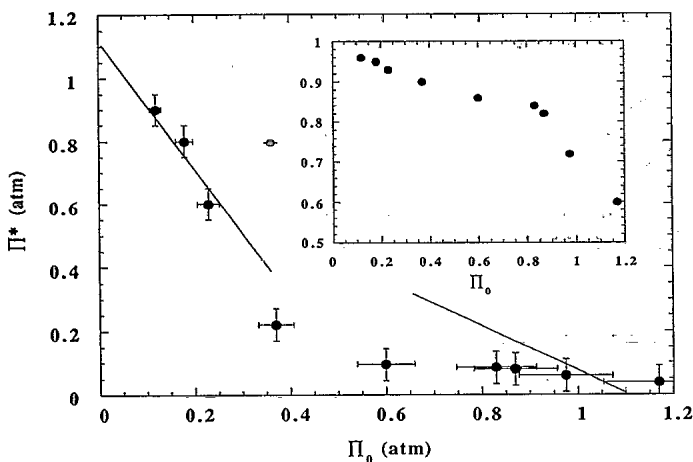


FIG. 3. Dependence of the threshold osmotic pressure  $\Pi^*$  on the Laplace pressure  $\Pi_0 = 4\gamma/\sigma$  of the undeformed droplets. Coalescence is rapid for all  $(\Pi_0, \Pi)$  above this curve. Solid lines are theoretical predictions for the limits of strong and weak droplet deformation, assuming  $\Pi_i^* = 1.1$  atm and an ordered fcc lattice. Inset: Threshold volume fraction of oil  $\phi^*$  plotted vs  $\Pi_0$ .

scaling form  $\Pi^* = \Pi_i^* f(\Pi_0/\Pi_i^*)$ , where  $f(x)$  is a universal function determined by geometry. While we cannot obtain a full analytic solution for  $f(x)$ , we can calculate its asymptotic behavior in the limits of very strong or weak deformation. To do so we will assume that the droplets form an ordered fcc lattice. This assumption is a reasonable starting point for describing the more strongly deformed large- $\sigma$  emulsions, but gives a poor description of the smaller- $\sigma$  emulsions, which seem to form a random close packing at coalescence. To treat the strongly deformed limit, we note that the facet areas  $a$  differ from  $a_p$  only because of the slight rounding of the droplet surface along each edge of the polyhedral cage. Using Eq. (1) to obtain the curvature along these edges, it is straightforward to calculate  $a/a_p$ , and thus obtain  $\Pi/\Pi_i$ . In the weakly deformed limit, we can calculate the linear response of the droplet shape to small forces applied at the surface, determining the pressure shift  $\delta\Pi_i = \Pi_i - \Pi_0$  from the requirement that the droplet volume remain unchanged [12]. This requirement is satisfied when the extra outward force associated with  $\delta\Pi_i$ , i.e.,  $\delta\Pi_i A_0$ , where  $A_0$  is the area of the undeformed sphere, exactly cancels the total  $\Pi A_p$  of the inward interdroplet forces, where  $A_p$  is the surface area of the surrounding Wigner-Seitz cell.

The resulting theoretical asymptotes are indicated in Fig. 3 by solid lines. The intercepts of both lines are given by the adjustable parameter  $\Pi_i^*$ , which we set to 1.1 atm, while the slopes are geometrical constants. In the weakly deformed regime, agreement between theory and experiment is rather poor, since the measured slope of  $\Pi^*$  vs  $\Pi_0$  is significantly lower than the theoretical prediction. There are many possible reasons for this failure, the most obvious of which is the fact that in this regime the droplets are not ordered, but randomly packed. In the strongly deformed regime, however, the agreement between the theoretical and experimental slopes is surprisingly good.

We conclude by suggesting a possible explanation for these results. The disjoining pressure  $\Pi(h)$  exerted between the interfaces of a fluid film is generally not a monotonic function of the film thickness  $h$  [9]. Upon decreasing  $h$ ,  $\Pi(h)$  may initially rise, due to double-layer repulsion, but then reach a maximum value and decrease, due to van der Waals attraction. A metastable equilibrium thickness thus exists only at applied pressures less

than the maximum disjoining pressure  $\Pi_{\max}$ : At pressures  $\Pi > \Pi_{\max}$  the film drains continuously, leading eventually to either film rupture or the formation of a Newtonian black film [9]. We thus tentatively associate our threshold  $\Pi_i^*$  with the pressure  $\Pi_{\max}$  at which the energy barrier to draining vanishes. The sharpness of the observed stability threshold further suggests that this barrier is of order  $k_B T$  only in a narrow range of pressures before vanishing. Our results raise the exciting possibility that the microscopic criteria for emulsion stability can be isolated and identified. It should be within the reach of future experiments to explore the generality and limitations of the ideas presented here.

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