Noncoalescing Drops

Y. Amarouchene, G. Cristobal, and H. Kellay

Centre de Physique Moléculaire Optique et Hertzienne (UMR 5689), Université Bordeaux I,
351 cours de la Libération, 33405 Talence, France
(Received 4 May 2001; published 29 October 2001)

A pure water drop coalesces almost immediately with a pure water surface. Minute amounts of surfactant can alter this process dramatically. When the drop is released towards the surface of the solution from a certain height smaller than a well defined critical height, the drop of surfactant solution either remains on the surface for a specific time or coalesces immediately. The statistics of the residence time are systematically measured along with the critical heights necessary for coalescence. It turns out that the surface elasticity controls coalescence in such a situation.

Fusion between two fluid bodies or the fission of a fluid body into two is of both fundamental and practical interest. The detachment of a fluid drop from a faucet or the breaking of a fluid jet are examples of a fission problem which has provided a wealth of information on the nonlinear dynamics of the processes leading to the observed singular behavior [1]. On the practical side, the stability of liquid foams and emulsions which are very widespread is also a problem of either enhancing the coalescence rates or inhibiting them [2]. The mechanisms that enter into play [3] are, however, not completely known and understood since it amounts to resolving the problem of thin film rupture which remains an active research area [4,5]. Here we revisit the case of a liquid drop that can sit on top of the same liquid for some time before coalescing with the liquid surface as is well known [6,7]. Reynolds pointed out this phenomenon more than a hundred years ago [8]. These drops can float on top of the surface for long times by simply setting the drop into motion as is well documented even for pure liquids or by imposing temperature gradients as has been recently put forth and quantified [9].

The aim of this contribution is to characterize this process in a simple example where the coalescence is inhibited for a short time by the presence of surfactants. Basically we use pure water with variable amounts of surfactant and study the coalescence of drops of this solution with the surface of the same solution. For pure water, the drop coalesces with the surface in a matter of milliseconds or less [10], but for very small quantities of surfactant added the time the drop rests on the surface is at least 2 orders of magnitude larger. Here two quantities are determined, namely, a critical height h_c such that if the drop is released towards the surface of the solution from a position higher than h_c, it coalesces immediately with the surface; this gives the energy barrier necessary for coalescence to occur. The other quantity we measure is the residence time t_c the drop stays on the surface when released from a height smaller than h_c. We construct histograms of the residence time of the drop and from such histograms we determine the critical height. An intriguing feature of our results is the existence of a range of heights below the critical height

h_c, for which the histograms of t_c show two bumps; the distribution of residence times is bimodal. A simple picture of coalescence emerges from the observations we have made. It turns out that the surface elasticity of the surfactant monolayers governs the barrier to coalescence as we show in a semiquantitative way.

The experiments use a fast video camera and a VCR to record the sequence of images before the drops coalesce to determine the time of residence. The drops of fluid are released from a pipette mounted on a translation stage for precise vertical positioning. The noncoalescence is observed for different surfactants of both the ionic and the nonionic type. Here we present results for two different surfactant systems. The surfactant solutions used are prepared using ultrapure water and a commercial pure ionic surfactant (AOT: bis-ethylhexylsulfosuccinate) or a nonionic surfactant (Triton X-100). The critical micellar concentration (cmc) for the AOT surfactant in water is 1.33 g/L, while for the Triton X-100 it is 0.5 g/L. Above this concentration aggregates start to form in the bulk of the solution. The surface tension of the solution was determined using the drop weight method.

Figure 1 shows photographs of a drop approaching, impacting, and rebounding before coming to rest on the surface of the solution it was made from. The resting drop deforms the surface underneath it due to its weight. The drop is slightly elliptical giving a high contact angle (close to 180°) with the surface. This indicates a nonwetting situation which implies directly the existence of an air film between the drop and the surface. Despite the dramatic impact of the drop with the surface which can make the drop penetrate almost in its entirety in the solution it still does not coalesce with the surface (Fig. 1b). Figure 2 is a typical series of histograms of the time the drop stays on the surface for a fixed concentration but for different release heights. For small heights, the histogram is wide and presents only a rounded bump at a finite time. As the height is increased, the bump becomes sharper with a distinct peak at 6/25 s, while a peak at zero time indicating almost immediate coalescence events starts to emerge. Once a certain height which we call h_c is reached, the
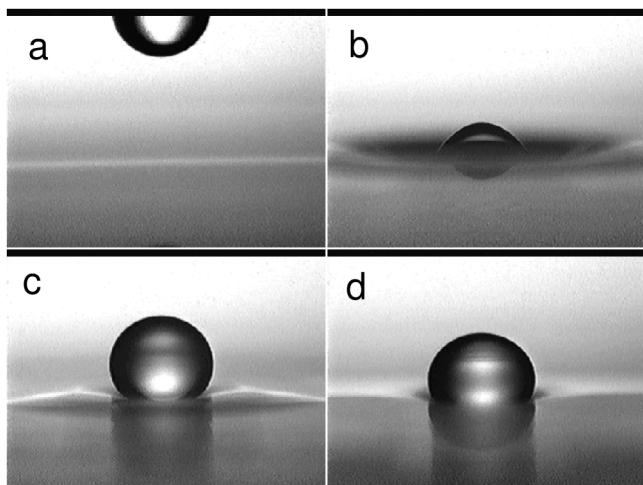
FIG. 1. Photograph of a drop of surfactant falling (a), impacting the surface (b), and rebounding (c) before coming to rest (d).

peak at zero is the only thing left and coalescence occurs almost immediately. Different concentrations of surfactant gave very similar behavior as the height changes. The only difference is a change of h_c versus concentration. While h_c is only 6.7 mm for the solution at 10^{-4} times the cmc, it is almost 25 mm for the solution at the cmc/3 for the AOT surfactant. As explained below, the peak at finite time reflects the slow drainage of the air film trapped between the drop and the surface. The peak at zero time, however, may indicate the presence of some roughness or inhomogeneities at the interfaces which alter the way the air escapes from the layer between the drop and the surface. Whether they are created by the air flow as the drop is approaching the flat surface or whether they are created by the impact itself is an open question. The coexistence of both immediate and delayed coalescence has not been reported before and may provide new insights on the coarsening of foams and emulsions even though the physics of

the impact used here is different from the collisions which occur in such systems.

Figure 3 shows the critical height h_c and the surface tension of the solution-air interface as a function of concentration for the two surfactant systems. h_c starts out small at low concentrations, then starts to increase up to concentrations well below the cmc; h_c then goes through a maximum and starts decreasing just below the cmc. Above the cmc, h_c saturates at a constant value up to at least 10 times the cmc. The variation of h_c clearly indicates that the barrier for coalescence changes in a similar fashion versus concentration; note that there is no resemblance with the variation of the surface tension. A better estimate of the barrier to coalescence is mgh_c, where m is the mass of the drop and g is the gravitational constant. This energy barrier also goes through a maximum at a concentration well below the cmc and then decreases to saturate at concentrations above the cmc.

This barrier could be directly related to the surface elasticity of the monolayers. To tear up the surfactant monolayers, large concentration gradients must be generated at the interface. The surface elasticity also known as a Marangoni elasticity normally measures the energy necessary for such gradients. Basically, the drop impacts the surface with a typical velocity $\sim\sqrt{2gh}$; part of the impact energy goes into the deformations of the surface and part of it goes into the draining of the air film. Both processes can reduce the surfactant surface concentration by increasing the surface area or, if the velocity of the draining is high, by flow entrainment of the surfactant molecules. If these gradients are large enough, the surface resembles water and coalescence may occur.

A direct test of the relevance of some surface elasticity in determining the barrier to coalescence comes from measurements done at a fixed concentration but varying drop radius R. Figure 4 shows h_c versus R in the inset and
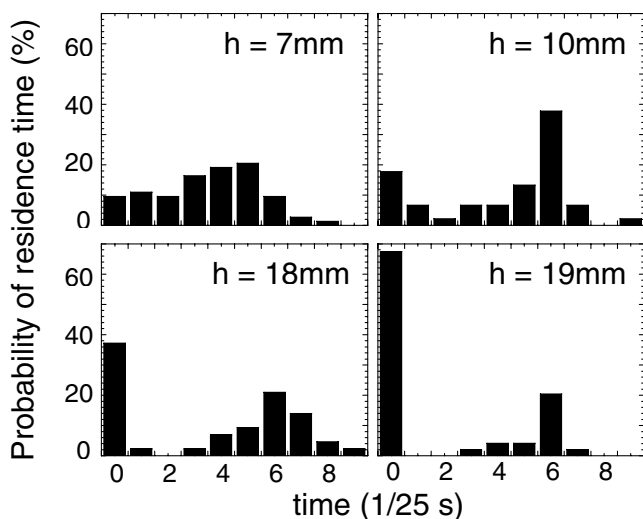

FIG. 2. Probability distributions of the residence time of a drop on the surface of the liquid for four different heights of release and 1 mM AOT solution.
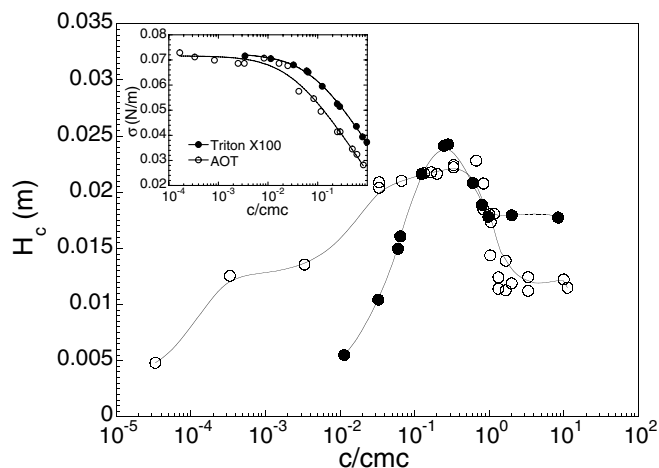

FIG. 3. The critical release height for coalescence to occur versus surfactant concentration and two different surfactant systems. Inset: Variation of surface tension versus concentration; the solid lines are fits using the Langmuir-Szyszkowski adsorption isotherm.
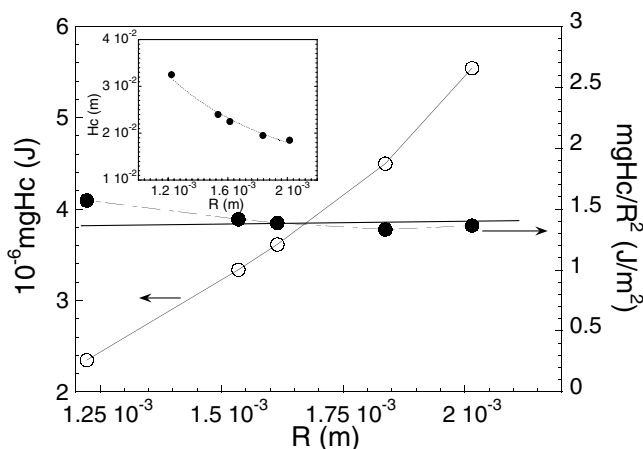
FIG. 4.   Energy barrier and energy barrier normalized by the square of the drop radius R versus R for a concentration of 1 mM AOT. Inset: Variation of h_c versus R.

the energy mgh_c as well as the energy normalized by the surface of the drop mgh_c/R^2 in the main figure. h_c decreases with R, while mgh_c seems to increase. The most surprising feature which points to the relevance of some surface elasticity is that the energy normalized by the surface of the drop turns out to be constant as a function of the radius. Clearly the physical parameter governing this process is an energy per unit surface. More quantitatively, we compare the extracted values for this energy barrier normalized by the surface of the drop to models of the surface elasticity developed by Lucassen *et al.* [11,12] in Fig. 5. It turns out that such simple models can account reasonably well for the variation of this barrier to coalescence versus concentration. The Lucassen model for the surface elasticity of monolayers of soluble surfactants predicts that $\epsilon = d\gamma/d\ln a = \epsilon_0 \frac{1+\Omega}{1+2\Omega+2\Omega^2}$, where a is a surface element, γ is the surface tension, and Ω is a reduced frequency given by $\sqrt{D/2\omega}\, \partial c/\partial \Gamma$. Here D is the diffusion constant of the surfactant molecules in the bulk solution (typically 6×10^{-10} m²/s [11]) and its presence
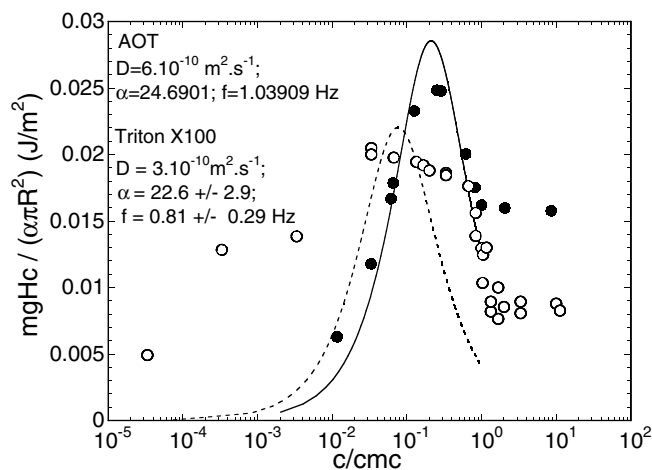

FIG. 5.   The energy barrier per unit surface versus concentration for the two surfactant systems. The solid lines are fits using the Lucassen model.

reflects the fact that the model uses diffusion from the bulk to the surface as the main factor governing surfactant adsorption and desorption at the interface. ω is the frequency of the perturbation at the surface, c is the bulk surfactant concentration, and Γ is the surface concentration of surfactant. The variation of surface versus bulk concentration is obtained from the surface tension variation versus concentration using the Langmuir-Szyszkowski adsorption isotherm [13] (Fig. 3 inset). The intrinsic surface elasticity ϵ_0 (also known as the Marangoni elasticity which measures the Marangoni interfacial stress) is given by $-\Gamma d\gamma/d\Gamma$ and is the elastic response of the surface for an infinite frequency of the perturbation. If the frequency of the excitation is reduced, the surfactant in the bulk can have enough time to adsorb at the interface and relax the increase in area giving a reduction of the elastic response of the monolayer. The fits have two free parameters which are the frequency of the excitation and the area with which the energy barrier is normalized ($S = \alpha\pi R^2$). The frequency comes out to be about 1 Hz which could be related to the rate of increase of the surface area ($\frac{\partial a/\partial t}{a}$), while the area S comes out to be about 5 times the drop surface and may be assimilated to the increase in area of the liquid surface upon impact. We find a much better agreement in the case of Triton X-100 (the nonionic surfactant) since the model does not take the electrostatic effects into consideration. These electrostatic effects are important for the ionic surfactant AOT and are expected to create additional barriers to the surfactant adsorption at the interface [14].

As in previous studies of noncoalescing drops, the air layer trapped between the drop and the surface can take a long time to thin when other forces can maintain it [9]. When surfactants are present it is probably the friction of air against the surfactant layer which is responsible for the delay in the thinning of the air film. The air film can thin very fast when pure water is used since the surface of pure water can move freely with little resistance to the air which entrains it. The only resistance would be viscous dissipation in the bulk which is small considering the small value of the water viscosity. When surfactants are present, the surface possesses its own rheological properties such as a surface viscosity and a surface elasticity associated with surfactant concentration gradients at the surface giving rise to Marangoni stresses [11,14,15]. In short, the surface of the surfactant solution presents extra resistance to the flow of air trapped in the layer. The boundary conditions on the surface of the drop and on the surface of the solution with respect to air flow would change from slip (for water) to at least partial nonslip for the surfactant solutions [16]. Theoretical work has recently addressed the complicated issue of the coupling between the bulk flow and the interfacial dynamics due to surfactant redistribution at interfaces for insoluble surfactants [17,18].

The mean residence time of the drop at the surface of the solution depends on the radius of the drop. This variation turns out to be roughly linear as shown in Fig. 6. Such a linear variation may seem to be consistent with a simple
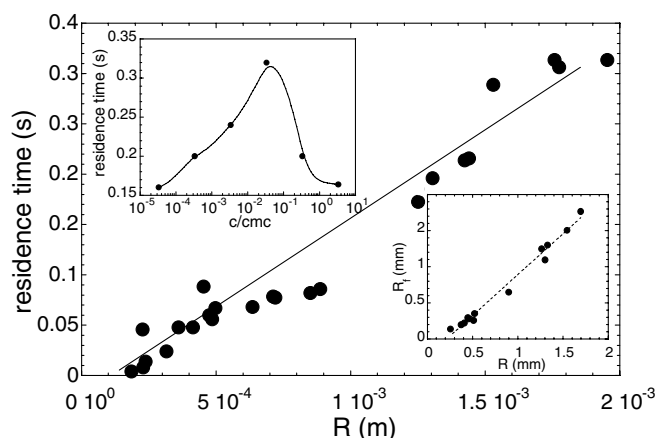
FIG. 6. Residence time versus drop radius for a fixed surfactant concentration (10 mM AOT). Upper inset: Variation of the residence time versus concentration (AOT system). Lower inset: Radius R_f of the contact area (A) between drop and surface versus R.

draining law for the thickness of the air film between the drop and the surface. One has to assume that the area of contact between the drop and the surface is proportional to the square of the drop radius [the radius R_f of this contact area is proportional to R (see lower inset)] and that the trapped film drains under the action of gravity. The residence time under these conditions can be written as $t_c \sim A^2 \mu / F(d_c^{-2} - d_i^{-2})$, where the force $F = mg$, m is the drop mass, g is the gravitational constant, A is the area of the film between the drop and the surface, μ is the viscosity of the intermediate fluid (air), and d_c is the critical thickness of the air film at breakup, while d_i is the initial thickness of this film. This would surprisingly indicate that this film drains in a similar fashion as in the so called Reynolds limit for the draining of a fluid between two rigid plates of finite radius. An estimate of d_c from such an expression gives a value of about 1 μm which appears quite large. Usually in previous studies this length was estimated to be close to 1000 Å. It has been argued theoretically that the mobility of the interfaces may contribute to the dynamics of thinning of thin fluid films and renders the thinning much faster [19]. Other effects which are hydrodynamic in origin or geometrical such as the formation of a dimple also affect the draining [20]. The physics is that of a less dense layer of fluid between two layers that are more dense, a typical scenario for the development of a Rayleigh-Taylor instability. Such a situation has been studied for the case where the liquids are confined in a Hele-Shaw cell where it was shown that rupture occurs in finite time [4]. The case in our experiment is different as we have two flat planes approaching each other. When the two interfaces are coated with surfactant, there is more friction of the air against the interfaces which would increase the time of draining of the air film. At some point rupture would occur triggered by the instability of the interfaces [21]. In any case, the residence time given by the above expression is only indicative; the rupture of the film is a difficult nonlinear process to understand fully. The upper inset (Fig. 6) shows that the residence time depends on the concentration of surfactant and goes through a maximum just as the barrier to coalescence which points to the relevance of the surface viscoelasticity in the draining and breakup of thin films. Above the cmc the residence time stays roughly constant just as the surface elasticity mentioned above.

In summary, we present a detailed study of the coalescence of surfactant laden drops on surfactant laden interfaces. The existence of a well defined energy barrier for coalescence to occur and the existence of a well defined residence time of the drop on the surface gives rise to a simple picture for this coalescence process. The energy barrier is controlled by a surface elasticity while the well defined residence time indicates that this process resembles finite time singularities as is the case in droplet fission.

We thank J. Meunier, D. Bonn, J. Eggers, and R. Blossey for discussions.

[1] J. Eggers, Rev. Mod. Phys. **60**, 3 (1997); **60**, 865 (1997).
[2] J. Bibette, F. Leal Calderon, and P. Poulin, Rep. Prog. Phys. **62**, 969 (1999).
[3] J. Eggers, J. R. Lister, and H. A. Stone, J. Fluid Mech. **401**, 293 (1999).
[4] T. F. Dupont *et al.,* Phys. Rev. E **47**, 4182 (1993).
[5] A. Oron, S. H. Davis, and G. Bankoff, Rev. Mod. Phys. **69**, 931 (1997).
[6] J. Walker, Sci. Am. **238**, No. 6, 123 (1978).
[7] G. E. Charles and S. G. Mason, J. Colloid Sci. **15**, 236 (1960); G. D. M. MacKay and S. G. Mason, Can. J. Chem. Eng. **41**, 203 (1963).
[8] O. Reynolds, Chem. News **44**, 211 (1881); O. Reynolds, Philos. Trans. R. Soc. London A **177**, 157 (1886).
[9] P. Dell'Aversana, J. R. Banavar, and J. Koplik, Phys. Fluids **8**, 15 (1996); P. Dell'Aversana and G. P. Neitzel, Phys. Today **51**, No. 1, 38 (1998).
[10] S. T. Thoroddsen and K. Takehara, Phys. Fluids **12**, 1265 (2000).
[11] J. Lucassen and M. Van Den Temple, J. Colloid Interface Sci. **41**, 491 (1972); Chem. Eng. Sci. **271**, 1283 (1972).
[12] R. Miller *et al.,* Colloids Surf. A **111**, 75 (1996).
[13] C-H. Chang and E. Franses, Colloids Surf. A **100**, 1 (1995).
[14] A. Bonfillon-Colin, Ph.D. thesis, University of Paris 6, 1994.
[15] D. E. Tambe and M. M. Sharma, J. Colloid Interface Sci. **147**, 137 (1991).
[16] S. A. Koehler, S. Hilgenfeldt, and H. A. Stone, Phys. Rev. Lett. **82**, 4232 (1999).
[17] J. M. Lopez and A. H. Hirsa, J. Colloid Interface Sci. **229**, 575 (2000).
[18] V. Cristini, J. Blawzdziewicz, and M. Loewenberg, J. Fluid Mech. **366**, 259 (1998).
[19] S. A. K. Jeelani and S. Hartland, J. Colloid Interface Sci. **156**, 467 (1993).
[20] A. F. Jones and S. D. R. Wilson, J. Fluid Mech. **87**, 263 (1978).
[21] S. B. Lang and C. R. Wilke, Ind. Eng. Chem. Fundam. **10**, 329 (1971).