Coalescence in Draining Foams

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Cellular material (emulsions, foams) made out of two different phases, one dispersed in another, may coarsen with time through coalescence, which is the rupture of the thin liquid film that separates two adjacent droplets or bubbles. In this Letter, we study destruction through coalescence of a model cellular material: a monodisperse soap foam. We report the existence of a sharp destabilization threshold controlled only by the liquid fraction of the foam at which the rate of coalescence increases dramatically. We point out a coupling between drainage and coalescence. We suggest that the rearrangements of the bubbles during the drainage of the foam induce an increase of the area of the bubbles which decreases temporarily the amount of adsorbed surfactant by unit area and weakens the interfaces.

Foams are a mixture of gas and liquid stabilized by surfactant, consisting of gas bubbles dispersed in a liquid.1 They are metastable, so that the mean size of the bubbles tends to increase with time. They belong to a wide class of nonequilibrium systems such as emulsions or off-critical decomposing mixtures that rearrange and coarsen with time. The characteristic time for coarsening of foams spans a remarkably wide range, from a few seconds to a few months. Foams are extremely important for a variety of applications such as detergency, food processing, or cosmetology, and their stability is a key factor for all applications.

Two limiting mechanisms are responsible for their evolution. One, Ostwald ripening, is due to the diffusion of the dispersed phase out of the smaller bubbles into the bigger ones through the continuous phase driven by the higher Laplace pressure in the smaller droplets. The second mechanism (coalescence) is due to the rupturing of the thin liquid film that separates two adjacent cells. A fundamental question concerns the determination of the critical parameters that govern the destruction of foams. This question has motivated a lot of studies. However, no simple conclusions emerged from these studies.2-5 The role of the film size in the coalescence process remains, for example, very unclear. A widely accepted and intuitive argument is that large bubbles are more fragile than the smallest ones and that the probability of rupture of a film is simply proportional to its surface area.2,6-8 On the contrary, acoustic experiments have demonstrated that small and large bubbles are involved in the avalanche process during the dynamics of a collapsing foam. The authors conclude that the radii of the bubbles do not govern the stability of the draining foam.4,5

To better understand the role of the film size in the destruction of the foam, we study draining foams comprised of initially monodisperse bubbles. We perform dielectric experiments and visual observations, and we measure the evolution of the liquid fraction of the foam during the collapsing process.

Figure 1. Experimental set up.

Foams of sodium dodecylbenzenesulfonate (SDBS), poly(ethylene glycol) surfactant (C10E10), and tetradecyltrimethylammonium bromide (TTAB) were made; SDBS and TTAB were purchased at Aldrich and used as received. C10E10 was provided by Atofina Company. The foaming solutions were prepared with deionized water. Various concentrations and mixtures of surfactants above and below the critical micellar concentration have been used. Foams have been created by continuously bubbling perfluorohexane saturated nitrogen through a capillary (hole diameter: 1, 0.5, 0.2, and 0.1 mm) or a porous glass disk (porosity: 150–200, 90–150, and 40–90 μm) into the foaming solution, inside a Plexiglas column (25 cm × 25 cm × 60 cm high) equipped with 25 electrodes and counter electrodes (Figure 1). During the bubbling, we wet the foam from above with the foaming solution at a constant rate by using a peristaltic pump. Before reaching the foam, the foaming solution falls on the wall of the column. This avoids wetting to induce coalescence. The column has an overflow pipe at its bottom. This method allows us to produce a monodisperse foam with an initial liquid fraction homogeneous in the entire column. By choosing a mixture of gas that has a very low diffusivity in water, we eliminate on the timescale of the experiment one class of destabilizing phenomena, that of Ostwald ripening, and we can study the evolution of the coalescence process only.9

Determination of the bubble size is made by image analysis of the plateau borders on the border of the column.

Plateau borders are the channels formed in the region where three films meet. Statistics are made over 50 bubbles. The polydispersity of the foam is measured by calculating the standard deviation $\delta = \sqrt{\frac{\sum (x - \bar{x})^2}{n(n - 1)}}$, where $n$ is the number of data points, $x_i$ is a data value, and $\bar{x}$ is the mean. To know the amount of water present in the foam, we measured the liquid fraction $\phi$ by conductivity using the models developed by Lemlich, Peters, and Phelan. The liquid fraction is equal to the volume of liquid in a macroscopic foam region divided by the total volume of the region.

At the beginning of experiments, bubbling is stopped and the pump is turned off. The column is hermetically closed with a Plexiglas cover and a polymer film in order to avoid evaporation. The foam is left to coalesce and collapse freely. Three successive regimes are observed. First, the height of the foam remains constant. Due to gravity, liquid flows and the foam dries. Second, the foam continues to dry but the bubbles present at the air/foam interface rupture. A rupture front propagates in the foam, and the height of the foam decreases. This evolution is discontinuous; it evolves by avalanches separated by periods of stasis. Visual observations suggest that coalescence events occur only at the top of the foam. We checked this by rewetting the foam from above with the flow used for the preparation of the sample and by measuring the liquid fraction. Comparing this to the liquid fraction measured during the preparation of the sample, it can be concluded that the number of bubbles is unchanged before the arrival of the rupture front. The third regime corresponds to the end of the experiments. In the lower part of the column, a residual height of bubbles persists. This foam is stable and no more evolves or coalesces.

To determine the parameters that govern the stability of the foam, we recorded the evolution of the liquid fraction as a function of time for various positions in the column.

Figure 2 presents the evolution of the liquid fraction $\phi$ versus time for a fixed position in the column. The soapy solution used to make the foam is a mixture of 70% SDBS and 30% C10E10. The concentration of surfactant is 1% in weight. The length of the plateau borders is 2 mm, and the standard deviation is 0.5 mm. First, liquid drains in the foam. When the drying front reaches the position where the measurement is made, the liquid fraction begins to decrease. The discontinuous drop down of the liquid fraction that occurs at longer time corresponds to the breaking of the foam. A nonzero signal is measured after rupture because some water is expelled on the walls and builds a wetting film that drives the electrical current. By comparing the signals at different positions, we note (Figure 3) that rupture arises nearly always at the same liquid fraction. More precisely, destruction occurs in a narrow field of liquid fraction ranging from 0.0005 to 0.0007 (Figure 3). It is important to note that the drainage of the foam is not ended when the rupture front propagates. This means that coalescence in this study occurs under dynamic conditions. This implies that there is a coupling between drainage and coalescence. At the end of the experiment, a residual height of foam persists in the lower part of the column. No coalescence events occur in this residual foam. In this part of the foam, the liquid fraction has reached an equilibrium value corresponding to the balance between the capillary and gravity forces. This equilibrium value is higher than the critical liquid fraction involved in the rupture front. This shows that the top of the foam is not a particular place for coalescence.

All these points suggest to us the existence of a sharp threshold controlled by the liquid fraction. To support our assumption, we carried out a forced drainage measurement. The soapy solution used to make the foam is a...
The total concentration of surfactant is 1% in weight. The length of the plateau borders is 2 mm, and the standard deviation is 0.5 mm. At the beginning of the experiments, the foam is wetted from above with a constant flow rate of 0.0004 mm/s. At t equals 130 s the flow rate is decreased to 0.0001 mm/s. The foam breaks in ~2 min. Coalescence occurs simultaneously in the middle (18 cm) and in the bottom of the foam (8 cm).

The novelty of our work is to demonstrate clearly the role of the liquid fraction. Coalescence events are dramatically enhanced below a critical liquid fraction. This critical liquid fraction is a function of the nature of the surfactant and of its concentration. It does not depend on the size of the bubbles. The coalescence process occurs then at a critical liquid fraction. More precisely, destruction occurs in a narrow field of liquid fraction ranging from 0.0005 to 0.0007 (Figure 5).

The velocity of the fluid in the drainage process is slowed down as the pressure criterion. Hence, if it were the case, then the radius of the bubbles does not govern the stability of draining foams. However, we show that the lifetime of a foam is enhanced when the bubbles are smaller because it takes more time for a fine foam to drain and to reach the critical liquid fraction. This fact may explain the widely accepted idea that foams with small bubbles are more stable.

Some previous studies on isolated films or in emulsions have suggested that thin liquid films become unstable at a critical value of the microscopic pressure exerted on them. This inward pressure, called the disjoining pressure, is opposed by the interactions (electrostatic or steric interactions) between the two interfaces of the film and determines its thickness. Our results demonstrate that coalescence in foam is not governed by a disjoining pressure criterion. Hence, if it were the case, then the critical liquid fraction measured for a monodisperse foam would vary as the square of the inverse of the radius of the bubbles. We thus confirm here the results obtained by Vandevallée and point out that the radius of the bubbles does not govern the stability of draining foams. However, we show that the lifetime of a foam is enhanced when the bubbles are smaller because it takes more time for a fine foam to drain and to reach the critical liquid fraction.
and of the plateau borders by the following formula $\phi = (0.36r/L_{pp})^2$. Moreover, the value of the disjoining pressure exerted on the films in the foam when coalescence occurs is very small compared to the disjoining pressure that isolated films are able to support before breaking. Indeed, in the case of the TTAB solution, the critical liquid fraction, for a surfactant solution near the critical micellar concentration, is equal to 0.0008. In this experiment, the length of the plateau borders is 1.5 mm, and the surface tension is $39 \times 10^{-3}$ N m$^{-1}$. The disjoining pressure applied to the films in the foam just before coalescence events is thus equal to 351 Pa. This value is 2 orders of magnitude smaller than the values that isolated films are able to support without breaking for the same solution.

Therefore, another mechanism must be responsible for coalescence in draining foams. This work proposes a mechanism based on a critical film dilatation. It takes into account the dynamical conditions induced by the drainage. Once the foam dries, elementary movements are still observed. These movements resemble what is known as T1 in 2D foams. They are very rapid and occur in less than $1/25$ s (we have been unable to record and define them using a classical video camera). These movements are induced by a change in liquid fraction and are a surface minimization process. For 2D foams, Princen has shown that the maximum strain reached in a T1 process strongly increases with foam dryness, noticeably for liquid fractions as low as 0.3%. This maximum strain, from a dimensional analysis, is not dependent on bubble size but rather depends only on the liquid fraction. It can thus be conceived that when the liquid fraction becomes too low, the fast relative surface area increase produced by an elementary movement will be too high to be stabilized by the surfactants. However, we need to know the time required for the surfactant molecules present in the liquid to reach the surface and recover it to claim this. As noticed previously, the answer to this question is delicate.

This time decreases when the surfactant concentration increases. Dynamic surface tension studies shows that it spans from 1 to 0.003 s in the studied concentration domain. We recall that, at a critical dilatation, we are able to describe the obtained evolution of the critical liquid fraction as a function of the surfactant concentration. Figure 6 presents the evolution of this critical liquid fraction as a function of the surfactant concentration for various plateau border lengths. As previously, our data evidenced that the range of critical liquid fraction does not depend on the length of the plateau borders. Moreover, when the surfactant concentration is increased, the critical liquid fraction decreases rapidly in the neighborhood of the critical micellar concentration (0.12% in weight) and almost saturates at higher concentrations.

This curious observation that the critical liquid fraction does not depend on the surfactant concentration above a few times the cmc can be explained by our mechanism: the limiting diffusion mechanism from the bulk to the surface in the convection of dissociated surfactant molecules and not of molecules associated in micelles, which have a far slower dynamic. We recall that, far from the critical micellar concentration, the adsorption is limited first by the splitting time of the micelles and after by the adsorption of the dissociated molecules. Thus, the critical dilution at which the bubbles can no more be saturated by surfactant strongly depends on the surfactant concentration around the cmc, but not far above.

In this Letter, we have studied coalescence in draining foam through visual observations and dielectric measurement. It is important to note that, in this study, the destruction of the foam occurs under dynamic conditions. Bubbles rearrange and liquid flows through the foam. Under those dynamic conditions, we point out the fundamental role played by the size of the bubbles. The coalescence process is dramatically enhanced below a critical liquid fraction. This critical range of liquid fraction depends on the surfactant concentration and the nature of the surfactant but does not depend on the size of the bubbles. Moreover, we have proposed a mechanism based on the dilatation of the films and on the coupling between drainage and coalescence. Assuming that the films break at a critical dilatation, we are able to describe the obtained results.

Future experiments concern the analysis of the avalanche process and their localization by ultrafast camera and acoustic experiments.