Coalescence In Draining Foams Made of Very Small Bubbles

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(Received 4 December 2015; published 22 March 2016)

We studied the stability of foams containing small bubbles (radius $\lesssim 50\ \mu$m). The foams are made from aqueous surfactant solutions containing various amounts of glycerol. The foams start breaking at their top, when the liquid volume fraction has decreased sufficiently during liquid drainage. Unlike in foams with larger bubbles, the liquid fraction at which the foam destabilizes is surprisingly high. In order to interpret this observation we propose that film rupture occurs during reorganization events ($T1$) induced by bubble coarsening, which is particularly rapid in the case of small bubbles. New films are therefore formed rapidly and if their thickness is too small, they cannot be sufficiently covered by surfactant and they break. Using literature data for the duration of $T1$ events and the thickness of the new films, we show that this mechanism is consistent with the behavior of the foams studied.

DOI: 10.1103/PhysRevLett.116.128302

Liquid foams are dispersions of gas bubbles in liquids, stabilized by surface active agents such as surfactants, polymers, or particles [1]. The liquid fraction ϕ is usually smaller than the *jamming* fraction ϕ_J at which bubbles come in contact ($\phi_J \sim 36\%$ for foams with modest polydispersity). The bubbles take polyhedral shapes, separated by liquid films connected in channels called *Plateau border* (PBs), themselves connected in *vertices* or *nodes*. Foams have a variety of applications in detergency, food, cosmetics, medicine, fire-fighting, oil recovery, and flotation of minerals. They are precursors of solid foams, used for heat and sound insulation or for manufacturing cushions and to lighten materials without losing mechanical resistance, such as metallic foams for cars and space vehicles.

Despite these many applications, our understanding of foams is still limited. Liquid foams are intrinsically unstable and disappear typically after a few hours. Foam destabilization occurs via mechanisms coupled together: gravity-driven *drainage* of the liquid, bubble *coarsening* (transfer of gas between bubbles driven by pressure differences), and bubble *coalescence* (rupture of films between bubbles leading to foam collapse) [1–3]. While foam drainage and coarsening can be modeled, coalescence remains little understood. Different observations are reported in the literature, in which coalescence of bubbles of radius R occurs: (i) when R reaches a critical value R^* [4] (as in emulsions, which are dispersions of oil and water [5]), (ii) when the pressure difference P_c between the gas and the liquid in the PBs (called capillary pressure) reaches a critical value P_c^* [6] (also as in emulsions [7]). R and P_c are related: for dry foams (small ϕ) $P_c \simeq \gamma/(R\sqrt{\phi})$ [1]. The observation of different thresholds can therefore be the manifestation of the same phenomenon.

It is sometimes proposed that P_c^* is equal to the maximum of the disjoining pressure (force per unit area between film surfaces) when only long range forces are taken into account [3]. P_c^* is, however, frequently smaller [8] and even depends on R: measured critical capillary pressures decrease as R increases [6], making the identification of a critical parameter difficult.

Two other destabilization mechanisms have been proposed, more dynamic in character. They are related to fast rearrangements taking place during foam coarsening, known as $T1$ processes: adjacent bubbles change neighbors and new liquid films are withdrawn from the PBs. Carrier and Colin [9] proposed that when the adsorption time of the surfactant is longer than the duration of the $T1$ process, the films break, and the foam collapses. Biance *et al.* [10] proposed that when the liquid fraction reaches a critical value ϕ^*, there is not enough liquid in the foam to allow for bubble rearrangements.

In order to clarify the interplay between the different destabilization mechanisms, we have worked with foams made with aqueous solutions of a widely used model surfactant, sodium dodecyl sulfate (SDS) and glycerol, in order to change the solution viscosity which influences drainage in a controlled way. The surfactant concentration used was 6 g/L, three times the critical micellar concentration (CMC). The amount of surfactant in excess to the CMC available to cover the bubble surfaces is, therefore, 4 g/L. This is much larger than the minimum amount needed, C_{ads}, in order to fill the bubble surfaces: $C_{\text{ads}} \sim 3(1-\phi)M_s/(N\Sigma R\phi)$, M_s being the surfactant molecular weight, N the Avogadro number, and Σ the area per surfactant molecule at the bubble surface. Using $\phi = 33\%$, $M_s = 288$, and $\Sigma \sim 0.5\ \text{nm}^2/\text{molecule}$, one finds $C_{\text{ads}} \sim 0.6$ g/L, for the smallest bubbles produced in this study, $R \sim 10\ \mu$m, i.e., smaller than the available 4 g/L. The water was from a Millipore system, the chemicals from Sigma Aldrich.

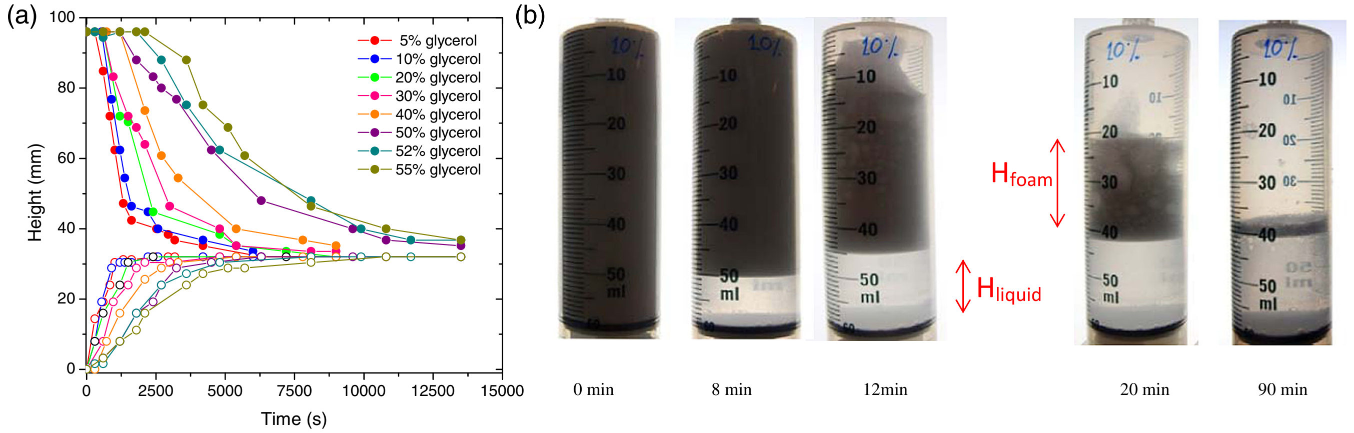

FIG. 1. (a) Time evolution of the total height of foam + drained liquid (closed circles) and height of drained liquid (open circles) for different amounts of glycerol in water and $\phi_0 = 33\%$. (b) Aspect of samples containing 10% glycerol after different times as indicated.

The foams were made using a device made of two identical syringes connected by a narrow tube. One syringe is first filled with a controlled volume V_G of gas (air in the present study) and liquid V_L, giving an initial liquid fraction $\phi_0 = V_L/(V_L + V_G)$. The total volume of the syringe (and generated foam) is 60 cm^3 (total length of about 10 cm). The two syringes were washed carefully before use (five times with the SDS solution, then with ultrapure water to remove the surfactant). In this way, the time evolution of the foams is fully reproducible. A series of ten back-and-forth cycles is then performed, the content of one syringe being emptied periodically into the second one, the pistons of the two syringes being controlled by a motor. This device produces foams of well-defined initial liquid fraction ϕ_0 and very small bubble radii (a few tens of microns) [11]. The time evolution of foam height and drained liquid is measured directly after foam generation in the syringe, which is set vertically for this purpose.

Figure 1(a) shows the evolution of the total height of foam + drained liquid (closed circles) and of the drained liquid height (open circles) for different amounts of glycerol in water and an initial liquid fraction $\phi_0 = 33\%$. Figure 1(b) shows pictures for the sample with 10% glycerol.

The total height of the foam and of the drained liquid $H_T = H_{\mathrm{foam}} + H_{\mathrm{liquid}}$ is constant at short times [Fig. 1(a)]. This indicates that the overall amount of gas and liquid in the system stays constant. Here the foam only coarsens. After some time, coalescence events are observed at the top of the foam and H_T starts decreasing, while no coalescence is seen in the lower parts of the foam [Fig. 1(b)].

Figure 2(a) shows the variation with liquid viscosity of the "half lifetime $T_{1/2}$" after which the foam height H_{foam} has decreased by a factor of 2.

The data points are averages over three independent measurements. These results show first that, contrary to isolated film rupture, which is stochastic [17], foam collapse is deterministic. Second, $T_{1/2}$ is significantly smaller than for foams made with the same surfactant, but containing larger bubbles ($T_{1/2} \sim 100$ min with millimetric bubbles and no glycerol [18], instead of 15 min here), a puzzling feature. Third, the linear variation of $T_{1/2}$ with viscosity suggests that foam drainage, which is very sensitive to the viscosity, plays an important role. This is confirmed by replotting the data of Fig. 2(a) vs a reduced time $\tilde{t} = t\eta_w/\eta$, η being the viscosity of the foaming liquid and η_w the water viscosity: all the curves collapse into two single master curves [Fig. 2(b)].

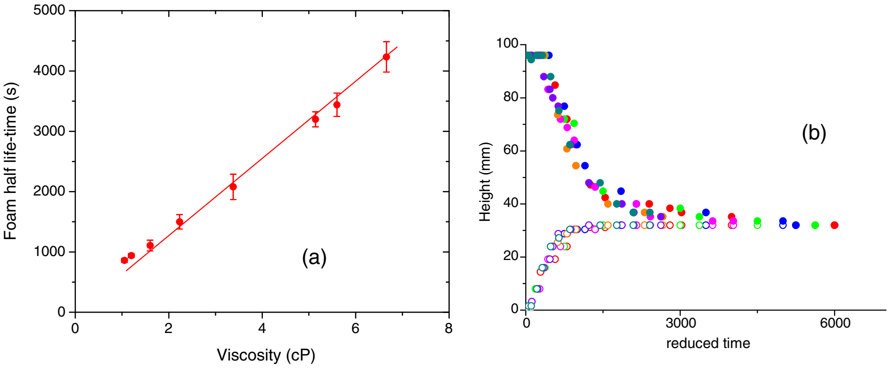

FIG. 2. (a) Foam half lifetime vs solution viscosity for $\phi_0 = 33\%$. (b) Height data of Fig. 1 plotted vs the reduced time $\tilde{t} = t\eta_w/\eta$ Additional data can be found in the Supplemental Material [12].

The basics of foam drainage is recalled in the Supplemental Material [12]. The *drainage equation* becomes nondimensional when using a characteristic time $t_{\mathrm{ch}} = \eta/(\gamma\rho g)^{1/2}$. For a given surfactant (given surface tension), the drainage time is therefore proportional to the viscosity η, as found in our experiments (Fig. 2b).

Because bubbles are small in our study, coarsening is significant. We, therefore, also measured the time evolution of the bubble size. For this purpose, small foam samples (1–2 mm thick) are extracted at the top of the syringe, set vertically as for the stability study. The first sample is discarded and the second is used to form a monolayer of bubbles between glass slides and visualized under microscope. The bubble size distribution was subsequently obtained using the ImageJ software. The detailed results are shown in the Supplemental Material [12].

As the foam becomes rapidly drier at the top than in the interior, the bubbles coarsen more rapidly at the top, where the size measurements are made. Indeed, the rate of gas transfer increases when ϕ decreases, because the size of the films between bubbles increases (see the Supplemental Material [12]).

The average bubble radius R^* at the onset of coalescence is about 60–90 μm for all the foams, whatever ϕ_0 and η. However, the time needed to reach this radius is roughly proportional to η (see Supplemental Material [12]). Drainage stops when the liquid fraction equilibrium profile is attained, i.e., when the hydrostatic pressure is in equilibrium with the osmotic pressure Π in the foam [19]. For bubble radii of 75 μm and a foam height of 10 cm, the equilibrium liquid fraction at the top of the foam is about 2% according to Ref. [19]. This leads to a capillary pressure of about 2 kPa, much smaller than the capillary pressures of 70 kPa at which rupture is observed for isolated films stabilized by the same surfactant SDS [20]. So, contrary to foams made with larger bubbles that were reported to collapse once the capillary pressure exceeds P_c^* [6], the present foams collapse earlier.

Another reported mechanism for foam collapse is dynamic in nature: when the liquid fraction reaches a critical value ϕ^*, there is not enough liquid in the foam for bubble reorganization to occur during coarsening ($T1$ process; see Fig. 3). It was predicted that $\phi^* \sim (\eta R/\tau\gamma)^{4/3}$, τ being the duration of a $T1$ event [10]. It was shown later [21] that τ is a universal function of the osmotic pressure Π in the foam

$$\tau = 0.33\frac{\eta}{\Pi}\frac{\phi}{\alpha}, \qquad (1)$$

where α is a permeability coefficient such as $\alpha = 10^{-3}$ $(2.1\phi^2 + 0.27\phi^{3/2})$ in the case of mobile surfaces. The osmotic pressure can be calculated using

$$\Pi = k\frac{\gamma}{R_{32}}\frac{(\phi_c - \phi)^2}{\phi^{1/2}}, \qquad (2)$$

in which $R_{32} = \langle R^3\rangle/\langle R^2\rangle$ is the Sauter-mean bubble radius, $k = 3.2$, and $\phi_c = 0.36$ [19].

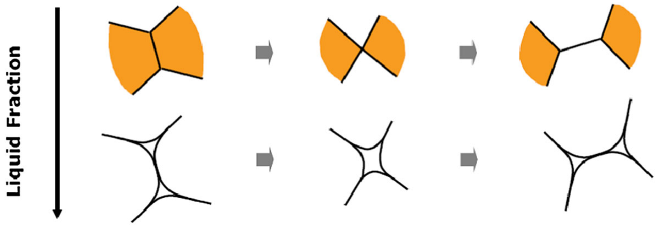

FIG. 3. Scheme of $T1$ events for a very dry foam (top) and a wetter foam (bottom).

As a consequence, ϕ^* should neither depend on the viscosity nor on the bubble size, as reported previously [9,10]. However, ϕ^* is less than 10^{-3}, which is much smaller than the liquid volume fractions of the foams studied here. The mechanism above can, therefore, not explain our observations.

A last mechanism is the surfactant depletion during the rapid stretching of liquid films in the T1 process [9]. When the bubbles are small, the process is very rapid, and depends on the osmotic pressure Π.

Using Eqs. (1) and (2) with $R = 75$ μm and $\phi = 2\%$, we obtain $\tau = 3.8$ ms for the foams under study and $\eta = \eta_w$. The stretching velocity $V_{\mathrm{st}} = L/\tau$—where L is the length of a Plateau Border ($L \sim R/1.4$)—is about 36 mm/s. As demonstrated in recent investigations of bubble clusters [22], the thickness h of the new film withdrawn from the PB can be estimated using $h = 2.68\, R_c\ \mathrm{Ca}^{2/3}$, where R_c is the PB curvature radius and Ca the capillary number ($\mathrm{Ca} = \eta V_{st}/\gamma$) [23]. Taking $R_c \sim R\sqrt{(\phi/0.33)}$, one finds $R_c \sim 18$ μm, leading to $h \sim 430$ nm for $\eta = \eta_w$. In order to know if there is enough surfactant in this film to replenish the film surfaces, we will introduce the length $l_{\mathrm{surf}} = \Gamma/C$, Γ and C being, respectively, the surface and bulk surfactant concentrations; l_{surf} corresponds to the thickness of a liquid layer containing the same amount of surfactant than the amount adsorbed at the surface. Neglecting the change in surfactant amount adsorbed at the bubble surfaces (which has decreased during coarsening), the available surfactant concentration is $C = 4$ g/L. With $\Gamma \sim 1$ mg/m^2 one has $l_{\mathrm{surf}} \sim 240$ nm and $h < h^* = 2l_{\mathrm{surf}}$, so there is not enough surfactant in the films generated to cover their surfaces [24]. Replenishment is, however, possible, but the time τ_{diff} taken by the surfactant to diffuse from the PBs to the films is long: $\tau_{\mathrm{diff}} \sim L^2/(24D_{\mathrm{surf}})$, and with $D_{\mathrm{surf}} \sim 5\, 10^{-10}$ m^2/s, $\tau_{\mathrm{diff}} \sim 200$ ms $\gg \tau$. As a consequence, there will not be enough surfactant to maintain the repulsive forces protecting the films against rupture.

It is also possible that surfactant replenishment is achieved by Marangoni convection. The characteristic time can be estimated as $t_M \sim \Delta\gamma/\eta_C$, where $\Delta\gamma$ is the surface tension gradient and η_C the surface compression viscosity. We can use $\Delta\gamma \sim 30$ mN/m (difference between surface tension of water and of the solution). Measurements of η_C have been made in the kHz range at concentrations 100 times smaller than the critical micellar concentration where the surface layer is very dilute (surface tension close to γ_w): $\eta_C \sim 10^{-3}$ N s/m [25]. This surface viscosity increases rapidly with increasing surfactant concentration and should decrease with decreasing frequency, so the replenishment time t_M is certainly larger than 20 ms. This time is longer than the time of the rearrangements. Other experimental findings show unambiguously that the Marangoni convection in foam films is slow ($t_M > 1$ s); otherwise, the drainage times of thin foam films would be as fast as those of air films in antibubbles, while they differ by orders of magnitude [26,27]. We have shown earlier that the film surface is depleted in surfactant during foam film thinning and that there is no surface replenishment, either by diffusion in the film or by Marangoni convection along the surface [26]. On the contrary, surfaces are replenished rapidly in antibubbles, because the film surfaces are in contact with a large aqueous phase; hence, the surfactant concentration at the film surfaces remains constant [27].

In Ref. [9], the authors compared the time of rearrangement τ to another characteristic time, the surfactant adsorption time τ_{ads}. Adsorption being diffusion controlled, $\tau_{\text{ads}} \sim l_{\text{surf}}^2/D_{\text{surf}} \sim 100\ \mu\text{s} \ll \tau$. Adsorption can therefore not be limiting. In addition, τ_{ads} decreases with surfactant concentration as C^2, so if this time was limiting, the stability would vary appreciable with C. This is not the case in our experiments: for foams made with aqueous surfactant solutions (no glycerol added) $T_{1/2}$ vary between 8 and 10 min when the concentration increases from 3 to 30 CMC. We can therefore exclude this mechanism in our study.

It remains to explain why the foam starts breaking when R and ϕ_{top} reach values of order 75 μm and 2%, respectively. For osmotic pressures larger than 1000 Pa [21], the reorganization time τ increases linearly with R, whereas the diffusion time increases quadratically, both times being independent of ϕ: τ will then remain smaller than τ_{diff} during the coarsening process. The crucial parameter could therefore be the thickness h of the films withdrawn from the PBs during the $T1$ events. Because both L and τ are linear in R and independent of ϕ, the velocity V is constant and h varies as $R_c = R\sqrt{(\phi/0.33)}$. Taking $R = 75\ \mu$m, h becomes equal to h^* when $\phi = 2.5\%$, i.e., close to the expected value. These estimations should be considered as indicative, as there are many uncertainties concerning the exact values of the reorganization time τ and of the thickness h of the films generated during the $T1$ events. However, the estimations are consistent and indicate that there is a conjunction due to the simultaneous increase in R and decrease in ϕ_{top}. This leads to a decrease of h until it reaches the critical value h^*, below which the films are insufficiently covered and rupture. The foam films at the top, where ϕ is the lowest, rupture first, and the rupture propagates downwards, as observed.

One could wonder above which bubble radius the proposed coalescence mechanism postulated above will no longer operate. Calculations show that for $R = 100\ \mu$m, $h = 580$ nm, already larger than h^*. The radius threshold is thus likely close to 100 μm; i.e., the mechanism applies only to very small bubbles. Note also that the calculations were made for a liquid volume fraction of 2%, and different ϕ (different foam heights) will lead to somewhat different thresholds.

All the characteristic times of drainage, coarsening (see the Supplemental Material [12]) and reorganization being proportional to the viscosity η, this mechanism leads to lifetimes also proportional to η, as observed.

The case of rigid surfactant layers should be different: drainage is slower, τ is larger and independent of the liquid fraction: $\tau \sim 200$ ms [21]. In order to check if this was consistent with the mechanism proposed here, we investigated foams made with mixtures of SDS (3 CMC) and dodecanol (0.6 g/L) in water containing 20% glycerol, in order to create rigid surfaces. Figure 4 shows the time evolution of the foam and liquid height in the presence and in the absence of dodecanol. The total height of foam + drained liquid in the presence of dodecanol does not decrease for more than 50 h, which is 2 orders of magnitude longer than for foams without dodecanol. It can be shown with the estimations made above, that for similar foam heights, if the bubble radius reaches values of 100 μm when ϕ becomes close to 2%, h is larger than h^*, so the mechanism active for small bubbles no longer holds for slightly larger ones. The foam lifetime is therefore greatly enhanced in the case of rigid interfaces, as expected from the coalescence mechanism proposed in this Letter.

Coalescence in the foams containing dodecanol sets in when the bubbles are centrimetric in size. As discussed

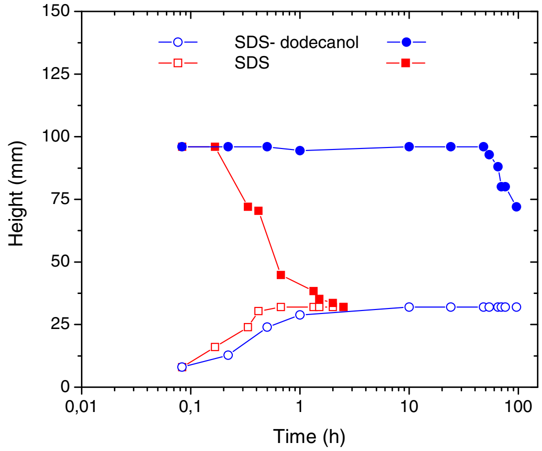

FIG. 4. Time evolution of the total height of foam + drained liquid (closed symbols) and height of drained liquid (open symbols) for pure SDS foams (squares) and SDS-dodecanol foams (circles). The foaming liquids contain 20% glycerol and the initial liquid fractions are $\phi_0 = 33\%$ for both types of foams.

earlier, foams with large bubbles collapse through different mechanisms (critical capillary pressure, ultrasmall critical liquid fraction). A systematic study of coalescence in foams made with bubbles of different sizes will be very valuable, implying the use of different types of foam production.

In conclusion, we propose a new mechanism of destabilization of foams made of small bubbles and fluid surface layers. The foams start breaking at their top, when the liquid volume fraction has decreased sufficiently and film rupture occurs during reorganization events induced by bubble coarsening ($T1$). New films are formed rapidly and their thickness is too small, they cannot be sufficiently covered by surfactant and they break. Because all the characteristic time scales depend linearly on the bulk viscosity of the solution, the foam lifetimes also depend linearly on this viscosity. Our numerical estimations indicate that the proposed mechanism is only possible for foams made with very small bubbles as in this study. This is consistent with the fact that foams made of larger bubbles are more stable. Addition of dodecanol increases the foam lifetime by orders of magnitude, showing that the proposed destabilization mechanism is not effective in the case of rigid surface layers.

We acknowledge fruitful discussions with Emmanuelle Rio and Anniina Salonen. Z. B. acknowledges financial support from Consejo Nacional de Ciencia y Tecnología, Mexico and European Space Agency. W. D. acknowledges funding from the European Research Council (FP7/2007-2013/307280-POMCAPS).

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[1] I. Cantat, S. Cohen-Addad, F. Elias, F. Graner, R. Hohler, O. Pitois, F. Rouyer, and A. Saint-Jalmes, *Foams—Structure and Dynamics* (Oxford University Press, New York, 2013).
[2] E. Rio and A.-L. Biance, Thermodynamic and mechanical timescales involved in foam film rupture and liquid foam coalescence, ChemPhysChem **15**, 3692 (2014).
[3] D. Langevin, Bubble coalescence in pure liquids and in surfactant solutions, Curr. Opin. Colloid Interface Sci. **20**, 92 (2015).
[4] D. Georgieva, A. Cagna, and D. Langevin, Link between surface elasticity and foam stability, Soft Matter **5**, 2063 (2009).
[5] J. Bibette, F. Leal Calderon, V. Schmitt, and P. Poulin, *Emulsion Science: Basic Principles*, 2nd ed. (Springer, New York, 2007).
[6] K. Khristov, D. Exerowa, and G. Minkov, Critical capillary pressure for destruction of single foam films and foam: effect of foam film size, Colloids Surf. A **210**, 159 (2002).
[7] S. Tcholakova, N. D. Denkov, and A. Lips, Comparison of solid particles, globular proteins and surfactants as emulsifiers, Phys. Chem. Chem. Phys. **10**, 1608 (2008).
[8] V. Bergeron, Disjoining pressures and film stability of alkyltrimethylammonium bromide foam films, Langmuir **13**, 3474 (1997).
[9] V. Carrier and A. Colin, Coalescence in draining foams, Langmuir **19**, 4535 (2003).
[10] A. L. Biance, A. Delbos, and O. Pitois, How Topological Rearrangements and Liquid Fraction Control Liquid Foam Stability, Phys. Rev. Lett. **106**, 068301 (2011).
[11] T. Gaillard, M. Roché, C. Honorez, A. Balan, M. Jumeau, and W. Drenckhan, Controlled foam generation using cyclic two-phase flows [Int. J. Multiphase Flow (to be published)].
[12] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.116.128302 for interpretation of additional drainage experiments and coarsening experiments using available theories, including Refs. [13–16].
[13] M. Durand, G. Martinoty, and D. Langevin, Liquid flow through aqueous foams: From the plateau border-dominated regime to the node-dominated regime, Phys. Rev. E **60**, R6307 (1999).
[14] S. Hilgenfeldt, S. A. Koehler, and H. A. Stone, Dynamics of Coarsening Foams: Accelerated and Self-Limiting Drainage, Phys. Rev. Lett. **86**, 4704 (2001).
[15] R. M. C. de Almeida, G. L. Thomas, and F. Graner, Universal, statistically scale-invariant regime in 3D cellular systems, Physica (Amsterdam) **371A**, 67 (2006).
[16] A. Saint-Jalmes, Physical chemistry in foam drainage and coarsening, Soft Matter **2**, 836 (2006); N. Isert, G. Maret, and C. M. Aegerter, Coarsening dynamics of three-dimensional levitated foams: From wet to dry, Eur. Phys. J. E **36**, 116 (2013).
[17] S. T. Tobin, A. J. Meagher, B. Bulfin, M. Mobius, and S. Hutzler, A public study of the lifetime distribution of soap films, Am. J. Phys. **79**, 819 (2011).
[18] K. Osei-Bonsu, N. Shokri, and P. Grassia, Foam stability in the presence and absence of hydrocarbons: From bubble- to bulk-scale, Colloids Surf. A **481**, 514 (2015).
[19] A. Maestro, W. Drenckhan, E. Rio, and R. Hohler, Liquid dispersions under gravity: volume fraction profile and osmotic pressure, Soft Matter **9**, 2531 (2013).
[20] V. Bergeron and C. J. Radke, Equilibrium measurements of oscillatory disjoining pressures in aqueous foam films, Langmuir **8**, 3020 (1992).
[21] M. Le Merrer, S. Cohen-Addad, and R. Höhler, Duration of bubble rearrangements in a coarsening foam probed by time-resolved diffusing-wave spectroscopy: Impact of interfacial rigidity, Phys. Rev. E **88**, 022303 (2013).
[22] K. J. Mysels and S. P. Frankel, The effect of a surface-induced gradual viscosity increase upon the thickness of entrained liquid films and the flow in narrow channels, J. Colloid Interface Sci. **66**, 166 (1978).
[23] P. Petit, PhD thesis, Université de Lyon, 2014.
[24] L. Saulnier, L. Champougny, G. Bastien, F. Restagno, D. Langevin, and E. Rio, A study of generation and rupture of soap films, Soft Matter **10**, 2899 (2014).
[25] V. Thominet, C. Stenvot, and D. Langevin, Light-scattering study of the viscoelasticity of soluble monolayers, J. Colloid Interface Sci. **126**, 54 (1988).
[26] A. A. Sonin, A. Bonfillon, and D. Langevin, Role of surface elasticity in the drainage of soap films, Phys. Rev. Lett. **71**, 2342 (1993).
[27] B. Scheid, S. Dorbolo, L. R. Arriaga, and E. Rio, Antibubble Dynamics: The Drainage of an Air Film with Viscous Interfaces, Phys. Rev. Lett. **109**, 264502 (2012).