2-25-2002

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Recommended Citation

Vera, M. U., & Durian, D. J. (2002). Enhanced Drainage and Coarsening in Aqueous Foams. *Physical Review Letters, 88* (8), 088304-1-088304-4. http://dx.doi.org/10.1103/PhysRevLett.88.088304

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Abstract

Experiments are presented elucidating how the evolution of foam microstructure by gas diffusion from high to low pressure bubbles can significantly speed up the rate of gravitational drainage, and vice versa. This includes detailed data on the liquid-fraction dependence of the coarsening rate, and on the liquid-fraction and the bubble-size profiles across a sample. These results can be described by a “coarsening equation” for the increase of bubble growth rate for drier foams. Spatial variation of the average bubble size and liquid fraction can also affect the growth and drainage rates.

Disciplines

Physical Sciences and Mathematics | Physics

Comments

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Enhanced Drainage and Coarsening in Aqueous Foams

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(Received 15 September 2000; published 11 February 2002)

Experiments are presented elucidating how the evolution of foam microstructure by gas diffusion from high to low pressure bubbles can significantly speed up the rate of gravitational drainage, and vice versa. This includes detailed data on the liquid-fraction dependence of the coarsening rate, and on the liquid-fraction and the bubble-size profiles across a sample. These results can be described by a "coarsening equation" for the increase of bubble growth rate for drier foams. Spatial variation of the average bubble size and liquid fraction can also affect the growth and drainage rates.

DOI: 10.1103/PhysRevLett.88.088304 PACS numbers: 82.70.Rr, 02.30.Jr, 47.55.Mh, 83.80.Hj

Aqueous foams are far from equilibrium. With time, they *drain* by flow of liquid in response to gravity and they *coarsen* by diffusion of gas from smaller to larger bubbles [1]. These phenomena are of fundamental interest for their interplay with the disordered packing structure of the bubbles and the topology of the random network of soap films. Stability issues are also crucial for applications, whether the foam is an unwanted byproduct or a specially designed material. In the past, drainage and coarsening have been investigated separately, assuming that only one effect dominates. This has led to a good understanding of coarsening in dry foams [2], and of forced drainage [1,3] where liquid is poured onto a foam from above. However, the common situation of free drainage, in which a foam is allowed to drain without interference, remains puzzling. Rates are faster, and have a different time- and sample-height dependence, than expected [4,5].

In this paper, we explore the idea [5] that coarsening plays an unavoidable role in free drainage. As a foam becomes drier from drainage, the rate of gas diffusion increases; as the average bubble size becomes larger from coarsening, the rate of drainage increases; and so on. This vicious cycle can be seen by shaking a bottle of soapy water until the foam is uniform and then waiting: as drained liquid emerges underneath the foam, the bubbles near the top become more polyhedral (dry) and grow rapidly, while the bubbles near the bottom become more spherical (wet) and grow slowly. This can also be demonstrated by the variation of drainage rate with the solubility of the gas [6]. Here, we quantify the coarsening/free-drainage connection in terms of foam microstructural evolution by imaging and by novel use of multiple light scattering. The results can be summarized in terms of a "coarsening equation" for the growth rate of bubbles. Taken together with a modified version of the standard drainage equation, this gives good predictions for the free drainage problem.

The most straightforward measure of drainage is the volume of liquid that seeps out underneath a foam vs time. Example data are shown by open circles in Fig. 1 for two different samples. Both foams consist of polydisperse N_2 gas bubbles, initial average diameter $\sim 100\ \mu$m, dispersed in an aqueous solution of AOS (alpha-olefinsulfonate) as in [4]. The first has an initial liquid fraction of $\varepsilon_0 = 0.08$, and is in a rectangular tank of height $H = 25$ cm, thickness 11.7 mm, and width 17 cm. The second has an initial liquid fraction of $\varepsilon_0 = 0.36$, and is in an "Eiffel Tower" tank of height $H = 70$ cm, thickness 1.25 cm, and width that grows with depth (measured downward in the direction of gravity) as $\exp(z/25\ \text{cm})$. If coarsening did not occur, then drainage would proceed only until capillary forces balanced gravity, which for these samples would be when roughly half the liquid has escaped. By contrast, the actual drainage in Fig. 1 continues past this point and is bounded only by the total volume of liquid in the sample. Consequently, the predictions of the standard drainage equation, shown as dashed curves, are dramatically wrong in both shape and time scale.

Recently we hypothesized [5] that coarsening is responsible for the accelerated drainage behavior seen in Refs. [4,5] and highlighted here in Fig. 1. To truly test

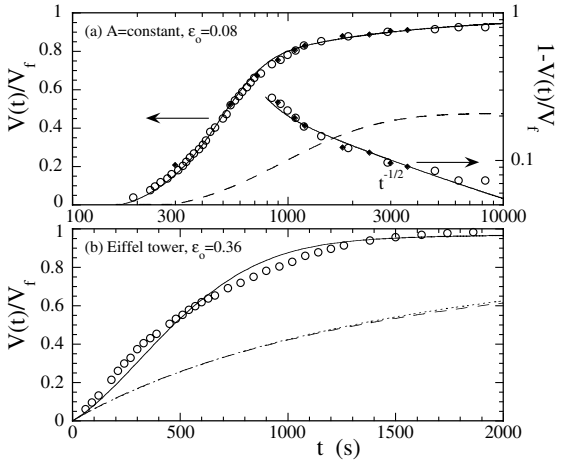

FIG. 1. Volume of drained liquid vs time. Open circles are from the height of liquid underneath the foam; solid diamonds are from the liquid-fraction profile inside the foam. Solid (dashed) curves are from numerical solution of the drainage equation with (without) effects of coarsening; the dotted curve in (b) is for Eq. 6 of Ref. [5].

this, it is necessary to characterize the average bubble size $R(z,t)$ and the volume fraction of liquid $\varepsilon(z,t)$ as a function of both time and depth throughout the sample. To deduce the former, we simply count the number of bubbles per unit length along the surface using video microscopy. Though this is straightforward, if laborious, such data have not been reported previously since it was always assumed that the bubble size distribution did not coarsen during drainage. Our results, in Fig. 2(a), show that this need not hold. As early as 200 s, when drained liquid has only first begun to emerge, the bubbles have grown noticeably larger. Note that the growth is fastest (slowest) near the top (bottom) where the foam is most dry (wet). Near the middle of the sample, R grows by a factor of nearly 4 (10) at $t = 540$ s (2400 s), when 50% (90%) of the liquid has leaked out.

To deduce $\varepsilon(z,t)$ we exploit diffuse light transmission. For this, two vertical fluorescent lights are arranged behind the sample so that unscattered light cannot reach the CCD camera. Initially the foam is opaque, so the diffuse transmission scales with the photon transport mean free path and sample thickness as $T_d \sim l^*/L \ll 1$. After significant drainage and coarsening, the foam becomes nearly transparent with $T_d \sim L/l^* \ll 1$. The full dependence of T_d exhibits a maximum near $L = l^*$ [7] that we use to normalize the data. This maximum depends on the boundary reflectivity, which is known from refractive indices, and on the average cosine of the scattering angle, which is about 0.5 [8]. Using both $l^*(z,t)$ and $R(z,t)$ data we deduce $\varepsilon(z,t)$ from the foam optics relation $l^* = R(3.0 + 0.28/\varepsilon)$ [8], which describes how photons are scattered more strongly for wetter foams with smaller bubbles. Results are shown in Fig. 2(b). The integrity

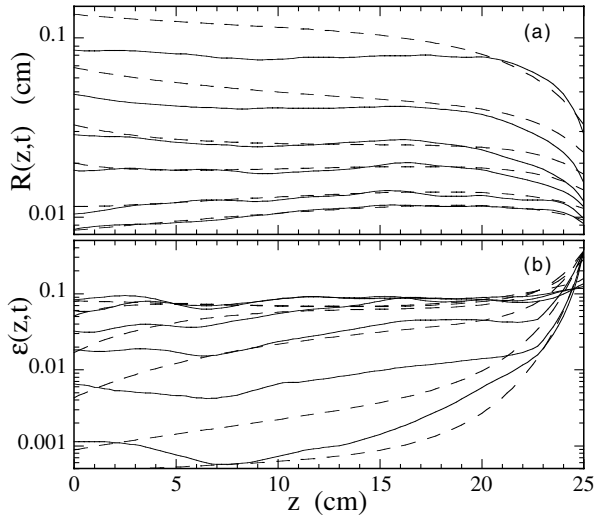

FIG. 2. Bubble radius and liquid fraction vs depth z for the draining foam of Fig. 1a. Solid curves are from video and diffuse transmission data; dashed curves are from the numerical solution of the coupled drainage and coarsening equations. The time sequence is $t = 60$, 120, 300, 540, 1080, and 2400 s.

of these procedures is checked by computing the volume of drained liquid from the amount still remaining in the sample $\int A(z)\varepsilon(z,t)\,dz$. As shown by the solid diamonds in Fig. 1(a), the agreement with direct measurement is quite good. Together, the complete data set of Figs. 1-2 constitutes the most detailed experimental description of a freely draining foam currently available.

The coupling between drainage and coarsening may be studied most cleanly by isolating the liquid-fraction dependence of the coarsening rate. The classic result for bubble growth by gas diffusion is $R(t) \propto \sqrt{t - t_o}$ for uniform foams [2]. In other words, the average bubble radius obeys

$$R(dR/dt) = DF(\varepsilon), \tag{1}$$

where D is a materials-dependent number with units of a diffusion coefficient and $F(\varepsilon)$ is a (presumably) universal function of only ε that we wish to determine. Note particularly that the combination $R(dR/dt)$ is independent of R. In Fig. 3 we display experimental results for this quantity, obtained by two means. In the first, we merely compute $R(\partial R/\partial t)$ for the data of Fig. 2 and plot it vs ε as a parametric function of time and depth. Clearly the coarsening rate increases for drier foams. Unfortunately there is considerable spread in the rate, due in part to numerical differentiation of radius data that are sparsely based in time. Systematic error is also present if the local coarsening rate depends on spatial derivatives of R and/or ε (as will be argued later), or if the foam-optics calibration between l^*/R and ε is incorrect for $\varepsilon < 0.008$ (i.e., outside the observation range from which it was deduced), or if the diffusion theory prediction of T_d is flawed for dry foams in the notoriously difficult regime $L/l^* < 3$. For a much better measure of the $F(\varepsilon)$ (which in fact was our original experiment), we use a series of uniform foams with accurately known liquid fractions. These are constructed one-at-a-time across the range $0.02 < \varepsilon_0 < 0.35$ and placed in a rectangular tank. During the initial stages of evolution, the central portion of the foam maintains the original liquid fraction while the top and bottom, respectively, become drier and wetter. Since these samples are opaque, the average bubble radius is deduced from $T_d \propto l^* \propto R$ with little error; note that this probes bulk bubbles, superior to video measurement of surface bubbles. With time $R(t)$ grows by a factor of slightly greater than 2 before the drying front sweeps through the measurement region and alters ε. The observed time dependence is always $R(t) \propto \sqrt{t - t_0}$, as expected. By fitting to this simple form, an accurate value of $R(dR/dt)$ may be deduced. The results in Fig. 3 (large diamonds) show that the previous data (small dots) are not grossly incorrect. Both sets of data, especially the highly reliable one, may be described by Eq. (1) with the empirical form $F(\varepsilon) = 1/\sqrt{\varepsilon}$.

Our data for the ε dependence of the coarsening rate make it possible, for the first time, to compare directly

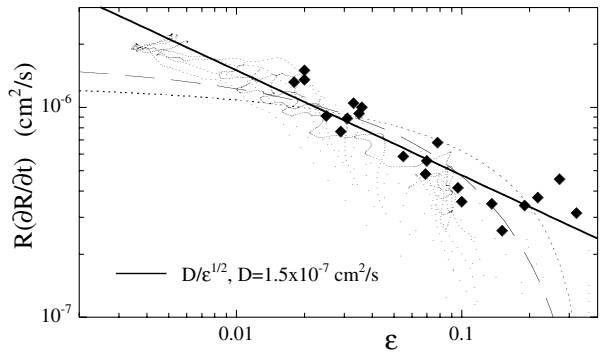

FIG. 3. Bubble growth rate vs liquid fraction $R(\partial R/\partial t) = DF(\varepsilon)$. Solid diamonds are from $R(t)$ data for foams with constant ε; small dots are from $R(z,t)$ and $\varepsilon(z,t)$ data for a single foam sample with initial $\varepsilon_0 = 0.08$. As explained in the text, the latter is subject to several sources of systematic error. Fits to the reliable data set are shown as follows: solid line for $F(\varepsilon) = 1/\sqrt{\varepsilon}$; dotted curve for $F(\varepsilon) = (1 - \sqrt{\varepsilon/\varepsilon_c})$ [9,10]; dashed curve for $F(\varepsilon) = (1 - \sqrt{\varepsilon/0.44})^2$ [11].

with expectation. For fairly dry foams, the liquid can be cleanly partitioned into three distinct structures: (a) thin soap films; (b) plateau borders, at which three films meet; and (c) vertices, at which four borders meet. The film thickness, $\ell \approx 100$ nm, is assumed to be set by interfacial forces independent of ε. Typically, ℓ is much smaller than the radius of curvature r of the plateau borders, which in turn is much smaller than the sphere-equivalent radius R of the bubbles. Therefore, essentially all liquid resides in the plateau borders, whose thickness varies with liquid-fraction according to $\varepsilon \propto (r/R)^2$ [1,3]. Additional liquid merely "decorates" the plateau borders, without any changes to vertex positions or film curvatures [1,9]. Consequently, drainage proceeds by flow of liquid through the plateau borders; flow within the films does not contribute [1,3]. Similarly, coarsening proceeds by diffusion of gas across the films; diffusion across the borders does not contribute [9]. Drier foams have thinner borders, wider films, and correspondingly faster coarsening rates. Based on such geometrical considerations alone, the liquid-fraction dependence of the coarsening rate is given to leading order by $F(\varepsilon) = 1 - \sqrt{\varepsilon/\varepsilon_c}$ [9,10]. Decoration of the plateau borders in a monodisperse foam gives $F(\varepsilon) = (1 - \sqrt{\varepsilon/0.44})^2$ [11]. By contrast with the coarsening rate data in Fig. 3, these predictions appear to saturate too readily at low ε and to decrease too rapidly at high ε. The cause for the latter is probably that gas diffusion through borders and vertices cannot be neglected for wet foams, where the bubbles are nearly spherical and the films are only vanishingly wide.

The cause for the observed behavior of $F(\varepsilon)$ at low ε is not as obvious. One possibility is that the film thickness is not truly constant. If ε is less than on the order of ℓ/R, then borders and films will compete for liquid; the film thickness will hence be smaller than the minimum in the effective interfacial potential and the film tension will be larger than twice the bare liquid-vapor surface tension. Both effects would cause a faster coarsening rate at small ε. This must eventually come into play, but not necessarily here since $\ell/R \sim 10^{-3}$ is drier than the onset of deviation. However, recent experiments suggest that the film thickness increases linearly with ε under conditions of steady forced drainage [12]. A more geometrical possibility is that the film curvature is not truly independent of ε. The notion that the addition of liquid merely "decorates" plateau borders, without changing film curvatures, is actually a theorem for sufficiently dry two-dimensional foams [9]. But the proof cannot be carried into three dimensions unless all films are perfectly spherical [1], which they are not. Since a change in film curvature is not strictly forbidden, the pressure difference between bubbles and the resulting rate of gas diffusion per unit area are free to vary with ε. Another geometrical possibility is that polydispersity in bubble sizes and films plays a role. Further research is needed to sort out the relative importance of these varied effects.

We now turn to incorporating the effects of coarsening on drainage, particularly for comparison with the drainage curves of Fig. 1. Prior treatments of coarsening all assume that the liquid-fraction and the bubble radius distribution are homogeneous throughout the sample. This isn't the case for free drainage and, in fact, gives rise to an additional coarsening and drainage mechanism. For example, if ε is uniform but R varies monotonically across the system, there must be a net coarsening-driven transport of gas in the direction of increasing average bubble size. Furthermore, gradients in this flux should contribute to the local coarsening rate. Such coarsening-driven transport effects must also arise if R is uniform but ε varies across the sample. Evidently, the bubble growth law must be generalized to the following partial differential "coarsening equation":

$$\frac{\partial R}{\partial t} = D\left\{\frac{F(\varepsilon)}{R} + \frac{R^2}{\alpha}\,\frac{\partial^2}{\partial z^2}\left[\frac{F(\varepsilon)}{R}\right]\right\}, \qquad (2)$$

whatever the form of $F(\varepsilon)$. Here α is a numerical constant, not fixed by dimensional arguments. Its value is expected to be set by $(R - R_c)/R \sim 0.01$, the difference between the radii of the average bubble and the crossover bubble, for which $dR_c/dt = 0$ instantaneously holds. This is because the usual coarsening rate depends on this difference, while coarsening-driven transport depends on the spatial variation of averages.

For drainage, the downward liquid flow speed $u(z,t)$ is set by the forces of gravity, capillarity, and viscosity [1,3]. But as noted above there can also be a coarsening-driven flux of gas, the gradient of which is the second term in Eq. (2). To conserve volume, there must be an opposite "displacement" flow of liquid that is $(1 - \varepsilon)/\varepsilon$ times larger. The sum of gravity-driven and coarsening-driven flows is

$$u = K_m \frac{\rho g R^2}{\eta c^2}\, \varepsilon^m \left[1 + 0.41 \frac{\gamma c}{\rho g}\, \frac{\partial}{\partial z}\left(\frac{1}{\sqrt{\varepsilon} R} \right) \right] + \left(\frac{1-\varepsilon}{\varepsilon} \right) \frac{DR}{\alpha}\, \frac{\partial}{\partial z}\left[\frac{F(\varepsilon)}{R} \right]. \quad (3)$$

Note that the latter may become very large for small ε, as in the late stages of drainage. The exponent is $m = 1(1/2)$ when the surfactants provide a no-slip (free-slip) boundary condition to liquid flow inside the plateau borders [1,3]. For our foams, observable swirling in the soap films implies $m = 1/2$ is appropriate. See Ref. [3] for the other constants. The "drainage equation" is finally obtained by expressing continuity of the total liquid flux, $\partial\varepsilon/\partial t + \partial(u\varepsilon)/\partial z + (u\varepsilon/A)dA/dz = 0$.

Taken together, the coarsening and drainage equations are coupled partial differential equations that may be solved numerically for $R(z,t)$ and $\varepsilon(z,t)$. Here we discretize space and use a variable time step 4th-order Runge-Kutta method. And we use the empirical rule $F(\varepsilon) = 1/\sqrt{\varepsilon}$. Accuracy is checked by reproducing known soliton solutions for forced drainage, and by confirming the equality of drainage curves computed from the flux of liquid out the bottom and from the total liquid remaining in the sample. For our $\varepsilon_0 = 0.08$ foam, numerical evolution is started from the measured profiles at $t = 60$ s. Of all the physical constants in Eqs. (2) and (3), all are independently known except $K_{1/2}$ and α. We take $\alpha = 0.01$ (variation by $\times 10^{\pm 1}$ has little effect until late times), and adjust only $K_{1/2}$ in order to fit the drainage curves in Figs. 1(a) and 1(b). The best value is $K_{1/2} = 8 \times 10^{-3}$, which is three times the fitting result of [3]. The agreement for the $\varepsilon_0 = 0.08$ foam in the rectangular tank, Fig. 1(a), is excellent; the agreement for the $\varepsilon_0 = 0.35$ foam in the Eiffel Tower tank, Fig. 1(b), is also quite good. The agreement between measured and predicted bubble-size profiles in Fig. 2 (not optimized by the fits) is good-to-fair. To highlight the role of coarsening, predictions are shown as dashed curves in Fig. 1 for the case $D = 0$ where coarsening effects are completely absent. Finally, note that a regime of coarsening-controlled drainage begins at about 1000 s. Here gravity is nearly balanced by capillarity, and liquid is released only as the bubbles grow larger. The liquid remaining in the foam is mostly within a capillary rise length of the bottom, and hence has a volume of order $\varepsilon_c A\gamma/[\rho g R(H,t)]$ with $R(H,t) \sim \sqrt{t}$. This explains why the drainage curve in Fig. 1(a) approaches 1 as $1/\sqrt{t}$.

In conclusion, coarsening is unavoidable for freely draining foams. Comprehensive data for the drainage of liquid out from under a foam, and for $R(z,t)$ and $\varepsilon(z,t)$ obtained via imaging and light scattering probes, may be described via the "coarsening equation" (2) and the displacement flow in Eq. (3). Besides an explanation for the observed liquid-fraction dependence of the coarsening rate, $F(\varepsilon) = 1/\sqrt{\varepsilon}$, several important issues remain. First, the value of $K_{1/2}$ has been inferred only by experiment, with results for forced and free drainage differing by $\times 3$. Second, the value of α needs to be determined by direct experimental measurement of the consequences of spatial variation of R and ε. These coarsening-driven transport effects are previously unrecognized, but should occur in any phase separating system with large-scale structure, such as a polymer solution or metal alloy near a wall or in a temperature gradient. Third, the failure of the coarsening and drainage equations in the very dry and wet limits, where $\varepsilon \propto (r/R)^2$ becomes invalid, needs to be investigated. Both extremes should be important for the free drainage problem, where the liquid fraction vanishes near the top and remains large near the bottom.

This work was supported by NASA Microgravity Fluid Physics Grant No. NAG3-2481.

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