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Coupling between drainage and coarsening in wet foam

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Abstract. Drainage and coarsening are two coupled phenomena during the evolution of wet foam. We show the variation in the growth rate of bubble size, along the height in a column of Gillette shaving foam, by microscope imaging. Simultaneously, the drainage of liquid at the same heights has been investigated by Raman spectroscopic measurements. The observations made in these two sets of experiments indicate the coupling between drainage and coarsening in wet foam. We could explain the correlation between our observed data on drainage and coarsening by the empirical relation, proposed by others, in the literature.

Keywords. Foam; drainage; coarsening

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1. Introduction

Foam is a two-phase system in which gas bubbles are enclosed by liquid boundaries. The liquid in foam primarily resides in (a) the thin films, (b) plateau borders, at which three films meet and (c) at the vertex, the junction of four borders. When the foam is allowed to drain freely, the liquid in it drains through the random network of plateau borders and/or vertices because of gravity. After a considerable period of time, all the liquid accumulates at the bottom, leaving the top dry. Adjacent bubbles coalesce when the liquid border becomes too thin. In addition to drainage, the other process, which changes the macroscopic appearance of foam is the coarsening. This occurs due to the gas diffusion from smaller to larger bubbles following the well-known Laplace–Young law [1]. Both effects, drainage and coarsening, in wet foam can occur at the same time-scale and can thus be coupled. If free drainage was a consequence of gravity, capillary and viscous forces alone, the drainage would have saturated when gravity balanced the capillary and viscous forces. However, it is quite evident from the experimental observations that drainage proceeds past this point and continues till most of the liquid is drained from the foam [2,3]. In freely draining foam, coarsening plays an inevitable role and is the reason for the accelerated drainage behaviour. The dynamics of free-drainage experiments with slow- and fast-coarsening of gases are reported to be markedly different [4]. On the other hand, the different rates of coarsening along the height of a column of foam, could not be explained by taking into account only the effect of diffusion [5,6]. It has been observed that drier foam coarsens more rapidly and coarser foam drains more rapidly [3,7].

In the literature, we find several reports, in which the coupling between drainage and coarsening has been investigated [8–10]. Different forms have been suggested in determining the dependance between the liquid-fraction and the rate of coarsening. For a polydisperse foam network, the evolution of the average bubble radius (R) may be modelled as [11]

$$\frac{\mathrm{d}R}{\mathrm{d}t} = D_{\mathrm{eff}}\frac{F(\epsilon)}{R}. \tag{1}$$

Here, D_{eff} is a materials constant in unit of cm^2/s. It is proportional to gas diffusivity, solubility and inversely proportional to the film thickness [11]. ϵ is the liquid fraction in the foam and $F(\epsilon)$ is a functional form of ϵ, which determines the liquid fraction dependence of the rate of coarsening. Hilgenfeldt and his co-workers [4] suggested the form of $F(\epsilon)$ to be $F(\epsilon) = (\sqrt{1-\epsilon/0.44})^2$, by incorporating the node-based drainage and diffusive coarsening in the wet foam. A slightly different form $F(\epsilon) = 1 - \sqrt{\epsilon/0.36}$ is proposed in ref. [7]. By studying micro-structural evolution by imaging and multiple light scattering, Vera and Durian proposed $F(\epsilon) = 1/\sqrt{\epsilon}$ [10]. An extensive review on the physical chemistry in foam drainage and coarsening and coupling between these two phenomena under different experimental conditions, are available in ref. [2].

In the present article, we focus on the coupling between drainage and coarsening in a uniform column of Gillette foam, via microscope imaging and Raman scattering techniques. We show the difference in the rate of evolution of the bubble diameter at different heights in the column of foam, which, in turn, indicates that the rate of coarsening cannot be explained only by the diffusion process. In addition, we measured the rate of drainage of water along the same heights, via Raman measurements. Next, we demonstrate the inter-dependence of these two observations on coarsening and drainage. Here we would like to point out that though Raman scattering is not a commonly used tool to study wet foam, the characteristics of wet foam, obtained from our measurements, match quite well with those obtained by others in the literature, using more standard techniques, like diffusive wave spectroscopy/dynamic light scattering [3,8]. In a way, this article indicates the efficacy of Raman spectroscopy to study this system (to the best of our knowledge, in the literature there are only a few reports [12–14], in which Raman spectroscopy has been used to study the behaviour of wet foam). Section 2 of this article describes the details of the experimental set-up. Discussion on coarsening and drainage along different heights in a column of foam is presented in §3. The coupling of these two phenomena, drainage and coarsening, has been discussed in §4. Finally, in §5, we summarize our results with a few comments.

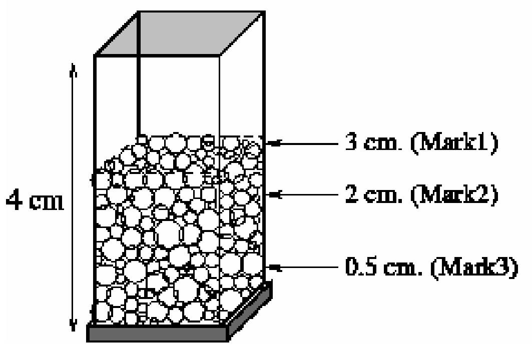

Figure 1. Schematic of the foam container.

2. Experiments

We have used commercial Gillette shaving foam, which is reproducible and stable over the duration required for an optical measurement. In this wet foam, the basic ingredients (triethanolamine stearate with small amount ($<1\%$) of sodium laurel sulphate and polyethylene glycol laurel ether and emulsified liquid hydrocarbon gases) are kept in an aqueous solution under high pressure. The expansion of the above mixture in air produces the foam. The experiments have been carried out by taking the foam in a closed rectangular quartz cell of length 4 cm and area 1 cm^2. Initially, the material fills about three-fourth of the whole cell volume (see figure 1). The cell is then sealed with a paraffin film to prevent direct evaporation. The experiments start with a fresh column of foam. We assume a uniform liquid fraction throughout the column in the beginning [13]. By microscope imaging the initial average bubble diameter at any height is also measured to be the same (refer to figure 2). The effect of aging on the foam in this sealed cell is then investigated. In this article, we discuss the results of two sets of experiments: (a) microscope images of the foam are recorded at different levels (Marks 1–3 in figure 1; at 3.0 cm, 2.0 cm and 0.5 cm from the bottom of the cell, respectively) along the height of the rectangular cell for a duration of 9 h with 1 h interval and (b) simultaneous Raman spectra are recorded at all the three heights. The images have been recorded by the Metzer Biomedical (model: MEGA-6021) optical microscope equipped with a CCD camera. Microscope images are analysed using Image J image-processing software. Raman spectra are taken in a back-scattering geometry using TRIAX550 single monochromator equipped with a notch filter and CCD as a detector. An argon ion laser of 488 nm wavelength has been used as an excitation source.

3. Variation in rate of coarsening and drainage along the height in a column of foam

3.1 *Rate of coarsening*

The pressure difference between the bubbles of foam drives the diffusion of gas through the thin film, which separates them. This is the process of coarsening.

The increase in the average bubble size with time is obtained from the fact that the rate of change of a bubble's volume is proportional to its surface area and to its Laplace pressure difference, with respect to a certain mean or critical bubble radius [7]. Hence, the time-scale of evolution of the cellular pattern slows down in inverse proportion to the length-scale. The above law of diffusion predicts that the rate of growth of average diameter of the bubbles should follow the scaling behaviour $R(t) \sim (t - t_0)^{1/2}$. If the process of coarsening could be explained only by the gas diffusion process, then one would expect the above equation to hold good at all points in a column of foam – as in the beginning there were uniform liquid fraction and average bubble diameter throughout.

The microscope images of foam are recorded at Marks 1–3 at a regular interval of time for 9 h. The characteristic images taken after 40 min and 2 h at these marks are shown in figure 2. From microscope images, the mean diameter of the bubbles is estimated by averaging the diameter of >100 bubbles for each time frame. In figure 3, the filled squares, circles and open diamonds show the variation in the average diameter of the bubbles at Marks 1–3 in figure 1, as computed from the images and the solid lines are the best fit to the experimental data points using the empirical relation

$$R(t) \sim (t - t_0)^{s_1}, \tag{2}$$

with s_1 as the free scaling factor for the bubble growth. We observe that the rate of growth of the bubble diameter at the bottom is much slower as compared to that of the bubbles at the top of the column, though the scaling factor, s_1, for the top layer is ∼0.5, for Mark 3 it is 0.42. The failure of the exponent $s_1 = 0.5$ to fit the evolution of bubbles with time at all points in a column of foam indicates that the process of coarsening cannot be explained only by diffusion of gas between bubbles.

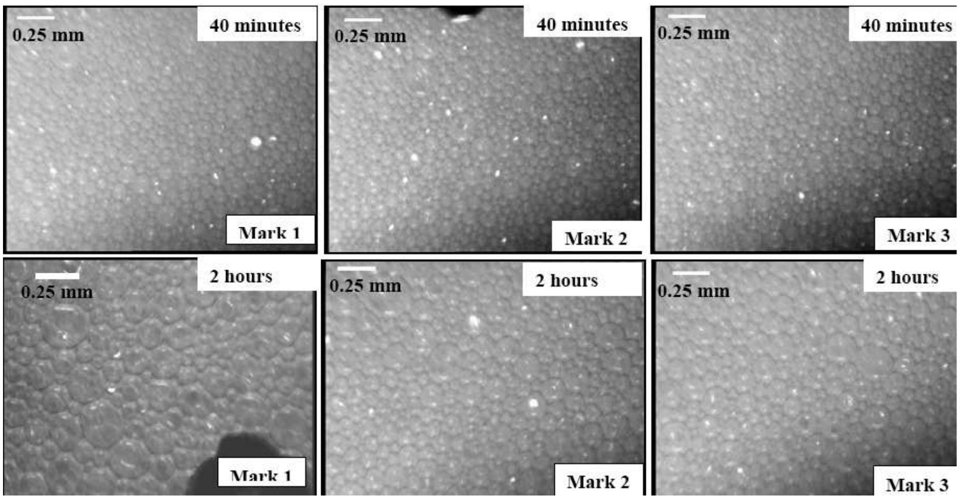

Figure 2. Microscope image of foam taken at Mark 1, Mark 2 and Mark 3 after 40 min and after 2 h.

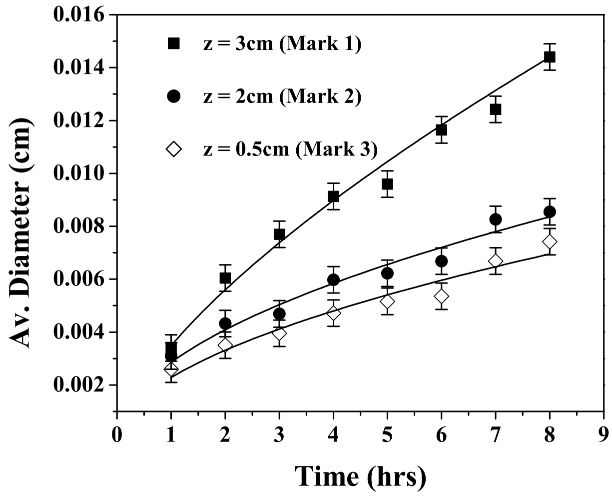

Figure 3. Different rates of coarsening along the height of the column of foam.

During drainage, the gradient of liquid is established along the length of the foam column [3]. For drier foam the rate of gas diffusion is expected to be higher than in wet foam [11]. Thus, referring to figures 2 and 3, we can conclude that the bubbles near the top become more polyhedral (dry) and grow more quickly, whereas the bubbles at the bottom are spherical (wet) and grow slowly.

3.2 *Rate of drainage*

Next, we report the Raman spectra, recorded at Mark 1 of figure 1. The spectra and image (discussed in §3.1) are measured simultaneously. A few characteristic spectra taken at different times are shown in figure 4. It is to be noted that Raman measurement is a reliable tool to study the characteristic water drainage in the wet foam [12]. In the spectral profile the broadband is the fingerprint of free water molecules in wet foam. Sharp lines can also be observed (not shown in this article) over this spectral window, when the excitation source is focussed to maximize the Raman signal of the surfactant molecules. These sharp lines correspond to water molecules either in the form of a cluster connected by strong hydrogen bonds or in the form of a complex with surfactant molecules in the foam. For details, one can refer to refs [12,15]. Due to the drainage of water molecules, the intensity of the broadband decreases with time. Each recorded Raman spectrum has been fitted with Lorentzian lineshape keeping peak position, width and intensity as free fitting parameters. This procedure ensures the proper estimation of these quantities. It is to be noted that the intensity of the spectral line does not provide the exact amount of water in the foam. However, the ratio of the intensity of the spectrum at any instant of time to that of the initial spectrum is proportional to the water fraction, ϵ, in foam, at that instant. The above spectral analysis provides the trend in the change in liquid fraction in the foam with time. It is to be noted that during

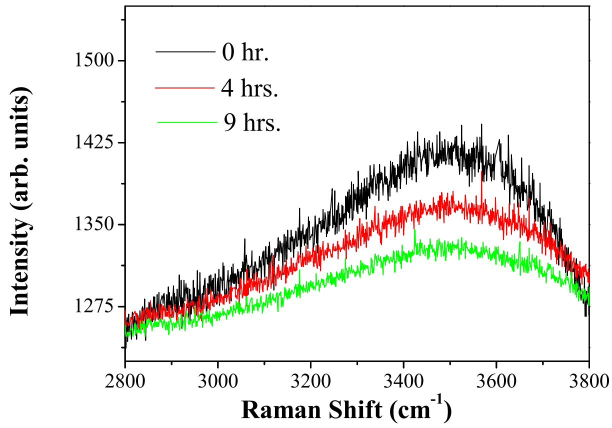

Figure 4. Characteristic Raman spectra recorded at Mark 1 for fresh foam (black line), after 4 h and after 9 h.

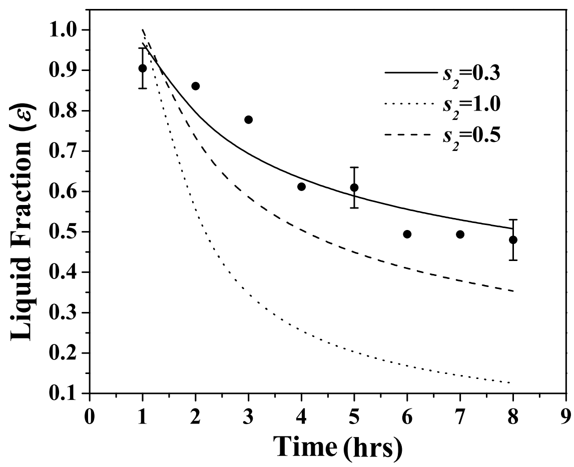

Figure 5. Variation in volume fraction in Mark 1 with time.

drainage of water molecules, other surfactant molecules also drain out. Similar measurements have been carried out at Mark 2 and Mark 3 in figure 1. However, for these two points we did not observe significant and consistent change in liquid fraction within the time-scale of our experiment. It is to be noted that the rate of coarsening is also less at these points (refer to figure 3). We believe that in our experiment the height of the column is short to exhibit the decrease in liquid fraction at lower points. In general, a column of 60–150 cm has been used by others to demonstrate the variation in liquid fraction along the height in a column of foam [3,4,11]. Unfortunately, our present experimental set-up does not allow us to carry out imaging and Raman measurements simultaneously on a longer column of foam.

In figure 5 we have plotted the variation in liquid fraction with time at Mark 1 of the foam column, as obtained from the above analysis. It has been derived that under gravity and viscous force and in the absence of capillary flow of the liquid the liquid fraction (ϵ) in a uniform column of wet foam varies with time as $1/t^m$, where $m = 1$ for plateau border dissipation and $m = 0.5$ for vertex dissipation in wet foam [3]. However, the capillary effect is known to be a crucial factor for a short column and at late times. Thus, to estimate the rate of drainage the data points in figure 5 are fitted with an empirical relation

$$\epsilon(t) \sim (1/t)^{s_2}, \tag{3}$$

with s_2 as a scaling factor. The best fit to the experimental data points is shown by the black solid line in figure 5 with $s_2 = 0.35$. The expected variation of ϵ with time with $s_2 = 0.5$ and 1 are shown by dashed and dotted lines in figure 5. We observe that, though they fail to fit, the dashed line with $m = 0.5$ is closer to the experimental data points than the dotted line with $m = 1$. Our previous work in ref. [12] also indicated that the liquid drainage in Gillette shaving foam under the given experimental condition is more like vertex dissipation rather than like plateau border dissipation. The effect of capillary flow of liquid also was evident in our experimental observation.

4. Coupling between drainage and coarsening

In the previous section we have discussed the observed results on the rate of coarsening of bubbles and the water (liquid, in general) fraction at Mark 1 in the column of foam in figure 1. Prompted by the fact that these two factors are coupled in the ageing process of the foam, we now use eq. (1) to correlate our observations shown in figures 3 and 5. In figure 6, we plot $F(\epsilon)/R$ vs. $\mathrm{d}R/\mathrm{d}t$ with $F(\epsilon) = (1-\sqrt{\epsilon/0.44})^2$ (filled circles) and $F(\epsilon) = 1/\sqrt{\epsilon}$ (filled squares). From the least square fit to the data points with a straight line, we expect to obtain D_{eff}. The solid line corresponds to a negative intercept on y-axis – which is unphysical for the form of $F(\epsilon)$ used. On the other hand, the dashed line corresponds to $D_{\mathrm{eff}} = 2 \pm 0.6 \times 10^{-6}$ cm^2/s with a reasonable value of positive intercept. Thus, from our experimental observation we could obtain $F(\epsilon)$, which holds true for Gillette shaving foam and also could estimate the value of D_{eff} for the same wet foam.

5. Summary

In this article we have shown the fast and slow coarsening of bubbles along the height of the foam-column during ageing. In addition, during free drainage, the liquid flows down under gravity. On the other hand, due to the capillary effect, some amount of liquid is pushed up. These two effects, together, determine the liquid fraction at any point in a column of foam at a certain time. As the column of foam is quite small in the present experiment, the net drainage of liquid during our time-scale of experiment is not significant for lower region of the column. However, we could carry out simultaneous measurements on the rate of coarsening and change in liquid volume fraction at the top layer of a column of foam at height ~3 cm. Next, we couple the rate of coarsening and drainage in our sample using the existing

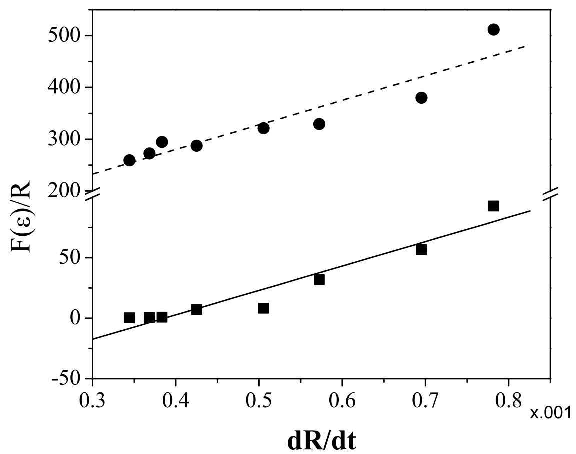

Figure 6. Variation of $F(\epsilon)/R$ with bubble growth rate $\mathrm{d}R/\mathrm{d}t$. The filled squares are for $F(\epsilon) = (1 - \sqrt{\epsilon/0.44})^2$ and the filled circles are for $F(\epsilon) = 1/\sqrt{\epsilon}$. The solid and dashed lines correspond to the best linear fit to the data points.

models available in the literature. From our analysis we have estimated the value of D_{eff} for Gillette shaving foam. This article also demonstrates the efficacy of Raman scattering to study wet foam.

References

[1] D Weaire and S Hutzler, *The physics of foams* (Clarendon Press, Oxford, 1999) pp. 215–217
[2] A S-Jalmes, *Soft Matter* **2**, 836 (2006)
[3] A S-Jalmes, M U Vera and D J Durian, *Europhys. Lett.* **50**, 695 (2000)
[4] S Hilgenfeldt, S A Koehler and H A Stone, *Phys. Rev. Lett.* **86**, 4704 (2001)
[5] L Pilon, A G Fedorov and R Viskanta, *J. Coll. Int. Sci.* **242**, 425 (2001)
[6] N Barbian, E Ventura-Medina and J J Cilliers, *Min. Eng.* **16**, 1111 (2003)
[7] S Hutzler and D Weaire, *Phil. Mag. Lett.* **80**, 419 (2000)
[8] A S-Jalmes, M U Vera and D J Durian, *Europhys. Lett.* **55**, 447 (2001)
[9] A S-Jalmes, M U Vera and D J Durian, *Euro. Phys. J.* **B12**, 67 (1999)
[10] M U Vera and D J Durian, *Phys. Rev. Lett.* **88**, 088304 (2002)
[11] K Feitosa, O L Halt, R D Kamien and D J Durian, *Europhys. Lett.* **76**, 683 (2006)
[12] P Bandyopadhyay, A K Ojha, T K Barik and A Roy, *J. Raman Spectrosc.* **39**, 827 (2008)
[13] T K Barik, P Bandyopadhyay and A Roy, *Int. J. Mod. Phys. B* (in press)
[14] N Gautev and Zh S Nikolov, *Phys. Rev.* **E54**, 1725 (1996)
[15] Q Du, Q R Superfine, E Freysz and Y R Shen, *Phys. Rev. Lett.* **70**, 2313 (1993)