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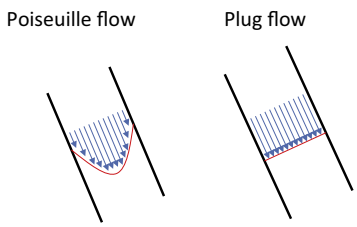
Foam drainage. Possible influence of a non-newtonian surface shear viscosity

Sébastien Gauchet [a], Marc Durand [b], Dominique Langevin [a,*]

[a] Laboratoire de Physique des Solides, Université Paris Sud 11, CNRS UMR 8502, Orsay, France
[b] Laboratoire MSC, Université Paris Diderot, CNRS UMR 7057, Paris, France

GRAPHICAL ABSTRACT

Flow types in foam Plateau borders



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ABSTRACT

We describe forced drainage experiments of foams made with model surfactant solutions with different surface rheology. We analyze the origin of two distinct drainage transitions reported in the literature, between regimes where the bubble surfaces are mobile or rigid. We propose that both transitions are related to the surface shear viscosity and to its shear thinning behavior. Shear thinning could also account for the huge discrepancies between measurements reported in the literature. The role of surface tension gradients, i.e. Marangoni effect, could not possibly explain the behavior observed with the different solutions.

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1. Introduction

Foam drainage [1] is the process during which the liquid initially incorporated in the foam during its creation drains due to gravity, until an equilibrium liquid volume fraction vertical profile is reached [2]. The topic was studied extensively, and during the recent years, experiments called *forced drainage* were proposed. In these experiments, a foam is initially left to dry and then wetted with liquid at a constant flow rate. In this case, a liquid front is formed and travels down at a constant velocity V varying as a power law of the liquid flow rate Q: $V \sim Q^{\alpha}$. The exponent α depends on the mobility of the surface of the bubbles: $\alpha = 0.5$ for rigid surfaces, for which the flow in the spaces between bubbles (*Plateau borders*) is Poiseuille-like, and $\alpha = 0.33$ for fluid surfaces, for which the flow is a plug flow. In practice, the measured exponents are intermediate between these two values [3–5].

The surface mobility depends primarily on the surface active species used to stabilize the foam: surfactants such as sodium dodecyl sulfate (SDS) lead to mobile surfaces, while proteins or surfactant mixtures (SDS–dodecanol for instance) lead to rigid surfaces. However, the behavior observed does not depend only on the surface-active species; it depends also on the viscosity of the foaming solution and on the bubble size. Indeed a transition between the regime with rigid surfaces toward the regime with fluid surfaces was observed by increasing the bulk viscosity or the bubble size [6]. This can be rationalized by using the Boussinesq number $B = \eta_S/(\eta R)$, η_S being the surface shear viscosity, η the bulk viscosity

* Corresponding author. Fax: +33 1 6915 6086.
E-mail address: dominique.langevin@u-psud.fr (D. Langevin).

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and R the bubble radius: B quantifies the relative role of surface and bulk dissipation. When B is large, the dissipation by the surface dominates, when B is small, the dissipation by the bulk dominates. Note that the transition is not sharp, the variation of the exponent occurs over a range of bulk viscosity and bubble size values (see for instance Fig. 3 later in the discussion).

Earlier studies of the drainage transition made it possible to estimate the surface shear viscosity: 0.08 μPa m s for SDS solutions and 1.8 μPa m s for SDS–dodecanol solutions [4]. In these experiments, the SDS concentration was above the *critical micellar concentration* (*cmc*) where the monolayer density changes little. It can thus be expected that the experiments performed with different SDS solutions can be safely compared, even if the concentrations are not exactly the same. For instance, in other foam drainage experiments [7], the surface viscosity was deduced from the velocity profiles in the Plateau borders and found to be 0.036 μPa m s, similar to the value deduced from the drainage transition.

It has to be noted that there are large discrepancies between surface viscosity values measured with other methods: these values are close to the limit of accuracy of the instruments used, and precise values of the surface shear viscosities are difficult to obtain for surfactants. SDS monolayers were among the most studied: the measured values of the surface shear viscosity above the *cmc* range from 2.3 μPa m s (measured with a rotating wall knife edge) [8], 1.45 μPa m s (drag of a small spherical float) [9] 0.6 μPa m s (magnetic disc oscillating in a soap film) [10], 0.1 μPa m s (deep channel viscometer) [11] and less than 0.01 μPa m s (drag of a microbutton) [12]. These values span an interval of three orders of magnitude and it is not easy to identify the source of discrepancies. The value determined by Djabbarah and Wasan (Ref. [11]) with the deep channel viscometer is the closest to that deduced from drainage experiments. Fewer experiments were performed with SDS–dodecanol solutions above the *cmc. The* surface viscosities are larger, but similarly scattered: 100 μPa m s [11] and 5 μPa m s [8], larger than the value determined from foam drainage transitions 1.8 μPa m s [4], without correlations with the amount of dodecanol (resp 0.4 wt%, 0.1 wt% and 1 wt%). Again, it is not easy to identify the source of discrepancies. One possibility would be to investigate if theses viscosities are frequency and shear rate dependent.

Another drainage transition was observed with SDS while decreasing the bubble size: the surfaces become again mobile [4]. This puzzling observation could be due to another parameter characterizing the surface behavior, namely the surface elastic compression modulus E. Indeed both the modulus E and the viscosity η_S influence the surface motion in surfactant systems, and it is usually quite difficult to disentangle their role, as for instance in film coating experiments with surfactant solutions [13]. In the case of surface compression, the number comparing surface and bulk dissipation is a Marangoni number. For insoluble surface layers, $M = E\ R/(\eta D_S)$, where D_S is the surface diffusion coefficient [14]. We have considered here the inverse of the Marangoni number of Ref. [14] for the consistency of the discussion with the Boussinesq number. When the surface-active species can exchange freely with the bulk liquid, the Marangoni number becomes $M = E\ R\ \gamma/(\eta D)$, where D is the bulk diffusion coefficient and γ is the equilibrium value of $C/\Gamma\ d\Gamma/dC$, Γ and C being respectively the surface and bulk concentration of the surface-active species. The Marangoni number increases when the bubble size increases, while the Boussinesq number decreases. Hence M is an interesting candidate to explain the transition observed upon decreasing bubble size.

In order to clarify the question, we performed new experiments with foaming solutions containing SDS and various additives, dodecanol and salt, aiming to change the surface compression modulus.

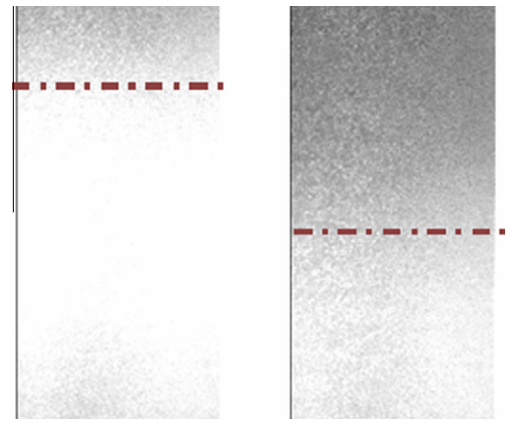

Fig. 1. Images of transmitted light through the foam column at two successive times, in a forced drainage experiment. The dashed-dotted lines show the liquid front position.

2. Materials and methods

The chemicals used were purchased from Aldrich and used as received. We fixed the surfactant concentration to 24 mM, about 3 times the critical micellar concentration, in order to achieve a full coverage of the bubble surfaces [15]. The dodecanol was added to specified samples with a mole ratio of 200 (moles of SDS/moles of dodecanol). A quantity of 100 mM sodium chloride was added to other specified samples.

The drainage front was followed using transmission of light from a foam column at the top of which liquid is added with the help of a pump. The device is very similar to that of Ref. [3]. The front was however detected using light transmission. The column was a sealed plastic container, with a rectangular section (2.5 cm × 13.5 cm) and a height of 39.9 cm. The cell bottom had two holes: one is equipped with a small porous glass cylinder through which pressurized gas can be injected. The second hole is connected by a hose to a beaker, in order to keep the foam level constant during the experiment. The cell bottom is first filled with a surfactant solution, until the porous disk is completely immersed. The foam is then created by injecting nitrogen through the porous cylinder. In this way, we obtained foams with bubble diameters of 800 μm. Foams with smaller bubbles, diameters 250 and 300 μm, were obtained using a turbulent mixing device [16].

The foam was then left to dry, after which liquid is injected at the top using a flow controller allowing to set a given flow rate.

We have used a camera and a bright screen (Holtex +), in order to illuminate uniformly the column. The images were analyzed with Image J, an open source software, to which a macro was added in order to follow the changes in the position of liquid fronts. The software detects a variation of 5% of gray levels and calculates the front position by averaging over the width of the selected area. Fig. 1 shows two typical images with front positions.

3. Results

Fig. 2 shows an example of the variation of the front velocity V with flow rate Q. The slope of the line gives the exponent α, equal to 0.467 in the example shown. The accuracy on α is typically ± 0.1–0.2. The Table 1 below gives the values of the exponent measured for the different samples studied.

One sees that the exponent α increases when the bubble size increases for the salt-free solutions, while α does not vary appreciably when salt is present.

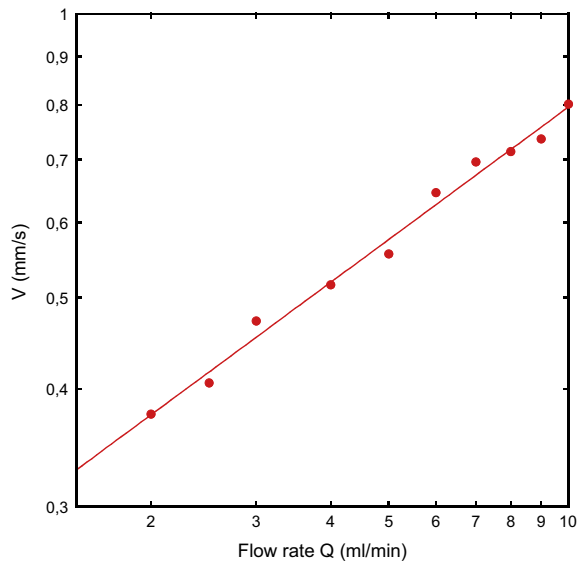

Fig. 2. Front velocity versus flow rate. The sample is a foam made with the SDS–dodecanol–salt solution with bubble diameter 800 μm.

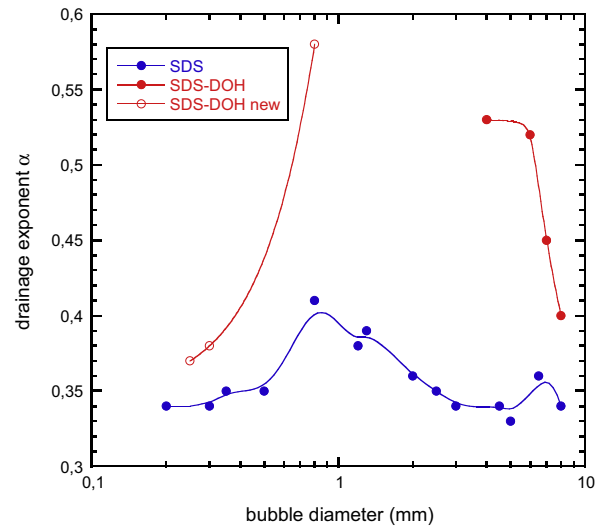

Fig. 3. Drainage exponent for foaming solutions made with SDS and SDS + dodecanol. Full circles: data taken from Ref. [4], empty circles: data from the present study. The lines are guides to the eyes: they show that the transitions between rigid and fluid surface regimes are rather smooth.

Table 1
Values of the drainage exponent α for the different foams studied.

Bubble diameter (μm)	SDS	SDS–dodecanol	SDS–salt	SDS–dodecanol–salt
250		0.37		0.47
300	0.34	0.38	0.47	0.49
800	0.49	0.58	0.46	0.47

4. Discussion

Fig. 3 shows the measured exponents α for SDS and SDS + dodecanol. The data for large bubbles is taken from Ref. [4] for which the SDS and dodecanol concentrations were somewhat higher than in the present study, 10 g/l and 0.1 g/l respectively. The data for SDS–dodecanol and small bubbles is from the present study. In the case of SDS solutions, the values of α are compatible with those of Ref. [4].

Fig. 3 clearly shows the two drainage transitions between rigid and fluid interface conditions: one is observed upon increasing bubble size, and can be explained by considering the Boussinesq number B as explained in the introduction. The second transition, observed upon decreasing the bubble size could correspond to the Marangoni number M. Let us recall that for insoluble layers [14]:

$$M = \frac{ER}{\eta D_S} \tag{1}$$

and for soluble layers

$$M = \frac{ER\gamma}{\eta D} \tag{2}$$

with

$$\gamma = \left[\frac{C}{\Gamma}\frac{d\Gamma}{dC}\right]_{eq} \tag{3}$$

By comparing Eqs. (1) and (2), one sees that soluble layers behave as if they had an effective elastic modulus: $E_{\text{eff}} = E\ \gamma\ D_S/D$.

Let us transform Eq. (2) using the definition of the modulus E:

$$E = -\Gamma\frac{d\sigma}{d\Gamma} = -\frac{\Gamma}{C}\frac{d\sigma}{dC}\frac{dC}{d\Gamma} = \frac{1}{\gamma}\frac{d\sigma}{d\ln C} = \frac{1}{\gamma}k_BT\Gamma \tag{4}$$

Here, we have used the Gibbs equation relating the surface concentration Γ to the derivative of the surface tension σ with respect to bulk concentration, valid for a surfactant concentration below *cmc*:

$$\Gamma = \frac{1}{k_BT}\frac{d\sigma}{d\ln C} \tag{5}$$

It follows that:

$$M = \frac{k_BT\Gamma R}{\eta D} \tag{6}$$

Let us estimate the value of M taking $k_BT = 4{\cdot}10^{-21}$ J, $\Gamma = 2{\cdot}10^{18}$ molecules/m^2, $R = 100$ μm, $\eta = 1$ mPa s, $D = 4\ 10^{-10}$ m^2/s. One finds $M \sim 10^6$, suggesting that whatever the bubble size, the surface conditions should be of the rigid-type for surfactant concentrations below *cmc*.

In foams in practice, the surfactant concentration is always above *cmc*, in which case Eq. (4) no longer applies. The Gibbs equation is still valid, but using for C the surfactant monomer concentration C_{mono} instead of the total surfactant concentration. Since C_{mono} remains approximately constant and equal to the *cmc*, the surface concentration Γ and the modulus E do not change much with bulk concentration either, while γ becomes very small and close to zero. It is then possible that, according to Eq. (2), M becomes small and the surface conditions become of the fluid-type. This would be consistent with the fact that at small and large bubble sizes, the fluid conditions are observed (Fig. 3). However, if the Boussinesq number remains large, the rigid conditions will prevail for small bubbles, even if the Marangoni number is small.

The only possible interpretation of the behavior observed in Fig. 3 is that the surface shear viscosity is smaller in the case of small bubbles. This could arise because of a possible dependence of the viscosity on shear rate. Indeed, the shear rate increases when the bubble size decrease, because the size of the Plateau border decreases while the drainage velocity does not change appreciably, ranging from 0.5 mm/s for the smallest bubbles ($R = 125$ μm) to 1 mm/s for the largest ones ($R = 500$ μm) in the experiments performed. With typical liquid volume fractions ϕ of 4%, the radius r_{PB} of the Plateau borders can be estimated using $r_{\text{PB}} \sim R\sqrt{(\phi/0.34)}$

[17]. Estimated shear rates are then 3 s^{-1} for R = 500 μm and 10 s^{-1} for R = 100 μm. Clear frequency variations have been evidenced recently in this range of shear rates for surfactant solutions [18]. This could be possibly why the surface viscosity of SDS solutions measured by Djabbarah and Wasan (deep channel viscosimeter, Ref. [11]) is larger than that by Squires and coworkers (microbutton, Ref. [12]). Indeed, the frequencies used were respectively 0.129 s^{-1} and 6.3 s^{-1}.

When salt is added to both SDS and SDS–dodecanol solutions, no transition is observed in the small bubble range. This could be either because the surface viscosity is much higher and did not decrease yet to small enough values and the Boussinesq number is still high. Unfortunately, no surface shear viscosity measurements could be found in the literature for these solutions. It is also possible that the Marangoni number becomes larger when salt is present. However, salt was added in order to rather decrease this Marangoni number. Indeed, salt screens the repulsive interactions between the surface layer and the monomers in bulk, therefore speeding up diffusion. This feature that can be qualitatively taken into account by introducing an effective diffusion coefficient $D_{\mathrm{eff}} = D\ \exp(-E_a/k_BT)$, where E_a is an adsorption energy that can be several k_BT in salt free solutions [19]. The decrease of the effective elastic modulus with added salt has been also observed [20]. In the presence of salt, D is larger or equivalently the effective modulus E_{eff} is smaller, so M should be smaller. The change in Marangoni number cannot therefore explain the absence of drainage transition in the investigated range of small bubble sizes.

5. Conclusion

We have proposed a possible interpretation for the transition in drainage regimes observed with small bubbles and foams made with SDS and SDS-dodecanol solutions. The idea is that the local shear rate increases with decreasing bubble size, so the surface shear viscosity could possibly decrease. This hypothesis is consistent with literature data that report vanishingly small viscosities at shear rates above a few s^{-1} for SDS solutions. Unfortunately, the precise frequency variation of the surface viscosity has not been reported yet. Such a study would be very valuable and will possibly clarify all the inconsistencies reported since many years in surface viscosity determinations. Surface viscosity determinations for solutions containing salt would also be very valuable to possibly confirm the interpretations proposed.

Acknowledgments

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