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Historical Perspective

On the influence of surfactant on the coarsening of aqueous foams

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ABSTRACT

We review the coarsening process of foams made with various surfactants and gases, focusing on physico-chemical aspects. Several parameters strongly affect coarsening: foam liquid fraction and foam film permeability, this permeability depending on the surfactant used. Both parameters may evolve with time: the liquid fraction, due to gravity drainage, and the film permeability, due to the decrease of capillary pressure during bubble growth, and to the subsequent increase in film thickness. Bubble coalescence may enhance the bubble's growth rate, in which case the bubble polydispersity increases. The differences found between the experiments reported in the literature and between experiments and theories are discussed.

Contents

1. Introduction

Aqueous foams are dispersions of gas bubbles in water containing stabilizing surface active species, such as surfactants, proteins of small particles. Despite the presence of these species, foams are metastable systems and destabilize through different processes: gravity drainage, coalescence (rupture of liquid films between bubbles) and coarsening (transfer of gas between bubbles due to pressure differences) [1,2]. In this paper, we will focus on the coarsening process occurring in foams made with surfactant solutions.

Coarsening has been extensively studied in two-dimensional (2D) foams, made in general by confining bubbles between two plates, separated by a distance *d* much smaller than the size of the bubbles. It has been shown that the evolution of bubbles depends on the number of their sides: bubbles with more than 6 sides grow, bubbles with less than 6 sides shrink, while bubbles with 6 sides remain stationary. After a lag-time that depends on the initial bubble distribution, a self-similar regime is reached where the average bubble size grows as the square root of time. A summary of existing work can be found in refs. [1,2].

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Coarsening of three dimensional (3D) foams is less documented. Apart from the scaling of the average bubble size with the square root of time, exact theoretical results, such as those established for 2D foams, cannot be derived. In particular, there is no critical number of faces, the growth and shrinkage of bubbles also depend on the number of sides of their faces. It was nevertheless shown experimentally and with simulations that bubbles with 13 to 17 faces evolve much more slowly with time than those with less than 13 faces or those with more than 17 faces [3,4]. Simulations showed recently the existence of a self-similar regime with a bubble size distribution similar to that derived by Lifshitz and Slyozov for the Ostwald ripening process [5], although wider and more extended [6], as found experimentally [7]. Let us recall that Ostwald ripening describes the gas transfer in dispersions of spherical bubbles (bubbly liquids) and that the growth law is different: the average bubble size increases as the cubic root of time (instead of the square root).

A number of recent papers concern foams in which coarsening is arrested. This arrest was predicted by Gibbs for a single spherical bubble [8] and later by simulations with dispersions of spherical bubbles [9]. The arrest should occur when the surface compression modulus E of the surface layer stabilizing the bubbles reaches a value equal to half the surface tension γ. Coarsening arrest has been observed in foams stabilized by partially hydrophobic nanoparticles [10] and by particular proteins, such as hydrophobins [11]. It has not been observed with most other proteins [12] or with surfactants, although the modulus E can be larger than $\gamma/2$. This apparent contradiction arises from the fact that the models assume that E is constant. When a bubble covered with proteins is compressed, at some point, the protein layer saturates, and a second layer is formed above the first one, hence the effective resistance to compression vanishes. When a bubble is expanded, the surface coverage decreases, E decreases and, at some point, becomes smaller than $\gamma/2$. In the case of surfactants, during expansion of compression of the bubbles, the surfactant can adsorb or desorb while maintaining constant surface coverage. This means that, again, the effective resistance to compression and expansion vanishes. Of course, this argument is only valid when there are no adsorption or desorption energy barriers [13]. Note that coarsening was also shown to be arrested in viscoelastic fluids having a yield stress larger than the capillary pressure in the bubbles [14].

It has been argued that the coarsening rate should be similar for all surfactant foams because the coarsening rate is proportional to the surface tension of the surfactant solutions, these tensions being comparable (of order 30–40 mN/m). Recent studies showed that in fact, different surfactant mixtures led to different coarsening rates [15]. Other studies in concentrated dispersions of oil drops in water (emulsions) made with pure surfactants also showed that the coarsening rates depend on the surfactant [16].

The aim of the present review is to collect existing data of coarsening in foams stabilized with surfactants and to compare these data with existing theories, focusing on the influence of physico-chemical parameters. In studies of Ostwald ripening of emulsions, it is known that the growth law (average drop size ~ time$^{1/3}$) is well followed, but the measured coarsening rates differ generally from theoretically predicted rates by factors of order 10, and sometimes more [17]. One of the unsolved issues is the influence of the surfactant's concentration. It has been postulated that surfactant micelles could also participate in oil transport in the case of oil in water emulsions, but so far, recent careful measurements do not support this picture [18]. It is therefore interesting to investigate if similar discrepancies are found in foam coarsening studies. New data for foams made with the surfactants used in the emulsion studies from ref. [16] will be included in the discussion.

2. Theoretical background

Foams are dispersions of gas in a liquid. The bubbles have polyhedrical shapes and are separated by thin liquid films; the films are connected to plateau borders (PB), which are themselves connected to nodes [1]. In such a structure, the gas mainly diffuses through the thin films between bubbles for which the diffusion path is the smallest. As a consequence, the bubble growth law is different from that of Ostwald ripening: $D \sim t^{1/2}$, D being an equivalent bubble diameter (diameter of the sphere having the same volume as the bubbles).

The growth rate of an individual bubble of volume V in a foam can be written as: $dV/dt = V^{1/3}G$, G depending both on the shape of the bubble and on the physico-chemical properties of the liquid, gas and surfactant through the effective gas diffusion coefficient D_f:

$$G = -D_f \int_S \frac{HdS}{V^{1/3}}$$

H being the mean curvature of a bubble surface element dS [19,20]. Bubbles with a small number of faces shrink, while those with a large number of faces grow, bubbles with 13–17 faces remain quasi-stationary [3,4]. When averages over suitable distributions of bubble geometry are performed [21], it can be shown that coarsening obeys the relation $dD^2/dt = \Omega$, with:

$$\Omega = \frac{8\delta_A}{3\pi\delta_V\beta}\frac{\gamma D_m He V_m}{h} f(\phi) \tag{1}$$

where δ_A, δ_B and β are geometrical factors, γ is the surface tension of the liquid used to make the foam, D_m is the diffusion coefficient of the gas molecules into the liquid, V_m the gas molar volume, He is the Henry constant (gas solubility in water expressed in mole m^{-3} Pa^{-1}) and h is the average thickness of the liquid films separating the bubbles.

The factor $f(\phi)$ in Eq. (1) is the fraction of bubble area covered by liquid films, ϕ being the liquid fraction in the foam; $f(\phi)$ is close to one for very dry foams and decreases when ϕ increases. Various forms of $f(\phi)$ were proposed and, currently, the most frequently used is $f(\phi) \approx (1\text{–}1.52\,\phi^{1/2})^2$ [22]. Experiments or theories could not yet establish which is the more suitable expression for $f(\phi)$ [23].

In ref. [21], δ_A, δ_B and β were calculated for bubbles having the shape of Kelvin tetradecahedra: L being the length of the plateau borders, the bubble volume is $V = \delta_V L^3$, with $\delta_V \sim 11.3$ and the bubble area $A = \delta_A L^2$ with $\delta_A \sim 27$. The effective mean curvature is such as $H \approx 1/(\beta L)$ with $\beta \sim 10$ for dry foams. The diameter of a sphere that has the same volume as the average polyhedron is $D = (6\delta_V/\pi)^{1/3} L \sim 2.78$ L. This is close to the diameter of a sphere that has the same area than this polyhedron: $D = (\delta_A/\pi)^{1/2} L \sim 2.93$ L.

The quantity $D_m He V_m/h = D_m He^*/h$ (He^* being the gas volume fraction in water) is the foam film permeability κ. For pure water films in air, $He^* = 0.013$ and $D_m = 2.6\ 10^{-9}$ m^2/s [24]; for a film 35 nm thick, κ is about 1 mm/s, comparable to the permeabilities measured for such thin films [25]. In the case of very thin films, in particular, Newton black films (NBF, which are surfactant bilayers containing little water), the surfactant molecular layers at the film surface usually affect gas transfer. In this case, $D_m He^*/h$ needs to be replaced by the expression:

$$\kappa = \frac{D_m He*}{h + 2D_m/\kappa_s} \tag{2}$$

where κ_s is the gas permeability across a surfactant monolayer. Eq. (1) then becomes:

$$\Omega = \frac{8\delta_A}{3\pi\delta_V\beta} 10^5 \gamma\kappa f(\phi) \tag{3}$$

Eqs. (1) and (3) apply when the self-similar regime is reached. The bubble size distribution remains unchanged afterwards. This distribution

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