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Bubble coalescence in pure liquids and in surfactant solutions

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ABSTRACT

The mechanisms for bubble coalescence in the absence of surfactants were clarified, including for salt solutions. No complete model is available yet for surfactant solutions. The notion of critical applied pressure for film rupture, decreasing with increasing film size, appears applicable to foam films, emulsion films and even asymmetric films.

1. Introduction

Foams evolve with time through different mechanisms: gravity drainage, coarsening due to gas transfer between bubbles because of capillary pressure differences and bubble coalescence due to the rupture of liquid films between adjacent bubbles [1]. Foam drainage is rather well understood, coarsening less well (in particular the physico–chemical aspects are still unclear), but coalescence is certainly the less well understood aspect [2,3]. In particular, the role of surface-active agents remains unclear. Recent advances were made in the bubble coalescence topic and will be described in the present paper, which will focus mainly on single film rupture. The recent work on foams produced in microgravity conditions, including foams made without surface-active agents, will also be discussed.

The topic has been active for many years and the reader could find relevant information and references in the comprehensive book by Exerowa and Kruglyakov [4]. In this review, we will limit the references mostly to recent work. We will not address the case of foams stabilized by insoluble surfactants, polymers, proteins or particles. Because the mechanisms involved in the rupture of foam and emulsion films appear similar, examples of studies with emulsions will also be given.

2. Surfactant-free films

When two bubbles approach at a velocity V and when the distance h between their surfaces becomes small, these surfaces deform and become flatter. The flattening occurs when the hydrodynamic pressure P_{hyd} at the film center exceeds the capillary pressure P_{cap} in the bubbles. It is only then that films form strictly speaking. For spherical bubbles of radius R and no-slip boundary conditions, $P_{hyd} > P_{cap}$ when h is less than a distance h^*:

$$h_* \sim R\sqrt{\frac{\eta V}{\gamma}} \tag{1}$$

where γ is the surface tension and η the liquid viscosity. When there are no forces between film surfaces, it can be shown that the flattened region deforms and that a dimple always form [5••] (see Fig. 1). In fact, there are always van der Waals forces between film surfaces, but dimples are formed in this case as well, excepted when the velocity V is very small, in which case a pimple is formed [5••]. At very high velocities, the bubbles may rebound after the collision.

2.1. Films made of pure liquids

The first model describing film rupture of liquid films was proposed by Sheludko [6] and refined later by Vrij [7]. They ascribed film rupture to the growth of thermal fluctuations in film thickness once the film becomes thin enough for the attractive van der Waals forces between film surfaces to play a role. This leads to an instability of wavelength λ_c that grows faster than the others. The calculated film lifetime depends on the surface tension γ and on the Hamaker constant *A*. Clear evidence of film rupture due to thickness thermal fluctuations was given much later in systems with extremely low interfacial tensions, where these fluctuations become visible by eye [8].

An output of the model is the critical thickness at which films rupture:

$$h_c \sim 0.1\left(r^2 A/\gamma\right)^{1/4} \tag{2}$$

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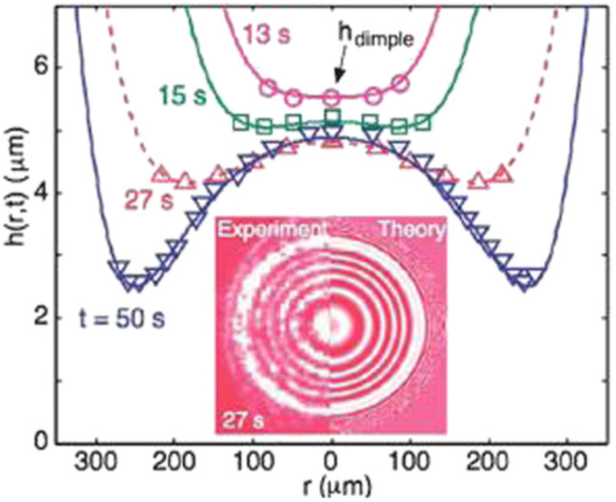

Fig. 1. Silicone oil film profile between glycerol drops at various times after the formation of the dimple: experiments (symbols) and theory (lines). The inset shows interference fringes observed when illuminating the film perpendicularly to its interfaces. From ref. [5].

where r is the film radius. For r ~ 100 μm, λ_c ~ 20 μm and h_c ~ 100 nm. The notion of critical thickness has been used in many coalescence models elaborated afterwards.

One of the main difficulties encountered when applying the model to pure liquid films is that the films surfaces are never flat and parallel. As seen above, films form when the distance between bubbles is smaller than h^*, but if no repulsive forces are present, a dimpling instability rapidly develops. Film rupture occurs once the dimple borders come close enough, allowing the van der Waals forces to play a role (see Fig. 1). A purely hydrodynamic model was developed to account for film lifetimes and is in perfect numerical agreement with the experiments [5••].

In the recent experiments performed with bubbles in pure water, the Sheludko–Vrij mechanism is not expected to play a role, because the critical wavelength of the thickness fluctuations exceeds the film size. For bubbles in the 100 μm size range in water, the coalescence times are quite short, less than 100 ms [9••].

This model also accounts for longer coalescence times upon bubble approach than upon retraction, because during retraction, the hydrodynamic pressure is larger [9••]. A similar observation was made for drops in microfluidic devices [10].

Although the assumption of deformable interfaces appears logical in the case of pure fluids, the no slip boundary condition used in ref [5••,9••] is by no means obvious. However, very small surface tension gradients $\Delta\gamma$ can immobilize a bubble surface [11••]:

$$\Delta\gamma \gtrsim \frac{\eta R V}{h}. \qquad (3)$$

These surface tension gradients can come from small amounts of residual impurities, and even from adsorption of ions, including OH^- ions, which are claimed to be responsible for the negative surface potential of pure water. In the experiments of ref [11••], the condition 3 was fulfilled for water films until the approach velocity of bubbles reached values of the order of 100 μm/s. At larger velocities, the surface become mobile and the velocity profile evolves from Poiseuille parabolic profiles toward plug-flow profiles. The film drainage then is controlled by inertial effects rather than by viscous effects and coalescence is much more rapid.

When the velocity of approach is very small (less than 1 μm/s, quasi-static conditions as opposed to the dynamic conditions discussed before), a very different behavior is observed: pure water film lifetimes could be hours and even days. It was shown that dimples are not formed, the film surfaces flatten instead. An interpretation of this surprising feature was attributed to the repulsive interaction between film surfaces due to OH^- adsorption at film surfaces [11••]. Further studies of water films exposed to various gases showed that the gas has a significant influence of film stability [12•]. Very recent studies showed that the long lifetimes of water films in quasi-static conditions originate from adsorption of carbonic acid at the water surface. Indeed, when carbon dioxide is removed, film rupture is very rapid [13•].

Microgravity studies of water foams were recently performed [14]. It was shown that very stable foams could be obtained, but only for liquid volume fractions larger than about 35%. This is the limit corresponding to the random packing of monodisperse hard spheres (jamming limit). Because bubbles are deformable, much smaller volume fractions can be obtained. However, the previous discussion showed that when bubbles are deformed, coalescence is fast in dynamic conditions. When foams are in a microgravity environment, the films between bubbles still drain because of the capillary pressure in film borders. This type of foam drainage was demonstrated in earlier microgravity experiments [15]. Water foams made of spherical bubbles are on the contrary very stable. It was also shown that gas incorporation was difficult in these very wet water foams, the foam volume being much less than for a surfactant foam in the same conditions. This is because during the foaming process, there is a competition between bubble formation and coalescence, and since the coalescence rate is high, it can only be partially compensated by a high bubble formation rate: the higher the mechanical energy provided, the higher the foam volume, as on Earth.

2.2. Aqueous salt solutions

A long standing problem deals with the lifetimes of films made from aqueous salt solutions: above a critical salt concentration (typically 0.1 M), specific to the ions used, the film lifetimes can be rather long. This is the opposite of what could be expected from the screening of electrostatic forces, which furthermore is not ion-specific. The stabilization is observed when the ions can either both form strong acids or bases, or both form weak acids or bases. Combinations of ions that form each strong and weak species lead to films that rapidly rupture.

It was shown recently that the behavior of the films in quasi-static conditions in fact follows current expectations based on charge screening: although pure water films are stable, films from salt solutions are very unstable [11••], whatever the couple of ions chosen [13•]. The abnormal behavior is observed only in the dynamic approach case. It was demonstrated that a surface potential can only be created with ion couples for which one ion adsorbs in larger amounts than the other. Charge separation at the film surface occurs and results in strong electrostatic repulsion and long film lifetimes [16••]. However, it is not clear why the charge separation does not lead to film stability in quasi-static conditions as well. The adsorbed ions may be displaced toward film borders during film thinning and their replacement might be possible in quasy-static conditions (surfactant diffusion between film borders and center is slow).

2.3. Films made of liquid mixtures

As discussed long ago by Ross [17], a dissolved component may demonstrates surface activity by reducing the surface tension of the solvent and by creating an excess concentration at the surface. These effects lead directly to a stabilizing mechanism for foam films, by the creation of surface tension gradients. The mechanism was found effective if the lower tension liquid is the minor component and the film stability is maximum close to the critical consolute point.

We have seen above that in the case of water, surface tension gradients due to adsorbed ions are frequently present, and even being weak, they can immobilize film surfaces. In the case of organic liquids, no ions are present and films and foams are very unstable, unless mixed with other liquids [18]. Liquid mixtures indeed lead to moderately stable films, as for instance water–alcohol mixtures: significant volume of