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Aqueous foams and foam films stabilised by surfactants. Gravity-free studies

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ARTICLE INFO

Article history: Received 8 March 2016 Accepted 10 June 2016 Available online xxxx

Keywords: Microgravity Aqeous foams Foam films

ABSTRACT

There are still many open questions and problems in both fundamental research and practical applications of foams. Despite the fact that foams have been extensively studied, many aspects of foam physics and chemistry still remain unclear. Experiments on foams performed under microgravity allow studying wet foams, such as those obtained early during the foaming process. On Earth, wet foams evolve too quickly due to gravity drainage and only dry foams can be studied. This paper reviews the foam and foam film studies that we have performed in gravity-free conditions. It highlights the importance of surface rheology as well as of confinement effects in foams and foam films behaviour.

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1. Introduction

Foams are dispersions of gas bubbles in liquids or solid matrices [1]. They occur widely in nature and are used in important industrial processes and commercial applications [2,3]. Liquid foams are an essential part of gas/liquid contacting processes such as distillation and flotation of minerals. Foams made with aqueous surfactant solutions are widely used for detergency purposes, while foams made with protein solutions are the base of many food products. Other applications of liquid foams include cosmetics, fire-fighting, oil recovery, and others. Solid polymeric foams, such as polystyrene and polyurethane, find applications as insulation panels in the construction industry and as packing and cushioning materials. Solid foams can also be made of metals, nowadays used in car and space industries.

Foams are usually prepared with liquid matrices. Because of the large density difference between air and the liquid, this liquid drains rapidly due to gravity and *dry* foams are obtained. Great progress has been made over the last thirty years in making the science of dry foams a sound and systematic discipline, with theories based on well-defined models being compared with well-characterised experiments. Properties of interest have included: the details of foam *structure* (shapes and arrangements of bubbles), capillary and gravity driven *drainage, rheology, coarsening* due to diffusion of gas (growth of large bubbles, shrinkage of small ones) and *coalescence* due to rupture of the films between bubbles [1,3].

Foam dynamics involves a variety of phenomena occurring at different length scales: molecular (monolayers of surface active agents at the air-water interface, thickness $\sim 1-10$ nm), mesoscopic (films between bubbles, thickness ~ 10 nm-1 µm), and macroscopic (bubbles and channels between bubbles called *Plateau borders*, ~ 100 µm-1 cm). These phenomena occur at different timescales, typically microseconds to hours. Furthermore, coarsening and coalescence are coupled with gravity drainage and are faster when the foam liquid fraction is lower. Due to this complexity, we still know little about coarsening and coalescence, a serious drawback for the prediction of dry foam stability. The study of the be-

http://dx.doi.org/10.1016/j.crme.2016.10.009

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Please cite this article in press as: D. Langevin, Aqueous foams and foam films stabilised by surfactants. Gravity-free studies, C. R. Mecanique (2016), http://dx.doi.org/10.1016/j.crme.2016.10.009

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Fig. 1. Scheme of foam aspects for different liquid volume fractions ϕ .

haviour of the foam in the early stages, when it still contains large amounts of liquid, remains still more elusive. As a consequence, it is difficult to predict what will be the final foam structure although this knowledge would help to better target the applications.

All these open questions have motivated foam investigations in microgravity. Microgravity is indeed a helpful tool to suppress drainage and gain more insight into the coarsening and coalescence mechanisms and into the behaviour of wet foams. In this paper, we will briefly summarise the work that we have done over the years thank to the support of CNES, in order to elucidate aqueous foams and foam films behaviour. We will focus on aqueous foams stabilised by surfactants. Part of this work has also been supported by ESA through a MAP program. Various experiments were performed in gravity-free conditions; others are scheduled in the near future. In the following, we will first recall some general concepts in foam science, then describe the different experiments and end with the plans for the near future.

2. General concepts for foams

The liquid volume fraction in foam, ϕ , may vary from less than one percent (*dry* foam) to more than 10% (*wet* foam) (Fig. 1). At low liquid fractions, the bubbles are deformed into polyhedra with both quasi-flat faces (bordering films) and curved faces (at the edges). When ϕ is larger than a critical value ϕ_c (~35% for disordered foams and 25% for ordered ones), the bubbles are spherical and move independently; in this case, the term *bubbly liquid* is used instead of foam. An interesting transition occurs at ϕ_c where the foam changes from solid-like (finite shear modulus G) to liquid-like (disconnected bubbles). This is the *jamming transition*, also encountered in other assemblies of randomly packed objects, such as emulsions, sand, clays, etc., and presently the object of numerous studies [4].

In order to generate a foam, an energy is needed to create the bubble surfaces, equal to γA , γ being the surface tension and *A* the area created. This energy is orders of magnitude larger than thermal energies and is not minimised: as a consequence, liquid foams are thermodynamically unstable. However, metastable configurations can be produced, in which each bubble takes a shape having minimal area for the given configuration: spheres for isolated bubbles and polyhedra (like the well-known tetrakaidecahedron proposed by Kelvin) in foams with small liquid volume fractions. Most of the liquid is confined to the edges called *Plateau borders* (PB), connecting three films and junctions or *nodes* connecting four PBs (Fig. 2).

Because liquid foams are metastable, the use of stabilising agents is required, which are generally surfactant molecules (Fig. 2), but polymers, proteins or particles can also be used. The stabiliser role is to slow down the different mechanisms of foam ageing: drainage, coalescence and coarsening. After formation, foams evolve with time until they fully disappear, typically a few hours later with surfactant foams. The foam destruction starts with the rupture of foam films, hence foam films have also been extensively studied in link with foam stability.

3. Experiments on foam films

We started our studies with model foam films, an activity supported by CNES in the 1990s. It was easy in this case to simulate microgravity conditions by studying horizontal films. We constructed devices similar to those proposed by Sheludko [5] and Mysels [6], later called *thin film balances* (TFBs). In the Sheludko device, horizontal films are formed in capillaries connected to a liquid reservoir of controlled hydrostatic pressure. The film thickness is measured by optical reflectivity. The Mysels' device is similar, but it makes use of a porous plate instead of a capillary tube, allowing accessing much larger pressures. In both cases, the pressure in the film holder is lower than the pressure in the film centre by a quantity ΔP . As a result and despite the absence of gravity force, the films drain because of the imposed pressure difference ΔP . Note that horizontal foam films also drain, because in this case, the pressure difference is the capillary pressure arising from the PB's curvature (Fig. 2). This type of drainage is called *capillary drainage*.

After drainage in a TFB, the film reaches an equilibrium thickness *h* at which the applied pressure is equal to the force between film surfaces counted per unit area, also called *disjoining pressure* Π_d (for a recent review, see [7]). TFBs therefore allow measuring disjoining pressures, an important property controlling foam stability (for a recent review, see [8]). Note that only repulsive forces can be measured with TFBs, at the difference of the well-known atomic force microscopy (AFM) instruments.

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