Historical perspective

Structure and energy of liquid foams

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ABSTRACT

We present an overview of recent advances in the understanding of foam structure and energy and their dependence on liquid volume fraction. We consider liquid foams in equilibrium for which the relevant energy is surface energy. Measurements of osmotic pressure can be used to determine this as a function of liquid fraction in good agreement with results from computer simulations. This approach is particularly useful in the description of foams with high liquid content, so-called *wet* foams. For such foams X-ray tomography proves to be an important technique in analysing order and disorder. Much of the discussion in this article is also relevant to bi-liquid foams, i.e. emulsions, and to solid foams, provided that the solidification preserves the structure of the initially liquid foam template.

Contents

1. Introduction

Many properties of liquid foams are a direct consequence of their detailed geometrical structure. The opacity of foam samples, for example, is due to the diffusive light scattering from both liquid films and their intersections (Plateau borders). Foam drainage under gravity propagates mainly via the flow of liquid through the network of Plateau borders.

Also the electrical conductivity of a foam is determined by this network. The complex flow behaviour of foams under shear is due to the requirement of structural rearrangements. In this section we present a general overview of foam structure and introduce several quantities for its description.

In equilibrium, foam structure is determined by the minimisation of surface energy for a given volume fraction of liquid. When considering foams under gravity, this corresponds to the experimental situation where a freshly formed foam has been allowed to drain so that an equilibrium profile of liquid content is established — as can be seen in Fig. 1. Furthermore, the time scale of observation needs to be short enough to make foam ageing effects – such as volume changes due to gas diffusion
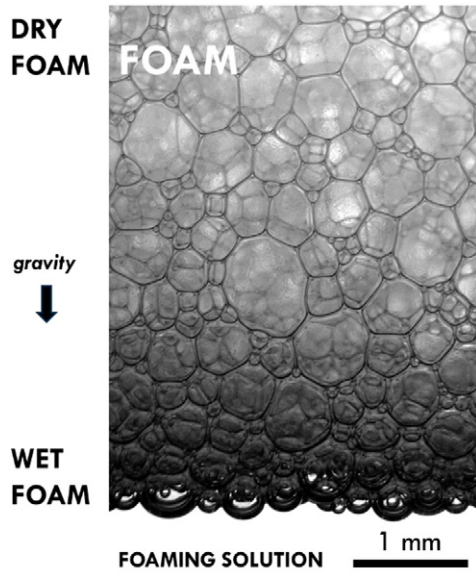
Fig. 1. Example of a liquid foam floating on top of its foaming solution (in this case the detergent "Fairy Liquid"). Liquid drainage under gravity results in a gradient of liquid fraction. At the top (dry foam) the bubbles take on polyhedral shapes while at the bottom (wet foam) they are nearly spherical.

between neighbouring bubbles (coarsening) or breaking films (coalescence) – negligible. Surface tension may then be treated as constant throughout the foam.

The excess pressure of a bubble inside a liquid with surface tension γ and radius R is given by the Young–Laplace law as $\Delta P = 2\gamma/R$. For a typical bubble of $R \approx 100\,\mu m$ and $\gamma \approx 0.03$ N/m, this leads to a pressure difference of the order of 1000 Pa. This is sufficiently small in comparison with the atmospheric pressure of 10^5 Pa, which is why bubbles in foams may be considered as incompressible.

The energy E of a foam with n bubbles is then simply

$$E = \gamma \sum_{i=1}^{n} S_i = \gamma S_{tot},$$ (1)

where S_i is the surface area of bubble "i" and S_{tot} is the total surface area of the foam.

The surface energy of the 100 μm bubble considered above is thus of the order of 10^{-8} J, i.e. about 10^{13} times larger than the thermal energy $kT \sim 10^{-21}$ J. Note that also its potential energy $\Delta \rho g R^4$ due to buoyancy is about 10^9 times larger than kT. Thermal energies therefore play no role in the organisation of bubble packings. This can be different in the case of emulsions, where density differences, values of surface tension and droplet sizes are often much smaller so that thermal effects (such as Brownian motion) need to be taken into account.

A photograph of a typical liquid foam in equilibrium under gravity is shown in Fig. 1. It reveals that bubble shape is dependent on the value of the local *liquid fraction* φ of the foam, i.e. the ratio of the liquid volume to the foam volume under consideration. Close to the foam–liquid interface, at the bottom of the foam column, the bubbles are well approximated by contacting, deformed spheres (Section 3). This is often referred to as the *wet limit*. For foams with modest polydispersity (i.e. containing different-sized bubbles), the maximum value of liquid fraction, or *critical liquid fraction* φ_C, is thus $\varphi_C \approx 0.36$, as obtained for random packings of (monodisperse) hard spheres (Section 3). Foams with liquid fraction higher than about 0.15 are referred to as *wet* foams. For decreasing values of liquid fraction, further away from the liquid interface, the bubbles are increasingly deformed, with curved films between them. Foams with φ less than about 0.05 are called *dry* (Section 2), their bubbles being nearly polyhedral in shape. The setting of precise values is quite arbitrary (see Weaire and Hutzler [1]). However, it helps to distinguish between dry foams, whose cellular structure is

still well described by Plateau's rules (Section 2), and wet foams (Section 3) which resemble aggregations of near spherical bubbles.

Considering such a column of foam in equilibrium, floating on an underlying liquid, the height of the wet foam layer may be estimated as l_c^2/D for bubbles of diameter D. Here l_c is the capillary length given by $l_c^2 = \gamma/(\Delta \rho g)$, g is the gravitational acceleration and $\Delta \rho$ is the liquid density. A wet foam thus contains about

$$Pri = \left(\frac{l_c}{D}\right)^2$$ (2)

layers of bubbles, where Pri has been called the dimensionless *Princen number* in honour of the foam pioneer Henry Princen (Chapter 1 in [2]). For a typical foaming solution, with say $l_c \approx 1.6$ mm, it follows that the average bubble diameter should not exceed 500 μm if one wants to produce wet foams of more than 10 layers of bubbles.

The example shown in Fig. 1 is that of a polydisperse, disordered foam, typical of foams found in nature and many industrial applications. Foams that are currently in vogue in research laboratories are monodisperse, i.e. contain equal-volume bubbles with polydispersity of less than about five percent in radius. Fig. 2 shows the example of such a foam floating on its foaming solution. As can be seen, these foams have the tendency to *order* [3–6], especially in the presence of templating boundaries (Section 3) or when confined in narrow tubes. A selection of experimental realisations of such ordered foams is shown in Fig. 3. In sufficiently wet monodisperse foams ordering might also occur spontaneously in the bulk, as discussed in Section 3.

The surface energy of a foam depends on bubble size, foam structure and liquid fraction. The dependence on bubble size can be removed by introducing the (dimensionless) scaled energy $\hat{E}$ as

$$\hat{E} = \frac{\langle S \rangle}{\langle V \rangle^{2/3}}$$ (3)

where $\langle V \rangle$ and $\langle S \rangle$ are mean bubble volume and surface area in a foam, respectively. Hence, $\hat{E}$ is a measure of how much bubbles are deformed away from their ideal spherical shape. For finite values of liquid fraction it is more convenient to introduce the relative surface excess $\varepsilon(\varphi)$ as

$$\varepsilon(\varphi) = \frac{\langle S(\varphi) \rangle - \langle S_0 \rangle}{\langle S_0 \rangle},$$ (4)
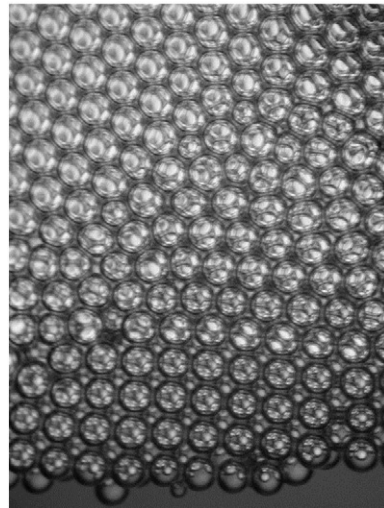
Fig. 2. Example of a monodisperse foam, floating on its foaming solution. It demonstrates the tendency of equal-volume bubbles to order (bubble size ~ 500 μm, see also [7]).