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The physics of foam

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Abstract. Some recent progress in the study of liquid foams is reviewed in outline. Calculations of foam conductivity are presented, which further improve upon the approximation recently proposed by us, in accounting for the nonlinearity in the dependence of conductivity on liquid fraction.

1. Introduction

The list of important scientists who have taken an interest in foams is impressive. Nevertheless the subject has remained largely unsystematic and empirical in style. Few have followed the lead of J A F Plateau (1873), whose painstaking investigations established some basic principles over a century ago. For most of this century the dominant style of research has been that of the chemical engineer, whose elaborate apparatus and multitudinous equations may have resulted in useful practical knowledge but generally added little to our insight.

At first glance the disordered unstable mass of bubbles which constitutes a foam may appear to be an unpromising system in which to apply the physicist's more refined discipline of sharply focused experiments, well-defined models and systematic approximations. But a closer look reveals a great deal of inner order, as Plateau discerned. The basic structural elements are simple in form and arise from the most elementary of physical principles. It is by no means a hopeless case.

2. Dry foam

Dry foam, an apparent contradiction in terms, is the conventional term for a foam in which there is little liquid. Ideally we may consider the volume fraction of liquid, ϕ_l , to be infinitesimal.

A dry foam consists of polyhedral cells with curved walls. These are thin films whose curvatures and angles of intersection are the subject of Plateau's rules. His geometrical rules express no more than the equilibrium of surface tension forces and gas pressures in the cells. Plateau adduced further topological rules: no more than three of the faces can meet in a line, no more than four of these lines can meet in a vertex. These are requirements for stability. The last rule is subtle, and was made mathematically rigorous only recently (Taylor 1976).

3. Wet foams

In the opposite limit, that of a wet foam, there is sufficient liquid to render the gas bubbles spherical, or almost so. The gas fraction at which this limit is reached is simply the packing density of hard spheres. Close to the limit, the bubbles are slightly deformed where they contact.



Figure 1. A tetrahedral vertex at which four Plateau borders come together.

All real foams lie somewhere between the above extremes. As we add liquid to a dry foam, the lines thicken to form Plateau borders (figure 1).

On the way to the wet limit various sorts of topological changes and associated instabilities rearrange the structure locally.

4. Monodisperse foams

The first concern of a systematic theory must be to understand the changes of structure, together with their consequences, as the liquid fraction is varied. The question may be posed for a monodisperse system (Weaire 1994), or indeed for analogous emulsions. When Weaire and Phelan (1994) embarked on a study aimed at this, using the Surface Evolver package of Brakke (1992), a startling discovery emerged for the dry foam.

Whereas the Kelvin structure (b.c.c.) had stood for a century as the conjectured structure of lowest energy (or surface area), a better one was found, having eight bubbles per periodic unit cell (figure 2). Two years later, this remains the best known solution for monodisperse dry foam.



Figure 2. A coarsely triangulated unit cell of the Weaire–Phelan bulk structure modelled using the 'Surface Evolver'.

The comparison of rival structures for wet foams has in due course been pursued (Phelan *et al* 1995), although the picture is not yet clear in all respects. Some results are indicated in figure 3.

One surprise has been the finding that the f.c.c. structure apparently remains at least metastable throughout the entire range of liquid fraction, despite the rule of Plateau which dictates its instability for a dry foam. We have suggested that it is indeed metastable for arbitrarily small liquid fraction (Weaire and Phelan 1996), but this has been queried, and may not be quite the case (Brakke 1996).

5. Polydisperse foams

Everyday foams are polydisperse. Their structures change continuously with increasing liquid fraction, both geometrically (swelling of Plateau borders and their junctions) and topologically. We are not quite at the point at which they can be directly simulated for large numbers of bubbles, in the manner of figure 2. In any case, simple analytical theories



Figure 3. Ranges of stability (solid) and metastability (hatched) of various structures. A 'stable' structure is here defined as that of lowest energy among those considered; a 'metastable' structure is simply mechanically stable. The question of f.c.c. metastability in the limit $\phi_l \rightarrow 0$ remains to be fully resolved.

are of obvious value and they can be developed for low liquid fractions. Limitations of space permit only two topics to be mentioned: drainage and conductivity.

6. Drainage

The drainage of liquid through a foam occurs most commonly when a freshly formed foam approaches static equilibrium. However, the most productive experimental procedure involves the continuous addition of liquid solution at the top of the sample (e.g. see Weaire *et al* 1993). When the flow rate is increased from zero or a steady value, a solitary wave is observed: for a review of the relevant theory see Verbist and Weaire (1996). The combination of easy experiments and an elegant first-order theory, which is quite successful, make this solitary wave a most attractive object of investigation. It has in turn spawned a new generation of drainage experiments under other conditions.

The theory assumes that drainage takes place mainly along Plateau borders, which are treated as uniform in cross-section. Corrections will surely be required when high liquid fractions are considered more carefully (Boltenhagen and Pittet 1996).

7. Conductivity

The conductance of a foam may be measured to determine its liquid fraction, and this has indeed proved useful in confirming the validity of the drainage theory mentioned above (Peters 1995). Lemlich (1977), whose early contributions contained many of the seeds of our present understanding, derived a remarkable relation between conductivity and liquid fraction, which is

$$\frac{\sigma_f}{\sigma_l} = \frac{1}{3}\phi_l \tag{1}$$

where σ_f / σ_l is the conductivity of the foam, σ_f , relative to that of the liquid, σ_l .

This follows from some reasonable geometrical idealizations of the random network of Plateau borders (assumed to make the dominant contribution), which are appropriate in the dry limit. The theory is in the same spirit as that mentioned for drainage: we possess quite a coherent model for most properties in this limit.



Figure 4. Experimental measurements (+) of the conductivity of an aqueous foam, σ_f , measured relative to the liquid conductivity, σ_l . The linear approximation is due to Lemlich. The solid curve shows the relationship based on equations (2) and (3) which include the concept of 'vertex corrections'. The dashed curve indicates the results of direct calculations (×).

Calibration curves, such as that of figure 4, are in accord with the Lemlich limit, but depart significantly from linearity when the liquid fraction is of the order of ten per cent. We attribute this to the effect of the swelling of the junctions of the Plateau borders, and have recently calculated these by computing the resistance of the junctions (Phelan *et al* 1996). This analysis has led to the simple parametric formulae

$$\phi_l = L_v c_g \delta^2 \left(1 + 1.50 \frac{\delta}{L} \right) \tag{2}$$

$$\frac{\sigma_f}{\sigma_l} = \frac{1}{3} \frac{L_v c_g \delta^2}{(1 - 1.27\delta/L)} \tag{3}$$

parametrized by δ and where c_g is a geometrical constant. L_v and L are constants describing the bulk foam structure.

These relations work quite well, as figure 3 indicates. Equations (2) and (3) were derived from detailed calculations of the volume and conductance of a typical foam vertex of the type shown in figure 1. The result is even more impressive if the calculations are used directly, and we present this for the first time here, also in figure 3.

8. Conclusion

For further details of recent progress, the references already cited may be consulted, together with Weaire and Fortes (1994) for rheological properties, and a forthcoming special issue of *Forma*, entitled 'The Kelvin Problem'.

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