

# Liquid Foams

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## Abstract

The elegant structure of a liquid foam and its constituent parts have fascinated scientists for centuries. A combination of experiments, theory and simulations has elucidated most of its static and quasi-static properties. However, this is only part of a wider subject: dynamic effects remain as a considerable challenge, particularly for wet foams.

## 1 The structure of a liquid foam

In 1873 the blind Belgian physicist Joseph Plateau (figure 1), Professor at the University of Ghent, published his life's work, "Experimental and Theoretical Statics of Liquids Subject to Molecular Forces Only" [1]. Translated in this way the title is clumsy in English, and it is elusive in French. The book is mainly based upon a series of papers in the Memoirs of the Belgian Academy which referred to "figures of equilibrium of a liquid mass without weight". In both cases a direct reference to effects of surface tension as the main object of enquiry might have been more helpful.

The book deserves its frequent citation as the standard historical reference on the geometric structure of a liquid foam. Plateau's name is often invoked for the attribution of basic geometrical and topological laws of equilibrium, which he established experimentally (with theoretical underpinning from his mathematical colleague Ernest Lamarle). But the scope of Plateau's work is really much wider. It included topics considered "advanced" today, such as rupture mechanisms, surface viscosity and the Marangoni effect. His work is not matched in its thoroughness by any modern text.

In the twentieth century, the books of Lawrence [2] and Mysels et al. [3] are largely concerned with individual films or bubbles. Chemical industries sponsored extensive research, usually aimed at understanding the role of surfactants. The book of Bikerman [4] gives the flavour of that work. Generally speaking, the essential simplicity of Plateau's vision was lost in this application-driven research. Inspired by C.S. Smith [5], various physicists turned their attention to the subject in the 1980s. Drawing on the best of the work in chemical engineering, including that of Princen (see his review article Princen [6]) and Lemlich (for example [7]), they began to build a systematic theory of foam properties. The recent *Physics of Foams* [8] is a broad introduction, mostly concentrating on liquid foams, based upon two decades of progress towards that goal. It concludes with a figure (our figure 2) which has proven useful as a conceptual map of our present stage of knowledge. This

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is intended to convey the existence of successful theory and experiment for dry, static foams, while a host of interesting and awkward problems are posed by wet and/or deforming foams. By *wet* we imply a relatively high value of the liquid fraction  $\Phi_l$ . Other recent works include those of Isenberg [9], who describes the mathematics of soap films and bubbles, and Exerowa and Kruglyakov [10], who provide in particular a detailed discussion of the physical chemistry of soap films.

A well-developed science of dry, static (or quasi-static) foams is a valuable first step. Most common foams are quite dry when in equilibrium under gravity, and we can understand most of their properties when they are in this condition. These include the essential structure, as Plateau described it long ago, the statistics associated with that structure, its coarsening with time due to gas diffusion, its elastic and plastic properties, and the drainage of liquid through it when equilibrium is disturbed.

The completion of this picture by the pursuit of dynamic effects and high liquid fractions is under way. Experiments are even undertaken in the microgravity environment of space, where homogeneous wet foams can exist in equilibrium [11].

Part of the motivation of the subject lies in its relation to solid foams. Most of these have a liquid foam as a precursor, so that a solid foam is usually a frozen (and perhaps processed) liquid foam. As such, it retains all or some of the characteristics of the pre-existing liquid structure. That elegant form has advantages for some purposes. It is, for example, close to the optimum for electrical or thermal conductivity [12]. For other properties, such as mechanical strength, it is more of a mixed blessing.

Many examples of such solid foams are to be found in this book. Others include the metallic foams that have begun to attract serious commercial interest, and biological foams such as bone or cork. At this point we must also draw attention to the distinction between open- and closed-cell foams. The former have two continuous phases, while in the latter one of the phases is separated into discrete units. In both cases, the structure is similar: open-cell foams can be thought of as solid closed-cell foams with the thin films removed. This is precisely how they are made in many cases.

In the case of ceramics, such open-cell foams are commonly made by replication of a polymeric foam. On the other hand, closed-cell foams may be formed by direct foaming of a ceramic slurry, followed by solidification. These processes are explained in Chapter 2.1.

So a good starting point for understanding such foams and striving for innovation in their fabrication is a study of the liquid foam structure from which they are derived.

The favoured tool for approaching the subject by simulation is the Surface Evolver [13]. This consists of software expressly designed for the modeling of soap bubbles, foams, and other liquid surfaces shaped by minimizing energy (such as surface tension and gravity), and subject to various constraints (such as bubble volumes and fixed frames). The surface is represented as a collection of triangular tiles. The complicated topologies found in foams are routinely handled. In particular, the Evolver can deal with the topological changes encountered during foam coarsening and quasi-static flow. It provides interactive 3D graphics and an extensive command language. The Surface Evolver is freely available from <http://www.susqu.edu/brakke/evolver/>, and is regularly updated. With the help of this software, realistic structures representing foams in equilibrium may be created, which may then be used for a variety of purposes in the physics of both liquid foams and their solidified counterparts. We shall use it to create many of the illustrations that follow.

## 2 The elements of liquid foam structure

Foam may be analysed in terms of distinct interrelated structural elements (bubbles, films, Plateau borders and junctions) with precise and simple geometry. This elegant structure is illustrated beautifully in the images of the photographer-artist Michael Boran, one of which is shown in figure 3.

**Films:** The bubbles which are pressed together to form the foam are separated by thin films. Although these are the most evident feature of the foam structure, they play only an incidental role in many of its properties. (One exception is stability, since foams collapse because of film rupture.)

**Plateau borders:** Where films meet along a line or curve, there is a liquid-filled interstitial channel called a Plateau border.

**Junctions:** Where several Plateau borders meet to form an interconnected network, they do so at a junction.

Hence each bubble may be represented as a polyhedral shape, such that faces are identified with films, edges with Plateau borders, and junctions with vertices. Plateau's equilibrium rules apply to a dry foam (a liquid fraction of  $\Phi_l = 0$  or, in practice, much less than 0.01) at equilibrium. They are:

- Only *three* films may meet at a Plateau border, and they meet at equal angles (figure 4a);
- Only *four* Plateau borders may meet at a junction, and they meet at equal angles (figure 4b).

These have been proved most rigorously by Taylor [14].

To these rules we may add the Laplace-Young law which states that the pressure difference  $\Delta p$  across a film is proportional to its mean curvature  $\kappa$ :

$$\Delta p = 4\gamma\kappa. \quad (1)$$

Here  $\gamma$  is the surface tension of a single air-liquid interface: the surface tension of the film is  $2\gamma$ . The mean curvature  $\kappa$  is the mean of the reciprocals of the radii of curvature in two orthogonal directions,

$$\kappa = \frac{1}{2} \left( \frac{1}{r_1} + \frac{1}{r_2} \right). \quad (2)$$

This law dictates, in particular, that the film must have curvatures consistent with the pressures in adjacent bubbles. If we look closely at a single surface of a Plateau border the same law applies, with an extra factor of one-half, and it implies that they have negative pressure with respect to the adjacent bubbles, as in figure 4c,d.

A foam can have any liquid fraction in a range from zero to about 36%, the *wet limit*, at which the bubbles come apart. This is the limit appropriate to a typical disordered foam, being related to the dense random packing of hard spheres with relative density 64%. In both the wet and dry limits the structure is relatively simple. Figure 5 shows simulated foams with  $\Phi_l \approx 0.5\%$  and 5%. In the middle of this range of liquid fraction, however, the structure is much more difficult to analyse and its properties remain somewhat obscure. Moreover, real foams are disordered, as indicated in figure 6. Beyond a liquid fraction of a few percent, multiple junctions may form, instead of the tetrahedral ones which are idealized in the confluence of four lines in the dry limit. In that limit such multiple junctions are explicitly forbidden by Plateau's rules, but they can become stable for finite liquid fraction, as illustrated in figure 7.

### 3 Real liquid foams

Real liquid foams are generally only stable if they contain surfactants. Their most important effect is not simply that of lowering the surface tension, although it is closely related. Rather, it is the dynamical properties of the surface tension which serve to stabilize the films. The surface tension  $\gamma$  increases whenever a film is suddenly stretched locally, resulting in increased forces which oppose that tendency.

Also of importance for the stability of the films is the so-called *disjoining pressure*, which expresses the mutually repulsive force between the two faces of a film. It opposes further thinning once the film thickness has been reduced to a value at which this repulsive force is significant. As the liquid pressure decreases to a large, negative, value (relative to atmospheric pressure) the Plateau borders shrink and increase in curvature in accordance with the Laplace-Young law, but the films do not thin indefinitely. The film thickness at which equilibrium is achieved is therefore determined by the balance between the disjoining pressure and the bulk pressure of the liquid.

Up to a point, all this can be ignored, the films being stable and of negligible thickness in accounting for the total liquid content or such properties as conductivity. Some of the simplicity of the various formulae which express properties in terms of liquid fraction [8] arise from such an assumption.

At the leading edge of the subject, the films are coming back into play. And there can be no doubting their primary importance in relation to stability.

### 4 Quasi-static processes

A quasi-static process in a foam is one in which the relaxation of the structure back to equilibrium is much faster than the time-scale at which the foam is perturbed. In this limit, we can use the Surface Evolver to probe the slow dynamics of foams. Topics of interest in this area fall roughly into three categories: gas diffusion, liquid motion and bubble motion.

#### 4.1 Coarsening

*Coarsening* is the gradual change of the foam structure due to gas diffusion through the films. This diffusion is driven by the pressure differences between bubbles, and can therefore be related to the curvature of the films by the Laplace-Young law. Small bubbles have high pressure, so that they lose gas and disappear. Thus the average bubble size increases with time, that is, the foam coarsens, typically on a time-scale of about 30 minutes [15]. In two dimensions there is an exact law, due to von Neumann [16], which states that the rate of change of area of a bubble depends only upon its number of sides.

In three dimensions there is no such exact result. It is known that the growth of a bubble does not depend only upon its number of faces, although this is a reasonable approximation for most cases, as evidenced by theory, simulation and experiment [17, 18, 19].

#### 4.2 Drainage

Whenever there is a finite amount of liquid in the foam, it is subject to gravity-driven drainage, unless it has already come into equilibrium under gravity [20]. In this state, there is a vertical profile of liquid fraction. This is related to a variation of the local pressure in the liquid according to the hydrostatic pressure law, necessary for equilibrium under gravity.

More generally, the liquid moves through the Plateau borders and junctions of the static foam structure (and to a lesser extent the films) in response to gravity and local pressure variations. An understanding of this process, particularly in the limit of low liquid fraction, has been aided by the development of nonlinear foam drainage equations [21, 22, 23].

The most striking manifestation of drainage is the solitary wave-front which propagates down through the foam when liquid is added to the top at constant flow-rate. See figure 8. This is known as a *forced drainage* experiment. The velocity of the front is constant to a good approximation, and easily observed. This simple measurement is a good starting point in exploring drainage, and its dependence on the nature of surfactants [24].

### 4.3 Rheology

In all of the above, the bubbles themselves have essentially remained stationary. But recently the deformation and flow of the foam, in which the bubbles are rearranged, has been a focus of experiment and theoretical debate [25]. We have known for a long time that a liquid foam has a well-defined shear modulus, proportional to surface tension and many orders of magnitude less than its bulk modulus (which is essentially that of the enclosed gas). Moreover, large shear strains may be imposed before substantial rearrangements (topological changes) are incurred, leading to plastic behaviour, a yield stress, and so on. This is summarized in figure 9, which schematically illustrates the results of an experiment in which a foam is sheared. In the elastic regime, the structure deforms without topological changes. At the yield stress, topological changes occur and the plastic regime is entered. Finally, the topological changes lead to flow.

Beyond this simple and well-understood picture, much remains to be explored as regards strain-rate dependent effects, localization of shear (shear-banding) etcetera. Further details can be found in the review by Weaire and Fortes [26]. Recent references include [27, 28, 29, 30].

## 5 Beyond quasi-statics

In order to understand the role of viscosity, for example, or the effects of combinations of the above processes, we must progress beyond the quasi-static picture.

In the latter category, one area of interest is the *convective instability* which occurs when liquid is added to a dry foam at a high flow-rate. The drainage causes the foam to become wet enough that it overcomes its yield-stress and begins to move, as illustrated in figure 10. There are at least two possible modes of instability in which the foam circulates [31, 32, 33]. In order to predict parameters such as the critical flow-rate for the onset of motion as a function of bubble size, we must combine theories of drainage and rheology, a challenge yet to be met.

For the rheology of real foams, we must in some sense understand the effects of viscous drag on the structure. Our attempts to model this in two dimensions [34] require a modification of the Laplace-Young law (1) to the following form

$$\Delta p = 2\gamma\kappa + \lambda v, \tag{3}$$

in which  $v$  is the normal velocity of a film, and all viscous effects are included in the parameter  $\lambda$ . (The factor of 2 rather than 4 arises because we are in two dimensions.) This *viscous froth* model shows good qualitative agreement with experiments, but has yet to be extended to three dimensions. It is no more than a tentative start to a difficult problem.

Three-dimensional modelling of viscous effects is essential to a full understanding of solid foam formation, whether consisting of ceramics, metals or plastics. There has undoubtedly been a good deal of work done on this in the polyurethane industry in particular, but much of it seems to

have been proprietary. There is also an extensive literature in the domain of chemical engineering for viscous effects in ordinary liquid foams (for example [35, 36, 37, 6]). It is largely empirically based, and this makes it difficult to assess its validity. Most of the subject of foam rheology remains in the *terra incognita* depicted in figure 2.

## 6 Conclusions

The equilibrium structure of a foam is an elegant and well-defined arrangement of films, Plateau borders and junctions. This structure is largely independent of the material from which the foam is constructed and its method of production. As ever more diverse materials are foamed with many different applications in mind, it should be remembered that the one-hundred-year-old laws of Plateau are still essential in describing the structure of the foam.

In the static state, our knowledge of the behaviour of both solid and liquid foams is good, particularly in the dry limit. Moreover, this understanding extends to many properties of a liquid foam's quasi-static motion. We now seek to extend theories to cope with wet foams in dynamic situations. A promising step in this direction is the use of *microgravity* experiments aboard parabolic flights, sounding rockets and potentially the International Space Station. The current generation of these experiments aims to study the drainage and rheology of wet foams and the formation and collapse of metallic foams in the absence of gravity.

## Acknowledgements

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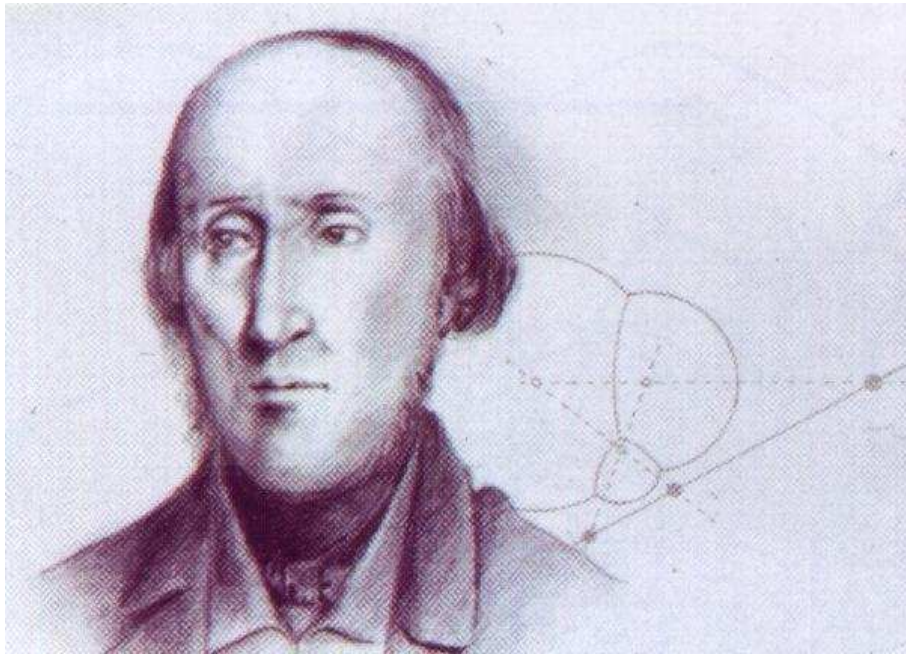


Figure 1: Joseph Plateau, the blind Belgian physicist who established the basic geometrical and topological laws of foam equilibrium.

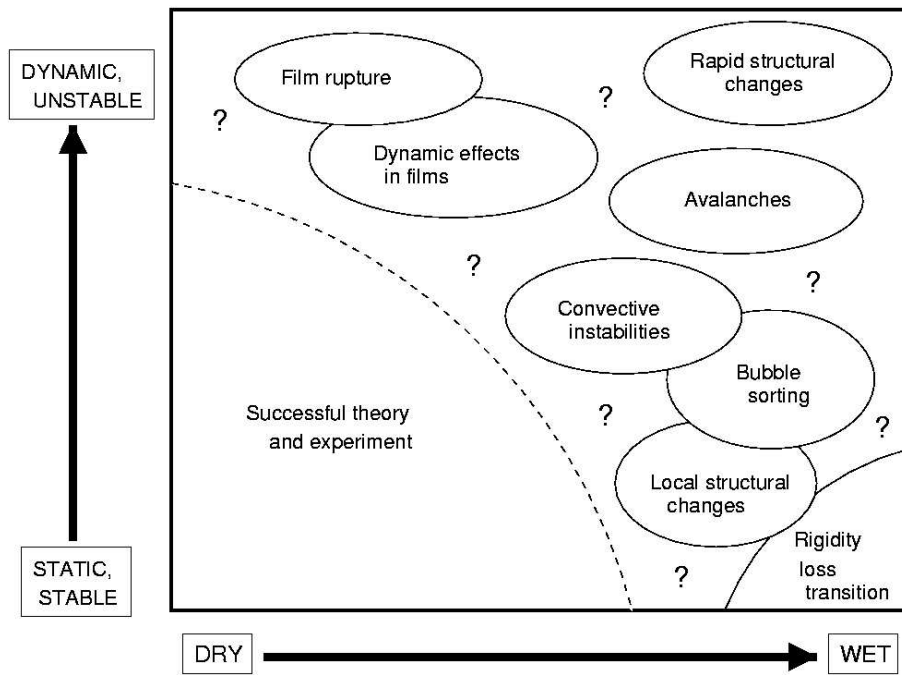


Figure 2: A schematic “phase-diagram” illustrating our current understanding of liquid foams, extending from dry to wet structures and from static to dynamic processes.

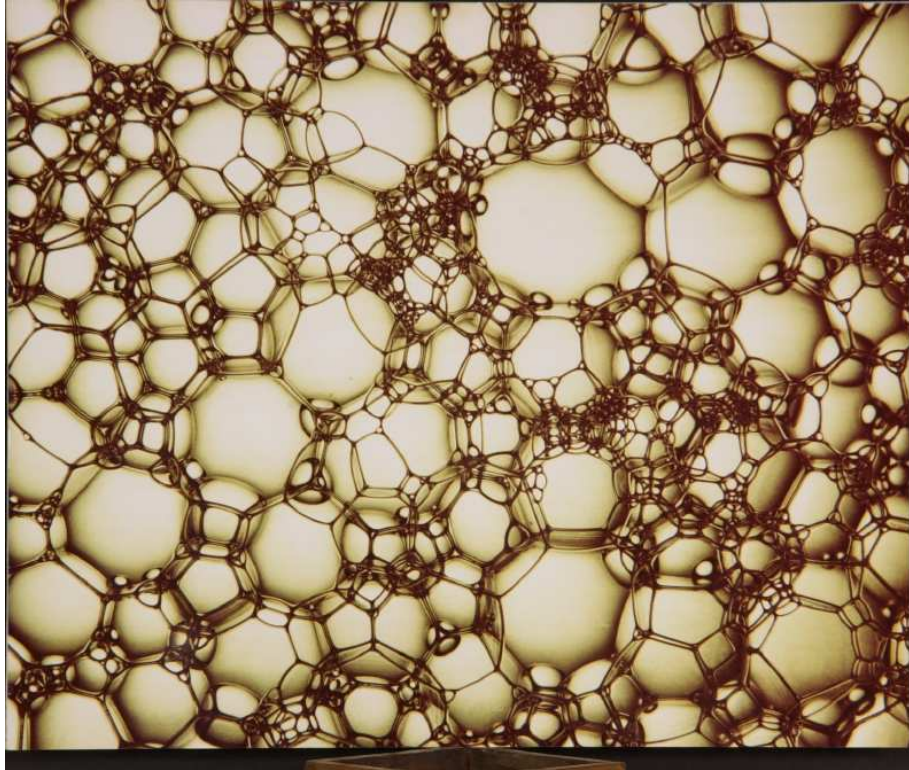


Figure 3: The structure of a liquid foam as seen by the photographer-artist Michael Boran.

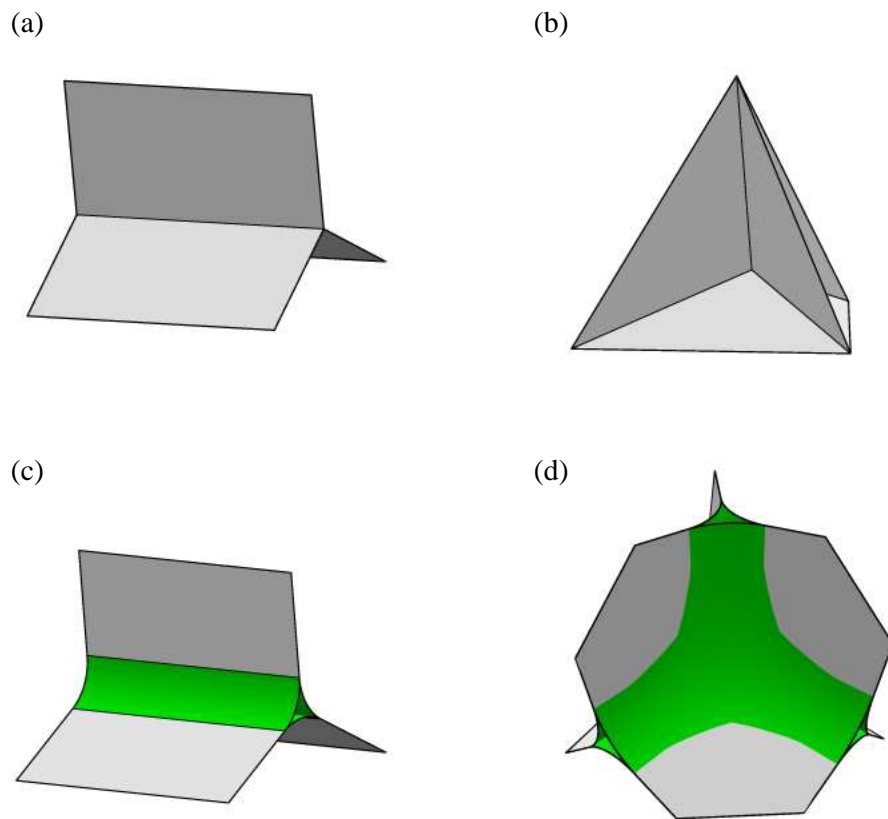


Figure 4: The elements of a foam, illustrating Plateau's laws. In the dry limit, (a) three films meet in a single Plateau border and (b) four Plateau borders meet in a single junction. This junction is formed at the meeting point of six films in a tetrahedral-shaped wire frame, such as Plateau used to discover the laws which bear his name. When liquid is added to a foam, the Plateau borders (c) and junctions (d) become swollen, meeting the films with a zero contact angle. These images were generated with the Surface Evolver.

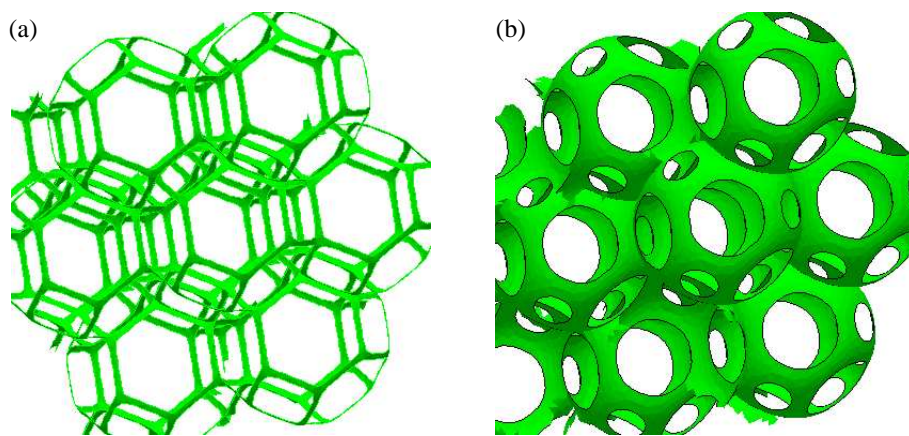


Figure 5: A simulated wet foam with liquid fraction of (a) 0.5% and (b) 5%, in the case of the tetrakaidecahedral structure proposed by Lord Kelvin for the structure of the ether. The films have been removed from this Surface Evolver calculation, giving the impression of an open-celled rather than a closed-cell foam.

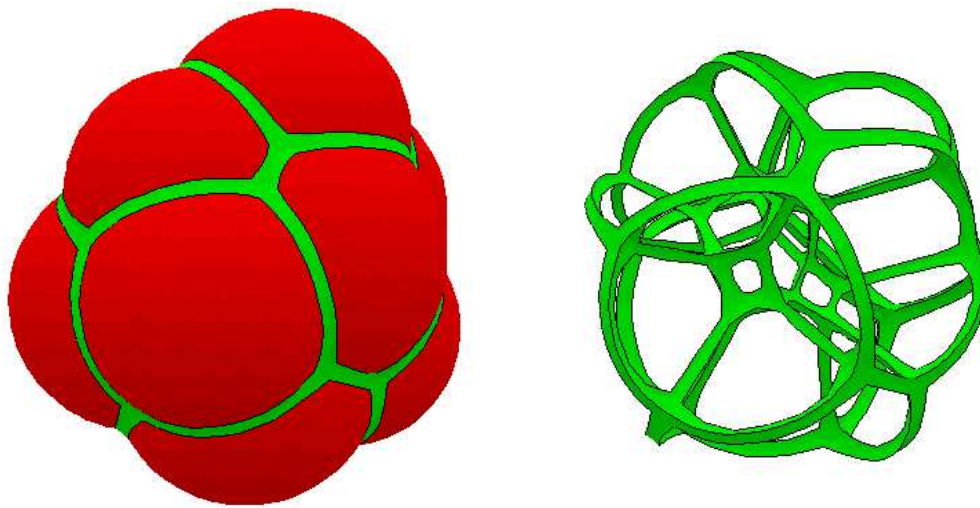


Figure 6: A finite, wet, polydisperse, closed-cell foam, such as this simulated cluster of bubbles, reveals a complex liquid network when the films are removed.

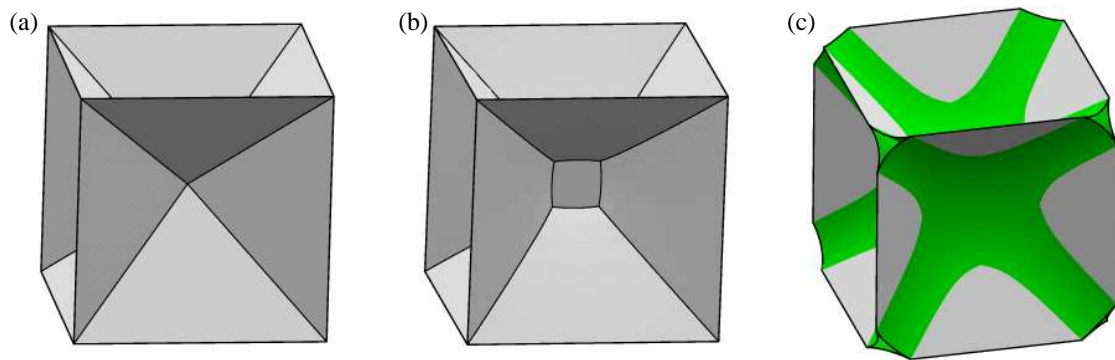
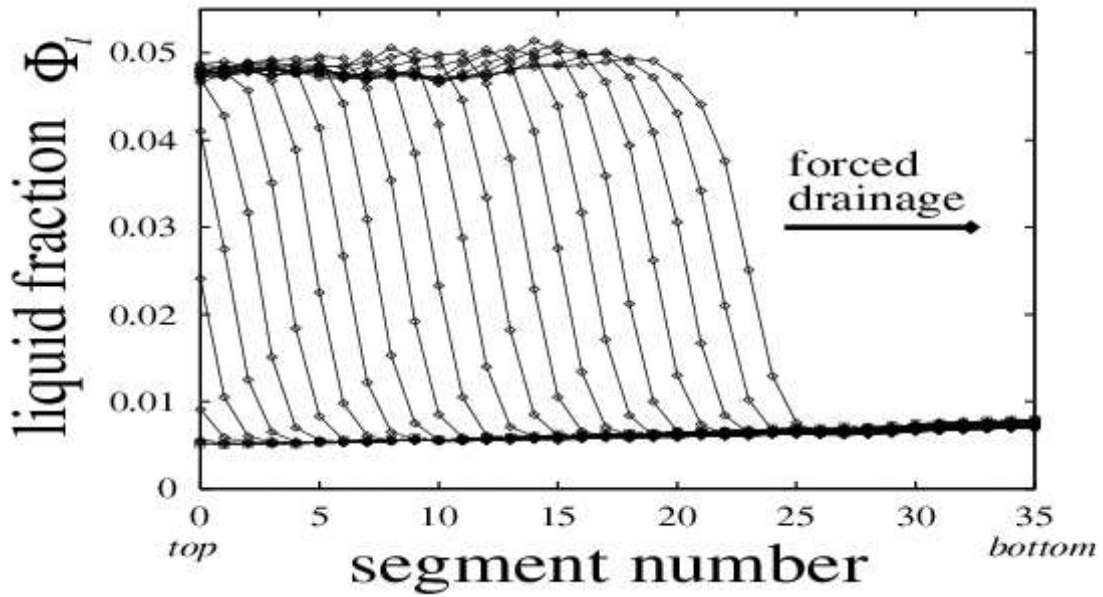


Figure 7: Higher-order junctions are only possible when the structure is sufficiently wet, as seen in these Surface Evolver simulations. In a cubic wire frame, such as that used by Plateau, the *dry* eight-fold symmetric vertex (a) is unstable: the vertex dissociates into four four-fold junctions (b). When sufficient liquid is added however, the eight-fold vertex (c) can be stable.

(a)



(b)

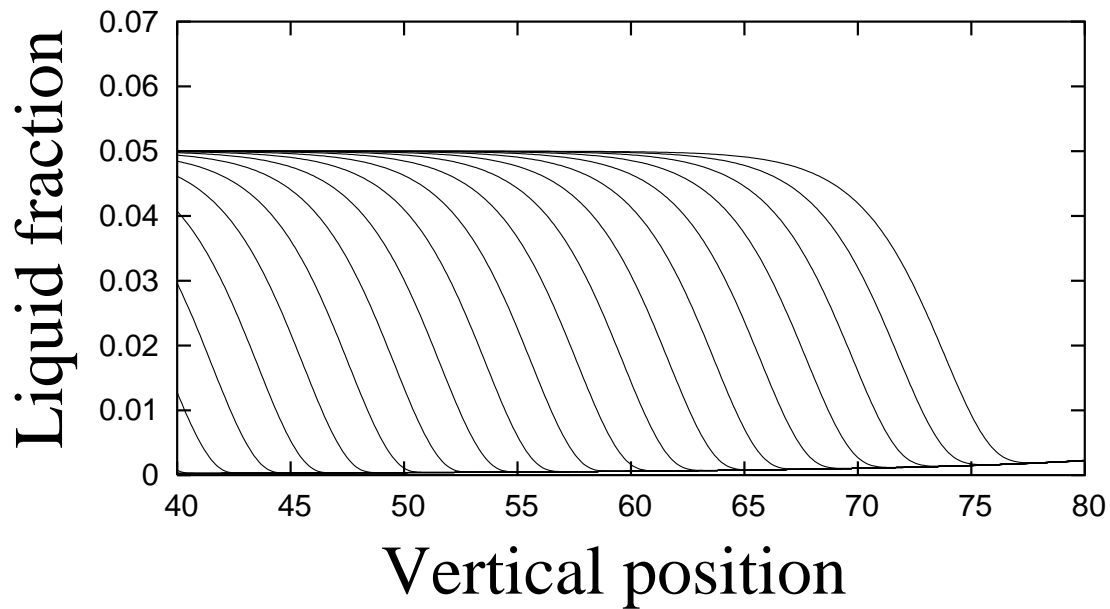


Figure 8: (a) The forced-drainage experiment, in which a solitary wave is observed to descend through the foam, has greatly improved our understanding of liquid drainage through foams. In this case the position of the wave-front was measured using conductivity. (b) The numerical solution of a foam drainage equation allows us to verify the agreement between theory and experiment.



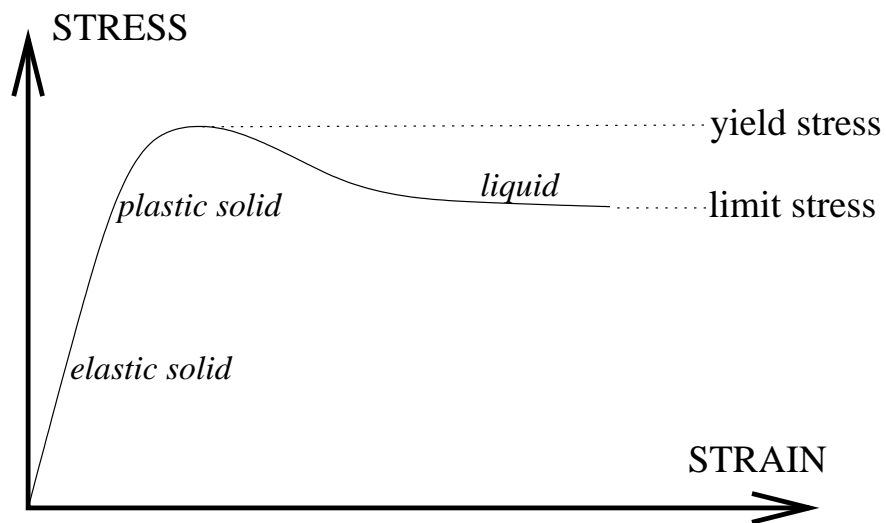


Figure 9: In an experiment in which the strain is slowly increased, the stress first increases linearly. The slope is the elastic shear modulus. This increase continues until the plastic limit, at which the first topological changes occur and the foam yields. The system shows hysteresis in the sense that once the foam has yielded, the stress drops to a lower limit stress characterised by further intermittent topological changes and liquid-like behaviour (flow). In practice, the difference between the limit stress and the yield stress is small, and both depend significantly upon the strain-rate.

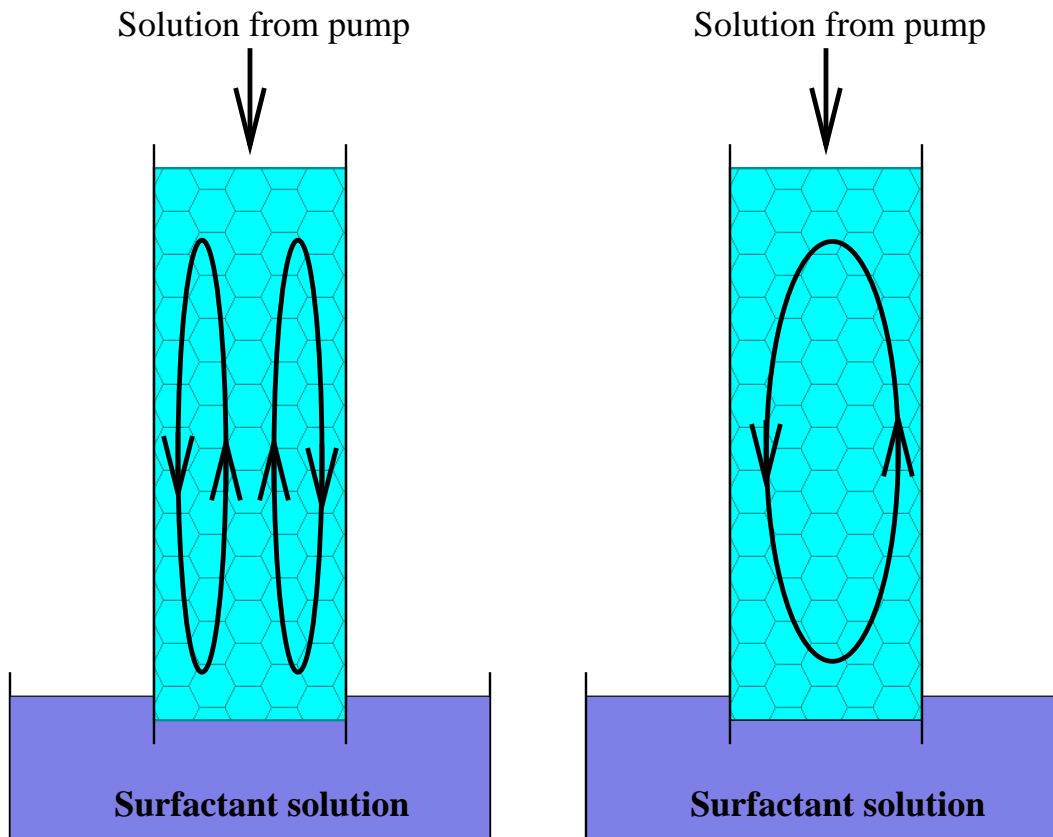


Figure 10: A forced drainage experiment at high flow-rate leads to one of a number of convective instabilities, in which the foam itself is continuously deformed. Two possibilities are illustrated here: the first is a cylindrically symmetric motion in which bubbles in the centre of the foam rise and those on the outside descend, while the second is a solid-body rotation.