THE PHYSICS OF FOAM DRAINAGE

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ABSTRACT
Foam drainage describes the flow of liquid through a foam, driven by gravity and capillarity. It is an important factor for foam stability, and thus of great relevance to the detergent industry.

Over the last decade substantial progress has been made in understanding the relevant physics behind foam drainage and the related issue of drainage or creaming in emulsions. This was instigated largely by so-called forced drainage experiments, in which the foam is fed at the top with a supply of liquid and its spatial and temporal variation of liquid fraction is determined.

We review key experiments and theory and also address remaining questions concerning convective bubble motion in foams with high liquid content and the local flow mechanism of drainage.

INTRODUCTION
Sipping a glass of champagne while sitting in a bubble bath conjures up an image of perfect relaxation for many of us. But while we want the foam in the bath tub to remain there for as long as possible, champagne is meant to foam up quickly when poured, and then collapse leaving only a necklace of bubbles remaining along the side of the glass. Anything else would look suspicious: was that glass properly rinsed?

The lifetime of a foam is controlled by a variety of factors (Weaire and Hutzler, 1999). Ultimately the thin films are stabilised against rupture by surfactants. These surface active molecules position themselves at the air-liquid interfaces and lower the surface tension of the liquid. Important for the enhancement of film stability is, however, the possibility of surface tension *gradients* in surfactant solutions.

Evaporation of liquid is one lifetime-limiting factor, as is coarsening, i.e. the increase in average bubble size (or decrease of the total number of bubbles in a foam) due to the diffusion of gas through the liquid films. The main limiting factor for foam stability is however foam drainage; driven by gravity, liquid flows from the top to the bottom of a foam (figure 1). As this leads to an ever decreasing liquid content it results in a so-called *dry* foam, which is considerably less stable as its thinner films are more likely to break and coarsening proceeds at a faster rate.

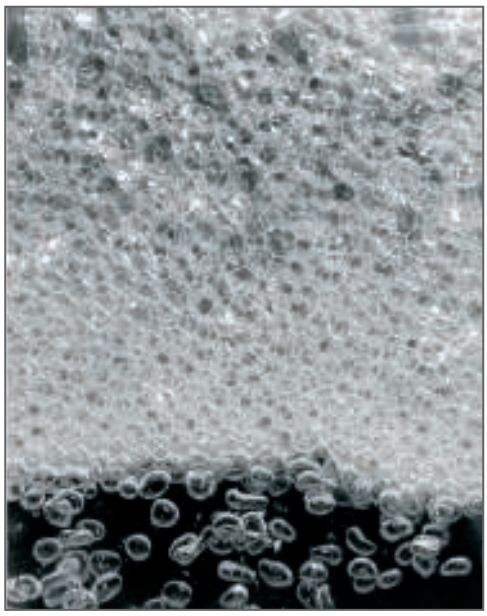

Figure 1: Free drainage results in the establishment of foams with a non-uniform liquid content, dry at the top, wet at the bottom.
Photograph by J. Cilliers, UMIST).

Considerable progress in undermade over the last 15 years by physicists who developed simple theoretical models of drainage and also designed new types of experiments (Weaire and Hutzler, 1999). The key ingredients of drainage are at this stage well understood. Remaining tasks include the coupling of the description of local flow properties to surfactant chemistry and rheology and also the bubble movement in foams with high liquid fraction, as in the pouring of beer, or a multitude of industrial chemical processes.

The aim of this paper is to provide a brief overview of the physics of foam drainage, with links to relevant recent research and review articles. It is hoped that this might demonstrate the industrial relevance of this work, and perhaps stimulate its use for the design of novel foam characterisation procedures.

The Structure of Foam

A foam is a collection of gas bubbles separated by liquid films. Many of the physical properties of a foam depend on its liquid fraction, Φ i.e. the volume ratio of liquid and gas. *Dry* foams refer to Φ less than about 0.05 (as generally holds for detergent foams), *wet* foams refer to Φ higher than about 0.15 (as in freshly poured beer). Values of liquid fraction higher than 0.36 correspond to *bubbly liquids*. In equilibrium under gravity, most common foams are quite dry.

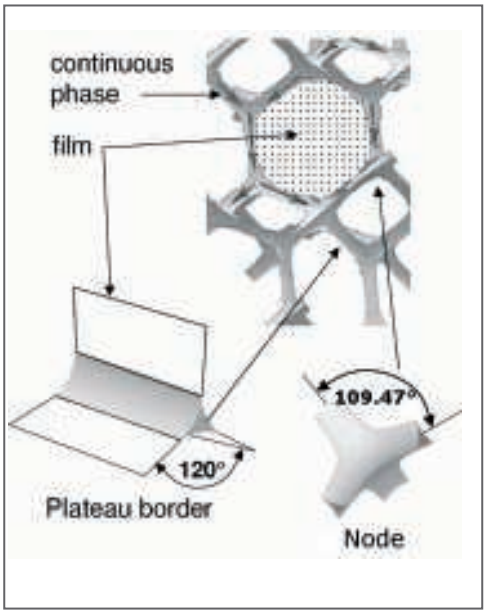

Figure 2: Structure and geometry of dry foam

The geometry of dry foams is well defined (figure 2). Three films meet symmetrically in a line at angles of 120 degrees and four such lines meet in a vertex at the tetrahedral angle of 109.47 degrees. The lines of intersection of three films are called Plateau borders, after 19th century scientist Joseph Plateau who was the first to describe the structure of dry foams. Starting from such a dry skeleton and increasing the liquid fraction leads to an increase of the cross-section of the Plateau borders, until at about $\Phi \approx 0.05$, also a swelling of the junctions becomes visible. At a further increase of Φ, the polyhedral char-

acter of the bubble packing (also called *polyederschaum*) vanishes completely and one arrives at what has been called *kugelschaum*, in which the bubbles are nearly spheres.

Relevant physical parameters for the constituents of a foam are the density ρ and the bulk viscosity η of the liquid, the surfactant-dependent surface tension γ and surface viscosity η_s, and the diffusivity of the gas. Depending on the method by which the foam has been generated there will be a certain size distribution for the bubble diameter d. Foam drainage experiments are often performed on foams with narrow size distributions or even monodisperse foams. This allows for systematic studies of the effect of bubble size on drainage and also avoids size sorting, see below. The average bubble diameter also determines the thickness W_{wet} of the layer of wet foam at the bottom of a drained foam. This is given by $W_{wet} \approx l_0^2/d$ where l_0 is the capillarity length, $l_0^2 = \gamma/\rho g$, and g is the acceleration due to gravity (Weaire and Hutzler, 1999).

Foams are generally disordered. In practice only the confinement of relatively small numbers of equal-sized bubbles by suitable boundaries can lead to ordering, at least in the case of dry foams (figure 3). This is exploited in the recently developed field of discrete micro-fluidics where ordered foam is transported through narrow channels. A series of tools has been developed for a controlled manipulation of such trains of bubbles, with great technological potential for the analysis and manipulation of gaseous and liquid samples (Drenckhan et al., 2005).

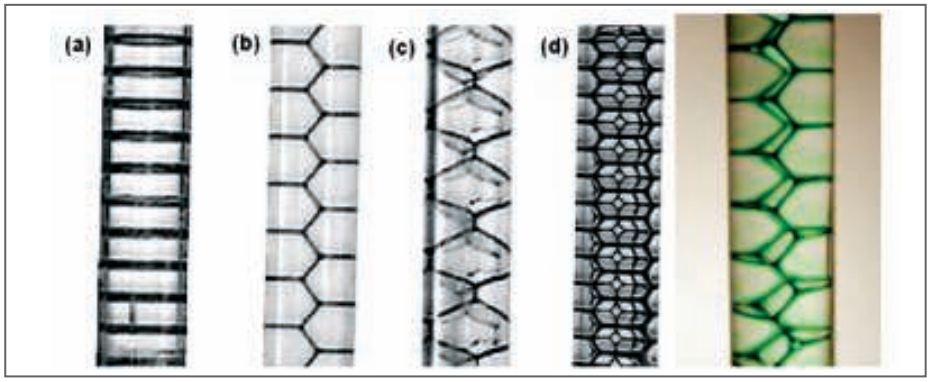

Figure 3: Confining foams (a-d) or emulsions in cylinders with diameter similar to the bubble diameter results in ordered sructures

The theoretical interest in monodisperse foam relates to the problem of finding the structure of lowest surface area for a given bubble size (Weaire, 1997). Lord Kelvin's suggested structure was outperformed only in 1993, by a structure computed by Weaire and Phelan, over one hundred years after the original finding (figure 4). A rigorous mathematical determination whether this is the optimal solution remains, however, elusive.

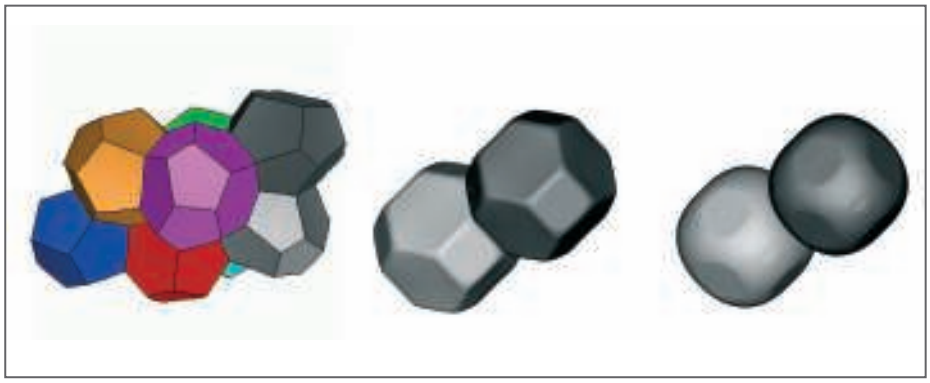

Figure 4: Foam structures can be computed using the Suface Evolver software (Brakke, 1992). The examples shown here are the Waire-Phelan structure for $\Phi = 0$ and Kelvin cells for $\Phi = 0.01$ and $\Phi = 0.10$.

All of the above remarks on the structure of foams also hold for emulsions, i.e. dispersions of one liquid in another liquid. This was shown recently for monodisperse oil-in-water emulsions with drop diameters of a few millimetres (figure 3) (Hutzler et al., 2004). The same experiments also demonstrated that the foam-emulsion analogy is also valid when describing the dynamics of drainage.

Free drainage and forced drainage

Typically, the liquid of a freshly made foam drains immediately and the foam eventually approaches an equilibrium state under to the forces of gravity and capillarity. This naturally occuring process is called *free* drainage, to distinguish it from the experimental technique of *forced* drainage which we will describe below.

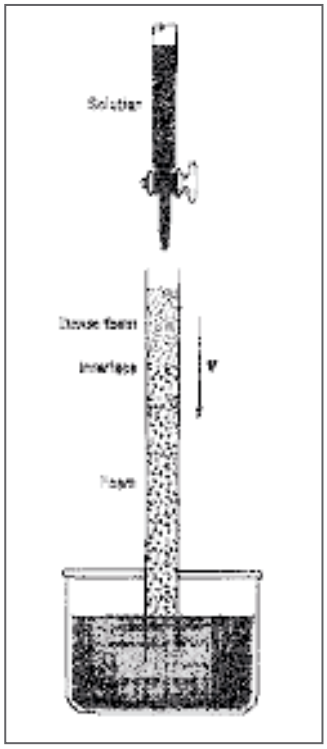

Figure 5: In forced drainage experiments surfactant solution is added onto a dry foam at a fixed flow rate. This results in the propagation of a drainage wave through the foam.

Free drainage was the natural choice for many experiments carried out in the middle of the 20th century, as reported in the classic book by Bikerman (1953). Essentially a liquid is foamed up with a fixed amount of gas and the volume of the liquid draining from the foam is measured as a function of time. Several variations of this theme are in use today, for example in the beer brewing industry (Rudin test, NIBEM method (Weaire and Hutzler, 1999)).

The main problems with such free drainage experiments relate to the definition of the start of the experiment, since the foam starts draining as soon as it is formed. A theoretical analysis of the drainage equations described below shows that there are several time regimes in free drainage, each leading to a different drainage rate. This appears to be the reason why Bikerman quotes no less than five different equations that supposedly govern free drainage.

A controlled *forced* drainage experiment was first described by Leonard and Lemlich and consists of injecting surfactant solution at a constant rate into a dry foam (Leonard and Lemlich, 1965). This results in a rather sharp interface between wet and dry foam moving down-

wards with a constant velocity (figure 5), an observation which surprisingly was not noted by Leonard and Lemlich and only reported in 1993 (Weaire et al., 1993). The velocity υ of this solitary wave scales with the flow rate of added solution Q in the form of a power law, $\upsilon \sim Q^{\beta}$. Two regimes have been identified, corresponding to the opposite limits of zero and infinite surfactant surface viscosity: these correspond to β= *1/3, 1/2,* respectively. Many common foams confirm roughly to one or the other power law.

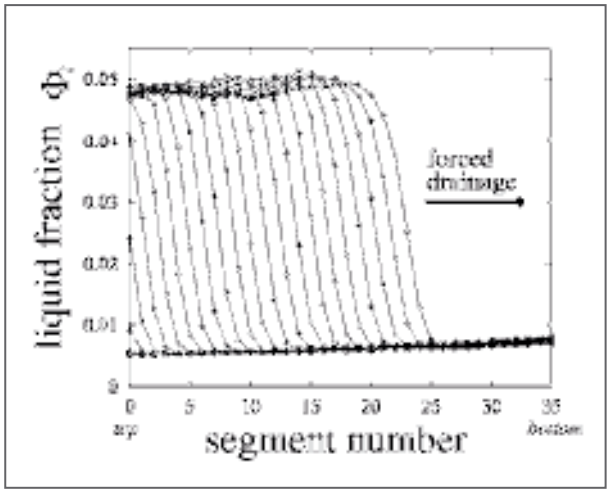

Figure 6: Experimental data for the propagation of a drainage wave through a foam. The vertical profiles of liquid fraction were obtained using segmented electrodes and monitoring electrical capacitance.

Since dry foam is transparent and wet foam is opaque due to diffusive light scattering the motion of the interface can generally easily be observed by eye. Measurements of optical transmission are relatively simple and require only a CCD camera, a diffusive white light source and image analysis software. Alternatively, local electrical properties of the foam can be monitored. For this purpose a foam cell is fitted with an array of regularly spaced electrodes and the local electrical conductivity or capacity is measured. All of these measurements can be calibrated to give the variation of liquid fraction with vertical position and time, $\Phi(x,t)$ (figure 6).

Foam drainage equation

In the now prevailing theory of foam drainage, based on a dry foam model but in practise successful up to moderate liquid fractions, liquid flows through a network of Plateau borders and their junctions. The contribution of the thin films is neglected. The cross section of borders and the size of nodes, which are a measure of liquid fraction, are not fixed, but are adapted to the flow rate of liquid. It is this feature of foam drainage that leads to the possibility of a solitary wave, as described above.

Of great importance is the treatment of the boundary conditions for the flow. Two extreme cases are readily accessible to theory. Rigid interfaces lead to zero flow at the liquid-gas interfaces and corresponds to Poiseuille flow, i.e. an essentially parabolic profile of flow velocity (Weaire *et al*., 1997). Fully mobile interfaces result in plug-flow, i.e. uniform flow velocity across a Plateau border. In this case dissipation takes place only in the nodes, where incoming liquid is redirected into three different directions (Koehler *et al*., 1999).

Both flow situations can be captured in one drainage equation. Here we give its one-dimensional formulation (Koehler *et al*., 2000), which is sufficient to describe most forced drainage experiments where one is generally only interested in the *vertical* variation of liquid fraction with time, in a cylindrical column.

$$\frac{\partial \alpha}{\partial \tau} = \frac{\partial}{\partial \xi}\left(\frac{1}{2k+1} \frac{\partial \alpha^{k+1/2}}{\partial \xi} - \alpha^{k+1} \right)$$

In this non-linear partial differential equation ζ and τ are (non-dimensionalised) vertical position and time, α is proportional to the liquid fraction and the value of κ specifies the type of flow. Plateau border or channel dominated Poiseuille flow corresponds to $\kappa=1$, node dominated plug flow corresponds to $\kappa=1/2$.

For forced drainage the solution of the drainage equation is given by a solitary wave profile, in excellent agreement with experimental data (figure 6). The wave propagates downwards through the foam with velocity $v \sim Q^{\beta}$ where $\beta = 1/2$ for Poiseuille flow and $\beta = 1/3$ for plug flow. All experimentally obtained values for β are bracketed by these theoretical limits, and most are close to them.

The foam drainage equation is, however, not restricted to modelling forced drainage. With a choice of appropriate mathematical boundary conditions, solutions for the case of free drainage can be obtained (Verbist et al., 1996). These successfully predict the rate of drained liquid as as a function of time and also the asymptotic equilibrium profile of liquid fraction (figure 7) (Cox et al. 2000).

In its two-dimensional formulation the drainage equation models liquid which not only propagates vertically through the foam but also horizontally (figure 8). This can be experimentally realised by containing the foam in wide Hele-Shaw cells and adding surfactant solution only at a narrow input (Hutzler *et al.* 2005). The horizontal spreading is due to *capillarity*, which is also the main driving factor of foam drainage under conditions of microgravity (Caps *et al*., 2005)[2].

[2] The word capillarity is often used rather vaguely in this subject. It can be taken to mean the local variation of liquid pressure (and its consequences): this is linked to surface geometry by the Young-Laplace equation, whenever the surface is in equilibrium.

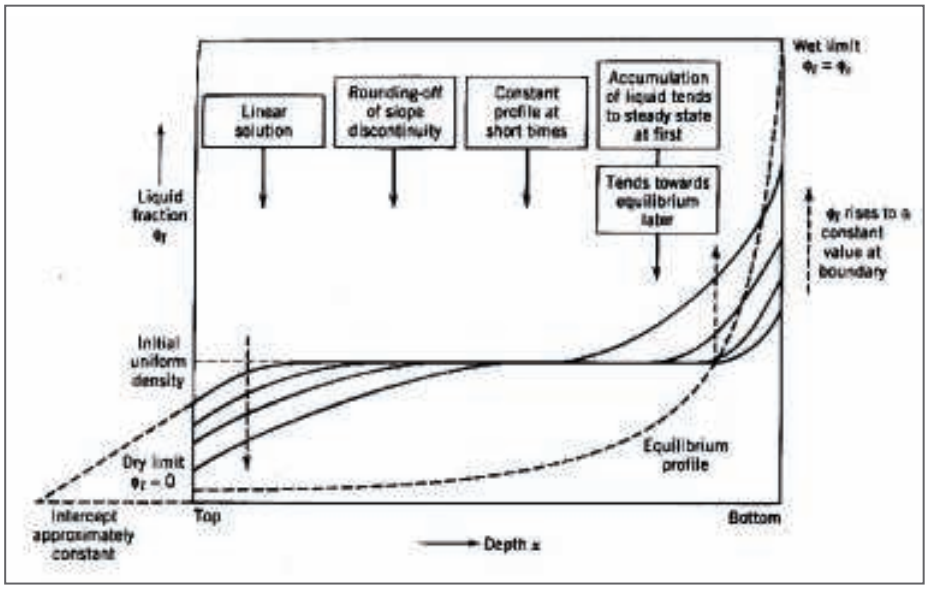

Figure 7: Free drainage of an initially uniformly wet foam proceeds in a very complex manner. Theory enables us to distinguish several regimes before an equilibrium state is reached.

Figure 8: In a two-dimensional drainage experiment the drainage wave spreads in both vertical and horizontal directions. Here food volouring was added to the surfactant solution. Values of local liquid fraction can be obtained from digitized images and an appropriate calibration procedure.

Remaining Challenges

Despite the success of the above drainage theory, which qualitatively describes a wide variety of drainage experiments, challenges remain concerning detailed comparisons, and wet foams.

The theory was developed for low values of liquid fraction, Φ less than about *0.05*, in terms of the assumption of a network of Plateau borders. For higher values of Φ the nodes begin to swell and need to be taken into account even when the flow is of the Poiseuille type, as the relative contribution of dissipation in the junction increases. The need for a combination of both channel and node dominated drainage is evident from the fact that realistic boundary conditions for the flow at the liquid-gas interface are always somewhere between no-slip (Poiseuille flow) and full-slip (plug flow). In this case the dissipation in the nodes cannot be neglected even for low values of Φ. Such a combined drainage model can be achieved by treating channels and nodes as distinct elements with individual hydrodynamic flow resistances which are mounted in series (Stone *et al*. 2003, Saint-Jalmes *et al*. 2004).

In order to account for finite interface velocities one may introduce the dimensionless mobility parameter $M=\eta r/\eta_s$, where r is the radius of curvature of a Plateau border, η is the liquid bulk and η_s the surface viscosity. Since a surfactant stabilised surface is highly viscoelastic, this is not the only possible choice to characterise its resistance to shear, although it is supported by recent experimental work (Saint-Jalmes *et al*. 2004).

The flow through a single Plateau border for a range of values of M was already studied computationally by Lemlich in the 1960s. Results for a similar computation for a node are only now beginning to emerge (figure 9). The difficulty in obtaining these is due to the complicated shape of the node, which requires sophisticated interfacing of various types of software.

Experimental studies encounter similar difficulties when addressing the flow in nodes. For the Plateau borders the experimental determination of velocity profiles employs confocal microscopy using tracer particles. This leads to a clear distinction between plug and Poiseuille flow for surfactant and protein stabilised foams, respectively (Koehler *et al*. 2004).

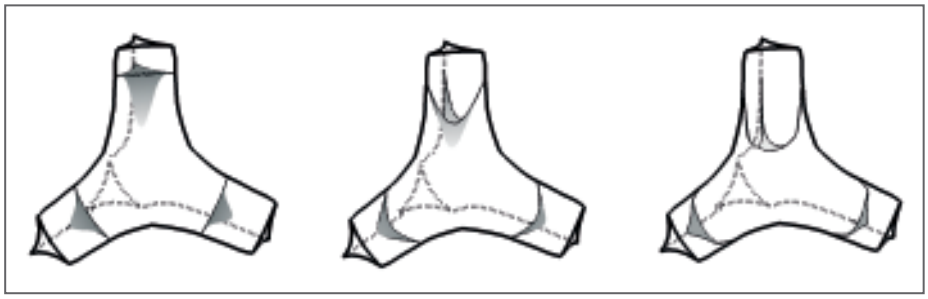

Figure 9: Simulations of the flow through nodes. Shown are flow velocity profiles for the two extreme cases of Poiseuille flow, $M=0$ (left) and plug flow, $M= \infty$ (right). A computation for a finite value of M, as in actual surfactants, is shown in the middle.

Quantitative predictions of drainage theory are currently available only in the limit of low liquid fractions and pure Poiseuille flow *(M=0)*, realised to a good approximation for example in protein foams or water silicone-oil emulsions. It is generally found that theory underestimates the speed of the drainage wave as a function of flow rate Q by a factor of about 2. Various effects may be responsible for this deviation, they include for example the role of Plateau borders and junctions at the container walls.

Saint-Jalmes *et al*. (2004) take an alternative approach of dealing with the numerical discrepancy of the pure Poiseuille flow model. They use their combined drainage model (channel *and* node flow) to obtain mobility parameters M for various surfactant and protein solutions from measurements of forced drainage waves. The corresponding values for surface viscosities are consistent with published data. In addition to this the drainage experiments were used to find an estimate for the flow resistance of a node data which compares well with theoretical expectations.

Disagreement with the combined drainage model appears for very small bubbles with diameter less than about 0.5 mm (Durand and Langevin, 2002, Saint-Jalmes *et al*. 2004). Carrier *et al*. (2002) attribute this to the contribution of drainage in films, since the liquid fraction due to the finite film thickness (*about 2 μm*) is about $\Phi_{film} \approx 0.004$, and thus no longer negligible compared to the liquid fraction due to the Plateau borders.

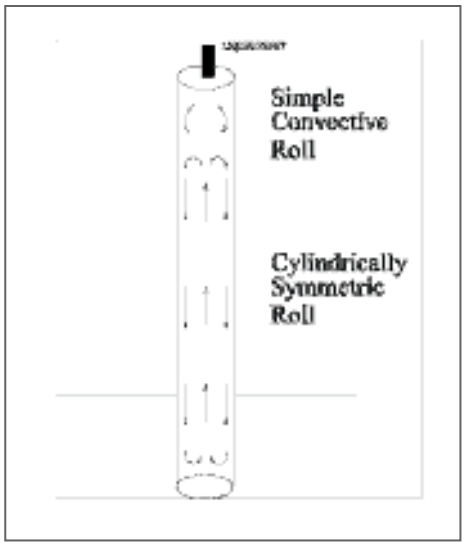

Figure 10: Once a critical flow rate is exceeded in a forced drainage experiment, bubbles take part in various types of convective motion.

Probably the most significant theoretical challenge posed by foam drainage is the occurrence of convective bubble motion, once a critical flow rate has been exceeded (Hutzler *et al*. 1998, Vera *et al*. 2000). This convection can take on various forms, including a cylindrically symmetric roll and is also prone to hysteresis (figure 10). An explanation of this phenomenon requires a coupling of the drainage equation to foam rheology, i.e. the study of the viscoelastic character of foam. Only a modified form of the experiment, where the column of foam is tilted against the vertical, has so far been accessible to theory (Cox *et al*. 2005). Of potential industrial relevance is the related effect of size sorting of bubbles (Hutzler *et al*., 2000). This occurs for sufficiently large flow rates in forced drainage experiments performed on polydisperse foams, where the largest bubbles rise to the top while the smalles bubbles migrate to the bottom.

Flow instabilities are also found in experiments using emulsions. However, these are not of a convective nature and may be associated with the transition of the emulsion to a bubbly liquid at high enough flow rates (Hutzler *et al*. 2004).

ACKNOWLEDGEMENTS

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REFERENCES

Bikerman, J.J., 1953, »Foams: Theory and Industrial Applications«, Reinhold Publishing Corporation, New York (also Springer, New York, 1973).

Brakke, K., 1992, »The Surface Evolver«, *Experimental Mathematics* **1**, 141-165.

Caps H., Cox S.J., Decauwer H., Weaire D. and Vandewalle N., 2005, »Capillary rise in foams under microgravity«, Colloids and Surfaces A: *Physicochemical Engineering Aspects* **261**, 131-134.

Carrier V., Destouesse S. and Colin A., 2002, »Foam drainage: A film contribution?«, *Physical Review E* **65**, 061401 (9 pages).

Cox S.J., Alonso, M.D., Weaire D. and Hutzler S., 2005, »Drainage induced convection rolls in foams I: Convective bubble motion in a tilted tube«, *in preparation*.

Cox S.J., Weaire D., Hutzler S., Murphy J., Phelan R. and Verbist G., 2000, »Applications and generalizations of the foam drainage equation«, *Proceedings of the Royal Society of London Series A: Mathematical, Physical and Engineering Sciences* **456**, 2441-2464.

Drenckhan W., Cox S.J., Delaney G., Holste H., Weaire D. and Kern N., 2005, »Rheology of ordered foams – on the way to Discrete Microfluidics«, *Colloids and Surfaces A: Physicochemical Engineering Aspects* **263**, 52-64.

Durand M. and Langevin D., 2002, »Physicochemical approach to the theory of foam drainage«, *European Physical Journal E* **7**, 35-44.

Hutzler S., Cox S.J. and Wang G., 2005, »Foam drainage in two dimensions«, *Colloids and Surfaces A: Physicochemical Engineering Aspects* **263**, 178-183.

Hutzler S., Péron N., Weaire D. and Drenckhan W., 2004, »The foam/emulsion analogy in structure and drainage«, *European Physical Journal. E* **14**, 381-386.

Hutzler S., Weaire D. and Shah S., 2000, »Bubble sorting in a foam under forced drainage«, *Philosophical Magazine Letters* **80**, 41-48.

Hutzler S., Weaire D., and Crawford R., 1998, »Convective instability in foam drainage«, *Europhysics Letters* **41**, 461-465.

Koehler S. A., Hilgenfeldt S., Weeks E.R. and Stone H.A., 2004, »Foam drainage on the microscale. II. Imaging flow through single Plateau borders«, *Journal of Colloid and Interface Science* **276**, 439-449.

Koehler S. A., Hilgenfeldt S., Stone H.A., 2000, »A generalized view of foam drainage: experiment and theory«, *Langmuir* **16**, 6327-6341.

Koehler S. A., Hilgenfeldt S., Stone H.A., 1999, »Liquid flow through aqueous foams: the node dominated drainage equation«, *Physical Review Letters* **82**, 4232-4235.

Leonard R. A. and Lemlich R., 1965, »A study of interstitial liquid flow in foam. I. Theoretical model and application to foam fractionation«, *American Institute of Chemical Engineers Journal,* **11**, 18-25.

Leonard R. A. and Lemlich R., 1965, »Experimental verifications and observations«, *American Institute of Chemical Engineers Journal* **11**, 25-29.

Saint-Jalmes A., Zhang Y., Langevin D., 2004, »Quantitative description of foam drainage: transitions with surface mobility«, *European Physical Journal E* **15**, 53-60.

Stone H.A., Koehler S.A., Hilgenfeldt S. and Durand J., 2003, »Perspectives on foam drainage and the influence of interfacial rheology«, *Journal of Physics: Condensed Matter* **15**, S283-S290.

Vera M.U., Saint-Jalmes A. and Durian D.J., 2000, »Instabilities in a liquid-fluidized bed of gas bubbles«, *Physical Review Letters* **84**, 3001-3004.

Verbist G., Weaire D. and Kraynik A.M., 1996, »The foam drainage equation«, *Journal of Physics: Condensed Matter* **8**, 3715-3731.

Weaire D. and Hutzler S., 1999, »The physics of foams«.
(Oxford: Oxford University Press).

Weaire D. (ed.), 1997, »The Kelvin Problem«, UK, Taylor and Francis.

Weaire D., Hutzler S., Verbist G. and Peters E., 1997, »A review of foam drainage«, *Advances in Chemical Physics* **102**, 315-374.

Weaire D., Pittet N., Hutzler S. and Pardal N., 1993, »Steady state drainage of an aqueous foam«, *Physical Review Letters* **71**, 2670-2673.

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