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The Rheology of Foams

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Abstract We review recent progress concerning an understanding of the rheological properties of foams, both in bulk form and confined in narrow channels, and including the problem of foam sliding along a solid wall. Our calculations contribute not only to the interpretation of rheological data, but also to the coupling of foam drainage and rheology.

Keywords Rheology · Foams · Complex fluids · Dilatancy

Introduction

Much of the usefulness and appeal of liquid foams lies in their rheological properties. They combine the properties of an elastic solid at low stress with those of a liquid when the yield stress is exceeded [1]. It is this that makes shaving easy.

There is no mystery in their dual nature. Above the yield stress, rearrangements of bubbles become possible – or *topological changes*, in the language preferred for relatively dry foams.

Many other substances behave in much the same way, yet this side of the general theory of rheology seems curiously neglected in favour of viscoelastic materials. In getting to grips with foam rheology we have been hampered by this lack of an adequate theoretical background.

In the present paper we review some of the faltering attempts to overcome this difficulty¹. In addition to surveying bulk rheology we shall report recent progress on confined foam structures, and the problem of slip at a wall – the so-called Bretherton problem.

¹ An excellent collection of recent papers on foam rheology can be found in *Colloids and Surfaces A: Physicochem. Eng. Aspects*, **263**, August 2005.

Structure and Properties

The equilibrium structure that undergoes rearrangement under high stress is surely one of the most beautiful in nature (Fig. 1), a thicket of thin films conspiring to meet everywhere in the manner prescribed by the rules of Plateau, with surface tension in balance with pressure differences across each film. Most basic theories of foam proper-

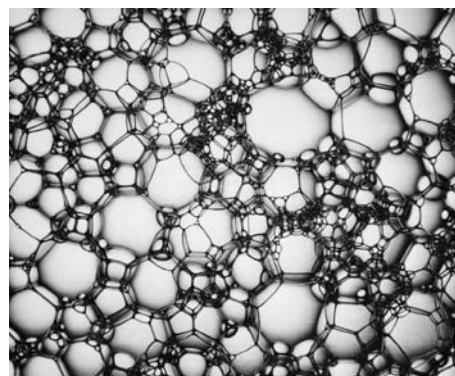


Fig. 1 An aqueous foam as seen by the photographer Michael Boran

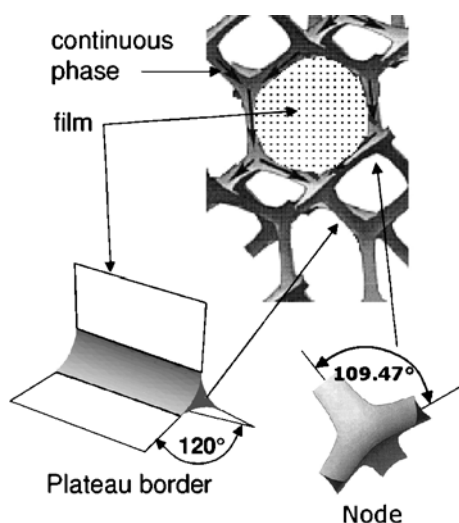


Fig. 2 The structure and geometry of dry foam was first described by the 19th century scientist Joseph Plateau [1]

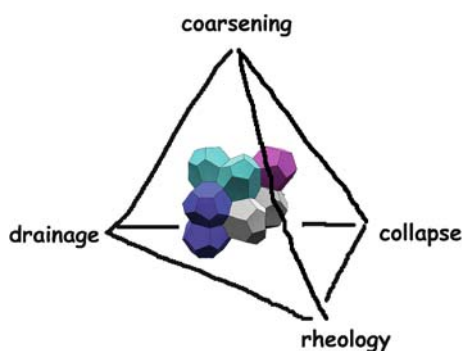


Fig. 3 The properties of a foam are interdependent and linked to its structure

ties find their way back to some aspect of that structure (Fig. 2).

Four main dynamic properties may be identified. *Drainage* is the transport of liquid through the foam, *rheology* is the description of the response to stress, *coarsening* is the gradual growth of average bubble size (and progressive elimination of bubbles) by gas diffusion through the films, and *collapse* is the eventual fate of most foams, as films rupture. In practice they are often interdependent. For example, drainage may be the precursor of collapse, and slow creep below the yield stress may be attributable to the gradual change of structure associated with coarsening (Fig. 3).

Foam Flows

This heading is the title of an excellent review by A. Kraynik [2] in which he stressed from the outset the importance of the ratio of average bubble diameter d to the characteristic length scale L of the vessel that contains the foam. A *microflow* regime ($d \approx L$), may be found in foam flow in

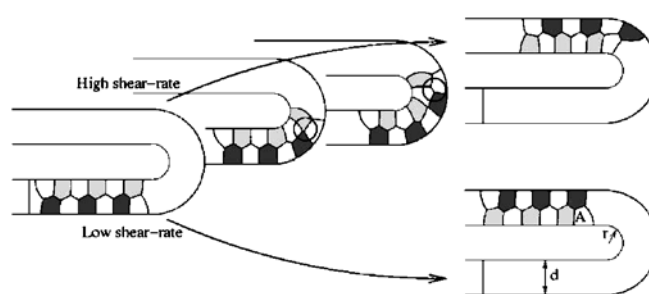


Fig. 4 Viscous froth simulation of a 2D ordered foam flowing around a U-bend. As seen in experiments, at a sufficiently high velocity the bubbles successively change neighbours [4]

a porous medium, but also in the recent area that has been called “Discrete Microfluidics” [3]. In the latter, individual bubbles are pushed through a network of specifically designed channels with the aim of controlled transport and manipulation of small amounts of gases (or liquids, in the analogous case of emulsions). An example is shown in Fig. 4. Relevant experiments pose a variety of questions concerning the detailed local mechanism of bubble transport, and relate to the Bretherton problem, as described below.

A continuum description of bulk foam is valid for $d/L \ll 1$. Such *macroflow* is challenging to theory, partly due to the non-linearity of the constitutive flow equations. Above the yield stress, S_y (which depends non-linearly on the liquid fraction of the foam), the shear stress S may be described by the *Herschel–Bulkley relation* as

$$S = S_y + \eta_p \dot{\epsilon}^m,$$

where $\dot{\epsilon}$ is the strain rate, and η_p is some asymptotic plastic viscosity (at high strain rate), also called foam consistency. In the *Bingham model* the exponent $m = 1$, but in the absence of convincing experimental data this is only one possible choice. The corresponding decrease of effective viscosity ($S/\dot{\epsilon}$) with strain rate is often called shear thinning [1].

However, the above equation is of limited applicability, if any. It may be appropriate for such cases as the continuous application of a positive shear rate, but there is hysteresis upon its reversal. Various attempts are underway to encapsulate such *history dependence* in a workable formulation. If the goal of our research is to find a continuum description, it faces this obstacle, which may well be the root cause of the deficiency in adequate treatments of rheology for yield stress materials, lamented above. So long as it is not overcome, a simulation (whether realistic or simplified) capturing all the local dynamics of the thin films is the more practical approach in many cases.

Dilatancy

Dilatancy traditionally describes the expansion of a dense packing of granular material when sheared [5] and was

first described by Osborne Reynolds in 1885 [6]. In 2003 quasi-static computer simulations were reported which feature the same effect in liquid foams [7]. Its possible importance was suggested by the late pioneer of foam rheology, Henry Princen, in 1989 [8]. In foams, dilatancy constitutes the local increase of liquid fraction due to shear. Experimental evidence is still sparse. Marze et al. [9] designed an experiment where a foam is continuously locally sheared. Observations and measurements of local electrical conductivity (which increases with liquid fraction) show that the sheared region is wetter. This is attributed to *dynamic* dilatancy, i.e. a shear-rate dependent effect which differs from the static dilatancy described by current theory [7, 10], and is less easily calculated (see however our discussion of the Bretherton problem below).

Real Foams

Foams are usually polydisperse and disordered. Around the time of Kraynik's review, it began to be possible to simulate reasonably large (static) samples of disordered

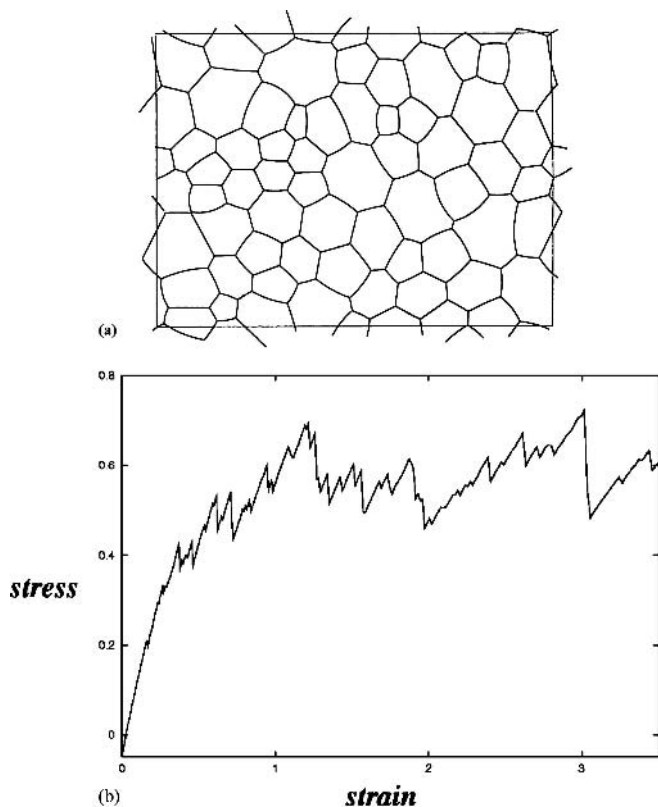


Fig. 5 (a) Early computer simulation of a two dimensional liquid foam [11] which can be used for the computation of a stress–strain curve as shown in (b) [12]. The slope of the initially linear variation of stress with strain is proportional to the shear modulus of the foam. In large bulk sample the jagged curve is smoothed out

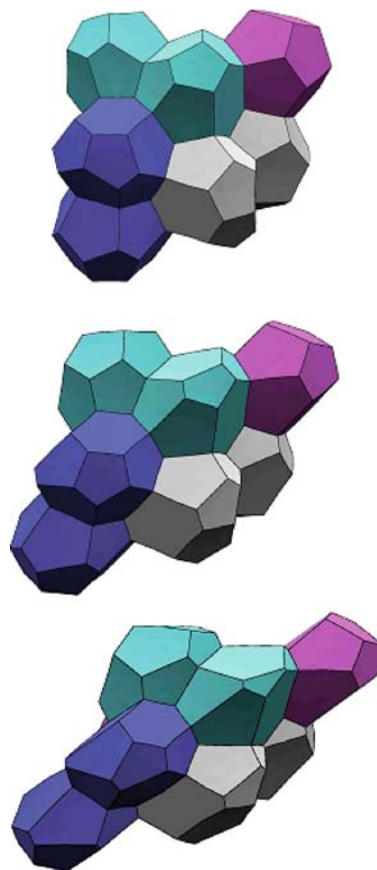


Fig. 6 The structure of three dimensional foams is conveniently computed using the Surface Evolver software of Ken Brakke [14] (free download at <http://www.susqu.edu/brakke/>). Here we show a simulation of the shearing of a Weaire–Phelan foam [13]. (Reproduced with kind permission of A.M. Kraynik)

foam, if only in two dimensions [11], and to compute stress/strain curves [12] (Fig. 5), and hence shear modulus and yield stress.

In some ways, such a disordered system is much simpler than the ideal ordered one: for example the yield stress is not dependent on orientation. The shear elastic modulus is close to that of the honeycomb structure with the same mean cell area.

Nowadays similar calculations are pursued for 3d foams [13] as illustrated in Fig. 6, so we have a good appreciation of many quasi-static properties in both cases. There is good general agreement with experiment.

Experiments

We have not paid enough attention to experiment up to this point. There exists a plethora of rheological measurements in foams, with a variety of rheometers, pipes with and without constrictions etc. Mostly this has drawn on

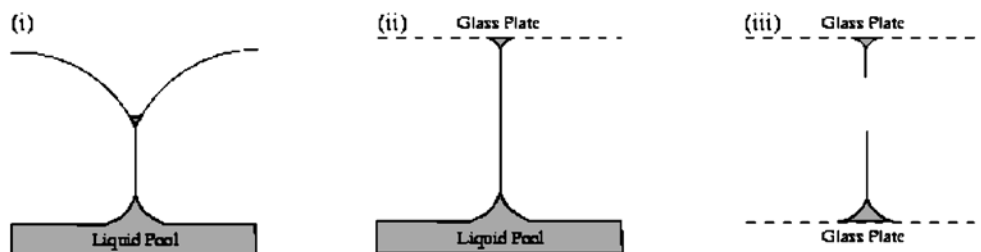


Fig. 7 Three different set-ups used for experiments with so-called two-dimensional foam. (i) Bragg raft, (ii) bubbles between a liquid pool and a glass-plate, (iii) bubbles trapped between two glass plates [19]

strong practical motivations in the field of chemical engineering: the consequent spirit of empiricism has not been very fruitful. Hence, as a greater interest in basic understanding developed in recent years, several groups have resorted to a familiar tactic of the foam physicist: a retreat into two dimensions. The shearing of a 2d foam sample can be viewed and imaged directly, recorded by video, and analysed in complete detail, in addition to relating the applied stress to the shear rate [15].

Such experiments have included the 2d equivalent of a Couette viscometer [16], as well as flow around obstacles [17] and through constrictions [18]. The recorded results have revealed some surprises and are still being digested.

There are qualitative disagreements between some of the experiments, which may be due to the use of different kinds of 2d foam. There are at least three kinds, depending on whether the bubbles are trapped between two plates, one plate and underlying liquid, or just floating on the liquid (Fig. 7) [19].

Simulations

If such experiments are to be simulated beyond the quasi-static approximation, we require the inclusion of dissipative forces. In an attempt to do this, we have developed the ideal *2d viscous froth model* [20]. In this the normal motion of each line (representing a film) is opposed by a drag force proportional to velocity. As will be explained below, this simple linear relation is usually not correct, but it has served to simplify the computational algorithm used in an initial search for qualitative understanding. It also has the merit of forming a bridge between foams and the curvature-driven boundary problems which are standard in the description of grain boundary motion [21].

Such understanding can only be transferred to 3d in the most general, qualitative way. The origin of viscous drag in that case must be completely different. It was considered long ago by Kravynik and others [2, 22, 23] but is still a region of uncharted waters.

One of the first specific applications of the 2d model concerned the flow of an ordered foam structure around a narrow bend as part of a feasibility study of discrete mi-

crofluidics [20]. The computer simulations successfully reproduced the experimentally observed swapping of neighbours of bubbles once a certain flow velocity is exceeded; see Fig. 4. Whereas it was initially thought that quasi-static simulations would be a sufficient guide for the design of components for the use in discrete microfluidics, we have found that there are large velocity-dependent effects, as illustrated by this case.

To date, a variety of standard rheological experiments, such as Couette shear (Fig. 8), creep (due to coarsening) or constant stress experiments have become accessible to similar modelling [24].

Our intention in introducing the viscous froth model has been to explore it exhaustively in a search for qualitative understanding of the role of dissipative effects. Its dir-

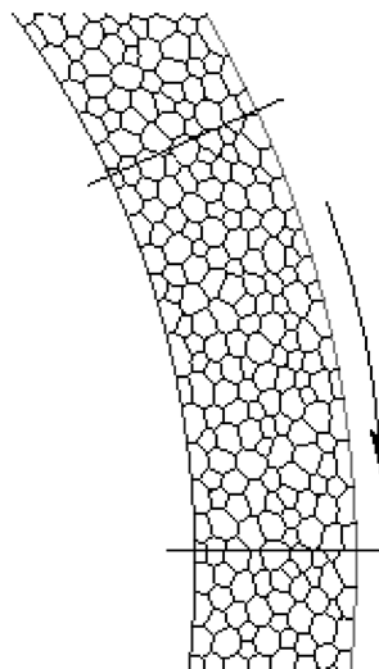


Fig. 8 Viscous froth simulation of a Couette shear experiment in which the outer boundary (with its contacting vertices) is moved clockwise, while the inner boundary (and its associated vertices) remains fixed. The *solid lines* demarcate the region used in the actual computation [24]

ect relevance to any particular system is questionable since other kinds of dissipative forces may well enter. Indeed Durand and Stone [25] have performed experiments with simple 2d configurations, accurately measuring their relaxation to equilibrium, and found rather different behaviour in some cases. Whenever a T1 change was produced the initial displacement of the vertices scaled linearly with time rather than with the square root which is the implication of the viscous froth model.

Moreover, the present viscous froth model is confined to the simulation of dynamic effects in dry foams. A recently developed lattice-gas based model allows for the simulation of foams over the entire range of liquid fraction [26]. It was applied to the flow of foam past an obstacle with the aim of determining the scale of the resulting bubble rearrangements [27]. Although this is a dynamic model, its representation of viscosity is inherently undetermined in lattice-gas models.

Weaire et al. [30] have recently formulated an elementary continuum model which can account for the localisation in the experiment of Debregeas et al. [16]. It combines the elements of the Bingham model with a viscous drag term associated with the two plates; the localisation length is given by the square root of ratio of the coefficients of Bingham viscosity and viscous drag.

The Bretherton Problem

One important source of drag in the 2d case is a wall effect. Whenever a foam slides along a wall, as in two of the 2d foams shown in Fig. 5, it is opposed by a dissipative force that depends on its velocity, which we had in mind in framing the viscous froth model.

It arises in 3d foam rheology as well, wherever there are walls. It is also a key factor in the motion of bubbles in channels (Fig. 4), in the context of the kind of microfluidics mentioned above.

In a classic paper [22], Bretherton concluded that the wall stress due to the frictional force of a single bubble rising in a tube scales as $\tau_w \propto (Ca)^{2/3}$, where the capillary number Ca is given by $Ca = \eta V / \gamma$ (for many purposes it represents velocity). Here η is the liquid viscosity, γ is the surface tension and V is the relative velocity of the bubble with respect to the wall. Naively, the power-law index for this viscous effect might be expected to be unity: it is the presence of free surfaces in the system and their variation with velocity that lies behind this non-trivial result.

This result has been found to apply to other situations that involve wall slip. Further afield, but still highly relevant here, is the relationship found for tension and rate of extension for the pulling of a film out of a Plateau border.

Bretherton's result was derived for a model in which the surfaces are mobile (that is, have zero surface viscosity). Denkov pursued the same approximations for immobile surfaces and found the exponent 1/2 in this case [28].

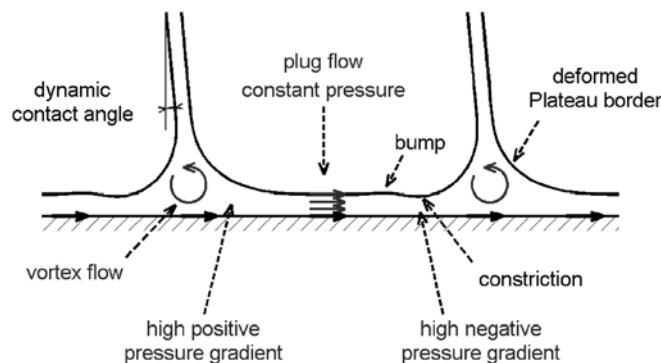


Fig. 9 Schematic of the key features of foam flow along a wall

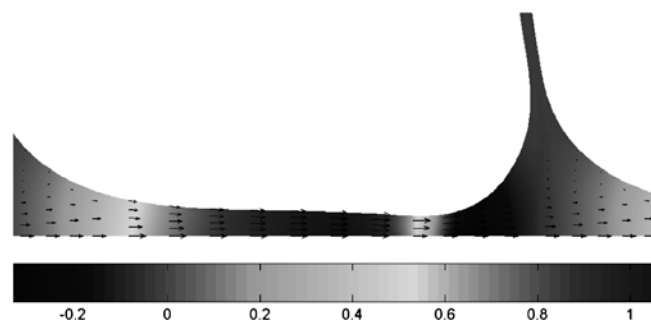


Fig. 10 Computed velocity profile and pressure fields for the flow of a foam along a wall

All of this has been based on analytic approximations for the flow in the thin film which adjoins the wall. It is the variation of the thickness of this film with velocity that is the root cause of the surprising nonlinear relationships that have been found in the above theories (and confirmed to a large degree by experiment).

We have recently succeeded in setting up a complete 2d simulation of the Bretherton problem, including the free surfaces which lie at its heart [29]. This exposes the full details of flow and the associated dissipation. At low velocities, Bretherton's semi-analytic result was confirmed. The simulation will be helpful in understanding the previous work and extending it to other situations.

Figure 9 illustrates the essential features of these calculations, and Fig. 10 is a detailed example. These calculations corroborate all of Bretherton's findings. In the case of wholly or partially immobile surfaces, there are difficulties in developing a 2d model. Pursuing the same line as Denkov, the same result was found. However, the role of surface stresses has yet to be incorporated.

Conclusions

Foams can provide a prototype for all those complex fluids that exhibit a yield stress. For that reason, as well as their intrinsic interest and applications, the rheological proper-

ties of foams are likely to be assiduously pursued in the years to come. It will take some time to reach the same competence that we enjoy in relation to static properties, but that end is almost in sight. Systematic and disciplined simulations offer a way forward.

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