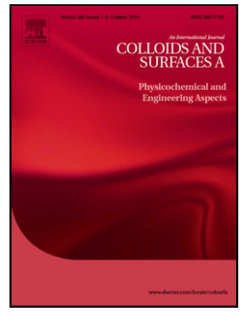

Title: The mechanics of liquid foams: history and new developments

Authors: S. Hutzler, D. Weaire

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The mechanics of liquid foams: history and new developments

S. Hutzler[1] and D Weaire
School of Physics
Trinity College Dublin
Dublin 2
Ireland

Abstract

The story of some recent developments in foam rheology is related at key points to the remarkable early contributions of Henry Princen, who pioneered the rigorous modern development of the subject. His general approach of introducing tractable geometrical models for foam structure and linking them to physicochemical properties at a smaller scale is still valid. It has however been amended to include the effects of disorder which are essential to the understanding of some properties, such as the variation of elastic modulus and yield stress with liquid fraction. Recent interest in foam rheology concerned the effect of shear localization in 2D foams, as was definitively demonstrated in 2001. This remains a challenge to theory, although continuum models have proved to be tractable and transparent, and have enjoyed some success.

1. Introduction

Just outside our laboratory, a bridge spanning a river of congested vehicular traffic carried for some years an advertisement, aimed at the frustrated motorists below. It showed the swirling bubbles of a pint of Guinness, with the taunting message:

IF ONLY EVERYTHING FLOWED SO FREELY.

[1]email:stefan.hutzler@tcd.ie

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But the contemplative drinker observes that the bubbles gathering in the head of a beer eventually form a more or less *solid* mass. The contemplative physicist decides that this foam is a *complex fluid*, with dual solid/liquid properties.

Here we review progress in capturing some of the subtleties of foam rheology, including some of the achievements of several contemporary groups, in addition to our own.

In tracing the origins of this progress we have been repeatedly impressed by the seminal role of Henry Princen, an industrial and industrious researcher who died in 2004. (An obituary was published in the EUFOAM 2004 Proceedings in *Colloids and Surfaces A: Physicochem. Eng. Aspects* [1].)

Nobody did more than Henry Princen to bring the whole subject of foam physics (equilibrium, drainage, mechanics, rheology, film permeability ...) out of the mire of mere empiricism and put it on a sound scientific footing. He was not always well appreciated and he deserves to be well remembered. We will weave into this review some mention of his precise and prescient contributions.

2. Wet and dry foams

In the late 1970s Princen developed simple two-dimensional (2d) models of foam, in order to clarify the role of liquid fraction and what he called *osmotic pressure* [2], adapting this term from physical chemistry. Not much experimentation has been done on this quantity: but see the recent measurements of Höhler *et al.* for monodisperse ordered foams [3].

In 1980 (perhaps to be considered the date of initiation of the present era of foam physics) Princen and co-workers (including his later wife A.D. Kiss) started a series of relevant experiments using oil-in-water emulsions. They chose this system rather than a foam for the following “practical reasons” [4]: increased stability of emulsions with respect to coarsening, reduced drainage due to smaller density difference of the two phases, and smaller drop size, leading to larger values for the yield stress.

The initial experiments concerned the volume fraction ϕ of the dispersed phase (analogous to gas fraction in a foam) of an *uncompressed* emulsion (corresponding to drops that are nearly spherical) which was found to take on values between 0.70 and 0.74. Princen then measured yield stress [5, 6] and shear modulus [7] as functions of ϕ. Both went smoothly to zero as ϕ was reduced to around 0.71 (see figure 1), a result that was not predicted by theory at the time.

Princen remarked much later [8] that the finite film thickness in his emulsions might lead to a significant downward correction to the measured values of ϕ. At the time of his initial measurements, however, he was not aware of the work of Bernal who in the 1950/60s had identified the value of $\phi \simeq 0.64$ for the packing fraction of disordered packings of equal volume hard spheres [9, 10, 11].

Princen's elementary 2d models had been ordered: he did not readily make the transition to thinking about the role of disorder, other than speculating that it was responsible for finding critical volume fractions that were less than the value of 0.7405 for an ordered close packing. Perhaps for this reason, his important findings were largely overlooked.

In fact, disorder is crucial to the understanding of the variation of elastic properties with gas fraction. The early simulations of Weaire and Kermode [14, 15] for dry foams (for an example computation see figure 2), and of Bolton and Weaire for wet foams quite a few years later [12], demonstrated this (see figure 1).

Today this variation is pursued to its limit in various investigations, both theoretical and experimental; see for example the review by van Hecke [16]. They are in particular addressed to the precise critical behaviour at the wet limit, where the foam falls apart. Physicists delight in such delicate critical phenomena, and this one has much in common with *jamming* phenomena in granular materials. Foam is proving to be an ideal model system for this purpose, avoiding many of the complications of real granular systems.

Engineers of the practical kind may fail to see the point of this somewhat arcane pursuit of singularities. However, if we return to a wider perspective

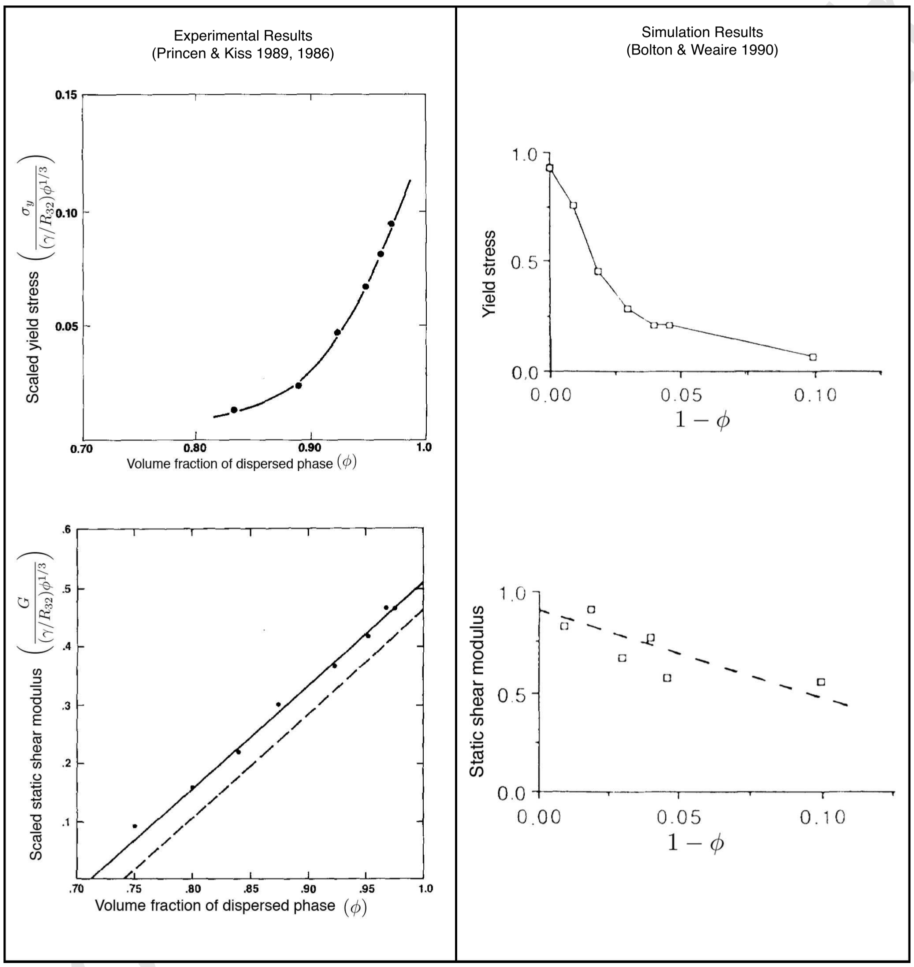

Figure 1: In experiments with emulsions Princen and Kiss found that both yield stress and shear modulus decrease smoothly to zero as a critical packing fraction is approached [5, 6, 7]. A few years later such a behaviour was also found in computer simulations of 2d wet foams by Bolton and Weaire who called it "rigidity loss transition" [12]. At the time of their publication these authors were not aware of Princen's experimental findings. (Princen's data is reproduced by permission of the Journal of Colloid and Interface Science.)

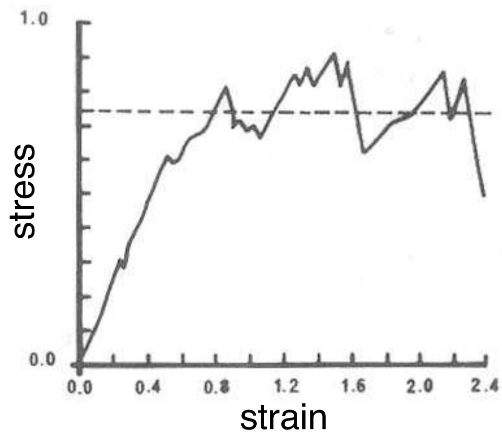

Figure 2: Example of an early computation of a stress-strain curve for a disordered dry 2d foam [13], obtained using the computer code by Weaire and Kermode[14, 15]. The yield stress is indicated by a dashed line. The fluctuations in stress are due to individual topological T1 events (whereby cells swap their neighbours as the foam flows due to shear) in this small sample (of not more than 100 bubbles).

of the overall variation of mechanical properties with ϕ, there is no doubting the practical importance of the subject introduced to us by Princen. This is especially so if we take it (as he did) a stage further, to consider the nature of the flow that results when the stress exceeds the yield stress.

3. Foam flows

Our section heading is the title of another seminal contribution, an early review by Kraynik [17] which contains some of Princen's work as well as his own. It suffered from the same deficiency that we identified above, being based entirely on models of *ordered* 2d foams. Nevertheless it raised questions that remain with us today: in particular, what are the local dissipative mechanisms that underlie the phenomena of foam flow?

The question is often posed in relation to the traditional Herschel-Bulkley constitutive relation

$$\sigma = \sigma_y + c_v \dot{\gamma}^a, \tag{1}$$

linking stress σ to yield stress σ_y and shear rate $\dot{\gamma}$, where the coefficient c_v is called consistency.

Incidentally, in the original 1926 paper by the National Bureau of Standards employees Herschel and Bulkley [18], which described the flow of benzol solutions of rubber, the authors consider the *inverse* of the above exponent a. They invented a "consistometer" but the term seems not to have enjoyed much currency.

What determines the value of the exponent a in the consistency term? It is often found to have a value around 0.5.

There are two schools of thought in current attempts to answer this question. The reconciliation of their assertions, with each other and with experiment, has not yet been reached.

Princen concluded his 1983 paper on a static model of foam elasticity and yield stress with the statement that in order "[...] to predict the dependence of shear stress on shear rate, a detailed understanding is required of the various dissipative processes involved"[19]. According to this approach the value of a is associated with the nonlinear dependence of local dissipative forces, such as those due to film stretching, upon rate of local deformation. Several different local sources of dissipation have been postulated; furthermore in each case the nature of the surfactant radically affects the relative importance of bulk and surface dissipation. Dating back to the work of Princen and his contemporaries [20, 21, 22], today this approach is most notably pursued in the group of Denkov (for a recent review see [23]).

But there is evidence that points us in an entirely different direction in the attempt to explain the value of a. It is found in simulations that do not contain any of the local nonlinearities to which we have referred. The value of a seems to arise in these cases from complex global dynamics, not yet elucidated. Our own simulations of this kind [24], using a variation of the simulation model developed by Durian [25], resulted in $a = 0.54 \pm 0.01$. The complexity of the dynamics is also evident in the experimental [26] and numerical [27] results of Möbius *et al.*, which suggest a nontrivial scaling of the relaxation time of the

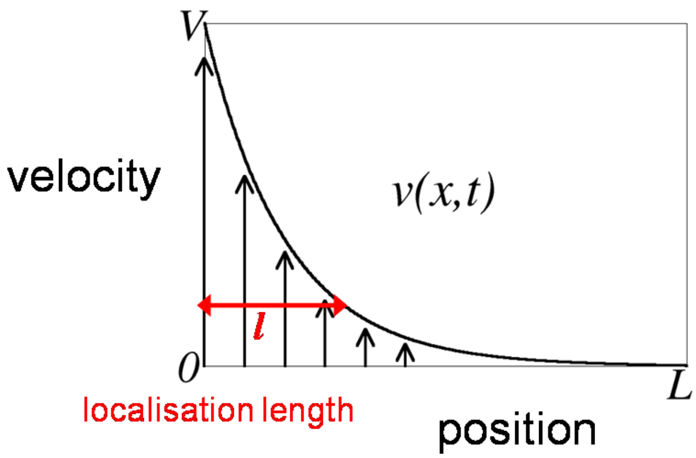

Figure 3: Sketch of a velocity profile, as obtained in a simple shear experiment of two-dimensional confined foams. The boundary at 0 is moving while the boundary at L is kept stationary. A variety of different definitions for a localization length l are in use [29].
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shear-induced diffusive bubble motion with the local shear rate.

4. Shear localization in 2d

The debate on the origins of the Herschel-Bulkley exponent intersects with another current theme of research, sparked off by the experiment of the Debrégeas group in 2001 [28].

Many experiments have now demonstrated what was seen in that key observation – the concentration of shearing motion near a moving boundary in a 2d foam, as illustrated in figure 3. One may express the results (with some choice of definition) in terms of a localization length, l. The localization length is generally found to depend on the boundary velocity, V, although this was not reported in the Debrégeas paper.

What is the source of this localization? Our own work has offered one possible answer, and there is plenty of experimental evidence (reviewed and summarised in [29]) that it provides us with at least an important factor, towards a more complete picture. It attributes localization primarily to the drag force exerted on the 2d foam by a confining plate. Indeed an *experimentum crucis* by the group of Dennin employs a sheared bubble raft both with and without confining top plate and finds *no* localization in the case where the top plate is removed [30].

The theory combines the Herschel-Bulkley relation, eqn.(1), with an equation for the drag force F (per unit area) as a function of the sliding velocity, v,

$$F = -c_d v^b, \tag{2}$$

where c_d is a constant.

Note in particular the two indices a and b in these generally nonlinear relations (1) and (2).

In due course we realised that an analytical formula for the localization length could be derived from the model [31]. Such a formula is often more convincing than obscure numerical calculations!

The formula gives the following velocity-dependence (if we set aside the (also known) coefficient):

$$l \propto V^{\frac{a-b}{1+a}}. \tag{3}$$

It is fully in accord with some of the experiments of the Leiden group [32], using $a = 0.36$ (fitted to their data) and $b = 0.67$ (independently determined).

This is highly satisfactory, but it was clear at the outset that it cannot be the whole story, because various quasistatic simulations [33, 34, 35] have found localization and they cannot, by their nature, include wall drag. The refinement outlined in the following section may be relevant to this paradox.

5. Refinement of the continuum model

The original formulation of this model makes no distinction between *yield* stress and *limit* stress, but we have known for a long time that there is a small difference between them, as is sketched (and slightly exaggerated) in Figure 4. A refinement can build in this complication, with interesting consequences.

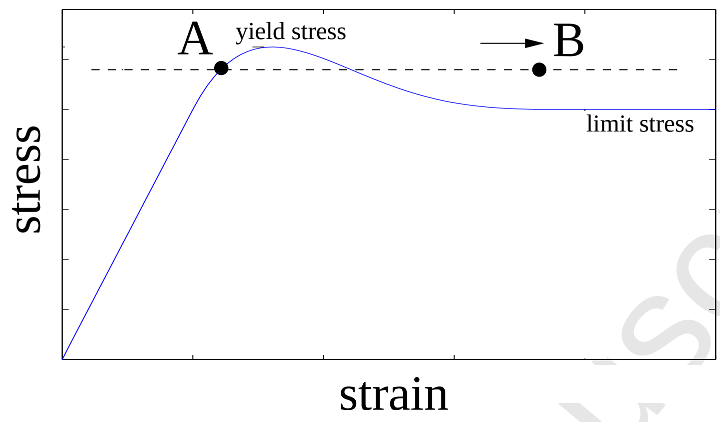

Figure 4: Sketch of stress-strain curve for a foam, featuring a small stress overshoot as strain is increased. There is a certain range of values of stress for which a *co-existence* of flowing (B) and static (A) regions of the foam is possible.

Even in the absence of wall drag, the foam can sustain a shear confined to a finite region (corresponding to the moving point B in Figure 4), while the remainder is static (point A). For B the stress is the limit stress plus the shear-rate-dependent term of the Herschel-Bulkley relation, which brings it into equality with that of A.

Note that such a solution can be envisaged for any stress that lies between yield and limit stress, giving localization of different extent according to the choice.

So what happens if we reformulate the continuum model to include this, in addition to the previously described ingredients?

We find that a *range* of solutions is possible, particularly at low values of the boundary velocity V, as shown in figure 5. This remains unconfirmed by experiment but is consistent with our computer simulations using the dynamic viscous froth model [36]. We cannot be sure whether some consideration of the stability of the solutions favours a particular choice in experiment. If this is not the case, the full range should be accessible for low V, by appropriate experiments, involving different histories (schedules of imposed V).

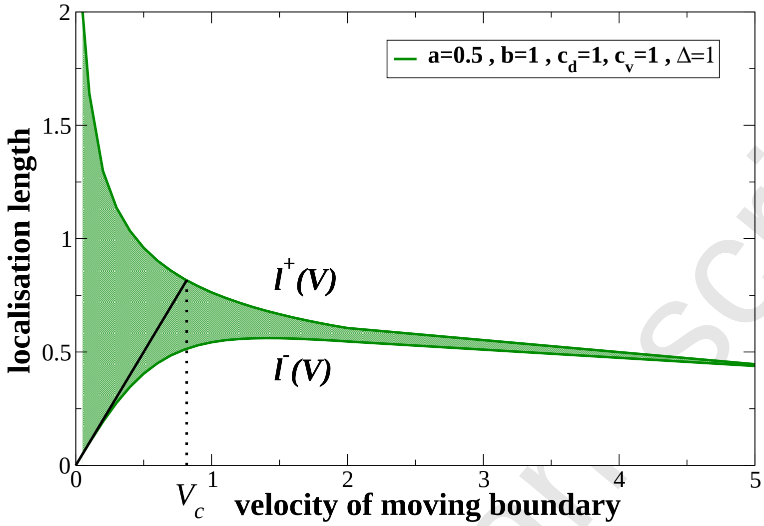

Figure 5: Example of predicted range of values for the localization length as a function of velocity V of the moving boundary in the case of distinct yield and limit stress, as sketched in figure 4 (arbitrary units, see [29]).

6. Another refinement

Quite recently, Goyon *et al.* have introduced a new dimension to foam rheology, which must bear on the continuum theory of localization [37]. Its motivation is best understood by considering the local processes of rearrangement (T1 processes) that underlie the shearing motion. These would appear to involve only a cluster of bubbles with a size of only a couple of bubble diameters. But T1 processes immediately trigger further ones in their vicinity, a few bubble diameters away. Goyon *et al.* therefore argue that this introduces nonlocal effects in rheology.

The formalism that incorporates this nonlocal effect may be applied to make allowance for it in the continuum theory (see figure 6). In preliminary calculations we have estimated the consequent increase in the localization length [38]. Recent localization experiments in the circular Couette geometry, carried out by the group of van Hecke in Leiden, also address this matter [39], and appear to vindicate the ideas of Goyon *et al.*

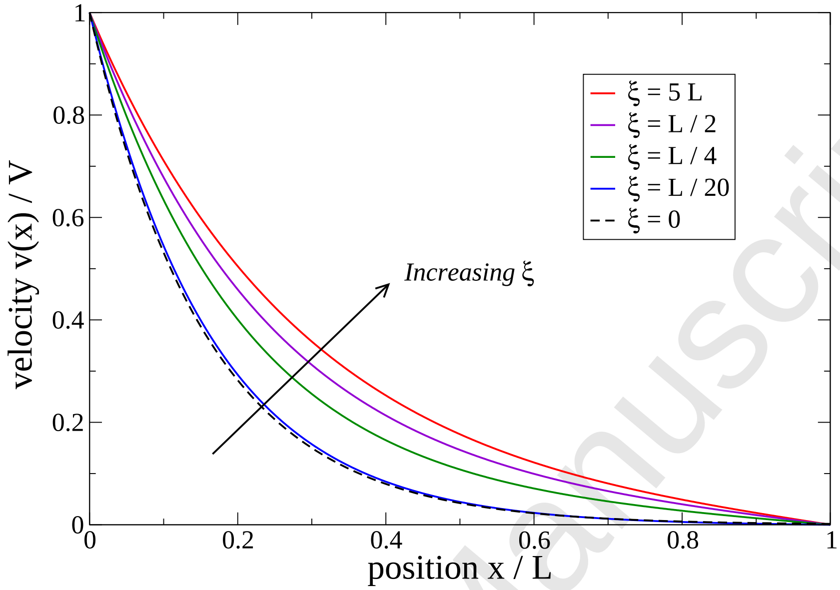

Figure 6: Example computations of velocity profiles using a nonlocal continuum theory. As the nonlocality length ξ is increased the profiles become less localized. (L is the width of the sample and V is the velocity of the moving boundary.)

7. Conclusion

The 2d rheology experiments that we have cited were set up with deliberately simple geometries. Some used cylindrical rheometers but they can be interpreted using the theory of an imposed simple shear, whenever the localization is on a length scale much less that the inner radius and the difference between the radii, as is commonly the case. The usual experimental protocol is to impose a steady boundary velocity and look for a steady state of shear after some time, ignoring transients.

Hence the possibility of such an elementary theory, in which stress, strain and strain rate are treated as scalars obeying a few simple equations. The continuum model also allows for the study of transient effects but this has so far only been explored for the most basic version of the model ($a = b = 1$, i.e. linear expressions for both drag force, eqn.(2), and Herschel-Bulkley relation, eqn.(1)) [40].

Practical applications of rheology are not so straightforward: they may involve foams with finite liquid fraction (for which Debrégeas *et al.* found an increase in localization length [28], but this work does not seem to have been followed up), awkward 2d geometries and time-varying flows. The group of Graner has concentrated on the latter two aspects, producing a more elaborate tensorial formalism [41] that can cope with such generality and also addressing the stress overshoot [42].

There is much to be satisfied with in all of this, but let us end on a less positive note. Real foams in real situations in industry and everyday life may undergo bubble break-up, coalescence, coarsening and liquid transport while they flow in complicated geometries. It seems that no-one has attempted even a minimally implausible "toy" model that addresses the entirety of this multiply complex scenario – indeed it might still be rash to do so.

That remains for another day, another Eufoam conference ...

Acknowledgements

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