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LETTER TO THE EDITOR

On the Validity of the Foam Drainage Equation

In the past decades, a "foam drainage equation" has been derived (1–3) for describing the drainage of "dry" (i.e., polyhedral) foams. The validity of this equation in a specific situation depends on whether the assumptions, on which it is based, are fulfilled in the case concerned. Foam drainage is a complex process, and even if, in certain cases, a confirmation of the validity of the assumptions involved can be obtained, it is far from certain that the equation is applicable in other cases as well. The present paper reviews the assumptions, on which the foam drainage equation is based; summarizes what type of confirmation of them has been reported for certain cases; and points to some of the discrepancies between theory and experiment found in other cases.

The foam drainage equation reads as follows:

$$\frac{\partial \alpha}{\partial \tau} + \frac{\partial}{\partial \xi}\left(\alpha^2 - \frac{\sqrt{\alpha}}{2}\frac{\partial \alpha}{\partial \xi}\right) = 0, \qquad [1]$$

where

$\alpha =$ the cross section of a channel formed where three films meet, usually indicated as "Plateau border"; α is dimensionless, defined as $\alpha = A/x_0^2$ with $A =$ the area of the cross section in m^2; $x_0 = \sqrt{(C\gamma/\rho g)}$;
$\xi = x/x_0$;
$x =$ the distance from the top of the foam downward;
$\gamma =$ the surface tension of the liquid in the foam;
$\rho =$ its density;
$\eta =$ its viscosity;
$g =$ acceleration by gravity;
$\tau =$ a dimensionless time $= t/t_0$, with $t_0 = \eta/\sqrt{(C\gamma\rho g)}$;

C is a geometrical constant relating the geometry assumed for a Plateau border channel (see Fig. 1) to a channel with circular cross section; $C = \sqrt{(\sqrt{3} - \pi/2)}$.

In Eq. [1], the first term between brackets refers to the flow induced by gravity, while the second is related with the gradient in capillary pressure along a channel. In the context of the present paper, the steps in the derivation of this equation are less important than the assumptions on which it is based. These assumptions are the following:

1. The drainage in polyhedric foams occurs in the Plateau border channels, i.e., on places where three films meet.
2. These channels have a shape as drawn in Fig. 1, and their liquid/gas boundaries behave as solid walls.
3. Flow in such a channel is described as a Poiseuille flow in a cylindrical tube with the same cross-sectional area, while the difference between the cross section as shown in Fig. 1 and that belonging to a cylindrical tube is taken into account by replacing the physical viscosity η_{phys} in the flow equation by an "effective" viscosity. For flow in a cylindrical tube, $\eta_{eff} = 8\pi\eta_{phys}$, while for a channel with cross section as shown in Fig. 1, $\eta_{eff} \cong 50\ \eta_{phys}$.
4. All gas cells have equal pressure.
5. Transport from foam films to the Plateau borders does not significantly influence foam drainage, and effects of film rupture are negligible.
6. The channels have a random orientation toward the direction of gravity, and their cross sections are independent of their orientation.
7. Liquid/gas interfaces of the Plateau borders are flexible enough to permit instantaneous establishment of a Laplace pressure difference between liquid and adjacent gas phases, yet rigid enough to act as rigid interfaces for flow in the channels.

Support for the model was reported by Leonard and Lemlich (4), and by Weaire *et al.* (5–7). Leonard and Lemlich compared experimental flow rates through the foam with those predicted by the theory, using an average value of the Plateau border cross section obtained from values of the liquid volume fraction, the average bubble diameter, and the film thickness values. The most important observation reported by Weaire *et al.* was for "forced drainage" of the foam. By this, the authors understand a drainage triggered by wetting of a dry foam, by introduction of fresh surfactant solution on top of the foam. This liquid penetrates downward through the foam, replacing a part of the original dry foam (at its top) by a wet foam. The boundary between wet foam and dry foam remains sharp, and its propagation velocity in the downward direction can be measured. It appears to move into the foam as a solitary wave with a constant velocity V. V is made dimensionless by expressing it in the units x_0 and t_0. Thus the dimensionless propagation velocity of the wave is given by $\upsilon = Vt_0/x_0$. In the case of forced drainage, Eq. [1] can be solved analytically to give

$$\begin{aligned} &\alpha(\xi, \tau) = \upsilon \tanh^2(\sqrt{\upsilon}|\xi - \upsilon\tau|) \qquad \text{if} \qquad \xi \le \upsilon\tau \\ &\alpha(\xi, \tau) = 0 \qquad \text{if} \qquad \xi \ge \upsilon\tau. \end{aligned} \qquad [2]$$

In this case, the Plateau border cross section behind the solitary wave can be chosen by changing the volume flow rate at the top of the foam (on the assumption that at the transition from the wet foam to the dry foam, no changes in the number of Plateau border channels occur). The wave front propagation velocity V and the volumetric flow rate Q are thought to be related by a power law relationship:

$$V \sim Q^p. \qquad [3]$$

In some cases, V is found to be proportional to the square root of Q. Then, $p = 0.5$; this was considered to support the assumptions underlying Eqs. [1] and [2], since the foam drainage equation mentioned predicts such behavior (see Ref. (3)).

However, the validity of the foam drainage equation appears to be far from general. Here we raise six points to illustrate this:

1. The equation should be applied only to the drainage of foams that are sufficiently stable to make assumption 5 applicable. Unless arguments can be presented that processes such as film drainage by marginal regeneration and film rupture are really negligible, there remains the uncertainty of whether the foam is sufficiently stable for assumption 5 to apply. Arguments based on the behavior of foams formed from solutions of similar surfactants may be deceptive. This is illustrated by experiments reported by Stoyanov *et al.* (7): foams which were sufficiently stable for forced drainage experiments could be obtained from solutions of Na dodecylsulfate (at a concentration 10 × CMC) and from solutions of cetyltrimethylammonium bromide (at concentrations 0.6 and 10 × CMC), but foams obtained from solutions of dodecyltrimethylammonium bromide were too unstable. In the case of the investigation reported by Stoyanov *et al.*, instability appeared soon enough during the experiment; but there may be cases in which this is more difficult to notice.

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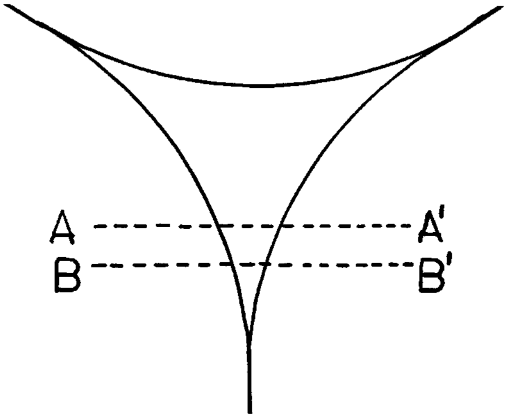

FIG. 1. Horizontal cross section through a Plateau border, assumed in the foam drainage equation. A–A′: line along which the Plateau border can be viewed, e.g., by microscope, where the downward motion due to gravity predominates; B–B′: line along which the Plateau border can be viewed where the motion caused by the surface tension gradient due to drainage from an adjacent film predominates.

2. The proportionality of V with $\sqrt{Q}$ is not always found. Koehler *et al.* (8) report, for foams formed from Dawn soap solutions "well above the CMC," an exponent p in Eq. [3] of 0.36 rather than 0.5; when error bars are taken into account, the data are also consistent with $p = 0.33$ (9). Koehler *et al.* ascribed the difference between theory and experiment to a "plug-like" flow in the Plateau border. The flow rate is then considered to be dominated by the flow into the nodes that connect different Plateau borders. These results are consistent with the results reported by Durand *et al.* (9): increasing quantities of dodecanol in a 0.012 M SDS solution (known to substantially increase the surface viscosity) result in changing the exponent p from 0.39 (for dodecanol/SDS (w : w) = 1/2000) to 0.54 (for dodecanol/SDS (w : w) = 1/1000). This was ascribed to the transition of the flow in Plateau borders from a "node-dominated region" (for nonstiff interfaces) to a "border-dominated region" (with stiff interfaces). Table 1 shows a survey over the different values of p in Eq. [3] reported by various investigators.

3. Kuznetsova and Kruglyakov (10, 11) reported differences between the drainage rates predicted by the foam drainage equation and those found experimentally. The cross-sectional areas of the Plateau border channels had been calculated from the volume fraction of liquid in the foam determined by electrical resistivity measurements. The drainage rate found experimentally was, in all cases investigated by those authors, substantially (factor of 2–5) *larger* than expected from the foam drainage equation. These authors ascribed the difference between theory and experiment to mobility of the Plateau border wall, i.e., to disagreement with assumption 3 about the "rigid wall" behaviour of the Plateau border/gas interfaces.

4. It was found experimentally, that a foam formed from a 0.0025 M SDS solution (about 0.3 × CMC) is destroyed by ultrasonic waves (12). This could be explained by stimulation of drainage from films to the Plateau borders through stimulation of squeezing mode vibrations in the film along the vertical Plateau borders; whereas there is no obvious way of explaining the effect of ultrasonic waves by an action on the flow through Plateau border channels with rigid walls. In this case again, the foam apparently was not stable enough for application of the foam drainage equation.

TABLE 1

Exponent *p* in the Relation between Linear Front Velocity and Volumetric Flow Rate in Forced Drainage Experiments According to Different Investigators

Investigator	System	p	Proposed explanation
Verbist, Weaire, *et al.* (1–3)	Theory	0.5	Poiseuille flow
Koehler *et al.* (8)	Dawn soap ≫ CMC	0.36	Plug flow
Durand *et al.* (9)	Dodecanol + 0.012 M SDS	0.39	Nonstiff interface
Durand *et al.* (9)	Dodecanol + 0.012 M SDS	0.54	Stiff interface

5. Assumption 2 is particularly doubtful, since it excludes the effect of the motion of the liquid/gas interfaces under the action of a surface tension gradient; which has been known in principle since the work of Gibbs (13), and which is very important in the drainage of films (14). Thus, as soon as the Plateau border wall does not behave as a solid, the dissipative force associated with flow may be balanced not only by gravity and by the pressure gradient (as assumed, e.g., by Verbist and Weaire (6)), but by a surface tension gradient as well, and Eq. [3] in the latter paper should be replaced by

$$\rho g - \frac{\partial p_l}{\partial x} - \frac{\omega}{A}\frac{\partial \gamma}{\partial x} - \frac{\eta_{\text{eff}} u}{A} = 0, \qquad [4]$$

where

ω = the length of the periphery of the Plateau border considered;
p_l = the pressure in the Plateau border.

6. That the effect of a surface tension gradient is not negligible, at least when drainage from films to the Plateau borders occurs, introducing surface tension gradients along the Plateau borders, has been shown by Hudales *et al.* (15, 16). This effect has been found to predominate especially near the pointed "edges" of a Plateau border cross section, as may be seen when observing the film, e.g., by microscope, along the line B–B′ in Fig. 1. This situation will change into a situation in which gravity-induced flow predominates, e.g., when looking along the line A–A′ in Fig. 1. The place where this transition occurs depends both on the size of the Plateau border cross section and on the magnitude of the induced surface tension gradient; but the Plateau border wall cannot be relied upon to act as a solid wall if marginal regeneration occurs.

The effect of a surface tension gradient along the Plateau border may work both in the same direction as gravity, and in the reverse direction. The evidence available at present from Refs. (15) and (16) concerns flow directed aginst the direction of gravity, since in those cases the surface tension increases with increasing height. However, in forced drainage experiments a fresh surfactant solution is introduced at the top of the foam. Then the surface tension gradient can easily be imagined to be in the same direction as gravity: in the foam, the surface tension along a Plateau border increases with increasing height (13); therefore, the surface tension of the fresh surfactant solution introduced at the top of the foam in a forced drainage experiment will in general be lower than that in the foam. A similar effect could occur when a film ruptures: then a relatively large quantity of surfactant, which had been present in the film walls, will enter the Plateau borders in the vicinity of the ruptured film and will locally enrich these Plateau borders with surfactant.

Thus, although there may be situations in which the foam drainage equation can be assumed to be valid, its validity cannot be claimed to be general. The best chance for the foam drainage equation to be valid appears to be in the case when surfactant solutions of rather high concentrations are involved such as to make the surfaces of both Plateau borders and films rigid, suppressing marginal regeneration and drainage from films, and when the Plateau borders are relatively large such as to suppress the effect of any surface tension gradient present, by decreasing the factor ω/A in Eq. [4].

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