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A note on the effects of liquid viscoelasticity and wall slip on foam drainage

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Abstract

A foam drainage model is modified to attempt the description of foams made of viscoelastic liquids (such as polymer solutions). In particular, the standard approach to foam drainage dominated by viscous dissipation in Plateau borders is modified to take into account the elastic forces acting on the fluid within Plateau borders, and slipping of the polymer solution at the walls of Plateau borders. It is shown that, in the case of forced drainage, the resulting differential equations reduce to the same one obtained in the case of Newtonian liquids, which is satisfied by the well-known solitary wave solution. According to these results, the fluid elasticity has no effect on the drainage velocity, while the wall slip assumption is compatible with recent observations showing a faster drainage velocity in the forced drainage experiment.

1. Introduction

The first attempt to obtain a simple mathematical description of foam drainage was carried out by Goldfarb *et al* [1], assuming that the liquid flow in the network of Plateau borders is analogous to Hagen–Poiseuille flow. In dimensionless form, this equation can be written as

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

where α is the dimensionless cross-sectional liquid fraction, and ξ the dimensionless coordinate in the direction of drainage. The same equation was obtained independently by Verbist and Weaire [2], and it has been studied extensively in the past years [3–5]. A peculiar solution of equation (1) consists of a solitary wave, which is usually written in the following approximate form:

$$\begin{array}{ll} \alpha = c\tanh^2\left(\sqrt{c}\,|\xi - c\tau|\right) & \xi \leqslant c\tau \\ \alpha = 0 & \xi > c\tau. \end{array} \tag{2}$$

This solution can be realized physically in the so-called forced drainage experiment [6], in which liquid is fed continuously at the top of a cylindrical column of foam, so that a state of steady drainage rather than that of equilibrium is approached. This generates a downward-moving wavefront between a region of high liquid fraction (wet foam) and one of low liquid fraction (dry foam). The wave amplitude and propagation velocity are determined by the flow rate of liquid supplied to the system.

There is, however, an alternative approach to foam drainage modelling, based on the assumption that mechanical energy is dissipated in the nodes rather in the Plateau borders, which leads to the so-called node-dominated foam drainage equation [7, 8]:

$$\frac{\partial \alpha}{\partial \tau} + \frac{\partial}{\partial \xi}\left(\alpha^{\frac{3}{2}} - \frac{1}{2}\frac{\partial \alpha}{\partial \xi}\right) = 0. \tag{3}$$

More recent studies have shown that the surface rheology of soap films plays a major role in determining the physical mechanism of the liquid flow in the network of Plateau borders, and therefore the appropriate model to describe foam drainage [9–11]. Roughly speaking, the former approach (equation (1)) is suitable for the high surface viscosity of soap films (that is, low surfactant mobility), whereas the latter (equation (3)) can be used to describe foams where the surfactant is easily soluble in the liquid.

Here, the standard theory of foam drainage for high surface viscosity is extended to viscoelastic liquids, such as solutions of flexible polymers. These fluids have a great and continuously growing importance in several applications of practical interest. Among others, examples are the reduction of turbulent drag in wall-bounded flows [12], and the control of drop impact on solid surfaces (either homo-thermal [13] or heated [14]).

As it is well known, the shear viscosity of dilute polymer solutions is almost identical to that of the solvent [15, 16], and very often polymer molecules have little or no surface activity, so they do not change the surface tension of the pure solvent. However, when polymers are dissolved in a liquid they do change its fluid-dynamic behaviour: in general, the two most noticeable effects are viscoelasticity and, in some cases, apparent slip at the walls (which breaks down the well-known no-slip boundary condition universally used for simple fluids).

At a microscopic level, viscoelasticity is due to the response of the polymer in elongational flow, where an elementary volume of fluid stretches under the action of the normal components of the stress tensor. In this case polymer molecules, which are coiled at rest to assume a state of maximum conformational entropy, unfold under the hydrodynamic action, generating an elastic force [17]. Such behaviour can be described from a macroscopic standpoint by introducing the concept of elongational (or extensional) viscosity, the ratio of the first normal stress difference to the rate of elongation of the fluid:

$$\eta_E = \frac{\sigma_{xx} - \sigma_{yy}}{\dot{\varepsilon}_{xx}} \tag{4}$$

where $\dot{\varepsilon}_{xx} = \mathrm{d}u/\mathrm{d}x$ is the velocity gradient in the direction of the elongation. For a Newtonian incompressible fluid, one can easily verify that the elongational viscosity is three times the shear viscosity [18]. For a polymer solution the ratio η_E/η, also known as the Trouton ratio, can be of the order of 10^3–10^4.

When the polymer concentration in the solvent exceeds the so-called overlap concentration, polymer molecules are not isolated but form entangled networks, which resist shear and tend to slip over the boundaries. For this reason, it was proposed [19, 20] that a polymer liquid near a solid surface does not obey the standard no-slip boundary conditions but, instead, that it should be allowed to slip with a (relative) velocity u_S, proportional to the applied viscous stress:

$$\sigma_{xy} = K_S u_S. \tag{5}$$

This effect is similar to the well-known apparent wall slip observed in many yield-stress fluids made of dense particle suspensions [21, 22] (note that in this case the slip velocity may also depend on the tube diameter [23]). In the case of flow within the Plateau borders, the polymer solution would tend to slip over the surfactant-covered film, provided that there is no strong attraction between the polymer chains and the surface. Both viscoelasticity and wall slip are known to affect the formation of soap films, which are made of a liquid layer enclosed between two surfactant layers and hence are very similar to Plateau borders [24].

This work was motivated by some recent experimental observations on tetradecyltrimethylammonium bromide/dodecanol (TTAB/DOH) aqueous foams, showing that tiny amounts of polyethylene oxide (PEO) dissolved into the liquid cause a faster displacement of the front between wet foam and dry foam in the forced drainage experiment [25, 26]. Independent experiments [27] on commercial aqueous film forming foams (AFFFs) showed that the addition of PEO significantly increased the foam lifetime, from which a reduction of the drainage rate was suggested.

In principle, both results could be explained by an increase of the surface tension due to the interaction between the oxygen atoms of the polymer and the polar head of the surfactant at the monolayer, which was actually observed in experiments on AFFFs. However, measurements on the TTAB/DOH foam showed that the PEO has no significant effect on the surface tension: for this system, it was suggested that the elongational viscosity plays a major role in changing the drainage velocity. Moreover, the increased lifetime of AFFF/PEO systems may not be simply due to a slower drainage: in fact, the absorption of PEO molecules at the film surfaces might also retard the collapse of the metastable surfactant bilayer that remains when all the liquid has been drained. For these reasons, the potential effects of the fluid elasticity and wall slip on foam drainage deserve some further investigation.

2. Analysis

A modified foam drainage equation suitable for describing the behaviour of polymeric liquids can be obtained following the same procedure used to derive the foam drainage equation for Newtonian liquids, that is, by writing a force balance over a small volume of fluid in a vertical Plateau border of cross-sectional area A. Assuming that the Plateau border is delimited by three cylindrical surfaces of radius R in mutual contact, simple geometrical considerations allow one to find that $A = \beta^2 R^2$, with $\beta^2 = \sqrt{3} - \pi/2$.

For Newtonian fluids, the forces acting on a volume $A\,\mathrm{d}x$ in the flow direction are gravity, the capillary force and the viscous resistance, so the force balance can be written as

$$\rho g - \frac{\beta\gamma}{2} A^{-\frac{3}{2}} \frac{\partial A}{\partial x} - \frac{k\eta u}{A} = 0 \tag{6}$$

where ρ, γ and η are the liquid density, surface tension and shear viscosity, respectively, u is the cross-sectional average velocity, and k is a geometric factor. For a circular cross-section $k = 8\pi$, whereas for Plateau borders the value $k = 49$ has been obtained numerically [28].

2.1. Effect of viscoelasticity

To account for the fluid viscoelasticity, one can start from equation (4), which relates the viscoelastic extra stress to the elongational viscosity; since the flow occurs in the x-direction, one can assume that $\sigma_{xx} \gg \sigma_{yy}$, so

$$\sigma_{xx} \approx \eta_E \frac{\partial u}{\partial x} \tag{7}$$

and the resulting elastic force in the x-direction is

$$F_{\mathrm{el}} = \frac{\partial}{\partial x}\left(\eta_E \frac{\partial u}{\partial x}\right). \tag{8}$$

For small velocity gradients, which are likely to occur during foam drainage, one can assume that the elongational viscosity is almost constant, so the elastic force becomes

$$F_{\mathrm{el}} = \eta_E \frac{\partial^2 u}{\partial x^2}. \tag{9}$$

The assumption of constant elongational viscosity is justified in the light of the well-known finite extensibility rheological models [29], which show that the elongational viscosity of polymer solutions does not vary significantly until the inverse of the elongation rate is of the same order as the characteristic time of the solution, a quantity proportional to the difference between the shear viscosities of the solution and of the solvent. Since for dilute solutions the difference is very small, significant variations of η_E occur only for velocity gradients as large as 10^3, which are not attained during foam drainage.

Taking into account the elastic component, the resulting force balance in the x-direction is

$$\rho g - \frac{\beta\gamma}{2} A^{-\frac{3}{2}} \frac{\partial A}{\partial x} + \eta_E \frac{\partial^2 u}{\partial x^2} - \frac{k\eta u}{A} = 0. \tag{10}$$

This equation must be modified to take into account the random orientation of Plateau borders in a real foam, with the substitutions $x \to x/\cos\theta$, $\rho g \to \rho g \cos\theta$, and $u \to u/\cos\theta$, and averaging over all possible directions using the following average operator:

$$\langle \circ \rangle = \frac{\int_0^\pi \circ \sin\theta \, \mathrm{d}\theta}{\int_0^\pi \sin\theta \, \mathrm{d}\theta}. \tag{11}$$

The resulting averaged equation is

$$\rho g - \frac{\beta\gamma}{2} A^{-\frac{3}{2}} \frac{\partial A}{\partial x} + \eta_E \frac{\partial^2 u}{\partial x^2} - \frac{3k\eta u}{A} = 0. \tag{12}$$

Equation (12) can be rewritten in a dimensionless form by the substitutions $x \to x\sqrt{\frac{\beta\gamma}{\rho g}}$ and $t \to t\frac{3k\eta}{\sqrt{\beta\gamma\rho g}}$:

$$u = A - \frac{1}{2\sqrt{A}} \frac{\partial A}{\partial x} + K A \frac{\partial^2 u}{\partial x^2} \tag{13}$$

where $K = \eta_E/3k\eta$. With $k \approx 50$ and $\eta_E \leqslant 100\eta$, a numeric estimate of this coefficient is $K \leqslant 2/3$.

To solve the problem for the cross-sectional area of the Plateau borders $A(x,t)$, the force balance must be coupled with the continuity equation:

$$\frac{\partial A}{\partial t} + \frac{\partial}{\partial x}(Au) = 0. \tag{14}$$

To do so, an explicit expression for the velocity u must be derived from equation (13), and introduced into equation (14). This is not immediately possible, due to the unknown second derivative of u existing in equation (13). To solve this problem, one can obtain the unknown term by deriving the continuity equation once with respect to x:

$$\frac{\partial^2 u}{\partial x^2} = -\frac{1}{A}\left\{\frac{\partial^2 A}{\partial x \partial t} + u\frac{\partial^2 A}{\partial x^2} - \frac{2}{A}\left[\frac{\partial A}{\partial x}\frac{\partial A}{\partial t} + u\left(\frac{\partial A}{\partial x}\right)^2\right]\right\}. \tag{15}$$

Introducing this result into equation (14) yields an explicit expression for u:

$$u = \frac{\frac{1}{2K\sqrt{A}}\frac{\partial A}{\partial x} - \frac{A}{K} + \frac{\partial^2 A}{\partial x \partial t} - \frac{2}{A}\frac{\partial A}{\partial x}\frac{\partial A}{\partial t}}{\frac{2}{A}\left(\frac{\partial A}{\partial x}\right)^2 - \frac{\partial^2 A}{\partial x^2} - \frac{1}{K}}. \tag{16}$$

Now, equation (16) can be used in (14) to obtain the foam drainage equation:

$$\frac{\partial A}{\partial t}+\frac{\partial}{\partial x}\left(\frac{\frac{\sqrt{A}}{2K}\frac{\partial A}{\partial x}-\frac{A^2}{K}+\frac{\partial^2 A}{\partial x\partial t}A-2\frac{\partial A}{\partial x}\frac{\partial A}{\partial t}}{\frac{2}{A}\left(\frac{\partial A}{\partial x}\right)^2-\frac{\partial^2 A}{\partial x^2}-\frac{1}{K}}\right)=0 \tag{17}$$

where the liquid flow rate $Q(x,t)$ is given by the expression between brackets.

To solve equation (17), for the problem of forced drainage, we search for solutions in the form of travelling waves, i.e. solutions of the form $A = A(x - ct)$; with the change of variable $X = x - ct$, equation (17) becomes

$$\frac{\mathrm{d}}{\mathrm{d}X}\left(-cA+\frac{\frac{\sqrt{A}}{2K}\frac{\mathrm{d}A}{\mathrm{d}X}-\frac{A^2}{K}-cA\frac{\mathrm{d}^2A}{\mathrm{d}X^2}+2c\left(\frac{\mathrm{d}A}{\mathrm{d}X}\right)^2}{\frac{2}{A}\left(\frac{\mathrm{d}A}{\mathrm{d}X}\right)^2-\frac{\mathrm{d}^2A}{\mathrm{d}X^2}-\frac{1}{K}}\right)=0; \tag{18}$$

that is,

$$\frac{cA+\frac{\sqrt{A}}{2}\frac{\mathrm{d}A}{\mathrm{d}X}-A^2}{K\left[\frac{2}{A}\left(\frac{\mathrm{d}A}{\mathrm{d}X}\right)^2-\frac{\mathrm{d}^2A}{\mathrm{d}X^2}\right]-1}=\text{const.} \tag{19}$$

For $K \to 0$ (i.e., when the viscoelastic term in equation (13) is removed) one obtains the standard foam drainage equation for Newtonian liquids. Note that due to the approximations introduced into the model, equation (19) does not converge to the Newtonian equation when $\eta_E \to 3\eta$ (i.e., $K \to 1/k$).

When the liquid is poured from the top into a column of dry foam, the wetted area becomes very small (and constant) for $X \to +\infty$, so setting the constant in equation (19) equal to zero is an acceptable approximation. In this case, provided that $K[\frac{2}{A}(\frac{\mathrm{d}A}{\mathrm{d}X})^2 - \frac{\mathrm{d}^2A}{\mathrm{d}X^2}] \neq 1$, equation (19) reduces to the same equation for Newtonian liquids, which can be obtained from equation (1) by imposing a solution in the form of a travelling wave.

2.2. *Effect of wall slip*

If the polymer solution tends to slip at the boundary of Plateau borders during foam drainage, the shear stress is no longer due to the liquid viscosity, but is related to the slip velocity according to equation (5). Thus, the force balance given by equation (6) should be rewritten as

$$\rho g-\frac{\beta\gamma}{2}A^{-\frac{3}{2}}\frac{\partial A}{\partial x}-\frac{K_S u_S}{A}=0. \tag{20}$$

In general $0 < K_S < k\eta$, where the lower limit corresponds to an infinite slip velocity and the upper limit to no slip.

From equation (20) one can find immediately an explicit expression for the slip velocity; however, this is not the actual mean velocity of the fluid inside the Plateau border (i.e., the velocity we need to substitute in the continuity equation). In general, one can write that the mean velocity is given by

$$u = u_S + u' \tag{21}$$

where u' depends on the liquid flow rate in the Plateau border.

Using the averaging procedure outlined above, one can find the expression for the averaged velocity in a network of randomly oriented Plateau borders:

$$u=\frac{1}{3K_S}\left(\rho gA-\frac{\beta\gamma}{2}A^{-\frac{1}{2}}\frac{\partial A}{\partial x}\right)+u'. \tag{22}$$

The dimensionless form is now obtained with the substitutions $x \to x\sqrt{\frac{\beta\gamma}{\rho g}}$ and $t \to t\frac{3K_S}{\sqrt{\beta\gamma\rho g}}$, and substituting into the continuity equation (equation (14)) yields

$$\frac{\partial A}{\partial t} + \frac{\partial}{\partial x}\left(A^2 - \frac{\sqrt{A}}{2}\frac{\partial A}{\partial x} + Au'\right) = 0. \tag{23}$$

With the variable change $X = x - ct$ one can integrate this equation to search for solutions in the form of travelling waves, and find that

$$\begin{array}{ll} A = (c-u')\tanh^2\left(\sqrt{c-u'}|x-ct|\right) & x \leqslant ct \\ A = 0 & x > ct. \end{array} \tag{24}$$

This solution is formally similar to the forced drainage solution for Newtonian liquids (equation (2)), the main difference being that in the case of wall slip the cross-sectional area occupied by the liquid is smaller due to the different pre-factor.

To obtain the relationship between the wavefront velocity and the liquid flow rate during forced drainage, one can observe that the flow rate (i.e., the expression between brackets in equation (23)) is constant for $x = 0$, and substitute the values $A = c - u'$ and $\partial A/\partial x = 0$ returned by equation (24) when the wavefront is far away from that point (i.e., $x \ll ct$), so that

$$Q(0,t) = c^2 - cu'. \tag{25}$$

Solving equation (25) for c and discarding the negative root yields

$$c = 0.5u' + \sqrt{Q + 0.25u'^2}. \tag{26}$$

This shows that when one assumes that the liquid may slip at the walls of Plateau borders the theoretical drainage velocity is faster than it would be if there was no wall slip. In fact, when the slip velocity vanishes equation (24) reduces to equation (2), and imposing the boundary condition on the flow rate yields $c = \sqrt{Q}$.

Now, one can compare the trend predicted by equation (26) with the drainage velocity measured in foams made of PEO solutions [25, 26]. According to these results, the wavefront velocity is proportional to the square root of the flow rate (within experimental error), but drainage is always faster than in foams made of a Newtonian liquid having the same viscosity. Thus, equation (26) is consistent with the experimental observations, in the sense that it is able to predict a qualitative increase of the drainage velocity. Unfortunately, a quantitative assessment has not been possible so far, because the actual value of the slip coefficient (and hence the slip velocity) in a real foam is not known, and is probably too difficult (if not impossible) to be measured directly.

3. Conclusions

The two simple foam drainage models described above allow one to get a deeper insight in the behaviour of foams made of viscoelastic liquids during forced drainage, and can be used to explain why some experiments [25, 26] show that drainage is faster with respect to the case of Newtonian liquids.

When an elastic force is included explicitly in the foam drainage equation, forced drainage is not affected: as a consequence, the fluid elasticity (or its elongational viscosity) appears to play no role in the phenomenon. However, this is not sufficient to rule out the elongational viscosity completely, because the model might miss some important physics (in particular, the proposed approach may not describe the action of normal stresses on the walls of Plateau borders appropriately).

If the no-slip boundary condition for the flow inside Plateau borders is relaxed by introducing a slip velocity proportional to the wall shear stress, the foam drainage model yields an expression of the drainage velocity which is consistent with the experimental data. Although this argument seems to provide a reasonable explanation for the increase of the drainage velocity, it should be verified by more systematic experiments. In particular, one should check the behaviour of dilute polymer solutions (i.e., solutions below the overlap concentration), which should not exhibit significant wall slip.

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