

# Physicochemical approach to the theory of foam drainage

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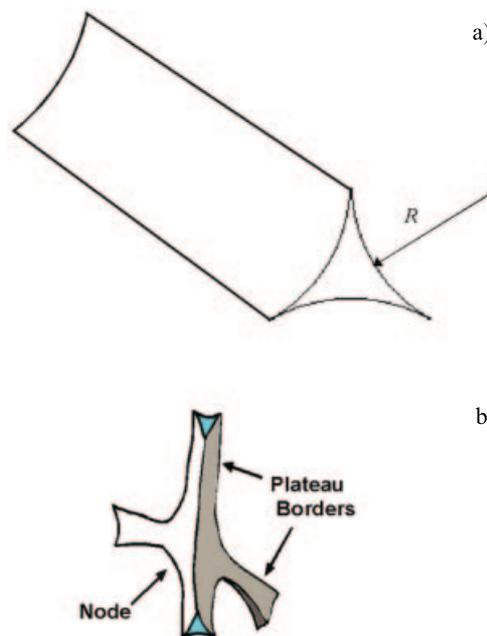
**Abstract.** We have investigated theoretically the effect of surface viscoelasticity on the drainage of an aqueous foam. Former theories consider that the flow in Plateau borders is either Poiseuille flow or plug-flow. In the last case, the dissipation is attributed to flow in the nodes connecting Plateau borders. Although we do not include this dissipation in our model, we obtain a drainage equation that includes terms equivalent to those of the earlier models. We show that when the water solubility of the surfactant stabilizing the foam is low, the control parameter  $M$  for the transition between the two regimes is the ratio  $\frac{\mu D_s}{\varepsilon R}$ , where  $\mu$  is the bulk viscosity,  $D_s$  the surface diffusion coefficient,  $R$  the radius of curvature of the Plateau border and  $\varepsilon$  the surface elasticity. When the surfactant is more soluble  $M$  is rather related to the bulk diffusion coefficient. Within the frame of this approach and in view of the estimated  $M$  values, we show that the flow in Plateau borders is Poiseuille-like.

**PACS.** 47.60.+i Flow in ducts, channels, nozzles, and conduits – 82.70.Rr Aerosols and foams – 68.03.Kn Dynamics (capillary waves)

## 1 Introduction

Liquid foams have interesting topological and rheological properties and also many industrial applications: fractionation, oil recovery, fire-fighting, cosmetics, food processing, among others [1]. Because of their limited time stability and despite the numerous studies reported in the literature, many of their properties are still not well understood, in particular the drainage of the liquid in between the bubbles under the influence of gravity [2,3]. Drainage plays an important role in foam stability: indeed, when a foam dries, its structure becomes more fragile; the liquid films between adjacent bubbles being thinner, then can break, leading to foam collapse. In the case of aqueous foams, surfactant is added into water and it adsorbs at the surface of the films, protecting them against rupture. Modelling of drainage is especially difficult when the water volume fraction in the foam is small, and the bubbles are distorted into polyhedra separated by liquid films. Three liquid films connect to form objects containing larger water quantities, called “Plateau borders” (Fig. 1). Four Plateau borders themselves connect to form regions called “nodes” [1].

In the late '60s, Leonard and Lemlich recognized that the effect of films on the drainage is negligible in dry foams and that the liquid flows essentially through a network of Plateau borders. They attempted to describe in detail the topology of the Plateau borders instead of replacing them by cylinders as in previous studies. They also included surface dissipation in the form of a surface shear viscosity  $\mu_s$



**Fig. 1.** a) Schematic representation of a channel or “Plateau border”, which connects three bubbles. b) Schematic representation of a “node” which connects four Plateau borders.

and allowed for motion at the surface of the Plateau borders: the flow is Poiseuille-like for large  $\mu_s$  and plug-like for small  $\mu_s$ . Within this elaborated framework, they proposed a drainage theory together with several numerical

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solutions [4]. In 1983 a new analysis was made by Kraynik [5] who neglected capillary forces and obtained simple analytical solutions in the case of Poiseuille flow in Plateau borders: the drainage velocity  $V$  is constant until the kink of the water density profile reaches the bottom of the container, then  $V$  becomes inversely proportional to the square of time. Note that in the initial stage,  $V$  is zero until the liquid volume fraction  $\phi$  reaches a value close to 35% and the bubbles become locally spherical. The regime of constant velocity is indeed observed in the experiments if the foam height is large enough. Kraynik gives as criteria for the transition between Poiseuille-flow and plug-flow regimes in the Plateau borders:  $M_K = 2R \mu/\mu_s \sim 10^{-1}$ , where  $R$  is the radius of curvature of the Plateau border and  $\mu$  is the liquid viscosity;  $R \sim a\sqrt{\phi}$ , where  $a$  is the bubble radius (large  $M$  corresponds to plug-flow regime). The drainage equation was generalized later to include capillary forces by Weaire and co-workers (Trinity model) [2]. More recently, Koehler and co-workers (Harvard model) [6] implemented further the equation including dissipation in nodes.

Solutions of the drainage equation cannot be easily obtained. When a freshly made foam is allowed to drain, a situation called “free drainage”, the amount of liquid in the foam depends on height and time. Only with special containers such as the “Eiffel tower” of St Jalmes and coworkers, more liquid can be passed down than received from above and the foam can become uniformly drier with time [7]. Recent experimental studies focused on gravity-driven flow with continuous supply of liquid, a process called “forced drainage”, which bears some resemblance to flow through porous media. However, in contrast to solid porous materials, the liquid channels between bubbles (Plateau borders) expand when liquid is forced into the foam. For this case the drainage equation can also be solved. Assuming rigid walls and Poiseuille flow throughout the network of Plateau borders, the velocity of the liquid front  $V$  is found constant (soliton wave) and proportional to  $Q^\alpha$ , where  $Q$  is the flow rate and  $\alpha = \frac{1}{2}$  [8,9]. Several series of experiments support these predictions [10,11].

However, in more recent experiments with different surfactants, Koehler *et al.* found that  $\alpha \sim 0.36$  [6]. They suggest that the rigid-wall condition may not be valid, they assume that the flow in the Plateau borders is plug-like and that the dissipation is dominated by the flow into the nodes. The solution of this hydrodynamic problem is again a soliton wave, with  $V \sim Q^\alpha$  and  $\alpha = \frac{1}{3}$ , in excellent agreement with their experimental findings.

In their early work, Leonard and Lemlich had already noted that the rigid-walls assumption could fail in some cases [4]. Indeed, aqueous foams are made with surfactant solutions, and they are stabilized by the surfactant monolayers adsorbed at the air-water interfaces. The rheological properties of these monolayers strongly depend upon surfactant nature and concentration. In order to check for their influence on forced drainage, different solutions of pure surfactants were studied later by Stoyanov and coworkers, and no significant variations of the flow

velocity were observed [11]. However, it is not easy to distinguish experimentally between power law exponents 1/2 and 1/3. In references [10] and [11], the range of flow rates was too limited, less than two decades. More recently, new measurements were performed with a larger range of flow rates [12] using mixed surfactants solutions containing sodium dodecyl sulfate (SDS) and minor amounts of dodecanol (weight ratio SDS/dodecanol above  $10^3$ ). Dodecanol is known to substantially increase the foam stability, by forming mixed monolayers with SDS at the air-water surface with high surface viscosities [13,14]. The exponent measured was close to 0.5 for the highest amount of dodecanol, and close to 0.4 for the smallest. This was associated to the transition between Poiseuille flow and plug-flow regimes.

The experiments of [12] confirm that the nature of the surfactant monolayer does influence the flow process. Qualitatively, it can be said that if the surface of the Plateau borders behaves as a solid, it is natural to find a situation where the flow is Poiseuille-like. On the contrary, when the surface is fluid, it moves along with the liquid and the flow should rather be plug-like. It is not yet clear whether this difference in behaviour is due to differences between surface viscosities, and which surface viscosity needs to be considered, shear or dilational. The surface dilational elasticity  $\varepsilon$  associated with surface Marangoni stresses can also play a role. All three properties increase with dodecanol content in the monolayer [13,14]. However, according to the Kraynik criteria,  $M_K = 2R \mu/\mu_s < 10^{-1}$ , the influence of the surface shear can be neglected in these systems. Indeed, in the case of the SDS-dodecanol solutions tested in [12],  $\mu_s \leq 10^{-4}$  kg/s,  $R \sim 0.1$  mm (for bubbles of millimeter size and water volume fractions of order 1%), leading to  $M_K \sim 10^{-3}$ .

It was shown by Boussinesq that a single (isolated) bubble rising in a liquid of viscosity  $\mu$  behaves as a solid sphere if  $\kappa/\mu a > 1$ , where  $\kappa$  is the surface dilational viscosity and  $a$  the bubble radius [15]. This criteria resembles that of Leonard and Lemlich, although the surface viscosity that they considered is a shear viscosity: in the isolated bubble problem, the surface is not sheared. Levich showed later that the Boussinesq dilational viscosity should be replaced by terms making use of the Gibbs elasticity  $\varepsilon = \Gamma \partial \gamma / \partial \Gamma$ ,  $\gamma$  being the surface tension and  $\Gamma$  the surface concentration. If the surface monolayer is insoluble,  $\kappa = \varepsilon a^2 / D_s$ ,  $D_s$  being the surface diffusion coefficient and if it is soluble,  $\kappa = \varepsilon \delta \beta / D$ ,  $\delta$  being the thickness of the diffusion layer,  $\beta$  an equivalent layer thickness  $\beta = (\partial \Gamma / \partial C)$ ,  $C$  the bulk concentration and  $D$  the bulk diffusion coefficient [16].

Similar hydrodynamic calculations have been performed with foam films to investigate the influence of surface elasticity and viscosities [17,18]. When the surfactant is soluble and the film thickness not too small, diffusion is not fast enough to replenish the film surfaces, and the surfactant behaves as if it were insoluble [18]. For thinner films, local equilibrium between surface and bulk is preserved and results similar to those of bubbles are obtained for the velocity of drainage  $V$ :

$V/V_0 = 1 + 3\mu D/(\varepsilon\beta) + 6\mu D_s/(\varepsilon h)$ , where  $V_0$  is the velocity of drainage for films with rigid surfaces and  $h$  the film thickness.

The problem of foams is much more complex. In this paper we will try to clarify which surface parameter — elasticity, shear or surface dilational viscosity— plays the more important role. We will also try to compare the role of the boundary conditions at the surface of the Plateau borders with the role of the dissipation in the nodes. We will first establish a new drainage equation considering the dissipation in the Plateau borders and at their surface. We will allow for partial slip at the surface and not make any hypothesis about the value of the surface velocity  $U$ . In this way a drainage equation containing both the terms of channel-dominated drainage equation and those of node-dominated drainage equation is recovered. Situations where the surfactant solubility in water is either small or large will be both considered. Numerical calculations of the water volume fraction vertical profile will be presented.

## 2 Governing equations

We address first the problem of dissipation in the Plateau borders and will discuss the contribution of the nodes later. We begin with the simplified case of one cylindrical channel. Let  $z'$  be the coordinate along the principal axis of the channel, tilted at an angle  $\theta$  with respect to the vertical axis  $z$ , and  $R(z')$  be the radius of the channel at the coordinate  $z'$ . We use cylindrical coordinates  $(r, \varphi, z')$  as shown in Figure 2.

### 2.1 Velocity

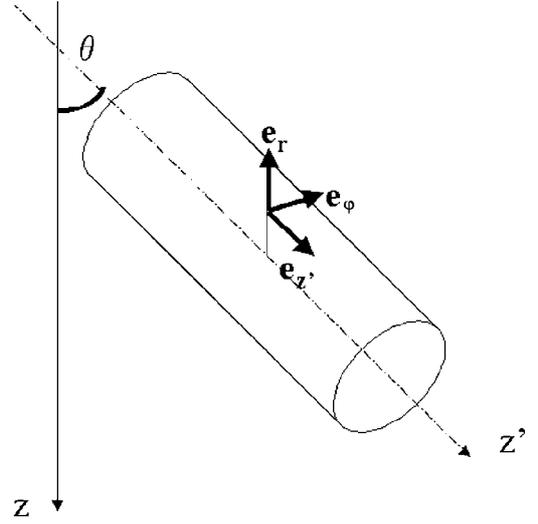
We consider that the liquid is an isotropic and incompressible Newtonian fluid. The expression of the velocity  $\mathbf{v}(\mathbf{r}, t)$  is then given by the Navier-Stokes equation:

$$\rho \frac{d\mathbf{v}}{dt} = \rho \mathbf{g} - \nabla p + \mu \Delta \mathbf{v}, \quad (1)$$

where  $\rho$  is the density,  $\mu$  the shear bulk viscosity and  $p$  the pressure.

Let us make the following assumptions:

- i) Inertial effects are negligible (small Reynolds number).
- ii) Gravity is too small to affect the revolution symmetry and so in equation (1) the  $\varphi$  derivatives are zero. Within this approximation, the surface is not sheared laterally. In their model, Leonard and Lemlich assumed that the  $\varphi$  derivatives are not zero, but they took into account the exact shape of the Plateau border. We will come back to the shape problem later on.
- iii) The lubrication approximation is valid: the flow is along the  $z'$ -axis and the variation of velocity with the normal coordinates  $r$  is much larger than with the axial coordinate  $z'$ . Note that this approximation implies that the variation of the radius with the axial coordinate is small:  $\frac{\partial R}{\partial z'} \ll 1$ .



**Fig. 2.** Geometry of the cylinder used to model a Plateau border.

Let  $U(z', t)$  be the velocity at the surface of the channel and  $R(z', t)$  the radius of the channel.

By writing

$$\mathbf{v}(\mathbf{r}, t) = v(r, z', t) \mathbf{e}_{z'}$$

and

$$P = p - \rho g \cos \theta z' \quad (2)$$

( $P$  is a function of only the axial coordinate and time:  $P(\mathbf{r}, t) = P(z', t)$ ) the solution of equation (1) is then

$$v(r, z', t) = \frac{1}{4\mu} \frac{\partial P}{\partial z'} (r^2 - R^2(z', t)) + U(z', t). \quad (3)$$

It is worth noting that for a given  $z'$  the velocity profile may be seen as the superposition of a Poiseuille-flow profile and a plug-flow profile.

### 2.2 Mass conservation

Assuming that the bulk liquid is incompressible, and introducing the mean velocity  $\bar{v}(z', t)$  through the channel section  $A(z', t)$

$$\bar{v}(z', t) = \frac{1}{A(z', t)} \iint_{A(z', t)} v(r, z', t) r dr d\varphi,$$

the equation for mass conservation is

$$\frac{\partial (A\bar{v})}{\partial z'} + \frac{\partial A}{\partial t} = 0. \quad (4)$$

The expression of  $\bar{v}$  is

$$\bar{v}(z', t) = -\frac{R^2}{8\mu} \frac{\partial P}{\partial z'} + U(z', t).$$

Substituting the expression of  $\bar{v}$  in equation (4), it follows that

$$\frac{\partial R^2}{\partial t} + \frac{\partial}{\partial z'} \left( -\frac{R^4}{8\mu} \frac{\partial P}{\partial z'} + R^2 U \right) = 0. \quad (5)$$

### 2.3 Bulk surfactant molecules conservation

Although the bulk fluid density is constant, the bulk surfactant concentration  $C$  varies. The conservation equation for the bulk surfactant is

$$\frac{\partial C}{\partial t} + \text{div } \mathbf{j}_c = 0, \quad (6)$$

with

$$\mathbf{j}_c = C\mathbf{v} - D\nabla C.$$

$\mathbf{j}_c$  is the bulk surfactant flux density and  $D$  is the bulk diffusion coefficient. We assumed that gravity does not affect the revolution symmetry, so  $C(\mathbf{r}, t)$  is independent of the  $\varphi$  coordinate and equation (6) becomes

$$\frac{\partial C}{\partial t} + \frac{\partial(Cv)}{\partial z'} - \frac{D}{r} \frac{\partial}{\partial r} \left( r \frac{\partial C}{\partial r} \right) - D \frac{\partial^2 C}{\partial z'^2} = 0. \quad (7)$$

### 2.4 Surface surfactant molecules conservation

A continuity equation for surfactant concentration for the entire surface of the foam should be written. Unlike for their liquid content, the surface area of films is not negligible compared to the surface area of Plateau borders. However, since the film thickness is small the drainage velocity of films is small too. So the film surfaces are dragged very slowly by the flow in films, and it is sufficient to consider the Plateau borders surface only in the continuity equation.

We can then make the following simplification: when the Plateau border volume increases, its surface increases too and part of the films surface becomes part of the Plateau border surface. The films act as surfactant molecules reservoir and reduce the variations of surface concentration.

The surface of a channel is made of three adjacent bubble surfaces. Since the flow is along the channel axis and since the conservation law is local, these three surfaces can be connected and modelled with a cylindrical surface.

Let  $\Gamma(r, z', t)$  be the surface concentration of surfactant. If we assume that the surfactant transport between the bulk fluid and the interface is diffusion controlled, the mass conservation equation at the surface is

$$\frac{\partial \Gamma}{\partial t} + \text{div}_s \mathbf{j}_s + D \left( \frac{\partial \Gamma}{\partial r} \right)_{r=R} = 0,$$

with

$$\mathbf{j}_s = \Gamma U \mathbf{e}_{z'} - D_s \nabla_s \Gamma.$$

$\mathbf{j}_s$  is the surface surfactant flux density,  $D_s$  is the surface diffusion coefficient and  $\nabla_s$  is the two-dimensional surface gradient.

Since it was assumed that gravity does not affect the revolution symmetry, one has

$$\frac{\partial \Gamma}{\partial t} + \frac{\partial(\Gamma U)}{\partial z'} - D_s \frac{\partial^2 \Gamma}{\partial z'^2} = -D \left( \frac{\partial \Gamma}{\partial r} \right)_{r=R}. \quad (8)$$

### 2.5 Stress balance

Before calculating the stress balance, let us make the following assumptions:

- i) The pressure is the same inside the bubbles and equal to  $p_0$ .
- ii) There are no shear stresses in the gas phase.
- iii) The bulk liquid is incompressible.
- iv) The mass of the interface is supposed to be sufficiently small so that the inertia term and the gravity force acting on the surface may be neglected [19].
- v) The surface transverse viscosity is small compared to the surface shear viscosity  $\mu_s$  and surface dilational viscosity  $\kappa$  [20].

With these assumptions, the stress balance equation in the cylindrical coordinates system gives [19]

$$f_\varphi^{\text{s(fluid)}} - f_\varphi^{\text{s(gas)}} = 0, \quad (9)$$

$$f_{z'}^{\text{s(fluid)}} - f_{z'}^{\text{s(gas)}} = -\frac{\partial \gamma}{\partial z'} - (\mu_s + \kappa) \frac{\partial^2 U}{\partial z'^2} \quad (10)$$

and

$$f_r^{\text{s(fluid)}} - f_r^{\text{s(gas)}} = \frac{\gamma}{R(z', t)} - \frac{(\mu_s - \kappa)}{R(z', t)} \frac{\partial U}{\partial z'}, \quad (11)$$

where  $f_i^{\text{s(fluid)}}$  and  $f_i^{\text{s(gas)}}$  are, respectively, the force exerted by the bulk fluid and the gas upon an element of the interface along the unit vector  $\mathbf{e}_i$ .

Note that our dilational viscosity  $\kappa$  is the Scriven's one [19], defined to be half the Boussinesq's one [15].

The stress tensors in the bulk liquid and in the gas (in cylindrical coordinates) are

$$[\sigma^{\text{fluid}}] = \begin{bmatrix} -p & 0 & \mu \frac{\partial v}{\partial r} \\ 0 & -p & 0 \\ \mu \frac{\partial v}{\partial r} & 0 & -p + 2\mu \frac{\partial v}{\partial z'} \end{bmatrix},$$

$$[\sigma^{\text{gas}}] = -p_0 [\mathbb{I}_3]$$

(where  $[\mathbb{I}_3]$  is the unit tensor).

Since the forces acting on the surface are  $f_i^{\text{s(fluid)}} = [\sigma^{\text{fluid}}] \cdot (-\mathbf{e}_r)$  and  $f_i^{\text{s(gas)}} = [\sigma^{\text{gas}}] \cdot (\mathbf{e}_r)$ , equations (10) and (11) become

$$\mu \left( \frac{\partial v}{\partial r} \right)_{r=R} = \frac{\partial \gamma}{\partial z'} + (\mu_s + \kappa) \frac{\partial^2 U}{\partial z'^2}, \quad (12)$$

$$p - p_0 = \frac{\gamma}{R(z', t)} - \frac{(\mu_s - \kappa)}{R(z', t)} \frac{\partial U}{\partial z'}. \quad (13)$$

The surface shear viscosity appears in the above equations because surface flow involves a combination of dilatation and shear. Substituting equation (3) in equation (12), it follows that

$$\frac{R}{2} \frac{\partial P}{\partial z'} = \frac{\partial \gamma}{\partial z'} + (\mu_s + \kappa) \frac{\partial^2 U}{\partial z'^2}. \quad (14)$$

### 3 Drainage equation

The governing equations are (3, 5, 7, 8, 13) and (14). In order to obtain the equation of evolution for  $R(z', t)$ , let us make the following assumptions:

- i) We assume that the quasi-steady-state assumption is valid, *i.e.* all variables depend implicitly on time through the channel radius  $R(z', t)$ .
- ii) Deviations of surface concentration with respect to equilibrium are supposed to be small:  $\Gamma = \Gamma_{\text{eq}} + \delta\Gamma$  with  $\delta\Gamma \ll \Gamma_{\text{eq}}$ . As a consequence,  $\gamma = \gamma_{\text{eq}} + \delta\gamma$  with  $\delta\gamma = \varepsilon\delta\Gamma/\Gamma_{\text{eq}} \ll \gamma_{\text{eq}}$ , and

$$\frac{\partial\gamma}{\partial z'} = \frac{d\gamma}{d\Gamma} \frac{\partial\Gamma}{\partial z'} \simeq \left( \frac{d\gamma}{d\Gamma} \right)_{\text{eq}} \frac{\partial\Gamma}{\partial z'}.$$

Let us introduce the surface Gibbs elasticity:

$$\varepsilon = -\Gamma \left( \frac{d\gamma}{d\Gamma} \right) \simeq -\Gamma_{\text{eq}} \left( \frac{d\gamma}{d\Gamma} \right)_{\text{eq}}.$$

Equation (14) then becomes

$$-\frac{\varepsilon}{\Gamma_{\text{eq}}} \frac{\partial\Gamma}{\partial z'} + (\mu_s + \kappa) \frac{\partial^2 U}{\partial z'^2} = \frac{R}{2} \frac{\partial P}{\partial z'}. \quad (15)$$

#### 3.1 Case of insoluble monolayers

Let us first assume that the surfactant solubility in water is very small. This is equivalent to setting  $D \left( \frac{\partial C}{\partial r} \right)_{r=R} = 0$  in equation (8). Furthermore, within the quasi-steady-state assumption, we can neglect the term  $\frac{\partial\Gamma}{\partial t}$ . Equation (8) then simplifies to

$$\frac{\partial}{\partial z'} (\Gamma U) - D_s \frac{\partial^2 \Gamma}{\partial z'^2} = 0, \quad (16)$$

which becomes, by integration,

$$U(z', t) = \frac{D_s}{\Gamma} \frac{\partial\Gamma}{\partial z'} + K_0$$

or, since  $\Gamma \simeq \Gamma_{\text{eq}}$ ,

$$\frac{\partial\Gamma}{\partial z'} = \frac{\Gamma_{\text{eq}}}{D_s} (U(z', t) - K_0), \quad (17)$$

where  $K_0$  is a constant of integration that can be determined by the following argument: at the bottom of the column (supposed to be very long), the liquid in the foam is in equilibrium with the solution. The surface (and bulk) velocity must vanish at the bottom. The gradient of surface concentration must also vanish (the surface tension is equal to its equilibrium value) implying  $K_0 = 0$ . The above equation becomes

$$\frac{\partial\Gamma}{\partial z'} = \frac{\Gamma_{\text{eq}}}{D_s} U(z', t), \quad (18)$$

physically meaning that there is no surface velocity when the surface concentration is constant.

Substituting equation (18) in equation (15), we obtain the differential equation of the surface velocity:

$$-\frac{\varepsilon}{(\mu_s + \kappa)D_s} U(z', t) + \frac{\partial^2 U}{\partial z'^2} = \frac{R}{2(\mu_s + \kappa)} \frac{\partial P}{\partial z'}.$$

$\frac{\partial^2 U}{\partial z'^2}$  is roughly equal to  $\frac{U}{l^2}$ , where  $l$  is the length of a Plateau border. Typically  $l \sim 10^{-3}$  m,  $\varepsilon \sim 10$  mN/m,  $D_s \sim 10^{-11}$  m<sup>2</sup>/s,  $\mu_s \sim \kappa \lesssim 10^{-6}$  kg/s, so  $\frac{\varepsilon}{(\mu_s + \kappa)D_s} \gtrsim 10^{15}$  and

$$\frac{\varepsilon}{(\mu_s + \kappa)D_s} U(z', t) \gg \frac{\partial^2 U}{\partial z'^2}.$$

The expression of the surface velocity is then

$$U(z', t) = -\frac{D_s}{2\varepsilon} R \frac{\partial P}{\partial z'}. \quad (19)$$

The ratio between the term  $p - p_0$  and  $\frac{(\mu_s - \kappa)}{R(z', t)} \frac{\partial U}{\partial z'}$  in equation (13) is also  $\frac{\varepsilon l^2}{(\mu_s + \kappa)D_s}$  so that the second term on the right-hand side in that equation can be neglected. We obtain

$$p - p_0 = \frac{\gamma}{R(z', t)},$$

which is simply the Laplace equation. Substituting equation (2), it follows that

$$P = p_0 + \frac{\gamma}{R(z', t)} - \rho g \cos \theta z'. \quad (20)$$

As a result, the governing equations are independent of the actual values of the surface viscosities. However, the dependence is somewhat hidden in the surface diffusion coefficient  $D_s$  whose variation probably follows that of surface viscosities.

Substituting equation (19) in equation (5), we obtain

$$\frac{\partial R^2}{\partial t} - \frac{\partial}{\partial z'} \left( \frac{R^4}{8\mu} \frac{\partial P}{\partial z'} + \frac{D_s R^3}{2\varepsilon} \frac{\partial P}{\partial z'} \right) = 0 \quad (21)$$

and from equation (20)

$$\frac{\partial P}{\partial z'} = \frac{\partial}{\partial z'} \left( \frac{\gamma}{R(z', t)} \right) - \rho g \cos \theta. \quad (22)$$

Deviations of surface tension with respect to equilibrium being small, equation (22) simplifies to

$$\frac{\partial P}{\partial z'} = \gamma_{\text{eq}} \frac{\partial}{\partial z'} \left( \frac{1}{R(z', t)} \right) - \rho g \cos \theta. \quad (23)$$

Substituting equation (23) in equation (21), it follows that

$$\begin{aligned} \frac{\partial R^2}{\partial t} + \frac{\partial}{\partial z'} \left[ \frac{1}{8\mu} \left( \gamma_{\text{eq}} R^2 \frac{\partial R}{\partial z'} + R^4 \rho g \cos \theta \right) \right. \\ \left. + \frac{D_s}{2\varepsilon} \left( \gamma_{\text{eq}} R \frac{\partial R}{\partial z'} + R^3 \rho g \cos \theta \right) \right] = 0. \end{aligned} \quad (24)$$

This is the evolution equation of the radius  $R(z', t)$  for a channel tilted at an angle  $\theta$  with respect to the vertical axis.

### 3.2 Foam drainage equation

With a good approximation, we can assume that Plateau borders in a foam are randomly oriented. The foam drainage equation is obtained by averaging equation (24) over  $\theta$ . We replace the  $z'$  coordinate by the vertical coordinate  $z = z' \cos \theta$ . Thus

$$\frac{\partial}{\partial z'} \equiv \cos \theta \frac{\partial}{\partial z}.$$

As

$$\langle \cos^2 \theta \rangle = \frac{1}{3},$$

it follows that

$$\begin{aligned} \frac{\partial R^2}{\partial t} + \frac{\partial}{\partial z} \left[ \frac{1}{24\mu} \left( \gamma_{\text{eq}} R^2 \frac{\partial R}{\partial z} + \rho g R^4 \right) \right. \\ \left. + \frac{D_s}{6\varepsilon} \left( \gamma_{\text{eq}} R \frac{\partial R}{\partial z} + \rho g R^3 \right) \right] = 0. \end{aligned} \quad (25)$$

In order to derive the drainage equation, we now introduce the channel cross-section  $A(z, t)$ . If we replace the channel by a cylinder, it follows that

$$\begin{aligned} \frac{\partial A}{\partial t} + \frac{\partial}{\partial z} \left[ \frac{1}{24\mu} \left( \frac{\gamma \sqrt{A}}{2\sqrt{\pi}} \frac{\partial A}{\partial z} + \frac{\rho g}{\pi} A^2 \right) \right. \\ \left. + \frac{D_s}{6\varepsilon} \left( \frac{\gamma}{2} \frac{\partial A}{\partial z} + \frac{\rho g}{\sqrt{\pi}} A^{\frac{3}{2}} \right) \right] = 0. \end{aligned} \quad (26)$$

This is the foam drainage equation for cylindrical channels. Since the liquid fraction  $\phi$  is proportional to  $A$ , this equation describes the evolution of the liquid fraction in space and time.

The actual channels being Plateau borders, the surface curvature has the opposite sign. This is equivalent to changing the sign of  $\gamma$  in equation (26). The numerical prefactors should also be modified.

Interestingly, the second term of the above drainage equation is a sum of the corresponding terms in the Trinity model [2] and in the Harvard model [6].

When  $M = \frac{\mu D_s}{\varepsilon R} \ll 1$ , it simplifies to

$$\frac{\partial A}{\partial t} + \frac{1}{24\mu} \frac{\partial}{\partial z} \left( \frac{\gamma_{\text{eq}} \sqrt{A}}{2\sqrt{\pi}} \frac{\partial A}{\partial z} + \frac{\rho g}{\pi} A^2 \right) = 0,$$

which is the Trinity drainage equation.

If  $M \gg 1$ , equation (26) simplifies to

$$\frac{\partial A}{\partial t} + \frac{D_s}{6\varepsilon} \frac{\partial}{\partial z} \left( \frac{\gamma_{\text{eq}}}{2} \frac{\partial A}{\partial z} + \frac{\rho g}{\sqrt{\pi}} A^{\frac{3}{2}} \right) = 0,$$

which is the Harvard drainage equation. However, in reference [6], the second term arises from dissipation in the nodes, whereas in the present calculation they arise from dissipation at the surface of the Plateau borders.

The dissipation in the nodes, if present, should also be accounted for. In the Harvard model [6], a foam permeability  $k(\phi)$  is introduced by analogy with porous media.

By considering the balance energy over a ‘‘dog-bone’’ foam network unit, the authors obtain an expression for its dependence upon liquid fraction:

$$k(\phi) = \left( \frac{K_{\text{vertex}}}{\phi^{1/2}} + \frac{K_{\perp \text{channel}}}{\phi} + K_{\parallel \text{channel}} \right)^{-1},$$

where  $K_{\text{vertex}}$ ,  $K_{\perp \text{channel}}$ ,  $K_{\parallel \text{channel}}$  are, respectively, related to dissipation in nodes, transverse dissipation in channels and longitudinal dissipation in channels. They then use Darcy law to relate velocity and pressure:

$$\mathbf{v} = -\frac{k(\phi)}{\mu} \nabla P$$

(where  $P$  is defined by Eq. (2)) to obtain the drainage equation [6]. Since  $k(\phi)$  is not a sum of contributions of dissipation in nodes and channels, the overall contribution of the nodes will not be a simple addition of a new term in our drainage equation.

Without nodes dissipation,  $M = \frac{\mu D_s}{\varepsilon R}$  is the control parameter describing the balance between bulk and surface dissipation. This parameter is different from that of Kraynik  $M_K = \frac{\mu R}{\mu_s}$  which involves surface shear viscosity. Here we have assumed that the surface velocity is independent of the azimuthal angle  $\varphi$ , so that flow does not produce pure shear in the surface monolayer (the surface is nevertheless sheared, because the flow is not purely dilatational). On the other hand, Leonard and Lemlich did not account for the surface tension gradients considered here. It is interesting to note that the ratio between the two  $M$  numbers is equal to the ratio of the surface dilational viscosity of Boussinesq  $\kappa$  and of its equivalent calculated by Levich for insoluble monolayers  $\varepsilon a^2/D_s$  for the problem of rising bubbles (with  $a$  the bubble radius instead of the radius of curvature of the Plateau border).

Let us now estimate the value of  $M$ . With  $\varepsilon \sim 10$  mN/m,  $D_s \sim 10^{-11}$  m<sup>2</sup>/s [21,22]  $\mu \sim 10^{-3}$  Pa.s,  $R \sim 0.1$  mm (millimeter bubbles,  $\phi \sim 1\%$ ), one finds  $M \sim 10^{-8}$ . Therefore, it can be concluded that for surfactants with very small water solubilities, the flow in the Plateau borders will always be Poiseuille-like, and drainage will follow the Trinity model equation provided node dissipation is not too large.

### 3.3 Case of soluble monolayers

We now extend the analytical solution of the previous section to the more general case of a surfactant soluble in the liquid phase. In our analysis we include both surfactant diffusion and convection.

We follow exactly the same methodology as we did in the insoluble surfactant case; *i.e.* we assume that all variables depend implicitly on time through the channel radius and that deviations of surface and bulk concentration with respect to equilibrium are small:  $\Gamma = \Gamma_{\text{eq}} + \delta\Gamma$ , with  $\delta\Gamma \ll \Gamma_{\text{eq}}$  implying that  $\gamma = \gamma_{\text{eq}} + \delta\gamma$ , with  $\delta\gamma = \varepsilon \delta\Gamma/\Gamma_{\text{eq}} \ll \gamma_{\text{eq}}$ .

Introducing the mean concentration  $\bar{C}(z', t)$ :

$$\bar{C}(z', t) = \frac{1}{A(z', t)} \iint_{A(z', t)} C(r, z', t) r dr d\varphi,$$

we also assume that  $\bar{C} = C_{\text{eq}} + \delta\bar{C}$ , with  $\delta\bar{C} \ll C_{\text{eq}}$ .

With these assumptions equations (7) and (8) simplify to

$$C_{\text{eq}} \frac{\partial v}{\partial z'} - \frac{D}{r} \frac{\partial}{\partial r} \left( r \frac{\partial C}{\partial r} \right) - D \frac{\partial^2 C}{\partial z'^2} = 0, \quad (27)$$

$$\Gamma_{\text{eq}} \frac{\partial U}{\partial z'} - D_s \frac{\partial^2 \Gamma}{\partial z'^2} = -D \left( \frac{\partial C}{\partial r} \right)_{r=R}. \quad (28)$$

Integrating equation (27), we obtain

$$\int_0^{R(z', t)} \left( C_{\text{eq}} \frac{\partial v}{\partial z'} - D \frac{\partial^2 C}{\partial z'^2} \right) r dr = DR \left( \frac{\partial C}{\partial r} \right)_{r=R}.$$

Thus

$$\int_0^{R(z', t)} \left( C_{\text{eq}} \frac{\partial v}{\partial z'} - D \frac{\partial^2 C}{\partial z'^2} \right) r dr + \Gamma_{\text{eq}} R \frac{\partial U}{\partial z'} - D_s R \frac{\partial^2 \Gamma}{\partial z'^2} = 0.$$

In the lubrication approximation,  $\frac{\partial v}{\partial z'}$  and  $\frac{\partial^2 C}{\partial z'^2}$  can be calculated at fixed  $R(z', t)$ , (*i.e.* by considering that  $\frac{\partial R}{\partial z'} = 0$ ). The above equation then simplifies to (since  $\frac{\partial v}{\partial z'} = \frac{\partial U}{\partial z'}$ )

$$C_{\text{eq}} \frac{R^2}{2} \frac{\partial U}{\partial z'} - D \frac{R^2}{2} \frac{\partial^2 \bar{C}}{\partial z'^2} + \Gamma_{\text{eq}} R \frac{\partial U}{\partial z'} - D_s R \frac{\partial^2 \Gamma}{\partial z'^2} = 0. \quad (29)$$

Assuming that adsorption and desorption are very fast so that interface and bulk are in local equilibrium, we can relate the average bulk and surface concentrations through an equation of state (*e.g.*, Langmuir, Frumkin, etc. [23]) as

$$\frac{\partial \bar{C}}{\partial z'} = \frac{1}{\beta} \frac{\partial \Gamma}{\partial z'},$$

where  $\beta = \left( \frac{d\Gamma}{d\bar{C}} \right)_{\text{eq}}$ .

Substituting the expression of  $\frac{\partial \bar{C}}{\partial z'}$  into equation (29), we finally obtain

$$\left( \Gamma_{\text{eq}} + C_{\text{eq}} \frac{R}{2} \right) \frac{\partial U}{\partial z'} - \left( D_s + D \frac{R}{2\beta} \right) \frac{\partial^2 \Gamma}{\partial z'^2} = 0.$$

With the Langmuir equation of state,  $\beta = \frac{C_a \Gamma_{\text{eq}}}{C_{\text{eq}}^2}$ , where  $C_a$  is the Szykowski concentration. Typically,  $\Gamma_{\text{eq}} \sim 10^{-6}$  kg/m<sup>2</sup>,  $C_{\text{eq}} \sim 1$  kg/m<sup>3</sup>,  $C_a \sim 10^{-1}$  kg/m<sup>3</sup>,  $\beta \sim 10^{-7}$  m,  $D_s \sim 10^{-11}$  m<sup>2</sup>/s,  $D \sim 10^{-9}$  m<sup>2</sup>/s,  $R \gtrsim 10^{-4}$  m, so  $C_{\text{eq}} \frac{R}{2} \gg \Gamma_{\text{eq}}$  and  $D \frac{R}{2\beta} \gg D_s$ . The above equation then simplifies to

$$C_{\text{eq}} \frac{\partial U}{\partial z'} - \frac{D}{\beta} \frac{\partial^2 \Gamma}{\partial z'^2} = 0. \quad (30)$$

Equation (30) is formally equivalent to equation (16) for an insoluble monolayer with  $\Gamma_{\text{eq}}$  and  $D_s$  replaced, respectively, by  $\beta C_{\text{eq}}$  and  $D$ .

By integrating equation (30), we obtain

$$\frac{\partial \Gamma}{\partial z'} = \frac{\beta C_{\text{eq}}}{D} (U(z', t) - K_1), \quad (31)$$

where  $K_1$  is an integration constant that we can choose equal to zero following the same arguments as for the insoluble monolayer. Substituting the above expression for  $\frac{\partial \Gamma}{\partial z'}$  in equation (15), we obtain

$$-\frac{\varepsilon \beta C_{\text{eq}}}{D \Gamma_{\text{eq}}} U(z', t) + (\mu_s + \kappa) \frac{\partial^2 U}{\partial z'^2} = \frac{R}{2} \frac{\partial P}{\partial z'}.$$

In view of the order of magnitude of the various coefficients, the viscous term in the above equation is negligible as for the case of an insoluble monolayer. Thus

$$U(z', t) = -\frac{D \Gamma_{\text{eq}}}{\varepsilon \beta C_{\text{eq}}} \frac{R}{2} \frac{\partial P}{\partial z'}.$$

Now we follow the same methodology as for the insoluble monolayer: substituting the above expression for  $U$  and the expression for  $\frac{\partial \Gamma}{\partial z'}$  (Eq. (23)) in equation (5), then averaging over  $\theta$  and introducing channel cross-section  $A$  rather than the radius, we finally obtain the evolution equation

$$\frac{\partial A}{\partial t} + \frac{\partial}{\partial z} \left[ \frac{1}{24\mu} \left( \frac{\gamma_{\text{eq}} \sqrt{A}}{2\sqrt{\pi}} \frac{\partial A}{\partial z} + \frac{\rho g}{\pi} A^2 \right) + \frac{D \Gamma_{\text{eq}}}{6\varepsilon \beta C_{\text{eq}}} \left( \frac{\gamma_{\text{eq}}}{2} \frac{\partial A}{\partial z} + \frac{\rho g}{\sqrt{\pi}} A^{\frac{3}{2}} \right) \right] = 0. \quad (32)$$

We see that equation (32) is formally identical to equation (26) provided  $D_s$  is replaced by  $\frac{D \Gamma_{\text{eq}}}{\beta C_{\text{eq}}}$ . The control parameter is now  $M = \frac{\mu D \Gamma_{\text{eq}}}{R \varepsilon \beta C_{\text{eq}}}$ . Numerically  $\frac{D \Gamma_{\text{eq}}}{\beta C_{\text{eq}}} \sim 10^3 D_s$ , so that  $M \sim 10^{-5}$ , still very small. The flow in the Plateau border is therefore still Poiseuille flow, and no transition towards the plug-flow regime is expected.

If the surfactant concentration is high enough, micelles could be present. It was shown by Joos and coworkers that micelles do not adsorb at the interface, but exchange their monomeric surfactants with the bulk solution, allowing these monomers to adsorb afterwards [24]. Consequently, the process implies exchanges of monomers between micelles and bulk solution, that can only slow down the process. In the above equations, an apparent diffusion coefficient  $D_{\text{app}}$  could be used with  $D_{\text{app}} \lesssim D$ . As a result, no transition towards plug-flow regime could be expected from the presence of micelles.

## 4 Solutions of the drainage equation

Let us now look for solutions to the drainage equations for a more realistic Plateau border. Let us first inspect how drainage equations (26) and (32) are to be changed:

- $R$  will be now the radius of curvature of the Plateau border.

- The curvature of the surface is of opposite sign. This is equivalent to changing the sign of  $\gamma$  in equation (13).
- $\pi$  is replaced with  $C_{\text{area}} = A/R^2 = \sqrt{3} - \pi/2$ .
- We introduce a form factor  $f_1 = 49.5$  [2,4] in the expression of the mean velocity in such a way that the expression of the mean velocity is

$$\bar{v}(z', t) = -\frac{A}{f_1\mu} \frac{\partial P}{\partial z'} + U(z', t).$$

- Because we lose the symmetry condition, the variables are dependent on the  $\varphi$  coordinate even in the absence of gravity. However, using the symmetry properties of the Plateau border (cf. Fig. 1a) we assume that the mean normal gradient or the velocity at the surface is given by

$$\frac{1}{\pi R} \oint_{\mathcal{C}} \left( \frac{\partial v}{\partial r} \right)_{r=R} dl = \frac{R}{f_2\mu} \frac{\partial P}{\partial z'},$$

where  $\mathcal{C}$  is the perimeter of the Plateau border:  $\mathcal{C} = \pi R$  and  $f_2$  is a second form factor. For a cylindrical channel,  $f_2 = 2$ .

In that case we replace the tangential stress balance equation (14) by the following ‘‘averaged’’ equation:

$$\frac{R}{f_2} \frac{\partial P}{\partial z'} = \frac{\partial \gamma}{\partial z'} + (\mu_s + \kappa) \frac{\partial^2 U}{\partial z'^2}.$$

It should be noted that since we neglect the  $\varphi$ -dependence of the velocity, our approach is simplistic [4, 5].

After carrying out these modifications, the drainage equation (26) for an insoluble monolayer becomes

$$\begin{aligned} \frac{\partial A}{\partial t} + \frac{\partial}{\partial z} \left[ \frac{1}{3f_1\mu} \left( \rho g A^2 - \frac{\gamma_{\text{eq}} \sqrt{C_{\text{area}}}}{2} \sqrt{A} \frac{\partial A}{\partial z} \right) \right. \\ \left. + \frac{D_s}{3f_2\varepsilon \sqrt{C_{\text{area}}}} \left( \rho g A^{\frac{3}{2}} - \frac{\gamma_{\text{eq}} \sqrt{C_{\text{area}}}}{2} \frac{\partial A}{\partial z} \right) \right] = 0. \end{aligned}$$

For the soluble monolayer, the drainage equation is the same, with  $D_s$  replaced by  $\frac{D\Gamma_{\text{eq}}}{\beta C_{\text{eq}}}$ .

It is convenient to introduce reduced units: a characteristic distance  $z_0$ , a characteristic time  $t_0$  and a characteristic area  $a_0$  such as

$$z = z_0\zeta, \quad t = t_0\tau, \quad A = a_0\alpha,$$

where  $\zeta, \tau, \alpha$  are dimensionless variables, and  $z_0 = \sqrt{\frac{\gamma}{\rho g}}$ ,

$$t_0 = \frac{3f_1\mu}{C_{\text{area}}} \sqrt{\frac{1}{\rho g \gamma}}, \quad a_0 = C_{\text{area}} z_0^2.$$

The drainage equation becomes

$$\frac{\partial \alpha}{\partial \tau} + \frac{\partial}{\partial \zeta} \left[ \left( \alpha^2 - \frac{\sqrt{\alpha}}{2} \frac{\partial \alpha}{\partial \zeta} \right) + N \left( \alpha^{\frac{3}{2}} - \frac{1}{2} \frac{\partial \alpha}{\partial \zeta} \right) \right] = 0, \quad (33)$$

where  $N$  is a new control parameter:  $N = \frac{f_1\mu D_s}{f_2 C_{\text{area}} \varepsilon} \sqrt{\frac{\rho g}{\gamma}}$  for insoluble surfactants and  $N = \frac{f_1\mu D\Gamma_{\text{eq}}}{f_2 C_{\text{area}} \varepsilon \beta C_{\text{eq}}} \sqrt{\frac{\rho g}{\gamma}}$  for soluble ones.

$z_0 = \sqrt{\frac{\gamma}{\rho g}}$  is the capillary length, typically of the order of 1 mm. Then  $N$  represents the ratio between the length  $\frac{f_1\mu D_s}{f_2 C_{\text{area}} \varepsilon}$  (or  $\frac{f_1\mu D\Gamma_{\text{eq}}}{f_2 C_{\text{area}} \varepsilon \beta C_{\text{eq}}}$ ) and the capillary length.

#### 4.1 The static case —equilibrium

The second term of equation (33) is the local dimensionless flow rate. In the static case, the flow is zero everywhere:

$$\alpha^2 - \frac{\sqrt{\alpha}}{2} \frac{\partial \alpha}{\partial \zeta} + N \left( \alpha^{\frac{3}{2}} - \frac{1}{2} \frac{\partial \alpha}{\partial \zeta} \right) = 0;$$

the solution is

$$\alpha(\zeta) = \frac{1}{(\zeta - \zeta_0)^2}.$$

The static profile is independent of the parameter  $N$ , meaning that, as expected, the equilibrium state is independent of the flow regime in the Plateau border.

#### 4.2 The stationary case —steady drainage

In the stationary case the flow is constant:

$$\alpha^2 - \frac{\sqrt{\alpha}}{2} \frac{\partial \alpha}{\partial \zeta} + N \left( \alpha^{\frac{3}{2}} - \frac{1}{2} \frac{\partial \alpha}{\partial \zeta} \right) = \text{const.}$$

The solution corresponding to a steady-state flow is  $\alpha(\zeta, \tau) = \alpha_0$  and the dimensionless flow rate is then

$$q = \alpha_0^2 + N\alpha_0^{\frac{3}{2}}. \quad (34)$$

#### 4.3 The solitary wave solution

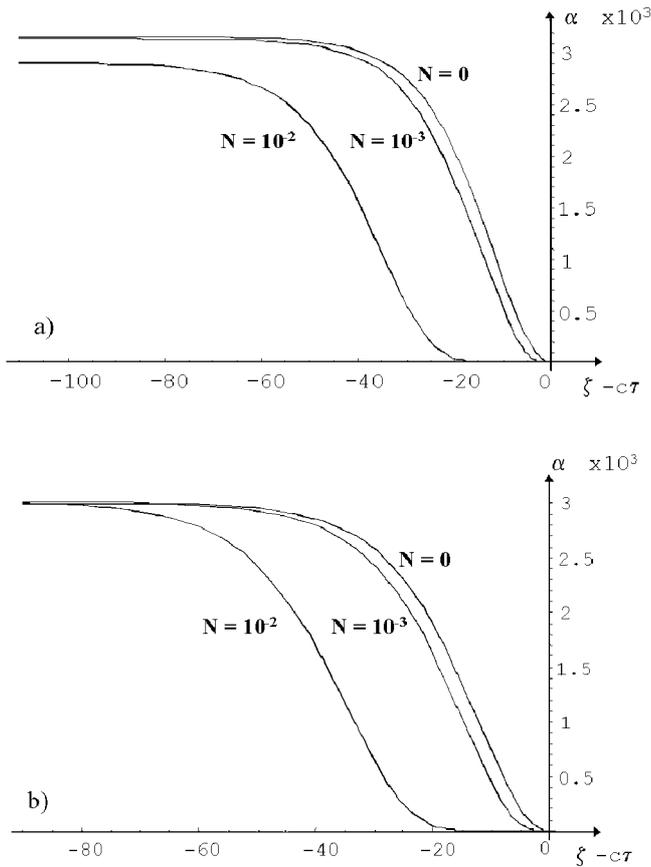
Equation (33) has no exact general solution. Solitary wave solutions in the form  $\alpha(\zeta, \tau) = f(\zeta - c\tau)$  (where  $c$  is the dimensionless front velocity) have been found in the cases  $N \gg 1$  and  $N \ll 1$ . We have calculated numerical solutions for intermediate values of  $N$ . Figures 3a) and b) represent the profile for different values of the parameter  $N$ , respectively, at fixed flow rate and at fixed downstream value of the dimensionless area  $\alpha_0 = f(-\infty)$ . We see that, as expected, the shape of the profile evolves continuously between the extreme shapes.

Long after the front passage, the downstream value of the area  $\alpha_0$  is related to the (dimensionless) flow rate  $q$  by equation (34). Thus the front velocity is given by

$$c = \alpha_0 + N\sqrt{\alpha_0}.$$

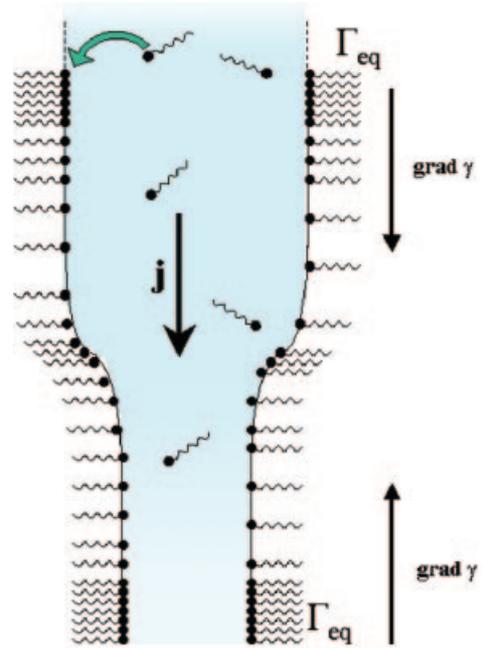
### 5 Non-linear behaviour

Up to now, we have considered that the bulk solution and the liquid surface were in equilibrium. During forced drainage, the size of the Plateau borders changes rapidly in the region of the water front, which is at least two to three bubbles thick. Since  $R$  is proportional to  $\sqrt{\phi}$  and typically above the front  $\phi \sim 10\%$  and below the front  $\phi \sim 1\%$ , the radius changes by a factor 3, and the area by a factor 10. The surfactant is therefore rapidly depleted, and important Marangoni flows are generated, as shown in Figure 4. This situation resembles that observed with an



**Fig. 3.** a) Numerical solutions for forced drainage at a fixed dimensionless flow rate ( $q = 10^{-5}$ ) for  $N = 0$ ,  $N = 10^{-3}$  and  $N = 10^{-2}$ . The front of the wet foam moves with a constant (dimensionless) velocity  $c$  and without deformation. b) Numerical solutions for forced drainage at fixed dimensionless area ( $\alpha_0 = 3 \cdot 10^{-3}$ ) for  $N = 0$ ,  $N = 10^{-3}$  and  $N = 10^{-2}$ . The curve  $N = 0$  corresponds to the solution of the Trinity model (Poiseuille flow). When  $N$  increases the curve tends to the solution of the Harvard model (plug flow).

overflowing cylinder [25], in which a liquid is pumped upward through a metal cylinder and allowed to flow freely over its top rim, accomplishing a steady-state dilation of the horizontal surface. It was found that with this device, the surface velocity is increased by factors up to ten when a surfactant is added to water, with a maximum around the critical micellar concentration (concentrated solutions flow as pure water). In these conditions,  $d \ln A / dt \sim 10 \text{ s}^{-1}$ , a value comparable to that achieved in forced drainage experiments. If we stick to the approximations of Section 3, it is impossible to predict a large increase in surface velocity. It is unfortunately very difficult to go beyond the approximations made up to now in the calculations. We can, at this point, only make some comments about a possible connection with the experimentally observed evolution towards the plug-flow regime. One possibility is to assume that the calculation can still be used provided the Gibbs elasticity is replaced by its actual value, very small in the depleted region. The number  $M$  will then be much larger than that calculated in Sec-



**Fig. 4.** Schematic representation of Marangoni flows occurring in a channel, due to surface concentration variations.

tion 3. Another possibility is to find out which  $M$  number is responsible for an increase of velocity by a factor of say 10. Kraynik made use of the results of Leonard and Lemlich to calculate the liquid velocity through the Plateau borders as a function of  $M$  [5]. In order to have the required velocity increase,  $M$  should be around 10, a value which would account for predominantly plug-like flow.

## 6 Conclusion

We have obtained a drainage equation which applies to the most general boundary conditions at the surface of the Plateau borders. In the limit of rigid boundary conditions, the equation reduces to the Trinity equation and in the limit of fluid boundary conditions to the Harvard equation. In this last case, however, the equation is derived considering the dissipation in the nodes which we have not included in our model.

Our equation allows to clarify the role of the surface parameters in drainage and shows that the main contribution comes from the surface elasticity, the role of surface viscosities being negligible. The influence of surfactant solubility is the same as in the problem of rising velocity of isolated bubbles and of drainage of soap films. Our calculations predict that for admitted values of the surface parameters, the drainage regime should always correspond to the rigid boundary conditions. We are therefore led to propose other possible origins for the plug flow regime:

- Viscous dissipation in the nodes dominating over dissipation into Plateau borders (Harvard model).
- The velocity lacks circular symmetry in the Plateau border sections, and the surface is sheared (Leonard-

Lemlich model). However,  $M \sim 10^{-3}$  with the SDS-dodecanol systems tested in [12] for which this origin can be excluded.

- The large expansion of Plateau borders during drainage that produces large Marangoni flows as proposed in Section 5.

It is unfortunate that no complete and exact drainage equation can be found in any of these cases. The only complete solution found here in the small perturbation approximation is unable to predict a plug-flow regime when the actual values of the surface parameters are considered.

Clearly, more experimental work is needed to discriminate between the possible origins of the plug-flow regime.

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## References

1. D. Weaire, S. Hutzler, *The Physics of Foams* (Oxford Press, 1999).
2. D. Weaire, S. Hutzler, G. Verbist, E.A.J. Peters, *Adv. Chem. Phys.* **102**, 315 (1997).
3. A. Bhakta, E. Ruckenstein, *Adv. Colloid Interface Sci.* **70**, 1 (1997).
4. R.A. Leonard, R. Lemlich, *AIChEJ* **11**, 18 (1965).
5. A.M. Kraynik, Sandia Report SAND 83-0844 (1983).
6. S.A. Koehler, S. Hilgenfeldt, H.A. Stone, *Phys. Rev. Lett.* **82**, 4232 (1999); *Langmuir* **16**, 6327 (2000).
7. A. St Jalmes, M.U. Vera, D.J. Durian, *Europhys. Lett.* **50**, 695 (2000).
8. G. Verbist, D. Weaire, *Europhys. Lett.* **26**, 631 (1994).
9. V. Goldshtein, I. Goldfarb, I. Schreiber, *Int. J. Multiphase Flow* **22**, 991 (1996).
10. D. Weaire, N. Pittet, S. Hutzler, D. Pardal, *Phys. Rev. Lett.* **71**, 2670 (1993); S. Hutzler, G. Verbist, D. Weaire, J.A. van der Steen, *Europhys. Lett.* **31**, 497 (1995).
11. S. Stoyanov, C. Dushkin, D. Langevin, D. Weaire, G. Verbist, *Langmuir* **14**, 4663 (1998).
12. M. Durand, G. Martinoty, D. Langevin, *Phys. Rev. E* **60**, R6307 (1999).
13. A.M. Poskanzer, F. Goodrich, *J. Phys. Chem.* **79**, 2122 (1975).
14. N.F. Djabbarah, D.T. Wasan, *Chem. Eng. Sci.* **37**, 175 (1982).
15. J. Boussinesq, *Ann. Chim. Phys.* **29**, 349, 357, 364 (1913).
16. V.G. Levich, *Physico-Chemical Hydrodynamics* (Prentice Hall, 1962), Chapt. 8.
17. I.B. Ivanov, D.S. Dimitrov, *Thin Liquid Films*, edited by I.B. Ivanov (Marcel Dekker, 1988).
18. A. Sonin, A. Bonfillon, D. Langevin, *J. Colloid Interface Sci.* **162**, 323 (1994).
19. L.E. Scriven, *Chem. Eng. Sci.* **12**, 98 (1960).
20. F. Goodrich, *Proc. R. Soc. London, Ser. A* **374**, 341 (1981).
21. K. Tamada, S. Kim, H. Yu, *Langmuir* **9**, 1545 (1993).
22. M. Forstner, J. Käs, D. Martin, *Langmuir* **17**, 567 (2001).
23. E. Lucassen, *Prog. Surf. Sci. Membrane Sci.* **10**, 253 (1976).
24. P. Joos, J. van Hunsel, *Colloids Surf.* **33**, 99 (1988).
25. D.J.M. Berjink-Martens, H.J. Bos, A. Prins, *J. Colloid Interface Sci.* **165**, 221 (1994).

## List of parameters

$\varepsilon$	Gibbs elasticity
$\mu$	bulk viscosity
$\mu_s$	surface shear viscosity
$\kappa$	dilational surface viscosity
$D$	bulk diffusion coefficient
$D_s$	surface diffusion coefficient
$C$	bulk surfactant concentration
$\Gamma$	surface surfactant concentration
$R$	channel radius
$A$	channel area
$\alpha$	dimensionless area
$\zeta$	dimensionless vertical coordinate
$\tau$	dimensionless time
$z_0$	characteristic length $\sqrt{\frac{\gamma}{\rho g}}$
$t_0$	characteristic time $\frac{24\mu}{\sqrt{\rho g \gamma}}$
$a_0$	characteristic area $\pi z_0^2$
$v$	velocity inside a channel
$U$	surface velocity
$p$	pressure inside a channel