Influence of surfactant on rounded and pointed bubbles in 2-D Stokes flow

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Abstract

A simple plane flow model is used to examine the effects of surfactant on bubbles evolving in slow viscous flow. General properties of the time-dependent evolution as well as exact solutions for the steady state shape of the interface and distribution of surfactant are obtained for a rather general class of far-field extensional flows. The steady solutions include a class for which 'stagnant caps' of surfactant partially coat the bubble surface. The governing equations for these stagnant cap bubbles feature boundary data which switches across free boundary points representing the cap edges. These points are shown to correspond to singularities in the surfactant distribution, the location and strength of which are determined as part of the solution. Our steady bubble solutions comprise shapes with rounded as well as pointed ends, depending on the far-field flow conditions. Unlike the clean flow problem, we find in all cases an upper bound on the strain rate for which steady solutions exist. A possible connection with the phenomenon of tip streaming is suggested.

Key words. surfactant, bubbles, tip streaming, singularity.

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1 Introduction

Studies of the deformation and burst of bubbles and drops subject to extensional flows at low Reynolds have uncovered a wide variety of interesting phenomena. The pioneering experiments of G. I. Taylor [37], in which a single drop placed in a highly viscous fluid was subjected to shear and strain type flows, revealed the existence of steady rounded and pointed drops, as well as bursting drops of each type. Later experiments [8, 29, 38] have confirmed and extended Taylor's results. In many of these early studies the word "bursting" refers to the non-existence of a steady drop shape when the applied shear or strain exceeds a critical value, rather than the actual break-up of the drop. Reviews by Acrivos [1] and Rallison [25] summarize some of the early experiments, while that of Stone [34] covers more recent developments.

One of the most interesting phenomena observed in drops and bubbles subjected to extensional flows is the process of tip streaming. Tip streaming is a mode of breakup where a drop develops a deformed shape featuring cusp-like ends, from which small drops are emitted into the exterior fluid (see e.g., [8, 10, 29] for experimental results). The shear or strain rate required for this type of breakup is typically much less than that required for the normal mode of breakup (fracture), in which a drop ruptures into two or three pieces of similar size, with a few tiny satellite drops in between [8]. Furthermore, the droplets produced by tip streaming can be much smaller than those produced by fracture. The experiments of [8] provide strong evidence that tip streaming occurs when interfacial tension gradients develop due to the presence of surfactant. Therefore, it is vital to take the influence of surfactant into account when examining the various modes of breakup in a drop exposed to shearing or straining flows.

There are a number of numerical studies concerning the influence of surfactant on the deformation of drops and bubbles in extensional flows. Stone and Leal [32] employ a boundary integral method to study the time dependent evolution of a drop in an axisymmetric pure straining flow. Milliken, Stone and Leal [21] study the effect of varying the viscosity ratio between the drop and ambient fluid, as well as the consequences of using a nonlinear equation of state. Other numerical studies include [18, 20]. In each of these studies, steady state solutions are characterized by following the time dependent evolution until a steady bubble profile is reached. In this way, the time dependent calculations are able to piece together the branch of steady state solutions from a sphere at zero strain rate to the point at which a steady solution no longer exists. However, none of these studies construct a complete steady solution branch (including unstable steady states) by directly solving the steady state equations. In addition, pointed bubbles are not resolved in detail, and there is no extensive examination of the tip streaming mode of breakup.

Theoretical studies of deforming drops which incorporate surfactant effects are scant. Flumerfelt [9] employed asymptotic analysis to examine small deformations of spherical drops in extensional flows. This calculation was repeated and extended in [20, 32]. A theoretical treatment of surfactant effects in the large deformation regime is presently not available.

There is a much larger body of literature investigating the influence of surfactant on a steadily translating drop in an otherwise quiescent fluid. Harper [12] provides an early review. Here, the surfactant often accumulates in the form of a stagnant cap at the rear of the drop (Figure 1a). This results in a surface tension gradient which retards the motion of the drop. Theoretical analysis of steady creeping flow past a circular drop with a stagnant cap has been considered in [7, 11, 30]. Under certain assumptions, Sadhal and Johnson [30] obtained an analytical expression for the stream function as an infinite series whose coefficients are functions of the cap angle. However, these studies were limited to spherical bubbles. Furthermore, the concentration of surfactant on the bubble surface was not obtained, and the nature of a potential singularity at the endpoints of the surfactant cap was not examined.

The boundary value problem associated with a stagnant cap bubble in Stokes flow is characterized by linear field equations, mixed boundary conditions at the bubble surface, and free boundary *curves* (or points in two-dimensional flow) that define the edges of the cap. The location of these curves needs to be determined as part of the solution. For spherical bubbles, these free curves are the only geometric unknown, whereas for deformable bubbles the entire bubble surface forms an additional free boundary. This boundary value problem possesses a number of features in common with the codimension-two free boundary problems discussed in the review [16], where the presence of boundary data that switches across codimension two free boundaries is a distinguishing trait.

In this paper, a simple plane flow model is employed to examine the evolution of a bubble in strain type flows, taking into account the influence of surfactant. Plane flow models have the advantage that powerful techniques from complex analysis may be utilized to obtain analytical solutions. The hope is that these can shed light on the qualitative aspects of three dimensional flows. In this spirit, Richardson [26, 27] obtained exact solutions for an inviscid two dimensional bubble in a linear and parabolic flow field, in the case when surfactant is absent. These solutions were later generalized by Antanovskii [3] and by Tanveer and Vasconcelos [35] to time evolving bubbles, and by Antanovskii [4, 5] to more general polynomial flow fields at infinity. This latter work includes a remarkable class of explicit steady solutions in which the bubble exhibits cusp-like ends. Related analyses of two-dimensional flows include [6, 13, 15, 14, 28]. The striking similarities of the cusped bubble profiles computed in [27] and [4, 5] with experimentally observed three-dimensional bubbles suggests that the two-dimensional model may capture much of the essential physics.

The application of complex variable techniques allows us to derive a number of properties of the time dependent evolution, and to formulate *exact solutions* for the steady state shape of the interface and the distribution of surfactant for a rather general class of far-field flow conditions. Our steady solutions include those for which the bubble is covered with a nonzero concentration of surfactant, as well as bubbles with stagnant caps of surfactant that collect on the bubble sides (Figure 1b). In the latter case, the closed form solution is obtained by reducing the singular integral equation for the surfactant concentration to the so-called Riemann problem. The free boundary points at the cap edges are shown to correspond to singularities in the surfactant concentration function. Physical constraints on the severity of these singularities then provides a unique solution to the steady problem.

Unlike the earlier studies of a translating drop, we are able to characterize the deformation of the steady bubble, as well as the size of the stagnant cap and distribution of surfactant, as a function of the far-field flow conditions. We find nonuniqueness in the form of two solutions for certain strain rates, and a lack of a steady solution at other strain rates. For polynomial far-field boundary conditions corresponding to flow in a four roller mill, both rounded and cusped steady bubble solutions are found. In contrast to the clean flow problem, we find an upper bound on the strain rate for which a steady solution exists. Possible connections with the tip streaming phenomenon are suggested. Since the main purpose of this paper is to formulate the mathematical theory and present the steady solutions, these connections will be further explored in a future paper.

2 Mathematical Formulation

2.1 Governing Equations

Consider an inviscid bubble placed in two dimensional slow viscous flow. The fluid outside of the bubble has a large viscosity μ and is taken to be incompressible, with the same density as the inner fluid. Since the fluid inside the bubble has negligible viscosity, the bubble pressure is constant; without loss of generality the constant is chosen to be zero. In addition, the bubble is considered to be neutrally buoyant in the exterior fluid, so that gravitational effects can be ignored. Neglecting inertial effects, the fluid motion is governed by the Stokes equations

$$\begin{aligned} \mu\nabla^2\mathbf{u} &= \nabla p \\ \nabla\cdot\mathbf{u} &= 0 \end{aligned} \tag{1}$$

where $\mathbf{u}(x, y)$ is the fluid velocity and p is the pressure.

On the bubble boundary we impose the kinematic condition that the normal velocity of a point on the boundary equal the corresponding velocity of the fluid at that point, i.e.,

$$\mathbf{u}\cdot\mathbf{n} = U_n$$

In addition we require a balance of stresses, which is written as

$$-p\mathbf{n} + 2\mu\mathbf{n}\cdot\mathbf{S} = \sigma\kappa\mathbf{n} - \nabla_s\sigma \tag{2}$$

where $\mathbf{n}$ is the outward normal unit vector, $\mathbf{S}$ is the rate of strain tensor whose j, k component is given by

$$s_{j,k} = \frac{1}{2}\left(\frac{\partial u_j}{\partial x_k} + \frac{\partial u_k}{\partial x_j}\right),$$

κ is the interfacial curvature, σ is the surface tension, and ∇_s is the surface gradient operator. The last term in (2) represents the tangential stress (Marangoni force) which results from the dependence of the interfacial tension σ on the non-uniform surfactant concentration , . This concentration is expressed in units of mass of surfactant per unit of interfacial length. The presence of surfactant generally acts to lower interfacial tension, owing to the repulsion of the polar surfactant molecules.

The precise nature of the dependence of surface tension on , is given by an equation of state of the form

$$\sigma = \sigma(,)$$

If the surfactant is present in dilute concentration, a linear relationship between σ and , may be assumed, i.e.,

$$\sigma = \sigma_0(1 - \beta, /, _0) \tag{3}$$

where σ_0 is the surface tension of the clean interface, $,_0$ is the uniform concentration of surfactant that exists in the absence of flow, and β is a parameter that determines the sensitivity of the interfacial tension to changes in surfactant concentration. [1] The linear equation of state has been widely used, even in situations for which the surfactant accumulates due to the action of the flow and thus can no longer be be considered as dilute [20, 32]. Other relations between σ and , are possible. For simplicity, we employ the linear relation (3) although the theory developed here applies equally well with other equations of state.

Since interfacial mobility and flow induced shape changes in the interface combine to lead to a non-uniform surfactant distribution, an equation describing the time-dependent behavior of , is required. This equation takes the form of a convection- diffusion equation (see, e.g., Stone [33], Wong et. al. [39])

$$\frac{\partial ,}{\partial t}|_s - \frac{\partial \mathbf{X}}{\partial t} \cdot \nabla_{\mathbf{s}} , + \nabla_{\mathbf{s}} \cdot (, \mathbf{u_s}) - D_s \nabla_{\mathbf{s}}^{\mathbf{2}} , + , \kappa \mathbf{u} \cdot \mathbf{n} = 0, \tag{4}$$

where $\nabla_{\mathbf{s}}$ is the surface gradient, $\mathbf{u_s}$ represents the velocity vector tangent to the interface, $\mathbf{X}(s,t)$ is a parametric representation of the interface, and D_s is the surface diffusivity. Here we have considered the surfactant to be insoluble, i.e., there is no net flux of surfactant to and from the interface from the bulk liquid. The fifth term in (4) governs changes in the local surface concentration due to stretching and distortion of the interface. Note that the time derivative is taken with respect to fixed s.

To completely specify the problem, boundary conditions are required at infinity. We shall allow rather general (polynomial) behavior at infinity. A commonly considered special case is that of a linear flow field, given by

$$u = \mathbf{E} \cdot \hat{\mathbf{x}} = \begin{pmatrix} G & B - \omega_0/2 \\ B + \omega_0/2 & -G \end{pmatrix} \cdot \hat{\mathbf{x}} \quad \text{as } \hat{\mathbf{x}} \to \infty. \tag{5}$$

The parameters G and B characterize the strain of the external flow, whereas ω_0 is the vorticity.

The preceding problem can be recast in terms of nondimensional quantities if the velocity is rescaled by σ_0/μ, pressure by σ_0/R (where πR^2 is the initial bubble area), surfactant concentration by $,_0$, and length and time by R and $R\mu/\sigma_0$. The problem is then characterized by the dimensionless parameters

$$\mathbf{E}' = \frac{\mu R}{\sigma_0}\mathbf{E}, \quad Pe_s = \frac{\sigma_0 R}{\mu D_s}, \quad \text{and } \beta$$

where Pe_s is the modified surface Peclet number. However, for the remainder of this section we follow [35] and use dimensional quantities.

[1]In terms of physical quantities, $\beta = \frac{RT\Gamma_0}{\sigma_0}$, where R is the gas constant and T is the absolute temperature.

2.2 Complex Variable Formulation

The basic formulae in the complex variable representation of two-dimensional Stokes flow (in the absence of surfactant) are given by Langlois [17]. The formalism has been used to study the motion of bubbles by a number of authors (see Tanveer and Vasconcelos [35] and references therein). Antanovskii [2] generalized the formalism to include the effects of insoluble surfactant for steady flow in a different geometry.

We follow the time-dependent formulation in [35], with modifications to account for the presence of surfactant. Introduce a stream function $\psi(x, y)$ and a stress function $\phi(x, y)$ which satisfy

$$\nabla^2 \psi = -\omega; \quad \nabla^2 \phi = \frac{p}{\mu}.$$

where ω is the fluid vorticity. It is easily seen that ϕ and ψ obey the biharmonic equation

$$\nabla^4 \phi = \nabla^4 \psi = 0.$$

Next introduce the stress-stream function $W(z, \bar{z}) = \phi(x, y) + i\psi(x, y)$ where $z = x + iy$ and the bar denotes complex conjugate. According to the Goursat representation for biharmonic functions (Mikhlin [19]) $W(z, \bar{z})$ can be written

$$W(z, \bar{z}) = \bar{z} f(z) + g(z)$$

where f and g are analytic functions in the fluid region. It is easily seen that the relevant physical quantities can be expressed in terms of f and g as (Langlois [17])

$$\frac{p}{\mu} - i\omega = 4f'(z) \tag{6}$$

$$u_1 + iu_2 = -f(z) + z\bar{f}'(\bar{z}) + \bar{g}'(\bar{z}) \tag{7}$$

$$s_{11} + is_{12} = z\bar{f}''(\bar{z}) + \bar{g}''(\bar{z}) \tag{8}$$

where $\bar{f}$ denotes the operation $\bar{f}(z) = \overline{f(\bar{z})}$ and the prime denotes derivative.

The outward unit normal to the bubble surface can be represented as

$$N = n_1 + in_2 = iz_s = ie^{i\theta} \tag{9}$$

where n_1 and n_2 are the x and y component of $\mathbf{n}$, s is arclength traversed in the clockwise direction, and θ is the angle between the tangent and the real positive x-axis. Using the expression (9), the stress balance equation (2) can be written

$$\begin{aligned} -i[pz_s + 2\mu(s_{11} + is_{12})\bar{z}_s] &= \sigma\kappa(iz_s) - \frac{\partial\sigma}{\partial s} z_s \\ &= -(\sigma z_s)_s \end{aligned} \tag{10}$$

where in the last equality we have used the fact that $\kappa = -\theta_s$ so that $z_{ss} = -i\kappa z_s$. Note that the single term on the righthand side of (10) represents the normal force due to surface tension as well as the Marangoni force. Substituting (6) and (8) into the above equation and integrating the resulting expression with respect to s

$$f(z) + z\bar{f}'(\bar{z}) + \bar{g}'(\bar{z}) = -i\frac{\sigma(s,t)}{2\mu} z_s. \tag{11}$$

Here, we have used some arbitrariness in the specification of the Goursat functions f and g to set the integration constant to zero. Equation (11) constitutes the dynamic boundary condition. We mention in passing that, for steady flow, $\phi = \psi = 0$ which leads to the simplified dynamic boundary condition

$$W = \phi + i\psi = \bar{z}f + g = 0.$$

We turn now to the kinematic boundary condition. Upon inserting (7) into (11) one obtains the identity

$$u_1 + iu_2 = -i\frac{\sigma(s,t)}{2\mu} z_s - 2f(z). \tag{12}$$

At this point it is convenient to consider the conformal map $z(\zeta, t)$ which takes the unit disc in the ζ-plane into the fluid region of the z-plane. This map takes the form

$$z(\zeta, t) = \frac{a(t)}{\zeta} + h(\zeta, t)$$

where h is analytic and $z_\zeta \neq 0$ in the region $|\zeta| \leq 1$ over some nonzero time interval. The extra degree of freedom allowed by the Riemann Mapping Theorem permits a to be chosen real and negative. Symmetry about the x and y axes is enforced by requiring

$$-z(-\zeta) = z(\zeta); \quad \bar{z}(\bar{\zeta}) = z(\zeta). \tag{13}$$

From (12) and the fact that $z_s = i\zeta z_\zeta / |z_\zeta|$ on $|\zeta| = 1$, it is easily seen that the kinematic condition can be written

$$Re\left\{\frac{z_t + 2f(\zeta,t)}{\zeta z_\zeta}\right\} = \frac{\sigma(,\,(\zeta,t))}{2\mu|z_\zeta|} \quad on\ |\zeta| = 1 \tag{14}$$

where the term f is written as shown to stress its functional dependence on ζ. This equation differs from the corresponding clean flow equation only in the dependence of σ on $,(\zeta,t)$.

The complex variable formulation of the equation for $,(\zeta = e^{i\nu}, t)$ is obtained from (4), with the result

$$\frac{\partial ,}{\partial t}|_\nu - Re\left(\frac{,_\nu}{z_\nu} z_t\right) + \frac{1}{|z_\nu|}\frac{\partial}{\partial \nu} Re\, P(\nu,t) - \frac{1}{|z_\nu|} Im\left(\frac{z_{\nu\nu}}{z_\nu}\right) Im\, P(\nu,t) = \frac{1}{|z_\nu|} D_s \frac{\partial}{\partial \nu}\left(\frac{,_\nu}{|z_\nu|}\right) \tag{15}$$

where

$$P(\nu,t) = \frac{(u_1 + iu_2)\bar{z}_\nu ,}{|z_\nu|}; \tag{16}$$

and the subscripts denote partial derivatives. The function $,$ is required to satisfy the imposed symmetries

$$,(-\nu,t) = ,(\nu,t), \quad ,(\pi+\nu,t) = ,(\nu,t) \tag{17}$$

Note that the total amount of surfactant is fixed, so that the integral

$$T = \int_0^{2\pi} ,|z_\nu| d\nu \tag{18}$$

is a conserved quantity.

3 Linear far-field flow

We first consider the far-field velocity field to be that of linear flow, given by (5). For convenience, the constants B and ω_0 are set to zero, although these terms may be easily included in the analysis if desired. Also, the results in this section are presented in non-dimensional form using the nondimensional groups defined at the end of section 2.1; all quantities will be denoted by the same symbol as before, with the understanding that they are nondimensional.

For a linear flow field, it is easily seen from (5), (6), and (7) that f and g' have the following behavior as $\zeta \to 0$ (corresponding to $z \to \infty$)

$$\begin{aligned} f(\zeta,t) &\sim \frac{ap_\infty}{4\zeta} + O(1) \\ g'(\zeta,t) &\sim \frac{Qa}{\zeta} + O(1). \end{aligned}$$

Here we have introduced the capillary number, defined by

$$Q = \frac{RG\mu}{\sigma_0}$$

and the non-dimensional pressure at infinity p_∞. Thus, the quantity in brackets in (14) is an analytic function of ζ for $|\zeta| \leq 1$. An evolution equation for the map $z(\zeta, t)$ for $|\zeta| < 1$ can therefore be obtained by an application of the Poisson Integral Formula with the result

$$z_t + 2f(\zeta, t) = \zeta \left[I(\zeta, t) \right] z_\zeta \tag{19}$$

where

$$I(\zeta, t) = \frac{1}{4\pi i} \oint_{|\zeta'|=1} \frac{d\zeta'}{\zeta'} \left[\frac{\zeta' + \zeta}{\zeta' - \zeta} \right] \frac{\tau(\zeta', t)}{|z_\zeta(\zeta', t)|} \tag{20}$$

and $\tau(\zeta, t) = 1 - \beta$, (ζ, t) is a non-dimensional surface tension. Note that $I(\zeta, t)$ depends on the surfactant distribution via the term $\tau(\zeta, t)$ in the integrand.

Analytic continuation of (19) into the domain $|\zeta| > 1$ allows one to derive several properties of the mapping function $z(\zeta, t)$. The analysis proceeds as in the clean flow problem (see [35]), i.e., deforming the contour and using the dynamic boundary condition to eliminate certain terms, one arrives at the equation

$$z_t = q_1 z_\zeta + q_3 z + q_2$$

where

$$\begin{aligned} q_1(\zeta, t) &= \zeta I(\zeta, t) \\ q_2(\zeta, t) &= 2\bar{g}'(\zeta^{-1}, t) \\ q_3(\zeta, t) &= \frac{2\bar{f}(\zeta^{-1}, t)}{\bar{z}(\zeta^{-1}, t)}. \end{aligned} \tag{21}$$

The important feature here is that, despite the spatial variability of τ, the function $I(\zeta, t)$ defined by (20) is analytic in $|\zeta| > 1$. Thus $\zeta^{-1} q_1$, q_2, and q_3 are analytic in $|\zeta| > 1$, and the Laurent series of each of these terms on $|\zeta| = 1$ will contain only non-positive powers of ζ.

The properties of $\zeta^{-1} q_1$, q_2, and q_3 described above have several important consequences. For convenience of the reader, we provide a summary of what is known [35] ([36] gives related results for a different flow):

1. Initial data of the form $z(\zeta,0) = a(0)/\zeta + h(\zeta,0)$ with $h(\zeta,0)$ an nth order polynomial leads to a solution of the form $z(\zeta,t) = a(t)/\zeta + h(\zeta,t)$ where $h(\zeta,t)$ is a polynomial of the same order, regardless of , (ζ,t).

2. There is no spontaneous generation of singularities in z in the finite complex plane. Furthermore, the form of a singularity which is present initially in $|\zeta| > 1$ is invariant with time.

3. Singularities in z move away from the unit circle. As a result, no finite angle corners can form.

4. Zeros in z_ζ may impinge on the unit disc in finite time, causing a zero angled cusp on the interface. If a cusp is present on a steady interface, then the analysis of [24] shows that surface tension must be zero at the cusp point. The presence of surfactant may facilitate cusp formation.

For later use, we note that (12) may be used to eliminate $f(\zeta,t)$ from (19) in favor of $u_1 + iu_2$. First, equation (19) is evaluated on $|\zeta| = 1$ by deforming the contour in the usual way. After elimination of f using (12), the result reads

$$z_t - (u_1 + iu_2) = \zeta z_\zeta \left[\frac{1}{4\pi i} PV \int_0^{2\pi} \frac{\tau(,\ (\nu',t))}{|z_\nu(\nu',t)|} \cot \frac{(\nu' - \nu)}{2} d\nu' \right] \tag{22}$$

where PV denotes Cauchy principal value integral. We also note that equation (19) can be used to eliminate f from (11) and express $g'(\zeta,t)$ in terms of $z(\zeta,t)$. This results in (see [35])

$$\begin{aligned} g'(\zeta,t) &= \frac{\bar{z}(\zeta^{-1},t)}{2} \left\{ \frac{z_{\zeta t}(\zeta,t)}{z_\zeta(\zeta,t)} - \zeta I_\zeta(\zeta,t) - \left[1 + \frac{\zeta z_{\zeta\zeta}(\zeta,t)}{z_\zeta(\zeta,t)} \right] I(\zeta,t) \right\} \\ &+ \frac{\bar{z}_\zeta(\zeta^{-1},t)}{2\zeta} I(\zeta,t) + \frac{\bar{z}_t(\zeta^{-1},t)}{2} \end{aligned} \tag{23}$$

which is originally valid on the unit circle but is extended off through analytic continuation. The requirement that the right hand side of (23) is analytic in $|\zeta| < 1$ (except for a known pole at $\zeta = 0$) determines the time evolution of the map $z(\zeta,t)$.

3.1 Polynomial solutions

In the clean flow problem, Tanveer and Vasconcelos [35] present a class of exact solutions for the interface shape, for which $h(\zeta,0)$ is a polynomial of degree

N. Such initial conditions form a dense set in the space of smooth initial shapes. These solutions are easily generalized to take into account the presence of surfactant.

Following [35] we look for solutions of the form

$$z(\zeta, t) = \frac{a(t)}{\zeta} + \sum_{j=1}^{N} b_j(t)\zeta^j \tag{24}$$

where the b_j's are complex coefficients. Evolution equations for the coefficients $a(t)$, $b_j(t)$ are obtained by enforcing the analyticity of the right hand side of (23) in $|\zeta| < 1$. Define the Taylor's series coefficients $\hat{I}_0(t)$, $\hat{I}_k(t)$ by

$$I(\zeta, t) = \hat{I}_0(t) + \sum_{k=1}^{\infty} \hat{I}_k(t)\zeta^k$$

where (see (20))

$$\begin{aligned} \hat{I}_0 &= \frac{1}{4\pi}\int_0^{2\pi} \frac{\tau(\nu, t)}{|z_\zeta(e^{i\nu}, t)|} d\nu \\ \hat{I}_k &= \frac{1}{2\pi}\int_0^{2\pi} \frac{\tau(\nu, t)e^{-ik\nu}}{|z_\zeta(e^{i\nu}, t)|} d\nu. \end{aligned} \tag{25}$$

Substitution of (24), (25) into the right hand side of (23) leads to a Laurent series in ζ. Matching the Laurent series coefficients from the right and left hand sides of this equation then leads to a system of ODE's for $a(t)$, $b_j(t)$ (in particular, the coefficient of $1/\zeta^k$ is zero for $k \geq 2$ and $Qa(t)/2$ for $k = 1$). This system is most conveniently written by defining the quantities c_k

$$\begin{aligned} c_{N+1} &= a\bar{b}_N \\ c_N &= a\bar{b}_{N-1} \\ c_k &= a\bar{b}_{k-1} - \sum_{j=1}^{N-k} j b_j \bar{b}_{k+j}, \quad 2 \leq k \leq N-1 \\ c_1 &= a^2 - \sum_{j=1}^{N} j|b_j|^2. \end{aligned} \tag{26}$$

The ODE's then take the form

$$\begin{aligned} \dot{c}_1 &= 0 \\ \dot{c}_k &= -k \sum_{j=0}^{N+1-k} \hat{I}_j c_{k+j+1} + a^2 Q \delta_{k+1,3}, \quad 2 \leq k \leq N+1. \end{aligned} \tag{27}$$

Equations (26,27) and the governing equation for the surfactant concentration (15) completely specify our problem. The initial data consists of , $(\nu, 0)$ and the initial interface shape $a(0),\ b_j(0)$. Note that the presence of surfactant affects the magnitude of the shape coefficients $a(t),\ b_j(t)$ through the dependence of $\hat{I}_k(t)$ on $\tau(\nu, t)$. This dependence can be significant.

3.2 Pure strain flow

We now focus our attention on the dynamics of an initially circular bubble with uniform initial surfactant concentration subject to a pure strain flow. The analysis reported here can be repeated, with slight modification, to the case of a bubble in a simple shear flow.

Consider a pure strain flow of the form $u \sim (Qx, -Qy)$ as $x, y \to \infty$. As in the constant surface tension problem, the general solution (24)–(27) indicates that the conformal map $z(\zeta, t)$ governing the evolution of an initially circular bubble contains only two terms. Specifically, the map is given by

$$z(\zeta, t) = a(t)/\zeta + b(t)\zeta \tag{28}$$

where $a(t) < 0$ and $b(t)$ real satisfy the ODE

$$\frac{d}{dt}(ab) = -2\hat{I}_0 ab + Qa^2 \quad a(0) = -1;\ b(0) = 0 \tag{29}$$

along with the area condition

$$a^2 - b^2 = 1. \tag{30}$$

The surfactant concentration , (ν, t) satisfies the non-dimensional form of (15), with $1/Pe_s$ in place of D_s. Interestingly, the overall bubble shape is an ellipse, regardless of the concentration of surfactant. However, the aspect ratio of the ellipse at a given t does depend on the surfactant distribution.

We now examine the conditions under which the interface evolves toward a steady-state shape and surfactant distribution. In order to characterize the steady state shapes, introduce the deformation parameter

$$D = \frac{R_{max} - R_{min}}{R_{max} + R_{min}}$$

where R_{max} and R_{min} are the maximum and minimum radial distance of a point on the interface from the bubble center. The steady state *shape* of the interface is given by the solution to

$$Qa - 2\hat{I}_0 b = 0 \tag{31}$$

together with the area condition (30). The integral term $\hat{I}_0$ depends on the steady state surfactant distribution. This distribution is obtained from equation (15) with the first, second and fourth terms set to zero (recall the fourth term is the complex variable representation of $,\, \kappa \mathbf{u} \cdot \mathbf{n}$ and is zero for the steady solution). After integrating the resulting equation with respect to ν, we obtain

$$, \;\; Re \left[\frac{(u_1 + iu_2)\bar{z}_\nu}{|z_\nu|} \right] = \frac{1}{Pe_s} \left(\frac{,_{\nu}}{|z_\nu|} \right) + C \qquad (32)$$

where C is an integration constant and z is given by (28). Note that this is simply the complex variable statement of $,\, \mathbf{u_s} = (1/Pe_s) ,_s + C$. By symmetry, $\int_0^{2\pi} ,\, \mathbf{u_s} d\nu = \int_0^{2\pi} ,_s d\nu = 0$, implying that $C = 0$.

If the functions appearing in (32) are evaluated at N equally spaced points $\nu_j = 2\pi(j-1)/N, \;\; j = 1, \ldots, N$, then the discretized version of (30)–(32) provides $N+2$ equations for the $N+2$ unknowns a, b and $,_j$. In practice, it is easier to specify b and solve for Q as part of the solution. The resulting system of nonlinear equations can be solved using Newton's method for an increasing sequence of b. We have found that the method works best when the normalization condition (18) is enforced as a constraint on the solution $,_j$.

The results of this computation are illustrated by the dashed curves in Figure 2, where the response curve is plotted for three values of β in the case $Pe_s \to \infty$. (In real physical systems Pe_s is quite large, and surface diffusion is often neglected). In each case, Newton's method converges with quadratic convergence rate, as long as the shape parameter b is less than a critical value b_{crit} which depends on β. The method fails to converge for $b > b_{crit}$.

The termination of a solution branch does not correspond to the non-existence of steady solutions for $b > b_{crit}$, but rather to a singularity in the surfactant concentration function $,(\nu)$. This is readily apparent from Figure 3a, in which $,(\nu)$ is plotted for b near b_{crit}. Here the steady surfactant distribution reaches zero at $\nu = \pm\pi/2$, corresponding to the top and bottom of the bubble. The applied strain Q_{crit} is large enough to sweep all of the surfactant away from these two points on the bubble surface. Further increases in Q should sweep away more surfactant, thus enlarging the region over which $, = 0$. Thus, for more deformed bubbles with $b > b_{crit}$ we expect that the bubble will contain 'surfactant caps' near convergent stagnation points in the flow, and regions where $,(\nu) = 0$ about divergent stagnation points. Since a non-zero analytic function cannot be zero along a curve in the complex plane, the function $,(\zeta)$ must be singular at the edges of the surfactant caps. We later characterize the nature of these singularities.

As shown in Figure 5, allowing a small amount of surface diffusion in equation (32) smooths out the singularities and prevents the surfactant concentration , (ν) from reaching zero. Nevertheless, the qualitative behavior is similar to that for $Pe_s = \infty$, in that there are intervals where , ~ 0, interspersed with surfactant cap regions where , $>> 0$. Beyond the last curve depicted in Figure 5 the Newton iterations fail to converge, due to insufficient resolution at the edges of the cap, where there is near singular behavior. This situation is compounded as Pe_s is increased. Clearly it would be useful to have available exact solutions in the ideal case $Pe_s = \infty$, so as to shed light on the large Pe_s behavior. These solutions are constructed in the next section, and enable us to extend the response curve beyond the point of singularity formation in , (ν).

3.3 Exact solutions

We deviate from the infinite series approach of [30], and instead use the theory of singular integral equations to obtain exact solutions for the bubble shape and surfactant concentration in the case of *deformed* bubbles in pure strain flow. With some modifications, the analysis applies to bubbles in shear flows.

Under the assumption $Pe_s \to \infty$, the steady state surfactant equation becomes (see (32))

$$, \;\; Re \left[\frac{(u_1 + iu_2)\bar{z}_\nu}{|z_\nu|} \right] = 0 \quad on \quad |\zeta| = 1 \tag{33}$$

which is simply the complex variable statement of , $\mathbf{u_s} = 0$. It follows that on any part of the interface $|\zeta| = 1$ either

$$, \; = 0$$

or

$$Re \left[\frac{(u_1 + iu_2)\bar{z}_\nu}{|z_\nu|} \right] = 0. \tag{34}$$

Since $z_\nu / |z_\nu| \neq 0$, the latter is equivalent to the no-slip condition

$$u_1 + iu_2 = 0 \tag{35}$$

which is required to hold in steady state flow over regions in which surfactant is present, whereas slip is allowed where , $= 0$.

Upon taking the steady state limit $z_t \to 0$ in (22) and using (35), one arrives at

$$\frac{1}{4\pi i} PV \int_0^{2\pi} \frac{\tau(\nu')}{|z_\nu(\nu')|} \cot \frac{(\nu' - \nu)}{2} d\nu' = 0. \tag{36}$$

For sufficiently small capillary Q, the bubble is covered with surfactant and equations (35,36) holds over the entire bubble surface $\nu \in [0, 2\pi]$. According to the Hilbert formula (Mikhlin [19]) the solution to (36) is

$$\frac{\tau}{|z_\zeta|} = A \tag{37}$$

where A is a constant. Substitution of the nondimensional equation of state $\tau = 1 - \beta$, into (37) leads to an expression for ,

$$, (\nu) = \frac{1 - A|z_\nu|}{\beta}. \tag{38}$$

Using this expression to eliminate , in the normalization condition (18) and solving for A gives

$$A = \frac{\frac{1}{2\pi}\int_0^{2\pi}[B(b,\nu)]^{1/2} d\nu - \beta}{\frac{1}{2\pi}\int_0^{2\pi} B(b,\nu) d\nu} \tag{39}$$

where $B(b,\nu) = 1 + 2b^2 - 2(1+b^2)^{1/2} b\, cos(2\nu)$ and the total amount of surfactant is chosen as 2π. In deriving this we have used (28) to obtain a relation for $|z_\nu|$ and employed the area condition (30) to cast the map parameter a in terms of b. Note that A is a function of the deformation of the bubble through b, and that $A > 0$.

Equation (31) governing the shape of the steady state ellipse now takes a particularly simple form. Upon substituting $I_0 = A/2$, which follows from (25) and (37), and replacing a with $-(1+b^2)^{1/2}$ one obtains

$$Q = -\frac{Ab}{(1+b^2)^{1/2}}. \tag{40}$$

The collection of equations (30 – 31) and (38) – (40) provides an exact solution for the interface shape and surfactant concentration, given a value of the shape parameter b. The solution is valid as long as the , so obtained remains non-negative. This condition is eventually violated for sufficiently large b, i.e., for sufficiently deformed bubbles.

Numerical evaluation of the exact solution (i.e., trapezoidal rule evaluation of the integrals) gives results which are in complete agreement with the steady state simulations reported in the previous subsection. Furthermore, the solutions explicitly show that the surfactant distribution reaches zero at critical values of b and Q. For larger b, corresponding to more deformed shapes, the surfactant distribution exhibits singularities. The theory of singular integral equations is applied in the next section to obtain analytical formulas for the solution which explicitly reveal the form of the singularities.

3.3.1 Stagnant cap solutions

For $b > b_{crit}$ the natural extension of the above solution contains regions over which , $= 0$, interspersed with stagnant caps for which , > 0. Let $L = \{\nu :$, $(\nu) > 0\}$, and denote the complement of L by $\bar{L}$. From the imposed symmetry L consists of the intervals $[-\theta, \theta]$ and $[\pi - \theta, \pi + \theta]$, where θ is a function of b and needs to be determined as part of the solution.[2]

On the portion of the bubble where the surfactant concentration is nonzero $u_1 + iu_2 = 0$, i.e., the singular equation (36) holds for $\nu \in L$, whereas , $= 0$ for $\nu \in \bar{L}$. Using the latter fact, we rewrite (36) as

$$\frac{1}{4\pi i} PV \int_L \left(\frac{\tau(\nu')}{|z_\nu|} - \frac{1}{|z_\nu|} \right) \cot \frac{(\nu' - \nu)}{2} d\nu' = r(\nu) \tag{41}$$

for $\nu \in L$ where

$$r(\nu) = -\frac{1}{4\pi i} PV \int_0^{2\pi} \frac{1}{|z_\nu|} \cot \frac{(\nu' - \nu)}{2} d\nu'. \tag{42}$$

Note that $(\frac{\tau}{z_\nu} - \frac{1}{|z_\nu|}) \to 0$ as $\nu \to \theta$, so that the principal value integral on the left hand side of (41) is well defined at $\nu = \theta$ as well as the other endpoints of the set L.

Since (41) does not hold for all ν, the Hilbert formula for the compounding of singular integrals does not apply. Hence the usual solution method is not applicable here. Instead, we apply a method based on the reduction of the singular integral equation to the so-called Riemann problem [19, 22]. Define

$$\tilde{\tau}(\zeta) = \frac{\tau}{|z_\zeta|} - \frac{1}{|z_\zeta|}$$

[2] In theory L could consist of 2^n such intervals separated by regions where , $= 0$. However, these solutions do not seem to be connected to the solution branch corresponding to our initial configuration

and introduce the function

$$F(\zeta) = \frac{1}{2\pi i} \int_{L_\zeta} \tilde{\tau}(\zeta') \left[\frac{\zeta' + \zeta}{\zeta' - \zeta} \right] \frac{d\zeta'}{\zeta'} \tag{43}$$

where $L_\zeta = \{e^{i\nu} : \nu \in L\}$. Let $F_i(\zeta)$ ($F_o(\zeta)$) denote the value of $F(\zeta)$ as ζ approaches the contour L_ζ from the inside (outside). Expressions for these quantities are obtained from (43) via contour deformation. From these it is easy to demonstrate that

$$\begin{aligned} F_i(\nu) - F_o(\nu) &= 2\tilde{\tau}(\nu) & (44) \\ F_i(\nu) + F_o(\nu) &= \frac{1}{\pi i} PV \int_L \tilde{\tau}(\nu') \cot \frac{(\nu' - \nu)}{2} d\nu' \\ &= 4r(\nu) & (45) \end{aligned}$$

where the last equality follows from (41). Here and in the remainder we use the convention that quantities $F(\zeta)$ evaluated on $\zeta = e^{i\nu}$ are denoted $F(\nu)$. Equations (44,45) constitute the Riemann problem, i.e., to find a function given a linear relation between its limiting values on the inside and outside of a curve.

Now consider the function

$$\omega(\zeta) = \left[\frac{(\zeta - \bar{\alpha})(\zeta + \bar{\alpha})}{(\zeta - \alpha)(\zeta + \alpha)} \right]^{1/2}$$

where $\alpha = e^{i\theta}$ and $\bar{\alpha}$ are the endpoints of one arc constituting L_ζ, and $-\bar{\alpha}$, $-\alpha$ are the endpoints of the other arc. Branch cuts are chosen to lie along the contour L_ζ. We select the particular branch satisfying $\omega(\zeta) \to 1$ as $\zeta \to \infty$. Since the function $\omega(\zeta)$ is multiplied by -1 upon making a circuit of any one of the points $\alpha, \bar{\alpha}, -\alpha, -\bar{\alpha}$, it is a solution to the homogenous Riemann problem

$$\omega_i(\nu) + \omega_o(\nu) = 0 \tag{46}$$

for $\nu \in L$.

Next introduce the function $\Phi(\zeta)$, defined by

$$F(\zeta) = \Phi(\zeta)\omega(\zeta)$$

From (45), (46) it follows that

$$\Phi_i(\nu) - \Phi_o(\nu) = \frac{4r(\nu)}{\omega(\nu)}$$

for $\nu \in L$, which is a form of the Riemann problem that is easily solved. Indeed, from (44) we surmise that

$$\Phi(\zeta) = \frac{1}{\pi i} \int_{L_\zeta} \left(\frac{r(\zeta')}{\omega(\zeta')} \right) \left[\frac{\zeta' + \zeta}{\zeta' - \zeta} \right] \frac{d\zeta'}{\zeta'}$$

which in turn implies

$$F(\zeta) = \frac{1}{\pi i} \omega(\zeta) \int_{L_\zeta} \left(\frac{r(\zeta')}{\omega(\zeta')} \right) \left[\frac{\zeta' + \zeta}{\zeta' - \zeta} \right] \frac{d\zeta'}{\zeta'}.$$

The functions $F_i(\nu)$ and $F_o(\nu)$ are computed from the above using contour deformation, after which equation (45) is employed to obtain a *particular* solution τ_p of the integral equation (41)

$$\tau_p(\nu) = \frac{1}{\pi i} \omega(\nu) PV \int_L \left(\frac{r(\nu')}{\omega(\nu')} \right) \cot \frac{(\nu' - \nu)}{2} d\nu'. \qquad (47)$$

As it stands, this particular solution does not satisfy the symmetry requirements (17). It is therefore convenient to modify it slightly. Noting that (47) remains a particular solution when $\omega^{-1}(\zeta)$ is substituted for $\omega(\zeta)$, we instead consider

$$\tilde{\tau}_p(\nu) = \frac{\omega(\nu)}{2\pi 1} PV \int_L \left(\frac{r(\nu')}{\omega(\nu')} \right) \cot \frac{(\nu' - \nu)}{2} d\nu' + \frac{1}{2\pi i \omega(\nu)} PV \int_L \left(r(\nu') \omega(\nu') \right) \cot \frac{(\nu' - \nu)}{2} d\nu'. \qquad (48)$$

From the symmetries of ω and r expressed in Table 1, it is readily verified that $\tilde{\tau}_p$ is real and that

$$\begin{aligned} \tilde{\tau}_p(-\nu) &= \tilde{\tau}_p(\nu) \\ \tilde{\tau}_p(\nu + \pi) &= \tilde{\tau}_p(\nu) \end{aligned}$$

in accordance with (17).

The solution (48) is not unique. In the appendix, a general solution to the homogeneous equation

$$\frac{1}{4\pi i} PV \int_L \tilde{\tau}_0(\nu') \cot \frac{(\nu' - \nu)}{2} d\nu' = 0 \qquad (49)$$

is computed, with the result

$$\tilde{\tau}_0 = c' \left(\alpha \omega - \bar{\alpha} / \omega \right), \qquad (50)$$

where c' is a complex constant. The form of the c' is restricted by the requirement that $\tilde{\tau}_0$ be real. Consulting the first row of Table I, we calculate

$$\overline{c'\left(\alpha\omega - \bar{\alpha}/\omega\right)} = -\bar{c}'(e^{2i\theta}\bar{\alpha}\omega - e^{-2i\theta}\alpha/\omega)$$

which equals $\tilde{\tau}_0$ if and only if

$$c' = iR_1$$

where R_1 is a real number. A quick check of Table I verifies that $\tilde{\tau}_0$ satisfies the other required symmetries.

The discussion above indicates that the general solution to the integral equation (41) takes the form

$$\tilde{\tau} = \tilde{\tau}_p + iR_1\left(\alpha\omega - \bar{\alpha}/\omega\right), \tag{51}$$

where $\tilde{\tau}_p$ is the particular solution (48). There are still two free parameters in the solution, R_1 and θ. Two conditions are required of the solution to fix these parameters and pick out a unique solution from the family of allowable ones. One follows from the physical requirement that the total stress on the bubble be finite. This implies that the rate of strain function $s_{11} + is_{12}$ is integrable over the bubble surface, which in turn implies that the integral of , $_{\nu}$ is finite. The second condition is that the total amount of surfactant on the bubble surface equal 2π.

To enforce the first condition, we expand the solution (51) in powers of $(\zeta - \alpha)^{1/2}$, and ask that the coefficient of the leading order singular term $(\zeta-\alpha)^{-1/2}$ equal zero. From symmetry, this also removes the singular terms corresponding to $(\zeta - \bar{\alpha})^{-1/2}$, $(\zeta + \alpha)^{-1/2}$, and $(\zeta + \bar{\alpha})^{-1/2}$. This procedure results in the condition

$$\frac{J(\theta)}{2\pi} - R_1 e^{i\theta} = 0$$

where $J(\theta)$ refers to the first integral in (48), evaluated at $\nu = \theta$. It is argued that the complex number $J(\theta)$ may be represented as

$$J(\theta) = |J|e^{i(\theta+k\pi)}, \quad k = 0 \ or \ 1$$

i.e., the principal argument of $J(\theta)$ is either θ or $\theta + \pi$. To see this, we use Table I to infer that $\omega J(\theta)/(2\pi i)$ is real, so that $arg[J(\theta)] + arg[\omega/(2\pi i)] = k\pi$. The identity $arg[J(\theta)] = \theta + k\pi$ then follows from the fact that $arg[\omega] = -\theta + \pi/2$. The parameter R_1 is therefore determined in terms of the quantity $|J|$ by

$$R_1 = \frac{|J|}{2\pi}e^{ik\pi} \quad k = 0 \ or \ 1 \tag{52}$$

Together with the normalization condition (18), this provides a pair of equations for the unknowns θ and R_1. Note that as $\theta \to \pi/2$, then $\omega \to 1$ and $\tilde{\tau}_0 \to -2R_1$, where R_1 is a negative real constant (i.e. $k = 1$ in (52)). After application of the Hilbert formula to (48), it follows that $\tau/|z_\nu| = -2R_1$=constant. Thus, equation (37), which holds when the bubble is covered by the surfactant layer, is reproduced.

In summary, equations (48), (51)–(52) completely determine the surfactant concentration function , (ν), given the interfacial shape (as specified by the map parameters a and b). Equation (31) then gives the value of Q corresponding to this shape and surfactant distribution. This solution is exact in the sense that determination of Q and the surfactant concentration is reduced to performing quadratures. However, application of the normalization condition (18) to determine the value of a single free parameter (say, θ) leads to a nonlinear equation. In general some form of iteration must be used to set the value of this last parameter. Nevertheless, we shall refer to this solution as exact. For problems lacking symmetry, there are more free parameters but also correspondingly more conditions, making a unique determination of the surfactant concentration possible.

An interesting feature of the solution is the presence of singularities at $\nu_0 = \pm\theta, \pi \pm \theta$ where the behavior of , satisfies

$$, (\nu) \sim d\ (\nu - \nu_0)^{1/2} \tag{53}$$

where d is a constant. For $b > b_{crit}$ the presence of these singularities prevents the Newton's method from converging in the computations reported in the previous subsection. Although these are smoothed out by the presence of surface diffusion, for small diffusion the function , (ν) still reflects the behavior (53) in the outer asymptotic sense, i.e., (53) still holds for $0 << |\nu - \nu_0| << 1$.

3.4 Numerical evaluation of solutions

The exact steady solutions described in the previous section have been numerically evaluated for several values of β. When the shape coefficient b is small enough for , > 0 over the entire bubble surface, equations (38)–(40) apply. Given b, the integral terms in (39) are evaluated using trapezoidal rule integration. This in turn allows one to calculate , via (38) and Q through (40).

For $b > b_{crit}$, equations (48), (51)–(52) apply. In this case the angle θ is specified. If we also provide a value of b, then R_1 may be computed using the relation (52); $\tilde{\tau}$ is then determined by performing the integration in (48) and adding the result to the homogeneous solution. However, in general the function , so obtained will not satisfy the normalization condition (18). We therefore use Newton's Method to adjust the value of b (iterating over the above process) so that (18) is exactly satisfied.

The most difficult part of this process is the evaluation of the integrals in (48), in which the kernels contain principal value singularities in addition to the square root singularities at the endpoints of the intervals of integration. Consider the first integral in (48). To remove the principal value singularity, we subtract from the kernel the expression $p(\nu')r(\nu)/(p(\nu)\omega(\nu')) \cot \frac{(\nu'-\nu)}{2}$, where $p(\nu) = \alpha\omega^2 - \bar{\alpha}$. Since the integral of this function over L is zero, our original equation is unchanged by this operation. However, the modified kernel has the finite value $2[r'(\nu) - (p'(\nu)/p(\nu))r(\nu)]$ at $\nu' = \nu$, so that trapezoidal rule integration may be performed in a straightforward manner. In order for the trapezoidal rule evaluation of this integral to be second order accurate, we also need to remove the leading order singularity of the kernel at one of the endpoints of L. From the imposed symmetry, this is equivalent to removing the leading order singular behavior at each of the endpoints of the intervals comprising L. Here, we follow the standard trick of subtracting out the singularity from the integrand in a form that is analytically integrable. The second integral is treated analogously.

3.4.1 Numerical results

Figure 2 shows the response curves (i.e., D versus Q) for three representative values of β. When , $(\nu) > 0$ for all ν, solution (38)-(40) holds, and the resulting portion of the response curve is shown as a dashed line. The dashed part of each curve agrees with the solution obtained in subsection 2.2 using Newton's method. The portion of the response curve corresponding to the surfactant cap solution is represented by a solid line. Note that the two different forms of solution merge smoothly into one another.

Each response curve shows that there are two steady state solutions for a given value of Q satisfying $Q < Q_t(\beta)$, where Q_t marks the turning point. Similar behavior is observed in the clean flow (, $= 0$) problem. Evidence is provided below that the turning point corresponds to a change in stability for the steady solution; the lower branch solutions correspond to stable steady states whereas the upper branch solutions are unstable. The turning point Q_t represents the maximum possible strain rate for which the bubble will advance to a steady state; for $Q > Q_t$ the bubble will burst.

Figure 3 presents the surfactant distribution function , (ν) at four representative points $A - D$ along the $\beta = .1$ response curve. Figure 4 depicts the corresponding interfacial profiles. In Figure 3a the steady surfactant concentration is plotted at the largest strain rate for which the solution (38)–(40) is valid; we see that the surfactant concentration is zero at $\nu = \pm\pi/2$, corresponding to the top and bottom of the bubble. Further increases in the strain rate Q leads to bubbles with surfactant caps. Figure 3b clearly depicts the formation of surfactant caps with square root singularities in the surfactant distribution at the terminal points of the cap. Further along the response curves at points C and D the surfactant distribution gets more concentrated about the ends of the bubble, i.e., the surfactant caps are narrower and stronger, and the bubbles are more deformed. Interestingly, this is true even though the strain rate decreases as one moves along the upper branch of the response curve from C toward D and beyond. The response curves in the figure are terminated due to loss of resolution. Increasing the resolution suggests that the curves continue toward the $Q = 0$ axis, and that the minimum value of $\sigma(,\ )$ approaches zero but does not reach this value for nonzero Q.

To determine the stability of a given solution branch, time dependent numerical simulations were performed on the initial value problem (15), (28)–(30) starting from an initially circular or elliptical bubble shape. A variety of smooth initial surfactant distributions have been considered. For a given Q, it was found that initial shapes and surfactant distributions that are 'near' a steady solution on the upper branch of the response curve did not evolve to a steady shape, i.e., the bubble evolved without limit. Hence, the upper portion of each response curve is a branch of unstable solutions. In contrast, initial shape deformations and surfactant concentrations which lie near the lower branch tend toward the steady solution on the lower branch corresponding to that particular value of Q, as long as $Q < Q_t$. By way of illustration, Figure 6 depicts the unsteady evolution for $Q = .15$, starting from an initially circular bubble and uniform surfactant concentration. The corresponding exact steady surfactant cap solution is also shown. Clearly, the time dependent solution evolves toward the predicted steady state surfactant profile.

The results above provide strong evidence that the lower part of the response curve is a branch of stable steady solutions, although this conclusion can not be definitively made on the basis of the reported tests. The reason is that we have restricted ourselves to elliptical perturbations of the steady solution, rather than arbitrary perturbations. However, it is easily shown that small non-elliptical perturbations die out.

These results also suggest that the turning point in each response curve corresponds to the maximally deformed bubble that can be observed for given β (alternatively, the turning point Q_t represents the maximum possible strain rate for which the bubble will advance to a steady state; for $Q > Q_t$ the bubble will burst). Figure 7 presents the surfactant concentration at the turning point for the values of β used in Figure 2. Note that the $\beta = .5$ and $\beta = .9$ bubbles do not contain surfactant caps at the turning point. In fact, there is a critical value of β above which stable, steady bubbles with surfactant caps do not exist. Here, the critical value is roughly $\beta = .35$. For the purpose of comparison, the locations of the $\beta = .5$ response curves for nonzero surface diffusion are computed as described in subsection 3.2 and illustrated in Fig. 8. In particular, the value of Q at the turning point (corresponding to the maximally deformed steady bubble) increases as diffusion increases.

4 Flow in a four roller mill

Taylor [37] devised the four roller mill depicted in Figure 9 to study mixing processes in two fluid emulsions. The mill is filled with a highly viscous liquid and the four cylinders rotated in the directions shown, producing a strain flow in the neighborhood of a bubble at the center of the mill. The effect of increasing strain can be measured by increasing the roller velocity in small increments and documenting the eventual steady bubble shape at each roller speed. In this way one can calculate the dependence of bubble shape, as measured by the deformation parameter D, on the capillary number Q', defined here as

$$Q' = \frac{2\mu G R}{\sigma_0}$$

where the extra factor of 2 is included to conform to Taylor's definition.

In the case where the viscosity of the drop is small enough compared with the outer fluid to treat the drop as inviscid, Taylor observed the following behavior. At a low rotation rate, the drop distorted only slightly and was ellipsoidal in shape. However, at a critical rotation rate $Q' = .41$ the drop suddenly developed pointed ends. Taylor noted that in fact this state was not a true steady state as “a thin skin appeared to slip off the bubble surface”. Later experiments showed the unsteady motion to often include small bubbles emitted from the pointed ends, a process known as tip streaming. After a certain time passed (holding the rotation rate constant) Taylor observed that the rounded bubble ends reemerged, and the resulting drop was smaller than the original drop. This rounded configuration persisted until $Q' = .65$, at which point the ends once again became pointed. This new pointed configuration remained stable as the strain was further increased; at the maximum attainable strain ($Q' = 2.45$) the drop still showed no sign of burst. The experiment was repeated and extended by others, with similar results (see, e.g., [29, 38, 8])

The experiments of de Bruijn [8] suggest that tip streaming occurs when interfacial tension gradients develop due to the presence of surfactant. Although de Bruijn's experiments were performed on drops in a simple shear flow, the behavior is similar in that the drop makes a sudden transition to a pointed (sigmoidal) shape and can exhibit tip streaming. In the experiments, systems with no or extremely low levels of the surfactant (glycerol-1-mono-oleate) did not exhibit tip streaming. Above a certain level of surfactant, tip streaming was observed. At very high levels of surfactant tip streaming was again suppressed, presumably due to the inability of a large surface tension gradient to develop. At this level, droplets could only be broken up via the "normal" mode of fracture.

Other behavior observed in the experiments points to the importance of surfactant in the tip streaming mode of breakup. For example, the interfacial tension of the emitted droplets was estimated to be much lower than that of the mother drop, suggesting that the emitted drops are covered with surfactant shed by the mother drop.[3] Although circumferential curvature is likely to be important in the actual breakup of a jet into small bubbles, we suggest that the *onset* of tip streaming, which corresponds in Taylor's experiments to a sudden transformation from a rounded steady bubble to an *unsteady* cusp-like bubble, can be captured by a two dimensional model.

Recently, Antanovskii [5] employed a plane flow model to examine the formation of a pointed drop in Taylor's experiment. The two dimensional "outer" velocity field produced by the four rotating rollers (with no drop present) was computed numerically by means of a boundary integral method. This was used to obtain the parameters in a local expansion of the flow field at the center of the mill, where the bubble is located. The resulting expression then provides the far-field for the "inner" flow around a drop in an unbounded fluid. The inner flow problem is solved using complex variable techniques.

The far-field flow computed by Antanovskii leads to the following expression

[3] Other factors were ruled out in importance. For instance, the particular viscosity ratio was not found to be crucial, as long as it is much less than one.

for the stress-stream function as $z \to \infty$

$$W_\infty(z) = \frac{1}{2}\left[\left(G + G_1|z|^2\right) z^2 + \frac{p_\infty}{2\mu}|z|^2\right]$$

so that, in the notation of Subsection 2.2,

$$f \sim \frac{1}{2}G_1 z^3 + \frac{p_\infty}{4\mu} z \quad g \sim \frac{1}{2}G z^2 \tag{54}$$

as $z \to \infty$. Note that this is just the superposition of a linear (pure strain) velocity field considered previously and a motion described by cubic terms (characterized by the additional rate of strain parameter G_1). Introduce the nondimensional parameter ϵ defined by

$$\epsilon = \frac{G_1 R^2}{G}.$$

In the presence of insoluble surfactant, the evolution is completely characterized by the parameters Q', ϵ, β, and Pe_s.

We consider the problem of specifying the steady state shape of the bubble when surfactant is present, under the assumptions of insoluble surfactant and $Pe_s \to \infty$. As before introduce a conformal map $z(\zeta)$ satisfying the condition $z(0) = \infty$ and the symmetry condition (13). For the far-field conditions (54) it is shown in [5] that in the absence of surfactant the map takes the form of a rational function, namely

$$z(\zeta) = \frac{\gamma_0 + \gamma_1\zeta^2}{\zeta(1 - \gamma_2\zeta^2)}$$

where γ_0, γ_1 and γ_2 are dimensionless coefficients with $\gamma_2 = \epsilon\gamma_0\gamma_1$. This conclusion is not altered by the presence of surfactant.

Enforcing the analyticity of $f(\zeta)$ at $\pm\gamma_2^{1/2}$ leads to an expression for Q' in terms of the map parameters γ_i and ϵ [5]. Modifying the expression so obtained to include the presence of surfactant, we find

$$Q' = \frac{\gamma_1}{\pi\gamma_0}\int_0^\pi \frac{1 - \beta,\,(\nu')}{|\gamma_0(1 - 3\gamma_2 e^{i\nu'}) - \gamma_1 e^{i\nu'}(1 + \gamma_2 e^{i\nu'})|}. \tag{55}$$

The condition that the drop area equal π leads to the constraint

$$\gamma_0 = \left[\frac{2(1+\gamma_1^2)}{c_1 + (c_1^2 - c_2)^{1/2}}\right]^{1/2}$$

where

$$\begin{aligned} c_1 &= 1 - \epsilon\gamma_1^2[2(1-\epsilon) + \epsilon\gamma_1^2] \\ c_2 &= 4\epsilon^2\gamma_1^2(1+\gamma_1^2)[3 + \epsilon(2+\epsilon)\gamma_1^2]. \end{aligned}$$

This reduces the number of free parameters by one.

We now consider the steady surfactant distribution. For this flow, the analogue of equation (36) governing the steady surfactant concentration can be shown to be

$$\begin{aligned} \frac{1}{4\pi i} PV \int_0^{2\pi} \frac{\tau(\nu')}{|z_\nu|} \cot\frac{(\nu'-\nu)}{2} d\nu' &= -\frac{1}{2}\epsilon\ Q'\ \gamma_0^2\ (\zeta^2 - \frac{1}{\zeta^2}) \\ &= s(\nu). \end{aligned} \tag{56}$$

When the bubble is covered with surfactant the above equation holds for $\nu \in [0, 2\pi]$ and is easily solved, with the result

$$,\ = \frac{1}{\beta}\left[1 - (A - 2\epsilon\ Q'\ \gamma_0^2\ cos\ 2\nu)|z_\nu|\right] \tag{57}$$

where

$$A = \frac{-2\pi\beta + \int_0^{2\pi} |z_\nu| d\nu' + 2\epsilon Q' \gamma_0^2 \int_0^{2\pi} cos\ 2\nu |z_\nu|^2 d\nu'}{\int_0^{2\pi} |z_\nu|^2 d\nu'}. \tag{58}$$

Given γ_1 and ϵ, the system of equations (55), (57)–(58) can be easily evaluated to obtain the strain rate Q' and surfactant distribution , (ν).[4] For γ_1 sufficiently large, the surfactant distribution contains stagnant caps. In this case equation (56) can be shown to be equivalent to (41), but with $r(\nu)$ now given by

$$r(\nu) = -\frac{1}{4\pi i} PV \int_0^{2\pi} \frac{1}{|z_\nu|} \cot\frac{(\nu'-\nu)}{2} d\nu' + s(\nu).$$

The surfactant distribution is therefore represented by (48,51), using the above expression for r. Given γ_1, ϵ, a surfactant cap angel θ and a guess for Q', the surfactant distribution is determined by solving equation (51) as outlined in Subsection 3.5. As before, Newton-Raphson iteration is employed to adjust γ_1 so that the normalization condition (18) is satisfied. A new value for Q' is then computed from (55), and the process is repeated until convergence.

[4] This exact solution was checked for agreement with the solution obtained by numerically solving (32) as indicated in Subsection 3.2.

The response diagram in the case $\beta = 0$ (no surfactant), first presented in [4], contains some remarkable features. As an example we show the curve for $\epsilon = .002$ (Figure 10a). Unlike the case of a bubble in a linear flow field, the steady solution persists for all strains. At the top, flat portion of the branch the interfacial profiles have cusp-like (although smooth) ends. These profiles show a remarkable similarity with the bubbles observed in the experiments of Taylor. The time dependent simulations of [23] indicate that these bubbles are stable. Note that there is a multi-valued dependence of D on Q' over part of the response curve. It has been conjectured that the solution described by a decreasing dependence of D on Q' is unstable [5]. If so, then at the lower turning point of the response curve the solution might jump to a solution on the upper branch, causing a sudden transition to a stable cusp-like bubble.

The time dependent simulations of [23] suggest that stable bubbles survive for *all strains* when surfactant is absent. Thus, the $\beta = 0$ solutions do not describe the transition to an unsteady cusp-like bubble, seen as a precursor to tip streaming. The presence of surfactant could alter this situation in a number of ways. For instance, it could modify the response curve or alter the stability at some point on the curve. The steady state calculations presented below show that the response curve is altered, at least for the simple model considered here. Models incorporating other physical effects will be considered in a future paper.

4.1 Numerical results

Figure 10b presents the response curve, and Figures 11a and b display the surfactant distribution and bubble profiles at the representative points A–E along the response curve. The most interesting feature of the response curve is the absence of the upper portion of the S-shaped solution branch; there now exists a critical value Q'_{crit} above which no steady bubble solution exists. Physically, enough surfactant is swept to the ends of the bubble that the restoring force of surface tension is no longer adequate to balance the extensional motion produced by the external flow. Interestingly, the upper part of the S-shaped curve does not reemerge as $\beta \to 0$, although the lower branch approaches the corresponding part of the $\beta = 0$ curve. It is expected that an additional physical effect, such as surface diffusion, will be required for the $\beta \to 0$ solution curve to tend to the $\beta = 0$ curve. This is considered in a future paper.

At the terminal point of the response curve, the surface tension equals zero and the curvature is infinite for $\nu = 0$, i.e., a true cusp is formed (see Figure 11c). This behavior has been numerically verified by evaluating the solution at increasing resolution. These trends indicate that the simple model used here employing a linear equation of state breaks down as the terminal point of the response curve is approached. Nevertheless, this result is suggestive as to the possible role of surfactant in tip streaming. In contrast to the clean flow problem, the time dependent evolution for $Q' > Q'_{crit}$ now consists of an ever lengthening bubble. It is likely that the bubble to passes through an unsteady cusp-shaped formation as it lengthens. This would be similar to the sudden transition from a steady rounded bubble to an unsteady cusp-like bubble that occurred immediately prior to tip streaming, as Q was increased in Taylor's experiments. This possibility, as well as the role of surface diffusion, surfactant solubility, and alternative equations of state, will be considered in a future paper.

5 Conclusions

We have obtained a complex variable formulation for a bubble evolving in two-dimensional Stokes flow, when a layer of surfactant is present on the bubble surface. This formulation is used to derive exact solutions for the steady state shape of the interface and distribution of surfactant when the bubble is subjected to an extensional flow. Properties of the corresponding time-dependent evolution are also derived.

Our solutions include bubbles that are completely covered by a non-uniform distribution of surfactant, as well as bubbles that are only partially coated by stagnant caps of surfactant. These stagnant cap bubbles satisfy a boundary value problem featuring mixed boundary data, with the no-slip condition enforced at the stagnant caps but slip allowed elsewhere. The singular integral equation governing the surfactant concentration is exactly solved to obtain a unique surfactant distribution, given the values of certain parameters. This solution features singularities in the surfactant distribution at the cap edges; the location and strength of these singularities is determined as part of the solution.

Both linear and cubic polynomial far-field flow conditions have been considered. For linear strain fields, only rounded bubbles are found. For cubic polynomial strain fields, both rounded and cusp-like bubbles are found. In all cases there is a maximum strain rate beyond which steady bubble solutions of the type considered here no longer exist. The possible relevance of this fact to the onset of tip streaming has been discussed. Of course, certain physical effects neglected in the treatment here (such as surface diffusion and diffusion of surfactant to and from the bulk liquid) may play a prominent role in the form of the steady solution branch. Nevertheless, it is possible that the behavior uncovered here survives in the limit as these physical effects become vanishingly small. The formulation developed here may be used to study the role of these additional elements, and will be the topic of a future paper.

6 Appendix

In this section, we derive all solutions to the homogeneous equation (49). Proceeding as in Subsection 3.3.1, introduce the integral

$$F_0(\zeta) = \frac{1}{2\pi i}\int_{L_\zeta} \tilde{\tau}_0(\zeta')\left[\frac{\zeta'+\zeta}{\zeta'-\zeta}\right]\frac{d\zeta'}{\zeta'}$$

and define $\Phi_0(\zeta)$ through the equation

$$F_0(\zeta) = \omega(\zeta)\Phi_0(\zeta).$$

Note that $F_0(\zeta \to \infty) = A_\infty > 0$, where the inequality follows from the fact that $\tilde{\tau}_0 \leq 0$ and is not identically zero. The important feature here is that this limit is neither zero nor infinite. Also, note that $F_0(0) = -A_\infty$.

Now, clearly Φ_0 is bounded (and nonzero) as $\zeta \to \infty$ and satisfies the equation

$$\Phi_{0i}(\nu) - \Phi_{0o}(\nu) = 0.$$

Since $\Phi_0(\zeta)$ takes the same values on both sides of L_ζ, it follows that this function is regular in the entire plane, except possibly at $\pm\alpha$ or $\pm\bar{\alpha}$. If we require $F_0(\zeta)$ to be integrable along a path joining any two of the points $\pm\alpha, \pm\bar{\alpha}$ and having no other point in common with L_ζ, then an argument similar to that given in Mikhlin [19] (p. 129) shows that $\pm\alpha$ are regular points of the function $\Phi_0(\zeta)$, and $\pm\bar{\alpha}$ are either simple poles or regular points.

The above arguments show that the most general form for Φ_0 is

$$\Phi_0 = \frac{a_1\zeta^2 + a_2\zeta + a_3}{(\zeta-\bar{\alpha})(\zeta+\bar{\alpha})}.$$

The constants a_1 and a_3 are fixed by the behavior of F_0 at $\zeta = \infty$ and $\zeta = 0$. Thus,

$$a_1 = A_\infty \quad \text{and} \quad a_3 = A_\infty|\alpha|^2.$$

Symmetry requirements force $a_2 = 0$. Hence

$$F(\zeta) = \frac{A_\infty(\zeta^2 + |\alpha|^2)}{[(\zeta - \bar{\alpha})(\zeta + \bar{\alpha})(\zeta - \alpha)(\zeta + \alpha)]^{1/2}}$$

and after invoking (44) it follows that the general solution to (49) is

$$\tilde{\tau}_0 = \frac{c\ (\zeta^2 + |\alpha|^2)}{[(\zeta - \bar{\alpha})(\zeta + \bar{\alpha})(\zeta - \alpha)(\zeta + \alpha)]^{1/2}} \tag{59}$$

where c is an arbitrary complex constant. It is easily seen that an equivalent form of (59) is

$$\tilde{\tau}_0 = c'\ (\alpha\omega - \bar{\alpha}/\omega). \tag{60}$$

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References

[1] Acrivos, A. 1983. The breakup of small drops and bubbles in shear flows. *Ann. NY Acad. Sci.*, 404:1–11.

[2] Antanovskii, L. K. 1994a. Influence of surfactants on a creeping free-boundary flow induced by two counter-rotating horizontal thin cylinders. *Eur. J. Mech. B/Fluids*, 13(6):73–92.

[3] Antanovskii, L. K. 1994a. Quasi-steady deformation of a two-dimensional bubble placed within a potential flow. *Meccanica-J. Ital. Assoc. Teor. Appl. Mech.*, 29:27–42.

[4] Antanovskii, L. K. 1994b. A plane inviscid incompressible bubble placed within a creeping viscous flow: Formation of a cusped bubble. *Eur. J. Mech. B/Fluids*, 13:491–509.

[5] Antanovskii, L. K. 1996. Formation of a pointed drop in taylor's four-roller mill. *J. Fluid Mech.*, 327:325–341.

[6] Buckmaster, J. D. & Flaherty, J. E. 1973. The bursting of two-dimensional drops in slow viscous flow. *J. Fluid Mech.*, 60:625–639.

[7] Davis, R. E. & Acrivos, A. 1966. The influence of surfactants on creeping motion of bubbles. *Chem. Engng Sci.*, 21:681.

[8] De Bruijn, R. A. 1993. Tipstreaming of drops in simple shear flows. *Chem. Eng. Sci.*, 48:277–284.

[9] Flumerfelt, R. W. 1980. Effects of dynamic interfacial properties on drop deformation and orientation in shear and extensional flow fields. *J. Colloid Interface Sci.*, 76:330–349.

[10] Grace, H. P. 1982. Dispersion phenomena in high viscosity immiscible fluid systems and application of static mixers as dispersion devices in such systems. *Chem. Eng. Commun.*, 14:225–277.

[11] Harper, J. F. 1973. On bubbles with small immobile adsorbed films rising in liquids at low reynolds numbers. *J. Fluid Mech.*, 58:539.

[12] Harper, J. F. 1982. Surface activity and bubble motion. *Appl. Scientific Research*, 38:343–352.

[13] Hopper, R.W. 1990. Plane stokes flow driven by capillarity on a free surface. *J. Fluid Mech.*, 213:349–375.

[14] Hopper, R.W. 1991. Plane stokes flow driven by capillarity on a free surface, part 2. further developments. *J. Fluid Mech.*, 230:355–364.

[15] Howison, S. D. & Richardson, S. 1994. Cusp development in free boundaries, and two-dimensional slow viscous flows. *Eur. J. Appl. Maths (submitted)*.

[16] Howison, S. D., Morgan, J. D. & Ockendon, J. R. 1997. A class of codimension-two free boundary problems. *SIAM Rev.*, 39(2):221–253.

[17] Langlois, W. E. 1964. *Slow Viscous Flow.* Macmillan.

[18] Li, Xiaofan & Pozrikidis, C. 1997. Effects of surfactants on drop deformation and on the rheology of dilute emulsions in stokes flow. To appear in J. Fluid Mech.

[19] Mikhlin, S. G. 1957. *Integral Equations.* Pergamon Press, New York.

[20] Milliken, W. J. & Leal L. G. 1994. The influence of surfactant on the deformation and breakup of viscous drop: The effect of surfactant solubility. *J. Colloid Interface Sci.*, 166:275–285.

[21] Milliken, W.J., Stone, H.A.& Leal L.G. 1993. The effect of surfactant on transient motion of newtonian drops. *Phys. Fluids A*, 5:69–79.

[22] Muskhelishvili, N.I. 1953. *Singular Integral Equations.* P. Noordhoff, Groningen.

[23] Pozrikidis, C. 1997. Numerical studies of singularity formation at free surfaces and fluid interfaces in two-dimensional stokes flow. *J. Fluid Mech.*, 331:145–167.

[24] Pukhnachov, V. V. 1973. On smoothness of the steady-state solutions of the navier- stokes equations near the free boundary. *Dinamika Sploshnoi Sredy*, 15:133–144.

[25] Rallison, J.M. 1984. The deformation of small viscous drops and bubbles in shear flows. *Ann. Rev. Fluid Mech.*, 16:45–66.

[26] Richardson, S. 1968. Two-dimensional bubbles in slow-viscous flow. *J. Fluid Mech.*, 33:475–493.

[27] Richardson, S. 1973. Two-dimensional bubbles in slow-viscous flow. part 2. *J. Fluid Mech.*, 58:115–127.

[28] Richardson, S. 1992. Two-dimensional slow-viscous flows with time-dependent free boundaries driven by surface tension. *Eur. J. Appl. Maths*, 3:193–207.

[29] Rumscheidt, F. D. & Mason, S. G. 1961. Particle motions in sheared suspensions xii. deformation and burst of liquid drops in shear and hyperbolic flow. *J. Coll. Int. Sci.*, 16:238–261.

[30] Sadhal, S. S. & Johnson, R. E. 1983. Stokes flow past bubbles and drops partially coated with thin films. part 1: Stagnant cap of surfactant film - exact solution. *J. Fluid Mech.*, 126:237–250.

[31] SIEGEL, M.. 1992. The effects of surface tension in the Kelvin-Helmholtz and Rayleigh-Taylor problems. Preprint.

[32] Stone, H. A. & Leal, L.G. 1990. The effects of surfactants on drop deformation and breakup. *J. Fluid Mech.*, 222:161–186.

[33] Stone, H. A. 1990. A simple derivation of the time-dependent convection-diffusion equation for surfactant transport along a deforming interface. *Phys. Fluids A*, 2:111–112.

[34] Stone, H. A. 1994. Dynamics of drop deformation and breakup in viscous fluids. *Annu. Rev. Fluid Mech.*, 26:65–102.

[35] Tanveer, S. & Vasconcelos, G. L. 1995. Time-evolving bubbles in two-dimensional stokes flow. *J. Fluid Mech.*, 301:325–344.

[36] Tanveer, S. 1993. Evolution of hele-shaw interface for small surface tension. *Phil. Trans. R. Soc. Lond. A*, 343:155–204.

[37] Taylor, G. I. 1934. The formation of emulsions in definable fields of flow. *Proc. R. Soc. Lond. A*, 146:501–523.

[38] Torza, S., Cox, R. G., & Mason, S. G. 1972. Particle motions in sheared suspensions xxvii. transient and steady deformation and burst of liquid drops. *J. Coll. Int. Sci.*, 38:395–411.

[39] Wong, H., Rumschitzki, D. & Maldarelli, C. 1996. On the surfactant mass balance at a deforming fluid interface. *Phys. Fluids A*, 8:3203–3204.

List of Figure Captions

1. (a) Bubble with surfactant rising in a quiescent fluid. The stagnant layer of surfactant is denoted by a heavy line.

   (b) Deformed bubble in a strain flow, with surfactant caps on the bubble sides.

2. Response curves (D versus Q) for bubble in a linear strain flow. Curves are shown for $\beta = .1,\ .5$, and .9. Dashed curves represent steady bubbles covered with a nonzero distribution of surfactant. Solid curves denote steady states with surfactant caps. Capital letters mark the locations of the plots in Figures 3 and 4.

3. Surfactant concentration , versus ν, plotted at four represetative points (marked A–D) along the $\beta = .1$ response curve (see Figure 2).

4. Bubble profiles at points marked A–D on the $\beta = .1$ response curve. The crosses mark the location of the surfactant cap edges.

5. Steady surfactant concentration , (ν), evaluated at $Pe_s = 1000$ and $\beta = .1$. The curves shown correspond to $Q = .054$ (least deformed profile), .106 and .162 (most deformed profile).

6. Comparison of surfactant distribution for time-dependent evolution (solid curves) with that for the exact steady-state solution (dotted curve). Initial data consists of a circular bubble with , $(\nu, 0) = 1$. The time interval between successive plots of the time-dependent solution is $\Delta t_p = 16.0$.

7. Surfactant concentration , versus ν, plotted at the turning point of each response curve shown in Figure 2.

8. Comparison of the response curves for three representative values of Pe_s and $\beta = .5$. The two curves for $Pe_s < \infty$ are terminated when the Newton iteration no longer converges due to insufficient resolution.

9. Taylor's four-roller mill.

10. Response curve for strain flow with cubic terms. (a) $\epsilon = .002,\ \beta = 0$ (b) $\epsilon = .002,\ \beta = .1$. The surfactant concentration and bubble profiles at the marked locations are plotted in Figure 10.

11. (a) Surfactant concentration , versus ν at points marked A–E near the terminal end of the response curve for $\beta = .1$ (see Figure 9).

(b) Bubble profiles at points A–E.

(c) Radius of curvature at the point $\nu = 0$ plotted versus the map parameter γ_1 (used to characterize the deformation of the bubble) for the $\beta = .1$ branch of steady solutions.