# Cusp formation for evolving bubbles in 2-D Stokes flow: the effect of variable surface tension

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**Abstract**

Analytical and numerical methods are applied to investigate the effect of variable surface tension, induced by the presence of surfactant, on a bubble evolving in 2-D Stokes flow. The evolution is driven by an extensional flow from a four roller mill. Of particular interest is the possible spontaneous occurrence of a cusp singularity on the bubble surface. Using complex variable methods, exact solutions for the steady interface shape and distribution of surfactant are obtained, in the case when surface diffusion of surfactant is negligible. The steady solutions include those for which the bubble is covered in a nonzero concentration of surfactant, as well as bubbles with 'surfactant caps' that collect on the bubble sides. The branch of steady state solutions is shown to terminate at a steady cusped bubble with zero surface tension at the bubble tips. Thus, in contrast to the clean flow (i.e., constant surface tension) problem, there exists an upper bound $Q = Q_c$ on the non-dimensional strain rate for which steady bubble solutions exist. Numerical calculations of the transient evolution for $Q > Q_c$ suggest that the bubble achieves an unsteady cusped formation in finite time. The numerical computations are greatly simplified by exploiting the analytic structure of the governing equations and interfacial shape. This enables the interfacial evolution to be followed nearly up to cusp formation. The role of a nonlinear equation of state and the influence of surface diffusion of surfactant are both considered. Comparison with experiment reveals some interesting similarities, and a possible connection between the observed behavior and the phenomenon of tip streaming is discussed.

# 1 Introduction

In a pioneering set of experiments, G. I. Taylor employed a four roller mill to subject isolated drops and bubbles to an extensional flow at low Reynolds number [33]. The purpose of these experiments was to explore the manner in which two fluids can be stirred together to form an emulsion. In the experiments the four roller mill (Fig. 1) was filled with a highly viscous fluid and the four rollers rotated in the directions shown, producing a strain flow in the neighborhood of a drop or bubble at the center of the mill. The effect of increasing strain was measured by increasing the roller velocity in small increments and documenting the eventual steady drop shape at each roller speed. In this way Taylor was able to calculate the dependence of drop deformation on a non-dimensional strain parameter $Q = 2\mu GR/\sigma_0$, where $\mu$ is the viscosity of the outer fluid, $G$ is a parameter characterizing the strain rate far from the drop ($G$ is related to the rotation rate of the rollers), and $R$ is the undeformed drop radius.

The experiments revealed a wide variety of phenomena, depending on the ratio of the drop viscosity to that of the ambient fluid. The most interesting behavior occurred when the drop viscosity was much less than that of the exterior fluid, so that the drop could be treated as an essentially inviscid bubble. In this case, the following behavior was observed. At a low rotation rate, the bubble distorted only slightly and was ellipsoidal in shape. However, at a critical rotation rate $Q = 0.41$ the bubble 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 (see e.g. [8] and references therein) showed that jets or small bubbles may be emitted form 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 steady bubble was smaller than the original one. This rounded configuration persisted until $Q = 0.65$, at which point the ends once again suddenly became pointed. This new pointed configuration remained stable as the strain was further increased, and there was no sign of tip streaming. 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., [8], [10], [34]).

Among the most interesting phenomena observed in the experiments is the sudden formation of cusp-like ends, in some cases followed by tip streaming. The spontaneous formation of regions of very high curvature in similar experiments has motivated theoretical studies of singularity formation at an interface in Stokes flow. Singularity formation on a free surface produced by counter rotating cylinders in various classes of steady flows has been considered in [5], [15], [16], and [17]. For nonvanishing surface tension the interface in each case is found to be smooth but with regions of high curvature that can exhibit the form of apparent cusps. In the limit of vanishing surface tension, the steady 'near' cusps become true cusps with infinite curvature. The unsteady version of some of these flows is investigated via numerical simulation in [23], [24]. True singularity formation is found in certain instances of vanishing tension (e.g., in the motion of a free surface driven by a point vortex dipole) but not observed in others (e.g., bubble motion in a four roller mill, for which the steady cusped solution at zero surface tension is not observed to be stable). It is important to note that whereas steady cusps may occur only for vanishing tension, transient cusps are allowed in principle for any value of tension. However, to our knowledge the only example of a true singularity in time-dependent flow for non-vanishing tension is that due to Richardson [26], involving the coalescence of five liquid cylinders.

One of the objectives of the present paper is to explore the sudden transition from a steady rounded bubble to an unsteady cusped bubble, observed as a precursor to tip streaming in Taylor's experiment. In this regard, the experiments of de Bruijn [8] are relevant. These experiments 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 surfactant 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. Additional evidence for the importance of surfactant comes from a measurement of the interfacial tension of the emitted droplets, which 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. The experimental results suggest that it is vital to take into account the influence of variable surface tension when examining the formation of cusp-like interfaces and exploring the dynamics at the onset of tip streaming.

Although the flow field in Taylor's experiment is genuinely three dimensional, the two simplest mathematical models which suggest themselves involve plane or axisymmetric flow. Asymptotic analysis using a slender drop assumption in axisymmetric flow has been performed by several authors (see, e.g., [1], [7], [11], and [29]). However, these analyses encounter difficulties resolving details of the flow and drop shape near the pointed ends. In addition, it is not possible to obtain the branch of steady solutions starting from a sphere at $Q = 0$ up to the point of nonexistence. Indeed, it is possible that slender drop solutions correspond to a physically unattainable branch. In addition, these analyses do not take into account the presence of surfactant. By contrast, the 2-D models would appear to suffer from an oversimplification of the relevant physics. However, a more complete analysis of the 2-D models is possible by taking advantage of the powerful techniques from complex analysis. This can provide an important adjunct to analytical and numerical studies for axisymmetric flow. It is worth mentioning that there are some arguments that the experimentally observed cusp is in fact a two dimensional edge in the plane of the rollers' axle (see [5]). Skirt formation on spherical gas caps may be another manifestation of such an edge formation.

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. Previously, 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 [4] and by Tanveer and Vasconcelos [32] to time evolving bubbles, and by Antanovskii [3, 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. Antanovskii [2] considered the effect of surfactant on the steady state interfacial profiles induced by a pair of counter-rotating point vortices below a free surface, and showed that it can promote cusp formation, although the transient evolution was not considered. Related analyses of two-dimensional flows include [6, 12, 14, 13, 28]. The striking similarities of the cusped bubble profiles computed in [27] and [3, 5] with experimentally observed three-dimensional bubbles suggests that the two-dimensional model may capture much of the essential physics.

In a previous paper [30] a similar plane flow model was employed to investigate the effect of surfactant on steady cusp formation in bubbles, but under the assumption that the surfactant obeys a linear equation of state (i.e., a linear relation between surfactant concentration and surface tension). It was possible to find exact solutions for the steady state shape of the interface and distribution of surfactant for a general class of far-field extensional flows. For boundary conditions corresponding to flow in a four roller mill, both rounded and cusp-like steady bubble solutions were found. In contrast to the clean flow problem, the steady solution branches were found to terminate, with the termination point corresponding to a bubble with a true cusp (i.e., infinite curvature). This behavior implies that there is an an upper bound on the strain rate for which a steady bubble solution can exist. It was suggested that for larger strains, the time dependent evolution would lead to unsteady cusp shaped profiles, much like that seen in experiments. However, time dependent solutions for bubble evolution in Taylor's four roller mill were not obtained. In addition, since the linear equation of state only applies to dilute concentrations of surfactant, this model breaks down before the terminal point is reached.

In the present paper, the previous work is extended to include the time dependent evolution as well as the behavior due to more realistic nonlinear equations of state. The effect of surface diffusion of surfactant is also considered. The use of a nonlinear equation of state is particularly important, for the following reason. As surfactant is convected with the outer flow toward the bubble tips there is a decrease in surface tension there, which in turn promotes high curvature. Counteracting this tendency are the Marangoni stresses which are created at the bubble surface. These stresses oppose the motion due to the external flow, thus retarding further build-up of surfactant and discouraging cusp formation. The nonlinear equation of state enhances the magnitude of Marangoni stresses in regions of relatively large surfactant concentration (when compared with the linear equation of state) and therefore provides a strong impediment to cusp formation.

The application of complex variable techniques allows us to formulate exact solutions for the steady state shape of the interface and the distribution of surfactant. 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, interspersed with regions of zero surfactant concentration. The closed form solution for these cap bubbles 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.

We find that, under certain conditions, the nonlinear equation of state does not prevent the existence of steady bubbles with a true cusp singularity. A given branch of steady state solutions therefore terminates in a cusped bubble, just as it does when the linear equation of state is used. Hence, unlike the clean flow problem, there exists an upper bound $Q_c$ on the non-dimensional strain rate for which steady bubble solutions exist. Numerical simulations of the transient evolution explicitly show that for $Q > Q_c$ the bubble reaches an unsteady cusped formation, much as in Taylor's experiments. Such a bubble is viewed as a precursor to tip streaming. The presence of surface diffusion is shown to enable the behavior for diminishing surfactant concentration to approach that for zero surfactant. Comparison with experiments show some intriguing similarities, despite the drastic simplifications employed in the model.

# 2 Mathematical Formulation

## 2.1 Governing Equations

Consider an inviscid bubble placed in two dimensional slow viscous flow. The bubble is considered to be neutrally buoyant, so that gravitational effects can be ignored. The fluid outside of the bubble has a large viscosity $\mu$ and is taken to be incompressible, whereas the fluid inside the bubble is assumed to have negligible viscosity. Thus the bubble pressure is constant; without loss of generality the constant is chosen to be zero. 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 the kinematic condition

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

holds, where $U_n$ is the normal velocity of the interface. 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

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

$\kappa$ is the interfacial curvature, $\sigma$ is the surface tension, and $\nabla_s$ 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 $\sigma$ on the non-uniform surfactant concentration $\Gamma$. The presence of surfactant generally acts to lower interfacial tension.

The bubble is considered to contain a fixed amount of insoluble surfactant. The relationship between the surface tension and surfactant concentration (measured in units of mass of surfactant per unit of interfacial length) is given by an equation of state of the form

$$\sigma = \sigma(\Gamma).$$

One of the goals of this study is to examine the importance of the equation of state on the phenomena discussed in [30]. In that paper, a linear equation of state

$$\sigma = \sigma_0(1 - \tilde{\beta}\Gamma/\Gamma_0)$$

was employed to examine the effect of surfactant on bubbles in extensional flows. Here $\sigma_0$ is the surface tension of the clean interface, $\Gamma_0$ is the uniform concentration of surfactant that exists in the absence of flow, and $\tilde{\beta}$ is a parameter that determines the sensitivity of the interfacial tension to changes in surfactant concentration. Such a relationship is valid for dilute surfactant concentrations. However, for large non-dimensional strain $Q$ the surfactant accumulates near convergent stagnation points in the flow and so the surfactant concentration can no longer be considered dilute.

There are a large number of nonlinear equations available in the literature. We choose to employ the Langmuir equation [9]

$$\sigma = \sigma_0[1 + \beta \ln(1 - \Gamma/\Gamma_\infty)],$$

where $\Gamma_\infty$ is the maximum concentration of surfactant (producing complete coverage of the bubble as a unimolecular film) and $\beta$ is a dimensionless parameter defined by $\beta = \frac{RT\Gamma_\infty}{\sigma_0}$. Strictly speaking, this equation applies for soluble surfactant. However, it has been previously used in studies involving insoluble surfactant [21]. Furthermore, it is important to understand the zero solubility problem since this will serve as the base solution in a study of the effect of small surfactant solubility.

An equation describing the time-dependent behavior of $\Gamma$ is also required. This equation takes the form of a convection-diffusion equation (see Wong et.

al. [35])

$$\frac{\partial ,}{\partial t}|_s - \frac{\partial \mathbf{X}}{\partial t} \cdot \nabla_{\mathbf{s}} , \; + \nabla_{\mathbf{s}} \cdot ( , \; \mathbf{u_s}) - D_s \nabla_{\mathbf{s}}^{\mathbf{2}} , \; + \, , \; \kappa \mathbf{u} \cdot \mathbf{n} = 0, \tag{3}$$

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. Note that the time derivative is taken with respect to fixed $s$.

To complete the problem statement, the following flow is specified at infinity

$$\begin{aligned} \mathbf{u}_\infty &= (Gx + G_1[x^3 + 3xy^2], -Gy - G_1[3x^2y + y^3]) \\ p_\infty &= P_\infty + 6 \; G_1 \; \mu(x^2 - y^2) \end{aligned} \tag{4}$$

where $G$ and $G_1$ are parameters characterizing the rate of strain and $P_\infty$ is an as yet undetermined pressure at the mill center. This form of the far-field flow was determined by Antanovskii [5], who used a boundary integral method to numerically compute the two dimensional velocity field produced by the four rotating rollers when no drop is present. This was then used to obtain the parameters in a local expansion of the flow field at the center of the mill. The result is expression (4), which is used as the far-field for the inner flow around a drop in an unbounded fluid. Note that this far-field flow is the superposition of a linear (pure strain) velocity field, characterized by rate of strain parameter $G$, and a motion describe by cubic terms, characterized by the additional rate of strain parameter $G_1$.

The preceding problem can be recast in terms of nondimensional quantities if the velocity is rescaled by $GR$ (where $\pi R^2$ is the initial bubble area), surface tension by $\sigma_0$, pressure by $G\mu$, surfactant concentration by $,_\infty$, and length and time by $R$ and $1/G$. The problem is then completely characterized by the dimensionless parameters

$$Q = \frac{2\mu G R}{\sigma_0}, \quad \epsilon = \frac{G_1 R^2}{G}, \quad Pe_s = \frac{\sigma_0 R}{\mu D_s}, \quad \chi = \frac{,_i}{,_\infty}, \text{and } \beta,$$

where $Q$ is the non-dimensional strain ($Q$ is of the form of a capillary number; the extra factor of 2 is included to correspond to Taylor's definition), $Pe_s$ is the modified surface Peclet number and $2\pi ,_i$ is the fixed amount of surfactant on the bubble surface. [1] However, for the next subsection, in which the basic formula for the complex variable representation of Stokes flow are given, we follow previous treatments (see e.g. [32]) and use dimensional quantities.

## 2.2 Complex Variable Formulation

The complex variable representation of two-dimensional Stokes flow has been widely employed to study the motion of drops and bubbles in various flows (see, e. g., [13], [28], [32] and references therein). Here the time-dependent formulation of [30] is summarized and modified to account for the cubic terms in the far-field flow.

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 $\omega$ is the fluid vorticity. The functions $\phi$ and $\psi$ 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 [20]) $W(z,\bar{z})$ 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 [19])

$$\frac{p}{\mu} - i\omega = 4f'(z) \tag{5}$$

$$u_1 + iu_2 = -f(z) + z\bar{f}'(\bar{z}) + \bar{g}'(\bar{z}) \tag{6}$$

$$s_{11} + is_{12} = z\bar{f}''(\bar{z}) + \bar{g}''(\bar{z}) \tag{7}$$

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

[1] Alternatively, the velocity may be rescaled by $\sigma_0/\mu$, pressure by $\sigma_0/R$, and time by $R\mu/\sigma_0$. The modified Peclet number is related to the usual Peclet number $Pe = GR^2/D_s$ by $Pe = QPe_s/2$. The modified Peclet number is preferable in studies of shear induced drop deformation, since it depends on material properties only.

The outward unit normal to the bubble surface can be represented as $N = ie^{i\theta}$, where $\theta$ is the angle between the tangent and the real positive x-axis. Using this, the stress balance equation (2) can be written

$$\begin{aligned} -i[pz_s + 2\mu(s_{11} + is_{12})\bar{z}_s] &= \sigma\kappa(iz_s) - \frac{\partial\sigma}{\partial s} z_s \\ &= -(\sigma z_s)_s \end{aligned} \tag{8}$$

where $s$ denotes arclength traversed in the clockwise direction and a subscript denotes partial differentiation. 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 (8) represents the normal force due to surface tension as well as the Marangoni force. Substituting (5) and (7) into the above equation and integrating the resulting expression with respect to $s$ gives the dynamic boundary equation

$$f(z) + z\bar{f}'(\bar{z}) + \bar{g}'(\bar{z}) = -i\frac{\sigma(s,t)}{2\mu} z_s. \tag{9}$$

Here, we have used some arbitrariness in the specification of the Goursat functions $f$ and $g$ to set the integration constant to zero.

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

$$z(\zeta, t) = \frac{\gamma_0(t)}{\zeta} + h(\zeta, t)$$

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 $\gamma_0$ to be chosen real and positive. Symmetry about the $x$ and $y$ axes is enforced by requiring

$$-z(-\zeta) = z(\zeta); \quad \bar{z}(\bar{\zeta}) = z(\zeta). \tag{10}$$

From (6) and (9) it can now be shown that the kinematic condition takes the form [30, 32]

$$Re\left\{\frac{z_t + 2f(\zeta,t)}{\zeta z_\zeta}\right\} = \frac{\sigma(,\ (\zeta,t))}{2\mu|z_\zeta|} \quad on\ |\zeta| = 1 \tag{11}$$

where the terms $f$ and $\sigma$ are written as shown to stress their dependence on $\zeta$. This equation differs from the corresponding clean flow equation only in the dependence of $\sigma$ on , $(\zeta, t)$.

The complex variable formulation of the equation for , $(\zeta = e^{i\nu}, t)$ is obtained from (3). For later use this equation is presented in dimensionless form, using the nondimensional quantities defined in subsection 2.1. The result is

$$\frac{\partial ,}{\partial t}\Big|_\nu - Re\,\left(\frac{,_\nu}{z_\nu} z_t\right) + \frac{1}{|z_\nu|}\frac{\partial}{\partial \nu} Re\, P(\nu,t) - \frac{1}{|z_\nu|} Im\,\left(\frac{z_{\nu\nu}}{z_\nu}\right) Im\, P(\nu,t) = \frac{2}{Q\ Pe_s}\frac{1}{|z_\nu|}\frac{\partial}{\partial \nu}\left(\frac{,_\nu}{|z_\nu|}\right) \tag{12}$$

where

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

The function , is required to satisfy the imposed symmetries

$$,(-\nu,t) = ,(\nu,t), \quad ,(\pi+\nu,t) = ,(\nu,t)$$

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

$$T = \int_0^{2\pi} ,\,|z_\nu| d\nu \tag{13}$$

is a conserved quantity.

# 3 Evolution equation for $z$

In this section an evolution equation for the conformal map $z(\zeta,t)$ is derived. The results in this section are presented in dimensionless form after rescaling and using the nondimensional groups discussed at the end of subsection 2.1. All quantities will be denoted by the same symbol as before, with the understanding that they are nondimensional.

## 3.1 Analytic continuation to $|\zeta| < 1$

In order to derive an evolution equation for the map $z(\zeta,t)$, equations (9) and (11) are analytically continued to the interior of the unit disk $|\zeta| < 1$. First, we observe that the form of the far-field flow (4) computed by Antanovskii [5] leads to the following nondimensional expression for the stress-stream function as $z \to \infty$

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

so that, in the notation of subsection 2.2,

$$\begin{aligned} f(\zeta,t) &\sim \frac{\epsilon\gamma_0^3}{2\zeta^3}+\frac{p_\infty\gamma_0}{4\zeta}+O(1) \\ g'(\zeta,t) &\sim \frac{\gamma_0}{2\zeta}+O(1) \end{aligned} \tag{14}$$

as $\zeta\to\infty$. Consequently, the quantity in braces in (11) behaves like $O(1/\zeta^2)$ as $\zeta\to\infty$; in order to remove the singularity from this term we rewrite this equation as

$$Re\left\{\frac{z_t+2f}{\zeta z_\zeta}+\frac{\epsilon\gamma_0^2}{\zeta^2}\right\}=\frac{\tau}{Q|z_\zeta|}+Re\left[\frac{\epsilon\gamma_0^2}{\zeta^2}.\right] \tag{15}$$

where $\tau=1+\beta\ln(1-,)$ is the nondimensional surface tension. The quantity in braces in the above equation is now an analytic function of $\zeta$ for $|\zeta|\leq 1$.

An evolution equation for the map $z(\zeta,t)$ for $|\zeta|<1$ can now be obtained by an application of the Poisson Integral Formula [20] to (15), with the result

$$z_t+2f(\zeta,t)=\zeta z_\zeta\left[\frac{-\epsilon\gamma_0^2}{\zeta^2}+I(\zeta,t)+iK\right] \tag{16}$$

where $K$ is a real constant and

$$I(\zeta,t)=\frac{1}{2\pi i}\oint_{|\zeta'|=1}\frac{d\zeta'}{\zeta'}\left[\frac{\zeta'+\zeta}{\zeta'-\zeta}\right]\left\{\frac{\tau(\zeta',t)}{Q|z_\zeta(\zeta',t)|}+Re\left[\frac{\epsilon\gamma_0^2}{\zeta^2}\right]\right\}. \tag{17}$$

Note that $I(\zeta,t)$ depends on the surfactant distribution via the term $\tau(\zeta',t)$ in the integrand. By examining the behavior of (16) in the limit $\zeta\to 0$, it follows that

$$\begin{aligned} K &= 0 \\ P_\infty(t) &= -2\left[I(0,t)+\frac{\dot\gamma_0}{\gamma_0}\right]. \end{aligned}$$

Although equation (16) describes the time evolution of the conformal map, it is more appropriate to view it as providing an equation for $f(\zeta,t)$. A more useful evolution equation for $z(\zeta,t)$ is then derived as follows. Take the complex conjugate of (9) and reorder the terms to obtain

$$g'(\zeta,t)=-\bar f(\zeta^{-1},t)-\bar z(\zeta^{-1},t)\frac{f_\zeta(\zeta,t)}{z_\zeta(\zeta,t)}+\frac{\tau(\zeta,t)}{Q}\frac{\bar z_\zeta^{1/2}(\zeta,t)}{\zeta z_\zeta^{1/2}(\zeta,t)}$$

where we have used the fact that on $|\zeta| = 1$ the relation $z_s = i\zeta z_\zeta/|z_\zeta|$ holds. Next, use (16) to eliminate $f$ from (9) and express $g'(\zeta, t)$ in terms of $z(\zeta, t)$. After some straightforward manipulations, this results in

$$g'(\zeta,t) = \frac{\bar{z}(\zeta^{-1},t)}{2}\left\{\frac{z_{\zeta t}(\zeta,t)}{z_\zeta(\zeta,t)} - \zeta[I_\zeta(\zeta,t) + \frac{2\epsilon\gamma_0^2}{\zeta^3}] - \left[1 + \frac{\zeta z_{\zeta\zeta}(\zeta,t)}{z_\zeta(\zeta,t)}\right]\left[I(\zeta,t) - \frac{\epsilon\gamma_0^2}{\zeta^2}\right]\right\}$$
$$+ \frac{1}{2}\left\{\frac{\bar{z}_\zeta(\zeta^{-1},t)}{\zeta} I(\zeta,t) + \bar{z}_t(\zeta^{-1},t) - \bar{z}_\zeta(\zeta^{-1},t)\frac{\epsilon\gamma_0^2}{\zeta^3}\right\} \qquad (18)$$

which is originally valid on the unit circle but is extended off through analytic continuation. In deriving this we have made use of the equality

$$\frac{I(\zeta,t) + \bar{I}(\zeta^{-1},t)}{2} = \frac{\tau}{Q z_\zeta^{1/2}(\zeta,t)\bar{z}_\zeta^{1/2}(\zeta^{-1},t)} + Re\left(\frac{\epsilon\gamma_0^2}{\zeta^2}\right)$$

which readily follows from (17). Note that in the case of linear far-field flow, with $\epsilon = 0$, the expression (18) agrees with that previously derived in [32].

The requirement that the right hand side of (18) is analytic in $|\zeta| < 1$ (except for a known singularity at $\zeta = 0$) determines the time evolution of the map $z(\zeta, t)$. Explicit evolution equations for the map parameters such as $\gamma_0(t)$ will be provided in the next section.

For later use, we note that (6) and (9) may be used to eliminate $f(\zeta, t)$ from (11) in favor of $u_1 + iu_2$. First, equation (16) is evaluated on $|\zeta| = 1$ by deforming the contour in the usual way. After elimination of $f$ using (6) and (9) and employing the identity $\frac{1}{2\pi} PV \int_0^{2\pi} Re\{\frac{\epsilon\gamma_0^2}{\zeta^2}\} \cot\frac{(\nu'-\nu)}{2} d\nu' = -\epsilon\ \gamma_0^2\ \sin 2\nu$, one obtains

$$z_t - (u_1 + iu_2) = -z_\nu\left[\frac{1}{2\pi Q} PV \int_0^{2\pi} \frac{\tau(,\ (\nu,t))}{|z_\nu(\nu,t)|} \cot\frac{(\nu'-\nu)}{2} d\nu' - 2\ \epsilon\ \gamma_0^2\ \sin 2\nu\right] \qquad (19)$$

where $PV$ denotes Cauchy principal value integral.

## 3.2 Time evolution equations

The steady state problem (in the absence of surfactant) is considered in [5]. By analyzing the possible singularities of $z(\zeta)$ given the far-field conditions (14), and applying the symmetry condition (10), it is shown that the mapping must be a rational function of the form

$$z(\zeta) = \frac{\gamma_0 + \gamma_1\zeta^2}{\zeta(1 - \gamma_2\zeta^2)} \qquad (20)$$

where the $\gamma_i$ are real parameters with $\gamma_0 > 0$ and $|\gamma_2| < 1$. The same argument with minor modifications shows that the mapping for the time dependent problem also has this form but with coefficients $\gamma_i(t)$ that are functions of time. The presence of surfactant does not affect these conclusions. [2]

We now proceed to derive evolution equations for the coefficients $\gamma_i(t)$ when surfactant is present. These equations follow from enforcing the analyticity of the right hand side of (18) in $0 < |\zeta| < 1$ and matching the form of the singularity at $\zeta = 0$.

The requirement that the right hand side of equation (18) is analytic at $\zeta^2 = \gamma_2$ gives one relation among the map parameters. The dominant singular behavior at $\zeta^2 = \gamma_2$ is contained in the terms $\bar{z}_\zeta(\zeta^{-1}, t)$ and $\bar{z}_t(\zeta^{-1}, t)$. If we define

$$\begin{aligned} Z_1(\zeta, t) &= \bar{z}_\zeta(\zeta^{-1}, t)(1 - \gamma_2/\zeta^2)^2 \\ Z_2(\zeta, t) &= \bar{z}_t(\zeta^{-1}, t)(1 - \gamma_2/\zeta^2)^2, \end{aligned}$$

then after multiplying equation (18) by $(1 - \gamma_2/\zeta^2)^2$ it is clear that this analyticity condition will be satisfied only if

$$\left\{ \frac{Z_1(\gamma_2^{1/2}, t)}{\gamma_2^{1/2}} \left[ I(\gamma_2^{1/2}, t) - \frac{\epsilon\gamma_0^2}{\gamma_2} \right] + Z_2(\gamma_2^{1/2}, t) \right\} = 0. \tag{21}$$

Upon noting that

$$\begin{aligned} Z_1(\gamma_2^{1/2}, t) &= 2(\gamma_0\gamma_2 + \gamma_1) \\ Z_2(\gamma_2^{1/2}, t) &= \frac{(\gamma_0\gamma_2 + \gamma_1)\dot{\gamma}_2}{\gamma_2^{3/2}} \end{aligned}$$

equation (21) simplifies to

$$\dot{\gamma}_2 = -2\gamma_2 \left[ I(\gamma_2^{1/2}, t) + \frac{\epsilon\gamma_0^2}{\gamma_2} \right] \tag{22}$$

Now, in the appendix it is demonstrated that

$$I(\gamma_2^{1/2}, t) = \frac{\epsilon\gamma_0^2}{\gamma_2} - \left[ \epsilon\gamma_0^2 \left( \frac{1-\gamma_2^2}{\gamma_2} \right) - \frac{1-\gamma_2^2}{\pi Q} \int_0^\pi \frac{\tau(\nu', t)}{|\gamma_0(1 - 3\gamma_2 e^{i\nu'}) - \gamma_1 e^{i\nu'}(1 + \gamma_2 e^{i\nu'})|} d\nu' \right]. \tag{23}$$

[2]The form of $z$ in (20) is based on the analytic properties (location of singularities, etc.) of terms in equation (18). Although the surfactant enters this equation through the term $I(\zeta, t)$, it does not affect any of the analytic properties.

Substituting this into (22) and simplifying leads to

$$\dot{\gamma_2} = 2\gamma_2 \left[ \epsilon\gamma_0^2 \left( \frac{1-\gamma_2^2}{\gamma_2} \right) - \frac{1-\gamma_2^2}{\pi Q} \int_0^{\pi} \frac{\tau(\nu',t)}{|\gamma_0(1-3\gamma_2 e^{i\nu'}) - \gamma_1 e^{i\nu'}(1+\gamma_2 e^{i\nu'})|} d\nu' \right] \tag{24}$$

which is the desired evolution equation for $\gamma_2$.

A second equation is obtained by equating the coefficient of the $O(1/\zeta)$ term on the right hand side of (18) with the known coefficient of this term in the Laurent series expansion of $g'(\zeta,t)$. To facilitate this task, the asymptotic behavior in the limit $\zeta \to 0$ of several terms is given below:

$$\begin{aligned} g'(\zeta,t) &\sim \frac{\gamma_0}{2\zeta} + O(1) \qquad z(\zeta,t) \sim \frac{\gamma_0}{\zeta} + (\gamma_1 + \gamma_0\gamma_2)\zeta + O(\zeta^3) \\ \bar{z}(\zeta^{-1},t) &\sim -\frac{\gamma_1}{\gamma_2}\zeta + O(\zeta^3) \qquad z_t(\zeta^{-1},t) \sim \frac{\gamma_1\dot{\gamma}_2 - \dot{\gamma}_1\gamma_2}{\gamma_2^2}\zeta + O(\zeta^3) \\ \bar{z}_\zeta(\zeta^{-1},t) &\sim \frac{\gamma_1}{\gamma_2}\zeta^2 + O(\zeta^4). \end{aligned} \tag{25}$$

The asymptotic behavior of $I(\zeta,t)$ at $\zeta = 0$ readily follows from the Taylor's expansion

$$I(\zeta,t) = I_0(t) + \sum_{k=1}^{\infty} \hat{I}_k(t)\zeta^k$$

where (see (17))

$$\begin{aligned} I_0 &= \frac{1}{2\pi Q} \int_0^{2\pi} \frac{\tau(\nu,t)}{|z_\zeta(e^{i\nu},t)|} d\nu \\ \hat{I}_k &= \frac{1}{\pi} \int_0^{2\pi} \left( \frac{\tau(\nu,t)}{Q\ |z_\zeta(e^{i\nu},t)|} + 2\ \epsilon\ \gamma_0^2\ \cos 2\nu \right) e^{-ik\nu} d\nu. \end{aligned}$$

Now, equating the coefficients of the $O(1/\zeta)$ terms in equation (18) yields, upon simplification,

$$\gamma_1 = \frac{\gamma_2}{\epsilon\gamma_0}. \tag{26}$$

Finally, a third relation among the conformal mapping coefficients results from the condition that the drop area equal $\pi$. This leads to the constraint [5]

$$\gamma_0 = \left[ \frac{2(1+\gamma_1^2)}{c_1 + (c_1^2 - c_2)^{1/2}} \right]^{1/2} \tag{27}$$

where

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

In summary, the three equations (24), (26), and (27) determine the time evolution of the conformal map parameters $\gamma_i,\ i = 0, \ldots, 2$ (and the dynamics of the map $z(\zeta, t)$ itself) and are the main results of this section. Note that these parameters are functions of the surfactant concentration , $(\zeta, t)$, which in turn evolves according to equation (12).

# 4 Steady-state solutions

We now derive a simplified set of equations which describe the steady-state interface shape and distribution of surfactant. Under the assumption $Pe_s \to \infty$, exact solutions to these equations will be constructed.

Upon setting the time derivatives to zero, the non-dimensional surfactant evolution equation takes the form (see (12))

$$\frac{\partial}{\partial\nu} Re\left[\frac{(u_1 + iu_2)\bar{z}_\nu ,}{|z_\nu|}\right] = \frac{2}{Q\ Pe_s}\frac{\partial}{\partial\nu}\frac{,\ _\nu}{|z_\nu|}$$

which is just the complex variable representation of $\nabla_s \cdot (,\ \mathbf{u}_s) = \frac{2}{Q\ Pe_s}\frac{\partial^2}{\partial s^2},$ . Here we have used the fact that the fourth term in (12), i.e., the complex variable representation of $,\ u_n\kappa$, is zero for the steady-state problem. Integrating with respect to $\nu$ gives

$$Re\left[\frac{(u_1 + iu_2)\bar{z}_\nu ,}{|z_\nu|}\right] = \frac{2}{Q\ Pe_s}\frac{,\ _\nu}{|z_\nu|} + C$$

where $C$ is an integration constant. By symmetry, $\int_0^{2\pi} ,\ \mathbf{u}_s d\nu = 0$, which implies $C = 0$. Using equation (19) (with $z_t$ set to zero) to eliminate $u_1 + iu_2$ then leads to the singular integral equation

$$\frac{1}{4\pi} PV \int_0^{2\pi} \frac{\tau(\nu')}{|z_\nu|} \cot\frac{(\nu' - \nu)}{2} d\nu' = \frac{1}{Pe_s\ ,}\frac{,\ _\nu}{|z_\nu|^2} + \epsilon\ Q\ \gamma_0^2\ \sin 2\nu. \qquad (28)$$

The above equation determines the surfactant concentration, given the steady interface shape $z(\zeta, t)$. This shape, in turn, is determined from (24) (with

$\dot{\gamma}_2 = 0$), (26), and (27). An expression relating the capillary number $Q$ to the interface shape and surfactant concentration is determined from equation (24) by setting $\dot{\gamma}_2 = 0$. This leads to the equation

$$Q = \frac{\gamma_1}{\pi \gamma_0} \int_0^{\pi} \frac{\tau(\nu')}{|\gamma_0(1 - 3\gamma_2 e^{i\nu'}) - \gamma_1 e^{i\nu'}(1 + \gamma_2 e^{i\nu'})|}. \tag{29}$$

## 4.1 Exact solutions

Under the assumption $Pe_s \to \infty$ exact solutions for the steady-state interface shape and surfactant distribution may be constructed. In real physical systems, $Pe_s$ is typically quite large and hence the third term in (12) is often neglected.

Depending on the non-dimensional strain and shape of the bubble, the surface can be either completely covered with surfactant or contain 'stagnant caps' of surfactant, i.e., regions where , $> 0$ interspersed with regions where , $= 0$ [30]. 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 $\theta$ needs to be determined as part of the solution.

On the portion of the bubble where the surfactant concentration is nonzero $u_1 + iu_2 = 0$, i.e., the singular equation (28) holds for $\nu \in L$, whereas , $= 0$ for $\nu \in \bar{L}$. Using the latter fact, we rewrite (28) as

$$\frac{1}{4\pi} PV \int_L \tilde{\tau}(\nu') \cot \frac{(\nu' - \nu)}{2} d\nu' = r(\nu) \tag{30}$$

for $\nu \in L$ where

$$\begin{aligned} \tilde{\tau}(\nu) &= \frac{\tau(\nu)}{|z_\nu|} - \frac{1}{|z_\nu|} \\ r(\nu) &= -\frac{1}{4\pi} PV \int_0^{2\pi} \frac{1}{|z_\nu|} \cot \frac{(\nu' - \nu)}{2} d\nu' + \epsilon\ Q\ \gamma_0^2 \ \sin 2\nu. \end{aligned}$$

Later it is shown that , $(\nu) \to 0$ as $\nu \to \theta$, so that $(\frac{\tau}{|z_\nu|} - \frac{1}{|z_\nu|}) \to 0$ in this limit. Hence the principal value integral on the left hand side of (30) is well defined at $\nu = \theta$ as well as the other endpoints of the set $L$.

### 4.1.1 Bubble covered with surfactant

In the case where the bubble surface is completely covered with surfactant, equation (30) simplifies to

$$\frac{1}{2\pi} PV \int_0^{2\pi} \frac{\tau(\nu')}{|z_\nu|} \cot \frac{(\nu' - \nu)}{2} d\nu' = 2\ \epsilon\ Q\ \gamma_0^2\ \sin 2\nu.$$

According to the Hilbert formula [20] the solution is

$$\frac{\tau(\nu)}{|z_\nu|} = -2\ \epsilon\ Q\ \gamma_0^2\ \cos 2\nu + A$$

where A is a constant. Solving for the nondimensional surfactant concentration , then gives

$$, = \left\{ 1 - \exp\left[ \frac{(A - 2\epsilon Q \gamma_0^2 \cos 2\nu)|z_\nu| - 1}{\beta} \right] \right\}. \tag{31}$$

The value of the constant $A$ is determined form the normalization condition (13). This requirement leads to the equation

$$\int_0^{2\pi} |z_\nu| \left\{ 1 - \exp\left[ \frac{(A - 2\epsilon Q \gamma_0^2 \cos 2\nu)|z_\nu| - 1}{\beta} \right] \right\} = 2\pi\chi. \tag{32}$$

Given $z(\nu)$, it is a simple matter to solve (29) and (32) for $A$ and $Q$ (and hence $,(\nu)$) using a nonlinear equation solver such as Newton's method. The results of such a computation are best illustrated in the form of a response curve, which charts the deformation of the bubble versus the non-dimensional strain $Q$. The deformation of the bubble is defined as

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

where $R_{max}$and $R_{min}$ are the maximum and minimum distances from the origin to a point on the bubble surface. The response curves when the bubble is completely covered with surfactant are represented by the *dashed* curves in Figure 2b. These curves are obtained by solving for $\gamma_0$, $\gamma_2$, $Q$ and $,(\nu)$ for an increasing sequence of $\gamma_1$ (corresponding to increasingly deformed bubbles). At the terminal (right) endpoint of each dashed line the steady surfactant distribution reaches zero at $\nu = \pm\pi/2$, i.e., at the top and bottom of the bubble. Bubbles with a greater deformation will therefore exhibit 'surfactant caps' with $, > 0$ near convergent stagnation points in the flow and regions with $, = 0$ near divergent stagnation points.

#### 4.1.2 Surfactant cap solutions

In the case of surfactant cap bubbles equation (30) does not hold for all $\nu$, so that the Hilbert formula for the compounding of singular integrals does not apply. However, an analytical solution to this equation can be obtained by applying a method based on the reduction of the singular integral equation to the so-called Riemann problem [20, 22]. Details in the case of a linear equation of state are given in [30]. Since the analysis presented there generalizes in a straightforward manner to account for the nonlinear equation of state, only the results are furnished here. The exact solution takes the form

$$\frac{\tau}{|z_\nu|} = \frac{1}{|z_\nu|} + \tau_p + iR_1(\alpha\omega - \bar{\alpha}/\omega) \tag{33}$$

where

$$\tau_p(\nu) = \frac{\omega(\nu)}{2\pi i} PV \int_L \frac{r(\nu')}{\omega(\nu')} \cot\frac{(\nu'-\nu)}{2} d\nu' + \frac{1}{2\pi i\omega(\nu)} PV \int_L r(\nu')\omega(\nu') \cot\frac{(\nu'-\nu)}{2} d\nu' \tag{34}$$

is a particular solution to equation (30) and

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

Here $\alpha = e^{i\theta}$ and $\bar{\alpha}$ are the endpoints of one arc constituting $L_\zeta$, ($-\bar{\alpha}$, $-\alpha$ are the endpoints of the other arc). Branch cuts are chosen to lie along the contour $L_\zeta$. We select the particular branch satisfying $\omega(\zeta) \to 1$ as $\zeta \to \infty$. The last term in (33) is a solution of the homogeneous version of (30). This term contains two free parameters, $R_1$ and $\theta$ (note that the interval of integration $L$ in (34) also depends on $\theta$). Two conditions are required of the solution to fix these parameters. One is that the total stress on the bubble is required to 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 $,_\nu$ is integrable. The second condition is that the total amount of surfactant on the bubble surface equal $2\pi\chi$.

To enforce the first condition, we expand the solution (34) 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 (see [30])

$$R_1 = -\frac{|J(\theta)|}{2\pi} \tag{35}$$

where $J(\theta)$ refers to the first integral in (34), evaluated at $\nu = \theta$. Together with the normalization condition (13), this provides a pair of equations for the unknowns $\theta$ and $R_1$.

The resulting leading order singularity at the edge of the surfactant cap has the form

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

where $\nu_0 = \pm\theta,\ \pi \pm \theta$ and $d$ is a constant. Equation (19) implies that the fluid velocity at the cap edges (on the bubble surface) has a singularity of the same form.

Equations (31)-(32) provide an exact solution for the steady-state shape of the interface and distribution of surfactant in the case where the bubble is covered by surfactant. Equations (33)–(35) apply the when the bubble contains surfactant caps. These solutions are exact in the sense that determination of the bubble shape and surfactant concentration are reduced to performing quadratures. However, application of the normalization condition (13) to determine the value of a remaining free parameter ($A$ or $\theta$, depending on whether the bubble is covered with surfactant or contains surfactant caps) leads to a nonlinear equation. In general some form of iteration must be used to set the value of this last parameter. Nevertheless, the solutions reported in this section will be referred to as exact solutions.

# 5 Numerical results: steady-state solutions

## 5.1 $Pe_s = \infty$

We first consider steady state solutions for $Pe_s = \infty$. The exact solution in the previous section is most conveniently evaluated by specifying one of the conformal map parameters, say $\gamma_1$, and then using (26) and (27) to determine the other map parameters. Once the map form is known, (31–32) is employed to determine the surfactant distribution in the case where the bubble is covered with surfactant, whereas (33–35) is used in the case of surfactant cap bubbles. The value of $Q$ corresponding to the solution is given by (29).

The most difficult part of this process is the evaluation of the integrals in (34), in which the kernels contain principal value singularities in addition to the square root singularities at the endpoints of the intervals of integration. 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. The leading order square root singularities at the endpoints of $L$ are removed by following the standard trick of subtracting out the singularity from the integrand in a form that is analytically integrable. To evaluate these integrals, the surfactant cap angle needs to be specified. In general, for arbitrary cap angles, the normalization condition (13) will not be satisfied. We therefore adjust the parameter $\gamma_1$ in a Newton iteration until the normalization condition is satisfied.

We contrast the behavior with and without surfactant in the case $\epsilon=0.01$, which corresponds to the value of $\epsilon$ in Taylor's experiments.[3] First consider $\beta=0$ (i.e., no surfactant). The response diagram plotting $D$ versus $Q$ in this case, first presented in [3], contains a number of interesting features (see the $\epsilon=0.01$ curve in Fig. 2a). The leftmost portion of the curve, between $Q=0$ and $Q=0.6$, represents rounded bubble profiles. In contrast the bubble shapes along the flat upper portion of the curve are cusp-like (although smooth) and show a remarkable similarity with the bubble profiles observed in the experiments of Taylor. Numerical calculations of the full time dependent evolution for $\epsilon\geq 0.01$ performed in [23], [24] suggest that the steady solutions are stable for values of $Q$ up to 0.7. Numerical difficulties due to the large magnitude of curvature at the bubble tips prevented the calculations from treating (finite) $Q$ values above 0.7. Nevertheless, these results indicate that in the absence of surfactant the steady 2-D bubbles are stable for values of the capillary number well above that for which Taylor first observed the sudden transition to a transient cusp-like bubble. It has been suggested [5] that the steady solutions are stable for all finite $Q$ when $\epsilon$ is sufficiently large.[4] If this is the case then the $\beta=0$ model would not describe tip streaming for the value of $\epsilon$ employed by Taylor, i.e., cusp-like bubbles would survive for all strains. This behavior is consistent with

[3] The numerical simulations in [5] of the 2-D outer flow field produced by Taylor's four roller mill lead to a value of $\epsilon=0.01$ prior to tip streaming, with the value dropping to 0.0025 for the smaller bubble remaining after tip streaming.

[4] When $\epsilon<0.004$ the response curve is no longer a single valued function of $Q$, and a portion of curve is expected to represent unstable steady solutions. More will be said about this situation in section 7.

the experiments of DeBruijn [8], which show that there is no tip-streaming when surfactant is absent.

The situation changes when surfactant is present. Figure 2b shows the $\beta > 0$ response curves for three representative values of $\beta$. When the bubble is covered with surfactant, the exact solution (31)–(32) holds, and the resulting portion of the response curve is shown as a dashed line. The portion of the response curve corresponding to the surfactant cap solution (33)–(35) is represented by a solid line. Note that the two different forms of solution merge smoothly into one another.

The most interesting feature of the $\beta > 0$ curves is the absence of the flat upper portion of the $S$-shaped curve seen when their is no surfactant. Instead the response curves terminate after a single turning point. In this respect these response curves, utilizing the nonlinear equation of state, are similar to the curves obtained in [30] using the linear equation of state. Figures 3a and 3b depict the surfactant concentration and bubble profiles at the representative points $A-E$ along the $\beta = 0.1$ response curve. Note that the lower portion of the curve corresponds to rounded bubbles, whereas the upper portion of the curve (points $D$ and $E$) represents cusp-like bubbles. The surfactant concentration shown in Figure 3a clearly depicts the formation of surfactant caps with square root singularities at the cap endpoints.

At the terminal point of the response curve (point $E$) a true cusped bubble is formed, i.e., the radius of curvature tends to zero at $\nu = 0$ (see Figure 3c). At this point the surface tension also reaches zero, consistent with rigorous theory [25]. This behavior is numerically verified by evaluating the integrals in the exact solution at increasing resolution. The terminal state is reached in spite of the strong Marangoni force opposing the accumulation of surfactant as surface tension tends to zero.

Evidence is provided below that the turning point corresponds to a change in stability for the steady solutions; the lower branch solutions correspond to stable steady states whereas the upper branch solutions are unstable. Thus for capillary numbers less than the value $Q_c$ at a turning point, the time dependent solution will evolve toward the proper rounded bubble steady state. For $Q > Q_c$ the bubble does not reach a steady state. These facts hint at a time dependent evolution for $Q > Q_c$ in which the bubble continuously evolves until an unsteady cusped (i.e., infinite curvature) formation is achieved, much as in Taylor's experiment. The surmised time dependent behavior is verified in the section 6.

## 5.2 $Pe_s < \infty$

Numerical solutions for $Pe_s < \infty$ are considered in this section in order to examine the role of surface diffusion on the steady state interfacial shape. In the case $Pe_s > 1$, steady state solutions are evaluated as follows. The interface shape $z(\nu)$ is computed from the specification of a single conformal map parameter, say $\gamma_1$, with the other two parameters are determined from (26) and (27). This in turn determines the surfactant distribution through the integral equation (28). If the functions appearing in (28) are evaluated at $n$ equally spaced points $\nu_j = 2\pi(j-1)/N,\ j = 1, \ldots, N$, then the discretized version of (28) provides $N$ equations for the $N$ unknowns $,_j$. The four fold symmetry is utilized so that only one quarter of the interface needs to be discretized. The principal value integral term on the left hand side of (28), which we denote by $H[\tau/|z_\nu|](\nu)$, is evaluated with spectral accuracy using the relation (see e.g. [18])

$$H[\tau/|z_\nu|](\nu) = \frac{i}{2}[(\frac{\tau}{|z_\nu|})_+ - (\frac{\tau}{|z_\nu|})_-].$$

Here the plus subscript denotes a sum over positive wavenumber Fourier modes, whereas the minus subscript denotes the sum over negative wavenumber modes.

The resulting set of equations can be solved using Newton's method for an increasing sequence of $\gamma_1$ (i.e., for an increasingly deformed interface). The normalization condition (13) is enforced as a constraint on the solutions $,_j$. Agreement with the exact solution of the previous section is verified for $Pe_s$ large enough, although the Newton's method here does not converge for bubbles sufficiently close to cusping or for surfactant distributions that are near the singular 'cap' distribution.

It is found that a very large number of points is necessary to obtain an accurate solution for bubbles near cusping when $Pe_s$ is small (i.e., $Pe_s \lesssim 1$). Newton's method, which involves the solution of an $N \times N$ matrix equation at each iteration, is prohibitively slow for $N$ much greater than 1024. In this range, we have found that a method involving fixed point iteration is more efficient. The fixed point iteration scheme employed here takes the form (see (28))

$$,_\nu^{(k+1)} = \frac{1}{2}\ Pe_s\ |z_\nu|^2\ ,\ \ H\left(\frac{\tau^{(k)}}{|z_\nu|}\right) - \epsilon\ Q\ Pe_s\ ,^{(k)}\ |z_\nu|^2\ \gamma_0^2\ \sin 2\nu$$

where $,^{(k)}$ denotes the kth iterate of $,(\nu)$ and $\tau^{(k)}$ is the value of $\tau$ evaluated using $,^{(k)}$. Spectral integration is employed to produce $,^{(k+1)}$. The constant of integration $\Gamma_0$ is determined from the normalization condition (13). This leads to

$$\Gamma_0 = \frac{2\pi\chi - \int_0^{2\pi} \Gamma_1(\nu')d\nu'}{\int_0^{2\pi} |z_\nu| d\nu'}$$

where $\Gamma_1(\nu) = \Gamma(\nu) - \Gamma_0$ is the periodic part of $\Gamma$. Although the convergence of the iterative scheme is linear, this algorithm requires only $O(n \ln n)$ operations per iteration, so that a very large number of points may be used. Up to $N = 8192$ points are used in the simulations reported here. For $Pe_s \lesssim 1$, the iteration converges even for bubble shapes that are very near cusped. This is not the case for $Pe_s$ much greater than one, so in this regime the scheme based on Newton's method is employed.

Fig. 4 presents the response curves at $\beta = 0.5$ for several $Pe_s$ values. At the terminal point of each curve the implemented iteration scheme no longer converges. However, it appears that the computed termination point lies near the actual termination point, where the bubble develops a true cusp and where the surface tension is zero at $\nu = 0$. This is supported by the curvature and surface tension trends as the terminal point is approached.

Fig. 4 clearly shows that as surface diffusion increases, the response curve smoothly transforms from its form at $Pe_s = \infty$ to the form observed in the absence of surfactant. This behavior might be expected, since the surfactant distribution is nearly constant when $Pe_s$ is small and $Q$ is not too large. In this condition the surface tension is nearly uniform along the bubble surface and surfactant merely reduces overall magnitude of surface tension from its clean flow value.

Similar behavior is observed as the total amount of surfactant (as measured by $\chi$) is decreased. Specifically, Fig. 5 shows that as $\chi$ is reduced with $Pe_s$ held fixed, the response curve again deforms toward the form exhibited in the absence of surfactant (compare with Fig. 2a). The presence of nonzero diffusion appears to be important for this trend. In particular, when $Pe_s = \infty$ the upper, flat portion of the response curve is absent, regardless of the value of $\chi$.

# 6 Numerical results: time dependent evolution

In this section the time dependent behavior of the interface is examined. Of particular interest are the details of the transient dynamics for small surface diffusion and for capillary numbers greater than the turning point value $Q_c$. The calculations are greatly simplified by exploiting the known analytic structure of the conformal map solution.

## 6.1 Numerical Method

The numerical method used to follow the time dependent evolution is outlined in this subsection. We start by presenting some preliminary calculations to transform the governing equations into a form convenient for numerical computation. First differentiate the area equation (27) to obtain an equation of the form $\dot{\gamma}_0 = q[\gamma_1]\dot{\gamma}_1$. Upon introducing the function

$$h(\gamma_1) = c_1 + ({c_1}^2 - c_2)$$

and differentiating the relation (26) one obtains the expression

$$\dot{\gamma}_1 = \frac{\dot{\gamma}_2}{\epsilon[\gamma_0 + \gamma_1 s(\gamma_1)]} \tag{36}$$

where

$$s(\gamma_1) = \frac{2\gamma_1 h - h'(1 + {\gamma_1}^2)}{[2h^3(1 + {\gamma_1}^2)]^{1/2}}$$

and $h' = \partial h/\partial\gamma_1$. Substitution of (24) into (36) leads to an expression for $\dot{\gamma}_1$ in terms of the other map parameters $\gamma_i$. Given the surfactant distribution at time $t$, an explicit scheme is applied to equations (24), (26) and (36) to obtain the map parameters at time $t + \Delta t$.

To describe how the surfactant distribution $,(\nu, t)$ is updated, it is convenient to write equation (12) as

$$\frac{\partial ,}{\partial t} + \Lambda_1(\nu, t) ,_{\nu\nu} = F(, , ,_\nu, t)$$

where $F(, , ,_\nu, t)$ takes the form

$$F(, , ,_\nu, t) = \Lambda_2(\nu, t) ,_\nu + \Lambda_3(\nu, t),$$

and the coefficients $\Lambda_i(\nu, t),\ i = 1, \ldots, 3$ depend on the interface shape. Assuming that this shape is known at time $t + \Delta t$ and that $,(\nu, t)$ is known, then equation (12) is discretized as

$$\frac{,_j^{n+1} - ,_j^n}{\Delta t} + \frac{\Lambda_1(\nu_j, t_n)}{2\Delta t}(,_{j+1}^{n+1} + ,_{j-1}^{n+1} - 2,_j^{n+1}) = F(,_j^n, ,_{\nu j}^n, t_n)$$

where we have introduced the notation $,^n_j = ,(\nu_j, t_n)$ and where $,^n_{\nu j}$ denotes the standard centered difference formula for $,_\nu$, centered at $\nu_j$. The resulting tridiagonal system can be inverted using standard techniques. Although this implicit Euler method is only first order accurate in time, we have found this sufficient for our purposes. In is not difficult to adapt the method to achieve second order accuracy. Computations for $Pe_s = \infty$ were performed with a straightforward explicit method, fourth order accurate in time and pseudospectral in space. A useful check on the accuracy of either method is to monitor the total amount of surfactant, which must remain constant. The total amount of surfactant was found to change by $0.1 - 0.001\%$ over the length of a calculation, depending on the time and space intervals and the method used. Thus, there was no need to renormalize the surfactant concentration periodically throughout the calculation as has often been found necessary to prevent degradation of accuracy (see e.g., [31]). For all the results reported in the next section, it was checked that decreasing the time step or the space interval did not affect the results. As a means of verification, it was checked that the transient calculations gave results in complete agreement with the exact steady state solutions exhibited in the previous section.

## 6.2 Transient behavior, numerical results

Transient calculations were performed with two main objectives: to determine the stability of steady solutions along the branches depicted in Fig. 2b, and to investigate the ultimate status of the time dependent evolution when $Q > Q_c$. Concerning the stability of the solution branches in Fig. 2b, 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 $Q < Q_c$. By way of illustration, Figure 6 depicts the transient surfactant distribution 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. This result suggests that the lower part of the response curve is a branch of stable steady solutions.

A comparison of the steady state response curve with the results of transient calculations for several values of the capillary number $Q$ is shown in Fig. 7. The parameter values are $\beta = 0.5, \chi = 0.5$, and $Pe_s = \infty$. The markers for fixed $Q$ depict the deformation of a time evolving bubble starting from a circle with $D = 0$ at $t = 0$. Note that for $Q < Q_c$ the markers indicate that a steady bubble solution is quickly reached, and the steady deformation is in precise agreement with the exact steady solution of the previous section (denoted by a solid curve). In contrast, when $Q > Q_c$ there is no allowable steady state solution. Thus, the bubble evolves without limit. Only a couple of outcomes are consistent with the form (20) of the conformal map and conditions (26, 27). One is that the bubble oscillates indefinitely, i.e., a limit cycle is approached. The other is that an unsteady cusped formation is achieved. Our numerical evidence for $Q = 0.4 > Q_c$ suggests that the latter outcome comes to pass.

The transient bubble profiles for $Q = 0.4$ are displayed in Fig. 8a. A plot of $\ln \kappa$ versus time (Fig. 8b), where $\kappa$ is the tip curvature, provides strong evidence that a true cusp singularity is realized in finite time. The figure demonstrates that the transient evolution for $Pe_s = \infty$ exhibits superexponential growth in the tip curvature during the late stages of evolution. Similar behavior is expected for sufficiently large but finite $Pe_s$ (i.e., weak surfactant diffusion), since the response curve has the same form as for $Pe_s = \infty$. This expectation is verified in Fig. 8b, for which a plot of $\ln \kappa$ versus time at $Pe_s = 10$ also exhibits superexponential growth. For comparison, the log-curvature is also plotted using the parameter values $Q = 0.3,\ Pe_s = \infty$, for which the evolution approaches a steady state.

Finally, the effect of increasing surface diffusion is illustrated in Fig. 9. Here the time dependent interface profiles and curvature are shown for parameter values $Q = 0.6$ and $Pe_s = 0.1$. As expected, the evolution approaches a steady state, despite a value of $Q$ that is considerably higher than that which led to unsteady cusped bubbles for $Pe_s >> 1$.

In summary, the numerical results provide strong evidence that a true cusp singularity occurs in finite time for a bubble evolving in an Antanovskii type straining flow with variable surface tension. The singularity is avoided in the case of constant surface tension. The formation of an unsteady cusped bubble at a critical value of capillary number $Q$ is viewed as the onset to tip streaming.

# 7 Discussion

Despite the drastic simplifications employed in our analysis, it is interesting to compare the theoretically predicted $Q_c$ at which point the bubble makes a transition from a steady rounded configuration to the unsteady cusp-like formation, to the values obtained in Taylor's experiment. There are three parameters, $\beta$, $\chi$, and $Pe_s$, that need to be determined from the experimental conditions. Although this cannot be precisely done for the fluids employed by Taylor[5] the parameter values can be estimated using representative values for the physical constants. The modified surface Peclet number typically satisfies $Pe_s >> 1$ and is set to infinity. A representative range of values for the surface tension $\sigma_0$ at a *clean* interface in an oil-water combination at room temperature is $25 - 50$ dyn/cm. A typical value for the product $RT, _\infty$ is 5 dyn/cm at room temperature (the maximum packing density $, _\infty$ does not vary greatly among fluid combinations).[6] This gives a value for $\beta = RT, _\infty/\sigma_0$ in the range $0.1 - 0.2$. Since there is no obvious characteristic value for $\chi$, we will present values of the critical capillary number for a range of this parameter.

Table *I* presents the calculated value of the critical capillary number for $\beta = 0.1$ and a range of $\chi$. This calculated values of $Q_c$ are not very sensitive to the value of $\chi$, and they compare favorably with the experimentally observed value $Q_c = 0.41$ (see also Fig. 2b). It is mentioned in passing that for smaller $\epsilon$ the $\beta = 0$ response curve takes on a $S$ shape (see Fig. 2a), and it has been suggested that the portion of the curve between the turning points is a branch of unstable steady solutions. If so, then the first turning point would correspond to a sudden transition to a steady cusped bubble (if the upper branch is stable) or to an unsteady cusped bubble (if the upper branch is unstable). However, the values of $\epsilon$ and $Q_c$ required for this to happen, namely $\epsilon < 0.004$ and $Q_c = 0.61$, do not match the experimental values at the first transition, given by $\epsilon = 0.01$ and $Q_c = 0.41$. Instead, they are consistent with the parameter values at the *second* transition observed by Taylor, occurring at $Q = 0.65$ and $\epsilon = 0.0025$, in which a steady rounded bubble suddenly transforms to a *steady* cusp-like bubble. Thus, the 2-D model gives results that are consistent with experimental

[5]Taylor [33] filled the four roller mill with 'golden syrup', which is a concentrated sugar solution. A number of liquids were used for the drop phase, so as to cover a large range of drop to liquid viscosity ratios. A mixture of carbon tetrachloride and parrafin oil was utilized to obtain the lowest ratio $\mu_{drop}/\mu_{liquid} = 0.0003$. This leads to the experimental results described in section 1.

[6]Charles Malderelli, private communication.

observation, if we use the $\beta > 0$ model with $\epsilon = 0.01$ to describe the first transition and the $\beta = 0$ model with $\epsilon < 0.004$ to describe the second one. Justification for using the two different models follows from the supposition that surfactant is removed from the bubble during tip streaming, and that the bubble remaining after tip streaming is smaller in size. The match between theory and experiment may indicate that the simplified model employed here still incorporates much of the relevant physics.

# 8 Conclusion

We have considered the effect of variable surface tension, caused by the presence of surfactant, on the steady state shape and time dependent evolution of a bubble in a four roller mill. At issue is the possible spontaneous occurrence of singularities on the bubble surface. Despite the use of a nonlinear equation of state, which enhances the magnitude of Marangoni stresses in regions of large surfactant concentration and thus hinders cusp formation, we find exact steady solutions that consist of cusped bubble profiles with zero tension at the tips. The form of the steady state solution branch is suggestive of spontaneous singularity formation in the time-dependent evolution for $Q > Q_c$. Actual finite time singularity formation in the transient evolution is verified through numerical calculation. The numerical calculations are greatly simplified by the analytic structure of the conformal map solution. Analogous behavior is observed for finite $Pe_s$.

After the analytical and numerical work for this paper was completed, the author became aware of the careful computational study of Pozrikidis [24], in which full numerical simulation of a time-evolving bubble in an Antanovskii type straining flow was performed using an adaptive boundary integral method. The evolution was considered both with and without surfactant. The results are for the most part consistent with the present work. For example, when $\epsilon = 0.05$, $\beta = 0.5$, $Q = 0.6$ and $Pe_s = 20$ or 200 the computations in [24] show that the bubble evolves toward an unsteady cusped shape much like that shown in Fig. 8. However, the numerics breaks down before the curvature gets too large, and evidence of superexponential growth of curvature is not as strong as in the present work. The results do differ somewhat from those presented here in the case $\beta = 0.2$, $Pe_s = 20$. For these parameter values, the bubble is observed to evolve toward a cusped shape as in the previous example, but instead of achieving a true cusp (as occurs for the exact mathematical solution of the form (20)) the curvature saturates and narrow jets stream out from the bubble tips. Since the numerical algorithm of [24] does not restrict the solution to the form (20), this could be an indication that this form is unstable to small disturbances as the cusp singularity is approached, when $\beta$ is sufficiently small. However, further study is required to uncover the precise cause of the differences in behavior. Other factors not considered in these studies, such as diffusion and/or transport of surfactant from the interface to the bulk fluid, may also influence the formation of cusped solutions. This will be considered in future work.

# 9 Appendix

We present a derivation of equation (23). First evaluate the expression (17) at $\zeta = \gamma_2^{1/2}$. Upon performing the expansion

$$\frac{1}{\zeta'}\left[\frac{\zeta'+\zeta}{\zeta'-\zeta}\right] = \frac{1}{\zeta'} + 2\sum_{n=1}^{\infty}\frac{\gamma_2^{n/2}}{\zeta'^{n+1}},$$

which holds for $\gamma_2 < 1$, it is easy to see that

$$\frac{1}{2\pi i}\frac{d\zeta'}{\zeta'}\left[\frac{\zeta'+\zeta}{\zeta'-\zeta}\right] Re \left[\frac{\epsilon\gamma_0^2}{\zeta'^2}\right] = \epsilon\gamma_0^2\gamma_2.$$

It follows that

$$I(\gamma_2^{1/2},t) = \frac{\epsilon\gamma_0^2}{\gamma_2} - \left[\epsilon\gamma_0^2\frac{1-\gamma_2^2}{\gamma_2} - \frac{1}{2\pi i Q}\frac{d\zeta'}{\zeta'}\left[\frac{\zeta'+\zeta}{\zeta'-\zeta}\right]\frac{\tau}{|z_\zeta|}\right].$$

Some tedious but straightforward algebra can then be performed to obtain the identity

$$\frac{\tau}{|z(\zeta)|}\frac{\zeta'+\gamma_2^{1/2}}{\zeta'-\gamma_2^{1/2}} = \tau\;\frac{1-\gamma_2^2+\gamma_2/\zeta'^2+2\gamma_2^{1/2}/\zeta'-\gamma_2\zeta'^2-2\gamma_2^{3/2}\zeta'}{|\gamma_0(1-3\gamma_2\zeta^2)-\gamma_1\zeta^2(1+\gamma_2\zeta^2)|}.$$

Symmetry arguments can be employed to show that only the first two (i.e., constant) terms in the numerator of the above expression remain after integration over the unit circle. As a result

$$I(\gamma_2^{1/2},t) = \frac{\epsilon\gamma_0^2}{\gamma_2} - \left[\epsilon\gamma_0^2\frac{1-\gamma_2^2}{\gamma_2} - \frac{1-\gamma_2^2}{2\pi Q}\int_0^{2\pi}\frac{\tau(\nu',t)}{|\gamma_0(1-3\gamma_2\zeta^2)-\gamma_1\zeta^2(1+\gamma_2\zeta^2)|}d\nu'\right]$$

Simplifying the integral term through a change of leads to the desired equation (23).

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## List of Figure Captions

1. Taylor's four-roller mill. The four cylindrical rollers are rotated in the directions shown, producing a strain flow at the bubble in the center of the mill.

2. (a) Response curves for $\beta = 0$ (i.e., no surfactant). Branches are shown for $\epsilon = 0.01$ and $\epsilon = 0.0025$.

   (b) Response curves (deformation $D$ versus capillary number $Q$) for $\beta = 0.1,\ 0.5$, and $0.9$. Parameter values are $\epsilon = 0.01,\ Pe_s = \infty$ and $\chi = 0.5$. Dashed curves represent steady bubbles covered with a nonzero distribution of surfactant. Solid curves denote steady states with surfactant caps. Capital letters show the parameter values for the plots in Figure 3.

3. (a) Surfactant concentration , versus $\nu$, plotted at five representative points (marked $A$–$E$) along the $\beta = 0.1$ response curve (see Figure 2). Surfactant caps are centered at $\nu = 0$ and $\nu = \pi$, with regions of zero surfactant concentration in between.

   (b) Bubble profiles at points marked $A$–$E$ on the $\beta = 0.1$ response curve.

   (c) Radius of curvature $1/\kappa$ and nondimensional surface tension $\tau$ at the point $\nu = 0$, plotted at $\beta = 0.1$ and for a range of the map parameter $\gamma_1$ (used to characterize the deformation of the bubble). Note that the surface tension tends to zero at the point when a cusped bubble is formed.

4. Response curves plotted for several values of $Pe_s$. Parameter values are $\epsilon = 0.01,\ \beta = 0.5$, and $\chi = 0.5$. The curve for $Pe_s = 0.1$ actually extends out to $Q = 2.419$ (not shown)

5. Comparison of response curves for two different values of $\chi$. Parameter values are $\epsilon = 0.01,\ \beta = 0.1$, and $Pe_s = 5$.

6. Comparison of surfactant distribution for the time dependent evolution (solid curves) with that for the exact steady state solution (dotted curve). Parameter values are $Pe_s = \infty,\ \chi = 0.5$, and $\beta = 0.1$. Initial data for the unsteady calculation consists of a circular bubble with , $(\nu, 0) = 1.0$. The time interval between successive plots for the time-dependent solution is $\Delta t_p = 0.6$.

7. Comparison of steady state response curve with the computed transient evolution for various $Q$. Parameter values are $Pe_s = \infty$, $\beta = 0.5$, and $\chi = 0.5$. For each $Q$, the markers represent the deformation of a time evolving bubble starting form a circle ($D = 0$) at $t = 0$. The time increment between markers is $\Delta t_m = 0.75$ for $Q = 0.1,\ 0.2,\ ,0.3$ and $\Delta t_m = 0.5$ for $Q = 0.4$, with the final increment given by $\Delta t_m = 0.4$. For $Q = 0.1,\ 0.2,$ and 0.3 the time dependent evolution approaches a steady state, whereas for $Q = 0.4$ the bubble evolves without limit until an unsteady cusped formation is reached (see Fig. 8).

8. (a) Bubble profiles for the time dependent evolution described in Fig. 7, in the case $Q = 0.4$.

   (b) Plot of $\ln\kappa$ versus time for the unsteady calculations of Fig. 7, in the cases $Q = 0.3$ and $Q = 0.4$. For $Q = 0.3$ the evolution approaches a steady state, whereas for $Q = 0.4$ it grows superexponentially. Superexponential growth is also observed for $Q = 0.4$ and $Pe_s = 10$ (weak diffusion).

9. (a) Bubble profiles for transient evolution with parameter values $Pe_s = 0.1,\ \beta = 0.5,\ \chi = 0.5,$ and $Q = 0.6$. The time interval between successive profiles is $\Delta t_p = 1.0$.

   (b) Plot of $\ln\kappa$ versus time for the parameter values in (a). The evolution approaches a steady state.