Surfactant effect on the motion of long bubbles in horizontal capillary tubes

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Abstract

In experiments involving slow steady motion of a long finite bubble of fluid with very small viscosity in a capillary tube filled with a liquid of viscosity μ, a thin film of liquid of uniform thickness adheres to the tube walls between the front and the rear menisci of the bubble. Taking the contact angle of the liquid at the walls zero and neglecting the gravitational effects, Bretherton (1961) obtained the film thickness proportional to $Ca^{2/3}$ where Ca is the capillary number. In the range $Ca < 5 \cdot 10^{-3}$, however, experimentally obtained thickness was significantly larger than the theoretical values. **Bretherton** speculated that the presence of small traces of surfactant on the bubble-liquid interface may explain this thickening phenomenon and could be the source of this discrepancy, but he did not provide a proof. In this article we give a theoretical proof of the above thickening phenomenon using perturbation theory and lubrication approximation of the flow equations. We consider the case of a small amount of surfactant on the bubble interface with a small variation of concentration. The main new result is a lower bound of the film thickness in terms of the Marangoni number M and Γ for small capillary number. A comparison with the "clean" case proves the thickening effect of the interfacial surfactant.

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1 Introduction

The displacement of a viscous liquid by a gas bubble in capillary tubes has been studied by many and findings have been reported in a large number of papers ([5], [7], [9], [10], [11], [20], [23], [24], [25]). An important parameter in this flow is the capillary number defined as $Ca = \mu U/\gamma$ where U is the bubble velocity, μ is the liquid viscosity and γ is the surface tension on the bubble-liquid interface. In the general case, a surfactant can exist on the bubble-liquid interface (or in the bulk liquid) and the surface tension γ is a function of the concentration of the surfactant. If we do not have surfactant along the interface, then the surface tension on the bubble-liquid interface is constant. In this connection, the book of Levich [15] should be mentioned. When the displaced viscous liquid is wetting, a thin film of liquid is deposited on the walls. In the case of constant γ, this phenomenon was first studied by **Fairbrother and Stubbs (1935)**. A dimensional analysis was performed and the film thickness was found to be proportional to $Ca^{1/2}$ in the range $7.5 \times 10^{-5} \le Ca \le 0.14$. Some experiments were carried out by **Taylor (1961)** who confirmed the above result and extended it for large Ca. There are other parameters based on other effects beside the Capillary number which play a role but to a negligible proportion comparison to Ca. In order to place our work here in proper perspective, it is appropriate here for us to comment on these additional effects within a broader framework which we do next before reverting back to the essential aspects of our problem.

In general, there are many effects that play a role on the motion of a bubble. However, depending on the specific problem and the specific flow regime of interest, some of the effects may be negligible in comparison to the others. Dropping the negligible effects can simplify the mathematical formulation of the problem, thereby making the problem easier to analyze. This process of analysis has the potential to either explain some of the experimentally observed phenomena or discover the most important effects causing an experimentally observed phenomenon. For example, this approach has been successful in explaining thickening effect in Landau-levich problem (See **Daripa & Pasa (2009)**). In this paper, we show similarly the thickening effect in the problem of bubble motion through a capillary tube (see **Fairbrother & Stubbs (1935)** and **Bretherton (1961)**). In the bubble motion through a capillary tube, number of effects that come into play also depends on the nature of the displaced fluid and the type of the interface displacing the fluid. For complex fluids (we do not consider such fluids in this paper) being displaced by a surfactant laden interface of a bubble, there are many more effects that can come into play. For example, consider polymer and surfactant laden complex fluids which are used in chemical enhanced oil recovery

process. Presence of polymer and surfactant in the aqueous solution changes the rheological properties of the fluid as well as properties on the interface. Due to polymer, viscosity of the fluid depends non-linearly on the local shear rate or equivalently local velocity.

The presence of surfactant also induces nonlinear effects on the overall flow characteristics. If the surfactant is soluble in the bulk, then transfer of surfactant from the bulk into the interface and vice-verse causes **non-uniform** interfacial surface tension. Moreover, surface tension is usually dynamic and anisotropic (see Bonn et.al. [3], [4]). In addition, surface tension will depend on a characteristic velocity defined by the rate of transfer of surfactant from the bulk into the interface. These issues are not important for this paper since we do not consider surfactant in the bulk. However, we refer the reader to a series of papers by Bonn et.al., and Ben Amar et. al. ([1], [6], [3], [4], [16], [17], [18], [19]). In these papers, authors study mostly the effect of complex fluids on the viscous finger dynamics through a Hele-Shaw cell. We study only the effect of interfacial surfactant. This will be the case in general when the surfactant is insoluble in the bulk. We study this specific case for several reasons: (i) it allows us to distinguish the effect of interfacial surfactant on the problem; (ii) it makes the problem relatively simpler allowing analysis that is otherwise not possible; and lastly (iii) we believe that it possibly captures the essence of the problem even when surfactant is present in the bulk.

Evolution of interfacial surfactant concentration from any initial distribution is governed by a convection-diffusion equation with a source term to account for the stretching/shrinkage of the interface ([27]). In this interfacial dynamics, Peclet number (which is a measure of the ratio of interfacial advection and interfacial diffusion) is the main parameter. For the steady state motion of the bubble as is the case in this paper, the equilibrium distribution of surfactant concentration is determined by a balance of advection and diffusion along the interface. Thus, in general, concentration and hence the surface tension is not uniform along the interface which gives rise to Marangoni stress. However, the surface tension is not dynamic as would be the case during the transient stage until an equilibrium profile along with steady motion of the bubble sets in. Again we want to emphasize here that the problem we consider has only insoluble surfactant at the interface and nothing in the bulk.

In the bubble motion through a capillary tube of simple Newtonian fluid that we consider here, surface tension, viscous force, gravity, inertia all play a role to various degrees. The dimensionless numbers associated with these forces are

$$\rho\,rU^2/\gamma, \quad \rho\,gr^2/\gamma, \quad \mu U/\gamma,$$

where ρ is the density, r is the radius of the capillary tube and g is the gravitational accelera-

tion. In the steady state where there is a thin film on the wall and the bubble moving with a constant speed U, experiments of **Fairbrother & Stubbs (1935)** and **Bretherton (1961)** have confirmed that Reynolds number based on the tube radius, namely $\rho\, rU/\mu \ll 1$, and the surface tension forces are much more dominant than the gravitational forces, i.e., $\rho\, gr^2/\gamma \ll 1$. Under these conditions, only parameter of importance for our problem here is the Capillary number. Thus other dimensionless parameters as mentioned above are essentially dropped in the formulation of the problem. The justification of this has been shown by **Bretherton (1961)**.

An important contribution in this field was made by **Bretherton (1961)**: he used the asymptotic analysis in terms of Ca and a matching procedure to estimate the film thickness. The flow was approximated by the lubrication equations and the solution was matched with constant curvature solution near the front of the gas bubble. A quite similar matching procedure was used by **Landau and Levich (1942)** in the case of coating of a flat plate by withdrawing it from a stagnant liquid bath. In the paper of **Bretherton (1961)** a good agreement between theoretical and experimental results was reported only for $Ca > 5 \times 10^{-3}$. However, the experimentally obtained thickness was significantly larger than the theoretical values in the range $Ca < 5 \times 10^{-3}$. This was very unusual because an asymptotic method is conventionally expected to give more accurate results when the small parameter tends to zero but that was not the case here for $Ca < 5 \times 10^{-3}$. **Bretherton** speculated that the presence of small traces of surfactant on the bubble-liquid interface could be the source of this discrepancy, but he did not provide a proof. The formal perturbations techniques were used by **Park and Homsy (1984)** where the Bretherton's results were confirmed. They also extended the technique to two-phase displacements in Hele-Shaw cells.

Theoretical, numerical and experimental results concerning the displacement in capillary tubes were obtained by **Marchessault and Mason (1960), Goldsmith and Mason (1963), Teletzke (1983), Schwartz, Princen and Kiss (1986)**, but no theoretical explanation was given for the discrepancy reported by Bretherton. The experimental results of **Chen (1986)** confirmed the significant deviation at low Ca from the **Bretherton** theory. In all of the works done to-date on this bubble problem, the surfactant concentration has been small. To the authors' best knowledge to-date, effect of large concentration of surfactant on the bubble motion has not been studied yet.

Ginley and Radke (1989) studied the influence of soluble surfactants on the long bubbles through capillaries. In foam transport through porous media (one of the enhanced oil recovery processes), bubbles surrounded by aqueous surfactant solutions in the pores

appear all over in the media. Thus, motion of bubbles through the aqueous surfactant plays an important role in the process of which there is very little quantitative understanding. Motivated by this fact, **Ginley and Radke (1989)** studied the role of soluble surfactants in bubble flow using regular perturbation expansion in large adsorption rates within the low capillary number, singular perturbation hydrodynamic theory of Bretherton. They solve the equations numerically using Runga-Kutta scheme and find the two-third power law to hold in the presence of bulk surfactant.

Some analytical-cum-numerical results concerning the surfactant effect in the Bretherton problem were obtained by **Ratulowski and Chang (1990)**. A numerical approach used there showed an increase in liquid film thickness due to the surfactant. Compared with the "clean" case, they reported an increase of the film thickness with the multiplicative factor $4^{2/3}$. A similar thickening effect of surfactant was reported by **Park (1991)** for the **Landau-Levich** problem. Numerical results were obtained in support of an increase in the film thickness with the same multiplicative factor $4^{2/3}$, compared with the "clean" case. **Krechetnikov and Homsy (2005)** considered the **Landau-Levich problem** taking into account the dynamic menisci in the matching procedure. The numerical method of boundary-element was used. The conclusion of this paper is that, in general, the surfactant can produce also a **thinning** effect of the liquid film adhering on the plate and that a pure hydrodynamic approach can not yet explain the discrepancy reported by **Bretherton**.

Daripa and Pasa (2009) studied the surfactant effect in the Landau-Levich problem. An asymptotic analysis was used. The film thickness in the "clean" case (respectively surfactant case) was denoted by H_c (respectively H_s). An upper bound for H_c and a lower bound for H_s were obtained in terms of Marangoni and Capillary numbers (Marangoni number is related with the derivative of the surface tension as function of the surfactant concentration). In particular, their main result is the following inequality: $H_c \leq Ca^{1/2} \leq H_s$, thereby proving the thickening effect of the surfactant.

In this letter, using the boundary layer method and lubrication approximation we prove the thickening effect of surfactants for the **Bretherton** problem. On the bubble-liquid interface, the surfactant concentration Γ is taken very small. The tangential stress along the interface in the liquid is related with the surface tension γ which is a function of Γ and the normal stress obeys the the Laplace's law. Using the matching procedure described in **Landau-Levich (1942)** and **Bretherton (1961)**, we obtain a lower bound on the thickness b_S in the presence of surfactant. This lower bound is shown to be greater than the thickness b_C for the clean case by at least $\frac{3r}{2}M\Gamma(x_B)$ where M is the Marangoni number, r

is the radius of the tube and $\Gamma(x_B)$ is the surfactant concentration at the point connecting the front menisci to the transition region. This proves the thickening effect of surfactant. Moreover, it shows that b_S is in excess of b_C by at least an amount proportional to r, M and Γ. Below, this proof is given in detail.

In the next two sections 2 and 3, we discuss the model and the estimate of the thickness of the thin-film in the presence of interfacial surfactant. Lastly, we conclude in section 4.

2   The model

We describe here the mathematical model of slow steady flow of a long bubble in a horizontal capillary tube of radius r filled with a liquid of viscosity μ. The bubble velocity is denoted by U and the fluid inside the bubble is of negligible viscosity. The flow is considered *axisymmetric* and analogous to that used in **Bretherton (1961)**. It is known that only axisymmetric shape with no singularities on the tube axis is a portion of a sphere if the contact angle with the tube walls is zero as is the case here. Therefore, for small U, the front and the rear menisci must have shapes of hemispheres.
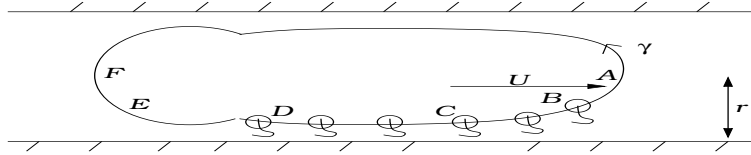

Figure 1: The bubble in the capillary tube. The transition region BC is matched with the constant film thickness region CD and with the constant curvature region AB.
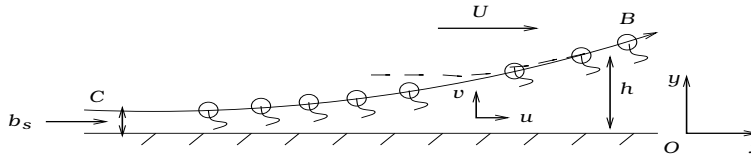

Figure 2: The transition region BC

We follow the boundary layer method, used by Bretherton, by decomposing the bubble interface in several regions starting with the edge of the front meniscus, denoted by A, on

the tube symmetry axis. The edge point of the rear meniscus of the bubble is also on the tube axis and is denoted by F as shown in the Figure 1. The two menisci are separated by a region CD where a thin film of liquid of viscosity μ and uniform thickness $b_S << r$ adheres on the walls of the tube. We consider this region to be long compared with the film thickness. Near the wall tube, we consider a planar approximation of the flow. The positive Ox axis is in the flow direction of the bubble. The axis Oy is orthogonal to Ox. Between the points C and A along the interface, we consider two regions: the part AB of the front meniscus, starting from the point A, will be of one shape in its entirety. Therefore curvature in this region AB is a constant given by $1/r$ approximately. The segment BC shown in Figure 2 is a transition (or intermediate) region between the constant curvature (or inner) region AB and the constant thickness film (outer) region CD. The goal is to obtain the solution of flow equations in the region BC using a matching procedure prevalent in boundary layer theory.

The surface tension gradient on the interface CD in the outer region is zero. It has been observed experimentally (see Bretherton (1961)) that the thin film region CD of constant thickness is almost stationary as the bubble moves with speed U. This is possibly due to the fact the film is so thin that no slip condition on the wall and the slip condition on the portion CD does not generate any flow in the film. Thus there is no flux through in the region CD. On the other hand the bubble interface BC in the transition region pushes the fluid generating flow in the region between the wall and BC and beyond. This is the flow scenario at any instant and as bubble moves so does the interface between the wall and point C on the interface. The best way to understand the flow in the region ahead of the thin-film is through the analogy: think of the thin-film as a piston and the bubble ahead pushing the fluid. We direct the readers to **Fairbrother & Stubbs (1935)**, **Bretherton (1961)** and **Ginley and Radke (1989)** for an understanding of the flow between the bubble and the wall tube.

In the region between BC and the tube wall, the flow equations within the lubrication approximation are:

$$u_x + v_y = 0, \quad \mu u_{yy} = p_x, \quad 0 = p_y, \tag{1}$$

where $\mathbf{u} = (u, v), p$ are velocity and pressure respectively and subscripts x and y denote the partial derivatives. These equations need to be solved subject to no-slip boundary condition on the wall, namely

$$\mathbf{u} = 0, \quad \text{on the wall} \quad y = 0, \tag{2}$$

the kinematic boundary condition, again approximating, $u(h(x)) = U$ (see Bretherton (1961)), $\mathbf{u} \cdot \mathbf{n} = Uh_x$ on $y = h(x)$ neglecting higher order terms in $h(x)$, and the dynamic

boundary conditions on the interface $y = h(x)$:

$$\mathbf{n} \cdot \mathbf{Tn} = \gamma(\nabla_s \cdot \mathbf{n}), \quad \mathbf{t} \cdot \mathbf{Tn} = -\mathbf{t} \cdot \nabla_s \gamma. \tag{3}$$

$$\frac{\partial \Gamma_1}{\partial t} + \nabla_s \cdot (\Gamma_1 \mathbf{u}^s) = D_s \nabla_s^2 \Gamma_1. \tag{4}$$

Above $\mathbf{n}, \mathbf{t}$ are the normal and the tangent to the interface respectively, $\mathbf{T}$ is the stress tensor, and $\nabla_s = \nabla - \mathbf{n}(\mathbf{n}.\nabla)$ is the surface gradient operator on $y = h(x)$. Also $\mathbf{u^s} = \mathbf{u} - (\mathbf{n} \cdot \mathbf{u})\mathbf{n}$ is the surface velocity and D_s is the surface diffusion coefficient. Since the steady state case is of interest here, the interfacial advection-transport of surfactant only fixes the steady state profile of the variable surface tension. Since the exact profile of the variable surface tension is not of interest, we do not need to consider this equation in our treatment here. The interfacial advection-transport equation is thus neglected as has been done in other similar problems (see Daripa (2009)).

It is necessary to rewrite these boundary conditions in terms of $h(x)$ which we do next. The normal $\mathbf{n}$ and tangent $\mathbf{t}$ to the free surface $y = h(x)$ are given by

$$\mathbf{n} = (-h_x, 1)/(1 + h_x^2)^{1/2}, \quad \mathbf{t} = (1, h_x)/(1 + h_x^2)^{1/2}. \tag{5}$$

The surface gradient operator is then given by

$$\nabla_s = \nabla - \mathbf{n}(\mathbf{n}.\nabla) = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}\right) - \frac{(-h_x, 1)}{1 + h_x^2}\left(-h_x \frac{\partial}{\partial x} + \frac{\partial}{\partial y}\right)$$

$$= \frac{1}{1 + h_x^2}\left(\frac{\partial}{\partial x}, h_x \frac{\partial}{\partial x}\right). \tag{6}$$

The last equality above is obtained after dropping the y-derivative terms which is valid in lubrication approximation. From the above relations we get

$$\nabla_s \cdot \mathbf{n} = (\nabla_s)_1 n_1 + (\nabla_s)_2 n_2 = \frac{1}{1 + h_x^2}\left((n_1)_x + h_x(n_2)_x\right). \tag{7}$$

Since

$$(n_1)_x = -\frac{(1 + h_x^2)h_{xx} - h_x^2 h_{xx}}{(1 + h_x^2)^{3/2}} = -\frac{h_{xx}}{(1 + h_x^2)^{3/2}}, \quad (n_2)_x = -\frac{h_x h_{xx}}{(1 + h_x^2)^{3/2}}, \tag{8}$$

we finally obtain from substituting (8) in (7) the following expression for the curvature.

$$\nabla_s \cdot \mathbf{n} = -\frac{h_{xx}}{(1 + h_x^2)^{3/2}}. \tag{9}$$

Using the stress tensor

$$T_{ij} = p\delta_{ij} - \mu\left\{(u_i)_{x_j} + (u_j)_{x_i}\right\} = p\delta_{ij} - \tau_{ij}, \tag{10}$$

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we find

$$\mathbf{n} \cdot T\,\mathbf{n} \equiv n_i(p\delta_{ij} - \tau_{ij})n_j$$

$$= p - [n_1\tau_{11}n_1 + 2n_1\tau_{12}n_2 + n_2\tau_{22}n_2]$$

$$= p - \frac{2}{1+h_x^2}(h_x^2\mu u_x - h_x\,\mu(u_y + v_x) + \mu v_y), \tag{11}$$

and

$$\mathbf{t} \cdot T\,\mathbf{n} \equiv t_i(p\delta_{ij} - \tau_{ij})n_j$$

$$= -[t_1\tau_{11}n_1 + t_1\tau_{12}n_2 + t_2\tau_{21}n_1 + t_2\tau_{22}n_2]$$

$$= (2\mu u_x h_x - \mu\,(u_y + v_x) + \mu\,h_x^2(v_x + u_y) - 2\,\mu h_x v_y)/(1+h_x^2)$$

$$= \frac{2}{1+h_x^2}\left[\mu h_x(u_x - v_y) - \frac{\mu}{2}(u_y + v_x)(1 - h_x^2)\right]. \tag{12}$$

It also follows from $(5)_2$ and (6) that

$$-\nabla_s\gamma \cdot \mathbf{t} = -(\mathbf{i} + \mathbf{j}h_x)\frac{\gamma_x}{1+h_x^2} \cdot (\mathbf{i} + \mathbf{j}h_x)\frac{1}{\sqrt{1+h_x^2}} = -\frac{\gamma_x}{\sqrt{1+h_x^2}}. \tag{13}$$

Using calculus and leaving out the details of calculations, the above dynamic boundary conditions are reduced to the following useful forms:

$$p - \frac{2}{(1+h_x^2)}[\mu v_y - h_x\mu(v_x + u_y) + h_x^2\mu u_x] = -\frac{\gamma \cdot h_{xx}}{(1+h_x^2)^{3/2}}, \tag{14}$$

and

$$\mu[(1 - h_x^2)(u_y + v_x) + 2h_x(v_y - u_x)] = \gamma_x\sqrt{1+h_x^2}. \tag{15}$$

Equation (14) above is the modified Laplace's law at an interface displacing viscous fluid within lubrication approximation. If it were not for the lubrication approximation, this law will depend on the gradient of surface tension (see [4]). However, above derivation shows such gradients within lubrication approximation does not appear in equation (14). Again approximating the boundary conditions (14) and (15) for the thin film within lubrication theory, we obtain following useful forms of these conditions.

$$p = -\gamma\,h_{xx} \quad \text{and} \quad \mu u_y = \gamma_x, \quad \text{on } y = h(x). \tag{16}$$

Note from $(16)_1$ that the viscous stress on the interface does not contribute anything in the normal direction which is a consequence of the steady state and is consistent with the treatment in Bretherton (1961). In the paper of Bretherton (1961), the surface tension γ is constant in equations $(16)_1$ and $(16)_2$. In this paper, the surface tension γ varies along the

interface according to some prescribed function. It is perhaps worth-mentioning that surface tension is a surface force and not a volume one. Therefore, Laplace's law $(3)_1$ does not change even in the presence of Marangoni convection (non-zero gradient of surface tension). It has been argued (see Bonn et.al. (1995)) that the γ in the right hand side of the Laplace's law $(3)_1$ should have an additive term γ'' where a prime denotes derivative of surface tension γ with respect to an interface parameter. However, we find here that for low concentration of Γ all variations in surface tension are of lower order than the surface tension itself. It is easy to see in the forgoing analysis that additive term γ'' in (3) drops out during lubrication approximation process leaving the equation (16) same.

3 Estimate on the thickness of the thin-film

Next we get the film thickness b_S in the region CD by solving the above equations in the region BC and using matching conditions with the inner and outer regions AB and CD respectively. A comparison with thickness b_C for the "clean" case is given later (subscript 'C' has been used to refer to the clean case). Taking pressure p as a function of x only due to $(1)_3$, solution of the problem defined by $(1)_2$, (2) and $(16)_2$ is then given by

$$u = \frac{p_x}{\mu}\left(\frac{y^2}{2} - yh\right) + \frac{\gamma_x}{\mu}y. \tag{17}$$

We eliminate the pressure term in (17) using the dynamical boundary condition $(16)_1$.

$$u(y) = -\frac{1}{\mu}(\gamma\,h_{xx})_x\left(\frac{y^2}{2} - yh\right) + \frac{\gamma_x}{\mu}y. \tag{18}$$

This can be used to compute the flux Q through the thin film which is

$$Q = \int_0^{h(x)} u(y)dy = \frac{h^3}{3\mu}(\gamma h_{xx})_x + \frac{h^2}{2\mu}\gamma_x. \tag{19}$$

The flux Q can also be easily calculated using conservation of mass and the kinematic boundary condition. It turns out within an approximation (see Bretherton (1961)) that

$$Q = U(h(x) - c), \tag{20}$$

where c is a constant. It follows from (19) and (20) that

$$6U\mu(h(x) - c) = 2(\gamma\,h_{xx})_x h^3 + 3\gamma_x h^2. \tag{21}$$

This is valid in the transition region BC. Matching this with the outer region CD where $h(x) = b_S$, all its derivatives are zero, and $\gamma_x = 0$, we obtain $c = b_S$. Therefore, for the region BC we get

$$6U\mu(h(x) - b_S) = 2(\gamma\, h_{xx})_x h^3 + 3\gamma_x h^2. \tag{22}$$

Following Bretherton (1961), we introduce here the non-dimensional function g and the non-dimensional variable z:

$$h(x) = b_S\, g(x), \quad x = b_S\, (3Ca)^{-1/3} z, \tag{23}$$

where $Ca = U\mu/\gamma_0$ is the capillary number based on the surface tension γ_0 of the clean interface. The above equation (22) then becomes

$$\frac{g-1}{g^3} = \{\tilde{\gamma}g_{zz}\}_z + \frac{3\tilde{\gamma}_z}{2g(3Ca)^{2/3}}, \tag{24}$$

where $\tilde{\gamma} = \gamma/\gamma_0$. The scaling (23) shows us that for small enough Ca and for a given solution of the above equation, we have regions where

$$g = h/b_S \gg 1, \quad h/r = b_S\, g/r \ll 1, \quad h_x = (3Ca)^{1/3}g_z \ll 1, \tag{25}$$

and the equation (24) still holds. Since the goal is to match the inner region with the transition region, it is convenient to select in the transition region for matching purpose the region where $g \approx 1$ and therefore we are interested to characterize the region where $g \approx 1$. The flow equation and the above considerations show us that in this region the interface can be approximated by

$$(\tilde{\gamma}g_{zz})_z \sim -\frac{3\tilde{\gamma}_z}{2(3Ca)^{2/3}}. \tag{26}$$

We integrate once and then divide by $\tilde{\gamma}$ to obtain

$$g_{zz} \approx -\frac{3}{2(3Ca)^{2/3}} + \frac{K}{\tilde{\gamma}}, \tag{27}$$

where K is a constant independent of z. Reverting back to dimensional variables x and $h(x)$, (27) becomes

$$b_S\, h_{xx}(3Ca)^{-2/3} \approx -\frac{3}{2(3Ca)^{2/3}} + \frac{K}{\tilde{\gamma}}. \tag{28}$$

The matching of the intermediate region BC and the inner region AB is achieved by equating the surface curvature at point B of these two regions. order. The approximate curvature at B of the transition region is h_{xx} and that of the inner region is $\frac{1}{r-b_s} \approx \frac{1}{r}$ since $b_s \ll r$. In the case of clean interface, the same matching procedure between these two regions has

been used in Bretherton (1961). Using this matching at B and re-arranging the relation (28) which is valid at $x = x_B$, we obtain

$$b_S = -\frac{3r}{2} + \frac{r\,K(3Ca)^{2/3}}{\tilde{\gamma}(x_B)}. \tag{29}$$

Note that this is a very approximate estimate of the thickness of the thin film in terms of surface tension at $x = x_B$ and the as yet unknown constant K. It is worth mentioning that we have an exact approximate formula for the thickness b_S as opposed to the thickening effect proved for the LLD problem (Daripa & Pasa (2009)) by estimation of the upper and the lower bounds. However, below we prove the thickening effect by giving a lower bound on b_S which does not depend on the unknown constant K. Another distinction worth mentioning is that the formula here is in terms of the surface tension at $x = x_B$ where as in the LLD problem the bounds were obtained in terms of gradient of surface tension.

For the clean interface case, $\tilde{\gamma} = 1$ and the above formula (29) becomes

$$b_C = -\frac{3r}{2} + r\,K(3Ca)^{2/3}, \tag{30}$$

where subscript C has been used to refer to the clean interface. Since $b_C > 0$, this formula suggests that the constant K must be positive and in particular,

$$K > \frac{3}{2(3Ca)^{2/3}}. \tag{31}$$

Due to small traces of surfactants on the bubble interface, the surface tension decreases from its value γ_0 for the clean surface and hence $\tilde{\gamma} < 1$. Hence it is proved here that the film in the region CD thickens due to surfactant as was speculated by Bretherton due to discrepancy in the experimental value exceeding the computed value of b_C in the low Capillary number regime.

Towards this end, we give the above formula for the thickness in terms of Marangoni number and surfactant concentration Γ when Γ is small. Within linear approximation, we can write

$$\gamma(\Gamma) = \gamma_0(1 - M\Gamma), \quad \text{where} \quad M = -\frac{1}{\gamma_0}\frac{\partial\gamma}{\partial\Gamma}\bigg|_{\Gamma=0}. \tag{32}$$

Here M is the positive Marangoni number and γ_0 is the surface tension of the clean interface with no surfactant. Thus, we have $\tilde{\gamma} = (1 - M\Gamma)$ and $1/\tilde{\gamma} \approx (1 + M\Gamma)$ for Γ small. Substituting these in (29), we obtain

$$b_S = -\frac{3r}{2} + r\,K(3Ca)^{2/3}(1 + M\Gamma(x_B)), \tag{33}$$

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and rearranging above we can write b_S in terms of b_C (see (30)) as

$$b_S = b_C + r\,K(3Ca)^{2/3}M\Gamma(x_B). \qquad (34)$$

It follows from using (31) in (34) that

$$b_S > b_C + \frac{3r}{2}M\Gamma(x_B). \qquad (35)$$

Thus we have a lower bound on b_S which is greater that b_C by at least $\frac{3r}{2}M\Gamma(x_B)$. This proves the thickening effect of surfactant and moreover it shows that b_S is in excess of b_C by at least an amount proportional to r, M and $\Gamma(x_B)$.

It is worth emphasizing that the main result (35) is a strict inequality which supports the experimentally observed phenomenon. Unfortunately, we do not have an exact formula in an equality form or else it could have had a wide range of repercussions. We mention this here in the hope that may be some readers will see more implications of the inequality (35) than we have. The strict inequality (35) is valid in the presence of non-uniform interfacial surfactant concentration. Note that it does not depend on γ', the gradient of surface tension (or equivalently gradient of Γ), along the interface. However it does not mean that b_S does not depend on γ'.

4 Conclusion

Using the leading order approximation within the boundary layer theory and the lubrication approximation, we have obtained a relation in **a strict inequality form** between the thickness of the clean thin-film and that of the interfacial surfactant laden thin-film. This inequality (see (35)) clearly establishes the thickening effect of the surfactant in the low concentration regime of surfactant. It is well known (see Bender & Orszag (1978)) in th boundary layer theory, that solution obtained by matching procedure we have used is an approximate one. Inner or outer region solution alone is not sufficient to recover the solution that is valid in the entire domain in the boundary layer theory. Therefore, even if the film thickness (i.e., the outer solution) found matches an experimental value, it does not imply that shape (i.e., the entire solution) of the bubble has to follow. The appearance of the point x_B in the inequality (35) should be a reminder of this fact.

We have not made any assumptions beyond the fact that the parameters that are not relevant according to experiments as mentioned in Bretherton (1961) have been ignored as well. The work here was inspired by an experimentally observed phenomenon, namely

the thickening effect of interfacial surfactant on the thin-film. The finding here is a strict inequality (35) that proves the observed phenomenon. Thus, de facto, the finding (35) is valid and hence does not need any discussion of the validity of this finding.

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