The effect of surfactant on long bubbles rising in vertical capillary tubes

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Abstract. In this letter we investigate the effect of interfacial surfactant on the motion of an air bubble rising in a vertical capillary tube filled with a viscous fluid and sealed at one end. A thin layer of liquid, with almost constant thickness $b$, exists between the bubble interface and the tube wall. The fluid displaced by the front meniscus flows down through this layer because the tube is sealed far up at the top. The steady rising velocity $U$ of the bubble is related to the thickness $b$. An upper bound for $U$ is obtained in terms of $b$ and other physical data of the problem, which is in good agreement with previous experimental results. It is proved here analytically that the presence of surfactant on the bubble interface causes a thinning and a delay effect: the thickness of the liquid layer behind the bubble and the rise velocity of the bubble are smaller than those for the ‘clean’ case. Exactly the opposite effect of surfactant in the horizontal case has been derived analytically by Daripa and Pasa (2010 \textit{J. Stat. Mech.} L02002) and numerically by Ratulowski and Chang (1990 \textit{J. Fluid Mech.} 210 303). These effects of interfacial surfactant are consistent with previous experimental and numerical results.

Keywords: bubbles and drops, films, foams and surfactants, hydrodynamics of complex fluids and biological fluid dynamics

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1. Introduction

Motion of bubbles through viscous fluids has received much attention over the years because of its relevance to many problems of fundamental scientific and of technological interest. For example, motion of two-dimensional bubbles in tubes has been studied using potential analysis by many investigators including [5, 6]. Displacement of a viscous fluid by a gas bubble in capillary tubes has been studied by Schwartz and Princen [23]. A general review concerning the long bubble propagation is given in [10]. The rise of bubbles in angular capillary tubes has been studied by Bico and Quere [2]. The bubble propagation in capillary tubes with non-circular cross-section has been studied by Liao and Zhao [14] and Clanet et al [4].

One of the first theoretical and experimental results concerning this flow was given by Bretherton [3]. As pointed out in [3] and reinforced in [18], the shape of the cap and the base of the bubble are independent of the size of the bubble. The midsection of the bubble is almost cylindrical, of radius of $\beta R$. The thickness of the layer between the wall of the tube and the bubble interface is $b = R - \beta R = R(1 - \beta)$. For large surface tension $\gamma$, this layer of fluid is very thin; we refer to this as a thin film. The thickness $b$ of this thin film and the speed of $U$ of the bubble have usually been of interest in many studies by various investigators. For example, with motivation from submarine technology, [9] was one of the earliest studies this problem. Motivated by oil recovery technology and fingering phenomena in displacement processes, Saffman and Taylor [20] also studied a similar problem: displacement of a viscous fluid by a less viscous one. Extensive studies on the long air bubbles in vertical cylindrical tubes have also been carried out by Zukoski [27] and White and Beardmore [26].

There are several forces that come into play in this problem: surface tension (denoted by $\gamma_0$ in the clean case), viscous force, gravity and inertia. There are three dimensionless associated parameters: the Reynolds number $Re$, the capillary number $Ca$ and the bond number $B$, defined as

$$Re = \rho U R / \mu, \quad Ca = \mu U / \gamma_0, \quad B = \rho g R^2 / \gamma_0,$$

where $\rho$ is the density of the fluid neglecting the density of the air, $R$ is the radius of the capillary tube and $g$ is the gravitational acceleration. The Reynolds number is the ratio of
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the force of inertia to the viscous force, the capillary number is the ratio of the viscous force to the surface tension, and the bond number is the ratio of the force of gravity to the surface tension. For the steady state where there is a thin film on the wall and the bubble rises with a constant speed \( U \), the experiment of Bretherton [3] suggests that the Reynolds number is negligible in comparison to other parameters. Dropping \( Re \) from the problem, there are now two parameters, \( Ca \) and \( B \), in the problem. A simple dimensional analysis shows then that the \( Ca \) and, hence, the speed \( U \) of the bubble are functions of the bond number. The geometric parameter \( \beta \), the ratio of the radius of the midsection of the bubble to the radius of the tube, has been shown in [3,18] to be a function of the bond number. Bretherton used matched asymptotic expansion in powers of the capillary number \( Ca \) to obtain the shape of the bubble. In so doing, he concluded that the bubble will not rise at a constant velocity \( U \) if \( B < 0.842 \) and speculated that it may rise unsteadily for \( B < 0.842 \). For \( B > 0.842 \), he obtained the following expression for very small values of \( Ca \):

\[
B - 0.842 \sim 1.25Ca^{2/3} + 2.24Ca^{1/3}.
\]  

This being an asymptotic series, the error can be estimated. This was done by Bretherton. He found the error to be about 10% when \( Ca = 8 \times 10^{-5} \). Even smaller values than this are required to make his analysis hold in practice. Later, Reinelt [18] constructed a numerical approach based on the Stokes equation for computing the shape of the bubble for values of the capillary number in the range \( 1 \times 10^{-4} < Ca < 1 \times 10^{-1} \). Reinelt’s results compare favorably with that of Bretherton for very low values of \( Ca < 10^{-5} \). In [26], based on experimental data for the rising velocity (cited also by Clanet et al [4]), the formula \( U = C\rho gR^2/\mu \) was proposed, which merely confirms that the Stokes law is valid for low Reynolds number bubble flow in vertical tubes, namely the rising velocity of the bubble is proportional to \( gR^2/\mu \). This formula in terms of dimensionless numbers is equivalent to \( B = C^{-1}(Ca) \) where the constant \( C \approx 0.038 \) for the experimental setup of [26]. According to [26], the value of this constant \( C \) monotonically decreases with decreasing bond number \( B \). Experimental verifications of the formula (1) for low values of \( Ca < 10^{-5} \) and of the prediction that the bubble will not rise at a constant speed for values of \( B < 0.842 \) were attempted by Bretherton. He validated these qualitatively but not quantitatively, without attributing the quantitative discrepancies to the presence of impurities on the bubble surface.

In this letter, we study the effect of small traces of surfactant on the thickness \( b \) of the thin film between the rising bubble interface and the vertical tube wall. Below, we give some details concerning two related problems: surfactant effects on the bubble flow in horizontal capillary tubes and in the Landau–Levich (LL for short in what follows) problem (see [12]). Recently, [7] has studied the effect of surfactant in horizontal capillary tubes. Using only theoretical estimates of the film thickness \( b \) in terms of the surface tension, there it was shown that the interfacial surfactant thickens the thin film in comparison to the clean case. This result was obtained also by Ratulowski and Chang [17], but using a numerical method to compute solutions with and without surfactant. The thickening factor obtained there is \( 4^{2/3} \) (about 2.5).

The thickening effect of surfactant on the thin film in the LL problem has been theoretically explained in [8] using two bounds for film thickness \( b \). The upper bound in
the clean case has been shown to be less than the lower bound in the surfactant case. The same result was obtained by Park [15] but using a ‘shooting’ method to compute solutions in clean and surfactant cases. Park obtained the same thickening factor, $4^{2/3}$, as is given by Ratulowski and Chang [17]. This is not surprising because the bubble in horizontal tubes and the thin film LL problems are quite similar. A very interesting discussion of these results can be found in [11] where a careful analysis and a numerical method are given for the study of surfactant effect in the LL problem. In [7], other investigators’ work on the effect of surfactant on the bubble motion in horizontal tubes, on the motion of fingers in Hele-Shaw cells and on the thin film in the LL problem has been discussed in detail. We refer the reader to [7] for these works as well as for many references cited there. We also mention here that the basic models for surfactant behavior on interfaces between fluids can be found in [13].

The vertical case which we study here is different from the two problems above. The bubble rises only if certain conditions (see [3]) are satisfied. In contrast, the bubble is pushed in the horizontal tube and the plate is withdrawn from a bath in the (LL) problem. For the vertical case, we suppose that appropriate conditions prevail (see [3]) for the bubble to rise in the tube. The tube is sealed and hence the fluid displaced by the front meniscus of the bubble must flow down through the thin film between the bubble surface and the tube walls. For this case, we have the direct relation (10) between $U$ and $b$ which does not depend on the surface tension. This is not the case for the thin film problem in the horizontal capillary tube and for the Landau–Levich LL problem, both of which have the thin film almost at rest. The details about the governing equations for the gas bubble motion (with surfactant concentration on the interface) in a tube are given in [7]. We later mention only basic equations and boundary conditions.

The main result of this letter is the following: the interfacial surfactant gives a thinning effect. The thickness $b$ of the thin film and the rising velocity $U$ of the bubble are both smaller when compared with the ‘clean’ case. An upper bound of the rising velocity $U$ for the clean case is derived which is similar to the formula $B = C^{-1}(Ca)$ of [26], discussed above. We obtain an upper bound of the constant $C$ which is approximately 0.018 as opposed to $C \approx 0.038$ for the experimental setup of [26]. This is not in contradiction with the value $C = 0.038$ obtained experimentally by White and Beardmore [26], who noted that the value of the constant $C$ decreases with increasing $\gamma$. We give also an (nonlinear) algebraic formula for $b$ and $U$ in terms of the problem data. The retardation of moving bubbles due to the presence of surfactants has been confirmed in the literature by the experimental results of [1] and numerical results of [24].

The analysis is based on the experimental observation as well as physical intuition that the flow past the bubble as it rises in a capillary tube is two-dimensional with hardly any motion in the azimuthal, i.e., circumferential, direction. Therefore, equations of motion for this axisymmetric flow can in principle be considered for analysis either in local Cartesian coordinates like in [3] or in cylindrical coordinates like in [18]. We use both of these approaches in our analysis, which leads to interesting results. The letter is laid out as follows. In section 2 we obtain the thinning and delay effect of surfactant. In section 3 we give some upper bounds of the rising velocity. Finally we conclude in section 4, which also contains an unusually long discussion of many of the recent results relating to the LL problem in complex fluids and of various time scales associated with thin film problems in complex fluids.
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Figure 1. Section of a bubble in a vertical tube.

2. The thinning effect of surfactant

The section of the tube including the bubble is shown in figure 1. In the Cartesian frame, the $x$ axis is taken to be parallel to the right wall and its positive direction points upward. The $y$ axis is orthogonal to the right wall and its positive direction is towards the interior of the tube, from the liquid to the gas. The gravity force is parallel with the $x$ axis but points downward. We recall that $b$ denotes the thickness of the thin liquid layer behind the front of the bubble, $U$ is the rising velocity and $R$ is the tube radius. The flow is ‘divided’ into three regions: the region $AB$ of the front meniscus of the bubble, the intermediate region $BC$ and the flat region $CD$. The free surface of the bubble in the transition region $BC$ is denoted by $h(x)$.

In the ‘clean’ case, the surface tension on the bubble interface is constant, denoted by $\gamma_0$. In the presence of insoluble interfacial surfactant, the surface tension on the interface will not be constant. Due to the motion of the bubble, surfactant along the interface will be swept downstream along the interface. This will cause the surfactant concentration to increase and hence surface tension $\gamma$ to decrease away from the front end of the bubble along its interface. Therefore it seems natural to suppose that the surface tension $\gamma$ decreases on the bubble interface as the distance from $A$ along the interface increases. Since the positive $x$ axis is upward (see figure 1), it follows that $\gamma_x > 0$ on $ABC$. This may seem to be an assumption in the absence of detailed treatment of interfacial surfactant motion by using an appropriate advection–diffusion equation that also accounts for stretching of the interface. However, this assumption is physically sound, especially
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when the time associated with interfacial diffusion of surfactant is much longer than the transit time associated with convection, i.e. $Ca \gg Pe^{-3}$ (see [19]) where $Pe = bU/D_s$ with $D_s$ as the surface diffusion coefficient is the Peclet number. This condition will also hold unless the bubble speed is very small. Thus, our results in this letter certainly hold under these qualifications. However, our results in this letter will hold even in the absence of the above assumption because the mere presence of surfactant, even if it were uniform, would reduce the surface tension from its value for a clean surface. This fact together with the formula (22) given below will then show, as we will see, the thinning effect of interfacial surfactant. Thus this is a special case that is covered within our general treatment for the case when $Ca \gg Pe^{-3}$. More comments on these issues are given in the last section, ‘Conclusion and discussion’.

In the transition zone $BC$, we use the lubrication approximation

\[ u_{yy} = \frac{1}{\mu} (p_x + \rho g), \quad p_y = 0. \] (2)

These equations need to be solved subject to the following boundary conditions (see [7, 15, 17]):

\[ u(y = 0) = 0, \quad u_y(y = h(x)) = \gamma_x/\mu, \quad \text{and} \quad p(y = h(x)) = -\gamma h_{xx}. \] (3)

The solution of the problem defined by (2), (3)\(_1\), and (3)\(_2\) is given by

\[ u = \frac{1}{\mu} (p_x + \rho g) \left( y^2/2 - yh \right) + \gamma_x y/\mu. \] (4)

We use the above expression for the liquid velocity and get the flux $Q(x) = \int_0^{h(x)} u(y) \, dy$ through the film at an arbitrary point $x$ in the transition region $BC$, which is

\[ Q(x) = \frac{1}{\mu} (p_x + \rho g) \left( -h^3/3 \right) + \gamma_x \frac{h^2}{2\mu}. \] (5)

On the other hand, as specified in [3], $Q(x) = Uh(x) + C_1$, where $U$ is the rising velocity and $C_1$ is a constant. Therefore we obtain

\[ \frac{1}{\mu} (p_x + \rho g) \left( -h^3/3 \right) + \gamma_x \frac{h^2}{2\mu} = Uh + Ud. \] (6)

The matching procedure allows us to consider that the above relation holds also near the point $C$, where the flat region begins. As in $CD$ we have $p_x = 0$, $\gamma_x = 0$, and $h = b$, the last relation gives

\[ -\frac{\rho gb^3}{3\mu} =Ub + C_1, \]

and we obtain the flow equation in the region $BC$:

\[ \frac{1}{\mu} (p_x + \rho g) \left( -h^3/3 \right) + \gamma_x \frac{h^2}{2\mu} = U \left( h - b - \frac{\rho gb^3}{3\mu U} \right). \] (7)

Therefore the flux at $x = -\infty$ in the region $CD$ is given by

\[ Q(-\infty) = -\frac{\rho gb^3}{3\mu}. \] (8)

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The flux in front of the bubble is given by the flow with speed $U$ through the area with radius $(R - b)$ and we obtain the following expression (per unit circumferential length):

$$Q(\infty) = -U \pi(R - b)^2 / (2\pi R) \approx -UR/2, \quad b \ll R. \quad (9)$$

Let $\beta = 1 - b/R = 1 - \delta$. We use $Q(-\infty) = Q(\infty)$ and get

$$U = \frac{2\rho gb^3}{3\mu R} = \left( \frac{\rho g R^2}{\mu} \right) \frac{2(1 - \beta)^3}{3}. \quad (10)$$

The relation (10) is used to estimate the magnitude of the terms in the right part of (7). We have

$$\frac{\rho gb^2}{3\mu U} = \frac{R}{2b} \gg 1, \quad (11)$$

because $b \ll R$. Then the above term greatly exceeds $(h - b)$ and we get

$$h - b - \frac{\rho gb^3}{3\mu U} = b \left( \frac{h}{b} - 1 - \frac{\rho gb^2}{3\mu U} \right) \approx -\frac{\rho gb^3}{3\mu U}.$$

The relation (7) and above magnitude analysis give the final form of flow equation in $BC$ which is

$$(\gamma h_{xx})_x - \rho g + \gamma_x \frac{3}{2h} = -\frac{\rho gb^3}{h^3}. \quad (12)$$

We considered here that the relation $p = -\gamma h_{xx}$ holds also in the film and not only on the free surface $h(x)$, because $p$ is not dependent on $y$.

We introduce the following dimensionless quantities:

$$\bar{\gamma} = \frac{\gamma}{\gamma_0}, \quad h = b\eta, \quad x = \frac{b^{1/3}}{T^{1/3}} z, \quad T = \frac{\rho g}{\gamma_0}, \quad (13)$$

and from the equation (12) we obtain

$$(\bar{\gamma} \eta_{zz})_z = \left( 1 - \frac{1}{\eta^2} \right) - \frac{3}{2} \frac{\bar{\gamma}_z}{T^{2/3}} \frac{1}{b^{4/3}}. \quad (14)$$

As the equation (14) holds also near the point $C$, we can consider $\eta \approx 1$ and the interface equation becomes

$$(\bar{\gamma} \eta_{zz})_z \approx -\frac{3}{2} \frac{\bar{\gamma}_z}{T^{2/3}} \frac{1}{b^{4/3}}. \quad (15)$$

We integrate equation (15) and get

$$\eta_{zz} \approx -\frac{3}{2} \frac{1}{T^{2/3} b^{4/3}} + \frac{K}{\bar{\gamma}}, \quad (16)$$

where $K$ is a constant with respect to $z$. We use the relations (13) and return to the function $f$ and the variable $x$. From (16) we obtain

$$\frac{h_{xx}}{b^{1/3} T^{2/3}} \approx -\frac{3}{2} \frac{1}{T^{2/3} b^{4/3}} + \frac{K}{\bar{\gamma}}. \quad (17)$$

The above relation holds also near the point $B$, which belongs to the top meniscus $AB$. Here Laplace’s law holds, and the (hydrostatic) pressure $\rho g x_B \eta$ is balanced by the pressure difference at the interface.
surface tension times the curvature. We approximate the (dimensional) curvature by $h_{xx}(x_B)$. Then we obtain
\[ h_{xx}(x_B) = \rho g x_B / \gamma(x_B), \tag{18} \]
where $x_B > 0$ is the height of the location $B$ above some fixed reference level. Similar relations have also been used by Bretherton [3]. Using this relation in equation (17), we obtain
\[ \rho g x_B / \gamma(x_B) \approx K / \tilde{\gamma}(x_B), \tag{19} \]
We consider the bond number $B = \rho g R^2 / \gamma_0 > 0.842, B \approx O(1)$. With $\delta = b/R$, the above equation becomes
\[ \frac{1}{\tilde{\gamma}(x_B)} \left( \frac{x_B}{R} \right) B^{1/3} \frac{\delta^{1/3}}{\delta^{1/3}} + \frac{3}{2} B^{2/3} \delta^{4/3} \approx \frac{K}{\tilde{\gamma}(x_B)}. \tag{20} \]
We analyze the magnitude of the two terms in the left hand side. We have $\delta \ll 1$; thus $\delta^{1/3} \ll \delta^{1/3}$. Therefore, all other entries in the terms being of the order $O(1)$, we can write
\[ \frac{1}{\tilde{\gamma}(x_B)} \left( \frac{x_B}{R} \right) B^{1/3} \frac{\delta^{1/3}}{\delta^{1/3}} \ll \frac{3}{2} B^{2/3} \delta^{4/3}. \tag{21} \]
Therefore it follows from (20) and (21) that $(3/2) B^{-2/3} \delta^{-4/3} \approx K / (\tilde{\gamma}(x_B))$ and we obtain
\[ b^{1/3} \approx \frac{3}{2} \frac{\tilde{\gamma}(x_B)}{K} T^{2/3}, \tag{22} \]
which is an approximate formula for the film thickness in terms of the surface tension at the point $x_B$. We recall here the relation between the surface tension and the surfactant concentration. Within the linear approximation, for small $\Gamma$, we have
\[ \gamma(\Gamma) = \gamma_0 (1 - M \Gamma), \quad M = -\frac{1}{\gamma_0} \frac{\partial \gamma}{\partial \Gamma} \bigg|_{\Gamma=0}, \]
where $M$ is the positive Marangoni number, $\gamma_0$ is the surface tension in the ‘clean’ case and $\Gamma$ is the surfactant concentration. The maximum value of $\gamma = \gamma / \gamma_0$ is 1 for the clean case when $\Gamma = 0$, and since the film thickness is an increasing function of $\gamma(x_B)$ according to the relation (22), it then follows that we get as a limit process
\[ b < b_{cl}, \tag{23} \]
where $b_{cl}$ is the film thickness in the clean case, $\gamma = 1$. In this way, we show the thinning effect of surfactant.

Next we show the delay effect due to the surfactant. In the clean case, $\gamma_x = 0$ at all points of the bubble surface and $Q(-\infty)$ (see (8)) is given in terms of the film thickness $b_{cl}$. Therefore the formula (10) which holds for the clean case as well becomes
\[ U_{cl} = \frac{2\rho g b_{cl}^3}{3 \mu R}, \tag{24} \]
From the relations (10), (23) and (24) we obtain the delay effect
\[ U < U_{cl}. \tag{25} \]
3. An upper bound of the rising velocity

In this section we consider that the bubble is axisymmetric. Therefore, the flow in the transition region is also axisymmetric and we use the equations in cylindrical coordinates which we introduce here. The O$x$ axis now is the upward symmetry axis of the tube (which is different from the convention used in the Cartesian frame before) and $r$ is the radial distance from the tube center to the tube walls. The gravity force is downward. We use the moving reference with the bubble speed $U$. The flow equations in the transition region $BC$ are

$$\frac{1}{r} \frac{d}{dr}(ru_r) = \frac{1}{\mu} (p_x + \rho g), \quad p_r = 0,$$

which need to be solved subject to the boundary conditions

$$u(r = R) = -U, \quad u_r[r = R - h(x)] = -\gamma_x/\mu, \quad p[r = R - h(x)] = -\gamma h_{xx},$$

where $r = R - h(x)$ is the bubble interface. The condition (27)$_2$ involves $(-\gamma_x)$, because $r$ is pointed from the gas (bubble) to the fluid. In section 2, the coordinate $y$ was pointed from the wall tube (the fluid) to the bubble interface (gas).

The solution of the above problem (26) and (27) in the transition region $BC$ is

$$u(x, r) = -\frac{\gamma h_{xx} + \rho g}{4\mu} \left\{ R^2 - r^2 + 2[R - h(x)]^2 \ln \left( \frac{r}{R} \right) \right\}$$

$$- \frac{\gamma_x}{\mu} [R - h(x)] \ln \left( \frac{r}{R} \right) - U.$$

The matching procedure allows us to consider that the relation (28) holds also near the point $C$. Therefore far behind the top meniscus $AB$, in the flat region $CD$, the solution is (because here $h_{xx}, \gamma_x = 0$ and $h = b$)

$$u(-\infty, r) = -\frac{\rho g}{4\mu} \left\{ R^2 - r^2 + 2(R - b)^2 \ln \left( \frac{r}{R} \right) \right\} - U.$$

The flux at a point $x \in BC$ is given by $Q(x) = \int_{0}^{2\pi} \int_{R - h(x)}^{R} u(x, r) r \, dr \, d\theta$. Therefore far behind $AB$, in the flat region $CD$, we get

$$Q(-\infty) = -2\pi \frac{\rho g}{16\mu} R^4 E(\beta) - 2\pi U \left[ \frac{R^2 - (R - b)^2}{2} \right]$$

where (recall $\beta = 1 - b/R$)

$$E(\beta) = 1 - 4\beta^2 + 3\beta^4 - 4\beta^4 \ln(\beta).$$

With respect to our reference frame, the flux $Q(\infty)$ far up in front of the bubble is given by

$$Q(\infty) = -U \pi (R - b)^2.$$

Equating (30) and (32) we obtain

$$U = \frac{\rho g R^2 E(\beta)}{8\mu (2\beta^2 - 1)}.$$
We prove that $E(\beta) > 0$ for $\beta \in (0, 1)$. We have $E'(\beta) = (-8\beta)D(\beta)$ where

$$D(\beta) = 1 - \beta^2 + 2\beta^2 \ln(\beta).$$ (34)

For our domain of interest $\beta \in (0, 1)$, $D'(\beta) = (4\beta) \ln(\beta) < 0$, with $D(0) = 1$ and $D(1) = 0$. It follows that $D(\beta) > 0 \forall \beta \in (0, 1)$ and hence $E'(\beta) = (-8\beta)D(\beta) < 0$. Therefore $E(\beta)$ is a strictly decreasing function. We have $E(0) = 1$, $E(1) = 0$; then $E(\beta) > 0 \forall \beta \in (0, 1)$.

Since $E(\beta) > 0$ and $U > 0$, from the relation (33) it follows that

$$(2\beta^2 - 1) > 0 \Rightarrow b < R(1 - 1/\sqrt{2}) = 0.292893R.$$ (35)

The relations (10) and (35) are used to obtain the following upper limit for $U$ in the surfactant case:

$$U < \frac{2\rho g R^2}{3\mu} (1 - 1/\sqrt{2})^3 \approx 0.018 \frac{\rho g R^2}{\mu}.$$ (36)

Consider now the clean case (without surfactant). The same upper bound of the rising velocity can be obtained. For this, we see that in the clean case the boundary conditions (27), the solution (29) and the flux (30) do not depend on $\gamma_x$. That means that in both the surfactant and the clean cases, the solution and the flux at $x \to -\infty$ are given in terms of the thin film thickness and do not contain $\gamma_x$. Then the rising velocity $U_{cl}$ in the clean case is given by a formula similar to (33):

$$U_{cl} = \frac{\rho g R^2 E(\beta_{cl})}{8\mu(2\beta_{cl}^2 - 1)},$$ (37)

where $b_{cl} = R(1 - \beta_{cl})$ is the film thickness in the clean case. We use again the analysis following (33) and obtain $2\beta_{cl}^2 - 1 > 0$; then we get $b_{cl} < R(1 - 1/\sqrt{2})$. Therefore the relation (24) gives the same upper bound (36) for $U_{cl}$.

The delay effect also holds in the case of an axisymmetric bubble considered here. For this, we prove that the function $F(x) = E(x)/(2x^2 - 1)$ is decreasing in the interval $x \in (1/\sqrt{2}, 1)$. We have

$$F'(x) = \frac{E'(x)(2x^2 - 1) - 4x E(x)}{(2x^2 - 1)^2}.$$ (38)

The analysis after (33) gives us $E'(x) < 0$ and $E(x) > 0$. Therefore the numerator of the above ratio is negative and we get $F'(x) < 0$. We obtained in section 2 the thinning effect $b < b_{cl}$. Therefore we have $\beta > \beta_{cl}$. Since $F(\beta)$ is a decreasing function of $\beta$, it follows that $U < U_{cl}$.

4. Conclusion and discussion

In this letter, we have studied the effect of interfacial surfactant on the thin layer entrained between a bubble rising through a viscous fluid in a capillary tube sealed at one end and the tube wall. The fluid drains under the gravity effect and is not at rest. This is in contrast with the horizontal case [7] in which the fluid in the thin layer between the bubble and the wall is essentially at rest. In this letter, we obtain analytically that the presence of surfactant on the bubble interface gives a thinning and a delay effect: the

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thickness of the liquid layer behind the bubble and the rising velocity of the bubble are smaller than those for the clean case (see formulas (23) and (25)). It is worth recalling here the exactly opposite effect of surfactant in the horizontal case, namely thickening of the thin film [3, 7]. An upper bound (see (36)) for the rising velocity is also given, varying widely depending on the radius of the tube, as has also been observed in [26]. These effects of surfactants have been confirmed by previous experimental and numerical results in which surfactants were in the bulk as well as on the interface, though our study here considers only interfacial surfactant.

Towards this end, it is worth discussing briefly some research results on very similar problems, namely on thin film problems in the Landau–Levich geometry. These problems arising in thin film coating on flat plates, on fibers, and on similar other geometries have been studied in a lot more detail (see [19, 16, 22, 21]) than the rising bubble problem studied in this letter. This discussion is necessary here as it may have a bearing on providing directions for future studies of the problem studied here in the presence of many other effects. The thickness \( b \) of the entrained film on a LL geometry being withdrawn at speed \( U \) usually follows from the formula

\[
b = 0.9458 \alpha \frac{\sigma}{\rho g} \frac{C_0}{C_a}^{2/3},
\]

where \( \sigma / (\rho g) \) is the capillary length and \( C_a = \mu U / \sigma \) is the capillary number with \( \rho \) the density, \( \mu \) the viscosity, and \( g \) the gravitational acceleration. Here \( \alpha \) is the thickening factor whose value is 1 for the pure Newtonian fluid with no trace of impurities (surfactant) either in the bulk or on the interface. It takes the extreme value of \( 4^{2/3} \) (about 2.5) in the presence of surfactants when the interface is immobile with respect to the substrate. A thickening factor of \( 4^{2/3} \) has been obtained by Park [15] by numerically solving this problem in the presence of surfactants.

Actually, the problem of Marangoni thin film in the presence of insoluble interfacial surfactant within Newtonian fluid approximation contains just about enough mechanisms to lead to film thickening in Landau–Levich geometries and in horizontal capillary tubes (see [7]) and film thinning in the present case of a vertical capillary tube. In problems of this type involving only interfacial surfactant, there are only two time scales: one set by the diffusion process and the other set by the interfacial advection process. Diffusion takes place at a slower time scale than advection unless the velocity of the substrate (in the Landau–Levich geometry) or the bubble (in the capillary tube case) is very small, in which case Marangoni stress will be quickly wiped out, rendering the problem to be one of equivalent pure fluid with the surface tension appropriately modified by the uniform distribution of the surfactant. However, typically this is not the case and the time associated with diffusion is much longer than the transit time associated with convection, i.e. \( C_a \gg Pe^{-3} \) (see [19]) where \( Pe = bU / D_s \), with \( D_s \) as the surface diffusion coefficient, is the Peclet number. More precise modeling of interfacial transport of the surfactants can be done using an advection–diffusion equation with a source term to account for interfacial stretching (see [25]).

Challenging cases are the ones in which the surfactant is present in the bulk as well as on the interface. The thickness of the thin film is then governed by not only the interfacial advection–diffusion equation for the surfactant but also additional transport equations that account for the exchange of surfactant between the bulk and the interface and also between the bulk and the substrate due to adsorption. These processes set their
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own characteristic time scales and the relative importance of these processes dictates the thickness of the thin film. Such surfactant laden fluids are realistically complex fluids and proper treatment (analysis, simulation) requires taking into account the non-Newtonian character of these fluids as well as surface rheology/viscosity. There are more recent experimental data (see [21]) in support of the thickening factor taking values between extreme values 1 (pure Newtonian fluid) and \(4^{2/3}\) (immobile surface). In [21], it has been shown that the thickening factor depends on a parameter (introduced by Quere and Ryck [16]) which essentially measures the capacity of the ‘bulk reservoir’ to replenish the interface with surfactant as necessary due to stretching of the interface. In experiments where the surfactant concentrations were a few times the critical micellar concentration, interesting results on a ‘dynamic transition of thickening’ occurring on increasing the speed of the substrate speed (i.e. \(Ca\)) have been obtained by Scheid et al [21]. In their studies, Scheid et al have demonstrated that thickening beyond the transition can be rationalized by surface viscous effects.

In view of the results mentioned above, it would be interesting to do similar studies on thin films entrained between a tube wall and moving bubble in horizontal and vertical capillary tubes. Such exhaustive studies on thin film problems in capillary tubes have not been done to date. In this letter, we have not studied the influence of surfactant in the bulk or the effect of adsorption on the film thickness. In particular, it will be interesting to do such studies in inclined tubes for various angles of inclination and for various bulk surfactant concentrations, above and below the critical micellar concentrations. These are open problems which will we hope be studied in the future.

In closing this section, after discussing above the frontiers of research in this area, it is important that we explain very concisely why our results, even though different from what is observed and predicted in the Landau–Levich geometry (a fiber or a plate pulled out of a bath) where the surfactants induce systematically a thickening of the entrained film, are not at all surprising. For this, one has to recognize the basic differences between our problem in this letter and the other thin film problems (i.e. the thin film problem in LL geometries and in a horizontal capillary tube with bubble motion inside).

In the Landau–Levich problem, the fiber or the plate is pulled up. In our case, the bubble is self-rising in a capillary tube that is sealed at one end. Because the tube is sealed, the fluid displaced by the front of the bubble must flow back exactly through the thin layer between the bubble surface and the tube wall. This condition leads to formula (10) through (8) and (9). From this follows the thickness, first given by Bretherton 1961 [3],

\[
b = \left( \frac{3\mu RU}{2\rho g} \right)^{1/3}
\]

which remarkably does not depend on the surface tension \(\sigma\). On the contrary, the thickness depends on the surface tension \(\sigma\) in the Landau–Levich geometry (see (39)) and also in the horizontal tubes with a bubble moving inside (see [3, 7]). In the latter case the formula, given below, is also seen to be similar to the LL law (39):

\[
b = 0.643R (3Ca)^{2/3}.
\]

Thus, the thin film problems in a horizontal capillary tube with a moving bubble inside and the Landau–Levich problem are indeed similar, but some differences still exist for which we refer the reader to [11]. One more instance of similarity between these two
problems is hidden in the equation for the free surface: this equation for the LL problem (see [8]) as well as for the horizontal capillary tube (see [3]) contains both \( b \) and \( U \). However, this is not so for the thin film problem in the vertical capillary tube considered in this letter. In our case in this letter, the free surface equation contains only \( b \) (see equation (12)). Of course, we can put \( b \) in terms of \( U \) using (40), but we do not need both \( b \) and \( U \). An estimate of \( b \) can be obtained directly from (22). In their experimental study, Amatroushi and Borhan [1] proved the delay effect of surfactant, meaning that the rising velocity \( U \) of the bubble is smaller in the presence of surfactants. Then the quantity of fluid displaced by the bubble is smaller, and using (40) we find that the thickness \( b \) is also smaller. A similar delay effect of surfactant has also been obtained by Tasoglu et al [24]. Thus our results on the thinning and delay effects are not so surprising and are consistent with experimental results.

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