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# On bubbles with small immobile adsorbed films rising in liquids at low Reynolds numbers

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Surface-active impurities may collect as a stationary film on the lowest part of a bubble rising in liquid while the remainder of the surface moves freely. Numerical approximations for the motion are available if the Reynolds number is low, but they fail for small films. We give the steady-state asymptotic solution for that case, and obtain the perturbation of the drag coefficient from its value for a completely free surface. It depends on the amount by which the surface tension is reduced at the rear stagnation point. This reduction has usually been taken to be the maximum possible for the particular impurity; we consider also the case where dilution is so great that that maximum cannot be reached because the impurity would then be diffusing off the surface at the rear faster than onto it elsewhere.

## 1. Introduction

When a bubble rises through a liquid containing surface-active impurities, the fluid motion near to its surface is slowed down or stopped. In suitable circumstances, a motionless film is adsorbed onto the rear part of the surface, while the remainder of the surface is practically free to move and has very little material adsorbed on it. Savic (1953) first observed the phenomenon. It has since been confirmed experimentally by many workers; see Huang & Kintner (1969). Savic also began its theoretical study, for the case of spherical drops moving at Reynolds numbers much smaller than unity, with negligibly small interior viscosity and bearing rigid spherical caps. His approximate numerical solution has been improved by Davis & Acrivos (1966), but even they reported numerical difficulties for small caps.

It is the purpose of this paper to supplement their theory by giving an analytic solution valid asymptotically for small rigid caps, the rest of the bubble being assumed tangentially stress-free, the shape spherical, and the Reynolds number small. These assumptions are also those of Savic and Davis & Acrivos; the only theory yet available for large Reynolds numbers is an order-of-magnitude analysis by Levich (1962, pp. 447–8).

The fluid motion is determined in § 2, in terms of the cap angle, which is proportional to the surface pressure at the rear stagnation point. This is very nearly the difference in surface tension between the front and rear stagnation points; it may be limited only by the chemical nature of the liquid and its surfactant, as was assumed by Davis & Acrivos, but there is another possibility, discussed in § 3. In a steady state the mass flux onto the free part of the surface will be equal to the mass flux off the rigid part, and in very dilute solutions of surfactants the maximum surface pressure allowable by this condition is less than the 'chemical' limit. The consistency of our assumptions is checked in § 4. It appears that either mechanism for limiting the surface pressure may arise in experiments.

## 2. Theory of the fluid motion

Consider a bubble rising steadily at speed $U$ in an unbounded liquid of density $\rho$ and dynamic viscosity $\eta = \nu\rho$. The surface tension $\sigma$ will vary around the surface, but if it is high enough everywhere the bubble will be very nearly a sphere, of radius $a$. The surface pressure $\Pi$ is defined to be $\sigma_p - \sigma$, where $\sigma_p$ is the surface tension of pure liquid. We assume, with Savic (1953) and Davis & Acrivos (1966), that $\Pi = 0$ on the leading part of the surface $0 \leqslant \theta < \pi - \phi^*$, that $\Pi$ takes whatever values are necessary to stop surface movement on $\pi - \phi^* < \theta \leqslant \pi$, and that surface viscosity and elasticity may be ignored. Here $\theta$ is the polar angle of a spherical co-ordinate system centred on the bubble, and $\phi^*$ is the angular extent of the stagnant cap from the rear stagnation point. We assume also that the Reynolds number $R = 2Ua/\nu \ll 1$ and $\phi^* \ll 1$. We write

$$\Pi = \Pi^*(\phi^*) f(m), \tag{2.1}$$

where $m = (\pi - \theta)/\phi^*$ and $f(0) = 1$, so that $\Pi^*$ is the surface pressure at the rear stagnation point, and $f(m) = 0$ for $m > 1$. In the region $m \leqslant 1$ we may put $\cos\theta = \mu = -1 + \frac{1}{2}m^2\phi^{*2}$, to a first approximation. To find the function $f(m)$, we observe that the rigid part of the bubble surface is almost plane if $\phi^* \ll 1$, and far from it the fluid motion is very nearly the Rybczynski–Hadamard flow past a bubble whose surface is entirely free of surfactant. Also $m = m'/\phi^* a$ is very nearly a dimensionless cylindrical polar radial co-ordinate in the stagnation region, $m'$ being the corresponding physical co-ordinate. Let us take $s$ and $s'$ to be the dimensionless and physical axial co-ordinates, where $s = s'/\phi^* a > 0$ outside the bubble.

Then the boundary conditions on the stream function $\psi$ are that

$$\psi \sim \tfrac{1}{2} U a^2 \phi^{*3} m^2 s \quad \text{at} \quad m^2 s \gg 1;$$

$\psi = 0$ on the axis ($m = 0, s \geqslant 0$); $\psi = \partial\psi/\partial s = 0$ on the stagnant cap ($0 \leqslant m < 1$, $s = 0$); and $\psi = \partial^2\psi/\partial s^2 = 0$ on the free surface ($m > 1$, $s = 0$). The differential equation for $\psi$ in creeping flow is, of course,

$$\{\partial^2/\partial m^2 - m^{-1}\,\partial/\partial m + \partial^2/\partial s^2\}^2 \psi = 0$$

in the region $m \geqslant 0$, $s \geqslant 0$.

This boundary-value problem is easily solved by observing that there must be a solution of the form

$$\psi = \tfrac{1}{2} U a^2 \phi^{*3} m^2 s \{1 - \Sigma A_n Q_n^{(1)}(i\tau)\, P_n^{(1)}(t)\} \tag{2.2}$$

(see Payne & Pell 1960), where $\tau$ and $t$ are oblate spheroidal co-ordinates given by $s = \tau t$, and $m^2 = (\tau^2+1)(1-t^2)$, and $Q_n^{(1)}$ and $P_n^{(1)}$ are first derivatives of Legendre functions. One finds that $A_n = 0$ unless $n = 1$, and hence

$$\psi = \pi^{-1}Ua^2\phi^{*3}m^2s\{\tan^{-1}\tau+\tau/(\tau^2+1)\}. \tag{2.3}$$

This solution resembles that of Reissner & Sagoci (1944) for the displacement of an elastic half-space when a circular portion of its surface is rotated through a fixed angle; the singularities at the circumference of the circle are of square-root type in both problems, as we now see. The surface velocity given by

$$-u_m = (1/a^2\phi^{*2}m)\,\partial\psi/\partial s$$

on the free surface ($m > 1$, $s = 0$; i.e. $t = 0$) is

$$u_m = \pi^{-1}U\phi^*m\{\sec^{-1}m+(m^2-1)^{\frac{1}{2}}/m^2\}; \tag{2.4}$$

for $m \rightarrow 1+$ this is asymptotically $2U\phi^*(m^2-1)^{\frac{1}{2}}/\pi$, so that $u_m$ comes sharply down to zero at $m = 1$. For large $m$, $u_m$ tends to $\frac{1}{2}U\phi^*m$, which is the Rybczynski–Hadamard surface velocity.

There is also a square-root singularity of the rate of shear $E$; on the stagnant cap ($m < 1$, $s = 0$; i.e. $\tau = 0$) we find that

$$E = 4Um/\pi a(1-m^2)^{\frac{1}{2}} = -(1/\eta a\phi^*)\,\partial\Pi/\partial m = -(\Pi^*/\eta a\phi^*)\,df/dm; \tag{2.5}$$

the latter two expressions for $E$ come respectively from our assumption that the viscous shear stress $\eta E$ is balanced by a surface tension gradient and from (2.1). Because $f(0) = 1$, it follows that

$$f(m) = (1-m^2)^{\frac{1}{2}} \tag{2.6}$$

and

$$\Pi^* = 4U\eta\phi^*/\pi. \tag{2.7}$$

The simplest way to find the drag coefficient $C_D$, given by

$$C_D = (\text{drag force})/\tfrac{1}{2}\rho U^2\pi a^2 = 8ga/3U^2,$$

where $g$ is the acceleration due to gravity, is to use Harper's (1972) equation (4.52), and so

$$\frac{RC_D}{16} = 1-\frac{1}{2U\eta}\int_{-1}^{1}\mu\Pi\,d\mu = 1+\frac{2\phi^{*3}}{3\pi} = 1+\frac{\pi^2}{96}\left(\frac{\Pi^*}{U\eta}\right)^3. \tag{2.8}$$

Equation (2.7) is very close to the corresponding result of Davis & Acrivos (1966) for values of $\Pi^*/U\eta$ up to about one, but (2.8) gives rather different effects of the surfactant on the drag. For $\Pi^*/U\eta < 1$, the present theory gives lower values of $RC_D$ and should be more accurate than that of Davis & Acrivos; the theories agree near $\Pi^*/U\eta = 1$; and Davis & Acrivos give smaller and better drag values if $\Pi^*/U\eta > 1$, or $\phi^* > 45°$. Our method fails, of course, for $\phi^*$ as large as this, while Davis & Acrivos reported numerical troubles for small cap angles.

## 3. Determination of $\Pi^*$

So far, $\Pi^*$ is a free parameter in the theory. Davis & Acrivos fixed it by putting it equal to the maximum possible surface pressure the given surfactant could provide, $\Pi_{\text{max}}$ say. (For many surfactants, $\Pi$ is known to be approximately proportional to the concentration in the solution up to a limiting value, and more concentrated solutions have nearly constant surface pressures; see, for example, Shaw (1970, p. 71).) To assume $\Pi^* = \Pi_{\max}$ is reasonable if the solution is sufficiently concentrated, but it seems worthwhile also to consider the possibility for small $\phi^*$ that $\Pi^*$ is limited to a value lower than $\Pi_{\max}$ by the available supply of surfactant. If the equilibrium surface pressure of the solution far from the bubble is $\Pi_\infty$, it is clear that $\Pi \ll \Pi_\infty$ over almost the entire free part of the surface when the surface activity is high enough (see Harper 1972, p. 115); and surfactant will diffuse towards that part of the surface. In a steady state, when the total quantity of adsorbed material is constant, $\Pi$ must be greater than $\Pi_\infty$ over some part of the surface, and in fact $\Pi \gg \Pi_\infty$ over almost the whole of the rigid part. (Mass transfer is less effective at a rigid than a free surface at high Péclet numbers, and our rigid surface is of small area.)

If, then, $\Pi < \Pi_{\max}$ everywhere, and $\Pi^*$ is limited by the possible rate of convective diffusion to the surface, let us suppose that the surfactant solution is 'ideal' (by analogy with ideal gases), i.e. that $\Pi = R_g T\Gamma = R_g Thc$, where $R_g$ is the gas constant, $\Gamma$ the surface excess of adsorbed surfactant (in moles per unit area), $c$ the concentration of surfactant in the adjacent solution (in moles per unit volume), and $h$ is a constant with the dimensions of length, the 'adsorption depth'. (A cylinder of the solution of depth $h$ would have equal amounts of surfactant dissolved within it and adsorbed on the surface, in equilibrium.) We also suppose that the diffusivity $D$ is constant in the solution, that $c = 0$ in the gas in the bubble, and that chemical equilibrium is maintained at the surface, so that $\Pi = R_g Thc$ at each point, although gradients of $\Pi$ and $c$ exist and cause diffusion. To simplify subsequent calculations, we define $\Pi$ by that equation throughout the liquid – $\Pi$ is a constant multiple of $c$ – and work in terms of $\Pi$.

In a steady state, the total net diffusion flux to the surface vanishes, and so

$$\int_0^\pi \sin\theta \left(\frac{\partial \Pi}{\partial r}\right)_s d\theta = 0, \tag{3.1}$$

with our assumptions, where the subscript $s$ indicates the bubble surface. To evaluate $(\partial\Pi/\partial r)_s$, we assume a high Péclet number and so a thin diffusion boundary layer; the contrary hypothesis does not lead to stagnant caps (Harper 1972, p. 110).

On the free part of the surface, where $\Pi \ll \Pi_\infty$ and $u \doteqdot \frac{1}{2}U\sin\theta$ except in a neighbourhood of the rear end which is too small to matter, we may use Levich's (1962, p. 407) analysis to write

$$\partial\Pi/\partial r = (3U/2\pi Da)^{\frac{1}{2}}\,\Pi_\infty(1+\mu)\,(2+\mu)^{-\frac{1}{2}},$$

and so the contribution to the integral in (3.1) from this part of the surface is

$$\int_0^{\pi-\phi^*} \sin\theta \left(\frac{\partial \Pi}{\partial r}\right)_s d\theta \doteqdot (8U/3\pi Da)^{\frac{1}{2}}\,\Pi_\infty. \tag{3.2}$$

On the rigid part, we find the distribution of $(\partial\Pi/\partial r)_s$ by the method of Lighthill (1950), modified slightly as required for an axially symmetric flow. Because the rate of shear at the surface is known from equation (2.5) we may take $\psi$ to be of the form

$$\psi = \tfrac{1}{2}Em'^2s'^2 = (324UD^2\phi^{*5}a^4/\pi)^{\frac{1}{3}}\,Y^2, \tag{3.3}$$

in the diffusion layer, and so obtain the convective diffusion equation in the form

$$\frac{1}{Y}\frac{\partial^2 \Pi}{\partial Y^2} = 9\frac{\partial \Pi}{\partial X}, \tag{3.4}$$

where $X$ depends only on $m$, being given for our distribution of $E$ by

$$X = \int_m^1 \frac{m_1^2\,dm_1}{(1-m_1^2)^{\frac{1}{4}}}, \tag{3.5}$$

so that, as $m$ varies from 1 to 0, $X$ varies from 0 to $\frac{1}{2}B(\frac{3}{2},\frac{3}{4}) = 0{\cdot}479$. Equation (2.6) gives us the surface boundary condition in the form

$$\Pi = \Pi^*(1-m^2)^{\frac{1}{2}} = \Pi^* F(X), \quad \text{say}, \tag{3.6}$$

on $Y = 0$, and the other boundary conditions are $\Pi \to \Pi_\infty \ll \Pi^*$ as $Y \to \infty$, and $\Pi \ll \Pi^*$ on $X = 0$.

Lighthill (1950) showed how to solve (3.4) with these conditions; on neglecting $\Pi_\infty$ completely we obtain

$$\Pi = \Pi^* \int_0^X \frac{dF(t)}{dt}\, h(Y/\{X-t\}^{\frac{1}{3}})\,dt, \tag{3.7}$$

where $$h(x) = \int_x^\infty \frac{\exp(-t^3)\,dt}{(\frac{1}{3})!}.$$

Hence we find that

$$\int_{\pi-\phi^*}^{\pi} \sin\theta \left(\frac{\partial \Pi}{\partial r}\right)_s d\theta = -\{24 \times 2^{\frac{1}{2}} X(0)^2 \phi^{*8} Ua/\pi^4 D\}^{\frac{1}{3}}\, U\eta/(\tfrac{1}{3})!\,a, \tag{3.8}$$

and then from (3.1) and (3.2) that

$$\phi^* = 1{\cdot}761(\Pi_\infty/U\eta)^{\frac{3}{8}}(Ua/D)^{\frac{1}{16}}, \tag{3.9}$$

therefore

$$\Pi^*/\Pi_\infty = 2{\cdot}242(U\eta/\Pi_\infty)^{\frac{5}{8}}(Ua/D)^{\frac{1}{16}} = 2{\cdot}431(Ua/D)^{\frac{1}{6}}\phi^{*-\frac{5}{3}}. \tag{3.10}$$

Because $(Ua/D)^{\frac{1}{6}} > 1$ and $\phi^* \ll 1$, the second part of (3.10) reveals that our assumption $\Pi^* \gg \Pi_\infty$ was self-consistent. One would only increase $\Pi^*$ by including the effects of $\Pi_\infty$ in the calculation, and so the assumption was valid: to discard it would introduce complication without significantly improving accuracy. The first part of (3.10) shows that $\Pi^*/\Pi_\infty$ increases with bubble size in a given liquid (constant $\eta$, $D$, $\Pi_\infty$), because if $RC_D$ remains close to 16, $U \propto a^2$ approximately, and so $\Pi^*/\Pi_\infty \propto a^{\frac{23}{16}}$. Because it is required that $\Pi^* < \Pi_{\max}$ for diffusion to limit the surface pressure, we see that this mechanism operates only in sufficiently dilute solutions. On the other hand, the solution must be concentrated enough to stop the motion over a part of the surface.

## 4. Conditions for validity

If a bubble is to rise as predicted by the present theory, a number of conditions must be satisfied. We collect them below.

(i) For the creeping-flow equations to be used, $R = 2Ua/\nu \ll 1$.

(ii) For the bubble to be nearly spherical, $\sigma/U\eta \gg 1$ according to Savic (1953); $\sigma$ is, of course, lowest at the rear stagnation point.

(iii) For $\Pi$ at the front stagnation point to be much less than $\Pi_\infty$, the Péclet number $P = 2Ua/D \gg 1$ and also the appetite of the surface there for surfactant must be too great for the diffusion through the bulk solution to satisfy, so that

$$h/a \gg P^{-\frac{1}{2}}, \tag{4.1}$$

according to Harper (1972, equations 4.46 and 4.48). Values of the adsorption depth $h$ vary from molecular sizes for weakly surface-active solutes, to 0·3 mm for dodecanol ($C_{12}H_{25}OH$) in water, and even more for highly surface-active nearly insoluble substances.

(iv) For the thickness $\delta$ of the diffusion boundary layer on the stagnant cap to be much less than its radius,

$$\delta \sim a\phi^{*\frac{1}{3}}P^{-\frac{1}{3}} \ll a\phi^*, \quad \text{so} \quad \phi^* \gg P^{-\frac{1}{2}}. \tag{4.2}$$

(v) For the stagnant cap to be small, $\phi^* \ll 1$.

(vi) For Lighthill's diffusion theory to hold, $u_\theta \ll E\delta$ on the stagnant cap. To estimate $u_\theta$, we write the equation for the material balance at the surface in the form

$$a\frac{\partial}{\partial\theta}(\Pi u_\theta \sin\theta) = D_s\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Pi}{\partial\theta}\right) + \frac{a^2D}{h}\sin\theta\frac{\partial\Pi}{\partial r}, \tag{4.3}$$

(see Harper 1972, equation 4.42), where $D_s$ is the surface diffusion coefficient. As $\Pi$ is already known, we find that $u_\theta \ll E\delta$ requires both that

$$\phi^{*\frac{4}{3}}P^{\frac{2}{3}}D/D_s \gg 1, \tag{4.4}$$

and that

$$\phi^{*-\frac{1}{3}}P^{\frac{1}{3}}h/a \gg 1. \tag{4.5}$$

Condition (4.4) will always hold, because of (4.2), if $D$ and $D_s$ are of the same order. Condition (4.5) requires a sufficiently large value of $h$, and is more restrictive than (4.1). The analysis leading to (4.4) and (4.5) fails near the transition from free to effectively stagnant surfaces, but the above conditions will ensure suitably small values of $u_\theta$ over most of the cap, and so the transition zone will be narrow enough to ignore.

## 5. Conclusions

The stagnant-cap model for the flow is often a good one; its principal requirements are a highly surface-active solute and a high Péclet number. But previous calculations of the viscous drag are somewhat misleading for small cap angles, and they cover only the case $\Pi^* = \Pi_{\max}$, i.e. a solution concentrated enough for the surface pressure to reach its upper bound for a given surfactant. Calculations for the simplest alternative case, $\Pi^*$ low enough for the solution to be everywhere ideal, give markedly different results. We find that $RC_D - 16 \propto a^n$ when $C_D$ is close to $16/R$, where $n = -6$ if $\Pi^* = \Pi_{\max}$ and $n = -\frac{27}{16}$ if the solution is ideal. (Compare the values $n = -2$ for strong and $n = -\frac{3}{2}$ for weak surfactants in solutions so dilute that $u_\theta$ is close to $\frac{1}{2}U\sin\theta$ even near the rear stagnation point, due respectively to Harper (1973) and Levich (1962).)

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