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Stagnant-cap bubbles with both diffusion and adsorption rate-determining

By J. F. HARPER

School of Mathematics, Statistics and Computer Science, Victoria University, Wellington, New Zealand
john.harper@vuw.ac.nz

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When a gas bubble rises in an impure liquid, its surface often has an upper spherical cap with negligible shear stress, a lower spherical cap with negligible tangential velocity, and a very small transition region between the two caps.

This paper gives the diffusion boundary-layer theory for the distribution of surfactant around a stagnant-cap bubble, allowing for slowness of both adsorption and diffusion. The resulting singular Volterra integro-differential equations are solved numerically for creeping flow (small Reynolds number). The main result is the relation between the surface pressure of surfactant in the bulk solution, the cap angle and Péclet number of the bubble, and the adsorption depth and adsorption speed of the surfactant. The values of the latter two parameters affect the validity of the approximations much more than the numerical results.

1. Introduction

Let us consider the theory of a gas bubble of constant volume rising steadily at high Péclet number in a dilute solution of a surfactant, in the common 'stagnant cap' situation first described by Savic (1953) of a spherical bubble on which an upper spherical cap is effectively free of shear stress, a lower spherical cap is effectively stagnant, i.e. with negligible tangential velocity, and the transition region between the two caps (Harper 1992) is negligibly small. For brevity we refer to the two caps as free and rigid, even though the upper one is not perfectly shear-free and the lower one is not perfectly rigid.

Some previous work on the subject has taken account of surfactant diffusion in the liquid and ignored slowness of adsorption and desorption (Levich 1962; Harper 1972, 1973; Lerner & Harper 1991). Some has dealt with slow adsorption and desorption but assumed that diffusion was very fast (Levich 1962; He, Maldarelli & Dagan 1991; Bel Fdhila & Duineveld 1996). There are also two recent papers allowing for both processes (Cuenot, Magnaudet & Spennato 1997; Ybert & di Meglio 2000). Both of these used full numerical simulations, but gave detailed results only at one Reynolds number: 100.

This paper goes some way towards overcoming that limitation by assuming a thin diffusion boundary layer of an ideal solution of surfactant. Much of the theory is then independent of Reynolds number, provided that no eddy appears in the wake. That condition imposes an upper bound on the Reynolds number; the bound increases with free-cap size. For very small Reynolds numbers Sadhal & Johnson (1983) solved the fluid mechanical problem, and found closed forms in elementary functions for some useful results. More will be given herein.

The problem of surfactant transfer reduces to a pair of linear Volterra integro-differential equations, which are solved numerically. Thinness of the diffusion layer implies that surface diffusion is negligible (Harper 1992) if, as usual, surface and bulk diffusivities are of the same order.

2. Governing equations

We use spherical polar coordinates (r, θ); the bubble surface is $r = a$, the free cap is $0 \leqslant \theta < \theta_T$, the rigid cap $\theta_T < \theta \leqslant \pi$. Subscripts t, T, b, and ∞ refer to values of variables at the top stagnation point of the bubble, the surface transition, the bottom stagnation point, and at large distances. Let $\hat{c}$ be the concentration (mol m^{-3}) of dissolved surfactant, D its diffusivity (m^2 s^{-1}), and $\hat{\Gamma}$ its surface excess (mol m^{-2}), not to be confused with the gamma function Γ whose complete and incomplete versions are both used below. Let $\hat{\Pi}$ be the surface pressure (i.e. the reduction in surface tension due to the surfactant), U the bubble speed, and $Pe = 2Ua/D$ the Péclet number.

2.1. *Differential equations*

We assume that $Pe \gg 1$. The thickness of the diffusion layer on the free cap is then $O(aPe^{-1/2})$. Let the tangential velocity on it be $u = Uf(\theta)$, where U is the speed of the bubble relative to the fluid far away. On the rigid cap we assume $u \ll UPe^{-1/3}$, so the diffusion layer thickness is $O(aPe^{-1/3})$, and if the shear rate is $UF(\theta)/a$, then $u \sim U(r-a)F(\theta)/a$ in the layer. To leading order the stream functions in the diffusion layers are then

$$\psi = Ua(r-a)f(\theta)\sin\theta, \quad \text{free cap}, \quad 0 < \theta < \theta_T, \tag{2.1}$$

$$\psi = \tfrac{1}{2}U(r-a)^2F(\theta)\sin\theta, \quad \text{rigid cap}, \quad \theta_T < \theta < \pi. \tag{2.2}$$

If we put $k = 2^{-3/2}Pe^{1/2}(Ua^2)^{-1}$, $K = 2^{1/6}3^{-2/3}Pe^{1/3}(Ua^2)^{-1/2}$, and

$$x = \int_0^\theta f(\theta')\sin^2\theta'\,\mathrm{d}\theta', \quad y = k\psi, \quad 0 < \theta < \theta_T, \tag{2.3}$$

$$X = \int_{\theta_T}^\theta \{F(\theta')\sin^3\theta'\}^{1/2}\,\mathrm{d}\theta', \quad Y = K\psi^{1/2}, \quad \theta_T < \theta < \pi, \tag{2.4}$$

then the diffusion-layer equations and their most useful similarity solutions become (Levich 1962; Harper 1972; Dukhin, Kretzschmar & Miller 1995)

$$4\frac{\partial\hat{c}}{\partial x} = \frac{\partial^2\hat{c}}{\partial y^2}, \quad \mathrm{erfc}_2\left(\frac{y}{[x-x']^{1/2}}\right), \quad 0 < \theta < \theta_T, \tag{2.5}$$

$$9\frac{\partial\hat{c}}{\partial X} = \frac{1}{Y}\frac{\partial^2\hat{c}}{\partial Y^2}, \quad \mathrm{erfc}_3\left(\frac{Y}{[X-X']^{1/3}}\right), \quad \theta_T < \theta < \pi, \tag{2.6}$$

if $\hat{c}$ is the surfactant concentration, x', X' are constants, and for $n > 0$ we define

$$\mathrm{erfc}_n(z) = \int_z^\infty \exp(-w^n)\,\mathrm{d}w \Big/ \int_0^\infty \exp(-w^n)\,\mathrm{d}w = \frac{\Gamma(1/n, z^n)}{\Gamma(1/n)}. \tag{2.7}$$

The usual error function erfc is erfc_2 in this notation.

2.2. *Boundary conditions*

Harper (1992) and Cuenot *et al.* (1997) explained why surface diffusion was unimportant at large Péclet numbers, and it will be ignored here. Cuenot *et al.* used

Langmuir surface kinetics, but if $\hat{\Gamma}$ is much smaller than its saturation value $\hat{\Gamma}_{sat}$, their surface boundary conditions reduce to the ideal-solution limits

$$D\frac{\partial \hat{c}}{\partial r} = V(\hat{c} - \hat{\Gamma}/h), \tag{2.8}$$

$$\hat{\Pi} = RT\hat{\Gamma}, \tag{2.9}$$

where V is the adsorption speed of the surfactant, $h = \lim_{\hat{c}\to 0}(\hat{\Gamma}/\hat{c})$ is its adsorption depth, R is the gas constant and T is the absolute temperature. Our parameters V, h which characterize the surface chemistry are more convenient than the adsorption and desorption parameters k_a and β of Cuenot *et al.*, in terms of which $V = \hat{\Gamma}_{sat}k_a$, $h = \hat{\Gamma}_{sat}/\beta$. Cuenot *et al.* used the symbol Γ_∞ for $\hat{\Gamma}_{sat}$, but we use the subscript ∞ to denote conditions far from the bubble. Numerical values for the decanoic acid of Cuenot *et al.* are $V = 2\times 10^{-4}\ \mathrm{m\,s^{-1}}$, $h = 56\ \mu\mathrm{m}$, and for many other surfactants can be found in Chang & Franses (1995); in the notation of their table 3, $V = k^{\mathrm{a}}$, $h = k^{\mathrm{a}}/k^{\mathrm{d}}$.

If there were a surface in equilibrium anywhere in the liquid with no diffusion to or from it, $\partial\hat{c}/\partial r = 0$ there, and (2.8) and (2.9) would imply $\hat{\Pi} = RT\hat{\Gamma} = RTh\hat{c}$. We use that equation to define $\hat{\Pi}$ and $\hat{\Gamma}$ throughout the liquid except at its surface in terms of the local value of $\hat{c}$. We assume that the surfactant concentration becomes uniform far from the bubble: $\hat{c}\to\hat{c}_\infty$, $\hat{\Pi}\to\hat{\Pi}_\infty$, $\hat{\Gamma}\to\hat{\Gamma}_\infty = h\hat{c}_\infty$ as $r\to\infty$. It is convenient to define a dimensionless bulk concentration $c = \hat{c}/\hat{c}_\infty$ and a dimensionless surface pressure $\Pi = \hat{\Pi}/\hat{\Pi}_\infty$, which is equal to $\hat{\Gamma}/\hat{\Gamma}_\infty$, by (2.9).

At the bubble surface, (2.8) and conservation of mass of surfactant imply that

$$U\frac{h}{a}\frac{\partial}{\partial\theta}\{\Pi f(\theta)\sin\theta\} = D\frac{\partial c}{\partial r}\sin\theta = V(c-\Pi)\sin\theta. \tag{2.10}$$

If η is the dynamic viscosity of the liquid, the surface shear stress $\sigma_{r\theta}$ obeys

$$\sigma_{r\theta} = \eta\frac{\partial u}{\partial r} = \frac{\eta U F(\theta)}{a} = \frac{1}{a}\frac{\partial\hat{\Pi}}{\partial\theta}, \tag{2.11}$$

if the dynamic viscosity of the gas in the bubble is negligibly small.

2.3. *Integro-differential equation: free cap*

Let $c = c_t$, $\Pi = \Pi_t$ at the top stagnation point, let $f_S(x) = f(\theta)\sin\theta$, and let $j(x)$ be the dimensionless surfactant flux along the surface given by

$$j(x) = \Pi f_S(x), \tag{2.12}$$

so that the molar flux is $2\pi aU\hat{\Gamma}_\infty j(x)$. Then (2.3), (2.5) and the boundary conditions give $j(x)$ and $c(x, y)$ on the surface $y = 0$ as

$$j(x) = \beta_1\left\{x^{1/2} - \int_0^x \frac{c(t,0)\,\mathrm{d}t}{2(x-t)^{1/2}}\right\}, \tag{2.13}$$

$$c(x,0) = \frac{j(x)}{f_S(x)} + \frac{Uh}{Va}f_S(x)\frac{\mathrm{d}j(x)}{\mathrm{d}x} \tag{2.14}$$

$$= \frac{j(x)}{f_S(x)} + \beta_2 f_S(x)\left\{\frac{1-c_t}{x^{1/2}} - \int_0^x \frac{\partial c(t,0)}{\partial t}\frac{\mathrm{d}t}{(x-t)^{1/2}}\right\}, \tag{2.15}$$

where each of the two parameters

$$\beta_1 = (8/\pi)^{1/2}Pe^{-1/2}(a/h), \qquad \beta_2 = (2/\pi)^{1/2}Pe^{-1/2}(U/V), \tag{2.16}$$

involves the Péclet number and a dimensionless ratio of a physical parameter, a or U, to a chemical parameter, h or V.

Near $\theta = 0$, $f(\theta) \sim E\theta$, say, so $x \sim \frac{1}{4}E\theta^4$, and $f_S \sim 2E^{1/2}x^{1/2}$. In creeping flow $E = \frac{1}{2}(\theta_T + \sin\theta_T)/\pi$, so if both caps exist, $0 < E < \frac{1}{2}$. At higher Reynolds numbers, $0 < E < \frac{3}{2}$. Equation (2.15) implies that

$$c_t = \frac{\beta_1 + 4E\beta_2}{\beta_1 + 4E\beta_2 + 2E^{1/2}}, \tag{2.17}$$

$$\Pi_t = \frac{\beta_1}{\beta_1 + 4E\beta_2 + 2E^{1/2}}. \tag{2.18}$$

As one might expect, $c_t > \Pi_t$ unless $\beta_2 = 0$. Slowness of adsorption implies that where elements of surface area are growing the surface pressure is below the equilibrium value for the local bulk concentration.

In exact stagnant-cap theory $\Pi = 0$ on the free cap. Our theory is an approximation, valid only if either $\beta_1 \ll 1$, i.e. $a/h \ll Pe^{1/2}$ (Harper 1973), or $\beta_1 \ll \beta_2$, i.e. $a/h \ll U/V$ (Cuenot *et al.* 1997).

The upstream condition on the rigid cap requires $\gamma(Y) = c(x_T, kY^2/K^2) - 1$; it is obtainable from (2.3), (2.4), (2.5) and the solution of (2.15) as

$$\gamma(Y) = (c_t - 1)\,\mathrm{erfc}(gY^2) + \int_0^x \frac{\partial c(t,0)}{\partial t}\,\mathrm{erfc}\left(\frac{gY^2}{[1 - t/x_T]^{1/2}}\right)\mathrm{d}t, \tag{2.19}$$

if $g = 2^{-11/6}3^{4/3}Pe^{-1/6}x_T^{-1/2}$. The total molar flux of surfactant to the free cap is

$$2\pi a^2 D\hat{c}_\infty \int_0^{\theta_T} \frac{\partial c}{\partial r}\sin\theta\,\mathrm{d}\theta = 2\pi a U\hat{\Gamma}_\infty j(x_T), \tag{2.20}$$

which has a non-zero limit at $\theta \to \theta_T$. As $f(\theta_T) \to 0$ there, it would seem that $\Pi \to \infty$. In reality a transition region like that of Harper (1992) keeps Π finite, and the main use of that theory is in checking validity of the approximations; see § 3.2 below.

2.4. *Integro-differential equation: rigid cap $\theta > \theta_T$*

On the rigid cap we have $c = 1 + \gamma(Y)$ at $X = 0$, by (2.19). On the surface $Y = 0$ we use (2.8) and put $c = 1 + c_1(X,Y) + c_2(X,Y) + c_3(X,Y) + c_4(X,Y)/\Pi_U$, where all four c_i obey the partial differential equation (2.6), and if $k = 3, 4$,

$$c_1(0,Y) = 0 \qquad \text{if } Y > 0; \qquad c_1(X,0) = \gamma(0); \tag{2.21}$$

$$c_2(0,Y) = \gamma(Y) \qquad \text{if } Y > 0; \qquad c_2(X,0) = 0; \tag{2.22}$$

$$c_k(0,Y) = 0 \qquad \text{if } Y \geqslant 0; \qquad c_k(X,0) - \Gamma\left(\tfrac{4}{3}\right)\beta_3 F_S(X)c_{kY}(X) = g_k(X), \tag{2.23}$$

where $c_{iY}(X)$ is $\partial c_i(X,Y)/\partial Y$ at $Y = 0$ for $i = 1, 2, 3, 4$, and F_S, g_k, β_3 and Π_U are

$$F_S(X) = \{F(\theta)\sin\theta\}^{1/2}, \tag{2.24}$$

$$g_3(X) = \Pi_T - 1 - \gamma(0) + \Gamma\left(\tfrac{4}{3}\right)\beta_3 F_S(X)\{c_{1Y}(X) + c_{2Y}(X)\}, \tag{2.25}$$

$$g_4(X) = (\Pi - \Pi_T)\Pi_U = \int_{\theta_T}^{\theta} F(\theta')\,\mathrm{d}\theta', \tag{2.26}$$

$$\beta_3 = \frac{2^{2/3}Pe^{-2/3}}{3^{2/3}\Gamma\left(\frac{4}{3}\right)}\frac{U}{V} = \frac{2^{1/6}\pi^{1/2}}{3^{2/3}\Gamma\left(\frac{4}{3}\right)}Pe^{-1/6}\beta_2, \tag{2.27}$$

$$\Pi_U = \frac{\hat{\Pi}_\infty}{\eta U}. \tag{2.28}$$

Now $c_1(X, Y) = \gamma(0)\,\mathrm{erfc}_3(Y/X^{1/3})$. If λ is any constant and $J_{1/3}$ denotes a Bessel function, $\exp(-\frac{1}{4}\lambda^2 X)Y^{1/2}J_{1/3}(\lambda Y^{3/2})$ obeys the diffusion-layer equation (2.6) and vanishes at $Y = 0$, so $c_{2Y}(X)$ can be found as follows. We begin with $\gamma(Y) = \mathrm{erfc}(mY^2)$, and then superpose the results with the various values of m required by (2.19). If

$$c_2(X, Y) = \int_0^\infty H(\lambda)(\lambda Y)^{1/2} \exp\left(-\tfrac{1}{4}\lambda^2 X\right) J_{1/3}\left(\lambda Y^{3/2}\right) \mathrm{d}\lambda, \tag{2.29}$$

the theory of Hankel transforms (Erdelyi *et al.* 1954) shows for that $\gamma(Y)$ that

$$H(\lambda) = \tfrac{3}{2}\lambda^{1/2} \int_0^\infty Y^{3/2}\,\mathrm{erfc}(mY^2) J_{1/3}\left(\lambda Y^{3/2}\right) \mathrm{d}Y, \tag{2.30}$$

$$\therefore \quad c_{1Y}(X) + c_{2Y}(X) = -\frac{\zeta\left(mX^{2/3}\right)}{\Gamma\left(\frac{4}{3}\right)X^{1/3}}, \tag{2.31}$$

where

$$\zeta(t) = \frac{4t}{\sqrt{\pi}} \int_0^\infty x \exp\left(-x^3 - t^2x^4\right) \mathrm{d}x = \frac{4}{\sqrt{\pi}} \int_0^\infty x \exp\left(-x^3t^{-3/2} - x^4\right) \mathrm{d}x \tag{2.32}$$

$$= \frac{1}{\sqrt{\pi}} \sum_{n=0}^{n=\infty} \frac{(-1)^n \Gamma\left(\frac{3}{4}n + \frac{1}{2}\right)}{n!\, t^{3n/2}} \quad \text{(convergent)}, \tag{2.33}$$

$$\sim \frac{4}{3\sqrt{\pi}} \sum_{n=0}^{n=\infty} \frac{(-1)^n \Gamma\left(\frac{4}{3}n + \frac{2}{3}\right) t^{2n+1}}{n!} \quad \text{(asymptotic as } t \to 0\text{)}, \tag{2.34}$$

if $|\arg t| < \frac{1}{4}\pi$. We also need $\delta(t) = \int_0^t \zeta(u)\,\mathrm{d}u$. Integration of the series (2.34) gives $\delta(t)$ for small t, and (2.32) gives $\zeta(u) = 1 - \int_0^\infty 3x^2\,\mathrm{erfc}(ux^2)\exp(-x^3)\,\mathrm{d}x$, leading to

$$\delta(t) \sim t - 3\Gamma\left(\tfrac{4}{3}\right)/\sqrt{\pi} + O\left(t^{-1/2}\right) \text{ as } t \to \infty. \tag{2.35}$$

Equations (2.19), (2.25) then lead to

$$g_3(X) = \Pi_T - 1 - \gamma(0) - \frac{\beta_3 F_S(X)}{X^{1/3}} \left\{ (c_t - 1)\zeta\left(gX^{2/3}\right) + \int_0^{x_T} \frac{\partial c(t, 0)}{\partial t} \zeta\left(\frac{gX^{2/3}}{[1 - t/x_T]^{1/2}}\right) \mathrm{d}t \right\}, \tag{2.36}$$

and (2.23) to the rigid-cap integro-differential equations:

$$c_k(X, 0) + \beta_3 F_S(X) \int_0^X \frac{\mathrm{d}c_k(T, 0)}{\mathrm{d}T} \frac{\mathrm{d}T}{(X - T)^{1/3}} = g_k(X), \quad k = 3, 4. \tag{2.37}$$

If $\beta_3 = 0$, this equation is trivial. If not, we may write it as $F_S(X)L(X) = 0$ and use Abel's transformation $\int_0^X L(X')(X - X')^{-2/3}\,\mathrm{d}X' = 0$ to obtain

$$\beta_3 h_k(X) + \frac{\sqrt{3}}{2\pi} \int_0^X \frac{h_k(T)\,\mathrm{d}T}{F_S(T)(X - T)^{2/3}} = -\beta_3 g_k(X), \tag{2.38}$$

where $h_k(X) = c_k(X, 0) - g_k(X)$.

3. Creeping flow

3.1. *Free cap*

For the Reynolds number $Re = 2Ua/\nu \ll 1$, where ν is the liquid kinematic viscosity, Sadhal & Johnson (1983) gave an analytical solution for the fluid mechanics of a

stagnant-cap bubble. Equation (2.15) requires f_S and x on the free cap, which are given by

$$f_S = (\sin^2\theta)(z + \sin z \cos z)/\pi, \tag{3.1}$$

$$9\pi x = 6\theta_T - 3z(1+\mu)^2(2-\mu) - 3S(1+C)(2-C)(1-T) + S(1-C)\{(5-4C)(1-T^3) - 3(1-C)(1-T^5)\}, \tag{3.2}$$

where $S = \sin\theta_T$, $C = \cos\theta_T$, $\mu = \cos\theta$, $z = \cos^{-1}(\cos\frac{1}{2}\theta_T/\cos\frac{1}{2}\theta)$, $T = \tan z/\tan\frac{1}{2}\theta_T$, or $T^2 = (\mu - C)/(1 - C)$, so that $T_t = 1$, $T_T = 0$. We shall also use $S_2 = \sin\frac{1}{2}\theta_T$, $C_2 = \cos\frac{1}{2}\theta_T$.

Harper (1988) developed a numerical method to solve the special case of (2.15) with $\theta_T = \pi$, $\beta_2 = 0$. It was used to solve the more general case here. One takes a set of $(n+1)$ angles θ_i such that $\theta_0 = 0$, $\theta_n = \theta_T - 0.1^\circ$, and the numbers $(\theta_T - \theta_i)$ form a geometric progression, more closely spaced near θ_T, and approximates the integrals in the obvious way, and uses the following second-order approximation to $\partial c(t,0)/\partial t$. If c, x at grid point i are c_i, x_i, and $h_{i1} = x_i - x_{i-1}$, $h_{i2} = x_i - x_{i-2}$, then at $t = x_i$

$$\frac{\partial c(t,0)}{\partial t} \approx \frac{h_{i2}^2(c_i - c_{i-1}) - h_{i1}^2(c_i - c_{i-2})}{h_{i1}h_{i2}(h_{i2} - h_{i1})}. \tag{3.3}$$

3.2. *Transition region*

Let $\phi = \pi - \theta_T$, and near the free–rigid transition let $\xi = a(\theta - \theta_T)$. Harper (1992) showed that the theory of the transition depends on two constants A, B such that if $|\xi| \ll a\phi$,

$$u\hat{\Pi} \sim A^2\eta, \qquad \text{for all such } \xi, \tag{3.4}$$

$$u \sim B|\xi|^{1/2} \qquad \text{if } \xi < 0, \quad |\xi| \gg d = A^2/B^2, \tag{3.5}$$

$$\hat{\Pi} \sim 2B\eta\xi^{1/2} \qquad \text{if } \xi > 0, \quad |\xi| \gg d = A^2/B^2, \tag{3.6}$$

where d is the transition length scale. Stagnant caps require $d \ll a\phi$, $d \ll a\theta_T$.

We have $A^2 = U^2\Pi_U j(x_T)/S$, $B = \pi^{-1}Ua^{-1/2}(8S)^{1/2}S_2 = O(Ua^{-1/2}\phi^{1/2})$. Section 4.2 of Harper (1992) erroneously gave $B = O(Ua^{-1/2}\phi)$, had $\sin\theta$ in a denominator in (26) that should have been in a numerator, and gave $\partial\Pi/\partial r = O(P^{-1/2}\Pi_\infty a^{-1})$, in which $P^{-1/2}$ should have been $P^{1/2}$. His equations (28) to (31) need corrections, but the physical conclusion that surface diffusion is usually negligible still stands. The corrected analogues of (30) and (31) are

$$Pe^{-1/16}(D_s/D)^{2/3}\Pi_U^{-3/8} \ll a/h \ll Pe^{11/16}\Pi_U^{1/8}, \tag{3.7}$$

in which the left-hand conditions ensure that surface diffusion is negligible, and the right-hand ones are necessary for rigid caps to exist. If the conditions are satisfied, and $|\xi/a\phi| \ll 1$ but $|\xi/d|$ is unrestricted, then the generalizations of (3.5) and (3.6) are

$$u \sim 2^{-1/2}A\left\{(1 + \xi^2/d^2)^{1/2} - \xi/d\right\}^{1/2}, \tag{3.8}$$

$$\hat{\Pi} \sim 2^{1/2}A\eta\left\{(1 + \xi^2/d^2)^{1/2} + \xi/d\right\}^{1/2}. \tag{3.9}$$

3.3. *Rigid cap*

On the rigid cap, if $Z = \cos^{-1}(S_2/\sin\frac{1}{2}\theta)$, from Sadhal & Johnson (1983) we obtain

$$F(\theta) = (\sin\theta)(3Z + 2\cot Z + \sin Z\cos Z)/\pi, \tag{3.10}$$

$$\Pi = \Pi_T + (1 - C)(3Z\tan^2 Z + 3\tan Z + Z)/(\pi\Pi_U). \tag{3.11}$$

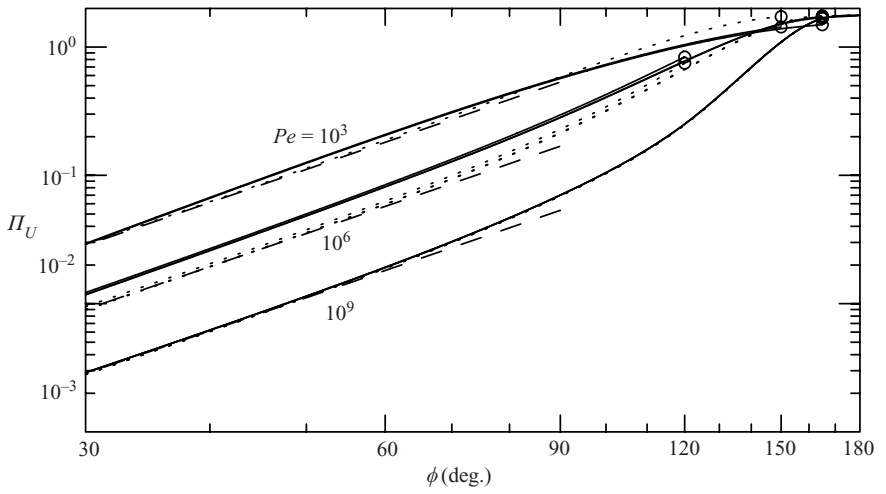

FIGURE 1. Π_U as a function of ϕ for $Pe = 10^3$, 10^6, 10^9. Solid curves: $U/V = 1000$, dotted curves: $U/V = 0$, dashed lines: $\Pi_U \sim 0.506\phi^{8/3}Pe^{-1/6}$ (ϕ in radians). At the ends of curves, ○ symbols show where the approximations fail. Curves have these values of $(a/h, U/V)$ in order of decreasing Π_U at their left-hand ends:
$Pe = 10^3$: $(1, 10^3)(0.1, 10^3)$ $(0.1, 0)$,
$Pe = 10^6$: $(10, 10^3)(1, 10^3)(0.1, 10^3)(10, 0)(1, 0)(0.1, 0)$,
$Pe = 10^9$: $(10, 10^3)(1, 10^3)(0.1, 10^3)(10, 0)(1, 0)(0.1, 0)$.

X had to be found numerically, though if $\theta - \theta_T \ll \theta_T$, i.e. $X \to 0+$,

$$X \sim 2^{9/2}3^{-1}\pi^{-1/2}S_2^{9/4}C_2^{7/4}(\theta - \theta_T)^{3/4}, \tag{3.12}$$

$$F_S \sim 2^3 3^{-1/3}\pi^{-2/3}S_2^2 C_2^{4/3}X^{-1/3}. \tag{3.13}$$

Because there is a singularity at transition but none at the rear stagnation point in (2.37), the grid points θ_i were chosen to make $\theta_n = \pi$ and $\theta_i - \theta_T \propto i^2$, $i = 0, \ldots, n$, but the method was otherwise the same as for the free cap.

4. Numerical results for creeping flow

We now solve (2.15) and (2.37) for c on each cap. Specifying a/h, U/V and Pe fixes β_1, β_2 and β_3; the value of Π_U, which is a dimensionless surface pressure far from the bubble, is then found by imposing the condition that in steady flow the total surfactant flux to the surface is zero. Figure 1 shows the results for Π_U for some representative values of a/h, U/V, Pe and the stagnant cap angle ϕ. Calculations were done with $n = 512$, 1024 and 2048 (and a few with 4096) to check the discretization.

The most striking feature of the results is the sensitivity of Π_U to Pe and especially to ϕ, and the comparative insensitivity to a/h and U/V, apart from their effect on whether the stagnant-cap flow model is valid. Assuming that $Re = DPe/\nu \ll 1$, and $\hat{\Pi}$ is small enough for the surfactant solution to be nearly ideal, the model is valid if Pe is large enough, and ϕ and a/h small enough. If the model predicts $d/a > 0.1 \min(\theta_T, \phi)$, $\Gamma_T > 0.1\Gamma_b$, or $u_T > 0.1U$, that failure of the approximations is marked on figure 1.

The condition on Reynolds number requires that the Schmidt number $Sc = \nu/D \gg 1$; it is of order 10^3 to 10^4 in dilute aqueous solutions and even higher in more viscous liquids. The assumption of an ideal solution may fail in dilute surfactant solutions with bubbles small enough to be nearly spherical, but only if the liquid is highly

viscous. If g is the acceleration due to gravity, then $\eta U/\rho g a^2$ is between $\frac{1}{3}\pi$ and $\frac{2}{9}\pi$. For liquid density $\rho = 1\,\mathrm{Mg\,m^{-3}}$, radius $a = 1\,\mathrm{mm}$ and large stagnant caps, then $\hat{\Pi}_\infty = 18\,\mathrm{mN\,m^{-1}}$. However bubbles as large as 1 mm radius can only occur at $Re < 1$ if $\nu > 10^{-4}\,\mathrm{m^2\,s^{-1}}$, about 100 times the viscosity of water, and smaller bubbles imply smaller $\hat{\Pi}_\infty$, as it is proportional to a^2.

Previous theoretical results consistent with figure 1 are $\Pi_U = 1.768$ if $\theta_T = U/V = 0$ (Dukhin & Buikov 1965; Harper 1972), and

$$\Pi_U \sim 0.506\phi^{8/3} Pe^{-1/6} \tag{4.1}$$

if $U/V = 0$, $\phi \to 0$, $Pe \to \infty$ (Harper 1973; Lerner & Harper 1991; Dukhin *et al.* 1995). Experimental work at low Reynolds numbers (Haberman & Morton 1953; Maxworthy *et al.* 1996) has concentrated on reporting the drag on the bubble. Sadhal & Johnson (1983) found it analytically in terms of ϕ:

$$F_{RH} = \frac{ReC_D}{16} = \frac{gd^2}{12\nu U} = 1 + \frac{2\phi + \sin\phi - \sin 2\phi - \frac{1}{3}\sin 3\phi}{4\pi}, \tag{4.2}$$

where F_{RH} is the drag force divided by the Rybczyński–Hadamard drag $4\pi\eta U a$ for $\phi = 0$, and C_D is the conventional drag coefficient. In each liquid the experiments showed a very gradual change from rigid to free behaviour, with F_{RH} decreasing from 1.5 to 1 as Re (hence also Pe) increased by a factor of about 100. Because

$$\Pi_U = (\hat{\Pi}_\infty/\eta)(12F_{RH}/g\nu)^{1/3} Re^{-2/3}, \tag{4.3}$$

the change from rigid to free requires a change of Π_U by a factor of about $1.5^{1/3}100^{2/3}$, or 25. That is also consistent with figure 1, in which Π_U is near 1.5 when $\Pi_U \geqslant 1$ ($\phi > 150°$) and near 1.0 when $\Pi_U \leqslant 0.04$ ($\phi < 35°$). Figure 1 also shows that the small-ϕ approximation (4.1) is quite good up to about $\phi = 90°$.

One might imagine that because surfactant diffuses onto the free cap through a boundary layer of thickness $O(aPe^{-1/2})$ and off the rigid cap through a boundary layer of thickness $O(aPe^{-1/3})$, the free-cap size must be $O(Pe^{-1/6})$. That is not so, because the diffusion is also onto the forward part of the rigid cap.

5. Conclusions

Diffusion boundary-layer theory and the stagnant-cap approximation allow the fluid mechanics and the convective diffusion around a rising bubble to be solved as separate problems. For $Re \ll 1$ only the latter is new, and one obtain reasonable results with a theory much simpler than ordinary computational fluid dynamics.

For rigid caps smaller than 90°, the known result for small rigid caps (4.1) remains a rough but useful approximation up to 90°.

In the mathematics one takes a/h, U/V, θ_T, Pe as given and deduces Π_U, finding that the first two of those dimensionless parameters affect the validity of the approximations more than the numerical results, while Π_U is much more sensitive to θ_T and Pe. In physical fact, of course, a given bubble in a given liquid would have particular values of $\hat{\Pi}_\infty$, a, h, V and D, and the bubble's transition angle θ_T would have to be solved for as an inverse problem.

Bubbles are likely to rise as in this theory if they neither grow nor shrink, if they are not too large (otherwise the shape may be non-spherical or the surfactant solution not nearly ideal), and if the surface activity is high and the Péclet number large.

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