# Surface activity and bubble motion

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**Abstract.** This paper reviews recent progress in the theories of the surface boundary conditions of adsorbed solutes in liquids, and of the effects of those solutes on the steady motion of a bubble or drop in the liquid. Both singular perturbation theory and numerical solutions have useful roles in this problem, and their relationship is explored. In addition, analytical solutions are given to two problems concerning a spherical bubble rising steadily at low Reynolds number in a viscous fluid. One of these is displacement of the internal vortex centre from its position in the absence of surface activity when there is a small stagnant cap of surfactant at the rear. The results agree with experimental data in the direction of that displacement but give only about half its amount. The other problem is the velocity perturbation all round the surface caused by a very dilute solution of a weak surfactant at high Péclet number. This compares quite well with the numerical solution for a Péclet number of 60, having relative errors of order $(60)^{-1/2}$ as would be expected.

## Introduction

In recent years two reviews [4, 11] have appeared which describe the motion under gravity of a drop or bubble and the subtle effects on it of surface activity. These reviews make it unnecessary to start again from scratch, and so this paper concentrates on recent work not described in them. It also gives for the first time some theoretical contributions related to that work. One of these new contributions is a pair of integrals giving the first-order displacement of the internal vortex centre in slow (Stokes) flow of a drop moving under gravity in a surfactant solution. The other is the perturbation velocity field near the rear stagnation point of a bubble rising in a very dilute solution of a weak surfactant (in the sense of [13]) at high Péclet number.

This paper begins by reviewing a topic which comes logically before the theory of bubble or drop motion: the surface boundary conditions. It then collects the various theorems for Stokes flow which give properties of the motion of a spherical bubble or drop in terms of integral transforms of the surface pressure distribution, including the new formulae of this kind for the internal vortex position. The next section concerns rear stagnation regions and the difficulties they cause for both numerical and analytical theory. Singular perturbation theory is an essential tool for the latter, but its proper relation to the former still seems to need comment over twenty-five years after its use in fluid mechanics was first elucidated [18].

## Surface boundary conditions

It has long been known what the boundary conditions are at a fluid interface: normal stress-difference between the two sides equal to the surface tension



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times the sum of the principal curvatures; tangential stress-difference equal to the surface gradient of interfacial tension; and conservation of mass of any surfactants, so that the convective and diffusive fluxes of each adsorbed component along the interface, taken together, must balance the convective and diffusive fluxes towards the interface from the bulk fluids on each side of it. (In problems where the interface changes its shape, this condition requires some care in its mathematical formulation. It is given, for example, in a recent paper [23] on wave propagation on a contaminated surface.)

Most previous proofs of the surface boundary conditions have used phenomenological assumptions about the stress distribution nearby. These can be avoided [2] by considering the intermolecular forces in a system where all properties such as pressure, number densities and chemical potentials are assumed continuous functions of position on a (microscopic) length scale $l$, but in one special direction ($y$, say) these properties change so rapidly that when viewed on a coarser (macroscopic) length scale $L \gg l$ they no longer appear to be continuous. Brenner [2] then goes on to point out that the concept of an interface at $y = 0$ is macroscopic, that the interface is in fact diffuse on the microscale, and, the new feature of his work, that singular perturbation theory of kind long used to cope with boundary layers [16, 18] is the natural way to bring surface tension and surface excesses out of the mathematical analysis. The paper does make the common assumption of local chemical equilibrium (at least on the length scale $l$); it is often a good assumption, but there are cases where it is not, e.g. bipolar solute molecules, which often have adsorption barriers [21].

## Integral theorems for stokes flow of spherical bubbles or drops

Suppose that a spherical drop or bubble of radius $a$ moves steadily at speed $U$ because of some external force (usually gravity) in an unbounded fluid. Suppose also that the Reynolds number is much less than one both inside (where the density is $\rho_1$ and the dynamic viscosity is $\eta_1$) and outside (where they are $\rho_0$, $\eta_0$), and that, owing to surface activity, the surface pressure $\Pi(\mu) = \sigma_p - \sigma(\mu)$ varies around the surface. In this equation $\sigma_p$ and $\sigma$ are the surface tensions of pure and contaminated fluid, and $\mu = \cos\theta$, where $\theta$ is the angular distance from the front stagnation point.

Then the first integral theorem [11] gives the drag coefficient $C_D$, defined as usual by $C_D = (\text{drag force})/\frac{1}{2}\rho_0 U^2 \pi a^2$, as

$$C_D = \frac{8}{R(\eta_0 + \eta_1)}\left(2\eta_0 + 3\eta_1 - \frac{1}{U}\int_{-1}^{1} \mu\Pi(\mu)\,\mathrm{d}\mu\right), \tag{1}$$

where $R$ is the external Reynolds number equal to $2Ua\rho_0/\eta_0$. The second theorem, first given [13] only for $\eta_1 = 0$, gives the dimensionless rate of strain $A$ at the near stagnation point as

$$A = \frac{1}{2(\eta_0 + \eta_1)} \eta_0 + \frac{1}{4\sqrt{2}U} \int_{-1}^{1} \frac{(1-\mu)}{(1+\mu)^{1/2}} \frac{\mathrm{d}\Pi(\mu)}{\mathrm{d}\mu} \mathrm{d}\mu \quad , \quad (2)$$

where $A$ is the coefficient in the asymptotic expression $u_\theta \sim UA \sin\theta$ for the tangential velocity component $u_\theta$ near the rear stagnation point. This theorem is a special case of the following [19], which unfortunately seems to have no simple expression in closed form:

$$\frac{u_\theta}{U \sin\theta} = \frac{\eta_0}{2(\eta_0 + \eta_1)} \left(1 + \sum_{n=1}^{\infty} c_n P'_n(\mu)\right), \quad (3)$$

where

$$c_n = \frac{1}{\eta_0 U} \int_{-1}^{1} \Pi(\mu) P_n(\mu)\, \mathrm{d}\mu, \quad (4)$$

and $P'_n(\mu)$ denotes the derivative of the Legendre polynomial $P_n(\mu)$. All these theorems are proved by expanding the surface pressure in a series of Legendre polynomials in $\mu$, expanding the stream functions inside and out in a series of integrals of Legendre polynomials in $\mu$ multiplied by appropriate powers of $r$, the distance from the centre, and using the boundary conditions and the orthogonality properties of Legendre polynomials.

One can similarly calculate the velocity components $(v_r, v_\theta)$ at the point $P: r = a/\sqrt{2}$, $\theta = \frac{1}{2}\pi$, which is the centre of Hill's spherical vortex [14], the internal flow when $\Pi$ = constant all round the drop or when the Péclet numbers inside and out are much less than one [11], but not in general otherwise. If the internal vortex centre moves a distance $\Delta R$ outwards and $\Delta Z$ forwards from $P$, and if $\Delta R$ and $\Delta Z$ are both much less than $a$, the results are

$$v_r = \frac{1}{\eta_0 + \eta_1} \int_{-1}^{1} \Pi(\mu) V_r(\mu)\, \mathrm{d}\mu \approx -\frac{\sqrt{2} U \eta_0\, a\, \Delta Z}{4(\eta_0 + \eta_1)}, \quad (5)$$

$$v_\theta = \frac{1}{\eta_0 + \eta_1} \int_{-1}^{1} \Pi(\mu) V_\theta(\mu)\, \mathrm{d}\mu \approx -\frac{\sqrt{2} U \eta_0\, a\, \Delta R}{4(\eta_0 + \eta_1)}; \quad (6)$$

in these equations the functions $V_r$ and $V_\theta$ are given by the following series of Legendre polynomials wich converge fast enough for all relevant $\mu$ to be easily computed:

$$V_r(\mu) = \frac{1}{4\sqrt{2}} \sum_{n=2}^{\infty} \frac{n(n+1) P_n(0) P_n(\mu)}{2^{n/2}}, \quad (7)$$

$$V_\theta(\mu) = -\frac{1}{8} \sum_{n=2}^{\infty} \frac{n(n+1) P_n(0) P_{n+1}(\mu)}{2^{n/2}}. \quad (8)$$

In many practical cases, $\Pi$ is very small except close to the rear stagnation point $\mu = -1$. Then the integrals in (1) to (6) are insensitive to the values of their integrands except in that neighbourhood. To evaluate (7) and (8) at $\mu = -1$, we use the function $f(x)$ defined for $|x| < \sqrt{2}$ by the series

$$f(x) = \sum_{n=2}^{\infty} n(n+1)P_n(0)\,(x/\sqrt{2})^n$$
$$= -3x/\{2(1+\tfrac{1}{2}x^2)^{5/2}\},$$

and so

$$V_r(-1) = \sqrt{2}\,V_\theta(-1) = f(1)/4\sqrt{2} = -1/6\sqrt{3} \tag{9}$$

Equations (1), (5), (6) and (9) then give, for this case,

$$\Delta Z \approx 4\sqrt{2}\,\Delta R \approx \frac{\sqrt{2}(2\eta_0 + 3\eta_1)\,a\,\Delta C_D}{3\sqrt{3}\,\eta_0\,C_D}, \tag{10}$$

where $\Delta C_D$ is the increase in the drag coefficient above its value for uncontaminated fluids. The vortex core thus begins to move, as surface contamination builds up from zero, outwards and forwards, in a direction making an angle initially equal to $\tan^{-1}(4\sqrt{2}) \approx 80°$ with the drop's equatorial plane.

## Stagnant caps

Savic [24] first showed that bubbles and drops in surfactant solutions often sweep their surface contamination around to the rear, where it collects in an immobile spherical cap, while the rest of the surface is free to move. Many subsequent authors have studied this 'stagnant-cap' regime [4], experimentally, computationally and analytically in the limit of very small caps. This last calculation can now be simplified slightly and extended to drops as well as bubbles by the use of (1) and (2). One follows the previous work [12] as far as

$$\Pi = \Pi^*(1 - \varphi^2/\varphi^{*2}) \quad \text{for} \quad 0 \leqslant \varphi \leqslant \varphi^* \leqslant \pi, \tag{11}$$

where $\varphi = \pi - \theta$, $\varphi^*$ is the cap angle, and $\Pi^*$ is the surface pressure at the rear stagnation point. Then a stagnant cap obviously requires $A = 0$ in (2), to which a first approximation is

$$\Pi^* = 4\eta_0\,U\varphi^*/\pi, \tag{12}$$

and then (1) yields

$$C_D = \frac{8}{R(\eta_0 + \eta_1)}\,(2\eta_0 + 3\eta_1 + 4\eta_0\varphi^{*3}/3\pi). \tag{13}$$

Because (11) must hold for either a drop or a bubble with a small stagnant cap, so must (12) and (13), unlike their analogues in [12].

To test the theory in (10) and (13) the most accurate experiments appear to be those of Horton reported by Huang and Kintner [15], in which $\Delta Z$ and $\Delta R$ were reported for various values of $\varphi^*$. The results, in Figure 1, show that the simple asymptotic theory gives a good initial direction of vortex-centre displacement but underestimates its magnitude as a function of $\varphi^*$. Presumably the asymptotic solution for small $\varphi^*$ ceases to hold before $\varphi^* = 42.5^\circ$, the smallest cap angle in the experiments [15].

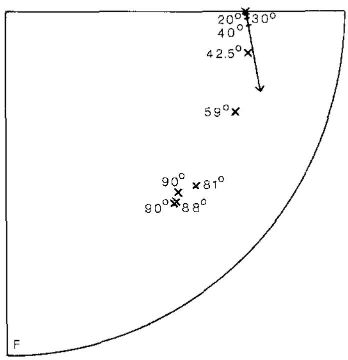


Figure 1. One quadrant of a falling drop, showing the position of the internal vortex core for various stagnant cap angles. Experimental data shown by crosses [15], theoretical points on the arrow making the initial direction (10). $F$ = front stagnation point.

Bubbles and drops with stagnant caps appear to present several as yet unexploited possibilities for both experimenters and theoreticians. They give a problem where non-ideal surfactant solutions can be readily incorporated in the theory, because the fluid mechanics gives $\Pi$ as a function of $\theta$ (or $\varphi$) for any given cap angle $\varphi^*$, the adsorption isotherm then determines the concentration in the immediately adjacent bulk solutions, and one could proceed to use the theory of convective diffusion in the way already known for ideal solutions [12]. Another problem waiting to be attacked (for any flow regime, including stagnant caps) is a surfactant soluble in the dispersed phase rather than the continuous phase, though there has been some work on the nature of convective diffusion inside a drop [3, 17].

## Bubbles in nearly pure liquids with high Péclet numbers

Suppose that a spherical bubble rises at low Reynolds but high Péclet number, and the surfactant is so dilute that the motion is only slightly affected by it, even near the rear stagnation point. Then the theoretician faces in the first instance a Stokes flow problem, with a thin diffusion boundary layer around the surface [7, 8, 9]. An analytical solution is feasible only for very low or very high surface activity, in the sense that $k$, the ratio of the amount of adsorbed surfactant to the amount in solution in the diffusion layer, has to be either much less or much greater than one [13]. Saville [25] has extended the calculation by computer to intermediate values of $k$, but one problem remained. The method fails in the rear stagnation region where $\varphi$ is small, both because the assumptions underlying the approximation of a thin boundary layer fail and because the calculated concentration tends to infinity as $\varphi \to 0$, like $ln\, \varphi$ or $1/\varphi^2$ for $k \ll 1$ and $k \gg 1$ respectively. Saville found behaviour as $ln\, \varphi$ for all finite values of $k$ he investigated: reconciling this with the asymptotic results in an unsolved problem in singular perturbation theory.

Overcoming the infinite values is another singular perturbation problem, whose results for the surfactant distribution have been given [13] in the limiting cases $k \ll 1$ and $k \gg 1$. The boundary-layer solution is treated as an outer approximation and matched asymptotically to a solution of the full diffusion equation valid in the rear stagnation region, where diffusion along streamlines is as important as across them but curvature of the bubble surface can be ignored.

In a new attack on the problem [19], the boundary layer and its singularities have been circumvented by the use of a finite-difference computation. That required particular numerical values to be chosen (a disadvantage of computer solutions when, as here, there are several independent dimensionless parameters): radius $a = 1.095 \times 10^{-5}$ m, viscosity $\eta_0 = 1.140 \times 10^{-3}$ Pa s, diffusivity $D = 1.25 \times 10^{-10}$ m$^2$ s$^{-1}$, speed $U = 3.43 \times 10^{-4}$ m s$^{-1}$. Reynolds number $6.6 \times 10^{-3}$, Péclet number $\mathrm{P} = 2Ua/D = 60$, and surface activity parameter $k = \Gamma \mathrm{P}^{1/2}/2ac = 0.155$, where $\Gamma$ is the surface excess in equilibrium with a solution of bulk concentration $c$. In an ideal solution, of course, $\Pi = R_g T \Gamma$ where $R_g$ is the gas constant and $T$ the absolute temperature. The analysis provides a useful test for the applicability of the singular perturbation method, which assumes $\mathrm{P}^{1/2} \gg 1$, $k \ll 1$: two conditions which are barely met in the calculated example.

The results for surfactant concentration are shown in Figure 2. The boundary-layer theory gives a value about 10% lower than the computation near the front stagnation point, rises to be very close to it from about $\theta = 90^\circ$ to $\theta = 150^\circ$, and then tends to infinity as $\theta \to 180^\circ$. The first-order rear stagnation correction removes the singularity and gives an answer only 4% too low at the rear stagnation point. The results are as good as one could expect with the 'small' parameters $\mathrm{P}^{-1/2}$ and $k$ as large as they are here.

Results were also given [19] for the perturbation of surface velocity from that in pure liquid, using equation (3) above and the numerical solution for $\Gamma$. That equation can also be used to find the surface velocity from the boundary-layer, theory, except in the rear stagnation region where the number of terms needed increases without bound. It turns out that the

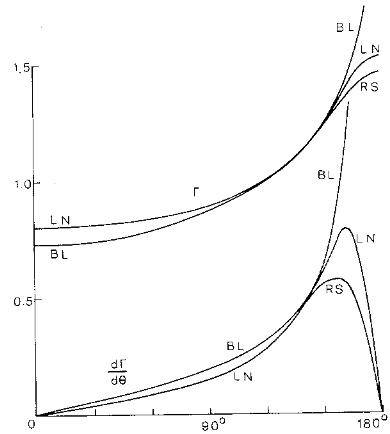


Figure 2. The distribution of adsorbed surfactant on Le Van and Newman's bubble, with $\theta$ in degrees from the forward stagnation point, $\Gamma$ and $\mathrm{d}\Gamma/\mathrm{d}\theta$ in units of the equilibrium surface excess with no bubble motion. LN indicates LeVan and Newman's solution [19], BL the boundary-layer outer approximation and RS the inner approximation in the rear stagnation region.

velocity perturbation in that region depedns mainly on the surfactant distribution there, that distribution is badly approximated by the boundary-layer solution, but that an analytical inner approximation can be given for the velocity as for $\Gamma$ (or $\Pi$).

That inner approximation is given here (for the first time). Define [13] dimensionless cylindrical polar coordinates $(m, s)$ by

$$(m,s) = (r\sin\theta/\delta, (-r\cos\theta + a)/\delta), \tag{14}$$

which are O(1) in the rear stagnation region. In this equation $\delta = 2\mathrm{P}^{-1/2}a$. The bubble's vertical axis is $m = 0$, and $s$ increases down the wake from (essentially) zero at the surface. The perturbation stream function $\psi(m,s)$ is then zero on $m = 0$ and $s = 0$, and the surface shear stress condition [4] becomes

$$\frac{\partial^2\psi}{\partial s^2} = \frac{16a^2k\Pi_\infty}{\sqrt{\pi}\eta_0\mathrm{P}}(\mathrm{e}^{-m^2/2} - 1) = B(\mathrm{e}^{-m^2/2} - 1), \text{say}, \tag{15}$$

on $s = 0$, where $\Pi_\infty$ is the surface pressure of undisturbed liquid. Put [23] $\psi = m^2 s\psi_3$, where $\psi_3$ must obey

$$\frac{\partial^2\psi_3}{\partial m^2} + \frac{3}{m}\frac{\partial\psi}{\partial m} + \frac{\partial^2\psi}{\partial s^2} = 0, \tag{16}$$

and then we deduce that

$$\psi = \int_0^\infty ms\, f(\alpha)\,\mathrm{e}^{-\alpha s} J_1(\alpha m)\,\mathrm{d}\alpha \tag{17}$$

for some function $f$, where $J_1$ denotes the usual Bessel function. Equation (15) gives

$$B(e^{-m^2/2} - 1) = \int_0^\infty -2\alpha m f(\alpha) J_1(\alpha m)\, d\alpha,$$

from which [10, p. 717] we find $f(\alpha) = B\, e^{-\alpha^2/2}/2\alpha$. The integrals can now be manipulated [10] to give the perturbation $u_m$ to the surface velocity component for $m = 0(1)$ as

$$u_m = \frac{1}{\delta^2 m} \frac{\partial \psi}{\partial s}\bigg|_{s=0} = -\frac{k\Pi_\infty P^{1/2}}{2\sqrt{2\eta_0}} \sin\theta \cdot e^{-m^2/4} \times \{I_0(\tfrac{1}{4}m^2) + I_1(\tfrac{1}{4}m^2)\}, \qquad (18)$$

where $I_0$ and $I_1$ denote, as usual, Bessel functions of imaginary argument.

The results of this inner approximation for the rear stagnation region are presented in Figure 3, together with the boundary-layer outer approximation and the numerical solution, all three for the same hypothetical bubble mentioned earlier. In this figure, $-\beta(\theta)c_\infty$ is the velocity perturbation due to the surface activity divided by the unperturbed surface velocity, where $c_\infty$ is the surfactant concentration at a great distance from the bubble, i.e.,

$$u_\theta = \tfrac{1}{2} U \sin\theta\, (1 - \beta(\theta)c_\infty). \qquad (19)$$

We see that, as was already known [26] the boundary-layer approximation gives a fairly good result over most of the surface by comparison with the numerical solution, with much less effort, though it is not as good for velocity perturbations as it was for the surfactant distribution. Also, as was already known [13, 20], that approximation fails and becomes singular near

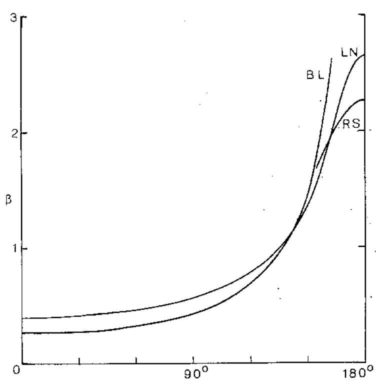


Figure 3. The distribution of surface velocity perturbation on LeVan and Newman's bubble, with $\beta$ as in (19), in units of $10^3$ m$^3$/mol. Other data as for Figure 2.

the rear stagnation point. What is new in the present work is the appropriate inner approximation, which removes the singularity and reduces the error to about 15% even at the rear stagnation point. As in the theory of the surfactant distribution, the error would become smaller at higher Péclet numbers. This is just the range where numerical solutions are hardest to do, because many terms of the series (3) are needed to convergence and the integrands in (4) for large $n$ are rapidly oscillating.

This theory, which ignores the consequence for convective diffusion of the slowed-down velocity field, even near the rear stagnation point where those consequences are greatest, has little physical importance. Its main practical use seems to be in testing methods of numerical calculation [25]. Like many other singular-perturbation theories, it gives answers for extreme values of the physical parameters at which the solution becomes singular in some way. Numerical solutions, on the other hand, are often better suited to filling in the intermediate values, and a good test for their accuracy is their ability to reproduce the singular-perturbation answers in the appropriate limits. One sometimes has to be depressingly close to those limits, though. The singular perturbation expansion for the drag coefficient of a spherical drop, bubble or solid particle at low $R$ is now known to order $R^4 \ln R$ [1], but it gives better information about the drag than Oseen's order $R$ term only at Reynolds numbers so small that the higher-order corrections are unimportant in practice. This is a penalty that has to be paid for using asymptotic, instead of convergent, series.

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