THE REAR STAGNATION REGION OF A BUBBLE RISING STEADILY IN A DILUTE SURFACTANT SOLUTION

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SUMMARY

Suppose that a gas bubble rises steadily in a very dilute surface-active solution, with very small Weber number, very large Péclet number, and either very small or very large Reynolds number. Define k, the dimensionless surface activity, as the ratio of the amount of contaminant absorbed on the surface to the amount dissolved in the diffusion boundary layer (in a sense which can be made precise). The diffusion boundary-layer equation was solved by the author in 1974 as a singular perturbation problem for k either very small or very large compared with unity.

Numerical work by Saville confirmed the form of the singularity at the rear stagnation point in the limit $k \to 0$, but not for $k \to \infty$. The problem is now re-examined for all positive k both analytically and numerically. The author's large-k result turns out to be valid for all positive k bounded away from zero.

Mathematically, the problem can be reduced to a weakly singular Volterra integral equation with its singularity at the rear stagnation point. After a coordinate transformation sends the singularity to infinity, a Laplace transformation of the equation can usefully be taken. This gives the asymptotic form which is needed, but is too complicated to give the full solution. Numerical integration of the original equation can be proved to converge; it confirms the form of the singularity, and finds the solution.

1. Introduction

CONSIDER a gas bubble of volume $\frac{4}{3}\pi a^3$ rising steadily at speed U in an unbounded liquid whose density ρ and dynamic viscosity $\eta = \rho\nu$ are both much greater than that of the gas. If the Weber number $W = 2\rho U^2 a/\sigma \ll 1$, where σ is the surface tension, then the bubble is known to be very nearly a sphere of radius a, whether the Reynolds number $\mathrm{R} = 2Ua/\nu$ is much less than one (**1, 2**) or much greater (**3, 4**). Using spherical polar coordinates (r, θ) centred at the centre of mass of the bubble, with $\theta = 0$ pointing upstream, it is also known that in the absence of impurities the surface velocity $u_\theta = v_0 \sin\theta$, where $v_0 = \frac{1}{2}U$ if $\mathrm{R} \ll 1$ (**5, 6**) and $v_0 = \frac{3}{2}U$ if $\mathrm{R} \gg 1$ (**3**).

Surface-active solutes in the liquid, or surfactants, slow down the motion (**7, 8, 9**) for the following reason: they move with the flow at the surface and so accumulate at the rear, thereby reducing the surface tension. This causes a tangential shear stress opposing the motion, especially near the rear stagnation point. If the surfactant is concentrated enough and the Péclet number high enough, u_θ may be reduced practically to zero over all (**7**) or part (**9, 10, 11, 12**) of the surface. This paper, however, is concerned with a very dilute surfactant, for which u_θ is close to $v_0 \sin\theta$ everywhere on the surface. The surfactant will also be assumed to be an ideal solution (**13**), for which the surface pressure $\Pi = \sigma_p - \sigma$ obeys

$$\Pi = R_g T\Gamma = R_g Thc, \tag{1.1}$$

where σ_p is the surface tension of pure solvent, σ that of the actual liquid, which varies from point to point, R_g is the gas constant, T is the temperature, Γ is the surface excess of absorbed surfactant (moles per unit volume), c is the concentration of surfactant in the solution, and h is a constant with the dimensions of length, the adsorption depth (**8, 14**). Physically, a depth h of solution contains the same amount of dissolved surfactant as is adsorbed on its surface.

We work in terms of Π, using equations (1.1) to define it everywhere in the liquid in terms of the local value of c. If $\Pi \to \Pi_\infty =$ constant at a large distance, the bulk diffusion coefficient of the surfactant in the liquid is D, and the Péclet number $P_v = v_0 a/D \gg 1$, then the equations for convective diffusion of surfactant can be written (**14**) in the form

$$4\frac{\partial \Pi}{\partial x} = \frac{\partial^2 \Pi}{\partial y^2} \tag{1.2}$$

in $0 < x < 1$, $0 < y < \infty$, with boundary conditions $\Pi \to \Pi_\infty$ as $y \to \infty$ and as $x \to 0$, and

$$\frac{\partial \Pi}{\partial y} = 3^{\frac{1}{2}} k \frac{\partial}{\partial x}\{(1-\mu^2)\Pi\} \tag{1.3}$$

on $y = 0$, where $k = hP_v^{\frac{1}{2}}/a$, $\mu = \cos\theta$, and the coordinates (x, y) are given by

$$x = \tfrac{1}{4}(2 - 3\mu + \mu^3) = \tfrac{1}{4}(1-\mu)^2(2+\mu), \tag{1.4}$$

$$y = (3P_v)^{\frac{1}{2}}(r-a)(1-\mu^2)/4a. \tag{1.5}$$

Thus x is the fraction of the volume of the sphere above the level μa shown shaded in Fig. 1, and the functions $x(\mu)$ and $\mu(x)$ defined by (1.4) are both one-to-one for $0 \leqslant x \leqslant 1$, $1 \geqslant \mu \geqslant -1$. A property of equation (1.4) useful in what follows is that

$$x(1-x) = (1-\mu^2)^2(4-\mu^2)/16, \tag{1.6}$$

which gives

$$2x^{\frac{1}{2}}(1-x)^{\frac{1}{2}} \leqslant 1 - \mu^2 \leqslant (4/3^{\frac{1}{2}})x^{\frac{1}{2}}(1-x)^{\frac{1}{2}}, \tag{1.7}$$

with the lower bound being attained at $\mu = 0$ and the upper bound at $\mu = \pm 1$. The other variable y required to obtain the canonical diffusion equation (1.2) is proportional to the stream function near the surface.

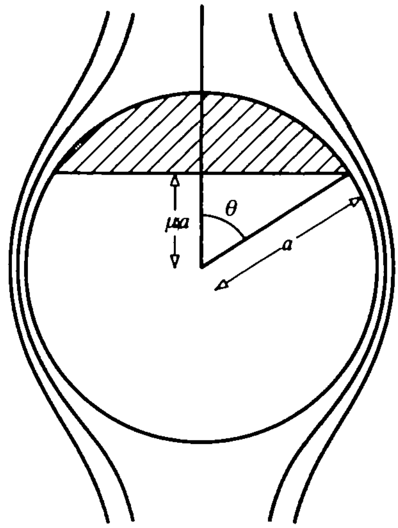

FIG. 1. Geometrical interpretation of coordinates: θ is the angle from the top (front) stagnation point, $\mu = \cos\theta$, x is the fraction of the volume of the sphere which is shaded, y is constant on streamlines, two of which are indicated on each side of the bubble

In deriving equations (1.2) and (1.3) surface diffusion was ignored; that is known (**14**) to be a good approximation except very near the rear stagnation point, where $1 - x = O(P_v^{-2})$. The inner expansion near that point has already been described (**14**); this paper concentrates on how the outer expansion matches to it as $x \to 1$. This problem has already been considered in some detail (**14**, **15**), but one difficulty remains. As $x \to 1$ the outer expansion for Π certainly tends to infinity, but Harper (**14**) found an algebraic singularity for $k \gg 1$ and a logarithmic one for $k \ll 1$, while Saville (**15**) suggested that it was logarithmic for all k.

Our tool for resolving this question is an integral equation, which will now be derived.

2. The integral equation

Let the surface value of $\Pi(x, y)$ be $\Pi_\infty f(x) = \Pi(x, 0)$. The diffusion equation (1.2) with its boundary conditions involving Π_∞ gives

$$\frac{\Pi(x, y)}{\Pi_\infty} = 1 + \{f(0) - 1\}\operatorname{erfc}(yx^{-\frac{1}{2}}) + \int_0^x f'(t)\operatorname{erfc}(y\{x - t\}^{-\frac{1}{2}})\,dt,$$

so that on the surface

$$\frac{1}{\Pi_\infty}\frac{\partial \Pi}{\partial y} = 2(\pi x)^{-\frac{1}{2}}\{1 - f(0)\} - 2\pi^{-\frac{1}{2}}\int_0^x f'(t)(x - t)^{-\frac{1}{2}}\,dt. \qquad (2.1)$$

It is convenient now to follow a standard sequence of manipulations (**16**) for equations with $(x-t)^{-\frac{1}{2}}$-kernels. On substituting (2.1) into equation (1.3) and integrating both sides from 0 to X one obtains

$$4\{1-f(0)\}\pi^{-\frac{1}{2}}X^{\frac{1}{2}}-2\pi^{-\frac{1}{2}}\int_0^X\int_0^x f'(t)(x-t)^{-\frac{1}{2}}\,dt\,dx=\sqrt{3}k\{1-\mu(X)^2\}f(X).$$

Finally, on reversing the order of the integration in the double integral and replacing X by x, one obtains

$$a(x)f(x)=b(x)-\lambda\int_0^x f(t)(x-t)^{-\frac{1}{2}}\,dt, \tag{2.2}$$

where

$$a(x)=(3\pi)^{\frac{1}{2}}\{1-\mu(x)^2\}, \tag{2.3}$$

$$b(x)=2\lambda x^{\frac{1}{2}}, \tag{2.4}$$

$$\lambda=2/k=(4aD/v_0)^{\frac{1}{2}}/h. \tag{2.5}$$

The Volterra equation (2.2) is weakly singular because of the factor $(x-t)^{-\frac{1}{2}}$ on the right-hand side. Its solution is not quite obvious because $a(x)\to 0$ as $x\to 0$ and $x\to 1$ and, as we shall see, $f(x)\to\infty$ as $x\to 1$. The main point of this paper is the elucidation of the singularity in $f(x)$ as $x\to 1$ from below. It is already known (**14**) that it will match an appropriate inner expansion near $x=1$, where $a(x)\sim 4\pi^{\frac{1}{2}}(1-x)^{\frac{1}{2}}$, only if

$$f(x)\sim A(1-x)^c \tag{2.6}$$

for some constant A, where (in the present notation)

$$\lambda=\frac{-4\Gamma(-c)}{\Gamma(-\frac{1}{2}-c)}=\frac{-4(c+\frac{1}{2})\Gamma(1-c)}{c\Gamma(\frac{1}{2}-c)} \tag{2.7}$$

and $-\frac{1}{2}<c<0$, with limiting values $c\to 0$ as $\lambda\to\infty$ and $c\to-\frac{1}{2}$ as $\lambda\to 0$. Thus both sides of (2.2) are finite near $x=1$. (There are of course other roots of equation (2.7) which do not at present concern us.) However, it has not previously been shown that the power law (2.6) emerges also from the outer expansion, that is, from equation (1.2) and hence from (2.2). Physically that needs to be done, because the outer expansion is parabolic: surfactant is carried from it into the inner region, and so the outer expansion imposes the upstream conditions on the inner one, not the inner on the outer.

Until (2.6) is confirmed from the outer expansion alone, its validity is at best tentative. The first step is to use a series in powers of $x^{\frac{1}{2}}$ to establish that $f(x)$ is positive (and monotonic). The second step is a change of variable and a Laplace transformation which, with the information gained in the first step, proves that equations (2.6) and (2.7) do indeed hold. The outer expansion thus leads into the inner one with precisely the asymptotic behaviour required for matching to occur. In physical coordinates, the outer expansion holds in the major part of the diffusion boundary layer:

$$r - a = O(aP_v^{-\frac{1}{2}}), \qquad \pi - \theta > O(P_v^{-\frac{1}{4}}).$$

The inner expansion holds within a distance $O(aP_v^{-\frac{1}{4}})$ of the rear stagnation point (**14**).

3. Series solution

If $x^{\frac{1}{2}} = z$ we may write

$$a(x) = \sum_{n=1}^{\infty} a_n z^n, \tag{3.1}$$

$$b(x) = 2\lambda z, \tag{3.2}$$

and solve equation (2.2) with a series

$$f(x) = \sum_{n=0}^{\infty} f_n z^n. \tag{3.3}$$

The coefficients a_n are easier to find than might at first appear. The usual trigonometrical solution of the cubic equation (1.4) gives

$$\mu = 2 \cos \tfrac{1}{3}(\phi + 4\pi),$$

where $\cos \phi = 2x - 1$, or $\phi = \pi - 2 \sin^{-1} z$. From this, (**17**, equations (15.1.15) and (15.1.17)) lead to

$$\begin{aligned} a(x) = (3\pi)^{\frac{1}{2}}(1-\mu^2) &= (3\pi)^{\frac{1}{2}}\{-1 + \cos(4/3 \sin^{-1} z) + \sqrt{3} \sin(4/3 \sin^{-1} z)\} \\ &= (3\pi)^{\frac{1}{2}}\{-1 + {}_2F_1(\tfrac{2}{3}, -\tfrac{2}{3}; \tfrac{1}{2}; z) + (4/\sqrt{3}) \times \\ &\quad \times {}_2F_1(\tfrac{7}{6}, -\tfrac{1}{6}; \tfrac{3}{2}; z)\}. \end{aligned}$$

The hypergeometric series now give the coefficients a_n in (3.1) and the series is absolutely convergent if $|z| \leq 1$. It transpires that $a_1 = 4\pi^{\frac{1}{2}}$, every a_n except a_1 is negative, and by Abel's theorem

$$a_1 = -a_2 - a_3 - a_4 - \dots . \tag{3.4}$$

Direct substitution from equations (3.1), (3.2), (3.3) into (2.2) produces

$$f_n = \begin{cases} \lambda/(\lambda + 2\pi^{\frac{1}{2}}), & n = 0, \\ -\dfrac{a_2 f_{n-1} + a_3 f_{n-2} + \dots + a_{n+1} f_0}{a_1 + \lambda B(\frac{1}{2}, \frac{1}{2}n + 1)}, & n > 0, \end{cases} \tag{3.5}$$

where B indicates the usual beta function.

Immediate consequences of equation (3.5) are that (a) every f_n is positive, and so $f(x)$ is a monotonically increasing positive function of z, and hence of x; (b) $f(x)/f_0$, which is equal to one when $x = 0$, increases monotonically as λ decreases through positive values for any fixed x in $(0, 1)$. Both conclusions are physically reasonable. The second shows that the concentration of surfactant and the surface pressure increase faster for more highly surface-active solutes (larger k, thus smaller λ). The monotonicity with λ also shows that the singularity of $f(x)$ at $x=1$ is between those appropriate to $\lambda=0$ and to $\lambda=\infty$, that is, between $(1-x)^{-\frac{1}{2}}$ and $(1-x)^0$. As both previous estimates (**14**, **15**) lie between these limits, more delicate analysis is needed to clarify the matter.

4. Laplace transformation

The series just considered do not seem to solve our main problem, but as $a(x)=a(1-x)$ by equation (1.6) they allow us to rewrite equation (2.2) as

$$\sum_{n=0}^{\infty} a_{n+1}e^{-\frac{1}{2}nu}F(u) = 2\lambda\Pi_\infty(1-e^{-u})^{\frac{1}{2}} - \lambda\int_0^u \{1-e^{-(u-w)}\}^{-\frac{1}{2}}F(w)\,dw, \quad (4.1)$$

where $1-x=e^{-u}$, and $F(u)=(1-x)^{\frac{1}{2}}f(x)$, $f(x)=e^{\frac{1}{2}u}F(u)$. The merits of this change of dependent and independent variables are that u goes from 0 to ∞ as x goes from 0 to 1, the integral is still of convolution type, and the series involve only exponential functions times $F(u)$. All three properties simplify the use of the Laplace transform

$$\hat{F}(p) = \int_0^\infty e^{-pu}F(u)\,du.$$

Transforming equation (4.1), one finds that

$$Q(p)\hat{F}(p) = 2\lambda R(p) - \pi^{-\frac{1}{2}}\sum_{n=1}^{\infty} a_{n+1}\hat{F}(p+\tfrac{1}{2}n) = S(p), \quad \text{say}, \quad (4.2)$$

where

$$Q(p) = 4 + \lambda\Gamma(p)/\Gamma(p+\tfrac{1}{2}), \quad (4.3)$$

$$R(p) = \Gamma(p)/\Gamma(p+\tfrac{3}{2}). \quad (4.4)$$

The asymptotic behaviour of $F(u)$ as $u\to\infty$ is determined by the singularities of $\hat{F}(p)$ with the largest real parts. To find them, we note that if $u\geq 0$, then $F(u)>0$ and so $\hat{F}(p)$ is real, positive and monotonic decreasing for all real p greater than its abscissa of convergence p_c. Then equation (3.4) shows that the series on the right-hand side of equation (4.2) is analytic for $\operatorname{Re}(p)>p_c-\frac{1}{2}$. There is no singularity of $\hat{F}(p)$ at any pole of $R(p)$, because $Q(p)$ has the same poles, and they are all simple poles for both functions. All singularities of $\hat{F}(p)$ with real parts greater than $p_c-\frac{1}{2}$ are therefore at zeros of $Q(p)$.

There is one zero of $Q(p)$ in each interval $-n-\frac{1}{2}<p<-n$ if $\lambda>0$, where $n=0, 1, \dots$, because $\Gamma(p)$ and $\Gamma(p+\frac{1}{2})$ have opposite signs in these intervals, and $|\Gamma(p)|\to\infty$ as $p\to -n$, $|\Gamma(p+\frac{1}{2})|\to\infty$ as $p\to -n-\frac{1}{2}$. There are no other zeros, for the following reasons. Stirling's formula shows that $\Gamma(p)/\Gamma(p+\frac{1}{2}) = O(m^{-\frac{1}{2}})$ on the circular arc $|p|=m+\frac{3}{4}$, $|\arg p|\leq \pi-\varepsilon<\pi$

in the complex p-plane, where m is an integer; the reflection formula for the gamma function establishes the same $O(m^{-\frac{1}{2}})$-result on the rest of that circle. For sufficiently large m, then, $|\arg Q(p)| < \frac{1}{2}\pi$ on the circle, and so $Q(p)$ has the same number of poles and zeros inside it (**16**). There are $m+1$ poles at $p = 0, -1, -2, \ldots, -m$, and thus the $m+1$ zeros already found on the negative real axis are all that exist.

Let the zero of $Q(p)$ between $-n$ and $-n-\frac{1}{2}$ be p_n. If $S(p_0) \neq 0$, then $\hat{F}(p)$ has a simple pole at p_0 with some residue A, say, and no other singularity with real part greater than $p_0 - \frac{1}{2}$, by equation (4.2). Hence

$$f(x) = A(1-x)^{-p_0-\frac{1}{2}} + g(x), \tag{4.5}$$

where $\int_0^1 g(x)(1-x)^{q-1}\,dx$ converges for every $q > p_0$. The leading term on the right-hand side of equation (4.5) is thus the first, and it gives exactly the same results as equations (2.6) and (2.7) if $A \neq 0$.

If, on the other hand, $A = 0$, the abscissa of convergence of $\hat{F}(p)$ would be p_1, or some higher p_n, instead of p_0. That would imply that $\int_0^1 f(x)(1-x)^{-\frac{3}{2}}\,dx$ converged, which is impossible because $f(x)$ is monotonically increasing and positive.

It is perhaps worth remarking that this Laplace-transformation method also works on the slightly more general integral equation

$$a(x)f(x) = b(x) - \lambda \int_0^x \frac{f(t)}{(x-t)^\beta}\,dt, \tag{4.6}$$

where $0 < \beta < 1$: the preliminary transformations are

$$1 - x = e^{-u}, \quad f(x) = e^{(1-\beta)u}F(u), \quad a(x) = \sum_{n=1}^{\infty} a_n(1-x)^{\alpha_n},$$

and then the equation obtained by taking the Laplace transform of (4.6) is

$$a_1\hat{F}(p+\alpha_1+\beta-1) + \lambda\hat{F}(p)\Gamma(p)\Gamma(\beta)/\Gamma(p+\beta)$$
$$= \hat{B}(p) - \sum_{n=2}^{\infty} a_n\hat{F}(p+\alpha_n+\beta-1), \tag{4.7}$$

from which the abscissa of convergence can be found as before if the series for $a(x)$ is absolutely convergent in $0 \leqslant x \leqslant 1$. Our previous case had $\alpha_1 + \beta - 1 = 0$, so that both terms on the left-hand side of equation (4.7) contributed: the problem of finding asymptotic behaviour would actually be easier if $\alpha_1 + \beta - 1 \neq 0$.

5. Numerical evaluation

If one wants to know the actual values of $f(x)$ instead of its asymptotic form near $x - 1$, it seems simpler and more accurate to attack equation (2.2) directly than to try and evaluate either the series or the Laplace transform. The results shown in Fig. 2, which plots $f(x)$ against μ, were obtained by

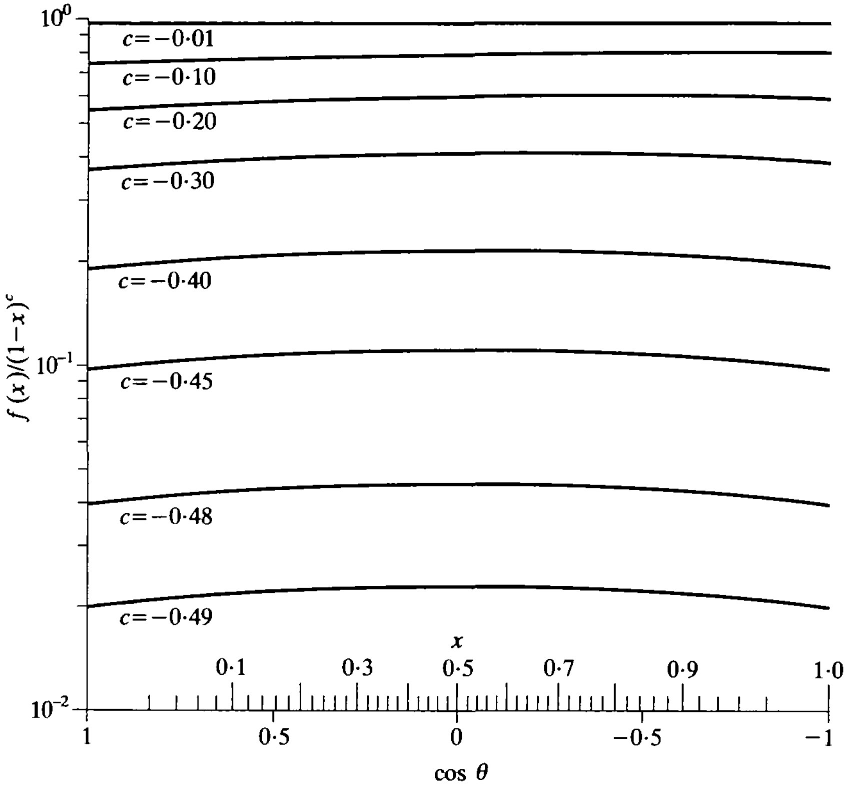

FIG. 2. Linear–logarithmic plot of $f(x)/(1-x)^c$ as a function of μ, for various values of the constant c. Values of x are indicated along the μ-axis

the following method. A set of $n = 1024$ angles θ_i°, $i = 1, 2, \ldots, n$, was chosen such that $\theta_1 = 0$, $\theta_n = 179$ and the numbers $(180 - \theta_i)$ were a geometric progression, so that they are more closely spaced near θ_n. Let $\mu_i = \cos\theta_i^\circ$, $x_i = \frac{1}{4}(2 - 3\mu_i + \mu_i^3)$ as in equation (1.4). The integral equation (2.2) was approximated by

$$a(x_i)f(x_i) = 2\lambda x_i^{\frac{1}{2}} - \lambda \sum_{j=2}^{j=i} \tfrac{1}{2}\{f(x_j) + f(x_{j-1})\} \int_{x_{j-1}}^{x_j} (x_i - t)^{-\frac{1}{2}}\, dt$$

$$= 2\lambda x_i^{\frac{1}{2}} - \lambda \sum_{j=2}^{j=i} \{f(x_j) + f(x_{j-1})\}\{(x_i - x_j)^{\frac{1}{2}} - (x_i - x_{j-1})^{\frac{1}{2}}\}. \qquad (5.1)$$

Equation (5.1) is tantamount to using a trapezoidal rule weighted by the $(x-t)^{-\frac{1}{2}}$-integrand. It is known (**16**, pp. 411–12) that this is sufficiently weakly singular that iteration would converge if the integral were evaluated exactly; in practice equation (5.1) was used for each i to calculate $f(x_i)$ from $f(x_1), f(x_2), \ldots, f(x_{i-1})$, starting with $f(x_1) = \lambda/(\lambda + 2\pi^{\frac{1}{2}})$ from equation

TABLE 1. *The variation of k and λ with c as given by equations* (2.5) *and* (2.7)

c	k	λ
−0·01	0·01784	112·11
−0·10	0·19567	10·221
−0·20	0·47125	4·2440
−0·30	0·97293	2·0557
−0·40	2·40882	0·8303
−0·45	5·24076	0·3816
−0·48	13·7097	0·1459
−0·49	27·8165	0·0719

(3.5). The computations were done for various values of c between −0·01 and −0·49, as shown on Fig. 2, λ being calculated from equation (2.7). Table 1 shows how λ varies with c. The numerical accuracy for $n = 1024$ was checked by repeating some of the work with $n = 256$ or 512; the differences were not visible on the scale of Fig. 2.

We can estimate the discretization error formally as follows. If h_j is the step-length $x_j - x_{j-1}$ in equation (5.1) the error from the trapezoidal rule in each step is of order $h_j^{\frac{3}{2}}$ if $i = j$, h_j^2 if not. (The exact trapezoidal rule would have given h_j^3 but would not have coped so well with the weak singularity at $i = j$.) The error in the integral is of order $nh_j^2 = O(n^{-1})$ at worst; in practice it proved to be between n^{-1} and $n^{-\frac{3}{2}}$ for the values of n used, depending on the value of c.

Figure 2 shows that a fair approximation to $f(x)$ is the very simple form $\lambda(1-x)^c/(\lambda + 2\pi^{\frac{1}{2}})$ for all x and all c: it is nowhere in error by more than 15 per cent.

From equation (2.6) the bubble surface pressure is

$$\Pi \sim \Pi_\infty A(3\Theta^4/16)^c \tag{5.2}$$

for $P_v^{-\frac{1}{2}} \ll \Theta = \pi - \theta \ll 1$; the left-hand inequality is because the result is valid only in the outer boundary-layer approximation (**14**). In the inner approximation we use the variable $m = \Theta P_v^{\frac{1}{2}}$, so that equation (5.2) becomes $\Pi \sim \Pi_\infty A P_v^{-2c}(3m^4/16)^c$ for $m \gg 1$. The appropriate inner solution matching this for large m and valid for finite m is (**14**)

$$\Pi = \Pi_\infty A P_v^{-2c}(\tfrac{3}{4})^c \Gamma(2c+1) e^{-\frac{1}{2}m^2} M(2c+1, 1, \tfrac{1}{2}m^2), \tag{5.3}$$

where M is the confluent hypergeometric function (**17**), and hence the surface pressure Π_{RSP} at the rear stagnation point is

$$\Pi_{RSP} = \Pi_\infty A P_v^{-2c}(\tfrac{3}{4})^c \Gamma(2c+1). \tag{5.4}$$

This is very much larger than Π_∞ because P_v is large and c is negative. As A is close to $\lambda/(\lambda + 2\pi^{\frac{1}{2}})$, Π_{RSP} can be shown to reduce to the previous special cases (14) $\Pi_{RSP} \sim 2P_v\Pi_\infty/\sqrt{3}$ for $k \to \infty$, $\Pi_{RSP} \sim 2\pi^{-\frac{1}{2}}\Pi_\infty k \ln P_v$ for $k \to 0$. (It should be noted that λ is $2/k$ in this paper, but λ in (14) is the same as $2c+1$ in this paper. Other variables such as Π, Π_∞, k, P_v, x, y, θ, m have the same meanings in both.)

6. Conclusions

If one uses the diffusion boundary-layer approximation, a singularity exists at the rear stagnation point of a bubble rising in a very dilute solution of a surfactant. It is algebraic in nature, being asymptotically a power law of the form $(1-x)^c$ or $(1+\mu)^{2c}$ near the rear stagnation point $x=1$, $\mu=-1$, where $0 > c > -\frac{1}{2}$, the value of c depending on the surface activity of the solute. One previous calculation (15) which gave a logarithmic singularity seems to have fallen into some numerical error; the present work has also given an analytical proof in order to check on this point. The methods make use of the integral equation for surface concentration which can be derived from the Green's function for concentration in the diffusion boundary layer; this reduces the dimensionality of the problem from 2 to 1 and simplifies both numerical and analytical work.

Physically, the most interesting of our results is probably equation (5.4), which explains just how large a magnification factor the surface pressure receives at the rear stagnation point, owing to the inefficiency of boundary-layer diffusion at removing surfactant swept towards that point. As might be expected, the magnification factor at the rear stagnation point increases with the surface activity, and so does the rapidity with which the surface pressure approaches its maximum value.

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REFERENCES

1. T. D. Taylor and A. Acrivos, *J. Fluid Mech.* **18** (1964) 466–476.
2. A. S. Brignell, *Q. Jl Mech. appl. Math.* **26** (1973) 99–107.
3. D. W. Moore, *J. Fluid Mech.* **6** (1959) 113–130.
4. ——, *ibid.* **23** (1965) 749–766.
5. W. Rybczynski, *Bull. int. Acad. pol. Sci. Lett. Cl. Sci. Math. Natur.* A (1911) 40–46.
6. J. Hadamard, *C. r. hebd. Seanc. Acad. Sci. Paris* **152** (1911) 1735–1738.
7. V. G. Levich, *Physicochemical Hydrodynamics* (Prentice–Hall, Englewood Cliffs 1962).
8. J. F. Harper, *Adv. appl. Mech.* **12** (1972) 59–129.
9. R. Clift, J. R. Grace and M. E. Weber, *Bubbles, Drops and Particles* (Academic Press, New York 1978).
10. P. Savic, *Rep. Div. mech. Engng natn. Res. Coun. Can.* MT **22** (1953).
11. J. F. Harper, *J. Fluid Mech.* **58** (1973) 539–545.

12. S. S. SADHAL and R. E. JOHNSON, *ibid.* **126** (1983) 237–250.
13. N. K. ADAM, *The Physics and Chemistry of Surfaces* (Dover, New York 1978).
14. J. F. HARPER, *Q. Jl Mech. appl. Math.* **27** (1974) 87–100.
15. D. A. SAVILLE, *Chem. Eng. J.* **5** (1973) 251–259.
16. G. F. CARRIER, M. KROOK and C. E. PEARSON, *Functions of a Complex Variable: Theory and Technique* (McGraw–Hill, New York 1966).
17. M. ABRAMOWITZ and I. A. STEGUN, *Handbook of Mathematical Functions* (Dover, New York 1965).