

# The leading edge of an oil slick, soap film, or bubble stagnant cap in Stokes flow

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Trace impurities often collect on the upstream side of an obstacle in the surface of flowing liquid. The transition from practically free surface to surface sufficiently clogged to be treated as stationary can be quite sharp. The viscous flow underneath is nonlinearly coupled to the convective mass transfer of surface-active material. For two-dimensional flow at high Reynolds number the first observations were due to Thoreau, Langton and Reynolds over 100 years ago, and the theory was given by Harper & Dixon in 1974. If the whole problem is considered from a frame of reference moving with the stream instead of fixed to the downstream surface film, the solution refers to the leading edge of a slowly spreading oil slick.

The present work gives the theory corresponding to Harper & Dixon's for low Reynolds numbers (Stokes flow), for which there is a very simple leading approximation near the transition for a soluble surfactant, and a more complicated one, which can still be found exactly, for an insoluble surfactant which spreads onto clear liquid by surface diffusion. In both cases the surface remains flat: the ridge often observed is not a Stokes flow phenomenon.

The results are used to clarify the circumstances in which Savic's stagnant-cap approximation is useful for a bubble rising in a viscous liquid: the rear stagnation point now plays the role of the obstacle in the surface, and the flow near the surface transition can be treated locally as if it were two-dimensional instead of axisymmetric.

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## 1. Introduction

The 'Reynolds ridge' at the leading edge of a region of surface-contaminated liquid has been known (but not well known) for a long time. Scott (1982) investigated the history, pointing out that Thoreau observed the phenomenon in 1854, Langton (1872) first published an account of it, and Reynolds (1881) seems to have been the first of many independent rediscoverers. The ridge is seen as a slight rise in the surface level at the leading edge of a spreading oil slick, or equivalently, where surfactant collects on the upstream side of an obstacle in the surface of flowing water, at the transition from apparently free surface to almost stationary surface which is caused by a gradient of surface tension. At high Reynolds numbers, this flow (relative to the transition region) is approximately a steady irrotational uniform stream past a surface which at each point is shifted downwards from the true liquid surface by the displacement thickness of the viscous boundary layer. Harper & Dixon (1974) gave the theory for a soluble surfactant, such as soap, and Scott (1982) confirmed it experimentally, though it must be said that his results were not sensitive to the difference between soluble and insoluble surfactants, nor to the precise nature

of the surface film, whether a 'gaseous film' on an ideal solution or a monolayer on a solution too concentrated to be ideal (Adam 1968). The problem for an insoluble surfactant (oil floating on water) was also attacked by Di Pietro (1975), Di Pietro, Huh & Cox (1978) and Di Pietro & Cox (1980), who considered both a bulk layer of oil and the monolayer which forms on the surface upstream of it, at a high Reynolds number. If both bulk layer and monolayer are present, the Thoreau-Langton-Reynolds ridge is at the upstream edge of the monolayer.

This paper discusses the transition from free to clogged on a surface with either kind of surfactant. Unlike Harper & Dixon (1974), the Reynolds number will be assumed to be low enough for the Stokes-flow approximation to hold. Throughout, the word 'clogged' is used to mean 'covered with enough surfactant to prevent tangential motion'; this usually requires the surfactant molecules to cover only a small fraction of the surface, so that a gaseous adsorbed film on an ideal solution is a good approximation, at least in the upstream parts of the clogged region. Besides the soap film and the oil slick, either spreading on water at rest or stationary on flowing water, there is a third physical application: the upstream edge of the 'stagnant cap' which may form on a bubble or drop moving steadily in a liquid (Savic 1953; Davis & Acrivos 1966; Harper 1973; Sadhal & Johnson 1983; Lerner 1985; Lerner & Harper 1991). In that theory there is assumed to be a transition from free to stagnant surface over a distance much smaller than the size of the cap; one aim of this paper is to clarify when that assumption holds, as most of the papers just cited do not mention the point, and Sadhal & Johnson omitted one of the necessary conditions.

The analysis is local, in the sense that at a distance from the origin the flow is assumed to tend to the two-dimensional Stokes flow past the leading edge of a flat plate end-on to a stream (Carrier & Lin 1948). This is one of the situations covered by the well-known remark of Conti & Van Dyke (1969) that 'under the eye of a sufficiently powerful glass most regions of most continuum flows dissolve into a uniform stream. Embedded in this local monotone there are, nevertheless, exceptional points that will not give up their identity under any magnification. Stagnation points, points of flow separation, and the eyes of vortices are some of these ... This results in simple local solutions ...'. In the present case there is a limit to the power of the glass, which will be found: the surface transition is sharp only on a large enough lengthscale, and its local solution on that large scale is used as the boundary condition at infinity for the problem of the small-scale transition from free to clogged surface.

## 2. Formulation

Consider a fluid of dynamic viscosity  $\mu$  flowing steadily and two-dimensionally at very low Reynolds number beneath a surface on which is adsorbed a surfactant whose surface excess per unit area (Guggenheim 1957; Harper 1972) is  $\Gamma$ . Ignore any variation of the surface from a plane for the moment, and take Cartesian coordinates  $(x, y)$  with the origin in the surface, the  $x$ -axis in the plane along the direction of flow and  $y$  into the fluid. It will also be convenient to use the complex  $z$ -plane and polar coordinates  $(r, \theta)$  where  $z = x + iy = r e^{i\theta}$ . Suppose that if the surfactant is soluble it has been diffusing from solution onto the surface upstream of the region of interest, that the surface diffusivity of adsorbed surfactant is  $D_s$ , and that the transition from almost free surface (shear stress  $\sigma_{xy}$  negligible) to almost clogged surface (surface

velocity  $u$  negligible) occurs over a distance too small for diffusion in or out of the surface to be significant. Then we may write

$$\frac{\partial}{\partial x}(u\Gamma) = D_s \frac{\partial^2 \Gamma}{\partial x^2} \quad (1)$$

in the transition region (Levich 1962; Harper 1972).

If the surfactant film may be treated as gaseous (Adam 1968), the surface pressure  $\Pi$  is given by

$$\Pi = \sigma_p - \sigma = RT\Gamma, \quad (2)$$

where  $\sigma_p$  is the surface tension of pure solvent,  $\sigma$  is the surface tension of the actual liquid,  $R$  is the gas constant and  $T$  the absolute temperature. In (2), the first equality is the definition of  $\Pi$  and the second is the condition for a gaseous film, which is a good approximation for sufficiently small  $\Gamma$ . In §4.2, but nowhere else in this paper, we assume an ideal solution obeying the condition  $\Gamma = hc$ , where  $c$  is the concentration in the solution and  $h$  is the adsorption depth (Harper 1972). Equation (2) gives

$$u\Pi - D_s \frac{\partial \Pi}{\partial x} = A^2\mu \quad \text{on } y = 0, \quad (3)$$

where  $A$  is a positive constant with the dimensions of velocity. Equation (3) is a nonlinear surface boundary condition for the viscous flow beneath the surface as well as the surfactant concentration by virtue of the dynamical boundary condition that the surface shear stress  $\sigma_{xy}$  obeys

$$\sigma_{xy} = \mu \frac{\partial u}{\partial y} = \frac{\partial \Pi}{\partial x} \quad \text{on } y = 0. \quad (4)$$

The remaining conditions to be satisfied by the stream function  $\psi$  such that

$$u = \frac{\partial \psi}{\partial y}, \quad v = -\frac{\partial \psi}{\partial x}, \quad (5)$$

are that in Stokes flow

$$\nabla^4 \psi = 0 \quad \text{for } y > 0, \quad (6)$$

$$\psi = 0 \quad \text{on } y = 0, \quad (7)$$

and that  $\psi$  should tend to the asymptotic form that

$$\psi \sim By \operatorname{Im}(z^{\frac{1}{2}}) = Br^{\frac{1}{2}} \sin \theta \sin \frac{1}{2}\theta, \quad (8)$$

as  $x \rightarrow \pm \infty, y \geq 0$ , where  $B$  is a constant with dimensions  $L^{\frac{1}{2}}T^{-1}$  which is determined by the details of the flow far from the transition region (Carrier & Lin 1948; van de Vooren & Dijkstra 1970; Botta & Dijkstra 1970; Van Dyke 1975).

There are square-root singularities of the velocity and surface pressure at the origin in the fluid motion given by (8); on  $y = 0$  they are given by

$$\left. \begin{aligned} u &= B(|x|)^{\frac{1}{2}} \quad \text{for } x < 0, & u &= 0 \quad \text{for } x > 0, \\ \Pi &= 0 \quad \text{for } x < 0, & \Pi &= 2B\mu x^{\frac{1}{2}} \quad \text{for } x > 0. \end{aligned} \right\} \quad (9)$$

Equation (8) is the local solution near the leading edge of a flat plate tangential to the flow, and it also applies to the locally two-dimensional flow at the leading edge of the stagnant cap on a rising bubble (Davis & Acrivos 1966).

### 3. Solution

In the transition region from free to clogged surface, we may write the general solution of (6) as

$$\psi = y \operatorname{Im}(w_1) + \operatorname{Im}(w_2), \quad (10)$$

where  $w_1$  and  $w_2$  are functions of  $z = x + iy$  analytic in the half-plane  $y \geq 0$ . On  $y = 0$  we have  $\psi = 0$ , so that  $w_2$  is real on the whole  $x$ -axis. By (8),  $w_1 \sim Bz^{\frac{1}{2}}$  and  $w_2 = o(z^{\frac{3}{2}})$  at infinity. With the Schwarz reflection principle to ensure that  $w_2$  has no singularities anywhere, we obtain  $w_2 = Uz + W$ , where  $U$  and  $W$  are real constants. It makes no difference to  $\psi$  to put  $W = 0$ . We may then delete the term  $\operatorname{Im}(w_2)$  from (10) if we simultaneously add the constant  $iU$  to  $w_1$ . Accordingly, let  $w_1 + iU = w$ ,  $\operatorname{Re}(w) = f(x, y)$ ,  $\operatorname{Im}(w) = g(x, y)$ . Then the surface boundary conditions are

$$u = g, \quad (11)$$

$$\frac{\sigma_{xy}}{\mu} = 2 \frac{\partial g}{\partial y} = 2 \frac{\partial f}{\partial x}, \quad (12)$$

by one of the Cauchy–Riemann equations, and so

$$\Pi = \int \sigma_{xy} dx = 2\mu f, \quad (13)$$

if  $f \rightarrow 0$  as  $\Pi \rightarrow 0$  far upstream.

The normal stress component  $\sigma_{yy}$  is constant on  $y = 0$  in any two-dimensional Stokes flow in which  $\psi = yg(x, y)$ , with  $\nabla^2 g = 0$ , because

$$\frac{\partial p}{\partial x} = \mu \nabla^2 u = \mu \nabla^2 \frac{\partial \psi}{\partial y} = 2\mu \frac{\partial^2 g}{\partial y^2} = -2\mu \frac{\partial^2 g}{\partial x^2},$$

and so  $p = -2\mu \partial g / \partial x + \text{constant}$ , everywhere in the flow; also

$$2\mu \frac{\partial v}{\partial y} = -2\mu \left( \frac{\partial g}{\partial x} + y \frac{\partial^2 g}{\partial x \partial y} \right) = -2\mu \frac{\partial g}{\partial x} \quad \text{on } y = 0,$$

and so  $\sigma_{yy} = -p + 2\mu \partial v / \partial y = \text{constant}$  there. It follows that the Thoreau–Langton–Reynolds ridge, which is caused by gradients of normal stress in the flow under the clogged surface, is a phenomenon of finite and large Reynolds numbers.

#### 3.1. Surface diffusion negligible

Let us deal first with an important simple special case. If the term in (3) involving  $D_s$  is small enough to ignore (the precise condition for which will be found later), (3), (11) and (13) reduce to

$$2fg = \operatorname{Im}(w^2) = A^2 \quad (14)$$

on  $y = 0$ , so that  $w^2 - iA^2$  is real at all points there. By (8),  $w^2 \sim B^2 z$  for large  $|z|$ , and if there are to be no singularities in the flow field, analytic continuation gives

$$w^2 - iA^2 = B^2 z + C, \quad (15)$$

where  $C$  is an arbitrary real constant, which may be equated to zero by shifting the origin to a suitable point on the surface. Supposing that done, we find the exact solution in the transition region as

$$w = B(z + id)^{\frac{1}{2}} = Bz_1^{\frac{1}{2}}, \quad \psi = Byr_1^{\frac{1}{2}} \sin \frac{1}{2}\theta_1, \quad (16)$$

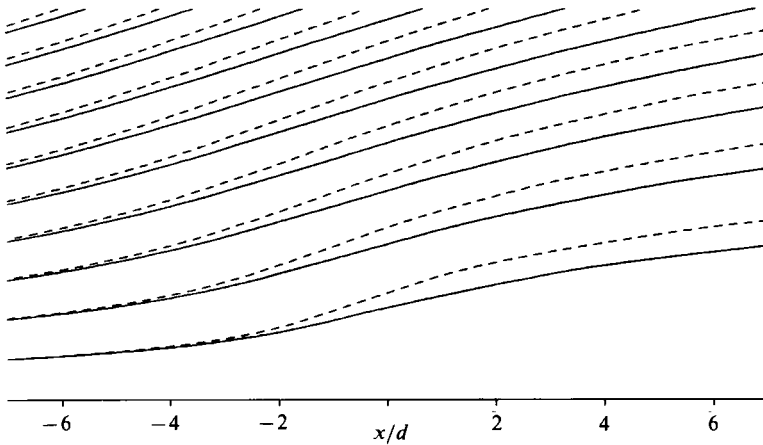


FIGURE 1. The streamline pattern for a soluble surfactant: —, the inner solution (equation (16)); ---, the outer solution (equation (8)).

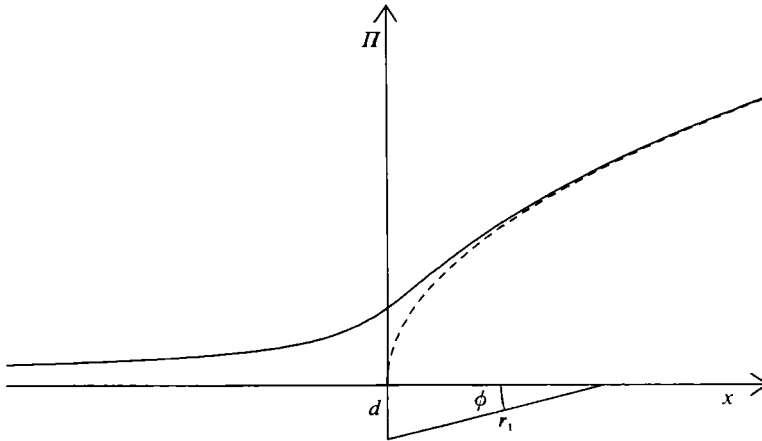


FIGURE 2.  $\Pi$  as a function of  $x$  for a soluble surfactant: —, the inner solution (equation (17)); ---, the outer solution (equation (9)). In both cases the graph of  $2\mu u$  is the same shape but reflected in the  $\Pi$ -axis.

where  $z_1 = z + id = r_1 \exp(i\theta_1)$ , so that  $(r_1, \theta_1)$  are polar coordinates centred at the point  $z = -id$ , and  $d = A^2/B^2$  is a constant, which is the lengthscale of the transition. Equations (8) and (16) now give the surface velocity and shear stress as

$$u = A(\frac{1}{2} \tan \frac{1}{2}\phi)^{\frac{1}{2}}, \quad \Pi = \mu A(2 \cot \frac{1}{2}\phi)^{\frac{1}{2}}, \quad (17)$$

where  $\phi$  is the value of  $\theta_1$  for points on the surface, so that  $\tan \phi = d/x$ , and

$$\tan \frac{1}{2}\phi = [1 + (x/d)^2]^{\frac{1}{2}} - (x/d) \sim \begin{cases} d/2x & \text{as } x \rightarrow +\infty, \\ 2|x|/d & \text{as } x \rightarrow -\infty. \end{cases} \quad (18)$$

The outer solution (8) is evidently the same as the inner solution (16) if  $d = 0$ , and the inner solution tends to it as  $|z|/d \rightarrow \infty$ . Figure 1 shows a streamline plot and figure 2 shows the variation of  $\Pi$  with  $x$  and the geometrical interpretation of  $\phi$ ; the variation of  $u$  with  $x$  is the same as that of  $\Pi$  reflected in the line  $x = 0$ , apart from a factor  $2\mu$ , by (17).

## 3.2. Surface diffusion included

If terms in  $D_s$  are included, calculations like those leading to (14) give

$$2fg = \text{Im}(w^2) = 2D_s \partial f / \partial x + A^2, \quad (19)$$

on the surface  $y = 0$ , so that  $w^2 - 2iD_s dw/dz - iA^2$  is real there, and  $w \sim Bz_1^{\frac{1}{2}}$  and  $dw/dz \rightarrow 0$  at infinity, and analytic continuation now gives

$$-2iD_s \frac{dw}{dz_1} + w^2 = B^2 z_1, \quad (20)$$

throughout the flow field, with the same  $z_1$  as in (16). This Riccati equation is solved, as usual, by putting

$$w = -\frac{2iD_s}{\xi} \frac{d\xi}{dz_1},$$

to obtain the Airy equation

$$\frac{d^2 \xi}{dz_1^2} - z_2 \xi = 0,$$

if

$$z_2 = (B/2D_s)^{\frac{2}{3}} \exp[-\frac{1}{3}i\pi] z_1 = \exp[-\frac{1}{3}i\pi] z_1/s = \beta z_1, \quad (21)$$

where  $s = (2D_s/B)^{\frac{3}{2}}$  is the lengthscale on which surface diffusion is relevant, and  $\beta$  is a complex constant. Hence

$$w = -2iD_s \beta \frac{\gamma \text{Ai}'(z_2) + \delta \text{Bi}'(z_2)}{\gamma \text{Ai}(z_2) + \delta \text{Bi}(z_2)}.$$

If  $|z_1| \rightarrow \infty$  with  $\theta_1 = \arg z_1 = \frac{1}{3}\pi$ , which is in the flow field  $0 \leq \theta_1 \leq \pi$ , then  $z_2 \rightarrow +\infty$ , both  $\text{Ai}(z_2)$  and  $\text{Bi}(z_2)$  are real,  $\text{Bi}(z_2) \gg \text{Ai}(z_2)$ ,  $\text{Bi}'(z_2) \gg |\text{Ai}'(z_2)|$ , and so  $w \sim 2iD_s \beta \text{Bi}'(z_2)/\text{Bi}(z_2)$  if  $\delta \neq 0$ . In that case  $w \sim -2iD_s \beta z_2^{\frac{1}{2}} \sim -Bz_1^{\frac{1}{2}}$ , which has the wrong sign. Hence  $\delta = 0$ , and

$$w = -2iD_s \beta \text{Ai}'(z_2)/\text{Ai}(z_2) \sim +Bz_1^{\frac{1}{2}}, \quad (22)$$

as  $|z_2| \rightarrow \infty$  if  $|\arg z_2| < \pi$ , which includes the whole flow field. The poles of  $w$  are all on the negative  $z_2$ -axis, which is outside the flow field. The particular cube root of  $-1$  in the definition of  $\beta$  was chosen to ensure this. Properties of Airy functions were taken from Abramowitz & Stegun (1970); some earlier printings of that book had an error in the asymptotic expansion of the function  $\text{Bi}'$ . It is perhaps worth noting that on the free surface  $w = f + ig$  has a pure imaginary limit as  $z_1 \rightarrow -\infty$ , and that  $g$  increases algebraically like  $B|z_1|^{\frac{1}{2}}$ , but that if  $A = 0$  then  $f$  decreases exponentially. The easiest way to see this is by (19) which reduces to

$$\frac{1}{f} \frac{\partial f}{\partial x} = \frac{g}{D_s}.$$

If, on the other hand,

$$s = (2D_s/B)^{\frac{3}{2}} \ll d = A^2/B^2, \quad (23)$$

then  $|z_2| \gg 1$  throughout the flow field. Mathematically, that means that the Airy functions may be replaced by their asymptotic approximations everywhere, and we may use the simple theory of §3.1 instead of the more elaborate theory of this section. Physically, it means that surface diffusion is irrelevant to the dynamics because  $D_s$  is too small for the term including it in (3) to be important anywhere on the surface.

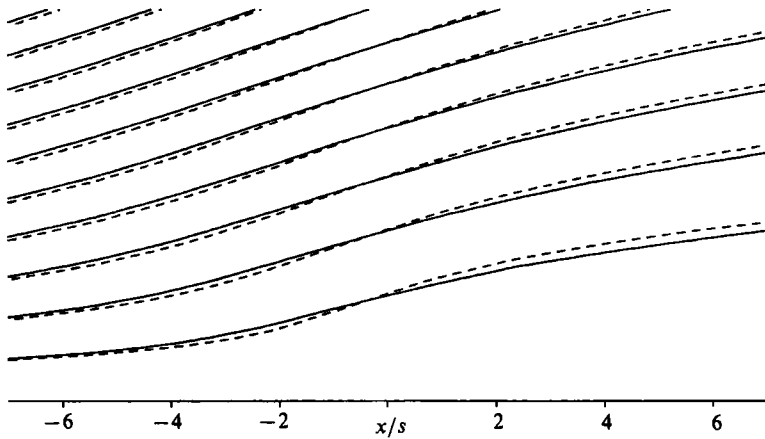


FIGURE 3. The streamline pattern for an insoluble surfactant: —, the inner solution (equation(22)); ---, the outer solution (equation (8)).

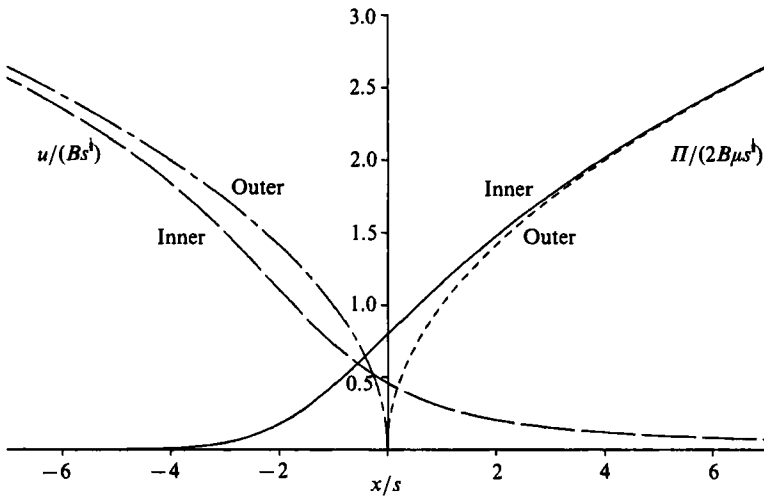


FIGURE 4. Surface pressure and velocity as functions of  $x/s$  for an insoluble surfactant: —,  $\Pi/(2B\mu s^{1/2})$  from equation (22); —,  $u/(Bs^{1/2})$  from equation (22); ---,  $\Pi/(2B\mu s^{1/2})$  from the outer approximation (equation (8)); ---,  $u/(Bs^{1/2})$  from the outer approximation (equation (8)).

Figure 3 shows graphs of  $u$  and  $\Pi$  on the surface and figure 4 shows a streamline plot for this case.

## 4. Applications

### 4.1. Spreading film

Suppose that a film of surfactant spreads at constant speed  $U$  across a fluid of kinematic viscosity  $\nu$  which is at rest at a great distance. The outer solution is the flow past a thin rigid flat plate, for which the numerical solution of the full Navier–Stokes equations was given by van de Vooren & Dijkstra (1970) and Botta & Dijkstra (1970). Close to the origin ( $r \ll \nu/U$ ) this solution reduces to a Stokes flow of the form (8) with

$$B = 3.0190U^{2/3}\nu^{-1/3}. \tag{24}$$

Carrier & Lin (1948) had given an equation equivalent to (24) with 3.0190 replaced by  $8 \times 0.3321 = 2.657$  after Van Dyke's (1975) correction is applied, but they assumed that the outer limit of the Stokes flow matched the inner limit of the Blasius boundary layer; there is of course an intermediate region when neither simplification holds. If the surface pressure at the downstream end of the free surface is  $\Pi_t$ , we have  $A^2 = \Pi_t U/\mu$ , and hence negligible surface diffusion if

$$\Pi_t/U\mu \gg 6.9(D_s/\nu)^{\frac{3}{2}}, \quad (25)$$

by (23). In this case, the transition lengthscale is  $d = 0.11\Pi_t/\rho U^2$ , where  $\rho$  is the density of the liquid. Unfortunately, values of  $D_s$  are not well known. If, as seems likely (Levich 1962),  $D_s$  is close to  $D$ , the bulk diffusivity of dissolved surfactant, then ordinary surfactants on water will have  $D_s/\nu$  of order  $4 \times 10^{-4}$ , and surface diffusion will be negligible if  $\Pi_t/U\mu \gg 0.005$ .

It has been assumed above the transition lengthscale  $d$  is much less than the size of the region where (8) and (24) hold, which is  $O(\nu/U)$ . This requires  $(\Pi_t/U\mu) \ll 9$ ; there is thus a reasonable range of upstream surface pressures over which the theory of §3.1 holds. If  $\Pi_t/U\mu \gg 9$  the theory of Harper & Dixon (1974) applies instead of the present work. In experiments on the Thoreau–Langton–Reynolds ridge  $U\mu$  is typically of order  $0.1 \text{ mN m}^{-1}$ .

For an oil slick of insoluble surfactant spreading on otherwise pure water,  $\Pi_t$  may be so small upstream that the inequality (25) is reversed. In that case it is a good approximation to put  $d = 0$  in the theory of §2.2, and the transition lengthscale is  $s = 0.7599D^{\frac{2}{3}}\nu^{\frac{1}{3}}U^{-1}$ .

#### 4.2. Stagnant-cap bubble

If our surfactant film is on the surface of an isolated stagnant-cap bubble of radius  $a$  and cap angle  $\alpha$  rising steadily at speed  $U$ , with the Reynolds number  $Re = Ua/\nu \ll 1$ , then  $B$  is of order  $Ua^{-\frac{1}{2}}\alpha$  (Harper 1973; Sadhal & Johnson 1983). If the surfactant solution is ideal and the diffusivity of dissolved surfactant is  $D$ , the kinematic surface boundary condition may be written

$$a \frac{\partial}{\partial \theta} (\Pi u_\theta \sin \theta) = D_s \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \Pi}{\partial \theta} \right) + \frac{a^2 D}{h \sin \theta} \frac{\partial \Pi}{\partial r}, \quad (26)$$

in spherical polar coordinates  $(r, \theta)$ . If the Péclet number  $P = Ua/D \gg 1$  (which is a necessary condition for stagnant caps to form), the first term on the right-hand side is negligible except possibly in the transition region. Upstream from that region  $\partial \Pi / \partial r = O(P^{-\frac{1}{2}}\Pi_\infty a^{-1})$ , where  $\Pi_\infty$  is the surface pressure at a great distance from the bubble, and so

$$A^2 \mu \alpha = O(P^{-\frac{1}{2}} U \Pi_\infty a/h). \quad (27)$$

The ratio of transition region lengthscale to cap size is of order  $d/\alpha a$  if surface diffusion is ignored, and

$$d/\alpha a = O(A^2/B^2 \alpha a) = O(P^{-\frac{1}{2}} (\Pi_\infty/U\mu) (a/h) \alpha^{-4}), \quad (28)$$

but  $\alpha$  is of order  $(\Pi_\infty/U\mu)^{\frac{3}{8}} P^{\frac{1}{8}}$  (Harper 1973; Lerner & Harper 1991), so that

$$d/\alpha a = O(P^{-\frac{3}{4}} (\Pi_\infty/U\mu)^{-\frac{1}{2}} (a/h)). \quad (29)$$

The stagnant-cap approximation requires  $d \ll \alpha a$ , and so (29) really shows that a necessary condition for its validity is

$$h/a \gg P^{-\frac{3}{4}} (\Pi_\infty/U\mu)^{-\frac{1}{2}}. \quad (30)$$



If  $\alpha$  is of order unity,  $\Pi_\infty/U\mu$  is of order  $P^{-\frac{1}{2}}$  and the condition becomes  $h/a \gg P^{-\frac{1}{2}}$ . This necessary condition for stagnant caps was not given by Sadhal & Johnson (1983), who required only that  $P \gg 1$ ,  $PD/D_s \gg 1$  and  $Re \ll 1$  in the present case of a surfactant soluble only in the continuous phase and with insignificant barriers to adsorption and desorption.

Surface diffusion was neglected above. That will usually be a good approximation, for the following reason. Terms in  $D_s$  are negligible if  $(2D_s/B)^{\frac{1}{2}} \ll A^2/B^2$ , which is equivalent to

$$h/a \ll P^{-\frac{1}{2}}(Ua/D_s)^{\frac{1}{2}}(\Pi_\infty/U\mu)\alpha^{-\frac{1}{2}} \sim P^{\frac{1}{4}}(D/D_s)^{\frac{1}{2}}(\Pi_\infty/U\mu)^{\frac{1}{2}}. \quad (31)$$

All three of the factors on the right-hand side are likely to be near 1, and  $h$  for most ordinary surfactants is much smaller than  $a$  for most ordinary bubbles. The inequality (31) therefore will usually be satisfied. The contrary hypothesis will not be investigated here.

## 5. Conclusions

Exact solutions have been found for the transition from free to clogged surface on a surface-contaminated liquid both for negligible surface diffusion (equations (16), (17)) and in general (equation (22)). The first case applies to a surfactant film spreading on a flat surface (or to a Thoreau–Langton–Reynolds ridge) if the liquid upstream of it is already somewhat polluted with a soluble surfactant. The second more complicated case applies to very small amounts of upstream contamination, possibly due to an insoluble surfactant, as described in §4.1.

The theory also applies to stagnant caps on rising bubbles, for which surface diffusion will normally be negligible in practice. Inequality (30) is a necessary condition for the stagnant-cap approximation to be a good one for bubbles at low Reynolds numbers; none of the extensive previous work on the subject seems to have mentioned it.

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## REFERENCES

- ABRAMOWITZ, M. & STEGUN, I. A. 1970 *Handbook of Mathematical Functions*, 9th printing. Dover.
- ADAM, N. K. 1968 *The Physics and Chemistry of Surfaces*. Dover.
- BOTTA, E. F. F. & DIJKSTRA, D. 1970 An improved numerical solution of the Navier–Stokes equations for the laminar flow past a semi-infinite flat plate. *Rep. Math. Inst. Univ. Groningen* TW-80.
- CARRIER, G. F. & LIN, C. C. 1948 On the nature of the boundary layer near the leading edge of a flat plate. *Q. Appl. Maths* **6**, 63–68.
- CONTI, R. & VAN DYKE, M. 1969 Inviscid reacting flow near a stagnation point. *J. Fluid Mech.* **35**, 799–813.
- DAVIS, R. E. & ACRIVOS, A. 1966 The influence of surfactants on the creeping motion of bubbles. *Chem. Engng Sci.* **21**, 681–685.

- DI PIETRO, N. D. 1975 The motion of oil slicks on a calm sea. MSc dissertation, McGill University, Montreal.
- DI PIETRO, N. D. & COX, R. G. 1980 The containment of an oil slick by a boom placed across a uniform stream. *J. Fluid Mech.* **96**, 613–640.
- DI PIETRO, N. D., HUH, C. & COX, R. G. 1978 The hydrodynamics of the spreading of one liquid on the surface of another. *J. Fluid Mech.* **84**, 529–549.
- GUGGENHEIM, E. A. 1957 *Thermodynamics*, 3rd edn. North-Holland.
- HARPER, J. F. 1972 The motion of bubbles and drops through liquids. *Adv. Appl. Mech.* **12**, 59–129.
- HARPER, J. F. 1973 On bubbles with small adsorbed films rising in liquids at low Reynolds numbers. *J. Fluid Mech.* **58**, 539–545.
- HARPER, J. F. & DIXON, J. N. 1974 The leading edge of a surface film on contaminated flowing water. *Proc. Fifth Australasian Conf. Hydraulics Fluid Mech., Christchurch, NZ* vol. 2, pp. 499–505.
- LANGTON, J. 1872 Ripples and waves. *Nature* **5**, 241–242.
- LERNER, L. 1985 The interaction of surface-contaminated drops in Stokes flow. MSc thesis, Victoria University of Wellington, NZ.
- LERNER, L. & HARPER, J. F. 1991 Stokes flow past a pair of stagnant-cap bubbles. *J. Fluid Mech.* **232**, 167–190.
- LEVICH, V. G. 1962 *Physicochemical Hydrodynamics*. Prentice-Hall.
- REYNOLDS, O. 1881 On surface-tension and capillary action. *Rep. Br. Ass. Adv. Sci.* **51**, 524–525.
- SADHAL, S. S. & JOHNSON, R. E. 1983 Stokes flow past bubbles and drops partially coated with thin films. Part 1. Stagnant cap of surfactant film – exact solution. *J. Fluid Mech.* **126**, 237–250.
- SAVIC, P. 1953 Circulation and distortion of liquid drops falling through a viscous medium. *Nat. Res. Council. Can., Div. Mech. Engng Rep.* MT-22.
- SCOTT, J. C. 1982 Flow beneath a stagnant film on water: the Reynolds ridge. *J. Fluid Mech.* **116**, 283–296.
- VAN DYKE, M. 1975 *Perturbation Methods in Fluid Mechanics*, annotated edn. Stanford, CA: Parabolic.
- VOOREN, A. I. VAN DE & DIJKSTRA, D. 1970 The Navier–Stokes solution for laminar flow past a semi-infinite flat plate. *J. Engng Maths* **4**, 9–27.