Int. J. Multiphase Flow Vol. 8, No. 6, pp. 627–639, 1982
Printed in Great Britain.

0301-9322/82/060627-13$03.00/0
Pergamon/Elsevier

ON THE SLOW TRANSLATION OF A SOLID SUBMERGED IN A FLUID WITH A SURFACTANT SURFACE FILM—I

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(*Received* 10 *November* 1981; *in revised form* 9 *April* 1982)

Abstract—In this paper a class of problems is examined in which a solid particle translates in a semi-infinite fluid whose surface is contaminated with a surfactant film. The fluid motion generated is assumed to be slow,. quasi-steady, and axisymmetric. Various linearised models governing the variation of film concentration are encompassed, and the constitutive properties of the film are described in terms of coefficients of surface shear and surface dilatational viscosity. The problem of a Stokeslet whose direction is normal to the film is solved, and the results are applied to computing approximate expressions for the force on a translating particle when far from the surface.

1. INTRODUCTION

The last two decades have seen a surge of interest in the design and theoretical analysis of instruments for the measurement of the coefficient of surface shear viscosity of monomolecular surfactants adsorbed in the surface of a bulk fluid. Much of this work is reviewed by Goodrich (1973), and further recent references are Briley *et al.* (1976), Oh & Slattery (1978), Shail (1978, 1979), Shail & Gooden (1981), etc. From the theoretical point of view most authors have considered either systems in which bodies rotate (either immersed within the bulk fluid or in contact with the surfactant layer), or parallel-flow configurations. In contrast with early calculations, full allowance is now made, via the boundary condition imposed at the surfactant surface layer, for the hydrodynamic interaction of the film with the motion of the substrate bulk fluid.

The form of the dynamic boundary condition on the velocity components in the surfactant film was investigated in detail by Scriven (1960), using a rheological model in which the properties of the film are described in terms of the Boussinesq coefficients of surface shear viscosity η, and surface dilatational viscosity κ. For a film incident with the plane $z = 0$, and separating two incompressible bulk phases with viscosities μ_1 and μ_2, occupying $z > 0$ and $z < 0$ respectively, these boundary conditions take the form

$$\tau_{xz}^{(1)} - \tau_{xz}^{(2)} = -\frac{\partial p_s}{\partial x} + (\kappa + \eta)\frac{\partial}{\partial x}\left(\frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y}\right) + \eta\frac{\partial}{\partial y}\left(\frac{\partial u_x}{\partial y} - \frac{\partial u_y}{\partial x}\right), \qquad [1]$$

and

$$\tau_{yz}^{(1)} - \tau_{yz}^{(2)} = -\frac{\partial p_s}{\partial y} + (\kappa + \eta)\frac{\partial}{\partial y}\left(\frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y}\right) - \eta\frac{\partial}{\partial x}\left(\frac{\partial u_x}{\partial y} - \frac{\partial u_y}{\partial x}\right), \qquad [2]$$

on $z = 0$, where $\tau_{xz}^{(1)}$, $\tau_{xz}^{(2)}$ etc. are the shear stresses exerted on the interface by the substrate bulk fluids in $z > 0$ and $z < 0$. In [1] and [2], u_x and u_y are the rectangular components of fluid velocity in the film, p_s is the surface pressure which is related to surface concentration of surfactant by an equation of state, the motion is assumed to be slow enough for the Stokes linearisation to be valid, and the inertia of the film has been neglected.

For steady axisymmetric Stokes-flow rotation problems (*loc. cit.*) the velocity vector field in all three phases of the system is in the aximuthal ϕ-direction of a cylindrical polar coordinate system (ρ, ϕ, z). All fluid particles describe circles, with centres on the z-axis of rotation, and in planes perpendicular to the axis of rotation. In this case, for an insoluble surfactant, the surface pressure (and hence surface concentration) can be taken as constant, and [1], [2] reduce to the simple form

$$\eta \frac{\partial^2 v_1}{\partial z^2} - \mu_1 \frac{\partial v_1}{\partial z} + \mu_2 \frac{\partial v_2}{\partial z} = 0 \text{ on } z = 0, \qquad [3]$$

where v_1 and v_2 are the azimuthal velocity components in $z > 0$ and $z < 0$ (note that $v_1 = v_2$ on $z = 0$). In the bulk phases, v_1 and v_2 both satisfy the equation

$$\frac{\partial^2 v}{\partial \rho^2} + \frac{1}{\rho}\frac{\partial v}{\partial \rho} + \frac{\partial^2 v}{\partial z^2} - \frac{v}{\rho^2} = 0, \qquad [4]$$

the pressure being constant throughout each phase.

It is the object of this and subsequent articles to investigate axisymmetric motions without swirl, i.e. the fluid velocity vector $\mathbf{v}$ has the form $\mathbf{v} = u(\rho, z)\hat{\rho} + w(\rho, z)\hat{z}$ where $\hat{\rho}$ and $\hat{z}$ are unit vectors in the directions of ρ- and z-increasing. With the exception of parallel flows, there seems to be little published work on this topic, and we wish to investigate the motion generated in a semi-infinite surfactant-covered fluid by an axisymmetric solid, which moves parallel to one of its axes of symmetry in a direction normal to the fluid surface. Assuming that the interfacial film remains plane, [1] and [2] are replaced, in an obvious notation, by

$$\tau_{\rho z}^{(1)} - \tau_{\rho z}^{(2)} = -\frac{\partial p_s}{\partial \rho} + (\eta + \kappa)\left\{\frac{1}{\rho}\frac{\partial}{\partial \rho}\left(\rho \frac{\partial u}{\partial \rho}\right) - \frac{u}{\rho^2}\right\} \text{ on } z = 0. \qquad [5]$$

Such problems are more difficult than the rotation configurations, since the fluid motion in the film is no longer consistent with constant surface pressure. It is therefore necessary to consider, along with the bulk-fluid dynamical equations, models for the determination of the surface pressure p_s and the molecular surface concentration n in the film.

In writing down equations for the calculation of n, various processes can be considered. For surfactants insoluble in the bulk phases, surface diffusion is a possible rate-determining process. For soluble surfactants the mechanisms of adsorption and desorption, and of bulk diffusion into the film from the substrates merit attention. The resulting equations, together with [5], couple the film velocity component u, the concentration n, and therefore p_s via the equation of state of the film, in a nonlinear manner, and in order to make analytic progress with the solution of specific boundary-value problems, it seems to be necessary to linearise about an equilibrium state in the manner suggested by Levich (1962).

The basic configuration and plan of this paper is as follows. An axisymmetric solid translates steadily, parallel to an axis of symmetry, through the bulk phase 1 normal to the surfactant film, which is assumed to remain plane. For simplicity the bulk fluid labelled 2 above is replaced by a vacuum, but there is no essential difficulty in extending the analysis to the three-phase system. In section 2 the basic equations of motion are formulated, the fluid motion being sufficiently slow to allow the quasi-steady Stokes approximation to be made. Each of the model film behaviours outlined in the previous paragraph is considered, and appropriate linearised forms are discussed.

In section 3 the various models are applied to the problem of finding the fluid motion generated by an axial Stokeslet in the bulk fluid. Using the approach of Brenner (1962), approximate expressions are derived in section 4 for the drag on an arbitrary axisymmetric body which translates perpendicularly to the surfactant film. These drag formulae are valid when $a/h \ll 1$ and are correct to $O(a^2/h^2)$, where a is a typical dimension of the solid and h a representative distance of the solid from the surface film [for analagous consideration in the rotation problem see Shail & Gooden (1981)]. The analysis generates no fewer than five dimensionless groups, so that a large variety of asymptotic behaviours is possible.

2. BASIC FORMULATION

The geometrical configuration considered is as follows. A semi-infinite expanse of viscous incompressible fluid, with coefficient of viscosity μ, occupies the region $z > 0$, where (ρ, ϕ, z) are cylindrical polar coordinates whose z-axis is drawn vertically downwards. The plane horizontal surface $z = 0$ of the bulk fluid is covered by a thin surfactant film a few molecules thick. The Boussinesq coefficients of surface shear viscosity and surface dilatational viscosity of the film are denoted by η and κ.† Within the bulk fluid there is a solid body, surface S, such that the z-axis is an axis of rotational symmetry of the solid. This body moves slowly with constant speed U parallel to the z-axis, i.e. normal to the undisturbed surface film, and a, h denote a typical dimension of the body, and the distance of a suitable 'centre' of the body from the film.

The fluid motion induced by the moving solid is unsteady, and in general the surface film will not remain plane. However, a first simplification occurs if we assume that the fluid motion is sufficiently slow for the quasi-steady Stokes creeping-motion approximation to be made. Sufficient conditions for the validity of this approximation are $Ua/\nu \ll 1$ and $Ua^2/\nu h \ll 1$, where ν is the kinematic viscosity of the bulk fluid (see Happel & Brenner 1965). The time t no longer appears explicitly in the problem, and the bulk-fluid velocity vector $\mathbf{v}$ satisfies the linear equations

$$\mu \operatorname{curl}\operatorname{curl}\mathbf{v} = -\nabla p, \qquad [6]$$

and

$$\operatorname{div}\mathbf{v} = 0, \qquad [7]$$

where p is the pressure field. On S, $\mathbf{v}$ satisfies the no-slip kinematic boundary condition, i.e.

$$\mathbf{v} = U\hat{\mathbf{z}} \text{ on } S, \qquad [8]$$

and further $\mathbf{v}$ must tend to zero at large distances from S.

Consider next the surface film. We propose to treat this as remaining plane and incident with $z = 0$ throughout the motion. An approximation of this type has been widely used by various authors (see e.g. Brenner 1961, Bart 1968, Lee *et al.* 1979, 1980) in discussing the motion of spheres near clean free surfaces and fluid interfaces, and can be realised in a number of ways. Thus, if $a/h \ll 1$, or if the surface tension is sufficiently large to prevent distortion,‡ the surface remains plane in a first approximation; alternatively, if we revert to the three-phase system, a sufficiently large density difference between the upper and lower bulk fluids will achieve approximate planarity of the interface. Thus, the appropriate form of [5] is taken to be

$$-\mu\frac{\partial u}{\partial z} = -\frac{\partial p_s}{\partial \rho} + (\eta + \kappa)\left\{\frac{1}{\rho}\frac{\partial}{\partial \rho}\left(\rho\frac{\partial u}{\partial \rho}\right) - \frac{u}{\rho^2}\right\} \text{ on } z = 0, \qquad [9]$$

$u = u(\rho, 0)$ being the radial component of fluid velocity in the film (equal of course to the

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†Experimentally, for some surfactants η is found to depend on surface concentration and on shear rate in the film. In this paper η and κ are treated as constants.

‡Specifically, this requires that $U\mu/\min \sigma \ll 1$, where σ is the surface tension of the film. Note that $\sigma = \sigma_0 - p_s$, where σ_0 is the surface tension of the pure bulk liquid.

bulk-fluid value at $z = 0$). Further, the requirement that the surface remain in $z = 0$ implies that

$$w = 0 \text{ on } z = 0, \quad 0 \leq \rho < \infty, \tag{10}$$

where $w(\rho, z)$ is the z-component of fluid velocity. Note that it is not possible to impose simultaneously with [9] and [10] the requirement of the vanishing of normal stress τ_{zz} at the surface. This normal stress imbalance is found in all the references quoted above, and is assumed to be compensated by surface tension effects.

In order to eliminate the surface pressure p_s in [9], the processes governing changes in film concentration must be considered. It is envisaged that the surface of the bulk fluid remains everywhere covered with surfactant throughout the motion; thus, for example, we exclude concentrations sufficiently large so as to cause phase changes such as micelle formation. Let the surfactant concentration be n molecules per cm^2. Then n is a function of ρ and is related to the surface pressure by an "equation of state" of the general form

$$p_s = f(T, n),$$

where T is the temperature. Here attention is restricted to isothermal situations, and the reader is referred to the texts of Adamson (1976), and Davies & Rideal (1961) for experimental data on the (n, p_s)-isotherms for various surfactants. For weak surfactants a linear relationship of the form

$$p_s = kTn, \tag{11}$$

where k is the Boltzmann constants, is often found; [11] is the equation of state of the so-called gaseous film. Wrinting $n = n_0 + n'$, where n_0 is the constant equilibrium concentration of the film, [11] gives

$$\frac{\partial p_s}{\partial \rho} = kT\frac{\partial n'}{\partial \rho}. \tag{12}$$

For a general equation of state this may be replaced, for small deviations n' from equilibrium, by

$$\frac{\partial p_s}{\partial \rho} = \left(\frac{\partial f}{\partial n'}\right)_0 \frac{\partial n'}{\partial \rho}, \tag{13}$$

where the derivative $\partial f/\partial n'$ is evaluated at $n' = 0$, and can be estimated from experimental isotherms.

To relate n and u, consider first the case in which there is surface diffusion in the film, together with adsorption from and desorption to the bulk fluid. In polar coordinates the equation of continuity for the surface molecules is (Levich 1962; Kenning 1968)

$$\frac{1}{\rho}\frac{\partial}{\partial \rho}(\rho n u) = D_s \frac{1}{\rho}\frac{\partial}{\partial \rho}\left(\rho \frac{\partial n}{\partial \rho}\right) + j, \tag{14}$$

where j is a source term which accounts for the adsorbtion and desorption processes, and D_s is the coefficient of surface diffusion. For small departures from the equilibrium concentration, Levich (1962) has derived the form

$$j = -\beta(n - n_0) = -\beta n', \tag{15}$$

where $\beta > 0$ is a constant. Physically β^{-1} is a measure of the time required for the establishment of an adsorption equilibrium, and varies from seconds to milliseconds. Thus, from [14] and [15],

$$\frac{1}{\rho}\frac{\partial}{\partial\rho}(\rho nu) = D_s\frac{1}{\rho}\frac{\partial}{\partial\rho}\left(\rho\frac{\partial n'}{\partial\rho}\right) - \beta n'. \qquad [16]$$

In order to make analytic progress, suppose now that during the creeping motion n does not vary much from the equilibrium concentration n_0, i.e. $n'/n_0 \ll 1$. Condition [16] can then be replaced by

$$\frac{n_0}{\rho}\frac{\partial}{\partial\rho}(\rho u) = D_s\frac{1}{\rho}\frac{\partial}{\partial\rho}\left(\rho\frac{\partial n'}{\partial\rho}\right) - \beta n', \qquad [17]$$

a linearisation which dimensional considerations show to be valid when the surface Peclet number $Ua/D_s \ll 1$, and $U/a\beta \ll 1$. There appears to be little experimental data on surface diffusion coefficients, but suggested values are of the order of $10^{-5}\,\text{cm}^2\,\text{sec}^{-1}$ (Levich 1962). Thus, $Ua/D_s \ll 1$ can only be satisfied for sufficiently small Ua. Equations [9], [12] (or [13]) and [17] now combine to provide the appropriate film boundary conditions, and they can be simplified in the special cases (i) $\beta = 0$, and (ii) $D_s = 0$.

When $\beta = 0$, i.e. the surfactant is insoluble in the bulk fluid, [17] can be integrated immediately to give

$$n_0 u = D_s\frac{\partial n'}{\partial\rho} + \frac{A}{\rho}, \qquad [18]$$

where A is a constant of integration. Finiteness of u and n' at $\rho = 0$ implies that $A = 0$, and on combining [9], [12] and [18] we find the film boundary condition

$$-\mu\frac{\partial u}{\partial z} = -\alpha u + (\eta + \kappa)\left\{\frac{1}{\rho}\frac{\partial}{\partial\rho}\left(\rho\frac{\partial u}{\partial\rho}\right) - \frac{u}{\rho^2}\right\} \text{ on } z = 0, \qquad [19]$$

where $\alpha = kTn_0/D_s$. In the case $D_s = 0$, $\beta \neq 0$, from [12] and [17]

$$\frac{\partial p_s}{\partial\rho} = -\frac{n_0kT}{\beta}\left\{\frac{1}{\rho}\frac{\partial}{\partial\rho}\left(\rho\frac{\partial u}{\partial\rho}\right) - \frac{u}{\rho^2}\right\}. \qquad [20]$$

It follows from [9] and [20] that

$$-\mu\frac{\partial u}{\partial z} = \left(\eta + \kappa + \frac{n_0kT}{\beta}\right)\left\{\frac{1}{\rho}\frac{\partial}{\partial\rho}\left(\rho\frac{\partial u}{\partial\rho}\right) - \frac{u}{\rho^2}\right\} \text{ on } z = 0. \qquad [21]$$

To complete the discussion of possible film processes we consider diffusion of a soluble surfactant from the bulk fluid into the film. Let $c(\rho, z)$ denote the concentration of solute in the bulk. For dilute systems it is found that $n(\rho) = h_0c(\rho, 0)$, where h_0 is the adsorption depth as defined by Harper (1972), who also gives some typical values (in the nm or μm range). Throughout the bulk fluid, c satisfies, in the quasi-steady approximation, the convective diffusion equation

$$D_0\nabla^2 c = \mathbf{v}\cdot\nabla c, \qquad [22]$$

where D_0 is the bulk diffusion coefficient. If the Peclet number $Ua/D_0 \ll 1$, then bulk diffusion dominates over convection and c satisfies Laplace's equation

$$\nabla^2 c = 0. \tag{23}$$

(Alternatively, an Oseen-type linearisation could be used.)

It is convenient to define a fictitious "surface pressure" p_s and "surface concentration" n throughout the fluid by

$$p_s = kTh_0 c, \quad n = h_0 c, \tag{24}$$

where the film has been assumed to be gaseous. We also wish to linearise about the equilibrium concentrations n_0 and c_0, and write

$$n = n_0 + n', \quad c = c_0 + c',$$

where, from [23] and [24],

$$\nabla^2 c' = \nabla^2 n' = 0, \tag{25}$$

throughout the bulk fluid. With these definitions, and allowing for surface diffusion, the surface mass-balance condition [14] has the linearised form

$$\frac{n_0}{\rho}\frac{\partial}{\partial \rho}(\rho u) = D_s \frac{1}{\rho}\frac{\partial}{\partial \rho}\left(\rho \frac{\partial n'}{\partial \rho}\right) + D_0\left(\frac{\partial c'}{\partial z}\right)_{z=0}, \tag{26}$$

where the final term represents the diffusion flux to the film from the bulk. As with [17], this linearisation requires that $Ua/D_s \ll 1$. Using the second of equations [24] and [25], [26] may be written in the alternative form

$$\frac{n_0}{\rho}\frac{\partial}{\partial \rho}(\rho u) = -D_s\left(\frac{\partial^2 n'}{\partial z^2}\right)_{z=0} + \frac{D_0}{h_0}\left(\frac{\partial n'}{\partial z}\right)_{z=0}, \tag{27}$$

which must be considered in conjunction with [9] and [11]. Thus, the surface boundary conditions are complete; however we must also supply a boundary condition for c' at the moving solid reaction surface S. The simplest forms of this condition are of either the Dirichlet, Neumann or impedance type. For example, $\partial c'/\partial \nu = 0$ on S, where $\partial/\partial \nu$ denotes differentiation normal to S, corresponds to an impermeable sealed surface.

3. THE STOKESLET PROBLEM

To demonstrate the use of the linearised boundary conditions derived in the previous section, the problem of an axial Stokeslet of strengh $f\hat{\mathbf{z}}$, placed at $\rho = 0$, $z = h$, is considered. In an unbounded fluid the Stokeslet produces a velocity field $\mathbf{v}_0$ with components (u_0, w_0), and a pressure distribution p_0 given by

$$\left.\begin{aligned} u_0 &= \frac{f\rho(z-h)}{R_1^3}, \quad w_0 = f\left(\frac{2}{R_1} - \frac{\rho^2}{R_1^3}\right), \\ p_0 &= \frac{2\mu f(z-h)}{R_1^3} \end{aligned}\right\}. \tag{28}$$

In [28], $R_1 = \{\rho^2 + (z-h)^2\}^{1/2}$, and the pressure at infinity is taken to be zero.

It is readily verified that two solutions of [6] and [7] are furnished by

$$\mathbf{v}_1 = z\nabla\psi - \psi\hat{\mathbf{z}}, \quad p_1 = 2\mu\frac{\partial\psi}{\partial z}, \tag{29}$$

and

$$\mathbf{v}_2 = z\nabla\left(\frac{\partial\chi}{\partial z}\right) - \frac{\partial\chi}{\partial z}\hat{\mathbf{z}} + \nabla\chi, \quad p_2 = 2\mu\frac{\partial^2\chi}{\partial z^2}, \tag{30}$$

where $\psi(\rho, z)$ and $\chi(\rho, z)$ are axisymmetric harmonic functions. Further, $\mathbf{v}_1\cdot\hat{\boldsymbol{\rho}} = 0$ and $\mathbf{v}_2\cdot\hat{\mathbf{z}} = 0$ on $z = 0$. We now represent the velocity and pressure fields in the semi-infinite bulk fluid as

$$\mathbf{v} = \mathbf{v}_0 + \mathbf{v}_1 + \mathbf{v}_2, \quad p = p_0 + p_1 + p_2.$$

The harmonic functions ψ, χ and $n'(\rho, z)$ must be chosen so that on $z = 0$ we have that

$$w = 0, \tag{10}$$

$$kT\frac{\partial n'}{\partial\rho} - \mu\frac{\partial u}{\partial z} - (\eta + \kappa)\left\{\frac{1}{\rho}\frac{\partial}{\partial\rho}\left(\rho\frac{\partial u}{\partial\rho}\right) - \frac{u}{\rho^2}\right\} = 0, \tag{31}$$

$$\frac{n_0}{\rho}\frac{\partial}{\partial\rho}(\rho u) = -D_s\left(\frac{\partial^2 n'}{\partial z^2}\right)_{z=0} + \frac{D_0}{h_0}\left(\frac{\partial n'}{\partial z}\right)_{z=0} - \beta n', \tag{32}$$

where [32] subsumes, for appropriate values of D_s, D_0 and β, each of the models of the previous section.

Suitable representations of ψ, χ and the fictitious surface concentration $n'(\rho, z)$, vanishing as $\rho^2 + z^2 \to \infty$, are

$$\psi(\rho, z) = \int_0^\infty A(s)\,J_0(s\rho)\,\mathrm{e}^{-sz}\,\mathrm{d}s, \tag{33}$$

$$\chi(\rho, z) = \int_0^\infty B(s)\,J_0(s\rho)\,\mathrm{e}^{-sz}\,\mathrm{d}s, \tag{34}$$

and

$$n'(\rho, z) = \int_0^\infty C(s)\,J_0(s\rho)\,\mathrm{e}^{-sz}\,\mathrm{d}s, \tag{35}$$

where ψ, χ, n' are all $o(1)$ as $h \to \infty$ with $Z = z - h$ fixed. Condition [10] implies that

$$\int_0^\infty A(s)\,J_0(s\rho)\,\mathrm{d}s = f\left\{\frac{2}{(\rho^2 + h^2)^{1/2}} - \frac{\rho^2}{(\rho^2 + h^2)^{3/2}}\right\}, \quad 0 \le \rho < \infty; \tag{36}$$

thus, invoking the Hankel inversion theorem, we find that

$$A(s) = f(1 + sh)\,\mathrm{e}^{-hs}. \tag{37}$$

Substituting [37] in [33] and evaluating the infinite integral gives the simple closed form

$$\psi(\rho, z) = f\left\{\frac{1}{R_2} + \frac{h(z + h)}{R_2^3}\right\}, \tag{38}$$

where $R_2 = \{\rho^2 + (z + h)^2\}^{1/2}$.

It remains to determine χ and n'; substituting [34] and [35] into [31] and [32], and subsequent simplification give the relations

$$\int_0^\infty s\{s(2\mu+\gamma s)B(s)+kTC(s)\}J_1(s\rho)\,\mathrm{d}s=\frac{6\mu fh^2\rho}{(\rho^2+h^2)^{5/2}}-\gamma fh\rho\left\{\frac{15h^2}{(\rho^2+h^2)^{7/2}}-\frac{3}{(\rho^2+h^2)^{5/2}}\right\},\tag{39}$$

where $\gamma=\eta+\kappa$, and

$$\int^\infty\left\{-n_0s^2B(s)+\left(D_ss^2+\frac{D_0}{h_0}s+\beta\right)C(s)\right\}J_0(s\rho)\,\mathrm{d}s=\frac{n_0fh(2h^2-\rho^2)}{(\rho^2+h^2)^{5/2}},\quad 0\leqslant\rho<\infty.\tag{40}$$

Applying the Hankel inversion theorem,

$$s(2\mu+\gamma s)B(s)+kTC(s)=fhs(2\mu-\gamma s)\,\mathrm{e}^{-hs},\tag{41}$$

and

$$n_0sB(s)+s^{-1}\Delta(s)C(s)=n_0fhs\,\mathrm{e}^{-hs},\tag{42}$$

where $\Delta(s)=D_ss^2+(D_0/h_0)s+\beta$. $B(s)$ and $C(s)$ are now found as

$$B(s)=-fh\frac{\{n_0kTs+(-2\mu+\gamma s)\Delta\}}{n_0kTs+(2\mu+\gamma s)\Delta}\,\mathrm{e}^{-hs},\tag{43}$$

and

$$C(s)=\frac{4\mu n_0fhs^2}{n_0kTs+(2\mu+\gamma s)\Delta}\,\mathrm{e}^{-hs},\tag{44}$$

thereby completing the computation of χ and n'.

The surface velocity profile is given by

$$u(\rho,0)=-\frac{fh\rho}{(\rho^2+h^2)^{3/2}}+\left(\frac{\partial\chi}{\partial\rho}\right)_{z=0},$$

which, using [34] and [35], can be reduced to

$$u(\rho,0)=-4\mu fh\int_0^\infty\frac{s\Delta}{n_0kTs+(2\mu+\gamma s)\Delta}\,\mathrm{e}^{-hs}J_1(s\rho)\,\mathrm{d}s.\tag{45}$$

It is also a simple matter in this problem to evaluate the unbalanced normal stress at the surface. In terms of ψ and χ, the stress component τ_{zz} is

$$\tau_{zz}=-\frac{6\mu f(z-h)^3}{R_1^5}+2\mu\left(-\frac{\partial\psi}{\partial z}+z\frac{\partial^2\psi}{\partial z^2}+z\frac{\partial^3\chi}{\partial z^3}\right).\tag{46}$$

Thus, on $z=0$, [38] and [46] show that

$$\tau_{zz}=\frac{12\mu fh^3}{(\rho^2+h^2)^{5/2}},\tag{47}$$

a result in accord with that of Lee *et al.* (1979).

4. DRAG FORMULAE

In this section the method of Brenner (1962) is used in conjunction with the results of the previous paragraphs to derive approximate expressions for the drag on an arbitrary axisymmetric particle which moves with velocity $U\hat{\mathbf{z}}$. The z-axis is an axis of rotational symmetry of the particle, and $-F\hat{\mathbf{z}}$, $-F_\infty\hat{\mathbf{z}}$ denote the hydrodynamical drag forces for the semi-infinite and an everywhere infinite bulk fluid, respectively. Our calculations provide formulae for F correct to $O(a^2/h^2)$, where a is a typical particle dimension, and h is the distance of a suitable centre in the solid from the surfactant film.

Brenner's result for the estimation of F when $\epsilon = a/h \ll 1$ depends on the use of the method of reflexions, and is valid for any surface limiting the fluid on which the boundary conditions are linear and homogeneous, requirements satisfied in the present work. Explicitly, F is expressed in the form

$$\frac{F}{F_\infty} = \frac{1}{1 - K(F_\infty/6\pi\mu Ua)\epsilon + O(\epsilon^3)}, \qquad [48]$$

where K is a constant depending only on the presence of the surfactant-covered plane surface, and not on the particle geometry.†

To compute K we first identify the Stokeslet strength f in section 3 with $F_\infty/8\pi\mu$ (see equation (2.15) in Brenner 1962). If $\mathbf{v}_0^{(2)}$ denotes the value of $\mathbf{v}_1 + \mathbf{v}_2$ (given by [29] and [30]), evaluated at the "centre" $\rho = 0$, $z = h$ of the particle (i.e. at the singularity of $\mathbf{v}_0$), then K is given by

$$K = \frac{6\pi\mu h}{F_\infty}(\mathbf{v}_0^{(2)} \cdot \hat{\mathbf{z}}). \qquad [49]$$

Thus, from [29], [30], [34], [38] and [43], K is found as

$$K = \frac{15}{16} + \frac{3h^3}{4}\int_0^\infty s^2 \frac{\{n_0kTs + (-2\mu + \gamma s)\Delta\}}{n_0kTs + (2\mu + \gamma s)\Delta} \mathrm{e}^{-2hs}\,\mathrm{d}s. \qquad [50]$$

Bearing in mind the error estimate in the denominator of [48], the asymptotic expansion of [50], correct to $O(\epsilon)$, is required for insertion in [48].

We proceed to examine the drag formulae supplied by [48] and [50] in various situations. Suppose first that the surfactant is insoluble with surface diffusion as the controlling process. Then $\Delta(s) = D_s s^2$. and

$$K = \frac{15}{16} + \frac{3}{4}K_1, \qquad [51]$$

where

$$K_1 = \int_0^\infty t^2 \frac{(1 - N_1\epsilon t + N_2\epsilon^2 t^2)}{1 + N_1\epsilon t + N_2\epsilon^2 t^2} \mathrm{e}^{-2t}\,\mathrm{d}t, \qquad [52]$$

with $N_1 = 2\mu D_s/n_0kTa$, $N_2 = (\eta + \kappa)D_s/n_0kTa^2$, both dimensionless groups. The ratio $N_2/N_1 = (\eta + \kappa)/2\mu a$ is analagous to the parameter $\lambda = \eta/\mu a$ in the rotation problems (*loc. cit.*). If, for example, N_1, N_2 are both $O(1)$, then

$$K_1 = \frac{1}{4} - \frac{3}{4}N_1\epsilon + O(\epsilon^2),$$

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†That the error term in [48] is $O(\epsilon^3)$ for bodies possessing the symmetry which we envisage has also been established by Williams (1966), using integral-equation methods.

and

$$K = \frac{9}{8}\left(1 - \frac{1}{2}N_1\epsilon\right) + O(\epsilon^2).$$

It follows from [48] that

$$\frac{F}{F_\infty} = 1 + \frac{9}{8}\Phi\epsilon + \frac{9}{16}\Phi\left(\frac{9}{4}\Phi - N_1\right)\epsilon^2 + O(\epsilon^3), \qquad [53]$$

where $\Phi = F_\infty/6\pi\mu Ua$. For a spherical particle, $\Phi = 1$, whereas for a disk-shaped particle moving normal to its plane, $\Phi = 8/3\pi$.

Various other asymptotic limits of [52] can be found for different relative magnitudes of N_1 and N_2 in terms of ϵ, and it is of interest to enquire what numerical values of N_1 and N_2 can be expected. For a surfactant such as stearic acid on an aqueous substrate, $\eta \simeq 10^{-3}$ surface poise, and $\mu \simeq 10^{-2}$ poise. A typical weak concentration has $\eta_0 \sim 10^{12}$ molecules cm^{-2}, and at 25°C, $kT \sim 4 \times 10^{-14}$ erg. There seems to be little experimental information available on D_s, but Levich suggests that it is of the order of the bulk diffusion coefficient, i.e. $D_s \sim 10^{-5}\ \text{cm}^2\ \text{sec}^{-1}$.

We then find that

$$N_1 \sim 10^{-5}/a, \quad N_2 \sim 10^{-6}/a^2.$$

Only for $a \sim 10^{-3}$ cm is $N_2 \sim 1$, and then $N_1 \sim 10^{-2}$. With $N_2/N_1 \sim 100$, the surface is responding to the substrate fluid motion much like a rigid plane. For instance, with $\epsilon \sim 0.1$, $N_1 \sim \epsilon^2$ and correct to $O(\epsilon)$, $K_1 = 1/4$ with $K = 9/8$, the value given by Brenner (1962) for a solid bounding plane.

Consider next the situation in which adsorption and desorption dominate in the film, i.e. $D_s = D_0 = 0$. Then $\Delta(s) = \beta$ and

$$K = \frac{15}{16} + \frac{3}{4}K_2, \qquad [54]$$

where

$$K_2 = \int_0^\infty t^2 \frac{(-1 + N_3\epsilon t)}{1 + N_3\epsilon t} e^{-2t}\, dt, \qquad [55]$$

with $N_3 = (n_0 kT\beta^{-1} + \eta + \kappa)/2\mu a$, a further dimensionless group. As a first example of this situation, suppose that $N_3 \gg 1$ with $\Lambda = N_3\epsilon = O(1)$. Then K_2 can be expressed in terms of the exponential integral $E_1(x)$ (Shail 1979), and

$$K = \frac{3}{8}\left\{3 - \frac{4}{\Lambda^3}e^{2/\Lambda}E_1(2/\Lambda) + \frac{2}{\Lambda^2} - \frac{1}{\Lambda}\right\}. \qquad [56]$$

Thus, since $K = O(1)$, [48] yields, on expansion in powers of ϵ,

$$\frac{F}{F_\infty} = 1 + K\Phi\epsilon + K^2\Phi^2\epsilon^2 + O(\epsilon^3). \qquad [57]$$

If $N_3 = O(1)$, then from [54] and [55]

$$K = \frac{3}{4}\left(1 + \frac{3}{4}N_3\epsilon\right) + O(\epsilon^2). \qquad [58]$$

The appropriate expression for F/F_∞ is now

$$\frac{F}{F_\infty} = 1 + \frac{3}{4}\Phi\epsilon + \frac{9}{16}\Phi(\Phi + N_3)\epsilon^2 + O(\epsilon^3). \qquad [59]$$

A wide variation seems possible for N_3; for $\beta \sim 10^3\,\text{sec}^{-1}$ with the values of η and μ used previously, $N_3 \sim 10^{-1}/a$. For $\beta \sim 10^{-2}\,\text{sec}^{-1}$, we find $N_3 \sim 100/a$. However, little concrete information seems to be available for β in practical situations. Note that for $N_3 = 0$, we recover from [58] and [59] the results for a contaminant-free bounding surface, for which $K = 3/4$.

It remains to discuss the bulk-diffusion dominated model with $D_s = \beta = 0$ and $\Delta(s) = (D_0/h_0)s$. Here,

$$K = \frac{15}{16} + \frac{3}{4}K_3, \qquad [60]$$

where

$$K_3 = \int_0^\infty t^2 \frac{(N_4 - 1 + N_5\epsilon t)}{N_4 + 1 + N_5\epsilon t}\,\mathrm{e}^{-2t}\,\mathrm{d}t, \qquad [61]$$

with $N_4 = h_0 n_0 kT/2\mu D_0$ and $N_5 = (\eta + \kappa)/2\mu a$, the final two dimensionless groups. (N_5 has the structure of the λ-parameter of the rotation problems.) As an illustration we consider F/F_∞ when N_4, N_5 are both $O(1)$. The direct expansion of [61] shows that

$$K_3 = \frac{N_4 - 1}{4(N_4 + 1)} + \frac{3N_5}{4(N_4 + 1)^2}\epsilon + O(\epsilon^2),$$

whence

$$K = \frac{3(3N_4 + 2)}{8(N_4 + 1)} + \frac{9N_5}{16(N_4 + 1)^2}\epsilon + O(\epsilon^2). \qquad [62]$$

Thus, [48] predicts that

$$\frac{F}{F_\infty} = 1 + \frac{3(3N_4 + 2)}{8(N_4 + 1)}\Phi\epsilon + \frac{9\Phi}{64(N_4 + 1)^2}\{4N_5 + (3N_4 + 2)^2\Phi\}\epsilon^2 + O(\epsilon^3). \qquad [63]$$

However, the validity of [63] needs further consideration.

In the solution of the Stokeslet problem and its subsequent application to the translating particle, the boundary condition satisfied by c' at the particle surface is not invoked. This is consistent within the first-reflexion process, since c' is $O(\epsilon)$, as may be verified *a posteriori*, and c' supplies the first-order correction, demanded by the boundary conditions on $z = 0$, to the unperturbed uniform concentration situation. It follows that the $O(\epsilon)$- contribution to [63] is valid, irrespective of the boundary condition on c' at S, the surface of the particle. The same cannot be said of the $O(\epsilon^2)$-term, which only remains correct if the effect of the translating particle on the solute concentration is ignored, i.e. the concentration in the bulk fluid merely adjusts itself in accordance with the boundary conditions on $z = 0$. If this unconvincing approximation cannot be made, then form of the $O(\epsilon^2)$-term in [63] becomes dependent on the boundary condition applied to c' at S. Some examples of this will be given in a subsequent paper, wherein the restriction $a/h \ll 1$ is relaxed.

Further asymptotic limits of [61] can be written down for different relative magnitudes of N_4, N_5 in terms of ϵ. To estimate possible values for N_4 and N_5 we note that a typical adsorption length h_0 is 10^{-4} cm, and bulk diffusion constants of the order of $10^{-5}\,\mathrm{cm}^2\,\mathrm{sec}^{-1}$ are found. Thus for a surfactant with $n_0 \sim 10^{12}$, $\eta \sim 10^{-3}$ and $\mu \sim 10^{-2}$, we have that $N_4 \sim 10$ and $N_5 \sim 1/10a$. It must also be remembered that this bulk-diffusion model refers to small Peclet numbers Ua/D_0.

5. CONCLUDING REMARKS

In this paper a number of linearised models have been considered for the behaviour of the two-phase system in which a surfactant film coats a semi-infinite substrate fluid. In particular, the response of such films, both soluble and insoluble, to the axisymmetric motion generated by a particle of suitable symmetry has been examined. In situations in which the particle is a comparatively large distance from the film, it behaves in first approximation like a point force or Stokeslet applied in the bulk fluid, thus motivating the calculations of Sections 3 and 4 which lead to expressions for the drag force on the particle. In these sections some five dimensionless numbers are introduced, and the asymptotics of estimating the drag force on the particle is seen to depend on the relative magnitudes of these numbers. Thus a plethora of different formulae for F/F_∞ become possible, and a representative selection is given in Section 4.

The number of different physical parameters in the configuration under investigation is relatively large, and values of some of them (e.g. D_s, β) seem to be rare in the literature. However, the linearised models adopted in this paper do allow analytic progress to be made in the solution of meaningful axisymmetric fluid mechanical problems, always within the compass of the quasi-steady Stokes approximation. Future papers in this series will attempt to remove some of the restrictions of this first work, notably with regard to the allowed magnitudes of ϵ and N_i, $i = 1,..,5$. In particular, attention will be focussed on the translating circular disk and sphere. In the former case the well-developed methods for the solution of mixed boundary-value problems are available, and in the latter the use of bispherical coordinates allows progress to be made. External container boundaries for the bulk fluid can also be included.

Further generalisations involve non-axially symmetric situations, typified by a Stokeslet placed in the bulk fluid with its axis parallel to the surfactant film. This configuration models a first approximation to a body moving parallel to the surface, but these and other relevant aspects will be treated elsewhere.

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