Creeping Flow Past a Fluid Globule When a Trace of Surfactant is Present

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The effects of a trace quantity of a surface-active agent on creeping flow past a bubble or droplet are investigated. The equations describing mass and momentum transfer are simultaneously solved by a perturbation technique, consistent with the jump mass and momentum balances at the phase interface. The stream function for the velocity distribution is evaluated as an infinite series of spherical harmonics. Galerkin's method, which reduces the partial differential equation of continuity to a set of ordinary differential equations, is used to evaluate the concentration distribution of surfactant.

A sample calculation is carried out for relative motion between an air bubble and an infinite body of water which contains a trace of isoamyl alcohol. The relative velocity of the water at an infinite distance from the bubble is found to be highly sensitive to small changes in surfactant concentration from zero, although the bubble varies imperceptibly from a spherical shape.

Consider a fluid globule which moves at a constant velocity under the action of gravity through a second immiscible phase. Hadamard and Rybczynski (*1*, p. 395) independently presented a solution to this problem which neglects interfacial effects, but their results failed to explain available experimental data for settling velocities.

This led Boussinesq (*2*) to hypothesize that a skin which inhibits the internal circulation can form around a moving droplet. He described this quantitatively by a constitutive equation which expresses the stress in the interface as a linear function of the rate of deformation of the interface. This relationship, often called the *Newtonian surface fluid model* (*3* to *6*), has two parameters in addition to surface tension: surface shear viscosity and surface dilatational viscosity. Acceptable laboratory measurements of these surface viscosities have not been obtained to date (*7*). Boussinesq (*2*) obtained an exact solution for creeping flow past a droplet under the assumptions that interfacial behavior could be described by the Newtonian surface fluid model and that surface tension and the two surface viscosities were independent of position on the phase interface. The results of Boussinesq's analysis do not appear to be in any better agreement with available experimental data than those of Hadamard and Rybczynski (*1*, p. 403).

Neither the analysis of Boussinesq nor the theory of Hadamard-Rybczynski considers the possible presence of surfactants (materials which have an affinity for a phase interface and which consequently alter the surface tension of a system). In practice it is very difficult to eliminate trace quantities of surface-active materials from an experiment. The observation of a fairly immobile cap on the trailing surface of a droplet (*8*) suggests that any surface-active agents present are not uniformly distributed around the surface, but rather that they are continuously swept toward the rear of the droplet by the fluid motion. If we express surface stress in terms of surface tension alone, the resultant accumulation of surfactants lowers the surface tension at the rear of the droplet and establishes a gradient of surface tension in the surface of the droplet. This gradient induces a shear stress over the droplet's surface which opposes the stress caused by the motion of the droplet relative to the continuous phase.

It is the purpose of this paper to describe quantitatively the effects of trace quantities of surfactants on the motion of a liquid droplet or vapor bubble. To do this, the fluid mechanics problem is solved simultaneously with the associated mass transfer problem.

PREVIOUS WORK

Bond (*9*), and Bond and Newton (*10*) established that drops of sufficiently large dimensions fall at velocities close to those given by Hadamard and Rybczynski, while small drops fall as solid spheres. Bond and Newton (*10*) observed a transition from the Stokes regime of flow (solid sphere) to the Hadamard-Rybczynski regime when the drop's radius passes through a critical value. Haberman and Morton (*11*) reviewed the literature and presented extensive experimental data on the drag and shape of single air bubbles rising freely through various liquids.

Garner and Skelland (*30*) describe the effects of surfactants upon circulation within a droplet and the time of fall of a droplet. Griffith (*8*) discussed the possibility of the formation of immobile caps over the rear of droplets; these caps retard surface flow at the rear surface but leave the forward surface flow unimpeded. Schechter and Farley (*12*) assumed a surface tension distribution which is consistent with a spherical interface and observed that this distribution does not adequately describe observed droplet behavior. They concluded that an explanation is impossible unless the droplet is nonspherical. Matunobu (*13*) attempted an analysis of creeping flow past a deformed droplet in the absence of all interfacial effects. Since the exact solution of this problem given by Hadamard and Rybczynski (*1*, p. 395) shows that the droplet is spherical, Matunobu was not able to find a solution for the deformed droplet which satisfied all of the required boundary conditions.

Levich (*1*, p. 395) presented an extensive treatment of the fall of drops under circumstances such that only the continuous phase contains surfactants. He cited two limiting cases of interest: the magnitude of the flux of surface-

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active material in the bulk liquid at the surface of the droplet is controlled either by adsorption (desorption) at the interface or by diffusion in the bulk liquid. By assuming small deviations of the adsorbed surfactant concentration from that which would exist at equilibrium, Levich obtained a solution for the former case which is consistent with the assumption of a spherical interface. The latter case necessitates a simultaneous solution of the mass and momentum transfer problems and was treated qualitatively.

Lochiel (*14*) presented empirical equations which predict the effect of small quantities of surfactants on mass transfer across a spherical interface, for both small and large Reynolds numbers.

STATEMENT OF PROBLEM

A droplet of known volume of a fluid with density, $\hat{\rho}^*$, and viscosity, $\hat{\eta}^*$, falls by gravity through a second immiscible, unbounded fluid with corresponding properties, ρ^* and η^*. The motion is assumed to be so slow that inertial effects may be neglected in both phases. A small amount of surfactant is present, but is restricted to the unbounded phase. It is assumed that ρ^* and η^* are not functions of the surfactant concentration. We seek the velocity distribution in both phases, the terminal velocity of the droplet, and the shape of the droplet. Surface stress is expressed in terms of surface tension alone, which in turn is allowed to depend upon surfactant concentration.

The problem is discussed in terms of spherical coordinates (Figure 1). For convenience, the unbounded fluid is taken to stream past the droplet in the positive z-direction. The center of mass of the droplet is the origin of the coordinate system.

In order to generalize the results of this calculation, dimensionless variables are used throughout. They are defined by the following scheme.

1. All velocities are normalized with respect to v_∞^*, the magnitude of the velocity of the exterior fluid at infinity in the absence of surfactants. This is the speed calculated by Hadamard and Rybczynski (*1*, equation 70.35) (when the effect of a uniform surface tension is included in their analysis, the same velocity distribution is obtained).
2. All lengths are divided by R^*, where R^* is the radius of a sphere with the same volume as the falling drop.
3. All stresses are divided by $\rho^* v_\infty^{*2}$.

All dimensional variables are distinguished by a superscript asterisk.

GENERAL PLAN OF SOLUTION

The approach used here is generally applicable to free surface problems (*7*).

The first step is to go as far as possible in solving for the velocity distribution and pressure distribution in each of the bulk phases.

(A) Assumptions are made concerning the functional dependence of the three components of velocity in each of the bulk phases.

(B) A relation between stress and deformation is assumed for each of the bulk phases.

(C) For each phase the equation of continuity and the equation of motion are solved simultaneously to obtain a velocity distribution which is consistent with the assumptions in (A) and all boundary conditions other than those at the phase interface.

The phase interfaces are next considered. For simplicity we assume there is only one, as in the problem to be discussed here.

(D) An assumption expressing symmetry may be made about the shape of the phase interface.

(E) An equation relating surface stress and surface deformation (for example, the Newtonian surface fluid model) is assumed. This equation contains parameters which may be affected by surfactants. These parameters may be regarded as functions of the concentration of surfactant in the interface.

(F) In the event a surfactant is present, the equation of continuity is solved to determine its concentration distribution in the interface.

(G) The requirement of continuity of the tangential components of velocity at the phase interface is imposed upon the velocity distributions found in (C).

(H) The velocity distributions within each of the bulk phases are forced to satisfy the jump balances for mass and momentum (3 to 6) and the constitutive equation for surface stress assumed in (E). This may lead to a differential equation describing the shape of the phase interface.

(I) The calculation is checked to see whether there are any contradictions met, such as not being able to satisfy a boundary condition. If all assumptions are correct, there should be no inconsistencies.

BULK FLOWS

The following assumptions are made regarding the flows in the two bulk phases.

1. The flows are time independent and symmetric with respect to the z-axis in Figure 1.
2. There are only two nonzero components of velocity in spherical coordinates: v_r and v_θ in the outer phase and $\hat{v}_r$ and $\hat{v}_\theta$ in the droplet.
3. Inertial terms of the equation of motion are negligible in both phases with respect to the viscous terms.
4. The immiscible bulk fluids are Newtonian and incompressible.

The equation of continuity in the outer phase is automatically satisfied if we express the velocity components, v_r and v_θ, in terms of a stream function ψ,

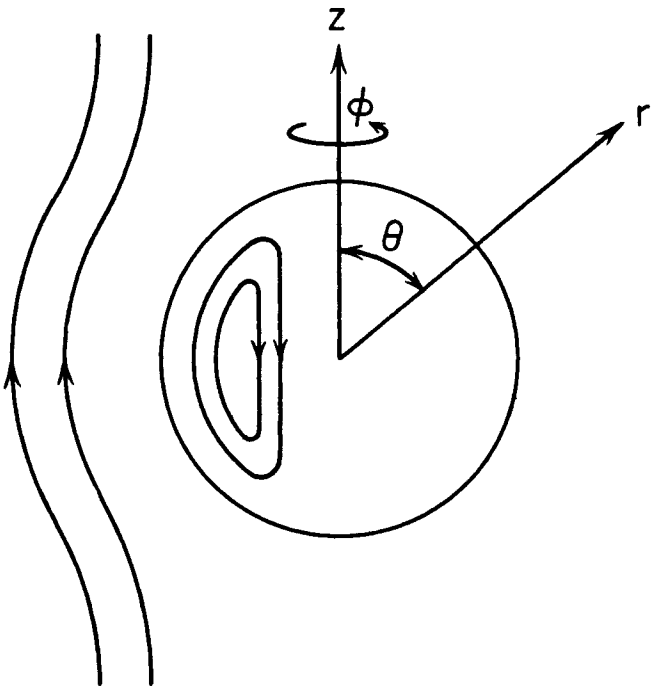

Fig. 1. Coordinate system for droplet.

$$v_r = \frac{1}{r^2}\frac{\partial \psi}{\partial \mu} \tag{1}$$

and

$$v_\theta = \frac{1}{r(1-\mu^2)^{1/2}}\frac{\partial \psi}{\partial r} \tag{2}$$

Here we denote $\mu = \cos\theta$. In a similar manner, we satisfy the equation of continuity for the interior phase by the introduction of a stream function $\hat{\psi}$. After application of the four assumptions above, the equations of motion for the inner and outer fluids are respectively equivalent to (*15*, p. 131)

$$E^4\,\psi = 0 \tag{3}$$

and

$$E^4\,\hat{\psi} = 0 \tag{4}$$

where

$$E^2 = \frac{\partial^2}{\partial r^2} + \frac{(1-\mu^2)}{r^2}\frac{\partial^2}{\partial \mu^2} \tag{5}$$

Other than the requirements to be met at the phase interface, we have the following restrictions on the bulk flows.

(a) The velocity very far from the droplet is uniform and in the positive z-direction,

$$r \to \infty: \quad \psi \to -\tfrac{1}{2}\, r^2\, v_t\,(1-\mu^2) \tag{6}$$

Here v_t is the dimensionless magnitude of the velocity of the exterior fluid at infinity relative to the droplet ($v_t = 1$ when surfactants are absent).

(b) Since we require velocity to be bounded everywhere,

$$r \to 0: \quad \hat{v}_r,\ \hat{v}_\theta \text{ are bounded} \tag{7}$$

and

$$r \to \infty: \quad v_r,\ v_\theta \text{ are bounded} \tag{8}$$

PHASE INTERFACE

We make the following assumptions concerning the phase interface.

5. All interfacial effects associated with momentum transfer are attributed to surface tension and the dependence of surface tension upon the local concentration of surfactant. The Newtonian surface fluid model (*3* to *6*), with the coefficients of surface shear viscosity and surface dilational viscosity identically zero, is used to represent surface stress.

6. It is assumed that there is no mass transfer across the phase interface. Surfactant may be transferred into and out of the interface from the outer phase, but the surfactant is insoluble in the droplet.

7. The interface is fixed in space as a function of time.

8. The tangential components of velocity are continuous across the phase interface.

9. The interface is symmetric with respect to the z-axis.

Before proceeding, it is necessary to discuss the tensor notation used. Latin indices indicate tensor components in three-space; Greek indices denote surface components or tensor components in two-space (*16*). Comma notation stands for covariant differentiation (*16*, p. 197), and the summation convention is employed throughout. Let the x^i ($i = 1, 2, 3$) be a set of curvilinear spatial coordinates; the associated covariant spatial metric tensor components are the g_{ij}. The equations which specify a surface in space are of the form

$$x^i = h^i(u^1, u^2), \quad i = 1, 2, 3 \tag{9}$$

where u^1 and u^2 are two parameters we hereafter refer to as the surface coordinates. The covariant surface metric tensor components, $a_{\alpha\beta}$, are defined as

$$a_{\alpha\beta} = g_{ij}\frac{\partial x^i}{\partial u^\alpha}\frac{\partial x^j}{\partial u^\beta} \tag{10}$$

the determinant of the matrix of these components is denoted by a. The contravariant surface metric tensor components are given by

$$a^{\alpha\beta} = \epsilon^{\alpha\mu}\ \epsilon^{\beta\nu}\ a_{\mu\nu} \tag{11}$$

where $\epsilon^{\alpha\beta} = e^{\alpha\beta}/a^{1/2}$. The quantity $e^{\alpha\beta}$ is skew-symmetric in the two indices with $e^{12} = 1$.

If $\underset{\sim}{\mathrm{p}}$ denotes a position vector, the unit vector $\underset{\sim}{\mathrm{n}}$ normal to the surface is defined such that $\left\{\dfrac{\partial \underset{\sim}{\mathrm{p}}}{\partial u^1},\ \dfrac{\partial \underset{\sim}{\mathrm{p}}}{\partial u^2},\ \underset{\sim}{\mathrm{n}}\right\}$ have the same orientation as the tangents to the spatial coordinate curves (*16*, p. 197),

$$n_i = \frac{1}{2}\ \epsilon^{\alpha\beta}\ \epsilon_{ijk}\frac{\partial x^j}{\partial u^\alpha}\ \frac{\partial x^k}{\partial u^\beta} \tag{12}$$

The quantity ϵ_{ijk} is defined as $g^{1/2}e_{ijk}$, where g is the determinant of the matrix of the covariant spatial metric tensor components, g_{mn}; e_{ijk} is skew-symmetric with $e_{123} = 1$. The mean curvature of a surface, H, is defined as (*16*, p. 205)

$$H = \tfrac{1}{2}\ a^{\alpha\beta}\ b_{\alpha\beta} \tag{13}$$

where the $b_{\alpha\beta}$ are the components of the symmetric tensor in Gauss's formulae (*16*, pp. 200, 203),

$$b_{\alpha\beta} = -\,g_{mn}\ n^m{}_{,\alpha}\frac{\partial x^n}{\partial u^\beta} \tag{14}$$

The application of the preceding formulae to the problem under consideration is summarized here. For a spherical coordinate system in three space, we take

$$x^1 = \theta,\ x^2 = \phi,\ x^3 = r \tag{15}$$

and

$$u^1 = \theta,\ u^2 = \phi \tag{16}$$

It is important to note here that the radial coordinate r is dimensionless; it represents the spherical radial coordinate divided by R^*, where R^* is the radius of a sphere with the same volume as the drop. By assumption 9, the shape of the phase interface is independent of ϕ, so that on the free surface r may be considered to be a function only of θ,

$$x^3 = r = f(\theta) = f(u^1) \tag{17}$$

The covariant spatial metric tensor components are

$$g_{11} = r^2,\ g_{22} = r^2\sin^2\theta,\ g_{33} = 1 \tag{18}$$

The covariant surface metric tensor components are obtained from Equation (10),

$$a_{11} = f^2 + (f')^2,\ a_{22} = f^2\sin^2\theta,\ a_{12} = 0 \tag{19}$$

By f' we mean here the derivative of f with respect to u^1. From Equation (12), the components of the unit normal vector to the surface may be computed to be

$$n^1 = \frac{-f'}{f[f^2 + (f')^2]^{1/2}},\ n^2 = 0,\ n^3 = \frac{f}{[f^2 + (f')^2]^{1/2}} \tag{20}$$

The mean curvature as computed by Equations (13) and (14) is

$$H = -\frac{1}{2[f^2 + (f')^2]^{1/2}}\left[\frac{2(f')^2 - ff'' + f^2}{f^2 + (f')^2} + \frac{f - f'\cot\theta}{f}\right] \tag{21}$$

The interface is represented here by a singular surface or surface of discontinuity. Accordingly, constitutive equations for the stress tensor and mass flux vector (Newton's law of viscosity and Fick's law of diffusion), applicable in each phase at points removed from the interface, are applied in each phase all the way up to the singular surface. In a more detailed description of the problem, these constitutive equations would not be valid in an interfacial region of some thickness, which might or might not include a surface of discontinuity. In order to properly represent the effects of this interfacial region in terms of the singular surface model for the phase interface, artificial sources of mass and momentum are postulated for the singular surface. In keeping with the usual practice in this area, these artificial sources are expressed in terms of a surface stress tensor and a surface mass flux vector. The philosophy of balance equations for the phase interface has been discussed elsewhere (*6*).

In interpreting assumptions 6 and 7, we must remember that we are allowing surfactant from the outer phase to move into and out of the interface. It is assumed that there is no surfactant in the interior phase. One statement equivalent to assumptions 6 and 7 is to say that

$$r = f(\theta): \quad \hat{v}{}^i \; n_i = 0 \tag{22}$$

The overall jump mass balance (*6*, equation 6.6) says that under these circumstances

$$r = f(\theta): \quad v^i \; n_i = 0 \tag{23}$$

Assumption 8 gives a further restriction at the singular surface which represents the phase interface,

$$r = f(\theta): \quad v_i \frac{\partial x^i}{\partial u^\alpha} = \hat{v}_i \frac{\partial x^i}{\partial u^\alpha} \tag{24}$$

In view of assumption 7 and Equations (22) and (23), the jump balance for momentum at the phase interface becomes (*3* to *5*; *6*, equation 7.9)

$$r = f(\theta): \; \hat{t}{}^{ij} \; n_j - t^{ij} \; n_j = \left(\frac{\partial x^i}{\partial u^\alpha} \; t^{\alpha\beta} \right)_{,\beta} \tag{25}$$

where, for the Newtonian surface fluid model under the conditions of assumption 5, the components of the surface stress tensor are given by

$$t^{\alpha\beta} = \sigma \; a^{\alpha\beta} \tag{26}$$

By σ we mean the dimensionless surface tension,

$$\sigma = \sigma^*/\sigma_o^* \tag{27}$$

The reference surface tension σ_o^* will be defined shortly.

After substituting Equation (26) into Equation (25), the two nonzero components of the jump balance for momentum become at $r = f(\theta)$ (*5*, equation 4.7):

$$[\hat{t}{}^{1j} - t^{1j}] \; n_j = \frac{1}{N_{We}} \left[a^{11} \frac{d\sigma}{d\theta} + 2H \; n^1 \; \sigma \right] \tag{28}$$

and

$$[\hat{t}{}^{3j} - t^{3j}] \; n_j = \frac{1}{N_{We}} \left[a^{11} \; f' \frac{d\sigma}{d\theta} + 2H \; n^3 \; \sigma \right] \tag{29}$$

Here N_{We} is the Weber number,

$$N_{We} = \rho^* \; v_\infty{}^{*2} \; R^*/\sigma_o^* \tag{30}$$

Equations (22) to (24), (28) and (29) comprise the set of boundary conditions which the bulk phase velocity distributions must satisfy at the phase interface.

A knowledge of σ as a function of θ on the surface of the droplet is necessary in order to use Equations (28) and (29). Surface tension may be related to the surfactant concentration of the unbounded fluid as follows. The concentration of surfactant in the surface, Γ^* (moles/area), is related to the bulk fluid surfactant concentration, c^* (moles/volume), by Langmuir's adsorption isotherm for un-ionized solutes (*17*, p. 184),

$$\Gamma^* = \frac{k^* c^*}{1 + \dfrac{k^* c^*}{\Gamma_\infty^*}} \tag{31}$$

Here k^* is the Langmuir adsorption coefficient and Γ_∞^* is the limiting value of Γ^* as c^* becomes very large. The surface tension may be related to Γ^* by a form of Gibb's equation (*17*, p. 198),

$$\frac{d\sigma^*}{dc^*} = -\frac{\tilde{R}^* \; T^* \; \Gamma^*}{c^*} \tag{32}$$

Here $\tilde{R}^*$ is the gas constant and T^* is the absolute temperature. After eliminating Γ^* by Equation (31), we may integrate Equation (32) to obtain Szyszkowski's Equation (*18*, p. 62),

$$\sigma = 1 - N_2 \; \ln \left(1 + \frac{k^* c^*}{\Gamma_\infty^*} \right) \tag{33}$$

where $N_2 = \tilde{R}^* \; T^* \; \Gamma_\infty^*/\sigma_o^*$. In this integration we identify σ_o^*, introduced in Equation (27), with the surface tension obtained in the absence of surfactants.

The amount of surfactant adsorbed at the interface must satisfy the jump mass balance (*1*, p. 393; *6*, equation 5.23), which in view of assumption 7 and Equations (22) and (23) may be written as

$$r = f(\theta): \quad j_i \; n^i = -j_{(s)\alpha,\beta} a^{\alpha\beta} \tag{34}$$

where the j_i ($i = 1, 2, 3$) are the components of the dimensionless mass flux vector with respect to the mass average velocity and the $j_{(s)\alpha}$ ($\alpha = 1, 2$) are the components of the dimensionless surface mass flux vector. (In arriving at this equation, we understand equation 5.23 of reference *6* to be written for a particular component in a multicomponent mixture. The mass balance for the particular component is obtained by taking $\psi = 1$ and $\phi_{(\xi)} = 0$.) We are forced to make an assumption about the surface mass flux vector.

10. We use the constitutive equation for surface mass flux vector suggested by Levich (*1*, p. 393), but neglect the effects of surface diffusion,

$$j_{(s)\alpha} = \Gamma \; v_i \frac{\partial x^i}{\partial u^\alpha} \tag{35}$$

Here we introduce

$$\Gamma = \frac{\Gamma^*}{c_\infty^* \; R^*} \tag{36}$$

where c_∞^* is a reference concentration of surfactant in the continuous phase to be defined shortly. If we interpret Equation (34) in the context of reference *6*, the introduction of Equation (35) implies that we assume the kinetics of adsorption (desorption) to be rapid, compared to diffusion of surfactant from the bulk fluid to the drops surface. In the context of Levich's discussion, this last is an additional assumption we make, distinct from Equation (35). Equation (35) allows Equation (34) to be written as

$$r = f(\theta): \; \frac{1}{N_{Pe}} \frac{\partial c}{\partial x^i} \; n^i = \left(\Gamma \; v_i \frac{\partial x^i}{\partial u^\alpha} \; a^{\alpha\beta} \right)_{,\beta} \tag{37}$$

where

$$N_{Pe} = R^* \; v_\infty{}^*/\mathcal{D}^*, \quad c = c^*/c_\infty^* \tag{38}$$

and $\mathcal{D}^*$ is the binary diffusion coefficient for the surfactant

in the bulk phase.

Equation (37) is a boundary condition for the differential mass balance for the surfactant in the outer phase (*15*, p. 559),

$$v_r \frac{\partial c}{\partial r} - (1-\mu^2)^{1/2} \frac{v_\theta}{r} \frac{\partial c}{\partial \mu} = \frac{1}{N_{Pe}} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial c}{\partial r} \right) + \frac{1}{r^2} \frac{\partial}{\partial \mu} \left\{ (1-\mu^2) \frac{\partial c}{\partial \mu} \right\} \right] \tag{39}$$

The other boundary condition is that the concentration of surfactant far from the droplet is c_∞^*,

$$r \to \infty: \quad c \to 1 \tag{40}$$

This completes the formulation of the problem. To summarize, partial differential Equations (3) and (4) must be solved simultaneously with partial differential Equation (39). The boundary conditions for Equations (3) and (4) are Equations (6) to (8), (22) to (24), and (28) to (29), while those for Equation (39) are Equations (37) and (40).

PERTURBATION EQUATIONS FOR SMALL CONCENTRATIONS OF SURFACTANT

An exact solution of the system of equations discussed above does not seem possible at this time. Since the shape of the phase interface is unknown, the problem is necessarily nonlinear.

One method for obtaining a limiting solution to a nonlinear problem is a perturbation analysis. A simple example illustrates the method. Suppose we require u as a function of position, the solution to the partial differential equation $L(u) - w = 0$ with the boundary condition $p(u, \epsilon) = 0$. Here ϵ, a scalar, is a parameter of the problem. We can imagine that, if we were able to obtain an exact solution to the problem and if the solution were suitably continuous as a function of ϵ, the solution could be expanded in a Taylor series of the form

$$u = u^{(0)} + \epsilon\, u^{(1)} + \epsilon^2\, u^{(2)} + \dots \tag{41}$$

This suggests that we assume the solution for u is of the form shown in Equation (41) and that we attempt to determine the first terms in this series. In this way we hope to obtain a solution valid for small values of ϵ. For this reason ϵ is called the perturbation parameter. The analysis proceeds as follows.

1. Solve $L(u) - w = 0$ with $p(u, \epsilon) = 0$, neglecting terms of $0(\epsilon)$ [we write $0(\epsilon)$ for order of ϵ]. The equations are such that this results in a linear problem for $u^{(0)}$, which is more easily solved.
2. Solve $L(u) - w = 0$ with $p(u, \epsilon) = 0$ neglecting terms of $0(\epsilon^2)$. This gives us a linear problem for $u^{(1)}$, which hopefully we may be able to solve also.
3. The process may be repeated, though usually the linear problems encountered at each stage are progressively more difficult to handle.

Van Dyke (*28*) gives a more complete discussion of perturbation methods.

In the sections which follow a perturbation solution to $0(\epsilon)$ is found for Equations (3), (4), and (39) with boundary conditions (6) to (8), (22) to (24), (28) to (29), (37), and (40).

In order to make a choice of perturbation parameters, it is best to have an idea as to which limiting physical situation one wishes to examine. Since we have a solution to our problem for the case of a uniform surface tension [essentially the Hadamard-Rybczynski solution (*1*, p. 395)], it seems most natural to examine the case where very little surfactant is present in the continuous phase or the case where c_∞^* is very small. But the perturbation parameter should be dimensionless. For very small values of $k^* c_\infty^* / \Gamma_\infty^*$ in Equation (33),

$$\sigma = 1 - N_2 \left\{ \frac{k^*\, c_\infty^*}{\Gamma_\infty^*}\, c - \frac{1}{2} \left(\frac{k^*\, c_\infty^*}{\Gamma_\infty^*} \right)^2 c^2 + \frac{1}{3} \left(\frac{k^*\, c_\infty^*}{\Gamma_\infty^*} \right)^3 c^3 + \dots \right\} \tag{42}$$

This suggests defining the perturbation parameter ϵ as

$$\epsilon = \frac{k^*\, c_\infty^*}{\Gamma_\infty^*} \tag{43}$$

so that we may write

$$\sigma = 1 + \epsilon\, \sigma^{(1)} + \epsilon^2\, \sigma^{(2)} + 0(\epsilon^3) \tag{44}$$

or

$$\sigma = 1 - \epsilon\, N_2\, c + 0(\epsilon^2) \tag{45}$$

When ϵ is identically zero, the problem reduces to that solved by Hadamard and Rybczynski. By analogy with Equation (41), we write all of the dependent variables in the problem as Taylor series in ϵ; for example we have

$$\left.\begin{aligned} c &= c^{(0)} + \epsilon\, c^{(1)} + 0(\epsilon^2) \\ \psi &= \psi^{(0)} + \epsilon\, \psi^{(1)} + 0(\epsilon^2) \\ t^{ij} &= t^{(0)ij} + \epsilon\, t^{(1)ij} + 0(\epsilon^2) \\ v_t &= 1 + \epsilon\, v_t^{(1)} + 0(\epsilon^2) \\ f(\theta) &= 1 + \epsilon\, f^{(1)}\theta + 0(\epsilon^2) \end{aligned}\right\} \tag{46}$$

In the next three sections we formulate the equations and boundary conditions appropriate to the perturbation problem before going into the details of the solution.

Bulk Flow Equations for Perturbed System

It follows readily from Equation (3) and (46) that the equations for the zeroth and first perturbations in the outer stream function are respectively

$$E^4\, \psi^{(0)} = 0 \tag{47}$$

and

$$E^4\, \psi^{(1)} = 0 \tag{48}$$

The equations for the zeroth and first perturbations in the inner stream function are analogous.

The zeroth perturbation of the outer velocity components may be expressed in terms of the zeroth perturbation of the outer stream function

$$v_r^{(0)} = \frac{1}{r^2} \frac{\partial \psi^{(0)}}{\partial \mu} \tag{49}$$

and

$$v_\theta^{(0)} = \frac{1}{r(1-\mu^2)^{1/2}} \frac{\partial \psi^{(0)}}{\partial r} \tag{50}$$

Similar expressions may be written for $v_r^{(1)}$, $v_\theta^{(1)}$, $\hat{v}_r^{(0)}$, $\hat{v}_\theta^{(0)}$, $\hat{v}_r^{(1)}$, and $\hat{v}_\theta^{(1)}$.

The boundary conditions at infinity are of the form

$$r \to \infty: \quad \psi^{(0)} \to -\tfrac{1}{2}\, r^2 (1-\mu^2) \tag{51}$$

and

$$r \to \infty: \quad \psi^{(1)} \to -\tfrac{1}{2}\, r^2 (1-\mu^2)\, v_t^{(1)} \tag{52}$$

An entirely equivalent set of boundary conditions adopted here are

$$r \to \infty: \quad \psi^{(0)} \to -\tfrac{1}{2}\, r^2 (1-\mu^2)\, v_t \tag{53}$$

and

$$r \to \infty: \quad \psi^{(1)} \to \text{terms of } 0(r^m) \text{ with } m < 2 \tag{54}$$

In writing Equation (53) we include higher order perturbations in a low order term. This is not incorrect, since terms containing powers of ϵ are collected in ascending order, but it is not customary. When we neglect terms of $0(\epsilon)$, Equations (51) and (53) are equivalent; when terms of $0(\epsilon)$ are included [but terms of $0(\epsilon^2)$ neglected], then $\psi = \psi^{(0)} + \epsilon\ \psi^{(1)}$ calculated by Equations (51) and (52) is equivalent to ψ calculated by Equations (53) and (54).

Equations (7) and (8) may be interpreted by requiring each perturbation in the velocity components to be bounded.

Phase Interface Conditions for Perturbed System

Consider Equations (28) and (29). The covariant stress tensor components for the outer fluid, for example, are

$$t_{ij} = -\ p\ g_{ij} + \frac{1}{N_{Re}}\left[v_{i,j} + v_{j,i}\right] \tag{55}$$

where the nonzero components of $\nabla \underset{\sim}{v}$ are

$$v_{1,1} = -\ (1-\mu^2)^{1/2}\frac{\partial}{\partial \mu}\left(r\ v_\theta\right) + r\ v_r \tag{56}$$

$$v_{1,3} = r\frac{\partial v_\theta}{\partial r} \tag{57}$$

$$v_{2,2} = r\ (1-\mu^2)\ v_r + r\ \mu(1-\mu^2)^{1/2}\ v_\theta \tag{58}$$

$$v_{3,1} = -\ (1-\mu^2)^{1/2}\frac{\partial v_r}{\partial \mu} - v_\theta \tag{59}$$

and

$$v_{3,3} = \frac{\partial v_r}{\partial r} \tag{60}$$

Here p is the (dimensionless) pressure and $N_{Re} = \dfrac{R^*\ v_\infty^*\ \rho^*}{\eta^*}$. Similar equations may be written for the inner fluid. From Equation (20), the perturbed components of the normal to the surface are

$$n^1 = \epsilon(1-\mu^2)^{1/2}\frac{df^{(1)}}{d\mu} + 0(\epsilon^2),\ n^2 = 0,\ n^3 = 1 + 0(\epsilon^2) \tag{61}$$

Equations (55) to (61) may be combined to generate the left side of Equations (28) and (29).

From Equations (21) and (46), we have for the mean curvature H,

$$H = -1 + \epsilon\left\{f^{(1)} + \frac{1}{2}\frac{d}{d\mu}\left[\ (1-\mu^2)\frac{df^{(1)}}{d\mu}\ \right]\right\} + 0(\epsilon^2) \tag{62}$$

This allows us to write the terms on the right of Equations (28) and (29) respectively as

$$a^{11}\frac{d\sigma}{d\theta} + 2H\ n^1\sigma = \epsilon\left[\ N_2\ (1-\mu^2)^{1/2}\frac{dc^{(0)}}{d\mu} - 2(1-\mu^2)^{1/2}\frac{df^{(1)}}{d\mu}\ \right] + 0(\epsilon^2) \tag{63}$$

and

$$a^{11}\ f'\frac{d\sigma}{d\theta} + 2H\ n^3\sigma = -\ 2 + \epsilon\left\{\ 2f^{(1)} + 2N_2\ c^{(0)} + \frac{d\sigma}{d\mu}\left[\ (1-\mu^2)\frac{df^{(1)}}{d\mu}\ \right]\right\} + 0(\epsilon^2) \tag{64}$$

Equations (63) and (64) indicate that it is necessary to evaluate only the zeroth perturbation of the equation of continuity for the surfactant, Equation (39), in order to obtain the information needed to solve for the first perturbation of the stream functions.

The remaining conditions to be satisfied at the phase interface are Equations (22) to (24). These equations imply that at the phase interface $v^i = \hat{v}^i$, which in turn implies that to order zero in the power of ϵ

$$\text{at } r = 1:\quad v_r^{(0)} = \hat{v}_r^{(0)},\quad v_\theta^{(0)} = \hat{v}_\theta^{(0)} \tag{65}$$

and to first-order in the power of ϵ

$$\text{at } r = 1:\ \left\{\frac{\partial v_r^{(0)}}{\partial r} - \frac{\partial \hat{v}_r^{(0)}}{\partial r}\right\} f^{(1)} + v_r^{(1)} = \hat{v}_r^{(1)} \tag{66}$$

$$\text{at } r = 1:\ \left\{\frac{\partial v_\theta^{(0)}}{\partial r} - \frac{\partial \hat{v}_\theta^{(0)}}{\partial r}\right\} f^{(1)} + v_\theta^{(1)} = \hat{v}_\theta^{(1)} \tag{66a}$$

A Taylor series expansion around $r = 1$ is used to evaluate $v_r^{(0)}$ and $v_\theta^{(0)}$ at $r = 1 + \epsilon\ f^{(1)}$. A similar analysis of Equation (23) [which employs Equation (61) for n^i] shows that to order zero in the power of ϵ

$$\text{at } r = 1:\quad v_r^{(0)} = 0 \tag{67}$$

and to first-order in the power of ϵ at $r = 1$:

$$\frac{\partial v_r^{(0)}}{\partial r}\ f^{(1)} + v_r^{(1)} = -\ v_\theta^{(0)}\ (1-\mu^2)^{1/2}\frac{df^{(1)}}{d\mu} \tag{68}$$

Mass Transfer Equations for Perturbed System

Since only the zeroth perturbation of the concentration of surfactant is required, all terms of $0(\epsilon)$ and higher may be neglected in Equation (39) and boundary conditions (37) and (40). The zeroth perturbations of Equations (39) (differential mass balance in outer phase) and (40) are respectively:

$$v_r^{(0)}\frac{\partial c^{(0)}}{\partial r} - (1-\mu^2)^{1/2}\frac{v_\theta^{(0)}}{r}\frac{\partial c^{(0)}}{\partial \mu} = \frac{1}{N_{Pe}}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial c^{(0)}}{\partial r}\right) + \frac{1}{r^2}\frac{\partial}{\partial \mu}\left\{(1-\mu^2)\frac{\partial c^{(0)}}{\partial \mu}\right\}\right] \tag{69}$$

and

$$r \to \infty:\quad c^{(0)} \to 1 \tag{70}$$

Some manipulation is required to obtain the zeroth perturbation of Equation (37). The right side of this equation may be rewritten using an alternate expression for the surface divergence (*16*, p. 187), thus

$$\left(\Gamma\ v_i\frac{\partial x^i}{\partial u^\alpha}\ a^{\alpha\beta}\right)_{,\beta} = \frac{1}{\sqrt{a}}\frac{\partial}{\partial u^\beta}\left(\sqrt{a}\ \Gamma\ v_i\frac{\partial x^i}{\partial u^\alpha}\ a^{\alpha\beta}\right) \tag{71}$$

From Equations (19) and (46), we have

$$\sqrt{a} = [a_{11}\ a_{22}]^{1/2} = (1-\mu^2)^{1/2} + 0(\epsilon) \tag{72}$$

Retaining only those terms of order zero in ϵ, we may obtain from Equation (71),

$$\left(\Gamma\ v_i\frac{\partial x^i}{\partial u^\alpha}\ a^{\alpha\beta}\right)_{,\beta}$$

$$= \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\ \Gamma\ v_i\frac{\partial x^i}{\partial u^1}a^{11}\right) + 0(\epsilon)$$

$$= \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\frac{\sin\theta}{a_{11}}\ \Gamma\ v_1\right) + 0(\epsilon)$$

$$= \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\frac{\sin\theta\sqrt{g_{11}}}{a_{11}}\frac{k^*}{R^*}c^{(0)}\ v_\theta{}^{(0)}\right) + 0(\epsilon)$$

$$= -\frac{k^*}{R^*}\frac{\partial}{\partial\mu}\left[(1-\mu^2)^{1/2}\ c^{(0)}\ v_\theta{}^{(0)}\right] + 0(\epsilon) \qquad (73)$$

In the first stage of this development, we make use of Equation (72) and the assumed symmetry with respect to ϕ; at the second stage we recognize Equations (65) and (67); at the third stage we introduce the physical component of velocity and eliminate Γ by Equation (31). Recognizing Equations (61), we are able to reduce the left side of Equation (37) to

$$\frac{1}{N_{Pe}}\frac{\partial c}{\partial x^i}n^i = \frac{1}{N_{Pe}}\frac{\partial c^{(0)}}{\partial r} + 0(\epsilon) \qquad (74)$$

Equations (73) and (74) together give us the zeroth perturbation of Equation (37) (jump mass balance) in dimensionless form:

at $r = 1 + 0(\epsilon)$:

$$\frac{1}{N_{Pe}}\frac{\partial c^{(0)}}{\partial r} = -\frac{k^*}{R^*}\frac{\partial}{\partial\mu}\left[(1-\mu^2)^{1/2}\ c^{(0)}\ v^{(}{}_\theta{}^{0)}\right] + 0(\epsilon) \qquad (75)$$

Solution of Bulk Flow Equations

A general solution of $E^4\psi = 0$ is (*19* to *22*)

$$\psi = \sum_{n=1}^{\infty}\left[A_n\ r^{n+3} + B_n\ r^{n+1} + C_n\ r^{2-n} + D_n\ r^{-n}\right]Q_n(\mu) \qquad (76)$$

where

$$Q_n(\mu) = \int_\mu^{-1} P_n(\alpha)\ d\alpha \qquad (77)$$

and $P_n(\mu)$ is the Legendre polynomial of degree n. [The quantity $Q_n(\mu)$, defined by Equation (77), is the negative of that introduced by Proudman and Pearson (*20*). The quantity $\{-Q_n(\mu)\}$ is the Gegenbauer polynomial of order $n+1$ and degree $-\frac{1}{2}$; it has been given the symbol $C^{-1/2}{}_{n+1}$ (*26*, p. 125) or $\mathcal{D}_{n+1}$ (*29*, p. 135). Do not mistake $Q_n(\mu)$ for the Legendre function of the second kind.]

The quantities $\psi^{(0)}$ and $\hat{\psi}^{(0)}$ may be obtained either from the Hadamard-Rybczynski solution (*1*, p. 396) or by a solution of the zeroth perturbation problem discussed in the preceding sections. Their values are

$$\psi^{(0)} = \left[-r^2 + \frac{2+3N_3}{2(1+N_3)}\ r - \frac{N_3}{2(1+N_3)}\ \frac{1}{r}\right]Q_1(\mu)\ v_t \qquad (78)$$

and

$$\hat{\psi}^{(0)} = \left[\frac{r^2-r^4}{2(1+N_3)}\right]Q_1(\mu)\ v_t \qquad (79)$$

with $N_3 = \hat{\eta}^*/\eta^*$. The corresponding velocity components may be computed from the stream functions by means of Equations (49) and (50) and the analogous equations for the inner fluid.

The first perturbations of the stream functions, $\psi^{(1)}$ and $\hat{\psi}^{(1)}$, are solutions of Equation (48) and the analogous equation for the inner fluid. From Equation (76), if $\psi^{(1)}$ is required to give bounded velocities far from the droplet, it must be of the form

$$\psi^{(1)} = \sum_{n=1}^{\infty}\left[C_n\ r^{2-n} + D_n\ r^{-n}\right]Q_n(\mu) \qquad (80)$$

In order that velocity components remain bounded at $r = 0$, from Equation (76)

$$\hat{\psi}^{(1)} = \sum_{n=1}^{\infty}\left[A_n\ r^{n+3} + B_n\ r^{n+1}\right]Q_n(\mu) \qquad (81)$$

First perturbation velocity components may be computed from stream functions (80) and (81) by equations similar in form to Equations (49) and (50).

The first perturbation velocity components substituted into Equations (66) (continuity of normal component of velocity), (66*a*) (continuity of tangential component of velocity), and (68) (overall jump mass balance) give respectively three equations relating A_n, B_n, C_n, D_n and $f^{(1)}(\mu)$:

$$A_n + B_n = C_n + D_n \qquad (82)$$

$$(2n+3)A_n + (2n+1)B_n - 2C_n = \frac{3(1-N_3)}{4(1+N_3)}\,n(n+1)\int_{-1}^{1} f^{(1)}\left[P_{n-1}(\mu) - P_{n+2}(\mu)\right]d\mu \qquad (83)$$

and

$$C_n + D_n = \frac{2n+1}{2(1+N_3)}\int_{-1}^{1}\left[\mu\ f^{(1)} - \frac{(1-\mu^2)}{2}\frac{df^{(1)}}{d\mu}\right]P_n(\mu)\ d\mu \qquad (84)$$

Identities (A1), (A2) and (A3) of Appendix A were used in the derivation of Equations (82) to (84).

The components of the jump momentum balance, Equations (28) and (29), yield two additional equations relating A_n, B_n, C_n, D_n and $f^{(1)}(\mu)$. The terms required for evaluation of the left sides of these equations are shown in Equations (55) to (61). Some helpful intermediate relations are given in Appendix B.* The bulk fluid pressures are directly evaluated from the Navier-Stokes equation (*15*, p. 87):

$$N_{Re}\,p = \frac{-(2+3N_3)}{2(1+N_3)}\frac{\mu}{r^2}\left[1+\epsilon v_t{}^{(1)}\right] - \epsilon\sum_{n=1}^{\infty}\frac{2(2n-1)}{n+1}C_n\ r^{-(n+1)}\ P_n(\mu)$$

$$\frac{-N_{Re}}{N_{Fr}}\,r\mu + C_1\ N_{Re} + \epsilon\ C'_1\ N_{Re} + 0(\epsilon^2) \qquad (85)$$

and

$$N_{Re}\,\hat{p} = \frac{5N_3}{1+N_3}\,r\mu\left[1+\epsilon v_t{}^{(1)}\right] - \epsilon\sum_{n=1}^{\infty}\frac{2(2n+3)}{n}N_3\ A_n\ r^n\ P_n(\mu)$$

$$\frac{-N_4\ N_{Re}}{N_{Fr}}\,r\mu + C_{11}\ N_{Re} + \epsilon\ C'_{11}\ N_{Re} + 0(\epsilon^2) \qquad (86)$$

Here

$$N_{Re} = \frac{R^*\ v_\infty{}^*\ \rho^*}{\eta^*} \qquad (87)$$

* Appendix B has been deposited as document NAPS-00384 with the ASIS National Auxiliary Publications Service, c/o CCM Information Sciences, Inc., 22 W. 34th St., New York 10001 and may be obtained for $1.00 for microfiche or $3.00 for photocopies.

and

$$N_{Fr} = \frac{v_\infty^{*2}}{R^* g^*} \tag{88}$$

where g^* is the acceleration of gravity, $N_4 = \hat{\rho}^*/\rho^*$, and C'_I, C_I, C'_{II}, and C_{II} are constants of integration for the pressure. The right sides of Equations (28) and (29) are found in Equations (63) and (64).

Evaluation of Equation (29) yields for the terms of order zero in ϵ:

$$C_I - C_{II} = -2/N_{We} \tag{89}$$

and

$$\frac{N_{Re}}{N_{Fr}}(N_4 - 1) = \frac{3(2 + 3N_3)}{2(1 + N_3)} \tag{90}$$

Equation (29) (r-component of jump momentum balance) to order unity in the power of ϵ is

$$\sum_{n=1}^{\infty} \left\{ \left[2(N_3 - 2) - 2n(1 + N_3) + \frac{6N_3}{n} \right] A_n + [2N_3(1-n) - 2(n+2)] B_n + \frac{6}{n+1} C_n \right\} P_n(\mu) + \frac{6\mu f^{(1)}(1 - N_3)}{1 + N_3} + \frac{(N_4 - 1) N_{Re}}{N_{Fr}} + (C'_I - C'_{II}) N_{Re} - \frac{3(2 + 3N_3)}{2(1 + N_3)} \mu v_t^{(1)} = \frac{N_{Re}}{N_{We}} \left\{ 2 N_2 C^{(0)} + 2f^{(1)} + \frac{d}{d\mu} \left[(1 - \mu^2) \frac{df^{(1)}}{d\mu} \right] \right\} \tag{91}$$

Multiplying Equation (28) (θ-component of jump momentum balance) by n^3, subtracting from that the product of Equation (29) (r-component of jump momentum balance) with n^1, and collecting the first-order terms in ϵ (there are no zero-order terms in ϵ) gives

$$\sum_{n=1}^{\infty} \{2(N_3 - 1) n(n+2) A_n + [2(n^2 - 1) N_3 - 2n(n+2)] B_n + 2(2n+1) C_n\} Q_n(\mu) + \frac{3\mu(1 - \mu^2)}{1 + N_3} \frac{df^{(1)}}{d\mu} (1 - N_3) - \frac{15 N_3}{2(1 + N_3)} f^{(1)}(1 - \mu^2) = \frac{N_2 N_{Re}}{N_{We}} (1 - \mu^2) \frac{dc^{(0)}}{d\mu} \tag{92}$$

Equations (82), (83), (84), (91), and (92) are now simplified. Since the Legendre Polynomials, $P_n(\mu)$, form a complete orthogonal set of functions in the interval $-1 \leq \mu \leq 1$, we may express

$$C^{(0)}|_{r=1} = \sum_{n=0}^{\infty} \gamma_n P_n(\mu) \tag{93}$$

and

$$f^{(1)}(\mu) = \sum_{n=0}^{\infty} \alpha_n P_n(\mu) \tag{94}$$

Since the volume of the distorted drop is equal to the volume of a sphere of radius R^*,

$$\int_{-1}^{1} f^{(1)}(\mu) d\mu = 0 + 0(\epsilon^2) \tag{95}$$

which implies that $\alpha_0 = 0$. The quantity R^* is independent of ϵ, since the interior fluid is assumed to be incompressible. The choice of the droplet's center of mass as the center of the spherical coordinate system requires that

$$\int_{-1}^{1} \mu f^{(1)}(\mu) d\mu = 0 + 0(\epsilon^2) \tag{96}$$

which means that $\alpha_1 = 0$.

After elimination of D_n by use of Equation (82), substitution of Equations (93) and (94), and application of the identities of Appendix A, Equations (83) (continuity of tangential component of velocity), (84) (overall jump mass balance), (91) (r-component of jump momentum balance), and (92) (combination of r- and θ-components of jump momentum balance) become respectively ($n = 1, 2, \ldots$):

$$(2n+3) A_n + (2n+1) B_n - 2C_n = \frac{3(1 - N_3) n(n+1)}{2(1 + N_3)(2n-1)} \alpha_{n-1} - \frac{3(1 - N_3) n(n+1)}{2(1 + N_3)(2n+3)} \alpha_{n+1} \tag{97}$$

$$A_n + B_n = \frac{n(n+1)}{2(1 + N_3)} \left[\frac{\alpha_{n-1}}{2n-1} - \frac{\alpha_{n+1}}{2n+3} \right] \tag{98}$$

$$\left[2(N_3 - 2) - 2n(1 + N_3) + \frac{6N_3}{n} \right] A_n + [2N_3(1-n) - 2(n+2)] B_n + \frac{6}{n+1} C_n - \frac{3(2 + 3N_3)}{2(1 + N_3)} v_t^{(1)} \delta_n^1 = -\left[\frac{6(1 - N_3)}{1 + N_3} + \frac{(N_4 - 1) N_{Re}}{N_{Fr}} \right] \left[\frac{n+1}{2n+3} \alpha_{n+1} + \frac{n}{2n-1} \alpha_{n-1} \right] + \frac{N_{Re}}{N_{We}} [2 - n(n+1)] \alpha_n + \frac{2 N_2 N_{Re}}{N_{We}} \gamma_n \tag{99}$$

and

$$\frac{1}{n(n+1)} [2n(n+2)(N_3 - 1) A_n + \{2(n^2 - 1) N_3 - 2n(n+2)\} B_n + 2(2n+1) C_n] = \frac{[6n(N_3 - 1) - 3(4 + N_3)]}{2(1 + N_3)(2n+3)} \alpha_{n+1} + \frac{[3(3N_3 + 2) + 6n(N_3 - 1)]}{2(1 + N_3)(2n-1)} \alpha_{n-1} + \frac{N_2 N_{Re}}{N_{We}} \gamma_n \tag{100}$$

Here

$$\delta_n^1 = \begin{cases} 0, & n \neq 1 \\ 1, & n = 1 \end{cases} \tag{101}$$

To obtain Equations (97) to (100), the coefficients of $P_n(\mu)$ or $Q_n(\mu)$ were equated to zero for $n = 1, 2, 3, \ldots$. In this way we took advantage of the linear independence of the $P_n(\mu)$ ($n = 1, 2, 3, \ldots$) and of the linear independence of the $Q_n(\mu)$ ($n = 1, 2, 3, \ldots$).

When $n > 1$, Equations (97) to (100) are a system of four simultaneous linear equations with four unknowns (A_n, B_n, C_n, α_{n+1}). [By Equations (95) and (96) we determined that $\alpha_0 = \alpha_1 = 0$.] When $n = 1$, however, an additional unknown, $v_t^{(1)}$, must be determined.

For $n = 1$, Equations (97) to (100) reduce to

$$5A_1 + 3B_1 - 2C_1 = \frac{-3(1 - N_3)}{5(1 + N_3)} \alpha_2 \tag{102}$$

$$A_1 + B_1 = \frac{-\alpha_2}{5(1 + N_3)} \tag{103}$$

$$3(N_3-1)\,A_1-3B_1+\frac{3}{2}\,C_1-\frac{3(2+3N_3)}{4(1+N_3)}\,v_t^{(1)}=$$
$$-\left[\frac{6(1-N_3)}{5(1+N_3)}+\frac{(N_4-1)\,N_{Re}}{5N_{Fr}}\right]\alpha_2+\frac{N_2\,N_{Re}}{N_{We}}\,\gamma_1 \quad (104)$$

and

$$3(N_3-1)\,A_1-3B_1+3C_1=\frac{3(N_3-6)}{10(1+N_3)}\,\alpha_2+\frac{N_2\,N_{Re}}{N_{We}}\,\gamma_1 \quad (105)$$

From Equation (90),

$$\frac{3(N_3-6)}{10(1+N_3)}=-\left[\frac{6(1-N_3)}{5(1+N_3)}+\frac{(N_4-1)\,N_{Re}}{5N_{Fr}}\right] \quad (106)$$

which means that a comparison of Equations (104) and (105) gives

$$v_t^{(1)}=\frac{-2(1+N_3)}{2+3N_3}\,C_1 \quad (107)$$

Equations (102), (103), and (105) contain four unknowns: A_1, B_1, C_1, and α_2. We examine this point further in the next section.

AUXILIARY CONDITIONS

One of the basic steps in the solution of a free-surface problem is to check the calculation to see whether any contradictions are met (see paragraph 1 of the general plan of solution). Three points must be checked for this calculation.

1. Why are there three equations with four unknowns when $n = 1$? (See preceding discussion.)
2. Under what conditions does the Legendre polynomial series for $f^{(1)}(\mu)$, Equation (94), converge? (If this series converges, the velocity expressions converge as well.)
3. Is the macroscopic force balance on the droplet satisfied?

Questions 1 and 2 are related. Our approach yields a solution only if the series for $f^{(1)}(\mu)$ converges. If such a solution exists, then the series for $f^{(1)}(\mu)$ should converge when $\mu = 1$, so that

$$\sum_{n=1}^{\infty}\alpha_n=\text{finite value.} \quad (108)$$

To ensure that this sequence is convergent, we require that it satisfy the ratio test,

$$\lim_{n\to\infty}\left|\frac{\alpha_n}{\alpha_{n-1}}\right|<1 \quad (109)$$

If our sequence $\{\alpha_n\}$ satisfies the ratio test, it is absolutely convergent, which means that $f^{(1)}(\mu)$ is bounded for all values of μ. Equations (97) to (100) may be solved for α_{n+1} by Cramer's rule. When the limit as $n \to \infty$ of this solution is taken, we find that

$$\lim_{n\to\infty}:\frac{\alpha_{n+1}}{\alpha_n}=\frac{-2N_{Re}}{N_{We}}+\frac{\alpha_{n-1}}{\alpha_n} \quad (110)$$

Let us define

$$\lambda_n\equiv\frac{\alpha_n}{\alpha_{n-1}} \quad (111)$$

and

$$\Omega\equiv\frac{2N_{Re}}{N_{We}} \quad (112)$$

This allows us to write Equation (110) more briefly as

$$\lambda_{n+1}=-\Omega+\frac{1}{\lambda_n} \quad (113)$$

Equation (113) is a special case of the Ricatti difference equation; the solution for λ_{n+k}, given λ_n, is (23, p. 324)

$$\lambda_{n+k}=\xi+\left[(-1)^k\left(\frac{\xi}{\Omega+\xi}\right)^k F(\lambda_n)+\frac{1}{\Omega-2\xi}\right]^{-1} \quad k=0,1,2,\ldots, \quad (114)$$

where $F(\lambda_n)$ is a function of λ_n (λ_n is known and fixed) and ξ is defined as

$$\xi\equiv-\frac{\Omega}{2}\pm\left(1+\frac{\Omega^2}{4}\right)^{1/2} \quad (115)$$

When $\Omega/\xi > 0$, λ_{n+k} is bounded as $k \to \infty$ and assumes the value of $+\xi$. In order that $\Omega/\xi > 0$, the positive square root must be chosen in Equation (115) when Ω is positive, and the negative square root must be chosen when Ω is negative. It is seen that $|\xi| < 1$ when ξ is chosen by the above procedure.

A unique value of α_2 may now be computed. By recursive solution of Equations (97) to (100), α_{n-1} is obtained as a linear function of α_2. Similarly α_n may be written as a linear function of α_2. A solution of the linear equation

$$\lim_{n\to\infty}:\frac{\alpha_n}{\alpha_{n-1}}=\xi \quad (116)$$

yields the unique value of α_2. This procedure is illustrated in a subsequent example.

Now let us turn our attention to question (c). Let F_z^* represent z-component of the force which the exterior fluid exerts on the droplet,

$$F_z\equiv\frac{F_z^*}{\rho^*\,R^{*2}\,v_\infty^{*2}}=\int_{S_{\text{drop}}}\frac{\partial z}{\partial x^i}\,t^{ij}\,n_j\,dS \quad (117)$$

At the surface of the droplet we have

$$\frac{\partial z}{\partial x^1}=-f(\mu)\,[1-{}^2\mu]^{1/2},\quad \frac{\partial z}{\partial x^2}=0,\quad \frac{\partial z}{\partial x^3}=\mu \quad (118)$$

From Equation (117) and (118) we obtain

$$F_z=-2\pi\int_{-1}^{1}[(f)^3\,t^{1k}\,n_k\,(1-\mu^2)^{1/2}-(f)^2\,\mu\,t^{3k}\,n_k]\,d\mu \quad (119)$$

In evaluating this integral using the expressions for the stress tensor and unit normal vector previously developed, we find that

$$F_z=\frac{4\pi}{3}\,\frac{N_4}{N_{Fr}}+0(\epsilon^2) \quad (120)$$

But an overall force balance on the droplet indicates that the z-component of the force exerted on the droplet by the exterior fluid should be equal in magnitude and opposite in direction to the action of gravity on the droplet,

$$F_z=\frac{4\pi}{3}\,\frac{N_4}{N_{Fr}} \quad (121)$$

In this way we see that the macroscopic force balance on the droplet is satisfied.

SOLUTION OF MASS TRANSFER PROBLEM

In Equation (93), we assumed that the zeroth-order concentration distribution of surfactant evaluated at the zeroth-order droplet surface, $c^{(0)}|_{r=1}$, could be represented in the form of a series. In this section a method for evalu-

ating the coefficients in this series, γ_i $(i = 0, 1, 2, \ldots)$, is shown.

A solution to partial differential Equation (69) satisfying boundary conditions (70) and (75) is sought. When $v_\theta^{(0)}$ from Equations (50) and (78) is evaluated at $r = 1$, *boundary condition* (75) (jump mass balance) becomes

$$\text{at } r = 1: \quad \frac{\partial c^{(0)}}{\partial r} = \kappa \frac{\partial}{\partial \mu} \left[(1 - \mu^2)\, C^{(0)} \right] \tag{122}$$

where we define

$$\kappa \equiv \frac{k^* N_{Pe}}{2R^*(1 + N_3)} \tag{123}$$

An approximate solution to the mass transfer system may be obtained by Galerkin's method (*24*, p. 261). A trial solution of the form

$$c^{(0)} = \sum_{i=0}^{n} E_i(r)\; P_i(\mu) \tag{124}$$

is assumed. Substituting this trial function into Equation (69) (differential mass balance in outer phase), using previously computed values for $v_r^{(0)}$ and $v_\theta^{(0)}$, and equating multipliers of $P_n(\mu)$ for each n, we obtain the following set of linear ordinary differential equations $(n = 0, 1, 2, \ldots)$

$$E''_n + \frac{2}{r} E_n' - \frac{n(n+1)}{r^2} E_n + \left[-1 + \frac{2 + 3N_3}{4(1 + N_3)} \frac{1}{r} + \frac{N_3}{4(1 + N_3)} \frac{1}{r^3} \right] \left[\frac{n(1-n)}{2n-1} E_{n-1} + \frac{(n+1)(n+2)}{2n+3} E_{n+1} \right] \frac{N_{Pe}}{r} - \left[1 - \frac{(2 + 3N_3)}{2(1 + N_3)} \frac{1}{r} + \frac{N_3}{2(1 + N_3)} \frac{1}{r^2} \right] \left[\frac{n}{2n-1} E'_{n-1} + \frac{n+1}{2n+3} E'_{n+1} \right] N_{Pe} = 0 \tag{125}$$

The prime notation denotes differentiation with respect to r. Substitution of the trial solution, Equation (124), into the boundary conditions, Equations (70) and (75), and equating coefficients of the $P_n(\mu)$ gives $(n = 1, 2, \ldots)$

$$\text{as } r \to \infty: \quad E_0 \to 1, \quad E_n \to 0 \tag{126}$$

and

$$\text{at } r = 1: \quad E'_0 = 0,$$

$$E'_n = \kappa \left[\frac{n(n+1)}{2n+3} E_{n+1} - \frac{n(n+1)}{2n-1} E_{n-1} \right] \tag{127}$$

When Equation (125) is satisfied at all interior points, the truncation error for the differential equation at any interior point, induced by truncating the function after n terms, is proportional to a linear combination of E_n and E'_n. The boundary error is proportional to E_n and is given by

$$-\kappa \left[\frac{(n+1)(n+2)}{2n+1} E_n \right] P_{n+1}(\mu) \tag{128}$$

If the series solution for $c^{(0)}$ is convergent, then $E_n(r) \to 0$ as $n \to \infty$ for all values of r. This means that the truncation errors approach zero as $n \to \infty$.

The coupled, linear system of ordinary differential equations, Equation (125), was solved numerically using a Runge-Kutta integration routine with Simpson's rule check. Each second-order equation is a two-point boundary value problem. We handled these problems by systematically varying the initial values of the dependent variables until, for some practical infinity, the terminal values of the E_n $(n \neq 0)$ approached zero and E_0 approached unity. Further details are given elsewhere (*25*, p. 40).

When N_{Pe} equals zero, a solution of Equation (125) which satisfies the boundary conditions may be obtained in closed form $(n = 1, 2, \ldots)$,

$$\text{for } N_{Pe} = 0: \quad A_0 = 1, \quad A_n = G_n\, r^{-n-1} \tag{129}$$

From the boundary conditions, we find that $(n = 2, 3, \ldots)$

$$G_2 = 5\left(1 - \frac{G_1}{\kappa}\right)$$

$$-\frac{G_n}{\kappa} = \frac{-n}{2n-1} G_{n-1} + \frac{n}{2n+3} G_{n+1} \tag{130}$$

The solution of the entire system is

$$G_1 = \left[\frac{1}{\kappa} + \cfrac{2/15}{1/\kappa + \cfrac{6/35}{1/\kappa + \cfrac{k(k+1)}{(2k+1)(2k+3)}{1/\kappa + \ddots}}} \right]^{-1} \tag{131}$$

$$G_2 = \frac{2}{3} \left[\cfrac{1/\kappa + 6/35}{1/\kappa + \cfrac{4/21}{1/\kappa + \ddots}} \right]^{-1} \tag{132}$$

$$G_3 = \frac{3}{5} \left[\cfrac{1/\kappa + 4/21}{1/\kappa + \cfrac{20/99}{1/\kappa + \ddots}} \right]^{-1} \tag{133}$$

$$G_n = \frac{n}{2n-1} \left[\cfrac{1/\kappa + n(n+1)}{1/\kappa + \cfrac{(2n+1)(2n+3)}{1/\kappa + \ddots}} \right]^{-1} \tag{134}$$

This solution provides a convenient check on the accuracy of the Galerkin computation.

Computations for $n = 5$ using the trial function Equation (124) have been carried out; results are summarized

in Table 1 for the zeroth-order concentration distribution at the droplet surface in terms of the coefficients in Equation (93). Exact solutions for $N_{Pe} = 0$ are tabulated in Table 2.

TABLE 1. THE COEFFICIENTS IN EQUATION (93) FROM THE GALERKIN SOLUTION FOR SEVERAL SETS OF PARAMETERS

κ	N_{Pe}	N_3	γ_0	γ_1	γ_2	γ_3	γ_4	γ_5	r_∞
0.600	0.0	0.00	1.000	0.5731	0.2167	0.07332	0.02343	0.007811	10.0
			1.000	0.5674	0.2144	0.07255	0.02319	0.007729	5.0
			1.000	0.5230	0.1946	0.06567	0.02098	0.006993	2.5
0.600	1.0	0.25	0.9678	0.5275	0.2197	0.08014	0.02694	0.009364	10.0
0.600	10.0	0.25	0.9484	0.3764	0.1855	0.09746	0.04458	0.02440	4.2
0.600	10.0	0.40	0.9442	0.3381	0.1745	0.1021	0.05012	0.03325	4.0
0.600	30.0	0.00	0.9583	0.2244	0.1057	0.09437	0.03760	0.05657	2.0
0.600	100.0	0.25	0.9535	0.2142	0.07373	0.08645	0.02619	0.05228	2.0
0.600	10^3	0.25	0.9746	0.0977	0.01561	0.04796	0.003480	0.03206	1.33
1.00	0.0	0.00	1.000	0.8947	0.5196	0.2691	0.1279	0.07107	10.0
			1.000	0.8864	0.5145	0.2665	0.1267	0.07038	5.0
			1.000	0.8217	0.4703	0.2430	0.1155	0.06414	2.5
1.00	1.0	0.25	0.9514	0.8057	0.4913	0.2643	0.1286	0.07318	10.0
			0.9526	0.8068	0.4920	0.2647	0.1287	0.07327	7.0
			0.9574	0.8103	0.4937	0.2655	0.1291	0.07349	5.0
			0.9636	0.8123	0.4937	0.2653	0.1290	0.07342	4.0
			0.9904	0.7364	0.4210	0.2215	0.1070	0.06079	2.0
1.00	10.0	0.25	0.9216	0.5738	0.3657	0.2385	0.1313	0.09673	4.5
1.00	10.0	0.40	0.9149	0.5160	0.3312	0.2318	0.1301	0.1103	4.3
1.00	10.0	1.00	0.9185	0.5425	0.3483	0.2356	0.1315	0.1042	4.0
1.00	100.0	0.25	0.9261	0.3396	0.1372	0.1662	0.05640	0.1124	2.0
0.059	44.6	0.683	0.9951	0.0243	0.00764	0.00675	0.00205	0.00327	2.0

An inspection of Table 1 shows that the γ_i are relatively insensitive to changes in N_3. All the γ_i, with the exception of γ_0, decrease markedly with an increase in κ. A comparison of the exact results of Table 2 with the computed results of Table 1 indicates excellent agreement, with the exception of the last tabulated coefficient, which is probably most sensitive to the truncation. The exact solution for $\kappa = 10$ indicates a seeming divergence of the γ_i; the γ_i do not begin to converge until $n = 10$. Consequently, accurate solutions for large values of κ may not be obtainable unless a large number of trial functions are used. Table 1 also shows the effect upon $A_i(1)$, of r_∞, the value r taken as the practical infinity in the Galerkin computation. One method of finding values of $A_i(1)$ when $r_\infty = \infty$ is to plot $A_i(1)$ against $1/r_\infty$ and extrapolate the curve to $1/r_\infty = 0$.

An important observation may be made. In every case, when the values of γ_i are substituted back into the trial function for the zeroth-order surfactant concentration on the surface of the droplet, Equation (93), we find that a maximum value for concentration exists at the rear of the droplet ($\mu = 1$).

TABLE 2. COEFFICIENTS IN EQUATION (93) FROM EXACT SOLUTION FOR $N_{Pe} = 0$

κ	0.6	1.0	10.0
n	γ_n	γ_n	γ_n
1	0.57396	0.89590	2.5453
2	0.21700	0.52051	3.7274
3	0.07341	0.26863	4.6344
4	0.02357	0.13103	5.3190
5	0.734×10^{-2}	0.06182	5.8198
6	0.224×10^{-2}	0.02533	6.1698
7	0.674×10^{-3}	0.01297	6.3937
8			6.5154
9			6.5513
10			6.5198
11			6.4309
12			6.3001
13			6.1318
14			5.9403
15	0.355×10^{-7}	0.180×10^{-4}	5.7249

Solution for Rising Gas Bubble

Up until now, we have assumed the droplet to be composed of an incompressible viscous fluid. In what follows, we extend our preceding calculations by treating the droplet as a compressible gas bubble. We assume that the density and viscosity of the gas composing the bubble are much less than those for the surrounding liquid, such that

$$N_3/N_{Re} = 0 \tag{135}$$

and

$$N_4/N_{Fr} = 0 \tag{136}$$

All quantities are taken to be independent of time; this might be achieved by balancing the buoyancy of the bubble by the drag of the exterior fluid moving down past it.

Effects of Compressibility

It is easy to show that pressure within the gas bubble must be independent of position as the result of Equations (135) and (136) as well as the absence of inertial effects.

The volume of the bubble is no longer a constant; it is a function of the pressure within the bubble. This pressure depends upon surface tension; surface tension depends upon local surfactant concentration, and local surfactant concentration in the phase interface depends upon concentration of surfactant at infinity in the exterior fluid through the equation of continuity for the surfactant. In order to specify the bubble's pressure, a datum or reference pressure for the system must be chosen. We specify

$$\text{as } r \to \infty \text{ for } \theta = \frac{\pi}{2}: \quad p = \frac{p^*}{\rho^* v_\infty^{*2}} \to p_\infty \tag{137}$$

Here p_∞ is a constant independent of surfactant concentration. If, for example, the system were vented to the atmosphere at $r \to \infty$, $\theta = \pi/2$, then p^* would be one atmosphere at this point. When Equation (137) is applied to Equation (85), we have from the coefficients of the terms of order unity

$$C_1 = p_\infty \tag{138}$$

and from the terms of order ϵ,

$$C'_1 = 0 \tag{139}$$

From Equations (86), (135), and (136), the dimensionless pressure for the gas which composes the bubble is

$$\hat{p} = C_{11} + \epsilon C'_{11} + 0(\epsilon^2) \tag{140}$$

When all coefficients of $P_0(\mu) = 1$ are collected in Equation (91), we have

$$C'_{11} = -\frac{1}{N_{We}} [2N_2\ \gamma_0 + 2\alpha_0] \tag{141}$$

In arriving at this result, we make use of Legendre's differential equation (*26*, p. 82). From Equation (89), we obtain

$$C_{11} = C_1 + \frac{2}{N_{We}} = p_\infty + \frac{2}{N_{We}} \tag{142}$$

We are now ready to compute the volume of the bubble. In the absence of surfactants, the bubble is a sphere of radius R^* and volume

$$V^{*(0)} = \frac{4}{3}\pi R^{*3} \tag{143}$$

The corresponding bubble pressure is

$$\hat{p}^{*(0)} = C_{11}\ \rho^*\ v_\infty^{*2}$$

When surfactants are present, the bubble pressure is

$$\hat{p}^* = \rho^*\ v_\infty^{*2} [C_{11} + \epsilon C'_{11} + 0(\epsilon^2)]$$

and the volume of the bubble is

$$V^* = \frac{2\pi R^{*3}}{3} \int_{-1}^{1} [1 + \epsilon f^{(1)} + 0(\epsilon^2)]^3\ d\mu$$

$$= \frac{2\pi R^{*3}}{3} \int_{-1}^{1} [1 + 3\epsilon f^{(1)}]\ d\mu + 0(\epsilon^2) \tag{144}$$

When $f^{(1)}$ is given by Equation (94), this reduces to

$$V^* = V^{*(0)} + 4\pi R^{*3}\ \alpha_0\ \epsilon + 0(\epsilon^3) \tag{145}$$

If the gas within the bubble is assumed to behave ideally and if the temperature of the system and the mass of the bubble are constant, we have

$$\hat{p}^{*(0)}\ V^{*(0)} = p^*\ V^* \tag{146}$$

After the appropriate substitutions have been made in Equation (146) for the pressures and volumes, we obtain

$$\alpha_0 = \frac{2\gamma_0\ N_2}{N_{We}\left[3p_\infty + \dfrac{4}{N_{We}}\right]} \tag{147}$$

We may conclude from this computation that it is only α_0 which is altered by the assumption of a compressible gas in the first-order solution. Had the gas been assumed incompressible, α_0 would be zero.

PROBLEM SOLUTION

As the result of Equation (135), the velocity distribution within the bubble can no longer affect the exterior velocity distribution through Equation (25). Equations (22) and (24) may be looked upon as boundary conditions on the interior velocity distribution. This means that the velocity distribution in the exterior fluid is independent of that in the gas bubble. Since we are primarily concerned with the motion of the exterior fluid, we will not determine the stream function for the gas phase.

The stream function for the exterior fluid must satisfy Equations (23) and (25). The equations equivalent to Equations (98) (overall jump mass balance), (99) (r-component of jump momentum balance), and (100) (combination of r- and θ-components of jump momentum balance) are respectively ($n = 1, 2, \ldots$)

$$C_n + D_n = \frac{n(n+1)}{2}\left[\frac{\alpha_{n-1}}{2n-1} - \frac{\alpha_{n+1}}{2n+3}\right] \tag{148}$$

$$\frac{-2(n^2+3n-1)}{n+1} C_n - 2(n+2)\ D_n + \left[6 - \frac{N_{Re}}{N_{Fr}}\right]\left[\frac{n+1}{2n+3}\right]\alpha_{n+1} - 3v_t^{(1)}\ \delta_n{}^1 = \frac{N_{Re}}{N_{We}}[2 - n(n+1)]\,\alpha_n - \left[6 - \frac{N_{Re}}{N_{Fr}}\right]\left[\frac{n}{2n-1}\right]\alpha_{n-1} + \frac{2N_{Re}\,N_2}{N_{We}}\gamma_n \tag{149}$$

and

$$\frac{2(1-n)}{n} C_n - \frac{2(n+2)}{n+1} D_n + \frac{3(n+2)}{2n+3}\alpha_{n+1} = \frac{3(1-n)}{2n-1}\alpha_{n-1} + \frac{N_2\,N_{Re}}{N_{We}}\gamma_n \tag{150}$$

In Equation (149), $\delta_n{}^1$ is the Kronecker delta defined by Equation (101).

Evaluation of Equations (148) to (150) for $n = 1$ yields

$$C_1 + D_1 = \alpha_0 - \alpha_2/5 \tag{151}$$

$$-3D_1 + 1.8\alpha_2 = \frac{N_2\,N_{Re}}{N_{We}}\gamma_1 \tag{152}$$

$$-3C_1 - 6D_1 + 0.4\left[6 - \frac{N_{Re}}{N_{Fr}}\right]\alpha_2 - 3v_t^{(1)} = \left[\frac{N_{Re}}{N_{Fr}} - 6\right]\alpha_0 + \frac{2N_2\,N_{Re}}{N_{We}}\gamma_1 \tag{153}$$

Equations (90), (135), and (136) specify

$$\frac{N_{Re}}{N_{Fr}} = -3 \tag{154}$$

which means that

$$D_1 = 3\alpha_2/5 - \frac{N_2\,N_{Re}}{3N_{We}}\gamma_1 \tag{155}$$

$$C_1 = \alpha_0 - 4\alpha_2/5 + \frac{N_2\,N_{Re}}{3N_{We}}\gamma_1 \tag{156}$$

and

$$v_t^{(1)} = 2\alpha_0 - \frac{N_2\,N_{Re}}{3N_{We}}\gamma_1 + 0.8\alpha_2 \tag{157}$$

[The exterior fluid at infinity must move in the direction of gravity, the negative z-direction, in order to keep the gas bubble suspended in a fixed position as specified earlier. This means that N_{Re} must be negative, which accounts for the sign in Equation (154)]. The coefficient α_2 must be determined by the criteria established in Equations (108) to (116).

Equations (148) to (150), a linear system, may be solved by Cramer's rule. The result is ($n = 2, 3, \ldots$)

$$\alpha_{n+1} = A(n)\ \alpha_n + B(n)\ \alpha_{n-1} + C(n) \tag{158}$$

Here

$$A(n) = \frac{-\Omega\,(n+1)(2n+3)\,[n(n+1)-2]}{2(n^4+n^3-n^2+2n+9)} \tag{159}$$

$$B(n) = \frac{n(2n+3)(n^3+n^2-n-15)}{(2n-1)(n^4+n^3-n^2+2n+9)} \tag{160}$$

and

$$C(n) = \frac{-(2n+3)(n-2)\,\Omega\,N_2\,\gamma_n}{2(n^4+n^3-n^2+2n+9)} \qquad (161)$$

where Ω is defined by Equation (112).

We may now compute a value of α_2. Equation (158) gives for $n = 2$

$$\alpha_3 = A(2)\alpha_2$$

for $n = 3$, we have

$$\alpha_4 = \{A(3)\ A(2) + B(3)\}\,\alpha_2 + C(3)$$

Following this procedure, we find that we may write by induction

$$\alpha_{n+1} = E(n)\alpha_2 + F(n), \quad n = 2, 3, \ldots. \qquad (162)$$

where

$$E(2) \equiv A(2),\ E(3) \equiv A(3)\ E(2) + B(3)$$

$$E(n) \equiv A(n)\ E(n-1) + B(n)\ E(n-2) \quad \text{for } n = 4, 5, \ldots$$

$$F(2) \equiv 0,\ F(3) \equiv C(3)$$

$$F(n) \equiv A(n)\ F(n-1) + B(n)\ F(n-2) \quad \text{for } n = 4, 5, \ldots \qquad (163)$$

From Equations (116) and (162), we may write

$$\lim_{n\to\infty} : \frac{E(n)\,\alpha_2 + F(n)}{E(n-1)\,\alpha_2 + F(n-1)} = \xi$$

or

$$\alpha_2 = \lim_{n\to\infty} : \frac{F(n) - \xi F(n-1)}{\xi E(n-1) - E(n)} \qquad (164)$$

Equation (164) in general must be evaluated by means of a computer. However, if $\Omega >> 1$, Equations (159) and (160) indicate that $|A(n)| >> |B(n)|$. This means that

$$E(n) = A(n)\ E(n-1) \text{ and } F(n) \doteq A(n)\ F(n-1)$$

Referring to Equation (164), we consequently have

$$\frac{F(n) - \xi F(n-1)}{\xi E(n-1) - E(n)} \doteq \frac{-F(n-1)}{E(n-1)} \doteq \frac{-F(n-2)}{E(n-2)} \doteq \ldots \doteq \frac{-F(3)}{E(3)} \qquad (165)$$

Equations (164) to (164) imply

$$\alpha_2 \doteq -\frac{F(3)}{E(3)} \qquad (166)$$

The solution for flow past a stationary gas bubble is illustrated by an example problem in the next section.

Example Problem

Consider an air bubble with an equivalent spherical radius of 1.095×10^{-3} cm. This bubble is held stationary in space by 15°C. water flowing down past it. The water contains a trace of isoamyl alcohol. We seek to determine the velocity of the water at infinity in terms of the alcohol concentration and we wish to evaluate the droplet's shape.

The data for this example are (27), unless noted otherwise:

$$\rho^*_{\text{water}} = 1.00 \text{ g./cc.},$$

$$\eta^*_{\text{water}} = 1.140 \times 10^{-2} \frac{\text{dynes sec.}}{\text{sq.cm.}}$$

$$\sigma_o^* = 73.5 \text{ dynes/cm.},$$

$$N_2 = 0.2019 \ (18, \text{p. } 65),$$

$$\Gamma_\infty^*/k^* = 1.42 \times 10^{-5} \text{ moles/cc. } (18, \text{p. } 65)$$

$$\mathcal{D}^* = 1.25 \times 10^{-6} \text{ sq.cm./sec. (assumed)}$$

By dividing $N_2 \left(= \frac{\tilde{R}\,T^*\,\Gamma_\infty^*}{\sigma_o^*} \right)$ by Γ_∞^*/k^* we find that $k^* = 4.37 \times 10^{-5}$ cm. From Equation (154), we find that $v_\infty^* = -3.43 \times 10^{-2}$ cm./sec. The Reynolds number based upon the radius of the equivalent spherical droplet is $N_{Re} = -3.30 \times 10^{-3}$. The other dimensionless groups required are $N_{Pe} = -30.0$, $\kappa = -0.6$, and $N_{We} = 1.75 \times 10^{-8}$.

When both κ and N_{Pe} are negative (indicating a flow at infinity in the direction of gravity), we may write instead of Equation (124)

$$c^{(0)} = \sum_{i=0}^{n} A_i(r)\ P_i(-\mu) = \sum_{i=0}^{n} (-1)^i\, A_i(r)\ P_i(\mu) \qquad (167)$$

Essentially, when we use this expression, we have made a change of variable $\tilde{\mu} = -\mu$ in Equations (1), (2), (69), (70), and (122). This allows us to use Table 1 to write for this problem

$$c^{(0)}|_{r=1} = 0.9484 - 0.2307\ P_1(\mu) + 0.1003\ P_2(\mu) - 0.09525\ P_3(\mu) + 0.03719\ P_4(\mu) - 0.05622\ P_5(\mu) + \ldots \qquad (168)$$

Since $\Omega\ (= 2N_{Re}/N_{We})$ is very large for this example, we may use Equation (166) to estimate α_2. This indicates that α_2 is of the order 10^{-9} and α_3, α_4, ... are of the same order of magnitude.

If we assume that the pressure in the exterior fluid approaches 1 atm. as $r \to \infty$ for $\theta = \pi/2$, p_∞ is fixed and we estimate from Equation (147) $\alpha_0 = 7.75 \times 10^{-3}$. Since Equation (96) requires that $\alpha_1 = 0$, we see from Equations (46) line 5, and (94) that

$$f(\theta) = 1 + 7.75 \times 10^{-3}\,\epsilon + 0(\epsilon^2) \qquad (169)$$

In order that this first order perturbation solution be meaningful, we must require $\epsilon << 1$ or $c_\infty^* << 1.42 \times 10^{-2}$ moles/liter of isoamyl alcohol. Equation (169) indicates that the air bubble will remain essentially spherical when a trace of isoamyl alcohol is added to the water.

To order ϵ, the velocity of the exterior fluid at infinity is specified by the fourth line in Equation (46) and Equation (157). From the estimates given above, we have

$$v_t = 1 - 2.93 \times 10^3\,\epsilon + 0(\epsilon^2) \qquad (170)$$

or

$$v_t \doteq 1 - 2 \times 10^8\ c_\infty^*. \qquad (171)$$

Here c_∞^* is to be given as moles/cc. This indicates that, even though only a trace of isoamyl alcohol might be present in the system ($\epsilon << 1$), the velocity of the fluid at infinity necessary to balance the buoyancy force and hold the bubble suspended in space might be drastically altered.

DISCUSSION OF OTHER WORK

Levich discusses several mechanisms by which the terminal velocity (velocity of the fluid at infinity required to balance the buoyancy force on the droplet) of the droplet might be decreased (*1*, Sections 74-6):

1. retardation because of surface viscosity (2)
2. retardation because of surface elasticity
3. retardation because of presence of surfactants
   (a) adsorption of surfactant controlling
   (b) bulk diffusion of surfactant controlling
   (c) surface diffusion of surfactant controlling

In all of these cases Levich assumes that the droplet is spherical. He presents his results in terms of a modification of the Hadamard-Rybczynski expression, which becomes in our notation (*1*, Equation 74.10)

$$v_t = \left[\frac{1 + N_3 + e/\eta^*}{2 + 3N_3 + 3e/\eta^*}\right]\left[\frac{2 + 3N_3}{1 + N_3}\right] \quad (172)$$

The value of the coefficient e is dependent upon the mechanism assumed to account for retardation. When $e = 0$, the droplet falls as a fluid sphere (the Hadamard-Rybczynski expression); as $e \to \infty$, the droplet falls as a solid sphere (Stokes law).

Only case 3b above is comparable to the problems discussed here. Levich places no restriction on the concentration of surfactant in the exterior fluid, but does assume that the concentration of surfactant in the surface varies only slightly about some equilibrium value. If we interpret Levich's work in terms of a perturbation solution, the zeroth perturbation corresponds to a droplet suspended in an infinite stagnant fluid containing an arbitrary amount of surfactant. The perturbation parameter would be proportional to the difference in densities of the two fluids. In review, our perturbation parameter is proportional to the concentration of the surfactant at infinity [Equation (43)]; no further restriction is placed upon the concentration distribution in the surface of the droplet (beyond neglecting inertial effects in the equation of motion). Our zeroth perturbation corresponds to the Hadamard-Rybczynski results.

Levich finds for case 3-b that (*1*, Equation 75.8_1)

$$e = \frac{2\tilde{R}\ T^*\ \delta^*}{3D^*\ R^*}\ \frac{k^{*2}\ c_\infty^*}{\left[1 + \dfrac{k^*\ c_\infty^*}{\Gamma_\infty^*}\right]^2} \quad (173)$$

Here δ^* is the average thickness of the diffusion boundary layer. We can compare our results with those of Levich only for sufficiently small values of $\epsilon = \dfrac{k^*\ c_\infty^*}{\Gamma_\infty^*}$, for which Equations (172) and (173) yield

$$v_t = 1 - \frac{2\tilde{R}\ T^*\ \delta^*\ k^{*2}\ c_\infty^*}{3\mathcal{D}^*\ R^*\ \eta^*\ (2 + 3N_3)(1 + N_3)} + 0(\epsilon^2) \quad (174)$$

For the numerical example given previously, Equation (174) gives

$$v_t \doteq 1 - 0.98 \times 10^{12}\ \delta^*\ c_\infty^* \quad (175)$$

where δ^* is measured in centimeters and c_∞^* in moles/cc. The value of δ^* given by Levich (*1*, compare Equations 75.8 and 75.11) assumes $N_{Pe} >> 1$, which does not appear applicable here. There is some further question whether the difference in densities for this example (air-water) is sufficiently small to satisfy Levich s requirement that the concentration of surfactant in the phase interface vary only slightly about some equilibrium value.

CONCLUSIONS

The effects of trace quantities of surface active agents on the motion of a droplet or gas bubble, moving slowly through an unbounded fluid, have been evaluated. Mass transfer of surfactant molecules from the unbounded fluid to the droplet's surface was assumed to be controlled by molecular and convective diffusion in the unbounded fluid. A perturbation solution indicates that the terminal velocity of the droplet can be very sensitive to slight changes of surfactant concentration in the unbounded fluid even though the droplet does not lose its spherical shape.

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NOTATION

a = determinant whose elements are the $a_{\alpha\beta}$ ($\alpha, \beta = 1, 2$)

$a_{\alpha\beta}(a^{\alpha\beta})$ = covariant (contravariant) surface metric tensor components defined by Equations (10) and (11)

$A_n, B_n, C_n, D_n (n=1, 2, \ldots)$ = coefficients in Equations (80) and (81)

$A(n), B(n), C(n)$ = functions of n in Equation (158)

c = dimensionless concentration of surfactant in the exterior fluid defined by Equation (38) line 2

c_∞^* = concentration of surfactant in the exterior fluid at infinity

$C_1, C'_1, C_{11}, C'_{11}$ = constants in Equations (85) and (86)

$\mathcal{D}^*$ = binary diffusion coefficient for the surfactant in the exterior fluid

e = coefficient in Equation (172)

$E_i (i=1, 2, \ldots, n)$ = coefficients in Equation (124)

$E(n), F(n)$ = functions of n in Equation (162)

f = dimensionless function defining the droplet surface in Equation (17)

F_z = dimensionless z-component of the force which the exterior fluid exerts on the droplet; defined by Equation (117), line 1

g^* = acceleration of gravity

g_{ij} = dimensionless metric tensor components (*16* p. 134)

$G_n (n=1, 2, \ldots, n)$ = defined by Equation (129)

H = dimensionless mean curvature of surface; defined by Equation (13)

k^* = Langmuir adsorption coefficient

$n_i(n^i)$ = covariant (contravariant) components of the unit normal to the surface defined such that ($\partial p/\partial u^1$, $\partial p/\partial u^2$, n) have the same orientation as the tangents to the spatial coordinate curves (*16*, p. 197)

$N_2 = \tilde{R}^*\ T^*\ \Gamma_\infty^*/\sigma_o^*$

$N_3 = \hat{\eta}^*/\eta^*$

$N_4 = \hat{\rho}^*/\rho^*$

N_{Fr} = Fronde number defined by Equation (88)

N_{Pe} = Peclet number defined by Equation (38), line 1

N_{Re} = Reynolds number defined by Equation (87)

N_{We} = Weber number defined by Equation (30)

p = pressure made dimensionless with respect to $\rho^*\ v_\infty^{*2}$

p_∞ = limiting value of p as $r \to \infty$ as for $\theta = \pi/2$

$P_n(\mu)$ = Legendre polynomial of degree n

$Q_n(\mu)$ = defined by Equation (77)

r = radial spherical coordinate; made dimensionless with respect to R^*

r_∞ = The practical infinity assumed in the Galerkin computation

R^* = radius of sphere with same volume as droplet

$\tilde{R}^*$ = gas constant

$t_{ij}(t^{ij})$ = dimensionless covariant (contravariant) components of the stress tensor for the exterior fluid; physical components made dimensionless with respect to $\rho^*\ v_\infty^{*2}$

$t^{\alpha\beta}$ = dimenionless contravariant components of the surface stress tensor
T^* = absolute temperature
$u^\alpha (\alpha=1, 2)$ = surface coordinates defined by Equation (16)
$v_i (v^i)$ = dimensionless covariant (contravariant) components of the velocity vector for the exterior fluid
v_r, v_θ = physical components of the velocity vector for the exterior fluid in spherical coordinates; made dimensionless with respect to v_∞^*
v_t = magnitude of velocity of the exterior fluid at infinity in the positive z-direction; made dimensionless with respect to v_∞^*
v_∞^* = terminal speed of droplet (speed of the fluid at infinity in the absence of surfactants)
V^* = volume of gas bubble
$x^i (i=1,2,3)$ = dimensionless curvilinear coordinates; defined by Equation (15)

Greek Letters

$\alpha_n (n=0, 1, \ldots)$ = coefficients in Equation (94)
$\gamma_n (n=0, 1, \ldots)$ = coefficients in Equation (93)
Γ = dimensionless concentration of surfactant in the surface defined by Equation (36)
Γ_∞^* = limiting value of Γ^* as the concentration of surfactant in the exterior fluid becomes very large
δ^* = average thickness of the diffusion boundary layer
ϵ = perturbation parameter defined by Equation (43)
η^* = viscosity of the exterior fluid
θ, φ = spherical coordinate; θ is angle measured from the positive z-axis and φ is angle measured from positive z-axis in the x-y phase
κ = defined by Equation (123)
λ_n = defined by Equation (111)
μ = stands for cos θ
ξ = defined by Equation (115)
ρ^* = density of the exterior fluid
σ = dimensionless surface tension defined by Equation (27)
σ_o^* = surface tension in the absence of surfactants
ψ = dimensionless stream function; defined by Equation (1) and (2)
Ω = defined by Equation (112)

Special Symbols

$\wedge$ = this mark over a quantity indicates an association with the interior fluid
* = as a superscript, this indicates a dimensional quantity
(i) = as a superscript, this indicates the ith perturbation
$,i$ = as a subscript, this indicates covariant differentiation with respect to the curvilinear coordinate x^i (*16*, p. 140)
$,\alpha$ = as a subscript, this indicates covariant differentiation with respect to the surface coordinate u^α (*16*, p. 197)

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APPENDIX A: LEGENDRE POLYNOMIAL IDENTITIES

$$Q_n(\mu) = \frac{1}{2n+1}\left[P_{n-1}(\mu) - P_{n+1}(\mu)\right] \qquad \text{(A-1)}$$

$$(1-\mu^2)\frac{d\,P_n(\mu)}{d\mu} = n(n+1)\,Q_n(\mu) \qquad \text{(A-2)}$$

$$\int_{-1}^{1} Q_n(\mu)\frac{d\,P_m(\mu)}{d\mu}\,d\,\mu = \begin{cases} 0, & m \neq n \\ \dfrac{2}{2n+1}, & m = n \end{cases} \qquad \text{(A-3)}$$

$$\int_{-1}^{1} P_n(\mu)\,P_m(\mu)\,d\,\mu = \begin{cases} 0, & m \neq n \\ \dfrac{2}{2n+1}, & m = n \end{cases} \qquad \text{(A-4)}$$

$$\mu\,Q_n(\mu) = \frac{n-1}{2n+1}Q_{n-1}(\mu) + \frac{n+2}{2n+1}Q_{n+1}(\mu) \qquad \text{(A-5)}$$

$$(1-\mu^2)\,P_n(\mu) = \frac{(n+1)(n+2)}{2n+1}Q_{n+1}(\mu) - \frac{n(n-1)}{2n+1}Q_{n-1}(\mu) \qquad \text{(A-6)}$$

$$(1-\mu^2)\,\mu\frac{d\,P_n(\mu)}{d\,\mu} = n(n+1)\left[\frac{n-1}{2n+1}Q_{n-1}(\mu) + \frac{n+2}{2n+1}Q_{n+1}(\mu)\right] \qquad \text{(A-7)}$$