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# Stokes flow past bubbles and drops partially coated with thin films. Part 1. Stagnant cap of surfactant film – exact solution

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In this investigation the creeping flow due to the motion of a liquid drop or a bubble in another immiscible fluid is examined when the interface is partially covered by a stagnant layer of surfactant. The associated boundary-value problem involves mixed boundary conditions at the interface, which lead to a set of dual series equations. An inversion of these equations yields the exact solution to the stagnant cap problem.

Several useful results are obtained in closed form. Among these are the expressions for the drag force, the difference between the maximum and the minimum interfacial tensions, and the amount of adsorbed surfactant. A shifting of the centre of the internal vortex is observed.

## 1. Introduction

The motion of liquid drops and gas bubbles has aroused a lot of interest for many years. The earliest investigations of the motion of a liquid drop in another immiscible liquid were carried out by Rybczynski (1911) and independetly by Hadamard (1911). The question about the effect of a third component as an impurity has been addressed by numerous investigators. The principal role of the impurity is in the form of a surfactant, which retards the motion by setting up a surface-tension gradient.

Experimental observations by Savic (1953), Garner & Skelland (1955), Elzinga & Banchero (1961), Griffith (1962), Horton, Fritsch & Kintner (1965), Huang & Kintner (1969) and Beitel & Heideger (1971) have all shown that the surfactant often collects in the form of a stagnant cap at the rear of the drop or the bubble, as shown in figure 1. The velocity on each side of the cap has been experimentally observed to vanish. This is frequently the case except for highly soluble surfactants (low Péclet number), for which there is a non-zero velocity over the entire interface. Such flows have been modelled by Levich (1962), Schechter & Farley (1963), Newman (1967), Wasserman & Slattery (1969), Harper (1972, 1982), Saville (1973), Lucassen & Giles (1975), and Levan & Newman (1976). An application of surface shear and surface dilatational viscosities was recently carried out for drops and bubbles by Levan (1981).

The case of creeping flow past a bubble with a stagnant cap has been investigated

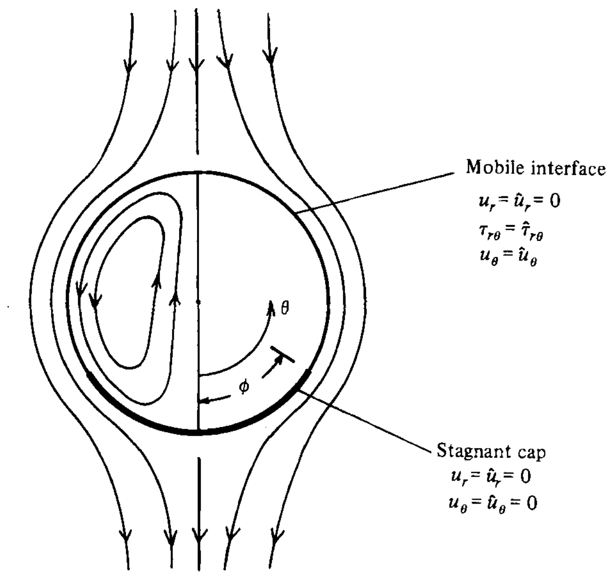


FIGURE 1. A schematic of the physical phenomenon being modelled. The spherical cap having a no-slip condition is denoted by a heavy line.

by Savic (1953), Davis & Acrivos (1966) and Harper (1973, 1982). In each case the difficulty came about in dealing with the mixed boundary conditions due to the stagnant cap. The formulation led to an infinite set of algebraic equations for the coefficients of a series solution. Savic (1953) truncated the series at six terms, while Davis & Acrivos (1966) used 150 terms. Harper (1973, 1982) studied the case of small cap angles and carried out an asymptotic analysis using oblate spheroidal coordinates.

In the present study the problem is generalized to include both drops and bubbles by allowing internal circulation within the drop. We first examine the limits of low Reynolds number and high Péclet number and formally establish the interface conditions appropriate to a stagnant cap. An exact solution is found for the resulting problem for an arbitrary cap angle. Further, a closed-form expression is found for the drag force in terms of viscosities and the cap angle. Also obtained are the closed-form expressions for the difference between the maximum and the minimum interfacial tensions, and the amount of surfactant present on the interface. Both are found as functions of the cap angle.

In addition to being a contribution in the study of surfactants, the present solution is a fundamental building block in the study of another class of flows. These flows will be treated in Part 2, which will consist of an examination of the cases in which the thin film is a liquid continuum with a weak internal circulation. A great deal of interest has been expressed in the study of these flows. Recent laboratory investigations by Mori (1978) have shown some of the characteristics of such flows. Among the specific areas of application are direct-contact heat exchangers (Sideman & Taitel 1964) and artificial blood oxygenation (Li & Asher 1973).

## 2. Governing equations

In this section the governing differential equations are examined in non-dimensional form, and approximations are made in the limits of low Reynolds number and high Péclet number. The resulting mathematical description of a stagnant cap is formally derived for these limits.

For the motion of a drop in an unbounded fluid we employ a fixed coordinate system. The centre of the drop is taken to be the origin. The interface is defined by $r = R$ and we assume that the shape of the drop is spherical. This assumption requires the surface tension force perpendicular to the interface to be large compared with the corresponding viscous force.

The governing equations are given below in non-dimensional form. The physical parameters pertaining to the interior of the drop ($0 \leqslant r < R$) are distinguished from those pertaining to the exterior bulk fluid ($R < r < \infty$) by a 'hat'. The surface phase is denoted by a subscript s.

Continuity:
$$\nabla \cdot \mathbf{u} = 0, \tag{1}$$
$$\nabla \cdot \hat{\mathbf{u}} = 0. \tag{2}$$

Momentum:
$$Re\, \mathbf{u} \cdot \nabla \mathbf{u} = -\nabla p + \nabla^2 \mathbf{u}, \tag{3}$$
$$\widehat{Re}\, \hat{\mathbf{u}} \cdot \nabla \hat{\mathbf{u}} = -\nabla \hat{p} + \nabla^2 \hat{\mathbf{u}}. \tag{4}$$

Surfactant transport (bulk phases):
$$\nabla \cdot (c\mathbf{u}) = \frac{1}{Pe} \nabla^2 c, \tag{5}$$
$$\nabla \cdot (\hat{c}\hat{\mathbf{u}}) = \frac{1}{\widehat{Pe}} \nabla^2 \hat{c}. \tag{6}$$

Surfactant transport (surface phase):
$$\nabla_{\mathrm{s}} \cdot (\mathbf{u}_{\mathrm{s}} \Gamma) - \frac{1}{Pe_{\mathrm{s}}^*} \nabla_{\mathrm{s}}^2 \Gamma = \left[\mathbf{n} \cdot \nabla\left(\frac{c}{Pe_{\mathrm{s}}} - \frac{\hat{c}}{\widehat{Pe}_{\mathrm{s}}}\right)\right]_{\mathrm{s}}. \tag{7}$$

Surface kinetics of adsorption:
$$\left[\mathbf{n} \cdot \nabla\left(\frac{c}{Pe_s} - \frac{\hat{c}}{\widehat{Pe}_{\mathrm{s}}}\right)\right]_{\mathrm{s}} = \frac{K_1 R}{U}\left(\Gamma - \frac{\hat{K}_{-1} \hat{c} c_\infty}{K_1 \Gamma_{\max}} - \frac{K_{-1} c c_\infty}{K_1 \Gamma_{\max}}\right)_{\mathrm{s}}. \tag{8}$$

The dimensionless groups are defined as $Re = UR/\nu$, $\widehat{Re} = UR/\hat{\nu}$, $Pe = UR/D$, $\widehat{Pe} = UR/\hat{D}$, $Pe_{\mathrm{s}}^* = UR/D_{\mathrm{s}}$, $Pe_{\mathrm{s}} = U\Gamma_{\max}/Dc_\infty$, and $\widehat{Pe}_{\mathrm{s}} = U\Gamma_{\max}/\hat{D}c_\infty$. Here $U$ is the velocity of the uniform stream, $\mathbf{u}U$ is the fluid velocity field, $c_\infty$ is the far-field surfactant concentration, $cc_\infty$ is the bulk phase surfactant distribution, $\Gamma_{\max}$ is the maximum concentration in the surface phase, $\Gamma\Gamma_{\max}$ is the surface distribution of surfactant, and $D$ the mass-diffusion coefficient. The pressures are given by $p(\mu U/R)$ and $\hat{p}(\hat{\mu}U/R)$. The constants $K_i$, $K_{-1}$ and $\hat{K}_{-1}$ pertain to the kinetics of adsorption.

We consider the situation $Re$, $\widehat{Re} \to 0$ and first examine the case $Pe$, $\widehat{Pe}$, $Pe_{\mathrm{s}}^* \to \infty$. The latter condition corresponds to either a low solubility of the surfactant or a large translational velocity of the drop. For moderate solubilities and large $U$ the condition $Re$, $\widehat{Re} \to 0$ is only satisfied for the case of very large kinematic viscosities.

With these limiting approximations we have, to leading order, the following description:

$$\nabla p = \nabla^2 \mathbf{u}, \tag{9}$$

$$\nabla \hat{p} = \nabla^2 \hat{\mathbf{u}}, \tag{10}$$

$$\nabla . (c\mathbf{u}) = 0, \tag{11}$$

$$\nabla . (\hat{c}\hat{\mathbf{u}}) = 0, \tag{12}$$

The surface mass conservation condition (7) reduces to

$$\nabla_{\mathrm{s}} . (\Gamma \mathbf{u}_{\mathrm{s}}) = 0. \tag{13}$$

This condition also results for the non-equilibrium limit when a strong adsorption barrier is present. Such a situation corresponds to the case for which $K_1 R/U$, $K_{-1} c_\infty R/\Gamma_{\max} U$, $\hat{K}_{-1} c_\infty R/\Gamma_{\max} U \to 0$. By applying this limit we obtain

$$\left[\mathbf{n}.\nabla\left(\frac{c}{Pe_{\mathrm{s}}} - \frac{\hat{c}}{\widehat{Pe}_{\mathrm{s}}}\right)\right]_{\mathrm{s}} = 0. \tag{14}$$

In this case, the bulk diffusion is much faster than the adsorption–desorption, which therefore controls the process. By substituting (14) into (7) and neglecting surface diffusion ($Pe_{\mathrm{s}}^* \to \infty$), we obtain (13).

The integration of (13) in spherical coordinates leads to

$$u_{\mathrm{s}} \Gamma = \frac{A}{\sin\theta}, \tag{15}$$

where $A$ is an integration constant. In order to have bounded solutions at $\theta = 0$ and $\theta = \pi$ we must set $A \equiv 0$. Therefore

$$u_{\mathrm{s}} \Gamma = 0, \tag{16}$$

which implies that on any part of the interface we have either

$$u_{\mathrm{s}} = 0 \tag{17}$$

or

$$\Gamma = 0. \tag{18}$$

Hence we impose the interface condition that wherever the surfactant is present ($\Gamma \neq 0$) we have the no-slip condition

$$u_{\mathrm{s}} = 0 \quad (0 \leqslant \theta < \phi), \tag{19}$$

and on the regions where the interface is mobile ($u_{\mathrm{s}} \neq 0$), we have

$$\Gamma = 0 \quad (\phi < \theta \leqslant \pi), \tag{20}$$

which leads to the continuity condition that the shear stresses on each side of the interface are equal over the region $\phi < \theta \leqslant \pi$.

## 3. Solution

In order to solve this set of equations we introduce dimensionless axially symmetric stream functions, viz

$$u_r = \frac{1}{r^2 \sin\theta}\frac{\partial\psi}{\partial\theta}, \quad u_\theta = \frac{-1}{r\sin\theta}\frac{\partial\psi}{\partial r} \quad (1 < r < \infty), \tag{21}$$

$$\hat{u}_r = \frac{1}{r^2 \sin\theta}\frac{\partial\hat{\psi}}{\partial\theta}, \quad \hat{u}_\theta = \frac{-1}{r\sin\theta}\frac{\partial\hat{\psi}}{\partial r} \quad (0 \leqslant r < 1). \tag{22}$$

Here the radial coordinate is nondimensionalized with respect to the drop radius $R$.

For creeping flow the stream functions obey the Stokes equations

$$L_{-1}^2(\psi) = 0, \tag{23}$$

$$L_{-1}^2(\hat{\psi}) = 0, \tag{24}$$

where
$$L_{-1} = \frac{\partial^2}{\partial r^2}+\frac{1}{r^2}\sin\theta\frac{\partial}{\partial\theta}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\right). \tag{25}$$

The boundary and interface conditions are as follows.

(i) Uniform stream at $\infty$:
$$\psi|_{r\to\infty} = \tfrac{1}{2}r^2\sin^2\theta. \tag{26}$$

(ii) Vanishing radial velocity at the interface:

$$\psi|_{r=1} = \hat{\psi}|_{r=1} = 0 \quad (0 \leqslant \theta \leqslant \pi). \tag{27}$$

(iii) Vanishing tangential velocity along the stagnant cap:

$$\left.\frac{\partial\psi}{\partial r}\right|_{r=1} = \left.\frac{\partial\hat{\psi}}{\partial r}\right|_{r=1} = 0 \quad (0 \leqslant \theta < \phi). \tag{28}$$

(iv) Continuity of the tangential velocity along the 'clean' interface:

$$\left.\frac{\partial\psi}{\partial r}\right|_{r=1} = \left.\frac{\partial\hat{\psi}}{\partial r}\right|_{r=1} \quad (\phi < \theta \leqslant \pi). \tag{29}$$

(v) Continuity of the shear stress along the 'clean' interface:

$$\left.\frac{\partial}{\partial r}\left(\frac{1}{r^2}\frac{\partial\psi}{\partial r}\right)\right|_{r=1} = \frac{\hat{\mu}}{\mu}\left.\frac{\partial}{\partial r}\left(\frac{1}{r^2}\frac{\partial\hat{\psi}}{\partial r}\right)\right|_{r=1} \quad (\phi \leqslant \theta < \pi). \tag{30}$$

(vi) Finite velocity at the origin:

$$\frac{1}{r^2}\hat{\psi}|_{r\to 0} < \infty. \tag{31}$$

Here $\mu$ and $\hat{\mu}$ are the exterior and the drop-interior viscosities respectively.

The general solution of (23) and (24) satisfying the boundary conditions (26), (27), (29) and (31) is

$$\psi = \left\{\left(r^2-\frac{1}{r}\right)\int_{\cos\theta}^{1} P_1(x)\,dx + \sum_{k=1}^{\infty} C_k^*[r^{-k+2}-r^{-k}]\int_{\cos\theta}^{1} P_k(x)\,dx\right\}, \tag{32}$$

$$\hat{\psi} = \left\{\tfrac{3}{2}(r^4-r^2)\int_{\cos\theta}^{1} P_1(x)\,dx + \sum_{k=1}^{\infty} C_k^*[r^{k+3}-r^{k+1}]\int_{\cos\theta}^{1} P_k(x)\,dx\right\}, \tag{33}$$

where $P_k(x)$ is the Legendre polynomial.

An attempt to satisfy (28) and (30) yields the following set of dual series equations:

$$\sum_{k=1}^{\infty} C_k^*\int_{\cos\theta}^{1} P_k(x)\,dx = -\frac{3}{2}\int_{\cos\theta}^{1} P_1(x)\,dx \quad (0 \leqslant \theta < \phi), \tag{34}$$

$$\sum_{k=1}^{\infty} (2k+1)\,C_k^*\int_{\cos\theta}^{1} P_k(x)\,dx = -\frac{3(2\mu+3\hat{\mu})}{2(\mu+\hat{\mu})}\int_{\cos\theta}^{1} P_1(x)\,dx \quad (\phi < \theta \leqslant \pi). \tag{35}$$

The integrals of the Legendre polynomials may expressed as

$$\int_{\cos\theta}^{1} P_k(x)\,dx = \sin\theta\, T_k^{-1}(\cos\theta), \tag{36}$$

where $T_k^m(\cos\theta)$ denotes the associated Legendre functions. With this notation, and by defining

$$C_1 = C_1^* + \frac{2\mu+3\hat{\mu}}{2(\mu+\hat{\mu})}, \tag{37}$$

$$C_k = C_k^* \quad (k \geqslant 2), \tag{38}$$

we find that the set of dual series equations (34), (35) takes the form

$$\sum_{k=1}^{\infty} C_k T_k^{-1}(\cos\theta) = -\frac{\mu}{4(\mu+\hat{\mu})}\sin\theta \quad (0 \leqslant \theta < \phi), \tag{39}$$

$$\sum_{k=1}^{\infty} C_k(2k+1)\, T_k^{-1}(\cos\theta) = 0 \quad (\phi < \theta \leqslant \pi). \tag{40}$$

An exact solution to this set of dual series equations is found by using the method introduced by Collins (1961). We first find an expression for

$$h(\theta) = \sum_{k=1}^{\infty} C_k(2k+1)\, T_k^{-1}(\cos\theta) \quad (0 \leqslant \theta < \phi). \tag{41}$$

Upon following Collins (1961), we find this to be given by

$$h(\theta) = -2\operatorname{cosec}\theta \tan\tfrac{1}{2}\theta \frac{d}{d\theta}\int_\theta^\phi \frac{H(\xi)\sin\xi\, d\xi}{(\cos\theta-\cos\xi)^{\frac{1}{2}}}, \tag{42}$$

where
$$H(\xi) = \frac{(\cot\frac{1}{2}\xi)^2}{\pi}\frac{d}{d\xi}\int_0^\xi \frac{\sin\theta\tan\frac{1}{2}\theta\,[-\mu/4(\mu+\hat{\mu})\sin\theta]\,d\theta}{(\cos\theta-\cos\xi)^{\frac{1}{2}}}. \tag{43}$$

After some manipulation of (42) and (43), $h(\theta)$ is found to be

$$h(\theta) = -\frac{\mu}{\pi(\mu+\hat{\mu})}\tan\tfrac{1}{2}\theta\left\{\tfrac{3}{2}(1+\cos\theta)\left[\arcsin\left(\frac{\cos\theta-\cos\phi}{1+\cos\theta}\right)^{\frac{1}{2}} + \frac{(\cos\theta-\cos\phi)^{\frac{1}{2}}(1+\cos\phi)^{\frac{1}{2}}}{1+\cos\theta}\right] + \frac{(1+\cos\phi)^{\frac{3}{2}}}{(\cos\theta-\cos\phi)^{\frac{1}{2}}}\right\}. \tag{44}$$

Upon the application of the orthogonality principle for the set

$$\{T_k^{-1}(\cos\theta),\ k = 1,2,3,\ldots\}$$

in the Legendre series

$$\sum_{k=1}^{\infty} C_k(2k+1)\, T_k^{-1}(\cos\theta) = \begin{Bmatrix} h(\theta) & (0 \leqslant \theta < \phi) \\ 0 & (\phi < \theta \leqslant \pi)\end{Bmatrix} \tag{45}$$

we find

$$C_k = C_k^* = \frac{\mu}{4\pi(\mu+\hat{\mu})}\left\{\sin(k+2)\phi - \sin k\phi + \sin(k+1)\phi - \sin(k-1)\phi - 2\left[\frac{\sin(k+2)\phi}{k+2} + \frac{\sin(k-1)\phi}{k-1}\right]\right\} \quad (k \geqslant 2), \tag{46}$$

$$C_1 = -\frac{\mu}{4\pi(\mu+\hat{\mu})}\,[2\phi + \sin\phi - \sin 2\phi - \tfrac{1}{3}\sin 3\phi], \tag{47}$$

$$C_1^* = -\left\{\frac{\mu}{4\pi(\mu+\hat{\mu})}\,[2\phi + \sin\phi - \sin 2\phi - \tfrac{1}{3}\sin 3\phi] + \frac{2\mu+3\hat{\mu}}{2(\mu+\hat{\mu})}\right\}. \tag{48}$$

The complete solution is given by equations (32)–(33) with $C_k^*$ given by (46)–(48). A discussion of several pieces of useful information that can be obtained from this solution is presented in §4.

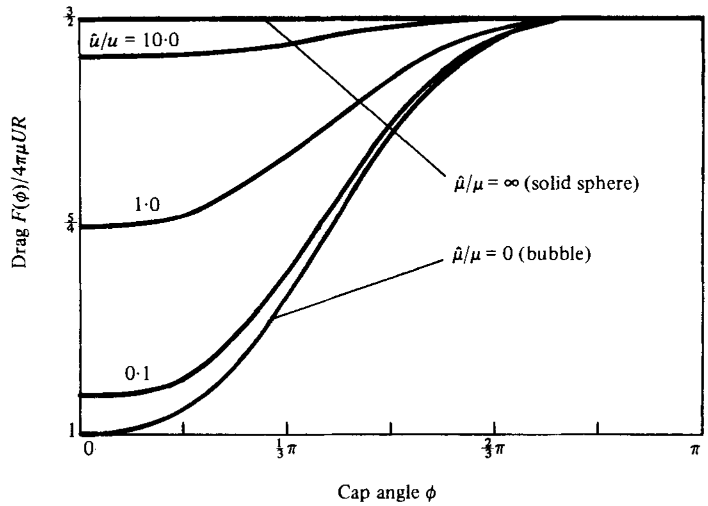


FIGURE 2. The drag force as a function of the cap angle $\phi$ for various values of the viscosities ratio $\hat{\mu}/\mu$.

## 4. Results and discussion

### 4.1. *The drag force*

An expression for the drag force is of fundamental interest in the type of flow being examined. For axisymmetric creeping flows, the drag force is given by Payne & Pell (1960) as

$$F = -8\pi\mu UR \lim_{r\to\infty} \frac{\psi - \frac{1}{2}r^2 \sin^2\theta}{r\sin^2\theta}, \tag{49}$$

where $R$ is the drop radius. For the present case the following closed-form expression for the drag is found:

$$F(\phi) = 4\pi\mu UR \left\{\frac{\mu}{4\pi(\mu+\hat{\mu})}[2\phi + \sin\phi - \sin 2\phi - \tfrac{1}{3}\sin 3\phi] + \frac{2\mu+3\hat{\mu}}{2\mu+2\hat{\mu}}\right\}. \tag{50}$$

This result for the drag is plotted in figure 2 as a function of the cap angle $\phi$ for various values of the viscosity ratio $\hat{\mu}/\mu$.

For the limiting case of $\phi = 0$ (no surfactant), we recover the Hadamard–Rybczynski result

$$F(0) = 4\pi\mu UR\,\frac{2\mu+3\hat{\mu}}{2\mu+2\hat{\mu}}. \tag{51}$$

For the case $\phi = \pi$ (completely stagnant interface), we obtain the solid-sphere result

$$F(\pi) = 6\pi\mu UR. \tag{52}$$

In the limit of the drop viscosity becoming infinitely large ($\hat{\mu}\to\infty$), the solid-sphere drag is also obtained. The drag force for the special case of a bubble is easily obtained from (50) by letting $\hat{\mu}\to 0$. This yields

$$F(\phi)_{\text{bubble}} = 4\pi\mu UR\left\{\frac{1}{4\pi}[2\phi+\sin\phi - \sin 2\phi - \tfrac{1}{3}\sin 3\phi] + 1\right\}. \tag{53}$$

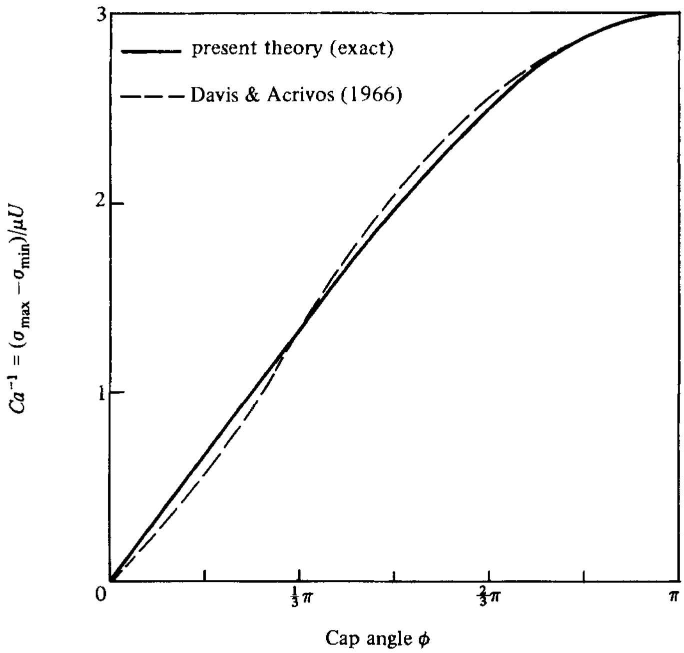


FIGURE 3. The reciprocal of the capillary number as a function of the cap angle $\phi$.

A Taylor-series expansion of (50) for small $\phi$ leads to Harper's (1982) result

$$F(\phi) \sim \frac{2\pi\mu UR}{\mu+\hat{\mu}}\left[(2\mu+3\hat{\mu})+\frac{4\phi^3}{3\pi}\mu\right]. \tag{54}$$

The recovery of this result from the present generalization indeed provides mutual confirmation about the accuracy.

### 4.2. *The interfacial tension*

The usefulness of the present result can be considerably enhanced by relating it to as many physically measurable quantities as possible. The difference between the maximum and the minimum interfacial tensions is one measurable quantity. It is possible to relate this difference to the cap angle. Since the jump in the interfacial shear stress is proportional to the interfacial tension gradient, we have

$$\frac{1}{R}\frac{d\sigma}{d\theta} = \tau_{r\theta}-\hat{\tau}_{r\theta} = -\frac{U}{R}\frac{r}{\sin\theta}\frac{\partial}{\partial r}\left[\frac{1}{r^2}\frac{\partial}{\partial r}(\mu\psi-\hat{\mu}\hat{\psi})\right], \tag{55}$$

where $\sigma(\theta)$ is the interfacial tension and $\tau_{r\theta}$ and $\hat{\tau}_{r\theta}$ are the appropriate shear stresses. Upon the substitution of (32), (33) into (55), and with the use of (41), we find that

$$\frac{1}{\mu U}\frac{d\sigma}{d\theta} = \sum_{k=1}^{\infty} C_k(2k+1)\,T_k^{-1}(\cos\theta) = h(\theta), \tag{56}$$

where $h(\theta)$ is given by (42)–(44).

Davis & Acrivos (1966) integrated (55) for bubbles ($\hat{\tau}_{r\theta} = 0$) and obtained a numerical relationship between ($\sigma_{max}-\sigma_{min}$) and $\phi$. The integration of (56) for the present case yields the following closed-form result:

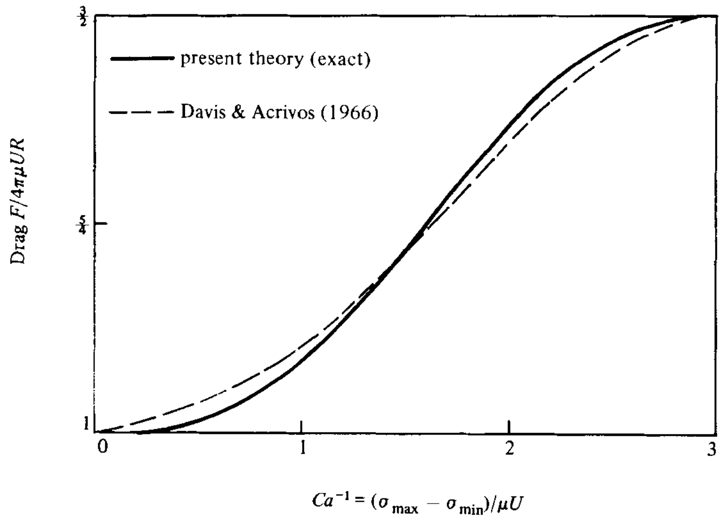


FIGURE 4. The drag force as a function of $Ca^{-1}$.

$$Ca^{-1} = \frac{1}{\pi}[3\phi + 3\sin\phi - \phi(1+\cos\phi)], \tag{57}$$

where we define the capillary number $Ca$ as

$$Ca^{-1} = \frac{(\sigma_{\max} - \sigma_{\min})}{\mu U} = \frac{1}{\mu U}\int_0^\phi \frac{d\sigma}{d\theta}\,d\theta. \tag{58}$$

The expression (57) for $Ca^{-1}$ is plotted in figure 3 along with the 150-term approximation of Davis & Acrivos (1966). In figure 4 the drag coefficient for bubbles is plotted as a function of $Ca^{-1}$. In each case the agreement is fairly good.

### 4.3. *The amount of surfactant adsorbed*

The possibility of obtaining an expression for the total amount of surfactant at the bubble surface was suggested by Dussan V. (personal communication). An examination of the problem led to some useful results. By following Gibbs (1878) and treating the interface as a discontinuity, the thermodynamic equilibrium at the interface and the adjacent liquid is described by

$$\Gamma = -\frac{1}{\mathscr{R}T}\frac{\partial\sigma}{\partial\mu}, \tag{59}$$

where $\Gamma$ is the dimensional surface concentration, $\mu$ is the chemical potential and $\mathscr{R}$ is the gas constant. For a constant activity-coefficient we have

$$d\mu = \frac{\mathscr{R}T}{\Gamma}\,d\Gamma. \tag{60}$$

As a result we obtain

$$\frac{d\sigma}{d\Gamma} = -\mathscr{R}T, \tag{61}$$

or

$$\Gamma(\theta) = \frac{1}{\mathscr{R}T}[\sigma_{\max} - \sigma(\theta)]. \tag{62}$$

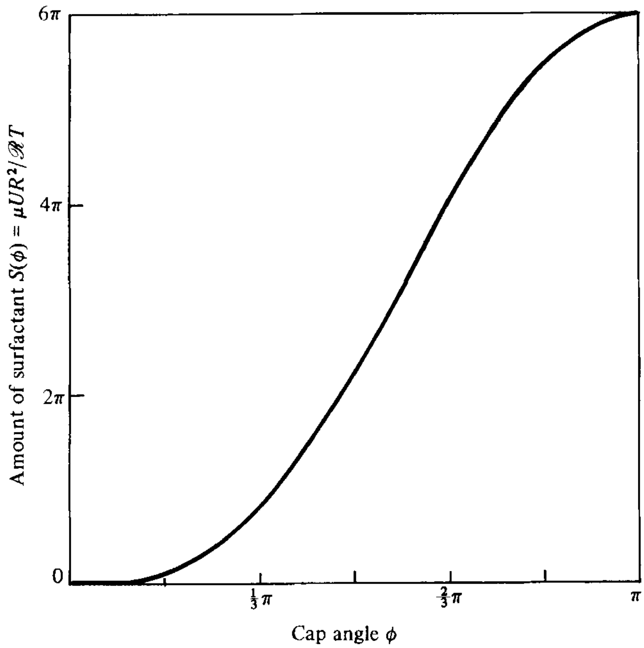


FIGURE 5. The amount of surfactant as a function of the cap angle $\phi$.

Clearly

$$\Gamma_{\max} = \frac{1}{\mathscr{R}T}[\sigma_{\max} - \sigma_{\min}]. \tag{63}$$

In order to calculate the total amount of surfactant at the interface, we need to evaluate

$$S = 2\pi R^2 \int_0^\phi \Gamma(\theta) \sin\theta \, d\theta. \tag{64}$$

After using (56) and (62) in (64) we obtain

$$S(\phi) = \frac{2\pi R^2}{\mathscr{R}T}\left\{(\sigma_{\max} - \sigma_{\min})(1-\cos\phi) - \mu U \int_0^\phi \left[\int_0^\theta h(\theta')\,d\theta'\right] d\theta\right\}. \tag{65}$$

Upon integrating by parts we find that

$$S(\phi) = \frac{\mu U R^2}{\mathscr{R}T}[2\phi - 4\phi\cos\phi - \sin 2\phi + 4\sin\phi]. \tag{66}$$

A plot of this result is given in figure 5. We notice that for small cap angles the amount of surfactant is indeed small. A steep increase is noticed for cap angles between $\phi = \frac{1}{3}\pi$ and $\phi = \frac{2}{3}\pi$.

### 4.4. *The internal vortex*

The stream functions given by (32), (33) were numerically evaluated and the streamlines located. An interesting flow pattern is exhibited within the drop, as shown in figure 6. With increasing cap angle we find that the centre of the vortex shifts towards the front of the drop. This vortex-shifting was observed experimentally by Huang & Kintner (1969). Our theory, however, underpredicts the shift in the position of the centre of the vortex. Harper (1982) also theoretically estimated the shift in the vortex and found disagreement with the Huang–Kintner measurement. It was originally felt that the disagreement was probably due to the limitation of Harper's

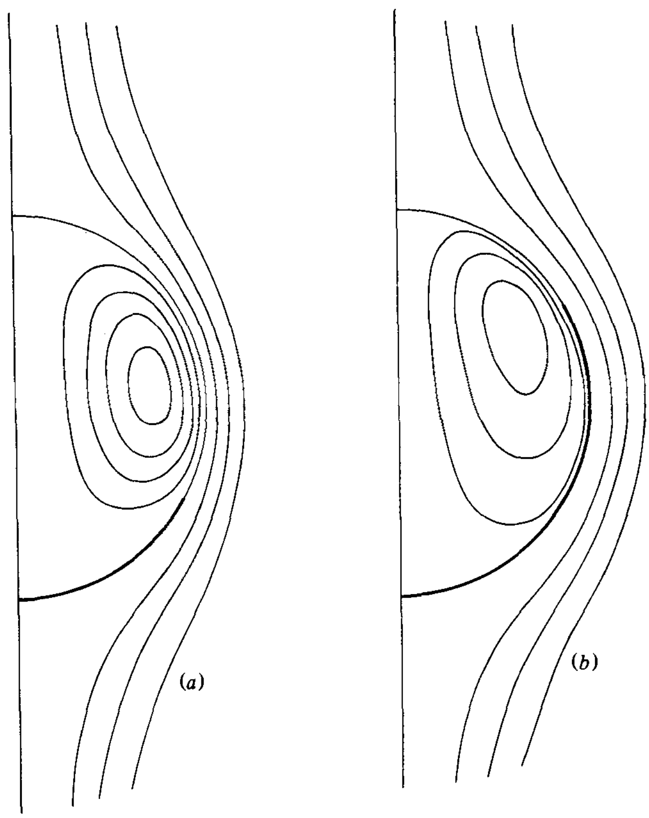


FIGURE 6. Streamlines for (a) $\phi = \frac{1}{3}\pi$ and (b) $\phi = \frac{2}{3}\pi$, with $\hat{\mu}/\mu = \frac{1}{2}$. The no-slip interface is indicated by a heavy line.

(1982) result to small cap angles. This suspicion may now be ruled out because the present theory, which is valid for all cap angles, still disagrees with the experiment. With this issue resolved the disagreement may now be attributed to the fact that the theory assumes that a part of the interface is completely surfactant-free. This was probably not the case in the Huang–Kintner experiment. A model accounting for this effect needs to be examined.

An interesting feature of the predicted vortex flow pattern is that it is independent of the drop viscosity. Only the strength of the vortex is governed by the viscosities of the drop and the surrounding fluid. This behaviour is quite obvious when we examine the development from (32)–(40). From this result an important deduction may be made about the 'degree of circulation'. The concept was proposed by Davies (1963), but a precise definition was given by Clift, Grace & Weber (1978) in the following form:

$$U_T = U_{TS}\,(1+\tfrac{1}{2}Z). \tag{67}$$

Here the 'degree of circulation' is denoted by $Z$, $U_T$ is the terminal velocity of the drop/bubble and $U_{TS}$ is the Stokes terminal velocity for a solid sphere. Griffith (1962) guessed an expression for $Z$ on the basis of Savic's (1953) approximation. In Clift's notation, this expression is

$$Z = \frac{2}{2+3\hat{\mu}/\mu}\,[2(Y-1)], \tag{68}$$

where $Y$ denotes the surface-contamination effects.

The present exact solution yields the following expression for $Z$:

$$Z = \frac{2}{2+3\hat{\mu}/\mu}\left[\frac{1-m(\phi)}{1+m(\phi)/(2+3\hat{\mu}/\mu)}\right]. \tag{69}$$

where $m(\phi)$ is the contamination term given by

$$m(\phi) = \frac{1}{2\pi}\,[2\phi+\sin\phi-\sin 2\phi-\tfrac{1}{3}\sin 3\phi]. \tag{70}$$

For small cap angles, $m(\phi)$ is also small, and we may write, to leading order,

$$Z \sim \frac{2}{2+3\hat{\mu}/\mu}\left\{1-m(\phi)\left[1+\frac{1}{2+3\hat{\mu}/\mu}\right]\right\}. \tag{71}$$

This does not correspond to Griffith's (1962) leading-order approximation, in which the surface contamination effects and the viscous effects are separated.

It is quite clear that with the definition of $Z$ given by Clift *et al.* (1978) we cannot separate the surface and viscous effects, even in the leading order. However, an examination of the drag force given by (50) shows that if we define the degree of circulation $Z^*$ as

$$F(\phi) = F_{\text{Stokes}}\,(1-\tfrac{1}{3}Z^*), \tag{72}$$

or equivalently

$$U_{\text{TS}} = U_{\text{T}}\,(1-\tfrac{1}{3}Z^*), \tag{73}$$

then we obtain

$$Z^* = \frac{1-m(\phi)}{1+\hat{\mu}/\mu}. \tag{74}$$

Here we can clearly separate the viscous effects from the surface effects, even for the exact case. It is therefore more convenient to define the degree of circulation in the form given by either (72) or (73).

## 5. Conclusion

The boundary conditions appropriate to drops in the presence of surfactants are formally derived in the limit of high Péclet numbers. A number of useful results are obtained from the solution, particularly the closed-form expressions for the drag force, the capillary number and the amount of surfactant adsorbed on the bubble surface. Since the drop viscosity is taken to be completely arbitrary, most of the results apply to both bubbles and drops.

The 150-term solution of Davis & Acrivos (1966) shows reasonable agreement with the present exact results for the drag force and for $(\sigma_{\max}-\sigma_{\min})/\mu U$. Also, Harper's (1982) asymptotic solution is in perfect agreement with the leading-order expansion of the present solution.

As mentioned earlier, the present solution is to be used as a leading-order term for the case when the thin film is a continuum having a weak internal circulation. A full development will be presented in Part 2 of this series of investigations. The case of thin liquid films on solid spheres was given by Johnson (1981). The situation when the coating is no longer thin is also under examination. In subsequent parts of this series we will be examining the heat-transfer and phase-change processes for application to direct-contact heat-transfer operations.

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