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Stokes flow in the presence of a planar interface covered with incompressible surfactant

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The Lorentz solution for Stokes flow in the presence of a plane wall is generalized to a surfactant-covered interface, and the Stokeslet solution is derived. The result is used to describe the motion of a small particle in the presence of the interface. The surfactant is insoluble and nondiffusing. The effects of surface viscosity are included. Small variations in surfactant concentration are assumed; this assumption usually holds under small capillary number conditions.
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I. INTRODUCTION

The Stokes flow scattered from a planar boundary has been the subject of many studies that are reviewed in Refs. 1, 2. The scattered field is known for a rigid wall[3–5] and a clean fluid–fluid interface.[6] In this paper we consider hydrodynamic interactions with a surfactant-covered interface.

Adsorbed surfactants modify the hydrodynamic boundary conditions at a fluid–fluid interface: bulk stresses are coupled to surface stresses that arise from surface viscosity and surface tension gradients resulting from the redistribution of surfactant.[7] Thus, the motion of particles and drops near the interface is qualitatively affected by adsorbed surfactant. In general, surfactant convection introduces nonlinearity into the problem.

Herein we develop a theory for hydrodynamic interactions with planar interfaces covered with insoluble nondiffusing surfactant under flow conditions for which the surfactant is incompressible. Long-aliphatic-chain surfactants may be insoluble; moreover, surfactant solubility is unimportant if the adsorption/desorption time scale is long compared to the flow time scale. Typically, surfactant diffusion is unimportant except at very small length scales (e.g., drops in near-contact motion[8,9]). As shown in the following section, incompressibility usually holds under low-capillary-number conditions. Thus, our theory can be used to describe a wide range of systems that involve motion of small particles in the presence of a surfactant-covered interface.

Under the assumption of incompressibility, the concentration of adsorbed surfactant is uniform. Thus, the surfactant conservation equation implies that the surface divergence of the velocity field is zero at the interface (however, the interfacial velocity does not generally vanish). Uniform surfactant concentration is maintained by gradients of surface tension. The situation is analogous to the three-dimensional incompressible flow, where constant fluid density is maintained by pressure gradients, and three-dimensional divergence of fluid velocity vanishes.

As a result of surfactant incompressibility, the boundary condition at the interface is linear, and the Stokes-flow problem can be solved for an arbitrary incident flow. In this paper we present the general solution and use it to find the flow field generated by a point force (Stokeslet). The result is applied to describe the motion of a small particle in the presence of the interface. Further applications of the Stokeslet solution include the motion of finite-size particles and drops near a much larger drop or near a flat interface.

The assumption of incompressibility and the resulting boundary conditions for the Stokes flow are discussed in Sec. II. The boundary-value problem is simplified in Sec. III by decomposing the flow into two components: (1) a component that is surface solenoidal on planes parallel to the interface, and (2) a component that is surface irrotational. In Sec. IV, the Stokes equations are solved with the help of this decomposition and a general expression for the scattered flow field is found in terms of the incident flow. In Sec. V, an explicit expression is derived for the Stokeslet in the presence of a surfactant-covered interface. The result is used in Sec. VI to determine the mobility of a small sphere near an interface, the resulting (small) deformation of the interface, and the surface tension distribution. The paper concludes with a discussion in Sec. VII.

II. INTERFACE COVERED WITH INCOMPRESSIBLE SURFACTANT

We consider Stokes flow in the presence of a planar surfactant-covered fluid–fluid interface at $z=0$, with normal vector $\mathbf{e}_z$. The surfactant is incompressible, nondiffusing, and insoluble in the bulk phases. Fluid (1) with viscosity η_1 occupies the half-space $z>0$ and fluid (2) with viscosity η_2

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occupies the half-space $z<0$; the interface has shear viscosity η_s. The equilibrium concentration of adsorbed surfactant is c_0, and the equilibrium surface tension is σ_0. We assume that the imposed flow (generated in the half-space $z>0$) is characterized by a length l_c and a velocity u_c.

The problem is nondimensionalized using c_0 for the concentration, and η_1, l_c, and u_c for all other quantities. The bulk and surface viscosity parameters are $\lambda=\eta_2/\eta_1$ and $\beta=(\eta_s/\eta_1)l_c^{-1}$. The scale for bulk stresses is $\tau_c=\eta_1 u_c/l_c$, and the scale for surface stresses (including surface tension) is $\tau_{sc}=l_c\tau_c$.

A. Incompressibility conditions

Surface tension gradients (Marangoni stresses) resulting from surfactant redistribution are balanced by the jump in tangential viscous tractions across the interface. Assuming that the magnitude of the viscous tractions is comparable to τ_c, and that the variation of the surface tension occurs on the length scale l_c, we find that in dimensionless variables,

$$\delta\sigma=O(1), \tag{1}$$

where $\delta\sigma$ is the perturbation of the surface tension σ (scaled by τ_{sc}) from the equilibrium value.

We seek conditions under which the perturbation $\delta c=c-1$ is small, where c is the normalized surfactant concentration. Accordingly, we expand σ in δc at $c=1$, which to the leading order yields

$$\delta\sigma=-\mathrm{Ma}\,\delta c, \tag{2}$$

where

$$\mathrm{Ma}=\frac{E}{\mathrm{Ca}} \tag{3}$$

is the Marangoni number; here

$$\mathrm{Ca}=\frac{\tau_c l_c}{\sigma_0} \tag{4}$$

is the capillary number, and

$$E=-\frac{c_0}{\sigma_0}\left(\frac{d\sigma'}{dc'}\right)_0 \tag{5}$$

is the surfactant elasticity, where a prime denotes unscaled variables, and the derivative is evaluated at $c'=c_0$.

Equations (1) and (2) indicate that

$$\delta c=O(\mathrm{Ma}^{-1}). \tag{6}$$

Thus, in the limit

$$\mathrm{Ma}\to\infty, \tag{7}$$

the surfactant becomes incompressible: a finite change of surface tension corresponds to an infinitesimal change of surfactant concentration. The situation is analogous to incompressible fluids, where finite changes of pressure produce only negligible changes of fluid density.

In order to find the range of applicability of the incompressibility limit (7), we note that typically

$$E=O(1) \tag{8}$$

at surfactant concentrations that correspond to an $O(1)$ relative change of surface tension from the clean-interface value. The only exceptions are surfactants close to interfacial phase transitions or critical points. In the absence of gravitational restoring forces, a small deformation of the interface requires[10]

$$\mathrm{Ca}\ll 1. \tag{9}$$

Conditions (8) and (9) imply that

$$\mathrm{Ma}\gg 1. \tag{10}$$

Thus, surfactant is usually incompressible under low-capillary-number conditions. The limit of an incompressible adsorbed film has been previously recognized.[11,12]

B. Equations of motion

At finite Marangoni numbers, the transport of insoluble, nondiffusing surfactant adsorbed on a constant-shape interface is described by the continuity equation

$$\frac{\partial c}{\partial t}=-\boldsymbol{\nabla}_s\cdot(c\mathbf{u}_s), \tag{11}$$

where $\mathbf{u}_s$ is the interfacial velocity, and $\boldsymbol{\nabla}_s$ is the two-dimensional gradient operator at a surface perpendicular to the z axis.

However, in the limit (7) the surfactant concentration becomes constant. Thus, in analogy with three-dimensional flow of an incompressible, constant density fluid, the interfacial continuity equation reduces to

$$\boldsymbol{\nabla}_s\cdot\mathbf{u}_s=0. \tag{12}$$

We note that Eq. (12) does not imply that the interfacial velocity vanishes; e.g., shearing motion at the interface is still possible.

Surface stresses that arise at the interface due to surface viscosity and surface tension are

$$\boldsymbol{\tau}_s=\beta[\boldsymbol{\nabla}_s\mathbf{u}_s+(\boldsymbol{\nabla}_s\mathbf{u}_s)^T]+\sigma\mathbf{I}_s, \tag{13}$$

where $\mathbf{I}_s=\mathbf{e}_x\mathbf{e}_x+\mathbf{e}_y\mathbf{e}_y$. The dilatational surface viscosity does not enter this expression because of the incompressibility condition (12). The tangential stress balance at the interface is

$$\begin{aligned}\mathbf{I}_s\cdot(\boldsymbol{\tau}_2-\boldsymbol{\tau}_1)\cdot\mathbf{e}_z&=\boldsymbol{\nabla}_s\cdot\boldsymbol{\tau}_s\\&=\beta\nabla_s^2\mathbf{u}_s+\boldsymbol{\nabla}_s\sigma,\end{aligned} \tag{14}$$

where $\boldsymbol{\tau}_i$ is the stress in the bulk fluid (i) at $z=0$.

According to Eqs. (12) and (14), surfactant distribution is eliminated from the description in the incompressibility limit (7), and surface tension becomes an independent variable; in an analogous procedure for three-dimensional incompressible flows, fluid density is eliminated and pressure becomes a field variable.

The remaining boundary conditions at the interface,

$$\mathbf{u}_1=\mathbf{u}_2, \tag{15a}$$

$$\text{at } z=0,$$

$$\mathbf{e}_z\cdot\mathbf{u}_i=0, \tag{15b}$$

do not depend on the presence of surfactant. The flow in the bulk fluid is described by Stokes equations,

$$\lambda_i \nabla^2 \mathbf{u}_i - \boldsymbol{\nabla} p_i = 0, \tag{16a}$$

$$\boldsymbol{\nabla} \cdot \mathbf{u}_i = 0. \tag{16b}$$

Here $\mathbf{u}_i(\mathbf{r})$ and $p_i(\mathbf{r})$ are the velocity and pressure at a position $\mathbf{r}$ in fluid (i), with the corresponding viscosity parameter $\lambda_1 = 1$ and $\lambda_2 = \lambda$. Equations (12)–(16) form a well posed boundary-value problem with a unique solution.[9] In general, normal tractions do not balance at the interface; we assume that the resulting deformation of the interface is small.

III. DECOMPOSITION OF STOKES FLOW

For certain flows, boundary condition (12) implies vanishing interfacial velocity. However, there are other flows that satisfy (12) with nonzero surface velocity. Examples of the former include potential flows and axisymmetric flows without swirl; examples of the latter include two-dimensional incompressible flows such as shear flow and rigid-body rotation. Here we show that a general Stokes flow can be decomposed into two components with these complementary characteristics.

For this purpose, we use a two-dimensional analog of the Helmholtz decomposition of vector fields on the family of planes parallel to the interface. Accordingly, a vector field $\mathbf{u}$ is decomposed into a surface-irrotational and a surface-solenoidal component:

$$\mathbf{u} = \mathbf{u}^{\mathrm{irr}} + \mathbf{u}^{\mathrm{sol}}, \tag{17}$$

where

$$\mathbf{e}_z \cdot \boldsymbol{\nabla}_s \times \mathbf{u}^{\mathrm{irr}} = 0, \tag{18}$$

$$\boldsymbol{\nabla}_s \cdot \mathbf{u}^{\mathrm{sol}} = 0, \tag{19a}$$

$$\mathbf{e}_z \cdot \mathbf{u}^{\mathrm{sol}} = 0. \tag{19b}$$

The fields $\mathbf{u}^{\mathrm{sol}}$ and the tangential component of $\mathbf{u}^{\mathrm{irr}}$ are derivable from scalar potentials:

$$\mathbf{u}^{\mathrm{irr}} = \boldsymbol{\nabla}_s \chi + u_z \mathbf{e}_z, \tag{20}$$

$$\mathbf{u}^{\mathrm{sol}} = \mathbf{e}_z \times \boldsymbol{\nabla}_s \psi, \tag{21}$$

where

$$\nabla_s^2 \chi = \zeta, \tag{22a}$$

$$\nabla_s^2 \psi = \rho, \tag{22b}$$

and

$$\zeta = \boldsymbol{\nabla}_s \cdot \mathbf{u}, \tag{23a}$$

$$\rho = \mathbf{e}_z \cdot \boldsymbol{\nabla}_s \times \mathbf{u}. \tag{23b}$$

For (bulk) solenoidal $\mathbf{u}$, relations (19) and (20) yield

$$\frac{\partial u_z}{\partial z} = -\nabla_s^2 \chi, \tag{24}$$

which indicates that u_z is also derivable from χ. The decomposition (17)–(19) is unique provided that $\mathbf{u} \to 0$ as $x^2 + y^2 \to \infty$.

Potential flows and axisymmetric flows with no azimuthal component (where z is the axis of symmetry) are surface irrotational; two-dimensional incompressible flows are surface solenoidal.

The following properties are shown in the Appendix. If $\mathbf{u}$ is a solution of Stokes equations with pressure p, then $\mathbf{u}^{\mathrm{irr}}$ and $\mathbf{u}^{\mathrm{sol}}$ are also solutions of Stokes equations, with corresponding pressures

$$p^{\mathrm{irr}} = p, \tag{25a}$$

$$p^{\mathrm{sol}} = 0. \tag{25b}$$

For Stokes flow, the potential χ is a biharmonic function and ψ is a harmonic function.

At the interface, Eqs. (12) and (18) imply that the surface-irrotational component $\mathbf{u}^{\mathrm{irr}}$ satisfies the no-slip boundary condition

$$\mathbf{u}_s^{\mathrm{irr}} = 0; \tag{26}$$

boundary condition (14) becomes

$$\mathbf{I}_s \cdot (\boldsymbol{\tau}_2^{\mathrm{irr}} - \boldsymbol{\tau}_1^{\mathrm{irr}}) \cdot \mathbf{e}_z = \boldsymbol{\nabla}_s \sigma, \tag{27}$$

because decomposition (17)–(19) is unique, the fields $\mathbf{I}_s \cdot \boldsymbol{\tau}_i^{\mathrm{irr}} \cdot \mathbf{e}_z$ and $\boldsymbol{\nabla}_s \sigma$ are surface irrotational, and the fields $\mathbf{I}_s \cdot \boldsymbol{\tau}_i^{\mathrm{sol}} \cdot \mathbf{e}_z$ and $\nabla_s^2 \mathbf{u}_s^{\mathrm{sol}}$ are surface solenoidal. The stress balance (27) determines the surface tension gradient needed to maintain the incompressible surface flow. For $\mathbf{u}^{\mathrm{sol}}$, the definition (19a) implies that boundary condition (12) is automatically satisfied; boundary condition (14) becomes

$$\mathbf{I}_s \cdot (\boldsymbol{\tau}_2^{\mathrm{sol}} - \boldsymbol{\tau}_1^{\mathrm{sol}}) \cdot \mathbf{e}_z = \beta \nabla_s^2 \mathbf{u}_s^{\mathrm{sol}}. \tag{28}$$

IV. GENERAL SOLUTION

A. Surface-irrotational flow

A surface-irrotational flow field satisfies Stokes equations with the no-slip boundary condition (26). Thus, Lorentz's[2,3] solution applies:

$$\mathbf{u}_1 = \mathbf{u}_e + \hat{\mathsf{P}} \hat{\mathbf{u}}_e, \quad p_1 = p_e + \hat{\mathsf{P}} \hat{p}_e, \quad z \geqslant 0, \tag{29a}$$

$$\mathbf{u}_2 = 0, \quad p_2 = 0, \quad z \leqslant 0; \tag{29b}$$

where $\mathbf{u}_e$ and p_e denote the incident fields that are generated by forces in the half-space $z > 0$ in an unbounded fluid (1). The reflection operator $\hat{\mathsf{P}}$ is defined by

$$\hat{\mathsf{P}} \mathbf{u} = (\mathbf{I} - 2\mathbf{e}_z \mathbf{e}_z) \cdot \mathbf{u}(x, y, -z), \tag{30a}$$

$$\hat{\mathsf{P}} p = p(x, y, -z); \tag{30b}$$

and

$$\hat{\mathbf{u}} = -(\mathbf{I} - 2\mathbf{e}_z \mathbf{e}_z) \cdot \mathbf{u} - 2z \boldsymbol{\nabla} u_z + z^2 \nabla^2 \mathbf{u}, \tag{31a}$$

$$\hat{p} = p + 2z \frac{\partial p}{\partial z} - 4 \frac{\partial u_z}{\partial z}, \tag{31b}$$

where $\mathbf{I}$ is the identity tensor. The flow field $\mathbf{u}_1$ is surface irrotational for a surface-irrotational incident flow.

In a system with a rigid wall, Lorentz's solution (29)–(31) is valid for an arbitrary incident flow.

B. Surface-solenoidal flow

In the absence of surface viscosity, a surface-solenoidal flow $\mathbf{u}$ is a solution of Stokes equations in the presence of a clean fluid–fluid interface, as indicated by boundary condition (28); thus, the solution is known.[6] For $\beta \neq 0$ the surface-solenoidal flow field can be determined by a Fourier analysis.

Equation (21) indicates that the Fourier decomposition of $\mathbf{u}$ in a plane $z=\text{const}$ has the form

$$\mathbf{u}(\mathbf{s},z)=\frac{1}{2\pi}\mathbf{e}_z\times\int i\mathbf{k}\tilde{\psi}(\mathbf{k},z)e^{i\mathbf{k}\cdot\mathbf{s}}d^2k, \tag{32}$$

where $\mathbf{k}=k_x\mathbf{e}_x+k_y\mathbf{e}_y$ is the wave vector; $\mathbf{s}=x\mathbf{e}_x+y\mathbf{e}_y$; $\tilde{\psi}$ is the Fourier transform of the potential ψ,

$$\tilde{\psi}(\mathbf{k},z)=\frac{1}{2\pi}\int \psi(\mathbf{s},z)e^{-i\mathbf{k}\cdot\mathbf{s}}d^2s; \tag{33}$$

and the integrations are over the entire plane.

Let $\mathbf{u}_e$ denote the incident surface-solenoidal flow field produced by forces in the half-space $z>z_0>0$ in an unbounded fluid (1). The Fourier expansion coefficients of $\mathbf{u}_e$ in the half-space $z<z_0$ have the form

$$\tilde{\psi}_e(\mathbf{k},z)=\tilde{\psi}_e^+(\mathbf{k})e^{kz}, \tag{34}$$

which follows from (32), Stokes equation (A4), and the behavior $\mathbf{u}_e\to 0$ for $z\to-\infty$. In the presence of the interface, the flow field $\mathbf{u}_i$ can be expressed as a sum of the incident and the scattered flow:

$$\mathbf{u}_i=\mathbf{u}_e+\mathbf{v}_i\,. \tag{35}$$

The Fourier expansion coefficients $\tilde{\xi}_i(\mathbf{k},z)$ of the scattered flow field $\mathbf{v}_i$ have the form

$$\tilde{\xi}_1(\mathbf{k},z)=A(k)\tilde{\psi}_e^+(\mathbf{k})e^{-kz},\quad z\geqslant 0; \tag{36}$$

$$\tilde{\xi}_2(\mathbf{k},z)=A(k)\tilde{\psi}_e^+(\mathbf{k})e^{kz},\quad z\leqslant 0; \tag{37}$$

which follows from (32), Stokes equation (A4), the behavior of the scattered fields at infinity, and continuity of the velocity. The scattering amplitudes,

$$A(k)=\frac{1-(\lambda+\beta k)}{1+(\lambda+\beta k)}, \tag{38}$$

are obtained from the stress balance (28), where the viscous stresses are evaluated using (32) with Fourier coefficients (34) and (36)–(37).

Surface viscosity introduces a length scale. For $\beta k\ll 1$ surface viscosity is unimportant; the interface behaves like a clean fluid–fluid interface according to boundary condition (28). For $\beta k\gg 1$ the scattering amplitude is $A(k)=-1$ thus, $\mathbf{u}_i=0$ at $z=0$ according to (34), (35), and (37); the interface behaves as a rigid wall. The rigid-wall behavior is also attained for $\lambda\to\infty$.

In real space, relations (35)–(38) and (25b) yield

$$\mathbf{u}_1=(1-\hat{\mathsf{P}})\mathbf{u}_e+\hat{\mathsf{P}}\hat{\mathsf{K}}\mathbf{u}_e\,,\quad p_1=0,\quad z\geqslant 0, \tag{39a}$$

$$\mathbf{u}_2=\hat{\mathsf{K}}\mathbf{u}_e\,,\quad p_2=0,\quad z\leqslant 0, \tag{39b}$$

where

$$[\hat{\mathsf{K}}\mathbf{w}](\mathbf{s})=\frac{b^2}{\pi(1+\lambda)}\int K(bs')\mathbf{w}(\mathbf{s}-\mathbf{s}')d^2s', \tag{40}$$

$$b=\frac{1+\lambda}{\beta}, \tag{41}$$

and

$$K(t)=\int_0^\infty \frac{k}{1+k}J_0(kt)dk \tag{42a}$$

$$=\frac{1}{t}+\frac{\pi}{2}[N_0(t)-\mathbf{H}_0(t)]. \tag{42b}$$

Herein J_n and N_n are Bessel functions of the first and second kind, and $\mathbf{H}_n$ is the Struve function.[13] The asymptotic behavior,

$$K(t)=O(t^{-1}),\quad \text{for } t\ll 1, \tag{43a}$$

$$K(t)=O(t^{-3}),\quad \text{for } t\gg 1, \tag{43b}$$

assures that the kernel K is integrable on a plane.

The limiting values of the operator $\hat{\mathsf{K}}$ can be most easily derived in Fourier space by comparing the limiting behavior of (37)–(38) with the expression (39b). The limits

$$\lim_{\lambda\to\infty}\hat{\mathsf{K}}=0,\quad \lim_{\beta\to\infty}\hat{\mathsf{K}}=0 \tag{44}$$

correspond to the no-slip boundary condition; clean-interface behavior is obtained from

$$\lim_{\beta\to 0}\hat{\mathsf{K}}=\frac{2}{1+\lambda}\hat{\mathsf{I}}, \tag{45}$$

where $\hat{\mathsf{I}}$ is the identity operator.

C. General flow

For a general incident flow fields $(\mathbf{u}_e,p_e)$, the velocity and pressure fields in the presence of a surfactant-covered interface can be expressed in a compact form:

$$\mathbf{u}_1=\mathbf{u}_e+\hat{\mathsf{P}}\hat{\mathbf{u}}_e+\hat{\mathsf{P}}\hat{\mathsf{K}}\hat{\mathsf{S}}\mathbf{u}_e\,,\quad p_1=p_e+\hat{\mathsf{P}}\hat{p}_e\,,\quad z\geqslant 0, \tag{46a}$$

$$\mathbf{u}_2=\hat{\mathsf{K}}\hat{\mathsf{S}}\mathbf{u}_e\,,\quad p_2=0,\quad z\leqslant 0, \tag{46b}$$

where $\hat{\mathsf{S}}\mathbf{u}=\mathbf{u}^{\text{sol}}$. The result follows from superposition of the surface-irrotational and surface-solenoidal components (29) and (39) by application of the identity $\hat{\mathbf{u}}_e^{\text{sol}}=-\mathbf{u}_e^{\text{sol}}$.

For $\hat{\mathsf{K}}=0$ (limits $\lambda\to\infty$ or $\beta\to\infty$) result (46) is identical to the solution for a rigid-wall;[2,3] however, in the limit $\beta\to 0$ expressions (46) tend to the clean-interface solution only for a surface-solenoidal incident flow.

D. Stresses at the interface

Normal and tangential tractions can be used to determine a small deformation of the interface and the perturbation of the surface tension.

Normal tractions are obtained from general solution (46) using (19b) and definitions (30)–(31):

$$\tau_{1zz}=4\frac{\partial u_{ez}}{\partial z}-2p_e,\quad \tau_{2zz}=0, \tag{47}$$

at $z=0$. According to (19b) and (25), normal tractions result entirely from the surface-irrotational component of the flow and are therefore independent of the viscosity parameters λ and β. It can be shown that normal tractions on a surfactant-covered interface are the same as on a clean interface.

According to (27), the surface tension gradient is associated with the jump of surface-irrotational tangential tractions. From the solution (29) and definitions (30)–(31), we obtain

$$\mathbf{I}_s\cdot\boldsymbol{\tau}_1^{\rm irr}\cdot\mathbf{e}_z=2\mathbf{I}_s\cdot\boldsymbol{\tau}_e^{\rm irr}\cdot\mathbf{e}_z,\quad \mathbf{I}_s\cdot\boldsymbol{\tau}_2^{\rm irr}\cdot\mathbf{e}_z=0, \tag{48}$$

at $z=0$, where $\boldsymbol{\tau}_e$ is the stress associated with the incident flow. The deviation of surface tension from the unperturbed value is obtained from (27) and (48):

$$\sigma=-2\left(u_{ez}+\frac{\partial\chi_e}{\partial z}\right), \tag{49}$$

where χ_e is the scalar potential (20) associated with the irrotational component of $\mathbf{u}_e$.

V. STOKESLET

We use the formalism developed in the previous sections to find the flow field generated by a point force in the presence of a surfactant-covered interface. The axisymmetric flow field generated by the force normal to the interface is the same as for a rigid-wall[4] because flow is surface irrotational and thus, the no-slip boundary condition applies. Here, we find the velocity field generated by a point force parallel to the interface.

We consider a force $\mathbf{f}=f\mathbf{e}_x$ on the z axis at a distance $z_0>0$ from the interface. The characteristic scales $l_c=z_0$ and $u_c=f/(8\pi\eta_1 z_0)$ are adopted. In dimensionless variables, the plane is at $z=0$ and the Stokeslet is at $z=1$. In an unbounded fluid (1), the velocity and pressure fields generated by the point force are

$$u_{es}(\mathbf{s},z)=\frac{(\bar{z}^2+2s^2)\cos\phi}{\bar{r}^3},\quad u_{e\phi}(\mathbf{s},z)=-\frac{\sin\phi}{\bar{r}}, \tag{50a}$$

$$u_{ez}(\mathbf{s},z)=\frac{s\bar{z}\cos\phi}{\bar{r}^3},\quad p_e(\mathbf{s},z)=\frac{2s\cos\phi}{\bar{r}^3}, \tag{50b}$$

where $s,\ \phi,\ z$ are the cylindrical coordinates, $\bar{z}=z-1$, and $\bar{r}=(s^2+\bar{z}^2)^{1/2}$.

A. Rigid-wall contribution

The rigid-wall contributions $\hat{\mathsf{P}}\hat{\mathbf{u}}_e$ and $\hat{\mathsf{P}}\hat{p}_e$ in (46a) are known.[2,4] In cylindrical coordinates the explicit expressions for $\hat{\mathbf{u}}_e$ and $\hat{p}_e$ are

$$\hat{\mathbf{u}}_e=-\mathbf{u}_e+\hat{\mathbf{u}}_e',\quad \hat{p}_e=-p_e+\hat{p}_e', \tag{51a}$$

where $\hat{\mathbf{u}}_e'$ and $\hat{p}_e'$ are

$$\hat{u}_{es}'=\frac{2z(\bar{z}^2-2s^2)\cos\phi}{\bar{r}^5},\quad \hat{u}_{e\phi}'=-\frac{2z\sin\phi}{\bar{r}^3}, \tag{51b}$$

$$\hat{u}_{ez}'=-2s\left(\frac{1}{\bar{r}^3}+\frac{3z\bar{z}}{\bar{r}^5}\right)\cos\phi,\quad \hat{p}_e'=-\frac{12s\bar{z}\cos\phi}{\bar{r}^5}, \tag{51c}$$

from which the rigid-wall contributions are obtained by applying the reflection operator (30).

B. Surface-solenoidal contribution

To find the transmitted velocity field $\hat{\mathsf{K}}\hat{\mathsf{S}}\mathbf{u}_e$ we first evaluate the surface-solenoidal component of $\mathbf{u}_e$. From (23b) and (50a) we find

$$\rho_e(\mathbf{s},z)=\frac{2s\sin\phi}{\bar{r}^3}; \tag{52}$$

then, the Poisson equation (22b) is solved for the potential of the surface-solenoidal component of the flow to obtain

$$\psi_e(\mathbf{s},z)=\frac{2(|\bar{z}|-\bar{r})\sin\phi}{s}, \tag{53}$$

which is well behaved at infinity. According to (21) and the above relation, the surface-solenoidal velocity field is

$$[\hat{\mathsf{S}}\mathbf{u}_e](\mathbf{s},z)=-\frac{2(|\bar{z}|-\bar{r})\cos\phi}{s^2}\mathbf{e}_s+\frac{2(|\bar{z}|-\bar{r})|\bar{z}|\sin\phi}{\bar{r}s^2}\mathbf{e}_\phi, \tag{54}$$

where $\mathbf{e}_s,\ \mathbf{e}_\phi$ are unit vectors in cylindrical coordinates.

The Fourier transform of the potential ψ_e is

$$\tilde{\psi}_e(\mathbf{k},z)=\frac{2ie^{-k|\bar{z}|}}{k^2}\sin\phi', \tag{55}$$

where ϕ' is the azimuthal angle in the Fourier space. The result (55) corresponds to the principal-value interpretation of the integration (33) in the vicinity of $\mathbf{k}=0$.

The Fourier coefficients of the transmitted surface-solenoidal velocity field are obtained from (55) and (37)–(38). After inverting the Fourier transform, we obtain the potential of the transmitted field:

$$\xi_2(\mathbf{s},z)=-2\sin\phi\int_0^\infty A(k)\frac{e^{-k|\bar{z}|}}{k}J_1(ks)dk,\quad z\leqslant 0. \tag{56}$$

After some manipulations involving the partial-fraction decomposition of $A(k)/k$ and integration by parts, this expression simplifies to

$$\xi_2(\mathbf{s},z)=-\psi_e(\mathbf{s},z)+\Xi(\mathbf{s},z), \tag{57}$$

where

$$\Xi(\mathbf{s},z)=\frac{2}{\beta}\int_{|\bar{z}|}^\infty e^{-b(t-|\bar{z}|)}\psi_e(\mathbf{s},1+t)dt, \tag{58}$$

and ψ_e is given by (53). By inserting the potential (57)–(58) into expression (21) for the solenoidal velocity field, and by comparing the result to (35) and (39b) we obtain

$$[\hat{\mathsf{K}}\hat{\mathsf{S}}\mathbf{u}_e](\mathbf{s},z)=\frac{2}{\beta}\int_{|\overline{z}|}^{\infty}e^{-b(t-|\overline{z}|)}[\hat{\mathsf{S}}\mathbf{u}_e](\mathbf{s},1+t)\,dt, \tag{59}$$

where the surface-solenoidal component of the incident flow is given by (54). The result reduces to (44) and (45) in the appropriate limits.

The complete reflected and transmitted velocity fields are given by Eqs. (46) supplemented with (51), (54), and (59).

C. Singularity representation of surface-solenoidal contribution

An analysis of the singular behavior of the potential (53) for small s indicates that the surface-solenoidal component (54) of the Stokeslet can be represented by an integral over a line of singularities along the half z axis:

$$[\hat{\mathsf{S}}\mathbf{u}_e](\mathbf{s},z)=\int_0^{\infty}t\,\mathbf{G}(\mathbf{s},\overline{z}\mp t)\,dt, \tag{60}$$

where

$$\mathbf{G}(\mathbf{s},z)=-\mathbf{e}_z\times\boldsymbol{\nabla}_s\frac{2s\sin\phi}{(s^2+z^2)^{3/2}}, \tag{61}$$

and the upper (lower) sign corresponds to $\overline{z}\leqslant 0$ $(\overline{z}\geqslant 0)$. The validity of the above representation can be verified by direct integration. The kernel function $\mathbf{G}(\mathbf{s},z)$ is a singular surface-solenoidal solution of the Stokes equations. Inserting (60) into (59) and integrating yields the singularity representation for the transmitted velocity field (46b):

$$[\hat{\mathsf{K}}\hat{\mathsf{S}}\mathbf{u}_e](\mathbf{s},z)=\int_0^{\infty}\gamma(t)\,\mathbf{G}(\mathbf{s},\overline{z}\mp t)\,dt, \tag{62}$$

where the line density γ is

$$\gamma(t)=\frac{2}{1+\lambda}\left(t-\frac{1-\mathrm{e}^{-bt}}{b}\right). \tag{63}$$

The rigid-wall limit $\gamma\to 0$ is recovered for $\beta\to\infty$ or $\lambda\to\infty$, and the clean-interface limit $\gamma\to 2t/(1+\lambda)$ is obtained for $\beta\to 0$.

Equations (60)–(62) indicate that the reflected flow field obtained from (35) and (46a) is represented in terms of a line singularity on the half-axis $z\leqslant -1$, and the transmitted flow field (46b) is represented in terms of a line singularity on the half-axis $z\geqslant 1$. In contrast, for a rigid wall[4] or a clean fluid–fluid interface[6] the transmitted and scattered fields can be represented in terms of point singularities.

D. Stresses at the interface

For a force $\mathbf{f}=f\mathbf{e}_x$ parallel to the interface, the jump of normal tractions at $z=0$ is obtained from (47) and (50b):

$$\tau_{2zz}-\tau_{1zz}=12r_0^{-5}s\cos\phi, \tag{64}$$

where $r_0=(s^2+1)^{1/2}$. For a normal force $\mathbf{f}=f\mathbf{e}_z$, the jump of normal tractions, obtained from the rigid-wall solution,[1] is

$$\tau_{2zz}-\tau_{1zz}=-12r_0^{-5}. \tag{65}$$

Equations (64)–(65) apply also to the case of a clean fluid–fluid interface.[6]

For a force parallel to the interface, the potential χ_e of the irrotational component of the Stokeslet (50) is obtained by solving (22a) and (23a):

$$\chi_e(\mathbf{s},z)=\frac{(|\overline{z}|-\overline{r})^2\cos\phi}{s\overline{r}}. \tag{66}$$

The perturbation of surface tension is obtained from (49), (50b), and the above equation:

$$\sigma(\mathbf{s})=-4\left[\frac{1}{s}\left(1-\frac{1}{r_0}\right)-\frac{s}{r_0^3}\right]\cos\phi. \tag{67}$$

For a force normal to the interface, a similar analysis yields

$$\sigma(\mathbf{s})=-4r_0^{-3}. \tag{68}$$

VI. SMALL SPHERE NEAR AN INTERFACE

As an application of the results obtained in the previous section, we consider the motion of a small spherical particle in the presence of a surfactant-covered interface. The particle is at a distance z_0 from the interface and has dimensionless radius $\delta=a/z_0\ll 1$.

A. Mobility of the sphere

To the leading order,

$$\mu=1-\mu_1+O(\delta^3), \tag{69}$$

where μ is the nondimensional particle mobility normalized by the mobility of an isolated particle $(6\pi\eta_1 a)^{-1}$. The first-order correction μ_1 due to the interaction with the interface is

$$\mu_1=-\tfrac{3}{4}\delta v_1(\mathbf{0},1), \tag{70}$$

where the reflected velocity field $v_1(\mathbf{s},z)$ for the Stokeslet is obtained from (35) and (46a).

For motion parallel to the interface, the above relation and the expression for v_1 obtained from (30a), (54), and (59) yield

$$\mu_{1\parallel}(\lambda,\beta)=\mu_{1\parallel}^{R}\left[1-\frac{8bE_1(2b)\mathrm{e}^{2b}}{3(1+\lambda)}\right], \tag{71}$$

where

$$\mu_{1\parallel}^{R}=\tfrac{9}{16}\delta \tag{72}$$

is the result for rigid wall and E_1 is the exponential integral.[14] Relation (71) indicates that

$$\mu_{1\parallel}^{R}>\mu_{1\parallel}(\lambda,\beta)\geqslant\mu_{1\parallel}(\lambda,0)>\mu_{1\parallel}^{C}, \tag{73}$$

where

$$\mu_{1\parallel}^{C}=\mu_{1\parallel}^{R}\left[1-\frac{5}{3(1+\lambda)}\right] \tag{74}$$

is the result for a clean fluid–fluid interface.[6] In the absence of surface viscosity,

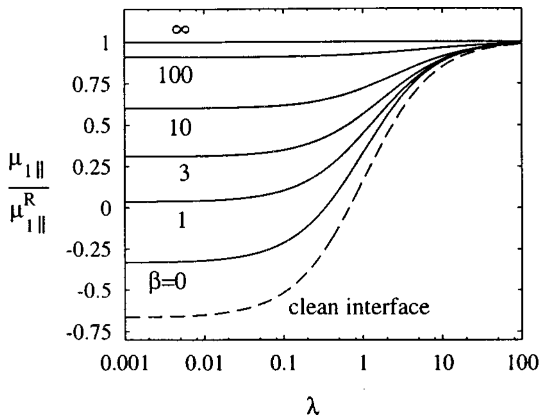

FIG. 1. Mobility coefficient $\mu_{1\|}$ normalized by the result for a rigid wall, as function of viscosity ratio λ. Result (71) for surfactant-covered interface with different values of surface viscosity parameter β, as labeled (solid curves); Result (74) for the surfactant-free interface with no surface viscosity (dashed curve).

$$\mu_{1\|}(\lambda,0)=\mu^R_{1\|}\left[1-\frac{4}{3(1+\lambda)}\right]. \tag{75}$$

For normal motion, the no-slip boundary condition applies at the interface. The exact expression for the mobility is given in Ref. 1; to the leading order the result is

$$\mu_{1\perp}(\lambda,\beta)=\mu^R_{1\perp}=2\mu^R_{1\|}, \tag{76}$$

where $\mu^R_{1\|}$ is given in (72).

The mobility coefficient (71) for a particle moving parallel to a surfactant covered interface is depicted in Fig. 1, along with the corresponding result (74) for a clean interface. Consistently with (73), the result for a surfactant-covered interface differs both from the results for a rigid-wall and for a clean interface. In the absence of surface viscosity, the difference with respect to a clean-interface is smaller, which contrasts with the corresponding result for equal-size surfactant-covered drops, where the transverse mobility at large separations is the same as for rigid spheres.[9] A transition to rigid-wall behavior occurs for λ or $\beta \gg 1$. The mobility correction changes sign: for small λ and β the particle mobility is enhanced, otherwise it is reduced.

Optical techniques are available for measuring single particle mobilities in the presence of an interface.[15,16] Thus, it may be possible to construct a device for directly measuring surface viscosity using formula (71).

B. Deformation of the interface

The motion of the sphere deforms the interface and perturbs the surface tension. The surface tension distribution resulting from the motion of the sphere is given by (67) and (68).

We consider the small deformation of an interface whose equilibrium planar shape is maintained by surface tension. The deformation is determined by the normal stress balance; in dimensionless variables,

$$\tau_{2zz}-\tau_{1zz}=\mathrm{Ca}^{-1}\nabla_s^2 h, \tag{77}$$

where h is the nondimensional deformation, $\mathrm{Ca}=f/(4\pi\sigma_0 z_0)\ll 1$ is the capillary number, f is the force acting on the sphere, and σ_0 is the surface tension corresponding to the unperturbed surfactant distribution.

For a parallel force $\mathbf{f}=f\mathbf{e}_x$, the solution of (64) and (77) is

$$\mathrm{Ca}^{-1}h=\frac{4(1-r_0)\cos\phi}{sr_0}, \tag{78}$$

which decays as $1/s$ at infinity. For a normal force $\mathbf{f}=f\mathbf{e}_z$, the solution of Eqs. (65) and (77), nonsingular at $s=0$, is

$$\mathrm{Ca}^{-1}h=4\left(\frac{1}{r_0}-\log(1+r_0)\right)+\text{const}, \tag{79}$$

which diverges logarithmically for $s\gg 1$ and matches to an outer solution for a finite-size interface or a weak buoyancy restoring force.

The jump in normal tractions and thus the dependence of the deformation on capillary number are the same for clean and surfactant-covered interfaces. The results for a clean interface with both surface-tension and buoyancy restoring forces have been studied.[10,17]

VII. CONCLUSIONS

We have analyzed Stokes flow in the presence of a planar interface covered with incompressible insoluble nondiffusing surfactant. The effects of surface viscosity have been included.

Surfactant is incompressible for Marangoni number $\mathrm{Ma}\gg 1$. For undeformed interfaces ($\mathrm{Ca}\ll 1$), the Marangoni number is usually large because the surfactant elasticity $E=O(1)$, except at small surfactant concentrations or near interfacial phase transitions. For an incompressible surfactant, finite gradients of surface tension induced by the flow correspond to infinitesimal changes of concentration. Thus, surfactant concentration remains uniform, and the divergence of the interfacial velocity vanishes.

We have developed a general method to construct the flow field produced by an arbitrary incident flow in the presence of an interface covered with incompressible surfactant. Accordingly, the flow field is decomposed into a component that is surface irrotational on planes parallel to the interface and a component that is surface solenoidal. The surface-irrotational component satisfies no-slip boundary conditions on the interface and the surface-solenoidal component satisfies boundary conditions characteristic of a fluid–fluid interface with surface viscous stresses but not Marangoni stresses.

The method has been used to calculate the flow generated by a point force in the presence of a surfactant-covered interface. For a force parallel to the interface, the solution is given by a line distribution of singularities on the axis normal to the interface. For a normal force, the flow in the presence of a surfactant-covered fluid–fluid interface is the same as for a rigid boundary.

The solution for a point force is the Green's function for Stokes flow with a planar surfactant-covered boundary and therefore, has an application to particle and drop dynamics in the presence of planar fluid–fluid interfaces or much larger drops. As an application, the mobility of a small sphere in the presence of a surfactant-covered interface and the associated interface deformation and surface tension distribution was found. The results have relevance to particle capture processes such as microflotation. Using our results, it may be possible to develop an apparatus for direct measurements of surface viscosity.

The scattered flow produced by higher-order force multipoles is needed to construct multiple scattering expansions for the motion of finite-size particles and drops. A systematic analysis of multipole solutions for a rigid boundary has been performed by Cichocki and Jones.[5] We are working on an extension of this analysis for a surfactant-covered interface.

Decomposition of the flow into surface-solenoidal and surface-irrotational components can also be applied to flows in the presence of nonplanar fixed-shape surfactant-covered interfaces. In a recent work,[9] we used the decomposition on concentric spherical surfaces to evaluate hydrodynamic interactions between spherical drops covered with an incompressible surfactant.

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APPENDIX: PROPERTIES OF DECOMPOSITION (17)

Assume that $(\mathbf{u},p)$ is a solution of the Stokes equations in a fluid with the viscosity λ_i. By applying the operator $\mathbf{e}_z\cdot\boldsymbol{\nabla}_s\times$ to both sides of Stokes equation (16a) and using decomposition (17), we obtain

$$\mathbf{e}_z\cdot\boldsymbol{\nabla}_s\times[\lambda_i\nabla^2(\mathbf{u}^{\mathrm{irr}}+\mathbf{u}^{\mathrm{sol}})-\boldsymbol{\nabla}p]=0, \tag{A1}$$

which, using (18), can be reduced to

$$\mathbf{e}_z\cdot\boldsymbol{\nabla}_s\times\nabla^2\mathbf{u}^{\mathrm{sol}}=0. \tag{A2}$$

Equation (19) indicates that

$$\boldsymbol{\nabla}_s\cdot\nabla^2\mathbf{u}^{\mathrm{sol}}=0. \tag{A3}$$

Assuming that $\mathbf{u}^{\mathrm{sol}}\to0$ as $x^2+y^2\to\infty$, relations (A2)–(A3) and (19b) imply that

$$\nabla^2\mathbf{u}^{\mathrm{sol}}=0; \tag{A4}$$

thus, from Eq. (16a) we obtain

$$\lambda_i\nabla^2\mathbf{u}^{\mathrm{irr}}=\boldsymbol{\nabla}p. \tag{A5}$$

From (A4)–(A5) and definitions (20) and (21) of the potentials χ and ψ, we find that

$$\lambda_i\nabla^2\chi=p, \tag{A6a}$$

$$\nabla^2\psi=0, \tag{A6b}$$

where we assume that p vanishes at infinity. The potential χ is a biharmonic function because $\nabla^2 p=0$.

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