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Interfacial effects on droplet dynamics in Poiseuille flow†

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Many properties of emulsions arise from interfacial rheology, but a theoretical understanding of the effect of interfacial viscosities on droplet dynamics is lacking. Here we report a theory, relating to isolated spherical drops in a Poiseuille flow. Stokes flow is assumed in the bulk phases, and a jump in hydrodynamic stress at the interface is balanced by Marangoni and surface viscous forces according to the Boussinesq–Scriven constitutive law. Our model employs a linear equation of state for the surfactant. Our analysis predicts slip, cross-stream migration and droplet-circulation velocities. These results and the corresponding interfacial parameters are separable: e.g., cross-stream migration occurs only if gradients in surfactant concentration are present; slip velocity depends on viscosity contrast and dilatational properties, but not on shear Boussinesq number. This separability allows a new and advantageous means to measure surface viscous and elastic forces directly from the drop interface.

1. Introduction

Droplet dynamics in flow reflects a number of properties of the drop interface, and influences emulsion rheology and stability.1 For some time now, it has been understood that droplets placed in a pressure-driven flow tend to be transported at a velocity less than that of the undisturbed flow. For example, a clean spherical viscous droplet lags behind the flow with a slip velocity given by (2) and undergoes no lateral migration.2 In addition, depending on the viscosity contrast, deformable particles migrate either towards the flow centerline or away if initially placed off-center.3,4 Recently, it was found that the presence of insoluble surfactant would induce a cross-stream migration in a spherical droplet.5 In this case, the symmetry present in the spherical shape limit of a clean drop (prohibiting the lateral migration of the droplet6) is broken, and the spherical surfactant-covered droplet migrates toward the centerline of the flow.

Analysis of drop dynamics within the limit of Stokes flow and micron-sized droplets are not limited to theoretical studies. For example, migration of a droplet has been observed experimentally.8,9 Additionally, experiments using a microfluidic interfacial tensiometer have been developed to probe interfacial dynamics and mass transfer processes for a micron-sized droplet in a confined rectangular channel.10 Previous studies have yielded measurements of dynamic multi-component interfacial tension,11,12 and insights into other processes such as tip streaming.13,14

Droplet dynamics in flow fields represents a long-standing problem, both theoretically and experimentally. However, investigation into the effects of surface viscous forces has been limited. In this work we generalize the results of Hanna and Vlahovskab to include the effects of surface viscous forces. Their results are for a drop which remains spherical by assuming that the capillary number is small; we adopt this assumption here as well. This aids isolation of the effects of the surfactant on the interface.

In order to avoid confusion when discussing interfaces free of surfactant, when no surface viscosity is present the interface is said to be clean. If surface viscosities are non-negligible (arising from some surface agent whose total concentration remains constant), the interface is referred to as being viscous. Interfacial viscosity and elasticity correlates to and retards the rate of droplet coalescence in emulsions.15,16 Here we determine their effects on the dynamics of a spherical drop. We suggest that measurement of these quantities yields a new route to characterize interfacial viscosities, and therefore a new way to evaluate emulsion properties.

2. Problem formulation

In this study, we will consider a neutrally buoyant drop of radius $a$. The viscosity of the droplet is $\eta$ while the embedding ambient fluid has a viscosity of $\eta$. The drop interface is considered Newtonian, with surface shear viscosity $\mu$ and dilatational viscosity $\kappa$. The drop is placed in unbounded plane Poiseuille flow, $v^* = (U - a\beta \dot{x})x$, where $U$ is the speed of the flow at the centerline, and $\alpha$ is proportional to the curvature of the flow profile. This flow is chosen because it excites both dilatational and shear deformations of the droplet, in similar magnitudes. We will consider initial drop locations both on and off the centerline...
of the flow. It therefore is convenient to express the applied
velocity in a coordinate system centered on, and translating with
the droplet. In dimensional units, the velocity profile is
\[ \mathbf{v}^* = (-\dot{\gamma} y - \alpha y^2) \hat{x} - U_{\text{mig}}' \] (1)
where the local shear rate experienced by the drop is \( \dot{\gamma} = 2\alpha y \), and
\( y \) is the position of the droplet off the centerline of the flow. The
migration velocity \( U_{\text{mig}}' \) is the difference between the drop’s
velocity and the velocity of the undisturbed flow. In the absence of
surface viscous forces,\(^2\)
\[ U_{\text{mig}}' = -\frac{\lambda}{2 \alpha^2} \nabla^2 \mathbf{x}. \] (2)

We consider that the drop may be covered with an insoluble,
non-diffusive, surfactant whose surface concentration on the
interface is given by \( \Gamma_{\text{eq}} \). The corresponding tension in the
membrane is \( \sigma_{\text{eq}} \). When the interfacial surfactant concentration
is uniform, the interface is viscous; Marangoni effects arise when
the concentration has local variations.

In the absence of an imposed flow, the equilibrium shape of
the droplet is spherical due to surface tension effects. If creeping
flow conditions are assumed in the bulk phases, this shape can
be maintained in the presence of flow if the capillary number,
\( C_a = \eta U_c / (\sigma_{\text{eq}} \Gamma_{\text{eq}}) \), remains small. Here \( U_c \) is the characteristic velocity, \( U_c = a a^2 \). The strength of surface viscous forces relative
to the bulk viscous forces acting on the interface are characterized
by the dimensionless shear and dilational Boussinesq numbers,
\[ \text{Bo}^s = \frac{\mu a}{\eta a}, \quad \text{Bo}^d = \frac{\kappa a}{\eta a}. \] (3)

Gradients in the surface tension may arise due to non-uniformities
in the surfactant distribution stemming from convection of
surfactant on the interface. The ratio of viscous stresses to these
surface tension gradients defines the Marangoni number, \( \text{Ma}^{-1} = \eta U_c / (\sigma_{\text{eq}} \Gamma_{\text{eq}}) \). The surface tension dependence on the local
surfacing gradient is nonlinear for arbitrary concentrations.\(^1\) Here, however, we assume a linear equation of state
(for small deviations on local interfacial concentration \( \Gamma \) from its
equilibrium value \( \Gamma_{\text{eq}} \))
\[ \sigma(\Gamma) = \text{Ma}(1 - \Gamma/\Gamma_{\text{eq}}) + \sigma_{\text{eq}}. \] (4)

In general, it is possible that surface viscosities depend on the
nonuniformities in \( \Gamma \), but in the absence of any such model, we
ignore this possibility, implying that \( \text{Bo}^d \) and \( \text{Bo}^s \) are functions of
\( \Gamma_{\text{eq}} \) only. Henceforth, all variables are rescaled with \( a, \eta, \sigma_{\text{eq}}, \Gamma_{\text{eq}} \)
as characteristic quantities.

### 2.1 Governing equations

The flow in the bulk phases is described using the Stokes equations,
where the velocity \( \mathbf{v} \) and pressure \( p \) satisfy
\[ \nabla p = \eta \nabla \mathbf{v}, \quad \nabla \cdot \mathbf{v} = 0, \] (5)
with \( \hat{\eta} = 1 \) in the suspending fluid and \( \hat{\eta} = \lambda \) in the droplet. The velocity field is continuous across the interface. Far from the
droplet, the velocity tends to the unperturbed imposed flow. At
the interface, the jump in the viscous hydrodynamic stresses is
balanced by membrane surface forces,
\[ \| \mathbf{T}^s \| \cdot \n = -2H \sigma \n + \n \nabla \sigma - \n \sigma \n \cdot \mathbf{r}. \] (6)
where \( \n \) is the surface gradient operator, \( \sigma \) is the surface stress
tensor, \( H \) is the mean curvature of the interface, \( \n \) is the outward
point unit normal vector (for a sphere \( \n = \mathbf{r} \)), and \( \| \cdot \| \) denotes a jump in the quantity enclosed from the inside to the outside.
Here \( \mathbf{T}^s = -\rho \mathbf{I} + \eta [\nabla \mathbf{v} + (\nabla \mathbf{v})^T] \) is the bulk hydrodynamic stress tensor, \( \mathbf{I} \) is the unit tensor, and \( \dagger \) denotes the transpose. For a
spherical droplet, the dimensionless mean curvature is \( 1 \). The third
term on the right-hand side of (6) is the force exerted on the
interface from surface viscous effects. Adopting the Boussinesq–
Seriven constitutive law for Newtonian interfaces gives\(^1\)
\[ \n \nabla \cdot \mathbf{v} = 2 \text{Bo}^d \mathbf{D}_s + (\text{Bo}^d - \text{Bo}^s)(\mathbf{I}_s - \mathbf{D}_s \mathbf{I}_s). \] (7)
where
\[ \mathbf{D}_s = \frac{1}{2} \left[ \nabla \mathbf{v} \mathbf{I}_s + \mathbf{I}_s \nabla \mathbf{v} \right] \] (8)
is the rate of deformation tensor, and \( \mathbf{I}_s = \mathbf{I} - \n \n \). Inserting (8) into (7) gives\(^1\)
\[ \n \nabla \cdot \mathbf{v} = (\text{Bo}^d + \text{Bo}^s) \n \nabla \cdot \mathbf{v} + \n \left[ 2 \text{Bo}^s \mathbf{b} : \nabla \mathbf{v} + (\text{Bo}^d + \text{Bo}^s) 2H \nabla \cdot \mathbf{v} \right] \\
+ \text{Bo}^d \left[ - \n \nabla \cdot \mathbf{v} \times \mathbf{v} \times \mathbf{k} + 2H (\nabla \cdot \mathbf{v}) \cdot \n \right] \\
- 2(\mathbf{b} - 2H \mathbf{I}_s) : \nabla \cdot (\n \mathbf{v} \n \mathbf{u}) \] (9)
where \( \mathbf{b} = -\n \n \nabla \cdot \mathbf{v}, \mathbf{v} = \mathbf{I}_s : \mathbf{v}, \) and \( K \) is the Gaussian curvature.

For a viscous interface with a constant tension \( \sigma = \sigma_{\text{eq}} \), (6) in
conjunction with the conditions on the velocity field is sufficient
to solve for the flow past the spherical droplet. On the other
hand, if an insoluble surfactant is present and gradients in its
interfacial concentration develop, (4) modifies (6),
\[ \| \mathbf{T}^s \| \cdot \n = 2 \text{Ma}(1 - \Gamma) \n - \text{Ma} \n \nabla \Gamma - \n \n \cdot \mathbf{r}. \] (10)

In this situation, in order to close the problem, a conservation
equation for the surfactant concentration is employed as an
evolution equation for \( \Gamma \),
\[ \frac{\partial \Gamma}{\partial t} + \n \nabla \cdot (\n \mathbf{v} \Gamma) + \Gamma (\n \mathbf{v} \cdot \n) (\n \cdot \mathbf{v}) = 0, \] (11)
where any diffusion flux has been neglected. On a sphere, \( \n \nabla \cdot \mathbf{v} = 2 \). Lastly, \( \mathbf{v} \) is the tangential surface velocity.

### 3. Solution for a spherical droplet

In the limit of a spherical droplet, exact expressions for the
velocity field can be obtained as a function of \( \lambda \), \( \text{Bo}^d \), \( \text{Bo}^s \), and, if
present, the concentration of surfactant. From the linearity of the
Stokes equations, the perturbation of the flow field about the
surfactant-covered droplet can be decomposed into two parts:
flow about a viscous drop, and flow induced from Marangoni
stresses.\(^1\) Therefore \( U_{\text{mig}} \) will be decomposed as
\[ U_{\text{mig}} = U_{\text{mig}}^d + U_{\text{mig}}^s. \] (12)
Henceforth, excluding previously defined terms, a superscript ‘s’ will indicate terms arising from surfactant concentration gradient effects, and a superscript 0 will indicate a viscous interface. Owing to the spherical nature of the droplet, the spherical coordinate system, \((r, \theta, \phi)\), is adopted and all fields are expanded in the basis of spherical harmonics (see Appendix A). Using spherical harmonics, the fundamental set of velocity fields is given by

\[
\mathbf{v}_{\text{out}} = c_{\text{jm}m}\mathbf{u}_{\text{jm}}(r) - \mathbf{u}_{\text{jm}}(r) + c_{\text{jm}m}\mathbf{u}_{\text{jm}}(r)
\]

(13)

where summation over repeated indices is implied. Details of the basis functions, \(\mathbf{u}_{\text{jm}}(r)\), can be found in Appendix D.\(^{1,20}\) Note that this velocity field is naturally continuous across the interface. The coefficients which define the far field velocity, \(c_{\text{jm}m}^*\), can be found in Appendix C. Similar to (12), the coefficients \(c_{\text{jm}m}\) are decomposed as \(c_{\text{jm}m} = c_{\text{jm}m}^0 + c_{\text{jm}m}.\) Moreover, in the limit of a spherical droplet, (9) simplifies by recognizing \(K = 1\), and \(b = -1\).

Therefore, on a sphere, (9) reduces to

\[
\nabla_i \cdot \mathbf{v} = (Bo^d + Bo^o)\nabla_i \nabla_i \mathbf{v} - 2Bo^o(\nabla_i \cdot \mathbf{v})\hat{r} + Bo^d[\nabla \times \nabla \times \mathbf{v}_s + \mathbf{v}_s - 3\mathbf{v}_s - 2\nabla_s(\mathbf{v} \cdot \hat{r})].
\]

(14)

\[c_{\text{jm}0} = \frac{2j + 1}{\sqrt{j(j + 1)}} \left(\frac{2\sqrt{j(j + 1)}c_{\text{jm}m}^* - 3c_{\text{jm}m}^*}{1 + \lambda - 2Bo^d + j\delta}\right)
\]

\[c_{\text{jm}1} = \frac{1}{\delta}(2j + 1)c_{\text{jm}1}^*
\]

\[c_{\text{jm}2} = 0
\]

(19)

where \(\delta = 2 + 2\lambda + (1 + j)(Bo^d + Bo^o)\). Note how when \(j = 1\), \(Bo\) does not enter \(c_{\text{jm}m}\), and when \(Bo^d = 0\), and \(Bo^o = 0\), the solution was previously identified by Hanna and Vlahovska.\(^6\) Obtaining an expression for the migration velocity similar to (2) requires determining the difference between the undisturbed imposed flow and the volume averaged velocity of the drop,

\[\mathbf{U}_{\text{mig}} = -\mathbf{v}^*(0) + \frac{3}{4\pi} \int_{\text{drop}} \mathbf{v}(r) \, dr.
\]

(20)

The only nonzero contribution to this integral are the \(\mathbf{u}_{\text{jm}m}\) modes, yielding

\[\mathbf{U}_{\text{mig}} = \sqrt{\frac{3}{8\pi}} \left[ - (c_{112} - c_{12})\hat{x} - i(c_{112} + c_{12})\hat{y} + \sqrt{2}c_{102}\hat{z}\right]
\]

(21)

This shows that the migration velocity of a spherical droplet is only given by the \(j = 1\) modes. In the absence of surfactant, these modes are not coupled to any other of higher order, and the solution can be given in closed form.

### 3.1 Viscous interface solution

Neglecting the effects of surfactant concentration gradients, the coefficients \(c_{\text{jm}m}\) are determined from the stress balance given by (6). The condition that the drop remains spherical places an extra constraint on the system, which overdetermines it if both the normal and tangential components of (6) are employed.\(^6\) In order to maintain sphericity, \(c_{\text{jm}2} = 0\) for \(j > 1\) leaving \(c_{\text{jm}0}\) and \(c_{\text{jm}1}\) to be determined from the tangential components of (6). For \(j = 1\), all three components of (6) are used. Additionally, in order to maintain sphericity, the jump in hydrostatic pressure across the interface is balanced by a large tension \((Ca \ll 1)\) and therefore the effects of \(\sigma_{\text{eq}}\) are not felt here.

Expressed in component form, (6), in conjunction with the spherical harmonic expansion of (9), becomes

\[\tau_{mj0}^* - \tau_{mj0} = -2Bo^d \sqrt{j(j + 1)}c_{\text{jm}2}^0
\]

\[+ [Bo^d(j + 2)(j - 1) + Bo^o(j + 1)] c_{\text{jm}0}^0
\]

\[= 0
\]

(15)

\[c_{\text{jm}1}^0 = c_{\text{jm}1}
\]

(16)

\[c_{\text{jm}2}^0 = 2Bo^d \left[2c_{\text{jm}2} - \sqrt{j(j + 1)}c_{\text{jm}0}^0\right]
\]

(17)

Solving the above system for the coefficients \(c_{\text{jm}m}\) yields, for \(j = 1\),

\[c_{\text{jm}0}^0 = \frac{1}{3\beta} \left[\sqrt{2\beta} c_{\text{jm}0} - (9 + 4Bo^d + 6\lambda) c_{\text{jm}0}^0\right]
\]

\[c_{\text{jm}1}^0 = c_{\text{jm}1}
\]

(18)

\[c_{\text{jm}2}^0 = \frac{1}{3\beta} \left[\sqrt{2\beta} c_{\text{jm}2} + (12 + 2Bo^d + 3\lambda) c_{\text{jm}2}^0\right]
\]

where \(\beta = 2 + 2Bo^d + 3\lambda\) and \(\tilde{\beta} = 2Bo^d - 3 + 3\lambda\). When \(j > 1\) we have

\[c_{\text{jm}m}^0 = \frac{2j + 1}{\sqrt{j(j + 1)}} \left(\frac{2\sqrt{j(j + 1)}c_{\text{jm}m}^* - 3c_{\text{jm}m}^*}{1 + \lambda - 2Bo^d + j\delta}\right)
\]

\[\mathbf{U}_{\text{mig}} = \frac{Ma}{\sqrt{6\pi(3\lambda + 2)}} \left[ - (g_{11} - g_{1-1})\hat{x} - i(g_{11} + g_{1-1})\hat{y} + \sqrt{2}g_{102}\hat{z}\right]
\]

(24)
as a migration velocity induced by gradients in surfactant concentration. 

4. Results and discussion

In this section, first the results concerning a viscous interface are shown, which include analytical expressions for a new slip velocity and drop fluid circulation patterns observable in laboratory experiments. Following that discussion, surfactant gradient effects are introduced, the asymptotic limit of an incompressible interface is explored, and the lateral migration velocity is calculated as a function of \( \text{Bo}^d \) and \( \text{Bo}^s \). Lastly, numerical solutions for arbitrary surfactant concentration gradients are discussed.

4.1 Viscous interface

To begin, we derive here the slip velocity of a drop with surface viscosity and without surfactant concentration gradients. Inserting the appropriate terms from (18), (19) and (47) into (21) yields

\[
U_{\text{mig}} = -\frac{2\text{Bo}^d + 3\lambda}{2 + 2\text{Bo}^d + 3\lambda} \hat{x}.
\]  

In the limit of either high drop viscosity, or large dilational viscosity, the rigid sphere slip migration is recovered, namely

\[
U_{\text{mig}} = -\frac{1}{\text{Bo}^d} \hat{x}.
\]

Moreover, it should be noted that the above slip velocity is independent of the shear surface viscosity, \( \text{Bo}^s \), a result of the fact that \( \text{Bo}^s \) does not appear in (18). Therefore, if \( \text{Bo}^s \) is small and \( \text{Bo}^d \) is large, there is fluid circulation in the drop, yet it lags behind the flow as for a rigid sphere. As a final comment, when \( \text{Bo}^d = 0 \), (25) reduces to (2). The absence of \( \text{Bo}^s \) dependence in the slip velocity is in agreement with Felderhof, who found a velocity independent of \( \text{Bo}^s \) would be ideal as well. The following combination of points \( A \), \( B \), and \( C \) yield an \( x \) velocity component given by

\[
v_x(A) = \frac{5}{3(4 + 4\text{Bo}^d + \lambda)} - \frac{1}{2 + 2\text{Bo}^d + 3\lambda} + \frac{7}{12\nu} \]

and

\[
v_x(B) = -\frac{5}{3(4 + 4\text{Bo}^d + \lambda)} - \frac{1}{2 + 2\text{Bo}^d + 3\lambda} - \frac{7}{3\nu} \]

where \( \nu = (1 + \lambda) + 12\text{Bo}^d + 10\text{Bo}^s \). These velocity components are dependent on the values of both \( \text{Bo}^d \) and \( \text{Bo}^s \). Fluid at the center of the droplet, denoted by point \( C \), has an \( x \) velocity component given by

\[
v_x(C) = \frac{1}{2 + 2\text{Bo}^d + 3\lambda} \]

which clearly has no dependence on \( \text{Bo}^s \). In the limit of large \( \text{Bo}^d \) this becomes \( v_x(C) = 0 \). The other velocity components here are zero for all values of the parameters (at \( y_0 = 0 \)). In (25) and (28) we have isolated velocities that depend only on \( \lambda \) and \( \text{Bo}^d \); a velocity independent of \( \text{Bo}^s \) would be ideal as well. The following combination of points \( A \), \( B \), and \( C \) yield an \( x \)-velocity which depends only on \( \lambda \) and \( \text{Bo}^d \),

\[
\frac{4}{5}v_x(A) + \frac{1}{5}v_x(B) + v_x(C) = \frac{1}{4 + 4\text{Bo}^d + \lambda}.
\]

The combination \( \frac{4}{5}v_x(A) + \frac{1}{5}v_x(B) \) can be obtained from the interfacial velocity measured \( 26^\circ \) from the azimuthal axis from \( A \) towards \( B \).

Fig. 2 shows streamlines within the droplet in the \( x-y \) coordinate plane. The figure contains three parts. In Fig. 2a, the shear and dilational Boussinesq numbers are zero. Effects of \( \text{Bo}^d \) become apparent in Fig. 2b, where \( \text{Bo}^d = 10 \) while \( \text{Bo}^s = 0 \). The magnitude of the fluid velocity near the center of the drop has greatly decreased. Lastly, the influence of \( \text{Bo}^s \) is isolated in Fig. 2c in the case of \( \text{Bo}^d = 10 \) and \( \text{Bo}^s = 0 \). Streamline profiles with other combinations of \( \text{Bo}^d \) and \( \text{Bo}^s \) are readily calculated; in general, these are not qualitatively different from what is shown in Fig. 2.

The position of the stagnation points located along the \( y \) axis (\( y_s \)) are given by solutions of the following 4th-order polynomial equation for \( y_s \)

\[
0 = \frac{5y^2}{4 + 4\text{Bo}^d + \lambda} + \frac{3(2y^2 - 1)}{2 + 2\text{Bo}^d + 3\lambda} + \frac{7}{\nu}y^2(3y^2 - 2)).
\]

It should be noted that although four solutions to (30) exist, only one of them satisfies the criteria that it be both real and less than one. Although analytical solutions to (30) exist, a more illustrative discussion of these solutions is obtained by examining the limit of large Boussinesq number. In the limit of \( \text{Bo}^d \rightarrow \infty \), only the first term in (30) survives, therefore \( y_s = 0 \). On the other hand, in the limit of \( \text{Bo}^s \rightarrow \infty \), the second term in (30) survives, giving the condition \( y_s = \pm 1/\sqrt{2} \approx 0.707 \).
and Bo all plots. In this limit obtained for large Bo in (25), which is another way an incompressible interface can be obtained within the context of this problem. Thus, as regards steady-state interfacial dilatation, both high elasticity or dilational viscosity achieve the same limit.

At the next order in perturbation the relevant terms in (23) are

\[
0 = \left[ \Omega_{m_2n_2} + \mathcal{A}_{m_2n_2} \right] g_{n_2m_2}^{(0)} + W(j) g_{n_2m_2}^{(1)} + \Psi_{m_2n_2}^{(0)} g_{n_2m_2}^{(0)},
\]

Solving the above for \( g_{n_2m_2}^{(1)} \) and inserting it into (24) and using (31) we find that a cross-stream (lateral) migration enters the system

\[
U_{n_2m_2}^{(1)} = \gamma_0 \left( 2\lambda + 3 \right) \left[ 48(\text{Bo}^d)^2 + 56\text{Bo}^o(3 + 2\lambda) + 5(1 + \lambda)(17 + 3\lambda) \right] \\
+ 2\text{Bo}^d[97 + 36\text{Bo}^o(2 + 3\lambda) + \lambda(151 + 27\lambda)\hat{\delta}^{-1}\hat{y}],
\]

where

\[
\hat{\delta} = 9(4 + 4\text{Bo}^d + \lambda)(2 + 2\text{Bo}^d + 3\lambda)(5 + 6\text{Bo}^d + 4\text{Bo}^o + 5\lambda).
\]

Surfactant gradients induce a cross-stream migration of the drop in the flow. This effect is not seen in the incompressible limit of a clean (or viscous interface) spherical drop. This migration velocity depends linearly on \( \gamma_0 \), and is directed towards the flow centerline for all values of \( \lambda, \text{Bo}^d, \) and \( \text{Bo}^o \).

When \( \text{Bo}^d = \text{Bo}^o = 0, U_{n_2m_2}^{(1)} \hat{y} \) decreases monotonically with increasing \( \lambda \) until a rigid-sphere limit is reached. On the other hand, if \( \text{Bo}^d > 0, U_{n_2m_2}^{(1)} \hat{y} \) approaches the rigid-sphere limit either monotonically (\( \text{Bo}^d > \text{Bo}^o \)) or non-monotonically (\( \text{Bo}^d > \text{Bo}^o \)). Here \( \text{Bo}^d \) is the value of \( \text{Bo}^d \) below which (33) has an extremum on the positive \( \lambda \) line, and above which it does not. This behavior is seen in Fig. 3a. If, on the other hand, \( \text{Bo}^o \) were varied while keeping \( \text{Bo}^d = 0, \) non-monotonic behavior is seen in \( U_{n_2m_2}^{(1)} \hat{y} \) for all values of \( \lambda \). It should be noted that in the limit of large \( \lambda, \) the addition of the surface viscous forces does not modify the conclusions reached in ref. 6. In the presence of both shear and dilatational forces, dilatation dominates, and thus the addition of even large values \( \text{Bo}^o \) (e.g. \( 10^6 \)) results in only a minor change to the curves in Fig. 3a.

Results for an arbitrary distribution of surfactant on the surface can be obtained by solving (23) numerically. In this case, all modes are coupled and the (23) represents an infinite sum. For numerical convenience, the series is truncated at the \( j = 6 \) harmonic mode. The trajectory of the droplet in the channel \( (y_j(t)) \) is found by numerically solving
Previous works on capsules\textsuperscript{23,24} found that the motion of an object in unbounded parabolic flow is directed towards the centerline of the flow. This observation is consistent with the results of Fig. 4, where the trajectory, $y_s$, is shown for a spherical surfactant-covered droplet. Increasing either Bo\textsuperscript{d} or Bo\textsuperscript{s} will increase the time needed for the drop to reach the equilibrium centerline of the flow field. However, dilatational surface viscosity severely delays cross-stream migration of the droplet, while the effects of shear surface viscosity effects are not as strong. Surfactant concentration profiles are qualitatively similar to those of Fig. 2 in Hanna and Vlahovska,\textsuperscript{6} and are essentially combinations of $j = 3$ and $j = 2$ harmonic modes.

5. Conclusions

We have shown here that interfacial viscous forces can modify the dynamics of a spherical droplet in a plane unbounded Poiseuille flow. A modified slip velocity was found which depends only on the viscosity of the drop and surface dilatation. Additionally, several locations on and within the drop were found where components of the velocity field were either independent of Bo\textsuperscript{d} or Bo\textsuperscript{s}, or where a combination eliminated the dependence of one Boussinesq number. These points are ideal locations for experimental measurements to obtain information about surface viscosities.

When Marangoni effects (i.e. concentration gradients in surfactant) are considered, the limit of incompressibility reveals a slip coefficient identical to that of a clean droplet with high surface dilational viscosity. Concentration gradients still break the symmetry and induce a cross-stream migration. For arbitrary surfactant concentrations, drop trajectories were numerically found which highlight the effects of surface viscous forces.

Whether for viscous interfaces or those where surfactant concentration is explicit, we have considered the effect of an interfacial agent, i.e., of some agent which forms on the interface and modifies its properties. The viscous interface was assumed to have constant properties if other transport mechanisms are sufficiently active to maintain a uniform concentration of interfacial agents. Motivated by the results obtained here, an investigation into deformable droplets in flow with viscous interfaces is warranted.

Appendix A – Spherical harmonics

The normalized scalar spherical harmonics are defined as

$$Y_{jm}(\theta, \phi) = \frac{2j + 1}{4\pi} \frac{(j - n)!}{(j + n)!} (-1)^m P^n_m(\cos \theta) e^{im\phi},$$

where $P^n_m(\cos \theta)$ are the associated Legendre polynomials. From the scalar harmonics, the vector spherical harmonics relevant to our study are defined as

$$y_{jm0} = [j(j + 1)]^{-1/2} \mathbf{\nabla}_\Omega Y_{jm},$$

$$y_{jm1} = -i \mathbf{r} \times y_{jm0},$$

$$y_{jm2} = \mathbf{r} Y_{jm},$$

where $\mathbf{\nabla}_\Omega$ is the angular part of the gradient operator in spherical coordinates.
Appendix B – Coupling of scalar and vector harmonics

Within this study, the coupling between scalar and vector spherical harmonics is inevitable. In this section, formulas developed in ref. 25 and given in ref. 26 for this coupling are shown for completeness. The product of scalar harmonics is recoupled as

\[ Y_{jm} Y_{jm'} = 2 \zeta(j_1 j_2 m m_1 m_2, 2) Y_{jm'} \]  

(38)

Summation over repeated indices is implied. The coupling formula between scalar and vector harmonics is

\[ y_{jqm} Y_{jm} = C_{jqm} (j_1 j_2) \times \zeta(j_1 j_2 m m_1 m_2, 2) y_{jm} Y_{jm'} \]  

(39)

The entries in the coupling matrix \( C_{jqm} \) are

\[ C_{00} = C_{10} = [j(j + 1) j_2(j_2 + 1)]^{1/2} \chi(j_1 j_2) \]
\[ C_{01} = -[j(j + 1) j_2(j_2 + 1)]^{1/2} \theta(j_1 j_2) \]
\[ C_{22} = 2. \]

All other entries are zero. In the above,

\[ \chi(j_1 j_2) = j(j + 1) + j_2(j_2 + 1) - j_1(j_1 + 1) \]  

(41)

and

\[ \theta(j_1 j_2) = [(j + 1) j_2 j_2(j_2 + 1)]^{1/2} \times (j(j + 1) + j_2(j_2 + 1))^{1/2} \]  

(42)

The coupling between two vector harmonics produces a scalar harmonic in the following way

\[ y_{jqm} Y_{jm'} = C_{jqm} (j_1 j_2) (-1)^{j_1 j_2} \times \zeta(j_1 j_2 m m_1 m_2, 2) Y_{jm'} \]  

(43)

In (38), (39), and (43), \( \zeta \) are the Clebsch–Gordan coefficients

\[ \zeta(j_1 j_2 m m_1 m_2, 2) = \frac{(-1)^{j_2}}{2 \pi^{1/2}} \left( \begin{array}{ccc} 2j + 1 & 2j_2 + 1 & 2j_2 + 1 \end{array} \right) \left( \begin{array}{ccc} j_1 & j_2 & j_2 \\ 0 & m & 0 \end{array} \right) \]

where \( \xi = 0 \) if \( q + q_2 \) is odd, and \( \xi = 1 \) if \( q + q_2 \) is either even or zero. Lastly,

\[ \left( \begin{array}{ccc} j & j_1 & j_2 \\ m & m_1 & m_2 \end{array} \right) \]  

(45)

is the Wigner 3j symbol.\(^{25}\) Properties of the 3j symbol can be found in ref. 26. For later convenience, let

\[ G_{jqm}^{lm} = C_{jqm} (j_2 j_1 m m_1 m_2) \]  

(46)

Appendix C – Coefficients of unbounded plane Poiseuille flow

For completeness, in this section, the coefficients \( c_{jqm} \), for plane Poiseuille flow are given. The full flow field is therefore given by \( v^* = c_{jqm} u_{jqm}^* \). These were taken from ref. 6 and are

\[ c_{jqm} = \alpha \sqrt{\frac{4 \pi}{105}} c_{jqm} \]  

(47a)

\[ c_{jqm} = \alpha \sqrt{\frac{2}{15}} \sqrt{\frac{\pi}{7}} c_{jqm} \]  

(47b)

\[ c_{jqm} = \pm i \gamma \sqrt{\frac{\pi}{5}} c_{jqm} \]  

(47c)

\[ c_{jqm} = \pm i \gamma \sqrt{\frac{\pi}{15}} \]  

(47d)

\[ c_{jqm} = \pm i \gamma \sqrt{\frac{\pi}{3}} \]  

(47e)

Appendix D – Fundamental set of velocity fields

Following the definitions given in Blawzdziewicz et al.,\(^{3} \) we list the expressions for the functions \( u_{jqm}^* (r, \theta, \phi) \). The velocity field outside the vesicle is described by

\[ u_{jqm} = \frac{1}{2} r^{j-1} (2 - j + j r^{-2}) y_{jqm} \]  

(48a)

\[ \frac{1}{2} r^{-j} (j + 1, j + 1) y_{jqm} \]  

(48b)

\[ \frac{1}{2} r^{-j} (j + 2, j + 2) y_{jqm} \]  

(48c)

The velocity field inside the vesicle is described by

\[ u_{jqm} = \frac{1}{2} r^{j-1} (-(j + 1) + j + 3) y_{jqm} \]  

(49a)

\[ \frac{1}{2} r^{-j} (j + 1, j + 1) y_{jqm} \]  

(49b)

\[ \frac{1}{2} r^{-j} (3 + j, 3 + j) y_{jqm} \]  

(49c)

On a sphere with \( r = 1 \) these velocity fields reduce to the vector spherical harmonics defined by (37)

\[ u_{jqm}^+ = u_{jqm} \]  

(50)

Hence, \( u_{jqm}^+ \) is tangential, and \( u_{jqm}^+ \) is normal to a sphere. In addition, \( u_{jqm} \) defines an irrotational velocity field.

Appendix E – Hydrodynamic tractions

The hydrodynamic tractions associated with the velocity fields (13) can be represented in vector spherical harmonics, \( T^{\mu v} = \varepsilon_{\mu v q} y_{jqm} \)\(^{27} \) where
\[ e_{jm}^\text{out} = c_{jm}^\text{in} \left( \Theta_q^+ q - \Theta_q^+ q' \right) + c_{jm} \Theta_q^+ q \]

\[ e_{jm}^\text{in} = \lambda c_{jm} \Theta_q^+ q \]

where summation over \( q' \) is implied. The symmetric matrices \( \Theta_q^+ q \) are

\[ \Theta_q^+ q = \begin{pmatrix}
2j + 1 & 0 & -3 \sqrt{\frac{j + 1}{j}} \\
0 & j - 1 & 0 \\
-3 \sqrt{\frac{j + 1}{j}} & 0 & 2j + 3 \sqrt{\frac{j + 1}{j}}
\end{pmatrix} \]

\[ \Theta_q^+ q = \begin{pmatrix}
2j - 1 & 0 & -3 \sqrt{\frac{j + 1}{j}} \\
0 & -j - 1 & 0 \\
-3 \sqrt{\frac{j + 1}{j}} & -2j + 1 & -\frac{3}{j}
\end{pmatrix} \]

The reader should note that the indexing of the matrices begins with 0.

**Appendix F – Surfactant-induced velocity field and evolution equations**

The Marangoni terms present in (10) give rise to the following coefficients found in ref. 6:

\[ c_{jm0}^a = -\delta_{lj} \sqrt{\frac{2}{\lambda + 2}} \frac{Ma}{2} g_{jm} - \frac{(1 - \delta_{lj}) Ma}{1 + \lambda} g_{jm} \]

\[ c_{jm1}^a = 0 \]

\[ c_{jm2}^a = \frac{\delta_{lj}}{3\lambda + 2} \frac{Ma}{2} g_{jm} \]

where as before, \( \delta_{lj} \) is the Kronecker delta.

The terms present in (23) are of two forms: clean drop and surfactant terms. The clean drop terms are

\[ C_{jm} = \sqrt{j(j + 1)} e_{jm2}^0 - 2c_{jm2}^a \]

\[ \Omega_{jm0jm1} = \sqrt{j(j + 1)} e_{jm0jm1}^0 \]

\[ \Lambda = \sqrt{j(j + 1)} e_{jm0jm1}^0 e_{jm2}^0 - 2e_{jm0jm2jm2}^{02} - 2e_{jm0jm1jm2jm2}^{02} \]

\[ \Psi_{jm0jm1jm2jm3jm2} = \sqrt{j(j + 1)} \psi_{jm0jm1jm2jm3jm2}^{02} - 2\psi_{jm0jm1jm2jm3jm2}^{02} \]

\[ \psi_{jm0jm1jm2jm3jm2}^{02} = \sqrt{j(j + 1)} \psi_{jm0jm1jm2jm3jm2}^{02} - 2\psi_{jm0jm1jm2jm3jm2}^{02} \]

**Appendix G – Expressions for \( g_{jm} \)**

In the limit of a nearly incompressible surfactant (\( Ma^{-1} \ll 1 \)), the leading-order evolution equation for \( g_{jm} \) (23) admits the following solution for \( j = 1 \)

\[ g_{jm}^{(0)} = \frac{2 + 3\lambda}{2 + 2Bo^d} \left[ \sqrt{2(2Bo^d - 3 + 3\lambda)} c_{jm2}^a \right. \]

\[ + (9 + 4Bo^d + 6\lambda) c_{jm0}^a \]

and for \( j > 1 \),

\[ g_{jm}^{(0)} = \frac{2j + 1}{\sqrt{j(j + 1)(1 + \lambda - 2Bo^d + j\lambda)}} \]

\[ 3c_{jm2}^a - 2\sqrt{j(j + 1)} c_{jm0}^a \]

The migration induced by the conception of surfactant can be obtained by inserting (57) into (24).

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**References**