

Effect of interfacial viscosities on droplet migration at low surfactant concentrations

Rajat Dandekar¹ and Arezoo M. Ardekani¹

¹School of Mechanical Engineering, Purdue University, West Lafayette, IN 49707, USA

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In this paper, we theoretically investigate the migration of a surfactant covered droplet in a Poiseuille flow by including the surface viscosities of the droplet. We employ a regular perturbation expansion for low surface Péclet numbers and solve the problem upto a second order approximation. We represent the drop surface as a two-dimensional homogeneous fluid using the Bousinessq-Scriven law and employ the Lamb's general solution to represent the velocity fields inside and outside the droplet. We obtain an expression for the cross-stream migration velocity of the droplet, where the surface viscosities are captured by the Bousinessq numbers for surface shear and surface dilatation. We elucidate the influence of the surface viscosities on the migration characteristics of the droplet and the surfactant redistribution on the droplet surface. Our study sheds light upon the importance of the inclusion of droplet surface viscosity in theoretical models aimed at predicting the droplet migration characteristics in experiments involving droplet manipulation.

1. Introduction

Migration of droplets plays an important role in microfluidic devices (Pamme 2007). Some important applications involving droplet manipulation include cell sorting, separation of particles and drug delivery (Karimi *et al.* 2013; Stone *et al.* 2004; Di Carlo *et al.* 2007; Gascoyne *et al.* 2004). In such applications, accurate control of the droplet motion is important for realizing optimum process capabilities. The Reynolds number in such applications is typically much smaller than unity ($Re \ll 1$) due to the small channel dimensions as well as the droplet size. It is known that a non-deformable droplet placed in a purely viscous Newtonian fluid only translates in the flow direction with a lower velocity than the background flow at the drop center (Hetsroni & Haber 1970). It does not experience any lateral motion across streamlines due to the reversibility of the Stokes flow. However, the presence of non-linearities can break the fore-aft symmetry and consequently the reversible nature of the flow. In such a case, the droplet can exhibit a cross-stream migration as well. Some significant mechanisms through which non-linearities can be introduced in the system are in the form of fluid inertia, particle surface deformation and non-Newtonian rheology of the suspending fluid (Leal 2007). Initial works started with the analysis of migration of solid particles in the presence of fluid inertia (Segre & Silberberg 1961; Rubinow & Keller 1961; Saffman 1965; Cox & Brenner 1968; Ho & Leal 1974; Vasseur & Cox 1976). Subsequently, several works have focused on the cross-stream migration of droplets due to surface deformation (Haber & Hetsroni 1971; Wohl & Rubinow 1974; Chan & Leal 1979; Stan *et al.* 2011; Mandal & Chakraborty 2015; Mandal *et al.* 2016) and the non-Newtonian rheology of the suspending fluid (Chan & Leal 1979; Mukherjee & Sarkar 2013, 2014).

Most of the microfluidic systems involving manipulation of droplets are expected to

Work	Regime
Hanna & Vlahovska (2010)	$Pe_s \rightarrow \infty, \eta_\mu = 0, \eta_\kappa = 0$
Pak <i>et al.</i> (2014)	$Pe_s \ll 1, \eta_\mu = 0, \eta_\kappa = 0$
Schwalbe <i>et al.</i> (2011)	$Pe_s \rightarrow \infty, \eta_\mu \neq 0, \eta_\kappa \neq 0$
This work	$Pe_s \ll 1, \eta_\mu \neq 0, \eta_\kappa \neq 0$

Table 1: List of previous works studying the cross-stream migration of an eccentrically placed surfactant laden droplet in an unbounded Poiseuille flow. Pe_s represents the surface Péclet number, η_μ and η_κ represent the surface shear and dilatation viscosity respectively.

contain surfactants which might be present as contaminants, additives or impurities (Stan *et al.* 2013). The surfactant molecules have two distinct chemical moieties which allows them to adsorb at interfaces between immiscible liquids. In the presence of an external flow, surface advection causes the surfactant molecules to redistribute along the interface. An asymmetric redistribution leads to interfacial tension gradients along the interface which drives a flow in the surrounding fluid known as the Marangoni flow. This phenomenon breaks the fore-aft symmetry of the problem and thereby the reversibility which causes a surfactant laden droplet to migrate across the streamlines. This is a relatively unexplored phenomena in literature which compels us to focus on this problem.

Theoretical work in this direction started within the last decade, when Hanna & Vlahovska (2010) predicted the cross-stream migration velocity of a surfactant laden droplet in a Poiseuille flow with negligible surface diffusion ($Pe_s \rightarrow \infty$), where Pe_s represents the surface Péclet number. They performed their analysis for the cases of high Marangoni number and high drop viscosity, by employing a regular perturbation expansion approach to solve the problem. Through their analysis, they found that, for both the cases, the drop always migrates towards the center of the channel. Later, Pak *et al.* (2014) extended their analysis as they explored the opposite limit of small surface Péclet numbers ($Pe_s \ll 1$). They employed a regular perturbation expansion method with the small parameter as Pe_s combined with an efficient use of the Lorentz reciprocal theorem to bypass the detailed calculations of the full flow problem. Interestingly, they found that, the cross stream velocity is zero upto first order in the surface Péclet number and the first non-zero term only appears at the second order. Again, they observed that the drop migrates towards the center of the channel with a velocity directly proportional to the distance of the drop from the centerline of the Poiseuille flow. Das *et al.* (2017) considered the droplet to be deformable and predicted the migration velocity of the droplet in terms of an asymptotic expansion with the small parameter as the capillary number (Ca). They found that, for small surface Péclet numbers ($Pe_s \ll 1$), the drop has a tendency to migrate towards or away from the centerline depending on the viscosity ratio of the fluid inside and outside the drop. More recently, Santra *et al.* (2018) experimentally measured the cross-stream migration velocity of a surfactant laden droplet subjected to an imposed flow in a confined fluidic environment. Panigrahi *et al.* (2018) explored the effect of interfacial viscosities on the droplet motion in a non-

isothermal Poiseuille flow. Gounley *et al.* (2016) provided a comprehensive numerical analysis regarding the effect of surface viscosities on droplets immersed in shear flow. However, in their analysis, they neglect the surfactant transport on the surface of the drop and the Marangoni stresses which arise from gradients in the surface tension.

The variation of the surface tension with the surfactant concentration gives rise to Gibbs elasticity which provides a measure of the sensitivity of the surface tension with the surfactant concentration, as well as Marangoni stresses at the interface (Leal 2007). In addition, surfactants also give rise to a surface excess rheology in comparison with a clean interface. In particular, the interface between two fluids can exhibit a complex rheological behavior, which can comprise of a surface viscosity as well as surface elasticity. In the present analysis, we neglected the elastic effects on the surface rheology and only focus on the effects of the surface viscosity. The surface viscosity arises from the rate dependent resistance of the interface to velocity gradients in the plane of the interface. We thus expect that interfacial viscosity combined with the interfacial tension will provide a more realistic depiction of the fluid-fluid interface. The simplest model which describes the mechanics of an interface is the Boussinesq-Scriven law (Boussinesq 1913; Scriven 1960) which treats the interface as a homogeneous two-dimensional fluid with surface shear and dilatation viscosities. Using the Boussinesq-Scriven model to represent the interfacial viscosities, Schwalbe *et al.* (2011) predicted the cross-stream migration velocity of an eccentrically placed surfactant covered droplet in a Poiseuille flow with negligible surface diffusion ($Pe_s \rightarrow \infty$). In addition, they found that the presence of interfacial stresses significantly altered the slip velocity and the droplet-circulation velocities.

Currently, we are unaware of the effect of the interfacial stresses on the droplet dynamics in limit of small surface Péclet number ($Pe_s \ll 1$). Analysis of this limit will allow us to close the current literature gap and provide a more complete picture regarding the cross-stream migration of a surfactant covered droplet in an unbounded Poiseuille flow (refer to Table 1). In this work, we explore the migration of a surfactant covered non-deformable droplet in an unbounded Poiseuille flow including the effects of interfacial stresses, at low surface Péclet numbers. We assume that the surfactant is insoluble in the bulk fluid and that a small amount of surfactant is adsorbed on the drop surface. We note that, the assumption of a dilute surfactant concentration considerably limits the extension of our analysis to biological flows, where the surfactants are expected to be more tightly packed and the intermolecular interactions between the adsorbed surfactant molecules should be considered (Manikantan & Squires 2020). We use the Boussinesq-Scriven law to represent the interface as a two-dimensional fluid with surface shear and dilatation viscosities. We neglect the elasticity of the interface and assume the interfacial viscosities to be independent of the surfactant concentration. This allows us to examine the effect of interfacial rheology on the droplet dynamics. Section 2 summarizes the problem formulation and the governing equations for the problem. Section 3 focuses on the solution methodology and important results from our study.

2. Problem Formulation

Figure 1 shows a surfactant covered neutrally buoyant droplet of radius a and viscosity $\lambda\eta$ immersed in a fluid of viscosity η and density ρ . There are two coordinate systems defined in the manuscript (x, y, z) and (r, θ, ϕ) . θ is the angle made by the vector shown as \mathbf{r} in the figure with the z -axis. ϕ is the angle made by the projection of the vector \mathbf{r} on the $x - y$ plane with the x -axis. The dashed blue line represents the projection operation which transforms the vector \mathbf{r} to a vector in the $x - y$ plane. The migration velocity of the droplet is represented as \mathbf{U} . The droplet is subjected to an external Poiseuille flow

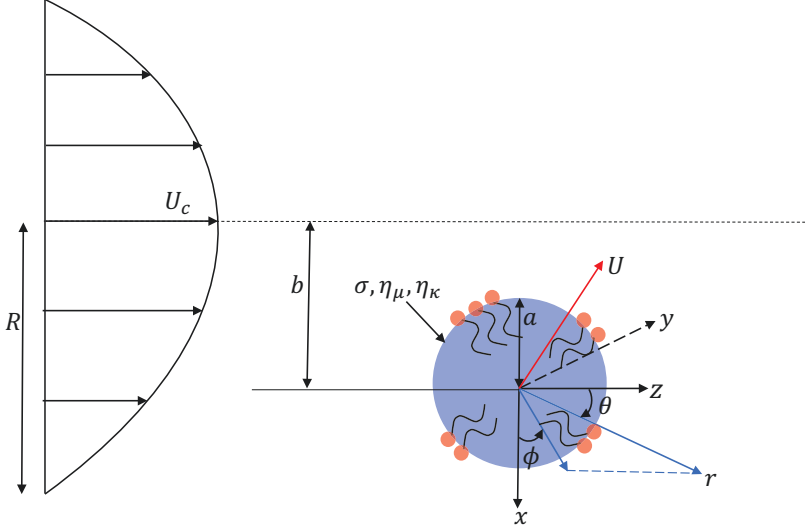


Figure 1: Surfactant laden droplet of radius a immersed in a cylindrical Poiseuille flow at a radial distance of b from the flow axis. (x, y, z) and (r, θ, ϕ) represent the Cartesian and spherical coordinate systems attached to the centre of the droplet respectively. Here, θ is the angle made by the vector shown as \mathbf{r} in the figure with the z -axis, ϕ is the angle made by the projection of the vector \mathbf{r} on the $x - y$ plane (shown as a blue vector) with the x -axis. The dashed blue line represents the z - coordinate of the vector \mathbf{r}

which is given by,

$$\mathbf{U}_\infty = U_c \left(1 - \frac{r_0^2}{R^2} \right) \mathbf{e}_z$$

Here, r_0 is the radial distance measured from the flow axis and U_c is the fluid velocity at $r_0 = 0$. The droplet is eccentrically located at a radial distance of b from the flow axis. In the absence of any flow, the surfactant distributes itself uniformly on the droplet surface at equilibrium. The equilibrium surfactant concentration is given by Γ_{eq} . For a clean drop, the interfacial tension is represented by σ_c . However, due to the presence of the surfactant, the interfacial tension is lowered. If the surfactant concentration is small, the surface tension can be described by the following linear relationship (Leal 2007),

$$\sigma = \sigma_c - RT\Gamma \quad (2.1)$$

Here, Γ denotes the surfactant concentration, R is the gas constant and T is the ambient temperature. We assume that the surfactant is insoluble in both the fluids inside and outside the drop. The interfacial viscosities are represented by η_μ and η_κ , which signify the surface shear and dilatational viscosities respectively.

We solve the problem in the creeping flow limit ($Re = 0$). In this limit, we can neglect the inertial forces exerted on the drop and the velocity field can be assumed to be setup instantaneously. We also assume that the drop is non-deformable. This assumption is valid if the surface tension forces dominate the viscous forces and the capillary number $\eta U_c / \sigma_c$ is small. We use a quasi-steady approximation and assume that the time taken for the surfactant redistribution is very small compared to the time scale associated with the

drop migration. Owing to the use of a regular perturbation methodology with Pe_s as the small parameter, we expect the characteristic velocity scale in the transverse direction to be expressed as $Pe_s^n U_c$. Here, $n \geq 1$ and represents the order of approximation at which the transverse migration velocity first becomes non-zero. When interfacial stresses are not considered, Pak *et al.* (2014) showed that the migration velocity is zero upto the first order and thus $n = 2$. Although in our problem we cannot predict the value of n a priori, we expect the magnitude of the velocity scale in the transverse direction to be at least an order of magnitude less than the longitudinal velocity scale U_c as $Pe_s \ll 1$. Hence, in order to check the validity of the quasi-steady approximation, the surfactant redistribution time scale (a^2/D_s) should be compared with the time scale associated with the motion of the droplet in the longitudinal direction (a/U_c). This implies that $Pe_s \ll 1$ which is the regime of analysis in our work.

2.1. Governing Equations

We express the equations of motion in a frame of reference translating with the drop (refer to the (r, θ, ϕ) coordinate system in figure 1). The velocity and pressure fields inside and outside the drop are represented by (\mathbf{u}_i, p_i) and (\mathbf{u}_e, p_e) respectively. We make the governing equations dimensionless by using the following scales: length scale (l_c) = a , velocity scale (u_c) = U_c , pressure scale (p_c) = $\eta U_c/a$. As inertia is considered to be negligible, the creeping flow dimensionless equations inside and outside the drop are given by,

$$-\nabla p_i + \lambda \nabla^2 \mathbf{u}_i = \mathbf{0}, \quad \nabla \cdot \mathbf{u}_i = 0, \quad (2.2a)$$

$$-\nabla p_e + \nabla^2 \mathbf{u}_e = \mathbf{0}, \quad \nabla \cdot \mathbf{u}_e = 0. \quad (2.2b)$$

Additionally, we have the surfactant transport equation for an insoluble surfactant which describes the steady state convection and diffusion processes on the interface as follows (Leal 2007),

$$Pe_s (\nabla_s \cdot (\Gamma \mathbf{u}_s) + \Gamma (\nabla_s \cdot \mathbf{n})(\mathbf{u} \cdot \mathbf{n})) = \nabla_s^2 \Gamma \quad (2.3)$$

We have made the equation dimensionless by using Γ_{eq} as the characteristic concentration scale. Here, $Pe_s = U_c a/D_s$ is the surface Péclet number, where D_s represents the diffusivity of the surfactant. Γ is the surfactant concentration at the interface, \mathbf{u}_s is the interface velocity, \mathbf{n} is the normal vector at the interface and $\nabla_s = \nabla - \mathbf{n}(\mathbf{n} \cdot \nabla)$ represents the gradient operator in the plane of the interface. Here, it should be noted that the unsteady term has been neglected in the above equation due to the quasi-steady approximation discussed in the previous section.

2.2. Boundary conditions

Far away from the drop, the velocity field is given by the difference between the background flow and the drop migration velocity as follows,

$$\mathbf{u}_e(r \rightarrow \infty) = \mathbf{U}_\infty - \mathbf{U}. \quad (2.4)$$

At the surface of the droplet, we apply the condition of velocity continuity and the kinematic boundary condition for a non-deforming interface to yield the following,

$$\mathbf{u}_i = \mathbf{u}_e \quad \text{at } r = 1, \quad (2.5a)$$

$$\mathbf{u}_i \cdot \mathbf{n} = 0 \quad \text{at } r = 1. \quad (2.5b)$$

Finally, we write the tangential stress balance at the surface of the drop as follows,

$$\mathbf{n} \cdot (\boldsymbol{\sigma}_e - \lambda \boldsymbol{\sigma}_i) \cdot (\mathbf{I} - \mathbf{n}\mathbf{n}) = Ma \nabla_s \Gamma - \nabla_s \cdot \boldsymbol{\tau}_s. \quad (2.6)$$

Here, $Ma = RT\Gamma_{eq}/U_c\eta$ is the Marangoni number which signifies the relative strength of the characteristic Marangoni stresses and viscous stresses. We have used equation (2.1) to express the surface tension in terms of the surfactant concentration. $\boldsymbol{\tau}_s$ represents the interfacial stress which arises due to the presence of surface viscosities. We use the Bousinessq-Scriven constitutive law to represent the interfacial stress as follows,

$$\boldsymbol{\tau}_s = 2Bq_\mu \mathbf{D}_s + (Bq_\kappa - Bq_\mu)(\nabla_s \cdot \mathbf{u}_s) \mathbf{I}_s \quad (2.7)$$

Here, $\mathbf{D}_s = \frac{1}{2}((\nabla_s \mathbf{u}_s) \cdot \mathbf{I}_s + \mathbf{I}_s \cdot (\nabla_s \mathbf{u}_s)^T)$ and $\mathbf{I}_s = \mathbf{I} - \mathbf{n}\mathbf{n}$, where \mathbf{I} is the identity tensor. $Bq_\mu = \eta_\mu/\eta a$ is the Bousinessq number for surface shear viscosity and $Bq_\kappa = \eta_\kappa/\eta a$ is the Bousinessq number for surface dilatation viscosity. In the normal direction, the viscous pressure and the stress contributions across the interface are balanced by the capillary pressure and a contribution from the surface tension variation with the surfactant concentration. In particular, the normal stress balance across the interface can be written as follows,

$$\mathbf{n} \cdot (\boldsymbol{\sigma}_e - \lambda \boldsymbol{\sigma}_i) \cdot \mathbf{n} = \frac{1}{Ca} \nabla_s \cdot \mathbf{n} - \frac{\beta \Gamma}{Ca} \nabla_s \cdot \mathbf{n}. \quad (2.8)$$

Here, $\beta = RT\Gamma_{eq}/\sigma_c$ is the Gibbs elasticity parameter which measures the sensitivity of the variation of the surface tension with the surfactant concentration. Typical values of β lie between 0 and 1 (Das *et al.* 2017). This implies that, if $Ca \ll 1$, the difference in the normal stresses can be balanced by a very small contribution from the term $\nabla_s \cdot \mathbf{n}$ and the droplet deformation can be neglected (Leal 2007)

Additionally, we note that, due to the kinematic boundary condition (refer to equation (2.5b)), the second term in the surfactant transport equation (refer to equation (2.3)) is identically zero.

3. Solution

In order to solve equations (2.2) and (2.3), we use a regular perturbation expansion approach with Pe_s as the small parameter. We express the unknown variables in the following form,

$$h = h^{(0)} + Pe_s h^{(1)} + Pe_s^2 h^{(2)} + O(Pe_s^3), \quad h = \{\mathbf{u}_i, \mathbf{u}_e, p_i, p_e, \Gamma, \mathbf{U}\}.$$

As the velocity fields at every order in Pe_s satisfy the Stokes equations (refer to equation (2.2)), we use the Lamb's general solution to express the velocity and pressure fields in terms of spherical harmonics. The velocity and pressure fields inside the droplet can be represented in terms of growing spherical harmonics as follows,

$$\mathbf{u}_i^{(q)} = \sum_{n=1}^{\infty} \nabla \times (\mathbf{r} \chi_n) + \nabla \phi_n + \frac{n+3}{2(n+1)(2n+3)\lambda} r^2 \nabla p_n - \frac{n}{(n+1)(2n+3)\lambda} \mathbf{r} p_n, \quad (3.1a)$$

$$p_i^{(q)} = \sum_{n=0}^{\infty} p_n \quad (3.1b)$$

Expressions for p_n , ϕ_n and χ_n are given in Appendix A. Similarly, we can express the velocity field outside the droplet as follows,

$$\mathbf{u}_e^{(q)} = (\mathbf{U}_\infty - \mathbf{U}) + \sum_{n=1}^{\infty} \nabla \times (\mathbf{r} \chi_{-n-1}) + \nabla \phi_{-n-1} - \frac{n-2}{2n(2n-1)} r^2 \nabla p_{-n-1} + \frac{n+1}{n(2n-1)} \mathbf{r} p_{-n-1}, \quad (3.2a)$$

$$p_e^{(q)} = \sum_{n=0}^{\infty} p_{-n-1} \quad (3.2b)$$

Expressions for p_{-n-1} , ϕ_{-n-1} and χ_{-n-1} are given in Appendix A. Finally, we express the surfactant concentration at the drop surface in terms of solid spherical harmonics as follows,

$$\Gamma^{(q)} = \sum_{n=0}^{\infty} \sum_{m=0}^n \left(\Gamma_{n,m}^{(q)} \cos(m\phi) + \hat{\Gamma}_{n,m}^{(q)} \sin(m\phi) \right) P_{n,m}(\cos\theta). \quad (3.3)$$

The unknown coefficients are determined by substituting the velocity fields as described above in the surfactant transport equation (refer to equation (2.3)) and the boundary conditions at the drop surface (refer to equations (2.5) and (2.6)). Here, we note that the drop migration velocity \mathbf{U} is still an unknown and yet to be determined. As the inertia of the drop is neglected in our analysis, the net force exerted on the drop is zero. For a neutrally buoyant drop, this implies that the hydrodynamic force acting on the drop is zero. Consequently, we have an additional equation as follows,

$$\mathbf{F}_h^{(q)} = 4\pi \nabla (r^3 p_{-2}) = \mathbf{0}. \quad (3.4)$$

Next, we substitute the perturbation expansions of the velocity, pressure and the surfactant fields in the equations of motion and obtain the governing equations and boundary conditions at various orders in Pe_s .

3.1. Solution at leading order

At leading order, the creeping flow and the surfactant transport equations are given by,

$$-\nabla p_i^{(0)} + \lambda \nabla^2 \mathbf{u}_i^{(0)} = \mathbf{0}, \quad (3.5a)$$

$$-\nabla p_e^{(0)} + \nabla^2 \mathbf{u}_e^{(0)} = \mathbf{0}, \quad (3.5b)$$

$$\nabla^2 \Gamma^{(0)} = 0. \quad (3.5c)$$

We observe that, at leading order, the fluid flow has no effect on the surfactant concentration. Consequently, the surfactant is distributed uniformly along the drop surface. The Stokes equations are subjected to the following boundary conditions,

$$\mathbf{u}_i^{(0)} = \mathbf{u}_e^{(0)} \quad \text{at } r = 1,$$

$$\mathbf{u}_i^{(0)} \cdot \mathbf{n} = 0 \quad \text{at } r = 1.$$

$$\mathbf{n} \cdot \left(\boldsymbol{\sigma}_e^{(0)} - \lambda \boldsymbol{\sigma}_i^{(0)} \right) \cdot (\mathbf{I} - \mathbf{n}\mathbf{n}) = -\nabla_s \cdot \boldsymbol{\tau}_s^{(0)}.$$

We use equations (3.1) and (3.2) to express the velocity fields inside and outside the drop respectively. We then obtain the unknown coefficients in the velocity field expansions by satisfying the above boundary conditions and the force free condition expressed in equation (3.4). We find that, at leading order, the drop only translates in the direction of the flow without any motion across the streamlines. The translational velocity of the drop at leading order is given as follows,

$$\mathbf{U}^{(0)} = \left(1 - \frac{b^2}{R^2} - \frac{2a^2(2Bq_\kappa + 3\lambda)}{3R^2(2 + 2Bq_\kappa + 3\lambda)} \right) \mathbf{e}_z. \quad (3.6)$$

As the surfactant effects influence the droplet motion only at higher orders, Schwalbe *et al.* (2011) obtained the same expression for the drop migration velocity at the leading order for the limit of $Pe_s \rightarrow \infty$, which is the opposite of the regime considered in our

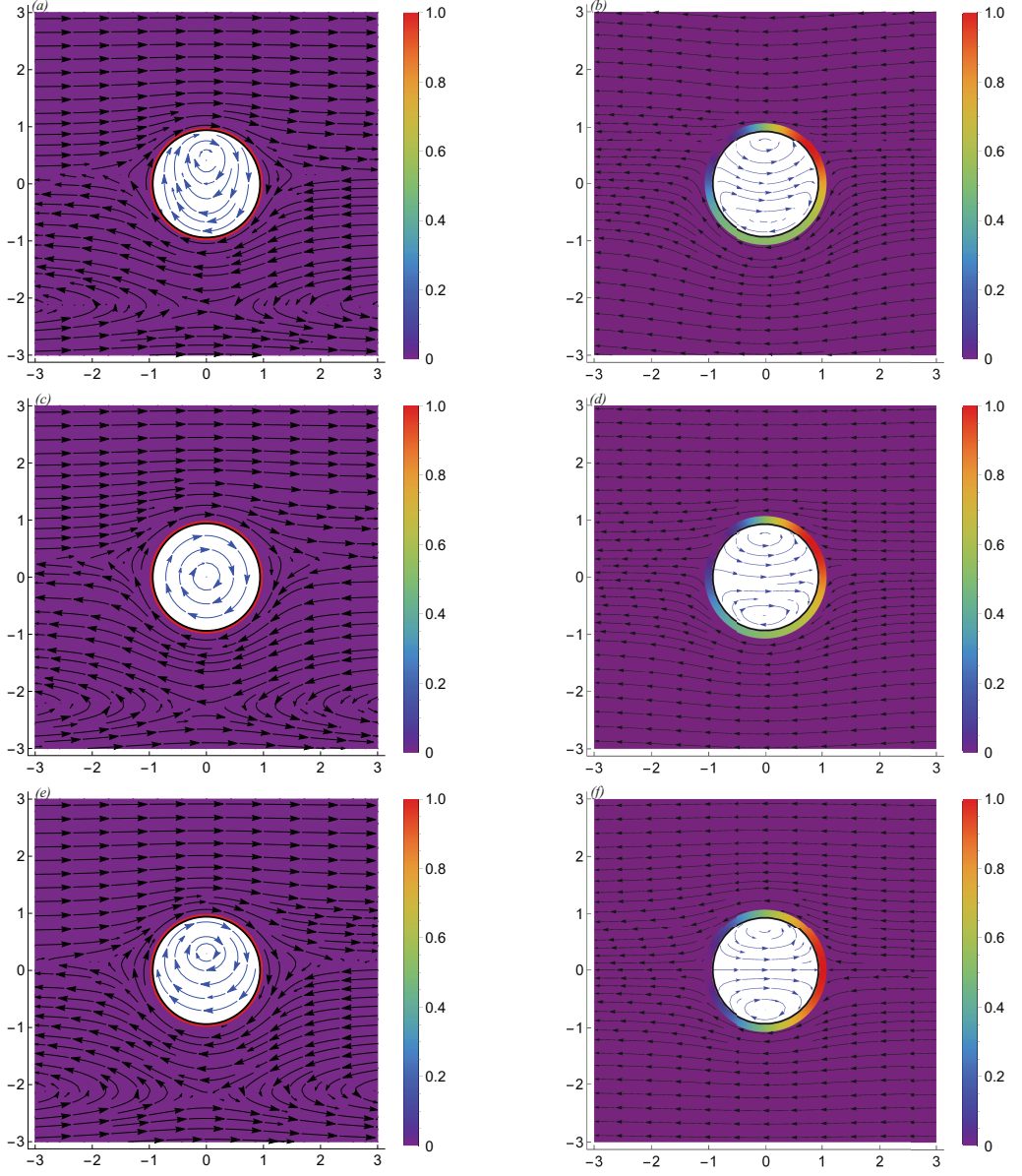


Figure 2: Figures on the left (*a, c, e*) show the leading order velocity vectors both inside (shown in blue) and outside the drop (shown in black) superimposed with the leading order surfactant concentration field, figures on the right (*b, d, f*) show the first order velocity vectors both inside (shown in blue) and outside the drop (shown in black) superimposed with the first order surfactant concentration field for (*a, b*) $Bq_\kappa = 0, Bq_\mu = 0$, (*c, d*) $Bq_\kappa = 100, Bq_\mu = 0$ and (*e, f*) $Bq_\kappa = 0, Bq_\mu = 100$. For all the cases shown, $a/R = 1, b/R = 1, \lambda = 1, Ma = 1$. The flow direction is from left to right.

analysis. We note that, the drop lags the flow for all values of Bq_κ and the migration velocity is independent of the surface shear viscosity. This observation can be supported by studying the leading order velocity vectors as shown in figures 2a,c,e. From the flow patterns, we find that, shear viscosity (Bq_μ) has a negligible effect on the leading order velocity field (refer to figures 2a,e), while the dilatation viscosity (Bq_κ) alters the circulation pattern inside the drop significantly (refer to figure 2c). The detailed expression for the leading order velocity field is provided in Appendix B. Note that, the surfactant is bulk insoluble and the surfactant concentration in the bulk is zero which is indicated by the purple color in figure 2.

3.2. Solution at first order

At first order, the creeping flow and the surfactant transport equations are given by,

$$-\nabla p_i^{(1)} + \lambda \nabla^2 \mathbf{u}_i^{(1)} = \mathbf{0}, \quad (3.7a)$$

$$-\nabla p_e^{(1)} + \nabla^2 \mathbf{u}_e^{(1)} = \mathbf{0}, \quad (3.7b)$$

$$\nabla^2 \Gamma^{(1)} = \nabla_s \cdot \mathbf{u}_s^{(0)}. \quad (3.7c)$$

The above equations are subjected to the following boundary conditions,

$$\mathbf{u}_i^{(1)} = \mathbf{u}_e^{(1)} \quad \text{at } r = 1,$$

$$\mathbf{u}_i^{(1)} \cdot \mathbf{n} = 0 \quad \text{at } r = 1.$$

$$\mathbf{n} \cdot \left(\boldsymbol{\sigma}_e^{(1)} - \lambda \boldsymbol{\sigma}_i^{(1)} \right) \cdot (\mathbf{I} - \mathbf{n}\mathbf{n}) = Ma \nabla_s \Gamma^{(1)} - \nabla_s \cdot \boldsymbol{\tau}_s^{(1)}.$$

From the surfactant transport equation, we observe that, at first order, the surfactant will redistribute itself along the interface due to convection of the leading order velocity along the drop surface. Consequently, the Marangoni stress term appears in the tangential stress continuity boundary condition. After solving the equations of motion, we obtain the equilibrium surfactant concentration as follows,

$$\Gamma^{(1)} = \frac{a^2}{R^2} \left(-\frac{2}{2 + 2Bq_\kappa + 3\lambda} P_1^0(\cos\theta) + \frac{7}{7 + 12Bq_\kappa + 10Bq_\mu + 7\lambda} P_3^0(\cos\theta) + \frac{5b}{a(5 + 6Bq_\kappa + 4Bq_\mu + 5\lambda)} P_2^1(\cos\theta)\cos\phi \right). \quad (3.8)$$

However, we find that, despite the surfactant redistribution, the drop migrates only in the direction of the flow and the cross-stream migration velocity is zero upto the first order in Pe_s . Here, we note that, Pak *et al.* (2014) made a similar observation for a non viscous interface. The first order migration velocity is given as follows,

$$\mathbf{U}^{(1)} = -\frac{a^2}{R^2} \left(\frac{4Ma}{3(2 + 2Bq_\kappa + 3\lambda)^2} \right) \hat{\mathbf{e}}_z. \quad (3.9)$$

The negative sign indicates that the first order velocity causes the drop to further lag the flow. This lag is decreased due to the surface dilatation viscosity as Bq_κ appears in the denominator. However, the surface shear viscosity has no effect on the droplet longitudinal speed. The first order velocity field vectors are displayed in figures 2b,d,f for different values of surface viscosities. In all the cases, the velocity vectors outside the drop are oriented in a direction opposite to the external flow, which reduces the longitudinal speed of the droplet as seen from equation (3.9). We further observe that, an increase in the surface shear viscosity, increases the resistance of the drop to surface shear forces

which consequently reduces the compression of the streamlines in the vicinity of the drop in comparison with the non-viscous drop (refer to figures 2b,f). However, surface dilatation viscosity does not cause any significant changes in the streamlines pattern. The detailed expression for the first order velocity field is provided in Appendix B.

From the surfactant concentration fields in figure 2, we observe that, in all the cases, the first order velocity creates a surplus of surfactant (shown in red) at the rear end of the drop and a deficit at the front end (shown in blue). This generates a Marangoni flow from the rear end to the front end of the droplet as shown in the figure. For a drop without any interfacial viscosities, as the drop is located away from the flow axis, we observe that the peaks in the surfactant concentration is not on the z -axis passing through the sphere center (refer to figure 2b). Introduction of the dilatation viscosity generates a similar surfactant distribution pattern (refer to figure 2d); however, the shear viscosity causes the surfactant concentration peaks to align with the sphere axis (refer to figure 2f).

3.3. Solution at second order

At second order, the creeping flow and the surfactant transport equations are given by,

$$-\nabla p_i^{(2)} + \lambda \nabla^2 \mathbf{u}_i^{(2)} = \mathbf{0}, \quad (3.10a)$$

$$-\nabla p_e^{(2)} + \nabla^2 \mathbf{u}_e^{(2)} = \mathbf{0}, \quad (3.10b)$$

$$\nabla^2 \Gamma^{(2)} = \nabla_s \cdot (\Gamma^{(0)} \mathbf{u}_s^{(1)} + \Gamma^{(1)} \mathbf{u}_s^{(0)}). \quad (3.10c)$$

The above equations are subjected to the following boundary conditions,

$$\mathbf{u}_i^{(2)} = \mathbf{u}_e^{(2)} \quad \text{at } r = 1,$$

$$\mathbf{u}_i^{(2)} \cdot \mathbf{n} = 0 \quad \text{at } r = 1.$$

$$\mathbf{n} \cdot \left(\boldsymbol{\sigma}_e^{(2)} - \lambda \boldsymbol{\sigma}_i^{(2)} \right) \cdot (\mathbf{I} - \mathbf{n}\mathbf{n}) = Ma \nabla_s \Gamma^{(2)} - \nabla_s \cdot \boldsymbol{\tau}_s^{(2)}.$$

We find that, the drop exhibits a cross-stream migration velocity in the x -direction at this order in Pe^s . The net migration velocity of the drop at this order is given by,

$$\mathbf{U}^{(2)} = -\frac{a^2}{R^2} \left(\frac{4Ma}{3(2+2Bq_\kappa+3\lambda)^3} \right) \mathbf{e}_z - \frac{a^3 b}{R^4} f(Ma, \lambda, Bq_\kappa, Bq_\mu) \mathbf{e}_x. \quad (3.11)$$

Here, $f(Ma, \lambda, Bq_\kappa, Bq_\mu)$ is given by,

$$\left(\frac{Ma(40 + 109\lambda + 70\lambda^2 + 144Bq_\kappa^2 + 80Bq_\mu^2 + 4Bq_\mu(29 + 39\lambda) + 2Bq_\kappa(77 + 108Bq_\mu + 102\lambda))}{3(2+3\lambda)(2+2Bq_\kappa+3\lambda)(5+6Bq_\kappa+4Bq_\mu+5\lambda)(7+12Bq_\kappa+10Bq_\mu+7\lambda)} \right)$$

From the above expression, we observe that, inclusion of the interfacial stress does not change the direction of the droplet migration and it always moves towards the centre of the channel irrespective of the values of the Bousinessq numbers. Additionally, we find that the cross-stream migration velocity depends on both the interfacial viscosities. If we substitute $Bq_\mu = Bq_\kappa = 0$, we obtain the expression for the cross-stream migration velocity obtained by Pak *et al.* (2014) for a non-viscous interface as follows,

$$U_x^{(2)} = -\frac{a^3 b}{R^4} \left(\frac{Ma(40 + 109\lambda + 70\lambda^2)}{105(1+\lambda)^2(2+3\lambda)^2} \right)$$

The detailed expression for the surfactant concentration at this order is provided in Appendix B.

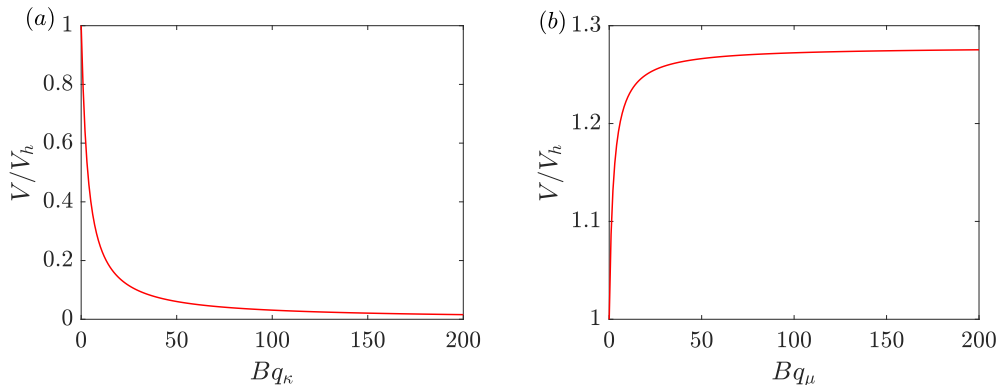


Figure 3: Variation of the drop cross-stream migration velocity with (a) Boussinesq number for surface dilatation for $Bq_\mu = 0, \lambda = 1$ and (b) Boussinesq number for surface shear for $Bq_\kappa = 0, \lambda = 1$.

Figure 3 shows the effect of the interfacial viscosities on the cross-stream velocity of the droplet (shown by symbol V). V_h denotes the cross-stream migration velocity for a droplet with a non-viscous interface ($Bq_\kappa = Bq_\mu = 0$). We observe that, both the viscosities influence the droplet motion in different ways. Surface dilatation reduces the migration velocity of the droplet, and for high Boussinesq numbers ($Bq_\kappa \gg 1$), the cross-stream migration of the droplet is greatly suppressed. On the other hand, surface shear increases the migration velocity of the drop, which tends to reduce the time taken by drop to reach the channel centre. Additionally, we find that, increasing the shear Boussinesq number beyond a value of $Bq_\mu \approx 100$ has no effect on the droplet motion and the curve reaches a plateau of $V/V_h \approx 1.275$. It is experimentally observed that, for higher surface pressures, the surface Boussinesq numbers can attain high values ($Bq_\kappa, Bq_\mu \gg Ma$) (Bhamla *et al.* 2017), which can affect the droplet dynamics considerably as seen from figure 3. Experimentally measured values of surface shear viscosities are on the order of magnitude of $\sim 10^{-3} \text{gs}^{-1}$ (Gupta & Wasan 1974), while the surface dilatational viscosities are usually higher. In particular, for a number of surfactant solutions (e.g., dodecanediol, lauryl alcohol), it was found that the surface dilatational viscosities are on the order of magnitude of $\sim 10^3 \text{gs}^{-1}$ (van Voorst Vader *et al.* 1964). Assuming a surfactant solution in water with a micrometer size droplet we obtain the estimates for the surface shear and dilatational Boussinesq numbers to be $Bq_\mu \sim 10^3$ and $Bq_\kappa \sim 10^9$ respectively. The Marangoni number (Ma) can be expressed as the ratio of the Gibbs elasticity parameter ($0 < \beta < 1$) and the capillary number ($Ca \ll 1$). We thus expect typical values of Marangoni numbers to be high ($Ma \sim 10 - 1000$). For example, Wang *et al.* (2017) performed experiments with surfactant laden bubbles with a Marangoni number of ~ 30 . From the above estimates and figure 3, we find that, for commonly used surfactant solutions, the effect of the dilatation viscosity is to completely inhibit the cross-stream motion of the droplet, while the surface shear viscosity enhances the migration velocity by a factor of ~ 1.275 .

For experiments involving droplet migration in microchannels, the lift forces acting on the drops due to the fluid inertia and the droplet deformation are considered to be important. We seek to analyze the relative magnitudes of inertial, deformation and surfactant induced lift forces acting on a droplet in a microchannel experiment. Asmolov (1999) derived an expression for the inertial lift force acting on particles suspended in a

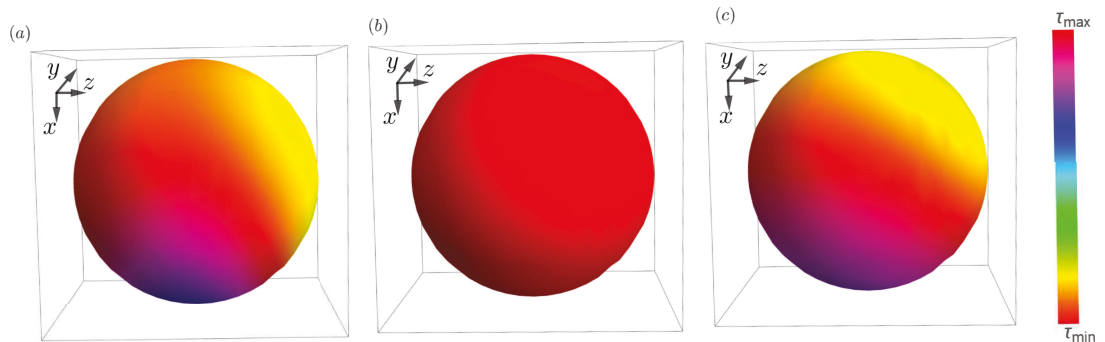


Figure 4: Second order surfactant distribution $\Gamma^{(2)}$ for a) $Bq_\kappa = 0, Bq_\mu = 0$, b) $Bq_\kappa = 100, Bq_\mu = 0$ and c) $Bq_\kappa = 0, Bq_\mu = 100$. In all the cases, $a/R = 1, b/R = 1, \lambda = 1, Ma = 1$ and the external flow is along the z -axis.

Poiseuille flow. In particular their analysis is valid for small particle Reynolds numbers denoted as R_p . The theoretical expression for the deformation induced lift forces was given by Chan & Leal (1979). For small droplets located away from the channel walls ($a/R = b/R \sim 0.1$), surface Péclet number $Pe_s \sim 0.1$, viscosity ratio $\lambda = 1$, particle Reynolds number $R_p \sim 10^{-3} - 1$ and a capillary number $Ca \sim 10^{-3} - 0.1$, we find the relative magnitudes of the surfactant induced lift force (F^s), inertial induced lift force (F^i) and deformation induced lift force (F^d) to be as follows,

$$\frac{F^s}{F^i} \sim 2.6 \times 10^{-6} Ma - 2.6 \times 10^{-3} Ma, \quad \frac{F^s}{F^d} \sim 5 \times 10^{-4} Ma - 5 \times 10^{-2} Ma.$$

We thus find that, for large Marangoni numbers, $Ma \sim 10^2 - 10^3$, the surfactant induced lift forces would be comparable to the inertial and the deformation induced lift forces for small particle Reynolds numbers and capillary numbers.

We can qualitatively understand the influence of the surface viscosities on the cross-stream migration velocity by analyzing the surfactant distribution on the droplet surface at this order (refer to figure 4). For the case of a large surface dilatation viscosity ($Bq_\kappa = 100$), we observe that the surfactant redistribution is greatly suppressed as the surface concentration appears to be uniform. We expect that, a suppression in the surfactant redistribution decreases the strength of the Marangoni flow and consequently the cross-stream migration velocity is reduced significantly as seen from figure 3a. On the other hand, a large surface shear viscosity causes the surfactant to be redistributed, but in a different manner as compared to a non-viscous interface. In particular, the minimum surfactant concentration (shown in yellow-orange) is observed near a region located further away from the the local z -axis passing through the sphere center which is parallel to the flow direction. We expect this redistribution to generate a stronger Marangoni flow in the cross-stream direction (along the x -axis), which consequently increases the cross-stream migration velocity of the droplet as seen from figure 3b.

Our work is applicable in the limit of small Reynolds number ($Re \ll 1$) based on the particle size, small surface Péclet number ($Pe_s \ll 1$) and a small capillary number ($Ca \ll 1$). In addition, we assume the surfactant concentration to be negligible ($\Gamma_{eq} \ll 1$), i.e., we neglect any intermolecular interactions between the surfactant molecules which are adsorbed on the droplet surface. As the cross-stream migration occurs as a second order effect in the surface Péclet number, the effect of the droplet capillary number (i.e, drop deformation) might become important even if the value of the capillary number is

small. Hence, for our results to be applicable in practical scenarios, the neglect of the drop deformation is justified if $Ca \ll Pe_s^2$. For surfactant laden droplets of size $\sim O(\mu\text{m})$ immersed in water with an average flow speed $\sim 10^{-3}\text{ms}^{-1}$, the Reynolds number is $\sim 10^{-3}$. Assuming a surface tension of $\sim 10^{-3}\text{kgs}^{-2}$, the capillary number can be estimated to be $\sim O(10^{-3})$. These requirements have been satisfied in number of experiments in the literature including the comprehensive analysis by Stan *et al.* (2013) which estimated the lift forces acting on a droplet in a microchannel for different pairs of continuous and dispersed phase fluids. The condition of small Péclet number ($Pe_s \sim 0.1$), would be satisfied for surfactant diffusivity values which are $\sim 10^{-8}\text{m}^2\text{s}^{-1}$. This requirement seems reasonable as typical values of surfactant diffusivity are expected to lie between $\sim 10^{-8}\text{m}^2\text{s}^{-1}$ and $\sim 10^{-10}\text{m}^2\text{s}^{-1}$ (van Voorst Vader *et al.* 1964; Das *et al.* 2017).

4. Conclusion

We predicted the migration velocity of a surfactant covered droplet in a Poiseuille flow including the interfacial viscosities of the drop. We performed a regular perturbation expansion for low surface Péclet numbers (Pe_s) and solved the problem upto the second order in Pe_s . We represented the interface as a two-dimensional homogeneous fluid using the Boussinesq-Scriven constitutive equation and employed the Lamb's general solution for representing the velocity fields both inside and outside the droplet. We obtained an expression of the cross-stream migration velocity of the droplet, where the interfacial effects were captured by Boussinesq numbers for surface shear and surface dilatation (Bq_μ, Bq_κ).

We found that, even when interfacial effects are included, the cross-stream migration velocity of the droplet is zero upto the first order in the surface Péclet number and the first non-zero term only appears at the second order. Surface dilatation viscosity restricts the surfactant redistribution on the droplet surface which suppresses the Marangoni flow around the droplet. This causes the cross-stream velocity to decrease with the dilatation viscosity. For a large dilatation viscosity ($Bq_\kappa > 100$), the cross-stream migration almost vanishes completely. On the other hand, surface shear viscosity redistributes more surfactant along the cross-stream axis of the sphere, which drives a stronger Marangoni flow in the cross-stream direction. Consequently, the migration velocity of the drop increases with the surface dilatation viscosity. However, increasing the shear Boussinesq number beyond a certain value ($Bq_\mu \approx 100$) has no effect on the migration velocity and the maximum velocity enhancement is ≈ 1.275 times more than the cross-stream velocity of a non-viscous droplet. We found that, only the surface dilatation viscosity affects the longitudinal speed of the droplet. In particular, the dilatation viscosity reduces the lag experienced the drop due to the Marangoni flows from the droplet rear to the front. Additionally, a high surface shear viscosity suppresses the compression of the streamlines in the vicinity of the droplet. From our analysis, we emphasize that, inclusion of interfacial viscosities is important to accurately model the migration characteristics of droplets for experiments involving droplet manipulation.

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Appendix A

Spherical harmonics in Lamb's general solution for flow inside the droplet:

$$p_n = \lambda r^n \sum_{m=0}^n \left(A_{n,m}^{(q)} \cos(m\phi) + \hat{A}_{n,m}^{(q)} \sin(m\phi) \right) P_{n,m}(\cos\theta),$$

$$\phi_n = r^n \sum_{m=0}^n \left(B_{n,m}^{(q)} \cos(m\phi) + \hat{B}_{n,m}^{(q)} \sin(m\phi) \right) P_{n,m}(\cos\theta),$$

$$\chi_n = r^n \sum_{m=0}^n \left(C_{n,m}^{(q)} \cos(m\phi) + \hat{C}_{n,m}^{(q)} \sin(m\phi) \right) P_{n,m}(\cos\theta).$$

where, $P_{n,m}(\cos\theta)$ are associated Legendre polynomials of degree n and order m .
Spherical harmonics in Lamb's general solution for flow outside the droplet:

$$p_{-n-1} = r^{-n-1} \sum_{m=0}^n \left(A_{-n-1,m}^{(q)} \cos(m\phi) + \hat{A}_{-n-1,m}^{(q)} \sin(m\phi) \right) P_{n,m}(\cos\theta),$$

$$\phi_{-n-1} = r^{-n-1} \sum_{m=0}^n \left(B_{-n-1,m}^{(q)} \cos(m\phi) + \hat{B}_{-n-1,m}^{(q)} \sin(m\phi) \right) P_{n,m}(\cos\theta),$$

$$\chi_{-n-1} = r^{-n-1} \sum_{m=0}^n \left(C_{-n-1,m}^{(q)} \cos(m\phi) + \hat{C}_{-n-1,m}^{(q)} \sin(m\phi) \right) P_{n,m}(\cos\theta).$$

Appendix B

Leading order velocity and pressure fields inside and outside the droplet:

$$\mathbf{u}_{i,r}^{(0)} = \frac{a(r^2 - 1)}{8R^2} \left(-\frac{16a\cos\theta}{2 + 2Bq_\kappa + 3\lambda} + \frac{7ar^2(3\cos\theta + 5\cos 3\theta)}{7 + 12Bq_\kappa + 10Bq_\mu + 7\lambda} - \frac{60br\cos\phi\sin 2\theta}{5 + 6Bq_\kappa + 4Bq_\mu + 5\lambda} \right).$$

$$\mathbf{u}_{i,\theta}^{(0)} = \frac{a}{8R^2} \left(8br\cos\phi - \frac{20br(-3 + 5r^2)\cos 2\theta\cos\phi}{5 + 6Bq_\kappa + 4Bq_\mu + 5\lambda} + \frac{16a(-1 + 2r^2)\sin\theta}{2 + 2Bq_\kappa + 3\lambda} - \frac{7br^2(-2 + 3r^2)(3 + 5\cos 2\theta)\sin\theta}{7 + 12Bq_\kappa + 10Bq_\mu + 7\lambda} \right).$$

$$\mathbf{u}_{i,\phi}^{(0)} = \frac{abr(-12Bq_\kappa - 8Bq_\mu + 5(-5 + 5r^2 - 2\lambda))\cos\theta\sin\phi}{2R^2(5 + 6Bq_\kappa + 4Bq_\mu + 5\lambda)}.$$

$$\begin{aligned} \mathbf{u}_{e,r}^{(0)} = & \frac{a\cos\theta}{60R^2} \left(-\frac{16a(-3 + 2Bq_\kappa + 3\lambda)}{r^3(2 + 2Bq_\kappa + 3\lambda)} + 40a\frac{(2Bq_\kappa + 3\lambda)}{2 + 2Bq_\kappa + 3\lambda} \right. \\ & - \frac{3a(12Bq_\kappa(-5 + 7r^2) + 10Bq_\mu(-5 + 7r^2) - 35\lambda + 7r^2(2 + 7\lambda))(-1 + 5\cos 2\theta)}{r^5(7 + 12Bq_\kappa + 10Bq_\mu + 7\lambda)} \\ & - 120br\cos\phi\sin\theta \\ & + \frac{60b(-6(3Bq_\kappa + 2Bq_\mu) + 10(-1 + 3Bq_\kappa + 2Bq_\mu)r^2 + 5\lambda(-3 + 5r^2))\cos\phi\sin\theta}{r^4(5 + 6Bq_\kappa + 4Bq_\mu + 5\lambda)} \\ & \left. - 60ar^2\sin^2\theta \right). \end{aligned}$$

$$\mathbf{u}_{e,\theta}^{(0)} = \frac{a}{48r^5R^2} \left(3\cos 2\theta \left(\frac{16br(6Bq_\kappa + 4Bq_\mu + 5\lambda)\cos\phi}{5 + 6Bq_\kappa + 4Bq_\mu + 5\lambda} - \frac{a(-30(6Bq_\kappa + 5Bq_\mu) + 14(1 + 6Bq_\kappa + 5Bq_\mu)r^2 + 7\lambda(-15 + 7r^2)\sin\theta)}{7 + 12Bq_\kappa + 10Bq_\mu + 7\lambda} \right) + \sin\theta \left(a(27 - 19r^2 - 32r^5) + \frac{32(r^2 + 2r^5)}{2 + 2Bq_\kappa + 3\lambda} + \frac{63(-3 + r^2)}{7 + 12Bq_\kappa + 10Bq_\mu + 7\lambda} + 48r^6\sin\theta(2b\cos\phi + ar\sin\phi) \right) \right).$$

$$\mathbf{u}_{e,\phi}^{(0)} = -\frac{ab(6Bq_\kappa + 4Bq_\mu + 5\lambda)\cos\theta\sin\phi}{r^4R^2(5 + 6Bq_\kappa + 4Bq_\mu + 5\lambda)}.$$

$$p_i^0 = \frac{ar\lambda\cos\theta}{R^2} \left(-\frac{20a}{2 + 2Bq_\kappa + 3\lambda} + \frac{21ar^2(-3 + 5\cos^2\theta)}{7 + 12Bq_\kappa + 10Bq_\mu + 7\lambda} - \frac{105br\cos\phi\sin\theta}{5 + 6Bq_\kappa + 4Bq_\mu + 5\lambda} \right).$$

$$p_e^0 = \frac{a}{4r^4R^2} \left(-\frac{7a(2 + 12Bq_\kappa + 10Bq_\mu + 7\lambda)\cos\theta(-3 + 5\cos^2\theta)}{7 + 12Bq_\kappa + 10Bq_\mu + 7\lambda} + \frac{20br(2 + 6Bq_\kappa + 4Bq_\mu + 5\lambda)\cos\phi\sin 2\theta}{5 + 6Bq_\kappa + 4Bq_\mu + 5\lambda} \right)$$

First order velocity and pressure fields inside and outside the droplet:

$$\mathbf{u}_{i,r}^{(1)} = \frac{aMa(r^2 - 1)}{8R^2} \left(\frac{16a\cos\theta}{(2 + 2Bq_\kappa + 3\lambda)^2} - \frac{7ar^2(3\cos\theta + 5\cos 3\theta)}{(7 + 12Bq_\kappa + 10Bq_\mu + 7\lambda)^2} + \frac{60br\cos\phi\sin 2\theta}{(5 + 6Bq_\kappa + 4Bq_\mu + 5\lambda)^2} \right).$$

$$\mathbf{u}_{i,\theta}^{(1)} = \frac{aMa}{8R^2} \left(\frac{20br(-3 + 5r^2)\cos 2\theta\cos\phi}{(5 + 6Bq_\kappa + 4Bq_\mu + 5\lambda)^2} + \frac{16a(1 - 2r^2)\sin\theta}{(2 + 2Bq_\kappa + 3\lambda)^2} + \frac{7ar^2(-2 + 3r^2)(3 + 5\cos 2\theta)\sin\theta}{(7 + 12Bq_\kappa + 10Bq_\mu + 7\lambda)^2} \right).$$

$$\mathbf{u}_{i,\phi}^{(1)} = -\frac{5abMar(-3 + 5r^2)\cos\theta\sin\phi}{2R^2(5 + 6Bq_\kappa + 4Bq_\mu + 5\lambda)^2}.$$

$$\mathbf{u}_{e,r}^{(1)} = \frac{aMa}{6R^2} \left(\frac{8a\cos\theta}{(2 + 2Bq_\kappa + 3\lambda)^2} - \frac{8a\cos\theta}{r^3(2 + 2Bq_\kappa + 3\lambda)^2} - \frac{21a(-1 + r^2)\cos\theta(-3 + 5\cos^2\theta)}{r^5(7 + 12Bq_\kappa + 10Bq_\mu + 7\lambda)^2} + \frac{45b(-1 + r^2)\cos\phi\sin 2\theta}{r^4(5 + 6Bq_\kappa + 4Bq_\mu + 5\lambda)^2} \right).$$

$$\mathbf{u}_{e,\theta}^{(1)} = \frac{aMa}{48R^2} \left(-\frac{64a\sin\theta}{(2 + 2Bq_\kappa + 3\lambda)^2} - \frac{32a\sin\theta}{r^3(2 + 2Bq_\kappa + 3\lambda)^2} - \frac{21a(-3 + r^2)\sin\theta(3 + 5\cos^2\theta)}{r^5(7 + 12Bq_\kappa + 10Bq_\mu + 7\lambda)^2} + \frac{240b\cos\phi\cos 2\theta}{r^4(5 + 6Bq_\kappa + 4Bq_\mu + 5\lambda)^2} \right).$$

$$\mathbf{u}_{e,\phi}^{(1)} = -\frac{5abMacos\theta\sin\phi}{r^4R^2(5 + 6Bq_\kappa + 4Bq_\mu + 5\lambda)^2}.$$

$$p_i^{(1)} = \frac{aMa\lambda\cos\theta}{R^2} \left(\frac{20a}{(2+2Bq_\kappa+3\lambda)^2} - \frac{21a(-r^2)(-3+5\cos^2\theta)}{(7+12Bq_\kappa+10Bq_\mu+7\lambda)^2} + \frac{105br\cos\phi\sin\theta}{(5+6Bq_\kappa+4Bq_\mu+5\lambda)^2} \right).$$

$$p_e^{(1)} = \frac{5aMa}{4r^4R^2} \left(-\frac{7a\cos\theta(-3+5\cos^2\theta)}{(7+12Bq_\kappa+10Bq_\mu+7\lambda)^2} + \frac{12br\cos\phi\sin2\theta}{(5+6Bq_\kappa+4Bq_\mu+5\lambda)^2} \right).$$

Second order surfactant concentration distribution:

$$\begin{aligned} \Gamma^{(2)} = & P_1^0(\cos\theta) \left(\frac{2a^2Ma}{R^2(2+2Bq_\kappa+3\lambda)^2} \right) \\ & + P_2^0(\cos\theta) \frac{a^2}{378R^4} \left(\frac{45b^2(40+42Bq_\kappa+28Bq_\mu+35\lambda)}{(5+6Bq_\kappa+4Bq_\mu+5\lambda)^2} + \frac{504a^2}{(2+2Bq_\kappa+3\lambda)^2} \right. \\ & \quad \left. + \frac{49a^2}{(7+12Bq_\kappa+10Bq_\mu+7\lambda)^2} - \frac{378a^2}{(2+2Bq_\kappa+3\lambda)(7+12Bq_\kappa+10Bq_\mu+7\lambda)} \right) \\ & + P_3^0(\cos\theta) \left(-\frac{7a^2Ma}{6R^2(7+12Bq_\kappa+10Bq_\mu+7\lambda)^2} \right) \\ & + P_4^0(\cos\theta) \frac{a^2}{924R^4} \left(-\frac{1320e^2}{(5+6Bq_\kappa+4Bq_\mu+5\lambda)^2} \right. \\ & \quad \left. - \frac{7a^2(1190+2070Bq_\kappa+1760Bq_\mu+1169\lambda)}{(2+2Bq_\kappa+3\lambda)(7+12Bq_\kappa+10Bq_\mu+7\lambda)^2} \right) \\ & + P_6^0(\cos\theta) \left(\frac{175a^4}{594R^4(7+12Bq_\kappa+10Bq_\mu+7\lambda)^2} \right) \\ & + P_1^1(\cos\theta)\cos\phi \left(\frac{a^3b(40+144Bq_\kappa^2)+80Bq_\mu^2+109\lambda+70\lambda^2}{2R^4(2+2Bq_\kappa+3\lambda)(5+6Bq_\kappa+4Bq_\mu+5\lambda)(7+12Bq_\kappa+10Bq_\mu+7\lambda)} \right. \\ & \quad \left. + \frac{4Bq_\mu(29+39\lambda)+2Bq_\kappa(77+108Bq_\mu+102\lambda)}{R^4(2+2Bq_\kappa+3\lambda)(5+6Bq_\kappa+4Bq_\mu+5\lambda)(7+12Bq_\kappa+10Bq_\mu+7\lambda)} \right) \\ & + P_2^1(\cos\theta)\cos\phi \left(-\frac{5abMa}{3R^2(5+6Bq_\kappa+4Bq_\mu+5\lambda)^2} \right) \\ & + P_3^1(\cos\theta)\cos\phi \left(\frac{a^3b(2170+252Bq_\kappa^2)+2457\lambda+315\lambda^2}{216R^4(2+2Bq_\kappa+3\lambda)(5+6Bq_\kappa+4Bq_\mu+5\lambda)(7+12Bq_\kappa+10Bq_\mu+7\lambda)} \right. \\ & \quad \left. + \frac{12Bq_\mu(254+21\lambda)+2Bq_\kappa(1931+84Bq_\mu+294\lambda)}{216R^4(2+2Bq_\kappa+3\lambda)(5+6Bq_\kappa+4Bq_\mu+5\lambda)(7+12Bq_\kappa+10Bq_\mu+7\lambda)} \right) \\ & + P_5^1(\cos\theta)\cos\phi \left(-\frac{10a^3b}{27R^4(5+6Bq_\kappa+4Bq_\mu+5\lambda)(7+12Bq_\kappa+10Bq_\mu+7\lambda)} \right) \\ & + P_2^2(\cos\theta)\cos2\phi \left(-\frac{5a^2b^2(20+42Bq_\kappa+28Bq_\mu+35\lambda)}{252R^4(5+6Bq_\kappa+4Bq_\mu+5\lambda)^2} \right) \\ & + P_4^2(\cos\theta)\cos4\phi \left(\frac{5a^2b^2}{42R^4(5+6Bq_\kappa+4Bq_\mu+5\lambda)^2} \right). \end{aligned}$$

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