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Abstract
The steady-state migration velocity of a spherical droplet placed in a second liquid is calculated taking into account gravity and several interfacial effects. The effect of insoluble surfactants at the bubble surface, surface tension gradients, surface elasticity, interfacial dilatational viscosity, interfacial diffusivity and convective and diffusive surface excess heat fluxes on the terminal velocity of the droplet are included under the assumption of small Marangoni, Reynolds and capillary numbers. This work extends earlier results, which do not take into account interfacial diffusivity.

1. Introduction

Migration of droplets in a liquid can be stimulated by several mechanisms. One of them is the application of external forces such as gravity, which gives the Rybczynski–Hadamard law [1,2]. Other ways are surface tension gradients, produced from thermal and solutal gradients or electrical fields. They will introduce a tangential stress on the bubble's surface, causing a motion in the direction of decreasing interfacial tension, which is called Marangoni migration. This case was first considered by Young *et al* [3] for bubbles of clean surfaces, i.e. vanishing surface shear viscosity, dilatational viscosity and surface elasticity. They were concerned with the motion of a gas bubble under the assumption of low Reynolds ($Re = ua\rho/\eta$) and Marangoni ($Mg = ua/\beta$) numbers, where u is the migration velocity, a is the radius of the bubble, ρ the density, η the dynamical viscosity and β the temperature diffusivity of the fluid outside the bubble. The low Reynolds number causes the validity of the equations of creeping flow and a low Marangoni number indicates the negligibility of convective transport. Under the assumption of low capillary number ($Ca = u\eta/\sigma$), where σ denotes the surface tension, the shape of the bubbles can be treated as spherical. Subramanian [4] has provided a second-order perturbation expansion of the bubble velocity for small Marangoni numbers. In this treatment the first-order correction to the terminal velocity vanishes. On the other hand Bratukhin [5] has proved the same result in the case of small Reynolds numbers. Levich [6] has

addressed the question of how the presence of soluble surfactants could affect this migration velocity. The problem was treated by combining the hydrodynamic equations with the soluble surfactant transport equations. Chen [7] has investigated the movement of a fluid sphere within a constant applied temperature gradient in an arbitrary direction with respect to a rigid plane surface. Transient migration of bubbles and steady-state flow for high Reynolds and Marangoni numbers were considered experimentally by Treuner *et al* [8]. They compared their experimental observation with that of the theoretical model for the terminal velocity of the bubble. The main influence of high Marangoni numbers (i.e. convective transport) and high Reynolds numbers (i.e. inertial effects) is to lower the terminal velocity.

Similar effects occur when considering the settling or rising of droplets due to gravity. Here surface rheological effects in the low-Reynolds-number regime slow down the sedimentation velocity from the value predicted by Rybczynski and Hadamard [1, 2], to the value of the settling velocity of a solid surface as the importance of these effects increases. An overview on this issue in a broad range of parameters can be found in [9]. Edwards *et al* [10] calculated the effects of interfacial properties such as the dilatational viscosity, the Gibbs elasticity and the adsorption parameter of *soluble* surfactants on the settling velocity.

The aim of the present work is to calculate the effect of the diffusivity and elasticity of *insoluble* surfactants on the terminal velocity of a droplet placed in a combined gravitational field and a temperature gradient.

2. Analysis

Consider a migration of an incompressible liquid spherical droplet of radius a surrounded by an incompressible Newtonian liquid of temperature T, mass density ρ and viscosity η. We assume that Reynolds and Marangoni numbers are small such that the Stokes equations hold and heat conduction dominates convective heat transfer both in the droplet and in the surrounding fluid [11]. The linearized equations describing the flow are

$$\eta \nabla^2 \boldsymbol{v} = \nabla(p + \rho g z) \tag{1}$$

$$\nabla \cdot \boldsymbol{v} = 0 \tag{2}$$

$$\nabla^2 T = 0 \tag{3}$$

where $\boldsymbol{v}$ is the flow field velocity outside the droplet ($r > a$), p is the pressure and g is the gravity acceleration in the negative z direction. Identical equations hold inside the droplet ($r < a$; parameters are denoted by $\sim$). Owing to the axial symmetry of the problem the solution for the velocity, pressure and temperature outside and within the spherical droplet respectively reads [1, 2]

$$v_r = u\left(1 - \frac{2E}{r^3} - \frac{2C}{r}\right)\cos(\vartheta) \tag{4a}$$

$$v_\vartheta = u\left(-1 - \frac{E}{r^3} + \frac{C}{r}\right)\sin(\vartheta) \tag{4b}$$

$$\tilde{v}_r = -2u(A + Br^2)\cos(\vartheta) \tag{5a}$$

$$\tilde{v}_\vartheta = 2u(A + 2Br^2)\sin(\vartheta) \tag{5b}$$

$$p = K - \rho g r \cos(\vartheta) - 2\eta u \frac{C}{r^2}\cos(\vartheta) \tag{6a}$$

$$\tilde{p} = \tilde{K} - \tilde{\rho} g r \cos(\vartheta) - 20\tilde{\eta} u B r \cos(\vartheta) \tag{6b}$$

$$T = T_0 + T_1 \left(r + \frac{k}{r^2} \right) \cos(\vartheta) \tag{7a}$$

$$\tilde{T} = T_0 + T_1 \tilde{k} r \cos(\vartheta) \tag{7b}$$

where the constants A, B, C, E, K, k, $\tilde{k}$ and $\tilde{K}$ are to be determined from the boundary conditions, u is the droplet velocity in the laboratory frame and T_1 is the external temperature gradient pointing in the positive z direction. Since all equations that follow are linearized equations, this will justify choosing a solution which varies as simply as $\cos(\vartheta)$, $\sin(\vartheta)$, with the angle ϑ.

First, the condition of continuity of the velocity fields across the droplet interface (i.e. $r = a$) requires that $v_r(a) = \tilde{v}_r(a) = 0$, since there is no flow across the droplet interface. Second, the continuity of the transverse components of the flow field across the droplet interface requires $v_\vartheta(a) = \tilde{v}_\vartheta(a)$. The rest of the boundary conditions are summarized in the following.
(a) The tangential stress boundary condition across the droplet interface

$$r\tilde{\eta}\frac{\partial}{\partial r}\left(\frac{\tilde{v}_\vartheta}{r}\right) - r\eta\frac{\partial}{\partial r}\left(\frac{v_\vartheta}{r}\right)\bigg|_{r=a} = \frac{1}{a}\frac{\partial\sigma}{\partial\vartheta} + \eta^s\left(\frac{2v_\vartheta}{a^2}\right) + \frac{\kappa^s + \eta^s}{a}\frac{\partial}{\partial\vartheta}\frac{1}{a\sin(\vartheta)}\frac{\partial}{\partial\vartheta}(v_\vartheta\sin(\vartheta)), \tag{8}$$

where κ^s is the interfacial dilatational viscosity, η^s is the interfacial shear viscosity and σ the interfacial tension, which depends both on temperature T and molar surfactant surface concentration Γ.
(b) The normal stress boundary condition across the droplet interface

$$p - \tilde{p} + 2\tilde{\eta}\frac{\partial\tilde{v}_r}{\partial r} - 2\eta\frac{\partial v_r}{\partial r}\bigg|_{r=a} = -\frac{2\sigma}{a} - \frac{2\kappa^s}{a^2\sin(\vartheta)}\frac{\partial}{\partial\vartheta}(v_\vartheta\sin(\vartheta)). \tag{9}$$

(c) In addition, we require that the temperature across the droplet boundary is continuous,

$$T(a) = \tilde{T}(a) \tag{10}$$

and (d) that the heat flux into the interface is transported away by convective and diffusive surface currents,

$$h\frac{\partial T(a)}{\partial r} - \tilde{h}\frac{\partial\tilde{T}(a)}{\partial r} = \nabla_s \cdot \left[-\boldsymbol{v}c_\Gamma^s + c_{surf}\frac{D^s}{R}\nabla_s\frac{\mu^s}{T}\right] \tag{11}$$

where h $(\tilde{h})$ is the thermal conductivity outside (inside) the droplet, D^s the surface diffusion constant, R the gas constant,

$$c_\Gamma^s = T\frac{\partial\sigma}{\partial T}\bigg|_\Gamma, \qquad c_{surf}^s = T\Gamma\frac{\partial^2\sigma}{\partial T\partial\Gamma} \tag{12}$$

are the total and the partial surfactant surface excess specific heat of the surfactant covered surface and

$$\mu^s = \frac{\partial\sigma}{\partial\Gamma}\bigg|_T \tag{13}$$

the surface excess chemical potential of the surfactant. The terms on the left-hand side of equation (11) are the heat fluxes from the bulk into the interface. The first term on the right-hand side is the convective surface heat flux, first treated by Harper *et al* [12]. The last term is a surface excess heat conduction mediated via the diffusion of the surfactant.
(e) The distribution of the insoluble surfactant density Γ on the droplet surface is determined by the balance between advective transport due to the flow of the surface and the diffusive transport caused by the gradient of the surfactant chemical potential and the temperature gradient at the

interface. For a *poorly soluble* surfactant adsorption and desorption of surfactants competes with surface diffusion. The surface transport equation of surfactants reads

$$\nabla_s \cdot \left[\boldsymbol{v}\Gamma - \frac{D^s\Gamma}{R}\nabla_s\frac{\mu^s}{T} \right] = \alpha(\Gamma^0 - \Gamma), \tag{14}$$

where ∇_s is the surface gradient, D^s is the surface diffusion coefficient, α the surfactant adsorption parameter and Γ^0 is the equilibrium surfactant density. For insoluble surfactants for which $RT\alpha a^2/D^s\Gamma(\partial^2\sigma/\partial\Gamma^2)_T \ll 1$ we may neglect any dissolution of the surfactant in the bulk phases. The surfactant can be treated as insoluble, $\alpha = 0$.

(f) The full solution of such a hydrodynamical problem requires a simultaneous determination of the dependence of interfacial tension on surfactant surface concentration profile $\Gamma(\vartheta)$ which couples via the surface tension $\sigma(\Gamma; T)$ with the equation of motion. Hence, the surface equation of state, which poses an equilibrium relation between interfacial tension and the interfacial density and temperature gradient on the droplet, is one of the ingredients to complete the solution for this problem. The surface equation of state $\sigma(\Gamma; T)$ of insoluble surfactants is neither linear in the concentration nor linear in temperature [13, 14]. However, for small temperature and concentration gradients $a\nabla_s \ln T \ll 1$, $a\nabla_s \ln \Gamma \ll 1$ we might use a linearized equation of state which reads

$$\frac{\partial\sigma}{\partial\vartheta} = \frac{\partial\sigma}{\partial T}\bigg|_{\Gamma^0} \frac{\partial T}{\partial\vartheta} - \frac{E_0}{\Gamma^0}\frac{\partial\Gamma}{\partial\vartheta}, \tag{15}$$

where $E_0 = -\Gamma\partial\sigma/\partial\Gamma|_{\Gamma^0}$ is the Gibbs elasticity of the surfactant. Following Levich's classical approach [6] and solving only linearized equations, which is justified under the assumption that $|\Gamma^0 - \Gamma| \ll \Gamma^0$, we obtain from (12)

$$\frac{\partial\Gamma}{\partial\vartheta} = \frac{RTa}{D^s(\partial^2\sigma/\partial\Gamma^2)_T}v_\vartheta - \frac{\partial^2\sigma/\partial\Gamma\partial T - (\partial\sigma/\partial\Gamma)_T/T}{(\partial^2\sigma/\partial\Gamma^2)_T}\frac{\partial T}{\partial\vartheta}. \tag{16}$$

Solving the above set of equations for the terminal velocity of the droplet gives

$$\boldsymbol{u} = -\frac{2}{9}\left[1 + \frac{1}{2\Lambda}\right]\frac{a^2}{\eta}(\tilde{\rho} - \rho)g\boldsymbol{e}_z + \frac{1}{\Lambda}\frac{a(\partial\sigma/\partial T)_{eff}}{\eta(2 + \tilde{h}/h)}\nabla T \tag{17}$$

where

$$\Lambda = 1 + \frac{3}{2}\frac{\tilde{\eta}}{\eta} + \frac{\kappa}{\eta a} + \frac{1}{2}\frac{E_0 a}{\eta D^s_{eff}} + \frac{(\partial\sigma/\partial T)_{eff}\, c^s_{eff}}{h\eta(2 + \tilde{h}/h)} \tag{18}$$

and

$$\begin{aligned} D^s_{eff} &= D^s\frac{\Gamma(\partial^2\sigma/\partial\Gamma^2)_T}{RT} \\ c^s_{eff} &= T[(\partial\sigma/\partial T)_\Gamma - \Gamma\partial^2\sigma/\partial T\partial\Gamma] \\ (\partial\sigma/\partial T)_{eff} &= (\partial\sigma/\partial T)_\Gamma + \frac{(\partial\sigma/\partial\Gamma)_T}{(\partial^2\sigma/\partial\Gamma^2)_T}[(\partial\sigma/\partial\Gamma)_T/T - \partial^2\sigma/\partial T\partial\Gamma] \end{aligned} \tag{19}$$

are an effective surface diffusion, an effectively transported surface specific heat and an effective thermomechanical derivative of the surface tension with respect to temperature. Note that we wrote equation (17) in vector notation (arbitrary orientation of the external temperature gradient), although we derived it when aligned to the gravitational acceleration only. We are allowed to do so, since the z component of (17) is a solution to a linear system of differential equations and we might superimpose a solution with a temperature gradient in the x direction.

The above equation for the terminal velocity agrees with the calculations of Young *et al* if the coefficients κ, E_0 and c^s_{eff} are set equal to zero. The major correction to Young's result is due to the presence of the surfactant elasticity and diffusivity. For a typical surfactant-covered

gas bubble taking the values of $\tilde{\mu}/\mu = 10^{-3}$, $E_0 = 10$ mN m^{-1}, $D^s = 10^{-10}$ m^2 s^{-1} and $a = 1$ μm, the factor $E_0 a/\mu D^s_{eff}$ is the dominant one in Λ. The presence of surfactants at the interface tends to slow down the terminal velocity. A typical thermocapillary coefficient $\zeta = \frac{u}{\nabla T} = \frac{1}{2\Lambda} \frac{a}{\mu} \frac{\partial \sigma}{\partial T}$ is of the order of $\zeta \approx 3 \times 10^{-6}$ m^2 s^{-1} K^{-1} for microbubbles with clean surfaces, while for bubbles covered with insoluble surfactant ζ is reduced to the range of $\zeta \approx 3 \times 10^{-11}$ m^2 s^{-1} K^{-1}. If no external temperature gradient is present and in the absence of surfactant the result coincides with the result for the drag coefficient of Harper *et al* [12].

Note that the effect of surfactant is much more drastic for the thermocapillary motion of a droplet than for the settling mobility. The reason for this lies in the location where the major dissipation occurs during the motion. The surface rheological properties of the surfactant solidify the bubble surface. The dissipation in the settling case is mainly due to dissipation in the surrounding fluid as the elasticity of the surfactant increases: quite the contrary for the thermocapillary motion. Since there the driving force are surface tension gradients, the motion cannot be transferred to the droplet surroundings. The major dissipation remains at the surface, leading to the drastic decrease in capillary motion. Experiments with laser tweezers on surfactant-covered gas microbubbles in water indeed show that repulsive optical forces surmount the attractive thermocapillary forces caused by local heating of the bubble with the laser and it is not possible to capture bubbles with the tweezers. If one were able to produce clean microbubbles the thermocapillary forces should overcome the repulsive optical forces and one should be able to produce a thermocapillary trap.

3. Conclusion

The thermocapillary motion of a droplet covered with insoluble surfactant is calculated. The terminal velocity is affected by the temperature gradient, surface elasticity, the interfacial dilatational viscosity and surface diffusivity. For small gas bubbles the elasticity plays the major role in affecting the terminal velocity of the gas bubble. In the case of small elasticity in the absence of an external temperature gradient the terminal velocity is identical with the result of Edwards *et al* [10]. If both interfacial elasticity and dilatational viscosity vanish, the result of Young *et al* follows.

Acknowledgments

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