A Theoretical Study of Remobilizing Surfactant Retarded Fluid Particle Interfaces

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I. Introduction

Microgravity processes must rely on mechanisms other than bouyancy to move bubbles or droplets from one region to another in a continuous liquid phase. One suggested method is thermocapillary migration in which a temperature gradient is applied to the continuous phase[1]. When a fluid particle contacts this gradient, one pole of the particle becomes warmer than the opposing pole. The interfacial tension between the drop or bubble phase and the continuous phase usually decreases with temperature. Thus the cooler pole is of higher interfacial tension than the warmer pole, and the interface is tugged in the direction of the cooler end. This thermocapillary or thermally induced Marangoni surface stress causes a fluid streaming in the continuous phase from which develops a viscous shear traction and pressure gradient which together propel the particle in the direction of the warmer fluid.

A significant and as yet unresolved impediment to the use of thermocapillary migration to direct bubble or drop motion is that these migrations can be significantly retarded by the adsorption onto the fluid particle surface of surface active impurities dissolved in the continuous or (if the particle is a liquid) droplet phases. Surfactant adsorbs onto the surface of a moving fluid particle, where it is convected by the surface flow to the particle's trailing end. Accumulation at the back end causes kinetic desorption into the bulk sublayer, and the sublayer concentration increases above the value far from the interface. This difference gives rise to a diffusive flux away from the trailing end. Similarly at the front end kinetic adsorption occurs from the sublayer since the front surface is swept clean of surfactant. The sublayer concentration adjacent to the leading end of the particle decreases creating a bulk diffusive flux from the bulk to the front end. Eventually a steady state develops: In this state, the surface concentration at the back end has increased to the point where the desorption rate, proportional to the difference between the surface and sublayer concentration, balances the convective rate. In addition, the sublayer concentration has increased sufficiently so that the diffusive flux away from the particle surface, proportional to the difference between the sublayer and far field concentration, balances the kinetic desorption. At the front end, the surface concentration becomes reduced enough so that kinetic adsorption balances convection, and the sublayer concentration becomes reduced enough so that diffusion to the surface balances adsorption. Consequently, in this steady state the surface concentration is considerably higher at the rear than at the front of the particle, and the interfacial tension is lower at the back relative to the front. This interfacial tension difference creates a surfactant Marangoni stress along the surface as the front end tugs at the rear. The direction of this surface stress is opposite to that of the surface flow caused by the thermocapillary driven motion of the particle, and thus the adsorption of surfactant onto the particle interface acts to reduce the surface flow and hinder the interfacial mobility. The less mobile an interface, the more drag is exerted by the continuous phase on the particle as it moves through the medium, and the smaller is the thermocapillary migration velocity.

This reduction in surface mobility and migration velocity due to retarding Marangoni gradients caused by the convective partitioning of surfactant has been studied extensively for the buoyancy driven

motion in which fluid inertial is negligible (low Reynolds number) and the fluid particles take the shape of spheres (small Weber number). For this case, the terminal velocity becomes reduced from the clean, mobile surface value (the Hadamard-Rybczynski velocity, U_{HR}= $\rho g a^2/3\mu$ (for a bubble) where ρ and μ are the continuous phase density and viscosity, respectively, g the gravitational acceleration, and a the particle radius) to the Stokes velocity (U_{ST}= $2\rho g a^2/9\mu$) of a sphere when the interface mobility is completely arrested. When either the kinetic or diffusive transport is slow relative to interfacial convection, surfactant collects at the trailing pole in a stagnant cap of surfactant, and the terminal velocity is a function of the cap angle which is determined by the steady amount of surfactant adsorbed. [2-5] Theoretical studies for finite kinetic and diffusive transport have also been studied [6-10]. The effect of surfactant adsorption on thermocapillary motion has only recently been studied: Kim and Subramanian[11-12] and Nadim and Borhan[13] have theoretically examined the reduction in thermocapillary migration velocity due to surfactant adsorption, and find that, for the same amount of surfactant adsorbed onto the surface, the reduction (relative to the value for a completely mobile interface) is much greater for thermocapillary driven movement than it is for buoyancy driven motion. The reason, as they point out, is that in thermocapillary migration the strength of the streaming flow around the particle which is driven by the surface tension gradient, and which is responsible for propelling the particle forward, is directly proportional to the interface mobility. The less mobile the surface, the more reduced is the streaming flow due to a fixed surface tension gradient, and the smaller is the particle velocity. Thus thermocapillary migration is very sensitive to the surfactant adsorption, and this adsorption, even arising from surfactants dissolved in trace amounts, can reduce the thermocapillary movement to near zero.

Most experimental evidence in tests both on earth and under microgravity conditions indicate that it is difficult to achieve significant thermocapillary migrations in agreement with the Young et al value, and many studies have attributed the reduced migrations to the retarding effect of surfactant impurities unavoidably present in the bulk phases (see the review article of Subramanian[14]). In addition, Barton and Subramanian[15] demonstrated directly the retardation by the intentional addition of surfactant to a liquid phase in which droplets were moving by thermocapillarity. To date the problem of retardation of thermocapillary driven particle motion due to surfactant impurities remains unresolved. Thermocapillary motions in agreement with the expression of Young et al [1] can only be achieved in systems in which extreme precautions have been taken to remove impurities (as, for example, in Barton and Subramanian's[15] experiments using ethyl salicylate drops in ethylene glycol).

In this paper, we provide a theoretical basis for remobilizing surfactant retarded fluid particle interfaces in an effort to make more viable the use of thermocapillary migrations for the management of bubbles and drops in microgravity. The retarding Marangoni stresses arise because the rate of convection of surfactant to the trailing pole is much larger than either the kinetic or diffusive flux away from the particle surface. The scale for the convective flux is $\Gamma_o U a$, where U is the terminal velocity, a (as before) the radius and Γ_o is the surface concentration in equilibrium with the bulk concentration C_o far from the particle. In this study we will use Langmuir relations to describe surfactant exchange; thus the adsorption rate is $\beta C_s(\Gamma_\infty - \Gamma)$ and the desorption rate is $\alpha\Gamma$, C_s the surfactant concentration adjacent to the interface (the sublayer concentration), Γ_∞ is the maximum packing density, and α and β are kinetic coefficients. At equilibrium, the sublayer concentration is equal to C_o and the equilibrium surface concentration Γ_o is

$$\frac{\Gamma_o}{\Gamma_\infty} = \frac{C_o / b}{1 + C_o / b}$$

(1)

where b is an adsorption parameter equal to α/β. The scale for the diffusive flux is $[DC_o/a]\, a^2$, where D is the bulk diffusion coefficient. We assume surfactant concentrations are below the critical micelle concentration, so no surfactant aggregates are present in the bulk liquid. The scale for the kinetic desorptive flux is $\alpha\Gamma_o\, a^2$. Retarding surfactant gradients do not develop when

$$\alpha a / U >> 1$$

$$\chi(1 + C_o / b) / Pe >> 1 \tag{2a,b}$$

where χ=ba/Γ_α and Pe is the Peclet number Pe=Ua/D, because when these inequalities are met, kinetic and diffusive transport are sufficient to maintain the surface concentration uniform despite the action of convective redistribution. The diffusion criteria in (2) illustrates the reason   impurity or small concentrations of surfactant tend to retard interfaces: The diffusion coefficient of surfactant monomers is of the order of 10^{-6}cm^2/sec, and b/ Γ_α is of the order .01-1, so for typical values of a and U of 10^{-3} cm<a<10^{-4} cm and 10^{-3} cm/sec < U< 1 cm/sec, χ/Pe is not larger than 1. Thus diffusion alone reduces the surface mobility.   However, the criteria in (2) suggest a method for remobilizing interfaces which have been retarded by the adsorption of a surfactant impurity. Select a surfactant (which we term a remobilizing surfactant) whose kinetic desorption rate constant is larger than the convective rate U/a. There are not many reported measurements of surfactant kinetic rate constants, but the small amount of data derived from dynamic surface tension measurements indicates that α can be as large as 10^2 sec^{-1}, so that for U/a<10^2 sec^{-1}, surfactants whose desorptive rate is fast enough so that (2a) is satisfied can be identified. The second criteria can be satisfied if the bulk concentration is large enough; typically C_o/b can be as large as 10^3 or more, before Micellar aggregation initiates. When the bulk concentration of the remobilizing surfactant is high, the impurity does not have an opportunity to adsorb onto the surface because of the faster transport of the remobilizing surfactant. Thus the interface consists only of the remobilizing surfactant, which keeps the interface mobile by maintaining a uniform surface concentration.

To verify the above scaling arguments, we undertake numerical simulations of the effect of increasing the bulk concentration on the steady velocity of a gas bubble in a continuos liquid phase. In this first effort, we assume that buoyancy drives the bubble motion, and that surface tension forces are larger than inertial and viscous forces (small Weber and capillary numbers) so that the bubble retains its spherical shape as it moves. The kinetic exchange is assumed to be fast enough to insure that the surface and the sublayer are in equilibrium, as we have observed that surfactants can have fast kinetic regimes, and Peclet numbers for the bulk surfactant mass transfer are assumed of order one, as observed above. In addition, we retain the effects of fluid inertia by developing order one Reynolds number solutions since the Reynolds number is not small for bubble motions in the most common of continuous phases, water. In the following sections we detail the Formulation and the Numerical Solution Algorithim (Sec. II), and the Results (Sec. III).

II. Formulation and Solution Algorithim

We consider the axisymmetric, steady motion of a spherical bubble in an unbounded, Newtonian incompressible liquid in a spherical coordinate system (r,θ) with the bubble fixed, and the coordinate angle θ measured from the upstream pole. All fluid equations are written nondimensionally with the radial coordinate scaled by a, and the velocity by U, the terminal velocity. Because the fluid motion in the surrounding liquid is axisymmetric and incompressible, the velocities in the r (u_r) and θ (u_θ) directions can be specified in terms of a (nondimensional) stream function Ψ(r,θ) (scaled by a^{2}U):

$$u_r = -\frac{1}{r^2 \sin\theta} \frac{\partial\psi}{\partial\theta} ; u_\theta = \frac{1}{r\sin\theta} \frac{\partial\psi}{\partial r} \tag{3}$$

and the one component of the vorticity, w (in the azimuthal direction, scaled by U/a) is

$$rw(r,\theta) = \frac{1}{\sin\theta} \frac{\partial^2\psi}{\partial r^2} + \frac{1}{r^2} \frac{\partial}{\partial\theta}\left[\frac{1}{\sin\theta} \frac{\partial\psi}{\partial\theta}\right] \tag{4}$$

The fluid motion is governed by the Navier Stokes equations at order one Reynolds number, and we use the vorticity-stream function formulation to develop solutions:

$$\frac{\partial}{\partial r}(ru_r w) + \frac{\partial}{\partial \theta}(u_\theta w) = \frac{1}{Re}\left[\frac{\partial}{\partial r}\left(\frac{\partial}{\partial r}(rw)\right) + \frac{\partial}{\partial \theta}\left(\frac{1}{r\sin\theta}\frac{\partial}{\partial \theta}(w\sin\theta)\right)\right] \quad (5)$$

where Re is the Reynolds number ($=\rho Ua/\mu$). The boundary conditions on the stream function and vorticity are the matching to the free stream velocity at infinity ($r \to \infty$)

$$\psi \to \frac{1}{2}r^2\sin\theta \quad (6a,b)$$

$$w \to 0,$$

zero normal velocity, and the balance of the tangential stress with the Marangoni stress at the bubble interface $r=1$:

$$\psi = 0$$

$$w = \frac{2}{\sin\theta}\frac{\partial\psi}{\partial r} + \frac{Ma}{1-\Gamma}\frac{\partial\Gamma}{\partial\theta} \quad (7a,b)$$

where Γ is the surface concentration (nondimensionalized by Γ_∞) and Ma is the Marangoni number $RT\Gamma_\infty/\mu U$. The surface concentration is obtained from the solution of the convective diffusion equation,

$$u \bullet \nabla C = \frac{1}{Pe}\nabla^2 C \quad (8)$$

where $C(r,\theta)$ is the bulk concentration (nondimensionalized by the far field value Co) and Pe the Peclet number, and the surfactant boundary conditions at the bubble surface $r=1$:

$$\Gamma = \frac{kC_s}{1+kC_s}$$

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\Gamma u_\theta) = \frac{k\chi}{Pe}\frac{\partial C}{\partial r} \quad (9a,b)$$

where k=Co/b and χ=ba/Γ_∞ as in Sec. I. The nondimensional concentration must match to 1 as $r \to \infty$.

We use a finite difference method to solve the above equations. The infinite boundary is truncated to a value r =20, and the annular region from the bubble surface r=1 to the outer boundary r=20 is mapped to a unit square (x,y) by the transformations x=lnr/lnr$_\infty$ and y= π/θ. The square is discretized with Δx=.01 and Δy=.01. The discretized system is solved by using an ADI (Alternating Directions Implicit) scheme[16] in which the field equations (4,5 and 8) and boundary condition (9b) are made pseudo-unsteady in time, and equal part time steps (Δt=.005), implicit in either x or y, are taken. The convergence criteria in time is formulated in terms of the change in the maximum value of the vorticity and the stream function over Δt 10^2; this change is required to be less than 10^{-6}.

III. Simulation Results

We begin by first examining the case without inertia (Re=0). To illustrate remobilization, we fix the values of the Marangoni and Peclet numbers (Ma=5, Pe=1) and χ (=1), and we obtain solutions for increasing bulk concentrations by varying k. In Fig. 1, we plot the surface concentration profile for three different values of k (=.1,1 and 5) relative to the maximum packing concentration Γ_∞ (Fig. 1a) and the equilibrium concentration Γ_0 (Fig. 1b). The convective partioning of surfactant on the surface is evident for all values of k, as the surface concentration is higher at the downstream pole (θ=π) then the upstream pole (θ=0). We note that as k increases, Fig. 1a indicates clearly that the total amount of adsorbed surfactant increases. More importantly, as is evident in Fig. 1b, the aurface concentration becomes more uniform as k increases: The ratio of bulk diffusion to convection (χ(1+k)/Pe increases from 1.1 to 6 as k varies from .1

to 5, and diffusion therefore begins to outscale convection (see criteria 2b) to maintain a uniform surface concentration. The remobilization of the interfacial mobility is evident in Figs. 2 which plots the maximum interfacial velocity as a function of k over a much wider range of k ($10^{-2}<k<10^{2}$) with the same values of Ma, Pc and χ as in Fig.1. Note that for a clean interface, the surface velocity is equal to $(1/2)\sin\theta$, so the maximum velocity at the equator ($\theta=\pi/2$) is 1/2. As k increases from 0 to 1, the interfacial velocity decreases from the clean value of 1/2. This is the retardation that as we noted in the Introduction has been well documented in the literature. However, as k increases further and the surface concentration becomes uniform, the interfacial mobility is restored and the maximum surface velocity tends to .5 .

As the bulk concentration increases and the surface concentration becomes more uniform, the sublayer concentration (in equilibrium with the surface) also becomes more uniform. In Fig. 2a, we plot the sublayer concentration for k=.1,1 and 5 (for Ma=5,Pc=1 and $\chi=1$), and the tendency towards a more uniform concentration with increasing k is evident. With the sublayer concentration approaching 1, the concentration in the bulk also approaches one as the diffusion driving force disappears. In Fig.3, contours of constant bulk concentration are shown for k=.1 (Fig. 3a), k=1 (Fig. 3b) and k=10 (Fig.3c), and it is clear that as the interface remobilizes, the bulk concentration becomes uniform.

The effect of increasing the bulk concentration on the terminal velocity is examined in **Fig.** 4 which plots the drag on the nondimensional drag on the bubble (nondimensionalized by $\pi\mu aU$) as a function of k, for Ma=5 and $\chi=1$ and a few values of Pc (.1,1 and 10). In these nondimensional units, the drag on a clean bubble is 4 and the drag on a completely immobile surface (the Stokes drag) is equal to 6. For fixed Pc, we note that as k increases, the drag at first increases (corresponding to the decrease in interfacial mobility observed in Fig. 2b), but then decreases as the interface becomes remobilized. For fixed k, as Pc increases the drag increases. This elevation in drag, which begins to approach the Stokes value of 6 for Pc=10, can be directly attributed to the larger convective partitioning of surfactant on the surface relative to bulk diffusion; as Pc increases, $\chi(1+k)/Pc$ decreases. Importantly, the larger drags at high Peclet numbers can also be reduced to clean surface drags if the bulk concentration is taken large enough so as to increase the ratio $\chi(1+k)/Pc$.

The above simulations have been for Re=0; some preliminary results for a finite value of Re (Re=5) are given in Fig. 5 in which the drag is plotted as a function of k for Pc=1 and Ma=5. Again we note that as k increases, the drag can be reduced and the terminal velocity increased.

IV. References

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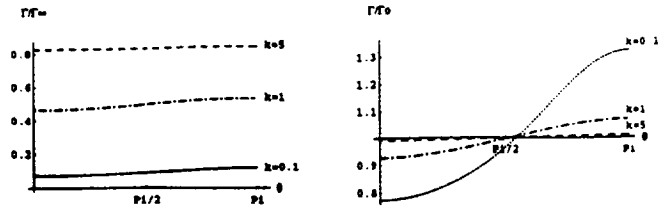[16] Ryskin, G. and Leal, L., J. Fluid Mech.,**148**, 1 and 19 (1984).

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Fig. 1 Surface concentration distribution as a function of k for Re=0, Ma=5, χ=1 and Pe=1.
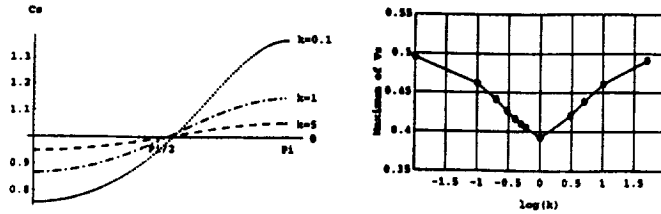

Fig. 2. The maximum interfacial velocity as a function of k and the sublayer concentration for Re=0, Ma=5, χ=1 and Pe=1
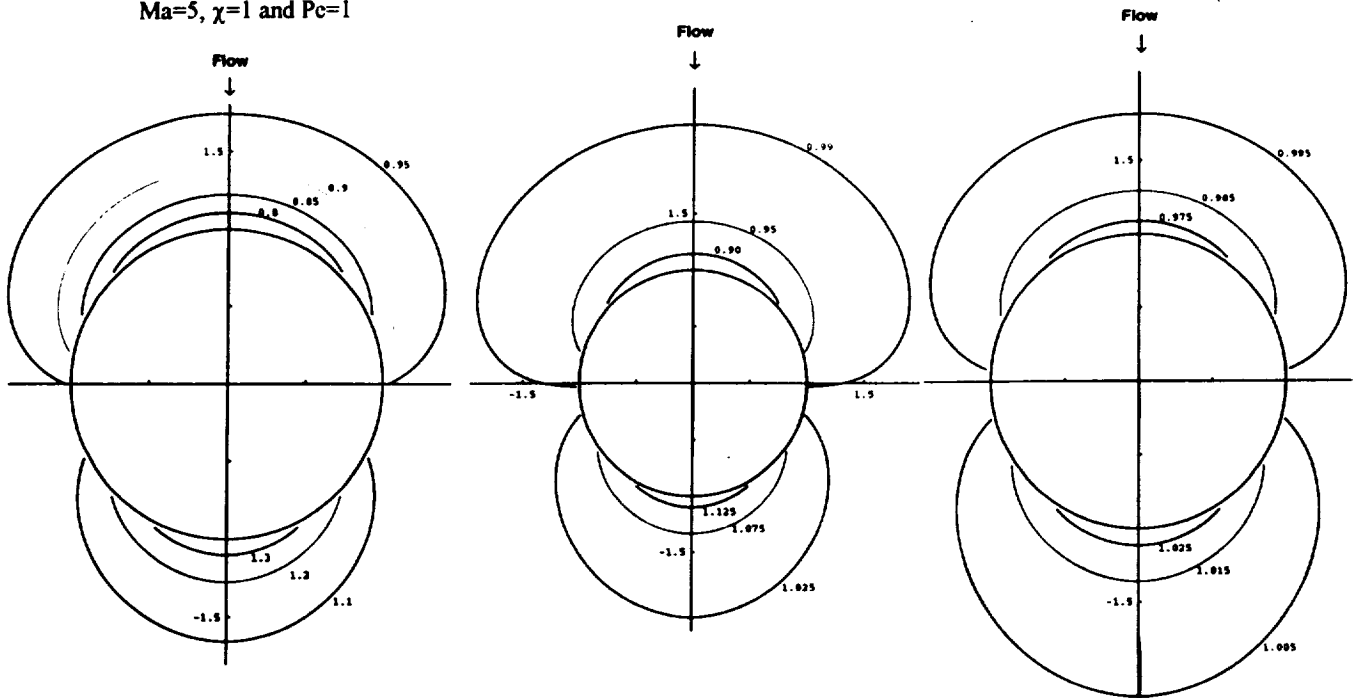

Fig. 3.Contours of constant concentration in the bulk for k=.1,1 and 10 and Re=0, Ma=5, χ=1 and Pe=1
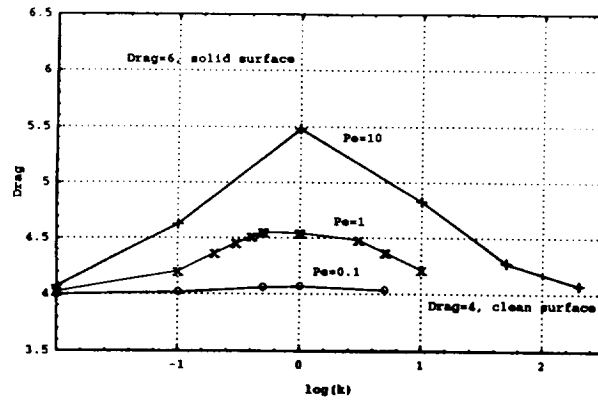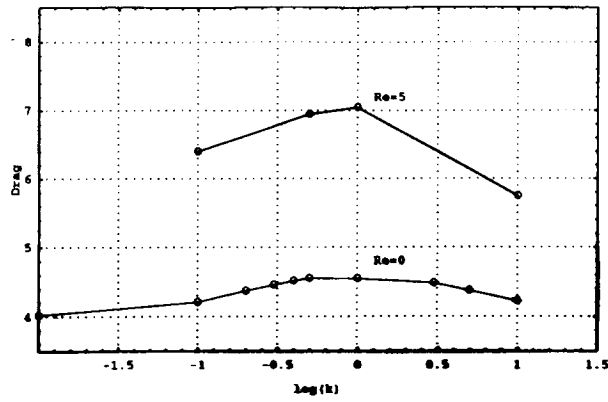
Fig. 4. Terminal velocity as a function of k for Rc=0

Fig. 5 Terminal velocity as a function of k for Rc=5