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Effect of non-homogeneous surface viscosity on the Marangoni migration of a droplet in viscous fluid

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Abstract

Marangoni migration of a single droplet in an unbounded viscous fluid under the additional effect of variable surface viscosity is studied. The surface tension and the surface viscosity depend on concentration of dissolved species. Cases of the motion induced by the presence of a point source and by a given constant concentration gradient are considered. The dependence of the migration velocity on the governing parameters is computed under quasi-stationary approximation. The effect of weak advective transport is studied making use of singular perturbations in the Peclet number, *Pe*. It is shown that, when the source is time dependent a Basset-type history term appears in the expansion of the concentration and, as a result, the leading order correction to the flow and to the migration velocity is of $O(Pe^{1/2})$. If the source of active substance driving the flow is steady, the effect of convective transport on the migration is weaker.

Keywords: Surface viscosity; Surface tension; Surfactant; Surface-active substance; Non-homogeneous distribution; Marangoni effect; Viscous drop; Advective transport; Singular perturbations; Matched asymptotic expansion

1. Introduction

The dynamics of drops and bubbles and their interaction is an important issue in many multiphase systems that involve simultaneous flow and mass transport. Analyses of such systems provide also methods for simulations of the dynamics of small biological bodies such as cells and intracellular particles. Surfactants adsorbed on an interface give rise to interfacial stresses, which may be of the form of surface tension gradients (the Marangoni effect) or those relating to the interfacial viscosities. These stresses may considerably influence the motion of drops in an immiscible medium, especially in the cases when the surface forces prevail over body ones (low gravity, small or nearly neutrally buoyant drops) [1].

The phenomenon of surface viscosity was suggested by Plateau, and used by Boussinesq to explain an anomaly that was observed in bubbles velocity. The discussed anomaly was the change of the characteristic velocity of a bubble in a viscous liquid with its size. It is known that the terminal settling velocity of relatively small bubbles and drops is close to that of a solid sphere (Stokes formula). On the other hand, larger bubbles and drops behave normally, in accordance with Hadmard and Rybczynski formula. The transition domain between these two types of behavior for bubbles and drops occurs in a relatively small interval of size (O (1 mm)). Boussinesq suggested that this "solidification" is due to the interfacial viscosity, which has strong influence with the reduction of bubble's size. Later on, Frumkin and Levich [2] suggested another explanation of the phenomenon based solely on the effect of surface tension gradient over the interface (Marangoni effect). Though it failed to account for all the changes in the characteristic velocities of bubbles, surface viscosity was found later on to be an existing and measurable quantity.

Marangoni migration of drops in a viscous medium is a subject of numerous analytical and experimental studies, while the effect of interfacial surface viscosity has attracted substantially less attention so far. However, in situations where a surfactant concentration at the interface is sufficiently large, or when the interface is composed of large molecules, the surface viscosity is not negligible and, therefore, must be accounted for.

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Moreover, the dependence of the surface viscosity on the concentration of surfactants may be extremely strong (see e.g. [3] and [4]).

Scriven [5] formulated the expressions for Boussinesq's surface viscosity and the expression for surface tension, γ, in a tensorial form and embedded them in a general surface stress balance. The interface is considered as a special 2-dimensional medium possessing its own specific energy and momentum. This medium is compressible even when both bulk phases are incompressible, hence, the surface viscosity has two independent contributions: Shear surface viscosity, ε, and dilatational surface viscosity, k [1,5,6]. Scriven's formula allowed measurements of surface viscosity and the development of continuum models for the effect of surface viscosity on the motion of bubbles and drops. The difficulty in measuring shear surface viscosity is relatively small. Thus, one decade after the appearance of Scriven's work, large amount of data related to shear surface viscosity magnitude and its dependence on various factors was published [3]. Dilatational surface viscosity is a different issue. Only in recent years suitable methods that eliminate the influence of other factors on the measurement were developed. Among the reports on measurements that were published are Stubenrauch and Miller [7], Koelsch and Motschmann [8], Wantke and Fruhner [9], Kostoglou and Karapantsios [10], Wang and Narsimhan [11] and others.

Agrawal and Wasan [12] presented a theoretical study of the creeping motion of a bubble under the combined effect of surface viscosity, surface tension and gravity. Effects of surface viscosity were added to earlier models and the final results of bubbles motion were compared. LeVan [13] and Holbrook and LeVan [14,15] solved the general problem that includes the effects of surface viscosity, surface tension and gravity on the motion of drop. Balasubramaniam and Subramanian [16] extended the analysis of LeVan to include convective transport of momentum and calculated the small deformations of the drop from the sphere.

The assumption of a constant surface viscosity was used in the earlier mentioned models and in measurements of surface viscosity. This assumption was made in order to achieve simplified analytical models. However, these simplifying assumptions were suspected to cause inaccurate predictions in analytical models in many physical systems [14]. Surface viscosity depends on many factors including surfactants concentrations, additives as ionic materials that change surfactants configuration, temperature, flow, fluids species and others [4]. Holbrook and LeVan [14] argued that due to the strong dependence of surface viscosity on these factors, the assumption of a constant surface viscosity would be reasonable only in very specific systems while it will cause some magnitude of error in models for most real systems. In addition, the use of constant surface viscosity is suspected to be the cause for many of the difficulties in dilatational surface viscosity measurements [17].

In the present work, the effect of variable surface viscosity on the Marangoni migration of a drop is investigated for isothermal conditions, where surface viscosity and surface tension depend solely on the concentration of a soluble surfactant. The interfacial surfactant transport is assumed to be diffusion-controlled, i.e. the interfacial concentration is taken to be proportional to the bulk concentration in the vicinity of the interface. Two kinds of concentration field are considered, the first results from a constant gradient far from the drop and the second is induced by a point source. The first type of the field is commonly used in the general problem of the Marangoni migration of drops and bubbles. For small drops, and in the absence of singularities, linear distribution provides a good approximation to an arbitrary one in the vicinity of the fluid particle. Nevertheless, in some applications a non-linear distribution may be important. For example distributions that result in spontaneous interactions of drops induced by interfacial mass transfer [18], or in biological applications, for which production of active substances is typical, e.g. Lavrenteva et al. [19] who considered a model of the locomotion of a drop induced by an internal point source of a surfactant. This highly simplified model ignored all the properties of the interface except surface tension. One of the goals of this paper is to extend these results to the case of a more involved rheology of the interface, which includes surface viscosity.

In Section 2, basic assumptions of the model are briefly discussed. Governing equations and boundary conditions are formulated. Most of the computations are performed making use of the quasi-stationary approximation described in Section 3, where the method of solution and results of calculations are discussed as well. In Section 4 we take into account a weak convection and include non-stationary effects by using the singular perturbation method of matched asymptotic expansions in the Peclet number, Pe. It is shown that a time-dependent point source gives rise to a correction of order $O(Pe^{1/2})$.

2. Statement of the problem

Consider a Newtonian viscous drop of radius a, submerged in an unbounded immiscible Newtonian viscous fluid, which is quiescent far from the drop. Around the drop there is a field of surfactants concentration c. It is supposed that the surfactants are weak or diluted so that their presence does not affect any physical property in the system other than the interfacial tension and the surface viscosity. Two kinds of surfactants distributions are considered. In case 'a,' a constant gradient of surfactants is assumed far from the drop. In case 'b,' a point source of surfactants is located in the vicinity of the drop surface. The intensity of the source may be time dependent, $Q = Q(t)$.

Values of variables and properties inside the drop are marked with the superscript $^{(1)}$. The superscript $^{(2)}$ is used for variables and properties outside the drop. Unmarked values are general. The following scaling is chosen: The radius of the drop, a, for the length, the characteristic change of the bulk mass concentration along the interface is $\hat{c} = |a\nabla c_\infty|$ for the case of constant gradient and $\hat{c} = \frac{Q^*}{D^{(2)}a}$ for the case of a point source with a characteristic strength Q^*. Since the flow is induced solely by the surface tension gradients, we chose Marangoni velocity, $\frac{|\Delta\gamma|}{\mu^{(2)}}$, for scaling of the velocity, $\frac{|\Delta\gamma|}{a}$ for the pressure or stress, and $\frac{\mu^{(2)}a}{|\Delta\gamma|}$ for time, with $\Delta\gamma$ being a characteristic drop of surface tension along the interface and μ denoting