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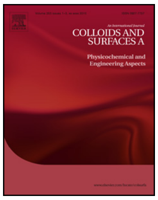

Transport of a partially wetted particle at the liquid/vapor interface under the influence of an externally imposed surfactant generated Marangoni stress

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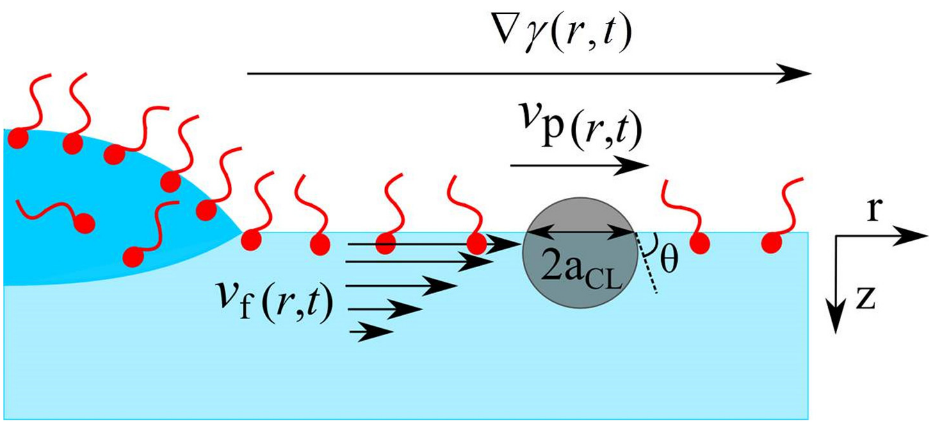
HIGHLIGHTS

- Spatiotemporally evolving surface tension & liquid velocity control particle dynamics.
- Subphase depth, particle size and wettability control dynamics.
- Surfactant solubility affects particle acceleration and deceleration regimes.

GRAPHICAL ABSTRACT



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ABSTRACT

Marangoni flows offer an interesting and useful means to transport particles at fluid interfaces with potential applications such as dry powder pulmonary drug delivery. In this article, we investigate the transport of partially wetted particles at a liquid/vapor interface under the influence of Marangoni flows driven by gradients in the surface excess concentration of surfactants. We deposit a microliter drop of soluble (sodium dodecyl sulfate) aqueous surfactant solution or pure insoluble liquid (oleic acid) surfactant on a water subphase and observe the transport of a pre-deposited particle. Following the previous observation by Wang et al. [1] that a surfactant front rapidly advances ahead of the deposited drop contact line and initiates particle motion but then moves beyond the particle, we now characterize the two dominant, time- and position-dependent forces acting on the moving particle:

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(1) a surface tension force acting on the three-phase contact line around the particle periphery due to the surface tension gradient at the liquid/vapor interface which always accelerates the particle and (2) a viscous force acting on the immersed surface area of the particle which accelerates or decelerates the particle depending on the difference in the velocities of the liquid and particle. We find that the particle velocity evolves over time in two regimes. In the acceleration regime, the net force on the particle acts in the direction of particle motion, and the particle quickly accelerates and reaches a maximum velocity. In the deceleration regime, the net force on the particle reverses and the particle decelerates gradually and stops. We identify the parameters that affect the two forces acting on the particle, including the initial particle position relative to the surfactant drop, particle diameter, particle wettability, subphase thickness, and surfactant solubility. We systematically vary these parameters and probe the spatial and temporal evolution of the two forces acting on the particle as it moves along its trajectory in both regimes. We find that a larger particle always lags behind the smaller particle when placed at an equal initial distance from the drop. Similarly, particles more deeply engulfed in the subphase lag behind those less deeply engulfed. Further, the extent of particle transport is reduced as the subphase thickness decreases due to the larger velocity gradients in the subphase recirculation flows.

1. Introduction

Surface tension driven (Marangoni) flow caused by the deposition of surfactants on a liquid subphase has been a topic of interest for many years. This phenomenon arises from a rich interplay of fluid mechanics and molecular properties of surfactants and has importance in several industrial and biomedical applications including ink-jet printing [2,3], coating flow technology [4,5], surfactant replacement therapies [6,7], and aerosol pulmonary drug delivery [8,9]. We have studied the use of surfactant-driven Marangoni stresses to transport solid particles across a liquid interface, [10,11] and solid particles placed at the interface have long been used as tracers to track the spreading of a surfactant front at a liquid/vapor interface [12,13]. However, a recent study has shown that talc particles, frequently used as tracers, actually lag behind the surfactant front and therefore may not be accurate tracers to mark the spreading of surfactant fronts [1].

When a liquid drop containing surfactant is deposited on a liquid subphase, surface tension gradients are developed at the drop/vapor, drop/subphase and subphase/vapor interfaces. These surface tension gradients cause the drop to spread convectively on the liquid subphase. As soon as the surfactant drop touches the liquid subphase, surfactant molecules escape ahead of the contact line and spread across the bare subphase/vapor interface [12,14,15]. The leading edge of this spreading monolayer is referred to as the surfactant front and is identifiable by a liquid ridge [16,17]. Many aspects of this spreading process have been studied, but particular attention has been paid to the speed at which the surfactant front spreads [16,18,19]. This speed depends on several variables, especially the surfactant solubility, subphase thickness and subphase viscosity. For an insoluble surfactant drop, it has been shown theoretically and experimentally that the surfactant front advances with time as $t^{0.75}$ [20–23]. For a soluble surfactant, the surfactant front spreads with a power law exponent of about 0.5 [18,24].

While the dynamics of surfactant drop and surfactant front spreading have received much attention, less attention has been paid to the transport of particles at the liquid/vapor interface under the influence of surfactant-induced Marangoni stresses. Unlike the work done on transport of self-propelled particles [25–27], in this study, the transport of particles solely by externally imposed Marangoni flows is considered. In the one prior study of partially wetted particle transport induced by a remotely deposited surfactant solution drop [1], it was determined that lateral particle transport is not initiated by the capillary waves generated by coalescence of the deposited drop with the subphase but rather is initiated by the passing surfactant front. As the surfactant front reaches the particle, it delivers a lateral impulse to initiate particle motion and then proceeds ahead of the particle.

The objective of the current work is to identify the main system parameters that govern the transport of a partially wetted particle at the liquid/vapor interface upon deposition of a surfactant drop at some distance from the particle. We identify and characterize the two transient forces acting on the particle that control the particle transport: (1) the surface tension force acting at the three-phase contact line on the partially wetted particle periphery due to the surface tension gradient along the liquid/vapor interface and (2) the viscous force associated with unequal velocities of the particle and liquid. As the particle moves along its trajectory, the particle velocity evolves spatially and temporally in two regimes: the acceleration regime, wherein the particle quickly accelerates to a maximum velocity and the deceleration regime, wherein the particle more gradually decelerates and eventually stops. We identify key parameters including particle size, particle initial position relative to the drop, particle wettability, subphase thickness and surfactant solubility that affect the two forces acting on the particle, and vary them independently to study their effect on the evolution of particle speed and the distance over which the particle is transported.

Interfacial transport of particles by Marangoni stresses is a physically rich problem with forces that evolve along the particle's trajectory in space and time. Full elucidation of the dependence of the spatial and temporal evolution of these forces on the key parameters demands both full mapping of the subphase velocities as well as measuring along overlapping particle trajectories as the parameters are varied. This makes a full experimental mapping of dependence of forces on the parameters difficult. Results from this work represent the first step towards this mapping: we characterize fluid mechanical regimes that must be considered for the full description of the problem.

2. Materials and methods

2.1. Materials

Surfactants were anionic sodium dodecyl sulfate (SDS; electrophoresis grade), purchased from Fisher Scientific (>99% purity) and oleic acid (>99% purity), purchased from Sigma Aldrich and used as received. The subphase used was water purified to 18 MΩ cm resistivity and 72.7 ± 0.7 mN/m surface tension (uncer-

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