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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Abstract

Marangoni flows offer an interesting and useful means to transport particles at fluid interfaces with application in 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 solution) 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 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: 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 M Ω •cm resistivity and 72.7 ± 0.7 mN/m surface tension (uncertainties in all reported measured quantities are the standard error of the mean unless otherwise noted) using a Milli-Q Academic unit (Millipore Corporation). An 8.3 mM (1 $\times$ critical micelle concentration, CMC) aqueous solution of SDS having a surface tension of 32.0 ± 0.7 mN/m was used for the soluble surfactant case. Pure oleic acid, with a surface tension of 32.4 ± 0.3 mN/m, was used as the insoluble surfactant.

All glassware was cleaned sequentially using ethanol, acetone, and deionized water several times and then dried under a nitrogen stream. All experiments were conducted at room temperature ($23 \pm 1^\circ\text{C}$).

Three different sizes of polymethylmethacrylate (PMMA; density 1.18 g/cm³) particles were used for particle transport experiments (diameter $\pm$ manufacturer-reported standard deviation): 0.50 ± 0.02 mm mean diameter PMMA particles were provided by Evonik Industries AG, and 1.50 ± 0.05 mm and 3.18 ± 0.05 mm particles were purchased from Goodfellow Cambridge Limited. The particles were cleaned by rinsing them with ethanol and water and spreading experiments were performed after the particles were completely dry. In addition, $3.1 \pm$

0.1 μm (diameter $\pm$ standard deviation) fluorescent microbeads, purchased from Polysciences, Inc., were used to trace the lateral flow within the bulk liquid subphase.

2.2. Methods

2.2.1. Surface tension measurement. All liquid/vapor surface tensions were measured with a Wilhelmy pin apparatus (Nima Technology Ltd.). Changes in surface tension of the subphase during spreading experiments were recorded by the Wilhelmy pin as a function of time after a surfactant drop was deposited. The pin was located in a subphase region well outside the final area covered by the spreading drop, which was determined in a separate study [1] by recording the movement of the spreading drop's contact line from a side view using a high speed camera. The drop's contact line disappeared after spreading to ~ 0.5 cm, thus any change in the subphase surface tension outside the spreading drop can be attributed solely to the spreading surfactant front. To verify that the transient Wilhelmy pin signal was indeed a surface tension change and not a perturbation caused by the physical surface disturbance, a water drop was deposited on the same subphase and was observed to produce no detectable Wilhelmy pin signal.

2.2.2. Particle surface modification. An oxygen plasma cleaner (Harrick plasma cleaner PDC-32G) was used to oxidize the surface and change the wettability of 1.5 mm PMMA particles. Cleaned particles were treated with oxygen plasma for 5 minutes to increase the surface hydrophilicity. The changed wettability of the particles was manifested as a change in the fraction of the particle immersed when placed on the subphase.

To measure the immersed depth of a PMMA particle, it was gently placed at the water/vapor interface in a square glass cuvette (2 cm x 2 cm). A solid state camera (Cohu, model #4115-5000-0000) with a zoom objective (Bausch and Lomb Monozoom 7) was focused at the three-phase contact line around the particle periphery, with illumination from behind the cuvette.

Captured images were analyzed (Nikon NIS-Elements Advanced Research microscope imaging software) to determine the immersed depth of particle, the distance from the interface where liquid meets the particle to the bottom of the particle. The immersed depths, of untreated 0.5 mm, 1.5 mm and 3.2 mm particles in water were 0.32 ± 0.02 mm, 0.86 ± 0.04 mm and 1.8 ± 0.1 mm, respectively. The immersed depth of the plasma treated 1.5 mm particle in water was 1.4 ± 0.1 mm.

2.2.3. Particle motion experiment. Fig. 1 shows a schematic of the experimental setup. Water subphases were contained at a depth of either 0.8 cm or 0.3 cm in a rectangular Pyrex glass trough with dimensions $39 \text{ cm} \times 26 \text{ cm} \times 6 \text{ cm}$ ($l \times w \times h$). A recirculating flow in the subphase after surfactant drop deposition was expected, and is experimentally observed, consistent with the value of the gravitational parameter, $G = \rho g H^2 / S > 1$, where ρ is the subphase density, 1000 kg/m^3 , g is acceleration due to gravity, 9.8 m/s^2 , H is subphase depth, $8 \times 10^{-3} \text{ m}$ or $3 \times 10^{-3} \text{ m}$ and S is the difference between the surface tensions of the subphase and surfactant drop, $\sim 40 \times 10^{-3} \text{ N/m}$ for both SDS solution and oleic acid drops. Theoretical models indicate that values of $G > 1$ also preclude subphase rupture during surfactant spreading [12]. Our experiments were conducted with $G \sim 16$ and $G \sim 2$. In addition, surfactant spreading in a finite subphase with $G > 1$ suggest that there would be bidirectional flow in the subphase for either subphase depth in our experiments as described below [28].

Figure 1. Schematic of the experimental setup to record the motion of a partially wetted particle at a liquid/vapor interface upon deposition of a surfactant drop.

Typically, five or six PMMA particles were placed at the water/vapor interface at different radial distances from the center of the water surface using tweezers. The particles were placed at different angular positions so they would not collide or exert capillary forces on one another during the experiments. Drops of 7 μL of SDS solution or 9 μL of oleic acid were deposited at the center of the liquid surface. A video camera (Sony, XC-555/555P) with 30 fps framerate was mounted above the experimental setup to record the particle movement. Videos were later analyzed (Nikon NIS software) to trace individual particle trajectories.

Particle velocity and acceleration were calculated by numerically differentiating the position versus time data (OriginPro 8 software). The differentiation was performed simultaneously with Savitzky-Golay smoothing [29] using a second degree polynomial and a 9 point window to reduce noise. The values of the maximum particle velocities (as discussed later) determined by this process or by simple differentiation by averaging the slopes of two adjacent

points vary by less than 10% and thus the smoothing technique does not affect any of the conclusions drawn. The average net force acting on a particle in the radial direction in any time interval Δt was calculated by determining the average acceleration and then multiplying by the particle mass m .

To trace the subsurface movement of the *bulk* liquid, a few spreading experiments were performed with 3 μm fluorescent microbeads mixed into the water subphase. To judge the suitability of these particles as bulk tracers, we calculated the Stokes number St [30],

$$St = \frac{\rho_p u_{\max} D^2}{18\mu r_d} \quad (1)$$

with $\rho_p = 1.05 \text{ g/mL}$ the density of the particle, $u_{\max} = 0.1 \text{ m s}^{-1}$ a typical value for the speed of the flow, $D = 3 \times 10^{-6} \text{ m}$ the diameter of the particle, $\mu = 10^{-3} \text{ Pa s}$ the viscosity of water and $r_d \sim 0.2 \text{ m}$ the distance between the drop and container wall, the length-scale at which the fluid flow is occurring. For our experiments, $St \sim 10^{-7} \ll 1$, indicating the absence of microbead inertial effects and confirming their suitability as tracers for the bulk flow.

The sub-surface microbead tracer experiments were performed under a fluorescence microscope operated in epi-illumination mode (Nikon Instruments, Inc., Nikon AZ 100 with an AZ-Plan Apo $0.5 \times$ objective, NA: 0.05/WD: 54 mm and fluorescein filter set Nikon B-1E), focused just below the water/vapor interface. A surfactant drop was deposited at the center of the container with the microscope focused at $\sim 9 \text{ cm}$ from the drop deposition point. Images were later analyzed to track microbead motion. Imaging tracer microbeads required a higher magnification, and thus a smaller field of view, than was needed to monitor the PMMA particle surface trajectories in the particle experiments. As a result, the subsurface flow fields could only be measured at a few isolated points and discrete time intervals after spreading. It was not

possible to measure the subsurface velocity at every point along the partially wetted particle trajectories in the particle motion experiments.

3. Forces acting on a partially wetted particle at an interface

The goal of this section is to provide a semi-quantitative description of the factors governing the transport of a partially immersed particle, rather than a full predictive model. As noted above, the particle starts moving only after it is passed by the advancing surfactant front [1]. After that, two forces act on the particle, the surface tension force on the contact line of the particle and the viscous drag force on the immersed surface area of the particle (**Fig. 2**).

Figure 2. Schematic showing developed surface tension gradient $\nabla\gamma$ across a particle moving at radial velocity v_p after deposition of a surfactant drop. a_{CL} is the contact line radius of the partially wetted particle, v_f is the subphase liquid velocity, θ is the contact angle and t is time.

The net surface tension force acting on the contact line of the particle is [31]

$$\overrightarrow{F}_{st} = \int_{CL} \gamma \hat{t} dl \quad (2)$$

where $\hat{t}$ is the unit vector normal to the three-phase contact line, CL , in the plane of the liquid/vapor interface. In the present context, the remote deposition of a surfactant drop

establishes a transient, radial surface tension gradient in which the particle is immersed, imparting a non-zero net force in the outward radial direction. Although the surface tension gradient is not linear along the radial direction [11,16], the discussion is simplified by approximating it as linear from the point of drop deposition to the surfactant front, $\nabla_r \gamma \approx (\gamma_{subphase} - \gamma_{drop}) / L_s(t)$ where ∇_r is the radial component of the gradient, $\gamma_{subphase}$ is the clean subphase surface tension, γ_{drop} is the drop surface tension and L_s is the time-dependent position of the surfactant front [17,32]. This formulation also neglects the change in drop surface tension due to surfactant inventory depletion in the drop. The surfactant front advances rapidly with a velocity on the order of tens of cm/s, and must eventually reach the container wall [1,15,33]. At times after the surfactant front has hit the edge of the container, $\nabla_r \gamma \approx (\gamma_{wall} - \gamma_{drop}) / r_{wall}$, where γ_{wall} is the time-varying surface tension at the wall of the container r_{wall} . On integrating along the particle's three-phase contact line, with the assumptions noted above, the surface tension force acting along the direction of motion at any given time can be approximated as

$$F_{st_r} = \pi a_{CL}^2 \nabla_r \gamma \quad (3)$$

where, a_{CL} is the contact line radius on the partially wetted particle, which depends on the particle diameter and its depth of immersion, and thus its wettability.

The second force acting on the particle in the radial direction is the viscous force F_{vis_r} which arises due to the difference in the radial components of the liquid velocity v_f and the particle velocity v_p . The same surface tension gradient that directly produces the surface tension

force on the particle also gives rise to subphase flow according to the tangential stress balance at the liquid/vapor interface [17,24]:

$$\nabla_r \gamma(r, t) = \mu \nabla_z v_f(r, z = 0, t) \quad (4)$$

where, z is the distance into the subphase from the liquid/vapor interface and t is time. When the surfactant front reaches a given location, the subphase flow is initiated at the surface and the velocity field propagates as a function of time into the subphase. For short times and short distances from surfaces, the liquid velocity decays exponentially in the z direction [17],

$$v_f(r, z, t) = v_f(r, z = 0, t) e^{z \sqrt{\rho/\mu t}} \quad (5)$$

where ρ is the density of the subphase liquid.

For particle Reynolds numbers (Re_p)

$$Re_p = \frac{\rho |v_f(r, t) - v_p(r, t)| D}{\mu} \quad (6)$$

greater than one (a typical maximum value of Re_p in our experiment is ~ 30), the radial component of the viscous force F_{vis_r} acting on a completely immersed particle in a uniform liquid velocity field is [34]

$$F_{vis_r} = \frac{\pi}{4} D^2 \rho C_d \frac{1}{2} |v_f(r, t) - v_p(r, t)| (v_f(r, t) - v_p(r, t)) \quad (7)$$

where the fluid velocity v_f depends on radial position, r , time, t , and the particle velocity, v_p is also a function of r and t . Equation (7) does not include unsteady forces acting on the particle. C_d

is the drag coefficient which for a fully submerged particle and $0 < Re_{particle} < 2500$ is given by [35]:

$$C_d = \frac{24}{Re_p} + \frac{6}{1 + \sqrt{Re_p}} + 0.4 \quad (8)$$

If the particle is partially immersed in the liquid, the viscous force applied on the particle will differ from equation (7) [36,37]. When the fluid velocity is uniform across the immersed portion of the particle, the radial component of the viscous force acting on a partially immersed particle at the liquid/vapor interface can be approximated by multiplying equation (7) by α , the fraction of the particle surface area immersed in the liquid [36],

$$F_{vis_r} = \alpha \frac{\pi}{4} D^2 \rho C_d \frac{1}{2} |v_f(r, t) - v_p(r, t)| (v_f(r, t) - v_p(r, t)) \quad (9)$$

The viscous force on a partially immersed particle in equation (9) is calculated assuming that the liquid/vapor interface is flat and that the fluid flow field induced by surface tension gradients is not significantly altered by the presence of the particle and is uniform across the immersed fraction of the particle. The area fraction α increases monotonically with decreasing contact angle θ measured through the liquid.

Applying Newton's second law of motion to a particle being transported under the influence of both a surface tension force and a viscous drag force:

$$\begin{aligned}
\frac{\partial v_p(r, t)}{\partial t} &= 0, \text{ for } t \leq T \\
\left\{ \begin{aligned} &\frac{\pi D^3}{6} \rho_p \frac{\partial v_p(r, t)}{\partial t} = \pi a_{CL}^2(D, \theta) \frac{\gamma_{subphase/wall} - \gamma_{drop}}{L_s(t)} \\ &+ \alpha(D, \theta) \frac{\pi}{4} D^2 \rho C_d \frac{1}{2} |v_f(r, t) - v_p(r, t)| (v_f(r, t) - v_p(r, t)) \end{aligned} \right\} \text{ for } t > T
\end{aligned} \tag{10}$$

where ρ_p is particle density, T is the time the surfactant front arrives at the particle and $\gamma_{subphase/wall}$ is either the surface tension of the bare subphase for times before the surfactant front hits the container wall or the (time-dependent) subphase surface tension immediately adjacent to the wall for times after the front has reached the wall. The net force acting on the particle is then a function of time and radial position due to the position and time dependence of the surface tension gradient and the subphase velocity. Thus, the net force varies along the particle *trajectory*. Equation (10) shows how the particle kinematics is dependent on different parameters including: initial particle position relative to the drop (implicitly through its effect on T), particle diameter (implicitly through its effect on a_{CL} and α), subphase thickness (implicitly through its effect on v_f), and particle wettability (implicitly through its effect on a_{CL} and α). In addition, the kinematics depend on the surfactant solubility through its impact on the surface tension gradient. The initial particle position relative to the drop impacts T , which serves as a time delay for the onset of forces on the particle and, since the surface tension gradient and fluid velocity profile evolve in time and space, determines the magnitude of the forces acting on the particle. The particle diameter affects the contact line radius (a_{CL}), the fraction of particle immersed in liquid (α) and the inertia of particle while its wettability affects only a_{CL} and α . The contact line diameter a_{CL} and particle immersed fraction α affect both the surface tension and viscous forces

but in different ways. Subphase thickness affects the fluid velocity (v_f), particularly its temporal decay at long times, thus affecting the viscous force acting on the particle. Surfactant solubility affects the surface tension gradient across the particle and fluid velocity (by placing different boundary conditions at the subphase surface at long times and by altering the temporal evolution of surface tension by the possibility of desorption into the subphase), thus influencing the surface tension and viscous forces acting on the particle. We systematically vary these parameters to study their effect on particle transport.

4. Results and Discussion

4.1. Particle motion induced by soluble surfactants

Fig. 3a shows a typical trajectory of a 0.5 mm particle on deposition of a 7 μ L drop of 1 $\times$ CMC SDS solution on a water subphase. The thickness of the water subphase in all experiments was 0.8 cm unless otherwise stated. The surfactant front induces motion in the particle and passes by the particle. The particle is transported by 9 cm over approximately 9 s and slows to nearly zero velocity (**Fig. 3b**) approximately 3 to 4 cm before it would hit the wall (at $r_{wall} \sim 20$ cm). This is approximately twenty times greater than the capillary length of water, so it is unlikely that the meniscus at the container wall is stopping or otherwise impacting the particle motion in this case.

Figure 3. A representative plot showing (a) particle position with time, (b) particle velocity with position and time and (c) net force acting on the particle with position and time for a 0.5 mm particle on deposition of a 1x CMC SDS solution drop on a water subphase. The schematics in (b) show the evolution of surface tension γ along the subphase with position r and time t . The particle was initially placed at 4.5 cm from the point of drop deposition.

Fig. 3b shows the corresponding velocity of the same particle as it moves in position and time on that trajectory. The particle velocity exhibits a distinct acceleration regime, where the particle rapidly accelerates from zero velocity to a maximum velocity of 7 cm/s, followed by an abrupt transition to a deceleration regime, where the particle more gradually decelerates back to zero velocity. The secondary ordinate of **Fig. 3b** shows the upper bound on the particle Reynolds number, $Re_{p, max} = \rho v_p D / \mu$, of a 0.5 mm particle as a function of time and position. Since we have not subtracted the fluid velocity, as it is unknown for this trajectory, the plotted values overestimate the Re_p value relevant for the calculation of the viscous force. Nonetheless, **Fig. 3b** shows that for most of the time the particle Reynolds number may be greater than one suggesting that (equations (7, 9)) are a safer representation for the viscous force than the simple Stokes analysis [34]. **Fig. 4a** shows that the velocity of a particle as its moves in space and time.

Figure 4. A representative 3D plot showing (a) particle velocity as a function of position and time and (b) net force acting on a particle as a function of position and time for a 0.5 mm particle on deposition of a 1× CMC SDS solution drop on a water subphase.

4.1.1. The acceleration regime. **Fig. 3c** shows the calculated net force acting on the particle. In the acceleration regime when the velocity of the particle is increasing with time (**Fig. 3b**), the net force acting on the particle is acting in the direction of particle motion. The schematics in **Fig. 3b** show the evolution of surface tension γ along the subphase with r and t . In these schematic illustrations, it is assumed for simplicity of presentation that the surface tension varies linearly with the radial position, while modeling predicts a monotonic but non-linear increase with increasing radial position [12,18]. At time $t = 0$, i.e. immediately upon deposition of a surfactant drop, the surface tension is smaller in the subphase region between the drop center and the drop contact line and higher (γ_{subphase}) beyond the drop contact line. As the surfactant front escapes across the contact line of the drop and spreads along the subphase surface, the surface excess concentration at the drop center decreases since the concentration of surfactant in drop was initially at $1 \times \text{CMC}$, and any dilution of the surfactant in the drop must decrease the surface excess concentration, thus increasing the surface tension. As the surfactant front passes by the particle, the particle experiences a gradient in surface tension along its contact line. This produces the unbalanced surface tension force on the particle captured in equation (3). As discussed previously, the surface tension gradients at the liquid interface also induce a flow in the subphase leading to a viscous force acting on the particle, represented in equation (9).

The net force on the particle achieves a maximum and then begins to decrease (**Fig. 3c**). The end of the acceleration regime is set as the time when the net force (acceleration) on the particle passes through zero. Lacking a mechanism to reverse the sign of the surface tension gradient, the surface tension force (equation (3)) is always acting in the direction of particle motion in either regime. It decreases monotonically with increasing time and radial position, along the trajectory after the surfactant front has passed the particle, but it never acts in

opposition to the particle motion. At some point in the acceleration regime, the viscous force on the particle begins to act in the opposite direction of the particle motion as the particle moves along its trajectory. At the position and time at the end of the acceleration regime, the viscous force balances the surface tension force thus making the net force acting on the particle zero. Using the surface tension force estimated from equation (3), 16×10^{-8} N and the net force, 4×10^{-8} N determined at the earliest possible time (~ 150 ms after drop deposition), we find that the viscous force on the particle is already negative at the earliest detected point along its trajectory. Whether the viscous force is ever in the positive direction even at the earliest time points depends on how the surface tension gradient accelerates the particle versus the fluid elements surrounding the particle. **Fig. 4(b)** shows the net force acting on the particle as it moves along its trajectory in space and time.

In the acceleration regime, the flow field is temporally developing both laterally across the particle and with depth into the subphase. An estimate of the time scale for development of fluid velocity across the particle along the interface is $t_{\text{interface}} \approx D / v_f$ [38]. With D as 0.5 mm and approximating v_f as the surfactant front velocity of ~ 10 cm/s, $t_{\text{interface}} \sim 1$ ms. The time scale for the evolution of the velocity in the bulk subphase across the particle's immersed length (equation (5)) is $t_{\text{bulk}} \approx L_{\text{Immersed}}^2 / \nu$ [39], where L_{Immersed} is the immersed length of the particle in the subphase, 0.3 mm for the 0.5 mm diameter particles, and ν is the kinematic viscosity. Thus, $t_{\text{bulk}} \sim 90$ ms which is comparable to our experimental observations of the duration of the acceleration regime for a 0.5 mm particle. Beyond the time evolution of the flow fields near the particle due to the above mentioned fluid relaxation, even more complicated temporally evolving flows are occurring as the surfactant front passes the particle [12] and recirculation flows develop [40].

4.1.2. The deceleration regime. In the deceleration regime, the net force on the particle is acting in the direction opposite to its motion (**Fig. 3c**) and its velocity decreases with time and position. While the surfactant front spreads radially outward and hits the container wall r_{wall} , the surface tension at the drop deposition point increases (**Fig. 3b**). Therefore, during the deceleration regime the surface tension force on the particle, as it moves along its trajectory, decreases but remains in the direction of the motion. The viscous force clearly must then oppose the motion ($v_p > v_f$) and has a larger magnitude than the surface tension force acting on the particle contact line throughout the deceleration regime where the net force is negative.

Experimental confirmation that v_p is greater than the local v_f and the viscous force is in opposite direction to the particle's motion is found by simultaneously tracking a single 3 μm fluorescent microbead in the bulk subphase $\sim 1 - 2$ mm below the surface and the 0.5 mm particle at the interface, after deposition of a surfactant solution drop. Although suspended fluorescent microbeads could be seen throughout the depth of subphase, we focused on a single microbead just underneath the fluid surface. That the microbead was just under the surface is supported by observing the multiple out of focus beads deeper in the subphase flowing backwards due to recirculation effects. The lateral distance between the particle and the microbead was 3 mm. Trajectory analysis indicated that $v_p - v_f \sim 0.3$ cm/s. With the measurement of v_f we confirm that the particle Reynolds number (equation (6)), calculated using the relative velocity of the particle and the fluorescent microbead bulk tracer particle is greater than one even in the later times of the deceleration regime.

In addition to spreading laterally, the soluble surfactant is desorbing from the surface during the particle motion along its trajectory. To estimate the portions of the particle trajectories where the surfactant is still present in significant amounts on the surface, we determine the

desorption time scale for SDS molecules from the water/vapor interface. This is done by recording the surface tension change at a remote location on the surface while simultaneously depositing the SDS solution drop.

Fig. 5a shows a decrease in the subphase surface tension upon deposition of a 7 μL drop of $1\times$ CMC SDS solution on the water subphase. The pin records a rapid surface tension decrease of approximately 2 mN/m after drop deposition, followed by an almost-as-rapid recovery to the baseline. Though small in magnitude, this change is reproducible. No change is seen when a pure water drop is deposited instead of the surfactant solution, confirming that the brief surface tension transient is not an artifact of any surface disturbance caused by drop deposition. After SDS deposition, the surface tension achieves a minimum as surfactants spread across the surface and recovers as the surfactant molecules simultaneously desorb from the interface [15,24,41]. Desorption to a surface concentration that produces no detectable surface tension reduction is complete within ~ 2 s after drop deposition. Thus, we may assume for our experiments that the SDS has disappeared from the surface about 2 s after the surfactant front passes that point. If a particle reached such a point in its trajectory, it would experience no surface tension force.

Figure 5. Representative plots showing surface tension change when (a) SDS ($1\times$ CMC) solution drop and water drop and (b) oleic acid drop are deposited on the water subphase as recorded by Wilhelmy pin. The drops were deposited ~ 7 cm from the pin. The arrow indicates the time at which the drops were deposited.

In addition to the desorption of surfactant, as the surfactant front spreads radially outward, the surface tension driving force $(\gamma_{\text{drop}} - \gamma_{\text{subphase}})/L_s$ acting on the particle decreases due to radial dilution. Therefore in the latter parts of the deceleration regime, along a trajectory the dominant force, and eventually the only force, is the viscous force acting on the particle in the opposite direction to its motion, as the net force is negative. At these points along the trajectory, the subphase flow is no longer directly driven by surface tension gradients and the flow decreases due to viscous dissipation. In summary, as the particle moves along its trajectory in the deceleration regime for a soluble surfactant, the viscous force opposes its motion. The surface tension forces acting on the particle and on the subphase decrease and disappear due to surfactant dissolution and radial dilution of the gradient. The fluid velocity along the trajectory also decreases both due to the radial geometry of the flow field and the viscous dissipation in the subphase. Inertia maintains the particle motion and the viscous force opposes the particle motion. Eventually the particle stops.

In following subsections, we systematically vary the key parameters that equation (10) suggests affect the surface tension force and viscous force acting on a particle. Although we see evident change in the forces acting on the particle and the extent of particle transport in response to these parameter variations, the quantitative effect of these parameters on the forces can only be established if the particle acceleration and velocity and the subphase velocities are known simultaneously at each point in space and time throughout the particle trajectories. Due to the noise in the force data, reliably comparing the forces at individual points in two separate trajectories is not possible. Separate trajectories with extended regions of overlap, which would allow direct comparisons to be made for different parameter values, cannot be obtained since varying the parameters causes the trajectories to cross rather than to overlap.

4.2. Effect of initial position. **Fig. 6a** shows the time evolution of position of three 0.5 mm particles after deposition of a 1× CMC SDS solution drop on a water subphase as a function of their initial distances from the point of drop deposition. The displacement of the particles recorded before their velocities approach zero decreases with increasing initial distance from the drop deposition site. **Fig. 6b** shows the corresponding particle velocity evolution. The maximum velocities of particles initially placed at 10.9 cm, 7.3 cm and 2.6 cm from the drop deposition site are ~ 11 cm/s, 5 cm/s, and 2 cm/s, respectively, decreasing with increasing initial distance from the deposition point.

Figure 6. Representative plots showing time evolution of (a) particle position (b) particle velocity and (c) net force acting on 0.5 mm particles as function of their initial distance R_0 from the deposited 7 μ L, 1 CMC SDS solution drop. The inset in (c) highlights forces at early times.

Note that the onset of particle motion is delayed for larger initial distances from the drop deposition and that delay correlates well with the speed of the surfactant front (~ 10 cm/s) which initiates the particle movement. **Fig. 6(c)** shows that the maximum net force on particles in the acceleration regime decreases from approximately $\sim 5 \times 10^{-8}$ N to 2×10^{-8} N to 1×10^{-8} N as the initial distance from the drop deposition site increases. The maximum opposite net force on particles in the deceleration regime also decreases from 2×10^{-8} N to 5×10^{-9} N to 2×10^{-9} N as the initial distance from the drop deposition site increases. Thus we observe that the maximum

acceleration net force and maximum deceleration net force shows the impact of the radial dilation of the surface tension gradient and subphase velocity field.

For each initial particle position, the deceleration regime begins in well under 2 s – well before the surfactant has desorbed. In the portion of the deceleration regime after surfactant has desorbed, the surface tension force is negligible; and only the viscous force is acting on the particle.

4.3. Effect of particle size. **Fig. 7a** shows the time evolution of the position of different size particles upon deposition of a 7 μL , $1\times$ CMC SDS solution drop. All the particles started 3.9 ± 0.5 cm from the drop deposition point. It is observed that the extent of particle transport over all time intervals decreases with increasing particle size. **Fig. 7b** shows the velocity profiles of the particles. The maximum velocity achieved by particles at the end of the acceleration regime decreases monotonically with increasing diameter: 7.0 cm/s, 5.5 cm/s and 2.4 cm/s for 0.5 mm, 1.5 mm and 3.2 mm diameter particles, respectively.

Figure 7. A representative plot showing time evolution of (a) particle position (b) velocity and (c) net force on 0.5 mm, 1.5 mm and 3.2 mm particles on deposition of a 7 μ L, 1 $\times$ CMC SDS solution drops. The inset in (c) shows the net force acting on the particles in the acceleration regime. In (c), Savitzky-Golay smoothing using a second degree polynomial and a twenty point window is used to reduce noise in the force curve for 3.2 mm particle in the decelerating regime. The particles initially started 3.9 ± 0.5 cm from the drop deposition point.

In the acceleration regime, the maximum net force on the particle increases with particle size (**Fig. 7c**), from 4×10^{-8} N, to 7×10^{-7} N to 2×10^{-6} N for 0.5 cm, 1.5 cm and 3.2 cm particles, respectively. We observe that the duration of the acceleration regime increases with an increase in the particle size (**Fig. 7c inset**), suggesting that a longer time is required for the subphase flow to develop across the immersed depth of the larger sized particles. In the

deceleration regime the maximum net opposing force acting on the particle increases with particle size from 1×10^{-8} N, to 1×10^{-7} N to 5×10^{-7} N for 0.5 cm, 1.5 cm and 3.2 cm particles, respectively (**Fig. 7c**).

4.4. Effect of immersed length. **Fig. 8a** shows the position of plasma treated and untreated 1.5 mm diameter particles with time after deposition of a 7 μ L, $1 \times$ CMC SDS solution drop. The particles started at 3.8 ± 0.1 cm from the drop. The immersed lengths of the untreated and plasma treated particles in water were 0.9 ± 0.1 mm and 1.4 ± 0.1 mm, respectively. After plasma treating the 1.5 mm particle, the contact line radius changed from 0.8 ± 0.1 mm to 0.3 ± 0.1 mm. As the particle becomes more deeply immersed, the area fraction of particle immersed in water, α , increases from 0.6 to 0.9. This has two consequences: i) the perimeter along which the surface tension force operates is smaller, and ii) the deeper immersion in the subphase increases the viscous force on the particle. After an initial period of less than 1 s where the two particles follow very similar trajectories, the plasma treated particle lags behind the untreated particle at all subsequent time intervals, producing significantly less displacement for the more deeply immersed, more hydrophilic particle. At the earliest times when the particles are close to each other in space and time, the surface tension force is smaller on the plasma treated particle because of the significantly reduced contact line radius (equation (3)), and the viscous force is higher on the plasma treated particle because of the larger immersed fraction (equation (9)).

Figure 8. Representative plots showing time evolution of (a) particle position (b) particle velocity and (c) net force acting on a 1.5 mm particle as a function of particle's engulfed length on deposition of a 7 μ L drop of 1 $\times$ CMC SDS solution. The particles started at 3.8 ± 0.1 cm from the drop.

Consistent with the different acceleration regime durations, the maximum velocity achieved by a particle at the end of the acceleration regime decreased from 5 cm/s to 3 cm/s with the increased immersed length of the particle (**Fig. 8b**). In the acceleration regime, the maximum net force on the plasma treated and untreated particles are $\sim 4 \times 10^{-7}$ N and 6×10^{-7} N respectively (**Fig. 8c**). In the deceleration regime the maximum net opposing force acting on the plasma treated and untreated particles are 7×10^{-8} N and 1×10^{-7} N respectively.

4.5. Effect of subphase thickness. **Fig. 9a** compares the time evolution of the position of an untreated 0.5 mm particle upon deposition of a 7 μL , 1 $\times$ CMC SDS solution drop on a thin subphase, $H_{\text{subphase}} = 0.3$ cm and a thicker subphase, $H_{\text{subphase}} = 0.8$ cm. Both particles were initially placed 2.9 ± 0.4 cm from the drop deposition point. Following a brief initial period where trajectories were similar, the particle on the thinner subphase lags behind in all subsequent time intervals, producing significantly greater displacement on the thicker subphase. The maximum particle velocity (**Fig. 9b**) and maximum force on the particle (**Fig. 9c**) during the acceleration regime both decrease with decreasing subphase thickness. The maximum net force acting on a 0.5 mm particle calculated on the thin subphase is 4×10^{-8} N and on the thicker subphase is $\sim 6 \times 10^{-8}$ N. In the deceleration regime the maximum net opposing force acting on the particle on both thin and thick subphase is $\sim 2 \times 10^{-8}$ N.

Figure 9. Representative plots showing time evolution of (a) particle position (b) particle velocity and (c) net force acting on a 0.5 mm particle as a function of subphase thickness H_{subphase} on deposition of a $1 \times \text{CMC}$ SDS solution drop. The particles started at $2.9 \pm 0.4 \text{ cm}$ from the drop.

In the deceleration regime, the particle decelerates much more rapidly on a thinner subphase as compared to thicker subphase. One effect of decreasing the subphase depth is to increase the velocity gradients in the z direction. For the same driving force, the velocity gradient in the recirculation flow in the subphase between the surface and the plane of zero velocity is steeper in the thinner subphase than in the thicker subphase. The steeper the velocity gradient, the smaller the average fluid velocity felt by the immersed portion of the particle will be relative to the surface velocity. Given the ratio of the immersed depth of the particle (0.3

mm) to the subphase depth is equal or smaller than 0.1, this may not be a large effect. However, the rate of viscous dissipation in the subphase flow increases with increasing velocity gradients in the subphase. Therefore, the fluid velocity decays more rapidly for the smaller subphase thickness due to increased viscous dissipation in the bulk, thus also reducing the particle velocity (**Fig. 9b**). We confirmed this by tracking bulk fluid flow using the 3 μm fluorescent microbeads. For the thin (0.3 cm) subphase, the fluid flow stopped abruptly by 2 s, approximately when the surface tension force had diminished due to surfactant desorption. In contrast, no abrupt stoppage of the bulk subphase fluid flow was observed for the thick (0.8 cm) subphase for as long as 20 s, beyond the timescale of the particle motion.

4.6. Particle motion induced by insoluble surfactants. **Fig. 10a** compares the time evolution of the position of 3.2 mm particles upon deposition of a soluble SDS solution drop and an insoluble oleic acid drop on water, for a subphase depth of 0.8 cm. In both the cases, the particles start at 3.2 ± 0.3 cm with respect to the drop deposition point. Recall that the surface tensions of the $1\times$ CMC SDS solution and pure oleic acid drops are nearly identical and thereby provide the same potential to create strong initial surface tension gradients. **Fig. 10a** shows that, except for a brief initial period that can be attributed to the small difference in initial particle placement, the particle transport on deposition of soluble SDS surfactant solution drop lags behind the particle for the insoluble surfactant case for all time intervals but continues for a longer time before stopping. **Fig. 10b** shows the corresponding particle velocity profiles. For oleic acid, the particle achieves a maximum velocity of ~ 5 cm/s, which is significantly larger than the SDS-induced velocity of ~ 2 cm/s. After achieving a maximum velocity, the particle driven by oleic acid maintains a nearly constant velocity for ~ 1 s before abruptly decreasing to zero velocity within 1 s of the end of the maximum velocity plateau, whereas for the SDS solution drop the particle

gradually decelerates from its maximum velocity to zero after ~ 7 s of attaining the maximum velocity. **Fig. 10c** shows that the net force on the particle in the acceleration regime is significantly greater in the oleic acid case.

Figure 10. Representative plots showing time evolution of (a) particle position (b) particle velocity and (c) net force acting on 3.2 mm particles on deposition of 7 μ L drop of $1 \times$ CMC SDS solution or a 9 μ L oleic acid drop. The particles started at 3.2 ± 0.3 cm from the drop.

In contrast to the SDS, the oleic acid is insoluble in water. **Fig. 5b** shows the surface tension change upon deposition of a 9 μ L drop of oleic acid on water at a position ~ 7 cm away from the drop deposition point. The subphase surface tension decreased by ~ 30 mN/m within 1 s of oleic acid deposition and did not recover over a period of tens of seconds. The deposited oleic

acid drop contained 5×10^{21} molecules, far exceeding the $\sim 4 \times 10^{17}$ required to form a densely packed monolayer at the water/vapor interface, assuming a packing density of $\sim 25 \text{ \AA}^2/\text{molecule}$ [14]. The excess supply of oleic acid molecules provides a temporally constant surface tension at the center of the drop deposition on the finite area surface, in contrast with the SDS case where the surface tension at the deposition point increases continually with time.

The oleic acid monolayer reaches the container wall around $\sim 0.8 \text{ s}$ based on the velocity of the surfactant front. After hitting the wall, the surfactant monolayer starts packing at the interface, with no desorption. The surface tension data shows that it takes 2 s from the time the surface tension starts to decrease until it achieves a constant value. After this time, the packing of the monolayer causes the surface excess concentration to become spatially uniform across the interface, reducing the surface tension gradient to zero. Indicative of formation of a saturated monolayer everywhere else at the liquid/vapor interface, we observe the formation of a small static oleic acid lens at the point of drop deposition at $\sim 3 \text{ s}$ [14].

In addition to removing the surface tension gradient that drives the subphase flow and applies the surface tension force to the particle contact line, the insoluble oleic acid monolayer affects the particle transport in two other ways. First, as the layer packs, it slows and then stops the surface flow on the subphase through the no-slip boundary condition. This increases the viscous force on the particle by rapidly decreasing v_f (**Fig. 10c**). Our observations with subsurface $3 \text{ }\mu\text{m}$ fluorescent microbeads show the abrupt slowing of the subsurface flow: the microbead marking the fluid flow abruptly stops $\sim 6 \text{ s}$ after oleic acid drop deposition. In contrast, no such abrupt stoppage was observed in the SDS case with the 0.8 cm deep subphase. Second, when the monolayer of oleic acid is packed, it increases the surface viscosity resistance to particle movement within the monolayer itself [42]. Thus, the particles experience an abrupt

decrease in velocity at ~ 1.5 s due to monolayer packing (**Fig. 10b**). This occurs just before the static lens of excess oleic acid is observed on the surface.

5. Conclusions

Motivated by the use of partially wetted tracer particles to track the motion of surfactant fronts, we have investigated the transport of particles at the liquid/vapor interface under the influence of externally imposed surfactant-induced Marangoni flows. Particles with different size or wettability experience significantly different spatiotemporal force evolution, and thereby respond quite differently to the surfactant-induced Marangoni flow. This should be considered when using such particles as Marangoni flow surface tracers.

In all cases, once the surfactant front moving ahead of the deposited surfactant drop contact line initiates particle lateral motion [1], the particle experiences a brief acceleration regime and a protracted deceleration regime in the case of a soluble surfactant. We show that there are two forces acting on the particle and these forces vary spatially and temporally along the particle trajectories. One of the two forces is the surface tension force (F_{st_r}) acting at the contact line of the particle due to surface tension gradients across the particle at the liquid/vapor interface. This surface tension gradient also induces a flow in the subphase which applies a viscous force (F_{vis_r}) on the immersed fraction of the particle in liquid. The viscous force arises due to the difference in velocities of the particle and fluid and its direction depends on their relative magnitudes.

As the particle moves along its trajectory, the surface tension force may decay in magnitude but always acts in the direction of particle motion whereas the viscous force changes direction depending on the relative magnitudes of velocities of the particle and fluid. In the acceleration regime the net force (F_{net_r}) acting on the particle is in the direction of particle

motion. While it is not possible to experimentally determine the direction of the viscous force (F_{vis_r}), estimates of the surface tension force combined with measurements of the net force acting on the particle suggest that the viscous force opposes particle motion already at the earliest detectable time point (~150 ms) in our experiments. In general, at some point along the particle trajectory during the acceleration regime the viscous force on the particle must oppose the motion of the particle and the net force reaches zero at the end of the regime.

The surface tension gradient felt by the particle as it moves along its trajectory decreases as the surfactant front radially spreads out. For drops of soluble surfactant solutions, two other effects decrease the surface tension gradients: surfactant molecules desorb from the interface (for SDS within 2-3 s of drop deposition) and the surface tension at the drop center increases as the surfactant concentration is diluted below the CMC. As the surface tension gradients decrease, the induced flow in the bulk subphase liquid also decreases. In the deceleration regime for soluble surfactants with sufficiently rapid desorption, the surface excess concentration drops to zero and the surface tension force acting on the particle becomes negligible. The viscous force acts on the particle in the opposite direction to its motion, thus retarding the transport of the particle and eventually stopping it. As we vary parameters such as particle initial position from drop, particle diameter, subphase thickness and particle wettability, significant changes in particle transport are observed. We find that a larger size particle always lags behind the smaller size particle when started from the same distance from the drop. This is also observed for particles more deeply immersed in the subphase compared to those less deeply immersed. We also observe that the extent of particle transport can be reduced by reducing the subphase thickness due to increased velocity gradients in the recirculation flows in the subphase.

For drops of insoluble oleic acid surfactants, a saturated monolayer of surfactant rapidly builds up and remains on the liquid/vapor interface. In contrast to the soluble SDS surfactant experiments, the acceleration regime is followed by a protracted period of approximately zero acceleration, followed by an abrupt deceleration regime. The surface excess concentration becomes uniform across the surface, and again the surface tension force drops to zero in the deceleration regime but now for a different reason than for the soluble surfactant case, where the force decayed primarily due to surfactant desorption. The surface viscosity of the insoluble monolayer further inhibits particle motion in the deceleration regime by slowing the fluid flow in the subphase and producing a surface with more intrinsic resistance to the particle motion.

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