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Effects of a surfactant monolayer on the measurement of equilibrium interfacial tension of a drop in extensional flow

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Abstract

The effect of surfactant monolayer concentration on the measurement of interfacial surface tension using transient drop deformation methods is studied using the Boundary Integral Method. Emulsion droplets with a surfactant monolayer modeled with the Langmuir equation of state initially in equilibrium are suddenly subjected to axisymmetric extensional flows until a steady-state deformation is reached. The external flow is then removed and the retraction of the drops to a spherical equilibrium shape in a quiescent state is simulated. The transient response of the drop to the imposed flow is analyzed to obtain a characteristic response time, τ_s^* . Neglecting the initial and final stages, the retraction process can be closely approximated by an exponential decay with a characteristic time, τ_r^* . The strength of the external flow on each model drop is increased in order to investigate the coupled effect of deformation and surfactant distribution on the characteristic relaxation time. Different model drops are considered by varying the internal viscosity and the equilibrium surfactant concentrations from a surfactant free state (clean) to high concentrations approaching the maximum packing limit. The characteristic times obtained from the simulated drop dynamics both in extension and retraction are used to determine an apparent surface tension employing linear theory. In extension the apparent surface tension under predicts the prescribed equilibrium surface tension. The error increases monotonically with the equilibrium surfactant concentration and diverges as the maximum packing limit is approached. In retraction the apparent surface tension under predicts the prescribed equilibrium surface tension depends non-monotonically on the equilibrium surfactant concentration. The error is highest for moderate surfactant concentrations and decreases as the maximum packing limit is approached. It was found that the difference between the prescribed surface tension and the apparent surface tension increased as the viscosity ratio decreased. Differences as large as 40% were seen between the prescribed surface tension and the apparent surface tension predicted by the linear theory.

1 INTRODUCTION

Material characteristics of a suspended particle can be ascertained by first deforming the particle, and then allowing the particle to retract (relax) to its initial state. The particle may be a bubble [1], a drop [2] or a biological cell [3]. The deformed drop retraction method (DDRM) relies on observation of the transient retraction of a drop to determine interfacial tension, usually following deformation due to a shear flow. Recently, Velankar et al. [4] used CFD to evaluate the DDRM for surfactant laden drops deformed by a shear flow and found that method

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significantly underestimates the equilibrium surface tension. In general the value of a material parameter extracted from transient experiments depends not only on the accuracy and precision of the measurements, but also on the selection of the theoretical model and its underlying assumptions.

Advances in optics and microfluidics have enabled the observation of micron scale particles deforming due to an extensional rate of strain in the external flow field [5]. A microfluidic device for measuring surface tension was developed that uses the transient deformation and retraction of drops and capsules as they flow through constrictions along a micro-channel [6]. These methods are based on the comparison of the rates of deformation or retraction measured experimentally with those obtained from the linearized solutions to the equations governing these transient processes [7]. Although it has been observed that the presence of surfactants on the interface affects the accuracy of the methods [8], no systematic study of the role that the surfactant monolayer plays during both the deformation in extensional flow and retraction process is available.

The objective of this work is to conduct numerical experiments, to isolate and investigate the effects of a monolayer of insoluble surfactant on the measurement of equilibrium interfacial tension. The transient response of the drop to an imposed extensional flow and corresponding retraction are simulated. The physical mechanisms leading to the simulated observations are discussed, as well as the accuracy of the equilibrium interfacial tension that is extracted from the transient behavior using linear theory. Interestingly, a monotonic dependence on equilibrium surfactant concentration is observed in extension, while in retraction a non-monotonic dependence is predicted.

II GOVERNING EQUATIONS

A droplet of a Newtonian incompressible liquid of viscosity $\lambda\mu$ is suspended in an immiscible Newtonian fluid of viscosity μ as shown in Figure 1. The density is assumed uniform throughout the fluid domain and thus the drop is neutrally buoyant. Initially the drop is spherical with radius R_0 and an insoluble surfactant monolayer with uniform concentration Γ_{eq} is distributed along the interface. The initial surfactant concentration gives an equilibrium surface tension, γ_{eq} . At time $t = 0$ the droplet is subjected to an axisymmetric pure extensional flow of strength G . The undisturbed flow has a velocity field described by

$$u^\infty = G(e \cdot x) \quad (1)$$

where e is the dimensionless rate of strain tensor and G defines the strength of the flow. The rate of strain tensor is given by

$$e = \begin{pmatrix} 2 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \quad (2)$$

The motion of internal and external incompressible Newtonian fluids is governed by the continuity equation:

$$\nabla \cdot u^d = 0; \quad \nabla \cdot u^e = 0 \quad (3)$$

which expresses conservation of mass, and the Stokes equation for viscous flow:

$$-\nabla P^d + \lambda \mu \nabla^2 u^d = 0; \quad -\nabla P^e + \mu \nabla^2 u^e = 0. \quad (4)$$

where the superscript d and e refer to the internal drop flow and the external flow, respectively. Since the droplet is considered to be neutrally buoyant, body forces have been omitted.

To complete the system of governing equations, we require a constitutive equation relating the surface tension γ' to the surfactant concentration Γ . The Langmuir surface equation of state in dimensional terms is given by:

$$\gamma' = \gamma_0 + RT\Gamma_\infty \left[\ln \left(1 - \frac{\bar{\Gamma}}{\Gamma_\infty} \right) \right] \quad (5)$$

where γ_0 is the surface tension of the surfactant-free interface and RT is the product of the universal gas constant and the absolute temperature. Since the surfactant molecules have finite dimensions, there is an upper bound to the surface concentration, Γ_∞ , that can be accommodated in a monolayer. The Langmuir surface equation of state thus takes into consideration surfactant molecular interactions.

The boundary conditions along the interface S are both the continuity of the velocity field,

$$u^d = u^e = u \quad (6)$$

and the kinematic condition,

$$\frac{ds}{dt}(S, t) = u_n \quad (7)$$

where s is the position vector of points along the interface S . Eq. (7) ensures the impermeability of the interface.

Far away from the drop the flow remains undisturbed and the velocity is equal to the free flow velocity,

$$u(x) = u^\infty(x) \quad \text{as} \quad x \rightarrow \infty. \quad (8)$$

Lengths are scaled with R_0 , time with t_0 , velocities by R_0/t_0 , viscous stresses by μ/t_0 and interfacial tensions by γ_{eq} . Since the drop has both surface tension and viscosity it is possible to define an intrinsic time scale for the drop [9],

$$t_c = \mu R_0 / \gamma_{eq} \quad (9)$$

When the drop is subjected to a pure extensional flow the obvious time scale is then $t_0 = G^{-1}$. A capillary number Ca that measures the ratio of the external viscous forces to the interfacial forces can then be defined by

$$Ca \equiv \mu G R_0 / \gamma_{eq} \quad (10)$$

The capillary number can be also be interpreted as the ratio of the intrinsic time scale t_c to the characteristic time scale of the incident flow field, G^{-1} . In the absence of an external forcing flow (e.g. during the retraction process) the proper characteristic time scale is then $t_0 = t_c$ and the capillary number $Ca = 1$.

Using these scaling factors a dimensionless equation of state is given by

$$\gamma = \frac{\gamma_0}{\gamma_{eq}} + E [\ln(1 - X\Gamma)] \quad (11)$$

where $\gamma = \gamma'/\gamma_{eq}$ is the dimensionless surface tension coefficient, $\Gamma = \frac{\bar{\Gamma}}{\Gamma_{eq}}$ is the dimensionless surface concentration and X is the fraction of the interfacial area that is initially covered by surfactant given by,

$$X = \frac{\Gamma_{eq}}{\Gamma_{\infty}}$$

and the elasticity number E is given by,

$$E = \frac{RT\Gamma_{\infty}}{\gamma_{eq}}.$$

E measures the sensitivity of the surface tension to Γ .

The transient deformation process is characterized by the competition between the shear stresses, acting to deform the drop, and the surface tension stresses opposing the deformation. Deformation is quantified using the Taylor deformation parameter defined as

$$DF = \frac{A - B}{A + B} \quad (12)$$

where A and B are the major and minor semi-axis as shown in Fig. 1. As long as the strength of the flow is below a certain critical value the drop will adopt a steady state shape at which viscous stresses and interfacial tractions are balanced [10]. The steady state deformation DF_{∞} as well the stress and surfactant distribution depends on both Γ_{eq} and Ca . When steady state is reached, the flow is turned off and the drop is allowed to return to its equilibrium spherical shape. During the retraction process the roles are inverted and motion is driven by the interfacial tension and is opposed by viscous stresses.

III SURFACTANT DYNAMICS

When an interface is occupied by an insoluble surfactant, the evolution of the surfactant concentration must be computed simultaneously with the motion of the interface. The components of the flow velocity at the interface are $\mathbf{u}_n$ in the normal direction and $\mathbf{u}_t$ in the tangential direction. Surfactant is convected along the interface by the tangential component of the fluid velocity. Including a diffusive contribution at the interface, the convective-diffusion equation for surfactant transport is [11]

$$\frac{\partial \Gamma}{\partial t} + \nabla_s \cdot (\Gamma \mathbf{u}_t) - \frac{1}{Pe_s} \nabla_s^2 \Gamma + 2\kappa \Gamma \mathbf{u}_n = 0 \quad (13)$$

where 2κ is the mean curvature of the interface and the dimensionless parameter Pe_s is the surface Péclet number defined as

$$Pe_s = Ca \Lambda \quad (14)$$

where

$$\Lambda = \frac{\gamma_{eq} R_0}{\mu D_s} \quad (15)$$

and D_s is the surface diffusivity of the surfactant molecule. Pe_s is the ratio between the surface convective flux that creates the gradients and the surface diffusion flux which acts to restore a uniform surfactant distribution [12]. The distribution of Γ along the interface is determined by the competition between the disruptive convective effects and the restoring surface diffusion effects. The second and third terms are the tangential convection and surface diffusion contributions, respectively. The last term is the surface dilution that results from the stretching of the interface [12]. Redistribution of surfactants leads to surface tension gradients and thus tangential Marangoni stresses [12]. The jump in the traction across the drop interface can be expressed in terms of the isotropic surface tension γ and the interface geometry in dimensionless variables by

$$\Delta f = 2\kappa \gamma \mathbf{n} - \nabla_s \gamma \quad (16)$$

where $\mathbf{n}$ is the surface normal pointing into the external fluid and $\nabla_s = \nabla \cdot (\mathbf{I} - \mathbf{n}\mathbf{n})$ is the surface gradient operator. The Laplace pressure, $2\kappa \gamma \mathbf{n}$, acts normally while the Marangoni stress, $\nabla_s \gamma$, is exerted tangentially.

IV BOUNDARY INTEGRAL FORMULATION

A boundary integral method arises from a reformulation of the Stokes equations (3) and (4) in terms of boundary integral expressions and the subsequent numerical solution of the integral equations. For more detailed information about the boundary integral method see the monograph by Pozrikidis [13]. The main advantage of the boundary integral method for a number of multiphase flow problems is that implementation involves integration on the interfaces only. Thus, discretization is required only of the interfaces, which allows for higher

accuracy and faster performance [14]. Another important feature of the mathematical model used here is that the velocity at a given time instant depends only on the position and properties of the interface at that instant. Boundary integral methods have been successfully used for simulations of complex multiphase flows: drop deformation and breakup [15]; drop-to-drop interaction [16, 17, 9, 18]; suspension of liquid drops in viscous flow [19, 20]; deformation of a liquid drop adhering to a solid surface [21, 22]. In the present work, Equations (3) and (4) with boundary condition Equations (6), (7) and (8) are solved using the boundary integral method (BIM). The BIM solves the system of equations in terms of generalized distributions of singularities over the boundaries [13, 23].

Consider the problem defined in Section II of an unbounded extensional flow past a deformable drop. The dimensionless equation for the velocity at a given position of the interface, x_0 , is represented in the form [13],

$$u_j(x_0) = \frac{2}{1+\lambda} u_j^\infty(x_0) - \frac{1}{(C_0 4\pi)(1+\lambda)} \int_S \Delta f_i(x) G_{ij}(x, x_0) dS(x) + \frac{1-\lambda}{4\pi(1+\lambda)} \int_S u_i(x) T_{ijk}(x, x_0) n_k(x) dS(x) \quad (17)$$

where the integration is over the total interfacial area S . The free-space velocity Green's function tensor G_{ij} and the associate stress tensor T_{ijk} , called Stokeslet and stresslet, respectively, and are defined in detail in [13].

The numerical method is based on a quasi-steady protocol for the evolution of the drop. Initially the steady state location of the drop interface is unknown. A time-marching numerical scheme is employed, tracing the evolution of an initially spherical drop as a function of time until steady state is attained. A time step of $dt = 0.0001$ was chosen in all cases. At each time step the normal and tangential velocity components are calculated at each node along the interface. The normal velocity is used along with the kinematic boundary condition (7) to obtain the new shape of the drop. The tangential component of the velocity is utilized in the mass balance equation (13) to calculate the new surfactant distribution at each time step. The surfactant distribution at each time step is determined by solving Equation (13) using a second order accurate finite difference scheme. See [24] for a detailed description of the method. Steady state is determined when the dimensionless velocity component normal to the interface is less than 0.001 everywhere along the interface.

V PARAMETER VALUES

Eggleton and Stebe [25] calculated the range of values of E to be 0.1 – 0.2. They adopted the value $E = 0.2$ and here for consistency the same value is used. Typically, surface diffusion is extremely weak. The value of Λ can be estimated to be 6×10^4 for drops with size on the order of microns. For consistency with previous works the value $\Lambda = 1000$ used in [24,25] will be used. This value for Λ is actually an underestimate for a typical surfactant. Although, for large values of Λ (i.e. $\Lambda > 1000$) the effects of diffusion become increasingly small. For $\Lambda = 1000$ diffusion effects are small enough that the overall response of the drop is not affected, however the small amount of diffusion helps stabilize the numerical algorithms.

VI SMALL DEFORMATION THEORY AND DYNAMIC INTERFACIAL MEASUREMENT

The deformation of nearly spherical drops and capsules has been studied by several authors in the limit of small deformations using perturbation methods [8,10,26]. This small deformation

theory, based on a constant surface tension interface, constitutes the basis of the transient methods for measuring surface tension.

Following the review by Rallison [8] the drop surface is taken to be a nearly spherical in shape, where

$$(x \cdot x)^{1/2} = 1 + \varepsilon x \cdot A \cdot x + O(\varepsilon^2) \quad \text{with } \varepsilon \ll 1, \quad (18)$$

and for the flow defined by Equations (1) and (2) the time evolution of the distortion is given by

$$\varepsilon \frac{\partial A}{\partial t} = \frac{5Ca\varepsilon}{2\lambda+3} - \frac{40(\lambda+1)\varepsilon A}{(2\lambda+3)19\lambda+16} + O(\varepsilon Ca, \varepsilon^2). \quad (19)$$

The second order tensor A is the distortion measured in a frame of reference that rotates with the drop. When the flow is weak $Ca \ll 1$ the distortion is limited by the strong surface tension. Thus, ε may be identified with Ca . The distortion tensor εA is then substituted by the scalar drop deformation parameter DF [27,8] in Eq. (19) which gives,

$$\frac{\partial DF}{\partial t} = \frac{5Ca(e_{max} - e_{min})}{4\lambda+6} - \frac{40(\lambda+1)DF}{(2\lambda+3)19\lambda+16}, \quad (20)$$

where e_{max} and e_{min} are the largest and smallest principal rates of strain.

A Extension method

Hudson *et al.* [5] defined the *Taylor plot* as the plot of $5(e_{max} - e_{min})/(4\lambda + 6) - (\partial DF)/(\partial t)$ vs DF . From Eq. (20) it can be seen that the slope of the Taylor plot is given by

$$\tau_s^{-1} \equiv \frac{40(\lambda+1)}{(2\lambda+3)19\lambda+16} \frac{1}{Ca} \quad (21)$$

where τ_s is the response time of the drop predicted by linear theory. Diaz *et al.* [28] found that the deformation of a capsule with an elastic interface could accurately be fitted to an equation of the form

$$DF(t) = DF_{\infty}(1 - e^{-t/\tau_s^*}) \quad (22)$$

where DF_{∞} is the steady state deformation as $t \rightarrow \infty$ and τ_s^* is the simulated response time.

Here, we find the rate of drop extension, τ_s^* , from our simulations using the following methodology. We consider only the simulated extension of drops in the range of deformation from $0 < DF < 0.3DF_{\infty}$. This portion of the simulated drop extension is fit to Eq. (22) above yielding both τ_s^* and DF_{∞} . The calculated value of τ_s^* can then be compared with the analytical prediction given by Eq. (21).

B Retraction method

In the absence of an external flow the strain-rate tensor $\mathbf{e} = 0$ and an expression for the time evolution of the deformation parameter $DF(t)$ can be obtained by solving Eq. (20) as

$$DF(t) = DF_0 e^{-t/\tau_r} \quad (23)$$

where DF_0 refers to the initial deformation of the drop during the retraction period which is the same as DF_∞ , the steady state deformation reached during flow. Linear theory predicts that the dimensionless analytical retraction time τ_r is given by

$$\tau_r \equiv \frac{(2\lambda+3)(19\lambda+16)}{40(\lambda+1)}. \quad (24)$$

In the deformed drop retraction method (DDRM) [27,29], an initially deformed drop retracts back to its spherical equilibrium shape in the absence of an external forcing flow. In the numerical experiments conducted here a model drop is allowed to reach equilibrium while deforming under a pure extensional flow. The imposed external flow is then turned off and the retraction of the drop back to its equilibrium spherical shape is simulated. A relaxation time, τ_r^* , is obtained from the simulated retraction in the following manner. The deformation DF is normalized with respect to the initial deformation at time $t = 0$, the time when the retraction is started, for the purpose of comparison. Thus all retractions that are shown start from $DF/DF_0 = 1.0$. A logarithmic scale is used for the ordinate axis as this is the form required by the DDRM. Although linear theory predicts a constant rate of retraction, previous observations have shown that there are start-up and end effects in experimental and simulated retraction processes (seen here as well) and that a drop retracts at nearly a constant rate intermediately. We exclude start-up and end-effects by considering the simulated retraction of drops from $DF/DF_0 = 0.6$ to $DF/DF_0 = 0.2$. The time history of DF/DF_0 in this range is fit to Eq. (23) above through linear regression on a semi-log scale. The linear regression fit yields a linear slope that is the simulated relaxation time, τ_r^* .

C Surface tension evaluation

In our numerical investigation, we have prescribed the equilibrium surface tension, γ_{eq} , and know a priori the value of interfacial surface tension. The small deformation theory introduced in this section constitutes the basis of the transient methods for measuring interfacial tension described in the following sections. An apparent surface tension can be obtained by equating the simulated response time, τ_s^* , and relaxation time, τ_r^* , to the expressions from linear theory predicting these quantities, Eqs. (21) and (24), respectively. These equations are then manipulated to yield expression for the apparent surface tension. Here, we assume that the dimensionless expressions from linear theory were normalized by the apparent surface tension. The expressions are then normalized by the prescribed equilibrium surface tension, γ_{eq} . More concretely the dimensionless apparent surface tension is given by

$$\gamma_{app,s} = \frac{Ca}{\tau_s^*} \frac{(2\lambda+3)(19\lambda+16)}{40(\lambda+1)}, \quad (25)$$

for drop extension methods and by

$$\gamma_{app,r} = \frac{1}{\tau_r^*} \frac{(2\lambda+3)(19\lambda+16)}{40(\lambda+1)}, \quad (26)$$

for the deformed drop retraction methods. A normalized (dimensionless) apparent surface tension value of 1 implies that response time predicted by linear theory is equal to that “measured” from our non-linear simulation data. More importantly, $\gamma_{app} = 1$ means that the measured value of interfacial surface tension extracted from transient drop deformation data using small deformation theory is equal to the prescribed value of surface tension, γ_{eq} . Similarly, non-unity values of normalized apparent surface tension indicate the error in the measured value of interfacial surface tension.

VII RESULTS

In this section we present our simulation results for the deformation of a drop with a monolayer of surfactant in an extensional flow. First we consider drops with $\lambda = 1$ for computational efficiency. Initially spherical drops with uniform surfactant coverage, denoted by X , are instantaneously subjected to extensional flows of increasing strength characterized by the capillary number, Ca . Once the drop reaches a steady state deformation in the extensional flow, we allow the drop to retract under quiescent conditions. The simulated extension and retraction are analyzed to obtain the dimensionless apparent surface tensions from extension $\gamma_{app,s}$ and relaxation $\gamma_{app,r}$.

Following the general procedure introduced in the previous section, the dimensionless apparent surface tension from extension $\gamma_{app,s}$ is calculated as a function of surfactant concentration as shown in Fig (2). It is seen that the method always underestimates surface tension. As the initial surfactant coverage increases, the value of $\gamma_{app,s}$ decreases. The worst case occurs for high surfactant concentrations and high Ca where surface tension can be underestimated by as much as 90%.

A Equilibrium conditions at steady state in an extensional flow

The steady state deformation DF_∞ of drops with different initial surfactant coverage X are shown as a function of Ca in Fig. 3. The steady-state deformation DF_∞ varies non-monotonically with X (Fig. 3) as previously shown in Eggleton *et al.* [24]. The deformation DF_∞ of a clean drop increases with increasing Ca . Small amounts of surfactant increase DF_∞ up to a critical concentration after which further increasing X leads to a decrease in magnitude of the steady state deformation. For larger values of Ca this behavior becomes more accentuated.

As the drop deforms, the local mean curvature increases at the pole, while it decreases at the equator. The increase in the curvature of the drop at the pole causes the Laplace pressure, $2\kappa\gamma$, to increase. Eventually, when the Laplace pressure is high enough, it will balance the viscous stress jump and the drop will reach steady state. Surfactant convection towards the poles causes the surface tension to decrease in this regions and thus higher curvatures will be necessary to balance the viscous stresses, thus the larger deformation.

When the initial surfactant coverage is small, $X \ll 1$, surfactant molecules are easily convected towards the pole leading to the formation of a high concentration cap and near depletion of surfactants at the equator. The surfactant distribution along the interface at equilibrium is shown in Fig. 4 for $Ca = 0.05$ for different values of X . When $X = 0.20$ a region of high surfactant concentration near the pole is observed where $X\Gamma \approx 0.90$, representing an increase of 450% from the initial surfactant concentration! Surfactant concentration decreases monotonically

along the interface and for $s > 1.2$, $X\Gamma$ approaches zero. Consequently, the surface tension at the pole is reduced to about 60% of its equilibrium value γ_{eq} (Fig. 5) favoring a deformation mode known as tip stretching and increased overall drop deformation.

B Retraction of a deformed drop in a quiescent fluid

In our numerical experiments a surfactant covered drop is allowed to reach steady state after deforming under a pure extensional flow. The extent of the deformation and the redistribution of surfactant on the interface are dependent on the strength of the external flow characterized by the capillary number, Ca , and the equilibrium surface coverage, X . The retraction of the drop to its equilibrium state is now simulated from the deformed state. As described in Section VI, the small deformation theory predicts that the retraction is governed by an exponential equation with a single relaxation time τ_r .

Fig. 6 shows the recovery of drops initially deformed by an extensional flow with $Ca = 0.05$. Deformation DF has been normalized using the initial deformation DF_0 . This is the deformation at time $t = 0$ when the retraction is started and thus all retractions shown start from $DF/DF_0 = 1.0$. This was done for comparison purposes since the steady state deformation DF_∞ for the extension is a function of X and Ca . A logarithmic scale is used for the ordinate axis as this is the form required by the DDRM. Experimentally, only an interval of the deformation process is exponential and agrees with Eq. 22 [5,27]. Hence, an interval has to be selected, for consistency between the different results shown, the interval $0.6DF_0 - 0.2DF_0$ is used to calculate τ_r^* in all cases. Within this time interval the recovery process is exponential for the range of Ca and values of X being considered.

The relaxation time τ_r^* as a function of X from our simulations are shown in Fig. 7. As with the response time, the relaxation time for a clean drop shows good agreement with the predicted value from Eq. 23 shown as a solid line. It is worth noting that the analytic solution considers a clean drop with uniform, constant surface tension. Surfactants are not considered in the small deformation theory. Our simulation demonstrate that the relaxation time τ_r^* is non-monotonic with respect to X . Initially it increases with increasing X , reaches a maximum for $0.4 < X < 0.6$ and decreases for larger values of X . It is interesting to note that linear theory predicts that $\tau_s/Ca = \tau_r$. In the case of $Ca = 0.05$ and $X = 0.2$, $\tau_s^*/Ca \sim 1.3\tau_r^*$. In our simulations this factor relating τ_s^*/Ca and τ_r varies with Ca and X . The apparent surface tension γ_{app} is calculated from Eq. (26) and is shown in Fig. 8. The measured surface tension depends non-monotonically on the surfactant concentration. Experimentally, this means that surface tension measurements made for drops with moderate to intermediate concentration of surfactants, e.g. $0.2 < X < 0.8$, will be the most inaccurate if small deformation theory is applied without any corrections. Depending on the initial conditions the measured surface tension could be under-predicted by over 30%. The tendency of linear theory to underpredict equilibrium surface tension is in agreement with the findings of Velankar et al. [4] for drops deformed by shear flow. Surface tension measurements of clean drop and with saturated surfactant monolayers will give better results.

The observed trends in apparent surface tension with equilibrium surface concentration are clearly related to the redistribution of surfactants and dynamic interfacial tension in the extension and retraction process. During the extension, surfactant is convected towards the poles by the external flow field lowering the local surface tension. The evolution of the normal stress jump at the pole, $2\kappa\gamma$ in time is shown in supporting material Fig. 1. For $X < 0.80$, the normal stress jump at the pole increases monotonically in time, however the time rate of change decreases as X increases from zero. The case where $X = 0.90$ is interesting in that the increase in curvature is balanced by the decrease in surface tension the normal stress jump at the pole remains almost constant. For $X = 0.975$ the normal stress jump at the pole decreases initially

and then increases. At a fixed capillary number, the normal stress jump at the pole decreases monotonically with equilibrium surface concentration in the extensional mode. As the maximum packing limit is approached, the normal stress jump actually decreases from its initial value. Similarly, the Marangoni stresses along the interface at early times in the extension process increase in magnitude monotonically with equilibrium surface concentration, see supporting material Figure 2. The monotonic trend in the apparent tension as the equilibrium surface concentration is increased is related to this physical mechanism. In retraction the non-monotonic trend in the apparent surface tension is related to the difference in the normal stress jump between the pole and the equator. Animations in the supporting material show the normal stress jump, $2\kappa\gamma$, over the interface during the retraction process. For the case, $X = 0.975$, the driving force for retraction, characterized by the normal stress at the pole minus the normal stress at the equator remains positive throughout, as it does for the clean interface. For $X = 0.2$, this is not the case, and the driving force for retraction actually becomes negative near the end of the process. That is, the normal stress jump at the equator is greater than that at the pole, resulting in the longer characteristic time for retraction.

C Effect of internal drop viscosity

In this section we expose drops with a surfactant monolayer to an extensional flow rate such that $Ca = 0.035$ until they reach equilibrium, and then turned off the external flow field in order to investigate the effect of the internal drop viscosity on the measurement of interfacial tension. The viscosity ratio, λ , (internal/external) is varied over four orders of magnitude ($\lambda = 0.1, 1, 10, 100$), while the equilibrium surface concentrations considered are $X = 0$ (clean), $X = 0.2$ (low-intermediate coverage) and $X = 0.975$ (approaching the maximum packing limit). Characteristic times, τ_s^* and τ_r^* are calculated from the drop deformation history. The apparent surface tensions are calculated as described above.

Internal drop viscosity effects the distribution of surfactants at equilibrium in the extensional flow, as shown in Fig. 9(a) for $X = 0.2$ and Fig. 9(b) for $X = 0.975$. For the intermediate equilibrium concentration $X = 0.2$ there is a wide variation in surfactant concentration at equilibrium in the extensional flow as a function of viscosity ratio. While at the high equilibrium concentration, $X = 0.975$, the magnitude of variation in surface concentration as the viscosity is varied is not as significant. Note however, that at concentrations approaching the maximum packing limit Γ_∞ small changes in surface concentration lead to large changes in surface tension.

The calculated apparent surface tensions based on the characteristic response time to the imposed flow, τ_s^* and the characteristic retraction time τ_r^* from the simulated deformations are shown in Figs. 10(a) and 10(b), respectively. In extension the apparent surface tension decreases monotonically with X at a fixed viscosity ratio. While in retraction, the apparent surface tension is lower than the prescribed equilibrium surface tension, and varies non-monotonically with X . At any given value of the internal viscosity ratio, the apparent surface tension is lowest at the intermediate equilibrium surface concentration, $X = 0.2$. In both cases the apparent surface tension is lowest for the lowest viscosity ratio, $\lambda = 0.1$. Thus, the simulations show that the effects of a surfactant monolayer are amplified as the viscosity ratio decreases, leading to significant error in the surface tension measurement. Correspondingly, these findings indicate that surface tension measurement is more accurate as the viscosity ratio λ increases.

VIII Conclusions

We have numerically investigated the effect of an insoluble surfactant monolayer on the measurement of interfacial tension by simulating the deformation of model drops in an extensional flow and their subsequent retraction under quiescent conditions. The characteristic

times for drop extension and retraction were obtained from these simulations and used in conjunction with linear theory to determine an apparent surface tension. This “measured” apparent surface tension was compared with the prescribed surface tension at equilibrium. Tests were conducted for equilibrium surface concentration of surfactant from clean to 0.975 of the maximum packing limit, a wide range of flow rates ($Ca = 0.01 - 0.05$), and for viscosity ratios from 0.1 through 100.

Our simulated data leads to the following conclusions. In extension, increasing the equilibrium surface concentration of surfactant leads to increasing dimensionless characteristic response times and decreasing apparent surface tensions. The error diverges as the equilibrium surface concentration approaches the maximum packing limit. A non-monotonic trend is observed in the retraction simulations. Maximum characteristic retraction times and corresponding minimum apparent surface tensions occur at intermediate values of the equilibrium surface concentration of surfactant. Deviations between the measured apparent surface tension and the known equilibrium surface tension that was prescribed in the simulations were high as 40% at an equilibrium surface concentration of 0.2 of the maximum packing limit. Interestingly, in the retraction mode the apparent surface tension approached 1, error decreased as the maximum packing limit is approached. Our simulations also show that the deviation (error) between the apparent and prescribed surface tension increased as the internal viscosity decreased and as the extensional flow rate (deformation) increased.

These deviations in the measured surface tension and the prescribed surface tension are introduced by fitting the observed rate of drop retraction to predictions of linear theory that assumes small deformations, and more importantly, neglects the effects of interfacial surfactants and is based on constant surface tension. Our simulations suggest that it is critical to measure the surfactant concentration on a drop interface, as well as the rate of drop retraction, in order to improve surface tension measurement using transient drop deformation methods.

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Figure 1.

Meridian of the trace of an axisymmetric drop with polar axis z at the plane where $\varphi = 0.0$. The drop is suspended in a fluid of viscosity μ , the internal viscosity is $\lambda\mu$. Deformation is defined in terms of the minor and major diameters $DF = (A-B)/(A+B)$. The interface is defined in terms of the arclength parameter S measured from the pole to the equator.

Figure 2.
Apparent surface tension $\gamma_{app,s}$ from Eq. (25) for $\lambda = 1$.

Figure 3. Steady state deformation DF_{∞} as a function of X for different values of Ca , $\lambda = 1$.

Figure 4. Steady state distribution of surfactant $X\Gamma$ along the drop interface for $Ca = 0.05$ and $\lambda = 1$.

Figure 5. Steady state surface tension γ along the drop interface for $Ca = 0.050$ and $\lambda = 1$.

Figure 6.

Normalized deformation parameter DF/DF_0 as a function of the dimensionless time t during retraction. The initial deformation DF_0 is that at equilibrium for $Ca = 0.050$. Lines indicate the subset of the retraction history used to obtain a retraction time, τ_r^* .

Figure 7. Retraction time as a function of the initial surfactant coverage X , for three capillary numbers, corresponding to weak, moderate and strong extensional flows.

Figure 8.

Apparent surface tension $\gamma_{app,r}$ as a function of X calculated from the retraction time τ_r^* .

(a)

(b)

Figure 9. Steady state distribution of surfactant XT along the drop interface for different viscosity ratio λ for (a) $X = 0.2$ (b) $X = 0.975$.

(a)

(b)

Figure 10. Apparent surface tension γ_{app} as a function of λ for three different X in (a) Extension (b) Retraction.