Effects of Surface Viscosity on Breakup of Viscous Threads

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In addition to surface tension lowering and Marangoni stresses, surfactants also induce surface rheological effects when they deform against themselves at fluid interfaces. Because surface viscosities are functions of surfactant concentration, surface rheological stresses can compete with capillary, Marangoni, and bulk stresses in surfactant-laden free surface flows with breakup. To elucidate the effects of surface rheology, we examine the breakup of a Stokes thread covered with a monolayer of insoluble surfactant when either surfactants are convected away from the space-time singularity or diffusion is dominant. Surprisingly, in both limits, surface rheological effects always enter the dominant balance of forces and alter the thread's thinning rate. Moreover, if surfactants are convected away from the singularity, we provide an analytical expression for thinning rate that explicitly depends on surface rheological parameters, providing a simple route for measuring surface viscosity.

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Introduction.—Adsorption onto and lowering the surface tension $\tilde{\sigma}$ of a fluid interface $\tilde{S}$ by surfactants are exploited in applications as diverse as enhanced oil recovery [1], treating respiratory diseases [2], and drop or jet breakup [3,4]. However, surfactant concentration $\tilde{\Gamma}$ can be nonuniform at $\tilde{S}$ because surfactant molecules can be transported along it by convection and diffusion and also due to normal dilatation and tangential stretching of $\tilde{S}$ [5–7]. Thus, aside from simply lowering $\tilde{\sigma}$, nonuniformity in $\tilde{\Gamma}$ causes gradients in $\tilde{\sigma}$ and gives rise to tangential interfacial (Marangoni) stresses. The latter brings about rich physics including tears of wine, interfacial turbulence in mass transfer, and droplet bouncing [8,9]. In addition to lowering $\tilde{\sigma}$ and the Marangoni effect, surfactants may also induce surface rheological effects as surfactant molecules deform against each other on $\tilde{S}$.

Here, we analyze the interesting but heretofore poorly understood physics that arises when surface rheology is accounted for in the breakup of a viscous liquid jet (thread). The motivation for this work comes from the need to develop a method to measure surface viscosities, which to date have proven difficult to determine [10], and improve the understanding of surface rheological effects in drop formation from nozzles (inkjet printing and sprays [4,11–13]). The role of surface rheology on thread pinch-off is best examined in two limits: when (i) surfactants are swept away from the space-time singularity and are hence highly nonuniformly distributed at the interface or (ii) they uniformly cover the surface of the thinning thread for all time. Surprisingly, little has been done on this important problem even though it has recently been shown that the increase in surfactant accumulation in satellite droplets during drop formation cannot be explained without accounting for surface viscosities [14].

Problem formulation.—To gain insights into thread breakup in the presence of surface viscous stresses, we use simulations and theory, and adopt the simplest configuration possible: a cylindrical, infinitely long column of liquid of radius R that is made to undergo capillary breakup by subjecting it to a shape perturbation. The thread is an incompressible Newtonian fluid of viscosity μ and surrounded by a passive gas (pressure datum). The surface tension of the interface between the pure liquid and the gas is σ_0. The thread's surface is initially covered uniformly with a monolayer of insoluble surfactant at concentration $\tilde{\Gamma}_0$. We nondimensionalize the problem by using R, σ_0/μ, and Γ_m, the maximum packing value of $\tilde{\Gamma}$, as characteristic length, velocity, and concentration. Hereafter, variables without tildes are dimensionless counterparts of ones with tildes. Thread shape and surfactant concentration are represented as $r = h(z,t)$ and $\Gamma(z,t)$ in cylindrical coordinates (r,z) (r and z: radial and axial coordinates), t time, and h the shape function. Thread breakup is initiated by subjecting the column's surface $S(t)$ to an axially periodic sinusoidal perturbation of wave number k and amplitude ϵ (Fig. 1).

Since thread shapes near breakup are slender, the dynamics is governed by a set of dimensionless 1D slender-jet equations [15]: $3(h^2 v_z)_z/h^2 + (2\mathcal{H}\sigma)_z + 2\sigma_z/h + (9B_s h v_z)_z/2h^2 + (B_d h v_z)_z/2h^2 = 0$, which is the 1D force balance or momentum equation in the Stokes limit, i.e., when $\sqrt{\rho R \sigma_0}/\mu \to 0$ (ρ: density), $h_t + v h_z + h v_z/2 = 0$, which is the kinematic boundary (KB) condition or 1D mass balance, and $\Gamma_t + v\Gamma_z + \Gamma v_z/2 - (\Gamma_{zz} + \Gamma_z h_z/h)/\mathrm{Pe} = 0$, which is the 1D convection-diffusion (CD) equation. Subscripts z and t indicate partial differentiation and $v = v(z,t)$ is axial velocity. $2\mathcal{H} = \{h_{zz}/[(1+h_z^2)^{3/2}]\} - \{1/[h(1+h_z^2)^{1/2}]\}$ is twice the mean curvature [16].

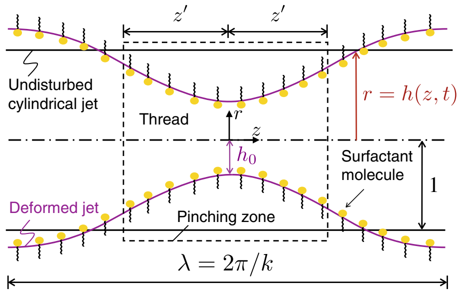

FIG. 1. Definition sketch showing the thread at $t = 0$ when the interface is subjected to a perturbation of wavelength $\lambda = 2\pi/k$. At that instant, $h(z,0) = 1 - \epsilon\cos(kz)$ and $\Gamma(z,0) = \Gamma_0$. The problem domain is $0 \le z \le \pi/k$. $h_0 \equiv h_{\min}(t=0) = h(0,0)$ denotes the initial minimum thread radius.

$\mathrm{Pe} \equiv R\sigma_0/\mu D$ is the Peclet number, where D stands for surfactant diffusivity. $B_s \equiv \mu^s/\mu R$ and $B_d \equiv \kappa^s/\mu R$ are the Boussinesq numbers defined in terms of the surface shear and dilatational viscosities μ^s and κ^s, respectively. The terms in the 1D force balance correspond to the axial derivatives of viscous stress, capillary pressure, Marangoni stress, and surface viscous stresses associated with surface shear deformation and dilatation, respectively. In arriving at the latter, we have used the Boussinesq-Scriven model [17]. Surface tension $\sigma(z,t)$ and surfactant concentration $\Gamma(z,t)$ are related via the Syzskowsky equation of state [18], $\sigma = 1 + \beta\ln(1-\Gamma)$. Here $\beta = \Gamma_m R_g T/\sigma_0$ is the surfactant activity or strength parameter, where R_g is the gas constant and T is the temperature. Note that surface shear and dilatational viscous stresses take on the same mathematical forms to leading order. Thus, we set $B_d = B_s$ for the sake of simplicity and use B_s in the rest of the Letter. To relate surface viscosity with surfactant concentration, we take the Boussinesq number to vary linearly with Γ, $B_s = B_{s0}\Gamma/\Gamma_0$ [14,19], where B_{s0} is the Boussinesq number at initial surfactant coverage Γ_0.

The governing equations are solved by a 1D finite element-based algorithm (FEA) and analyzed theoretically. Results obtained from 1D simulations have been verified by showing that they accord with predictions made with a 2D FEA algorithm that does not invoke the slender-jet assumption. In what follows, simulation results are reported when $\beta = 0.3$, $\Gamma_0 = 0.5$, and $k = 0.7$.

Results: Limit of $\mathrm{Pe} = \infty$.—In the absence of surface rheological effects, how much surfactant is present where a thread breaks is set by Peclet number $\mathrm{Pe} = Rv_c/D$ ($v_c \equiv \sigma_0/\mu$), which measures the importance of convection, which sweeps surfactant away, to diffusion, which replenishes it. In macroscale flows (crop spraying) where $\mathrm{Pe} \gg 1$, it accords with intuition and was shown in Refs. [20–22] that surfactants are convected out of the thinning neck, and have no effect on thinning rate. In other words, thinning rate for a surfactant-laden thread is identical to that of a surfactant-free one [18]. Although the rate of thread thinning is unchanged by surfactants, they impart a significant imprint by altering the thread's shape far away from the pinch point: Stokes threads can break asymmetrically and threads with inertia can exhibit microthread cascades [23,24]. Here, we show for the first time that thinning rate can be altered by surfactants when surface rheological effects are included.

Figure 2 shows the variation with time remaining until breakup $\tau \equiv t_0 - t$, where t_0 is the breakup time, of the thread's minimum radius $h_{\min}(t)$, the axial length scale $z' \equiv z_{\Lambda h_{\min}} - z_0$ where $1 < \Lambda < 1.2$, the axial velocity scale $v' \equiv v_{\Lambda h_{\min}}$, and surfactant concentration where thread radius is a minimum $\Gamma_{\min} \equiv \Gamma_{h_{\min}}$ for a thread of $\mathrm{Pe} = \infty$, $B_{s0} = 0.1$, and $h_0 = 1 - \epsilon = 0.6$. Henceforward, $\Lambda = 1.04$ wlog [24]. Figure 2 makes plain that all dynamical variables exhibit power-law dependencies on τ as $\tau \to 0$. Specifically, $h_{\min} \sim \tau$, $v' \sim \tau^{-0.825}$, $z' \sim \tau^{0.175}$, and $\Gamma_{\min} \sim \tau$. We note that the same axial scaling exponent of 0.175 is obtained if it is instead deduced by monitoring the variation of the planar curvature h_{zz} at $h_{\min}$ with τ. In the next three paragraphs, we predict all but one of the aforementioned scaling exponents and also the rate of thread thinning analytically.

First, we note that in the limit as $\mathrm{Pe} \to \infty$, the CD equation and the boundary conditions on $\Gamma(z,t)$ become

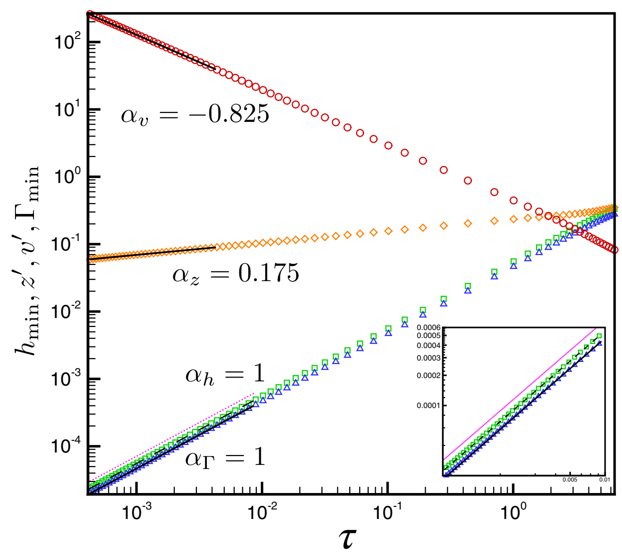

FIG. 2. Computed variation of $h_{\min}$ (green square symbols), $z' \equiv z_{1.04h_{\min}} - z_0$ (orange diamond symbols), $v' \equiv v_{1.04h_{\min}}$ (red circle symbols), and $\Gamma_{h_{\min}}$ (blue triangle symbols) with τ for a thread of $\mathrm{Pe} = \infty$. Here $B_{s0} = 0.1$ and $h_0 = 0.6$. The solid black lines of indicated slopes correspond to power-law exponents predicted from theory. The pink dotted line is Papageorgiou's solution, $h_{\min} = 0.0709\tau$, for a thread with a clean interface or a surfactant-covered thread without surface rheological effects. The black dashed line is the new analytical solution in the presence of surface rheological effects, $h_{\min} = [(0.0709)/(1 + 5B_{s0}/3h_0)]\tau$. Inset: Enlarged view of $h_{\min}$ and $\Gamma_{\min}$ versus τ as $\tau \to 0$.

identical to the KB condition and the boundary conditions on $h(z,t)$. Therefore, if $\Gamma(z,0)$ and $h(z,0)$ have the same functional form, $\Gamma(z,t) = c_0 h(z,t)$, where c_0 is a constant. If not, $\Gamma(z,t) = ch(z,t)$, where c is a function that obeys $Dc/Dt = 0$. In the former case, $c_0 = \Gamma_0/h_0$ and in the latter, $c|_{z=0} \equiv c_0 = \Gamma_0/h_0$. Given that as $h_{\min} \to 0$ and/or $\tau \to 0$, $\Gamma_{\min} \to 0$ (Fig. 2), the Szyskowski equation can be linearized near pinch-off as $\sigma = 1 - \beta\Gamma$, which is used below.

On account of the power-law dependencies revealed in Fig. 2 and the self-similarity of the dynamics for Stokes threads without [25] and with [26] surfactants, we adopt the self-similarity ansatz here and write $h(z,t) = \tau^{\alpha_h} H(\xi)$, $v(z,t) = \tau^{\alpha_v} V(\xi)$, $\Gamma(z,t) = \tau^{\alpha_\Gamma} G(\xi)$, and $\xi \equiv (z - z_0)/\tau^{\alpha_z}$, where ξ is the similarity variable, z_0 the axial location where the thread will pinch-off, α_h, α_v, α_Γ, and α_z are scaling exponents, and H, V, and G are similarity functions. Recasting the KB condition onto similarity space yields $-\alpha_h H + \alpha_z \xi H' + \tau^{1+\alpha_v-\alpha_z}(VH' + HV'/2) = 0$, where prime denotes differentiation with respect to ξ. Requiring that the ODE in similarity space cannot depend on τ, we deduce $\alpha_v = \alpha_z - 1$ [27]. Using the linearized form of the Szyskowski equation, the 1D force balance becomes $[3\tau^{\alpha_h+\alpha_v-\alpha_z} H^2 V' + H + (5B_{s0}/\Gamma_0)\tau^{\alpha_\Gamma+\alpha_v-\alpha_z} HGV']' = 0$. It is worth noting that the Marangoni force has dropped out as it is smaller than the other forces; balancing the remaining forces in the last equation and using the KB condition reveals $\alpha_h = \alpha_\Gamma = 1$. We further note that because this is a self-similarity of the second kind, α_z is left undetermined. A standard way of determining α_z is by solving the PDEs in physical space. However, it has already been shown in Fig. 2 that $\alpha_z = 0.175$ (and $\alpha_v = -0.825$). While the scaling exponents for h, z, and v are identical to those obtained by Papageorgiou for a Stokes thread in the absence of surfactants [25], his scaling law ($h_{\min} = 0.0709\tau$) does not exactly fit the simulation data in Fig. 2. Therefore, we will next perform a more careful analysis of the equations in similarity space.

We first note that the ODEs in similarity space are invariant under the transformation $\xi \to -\xi$, $V \to -V$, $H \to H$, and $G \to G$. Moreover, the KB and CD equation can be written as $H'/H = [1 - (1/2)V']/[V + \alpha_z \xi]$ and $G'/G = [1 - (1/2)V']/[V + \alpha_z \xi]$. Therefore, there is a point ξ_0, where $V + \alpha_z \xi = 0$. In order to remove the singularity, $1 - \frac{1}{2}V' = 0$ at ξ_0. Using the symmetry and asymmetry discussed previously, it can be readily shown that $V(\xi_0) = 0$ and $\xi_0 = 0$. Hence, $V'(\xi_0) = V'(0) = 2$. Thus, the similarity functions can be expanded in a series about $\xi = 0$ as $H(\xi) = \sum_{k=0}^{\infty} H_{2k}\xi^{2k}$, $V(\xi) = \sum_{k=0}^{\infty} V_{2k+1}\xi^{2k+1}$, and $G(\xi) = \sum_{k=0}^{\infty} G_{2k}\xi^{2k}$. Substitution of the series expansions into the ODEs yields the following recurrence relations for the coefficients H_{2k}, G_{2k}, and V_{2k+1} (note that $V_1 = 2$):

$$[\mathbf{A}]\begin{bmatrix} H_{2k} \\ V_{2k+1} \\ G_{2k} \end{bmatrix} = \begin{bmatrix} f_1(H_{2k-2}, V_{2k-1}, G_{2k-2}) \\ f_2(H_{2k-2}, V_{2k-1}) \\ f_3(V_{2k-1}, G_{2k-2}) \end{bmatrix}. \quad (1)$$

Nonzero elements of the coefficient matrix $\mathbf{A}$ are given by $A_{11} = 2k[12H_0 + 1 + (10B_{s0}/\Gamma_0)G_0]$, $A_{12} = 2k(2k+1) \times [3H_0^2 + (5B_{s0}/\Gamma_0)G_0 H_0]$, $A_{13} = 2k(10B_{s0}/\Gamma_0)H_0$, $A_{21} = 2(2+\alpha_z)(2k)$, $A_{22} = H_0(2k+1)$, $A_{32} = G_0(2k+1)$, and $A_{33} = 2(2+\alpha_z)(2k)$. The terms on the right side, f_1, f_2, and f_3, depend on lower-order coefficients. We note that $H = H_0$, $V = V_1\xi = 2\xi$, and $G = G_0$ is an exact solution of the ODEs and all the higher order terms involving H_{2k}, V_{2k+1}, and G_{2k} for $k \geq 1$ in the recurrence relations vanish unless the determinant of the 3×3 coefficient matrix $\mathbf{A}$ equals zero for some $k = m \geq 1$. When the determinant vanishes, it follows that $H_0 = \{1/(12[m(2+\alpha_z) - 1])\} - (5B_{s0}/3\Gamma_0)G_0$. If the value of m is set to unity [25], $H_0 = \{1/[12(1+\alpha_z)]\} - (5B_{s0}/3\Gamma_0)G_0$. Since $\Gamma = ch$ and solutions are symmetric, it can be shown that $G_0 = c_0 H_0 = (\Gamma_0/h_0)H_0$. With α_z determined from simulations, the theory developed here predicts that $h_{\min} = [(0.0709)/(1 + 5B_{s0}/3h_0)]\tau$ and can be seen to be in excellent agreement with simulation data reported in Fig. 2. It is worth noting that Papageorgiou's [25] solution is recovered when $B_{s0} = 0$ or surface rheological effects are absent, and $5B_{s0}G_0/3\Gamma_0 H_0$ represents the relative importance of surface viscous force to its bulk counterpart to leading order near pinch-off. Plainly, surface rheological effects compete with their bulk counterparts as $\tau \to 0$.

Results: Limit of Pe $= 0$.—Figure 3(a) shows the variation of $h_{\min}$ with t predicted from simulations when Pe $= 0$

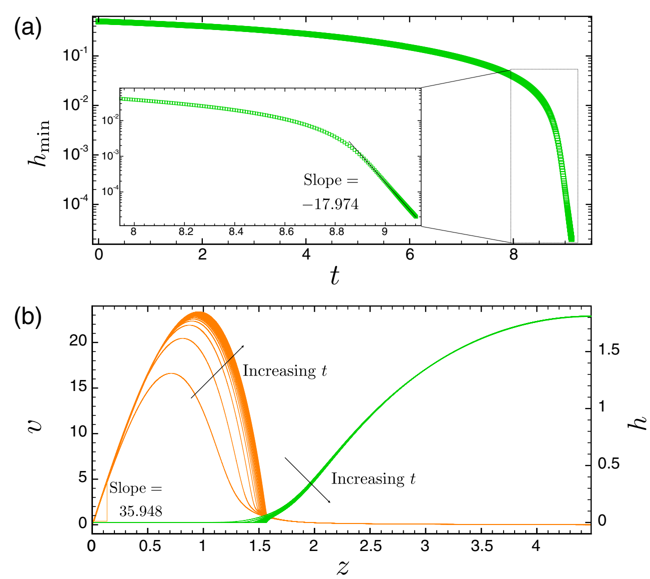

FIG. 3. (a) Variation of $h_{\min}$ with t when Pe $= 0$ and $B_{s0} = 0.001$. Inset: a blowup of the exponential thinning region. (b) Time evolution of the velocity profile $v(z,t)$ (orange) and thread shape $h(z,t)$ (green) during exponential thinning.

and $B_{s0} = 0.001$, and reveals that the asymptotic thinning is exponential and varies as $e^{-\omega t}$ (ω^{-1}: time constant). Figure 3(b) further shows that unlike surfactant-free threads or ones for which $\mathrm{Pe} = \infty$, the velocity in the thinning neck does not diverge in finite time but grows more slowly. Moreover, Fig. 3(b) reveals that near the midplane ($z \approx 0$), the transient velocity profiles collapse onto a straight line of constant slope. Taking $v_z = 2\omega$ near $z = 0$, and substituting this observed behavior into the KB condition yields $h_t = -\omega h$ at $z = 0$, confirming that thread thinning is exponential.

To gain insights into the balance of forces and deduce the constancy of v_z for $z \ll 1$ and $t \gg 1$, we turn to the CD equation and 1D force balance. When $\mathrm{Pe} = 0$, the former reduces to $\Gamma_z(z,t) = 0$; therefore, $\Gamma = \Gamma(t)$. Since the total amount of surfactant is conserved, it follows that $\Gamma(t) = \int_{S(t=0)} 2\pi h(z, t=0)\Gamma_0 dz / \int_{S(t)} 2\pi h dz$. Intuition dictates and simulations confirm that the surface area of the jet $S(t)$ tends to a virtually constant value as time grows without bound. Therefore, all parameters that depend on surfactant concentration, Γ, σ, and B_s, are constants. Rewriting the 1D force balance in a more convenient manner, $(\partial/\partial z)(3h^2 v_z + h\sigma + 5B_s h v_z) = 0$, reveals that as $t \to \infty$ and $h_{\min} \to 0$, and since the problem variables $\Gamma(z,t) = \Gamma, \sigma(z,t) = \sigma$, and $B_s(z,t) = B_s$, (i) bulk viscous force is negligible, (ii) capillary and surface viscous forces balance, and (iii) $v_z(z,t) = \mathrm{const}$.

In most cases involving breakup (cf. Ref. [28]), thread thinning follows self-similar dynamics and physical variables exhibit power-law dependencies on time. To address why the dynamics in this case does not behave in the typical way, we start by assuming such a dependence and demonstrate this leads to a contradiction. As in the large Pe limit, we assume that $h \sim \tau^{\alpha_h}$, $z' \sim \tau^{\alpha_z}$, $v' \sim \tau^{\alpha_v}$, and $\Gamma \sim \tau^{\alpha_\Gamma}$. Using the arguments made in the previous paragraph, it then follows that $\Gamma(z,t) = \Gamma$ or $\alpha_\Gamma = 0$. Clearly, in this case, Marangoni stress vanishes and the only remaining forces are bulk and surface viscous forces and capillary force. By considering the local Boussinesq number, $B_{\mathrm{loc}} \equiv B_s(\Gamma)/h(z,t)$, or ratio of surface to bulk viscous force, it can be shown that $B_{\mathrm{loc}} \to \infty$ as $\tau \to 0$, i.e., asymptotically, bulk viscous force is negligible in comparison to surface viscous force. Hence, the only two forces that can balance are surface viscous and capillary forces. Balancing them reveals $\alpha_v = \alpha_z$, a result that is in clear contradiction with the KB condition which predicts $\alpha_v = \alpha_z - 1$. Thus, it is not possible for the dynamical variables to exhibit a power-law dependence on time.

The only other situation in which a liquid thread thins exponentially is when it is viscoelastic (VE), e.g., a fluid whose rheology can be characterized by the Oldroyd-B constitutive relation [29–32]. Therefore, it is instructive to compare the dynamics of exponentially thinning VE threads and that of surfactant-covered threads when $\mathrm{Pe} = 0$. For a VE thread, the entire jet tends asymptotically to a long and slender, nearly perfectly ($h_z \approx 0$) cylindrical thread that connects to a nearly spherical drop with a corner region that forms at their junction [31,33]. Over the entirety of this thread, v_z is spatially uniform, and as $t \to \infty$, capillary stress grows and is balanced by axial elastic stress while radial elastic stress decays. For a surfactant-laden thread with surface rheological effects, only a short section but not the entirety of the thread is nearly cylindrical. Thus, over the entire thread, h_z is small but finite and v_z again varies slightly with z. As described above, surface viscous and capillary forces balance along the thread but radial stress does not decay. In other words, here *both* the axial and the radial components of the surface viscous force remain important as $t \to \infty$. The impact of this observation on the thread profile over the entire domain and what factors set the length of the cylindrical thread remain open problems.

Conclusions.—We have examined the effects of surface rheology on the thinning of a thread undergoing Stokes flow in two limits, $\mathrm{Pe} = \infty$ and 0. When $\mathrm{Pe} = \infty$, surfactants are asymptotically swept away from breakup but still play a crucial role in the dynamical balance of forces. We have shown that all three forces, bulk viscous, surface viscous and capillary, balance and give rise to a self-similarity of the second kind and to power-law scalings $h_{\min} \sim \Gamma_{\min} \sim \tau$, $z' \sim \tau^{0.175}$, and $v' \sim \tau^{-0.825}$. Specifically, it has been shown that $h_{\min} = [(0.0709)/(1 + 5B_{s0}/3h_0)]\tau$ from theory. This relation provides a correction to Papageorgiou's [25] result for clean interfaces, and reveals that surface rheological effects act to slow the rate of thinning, a finding that accords with intuition. Moreover, this result provides a route to measuring surface rheological properties. Alternatively, if $h(t)$ as well as $\Gamma(t)$ could be measured [34], then surface viscosity can be determined to leading order by using $h_{\min} = [0.0709 - (5B_{s0}/3\Gamma_0)G_0]\tau$, where G_0 is the surfactant depletion rate at $z = 0$.

It is remarkable but counterintuitive that surface viscosities can be important even when surfactants are swept away from the pinching zone. Indeed, surface viscous stress can remain comparable to bulk viscous stress as surfactants are swept away from the pinching region and surface viscosities vanish because surface area-to-volume ratio $1/h \to \infty$ as $h \to 0$ [35].

Extension of the results when $\mathrm{Pe} = \infty$ is worthwhile including generalization of the correction to Papageorgiou's result [37] and accounting for inertia [38]. A number of extensions when $\mathrm{Pe} = 0$ is also possible [39]. In both limits, it would be valuable to study effects of surfactant solubility [40] and intermolecular forces on thinning [41,42].

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Note added.—It was pointed out that exponential thinning of a viscous thread with a uniform surfactant concentration has been described recently in a preprint [43,44].

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[40] Even soluble surfactants can be considered insoluble so long as the timescale for surfactant adsorption or desorption from the interface is much larger than the timescale for pinch-off. The adsorption time is typically hundreds of milliseconds but the characteristic hydrodynamic time during pinch-off can be milliseconds or smaller [24]. See Supplemental Material at [35].

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