

Newtonian and non-Newtonian thin films create finite-time filaments: Experiments and theory

Saksham Sharma  and D. Ian Wilson *Department of Chemical Engineering and Biotechnology, [University of Cambridge](#), Philippa Fawcett Drive, Cambridge CB3 0AS, United Kingdom*

(Received 21 August 2023; accepted 16 June 2025; published 25 July 2025)

The sticky fluids found in pitcher plant traps leave behind dendritic, treelike filaments when the liquid dewets from a substrate. To understand the origin of these filaments, we investigate the retreating thin-film dynamics of aqueous glycerol and polyethylene oxide solutions on partially wetting polydimethyl siloxane substrates, conditionally generating regularly spaced filaments. We show that during the early-stage dynamics of these films, there is a critical average film thickness, h_f (governed by the interplay between van der Waals and capillary forces), below which the film will be unstable, giving rise to filaments. Conversely, filaments are not formed when the average film thickness $\bar{h}$ exceeds h_f . Experiments probing the conditions when filaments are formed and not formed show good agreement with the theory. After the early stage, filament dynamics enter an intermediate stage governed by a Plateau-Rayleigh instability. In this stage, the key scaling relation is $\lambda_f \eta / \gamma \propto \text{Ca}^s$ with $s \approx 1$, where λ_f is the average spacing between filaments, η and γ the viscosity and surface tension of the fluid, and Ca is the capillary number (given by $\eta U / \gamma$; U is the receding contact line velocity). The evolution of the thin-film shape is modeled numerically to show that the formation of filaments arises because the thin-film equation numerically hints at a singular solution after certain time t_f and when the thin-film thickness is below h_f .

DOI: [10.1103/wlft-3z16](https://doi.org/10.1103/wlft-3z16)

I. INTRODUCTION

Receding thin films arise in a range of fields and are important in coating, printing, and drying applications, where the stability of the thin film near the moving contact line will determine the uniformity of the product [1]. It was recently reported that *N. Rafflesiana* pitcher plants secrete digestive sticky fluids that exhibit discrete geometric features upon the receding motion of its contact line (see Fig. 1 caption) [2]. This could be seen as an anecdotal hint that a receding thin film is of crucial importance in biology. When the drop of this sticky fluid dries or is sucked up using a pipette, the contracting volume forms a receding thin film which leaves dendritic, treelike filaments behind as it retreats (Fig. 1). The filaments exhibit regular spacing on relatively smooth surfaces, indicating that the filaments arise from an instability in the thin film rather than the contact line pinning. While such filaments have been observed before with synthetic polymer solutions [3], the underlying physical principles governing the origin of such filaments are not yet known.

This article presents a theoretical treatment that can explain the origin of such filaments and predict their criterion of their formation. It draws on recent experimental work by Xue and Stone

Published by the American Physical Society under the terms of the [Creative Commons Attribution 4.0 International](#) license. Further distribution of this work must maintain attribution to the author(s) and the published article's title, journal citation, and DOI.

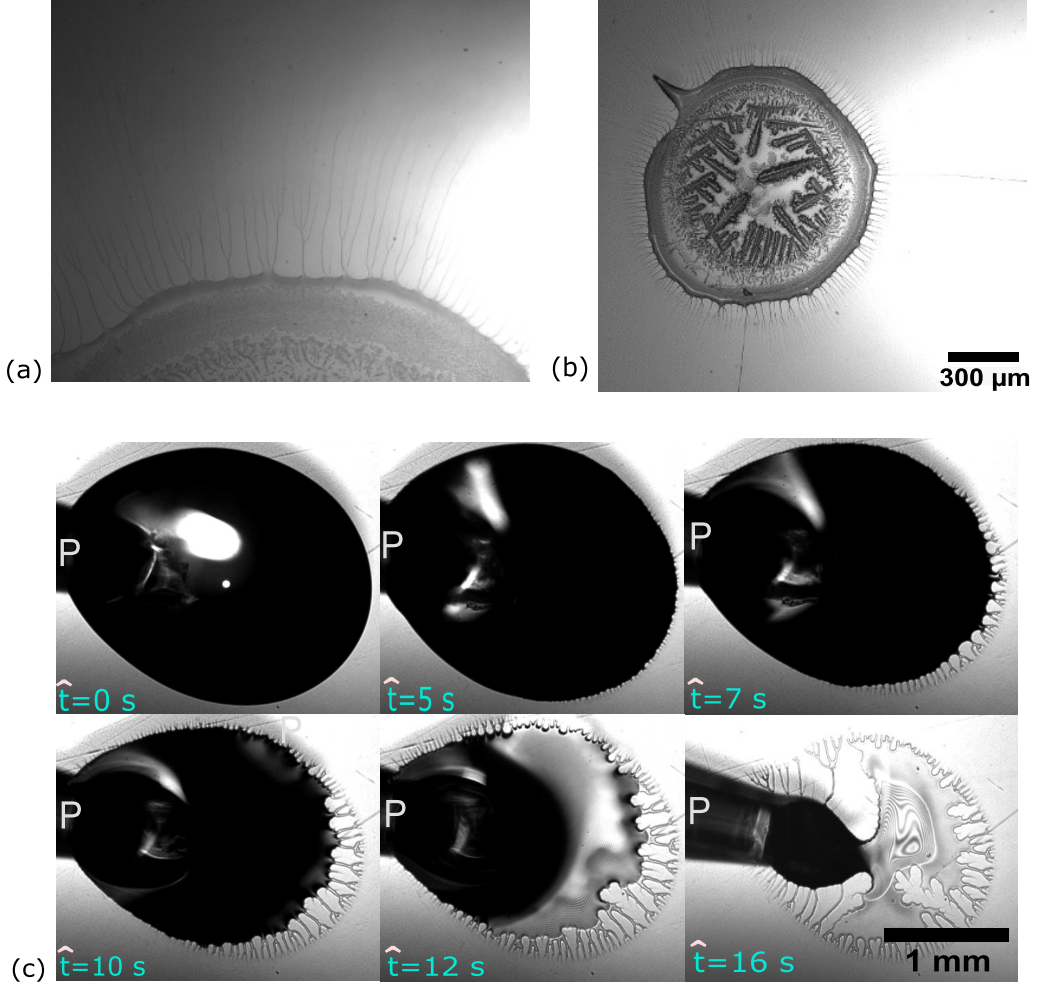


FIG. 1. Filaments formed by overnight evaporation of ground pitcher *N. Rafflesiana* fluid on (a) polystyrene and (b) borosilicate glass surfaces. (c) Forced shrinkage of a sessile drop of *N. Rafflesiana* on borosilicate glass, caused by withdrawal of liquid via pipette labeled P. The experimental configuration is shown in Fig. 2(a). Evaporation in (a) and (b) results in concentration of dissolved species in the drop, slowing evaporation and triggering the transition from a receding film to a pinned state and coffee-ring effect features. Liquid removal in (c) is faster and there is little evaporation: filaments are observed once the contact line starts to recede.

[4] on a liquid film draining down a glass slide under the action of gravity. The thin-film nonlinear partial differential equation (PDE) that is used to model the thin film considers three forces: viscous resistance, gravity, and surface tension. A major assumption there was the consideration of perfectly wetting (zero degree contact angle) fluids, arising from the difficulty of incorporating partial wetting in the model [5]. Partial wetting is included in the present study, following the work by Witelski and coworkers on the stability analysis and evolution of thin films [6–9] by employing expressions for the van der Waals forces’ dependency on the film thickness. We demonstrate that the formation of cusps and filaments observed during the dewetting of pitcher plant fluids has its roots in the inherent instability of the thin film. This instability gives rise to a singularity after a certain time t_f .

This article is organized as follows. Experimental methods are outlined in Sec. II. The hydrodynamic equations for the thin film are presented in Sec. III and stability analysis is then performed to

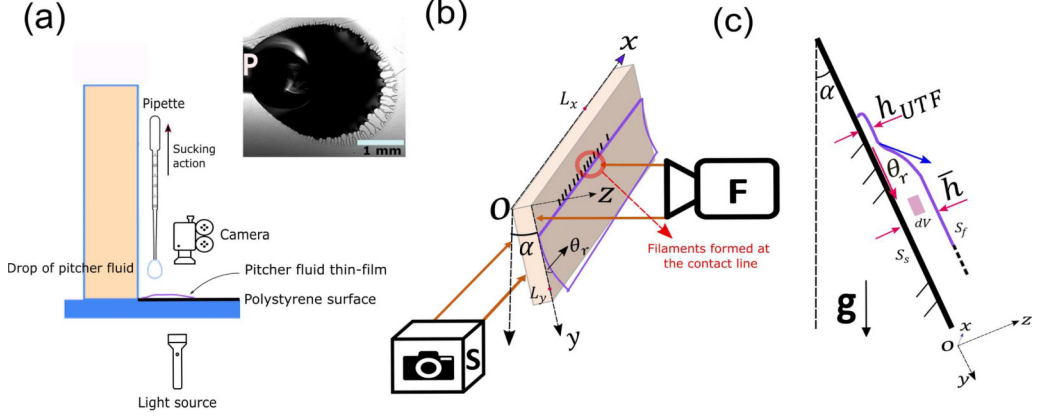


FIG. 2. Generation of filaments in natural and synthetic systems. (a) A schematic of the experimental set to suck fluid up using a pipette. A time series of images are available in Fig. 1(c). The inset shows a photograph of filaments formed by the receding contact line of *N. Rafflesiana* pitcher fluid on a polystyrene surface. (b) A PDMS coated glass microscope slide (size: 25×75 sq. mm) inclined at angle α to the vertical is wetted by raising a liquid bath containing the solution (not shown) upward to immerse the plate. The bath is withdrawn, leaving the thin film which dewets and drains downwards. The upward and downward motion of the liquid bath is generated using a $4'' \times 4''$ laboratory scissor jack, the motion of which does not affect the motion of draining film. (c) Side view of the receding film showing geometric features (dV , S_f , S_s) of the model: the macroscopic receding contact angle θ_r , film heights h_{UTF} and $\bar{h}$. Here, dV is the infinitesimal control volume, S_f is the top free surface of the liquid film, and S_s is the solid substrate. The control volume V is bounded below by the inclined substrate and above by the film surface $z = h(x, y, t)$, with periodic boundaries at $x = 0$ and $x = 1$.

find the criterion for filament formation (Sec. VI). The rationale behind the finite-time singularity feature of the thin-film equation is discussed in Sec. IV along with some numerical investigations. The criterion is compared with experimental results in Sec. V. A scaling law for the spacing between filaments is derived and compared with experimental data in Sec. VI. The key findings and potential further directions for this work are discussed in Sec. VII. Roman and Greek symbols used in this paper, alongside the acronyms, with their physical meanings are given in the Supplemental Material [10] (including Refs. [2, 11–18]).

II. MATERIALS AND METHODS

A. Experimental setup

The experimental setup for studying film dewetting is shown schematically in Fig. 2(b). A glass slide is held at angle α to the vertical above a bath of test liquid. The bath is then raised vertically upwards to wet the initially dry glass slide, and then lowered to its initial position to generate a thin-film which drains downwards under the action of gravity g . Camera F is used to capture the thin-film in the xy plane, and side camera S is used to capture the macroscopic receding contact angle θ_r of the thin-film in the yz plane and the thickness $\bar{h}$ of the thin-film. Movies of the receding film are recorded using a Ximea xiQ USB3.0 (F) camera at 17 fps and a Basler acA1300200um USB3.0 (S) camera at 50 fps. Subsequent image analysis is performed using ImageJ software. All experiments are performed at a laboratory temperature of 21°C .

Borosilicate glass slides with dimensions $25 \times 75 \text{ mm}^2$ and thickness 1 mm were coated with PDMS (polydimethylsiloxane) solution. PDMS polymer was prepared by mixing Sylgard 184 silicone elastomer (prepolymer) and curing agent in the weight ratio 10:1. Slides were prepared using the following protocol: cleansing with surface active cleaning agent (2 wt % aqueous Decon90 solution), rinsing with pure water, drying with an air gun, and further cleaning using an air plasma

cleaner. The PDMS film was then coated on the glass slide by spin coating at 3000 rpm for 30 s followed by curing at 70 °C in the oven.

B. Solution preparation

Polyethylene oxide (PEO) solutions (3500 to 11000 ppm) were prepared by adding the required amount of PEO powder (mol. wt. 8×10^6 , Acros Organics) to deionized water at room temperature and stirred at 800 rpm for 48 hours to obtain a uniform solution. Glycerol-water mixtures (80–100% v/v) were stirred for shorter periods.

C. Material characterization

This section describes the characterization of the liquids employed in the current work. These can be broadly classified as (i) Newtonian, glycerol-water mixtures and (ii) non-Newtonian, aqueous PEO solutions.

1. Shear rheology

The shear rheology of the liquids was studied using a Kinexus controlled shear rheometer (Malvern Instruments, UK) fitted with a Couette cell. The apparent viscosity, η_{app} , was measured using controlled stress ramps. Supplemental Material Fig. S1(a) [10] shows that the glycerol-water mixtures were Newtonian. The PEO solutions exhibit shear-thinning behavior, particularly in the experimentally relevant shear rate range of 0.1–60 s⁻¹. Supplemental Material Fig. S1(b) [10] shows the fit of the PEO data to the Cross model, $\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = \frac{1}{1 + (\tau_c \dot{\gamma})^c}$. The parameters η_0 , η_∞ , τ_c , c are the calculated fitting parameters. The model parameters are reported in Table S1 and the values of η_0 and τ_c for different PEO concentrations are plotted in Supplemental Material Fig. 2 [10].

2. Receding contact angle and surface tension

The receding angle θ_r of the thin film was measured using the side camera S , as shown in the schematic, Fig. 2(b). The surface tension γ of the liquids was measured using pendant droplet tensiometry (see Ref. [2]). The values obtained are reported in Supplemental Material Table S1 [10].

III. THEORY

Consider a thin liquid film of local thickness $h(x, y, t)$ on plane (Oxy) [Fig. 2(b)], with height h pointing toward Oz . Ox points horizontally along the liquid-substrate-air contact line and Oy points directly down the slope. The standard equation for a non-Newtonian thin-film [8] exhibiting power-law behavior with exponent n is

$$3\eta_{app}(\dot{\gamma}) \frac{\partial h}{\partial t} = \left(\frac{\partial}{\partial x} \left[m(h) \frac{\partial p}{\partial x} \right] + \frac{\partial}{\partial y} \left[m(h) \frac{\partial}{\partial y} (\rho g' h) \right] \right)^{1/n}, \quad (1)$$

where $\eta_{app}(\dot{\gamma})$ is the apparent viscosity (the ratio of shear stress and shear rate) at the characteristic shear rate in the film $\dot{\gamma} = \frac{\partial V_y}{\partial z} \big|_{z=0}$,¹ defined at the solid surface $z = 0$ [Fig. 2(c)] where $\mathbf{V}(x, y, t) = V_x \mathbf{e}_x + V_y \mathbf{e}_y$ is the depth-averaged fluid velocity inside the film, ρ the density, p is given by

¹Rather than performing a standard Nusselt film analysis to estimate the shear rate, we estimate the order of the shear rate as $\dot{\gamma} \sim U/\bar{h}$, where U is the surface velocity and $\bar{h}$ is the average film thickness. This estimate provides a characteristic range of shear rates for comparison with the flow curves (shear viscosity vs shear rate) in Fig. S1 and helps us to use the Cross model using the procedure in Supplemental Material Note 2 [10] to find the four Cross-model parameters.

$\Pi(h) - \gamma \frac{\partial^2 h}{\partial x^2}$, and γ is the surface tension of the thin film, $\Pi(h)$ is the disjoining pressure, accounting for van der Waals interactions between the thin film, the substrate, and the air [Ref. [8], see Eq. (1.3)], and $g' = g \cos \alpha$. The mobility coefficient $m(h)$, given by $m = h^k$ where $k \in [1, 3]$, quantifies the degree of slippage (hence, mobility) experienced by the thin film on the substrate [9,19,20]. The higher the value of k , the less the slip occurs: $k = 3$ for the no-slip case (see Eq. 2.31 in Ref. [1]) and $k = 1$ for a geometrical Hele-Shaw cell case with Darcy flows (see Eq. 6.14 in Ref. [1]); also see p. 2 in Ref. [20]. It is to be noted that different values of k between 1 and 3 would one-to-one map to different types of thin-film systems (aka, thin-film equations) with varying degrees of slippage: in Ref. [21], for example, increasing the effect of β^2 in Eq. (2.16) would increase the slip coefficient function $\kappa(h)$, which means that h^1 would dominate, as the slip increases. A similar expression for $m(h)$ also exists in the form of a Navier slip model [21]. Indices k and n are not related. We will see later, toward the end of this section, that the linear stability analysis on the thin-film perturbation is independent of k , and this is the reason we choose to start with a thin-film equation for a general k parameter. Furthermore,

$$\Pi(h) = \frac{A}{h^3} \left[1 - \frac{h_{\text{UTF}}}{h} \right], \quad (2)$$

where the van der Waals forces are characterized by the Hamaker constant A [$A > 0$ means the interaction is hydrophobic and $A < 0$ hydrophilic) and h_{UTF} is the height of the adsorbed precursor film shown in Fig. 2(c) [8], also termed the ultrathin film (UTF). This precursor film is very thin, of $O(10^{-9})$ m, and θ_r is the macroscopic (experimentally measured) receding contact angle. The second term on the right-hand side (RHS) of Eq. (1) accounts for the hydrostatic pressure contribution, equivalent to $-3\rho g' h^2 \frac{\partial h}{\partial y}$ for $m(h) = h^3$.

For a general $m(h) = h^k$, there are two timescales associated with Eq. (1): (i) T_x , when the pressure term (first term on the RHS) is dominant and (ii) T_y , when the gravity term (second term on the RHS) dominates. A scaling analysis yields

$$T_x = \frac{3\eta_{\text{app}} L_x^4}{\bar{h}^k \gamma}; \quad T_y = \frac{\eta_{\text{app}} L_y}{\rho g' \bar{h}^{k-1}}, \quad (3)$$

with $L_x = \bar{h} \sqrt{\gamma h_{\text{UTF}}^2 / A}$ [Ref. [8], p. 016301-2] is the length scale in the X direction, arising from the interplay between surface tension and van der Waals forces (scaled against average film height $\bar{h}$). L_y is the length of the glass substrate in the Oy direction (in these experiments 25 mm). For our experiments, $\bar{h} = O(10^{-4})$ m, $A = O(10^{-17})$ J, $h_{\text{UTF}} = O(10^{-9})$ m, and $\gamma = O(10^{-2})$ N/m, giving $T_x = O(10^{-8})$ s and $T_y = O(1)$ s. The former dominates and the early-stage dynamics of the thin film are characterized by a timescale of 10^{-8} s (Ref. [8], see p. 016301-2), where the van der Waals interactions are dominant at a length scale below the capillary length, without any additive effects of gravity (in Eq. (2), the validity range is $h > h_{\text{UTF}}$).

Newtonian (glycerol-water mixtures) and non-Newtonian solutions (aqueous polyethylene oxide, PEO, mol. wt. 8×10^6) were used in the experiments. Scaled viscosity given by $\hat{\eta}_{\text{scaled}}$ [scaling η with respect to $(\rho \gamma^3 / g \sin \alpha)^{1/4}$] characterizes the Newtonian liquids. The PEO solutions exhibited shear thinning over the range of shear rates encountered here and η_{app} could be described by the power law model (see Sec. 2, Supplemental Material [10], for fits to the more detailed Cross model).

The experiments feature two steps: Step (i) is wetting by raising a small bath of the liquid to contact the glass slide; step (ii) is lowering the bath and letting the thin film drain downwards [Fig. 2(b)]. Step (i) generates the microscopic UTF, thickness h_{UTF} , while step (ii) generates the macroscopic film, thickness $\bar{h}$. Further details are provided in Supplemental Material Secs. 1 and 5 [10]. In our calculations, we adopt an ultrathin film thickness $h_{\text{UTF}} = 1$ nm, consistent with the order of experimental values reported previously [22], which effectively prevents a singularity occurring

because of the disjoining pressure $\Pi(h) \sim \frac{A}{h^3}$ in Eq. (1) and remains insensitive to the exact value of h_f evaluated later in Eq. (22), due to five orders of scale separation from the film thickness h_f .

Focusing on the early-stage dynamics of the thin film, thus ignoring the gravity term, Eq. (1) gives

$$3\eta_{\text{app}} \frac{\partial h}{\partial t} = \frac{\partial}{\partial x} \left[h^k \frac{\partial}{\partial x} \left(\frac{A}{h^3} \left[1 - \frac{h_{\text{UTF}}}{h} \right] - \gamma \frac{\partial^2 h}{\partial x^2} \right) \right]^{1/n}. \quad (4)$$

Equation (4) is nondimensionalized by introducing scales

$$h = \bar{h}\hat{h}, \quad x = L_x\hat{x}, \quad t = T_x\hat{t}, \quad h_{\text{UTF}} = \bar{h}\hat{\zeta}, \quad (5)$$

where the variables with hats are dimensionless and $\hat{\zeta} = h_{\text{UTF}}/\bar{h} < 1$. Indices, e.g., n, k are hatless. This yields

$$\frac{\partial \hat{h}}{\partial \hat{t}} = \frac{\partial}{\partial \hat{x}} \left[\hat{h}^k \frac{\partial}{\partial \hat{x}} \left(\hat{\Gamma}(\hat{h}) - \frac{\partial^2 \hat{h}}{\partial \hat{x}^2} \right) \right]^{1/n}, \quad (6)$$

where $\hat{\Gamma}(\hat{h})$ is the dimensionless form of $\Pi(h)$,

$$\hat{\Gamma}(\hat{h}) = \frac{\hat{\zeta}^2}{\hat{h}^3} \left[1 - \frac{\hat{\zeta}}{\hat{h}} \right], \quad (7)$$

and the dimensionless pressure is

$$\hat{p} = \hat{\Gamma}(\hat{h}) - \frac{\partial^2 \hat{h}}{\partial \hat{x}^2}. \quad (8)$$

We investigate the nature of stability of the thin film at its early stage. Linear stability analysis is performed with respect to arbitrary infinitesimal perturbations. Since the existence of a Lyapunov function provides an indication of the nature of the stability of the system [23], we start by finding a Lyapunov function for Eq. (6). Consider

$$\hat{I}[\hat{h}] = \int_0^1 \left(\frac{1}{2} \left| \frac{\partial \hat{h}}{\partial \hat{x}} \right|^2 - \hat{\zeta}(\hat{h}) \right) d\hat{x}, \quad (9)$$

where $\partial \hat{\zeta}(\hat{h})/\partial \hat{h} = \hat{\Gamma}'(\hat{h})$. The reason behind choosing this integral is that its first derivative with respect to $\hat{h}$ gives

$$\frac{\partial \hat{I}}{\partial \hat{h}} = \frac{\partial}{\partial \hat{h}} \left(\frac{1}{2} \left| \frac{\partial \hat{h}}{\partial \hat{x}} \right|^2 - \hat{\zeta}(\hat{h}) \right) = \frac{\partial^2 \hat{h}}{\partial \hat{x}^2} - \hat{\Gamma}'(\hat{h}) = -\hat{p}. \quad (10)$$

This integral is the energy functional of the system. We define V as the three-dimensional volume occupied by the liquid film (for unit widths along x and y), bounded below by the inclined substrate and above by the film surface $z = h(x, y, t)$. The infinitesimal control volume is denoted dV , and the enclosing surface S comprises the top free surface S_f , the substrate S_s , and the periodic boundaries between $x = 0$ and $x = 1$. These geometric elements (except the periodic boundaries) are shown in Fig. 2(c). The rate of energy dissipation in control volume dV is

$$\frac{\partial \hat{I}}{\partial \hat{t}} = \frac{\partial \hat{I}}{\partial \hat{h}} \frac{\partial \hat{h}}{\partial \hat{t}} = -\hat{p} \nabla \cdot (\hat{h}^3 \nabla \hat{p}), \quad (11)$$

where the derivative is written in terms of ∇ . The total energy dissipation over volume V is

$$\frac{d\hat{I}}{d\hat{t}} = \int_V -\hat{p} \nabla \cdot (\hat{h}^3 \nabla \hat{p}) dV. \quad (12)$$

Integrating by parts

$$\frac{d\hat{I}}{d\hat{t}} = -\hat{p} \int_V \nabla \cdot (\hat{h}^3 \nabla \hat{p}) dV - \int_V \nabla \hat{p} \int \nabla \cdot (\hat{h}^3 \nabla \hat{p}) dV \quad (13)$$

and applying the divergence theorem yields

$$\frac{d\hat{I}}{d\hat{t}} = -\hat{p} \int_S \hat{h}^3 (\nabla \hat{p} \cdot \mathbf{n}) dS - \int_S \hat{h}^3 |\nabla \hat{p}|^2 dS. \quad (14)$$

The first term on the RHS is zero because of the boundary condition which assumes no flux of the liquid normal to the boundary, i.e., $\nabla \hat{p} \cdot \mathbf{n} = 0$ on surface dS . The net energy dissipation is then

$$\frac{d\hat{I}}{d\hat{t}} = - \int_S \hat{h}^3 |\nabla \hat{p}|^2 dS, \quad (15)$$

which is always ≤ 0 because $\hat{h} \geq 0$. The nonincreasing nature of Lyapunov function $\hat{I}[\hat{h}]$ confirms the direction of stability of the steady-state solution of Eq. (6) toward the higher value of $\hat{h}$. This allows us to find all possible time-independent solutions of Eq. (6) obeying Eq. (15), and these are (i) $\hat{h} = 0$ and (ii) $\nabla \hat{p} = 0$. The former corresponds to the absence of any fluid on the surface and the latter means that a uniform pressure field exists for the steady-state solution. The latter, with uniform pressure $\hat{p}$, is selected to proceed further, such that

$$\hat{\Gamma}(\hat{h}) - \frac{\partial^2 \hat{h}}{\partial \hat{x}^2} = \hat{p}. \quad (16)$$

This has a uniform solution, given by $\hat{h} = \hat{h}$ and $\hat{p} = \hat{\Gamma}(\hat{h}) = \frac{\hat{\zeta}^2}{\hat{h}^3} [1 - \frac{\hat{\zeta}}{\hat{h}}] > 0$. We are now interested in finding families of solutions (apart from $\hat{h} = \hat{h}$). To do this, we expand pressure and film thickness as

$$\hat{p} = \hat{p}_c + \hat{\delta} \quad (17a)$$

$$\hat{h}(\hat{x}) = \hat{h} + \hat{\epsilon} \hat{h}_1(\hat{x}) + \hat{\epsilon}^2 \hat{h}_2(\hat{x}) + \dots, \quad (17b)$$

where $\hat{\epsilon}, \hat{\delta} \ll 1$ are small perturbation parameters. At $O(\hat{\epsilon})$, Eq. (16) becomes

$$\frac{3\hat{\zeta}^2 \hat{h}_1}{\hat{h}^4} \left[1 - \frac{\hat{\zeta}}{\hat{h}} \right] + \frac{\partial^2 \hat{h}_1}{\partial \hat{x}^2} = 0, \quad (18)$$

which is second-order ordinary differential equation (ODE) upon ignoring higher order $\hat{\epsilon}^2$ terms. The equation is made closed form by considering it over a periodic domain, $0 \leq \hat{x} \leq 1$, with Neumann boundary condition $\hat{h}_x(0) = \hat{h}_x(1) = 0$ (subscript x denotes differentiation with respect to x). A periodic boundary condition explains the formation of periodic array of filaments in the Ox direction. Equation (18) can be written in the form of the harmonic oscillator equation,

$$\frac{\partial^2 \hat{h}_1}{\partial \hat{x}^2} + \hat{\Lambda}^2 \hat{h}_1 = 0, \quad (19)$$

where $\hat{\Lambda}^2 = 3\hat{\zeta}^2 [1 - \hat{\zeta}/\hat{h}]/\hat{h}^4$. Eigenvalues of this equation are $\hat{\Lambda}_i = i\pi$ for $i \in \mathbb{N}^*$. Solving for $\hat{h}$,

$$3 \frac{\hat{\zeta}^2}{\hat{h}^4} \left[1 - \frac{\hat{\zeta}}{\hat{h}} \right] = i^2 \pi^2, \quad (20)$$

with the solution

$$\hat{h}_i = 3^{1/4} \sqrt{\frac{\hat{\zeta}}{i\pi}}. \quad (21)$$

Solution $\hat{h}_1$ for $i = 1$ is the primary bifurcation point which demarcates the transition between stable and unstable solutions. Above the primary bifurcation point ($\hat{h} > \hat{h}_1$), the solution is stable, while below it ($\hat{h} < \hat{h}_1$) the solution is unstable (Ref. [6], p. 159). Higher order bifurcations for $i \geq 2$ are not considered because they involve only unstable modes (Ref. [24], Theorem 5).

To find a dimensional version of this solution, dimensional analysis of Eq. (4) is required, which yields the scaling relation $\bar{h} \sim \gamma T_x / \eta_{\text{app}}$. Using T_x from Eqs. (3) and $L_x = \bar{h}^2 \hat{\zeta} \sqrt{\gamma/A}$ gives the critical height of the thin film as

$$h_f = 3^{-5/16} \left(\frac{\hat{\zeta}}{\pi} \right)^{-1/8} \hat{\zeta}^{-1} \left(\frac{\gamma}{A} \right)^{-1/2}. \quad (22)$$

If $\bar{h} < h_f$, the thin film is unstable, and if $\bar{h} > h_f$, it is stable. It should be noted that this theoretical treatment does not predict the shape or behavior of the unstable film: it provides a criterion to compare the steady-state film thickness with a theoretical limit, above which the film is stable and below which it is unstable. This result is independent of the rheology of the fluid and the shear rate in the thin film. In addition, the expression does not depend on the value of k because the Lyapunov function [Eq. (9)] that enables us to find the steady-state solution and its subsequent perturbation, is also independent of k . This also hints at the potential universality of this instability phenomenon across wide-ranging systems with different values of k , such as Hele-Shaw cells ($k = 1$) and slip-conditioned systems ($1 < k < 3$). The physical rationale behind this is that the formation of filaments happens over a timescale significantly faster (theoretically, eight orders of magnitude) than the timescale of receding motion, and thus the shear rate or rheology of the thin film does not play any role in the critical film thickness $\hat{h}_f$. The reader is referred to the work of Xue and Stone [4] where the evolution of the shape of the thin film is considered.

An unstable filament evolves to yield the steady-state solution $h \approx 0$ (as discussed above). The dynamics of this transition are considered in the next section, where it is shown that the evolution of a thin film to approach zero film thickness in finite time is the reason for the origin of the filament.

IV. FINITE-TIME FILAMENT FORMATION

We start with a simplified form of (6) in this section, for a Newtonian fluid, to study the bounds or limits of the modified equation which features surface tension and van der Waals force terms. The motivation in the section is to understand the behavior of the solutions and thereby predict the conditions necessary for the solution to remain bounded or to blow up. A general form of (6) with $n = 1$ (see Ref. [25]) is

$$\frac{\partial h}{\partial t} = -\frac{\partial}{\partial x} \left(M(h) \frac{\partial}{\partial x} \left[-Q(h) + R(h) \frac{\partial^2 h}{\partial x^2} \right] \right), \quad (23)$$

with boundary condition $h(x+L) = h(x)$. If $M(h) = f(h)$, $R(h) = 1$ and $dQ(h)/dh = -g(h)/f(h)$, then the equation becomes

$$h_t = -(f(h)h_{xxx})_x - (g(h)h_x)_x, \quad (24)$$

where subscripts denote differentiation. For $f(h) = h^k$ ($1 \leq k \leq 3$) and $g(h) = 3\frac{\zeta^2}{h^4}(1 - \frac{4\zeta}{3h})$, (24) is equivalent to (6). It was proved in Ref. [7] that the solution of (24) blows up when

$$\lim_{s \rightarrow \infty} \frac{s^2 f(s)}{g(s)} < \infty \quad (25)$$

and when $s^2 f(s)/g(s) \rightarrow \infty$, as $s \rightarrow \infty$, the classical solution is uniformly bounded and positive. In the current work, i.e., (6) with $n = 1$, $s^2 f(s)/g(s) = s^{6+k}/(3\zeta^2(1 - 4\zeta/3s))$, which grows to ∞ as $s \rightarrow \infty$. Hence, the classical-positive solution of (6) (for $n = 1$) is bounded and finite. Having established the bounds of the equation, we next explore how the solution evolves over time.

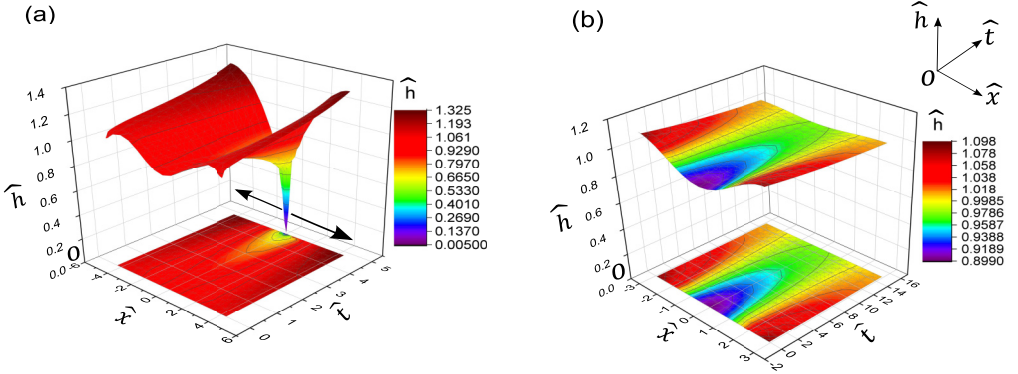


FIG. 3. Numerical solution of (4) (for $\hat{h}_{\text{UTF}} = 0$) over domain $-\hat{L}_d \leq \hat{x} \leq \hat{L}_d$. (a) For $\hat{L}_d = 4.34$, height $\hat{h}$ approaches zero at time $\hat{t}_f \approx 4.79$ after which the dry region grows in the direction of the arrows and the film splits to form two filaments (not shown). (b) For $\hat{L}_d = 2.94$, height $\hat{h}$ remains stable with time and does not tend toward zero.

Equation (4) states that the height of the film h is determined by two forces: van der Waals interactions and surface tension. For wetting liquids, the former is attractive in nature and brings the fluid in contact with the substrate; being inversely proportional to h , it increases in magnitude as $h \rightarrow 0$. The latter, on the other hand, tries to minimize the surface energy of the fluid by reducing the area of the liquid-vapor interface; it prefers a nonplanar film to a planar one. It is expected that the combination of these will lead to the presence of both features, namely, reduced film height and nonplanar film geometry, in the system. To focus on the highly nonlinear terms (van der Waals and surface tension forces) which grow very fast, we take $\hat{h}_{\text{UTF}} = 0$ (as the order of $\hat{h}_{\text{UTF}}$ is significantly lower than h) in (4), so only the first order term in van der Waals interaction and the surface tension is compared and evaluated in the numerical study. The numerical solution is evaluated using Wolfram Mathematica. A finite domain with width (in the $\hat{x}$ direction) $2\hat{L}_d$ is considered with the boundary condition $h(-\hat{L}_d, t) = h(\hat{L}_d, t) = H(t)$, $h_x(\hat{x} = -\hat{L}_d) = h_x(\hat{x} = \hat{L}_d) = 0$, and the initial condition $h(\hat{x}, 0) = \bar{h} - \delta \cos \frac{\pi \hat{x}}{\hat{L}_d}$ such that $\bar{h} = 1$ is the average film height and $\delta = 0.1$ is the amplitude of perturbation (0.1 being chosen to ease graphical visualization). As derived previously in Ref. [9] [see Eq. (3.3)], there is a critical thickness $\sqrt{\hat{L}_d/\pi}$ (following a similar stability analysis to that in the previous section) below which the uniform film is unstable and above which the uniform film is stable to small perturbations.

Figure 3(a) shows the former case, for $\hat{L}_d = 4.34 > \pi$, where the film height $\hat{h}$ approaches 0 at certain $\hat{t}_f \approx 4.79$. Near this time, the Mathematica software suspects a singularity to exist, hence it is not possible to find the solution at longer times. Figure 3(b) shows an example of the latter case, for $\hat{L}_d = 2.94$, where no such singularity is found even at larger times; the initial sinusoidal perturbation decays to the average film height $\hat{h} = 1$, suggesting that the film remains stable.

V. RESULTS

Our experimental results are presented in the form $\bar{h}/h_f$, the criterion for thin film stability, in Fig. 4. The abscissa captures the dimensionless viscosity of the liquid, i.e., $\hat{\eta}_{\text{scaled}}$ for Newtonian fluids, and the Cross model time parameter τ_c for the PEO solutions. Figure 4(a) shows good agreement with the stability criterion for the Newtonian liquids. If $\bar{h}/h_f < 1$, the thin film becomes unstable because the thinner film incurs larger van der Waals forces. A more viscous liquid results in a thicker film ($\bar{h}$ values, measured experimentally, are given in Supplemental Material Tables S3–S5 [10]), while h_f is independent of viscosity. Less viscous Newtonian films are therefore more likely to be unstable. The photograph in Fig. 4(a) shows that these unstable thin films form droplets: the

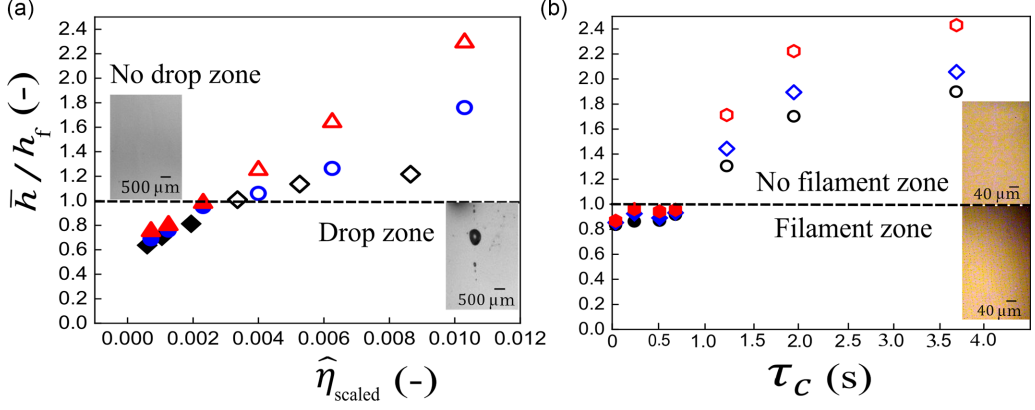


FIG. 4. Comparison of experimental results with theory: effect of dimensionless viscosity, $\hat{\eta}_{\text{scaled}}$ and Cross model parameter τ_c , on $\bar{h}/h_f$ for (a) glycerol-water mixtures and (b) PEO solutions. Solid symbols denote unstable film; hollow symbols denote a stable film. Symbol color indicates the angle of plate inclination: black for $\alpha = 0^\circ$, blue for $\alpha = 30^\circ$, red for $\alpha = 60^\circ$. Here, $\bar{h}$ is the experimentally measured film thickness and h_f is the theoretical critical film thickness.

initial filament creates a dry spot which grows (Ref. [9], see Fig. 5) and gives rise to satellite beads. Satellite beads have been reported previously, e.g., Ref. [26], in studies of large drops sliding down a partially wetting substrate which emit smaller drops from their cusped tail.

For the non-Newtonian case, Fig. 4(b), when $\bar{h}/h_f > 1$, the thin film again remains stable and does not yield a singularity. However, for $\bar{h}/h_f < 1$, the thin film yields a singular solution and filaments are observed. Experimentally observed zones of filament formation and nonformation are predicted very well by the stability theory. The crossover between the zones occurs at different η_{scaled} values for the two fluid types: elucidation of this aspect requires further work, as does testing on pitcher fluids.

It is to be noted that the current theory has not been tested for the pitcher fluids. Conducting these experiments on pitcher fluids, any other biological fluids, requires: (i) an ample amount of fluid (approximately 3–5 mL) for a series of tests across a wide range of parameters and (ii) knowledge

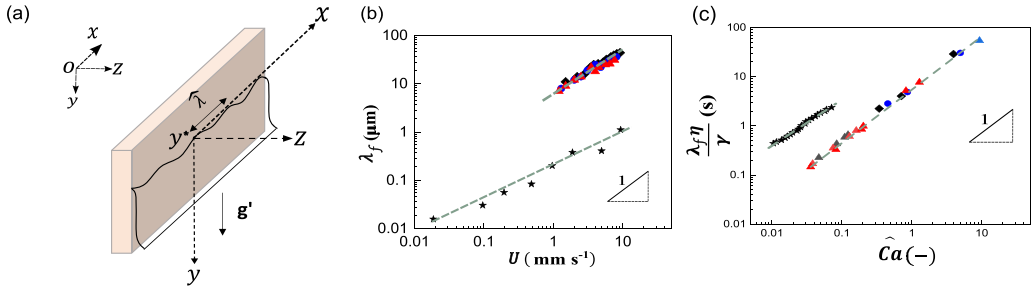


FIG. 5. Comparison of experimental data from literature and experiments in the current work on filament spacing, λ_f , alongside predictions. (a) Schematic of a moving contact line with disturbance wavelength $\hat{\lambda}$ in the x direction. (b) Effect of receding contact line velocity U on spacing between filaments λ_f for experiments reported in the literature (star symbols) [3] and performed by us (nonstar symbols). (c) Effect of Capillary number $\hat{Ca}$ on $\frac{\lambda_f \eta_{\text{app}}}{\gamma}$ for experiments reported in the literature (star symbols) [3] and performed by us (nonstar symbols); color of the nonstar symbol indicates angle of inclination: black for $\alpha = 0^\circ$, blue for $\alpha = 30^\circ$, red for $\alpha = 60^\circ$.

of the wetting and dispersive properties of the fluid. We invite future studies in this area, linking plant scientists and fluid mechanicians; the variation of pitcher fluid behaviors between different species and locations is a topic of ongoing research.

VI. STABILITY ANALYSIS OF MOVING CONTACT LINE

In previous sections, the condition for formation of droplets or filaments was determined using stability analysis of a young thin film. We now seek to determine how the spacing between such filaments depends on the contact line velocity. The theory developed in Ref. [27] is used to derive the scaling relation for the size and spacing of filaments, which is then compared with our experiments and experimental data reported in the literature.

The dimensionless lubrication equation for a moving contact line of a thin film of height $h(x, y, t)$ with slip at the fluid-solid interface is given by [1]

$$\partial_t h + \nabla \cdot (h \mathbf{V}) = 0, \quad (26a)$$

$$\nabla \kappa + \mathbf{e}_y + \frac{3(-\hat{C}a \mathbf{e}_y - \mathbf{V})}{h(h + 3l_s)} = 0, \quad (26b)$$

where $\mathbf{V}(x, y, t) = V_x \mathbf{e}_x + V_y \mathbf{e}_y$ is the depth-averaged fluid velocity inside the film, l_s is the slip length to ensure Navier slip along the substrate, $\hat{C}a$ is the capillary number given by $\eta(\dot{\gamma})U/\gamma$, U is the contact line velocity, and $\nabla = \mathbf{e}_x \partial_x + \mathbf{e}_y \partial_y$. All the terms are dimensionless. A linear stability analysis of (26) yields

$$h(x, y, t) = h_0(y) + \epsilon h_1(y) e^{-\sigma t + i q x}, \quad (27a)$$

$$\kappa(x, y, t) = \kappa_0(y) + \epsilon \kappa_1(y) e^{-\sigma t + i q x}, \quad (27b)$$

where κ is two times the mean curvature of the interface. $h_0(z)$ and $\kappa_0(z)$ denote the shape of the film as a result of balance between capillary forces and gravity; σ is the decay rate of perturbations; q is the wave number of the disturbance in the x direction [Fig. 5(a)]. The detailed stability analysis of (27) is given in the Appendix of Ref. [27], wherein the following analytical result for σ is derived:

$$\sigma = \frac{|q|\gamma}{\eta} \frac{\tan \theta_r}{\cos \theta_r} \left(\frac{d \tan \theta_r}{d \hat{C}a} \right)^{-1}, \quad (28)$$

where θ_r is the receding contact angle of the thin film, estimated using the Cox-Voinov law [28],

$$\theta_r^3 = \theta_e^3 - 9 \hat{C}a \ln(y/l_s) \quad (29)$$

where θ_e is the equilibrium contact angle, y is the distance from the contact line [Fig. 5(a)], and l_s is the slip length. Differentiating with respect to $\hat{C}a$ gives

$$3\theta_r^2 \frac{d\theta_r}{d\hat{C}a} = -9 \ln(y/l_s) \frac{d(y/l_s)}{d\hat{C}a} \quad (30)$$

such that $\frac{d(y/l_s)}{d\hat{C}a} \propto T_y$ because l_s is dependent only on molecular factors (self-diffusion coefficient and molecular size) [29]. Since θ_r is small, $\tan \theta_r \approx \theta_r$ and $\cos \theta_r \approx 1 - \theta_r^2/2$ and (28) becomes

$$\sigma \approx -|q| \frac{\gamma}{\eta} \frac{\theta_r}{1 - \theta_r^2/2} \left(\frac{3}{\theta_r^2} \ln \left(\frac{y}{l_s} \right) T_y \right)^{-1} \approx -|q| \frac{\gamma}{\eta} \frac{\theta_r^3}{3 \ln(y/l_s) T_y} \quad (31)$$

Ultimately, the expression for dimensionless wavelength $\hat{\lambda}$ of the contact line disturbance, using (31), is given by

$$\hat{\lambda} = \frac{2\pi}{|q|} = \frac{2\pi\gamma}{\sigma\eta} \frac{-\theta_r^3}{3 \ln(y/l_s) T_y}. \quad (32)$$

Substituting (29) in (32) gives

$$\hat{\lambda} = \frac{2\pi\gamma}{\sigma\eta T_y} \left[3\hat{Ca} - \frac{\theta_e^3}{3\ln(y/l_s)} \right], \quad (33)$$

with the first term on the RHS given by $\frac{6\pi\gamma}{\sigma T_y} \hat{Ca} = \frac{6\pi}{\sigma T_y} U$. This predicts that $\hat{\lambda}$ is dependent on the first power of U for a given decay rate σ . It should be noted that the decay rate in (28) is positive because receding angle θ_r increases with $\hat{Ca}$ [27]. Hence, any small perturbation ϵ on h will eventually die with a relaxation rate σ , which can be assumed to be constant for a given disturbance ϵ . Interestingly, a similar kind of stability analysis is performed while deriving the decay rate on numerous fluid dynamical instabilities. To give an example, in the case of the Plateau-Rayleigh instability, the wavelength of the most unstable mode is derived analytically, owing to imaginary values of decay rate σ [30]. However, in the present case, we have shown that wavelength λ is dependent on the first power of U .

In Sec. IV, it was shown that the thin film with a thickness lower than the critical film thickness h_f can break to form filaments and approach the interface to the solid surface in a self-similar manner. The origin of filament formation is then followed by the motion of contact line and formation of fluctuation-induced crests and troughs of wavelength λ as shown in Fig. 5(a), where it also apparent that filaments are experimentally observed to have a regular spacing between them, given by λ_f .

We now compare the above theory with (i) experimental data collected using PEO solutions in the setup in Fig. 2 and (ii) the experimental data reported for aqueous polyacrylamide solutions in Ref. [3]. For case (i), the spacing between filaments λ_f varies with U as $\lambda_f \propto U^{0.72}$ [Fig. 5(b)], whereas, for case (ii), it varies as $\lambda_f \propto U^{0.80}$ [Fig. 5(c)]. In terms of $\hat{Ca}$, for case (i), a plot of $\lambda_f\eta/\gamma$ versus $\hat{Ca}$ behaves as $\lambda_f\eta/\gamma \propto \hat{Ca}^{1.08}$, and for case (ii) it behaves as $\lambda_f\eta/\gamma \propto \hat{Ca}^{0.945}$. There is therefore good agreement between the experiments reported here [case (i)], those of Deblais *et al.* [3] [case (ii)], and the prediction from the stability analysis.

VII. CONCLUSION

The ability to predict regimes of filament/drop formation by a thin film is likely the result of simplifying the geometry of this problem and focusing on one single question: What drives the formation of these thin-film instabilities? The answer to this question inherently lies in the instability of a thin-film PDE which arises from a fourth-order parabolic degenerate PDE and undergoes a stable-to-unstable transition at a critical juncture. This juncture also dictates the criterion necessary for the formation of filaments, which explained what we originally observed with the biological pitcher fluids. A stability analysis of the thin-film equation allowed us to find the criterion to predict the conditions which makes the thin film unstable. Once it happens, the thin film evolves dynamically to touch the substrate and creates a dry spot region which grows in size and divides the film into multiple filaments. The spacing between filaments is explained by performing a stability analysis on the moving contact line to find out how λ_f depends on $\hat{U}$. We compared this scaling prediction with the experiments reported in the literature and our own experiments and found good agreement. A possible application of our theoretical and experimental study could be to engineer the deposition of electrically conductive filaments of PEDOT:PSS polymer on a transparent conducting substrate [such as indium tin oxide (ITO)], given that with our model, we can predict when filaments would form on the substrate. Traditional approaches of printing PEDOT:PSS usually employ lithography, direct ink writing, and electrohydrodynamic printing, which are expensive and cumbersome. A simple means of predictably depositing conductive filaments on a substrate can lay the foundation of a printing technology that can significantly save time and resources in the field of, say, biological printing for in vitro cellular modeling, where researchers are often interested in monitoring ion channels and its functioning in response to different drugs [31].

ACKNOWLEDGMENTS

We thank Professor W. Federle and Doctor V. Kang for experiments on filament formation with pitcher plant fluids inspiring this work and the AFM-FTIR setup (Doctor Mike Casford, Department of Chemistry, Cambridge). The experimental work benefited from insights provided by Doctor V. Kang, Doctor S. Middy, Doctor R. Das, Doctor S. Vema, and Doctor S. Pavagada on rig building and surface coating. Initial discussion in Graduate Parlour of Pembroke College, Cambridge with Professor A. J. D. Shaikeea (now at GALCIT, Caltech), Professor S. Das (now at IIT Madras), and final discussion on the bounded-ness/blowup condition with Professor E. Miranda and her group in the Special Lectures Differential Manifolds series at UPC Barcelona was helpful. S.S. was funded by the Cambridge-India Ramanujan and Cambridge Philosophical Society Scholarship from the Cambridge Commonwealth, European and International Trust.

-
- [1] A. Oron, S. H. Davis, and S. G. Bankoff, Long-scale evolution of thin liquid films, *Rev. Mod. Phys.* **69**, 931 (1997).
 - [2] V. Kang, H. Isermann, S. Sharma, D. I. Wilson, and W. Federle, How a sticky fluid facilitates prey retention in a carnivorous pitcher plant (*Nepenthes Rafflesiana*), *Acta Biomater.* **128**, 357 (2021).
 - [3] A. Deblais, R. Harich, A. Colin, and H. Kellay, Taming contact line instability for pattern formation, *Nat. Commun.* **7**, 12458 (2016).
 - [4] N. Xue and H. A. Stone, Self-similar draining near a vertical edge, *Phys. Rev. Lett.* **125**, 064502 (2020).
 - [5] H. Stone, Modern applications of classical ideas in fluid mechanics (2021), <https://youtu.be/s4Sqml7Kcec?t=3230>.
 - [6] T. P. Witelski and A. J. Bernoff, Dynamics of three-dimensional thin film rupture, *Physica D* **147**, 155 (2000).
 - [7] A. L. Bertozzi and M. C. Pugh, Long-wave instabilities and saturation in thin film equations, *Comm. Pure Appl. Math.* **51**, 625 (1998).
 - [8] M. B. Gratton and T. P. Witelski, Coarsening of unstable thin films subject to gravity, *Phys. Rev. E* **77**, 016301 (2008).
 - [9] T. P. Witelski, Nonlinear dynamics of dewetting thin films, *AIMS Math.* **5**, 4229 (2020).
 - [10] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/wlft-3zl6> for additional information about the experimental methods and a detailed discussion of the numerical simulations, includes supplemental text, Figs. S1 to S3 and Tables S1 to S5, which includes Refs. [2,11–18].
 - [11] E. M. Lifshitz and M. Hamermesh, The theory of molecular attractive forces between solids, in *Perspectives in Theoretical Physics* (Pergamon, Oxford, UK, 1992), pp. 329–349.
 - [12] C. J. Drummond and D. Y. Chan, van der Waals interaction, surface free energies, and contact angles: Dispersive polymers and liquids, *Langmuir* **13**, 3890 (1997).
 - [13] D. B. Hough and L. R. White, The calculation of Hamaker constants from Lifshitz theory with applications to wetting phenomena, *Adv. Colloid Interface Sci.* **14**, 3 (1980).
 - [14] L. Girifalco and R. J. Good, A theory for the estimation of surface and interfacial energies. I. Derivation and application to interfacial tension, *J. Phys. Chem.* **61**, 904 (1957).
 - [15] H. S. Nalwa, *Encyclopedia of Nanoscience and Nanotechnology* (American Scientific Publishers, Los Angeles, CA, 2004).
 - [16] J. N. Israelachvili, *Intermolecular and Surface Forces* (Academic Press, New York, 2011).
 - [17] M. I. Bahloul, K. Bekkour, A. Benchabane, Y. Hemar, and A. Nemdili, The effect of temperature on the rheological behavior of polyethylene oxide (PEO) solutions, *Appl. Rheology* **23**, 13435 (2013).
 - [18] A. Volk and C. J. Kähler, Density model for aqueous glycerol solutions, *Exp. Fluids* **59**, 75 (2018).
 - [19] M. Chugunova, J. R. King, and R. M. Taranets, Uniqueness of the regular waiting-time type solution of the thin film equation, *Eur. J. Appl. Math.* **23**, 537 (2012).

- [20] M. Chugunova, Y. Ruan, and R. Taranets, On qualitative behaviour of solutions to a thin film equation with a source term, *J. Nonlinear Sci.* **31**, 9 (2021).
- [21] H. P. Greenspan, On the motion of a small viscous droplet that wets a surface, *J. Fluid Mech.* **84**, 125 (1978).
- [22] C. Neto, K. Jacobs, R. Seemann, R. Blossey, J. Becker, and G. Grün, Correlated dewetting patterns in thin polystyrene films, *J. Phys.: Condens. Matter* **15**, S421 (2003).
- [23] S. H. Strogatz, *Nonlinear Dynamics and Chaos with Student Solutions Manual: With Applications to Physics, Biology, Chemistry, and Engineering* (CRC Press, Boca Raton, FL, 2018).
- [24] R. S. Laugesen and M. C. Pugh, Linear stability of steady states for thin film and Cahn-Hilliard type equations, *Arch. Ration. Mech. Anal.* **154**, 3 (2000).
- [25] T. Hocherman and P. Rosenau, On KS-type equations describing the evolution and rupture of a liquid interface, *Physica D* **67**, 113 (1993).
- [26] T. Podgorski, J. M. Flesselles, and L. Limat, Corners, cusps, and pearls in running drops, *Phys. Rev. Lett.* **87**, 036102 (2001).
- [27] J. H. Snoeijer, B. Andreotti, G. Delon, and M. Fermigier, Relaxation of a dewetting contact line. Part 1. A full-scale hydrodynamic calculation, *J. Fluid Mech.* **579**, 63 (2007).
- [28] R. G. Cox, The dynamics of the spreading of liquids on a solid surface. Part 1. Viscous flow, *J. Fluid Mech.* **168**, 169 (1986).
- [29] M. Do-Quang, Wetting contact angle (2010), https://www.mech.kth.se/~luca/Micro/WettingDynamics_Minh.pdf.
- [30] J. W. M. Bush, Lecture 11: Interfacial flows: Thin films, lubrication theory (2010), https://ocw.mit.edu/courses/18-357-interfacial-phenomena-fall-2010/resources/mit18_357f10_lecture11/, MIT OpenCourseWare, 18.357 Interfacial Phenomena, Fall 2010.
- [31] A.-M. Pappa, H.-Y. Liu, W. Traberg-Christensen, Q. Thiburce, A. Savva, A. Pavia, A. Salleo, S. Daniel, and R. M. Owens, Optical and electronic ion channel monitoring from native human membranes, *ACS Nano* **14**, 12538 (2020).