Spreading of Droplets on a Solid Surface

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We discuss a class of similarity solutions to the hydrodynamic equations that describe droplets spreading under capillarity. The spreading time scale of these solutions exhibits a subtle dependence on the microscopic length scale around the contact line. We show that such solutions are linearly stable to small perturbations away from the contact line, justifying the universality of experimental spreading laws. We discuss the transition between the two macroscopic spreading regimes. Our prediction for the transition time is consistent with experimental data.

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Liquid spreading on a solid surface [1] arises in many practical situations, ranging from the design of paints to oil recovery techniques. From the theoretical side, the dynamics of the liquid-solid interface raises interesting questions involving the physics of different length scales. It is well known [2] that a traditional hydrodynamic description—the Navier Stokes equation coupled with "no slip" boundary conditions—leads to a divergence in the energy dissipated at the contact line. Another important feature is that near the contact line where the film thickness is a few angstroms hydrodynamics itself breaks down. Two remedies have been proposed for cutting off the divergence: inclusion of long range van der Waals forces [1] and relaxing the "no slip" boundary conditions. Such "slip" arises in certain physical situations, such as when the surface is porous [3] or for polymer melts [1]. There is still much controversy over how (not) to treat the breakdown of hydrodynamics [4,5].

In the special case of complete wetting fluids, droplets exhibit hydrodynamic effects characteristic of both length scales. On the macroscopic scale, there are spreading laws which are universal, independent of the physics of the contact line. "Tanner's law" [6], which applies when capillarity dominates the spreading, dictates that

$$R(t)=c_1t^{1/10}, \tag{1a}$$

$$\theta_{\rm loc}^3=c_2\dot R, \tag{1b}$$

$$\theta_M^3=c_3\dot R, \tag{1c}$$

where $R(t)$ is the radius of the droplet, $\theta_{\rm loc}$ is the contact angle near the edge of the drop, and θ_M is the maximum height of the drop divided by its radius. The last two Tanner's laws (1b) and (1c) are usually grouped together, but they are actually not the same, for (1b) depends on the detailed shape of the droplet whereas (1c) does not. When gravitational forces dominate $R(t)=r_0t^{1/8}$ [7]. Many experiments verify the universality of the exponents in these spreading laws [8–11]. In 1919 Hardy [12] discovered a purely microscopic phenomenon, that the edge of a spreading droplet emits a thin layer of fluid. This "precursor film" has been observed in many subsequent experiments [9,13].

A significant question, not requiring detailed knowledge of the physics near the contact line, is to understand the universality of the macroscopic spreading laws. Dussan [14] constructed solutions for different slip models and showed that the solutions are universal away from the contact line, other than a weak dependence on the slip length. Hervet and de Gennes [15] proposed a theory in which a van der Waals region near the contact line matches a solution of the macroscopic equations. Their work demonstrates that the Tanner law (1b) is a consequence of the matching, and moreover that the coefficient c_2 is nonuniversal. However, to date we know of no study of the effect of dynamical perturbations to the spreading.

In this Letter we study a similarity solution to the hydrodynamic equations, originally introduced by Starov [16], that describes the macroscopic droplet with time dependences given by Tanner's laws. We show that there is actually a one parameter family of these solutions, the parameter being essentially the microscopic length scale. The consequence of this is that the coefficients c_1 and c_3 in Tanner's law are nonuniversal. Next we show that the Starov solution is linearly stable to perturbations away from the contact line. This provides a *dynamic* justification for the universality of Tanner's laws. Finally we discuss the transition between the two macroscopic spreading regimes. We derive a formula for the transition time which agrees with the experimental data of Cazabat and Cohen-Stuart [11]. Our explanation of the transition combined with the stability arguments clarifies the nonuniversal characteristics observed in the experiments.

The hydrodynamic equation for the height $h(r,\varphi,t)$ of the droplet is [17]

$$h_t+\frac{\gamma}{3\mu}\nabla\cdot\{h^3\nabla(\nabla^2h)+\mathbf{F}[h,r,\varphi,t]\}=0\,. \tag{2}$$

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The derivation uses a lubrication approximation of the Navier-Stokes equation, neglecting inertial terms. Capillarity dominates the pressure field. The function F contains additional physical effects. In general, $\mathbf{F}=-(\rho g/\gamma)h^3\nabla h+\mathbf{G}$ where the first term accounts for gravitational forces, and $\mathbf{G}$ is only important near the contact line, when h is of order of the microscopic length scale.

Our first step is to construct a solution for a macroscopic droplet spreading under capillarity, so that we neglect $\mathbf{F}$. It is convenient to nondimensionalize (2) by setting $h(r)=h_0\bar{h}(r,t)$, $r=\lambda r_0\bar{r}$, and $t=(3\mu\lambda r_0/\gamma)(\lambda r_0/h_0)^3\bar{t}$, where r_0 is the initial drop radius, and h_0 is the initial height. λ is a function of the microscopic length scale, which is fixed by constraints on the similarity solution, as we discuss below. The presence of λ is a consequence of a weak dependence of the macroscopic solutions on microscopic length scale, a dependence which is expected due to the previous work of Dussan [14] and de Gennes [1]. For the remainder of this Letter, all references to macroscopic and microscopic length scales should be interpreted through this rescaling. Also, for convenience, we assume that time starts at $t=1$.

Following Starov [16], we seek a radially symmetric similarity solution to

$$h_t=-\nabla\cdot h^3\nabla(\nabla^2 h)\,. \tag{3}$$

Volume conservation constrains the similarity solution to have the form $h(r,t)=(1/t^{1/5})H(r/t^{1/10})$, which satisfies Tanner's laws. H satisfies

$$\eta/10=H^2\partial_\eta(\partial_\eta+\eta^{-1})H_\eta\,. \tag{4}$$

For h to be smooth, we require H to be even in η. Furthermore, we set $H(0)=1$ and $H_{\eta\eta}(0)=-c$, yielding a "spherical cap" $H\sim 1-\frac{1}{2}c\eta^2$ for the center of the drop.

Remarkably, there are no solutions of (4) satisfying the given boundary conditions for which H goes to zero at a finite value of η [18]. For a fixed c, $H(\eta)$ has a minimum height $\tilde{h}$ at a value of η that we denote by η_0 (see Fig. 1). Near η_0, $H(\eta)=\tilde{h}F[(\eta_0-\eta)/\tilde{h}]$, where $F(x)$ has the asymptotic behavior $F(x)\sim x^2$ for large negative x and

$$F(x)\sim x[\log(x)]^{1/3} \tag{5}$$

for large positive x (see inset). A physical droplet, unlike this similarity solution, has compact support. The only reasonable conclusion is that forces other than capillarity must become important when h is of order $\tilde{h}$. That is, microscopic interactions control the shape of the droplet to the right of η_0. Joanny [19] showed that it is possible to match the Starov solution to a van der Waals precursor film. In fact the functional form (5) near the edge of the Starov solution is the same asymptotic behavior used by Hervet and de Gennes [15] to justify the Tanner law $\dot{R}\sim\theta_{\rm loc}^3$. Indeed the Starov solution also gives $\theta_{\rm loc}\sim t^{-0.3}\log(h_0/\tilde{h})$, a Tanner law with a nonuniversal logarithmic correction. Chen and Wada verified the $x[\log(x)]^{1/3}$ behavior near the edge of a spreading droplet in an experiment [10].

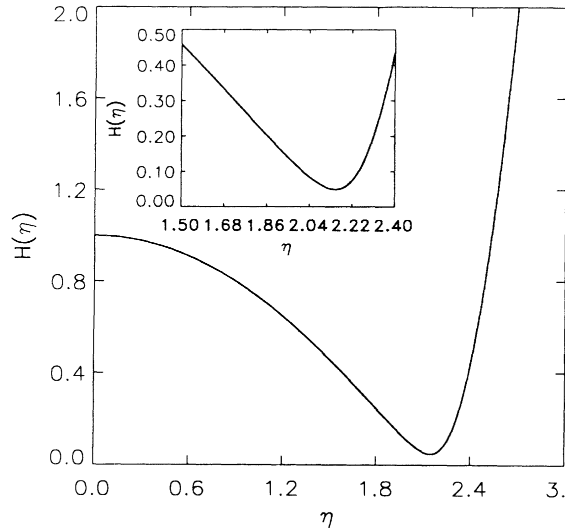

FIG. 1. Numerically integrated solution to similarity equation; here $H_{\eta\eta}(0)=-0.5$. Inset: Blowup of pinch region.

The microscopic length scale must be the same order as $\tilde{h}$. Fixing $\tilde{h}$ fixes c, and thus λ $(=1/\eta_0)$. The prefactors in the Tanner laws (1a) and (1c) are thus nonuniversal. The essential point is that straightforward dimensional analysis of the prefactors breaks down due to the presence of the additional length scale $\tilde{h}$ [20]. In Fig. 2 we show the variation of λ with $\tilde{h}$. Note that as $\tilde{h}\to 0$, $\lambda\to\infty$, indicating that the time scale becomes significantly different from that predicted by a dimensional analysis without $\tilde{h}$. In a typical experiment (a 1 mm drop spreading on a smooth surface) $\tilde{h}\sim 10^{-5}$ so that λ is around 1.15.

We now consider perturbations of h_S, the Starov solu-

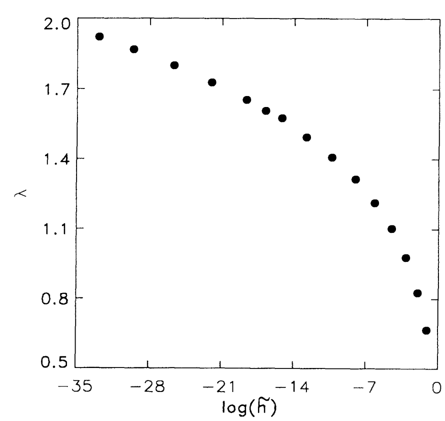

FIG. 2. λ as a function of the minimum height $\tilde{h}$ as determined by numerically integrating the similarity equation for different values of $H_{\eta\eta}(0)$.

tion modified by microscopics near $\tilde{h}$. First, we show that h_S is linearly stable to perturbations away from the contact line. Let $h(r,\varphi,t)=h_S(r,t)+w(r,\varphi,t)$ solve (3) on the macroscopic part of the drop. We assume that w is a small perturbation with support contained inside the macroscopic droplet for all time. The linearized evolution equation for w is

$$w_t+\nabla\cdot\{3wh_S^2[\nabla(\nabla^2 h_S)]\}+\nabla\cdot\{h_S^3[\nabla(\nabla^2 w)]\}=0\,. \quad (6)$$

Stability of the Starov solution follows from the fact that $\int|\nabla w|^2 dx\,dy$ dies much faster than $\int|\nabla h_S|^2 dx\,dy$ [21]. The proof is as follows: Taking the inner product of the gradient of (6) with ∇w and integrating by parts gives

$$\frac{d}{dt}\frac{1}{2}||\nabla w||_{L^2}^2=-\int 3wh_S^2(\nabla\nabla^2 h_S)\cdot\nabla\nabla^2 w - ||h_S^{3/2}\nabla\nabla^2 w||_{L^2}^2\,. \quad (7)$$

Integrating by parts and using the fact that $h_S^2\nabla\nabla^2 h_S=\hat{\mathbf{r}}r/10t$ on the support of w gives

$$\frac{d}{dt}\frac{1}{2}||\nabla w||_{L^2}^2=-\frac{3}{5t}||\nabla w||_{L^2}^2-||h_S^{3/2}\nabla\nabla^2 w||_{L^2}^2\,. \quad (8)$$

Thus,

$$||\nabla w(\cdot,t)||_{L^2}\le t^{-3/5}||\nabla w(\cdot,1)||_{L^2}$$

so that $||\nabla w(\cdot,t)||_{L^2}$ dies faster than $||\nabla h_S(\cdot,t)||_{L^2}$. Also, if

$$w(y,\varphi,t)\sim t^\gamma \sin(n\pi y)\sin(q\varphi)\,,$$

then $\gamma\sim -0.6-|P(n,q)|$, where $P(n,q)$ is a polynomial quartic in both n and q. The decay rate $-\gamma$ increases rapidly with the wave number of the perturbation.

The stability of the Starov solution justifies the selection of Tanner's laws for the macroscopic dynamics [22]. A droplet encounters many natural perturbations during its spreading, ranging from impurities on the liquid-solid interface to capillary wave excitations from the solid surface [23]. Whether the excitations have a characteristic wavelength of μm or Å is inconsequential for the macroscopic dynamics, as both die off very quickly.

The stability argument breaks down for perturbations which do not vanish at the edge of the Starov solution. Perturbations of this type are dynamically significant in a common macroscopic spreading phenomenon, the transition between the two macroscopic spreading regimes. The equation governing the transition is

$$h_t+\nabla\cdot\left(\frac{\gamma}{3\mu}h^3(\nabla(\nabla^2 h))\right)=\frac{\rho g}{3\mu}\nabla\cdot(h^3\nabla h)\,. \quad (9)$$

We consider an initial droplet in the Tanner's law regime. The gravitational term can be viewed as a source term which produces perturbations of the Starov solution.

The size of perturbation w produced by the source can be estimated by decomposing $h=h_S+w$, as above. Plugging into (9) gives that $w_t\sim(\rho g/\mu)\nabla\cdot(h_S^3\nabla h_S)$, or $w\sim V/l_{\text{cap}}^2$ where V is the volume of the drop and $l_{\text{cap}}=\sqrt{\gamma/\rho g}$ is the capillary length. The gravitational term tends to flatten out the drop, causing fluid to flow from the center of the drop to the edges. Near the edge, the perturbations compound. The size of the compounded perturbation is approximately

$$\int^t \frac{dt_0}{\tau}\frac{V}{l_{\text{cap}}^2}\sim\frac{V}{l_{\text{cap}}^2}\frac{t}{\tau}\,, \quad (10)$$

where τ is a time scale associated with the compounding. The time scale τ is independent of the volume of the droplet, and depends on both $\sqrt{\mu^2/\gamma\rho g}$ and microscopic parameters. The transition occurs when the size of the compounded perturbation is comparable to h_S or when

$$\frac{V^{3/5}t^{6/5}}{l_{\text{cap}}^2\tau}\left(\frac{\mu}{\gamma}\right)^{1/5}\sim 1\,. \quad (11)$$

This formula for the transition time is consistent with experimental data on the transition by Cazabat and Cohen-Stuart [11]. They find transition times ranging from around 50 to 500 s with volumes ranging from 37.9 to 0.35 μl, suggesting that the transition time varies approximately like $t=b/\sqrt{V}$. Moreover they discover that the prefactor b changes for fluids with different microscopic characteristics. This feature is consistent with the fact that the transition is controlled by perturbations compounding near the *edge* of the drop, where our stability analysis breaks down.

Finally we mention the work of Brochard-Wyart, Redon, and collaborators [24]. They study quasisteady solutions of Eq. (9) and compare with drop profiles measured from experiment, with excellent agreement. Their analysis shows that the drop profiles are not self-similar during the transition, complicating the time dependence. Equations (10) and (11) quantify the lack of self-similarity by considering the effects of perturbations produced by gravity explicitly.

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