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Spreading of Liquids on Highly Curved Surfaces

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wet conditions may already be occurring. With this possibility in mind, meteorologists need to develop a greater appreciation of the association between West African rainfall and the incidence of intense Atlantic hurricanes with a special focus on improved methods for monitoring and forecasting the West African weather conditions on weekly, monthly, and seasonal time scales. Coastal populations in the United States and Caribbean, as well as officials involved with disaster management, civil defense, and related activities should also be aware of the implications of increased West African rainfall for increases in intense hurricane activity. The observation and forecasting of West African precipitation and related large-scale circulations should now become a priority for all hurricane-related interests. Given the association of Sahel rainfall with patterns of Atlantic SST, wind, and pressure, it is likely that research aimed at developing explicit seasonal forecasts of Western Sahel rainfall should also contribute to significant improvements of seasonal hurricane prediction schemes.

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## Spreading of Liquids on Highly Curved Surfaces

DAVID QUÉRÉ, JEAN-MARC DI MEGLIO, FRANÇOISE BROCHARD-WYART

Because of surface tension, liquid films coating fibers or the insides of capillary tubes are usually unstable and break up into a periodic array of droplets. However, if these films are very thin (of thickness in the range of tens of angstroms), they can be stabilized by long-range van der Waals forces. A simple method for making such

wetting films consists of slowly drawing the fiber out of a bath of liquid; the thickness of the film is then measured using a method based on gas chromatography. If these liquid films are thick, and are forced to flow, they may then not break up: the instability becomes “saturated.”

**E**VEN THOSE WHO ARE FRIGHTENED BY SPIDERS MAY WONDER at the architecture of their webs. For instance, *Aranes diadematus*, the common diadema garden spider, builds a

radial structure (at the center of which the spider usually stands) and then superimposes a circumferential network consisting of capture threads. When these threads are extruded from the spinneret, they are uniformly coated with a sheath of glue that spontaneously breaks up into droplets upon which the spider’s victims become trapped. The instability of the liquid sheath has been used by spiders for hundreds of millions of years but has been studied by scientists for

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only one century. In this article, we will show how this old problem has raised new interests in contemporary physics.

Joseph Plateau (1801–1883), a Belgian physicist also known for his work on soap films, was the first to study the instability of cylindrical films (1). [More generally, liquid jets (2), annular films on fibers or in capillary tubes, and liquid ridges on solids are all prone to this type of instability.] Plateau understood that the instability of these films is driven by the liquid surface tension. When the free surface of a liquid cylinder undulates with a wavelength  $\lambda$ , its area decreases (3), provided that  $\lambda$  is larger than the circumference of the cylinder ( $2\pi R$  for a liquid jet of radius  $R$ , or  $2\pi b$  for a film of thickness  $e$  on a fiber of radius  $b$  for  $e \ll b$ ). Although the observed longitudinal curvature (Fig. 1) of the film should oppose the growth of the instability, the curvature associated with the cross-sectional area of the column, which is larger than the longitudinal curvature, actually governs the growth of the instability. The Laplace pressure is higher in the troughs than in the crests and thus the instability can develop.

In a series of papers written between 1878 and 1892 (1), Lord Rayleigh revisited and extended the work of Plateau. He showed that the instability of cylindrical films is established with a well-defined wavelength, and thus explained the regularity in spacing of the drops that form. The observed wavelength simply corresponds to the fastest growing mode and, for a thin film coating a fiber of radius  $b$ , is  $2\pi\sqrt{2}b$ , about  $10b$  (Fig. 2).

Many papers on this subject have been published since Rayleigh's time (4), but all of them have dealt with the idea that liquid films on (or in) highly curved solid cylinders were inevitably unstable. However, after the pioneering work by Dzyaloshinskii, Lifshitz, and Pitaevskii (5), both Starov and Churaev (6) and Brochard-Wyart (7) recently predicted that films on curved solids can be stabilized by long-range forces if the films are very thin.

## Spreading of Nonvolatile Liquids

*The spreading parameter.* We first need to make some general statements about the spreading of liquids (8). To determine whether a liquid drop deposited on a flat solid surface spreads or not, one must compare the energies (per unit area) of the bare solid and of the solid coated with a layer of liquid. In the former, the energy is just  $\gamma_{SG}$ , the interfacial tension between solid and air. In the latter, two interfaces contribute to the energy, which is written as  $\gamma_{SL} + \gamma$ , where  $\gamma_{SL}$  is the interfacial tension between solid and liquid, and  $\gamma$  is the interfacial tension between liquid and air. These two energies are compared by defining  $S$ , the “spreading parameter,” as

$$S = \gamma_{SG} - \gamma_{SL} - \gamma \quad (1)$$

If  $S$  is negative, the drop spreads partially and forms an angle  $\theta_e$  with the solid given by the Young-Laplace equation

$$\cos \theta_e = 1 + S/\gamma \quad (2)$$

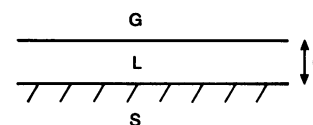


**Fig. 1.** Film of honey on a fishing line of radius  $b = 140 \mu\text{m}$ . The film is made by drawing the thread horizontally out of a large drop of honey. The instability is fully developed on the left, but still not on the right where the optimal wavelength  $\lambda$  has not yet been selected.



**Fig. 2.** Drops resulting from a thin film of silicone oil coating a nylon fiber (radius  $b = 80 \mu\text{m}$ ). The spacing between the droplets is regular and is about  $10b$  (as shown by Rayleigh) for thin films on fibers.

**Fig. 3.** Wetting film on a planar solid surrounded by air.



If  $S$  is positive, the drop spreads out completely. The resulting film is very thin, and long-range forces (the range of which can be on the order of the thickness of the film) must be introduced.

*Role of long-range forces in very thin films.* When a film is very thin, long-range forces cannot be neglected (5, 8). These forces may be electrostatic, steric, or van der Waals in nature. In the following, we restrict our attention to van der Waals interactions, which always exist between two atoms or molecules. The potential of interaction is attractive and decreases with intermolecular distance  $r$  as  $r^{-6}$ ; this is the so-called nonretarded regime. When this potential is integrated over all pairwise interactions between two half-spaces separated by a distance  $e$ , one finds a slow decreasing potential (9)

$$W(e) = -\frac{A}{12\pi e^2} \quad (3)$$

where  $A$  is an effective Hamaker constant (10), on the order of a few  $k_B T$  (where  $k_B$  is the Boltzmann constant and  $T$  is temperature). If  $A$  is positive, the interaction is attractive. ( $A$  is always positive between two identical bodies, which explains why particles in solution generally flocculate.)

In the case of a liquid film deposited on a solid surface, the two half-spaces are different (solid and gas) (Fig. 3), and the Hamaker constant can be either positive or negative. In wetting conditions,  $A$  is negative: solid and gas repel each other through liquid. The effect of long-range forces is then to make the film thicker, since  $W(e)$  has a minimum for an infinite liquid thickness ( $e = \infty$ ). One can determine the sign of  $A$  from approximate combining relations (10):  $A \cong A_{SV} + A_{LL} - A_{LV} - A_{SL}$ , where the  $A_{IJ}$  is the Hamaker constant between media  $I$  and  $J$ .  $A_{IJ}$  is proportional to the product of the densities of phases  $I$  and  $J$  and to the product of their polarizabilities  $\alpha_I \alpha_J$ . Because the density of the gaseous phase is generally negligible,  $A$  is negative when the polarizability of the solid is larger than that of the liquid. Therefore, a solid of high surface energy (that is, of large  $\alpha_S$ ), such as metal or clean glass, should be wet by all the usual liquids.

*The disjoining pressure.* The disjoining pressure  $\Pi_d$  introduced by Deryaguin in 1940 (11), can be derived from  $W(e)$ .

$$\Pi_d(e) = -\frac{dW}{de} \quad (4)$$

$\Pi_d(e)$  is the pressure that must be applied on a film to maintain it at constant thickness  $e$ . In wetting conditions ( $A < 0$ ),  $\Pi_d(e)$  is positive. This pressure can be supplied by gravity [wetting film climbing a vertical wall (12)] or by the Laplace pressure induced when the solid is curved (for example, a wetting film on a fiber or in a capillary tube).

## Spreading on Fibers

*Stabilizing effect of van der Waals interactions.* In wetting conditions ( $A < 0$ ), long-range forces tend to thicken liquid films because  $W(e)$  is minimum for an infinite thickness of the wetting film. On fibers (13), the situation is different because of the curvature of the solid surface; to increase the thickness of a film from  $e$  to  $e + \Delta e$  requires an additional surface energy of  $2\pi\Delta e\gamma$  per unit length. In wetting conditions, therefore, the thickness of liquid films on fibers cannot diverge and remain small because of this competition between disjoining and Laplace pressures (6, 7).

For a very thin, cylindrical film on a fiber, the internal pressure  $p$  is composed of two terms, the Laplace pressure and the pressure due to long-range interactions, which gives

$$p = \frac{\gamma}{b + e} - \Pi_d(e) \quad (5)$$

where  $b$  is the fiber radius.  $\Pi_d(e)$  can be derived from Eqs. 3 and 4, where we have introduced a convenient length,  $a$  (on the order of 1 Å), by setting  $A = -6\pi\gamma a^2$ .

The condition for stability of this annular film is that  $p$  is an increasing function of  $e$

$$\frac{\partial p}{\partial e} > 0 \quad (6)$$

which implies small film thicknesses

$$e < e_c = a^{1/2}b^{1/2} \quad (7)$$

For fibers with  $b$  in the range of 10 to 100  $\mu\text{m}$ , a wetting film should be stable if its thickness is smaller than a few hundred angstroms. Of course, inequality 6 has no solution if the system is nonwetting ( $A > 0$ ) or if the film is too thick [ $\Pi_d(\infty) = 0$ ]; in other words, a thick film remains unstable.

*Spontaneous spreading of a drop on a fiber.* When a drop is deposited on an infinite fiber, it should spontaneously spread if the spreading parameter is larger than a threshold value  $S_c$  (7), which is slightly but strictly positive [ $S_c$  decreases with  $b$ , and for a plane ( $b = \infty$ ) the spreading transition occurs for  $S_c = 0$ , as seen above]. When  $S$  is smaller than  $S_c$ , the liquid only partially wets the fiber (14), forming an angle of contact (which can be equal to zero, unlike the contact angle of a drop on a planar surface. For  $S$  larger than  $S_c$ , the thickness of the film results from a competition between spreading (expressed by  $S$ ) and thickening long-range effects (expressed by  $A$ ), but the film is generally of molecular thickness.

On a fiber of finite length, the volume of the drop generally exceeds the volume of this microscopic film, which means that the drop should coexist with the wetting film. For this equilibrium to exist, the pressures of both the drop and the film should be equal. If the drop is large enough to be considered of zero internal pressure, then, given  $p$  of the film (Eq. 5), one can calculate:

$$e_0 = a^{2/3}b^{1/3} \quad (8)$$

where  $e_0$  (on the order of 100 Å) is less than  $e_c$  (Eq. 7). Between  $e_0$  and  $e_c$ , the film is metastable.

To verify the existence of such microscopic films, we performed the following experiment (15). Two drops of a nonvolatile spin-finish oil (a lubricant used in spinning) were placed on a horizontal nylon fiber of radius  $b = 10 \mu\text{m}$ . Because this oil wet the fiber, conditions  $A < 0$  and  $S > S_c$  were fulfilled. The two drops were of different sizes and were placed very close to one another.

At first, nothing seemed to happen, but microscopic wetting films began to spread from the four menisci. Two of these menisci finally

joined, and the drops were linked by a thin, annular channel. The small drop, which had a larger  $p$ , slowly emptied into the large drop, by way of the macroscopically invisible channel (16). This is very similar to the classical problem of two soap bubbles of different size linked by a small pipe. From the kinetics of this process, we can estimate the thickness of the wetting film to be on the order of 200 Å, which is a little large compared with the predictions of Eq. 8 (on the order of 60 Å). This difference may be due to the fluorescent dye dissolved in the oil, the effect of which could be to increase  $a$ . Nevertheless, this simple experiment can be used to check whether a fiber is wetted or not by a given nonvolatile liquid.

This experiment also gives a qualitative feeling for the dynamics of these microscopic films. We calculated (17) that the diffusion rates that govern the progression of the film are extremely slow (the first centimeter is wetted in at least 1 day). We decided to make such films instead of letting them spontaneously spread.

*Making wetting films.* A very simple way to make an annular film on a fiber consists of drawing the fiber at constant velocity  $V_0$  out of a bath of liquid. At low velocity, the thickness  $e$  of this film is proportional to  $b$ , the fiber radius, and increases with the capillary number  $Ca$  ( $Ca = \eta V_0/\gamma$ , where  $\eta$  is the liquid viscosity). The exact law was first derived in the 1940s by Landau and Levich (18) and Deryaguin (19):

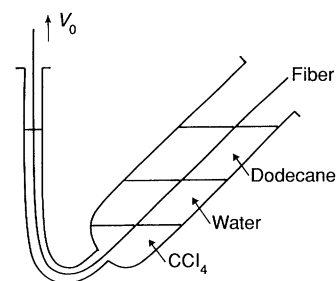
$$e = 1.33bCa^{2/3} \quad (9)$$

This equation should be valid only at intermediate  $Ca$  ( $10^{-5} < Ca < 10^{-2}$ ) (20, 21). In this regime, even if the fiber is vertically withdrawn,  $e$  does not depend on gravity, because gravitational pressure is small compared to Laplace pressure. The film becomes thinner as the fiber moves because the pressure inside the film is larger than in the unperturbed part of the meniscus (where it is zero). As long as the film is thick enough, the pressure in the film (Eq. 5) is dominated by the Laplace term  $\gamma/(b + e)$ , which causes the thinning, and gives rise to Eq. 9.

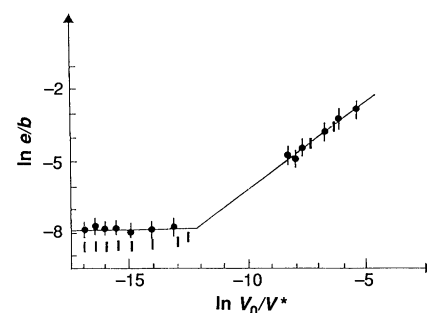
For high capillary numbers, the entrained film is thick and there are inertial effects. In this case, there is no analytical solution.

At very low capillary numbers, the entrained film is so thin that the long-range interactions may not be ignored; disjoining pressure must be considered in the expression of the internal pressure  $p$  of the film (Eq. 5). The film can then be in equilibrium with the meniscus,

**Fig. 4.** Experimental setup for making and measuring very thin films on fibers. The glass U-tube is about 4 cm high.



**Fig. 5.** Logarithm of the entrained thickness of the dodecane film as a function of the logarithm of the capillary number. The rectangles correspond to nylon fiber, and the circles to polyester fiber. Data points between  $\ln V_0/V^* = -7.5$  and  $-12$  were not obtained because they were out of the range of the motor.





and there is no more drainage. So below a certain capillary number, the thickness should no longer depend on  $Ca$ : the fiber carries a wetting film, the thickness of which is given by a coexistence condition between the film and the bath (of zero internal pressure). Hence we find again the result of Eq. 8, which gives the expression for the thickness of such a film in equilibrium with an infinite reservoir.

To verify this point, we ran a smooth fiber (either nylon or polyester, of radius  $b = 9.5 \mu\text{m}$ ) successively through three layers of liquid in a glass U-tube (Fig. 4) (22): first pure dodecane, then triply distilled water, and finally, carbon-tetrachloride ( $\text{CCl}_4$ ). As soon as the fiber was entrained (by a stepping motor), a film formed at the dodecane-water interface. Then it passed through the water layer and finally dissolved in  $\text{CCl}_4$ . The motor was stopped after about 15 cm of fiber had passed through all layers, and the  $\text{CCl}_4$  phase was picked up. We measured the fraction of dodecane in the  $\text{CCl}_4$  by gas chromatography (GC), using a flame ionization detector. The average thickness of the film could then be derived.

The results are displayed in Fig. 5. At high velocities (corresponding to  $V_0$  between 0.7 and 14 cm/s), the system is in the hydrodynamical regime:  $e$  increases with  $V_0$ , following a law in good agreement with the predictions of Deryaguin (Eq. 9). The exponent  $\pm$  SE that we determined was  $0.69 \pm 0.05$ , to be compared with  $2/3$ . However, the numerical coefficient was 1.75 instead of 1.33, probably because of the presence of surfactant at the oil-water interface: the film is then thicker because the drainage is less efficient (23).

At low speed (between 1 and 100  $\mu\text{m/s}$ ),  $e$  is independent of  $Ca$ : the system is in the wetting van der Waals regime. The films are thin because of the low value of the Hamaker constants due to the presence of water: we find  $e_{\text{nylon}} = 24 \pm 4 \text{ \AA}$  and  $e_{\text{polyester}} = 34 \pm 4 \text{ \AA}$ , in good agreement with values deduced from the literature (respectively, 27 and 32  $\text{\AA}$ ). The film on the polyester fiber is slightly thicker, probably because this solid is more polarizable than nylon. This difference in wetting behavior can be measured thanks to the extreme sensitivity of GC: it is possible to detect films that are 5  $\text{\AA}$  thick on an entrained fiber 20 cm long.

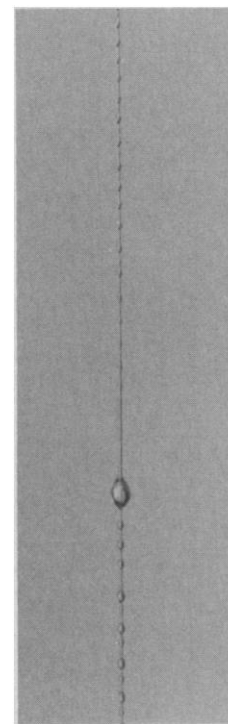
These two simple experiments seem to confirm the possible existence of stable microscopic films on fibers. All the arguments that we have given for fibers should also be valid in capillary tubes (24). For example, the thickness of a wetting film in contact with a drop trapped in a small tube (radius  $b$ ) is given by the equilibrium between internal pressures  $[-\gamma/(b-e) - \Pi_d(e)$  for the film and  $-2\gamma/b$  for the drop], and thus still is  $e_0 = a^{2/3}b^{1/3}$  (Eq. 8). Similarly, this film should be stable up to thickness  $e_c$  (Eq. 7).

## Influence of a Flow on Rayleigh Instability

When a vertical fiber is coated with liquid, the film flows by gravity. Can this flow perturb the growth of the instability, since the film is now thick enough ( $e \gg e_c$ ; Eq. 7) to be a priori unstable? We vertically withdrew a fiber from a bath of viscous oil (25), thus entraining a film, the thickness of which we could vary by changing the fiber velocity.

The behavior of the film depends on the radius of the fiber and on the velocity of the fiber withdrawal rate  $V_0$ : (i) When  $V_0$  is large ( $Ca > 10^{-2}$  for a fiber radius of 300  $\mu\text{m}$ ) the film is thick and the instability does not seem to be perturbed by the flow: drops appear quickly and fall down along the fiber. If one drop is slightly larger than the others (Fig. 6), it falls faster and in passing swallows the rest. But it cannot grow indefinitely, because it leaves a film behind itself. This film in turn breaks into droplets, and a new cascade of events begins. (ii) When the film is initially thin enough, it is

Fig. 6. In spite of the flow, a thick film is unstable on a vertical fiber (here, the initial thickness of the film was 100  $\mu\text{m}$  on a fiber of 90- $\mu\text{m}$  radius). Because small differences in droplet sizes are amplified, a large drop forms, "eating" all the other ones. It leaves behind it a film, which can be seen breaking into droplets. For thin films on thick fibers (for example,  $e$  smaller than 15  $\mu\text{m}$  on a fiber of 300- $\mu\text{m}$  radius), no drop formation (nor varicosities) can be seen (see text).



apparently stable. The flow prevents drops from developing. If the flow is stopped by extending the fiber horizontally, the instability reappears. By recording the thickness of the film versus time, we have seen that below a certain thickness ( $e_i$ ) there were no drops;  $e_i$  is an increasing function of the radius  $b$  of the fiber. (Therefore, to directly observe the phenomenon, thick fibers should be used: for example, for  $b = 300 \mu\text{m}$ , we measured  $e_i = 17 \mu\text{m}$ .) We experimentally determined that  $e_i$  scales as  $b^3$ .

The variation in behavior of these films is compatible with a theory of saturation of Rayleigh instability, such as the one recently developed by Frenkel *et al.* (26). When the film has coated the fiber, the instability develops immediately. The interface begins to undulate, and crests and troughs appear. But the flow, which we found to be a Poiseuille flow (27), causes the points at the interface to be convected at different velocities: that is, points on a crest move faster than points in a trough. The interface is distorted, and highly curved regions form. The surface tension opposes the creation of such regions and restores the interface; the instability cannot develop.

In this nonlinear scenario (which should only happen when the liquid layer is thin enough), the interface will not be smooth, but should ripple slightly in a way that Sivashinsky (28) showed to be spontaneously turbulent. In our case, where  $e$  and  $b$  are both small, the amplitude of this disordered ripple is probably microscopic, so that we only see a spectacular consequence of the gravitational flow: there are no more drops.

## Conclusions

We have shown two different ways to prevent the Rayleigh instability from developing on fibers coated with a liquid. If the liquid film is very thin (on the order of 100  $\text{\AA}$ ), long-range forces can stabilize it. If the liquid film is thicker (on the order of 1  $\mu\text{m}$ ), one can prevent the unstable sheath from breaking up by holding the fiber vertically and thus saturating the instability.

The study of the wetting of fibers has important implications in optical fiber processing, in textile spinning, and in the physical

chemistry of modern composites reinforced with carbon fibers. The saturated Rayleigh instability case might have applications as a simple model from which to approach the transition towards disorder (and chaos). Lastly, because they have no edges, fibers or capillary tubes provide a very convenient geometry for studying problems such as mobile contact lines, and, consequently, contact angle hysteresis.

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2. A sheath of glue on a thread is unstable and, because liquid jets also break into droplets, the spider's filaments should themselves be unstable. Actually, the thread is very viscous when just excreted and prone to rapid crosspolymerization; at worst, its diameter is slightly modulated because of the Rayleigh instability.
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13. We consider only nonvolatile liquids. On wetting transitions on thin cylinders, see, for example: M. P. Gelfand and R. Lipowsky, *Phys. Rev. B* **36**, 8725 (1987); R. Holyst and A. Poniewierski, *Physica A* **149**, 622 (1988); J. O. Indekeu, P. J. Upton, J. M. Yeomans, *Phys. Rev. B* **40**, 666 (1989). Bacri *et al.* have described the spreading transition of a ferrofluid on a wire [J. C. Bacri, C. Frenois, R. Perzynski, D. Salin, *Rev. Phys. Appl.* **23**, 1017 (1988)].
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16. Because of this microscopic film, the series of droplets (Fig. 2) should only be a stage in the evolution of the cylindrical film on a fiber: drops should empty into the other and finally form one single sphere. Actually, this succession of events takes too long to be achieved—only one or two phagocytes can be observed.
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20. In addition to (22), three experimental papers have been devoted to the measure of the entrained thickness by a fiber out of a bath of wetting liquid: F. S. Goucher and H. Ward, *Philos. Mag.* **44**, 1002 (1922); D. A. White and J. A. Tallmadge, *AIChE J.* **12**, 333 (1966); B. J. Carroll and J. Lucassen, *Chem. Eng. Sci.* **28**, 23 (1973). The results, apparently contradictory, are in fact coherent when gathered, as in (21).
21. D. Quéré, thesis, Université de Paris VI (1989).
22. ———, J.-M. di Meglio, F. Brochard-Wyart, *Europhys. Lett.* **10**, 335 (1989).
23. This point was first made in Carroll and Lucassen (19) and later discussed by Teletzke *et al.* (11).
24. For the spreading of microscopic films in capillary tubes, in addition to (5, 21), see: J.-M. di Meglio, F. Brochard-Wyart, D. Quéré, *C. R. Acad. Sci. Ser. II* **309**, 19 (1989). For making films in capillary tubes by displacing a drop of wetting liquid (which leaves behind a film), there is abundant experimental literature, particularly from Taylor and his co-workers referenced in J. D. Chen, *J. Colloid Interface Sci.* **109**, 341 (1986). For making wetting microscopic films, see: N. F. Bondarenko, B. V. Zheleznyi, Y. A. Osipov, N. S. Ostapenko, *Kolloidn. Zh.* **39**, 241 (1977).
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26. A. L. Frenkel, A. J. Babchin, B. G. Levich, T. Shlang, G. I. Sivashinsky, *J. Colloid Interface Sci.* **115**, 225 (1987); T. Shlang and G. I. Sivashinsky, *J. Phys. (Paris)* **43**, 459 (1982).
27. A Poiseuille flow is characteristic of thin films flowing on solids: the velocity distribution across the layer is parabolic, and the mass of fluid flowing per unit time is proportional to the pressure gradient responsible for the flow and to the cube of the film thickness.
28. This result was derived to explain the chaotic waves that sometimes appear at the free interface of a liquid layer flowing down an inclined plane [first described by Kapitza; see P. L. Kapitza and S. P. Kapitza, *Collected Works* (Pergamon, New York, 1965), p. 690]. For this derivation, see G. I. Sivashinsky and D. M. Michelson, *Prog. Theor. Phys.* **55**, 356 (1980).
29. We thank P. G. de Gennes for numerous fruitful discussions.