Slip-mediated dewetting of polymer microdroplets

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Classical hydrodynamic models predict that infinite work is required to move a three-phase contact line, defined here as the line where a liquid/vapor interface intersects a solid surface. Assuming a slip boundary condition, in which the liquid slides against the solid, such an unphysical prediction is avoided. In this article, we present the results of experiments in which a contact line moves and where slip is a dominating and controllable factor. Spherical cap-shaped polystyrene microdroplets, with nonequilibrium contact angle, are placed on solid self-assembled monolayer coatings from which they dewet. The relaxation is monitored using in situ atomic force microscopy. We find that slip has a strong influence on the droplet evolutions, both on the transient nonspherical shapes and contact line dynamics. The observations are in agreement with scaling analysis and boundary element numerical integration of the governing Stokes equations, including a Navier slip boundary condition.

slip | contact line motion | free-surface flows | microflows | nanoflows

Unexpected flow phenomena emerge when the size of a liquid system is reduced below a length scale typically on the order of a few, to hundreds of nanometers (1–3). Approaching this scale, effects associated with interfaces become increasingly important. One such effect is slip, wherein fluid slides along a solid boundary. Flow of single-component (4, 5) and complex fluids (6, 7) in micro- and nanochannels, as well as dewetting (8, 9) and interfacial instabilities (10) of molten polymer films, are systems and phenomena in which slip may have an effect. The present work demonstrates that the relaxation of micrometer-sized droplets in contact with a solid planar surface is strongly influenced by slip. The observed dewetting dynamics exhibits an unexpectedly rich phenomenology of transient droplet shapes.

The empirical no-slip boundary condition assumes no relative motion between liquid and solid at the phase boundary. This condition was historically assumed to be valid in all practical cases (3). However, Huh and Scriven discovered (11) that the no-slip boundary condition leads to infinite viscous dissipation at the tip of a liquid wedge, and thus implies that a contact line would never move—infinite force is required to overcome infinite dissipation. In common experience we are surrounded by liquid/vapor interfaces moving along solid surfaces, from water droplets on a wind screen, to the displacement of air by liquid through a capillary or porous medium. This apparent paradox of contact line motion has attracted the attention of many researchers over at least the last four decades (11–18).

Various mechanisms have been proposed to explain the existence of contact line motion. Precursor film models (13, 19–25) circumvent the Huh–Scriven paradox as they neglect the existence of a proper contact line. Models beyond a continuum hydrodynamic description include molecular transport mechanisms at the contact line (15, 26, 27). Another commonly used approach to avoid the paradox is to allow for a slip boundary condition at the substrate (11, 12, 18, 28–31). Importantly, all of these models used in previous studies (27, 32, 33) have in common a characteristic length scale, for example the extension of the slipping region (18, 30) or the molecular hopping length (15,

27). This length scale is typically of nanometric size yet much smaller than the lateral extension of the interface, which could be that of a millimetric droplet or meniscus. For this wide separation of length scales, being at least five orders of magnitude, the deformation of the interface by viscous stresses is noticed only in the direct vicinity of a moving contact line. On a macroscopic scale, the liquid interface remains close to a quasi-static shape (17, 34, 35). Millimetric sessile drops relaxing on a plane surface, for instance, are described by a sequence of spherical caps with a slowly changing apparent contact angle. In such a multiscale system, the microscopic length has only a weak (logarithmic) effect on the dynamics (13, 16).

Recently, the no-slip hypothesis has been critically assessed. Experimental techniques (1–3) to measure slip lengths b —defined as the distance beyond the solid over which a linear extrapolation of the liquid velocity field reaches zero (36)—have reached nanometric resolution. Values of b for small-molecule liquids on the order of tens (1–3, 37–40) up to a couple of hundred nanometers (41–43) are now reported. Polymer melts, containing chain-like molecules which can be highly coupled to one another (13, 44, 45), may show slip lengths from one up to tens of micrometers (9, 10, 46–51). The microscopic mechanisms responsible for such large slip lengths are not clear in all cases (52), e.g., for unentangled polymers dewetting from chemically similar substrates as used here (51). Whereas investigations into the molecular origin of these disparate and relatively large slip lengths continue, these self-assembled monolayers (SAMs) provide an ideal set of surfaces to study the impact of slip

Significance

Contact lines form at phase boundary intersections, quintessentially liquid/vapor interfaces at solid surfaces. Whereas classical hydrodynamic models predict that contact line motion requires infinite energy, common observations of moving droplets show that huge amounts of energy are unnecessary. Slip, wherein a fluid slides along a solid boundary, offers relief of such divergences, and has gained attention with the developing fields of micro- and nanofluidics. This article focuses on contact line motion of retracting liquid droplets with micrometric dimensions. Slip is tuned by changing a nanometric substrate surface layer. The resulting contact line motion and droplet evolutions are hugely influenced by slip, thus offering insights on the question: How do contact lines move?

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on small-scale interfacial flows. In contrast to systems with a wide separation of length scales, a qualitatively different interfacial dynamics may be found when system sizes become comparable to the slip length.

To explore the effect of slip on small-scale wetting flows, here we study polymer microdroplets dewetting from SAMs. The slip lengths involved are comparable to the typical droplet heights. Strikingly, we find that slip significantly influences the transient droplet profiles, which are nonspherical and thus not quasi-static (Fig. 1*A*). Velocities of the receding contact lines are orders of magnitude faster than expected for no-slip systems. The good agreement between the experimental results and hydrodynamic modeling, including a Navier slip boundary condition, shows that slip is the dominating factor in the shape evolution and contact line motion of the small dewetting droplets in our experiments. Any other processes occurring at the contact line play a minor role.

The experiments were performed using spherical cap-shaped polystyrene (PS) microdroplets as the initial state, with flows driven by unbalanced capillary forces. Because of the high viscosity of the nonvolatile PS melt, droplets with a typical diameter of 1 μm reach their new equilibrium conformation on the order of several minutes to hours, and can thus be monitored with high spatial resolution using atomic force microscopy (AFM). Prepared in the glassy state with a low contact angle of $\theta_0 = 9 \pm 3^\circ$ (24), the droplets are transferred onto Si wafers precoated with SAMs of octadecyl- or dodecyltrichlorosilane (OTS and DTS, respectively). In the liquid state, the PS/air interfaces on these two chemically similar SAMs exhibit the same equilibrium contact angles, $\theta_\infty = 62 \pm 3^\circ$. Despite the high similarity of OTS and DTS, the slip lengths of the PS melt on these SAMs are strikingly different: $b_{\text{OTS}} = 160 \pm 30$ nm and $b_{\text{DTS}} = 1,500 \pm 200$ nm are reported in ref. 51. These slip lengths were extracted from the rim shape and velocity of a dewetting PS layer with an initially constant thickness (50, 53). See *Materials and Methods* for further details on sample preparation and experimentation.

When heated above the glass transition temperature, we observe the contact line to move inward, while volume conservation ensures that material is collected toward the center of the droplet. Fig. 1*B* and *C* shows full sequences of axisymmetric droplet profiles, $h(r, t)$ with r and t the radial coordinate and time, respectively, observed during the dewetting process on OTS- and DTS-covered substrates. The shapes highlighted in Fig. 1*A* were chosen such that

the transient profiles deviate maximally from a spherical cap, as demonstrated in Fig. 1*B* and *C*, *Insets* (gray lines).

The PS droplet dewetting from OTS in Fig. 1*B* transiently forms a ridge and for some time exhibits a positive (inward) curvature at the droplet center. This qualitative feature was observed previously using numerical integration of a 2D thin-film equation including a precursor film (22). Additionally, the central droplet height does not change significantly until the width of the ridge is comparable to the time-dependent contact line radius, $R(t)$ (Fig. S1). In contrast to the evolution on OTS, the PS droplet dewetting from DTS does not show a pronounced ridge. Furthermore, at the earliest accessible experimental time (several minutes), the central droplet height is already increasing on DTS as seen in Fig. S1. At late times, for both OTS and DTS, the curvature is always negative (outward) as the droplets relax to their final spherical cap shapes with the same contact angle θ_∞ . In addition to the equilibrium contact angle θ_∞ , surface tension γ and viscosity η being identical for the PS droplets on OTS and DTS in Fig. 1, the initial contact line radii $R_0 = R(0)$ and initial contact angle were similar. The slip lengths, b , however, differ by an order of magnitude on these two substrates. The qualitative differences in the evolution are therefore expected to originate from the different values of the dimensionless slip length $B = b/R_0$, as can be seen for a similar shape transition in dewetting polymer films with slip (9, 49). Indeed, a gradual disappearance of the ridge at any point in the temporal evolutions can be observed by increasing B for PS on OTS—decreasing R_0 in this case, with identical $b, \theta_0, \theta_\infty$, a ridge can no longer be detected for $R_0 \lesssim 2.7$ μm (Fig. S2).

To investigate theoretically whether slip is the dominating factor that controls the dewetting of PS droplets, we numerically integrated the governing fluid mechanical equations. Inertial effects are neglected because the Reynolds number $\text{Re} = \rho R \dot{R} / \eta \approx 10^{-19}$, involving the mass density ρ and contact line velocity $\dot{R} = dR/dt$, is much less than unity. The flow is controlled by a balance of viscous and capillary stresses only. Solutions to the governing Stokes equation, $\nabla p = \eta \nabla^2 \mathbf{u}$, and incompressibility condition $\nabla \cdot \mathbf{u} = 0$ are numerically computed using a boundary element method (54). Here, p is the scalar pressure field and $\mathbf{u}$ is the velocity field. The normal stress component at the curved PS/air interface is balanced by surface tension according to Laplace's law, which reads $2\eta \partial_n u_n - p = 2\gamma C$, where C is the mean curvature of the liquid/vapor interface, and where ∂_n denotes the directional derivative normal to this interface. Hydrostatic contributions to the pressure, elasticity of

Fig. 1. (A) Experimental AFM data for 10.3-kg/mol PS microdroplets dewetting from OTS (*Top*) and DTS (*Bottom*) SAMs. (Scale bars: horizontal, 2 μm ; vertical scale according to gray lines in *B* and *C*.) (B) Experimental height profile evolution of the PS droplet dewetting from OTS shown in *A*. Time between subsequent lines is ~ 10 min. (C) Experimental height profile evolution of the PS droplet dewetting from DTS shown in *A*. Time between subsequent lines is ~ 4 min. (*Insets*) Height profiles, with the radial coordinate r and height profile $h(r, t)$ scaled by the contact line radius $R(t)$ and central droplet height $h(0, t)$. Inset color schemes as in the main figures.

the PS melt, and corrections of the normal stress by van der Waals forces are consistently neglected in the bulk equations. To account for slippage relative to the substrate, we impose a Navier slip condition, representing a balance of stresses parallel to the substrate. The radial velocity component u_r at the substrate then satisfies

$$\kappa u_r|_{z=0} = \eta \partial_z u_r|_{z=0}. \quad [1]$$

Eq. 1 allows for a definition of the slip length, $b = \eta/\kappa$, where κ is a constant friction coefficient. As a boundary condition on the height profile, we impose a microscopic contact angle equal to the final contact angle θ_∞ at the contact line position for all times (17, 18). This constant angle assumption is not strictly correct, yet, with the small variation observed in the experimental evolution, it is a reasonable approximation [examples for $\theta(t)$ are shown in Fig. S3]. In the following, we refer to this as the Navier–Young model (NYM). Given θ_0 and θ_∞ as control parameters, only two independent length scales can be found in the NYM for dewetting microdroplets. The droplet size represents the first length scale, e.g., R_0 , whereas the second one is the Navier slip length b . Rescaling all lengths with R_0 and using a dimensionless time $T \equiv \gamma t \eta^{-1} R_0^{-1}$, we end up with the three independent dimensionless control parameters: θ_0 , θ_∞ , and the rescaled slip length B defined above. The associated dimensionless contact line radius is $\mathcal{R}(T) = R(t)/R_0$, with velocity $\dot{\mathcal{R}} = d\mathcal{R}/dT$.

In Fig. 2 A and B we present temporal profile evolutions obtained from the NYM for $B=0.030$ and $B=0.47$. The droplets have geometrical and physical parameters that were chosen to match the experimental droplets shown in Fig. 1. Remarkably, these computed droplet evolutions reproduce the curvature inversion of Fig. 1B and its absence in Fig. 1C, confirming that slip plays a major role in determining the transient shape. In Fig. 2, we also add experimental data from Fig. 1 for the specific profiles that maximize the deviation from a spherical cap. Those experimental profiles show good quantitative agreement with the NYM profiles, with maximum relative deviations of $\sim 5\%$. Comparison with other experiments for different droplets, as well as for different times for the droplets presented in Fig. 2, shows similar agreement. We note that the deviation between experiments and the NYM is consistent with the typical experimental uncertainties, mainly comprising overshoot due to the large slopes encountered (55) (Fig. S4). Identifying the numerically computed shapes of Fig. 2A with the measured ones for the droplet on OTS of Fig. 1B, we note that $B=0.03$ corresponds to a slip length $b_{\text{OTS}} = 160$ nm, which is exactly the value measured in the hole-growth dewetting experiment (51), as given above. For the droplet of Fig. 2B, $B=0.47$ corresponds to a slip length $b_{\text{DTS}} = 2,250$ nm for the experimental droplet of Fig. 1C; this is similar to the measured slip length $b_{\text{DTS}} = 1,500 \pm 200$ nm in ref. 51.

To understand the different shape evolutions in terms of the flow structure inside the droplets, we computed the flow fields from the NYM. The numerical solutions, superimposed on the 3D renderings shown in Fig. 2C and D, reveal substantial qualitative differences in the spatial distribution of the flow inside the droplets at the early moment when $\mathcal{R}=0.91$. As illustrated in Fig. 2C, the velocity field for small rescaled slip length $B=0.03$ is concentrated near the contact line and contains mainly shear flow. The result is an upward motion of the interface near the contact line but not in the central part of the drop. The formation of a ridge is thus observed later. In contrast to the droplet in Fig. 2A and C, the flow field for a larger rescaled slip length $B=0.47$ in Fig. 2D is more delocalized, including a significant upward flow in the central part of the droplet. We note the disparity in arrow lengths and gray scale near the droplet centers in Fig. 2C and D. The velocity field of Fig. 2D corresponds more to elongational flow throughout the droplet, with the flow profile close to the contact line more resembling a plug flow (i.e., constant radial velocity with respect to the vertical direction). These

Fig. 2. (A and B) Normalized height profiles as a function of normalized radius, at different dimensionless times, T , for numerical droplet evolutions obtained from the NYM: (A) $0 \leq T \leq 14.5$, rescaled slip length $B=0.030$, $\theta_0=11^\circ$, and $\theta_\infty=62^\circ$, as for the PS droplet evolution on OTS in Fig. 1B; (B) $0 \leq T \leq 5.2$, $B=0.47$, $\theta_0=7.0^\circ$, and $\theta_\infty=62^\circ$, as for the PS droplet on DTS in Fig. 1C. For both A and B experimental data from the highlighted transient profiles (gray lines of Fig. 1) are shown as squares. (C and D) Three-dimensional renderings of the droplet surfaces (note exaggerated vertical scales) with the flow fields when $\mathcal{R}=0.91$ for the droplets shown in A and B. Gray scales indicate magnitudes of the dimensionless flow velocity for various r/R_0 , averaged through the local interface height. Arrow lengths and gray scales are normalized by the respective contact line speeds, $|\dot{\mathcal{R}}|=0.16$ and 1.19 for C and D.

differences between the two early flow fields are responsible for the transient ridge formation of the $B=0.03$ droplet and its absence for $B=0.47$.

Slip not only changes the structure of the flow field in the droplet, thus controlling the morphological evolution of the free interface during dewetting, but the magnitude of slip also has a significant impact on the rate of dewetting. The capillary numbers, $\text{Ca} \equiv \dot{\mathcal{R}} \eta / \gamma = \dot{\mathcal{R}}$, of the early flows are of order ~ 1 for DTS, and ~ 0.1 for OTS, which are much larger than those typically encountered in no-slip systems (16, 17, 27, 32, 33). To quantify the impact of slip on the dewetting dynamics, we consider the motion of the contact line. For ease of comparison, we normalize the displacement of the contact line, $R_0 - R(t)$, by the total change throughout the droplet equilibration, $R_0 - R_\infty$, where R_∞ is the asymptotically reached contact line radius in the equilibrium state. The evolution of the normalized contact line displacement as a function of time for the two droplets of Fig. 1 is shown in Fig. 3A; unscaled $R(t)$ are also shown in Fig. S1.

In both the OTS and DTS cases of Fig. 3, the contact line displacement during the earliest experimentally accessible time shows a power law $R_0 - R(t) \propto t^m$. In addition, we show in Fig. 3A (Inset) the measured exponents m of 10 other PS droplets as a function of $b\Omega^{-1/3}$, where Ω is the droplet volume. Remarkably, although the flow structure for different cases can be significantly

Fig. 3. (A) Experimental early-time dynamics of the normalized contact line radius, for the two PS droplets of Fig. 1, dewetting from OTS and DTS substrates. Solid lines represent power laws $\sim t^m$, with exponent $m = 0.54$. (Inset) Such exponents measured for all studied droplets for which an early-time dynamics was accessible, as a function of $b\Omega^{-1/3}$, where Ω is the droplet volume; the dashed lines indicate $m = 0.5$ and $m = 1$. (B) Numerical early-time dynamics obtained from the NYM using various $B = b/R_0$. Along with unit initial radius, parameters used were $\theta_0 = 9.9^\circ$, $\theta_\infty = 62^\circ$, leading to $R_\infty = R_0/\Omega \approx 0.54$.

different, the observed value of m is well represented by the average on all droplets $\langle m \rangle = 0.48 \pm 0.08$, with the error representing the SD. A power-law scaling of the contact line displacement in time similar to the experiments is obtained from the NYM (Fig. 3B) for rescaled slip length $0.03 \lesssim B \lesssim 1$, corresponding to the experimental range of B . Deviations from an ideal power law become clearly visible for $B = 0.005$ and $B \geq 10$.

In the numerical results of the NYM for both droplets represented in Fig. 2, we observe that the early-time frictional dissipation is concentrated near the contact line (Fig. S5). At early times, we thus assume the capillary driving power to be significantly dissipated by friction in the contact line region. Because the spreading parameter (14) reads $S = \gamma(\cos \theta_\infty - 1)$, the typical driving power is $\sim SR_0\dot{R} \sim -\gamma R_0\dot{R}$. On the other hand, because the frictional stress scales as $\sim \kappa\dot{R}$, the frictional dissipation power is $\sim \eta\dot{R}^2 R_0 \Delta/b$ (see Eq. 1), where $\Delta(t)$ is the typical horizontal extension of the flow region where friction is important. Supported by an argument based on a thin-film approximation of the flow and by the experimentally measured profiles near the contact line (Supporting Information and Fig. S6), we impose a proportionality between the vertical and horizontal extents of the slip region. Conservation of volume thus implies a scaling $R_0\Delta^2 \sim R_0(R_0 - R)^2$. Balancing the capillary driving power and the frictional dissipation power (56) thus leads to $\dot{R}(R - R_0) \sim \gamma b/\eta$, which can be integrated into

$$R_0 - R(t) \sim \left(\frac{\gamma b t}{\eta} \right)^{1/2}, \quad [2]$$

consistent with the values of m reported above in both experiments and numerics.

The scaling argument provided above assumes that friction at the substrate is a dominant dissipation mechanism, in addition to viscous processes (29). Using the NYM, we determine that friction at the substrate accounts for $\sim 60\%$ of the overall energy

dissipation for $B = 0.03$ (OTS), and $\sim 40\%$ for $B = 0.47$ (DTS) during the early-time regime. Although these are not necessarily dominating, it is clear that frictional dissipation is largest near the contact line where friction dominates over viscous dissipation (Fig. S5). In contrast to the slip friction dominated scaling derived above, no-slip hole-growth dewetting is known to show a linear power law in time (45) (with logarithmic corrections). Similarly, following the arguments preceding Eq. 2 but with the friction replaced by viscous shear dissipation and adding a regularization mechanism appropriate to the no-slip situation, a linear power law $R_0 - R(t) \sim t$ would be obtained. This shear dissipation dominated scaling prediction falls well outside our experimentally observed range of exponents in Fig. 3A (Inset), suggesting that dissipation in the contact line region is dominated by friction at early times.

For late-time dynamics of dewetting microdroplets, the precise value of the rescaled slip length B is also of great importance. In Fig. 4A and B, we show the displacement $R(t) - R_\infty$ of the contact line with respect to the final contact line radius R_∞ . As expected from a linear response, the contact line radius $R(t)$ saturates exponentially to the final equilibrium value R_∞ . The same features

Fig. 4. Late-time dynamics of normalized contact line radius for (A) PS droplets dewetting from OTS covered substrates, with $2.7 \mu\text{m} \leq R_0 \leq 5.3 \mu\text{m}$; (B) PS droplets dewetting from DTS covered substrates, with $1.8 \mu\text{m} \leq R_0 \leq 7.7 \mu\text{m}$; (C) numerical results from the NYM, with dimensionless slip lengths B as indicated on the curves. (D) Dimensionless relaxation time constant as a function of dimensionless slip length, for both the experiments and the NYM. The two lines depict the asymptotic behaviors (see text following Eqs. 3 and 4): (i) weak-slip logarithmic behavior; (ii) strong-slip constant behavior. (Insets) These recall intermediate-time droplet shapes, for the weak-slip (red substrate) and strong-slip (blue substrate) regimes.

are also clearly visible in the numerical solutions shown in Fig. 4C for various B . Furthermore, on DTS, for the smallest droplets on OTS, and at large B in the NYM, the droplets reach this late-time regime at much larger $R - R_\infty$. Interestingly, an exponential relaxation to a spherical shape is also characteristic of suspended viscous droplets (57, 58). Thus, a connection can be drawn between supported droplets with large slip lengths and free-standing droplets. In fact, by symmetry, the freely relaxing droplets are strictly equivalent to infinite-slip dewetting droplets when $\theta_\infty = 90^\circ$.

As for the early-time power law, the late-time exponential evolution can be understood from an energy balance. Close to equilibrium, the droplet shape is nearly a spherical cap, and the restoring capillary force is linear in $R - R_\infty$ (Eq. S20). The driving capillary power then scales as $\mathcal{P}_{\text{inj}} \sim -\gamma(R - R_\infty)\dot{R}$. On the other hand, the dissipation power $\mathcal{P}_{\text{dis}}$ depends on the four parameters, η , b , θ_∞ , and R_∞ and the one variable, R . By dimensional analysis (59), we can therefore write the dissipation power in the form $\mathcal{P}_{\text{dis}} \sim \eta R_\infty \dot{R}^2$, with a dimensionless prefactor that is a function of b/R_∞ and θ_∞ (recall that the latter is constant in this study). Equating the dissipation power with the driving one and integrating in time leads to

$$R(t) - R_\infty \sim e^{-t/\tau}, \quad [3]$$

$$\tau = \frac{\eta R_\infty}{\gamma} f\left(\frac{b}{R_\infty}, \theta_\infty\right), \quad [4]$$

where f absorbs the numerical prefactors missing in the scaling arguments presented above. Fig. 4D displays the experimentally measured time constants, after a rescaling according to Eq. 4, as a function of the dimensionless slip length b/R_∞ using $b_{\text{OTS}} = 160$ nm and $b_{\text{DTS}} = 2,250$ nm (Fig. 2). Numerically computed time constants from the NYM allow an estimate of the scaling function f in Eq. 4, which is logarithmically decreasing for small b/R_∞ but tends to a constant value for large b/R_∞ . Both asymptotic limits of the scaling function f can be understood from the viscous dissipation in the bulk flow during the late-time relaxation.

When $b/R_\infty \ll 1$, the dynamics can be analyzed in the framework of the classical wedge calculation (13, 16), where the slip length replaces the microscopic cutoff length scale in the logarithmic prefactor as discussed in the Introduction. In this limit, it follows for a spherical cap: $f = C_0 \ln(b/R_\infty) + C_1$, where $C_0 \approx -1.44$ for $\theta_\infty = 62^\circ$ (Supporting Information). In Fig. 4D, we obtain $C_0^{\text{NYM}} = -1.02$ and $C_1^{\text{NYM}} = -0.65$ by fitting the $B \leq 0.08$ NYM data. Although the experimental data deviate slightly (Supporting Information), the numerical results are in reasonable agreement with the analytical calculation above.

In contrast to weak slip, when $b/R_\infty \gg 1$ the assumption of a localized dissipation near the contact line, inherent to the classical wedge calculation, is violated. Friction at the substrate is negligible with respect to elongational viscous stresses, and a different retraction regime is entered. In this regime, we expect f to be independent of b/R_∞ . We find $f|_{b \rightarrow \infty} \approx 0.82$ for $\theta_\infty = 62^\circ$ in the NYM; the experiments on DTS support this finding. The

NYM value for the strong-slip relaxation time compares well with an estimate assuming viscous dissipation to occur only through elongational stresses. This simple model (Supporting Information) predicts $f|_{b \rightarrow \infty} \approx 1.05$ for $\theta_\infty = 62^\circ$.

To conclude, we have studied polymer microdroplets dewetting from substrates decorated with SAMs. The OTS SAM provides a weaker slip boundary condition compared with the DTS one, resulting in marked differences in the evolution of similarly sized droplets. Specifically, the weaker slip condition can give rise to a transient ridge. Increasing the ratio of slip length to droplet size, we observe a gradual disappearing of the ridge. These observations are explained through visualizations of the flow fields accessed through the NYM. At early times, we find that the dewetting dynamics is in agreement with a scaling argument predicting a temporal power-law evolution of the dewetted distance, with an exponent 1/2, consistent with the NYM. At late times, an exponential saturation of the contact line radius with time is observed. The time constants are in good agreement with the scaling analysis and numerical solution of the NYM. This simple system of dewetting microdroplets on different surfaces gives insights on the effects of slip in free-surface micro- and nanoflows. In the context of the Huh–Scriven paradox of contact line motion, our work offers a combined experimental and theoretical justification for slip as a major control factor in the motion of contact lines.

Materials and Methods

To prepare the nonequilibrium droplets, PS (Polymer Standards Service GmbH) with weight-averaged molecular weight 10.3 kg/mol and polydispersity index 1.03, was dissolved into toluene (chromatography grade, Merck), and spin-coated onto freshly cleaved mica sheets (grade V2, Plano GmbH). After a dewetting process in toluene-saturated atmosphere at room temperature, glassy spherical cap-shaped droplets on mica were produced with initial contact angles $\theta_0 = 9 \pm 3^\circ$, and contact line radii $2 \mu\text{m} \leq R_0 \leq 7 \mu\text{m}$ (measured using AFM; Dimension FastScan and FastScan A tips, Bruker).

Under ambient conditions, the glassy droplets were then floated from mica onto the surface of an ultraclean water bath (18 MΩ cm, total organic carbon content <6 ppb; TKA-GenPure, TKA Wasseraufbereitungssysteme GmbH), and transferred onto the SAM-coated silicon wafers [(100) crystal orientation with native oxide layer present; Si-Mat Silicon Materials]. Two types of SAMs were used, being prepared from either OTS or DTS; Sigma-Aldrich, with the self-assembly procedure and full characterization described in ref. 60. Both SAM coatings render the Si wafers hydrophobic, and lead to equilibrium PS contact angles in air of $\theta_\infty = 62 \pm 3^\circ$, as measured by AFM.

The droplets dewet when heated above the glass-transition temperature $\approx 90^\circ\text{C}$ (61). The heating stage on the AFM was set to 110°C and AFM was used to measure in situ height profiles of the dewetting microdroplets. This annealing temperature is low enough to ensure no loss of PS due to evaporation or degradation; volume conservation was verified. Finally, the capillary velocity of our system was measured using the stepped-film method (62) to be $\gamma/\eta = 0.07 \pm 0.01 \mu\text{m min}^{-1}$ at the experimental annealing temperature.

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