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Growth of Holes in Liquid Films with Partial Slippage

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We derive an expression for the temporal development of circular holes formed spontaneously in dewetting liquid films. Our formula is shown to interpolate between the known limiting cases of perfect sticking (purely viscous dissipation) and full slippage of the film on the substrate. Good agreement between experiment and theory is found. By fitting the theroetical curves to the data, we can derive the relative importance of slip in the dewetting process.

The rupture of a thin liquid film on a substrate which is not wetted by the liquid is frequently observed to proceed by the nucleation of circular dry patches ("holes") which grow with time, until finally the film has been transformed into a pattern of sessile droplets.[1,2] In the present note, we want to concentrate on the dynamics of growth of these circular holes. The energy released by the dewetting process is generally distributed among viscous dissipation within the rim of the hole and the friction of slip of the film along the substrate. Theories set up so far could only account for the two limiting cases, i.e., either no-slip conditions (only viscous dissipation) or full slippage (no viscous dissipation at all). We develop here a theoretical description of the growth dynamics which includes both slip and viscous dissipation and agrees well with our observations. We demonstrate that it is possible to derive quantitatively the relative importance of friction and viscous dissipation from experimental data.

Let us first recall the equations of motion for no-slip conditions and for full slippage. The main features of a hole are a circular "dry" region the radius of which, R, grows steadily with time, and an elevated rim consisting of the material removed from the dry area.[2,3] The rim profile is characterized by its width, b, and the contact angle, θ, at the three-phase contact line. It is not relevant how b is really defined (e.g., the full width at half-maximum or the width at the base), since differences arising from geometrical definitions can be absorbed into constants which are not of interest here. When the width of the rim is small as compared to the hole radius, it is sufficient to treat the problem as quasi-two-dimensional, with x for the coordinate in the direction of dewetting (perpendicular to the three-phase contact line), and z for the coordinate normal to the substrate. Our results are thereby equally relevant for a straight receding contact line. The growth velocity $v = \mathrm{d}R/\mathrm{d}t$ is determined by balancing the dewetting force, S, with the dissipation connected to the dynamics of the rim. S is defined here as the gain in free energy upon removal of the film from the substrate.

The power of viscous dissipation in the velocity field, $\boldsymbol{v}(x,z)$, within the rim is described by

$$P_{\mathrm{v}} = \int_{\mathrm{rim}} \eta[\mathrm{rot}\ \mathbf{v}(x, z)]^2\ \mathrm{d}x\ \mathrm{d}z = v_{\mathrm{v}}^{\ 2}\ K_{\mathrm{v}}(\theta) \qquad (1)$$

where η is the viscosity and v_{v} is the flow velocity at the three phase contact line. $K_{\mathrm{v}}(\theta)$ is a geometric factor depending on the contact angle, which describes the total viscous dissipation within the rim. As it is well-known, its value is dominated by a logarithmic divergence of the dissipated power at the three-phase contact line,[4,5] which depends only on the contact angle. Since we found the latter to be constant to a very good approximation for all stages of hole growth, K_{v} can be safely assumed to be constant during the process of growth.

The equation of motion is obtained by equating the dissipated power from eq 1 with the dewetting force, S, times the dewetting velocity, i.e., with $S(\mathrm{d}R/\mathrm{d}t)$. At no-slip conditions, we have $\mathrm{d}R/\mathrm{d}t = v_{\mathrm{v}}$,[4] and obtain

$$S = v_{\mathrm{v}}\ K_{\mathrm{v}}(\theta) \qquad (2)$$

The dynamics can thus be described by a constant friction coefficient, K_{v}, under the assumption of absence of slippage, regardless of the particular geometry of the rim profile. From eq 2, the radius of the hole as a function of time can immediately be obtained:

$$R(t) = \frac{S}{K_{\mathrm{v}}}\, t \qquad (3)$$

which is a well-known result for no-slip conditions.[5,6]

If, on the other hand, there is a certain slip of the liquid along the substrate surface, the mechanical resistance to this slip is expected to depend on the width of the rim, b. When the contact angle is constant, the height of the rim is expected to be directly proportional to its width. It is easy to see that in this case, b should scale as $b \propto \sqrt{R}$ due to mass conservation.[5,6] Let us consider the energy dissipated by the slip process. The velocity at which the liquid slips over the substrate is given by

$$v_{\mathrm{slip}}(x) = v_{\mathrm{s}}\ f\left(\frac{x}{b}\right) \qquad (4)$$

v_{s} is the slip velocity at the contact line where the lateral coordinate, x, is zero, and $f(w)$ is a monotonically decreasing function with $f(0) = 1$ and $f(w) = 0$ (or very small) for all

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w larger than one. Assuming this function to be independent of time, we obtain for the power dissipated in the slip process

$$P_{\text{slip}} = \kappa\, v_s^2 \int_0^b f^2\left(\frac{x}{b}\right) \mathrm{d}x = \tilde{\kappa} v_s^{\,2} b \tag{5}$$

with κ being the coefficient of friction between the film and the substrate and $\tilde{\kappa} := \kappa \int_0^1 f^2(w)\, \mathrm{d}w$. Since, on the other hand, the dissipated power is given by the dewetting force times the dewetting velocity, we obtain, for the slip process separately

$$S = v_s \tilde{\kappa} b =: \; v_s\, K_s \sqrt{R} \tag{6}$$

If the contact line recedes only by means of the slip process, $\mathrm{d}R/\mathrm{d}t = v_s$, and eq 6 can be directly integrated to yield the well-known result[6,8]

$$R(t) = \left(\frac{3S}{2K_s}\, t\right)^{2/3} \tag{7}$$

It has been observed[3,7] that experimental data for $R(t)$ could be fitted neither with eq 3 nor with eq 7, which is to be expected when the energy released upon dewetting is dissipated in part by the friction of slippage at the substrate and in part by viscous dissipation within the rim. Let us now derive the equation of motion for $R(t)$ for this general case. Since the stress must be continuous at the lower liquid interface, the friction process at the substrate is driven by the same force (namely, S) as the viscous flow. We thus have to add the velocities of the two contributing processes, such that $\mathrm{d}R/\mathrm{d}t = v_s + v_v$, and obtain

$$\mathrm{d}R/\mathrm{d}t = S\left(\frac{1}{K_v} + \frac{1}{K_s}\sqrt{R}\right) \tag{8}$$

This can be solved by separation of variables and leads to

$$t = \frac{K_v}{S}\left(R - 2\gamma\sqrt{R} + 2\gamma^2 \ln\left(1 + \frac{\sqrt{R}}{\gamma}\right)\right) + \tau_0 \tag{9}$$

with $\gamma := K_v/K_s$, and τ_0 is a rupture time which is particular to the hole nucleation process itself and is thus yet unknown. Full slippage corresponds to $\gamma = \infty$, while $\gamma = 0$ represents the no-slip case.

It can be seen from eq 9 that in the late stage, when R is large, the result from eq 3 is reobtained. Analogously, by expanding the logarithm in eq 9 in a power series, it is readily seen that at early times, the dynamics is described by eq 7. This suggests that in the early stage, slip is the dominating mechanism while in the late stage, dissipation takes place mainly by viscous flow in the rim.[3] This is quite expected since the wider the rim becomes, the stronger becomes the force required to slip it along the substrate. This suppresses the slip process in relation to viscous dissipation within the rim.

For our experiments, we have used thin films of polystyrene (M_w from 18 to 600 kg/mol, $M_w/M_n = 1.02$, $T_g = 100°$ C) which were prepared by spin-casting from toluene solution onto freshly cleaved mica sheets. They were subsequently floated onto a clean, deionized water surface and picked up with Si wafers which had been silanized before[9] following standard procedures.[10,11] To induce dewetting, the samples were annealed in situ under a light microscope at temperatures fixed between 115 and 135° C. Figure 1 shows a typical set of data obtained for $R(t)$. The dashed and the dotted line represent least-squares fits of eqs 3 and 7, corresponding to no-slip and full slip conditions, respectively. The discrepancy with our data is obvious. In contrast, the solid line, which represents a fit of eq 9 to the data, describes the dynamics very well. From the fit parameters, one can now obtain information on the relative importance of slip and nonslip dynamics in the dewetting liquid film.

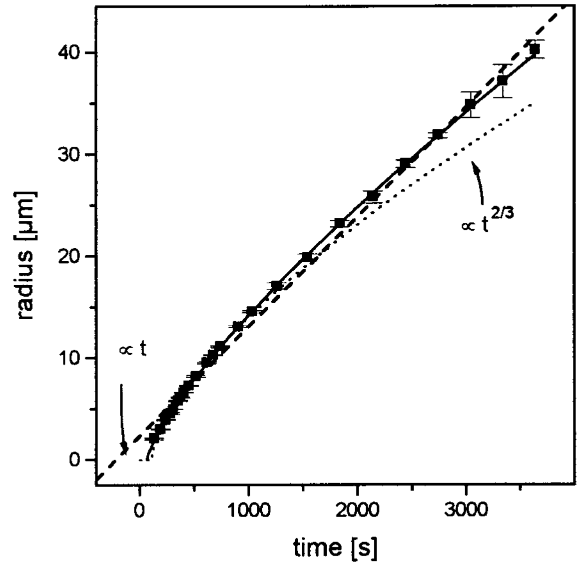

Figure 1. Typical behavior of the hole radius as a function of time. Dashed line: theoretical prediction for no-slip conditions. Dotted line: prediction for full slip, i.e., when dissipation takes place only by slippage of the film across the substrate. Solid line: our theory (eq 9) fitted to the data, which allows to extract the effective viscosity and the slip friction of the liquid film on the substrate.

Experiments have been performed with polymer film thicknesses ranging from 30 to 60 nm at various temperatures. The data obtained for the hole radii could all be well fitted with $K_s = 8.1 \times 10^4$ $Pas/m^{1/2}$, but with K_v depending strongly on temperature. The results for K_v are displayed in Figure 2a. As expected, there is (at least in the limited range of thicknesses investigated) no significant dependence upon the film thickness, but K_v is strongly increased when the temperature is reduced. Figure 2b shows the temperature dependence of K_v, averaged over film thickness. The dashed line gives a rough estimate of the temperature dependence of the viscosity of the films as taken from the literature.[12] Fair agreement is found with the observed behavior of K_v, as expected.

This leads us to the following conclusions. The friction of the polystyrene film at the silanized silicon surface is finite, such that there is a certain amount of slippage (as it can already be seen from the finite "curvature" of the data displayed in Figure 1). This friction is, within the

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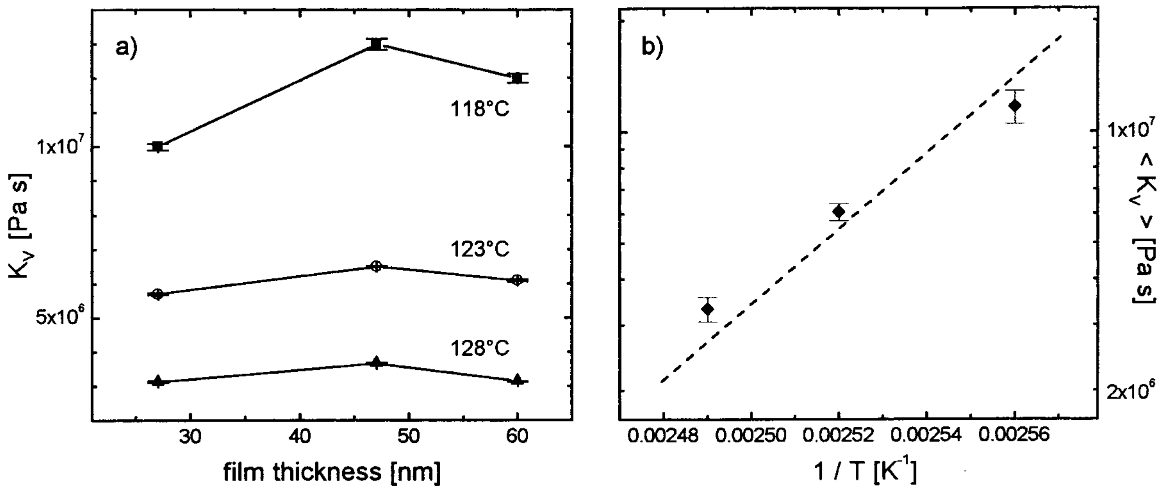

Figure 2. (a) the coefficient of viscous dissipation, K_v, for different film thicknesses and temperatures. All data correspond to $K_s = 8.1 \times 10^4$ Pa s/m$^{1/2}$, which gave the best fit results. (b) Arrhenius plot of K_v, averaged over the various film thicknesses used. The dashed line gives a rough estimate for the temperature dependence of the viscosity of polystyrene as taken from literature data.[12]

resolution of the experiments presented here, independent of film thickness and of temperature. In contrast, the viscous dissipation scales, as far as its temperature dependence is concerned, as the viscosity of the liquid. The apparent independence (or weak dependence) of the slip friction on temperature suggests that if slip is due to thermally activated elementary processes, the activation energy is much smaller than for bulk viscous transport.

It should be noted that γ^2, which has the dimension of a length, is orders of magnitude larger than the so-called extrapolation length,[5] which is frequently used as a convenient quantity to characterize the slip behavior of liquid flow at a wall. This illustrates the fact that by far most of the viscous dissipation takes place near the contact line. In contrast, the dissipation due to the Poiseuille flow away from it, which enters in the extrapolation length, is negligible. It furthermore corroborates that, at least as far as the viscous dissipation is concerned, the growth dynamics is largely independent of the rim geometry, rendering our considerations valid also at the very early stage of hole formation, when the rim is not yet large as compared to the film thickness.

In conclusion, we have presented a theory of hole growth in dewetting liquid films which accounts for both viscous dissipation and slippage along the substrate. It is well capable of describing the observed growth dynamics and allows one to extract the viscous dissipation as well as the slip friction from experimental data.

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