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The role of nonlinear friction in the dewetting of thin polymer films

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Abstract. – The study of the dewetting of very thin polymer films has recently revealed many unexpected features (*e.g.* unusual rim morphologies and front velocities) which have been the focus of several theoretical models. Surprisingly, one of the most striking features, that is the decrease of the rim width with time, has not yet been explained. In the present letter, we show how the combined effects of a non-linear friction between the film and the substrate, and the presence of residual stresses within the film, result in the presence of a maximum in the time evolution of the rim width. Our model allows a quantitative evaluation of the residual stresses and a characterization of the friction between the polymer film and the substrate. In addition, we show how the introduction of a non-linear friction simply explains the experimentally observed rapid decrease of the dewetting velocity with time.

Thin polymer films play a major role in the current manufacturing of nano-devices, and, consequently, have been the subject of a large amount of experimental and theoretical work in recent years [1–4]. Despite many efforts, the instability and the subsequent dewetting dynamics of these films are not yet fully understood. As shown by Brochard *et al.* in their pioneering work [5], wall slip (resulting from polymer chain entanglement within the film) is a key ingredient. When the dewetting is initiated from a straight edge [6], it leads first to a dewetting regime where an asymmetric rim builds up at the edge of the film (and where the surface tension plays almost no role), and then to a second regime (called the "mature rim" regime) where the rim is rounded by the surface tension [10–14]. Both regimes have been the subject of several experimental and theoretical studies. Particular attention has been paid to the building up of the rim, since the ineffectiveness of the surface tension in this first regime allows for unusual rim morphologies [7, 15–19]. The viscoelastic properties of the dewetting film (that are, too, related to chain entanglements) have been taken into account only very

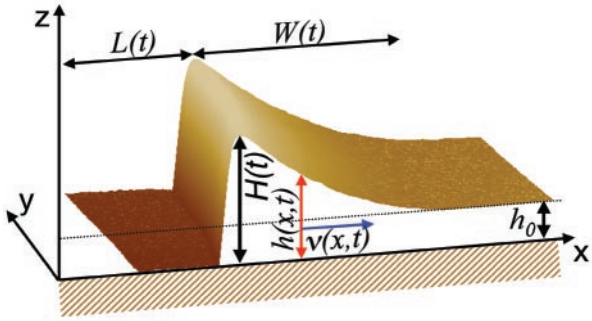

Fig. 1 – Film geometry: $h(x,t)$ is the profile of the film, h_0 is the initial height of the film, $H(t)$ is the height of the front, $L(t)$ is the dewetted distance, $W(t)$ is the width of the rim, and $v(x,t)$ is the velocity of the film.

recently [8, 12, 14, 19]. In the simplest cases, the film viscoelasticity can be characterized by an elastic modulus G, and a relaxation time τ_1 [20]. At times longer than τ_1, the film behaves like a Newtonian fluid of high viscosity $\eta_1 = \tau_1 G$, while at shorter times, it behaves like an elastic solid (of modulus G). At even shorter times ($t \ll \tau_0 \ll \tau_1$), the rheologic behavior of the film is dominated by the friction between monomers, leading to a Newtonian response of low viscosity, $\eta_0 = \tau_0 G$. Even if some light has been shed on the dewetting of thin polymer films by taking into account their viscoelasticity, the time evolution of the rim width, W (see fig. 1), exhibited in [7, 18, 21], is still a mystery. Indeed, these studies, which concern the building-up of the rim, indicate that W reaches a maximum after some time, and then decreases, an unexpected feature unexplained by the current theoretical models.

The aim of the present letter is to solve this puzzle, by showing that the decrease of the rim width is not a somewhat exotic feature, but a robust signature of two important characteristics of the system: the presence of residual stresses within the film, and a non-linear dependance of the friction between the film and the substrate on the sliding velocity. Residual stresses, the existence of which has been now attested by several works [9, 19, 21, 22], seem to be the result of the spin-coating fabrication process of polymer films. Indeed, spin coating leads to a fast evaporation of the solvent which leaves the polymer molecules in a non-equilibrium frozen-in state [22]. The evaluation of these stresses is of practical importance as they increase the film instability. Indeed, the residual stresses are part of the dewetting driving forces, even if they decrease with time as the film undertakes internal relaxation toward an equilibrated state [19,22]. The characterization of the friction force between a polymer film and a substrate is essential as the friction reduces the mobility of the liquid on the substrate and consequently stabilizes the film. We will show from recent dewetting experiments on thin polystyrene (PS) films deposited onto a silicon wafer coated with a polydimethylsiloxane (PDMS) mono-layer (preliminary results and the experimental setup have been described in [21]), that the friction force can be characterized and the residual stresses evaluated quantitatively.

Our experiments revealed a relation between the amplitude of the residual stresses and the age of the film conserved below the glass transition. The consequences of up to three hundred days of aging of the deposited film on the dewetting dynamics have systematically been investigated. While increasing the aging time, we observed a slowing-down of the dewetting process, as well as a decrease of the maximum rim width (see figs. 2 and 3). Eventually, at the longest aging time, almost no maximum rim width was observed. We interpreted these results as a manifestation of the very slow relaxation of the residual stresses within the film

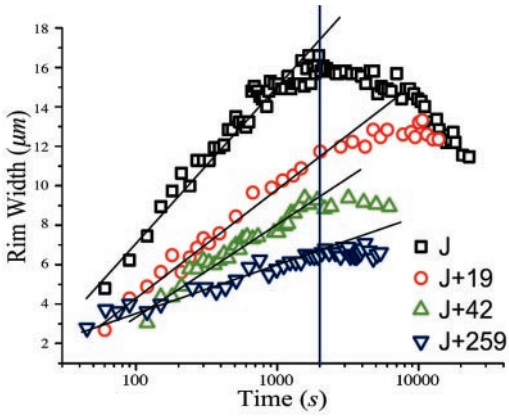

Fig. 2

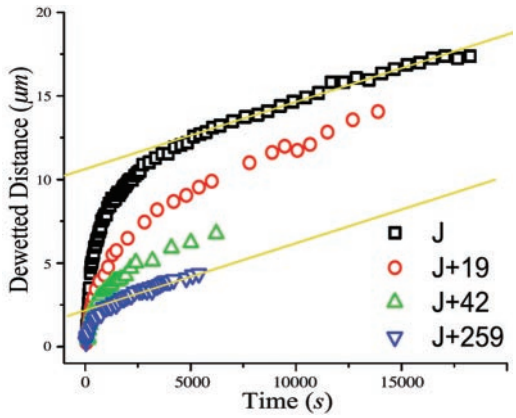

Fig. 3

Fig. 2 – Width of the rim as a function of dewetting time for films ($h_0 = 57nm$, $M_w = 233$ kg/mol, and $T = 125\,^{\circ}$C) aged at room temperature for days indicated in the figure. W is defined as the distance from the edge where $h - h_0 = 10$ nm.

Fig. 3 – Dewetted distance as a function of dewetting time for films ($h_0 = 57$ nm, $M_w = 233$ kg/mol, and $T = 125\,^{\circ}$C) aged at room temperature for days indicated in the figure.

with aging time. During each dewetting experiment, W increases logarithmically with time, proportionally to the dewetted distance L (see fig. 1), until it reaches a maximum. Then, it slowly deceases, while L seems to increase linearly with time. This decrease implies a sharpening of the rim shape. Let us note that the width of a "mature" rounded rim (for which the height of the rim $H \propto W$, and thus $W \propto L^{\frac{1}{2}}$) cannot decrease with time.

For the dewetting of a viscoelastic film, the proportionality between the rim width and the dewetted distance during the building-up of the rim has been shown to result from the elastic behavior of the film ($\tau_0 < t < \tau_1$). In the long-time Newtonian regime ($t > \tau_1$, but before reaching the "mature rim" regime), W stays approximately constant, of the order of $\Delta_1 = \sqrt{\eta_1 h_0/\zeta}$ [19] (h_0 is the initial thickness of the film, and ζ is the friction coefficient between the film and the substrate assumed to be constant [5]). Therefore, no decrease of the rim width with time is predicted. However, at the sight of the expression of Δ_1, we anticipate that W could decrease on the condition that the friction parameter increases with time. A non-constant friction parameter is possible if the friction force does not increase linearly with the sliding velocity. Such cases are indeed common in polymer physics. The friction of a PDMS elastomer on grafted or absorbed PDMS surfaces has been shown to increase only very slowly with velocity: Casoli *et al.* found a friction force increasing proportionally to $V^{\frac{1}{3}}$ on absorbed brushes, and like $V^{\frac{1}{6}}$ on dense grafted brushes, for sliding velocities being between 10 μm s^{-1} and 5 mm s^{-1} [23]. More recently, Bureau *et al.* showed a $V^{\frac{1}{5}}$-dependence of the friction force between an elastomer and a grafted brush, for sliding velocities ranging from 300 μm s^{-1} down to 0.01 μm s^{-1} [24], which is similar to the velocity range of our dewetting experiments.

A rather general expression of the friction force by unit surface, f_r, as a function of the sliding velocity, v, is given by

$$f_r = \begin{cases} \zeta v, & \text{for} \quad v < v_\alpha, \\ \zeta v_\alpha \left(\frac{v}{v_\alpha}\right)^{1-\alpha}, & \text{for} \quad v > v_\alpha. \end{cases} \tag{1}$$

The friction exponent α is smaller than one; it varies between 2/3 and 5/6 in the above-mentioned experiments of Casoli *et al.* and Bureau *et al.* Hereafter, we assume v_α to be small enough to omit the linear friction regime which should only be reached at the end of the dewetting process. The effective friction coefficient is then a decreasing function of v: $\zeta_{eff}(v) = \zeta\,(v_\alpha/v)^\alpha$. Using such a friction force, the height-integrated horizontal momentum equation reads

$$\zeta v_\alpha \left(\frac{v}{v_\alpha}\right)^{1-\alpha} = \frac{\partial}{\partial x}\left(h\sigma_x\right), \tag{2}$$

where σ_x is the normal stress component in the x-direction. The boundary conditions are a stress equal to S/H at the edge, and a vanishing velocity infinitely far from the edge. For a Newtonian fluid of viscosity η_1, the horizontal stress is $\sigma_x = \eta_1 \partial v/\partial x$. The resolution of this equation, hence, gives a time-independent dewetting velocity $V_{\alpha 1} \sim |S|^{\frac{2}{2-\alpha}}$ (where S is the spreading parameter [25]), as well as a constant rim width $\Delta_{\alpha 1} \sim |S|^{\frac{\alpha}{2-\alpha}}$ ([1]). These analytical results have been confirmed by numerically solving eq. (2) combined with the volume conservation equation and the boundary conditions specified earlier (same method as in [19]).

As expected, when the friction force is a non-linear function of the velocity, the rim width is a function of the amplitude of the dewetting driving forces (*i.e.* the capillary forces in cases without residual stresses: $\Delta_{\alpha 1} \sim |S|^{\frac{\alpha}{2-\alpha}}$). A decrease of the rim width can thus be expected if the driving forces decrease during the dewetting process. That is indeed what happens when a viscoelastic film presents residual stresses σ_0 at the onset of dewetting. As stated above, the residual stresses are driving forces that decrease over the relaxation time τ_1 [19,22]. At early times the stressed film is equivalent to an equilibrated film pushed by the force $|S| + h_0\sigma_0$ by unit of length. This force decreases down to $|S|$ at times longer than τ_1. This simple comparison allows to predict that W will increase proportionally to the dewetted distance L up to its maximum value:

$$\Delta_m \simeq \Delta_{\alpha 1}\left(1 + \frac{h_0\sigma_0}{|S|}\right)^{\frac{\alpha}{2-\alpha}} \tag{3}$$

during the elastic regime ($t < \tau_1$). Around the characteristic time τ_1, the residual stresses have decreased significantly, and the film begins to behave like a Newtonian liquid. Consequently, the rim width decreases down to $\Delta_{\alpha 1}$. Once again, we confirmed these results by numerical resolutions of the equations of the flow (see fig. 4). We notice that Δ_m is higher than $\Delta_{\alpha 1}$ only if the exponent α is not nil. The combination of non-linear friction together with residual stresses is thus necessary to explain the decrease of the rim width with time. The initial dewetting velocity is also modified by the presence of residual stresses([2]):

$$V_i = V_{\alpha 0}\left(1 + \frac{h_0\sigma_0}{|S|}\right)^{\frac{2}{2-\alpha}}. \tag{4}$$

Then, while the residual stresses relax, the dewetting velocity decreases down to $V_{\alpha 1}$.

([1])As long as h remains of the order of h_0, the solution is $v(x,t) = V_{\alpha 1}\left(1 - \frac{\alpha}{2}\frac{x - V_{\alpha 1}t}{\Delta_{\alpha 1}}\right)^{\frac{2}{\alpha}}$, when $x - V_{\alpha 1}t < \Delta_{\alpha 1}$, and $v(x,t) = 0$ elsewhere. Here, $V_{\alpha 1} = \left(\frac{2-\alpha}{2}\frac{V_1^\alpha}{v_\alpha^\alpha}\right)^{\frac{1}{2-\alpha}} V_1$, with $V_1 = \frac{|S|}{\sqrt{\eta_1 h_0 \zeta}}$, and $\Delta_{\alpha 1} = \left(\frac{2-\alpha}{2}\frac{V_1^\alpha}{v_\alpha^\alpha}\right)^{\frac{1}{2-\alpha}} \Delta_1$.

([2])At shorter times than τ_0 the film behaves like a Newtonian liquid of viscosity η_0, then $V_{\alpha 0} = \left(\frac{2-\alpha}{2}\frac{V_0^\alpha}{v_\alpha^\alpha}\right)^{\frac{1}{2-\alpha}} V_0$, with $V_0 = \frac{|S|}{\sqrt{\eta_0 h_0 \zeta}}$.

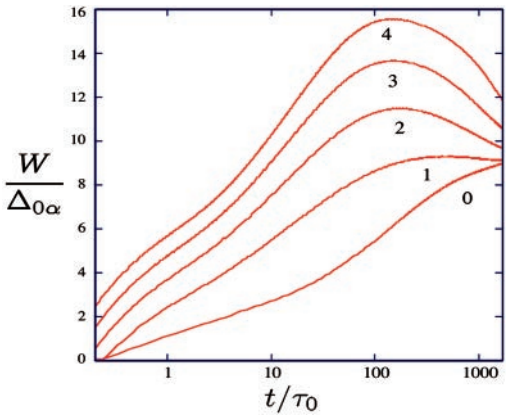

Fig. 4

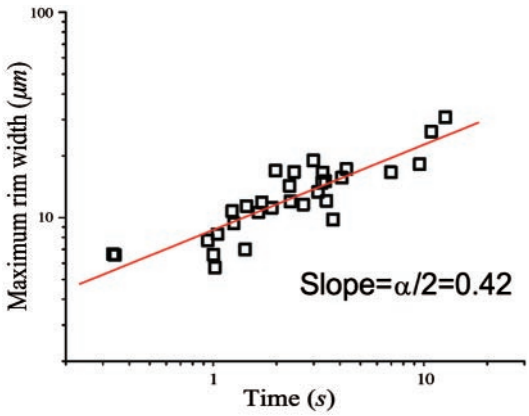

Fig. 5

Fig. 4 – Numerical calculations of the evolution of the rim width W for $h_0\sigma_0/|S| = 0$, 1, 2, 3, and 4, with a friction exponent $\alpha = 2/3$, and a ratio $\tau_1/\tau_0 = 100$. W is defined as the distance from the edge where $h - h_0 = h_0/5$.

Fig. 5 – Evolution of the maximum rim with as a function of the initial dewetting velocity for several aging times and PS molecular weights ranging from 35 kg/mol to 600 kg/mol.

Interestingly, the residual stresses σ_0 do not appear in the following relation between the initial dewetting velocity V_i and the maximum rim width Δ_m:

$$V_i \simeq V_{\alpha 0} \left(\frac{\Delta_m}{\Delta_{\alpha 1}} \right)^{\frac{2}{\alpha}} \tag{5}$$

The exponent α can thus be deduced from a log-log plot of V_i as a function of Δ_m, for various dewetting experiments considering different values of the residual stress. Furthermore, the ratio $V_i/\Delta_m^{\frac{2}{\alpha}}$ varies like the viscosity η_1 (and thus on the molecular weight of the polymer), to the power $-2(1-\alpha)/(2-\alpha)$, which is weak when α is close to unity. Then, various log-log plots, corresponding to different molecular weights, can be superposed in order to measure α. We have brought together log-log plots of the maximum rim width as a function of the initial ($t = 1\,\mathrm{s}$) dewetting velocity for several aging times and several PS molecular weight. This revealed a friction exponent $\alpha = 0.84 \pm 0.15$ (see fig. 5). This latter result is very close to the values discussed above for the PDMS elastomer-grafted brush friction, although almost no interpenetration is expected between the PS film and the PDMS layer (the non-linear relation between friction and velocity could thus be a consequence of the rheologic response of the brush itself to a shear strain, and not to the variations of the amount of interdigitation with the velocity). Dewetting unexpectedly reveals itself as a sensitive tribology tool.

Once the friction exponent α is determined, a quantitative evaluation of the residual stresses becomes possible. The quantities τ_1 (the time corresponding to the maximum rim width), $V_{\alpha 1}$, and $\Delta_{\alpha 1}$ can be directly deduced from the plots of $W(t)$ and $L(t)$. From these quantities we can then calculate the ratio $h_0 G/|S| = \Delta_{\alpha 1}/(\tau_1 V_{\alpha 1})$: $h_0 G/|S| = 4 \pm 1$. Then σ_0 is simply deduced from the measure of Δ_m: σ_0 lies between $0.2G$ and $1.2G$ in our experiments, which is not negligible (up to $6|S|/h_0$). Note that the time τ_0 cannot really be evaluated, which hinders any evaluation of ζ and v_α. Still, the comparisons between $W(t)$ and $L(t)$ obtained numerically and the experimental results are very satisfying, assuming τ_0 to be shorter than 10 s (see figs. 4 and 6).

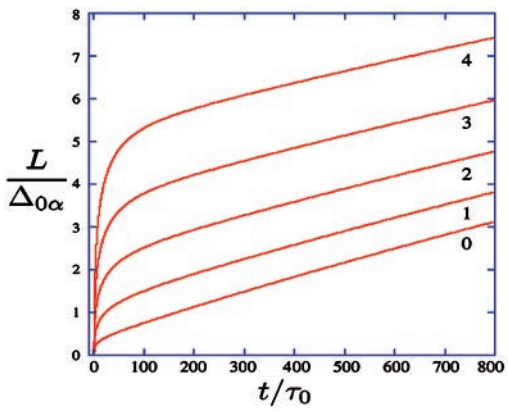

Fig. 6

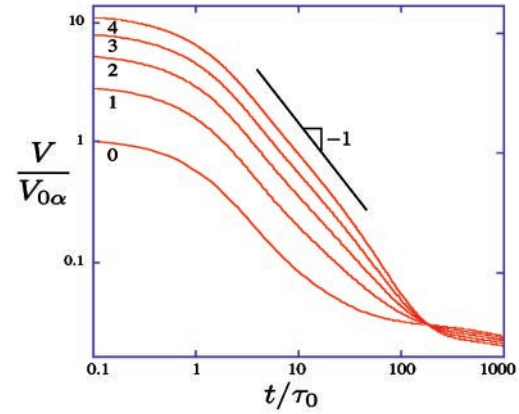

Fig. 7

Fig. 6 – Numerical calculations of the evolution of the dewetted distance for $h_0\sigma_0/|S| = 0$, 1, 2, 3, and 4, with the friction exponent $\alpha = 2/3$, and a ratio $\tau_1/\tau_0 = 100$.

Fig. 7 – Numerical calculations of the evolution of the dewetting velocity for $h_0\sigma_0/|S| = 0$, 1, 2, 3, and 4, with the friction exponent $\alpha = 2/3$, and a ratio $\tau_1/\tau_0 = 100$.

We also notice that the characteristic relaxation time of the elastic constraints, $\tau_1 \simeq 2000\,\mathrm{s}$, is significantly shorter than the corresponding relaxation time in the bulk (*i.e.* the reptation time of the polymer chains $\tau_{rept} \simeq 25000\,\mathrm{s}$), which is consistent with the fact that the entanglement length should be longer in films whose thickness is of the order of the size of the molecules [26, 27]. Note that other structural relaxation mechanisms related to the proximity of the glass transition might also be involved.

Another interesting result, in the absence of residual stress, is the power law form for the decrease of the dewetting velocity with time which can be obtained by a simple scaling analysis: from τ_0 to τ_1 the dewetting velocity decreases from $V_{\alpha 0}$ down to $V_{\alpha 1} = (\tau_0/\tau_1)^{\frac{1}{2-\alpha}} V_{\alpha 0}$. Then, the dewetting velocity reads

$$V = V_{\alpha 1} \left(\frac{t}{\tau_1} \right)^{-\frac{1}{2-\alpha}} \tag{6}$$

for $\tau_0 < t < \tau_1$. One can show that, even in the presence of residual stresses, eq. (6) remains valid, except in the close vicinity of τ_1 where the decrease is more rapid. Thus, the dewetting velocity has a power law close to t^{-1} if α is close to unity, as deduced from the plot of W_m *vs.* V_i (see fig. 5), implying a logarithmic increase of the dewetted distance. The decrease is made a little more rapid around τ_1 by the presence of residual stresses. This latter result is in complete agreement with our experiments (see also [7, 18]). We have also confirmed these analytical prediction by numerical resolutions (see figs. 6 and 7).

In conclusion, we have presented in this letter both experimental data and theoretical results which provide a deeper understanding of the mechanisms involved into the dewetting of thin polymer films. The non-linearity of the friction force between the substrate and the film, and the initial presence of residual stresses within the dewetting liquid are brought together to form a coherent theory which solves the mystery of the decrease of the rim width with time, and matches with the experimental data. Dewetting appears then as a powerful tool to characterize the friction between the film and the substrate and determine quantitatively a friction exponent α. The weak dependence of the friction force with the sliding velocity causes a fast initial

dewetting velocity. The dewetting process is accelerated by the presence of residual stresses σ_0, which we managed to quantitatively evaluate with the simple observation of the rim width and the dewetted distance. The rather large amplitude of these residual stresses makes their control of great technological importance. Finally, many questions, regarding the dynamics of confined polymers, remain open and will require additional experimental and theoretical work.

* * *

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