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Dewetting of thin viscoelastic polymer films on slippery substrates

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Abstract. – Dewetting of thin polystyrene films deposited onto silicon wafers exhibits unusual dynamics and rim morphologies. Here, we present a new theoretical approach of these phenomena taking into account both the viscoelastic properties of the film and the non-zero velocity of the film at the interface with the substrate (*i.e.* slippage). We show how these two ingredients lead to: a) a very asymmetric shape of the rim as the film dewets; b) a decrease of the dewetting velocity with time like $t^{-\frac{1}{2}}$ for times shorter than the reptation time (for larger times, the dewetting velocity reaches a constant value). Recent experiments by Damman, Baudelet and Reiter (*Phys. Rev. Lett.*, **91** (2003) 216101) present, however, a much faster decrease of the dewetting velocity. We then show how this striking result may be explained by the presence of residual stresses in the film.

Thin liquid films are of great scientific and technological importance, and display a variety of interesting dynamics phenomena [1–3]. In engineering, for instance, they serve to protect surfaces, and applications arise in adhesives, magnetic disks and membranes. They have therefore been the focus of many experimental and theoretical studies [4]. When forced to cover a non-wettable substrate, a thin liquid film is unstable and will dewet this substrate. Four years ago, Reiter studied the dewetting of ultrathin (*i.e.* thinner than the equilibrium size of the molecules), almost glassy polystyrene (PS) films deposited onto silicon wafers coated with a polydimethylsiloxane (PDMS) monolayer [5]. He found that a highly asymmetric rim, with an extremely steep side towards the interior of the hole and a much slower decay on the exterior side, builds up progressively. In order to explain these deviations from the behavior of simple Newtonian liquids, theoretical models based on the shear-thinning properties of polymer films (see the work of Dalnoki-Veress *et al.* [6]), and assuming radial geometry, have been proposed independently by Saulnier *et al.* [7] and Shenoy *et al.* [8]. Very recently, Damman, Reiter and collaborators compared the opening of cylindrical holes with the retraction of a straight contact line (edge geometries) [9, 10]. These experiments revealed the existence of a highly asymmetric rim and a strong decrease of the dewetting velocity as the rim builds up for both the radial and the edge geometries [11]. One has to note that the models proposed

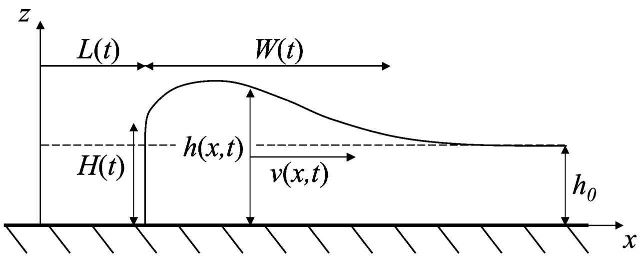

Fig. 1 – Film geometry: $h(r,t)$ is the profile of the film, h_0 is the initial height of the film, $H(t)$ is the height of the front, $L(t)$ is the dewetted distance, $W(t)$ is the width of the rim, and $v(x,t)$ is the velocity of the film.

in [7] and [8] strongly rely on the assumption of a radial geometry, and therefore cannot be readily transposed to the case of straight contact lines. In this letter, we thus present a new theoretical approach that shows how the friction (due to slippage) of the polymer film onto the substrate, combined with its viscoelastic properties, can explain the above-mentioned experimental results of Damman and Reiter [9, 10]. Herminghaus, Jacobs and collaborators have recently conducted thorough numerical studies of the dewetting process [12–14], mainly focussing their interest on the description of the morphology of a fully developed rim (*i.e.* rounded by surface tension). Here we present a simplified scaling analysis which allows us to gain some physical insights into how the morphology of the rim changes during the dewetting process, and how the dewetting velocity evolves with time.

Let us consider the dewetting of a straight contact line and assume that the thickness of the liquid film is smaller than the hydrodynamic extrapolation length $b = \eta/\zeta$ (where η is the viscosity of the liquid, which can be assumed to be very high since the experiments are conducted close to the glass transition, and ζ is the interfacial friction coefficient of the liquid on the substrate) [1]. We can thus use a simple plug-flow description and characterize the velocity field in the film, $v(x,t)$, and the film profile, $h(x,t)$, by two functions independent of the z-coordinate (see fig. 1). The horizontal stress, $\sigma(x,t)$, is related to the strain rate, $\dot\gamma = \partial v/\partial x$, by a constitutive equation (the form of which depends on the type of fluid under consideration; see below). Neglecting both the film surface tension and inertia, the local mechanical equilibrium between the friction forces (per unit surface) onto the substrate, $\zeta\, v(x,t)$, and the bulk viscous forces in the x-direction gives

$$\zeta\, v = \frac{\partial\,(h\sigma)}{\partial x}. \tag{1}$$

Assuming the fluid to be incompressible, volume conservation leads to

$$\frac{\partial h}{\partial t} + v\,\frac{\partial h}{\partial x} = -h\,\frac{\partial v}{\partial x}. \tag{2}$$

The applied force (per unit of length) on the rim , $|S|$ (where S is the spreading parameter [1] assumed to be negative), pushing the film away from the dry area, must be balanced by the the viscous force:

$$|S| = -H\,\sigma(x = L), \tag{3}$$

where $H = H(t)$ is the front height, and $L = L(t)$ is the dewetted distance (see fig. 1). Finally, far away from the rim (*i.e.* for large positive values of x), the velocity film must vanish (*i.e.* $v(+\infty) = 0$) . For a Newtonian liquid, the above equations can easily be solved at short times.

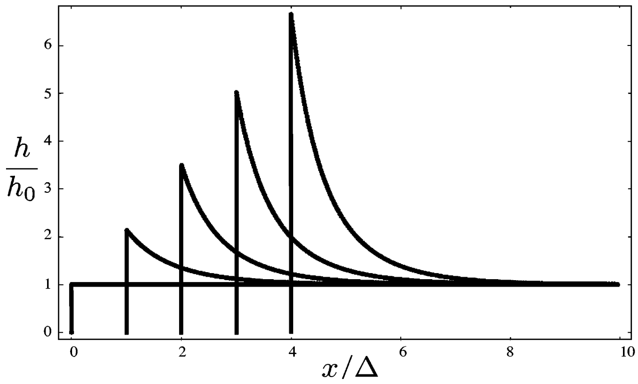

Fig. 2 – Numerical calculation of the shape of a Newtonian film dewetting on a slippery substrate at different times. The successive curves are separated by a time interval Δ/V_0.

Indeed, as long as $h(x,t)$ remains of the same order as the initial thickness of the film, h_0, eq. (1) —combined with the fact that for a Newtonian fluid $\sigma = \eta\,\dot{\gamma}$— leads to

$$\zeta\, v \;\simeq\; \eta\, h_0\, \frac{\partial^2 v}{\partial x^2}. \tag{4}$$

The velocity field is then given by $v(x) = V_0 \exp\left[-\frac{x-L}{\Delta}\right]$, where the distance Δ is equal to $\sqrt{h_0\eta/\zeta} = \sqrt{h_0 b}$, and the velocity V_0, deduced from eq. (3), is equal to $|S|/\sqrt{\zeta\eta h_0}$. At short times, a Newtonian liquid deposited onto a slippery substrate thus dewetts with a constant velocity V_0. This result was already obtained by Brochard-Wyart *et al.* [15] using energetic arguments, but the present mechanical point of view gives us additional information about the film morphology. Indeed, eqs. (2) and (3) give for the front height: $H(t) = h_0 + (|S|/\eta)\,t$. Since the velocity field decreases exponentially as one moves away from the front, the film profile exhibits at short times an asymmetric rim, with an exponential decrease of the thickness over the characteristic length Δ:

$$h(x,t) \;=\; h_0 \,+\, \frac{|S|}{\eta}\, t \exp\left[-\frac{x - V_0 t}{\Delta}\right]. \tag{5}$$

This behavior is indeed observed by Reiter on AFM images [5]. We have also completed our analysis by numerically solving eqs. (1)-(3) along with the condition $v(+\infty) = 0$, using the Euler method with implicit x discretisation; as shown in fig. 2, these numerical solutions confirm well the analytical predictions of a decreasing exponential shape of the rim, with $H(t) \sim t$, and $V(t) = V_0$. Our analysis also allows us to correct the assumption made by Brochard-Wyart *et al.* that the viscous dissipation should be negligible compared with the dissipation due to friction [15]. Indeed, a simple calculus based on the above results shows that the two dissipations are approximately equal. Note that due to surface tension, the rim presents in fact a cylindrical-like section at its front. The width of this section is approximately given by $\delta \simeq H/\theta_0$ (where θ_0 is the equilibrium contact angle [1]). The rim thus remains highly asymmetric if $\delta \ll \Delta$, that is to say as long as $H(t) \ll \theta_0\Delta$. Assuming $h_0 \ll \theta_0^2 b$ [16], the rim is highly asymmetric as long as $L(t) \ll \theta_0 b$. For $L \geq \theta_0 b$, the friction of this cylindrical section on the substrate begins to be more important than the friction of the rest of the film, and simultaneously the Laplace pressure due to the curvature of the exponentially decaying rim becomes stronger than the capillary pressure $|S|/H$. Thus, once $L \geq \theta_0 b$, the "mature rim" regime described by Brochard-Wyart *et al.* [15,17] (see also Damman *et al.* [9]) begins, and the rim becomes round and symmetric (with a width $W \sim \sqrt{h_0 L}$ simply given by volume conservation). It was shown in [12–14] that the combination of slippage and surface tension in the mature-rim regime can lead to an oscillatory profile. As surface tension is ineffective during the formation of the rim, no oscillations are predicted. In this regime, the viscous dissipation is negligible compared with the dissipation due to friction, and, consequently, the dewetting velocity is proportional to $t^{-\frac{1}{3}}$ [15]. Two important results arise from our analysis of the dewetting of a Newtonian fluid. Firstly, the ineffectiveness of the surface tension and the friction of the film onto the substrate give rise to an asymmetric rim, since the friction dumps the velocity field in the film over a length Δ (which depends on the liquid viscosity). Secondly, the viscous dissipation is approximately equal to interfacial dissipation due to friction during the formation of the rim, while it is negligible in the "mature rim" regime. We can therefore anticipate that for a viscoelastic fluid, the rheologic properties of the fluid will have no significant consequences on the dewetting velocity in the "mature rim" regime, but will play a major role during the formation of the rim.

Let us now consider in some details the dewetting of a viscoelastic film, assuming the following simplest (one relaxation time) constitutive equation [18]:

$$G\sigma + (\eta_0 + \eta_1)\dot{\sigma} = G\eta_1\dot{\gamma} + \eta_0\eta_1\ddot{\gamma}, \tag{6}$$

where G is an elastic modulus (due to entanglements), η_0 is a short-time viscosity (due to the friction between monomers) and η_1 is the usual melt viscosity ($\eta_1 \gg \eta_0$). The time response of such a liquid can be divided into three regimes: 1) At short times, $t < \tau_0 = \eta_0/G$, the liquid behaves like a simple Newtonian liquid with a weak viscosity η_0. 2) For $\tau_0 < t < \tau_1 = \eta_1/G$, where τ_1 is the relaxation time of the elastic stresses in the film (in the bulk, τ_1 would be the reptation time of the polymer chains, it can be different in thin films as shown in [19]) the liquid behaves like an elastic solid of elastic modulus G. 3) At long times ($t > \tau_1$), the liquid behaves like a very viscous Newtonian liquid of viscosity η_1. The above-mentioned time response of the liquid has direct consequences on the dewetting process. For times shorter than τ_0, the viscoelastic liquid dewets like a simple liquid, with a high constant velocity $V_0 = |S|/\sqrt{\zeta\eta_0 h_0}$, and with the formation of an asymmetric rim of width $\Delta_0 = \sqrt{h_0\eta_0/\zeta}$. At long times ($t > \tau_1$), the viscoelastic liquid also dewets like a simple liquid, with a constant velocity $V_1 = |S|/\sqrt{\zeta\eta_1 h_0}$, and with the formation of an asymmetric rim of width $\Delta_1 = \sqrt{h_0\eta_1/\zeta} \gg \Delta_0$. In between these two regimes, the viscoelastic behavior of the fluid will thus lead to a significant drop of the dewetting velocity (from V_0 to V_1). More precisely, in this intermediate-time regime ($\tau_0 < t < \tau_1$), the liquid behaves like an elastic solid and the height of the front increases very slowly with time: $H \simeq h_0 + |S|\,(1 + t/\tau_1)\,/G \approx h_0 + |S|/G$ [20]. Volume conservation then imposes that the width of the rim, W, increases proportionally to the dewetted distance, L:

$$W \simeq \frac{G}{|S|}\,h_0\,L. \tag{7}$$

Let us now assume that the bulk viscous dissipation is at most of the order of the dissipation due to friction. This assumption then allows us to determine the dynamic of the dewetting process from a simple energy balance (per unit of length) between the work done by the capillary force per unit of time and the dissipation due to friction:

$$|S|\,V \simeq \zeta\,W\,V^2 \tag{8}$$

(where, as anywhere else in this letter, numerical prefactors of order unity are neglected). The above equation, combined with eq. (7), gives $V(t) \simeq V_0\sqrt{\tau_0/t}$ for times t shorter than τ_1. Note

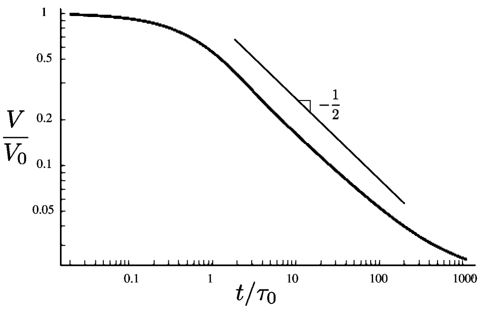

Fig. 3

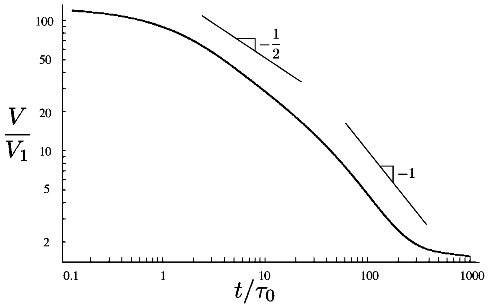

Fig. 4

Fig. 3 – Numerical calculation of the reduced dewetting velocity V/V_0 *vs.* the reduced time t/τ_0 for a viscoelastic film with $\tau_1 = 1000\,\tau_0$. The straight line represents $t^{-\frac{1}{2}}$.

Fig. 4 – Numerical calculation of the reduced dewetting velocity, V/V_1, *vs.* reduced time, t/τ_0, for a viscoelastic film ($\tau_1 = 100\,\tau_0$) with residual stresses ($\sigma_0 = G = 4|S|/h_0$). The straight lines represents $t^{-1/2}$ and t^{-1}, respectively.

that this $t^{-\frac{1}{2}}$ behavior might have been guessed directly from the fact that $V_1/V_0 = \sqrt{\tau_0/\tau_1}$. We have confirmed these results by numerically solving the equations of motion (1) (with the constitutive equation (6), (2) and the same boundary and initial conditions as for a Newtonian liquid (see fig. 3). The good agreement between our analytical and numerical results ($V \sim t^{-\frac{1}{2}}$ between τ_0 and τ_1) indicates that our assumption that the bulk viscous dissipation is smaller than (or equal to) interfacial dissipation does hold for a viscoelastic liquid described by eq. (6). For $t > \tau_1$, our model predicts a constant dewetting velocity V_1. This prediction holds as long as the height of the front H is small compared to the width $\theta_0\Delta_1$. Thereafter, as in the case of a Newtonian liquid, the "mature rim" regime is reached and the dewetting velocity then decreases like $t^{-\frac{1}{3}}$. We have thus shown that for a viscoelastic fluid in the time interval $\tau_0 < t < \tau_1$, and the dewetting velocity is initially very high ($V_0 \gg V_1$), and then decreases like $t^{-\frac{1}{2}}$, while the width of the rim W increases proportionally to the dewetted distance L. The former prediction is in good agreement with the experimental observations of Damman *et al.* [9]. While a $t^{-\frac{1}{2}}$ decrease of the dewetting velocity has indeed been occasionally observed by Damman [21], in most cases the measured dewetting velocity decreases like t^{-1} [9], much faster than predicted. In order to explain this striking result, let us assume that at the beginning of the dewetting process the polymer films are not at equilibrium, and display residual stresses due to the spin-coating fabrication process and fast evaporation of the solvent, as recently emphasized by Reiter and de Gennes [22]. We shall now show how these residual stresses, assumed to be essentially horizontal and of initial amplitude σ_0, cause a high initial dewetting velocity, followed by a strong slow-down.

The various time regimes of the dewetting process, when partially driven by residual stresses, are similar to the ones already described when the process is only driven by capillary forces. At times shorter than τ_0, we deduce from eq. (3) that the dewetting velocity is equal to $V_0 + \sigma_0\Delta_0/\eta_0$, where the second term denotes the contribution of the residual stresses. In this short-times regime, the residual stresses have no direct effects on the shape of the rim which thus keeps an exponential shape of characteristic width Δ_0. For $t > \tau_0$, the height of the front is given by $H = h_0 + h_0\sigma_0/G + |S|(1 + t/\tau_1)/G$ [23], and the width of the rim, W, is simply given by volume conservation: $W(H - h_0) \simeq h_0L$. Thus, as long as $t \ll \tau_1$, H is approximately constant and W increases proportionally to the dewetted distance. In order to obtain the dynamics of the dewetting process, the power (per unit of length) $h_0\sigma_0 \exp[-\frac{t}{\tau_1}]\, V$ [24] delivered by the residual stresses should be added to the l.h.s. of the energy balance eq. (8). The dewetting velocity is then given by

$$V \simeq \frac{V_1}{\sqrt{2}} \frac{(1+\epsilon+\frac{t}{\tau_1})(1+\epsilon e^{-\frac{t}{\tau_1}})}{\sqrt{\frac{t}{\tau_1}+\frac{1}{2}(\frac{t}{\tau_1})^2+\epsilon(2+\epsilon+\frac{t}{\tau_1})(1-e^{-\frac{t}{\tau_1}})}} \tag{9}$$

for $t > \tau_0$, where $\epsilon = h_0\sigma_0/|S|$. Around $t = \tau_0$, the velocity decreases like $t^{-\frac{1}{2}}$, and thereafter decreases more sharply as the residual stresses relax within the film. For large enough residual stresses ($\epsilon \geqslant 4$), the dewetting velocity behaves like t^{-1} around $t = 2\tau_1/3$. Note that when the capillary forces are negligible (*i.e.* when $\epsilon \gg 1$), the residual stresses alone are able to induce the dewetting process and lead to a decrease of the dewetting velocity like $\exp[-t/\tau_1]$ (in the range $\tau_1 < t < \tau_1 \ln(\epsilon+\epsilon^2)$).

The above analytical results are in good agreement with numerical solutions (same resolution as previously, with an additional homogeneous horizontal stress σ_0 at the onset of the dewetting, see fig. 4). Again, the simplified energy balance resulting from our assumption that the bulk dissipation is smaller than (or equal to) the interfacial dissipations gives very satisfying results. Residual stresses are thus a very good candidate to explain the experimental observations of Reiter and Damman since both morphological observations (rim width W proportional to the dewetted distance L) and dynamic measurements (variations with time of L and V) agree with the theoretical predictions. Additionally, it has been observed that the dewetting velocity of a circular hole, while much lower than the dewetting velocity of a straight contact line at the beginning of the dewetting process (due to radial deformations), systematically joins it after some time [9, 10]. The presence of residual stresses can simply explain this experimental observation. Indeed, as described above, the dewetting velocity is mainly controlled by residual stresses (for $\epsilon > 1$) which are evenly distributed throughout the film. Thus, when the size of a hole is large enough for the viscous dissipations due to radial deformations to be negligible compared with the friction onto the substrate, the hole becomes equivalent to a straight line, and both velocities become of the same order, even though the dewetted distances and the rim sizes are different.

In conclusion, we have shown that the friction of the liquid film onto the substrate can explain the building-up of the asymmetric rim observed by Reiter [5] during the dewetting of thin PS films on a PDMS monolayer. We have also shown that the viscoelastic properties of the PS are of great importance as they lead to a decrease of the dewetting velocity with time proportional to $t^{-\frac{1}{2}}$ for times shorter than the relaxation time of the elastic stresses in the film. This decrease is made sharper by the presence of residual stresses. A sharp decrease of the dewetting velocity ($V \sim t^{-1}$) as observed by Damman *et al.* [9] could thus be seen as an evidence of the presence of residual stresses in such viscoelastic films. Note that these residual stresses should also influence the initial stage of the opening of cylindrical holes (a situation where the dissipation due to radial deformations dominates over the friction). The residual stresses might also play a role in the surface instabilities of the film and in the rate of hole formation [22]. In this letter we did not talk about the shear thinning properties of PS films [6, 7], but one can show —using an analysis similar to the one used in this letter for viscoelastic film— that a shear-thinning behavior leads to a decrease of the dewetting velocity weaker than $t^{-\frac{1}{2}}$. Hence, in the absence of residual stresses, shear thinning alone cannot explain the obeservations of Reiter, Damman and colaborators, even combined with viscoelastic properties.

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