Shape of a liquid front upon dewetting

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We examine the profile of a liquid front of a film that is dewetting a solid substrate. Since volume is conserved, the material that once covered the substrate is accumulated in a rim close to the three phase contact line. Theoretically, such a profile of a Newtonian liquid resembles an exponentially decaying harmonic oscillation that relaxes into the prepared film thickness. For the first time, we were able to observe this behavior experimentally. A non-Newtonian liquid - a polymer melt - however, behaves differently. Here, viscoelastic properties come into play. We will demonstrate that by analyzing the shape of the rim profile. On a nm scale, we gain access to the rheology of a non-Newtonian liquid.

The interplay of viscous and viscoelastic properties of a fluid is of enormous technical importance. The rheology e.g. of a coating will be adjusted such that standard coating techniques may be applied. In those thin films, however, the typical rheological analyses techniques fail. In this Letter we will propose a method that can even be applied to nm thin films. We will moreover demonstrate the sensitivity of a liquid profile even to slight changes in the viscoelastic properties of the material. To the best of our knowledge, the analysis of a rim profile was only subject to theoretical studies, yet experimental studies concentrated on the characterization of the dynamics of dewetting, but not on the shape of the rim.

A liquid film on a non-wettatable substrate is not stable and will bead up: circular ‘dry’ regions (‘holes’) appear, the radius of which grows steadily with time. If mass conservation is valid, the material once at the inner part of the hole will be accumulated in a rim along the perimeter of the hole. Close to the three phase contact line of the liquid, i.e. on the ‘dry’ side of the rim, the rim shape is dominated by the receding contact angle \( \theta \) of the liquid on the surface. On the ‘wet’ side of the rim, where the actual contact angle is zero, the liquid merges somehow or other from the crest into the initial film thickness. From a theoretical point of view, the rim is a disturbance in the liquid and is expected to decay via an undulation, the wavelength of which is dominated by the surface tension of the liquid. To the best of our knowledge, however, this peculiar behavior was never reported on dewetting experiments. In our experimental system, short chain polystyrene (PS) on silicon wafers, an undulatory behavior is observed and measured for the first time. It is one of the aims of this Letter to explain why this behavior is only rarely found in experiments and how it can be induced. Moreover, as we will show in this study, the profile of the ‘wet’ side of the rim may serve as a fingerprint of the viscoelastic properties of the liquid.

Using thin atactic PS films on Si wafers as a model system for liquid front studies has several advantages: the PS melt has a very low vapor pressure, hence mass conservation is valid, its viscosity can be tuned by choosing various chain lengths and/or annealing temperatures, its physical properties are well-known and PS is available in high purity and low polydispersity. Moreover, PS films can be studied in the liquid state by atomic force microscopy (AFM). Polished Si wafers are ideal model substrates due to their very low surface roughness (rms values below 0.1 nm). The native oxide layer of the Si wafers renders the surface quite inert in air, and chemical homogeneity of the surface can be achieved by well-known cleaning procedures. Moreover, to check the influence of contact angle on the profile of the liquid front, the wettability of the Si wafer can be changed by the preparation of a self-assembled monolayer of octadecyl-trichlorosilane (OTS) on the surface.

Two types of substrates were used: Type A are Si wafers with a thin natural oxide layer of 1.6(2) nm (Wacker Chemtronics, Burghausen, Germany; crystal orientation (100), p-(boron-)doped, 6-12 \( \Omega \)cm) on top of which an OTS monolayer was prepared following standard procedures. Type B substrates are Si wafers with a thick oxide layer of 191(1) nm (Silchem GmbH, Freiberg, Germany; (100)-oriented, p-(boron-)doped, conductivity > 1 \( \Omega \)cm).

Thin polystyrene films (molecular weight between 2.05 kg/mol and 600 kg/mol, \( M_0/M_n = 1.02 - 1.05 \), purchased from PSS, Mainz, Germany and Polymer Labs, Church Stratton, UK) were spin cast from toluene solution onto the substrates. Before coating, type B substrates, cut in ca. 1 cm\(^2\) pieces, were freed from Si dust by treatment with a CO\(_2\)-jet. The samples were then ‘degreased’ by sonication in ethanol, acetone and toluene. Residual hydrocarbons were removed by immersing in a fresh 1:1 H\(_2\)O\(_2\) (conc.)/H\(_2\)O\(_2\) (30%) solution for 30 min, followed by a thorough rinse in hot MilliporeTM water. Due to the large contact angle of the toluene solution on type A substrates, PS films were first spin coated onto freshly cleaved mica surfaces (B & M Mica Co., Flushing, NY), then floated onto MilliporeTM water and picked up by the type A substrates.

Cleaning and coating was performed in a class 100 clean room atmosphere. The thickness of the Si wafer’s oxide layer and of the polymer films were measured by ellipsometry (Multiscope by Optrel GdBR, Berlin, Ger-
many) at various angles of incidence. Further characterization of wafers and polymer films was done by atomic force microscopy (AFM) (Multimode III by Digital Instruments, Santa Barbara, CA) in Tapping Mode™. Annealing took place on a temperature-controlled hot plate in a class 100 clean room atmosphere or in situ on top of the AFM sample holder.

The inset of Fig. 1 presents an AFM scan of a typical hole in a 6.6(2) nm [12] thick PS(2.24k) film on a wafer B. The diagram shows a radial cross section of this hole. Most outstanding feature of the cross section is the way the rim decays into the unperturbed film. The rim profile is asymmetric, with higher slopes near the three-phase contact line and a ‘trough’ on the wet side of the rim where it meets the undisturbed film. Here, the form resembles a damped harmonic oscillation. We describe the profile by the contact angle $\Theta$ of the liquid at the crest, the depth $B$ of the first trough and the slope $\tan \alpha$ of the rim profile on the wet side at the level of the initial film thickness $h_0$, as depicted in Fig. 1. The trough is also visible in the top view AFM scan in the form of a dark circle surrounding the wet side of the rim (inset of Fig. 1).

From the temporal evolution of the experimental rim profile as shown in Fig. 2, we can determine the width $a$ and height $A$ of the rim, the depth $B$ and the width $b$ of the trough, and the slope $\tan \alpha$ as a function of time. Moreover, by in situ AFM scanning, we can record the dewetting velocity $v$. Within the experimental error, the contact angle $\Theta$ stays constant during hole growth, which is consistent with other experimental and theoretical studies [2–17], Fig. 2b and c) show how $|B|$ and $\alpha$ vary with increasing height $A$ of the rim. From a certain value $A_{\text{exp}}^*$ of the rim height onwards, which will call the late stage in the following, both $B$ and $\alpha$ reach a plateau value. Below $A_{\text{exp}}^*$, in our terms now the early stage, $|B|$ as well as $\alpha$ increase - within the experimental error - linearly with $A$.

For a physical understanding of the occurrence and the temporal evolution of the trough we analytically solve in the following the linearized thin film equation in the lubrication approximation [13–17]:

$$\frac{\partial h}{\partial t} + \frac{\sigma h_0^2}{3\eta} \frac{\partial^4 h}{\partial x^4} - \frac{\partial h}{\partial x} = 0 ,$$

where $h$ is the film thickness, $\sigma$ and $\eta$ are the surface tension and viscosity, and $v$ the velocity of the three phase contact line. We hereby neglect the disjoining pressure $-\Phi'(h)$, since we know from an earlier study that its impact on the dewetting morphology is negligible as compared to the interfacial forces involved here [13–17]. The ‘traveling wave’ solution $h(\xi) = h(x - vt)$ of Eq. (1) reads

$$h(\xi) = \exp \left( -\frac{2\pi}{\sqrt{3}\lambda} \xi \right) \cdot \cos \left( \frac{2\pi}{\lambda} \xi \right) ,$$

where the wavelength $\lambda$ is defined as

$$\lambda := \frac{4\pi}{h_0\sqrt{3}} \cdot \sqrt{\frac{\sigma}{3\eta v}} .$$

Here, $\eta$ denotes the viscosity of the polymer. Eq. (2) represents a damped harmonic oscillation. The ratio of $h(\xi)$ at two consecutive extrema is:

$$\frac{B}{A} = \exp \left( -\frac{\pi}{\sqrt{3}} \right) \approx 0.163$$

and is plotted as the dotted line in Fig. 3. This ratio is independent of any experimental parameter of the system, in particular of the dewetting velocity. It is universal for any rim profile of a retracting Newtonian liquid if the film thickness is small as compared to the capillary length. Although, it cannot be valid for the entire process of dewetting. Due to accumulation of material inside the rim, its width $a$ will be much larger than the width $b$ of the trough. In other words, as soon as the crest of the rim exceeds a certain height $A_{\text{th}},\text{the description}$ of the entire rim profile as a damped harmonic oscillation with a single wavelength $\lambda = 2b$ in Eq. (2) will be no more adequate.

In Fig. 3, the experimental data of $|B/A|$ are plotted over $A$. They reveal that - within the experimental error - $B/A = \text{const.}$ for $A < A_{\text{exp}}^*$. Yet the constant is roughly a factor of two smaller than 0.163. For $A > A_{\text{exp}}^*$, $B/A$ decreases with increasing $A$.

In order to extend the theoretical description to the late stage of dewetting, we have to introduce a boundary condition. From experiment, we have learned that $B$ as well as $\alpha$ are constant in the late stage, c.f. Fig. 2b and c). For $A > A^*$ we therefore introduce into the calculation the experimental plateau value $\alpha = 1.0(1)^\circ$ as a boundary condition. The trough depth $B$ hence is simply obtained by identifying in Eq. (2) the slope of $h(\xi)$ at its first zero as $\tan \alpha$. So, $B$ is a function of the experimental parameters $\sigma$, $\eta$, $h_0$ and dewetting velocity $v$.

Figure 3 shows the result for $|B/A|$ obtained with the boundary condition $\alpha = 1.0(1)^\circ$ for $A > A_{\text{th}}$ (dashed line). Here, the trough depth $B$ is calculated with $\sigma = 30.8$ mN/m, $\eta = 300$ Pa·s (Ref. [16]), $h_0 = 11$ nm, and $v(t)$ taken from the online AFM measurement shown in Fig. 2 [20]. The point of intersection of dashed and dotted line at $A = A_{\text{th}}$ corresponds to the value of $A_{\text{exp}}^*$ at which the experimental values of $|B/A|$ are starting to decrease. This point hence is name $A^*$ in the following. For $A > A^*$, the course of the theoretical curve for $|B/A|$ resembles that of the experimental data, but the absolute values differ by a factor of about 1.5.

To sum up, one may say that the theoretical curves presented above well describe the qualitative development of the height of the rim with respect to the depth of the trough. A quantitative agreement, however, is
not reached yet. In fact, we found that the trough may even be completely suppressed by increasing the molecular weight of the polymer. In Fig. 4 we show profiles of holes in PS films on type A substrates of about the same film thickness (50 nm) and hole radius, yet of various molecular weight: 2 kg/mol, 18 kg/mol, 101 kg/mol and 600 kg/mol. The most outstanding feature in these profiles is that the trough vanishes and the width of the rim grows with increasing molecular weight of the polymer.

It is interesting to note that the PS(2k) and the PS(18k) profiles - both polymers are below the entanglement length [22] - look quite similar, yet the change in viscosity is about four orders of magnitude [23]. The other two profiles, however, greatly differ in shape, yet the increase in viscosity as compared to PS(18k) is only two (four) orders of magnitude for PS(101k) (PS(600k)).

These results suggest that the alteration in profile shape is caused by an increase in viscoelastic properties, i.e., the ratio of viscosity and elastic modulus at the typical shear rates to which the material is subject upon dewetting.

To corroborate this hypothesis, we performed dewetting experiments with an entangled polymer melt of a single chain length and varied the temperature. This is expected to change the viscoelastic response in a way completely different from changing the molecular weight. We prepared 50(2) nm thick PS(65k) films on type A wafers. The samples were heated up to different temperatures for a certain time, namely until the holes had reached a radius of about 5 μm. That way, we changed the viscosity from \(\eta = 4 \times 10^4\) Pa·s (T=145°C) to \(\eta = 5 \times 10^6\) Pa·s (T=125°C). The profiles are shown in the inset of Fig. 4. We have normalized the data to account for the slightly different hole sizes. As can be seen in the inset, the profiles are similar, as opposed to the large figure.

Since the substrate is identical for all polymer films shown, the friction at the interface between melt and substrate remains unchanged for all polymer films. The only difference is that with increasing chain length the viscoelasticity of the polymer melt plays a more and more pronounced role [24]. In a theoretical calculation of the stability condition of thin polymeric films, Safran and Klein [23] found that viscoelasticity stabilizes a liquid film against surface undulations, which corroborates our results.

In summary we may say that we report for the first time on an undulatory behavior of the rim of a dewetting polymer film. Most experiments done before with dewetting films were performed on polymers of much higher molecular weight than 2 kg/mol. Hence, the viscoelastic properties of the melt have suppressed the undulation. We introduced a simple model that is able to explain the qualitative behavior of rim and trough of a short-chain polymers melt. A quantitative comparison of theoretical and experimental results reveals a difference of roughly a factor of 2. For long-chain polymers, the model fails completely due to the absence of the trough. Analyzing the reason for the factor 2 or for the complete failure of the model, respectively, we came to the conclusion that the viscoelastic properties of the polymer melt are to blame.

In is interesting to note here that on the rim profiles an influence of the elastic properties of the melt can be found for chain lengths at which bulk rheometers detect purely viscous properties [24]. The rim profile therefore can be viewed as an extremely sensitive rheometer for small volumes on nm scales.

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For very small radii, the velocity of the contact line behaves like \( v \propto \sqrt{1/t} \) passing into a \( v = \text{const.} \) behavior for very large radii \([21]\). A similar result is given by the simulation in Ref. \([22]\). This is important due to the fact that the calculated depth of depression \(|B|\) increases with decreasing \( v \cdot \eta \). Hence, if \( v \) reaches a constant value, \(|B|\) reaches a maximum value \((|B| < h_0)\) and will not lead to an undulation-induced break-up of the film as it was speculated in Ref. \([1]\), even for very long times.

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\[ \eta = 500 \text{ Pa} \cdot \text{s (PS(2k) at } T=110{\degree}\text{C)}, \eta = 2 \times 10^6 \text{ Pa} \cdot \text{s (PS(18k) at } T=110{\degree}\text{C)}, \eta = 4 \times 10^9 \text{ Pa} \cdot \text{s (PS(390k) at } T=120{\degree}\text{C}) \text{ to } \eta = 2 \times 10^{10} \text{ Pa} \cdot \text{s (PS(600k) at } T=120{\degree}\text{C}). \]

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FIG. 1. Inset: AFM scan of a hole in a 6.6(2) nm thick PS(2.24k) film on a wafer B, 30 min at \( T = 80 \) °C. The large diagram shows a radial cross section of this hole, where \( A \) describes the height of the rim, \( B \) the depth of depression and \( L \) the length from the maximum of the rim to the point where the rim crosses the level of the unperturbed film.

FIG. 2. a) Cross sections of a growing hole in a 11.0(4) nm thick PS(2.05k) film on a type B wafer (191.2(2) nm thick oxide layer) at a temperature of \( T = 90{\degree}\text{C} \), as gained from an in situ AFM scan. Note that the profiles have been shifted laterally such that the three phase contact ‘points’ fall onto one single point. The maximum slope at the level of the unperturbed film thickness is \( \tan \alpha = 0.026 \). b) Depth of depression \( B \) over height of rim \( A \) of the hole and c) ‘wet’ contact angle \( \alpha \) plotted over height of rim \( A \) of the hole.

FIG. 3. Ratio \((B/A)\) over rim height \( A \). Dots: experimental data for a 11.0(4) nm thick PS(2.05k) film on a type B wafer at a temperature of \( T=90{\degree}\text{C} \). Lines: theoretical expectation in lubrication approximation for the same system gained from the analytic calculation without any elastic properties. Dotted line: solution for the early stage \( B/A \approx 0.163 \). Dashed line: solution for the later stage using reduced viscosity \( \eta = 300 \text{ Pas} \) with the boundary condition gained from experiment: \( \alpha_{\text{th,eo}} = 1.0{\degree} \).

FIG. 4. Cross sections as gained from AFM scans of holes in polystyrene films with different chain length on wafers of type B: solid line: PS(2k), dashed line: PS(18k), dot-dashed line: PS(101k), dotted line: PS(600k). The thickness \( h \) of the films and the diameters of the holes are chosen to be about the same. Inset: Hole profiles of PS(65k) taken temperatures between 125 - 145 °C. Differences in film thickness and hole size lead to slight differences of the profiles.
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