Sliding fluids: Dewetting experiments reveal the solid/liquid boundary condition

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Abstract. Nanoscale liquid polymer films are ideal candidates to probe the solid/liquid boundary condition: Prepared on hydrophobized Si wafer, the films are not stable, they dewet. The dewetting induces a flow without applying an external force. Probing the dynamics of the dewetting film and the morphology of the liquid front, we can deduce the slip length. A variation of the type of hydrophobic coating (silane or Teflon®) of the Si wafer enables us to tune the boundary condition from a no-slip to a nearly full-slip condition. For a short introduction to the topic, we offer a phenomenological approach and supply multimedia files.

The solid/liquid boundary condition is of great importance for a theoretical description of liquids in confined geometries. Usually it is assumed, that the velocity profile of the liquid extrapolates to zero at the solid/liquid boundary. This is called ‘no-slip’ boundary condition. At a gas/liquid interface, a ‘full-slip’ boundary condition is usually applied, describing a continuity of tangential stress across a fully mobile interface. To quantify the amount of slippage, a parameter is introduced, the slip length \( b \). It is defined as the extrapolation length of the velocity profile of the liquid ‘below’ the interface. Technically, the full slip condition (\( b \) infinite) or a very large \( b \) often is desirable since effects such as die swelling using extruder techniques can be reduced. Moreover, the throughput in pipes and channels can be substantially enhanced at the same applied pressure.

A number of different methods have been used to probe the boundary condition at various systems as discussed in recent review articles [1, 2, 3]. Most of them, like colloidal probe microscopy or particle imaging between two shearing plates, apply an external force to create the flow. For the studies presented here, a thin liquid film is observed as it beads off a solid surface, driven by internal forces only. We record the dewetted distance as a function of time, usually with an optical microscope. This gives us information about the dynamics of the dewetting film. Moreover, we characterize the shape of the liquid front as it retracts using atomic force microscopy (AFM). Both the dynamics and the front of the dewetting film are sensitive to the solid/liquid boundary condition.

Let us first look into how dewetting proceeds. An everyday dewetting experiment, the dewetting of honey from a buttered bread, can be performed on a breakfast table. A snapshot of a layer of honey dewetting from a buttered surface is shown in Fig. 1. A video can be found in the supplementary material. Initially, the liquid must be forced into a thin film. At the breakfast table, this is done with a knife, in the video we used a wooden stick. For a polymer melt, that blade technique is rarely used as it usually cannot generate films thinner than several
micrometers. For the preparation of films in the nm-range, the substrate is placed on a chuck that can spin from several hundreds up to ten thousands rounds per minute. A drop of polymer solution is then placed on the spinning sample. As the solvent evaporates, a smooth film of uniform film thickness is left behind. The film thickness depends on polymer concentration, spinning speed, acceleration, type of solvent and type of polymer and can be measured by e.g. ellipsometry.

On the breakfast table, the layer of honey immediately starts to bead off the buttered surface and dry patches (‘holes’) appear and grow in size. In case of a polymer instead of honey, it needs to be heated above the glass transition temperature to become liquid, because the polymer film is usually glassy as soon as the solvent has evaporated.

For honey as well as for many polymer films mass conservation is valid, at least for the usual times of observation, minutes to hours. This means that all material that was once on the surface as a flat film must stay on the surface. The material that was inside a hole is accumulated along its perimeter, forming a ‘rim’. As the hole grows, also its surrounding rim increases. Dewetting ends when holes meet. Their rims merge and form a common ribbon, a liquid cylinder with a certain contact angle. Due to the Rayleigh-Plateau-instability, the ribbon decays into droplets.

Why does a film dewet? Dewetting occurs if the film can gain energy by minimizing its interfacial area with the substrate (see [4, 5] and references therein). Dewetting of thin liquid films on solid substrates is a result of internal forces, which can be inferred from the effective interface potential \( \Phi \) [6, 7]. In case of several films of dielectric materials, \( \Phi \) is the sum of the van der Waals potentials involving gas layers, liquid layers and substrate and a repulsive short range potential, representing the steric repulsion. In case the substrate consists of different layers, the influence of each layer on the van der Waals potential has to be taken into account [5, 7, 10]. If \( \Phi \), which is a function of film thickness \( h \), has a global minimum at a finite film thickness, the film can dewet. In the region of \( \Phi \) where the second derivative of the potential with respect to film thickness, \( \Phi''(h) \) is negative, there is a driving force that promotes thinning of the film. In this case spinodal dewetting takes place [6, 11]. Most exiting feature of this case is that there is a wavelength in the capillary spectrum of the liquid film that is amplified.
Figure 2. Left: Spinodal dewetting 4 nm thick PS(2k) film on a Si wafer with a thick (191 nm) silicon oxide layer as seen by AFM. Height scale from black to white is 10 nm. Inset: Fourier transform of the AFM image. Right: AFM scan of a 6.6 nm thick PS (2k) film on a Si wafer with a thin (2.4 nm) silicon oxide layer; height scale 20 nm. Holes are randomly distributed and therefore generated by nucleation.

fastest. This wavelength can be observed experimentally, e.g. by an atomic force microscope (AFM). Recording the spinodal wavelength as a function of liquid film thickness can give access to the effective interface potential [7, 10] in the experiment. For a 4 nm thin PS film of 2 kg/mol molecular weight (a short-chained polymer, roughly 20 monomer units) on a Si wafer covered with a thick (191 nm), amorphous silicon oxide layer, spinodal dewetting can be observed, as depicted in the left image of Fig. 2. The inset shows a Fourier transform of the AFM image. Clearly, a preferred wavelength (415 nm ± 20 nm) can be observed.

To yield information about the dynamics of spinodal dewetting, in situ AFM scans can be performed. In order to not disturb the liquid surface, an especially soft, so-called ‘non-contact’ mode of scanning is used [12]. To get a reasonable time resolution below one minute, only a small area in the µm² range is scanned. In Fig. 3, an AFM image of a spinodally dewetting polystyrene (PS) film is shown. The area is (1.3 µm)², the height scale from black to white is 12 nm. Since the area is so small, a Fourier transform will not yield reliable results. Hence, the image has been analyzed by Minkowski measures and compared to numerical simulations [13, 15]. The surface undulations in both cases can be described by a Gaussian random field, which one theoretically would also expect for spinodal dewetting. By Minkowski measures, also the morphology of the pattern in the experiments and the simulations can be compared and have shown to match perfectly. The time scale, however, when e.g. first valleys of the undulation reach the solid surface, do not match in simulation and experiment. In the experiments, holes appear faster as compared to the simulations, yet in the simulations the coarsening of the rims and ribbons is quicker than in the experiments. The reason is not, as first suggested, a false assumption of the viscosity for the simulations, but rather the neglect of the thermal noise in them. Including this thermal noise, a perfect match of the dynamics of dewetting in experiments and simulations could be achieved [17].

If there is a global minimum of $\Phi(h)$ at finite $h$, but $\Phi''(h)$ is positive at the prepared film thickness $h$, the system needs to overcome a potential barrier to reach the minimum in $\Phi(h)$. A nucleus - whatever it may be (e.g. a chemical heterogeneity, a dust particle) - can locally change $\Phi(h)$. There, the film thins, a hole is generated and dewetting starts. If not intentionally prepared, nuclei are randomly distributed and so are the holes. An example is shown in Fig. 2, right. The analysis of the sites of holes by Minkowski measures confined a random distribution [13, 14].
Figure 3. Snapshot of a series of AFM images of a spinodally dewetting polystyrene film (2k) with a thickness of 4 nm on a Si wafer with 191 nm silicon oxide on top. The entire series can be found in the supplementary material. Height scale from black to white is 12 nm.

In everyday life, where films of some 100 nm to some 100 µm thickness are dominant, dewetting is usually initiated by nuclei since the time for the spinodal instability to grow in amplitude scales with $h^5$ [16]. Spinodal dewetting can therefore only be observed in films of a few nm thickness. For the dewetting experiments evaluating the solid/liquid boundary condition, the dewetting mechanism is not important. Dewetting is used as a tool to initiate a flow without applying an external force. Dewetting - and that is the main advantage - is only driven by internal, capillary forces. Viscous dissipation within the liquid (which mainly occurs at the three-phase contact line [8]) and friction at the solid/liquid interface (slippage) counteract these driving forces. For an overview about the basic models and experimental results concerning especially sliding polymeric melts, the reader is referred to [9], where also concepts that aim to explain slippage on the molecular scale are summarized and discussed.

Fig. 4 shows a sequence of micrographs of a 130 nm thick PS(13.7k) film at $T = 120$ °C from two different hydrophobic surfaces. The only difference of the two films is the type of hydrophobic layer on top of the Si wafer. In Fig. 4 left, a silanized wafer was used, in Fig. 4 right, a Teflon®-coated wafer [18]. Judging from the contact angle only (which corresponds to the depth of the global minimum in $\Phi(h)$ and, thus, to the driving force), one expects the polymer melt to dewet faster from the substrate with the larger contact angle (Teflon®, 88(2)°, compared to silanized wafer, 68(2)°). The experimental results, however, contradict this expectation: A snapshot of the experiment is shown in Fig. 4. In the supplementary material, a video sequence is given which shows the dynamics of the dewetting experiment: Both films are 130 nm thick and dewet at $T = 120$ °C. In both cases, the time when the first tiny hole can be detected by optical microscopy is set to $t = 0$. Clearly, dewetting proceeds faster on the left, the silanized wafer. Concerning silanization, two different types of molecules were used: Octadeyltrichlorosilane (OTS) consisting of a backbone of 18 carbon atoms and Doedecyltrichlorosilane (DTS), with 12 carbon atoms as backbone. Both are forming self-assembled monolayers on Si wafers covered with a native $SiO_2$-layer, leading to water contact angle above 110 °. Both hydrophobic layers have comparable surface roughness, surface tension and water contact angle hysteresis [21]. Data for the hole radius $R$ as function of time is shown in Fig. 5 left.

A detailed study reveals that on the silanized surfaces, slip lengths in the range of micrometers...
Figure 4. Dewetting of a 130 nm thick PS(13.7k) film at $T = 120^\circ C$ from two different surfaces as seen by reflective light microscopy. Left: Si wafer as a substrate, hydrophobized by dodecyltrichlorosilane (DTS). Right: Teflon®-coated Si wafer as substrate. The striped pattern in the surrounding of the hole stems from slight nm-sized height differences on a lateral scale of tens of $\mu m$ in the Teflon®-coating and do not affect dewetting.

can be achieved for unentangled polystyrene films. On the Teflon®-coated Si wafers, however, slip lengths below 100 nm are found [21]. The results for all three surfaces, Teflon®, OTS and DTS, are shown in Fig.5 right. Slip lengths are determined by either recording the dewetting velocity as a function of time [22] or by analyzing the rim profile as it ‘decays’ into the unperturbed film [23, 21]. The largest slip lengths range up to 10 $\mu m$ (at the film thickness of approx. 100 - 130 nm).

The relatively small slip lengths in case of the Teflon®-coated Si wafers are in good agreement with molecular dynamic simulations for a simple Newtonian liquid that predict slip lengths exceeding 30 times the molecular diameter of the liquid molecules [24]. For polystyrene chains like PS (13.7k) with a radius of gyration $R_G \approx 3$ nm, one would expect slip lengths up to roughly 100 nm. This raises the question of the underlying molecular mechanism of slippage. The fact that slip is substantially different on OTS-, DTS- and Teflon®-coated Si wafers is not obvious and various explanations are being discussed.

Figure 5. Left: Radius versus time of a growing hole on a 130 nm thick PS(13.7k) film at $T = 120^\circ C$ from different hydrophobic substrates measured by optical microscopy. Right: Slip length plotted versus dewetting temperature on DTS-, OTS- and Teflon®-coated surface. Both graphs adapted from [21].
the silane molecules takes place during the dewetting process. Another explanation blames an interpenetration of PS-chains into the silane monolayer. Both hypotheses imply a change of the solid/liquid interface. Recently performed neutron scattering experiments indeed corroborate a diffusion of PS chains into the silane layer [25], yet the exact molecular mechanism of the high slip lengths on the silane surfaces is still unclear. A third explanation is revealed with our newest experiments: Entangled polymer melts on hydrophobic, 'no slip', Teflon®-coated Si wafers showed a reduced number of entanglements of polymer chains at the solid/liquid interface and create by that a slip effect [20], which corroborates the hypothesis of a polymer interphase with properties different from the bulk. In this case, the slip lengths characterize apparent slip.

In summary, we have provided a short overview on dewetting experiments revealing the solid/liquid boundary condition, providing a 'dynamic' insight by including multimedia files of dewetting liquids. For thin polymer films on hydrophobic substrates, viscous dissipation as well as slippage are relevant. Future experiments will focus on the molecular origin of slippage and on the characterization of the lubrication layer.

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