# Experiments on Wetting on the Scale of Nanometers: Influence of the Surface Energy

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Via ellipsometry, the time-dependent profiles of liquid droplets spreading completely on plane solid substrates are measured in the range 0–200 Å. Two different surfaces are used, a "high-energy" surface and a "low-energy" surface. We have observed that the shape of spreading droplets of the same fluid are quite different on these two surfaces: On the low-energy surface, the spreading occurs by the macroscopic lateral spreading of essentially one monolayer. For the high-energy surface, spreading occurs by the macroscopic lateral spreading of several monolayers, in a kind of hierarchical process. Nevertheless, in both cases there is a signature of molecular structuring in the fluid flow at the center of the drop.

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Spreading and thin-film dynamics in the case of spontaneous dry spreading have recently been the subject of a number of theoretical[1-5] and experimental[6-13] papers. In the case of a positive initial spreading parameter[3,4] $S$, defined in Ref. 5, a microscopic film develops at the edge of the macroscopically observable front, and dissipates[4] all the excess, surface energy $S$. For the spreading of PDMS (polydimethylsiloxane) it was recently reported[8-11] that the spreading on oxide-covered silicon wafers occurs with the development of a foot of near-monomolecular thickness, extending over macroscopic distances. These experiments indicate the presence of molecular-size effects, of course not describable by hydrodynamic theories.[3,4] In this Letter, we present new experimental results on the influence of the surface free energy on the morphology and dynamics of spreading films of the same fluid.

The experimental setup used here is essentially the same as the one described in a preceding Letter[9] and we shall only emphasize a few key differences. Thicknesses are measured by single-wavelength ellipsometry[13-15] ($\lambda = 6328$ Å), with a focalized measurement spot. Lateral resolution is 30 $\mu$m by 120 $\mu$m as estimated from the half-width of the measured profile at the edge of a 30-Å-thick Langmuir-Blodgett layer. The measurement stability over one day is 0.2 Å rms with a time constant of 100 ms for the detection electronics. The fluid used is a low-molecular-mass PDMS (anionic polymerization leading to linear, tributyl-terminated chains[16] of polydispersity 1.6, viscosity 50 cP, and surface tension 21 mN m$^{-1}$). The "width" of the molecule (monomer thickness) is of the order[17] of 7 Å. The substrates are silicon wafers ([111] crystal facet, 2 in. diam, phosphorus doping, resistivity 4–6 $\Omega$ cm, "prime" quality, manufacturer Pensilco), covered with 14 Å of natural oxide. The experiments are performed at room temperature and pressure, under a constant flow of clean nitrogen gas (rate of 0.2 liter/min) evaporating from a Dewar containing liquid nitrogen. The gas-line tubing is made out of Pyrex glass, fired before use to remove organic contamination.

Two types of surfaces are used in the present experiment: "high-energy" ones designated by [++], and "low-energy" ones designated by [+]. The terminology refers to $\gamma_s$, the surface free energy per unit area of the solid. The [+] surface is prepared by monolayer deposition, using the Langmuir-Blodgett technique,[18] on a uv-ozone cleaned[19] silicon wafer. The molecule is a fatty acid with a chain of 23 carbon atoms, terminated by a double bond ($-CH=CH_2$). The thickness of the layer is about 30 Å. The critical surface tension[20] $\gamma_c$ of such a surface is estimated to be in the range $\gamma_c = 25$–$30$ dyn cm$^{-1}$.

The [++] surface is a uv-ozone cleaned wafer, used immediately after treatment. Such a surface is completely wettable by water. With the particular precautions described above, it is possible to keep the surface wettable by water for about 10–15 d. It was realized that in the preceding measurements,[11] although the initial cleaning procedure was the same, the surface lost its water wettability within a few hours after the beginning of the experiments. This contamination was later identified as outgassing from a Teflon tube that was used for the gas line. Those latter experiments were thus performed on a non-water-wettable surface ("medium-energy" surface, designated as [++−]).

Figures 1 and 3 correspond to ellipsometric profile measurements on [+] and [++] surfaces. On the figures, the horizontal axis (scan across the droplet) is graduated in millimeters, while the vertical axis (measured fluid thickness) is graduated in angstroms. Droplet volumes are estimated from integration of the profiles. For the initial profiles, the central part of the droplet is nonmeasurable (the measured point is out of the theoretical ellipsometric trajectory, the sign of a nonvalid thickness measurement[15,21,22]) because its slope is

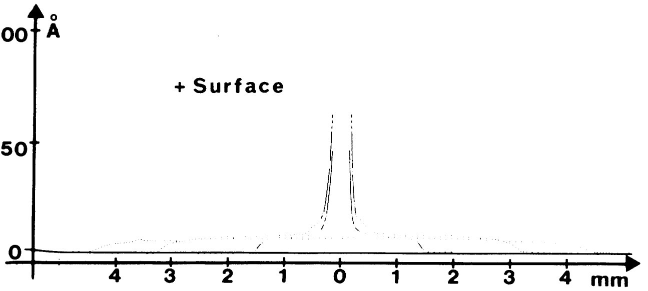

FIG. 1. Time evolution of the thickness profile of a $2\times10^{-5}$-$\mu$l PDMS droplet on a [+] surface. The times of measurement are 1 h 40, 10 h 30, and 30 h, respectively, after deposition of the drop.

too steep. Figure 1 corresponds to the spreading of a $2\times10^{-5}$-$\mu$l droplet, on a [+] surface. Originating from the central part, a "foot" spreads out. Its thickness $e_0$ decreases from 9 to 6 Å, and its lateral extension is macroscopic. This behavior is qualitatively independent of the drop volume and has already been observed[9-11] for PDMS droplets: The results were interpreted as molecules lying flat on the substrate and flowing out of the central cap. On one of the profiles, the presence of a second foot on top of the first one is faintly observable. The length of the first layer is observed to grow with the square root of time as long as the central reservoir is present. This behavior has been termed pseudodiffusive,[11] in the sense that the diffusion coefficient[3,23-25] $D(e)$ is thickness dependent. In the present experiment, the coefficient for the average thickness $e_0$ was determined to be $D(e_0)=(1.7\pm0.3)\times10^{-10}$ m$^2$s$^{-1}$ for the [+] surface. The height at the center of another drop was measured as a function of time. Figure 2 displays up to four distinct changes of the thinning rate, appearing every 7.5 ± 0.5 Å in thickness. This is a clear indication of molecular structuring of the fluid flow at the center of the drop.

PDMS spreading of a $8\times10^{-6}$-$\mu$l droplet on the [++] surface is shown in Fig. 3. Again a foot (thickness of the order of a molecular size, about 6–8 Å) develops from the base of the drop. But in contrast with the [+] surface where essentially one layer was observed to develop laterally, a second molecular layer of about the same thickness develops over a macroscopic distance and at a smaller rate on top of the first one, and a third less visible film on top of the second one. Again, those molecular features are qualitatively independent of the drop volume. (The steps were observed at the edge of a $5\times10^{-2}$-$\mu$l droplet, the height of the center still being macroscopic. Up to five steps were observed on such large drops.) All these layers continue to spread as long as the central part of the drop exists as a reservoir. When the drop has completely leaked into the spreading foot, the top layers (then receding) empty into the lower layers, down to the first one. The water wettability was tested at this stage: Water does not wet the surface covered by a single PDMS monolayer, but still wets the bare substrate. The successive layers of PDMS spreading on top of the first one see an effectively hydrophobic surface. In Fig. 4, the center height versus time measurement is plotted for another drop on the [++] surface. Here, the structuring is very evident and occurs at up to 4 times 7.5 ± 0.5 Å.

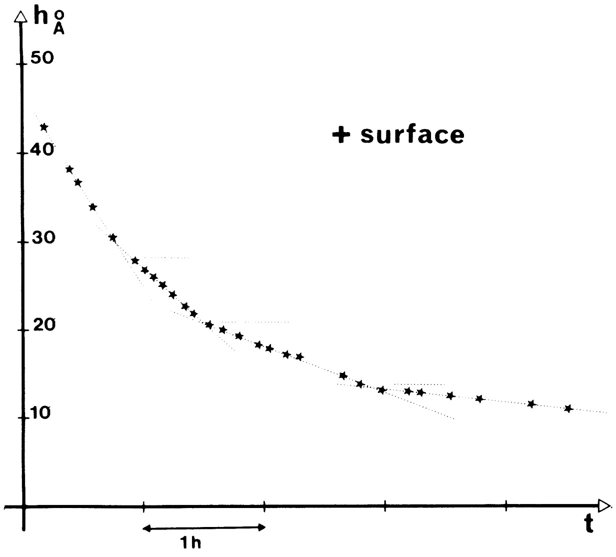

FIG. 2. Time evolution of the thickness at the center of a $3.5\times10^{-5}$-$\mu$l PDMS droplet on a [+] surface. Dotted lines are drawn every 7 Å in thickness, above the bare substrate. The origin of the time axis does not correspond to the deposition of the drop.

The spreading foot begins to slow down notably after only one or two layers are left. The last stages of this evolution have not yet been reached in Fig. 3. Of course, this last stage of spreading is more easily observed on a

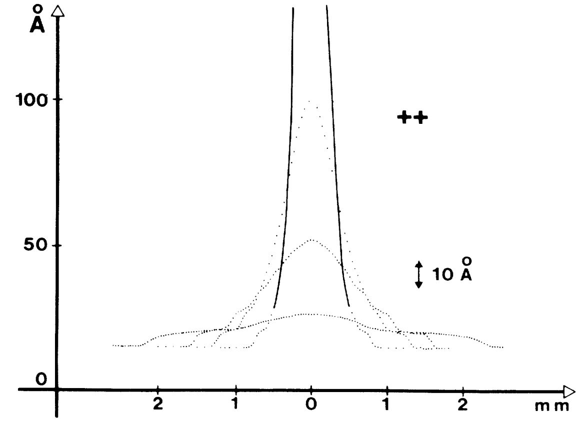

FIG. 3. Time evolution of the thickness profile of a $8\times10^{-6}$-$\mu$l PDMS droplet on a [++] surface. The times of measurement are 1 h 30, 6 h 10, 12 h, and 70 h, respectively, after deposition of the drop.

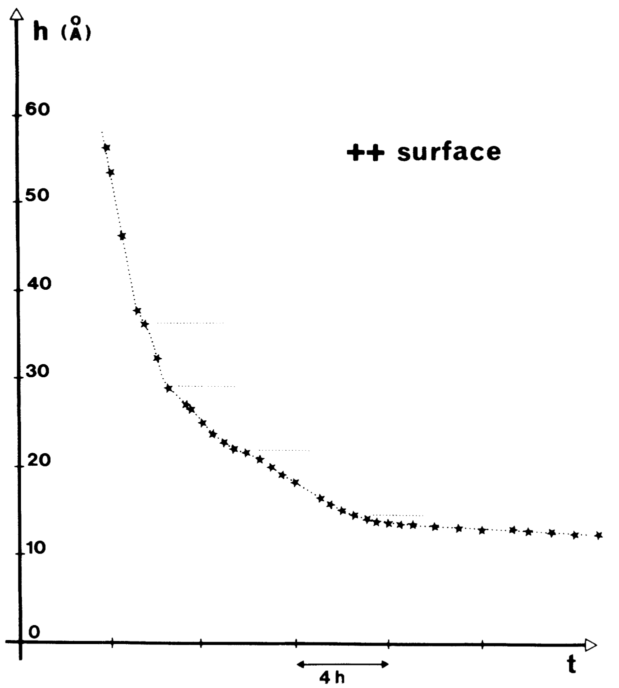

FIG. 4. Time evolution of the thickness at the center of a $3.4\times10^{-6}$-$\mu$l PDMS droplet on a [+ +] surface. Dotted lines are drawn every 7 Å in thickness, above the bare substrate. The origin of the time axis does not correspond to the deposition of the drop.

smaller drop (faster overall evolution[26]). One finds then the same kind of late evolution as with the [+] surface (the molecules tend to separate from each other).

In both cases of spreading on [+] or [+ +] surfaces, an intrinsic thickness appears, which is related to the width of the PDMS monomer. This is an indication that a molecular structuring and layering develops in the spreading process, up to several layers from the solid. This ordering may involve dynamic effects (steplike viscosity-versus-thickness dependence[27]) or static effects and be related to a kind of nematic order induced by the presence of the solid substrate[28] (behavior observed for liquid phases adsorbed from gas on graphite[29]). Such arguments have been developed[24,25] for thin-film dynamics. It seems clear that for a given layer, there is competition between exchange with the lower layer and advance at a given altitude. This kind of "staircase" shape has been previously observed[10] with another type of liquid on a [+ + −] surface. The configuration and chemistry of the molecule in that case were quite different. It was star shaped (silicon center, alkane arms), instead of the linear PDMS polymer used in the present work. Thus the structuring appears to be a rather general phenomenon.

The interpretation of the evolution of the coefficient of diffusion of the first foot versus the surface energy is not straightforward. One might expect that the film should advance faster on a high-energy surface. However, the driving force at the molecular scale is not $S$, but is the film pressure gradient and is therefore not necessarily larger on a high-energy surface.[24,25] Moreover, the friction is certainly much larger on such a surface, where adsorption takes place. Effectively, the diffusion coefficients were found to be $(1.7\pm0.3)\times10^{-10}$ and $(7\pm1)\times10^{-11}$ m$^2$s$^{-1}$, respectively, for the [+] and [+ +] surfaces. However, the dynamics of the front (all the steps together, with possible exchange between layers) should be treated as a whole, especially for the [+ +] case.

In conclusion, our experiment reports the first observation on the "nanoscopic" spreading behavior of PDMS, as a function of the surface energy. Molecular structuring occurs on [+] and [+ +] surfaces. For [+] surfaces, spreading occurs essentially via lateral extension of a film of near molecular thickness, over a macroscopic distance. The diameter of the central part of the drop is quasistatic and its edges are steep. For [+ +] surfaces, the profile displays a transient stage with several distinct molecular films advancing laterally over macroscopic distances on top of each other, and the whole film profile appears smoother. The last stages are the same, namely, all the initial volume is found after some time at molecular thickness, and the molecules tend to migrate away. Experimental studies are planned to characterize the interactions involved, beyond the simple van der Waals picture. The work presented here should initiate further theoretical developments in the field of wetting and thin-film dynamics.

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