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Existence and Role of the Precursor Film in the Spreading of Polymer Liquids

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We present investigations of the spreading behavior of nonvolatile liquids (high-molecular-weight polydimethylsiloxane) on smooth horizontal surfaces, and establish the following: (1) the existence of a thin precursor film extending progressively ahead of the macroscopic front of the drops, and that we directly visualize by polarized reflection microscopy; (2) the universality of the spreading kinetics, followed by means of simultaneous size and contact-angle measurements, which appears insensitive to the spreading parameter S. Both points give strong experimental support to recent theoretical developments.

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The spreading of a liquid on a solid substrate conditions a large number of practical situations such as metal or glass anticorrosive coating, textile dying, paint spreading, plant nutrition or treatments, enhanced oil recovery, etc. However, the basic processes involved in the spreading are still far from being elucidated.

Since the pioneering work of Young[1] and Zisman,[2] the role of the spreading parameter $S = \gamma_{SG} - \gamma_{SL} - \gamma$ (with γ_{SG}, γ_{SL}, γ respectively the solid-gas, solid-liquid, and liquid-gas interfacial tensions) has been recognized: If S is negative, a liquid drop deposited on the solid adopts an equilibrium shape corresponding to a finite contact angle θ_e defined by the Young's condition $\cos\theta_e = (\gamma_{SL} - \gamma_{SG})/\gamma$; if S is positive, spontaneous spreading occurs, and the equilibrium situation corresponds to a complete coverage of the solid by a thin liquid film. S measures the interfacial energy per unit area gained during the spreading. However, several measurements of the spreading kinetics of liquids on a large variety of substrates (different S values)[3-6] seem to give spreading kinetics approximately independent of S, and the adequacy of a description based on interfacial energies and simple hydrodynamic concepts has been widely debated (see the review by Marmur[7]). de Gennes[8] and Joanny[9] have recently proposed an explanation of that paradox, pointing out the role of long-range forces which may give rise to a precursor film. (A) If the liquid is volatile, and for positive S, the more efficient transport of molecules from the liquid to the solid surface takes place through the vapor phase. The surface is thus rapidly covered with a film of recondensed liquid molecules. The macroscopic part of the remaining liquid drop spreads on a "solid" of identical chemical structure, and S locks to zero.

(B) If the liquid is not volatile ("dry spreading") the only efficient transport of the liquid is by flow. S keeps playing an important role, and conditions the final equilibrium thickness e of the liquid film ($e \sim S^{-1/2}$ for van der Waals interactions). As a consequence, during the spreading, a drop of nonvolatile liquid should display several regions: (1) a macroscopic part in which van der Waals forces are not dominant and whose spreading is driven by the Laplace pressure due to the curved liquid-gas interface (S independent); (2) a microscopic almost flat precursor film, in which Laplace pressure is negligible, but whose thickness is governed by long-range forces, and decreases towards the equilibrium thickness e. Quantitative predictions have been proposed for the profile of that precursor film, and the way it connects to the macroscopic spherical cap,[8,9] with assumption of a dissipation in the precursor film which exactly compensates the surface energy gain, while the dissipation in the macroscopic part of the drop exactly compensates the work of the Laplace pressure forces. If such is the case, the spreading kinetics of a nonvolatile liquid should appear, when one monitors only the advance of the macroscopic part of the drop, independent of S, while a precursor film should develop progressively in front of the apparent contact line.

Several experimental studies have pointed out either the existence of a precursor film[10-12] or the S independence of the spreading kinetics.[3-6,13] However, these experiments are not completely conclusive: (1) The liquids used were not clearly nonvolatile, or were contaminated by volatile impurities which have been assessed to be at the origin of the formation of the precursor film; (2) spreading kinetics were followed over a relatively narrow time window; (3) the solid surface was not well defined; (4) the size of the drops was usually greater than the critical size for gravity effects.[7] Here we report investigations of the spreading behavior of nonvolatile liquids, performed on the macroscopic and on the microscopic scales, at the same time and on the same samples.

Special attention has been paid to the control of several crucial parameters of the system: The liquids are three narrow-distribution, high-molecular-weight fractions of polydimethylsiloxane (PDMS) which can be considered as model nonvolatile liquids. Their weight-average molecular weights are 79000, 160000, and 280000, with polydispersity index 1.15, 1.11, and 1.19, respectively. PDMS is known to spread spontaneously on silica surfaces[13]; the solids are silicon wafers, of controlled chemical constitution (a 20-Å SiO_2 layer on silicon) and with a residual surface roughness smaller than 30 Å. Two surface states have been achieved: (1) a high-energy surface (large positive S value) with the bare ultraclean wafer (in order to avoid degradation of the surface quality, we have used cleaning procedures based on local oxidation of impurities on the surface by UV irradiation under oxygen flow[14]); (2) a small-energy surface obtained by chemical grafting of octadecyltrichlorosilane, which leads to a critical surface tension[2] $\gamma_c \simeq 23$ dynes/cm.[15,16] As the surface tension of PDMS is $\gamma \simeq 21$ dynes/cm,[4] it still spreads spontaneously on the grafted wafer, but the spreading parameter is much smaller than for the bare wafer ($S \sim \gamma_c - \gamma \sim 2$ dynes/cm. Drops of very small volume ($\Omega \sim 10^{-2}$–10^{-1} mm^3) were deposited on the surface of the wafer which was then immediately enclosed in a sealed box in order to minimize dust deposition or contamination during the spreading. The boxes were equipped with flat windows, allowing for optical investigations of the sample. The drop sizes were always smaller than the capillary length K^{-1} (~ 2 mm for PDMS), even at the latest stages of the study, so that gravity effects could be neglected.

The macroscopic part of the drop has been characterized as a function of time by two kinds of measurements: the drop radius by direct microscope observation, and the apparent contact angle θ_a by a recently proposed light reflection technique,[16] where a parallel laser beam is sent onto the drop which acts as a convex mirror and shines the light back into a cone of angular aperture $2\theta_a$; on a far screen at a distance h from the substrate, one detects an illuminated disk with a diameter D related to θ_a through $\theta_a = \frac{1}{2}\tan^{-1}[\frac{1}{2}(D-2R)/h]$. By adjustment of h, θ_a values in the range 20°–0.1° can be measured with an accuracy better than 5%, and measurements on the whole periphery of the drop are performed simultaneously, leading to easy averaging procedures or detection of drop shape distortions.

Typical results for $R(t)$ and $\theta_a(t)$ on logarithmic scales are presented in Fig. 1 for a series of drops of different volumes and different molecular weights, and for the two types of surfaces. A linear behavior is observed in all cases over more than three decades, an indication of power-law dependences $R(t) \sim t^n$, $\theta(t) \sim t^{-p}$. The exponents appear to be independent of drop volume Ω, polymer molecular weight, and spreading parameter S as evidenced by the corresponding parallel lines in Fig. 1. For the set of 20 drops studied at the present time, we have obtained $n = 0.100 \pm 0.010$ and $p = 0.300 \pm 0.015$, in very good agreement with Tanner's predictions.[13]

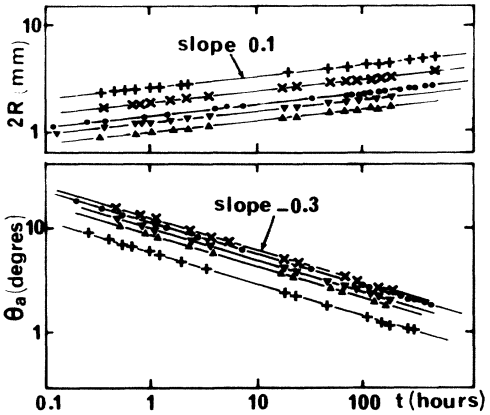

FIG. 1. Drop sizes R and apparent contact angles θ_a as functions of time (logarithmic scales) for five PDMS drops of different volumes, of different molecular weights M, and deposited on clean or silanated silicon wafers. Clean wafer, $M = 1.6 \times 10^5$, $\Omega = 6.5 \times 10^{-5}$ cm^3, circles; silanated wafer, $M = 1.6 \times 10^5$, $\Omega = 1.8 \times 10^{-4}$ cm^3, plusses; silanated wafer, $M = 1.6 \times 10^5$, $\Omega = 3.5 \times 10^{-5}$ cm^3, inverted triangles; silanated wafer, $M = 1.6 \times 10^5$, $\Omega = 1.5 \times 10^{-5}$ cm^3, triangles; silanated wafer, $M = 7.9 \times 10^4$, $\Omega = 2.1 \times 10^{-4}$ cm^3, plusses. Power laws are well observed over more than three time decades, and the corresponding exponents are insensitive to the spreading parameter, the molecular weight (viscosity), or the volume of the drop.

In order to investigate more microscopic scales, we have developed sensitive visualization procedures based on the optical properties of thin dielectric films in polarized reflected light. The reflection coefficient of a polarized beam depends on the direction of the polarization with respect to the plane of incidence, and one usually introduces two reflection coefficients $r_\perp$ and $r_\parallel = r_\perp (\tan\psi) e^{i\Delta}$, given by the Fresnel formula,[17] and corresponding respectively to an incident electric field normal or parallel to the plane of incidence.

A thin dielectric layer deposited on the surface affects both the amplitude ratio $\tan\psi$ and the phase difference Δ. The measurement of those two quantities is commonly used in ellipsometry to obtain the thickness and dielectric constants of the film.[18] The modifications of $r_\parallel$ and $r_\perp$, however, can be used in a slightly different way, combined with imaging through a microscope, to visualize a nonuniform film: The film is placed under a reflection polarizing microscope between two crossed polarizers. For a given incidence angle θ and for a given angle ϕ between the plane of incidence and the (first) polarizer axis, the reflected amplitude selected by the analyzer is

$$A(\theta,\phi) = A_i(\theta)[r_\perp(\theta) + r_\parallel(\theta)]\sin\phi\cos\phi = A_i(\theta) r_\perp(\theta)[1 + \tan\psi(\theta) e^{i\Delta(\theta)}]\sin\phi\cos\phi,$$

where $A_i(\theta)$ is the real incident amplitude at (θ,ϕ), with the sign conventions of Ref. 17. For incoherent light, averaging over ϕ leads to a reflected intensity

$$I(\theta) = \tfrac{1}{8} A_i(\theta)^2 |r_\perp(\theta)|^2 [1 + \tan^2\psi(\theta) + 2\tan\psi(\theta)\cos\Delta(\theta)].$$

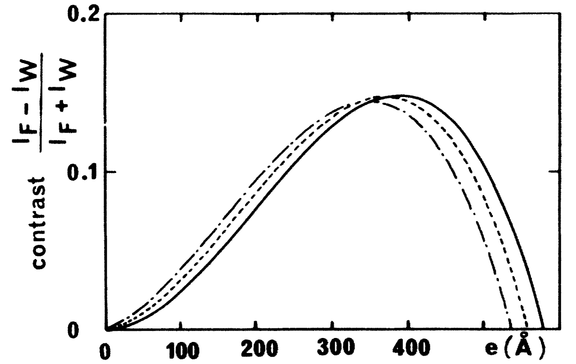

FIG. 2. Numerical evaluation of the contrast in reflected polarized light as a function of PDMS film thickness e, for an angle of incidence $\theta = 20°$. We have assumed a complex index of refraction for the silicon $n = 4 - 0.03i$, and for both PDMS and oxide layer $n = 1.43$. The different curves correspond to oxide layer thicknesses, $e = 0$ Å (solid line), 20 Å (dashed line), 40 Å (dash-dotted line).

Figure 2 presents a numerical evaluation of the contrast $(I_F - I_W)/(I_F + I_W)$ as a function of film thickness e for $\theta = 20°$. I_F and I_W are the reflected intensities with, respectively, a PDMS film of thickness e (index of refraction 1.43) or no PDMS (silicon covered with a 0-, 20-, or 40-Å-thick oxide layer of refractive index 1.43). A noticeable contrast appears for films of order 50 Å, increases with e, reaches a maximum for $e \sim 400$ Å, and then decreases for larger thicknesses as one reaches the first ordinary black fringe of equal thickness. A decrease of θ does not significantly displace the position of the maximum, but progressively decreases the total contrast, and Fig. 2 is representative of what can be expected from observation through a microscope when an average over all θ values in the aperture of the objective is performed. In the following, the method will be referred to as "ellipsometric contrast."

Typical pictures of the fronts of spreading drops are presented in Fig. 3, for a wafer grafted with silane. The bright area in front of the last interference fringe visible in Fig. 3 is a clear manifestation of the existence of a precursor film. This bright area progressively extends ahead of the drop macroscopic edge (that we localize at the position of the first black fringe) as time passes. For a given substrate and a given molecular weight, it extends more rapidly for smaller apparent contact angles, and may extend as far as 1 mm after several weeks of spreading. It also extends more rapidly on a bare wafer than on a silanated one. Moreover, the precursor film has a very different aspect on the two kinds of surfaces: On the high-energy surface the film appears homogeneous, and the contrast progressively dies out with distance from the drop edge, an indication of a slow decrease of the thickness towards molecular values. On the low energy surface, in contrast, the film appears quite inhomogeneous (while the surface roughness is the same in both cases) and stops more abruptly. A complete quantitative analysis of the film profile with a calibration of the reflected intensity as a function of film thickness is presently underway. The above results, however, still demonstrate that ellipsometric contrast can be a useful tool in the study of nonuniform thin films.

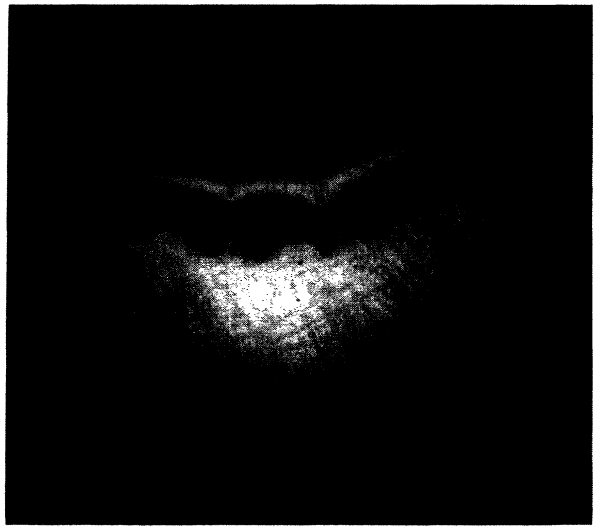

FIG. 3. Typical aspect of a PDMS drop (molecular weight 79000), deposited on a silanated wafer, as observed by ellipsometric contrast microscopy. Full-view diameter: 1800 μm. Fringes of equal thickness are visible in the macroscopic part of the drop (lower part of the figure). Above the last black fringe, the precursor film appears as a nonuniform bright area. Starting from the black fringe, the contrast increases rapidly, and then slowly decreases toward the top of the figure in correspondence with Fig. 2. Notice the stong fluctuations characteristic of silanated wafers.

In conclusion, the spreading of high-molecular-weight polydimethylsiloxane droplets deposited on smooth silicon surfaces has been investigated by three different optical techniques, on both macroscopic and microscopic scales. For the macroscopic part of the drop (thickness larger than 0.1 μm), our data confirm and extend previous results: The size and the apparent contact angle kinetics follow Tanner's scaling laws, which appear to be universal with respect to the viscosity of the liquid, the volume of the drop, and the spreading parameter S of the system. For smaller scales, we present what we think to be the first direct visualization of a thin precursor film (a few hundred angstroms thick) which progressively develops ahead of the macroscopic drop edge as time passes. The growing kinetics and the structure of this film are nonuniversal and, in particular, strongly depend on the spreading parameter S.

Both points give strong support to de Gennes's and Joanny's recent theoretical developments based on a separate treatment for two regions in space, respectively inside and outside the zone of influence of long-range forces. Our visualization method opens the way to quantitative investigations of the structure and dynamics of the precursor film.

The PDMS samples have been fractionated, characterized, and kindly given to us by C. Strazielle, Institut Charles Sadron, Strasbourg, France. We have benefitted from very helpful discussions with Professor F. Abeles, on the optical properties of thin films. F. Rondelez has pointed out to us the surface quality of silicon wafers, and supplied us with the wafers used in the present study. Physique de la Matière Condensée, Collège de France, is Unité Associé No. 792 au Centre National de la Recherche Scientifique.

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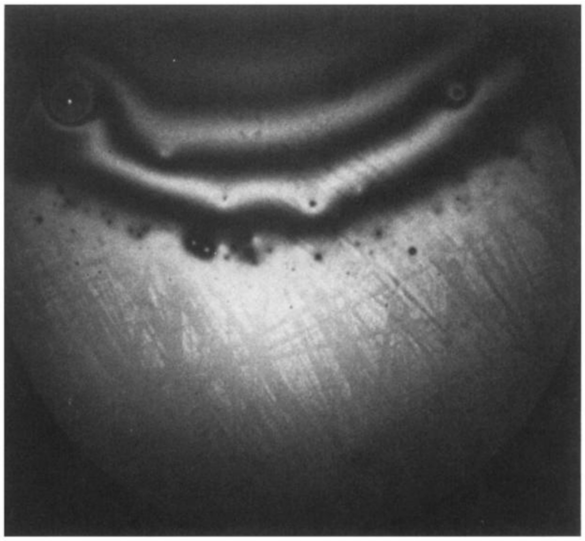

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