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Evidence for a New Spreading Regime between Partial and Total Wetting

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We present an investigation of the macroscopic spreading behavior of polydimethylsiloxane droplets on solid surfaces of adjustable spreading power. This is obtained through chemical grafting of mixed self-assembled monolayers on silicon wafers. Between partial wetting and high-energy-type total wetting, we identify for the first time a new regime in which the whole spreading kinetics is highly sensitive to the layer polarizability. This new regime can be interpreted in terms of oscillating van der Waals interactions, and identified with the pseudo partial wetting recently predicted.

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Wetting and spreading has recently become a field of renewed interest, both experimentally and theoretically, mainly due to a strong practical interest and to the now well accepted idea that thin liquid films in which disjoining pressure is important play a dominant role in the spreading process.[1,2] The situation is not yet totally clear, however: The theoretical models are mainly devoted to low-spreading-parameter (S) situations ($S = \gamma_{SG} - \gamma_{SL} - \gamma$ is the difference between the energy of a dry solid and that of a solid covered by a flat macroscopic layer of liquid, with γ_{SG}, γ_{SL}, and γ, respectively, the solid-gas, solid-liquid, and liquid-gas interfacial tensions), while experiments have been performed on high-energy surfaces[3] or on surfaces where S was relatively low, but unknown.[3(b),4]

The situation of particular interest is that of "dry wetting" in which spreading only takes place through liquid flow (no efficient transport through the vapor phase). Then S and the disjoining pressure are predicted[2] to control the late stages of a spreading drop (fixed volume) while its macroscopic part follows Tanner's law[5] independently of S, as has already been observed.[6]

Experimental investigations on high-energy surfaces have mainly revealed, at long times, the formation of a "tongue" of molecular thickness, in which the liquid progressively loses its cohesion,[3(b),3(c)] sometimes accompanied by a structuring of the liquid.[3(c)] On low-energy surfaces ($S < 1$ dyn/cm), the final state of spreading has been shown to be a "pancake," i.e., a film of uniform thickness surrounded by dry solid,[4] in agreement with de Gennes and Joanny's description.[2] The thickness e_c of this experimentally observed pancake is, however, still molecular, which makes any further comparison with theory difficult. Assuming van der Waals interactions, one expects $e_c = a\sqrt{3}\gamma/2S$ with a a molecular length.[2] Therefore, variations of S in the range $S > 0$ but very small (i.e., $S < 10^{-2}\gamma$) appear to be of particular interest.

In this Letter, we present a series of experiments conducted on controlled surfaces of adjusted surface energy. The whole spectrum of situations from partial wetting to high-energy-surface wetting, for the same liquid, has been continuously explored. We restrict our attention here to the spreading behavior of the macroscopic part of the drops and to thick precursor films when they are visible through optical microscopy in monochromatic polarized light. A detailed analysis of the very-thin-film profiles, when they exist, is presently under way and will be presented in a forthcoming paper.

The liquids used are narrow-molecular-weight fractions of polydimethylsiloxane (PDMS), $M_w \cong 18\,000$ and $M_w \cong 26\,500$; $M_w/M_n \cong 1.1$. High enough molecular weights have been chosen to avoid molecular-weight dependence of the surface tension for the different constituents of one fraction. Typical drop volumes are $\Omega \cong 10^{-8}$ cm^3.

The solid surfaces are chemically modified silica surfaces (native oxide, amorphous silica 20 Å thick) of a silicon wafer (Siltronix, France, cut along the [111] direction). Their roughness, characterized through x-ray reflectivity, is small ($\sigma \cong 5$ Å).[4] Modification of these surfaces has been performed by grafting long aliphatic chains using Sagiv's silanation procedure.[7,8] We have grafted mixtures of tetradecyltrichlorosilane [TTS: $Cl_3-Si-(CH_2)_{13}-CH_3$, synthesized using a Grignard-type procedure[8]] and unsaturated TTS [uTTS: $Cl_3-Si-(CH_2)_{12}-CH=CH_2$, Petrarch]. Taking advantage of the slightly higher polarizability of the vinyl group compared to the methyl group, the surface energy was adjusted by varying the relative proportions of uTTS and TTS in the grafted layer. The details of the experimental procedure will be presented elsewhere.[8] The monolayers, characterized by x-ray-reflectivity experiments,[9] appear dense with a thickness of 18 Å (the length of the fully extended aliphatic chains) whatever the relative concentrations of the two components. The chains are close packed, all extended in a *trans* conformation, perpendicular to the surface within ±5°.

The wafers have been individually characterized by contact-angle experiments using dodecane as a reference liquid (see Fig. 1). Hysteresis, defined as $\Delta = \cos\theta_r - \cos\theta_a$ (where θ_r and θ_a are, respectively, the advanc-

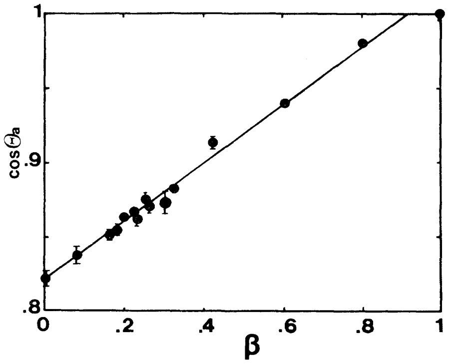

FIG. 1. Cosine of the advancing contact angle of dodecane as a function of a relative concentration of uTTS over TTS in the grafting solution.

ing and receding contact angles), does not show any significant variation with the fraction of uTTS in solution (β): $\Delta \cong 1.5\times 10^{-2}$. This seems to be in support of unsaturated groups uniformly and randomly distributed on the surface. If patches form, they are small enough to not affect Δ.[10] These surfaces can therefore be seen as model surfaces with a surface free energy continuously adjustable by varying the relative uTTS to TTS concentration β in the silanation solution.

One PDMS droplet is deposited on a treated wafer, inside a glove box in a filtered dry-nitrogen atmosphere. After deposition, each wafer is immediately enclosed in an airtight box equipped with a glass window. The spreading can then be studied by microscopy, out of the glove box, in a controlled atmosphere free of dust and further contamination, even for long times.

The profile of the macroscopic part of the drop is deduced from the location of the equal-thickness interference fringes obtained in natural monochromatic reflected light, down to $\lambda/4n$ (λ is the wavelength of light, and n the index of refraction of the liquid at λ), i.e., to approximately 700 Å for blue light. Smaller thicknesses, down to approximately 100 Å, can be probed at least qualitatively in reflected polarized light using ellipsocontrast.[6(a)]

For very small uTTS concentrations ($\beta<\beta_0$, $\beta_0 \cong 24\%$), PDMS is in the partial-wetting regime: the drops reach their static contact angle in times going from 10^{-3} s to several hours when the contact angle is small. Then the process stops and no further evolution of the drop can be detected; in particular, its volume remains constant over periods as long as six months, a test of the very low volatility of these liquids (this is not the case for unfractionated silicon oils which may contain a noticeable fraction of volatile low-molecular-weight molecules).

If the polarizability of the surface is slightly increased ($\beta_0<\beta<\beta_1$, $\beta_1 \cong 26\%$) a total-wetting regime is observed and very small drops ($\Omega \cong 10^{-10}$ cm^3) totally spread. Very surprisingly, however, the kinetics of evolution of the macroscopic cap is much slower than for the spreading of a drop of comparable volume deposited on a high-energy surface, as is immediately visible when comparing Figs. 2(a) and 2(c). Moreover, this kinetics is highly sensitive to the surface energy and slows down drastically when β is close to β_0. This behavior is in clear disagreement with Tanner's law[5] which was considered as well established for total-wetting situations.

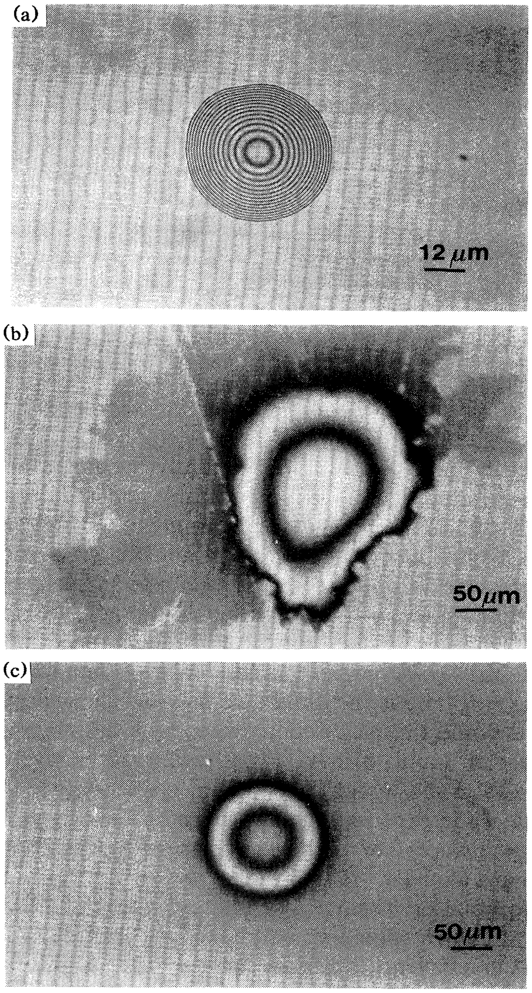

FIG. 2. Photographs of droplets of PDMS of comparable volumes (10^{-8} cm$^3 < \Omega < 10^{-7}$ cm^3) in the different regimes. Photographs (a) and (b) were taken about 24 h after deposition; photograph (c), 6 h after deposition (smaller volume). In all cases, the wavelength was 436 nm; light was polarized in cases (b) and (c) and natural in case (a). (a) $\beta_0<\beta<\beta_1$: The drop evolves very slowly. In this photograph, no difference can be observed compared with a drop in the partial-wetting regime. (b) $\beta_1<\beta<\beta_2$: The drop is surrounded by a thick film (30 nm $< e <$ 50 nm). Its kinetics begins to depart from Tanner's law. (c) $\beta_2<\beta$: The situation is a classical total-wetting situation. The slowly decreasing contrast from the last black fringe is the connection to a very thin precursor film.

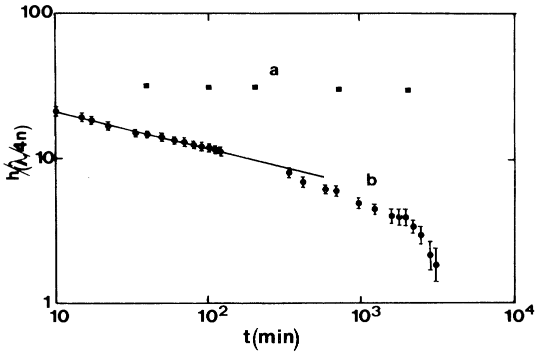

FIG. 3. Evolution of the maximum thickness h of droplets in two different regimes: curve a, $\beta_0 < \beta < \beta_1$; curve b, $\beta_1 < \beta < \beta_2$. Units for h are the total number of interference fringes. The difference in height between a dark and a clear fringe is $\lambda/4n \cong 770$ Å in our case. The solid line represents the corresponding Tanner's law for curve b. Experimental points depart from it when a thick film appears. Notice on curve a the very slow (but nonconstant) evolution of the drop.

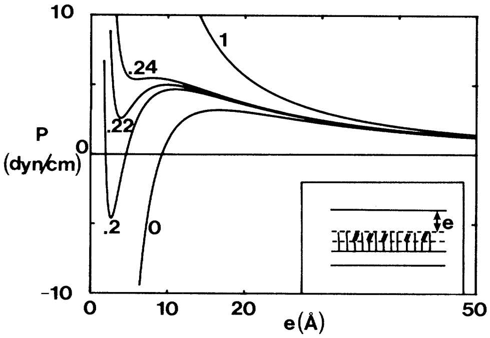

FIG. 4. $P(e)$ calculated for different values of the surface concentration in ethylene groups (β is noted for each curve). The system is modeled as a homogeneous stratified medium (see inset). From top to bottom, the layers are PDMS (thickness e), end of the grafted chains, grafted chains, silica, and silicon (as a semi-infinite medium). The other semi-infinite medium (over PDMS) is air. Hamaker-constant values used in this calculation are from Ref. 12.

Such a disagreement is illustrated by the kinetics depicted in Fig. 3.

If the surface polarizability is further increased, with $\beta_1 < \beta < \beta_2$, $\beta_2 \cong 27\%$, the situation is that of Fig. 3 (curve b) and Fig. 2(b): The macroscopic drop asymptotically follows Tanner's law at short times, but a thick film ($e \cong 500$ Å) clearly develops all around the drop when it has reached a small enough contact angle ($\theta \cong 5\times10^{-3}$ rad). When the volume of liquid involved in this film is no longer negligible compared to the total volume of the drop, the macroscopic kinetics departs from Tanner's law (which assumes a constant volume), the film extends as the drop drains into it, and it then thins out, becoming too thin to be observable with a microscope. An alternative technique, such as ellipsometry or x-ray reflectivity, becomes necessary.

Increasing again the surface energy ($\beta > \beta_2$), high-energy-type spreading comparable to what has previously been reported is recovered: The drop follows Tanner's law over several time decades. In Fig. 2(c) the continuous decrease in contrast from the last black fringe towards the edge of the wafer is indicative of a thin precursor film and, again, alternative techniques have to be used to obtain its detailed profile.

Brochard *et al.*[11] have recently pointed out that short-range interactions can have a drastic influence on the free energy $F(e)$ of the system constituted by a solid covered by a liquid layer of thickness e and could change the spreading criterion. $F(e) = \gamma_{SL} + \gamma + P(e)$, with $P(e)$ the contribution of the cohesive interactions within the liquid. As $F(e \to 0) = \gamma_{SG}$, one can easily see that $S = P(e \to 0)$. The spreading parameter is thus very sensitive to short-range interactions close to the surface, while at large enough e the behavior of the liquid can be described, if the solid is a semi-infinite medium, by the van der Waals expression $P(e) = A/12\pi e^2$ (A is the Hamaker constant of the system). Thus, S and $P(e)$ can be considered independently; in particular, they may have opposite signs in a certain range of thicknesses. In this case, a new regime, called pseudo partial wetting, can possibly take place[11] when a minimum at finite thickness appears in $F(e)$. In this regime, the drop drains into a thin film, but its profile and its connection to the macroscopic drop are completely different from the high-energy-wetting situation: In the latter, the thickness at which the film connects to the macroscopic drop increases with time like a/θ (where a is a molecular size and θ the apparent contact angle), while this thickness is time independent in the pseudo-partial-wetting regime, leading to a much steeper connection. This drastically slows down the spreading process and leads to a macroscopic drop in equilibrium with a thin film into which its drains very slowly. Only very small drops appear to totally spread.

The solids we use are not semi-infinite but rather are stratified media (Fig. 4, inset). We have estimated $P(e)$ for different values of β by simply adding up the different layers of elementary contributions[13] (Fig. 4). An absolute minimum shows up in a restricted range of β. Thus, the slow spreading observed in the range $\beta_0 < \beta < \beta_1$ renders plausible an interpretation in terms of pseudo partial wetting, the absolute minimum of $P(e)$ appearing in a range of β close to our experimental values (Fig. 4).

In conclusion, by continuously varying the surface energy of silicon wafers by chemical grafting of trichlorosilanes, we have characterized the macroscopic spreading kinetics of PDMS with special attention given to the vicinity of the zero spreading parameter. We have demonstrated the existence of a new spreading regime, distinct from both partial wetting (very small drops totally spread) and the usual, previously reported total-wetting situations, as the macroscopic kinetics of the drop is highly sensitive to the spreading-parameter value and incompatible with Tanner's laws. This behavior may be indicative of the recently predicted pseudo-partial-wetting regime, related to the existence of a minimum in the van der Waals energy term. If this is confirmed by further experiments, one can think of wetting experiments to experimentally determine Hamaker constants over a wider range of systems than what is presently possible.[14] The fact that the thick film observed in total wetting at low enough spreading-parameter values ($\beta_1 < \beta < \beta_2$) is unstable and thins out after a long time may also be indicative of oscillations in the force-versus-distance law.

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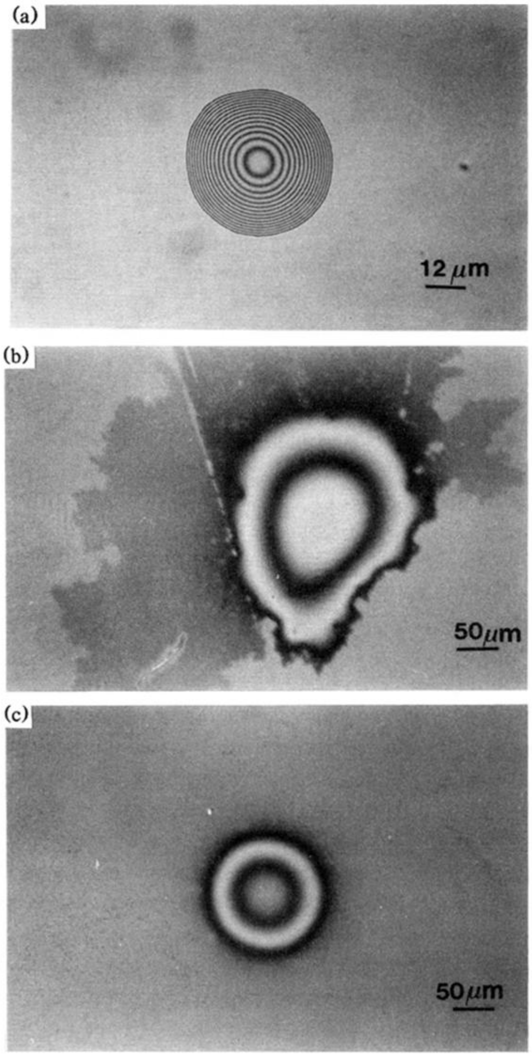

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