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Spreading dynamics of water droplets

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The spreading dynamics of water droplets on flat silicon surfaces is investigated. It is shown that, for situations close to complete wetting, the radius evolution with time can be described using a power law with a nonstandard exponent of 1/7. This dynamics is interpreted using a hydrodynamic model with an invariant dissipation profile. Such a description is also consistent with the slow dynamics observed for larger contact angles.

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The spreading dynamics of a liquid on a solid surface plays a key role in many practical processes ranging from agriculture (e.g., crop protection via pesticide spreading on plant leaves) to industry (e.g., painting, printing). Despite this broad interest, the physics underlying the spreading of a liquid on a solid surface has remained poorly understood until recently and some issues remain controversial. This lack of clarity is linked to the difficulty of preparing ideal experiments (i.e., using simple liquids and atomically flat solids). Experiments by Tanner [1] using silicone oils as a fluid have shown that the radius of a spreading droplet varies as the $\frac{1}{10}$ power of the time (the ''Tanner'' law). This finding was confirmed by other groups [2] using similar nonvolatile fluids and explained theoretically by de Gennes [3,4].

The present work was done with the aim of exploring ways to measure the hydrophilicity of silicon wafers that have experienced different microelectronic cleaning procedures. Measuring contact angles is a valuable tool in this respect as the equilibrium value of the angle is a direct manifestation of the balance between molecular forces, but such measurements are restricted to the case of partial wetting. In the case of total wetting, the question was whether the study of the dynamics of spreading could supplement the lack of information from equilibrium situations.

In this context, we used water as a fluid, i.e., a low-viscosity, volatile liquid made of small molecules. The solid surfaces were those of flat silicon wafers (covered with oxide), whose contact angle with water could be changed using the standard chemical cleaning procedures of microelectronics, while keeping extremely low surface roughness (1–2 Å rms). As problems of contact line pinning are avoided, our experiments should approach the ideal case situation and be suited for comparison with theory.

The experiments reported here were done in the so-called sessile drop geometry: At time $t=0$, a drop is formed from the needle of a syringe and deposited onto a flat horizontal silicon wafer. Using a video camera, the macroscopic profile of the drop is then recorded as a function of time (Fig. 1). During the experiment, the atmosphere was saturated with water vapor and temperature kept constant at a value of 21 °C. Care was taken to check reproducibility: Measurements were performed several times and no differences were found between subsequent spreading sequences. In the experiments, we measured simultaneously the size of the drop (radius) and the contact angle. To the accuracy of our measurement, they were always found to be consistent with the condition of constant volume. Receding and advancing contact angles when measured in quasistatic mode (slow speed) were similar. We shall compare in the following the situation for two surface treatments giving zero and finite (12°) static contact angles.

We first examined the spreading of droplets in the case of a hydrophilic substrate. The final contact angle was very close to zero (below 1°). For that purpose, wafers were cleaned using a ''standard clean'' procedure (SC1) (ammonium hydroxide–hydrogen peroxide mixture). The SC1 cleaning procedure is known to remove the oxide layer and its contaminants and freshly reoxide the silicon surface [5]. On Fig. 2, we have plotted experimental values for $\cos(\theta_f)-\cos\theta\approx 1-\cos(\theta)$ as a function of time t. We find that the time dependence of this quantity can be described by a power law, with an exponent $\alpha=-0.855\pm0.03$, close to $-\frac{6}{7}$. We shall discuss in the following how we can interpret this value.

The basic equation governing the dynamics of spreading is obtained by equating the power of the spreading force F to the dissipation in the liquid by viscous shear forces [3]:

$$\frac{dQ}{dt}=Fv, \tag{1}$$

where v is the velocity of the spreading drop edge and Q the

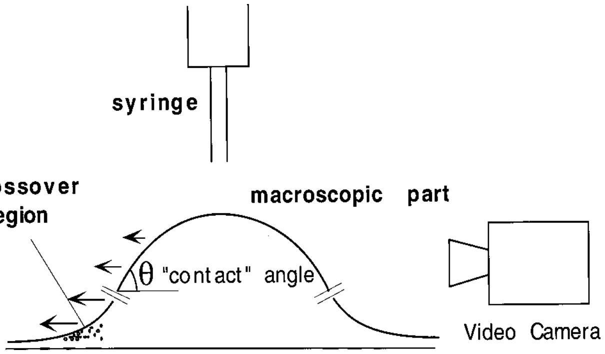

FIG. 1. Sketch of the experiment. Only the macroscopic part of the drop is visible with the optical video camera. Contact angle and drop radius are measured as a function of time.

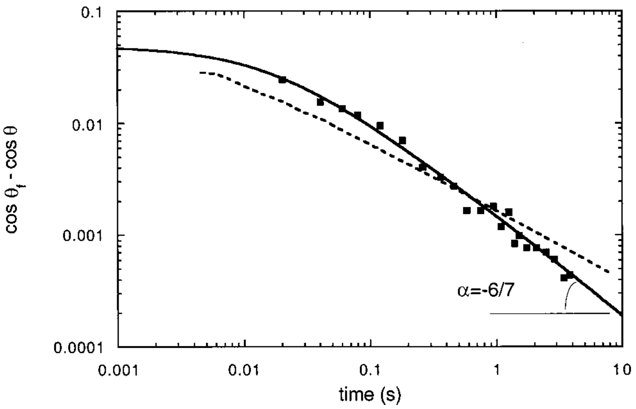

FIG. 2. Spreading force as a function of time for a hydrophilic substrate. Solid line is the model based on an invariant dissipative profile using $\tau_7 = 8$ ms, giving a power law at large times with exponent $\alpha = \frac{6}{7}$. Dashed line is the wedge model with $\tau_{10} = 0.74$ ms, giving $\alpha = -\frac{6}{10}$.

heat dissipated. Following the work of de Gennes [3], one obtains within the lubrication approximation (for small angles) the following expression for the viscous dissipation due to shear forces [η is the viscosity and $u(z)$ the fluid velocity profile]:

$$\int_{x_{\min}}^{x_{\max}} dx \int_0^{z(x)} \eta \left(\frac{\partial_\mu}{\partial z} \right)^2 dz = \gamma(\cos\theta_f - \cos\theta) v, \tag{2}$$

where γ is the liquid/vapor surface tension, θ the contact angle, and θ_f the equilibrium (final) value of this angle. The solution of these equations depends on the shape of the dissipative part and we shall make two different assumptions as follows.

If one models the drop shape close to the contact line as a wedge of angle θ extending from $x_{\min}$ to $x_{\max}$, one obtains for the dissipation, assuming a Poiseuille flow in the wedge,

$$\frac{dQ}{dt} = 3\, l\, \eta \frac{v^2}{\theta}, \quad l = \ln(x_{\max}/x_{\min}). \tag{3}$$

The parameter l depends on both the maximum size of the drop ($x_{\max}$=radius$r$) and the value of a microscopic cutoff ($x_{\min}$). For a millimeter-size drop with a molecular length cutoff $l = \ln(10^{-3}/10^{-10})$, so that physically relevant values for this parameter should not exceed $l = 16$. The velocity v of the advancing contact line is related to the time derivative of the contact angle via the expression for the volume Ω of a spherical cap (small angles)

$$\Omega = \frac{\pi}{4} \theta r^3 \Rightarrow v = \frac{dr}{dt} = \frac{d}{dt} \left[\left(\frac{4\Omega}{\pi\theta} \right)^{1/3} \right]. \tag{4}$$

Equation (2) yields a differential equation that describes the evolution with time of the contact angle θ:

$$\theta(\theta^2 - \theta_f^2) = \tau_{10} \frac{d}{dt} \left(\frac{1}{\theta^{1/3}} \right), \tag{5}$$

where $\tau_{10} = l(6\eta/\gamma)(4\Omega/\pi)^{1/3}$ is a characteristic time for spreading. The subscript 10 refers here to the exponent of the spreading law for the drop radius ($\frac{1}{10}$, see below). The differential equation (5) can be solved analytically in the form

$$\frac{1}{\theta_f^{10/3}} \left[F_{10}\left(\left(\frac{\theta_f}{\theta} \right)^{1/3} \right) - F_{10}\left(\left(\frac{\theta_f}{\theta_0} \right)^{1/3} \right) \right] = \frac{t}{\tau_{10}}, \tag{6}$$

where the expression for F_{10} is

$$F_{10}(\rho) = -\frac{\rho^4}{4} - \frac{1}{2\sqrt{3}} \arctan\left[\frac{\rho^2\sqrt{3}}{2+\rho^2} \right] + \frac{1}{12} \ln\left[\frac{1+\rho^2+\rho^4}{(1-\rho^2)^2} \right]. \tag{7}$$

For the first stages of spreading (short time, $\theta \gg \theta_f$, $\rho \ll 1$), $F(\rho) = \rho^{10}/10$ and Eq. (7) yields

$$\frac{1}{\theta^{10/3}} - \frac{1}{\theta_0^{10/3}} = 10 \frac{t}{\tau_{10}}, \tag{8}$$

i.e., the angle changes with time with exponent $-\frac{3}{10}$ and the radius r of the drop with exponent $\frac{1}{10}$ (the Tanner law). In the representation of $\cos\theta_f - \cos\theta = \theta^2/2$ as a function of time, an exponent of $-\frac{6}{10}$ would be obtained. From the plot of Fig. 2, it is clear that this power law does not describe the data correctly.

Let us now assume the dissipation takes place in a part of the drop profile $z(x)$, ranging from $x_{\min}$ to $x_{\max}$, whose shape does not depend on the macroscopic contact angle. Such an assumption is not necessarily unrealistic since most of the dissipation occurs very close to the contact line. Then the expression (3) for the viscous dissipation in the profile does not depend explicitly on the contact angle and the differential equation giving the time dependence of the contact angle can be expressed as

$$(\theta^2 - \theta_f^2) = \tau_7 \frac{d}{dt} \left(\frac{1}{\theta^{1/3}} \right), \tag{9}$$

with $\tau_7 = (6\eta/\gamma)(4\Omega/\pi)^{1/3} \int_{x\,\min}^{x\,\max} dx/z(x)$. One can define an effective angle θ_p for this profile part by setting $l/\theta_p = \int_{x\,\min}^{x\,\max} dx/z(x)$. Equation (9) can be solved again in a form similar to Eq. (6) but gives a different exponent for the time dependence of the contact angle:

$$\frac{1}{\theta_f^{7/3}} \left[F_7\left(\left(\frac{\theta_f}{\theta} \right)^{1/3} \right) - F_7\left(\left(\frac{\theta_f}{\theta_0} \right)^{1/3} \right) \right] = \frac{t}{\tau_7}, \tag{10}$$

where the expression for F_7 is now

$$F_7(\rho) = -\rho - \frac{1}{2\sqrt{3}} \arctan\left[\frac{\rho\sqrt{3}}{\rho^2 - 1} \right] + \frac{1}{12} \ln\left[\frac{(1+\rho+\rho^2)(\rho+1)^2}{(1-\rho+\rho^2)(\rho-1)^2} \right]. \tag{11}$$

The Taylor expansion of $F_7(\rho)$ close to $\rho = 0$ ($\theta/\theta_f \gg 1$) is now $\rho^7/7$, yielding

$$\frac{1}{\theta^{7/3}} - \frac{1}{\theta_0^{7/3}} = 7 \frac{t}{\tau_7}, \tag{12}$$

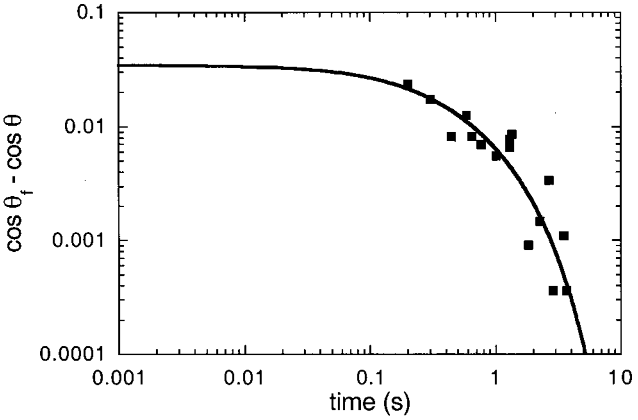

FIG. 3. Spreading force as a function of time for a hydrophobic substrate. Solid line is the model using $\tau_7 = 170\,\mathrm{ms}$.

so that for $\theta \ll \theta_0$ the angle changes with time with exponent $-\frac{3}{7}$ and the radius r of the drop with exponent $\frac{1}{7}$. When plotted as a function of $\cos(\theta_f) - \cos(\theta)$, we now obtain an exponent of $-\frac{6}{7}$, close to the experimental observation. Using this exponent, the value found for the characteristic time τ_7 is 8 ± 1 ms for a 2.3 μl drop. Our experimental data on oxidized silicon are not so far from observations of Marmur and Lelah for water spreading on a silica glass surface [6]. They described their data using a law of the form $A = \mathbf{k}\mathbf{t}^n$ for the area A of the drop as a function of time t. Using these variables, our data would give $k = 0.4$ (for a drop volume of 2.3 μl) and $n = \frac{2}{7} = 0.28$. Marmur and Lelah report values of $k = 0.31$ and $n = 0.25$.

Let us now consider the case of a large final contact angle (''hydrophobic'' substrates). These samples were prepared using standard sulfuric acid–hydrogen peroxide mixtures whose main effect is to remove heavy organic contaminants from the surface without etching the oxide. The drop volume is now 3 μl.

The previous considerations based on the wedge dissipation would predict a very fast spreading for the drop. For nonzero contact angles, spreading times of 10^{-5} s are expected [4]. However, the observed spreading kinetics is much slower. When plotted on a log-log plot, the driving force does not show a straight line due to absence of a regime where $\theta \gg \theta_f$ (Fig. 3). The full form of Eq. (10) has to be used and corresponds to an exponential relaxation when $\theta \rightarrow \theta_f$. One can fit both laws to the data and they give equally good results. Using Eq. (10), one finds $\tau_7 = 170\,\mathrm{ms}$. If Eq. (6) was used, one would obtain $\tau_{10} = 40\,\mathrm{ms}$.

These large values for the time constants give unphysical values for l (320) when the wedge model is applied with angles larger than $\theta_f = 0.2\,\mathrm{rad}$. This is a second indication that this model is not adapted to describe what happens close to the contact line where the angle θ_p is probably very small. Note that similar observations were made by de Ruijter and co-workers [7] on the spreading of a water-glycerol solution on poly (ethyleneterephtalate) (PET). In their experiments, the authors found values for l ranging from 19 to 46 with highest values for higher θ_f. The explanation for this behavior may just be that the value for l is compensating the underestimation of dissipation by the wedge model, which is larger for large angles. The unphysical values found for l have been put forward in favor of a molecular dynamics treatment of the spreading kinetics [7,8]. In this molecular approach, the spreading dynamics is limited by some kind of molecular static friction coefficient at the contact line. This coefficient being independent of the contact angle, this view yields a dynamical behavior similar to that predicted by Eq. (9). Models combining the two types of dissipation (viscous hydrodynamic and molecular) have also been proposed [9,10]. Here we suggest that, in the case of wetting with water, the situation is that of pure hydrodynamic dissipation in an invariant part of the drop profile determined only by the fluid/substrate interaction potential $P(z)$ [3]. Unfortunately an exact shape of the interaction potential is unavailable for such a complex fluid as water. It would be very important to be able to directly measure experimentally the profile of the drops close to the contact line. This appears to be a very difficult task, due to the high resolution required. For a drop in equilibrium, techniques such as ellipsometry and atomic force microscopy have been used [2,11] but they still lack lateral resolution. Dynamical measurements of the profile during spreading in the case of low-viscosity liquids are even more difficult as the measurements should be performed within a few milliseconds.

Pinning of the contact line is excluded here as values of the contact angle in the advancing and receding modes are very similar, a fact that is not very surprising on these very smooth substrates. Reactive spreading (i.e., modification of the chemical state of the substrate as the liquid advances) is also excluded as successive spreading experiments done on the same part of the wafer gave identical results. It should also be recalled that these experiment are done in a water saturated atmosphere, so that an adsorbed water film is already present on the wafer.

In conclusion, our findings indicate that the model of a liquid wedge with an angle equal to the macroscopic contact angle cannot be extended to microscopic distances in the case of water and that dissipation is independent of the actual contact angle value. This conclusion is backed, for total wetting, by the observation of a $\frac{1}{7}$ exponent for $r(t)$ instead of the $\frac{1}{10}$ exponent of the Tanner law, and, for partial wetting, by a dynamics much slower than expected using the wedge model. Such an observation can be related to the importance of dissipation within the precursor film in the case of total wetting for a nonvolatile liquid. It was shown in this case that most of the dissipation takes place in this narrow film region [3].

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