LETTER TO THE EDITOR

Diffusion-controlled wetting films

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Abstract. The dynamics of ultra-thin wetting films has been studied experimentally under a controlled atmosphere using a dynamic ellipsometric technique. The spreading fluid was PDMS and the substrates were oxide covered silicon wafers. The situations of capillary rise up a vertical wall, and the spreading of 'nanoscopic' drops, have been compared. The development of films of near-molecular thickness, over macroscopic distances, is observed in both cases. Two diffusive processes (early and late) have been identified for the dynamics of the tips of those films. This in turn requires theoretical effort in the field of ultra-thin-film dynamics.

Stimulated by recent theoretical analysis [1, 2] the field of wetting and adhesion [3] is at present the subject of an increasing number of experimental and theoretical studies. It has been observed for a long time [4] that a thin precursor film precedes the macroscopic edge of a completely wetting liquid. It is possible to study [5–13] these films by ellipsometry, x-ray reflectometry or in their thickest part by interferometry.

Thin film properties can be analysed in terms of the disjoining pressure first introduced by Derjaguin [3, 14], which expresses the action of molecular forces in the film–substrate system. Although the theory can be developed formally in the general case [1, 3], the resulting equations must be solved numerically for each particular disjoining pressure case and their predicting power is limited. The *hydrodynamic* treatment by de Gennes [2], who focused on long-range van der Waals forces, has a restricted validity at small thicknesses but may provide a first basis for qualitative discussions.

As a matter of fact, recent experiments [12,13] have shown the importance of the '*structuration' of the fluid*, of *short range molecular forces* and *molecular processes* in the dynamics of thin films. The aim of the present work is to provide detailed experimental results on the dynamics of ultra-thin films, which could be used in a forthcoming theoretical analysis.

We shall consider two experimental situations. One corresponds to the spreading of 'nanoscopic' droplets (about $10^{-4}\,\mu l$). The central part of the drop acts as a limited reservoir. The other situation corresponds to the capillary rise of the liquid up a vertical wall: the reservoir is nearly infinite and static. In this last case the hydrodynamic theory (with the assumption of a van der Waals interaction), predicts that the films obey a non-linear equation which is formally similar to a diffusion equation [15] with a *thickness-dependent diffusion coefficient*. In our case, we expect short-range forces also to be present at small thickness; these would lead to modifications of the predictions in the very-thin-film regime.

We have studied the spreading of low-molecular-mass methyl-terminated polydimethylsiloxame (PDMS, from Rhone-Poulenc) on silicon wafers covered with natural oxide. The light PDMS behaves as a simple, non-volatile liquid, with no specific polymeric effect. Here, the molecular mass is 2400, the viscosity $\eta = 20 \times 10^{-3}$ Pa s, the surface tension $\gamma = 20.6 \times 10^{-3}$ Nm^{-1}. The polydispersity index is 1.7 and no secondary peak is observed in the mass distribution (GPC results courtesy of S Boileau).

Silicon wafers (crystallographic plane 111, resistivity 4–6 Ω cm, doping: phosphorus) were purchased from the semiconductor industry. They are covered with natural silicon oxide (thickness of the order of 18 Å for this batch; the growth of the oxide is negligible over the experimental timescale). Film thicknesses are measured by fixed wavelength (6328 Å) ellipsometry [16–18].

The measured quantity at small thicknesses ($\leqslant 100$ Å) is a linear function of the total optical path through the sandwich: (oil film) + (silicon oxide); the refractive index is taken to be 1.4, and considered to be the same for the two layers [19]. The film thickness is obtained by comparison of wafer cartographies before deposition of the oil, and after. The thickness resolution with a 10 ms time constant is 0.1 Å and the measured values are averages over the light spot size: 200 μm by 1 mm.

Obviously, control of surface contamination is required. The experiment is performed in an atmosphere of dry filtered N$_2$. The sample holder is made of Teflon. The contamination (which may be monitored by the apparent thickness increase when no liquid is deposited), is less than 0.2 Å per week in these conditions. Various cleaning techniques were tried before starting the spreading experiments. All techniques involving wetting cleaning fluids were rejected as they have a tendency to leave inhomogeneous dry spots after drying. The wafers were used after plasma cleaning (UV-ozone) [20].

A second experimental point merits detailed discussion: what is the roughness of the substrates? Recent results provide various answers. Grazing-incidence x-ray reflectometry gives typical numbers of 4 to 6 Å RMS [9], but assumes a model with a random surface. On the other hand, force microscope measurements [21] on {111}-oxide-covered wafers show atomic smoothness over the scanned regions (200 Å $\times$ 200 Å), separated by steps of a few angstroms. Also, differential interferometry measurements [22] give a typical value of 10 Å RMS measured between spots of 2 μm separated by 2 μm. The conclusion is that the measured roughness depends to a large degree on the scale at which the measurement is performed. The surface is expected to be composed of patches of atomic smoothness.

Let us now discuss the experimental results. The first situation corresponds to the capillary rise up a vertical wall, dipping in a reservoir of PDMS. Figure 1 shows the profiles observed, as a function of time. A film of nearly constant thickness is advancing up the surface, and covers macroscopic distances (up to centimetres). The film thickness has to be compared with the thickness measured [23] by the surface force apparatus (7 Å). It is interpreted as a compact layer of molecules lying flat on the substrate. The film length nicely obeys a diffusion law (see inset) with $D = 2.8 \times 10^{-10}$ m^2 s^{-1}. This process will be designated as 'pseudo-diffusive' for reasons that will become clearer later in the text. This molecular scale is not described by a hydrodynamic theory. It is nevertheless informative to evaluate the order of magnitude of the diffusion coefficient predicted by such a hydrodynamic theory (with van der Waals interaction)

$$D(z) = A/6\pi\eta z.$$

Inserting thickness $z = 6$ Å, viscosity $\eta = \eta_{bulk} = 20 \times 10^{-3}$ Pa s, and Hamaker constant $A = 8 \times 10^{-21}$ J (the silica layer plays the major role for films thinner than 30 Å [24])
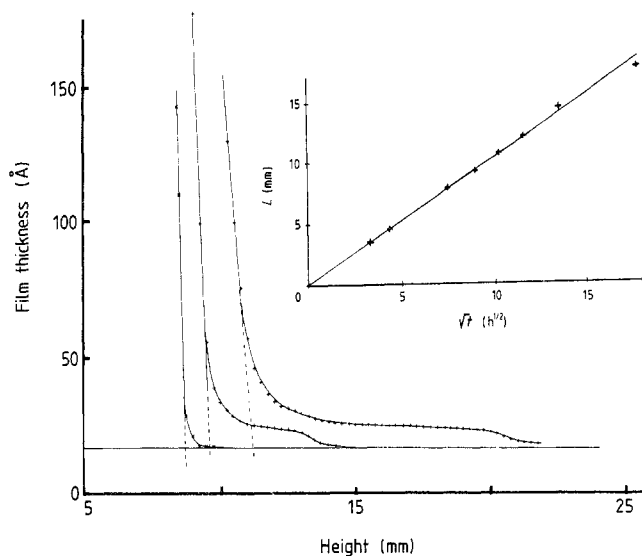
Figure 1. Ellipsometric profiles of films developing up a vertical wall. The thick part (left) is the beginning of the crossover toward the macroscopic meniscus. The x axis is the vertical distance (mm). The y axis is the thickness (Å). Curve A, 10 min after contact; curve B, 10 h; curve C, 56 h. Inset: film length L (measured from the broken line) as a function of the square root of time.

gives $D = 3 \times 10^{-11}$ m^2 s^{-1}, an order of magnitude too small. In order to understand part of the discrepancy, one could consider that a microscopic viscosity should be used at this scale (known to be much smaller than η_{bulk}). Also the van der Waals potential has to be supplemented by short-range forces, which may be dominant at the scale considered. Let us point out that it is possible to consider a very simple model [25] for the motion of a film of near constant thickness: the driving force is constant (constant energy gained by unit surface covered), and the friction (assumed to be constant per unit length of the film) is applied on a growing length of film.

Figure 2 shows the typical evolution of 'nanoscopic' PDMS droplets (total volume in the range of 10^{-4} μl). The profile of such droplets takes the shape of a 'mexican hat', and was first observed in [12]. We will focus here on the dynamics of the advancing thin film (the rim of the hat). Here again, the thinner part of the profile is interpreted as a compact layer of molecules lying flat on the substrate. At short times, the central part of the drop acts as a reservoir for this molecular layer. Not surprisingly, the layer grows approximately by a 'pseudo-diffusive' process, as in the previous case, with $D = 2.8 \times 10^{-10}$ m^2 s^{-1} independent of the drop volume (figure 3). Then the reservoir is consumed and the tip velocity decreases (its precise definition becomes questionable when the shape of the drop evolves from a 'mexican hat' to a 'bell'). Finally, the whole profile corresponds to submolecular thickness, i.e. the layer compactness is lost by diffusion of molecules on the solid surface. This last effect was first predicted in [26], and observed in [12]. Here, the ellipsometric measurement gives the local density of molecules averaged over the spot size. This last process is governed by a 'true' diffusion equation, with Ds the (constant) diffusion coefficient of molecules on the surface. The drop profile tends approximately towards a Gaussian. The accuracy here becomes poor, because this last evolution takes very long times (10 days typically; then the contamination is already
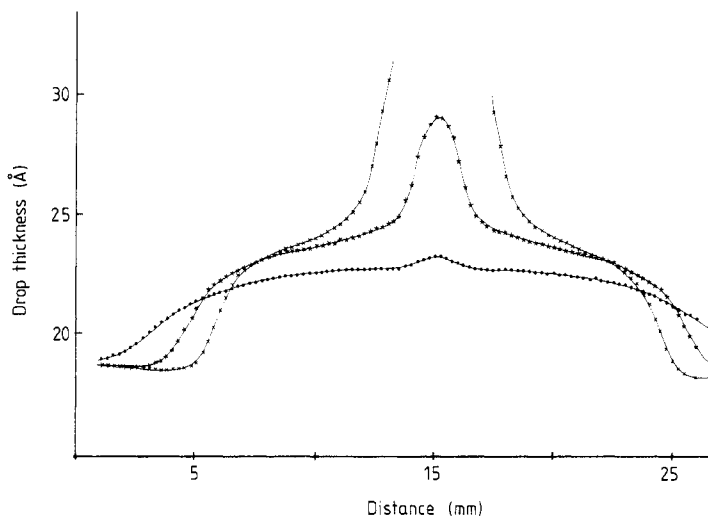
Figure 2. Ellipsometric scans across a PDMS drop. Direct measurement of thickness *before* subtraction of the oxide layer thickness (a variation of the oxide layer thickness accounts for the slight slope on the left of this figure). The drop volume (calculated from numerical integration of the profiles) is constant: $V = 2 \times 10^{-4}$ µl. Curve A, 56 h after deposition; curve B, 79 h; curve C, 167 h.
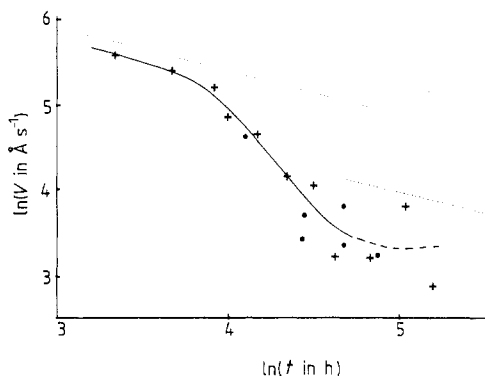

Figure 3. Log–Log plot of the tip velocity as a function of time for two drops: +, $V = 2 \times 10^{-4}$ µl; ●, $V = 1.2 \times 10^{-4}$ µl. Upper broken line: diffusion with $D = 2.8 \times 10^{-10}$ m^2 s^{-1}; lower broken line: diffusion coefficient with $D = 6 \times 10^{-11}$ m^2 s^{-1}.
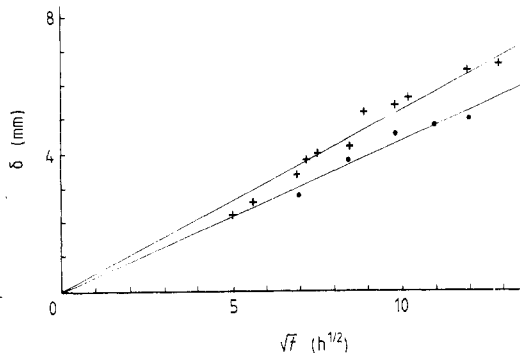
Figure 4. Width of the microscopic edge δ as a function of the square root of time for two drops: +, $V = 2 \times 10^{-4}$ µl; ●, $V = 1.2 \times 10^{-4}$ µl. The intrinsic width due to the limited spatial resolution has been subtracted.

0.3 Å, and the noise becomes significant). An evaluation of the molecular diffusion coefficient is possible at *intermediate times*: from the width of the edge (with an approximate error-function shape [27]), Ds_{edge} can be obtained. This width increases according to a diffusion law (figure 4). For two drops we find $Ds_{edge} = (6 \pm 2) \times 10^{-11}$ m^2 s^{-1}. This value was found to be the same for experiments performed on wafers of different batches, and in particular did not vary with the 'large scale' roughness measured by differential interferometry [22], which could vary by a factor of two. The question of the

possible role of molecular steps on the substrate has not yet been asserted experimentally. (Control experiments with out-of-crystallographic-axis wafers are planned). Nevertheless thin films, say below 50 Å, are expected to follow the surface profile [28]. Indeed, recent observations [13] of clear molecular 'structuration' of other fluids (several piled distinct molecular layers) on this kind of substrate reinforce this analysis.

As a conclusion, for the two types of experiments (droplets and capillary rise), the growth of a film of near-molecular thickness and macroscopic extent is observed. It has been shown experimentally that two different diffusion processes are involved. First the film length grows by a 'pseudo-diffusive' process, as long as a fluid reservoir is present. A second diffusive process, interpreted as molecular diffusion, is always present at the edge of the observed films (this process is slower at the start than the 'pseudo-diffusive' motion, and that is why a well defined film is observable). These experimental observations should stimulate new theoretical efforts to describe the dynamics of films at such molecular thicknesses satisfactorily.

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