

Structure and dynamics of thin liquid films on solid substrates

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Abstract

In the absence of surface tension gradients, and on smooth, chemically homogeneous substrates, wetting liquids build molecularly thin films, conveniently studied at the edge of spreading microdroplets. Spatially resolved ellipsometry is a relevant technique for this study. At the microscopic scale, microdroplets usually take a stepped pyramidal shape due to the layering induced by the solid surface. The thickness and growth dynamics of the successive layers give information on the behaviour of the liquid close to the solid. In particular, the friction process between the first molecular layer and the substrate is still only partially understood. We report studies of the spreading rate of polydimethylsiloxanes (PDMS) with different chain lengths. For moderate or high friction, the successive layers grow at a comparable rate and the spreading of the droplet is mainly controlled by the mesoscopic scale. Thus, the relevant parameter is the bulk viscosity η . For low friction, only the first layer grows significantly. Then the relevant parameter is the number N of monomers or the molar mass M of the polymer chain. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The spontaneous spreading of a liquid on a solid surface is controlled by the competition between driving terms and dissipative processes.

At a macroscopic scale, the film is a continuous medium whose thickness is much larger than the range of molecular interactions. In the partial

wetting case, the driving term is the unbalanced capillary force $\gamma(\cos \theta_0 - \cos \theta)$, where γ is the surface tension of the liquid, θ_0 the equilibrium contact angle, given by Young's equation, and θ is the dynamic contact angle [1–12]. In the case of complete wetting, and for nonvolatile liquids, this driving term becomes $S_0 + \gamma(1 - \cos \theta)$, where S_0 is the positive initial spreading parameter [8]. The dissipative process is the viscous friction in the liquid and is calculated assuming a no-slip condition on the solid. The relevant parameter is the bulk viscosity η . The dissipation in the macroscopic liquid wedge balances the term $\gamma(\cos \theta_0 -$

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$\cos \theta$) or $\gamma(1 - \cos \theta)$. In the complete wetting case, it has been shown by de Gennes [8] that S_0 is balanced by the dissipation in a thin precursor film growing ahead of the macroscopic liquid wedge [13].

The dynamics of the precursor film have been investigated at a mesoscopic scale by Derjaguin [5] and de Gennes [8]. At this scale, the film is still a continuous medium, but now the thickness is comparable to the range of intermolecular forces. This is taken into account by introducing the disjoining pressure term in the Navier–Stokes equation. Again, a no-slip condition on the solid is assumed and the dissipative term is still the viscous friction calculated from a Poiseuille flow in the liquid film. The behaviour of the film depends on the velocity U of the macroscopic liquid wedge. For non-vanishing velocities, adiabatic films are observed, the length L of which is inversely proportional to the velocity U and does not depend explicitly on time [8]. For vanishing U , i.e. at long times if one considers the spreading of a drop, one gets diffusive films, the length of which scales like the square root of time t . Here, the driving term is the gradient of the disjoining pressure $\Pi(z)$, where z is the local film thickness [5,8,14].

Ellipsometric observations of diffusive films show that for most of their length, these films are molecularly thin [15,16]. Moreover, stepped thickness profiles are frequent, due to surface induced layering [17,18]. There is no basic difficulty to calculate the driving term at the molecular scale. On the contrary, the dissipative process poses problems. What friction means at the molecular scale, and which parameters are relevant is still a matter of debate [19–22].

In the following, we shall report ellipsometric measurements of the thickness profiles of diffusive films growing at the quasi-static edge of spreading drops. Our aim is to identify the parameters relevant in the dissipative process in the specific case of low molecular weight polymers spreading on smooth surfaces.

In the next part (Section 2), we recall the main results of the available theories, both for mesoscopic [5,8,19] and molecular films [25,27,28]. Experimental systems and results are reported in

Section 3. Concluding remarks are given in Section 4.

2. Available theories of the dynamics of diffusive films

Let us first recall the main predictions for the mesoscopic scale in the one-dimensional case [5,8,19]. The film grows with time t in the x -direction from a quasi static macroscopic wedge which plays the role of a reservoir. The extension $L(z, t)$ of the film at thickness z obeys a diffusive-like equation with a thickness-dependent diffusion coefficient $D(z)$:

$$L(z, t) = \sqrt{D(z)t} \quad D(z) = -\frac{z^3}{3\eta} \frac{d\Pi}{dz} \quad (1)$$

These equations are expected to hold for mesoscopic thicknesses. However, three or four molecular layers are usually enough for the film to be considered as mesoscopic. Therefore, the problem of molecularly thin films concerns typically the very first layers.

For thinner films, two main analytical models are available.

A model for completely stratified, incompressible droplets has been proposed by de Gennes [19]. The model mimics the experimental situation, i.e. the thickness belongs to the molecular range while the lateral extension of the film is macroscopic. The driving term is the difference in the chemical potentials of the molecules in the different layers, while the dissipation is a viscous-like process, as expected for films of macroscopic extension. Friction coefficients between successive layers are introduced. For the upper layers, and in practice for all layers except the first one, these coefficients are supposed to be the same:

$$\zeta_{n,n-1} = \zeta = \eta \frac{\Sigma}{a} \quad n > 1 \quad \zeta_{1,0} = \zeta_1 \quad (2)$$

Here, Σ is the area per molecule in a layer and a is the layer thickness.

The dynamics of the successive layers obey a series of coupled differential equations. For the first layer:

$$R_1 \frac{dR_1}{dt} = \frac{W_2 - W_1}{\zeta_1 \ln \frac{R_1}{R_2}} \quad (3)$$

Here, W_1 and W_2 are the energies of the molecules in the first and second layer, respectively, and R_1 and R_2 are the corresponding radii. If the logarithmic term does not change too much with time, the dynamics of the first layer obeys a diffusion-like equation, with a diffusion coefficient D_1 such as:

$$D_1 \approx 2 \frac{W_2 - W_1}{\zeta_1 \ln \frac{R_1}{R_2}} \quad (4)$$

In this formula, ζ_1 is a molecular friction coefficient, but the upper layers intervene through R_2 which in turn depends on R_3 , etc. More specifically:

$$R_1 \frac{dR_1}{dt} + R_2 \frac{dR_2}{dt} = \frac{W_3 - W_2}{\zeta \ln \frac{R_2}{R_3}} \left[1 + 4 \frac{\zeta}{\zeta_1} \right] \quad (5)$$

Thus, the bulk viscosity will come into play if ζ_1 is larger than ζ or of similar magnitude. On the contrary, if ζ_1 is very small, ζ disappears from the equations.

The second model considers the case where a single monolayer grows from a macroscopic reservoir [21,22]. Now, the diffusive-like law is obtained over a much wider time scale and is written as follows:

$$R(t) = R_0 + \sqrt{2A_m D_0 t} \quad (6)$$

Here, D_0 is the diffusion coefficient of an isolated molecule on the surface, which is inversely proportional to ζ_1 , and A_m depends on the liquid–liquid and liquid–solid interactions. In an analogy with the previous formula, one may write:

$$D_1 \approx \frac{W}{\zeta_1} \quad (7)$$

where W is basically the chemical potential difference between a molecule in the reservoir and a molecule in the film. In this model, the mesoscopic scale does not play any role.

The diffusive-like law is also obtained in numerical simulations.

Indeed, various numerical studies have been carried out to recover the diffusive behaviour of the spreading droplets. This was first achieved by De Coninck et al. [23] using Kawasaki dynamics [24], a method analogous to the Monte-Carlo method with a local conservation law of the mass. These authors accounted for the two diffusion regimes experimentally observed in the early and late stages of the spreading of small droplets. However, the choice of such a Monte-Carlo type dynamics was not completely satisfactory because it implicitly contains the square-root of the time behavior and cannot be fully justified at the microscopic level.

In contrast, the molecular dynamics approach leads to a clear understanding of the detailed dynamics of spreading. This technique has been used by several research groups [25–30]. With that simulation technique, the diffusive behavior of the precursor film can only be recovered for a large number of polymer-like molecules and for a solid substrate taking account the surface structure at the molecular level [31,32]. Oversimplifying the solid substrate [33,34] or considering very small liquid molecules [35,36] led to dynamics for which the film length grows like $\sqrt{\ln t}$ instead of \sqrt{t} . This clearly supports the importance of a careful description of the properties of the solid and liquid at the atomic scale and, more specifically, of the friction process in the ‘solid–liquid’ interactions.

3. Experimental systems and results

The spreading of thin films has been studied extensively for years. Our experimental technique is spatially resolved ellipsometry, which allows the recording droplets profiles with a thickness resolution 0.2 Å and a lateral resolution of 25 μm. The set-up has been described elsewhere [23,24,37].

At relatively short times, when the center of the droplet plays as a reservoir for the film, i.e. when the conservation of the drop volume does not enter explicitly in the equations, the diffusive-like law is well obeyed [20–24,37].

In the mesoscopic part of the film, the diffusion coefficient is given by:

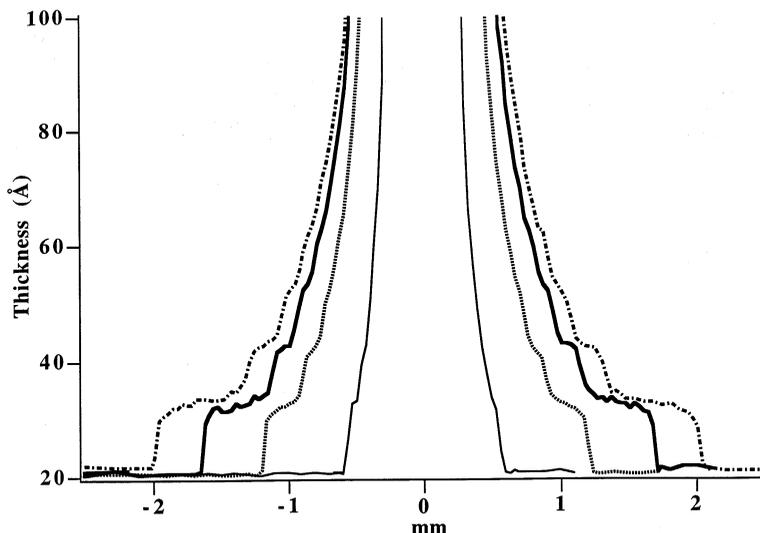


Fig. 1. Ellipsometric thickness profiles of a microdroplet of fractionated polydimethylsiloxane $M_p = 16\,000$, polydispersity index $I_p = 1.20$, viscosity $\eta = 0.420\text{ Pa}\cdot\text{s}$. The substrate is a silicon wafer bearing a loose layer of trimethyl groups. Critical surface tension for alkanes 25.5 mN m^{-1} . Measurement times after drop deposition: light full line 3 h 30 min; dotted line 22 h; heavy full line 45 h 30 min; dash-dotted line 70 h 30 min. The baseline at 20 Å is the silica plus the grafted layer.

$$D(z) = -\frac{z^3}{3\eta} \frac{d\Pi}{dz} \quad (8)$$

For van der Waals interactions, the disjoining pressure is:

$$\Pi(z) = \frac{A}{6\pi z^3} \quad (9)$$

where A is the absolute value of the effective Hamaker constant for the air/film/solid system. This gives:

$$D(z) = \frac{A}{6\pi\eta z} \quad (10)$$

in good quantitative agreement with the experiment [38].

In the thin part of the film, stepped profiles are the rule for nonvolatile liquids. For the upper layers, one may expect the W_n to scale like n^{-3} . However, W_1 and ζ_1 are unknown.

In the present paper, we report changes in the dynamics of the first layer for low MW polydimethylsiloxane (PDMS) oil droplets when the chain length of the molecule is varied. All oils are below the three dimensional disentanglement threshold, i.e. molar mass $M = 20\,000$. The sub-

strates are bare or grafted oxidized silicon wafers. The set-up and the cleaning and grafting procedures have been extensively described elsewhere [15–18,20,23,31,32]. Our aim is to discriminate from the diffusion coefficient D_1 the role of the bulk dissipation, i.e. the viscosity η and the role of the molecular friction term, i.e. ζ_1 .

Previous investigations of the change in spreading dynamics of very thin polymer films with chain length are available in the literature [31,33,34]. The thickness profiles were either smooth [33,34], or stepped but with several superimposed layers growing at similar rates [31]. In all cases, D_1 was found to vary like η^{-1} . For the PDMS investigated ($2000 \leq M \leq 20\,000$), the viscosity scales with $M^{1.7}$, which means that we are in the crossover between the short chains ($\eta \propto M$) and the long chains ($\eta \propto M^{3.4}$) [35]

A typical profile of this case is found in Fig. 1. All of the layers grow more or less at the same rate, and it is not too surprising to find that the dynamics of the first layer is controlled by the mesoscopic scale, and that D_1 scales like η^{-1} . This type of profile is obtained on surfaces with medium or high friction. In the case of PDMS and silicon wafers, these surfaces are for example:

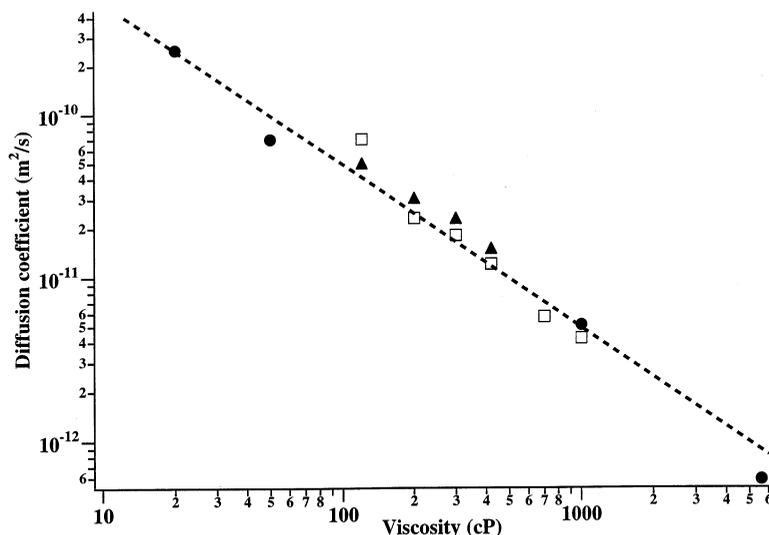


Fig. 2. Log–log plot of the diffusion coefficient of the first layer versus bulk viscosity on different substrates. Open squares: wafer bearing a loose trimethyl layer. Dots: bare, uncleaned wafer. Full triangles: bare, cleaned wafer, relative humidity $RH \approx 20\%$. Even if D_1 is more or less the same, the drop profiles differ significantly: less layers develop on the bare wafers.

- bare, cleaned silicon wafers at low relative humidity ($< 35\%$): high friction [36]. These cleaned wafers are water-wettable, but not very hydrophilic. Adsorption isotherms of water on these substrates show that the mean thickness of the adsorbed water film is only 4 Å at 75% RH.
- bare silicon wafers taken from the box and used without cleaning: medium friction: the high energy silanol sites are covered by organic contamination.
- silicon wafers bearing a loose grafted layer of trimethyls [36,37]. They are obtained by short time incubation of cleaned bare wafers with hexamethyldisilazane. The critical surface tension γ_c of these surfaces for the series of alkanes is $\sim 25\text{--}26 \text{ m Nm}^{-1}$. They behave like contaminated wafers.

Log–log plots of D_1 versus η for these three surfaces are given in Fig. 2. The expected slope -1 is well observed. The curves corresponding to the different surfaces are very close. In fact, driving terms and friction changes approximately compensate each other for the surfaces considered. This is not a general situation.

From the previous discussion, we expect molecular effects to become effective at low friction. It might be the case, either on cleaned bare silicon wafers at significant relative humidity [36], or on wafers bearing a compact grafted layer of trimethyls ($\gamma_c \approx 23 \text{ mN m}^{-1}$). Wafers covered by Langmuir–Blodgett films of behenic acid are also good candidates [38].

A typical profile is given in Fig. 3 where now, only one layer of molecular thickness grows at the bottom of the drop. The mesoscopic part is very short and almost static. A log–log plot of D_1 versus r does not give a slope of -1 . Instead, the relevant parameter becomes the molar mass M or equivalently the number of monomers N (the molar mass of the monomer is ~ 74). In this low friction case, we see in Fig. 4 that for compact grafted layers or bare wafers at intermediate relative humidity ($40\% \leq RH \leq 70\%$), D_1 scales like N^{-1} . As W is proportional to N , ζ_1 scales like N^2 . Note that at very low friction ($RH \leq 95\%$), ζ_1 becomes linear with N . This dependence corresponds to a change in the polymer behaviour from a reptation to the Rouse regime and is discussed elsewhere [35,39].

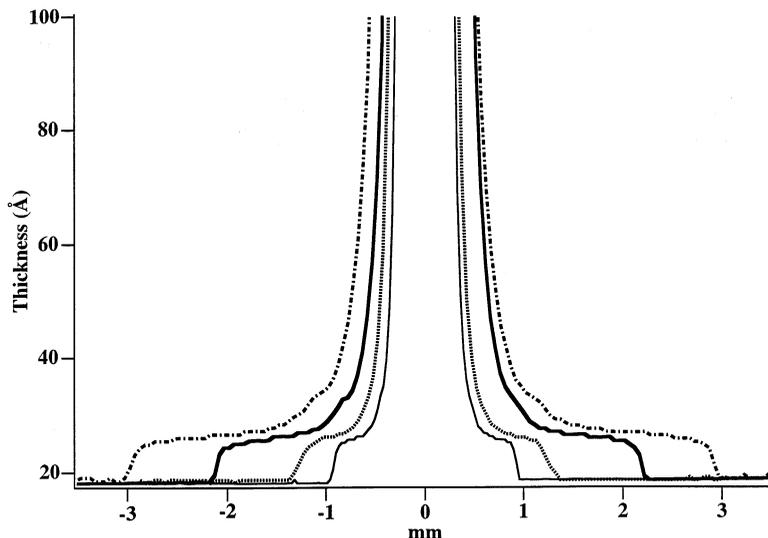


Fig. 3. Ellipsometric thickness profiles of a microdroplet of fractionated polydimethylsiloxane $M_p = 16\,000$, polydispersity index $I_p = 1.20$, viscosity $\eta = 0.420\text{ Pa}\cdot\text{s}$. The substrate is a silicon wafer bearing a compact layer of trimethyl groups. Critical surface tension for alkanes 23 m Nm^{-1} . Measurement times after drop deposition: light full line 3 h 30 min; dotted line 7 h 30 min; heavy full line 24 h; dash-dotted line 48 h. The baseline at 20 Å is the silica plus the grafted layer.

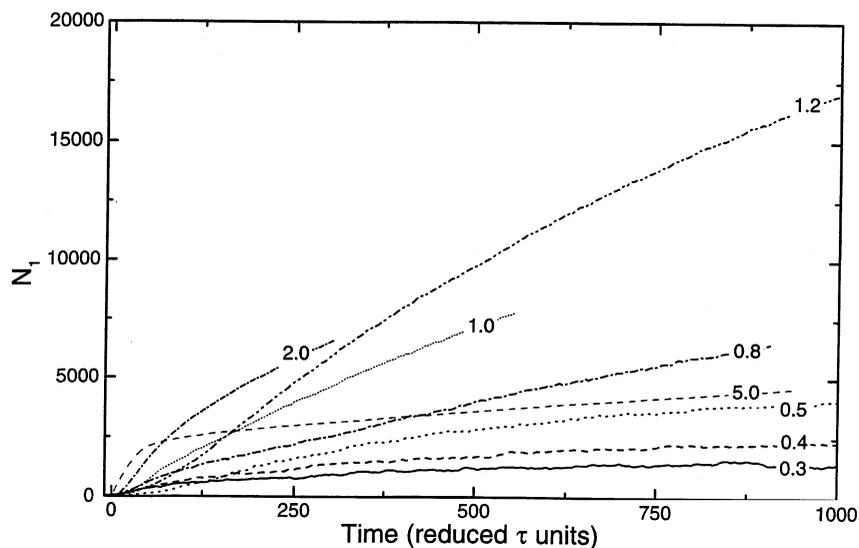


Fig. 4. Log-log plot of the diffusion coefficient of the first layer versus the number N of monomers in the polymer chain on different substrates. Bow ties: wafer bearing a compact trimethyl layer. Critical surface tension for alkanes 23 m Nm^{-1} . Dots: bare, cleaned wafer, relative humidity $RH \approx 40\%$. D_1 would be larger for increasing RH [36], or on Langmuir-Blodgett layers [37].

4. Discussion and conclusion

The respective roles of mesoscopic and molecular friction have been studied in the case of light

PDMS oils, taking advantage of the non linear behaviour of the viscosity with the molar mass in the range of masses investigated. Molecular effects control the spreading in the case of low

friction coefficient ζ_1 . The corresponding drop profiles are very typical, with a quasi static and very short mesoscopic part and only one layer spreading at the bottom. Such profiles can be understood intuitively, as the friction on the solid is low. On the contrary, for medium or high friction on the solid, all the layers grow more or less at the same rate and the dynamics is controlled by mesoscopic effects, i.e. by the bulk viscosity η .

Even if these results are satisfactory, one must admit that the process through which the molecules pass from the main drop to the monolayer is not fully understood. In particular, for low ζ_1 , one might expect the feeding of the film to act as a limiting process. This does not seem to be the case, and this means somewhere there is a missing link.

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