

Dynamics of Spreading of Liquid Microdroplets on Substrates of Increasing Surface Energies

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By spatially resolved single-wavelength ellipsometry, we investigate the spreading on a solid substrate of low molecular weight trimethyl-terminated poly(dimethylsiloxane) droplets. Especially, we focus our study on the dependence of the diffusion coefficient of the first molecular layer on the substrate surface energy, characterized by the critical surface tension γ_c measured for the alkane series. Our experimental data show that the diffusion coefficient D calculated from the film length reaches a maximum value for surfaces of intermediate energies. This result is shown to be consistent with the predictions of the available theoretical approaches and agrees quite well with molecular dynamics simulations reported in the third part of the paper.

I. Introduction

The spreading of liquids on top of solid substrates plays a major role in many technological processes such as painting, surface coating, oil recovery, plant protection, etc. Therefore the understanding of the variations of the spreading dynamics with the surface energy is of crucial importance. For example, studies carried out with "trisiloxane surfactant/water" macroscopic drops spreading on gold surfaces whose surface energy was controlled by the deposition of mixed organosulfur monolayers with different terminal chemical functionality brought experimental evidence that the spreading rate of the droplets exhibits a pronounced maximum for surface energies of moderate hydrophobicity.¹ The authors pointed out that, while not necessarily expected, the existence of such a maximum suggested the importance of the solid–liquid interactions at the interface. As a matter of fact, this has been already quoted in the review paper by Blake.² Stoebe et al. recently confirmed the results of their first study, highlighting the importance of the water layer in the spreading phenomenon.^{3–5} That water layer acts directly on the friction properties of the substrate: previous studies of Tiberg and Cazabat^{6,7} have demonstrated the influence of the relative humidity on the spreading of pure trisiloxane surfactant droplets. Increasing the relative humidity contributes to lowering the friction of the molecules on the substrate and to increasing the diffusion coefficient of the liquid. This result has also been experimentally demonstrated for poly(dimethylsiloxane) (PDMS) by Villette et al.⁸ More recently, Valignat et al.⁹

investigated the molecular weight dependence of the diffusion coefficient of such molecules on the friction properties of the substrate.

The present paper addresses the same problem at the molecular level; i.e., we investigate the dependency of the wetting film spreading rates for varying surface energies.

Since the first study of droplet spreading by Beaglehole,¹⁰ modulated polarization single wavelength ellipsometry has been successfully used to investigate the dynamics of the spreading of silicon oils (trimethyl-terminated poly(dimethylsiloxanes) or PDMSs) and other complex fluids (squalane, tetrakisilane, etc.) on grafted or bare silicon wafers.^{11,12}

In particular, it was recognized that these droplets take characteristic stepped pyramid shapes, the height of the steps being the molecular size.¹³ In some cases, the wetting film is just one monomolecular layer which develops at the bottom of the main droplet.

Close to the wetting transition, thick wetting films are expected.^{14–16} Several studies have been carried out to approach the transition either by changing the surface energy of the substrate¹⁷ or by considering a homologous series of liquids with decreasing surface tension.¹² In these experimental conditions the final state of the drop is a "pancake", as first predicted by de Gennes.¹⁴

Experiment shows that the length of the wetting film at short times (i.e., as long as the central part of the drop acts as a reservoir for the film) obeys a diffusion-like law $l_{\text{film}}(t) = (Dt)^{1/2}$, where D is referred to as the diffusion coefficient of the film.

In parallel to these ellipsometric studies, several theoretical models^{18,19} were proposed. In the past few

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years, for chainlike liquid molecules, atomistic representations of the solid, and sufficiently large systems to mimic the existence of a liquid reservoir (up to 250 000 atoms), it has been recognized that molecular dynamics (MD) techniques lead to the detailed recovery of the experimental observations.^{20,21}

The parameters controlling the values of the diffusion coefficient D are still not fully understood. However, the microscopic details of the mechanism of spreading and, in particular, the role of the friction at the microscopic level were recently investigated using MD simulations.²²

The paper is organized as follows: New experimental results are presented in section II. These results show the same tendency as the ones obtained at the macroscopic scale, i.e., nonmonotonic variation of the diffusion coefficient with the surface energy. This dependence is interpreted in terms of the models by de Gennes and Cazabat¹⁸ or Burlatzky and co-workers¹⁹ in section III. In section IV, we compare the experimental results with MD simulations. Concluding remarks are given in section V.

II. Experimental Results

Single-wavelength polarization modulated ellipsometry is a powerful tool for the investigation of the dynamics of the spreading of microdroplets on solid substrates.¹⁰ The experimental setup has been described in previous papers.^{11,13} We first remind the reader that this ellipsometer is working at the Brewster angle and has a lateral resolution of 30 μm . The thickness resolution is 0.02 nm.

The fluids used are low molecular weight trimethyl-terminated PDMSs purchased from Petrarch. Most of the experiments were done with "PDMS 20" (molecular mass, 2000; viscosity, 20 cP; surface tension, 20.6 mN m⁻¹). Complementary measurements used the lighter "PDMS 10" (molecular mass, 1250; viscosity, 10 cP; surface tension, 20.1 mN m⁻¹). These light oils are not fractionated. Care must be taken with the lighter one, which is slightly volatile. In that case, the drops must be extremely small to avoid thermally induced Marangoni effects, and the reservoir condition is difficult to fulfill. It is why this oil was not used in a systematic way.

The substrates are oxidized silicon wafers (Siltronix: type n, phosphorus doping, [100], 3–5 Ω cm) covered with a natural oxide layer (about 2.0 nm). It is well-known that these kind of surfaces are not very hydrophilic and are characterized by a low surface density of silanol groups. Even when cleaned by the UV–ozone procedure, these surfaces are not completely hydroxylated. The cleaning procedure reveals the Si–OH groups but does not induce a breaking of the Si–O–Si bonds and leads to intermediate values for the critical surface tension.

The different kinds of surfaces used in this study are as follows: (i) "Bare wafers" were taken from the box and used without a further cleaning procedure. (ii) "UV O₃ wafers" were UV–ozone cleaned wafers (1 h under a dry O₂ flow + 20 min under an O₂ flow saturated with H₂O). (iii) "UV O₃ protected wafers" were wafers cleaned according to the same procedure but protected after cleaning by aluminum foils and stored under nitrogen in the presence of silica gel to prevent a fast contamination of the reaction sites. (iv) "C₁₆ wafers" are surfaces obtained by chemical grafting of a 3.4 nm thick layer of hexadecyltrichlorosilane. The UV–ozone cleaned wafers are exposed to the hexadecyltrichlorosilane vapors during 12 h at 85 °C, according to the procedure used by Tiberget al.⁶ (v) "HMDZ₂₄" are obtained by exposing an UV–ozone cleaned wafer to hexamethyldisilazane vapors during 24 h at room temperature. This procedure results in the grafting of a 0.4 nm thick trimethyl layer. (vi) "OTS wafers"

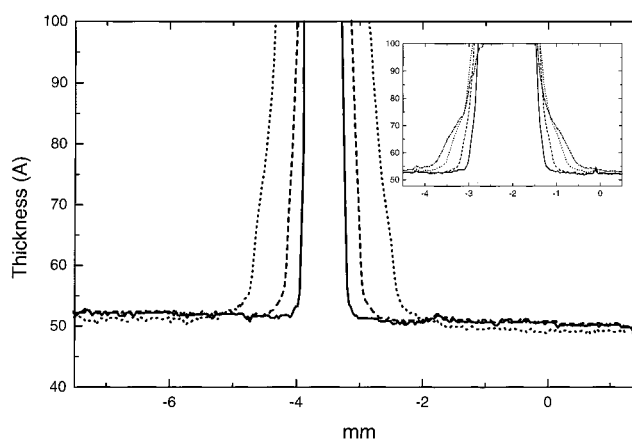


Figure 1. Ellipsometric thickness profiles of a PDMS 20 droplet on top of an octadecyltrichlorosilane-grafted silicon wafer. The profiles are taken 15 (plain line), 40 (dashed line), and 235 min (dotted line) after deposition of the droplet. The baseline (≈ 52 Å) corresponds to the thickness of the native oxide layer (≈ 20 Å) plus the grafted OTS layer (≈ 32 Å). No structure is visible on the drop profiles. The absence of a precursor film clearly shows that the oil is not wetting the OTS substrate and that the droplet is just relaxing to reach its equilibrium contact angle in the partial wetting regime. Inset: Thickness profiles of a PDMS 10 droplet on the same OTS wafer. Times after deposition are 15 (plain line), 30 (dashed line), 90 (dotted line), and 170 min (mixed line).

are obtained by chemical grafting of octadecyltrichlorosilane on a UV–ozone cleaned wafer. This procedure results in a 3.2 nm thick layer.

Leaving the cleaned surface in the UV chamber under an O₂ flow saturated by water between the cleaning phase and the grafting phase itself contributes to a decrease in the contamination of the substrate. The Si–OH groups are saturated by the adsorbed H₂O molecules, while the siloxane Si–O–Si groups are less easily contaminated. This is assessed by a high reproducibility of the experiments if the surface is saturated by water molecules. In these experimental conditions, the reported values of γ_c (from 25 to 28 mN m⁻¹) are normal values for the critical surface tension. It should also be pointed out that when a flow of dry nitrogen is used, already one molecule of water is adsorbed per silanol group.

All these surfaces were selected because, if the liquid spreads on the substrate, only one step—not necessarily of monomolecular thickness—grows at the bottom of the drop, contrary to what occurs on trimethyl-grafted wafers obtained by a shorter time grafting procedure for which stepped-pyramid shapes in the molecular range of thickness have been observed.²³

The value of the critical surface tension γ_c for the homologous series of alkanes is determined on each substrate using a Kruss goniometer for angles larger than 15°. When the contact angle appeared to be lower, its value was determined from the microscope measurement of the equal thickness interference fringes of the pattern which appears when monochromatic light is simultaneously reflected by the silicon wafer and by the nearly-flat "PDMS–air" interface of the microdroplet. The obtained values of γ_c range from 19 mN m⁻¹ for OTS to 28 mN m⁻¹ for UV–O₃ protected wafers. It should be kept in mind that the critical surface tensions determined with the alkane series are slightly shifted to higher values with respect to the one obtained using the PDMS series.²⁴

We now report the experimental results.

Thickness profiles of PDMS 10 and PDMS 20 droplets on top of an OTS wafer have been measured at increasing times. They are shown in Figure 1. In the PDMS 20 case ($\gamma = 20.6$ mN m⁻¹), no structure is visible on the drop profiles. The absence of a

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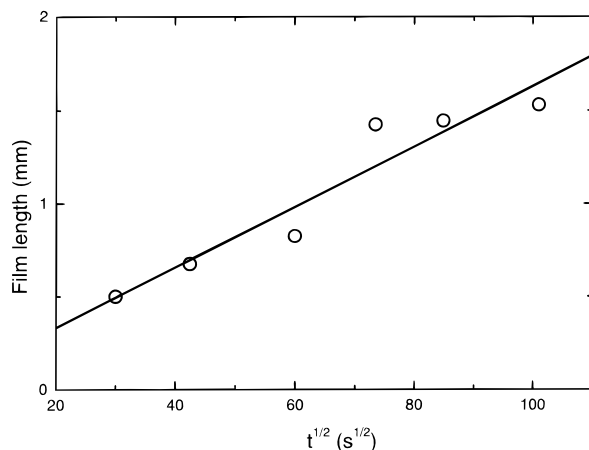


Figure 2. Film length versus the square root of the time. The liquid is a PDMS 10 spreading on an OTS-grafted silicon wafer. The calculated value of the diffusion coefficient is $D = 2.6 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$.

precursor film clearly shows that the oil is not wetting the OTS substrate and that the droplet is just relaxing to reach its equilibrium contact angle in the partial wetting regime. The equilibrium contact angle measured by the interferometric technique is 0.3° . With this liquid, we are just beyond the wetting–nonwetting transition.

The inset of Figure 1 shows the spreading characteristics of PDMS 10 ($\gamma = 20.1 \text{ mN m}^{-1}$) on the same OTS wafer. The usual 7 Å thick precursor film, corresponding to a monomolecular film of PDMS molecules flat on the surface, is not observed. Instead, a step about 20 Å thick is forming at the foot of the macroscopic part of the droplet, a result in agreement with the experimental behavior of a liquid just below the wetting–nonwetting transition¹² and with the theoretical predictions.^{14–16} The final state of such a structure is a pancake of thickness equal to the one of that step. We conclude that the critical surface tension of the OTS wafer for PDMS is between 20.1 and 20.6 mN m^{-1} . From these thickness profiles, we calculate the film length l_{film} by measuring the drop base radius at half-height of the first step and subtracting the reservoir radius measured 40 Å above the baseline. Using this method, it is possible to separate the contribution of the growth of the film from the one due to the possible spreading of the reservoir.

The growth of the film length l_{film} as a function of $t^{1/2}$, with t being the time after deposition and expressed in seconds, is presented in Figure 2 for the PDMS 10 on the OTS substrate. The value of the diffusion coefficient D calculated from the linear fit of the relation $l_{\text{film}}(t) = (Dt)^{1/2}$ to the experimental data is $2.6 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$.

We now consider the C_{16} substrate whose surface energy is, like the OTS one, close to the wetting transition for the considered liquids. We observe that both the PDMS 20 (Figure 3) and the PDMS 10 spread over the surface (Figure 3 inset). A thick wetting film is growing at the bottom of the reservoir. Diffusion coefficients D , calculated from the variations of the film length with the square root of the time, are 3.3×10^{-10} and $0.3 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, for the PDMS 10 and the PDMS 20, respectively (Figure 4). The ratio of these D values is about 11.6, a value which does not agree with the ratio 2.0 of the viscosity of the liquids as expected from Frayse et al.²³ This result clearly demonstrates the effect of the slowing down of the liquid spreading close to the wetting–nonwetting transition.

For the PDMS 20 droplet spreading on a HDMZ₂₄ wafer, we observe that a film of monomolecular thickness (7 Å) is forming at the foot of the drop at a growth rate of $D = 3.5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ (Figure 5).

Ellipsometric thickness profiles have also been measured during the spreading of PDMS 20 droplets on nongrafted surfaces: wafers taken directly from the box and used as they were, UV–O₃ cleaned wafers, and UV–O₃ cleaned wafers kept in a protected confined environment (silicagel and aluminum foils to prevent water vapor and contaminants adsorption). These surfaces are substrates with medium to high surface energies (γ_c

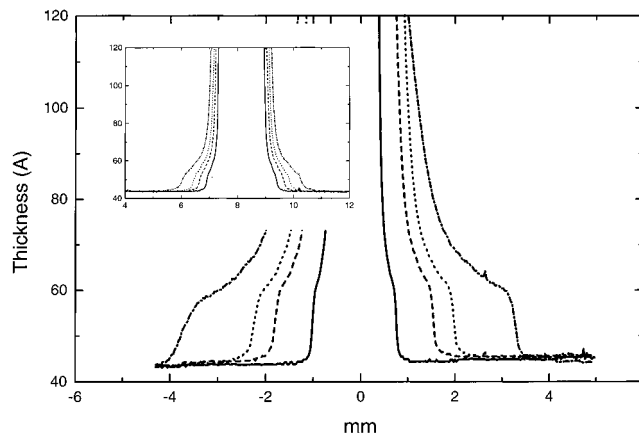


Figure 3. Ellipsometric thickness profile of a PDMS 20 microdroplet spreading on a C_{16} substrate. The profiles have been measured after 45 (plain line), 210 (dashed line), 360 (dotted line), and 1320 min (mixed line). A thick wetting film ($\approx 15 \text{ Å}$) is growing at the base of the drop. The baseline ($\approx 42 \text{ Å}$) corresponds to the thickness of the native oxide layer plus that of the C_{16} -grafted layer. Inset: Same experiment with PDMS 10. Times after deposition of the droplet on the surface are 20 (plain line), 40 (dashed line), 60 (dotted line), and 120 min (mixed line).

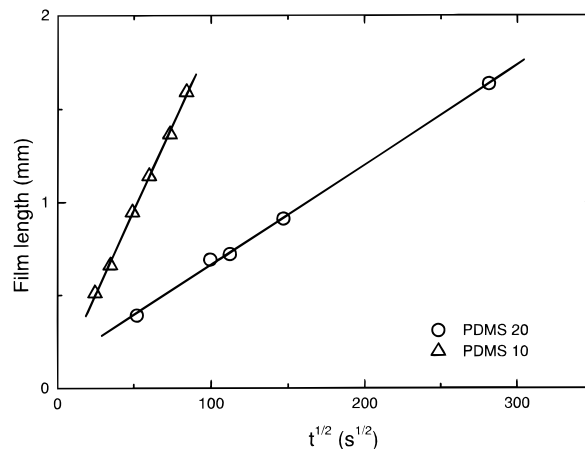


Figure 4. Film length versus the square root of the time. The liquids are PDMS 10 and PDMS 20 spreading on a C_{16} -grafted silicon wafer. The diffusion coefficient calculated from the film length variations are respectively $D = 3.3 \times 10^{-10}$ and $0.3 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$.

from 25.5 to 28.0 mN m^{-1}) for the series of alkanes. The wafers cleaned using the UV–ozone method are very sensitive to surface contaminants and therefore not easily reproducible. PDMS 20 spreads on these three kinds of surfaces. Profiles measured on unprotected and protected surfaces are represented in Figures 6 and 7.

On these substrates, a first step of molecular thickness ($\approx 7 \text{ Å}$) is forming in front of the macroscopic part of the droplet but no other structure appears. The dynamics of the film length is represented in Figure 8 versus the square root of the time. It appears that the protected wafer, i.e., the substrate with the highest surface energy, is characterized by a dynamics significantly slower than the one of the unprotected wafer, at least at short times. When the protection is removed and when the later stages of the spreading are considered, (Figure 8 inset), the film length is not linear anymore with respect to the square root of the time. The adsorption of water vapor and other surface contaminants induces a progressive increase of the growth rate of the film. The experimental results obtained with the non-cleaned wafer are not significantly different from those obtained with the unprotected UV–O₃ wafer.

The values of D measured in this study and those from refs 24 and 25 have been reported in Figure 9 as a function of the γ_c

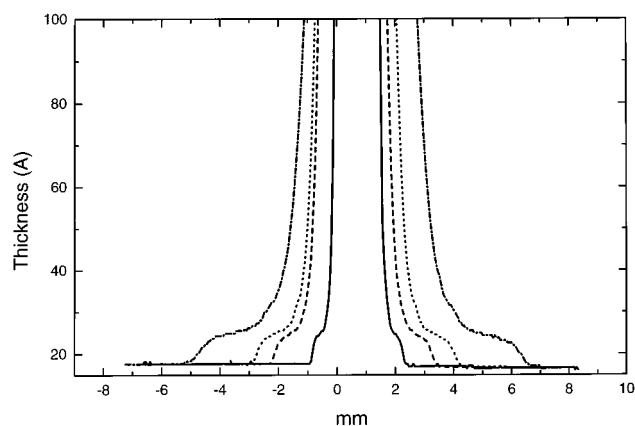


Figure 5. Thickness profile of a PDMS 20 microdroplet spreading on a HMDZ₂₄ wafer. A film of monomolecular thickness is growing at the foot of the droplet. Times after deposition are 75 (plain line), 280 (dashed line), 465 (dotted line), and 1386 min (mixed line). The diffusion coefficient $D = 3.5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$.

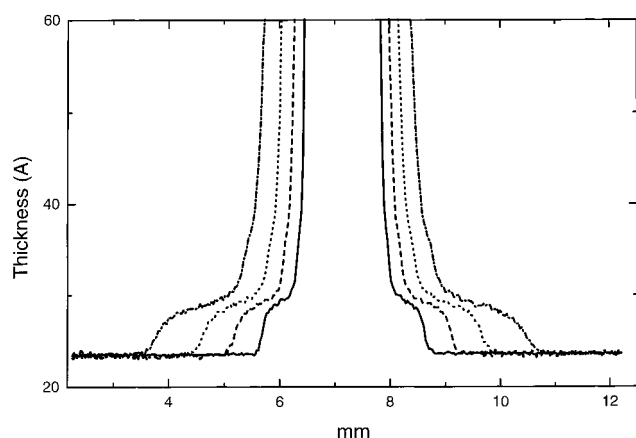


Figure 6. Thickness profiles of a PDMS 20 microdroplet spreading on an unprotected UV-O₃ surface. A first step (7 Å) is forming at the base of the droplet. Thickness profiles were measured 30 (plain line), 60 (dashed line), 105 (dotted line), and 230 min (mixed line) after deposition of the droplet on the bare substrate. The diffusion coefficient $D = 3.1 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$.

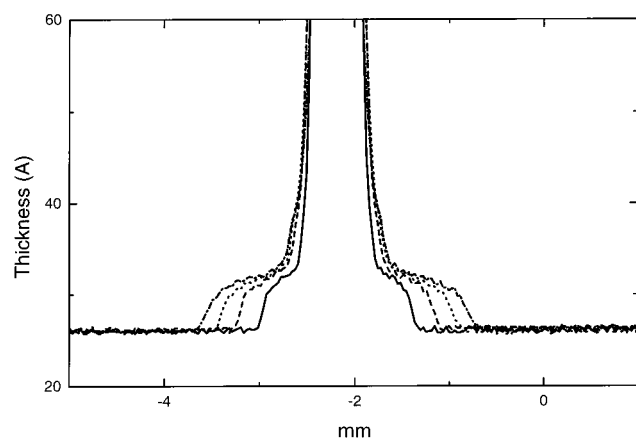


Figure 7. Same experiment as in Figure 6 but on a UV-O₃ surface protected by aluminum foils containing silica gel, under nitrogen. Ellipsometric measurements were carried out 15 (plain line), 28 (dashed line), 43 (dotted line), and 58 min (mixed line) after deposition of the droplet on the bare substrate. The diffusion coefficient $D = 1.9 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$.

measured on the different substrates for the alkane series. In the work of Stoebe et al.,^{1,3-5} the surface energy of the substrate was characterized by the cosine of the contact angle measured

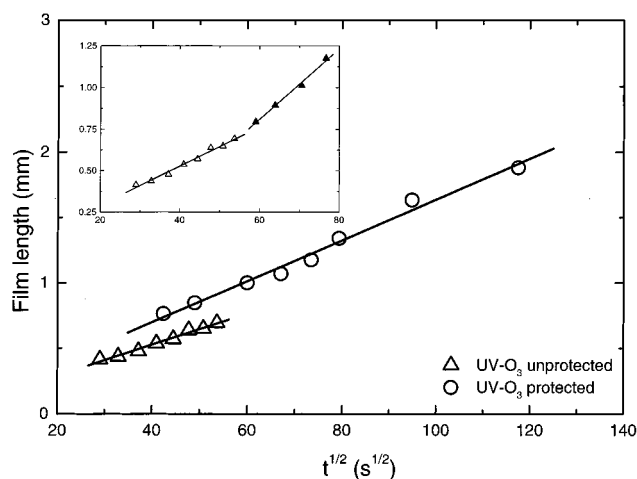


Figure 8. Length of the first step as a function of the square root of the time for the unprotected (open circles) and protected (open triangles) UV-ozone cleaned surfaces for PDMS 20. The coefficients D are equal to 3.1×10^{-10} and to $1.9 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ for the unprotected and for the protected surfaces, respectively. Inset: Effect of progressive contaminant adsorption on the dynamics of growth of a PDMS 20 film on a protected UV-O₃ surface. Protection has been removed 48 min ($t^{1/2} = 53 \text{ s}^{1/2}$) after drop deposition.

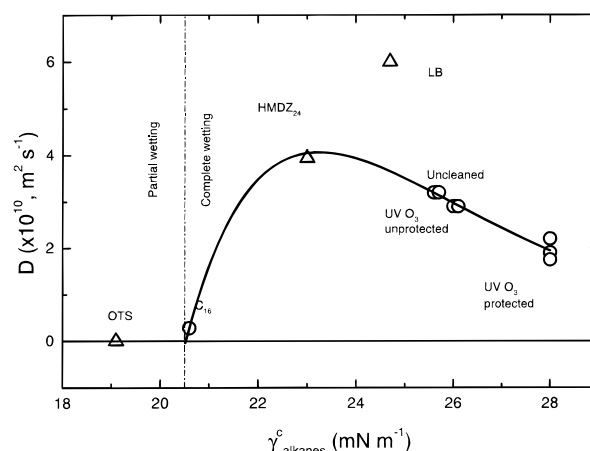


Figure 9. Film diffusion coefficient (D) for PDMS 20 versus critical surface tension ($\gamma_c^{\text{alkanes}}$) of the substrates evaluated with the alkane series. Full line corresponds to the best fit of the data represented by open circles with the bell-shaped function defined by eq 12. Data represented by open triangles correspond to chemically different substrates.

for pure water. In our study, we chose to characterize the surface energy using alkanes instead of water because their nonpolar behavior will be similar to that of PDMS.

When plotted versus the critical surface tension γ_c of the surface, the diffusion coefficient D of PDMS 20 exhibits a nonmonotonic behavior (Figure 9) with a maximum in the surface diffusion process observed for substrates with medium surface energies. This phenomenon is quite well-understood for the low- and high-energy surfaces but not for the medium ones. In the case of surfaces with low critical surface tensions, i.e., close or beyond the wetting–nonwetting transition, the PDMS 20 does not spread on the substrate or does it very slowly. For this range of surface energies, the driving term, which results from the competition between the “liquid–liquid” and “solid–liquid” interactions, tends to zero. This results in a very slow growth rate of the film. The decrease of the film growth rate for the high-energy surfaces can be explained by the increase of the friction at the microscopic level. The high-energy sites trap the

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liquid molecules and considerably increase the time they will spend in a given potential well. This phenomenon has been numerically demonstrated using the MD technique.²²

These results confirm the appropriate choice of the substrates: there was no need to investigate the behavior of the selected liquids on surfaces of lower or higher energies. In the former case, they would not be wet by the PDMS 20 or PDMS 10, while in the latter the dynamics of spreading would have been drastically reduced.

III. Comparison with Available Analytical Models

We now show that the nonmonotonic dependence of the precursor's diffusion coefficient D on the strength of liquid–solid interactions, ϵ_{sf} , revealed by experimental studies, is actually quite consistent with the predictions of available theoretical approaches.

Two theoretical models have been developed in order to account for the dynamics of the molecular precursor films. These are, namely, the hydrodynamic model of de Gennes and Cazabat¹⁸ and the microscopic dynamical model of Burlatsky et al.¹⁹ We start with the predictions of the hydrodynamic model,¹⁸ which allow for the most straightforward analysis.

In the hydrodynamic model, the liquid drop on solid substrate was considered as a completely layered structure, each layer being a two-dimensional incompressible fluid of molecular thickness but with a macroscopic radial extension. The interaction energy of a molecule in the n th layer with the solid substrate was taken in the general form as a negative, decreasing function of the distance from the substrate. Next, it was supposed that the spreading of successive layers proceeds due to penetration of the molecules from the upper layers to the lower ones, which process is favored by attractive liquid–solid interactions. In each layer there is a horizontal, radial current and vertical permeation fluxes, one from the upper layer and the second toward the lower layer, both being located in a narrow “permeation ribbon” just at the droplet's surface—the core droplet appears to be a “stagnant” liquid with respect to the vertical mass transfer.

Extending this model to the present situation of a single layer growing at the bottom of a macroscopic reservoir, the diffusion coefficient can be expressed as

$$D \approx \Delta W / \zeta \quad (1)$$

where ζ is the friction coefficient for motion of fluid molecules on top of solid surface, while ΔW denotes the difference

$$\Delta W = W_r - W_f \quad (2)$$

in which W_r and W_f are the interaction energies of particles being in the reservoir and in the film, respectively.

Now, each of W_i can be represented as the difference of two terms. The first term stems from the liquid–solid interactions and is proportional to ϵ_{sf} , the standard energy parameter of the Lennard-Jones interaction potential, while the second one is determined by the liquid–liquid interactions and is proportional to their strength, i.e., ϵ_{ff} . Physically, it means that each particle moving from the reservoir to the film gains some energy, because it moves along the gradient of the liquid–solid interactions, but also loses some portion of the liquid–liquid interactions energy, because the number of neighboring fluid molecules is effectively less in the film than in the reservoir. Consequently, we have that, in the general form, ΔW in eq 2 can be written as

$$\Delta W \sim \text{const}(\epsilon_{sf} - \epsilon_{crit}) \quad (3)$$

where ϵ_{crit} is a certain critical parameter depending on the strength of the liquid–liquid interactions. This equation, of course, makes sense only when $\epsilon_{sf} \geq \epsilon_{crit}$.

Further on, to estimate the ϵ_{sf} dependence of the molecular friction coefficient, we recall that, in virtue of the Einstein relation, ζ is inversely proportional to the diffusion coefficient D_0 , describing diffusion of an isolated molecule on a solid surface.

Diffusion of molecules adsorbed on top of a solid surface proceeds by rare events of hopping between the local minima of potential wells created by the liquid–solid interactions. To perform a hop from one well to another solely due to thermal agitation, a molecule has to overcome a barrier against lateral motion, whose magnitude is proportional to ϵ_{sf} .^{26,27} Neglecting the prefactors, we have then

$$D_0(\epsilon_{sf}) \sim \exp(-C_1 \epsilon_{sf}) \quad (4)$$

where C_1 is some constant, dependent on the temperature.^{26,27} Equation 4 thus means that the molecular friction coefficient ζ grows exponentially fast with ϵ_{sf} , i.e., apart from the prefactor, ζ is determined by

$$\zeta \sim \exp(C_1 \epsilon_{sf}) \quad (5)$$

Combining now eqs 5, 3, and 1, we find that the precursor's diffusion coefficient has the form

$$D \sim C_2(\epsilon_{sf} - \epsilon_{crit}) \exp(-C_1 \epsilon_{sf}) \quad (6)$$

where C_2 is some constant, which adsorbs the prefactors omitted in eqs 3 and 5. The precursor's diffusion coefficient D defined by eq 6 appears to be a bell-shaped function of ϵ_{sf} , which equals zero when either $\epsilon_{sf} = \epsilon_{crit}$ or $\epsilon_{sf} = \infty$ and which approaches its maximal value when $\epsilon_{sf} = \epsilon_{crit} + 1/C_1$.

We turn now to the predictions of the microscopic dynamical model of refs 19, 28, and 29, which requires a less straightforward analysis but, as we proceed to show, results in essentially the same type of the ϵ_{sf} dependence of the precursor's diffusion coefficient.

In the microscopic dynamical model of^{19,28,29} the macroscopic sessile drop on top of solid substrate was considered as the reservoir of molecules with constant molecular density ρ_r , while the film was modeled as a gas of interacting molecules, performing a hopping motion on top of the solid. It was assumed that the reservoir maintains constant the molecular density ρ_0 at the boundary between the film and the reservoir (Figure 10). In other words, the reservoir and the film are in equilibrium with each other so that there is no flow of molecules from the drop to the film, which may push the molecules on top of the solid to move away from the drop. This model allowed for an analytical solution, which yields the spreading of the film at the $t^{1/2}$ rate and which suggests that such a dynamical behavior is controlled by diffusive migration of vacancies from the advancing edge of the film to the reservoir, where these vacancies are filled by fluid molecules.

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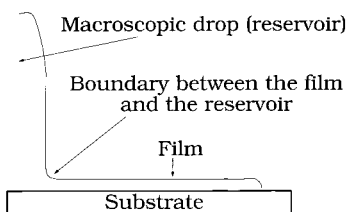


Figure 10. Schematic representation of the precursor film growing at the bottom of the macroscopic part of the drop.

More specifically, this model predicts that the length of the precursor film of molecular thickness grows as

$$l(t) = [2A_m D_0 t]^{1/2} \quad (7)$$

where D_0 is the “bare” diffusion coefficient, defined in eq 4, while the parameter A_m depends on the liquid–liquid and the liquid–solid interactions and is given implicitly as the solution of the following transcendental equation:

$$\left[\frac{\pi A_m}{2} \right]^{1/2} \exp\left(\frac{A_m}{2}\right) \operatorname{erf}\left(\left[\frac{A_m}{2}\right]^{1/2}\right) = \frac{\rho_0}{1 - \exp(-\beta W_T)} - 1 \quad (8)$$

In eq 8 $\operatorname{erf}(x)$ denotes the error function, β is the reciprocal temperature, and W_T stands for the work required to transport a vacancy from the edge of the film to the reservoir; W_T is a constant, dependent on the strength of the liquid–liquid interactions ϵ_{ff} (see for more discussion refs 19 and 30).

Now, one notices that not only D_0 in eq 4 but also A_m in eqs 7 and 8 is dependent on the strength of the liquid–solid interactions ϵ_{sf} . Here we present only some qualitative estimates of this dependence, aiming mostly to show that the prefactor in eq 7, i.e., $D = A_m D_0$, is actually a nonmonotonic function of the parameter ϵ_{sf} .

As a matter of fact, the ϵ_{sf} dependence of the parameter A_m results from its dependence on ρ_0 —the density in the transient region between the reservoir and the film. Following Burlatsky et al.,^{19,28} we consider the reservoir and the film as a two-level system and estimate ρ_0 using standard Langmuir-type arguments.²⁶ This gives

$$\rho_0 = \left[1 + \frac{1 - \rho_r}{\rho_r} \exp(-\beta \Delta W) \right]^{-1} \quad (9)$$

Therefore, the ϵ_{sf} dependence of the parameter A_m appears to be rather complex. First of all, eq 8 cannot be solved explicitly, and second, ρ_0 is itself a complicated function of ϵ_{sf} . Nonetheless, a qualitative and asymptotical behavior of A_m as a function of ϵ_{sf} can be readily deduced from eq 8. First of all, A_m appears to be exactly equal to zero for $\epsilon_{sf} \leq \epsilon'_{\text{crit}}$, whose value is given by

$$\epsilon'_{\text{crit}} \approx \epsilon_{ff} + \beta^{-1} \ln \left[\frac{\rho_r}{(1 - \rho_r)(\exp(\beta W_T) - 1)} \right] \quad (10)$$

This critical value is not necessarily the same as in the previous model. Then, for ϵ_{sf} only slightly exceeding ϵ'_{crit} , A_m varies linearly with the difference $\epsilon_{sf} - \epsilon'_{\text{crit}}$. Finally, for $\beta(\epsilon_{sf} - \epsilon'_{\text{crit}}) \gg 1$, one finds that A_m grows logarithmically with the difference $(\epsilon_{sf} - \epsilon'_{\text{crit}})$.

Now, since we are interested mostly in the behavior of the product $A_m D_0$, where the second multiplier is an

exponentially vanishing with the ϵ_{sf} function, we can majorize A_m by the term which is linear with the difference $(\epsilon_{sf} - \epsilon'_{\text{crit}})$. Consequently, the precursor’s diffusion coefficient can be written as

$$D = A_m D_0 \sim \text{const}(\epsilon_{sf} - \epsilon'_{\text{crit}}) \exp(-C_1 \epsilon_{sf}), \quad \text{for } \epsilon_{sf} \geq \epsilon'_{\text{crit}}$$

$$D = 0, \quad \text{for } \epsilon_{sf} \leq \epsilon'_{\text{crit}} \quad (11)$$

which differs from the result in eq 6 only by the value of the critical energy. Thus also in this model D appears to be a bell-shaped function.

Thus, these two theoretical approaches predict that the diffusion coefficient will exhibit a bell-shaped dependency with respect to the surface energy of the substrate and that the diffusion coefficient will tend to a zero value for both the low- and high-energy surfaces. This can be intuitively understood by considering the relative influence of the driving and friction terms that underlay the spreading process. For the low-energy surfaces, the balance between the liquid–liquid and the liquid–solid interactions results in a very low value of the driving term, whatever the friction. The spreading of the droplet—if any—occurs in these conditions at a very low rate. For the high-energy surfaces, the solid–liquid interaction increases. It turns out that the friction term increases faster than the driving term. This leads to the trapping of the liquid molecules within the potential wells of the solid substrate, yielding a slower spreading rate on such substrates than for the substrates of intermediate surface energy. This result is additionally supported by the results of a previous publication,²² where molecular dynamics simulations have been used to investigate at the microscopic level the mechanism of spreading of silicon oil microdroplets. In that study, it has been shown that, in agreement with the experiments reported in Heslot et al.¹³ and in Fraysse et al.,²³ D is the ratio of a driving term to the friction coefficient ζ_1 and is found to decrease as the “liquid–solid” interaction increases.

The curve drawn in Figure 9 is the best-fit curve for a bell-shaped function of the type

$$D \cong C_1 (X - X_{\text{crit}}) \exp(-C_2 X) \quad (12)$$

where X is a variable related to the surface energy of the substrate and C_1 , C_2 are numerical constants. The difficulty that we have to overcome is to compare bare and grafted substrates that are indeed characterized by different surface chemistry. The C_{16} wafer is close to the wetting–nonwetting transition (PDMS 10 wets that surface, but PDMS 20 does not), and these data are therefore representative of the zero value for the diffusion coefficients.

On the contrary, the values measured with HMDZ₂₄ and LB wafers cannot be quantitatively compared with the one measured on the bare substrates, even if they follow qualitatively the same trend: the preparation of these substrates could a priori induce an important modification of the surface properties of the silicon wafers. Therefore these values were excluded from the fitting procedure. OTS wafer was also excluded from the fit because this surface is beyond the wetting–nonwetting transition. We observe a fairly good agreement between eq 12 and the experimental data used for the fit. Even the HMDZ₂₄ value lays on the curve. This is not surprising to us because this experimental procedure leads to a 0.4 nm thick trimethyl layer grafted on the native silicon oxide surface, and therefore, although of lower surface energy,

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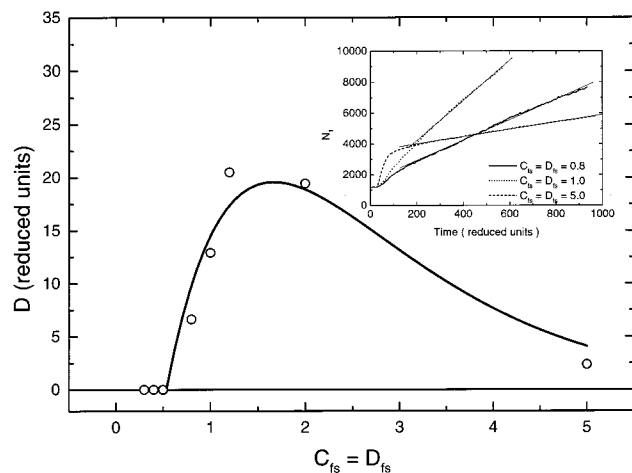


Figure 11. Film diffusion coefficients (D) calculated from MD simulations versus “liquid–solid” interaction parameters ($C_{fs} = D_{fs}$). Data for $C_{fs} = D_{fs} = 0.8, 1.0$, and 5.0 are from this study. D values corresponding to $C_{fs} = D_{fs} = 0.3, 0.4$, and 0.5 are from ref 25, and those corresponding to $C_{fs} = D_{fs} = 1.2$ and 2.0 are from ref 15. Inset: Number of atoms in the first layer as a function of the time for $C_{fs} = D_{fs} = 0.8, 1.0$, and 5.0 . This number is proportional to the square of the film lengths. The slopes of these curves correspond to the diffusion coefficients D .

the HMDZ₂₄ surface is not too different from the “original” wafers. More striking is the fact that the Langmuir–Blodgett wafer has a behavior completely different from the ones reported in this study. This clearly asserts that the stacking of the ω -tricosenoic acid layers drastically modify the chemistry of the surface. It is important to stress that modifying either the cleaning procedure of the wafers or their grafting conditions results in quantitative changes of both the critical surface tension of the wafer and of the D values, but not in a qualitative change of the curve shape.

IV. Molecular Dynamics

The way experiment allows modification of the surface energy without changing too much of the surface chemistry of the substrate is not fully satisfactory. For this reason, we have investigated the spreading of polymer-like liquid droplets on solid substrates using the molecular dynamics technique. That technique allows us to change interactions in an ideal way. We consider 16-atom polymer-like chains and mimic the variations of the substrate surface energy simply by using different values of the “liquid–solid” interaction parameter ϵ_{fs} .

For all the atoms that we consider here, we have taken a Lennard-Jones-type potential

$$V_{ij}(r) = \frac{C_{ij}}{r^{12}} - \frac{D_{ij}}{r^6} = 4\epsilon_{ij} \left\{ \left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right\} \quad (13)$$

where r denotes the distance between the two atoms i and j and C_{ij} and D_{ij} refer to the fluid/fluid (ff), fluid/solid (fs), and solid/solid (ss) interactions. ϵ_{ij} and σ are the standard parameters of the Lennard-Jones potential. Only short-range interactions are considered here, and, for computational convenience, they are cut off above $r_c = 2.5\sigma$ in reduced units, where σ is the hard core radius. These atoms are grouped in polymer-like molecules using a confining potential for adjoining atoms

$$V_{\text{conf}}(r) = Ar^6 \quad (14)$$

The power 6 is chosen here for computational convenience.

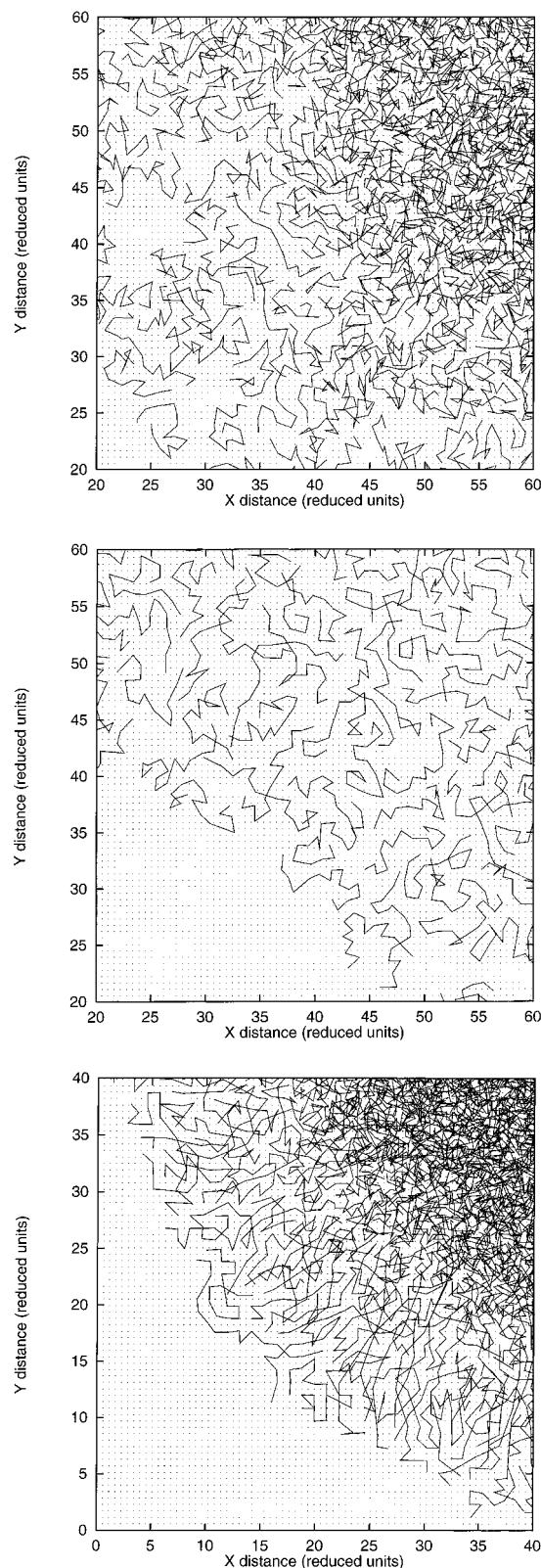


Figure 12. Snapshots ($t = 1005$, in reduced units) illustrating the molecular organization in the precursor film. The atoms of the substrates are represented by dots, and the 16 atoms of the polymer-like molecules are connected by plain lines. The interactions parameters are (a, top) $C_{fs} = D_{fs} = 0.8$, (b, middle) $C_{fs} = D_{fs} = 1.0$, and (c, bottom) $C_{fs} = D_{fs} = 5.0$. The chains in the precursor film are more segregated in the case of the medium surface energy substrates than in the high- or low-energy ones. In the latter case, the structure of the polymer molecules mimic the structure of the substrate.

The use of such a confining potential reduces the evaporation of the liquid, and the model allows us to mimic the dry spreading experiments described in this paper.

As in our previous studies, the solid is made by two layers of fcc(100) surface, at each site of which is an atom. These atoms are allowed to vibrate around their initial position with a deep restoring harmonic potential. For the simulations which are presented here, we have chosen the parameters $C_{ss} = 36.45$ and $D_{ss} = 5.0$ and a solid atom mass in solid ≈ 50 liquid atom mass to get a comparable time scale for the solid and the liquid atoms. The coupling parameters for the liquid–liquid interaction are $C_{ff} = D_{ff} = 1.0$.

We now briefly discuss the way the values of the solid–liquid coupling parameters can be related to the different wetting regimes. This MD model can be applied to describe the behavior of polymer-like liquids in the complete wetting regime,^{20–22} but it has also been recently applied to the partial wetting phenomenon.³¹ In a previous study²² coupling parameters $C_{fs} = D_{fs} = 1.2$ and 2.0 were used to describe a polymeric liquid which wets completely the considered solid surface, while, in the study of Blake and co-workers,³¹ the partial wetting regime was described using coupling parameters $C_{fs} = D_{fs} = 0.3, 0.4$, and 0.5 . These studies respectively refer to the behavior of liquids on substrates of medium and of low surface energy. In the paper, we consider two new cases: liquids on substrates of very high surface energy ($C_{fs} = D_{fs} = 5.0$) and liquids close to the wetting transition ($C_{fs} = D_{fs} = 0.8$ and 1.0).

Given the potentials, the motion follows by integrating Newton's equation of motion. After equilibration, the temperature of the solid is kept fixed by rescaling the speed of the solid atoms to mimic the dissipation of energy of the substrate. The characteristics of the spreading of such polymer-like liquids are studied using 25 600 atoms for the liquid, i.e., 1600 16-atom chains, and 300 000 atoms for the solid substrate. The initial configuration is the following. On top of a square of atoms of the solid, we first consider a sessile drop made by 25 600 atoms forming the polymer chains. To consider this sessile drop configuration, we let equilibrate that drop with solid–fluid couplings $C_{fs} = D_{fs} = 0.4$.³¹ This equilibration procedure was maintained during a time of the order of 10^6 time steps, with a time step $\Delta t = 0.005\tau$, where τ is the natural time unit, $(\epsilon/m\sigma^2)^{1/2}$ (m denotes the unitary mass of the considered fluid atoms, and ϵ and σ are associated with the standard form of the Lennard-Jones potential). After that, we initiate the change of couplings describing the solid–liquid interaction to reach the appropriate values in 10^4 time steps. This procedure allows us to end up with a sessile drop which is a piece of a sphere.

For each of the considered cases, we now analyze the dynamics of the first layer and, if any, of the precursor film to determine the diffusion coefficient D of the liquid on the substrate. As a function of time, we have plotted in the inset of Figure 11 the number of atoms which belong to the first layer.

After the equilibration time, it appears that the number of atoms in the first layer grows linearly with time, for

each of the sets of considered interaction parameters. The values of the diffusion coefficients calculated from these data are presented in Figure 11. Values for interaction parameters $C_{fs} = D_{fs} = 0.3, 0.4$, and 0.5 and for interaction parameters $C_{fs} = D_{fs} = 1.2$ and 2.0 are respectively calculated from the simulations reported in refs 31 and 22. As in the experimental study reported in the first part of this paper, the diffusion coefficient varies in a nonmonotonic way with respect to the interaction parameters.

Furthermore, if we analyze the structure of the precursor film (Figure 12), it appears that the 16-atom chains are more segregated when spreading on the substrates characterized by intermediate liquid–solid interaction parameters ($C_{fs} = D_{fs} = 0.8$, Figure 12a) than in the cases where low- or high-energy substrates are considered (Figure 12a,c). It also appears that, in the case of high-energy surfaces, the conformation of the polymer chains mimic the structure of the solid. It should be kept in mind that the MD simulations were carried out with linear free chain molecules, representative of the PDMS ones, but whose structure and stiffness are different from those of trisiloxanes or C_nE_m surfactant molecules. Nevertheless, the study of Tiberg and Cazabat⁶ has pointed out that, for such systems, the profile of the precursor film and their molecular organization is the outcome of the relative strengths of the “substrate–surfactant” and “surfactant–surfactant” interaction potentials as well as the molecular dynamic picture within the layer precursor.

V. Conclusions

The present investigations bring evidence that the diffusion coefficient D , calculated from the time variations of the film length, is a nonmonotonic function of the surface energy of the substrate, characterized by the critical surface tension. Starting from the partial wetting regime and increasing the surface energy of the substrate, our experiments show that the diffusion coefficient reaches a maximum value for substrates of intermediate surface energies. Our experimental observations are corroborated by an extension of the hydrodynamic model of de Gennes and Cazabat and by the model of Burlatzky and co-workers, which both predict that D varies as $D \sim C_2(\epsilon_{sf} - \epsilon_{crit}) \exp(-C_1\epsilon_{sf})$, where ϵ_{sf} is the energy parameter for the solid–liquid interactions and ϵ_{crit} is a critical energy parameter depending on the liquid–liquid interactions. Furthermore, the same behavior is observed from the molecular dynamics numerical experiments. Although that trend is unambiguous, these results should be considered as semiquantitative because modifying the surface energy of the substrates by grafting a monolayer on top of them also modifies their surface chemistry.

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