

Spreading on Heterogeneous Substrates

M. Voué¹ and J. De Coninck¹

¹ Centre de recherche en modélisation moléculaire, université de Mons-Hainaut, place du Parc, 20,
B-7000 Mons - Belgium
e-mail: michel.voue@galileo.umh.ac.be

Résumé — Étalement sur substrats hétérogènes — Dans cet article, nous considérons les propriétés de mouillabilité de surfaces recouvertes de monocouches organiques. Ces monocouches sont soit incomplètes soit chimiquement hétérogènes. La dynamique de relaxation de l'angle de contact d'avancée et l'ellipsométrie spectroscopique à haute résolution latérale (*High Lateral Resolution Spectroscopic Ellipsometry*, HRSE) sont utilisées pour caractériser les surfaces ainsi que l'étalement de gouttes d'alcanes ramifiés ou d'huiles silicones. L'influence de la concentration en hétérogénéités sur le coefficient de friction (régime de mouillage partiel) ou sur le pseudo-coefficient de diffusion (régime de mouillage complet) des molécules de liquide est présentée. Les résultats expérimentaux sont comparés aux résultats de simulations numériques.

Mots-clés : mouillabilité, monocouches auto-organisées, silanisation, hétérogénéité, dynamique moléculaire, ellipsométrie, angle de contact, friction.

Abstract — Spreading on Heterogeneous Substrates — In this article, we consider the wetting properties of surfaces coated by organic monolayers. These monolayers are either incomplete or chemically heterogeneous. Dynamics of relaxation of the advancing contact angle and high lateral resolution spectroscopic ellipsometry (HRSE) serve to characterize the surfaces and the spreading of branched hydrocarbon or of silicon oils droplets. Influence of the heterogeneity concentration on the friction coefficient (partial wetting regime) or on the pseudo diffusion coefficient (complete wetting regime) of the liquid molecules is presented. Comparisons are given with computer simulation results.

Keywords: wetting, self-assembled monolayers, silanization, heterogeneity, molecular dynamics, ellipsometry, contact angle, friction.

TABLE 1
Characterization of the mixed alkanethiol layers

	Hydroxylation degree C_{HUT} (%)						
	0	15	30	50	70	85	100
$r_{\text{O/C}}^{\text{exp}} / r_{\text{O/C}}^{\text{th}}$ ⁽¹⁾	–	–	1.19	1.02	0.98	1.03	1.08
γ_c (mN/m) ⁽²⁾	20.5	23.2	26.0	29.3	33.7	36.5	39.6 ⁽⁴⁾
CAH ($^\circ$) ⁽³⁾	3.0	4.0	7.0	10.0	9.0	6.0	4.0

(1) Oxygen to carbon ratio determined from XPS measurements.

(2) Determined using water/ethanol mixtures (± 0.4 mN/m).

(3) For water.

(4) 45.5 mN/m, if determined from the Good-Girifalco equation (Eq. (1)). No change for the other values.

between the experimental and the theoretical O/C atomic ratio shows that no preferential adsorption of the thiol compounds occurs (Table 1). The relative fractions in solution can therefore be unambiguously used as a reliable variable to characterize the organic monolayers.

1.3 Wettability Properties of the SAMs

These structural properties have to be correlated with the wettability ones. A first step in this correlation is the determination of the critical surface tension of the organic monolayers and of their contact angle hysteresis (CAH). The critical surface tension γ_c of the substrates has been determined by measuring the static contact angle of water/ethanol droplets. These mixtures were used to obtain surface tensions ranging from 23.0 mN/m for pure ethanol to 72.8 mN/m for water. This range is much wider than the one covered by the homologous series of alkanes (ranging from 23 to 27 mN/m, from hexane to hexadecane). The use of these mixtures allowed us to determine the critical surface tension of the whole set of surfaces, from the fully methylated surface (100% UDT) to the fully hydroxylated one (100% HUT). The values of γ_c , calculated using the Fox-Zismann approximation [9] as a function of the hydroxylation degree (C_{HUT}), are given in Table 1. They range from 21 to 39 mN/m, for the fully methylated and the fully hydroxylated surfaces, respectively. As discussed in [8], the Fox-Zismann approximation is not *per se* entirely justified, because the liquid used does not belong to a homologous series of liquids such as the alkanes, but can be understood as a first-order approximation of the Good-Girifalco equation [10, 11], or of related theories [12], for a surface tension of the liquid γ close to the critical surface tension of the solid. More explicitly, a better approximation is to plot $\cos \theta$ versus $\gamma^{-1/2}$ according to:

$$\cos \theta \cong -1 + 2(\gamma_c / \gamma)^{1/2} \quad (1)$$

which reduces to the linear approximation (*i.e.* the Fox-Zismann approximation):

$$\cos \theta \cong 1 - \frac{\gamma - \gamma_c}{\gamma_c} + O((\gamma - \gamma_c)^2) \quad (2)$$

in the vicinity of the critical surface tension γ_c .

The second step in the characterization of the wettability properties of these SAMs is the measurement of the CAH. These results are reported in Table 1 for water droplets. CAH is low on the pure substrates: 3° to 4° on the methylated and hydroxylated surfaces. It considerably increases with the molecular disorder on the surface, to reach a maximum value equal to about 10° at $C_{\text{HUT}} = 50\%$. This case corresponds to a maximum number of interfaces between the clusters of OH-terminated molecules and the clusters of CH_3 -terminated ones.

The final step of the characterization consists in the determination of the frictional properties of the substrates. To perform these investigations, we considered the relaxation of the advancing contact angle of a squalane droplet on top of these substrates. These data are reported in Figure 3. As expected, the equilibrium contact angle increases as the methylation degree of the surface increases and the relaxation of the contact angle towards its equilibrium value is less rapid on the hydroxylated surfaces.

Figure 3 also shows that the contact angle scales as $t^{-3/7}$, *i.e.* that the dissipation of energy related to the relaxation process of the contact angle is dominated by the molecular displacements of the liquid molecules at the contact line [13]. In this case, we may apply the molecular kinetics theory of wetting (MKT) [14, 15] to extract, from the relaxation curves, the information relative to the liquid/solid friction at the molecular scale. More precisely, using the linear version of the MKT, the speed of the contact line v is related to the out-of-balance driving force, *i.e.* the difference between the

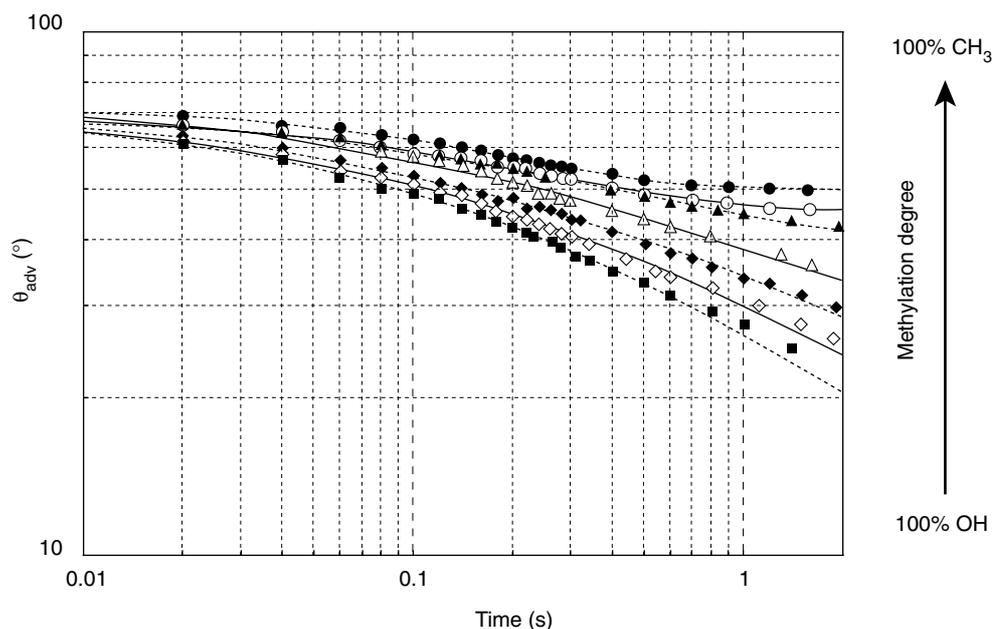


Figure 3

Relaxation of the advancing contact angle of a squalane droplet on top of mixed alkanethiol monolayers. The methylation degree of the SAM increases from top to bottom: 0%, 15%, 50%, 70%, 85% and 100%.

cosine of the equilibrium contact angle θ_0 and the cosine of the dynamic contact angle θ_t , via:

$$v = \frac{1}{\zeta} \gamma (\cos \theta_0 - \cos \theta_t) \quad (3)$$

where the friction coefficient ζ is given by: $\zeta = kT / K_0 \lambda^3$. K_0 and λ are respectively the frequency of the displacements of the liquid molecules at the contact line and the length of these jumps. The results of the modeling (in the least-square sense) of our experimental data by Equation (3) are represented by plain lines in Figure 3. Both the experiment and the computations are in close agreement with each other.

As shown in Figure 4, the friction ζ_{eff} , determined on the heterogeneous substrate, is approximately given by:

$$\zeta_{\text{eff}} = \zeta_{\text{UDT}} + \left(\zeta_L^* - \zeta_{\text{UDT}} \right) \frac{\gamma_c - \gamma_c^{\text{UDT}}}{\gamma_{LV} - \gamma_c^{\text{UDT}}}, \quad \gamma_c < \gamma_{LV} \quad (4)$$

$$\cong \zeta_L^* \quad , \quad \gamma_c \geq \gamma_{LV}$$

where ζ_L^* is the friction coefficient of the liquid, used to probe the relaxation process, on the substrate characteristics of the wetting/non-wetting transition. γ_{LV} is its surface tension. The two identified regimes have been respectively described elsewhere [16-18]. Using linear approximation, they cross each other for a critical surface tension equal to 32.6 mN/m, a value not too different from the squalane surface tension (31.1 mN/m). In [16], molecular dynamics (MD) has been used to assess the validity of Cassie's

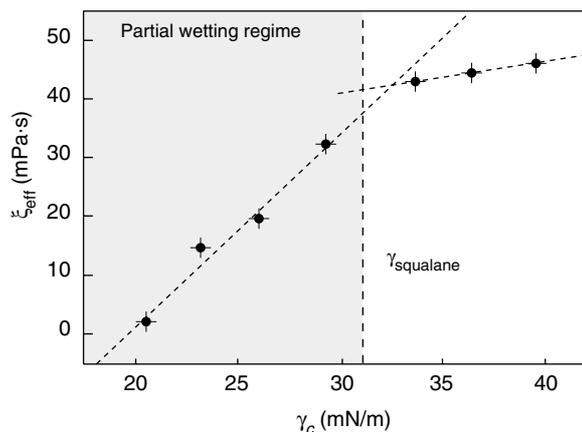


Figure 4

Influence of the substrate critical surface tension γ_c on the effective friction coefficient ζ_{eff} of the liquid molecules. The friction coefficient linearly varies with γ_c in the partial wetting regime and remains quasi-constant as soon as the liquid completely wets the substrate.

equation at the microscopic scale. Moreover, it was shown that the inverses of the jump frequencies (*i.e.* quantities proportional to the friction coefficients) are additive, provided they are weighed by the surface fraction of each material constituent. This was also validated by studying the relaxation of the advancing contact angle of squalane droplets on top of partially silanized silicon wafers [17]. This corresponds to the first regime observed in this paper. MD

simulations were also useful in the determination of the influence of the “solid/liquid” interaction strength on the jump frequency K_0 [18]. In that study, it was shown that K_0 and hence the friction ζ do not depend on the strength of “solid/liquid” interaction in the complete wetting regime. This corresponds to the second regime reported here.

2 COMPLETE WETTING REGIME: PARTIALLY OTS-GRAFTED SILICON WAFERS AND COMPLETE BINARY MONOLAYERS

Let us now consider the spreading of a liquid droplet on heterogeneous substrates in the complete wetting regime. By that we mean that both the matrix and the heterogeneities (or the patterning) are wet by the liquid. Experimental cases that are reported here are:

- partially OTS-grafted silicon wafers;
- binary (UTS/uUTS) complete monolayers.

2.1 Substrate Preparation

In the first case that we have to consider, the heterogeneous substrates were prepared according to the procedure described in [19]. The heterogeneities were obtained by varying the dipping time of the substrates in the OTS-grafting solution (Fig. 2c). In the second case, the grafting procedure is carried out till completion and the heterogeneity is obtained by mixing in the grafting solution UTS and uUTS molecules at varying relative volume fractions [20, 21]. The structure of these chemical compounds is represented in Figures 2d and 2e. The so-obtained substrates have a critical surface tension which ranges from 20.5 to 28.0 mN/m for the

partially OTS-grafted substrates and from 20.5 to 25.2 mN/m for the UTS/uUTS surfaces.

2.2 Diffusion Coefficients

As experimentally evidenced in the early '90s [22, 23], the complete spreading of a liquid microdroplet, typically a low molecular weight silicon oil, on top of a silanized silicon wafer is characterized by the formation of a transient pyramid shape. Each step of the pyramid corresponds to a layer of molecular thickness (about 7 Å for silicon oils). The length of the first layer (*i.e.* of the precursor film) and of all the subsequent ones follows a diffusion-like law:

$$l_{\text{film}} = (Dt)^{1/2} \quad \text{with: } D = \Delta W / \zeta \quad (5)$$

Here D has the physical dimension of a diffusion coefficient but has to be understood as the ratio of a driving term, the difference of energy of a liquid molecule between two successive layers (ΔW), and of the friction term (ζ) which describes, at the molecular level, the energy dissipation between the first liquid layer and the solid substrate.

Using high lateral resolution spectroscopic ellipsometry (HRSE), as reported in [24], we measured the time evolution of PDMS droplets on the two kinds of heterogeneous substrates. As an example, the profiles of a PDMS (PDMS_{10} , $\eta = 10 \text{ mPa}\cdot\text{s}$, $\gamma = 20.1 \text{ mN/m}$) microdroplet spreading on an 85% uUTS monolayer are represented in Figure 5a. The stratified structure of the droplet clearly appears as a function of time. In this case, the energy dissipation is controlled by the viscosity of the fluid [25].

For all the considered substrates, the pseudo diffusion coefficient has been calculated from the linear growth of the

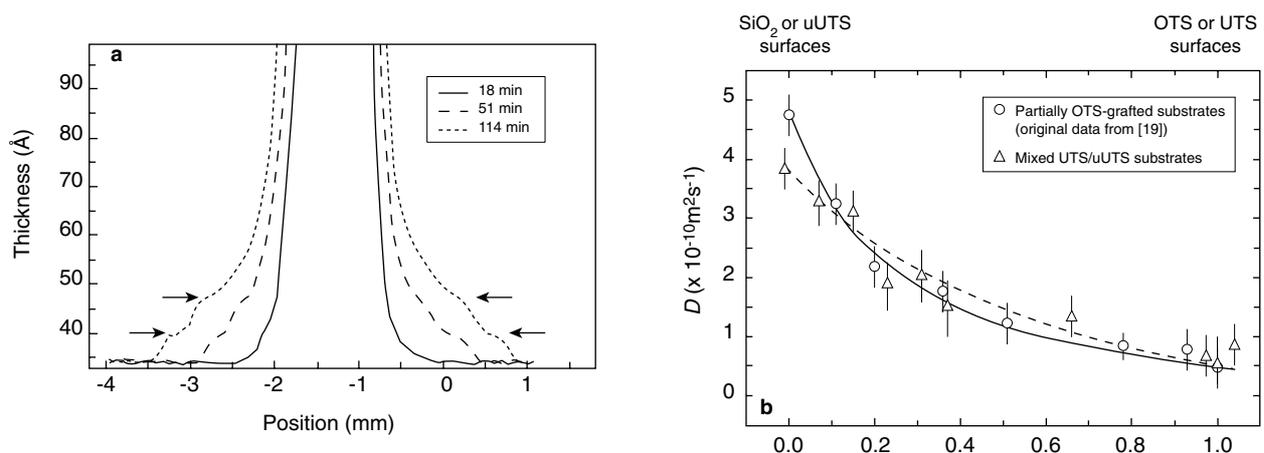


Figure 5

- (a) Time evolution of thickness profiles of a PDMS_{10} microdroplet spreading on an 85% uUTS substrate. The arrows indicate the monomolecular layers (thickness 7 Å) which are growing in front of the macroscopic part of the droplet.
- (b) Influence of the heterogeneity concentration C on the diffusion coefficient of the PDMS molecules.

precursor film length as a function of $t^{1/2}$. The results are presented in Figure 5b. We have recently shown [19] that, on heterogeneous substrates made of A and B materials at relative fractions C_A and $C_B = 1 - C_A$, the pseudo diffusion coefficient D_{AB} is a monotonous function of the fraction C_A or C_B and is related to the characteristics of the pure substrates, namely to the diffusion coefficients D_i and to the friction coefficients ζ_i , by:

$$D_{AB} = \frac{C_A D_A + (1 - C_A) D_B}{C_A + (1 - C_A) \Lambda} \quad \text{with: } \Lambda = \frac{\zeta_B}{\zeta_A} \quad (6)$$

This equation has been used in [19] to model the experimental data obtained for the partially OTS-grafted substrates. As in that case, the data obtained for the UTS/uUTS substrates are adequately fitted by the model (Fig. 5b—dashed line) and the best-fit Λ value is 0.41 ± 0.07 . This value is significantly different from the one obtained for the OTS substrates (0.21 ± 0.02). This difference in the Λ values is due to the change of the chemistry of the surface (SiO_2 to $-\text{CH}_3$ surfaces or $-\text{CH}_2$ to CH_3 surfaces) but could also find its origin in the microscopic structure of the heterogeneity: large OTS clusters in the first case and microscopic heterogeneity in the second one. This question is numerically addressed in the last part of the paper.

2.3 MD Simulations

Although we have tried to focus our experimental studies on the influence of the chemical heterogeneity by using chemical compounds characterized by equal chain lengths

and by different chemical end-groups ($-\text{OH}$, $-\text{CH}_2$, $-\text{CH}_3$), some undesirable effects, related to the physical heterogeneity (*i.e.* to the roughness of the SAMs at the molecular scale, whatever its definition), are difficult to avoid. From a numerical point of view, MD simulations are very appropriate tools because, by locally changing the strength of the “solid/liquid” interaction, we are able to tune the chemical affinity of the liquid molecules for the solid substrate, without having to reconsider the ideality of the surface. Furthermore, MD simulations allow us to consider heterogeneities of known shapes and to compare the results obtained for these to the ones obtained for randomly heterogeneous surfaces.

MD simulations of a pure liquid on top of an ideally flat substrate [26, 27], as well as the extensions of the model to the case of chemically heterogeneous substrates [16, 19], have been described in previous publications. Only the main features of the model are qualitatively given here. The liquid droplet is made of 16-atom Lennard-Jones chains whose monomers are interconnected *via* an r^6 intramolecular confining potential. The droplet spreads on a solid substrate whose atoms occupy, at rest, the position of one layer of faced cubic centered (fcc) cells. The “solid-liquid” interaction potential is based on the 6-12 Lennard-Jones potential. The substrate is made of A and B materials, with A more wettable than B . In this case, A will be considered as the most wettable heterogeneities and B as the matrix. In [19], we have reported the results obtained for patterned substrates. In this contribution, we have modeled the spreading of a liquid droplet on a randomly heterogeneous substrate, whose both components are wet by the liquid.

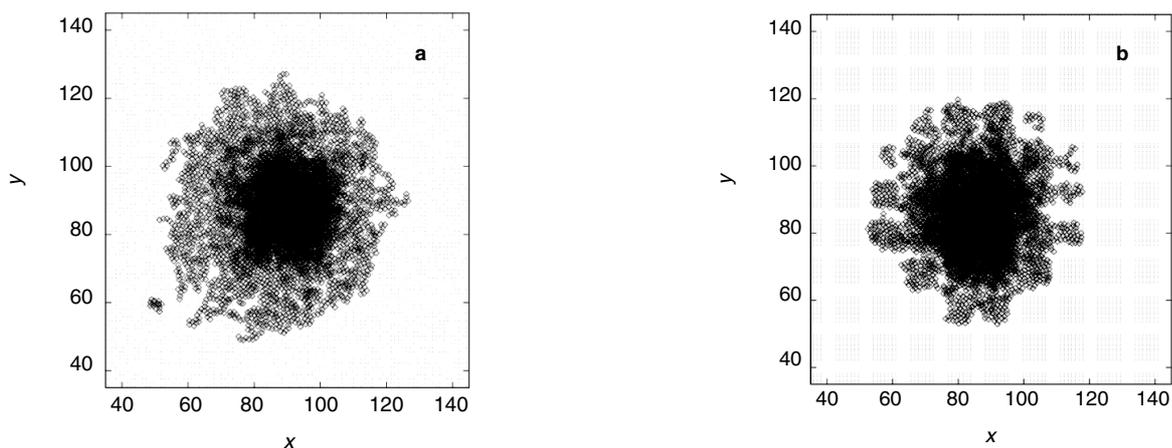


Figure 6

MD simulations of the microdroplets spreading on the heterogeneous substrates. The snapshots (top views) are taken after $100 \cdot 10^3$ time steps.

(a) Random substrates.

(b) Patterned substrates.

In both cases, the less wettable atoms contribute to 44.4% of the substrate surface.

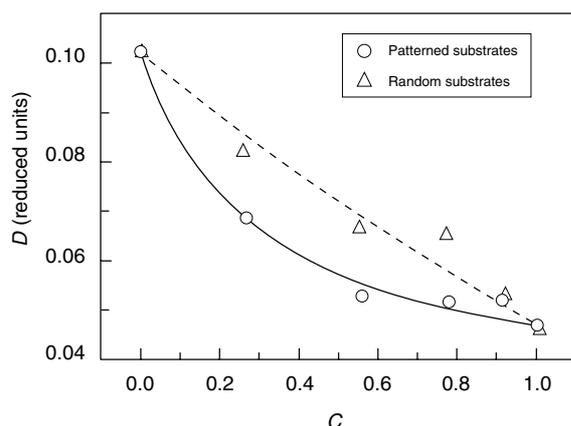


Figure 7

Influence of the concentration C of the less wettable heterogeneities on the pseudo diffusion coefficient D of the liquid molecules. The full and the dashed lines correspond to the best-fit results of Equation (6) to the numerical data with respect to Λ .

Contrarily to what has been observed in the partial wetting regime [16], the structure of the heterogeneity influences the spreading of the droplet (Figs. 6a and 6b). In the case of patterned substrates, the structure of the precursor film matches the structure of the more wettable sites of the substrates. In the case of random substrates, the contact line keeps a shape more circular than in the previous case, as shown by the snapshots. The fluctuations of this line will be quantitatively considered in a forthcoming paper. The structure of the heterogeneity modifies the structural aspects of the droplet during the spreading process but also influences the dynamics of this process, as shown in Figure 7 in which we have plotted the value of the pseudo diffusion coefficient as a function of the concentration of heterogeneity for both the random and the patterned substrates. The values of the ratios of the friction coefficients, calculated from Equation (6), appear to be significantly different from each other, although the “solid/liquid” interactions are the same in the two sets of simulations: $\Lambda_{\text{pattern}} = 0.24 \pm 0.04$ and $\Lambda_{\text{random}} = 0.82 \pm 0.15$. This ratio therefore implicitly includes the effects of the relative distribution of the heterogeneity with respect to the matrix.

CONCLUSIONS

In this article, we have considered the spreading of a pure liquid on various heterogeneous substrates, in the partial as well as in the complete wetting regime. Using the dynamics of the relaxation of the advancing contact angle and the molecular kinetics theory of wetting as a model for our experimental data, we have shown that:

- our experimental system exhibits a wetting/non-wetting transition;

- the friction varies linearly with the heterogeneity concentration in the partial wetting regime and remains constant as soon as the liquid wets the substrate.

This experimental result summarizes those obtained in previous numerical as well as experimental studies for the partial and the complete wetting regimes, separately. On the other hand, we have shown that the diffusion coefficient of silicon oils, as determined from the time evolution of thickness profiles, is a monotonous function of the heterogeneity concentration. This result has been confirmed by molecular dynamics simulations, which evidenced the influence of the structure of the heterogeneity patches on the dynamics of the spreading process.

ACKNOWLEDGEMENTS

This research is partially supported by the *ministère de la Région wallonne*. We gratefully thank S. Semal for the wettability analysis, R. Gouttebaron for the XPS measurements and P. Leclère for the AFM scans.

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Final manuscript received in November 2000