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Droplet spreading on heterogeneous substrates using molecular dynamics

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Using molecular dynamics, it is shown that the equilibrium contact angle of a sessile drop placed on a heterogeneous substrate follows Cassie's law [Discuss. Faraday Soc. **57**, 5041 (1952)]. The dynamics of the associated spreading is analyzed with the molecular kinetic theory. We show that the corresponding molecular parameters vary highly nonlinearly with the relative concentration of the heterogeneities. A model to explain this behavior is proposed. It is predicted that small quantities of wettable heterogeneities on a nonwettable substrate will change the spreading dynamics drastically. [S1063-651X(99)06101-2]

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I. INTRODUCTION

Spreading and wetting are very active research subjects. Many of the associated technological processes have been based on the well known Young equation. This equation describes how a surface liquid *L*, in coexistence with its vapor phase *V*, will equilibrate on a solid wall *W*, according to the equation

$$\gamma_{LV} \cos \theta = \gamma_{VW} - \gamma_{LW}, \tag{1}$$

where the γ_{ij} denote the different surface tensions characterizing the three pairs of media and θ is the contact angle, defined as usual. As already pointed out in several publications [1–3], the problem with this equation is that it refers to perfectly flat and homogeneous substrates. Such cases do not exist in practice. There is therefore a need to study the validity of this equation with realistic substrates. It is known that Young's equation may be replaced by Cassie's law [4] if macroscopical, chemical heterogeneities are present:

$$\gamma_{LV} \cos \theta = c(\gamma_{VW} - \gamma_{LW})_A + (1-c)(\gamma_{VW} - \gamma_{LW})_B, \tag{2}$$

where *c* represents the concentration of the species *A* and $1-c$ is the concentration of the species *B*. This relation refers to equilibrium properties of wall tensions. It is certainly correct for macroscopic heterogeneities for which the additivity of the associated free energies should hold but is questionable for microscopic heterogeneities. Moreover, it is not obvious that such an equilibrium can indeed be observed since, due to the metastable configurations, the time needed to reach equilibrium can be very large. It is, however, expected, on an experimental and also on a numerical basis [5], that if the heterogeneities are not too important, a drop put on a substrate should spread from its initial configuration to reach its equilibrium shape. Many experimental works have addressed this problem in the past [14]. It is, however, very difficult to have good control of the size and distribution of heterogeneities. Whether or not Cassie's law remains valid for microscopic heterogeneities is still an open question. Moreover, the dynamic process of spreading is also a very interesting problem in itself. Several theories have been proposed (see [6–8] for an overview), but all these models assume perfectly flat and homogeneous substrates.

It is therefore interesting to use molecular dynamics (MD) to study the spreading of sessile drops on well defined microscopically heterogeneous substrates. This work complements a previous analysis developed for lattice gas models in two dimensions [9]. Moreover, in [10] we already showed that MD techniques can be used to describe wetting on uniform substrates. This allowed us in particular to validate one of these dynamical theories [6–8] at the microscopical scale.

II. MODEL

Let us now present the liquid drop and the solid at the atomistic scale. For all the atoms considered, we apply a standard Lennard-Jones interaction of the form

$$U_{ij}(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^6 - \left(\frac{\sigma}{r}\right)^{12}\right] = \frac{C_{ij}}{r^6} - \frac{D_{ij}}{r^{12}}, \tag{3}$$

where *r* denotes the distance between any pairs of atoms *i* and *j*, σ is the characteristic radius of the atoms, and ϵ is the strength of the associated potential. The parameters C_{ij} and D_{ij} are, for simplicity, chosen constant for each species and refer thus to the fluid/fluid (ff), fluid/solid (fs), and solid/solid (ss) interactions. For computational convenience, the tail of the Lennard-Jones potentials are cut off at $r_c = 2.5$ in reduced units. This means that we take into account only short-range interactions. To mimic as much as possible the experimental conditions, we consider here chainlike molecules instead of overly simple single atoms. This choice reduces considerably the evaporation into vacuum and therefore improves the efficiency of the simulation. In practice, we incorporate a confining potential

$$U_{\text{conf}}(r) = r^6 \tag{4}$$

for adjoining atoms belonging to a given chain. The power 6 is chosen here for computational convenience. The solid is modeled by two layers of atoms. These atoms interact via the Lennard-Jones potential with $C_{ij} = 35$ and $D_{ij} = 5$. We ascribe to them a heavy mass $m_{\text{solid}} = 50 m_{\text{liquid}}$ so as to have a time scale comparable to the liquid. Each layer of atoms is initially fixed on a fcc(100) lattice and these atoms are then allowed to vibrate around their initial positions with a harmonic restoring potential.

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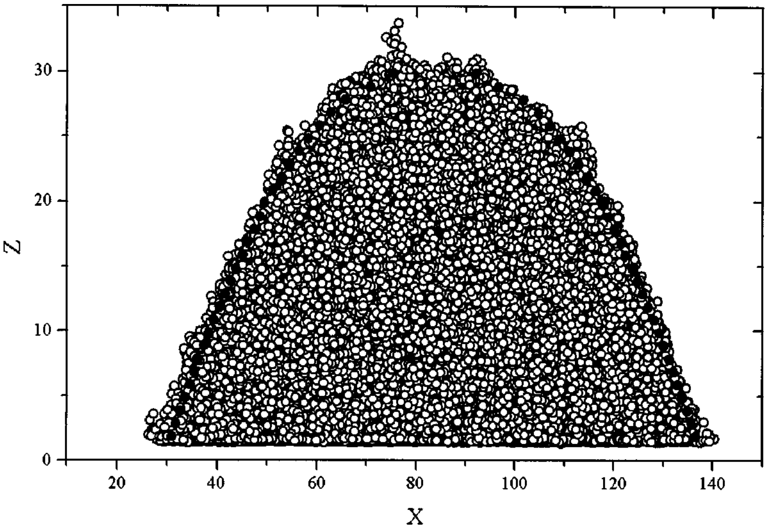

FIG. 1. Side view of a drop. The open circles are liquid atoms, the filled circles mark the average position of the interface.

The temperature of the system is maintained by rescaling the velocities of the atoms. We first equilibrate independently the drop of liquid and the solid. Once we have an equilibrated drop (constant energy), we move it into the vicinity of the solid and then we maintain the temperature of the solid only. This procedure is used to mimic the thermal exchange between the liquid and the thermalized solid, as in a real experiment. The time step δt is measured in units of $\tau=\sqrt{\epsilon m/\sigma^2}$ and its typical value is given by $\delta t=0.005\tau$, of the order of 5×10^{-15} s, with ϵ and σ defined as before. The trajectories of the atoms are then computed solving the associated Newton equations with $C_{\mathrm{ff}}=D_{\mathrm{ff}}=1.0$. The system size we consider in this paper is 25 600 atoms for the liquid (1600 16-atom chains) and 40 000 atoms to represent the wall. The interaction between the liquid and the solid itself is modulated by the constants C_{fs} and D_{fs}. To mimic the existence of two species in the substrate, we have considered $C_{\mathrm{fs}}=D_{\mathrm{fs}}=0.5$ for some solid atoms and $C_{\mathrm{fs}}=D_{\mathrm{fs}}=0.3$ for the others. That is to say, the substrate is constituted by one species *A*, which interacts strongly with the liquid, and another species *B*, which interacts weakly. Previous studies [10] have shown that the interactions of 0.5 and 0.3 lead to equilibrium contact angles of, respectively, 52° and 119°. The relative concentrations of *A* and *B* are, respectively, c and $1-c$. Intuitively, we may expect that the larger the concentration of *B*, the larger the contact angle. Several configurations for the distribution of these species may of course be considered: either regularly distributed or, closer to real experiments, randomly distributed. Both cases will be developed below.

III. RESULTS

To compute the associated contact angle, we proceed as follows. First, we subdivide the liquid droplet into several horizontal layers of arbitrary thickness. The constraint on the number of layers is provided by the need to maximize the number of layers while ensuring that each layer contains enough molecules to give a uniform density. For each layer, we locate its center by symmetry and compute the density of particles as a function of the distance to the center. We then locate the extremity of the layer as the distance where the density falls below a cutoff value of 0.5 times the liquid density. To check the consistency of the method, different layer thicknesses and cutoff values were considered and these gave almost identical results. A typical snapshot of the observed drops is given in Fig. 1 (see also [10]). Using a circular fit based on the extremities of the layers, we then can measure the contact angle θ of the drop versus time. This is also necessary to determine the corresponding value at equilibrium.

Let us first compare the effect of the shape of the patches of the different species on the results. For that we have considered with the same surface concentration of *A* and *B*, regular distributions (squares of 1×1 to 7×7 atoms), and random distributions in the two solid layers. The corresponding contact angle relaxations in time do not exhibit any significant differences as observed in Fig. 2. These results show, in agreement with the results presented earlier [9], that the geometry of microscopic patches seems not to play a significant role in determining the equilibrium contact angle. Presumably the patches are small enough so that the energy

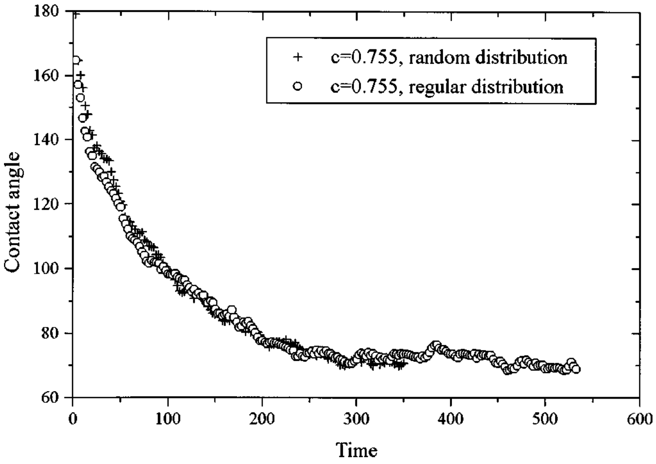

FIG. 2. Contact angle relaxation of drops in contact with a heterogeneous solid ($c=0.755$), with a random distribution (+) and with square patches (○).

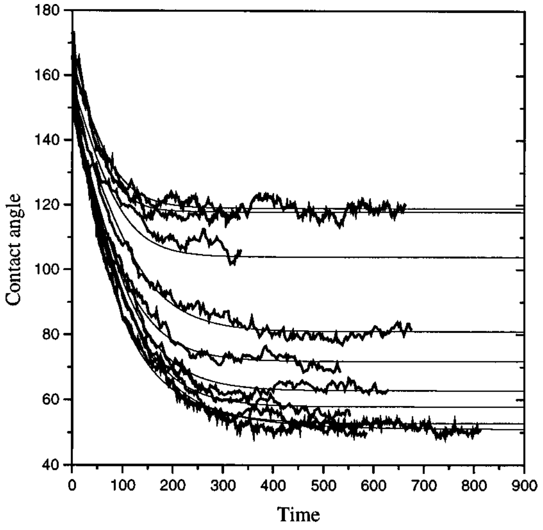

FIG. 3. Contact angle versus time. The fitted curves correspond to the MKT. From bottom to top, we have the following concentration of *A*: 1.0, 0.995, 0.98, 0.875, 0.755, 0.595, 0.245, 0.02, and 0.0.

required to cross them is comparable to *kT*.

Let us now present our results for regular patches. The contact angle relaxations in time for different concentrations of *A* and *B* are given in Fig. 3. To extract from these data the associated equilibrium angles, we need to fit them using some theoretical model. It has been shown in [10] that the molecular kinetic theory (MKT) can be applied very well for the pure cases $C_{\text{fs}}=D_{\text{fs}}=0.3$ and 0.5. Moreover, the parameters within the MKT can be linked to the molecular properties of the liquid and the solid. It is therefore meaningful to fit these data according to an effective MKT. Within this approach, Blake and Haynes [11] assumed the driving force for the wetting line to be the out of balance surface tension force γ_{LV} $(\cos\theta^0-\cos\theta)$. Using Eyring's activated rate theory for transport in liquids gave the final relationship between θ and the velocity of the wetting line v as

$$v=2K^0\lambda\,\sinh\left[\frac{\gamma_{LV}}{2nk_BT}\,(\cos\theta^0-\cos\theta)\right], \qquad (5)$$

where K^0 is the frequency of molecular displacement at equilibrium, λ is the average length of these displacements, n is the number of adsorption sites per unit of area, k_B is the Boltzmann constant, and T is the absolute temperature. No external forces are present in the simulation and the shape of the spreading drop will approximate a spherical cap [12]. If we assume no evaporation and a constant volume, which is indeed observed within the simulations, the following relationship can be derived [10]:

$$v=\frac{\partial R}{\partial t}=-\frac{\partial\theta}{\partial t}\left(\frac{3V}{\pi}\right)^{1/3}\frac{(1-\cos\theta)^2}{(2-3\cos\theta+\cos^3\theta)^{4/3}}, \qquad (6)$$

where V is the drop volume and R is the base radius. These equations are a linked set of partial differential equations with two adjustable parameters: the prefactor $a=2K^0\lambda$ and $b=\gamma_{LV}/2nk_BT$. The prefactor is a measure for the intrinsic velocity of the solid/liquid system. To keep the results as general as possible, we calculated all the parameters in reduced units. Since we do not change the site density n and the other parameters in b are independent of the interactions between the solid and the liquid, b should be the same in all the experiments. The best fit gave $b=0.21\pm0.06$ [10]. The differential equations were solved numerically using a fourth-order Runge-Kutta algorithm [13]. The difference between the numerical data and the theoretical curve was then minimized with a downhill simplex method [13]. The numerical fitted curves are also shown in Fig. 3. The associated equilibrium angles versus the concentration of *A* are given in Fig. 4.

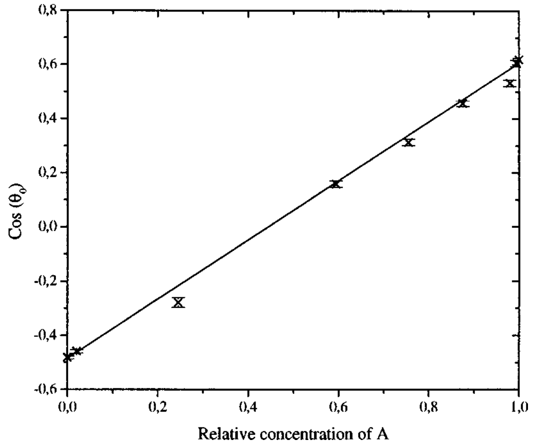

FIG. 4. Equilibrium contact angle as a function of the relative concentration of *A*. The solid line represents Cassie's law. The correlation coefficient of the straight line fit is 0.9994.

To estimate the errors on the parameters, we have applied the bootstrap method [13] using an estimated error of 2.5° on the measurement of the individual angles. Because, at longer times, the contact angles of our MD drops fluctuates more or less around a mean value, we conclude that the true equilibrium values are reached. As can be seen, the agreement with Cassie's law (shown as the straight line) is quite remarkable for these microscopic heterogeneities.

The associated prefactor a_{eff} resulting from every fit can then also be plotted versus the concentration of *A*. The corresponding data are given in Fig. 5. The prefactors on pure substrates a_B and a_A are the values at, respectively, $c=0$ and 1.

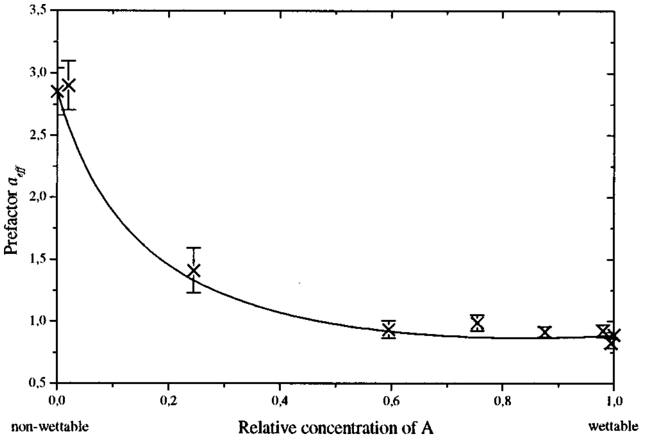

FIG. 5. Prefactor a_{eff} from fitting the MKT versus the relative concentration of *A*. The solid line represents Eq. (8).

The prefactor a_{eff} varies highly nonlinearly with the relative concentrations of the two species present at the substrate. The effective prefactor (with dimensions of velocity) for the mixed substrates seems to be constant when c is close to 1. Only as the relative concentration of A approaches 0 does the effect of B on the effective prefactor become significant. This behavior suggests that the effective dynamics of spreading on heterogeneous substrates is determined by the slowest process (a_A) occurring at the contact line. It is only when the concentration of the rate determining species becomes small that the effective prefactor takes an intermediate value.

Since $a=2K^0\lambda$ and in all the simulation the λ's are equal, we can describe the behavior of a_{eff} in terms of K^0_{eff}. In the original model of Blake and Haynes [11], K^0 could be seen as the inverse of the time required to jump from one site to another, including the residence time. On heterogeneous substrates with two constituents, four kinds of jumps may exist, namely, A-A, B-B, A-B, and B-A. It can be expected that a jump from one surface species to another is characterized by different asymmetric energy barriers and thus we may expect different and asymmetric jump frequencies. The average jump time is then the sum of all the individual jump times respectively multiplied by the probability of their occurrence. If we assume that the probability of jumps from one surface species to another can be approximated by $c(1-c)$, we then find

$$\frac{1}{K^0_{\mathrm{eff}}}=\frac{c}{K^0_{A\text{-}A}}+\frac{1-c}{K^0_{B\text{-}B}}+\frac{c(1-c)}{K^0_{A\text{-}B}}+\frac{c(1-c)}{K^0_{B\text{-}A}}. \tag{7}$$

If the wettabilities of A and B are very different, with A the most wettable species, so that $K^0_{A\text{-}B}\ll K^0_{B\text{-}A}$, and if, to a first approximation, it can also be expected that $K^0_{A\text{-}B}$ is of the order of $K^0_{A\text{-}A}$, this equation leads to

$$\frac{1}{a_{\mathrm{eff}}}=\frac{c(2-c)}{a_A}+\frac{1-c}{a_B}. \tag{8}$$

In Fig. 5 this equation is represented by the full line. The errors are calculated as before. It is clear that the proposed model fits the data very well.

In the general case, $K^0_{A\text{-}B}$ and $K^0_{B\text{-}A}$ should be treated as fitting parameters. Moreover, it should be clear that the probability of jumps across a given boundary depends on the geometry of the heterogeneities. However, if the heterogeneities are of microscopic size and they are not ordered in some special geometries (e.g., stripes), we expect $c(1-c)$ to be a good approximation. As explained before, no differences are seen between the contact angle relaxation on substrates with random and regular patches, with fixed relative concentration.

Taking a closer look at the equations, it is expected that a small quantity of heterogeneities of nonwettable species on a wettable surface (c close to 1) will not change the dynamic parameters significantly; only the driving force of spreading will be changed according to Cassie's law (linear with the concentration). On the other hand, a small quantity of wettable species on a nonwettable surface (c small) can drastically increase the dissipation at the contact line (smaller a_{eff}). Since the dissipation at the contact line is the rate determining factor within this approach, small wettable heterogeneities can significantly decrease the rate of spreading. This property can be related to the observation that the jump frequency of water on hydrophobic substrates can be orders of magnitudes larger than on hydrophobic substrates [7].

IV. CONCLUSIONS

In conclusion, we have been able to show the validity of Cassie's law for molecular heterogeneities using MD simulations. Moreover, we have shown that, provided the sizes of the heterogeneities are of molecular scale, their geometry does not change the equilibrium contact angle. The dynamics of the MD drops spreading on heterogeneous substrates can be described by the molecular kinetic theory. The effective kinetic parameters resulting from these fits change nonlinearly with the relative concentration of the heterogeneities. In the model proposed for the effective kinetic parameters, we assume different frequencies at the contact line: frequencies related to the movement of liquid molecules on patches that are locally pure and the frequencies related to the crossing of boundaries between the different species. This simple model represents the experimental behavior very well. It is shown that small quantities of wettable heterogeneities can decrease the jump frequency of wetting drastically.

To our knowledge, no experimental results on the effect of heterogeneities on contact angle relaxation have been published. However, intuitively, it can be understood that heterogeneities must influence the dynamics to a large extent. We hope these MD studies are a step towards a better understanding of the dynamics of spreading on heterogeneous and rough substrates.

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