Mechanisms of fluid spreading : Ising model simulations

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(Received 22 July 1994)

Mechanisms of fluid droplet spreading on atomically flat solids are studied using Monte Carlo lattice simulations with particle conservation. The early time nearly linear behavior of precursor spreading is observed to be dominated by the surface fluid flow on the bulk droplet to the solid. The late time nearly $t^{1/2}$ behavior is mostly due to migration of second layer particles to the holes and the perimeter of the precursor. Also, the roles of initial contact angle and Hamaker constant of the fluid-substrate system are discussed.

PACS number(s): 68.10.Jy, 05.50.+q, 68.10.Gw, 68.45.Gd

Recently, careful ellipsometric studies of the spreading of small droplets of silanols across atomically flat silicon wafers have revealed precursor films about one molecule thick [1,2]. These experiments also show the striking phenomenon of dynamical layering, which appears to have little, if anything, to do with the equilibrium layering phenomena seen at surfaces in the situation of partial wetting. Moreover, in the final stages of spreading, there is evidence for the formation of a surface gas of the molecular disk onto the substrate. These observations have not been corroborated fully by the hydrodynamic considerations [3]. However, with the exception of surface gas formation, these phenomena have been modeled analytically [4] and numerically with a rather simple horizontal solid on solid model [5]. Apart from the morphology of spreading droplets, the time dependence of the precursor width is of particular interest. Heslot *et al.* [2] did establish for squalane the $t^{1/2}$ law, with the exception that for early times there was a single datum that departed significantly from this law. This means that the work in Refs. [4] and [5] is not capturing this late time scale behavior for reasons which are explained in Ref. [6]. Based on our molecular dynamics simulations [7] we have shown that there is a preliminary time linear growth of the precursor width, as in [4,5], crossing over on some characterstic time t_c to the $t^{1/2}$ final law. It is noted that these continuum simulations also showed evidence of dynamical layering.

All these experimental and theoretical results about spreading indicate the need for a detailed mechanism at the molecular level. This need was further amplified by the most recent ellipsometric measurements by Forcade and Mate [8]. They claim that particle evaporation from the droplet into the vapor phase followed by readsorbtion plays the dominant role in spreading rather than molecular motion in the drop. It is worth noticing, however, that the ellipsometric technique allows subatomic resolution of the density profile normal to the substrate, but is insensitive to the possible existence of a cloud of particles surrounding the droplet. One reason why experimentalists appear to have overlooked the early time linear growth of the precursor might be the difficulty in controlling the initial contact angle θ_c with which the droplet is introduced on the substrate. However, at late times the initial contact angle is not expected to have any significant effect on growth of the precursor. To resolve this controversy about the dominant spreading mechanism we use a computational model in which the evaporation of particles from the droplet is also possible. We selected a stochastic Monte Carlo approach to study a lattice gas system instead of a molecular dynamics (MD) model.

As in Ref. [9], we consider an Ising model with spin variables $S_i = \pm 1$. This model maps to the lattice gas model with occupation numbers $n_i = (S_i + 1)/2$. The fluid particles interact with their nearest neighbors via the coupling constant J, which describes the cohesion between fluid particles and is closely related to the surface tension strength between fluid and vacuum. With these assumptions we may write the Hamiltonian as

$$H = -\frac{J}{2}\sum_i \sum_j S_i S_j + \sum_i S_i V(z_i),$$

where indices i and j run over the whole three-dimensional lattice. The initial droplet of $S_i = +1$ is made ridge shaped by imposing translationally invariant initial conditions in the direction that is perpendicular to the assumed spreading direction. We assume the interaction between the fixed structureless substrate and the liquid particles to be of the attractive van der Waals form $V(z) = -A/z^3$, where z is the distance from the substrate and A is proportional to the Hamaker constant; its value is chosen to guarantee complete wetting. This term provides the driving force for spreading as well.

The microscopic dynamics is governed by a stochastic process, constrained by the particle conservation requirement in the rectangular simulation box of size $W \times H \times L$. The precursor spreading takes place in the W direction and L is the direction of periodic boundaries. In the simulation, particle conservation is handled by using Kawasaki spin-exchange dynamics: opposite spins on neighboring sites can exchange positions, with a transition propability P dependent on the energy change δH

as $P = e^{-\delta H/kT}/\left(1+e^{-\delta H/kT}\right)$. Note that there is an arbitrary time scale in the dynamics. The experimental work indicates that the temperature kT/J must be small enough to give a very low vapor pressure, as the experiments require. This means that very little change is induced by the Kawasaki dynamics except at the liquid surface, since the spontaneous density — or magnetization in spin language — is nearly saturated. Thinking now in the particle-hole language, several mechanisms of particle transport can be considered.

(a) Near the surface of the reservoir droplet, the particles tend to move downward towards the attractive substrate when they are near it because of the van der Waals interaction. Unless the particle in question projects from the surface above a hole, several bonds must be broken in a preliminary step before the particle can stabilize by downward movement to a vacancy. Since the first step would be rather slow (in view of the size of kT/J), we add here that for testing purposes only we have allowed diagonal hopping, there obviating the first step above but at some cost in computer time, to check that this additional factor is qualitatively unimportant.

(b) Particles initially bonded to the reservoir can sever this connection either by evaporating into the vacuum or by moving across the substrate itself or on top of a molecular layer closer to the substrate. Given sufficiently large A/J and small kT/J values, the latter two processes are clearly energetically favored over the first.

(c) Consider the case where a precursor film has been formed. It can grow further by two processes. (i) The reservoir can evaporate particles into a dilute gas on lattice points immediately above the substrate as in (b). On reaching the extremum of the precursor film, particles fall (under the substrate attraction) into the growing edge. (ii) Holes formed in the precursor film at its extremum by spin exchange can propagate back towards the reservoir where they will be filled (driven by the van der Waals force). In assessing the relative importance of (i) and (ii), although the hopping rate of particles and holes would be the same in our model, we expect the particle transport in the dilute surface gas to dominate because the composite event creating a mobile particle is energetically favored.

(d) In case (c), particles can be deposited on top of a growing precursor not only from the reservoir, but also from the vapor phase, bringing in the ideas of Forcada and Mate [8]. If A is big enough, such particles will be more likely to fall over the edge of the precursor rather than to become attached to the reservoir drop, also producing a viable precursor film growth mechanism. In our case, it turns out not to be dominant. Evidently, holes in the precursor will tend to be filled by particles in the dilute gas when permissible.

It should be noted that with chosen simulation parameters and strict particle conservation, evaporation from the droplet will increase the partial vapor pressure slightly from its initial zero value. We have also tested this model by allowing the particles reaching the nonperiodic boundaries to irreversibly escape from the simulation box. Such a relaxation of strict particle conservation, as was done in our MD simulations [7], did not change the morphology and characteristic behavior of the droplet. Then it is obvious that our simulation model with a closed simulation box favors evaporation and overestimates its effects. However, we tried to keep the evaporation rate low by adjusting the simulation temperature kT/J, within the range from 1.5 and 6.0. For temperatures $kT/J<2.5$ and $A/J\geq 10$, evaporation did not seem significant and for the results presented in this paper we chose $kT/J=2.0$. In addition to temperature, we also varied the substrate potential strength A/J and found that, if precursor film motion is examined, the change in the substrate potential strength does not affect results very dramatically. The increase in A/J from 5 to 100 caused the precursor length to differ only less than 10 % after 150 000 steps (equivalent to Monte Carlo steps per lattice site). Increasing the substrate potential strength causes the layers above the precursor to spread faster, thus making the droplet cap wider. It is worth noticing that this change in the morphology of the droplet is qualitatively similar to that observed experimentally by Heslot *et al.* [10]. On the other hand, at low values of substrate potential ($A/J<5$), the evaporation rate increases clearly causing a considerable vapor pressure all over in the simulation volume. However, this does not seem to play any role in spreading.

In the simulations we first investigated the characteristic time behavior of the first few layers on the substrate. We used a system of 5000 particles with a substrate potential strength $A/J=10$ in a volume of $201\times25\times10$ lattice sites forming an initially rectangular ridge ($\theta_c = 90°$). To obtain sufficiently good statistics, we averaged over 20 runs. Our results for the characteristic precursor spreading show after a certain transient time $t_s\approx2000$ an early time linear growth to crossing over at about $t_c\approx13\,000$ to $t^{1/2}$ late time law until the droplet cap has disappeared. The remaining film, only one layer thick, breaks up after very long times to form a surface gas. These behaviors are in full qualitative agreement with our molecular dynamics results [7]. We also studied the effect of droplet size by changing its volume between 500 and 24 000 lattice sites, but have not seen any significant effects. As a further test for the growth behavior, we simulated a system with an increasing number of fluid particles in the middle section of the "initial" ridge after the particles there had moved away. Once again the crossover behavior was evident, but now the $t^{1/2}$ law persisted without showing the surface gas formation.

Next we studied the effect of initial contact angle by setting the substrate potential strength $A/J=50$ for a fluid ridge of 5760 particles in the simulation box of volume $201\times30\times10$ lattice sites and averaging over 10 runs. The initial contact angle was set to $\theta_c = 45°, 63°, 72°$, and $85°$. Also in these cases the results indicate that during the early time interval the precursor film grows nearly linearly in time until the precursor film grows too wide, whereafter this behavior changes to slower and contact-angle-independent $t^{1/2}$ behavior. However, when the initial contact angle is decreased, the transient time t_s becomes shorter and the late time spreading mechanism becomes earlier. Furthermore, it was found that the characteristic dynamics of the second layer is similar to the

precursor layer. However, the initial transients are longer and the ratios between the first and second layer velocities were about 0.5 for the chosen simulation parameters and dependent on the substrate potential strength.

To study the relative importance of different spreading mechanisms in detail, we calculated particle densities and fluxes at different heights above the substrate. For this purpose we used a somewhat smaller system consisting of 2100 particles in a rectangular fluid ridge, i.e., θ_c=90°, and setting A/J=10. First we show snapshots of fluid densities [Fig. 1(a)], which can be measured by ellipsometry. About three separate dynamic layers can clearly be distinguished and profiles resemble rather closely the experimentally observed structures [1]. From the density snapshots, indicated as gray scales in Figs. 1(b) and 1(c), it is seen that the vapor pressure is very small. It is also clear that particles migrate from the precursor film to move freely on the substrate, thus forming a two-dimensional surface gas. In order to get more detailed information about the movements of fluid particles during spreading, we calculate net fluxes of matter by using randomly chosen tracer particles. In the initial droplet about 10% of the tracer particles are in the first droplet cap layer, another 10% in the second, and the rest (80%) in the third and higher layers. In Fig. 2 we show the droplet profiles at two different times for (a) early and (b) late time growth. Within these equally long time intervals we also show the net flux vectors as a function of W position for the first three layers projected to the profile ($H \times W$) plane. It is noted that in the flux calculations, small horizontal components of the fourth and higher layers were added to the third layer fluxes. This tells us about particle transportation in a vapor phase. The vertical components were calculated as net fluxes through interfaces between consecutive layers. In order to find the total transport of matter away from each layer of the droplet cap, we have summed over the horizontal components of flux in each layer. Likewise we have calculated the total vertical transport of matter from the third to the second layer and from the second to the first layer.

From Fig. 2(a) it is evident that for early times the flow of matter is concentrated in the fluid interface region of the droplet cap and the fluxes are predominantly vertical towards the substrate. This results in a fast precursor growth and solely horizontal flux in the precursor, i.e., particles that reach the substrate also stay there forever. The total horizontal transport of the first layer is twice that of the second layer and more than five times that of each higher layer on average. On the other hand, the total vertical transport of matter from the third to the second layer is about 20% larger than that from the second to the first layer. This facilitates the growth of the second layer. From Fig. 1(b) it is also observed that the fluid wall is quite diffuse, providing an interface region in which particle flow down to the substrate is easy. At very early times a transient time (t_s) is needed to form this diffuse interface for the droplet cap. Then it is quite obvious that a large initial contact angle, i.e., flat fluid wall, requires a longer transient time than a small initial contact angle. We can now conclude that at early times the spreading is dominated by the fluid particle flow down along the diffuse droplet interface. This flow is driven by the van der Waals force of the substrate and thus shows a constant speed spreading of the precursor layer. The same is true also for the second layer, but

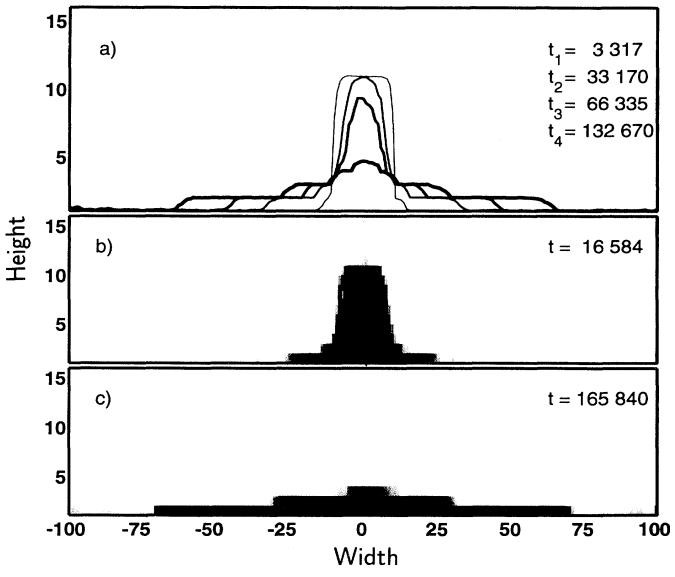

FIG. 1. Snapshot (a) shows the temporal development of the droplet profile. Average densities of the droplet are given in snapshots (b) and (c). Areas having density larger than 2% are visible and dark shading denotes the dense area.

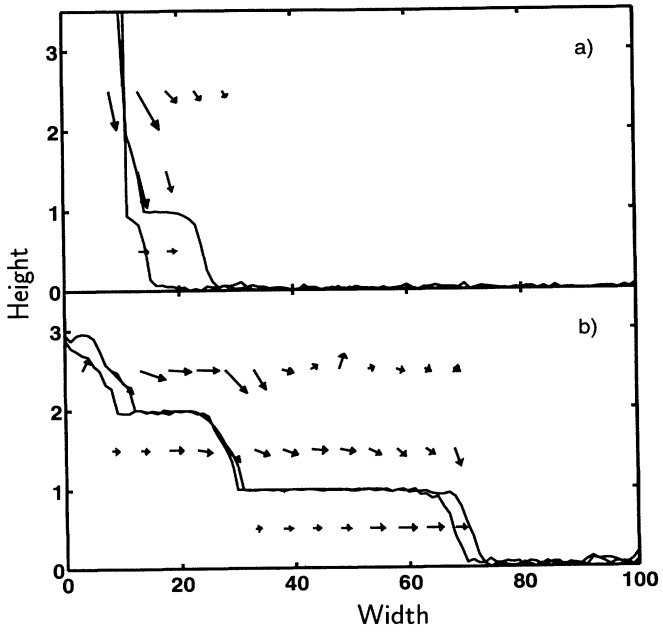

FIG. 2. Profiles and net fluxes of particles for (a) the early time interval of 3317–16 584 steps and (b) the late time interval 152 573–165 840 steps.

with much lower speed, because about 85% of the total vertical transport of matter from the third to the second layer continues to the first layer. Therefore, the early time spreading corresponds to the growth mechanism (a), described above.

For the late times the spreading is quite different, as depicted in Fig. 2(b). First of all, the precursor profile has spread only about 1/3 of the corresponding spreading for early times within an equal time interval. The second layer has spread only a very small amount, while the third layer already shrinks. This shrinking, due to the shortage of matter in the droplet cap, will also happen for the second layer at even later times. The flux vectors are seen to be purely horizontal in the precursor and predominantly horizontal for the second and the third layers. From the second and third layer of the droplet, there are slight downward vertical fluxes, which increase rapidly towards the edge of the precursor and second layer, respectively. This increase is caused by the increasing number of holes, which the flux of particles from upper layers fill in. The increasing number of holes towards the edge of otherwise complete precursor and second layer also explain the increasing horizontal fluxes within these fluid layers. From the third layer fluxes for $W \geq 38$, which include the horizontal components of fourth and higher layer fluxes, we see that these vapor particles have very small horizontal components. This behavior can be explained by the density gradient in the vapor caused by the small amount of particles that have evaporated originally from the droplet cap. The total horizontal transport of matter from $W = 38$ to $W = 58$ is for the second layer and vapor layers about 1.2 times and 0.6 times that of the first layer. Thus the transport of matter on the surface of the precursor dominates the precursor spreading. These particles on nearly complete precursor layer can be considered as random walkers with the *mean square displacement behaving linearly in time.* From estimating the total horizontal transport of matter within the fluid interface, on the surface of this interface, and outside this interface in the vapor, we find the surface transport to be about two times that inside the fluid and more than two times that in the vapor. The total vertical transport of matter from the second to the first layer is about 25% more than that from the third to the second layer. In Fig. 2(b) we see some upward vertical flux from roughly the middle of the second layer to the third layer, which could indicate either small evaporation or composite jumps on top of other second layer particles. Thus we can conclude that at late times the spreading of the precursor layer is dominated by particles migrating off from the second layer edge and performing random walks on the first layer until they find holes to fill or the rough edge of the precursor layer to stick with. Then the mechanism of spreading is the same as that described in (c(i)) and the random walkers dominate the $t^{1/2}$ late time growth.

Finally we conclude that although some small number of particles evaporate from the droplet cap and form vapor, they do not play a significant role in the precursor spreading. Increasing the temperature will increase particle evaporation, but at the same time particle flow in a diffuse droplet interface is enhanced. Similarly increasing the temperature will increase the amount of particles migrating off from layer edges. Thus we believe that the dominant early time fluid flow and late time second (and higher) layer migration mechanisms could explain the experimental results of the precursor growth also in the case of Forcada and Mate [8]. On the other hand, it is known that in a somewhat related phenomenon of surface flattening under suitable size conditions the process of evaporation and condensation can dominate over the diffusion mechanism [11]. Thus in the case of a large droplets we cannot rule out the evaporation-condensation process as a dominant mechanism.

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