

Simulating the Spreading of a Drop in the Terraced Wetting Regime

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(Received 10 November 1995)

For atomic fluids, droplet spreading in the terraced wetting regime is investigated using molecular dynamics. The radii of the terraced layers vary as \sqrt{t} regardless of system size, lattice geometry, and thermostating, in agreement with experimental data. Previous simulations are shown to disagree due to porosity of the lattice. The spreading proceeds initially via downward mass transfer in the outer regions of the drop. When layers close to the solid surface become impenetrable, mass transfer occurs only at the drop edges, as suggested by de Gennes and Cazabat. [S0031-9007(96)00120-2]

PACS numbers: 68.45.Gd, 61.20.Ja, 68.10.Gw

In 1989, Heslot, Cazabat, and Levinson [1,2] observed in a spatially resolved ellipsometry experiment that droplets of polydimethylsiloxane (PDMS) spread on a flat solid surface by forming distinct monomolecular layers. These layers diffuse outward until only the layer closest to the solid surface remains. This “terraced wetting” is a subcase of complete wetting. It occurs due to strong favorable interactions between the solid surface and droplet fluid. Experimentally, the radii of layers vary with time as \sqrt{t} . Kawasaki dynamics for a lattice gas [3] appear to recover the dependence of the radii of the layers on time, but the large number of parameters involved and non-first-principles make difficult direct comparisons with experiment.

In principle the molecular dynamics technique is the most appropriate technique to investigate the dynamics of spreading. Previous attempts by Yang, Koplik, and Banavar [4,5] to use molecular dynamics simulations show different spreading rates from the ones observed experimentally [3]. In particular, they found that the radii of the layers vary with time as $\sqrt{\log_{10}(t)}$. Yang, Koplik, and Banavar [5] believe that the difference in molecular size is the main reason for discrepancy between the simulations and experiments. They argue that atoms (used in simulations) diffuse by hopping between lattice sites, and are likely to be pinned to adsorption sites. Long chains, on the other hand, are unlikely to be pinned to the surface unless the nearest-neighbor distance matches exactly the lattice parameter. Therefore, one would expect a subdiffusive behavior of atoms. Recent molecular dynamics simulations do indeed show that for a nonvolatile droplet of chain molecules monomolecular layers vary with time as \sqrt{t} [6]. De Coninck *et al.* [3] suggested that the discrepancy between simulation and experiment is due to the huge disproportion between the longitudinal scales involved; i.e., in the simulations, thickness and longitudinal scales are microscopic where these are macroscopic experimentally [3]. Finally, Nieminen *et al.* [7] suggest that the discrepancy between simulation and experiment is due to the high volatility of the simulated droplet in comparison with PDMS droplets on silicon wafers.

In order to shed some insight on the spreading of a droplet consisting of an atomic fluid on a solid surface, and more specifically to explore the reasons behind the discrepancy between molecular dynamics (MD) results and very careful experimental data, we have performed several simulations using the MD technique. We have investigated the effect of droplet size, solid geometry, interaction between solid particles, and thermostating.

To mimic experimental conditions, gas, liquid, and solid phases have atomic details. Particles interact with each other through a Lennard-Jones (LJ) potential

$$V_{\alpha\beta}(r_{ij}) = 4\epsilon_{\alpha\beta} \left[\left(\frac{\sigma_{\alpha\beta}}{r_{ij}} \right)^{12} - C_{\alpha\beta} \left(\frac{\sigma_{\alpha\beta}}{r_{ij}} \right)^6 \right]. \quad (1)$$

Here, $r_{ij} = |\vec{r}_i - \vec{r}_j|$ is the distance between particles i and j with, respectively, position vectors \vec{r}_i and \vec{r}_j . The parameter $\sigma_{\alpha\beta}$ determines the sizes of the particles and $\epsilon_{\alpha\beta}$ is the depth of the potential well. For the interaction between fluid particles (f), C_{ff} is set equal to unity and σ_{ff} , ϵ_{ff} , and m_f are chosen as units of length, energy, and mass, respectively. Different solid (s) representations have been used in these simulations. The base case is a face centered cubic (fcc) lattice with cubic lattice constant $a = 2^{2/3}\sigma_{ff}$ such that the nearest-neighbor distance $d_{NN} = a/\sqrt{2} = 2^{1/6}\sigma_{ff}$, which equals the minimum-energy distance between fluid particles. Alternatively, we used a simple cubic (sc) lattice with the same d_{NN} (in this case, $a = 2^{1/6}\sigma_{ff}$). In both cases, particles are attached to their lattice positions $\vec{r}_{i,0}$ through a rigid-spring potential

$$V(r_i) = (k/2) |\vec{r}_i - \vec{r}_{i,0}|^2, \quad (2)$$

where k is the spring constant. Additionally, we introduced a LJ interaction between solid particles with $\epsilon_{ss} = C_{ss} = 1$ and $\sigma_{ss} = 1.1$ such that the distance of minimal LJ interaction is slightly larger than d_{NN} in order to facilitate thermostating. Solids constructed by these two types of forces are called type I solids. In one simulation, the solid has been modeled by using a deep potential well with $\epsilon_{ss} = 50\epsilon_{ff}$ and $\sigma_{ss} = 1$, which we call a type II

solid. Again this will lead to an fcc lattice with a nearest-neighbor distance $d_{\text{NN}} \approx 2^{1/6} \sigma_{ff}$. For all types of solids, $m_s = 5m_f$ and the Lindemann criterion [8] is fulfilled.

A spherical droplet is equilibrated and positioned near the surface using a gravitational force field. During this equilibration step the solid and drop particles are kept at a constant temperature of $kT/\epsilon = 0.8$ using a Nosé-Hoover thermostat, while the attraction between solid and drop particles is kept at zero. When the drop touches the surface, the gravitational field is turned off, the total momentum of the drop is scaled to zero, and the attraction between the solid and droplet is turned on. Only solid particles remain thermostated from here onwards. Several values of the attraction parameter between the solid and fluid particles C_{sf} have been tested. A value of 1.5 was found to lead to a terraced spreading regime. Several systems have been simulated with different numbers of particles and lattice geometries (see Table I). Our Nosé-Hoover thermostat has a constant of 0.01, and a time step of 0.004. In one case a velocity scaling thermostat was tested in order to compare with Refs. [4,5].

Figure 1 shows a typical case of terraced wetting. Initially one layer is formed close to the solid surface, then second and third layers are formed. Subsequently the third and second layers disappear, and only a monolayer remains. Snapshots from various solid lattices do not show a significant difference in the terracing of the droplet. The layering of fluids near a solid surface is in itself very usual, and well characterized experimentally, theoretically, and in molecular simulations [9]. The static side of terraced wetting is better characterized than its dynamics. Experiments [1,2] indicate clearly that the radii of the layers depend on time as \sqrt{t} .

To quantify the rate of spreading of the droplet, we have recorded the density profiles for the first layer at several time intervals. Subsequently, the radius R of the first layer at the cutoff density of 0.5, indicative of the liquid-vapor boundary, is noted at several time steps (no significant difference of the behavior of R exists among cutoff densities of 0.4, 0.5, and 0.6). Plots of R vs t in Fig. 2 clearly indicate that a reasonable fit of the data is $R(t) - R_0 = A\sqrt{t}$. The behavior of R is in agreement with experimental data [1,2].

Our simulations show that droplets consisting of 4224 and 8634 have the same \sqrt{t} dependence. Thus the spreading of a droplet of only 4224 particles is sufficient to reproduce the experimental dependence of radius on time, even though there is a huge disproportion between the longitudinal scales, which are microscopic in the simulations, and macroscopic in the experiment [3]. Similarly to our results, Yang, Koplik, and Banavar [5] found that simulations on a drop consisting of 9000 fluid particles showed the same dependence of the radius as that of a small drop of 4000 fluid particles. However, they found that R depends on time as $\sqrt{\log_{10}(t)}$ [4] for the large and small systems.

Discrepancy between our results and previous simulations [4,5] could be due to thermostating. Yang, Koplik, and Banavar thermostat the solid atoms by scaling the velocities of the atoms in the third layer of the lattice. In our simulations, thermostating by scaling the velocities or by applying a Nosé-Hoover formalism leads to the same spreading rates. Nieminen *et al.* [7,10] apply a Nosé-Hoover thermostat to atoms in the droplet, possibly inappropriate for an inhomogeneous system [6]. An additional reason for the subdiffusive regime seen in simulation could be the high volatility of the simulated droplet. Therefore, Nieminen *et al.* [7] suggested that the spreading of PDMS droplets on silicon wafers has a stronger dependence on time than the spreading of a volatile droplet of atomic fluid. This could be true if the condensate from the vapor mixes significantly with the first layer to slow down its spreading rate. However, our simulations show that the volatility of drops does not significantly weaken the spreading process. In addition, Yang, Koplik, and Banavar [5] have shown that the spreading of a nonvolatile drop of dimers had the same dependence on time as that of a volatile drop of atomic fluids.

It should be mentioned here that Yang, Koplik, and Banavar simulate an fcc lattice for which $d_{\text{NN}} = 2^{2/3} \sigma_{ff}$, which is a factor of $\sqrt{2}$ larger than in our simulations. This could be a reason for disagreement between simulations especially if fluid particles can penetrate into the solid in their case. To verify this we performed a simulation with the same lattice dimension as that of Yang, Koplik, and Banavar [4,5]. The dependence of layer

TABLE I. Summary of simulation runs. Solids are constructed with particles in a simple cubic (sc) or face centered cubic (fcc) lattice. Solid type I refers to lattices in which particles are fixed to their equilibrium positions through a rigid spring and have Lennard-Jones interactions. Solid type II refers to lattices in which particles interact only via a (strong) Lennard-Jones potential. Nosé-Hoover thermostats are indicated by NH, whereas Scaling refers to a velocity scaling scheme. The nearest-neighbor distance in the lattice d_{NN} is given in units of σ_{ff} .

Run	1	2	3	4	5	6
Lattice type	sc	fcc	fcc	fcc	fcc	fcc
No. solid particles	8978	13 254	10 086	13 254	13 254	8214
Solid interaction	I	I	I	II	I	I
Thermostat	NH	NH	NH	NH	Scaling	NH
No. fluid particles	8634	8634	4224	8634	8634	8634
$d_{\text{NN}}/\sigma_{ff}$	$2^{1/6}$	$2^{1/6}$	$2^{1/6}$	$2^{1/6}$	$2^{1/6}$	$2^{2/3}$

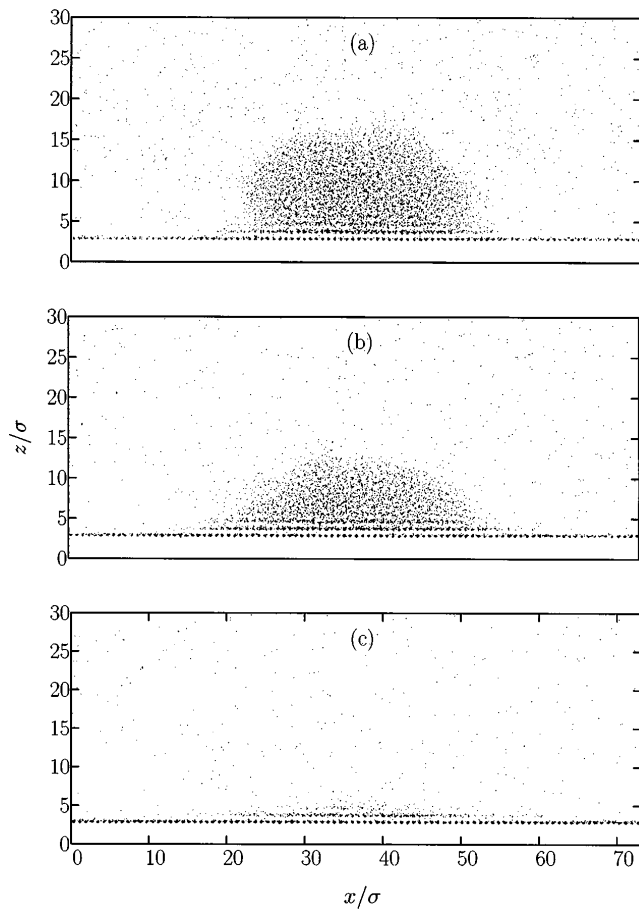


FIG. 1. Three snapshots of a droplet spreading on an fcc lattice in the terraced wetting regime (run 2): (a) $t = 44\tau$, (b) $t = 164\tau$, and (c) $t = 564\tau$, where $\tau = \sigma_{ff}\sqrt{m_f/\epsilon_{ff}}$.

radius on time is shown for the small and large lattice dimensions in Fig. 3. Clearly, one sees that for a large d_{NN} the first layer radius grows with time slower than \sqrt{t} . A snapshot of the spreading process (Fig. 4) shows that fluid

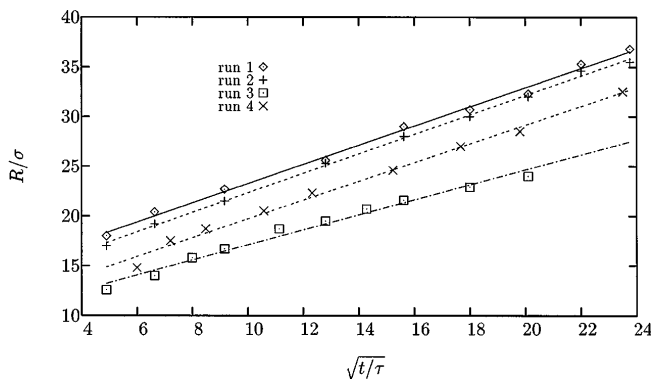


FIG. 2. Dependence of the spreading radius of the first layer of the droplet on various solids (fcc and sc), all with nearest-neighbor distances $d_{NN} = 2^{1/6}\sigma_{ff}$. Results are shown for small and large droplets consisting of, respectively, 8634 and 4224 particles. Thermostating of the solid atoms was performed using Nosé-Hoover.

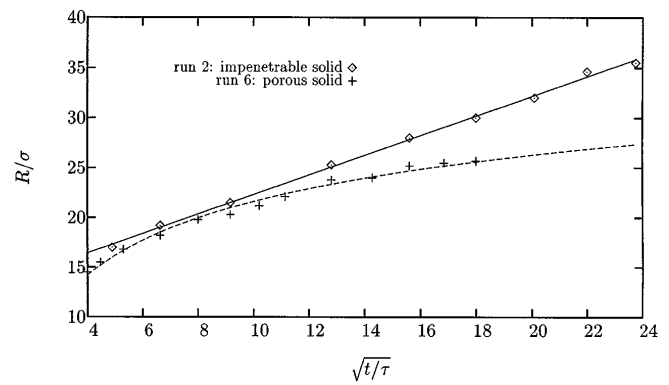


FIG. 3. Dependence of the radius of the first layer on time for a large droplet spreading on solids with nearest-neighbor distance $d_{NN} = 2^{1/6}\sigma_{ff}$ (run 2) for which the data are fitted by $R(t) - R_0 = \alpha\sqrt{t}$, and $d_{NN} = 2^{2/3}\sigma_{ff}$ (run 6) for which the data are fitted by $R(t) - R_0 \propto \sqrt{\log_{10}(t)}$. Thermostating of the solid atoms was performed using Nosé-Hoover.

particles penetrate the solid lattice if $d_{NN} = 2^{2/3}\sigma_{ff}$, and not if $d_{NN} = 2^{1/6}\sigma_{ff}$. Effectively, the dynamics simulated by Yang, Koplik, and Banavar combines spreading and penetration. This, in our view, is the most plausible reason for the subdiffusive regime found in Refs. [4,5].

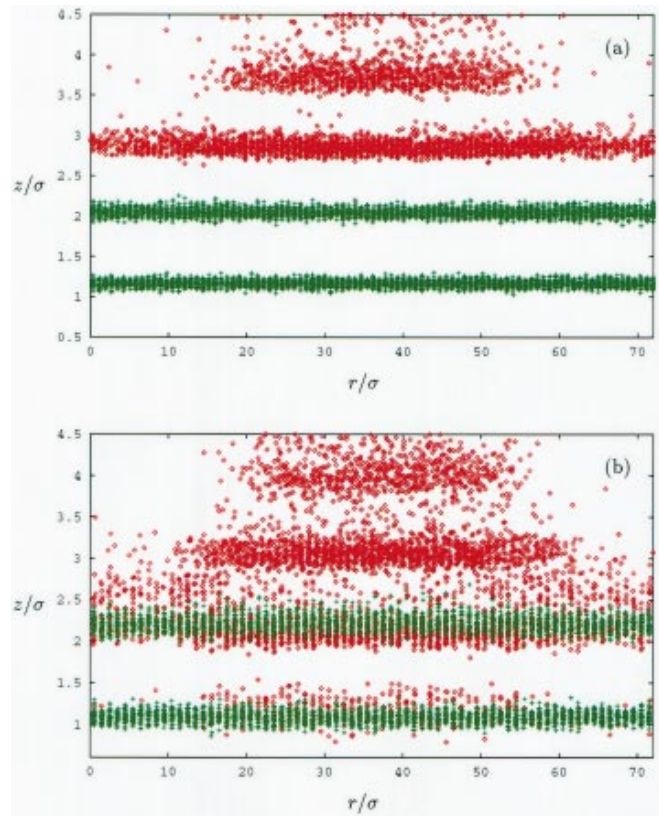


FIG. 4 (color). Upper layers of the solid (green +) and first layers of the fluid (red \diamond). In contrast to a solid with nearest-neighbor distance $d_{NN} = 2^{1/6}\sigma_{ff}$ [run 2, (a)], the solid with $d_{NN} = 2^{2/3}\sigma_{ff}$ [run 6, (b)] allows fluid particles to penetrate and therefore resembles a porous substance.

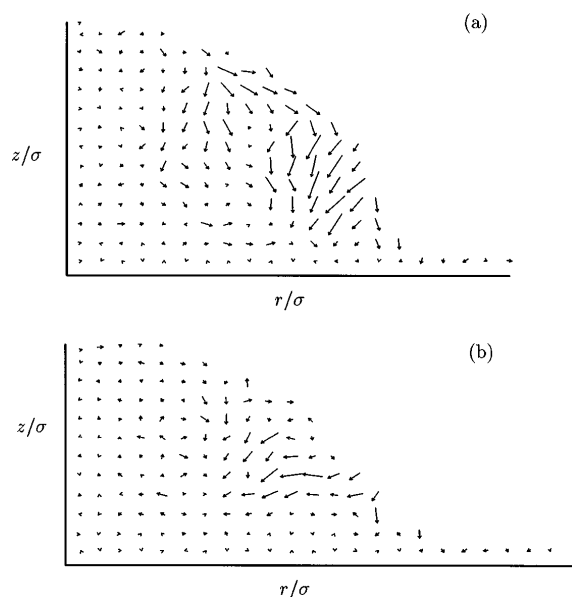


FIG. 5. Mass transfer profile within a large droplet spreading on an fcc lattice (run 2). Normal to the surface, the bin size $\Delta z = 2^{1/6}$. Tangential to the surface, the ring size $\Delta r = 2^{1/6}$. Results are shown at (a) $t = 44\tau$ and (b) $t = 84\tau$. Every profile has been averaged over 24τ .

The specific movement of particles in different regions of the droplet in the terraced spreading regime is an issue that has been raised first by de Gennes and Cazabat [11], who constructed a model that reproduces the \sqrt{t} behavior of R . This model assumes that molecules are added to layers only at the steplike edges of neighboring layers. Results from various simulations [4,5,7] have shown that the movement of molecules within the layers and between the layers does not agree with the theoretical picture. In view of the penetration of atoms in the solid lattice [4,5], we have performed some extensive analysis in the case of nonpenetration, in order to compare with theory [11]. We have calculated mass transfer profiles in various regions of the droplet, and at several stages of spreading. The results are shown in Fig. 5. One notes that at the center of the droplet there is hardly any mass transfer. Initially, when no layers are fully formed yet, mass transfer occurs only downward in the outer rings of the drop. As layers close to the solid lattice become filled, layer growth near the surface occurs only at the steplike edges of neighboring layers. A net upward interlayer or lateral intralayer mass transfer in regions slightly inside the droplet is noticed as lower layers become impenetrable for incoming particles from upper layers. This second regime confirms for the first time theoretical predictions of de Gennes and Cazabat [11,12]. Differences between earlier simulations [4,5] and theory must be due to the penetration of droplet atoms in the solid lattice. As a consequence layers adjacent to the surface become also penetrable from layers above them.

In summary, we have performed extensive molecular dynamics calculations of the spreading of a droplet of a volatile atomic fluid on a solid surface in the terraced wetting regime. Careful investigation of the effect of system size, lattice geometry, and thermostating technique shows that the radius of the first layer depends on time as \sqrt{t} . This is in agreement with experimental results [1,2]. The reason why previous molecular dynamics simulations [4,5] calculated a subdiffusive regime for layer spreading is, in our view, the penetration of fluid atoms in the solid lattice.

Two forms of mass transfer are noted in the course of spreading simulations: In the preterracing stage, mass transfer occurs only downward in the outer regions of the droplets, whereas in the partially layered stage, mass transfer occurs downward at the edges of the layers, and upwards or laterally far from the edges. Mass transfer in this stage is in agreement with theoretical predictions of de Gennes and Cazabat [11].

We thank A.M. Cazabat and A. Chesters for their comments on our manuscript, and R. Miesen for useful discussions on various simulation techniques.

Note added.—After submission of this Letter, we learned about a recent preprint of D’Ortona *et al.* [Phys. Rev. E **53**, 562 (1996)] in which the spreading of *chainlike* molecules is studied. Their results for the mass transfer are similar to the ones found here for a simple atomic fluid. We thank Professor J. De Coninck for sending this result prior to publication.

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