

Molecular Dynamics of Drop Spreading on a Solid Surface

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We have studied the spreading of liquid drops on a solid surface by molecular-dynamics simulations of Lennard-Jones systems of liquid, vapor, and solid. As the attraction between liquid and solid increases we observe a smooth transition from partial wetting to terraced wetting, with distinct molecular layers spreading with different velocities. In the terraced case the layers are ordered but not solid, with substantial molecular diffusion both within and between layers, and a growth rate that disagrees with experiments with nonvolatile liquids as well as recent calculations.

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The spreading of liquids on solid surfaces has lately received considerable attention both theoretically and experimentally [1-5]. The fine structure in the thin film often observed at the edge of the advancing liquid is usually discussed in terms of precursor films driven by van der Waals forces. Such an approach is successful for films much thicker than the size of their constituent molecules, which can be treated hydrodynamically. However, different behavior is seen in ultrathin films, whose thickness is only several molecular diameters [6]. Instead of a smoothly varying continuum, experiments find that the spreading liquid consists of distinct monomolecular layers which advance across the solid with different velocities, over distances of millimeters. Such films are too thin to be described by lubrication equations, and alternative models based on Langevin dynamics [7] or two-dimensional liquid layers [8] have been introduced. The experiments are interferometric in nature, and have much finer resolution normal to the layers than within them, and many open questions remain. We have been motivated thereby to conduct molecular-dynamics (MD) simulations of spreading. While we are restricted to small drops, whose initial radius is only about 10 atomic sizes, our results complement the experiments by providing detailed three-dimensional information about the spreading dynamics.

We consider a molecular system described by Lennard-Jones interaction potentials of the form

$$V(r) = \frac{\beta}{r^6} \left(\frac{1}{r^6} - \alpha \right),$$

where the coefficients are related to the conventional [9] Lennard-Jones energy and distance parameters ϵ and σ via $\alpha = \sigma^{-6}$ and $\beta = 4\epsilon\sigma^{12}$, respectively. The fluid subsystem is used as reference, with all distances expressed in terms of $\sigma \equiv \sigma_{ff}$, mass in terms of m_f , and times in terms of $\tau \equiv (m_f \sigma_{ff}^2 / \epsilon_{ff})^{1/2}$. The parameter $\alpha \equiv \alpha_{fs}$, the strength of the attraction between fluid and solid molecules, is varied from 1.0 to 1.4 to produce different wetting regimes, and ϵ_{ff} is kept at 1. For the solid-solid interac-

tions we choose $\epsilon_{ss} = 50$ and $\sigma_{ss} = 2^{-1/6}d$, where $d = \sqrt{2}$ is the lattice constant, so that the equilibrium position of the solid particles is also the minimum of the potential. The mass of the solid particles is $5m_f$. The potentials of fluid-fluid interactions and fluid-solid interactions are cut off at $2.5\sigma_{ff}$ and $2.5\sigma_{fs}$, respectively, and the potential of solid-solid interactions is cut off at $1.8\sigma_{ss}$.

In the simulations, 4000 fluid particles are confined in a cube of side $L = 60\sigma$. The boundaries at $z = 0$ and $z = L$ are replaced by a solid wall made of five layers of fcc solid, totaling 9000 molecules, with the (100) surface exposed to the fluid. The solid is thick enough to prevent a direct interaction between the fluid particles on either side, and the remaining directions have periodic boundary conditions imposed. The equations of motion are integrated using the Beeman algorithm [9], with a time step 0.005τ . The entire system is equilibrated at $T = 0.7$ with $\alpha = 0$ and $\beta_{fs} = 1$. The drop has then a roughly spherical shape of radius 10σ , surrounded by a cloud of vapor. The center of the drop is gradually moved to 16σ above the solid surface by time $t = 35$, whereupon the fluid-solid interactions attract the drop, leading to contact and subsequent spreading. The middle layer of the solid is kept at constant temperature $T = 0.7$ by rescaling of the velocities of the particles in that layer, in analogy to a laboratory experiment where the solid substrate is kept at a constant temperature.

We studied a range of solid-liquid interaction strengths from $\alpha = 1.0$ to 1.4, in steps of 0.1. For values $\alpha \leq 1.1$ we observed partial wetting, in which the drop reached a stable shape, while for $\alpha \geq 1.2$ the drop continues to spread up to the boundaries of the simulation box. In Figs. 1(a)-1(c) we illustrate the three types of behavior seen by showing the final states for $\alpha = 1.1$, 1.2, and 1.4, respectively. The points in the figures are the centers of the fluid molecules, where the three-dimensional system has been projected onto the two-dimensional surface of the box. Note that the vapor density decreases as α increases, due to the condensation of vapor molecules onto the solid wall, and in Fig. 1(c) a condensed layer of regu-

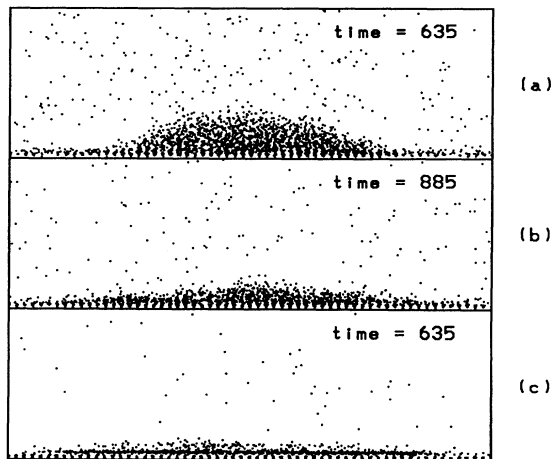


FIG. 1. The final states of spreading observed for (a) $\alpha=1.1$ at $t=635\tau$, (b) $\alpha=1.2$ at $t=885\tau$, and (c) $\alpha=1.4$ at $t=635\tau$. The points represent the centers of molecules in three dimensions, projected onto the x - z plane. Only molecules with $0 < z < 20$ are shown.

larly spaced molecules, commensurate with the solid structure, lies on the surface. There *appear* to be fewer molecules as α increases, but this illusion is caused by the enhanced ordering in the fluid. In Fig. 1(a) a true steady state is reached, with a well-defined contact angle. In contrast, in Fig. 1(b) the spreading is slow but does not terminate. Even at $t=885$ the height of the drop is still decreasing while the particle "reservoir" in the bulk of the drop is nearly depleted—this case corresponds to complete wetting. In Fig. 1(c), the spreading is complete, and the drop evolves into two distinct molecular layers; we consider this case in detail below.

One difference between the present simulations and laboratory experiments is that the solid-liquid interaction cuts off at a fixed distance, whereas a realistic long-range van der Waals potential, arising from a superposition of many layers of r^{-6} interaction, behaves approximately as r^{-3} [10]. In order to check that the partial wetting is not due to this cutoff, we ran a simulation with an extended fluid-solid interaction. This extra potential had the form $k/(z-z_0)^3$ for z (the coordinate normal to the solid surface) greater than the cutoff, with the constants k and r_0 determined by the continuity of the potential there. We compared the final states with and without this extended potential for $\alpha=1.0$ and did not see any qualitative changes.

The time evolution of the spreading drop is most interesting in the terraced case $\alpha=1.4$ [11], and Fig. 2 shows the snapshots of the profile at various stages, with the final state given in Fig. 1(c). At $t=140$, several liquid layers have formed, rather more prominently than in the $\alpha=1.1$ case, say, but layering in liquids near solid surfaces is not in itself unusual [10]. At $t=240$, however, it is evident that the first two layers spread faster than

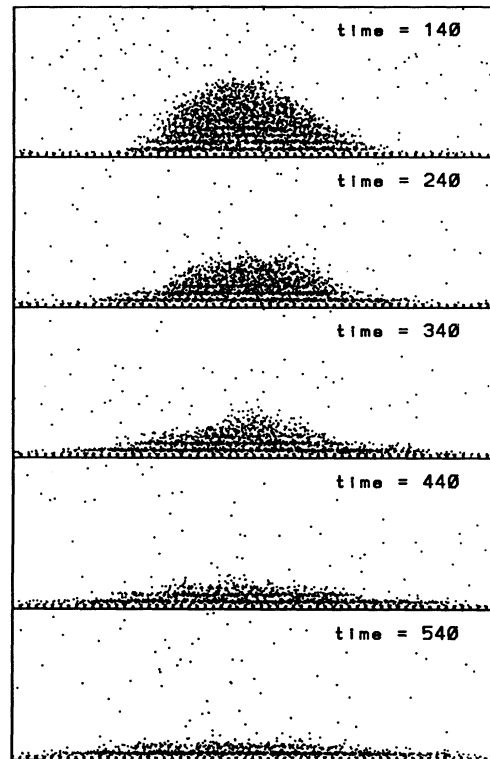


FIG. 2. Time evolution of complete terraced wetting at $\alpha=1.4$. The format is as in Fig. 1.

the bulk of the drop, and that first layer spreads faster than the second. Furthermore, a clear steplike structure has formed. At $t=340$ the spreading of the first layer continues, while the motion of the second layer has nearly come to a stop. At later times $t=440$ and 540 the first layer continues to move outward while depleting the central bulk of the drop.

The structures of the first and second layers in terraced spreading are quite strongly ordered. Figures 3(a) and 3(b) show typical x - y projections of the first and second layers for $\alpha=1.4$. The particles form a defective hexagonal lattice, with stronger ordering in the first layer than in the second, and within each layer the inner part is more ordered than the outer part. As the boundary of the layer moves outward, vacancies are created both in the interior and at the edge. When such plots are examined as a function of time, one sees that the vacancies in the first layer provide the likely sites for the particles to move in from above. Measurements of the in-plane radial distribution function for times after 250 show four clear peaks in the first layer and three in the second, the peaks having a half-width of about 0.3σ .

For comparison with other work, it is useful to quantify the rate of spreading of the drop. Figure 4 shows the evolution of the average radii of the first and second layers as a function of time. Evidently, a reasonable fit is $R^2(t)$

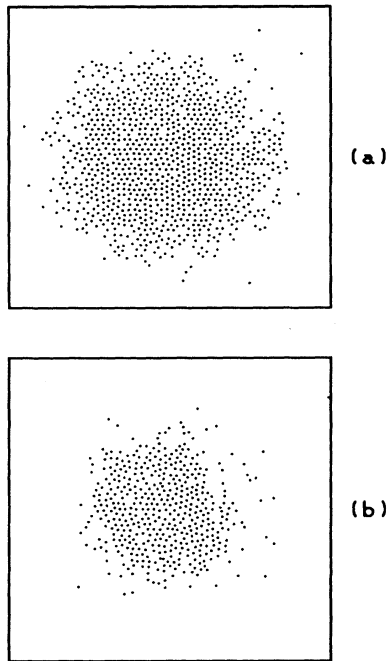


FIG. 3. x - y positions of (a) the first layer and (b) the second layer at $t = 340\tau$ for $\alpha = 1.4$.

$= C \log_{10} t + D$, with $C \approx 430$ and 272 for the first and second layers, respectively. Similar behavior is found for the other values of α where complete wetting occurs, with the same functional form and different values for the constants. This relation disagrees with the $R^2 \sim t$ behavior found in laboratory experiments with nonvolatile liquids [4,6] ("dry spreading"). One might suspect that the discrepancy is related to the fact that the condensation of vapor ahead of the drop reduces the degree of attraction of liquid to the surface. On the other hand, in this case the condensed vapor forms a distinct layer of fairly regular lattice, clearly separated from the spreading liquid,

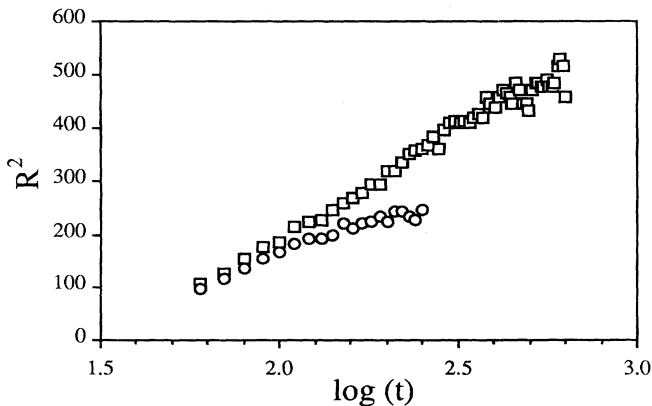


FIG. 4. Dependence of drop radius on time for $\alpha = 1.4$, for the first (squares) and second (circles) layers.

whereas only when α is smaller does the condensate mix with the drop. Another possible source of disagreement is the comparatively small number of molecules in the simulation. A laboratory drop has an enormous reservoir of molecules in its center available for continued spreading, whereas we have nearly exhausted the supply. Note, however, that the eventual leveling off of R^2 for the second layer resembles a simple finite-size effect, and suggests that a larger drop would continue to spread at the same rate. Indeed, a single run on a larger system, with 9000 fluid molecules and a maximum radius of 30, gives results consistent with those described above [11].

One key advantage of MD simulations is the ability to study the molecular motion in detail, and to this end we have examined the intralayer and interlayer movement of particles separately. Since the spreading is relatively slow, we considered a sliding time window of interval 50τ , averaging over configurations between $t = 336$ and 435 . We have obtained the vertical probability distribution function $P(\Delta z)$ for displacements normal to the solid, as well as the radial distribution $P(\Delta r)$ for motion parallel to the surface, separately for the first and second layers of the spreading drop and for various initial radial intervals. To be precise, we define the first layer as $0.8 < z < 1.5$ and the second as $1.5 < z < 2.5$, and in each layer we have three regions: I, $0 < r < 10$; II, $10 < r$

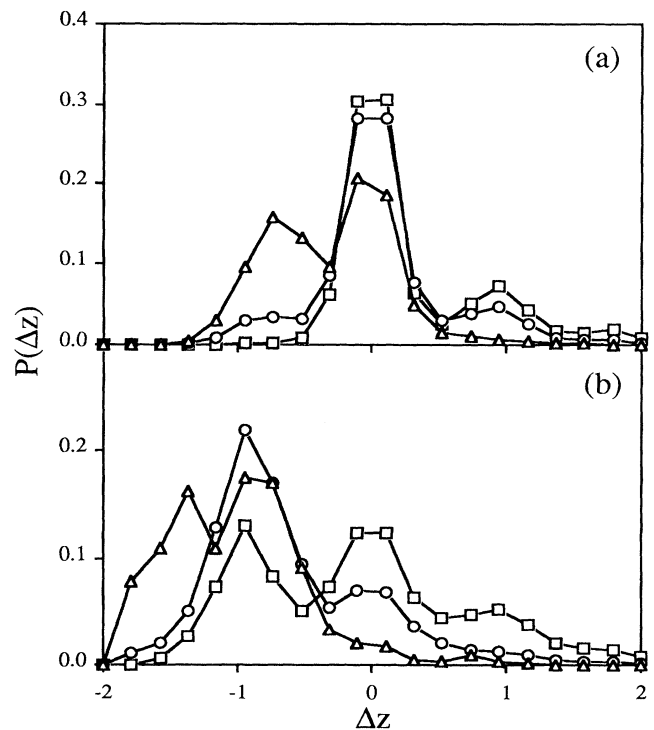


FIG. 5. Vertical distribution function $P(\Delta z)$ for (a) the first layer and (b) the second layer. The squares, circles, and triangles represent radial regions I, II, and III, respectively, as specified in the text.

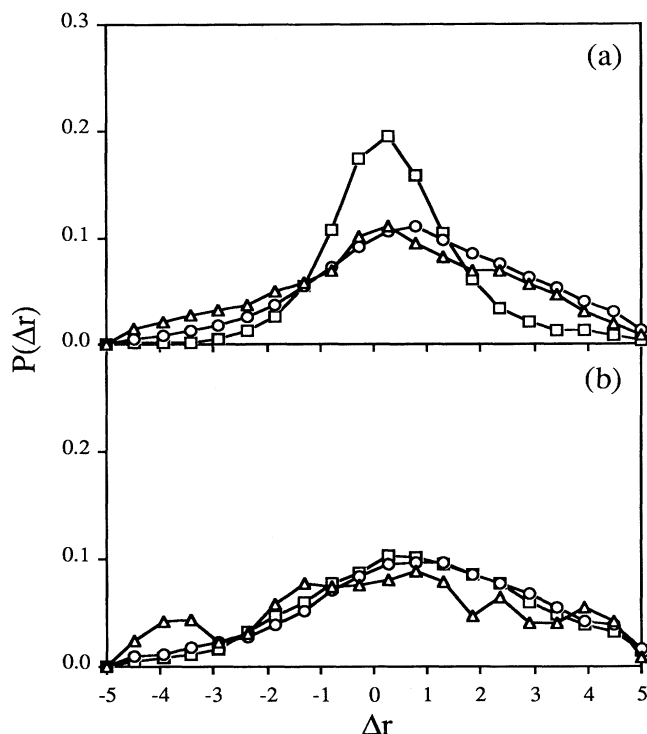


FIG. 6. Radial distribution function $P(\Delta r)$, in the same format as Fig. 5.

< 20 ; and III, $20 < r < 30$, where $r=0$ corresponds to the center of mass of the layer. Note that the vapor which condensed on the solid surface before the drop spread is rather static and has *not* been included in this analysis.

The distribution of vertical displacements for the first layer is given in Fig. 5(a); we see that for both inner regions I and II the principal peak at $\Delta z=0$ indicates that these molecules tend to stay in the first layer, while the secondary peak at $\Delta z=1$ indicates some probability to jump up to the second layer. In contrast, molecules in outer region III are quite likely to move closer to the solid. In Fig. 5(b) for the second layer, the peak at $\Delta z=-1$ indicates that the principal tendency is to move downwards to the first layer. This tendency decreases as one moves inwards from the outer edge of the layer, so that the inner core is somewhat persistent. Figures 6(a) and 6(b) give the corresponding radial distributions for the first and second layers, respectively. The inner ring of the first layer has a peak of unit width favoring small radial displacements, whereas the molecules in regions II and III, as well as those in the second layer, have rather broad distributions skewed towards positive Δr . The general conclusion here is that, except for perhaps the inner

ring of the first layer, the spreading liquid is not at all rigid or impenetrable.

To conclude, we have carried out systematic molecular-dynamics studies of drop spreading on a solid surface. We observe that fairly modest variations in the strength of the solid-liquid attraction potential lead to qualitatively different wetting regimes, each with a laboratory counterpart. We have focused on the novel terraced spreading case, where our results for the rate of spreading differ from experiment [6] for reasons which are perhaps related to the "dryness" of the solid, or to the size of the simulated system. These results for $R^2(t)$ are also in disagreement with theoretical models of ultrathin layers. One analysis [7] is based on a solid-on-solid-like model with thermal noise and predicts $R^2(t) \sim t \log t$, but there is no detailed relation between the model and the system. Another analysis [8], which yields $R^2(t) \sim t$ as in laboratory experiment, assumes that molecules are added to layers only at the steplike edges of adjoining layers. In the systems studied here, however, substantial molecular diffusion is observed throughout the layers and the theory is inapplicable. A theoretical understanding of terraced spreading remains to be found.

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