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WETTING AND SPREADING AT THE MOLECULAR SCALE

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ABSTRACT

We have studied the microscopic aspects of the spreading of liquid drops on a solid surface by molecular dynamics simulations of coexisting three-phase Lennard-Jones systems of liquid, vapor and solid. We consider both spherically symmetric atoms and chain-like molecules, and a range of interaction strengths. As the attraction between liquid and solid increases we observe a smooth transition in spreading regimes, from partial to complete to terraced wetting. In the terraced case, where distinct monomolecular layers spread with different velocities, the layers are ordered but not solid, with qualitative behavior resembling recent experimental findings, but with interesting differences in the spreading *rate*.

INTRODUCTION

The spreading of liquids on solid surfaces has lately received considerable attention, due to its crucial role in materials processing and its ubiquity in zero-gravity environments, as well as the fascinating scientific issues which arise. Wetting has long been studied both theoretically and experimentally [1-3], and many features are well understood within the context of the continuum equations augmented with van der Waals forces. However a number of significant microscopic issues are unresolved, such as the precise boundary condition appropriate to a moving contact line and the dynamics of contact angle hysteresis, and for such problems molecular scale calculations can provide invaluable information. Previous work has examined the contact line problem [4], showing that the no-slip boundary condition breaks down in regions of unusually high stress, and several calculations in progress address the effects of heterogeneities and hysteresis, but here we will consider the somewhat related ill-understood phenomenon of "terraced wetting." It has been observed, using interferometric techniques [5], that certain polymeric liquids spread on atomically smooth substrates in the form of distinct monomolecular layers of nanometer thickness, which extend laterally over millimeter distances to completely wet the solid. Such films are too thin for a lubrication analysis to be applicable, and only heuristic alternative models based on Langevin dynamics or two-dimensional liquid layers are available. This situation motivated us [6] to conduct molecular dynamics (MD) simulations of spreading, based on the atomic scale motion of the constituent atoms. 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.

SIMULATION METHOD

In an MD computer simulation [7], one places atoms in a region of space with random initial velocities corresponding to the desired temperature, and integrates Newton's equations of motion. The force on any one atom is due to interactions with the others, and we consider Lennard-Jones 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 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 $\sigma \equiv \sigma_{\text{ff}}$, mass in terms of m_{f} , and times in terms of $\tau \equiv (m_{\text{f}}\sigma_{\text{ff}}^2/\epsilon_{\text{ff}})^{1/2}$. The parameter $\alpha \equiv \alpha_{\text{fs}}$, 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 interactions we choose $\epsilon_{\text{ss}} = 50$ and $\sigma_{\text{ss}} = 2^{-1/6}d$, 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 $5m_{\text{f}}$. The potentials of fluid-fluid interactions and fluid-solid interactions are cut off at $2.5\sigma_{\text{ff}}$ and $2.5\sigma_{\text{fs}}$ respectively, and the potential of solid-solid interactions is cut off at $1.8\sigma_{\text{ss}}$.

The "computational protocol" in our simulations is to consider 4000 fluid particles confined to a cube of side $L = 60\sigma$, with the boundaries at $z = 0$ and $z = L$ are replaced by a solid wall made of 5 layers of fcc solid, totalling 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 [7], with a time step 0.005τ . The entire system is equilibrated at $T = 0.7$ with $\alpha = 0$ and $\beta_{\text{fs}} = 1$. 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. The computation ends when the drop attains a steady state, or reaches the edges of the simulation box.

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} [8]. 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.

We will also consider simple polyatomic molecules, made by introducing an attractive confining potential between adjoining atoms along a chain, e.g., $V_{12}(r) \sim r^{+12} + r^{-6}$. If non-adjoining atoms retain a Lennard-Jones attraction, the resulting molecule is compact rather

than elongated, while appropriate repulsive or orientational potentials may be introduced to maintain a long chain. At the expense of further computational effort, other MD practitioners often work with realistic specific materials.

MONATOMIC FLUIDS

First we consider the spreading of a simple monatomic fluid, such as Argon, where the Lennard-Jones potential above is qualitatively valid. 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 Fig. 1(a,b,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 regularly 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.

The time evolution of a terraced spreading drop is shown in Fig. 2, in the form of 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 [8]. At $t = 240$ however, it is evident that the first two layers spread faster than the bulk of the drop, and that the first layer spreads faster than the second. Furthermore, a clear step-like 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. The particles form a defective hexagonal lattice, with stronger ordering in the first layer than 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. Although ordered, the layers are by no means solid: since an MD simulation provides detailed information on the molecular motion, we have studied the intra-layer and inter-layer movement of particles in detail. Histograms of the horizontal and vertical displacements have a generally diffusive shape, with the trend that particles near the center of the first layer are most constrained, while the outer parts of the drop move most readily. In contrast to some theoretical models of terraced spreading, the conclusion here is that, except for perhaps the inner ring of the first layer, the liquid is not at all rigid or impenetrable.

For comparison with experiment, it is useful to quantify the rate of spreading of the drop. Fig. 3 shows the evolution of the average radii of the first and second layers as a function of time. Evidently, a reasonable fit is $R^2(t) = C \log t + D$, 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 non-volatile liquids [5] (“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, 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.

CHAIN MOLECULES

To further explore the differences between simulation and experiment in the growth rate of the layers, we have considered fluids made of more complicated molecules, by the simple device of combining Lennard–Jones atoms into chains. If the above simulations are repeated with diatomic dumbbell molecules, we see no significant difference in the spreading behavior – at large enough solid-liquid attraction the spreading is again in the form of sharp layers, whose growth rate is still $R^2 \sim \log t$. In this case however, the liquid’s volatility is considerably reduced so that the spreading is “dry”, without an adsorbed vapor layer on the substrate. For longer chains, however, the results do change in the direction of experiment. In work in progress [6], we have studied the spreading of chains of length 8; note that because of the Lennard–Jones attraction between non-adjacent atoms, the molecules are compact rather than elongated, and not at all entangled. Our preliminary results for this system give terraced spreading with a growth rate $R^2 \sim t^{0.8}$. At the extreme, other workers [9] have conducted MD simulations in which the substrate is a plane whose potential varies only with the normal distance, which can be thought of as the limit of molecule (or monomer) size much larger than the solid lattice spacing. Here one finds diffusive behavior, $R^2 \sim t$, in agreement with laboratory observation. We are now studying the case of length-16 chains, to elucidate the crossover behavior.

An intuitive picture of the results is as follows. The strong solid–liquid interaction draws fluid molecules to the solid, and the free energy is minimized by an ordered structure with well-defined layers, in which as many fluid atoms as possible are in positions favored by the periodic lattice potential. The temperature is still above melting, so the liquid atoms can diffuse between and within the layers, and layer growth involves vacancy creation and filling. If the fluid molecules are small, it is easy for most or all of their constituent atoms to find the preferred sites, and the growth is slow and sub-diffusive, in analogy to diffusion in the presence of traps. When the molecule size increases, steric and thermal effects make

it difficult for a significant fraction of the atoms to simultaneously be in preferred sites, so that the pinning effect is less effective and the growth is faster.

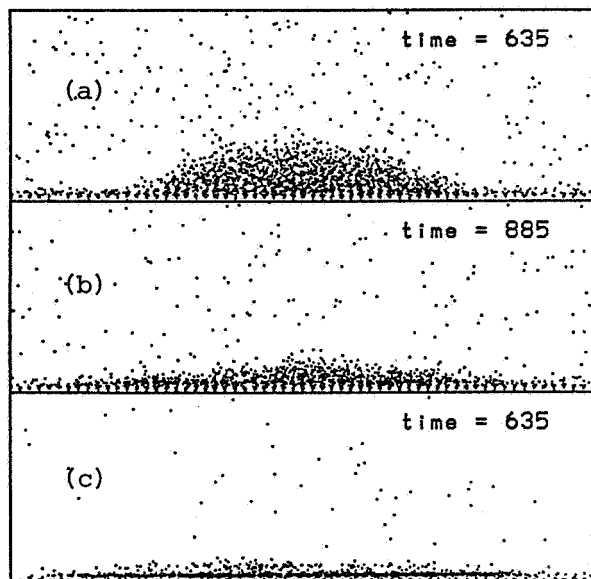
CONCLUSIONS

In summary, 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 give the internal dynamical structure for this spreading regime, and where we have shown that the rate of spreading depends on the size and nature of the fluid molecules.

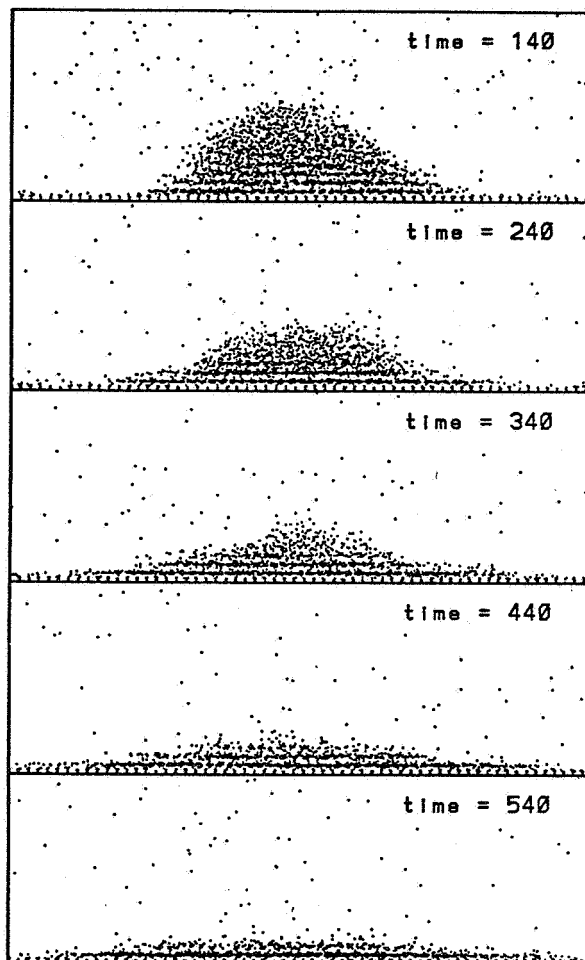
More generally, we have indicated how molecular simulation can complement theory and experiment, by providing otherwise unavailable small-scale information about the internal dynamics of a system, by providing "clean" results free of theoretical bias of laboratory contamination, and by allowing one to systematically vary significant parameters in a many-body problem and compute the consequences. In other related work in progress, we are exploring the relation between the presence of structural and chemical surface heterogeneity and contact line hysteresis. Here again, we can control the substrate's properties in complete detail, vary the fluid both in molecular size and in its Newtonian vs. non-Newtonian behavior, and observe the resulting dynamics at high resolution. We hope to help clarify these important issues in wetting as well.

REFERENCES

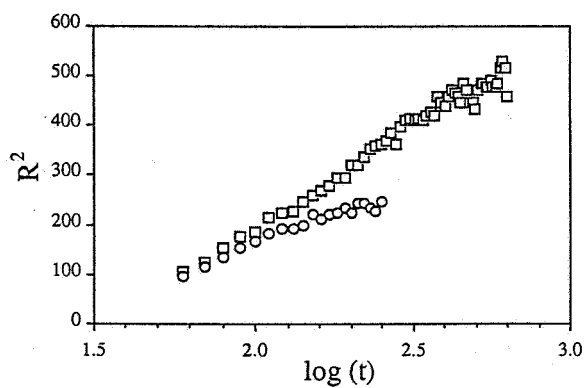
1. E. B. Dussan V., *Ann. Rev. Fluid Mech.* **11**, 371 (1979).
2. P. G. de Gennes, *Rev. Mod. Phys.* **57**, 827 (1985).
3. L. Leger and J. F. Joanny, *Rep. Prog. Phys.* **55**, 431 (1992).
4. J. Koplik, J. R. Banavar and J. F. Willemsen, *Phys. Fluids A* **1**, 784 (1989); P. A. Thompson and M. O. Robbins, *Phys. Rev. Lett.* **63**, 766 (1989).
5. F. Heslot, N. Fraysse and A. M. Cazabat, *Nature* **338**, 640 (1989); N. Fraysse et al., *J. Colloid Int. Sci.* **158**, 27 (1993).
6. J.-x. Yang, J. Koplik and J. R. Banavar, *Phys. Rev. Lett* **67**, 3539 (1991); *Phys. Rev. A* **46**, 7738 (1992); J. De Coninck, U. D'Ortona, J. Koplik and J. R. Banavar, in preparation (1994).
7. M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids*, Oxford (1987); see also J. Koplik and J. R. Banavar, *Ann. Rev. Fluid Mech.* **27**, in press (1995).
8. J. N. Israelachvili, *Intermolecular and Surface Forces*, Academic, 1985.
9. J. A. Niemenen, D. B. Abraham, M. Karttunen and K. Kaski, *Phys. Rev. Lett.* **69**, 124 (1992).



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 front plane.



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



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