

Wetting Hysteresis at the Molecular Scale

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The motion of a fluid-fluid-solid contact line on a rough surface is known to display hysteresis in the contact angle versus velocity relationship. To understand the phenomenon at the microscopic level, we have conducted molecular dynamics simulations of a Wilhelmy plate experiment in which a solid surface is dipped into a liquid bath, and the force-velocity characteristics are measured. We observe a systematic variation of force and contact angle with velocity, which is single valued for the case of an atomically smooth solid surface. If the surface is microscopically rough, however, we find a very irregular local interface shape, and an open hysteresis loop corresponding to a history-dependent force. [S0031-9007(97)02455-1]

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The contact angle at which a meniscus separating two fluids meets a solid surface is an important quantity for both static and moving fluid interfaces. The static angle determines the shape of drops, while the dynamic contact angle of a moving interface controls the time evolution of an interface. In both cases the angle is not unique, a phenomenon referred to as contact angle hysteresis [1,2]. In the static case, Young's equation relates the contact angle to the various interfacial free energies in the problem, and ostensibly implies a unique angle for a given solid-liquid-liquid system. In fact, one observes that a *range* of static angles is possible. The origin of this effect is believed to be surface heterogeneity, which can be either structural (a nonplanar shape at mesoscopic lengths greater than atomic size) or chemical (a fluctuating local variation in wetting properties). In this situation, even a unique microscopic or intrinsic angle on a fluctuating surface may give a range of apparent macroscopic angles. In the dynamic case, a second phenomenon arises—the observed contact angle varies with the velocity of the meniscus. Here, in addition to surface effects, the viscous stress resulting from fluid motion will certainly affect the interfacial shape away from the solid.

Although contact angle hysteresis has been well documented in the laboratory, and is a common ingredient in recent hydrodynamic calculations, its origins entail the difficult problem of the interplay of fluid dynamics and microscopic surface effects. In terms of quantitative calculations, several authors have considered the possible static interfacial configurations resulting from model surface heterogeneities. The latter have ranged from a 2D sinusoidal variation in the position of a solid surface [3] to a more realistic periodic pattern of wettability variation on a solid plate [4]. In the latter case, Schwartz and Garoff find multiple minima in the free energy, deducing that the meniscus motion consists of alternating stick

and jump events. Analytic time-dependent calculations of hysteresis have considered in detail only the effects of a localized region of different wettability [5], using various approximations, and with further statistical arguments required for the multiple-defect behavior. Molecular dynamics (MD) simulations aimed at the moving contact line singularity question [6,7] observed a systematic variation of contact angle with interface velocity, but have considered only the steady state behavior at a single velocity, and heretofore only molecularly smooth surfaces.

In this Letter we report on MD simulations of a Wilhelmy plate experiment in which hysteresis is the focus. The Wilhelmy configuration of a plate dipped into a bath at fixed velocity directly gives the force as a function of plate velocity. In this procedure, a direct measurement of angle is not needed, although the force could be converted to an apparent angle, which can be correlated with observation. The advantage of studying the force is that angles are difficult to observe directly in the laboratory at short distances from the solid, and difficult to quantify in molecular simulations due to small-system fluctuations. We consider structural heterogeneity only, and solid surfaces which are either atomically smooth, periodically rough, or randomly rough. A laboratory experiment similar to these simulations has been carried out by Di Meglio [8], but does not examine the microscopic configurations, and does not consider a hysteresis *loop*.

The computational procedure in the present simulations is quite similar to that used previously in MD studies of wetting processes [6,7,9]. We wish the atoms to be as simple as possible so that typical correlation lengths are small compared to the size of the whole system, and continuum behavior may be expected. A soft-sphere atomic fluid with Lennard-Jones potentials is then optimal, but unfortunately leads to a rather diffuse interface [10], whose contact angle is difficult to establish.

The interface may be sharpened up while retaining a monatomic fluid by considering the relative displacement of two immiscible viscous liquids, as in [6,7]. Since we are interested in fluid behavior near a solid surface, it is important to treat the solid as a collection of atoms. Surface roughness is straightforward to implement.

The interaction between atoms is a two-body potential of generalized Lennard-Jones form, $V_{ij}(r) = 4\epsilon[(r/\sigma)^{-12} - c_{ij}(r/\sigma)^{-6}]$, where ϵ and σ are energy and length scales, respectively. If m is the (common) atomic mass of the fluids, the appropriate time scale is $\tau = \sigma\sqrt{m/\epsilon}$, and all quantities discussed below are nondimensionalized using $\{\sigma, \tau, \epsilon\}$. The indices i, j label the atomic species, fluid-1, fluid-2, confining wall (W), and plate (P), and the coefficient matrix (c_{ij}) is chosen as follows. Between any two atoms of the same species, we use the standard interaction strength, $c_{ii} = 1$ for all i . Atoms of different immiscible fluids should have a weaker attraction, and we choose $c_{12} = 0$. The precise value controls the interfacial width, but we have not explored other choices. The fluid-plate interaction controls the wetting properties, and we choose the lower fluid to preferentially wet the plate, $c_{1P} = 0.75$ and $c_{2P} = 0.5$. The bottom wall of the vessel serves only to confine the fluid, and we take $c_{1W} = c_{2W} = c_{PW} = 0$. The r^{-12} term provides a strong short-distance repulsion to prevent overlap of the atoms, and we simply use the standard coefficient.

A snapshot of a typical simulated system is shown in Fig. 1. The system is fully three dimensional but shown in a projected view for clarity. The two fluids have 11 760 atoms each and are placed in a rectangular region with a solid plate running vertically down the center, straddling the interface. On all four vertical sides of the container, periodic boundary conditions are used. The plate is periodic in the vertical direction as well as the

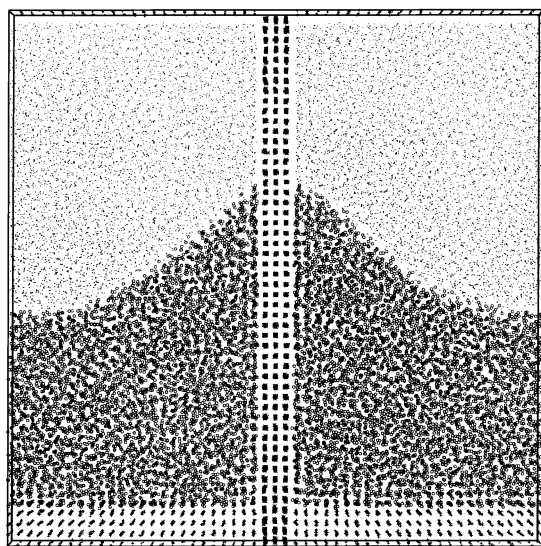


FIG. 1. Snapshot of a typical simulation: smooth-plate case with 27 040 atoms after 1800τ at $v = 0.07\sigma/\tau$.

direction normal to the figure, so as to allow a steady state to be established when it moves. At the top and bottom of the container there are solid walls, which prevent the fluids from simply translating along with the plate when it moves up and down. Initially, the fluid atoms are placed on lattice sites with density 0.8 and given a random initial velocity chosen from a Boltzmann distribution at temperature $T = 0.8$. After equilibration, the atomic positions become disordered, although one sees some layering near the solid. The solid atoms are localized for all times on an approximate crystal structure by tethering them to the sites of a regular lattice by linear springs.

Motion is produced by translating the lattice of plate tether sites vertically at a fixed velocity. The tethers then drag the plate atoms, and the plate atoms drag the fluid with them. During the simulation we record the atomic positions, from which the contact angle may be estimated, and the force on the plate—more precisely, the net force exerted by the fluid atoms on the plate atoms. In principle, the angle θ and the force F are related by $F = 2W\gamma \cos \theta - F_V$, where W is the plate width, γ is the surface tension (the 2 comes from the two sides of the plate), and F_V is the viscous drag exerted by the fluid on the plate, and the angle may be inferred from the force. In practice the force measurement is the most reliable—less susceptible to statistical fluctuations, while the angle is ambiguous, particularly in the rough case. We have also measured the local velocity and stress fields and F_V , but at the velocities considered here, thermal noise dominates and little information is present. We presume that the viscous drag on the plate makes a significant contribution to the force, but have not been able to obtain a reliable numerical estimate. One does, however, observe fluid slip at the contact line, as in [6,7]. Heat is generated due to the flow, and a thermostat is required; at low velocities it suffices to equilibrate the plate atoms (by kinetic energy rescaling), but at a higher velocity the fluid atoms are equilibrated as well. The equilibration is *local*, however, with the velocities of atoms in a small sampling bin rescaled about the average velocity in that bin, so that the average velocity field is unchanged. To study the force or contact angle as a function of velocity, a small positive plate velocity is applied and the system proceeds at this velocity until a steady state is reached, and the force averaged over an interval of typically 100τ . The velocity is then increased until a new steady state is reached. As the plate velocity increases, the fluid-fluid interface becomes increasingly distorted and eventually hits the top wall. This value is discarded, and the velocity is now *decreased* systematically until at large negative values the interface hits the bottom wall. This value is again discarded, and the velocity is gradually increased back to zero.

First we consider an atomically smooth plate. The resulting F - v plot in Fig. 2 is, within statistical fluctuations, a simple curve with a single value of force depending only on the current velocity and not on the system's history. (Note that when the plate velocity is upwards the resisting

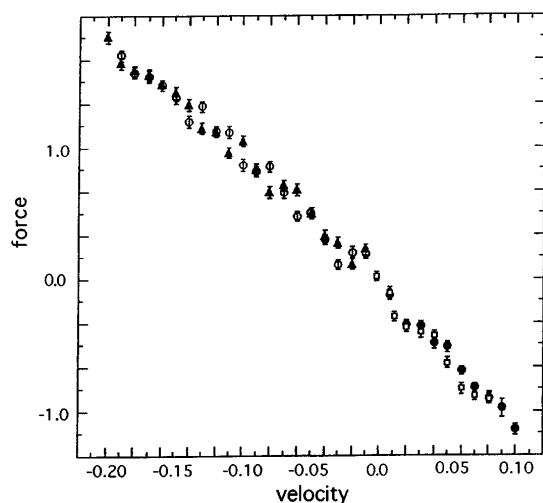


FIG. 2. Force vs velocity for the smooth plate: variation of the force (arbitrary units) exerted on the plate by the fluids as a function of the pulling velocity of the plate. The plate starts at rest, then the velocity increases to 0.1 (open markers), decreases to -0.2 (filled markers), then increases back to 0. The error bars are obtained by dividing the averaging interval into 10 subintervals.

force due to the fluids is downwards. The velocity range is asymmetric because the interface is asymmetric, concave upwards, and hits the top wall sooner on the upward cycle than it hits the bottom wall on the downward cycle.) The change in the contact angle itself at least qualitatively follows the same trend: Figure 3 gives snapshots of the three-phase region for various velocities. Evidently, the microscopic contact angle varies with velocity, in contrast to assumptions sometimes made in theoretical analyses. It is nontrivial to assign a numerical value to the contact angle because of the fluctuations in the interface position itself at a given speed, as well as the change in shape of the interface with distance from the contact line. Previous work [11] has addressed the latter issue, at least, and further work on the analysis of the angle versus velocity relationship and the interfacial shape is in progress. In this simulation, the Reynolds number based on the plate velocity and half-width of the cell is at maximum speed 1.2, while the capillary number extends up to 2.1. The variation of contact angle with speed observed here, a difference between *advancing* and *receding* angle, is often called contact angle hysteresis, but here there is no dependence on the history of the motion.

Next we consider two types of *rough* plate, obtained by displacing groups of solid atoms outward from their ideal-lattice positions. We first used weak periodic roughness, displacing outward the plate atoms in a periodic array of square regions as in [4]. The average displacement was only half a lattice spacing, and while the results suggested an open hysteresis loop, the error bars were too large to permit an unambiguous conclusion. We then considered surface roughness that was both stronger and random, with 60% of the outer plate atoms displaced

by 0.51 ± 0.72 lattice spacings. In this case, Fig. 4, we find an obvious open hysteresis loop: the force is a multiple-valued function of velocity, and depends on the past history of interface motion. (The rough plate system has a different size than the smooth plate case, and the numerical values of F are not directly comparable.) In this case it is impossible to define a local contact angle at the solid—see Fig. 5—while at larger distances from the plate the interface shape is strongly influenced by the finite size of the container. Note that the interface is a surface dividing two partially overlapping sets of atoms in space, and is intrinsically difficult to visualize. The principal point of Fig. 5 is the contrast with Fig. 3.

From snapshots of the atomic positions, as well as examining time-averaged density plots, the following explanation of the hysteresis loop emerges. Because of the irregularity of the plate surface normal to the plane of the figures, the interface cannot meet the solid at a single angle but tries to adjust itself locally. This produces an enhancement in the interface width beyond what occurs in the smooth case. As the plate moves upwards it tries to pull the interface along with it, but different parts of the interface see a differently shaped and time-dependent solid boundary. The result is an additional broadening of the interface, as it passes through some set of transient or metastable states. As the plate velocity increases on the upward ramp, the interface broadens still further, because

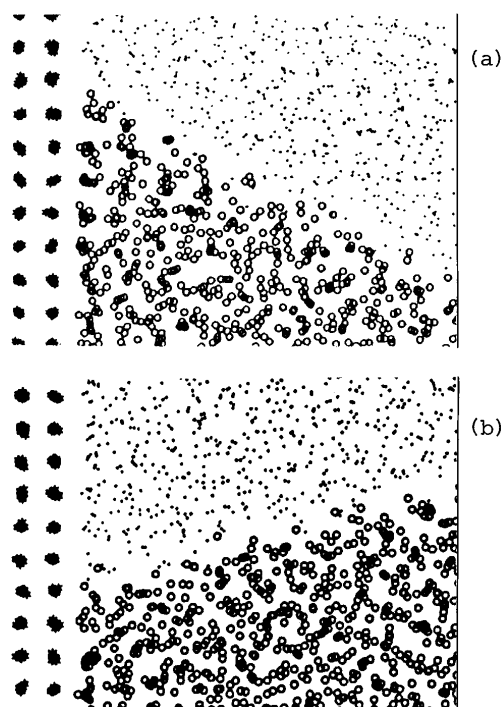


FIG. 3. Snapshots of the contact-line region for a smooth plate; (a) $v = +0.04$ and (b) $v = -0.12\sigma/\tau$. The solid, fluid-1, and fluid-2 atomic positions are indicated by *, o, and □, respectively.

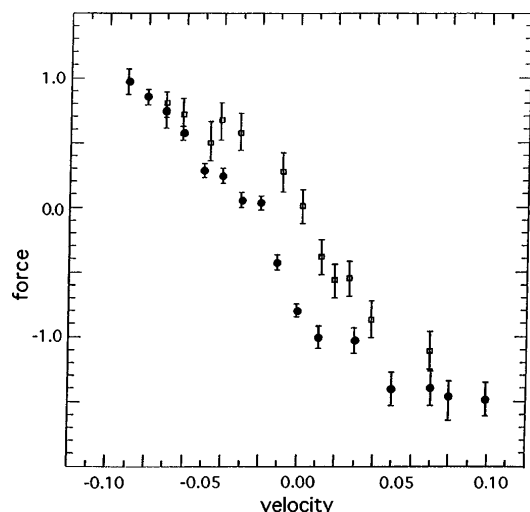


FIG. 4. Force vs velocity for an atomically rough plate; same format as Fig. 2.

different segments of its edge near the plate see more rapid fluctuations. The force increases as well because the additional distortion of the interface is resisted by surface tension. When the velocity is reduced on the downward ramp, the interface does not immediately relax to the shape on the upward ramp, as it is effectively sampling a larger set of metastable states. Thus at a given velocity on the downward ramp, the interface is more distorted than on the upward ramp, and the corresponding force at that point is larger in magnitude. This mechanism closely parallels the usual explanation for magnetic hysteresis in

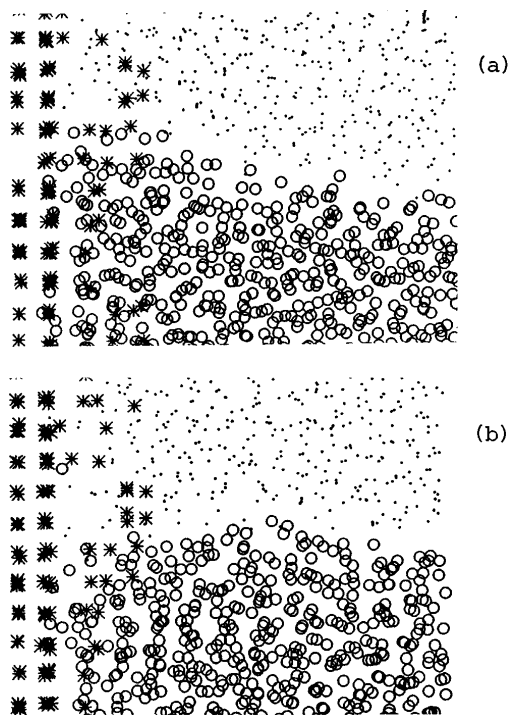


FIG. 5. Snapshots of the contact-line region for a rough plate; (a) $v = +0.04$ and (b) $v = -0.05\sigma/\tau$.

terms of the growth and breakup of oriented spin domains. Since the issue is one of metastable states, there is always the possibility that the effect might disappear in time, but we see no evidence for this. Note that the scale of the roughness should exceed the atomic spacing in the fluid in order that the (average) interface is substantially perturbed.

Although these simulations have for the first time directly demonstrated the role of surface heterogeneity in producing hysteresis in a *dynamic* wetting process, they have only begun to explore the problem. A number of further issues appear to be amenable to MD simulations, such as scanning loops, chemical rather than structural surface heterogeneity, the effects of nontrivial liquids such as surfactants or polymers [12], and so on. The fluid flow field and the role of dissipation [13] requires further study as well, perhaps using very long runs to improve the statistics, in order to connect these microscopic results to continuum calculations and experiments.

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- [1] *Wetting, Spreading and Adhesion*, edited by J.F. Padday (Academic, New York, 1978).
- [2] E. B. Dussan V, *Annu. Rev. Fluid Mech.* **11**, 371 (1979); P.G. de Gennes, *Rev. Mod. Phys.* **57**, 827 (1985); L. Leger and J.F. Joanny, *Rep. Prog. Phys.* **55**, 431 (1992).
- [3] R. E. Johnson, Jr. and R. H. Dettre, in *Surface and Colloid Science*, edited by E. Matejovic, **2**, 85 (Interscience, New York, 1969).
- [4] L. W. Schwartz and S. Garoff, *Langmuir* **1**, 219 (1985).
- [5] J.F. Joanny and P.G. de Gennes, *J. Chem. Phys.* **81**, 552 (1984); E. Raphael and P.G. de Gennes, *J. Chem. Phys.* **90**, 7577 (1989); J.F. Joanny and M.O. Robbins, *J. Chem. Phys.* **92**, 3206 (1990); A. Paterson, M. Fermigier, P. Jennfer, and L. Limat, *Phys. Rev. E* **51**, 1291 (1995).
- [6] J. Koplik, J.R. Banavar, and J.F. Willemsen, *Phys. Fluids A* **1**, 781 (1989).
- [7] P. A. Thompson and M. O. Robbins, *Phys. Rev. Lett.* **63**, 766 (1989).
- [8] J.-M. Di Meglio, *Europhys. Lett.* **17**, 607 (1992).
- [9] J.-x. Yang, J. Koplik, and J.R. Banavar, *Phys. Rev. A* **46**, 7738 (1992); J.A. Nieminen and T. Ala-Nissila, *Phys. Rev. E* **49**, 4228 (1994); U. d'Ortona, J. De Coninck, J. Koplik, and J.R. Banavar, *Phys. Rev. E* **53**, 562 (1996).
- [10] J. Koplik and J.R. Banavar, *Annu. Rev. Fluid Mech.* **27**, 257 (1995).
- [11] R. G. Cox, *J. Fluid Mech.* **168**, 169 (1986); J. A. Marsh, S. Garoff, and E. B. Dussan V, *Phys. Rev. Lett.* **70**, 2778 (1993).
- [12] K. R. Willson and S. Garoff, *Colloids Surf.* **89**, 263 (1994).
- [13] G. W. Young and S. H. Davis, *J. Fluid Mech.* **174**, 327 (1987).