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A Stochastic Method to Determine the Shape of a Drop on a Wall

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We present results of a stochastic simulation which determines the shape of a liquid drop, subject to gravity, on a wall. The system is modeled using an Ising model in a field gradient, with Kawasaki dynamics governing the time dependence. We can locate a phase transition between a hanging and a sliding phase with high precision and determine its critical exponents.

KEY WORDS: Ising model; Kawasaki dynamics; surface tension.

Liquid drops hanging or sliding down walls or tilted planes have been studied for a long time. It is known that, depending on the surface tension of the fluid, the adhesion force to the substrate, the tilting angle of the plane, and the volume, a drop will either hang or slide down, both with a characteristic shape and with well-defined contact angles which can be accurately determined experimentally.(1) The transition between the hanging and the sliding cases is characterized by a critical drop volume.

The theoretical determination of the shape of a hanging or sliding drop has long been a challenge; and very diverse methods have been used, some of them yielding rather good results. On one hand the Young–Laplace equations have been solved by Galerkian finite-element methods.(2) Lubrication theory has been used to obtain in particular the maximum drop volume.(3) The basic optimization problem of finding the shape that for given volume lowers the surface tension has been attacked by

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approximating the shape by spline functions[4] and, in a more refined way, by generalizations of Winterbottom functions.[5]

In this note we propose an alternative stochastic method for this optimization problem. For calculational simplicity we will work on a square lattice, i.e., restrict ourselves to the two-dimensional case, and consider Ising variables σ_i on each site i. Spin "$+1$" represents the fluid and "-1" the air. Our lattice has fixed boundary conditions. A drop is placed on the right vertical boundary. Spins on the boundary adjacent to the initial drop are made "$+1$" and all other boundary spins are made "-1." This right vertical boundary represents the wall on which the drop should hang or slide, and at the initial contact surface of this wall the drop should feel an adhesion force while the lower part is repulsive. This initial wetting of the boundary is kept wet all the time. Physically one can think of a drop that hangs on a part of the wall that it has already wetted, but does not slide down because the part below is not wetted yet (for instance, because of the presence of dirt).

The presence of gravity is introduced by a uniform field gradient g: On the top line we have a field h_1 with an energy $h_1 \sum_{\text{line } 1} \sigma_i$, on the bottom line ($L$th line) a field h_L is applied analogously, and for the lines in between, the linearly interpolated value $h_j = h_1 + (j-1)(h_L - h_1)/(L-1)$ is applied. We define the "gravity g" as $g = (h_L - h_1)/L$. Its value is always chosen to be positive.

We start with a semicircular drop of volume V, i.e., V "$+1$" spins, attached to the wall with topmost site of the drop four lattice sites below the top line of our lattice. In the subsequent time evolution of this drop three elements must be taken into account:

1. In order to take into account the effects of surface tension and surface rigidity using a thermodynamic approach, we introduce two energies, the nearest-neighbor attraction of spins of equal sign, which tends to reduce the surface of the drop, and the next-nearest-neighbor attraction, which is the first approach on a lattice to reduction of the curvature. We thus have a Hamiltonian

$$\mathscr{H} = \sum_{\text{nn}} \sigma_i \sigma_j + \sum_{\text{nnn}} \sigma_i \sigma_j + \sum_j h_j \sum_{\text{line } j} \sigma_i \tag{1}$$

in which we set the coupling constants to be unity, which means that surface tension and rigidity should be set to two if they are defined by the amount of energy change in a flip. On the right vertical boundary this Hamiltonian automatically has the effect of an attraction of the drop on the upper half and a repulsion on the lower half. This Hamiltonian is used to introduce a canonical spin-flip Monte Carlo dynamics.

2. In order to impose volume conservation (we consider an incompressible, nonvolatile fluid), long-range Kawasaki spin exchange is used. That means that two spins on the surface of the drop, i.e., the interface between the two types of spins, are chosen at random, one being "$+1$" and the other "-1." If a random number uniformly distributed between 0 and 1 is less than the spin-flip probability $p = \exp(\beta\, \Delta E)$, the two spins are interchanged (as long as condition 3 is fulfilled). ΔE is the energy difference between the configuration before and after the interchange given by Eq. (1).

3. The topmost and the lowest sites of the initial drop are pinned down, which means they are always "$+1$."

Using the above dynamics, we relaxed the initially semicircular drops by applying t_r spin exchange attempts. In Fig. 1 we see the result obtained in a lattice of $L = 257$ with $V = 6613$ and $g = 0.001$ after $t_r = 5 \times 10^7$ iterations at a temperature of $T/T_c = 0.25$, where T_c is the critical temperature of the Ising model. In fact, Fig. 1 is a shape averaged over 10 samples using an averaging procedure described below. We see that the drop has slid down and is already touching the bottom of the system. Note that since the upper part of the right vertical wall is "$+1$," it is technically treated as part of the drop, and so microdroplets are left behind like a thin film. Since the lower part of the wall is repulsive, the drop does not wet it. Due to the stochastic nature of our method, the surface of the drop has a certain roughness.

Essentially, the temperature only seems to change the speed of the dynamics. Although there is no finite roughening temperature in two dimensions, at very low temperatures one tends to get flat facets of a size that increases exponentially with decreasing temperature. These facets are

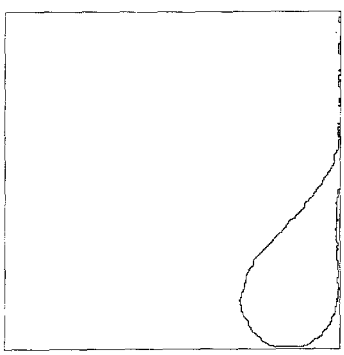

Fig. 1. Shape after 5×10^7 Monte Carlo exchanges starting with a semicircular drop of radius 65 in lattice units at $T/T_c = 0.25$ and $g = 0.001$. The averages are over ten independent runs and taking sites that belong to the drop more than five times.

artefacts of the underlying lattice and can in principle be removed by a more detailed, long-range definition of curvature in the Hamiltonian. The easiest way to reduce this lattice problem, however, is to increase the temperature sufficiently. As seen from Fig. 1, a very satisfactory result can already be obtained well below T_c.

Although real drops are subject to thermal fluctuations and should therefore not have completely smooth surfaces, the roughness is certainly less pronounced than for the drop obtained from a single time step of our simulation. However, it is well known that in stochastic methods one has to take averages over M statistically independent samples. One way to "average" the shape is to store the number of samples m_i for which spin i has the value "+1." Then one can define the interior of the drop as being comprised of all the sites j for which m_j is larger than $M/2$. In fact, the shape shown in Fig. 1 is the result of just such a calculation with $M = 10$. This average shape is certainly smoother than the nonaveraged case, but still consists of steps on the length scale of a lattice unit. This effect can also be removed by linearly interpolating the values of the m_i on the lattice and choosing the continuous line for which the field m defined by the interpolation equals $M/2$. A picture of such a drop is shown in Fig. 2 after averaging over 100 samples. In this case the parameters were chosen such that the drop does not slide.

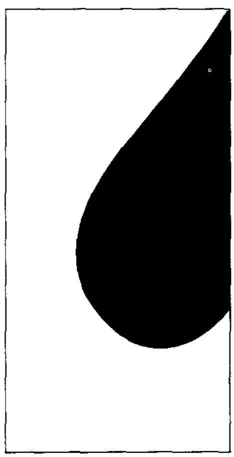

Fig. 2. Shape of drop of initial radius of 65 in lattice units (i.e., a volume of $V = 6702$) in a lattice of $L = 513$ after $t_r = 5 \times 10^7$ time steps and averaging over $M = 20$ independent samples (using for each one the last 1000 configurations at intervals of 100 time steps) and using an interpolation to get a smooth line. This simulation took 15 hr on one processor of an Alliant FX2800 at the GMD.

As has been previously discussed,[3,5] it is easy to see that the relevant parameter that determines if a drop hangs or slides is the product of volume and gravity: $H = Vg$. Using the model described above, we want to locate with high accuracy the critical value H^* above which the sliding sets in and determine the critical behavior of various physical properties around this point.

An interesting observation is that for H just above H^* the drop does not immediately slide down, but hangs on the wall for a while before suddenly breaking off after a time t_s that depends on H. This can be seen by calculating the height of the center of mass of the drop as a function of time (= Monte Carlo exchanges) as shown in Fig. 3 for the case of fixed volume $V = 1710$ and varying gravity g. From Fig. 3 one sees that the center of mass first moves down slowly, fluctuating due to the stochastic nature of the dynamics, and then at a sharply defined time t_s moves downward with high speed. When g^* is approached, the time t_s diverges. This effect can be analyzed quantitatively by calculating for fixed g the average $\langle t_s \rangle$ over many samples plotting $1/t_s$ as a function of g. The result of such a calculation is shown in Fig. 4 for the case of $V = 468$. From the data in this figure we determine that $\langle t_s \rangle$ diverges at $g^* = 0.0124 \pm 0.0001$, which gives a value of $H^* = 5.79$. For $V = 1710$ we find $H^* = 5.77$, a results which confirms our expectation that the product $H = Vg$ is the relevant parameter. Note that also the volume has an inaccuracy in the third digit due to the lattice discretization.

When the critical point is approached from above, $\langle t_s \rangle$ diverges with a power law. This can be seen in the double logarithmic plot of Fig. 5. There again the volume $V = 468$ is fixed and the distance from the critical

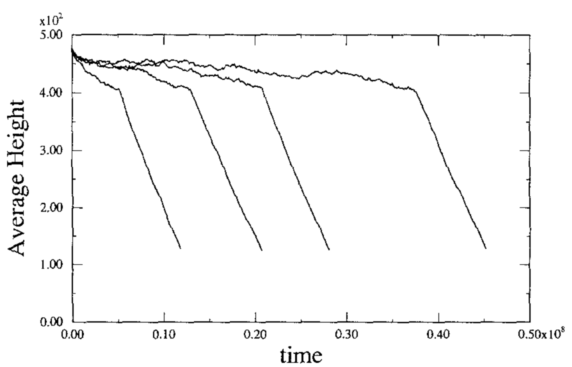

Fig. 3. Height of the position of the center of mass as a function of time for an initially circular drop of radius 33 in lattice units for $T/T_c = 0.25$ and $L = 513$ for different values of g: 0.004, 0.0035, 0.00343, and 0.0034 from left to right, each for one single configuration.

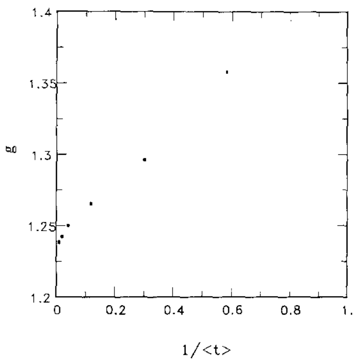

Fig. 4. Applied gravitation g vs. the inverse average breakup time $\langle t_s \rangle$ for an initially semicircular drop of radius 17 in lattice units ($V = 468$), $L = 513$, $M = 10$, and $T/T_c = 0.25$.

point is measured by $(g - g^*)/g^*$. We see that the points lie nicely on a straight line of slope 1.25. We conjecture that this exponent $x \approx 1.25$ defined by $\langle t_s \rangle \sim (g - g^*)^{-x}$ is universal.

When the critical point is approached from below, i.e., from the static case, one sees that the hanging drop deforms more and more, having an increasingly large overhang. This effect can be measured by monitoring the average number m_b of sites belonging to the drop with heights below the lower contact point of the drop with the wall, i.e., sites lying in the overhang. The log-log plot of Fig. 6 shows that the dependence is also numerically consistent with a power law: $m_b \sim (g^* - g)^{-y}$ with $y \approx 0.44$, which means that the size of the overhang diverges when the onset to sliding is

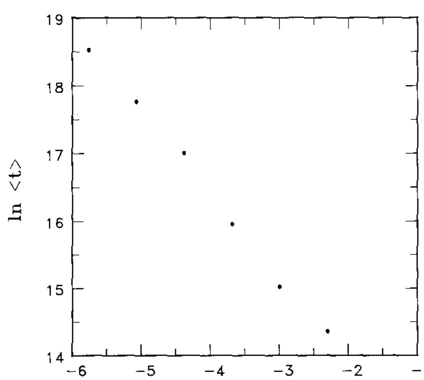

Fig. 5. Log-log plot of the average breakup time $\langle t_s \rangle$ as a function of the distance from the critical point $(g - g^*)/g^*$ for $g \geq g^*$.

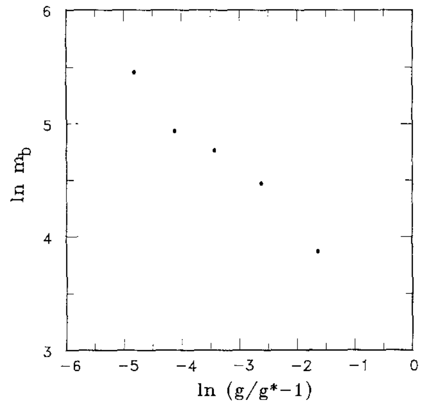

Fig. 6. Log-log plot of the average mass m_b in the overhang of the drop as a function of $(g^* - g)/g^*$ for $V = 468$, $L = 513$, $M = 10$, and $T/T_c = 0.25$.

approached. Since dominant terms in surface tension are taken into account in our model, we again conjecture that this exponent y is universal.

We also looked at the experimentally easily accessible lower contact angle θ, defined as the angle at the lower contact point of the drop with the wall measured from the tangential of the shape of the drop at this point to the axis of the wall pointing down (increasing gravity). For a given drop, this angle can be measured quite accurately with a ruler. This angle goes to zero when the critical point is approached from $g \leqslant g^*$, i.e., for the hanging drop presumably again with a power law defining a critical exponent. It is, however, not easy to measure very small angles, also due to the lattice effects, that tend to favor crystal planes as edges. Decreasing the temperature, one can in fact see that the contact angle tends to 45° irrespective of the value of g. In Fig. 7 we show this temperature dependence of the contact angle for $H = 4.18$ and see that the value of the contact angle does not saturate yet to a well-defined value at temperatures as high as $T_c/2$. Since we wanted to avoid getting close to the critical point of the Ising model, we preferred not to make predictions about the critical behavior of the contact angle.

For the above reason we also refrained from comparing our shapes directly to experimental photographs or other numerically obtained shapes. Another reason is that we have worked with a fixed set of values for surface tension, rigidity, and adhesion force and did not want to explore a large parameter space to fit the corresponding experimental values. Also, most experiments deal with three-dimensional systems.

In summary, we have presented a new stochastic method based on

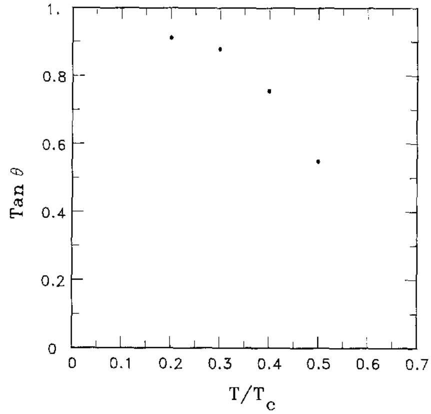

Fig. 7. Contact angle $\tan(\theta)$ as a function of reduced temperature T/T_c for $g = 6.3 \times 10^{-4}$, $V = 6702$, $L = 513$, $M = 10$, $t_r = 5 \times 10^7$.

Ising dynamics on a square lattice to obtain the shape of a drop and showed how this method works in the case of a two-dimensional drop hanging on a vertical wall. Similar stochastic methods using Ising variables on a lattice have in fact been formulated for sessile drops (no gravity),[6] wetting fronts,[7] and vesicles.[8] Our work can be trivially extended to the cases of tilted or horizontal walls, three-dimensional drops, and to arbitrary ratios of adhesion strengths and rigidity to surface tension. We found rather encouraging results concerning the determination of the critical point at which the drop starts sliding and its critical exponents. A drawback of our method is the presence of anisotropies generated due to the underlying lattice, but they can be minimized by increasing the temperature. Simulations in the continuum (tethered surfaces) or on random lattices could be used to avoid this effect altogether.

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