Molecular Simulations of Dewetting

Joel Koplik

*Benjamin Levich Institute and Department of Physics, City College of the City University of New York, New York, NY 10031*

Jayanth R. Banavar

*Department of Physics, The Pennsylvania State University, University Park, PA 16802*

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We have studied the breakup and subsequent fluid flow in very thin films of partially wetting liquid on solid substrates, using molecular dynamics simulations. The liquid is made of short chain molecules interacting with Lennard-Jones interactions, and the solid is modeled as a clean crystal lattice whose atoms have thermal oscillations. Films below a critical thickness are found to exhibit a spontaneous spinodal-like instability leading to dry patches, as predicted theoretically and observed in some experiments. Liquid withdrawing from a dry patch collects in a moving rim whose fluid dynamics is only partially in agreement with earlier predictions.

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The equilibrium configuration of a partially wetting liquid on a solid substrate is a drop, with finite contact angle given by Young’s equation. If the liquid is initially placed on the substrate in the form of a uniform coating film, however, it is potentially unstable and may “dewet” the solid so as to contract into drops, or perhaps other shapes. This process is obviously very relevant to applications in materials containment and transport, and at the same time involves a number of challenging scientific issues, such as the nature of the instability, the fluid dynamics of the dewetting liquid, and the shape selection problem for the final pattern. In this Letter, we describe the results of molecular dynamics (MD) simulations which address the first two issues. We first present new and independent confirmation of the spinodal dewetting scenario for very thin films, those of sub-micron thickness where gravity is negligible but Van der Waals interactions between the liquid and the solid are crucial. We observe unstable films whose behavior reflects spontaneous rather than nucleated instabilities. We then consider the hydrodynamics of a liquid film undergoing a dewetting flow, and determine the time evolution of the film length and shape, and the issues of internal flow and contact angle variability. Here we find only partial agreement with earlier theoretical proposals. The pattern selection issue unfortunately involves the dynamics on larger scales than those readily addressed with MD, and is not considered here. Several previous papers have used molecular simulations to study dewetting, but with an emphasis on different parameters and aspects of the instability, the behavior at shorter times than we consider, and no consideration of the hydrodynamics of the dewetting liquid. Furthermore, we disagree with some of their conclusions.

The behavior of a thin liquid film on a solid depends on Van der Waals (VdW) forces if the film is sufficiently thin, gravity otherwise, surface tension if its surface is not flat, and when motion occurs, viscosity. In the partially wetting case, the VdW forces favor a solid exposed to vapor rather than liquid, but for incompressible liquids any attempt to withdraw the liquid increases the liquid-vapor surface area. The competition between VdW and surface tension forces leads to an instability criterion that small sinusoidal perturbations of wavelength greater than \( \lambda_c = \sqrt{4/3\pi k_0 a} \) are unstable. Here \( a \) is a microscopic length given by \( a^2 = (A_{LL} - A_{LS})/6\pi\gamma \), where the \( A_{ij} \) (\( i,j = \text{liquid L, solid S or vapor V} \)) are the Hamaker constants, \( \gamma \) is the LV surface tension, \( \mu \) is the liquid viscosity, and \( h_0 \) is the unperturbed thickness. The linear stability calculation shows that there is a most unstable wavelength \( \sqrt{2}\lambda_c \) with corresponding growth rate \( \omega_{max} = 3\alpha^4/\mu h_0^3 \). Further analysis, using weakly nonlinear theory or lubrication modeling may then be used to discuss the final patterns. A long-standing issue has been whether the origin of observed dewetting phenomena is simply the evolution of these “spontaneous” instabilities, analogous to spinodal decomposition, or whether nucleation at impurity sites or by contaminants is required. Recent experiments and previous simulations favor the former mechanism, and we wish to provide further evidence, by systematically varying the film thickness. The procedure will be to simulate a clean substrate of width \( L \) with periodic boundary conditions, and films with various values of \( h_0 \). The maximum wavelength of any disturbance is on the order of magnitude of the substrate size, so an instability should occur only when \( \lambda_c(h_0) \) is less than \( O(L) \).

Our simulations are based on standard MD techniques applied to fluid flows, and the details are very similar to that used in our earlier studies of drop wetting. We consider a system with 18000 fluid molecules consisting of four atom FENE chains, placed on a substrate in the form of an fcc-crystal with atoms tethered by linear springs to regular lattice sites. All atoms interact via two-body Lennard-Jones interactions, \( V(r) = 4\epsilon[(r/\sigma)^{12} - c_{ij}(r/\sigma)^{6}] \), where \( i,j \) refer to the fluid and solid species present. The potential is cutoff at 2.5\( \sigma \) for computational speed, but a \( r^{-3} \) tail is added to the solid-liquid interaction above the cutoff distance, corresponding to the interaction due to a half-space of...
solid. The temperature is 1.0, maintained by a Nosé-Hoover thermostat, and the fluid density is 0.8σ⁻³. The solid has 34848 atoms, in the shape of a square substrate of side 102.6σ, and two fcc cells (four staggered layers) in thickness. We prefer to use molecular chains rather than a monatomic liquid so as to reduce the vapor pressure and have a sharper interface. FENE molecules have non-Newtonian behavior under high-stress conditions, but here the stress is usually weak (but see below) and any other potential confining atoms into molecules would suffice. Note that the r⁻³ tail in the potential and the z⁻³ tail are the microscopic basis of the semi-macroscopic VdW force, and the wettability of the solid is controlled by the Lennard-Jones solid-liquid interaction coefficient c_{LS}. By simulating the spreading of a liquid drop on this substrate, we find that c_{LS} = 1 gives complete wetting, while c_{LS} = 0.75 gives partial wetting. We observe in these microscopic simulations that the wetting and dewetting behavior is essentially the same if we remove the z⁻³ tail but increase c_{LS}. Similarly, although we prefer the use of a solid made of tethered molecules which can realistically exchange energy with the liquid, the dewetting behavior is not significantly modified if fixed potential sites are used. The in-plane variation of the wall interaction is crucial, however, because if the potential is purely a function of height, the liquid readily slips along the substrate.

We have simulated the free evolution of uniform liquid films of various initial thicknesses, and Fig. 1 shows snapshots for four choices near the onset of instability. Each frame is a top view of a liquid film, where a molecule is displayed as the three-segment broken line joining its four atomic centers, so that darkness increases with thickness. The initial film is slightly thicker than those shown, h_0 = 6.7σ, and is stable over a time 120τ, where τ = σ√ε/m is a characteristic molecular time (in the picosecond range). Thinner films, produced by skim- ming molecules off the surface of the liquid, are unstable; the different frames of the figure show films at an early stage of evolution just after one or more holes appear, corresponding to dry patches on the substrate. The solid is flat, aside from thermal fluctuations in its atomic positions, and the liquid is homogeneous, so there is no nucleation. Furthermore, the locations of the dry spots for various films are uncorrelated. Once a dry spot appears, it invariably continues to grow, and eventually the liquid withdraws into a single round drop. Liu et al. claim to the contrary to observe a nucleation mechanism, wherein dry patches smaller than some critical size heal. We find instead that once a dry region larger than a couple of molecular diameters appears, which is to say once the molecules on the two sides are out of mutual interaction range, it continues to grow.

The effect of varying the thickness in the unstable cases is that decreasing h_0 decreases the time before a dry spot appears, and also decreases the spacing between the spots. The stability calculation summarized above predicts that these two quantities would vary as h_0^2 and h_0^6, respectively. It would be prohibitive in computation time to test these results quantitatively, but the expected trend is clearly reproduced. A further difficulty in making a quantitative comparison is the unknown connection between the atomic interaction parameters and the Hamaker constants. There is a standard relation for a monatomic liquid neglecting thermal motion, A_{ij} = 4πρ_iρ_j c_{ij} where ρ_i is the density of species i, but not for molecules. If we use this expression anyway, along with measurements of γ and μ from earlier MD simulations, our results agree with the stability calculations to within factors of 2-3.

Now we turn to consideration of the fluid mechanics of the withdrawing liquid. Conventional theoretical and numerical studies of dewetting flows are plagued by several difficulties. In general, this is a moving boundary problem where disjoining pressure must be included to take account of VdW forces. Full Stokes equation calculations are difficult due to the fine resolution that would be required near the solid to capture this term. Furthermore, there is a moving contact line, with the usual accompanying shear stress singularity, and where one is completely ignorant of the appropriate dynamic contact angle. The singularity may be eliminated by use of a slip model for the boundary value of the fluids velocity, but the correct angle and its possible variation with flow conditions is simply unknown. The computational complexity may be significantly reduced by use of a depth-averaged or lubrication model, but the standard parameterization of disjoining pressure, as a single term proportional to the inverse square of the thickness, does not lead to an actual dewetting motion, but rather
pins the edge of the film. This deficiency can be remedied by modifications to the potential which give a minimum at a small value of thickness, but in this case a residual film is left behind, not usually seen in experiment.

The only quantitative theoretical attempt to consider the fluid mechanics of dewetting, by Brochard and collaborators [4], is based on the strong simplifying assumptions that the liquid collects into a growing rim as it dewets with negligible fluid motion elsewhere, that the rim is in the shape of an arc of a circle, and that particular contact angles appear at the two edges of the rim. It is then possible to derive power laws for the speed and shape evolution of the rim. Of the assumptions made in this treatment, it is entirely reasonable that the liquid in the center of the film would be static until it is swept up by a withdrawing rim, but the particular assumptions made about the shape of the rim are less compelling. The theoretically unbiased MD simulations reported here provide new information at microscopic resolution.

As in the previous calculations, we begin with a solid substrate initially covered by a thin uniform liquid film, with the same density and temperature as above, but thickness $12\sigma$. In order to maximize the time and space interval over which the film evolves, we take the substrate to be a long narrow strip, $547\sigma \times 17\sigma$, so as to discourage instabilities in the spanwise direction. The liquid film is first equilibrated with periodic boundary conditions and with $c_{LS}=1$, corresponding to complete wetting. A strip of liquid is removed “by hand” at one edge of the film while $c_{LS}$ is reduced to a dewetting value 0.75 for the solid atoms in the right-hand quarter of the substrate where motion occurs. The film at this stage is shown from the side in Fig. 2a, and in subsequent frames the liquid at the edge of the film withdraws from the sub-

state and collects in a rim which translates and grows, at least initially. As the film dewets, we occasionally extend the region of substrate where $c_{LS} = 0.75$ to keep it ahead of the advancing rim, while retaining the “wetting value” 1.0 elsewhere. In this way, the motion is purely from right to left, rather than inwards on both sides, and it is possible to study the behavior of a longer dewetted region.

We see that while the dewetted liquid indeed forms a rim which grows in size as it moves, only the outer edge is circular, while the inner boundary is more ramp-like. There is no second contact angle [4] where the rim meets the flat part of the film. The solid-liquid-vapor contact angle at the receding edge is seen to fluctuate with time, as usual at this scale, but its mean value is observed to be roughly 90° and is distinctly less than the static equilibrium value of 105° ± 5°. Hwang et al. [5] present plots of contact angle vs. time which suggest a smooth and systematic variation, but in our simulations (with larger scale and different parameters) substantial oscillation is seen. The position of the edge of the film as a function of time is shown in Fig. 3, and as predicted [4] its speed is roughly constant. The glitch around time 1000$\tau$ is related to the first appearance of an obvious rim, and the possible flattening at the largest times is probably due to gradual thickening of the immobile part of the film. Liu et al. [6] however find a different behavior at early times in other systems. The height and length of the rim were predicted theoretically to vary as $\sqrt{t}$, at least for non-volatile liquids, but we observe a much slower growth of the rim. The rim is subject to avalanching along its inner side, and grows irregularly at a rate very roughly $t^{1/4}$, Fig. 3, while the width of the rim region
appears to stabilize. Additional, more microscopic, information is provided by the simulation as well. Typical velocity fields are shown in the rim region and in the middle of the film, respectively, in Fig. 4. There is slip in the very near vicinity of the contact line but not elsewhere. The shear stress and pressure do not show any statistically significant variation, aside from a shear stress peak at the contact line which usually accompanies slip there [14]. The flow is essentially confined to the rim region, as predicted, but the details of the velocity field are hard to resolve because the values are small and subject to small-system thermal fluctuations. While there is little bulk motion in the plateau region of the film, there is some motion in the vapor and also along the surface however; the snapshots in Fig. 2 show some wave-like excitations on the film surface, and there is a non-zero velocity at the top of the liquid plateau indicated in Fig. 4.

![Velocity fields](image)

**FIG. 4.** Velocity fields at the edge (top) and in the middle (bottom) of a receding film, averaged over the time interval 3125-3150 $\tau$ and spatial bins of cross section 1.71$\sigma$. The largest velocity vector shown is 0.2$\sigma/\tau$.

Although in this Letter we have focused on the results of just two rather large scale simulation sequences, we emphasize that numerous smaller-sized runs with various alternative parameters exhibit essentially the same behavior. Among the variations we have explored in this way are different molecular sizes and bonding potentials, different substrate thicknesses, other values of the temperature, adding a (weak) gravitational force, and different methods for initialization. In particular, aside from the obvious expectation that decreasing the strength of the solid-fluid interaction enhances the rate of dewetting, we find that sufficiently thin dewetting films always follow the trends expected from the spinodal decomposition scenario and its linear stability analysis, and that dewetted fluid collects from the substrate into a rim moving with roughly constant velocity. The detailed fluid dynamics of flow in the rim region and the shape evolution of the front is unfortunately not yet predictable. A particularly fruitful area for further study might be the effects of molecular structure and interactions on dewetting dynamics. The advantage of having the forces and structures under explicit control may help in the design of controlled dewetting patterns.

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