Langevin Dynamics of Spreading and Wetting

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We propose a solid-on-solid-model description of the dynamics of wetting, using Langevin equations. The Gaussian version, appropriate to partial wetting, is solved exactly. The general version is solved using local equilibrium and scaling arguments. We obtain the dynamical contact angle, the shape of the profile near the substrate, and, for dry spreading, the occurrence, speed, and possible layering of a precursor film.

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There has been considerable interest in the dynamics of the wetting phenomena.[1] The current experimental picture in the case of complete wetting, which develops ideas of Hardy,[2] is one of a precursor film of molecular thickness advancing, as its name suggests, ahead of the macroscopically observable drop.[3] The most recent progress has resulted from refinement of experimental technique culminating in the surprising layering results of Heslot, Fraysse, and Cazabat.[4] Earlier work[5,6] gave results reasonably well explained by the theory of Joanny and de Gennes[7] based on continuum-theoretic or hydrodynamic ideas. Such ideas clearly cannot be expected to apply at a molecular level and, indeed, they do not explain the most recent experimental results. It is therefore of interest to investigate the dynamics of interfaces in statistical-mechanical models of wetting.

As a first step in this direction, we present in this work a simple, dynamical, coarse-grained model of wetting which we solve exactly in a special case appropriate to partial wetting. A more general locally equilibrated version is then given which allows treatment of the complete-wetting case and extraction of a precursor film which, as far as is known by the authors, has not been done before in a microscopic statistical-mechanics framework.

Our model is related to the Lifschitz equation[8] which describes the time evolution of an interface in a system with a second-order phase transition, focusing on the effects of surface tension rather than those of hydrodynamics. The normal component of velocity v_n is given in terms of the radius of curvature $r(x)$ by $v_n = \lambda r(x)^{-1}$, where λ is proportional to the surface tension. At this point, we are evidently dealing with a continuum theory. Referring to Fig. 1, the height i is replaced by a continuous variable x and the position of the interface is denoted by $h(x,t)$. Then,

$$r(x)^{-1} = h''(x)/\{1+[h'(x)]^2\}^{3/2}$$

and the normal component of velocity is $v_n \dot{h}(x)/\{1+[h'(x)]^2\}^{1/2}$ so that the Lifschitz equation becomes

$$\dot{h}(x) = \lambda h''(x)/\{1+[h'(x)]^2\} + \mu_0 \delta(x) ,$$

where the last term has been added to describe the propensity of the substrate to spread the drop. The origin of this seemingly arbitrary term will be made clear below.

This equation should be supplemented by fluctuations in the spirit of Langevin but its study then imposes serious conceptual and analytical problems which we avoid by changing x into a discrete variable i. In any case, since we are looking for a microscopic theory of dynamical profiles, discreteness has its advantages.

We consider a solid-on-solid model, the configurations of which are described in Fig. 1. A third dimension can be added, perpendicular to the figure, provided the initial and boundary conditions are translation invariant in this direction. The solid-on-solid models can only be expected to apply at equilibrium in a spatially coarse-grained sense;[9] the thickness of the layers ought to be of the order of the bulk phase correlation length. Langevin dynamics are then applied to the thermal motion of the layers. Let the displacement of the ith layer be h_i, $i=0,\ldots,L$. The h_i are taken to be continuous variables. Then h_i evolves in time according to the stochastic differential equation

$$\frac{dh_j}{dt} = -\lambda \frac{\partial F(\{h_i\})}{\partial h_j} + \xi_j, \quad j=0,1,\ldots,L , \tag{1}$$

where ξ_i is white noise such that

$$\langle \xi_i(t)\xi_j(u)\rangle = 2kT\lambda\delta_{ij}\delta(t-u) \tag{2}$$

and $F(\{h_i\})$ is the coarse-grained free-energy functional

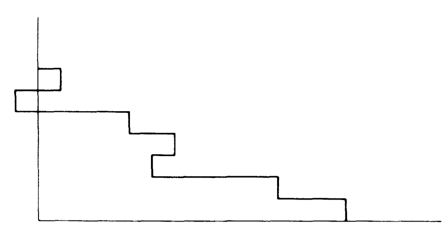

FIG. 1. Typical configuration showing displacement parallel to substrate as function of height above substrate.

of the profile which we take to be of the form

$$F(h_0,\ldots,h_L)=\sum_1^L P(h_{j-1}-h_j)-\mu_0 h_0 . \tag{3}$$

The term $\mu_0 h_0$ causes spreading; it expresses differential preference for the substrate to be covered by one of the phases. If γ_{ab} denotes the surface tension of the interface between phases a and b, then μ_0 can be expressed as

$$\mu_0=\gamma_{sv}-\gamma_{sl}\,, \tag{4}$$

where s, l, and v denote the substrate, the liquid (the spreading phase), and the vapor (or another phase), respectively. Moist spreading refers to a situation where the vapor is at coexistence with the liquid, so that Young's equation will ultimately be satisfied:

$$\gamma_{sv}-\gamma_{sl}=\gamma_{lv}\cos\theta .$$

This implies $\mu_0\le\gamma_{lv}$; the argument still holds when Young's equation is modified by anisotropy. In contrast, dry spreading refers to a situation where v has typically no thermodynamic-equilibrium relation to l, so that μ_0 should not be restricted. Spreading of a nonvolatile liquid is usually dry spreading, with a strictly positive spreading coefficient corresponding in our model to $\mu_0-\gamma_{lv}>0$.

The function $P(x)$ in (3) is chosen so as to give a realistic surface tension γ_{lv}, which may depend upon orientation and is then denoted by $\gamma_{lv}(\theta)$. Young's equation, modified by anisotropy, then reads[10,11]

$$\gamma_{sv}-\gamma_{sl}=\gamma_{lv}(\theta)\cos\theta-\frac{\partial\gamma_{lv}(\theta)}{\partial\theta}\sin\theta . \tag{5}$$

In order to be specific and yet consider the different wetting situations, one may choose

$$P(x)=J(1+x^2)^{1/2} . \tag{6}$$

Equation (1) is supplemented by the initial condition $h_j(0)=0$ for all $j=0,\ldots,L$. The height L of the profile may be thought of as much larger than the foot of the profile, but much smaller than the drop itself which will constitute a reservoir. This will appear to make sense for L large and time t much less than L^2.

When $x\ll 1$, a quadratic approximation to (6) is useful since the model can then be solved exactly, as has been done already for the case of the free interface.[12] Let $\langle\cdot\rangle$ denote the average with respect to the noise. The solution of (1) in the limit $L\to\infty$ now reads

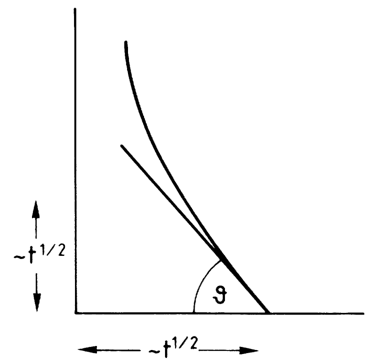

FIG. 2. Spreading profile: case of partial wetting.

$$\langle h_j(t)\rangle=\frac{\mu_0}{2\pi J}\int_0^\pi\{\cos(jx)+\cos[(j+1)x]\}\times\frac{1-e^{-\lambda J(1-\cos x)t}}{1-\cos x}\,dx . \tag{7}$$

As $t\to\infty$, the foot of the profile spreads out in a scale-invariant shape of size $t^{1/2}$ in both the spreading and the vertical direction:

$$\lim_{t\to\infty}\langle t^{-1/2}h_{yt^{1/2}}\rangle=\frac{\mu_0\sqrt{2}}{\pi\sqrt{J}}\int_0^\infty\cos\left(\frac{zy\sqrt{2}}{\sqrt{J}}\right)\frac{1-e^{-\lambda z^2}}{z^2}\,dz . \tag{8}$$

Indeed (8) tends to zero as $y\to\infty$ by the Riemann-Lebesgue lemma. The dynamical contact angle can be defined by

$$\cot\theta=\lim_{y\to 0}\lim_{t\to\infty}\frac{\langle h_0-h_{yt^{1/2}}\rangle}{yt^{1/2}}=\frac{\mu_0}{J}\,,$$

which is the equilibrium value (see Fig. 2).

Returning to the continuum model, when $h'(x)\ll 1$ exactly the same results are obtained.

Thus complete wetting cannot be obtained from the Gaussian model, as expected from equilibrium studies. From (6) it is seen that as soon as the interface tilts significantly, $P(x)=J|x|$ is a better approximation, but unfortunately not an exactly solvable one. Instead, mean values are examined under the assumption that local equilibrium obtains with $\langle P'(h_{i-1}-h_i)\rangle$ given as a function of the expected slope $\langle h_{i-1}-h_i\rangle$ by the same formula as in equilibrium. This gives[13]

$$\langle P'(h_{i-1}-h_i)\rangle=\mu(\langle h_{i-1}-h_i\rangle)\,, \tag{9}$$

where $\mu(y)$ is a field which, at equilibrium, would produce an average slope y for the interface. For the model studied here, $\mu(y)$ is given by

$$y=\int x\exp\left[-\frac{1}{kT}P(x)+\frac{1}{kT}\mu(y)x\right]dx\Big/\int\exp\left[-\frac{1}{kT}P(x)+\frac{1}{kT}\mu(y)x\right]dx . \tag{10}$$

The Langevin equations (1) now yield simple equations for the mean values:

$$\frac{d\langle h_0\rangle}{dt}=\lambda\mu_0-\lambda\mu(\langle h_0-h_1\rangle)\,, \tag{11}$$

$$\frac{d\langle h_i\rangle}{dt}=\lambda\mu(\langle h_{i-1}-h_i\rangle)-\lambda\mu(\langle h_i-h_{i+1}\rangle)\,,\ i=1,2,\ldots,L . \tag{12}$$

A sum rule is now constructed: Eqs. (11) and (12) give

$$\frac{d}{dt}\left\langle \sum_{0}^{L-1} h_i \right\rangle = \lambda\mu_0 - \lambda\mu(\langle h_{L-1} - h_L\rangle) \approx \lambda\mu_0 \qquad (13)$$

for $t \ll L^2$ because only the foot of the profile will have evolved. If the profile scales as t^a in the spreading direction, then (13) implies that it should scale as t^{1-a} vertically, giving

$$\langle h_j(t)\rangle = t^a \phi(jt^{a-1}) ,$$

with some smooth scaling function. Scale invariance in (12) demands $a=\frac{1}{2}$, not unexpected, and with $z = jt^{-1/2}$ as a continuous variable, (12) reduces to

$$\phi(z) - z\phi'(z) = 2\lambda\phi''(z)\mu'(\phi'(z)) , \qquad (14)$$

with $\phi(\infty)=0$ and

$$\int_0^\infty \phi(z)\,dz = \lambda\mu_0 = -\lambda\mu(\phi'(0)) \qquad (15)$$

by partial integration of (14). Equation (15), together with (4) and (9), can be checked to be equivalent to the modified Young equation (5). In the Gaussian case, the solution of (14) gives (8), an important test of consistency. With $P(x)=J(1+x^2)^{1/2}$, the inversion of (10) can be examined: $\mu(y)$ increases smoothly from 0 to J as y increases from 0 to ∞. For $0<\mu_0\le J$, Eqs. (14) and (15) have a solution, and the dynamical contact angle is equal to its equilibrium value. It vanishes for $\mu_0=J$, in accordance with Young's equation because the interfacial tension at angle $\theta=0$ is equal to J. There is no precursor film in this case, corresponding to moist spreading, but the scale-invariant profile coming out of (14) and (15) has an asymptote $\phi(z)\to\infty$ as $z\to 0$. In terms of the original variables, this asymptote takes the form of logarithmic factors multiplying the $t^{1/2}$ scale factor:

$$\langle h_0\rangle \approx t^{1/2}(\ln t)^{1/2} , \qquad (16)$$

$$\langle h_i - h_{i+1}\rangle \approx \left[\ln\left(\frac{i+1}{i}\right)\right] t^{1/2}(\ln t)^{-1/2} \quad (i \ll t^{1/2}) .$$

If a contact angle would be estimated from a finite number of $h_0, h_1, \ldots, h_i$, one should find $\theta \sim t^{-1/2} \times(\ln t)^{1/2}$, which may be compared to the generally accepted $\theta\sim t^{-0.3}$ behavior.

Everything said so far can be traced through the continuum model based on the Lifschitz equation provided the function μ is correctly identified. For example, looking for a solution of the form $t^{1/2}\phi(x/t^{1/2})$ gives the equation

$$\phi(z) - z\phi'(z) = 2\lambda\phi''(z)\{1+[\phi'(z)]^2\}^{-1} ,$$

which is (14) with $\mu(t)=\arctan t$. In the continuum theory, the sum-rule condition (15) emerges from the rate of change of the wedge volume.

For $\mu_0 > J$, corresponding to dry spreading, we cannot satisfy the boundary condition (15) because $-\mu(\phi'(0))$ lies in $[0,J]$. The deficiency in the sum rule is concentrated at $z=0$, and we deduce that

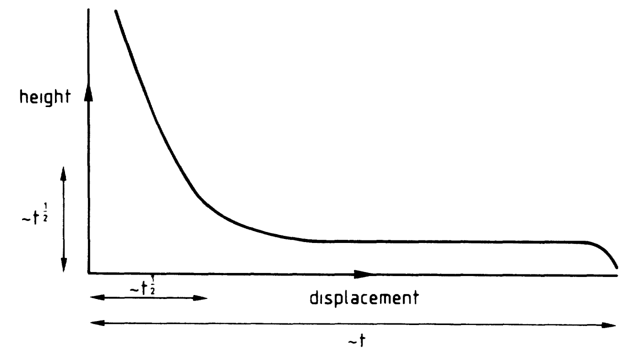

FIG. 3. Spreading profile with precursor film.

$$\langle h_0\rangle \approx \lambda(\mu_0 - J)t , \qquad (17)$$

but

$$\langle h_i\rangle \approx c_i t^{1/2}(\ln t)^{1/2}, \quad 1\le i \ll t^{1/2} .$$

Thus a precursor film is obtained of speed $\lambda(\mu_0 - J)$; the rest of the profile spreads on top of it exactly as for moist wetting (see Fig. 3). Heslot, Fraysse, and Cazabat[4] showed several precursor films stacked on top of one another. This structure may be related to details of the molecular interactions, which are clearly absent from our model. Yet if longer-range interactions with the substrate are included, it appears that layering of the precursor film may or may not occur, depending on the interactions. This can already be seen by adding a single term $\mu_1 h_1$ in our free energy, with $\mu_0 > \mu_1 > 0$ and $\mu_0 + \mu_1 > J$, which is the condition for a precursor film. If $\mu_1 < \mu_0 - J$, then the second layer will spread at a lower speed than the first layer; but if $\mu_1 > \mu_0 - J$ the two layers will be glued together, with a speed $\lambda(\mu_0 + \mu_1 - J)/2$. More details will be published in a forthcoming article.[14]

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