SCALING PROFILES OF A SPREADING DROP FROM LANGEVIN OR MONTE-CARLO DYNAMICS ♮

F. Dunlop[1] and M. Plapp[1]

1. Centre de Physique Théorique *(CNRS – UPR14)* , Ecole Polytechnique, 91128 Palaiseau, France

INTRODUCTION

[1] When a drop spreads on a plane solid surface under the influence of surface tensions, one has a reasonable macroscopic understanding of the shape of the bulk of the drop, and a good understanding of the contact angle, which quickly approaches the equilibrium angle θ satisfying Young's equation

$$\cos\theta\ \sigma_{AB}(\theta) - \sin\theta\ \sigma'_{AB}(\theta) = \sigma_{AW} - \sigma_{BW}\ , \tag{1}$$

where σ_{AB}, σ_{AW} and σ_{BW} are the appropriate surface tensions, and the prime denotes a derivative with respect to the angle. What has been less studied, and is more related to non-equilibrium, is the shape of the foot of the drop, where the interface bends to match the contact angle. There the scale is intermediate between molecular and macroscopic, which justifies a statistical mechanical study.

Such a study was initiated in ref.[1] for a two-dimensional model, where the one-dimensional moving interface was represented by a continuous Solid-On-Solid model with Langevin dynamics. An exact solution was given for a Gaussian Hamiltonian, and a solution derived from a local equilibrium assumption for a generic Hamiltonian. Both solutions were in terms of a deterministic equation for scaled variables, which reminds of a hydrodynamic limit. Hydrodynamic limits for interfaces have been the object of much interest recently[2,3,4], with the common feature that such limits are in terms of motion by curvature, whenever the phases are at coexistence and the respective volumes of the phases are not conserved.

In the next section, we review those results of ref.[1], which deal with the scaling limit as $1 \ll t \ll L^2$. We then use Spohn's study of the mobility to show that those results were indeed motion by curvature taking proper account of anisotropy. The following section is devoted to Monte-Carlo dynamics for the Restricted-Solid-On-Solid model, as applied to the study of spreading in ref.[5], which we also relate here to motion by curvature.

LANGEVIN DYNAMICS OF CONTINUOUS SOLID-ON-SOLID MODELS

Variables $h_0, h_1, ...h_L$ represent the spreading lengths of layers $0, 1, ...L$ on top of the substrate. The Hamiltonian is taken as

$$H(h_0, h_1, ...h_L) = \sum_{i=1}^{L} U(h_{i-1} - h_i) - (\sigma_{AW} - \sigma_{BW})h_0\ , \tag{2}$$

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where $U(x)$ is an even function increasing at least linearly when $x \to +\infty$. The corresponding Langevin dynamics is given by

$$dh_i = -\frac{\partial H}{\partial h_i} dt + (2\beta^{-1})^{1/2}\ d\omega_i \qquad i = 0, 1, ..., L-1\ , \tag{3}$$

where $\omega_i(t)$ are independent Brownian motions, with boundary condition $h_L(t) = 0\ \forall t$, and initial condition $h_i(0) = 0\ \forall i$. As $t \to \infty$, expectation values over the Brownians converge to expectation values computed with the Gibbs measure

$$\exp\Big(-\beta H(h_0, h_1, ...h_L)\Big) \prod_0^{L-1} dh_i\ . \tag{4}$$

The corresponding mean profile is a straight line making an angle θ_e satisfying Young's equation (1). In the Gaussian case, $U(x) = Jx^2$, the Langevin equation (3) is linear and can be solved explicitely at all times, showing relaxation to equilibrium in time $t \sim L^2$. Studying the scaling of the foot of the drop means studying the profile at times $1 \ll t \ll L^2$. There one finds, denoting by E the expectation over the Brownians,

$$\lim_{t\to\infty} \lim_{L\to\infty} t^{-1/2} \mathrm{E} h_{[yt^{1/2}]}(t) = (\sigma_{AW} - \sigma_{BW}) \int_0^\infty \frac{\cos yx}{x^2} \Big(1 - \exp(-x^2)\Big) dx \equiv \psi(y)\ , \tag{5}$$

so that $\psi(y)$ obeys

$$\psi(y) - y\psi'(y) = 2J\psi''(y)\ . \tag{6}$$

For a general $U(x)$, the Langevin equation (3) averaged over the Brownians reads

$$\frac{d}{dt}\mathrm{E}h_i(t) = \mathrm{E}\beta U'(h_{i-1} - h_i) - \mathrm{E}\beta U'(h_i - h_{i+1})\ . \tag{7}$$

At this point, the following ansatz is introduced: $\mathrm{E}U'(h_{i-1} - h_i)$ is taken as a function of $\mathrm{E}(h_{i-1} - h_i)$ up to an error $O(t^{-1})$, and this function is the same that gives the Gibbs average $\langle U'(h_{i-1} - h_i)\rangle$ as a function of $\langle h_{i-1} - h_i\rangle$ in the measure (4) with boundary conditions such that $\langle h_{i-1} - h_i\rangle$ is prescribed.

This ansatz is a weak but precise form of the following conjecture: as $t \to \infty$, a local equilibrium is approached; this local equilibrium can be thought of as a measure for local height differences; the conjecture is that this measure is nothing but the Gibbs measure corresponding to the average local slope.

The ansatz is convenient for computing. Indeed let $c(\tau)$ be the function defined by

$$\int_{-\infty}^{+\infty} dx(\tau - x) \exp\Big(-\beta U(x) + \beta c(\tau)x\Big) = 0\ . \tag{8}$$

Then applying the ansatz gives

$$\frac{d}{dt}\mathrm{E}h_i(t) = c(\mathrm{E}(h_{i-1} - h_i)) - c(\mathrm{E}(h_i - h_{i+1})) + O(t^{-1})\ . \tag{9}$$

The ansatz and eq.(9) do not depend in an essential way upon boundary conditions. A scaling assumption can also be made, depending upon boundary conditions, like the existence of

$$\psi(y) \equiv \lim_{t\to\infty} \lim_{L\to\infty} t^{-1/2} \mathrm{E} h_{[yt^{1/2}]}(t)\ . \tag{10}$$

Then $\psi(y)$ is found to obey

$$\psi(y) - y\psi'(y) = c'(\psi'(y))\psi''(y)\ . \tag{11}$$

In the next section, we show that eq.(9) corresponds to motion by curvature discretised in space, and eq.(11) to a scaling solution of motion by curvature, in both cases taking anisotropy into account. This gives a strong support, of course not a proof, to the conjecture.

MOTION BY CURVATURE

Starting point for this study is the Lifshitz equation which describes the time evolution of an interface in a system with a second-order phase transition. The normal component of velocity is given in terms of the mean curvature $K = R^{-1}$ by $v_n = \lambda \cdot K$ where λ is a constant proportional to the surface tension. This equation, stated for the isotropic case, can be generalized to take care of the anisotropy of σ: Let the (one-dimensional) interface be represented by a curve $C(l)$ parametrized by arc length. Then the curvature $K(l)$ and the angle $\theta(l)$ between the tangent at C and the x-axis can be expressed as functions of l, and we have $K(l) = d\theta(l)/dl$. We start from the formula for the surface free energy

$$F = \int_C \sigma(\theta(l))dl$$

and compute the variation of F under a small deformation $\delta\mathbf{r}(l)$:

$$\delta F = \int_C (\sigma + \sigma'') \cdot K \cdot dl \cdot \delta\mathbf{r} \cdot \hat{\mathbf{n}} \ , \tag{12}$$

where $\hat{\mathbf{n}}(l)$ is the unitary vector normal to the interface. The linear response argument which is the basis of the Lifshitz equation then gives

$$v_n = -\mu \cdot (\sigma + \sigma'') \cdot K \ , \tag{13}$$

where the the coefficient $\mu(\theta)$ called the mobility gives a time scale. As boundary conditions, we can have fixed points or fixed contact angles with walls.

Returning to the problem of the preceding section, and loking for solutions of eq. (13) scaling as $h(x,t) = t^{1/2} \cdot \psi(x \cdot t^{-1/2})$ we get

$$\psi(y) - y\psi'(y) = \mu \cdot (\sigma + \sigma'') \cdot (\cos\theta)^2 \cdot \psi'' \ . \tag{14}$$

Next, we remark that the stiffness $(\sigma + \sigma'')$ gives the fluctuations at equilibrium, which can be computed using eq. (8):

$$(\sigma + \sigma'') \cdot (\cos\theta)^3 = \frac{\int dx \exp\Big(-\beta U(x) + \beta c(\tan\theta)x\Big)}{\beta \int dx(\tan\theta - x)^2 \exp\Big(-\beta U(x) + \beta c(\tan\theta)x\Big)} = c'(\tan\theta) \ . \tag{15}$$

Finally, using[3] $\mu = \cos\theta$ in Langevin dynamics, eqs. (11) and (14) are found to be exactly the same. Similarly, we can rewrite eq. (13) using the identities $v_n = \cos\theta \cdot \dot{h}$, $\mu = \cos\theta$, $K = h'' \cdot (\cos\theta)^3$ and (15) as

$$\dot{h} = c'(\tan\theta) \cdot h'' \ . \tag{16}$$

But this, in the discrete case, is just the limit of eq. (9) for smooth interfaces. Hence we have shown that generalized motion by curvature and continuous Langevin dynamics with a local equilibrium assumption give the same results for smooth solutions, and have the same scaling limit when boundary conditions permit.

We can furthermore use motion by curvature to achieve a better understanding of interface motion at a macroscopic level. Suppose that we stick to a point of an interface, following motion by curvature, our point always moving in the direction of the local normal. We can develop an evolution equation for the curvature, similar to advective derivation in hydrodynamics. We find for the isotropic case, using the Lifshitz equation,

$$\frac{d}{dt}K = \lambda\left(K^3 + \frac{\partial^2}{\partial l^2}K\right) , \tag{17}$$

a nonlinear diffusion equation. This accounts very well for the different features of motion by curvature. The first term causes interface regions of constant curvature to shrink, whereas the second term describes a diffusion of curvature towards flat interface regions, as observed for interfaces near a wall or in a corner. For the anisotropic case the equation is slightly more complicated, but the structure is the same.

MONTE-CARLO DYNAMICS OF RESTRICTED-SOLID-ON-SOLID MODELS

We now return to the usual Solid-On-Solid model, where the variables $h_0 ... h_i ... h_l$ represent the height of the spreading phase on top of the plane solid surface, here a straight solid line in two-dimensional space. The allowed configurations are $\mathbf{h} = \{h_i\}_{i=0}^{\infty} \in Z^Z$ such that $\forall i \geq 0, \quad h_i \geq 0$ and $h_{i+1} - h_i \in \{-1, 0, 1\}$, and

$$\forall i \geq 0, \qquad h_i = 0 \Longrightarrow h_{i+1} = 0 \qquad \text{and} \qquad \max\{i | h_i > 0\} = l \ < \ \infty$$

The last condition means taking the foot of a single drop. The Hamiltonian is taken as

$$H(\mathbf{h}) = a_0 h_0 + \sum_{i=0}^{\infty}\Big(J|h_{i+1} - h_i| + (J - \sigma_{AW} + \sigma_{BW})(1 - \delta_{h_i,0})\Big) . \tag{18}$$

Letting $\mathbf{h} = (\mathbf{h}^o, \mathbf{h}^e)$ with $\mathbf{h}^o = \{h_{2j+1}\}_{j=0}^{\infty}$ and $\mathbf{h}^e = \{h_{2j}\}_{j=0}^{\infty}$, the discrete time dynamics is defined by the transition probabilities

$$Pr((\mathbf{h}^o, \mathbf{h}^e) \to (\mathbf{h}'^o, \mathbf{h}^e)) = \frac{1}{2}\frac{e^{-\beta H(\mathbf{h}'^o, \mathbf{h}^e)}}{\sum_{\mathbf{h}''^o} e^{-\beta H(\mathbf{h}''^o, \mathbf{h}^e)}}$$

$$Pr((\mathbf{h}^o, \mathbf{h}^e) \to (\mathbf{h}^o, \mathbf{h}'^e)) = \frac{1}{2}\frac{e^{-\beta H(\mathbf{h}^o, \mathbf{h}'^e)}}{\sum_{\mathbf{h}''^e} e^{-\beta H(\mathbf{h}^o, \mathbf{h}''^e)}}$$

where $\mathbf{h}'^o \neq \mathbf{h}^o$ and $\mathbf{h}'^e \neq \mathbf{h}^e$, and where the factors 1/2 correspond to the probability of either the odd sites, or the even sites being updated. Scaling profiles of the foot of a spreading drop have been obtained numerically within this model[5]: the initial condition was a straight line $h_i \simeq h_0 - i \tan\theta_0$ making an angle θ_0 larger than the equilibrium angle θ_e obeying eq.(1). At times $1 \ll t \ll h_0^2$, a scaling limit was obtained as

$$t^{-1/2}\Big(h_{l_0 + xt^{1/2}}(t) - h_{l_0 + xt^{1/2}}(0)\Big) \longrightarrow \Phi(x) \qquad \text{as} \qquad t \to \infty , \tag{20}$$

This scaling limit looks like motion by curvature, with boundary conditions such that curvature diffuses away from the original angle at l_0. In order to make a quantitative comparison, we estimate the mobility from the linear response: consider

$$H_\epsilon(\mathbf{h}) = \sum_{i=0}^{L-1}\Big(J|h_{i+1} - h_i| + c(\tan\theta)(h_{i+1} - h_i)\Big) + \epsilon\chi(t \geq 0)\sum_{i=0}^{L} h_i , \tag{21}$$

and run the associated dynamics from $t = -\infty$ up to $t = 0$ with the boundary condition $h_0 = 0$, and then with free boundary condition for $t > 0$. Then

$$\mu(\theta) = \cos\theta \lim_{L\to\infty} \frac{1}{L} \sum_{i=0}^{L-1} \lim_{\epsilon\to 0} \epsilon^{-1} \lim_{t\to+\infty} \Big(\mathrm{E}h_i(t+1) - \mathrm{E}h_i(t) \Big) \ . \tag{22}$$

An approximation to the mobility is obtained by taking (22) at $t = 0$, where the formula can be evaluated exactly from the Gibbs measure, giving

$$\mu(\theta) \simeq \cos\theta \ \frac{2e^{-2\beta J} + \frac{1}{2}e^{-\beta J}\Big(e^{\beta c(\tan\theta)} + e^{-\beta c(\tan\theta)}\Big)}{\Big(1 + e^{-\beta J}\Big(e^{\beta c(\tan\theta)} + e^{-\beta c(\tan\theta)}\Big)\Big)^2} \ , \tag{23}$$

with $c(.)$ defined by

$$\tau = \frac{e^{-\beta J}\Big(e^{\beta c(\tau)} - e^{-\beta c(\tau)}\Big)}{1 + e^{-\beta J}\Big(e^{\beta c(\tau)} + e^{-\beta c(\tau)}\Big)} \ . \tag{24}$$

This value of the mobility gives at least the right leading order at low temperatures. We have integrated numerically the corresponding equation for motion by curvature,

$$\dot{h} = \frac{\mu(\theta)}{\cos\theta} c'(\tan\theta) h'' \ , \tag{25}$$

and also the Monte-Carlo dynamics associated to (18), with various boundary and initial conditions, and found a good agreement even for long times. As a notable feature, the dynamics of wetting in a right-angle corner, with contact angle θ_1 on one boundary and θ_2 on the other, shows spreading if $\theta_1 + \theta_2 < \pi/2$ and shrinking if $\theta_1 + \theta_2 > \pi/2$.

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