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Conservative Langevin Dynamics of Solid-on-Solid Interfaces

Pierre Collet,[1] François Dunlop,[1,2] and Thierry Gobron[3]

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We study the dynamics of an interface between two phases in interaction with a wall in the case when the evolution is dominated by surface diffusion. For this, we use an SOS model governed by a conservative Langevin equation and suitable boundary conditions. In the partial wetting case, we study various scaling regimes and show oscillatory behavior in the relaxation of the interface toward its equilibrium shape. We also consider complete wetting and the structure of the precursor film.

KEY WORDS: Wetting; surface diffusion; conservative Langevin dynamics; solid-on-solid model.

1. INTRODUCTION

In recent years, a large amount of work, experimental as well as theoretical, has been done on the physics of wetting phenomena. Various treatments, mostly phenomenological, have been proposed to grasp some understanding of the dynamics. Recently, simplified models have been proposed which are amenable to the methods of statistical mechanics.[(1)]

The aim of the present work is to extend this kind of approach to the case of a conservative dynamics. A direct application of such a model can be found in the study of polycrystalline surfaces which develop grooves around grain boundaries, and whose evolution is dominated by surface diffusion.[(5)]

[1] Centre de Physique Théorique (CNRS-UPR14), Ecole Polytechnique, 91128 Palaiseau, France.

[2] Groupe de Physique Statistique, Université de Cergy-Pontoise, 95806 Cergy-Pontoise, France.

[3] Laboratoire de Physique de la Matière Condensée (CNRS-URA D1254), Ecole Polytechnique, 91128 Palaiseau, France.

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In the next section, we describe our model given by a Langevin equation for a solid-on-solid (SOS) type model. We derive the dynamics mostly by requiring that it should converge to the correct equilibrium measure (in the partial wetting case). As a consequence, we get a connection between the noise correlations induced by the conservation prescription and the structure of the drift term.

In Section 3, we study the simple case of a Gaussian interaction between the layers. In the limit of infinite volume, we show that for time $t \ll L^4$, L being the size of the system, the typical profile scales as $t^{1/4}$ with an oscillating shape, as for the surface diffusion equation previously devised by Mullins[5] and mathematically studied by Baras *et al.*[2]

In Section 4, we extend the results to the case of a general interaction, which we study under the hypothesis of local equilibrium. In particular, we show that the surface diffusion equation that we obtain under this hypothesis is the same as the one derived from a more phenomenological basis, along the lines proposed by Spohn.[7]

In the last section, we investigate the complete wetting case in a more heuristic fashion and show various new features related to the conservative character of the dynamics.

2. CONSERVATIVE LANGEVIN DYNAMICS

Let us consider an interface between two phases in a tube in two dimensions and describe it using some SOS-type model. We divide arbitrarily our system into $L+1$ layers parallel to the walls of the tube and assume that the interface crosses each layer i, $i \in \{0,..., L\}$, at a definite position h_i, thus neglecting possible overhangs. The energy of this interface can be written as

$$H(h_0,..., h_L) = \sum_{i=1}^{L} U(h_{i-1} - h_i) - \sum_{i=0}^{L} \mu_i h_i \tag{2.1}$$

where $U(x)$ is an even function, increasing at least linearly for $x > 0$, and $\{\mu_i\}_{i \in \{0,..., L\}}$ is a distribution of chemical potentials representing the interaction of each layer with the walls. Obviously enough, the fact that the dynamics we consider is conservative means that if we take an initial condition such that $\sum_{i=0}^{L} h_i = 0$, this constraint will be obeyed at all times; this has as a direct consequence that the chemical potentials μ_i are relevant up to a constant and for instance can be replaced in (2.1) by another distribution $\tilde{\mu}_i$ with zero average:

$$\tilde{\mu}_i = \mu_i - \frac{1}{L+1} \sum_{j=0}^{L} \mu_j \tag{2.2}$$

The finite-volume canonical Gibbs measure, to which the system should converge as time goes to infinity, has a density with respect to the Lebesgue measure, namely

$$\mathbb{P}(h_0, h_1,..., h_L) = \frac{1}{\mathscr{Z}} \exp[-\beta H(h_0, h_1,..., h_L)]\, \delta\left(\sum_{i=0}^{L} h_i\right) \tag{2.3}$$

The partition function $\mathscr{Z}$ normalizing the probability can be finite only if H is bounded from below, which requires a condition such as

$$\left|\sum_{i=0}^{j} \tilde{\mu}_i\right| < \lim_{x \to +\infty} \frac{U(x)}{x} = \lim_{x \to +\infty} U'(x) \leqslant +\infty \quad \forall j \tag{2.4}$$

where we assumed for simplicity that both limits in (2.4) exist.

In the case of contact interactions with the walls,

$$\mu_i = \mu_0 \delta_{i,0} + \mu_L \delta_{i,L}$$

the canonical Gibbs measure (2.3) describes an interface with fluctuations $\mathcal{O}(L^{1/2})$ around a Wulff shape.[3]

In order to set up a conservative dynamics which converges to the correct Gibbs measure (2.3), we start from a general form for the Langevin equation and look for sufficient conditions. Assume that $w_0(t), w_1(t),...,$ $w_L(t)$ are independent Wiener processes and consider the system of stochastic differential equations

$$dh_i(t) = F_i(\mathbf{h}(t))\, dt + \left(\frac{2}{\beta}\right)^{1/2} \sum_{j=0}^{L} \sigma_{ij}\, dw_j(t) \tag{2.5}$$

where the functions $F_i(\mathbf{x})$ are defined for $\mathbf{x} \in \mathbb{R}^{L+1}$ and $\boldsymbol{\sigma}$ is an $(L+1) \times (L+1)$ matrix with constant coefficients. The solution of Eq. (2.5) is a Markov process whose probability density $\mathbb{P}(\mathbf{h}, t)$ satisfies the Fokker–Planck equation:

$$\begin{aligned} \frac{\partial \mathbb{P}(\mathbf{h}, t)}{\partial t} = & -\sum_{i=0}^{L} \frac{\partial}{\partial h_i} (F_i(\mathbf{h})\, \mathbb{P}(\mathbf{h}, t)) \\ & + \frac{1}{\beta} \sum_{i,j,k=0}^{L} \sigma_{ik}\sigma_{jk} \frac{\partial^2}{\partial h_i\, \partial h_j} \mathbb{P}(\mathbf{h}, t) \end{aligned} \tag{2.6}$$

In order to check (2.6), it suffices to take any function g on $\mathbb{R}^{L+1}$ twice continuously differentiable with compact support, and define the process $\xi(t) = g(\mathbf{h}(t))$ whose stochastic differential is given by the Ito formula[8]:

$$d\xi(t) = \left\{ \sum_{i=0}^{L} \frac{\partial g(\mathbf{h}(t))}{\partial h_i} F_i(\mathbf{h}) + \frac{1}{\beta} \sum_{i,j,k=0}^{L} \frac{\partial^2 g(\mathbf{h}(t))}{\partial h_i \partial h_j} \sigma_{ik}\sigma_{jk} \right\} dt$$
$$+ \left(\frac{2}{\beta}\right)^{1/2} \sum_{i,k=0}^{L} \frac{\partial g(\mathbf{h}(t))}{\partial h_i} \sigma_{ik}\, dw_k(t) \tag{2.7}$$

By taking the expectation value in the integral form of (2.7), the third term in the right-hand side vanishes. Using

$$\mathbb{E}(g(\mathbf{h}(t))) = \int \prod_{i=0}^{L} dh_i\, \mathbb{P}(\mathbf{h}, t)\, g(\mathbf{h}) \tag{2.8}$$

and integrating by parts leads to the Fokker–Planck equation (2.6).

The condition that the Gibbs distribution (2.3) be the equilibrium distribution for the Fokker–Planck equation determines the functions $F_i(\mathbf{h})$ up to a divergence-free vector. We make the following choice:

$$F_i(\mathbf{h}) = -\sum_{j,k=0}^{L} \sigma_{ik}\sigma_{jk} \frac{\partial H(\mathbf{h})}{\partial h_j} \tag{2.9}$$

The conservation of volume in Eq. (2.5) then appears to be a consequence of taking a conservative noise:

$$\sum_{i=0}^{L} \sigma_{ik} = 0 \quad \forall k \in \{0,..., L\} \tag{2.10}$$

This choice does not fully prescribe Eq. (2.5) yet. Assuming that the random part in (2.5) is due only to local exchange between neighboring layers, we get an expression for the matrix $\boldsymbol{\sigma}$:

$$\boldsymbol{\sigma} = \begin{pmatrix} 1 & & & \\ -1 & \ddots & & \\ & \ddots & 1 & 0 \\ & & -1 & 0 \end{pmatrix} \tag{2.11}$$

and the conservative Langevin equation explicitly reads

$$\dot{h}_0 = -2U'(h_0 - h_1) + U'(h_1 - h_2) + \mu_0 - \mu_1 + \left(\frac{2}{\beta}\right)^{1/2} \dot{w}_{1/2}$$
$$\dot{h}_1 = 3U'(h_0 - h_1) - 3U'(h_1 - h_2) + U'(h_2 - h_3)$$
$$- \mu_0 + 2\mu_1 - \mu_2 + \left(\frac{2}{\beta}\right)^{1/2} (\dot{w}_{3/2} - \dot{w}_{1/2})$$

$$\dot{h}_2 = -U'(h_0 - h_1) + 3U'(h_1 - h_2) - 3U'(h_2 - h_3) + U'(h_3 - h_4)$$
$$-\mu_1 + 2\mu_2 - \mu_3 + \left(\frac{2}{\beta}\right)^{1/2} (\dot{w}_{5/2} - \dot{w}_{3/2}) \tag{2.12}$$
$$\vdots$$

where we have labeled the Wiener processes with half-integers to get a more symmetric expression. Using more compact notations, we can write (2.12) as

$$d\mathbf{h}(t) = -\boldsymbol{\sigma}\boldsymbol{\sigma}^\dagger(\boldsymbol{\sigma}\mathbf{U}'(\boldsymbol{\sigma}^\dagger \mathbf{h}) - \boldsymbol{\mu})\, dt + \left(\frac{2}{\beta}\right)^{1/2} \boldsymbol{\sigma}\, d\mathbf{w}(t) \tag{2.13}$$

where $\mathbf{U}'(\mathbf{x})$ is the vector whose ith component is $U'(x_i)$.

3. THE GAUSSIAN MODEL

In this section we investigate the dynamical behavior of the model when the function $U(x)$ is a parabola

$$U(x) = \frac{J}{2} x^2 \tag{3.1}$$

In this particular case, the Langevin equation (2.13) can be cast in the form

$$d\mathbf{h}(t) = (-J(\boldsymbol{\sigma}\boldsymbol{\sigma}^\dagger)^2\, \mathbf{h} + \boldsymbol{\sigma}\boldsymbol{\sigma}^\dagger \boldsymbol{\mu})\, dt + \left(\frac{2}{\beta}\right)^{1/2} \boldsymbol{\sigma}\, d\mathbf{w}(t) \tag{3.2}$$

The solution is easily found, given a flat initial profile:

$$\mathbf{h}(0) = \mathbf{0}$$

We get

$$\mathbf{h}(t) = (1 - e^{-J(\boldsymbol{\sigma}\boldsymbol{\sigma}^\dagger)^2 t})\, \mathbf{h}^e + \left(\frac{2}{\beta}\right)^{1/2} \int_0^t e^{-J(\boldsymbol{\sigma}\boldsymbol{\sigma}^\dagger)^2 t}\, \boldsymbol{\sigma}\, d\mathbf{w}(t) \tag{3.3}$$

The components of the equilibrium mean profile $\mathbf{h}^e$ are given by

$$h_k^e = h_0 - \frac{1}{J} \sum_{l=0}^{k-1} (k - l)\, \tilde{\mu}_l \tag{3.4}$$

where the $\tilde{\mu}_l$ are defined as in (2.2) and the value of h_0 is determined from the value of the (preserved) volume:

$$h_0 = \frac{1}{J} \sum_{l=0}^{L-1} \frac{(L-l)(L-l+1)}{2(L+1)} \tilde{\mu}_l \tag{3.5}$$

In order to push the computation a little bit forward, we need to compute the eigenvalues of the matrix $(\sigma\sigma^\dagger)^2$, which are

$$\lambda_q = 16 \sin^4\left(\frac{\pi q}{2(L+1)}\right), \qquad q \in \{0,..., L\} \tag{3.6}$$

The components of the associated normalized eigenvectors are

$$\varphi_k^0 = \frac{1}{(L+1)^{1/2}}; \qquad \varphi_k^q = \left(\frac{2}{L+1}\right)^{1/2} \cos\left[\frac{\pi q(2k+1)}{2(L+1)}\right], \quad q \in \{1,..., L\} \tag{3.7}$$

The mean profile averaged over the Brownians has components

$$\mathbb{E}(h_k(t)) = \sum_{q=1}^{L} \left(\sum_{l=0}^{L} \varphi_l^q h_l^e\right)(1 - e^{-J\lambda_q t})\, \varphi_k^q \tag{3.8}$$

while its variance is

$$\mathbb{E}(h_j(t)\, h_k(t)) - \mathbb{E}(h_j(t))\, \mathbb{E}(h_k(t)) = \sum_{q=1}^{L} \frac{1}{\beta J \sqrt{\lambda_q}} (1 - e^{-J\lambda_q t})\, \varphi_j^q \varphi_k^q \tag{3.9}$$

In the case of a contact interaction with the walls of the container, the chemical potential can be taken as zero except in the first and last layers:

$$\mu_0 = \mu_L = \mu, \qquad \mu_{i, i \neq 0, L} = 0 \tag{3.10}$$

In that particular case, the shape of the equilibrium mean profile is a parabola,

$$h_k^e = \frac{\mu}{J}\left[\frac{L(L-1)}{6(L+1)} - \frac{k(L-k)}{L+1}\right] \tag{3.11}$$

and the infinite-volume limit of Eqs. (3.8)–(3.9) can be cast in an integral form as

$$\lim_{L \to \infty} \mathbb{E}(h_k(t)) = \frac{\mu}{\pi J} \int_0^{\pi/2} dx\, (1 - e^{-16J \sin^4(x) t})\, \frac{\cos(x)}{\sin^2(x)} \cos[(2k+1)\, x] \tag{3.12}$$

$$\lim_{L \to \infty} [\mathbb{E}(h_j(t)\, h_k(t)) - \mathbb{E}(h_j(t))\, \mathbb{E}(h_k(t))]$$

$$= \frac{1}{\beta \pi J} \int_0^{\pi/2} dx\, \frac{1 - e^{-16J \sin^4(x) t}}{\sin^2(x)} \cos[(2j+1)\, x] \cos[(2k+1)\, x] \tag{3.13}$$

In order to study the behavior of the profile for times long enough but still small with respect to the equilibrium time, we need to scale the distances by a factor $t^{1/4}$ and study the limit

$$\lim_{t \to \infty} \lim_{L \to \infty} t^{-1/4} \mathbb{E}(h_{[y t^{1/4}]}) = -\frac{\mu}{J^{3/4}} \mathscr{X}(J^{-1/4} y) \tag{3.14}$$

where

$$\mathscr{X}(u) = -\frac{2}{\pi} \int_0^\infty dz\, \frac{1 - e^{-z^4}}{z^2} \cos(uz) \tag{3.15}$$

The function $\mathscr{X}$ is the explicit solution of the linearized surface diffusion equation (34) of ref. 5, namely

$$\mathscr{X}^{(4)}(u) = -\tfrac{1}{4}\{\mathscr{X}(u) - u\mathscr{X}'(u)\}, \qquad u > 0 \tag{3.16a}$$

together with the boundary conditions

$$\begin{aligned} \mathscr{X}(0_+) &= \frac{-1}{\sqrt{2}\, \Gamma(5/4)}, \qquad & \mathscr{X}'(0_+) &= 1 \\ \mathscr{X}''(0_+) &= \frac{-1}{\sqrt{2}\, \Gamma(3/4)}, \qquad & \mathscr{X}'''(0_+) &= 0 \end{aligned} \tag{3.16b}$$

In order to evaluate $\mathscr{X}(u)$, we consider the real function f defined by $f(\infty) = f'(\infty) = 0$ and

$$f''(x) = g(x) = \int_{-\infty}^{\infty} e^{ixy} e^{-y^4}\, dy \tag{3.17}$$

and determine its behavior for large x.

For $x > 0$ we change the variable in the integral to $y = x^{1/3} z$ and obtain

$$g(x) = x^{1/3} \int_{-\infty}^{\infty} e^{x^{4/3}(iz - z^4)}\, dz \tag{3.18}$$

We are now going to use the stationary phase method to estimate the above integral. The derivative of the phase has three simple zeros which are the three cubic roots of the number $i/4$. Among these three zeros, only two give a decreasing behavior to the integral, namely

$$z_{\pm} = \eta(\pm\sqrt{3} + i) \qquad \text{with} \quad \eta = 2^{-5/3} \tag{3.19}$$

We choose a contour parallel to the real axis and passing through the two previous points, namely $z = u + i\eta$. On this line the phase in the integral is given by

$$Q(u) \equiv iz - z^4 = -\eta + \eta^4 + 6u^2\eta^2 - u^4 + i[u(1 + 4\eta^3) - 4\eta u^3] \tag{3.20}$$

Moreover, at the critical points we have $Q(\pm\eta\sqrt{3}) = 3iz_{\pm}/4$ and $Q''(\pm\eta\sqrt{3}) = -12z_{\pm}^2$. By a standard steepest descent argument we obtain for large z

$$g(x) = \frac{2^{5/3}\sqrt{\pi}}{\sqrt{6}} x^{-1/3} e^{-3x^{4/3}2^{-11/3}} \cos(3^{3/2}2^{-11/3}x^{4/3} - \pi/6) + e^{-3x^{4/3}2^{-11/3}} \mathcal{O}(x^{-5/3}) \tag{3.21}$$

We now observe that if γ is a real number and ρ is a complex number with negative real part, we have for large x, using integration by parts,

$$\int_{+\infty}^{x} s^{\gamma} e^{\rho s^{4/3}}\, ds = \frac{3x^{\gamma - 1/3}}{4\rho} e^{\rho x^{4/3}} + e^{\Re(\rho) x^{4/3}} \mathcal{O}(x^{\gamma - 5/3}) \tag{3.22}$$

Therefore, integrating twice and using the boundary conditions at infinity, we obtain for large x

$$f(x) = -\frac{8x^{-1}}{(6\pi)^{1/2}} e^{-3x^{4/3}2^{-11/3}} \sin(3^{3/2}2^{-11/3}x^{4/3}) + e^{-3x^{4/3}2^{-11/3}} \mathcal{O}(x^{-7/3}) \tag{3.23}$$

Hence the long-time behavior of the profile in the range $t \ll L^4$ is dominated by an oscillating term with a rapidly decreasing amplitude.[6] For large y, we have

$$\lim_{t \to \infty} \lim_{L \to \infty} t^{-1/4} \mathbb{E}(h_{[yt^{1/4}]}) \simeq \frac{4\mu y^{-1}}{(6\pi J)^{1/2}} e^{-3J^{-1/3}y^{4/3}2^{-11/3}} \sin(3^{3/2}2^{-11/3}J^{-1/3}y^{4/3}) \tag{3.24}$$

An analogous reasoning can be applied to Eq. (3.13) and one finds that the mean amplitude of the fluctuations scales as $t^{1/8}$ in this regime, namely

$$\lim_{L \to \infty} [\mathbb{E}(h_j(t)\, h_k(t)) - \mathbb{E}(h_j(t))\, \mathbb{E}(h_k(t))] \approx t^{1/4} \qquad \text{as} \quad t \to \infty$$

4. LOCAL EQUILIBRIUM AND SURFACE DIFFUSION

At large times, we expect the profile to become smooth in average, and fluctuations to follow a Gibbsian local equilibrium. Assuming that these two assumptions hold true, we show that the corresponding hydrodynamic regime is described by surface diffusion, in agreement with a linear response argument.[7] This is analogue to the heuristic derivation of motion by curvature in the nonconservative Langevin dynamics.[4]

Before doing so, we recall some facts about one-dimensional interfaces at equilibrium in SOS models, in the grand canonical ensemble, with boundary conditions fixing the average slope. The free energy per unit length of interface is defined as usual by

$$\sigma(\theta) = -\frac{1}{\beta} \lim_{L \to \infty} \frac{\cos\theta}{L} \log \mathscr{Z}_\theta$$

with, similar to (2.3),

$$\mathscr{Z}_\theta = \int \exp[-\beta H(h_0, h_1, ..., h_L)]\, \delta(h_0)\, \delta(h_L - L\tan\theta) \prod_{i=0}^{L} dh_i$$

It is convenient to replace the boundary condition fixing the average slope by a slope chemical potential. This change of ensemble leads only to logarithmic corrections in the total free energy and does not modify $\sigma(\theta)$. The chemical potential $c(\tan\theta)$ conjugate to the desired slope can be defined for suitable U by

$$\int_{-\infty}^{+\infty} dx\, (x - \tan\theta) \exp\{-\beta[U(x) - c(\tan\theta)\, x]\} = 0 \tag{4.1}$$

Dropping the constraint $\delta(h_L - L\tan\theta)$ then leaves a random walk with independent steps, so that the free energy and local expectation values can be computed from the step distribution:

$$\sigma(\theta) = -\frac{1}{\beta} \cos\theta \log \int_{-\infty}^{+\infty} dx \exp\{-\beta[U(x) - c(\tan\theta)(x - \tan\theta)]\} \tag{4.2}$$

$$\langle U'(h_{i-1} - h_i)\rangle_\theta = c(\tan\theta) = \sigma\sin\theta + \sigma'\cos\theta \tag{4.3}$$

where σ' is the derivative of σ with respect to θ.

Let us now return to the dynamical problem, and take averages in (2.13) to obtain

$$\mathbb{E}\dot{\mathbf{h}} = -\boldsymbol{\sigma}\boldsymbol{\sigma}^\dagger\boldsymbol{\sigma}\mathbb{E}\mathbf{U}'(\boldsymbol{\sigma}^\dagger\mathbf{h}) \tag{4.4}$$

where $\mathbf{U}'(\mathbf{x})$ is the vector whose ith component is $U'(x_i)$. We then get an approximation to $\mathbb{E}U'(h_{i-1}-h_i)$, using the equilibrium Gibbs measure for a straight interface of slope $\mathbb{E}(h_{i-1}-h_i)$. Indeed, convergence to local Gibbs equilibrium applied to the observable $U'(h_{i-1}-h_i)$ means, using (4.3),

$$\mathbb{E}U'(h_{i-1}-h_i)-c(\mathbb{E}(h_{i-1}-h_i))\to 0 \qquad \text{as} \quad t\to\infty \tag{4.5}$$

More precisely, we assume

$$\boldsymbol{\sigma}\boldsymbol{\sigma}^{\dagger}\boldsymbol{\sigma}\mathbb{E}\mathbf{U}'(\boldsymbol{\sigma}^{\dagger}\mathbf{h})=\boldsymbol{\sigma}\boldsymbol{\sigma}^{\dagger}\boldsymbol{\sigma}\mathbf{c}(\boldsymbol{\sigma}^{\dagger}\mathbb{E}\mathbf{h})+\mathcal{O}(t^{-1}) \tag{4.6}$$

where $\mathbf{c}(\mathbf{x})$ is the vector whose ith component is $c(x_i)$, and obtain that the averages $\mathbb{E}\mathbf{h}$ follow approximately a simple deterministic equation,

$$\mathbb{E}\dot{\mathbf{h}}=-\boldsymbol{\sigma}\boldsymbol{\sigma}^{\dagger}\boldsymbol{\sigma}\mathbf{c}(\boldsymbol{\sigma}^{\dagger}\mathbb{E}\mathbf{h})+\mathcal{O}(t^{-1}) \tag{4.7}$$

or

$$\begin{aligned}\mathbb{E}\dot{h}_i= &-c(\mathbb{E}h_{i-2}-\mathbb{E}h_{i-1})+3c(\mathbb{E}h_{i-1}-\mathbb{E}h_i)\\ &-3c(\mathbb{E}h_i-\mathbb{E}h_{i+1})+c(\mathbb{E}h_{i+1}-\mathbb{E}h_{i+2})+\mathcal{O}(t^{-1})\end{aligned}$$

A further smoothness assumption gives

$$\begin{aligned}\mathbb{E}\dot{h}_i=\, &c'((\mathbb{E}h_{i-2}-\mathbb{E}h_i)/2)(-\mathbb{E}h_{i-2}+2\mathbb{E}h_{i-1}-\mathbb{E}h_i)\\ &-2c'((\mathbb{E}h_{i-1}-\mathbb{E}h_{i+1})/2)(-\mathbb{E}h_{i-1}+2\mathbb{E}h_i-\mathbb{E}h_{i+1})\\ &+c'((\mathbb{E}h_i-\mathbb{E}h_{i+2})/2)(-\mathbb{E}h_i+2\mathbb{E}h_{i+1}-\mathbb{E}h_{i+2})+\mathcal{O}(t^{-1})\end{aligned}$$

or, in sloppy notation,

$$\mathbb{E}\dot{h}=(c'(\mathbb{E}h')\,\mathbb{E}h'')''+\mathcal{O}(t^{-1}) \tag{4.8}$$

We shall show that this is surface diffusion, or linear response to a gradient of curvature, modified by anisotropy. The interface is now taken as a four-times differentiable curve $C(l)$ parametrized by arc length. The associated free energy functional is defined as

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

where $\sigma(\theta)$ is the free energy per unit length of a straight interface of slope $\tan\theta$, as computed in (4.2).

The variation of F under a small deformation $\delta\mathbf{r}(l)$ is

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

where K is the curvature and $\hat{\mathbf{n}}(l)$ is the unitary vector normal to the interface. The current is the basic linear response in conservative dynamics,

$$J(l)=-\mu(\theta)\frac{d}{dl}\frac{\delta F}{\delta(\delta\mathbf{r}(l)\cdot\hat{\mathbf{n}})}=\mu(\theta)\frac{d}{dl}((\sigma+\sigma'')\, K) \tag{4.9}$$

where the surface mobility $\mu(\theta)$ gives the time scale. The speed of the interface measured along the normal is then obtained from the conservation law:

$$v_n=-\frac{d}{dl}J=\frac{d}{dl}\mu(\theta)\frac{d}{dl}((\sigma+\sigma'')\, K) \tag{4.10}$$

In order to compare to (4.8), we change to h and x variables, using $v_n=\cos\theta\,\dot{h}$ to get an equation for $h(t,x)$,

$$\dot{h}=\frac{\partial}{\partial x}\left\{\mu(\theta)\cos\theta\frac{\partial}{\partial x}((\sigma+\sigma'')\, K)\right\} \tag{4.11}$$

which agrees with (4.8) if $\mu(\theta)=(\cos\theta)^{-1}$, because $K=h''(\cos\theta)^3$ and $(\sigma+\sigma'')(\cos\theta)^3=c'(\tan\theta)$. One should also note that Eq. (11) in ref. 5 can be recovered from (4.10) by taking μ and σ independent of the orientation and noting $\mu\sigma=B$.

5. COMPLETE WETTING

The Hamiltonian is here taken as

$$H(h_0, h_1,\ldots, h_L)=\sum_{i=1}^{L} U(h_{i-1}-h_i)-\mu(h_0+h_L) \tag{5.1}$$

with

$$J=\lim_{x\to+\infty}\frac{U(x)}{x}=\lim_{x\to+\infty}U'(x)<\mu<+\infty$$

The quantity $\mu-J$ is essentially what is called the spreading coefficient in dynamical studies of wetting. The condition $\mu>J$ corresponds to dry spreading, whereas $\mu=J$ would correspond to spreading at the wetting transition. We shall discuss only $\mu > J$, in which case the measure (2.3) cannot be normalized and the asymptotics as time goes to infinity are unusual. We shall only discuss the time evolution of quantities averaged over the Brownians, in a heuristic fashion. The evolution equations take the form

$$
\begin{aligned}
\mathbb{E}\dot{h}_0 &= \mu - 2\mathbb{E}U'(h_0 - h_1) + \mathbb{E}U'(h_1 - h_2)\\
\mathbb{E}\dot{h}_1 &= -\mu + 3\mathbb{E}U'(h_0 - h_1) - 3\mathbb{E}U'(h_1 - h_2) + \mathbb{E}U'(h_2 - h_3)\\
\mathbb{E}\dot{h}_2 &= -\mathbb{E}U'(h_0 - h_1) + 3\mathbb{E}U'(h_1 - h_2) - 3\mathbb{E}U'(h_2 - h_3) + \mathbb{E}U'(h_3 - h_4)\\
\cdots &= \cdots\\
\mathbb{E}\dot{h}_i &= -\mathbb{E}U'(h_{i-2} - h_{i-1}) + 3\mathbb{E}U'(h_{i-1} - h_i) - 3\mathbb{E}U'(h_i - h_{i+1})\\
&\quad + \mathbb{E}U'(h_{i+1} - h_{i+2})\\
\cdots &= \cdots
\end{aligned}
$$

Let us first consider the profile near one boundary ($i = 0$), while the other boundary ($i = L$) has been sent to infinity, before letting time go to infinity. The predictions should in fact be valid in the range $1 \ll t \ll L^4$. These predictions will now be given based on a few reasonable assumptions or ansätze.

For any fixed i, local equilibrium is approached as time goes to infinity. We assume the existence of the following limits:

$$
v_i = \lim_{t \to \infty} \mathbb{E}\dot{h}_i(t); \qquad U'_{i(i+1)} = \lim_{t \to \infty} \mathbb{E}U'(h_i(t) - h_{i+1}(t)) \tag{5.2}
$$

The first observation is that $v_i \neq v_{i+1}$ implies $U'_{i(i+1)} = J\,\mathrm{sign}(v_i - v_{i+1})$. Thus, for $i \geqslant 2$, whenever $v_{i-2} \neq v_{i-1} \neq v_i \neq v_{i+1} \neq v_{i+2}$, we have

$$
\begin{aligned}
v_i = J(&-\mathrm{sign}(v_{i-2} - v_{i-1}) + 3\,\mathrm{sign}(v_{i-1} - v_i)\\
&- 3\,\mathrm{sign}(v_i - v_{i+1}) + \mathrm{sign}(v_{i+1} - v_{i+2}))
\end{aligned}
$$

Therefore v_i maximum implies $v_i < -4J$ and v_i minimum implies $v_i > 4J$. Allowing negative maxima and positive minima, while forbidding positive maxima and negative minima, would be difficult to match with the boundary condition requiring $v_i \to 0$ as $i \to \infty$. This leads to

$$
v_0 > 0 > v_1 \leqslant v_2 \leqslant v_3 \leqslant \cdots \leqslant 0
$$

We next observe that a sequence which would be strictly monotonic over five layers around a given i,

$$
v_{i-2} < v_{i-1} < v_i < v_{i+1} < v_{i+2}
$$

would give $U'_{(i-2)(i-1)} = U'_{(i-1)i} = U'_{i(i+1)} = U'_{(i+1)(i+2)} = -J$, and thus $v_i = 0$, a contradiction. This leaves

$$v_0 > 0 > v_1 = v_2 = \cdots = v_k < v_{k+1} < v_{k+2} = 0$$

or

$$v_0 > 0 > v_1 = v_2 = \cdots = v_k < v_{k+1} < v_{k+2} < v_{k+3} = 0$$

We reject this last possibility by considering the match with the profile for $i > k+2$, which should have $h_{k+3}(t) \to -\infty$ as $t \to \infty$, and $U'_{(k+3)(k+4)} = -J$, implying $v_{k+2} = 0$. An independent argument in the same direction is to compute

$$\sum_{i=0}^{k+1} \mathbb{E}\dot{h}_i = \mathbb{E}U'(h_k - h_{k+1}) - 2\mathbb{E}U'(h_{k+1} - h_{k+2}) + \mathbb{E}U'(h_{k+2} - h_{k+3})$$

which tends to zero as $t \to \infty$ in both cases of the above alternative, indicating that $\mathbb{E}\dot{h}_{k+2}$ should also go to zero because of volume conservation. Our ansatz therefore takes the form

$$x = v_0 > y = v_1 = v_2 = \cdots = v_k < z = v_{k+1} < v_{k+2} = 0 \tag{5.3}$$

and $v_i = 0$, $\forall i \geqslant k+2$. We now proceed to determine k and the profile of the piece of interface moving at the speed y. The evolution equation together with the ansatz give

$$x = \mu - 2J + U'_{12}$$

$$y = -\mu + 3J - 3U'_{12} + U'_{23}$$

$$y = -J + 3U'_{12} - 3U'_{23} + U'_{34}$$

$$y = -U'_{12} + 3U'_{23} - 3U'_{34} + U'_{45}$$

$$\cdots$$

$$y = -U'_{(k-4)(k-3)} + 3U'_{(k-3)(k-2)} - 3U'_{(k-2)(k-1)} + U'_{(k-1)k}$$

$$y = -U'_{(k-3)(k-2)} + 3U'_{(k-2)(k-1)} - 3U'_{(k-1)k} - J$$

$$y = -U'_{(k-2)(k-1)} + 3U'_{(k-1)k} + 2J$$

$$z = -U'_{(k-1)k} - J$$

Solving this set of equations gives

$$x=\frac{2(2k+1)\mu-2(2k+7)J}{(k+1)(k+2)}$$
$$y=\frac{-6k\mu+6(k+4)J}{k(k+1)(k+2)} \tag{5.4}$$
$$z=\frac{2(k-1)\mu-2(k+5)J}{(k+1)(k+2)}$$

which can be consistent with the assumptions only when $y<z<0$, or

$$\frac{k+6}{k}J<\mu<\frac{k+5}{k-1}J$$

Given J and $\mu>J$, and leaving aside a discrete set of exceptional values, this gives

$$k=\left[\frac{5J+\mu}{\mu-J}\right]\approx 6J(\mu-J)^{-1} \qquad \text{as} \quad \mu\searrow J$$

while

$$x\simeq\frac{(\mu-J)^2}{3J}, \qquad y\simeq\frac{(\mu-J)^3}{18J^2}, \qquad \text{and} \qquad z=\mathcal{O}((\mu-J)^3) \qquad \text{as} \quad \mu\searrow J$$

The profile of these k layers satisfies

$$-U'_{(i-2)(i-1)}+3U'_{(i-1)i}-3U'_{i(i+1)}+U'_{(i+1)(i+2)}=y$$

If the constant y were zero, this would be a Wulff shape, but $y<0$, which is related to the flux going from the top layers down to the zero wetting layer h_0. However, since $y\sim k^{-3}$ as $\mu\searrow J$, the Wulff shape will be approached in this limit, the effect of the flux on $\mathbb{E}(h_i-h_j)$ being $\mathcal{O}((i-j)/k)$ compared to fluctuations $\mathcal{O}((i-j)^{1/2})$.

Let us now return to the tube $i=0,..., L$, and let the time go to infinity with L fixed. The same reasoning as before leads to

$$v_i=\lim_{t\to\infty}\mathbb{E}\dot{h}_i(t)=v \qquad \text{for} \quad i=k+2,..., L-k-2$$

and then

$$U'_{i(i+1)} = \lim_{t \to \infty} \mathbb{E} U'(h_i(t) - h_{i+1}(t)) = f\left(\frac{i}{L}\right) + \mathcal{O}\left(\frac{1}{L}\right)$$

giving in turn $v \sim L^{-3}$, and a shape differing from a Wulff shape only at $\mathcal{O}(1)$ compared to fluctuations $\mathcal{O}(L^{1/2})$.

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