Journal of Statistical Physics, Vol. 61, Nos. 3/4, 1990

Langevin Dynamics of an Interface near a Wall

Douglas Abraham,[1] Pierre Collet,[2] Joël De Coninck,[3] and François Dunlop[2]

Received October 31, 1989; final June 1, 1990

We study dynamical contact angles and precursor films using Langevin dynamics for SOS type models, near a wall which favors spreading. We first solve exactly the Gaussian model and discuss various asymptotic regimes. This is only appropriate to partial wetting. We then consider more general models. Using local equilibrium and scaling arguments, we derive the shape of the dynamical profile and the speed of the precursor film which exists when the spreading coefficient is strictly positive. Long-range potentials lead to a layered structure of the precursor film. We also consider the case of a meniscus in a capillary.

KEY WORDS: Langevin dynamics; SOS model; interface; contact angle; precursor film.

1. INTRODUCTION

The dynamics of wetting is a subject of considerable current interest, in no small part due to the experimental work of Cazabat, Heslot, and others.[1-5] A prominent feature is the occurrence of a precursor film, which can be of molecular thickness, in the spreading of a macroscopic drop when the parameters are such that, at equilibrium, there would be complete wetting.

Some understanding of the dynamics of wetting has been achieved at a phenomenological level, including hydrodynamic effects.[6-8] The present paper is devoted to a simplified model which can be treated within statistical mechanics.

[1] Department of Theoretical Chemistry, Oxford OX1 3UB, England.
[2] Ecole Polytechnique, Centre de Physique Théorique (CNRS Laboratoire UPR 14), 91128 Palaiseau Cedex, France.
[3] Université de Mons, Faculté des Sciences, 7000-Mons, Belgium.

0022-4715/90/1100-0509$06.00/0

The first rigorous discussion of wetting at equilibrium was conducted at a microscopic level for the planar Ising model.[9] An important feature to emerge from this exact work is its approximation by random walk or solid-on-solid (SOS) models; if the systems are viewed on a scale proportional to the bulk-phase correlation length, this approximation becomes essentially exact. This is of crucial importance in dynamical studies (other than numerical), since it appears hopeless to attempt to study stochastic dynamics of the Ising models themselves other than numerically. It turns out that significant progress can be made on the dynamics of SOS models.

In their usual formulation, the SOS phase-separating surface is described by a unique height variable $h(\mathbf{r})$ defined for $\mathbf{r} \in \mathbb{Z}^{d-1}$ in the d-dimensional case. In the wetting case we want the surface to lie above the boundary surface $z=0$; thus $h(\mathbf{r}) \geqslant 0$. The dynamics for a time-dependent interface described by $h(\mathbf{r}, t)$ is often formulated in terms of the Langevin equation[10–13]

$$\frac{\partial h(\mathbf{r}, t)}{\partial t} = -\frac{1}{2} \nabla U(\mathbf{h}(\mathbf{r}, t)) + \eta(\mathbf{r}, t)$$

where the function U describes the energy of the interface and $\eta(\mathbf{r}, t)$ is white noise with zero mean and covariance satisfying

$$\langle \eta(\mathbf{r}, t)\, \eta(\mathbf{r}', t') \rangle = \delta_{\mathbf{r},\mathbf{r}'} \delta(t-t')$$

Note that the usual friction and temperature parameters have been normalized to one for simplicity of notation.

Treating the white noise consistently demands that we violate the restriction $h(\mathbf{r}, t) \geqslant 0$. It is thus difficult if not impossible to attach a meaning to these models when applied to wetting rather than to free interfaces. Recently the exact Ising results for $d=2$ have been discussed from a different point of view, making the SOS restriction in a direction parallel, rather than normal, to the substrate plane.[14] We shall adopt this point of view (see Fig. 1). The variables $h(\mathbf{r}, t)$ are therefore not restricted to positive values and the Langevin equation is thus consistent with the allowed configurations.

Recently, there has been much study of growth processes where one of the phases is favored in the bulk (see in particular ref. 15). In this situation, one is therefore led to a Langevin equation with a term which does not derive from a potential. In our case, we consider a Langevin equation derived from a Hamiltonian and the motion of the interface is due to the difference of the wall free energies.

In Section 2, we introduce and discuss the various models at equi-

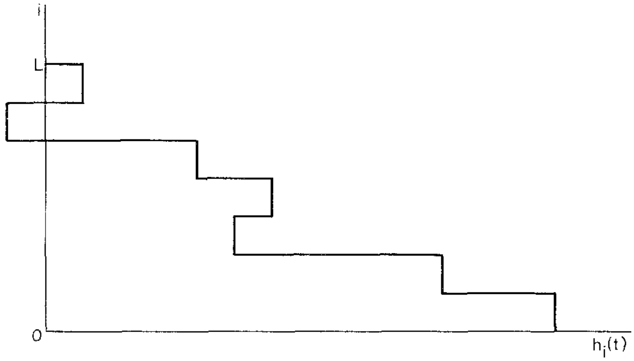

Fig. 1. Typical configuration showing displacement parallel to the substrate as a function of the height above the substrate.

librium. In Section 3 we solve completely the Gaussian version of our model, for which

$$U(h_0,..., h_L) = J \sum_{1}^{L} (h_i - h_{i-1})^2 - \mu_0 h_0$$

where $\mu_0 > 0$ favors the spreading of the interface. This model never shows complete wetting, but we can use it to define and calculate a dynamical contact angle. We can also exhibit scaling regimes where both $h(x, t)$ itself and x are scaled by $t^{1/2}$ for large times, L having been taken to infinity first. Then there is the final approach to equilibrium on a scale $t \sim L^2$. The mean profile becomes a straight line and the fluctuations about it scale as $L^{1/2}$ exactly as one would expect. We should point out that the finite-size behavior of the interface pinned at its ends but without other constraint has already been investigated in the Gaussian case.[16]

We then discuss more general models with

$$U(h_0,..., h_L) = \sum_{1}^{L} P(h_i - h_{i-1}) - \mu_0 h_0$$

which enable one to capture both partial wetting (Section 4) and complete wetting (Section 5) with, say, $P(x) \sim J|x|$ as $|x| \to \infty$. Assuming that there is local equilibrium and that there is a suitable scaling regime, we shall find the shape of the dynamical profile. For a strictly positive spreading coefficient, we establish the existence of a precursor film and show that it advances at a velocity which we calculate. We also display the shape of the profile which is left behind, which scales like $t^{1/2}$ in both directions.

In Section 6, we discuss the structure of the precursor film when the contact wall potential μ_0 is replaced by a longer-range potential.

Finally, in Section 7, we consider the dynamics of wetting in a capillary tube.

2. THE MODELS

Let us consider an interface between two phases, say A and B. Its position is characterized by the heights h_i as represented in Fig. 1 with $i=0, 1,\ldots, L$. If we do not consider overhangs, the "energetic" cost of this interface may be defined by some SOS type model

$$U(h_0,\ldots, h_L)=\sum_{i=1}^{L} P(h_i-h_{i-1})-\mu_0 h_0 \tag{1}$$

where $P(x)$ is an even function, increasing for $x>0$, and such that

$$\lim_{x\to+\infty} \frac{P(x)}{x}=+\infty \tag{2a}$$

or

$$P(x)=J|x|+\varepsilon(|x|) \qquad \text{with} \quad \gamma=\lim_{x\to\infty} \frac{\varepsilon(x)}{\log x}<2 \tag{2b}$$

(we have assumed for simplicity that the limit exists). A particular case is the Gaussian model defined by

$$U(h_0,\ldots, h_L)=J\sum_{1}^{L} (h_i-h_{i-1})^2-\mu_0 h_0$$

The term $-\mu_0 h_0$ simply takes into account a preference of the wall of the container for phase A. The other end of the interface will be pinned at $h_L=0$ for definiteness. At equilibrium, the partition function is given by (we fix the temperature at $kT=1$ for simplicity)

$$Z=\int_{-\infty}^{\infty} dh_0\cdots\int_{-\infty}^{+\infty} dh_L\, e^{-U(h_0\cdots h_L)}\delta(h_L)$$

Introducing $x_i=h_i-h_{i-1}$ leads to

$$Z=\int_{-\infty}^{+\infty} dx_1\cdots\int_{-\infty}^{+\infty} dx_L \exp\left[-\sum_{1}^{L} P(x_i)-\mu_0\sum_{1}^{L} x_i\right]$$

and therefore

$$-\frac{1}{L}\log Z = -\log \int_{-\infty}^{+\infty} dx\, e^{-P(x)-\mu_0 x}$$

In the Gaussian case, we get

$$-\frac{1}{L}\log Z = -\log \int_{-\infty}^{+\infty} dx\, e^{-Jx^2-\mu_0 x}$$

$$= -\frac{(\mu_0)^2}{4J} - \log\left(\frac{\pi}{J}\right)^{1/2}$$

The corresponding mean profile $\bar{x}_i$, $i = 1,..., L$, will therefore be given by

$$\bar{x}_i = -\frac{\mu_0}{2J} \tag{3}$$

for any $i = 1,..., L$ in the Gaussian case and by

$$\bar{x}_i = \frac{\int_{-\infty}^{+\infty} x e^{-P(x)-\mu_0 x}\, dx}{\int_{-\infty}^{+\infty} e^{-P(x)-\mu_0 x}\, dx} \tag{4}$$

for any $i = 1,..., L$ in the general case, i.e., in both cases, a straight line because the mean value of the increments is independent of i.

The contact angle θ_{eq} (see Fig. 2) satisfies obviously at equilibrium the equation

$$\cot \theta_{eq} = -\bar{x}_i \tag{5}$$

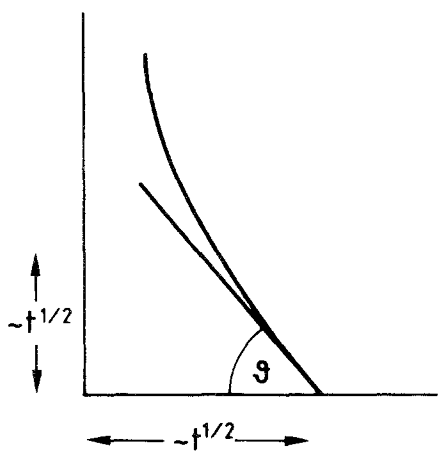

Fig. 2. Definition of the contact angle.

This contact angle obeys the modified Young equation[17,18]

$$\cos\theta\,\sigma_{AB}(\theta)-\sin\theta\,\sigma'_{AB}(\theta)=\sigma_{AW}-\sigma_{BW} \tag{6}$$

where

$$\sigma_{AW}-\sigma_{BW}=\mu_0$$

and

$$\sigma_{AB}(\theta)=-\sin\theta\log\int e^{-P(x)+\mu(\cot\theta)(x-\cot\theta)}\,dx \tag{7}$$

where the function $\mu(\cot\theta)$ solves the equation

$$\int e^{-P(x)+\mu(\cot\theta)x}(x-\cot\theta)\,dx=0 \tag{8}$$

which is always possible under condition (2a) or (2b) above. Knowing σ_{AB}, one can consider (7) and (8) as a system of equations for the functions P and μ.

We illustrate this point in the case $\sigma_{AB}(\theta)=\sigma$ independent of θ (isotropic) and for $\sigma_{AB}(\theta)=\sigma_{\mathrm{Ising}}(\theta)$ (SOS representation of the two-dimensional Ising model giving the exact surface tension for all angles, for any fixed temperature).

In the first case (7) and (8) lead to

$$\mu(t)=\frac{\sigma t}{(1+t^2)^{1/2}}$$

and

$$e^{-P(x)}=\int_{-\infty}^{\infty}e^{-\sigma(1+t^2)^{1/2}}\cos tx\,dt=\frac{2\sigma K_1((x^2+\sigma^2)^{1/2})}{(x^2+\sigma^2)^{1/2}}$$

where K_1 is a modified Bessel function.

In the second case, we have[19]

$$\beta\sigma\sin\theta+\beta\sigma'\cos\theta=\hat{\gamma}(i\mu(\theta))$$

where $\hat{\gamma}$ is Onsager's function, which is defined by

$$\cosh\hat{\gamma}(i\mu)=\cosh 2K\coth 2K-\cosh\mu$$

with $K=\beta J$, and $\mu(\theta)$ satisfies

$$\cot\theta=\frac{\partial\hat{\gamma}(i\mu)}{\partial\mu}$$

In this case, (7) and (8) lead to

$$e^{-P(x)}=\int_{-\pi}^{\pi} d\omega\, e^{i\omega x}\,\{(A-\cos\omega)-[(A-\cos\omega)^2-1]^{1/2}\}$$

with $A=\cosh 2K\coth 2K$. Here the variable x is an integer. Both the first and second cases lead to $\gamma=3/2$ in (2b).

Returning to the question of the equilibrium contact angle, we find that θ_{eq} as a function of μ_0 is obtained by solving

$$\mu(\cot\theta_{eq})=\mu_0$$

Let us now examine the dynamics of that interface. To describe the approach to equilibrium, we choose the Langevin dynamics given by

$$dh_i=-\frac{1}{2}\frac{\partial U}{\partial h_i}\,dt+d\beta_i,\qquad i=0,\ldots,L-1$$

i.e.,

$$\begin{aligned} dh_0&=[\tfrac{1}{2}\mu_0-\tfrac{1}{2}P'(h_0-h_1)]\,dt+d\beta_0\\ dh_i&=\tfrac{1}{2}[P'(h_{i-1}-h_i)-P'(h_i-h_{i+1})]\,dt+d\beta_i \end{aligned}\tag{9}$$

with the simplest initial conditions $h_i=0$ for any i at $t=0$ and with $h_L=0$ for all t.

Our model can also be compared to the Lifschitz equation[20] which has been used to describe 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. This equation states that the normal component v_n of the speed of the interface at the point x is proportional to the inverse of the radius of curvature $r(x)$,

$$v_n=\lambda r(x)^{-1}$$

where λ is proportional to the surface tension. This is of course 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 $h(x, t)$. From the well-known relations

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

the Lifschitz equation can be written as

$$\dot{h}=\frac{\lambda h''(x)}{1+[h'(x)]^2}$$

The analogous equation in the anisotropic case is given by

$$\dot{h} = \frac{\lambda h''(x)}{1 + [h'(x)]^2} [\sigma(\arctan h') + \sigma''(\arctan h')]$$

These equations should be supplemented first by a term describing the interaction with the substrate and second by fluctuations in the spirit of the Langevin equation. This leads to serious conceptual and analytical problems, in particular for the wetting regime with a microscopic precursor film, and we shall only consider below the discrete model.

3. DYNAMICS OF THE GAUSSIAN MODEL

We shall now solve explicitly the Langevin equation corresponding to the quadratic potential

$$U(\mathbf{h}) = J \sum_{0}^{L-1} (h_{i+1} - h_i)^2 - \mu_0 h_0$$

where we have assumed $h_L = 0$. For the associated Gaussian model, the Langevin equation is given by

$$d\mathbf{h} = \left(\frac{\mu_0}{2} \mathbf{e}_0 - JA\mathbf{h} \right) dt + d\boldsymbol{\beta}$$

where $\mathbf{e}_0$ is the L-dimensional vector $(1, 0,..., 0)$, $\boldsymbol{\beta}$ is an L-dimensional Brownian motion, and the L by L matrix A is given by

$$A = \begin{pmatrix} 1 & -1 & 0 & 0 & 0 & \cdots & \cdots \\ -1 & 2 & -1 & 0 & 0 & \cdots & \cdots \\ 0 & -1 & 2 & -1 & 0 & \cdots & \cdots \\ & & & \ddots & & & \\ & & & & \ddots & & \\ \cdots & \cdots & 0 & 0 & -1 & 2 & -1 \\ \cdots & \cdots & 0 & 0 & 0 & -1 & 2 \end{pmatrix}$$

The general solution of the Langevin equation is therefore given by

$$\mathbf{h}(t) = \frac{\mu_0}{2J} A^{-1}(\mathbf{e}_0 - e^{-JAt}\mathbf{e}_0) + \int_0^t e^{-JA(t-s)}\, d\boldsymbol{\beta}(s) + e^{-JAt}\mathbf{h}(0) \qquad (10)$$

The last term is a transient term which is absent if we start with the initial condition $\mathbf{h}(0) = \mathbf{0}$. The first term is the stationary solution of the deterministic problem. Finally, the second term is the (Gaussian) fluctuation (note that this simple decomposition is only true for quadratic potentials).

In order to compute the relevant quantities, we shall of course diagonalize the Hermitian matrix A. It is easy to verify that the eigenvalues are given by

$$\lambda_q = 2\{1 - \cos[\pi(2q+1)/(2L+1)]\}$$

with $q = 0, 1,..., L-1$. The associated normalized eigenvectors have components

$$S_j^q = [2/(L+1/2)]^{1/2} \cos[\pi(j+1/2)(2q+1)/(2L+1)]$$

$(j = 0, 1,..., L-1)$.

It is now convenient to perform the orthogonal transformation which diagonalizes the matrix A, and to integrate the stochastic differential equation. If we denote by h_q the component of the vector $\mathbf{h}$ on the qth eigenvector, we obtain the equation

$$dh_q = (\mu_0 S_0^q/2 - J\lambda_q h_q)\, dt + d\beta_q(t)$$

where β_q $(q = 0, 1, 2,..., L-1)$ is again a collection of independent one-dimensional Brownian motions (this is true because we have performed an orthogonal transformation). The solution with initial condition zero is therefore given by

$$h_q(t) = \frac{\mu_0}{2J\lambda_q} S_0^q(1 - e^{-J\lambda_q t}) + \int_0^t e^{-J\lambda_q(t-s)}\, d\beta_q(s)$$

It follows from the above formula that the mode number q relaxes to equilibrium with a time scale of order $J^{-1}\lambda_q^{-1}$. For q small this time scale is of order L^2, and of order unity for large values of q (q of order L).

Performing the inverse orthogonal transformation, we obtain for the components $(h_j(t))_{0 \leqslant j \leqslant L-1}$ of the vector $\mathbf{h}(t)$

$$h_j(t) = \sum_{q=0}^{L-1} \frac{\mu_0}{2J\lambda_q} S_j^q S_0^q(1 - e^{-J\lambda_q t}) + \sum_{q=0}^{L-1} S_j^q \int_0^t e^{-J\lambda_q(t-s)}\, d\beta_q(s) \qquad (11)$$

Again, the first term is the solution of the deterministic problem, while the second sum is the contribution of the fluctuations.

From this expression, we can obtain immediately an expression for the average of the Gaussian random variable $h_j(t)$,

$$\langle h_j(t) \rangle = \sum_{q=0}^{L-1} \frac{\mu_0}{2J\lambda_q} S_j^q S_0^q(1 - e^{-J\lambda_q t}) \qquad (12)$$

and for the variance

$$\langle h_j(t)^2\rangle - \langle h_j(t)\rangle^2 = \sum_q \frac{(S_j^q)^2}{2J\lambda_q}(1-e^{-2J\lambda_q t}) \tag{13}$$

As mentioned above, different modes have different relaxation times, and we shall now extract from the previous formula some interesting asymptotic behaviors in various regimes. We shall first consider the case where the position variable j is much smaller than the vertical size L and the time variable t is much smaller than L^2. It is tempting to replace the above sums on q by integrals, since they look like Riemann sums. There is, however, a difficulty coming from the divergence of λ_q^{-1} for q fixed and L large. To avoid this difficulty, one can observe that $\langle h_j(t)\rangle$ is analytic and uniformly bounded in the complex right half-plane in t. It is therefore enough to deal with the limiting problem for the time derivative, which avoids the previous difficulty. Integrating back, one gets the natural answer

$$\lim_{L\to\infty} \langle h_j(t)\rangle = \frac{\mu_0}{2\pi J}\int_0^\pi \cos\left[\left(j+\frac{1}{2}\right)x\right]\cos\left(\frac{x}{2}\right)\frac{1-e^{-2J(1-\cos x)t}}{1-\cos x}\,dx \tag{14}$$

It follows easily from the above formula that the result becomes simpler if we use a scale $t^{1/2}$ for j and h (see Fig. 3).

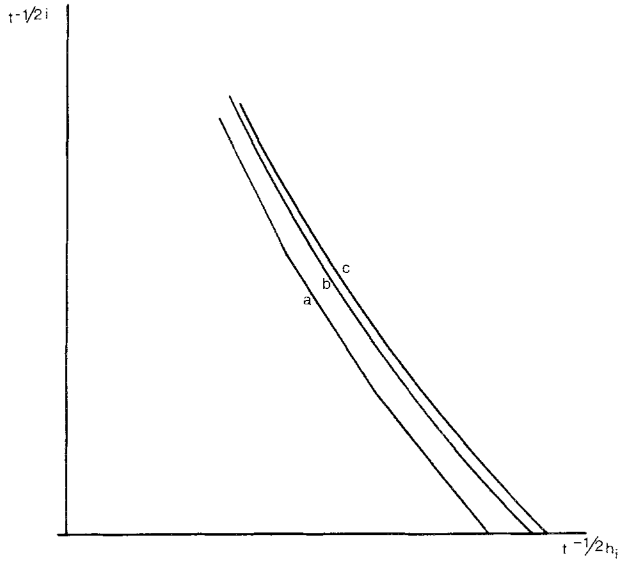

Fig. 3. Scaling behavior of the dynamical profile. (a) $t=10$, (b) $t=100$, (c) $t=1000$.

We shall see later on that this scaling is also relevant in more general situations. We get

$$\lim_{t\to\infty}\lim_{L\to\infty} t^{-1/2}\langle h_{yt^{1/2}}(t)\rangle=\frac{\mu_0}{\pi\sqrt{J}}\int_0^\infty \frac{\cos(zyJ^{-1/2})}{z^2}(1-e^{-z^2})\,dz \tag{15}$$

Note that the integral on the right-hand side can also be expressed in terms of a primitive of the error function. If we define the contact angle at the wall θ_W by

$$\cot\theta_W=\lim_{L\to\infty}\langle h_0-h_1\rangle$$

we obtain

$$\cot\theta_W=\frac{\mu_0}{2\pi J}\int_0^\pi (1+\cos x)(1-e^{-2J(1-\cos x)t})\,dx$$

which for t large is asymptotically equal to the equilibrium value of the cotangent of the contact angle, namely $\mu_0/2J$, the correction being $O(t^{-1/2})$. One can show even more, namely that with probability one

$$\lim_{\substack{j\to+\infty\\ t\to+\infty\\ j/\sqrt{t}\to 0}}\lim_{L\to\infty}\frac{h_0-h_j}{j}=\cot\theta_{\mathrm{eq}} \tag{16}$$

Returning to the continuum model, if we assume that the profile has a small slope

$$h'(x)\ll 1$$

we obtain exactly the same results.

We also can obtain a simple formula for the variance of the fluctuations, which is

$$\lim_{t\to\infty}\lim_{L\to\infty} t^{-1/2}(\langle h_{yt^{1/2}}(t)^2\rangle-\langle h_{yt^{1/2}}(t)\rangle^2)$$
$$=\frac{1}{\pi J}\int_0^\infty \cos^2(J^{-1/2}yz)\,z^{-2}(1-e^{-2z^2})\,dz$$

Note that in this limit, the amplitude of the fluctuations is of the order of $t^{1/4}$, whereas normal fluctuations of a string of length L with periodic boundary conditions would be of order $(t/L)^{1/2}$. The above result is also true for $\mu_0=0$, which corresponds to a string with one end loose and the other fixed. For $t \ll L^2$, the loose end has fluctuations of amplitude $t^{1/4}$ which matches $(t/L)^{1/2}$ for $t \sim L^2$.

Another interesting time scale is of course $t \approx L^2$, which is the final approach to equilibrium. The mean profile relaxes to a straight segment and the fluctuations are of order $L^{1/2}$. More precisely, we have in scaled variables

$$\lim_{L \to +\infty} L^{-1} \langle h_{yL}(\tau L^2) \rangle = \frac{\mu_0}{\pi^2 J} \sum_{q=0}^{q=\infty} \frac{\cos \pi y(q+1/2)}{(q+1/2)^2} (1 - e^{-J\pi^2(q+1/2)^2 \tau})$$

which implies for τ large enough

$$\lim_{L \to +\infty} L^{-1} \langle h_{yL}(\tau L^2) \rangle \approx \frac{\mu_0}{2J} \left[1 - y - 8\pi^{-2} \cos\left(\frac{\pi y}{2}\right) e^{-J\pi^2 \tau/4} + O(e^{-9J\pi^2\tau/4}) \right] \tag{17}$$

As a consequence, we can only have partial wetting in the Gaussian case.

4. LOCAL EQUILIBRIUM AND SCALING ARGUMENTS: PARTIAL WETTING

We shall now consider a general SOS type model with Hamiltonian

$$U(h_0, \ldots, h_L) = \sum_{i=1}^{L} P(h_i - h_{i-1}) - \mu_0 h_0$$

in a partial wetting case, i.e.,

$$0 < \mu_0 < \lim_{x \to \infty} \frac{P(x)}{x}$$

This condition implies that h_0/L will remain bounded, which corresponds to partial wetting. Complete wetting will be considered in Section 5. We recall that $P(x)$ is an even function increasing for $x > 0$.

The Langevin equations now read

$$\begin{aligned} dh_0 &= [\tfrac{1}{2}\mu_0 - \tfrac{1}{2}P'(h_0 - h_1)]\, dt + d\beta_0 \\ dh_i &= [\tfrac{1}{2}P'(h_{i-1} - h_i) - \tfrac{1}{2}P'(h_i - h_{i+1})]\, dt + d\beta_i, \qquad i = 1, \ldots, L-1 \end{aligned} \tag{18}$$

where we again fix $h_L = 0\ \forall t$. It is well known that the equilibrium Gibbs measure

$$\exp\{-U(h_0, \ldots, h_{L-1}, 0)\} \prod_{0}^{L-1} dh_i$$

is invariant under the Langevin dynamics. Rigorous results as to the approach to equilibrium could be formulated for L finite, but would be difficult to extend to the case of interest $L \to \infty$. We shall therefore begin with heuristic arguments and conjectures.

Suppose that the mean profile $\langle h_i(t) \rangle$ is a smooth function of i, for example, as in the Gaussian case

$$\langle 2h_i(t) - h_{i+1}(t) - h_{i-1}(t) \rangle \leqslant O(t^{-1/2}), \qquad 1 \ll t \ll L^2$$

Then, on a scale $l \ll t^{1/2}$, the profile is approximately a straight line. If we suppose also that the slope varies slowly with time, then we have local equilibrium. We shall assume that $\langle P' \rangle$ is a function of the local slope $\langle h_i - h_{i+1} \rangle$:

$$\langle P'(h_i - h_{i+1}) \rangle \simeq \mu(\langle h_i - h_{i+1} \rangle) \tag{19}$$

From the *local equilibrium* assumption, we expect the function μ to satisfy[21]

$$\bar{x} = \frac{\int x \exp[-P(x) + \mu(\bar{x})\, x]\, dx}{\int \exp[-P(x) + \mu(\bar{x})\, x]\, dx}$$

This local equilibrium argument leads to an equation for mean values: from (18) and (19) we obtain

$$\frac{d\langle h_i \rangle}{dt} = \frac{1}{2} \mu(\langle h_{i-1} - h_i \rangle) - \frac{1}{2} \mu(\langle h_i - h_{i+1} \rangle) \tag{20}$$

We hope of course that the error in this approximate formula will be negligible for $1 \ll t \ll L^2$. For this to be true, it is necessary that the error in (19) should be of second order [e.g., $O(t^{-1})$ if the scale is to be $O(t^{1/2})$], or that the errors in applying (19) to $\langle P'(h_{i-1} - h_i) \rangle$ and $\langle P'(h_i - h_{i+1}) \rangle$ cancel at first order in (20).

Let us now make a scaling argument: consider $t \gg 1$ and t small relative to L^2 in such a way that the spreading of the foot of the profile has not yet affected the top, $i = L$. The initial condition was indeed $h_i(0) = 0\ \forall i$, and the driving force comes from μ_0 which is applied to $i = 0$. Therefore we should have

$$\langle P'(h_{L-1} - h_L) \rangle \simeq 0$$

and summing (18) from $i = 0$ to $L - 1$ yields

$$\frac{d}{dt} \left\langle \sum_0^{L-1} h_i \right\rangle = \frac{1}{2} \mu_0 - \frac{1}{2} \langle P'(h_{L-1} - h_L) \rangle \simeq \frac{1}{2} \mu_0 \tag{21}$$

Suppose that the profile scales as t^λ on the h axis (spreading direction). In view of (21), it should then scale as $t^{1-\lambda}$ on the i axis:

$$\langle h_i(t)\rangle = t^\lambda \phi(it^{\lambda-1}) \tag{22}$$

for some smooth scaling function $\phi(\cdot)$.

Changing i into a continuous variable y and injecting (22) into (20), we get

$$\frac{d}{dt} t^\lambda \phi(yt^{\lambda-1}) = \frac{1}{2}\frac{d}{dy}\mu\left(\frac{d}{dy} t^\lambda \phi(yt^{\lambda-1})\right)$$

or

$$\begin{aligned}\lambda t^{\lambda-1/2}\phi(yt^{\lambda-1}) - (1-\lambda)\, t^{\lambda-1/2}(yt^{\lambda-1})\,\phi'(yt^{\lambda-1})\\ = \tfrac{1}{2} t^{3(\lambda-1/2)}\phi''(yt^{\lambda-1})\,\mu'(t^{2\lambda-1}\phi'(yt^{\lambda-1}))\end{aligned}$$

We see that $\lambda = 1/2$ is the only choice which gives a scale-invariant equation, whatever the function $\mu(\cdot)$ or the $P(\cdot)$ which defines the model. The function $\phi(z)$ with $z = yt^{-1/2}$ should then satisfy

$$\phi(z) - z\phi'(z) = \phi''(z)\cdot\mu'(\phi'(z)) \tag{23}$$

with two boundary conditions

$$\phi(\infty) = 0 \tag{24}$$

and

$$\int_0^\infty \phi(z)\, dz = \frac{\mu_0}{2}$$

This last condition can be related to the dynamical contact angle by integrating (23) once, which gives

$$2\int_0^\infty \phi(z)\, dz = -\mu(\phi'(0))$$

so that the boundary condition at $z = 0$ becomes

$$-\mu(\phi'(0)) = \mu_0 \tag{25}$$

This shows that the dynamical contact angle is stationary and equals the equilibrium contact angle. This is consistent with our local equilibrium assumption.

All the above results can be checked to hold true in the Gaussian case. In particular, (23) then reads

$$\phi(z) - z\phi'(z) - 2J\phi''(z) = 0 \tag{26}$$

which indeed has (15) as a solution. A notable difference in the general case is that the function $\mu(\cdot)$, and therefore (23) and the shape of the profile, depend upon the temperature, i.e., upon the variance of the Brownian (which we normalized to one for simplicity of notation).

Another question is whether relaxation to equilibrium occurs for $t \approx L^2$. The previous regime indicates that relaxation at the top $i \simeq L$ will not begin before $t \approx L^2$. One probably could prove that the relaxation time is in fact not larger than order L^2.

The above results can be traced through the continuum model based on the Lifschitz equation. For example, looking for a similarity solution of the Lifschitz equation of the form $\sqrt{t}\,\phi(x/\sqrt{t})$ gives the equation

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

which happens to be (23) with $\mu(t) = \arctan(t)$.

5. LOCAL EQUILIBRIUM AND SCALING ARGUMENTS: COMPLETE WETTING

We shall now consider

$$\mu_0 = J = \lim_{x \to \infty} P(x)/x \tag{27}$$

which is the wetting transition, and then $\mu_0 > J$, which corresponds to a strictly positive spreading coefficient (dry spreading).

The arguments leading to the scaling form (23) should still be valid, at least for i not too small (possibility of a precursor film). Let us therefore examine (23) with (24) and with (25), which should be understood as

$$\lim_{it^{-1/2} \to 0} -\mu(\phi'(it^{-1/2})) = \mu_0$$

Recall that $\mu(\cdot)$ is defined by

$$\bar{x} = \frac{\int x \exp[-P(x) + \mu(\bar{x})\, x]\, dx}{\int \exp[-P(x) + \mu(\bar{x})\, x]\, dx}$$

The function $\mu(\bar{x})$ increases from 0 to J as $\bar{x}$ increases from 0 to ∞. The contact angle θ is given by

$$\tan\theta = -\frac{1}{\phi'(0)}$$

and (25) shows that it goes to zero indeed as $\mu_0 \nearrow J$.

For $\mu_0 = J$, we have $\phi'(0) = -\infty$, and one may ask whether $\phi(z)$, solution of (23)–(25), has an asymptote $\phi(z) \to \infty$ as $z \to 0$, or whether it remains finite. To answer this question, we need the behavior of $\mu'(\bar{x})$ near $\bar{x} = \infty$ or equivalently the behavior of $\bar{x}'(\mu)$ near $\mu = J$.

We have

$$\bar{x}'(\mu) = \frac{\int x^2 e^{-J|x| - \varepsilon(x) + \mu x}\,dx}{\int e^{-J|x| - \varepsilon(x) + \mu x}\,dx} - \left(\frac{\int x e^{-J|x| - \varepsilon(x) + \mu x}\,dx}{\int e^{-J|x| - \varepsilon(x) + \mu x}\,dx}\right)^2$$

and the behavior for $J - \mu \to 0$ will depend on γ defined in (2b) by

$$\gamma = \lim_{x \to \infty} \frac{\varepsilon(x)}{\log x}$$

We first consider the case $1 < \gamma < 2$. An easy computation leads to

$$\bar{x}(\mu) \sim (J - \mu)^{\gamma - 2}$$

which implies

$$\mu'(\bar{x}) \sim \bar{x}^{-(3-\gamma)/(2-\gamma)}$$

for $\bar{x}$ large enough. Using this expression of μ' in Eq. (23), one can check that the ansatz

$$\phi(z) = \phi(0) - \lambda z^{\gamma - 1} + \text{higher-order terms}$$

solves the equation for z near zero. This implies

$$\lim_{t \to \infty} \langle h_0(t) \rangle\, t^{-1/2} < \infty$$

In other words, at the wetting transition the contact angle vanishes and there is neither an asymptote nor a precursor film.

In the case $\gamma < 1$, similar computations lead to

$$\bar{x}(\mu) = (J - \mu)^{-1}$$

and

$$\mu'(\bar{x}) \sim \bar{x}^{-2}$$

Taking this estimate into (23) yields

$$\phi(z) - z\phi'(z) \simeq \frac{\phi''(z)}{\phi'(z)^2} \tag{28}$$

which should be valid for $z \to 0$, with $\phi'(z) \to -\infty$. This second-order differential equation admits az and $(2 \log az^{-1})^{1/2}$ as asymptotic solutions for $z \to 0$. Only the second is compatible with the boundary conditions. Therefore

$$\phi(z) \sim (2 \log az^{-1})^{1/2} \to \infty \qquad \text{as} \quad z \to 0 \tag{29}$$

If we return to the original variables and invert h_i into i_h, we find the following asymptotics:

$$i_h \sim at^{1/2} \exp\left(-\frac{h^2}{2t}\right) \tag{30}$$

We can also express the result for $\gamma < 1$ as

$$\langle h_0 \rangle \approx t^{1/2} (\log t)^{1/2} \tag{31}$$

$$\langle h_i - h_{i+1} \rangle \approx \log \frac{i+2}{i+1} \cdot t^{1/2} (\log t)^{-1/2} \qquad \begin{cases} i = 0, 1,... \\ i \ll t^{1/2} \end{cases} \tag{32}$$

There is a significant point in Eq. (31). Suppose $h_1 < h_0$: then in the SOS dynamics $[P(x) = J\,|x|]$, only the noise term remains in dh_0, that is, $dh_0 = d\beta_0$, which seems to contradict (31). The fact is that h_1 catches up with h_0 sufficiently often to produce (31), contrary to what might have been thought to be the case.

It is worth noticing that the existence or not of an asymptote in the case of a contact angle equal to zero may also be investigated at equilibrium for a droplet in a corner as in the summertop construction.[22] In the framework of (2b) the question can be answered: for $2 > \gamma > 1$ there is no asymptote, as in our dynamical model. For $\gamma < 1$, there is an asymptote behaving as $\log z^{-1}$ [compared to $(\log z^{-1})^{1/2}$ in the dynamics; cf (29)]. For $\gamma > 2$, the contact angle cannot approach zero.

This concludes our analysis of the case $\mu_0 = J$, and we turn to $\mu_0 > J$. We first observe that the boundary condition (25) cannot be satisfied, because the range of $-\mu(\phi'(0))$ is between 0 and J. Yet we should have

$$\frac{d}{dt}\left\langle \sum_0^{L-1} h_i \right\rangle \simeq \frac{1}{2}\mu_0$$

Thus, a finite fraction of $\sum_0^{L-1} h_i$ is not seen on the scale $(t^{1/2}, t^{1/2})$ of the profile $\phi(z)$, and should therefore be concentrated at $z=0$, or $i \ll t^{1/2}$:

$$\frac{d}{dt}\left\langle \sum_{i \ll t^{1/2}} h_i \right\rangle = \frac{1}{2}(\mu_0 - J) \tag{33}$$

On the other hand, we have

$$\begin{aligned} \frac{d}{dt}\langle h_0 \rangle &= \frac{1}{2}\mu_0 - \frac{1}{2}\langle P'(h_0 - h_1)\rangle \\ &\geqslant \frac{1}{2}(\mu_0 - J) \end{aligned} \tag{34}$$

We conclude that the fraction of the spreading phase which is missing from the $t^{1/2}$ profile is entirely concentrated in h_0. Indeed, (33) and (34) imply

$$\langle h_0 \rangle \approx \tfrac{1}{2}(\mu_0 - J)\, t \tag{35}$$

and $\langle h_1 \rangle \ll t$. If we now look back at

$$\frac{d\langle h_1 \rangle}{dt} = \frac{1}{2}\langle P'(h_0 - h_1)\rangle - \frac{1}{2}\langle P'(h_1 - h_2)\rangle$$

we see that $h_0 - h_1$ is so large that we can set $P'(h_0 - h_1) = J$, and the equations for $h_1, h_2, \ldots, h_{L-1}$ become effectively the same as those for $h_0, \ldots, h_{L-1}$ at the transition point $\mu_0 = J$.

In conclusion, we get a precursor film of length $\sim t$ ahead of a profile scaling as $t^{1/2}$ in both directions (see Fig. 4).

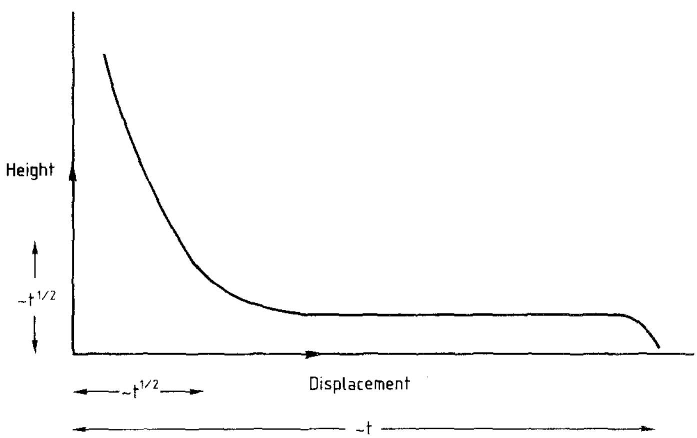

Fig. 4. Spreading profile with a precursor film.

6. LONG-RANGE POTENTIALS

One may ask what happens if the wall potential, which is just a contact one of the form $\mu_0 h_0$ in Eq. (1), is replaced by a long-range one. This can be taken in the form

$$\tilde{\mu}_0 h_0 - \sum_1^\infty u_j(h_{j-1} - h_j) = \sum_0^\infty \mu_j h_j$$

with $\mu_0 = \tilde{\mu}_0 - u_1$, and $\mu_j = u_j - u_{j+1}$. The physical interpretation is that u_j is the interaction of the interface with the wall at a distance j. It is expected that $u_j > u_{j+1}$ for $j \geqslant 1$. Finally, it should be kept in mind that the layer index $j = 0, 1,...,$ corresponds to a coarse-grained height.

We consider again models defined by (27). The first observation is

$$\frac{d}{dt}\left\langle \sum_0^n h_i \right\rangle = \frac{1}{2} \sum_0^n \mu_i - \frac{1}{2} \langle P'(h_n - h_{n+1}) \rangle \tag{36}$$

for any integer n, so that complete wetting will occur if and only if

$$\sum_0^\infty \mu_i \geqslant J$$

The second observation is that the front of a precursor film may have a thickness of several layers. As a first example consider

$$\mu_0 > \mu_1 > \mu_2 = \mu_3 = \cdots = 0$$

with

$$\mu_0 + \mu_1 > J$$

We have

$$\frac{d}{dt} \langle h_0 + h_1 \rangle = \frac{1}{2} (\mu_0 + \mu_1) - \frac{1}{2} \langle P'(h_1 - h_2) \rangle$$

Anticipating the result $h_1 \gg h_2$, we get

$$\frac{d}{dt} \langle h_0 + h_1 \rangle \simeq \frac{1}{2} (\mu_0 + \mu_1 - J) \tag{37}$$

and

$$\begin{aligned} \frac{d}{dt} \langle h_0 - h_1 \rangle &= \frac{1}{2} (\mu_0 - \mu_1) - \langle P'(h_0 - h_1) \rangle + \frac{1}{2} \langle P'(h_1 - h_2) \rangle \\ &\simeq \frac{1}{2} (\mu_0 - \mu_1 + J) - \langle P'(h_0 - h_1) \rangle \end{aligned} \tag{38}$$

If $\mu_1 > \mu_0 - J$, still with $\mu_1 < \mu_0$, then $h_0 \geqslant h_1$ and (38) imply

$$\langle P'(h_0 - h_1)\rangle < J$$

so that $h_0 - h_1$ remains bounded as $t \to \infty$ and the precursor film consists of two layers moving together at speed $\frac{1}{4}(\mu_0 + \mu_1 - J)$.

If $\mu_1 < \mu_0 - J$, then

$$\frac{d}{dt}\langle h_0 - h_1\rangle \geqslant \frac{1}{2}(\mu_0 - \mu_1 - J) > 0$$

which implies

$$\langle P'(h_0 - h_1)\rangle \simeq J$$

and the precursor film consists of a first layer moving at speed $\frac{1}{2}(\mu_0 - J)$ followed by a second layer moving at a lower speed $\frac{1}{2}\mu_1$.

Similarly, for a long-range potential

$$\mu_0 > \mu_1 > \mu_2 > \cdots > 0$$

with $\mu_i \downarrow 0$ as $i \uparrow \infty$ and

$$\sum_0^\infty \mu_i > J$$

let

$$n = \max\left\{ j \,\middle|\, \mu_j > \frac{1}{j}\left(\sum_{i=0}^{j-1} \mu_i - J\right)\right\} \tag{39}$$

and $n = 0$ if the set is empty. The assumptions imply n finite. The same argument as with μ_0, μ_1 alone now gives the following structure to the precursor film: $n+1$ layers moving together at speed

$$\frac{1}{2(n+1)}(\mu_0 + \mu_1 + \cdots + \mu_n) \tag{40}$$

followed by the other layers $i = n+1, n+2, \ldots$, moving each at its own speed $\frac{1}{2}\mu_{n+1}, \frac{1}{2}\mu_{n+2}, \ldots$.

Our third and last observation concerns the part of the profile which scales as $t^{1/2}$. Let us assume

$$\mu_i \ll i^{-1} \qquad \text{as} \quad i \to \infty$$

which is not a physical restriction. Then the precursor film, if there is one, will not be visible in the $t^{1/2}$ part of the profile. Indeed, if $i = t^{1/2}y$, the extension of the precursor film at i is of order $\mu_i t$, which satisfies

$$\mu_i t \ll i^{-1} t = y^{-1} t^{1/2}$$

and is therefore much smaller than the extension of the scaling profile, which is $O(t^{1/2})$.

Also, in case of partial wetting, $\mu_i \ll i^{-1}$ guarantees that the μ_i do not spoil the scaling form of the profile. In particular, a contact angle is well defined at the $t^{1/2}$ scale, and is equal to the equilibrium value, defined by [see (36) and (19)]

$$-\mu(\cot\theta) = \sum_{0}^{\infty} \mu_i \tag{41}$$

7. THE CAPILLARY CASE

In this section we shall consider the wetting problem in a two-dimensional strip (a model for a capillary tube). The Langevin system is now given by

$$dh_i = \tfrac{1}{2}[P'(h_{i-1} - h_i) - P'(h_i - h_{i+1})]\,dt + d\beta_i$$

for $i = 1,..., L-1$, and

$$dh_0 = \tfrac{1}{2}P'(h_1 - h_0)\,dt + d\beta_0 + \tfrac{1}{2}\mu_0\,dt$$
$$dh_L = \tfrac{1}{2}P'(h_{L-1} - h_L)\,dt + d\beta_L + \tfrac{1}{2}\mu_0\,dt$$

The hypotheses on the interaction P are the same as before. We shall now show that there is an equilibrium state in a moving frame with a well-defined speed. In a frame moving at speed v with respect to the laboratory frame, the Langevin system is essentially the same except that we have to subtract $-v\,dt$ to each equation. If we denote again by h_i for $i = 0,..., L$ the random variables in the moving frame, we obtain the equations

$$dh_i = \tfrac{1}{2}[P'(h_{i-1} - h_i) - P'(h_i - h_{i+1}) - 2v]\,dt + d\beta_i \tag{42}$$

for $i = 1,..., L-1$, and

$$\begin{aligned} dh_0 &= \tfrac{1}{2}P'(h_1 - h_0)\,dt + d\beta_0 + \tfrac{1}{2}\mu_0 dt - v\,dt \\ dh_L &= \tfrac{1}{2}P'(h_{L-1} - h_L)\,dt + d\beta_L + \tfrac{1}{2}\mu_0\,dt - v\,dt \end{aligned} \tag{43}$$

We easily get

$$\frac{d}{dt}\left\langle \sum_{0}^{L} h_i \right\rangle = \mu_0 - (L+1)\, v$$

This suggests that we look in the frame moving at speed

$$v = \frac{\mu_0}{L+1}$$

We shall now recover this formula from the existence of an equilibrium state only in this moving frame, in the nonwetting case. The (nonnormalized) density of an equilibrium state in a frame moving at speed v will be given by

$$e^{(h_0 + h_L)\mu_0} \prod_{j=0}^{j=L-1} e^{-P(h_j - h_{j+1})} \prod_{j=0}^{j=L} e^{-2vh_j}$$

We can now rearrange the above formula as follows:

$$\begin{aligned} &e^{(h_0 + h_L)\mu_0} \prod_{j=0}^{j=L-1} e^{-P(h_j - h_{j+1})} \prod_{j=0}^{j=L} e^{-2vh_j} \\ &\quad = e^{(h_0 + h_L)\mu_0} e^{-v(L+1)(h_0 + h_L)} \prod_{j=0}^{j=L-1} e^{-P(h_j - h_{j+1})} e^{-v(h_j - h_{j+1})(2j+1-L)} \end{aligned}$$

We can integrate this density over the variables $h_1, \ldots, h_{L-1}$ to get the effective density for the variables h_0 and h_L. This effective density is given by

$$e^{\mu_0(h_0 + h_L)} e^{-v(L+1)(h_0 + h_L)} R_L(h_0 - h_L)$$

where ($*$ denotes the convolution)

$$R_L(s) = r_{(0,L)} * r_{(1,L)} \cdots * r_{(L-1,L)}(s)$$

and

$$r_{(j,L)}(s) = e^{-P(s)} e^{-v(2j+1-L)s}$$

In the nonwetting case, the function R_L is integrable, and we get a normalizable state independent of the value of $h_0 + h_L$ if and only if

$$v = \frac{\mu_0}{L+1} \tag{44}$$

Let us therefore choose a frame moving at this speed, and such that

$$\sum h_i = 0 \qquad \text{at} \quad t = 0$$

We then have

$$\left\langle \sum h_i \right\rangle = 0 \qquad \forall t$$

As $t \to \infty$, the difference variables $x_j = h_j - h_{j+1}$ will become independent random variables distributed according to the unnormalized densities $r_{j,L}(x_j)$. The mean profile $\langle h_j \rangle$ will be a meniscus, e.g., a parabola if $P(\cdot)$ is Gaussian (see Fig. 5).

It is worth noting that this profile could be obtained by a Wulff construction, at least when $L \to \infty$: if the wall and interface free energies, corresponding to the Hamiltonian

$$\mu_0(h_0 + h_L) + \sum P(h_j - h_{j+1})$$

are minimized at fixed volume

$$\sum h_j = 0$$

then the same profile as above is obtained (see ref. 21 for a proof). In particular, the contact angle will obey the same Young equation. There will remain a slight difference between equilibrium expectation values and the expectation values coming out of the Langevin dynamics: the former are averages over configurations, whereas the latter are averages over the noise from $t = 0$ to the given time t, starting from fixed initial conditions. The difference will not be visible in expectation values involving only difference

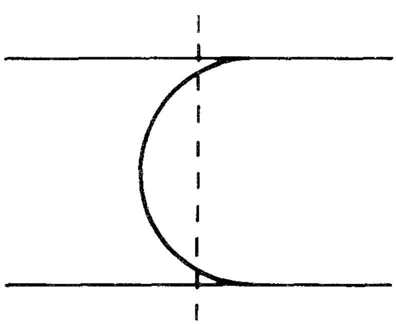

Fig. 5. Stationary profile of a meniscus in a moving frame.

variables, but the center of mass will drift away like $t^{1/2}$ in the Langevin dynamics, whereas it is held fixed at 0 in the equilibrium measure.

The above discussion concerns the equilibrium solution for the h_j, or the stationary solution for the original variables. These will be attained for $t \gg L^2$. The smaller time scales could be discussed as in the preceding sections.

ACKNOWLEDGMENTS

We thank the Royal Society, Communauté Française de Belgique, and CNRS for financial support, which permitted several study visits during which this work was done.

NOTE ADDED IN PROOF

We thank H. Spohn for drawing our attention to ref. 23, which contains mathematically related work, with a different physical motivation.

REFERENCES

1. A.-M. Cazabat, *Contemp. Phys.* **28**:347 (1987).
2. F. Heslot, N. Fraysse, and A.-M. Cazabat, *Nature* **338**:640 (1989).
3. F. Heslot, A.-M. Cazabat, and P. Levinson, *Phys. Rev. Lett.* **62**:1286 (1989).
4. L. Leger, M. Erman, A. M. Guinet-Picard, D. Ausserré, and G. Strazielle, *Phys. Rev. Lett.* **60**:2390 (1988).
5. D. Beaglehole, *J. Phys. Chem.* **93**:893 (1989).
6. J. Joanny and P. G. de Gennes, *J. Phys.* (Paris) **47**:121 (1986).
7. P. G. de Gennes, *Rev. Mod. Phys.* **57**:827 (1985).
8. E. B. Dussan V, *Annu. Rev. Fluid Mech.* **11**:371 (1979).
9. D. B. Abraham, *Phys. Rev. Lett.* **44**:1165 (1980).
10. M. Kac and J. Logan, in *Studies in Statistical Mechanics*, Vol. VII, E. W. Montroll and J. L. Lebowitz, eds. (North-Holland, Amsterdam, 1979).
11. P. C. Hohenberg and B. I. Halperin, *Rev. Mod Phys.* **49**:435 (1977).
12. J. D. Gunton, M. San Miguel, and P. S. Sahni, in *Phase Transitions and Critical Phenomena*, Vol. 8, C. Domb and J. L. Lebowitz, eds. (Academic Press, New York, 1983).
13. R. Bausch, V. Dohm, H. K. Janssen, and R. K. P. Zia, *Phys. Rev. Lett.* **47**:1837 (1981).
14. D. B. Abraham and D. A. Huse, *Phys. Rev. B* **38**:7169 (1988).
15. M. Kardar, G. Parisi, and Y.-C. Zhang, *Phys. Rev. Lett.* **56**:829 (1986).
16. D. B. Abraham and P. Upton, *Phys. Rev. B* **39**:736 (1989).
17. J. De Coninck and F. Dunlop, *J. Stat. Phys.* **47**:827 (1987).
18. D. B. Abraham and L. F. Ko, *Phys. Rev. Lett.* **63**:275 (1989).
19. D. B. Abraham, J. De Coninck, and F. Dunlop, *Phys. Rev. B* **39**:4708 (1989).
20. I. M. Lifschitz, *Sov. Phys. JETP* **15**:939 (1962).
21. J. De Coninck, F. Dunlop, and V. Rivasseau, *Commun. Math. Phys.* **121**:401 (1989).
22. R. K. P. Zia, J. E. Avron, and J. E. Taylor, *J. Stat. Phys.* **50**:727 (1988).
23. M. Z. Guo, G. C. Papanicolauo, and S. R. S. Varadhan, *Commun. Math. Phys.* **118**:31–59 (1988).