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LETTER TO THE EDITOR

Numerical simulations of a Langevin dynamics of wetting

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Abstract. We consider numerical simulations of the Langevin equations recently proposed by Abraham *et al* to model the spreading of a fluid on a substrate. A dependence upon the temperature is found in both the dynamical and the static properties. The contact angle, as a function of the parameters, is calculated in the partial wetting case. A precursor film with constant speed is observed in the complete wetting phase. The fluid above the precursor film is found to behave in time as t^{α}, with α function of the height of the fluid. At low temperature, α is smaller than $\frac{1}{2}$ and larger at high temperature. The profile of the fluid is found to be close to a parabola, at low temperature.

The spreading of fluids and wetting of surfaces is a problem of considerable interest in technical sciences (properties of lubricants, paints and so forth). It is also a very interesting problem for the physicist in order to understand the phenomena that take place in such a process. Recent experiments [1] have shown the formation of layers in a spreading fluid, whose thickness is typically of molecular size. In particular, a precursor film that moves faster than the rest of the fluid is seen at the interface with the solid substrate.

Hydrodynamics in its usual form might not be appropriate to describe the spreading of a fluid, due to the presence of these microscopic layers and also due to the type of boundary condition (slip or no slip) one has to impose at the interface [2].

Simple models of spreading giving predictions that can be tested experimentally are of interest. Abraham *et al* [3] have proposed such a simple model where a precursor film appears naturally. They have considered the case of a semi-infinite wedge of a non-volatile fluid, spreading on a smooth solid horizontal substrate. The idea of the model is to divide the fluid into L horizontal layers of thickness 1. The displacement of the ith layer is described by the quantity $h_i(t)$ and obeys the set of Langevin equations

$$\frac{\mathrm{d}}{\mathrm{d}t} h_i(t) = -\frac{\partial F}{\partial h_i} + \eta_i(t) \tag{1}$$

where the $\eta_i(t)$ are Gaussian uncorrelated white noises. The free energy $F(h)$ contains a contribution of the surface tension J and another one due to the interaction μ_0 between the fluid and the substrate. Its effect is to favour the coverage of the substrate by the fluid. In the case of a short range interaction, it only affects the very first layer h_0 and comes as an additive part in the free energy.

$$F = J \sum_{i=1}^{L-1} \sqrt{1+(h_i - h_{i-1})^2} - \mu_0 h_0. \tag{2}$$

Equation (1) has to be supplemented by the initial conditions $h_i(t=0)=0$ for all i, and the boundary condition $h_{L-1}=0$ for all times t.

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Our aim is not to discuss the validity of this model, but rather to investigate numerically the predictions it gives, with the hope that these predictions will be compared with other models [4, 5] and ultimately with real experiments. In particular, we would like to compare our results with the Monte Carlo simulations performed by Kaski *et al* [4], for the same model, but with a Hamiltonian derived from F by assuming $\sqrt{1+(h_i-h_{i-1})^2} \approx |h_i - h_{i-1}|$.

For the purpose of a numerical treatment, we have considered a discrete time version of (1):

$$h_0(t+1) = h_0(t) - J\frac{h_0(t)-h_1(t)}{\sqrt{1+(h_0(t)-h_1(t))^2}} + \mu_0 + \eta_0(t) \tag{3}$$

and, for $i = 1, \ldots, L-2$

$$h_i(t+1) = h_i(t) - \frac{J(h_i(t)-h_{i+1}(t))}{\sqrt{1+(h_i(t)-h_{i+1}(t))^2}} + \frac{J(h_{i-1}(t)-h_i(t))}{\sqrt{1+(h_{i-1}(t)-h_i(t))^2}} + \eta_i(t). \tag{4}$$

For simplicity, the $\eta_i(t)$ are taken as independent random variables, uniformly distributed between $-a/2$ and $a/2$, where

$$a = \sqrt{24 k_B T}$$

so that $\langle \eta_i^2(t) \rangle = 2k_B T$. The fact that the noise is not Gaussian distributed is found to have no effect on our results, at least in the case of partial wetting where analytical work is possible.

When $\mu_0 < J$, a numerical simulation of equations (3) and (4) show that a stationary regime is reached after a large enough number of iterations. The profile of the spreading fluid as a function of time is shown in figure 1(a).

The probability distribution $P(t, h_0, \ldots, h_{L-1})$ associated with the Langevin equation (1) is known to obey the Fokker–Planck equation

$$\partial_t P = -\sum_i \frac{\partial}{\partial h_i}\left(-\frac{\partial F}{\partial h_i} P\right) + k_B T \sum_i \frac{\partial^2 P}{\partial h_i^2}. \tag{5}$$

In this case, the stationary solution of Fokker–Planck equation is simply

$$P = K \exp(-F/k_B T). \tag{6}$$

The constant K is the normalization. This solution makes sense only when the integral of P is finite, i.e. when $\mu_0 < J$ as can be seen by inspection of (6).

The value of K as well as the average quantities $\langle h_i \rangle$ are difficult to obtain analytically from P. Figure 1(a) shows that the stationary profile is a straight line. In addition, simulations of various system sizes, show that the contact angle θ is independent of the number of layers L. Thus, only the value of h_0 is important. It turns out that considering a system with only one layer ($L = 1$) already gives quite good results for the contact angle defined in this case as

$$\tan \theta = \frac{1}{\langle h_0 \rangle}. \tag{7}$$

For $L = 1$, a simple numerical integration yields K and $\langle h_0 \rangle$. In figure 2, the results of this one-layer calculation is compared with the simulation of the Langevin equations of a sixteen layers system. We obtain a very satisfactory agreement.

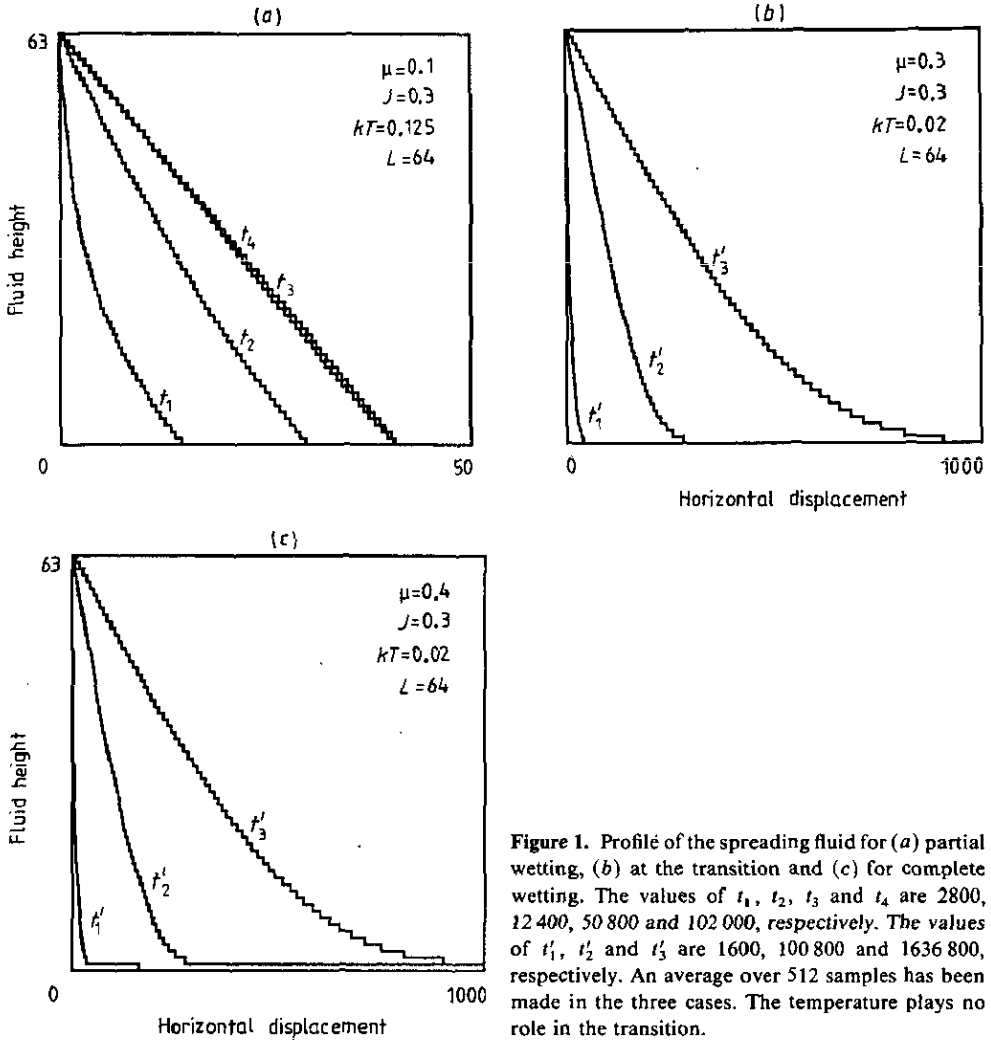

Figure 1. Profilé of the spreading fluid for (*a*) partial wetting, (*b*) at the transition and (*c*) for complete wetting. The values of t_1, t_2, t_3 and t_4 are 2800, 12 400, 50 800 and 102 000, respectively. The values of t'_1, t'_2 and t'_3 are 1600, 100 800 and 1636 800, respectively. An average over 512 samples has been made in the three cases. The temperature plays no role in the transition.

The behaviour near the transition and for high temperature can be obtained analytically for $L=1$, by assuming that $\sqrt{1+h_0^2} \approx |h_0|$. We get

$$\tan\theta = \frac{(J+\mu_0)}{2\mu_0}\frac{(J-\mu_0)}{k_B T}. \tag{8}$$

This behaviour is confirmed by the numerical measurements when $k_B T$ is large enough and μ_0 close to J (see figure 3). This shows that the temperature cannot induce a transition from partial to complete wetting.

In the limit of zero temperature, the contact angle is easily obtained from (3), with $\eta_0 = 0$. We find

$$\tan\theta = \frac{1}{h_0 - h_1} = \frac{\sqrt{J^2-\mu_0^2}}{\mu_0}$$

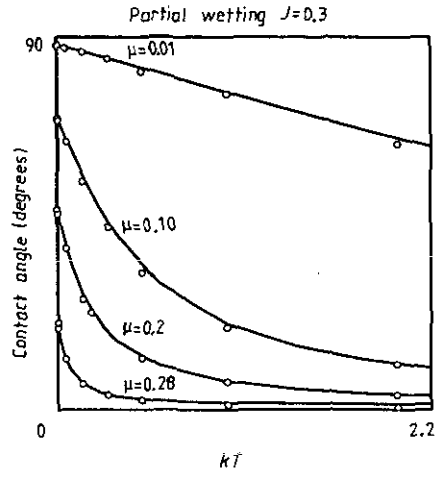

Figure 2. Contact angle against the temperature, for various values of μ_0, in the partially wet case. The full curves are obtained by integration of the probability distribution for $L=1$. The circles are the results of the numerical simulations of the Langevin equations for $L=16$, with an average over 256 samples.

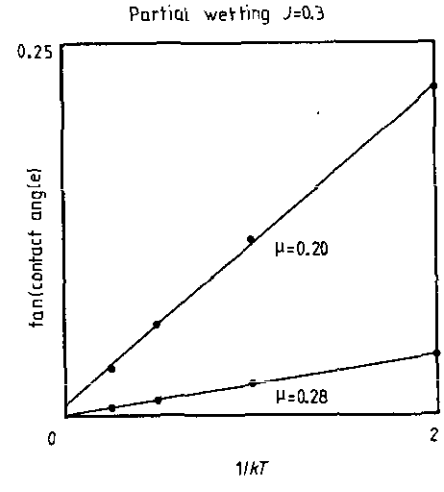

Figure 3. Behaviour of the contact angle for high temperature. The full circles correspond to the same numerical simulations as in figure 2. The slopes of the least-squares fits are 0.11 and 0.02 for $\mu_0=0.2$ and $\mu_0=0.28$, respectively. These values are in reasonable agreement with relation (8).

which, in the limit $\mu_0 \ll J$, gives the result of [3]. Indeed, when $\mu_0 \ll J$, θ is close to $\pi/2$ and $(h_{i+1}-h_i)^2$ is much smaller than 1. This makes it possible to use a Taylor expansion of F, which leads to an exact solution of the Langevin equations.

We also have investigated the dynamics of the partially wetting phase, i.e. how the stationary state is reached. If the time t is not too small, it is found that

$$h_i(t) = h_i(\infty)(1-\exp(-t/\tau))$$

where τ is the relaxation time which depends on both the system size and $(J-\mu_0)$.

For L ranging between 8 and 128, we found that τ tends to L^2, far from the transition and L near the transition. As μ tends to J, the amplitude increases as a power law of $J-\mu_0$ whose exponent seems to depend strongly on L, when L is small.

When $\mu_0 \geqslant J$, the probability distribution P given by (6) is no longer normalizable. Only a non-stationary state is possible and the fluid will move continuously on the substrate, giving rise to the complete wetting of the surface. This is illustrated in figures 1(b) and 1(c). The question we shall address now is to find out the time behaviour of the moving front and its shape. From the figures, it appears that, for $\mu_0 > J$, the first layer runs quickly ahead of the rest of the fluid. Such a precursor film has been observed in real experiment [1] and was already predicted in [3]. From our numerical simulations, we observed that

$$\langle h_0(t)\rangle = \text{constant} + (\mu_0 - J)t. \tag{9}$$

This relation is found to hold even if μ_0 is very close to J, provided that t is large enough. No dependence on the temperature is observed. Equation (9) is in agreement with [3]. As far as the above layers are concerned, the theoretical predictions of [3] and [6] suggest a behaviour in $\sqrt{t \ln t}$ for the first few layers. We obtain a different result from the numerical simulations, conducted on a 64 layers system. In the large time limit, it is found that

$$h_i(t) = b + a_i t^{\alpha_i} \tag{10}$$

where b is very small compared with h_i and α_i is temperature dependent. At low temperature ($k_B T = 0.02$ and $k_B T = 0.1$), α_i was found to slightly decrease with i, until it reaches a value α_∞, independent of i (0.42 and 0.47, respectively). At higher temperature ($k_B T = 1.0$), α_i turned out to increase from 0.52 for $i = 1$, to 0.55, at $i = 32$.

Although these values are very close to each other, their difference is significant when considering a least-squares fit.

An exponent α smaller than one half may be understood from equation (4), in the limit of zero noise. As the fluid spreads, the differences $h_i - h_{i+1}$ increase and a Taylor expansion of (4) for $1/(h_i - h_{i+1})^2$ yields

$$\frac{\mathrm{d}}{\mathrm{d}t} h_i = \frac{J}{2}\left(\frac{1}{(h_{i+1}-h_i)^2} - \frac{1}{(h_i - h_{i-1})^2}\right). \tag{11}$$

An ansatz such as (10) gives $\alpha_i = \frac{1}{3}$. The effect of the noise is to increase this exponent.

When $\mu_0 = J$, equation (9) is no longer correct. The very fast precursor film does not exist anymore. As suggested in figures 1(b) and 1(c), for the same value of temperature, we observe that h_i behaves very much as if the profile of the case $\mu_0 > J$ was shifted one layer down. The two situations seem equivalent, provided the index i goes to $i-1$.

Finally, we have studied the shape of the front, as a function of time, which amounts to the determination of the a_i in (10). For the temperatures $k_B T = 0.02$ and $k_B T = 0.1$, a shape close to a parabola is obtained, as shown in figure 4. More precisely, after having removed the precursor film, we define e as the thickness of the fluid ($e = i - 1$) and x as the horizontal displacement of the front ($x(e) = h_i$). We get

$$e = \sim \frac{(h_1(t) - x)^\gamma}{t^{\gamma \alpha_\infty}} \tag{12}$$

where $\gamma \approx 2$. It is important to note that this relation is well obeyed for the whole fluid, except, maybe, for the very first layers whose exponents α_i are different from the bulk.

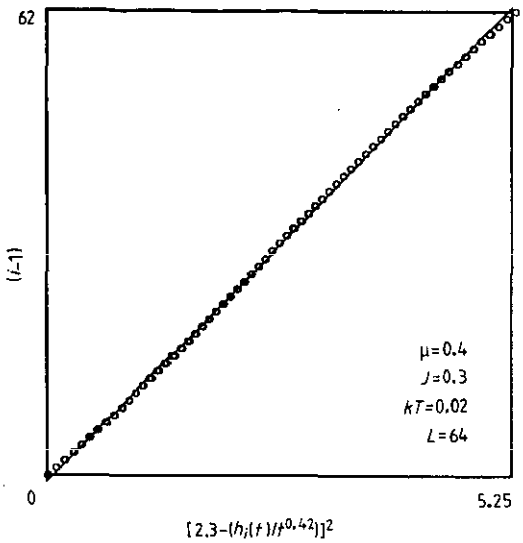

Figure 4. Complete wetting. The circles show a collapse of three numerical measurements of the profile $h_i(t)$, at time 2×10^6, 2.5×10^6 and 3.6×10^6, respectively, with an appropriate scaling of the horizontal axis. The fact that the three curves are almost indistinguishable shows a $t^{0.42}$ behaviour, valid for the temperature $k_BT=0.02$. The reasonable alignment of the data shows the parabolic shape of the spreading fluid.

This is a large time result which does not fully agree with the prediction $e\sim x^{-2}$ of the continuum theory [7]. When the temperature is changed, γ changes also. For $k_BT=0$, γ tends to 1.5, whereas $\gamma>4$ is observed when $k_BT=1.0$. In the case of high temperature, relation (12) turns out to be an unsatisfactory fit.

Our results are in qualitative agreement with those of [3–6]. However, the effect of the temperature clearly shows up in our simulations, introducing significant quantitative differences.

The more realistic case of a long range interaction (see [6]) between the substrate and the fluid is now under investigation.

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