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J. Phys. A: Math. Gen. 24 (1991) L309-L315. Printed in the UK

LETTER TO THE EDITOR

Computer simulation studies of fluid spreading

D B Abraham†, J Heiniö‡ and K Kaski†§

† Department of Theoretical Chemistry, Oxford University, Oxford OX1 3UB, UK
‡ Tampere University of Technology, PO Box 527, SF-33101 Tampere, Finland

Received 1 January 1991

Abstract. The spreading characteristics of a fluid wedge on an attractive substrate are studied with the Monte Carlo simulations in a horizontal solid-on-solid model and compared with the Langevin theory. In the partially wet case, relaxation to a stable wetting angle is observed, whereas in the completely wet system a precursor film is found to behave linearly in time and the layers next to the precursor as $(t \log t)^{1/2}$, in agreement with theory. The layers above the precursor film of molecular thickness seem to show diffusive fluid profiles as found previously in continuum theory.

Recently there has been renewed interest and progress in the study of wetting and spreading. This is a subject of great technical importance for lubrication, painting and adhesion (Ball 1989, Cazabat 1987 and de Gennes 1985). Hardy (1919) first demonstrated the remarkable property that a small droplet of an involatile, immiscible substance floating on water spreads out, driving before it specks of dust which happen to be in the way. A simple but not unreasonable continuity argument shows that the final film, if it is homogeneous, is surprisingly only of molecular thickness. If there is free space left on the water surface, the film will ultimately break up at its perimeter, although this is likely to be a very slow process. Hardy showed that the surface tension of that part of the water surface which is covered is decreased, as the molecular picture above would suggest. But this picture is only inferred from the macroscopic results. Nevertheless, the behaviour of the spreading drop at its perimeter is quite unknown.

Over the past few years, ellipsometric studies have changed this situation. The earliest results of these experiments (Leger *et al* 1988) were partly explained by a continuum theory (Joanny and de Gennes 1986). The resolution of the extremum of the droplet has revealed a rather flat precursor film of molecular thickness (~5 Å), with structure independent of the spreading coefficient, preceding the rest of the drop ultimately up to a distance of order 10^7 Å (Heslot *et al* 1989a). The experiments also give evidence that the final state of the spread drop is not a 'pancake' but more likely a surface gas, thus pointing out the ultimate domination of molecular diffusion over the liquid cohesion. In some cases, up to four such molecular films were found to be stacked on top of each other (Heslot *et al* 1989a, b). Clearly hydrodynamics (Joanny and de Gennes 1986) is not entirely appropriate here since viscosity is not a well defined concept on this length scale. Alternative theories, based on Langevin theory, have on the other hand had some success (Abraham *et al* 1990a, b).

§ Permanent address: Tampere University of Technology, PO Box 527, SF-33101 Tampere, Finland.

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The horizontal solid-on-solid (HSOS) model has been demonstrated to give a good account of the equilibrium wetting transition and interface profile near a substrate wall (Abraham and Huse 1988, Abraham and Ko 1989). In this model, instead of discussing a phase-separating surface which is a histogram above the substrate plane, as in the usual SOS model, we investigate a surface which is a histogram with respect to a plane normal to the substrate. In this letter we will consider a wedge of fluid spreading in the x direction (without overhangs with respect to this direction) across a flat substrate with normal z. The underlying space is discretized, since only then can an SOS model make sense physically (Kac and Logan 1979). The surface of the spreading droplet is described by a dynamic integer-valued variable $h_{j,k}(t)$, where j is a non-negative integer for the z coordinate and k is the remaining discrete y coordinate in the three-dimensional case. For the Langevin theory, which we will summarize in the $d=2$ case, $h_j(t)$ is continuous. Then we can write the equation of motion as

$$\frac{\partial h_j}{\partial t} = -\lambda \frac{\partial F}{\partial h_j} + \eta_j(t) \tag{1}$$

where the boundary conditions are $h_j(0)=0$, $j=0,\ldots,L-1$, $h_{L-1}(t)=0$, $\forall t \geqslant 0$, and $\eta_j(t)$ is white noise:

$$\langle \eta_j(t) \rangle = 0 \qquad \langle \eta_j(t)\eta_k(t') \rangle = 2kT\lambda\delta_{jk}\delta(t-t'). \tag{2}$$

In equation (1), λ is an arbitrary time scale and $F(\{h\})$ is a free energy functional taken to be

$$F(\{h\}) = \tau \sum_{j=1}^{L-1} \sqrt{1+(h_j-h_{j-1})^2} - \mu_0 h_0. \tag{3}$$

Such a model cannot be defined consistently for the usual SOS model since $h_j(t) \geqslant 0$ which is incompatible with the white noise term. In the simplest case; τ is the surface tension and μ_0 is an interaction favouring covering the substrate. The Gaussian approximation to (3) is exactly solvable (Abraham *et al* 1990a, b), but it does not give complete wetting at equilibrium unlike (3) itself. In any case, the quadratic truncation would be inappropriate. In these two papers a local equilibrium approximate treatment was given which produced a precursor film if $\mu_0 > \tau$. If we replace the free energy functional in (3) by

$$F(\{h\}) = \tau \sum_{j=1}^{L-1} |h_j - h_{j-1}| - \mu_0 h_0 \tag{4}$$

then an exact solution is still impossible it seems, but the existence of the precursor film is rather obvious since

$$\lambda^{-1} \frac{\partial h_0}{\partial t} = -\tau \operatorname{sgn}(h_0 - h_1) + \mu_0 + \eta_0(t). \tag{5}$$

Averaging over noise, we have

$$\lambda(\mu_0 + \tau) \geqslant \frac{\partial \langle h_0 \rangle}{\partial t} \geqslant \lambda(\mu_0 - \tau) \tag{6}$$

for all $t \geqslant 0$, from which the inequality $\lambda(\mu_0+\tau)t \geqslant \langle h_0 \rangle \geqslant \lambda(\mu_0-\tau)t$, follows by elementary calculus. Thus a precursor film exists whenever $\mu_0 > \tau$. Since we anticipate $h_0 > h_1$, ultimately we expect

$$h_0(t) \sim \lambda(\mu_0 - \tau) + \int_0^t \eta_0(s)\, \mathrm{d}s \tag{7}$$

only for the first layer. In Abraham *et al* (1990b) it is also suggested that in fact for $j \ll O(t^{1/2})$, we have $\langle h_j(t)\rangle \sim (t \log t)^{1/2}$.

In this work we examine, via Monte Carlo simulations, the time evolution of the related problem using the following HSOS Hamiltonian:

$$H = \tau \sum_{j=0}^{L-1} \sum_{k=1}^{M} |h_{j,k} - h_{j,k-1}| + \tau \sum_{j=0}^{L-1} \sum_{k=1}^{M} |h_{j+1,k} - h_{j,k}| - \mu_0 \sum_{k=1}^{M} h_{0,k}. \tag{8}$$

The first term and index k are to be dropped for the $d = 2$ system. We take the $h_{j,k}$ to be integers and impose the boundary conditions $h_{j,k}(0) = 0$ for all j, k and $h_{L-1,k}(t) = 0$ for all $t \geq 0$ and all k. Thus for the $d = 3$ case we have assumed the wedge geometry on top of a planar xy-substrate with additional periodic boundary conditions in the y-direction and fixed on top of the wedge at $z = (L-1)$. The $d = 2$ case is otherwise the same but without the y-direction and its boundary condition. It should be noted that this HSOS model can describe only the case of an involatile fluid. This model is also incapable of producing the surface gas, as found experimentally for final stages of spreading (Heslot *et al* 1989a). In order to include volatility, i.e. evaporation and redeposition, and a possibility for surface gas, Ising-type models should be used. The case of a surface gas, however, can also be studied with a vertical SOS model. In the Hamiltonian (8) no dynamics has yet been included. In Monte Carlo simulations the dynamics is based on the Markovian master equation. Thus the dynamics is not deterministic but stochastic in nature. It describes a random migration of the state of the system through the configurational phase space towards equilibrium as a result of the system being a contact with a heat bath and confirming the Hamiltonian via the detailed balance relation.

In these computer simulations the time proceeds in discrete steps and is measured by Monte Carlo steps/site (MCS/S). Within each time step, on average, every $h_{j,k}(t)$ is randomly updated with the transition probability

$$P(h_{j,k} \to h'_{j,k}) = \min\left\{1, \exp\left(\frac{-\Delta H}{kT}\right)\right\} \tag{9}$$

where ΔH is the energy difference between the final $(h'_{j,k})$ and initial $(h_{j,k})$ states. Hence the dynamics is described by a single-site event so no particle conservation is included. In fact we can then interpret the wedge as a limitless reservoir of particles for the spreading front. We believe that the simple Hamiltonian and dynamics models can capture some of the saliant features of fluid spreading specifically for precursor films at about molecular thickness, for which length scales hydrodynamics is inappropriate.

In this letter we will mainly consider the result for $d = 2$, although we will briefly mention the main results for the $d = 3$ case. In the computer simulations the dynamics of $h_{j,k}$ were followed up to the time when the precursor film had spread to about 10 000 lattice units. The dynamic averages were taken over at least 400 runs, so that a 'conservative' estimate for the error bars, based on the central limit theorem, is less than 5%. In our studies the system sizes were varied as $L = 40$, 60, 80, 120, 240 in two dimensions whereas smaller $L = M$ were used in three dimensions. No significant finite-size effects were detected; in fact the results for $h_{j,k}$ were the same within the error bars for all studied L. In figure 1 we show a time sequence of the fluid profile for the complete wetting case ($\mu_0 > \tau$). A very rapid precursor film layer is seen to precede all the other layers. Also it seems that for about ten layers from the second layer onwards the fluid's thickness (e) profile behaves diffusively as a function of

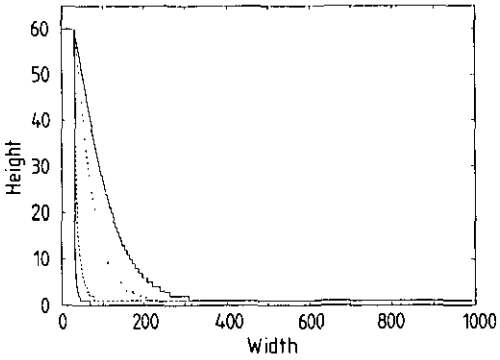

Figure 1. Snapshots of completely wetting fluid profiles at 100, 800, 2500, 7000 and 16 000 MCS/s. Results are averages over 500 independent runs with $\mu_0 = 0.15$, $\tau = 0.10$ and $kT = 0.04$.

spreading distance (x), $e \sim x^{-2}$. This was obtained previously from the continuum theory (Joanny and de Gennes 1986).

In figure 2 we show the results for the dynamics of first three layers in a partially wet system. For $\mu_0 = 0.5 \times \tau$ and $\mu_0 = 0.9 \times \tau$ these layers are found to relax to constant values and thus to finite wetting angles, clearly demonstrating that the system is partially wet. Although at early times the first layer precedes the second, and so on, giving rise to different spreading exponents we do not see a clear formation of a precursor film. Before equilibration the layers spread with an effective exponent being in the neighbourhood of the diffusive exponent, $\frac{1}{2}$.

The spreading in the case of complete wetting for various values of μ_0 is shown in figure 3. The first layer is found to form a clear precursor film, preceding rapidly ahead of the two next layers on top of the first one. The characteristic time behaviour for h_0, h_1 and h_2 persist after the initial transient period of about 100 MCS/s, within which the formation of the precursor film occurs. In figure 4 we demonstrate the success of the curve fitting over more than two orders of magnitude in time to find the dominant time behaviour for the first three layers, For the precursor film we have used $h_0(t) = A + B \times t^n$ as the fitting function either by forcing $n = 1$ and using least-squares analysis or letting n find its best value by using the Levenberg–Marquardt method (Press *et al*

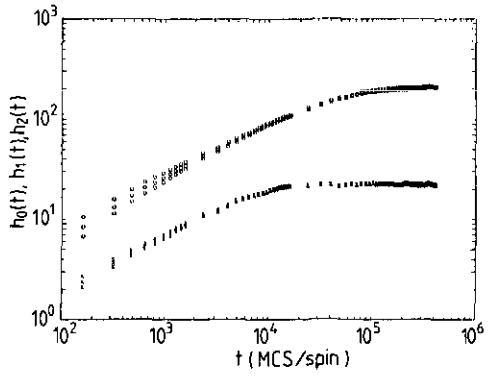

Figure 2. Dynamics of first three layers on an attractive substrate for two partially wet cases; $\mu_0 = 0.09$ (∘) and $\mu_0 = 0.05$ (×). In both cases $\tau = 0.10$ and $kT = 0.04$, with averages taken over 500 independent runs.

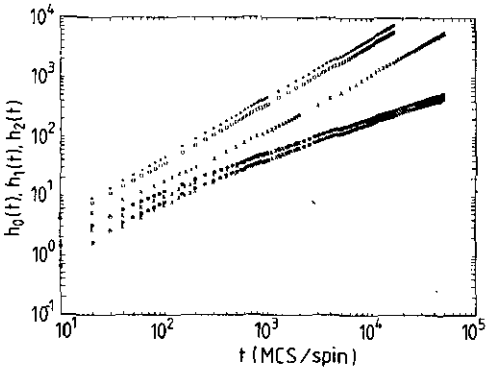

Figure 3. Dynamics of first layers for three completely wet cases; $\mu_0 = 0.20$ (*), $\mu_0 = 0.15$ (◦) and $\mu_0 = 0.11$ (×). Other parameters are the same as in figure 2.

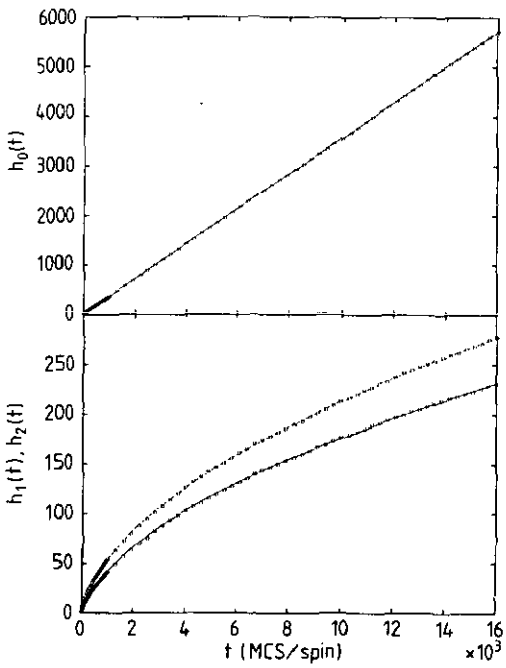

Figure 4. Curve fitting of the characteristic spreading dynamics in the complete wetting case ($\mu_0 = 0.15$ and other parameters are the same as in figure 2). Best fit curves are $h_0(t) = -1.56 + 0.357 \times t$, $h_1(t) = -5.51 + 0.720 \times (t \log t)^{1/2}$ and $h_2(t) = -8.43 + 0.609 \times (t \log t)^{1/2}$.

1986). In the latter case we find $n = 1.002$ with only a very slightly better sum of square residuals. For $h_1(t)$ and $h_2(t)$ we used either $h_i(t) = A + B \times t^n$ or $h_i(t) = A + B \times (t \log t)^{1/2}$ as fitting functions in the Levenberg–Marquardt method. A very good fit can be obtained by choosing $n = \frac{1}{2}$ in the former fitting function but a ten-fold improvement in the sum of square residuals can be achieved by letting n find their best values, $n = 0.556$ and $n = 0.567$ for h_1 and h_2, respectively. Using the latter fitting function we obtain the same sum of square residuals as for the unforced fitting function. These results are in excellent agreement with the analytical considerations by Abraham *et al*

(1990a, b) and the discussion above. It is worth mentioning that the sums of square residuals of these curve fittings can also be used as more accurate estimates for the error bars in $h_i(t)$. Thus we find that the error bars should be of the order of 0.8% instead of the earlier estimate of 5%.

We have carried out the same simulations and analysis for the $d=3$ case but by studying $\langle h_0(t)\rangle_s$, $\langle h_1(t)\rangle_s$ and $\langle h_2(t)\rangle_s$ instead. Here the subscript s stands for the spatial average over the y direction. As in two dimensions we find these averaged layers relaxing to equilibrium contact angle in the partially wet case. For complete wetting the average precursor film is once again found to be linear in time, i.e. $\langle h_0(t)\rangle_s \sim t$ and the two layers on top of it also behave as $\langle h_i(t)\rangle_s \sim (t \log t)^{1/2}$. A detailed analysis of the $d=3$ case will be presented elsewhere.

These simulations of the dynamic HSOS model show (a) a precursor film spreading as t, (b) some higher layers moving as $(t \log t)^{1/2}$ and (c) above that a profile as $e \sim x^{-2}$. Such results have been predicted by the Langevin theory (Abraham *et al* 1990a, b) (for (a) and (b)), and by the continuum theory (Joanny and de Gennes 1986) (for (c)) and experiments ((a), (b) and (c)), although in the latter two cases the geometry is spreading from a small drop rather than a wedge. It is very likely that this geometry produces significantly different results because in the drop case there is more likelihood of the spreading disc breaking up at its perimeter.

It is clear that our model contains significant over-simplifications. Firstly, the spreading interaction is assumed only to act on the first layer; this is easily remediable. Secondly, the substrate is taken to be smooth. A most serious approximation is the apparent lack of matter conservation. We assume that the wedge acts as a particle source for the precursor film and that particles move from there to the film front essentially instantaneously on the time scale of the simulation which is the ultimate one. If the precursor film is wide enough it is likely that evaporation from its front will become as fast as the spreading and the precursor will stop growing, much as seen with squalane (Heslot *et al* 1989a). Also it is clear that much remains to be done in this field.

In summary, we have shown that our dynamic HSOS model yields results in excellent agreement with the analytic Langevin theory. It even seems that this model shows similar fluid profiles as obtained from hydrodynamics, which on the other hand is not entirely appropriate for treating systems at molecular dimensions. In the future it should be very interesting to study volatile systems and systems with longer range substrate potentials.

The authors thank B Chopard, P Collet, J De Coninck, E Domany, F Dunlop, H Herrmann, J F Joanny and P J Upton for interesting discussions on related problems JH and KK would like to acknowledge the financial support from the Academy of Finland. KK would also like to thank SERC and Condensed Matter Theory Group (Oxford University) for financial support and hospitality.

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