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LETTER TO THE EDITOR

Dynamics of interfacial wetting near the roughening transition

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Abstract. Theoretical and computer simulation results are presented for the effect of fluctuations on the dynamics of layer growth during complete wetting. For example, in two dimensions we predict a crossover in the dynamics of the layer thickness W, from Lipowsky's result, $W \sim t^{1/4}$, for all non-zero temperatures in a lattice-gas system, to $W \sim (\ln t)^{1/2}$ at zero temperature (the roughening transition temperature) for intermediate times. Simulations of wetting in the three-state chiral Potts model give $W \sim t^{\psi}$, where ψ is 0.25 ± 0.03 for temperatures $T \geq 0.6\ T_c$, where T_c is the critical temperature, while the effective exponent ψ monotonically decreases with T below this temperature.

The physics by which layers grow on a substrate is a problem of interest in the fields of wetting, thin film growth and epitaxy (Pandit *et al* 1982, Wortis *et al* 1982, Venables *et al* 1984, Cahn 1977). The complete wetting of a substrate by a film can involve both the potential of interaction between the growing film and the substrate, as well as fluctuations which cause the film's interface to wander and become rough.

Previously, Lipowsky (1985) analysed the late-stage growth of layers during complete wetting. In the limit in which the substrate interaction is short ranged (and so can be neglected for large time values) he finds the root-mean-square thickness of the wetting layer to be

$$W(t) \sim t^{\psi} \tag{1}$$

for large time values, where $\psi = (3d)/4$, and dimension $d < 3$. In $d = 3$, $W \sim (\ln t)^{1/2}$ (Desai and Grant 1986). The value of the exponent ψ is essentially due to the effects of long-wavelength thermal fluctuations, which roughen the interface.

The question we shall address in this letter is, how universal is this result? We shall obtain results for different universality classes below. We consider the effects conservation laws, random impurities and, in particular, anisotropic surface tension and the roughening transition, have on this result.

Equation (1) follows from linearising the effects of inhomogeneities in a dynamical interface model. The equation describes, for example, a liquid-vapour interface after the chemical potential has been changed suddenly from a region in the phase diagram where only vapour is in equilibrium over the substrate, to a region of liquid-vapour coexistence. The liquid wets the substrate, and the flat liquid-vapour interface is repelled from the substrate. We shall be concerned with how that interface becomes more diffuse with increasing time.

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Let the substrate (and the interface at $t=0$) be a surface located in the $(d-1)$-dimensional X plane, which is orthogonal to the y axis. A single-valued variable $\zeta(x, t)$ gives the instantaneous position of the interface, relative to the y axis, as time goes on. For simplicity, we assume that the system can be prepared such that the interface, of area L^{d-1}, corresponds to the $y=0$ plane, at time $t=0$. That is, the interface is flat initially, as compared to its final rough configuration, so that $W(t=0)/W(t) \ll 1$, at the large time t. This idealisation simplifies the analysis, and is of no consequence for large times. The dynamical interface model is (Lipowsky 1985, Weeks 1980, Chui and Weeks 1978, Saito 1978, Allen and Cahn 1979, Bausch *et al* 1981, Kawasaki and Ohta 1982)

$$\partial\zeta/\partial t = D\delta F/\delta\zeta + \eta \tag{2}$$

where F is the free energy, D is a constant and η is the usual Gaussian thermal noise. (We neglect overhangs and bubbles, and additional factors required in general to enforce Euclidean invariance. This is allowable provided $W/L \ll 1$, as it is above the lower critical dimension. The results for $W(t)$ are of marginal validity at the lower critical dimension, which is $d=1$ here, unless there is a random field present, in which case it is $d=2$.)

The free energy can be written as $F[\zeta] = F_S[\zeta] + V[\zeta]$, where F_S is the surface free energy, and V gives the interaction with the substrate. Note that, for complete wetting, V is minimised by $\zeta \to \infty$. For the remainder of this letter we shall assume that V is sufficiently short ranged that its effects can be neglected for late times. (A Ginzburg criterion determines the upper critical dimension for short-range forces as the dimension at which roughening sets in (i.e. three dimensions for the Ising model).) In that case, the late stages of complete wetting are determined by roughening, i.e. by fluctuations entering through the form of the surface free energy. This causes $W(t) \equiv (\langle[\zeta - \langle\zeta\rangle]^2\rangle)^{1/2}(t)$ to grow. To obtain (1) with $\psi = (3-d)/4$, Lipowsky has assumed that the surface free energy is proportional to the surface area, i.e.

$$F_S = \sigma \int \mathrm{d}x^{d-1}[1 + (\nabla\zeta)^2]^{1/2} \tag{3}$$

where the proportionality constant σ is the surface tension. He then linearises around small ζ in (2) and solves for the correlation function which gives W. (One may linearise because the interface remains approximately flat during complete wetting, i.e. $W/L \ll 1$.)

One would expect that the large-time result of (1) might not apply if the long-wavelength properties of the dynamical equation, or the surface free energy, were significantly different from (2) and (3). For example, it is known that (2) follows from model A of critical dynamics (the continuum non-conserved Ising model) (Allen and Cahn 1979, Bausch *et al* 1981, Kawasaki and Ohta 1982). However, model B (the *conserved* Ising model) implies a much more complicated interface equation (Kawasaki and Ohta 1983, Kawasaki 1984). Nevertheless, if the conservation law is only enforced locally (in which case dynamics is limited by surface diffusion) one obtains a dynamical equation similar to (2), but with (Mullins 1957) $D \to D\nabla^2$. Linearising then gives $\psi = (3-d)/8$, for $d < 3$. (At the dimensions where the ψ vanish, $W(t) \sim (\ln t)^{1/2}$. Additional results, and further details of the theory, are given by Grant (1987).) Of course, the exponent is different because this is a different dynamical universality class.

Another example, where it is the long-wavelength behaviour of the free energy which changes, is given by the random-field Ising model (which provides a simple

model of the effects of impurities; a review is given by Imry (1984)). This is also in a different universality class from model A. That interface model corresponds to adding a term of the form

$$F_h = 2\int \mathrm{d}x^{d-1}\int_0^{\zeta} \mathrm{d}y\, h(x, y) \tag{4}$$

to the surface free energy (Grinstein and Ma 1983), where h is a time-independent Gaussian random variable. Linearising this equation gives $\psi = (5-d)/6$ for the late-stage growth of the wetting layer, in $d < 5$. It should be noted that metastable states have been observed to play an important role in the dynamics of equilibration of the random-field Ising model. The present results thus apply to a time regime which would precede that regime.

These two examples where the growth exponent ψ changes are not surprising; conservation laws, or a random external field, change the universality class of a system. We shall, however, consider a rather different example for the remainder of this letter: an anisotropic surface tension near the roughening transition temperature T_R. The roughening transition leads to significant changes to the long-wavelength properties of a system, and thus to significant changes in the late-stage growth of the wetting layer.

Below T_R (where $T_R = 0$ in $d = 2$, and $0 < T_R < T_C$ in $d = 3$), there is no longer an infrared divergence in ζ. The 'massive' behaviour of the interface implies that dynamics is limited to large fluctuations, the rate of which is proportional to their free energy (as in nucleation theory). Roughly, then, the timescale over which such fluctuations occur is $\tau \sim \exp(\text{constant})\, W^n$, where n depends on the form of the free energy. Thus, $W \sim (\ln t)^{1/n}$ below T_R. An exponent $n = 2$ corresponds to a quadratic free energy. Presumably the exponent would be difficult to determine numerically or experimentally, however.

Above T_R, we expect crossover behaviour which is affected by anisotropic surface tension over intermediate length scales (but not the strict limit $q \to 0$, for which Lipowsky's result applies). Furthermore, for our problem, this corresponds to intermediate times, but not $t \to \infty$. A model for 'lattice' effects which can be used for this purpose has been introduced by Grinstein and Ma (1983):

$$F \propto \int \mathrm{d}^{d-1}x(1+|\nabla\zeta|). \tag{5}$$

This model, we believe, has only a limited validity for intermediate length scales near T_R. In principle, a better approach for $d = 2$ would be to use the known anisotropic surface tension for, say, the Ising model (Avron *et al* 1982). However such a calculation appears quite formidable. We have obtained $W(t)$ from (5) by the following method. First, we expand F to quadratic order in ζ, since we are only considering small distortions of the interface. The coefficient of the quadratic term is evidently a function of the magnitude of $\boldsymbol{q}$, by translational invariance. We assume a power-law form for this coefficient, and determine the exponent self-consistently through the sum rule relating $\langle\zeta^2\rangle$ to $\delta^2 F/\delta\zeta^2$. (Details of this and other analyses are given by Grant (1987).) We eventually obtain $W \sim (\ln t)^{1/2}$ in $d = 2$. (Explicitly, $\psi = (2-d)/(3-d)$, for $d < 2$, and $\psi = 0$ in $d = 3$. If a random field is present, $\psi = (3-d)/(4-d)$. If the order parameter is locally conserved, the ψ are halved.) We emphasise again, however, that these results only apply to intermediate length scales (and so intermediate times) for $T \geqslant T_R$. For $t \to \infty$, the previous results, in particular Lipowsky's, apply. To summarise, our theoretical results suggest that there is rich behaviour near T_R: in $d = 2$, for all

$T > T_R$ (where $T_R = 0$), we expect $W \sim t^{1/4}$, as $t \to \infty$. However, for intermediate times and $T \geqslant T_R$ we expect crossover behaviour due to the proximity of the roughening transition; our analysis gives $W \sim (\ln t)^{1/2}$. This would lead to an effectively temperature-dependent ψ, with ψ close to 0 for low T, rising to $\frac{1}{4}$ for high T, for analysis over a limited time regime. In the second half of this letter we shall present the results of a Monte Carlo simulation which tests these predictions.

We have simulated the two-dimensional three-state chiral Potts model on a square lattice. This simple system is known to have a wetting transition, with a short-ranged 'substrate' interaction (Huse *et al* 1983, Selke and Huse 1983, Yeomans and Derrida 1985). Furthermore, at low temperatures, the square lattice gives rise to an anisotropic surface tension. Therefore we can test the above prediction. The details of the model are as follows. Its Hamiltonian is

$$H = -J \sum_{\langle ij \rangle}^{y} \cos[\tfrac{2}{3}\pi(n_i - n_j + \Delta)] - J \sum_{\langle ij \rangle}^{x} \cos[\tfrac{2}{3}\pi(n_i - n_j)] \tag{6}$$

where a variable $n_i = 0$, 1 or 2 is associated with each lattice site i, Δ is the chiral field, J is the interaction constant, and the sums are taken over nearest neighbours in the y and x directions, respectively. The equilibrium critical properties are fairly well known. Three phases are stable: a ferromagnetic phase, a paramagnetic phase and an incommensurate phase. Huse *et al* (1983) have recently pointed out that this model has interesting interface properties when Δ is varied, and in particular they have discussed complete wetting. Wetting of an interface occurs as follows. The free energy of an interface between spins taking values n_L and n_R (called a '$-$' interface) depends on $(n_R - n_L)$ (mod 3), such that for a value of 1 it corresponds to a free energy $F_+ = F_-$, but for increasing Δ, F_+ decreases relative to F_-. In particular, when $2F_+ = F_-$, a '$-$' interface will split into two '+' interfaces and hence become wet. At temperature $T = 0$ this occurs for $\Delta = \frac{1}{4}$.

We have simulated the kinetics of interfacial wetting in the model with Glauber spin-flip dynamics. Various values of T and Δ were studied within the wetting region of the phase diagram. Lattices of size $(N+2) \times N = 104 \times 102$, and 206×204 were prepared with the $y = 1$ row fixed to $n_1 = 0$, while the $y = N+2$ row was fixed to $n_{N+2} = 2$, so as to create a flat '$-$' interface at the $y \simeq (N+2)/2$ plane, initially. Periodic boundary conditions were used in the x direction. There were 100 runs done over 500 Monte Carlo timesteps for each temperature on the small lattice, while 100 runs over 5000 Monte Carlo steps were done on the larger lattice. The dynamics of the growth of the wet layer was measured by $W(t) = N_1^{(0,2)}(t) - N_1^{(0,0)}(t)$, where $N_\gamma^{(\alpha,\beta)}$ is the average number of spins per row in state γ with boundary conditons (α, β) on the y axis. After the early stages of wetting, this $W(t)$ is twice the root-mean-square position of the interface described by the above theory (because the 'substrate interaction' is short ranged). The total energy of the system was also calculated.

In figure 1 we show two representative configurations of a system which was prepared with one flat '$-$' interface. At very early times the interface is rapidly wetted by one layer of the third degenerate state. During this early stage, vertices (where the three phases meet) play a role in the dynamics. Since the total energy of the system was only found to change significantly during those early times, this stage seems to be primarily energy drives. At later times the observed occurrence of vertices is negligible, and the kinetics acts to make the two interfaces rougher as time goes on.

The time dependence of $W(\Delta = 0.4, t)$ is shown in figure 2 for temperatures $T/J =$ 0.2, 0.3, 0.4, 0.6, 0.8 and 1.0 (the critical temperature is $T_c(\Delta = 0.4) \simeq 1.05J$). The

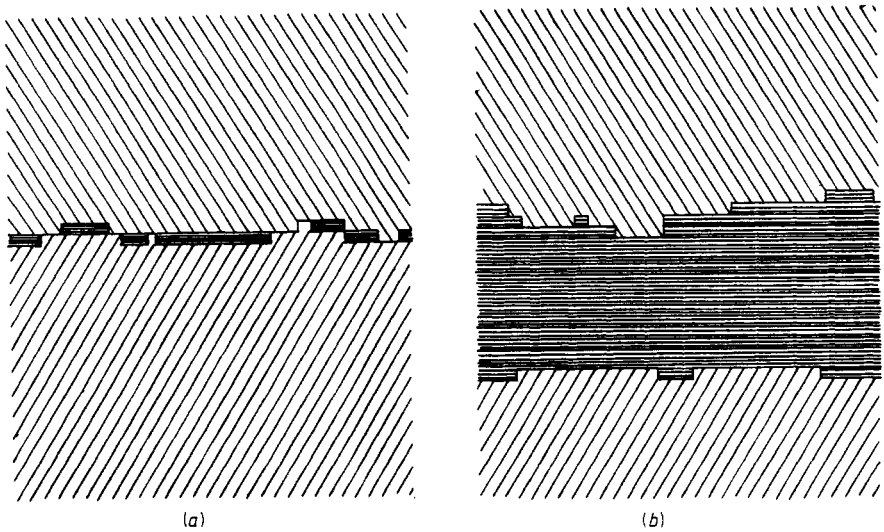

Figure 1. Two representative configurations are shown at $T = 0.6J$ and $\Delta = 0.4$. (a) shows the early stages of complete wetting, (b) the late stages.

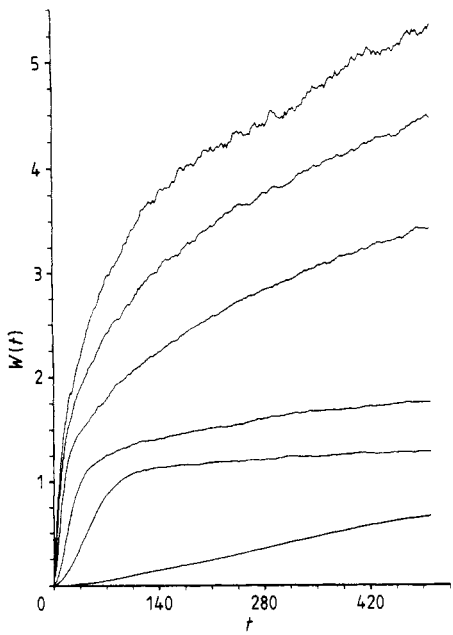

Figure 2. $W(t)$ against t is shown for $T/J = 0.2$, 0.3, 0.4, 0.6, 0.8 and 1.0, from bottom to top, over 500 Monte Carlo timesteps.

dynamics of wetting clearly separates into two time regimes: early-time wetting of the first layer, and late-time complete wetting. The wetting during the early stage is rapid for temperatures $T \gtrsim 0.3J$, and a strong temperature dependence is evident in figure 2. Indeed, the $T/J = 0.2$ curve only consists of that early stage, for the time regime shown in that figure. Thus wetting of the first layer involves strong temperature dependences and vertex dynamics. The present theory does not describe the early

stages of growth; presumably, this early stage involves the short-ranged 'substrate interaction' (i.e. the repulsive force between two '+' interfaces) which we have neglected to obtain a late-time solution.

The growth during the later stages is significantly slower. It is this aspect of the simulation which the theory discussed above addresses. Figure 2 shows a pronounced crossover from slow late-time growth at low temperatures to faster late-time growth at high temperatures, as we predicted above. We note that this temperature dependence of W is due to the limited time regime over which our simulations have been performed. For $t \to \infty$, we expect this crossover to only take place at $T = 0$. We have quantitatively characterised this effect by a power-law fit to the data from the larger system, namely $W(t) = W_0 + Ct^{\psi}$, where W_0 is the value of W at which the crossover to late-stage complete wetting occurs (that is, $W_0 \simeq 1$), and C is a constant. (If we fit with $W_0 \equiv 0$, then $\psi \simeq 0.2$ at high temperatures, while ψ becomes smaller as T is decreased. The physics of the problem requires $W_0 \simeq 1$, however, since we observe a clear distinction between early and late-stage wetting. Fits are also better in that case.) At high temperatures, $T \gtrsim 0.6J$, the effective growth exponent is approximately independent of temperature, being $\psi = 0.25 \bullet 0.03$, which is consistent with Lipowsky's prediction of $\psi = \frac{1}{4}$. Below this temperature, however, ψ becomes smaller. (For example, $\psi(T = 0.4J) \simeq 0.12$, and $\psi(T = 0.3J) < 0.05$.) This effective dependence upon temperature close to the roughening transition is in agreement with the theory presented above. (There is no special significance to the temperature $T = 0.6J$, that crossover temperature depends on the detailed form of the anisotropic σ for the chiral Potts model, as well as the time regime over which we analyse our data.) Other tests of theory, simulations in different regions of the phase diagram, and a study of the effects of wetting on the kinetics of ordering have been conducted and will be reported elsewhere.

To conclude, we have presented a study of the dynamics of complete wetting. A dynamical model was used to analyse the effects of fluctuations on layer growth near T_R. The results of this theory were then compared to computer simulation, where we verified our prediction of strong crossover behaviour due to anisotropic surface tension.

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