J. Phys. A: Math. Gen. **18** (1985) L585-L590. Printed in Great Britain

LETTER TO THE EDITOR

Nonlinear growth of wetting layers

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Received 16 April 1985

Abstract. The growth of wetting layers is studied as a function of time t in the framework of effective interface models. The thickness of such layers is found to grow as $t^{1/4}$ and $t^{1/5}$ for three-dimensional systems which are governed by non-retarded and retarded van der Waals forces. In the fluctuation regimes, a universal growth law t^{ψ} with $\psi = \frac{1}{4}(3-d)$ is found where d is the bulk dimensionality. It is also shown that the dynamic critical exponent z is super-universal: $z = 2$ holds both in the mean field and in the fluctuation regimes.

Considerable effort has been devoted recently to the study of wetting phenomena (see the reviews in Pandit *et al* 1982, and Sullivan and Telo da Gama 1985). Most of this work has focused on the properties of wetting layers in thermal equilibrium. It is also of interest, however, to study how such layers approach equilibrium if they are initially far away from it. Consider, for instance, a liquid layer between a gas of adatoms and a solid substrate surface. In equilibrium, its thickness is determined by the temperature T and by the chemical potential difference $\delta\mu \propto T \ln(p^*/p)$ where p is the pressure and p^* is its value at liquid-vapour coexistence. For $\delta\mu \gg 0$, the wetting layer is very thin. For $\delta\mu \simeq 0$, it is very thick. Thus, if one changes $\delta\mu$ from $\delta\mu \gg 0$ to $\delta\mu \simeq 0$, the thickness of the layer will steadily grow with time. This growth is studied here in the framework of effective interface models.

The equilibrium properties of wetting layers are most easily obtained from the free energy functional (Lipowsky 1984, 1985 and references therein)

$$F\{l\} = \int \mathrm{d}^{d-1}x[\tfrac{1}{2}\sigma(\nabla l)^2 + V(l)]/(K_{\mathrm{B}}T) \tag{1}$$

$l = l(x_1, \ldots, x_{d-1})$ is the distance between the $(d-1)$-dimensional interfaces which bound the wetting layer, σ is an appropriate interfacial tension, and the interface potential $V(l)$ is the free energy per unit area for a layer of constant thickness. Quite generally, $V(l)$ consists of a repulsive and an attractive part. For complete wetting, one has

$$V(l) = Wl^{-p} + \delta\mu l \tag{2}$$

with a positive Hamaker constant W. The first term in (2) is repulsive, i.e., it favours a larger value of l, the second term in (2) is attractive, i.e., it favours a smaller value of l. The exponent p in (2) is given by $p = \kappa - d - 1$ where $\kappa = 6$ and $\kappa = 7$ for non-retarded and retarded van der Waals forces (see, e.g., Dzyaloshinskii *et al* 1961).

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0305-4470/85/100585 + 06$02.25

The chemical potential difference $\delta\mu$ is the only scaling field which is relevant at complete wetting. As $\delta\mu \to 0$, the mean thickness $\langle l \rangle \equiv \bar{l}$ of the layer diverges as well as the correlation length $\xi_\parallel$ for interfacial fluctuations

$$\bar{l} \propto \delta\mu^{\beta_s} \qquad \beta_s < 0 \tag{3a}$$

$$\xi_\parallel \propto \delta\mu^{-\nu_\parallel} \qquad \nu_\parallel > 0. \tag{3b}$$

Two scaling regimes have to be distinguished; a mean field (MF) regime for $d > d^*(p)$ and a fluctuation (FL) regime for $d \leqslant d^*(p)$. The upper critical dimension $d^*(p) = (2+3p)/(2+p)$ depends only on the repulsive part of the interface potential (2) (Lipowsky 1984). In the MF regime, one has

$$\beta_s = -1/(1+p) \qquad \nu_\parallel = (2+p)/(2+2p). \tag{4a, b}$$

In the FL regime with $d \leqslant d^*(p)$, the values for β_s and $\nu_\parallel$ can be obtained from two simple and plausible assumptions: (1) that these critical exponents are universal, i.e., do not depend on p; and (2) that they are continuous at $d = d^*(p)$. These two assumptions together with (4) lead to

$$\beta_s = -(3-d)/(d+1) \qquad \nu_\parallel = 2/(d+1) \tag{5a, b}$$

for $d \leqslant d^*(p)$. The same values have been obtained from a self-consistent perturbation theory (Kroll *et al* 1985) and from a linear renormalisation group (Fisher and Huse 1985). They can also be obtained from the overall entropy loss of the two interfaces as given by Fisher and Fisher (1982).

The dynamical model studied here is defined by the Langevin equation

$$\partial l(\boldsymbol{x}, t)/\partial t = -\lambda \delta F\{l\}/\delta l + \zeta. \tag{6}$$

λ is an Onsager coefficient, $F\{l\}$ is given by (1), and ζ is a Gaussian random force with $\langle \zeta \rangle = 0$ and $\langle \zeta(\boldsymbol{x}, t)\zeta(\boldsymbol{x}', t') \rangle = 2\lambda\delta(\boldsymbol{x}-\boldsymbol{x}')\delta(t-t')$. Similar Langevin equations have been studied previously for the dynamics of the roughening transition (Chui and Weeks 1978) and as a dynamic version of the drumhead model (Bausch *et al* 1981). In the latter case, one has to include a generalised Onsager coefficient $\lambda = \lambda(l)$ in order to preserve the nonlinear symmetry of the drumhead model. Such a complication does not arise here since (1) does not possess such a symmetry. For convenience, I will put $K_B T \equiv 1$ and $\sigma \equiv 1$ in the rest of this paper.

Consider now a situation where the wetting layer has a finite thickness for $t < 0$ At $t = 0$, the field $\delta\mu$ is changed to $\delta\mu = 0$. As a consequence, the thickness $\bar{l}(t)$ will steadily grow towards its equilibrium value $\bar{l} = \infty$. In the MF approximation to (6) which should be valid for $d > d^*(p)$, this growth is determined by

$$\partial \bar{l}(t)/\partial t = -\lambda \partial V/\partial l|_{\bar{l}} = \lambda p W \bar{l}^{-(1+p)}. \tag{7}$$

The solutions of (7) behave like

$$\bar{l}(t) \propto t^{\psi} \tag{8a}$$

with

$$\psi = 1/(2+p) \tag{8b}$$

for large t. Thus, the thickness of the wetting layer grows as $t^{1/4}$ and $t^{1/5}$ for three-dimensional systems governed by non-retarded and retarded van der Waals forces, i.e., by $p = 2$ and $p = 3$

For short-range forces, on the other hand, the interface potential has the form

$$V(l) = W\,\mathrm{e}^{-l/\xi} + \delta\mu l \tag{9}$$

where ξ is the bulk correlation length. The corresponding MF equation leads to

$$\bar{l}(t) \propto \ln(t). \tag{10}$$

Such a logarithmic behaviour has been found previously from the numerical solution of a Ginzburg-Landau model for the fluid density (Riecke 1982).

The long-time behaviour (8) can be re-derived by a scaling argument. Assume that $\bar{l} = \bar{l}(\delta\mu, t)$ is a homogeneous function of its arguments, i.e.,

$$\begin{aligned}\bar{l}(\delta\mu, t) &= b^{-\beta_s/\nu_\parallel}\bar{l}(b^{1/\nu_\parallel}\delta\mu, b^{-z}t) \\ &= \delta\mu^{\beta_s} L(\xi_\parallel^{-z} t)\end{aligned} \tag{11}$$

where b is an arbitrary rescaling factor, and $L(x)$ a shape function. The dynamic exponent z in (11) is $z = 2$ in MF theory. This can be seen, for instance, from the Fourier transform $R(k, \omega)$ of the linear response function. In MF, one has

$$\begin{aligned}R(k, \omega) &= R_0(k, \omega) = [-\mathrm{i}\omega + \lambda(k^2 + \xi_\parallel^{-2})]^{-1} \\ &\equiv \xi_\parallel^2 \bar{R}(\xi_\parallel k, \xi_\parallel^2 \omega)\end{aligned} \tag{12}$$

which implies $z = 2$. The fact that $z = 2$ in the MF approximation for wetting has also been observed by Forgacs *et al* (1985) who studied a Ginzburg-Landau model for the fluid density.

The scaling form (11) implies

$$\bar{l}(0, t) \propto t^{-\beta_s/(\nu_\parallel z)}. \tag{13}$$

From (4), (8) and (13), one finds

$$-\beta_s/(\nu_\parallel z) = 1/(2+p) = \psi, \qquad d > d^*(p). \tag{14}$$

Note that this scaling relation is quite similar to the corresponding relation for the nonlinear relaxation of an order parameter near a bulk critical point. In the latter case, the order parameter decays as t^{ψ_b} with $\psi_b = -\beta_b/(\nu_b z_b) < 0$ (Fisher and Rácz 1976) where β_b, ν_b and z_b are bulk critical exponents in the usual notation.

The identity $z = 2$ for the dynamic critical exponent z holds also in the FL regime for $d \leqslant d^*(p)$. This is shown as follows by a self-consistency argument which is similar to the one used by Kroll *et al* (1985) for the time-independent case. First, let us consider the generalised interface potential

$$V(l) = Wl^{-p} + \delta\mu l^q \tag{15}$$

and put $l = \bar{l} + \phi$. This leads to a field theory for $\phi = l - \bar{l}$ with the potential

$$\bar{V}(\phi) \equiv V(l) - V(\bar{l}) = \sum_{n \geqslant 1} \frac{1}{n!} v_n \phi^n. \tag{16}$$

The vertices v_n are given by

$$v_n = \mathrm{d}^n V(l)/\mathrm{d}l^n|_{\bar{l}} \tag{17a}$$

and behave like

$$v_n \to \delta\mu\,\bar{l}^{q-n} \propto \delta\mu\,\xi_\parallel^{(q-n)(3-d)/2} \tag{17b}$$

as $\delta\mu \to 0$ where the scaling relation $\bar{l} \sim \xi_{\parallel}^{(3-d)/2}$ has been used. The Fourier transform $R(k, \omega)$ of the linear response function has the form

$$R(k, \omega) = [-i\omega + \lambda(k^2 + v_2) - \Sigma(k, \omega)]^{-1} \tag{18}$$

with $v_2 \propto \delta\mu \xi_{\parallel}^{(q-2)(3-d)/2}$ from (17*b*). The self-energy $\Sigma(k, \omega)$ can be expressed in terms of diagrams according to the usual rules (Bausch *et al* 1976, De Dominicis and Peliti 1978). There are two types of internal lines, namely response and correlation lines. After the integrations over internal times have been performed, each correlation line contributes a factor $(k^2 + v_2)^{-1}$, and each time interval gives a factor $[-i\omega + \lambda \sum_{\alpha} (k_{\alpha}^2 + v_2)]^{-1}$ where α runs over all momenta present in that time interval.

The correlation length $\xi_{\parallel}$ may now be determined self-consistently. First, it is assumed that

$$\xi_{\parallel}^{-2} \sim v_2 \tag{19}$$

which implies (3*b*) with

$$\nu_{\parallel} = 2/(-2 + 3q + 2d - qd). \tag{20}$$

For $q = 1$, (20) reduces to (5*b*). Due to (19), each diagram for $\Sigma(k, \omega)$ with a total number N of vertices yields a contribution of the form

$$\xi_{\parallel}^{-2} (\delta\mu \xi_{\parallel}^{1/\nu_{\parallel}})^N A(x, y) \tag{21}$$

where A depends on $\delta\mu$ only via

$$x \equiv (\xi_{\parallel} k)^2 \qquad y \equiv \xi_{\parallel}^2 i\omega. \tag{21a, b}$$

Self-consistency requires that $\Sigma(0, 0) \sim \xi_{\parallel}^{-2}$ yields again (20) which is found to be fulfilled. Furthermore, (21) implies

$$\xi_{\parallel}^{-2} A(x, y) = a\xi_{\parallel}^{-2} + bk^2 + ci\omega + \ldots \tag{22}$$

for small k and ω with $a \equiv A(0, 0)$, $b \equiv dA(x, 0)/dx|_0$, and $c \equiv dA(0, y)/dy|_0$. Thus, $\Sigma(k, 0) \sim k^2$ for small k which means that $\eta \equiv 0$. This identity has also been proven to be correct by transfer-matrix methods for two-dimensional systems (Lipowsky 1985). Similarly, one concludes from (22) that $\Sigma(0, \omega) \sim i\omega$ for small ω which implies that the dynamic exponent $z = 2$ in the FL regime.

One may now use the scaling form (13) in order to determine the nonlinear growth in the FL regime. It then follows from (5) and $z = 2$ that

$$\psi = -\beta_s/(\nu_{\parallel} z) = \tfrac{1}{4}(3 - d) \qquad d \leqslant d^*(p). \tag{23}$$

In particular, for $d = 2$ and $p \geqslant 2$, the wetting layer grows as t^{ψ} with the universal value $\psi = \frac{1}{4}$. This applies to all lattice models with short-range interactions ($p = \infty$) since the roughening temperature $T_R = 0$ in $d = 2$ and one may, therefore, use the continuum model studied here. As a consequence, the universal growth law $t^{1/4}$ should be accessible to Monte Carlo simulations of models such as the two-dimensional Ising model where $\delta\mu$ corresponds to the magnetic field h

The above scaling argument can also be applied to the length scale $\xi_{\parallel}$. As a result, one finds

$$\xi_{\parallel}(t) \propto t^{1/z} = t^{1/2}, \qquad \forall d. \tag{24}$$

Thus, the growth of this length scale is predicted to be completely independent of p, i.e., of the underlying microscopic forces for all d.

In an experiment, one cannot make $\delta\mu$ exactly equal to zero. If $\delta\mu$ is small and *positive,* the equilibrium thickness $\bar{l}(\infty)$ is large but finite. As a consequence, there is a characteristic time

$$t^* \sim \delta\mu^{\Delta} \tag{25a}$$

with

$$\Delta = \beta_s/\psi = -z\nu_{\parallel} = -2\nu_{\parallel}. \tag{25b}$$

For $0 \ll t \ll t^*$, the layer thickness grows as predicted by (8) and (10). For $t \leqslant t^*$, $\bar{l}(t)$ relaxes exponentially to $l = \bar{l}(\infty)$. On the other hand, if $\delta\mu$ is small and *negative,* one has $\partial\bar{l}/\partial t \sim \lambda\delta\mu$ from the MF approximation to (6). Thus, the wetting layer grows linearly in this case as long as the metastable or oversaturated bulk phase does not decay.

So far, the discussion has been confined to complete wetting. Very similar results can be obtained for critical and multicritical wetting. At bulk coexistence, the corresponding interface potentials have the form

$$V(l) = Al^{-s} + Bl^{-r}, \qquad s > r, \tag{26}$$

with $A > 0$ and $B < 0$. s depends on the type of criticality. For fixed s, different values for r correspond to different relevant perturbations. For each pair (s, r) one has two boundary dimensions and thus three different scaling regimes (Kroll *et al* 1985, Fisher and Huse 1985). As for complete wetting, the upper critical dimension d^* depends only on the repulsive part of (26): $d^*(s) = (2+3s)/(2+s)$. For $d \leqslant d^*(s)$, the correlation length $\xi_{\parallel} \propto |B|^{-\bar{\nu}_{\parallel}}$ as $B \to 0^-$ with $\bar{\nu}_{\parallel} = 2/(-2-3r+2d+rd)$. That exponent goes to infinity as $d \to d^{**}(r) = (2+3r)/(2+r)$. d^{**} is the second boundary dimension which depends only on the attractive part of (26). Thus, there is a MF regime for $d > d^*(s)$, a weak fluctuation (WFL) regime for $d^*(s) > d > d^{**}(r)$, and a strong fluctuation (SFL) regime for $d^{**}(r) > d$. The existence of three scaling regimes showed up first in an investigation of the interface potential $V(l) = A\,\mathrm{e}^{-l/\xi} + Bl^{-r}$ (Lipowsky 1984) which corresponds to $s \to \infty$ in (26). In the MF and in the WFL regime, the critical and multicritical transitions occur at $B = 0^-$. As a consequence, the nonlinear growth is solely determined by the repulsive l^{-s} term in (26). By analogy with (8) and (23), this immediately implies

$$\psi = \begin{cases} 1/(2+s) & \text{MF} \\ \frac{1}{4}(3-d) & \text{WFL.} \end{cases} \tag{27}$$

In fact, exact results in $d = 2$ and continuity arguments indicate that $\psi = \frac{1}{4}(3-d)$ holds also in the SFL regime where the transitions occur at finite $B < 0$

I thank Professor M E Fisher for his support and his hospitality at Cornell, and Professors B Widom and C Franck for stimulating discussions. I am grateful to Professor M E Fisher for a critical reading of the manuscript. This work is supported by a grant from the National Science Foundation.

Note added in proof. The predictions of this letter should also apply to thin films which grow via the Frank-van der Merwe mode. Physical systems which exhibit this growth behaviour can be found in Venables *et al* (1984).

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