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LETTER TO THE EDITOR

Universal and non-universal short-distance expansions in the strong, weak and intermediate fluctuation regimes of critical wetting

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Abstract. We study the scaling properties of the density profile $\rho(z)$ of a fluid near a wall undergoing a critical wetting transition in the strong-fluctuation and in the weak-fluctuation scaling regimes. A critical exponent θ describing the short-distance algebraic decay of the density profile (for distances z normal to the wall much less than the perpendicular correlation length $\xi_\perp$) is calculated explicitly in dimension $d=2$ using an effective interfacial Hamiltonian model. The exponent θ is found to be universal in the strong-fluctuation regime ($\theta=1$) and in the weak-fluctuation regime ($\theta=3$) In contrast to the other standard critical exponents θ is non-universal at the weak-fluctuation/mean-field borderline We discuss the origin of the universality of θ in the different fluctuation regimes and derive expressions for θ, valid for general d, in terms of known critical exponents

In a recent article (Parry (1991) hereafter referred to as I) the author has argued that, for systems with short-ranged forces and bulk dimension $d<3$, the density profile $\rho(z)$ of a thick liquid film adsorbed at a planar wall-vapour interface (bulk chemical potential $\mu\leq\mu_{\text{sat}}$) is a scaling function of the variables $z\tilde{t}^{\nu_\perp}$ and $h\tilde{t}^{-\Delta}$. Here z measures the distance normal to the wall whilst $\tilde{t}\equiv(T_w-T)/T_w$ and $h\propto(\mu-\mu_{\text{sat}})$ are the relevant scaling fields for the critical wetting transition which takes place at temperature $T=T_w$, $h=0^-$. The critical exponent $\nu_\perp$ characterizes the growth of the perpendicular (to the wall) correlation length $\xi_\perp\sim\tilde{t}^{-\nu_\perp}$ and Δ is the gap exponent (see below). In the present letter we extend the scaling theory to the weak-fluctuation regime of critical wetting. That is, we argue that the density profile retains a scaling form even in the presence of relevant long-range (algebraically decaying) intermolecular forces. To test the scaling theory developed herein we have analysed the critical wetting transition in $d=2$ using an effective interfacial Hamiltonian model. In addition to confirming the scaling hypothesis this analysis demonstrates that the density profile $\rho(z)$, at short distances $z\ll\xi_\perp$, may exhibit universal or non-universal algebraic behaviour depending upon the type of fluctuation regime that the critical wetting transition is described by. To proceed we recall some details of the critical wetting transition.

If the equilibrium thickness l_{eq} of a liquid film adsorbed at a wall-gas interface diverges continuously as the temperature T approaches some wetting temperature T_w at chemical potential $\mu=\mu_{\text{sat}}^-$ then the system is said to undergo a critical wetting transition. Excellent reviews of wetting transitions may be found in Dietrich (1988) and Schick (1990). Associated with the growth of the film thickness $l_{\text{eq}}\sim\tilde{t}^{-\beta_s}$ is the divergence of correlation lengths perpendicular ($\xi_\perp\sim\tilde{t}^{-\nu_\perp}$) and parallel ($\xi_\parallel\sim\tilde{t}^{-\nu_\parallel}$) to

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the substrate. Such divergences are due to the capillary-wave-like fluctuations of the depinning liquid–vapour interface. The approach to critical wetting is also associated with the vanishing of a singular term $\Sigma^{(s)} \sim \tilde{t}^{2-\alpha_s}$ in the excess grand potential per unit area $\Omega^{(s)}/A$. In addition to a relevant temperature variable $\tilde{t}$ the deviation of the chemical potential from saturation is also a relevant scaling field Thus, we write (Nakanishi and Fisher 1982)

$$\Sigma^{(s)} = \tilde{t}^{2-\alpha_s} W(h\tilde{t}^{-\Delta}) \tag{1}$$

where Δ is a gap exponent ($\Delta = 2 - \alpha_s + \beta_s$) and W is the scaling function Varying the temperature T is equivalent (for the critical wetting transition) to varying the strength ε of the attractive part of the wall–fluid external potential. Generally speaking such transitions are only found in systems where the attractive one-body wall–fluid interaction $V(z) \sim -\varepsilon z^{-m} (z \to \infty)$ has the same range as the attractive part of the two-body fluid–fluid interaction, i.e. $\phi(r_{12}) \propto -r_{12}^{-(d+m)} (r_{12} \to \infty)$. In addition, outside of the strong-fluctuation regime (SFR), the values of the critical exponents for critical wetting show a remarkable sensitivity to the range m of the forces At mean-field level the equilibrium film thickness in zero bulk field follows from minimizing the effective interfacial binding potential (Lipowsky and Fisher 1987)

$$U(l) = -ul^{-r} + wl^{-s} \qquad w > 0, h = 0. \tag{2}$$

In the presence of a bulk field there is an additional term $|h|l$ in (2). For critical wetting transitions $s = r + 1 = m$. The field u vanishes at the (mean-field) wetting temperature: $u \propto \tilde{t}$. Other critical exponents follow from the identifications $U''(l_{\mathrm{eq}}) \propto \xi_{\|}^{-2}$ and $U(l_{\mathrm{eq}}) \propto \Sigma^{(s)}$. In addition, for $d < 3$, the capillary-wave relation $\nu_\perp = (3-d)\nu_\|/2$ is generally valid. For $d > 3$ $\xi_\perp$ is finite. In fact the whole mean-field regime is characterized by the length scale inequality $l \gg \xi_\perp (\tilde{t} \to 0)$. The mean-field description is valid provided $d \geq d_1 = (3s+2)/(s+2)$ corresponding to the upper critical dimension for critical wetting. Below the upper critical dimension fluctuation effects (due to the capillary-wave-like modes of the liquid–vapour interface) alter the critical behaviour. An immediate and important consequence of the hyperscaling hypothesis $\Sigma^{(s)} \sim \xi_\|^{-(d-1)}$ (presumed valid $\forall d \leq d_1$) is $\beta_s = \nu_\perp$ (Kroll *et al* 1985). That is, for $d \leq d_1$, the perpendicular correlation length $\xi_\perp$, measuring the liquid–vapour interfacial roughness, is of the same order as the equilibrium film thickness l_{eq}. Thus $d < d_1$ corresponds to the fluctuation regime of critical wetting. The rich structure of this fluctuation regime is elegantly described by the heuristic scaling picture of Lipowsky and Fisher (1987). These authors argued that for $d < 3$ capillary-wave fluctuations (not accounted for in mean-field calculations) give rise to an effective entropic repulsion term in (2) $U_{\mathrm{FL}} \sim l^{-\tau}$ with $\tau = 2(d-1)/(3-d)$. The mean-field regime $d > d_1$ then follows from the requirement $\tau > s$, i.e. fluctuation effects are a negligible higher-order contribution. The fluctuation regime $d \leq d_1$ is then seen to comprise (*a*) a weak-fluctuation regime (WFR) where $r < \tau < s$ or equivalently $d_2 < d < d_1$ with $d_2 = (3r+2)/(r+2)$, (*b*) a strong-fluctuation regime (SFR) for $d < d_2$ where U_{FL} is larger than either term in (2). In the WFR the attractive part appearing in (2) is a relevant long-ranged perturbation (to the critical wetting fixed point potential) and hence the phase transition occurs at the mean-field boundary $u = 0$. The repulsive part in (2) is irrelevant in the WFR. The critical exponents in the WFR may be determined analytically, for arbitrary d, using the above scaling arguments. Alternatively they may be derived from perturbation theory (Kroll *et a.* 35) or by renormalization group analysis of an interfacial

Hamiltonian (Lipowsky and Fisher 1987)

$$\beta_s = \frac{1}{\tau - r}$$

and recall $\beta_s = \nu_\perp = \frac{1}{2}(3-d)\nu_\parallel$ and $(2-\alpha_s) = (d-1)\nu_\parallel$. This has been confirmed in $d=2$ in transfer-matrix studies of effective interfacial Hamiltonians (Kroll and Lipowsky 1983). The critical exponents in the WFR satisfy the exponent equality $1-\alpha_s = \beta_s r$. Together with the hyperscaling and capillary-wave relation this determines uniquely the critical exponents.

In the SFR critical exponents are universal (i.e. r, s independent since both terms in (2) constitute irrelevant operators) and the critical wetting transition occurs at $u>0$. The exponents for such transitions have been determined analytically for $d=2$ from exactly solved models (Abraham 1980) and effective interfacial Hamiltonians (see e.g. Lipowsky 1988) and numerically for $2 \leqslant d < 3$ using a nonlinear renormalization group analysis (Lipowsky and Fisher 1987, David and Leibler 1990). In $d=2$, $\alpha_s = 0$, $\beta_s = 1$ and $\nu_\parallel = 2$ For all $d<3$ the SFR describes the critical behaviour of systems with short-ranged forces.

In I it was argued that for $d<d_1$ the 'contact' condition $l \sim \xi_\perp$ implies that all distances to the wall appearing in thermodynamic response functions may be measured in terms of the single scaled variable $z\tilde{t}^{\beta_s}$. More precisely, the density profile $\rho(z)$ was assumed to have a singular, scaling contribution

$$\rho_{(z)}^{\text{sing}} = \rho_1 - (\rho_1 - \rho_g)\Xi(z\tilde{t}^{\beta_s}, h\tilde{t}^{-\Delta}). \tag{3}$$

Here ρ_1 and ρ_g denote the coexisting liquid and gas number densities whilst $\Xi(x, y)$ is a scaling function normalized such that $\Xi(\infty, y) = 1$. For systems with short-ranged forces exact statistical mechanical sum rule results (Henderson 1986, Evans and Parry 1989) determine the exponent θ of the short-distance expansion (SDE), defined quite generally $\forall d < d_1$ by

$$\Xi(x, 0) \sim x^\theta \qquad x \to 0 \tag{4}$$

in terms of standard critical exponents: $\theta = (1-\alpha_s)/\beta_s$. That is, for systems with short-ranged forces, the profile should decay algebraically like

$$\rho(z) \sim \rho_1 - \text{constant} \times \tilde{t}^{1-\alpha_s} z^{(1-\alpha_s)/\beta_s} + \ldots \qquad h=0$$

for distances $0 \ll z \ll \tilde{t}^{-\beta_s}$. This was verified in I for $d=2$ by explicit analysis for an effective interfacial Hamiltonian. Upon invoking the universality hypothesis it follows that the result $\theta = (1-\alpha_s)/\beta_s$ is expected to be valid for all systems where long-ranged forces are irrelevant, i.e. it should be valid for systems belonging to the SFR. We argue independently for this below. Note that since we expect the scaling function $\Xi(x, y)$ appearing in (3) to behave as $x^\theta Y(y)$ as $x \to 0$ (at least for y small) the exponent θ also determines the algebraic behaviour of the zero field derivative of $\rho(z)$ WRT h, i.e. the local susceptibility $\chi(z)$.

In the present letter we analyse the density scaling hypothesis (3) and SDE (4) in the WFR. In the presence of an attractive one-body force $V_{\text{att}} = -\varepsilon z^{-m}$ ($z > a$, a microscopic distance from the wall) the Henderson (1986) sum rule result for the variation of the excess grand potential with ε reads

$$\frac{\partial \Omega^{(s)}/A}{\partial \varepsilon} = -\int_a^\infty \mathrm{d}z\, \rho(z) z^{-m}. \tag{5}$$

Hereafter we work in the limit $h=0$ only. From (3) it follows from matching the singular contributions to either side of (5) that

$$\bar{t}^{1-\alpha_s} = \text{constant} \times \bar{t}^{\beta_s r} \int_{a\bar{t}^{\beta_s}}^{\infty} \mathrm{d}x\, \Xi(x,0) x^{-m}$$

$$\equiv \bar{t}^{\beta_s r} Q(a\bar{t}^{\beta_s}). \tag{6}$$

From (6) we conclude: (*a*) $Q(0)$ is finite in the WFR since $1-\alpha_s=\beta_s r$, (*b*) $Q(\omega)$ is singular as $\omega \to 0$ in the SFR. In fact, it is straightforward to show that the singular behaviour of Q in the SFR arises from the short-distance behaviour of the integrand in (6). From the definition (4) it then follows that $\theta=(1-\alpha_s)/\beta_s$ and hence is universal in the SFR provided that the profile has the assumed scaling form

It should be apparent that the present sum rule analysis does not determine θ in the WFR. Instead we are left with the weak inequality $\theta > r$ which follows from the condition that $Q(0)$ is finite. To continue we calculate θ explicitly for a given model belonging to the WFR.

In two dimensions the WFR for the potential (2) (with $s=r+1$) occurs for $1<r<2$. For r in this range we can ignore the repulsive term in (2) and consider the unbinding (critical wetting) transition that occurs, for $h=0$ in the limit $u \to 0^+$, with the potential

$$U(l) = \begin{cases} -ul^{-r} + |h|l & l>1 \\ \infty & l<1. \end{cases} \tag{7}$$

In order to model the effect of fluctuations we use the effective interfacial Hamiltonian

$$H_{\text{eff}} = \int_{-\infty}^{+\infty} \mathrm{d}x \left[\frac{\sigma}{2} \left(\frac{\mathrm{d}l}{\mathrm{d}x} \right)^2 + U(l(x)) \right] \tag{8}$$

where σ is the liquid–gas surface tension and $l(x)$ denotes the instantaneous height of the interface at position x along the wall. The application of such Hamiltonians to wetting transitions is well documented, we refer to the reader to reviews (e.g. Dietrich 1988). As pointed out by many authors determining the equilibrium statistical mechanics of the above Hamiltonian is equivalent to determining the eigenvalues E_i and eigenfunctions ϕ_i of the one-dimensional Schrödinger equation

$$-\frac{1}{2\beta^2\sigma} \frac{\mathrm{d}^2\phi_i(l)}{\mathrm{d}l^2} + U(l)\phi_i(l) = E_i\phi_i(l) \tag{9}$$

where β is the inverse temperature $\beta=(k_B T)^{-1}$. In particular the ground state energy E_0 may be identified with $\Sigma^{(s)}$. The density profile may be constructed in the usual solid-on-solid way (see e.g. Weeks 1977) by assuming that the graph $l(x)$ separates a high density liquid from a low density gas. Thus we write

$$\rho(z) = \rho_l - (\rho_l - \rho_g) \int_0^z \phi_0^2(z')\, \mathrm{d}z'. \tag{10}$$

Consider the solution of (8) for the potential (7) with $1<r<2$. Using the critical exponent results quoted earlier it follows immediately that ϕ_0 is a scaling function of $l\bar{t}^{\beta_s}$ and $h\bar{t}^{-\Delta}$ provided $E_0 (\equiv \Sigma^{(s)})$ has the scaling form (1). Thus the scaling of the density profile (equation (3)) follows from the scaling of the free energy. In zero bulk field $h=0$ the SDE exponent θ may be readily found from noting that ϕ_0 has the asymptotic solution

$$\phi_0(\bar{l}) \propto \bar{l}(1+O(\bar{l}^{2-r})+\ldots) \qquad h=0, \bar{l}\to 0$$

where $\bar{l} \equiv \tilde{t}^{1/(2-r)} l$. Thus we find that the profile has the short-distance behaviour

$$\rho(z)=\rho_1-\text{constant}\times(z\tilde{t}^{1/(2-r)})^3+\ldots \qquad h=0, z\tilde{t}^{1/(2-r)}\to 0 \tag{11}$$

corresponding to $\theta=3$. Thus in $d=2$ the SDE exponent θ is universal (r independent) in the WFR.

For $r=2$ corresponding to the intermediate regime between the WFR and SFR it follows immediately from the analysis of Kroll and Lipowsky (1983) that $\theta=2$ (ignoring logarithmic corrections). However a more general analysis of this intermediate fluctuation regime (Lipowsky and Nieuwenhuizen 1988) demonstrates that the critical behaviour of potentials that decay with exponent $r=2$ are sensitive to the short-range properties of $U(l)$ (i.e. $l<1$) which is set equal to infinity in (6). Further work is required to investigate the SDE exponent θ for this more general case.

For $r=1$ corresponding to the intermediate regime between the WFR and mean-field regime we uncover some unexpected richness. Consider the unbinding transition from the potential (3) with $r=1$, $s=2$. Note that now we must include the repulsive term wl^{-s} in the binding potential since this represents a marginal operator (Lipowsky and Fisher 1987). The critical exponents for the transition are believed to be $\nu_\perp=\beta_s=1$, $\nu_\parallel=2$, $\Delta=3$ and $\alpha_s=0$, i.e. they are not changed from their mean-field values. Using these results it follows that ϕ_0 (and hence $\rho(z)$) is a scaling function of lt^{β_s} and $h\tilde{t}^{-\Delta}$ provided that $\Sigma^{(s)}$ has the standard scaling form (1). Moreover, for $h=0$ equation (9) has the form of Whittakers equation the eigenfunctions of which are well known. We find

$$\phi_0(\bar{l}) \propto \bar{l}^{(1+\sqrt{1+8w\sigma\beta^2})/2} \qquad h=0, \bar{l}\to 0.$$

Consequently the SDE exponent θ is non-universal for $w\neq 0$:

$$\theta=2+\sqrt{1+8w\sigma\beta^2} \tag{12}$$

This result is intriguing since the standard critical exponents are universal (w independent). Similar remarks apply to the WFR/mean-field intermediate fluctuation regime for complete wetting (see section IV.F of Lipowsky 1985).

To conclude, we argue that the SDE exponent θ is universal in the WFR for arbitrary dimension. Consider the approach to a critical wetting transition belonging to the WFR but from off coexistence ($h\to 0$) and exactly at the wetting temperature. The only relevant operator in the binding potential (2) is the term $\propto|h|l$ since $u=0$ and w is an irrelevant scaling field. The critical behaviour of the system is therefore identical to that observed at fluctuation-dominated complete wetting transitions (Lipowsky 1985) which have been studied in I. It follows that the local susceptibility near the wall remains finite at the transition. This local condition on the susceptibility can then be used to determine the SDE of the susceptibility and density profile in the WFR as described in I. We find

$$\theta=\frac{(d+1)}{(3-d)} \qquad \text{WFR} \tag{13}$$

in agreement with our explicit result $\theta=3$ in $d=2$. The exponent is therefore universal in the WFR for arbitrary dimension.

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