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Short-distance expansion for the local susceptibility and pair correlation function at continuous wetting transitions

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Abstract. A scaling ansatz is proposed for the density profile $\rho(z)$ (with z the distance normal from the substrate) for a fluid undergoing a continuous wetting transition at a wall. The ansatz predicts that, in the fluctuation dominated regime, the local susceptibility $(\partial\rho(z)/\partial\mu)_T$, with μ the chemical potential, has a simple power law position dependence for short distances $z \ll \xi_\perp$, the perpendicular correlation length. The power law is determined by the wetting critical exponents, which is different for complete and critical wetting. The scaling predictions are confirmed in dimension $d=2$ by explicit analysis for an interfacial Hamiltonian model of the wetting transition. For critical wetting a scaling ansatz for the form of the transverse moments of the two-point correlation function G is postulated which now yields the z_1, z_2 dependence of G in terms of critical exponents. Calculations again confirm the scaling theory for $d=2$. The analysis highlights the different qualitative and quantitative features of the response functions for critical and complete wetting for fluids with short-ranged forces.

1. Introduction

In this paper we are concerned with the spatial dependence of the local susceptibility and pair correlation function when a thick wetting layer of liquid is adsorbed at a planar wall-vapour interface. We assume that the wall exerts an external potential $V(z)$, with z normal to the wall, on molecules in the fluid, which is sufficiently attractive to absorb a liquid film of thickness l (see figure 1). Close to the wall the fluid density

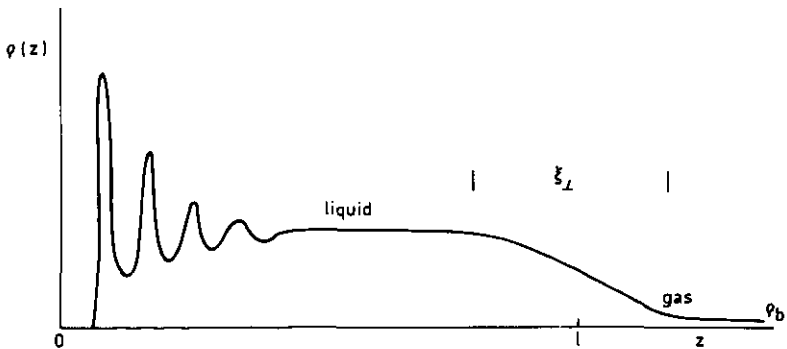


Figure 1. Schematic density profile for a liquid wetting film at a wall-vapour interface. In the limit of complete or critical wetting the thickness of the wetting film l diverges. For $d \leq 3$ the interfacial width ξ_\perp also diverges in this limit.

$\rho(z)$ exhibits oscillations due to packing and volume exclusion effects. Away from the wall, but for $z < l$, the number density is almost constant and that of a liquid, ρ_l . A liquid-vapour interface of width ξ_\perp is centred at $z \sim l$; over the distance ξ_\perp the density decays to that of the bulk vapour, ρ_b .

We will be considering the situation when l diverges to infinity in a continuous manner as some thermodynamic field approaches a critical value. Such wetting transitions have been the subject of much recent research—see for example the reviews of Dietrich (1988) and Schick (1990). Much of the interest stems from the fact that continuous wetting transitions constitute examples of critical phenomena in inhomogeneous systems. As l diverges, capillary-wave-like fluctuations of the liquid-vapour interface result in the divergence of a transverse correlation length ξ_\perp at the edge of the wetting film. For $d \leq 3$ the width of the liquid-vapour interface also diverges as l , $\xi_\parallel \rightarrow \infty$, i.e. $\xi_\perp \sim \xi_\parallel^{(3-d)/2}$.

The divergence of the lengths l , ξ_\parallel and ξ_\perp are characterized by critical exponents and we distinguish between two types of transition:

(a) *Critical wetting*. This occurs as the temperature T (or attractive external potential strength ε) is increased towards the wetting temperature T_w (field strength ε_w) whilst the bulk fluid is kept at saturation chemical potential $\mu = \mu_{\text{sat}}(T)$. The scaling fields $\tilde{t} \equiv |(T - T_w)/T_w|$ and $|(\varepsilon - \varepsilon_w)/\varepsilon_w|$ are equivalent for a critical wetting transition. The exponents are defined by

$$l \sim \tilde{t}^{-\beta}, \quad \mu = \mu_{\text{sat}} \quad (1a)$$

$$\xi_\perp \sim \tilde{t}^{-\nu_\perp}, \quad \mu = \mu_{\text{sat}} \quad (1b)$$

$$\xi_\parallel \sim \tilde{t}^{-\nu_\parallel}, \quad \mu = \mu_{\text{sat}} \quad (1c)$$

In addition, there is a singular contribution to the wall-gas excess grand potential per unit area $\Sigma^{(s)}$,

$$\Sigma_{\text{sing}}^{(s)} \sim \tilde{t}^{2-\alpha_s}, \quad \mu = \mu_{\text{sat}} \quad (1d)$$

There are two relevant scaling fields for critical wetting, \tilde{t} and h , where the latter measures the undersaturation of the bulk vapour: $h \propto (\mu_{\text{sat}} - \mu)$. Exponent relations can be established from thermodynamic arguments (Evans and Parry 1989) or from the appropriate scaling hypothesis for $\Sigma^{(s)}$ (Nakanishi and Fisher 1982),

$$\Sigma_{\text{sing}}^{(s)} = \tilde{t}^{2-\alpha_s} W(ht^{-\Delta}) \quad (2)$$

where Δ is a gap exponent ($\Delta = 2 - \alpha_s - \beta_s$) and W is the scaling function (see also Sullivan and Telo da Gama 1986).

(b) *Complete wetting*. Complete wetting occurs as $\mu \rightarrow \mu_{\text{sat}}(T)$ for $T > T_w$. There is only one relevant scaling field, h , and the analogous exponents are defined by

$$l \sim h^{-\beta_s^{\text{co}}} \quad (3a)$$

$$\xi_\perp \sim h^{-\nu_\perp^{\text{co}}} \quad (3b)$$

$$\xi_\parallel \sim h^{-\nu_\parallel^{\text{co}}} \quad (3c)$$

$$\Sigma_{\text{sing}}^{(s)} \sim h^{2-\alpha_s^{\text{co}}} \quad (3d)$$

In the present paper we ask the question, how do fluctuation effects at wetting transitions determine the spatial dependence of the local susceptibility $\chi(z) = (\partial\rho(z)/\partial\mu)_T$ and pair correlation function $G(r_1, r_2)$? A few facts are already known

about these quantities. By analogy with the well-studied problem of interface localization in a gravitational field ($V(z) = mgz$) it is known that $\chi(z)$ will exhibit a peak at the liquid-vapour edge of the wetting film due to capillary-wave-like fluctuations of the intrinsic interface (e.g. Evans 1979). The height of the peak should diverge as the film thickness increases, i.e.

$$\begin{aligned} \left(\frac{\partial \rho(z)}{\partial \mu}\right)_T &\sim \frac{d\rho(z)}{dz} \xi_{\parallel}^2 & z \sim l \\ &\sim \xi_{\perp}^{-1} \xi_{\parallel}^2 & z \sim l. \end{aligned} \tag{4}$$

This behaviour has been verified in a mean-field model where ξ_{\perp} remains finite (Tarazona and Evans 1982).

In addition, it is known that for systems with short-ranged forces the local susceptibility near the wall $\chi(z \sim 0)$ must diverge at a critical wetting transition (see for example Parry and Evans 1989), a fact that has been used to determine critical wetting exponents in computer simulations (Binder *et al* 1986). Similarly, one expects that the transverse Fourier transform of G exhibits a characteristic Ornstein-Zernike (oz) capillary-wave-like divergence when both particles are located in the edge of the wetting film; we return to this later. Recent sum rule results (Henderson 1986, Evans and Parry 1989) also predict that, at a critical wetting transition with short-ranged forces, G is singular when one or both particles are located near the wall.

In view of these considerations it is clear that, at least for critical wetting transitions, in systems with short-ranged forces the response function $\chi(z)$ and $G(r_1, r_2)$ exhibit singular behaviour throughout the inhomogeneous region. The situation is not unlike that of standard critical phenomena where surface and bulk quantities exhibit different singularities as $T \rightarrow T_c$. Recall that the local magnetic susceptibility $\chi(z) = \partial m(z) / \partial h$ diverges with exponent γ in the bulk, but as $|T_c - T|^{-\gamma_1}$ at the surface layer. Furthermore, renormalization group calculations predict that the local susceptibility exhibits an asymptotic scaling form $\chi(z) \sim (T_c - T)^{-\gamma_1} X(z/\xi_b)$, which results in a singular short-distance expansion (i.e. for $z \ll \xi_b$, the bulk correlation length) for $\chi(z)$ (Diehl 1986). Indeed, such spatial dependence should be expected generally when any local operator has different scaling dimensions at and away from the surface (Diehl 1986). With this observation in mind the present paper analyses the scaling properties of the local susceptibility and pair correlation function at fluctuation-dominated wetting transitions.

Hereafter we will be dealing with systems with short-ranged fluid-fluid and wall-fluid forces that are below their upper critical dimension. Such systems belong to the strong- and weak-fluctuation regime universality classes for critical and complete wetting, respectively. The critical exponents for complete and critical wetting with short-ranged forces are summarized in table 1. Table 2 lists the important exponent relations for the critical exponents defined in (1), (2) and (3) corresponding to systems

Table 1. Exponents for complete and critical wetting for systems with short-ranged forces.

| | α_s | β_s | ν_{\parallel} | ν_{\perp} | Δ | α_s^{co} | β_s^{co} | ν_{\parallel}^{co} | ν_{\perp}^{co} |
|---------|---------------|-----------|-------------------|---------------|----------|-----------------|----------------|------------------------|--------------------|
| $d = 2$ | 0 | 1 | 2 | 1 | 3 | $\frac{4}{3}$ | $\frac{1}{3}$ | $\frac{2}{3}$ | $\frac{1}{3}$ |
| $d = 3$ | Non-universal | | | | | 1 | $O(\ln)$ | $\frac{1}{2}$ | $O(\sqrt{\ln})$ |
| $d > 3$ | 0 | $O(\ln)$ | 1 | 0 | 2 | 1 | $O(\ln)$ | $\frac{1}{2}$ | 0 |

Table 2. Exponent relations for complete and critical wetting for systems below their upper critical dimension. For complete wetting these relations uniquely determine the critical exponents $\beta_s^{\text{co}} = \nu_{\perp}^{\text{co}} = (3-d)/(d+1)$, $\nu_{\parallel}^{\text{co}} = 2/(d+1)$, $\alpha_s^{\text{co}} = 4/(d+1)$.

| Complete wetting | Critical wetting |
|--|--|
| $2 - \alpha_s^{\text{co}} = (d-1)\nu_{\parallel}^{\text{co}}$ | $2 - \alpha_s = (d-1)\nu_{\parallel}$ |
| $1 - \alpha_s^{\text{co}} = -\beta_s^{\text{co}}$ | $2 - \alpha_s = 2\nu_{\parallel} - 2\beta_s$ |
| $\nu_{\perp}^{\text{co}} = [(3-d)\nu_{\parallel}^{\text{co}}]/2$ | $\nu_{\perp} = [(3-d)\nu_{\parallel}]/2$ |
| $\alpha_s^{\text{co}} = 2\nu_{\parallel}^{\text{co}}$ | $\Delta = [(d+1)/2]\nu_{\parallel}$ |

below their upper critical dimension. These exponent relations uniquely determine the complete wetting exponents. For critical wetting there is one free exponent.

The paper is arranged as follows. In section 2 we develop a scaling theory for the density profile $\rho(z)$ of a fluid near a (fluctuation-dominated) wetting transition. The scaling hypothesis allows the explicit short-distance position dependence of the local susceptibility to be calculated in terms of critical exponents. Here short distance means that $0 < z \ll \xi_{\perp}$. For critical wetting we find

$$\left(\frac{\partial \rho(z)}{\partial \mu}\right)_T \approx \tilde{t}^{-(1+\beta_s)} z^{(1-\alpha_s)/\beta_s} \quad z \ll \xi_{\perp} \quad (5a)$$

while for complete wetting

$$\left(\frac{\partial \rho(z)}{\partial \mu}\right)_T \approx z^{1/\beta_s^{\text{co}}} \quad z \ll \xi_{\perp}. \quad (5b)$$

In section 3 these predictions are confirmed in two dimensions by explicit analysis of two effective interfacial Hamiltonians. The results are compared with the corresponding mean-field predictions. Section 4 generalizes the scaling theory of section 2 to the transverse moments of $G(\mathbf{r}_1, \mathbf{r}_2)$ at a critical wetting transition. This theory predicts that the zeroth transverse moment $G_0(z_1, z_2)$ has the asymptotic form

$$G_0(z_1, z_2) \approx \tilde{t}^{-\alpha_s} (z_1 z_2)^{(1-\alpha_s)/\beta_s} \quad z_1, z_2 \ll \xi_{\perp} \quad (6)$$

which is confirmed in section 5 by analysis of Burkhardt's (1989) exact solution for the propagator at a critical wetting transition in $d = 2$ dimensions. Connection is made once more with the corresponding mean-field result. We conclude in section 6 with a summary of our results and some comments on the form of G for complete wetting in $d = 2$.

2. Scaling of the density profile and local susceptibility in the fluctuation-dominated regime

For short-ranged fluid-fluid and wall-fluid forces the upper critical dimension for both complete and critical wetting is $d_{\text{co}}^> = d_{\text{c}} = 3$. This dimension separates the mean-field regime from the fluctuation-dominated regime for both types of transition†. An important consequence of scaling (see for example Lipowsky and Fisher 1987) for systems

† Note that since we are dealing with short-ranged forces there is no weak-fluctuation regime for the critical wetting transition (Lipowsky and Fisher 1987).

below their upper critical dimension (table 2) is that $\beta_s = \nu_\perp$ and $\beta_s^{\text{co}} = \nu_\perp^{\text{co}}$, i.e.

$$l \sim \xi_\perp \quad d < d_> \text{ or } d < d_>^{\text{co}}$$

for critical and complete wetting. It follows that, for each transition, there is only one relevant length scale normal to the wall that sets the scale for long-ranged fluctuations. Using this idea it is straightforward to construct a scaling ansatz for $\chi(z)$ for each transition. Using (4) we suppose that $\chi(z)$ has a singular contribution which can be written as its maximal value (i.e. when $z \sim l$) modulated by a function of the single variable z/l . Thus we write

$$\chi_{(z)}^{\text{sing}} = \tilde{t}^{-(d+1)\nu_\parallel/2} X(z\tilde{t}^{\beta_s}) \quad h = 0, \text{ critical wetting} \quad (7a)$$

$$\chi_{(z)}^{\text{sing}} = h^{-(d+1)\nu_\parallel^{\text{co}}/2} X^{\text{co}}(zh^{\beta_s^{\text{co}}}) \quad \text{complete wetting} \quad (7b)$$

where we have omitted the metric factors for simplicity. The prefactors in (7) follow from (4) and the exponent relations. The scaling functions X and X^{co} must be of the order of unity when the particle is located at the edge of wetting layer ($X(1) \sim 1$, $X^{\text{co}}(1) \sim 1$) where $\chi(z)$ is maximal.

They must also tend to zero for vanishing and diverging arguments so that $\chi(z)$ has the appropriate peak.

It is interesting to note that (7a) and (7b) may be derived from a scaling ansatz for the density profile at each transition. Since the susceptibility involves a derivative with respect to the chemical potential it is necessary to maintain $h \neq 0$ in the scaling ansatz for $\rho(z)$ at a critical wetting transition. We split the density profile into a short-ranged contribution $\rho_{\text{SR}}(z)$ and a scaling contribution valid in the asymptotic limit $h \rightarrow 0$, $\tilde{t} \rightarrow 0$:

$$\rho(z) = \rho_{\text{SR}}(z) + \rho_l - (\rho_l - \rho_g) \Xi(z\tilde{t}^{\beta_s}, h\tilde{t}^{-\Delta}) \quad (8a)$$

and

$$\rho(z) = \rho_{\text{SR}}^{\text{co}}(z) + \rho_l - (\rho_l - \rho_g) \Xi^{\text{co}}(zh^{\beta_s^{\text{co}}}). \quad (8b)$$

The short-ranged contribution arises from the perturbation to the density profile due to packing effects at the wall. We expect that $\rho_{\text{SR}}(z)$ decays exponentially for $z \gg \xi_b$ (for $T < T_c$ and short-ranged forces). The scaling functions $\Xi(x, y)$ and $\Xi^{\text{co}}(x)$ have been normalized such that $\Xi(\infty, y) = \Xi^{\text{co}}(\infty) = 1$ and so that a bulk gas density ρ_g is reached at $z = \infty$. In the following we ignore any temperature and pressure dependence of the bulk densities. Note that the scaling of h with \tilde{t} in (8a) is identical to that found in the standard free-energy scaling hypothesis (2). Differentiating (8a) and (8b) yields the scaling form of $\chi(z)$:

$$\chi^{\text{sing}}(z) = \text{constant } \tilde{t}^{-\Delta} \Xi_{,y}(z\tilde{t}^{\beta_s}, 0) \quad h = 0 \quad (9a)$$

and

$$\chi^{\text{sing}}(z) = \text{constant } h^{-1} \Xi_x^{\text{co}}(zh^{\beta_s^{\text{co}}})(zh^{\beta_s^{\text{co}}}) \quad (9b)$$

where the subscript refers to a (partial) differential with respect to that variable. Equations (9a) and (9b) are equivalent to (7a) and (7b) since $\Delta = (d+1)\nu_\parallel/2$ and $\nu_\parallel^{\text{co}} = 2/(d+1)$ for $d < 3$. It is not within the scope of the scaling analysis to identify completely the form of the scaling functions X and X^{co} appearing in (7). However, it is possible to be precise about the nature of $X(x)$ and $X^{\text{co}}(x)$ for $x \rightarrow 0$. To do this we need some independent requirement on $\chi(z)$. This is not difficult to find. Henderson (1986) and Evans and Parry (1989) have identified an exact requirement for $\chi(a)$

where a is a microscopic distance from the wall (of the order of the range of the potential). They find

$$\chi(a) \propto \left(\frac{\partial l}{\partial \epsilon} \right)_{\mu, T} \quad (10)$$

which is simply the fluid generalization of a surface Maxwell relation for contact surface fields (Parry and Evans 1989). It follows from (10) that

$$\chi^{\text{sing}}(a) \propto \tilde{t}^{-(1+\beta_s)} \quad h=0, \text{ critical wetting} \quad (11)$$

and

$$\chi^{\text{sing}}(a) \approx \text{constant} \quad \text{complete wetting} \quad (12)$$

which illustrates that fluctuation effects are more pronounced at critical wetting transitions. Notice that (12) asserts that the singular contribution to $\chi(a)$ at complete wetting is a finite and non-zero constant. It does not mean that there is no singular contribution. Whilst (12) implies that $\chi(a)$ cannot diverge at a complete wetting transition, it has been found from mean-field analysis (Evans and Parry 1989) that there is an extra finite contribution to $\chi(a)$ when $\mu \rightarrow \mu_{\text{sat}}^-$, $T > T_w$ (where complete wetting occurs) compared with $\mu \rightarrow \mu_{\text{sat}}^+$ at the same temperature (no wetting film). It is unlikely that fluctuation effects in lower dimensions would reduce this finite contribution to zero.

If we assume that $X(x) \propto x^p$ and $X^{\text{co}}(x) \propto x^{p^{\text{co}}}$ as $x \rightarrow 0$, then (7), (11) and (12) may be combined to determine p and p^{co} in terms of exponents defined already. Finally, we arrive at the desired short-distance expansions for $\chi(z)$:

$$\chi^{\text{sing}}(z) \approx \text{constant} \tilde{t}^{-(1+\beta_s)} z^{(1-\alpha_s)/\beta_s}, \quad h=0, z\tilde{t}^\beta \ll 1 \quad (13)$$

and

$$\chi^{\text{sing}}(z) \approx \text{constant} z^{1/\beta_s^{\text{co}}} \quad zh^{\beta_s^{\text{co}}} \ll 1. \quad (14)$$

Equations (13) and (14) predict the explicit z dependence of the susceptibility for arbitrary large (but finite) z in the limit $l \rightarrow \infty$. For dimension $d=2$ they predict, using table 1,

$$\chi^{\text{sing}}(z) \propto \tilde{t}^{-2} z \quad h=0, z\tilde{t} \ll 1 \quad (15)$$

and

$$\chi^{\text{sing}}(z) \propto z^3 \quad zh^{1/3} \ll 1 \quad (16)$$

for complete and critical wetting, respectively. The latter result is particularly simple since it implies a cubic dependence $\forall z$ in the limit of complete wetting $h=0$.

It is also possible to derive a short-distance expansion for the singular part of the density profile at complete and critical wetting, i.e. to determine the power law decay of $\Xi(x, 0)$ and $\Xi^{\text{co}}(x)$ as $x \rightarrow 0$. For complete wetting this follows simply from the integration of (14):

$$\rho(z) \approx \rho_{\text{SR}}^{\text{co}}(z) + \rho_l - \text{constant} h z^{1/\beta_s^{\text{co}}} + \dots \quad zh^{\beta_s^{\text{co}}} \ll 1. \quad (17)$$

For critical wetting it is necessary to introduce a thermodynamic requirement which identifies the singular contribution to $\rho(a)$. This is provided by the sum rule result (Evans and Parry 1989)

$$\frac{\partial \Sigma^{(s)}}{\partial \epsilon} \propto \rho(a) \quad (18)$$

valid for systems with short-ranged forces. Equation (8) implies that $\rho(a)$ contains a singular piece $\sim \tilde{t}^{1-\alpha}$. It follows that for critical wetting

$$\rho(z) \approx \rho_{\text{SR}}(z) + \rho_l - \text{constant } \tilde{t}^{1-\alpha} z^{(1-\alpha)/\beta}, \quad h = 0, z \tilde{t}^{\beta} \ll 1. \quad (19)$$

These predictions are of rather less interest than the corresponding ones for the local susceptibility, however, since the singular contribution to the density profile must necessarily vanish at the appropriate transition.

In the next section we turn to a specific model of a two-dimensional wetting transition to test these scaling predictions.

3. Calculations for the local susceptibility: interfacial Hamiltonian and mean-field analysis

Two-dimensional solid-on-solid (sos) and effective interfacial Hamiltonians are an important class of exactly solvable models for wetting transitions. Whilst not being truly microscopic, the models are believed (see for example the discussion by Huse *et al* (1985)) to describe correctly the low-temperature fluctuations of an intrinsic interface bound by an external potential. Both critical wetting (Vallade and Lajzerowicz 1981; Burkhardt 1981; Chalker 1981) and complete wetting (van Leeuwen and Hilhorst 1981; Lipowsky 1985; Abraham and Smith 1986) have been studied using these models and it is a simple task to extend these analyses to calculate the local susceptibility. For completeness we recall briefly the details of the continuum interfacial Hamiltonian model and its transfer matrix analysis. Extensive details may be found in Lipowsky (1988). The Hamiltonian is

$$H = \int_{-\infty}^{+\infty} dx \left(\frac{\sigma}{2} (\nabla l(x))^2 + U(l(x)) \right) \quad (20)$$

where $l(x)$ denotes the instantaneous height of the fluctuating liquid-vapour interface (with surface tension σ) from the wall at position x . The interface height is allowed to vary continuously in the half space $0 < l(x) < \infty$. The lower bound on $l(x)$ may be imposed by introducing the hard-wall boundary condition $U(l < 0) = \infty$. The effective interface binding potential $U(l)$ depends on the microscopic details of the wall-fluid and fluid-fluid forces. In the presence of an undersaturated bulk vapour there is always a linear contribution:

$$U(l) = hl + U_w(l). \quad (21)$$

To describe critical and complete wetting transitions with short-ranged forces we follow Vallade and Lajzerowicz (1981) and Lipowsky (1985) and specify that $U_w(l)$ has the form

$$U_w(l) = \begin{cases} \infty & l < 0 \\ -|U_0| & 0 < l < a \\ 0 & l > a \end{cases} \quad (22a)$$

for critical wetting and

$$U_w(l) \equiv U_w^{\text{co}}(l)$$

with

$$U_w^{\text{co}}(l) = \begin{cases} \infty & l < 0 \\ 0 & l > 0 \end{cases} \quad (22b)$$

for complete wetting. The potentials (22a) and (22b) correspond to those of a square well and purely repulsive potential, respectively.

Returning to the formal analysis, the partition function for (20) may be easily evaluated using transfer matrix methods. This approach elegantly exploits the Feynman path-integral formulation of quantum mechanics. The thermodynamic observables and response functions of the system may be described by the eigenfunctions $\psi_i(l)$ and eigenvalues E_i satisfying the Schrödinger equation

$$\left(-\frac{1}{2\beta^2\sigma} \frac{d^2}{dl^2} + U(l)\right)\psi_i(l) = E_i\psi_i(l) \quad (23)$$

where $\beta = (K_B T)^{-1}$. In particular, the ground state (normalized) wave function $\psi_0(l)$ determines the probability $P(l)$ of finding the interface at height l , i.e.

$$P(l) = \psi_0^2(l) \quad (24)$$

whilst the ground state energy E_0 can be identified with the (singular) excess grand potential, i.e. $\Sigma^{(s)} = E_0$. The density profile $\rho(z)$ is constructed in the usual way by assuming that the instantaneous order parameter profile $l(x)$ separates a region of high-density liquid ρ_l below it from a low density gas ρ_g above it. Using (24), it follows that the average density $\rho(z)$ at height z is given by

$$\rho(z) = \rho_g + (\rho_l - \rho_g) \int_z^\infty \psi_0^2(l) dl \quad (25)$$

Whilst it is clear that the model cannot describe any short-ranged structure arising from packing effects near the wall it should accurately describe the effect of fluctuations. To proceed we consider the cases of critical and complete wetting separately.

3.1. Critical wetting

In the absence of a bulk field $h=0$ and for $T < T_w$ there is one bound state with $\psi_0(l) \propto e^{-\tilde{t}l}$ for $l > a$ and a continuum of scattering states. If a small bulk field h is applied, the ground state wave function ψ_0 will satisfy, asymptotically, the equation (Vallade and Lazjerowicz 1981)

$$\left(-\frac{d^2}{dl^2} + \tilde{t}^2 W(h\tilde{t}^{-3}) + hl\right)\psi_0(l) = 0 \quad l > a \quad (26)$$

where all constants of proportionality are set to unity. W is the scaling function for the free energy (i.e. (2)). Equation (26) allows the solution

$$\psi_0(l) \propto Ai(h^{1/3}l + \tilde{t}^2 h^{-2/3} W(h\tilde{t}^{-3})) \quad (27)$$

where Ai denotes the Airy function. It follows that the density profile $\rho(z)$ is given by

$$\rho(z) = \rho_l + (\rho_g - \rho_l) \frac{\int_0^z dl Ai^2(h^{1/3}l + \tilde{t}^2 h^{-2/3} W(h\tilde{t}^{-3}))}{\int_0^\infty dl Ai^2(h^{1/3}l + \tilde{t}^2 h^{-2/3} W(h\tilde{t}^{-3}))} \quad (28)$$

where, for simplicity, we have ignored the variation of ψ_0 when $l < a$. Equation (28) may be rewritten

$$\rho(z) = \rho_g + (\rho_l - \rho_g) \frac{\int_{Q_1}^\infty Ai^2(q) dq}{\int_{Q_2}^\infty Ai^2(q) dq} \quad (29a)$$

with

$$Q_1 = zt(h\tilde{t}^{-3})^{1/3} + (h\tilde{t}^{-3})^{-2/3} W(h\tilde{t}^{-3}) \tag{29b}$$

and

$$Q_2 = (h\tilde{t}^{-3})^{-2/3} W(h\tilde{t}^{-3}). \tag{29c}$$

Thus the density profile $\rho(z)$ is indeed a scaled function of $z\tilde{t}^{\beta_s}$ and $h\tilde{t}^{-\Delta}$ (note that $\beta_s = 1$ and $\Delta = 3$; table 1). For fixed $\tilde{t} \neq 0$ both Q_1 and Q_2 diverge as $h \rightarrow 0$. In this limit we may use the leading order asymptotic expansion of the Airy function to deduce

$$\rho(z) \approx \rho_g + (\rho_l - \rho_g) \frac{\Gamma(\frac{1}{3}, \frac{4}{3} Q_1^{3/2})}{\Gamma(\frac{1}{3}, \frac{4}{3} Q_2^{3/2})} \tag{30}$$

where Γ denotes the incomplete gamma function. Hereafter we work with the $h = 0$ limit only. Using the known asymptotic behaviour of the Γ function it is straightforward to derive the leading order asymptotic form of the density profile and local susceptibility. We find

$$\rho(z) \approx \rho_g + (\rho_l - \rho_g) e^{-2\tilde{t}z} \quad h = 0 \tag{31}$$

and

$$\chi(z) \approx (\rho_l - \rho_g) \tilde{t}^{-3} e^{-2\tilde{t}z} (cz\tilde{t} + (z\tilde{t})^2) \quad h = 0 \tag{32}$$

where c is a constant $O(1)$. The first result is not new. Abraham and Huse (1988) have derived an equivalent result in a more complex sos model of interfacial fluctuations. Note that in the limit $\tilde{t}z \rightarrow 0$, (31) is consistent with the short-distance expansion prediction (19) for the density profile. The second result (32) is the desired result for the asymptotic form of the local susceptibility. Note that it is indeed a scaled function of $z\tilde{t}^{\beta_s}$ multiplied by an amplitude $\propto \tilde{t}^{-\Delta}$ (recall (7a)). For fixed arbitrary (but large) z , (32) reduces, in the limit $\tilde{t} \rightarrow 0$, to

$$\chi(z) \propto \tilde{t}^{-2} z \quad h = 0, z\tilde{t} \ll 1$$

which is precisely the scaling prediction (13) in $d = 2$.

Before discussing the local susceptibility for complete wetting it is worthwhile recalling the mean-field result ($d > 3$) for $\chi(z)$ for critical wetting with short-ranged forces. An analytic solution of the Sullivan model (Tarazona and Evans 1982; Parry and Evans 1988) yields

$$\chi(z) \propto \tilde{t}^{-1} e^{(z/\xi_b)} \quad h = 0, l \geq z \geq \xi_b \tag{33}$$

where ξ_b denotes the bulk liquid correlation length which is finite at the wetting transition. The first factor is consistent with the sum rule requirement (11) since $\beta_s = O(\ln)$ in mean field whilst the exponential term is not inconsistent with the mean-field limit of the exponent combination $(1 - \alpha_s)/\beta_s$ appearing in (13). Comparison of the mean field and $d = 2$ results highlights the expected qualitative difference between fluctuations in the two cases. Fluctuations are more strongly localized to the interfacial region in higher dimensions.

3.2. Complete wetting

The analysis for complete wetting is somewhat easier. From Lipowsky (1985) the Schrödinger equation for the eigenfunctions for the potential (22b) is

$$\left(-\frac{d^2}{dl^2} + hl\right)\psi_i(l) = E_i\psi_i(l) \tag{34}$$

where we have set $2\beta^2\sigma = 1$. The boundary condition is $\psi_i(0) = 0$ which results from the hard-wall potential. It follows (van Leeuwen and Hilhorst 1981; Lipowsky 1985) that the lowest-energy eigenfunction is

$$\psi_0(l) \propto \text{Ai}(h^{1/3}l - |\lambda_0|) \tag{35}$$

with energy

$$E_0 = |\lambda_0|h^{2/3}. \tag{36}$$

Here λ_0 is largest zero of the Airy function Ai . It immediately follows the density profile $\rho(z)$ is given by

$$\rho(z) = \rho_l - (\rho_l - \rho_g) \frac{\int_0^{h^{1/3}z} \text{Ai}^2(q - |\lambda_0|) dq}{\int_0^\infty \text{Ai}^2(q - |\lambda_0|) dq}. \tag{37}$$

It is clear that the position dependence of the density profile is a function of the scaled variable $z/l \sim zh^{1/3}$ in $d = 2$ vindicating the scaling hypothesis. From (37) it follows that

$$\rho(z) = \rho_l - \text{constant } hz^3 + \dots \quad hz^3 \ll 1 \tag{38}$$

and

$$\chi(z) \approx \text{constant } z^3 \quad hz^3 \ll 1 \tag{39}$$

in accordance with the scaling predictions for $d = 2$. It is profitable to compare (39) with the mean-field ($d > 3$) result for complete wetting with short-ranged forces (Tarazona and Evans 1982; Parry and Evans 1988)

$$\chi(z) \propto e^{-(z/\xi_b)} \quad l \gg z \gg \xi_b. \tag{40}$$

As was the case for critical wetting, the exponential dependence of the local susceptibility would appear to be consistent with the mean-field limit of the exponent $1/\beta_s^{\text{co}}$.

4. Scaling of the pair correlation function for critical wetting

The two-point density-density correlation function $G(\mathbf{r}_1, \mathbf{r}_2)$ is defined by

$$G(\mathbf{r}_1, \mathbf{r}_2) = \beta^{-1} \frac{\delta\rho(\mathbf{r}_1)}{\delta(\mu - V(\mathbf{r}_2))} = \langle \rho(\mathbf{r}_1)\rho(\mathbf{r}_2) \rangle - \rho(\mathbf{r}_1)\rho(\mathbf{r}_2) + \delta(\mathbf{r}_1 - \mathbf{r}_2)\rho(\mathbf{r}_1) \tag{41}$$

where $\langle \cdot \rangle$ denotes the ensemble average. Given the translational invariance parallel to the substrate it is convenient to Fourier transform with respect to the transverse distance R between particles situated at distances z_1, z_2 from the wall:

$$G(z_1, z_2; Q) \equiv \int d\mathbf{R} e^{i\mathbf{Q}\cdot\mathbf{R}} G(z_1, z_2; \mathbf{R}) = G_0(z_1, z_2) + Q^2 G_2(z_1, z_2) + \dots \tag{42}$$

where the expansion is in wavevector Q . Equation (42) defines the transverse moments of the correlation function.

For critical wetting transitions there exists a number of powerful and exact sum rule results for the behaviour of the density-density correlation function near the

substrate (Henderson 1986; Evans and Parry 1989). These allow the identification of the singular contributions to $G_0(z_1, z_2)$ and $G_2(z_1, z_2)$ for $z_1, z_2 \sim a$:

$$G_0^{\text{sing}}(a, a) \propto \tilde{r}^{-\alpha}, \quad h = 0 \quad (43a)$$

$$G_2^{\text{sing}}(a, a) \propto \tilde{r}^{-2(1+\beta_s)}, \quad h = 0. \quad (43b)$$

Equations (43a) and (43b) allow the transverse correlation length to be defined near the wall

$$(\xi_{\parallel}^w)^2 \equiv -\frac{G_2^{\text{sing}}(a, a)}{G_0^{\text{sing}}(a, a)}. \quad (44)$$

Substitution of (43) in (44) leads to the conclusion that the transverse correlation length at the wall diverges with the same exponent ν_{\parallel} as the transverse correlation length defined at the fluctuating liquid-vapour edge of the wetting film (recall the exponent relation $2\nu_{\parallel} = 2 - \alpha_s + 2\beta_s$). It is quite remarkable that this conclusion follows from formal surface thermodynamic arguments.

The same cannot be said of complete wetting. Whilst sum rule results for complete wetting are very interesting (Henderson and van Swol 1984; Parry and Evans 1988) they do not facilitate the immediate identification of any singular contributions to G (see the discussion for further remarks).

Equations (43) and (44) complement the well known oz behaviour of G near the liquid-vapour edge of the wetting film:

$$G(z_1, z_2; Q) \approx \frac{d\rho(z_1)/dz_1 \cdot d\rho(z_2)/dz_2}{1 + \xi_{\parallel}^2 Q^2} \xi_{\parallel}^2 \quad z_1, z_2 \sim l. \quad (45)$$

This form is expected to be valid in all dimensions since the exponent analogous to η is zero (Lipowsky and Fisher 1987).

Explicit mean-field analysis has verified the sum rule predictions (43) for d above the upper critical dimension. In the next section we study the correlation function for an interfacial Hamiltonian model of two-dimensional critical wetting and confirm the sum rule predictions for this particular case. Before doing so we extend the scaling analysis of section 2 to the pair correlation function. Assuming that oz behaviour is valid throughout the system it suffices to consider scaling of the zeroth moment $G_0(z_1, z_2)$. From (45) it is apparent that

$$G_0(l, l) \sim \xi_{\perp}^{-2} \xi_{\parallel}^2 \sim \xi_{\parallel}^{d-1} \quad d < 3. \quad (46)$$

In the strong-fluctuation regime it is natural to suppose that $G_0(z_1, z_2)$ contains a singular piece that is a scaled function of $z_1/l, z_2/l$, i.e.

$$G_0^{\text{sing}}(z_1, z_2) = \xi_{\parallel}^{d-1} \phi(z_1 \tilde{r}^{\beta_s}, z_2 \tilde{r}^{\beta_s}) \quad h = 0 \quad (47)$$

which reduces to (46) when $z_1, z_2 \sim l$. In the limit $z_1 \tilde{r}^{\beta_s}, z_2 \tilde{r}^{\beta_s} \rightarrow 0$ it is plausible to assume that the leading term in the expression for the scaling function ϕ separates into a product of two separate functions, i.e.

$$\phi(z_1 \tilde{r}^{\beta_s}, z_2 \tilde{r}^{\beta_s}) \rightarrow \phi(z_1 \tilde{r}^{\beta_s}) \phi(z_2 \tilde{r}^{\beta_s}) + \dots \quad h = 0, z_1, z_2 \ll \tilde{r}^{-\beta_s}.$$

Assuming $\phi(\omega) \propto \omega^b$ as $\omega \rightarrow 0$ the index b can be identified since, from (43a), the behaviour near the wall is known. The result is a scaling prediction for the short-distance expansion for the zeroth moment in the strong-fluctuation regime

$$\begin{aligned} G_0^{\text{sing}}(z_1, z_2) &\propto \tilde{r}^{-\alpha_s} (z_1 z_2)^{(1-\alpha_s)/\beta_s}, \quad z_1, z_2 \ll \tilde{r}^{-\beta_s}, h = 0 \\ G^{\text{sing}}(z_1, z_2; Q) &\approx G_0^{\text{sing}}(z_1, z_2) (1 + \xi_{\parallel}^2 Q^2)^{-1}. \end{aligned} \quad (48)$$

For $d = 2$, the scaling predictions are particularly simple

$$G_0^{\text{sing}}(z_1, z_2) \propto z_1 z_2 \quad h = 0, z_1, z_2 \ll \tilde{t}^{-\beta}, \tag{49}$$

since $\alpha_s = 0$ (discontinuity) and

$$G_2^{\text{sing}}(z_1, z_2) \propto \tilde{t}^{-4} z_1 z_2 \quad h = 0, z_1, z_2 \ll \tilde{t}^{-\beta}. \tag{50}$$

In the next section we check (49) and (50) explicitly for an interfacial Hamiltonian.

5. Model calculations of the correlation function moments

In a recent article Burkhardt (1989) has evaluated analytically the partition function for the two-dimensional interfacial Hamiltonian (20) in the limit of a contact attractive surface field. The model retains a critical wetting transition in this limit. The solution allows the energy-energy correlation function $P(z_1, z_2; x_2 - x_1)$ for particles at (z_1, x_1) , (z_2, x_2) to be calculated in terms of elementary functions. In the thermodynamic limit of an infinitely long interface he finds

$$\xi_{\perp}^2 P(Z_1, Z_2; X_2 - X_1) = (\pi X)^{-1/2} e^{-X - \bar{Z}} (e^{-Z^2/4X} + e^{-\bar{Z}^2/4X}) + 2 e^{-2\bar{Z}} \text{erfc}\left(\frac{\bar{Z}}{2\sqrt{X}} - \sqrt{X}\right) \tag{51}$$

where erfc denotes the complementary error function and the scaled variables X, \bar{Z}, Z are defined by

$$X \equiv \frac{|x_2 - x_1|}{\xi_{\parallel}}, \quad \bar{Z} \equiv \frac{(z_1 + z_2)}{\xi_{\perp}}, \quad Z \equiv \frac{(z_2 - z_1)}{\xi_{\perp}}. \tag{52}$$

In terms of the scaled variables the energy-energy correlation function is a universal quantity and is identical to the explicit Ising model result of Ko and Abraham (1989). Further, Burkhardt provides a prescription for calculating a spin-spin correlation function which he denotes $Q(z_1, z_2; x_2 - x_1)$ in terms of P :

$$Q(z_1, z_2; x_2 - x_1) = \int_0^{\infty} \int_0^{\infty} dz'_1 dz'_2 \text{sgn}(z_1 - z'_1) \text{sgn}(z_2 - z'_2) P(z'_1, z'_2; x_2 - x_1). \tag{53}$$

It is a straightforward, though tedious, exercise to perform the integrations and hence deduce an explicit expression for the correlation function $G \propto Q(z_2, z_1; x_2 - x_1) - Q(z_2, z_1; \infty)$. We find

$$G(z_1, z_2; x) = \text{constant} \left[e^{-2z_1/\xi_{\perp}} \text{erfc}\left(\frac{(z_2 - z_1)}{2\xi_{\perp}} \sqrt{\frac{\xi_{\parallel}}{x}} + \sqrt{\frac{x}{\xi_{\parallel}}}\right) + e^{-2z_2/\xi_{\perp}} \text{erfc}\left(\frac{(z_1 - z_2)}{2\xi_{\perp}} \sqrt{\frac{\xi_{\parallel}}{x}} + \sqrt{\frac{x}{\xi_{\parallel}}}\right) - e^{-2(z_1+z_2)/\xi_{\perp}} \text{erfc}\left(-\frac{(z_1 + z_2)}{2\xi_{\perp}} \sqrt{\frac{\xi_{\parallel}}{x}} + \sqrt{\frac{x}{\xi_{\parallel}}}\right) - \text{erfc}\left(\frac{(z_1 + z_2)}{2\xi_{\perp}} \sqrt{\frac{\xi_{\parallel}}{x}} + \sqrt{\frac{x}{\xi_{\parallel}}}\right) \right]. \tag{54}$$

The moments of G can then be evaluated making use of the results in the appendix.

We find, for $z_2 \geq z_1$,

$$G_0(z_1, z_2) \propto \xi_{\parallel} \left[\left(1 + \frac{(z_2 - z_1)}{\xi_{\perp}} \right) e^{-2z_2/\xi_{\perp}} - \left(1 + \frac{(z_2 + z_1)}{\xi_{\perp}} \right) e^{-2(z_1 + z_2)/\xi_{\perp}} \right] \quad (55)$$

$$G_2(z_1, z_2) \propto -\xi_{\parallel}^3 e^{-2z_2/\xi_{\perp}} \left[\frac{5}{4} + \frac{5}{4} \frac{(z_2 - z_1)}{\xi_{\perp}} + \frac{1}{2} \frac{(z_2 - z_1)}{\xi_{\perp}^2} + \frac{(z_2 - z_1)^3}{12\xi_{\perp}^3} \right. \\ \left. - e^{-2z_1/\xi_{\perp}} \left(\frac{5}{4} + \frac{5}{4} \frac{(z_1 + z_2)}{\xi_{\perp}} + \frac{1}{2} \frac{(z_1 + z_2)^2}{\xi_{\perp}^2} + \frac{(z_1 + z_2)^3}{12\xi_{\perp}^3} \right) \right]. \quad (56)$$

From (55) and (56) it follows that

$$G_0(z_1, z_2) = \text{constant } z_1 z_2 \quad h = \tilde{t} = 0 \quad (57)$$

$$\frac{G_2(z_1, z_2)}{G_0(z_1, z_2)} \propto \tilde{t}^{-4} \quad h = 0, z_1 \tilde{t} \rightarrow 0, z_2 \tilde{t} \rightarrow 0 \quad (58)$$

which confirms the scaling predictions (49) and (50). However, from (55) and (56) it is apparent that the ratio $G_2(z_1, z_2)/G_0(z_1, z_2) \equiv -\xi_{\parallel}^2(z_1, z_2)$ is not exactly constant over all space. There is a slowly varying position dependent amplitude to $\xi_{\parallel}(z_1, z_2)$ but this does not effect the singular divergence, i.e. $\xi_{\parallel}^2(z_1, z_2) \sim \tilde{t}^{-4}$ independent of z_1, z_2 .

It is profitable to compare the form of $G_0(z_1, z_2)$ for $d=2$, exactly at the wetting transition, with that for $d>3$. The mean-field result ($d>3$) is given by (Evans and Parry 1989)

$$G_0(z_1, z_2) \approx \text{constant } e^{(z_1 + z_2)/\xi_b} \quad z_1, z_2 \geq \xi_b, h = \tilde{t} = 0 \quad (59)$$

which should be contrasted with (57) for $d=2$. Thus, the form of G_0 is very different in the mean-field and strong-fluctuation regime.

6. Discussion

A few remarks are needed to qualify the scaling predictions. Firstly, it was stated in the introduction that our results for the short-distance expansion apply only to systems with short-ranged forces and $d<3$. Such systems belong to the strong-fluctuation regime for critical wetting and the weak-fluctuation regime for complete wetting.

It is natural to invoke universality and postulate that the results are applicable to all fluid-fluid and wall-fluid forces (not just short ranged) provided that the system falls in the fluctuation dominated regime. Thus van der Waals forces in $d=2$ may result in the same singular short-distance expansion (for sufficiently large distances $z \ll l$) for $X(z)$ and $G_n(z_1, z_2)$ for critical and complete wetting, as in the case of short-ranged forces ((15), (16), (49) and (50)). However, the presence of long-range forces complicates the analysis considerably. This case will be dealt with in a separate publication.

It should be apparent that we have not dealt with the short-distance expansion of $G_0(z_1, z_2)$ at complete wetting. As stated earlier, the reason for this is that previous sum rule analyses of complete wetting have not yielded an unambiguous condition for the singular behaviour of $G_0(a, a)$ (see for example table 1 in Evans and Parry (1989)). However, the transfer matrix methods discussed earlier can be easily extended to calculate the moments of G for two-dimensional SOS models (see for example

Hemmer and Lund (1988)). We simply quote our final results for complete wetting obtained with the repulsive potential (22b):

$$G_0(z_1, z_2) \propto h^{4/3} (z_1 z_2)^3 \quad z_1, z_2 \ll h^{-1/3} \tag{60a}$$

$$G_2(z_1, z_2) \propto (z_1 z_2)^3 \quad z_1, z_2 \ll h^{-1/3}. \tag{60b}$$

In the absence of any appropriate sum rule result for $G_0(a, a)$ we must find an alternative method for developing its short-distance expansion consistent with the exact results (60a) and (60b). A simple argument which yields (60a) is the following. Consider the well known compressibility sum rule

$$\left(\frac{\partial \rho(z)}{\partial \mu} \right)_T = \beta \int dz_2 G_0(z_1, z_2). \tag{61}$$

Now assume that the short-distance expansion

$$G_0^{\text{sing}}(z_1, z_2) \approx h^\omega \phi^{\text{co}}(z_1 h^{\beta_s^{\text{co}}}) \phi^{\text{co}}(z_2 h^{\beta_s^{\text{co}}})$$

dominates the evaluation of (61) if $z_1 \ll h^{-\beta_s^{\text{co}}}$. This is not an unreasonable assumption and is justified *a posteriori*. However, the LHS of (61) is known since $\chi(z_1) \sim z_1^{1/\beta_s^{\text{co}}}$ for $z_1 \ll h^{-\beta_s^{\text{co}}}$. This determines ω . It follows that

$$G_0^{\text{sing}}(z_1, z_2) \approx h^{\alpha_s^{\text{co}}} (z_1, z_2)^{1/\beta_s^{\text{co}}} \quad z_1, z_2 \ll h^{-\beta_s^{\text{co}}}. \tag{62}$$

Together with the assumption that, within the weak-fluctuation regime, the oz relation $G_2(z_1, z_2) \sim -\xi_{\parallel}^2(z_1, z_2) G_0(z_1, z_2)$ remains valid for z_1, z_2 near the wall we find

$$G_2^{\text{sing}}(z_1, z_2) \approx (z_1 z_2)^{1/\beta_s^{\text{co}}} \quad z_1, z_2 \ll h^{-\beta_s^{\text{co}}}. \tag{63}$$

In deriving (63) we have made use of the exponent relation $\alpha_s^{\text{co}} = 2\nu_{\parallel}^{\text{co}}$. Equations (62) and (63) are in agreement with the explicit $d = 2$ results. Note that to derive $G_2^{\text{sing}}(z_1, z_2)$ from $G_0^{\text{sing}}(z_1, z_2)$ we have had to assume that the oz relation is correct near the wall. Recall that this is known to be true for critical wetting from formal arguments (see section 4).

The result (63) implies that $G_2^{\text{sing}}(a, a) \sim \text{constant}$ at complete wetting. This is in agreement with conclusions reached from sum rule analyses of complete wetting (Evans and Parry 1989).

Table 3 summarizes the scaling results for the singular short-distance expansion of the density profiles, local susceptibility and density-density correlation function at continuous wetting transitions.

Table 3. Singular short-distance expansions for the density profile, local susceptibility, zero moment correlation function and second moment correlation function for complete and critical wetting in systems with short-ranged forces. All constants of proportionality have been set to unity.

| | Complete wetting | Critical wetting |
|-----------------|--|--|
| $\rho(z)$ | $\rho_1 - h z^{1/\beta_s^{\text{co}}}$ | $\rho_1 - \tilde{t}^{1-\alpha_s} z^{(1-\alpha_s)/\beta_s}$ |
| $\chi(z)$ | $z^{1/\beta_s^{\text{co}}}$ | $\tilde{t}^{-(1+\beta_s)} z^{(1-\alpha_s)/\beta_s}$ |
| $G_0(z_1, z_2)$ | $h^{\alpha_s^{\text{co}}} (z_1 z_2)^{1/\beta_s^{\text{co}}}$ | $\tilde{t}^{-\alpha_s} (z_1 z_2)^{(1-\alpha_s)/\beta_s}$ |
| $G_2(z_1, z_2)$ | $(z_1 z_2)^{1/\beta_s^{\text{co}}}$ | $\tilde{t}^{-2(1+\beta_s)} (z_1 z_2)^{(1-\alpha_s)/\beta_s}$ |

Finally, we make contact with a previous scaling analysis of the correlation function $G(z_1, z_2; Q)$ at critical wetting (Parry and Evans 1989). There it was postulated that the 'Wertheim' form for $G(z_1, z_2; Q)$ given by (45) is modified for z_1, z_2 near the wall:

$$G^{\text{sing}}(z_1, z_2; Q) = \frac{d\rho_{\text{sing}}(z_1)/dz_1 \cdot d\rho_{\text{sing}}(z_2)/dz_2}{1 + \xi_{\parallel}^2 Q^2} F(z_1/\xi_{\perp}) F(z_2/\xi_{\perp}) \xi_{\parallel}^2 \quad (64)$$

where the scaling function $F(x) \sim x$ for $x \rightarrow 0$. One may now check the consistency of (64) with the scaling theory for $\rho(z)$ and $G_0^{\text{sing}}(z_1, z_2)$ developed in sections 2 and 4. Substitution of the scaling result (19) for ρ_{sing} into the $Q = 0$ limit of (64) yields

$$G_0^{\text{sing}}(z_1, z_2) = t^{2-2\alpha_s+2\nu_{\perp}-2\nu_{\parallel}} (z_1 z_2)^{(1-\alpha_s)/\beta}, \quad h = 0, z_1, z_2 \ll t^{-\beta},$$

which reduces to (49) for $G_0(z_1, z_2)$ using the exponent relation $2 - \alpha_s = 2\nu_{\parallel} - 2\beta_s$ (table 2). Thus the short-distance modification of the 'Wertheim' form for $G(z_1, z_2; Q)$ is indeed consistent with the scaling theory developed here. Note that the short-distance expansion for the density gradient appearing in (64) is not the same for $d < 3$ as that obtained from a Gaussian unfreezing of fluctuations on a mean-field profile. This latter procedure, which was assumed to be valid by Evans and Parry (1989) for $d < 3$, is not capable of deriving the correct critical exponents for $2 < d < 3$. Whilst such a 'Gaussian unfreezing' may work in $d = 3$, the present analysis demonstrates that it cannot be trusted in $d = 2$ where it yields the correct critical exponents. Inspection of (82) of Evans and Parry (1989) reveals that the 'Gaussian unfreezing' procedure does not yield a short-distance expansion. The resulting density profile is not a scaling function of z/ξ_{\perp} . This is not consistent with the exact two-dimensional interfacial Hamiltonian result (29). However, we emphasize that the expression (64) for the modified short-distance expansion of $G(z_1, z_2; Q)$ is consistent with the scaling arguments of sections 2 and 4.

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Appendix

In deriving G_0 and G_2 the following results have been used:

$$\int_0^{\infty} dq \operatorname{erfc}\left(\frac{\alpha}{\sqrt{q}} + \sqrt{q}\right) = \frac{1}{2} e^{-4\alpha} \quad (A1)$$

$$\int_0^{\infty} dq \operatorname{erfc}\left(\frac{-\alpha}{\sqrt{q}} + \sqrt{q}\right) = \frac{1}{2}(1 + 4\alpha) \quad (A2)$$

$$\int_0^{\infty} dq q^2 \operatorname{erfc}\left(\frac{\alpha}{\sqrt{q}} + \sqrt{q}\right) = e^{-4\alpha} \left(\frac{5}{8} + \alpha + \frac{\alpha}{2}\right) \quad (A3)$$

$$\int_0^{\infty} dq q^2 \operatorname{erfc}\left(\frac{-\alpha}{\sqrt{q}} + \sqrt{q}\right) = \frac{5}{8} + \frac{3\alpha}{2} + \frac{3\alpha^2}{2} + \frac{2\alpha^3}{3} \quad (A4)$$

where $\alpha \geq 0$.

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