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Wetting transitions in fluids with short-ranged forces: correlation functions and criticality

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Abstract. The nature of the pairwise correlation function G for a fluid undergoing critical and complete wetting transitions at an adsorbing substrate (wall) is examined using various statistical-mechanical treatments. Sum-rule and scaling arguments predict that, in critical wetting at bulk coexistence, capillary-wave fluctuations manifest themselves throughout the wetting film, up to the wall, so that the (divergent) transverse correlation length ξ_{\parallel} is the same for all pairs of particles. By contrast, in the case of complete wetting from off-bulk coexistence, a divergent correlation length is appropriate only for particles located in the liquid–gas edge of the wetting film. These predictions are confirmed by explicit formulae for the transverse moments of G derived from a mean-field, density-functional theory of a Yukawa fluid in the presence of a short-ranged (exponential) wall–fluid potential. The sum-rule analysis also provides a surface analogue of the C_p – C_v thermodynamic relation, which is used to determine a rigorous relationship between the exponents that characterise critical wetting. The same thermodynamic relation predicts corrections to scaling in bulk dimension $d = 3$ that are similar to those found in renormalisation-group (RG) studies of effective interfacial Hamiltonians.

By unfreezing capillary-wave fluctuations on a mean-field density profile and making use of a sum rule that relates a derivative of the surface tension to the profile near the wall, relationships between ξ_{\parallel} and the thickness t of the wetting film are derived for critical wetting with finite-ranged forces. For $d < 3$ this analysis predicts the correlation-length exponent $\nu_{\parallel} = 2/(3d - 5)$. For $d = 3$ critical exponents depend on the dimensionless parameter $\omega = k_B T/4\pi\sigma_{lg}\xi_b^2$, where σ_{lg} is the liquid–gas surface tension, ξ_b is a bulk correlation length and $t = (2 + \omega - 1/\nu_{\parallel})\xi_b \ln(\xi_{\parallel}/\xi_b)$ provided $\omega < 2$. Our procedure accounts for the other fluctuation regimes found in the RG studies and provides new insight into the origin of the ω -dependence of the exponents. The singularities that occur in critical wetting can be described in terms of a simple *ansatz* for G , similar but not identical to that proposed by Henderson.

1. Introduction

The subject of wetting transitions has attracted enormous theoretical and experimental effort since Cahn (1977) and Ebner and Saam (1977) first described a phase transition from partial to complete wetting by a fluid phase of the interface between an inert substrate, or spectator phase, and a second fluid phase that coexists with the first. Cahn (1977) and Ebner and Saam (1977) predicted that the transition would be first-order; for temperature $T < T_w$ the thickness t of the film of the intruding phase is finite, whereas for $T \geq T_w$ this is of macroscopic extent so that t diverges discontinuously at the transition

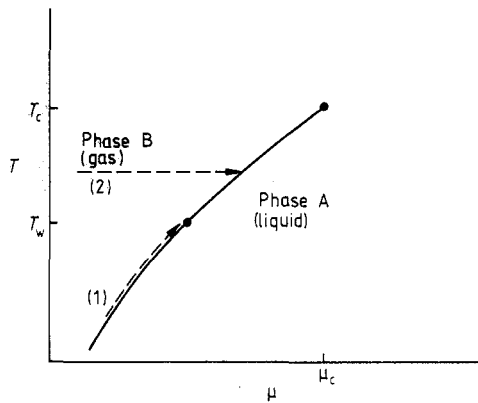


Figure 1. The two types of wetting transition. Critical wetting occurs on path (1) as the wetting transition temperature T_w is approached from below at bulk coexistence $\mu = \mu_{\text{sat}}(T)$ (full curve). Complete wetting from off-bulk coexistence occurs on path (2) as $\mu \rightarrow \mu_{\text{sat}}(T)$ for $T > T_w$. The bulk coexistence curve ends in a critical point (μ_c, T_c) .

temperature T_w . Later Sullivan (1979, 1981) showed, on the basis of a van der Waals (density-functional) treatment, that the transition could be continuous. Such a transition is now termed 'critical wetting'. In the complete wetting regime ($T \geq T_w$) the thickness of the wetting film diverges continuously as the chemical potential μ approaches its value at bulk coexistence $\mu_{\text{sat}}(T)$.

Critical behaviour accompanies film growth on both types of path (see figure 1). For *critical wetting* the relevant control field is $T_w - T$, at $\mu = \mu_{\text{sat}}$, whereas for *complete wetting* the relevant field is $\mu_{\text{sat}}(T) - \mu$, at $T \geq T_w$. By varying the strength ε of a substrate–fluid potential, so as to favour the adsorption of the intruding phase, critical wetting can be induced at fixed temperature. The relevant field is then $\varepsilon_w(T) - \varepsilon$, where $\varepsilon_w(T)$ is the strength of the potential at the transition. Excellent reviews of work on both types of wetting transition are given by Sullivan and Telo da Gama (1986), Dietrich (1988) and Shick (1989).

Although the basic physics is well established from mean-field treatments of lattice-gas models and density-functional calculations for continuum fluids, there has been relatively little work on understanding wetting phenomena from a more fundamental statistical-mechanical basis. Apart from a few valuable exact results for two-dimensional Ising-like or solid-on-solid models (e.g. Abraham 1986), almost all efforts at including the effects of critical fluctuations are based on the framework of effective interfacial Hamiltonians, of the type first used to investigate capillary-wave-like fluctuations at the free interface between two coexisting fluid phases. Detailed studies of such Hamiltonians—see the reviews above—have provided some insight into the nature of interfacial fluctuations and have demonstrated that wetting is an extremely rich critical phenomenon. Some of the predictions are very striking. The upper critical dimension d_c depends on the form of the substrate–fluid and fluid–fluid potentials. For algebraically decaying potentials, $d_c < 3$, and critical exponents for a real fluid should be described correctly by mean-field theories and should depend explicitly on the inter-molecular forces. For finite-ranged or exponential potential functions, $d_c = 3$ for complete and critical wetting. Fluctuation effects remain important in $d = 3$, especially for critical wetting, where intriguing, non-universal exponents are predicted.

In this paper we ask the following questions: (i) To what extent can the predictions from the interfacial Hamiltonians and other approaches be obtained from the formal statistical mechanics of inhomogeneous fluids, appropriate to a realistic many-body Hamiltonian for a continuum fluid in an external (substrate) potential? (ii) What is the

nature of the pairwise correlation function $G(\mathbf{r}_1, \mathbf{r}_2)$ in a fluid approaching a wetting transition? These questions are not unrelated. Both complete and critical wetting are characterised by the growth of capillary-wave-like fluctuations in the depinning fluid–fluid interface, and these fluctuations manifest themselves in Ornstein–Zernike behaviour of $G(\mathbf{r}_1, \mathbf{r}_2)$, provided both particles are located near t , i.e. in the edge of the wetting film. The associated transverse (parallel to the substrate) correlation length ξ_{\parallel} diverges in the approach to the transition. Relationships between the critical exponents that describe the divergence of $t(\beta_s)$, $\xi_{\parallel}(\nu_{\parallel})$ and the singular part of the surface excess free energy (α_s) are best understood, at the microscopic level, in terms of the singular behaviour of transverse moments of $G(\mathbf{r}_1, \mathbf{r}_2)$. Effective Hamiltonian approaches do not provide a description of the density profile of the fluid or of the pairwise correlation function; the order parameter is simply the fluctuating film thickness.

Our paper is arranged as follows: In § 2 we use statistical-mechanical sum rules and surface thermodynamics to derive critical exponent relationships. These are consistent with earlier results based on scaling ideas and with exact results in $d = 2$. With some mild assumptions the sum rules also allow us to make predictions for singularities in $G(\mathbf{r}_1, \mathbf{r}_2)$. Critical and complete wetting are signalled by very different behaviour of the zeroth transverse moment $G_0(t, 0)$, corresponding to one particle in the edge of the wetting film, $z_1 \sim t$, and one particle at the wall, $z_2 = 0$. $G_0(t, 0)$ remains finite as $t \rightarrow \infty$ for complete wetting, whereas this quantity diverges with a universal exponent for critical wetting. The local susceptibility at the wall and the second moment $G_2(0, 0)$ for both particles at the wall also remain finite at complete wetting but are divergent in critical wetting. In § 3 we investigate correlation functions in a mean-field density-functional theory of the inhomogeneous fluid. For particular choices of the attractive fluid–fluid (Yukawa) and substrate–fluid (exponential) potentials, explicit formulae for the transverse moments of $G(\mathbf{r}_1, \mathbf{r}_2)$ can be obtained. These enable us to examine in detail the nature of correlations at the different types of wetting transition and to test the general predictions arising from the formal sum-rule analysis. The results confirm, within mean-field theory, the predictions of § 2. Section 4 contains a derivation of certain relationships between correlation length ξ_{\parallel} and film thickness t for the important special case of critical wetting with short-ranged potentials in $d = 3$. Using thermodynamic arguments and the idea that there is only one diverging correlation length in the inhomogeneous fluid, we obtain relationships that are very similar to those obtained in explicit renormalisation-group calculations for interfacial Hamiltonians. In § 5 we derive the same relationships by unfreezing capillary-wave fluctuations on a bare (mean-field) density profile. This procedure also generates explicit results for exponents for critical wetting in $d < 3$. We conclude in § 6 with a summary of our results and some remarks about other aspects of wetting transitions.

To the best of our knowledge the only other work on wetting that adopts a similar (correlation-function) viewpoint is that of Henderson (1986, 1987a,b). While our present treatment of the sum rules owes much to his seminal papers, it differs in some important technical details and presents new results for the correlation functions at wetting transitions. We deliberately avoid making Henderson’s single-eigenfunction assumption at the outset, since we found that this is problematic for the case of complete drying at a hard wall (Parry and Evans 1988). That paper, hereafter referred to as I, contains a detailed analysis of correlation functions for the Sullivan (1979, 1981) density-functional model. Many of the results derived in I will be used here, but we have attempted to make the present paper self-contained.

2. Statistical-mechanical sum rules, relationships between critical exponents and form of correlation functions

In this section we recall the most important sum rules for the properties of inhomogeneous fluids in an external potential $V(\mathbf{r})$. These sum rules are then applied to complete and critical wetting transitions in order to derive relationships between the various critical exponents that characterise such transitions for fluids near walls. While our presentation of the sum relies on the work of Henderson and van Swol (1985) and Henderson (1986), our derivations of the exponent relationships and of the form of the correlation functions in the vicinity of transitions avoid making any specific *ansatz* for $G(\mathbf{r}_1, \mathbf{r}_2)$.

2.1. Sum rules

The hierarchy of distribution functions is generated by successive functional differentiation of the grand potential Ω with respect to $u(\mathbf{r}) \equiv \mu - V(\mathbf{r})$ at fixed temperature T :

$$\delta\Omega/\delta u(\mathbf{r}) = -\rho(\mathbf{r}) \quad (1a)$$

and

$$\beta^{-1} \delta\rho(\mathbf{r}_1)/\delta u(\mathbf{r}_2) = G(\mathbf{r}_1, \mathbf{r}_2) \equiv \rho(\mathbf{r}_1)\rho(\mathbf{r}_2)h(\mathbf{r}_1, \mathbf{r}_2) - \delta(\mathbf{r}_1 - \mathbf{r}_2)\rho(\mathbf{r}_1) \quad (1b)$$

where $\rho(\mathbf{r})$ is the equilibrium one-body density and $G(\mathbf{r}_1, \mathbf{r}_2)$, the density–density correlation function, is related to the total pairwise distribution function $h(\mathbf{r}_1, \mathbf{r}_2)$. Also, μ is the chemical potential and $\beta^{-1} \equiv k_B T$. For a fluid in an external potential $V(\mathbf{r}) \equiv V(z)$, the density of the fluid depends upon z only, $\rho(\mathbf{r}) \equiv \rho(z)$, and, at fixed μ , (1b) leads to

$$-\rho'(z_1) = \beta \int_{-\infty}^{\infty} dz_2 V'(z_2) G_0(z_1, z_2) \quad (2)$$

where the prime denotes differentiation with respect to z . The (dimensionless) local susceptibility, for fixed external potential, also follows from (1b):

$$\chi(z_1) \equiv \frac{1}{\beta\rho(z_1)} \left(\frac{\partial\rho(z_1)}{\partial\mu} \right)_T = \frac{1}{\rho(z_1)} \int_{-\infty}^{\infty} dz_2 G_0(z_1, z_2). \quad (3)$$

G_0 is defined via the transverse Fourier transform:

$$\begin{aligned} G(z_1, z_2; Q) &\equiv \int d\mathbf{R} \exp(i\mathbf{Q} \cdot \mathbf{R}) G(z_1, z_2; R) \\ &= G_0(z_1, z_2) + Q^2 G_2(z_1, z_2) + \dots \end{aligned} \quad (4)$$

Here \mathbf{R} and \mathbf{Q} are transverse vectors, parallel to the interface. (In three dimensions $R^2 = (x_1 - x_2)^2 + (y_1 - y_2)^2$.) Equation (4) assumes the existence of an expansion in powers of Q^2 and implies Ornstein–Zernike-like behaviour. We return to this point later.

Two quantities of central importance for wetting phenomena are the surface excess grand potential $\Omega^{(s)}$ and the adsorption, or coverage, Γ . The former is defined by

$$\Omega^{(s)} \equiv \Omega + pV_0$$

where p is the pressure of the bulk fluid, far from any interface, at given (μ, T) , and V_0 is the volume occupied by the fluid. Γ is given by the Gibbs adsorption equation

$$\Gamma = -\left(\frac{\partial \Omega^{(s)}/A}{\partial \mu}\right)_T \tag{5a}$$

and is the excess number of particles per unit area A :

$$\Gamma = \int_0^\infty dz [\rho(z) - \rho_b]. \tag{5b}$$

We have assumed that $V(z)$ is infinitely repulsive for $z < 0$ so that $\rho(z) = 0$ for $z < 0$. In (5b), $\rho_b(\mu, T)$ is the density of the bulk fluid. Differentiation of (5b) with respect to μ and use of (3) give a surface susceptibility sum rule

$$\left(\frac{\partial \Gamma}{\partial \mu}\right)_T = \beta \int_0^\infty dz [\rho(z)\chi(z) - \rho_b\chi_b] \tag{6a}$$

$$= \beta \int_0^\infty dz_1 \int_{-\infty}^\infty dz_2 [G_0(z_1, z_2) - G_0(|z_1 - z_2|)_b \theta(z_2)] \tag{6b}$$

where subscript b refers to a property of the bulk fluid. Equation (6) is the analogue of the well known sum rule that relates the bulk compressibility to the long-wavelength limit of the liquid structure factor.

The second transverse moment of G is related to the surface tension σ of the fluid in the external potential:

$$\sigma = -\beta \int_{-\infty}^\infty dz_1 \int_{-\infty}^\infty dz_2 V'(z_1)V'(z_2)G_2(z_1, z_2). \tag{7}$$

In general σ is not equal to $\Omega^{(s)}/A$; there is an additional one-body contribution:

$$\Omega^{(s)}/A = \sigma - \int_0^\infty dz z\rho(z)V'(z). \tag{8}$$

For the special case of a planar hard wall, with

$$V_{hw}(z) = \begin{cases} \infty & z < 0 \\ 0 & z > 0 \end{cases}$$

many of the sum rules simplify (Henderson and van Swol 1984):

$$\beta p = \rho_w \equiv \rho(0^+) \tag{9a}$$

$$G_0(z, 0) = \rho'(z) \quad z > 0 \tag{9b}$$

$$\chi(0^+) = \rho_b/\rho_w \tag{9c}$$

$$\Omega^{(s)}/A = \sigma = -\beta^{-1}G_2(0^+, 0^+). \tag{9d}$$

The implications of (9) for complete drying were discussed at length in I and we shall

recall some of these later when discussing effects beyond mean-field theory. Here we merely note that these results are exact and apply in any dimension d . For $d \geq 2$, where liquid-gas coexistence occurs in bulk, (9a) indicates that in the limit $\mu \rightarrow \mu_{\text{sat}}^+$ the density at contact ρ_w is slightly less than the density of the coexisting gas. This is consistent with the premise that the interface between a hard wall and a liquid should be wet completely by gas (complete drying) for any temperature for which bulk coexistence occurs.

Sum rules can also be derived by varying the strength of the attractive part of the external potential V_ε at fixed (μ, T) . These are especially revealing for the case of critical wetting transitions (Henderson 1986). We suppose that $V(z)$ is defined such that $\partial V(z)/\partial \varepsilon \equiv V_\varepsilon(z)/\varepsilon$ is independent of the well depth ε . Then from (5b), (1b) and (4) we obtain

$$\left(\frac{\partial \Gamma}{\partial \varepsilon}\right)_{\mu, T} = \int_0^\infty dz \frac{\partial \rho(z)}{\partial \varepsilon} = -\beta \int_0^\infty dz_1 \int_{-\infty}^\infty dz_2 \frac{V_\varepsilon(z_2)}{\varepsilon} G_0(z_1, z_2) \quad (10)$$

while from (1a), and the definition of $\Omega^{(s)}$, we have

$$\left(\frac{\partial^2 \Omega^{(s)}/A}{\partial \varepsilon^2}\right)_{\mu, T} = \frac{\partial}{\partial \varepsilon} \int_0^\infty dz \rho(z) \frac{V_\varepsilon(z)}{\varepsilon}. \quad (11a)$$

Since $V_\varepsilon(z)/\varepsilon$ is independent of ε , (11a) can be rewritten as

$$\left(\frac{\partial^2 \Omega^{(s)}/A}{\partial \varepsilon^2}\right)_{\mu, T} = -\beta \int_0^\infty dz_1 \frac{V_\varepsilon(z_1)}{\varepsilon} \int_{-\infty}^\infty dz_2 \frac{V_\varepsilon(z_2)}{\varepsilon} G_0(z_1, z_2). \quad (11b)$$

It is convenient to treat ε as a thermodynamic field. Then surface thermodynamics are obtained from

$$d(\Omega^{(s)}/A) = -s dT - \Gamma d\mu - \Theta d\varepsilon \quad (12)$$

where s is the surface excess entropy per unit area.

The conjugate density for ε is

$$\Theta = -\left(\frac{\partial \Omega^{(s)}/A}{\partial \varepsilon}\right)_{\mu, T} = -\int_0^\infty dz \rho(z) \frac{V_\varepsilon(z)}{\varepsilon} \quad (13)$$

From (12) it follows that, for fixed T ,

$$\left(\frac{\partial \Theta}{\partial \varepsilon}\right)_\mu = \left(\frac{\partial \Theta}{\partial \varepsilon}\right)_\Gamma - \left(\frac{\partial \Gamma}{\partial \varepsilon}\right)_\mu \left(\frac{\partial \mu}{\partial \varepsilon}\right)_\Gamma$$

which becomes, in terms of more convenient variables,

$$\left(\frac{\partial \Theta}{\partial \varepsilon}\right)_\mu = \left(\frac{\partial \Theta}{\partial \varepsilon}\right)_\Gamma + \left(\frac{\partial \Gamma}{\partial \varepsilon}\right)_\mu^2 \left(\frac{\partial \Gamma}{\partial \mu}\right)_\varepsilon^{-1}. \quad (14)$$

Equation (14) is a surface analogue of the standard C_P-C_V thermodynamic relation; it will prove to be important in determining relationships between critical exponents. Note that, for a magnetic (Ising) system, $\mu \rightarrow h$, the bulk external field, $\Gamma \rightarrow m_s$, the surface excess magnetisation, and $\varepsilon \rightarrow h_1$, the applied surface field. If the latter acts on the

surface layer ($n = 1$) only, then $\Theta \rightarrow m_1$, the magnetisation in that layer, and (14) transcribes to

$$\left(\frac{\partial m_1}{\partial h_1}\right)_h = \left(\frac{\partial m_1}{\partial h_1}\right)_{m_s} + \left(\frac{\partial m_s}{\partial h_1}\right)_h \left(\frac{\partial m_s}{\partial h}\right)_{h_1}^{-1} \quad (15)$$

which is somewhat easier to contemplate since m_1 is strictly local now. The LHS of (15) is simply the susceptibility

$$\chi_{11} = -(\partial^2 F^{(s)} / \partial h_1^2)_{h,T}$$

where $F^{(s)}$ is the (magnetic) surface excess free energy. We could, of course, have chosen to differentiate with respect to temperature T . This would have yielded equivalent equations but these are less useful for subsequent purposes.

2.2. Relationships between critical exponents

Complete or critical wetting transitions are signalled by the growth of thick wetting films and the development of capillary-wave-like fluctuations in the depinning liquid–gas interface. Such fluctuations give rise to Ornstein–Zernike behaviour of the density–density correlation function in the edge of the film, i.e.

$$G(z_1, z_2; Q) \sim G_0(z_1, z_2)(1 + \xi_{\parallel}^2 Q^2)^{-1} \quad z_1, z_2 \sim t \quad (16)$$

for small wavenumbers Q . The transverse correlation length $\xi_{\parallel} = [-G_2(t, t)/G_0(t, t)]^{1/2}$ and the zeroth moment

$$G_0(z_1, z_2) \sim \rho'(z_1)\rho'(z_2)\xi_{\parallel}^2/\beta\sigma_{\text{lg}} \quad z_1, z_2 \sim t \quad (17)$$

diverge as the film thickness t diverges at the appropriate transition (e.g. Tarazona and Evans 1982, Lipowsky 1985). Because the relevant fluctuations are capillary-wave-like, the analogue of the exponent η is zero for all wetting transitions (Lipowsky 1984, 1985, Dietrich 1988 and references therein) and the expansion (4) should be valid.

2.2.1. Complete wetting from off-bulk coexistence. In the complete wetting regime the transition occurs as $\mu \rightarrow \mu_{\text{sat}}$ at fixed $T > T_w$. The thickness of the liquid film and, hence, the adsorption diverge as

$$\Gamma \sim \Delta\rho t \sim |\delta\mu|^{-\beta_s} \quad (18a)$$

where $\delta\mu \equiv \mu_{\text{sat}} - \mu$ and $\Delta\rho \equiv \rho_l - \rho_g$ is the difference in densities of the two coexisting bulk phases. The correlation length diverges as

$$\xi_{\parallel} \sim |\delta\mu|^{-\nu_{\parallel}} \quad (18b)$$

while the singular part of the surface excess grand potential vanishes as

$$\Omega_{\text{sing}}^{(s)}/A \sim |\delta\mu|^{2-\alpha_s} \quad (18c)$$

The exponents β_s , ν_{\parallel} and α_s are not independent. From the Gibbs adsorption equation (5a) it follows that

$$1 - \alpha_s = -\beta_s \quad (19a)$$

while from (6) and (17) it follows that

$$1 + \beta_s = 2\nu_{\parallel} \quad (19b)$$

These relationships are valid for all types of wall–fluid and fluid–fluid potentials. For

short-ranged (exponential or finite-ranged) potentials the mean-field result is $t \sim -\ln |\delta\mu|$, so that $\beta_s = 0$, $\nu_{\parallel} = \frac{1}{2}$ and $\alpha_s = 1$. Inserting these values into the hyperscaling relation

$$2 - \alpha_s = (d - 1)\nu_{\parallel} \quad (19c)$$

it follows that the upper critical dimension $d_c = 3$ (e.g. Dietrich 1988). (Hyperscaling for the surface problem asserts $\xi_{\parallel}^{d-1} \Omega_{\text{sing}}^{(s)}/A \sim k_B T$.) Thus, for $d \leq 3$, the exponents are determined uniquely by (19), e.g.

$$\nu_{\parallel} = 2/(d + 1).$$

In $d = 2$, $\beta_s = \frac{1}{3}$, $\nu_{\parallel} = \frac{2}{3}$ and $\alpha_s = \frac{4}{3}$. These results agree with those from exact solution of a solid-on-solid model in an external field (e.g. Abraham 1986 and references therein).

The sum rules enable us to make some statements about the nature of correlation functions at complete wetting. Equations (17) and (3) imply that the local susceptibility in the edge of the film diverges as

$$\chi(z) \sim \rho'(z)\xi_{\parallel}^2 \quad z \sim t \quad (20)$$

for all potential functions. For the special case of a hard wall, (9) makes rather specific predictions for correlation functions in complete drying, $\mu \rightarrow \mu_{\text{sat}}^+$. Equation (9b) states that $G_0(z, 0)$ is equal to the density gradient $\rho'(z)$. Consider the situation where one particle is at the wall and the other is in the edge of the intruding gas film. Then $\rho'(t)$ becomes equal to the density gradient of a free liquid-gas interface as $t \rightarrow \infty$. Capillary-wave arguments then predict $\rho'(t) \sim \xi_{\perp}^{-1}$ as $\delta\mu \rightarrow 0^+$, where ξ_{\perp} is the width of the depinning interface, or the interfacial roughness:

$$\xi_{\perp} \sim \begin{cases} \text{constant} & d > 3 \\ (\ln \xi_{\parallel})^{1/2} & d = 3 \\ \xi_{\parallel}^{(3-d)/2} & d < 3. \end{cases} \quad (21)$$

Using the exponents quoted above we predict for complete drying with short-ranged potentials

$$G_0(t, 0) \sim \begin{cases} \text{constant} & d > 3 \\ t^{-1/2} & d = 3 \\ \xi_{\perp}^{-1} \sim t^{-1} & d < 3 \end{cases} \quad (22)$$

in the limit $t \rightarrow \infty$.

Sum rule (9c) shows that the local susceptibility at contact, $\chi(0^+)$, depends on the density of the *bulk liquid*, which is macroscopically far from the wall when the gas film intrudes in the limit $\delta\mu \rightarrow 0^+$. Equation (9d) asserts that the second transverse moment $G_2(0, 0)$ evaluated with both particles at the wall is proportional to the *total* surface tension σ_{wl} of the wall-liquid interface. In the limit $\delta\mu \rightarrow 0^+$, $\sigma_{\text{wl}} = \sigma_{\text{wg}} + \sigma_{\text{lg}}$, where σ_{wg} is the wall-gas gas tension. Thus $G_2(0, 0)$ depends on the tension, σ_{lg} , of the liquid-gas interface that is a macroscopic distance from the wall. (A detailed analysis of this curious result was given in I.) In contrast the zeroth moment $G_0(0, 0)$ depends only on the derivative of the density at the wall, which is characteristic of the wall-gas interface in the complete drying limit.

It is natural to enquire if these features of the correlation functions are specific to drying at a hard wall or whether they pertain, with minor alterations, to all complete

wetting or drying situations in systems with short-ranged potentials. Our explicit mean-field results for exponential potentials will shed light on this question

2.2.2. Critical wetting at bulk coexistence. We suppose that a critical wetting transition can be induced at a fixed value of (μ, T) on the bulk coexistence curve by increasing the strength ε of the attractive part of the wall–fluid potential. Then for $\varepsilon < \varepsilon_w(\mu, T)$ the wall–gas interface ($\delta\mu = 0^+$) is partially wet by liquid $\sigma_{wg} < \sigma_{wl} + \sigma_{lg}$, whereas for $\varepsilon \geq \varepsilon_w(\mu, T)$ this interface is completely wet and $\sigma_{wg} = \sigma_{wl} + \sigma_{lg}$. Alternatively we can envisage a critical drying transition induced by decreasing ε ; for $\varepsilon > \varepsilon_D(\mu, T)$ the wall–liquid interface ($\delta\mu = 0^-$) is partially wet (dried) by gas whereas for $\varepsilon \leq \varepsilon_D(\mu, T)$ this interface is completely dry. Critical behaviour, analogous to (18), will occur as $\varepsilon \rightarrow \varepsilon_w(\mu, T)$. We use the same notation for critical exponents but the values of these exponents will be different from those for the approach to complete wetting from off-bulk coexistence:

$$\Gamma \sim \Delta\rho t \sim |\delta\varepsilon|^{-\beta_s} \quad (23a)$$

$$\xi_{\parallel} \sim |\delta\varepsilon|^{-\nu_{\parallel}} \quad (23b)$$

$$\Omega_{\text{sing}}^{(s)}/A \sim |\delta\varepsilon|^{2-\alpha_s} \quad (23c)$$

with $\delta\varepsilon \equiv \varepsilon - \varepsilon_w(\mu, T)$. The fundamental relationship between the critical exponents now follows from the thermodynamic relation (14). The LHS is $-((\partial^2\Omega^{(s)}/A)/\partial\varepsilon^2)_{\mu, T}$ which has a ‘singular’ contribution $|\delta\varepsilon|^{-\alpha_s}$, while the second term on the RHS is the ratio of two diverging terms: from (6), (17) and (23b), $(\partial\Gamma/\partial\mu)_{\varepsilon, T} \sim |\delta\varepsilon|^{-2\nu_{\parallel}}$ whereas $(\partial\Gamma/\partial\varepsilon)_{\mu, T} \sim |\delta\varepsilon|^{-(1+\beta_s)}$ for $\varepsilon \rightarrow \varepsilon_w^-$. For finite-ranged potentials $\beta_s = 0(\ln)$, $\nu_{\parallel} = 1$ and $\alpha_s = 0$, corresponding to a finite singular contribution to $((\partial^2\Omega^{(s)}/A)/\partial\varepsilon^2)_{\mu, T}$ (e.g. Sullivan and Telo de Gama 1986) in mean-field approximation. Beyond mean-field theory it is feasible that $\alpha_s \neq 0$. Then, assuming $(\partial\Theta/\partial\varepsilon)_{\mu}$ (or further derivatives of $\Omega^{(s)}/A$) are not less singular than $(\partial\Theta/\partial\varepsilon)_{\Gamma}$ (or further derivatives of this quantity) it follows that

$$-\alpha_s = -2(1 + \beta_s) + 2\nu_{\parallel}$$

or

$$2 - \alpha_s = 2\nu_{\parallel} - 2\beta_s. \quad (24)$$

Clearly this is the analogue of the well known Rushbrooke exponent (in)equality for bulk systems. When $\alpha_s < 0$ the non-singular contribution to $(\partial\Theta/\partial\varepsilon)_{\mu}$ and $(\partial\Theta/\partial\varepsilon)_{\Gamma}$ must be identical at $\delta\varepsilon = 0$. In the vicinity of the transition

$$\Omega^{(s)}/A = \sigma_{wl}(\varepsilon) + \sigma_{lg} + \Omega_{\text{sing}}^{(s)}/A \quad (25)$$

and the (non-critical) wall–liquid tension, which is analytic in $\delta\varepsilon$, gives a constant contribution to $((\partial^2\Omega^{(s)}/A)/\partial\varepsilon^2)_{\mu, T}$. Note that (24) is obeyed by the mean-field results. Our present thermodynamic derivation of the exponent relation is more direct than previous derivations that were based on a scaling hypothesis for $\Omega_{\text{sing}}^{(s)}$ (e.g. Sullivan and Telo da Gama 1986, Schick 1989) or on an *ansatz* for $G_0(z_1, z_2)$ (Henderson 1986). Inserting the mean-field exponents into the hyperscaling relation (19c) we obtain $d_c = 3$ once more.

Combining (19c) and (24) we find

$$\beta_s = (3 - d)\nu_{\parallel}/2 \quad d \leq 3. \quad (26)$$

But (21) shows that the interfacial roughness $\xi_{\perp} \sim \xi_{\parallel}^{(3-d)/2}$ for $d < 3$. Thus ξ_{\perp} diverges

with the same exponent as that of the film thickness t , at critical wetting in $d < 3$. This was also the case for complete wetting in $d < 3$, reflecting the fact that for both types of transition strong fluctuations of the interface lead to excursions that are of the same order as the film thickness, i.e. $\xi_{\perp} \sim t$.

Unlike the complete wetting case we cannot determine the exponents uniquely from sum-rule and hyperscaling arguments because there are two relevant scaling fields—the chemical potential μ and the wall field ε —rather than the single field μ appropriate in complete wetting. However, since $\eta = 0$, all critical exponents can be expressed in terms of a single independent exponent ν_{\parallel} , say (Schick 1989). The exact results for the square Ising lattice with a contact surface field h_1 (Abraham 1986), $\beta_s = 1$, $\nu_{\parallel} = 2$ and $\alpha_s = 0$ satisfy (24) and (26).

Critical wetting is rather special in $d = 3$. If there is power-law growth of the correlation length (finite ν_{\parallel}), (26) implies $\beta_s = 0$, i.e. logarithmic growth of the film thickness. The magnitude of ν_{\parallel} is not determined but we would expect incorporation of fluctuations either to leave ν_{\parallel} unrenormalised or to increase ν_{\parallel} above the mean-field value (3 is the marginal dimension.) Then from hyperscaling, or from (24), α_s is either zero or negative. In the second case $((\partial^2 \Omega^{(s)}/A)/\partial \varepsilon^2)_{\mu, T}$ has a vanishing singular contribution at the transition—see (23c) and (25). Renormalisation-group (RG) calculations for effective interfacial Hamiltonians (e.g. Dietrich 1988) predict $\nu_{\parallel} > 1$ and, therefore, $\alpha_s < 0$ for short-ranged potentials in $d = 3$. We will comment on these predictions in § 4.

As emphasised earlier, this treatment is based on the assumption that the exponent $\eta_{\parallel} = 0$ for all wetting transitions. It is instructive to enquire how exponent relations for critical wetting would be modified if $\eta_{\parallel} \neq 0$. We suppose that $(\partial \Gamma / \partial \mu)_{\varepsilon, T} \sim |\delta \varepsilon|^{-\gamma_{\parallel}}$, with γ_{\parallel} , the analogue of the susceptibility exponent, related to the transverse correlation-length exponent via $\gamma_{\parallel} = \nu_{\parallel}(2 - \eta_{\parallel})$. Then the C_P - C_V relation implies, for finite ν_{\parallel} , that

$$2 - \alpha_s = \nu_{\parallel}(2 - \eta_{\parallel}) - 2\beta_s$$

rather than (24). Assuming hyperscaling remains valid we find

$$\nu_{\parallel}(d - 3 + \eta_{\parallel}) = -2\beta_s.$$

Since in $d = 3$ we require $\beta_s \geq 0$ and $\nu_{\parallel} \geq 1$ (the mean-field result), the above relation implies $\eta_{\parallel} \leq 0$. But η_{\parallel} cannot be negative, so we conclude that thermodynamic considerations plus hyperscaling enforce the condition $\eta_{\parallel} = 0$, in keeping with the general consensus concerning the nature of capillary-wave fluctuations (e.g. Dietrich 1988). Moreover, β_s is forced to be zero. If the correlation length diverges exponentially, the above argument is no longer applicable. Note that in $d = 2$ Abraham's (1986) explicit results for the Ising model require $\eta_{\parallel} = 0$.

As first recognised by Henderson (1986) the sum rules make specific predictions for the behaviour of correlation functions as $\delta \varepsilon \rightarrow 0$. The susceptibility in the edge of the film diverges as in (20), with the correlation-length exponent appropriate to critical wetting. More strikingly the local susceptibility also diverges for z near the wall. This becomes clear upon combining (10) and (3). If $V_{\varepsilon}(z)$ has a finite (microscopic) range a , then $\chi(a)$ diverges as $(\partial \Gamma / \partial \varepsilon)_{\mu, T}$.

It is natural to suppose that such a divergence in $\chi(a)$ is associated with the divergence of $G_0(a, t)$, i.e. the integral in (3) is dominated by the contribution from $z_2 \sim t$. A plausible form is

$$G_0(z, a) \sim \rho'(z)(\partial \Gamma / \partial \varepsilon)_{\mu, T} \quad z \sim t. \quad (27)$$

This yields the correct divergence for $\chi(a)$ and is consistent with the sum rule (10). Explicit density-functional results (see § 3) confirm the factor of $\rho'(z)$.

Using the exponents introduced above, (27) implies

$$G_0(t, a) \sim |\delta\varepsilon|^{-1} \quad \text{for all } d \tag{28}$$

as $\delta\varepsilon \rightarrow 0^-$. This result assumes that $\beta_s = 0$ in $d = 3$. If $\beta_s \neq 0$, as is expected for certain strong fluctuation regimes in $d = 3$, (28) will be modified. Critical wetting with short-ranged potentials is characterised by $G_0(t, a)$ diverging with an (almost) universal critical exponent. Such behaviour should be contrasted with (22) for complete wetting.

When both particles are close to the wall we must consider $\tilde{G}_0(a, a)$. This quantity is defined as $G_0(a, a)$ minus the delta function, i.e. $\tilde{G}_0(z, z) \equiv \rho^2(z)h_0(z, z)$ —see (1b). For critical wetting (11b) and (25) together imply that $\tilde{G}_0(a, a)$ acquires a ‘singular’ contribution $|\delta\varepsilon|^{-\alpha_s}$, from the ‘critical’ interface. Such a contribution is non-vanishing at the transition in mean-field approximation ($\alpha_s = 0$)—see § 3.4.

If $\alpha_s < 0$ any singular contribution to $\tilde{G}_0(a, a)$ must vanish for finite-ranged $V_\varepsilon(z)$ and we might expect $\tilde{G}_0(a, a)$, with $a \sim 0$, to be the same for the ‘critical’ ($\mu = \mu_{\text{sat}}^-$) and ‘non-critical’ ($\mu = \mu_{\text{sat}}^+$) interfaces at the transition.

The second transverse moment $G_2(z_1, z_2)$ is also of interest. When both particles are in the edge of the film, (16) and (17) imply

$$G_2(z_1, z_2) \sim -\rho'(z_1)\rho'(z_2) \xi_{\parallel}^4 / \beta\sigma_{\text{lg}} \quad z_1, z_2 \sim t.$$

As z_1 and z_2 move out of the liquid–gas interface, G_2 will decay. Any singular contribution can be estimated using the Ornstein–Zernike (OZ) relation, which defines a direct correlation function C as the inverse of G :

$$\int_{-\infty}^{\infty} dz_3 C(z_1, z_3; Q)G(z_3, z_1; Q) = \delta(z_1 - z_2). \tag{29}$$

Expanding C and G in powers of Q^2 , as in (4), it follows (e.g. Evans 1979) that

$$G_2(z_1, z_2) = -\int_{-\infty}^{\infty} dz_3 \int_{-\infty}^{\infty} dz_4 G_0(z_1, z_4)C_2(z_4, z_3)G_0(z_3, z_2) \tag{30}$$

where $C_2(z_1, z_2)$ is the second transverse moment of the direct correlation function. Using (27) in (30) it is clear that $G_2(a, a)$ should acquire a divergent contribution from z_3 and z_4 in the edge of the film:

$$G_2(a, a) \sim -\sigma_{\text{lg}}(\partial\Gamma/\partial\varepsilon)_{\mu, T}^2 \sim |\delta\varepsilon|^{-2(1+\beta_s)} \tag{31}$$

where the Triezenberg and Zwanzig (1972) formula (see also I) has been used to express the integral in terms of σ_{lg} . We are now in a position to examine the transverse correlation length

$$\xi_{\parallel}^{\text{w}} \equiv [-G_2(a, a)/\tilde{G}_0^{\text{sing}}(a, a)]^{1/2} \tag{32}$$

corresponding to correlations in which both particles are close to the wall. It is important to recognise that this definition employs only the singular contribution ($\propto |\delta\varepsilon|^{-\alpha_s}$) to $\tilde{G}_0(a, a)$, which, as we have seen, may vanish at the transition. Inserting (31) into (32) and making use of the exponent relation (24), we find $\xi_{\parallel}^{\text{w}} \sim \xi_{\parallel}$. In other words the transverse correlation length for particles near the wall diverges in the same manner as that for particles located in the depinning liquid–gas interface; there is only one diverging correlation length. For complete drying at a hard wall we found that both $G_2(0, 0)$ and $\tilde{G}_0(0, 0)$ are finite at $\mu = \mu_{\text{sat}}^+$. There is no divergent $\xi_{\parallel}^{\text{w}}$ in this case—see I.

3. Correlation functions from a mean-field free-energy functional

The sum-rule analysis of the previous section made some rather general predictions concerning the behaviour of pairwise correlation functions for fluids undergoing wetting transitions. In order to test and to understand better these formal results, it is instructive to examine the correlation functions obtained for a specific model of a fluid near a wall. Here we consider a simple, mean-field density-functional theory of the inhomogeneous fluid in which explicit formulae can be calculated for transverse moments of G . As the present discussion is an extension to critical wetting transitions of the density-functional theory developed in I for complete wetting, we make much use of results presented in that paper.

3.1. Specification of the free-energy functional and equations for G

As in I we consider the grand potential functional

$$\Omega_V[\rho(\mathbf{r})] = - \int d\mathbf{r} \rho(\mathbf{r})u(\mathbf{r}) + \mathcal{F}[\rho] \quad (33)$$

with the intrinsic Helmholtz free energy given by

$$\mathcal{F}[\rho] = \int d\mathbf{r} f_h(\rho(\mathbf{r})) + \frac{1}{2} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \rho(\mathbf{r}_1)\rho(\mathbf{r}_2)w_2(|\mathbf{r}_1 - \mathbf{r}_2|). \quad (34)$$

Minimisation of Ω_V with respect to $\rho(\mathbf{r})$ yields an integral equation for the equilibrium density profile:

$$u(\mathbf{r}) \equiv \mu - V(\mathbf{r}) = \mu_h(\rho(\mathbf{r})) + \int d\mathbf{r}' \rho(\mathbf{r}')w_2(|\mathbf{r} - \mathbf{r}'|). \quad (35)$$

The approximation (34) for $\mathcal{F}[\rho]$ has been widely used in studies of wetting phenomena and its limitations are well known (Sullivan and Telo da Gama 1986, Dietrich 1988). Equation (34) assumes that the free energy arising from repulsive interactions between fluid molecules can be treated in the local-density approximation: $f_h(\rho)$ is the Helmholtz free-energy density of a uniform hard-sphere fluid of density ρ . The second term in (34) treats attractive forces in mean-field fashion: $w_2(\mathbf{r})$ is the attractive part of the pairwise potential between two fluid molecules. Such a functional cannot describe oscillatory density profiles and it omits some of the effects of capillary-wave fluctuations. We will comment on this later. Finally, $\mu_h(\rho) \equiv df_h/d\rho$ is the chemical potential of the uniform hard-sphere fluid.

Within the context of density-functional theory, $G(\mathbf{r}_1, \mathbf{r}_2)$ is obtained via (29), i.e. as the inverse of the direct correlation function $C(\mathbf{r}_1, \mathbf{r}_2)$. The latter is the second functional derivative

$$C(\mathbf{r}_1, \mathbf{r}_2) = \beta \frac{\delta^2 \mathcal{F}[\rho]}{\delta \rho(\mathbf{r}_1) \delta \rho(\mathbf{r}_2)} \quad (36)$$

evaluated at the equilibrium density. In the present model C is very simple:

$$C(\mathbf{r}_1, \mathbf{r}_2) = \frac{\delta(\mathbf{r}_1 - \mathbf{r}_2)}{\rho(\mathbf{r}_1)\chi_h(\rho(\mathbf{r}_1))} + \beta w_2(|\mathbf{r}_1 - \mathbf{r}_2|) \quad (37)$$

where $\chi_h(\rho) \equiv (\beta\rho d\mu_h/d\rho)^{-1}$ is the susceptibility of the uniform hard-sphere fluid. If, in addition, the attractive fluid–fluid potential is chosen to be of Yukawa type,

$$w_2(\mathbf{r}) = - \frac{\alpha\lambda^3 \exp(-\lambda r)}{4\pi\lambda r} \quad (38)$$

where $\alpha = -\int d\mathbf{r} w_2(\mathbf{r})$ is the integrated strength and λ^{-1} is the decay length, the

transverse Fourier transform can be performed, giving an explicit expression for $C(z_1, z_2; Q)$ —see I. (We specialise once more to a three-dimensional fluid in a potential $V(z)$ where $\rho(\mathbf{r}) \equiv \rho(z)$.) The OZ equation (29) then yields an integral equation for $G(z_1, z_2; Q)$. In I it was shown that this equation can be converted into a second-order differential equation

$$\frac{\partial^2}{\partial x_2^2} \left(\frac{s(x_1, x_2; Q)}{\chi_h(\rho(x_2))} \right) = [1 + Q^2 \lambda^{-2} - \alpha \beta \rho(x_2) \chi_h(\rho(x_2))] \frac{s(x_1, x_2; Q)}{\chi_h(\rho(x_2))} \tag{39a}$$

with the boundary conditions for $x_1 = 0$

$$\lim_{x_2 \rightarrow 0} \frac{\partial}{\partial x_2} \left(\frac{s(0, x_2; Q)}{\chi_h(\rho(x_2))} \right) = -\alpha \beta \lambda \chi_h(\rho_w) + (1 + Q^2 \lambda^{-2})^{1/2} \frac{s(0, 0; Q)}{\chi_h(\rho_w)} \tag{39b}$$

and for $x_1 > 0$

$$\lim_{x_2 \rightarrow 0} \frac{\partial}{\partial x_2} \left(\frac{s(x_1, x_2; Q)}{\chi_h(\rho(x_2))} \right) = (1 + Q^2 \lambda^{-2})^{1/2} \frac{s(x_1, 0; Q)}{\chi_h(\rho_w)}. \tag{39c}$$

Here $x \equiv \lambda z$ and $\rho_w \equiv \rho(0^+)$ is the density of the fluid at contact with the wall; we assume $V(z)$ is infinitely repulsive for $z < 0$. The function s is defined as

$$s(z_1, z_2; Q) \equiv \frac{G(z_1, z_2; Q)}{\rho(z_1)\rho(z_2)} - \frac{\delta(z_1 - z_2)}{\rho(z_1)} \chi_h(\rho(z_1)). \tag{40}$$

It is important to recognise that (39) determines the pairwise correlation function of the Yukawa model fluid for any external (wall) potential—the dependence of s on $V(z)$ is implicit in the profile $\rho(z)$. Later we shall examine explicit solutions of (39) for different choices of $V(z)$ but first we deduce some consequences of (39) for a *general* wetting transition. We suppose that, beyond a certain distance from the wall, which we will denote Λ , the density profile is essentially constant and equal to ρ_l , the density of the liquid that coexists with the bulk gas at $\mu = \mu_{\text{sat}}^-$. The differential equation for the zeroth moment $s_0(x_1, x_2) \equiv s(x_1, x_2; 0)$ can then be approximated by

$$\frac{\partial^2}{\partial x_2^2} \left(\frac{s_0(x_1, x_2)}{\chi_h(\rho(x_2))} \right) = a_1^2 \left(\frac{s_0(x_1, x_2)}{\chi_h(\rho(x_2))} \right) \quad \lambda t \geq x_2 \geq \lambda \Lambda \tag{41}$$

where a_1 is the dimensionless inverse *bulk* liquid correlation length (see I)

$$a_1 = [1 - \alpha \beta \rho_l \chi_h(\rho_l)]^{1/2} = \left[1 - \alpha \left(\frac{d\mu_h}{d\rho_l} \right)^{-1} \right]^{1/2}. \tag{42}$$

Equation (41) predicts exponential increase of correlations with x_2 increasing towards λt , the thickness of the liquid film. Setting $z_1 = t$ and ignoring the variation of χ_h with z_2 it follows that

$$s_0(t, z_2) \sim s_0(t, \Lambda) \exp[\lambda a_1 (z_2 - \Lambda)] \quad t \geq z_2 > \Lambda.$$

When both particles lie in the edge of the film, $s_0(t, t) \sim \xi_{\parallel}^2$ since (17) is valid within the density-functional approximation, but with non-vanishing density gradients (Tarazona and Evans 1982) at a transition. Thus the zeroth moment should exhibit the following decay

$$s_0(t, z_2) \sim \xi_{\parallel}^2 \exp[-\lambda a_1 (t - z_2)] \quad t \geq z_2 > \Lambda \tag{43}$$

for both complete and critical wetting. The behaviour of $s_0(t, z_2)$ depends on the relative

strength of the singularities of ξ_{\parallel} and t , which differs between complete and critical wetting. More specifically, in the light of the sum-rule analysis, we might expect $G_0(t, \Lambda)$ to be singular for critical wetting but finite for complete wetting.

3.2. Wetting characteristics for exponential wall-fluid potentials

We consider an external potential of the form

$$V(z) = \begin{cases} \infty & z < 0 \\ -\varepsilon \exp(-\lambda_v z) & z > 0 \end{cases} \quad (44)$$

where ε is the well depth and $\lambda_v (>0)$ is the inverse decay length. In the special case $\lambda_v = \lambda$, so that fluid–fluid and wall–fluid potentials have identical decay lengths, the density-functional theory reduces to that employed by Sullivan (1979, 1981) in his pioneering study of wetting transitions. With this choice the integral equation (35) for the profile can be converted to a differential equation, which is easily solved by quadrature. Sullivan showed that the fluid undergoes a continuous (critical) wetting transition at bulk coexistence, $\mu = \mu_{\text{sat}}^-(T)$, when ε is increased to $\varepsilon_w(T)$ satisfying

$$\alpha \rho_l(T) = 2\varepsilon_w(T). \quad (45a)$$

A critical drying transition occurs when ε is decreased, at $\mu = \mu_{\text{sat}}^+(T)$, to the critical value $\varepsilon_D(T)$ satisfying

$$\alpha \rho_g(T) = 2\varepsilon_D(T). \quad (45b)$$

The wetting characteristics of the Sullivan model are well known (Sullivan 1979, 1981, Tarazona and Evans 1982). For *complete wetting*, $\varepsilon > \varepsilon_w(T)$, the thickness of the liquid film diverges as

$$\lambda t \sim -a_l^{-1} \ln |\delta\mu| \quad (46a)$$

the transverse correlation length as

$$\xi_{\parallel} = (\sigma_{lg}/\Delta\rho\lambda a_l |\delta\mu|)^{1/2} \quad (46b)$$

and $\alpha_s = 1$.

Equivalent results apply for complete drying with a_l replaced by a_g , the correlation length of the bulk gas. At the *critical wetting* transition we find

$$\lambda t \sim -a_l^{-1} \ln |\delta\varepsilon| \quad (47a)$$

$$\xi_{\parallel} = \left(\frac{\sigma_{lg} \alpha (1 - a_l^2)}{8\lambda a_l^3 \delta\varepsilon^2} \right)^{1/2} \quad (47b)$$

and

$$\alpha_s = 0 \quad (47c)$$

with equivalent results for the drying transition. The critical exponents have the appropriate mean-field values given in § 2. Only second-order transitions occur in the Sullivan model; there is no first-order wetting transition.

This situation changes dramatically when $\lambda_v \neq \lambda$ so that the potentials have different decay lengths. Numerical results by Tarazona and Evans (1983) and Teletzke *et al* (1983) showed that the wetting transition could become first-order when $\lambda_v < \lambda$, i.e. when

the wall–fluid potential is longer-ranged. Hauge and Schick (1983) reached the same conclusion from a perturbative treatment of the same model. More significantly for our present purposes, Aukrust and Hauge (1985, 1987) (AH)[†] considered the situation $b \equiv \lambda_v/\lambda > 1$, where the wall–fluid potential is *shorter*-ranged, and found critical wetting transitions with non-universal, b -dependent correlation-length exponents, provided $a_1 < b < 2a_1$.

The film still thickens logarithmically, but with a different amplitude

$$\lambda t \sim -(b - a_1)^{-1} \ln |\delta\varepsilon| \tag{48a}$$

whereas $\xi_{\parallel} \sim |\delta\varepsilon|^{-\nu_{\parallel}}$ with

$$\nu_{\parallel} = \frac{b}{2(b - a_1)} \quad a_1 < b < 2a_1, b > 1. \tag{48b}$$

Since $\nu_{\parallel} > 1$, in this regime the exponent relation (24) implies

$$\alpha_s = \frac{b - 2a_1}{b - a_1} < 0. \tag{48c}$$

AH showed that $b = 1$ (the Sullivan case) corresponds to the tricritical line of the model. When $b \geq 2a_1$, but $b > 1$, the critical wetting transition reverts to the Sullivan type with characteristics given by (47). The location of the wetting transition cannot be determined exactly when $b \neq 1$. From a perturbative analysis AH find

$$\alpha\rho_1(T) \frac{[b^2 - a_1^2(T)]}{[1 - a_1^2(T)]} \frac{2}{(1 + b)} = 2\varepsilon_w(T) \tag{49}$$

for $a_1 < b < 2a_1$, $b > 1$. This result connects smoothly to the Sullivan result (45a) at $b = 1$.

AH point out that it is remarkable that a system in which all the relevant potentials are exponential should exhibit such a diversity of critical behaviour[‡]. The fact that α_s is zero for certain regimes but negative for another has important repercussions for the behaviour of the pairwise correlation function near the wall, as we shall see in later sections.

3.3. Correlation functions for the Sullivan and AH models

We are now in a position to list some explicit formulae for moments of $G(\mathbf{r}_1, \mathbf{r}_2)$ for exponential wall–fluid potentials. In I we showed that for the Sullivan model a solution of (39a), with $Q = 0$, is $\rho'(x_2)/\rho(x_2)$. This result follows because the Sullivan differential equation for $\rho'(x)$ can be cast into the same form as (39a). The full solution for $s_0(x_1, x_2)$ is

$$s_0(x_1, x_2) = \frac{\lambda\rho'(x_1)\rho'(x_2)}{\rho(x_1)\rho(x_2)} \left\{ \frac{\chi_h(\rho_w)\rho_w}{(\rho_w - 2\alpha^{-1}\varepsilon)\rho'_w} + \frac{\alpha}{\beta} \left[\theta(x_1 - x_2) \int_{0^+}^{x_2} dx_3 \left(\frac{d\mu_h}{dx_3} \right)^{-2} + \theta(x_2 - x_1) \int_{0^+}^{x_1} dx_3 \left(\frac{d\mu_h}{dx_3} \right)^{-2} \right] \right\} \tag{50}$$

[†] Our notation differs from that of AH. They use β for our ratio b and λ for the inverse bulk correlation length a_1 .

[‡] The exponents for complete wetting are the same for all b .

where $\theta(x)$ is the Heaviside step function, $\rho'_w = d\rho/dx$ at $x = 0^+$ and $\mu_h \equiv \mu_h(\rho(x))$. The local susceptibility (see I) is

$$\chi(x_1) = \chi_h(\rho(x_1)) + \frac{\chi_h(\rho_w)(\rho_b - \rho_w)\rho'(x_1)\rho_w}{(\rho_w - 2\alpha^{-1}\varepsilon)\rho(x_1)\rho'_w} + \frac{\beta\alpha\rho'(x_1)}{\rho(x_1)} \\ \times \int_{0^+}^{x_1} dx_2 \left(\frac{\rho(x_2)\chi_h(\rho(x_2))}{\rho'(x_2)} \right)^2 [\rho_b - \rho(x_2)]. \quad (51)$$

Both equations simplify considerably for a particle at the wall. Reverting to the original variables and correlation function we find

$$G_0(z, 0) = \frac{\rho'(z)\chi_h(\rho_w)\rho_w}{(\rho_w - 2\alpha^{-1}\varepsilon)} \quad z > 0 \quad (52)$$

and

$$\chi(0^+) = \chi_h(\rho_w) \left(1 + \frac{(\rho_b - \rho_w)}{(\rho_w - 2\alpha^{-1}\varepsilon)} \right). \quad (53)$$

Equations (52) and (53) agree with the *exact* results (9b) and (9c) for a hard wall ($\varepsilon = 0$), apart from a factor of $\chi_h(\rho_w)$ in both equations. The origin of this factor was described in I; it arises from the failure of a local-density approximation to treat properly infinite repulsion at the wall—the sum rule (9a) is not satisfied exactly in this theory.

Using (30) another important formula was derived in I for the second moment $G_2(z_1, z_2)$. This simplifies to

$$\frac{-G_2(0^+, 0^+)}{\chi_h^2(\rho_w)} = \frac{\rho_w^2}{(\rho_w - 2\alpha^{-1}\varepsilon)^2} \int_{0^+}^{\infty} dx_1 \int_{0^+}^{\infty} dx_2 \rho'(x_1)\rho'(x_2)C_2(x_1, x_2) \\ + \frac{2\rho_w^2}{(\rho_w - 2\alpha^{-1}\varepsilon)} \int_{0^+}^{\infty} dx_2 \rho'(x_2)C_2(0, x_2) + \rho_w^2 C_2(0, 0) \quad (54)$$

when both particles are at the wall. Note that the second moment C_2 is a simple function for the Yukawa potential (38):

$$C_2(x_1, x_2) = \frac{\beta\alpha}{4\lambda}(1 + |x_1 - x_2|) \exp(-|x_1 - x_2|). \quad (55)$$

For the hard-wall case we showed that the RHS of (54) is $\beta\sigma (= \beta\Omega^{(s)}/A)$. In other words G_2 obtained from the Sullivan model is consistent with the exact result (9d), apart from an unimportant factor of $\chi_h^2(\rho_w)$.

The above formulae all refer to the Sullivan model, $b = 1$. When $b \neq 1$, (39a) remains valid but the equation for the derivative of the density profile no longer reduces to a second-order differential equation having the same form as (39a) at $Q = 0$. This means that $\rho'(x_2)/\rho(x_2)$ is not a solution and an explicit formula for $s_0(x_1, x_2)$ cannot be derived. However, another more transparent integral equation for $s_0(x, 0)$ can be obtained from (39a). Setting $s_0(x, 0) \equiv f(x)\chi_h(\rho(x)) d\mu_h/dx$, a second (integral) relationship between the arbitrary function $f(x)$ and $s_0(x, 0)$ follows from (39a) and the differential equation for $d\mu_h/dx$ resulting from (35). Eliminating f then yields a new equation for $s_0(x, 0)$ that

involves constants of integration. These can be evaluated using the various boundary conditions. We omit details and quote the final equation:

$$s_0(x_1, 0) = \frac{\lambda \rho'(x_1)}{\rho(x_1)} \left[B + \frac{b\varepsilon(1-b^2)}{\beta\lambda} \int_{0^+}^{x_1} dx_2 \left(\frac{d\mu_h}{dx_2} \right)^{-2} \times \int_{x_2}^{\infty} dx_3 \frac{s_0(x_3, 0) \exp(-bx_3)}{\chi_h(\rho(x_3))} \right] \tag{56a}$$

where B is a constant given by

$$B = \left[\alpha \chi_h(\rho_w) + \frac{b\varepsilon(1-b^2)}{\rho'_w \lambda} \rho_w \chi_h(\rho_w) \int_{0^+}^{\infty} dx \frac{s_0(x, 0) \exp(-bx)}{\chi_h(\rho(x))} \right] \times [\alpha \rho_w - b(1+b)\varepsilon]^{-1}. \tag{56b}$$

Although (56) reduces to the correct Sullivan limit (52) for $b = 1$, it is clear that, for any other value of b , $s_0(x, 0)$ is a much more complex function. Only when both particles are at the wall does (56) adopt a form *similar* to (52), i.e.

$$s_0(0, 0) = \lambda \rho'_w B / \rho_w. \tag{57}$$

We will make use of (56) and (57) in our discussion of critical wetting and the exponent α_s .

That these explicit formulae for correlation functions are consistent with the exact sum-rule predictions for the hard wall suggests that it is meaningful to investigate their consequences for models undergoing wetting transitions. (The particular case of complete drying at a hard wall was analysed in I.) The exact sum rules of § 2.1 simplify for the special case of an exponential wall–fluid potential. Since

$$V'(z) = -\lambda_v V_\varepsilon(z) \quad z > 0$$

(see (44)), equation (2) for the density profile can be written as

$$\rho'(z_1) = G_0(z_1, 0) + \beta \lambda_v \int_{0^+}^{\infty} dz_2 V_\varepsilon(z_2) G_0(z_1, z_2) \quad z_1 > 0$$

where the first term on the RHS arises from the hard-wall discontinuity, cf. (9b). This equation can then be used to reduce the RHS of (10) to a single integration

$$\left(\frac{\partial \Gamma}{\partial \varepsilon} \right)_{\mu, T} = (\varepsilon \lambda_v)^{-1} \left[\int_{0^+}^{\infty} dz G_0(z, 0) + \rho_w - \rho_b \right] \tag{58a}$$

$$= (\varepsilon \lambda_v)^{-1} [\rho_w \chi(0^+) - \rho_b]. \tag{58b}$$

Similarly the RHS of (11b) can be reduced to an expression involving $\tilde{G}_0(0, 0)$ only:

$$\left(\frac{\partial^2 \Omega^{(s)}/A}{\partial \varepsilon^2} \right)_{\mu, T} = (\beta \varepsilon^2 \lambda_v^2)^{-1} [\rho'_w - \tilde{G}_0(0, 0) - \lambda_v (\beta p - \rho_w)]. \tag{59}$$

As before, the quantity $\tilde{G}_0(0, 0)$ is $G_0(0, 0)$ minus the delta function contribution—see (1b). Note that for a hard wall ($\varepsilon = 0$) the terms in square brackets in (58) and (59) vanish identically by virtue of (9). We do not expect the correlation functions obtained from the density-functional approximation to satisfy sum rules (58) and (59) *identically*; factors of $\chi_h(\rho_w)$ will arise as in the hard-wall case. However, (58) and (59) require any

singular contributions to $G_0(t, 0)$ and $\tilde{G}_0(0, 0)$ obtained from our approximate theory to be consistent with the singularities in $(\partial\Gamma/\partial\varepsilon)_{\mu, T}$ and $((\partial^2\Omega^{(s)}/A)/\partial\varepsilon^2)_{\mu, T}$ respectively. In particular (59) requires[†] $\tilde{G}_0^{\text{sing}}(0, 0) \sim |\delta\varepsilon|^{-\alpha_s}$. Thus, these equations provide a useful check on the internal consistency of the density-functional results.

3.4. Behaviour of the correlation functions at wetting transitions

3.4.1. Complete wetting from off-bulk coexistence. Complete wetting and drying in the Sullivan model ($b = 1$) was analysed in I. The results can be summarised as follows. $G(z_1, z_2; Q)$ exhibits Ornstein–Zernike behaviour (16) when $z_1, z_2 \sim t$ and $\xi_{||}$ is given by (46b). The local susceptibility $\chi(t)$, obtained from (51), diverges as given in (20) (Tarazona and Evans 1982), i.e. as $\rho'(t)|\delta\mu|^{-1}$. For complete wetting $\varepsilon > \varepsilon_w(T)$ and $\rho_w > \rho_l(T)$; the density profile decreases monotonically with z . The denominator in (52) and (53) is non-zero, so that both $G_0(t, 0)$ and $\chi(0^+)$ remain finite at $\delta\mu = 0$. These results are consistent with the exact sum-rule predictions for drying at a hard wall (§ 2.1). That $G_0(t, 0)$ is finite is also consistent with (43) since, from (46), $\xi_{||}^2 \exp(-\lambda a_1 t) \sim 1$ for complete wetting. Caution must be exercised, however, in employing (43) in this case. More careful analysis shows that (43) applies for $z_2 > \Lambda \sim t/2$. When $z \rightarrow 0$ there is no ‘singular’ contribution to $G_0(z, 0)$ from the liquid–gas interface, as is evident from (52). When both particles are at the wall $\tilde{G}_0(0, 0)$ depends on purely local quantities ρ'_w and ρ_w . At complete wetting these are characteristic of the wall–liquid interface and contain no information about the liquid–gas interface.

The second moment $G_2(z_1, z_2)$ is somewhat more difficult to analyse. In I an explicit equation was obtained for $G_2(z, 0)$ for the particular case of a hard wall and we showed that

$$G_2(z, 0) \sim \frac{-\rho'(z)\chi_h(\rho_w)\sigma_{\text{lg}}}{\lambda a_g \Delta\rho|\delta\mu|} \quad t/2 < z < t. \quad (60)$$

Taking the ratio of (60) and (52) we obtain a transverse correlation length that diverges as $|\delta\mu|^{-1/2}$, i.e. in the same fashion as $\xi_{||}$ —see (46b). The capillary-wave fluctuations do not manifest themselves in this way when $z < t/2$. Then there is no diverging transverse correlation length. We would expect the same consequences for any complete wetting or drying situation in the Sullivan model. Equation (54) implies that $G_2(0, 0)$ acquires a contribution from the depinning liquid–gas portion of $\rho'(z)$ in the limit $\delta\mu \rightarrow 0^+$. Use of the Triezenberg and Zwanzig (1972) formula for σ_{lg} (see I) shows that this is a *finite* contribution $-\chi_h^2(\rho_w)\rho_w^2\sigma_{\text{lg}}\beta/(\rho_w - 2\alpha^{-1}\varepsilon)^2$.

Complete wetting when $b \neq 1$ is essentially the same as that for $b = 1$. As mentioned earlier the critical exponents are the same and the film thickens as in (46a) if $a_1 < b$, or as $\lambda t \sim -b^{-1} \ln |\delta\mu|$ if $a_1 > b$. In either case $s_0(t, 0)$ in (43) remains finite. This is confirmed by further analysis, which shows that there is no contribution to B , in (56a), from the liquid–gas interface and that the second term in this equation is non-singular.

3.4.2. Critical wetting at bulk coexistence. We focus on critical wetting $\varepsilon \rightarrow \varepsilon_w^-(T)$, where the bulk is gas at $\delta\mu = 0^+$. The Sullivan model ($b = 1$) is exceptional in that for $\varepsilon \leq \varepsilon_w(T)$ the density profile, at coexistence, is a portion of the free liquid–gas interface (Sullivan

[†] Equation (59) justifies, for the special case of exponential wall potentials, the argument, given in § 2.2, that $\tilde{G}_0^{\text{sing}}(a, a) \sim |\delta\varepsilon|^{-\alpha_s}$.

1979, 1981). At the transition $\rho_w = \rho_l(T)$ and $\rho'_w = 0$. From the equation for the density profile and the boundary condition at the wall, it is straightforward to show that

$$\left(\frac{d\mu_h}{dx}\right)_{x=0^+}^g = \frac{2a_1 \delta\varepsilon}{1 - a_1} \quad \delta\varepsilon \rightarrow 0^- \tag{61a}$$

for the (critical) wall–gas interface; $\delta\varepsilon \equiv \varepsilon - \varepsilon_w(T)$. It is instructive to consider also the (non-critical) wall–liquid interface ($\delta\mu = 0^-$), for which

$$\left(\frac{d\mu_h}{dx}\right)_{x=0^+}^l = \frac{-2a_1 \delta\varepsilon}{1 + a_1} \quad \delta\varepsilon \rightarrow 0^-. \tag{61b}$$

Thus ρ'_w is negative for wall–gas but positive for wall–liquid interfaces. (Note that $0 < a_1 < 1$.) When $\delta\varepsilon > 0$ the wall–gas interface is wet by liquid and (61b) applies to *both* the critical and non-critical interfaces. There is a discontinuous jump in $(\partial\rho'_w/\partial\varepsilon)_T$ on the critical interface at the transition. This gives rise, via (52), and some algebra, to an equivalent discontinuity in $\tilde{G}_0(0, 0)$, i.e.

$$\tilde{G}_0(0, 0)^g = \frac{\beta\alpha\lambda\rho_w^2}{1 - a_1} \chi_h^2(\rho_w) \quad \delta\varepsilon \rightarrow 0^- \tag{62a}$$

and

$$\tilde{G}_0(0, 0)^l = \frac{\beta\alpha\lambda\rho_w^2}{1 + a_1} \chi_h^2(\rho_w) \quad \delta\varepsilon \rightarrow 0^- \tag{62b}$$

with (62b) applying to both interfaces at $\delta\varepsilon = 0^+$. The difference between these results can be identified with the singular contribution:

$$\tilde{G}_0^{\text{sing}}(0, 0) \equiv \tilde{G}_0(0, 0)^g - \tilde{G}_0(0, 0)^l = \frac{2a_1\beta\alpha\lambda\rho_w^2}{1 - a_1^2} \chi_h^2(\rho_w) \quad \delta\varepsilon \rightarrow 0^-. \tag{63}$$

The sum rule (59) would identify this difference with

$$D \equiv \beta\varepsilon^2\lambda^2 \left[\left(\frac{\partial^2\Omega^{(s)}/A}{\partial\varepsilon^2}\right)_{\mu,T}^l - \left(\frac{\partial^2\Omega^{(s)}/A}{\partial\varepsilon^2}\right)_{\mu,T}^g \right]$$

since the other terms in (59) are identical on both interfaces at $\delta\varepsilon = 0$. Sullivan (1981) has investigated the dependence of the surface tension on $\delta\varepsilon$. Using the results in the appendix to his paper we have evaluated D and find this quantity is identical to the RHS of (63), apart from the expected factor of $\chi_h^2(\rho_w)$. That the two routes to $\tilde{G}_0^{\text{sing}}(0, 0)$ give consistent results attests to the internal consistency of the theory, as remarked in § 3.3.

We conclude that $\tilde{G}_0(0, 0)^g$ has a finite, singular contribution at the transition, consistent with exponent $\alpha_s = 0$. The second moment $G_2(0, 0)$, on the other hand, now diverges as $|\delta\varepsilon|^{-2}$. This follows directly from the explicit formula (54). The transverse correlation length at the wall (defined by (32) with $a = 0$), $\xi_{\parallel}^w \sim |\delta\varepsilon|^{-1}$, which is the same divergence as that of ξ_{\parallel} in (47b). More precisely, from (63), (54), (47b) and the definition (32), we find $\xi_{\parallel}^w = a_1\xi_{\parallel}$.

From (51) we find (Tarazona and Evans 1982) that $\chi(t)$ again diverges as predicted by (20), i.e. as $\rho'(t)|\delta\varepsilon|^{-2}$. The susceptibility at the wall $\chi(0^+)$ has, from (53), a singular contribution

$$\chi^{\text{sing}}(0^+) = \chi_h(\rho_w) \frac{(\rho_w - \rho_b)\alpha}{2\delta\varepsilon} \tag{64}$$

with $\rho_w - \rho_b \rightarrow \Delta\rho$ at the transition. ($\chi(0^+)$ is finite on the non-critical interface since $\rho_w - \rho_b$ vanishes as $\delta\varepsilon$.) Sum rule (58*b*) identifies $\chi^{\text{sing}}(0^+)$ with the singular part of $\varepsilon\lambda\rho_w^{-1}(\partial\Gamma/\partial\varepsilon)_{\mu,T}$. This latter quantity can be evaluated explicitly in the Sullivan model. Using methods given in the appendix of Tarazona and Evans (1982), we find

$$\varepsilon\lambda\rho_w^{-1} \left(\frac{\partial\Gamma}{\partial\varepsilon} \right)_{\mu,T} = \frac{2\varepsilon(\rho_w - \rho_b)}{\rho_w(2\varepsilon - \alpha\rho_w)} \tag{65}$$

which, apart from the factor of $\chi_h(\rho_w)$, reduces to (64) at the transition, again attesting to the internal consistency of the theory.

Equation (52) implies that $G_0(t, 0) \sim \rho'(t)|\delta\varepsilon|^{-1}$, which is consistent with the predictions (27) and (28), taking $a = 0$. The same exponent (-1) follows by inserting the critical wetting characteristics (47) into (43). In this case Λ is a *microscopic* distance, which can be taken to be zero, at the transition. Critical wetting in the Sullivan model is characterised by capillary-wave-like fluctuations that extend all the way to the wall.

A similar scenario emerges when $b \neq 1$. The details are sufficiently different to warrant separate discussion, however. Now the density profile at the transition is no longer a portion of the free interface and $\rho'_w \neq 0$. The constant B in (56) remains finite at the transition; the denominator in (56*b*) does not vanish when $\varepsilon \rightarrow \varepsilon_w(T)$ —see (49).

Direct analysis of the integral equation (56) is not straightforward. It is more convenient to return first to (43), which remains valid for $b \neq 1$. The exponent $\nu_{||}$ that describes the divergence of $\xi_{||}$ and the amplitude of t depend on b , however. If we insert the appropriate values, as given in § 3.2, (43) yields

$$G_0(t, \Lambda) \sim |\delta\varepsilon|^{-1} \tag{66}$$

for all b for which critical wetting occurs. This result is consistent with (28). Moreover we expect it to apply for $\Lambda = 0$, consistent with the divergence predicted by sum rule (58*a*); $\beta_s = 0$ for all relevant b . The argument that leads to (43) can be extended to give

$$\tilde{G}_0^{\text{sing}}(\Lambda, \Lambda) \sim \xi_{||}^2 \exp[-2\lambda a_1(t - \Lambda)]. \tag{67}$$

Setting $\Lambda = 0$ and inserting the wetting characteristics we obtain

$$\tilde{G}_0^{\text{sing}}(0, 0) \sim \begin{cases} \text{constant} & b \geq 2a_1 \\ |\delta\varepsilon|^{(2a_1-b)/(b-a_1)} & a_1 < b < 2a_1, b > 1 \end{cases} \tag{68}$$

which is consistent with the requirement $\tilde{G}_0^{\text{sing}}(0, 0) \sim |\delta\varepsilon|^{-\alpha_s}$. If we shift attention to (56) and (57) and recall that at contact the density profile and its derivative are the same on both the critical and non-critical interfaces, it follows that B must also be the same when the singular contribution to $s_0(0, 0)$ vanishes at the transition ($\alpha_s < 0$) but should be different when the singular contribution is non-vanishing ($\alpha_s = 0$). Any singular term must arise from the integral in (56*b*). But it is easy to see that the singular contribution to the integral is proportional to $\tilde{G}_0(0, 0)$, so B does indeed exhibit the correct behaviour.

There is no explicit formula for the second moment when $b \neq 1$ but the Ornstein-Zernike relation (30) combined with (66) gives, consistent with (31),

$$G_2(0, 0) \sim |\delta\varepsilon|^{-2} \quad (69)$$

for all relevant b . Although $G_2(0, 0)$ diverges more slowly than $G_2(t, t) \sim |\delta\varepsilon|^{-4\nu_{\parallel}}$, with $\nu_{\parallel} \geq 1$, the transverse correlation length ξ_{\perp}^w , obtained from the ratio of (69) and (68) still diverges as $\xi_{\perp} \sim |\delta\varepsilon|^{-\nu_{\parallel}}$.

4. Relationships between ξ_{\parallel} and t for critical wetting in three dimensions

Critical wetting in $d = 3$ with short-ranged potentials has received much attention recently (e.g. Dietrich 1988). The application of RG methods to effective interfacial Hamiltonians (Lipowsky *et al* 1983), Brezin *et al* 1983, Fisher and Huse 1985) leads to predictions of non-universal critical exponents that depend on the dimensionless parameter $\omega = (4\pi\beta\sigma_{lg}\xi_b^2)^{-1}$, where ξ_b is the bulk correlation length of the phase that is preferentially adsorbed. Such effective Hamiltonians consider the displacement of the liquid-gas edge of the wetting film in a 'pinning potential' that is identified with the mean-field wall-fluid interfacial tension; all fluctuations other than the capillary-wave-like fluctuations of the depinning interface are averaged out. In $d = 2$, exact solution of the interfacial Hamiltonian yields the exact Ising model results quoted earlier. In $d = 3$, Monte Carlo results for the same effective Hamiltonian (Gompper and Kroll 1988) are in agreement with the RG predictions, whereas extensive simulations (Binder *et al* 1986, Binder and Landau 1988) of an Ising model with a contact surface field appear to yield only the mean-field value $\nu_{\parallel} = 1$ for a situation where ω is such that RG theory would predict substantial renormalisation, $\nu_{\parallel} \sim 6$. Various explanations of the discrepancy between the results from the Ising simulations and those from study of the interfacial Hamiltonian have been put forward (Binder and Landau 1988, Dietrich 1988, Halpin-Healy and Brezin 1987, Mon *et al* 1988, Halpin-Healy 1989), none of which we find totally convincing. Given this background it is important to enquire whether the RG results can be derived by methods appropriate to a full many-body Hamiltonian description of a continuum fluid adsorbed at a wall. Henderson (1987b) has made a promising step towards this end using sum-rule arguments and making certain assumptions for the effects of capillary-wave fluctuations. Here we have the somewhat less ambitious aim of rederiving the RG relationships between the thickness t of the wetting film and the transverse correlation length ξ_{\perp} using results from § 2.

We begin by recalling that naive scaling analysis for critical wetting is problematic in $d = 3$. This follows as a consequence of the exponent relation (26) and from the fact that RG theory predicts exponential growth of ξ_{\parallel} ($\nu_{\parallel} = \infty$) for $\omega \geq 2$. A careful treatment of scaling (Parry and Evans 1989) implies the relationship

$$\xi_{\parallel} \sim \exp(ct) \quad (70a)$$

where c is a constant, which implies, in turn

$$\xi_{\perp} \sim (\ln \xi_{\parallel})^{1/2} \sim t^{1/2}. \quad (70b)$$

While the second of these is obeyed by the RG results for all ω , the first is obeyed exactly only if $\omega < \frac{1}{2}$. For $\omega > \frac{1}{2}$ there are logarithmic factors (see below) present in the RG results. In order to investigate the origin of these terms, which constitute corrections to the scaling prediction, we make use of the analogue of the $C_P - C_V$ thermodynamic

relation (14). Assuming hyperscaling is valid at the upper critical dimension, which is known to be correct within the RG analysis, we have, for $d = 3$, $\Omega_{\text{sing}}^{(s)}/A \sim \xi_{\parallel}^{-2}$. Then, since $(\partial\Gamma/\partial\mu)_{\epsilon,T} \sim \xi_{\parallel}^2$, equation (14) implies

$$\frac{\partial^2}{\partial\epsilon^2} \xi_{\parallel}^{-2}(\epsilon) = K \left(\frac{\partial t}{\partial\epsilon}\right)^2 \xi_{\parallel}^{-2}(\epsilon) \tag{71}$$

where K is some (unknown) constant and ϵ refers, as usual, to either the surface field or the temperature. Setting

$$y \equiv \frac{d}{d\epsilon} \ln \xi_{\parallel}^{-2}(\epsilon)$$

can be re-expressed as

$$\frac{dy}{d\epsilon} = -y^2(\epsilon) + K \left(\frac{dt}{d\epsilon}\right)^2. \tag{72}$$

In the light of the RG and scaling results we suppose that

$$\xi_{\parallel}(\epsilon) = \begin{cases} \text{constant} \times (\delta\epsilon)^{-n} & \tilde{\beta} = 0 \\ A(\delta\epsilon)^{-n} \exp[\phi(\delta\epsilon)^{-\tilde{\beta}}] & \tilde{\beta} > 0 \end{cases} \tag{73}$$

where A , n , ϕ and $\tilde{\beta}$ are constants, $\tilde{\beta}$ to be identified later with exponent β_s . It is then straightforward to determine $t(\epsilon)$ from (72) and show that

$$t(\epsilon) = \begin{cases} \text{constant} \times \ln(\delta\epsilon) & \tilde{\beta} = 0 \\ (2/K^{1/2})[\phi(\delta\epsilon)^{-\tilde{\beta}} - \frac{1}{4}(4n - \tilde{\beta} - 1) \ln \delta\epsilon] & \tilde{\beta} > 0 \end{cases} \tag{74}$$

in the limit $\delta\epsilon \rightarrow 0$. Then

$$\xi_{\parallel} = A(\delta\epsilon)^{-(\tilde{\beta}+1)/4} \exp(\frac{1}{2}K^{1/2}t) \quad \text{for all } n, \tilde{\beta} > 0$$

in the same limit. This last result can be expressed as

$$\xi_{\parallel}(\ln \xi_{\parallel})^{-(\tilde{\beta}+1)/4\tilde{\beta}} \propto \exp(\frac{1}{2}K^{1/2}t) \quad \tilde{\beta} > 0 \tag{75}$$

since, from (73), $\ln \xi_{\parallel} \sim (\delta\epsilon)^{-\tilde{\beta}}$ at leading order. Equation (75) is the main result of this section and we now compare its predictions with the RG results of Fisher and Huse (1985), which are summarised below:

$\beta_s = 0(\ln)$	$\nu_{\parallel} = (1 - \omega)^{-1}$	$\xi_{\parallel} \sim \exp[t(1 + 2\omega)^{-1}]$	$\omega \leq \frac{1}{2}$
$\beta_s = 0(\ln)$	$\nu_{\parallel} = (\sqrt{2} - \sqrt{\omega})^{-2}$	$\xi_{\parallel}(\ln \xi_{\parallel})^{-1/8} \sim \exp[t(8\omega)^{-1/2}]$	$\frac{1}{2} < \omega < 2$
$\beta_s = 2$	$\xi_{\parallel} \sim \exp[C'(\delta\epsilon)^{-2}]$	$\xi_{\parallel}(\ln \xi_{\parallel})^{-1/4} \sim \exp(t/4)$	$\omega = 2$
$\beta_s = 1$	$\xi_{\parallel} \sim \exp\{(C\delta\epsilon)^{-1}[\ln(C\delta\epsilon)^{-1} + \ln \ln(C\delta\epsilon)^{-1} + O(1)]\}$		
	$\xi_{\parallel}(\ln \xi_{\parallel})^{-3/8} \sim \exp[t(8\omega)^{-1/2}]$		$\omega > 2$

(76)

where C is an ω -independent constant and C' is a constant.

Comparison of (74) and (76) suggests that the relevant values of $\tilde{\beta} (\equiv \beta_s)$ are 0, 1 and 2, so that our present thermodynamic argument predicts (70a) for $\beta_s = 0$ and

$$\xi_{\parallel} (\ln \xi_{\parallel})^{-1/2} \sim \exp(\text{constant} \times t) \quad \beta_s = 1 \quad (77a)$$

or

$$\xi_{\parallel} (\ln \xi_{\parallel})^{-3/8} \sim \exp(\text{constant} \times t) \quad \beta_s = 2. \quad (77b)$$

These results are very similar to the explicit RG results (76) but, in each case, there is a discrepancy of a factor $(\ln \xi_{\parallel})^{1/8}$. This observation becomes even more puzzling when we recall that the RG treatment of Lipowsky *et al* (1983) yields *precisely* (77a) for $\beta_s = 1$. More specifically Lipowsky *et al* found

$$\begin{aligned} \beta_s = 0(\ln) \quad \nu_{\parallel} &= (1 - \omega)^{-1} \quad \xi_{\parallel} \sim \exp[t(1 + 2\omega)^{-1}] \quad \omega < 1 \\ \beta_s = 1 \quad \xi_{\parallel} &\sim \exp(\text{constant} \times \delta\epsilon^{-1}) \quad (78) \\ \xi_{\parallel} (\ln \xi_{\parallel})^{-1/2} &\sim \exp(t \times \text{constant}) \quad \omega > 1 \end{aligned}$$

in a theory based on a cruder renormalised effective potential, i.e. one that provides a less realistic description of a repulsive wall.

For the case $\tilde{\beta} \equiv \beta_s = 0(\ln)$ equation (71) has the simple solution (70a) with $\xi_{\parallel} \sim (\delta\epsilon)^{-n}$ and the exponent $n (\equiv \nu_{\parallel})$ is undetermined. Thus, the thermodynamic argument recovers the scaling result, which is in agreement with both RG analyses. That ν_{\parallel} is undetermined within the thermodynamic and scaling treatments is a direct consequence of (26).

Returning to the situation where $\beta_s \geq 1$ we are forced to conclude that, if (71) gives a complete description of the singularities, Lipowsky's RG analysis is the one that gives the correct relationship between ξ_{\parallel} and t . This is contrary to the 'accepted wisdom'. On the other hand, corrections to hyperscaling would, presumably, change our thermodynamic analysis, alter (71) and provide the factor of $(\ln \xi_{\parallel})^{1/8}$ that would bring our results into agreement with those of Fisher and Huse (1985), i.e. (76). The origin of any such correction terms remains obscure, however, and we shall see in § 5 that discrepancies of this sort also arise in alternative approaches to the problem.

The analysis of this section demonstrates that as well as yielding the fundamental exponent relationship (24) the thermodynamic argument is capable of accounting for remarkable, non-trivial relations between ξ_{\parallel} and t which supersede those from the scaling *ansatz*. Finally, we note that the solution (75) is unaffected by allowing ϕ to diverge as $\ln \delta\epsilon$.

5. Critical exponents for critical wetting via unfreezing of capillary-wave fluctuations on a mean-field profile

In this section we present the results of an analysis that has the same aim as that described in § 4 but which makes use of (13), or equivalently, the sum rule (11a), and an explicit model for the density profile $\rho(z)$ near the wall. For finite-ranged wall potentials (13) implies

$$\left(\frac{\partial \Omega^{(s)}/A}{\partial \epsilon} \right)_{\mu, T} \sim -a\rho(a) \quad (79)$$

where a is a microscopic distance. Clearly any singular behaviour in derivatives with

respect to ε of $\Omega^{(s)}$ is reflected in derivatives of $\rho(a)$. We assume that, in general, the profile near the wall can be expressed as a short-ranged, unrenormalised part $\rho_{sr}(z)$, associated with $(\partial\sigma_{wl}/\partial\varepsilon)_{\mu,T}$ in (25), plus a contribution $\bar{\rho}(z)$ arising from the unfreezing of the capillary-wave-like fluctuations on a bare profile $\bar{\rho}_{MF}(z)$ that corresponds to the mean-field solution for a liquid-gas profile whose dividing surface is located near the edge of the wetting film at $z \sim t$. For a fluid in which the intermolecular potential is short-ranged, the tails of the (mean-field) density profile decay exponentially towards their constant, bulk values and the profile takes the form

$$\bar{\rho}_{MF}(z - t) = -\bar{a} \exp[(z - t)/\xi_b] + \bar{b} \exp[2(z - t)/\xi_b] + \dots \quad z \ll t \tag{80}$$

where \bar{a} and \bar{b} are constants. In the particular case of the Yukawa fluid, the bulk liquid correlation length $\xi_b = (\lambda a_1)^{-1}$, with a_1 given by (42). The fluctuations are unfrozen on the bare profile according to the procedure of Percus (1981), as adopted by Henderson (1987b). The renormalised profile is given by

$$\bar{\rho}(z) = (2\pi\xi_{\perp}^2)^{-1/2} \int_{-t}^{\infty} dy \bar{\rho}_{MF}(z - t - y) \exp(-y^2/2\xi_{\perp}^2) \tag{81}$$

where ξ_{\perp} is the interfacial roughness introduced in (21). Equation (81) is an extension to films of the standard unfreezing procedure used for liquid-gas interfaces in the presence of a gravitational field, where it leads to the well known error-function profile, e.g. Bedeaux and Weeks (1985). Henderson (1987b) provides a careful discussion of the assumptions underlying (81) in the present context†. Combining (80) and (81) we obtain for z close to the wall

$$\bar{\rho}(z) = -\bar{a} \exp(z/\xi_b) I(\xi_b^{-1}) + \bar{b} \exp(2z/\xi_b) I(2\xi_b^{-1}) + \dots \tag{82}$$

with

$$I(p) \equiv (2\pi\xi_{\perp}^2)^{-1/2} \int_0^{\infty} dx \exp(-px) \exp[-(x - t)^2/2\xi_{\perp}^2]. \tag{83}$$

For $d \leq 3\xi_{\perp}$ diverges as t diverges (at the wetting transition) and it is evident that the form of $\bar{\rho}(z)$ will depend sensitively on the relative magnitudes of ξ_{\perp} and t , which depend, in turn, on the transverse correlation length ξ_{\parallel} . From the limiting behaviour of the error function it follows that

$$I(p) \xrightarrow{(t, \xi_{\perp} \rightarrow \infty)} \begin{cases} \exp(p^2\xi_{\perp}^2/2 - pt) & p\xi_{\perp}^2 < t \\ \frac{\exp(-t^2/2\xi_{\perp}^2)}{(2\pi)^{1/2}(p\xi_{\perp} - t/\xi_{\perp})} & p\xi_{\perp}^2 > t. \end{cases} \tag{84a, 84b}$$

In $d = 3$, the standard capillary-wave Hamiltonian yields (Buff *et al* 1965, Evans 1979, Bedeaux and Weeks 1985)

† The exponential in (81) takes into account Gaussian smearing about the mean field profile. In principle one should also include a term $\exp U(y, t)$ that accounts for wall-fluid and fluid-fluid contributions to the mean-field interfacial free energy. For short-ranged forces we can take

$$U = \begin{cases} \infty & y < -t \\ \text{constant} & -t < y < -t + a \\ 0 & \text{otherwise} \end{cases}$$

where a is a microscopic length. Including such a U alters the amplitude of $\bar{\rho}(z)$ but not the form of the singularity.

$$\begin{aligned} \xi_{\perp}^2 &= (4\pi\beta\sigma_{\text{ig}})^{-1} \ln(\xi_{\parallel}/\xi_b)^2 \\ &\equiv \omega \xi_b^2 \ln(\xi_{\parallel}/\xi_b)^2 \end{aligned} \tag{85}$$

when the cut-off for transverse wavenumbers $Q_{\text{max}} \equiv \xi_b^{-1}$. For sufficiently small ω , corresponding to a very stiff interface, we might suppose that the roughness is such that $2\xi_{\perp}^2 < \xi_b t$. Then both $I(\xi_b^{-1})$ and $I(2\xi_b^{-1})$ can be approximated according to (84a). Moreover we expect (70a) to be valid so that $t = c_1 \xi_b \ln(\xi_{\parallel}/\xi_b)$ with c_1 now an ω -dependent constant. Using (85) the leading term in (82) yields

$$\rho(z) = -\bar{a} \exp(z/\xi_b) \exp[(\omega - c_1) \ln(\xi_{\parallel}/\xi_b)] \quad \omega < c_1/4 \tag{86}$$

for the profile near the wall.

We now use (79), with (25) and (23a), to equate singular contributions. Since $\rho_{\text{st}}(a)$ is non-singular we find

$$\delta \varepsilon^{1-\alpha_s} \sim \xi_{\parallel}^{\omega-c_1}$$

which implies the exponent relationship $1 - \alpha_s = \nu_{\parallel}(c_1 - \omega)$. Then α_s can be eliminated using hyperscaling: $2 - \alpha_s = 2\nu_{\parallel}$. We obtain

$$\nu_{\parallel} = (2 + \omega - c_1)^{-1}. \tag{87}$$

As expected, our argument is not sufficient to determine ν_{\parallel} explicitly. However, it does provide a powerful consistency check on the RG results. The small- ω regime corresponds to the first of equations (76), so we assume $c_1 = 1 + 2\omega$. Then (87) yields $\nu_{\parallel} = (1 - \omega)^{-1}$, which is identical to the RG result for the exponent. Moreover, with this choice of c_1 the condition $2\xi_{\perp}^2 < \xi_b t$ requires $\omega < \frac{1}{2}$, which is precisely the RG requirement for this regime. If this requirement is met, the terms in $I(2\xi_b^{-1})$, $I(3\xi_b^{-1})$, etc., in (82) are of higher order than $I(\xi_b^{-1})$ and can be neglected.

For intermediate values of ω it is feasible that $\xi_{\perp}^2 < \xi_b t < 2\xi_{\perp}^2$. Then $I(\xi_b^{-1})$ is given by (84a) but $I(2\xi_b^{-1})$ must be approximated by (84b). The calculation proceeds as previously with $t = c_2 \xi_b \ln(\xi_{\parallel}/\xi_b)$ so that the condition on t and ξ_{\perp} requires $2\omega < c_2 < 4\omega$. Under these circumstances the terms in $I(2\xi_b^{-1})$, $I(3\xi_b^{-1})$, etc., are again of higher order than $I(\xi_b^{-1})$ and we obtain (87) for ν_{\parallel} , with c_1 replaced by c_2 . The RG result (76) for intermediate ω is

$$t = (8\omega)^{1/2} \xi_b [\ln(\xi_{\parallel}/\xi_b) - \frac{1}{8} \ln \ln(\xi_{\parallel}/\xi_b)].$$

If we assume $c_2 = (8\omega)^{1/2}$, equation (87) yields $\nu_{\parallel} = (\sqrt{2} - \sqrt{\omega})^{-2}$, in agreement with the RG exponent, and the condition becomes $\frac{1}{2} < \omega < 2$, which is the same as the RG requirement. In this case the procedure of equating leading singular contributions cannot determine the coefficient of any $\ln \ln \xi_{\parallel}$ term that might be present. Note that to leading order (87) implies

$$t = (2 + \omega - 1/\nu_{\parallel}) \xi_b \ln(\xi_{\parallel}/\xi_b) \quad \omega < 2. \tag{88}$$

The calculation can be extended to less stiff interfaces where ω is large and $\xi_{\perp}^2 > \xi_b t$. Then all the terms in (82) must be approximated using (84b). If we take

$$t = c_3 \xi_b [\ln(\xi_{\parallel}/\xi_b) - q \ln \ln(\xi_{\parallel}/\xi_b)]$$

with q a constant, as is suggested by the analysis of § 4, and allow for exponential growth of correlations, $\Omega_{\text{sing}}^{(s)}/A \sim \xi_{\parallel}^{-2}$, then (79), which now has the form

$$\frac{\partial}{\partial \varepsilon} \xi_{\parallel}^{-2}(\varepsilon) \propto \bar{\rho}(a)$$

can be solved for c_3 and q . (Now all the terms in (82) are $O(\xi_{\perp}^{-1})$ and we are forced to

make the assumption that the sum is a finite multiple of the first term.) We find $c_3 = (8\omega)^{1/2}$ and $q = (3\beta + 2)/8\beta$, where β is the exponent that characterises the ε -dependence of ξ_{\parallel} —see (73). Choosing $\beta(\equiv\beta_s) = 1$ or 2 , as in § 4, we obtain

$$\xi_{\parallel} (\ln \xi_{\parallel})^{-5/8} \sim \exp[t(8\omega)^{-1/2}] \quad \beta_s = 1 \quad (89a)$$

$$\xi_{\parallel} (\ln \xi_{\parallel})^{-1/2} \sim \exp[t(8\omega)^{-1/2}] \quad \beta_s = 2. \quad (89b)$$

The requirement $\xi_{\perp}^2 > \xi_{\parallel} t$ is equivalent to $\omega > c_3/2$, i.e. $\omega > 2$. Given that Fisher and Huse's (1985) RG results (76) assign $\beta_s = 1$ to the regime $\omega > 2$, it is natural to suppose that (89a) is the appropriate result to compare with RG theory. Our present theory yields the same coefficient $(8\omega)^{-1/2}$ in the exponential; when ξ_{\parallel} is exponentially diverging, equating leading singularities is sufficient to determine this coefficient. Equation (89a) exhibits a discrepancy with (76) of a factor $(\ln \xi_{\parallel})^{1/4}$. Furthermore this result differs from that of (77a) based on the C_p - C_v route. We do not have a convincing explanation for the discrepancies, other than to note that there might be problems with the convergence of (82).

It is instructive to examine the renormalisation when the wall–fluid potential is exponentially decaying as in (44). Then the sum rule (13) becomes, upon integrating by parts,

$$\left(\frac{\partial \Omega^{(s)}/A}{\partial \varepsilon}\right)_{\mu, T} = -\frac{\rho(0^+)}{\lambda_v} - \frac{1}{\lambda_v} \int_0^{\infty} dz \rho'(z) \exp(-\lambda_v z).$$

The contact density $\rho(0^+)$ can be considered as the sum of a short-ranged part, $\rho_{sr}(0^+)$, and a renormalised part given, as previously, by (82). However, the integral cannot be ignored. Using (81) and approximating $\bar{\rho}'_{MF}(z-t)$ by $-\Delta\rho\delta(z-t)$, the integral is proportional to $I(\lambda_v)$ so that

$$\left(\frac{\partial \Omega^{(s)}/A}{\partial \varepsilon}\right)_{\mu, T} = -\lambda_v^{-1}[\rho_{sr}(0^+) - \bar{a}I(\xi_b^{-1}) + \bar{b}I(2\xi_b^{-1}) + \dots + \bar{d}I(\lambda_v)]. \quad (90)$$

We are now in a position to return to the Yukawa fluid that was treated earlier in mean-field approximation. Then $\xi_b^{-1} \equiv \lambda a_1$ and $\lambda_v \equiv \lambda b$, where a_1 and b are the dimensionless quantities defined in § 3.2. Recall that the interesting case is when $a_1 < b < 2a_1$, since then the mean-field exponents for critical wetting are explicitly dependent upon b and a_1 —see (48). It is clear that we can carry through the previous calculation but now the boundaries between the different fluctuation regimes should depend on the magnitude of $\lambda_v \xi_{\perp}^2$. If $\lambda_v \xi_{\perp}^2 < t$ then both $I(\xi_b^{-1})$ and $I(\lambda_v)$ can be obtained from (84a). Assuming the former dominates, equating singular contributions in (90) again yields (87). Hauge and Olaussen (1985) extended the RG calculation of Brezin *et al* (1983) to a model Hamiltonian that included a term in $\exp(-\lambda_v t)$. From their paper one can show that $\lambda a_1 t = c_1 \ln \xi_{\parallel}$ with $c_1 = 2a_1/b + b\omega/a_1$, provided ω is less than a critical value $\omega_c \equiv 2(a_1/b)^2$. Using their result for c_1 in (87) we find

$$\nu_{\parallel} = \nu_{\parallel}(\omega = 0)/(1 - \omega b/2a_1) \quad \omega < \omega_c \quad (91)$$

where

$$\nu_{\parallel}(\omega = 0) \equiv \frac{b}{2(b - a_1)}$$

is the mean-field result (48b). Since $a_1 < b < 2a_1$, ω_c is restricted to the range $\frac{1}{2} < \omega_c < 2$.

This result for the renormalised exponent is identical to that obtained by Hauge and Olaussen (1985). Moreover the condition $\lambda_v \xi_{\perp}^2 < t$, which corresponds to $2b\omega < c_1 a_1$, is identical to the condition $\omega < \omega_c$, so we conclude that the present procedure is completely consistent with the RG treatment in this regime. With the above value for c_1 the terms in $I(\lambda_v)$, $I(2\xi_b^{-1})$, etc, are of higher order than $I(\xi_b^{-1})$. Note that when $b = 2a_1$, c_1 reduces to $1 + 2\omega$, (91) becomes $\nu_{\parallel} = (1 - \omega)^{-1}$ and $\omega_c = \frac{1}{2}$, so that we recover the earlier results for wall potentials of strictly finite range.

Hauge and Olaussen (1985) argue that for $2 > \omega > \omega_c$ the second regime in (76) will pertain and, by implication, so will the results for $\omega \geq 2$. In other words ν_{\parallel} should not depend on a_1 and b for $\omega > \omega_c$ —see also Dietrich (1988). This conclusion is consistent with the present treatment. The condition $\xi_b^{-1} \xi_{\perp}^2 < t < \lambda_v \xi_{\perp}^2$ is equivalent to $2 > \omega > \omega_c$ if the RG result $t \sim (8\omega)^{1/2} \ln \xi_{\parallel}$ is assumed. $I(\xi_b^{-1})$ remains the leading-order term in this regime.

Perhaps it is appropriate to emphasise (although it must be abundantly clear!) that our present procedure is not capable of determining *explicit* results for critical exponents in $d = 3$. The situation is markedly different for $d < 3$ where the fluctuations are stronger. Here we do obtain explicit exponents for critical wetting.

The procedure for unfreezing capillary-wave like fluctuations is not restricted to $d = 3$; equations (81) to (84) also apply for $d < 3$. In these lower dimensions $\xi_{\perp} \sim t$ (see § 2.2), so that (84b) is the only relevant limit and $\bar{\rho}(a) \propto \xi_{\perp}^{-1}$. Equating singular contributions in (79) gives a new exponent relation

$$1 - \alpha_s = \beta_s \quad d < 3 \quad (92)$$

which, combined with the other relations (24) and (26), yields the explicit result

$$\nu_{\parallel} = 2/(3d - 5) \quad d < 3 \quad (93)$$

from which all the other critical exponents can be determined. For $d = 2$ we find $\nu_{\parallel} = 2$, $\beta_s = 1$, $\alpha_s = 0$, which are the exact results quoted earlier. This gives us some confidence that summing the terms in (82), each of which is proportional to ξ_{\perp}^{-1} , does not introduce additional singularities. It is interesting that $\alpha_s = 4(d - 2)/(3d - 5)$ is *positive* for $2 < d < 3$. This implies that $\bar{G}_0(a, a)$ *diverges* in these dimensions.

Note that if (93) were to remain valid in $d = 3$ it would predict the incorrect result $\nu_{\parallel} = \frac{1}{2}$. However, as we have seen above, ξ_{\perp} is no longer proportional to t in $d = 3$ and the fluctuations manifest themselves in a very different fashion in this borderline dimension. The variation of ν_{\parallel} with dimension is a subtle matter that will be discussed elsewhere, when we make contact with the work of Kroll and Lipowsky (1982), who derived a formula equivalent to (93) using a very different procedure based on a field-theoretic treatment of domain wall pinning, and with the results of Lipowsky and Fisher (1987), who used a functional renormalisation-group treatment for an effective Hamiltonian to connect behaviour in $d = 3$ to that in $d < 3$. The numerical results of Lipowsky and Fisher are fitted by a formula that is quite different from (93). An explanation of the difference will be given in a forthcoming paper.

Before ending this section we note that our procedure for obtaining critical exponents or relationships between the various critical lengths differs from that of Henderson (1987b). Although $\bar{\rho}(a)$ is calculated from the same formulae (82)–(85), Henderson's subsequent analysis of the critical wetting transition makes several assumptions in addition to those described here. We believe that these are not fully justified and that

Table 1. Singular contributions to the transverse moments of the density–density correlation function G and the local susceptibility $\chi(z)$ at the two types of wetting transition. The tilde indicates that delta-function contributions are omitted—see text. The thickness of the wetting film, t , and the transverse correlation length, ξ_{\parallel} , diverge at the transition with critical exponents β_s and ν_{\parallel} , respectively; a is a microscopic distance. All unimportant factors of proportionality have been suppressed in this table.

	Complete	Critical
$\tilde{G}_0(t, t)$	$(\rho'(t))^2 \xi_{\parallel}^2$	$(\rho'(t))^2 \xi_{\parallel}^2$
$\tilde{G}_0(t, a)$	$\rho'(t)$	$\rho'(t) (\partial t / \partial \varepsilon)_{\mu, T}$
$\tilde{G}_0(a, a)$	0	$ \delta \varepsilon ^{-\alpha_s}$
$\tilde{G}_2(t, t)$	$-(\rho'(t))^2 \xi_{\parallel}^4$	$-(\rho'(t))^2 \xi_{\parallel}^4$
$\tilde{G}_2(a, a)$	$-\sigma_{\text{ig}}$	$-\sigma_{\text{ig}} (\partial t / \partial \varepsilon)_{\mu, T}^2$
$\tilde{\chi}(t)$	$\rho'(t) \xi_{\parallel}^2$	$\rho'(t) \xi_{\parallel}^2$
$\tilde{\chi}(a)$	ρ_b	$(\partial t / \partial \varepsilon)_{\mu, T}$

our present approach is more systematic[†]. It is clear that a simple unfreezing of the capillary-wave fluctuations on a mean-field profile leads to relations between ξ_{\parallel} and t that are consistent with the thermodynamic treatment of § 4 and with the RG results. The origin of the ω -dependence of the exponents and the amplitudes in $d = 3$ is transparent in this formulation; it is via the roughness ξ_{\perp} . In the purely thermodynamic treatment ω does not enter directly; the ω -dependence is contained in the constants of proportionality appearing in (71).

6. Discussion

In table 1 we summarise our main results for the singular behaviour of the transverse moments of G at wetting transitions. The explicit density-functional results of § 3 confirm the predictions extracted from the sum-rule analysis; they are completely consistent with the results in table 1, provided mean-field exponents are invoked and the interfacial roughness is ignored, i.e. ξ_{\perp} is set equal to a microscopic length. It is likely that a more sophisticated, non-local density-functional treatment of repulsive forces would satisfy the various sum rules exactly, but still with mean-field exponents, thereby removing the extraneous factors of $\chi_{\text{h}}(\rho_w)$ —see I. Incorporating capillary-wave fluctuations into a density-functional approach so that $\rho'(t)$ vanishes appropriately as $t \rightarrow \infty$ is difficult (e.g. Evans 1989). Nevertheless we expect the *form* of many of the results in § 3 to remain valid beyond mean-field approximation.

Although complete and critical wetting have many features in common it is clear from table 1 that correlation functions do differ significantly between the two types of transition. Singular behaviour, arising from the fluctuations, manifests itself more dramatically in critical wetting. This is a direct consequence of the result $\xi_{\parallel}^{\text{w}} \sim \xi_{\parallel}$; fluctuations extend all the way to the wall in critical wetting whereas they are modulated in a rather complex fashion in the case of complete wetting, for which there is no divergent transverse correlation length when both particles are near the wall. It is important to recognise that a divergent $G_2(a, a)$ does not imply a divergent (unphysical)

[†] Henderson does not attempt to derive exponents for $d < 3$ and he cannot describe the $\omega > 2$ regime in $d = 3$; however, he does obtain explicit exponents for $\omega < 2$.

surface tension. Careful analysis of (7), using (2), along with the explicit mean-field treatment, shows that σ remains finite at critical wetting.

One can ask how ξ_{\parallel}^w varies with $\delta\mu$ and $\delta\varepsilon$, i.e. how the transverse correlation length at the wall depends on the approach to the wetting transition. This is conveniently tackled by means of scaling arguments. From the definition (32), using the relations $G_2(a, a) \sim (\partial t/\partial \varepsilon)_{\mu, T}^2$ and $G_0^{\text{sing}}(a, a) \sim (\partial^2 \Omega_{\text{sing}}^{(s)}/\partial \varepsilon^2)_{\mu, T}$ and a scaling *ansatz* (see Parry and Evans 1989) for $\Omega_{\text{sing}}^{(s)}$ it is straightforward to show that

$$(\xi_{\parallel}^w(\delta\mu, \delta\varepsilon))^2 = \xi_{\parallel}^2 \tau(\delta\mu \xi_{\parallel}^2) \quad d = 3 \tag{94a}$$

where $\xi_{\parallel} = \xi_{\parallel}(\delta\varepsilon; \delta\mu = 0)$ and τ is a suitable scaling function: $\tau(0) = \text{constant}$. For $d < 3$ the corresponding result is

$$(\xi_{\parallel}^w(\delta\mu, \delta\varepsilon))^2 = \delta\varepsilon^{-2\nu} \bar{\tau}(\delta\mu \delta\varepsilon^{-\Delta}) \quad d < 3 \tag{94b}$$

with $\Delta = (d + 1)\nu/2$ and $\bar{\tau}$ another scaling function. The most interesting result emerges when we set $\delta\varepsilon = 0$ and take the limit $\delta\mu \rightarrow 0$. Then

$$\xi_{\parallel}^w(\delta\mu, 0) \sim \begin{cases} |\delta\mu|^{-1/2} & \delta\varepsilon = 0, d = 3 \\ |\delta\mu|^{-2/(d+1)} & \delta\varepsilon = 0, d < 3. \end{cases} \tag{95}$$

Thus (95) predicts that if we follow a path in figure 1 at fixed temperature $T = T_w$, the correlation length at the wall will diverge with the same exponent as that which describes the divergence of ξ_{\parallel} in complete wetting from off-bulk coexistence at $T > T_w$. Such behaviour is a further manifestation of the fact that fluctuations extend all the way to the wall in a critical wetting situation; $\xi_{\parallel}^w \sim \xi_{\parallel}$ on this path as well as on path (1).

Is there a simple approximation to G that will account for the various singularities that are encountered at both types of wetting transition for systems with short-ranged forces? Henderson invoked a single-eigenfunction *ansatz* for the singular or capillary-wave contribution at small wavenumbers Q :

$$G^{\text{cw}}(z_1, z_2; Q) \sim \frac{\bar{\rho}'(z_1)\bar{\rho}'(z_2)f(z_1)f(z_2)}{w(1 + \xi_{\parallel}^2 Q^2)}. \tag{96}$$

Here $\bar{\rho}(z)$ is, as in § 5, a portion of the ‘free’ liquid–gas profile whose dividing surface lies close to $z = t$; w and $f(z)$ are damping factors. The form of (96) is suggested by the corresponding result for the liquid–gas interface in a gravitational field. There $w = \beta mg \Delta \rho$ (Wertheim 1976, Evans 1979). When $z_1 \sim z_2 \sim t$, (96) must reduce to the Ornstein–Zernike result (16) and (17). Since in the edge of the film the density profile is that of the detaching liquid–gas interface, $\rho'(t) \rightarrow \bar{\rho}'(t)$ as $t \rightarrow \infty$, and we can make the identification

$$w \equiv \beta \sigma_{\text{lg}} \xi_{\parallel}^{-2} \tag{97a}$$

and

$$f(t) \equiv 1 \quad t \rightarrow \infty \tag{97b}$$

for both types of transition. Henderson argues that $f(z)$ should be a smoothly varying function that is unity for z greater than a microscopic distance but we will reconsider this function below.

Rather than following Henderson’s approach, which uses (96) as the basis for a theory of criticality, we first ask whether (96) is consistent with our results in table 1 and

then whether this *ansatz*, with the prescription for $\bar{\rho}(z)$ presented in § 5, does predict the correct critical exponents. The Ornstein–Zernike nature of (96) implies that fluctuations extend all the way to the wall; there is only one diverging correlation length ξ_{\parallel} . Consequently the formula is not appropriate for complete wetting and for this case it is necessary to go to a more sophisticated two-eigenfunction approximation to obtain a proper description of correlations†—see I. The formula is clearly more appropriate for critical wetting so we concentrate on this case here. When one particle is near the wall and the other is in the edge of the film $G_0^{\text{cw}}(t, a)$ should reproduce (27), i.e.

$$\bar{\rho}'(a)f(a) = \left(\frac{\partial \Gamma}{\partial \varepsilon}\right)_{\mu, T} w \sim \left(\frac{\partial t}{\partial \varepsilon}\right)_{\mu, T} \xi_{\parallel}^{-2}. \quad (98)$$

If both particles are at the wall we require

$$G_0^{\text{cw}}(a, a) = (\bar{\rho}'(a)f(a))^2 w^{-1} \sim |\delta \varepsilon|^{-\alpha_s}$$

which, using (97a) and (98), leads either to the exponent relation (24) or to (71) in the case of $d = 3$. The second moment

$$G_2^{\text{cw}}(a, a) = -(\bar{\rho}'(a)f(a))^2 \xi_{\parallel}^2 w^{-1} \sim -\sigma_{\text{lg}} \left(\frac{\partial t}{\partial \varepsilon}\right)_{\mu, T}^2$$

and (31) is automatically satisfied. Thus, provided (98) is valid, G^{cw} will account for the singularities at critical wetting.

We focus attention first on the mean-field case where there is no renormalisation of $\bar{\rho}_{\text{MF}}(z - t)$. From (80) we find for the Yukawa fluid

$$\bar{\rho}'_{\text{MF}}(a) \sim -\exp[\lambda a_1(a - t)] + \dots$$

As the film thickness t diverges logarithmically, with an amplitude that depends on the decay length of the exponential wall–fluid potential—see (47a) and (48a)—the tail of the liquid–gas profile vanishes as

$$\bar{\rho}'_{\text{MF}}(a) \sim \begin{cases} -|\delta \varepsilon| & b = 1 \\ -|\delta \varepsilon|^{|a_1|/(b-a_1)} & a_1 < b < 2a_1, b > 1 \end{cases}$$

as $t \rightarrow \infty$. Inserting this result in (98) implies that ξ_{\parallel} should diverge with the exponent $\nu_{\parallel} = 1$ or $b/2(b - a_1)$. But these are precisely the values obtained earlier from explicit calculations. Thus, provided $f(a)$ is a constant, G^{cw} does account for the singularities obtained in the detailed mean-field treatment.

Beyond mean-field theory, it is necessary to make some further *ansatz* regarding the damping function $f(z)$. We suppose that this has a scaling form

$$f(z) \equiv F(z/\xi_{\perp})$$

with $F(\theta)$ having a Taylor expansion about $\theta = 0$ and $F(1) = 1$. Whereas in mean-field theory the interfacial roughness ξ_{\perp} can be set equal to the length a so that $f(a)$ is irrelevant, we can expect the factor $f(a) \sim a \xi_{\perp}^{-1}$ to become relevant in strongly fluctuating

† Even in $d = 2$, when $\xi_{\perp} \sim t$ and fluctuations are extremely strong, a divergent ξ_{\parallel}^* does not exist for complete wetting or drying. The sum rules (9) for a hard wall also apply in $d = 2$ and $G_0(z, 0) = \rho'(z)$ must still be characteristic of the wall–gas interface for small z in the complete drying limit. Consequently there is no singular contribution to $\bar{G}_0(0, 0)$.

regimes. For $d < 3$ unfreezing the capillary-wave fluctuations gave the result $\bar{\rho}'(a) \sim \xi_{\perp}^{-1}$ so that (98) implies

$$\xi_{\perp}^{-2} \sim |d \varepsilon|^{-(1+\beta_s-2\nu_{\parallel})} \quad d < 3$$

and since $\xi_{\perp} \sim t$ and $\beta_s = (3-d)\nu_{\parallel}/2$ in this regime, we recover (93) for ν_{\parallel} . The calculation can be repeated in $d = 3$ for the various regimes of ω . Equation (86) yields $\bar{\rho}'(a) \sim \xi_{\parallel}^{\omega-c_1}$ for $\omega < \frac{1}{2}$ and $\frac{1}{2} < \omega < 2$. In both of these regimes t diverges logarithmically and (98) implies

$$\xi_{\perp}^{-1} \xi_{\parallel}^{\omega-c_1} \sim |\delta \varepsilon|^{-1} \xi_{\parallel}^{-2}$$

so that we recover (87) for ν_{\parallel} ; the factor of ξ_{\perp}^{-1} has no implication for the exponents if $\omega < 2$. When $\omega > 2$ and ξ_{\parallel} diverges exponentially we assume, as previously,

$$t = c_3 \xi_b [\ln(\xi_{\parallel}/\xi_b) - q \ln \ln(\xi_{\parallel}/\xi_b)]$$

with (73) for $\xi_{\parallel}(\varepsilon)$. Using (98) to determine the coefficients c_3 and q we find $c_3 = (8\omega)^{1/2}$, as before, but now $q = (4\beta + 2)/8\beta$ so that

$$\xi_{\parallel} (\ln \xi_{\parallel})^{-3/4} \sim \exp[t(8\omega)^{-1/2}] \quad \beta_s = 1 \quad (99a)$$

$$\xi_{\parallel} (\ln \xi_{\parallel})^{-5/8} \sim \exp[t(8\omega)^{-1/2}] \quad \beta_s = 2. \quad (99b)$$

These results differ (by yet another troublesome factor of $(\ln \xi_{\parallel})^{1/8}$) from those of (89). This factor can be traced to the factor of ξ_{\perp}^{-1} arising from our scaling *ansatz* for $f(a)$. We conclude that apart from this niggling discrepancy in the coefficient of the $\ln \ln \xi_{\parallel}$ term the simple *ansatz* for G^{cw} is remarkably successful in all dimensions and all fluctuation regimes for critical wetting with short-ranged forces. It would be worth while investigating two-point correlation functions in two-dimensional models to see whether a formula equivalent to (96) can be derived from a rigorous treatment.

In §§ 4 and 5 and in this concluding section we have sought to rederive or test the consistency of the RG results for critical wetting in $d = 3$. We find that these satisfy the various sum-rule requirements and that they are consistent with the explicit procedure of unfreezing capillary-wave fluctuations on the mean-field profile. It is important to recognise that the latter procedure leads directly to ω -dependent exponents and amplitudes, e.g. (87) and (88). The mean-field results are recovered if and only if $\omega = 0$. The ω enters our procedure via (85), i.e. as the parameter that measures the amplitude of the interfacial roughness ξ_{\perp} . Provided the detaching liquid–gas interface is rough, ω must be non-zero, and we conclude in keeping with Henderson that, if critical wetting does occur in a continuum fluid near an adsorbing wall, this transition should exhibit ω -dependent exponents. This conclusion is, of course, consistent with studies based on interfacial Hamiltonians. However, in those theories ω^{-1} enters from the outset as a measure of the increase in energy associated with an increase in area of the interface. Although our analysis is not immediately applicable to lattice models it does indicate that non-universal, ω -dependent exponents should arise for any proper many-body Hamiltonian in $d = 3$, with short-ranged forces, and does suggest that further simulations, for both Ising-like and continuum models, would be valuable. To the best of our knowledge, no critical wetting transition has been found in simulations of continuum fluids.

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References

- Abraham D B 1986 *Phase Transitions and Critical Phenomena* vol 10, ed. C Domb and J L Lebowitz (New York: Academic) p 1
- Aukrust T and Hauge E H 1985 *Phys. Rev. Lett.* **54** 1814
- 1987 *Physica* **141A** 427
- Bedeaux D and Weeks J D 1985 *J. Chem. Phys.* **82** 972
- Binder K and Landau D P 1988 *Phys. Rev. B* **37** 1745
- Binder K, Landau D P and Droll D M 1986 *Phys. Rev. Lett.* **56** 2272
- Brezin E, Halperin B I and Leibler 1983 *J. Physique* **44** 775
- Buff F P, Lovett R A and Stillinger F H 1965 *Phys. Rev. Lett.* **15** 621
- Cahn J W 1977 *J. Chem. Phys.* **66** 3667
- Dietrich S 1988 *Phase Transitions and Critical Phenomena* vol 12, ed. C Domb and L J Lebowitz (New York: Academic) p 1
- Ebner C and Saam W F 1977 *Phys. Rev. Lett.* **38** 1486
- Evans R 1979 *Adv. Phys.* **28** 143
- 1989 *Liquids at Interfaces* (Les Houches Session XLVIII) ed. J Charvolin, J F Joanny and J Zinn-Justin (Amsterdam: Elsevier)
- Fisher D S and Huse D A 1985 *Phys. Rev. B* **32** 247
- Gompper G and Kroll D M 1988 *Phys. Rev. B* **37** 3821
- Halpin-Healy T 1989 *Phys. Rev. B* **40** 772
- Halpin-Healy T and Brezin E 1987 *Phys. Rev. Lett.* **58** 1220
- Hauge E H and Olaussen K 1985 *Phys. Rev. B* **32** 4766
- Hauge E H and Schick M 1983 *Phys. Rev. B* **27** 4288
- Henderson J R 1986 *Mol. Phys.* **59** 1049
- 1987a *Phys. Rev. B* **35** 7303
- 1987b *Mol. Phys.* **62** 829
- Henderson J R and van Swol F 1984 *Mol. Phys.* **51** 991
- 1985 *Mol. Phys.* **56** 1313
- Kroll D M and Lipowsky R 1982 *Phys. Rev. B* **26** 5289
- Lipowsky R 1984 *Phys. Rev. Lett.* **52** 1429
- 1985 *Phys. Rev. B* **32** 1731
- Lipowsky R and Fisher M E 1987 *Phys. Rev. B* **36** 2126
- Lipowsky R, Kroll D M and Zia R K 1983 *Phys. Rev. B* **27** 4499
- Mon K K, Wansleben S, Landau D P and Binder K 1988 *Phys. Rev. Lett.* **60** 708
- Parry A O and Evans R 1988 *Mol. Phys.* **65** 455
- 1989 *Phys. Rev. B* **39** 12336
- Percus J K 1981 *Faraday Symp. Chem. Soc.* **16** 23
- Schick M 1989 *Liquids at Interfaces* (Lew Houches Session XLVIII) ed. J Charvolin, J F Joanny and J Zinn-Justin (Amsterdam: Elsevier)
- Sullivan D E 1979 *Phys. Rev. B* **20** 3991
- 1981 *J. Chem. Phys.* **74** 2604
- Sullivan D E and Telo da Gama M M 1986 *Fluid Interfacial Phenomena* ed. C A Croxton (New York: Wiley) p 45
- Tarazona P and Evans R 1982 *Mol. Phys.* **47** 1033
- 1983 *Mol. Phys.* **48** 799
- Teletzke G F, Scriven L E and Davis H T 1983 *J. Chem. Phys.* **78** 1431
- Triezenberg D G and Zwanzig R 1972 *Phys. Rev. Lett.* **28** 1183
- Wertheim M S 1976 *J. Chem. Phys.* **65** 2377