# Critical amplitudes for critical wetting with short-ranged forces: the approach to $d=3^-$



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# Critical amplitudes for critical wetting with short-ranged forces: the approach to $d = 3^-$

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**Abstract.** Critical wetting in fluids with short-ranged forces is investigated for dimensions $d \leqslant 3$. By combining statistical mechanical sum rules and capillary-wave theory with a standard scaling hypothesis for the singular part of the interfacial tension we show that, whilst the thickness $l$ of the wetting film and the interfacial roughness $\xi_\perp$ diverge with the same critical exponent for $d < 3$, the critical amplitudes are such that the ratio $l/\xi_\perp$ diverges as $(3-d)^{-1/2}$ in the limit $d \to 3^-$. Our analysis suggests that the extent of the critical regime becomes vanishingly small in the same limit and provides further insight into the crossover from $d < 3$, a strong-fluctuation regime with universal exponents, to $d = 3$, where $l \sim \xi_\perp^2$ and non-universal exponents occur.

## 1. Introduction

Consider an adsorbing planar substrate (wall) in contact with a reservoir of gas at fixed chemical potential $\mu$ and temperature $T$. The wall exerts an external potential $V_{\mathrm{ext}}(z)$, with $z$ normal to the wall, on molecules in the fluid which is sufficiently attractive to adsorb a liquid film of thickness $l$. Suppose that in bulk two-phase (liquid–gas) coexistence, where $\mu = \mu_{\mathrm{sat}}^-(T)$, $l$ diverges continuously as the temperature is increased towards the wetting transition temperature $T_\mathrm{w}$. Then a macroscopically thick film of liquid intrudes between the gas and the wall, corresponding to a phase transition from partial to complete wetting by liquid. The surface tension $\sigma_{\mathrm{wg}}$ of the wall–gas interface is then the sum of the wall–liquid surface tension $\sigma_{\mathrm{wl}}$ and the (free) liquid–gas surface tension $\sigma_{\mathrm{lg}}$, i.e. $\sigma_{\mathrm{wg}} = \sigma_{\mathrm{wl}} + \sigma_{\mathrm{lg}}$; $T \geqslant T_\mathrm{w}$. Such a critical wetting transition may also be induced by increasing the strength $\varepsilon$ of the attractive part of $V_{\mathrm{ext}}(z)$ at fixed $T$ and $\mu = \mu_{\mathrm{sat}}^-(T)$.

Critical wetting transitions have attracted much attention in recent years; see the reviews by Sullivan and Telo da Gama (1986) and by Dietrich (1988). The divergence of the film thickness and the transverse correlation length $\xi_\parallel$ and the singular contribution $\Sigma^{(\mathrm{s})}$ to the wall–gas tension are characterised by the critical exponents

$$l = c_l \xi_\mathrm{b}\, \delta\varepsilon^{-\beta_\mathrm{s}} \tag{1a}$$

$$\xi_\parallel = c_\parallel \xi_\mathrm{b}\, \delta\varepsilon^{-\nu_\parallel} \tag{1b}$$

$$\Sigma^{(\mathrm{s})} \equiv \sigma_{\mathrm{wg}} - (\sigma_{\mathrm{wl}} + \sigma_{\mathrm{lg}}) = k_\mathrm{B} T c_\mathrm{s} \xi_\mathrm{b}^{-(d-1)}\, \delta\varepsilon^{2-\alpha_\mathrm{s}} \tag{1c}$$

where $c_l$, $c_\parallel$ and $c_\mathrm{s}$ are dimensionless critical amplitudes, $\xi_\mathrm{b}$ is the bulk (liquid) correlation length and $\delta\varepsilon \equiv |(\varepsilon^\mathrm{T} - \varepsilon)/\varepsilon^\mathrm{T}|$ measures the deviation of the temperature or the field

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strength from that at the transition $\varepsilon^{\mathrm{T}}$. It is the build-up of capillary-wave-like fluctuations in the edge of the film that leads to the divergence of $\xi_{\|}$. Such fluctuations give rise to an Ornstein–Zernike type of behaviour of the (transverse) structure factor in the liquid–gas part of the interface, i.e. the exponent analogous to $\eta$ is zero for all (bulk) dimensions $d$. $\xi_{\|}$ may be defined rigorously in terms of the ratio of the second to zeroth moments of the transverse structure factor or pair correlation function in the vicinity of the liquid–gas edge of the wetting film (see later). For $d \leqslant 3$ the divergence of $\xi_{\|}$ is accompanied by the divergence of the interfacial roughness $\xi_{\perp}$, which is a measure of the interfacial width, i.e.

$$\xi_{\perp} = c_{\perp}\xi_{\mathrm{b}}\,\delta\varepsilon^{-\nu_{\perp}}. \tag{1$d$}$$

The divergence of $\xi_{\perp}$ is related to the divergence of $\xi_{\|}$ by standard capillary-wave theory (see, e.g., Bedeaux and Weeks 1985)

$$\xi_{\perp}^{2} = \begin{cases} \text{finite} & d > 3 \\ \omega\xi_{b}^{2}\ln(\xi_{\|}/\xi_{\mathrm{b}})^{2} & d = 3 \\ K(d)\xi_{\|}^{3-d} & d < 3 \end{cases} \tag{2}$$

where $\omega \equiv k_{\mathrm{B}}T/4\pi\sigma_{\mathrm{lg}}\xi_{\mathrm{b}}^{2}$ is a dimensionless parameter, and $K(d)$ is a function of $d$.

Of special interest is the case of short-ranged wall–fluid and fluid–fluid forces for which the upper critical dimenision $d_{\mathrm{u}} = 3$. The mean-field exponents are $\beta_{\mathrm{s}} = 0(\ln)$, $\nu_{\|} = 1$ and $\alpha_{\mathrm{s}} = 0$ (discontinuity). Approximate linear renormalisation group (RG) studies of effective interfacial Hamiltonians predict non-universal exponents for $d = 3$. To leading order the RG results (Brezin *et al* 1983a, b, Fisher and Huse 1985) are

$$l/\xi_{\mathrm{b}} = \begin{cases} (1+2\omega)\ln(\xi_{\|}/\xi_{\mathrm{b}}) & \nu_{\|} = (1-\omega)^{-1} \quad \omega \leqslant \tfrac{1}{2} \\ (8\omega)^{1/2}\ln(\xi_{\|}/\xi_{\mathrm{b}}) & \nu_{\|} = (\sqrt{2}-\sqrt{\omega})^{-2} \quad \tfrac{1}{2} < \omega < 2 \\ (8\omega)^{1/2}\ln(\xi_{\|}/\xi_{\mathrm{b}}) & \beta_{\mathrm{s}} = 2 \quad \nu_{\|} = \infty \quad \omega = 2 \\ (8\omega)^{1/2}\ln(\xi_{\|}/\xi_{\mathrm{b}}) & \beta_{\mathrm{s}} = 1 \quad \nu_{\|} = \infty \quad \omega > 2. \end{cases} \tag{3}$$

Monte Carlo results for the same interfacial Hamiltonian (Gompper and Kroll 1988) show that $\nu_{\|}$ is $\omega$ dependent and are consistent with (3) for the small values of $\omega$ at which the simulations were performed.

For $d = 2$, Abragam's (1980) exact solution for a square Ising lattice with a contact surface field exhibiting a critical wetting transition gives the exponents

$$\beta_{\mathrm{s}} = 1 \qquad \nu_{\|} = 2 \qquad \alpha_{\mathrm{s}} = 0\ \text{(discontinuity)} \qquad d = 2. \tag{4}$$

The same $d = 2$ results have been found in exact treatments of interfacial Hamiltonians (see, e.g., Sullivan and Telo de Gama 1986, Dietrich 1988). More recently a non-linear functional RG treatment (Lipowsky and Fisher 1986, 1987) has demonstrated that the linear RG approximation fails for $d < 3$. Whilst earlier linear RG studies (Kroll and Lipowsky 1982) indicated that only first-order wetting transitions could occur for $2 < d < 3$, the analysis of Lipowsky and Fisher indicates that for $d < 3$ a critical wetting transition does exist and this has $d$-dependent critical exponents. Their numerical results, obtained from iterations of the RG transformation, predict that $\nu_{\|}(d)$ diverges as $d \to 3^{-}$. They noted that an excellent fit to their data for $\nu_{\|}$ is provided by the formula

$$\nu_{\|} = (3-d)^{-1/2}\{\ln[3/(3-d)]^{1/2} + 3.65(3-d)\}^{1/2} \qquad 2 \leqslant d \leqslant 2.975. \tag{5}$$

It is striking that, as $d \to 3^{-}$, there appear to be critical exponents for critical exponents!

In addition, the non-linear RG analysis reveals an unusual fixed-point bifurcation property at $d = 3$ which suggests that non-universality in this dimension might be described correctly (at least for small $\omega$) by the linear RG treatment. Although the non-linear functional RG is certainly a powerful technique, it has not yet yielded a complete description of critical wetting as $d \to 3^-$ or for $d = 3$ (Fisher 1989).

It is the purpose of the present article to investigate further the nature of critical behaviour as $d \to 3^-$. In particular, we are concerned with the relationship between $l$ and $\xi_\perp$ in this limit. Using a standard scaling hypothesis for the singular part $\Sigma^{(s)}$ of the wall–gas interfacial tension together with some recently derived statistical mechanical sum rules, appropriate to a realistic many-body Hamiltonian, and thermodynamic requirements (Evans and Parry 1989, hereafter referred to as I), we derive a relationship between the critical amplitudes $c_l$ and $c_\parallel$ appearing in (1). Our analysis shows that in addition to the diverging critical exponents, as $d \to 3^-$, the ratio of length scales $l/\xi_\perp$ should diverge in the same limit. More precisely, we conclude that

$$l/\xi_\perp \sim (3-d)^{-1/2} \qquad d \to 3^-. \tag{6}$$

Thus the magnitude of the interfacial wandering $\xi_\perp$ decreases relative to that of the wetting film thickness $l$ as the bulk dimension $d$ increases towards $d = 3$. In order to appreciate the significance of this result we recall that scaling, sum rule (see I) and RG calculations (Brezin *et al* 1983a, b, Fisher and Huse 1985) conclude that to leading order, exactly at the upper critical dimension,

$$l \sim \xi_\perp^2 \qquad d = d_u = 3 \tag{7}$$

for critical wetting with short-ranged forces. The scaling hypothesis also yields (see e.g., Sullivan and Telo da Gama 1986) the well known exponent relation

$$2 - \alpha_s = 2\nu_\parallel - 2\beta_s. \tag{8}$$

This relation is analogous to the Rushbrooke (in)equality of bulk critical phenomena and can also be derived from thermodynamic arguments; see I. When combined with the hyperscaling relation

$$2 - \alpha_s = (d-1)\nu_\parallel \tag{9}$$

(8) implies that

$$\beta_s = (3-d)\nu_\parallel/2 \qquad d < 3. \tag{10}$$

Making use of the capillary-wave relation (2) it follows that, in the strong-fluctuation regime ($d < d_u$), $\beta_s = \nu_\perp$ and

$$l \sim \xi_\perp \qquad d < 3. \tag{11}$$

Thus for $d < 3$ the interfacial roughness diverges in the same way as the film thickness, whereas for $d = 3$ the roughness diverges much more slowly than the film thickness. The present article provides a means of understanding the crossover from one type of $l$ versus $\xi_\perp$ relationship to another as $d \to 3^-$. Since $\beta_s = \nu_\perp$ remains valid for all $d < 3$, $l/\xi_\perp = c_l/c_\perp$ for $d < 3$ and (6) reflects directly the divergence of the ratio of critical amplitudes in the limit $d \to 3^-$.

Our paper is arranged as follows: in section 2 we recall some relevant sum rules and thermodynamic relations from our earlier paper I. These allow us to introduce a transverse correlation length $\xi_\parallel^w$ for particles located near the wall. Assuming that hyperscaling is valid for all dimensions less than 3, we argue that the ratio of correlation lengths $\xi_\parallel^{\mathrm{w}}/\xi_\parallel$ should be O(1) and remain well behaved as $d \to 3^-$. In section 3, we combine a standard scaling hypothesis for $\Sigma^{(s)}$ with thermodynamic relations from section 2 and standard capillary-wave theory to deduce a formula for $c_l/c_\perp$ that depends on $\nu_\parallel(d)$ and the coefficient $Q$ of hyperscaling, as well as the ratio $\xi_\parallel^{\mathrm{w}}/\xi_\parallel$. Provided that the last two quantities are non-singular as $d \to 3^-$, we obtain (6) for any $\nu_\parallel(3^-) > \frac{1}{2}$, including a divergent $\nu_\parallel(3^-)$. If $\nu_\parallel(3^-) = \frac{1}{2}$, a result derived in I via Gaussian unfreezing of capillary-wave fluctuations on a mean-field interface, (6) is not valid and we find the less satisfactory result that $l/\xi_\perp$ remains constant as $d \to 3^-$. We also discuss the nature of the divergences of the individual amplitudes $c_l$ and $c_\perp$ and develop a criterion for the size of the critical regime for critical amplitudes. Our criterion implies that this size vanishes as $d \to 3^-$ if the exponent $\beta_s \to 0$. Section 4 contains concluding remarks.

## 2. Sum rules, thermodynamics and hyperscaling

We begin by recalling some of the main results of I. There exists a number of exact statistical mechanical sum rules which relate derivatives of thermodynamic functions (surface tension and adsorption) to transverse moments of the density–density correlation function

$$G(\boldsymbol{r}_1, \boldsymbol{r}_2) \equiv \rho(\boldsymbol{r}_1)\rho(\boldsymbol{r}_2)h(\boldsymbol{r}_1, \boldsymbol{r}_2) + \delta(\boldsymbol{r}_1 - \boldsymbol{r}_2)\rho(\boldsymbol{r}_1) \tag{12}$$

where $\rho(\boldsymbol{r}) \equiv \rho(z)$ is the equilibrium one-body density and $h(\boldsymbol{r}_1, \boldsymbol{r}_2)$ is the total pairwise distribution function. The appropriate moments of $G$ are defined via the transverse Fourier transform

$$G(z_1, z_2; Q) \equiv \int \mathrm{d}\boldsymbol{R} \exp(\mathrm{i}\boldsymbol{Q} \cdot \boldsymbol{R})\, G(z_1, z_2; R) \tag{13}$$

$$= G_0(z_1, z_2) + Q^2 G_2(z_1, z_2) + \dots \tag{14}$$

Here $\boldsymbol{R}$ and $\boldsymbol{Q}$ are transverse wavevectors, parallel to the interface. Two important quantities for wetting phenomena are the surface excess grand potential $\sigma$ per unit area (surface tension) and the adsorption, or coverage, $\Gamma$. The latter serves to define the thickness $l$ of the wetting film of liquid, say

$$\Gamma = \int_0^\infty \mathrm{d}z\, [\rho(z) - \rho_\mathrm{b}] \tag{15a}$$

$$\equiv (\rho_l - \rho_\mathrm{g})l \tag{15b}$$

where $\rho_\mathrm{b}$, $\rho_l$ and $\rho_\mathrm{g}$ are the bulk and coexisting liquid and gas number densities, respectively. We have assumed that $V_\mathrm{ext}$ is infinitely repulsive for $z < 0$ so that $\rho(z) = 0$ for $z < 0$. $\Gamma$ is related to $\sigma$ by the Gibbs adsorption equation

$$\Gamma = -(\partial\sigma/\partial\mu)_T. \tag{16}$$

Differentiating WRT $\mu$ yields the surface susceptibility sum rule

$$\left(\frac{\partial\Gamma}{\partial\mu}\right)_T = \frac{1}{k_\mathrm{B}T}\int_0^\infty \mathrm{d}z_1 \int_{-\infty}^\infty \mathrm{d}z_2\, [G_0(z_1, z_2) - G_0(|z_1 - z_2|)_\mathrm{b}\theta(z_2)] \tag{17}$$

where the subscript b refers to bulk properties. Henderson (1986) has derived some illuminating sum rules by differentiating $\Gamma$ and $\sigma$ WRT $\varepsilon$, the strength of the attractive part $V_\varepsilon(z)$ of $V_{ext}$. Assuming that $V_{ext}$ is defined so that $\partial V_{ext}(z)/\partial\varepsilon \equiv V_\varepsilon(z)/\varepsilon$ is independent of $\varepsilon$ it is possible to show (Henderson 1986) that

$$\left(\frac{\partial\Gamma}{\partial\varepsilon}\right)_{\mu,T} = -\frac{1}{k_B T}\int_0^\infty dz_1 \int_{-\infty}^\infty dz_2 \frac{V_\varepsilon(z_2)}{\varepsilon} G_0(z_1, z_2) \tag{18}$$

and

$$\left(\frac{\partial^2\sigma}{\partial\varepsilon^2}\right)_{\mu,T} = \frac{-1}{k_B T}\int_0^\infty dz_1 \frac{V_\varepsilon(z_1)}{\varepsilon}\int_{-\infty}^\infty dz_2 \frac{V_\varepsilon(z_2)}{\varepsilon} G_0(z_1, z_2). \tag{19}$$

These sum rules are formally exact. They are extremely useful since they relate singular behaviour in $G_0(z_1, z_2)$ to that of thermodynamic quantities. In I we argued that (18) and (19) could be used to determine the singular contributions to $G$ when one or both particles are located near the wall ($z = 0$):

$$G_0^{\text{sing}}(a, a) \sim -(k_B T/a^2)(\partial^2\Sigma^{(s)}/\partial\varepsilon^2)_{\mu,T} \tag{20a}$$

$$G_0^{\text{sing}}(a, z) \sim (k_B T/a)\,\rho'(z)(\partial l/\partial\varepsilon)_{\mu,T} \qquad z \sim l \tag{20b}$$

$$G_2^{\text{sing}}(a, a) \sim -(k_B T/a^2)\sigma_{\text{lg}}(\partial l/\partial\varepsilon)^2_{\mu,T}. \tag{20c}$$

Here $a$ is a microscopic length which is of the same order as the range of $V_\varepsilon(z)$ and the prime denotes differentiation WRT $z$. Note that $\Sigma^{(s)} \leqslant 0$ and $G_0^{\text{sing}}(a, a)$ is positive.

These results complement the well known result for $G(z_1, z_2; Q)$ that is valid at small $Q$ when both particles are near the liquid–gas edge of the wetting film:

$$G(z_1, z_2; Q) \sim G_0(z_1, z_2)(1 + \xi_\parallel^2 Q^2)^{-1} \qquad z_1, z_2 \sim l \tag{21a}$$

with

$$G_0(z_1, z_2) \sim k_B T\rho'(z_1)\rho'(z_2)\xi_\parallel^2/\sigma_{\text{lg}} \qquad z_1, z_2 \sim l. \tag{21b}$$

The transverse correlation length appearing in (21) is defined by

$$\xi_\parallel^2 \equiv -G_2(z_1, z_2)/G_0(z_1, z_2) \qquad z_1, z_2 \sim l. \tag{22a}$$

Using (21$b$) in (17) we obtain

$$\xi_\parallel^2 \sim \sigma_{\text{lg}}(\rho_l - \rho_g)^{-2}(\partial\Gamma/\partial\mu)_T. \tag{22b}$$

By analogy the sum rule results (20) can be used to determine a transverse correlation length when both particles are near the wall

$$\xi_\parallel^{w\,2} \equiv -G_2^{\text{sing}}(a, a)/G_0^{\text{sing}}(a, a) \tag{23a}$$

$$\sim -\sigma_{\text{lg}}(\partial l/\partial\varepsilon)^2_{\mu,T}/(\partial^2\Sigma^{(s)}/\partial\varepsilon^2)_{\mu,T}. \tag{23b}$$

It follows from the definitions of the exponents and the exponent relation (8) that $\xi_\parallel^w \sim \delta\varepsilon^{-\nu_\parallel}$. That is, the transverse correlation length diverges, for particles at the wall, with the same exponent as for particles in the liquid–gas interface. This startling manifestation of capillary-wave-like fluctuations is not associated with interfacial roughness. Explicit mean-field calculations (see I) have shown that $\xi_\parallel$, as defined by (22), is independent of $z_1$, $z_2$ for $z_1, z_2, \geqslant a$ and recall that in mean-field theory $\xi_\perp$ remains finite. The physically appealing interpretation of these results is that, for critical wetting, the transverse correlation length is essentially independent of particle position so that a simple O–Z contribution to $G(z_1, z_2; Q)$ is present throughout the inhomogeneous fluid. We might suppose, therefore, that the singular contribution to $G$ has the form

$$G^{\text{sing}}(z_1, z_2; Q) \sim G_0(z_1, z_2)(1 + \xi_\parallel^2 Q^2)^{-1} \qquad z_1, z_2 \gg a \tag{24}$$

at small $Q$. Such a form necessarily implies that $\xi_\parallel^{\text{w}} \equiv \xi_\parallel$. All we shall require is the weaker assumption that $\xi_\parallel^{\text{w}}/\xi_\parallel$ is O(1) and we justify this below.

In I we also introduced an important thermodynamic requirement for critical wetting. Treating $\varepsilon$ as a thermodynamic field, we derived a formal analogue of the bulk $c_P$–$c_V$ relation. Here we merely quote the result

$$(\partial\Theta/\partial\varepsilon)_{\mu,T} - (\partial\Theta/\partial\varepsilon)_{\Gamma,T} = (\partial\Gamma/\partial\varepsilon)^2_{\mu,T}(\partial\Gamma/\partial\mu)^{-1}_{\varepsilon,T} \tag{25}$$

where

$$\Theta = -(\partial\sigma/\partial\varepsilon)_{\mu,T}. \tag{26}$$

As mentioned in section 1, (25) provides a direct and rigorous route to the derivation of the exponent relation (8). We shall make use of (25) in the next section, introducing a scaling hypothesis for $\Sigma^{(s)}$, the singular part of $\sigma$.

Hyperscaling for the present problem can be expresed as

$$\Sigma^{(s)}/k_{\text{B}}T = -Q\xi_\parallel^{-(d-1)} \tag{27}$$

where $Q(>0)$ is a dimensionless coefficient. If, for a given $d$, $Q$ is a universal constant, critical wetting can be said to exhibit hyperuniversality. (Note that (27) implies (9).) The value of $Q$ can be ascertained for several models. An exact treatment of a continuum interfacial (solid on solid) Hamiltonian in $d = 2$ yields (Burkhardt 1989)

$$\Sigma^{(s)}/k_{\text{B}}T = -\xi_\parallel^{-1} \qquad d = 2 \tag{28}$$

so that $Q = 1$ in this case. Linear RG results imply that $Q$ depends on the value of $\omega$ when $d = 3$. Using the methods of Brezin *et al* (1983a, b) it is easy to show that

$$\Sigma^{(s)}/k_{\text{BT}} = \begin{cases} -(8\pi\omega)^{-1}\xi_\parallel^{-2} & \omega \leq \frac{1}{2} \quad d = 3 & (29a) \\ -(\pi\sqrt{32\omega})^{-1}\xi_\parallel^{-2} & \frac{1}{2} < \omega < 2 \quad d = 3 & (29b) \\ -(8\pi)^{-1}\xi_\parallel^{-2} & \omega > 2 \quad d = 3. & (29c) \end{cases}$$

It is significant that the small-$\omega$ result (29$a$) is identical with the mean-field result. That is, an explicit calculation, for the Sullivan (1979) model (see I) in three dimensions and for a'slab' model, in which a slab approximation is made for the density profile of the film, for any dimension, yields

$$\Sigma^{(s)}/k_{\text{B}}T = (-\sigma_{\text{lg}}\xi_{\text{b}}^2/2k_{\text{B}}T)\,\xi_\parallel^{-2} \qquad \text{mean field.} \tag{30}$$

In the strongest-fluctuation regime ($\omega > 2$) for $d = 3$, $Q$ is independent of $\omega$. Given that this is also the case for $d = 2$ it is tempting to speculate that hyperuniversality is a generic feature of the strong-fluctuation regime of critical wetting. Although we do not know how $Q$ varies with dimension $d$, we do not expect $Q(d)$ to exhibit any pathological behaviour as $d \to 3^-$.

We are now in a position to reconsider the ratio of correlation lengths $\xi_\parallel^{\text{w}}/\xi_\parallel$. Combining (30) and (23$b$) we find, using results in I, that, for the Sullivan model, $\xi_\parallel^{\text{w}} \approx \xi_\parallel$. On the other hand (see I) an explicit calcalation of the moments $G_0^{\text{sing}}(0, 0)$ and $G_2^{\text{sing}}(0, 0)$ and the definition (23$a$) gives $\xi_\parallel^{\text{w}} = a_1\xi_\parallel$, where $a_1$ is a dimensionless inverse correlation length which is O(1). This exercise gives us confidence that (23*b*) is a reliable approximation for $\xi_\parallel^{\mathrm{w}}$. If we follow the same procedure for a generalisation of the Sullivan model that allows the wall–fluid potential to be shorter ranged than the attractive fluid–fluid potential (both exhibit exponential decay), we find, once more, that $\xi_\parallel^{\mathrm{w}} \sim \xi_\parallel$. Beyond mean field, for $d = 3$, we combine (23*b*), (29) and (3) to obtain the linear RG predictions

$$\xi_\parallel^{\mathrm{w}}/\xi_\parallel \sim \begin{cases} (1+2\omega)/(1+\omega)^{1/2} & \omega \leqslant \frac{1}{2} \\ [2/(1-(\omega/8)^{1/2})]^{1/2} & \frac{1}{2} < \omega \leqslant 2 \\ 2 & 2 < \omega. \end{cases} \tag{31}$$

For $d = 2$, using the results of Burkhardt (1989) for $l(=\xi_\perp/2)$ and $\xi_\parallel$ in (23*b*) we find that $\xi_\parallel^{\mathrm{w}}/\xi_\parallel = \frac{1}{4}$. It appears that the ratio $\xi_\parallel^{\mathrm{w}}/\xi_\parallel$, like $Q$, is independent of $\omega$ in the strong-fluctuation regime. For the subsequent analysis it is sufficient to suppose that both $Q$ and $\xi_\parallel^{\mathrm{w}}/\xi_\parallel$ are well behaved, i.e. finite and non-zero, as $d \to 3^-$.

Before leaving this section we derive one further expression for $\xi_\parallel^{\mathrm{w}}/\xi_\parallel$ that will be used in section 3. From (22*b*), (25), (26) and (15*b*) it follows that near the edge of the wetting film

$$\xi_\parallel^2 = -\sigma_{\mathrm{lg}}(\partial l/\partial \varepsilon)^2\{(\partial^2\Sigma^{(\mathrm{s})}/\partial\varepsilon^2)_{\mu,T} - (\partial/\partial\varepsilon)[(\partial\Sigma^{(\mathrm{s})}/\partial\varepsilon)_{\mu,T}]_{\Gamma,T}\}^{-1} \tag{32}$$

whilst near the wall the transverse correlation length is given by (23*b*). The ratio of the two lengths is, therefore,

$$(\xi_\parallel^{\mathrm{w}}/\xi_\parallel)^2 = 1 - (\partial/\partial\varepsilon)[(\partial\Sigma^{(\mathrm{s})}/\partial\varepsilon)_{\mu,T}]_{\Gamma,T}/(\partial^2\Sigma^{(\mathrm{s})}/\partial\varepsilon^2)_{\mu,T} \tag{33}$$

where derivatives are evaluated at $\mu = \mu_{\mathrm{sat}}^-$.

## 3. Relationship between critical amplitudes

In this section we combine the formalism developed in section 2 with a standard scaling hypothesis for $\Sigma^{(\mathrm{s})}$ to deduce the behaviour of $\xi_\perp/l$ as $d \to 3^-$.

The scaling hypothesis for wetting transitions, proposed first by Nakanishi and Fisher (1982), is

$$\Sigma^{(\mathrm{s})}/k_{\mathrm{B}}T \sim -\delta\varepsilon^{2-\alpha_{\mathrm{s}}}\,W(\delta\mu\,\delta\varepsilon^{-\Delta})$$

where $\delta\mu \equiv |\mu_{\mathrm{sat}} - \mu|/k_{\mathrm{B}}T$ measures the deviation of the chemical potential from its value at bulk coexistence, $\Delta(=(d+1)\nu_\parallel/2)$ is a gap exponent and $W$ is the scaling function. While this simple scaling form is believed to be valid for $d < 3$, modifications are required for $d = 3$ (Parry and Evans 1989). For our present purposes it is necessary to include some metric factors, i.e. we write

$$\Sigma^{(\mathrm{s})}/k_{\mathrm{B}}T = -Qc_\parallel^{-(d-1)}\xi_{\mathrm{b}}^{-(d-1)}\,\delta\varepsilon^{(d-1)\nu_\parallel}\,W(A\,\delta\mu\,\delta\varepsilon^{-\Delta}) \tag{34}$$

where we have invoked hyperscaling (27) and the definition (1*b*) of the critical amplitude $c_\parallel$. $A$ is a dimensionless, presumably non-universal metric factor. The scaling function has been chosen so that $W(0) = 1$, i.e. (27) holds at $\delta\mu = 0$. The first derivative $W'(0)$ and second derivative $W''(0)$ should be finite constants.

We now employ (34) to evaluate the singular part of the LHS of (25). The first term is straightforward:

$$(1/k_BT)[\partial^2\Sigma^{(s)}/\partial(\delta\varepsilon)^2]_{T;\delta\mu=0}$$
$$= -Q(d-1)\nu_\parallel[(d-1)\nu_\parallel - 1]c_\parallel^{-(d-1)}\xi_b^{-(d-1)}\ \delta\varepsilon^{(d-1)\nu_\parallel - 2} \tag{35}$$

but the second term is somewhat more complicated since we need to take a derivative of $\Theta$ WRT $\varepsilon$ along a line of constant $\Gamma$ or $l$.

Using (34) in the Gibbs adsorption equation (16) we have

$$\Gamma \propto \delta\varepsilon^{(d-1)\nu_\parallel - \Delta} W'(A\ \delta\mu\ \delta\varepsilon^{-\Delta}). \tag{36}$$

Setting $\delta\mu = 0$ it follows that the exponent for the film thickness is given by $\beta_s = -(d-1)\nu_\parallel + \Delta$, which reduces to (10). Inverting (36) and differentiating we find that

$$[\partial(\delta\varepsilon)/\partial(\delta\mu)]_{\Gamma;\delta\mu=0} = (A/\beta_s)\ \delta\varepsilon^{1-\Delta}\ [W''(0)/W'(0)]. \tag{37}$$

This result can now be used to evaluate the singular part of $(\partial\Theta/\partial\varepsilon)_\Gamma$. After some tedious algebra it can be shown that this quantity has the same exponent but a different amplitude from $(\partial\Theta/\partial\varepsilon)_\mu$, and that the total singular contribution to the LHS of (25) is

$$k_BTQc_\parallel^{-(d-1)}\xi_b^{-(d-1)}\beta_s\nu_\parallel[(3-d)/2]\{[W'(0)]^2/W''(0)\}\ \delta\varepsilon^{(d-1)\nu_\parallel-2}.$$

The leading singular contribution to the RHS of the same equation is, using (22*b*),

$$\sigma_{lg}(\partial l/\partial\varepsilon)^2\xi_\parallel^{-2} = \sigma_{lg}\beta_s^2 c_l^2 c_\parallel^{-2}\ \delta\varepsilon^{-2(1+\beta_s)+2\nu_\parallel}.$$

Equating exponents in these last two expressions, we obtain $\beta_s = (3-d)\nu_\parallel/2$, i.e. we recover equation (10). The new result emerges from equating coefficients:

$$[W'(0)]^2/W''(0) = \sigma_{lg}\xi_b^{d-1}c_l^2 c_\parallel^{d-3}/k_BTQ. \tag{38}$$

This is an equation relating the critical amplitudes $c_l$ and $c_\parallel$; the same result can be derived using the scaling hypothesis to calculate $(\partial\Gamma/\partial\mu)_T$ and (22*b*) to relate the latter to $\xi_\parallel^2$.

As it stands, (38) is not particularly useful because the properties of the scaling function $W$ are not known. However, the ratio of derivatives of $W$ on the LHS can be eliminated in favour of a much more physically transparent quantity, i.e. the ratio $(\xi_\parallel^w/\xi_\parallel)^2$.

Using the scaling hypothesis in (33) we find that

$$(\xi_\parallel^w/\xi_\parallel)^2 = [W'(0)]^2(3-d)^2\nu_\parallel/W''(0)4(d-1)[(d-1)\nu_\parallel - 1]. \tag{39}$$

So (38) can be written as

$$(\xi_\parallel^w/\xi_\parallel)^2 = \{(3-d)^2\nu_\parallel/4(d-1)[(d-1)\nu_\parallel - 1]\}$$
$$\times (\sigma_{lg}\xi_b^{d-1}/Qk_BT)(c_\perp^2/c_\parallel^{3-d})(c_l^2/c_\perp^2). \tag{40}$$

This is the desired relationship between $c_l$ and $c_\parallel$. We can check its validity for the $d = 2$ continum solid on solid model mentioned earlier. In this case we have the explicit results (Burkhardt 1989):

$$Q = 1 \qquad c_l/c_\perp = \tfrac{1}{2} \qquad c_\parallel/c_\perp^2 = 2\sigma_{lg}\xi_b/k_BT \qquad \nu_\parallel = 2$$

and (40) gives $\xi_\parallel^w/\xi_\parallel = \frac{1}{4}$, the result obtained in section 2. Note that Burkhardt's result (see also Huse 1987) for $c_\parallel/c_\perp^2$ is identical with the standard ($d = 2$) capillary-wave result for the ratio $\xi_\parallel/\xi_\perp^2$.

In general, capillary-wave theory (Bedeaux and Weeks 1985) for the liquid–gas interface pinned by a gravitational field, say, predicts that

$$\xi_\perp^2 = \pi\xi_\parallel^{3-d}k_BT[(\tfrac{1}{2})^{-\lambda}/\Gamma(1-\lambda) - (\tfrac{1}{2})^{\lambda}y^{2\lambda}/\Gamma(1+\lambda)]/2(2\pi)^{(d-1)/2}\sigma_{lg}\sin(\lambda\pi) \tag{41}$$

where $\Gamma$ denotes the gamma function, $\lambda \equiv (3-d)/2$ and $y = \xi_b/\xi_\parallel$. Equation (41) is valid in the limit $y \to 0$; the bulk correlation length $\xi_b$ is always of microscopic extent. For fixed $\lambda$, i.e. fixed $d$, and $y \to 0$, (41) yields

$$\begin{aligned} c_\parallel^{3-d}/c_\perp^2 = {} & (2\sigma_{lg}\xi_b^{d-1}/\pi k_BT)(2\pi)^{(d-1)/2}(\tfrac{1}{2})^{(3-d)/2} \\ & \times \sin\{[(3-d)/2]\pi\}\,\Gamma((d-1)/2) \end{aligned} \tag{42}$$

which reduces to $2\sigma_{lg}\xi_b/k_BT$ for $d = 2$. In the limit $d \to 3^-$, (42) predicts that

$$c_\parallel^{3-d}/c_\perp^2 \to (2\pi/k_BT)\,\sigma_{lg}\xi_b^2(3-d). \tag{43}$$

This will be valid provided that we can ignore the second term in (41), i.e. iff $(\xi_\parallel/\xi_b)^{3-d} \gg 1$. If we now assume that (42) is appropriate for a critical wetting transition, for all $d < 3$, substituting (43) into (40) gives the following result for the ratio of critical amplitudes $c_l/c_\perp$:

$$(\xi_\parallel^w/\xi_\parallel)^2 = \nu_\parallel(3-d)c_l^2/16\pi Q(2\nu_\parallel - 1)c_\perp^2 \qquad d \to 3^- \tag{44}$$

provided that $(\xi_\parallel/\xi_b)^{3-d} \gg 1$. This result can be rewritten as

$$l/\xi_\perp = [32\pi Q(1 - 1/2\nu_\parallel)]^{1/2}(\xi_\parallel^w/\xi_\parallel)(3-d)^{-1/2} \qquad d \to 3^-. \tag{45}$$

Equation (45) is the main result of this paper and we consider its implications.

We argued at length in section 2 that the hyperscaling coefficient $Q$ and the ratio $\xi_\parallel^w/\xi_\parallel$ of transverse correlation lengths should be well behaved as $d \to 3^-$. It follows that

$$l/\xi_\perp \sim [(1 - 1/2\nu_\parallel)/(3-d)]^{1/2} \qquad d \to 3^-.$$

Whether or not this ratio diverges depends on the value of the exponent $\nu_\parallel$. This is not given by the present formalism. There are two candidates† for $\nu_\parallel(d)$. The first is the non-linear RG result (5) of Lipowsky and Fisher which implies that $\nu_\parallel \to \infty$ as $d \to 3^-$. With this choice $l/\xi_\perp \sim (3-d)^{-1/2}$ as $d \to 3^-$. The second candidate is the result of a procedure (see section 5 of I) that unfreezes Gaussian fluctuations on a mean-field density profile. This procedure, which can be viewed as a linearised treatment of fluctuations (see also appendix B of Lipowsky (1987)), gives the formula $\nu_\parallel = 2/(3d-5)$ for $d < 3$. The same formula was obtained (Kroll and Lipowsky 1982), but for $\frac{5}{3} < d \leqslant 2$, in an earlier approximate treatment of domain wall pinning. With this second choice, $l/\xi_\perp$ remains constant as $d \to 3^-$. As such a scenario is difficult to reconcile with the $d = 3$ relation $l \sim \xi_\perp^2$, we believe that this provides further evidence for the inadequacy of a linear theory in $d < 3$. Provided that $\nu_\parallel$ approaches *any* number greater than $\frac{1}{2}$, as $d \to 3^-$, $l/\xi_\perp$ diverges as $(3-d)^{-1/2}$.

We can go further and determine the form of the divergences of the individual critical amplitudes. From (43) we conclude that

$$c_\perp \sim (3-d)^{-1/2} \qquad d \to 3^- \tag{46a}$$

provided that $c_\parallel$ is less singular than $\exp[B(3-d)^q]$ with $q = -1$, i.e. if $c_\parallel$ diverges

† See note added in proof.

algebraically or exponentially with $q \geqslant -1$. Supposing that this condition is met it follows that

$$c_l \sim (3-d)^{-1} \qquad d \to 3^- \tag{46b}$$

and

$$c_l \propto c_\perp^2 \qquad d \to 3^- \tag{46c}$$

Interestingly, (46*c*) implies that the relative divergence of the critical amplitudes as $d \to 3^-$ is of the same form as that for the length scales ($l \sim \xi_\perp^2$) in $d = 3$. However, it is important to recall that our starting result (43) was qualified by the condition $(\xi_\|/\xi_b)^{3-d} \gg 1$. Under the same restrictions on $c_\|$ that lead to (46), this condition reduces to

$$\delta\varepsilon \ll \exp(-1/\beta_s) \tag{47}$$

where we have used the relation $\beta_s = (3-d)\nu_\|/2$. If (47) is not met, the second term in (41) becomes significant. Equation (47) can be regarded as a type of Ginzburg criterion for the critical amplitudes. If $\nu_\|$ diverges in the fashion suggested by the result (5) obtained by Lipowsky and Fisher, $\beta_s$ vanishes as $[-(3-d)\ln(3-d)]^{1/2}$ as $d \to 3^-$ and the size of the critical region becomes vanishing small in this limit.

It is tempting to speculate that a condition such as (47) should also be appropriate for the critical exponents. Outside the critical regime both terms in (41) are significant and we recover, for a fixed but large $\xi_\|$, the relation (quoted in (2)) $\xi_\perp^2 = \omega\xi_b^2 \ln(\xi_\|/\xi_b)^2$ in the limit $d \to 3^-$. Since this relation is the basis for the non-universality of critical wetting in $d = 3$, it is not unreasonable to suppose that for $d \leqslant 3$ and $\delta\varepsilon > \exp(-1/\beta_s)$ the growth of $l$, $\xi_\perp$ and $\xi_\|$ will be described by non-universal 'exponents' which extrapolate smoothly to the $d = 3$ results (3).

## 4. Concluding remarks

We have shown, on the basis of sum-rule arguments coupled with standard scaling and capillary-wave ideas, that the ratio of the wetting film thickness $l$ to the interfacial roughness $\xi_\perp$ diverges as $(3-d)^{-1/2}$ as $d$ approaches the upper critical dimension 3 from below. While $l$ and $\xi_\perp$ diverge with the same critical exponent ($\beta_s = \nu_\perp$) in this strong-fluctuation regime the ratio of their critical amplitudes diverges as $d \to 3^-$. Although the fact that such a divergence should occur could have been anticipated on the grounds that it provides a sensible mechanism for a smooth crossover to the behaviour expected in higher dimensions (recall that $l/\xi_\perp \to \infty$ as $\delta\varepsilon \to 0$ for $d \geqslant 3$), the present results establish the form of the divergences of the individual amplitudes $c_l$ and $c_\perp$, thereby enriching further the phenomenology of critical wetting transitions. The occurrence of critical exponents for critical amplitudes as $d \to 3^-$ is remarkable.

Since $l/\xi_\perp$ diverges as $d \to 3^-$, one can argue that the degree of interfacial wandering is reduced as the dimension $d$ increases. However, this does not necessarily imply that interfacial fluctuations become less important; the correlation length exponent $\nu_\|$ is predicted by RG to diverge as $d \to 3^-$! A fuller understanding of the nature of the fluctuations is required before we can ascertain whether the divergence of $c_l$ and $c_\perp$, or of their ratio, is a consequence of the divergence of $\nu_\|$, or vice versa. Our analysis does point to the existence of a non-universal pre-critical regime in which the various length scales behave similarly to those in $d = 3$. We find that the extent of the true critical region shrinks to zero as $d \rightarrow 3^-$, providing a means for smooth crossover to $d = 3$.

Finally we note that it is possible to derive a formula similar to (45) by making a single eigenfunction approximation (see I)

$$G_0^{\text{sing}}(z_1, z_2) \simeq \tilde{G}_0(z_1)\tilde{G}_0(z_2)$$

In the edge of the wetting film, $\tilde{G}_0(z) \sim \rho'(z)(k_B T\xi_\|^2/\sigma_{lg})^{1/2}$, (see (21($b$)). Using this approximation in the sum rules (18) and (19) it follows that

$$(\partial^2\Sigma^{(s)}/\partial\varepsilon^2)_{\mu,T} \approx -\sigma_{lg}\xi_\|^{-2}(\partial l/\partial\varepsilon)^2_{\mu,T} \tag{48}$$

a result derived earlier by Henderson (1987). If we use the hyperscaling form (27) for $\Sigma^{(s)}$, (48) provides an equation for $c_\|^{3-d}/c_l^2$ which is converted to one for $(c_l/c_\perp)^2$ by using the capillary-wave result (43). The final result is identical with (45) apart from the factor $\xi_\|^{w}/\xi_\|$. The single-eigenfunction approximation is equivalent to setting $\xi_\|^{w} = \xi_\|$, i.e. neglecting the second term in (33).

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**Note added in proof.** (i) Very recently David and Leibler (1990) have shown that an *analytical* treatment of the non-linear functional RG gives $\nu_\| \sim (3-d)^{-2/3}$ rather than the numerical result (5). This does not alter any of our conclusions. (ii) It is interesting to note that *complete wetting*, from off bulk coexistence, can be analysed in a similar fashion. For short-ranged forces and $d < 3$ the exponents are known explicitly (see I): $\nu_\| = 2/(d+1)$, $\beta_s = (3-d)/(d+1)$ and $\nu_\perp = \beta_s$, i.e. $\xi_\perp \sim l$. When $d = 3$ there is weak non-universality with the exponents remaining unrenormalised from their mean-field values ($\nu_\| = \frac{1}{2}$, $\beta_s = 0$) but with amplitudes and corrections to leading-order terms exhibiting dependence on $\omega$ (Fisher and Huse 1985). At the upper critical dimension $d_u = 3$, $l \sim \xi_\perp^2$, as for critical wetting. The sum rule analysis of the critical amplitudes is much simpler for complete wetting. From (22$b$) we find $c_\|^2 \propto \beta_s c_l$ and, hence $c_l \sim c_\|^2/(3-d)$ as $d \rightarrow 3^-$. (Now $l = c_l\xi_b\delta_\mu^{-\beta_s}$ etc.) Given that $\nu_\|$ approaches its $d = 3$ value smoothly from below it is natural to assume that $c_\|$ remains finite as $d \rightarrow 3^-$. Then $c_l$ diverges as $(3-d)^{-1}$ reflecting directly the vanishing of the film thickness exponent $\beta_s$ as $d \rightarrow 3^-$. With the same assumptions as in the text, the capillary-wave relation (43) yields $c_\perp \sim (3-d)^{-1/2}$ as $d \rightarrow 3^-$. In summary we find $l/\xi_\perp = c_l/c_\perp \sim (3-d)^{-1/2}$ for complete wetting in the limit $d \rightarrow 3^-$, provided $c_\|$ remains finite. Just as for critical wetting, the existence of diverging amplitudes leads to a possible crossover mechanism for the $l$ versus $\xi_\perp$ relationship.

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