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2002 J. Phys.: Condens. Matter 14 1169

(http://iopscience.iop.org/0953-8984/14/6/306)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **14** (2002) 1169–1198 PII: S0953-8984(02)29854-9

Wedge covariance for two-dimensional filling and wetting

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Received 18 October 2001, in final form 12 December 2001
Published 1 February 2002
Online at stacks.iop.org/JPhysCM/14/1169

Abstract

A comprehensive theory of interfacial fluctuation effects occurring at two-dimensional wedge (corner) filling transitions in pure (thermal disorder) and impure (random bond disorder) systems is presented. Scaling theory and the explicit results of transfer matrix and replica trick studies of interfacial Hamiltonian models reveal that, for almost all examples of intermolecular forces, the critical behaviour at filling is fluctuation dominated, characterized by universal critical exponents and scaling functions that depend only on the wandering exponent ζ. Within this filling-fluctuation (FFL) regime, the critical behaviour of the midpoint interfacial height, probability distribution function, local compressibility and wedge free energy are identical to corresponding quantities predicted for the strong-fluctuation (SFL) regime for critical wetting transitions at planar walls. In particular the wedge free energy is related to the SFL regime point tension, which is calculated for systems with random bond disorder using the replica trick. The connection with the SFL regime for all these quantities can be expressed precisely in terms of special wedge covariance relations, which complement standard scaling theory and restrict the allowed values of the critical exponents for both FFL filling and SFL critical wetting. The predictions for the values of the exponents in the SFL regime recover earlier results based on random walk arguments. The covariance of the wedge free energy leads to a new, general relation for the SFL regime point tension, which derives the conjectured Indekeu–Robledo critical exponent relation and also explains the origin of the logarithmic singularity for pure systems known from exact Ising studies due to Abraham and co-workers. Wedge covariance is also used to predict the numerical values of critical exponents and position dependence of universal one-point functions for pure systems.

0953-8984/02/061169+30$30.00

1. Introduction

Fluids adsorbed near wedges, cones and corners show filling phenomena [1–11] similar to the wetting of planar wall–fluid and fluid–fluid interfaces [12, 13][1]. Above a filling temperature T_{fill} a wedge (say) in contact with vapour at bulk coexistence is completely filled by liquid, analogous to the complete wetting of a planar wall–fluid interface above the wetting temperature T_{wet}. There are, however a number of notable distinctions between wetting and the different possible types of filling transition. Firstly, thermodynamic arguments [1–3] dictate that filling precedes wetting, occurring when the contact angle satisfies $\theta = \alpha$, where α is the wedge tilt angle (see figure 1). Thus filling may occur in the absence of any wetting transition, i.e. if the walls are partially wet up to the bulk critical temperature. Secondly the conditions for observing continuous (critical) filling [7, 9] in the laboratory are much less restrictive than for continuous (critical) wetting [12]. For example three-dimensional cone or corner filling should be continuous provided the line tension is negative. Finally, the critical singularities and fluctuation effects occurring at critical filling reflect the divergence of different length-scales compared with wetting. For example, in a three-dimensional wedge, long-wavelength fluctuations in the interfacial height along the wedge dominate and lead to an interfacial roughness that is much larger than for wetting at a planar wall and which exhibits universal properties [7, 9, 10].

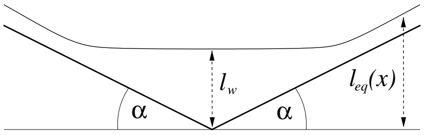

Figure 1. Schematic portrait of the equilibrium interfacial height $l_{\mathrm{eq}}(x)$ for a fluid adsorbed in a wedge close to a filling transition. l_{w} denotes the midpoint interfacial height.

For two-dimensional wedges (and three-dimensional cones) on the other hand something quite different and unexpected occurs. Recent studies based on effective interfacial Hamiltonians [5, 6, 9] and more microscopic Ising models [11] indicate that there is a fundamental connection with the strong-fluctuation (SFL) regime of critical wetting [13–17]. More specifically, even in the presence of long-ranged forces, the divergence of the interfacial height at critical filling together with the precise scaling form of the midpoint interfacial height probability distribution function (PDF) are identical to predictions for the critical wetting SFL regime. In other words the substrate geometry effectively turns off the influence of long-ranged solid–fluid and fluid–fluid forces so the fluid mimics fluctuation behaviour predicted for planar systems with short-ranged forces. In two dimensions this has been demonstrated for both pure and impure systems (with random bond disorder) and can be precisely expressed in terms of special wedge covariance laws which relate the interfacial heights and PDFs in the different geometries at bulk two-phase coexistence [6, 9]. Whilst the demonstration of these laws, particularly for impure systems, is rather technical, the final expressions are extremely simple and contain a great deal of information. Consider a fluctuation-dominated filling transition occurring in a two-dimensional wedge and let $l_{\mathrm{w}}(\theta, \alpha)$ and $P_{\mathrm{w}}(l; \theta, \alpha)$ denote the equilibrium midpoint interfacial height and corresponding PDF respectively. Now let $l_\pi(\theta)$ and $P_\pi(l; \theta)$ denote the interfacial height and PDF for an SFL regime wetting transition, occurring at a *planar* wall–fluid interface, written in terms of the contact angle. Covariance for the interfacial heights implies that at bulk coexistence and as $\theta \to \alpha$,

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[1] The fluctuation theory of wetting, including disordered systems, is discussed at length in [13].

$$l_{\mathrm{w}}(\theta, \alpha) = l_{\pi}(\theta - \alpha). \tag{1}$$

The statement of covariance for the PDFs is even stronger:

$$P_{\mathrm{w}}(l; \theta, \alpha) = P_{\pi}(l; \theta - \alpha) \tag{2}$$

implying that not only the interfacial height but also the roughness (and all moments of the distribution) at filling and wetting are similarly related.

In this paper we further investigate the connection between filling and wetting and demonstrate covariance relations for other quantities of interest. Again, because the derivation of these results is rather technical we quote their final form here. For the excess free energy of the wedge $f_{\mathrm{w}}(\theta, \alpha)$ at coexistence we find that for both pure and impure systems

$$f_{\mathrm{w}}(\theta, \alpha) = \tau(\theta) - \tau(\theta - \alpha) \tag{3}$$

where $\tau(\theta)$ denotes the point tension near an SFL regime critical wetting transition. We also consider the local compressibility for filling $\chi_{\mathrm{w}}(z; \theta, \alpha)$ corresponding to the derivative of the midpoint density profile w.r.t. chemical potential μ evaluated at two-phase coexistence. This is related to the corresponding expression $\chi_{\pi}(z; \theta)$ for SFL regime wetting by

$$\chi_{\mathrm{w}}(z; \theta, \alpha) = \left(\frac{\theta}{\alpha} - 1\right) \chi_{\pi}(z; \theta - \alpha) \tag{4}$$

where z is the direction normal to the wall.

These covariance relations complement the standard scaling hypothesis for the singular contribution to the corner free energy and may be understood heuristically by considering the special influence that the wedge (and also cone) geometry has on interfacial configurations. The relations are rather restrictive and from them we may deduce the allowed values of the critical exponents for both two-dimensional filling *and* critical wetting transitions without explicit model calculations. This is somewhat analogous to the restrictions imposed by the principle of conformal invariance for bulk and surface critical phenomena [18]. We shall also use the covariance relations to derive new results for the point tension and position dependence of the local compressibility. Indeed for the point tension we shall be able to derive a conjectured critical exponent relation due to Indekeu and Robledo [19, 20] and also explain why, for pure systems, the point tension shows a logarithmic singularity as $\theta \to 0$ [21].

Our paper is arranged as follows: in section 2 we present the necessary background theory for critical wetting describing, in turn, the derivation of critical exponent relations and fluctuation regimes from heuristic scaling theory and the scaling of the density profile, PDF and their short-distance expansions (SDEs). In section 3 we discuss the singularities of the point tension first recalling the scaling conjecture of Indekeu and Robledo [19] and exact Ising model results for pure systems due to Abraham *et al* [21]. We then present a lengthy calculation of the point tension τ for critical wetting in pure and impure systems using continuum interfacial models. As far as we are aware τ has not been calculated before for systems with random bond disorder and the derived expression shows singular behaviour as $\theta \to 0$ in full agreement with the Indekeu–Robledo conjecture. In section 4 we begin our discussion of two-dimensional filling transitions and first discuss critical exponent relations, heuristic fluctuation theory and the scaling of the density profile and PDF, which parallels our earlier discussion of critical wetting. In section 5 we recall the main results of explicit effective Hamiltonian studies of filling which will be further developed here. These calculations support the scaling theory developed in section 4 and also demonstrate the covariance laws (1)–(3) quoted above. The consequences of these relations and the restrictions they place on the allowed values of the critical exponents at two-dimensional filling and wetting (in systems with short-ranged forces) are discussed at length. A new and very simple result for the point tension is also discussed, from which we can derive the Indekeu–Robledo exponent relation. In section 6 we turn our attention to scaling behaviour occurring off bulk coexistence and focus on the position dependence of the local compressibility leading to the final covariance relation (4). Finally we revisit the nature of filling and wetting in pure systems and use the covariance relations to re-derive the specific results of the transfer matrix studies. We finish our article with a brief summary of our main results and discussion of future work.

2. Two-dimensional critical wetting and SFL regime

We begin with a brief survey of the central results from the theory of critical wetting paying special attention to critical exponents, fluctuation regimes and the scaling of the density profile and PDF. Further details and original references can be found in the excellent review articles [12, 13].

2.1. Critical exponents and exponent relations

Consider the interface between a planar substrate (wall), located in the $z = 0$ plane, and a bulk fluid phase at temperature T and chemical potential μ (and corresponding pressure p). The two-phase coexistence line is denoted $\mu = \mu_{\rm sat}(T)$ with corresponding bulk liquid and vapour phase densities $\rho_{\rm l}$ and $\rho_{\rm v}$ respectively. Throughout this article we set $k_{\rm B}T \equiv 1$ for convenience. We suppose the wall–vapour interface preferentially adsorbs the liquid phase and is completely wet above a wetting transition temperature $T_{\rm wet}$. Thus the wetting phase boundary is defined by the vanishing of the contact angle

$$\theta(T) = 0 \qquad T \geqslant T_{\rm wet}. \tag{5}$$

The wetting transition corresponds to a singularity in the excess free energy (surface tension) of the planar wall–vapour interface $\sigma_{\rm wv}$. This is defined [22] by subtracting the bulk contribution from the total grand potential Ω

$$\sigma_{\rm wv} = \frac{\Omega + pV}{A} \tag{6}$$

in the limit of infinite volume V and planar area A. On approaching a critical wetting transition the adsorption $\Gamma \approx (\rho_{\rm l} - \rho_{\rm v})l_\pi$, with l_π the equilibrium height of the liquid–vapour interface above the wall, diverges continuously. The critical wetting transition has two relevant scaling fields which we can identify (for fixed strength of the wall–fluid intermolecular potential) as $t' = (T_{\rm wet} - T)/T_{\rm wet}$ and $h = (\rho_{\rm l} - \rho_{\rm v})(\mu_{\rm sat} - \mu)$. From scaling theory we anticipate that off two-phase coexistence $\sigma_{\rm wv}$ contains a singular term, $f_{\rm sing}$, which vanishes at the critical wetting phase boundary and can be written

$$f_{\rm sing} = t'^{2-\alpha_{\rm s}} W_\pi(ht'^{-\Delta}) \tag{7}$$

where $\alpha_{\rm s}$, Δ are the surface specific heat and gap exponents respectively, $W_\pi(x)$ is the scaling function and we have restricted our attention to $t' \geqslant 0$. Now at coexistence we have, by definition, $f_{\rm sing} \equiv \sigma_{\rm wv} - (\sigma_{\rm wl} + \sigma_{\rm lv})$ so that from Young's equation [22] it follows that the contact angle vanishes as

$$\theta \sim t'^{(2-\alpha_{\rm s})/2} \tag{8}$$

and can be used as an alternative measure of the temperature-like scaling field. In addition to the mean interface height l_π we also need to consider the divergence of the r.m.s. interfacial width or roughness $\xi_\perp$ and the transverse correlation length $\xi_\parallel$ measuring the correlations in fluctuations of the interfacial height along the wall. At $h = 0$, the divergence of these length-scales is characterized by critical exponents defined by

$$l_\pi \sim t'^{-\beta_s} \qquad \xi_\perp \sim t'^{-\nu_\perp} \qquad \xi_\parallel \sim t'^{-\nu_\parallel} \tag{9}$$

and we expect scaling behaviour similar to (7) off coexistence. Thus, along the wetting critical isotherm ($T = T_{\rm wet}$, $h \to 0$) we define

$$l_\pi \sim h^{-\psi} \tag{10}$$

and anticipate that the critical exponent $\psi = \beta_s/\Delta$. Critical exponent relations immediately follow from the scaling hypothesis. Firstly from the Gibbs adsorption equation [12, 22]

$$\partial f_{\rm sing}/\partial h = l_\pi \tag{11}$$

we have

$$\Delta = 2 - \alpha_s + \beta_s \tag{12}$$

which identifies the gap exponent. Secondly, from the compressibility sum-rule (see for example [12])

$$\partial^2 f_{\rm sing}/\partial h^2 \propto \xi_\parallel^2 \tag{13}$$

we have $2 - \alpha_s - 2\Delta = -2\nu_\parallel$ so that on eliminating the gap exponent we arrive at the important relation

$$2 - \alpha_s = 2\nu_\parallel - 2\beta_s \tag{14}$$

which is valid for all dimensions, ranges of forces and fluctuation regimes of interest. The perpendicular and transverse correlation lengths are related through the wandering exponent defined by [15]

$$\xi_\perp \sim \xi_\parallel^\zeta \tag{15}$$

with the value of $\zeta \geqslant 0$ dependent on the dimensionality and qualitative type of disorder. For discussions of wetting and filling in two-dimensional systems the most relevant values are $\zeta = 1/2$ and $2/3$ for pure (thermal disorder) and impure systems (random bond disorder) respectively. Recall that random fields destroy phase coexistence in two dimensions so cannot be considered. Also whilst values of the wandering exponent $\zeta < 1/2$ have been predicted for some models of interfacial roughening transitions in quasi-crystalline materials this is not of particular importance to the general fluctuation theory of wetting (and filling) and will not be considered here. The predictions we make for the values of critical exponents at filling will assume that, in two dimensions, $1 > \zeta \geqslant 1/2$.

2.2. *Fluctuation regimes for wetting*

Quite generally, provided $\zeta > 0$, the critical singularities at wetting are believed to fall into *three* distinct classes depending on the interplay between interfacial wandering and the 'direct' influence of intermolecular forces [13–17]. The latter can be modelled by the binding potential

$$W(l) = -\frac{a}{l^p} + \frac{b}{l^q} + \cdots \qquad l > 0 \tag{16}$$

with a, b effective Hamaker constants and indices $q > p > 0$ depending on the range of the intermolecular forces. The binding potential describes the bare or mean-field (MF) wetting transition and in order for this to be continuous we require that $a = 0$, $b > 0$ at the (MF) phase boundary. Thus $a \propto (T_{\rm wet}^{\rm MF} - T)$ where $T_{\rm wet}^{\rm MF}$ is the MF wetting temperature. The existence of three regimes can be understood semi-quantitatively [16] by comparing the bare binding potential with an effective fluctuation contribution

$$W_{\mathrm{fl}}(l) \approx \frac{\Sigma\xi_\perp^2}{2\xi_\parallel^2} \tag{17}$$

the form of which is suggested by interfacial Hamiltonian models. Beyond MF level we anticipate large-scale fluctuation effects with $l_\pi \sim \xi_\perp$ and thus using (15) one can estimate

$$\frac{\xi_\perp}{\xi_\parallel} \approx l^{1-1/\zeta} \tag{18}$$

implying that $W_{\mathrm{fl}}(l) \approx l^{2(1-1/\zeta)}$. The competition between $W_{\mathrm{fl}}(l)$ and the bare potential leads to the following three fluctuation regimes.

- *Mean field (MF) regime*. If $q < 2(1/\zeta - 1)$ fluctuation effects are negligible, $l_\pi \gg \xi_\perp$ and the mean interface position remains close to the minimum of the binding potential. The phase boundary remains $a = 0$ with $\beta_{\mathrm{s}} = 1/(q-p)$.
- *Weak-fluctuation (WFL) regime*. If $q > 2(1/\zeta - 1)$ but $p < 2(1/\zeta - 1)$ the repulsion from the wall has an entropic origin but the attraction is still due to long-ranged forces. In this regime the phase boundary remains $a = 0$ with

  $$\beta_{\mathrm{s}} = \frac{1}{2(1/\zeta - 1) - p} \tag{19}$$

  with large-scale interfacial fluctuations $l_\pi \sim \xi_\perp$.
- *Strong-fluctuation (SFL) regime*. If $p > 2(1/\zeta - 1)$, fluctuations dominate leading to a renormalization of the phase boundary and universal critical behaviour. Because the wetting phase boundary no longer occurs at $a = 0$ one cannot use the above heuristic argument to determine the values of the critical exponents. However a remarkable feature of two-dimensional wetting is that the values of the SFL regime critical exponents can be explicitly related to the wandering exponent ζ using very general random walk arguments [15]. For wetting in systems with $\zeta \geqslant 1/2$ the full set of values for the critical exponents is

  $$\alpha_{\mathrm{s}} = 0 \qquad \beta_{\mathrm{s}} = \frac{\zeta}{1-\zeta} \qquad \nu_\parallel = \frac{1}{1-\zeta} \tag{20}$$

  and

  $$\Delta = \frac{2-\zeta}{1-\zeta} \qquad \psi = \frac{\zeta}{2-\zeta} \tag{21}$$

  which are in precise agreement with the explicit results of Ising model [23] and effective interfacial Hamiltonian studies [24–27]. The values of these critical exponents will play a central role in our discussion of two-dimensional filling.

Finally we point out that in both the WFL and SFL regimes, where $l_\pi \sim \xi_\perp$, the divergence of the interfacial height at $h = 0$ written in terms of the contact angle,

$$l_\pi(\theta) \sim \theta^{-\hat{\beta}_{\mathrm{s}}} \tag{22}$$

is characterized by a universal critical exponent

$$\hat{\beta}_{\mathrm{s}} \equiv \frac{2\beta_{\mathrm{s}}}{2-\alpha_{\mathrm{s}}} = \frac{\zeta}{1-\zeta} \tag{23}$$

which follows directly from the critical exponent relation (14) *without* using the explicit values of the critical exponents (19), (20). We shall return to this later when we use the covariance relations to determine the values of the critical exponents at two-dimensional filling.

2.3. Scaling of the PDF and the short-distance expansion

The position dependence of the equilibrium density profile, $\rho(z)$, local response functions such as the compressibility/susceptibility $\chi(z) \propto \partial\rho(z)/\partial\mu$ and also higher-point functions all show scaling behaviour in the WFL and SFL scaling regimes. The scaling emerges in the appropriate limits $z \to \infty, t' \to 0, h \to 0$ with $zt'^{\beta_s}, ht'^{-\Delta}$ arbitrary and for the profile we anticipate [28–30]

$$\rho(z) = \rho_l - (\rho_l - \rho_v)\Xi_\pi(zt'^{\beta_s}, ht'^{-\Delta}) \tag{24}$$

where $\Xi_\pi(x, y)$ is the scaling function satisfying $\Xi_\pi(0, y) = 0$, $\Xi_\pi(\infty, y) = 1$ and which is distinct in the SFL and WFL regimes. Clearly the scaling of $\rho(z)$ does not include oscillatory structure close to the wall or effects associated with bulk and surface criticality but rather reflects the large-scale fluctuations of the unbinding liquid–vapour interface. For large z but $zt'^{\beta_s} \to 0$ the profile has a characteristic algebraic SDE [28–30]

$$\rho(z) - \rho_l \approx (\rho_v - \rho_l)(zt'^{\beta_s})^\gamma \tag{25}$$

where, for simplicity we have set $h = 0$. The SDE critical exponent γ (referred to as θ in earlier work) also describes the behaviour of the local compressibility and pair-correlation functions close to the wall. The critical exponent γ is not independent, and can be related to others using standard surface Maxwell relations and sum-rules. Importantly it takes different universal values in the SFL and WFL regimes and can be identified as [29, 30]

$$\gamma^{\mathrm{SFL}} = 2(1/\zeta - 1) - 1/\beta_s \tag{26}$$

and

$$\gamma^{\mathrm{WFL}} = 2/\zeta - 1 \tag{27}$$

which are valid for arbitrary dimensions. The scaling of the profile is directly related to the scaling of the interfacial height PDF, $P_\pi(l)$, since interfacial fluctuations dominate the distribution of matter and we may write

$$\rho(z) = \rho_l - (\rho_l - \rho_v)\int_0^z P_\pi(l)\,\mathrm{d}l \tag{28}$$

where we have assumed the interface separates regions of bulk vapour and liquid density and we have omitted the field dependence of the PDF. Throughout this paper we shall omit the field dependence whenever the equation containing it is exact within effective Hamiltonian theory and not just restricted to the asymptotic critical regime. Since the contact angle θ is an equivalent (possibly nonlinear) measure of the temperature-like scaling field t' it is possible to write the scaling dependence as $P_\pi(l; \theta, h)$ rather than $P_\pi(l; t', h)$. Moreover for the next few sections we concentrate on behaviour occurring at $h = 0$ and define $P_\pi(l; \theta) \equiv P_\pi(l; \theta, 0)$. Scaling then implies that in the WFL and SFL regimes

$$P_\pi(l; \theta) = \tilde{a}\theta^{\hat{\beta}_s}\Lambda_\pi(\tilde{a}l\theta^{\hat{\beta}_s}) \tag{29}$$

where $\Lambda_\pi(x)$ is the scaling function and $\tilde{a}$ is a suitable metric factor having dimensions of inverse length. This may be chosen so that the argument of the scaling function is equivalent to the length-scale ratio $l/l_\pi(\theta)$. Notice that the power-law dependence of the contact angle follows from (23) and is the same in the WFL and SFL regimes. The different fluctuation effects occurring in these regimes are distinguished by the appropriate scaling functions $\Lambda_\pi^{\mathrm{SFL}}(x)$ and $\Lambda_\pi^{\mathrm{WFL}}(x)$. The two functions are similar at large distances where, out of the range of the binding potential, they decay exponentially quickly but have quite distinct SDEs $\Lambda_\pi(x) \sim x^{\gamma-1}$ describing the limit $l/l_\pi \to 0$. Using the appropriate values for the critical exponents in two dimensions it can be seen that, for both pure and impure systems, the interface makes many more excursions to the wall in the SFL regime than in the WFL regime. Hereafter we shall only need to deal with the properties of the SFL regime.

The explicit results of effective interfacial Hamiltonian studies are completely consistent with the scaling predictions and SDE. For pure systems with just thermal disorder the PDF in the SFL regime is particularly simple [6, 27]

$$P_\pi(l;\theta) = 2\Sigma\theta \mathrm{e}^{-2\Sigma\theta l} \tag{30}$$

where Σ denotes the stiffness coefficient of the unbinding interface and may be identified with σ_{lv} for continuum, fluid-like systems for which the interface is isotropic. For random bond disorder the expression for $P_\pi(l;\theta)$ is considerably more complicated but can still be calculated analytically using replica trick methods [13]

$$P_\pi(l;\theta) = \frac{\Sigma\theta}{\pi\sqrt{2l\kappa}}\mathrm{e}^{-l\theta^2\Sigma^2/2\kappa}\int_0^\infty \mathrm{d}s\, \frac{\sqrt{s}\mathrm{e}^{-s/4}}{s + 2l\theta^2\Sigma^2/\kappa} \tag{31}$$

where κ is the inverse length-scale associated with the disorder (see later). Note that in both these expressions the respective combinations $l\theta$ and $l\theta^2$, together with the SDEs, are in agreement with the above scaling theory.

3. The point tension for two-dimensional wetting in pure and impure systems

3.1. The Indekeu–Robledo conjecture

The one ingredient missing in our review of fluctuation effects at two-dimensional wetting is the nature of the point tension τ measuring the excess free energy associated with the point of three-phase contact between wall–vapour and wall–liquid interfaces [19–21, 31, 32]. The reason for this, as first pointed out by Abraham, Latrémolière and Upton (ALU) [21], is that beyond MF level, fluctuation effects make the definition of τ a rather subtle issue. The purpose of this long section is to identify a method of defining τ within continuum effective interfacial Hamiltonian theory that we can apply to the case of wetting with random bond disorder. To begin recall that within MF theory, it is straightforward to define the point/line tension τ by simply subtracting the necessary bulk and interfacial contributions from the grand-potential of the heterogeneous wall–fluid interface [19, 20, 31]. Such studies reveal that as $T \to T_{\mathrm{wet}}$ at $h = 0$, τ contains a singular contribution which we write

$$\tau_{\mathrm{sing}} \sim t'^{2-\alpha_{\mathrm{l}}} \tag{32}$$

with a point/line tension specific heat exponent α_{l} which depends sensitively on the range of the forces. A crucial insight into the singularities of the point/line tension was made by Indekeu and Robledo [19], who pointed out that within MF theory the singularities of τ were consistent with the scaling equation

$$\alpha_{\mathrm{l}} = \alpha_{\mathrm{s}} + \nu_\| \tag{33}$$

and conjectured that this is generally valid even in the presence of fluctuation effects. The Indekeu–Robledo conjecture is important because it relates the excess free energy of a heterogeneous wall–fluid interface to the properties of a homogeneous wall–vapour interface. As we shall show there are very good reasons for regarding this as the precursor of a covariance relationship between filling and critical wetting. Indeed, we shall be able to derive a precise relation for the point tension, valid for pure and impure systems, which is in perfect agreement with (33). Assuming the validity of the scaling relation for the point tension in two dimensions we can identify, in the SFL regime

$$2 - \alpha_l = \frac{1 - 2\zeta}{1 - \zeta} \tag{34}$$

which completes our list of critical wetting exponents.

Following our earlier discussion of the interfacial height and PDF it is convenient for later purposes to measure the singular contribution to the point tension as a function of the contact angle rather than t'. We shall only consider the point tension for systems with short-ranged forces (belonging to the SFL regime) and thus expect

$$\tau_{\text{sing}}(\theta) \sim \theta^{2-\alpha_l} \tag{35}$$

with $2 - \alpha_l$ given by (34) In fact, as we shall show, for interfacial models with strictly short-ranged (contact) forces there is no ambiguity defining the point tension itself $\tau(\theta)$ to be a function of θ, although, of course, such models are only well defined when θ is small. Thus, for pure systems with $\zeta = 1/2$, the Indekeu–Robledo scaling relation predicts $2 - \alpha_l = 0$, which may either mean that τ remains finite at T_w or diverges (or vanishes) more slowly than any power law. For random bonds however, the Indekeu–Robledo prediction is unambiguous: $\alpha_l = 3$ so that $\tau_{\text{sing}} \sim \theta^{-1}$. These predictions are discussed in detail below.

3.2. The ALU point tension for pure systems

ALU point out that, at least for two-dimensional systems, considerable care has to be taken in defining the point tension due to the influence of large-scale interfacial wandering, which smoothes out the point of contact. In MF theories, which ignore fluctuation effects, there is no pathology involved in constructing boundary conditions which induce a line of contact between a wall–vapour interface and the edge of an infinite drop. However, this latter concept becomes ill defined as soon as fluctuation effects are introduced since the surface of an infinite drop of liquid has unbounded fluctuations in the interfacial height. To overcome this problem ALU propose a fluctuation-theory-based definition of τ, involving a convolution of partition functions. This requires as input some appropriate choice for the partition function representing a finite-size liquid drop. In this way the thermodynamic limit can be taken yielding a well defined point tension, although the expression obtained depends crucially on the choice of restricted partition function used to model the edge of the liquid drop. The most satisfactory definition shows the singular behaviour

$$\tau_{\text{sing}}(\theta) \sim -\ln\theta \tag{36}$$

close to the wetting transition, which is indeed consistent with the Indekeu–Robledo exponent relation. The other fluctuation definitions considered by ALU yield point tensions that are either non-singular or have a different numerical pre-factor of the logarithm (other than unity). However as pointed out by ALU the above divergence is appealing since it coincides precisely with the singularity predicted by a heuristic energy–entropy balance argument. In an infinite Ising strip of width L lattice spacings and with opposing surface fields (which we refer to as a $+-$ strip), it is well understood that pseudo-phase coexistence only occurs below the wetting temperature and for sufficiently large strip widths [33–36]. This behaviour is characterized by an exponentially large correlation length (see their figure 3) reflecting the asymptotic degeneracy of the lowest two transfer matrix eigenvalues. Physically this means that the interface sticks to each wall over exponentially large distances, which can be estimated by

$$\frac{\xi_\parallel}{\xi_0} \sim \mathrm{e}^{\Sigma\theta L + 2\tau} \tag{37}$$

valid for large L, small θ and $\theta L \to \infty$. Here ξ_0 is an appropriate (non-singular) length-scale for measuring distances along the strip, which we anticipate is of the order of the bulk correlation length. This has to be introduced for dimensional reasons and plays no role in determining the divergence of τ near wetting. The argument of the exponential reflects the free-energy cost of an interface jump from one wall to the other with contributions arising from surface free-energies, leading to the $\Sigma\theta L$ term and two point tensions. Exact evaluation of the correlation length in the $+-$ Ising model and also in solid-on-solid approximation (valid at low temperatures away from the bulk critical point) yields a point tension in precise agreement with result (36) from the ALU convolution definition. Finally we note that, within the full transfer matrix theory discussed here, finite size effects in the point tension for systems (both pure and impure) with short-ranged forces are exponentially small in the strip width or length. Thus the thermodynamic limit of the point tension is well defined.

3.3. *Continuum interfacial models of the point tension in pure systems*

The purpose of this subsection is to show that one may also obtain the logarithmic singularity of the point tension for pure systems from the asymptotic scaling of the PDF as evaluated using a continuum effective interfacial Hamiltonian. The advantage of this approach is that it can be readily generalized to systems with random bond disorder, which we shall consider next. To begin, we introduce the interfacial model and explicitly evaluate the point tension using the ALU finite-size $+-$ strip identification discussed above.

The general fluctuation theory of wetting two dimensions in pure systems, without quenched impurities, is based on the interfacial model (see [13] and references therein)

$$H[l] = \int \mathrm{d}x \left\{ \frac{\Sigma}{2} \left(\frac{\mathrm{d}l}{\mathrm{d}x} \right)^2 + hl + W(l) \right\} \tag{38}$$

where $l(x)$ is the local height of the unbinding (liquid–vapour) at position x along the wall and $W(l)$, Σ are the binding potential and stiffness coefficient introduced earlier. We emphasize again that we shall focus on isotropic bulk fluid systems and identify Σ with the surface tension σ_{lv}. The partition function $Z_\pi(l_1, l_2; X)$ of an interface of length X with fixed end positions $l(0) = l, l(X) = l'$ is expressed in spectral form using continuum transfer matrix methods [27],

$$Z_\pi(l, l'; X) = \sum_n \psi_n^*(l')\psi_n(l)\mathrm{e}^{-E_n X} \tag{39}$$

where the eigenvalues and eigenfunctions, labelled $n = 0, 1, 2, \ldots$ satisfy the Schrödinger equation

$$-\frac{1}{2\Sigma}\frac{\mathrm{d}^2\psi_n}{\mathrm{d}l^2} + (hl + W(l))\psi_n(l) = E_n\psi_n(l). \tag{40}$$

Thus in the thermodynamic limit $X \to \infty$ the singular part to the free energy is simply

$$f_{\mathrm{sing}} = E_0 \tag{41}$$

which, for $h = 0$ and $T < T_{\mathrm{w}}$, allows us to identify the contact angle

$$\theta = \left(\frac{-2E_0}{\Sigma} \right)^{1/2}. \tag{42}$$

Here we have used Young's equation in the small-contact-angle limit, for which the interfacial model is valid. Similarly the normalized interfacial height PDF and parallel correlation length follow as

$$P_\pi(l) = |\psi_0(l)|^2 \tag{43}$$

and

$$\xi_{\parallel} = \frac{1}{E_1 - E_0} \tag{44}$$

respectively. For future reference we also define the matrix elements

$$\langle m|f(l)|n\rangle = \int \mathrm{d}l\, \psi_m^*(l) f(l) \psi_n(l) \tag{45}$$

which will appear in the transfer matrix theory for the wedge geometry. As discussed by Burkhardt [27], the scaling form of the PDF (30) at $h = 0$ characteristic of the SFL regime, together with the values of the critical exponents quoted earlier (with $\zeta = 1/2$), readily emerges from the transfer matrix formalism if, instead of the binding potential contribution to (38), one imposes the boundary condition on the wavefunctions

$$\psi_n'(0) = -\lambda\psi_n(0) \tag{46}$$

where, for pure systems, $\lambda \propto t'$. Specifically, the ground-state energy $E_0 = -\lambda^2/(2\Sigma)$, contact angle $\theta = \lambda/(\Sigma)$ and mean interfacial height $l_\pi = 1/(2\Sigma\theta)$.

Next consider the interfacial model of the finite width +− Ising strip at bulk coexistence. Since the system has short-ranged forces we can mimic the influence of the surface fields through the boundary conditions

$$\psi_n'(0) = -\lambda\psi_n(0) \qquad \psi_n'(L) = \lambda\psi_n(L). \tag{47}$$

For $T_{\mathrm{wet}} > T$ and large L the first two eigenfunctions are

$$\psi_0(l) \propto \cosh(\sqrt{(}2\Sigma|E_0|)(l - L/2)) \tag{48}$$

and

$$\psi_1(l) \propto \sinh(\sqrt{(}2\Sigma|E_1|)(l - L/2)). \tag{49}$$

Using the boundary conditions (47) we find for $\lambda L \to \infty$

$$E_0 = -\frac{\lambda^2}{2\Sigma}(1 + 4\mathrm{e}^{-\lambda L} + \cdots) \tag{50}$$

and

$$E_1 = -\frac{\lambda^2}{2\Sigma}(1 - 4\mathrm{e}^{-\lambda L} + \cdots). \tag{51}$$

Writing these in terms of the contact angle of the semi-infinite geometry we arrive at the desired expression for the parallel correlation length

$$\xi_{\parallel} \sim \frac{\mathrm{e}^{\Sigma\theta L}}{4\Sigma\theta^2}. \tag{52}$$

From this we can now extract the desired result for the point tension in the interfacial model using the ALU identification (37):

$$\tau = -\ln\theta + A \tag{53}$$

where $A = -\ln 2\sqrt{\Sigma\xi_0}$ may be regarded as an unimportant non-singular contribution, the value of which depends on the choice of reference length-scale ξ_0. In the interfacial model (38) with short-ranged forces the only possible choice of length-scale intrinsic to the interface is the inverse surface stiffness so that $\xi_0 = 1/\Sigma$, which is directly proportional to the bulk correlation length (and recall we have set $k_{\mathrm{B}}T \equiv 1$). With this choice of reference length-scale our expression for the point tension in pure systems is simply

$$\tau(\theta) = -\ln\theta - \ln 2. \tag{54}$$

In terms of the parameters Σ and λ this is equivalent to

$$\tau = -\ln \frac{\lambda}{\Sigma} - \ln 2 \tag{55}$$

which will be useful when we consider random bond systems.

Having derived this result using the ALU identification observe that the logarithmic divergence of the point tension for pure systems is also consistent with the behaviour of the PDF $P_\pi(l;\theta)$ for wetting at a single wall. To see this recall that, similar to the correlation length $\xi_\parallel$ (for the $+-$ strip geometry), the scaling form of the PDF $P_\pi(l;\theta)$ is also determined by the surface free energy and point tension. Ignoring the normalization constraint for the moment, notice that $P_\pi(l;\theta)$ may be identified as

$$P_\pi(l;\theta) \propto \mathrm{e}^{-f^\times(l)} \tag{56}$$

where $f^\times(l)$ denotes the excess free-energy cost of an interfacial configuration constrained to be at height l at some arbitrary position along the wall (which we can take to be the origin). For asymptotically large distances $l \gg l_\pi$ typical interfacial configurations determining $P_\pi(l;\theta)$ will have a triangular shape (see later) with incident angle θ. The free energy $f^\times(l)$ can therefore be estimated as

$$f^\times(l) = 2\Sigma\theta l + 2\tau \tag{57}$$

showing contributions from two point tensions and the surface free energies. Notice this latter term is precisely twice the value of the analogous contribution to the ALU correlation length (37) so we immediately recover the expression for the PDF (30). To extract the point tension from $P_\pi(l;\theta)$ we have to bear in mind that unlike the correlation length identification (37) the PDF satisfies the addition constraint of normalization. Moreover in two dimensions one is not capable of distinguishing the normalization constant from the point-tension term $\mathrm{e}^{-2\tau}$ since the latter term is simply another constant (independent of l). Turning this around we observe that the normalization constant $N(\theta)$ appearing in the asymptotic scaling form

$$P_\pi(l;\theta) = N(\theta)\mathrm{e}^{-f^\times(l)} \tag{58}$$

must be related to the (exponential) of the point tension. The ALU identification of τ through the correlation length $\xi_\parallel$ is in fact in precise accord with the behaviour of the PDF provided we identify

$$P_\pi(l;\theta) = \mathrm{e}^{-2\Sigma\theta l - \tau}/\xi_0 \tag{59}$$

or more simply

$$\tau = -\ln(N\xi_0) \tag{60}$$

where again ξ_0 is an appropriate intrinsic length-scale introduced for dimensional reasons and which plays no role in determining the divergence of τ. Using the choice $\xi_0 = 1/\Sigma$ appropriate to the interfacial model we recover the ALU identification (54).

3.4. The point tension for critical wetting with random bonds

We now turn to the evaluation of the point tension for two-dimensional critical wetting with random bond disorder. Together with the interfacial model result for pure systems this will be crucial in our discussion of the scaling connections between filling and the SFL regime of critical wetting. With random bond disorder the interfacial model for two-dimensional wetting is written [13, 26]

$$H[l] = \int \mathrm{d}x \left\{ \frac{\Sigma}{2}\left(\frac{\mathrm{d}l}{\mathrm{d}x}\right)^2 + hl + W(l) + V_r(x,l) \right\} \tag{61}$$

where the Gaussian random variable $V_r(x,l)$ has statistical properties

$$\overline{V_r(x,l)} = 0 \tag{62}$$

$$\overline{V_r(x,l)V_r(x',l')} - \overline{V_r(x,l)}\;\overline{V_r(x',l')} = \Delta\delta(x-x')\delta(l-l') \tag{63}$$

where the overbar denotes an average over the quenched disorder with strength Δ. It is convenient to introduce the inverse length-scale $\kappa = \Delta\Sigma/2$ as a measure of the bulk disorder which vanishes for the pure (thermal) system. As first shown by Kardar [26] the model can be studied using the replica trick identification

$$\overline{\ln Z_\pi} = \lim_{n\to 0} \frac{\overline{Z_\pi^n} - 1}{n} \tag{64}$$

where Z_π^n may be interpreted as the partition function for n non-interacting interfaces in an environment with bulk random bonds. Some details of this calculation are repeated below together with the results necessary for the calculation of the point tension and later the wedge interfacial height distribution function and free energy. Performing the disorder average introduces interactions described by the many-body Hamiltonian (ignoring l-independent terms)

$$H[\{l_i\}] = \int \mathrm{d}x \left\{ \sum_{i=1}^{n} \left(\frac{\Sigma}{2}\left(\frac{\mathrm{d}l_i}{\mathrm{d}x}\right)^2 + hl + W\left(l_i\right) \right) - \Delta \sum_{i<j}^{n} \delta\left(l_i - l_j\right) \right\} \tag{65}$$

so that the interacting n-body partition function for interfaces of length X with boundary values l_i at $x = 0$ and l_i' at $x = X$ has the spectral expansion

$$\overline{Z_\pi^n(\{l_i\},\{l_i'\};X)} = \sum_{m=0}^{\infty} \psi_m^{(n)*}(\{l_i'\})\psi_m^{(n)}(\{l_i\})\mathrm{e}^{-E_m X} \tag{66}$$

where $\psi_m^{(n)}$ is the mth state wavefunction with eigenvalue E_m for n interacting interfaces satisfying the Schrödinger equation $\hat{H}^{(n)}\psi_m^{(n)} = E_m\psi_m^{(n)}$. Again, ignoring constant terms, the Hamiltonian operator is

$$\hat{H}^{(n)} = \sum_{i=1}^{n} \left(-\frac{1}{2\Sigma}\frac{\partial^2}{\partial l_i^2} + hl + W(l_i) \right) - \Delta \sum_{i<j}^{n} \delta(l_i - l_j). \tag{67}$$

For systems with strictly short-ranged forces, characteristic of the SFL regime, it is convenient to adopt the natural generalization of the boundary condition (46) which reads [13]

$$\lim_{l_i\to 0} \frac{\partial\psi_m^{(n)}(\{l_j\})}{\partial l_i} = -\lambda\psi_m^{(n)}(\{l_j\})\Big|_{l_i=0} \tag{68}$$

for any l_j. Note that the inverse length-scale λ is characteristic of the pure wall–fluid interface and remains finite at the wetting transition in the presence of random bonds. The ground-state solution to the eigenvalue problem is given by the Bethe ansatz wavefunction [13, 26]

$$\psi_0^{(n)}(\{l_i\}) = C_n(\lambda,\kappa)\mathrm{e}^{-\lambda\sum l_i + \kappa\sum_{i<j}|l_i - l_j|} \tag{69}$$

with normalization constant

$$C_n(\lambda,\kappa) = (2\kappa)^{n/2}\left(\frac{\Gamma(\lambda/\kappa + 2n - 1)}{\Gamma(\lambda/\kappa + n - 1)}\right)^{1/2} \tag{70}$$

where $\Gamma(x)$ is the usual gamma function. From the wavefunction one can easily obtain the ground-state energy, and by considering the limit of $E_0^{(n)}/n$ as $n \to 0$ identify

$$f_{\mathrm{sing}} = -\frac{(\lambda-\kappa)^2}{2\Sigma} \tag{71}$$

as the singular contribution to the free energy. Thus the contact angle is simply

$$\theta = \frac{(\lambda - \kappa)}{\Sigma} \tag{72}$$

and note that these expressions identically reproduce the results for the pure system when $\kappa \to 0$. From the above it is clear that the disorder lowers the wetting transition temperature, which now occurs at $\lambda = \kappa$. We shall also need the expression for the mean interface height

$$l_\pi = \frac{1}{2\kappa}\psi'\left(\frac{\lambda}{\kappa} - 1\right) \tag{73}$$

which involves the derivative of the psi or digamma function defined by

$$\psi(x) = \frac{\mathrm{d}\ln\Gamma(x)}{\mathrm{d}x}. \tag{74}$$

Again in the limit $\kappa \to 0$ this reproduces the appropriate result $l_\pi = 1/(2\lambda)$ for pure systems. For finite κ however the asymptotic divergence of l_π as $\lambda \to \kappa$ is different to the pure system and

$$l_\pi \sim \frac{\kappa}{2(\lambda - \kappa)^2}. \tag{75}$$

From the results for the singular contribution to the free energy and divergence of the interfacial height we have $\alpha_\mathrm{s} = 0$ and $\beta_\mathrm{s} = 2$ in agreement with the general expectations for the SFL regime with $\zeta = 2/3$. The PDF $P_\pi(l;\theta)$ describing the fluctuations of the interfacial height in the asymptotic scaling regime is given by (31).

To evaluate the point tension for random bonds we use the properties of the PDF taking care to extract the relevant quantities at finite n before continuing to $n = 0$. The n-point PDF is the square of the ground-state wavefunction, which may be written as the ordered product

$$P^{(n)}(\{l_i\}) = C_n^2(\lambda,\kappa)\prod_{j=1}^{n}\mathrm{e}^{-2(\lambda+(n+1-2j)\kappa)l_j} \tag{76}$$

with $l_1 < l_2 < \cdots < l_n$. By analogy with the interpretation of the PDF for pure systems the coefficient of each l_j term appearing in the exponential may be viewed as the surface free-energy cost of constraining the height of the jth interface whilst the normalization constant contains the required information about the point tension. Using the appropriate replica trick identification we generalize the result (60) for the point tension in the pure system to

$$\tau = -\lim_{n\to 0}\frac{1}{n}\left(C_n^2(\lambda,\kappa)(\xi_0^{\mathrm{RB}})^n - 1\right) \tag{77}$$

where, in an obvious notation ξ_0^{RB} is a suitable choice of reference length-scale for the random bond system which plays the same, trivial-dimensional role as the length-scale ξ_0 for systems with purely thermal disorder. We emphasize that the choice of ξ_0^{RB} does not influence the asymptotic divergence of the point tensions as $T \to T_{\mathrm{wet}}$ and only contributes towards the non-singular, background term analogous to the constant A appearing in (54). Thus we find

$$\tau = -\psi\left(\frac{\lambda}{\kappa} - 1\right) - \ln 2\kappa\xi_0^{\mathrm{RB}} \tag{78}$$

which again introduces the digamma function. We now choose the value of ξ_0^{RB} so that upon taking the limit $\kappa \to 0$ we recover the correct background term for the pure system (55). As $\kappa \to 0$ the argument of the digamma function diverges and we can use the asymptotic large-x expansion

$$\psi(x) \sim \ln x - \frac{1}{2x} + \cdots. \tag{79}$$

Note that the necessary logarithmic singularity for the point tension in the pure system emerges naturally from the properties of the digamma function. The appropriate choice of reference length-scale is therefore $\xi_0^{\mathrm{RB}} = (\Sigma)^{-1} \equiv \xi_0$ and is *identical* to that chosen in our earlier discussion of purely thermal disorder. We regard this as a rather pleasing feature of the present replica trick definition of τ using the PDF. In terms of the inverse length-scales λ, κ and Σ our expression for the point tension with random bond disorder is therefore

$$\tau = -\psi\left(\frac{\lambda}{\kappa} - 1\right) + \ln\left(\frac{\Sigma}{2\kappa}\right). \tag{80}$$

Alternatively for fixed Σ and κ we can eliminate λ and rewrite this in terms of the contact angle θ recalling that $\theta \propto \lambda - \kappa \propto t'$. This is the form that is most convenient for discussing the connection with two-dimensional filling. Our final result is

$$\tau(\theta) = -\psi\left(\frac{\theta\Sigma}{\kappa}\right) + \ln\left(\frac{\Sigma}{2\kappa}\right) \tag{81}$$

which should be compared with (54) for the pure system. Equations (80) and (81) are the main new results of this section and will play an important role in our discussion of two-dimensional wedge filling with random bond disorder.

We are now in a position to test the validity of the Indekeu–Robledo critical exponent relation for the line/point tension. The singularities of the point tension occurring as $\theta \to 0$ are contained within the digamma function, which diverges as $\psi \sim -1/x$ as $x \to 0$. Thus we can identify the singular contribution to the point tension

$$\tau_{\mathrm{sing}} \sim \frac{\kappa}{\Sigma\theta} \tag{82}$$

implying $\alpha_{\mathrm{l}} = 3$, which is in precise agreement with the conjectured exponent relation. Note also that as with the pure system the point tension diverges to $+\infty$ as $T \to T_{\mathrm{wet}}$ although the quantitative divergence is much stronger.

4. Two-dimensional filling in pure and impure systems: I. Scaling theory

Our presentation of fluctuation effects occurring at two-dimensional filling transitions parallels our earlier treatment of critical wetting. In turn we shall consider (A) the definitions of critical exponents and the derivation of exponent relations, (B) a discussion of fluctuation regimes from heuristic scaling arguments and (C) the scaling and SDE of the density profile and PDF. From these preliminary considerations will emerge a possible fluctuation-induced connection with the SFL regime of critical wetting, which will be precised later using covariance relations.

4.1. Critical exponents and exponent relations

A two-dimensional wedge is a 'V'-shaped substrate formed from the junction of two linear (identical) walls that meet at the origin (say) with angles $+\alpha$ and $-\alpha$ measured w.r.t. to the $z = 0$ line. Thus the height of the wall above the line is described by a wall-function $z_{\mathrm{w}}(x) = \tan\alpha|x|$, where the x-axis runs across the wedge. The wedge is considered to be in contact with a bulk vapour phase at temperature T and chemical potential μ and is supposed to preferentially adsorb the liquid phase along the surface of the walls and, in particular, the wedge bottom. Thus the equilibrium density profile $\rho(z, x)$ is liquid-like in the filled region and will show packing effects very close to the wall although these will not be our concern here. Very general macroscopic, thermodynamic arguments [1–3] indicate that at bulk coexistence $\mu = \mu_{\mathrm{sat}}$ the wedge is completely filled by liquid provided the planar contact angle satisfies $\theta < \alpha$. Thus for the most common case where the contact angle decreases with increasing temperature, the transition from partial to complete filling occurs at a filling transition temperature T_{fill} satisfying

$$\theta(T_{\mathrm{fill}}) = \alpha. \tag{83}$$

This implies that complete filling precedes complete wetting and also that the filling temperature T_{fill} can be lowered simply by increasing the angle of the wedge. On approaching the filling phase boundary at $(T_{\mathrm{fill}}, \mu_{\mathrm{sat}}(T_{\mathrm{fill}}))$ the mean height of the interface l_{w}, as measured from the wedge bottom, diverges. The divergence is discontinuous and continuous for first-order and second-order (critical) filling respectively. Whilst in three dimensions both types of transition are possible, in two-dimensional filling transitions will almost always be continuous. At two-phase coexistence the equilibrium height profile $l_{\mathrm{eq}}(x)$ measured from the $z = 0$ line, with $l_{\mathrm{w}} \equiv l_{\mathrm{eq}}(0)$ is essentially flat in the filled region of the wedge owing to the absence of any macroscopic curvature as dictated by the Laplace equation. The lateral extent of the filled region is therefore controlled by a correlation length $\xi_x \approx 2l_{\mathrm{w}} \cot\alpha$ which is trivially related to the interfacial height. Critical effects at two-dimensional filling may be viewed as arising from breather-mode-like fluctuations in the interface height, which roll the points of contact up and down the sides of the wedge thus changing the height and volume of the filled region. A similar picture holds for three-dimensional conic filling but is modified in a three-dimensional wedge owing to long-wavelength fluctuations along the system. Similar to wetting the filling transition has two relevant scaling fields, which we can write $t = (T_{\mathrm{fill}} - T)/T_{\mathrm{fill}}$ and $h = (\rho_{\mathrm{l}} - \rho_{\mathrm{v}})(\mu_{\mathrm{sat}} - \mu)$ respectively. However for filling one has the additional possibility of using the wedge angle to control the deviation from the phase boundary. Thus for fixed T close to T_{fill} the combination $\theta - \alpha \propto t$ is a linear measure of the temperature-like scaling variable. At bulk coexistence $\mu = \mu_{\mathrm{sat}}$ the divergence of the midpoint interfacial height and roughness are characterized by critical exponents

$$l_{\mathrm{w}} \sim t^{-\beta_{\mathrm{w}}} \qquad \xi_{\perp} \sim t^{-\nu_{\perp}} \tag{84}$$

and we anticipate that in a fluctuation-dominated regime $\beta_{\mathrm{w}} = \nu_{\perp}$ so that $l_{\mathrm{w}} \sim \xi_{\perp}$. Along the filling critical isotherm $T = T_{\mathrm{fill}}$, $h \to 0$, the midpoint height l_{w} (and $\xi_{\perp}$) also diverges and we introduce the critical exponent

$$l_{\mathrm{w}} \sim h^{-\psi_{\mathrm{w}}} \tag{85}$$

to characterize this. Two other critical exponents are defined from the singularities of the wedge free energy $f_{\mathrm{w}}(\theta, \alpha, h)$, which, for later purposes, we have written as a function of the variables which highlight the covariance with wetting. Also for $h = 0$ we define $f_{\mathrm{w}}(\theta, \alpha) \equiv f_{\mathrm{w}}(\theta, \alpha, 0)$. At a thermodynamic level the wedge free energy is defined by subtracting from the total grand potential Ω the bulk free energy and the contribution from two (infinite) planar walls:

$$f_{\mathrm{w}}(\theta, \alpha, h) = \Omega + pV - \sigma_{\mathrm{wv}}^{(\pi)} A \tag{86}$$

where $\sigma_{\mathrm{wv}}^{(\pi)}$ is the wall–vapour tension for the planar ($\alpha = 0$) system and A is the *total* surface area exposed to fluid. By construction the wedge free energy vanishes in the planar limit $\alpha = 0$. On the other hand we expect that $f_{\mathrm{w}}(\alpha, \alpha)$ is unbounded due to the adsorption of a macroscopic amount of liquid. Near the filling transition we anticipate that f_{w} contains a singular contribution that the shows scaling behaviour depending on the variables h and $t \propto (\theta - \alpha)$ only. We write

$$f_{\mathrm{w}}^{\mathrm{sing}} \sim t^{2-\alpha_{\mathrm{w}}} W_{\mathrm{w}}(ht^{-\Delta_{\mathrm{w}}}) \tag{87}$$

which introduces the wedge specific heat exponent α_{w}, gap exponent Δ_{w} and free-energy scaling function $W_{\mathrm{w}}(x)$. Partial derivatives of the wedge free energy are related to thermodynamic observables, similar to the Gibbs adsorption equation for planar systems. Firstly, in the free energy the bulk ordering-field h is conjugate to the total two-dimensional volume of adsorbed fluid so that

$$\frac{\partial f_{\mathrm{w}}^{\mathrm{sing}}}{\partial h} \propto l_{\mathrm{w}}^2. \tag{88}$$

Secondly variation of the wedge angle α linearly changes the height and lateral extent of the filled region, implying [5]

$$\frac{\partial f_{\mathrm{w}}^{\mathrm{sing}}}{\partial t} \propto l_{\mathrm{w}}. \tag{89}$$

In this way we obtain the exponent relations

$$\Delta_{\mathrm{w}} = 2 - \alpha_{\mathrm{w}} + 2\beta_{\mathrm{w}} \tag{90}$$

and

$$1 - \alpha_{\mathrm{w}} = -\beta_{\mathrm{w}} \tag{91}$$

showing there is only one free critical exponent for two-dimensional filling.

4.2. Fluctuation regimes for two-dimensional filling

The classification of fluctuation regimes and also the values of the critical exponents for two-dimensional filling follow from a rather simple heuristic scaling theory somewhat analogous to the Lipowsky–Fisher treatment of critical wetting considered earlier. To begin we consider MF theory, which ignores the fluctuation effects arising from thermal excitations or quenched impurities. As first shown by Rejmer *et al* [4], interfacial models give a very elegant description of filling phenomena at MF level. For open wedges corresponding to small α (for which $\tan\alpha \approx \alpha$) the equilibrium MF profile $l_{\mathrm{eq}}(x)$ may be found from minimization of the effective interfacial free energy [4]

$$F_{\mathrm{w}}[l] = \int \mathrm{d}x \left\{ \frac{\Sigma}{2}\left(\frac{\mathrm{d}l}{\mathrm{d}x}\right)^2 + h(l - \alpha|x|) + W(l - \alpha|x|) \right\} \tag{92}$$

which can be justified from analysis of a more general drumhead-like model valid for larger α. As mentioned earlier, $l(x)$ denotes the interfacial height relative to the $z = 0$ line, whilst $W(l)$ is the binding potential appropriate to the *planar* system. We emphasize that the small-α approximation is not expected to introduce any peculiarities and the critical behaviour predicted by the model (at MF level and beyond) is believed to be valid for arbitrary wedge angles. The free-energy functional is minimized subject to the appropriate boundary conditions that the equilibrium profile $l_{\mathrm{eq}}(x) \to \alpha|x| + l_\pi$ as $|x| \to \infty$. The resulting Euler–Lagrange equation can be integrated once to give an explicit equation for the midpoint height (restricting our attention to $h = 0$) [4, 6, 7],

$$\frac{\Sigma(\alpha^2 - \theta^2)}{2} = W(l_{\mathrm{w}}) \tag{93}$$

which can be solved trivially. Thus for binding potentials of the form (16) the dependence on q is unimportant and the MF critical behaviour is determined solely by the leading-order index p. As $\theta \to \alpha$ we may expand the above equation

$$\theta = \alpha + \frac{a}{\alpha\Sigma} l_{\mathrm{w}}^{-p} + \cdots \tag{94}$$

recalling that a remains *finite* at the filling transitions since $T_{\mathrm{fill}} < T_{\mathrm{wet}}$. From this it follows immediately that the MF value of the height critical exponent at filling is $\beta_{\mathrm{w}} = 1/p$ [7].

The absence of any q dependence is a first indication that critical filling may be less sensitive to the nature of the intermolecular forces compared with critical wetting.

It is possible to extend this simple MF approach to include thermal and disorder-induced fluctuation effects in a heuristic way. The last equation tells us how the difference or shift between the contact angle and wedge tilt angle depends on the *direct* influence of the intermolecular forces. In the presence of fluctuation effects arising from either thermal or random bond disorder it is natural to suppose that (94) generalizes to

$$\theta = \alpha + \Delta\alpha_p(l_{\mathrm{w}}) + \Delta\alpha_{\mathrm{fl}}(l_{\mathrm{w}}) \tag{95}$$

where $\Delta\alpha_p(l) \sim l^{-p}$ is the direct angle shift and $\Delta\alpha_{\mathrm{fl}}(l)$ is the shift arising due to fluctuation effects, which we anticipate takes the form of a *ratio of length-scales*. Now by construction $\Delta\alpha_{\mathrm{fl}}(l)$ is *not* the ratio l_{w}/ξ_x since this is, essentially, the first term in (95) and is purely geometrical. Instead we write $\Delta\alpha_{\mathrm{fl}}(l) \propto \xi_\perp/\xi_{\mathrm{fl}}$, where ξ_{fl} is an appropriate fluctuation-related length-scale, which must be much larger than the midpoint height. If we also make the reasonable assumption that this length-scale is controlled by the wandering exponent ζ then the simplest possible choice given these constraints is $\xi_{\mathrm{fl}} \sim l_{\mathrm{w}}^{1/\zeta}$ similar to the relation $\xi_\parallel \sim l^{1/\zeta}$ appropriate to a fluctuation-dominated (WFL or SFL regime) wetting transition. Consequently if fluctuations dominate we anticipate

$$\Delta\alpha_{fl}(l) \sim l^{1-1/\zeta} \tag{96}$$

similar to the length-scale ratio $\xi_\perp/\xi_\parallel$ (18) appearing in the Lipowsky–Fisher analysis.

This simple, heuristic modification of the MF analysis is particularly powerful because for filling the phase boundary always remains $\theta = \alpha$ and is not modified by fluctuations. It follows that the critical behaviour should fall into two possible classes.

- *Filling mean field (FMF) regime.* If $p < 1/\zeta - 1$ fluctuation effects are negligible, $l_{\mathrm{w}} \gg \xi_\perp$ and the critical exponent $\beta_{\mathrm{w}} = 1/p$ is unchanged from its MF value.
- *Filling fluctuation (FFL) regime.* If $p > 1/\zeta - 1$ there are large-scale fluctuations, $l_f \sim \xi_\perp$, and the critical exponents are universal and determined by the wandering exponent. For the divergence of the filling height we predict

  $$\beta_{\mathrm{w}} = \frac{\zeta}{1-\zeta} \tag{97}$$

  with the values of the other critical exponents following from the relations (90) and (91).

At this point, a number of remarks are in order.

(I) These predictions are in perfect agreement with exact results known from transfer matrix and replica trick studies of interfacial models, which find $\beta_{\mathrm{w}} = 1$ and 2 for pure ($\zeta = 1/2$) and impure ($\zeta = 2/3$) systems with short-ranged forces [5, 6]. They are also consistent with studies of filling (corner wetting) in square lattice Ising models [11,37,38]. Moreover for pure systems it is possible to completely classify the critical behaviour using the interfacial model [5] and show that the criticality falls into the above two regimes with a marginal value $p = 1$ corresponding to the FFL/MF borderline. The critical exponent remains $\beta_{\mathrm{w}} = 1$ for this marginal case.

(II) The existence of two fluctuation regimes for filling clearly contrasts with the phenomenology of critical wetting, for which there are three. Also note that the borderline between the FFL and FMF regime occurs when $p = 1/\zeta - 1$, which is different to the SFL/WFL and WFL/MF borderlines for critical wetting, which happen when $p = 2(1/\zeta - 1)$ and $q = 2(1/\zeta - 1)$ respectively. The regime in which there is universal critical behaviour is broader for filling than for wetting.

(III) The value of the critical exponent $\beta_{\mathrm{w}} = 1/p$ in the FMF regime is different to the value $\beta_{\mathrm{s}} = 1/(q-p)$ in the MF regime of critical wetting. Therefore when the intermolecular forces are sufficiently long ranged to induce MF-like criticality, there is no apparent connection between filling and wetting. However for sufficiently short-ranged forces the predicted value for the critical exponent β_{w} (97), belonging to the FFL regime, is the same as the random-walk result for the critical exponent β_{s} for the critical wetting SFL regime (20). This is a first hint that there may be some fluctuation-induced connection between the two transitions.

4.3. Scaling of the PDF and short-distance expansion

In the FFL regime we anticipate that, within the filled region of the wedge, the density profile $\rho(z, x)$ exhibits universal scaling behaviour related to the scaling of the interfacial height PDF. We shall focus on the behaviour of the density profile and distribution function occurring at the centre of the wedge ($x = 0$) and define $\rho_{\mathrm{w}}(z) \equiv \rho(z, 0)$. Thus, for $z \to \infty, t \to 0, h \to 0$ with $zt^{\beta_{\mathrm{w}}}$ and $ht^{-\Delta_{\mathrm{w}}}$ arbitrary we expect

$$\rho_{\mathrm{w}}(z) = \rho_{\mathrm{l}} - (\rho_{\mathrm{l}} - \rho_{\mathrm{v}})\Xi_{\mathrm{w}}(zt^{\beta_{\mathrm{w}}}, ht^{-\Delta_{\mathrm{w}}}) \tag{98}$$

where the scaling function satisfies $\Xi_{\mathrm{w}}(\infty, y) = 1$ and $\Xi_{\mathrm{w}}(0, y) = 0$ for any y. Notice that unlike the case of critical wetting, where one has to distinguish between scaling behaviour in the SFL and WFL regimes, the scaling function for fluctuation-dominated filling is unique. Associated with the scaling of the profile is an SDE describing the algebraic behaviour close to the wall compared with the filling height. At $h = 0$ we write, analogous to (25)

$$\rho_{\mathrm{w}}(z) - \rho_{\mathrm{l}} \approx (\rho_{\mathrm{v}} - \rho_{\mathrm{l}})(zt^{\beta_{\mathrm{w}}})^{\gamma_{\mathrm{w}}} \tag{99}$$

which introduces our final critical exponent γ_{w} for filling and which is only defined for the FFL regime. Similar to SDE exponents for SFL and WFL regime wetting, the value of the critical exponent γ_{w} is not independent and can be related to the other exponents defined for filling. To see this, consider that the value of the wall–fluid intermolecular potential contains an additional short-ranged contribution of strength h_0 localized to the bottom of the wedge. In a magnetic (Ising) language this is would correspond to an incremental point field at the wedge apex and serves only to introduce a new non-singular length-scale proportional to the value of the field. This is useful because differentiation of the wedge free energy w.r.t. h_0 yields the value of the density at or near the wedge bottom. Now the field h_0 is irrelevant, in the renormalization group sense, and can be included in the scaling hypothesis for the free energy (87) by allowing for an additional scaling variable $h_0 t^{\beta_{\mathrm{w}}}$, which is simply the ratio of relevant length-scales. Differentiation of the singular contribution to the wedge free energy therefore implies that the singular contribution to the density at the wedge bottom is simply $\rho_{\mathrm{w}}(0) \sim t$, where we have used the exponent relation (91). However from the SDE we can also identify $\rho_{\mathrm{w}}(0) \sim t^{\beta_{\mathrm{w}}\gamma_{\mathrm{w}}}$ implying that

$$\gamma_{\mathrm{w}} = 1/\beta_{\mathrm{w}} \tag{100}$$

which will later prove to be an extremely useful exponent relation.

The scaling of the profile at filling follows from the scaling of the PDF for the midpoint interfacial height, written $P_{\mathrm{w}}(l; \theta, \alpha, h)$, similar to (28). At bulk coexistence, $h = 0$, we simply write

$$P_{\mathrm{w}}(l; \theta, \alpha) \equiv P_{\mathrm{w}}(l; \theta, \alpha, 0). \tag{101}$$

In the FFL regime we expect that $P_{\mathrm{w}}(l; \theta, \alpha)$ is characterized by a universal scaling function $\Lambda_{\mathrm{w}}(x)$ such that

$$P_{\mathrm{w}}(l; \theta, \alpha) = \tilde{a}(\theta - \alpha)^{\beta_{\mathrm{w}}}\Lambda_{\mathrm{w}}(\tilde{a}l(\theta - \alpha)^{\beta_{\mathrm{w}}}) \tag{102}$$

where $\Lambda_{\mathrm{w}}(x)$ is a universal function and the inverse length-scale $\tilde{a}$ is chosen, as with $\Lambda_{\pi}(x)$, so that the argument is simply l/l_{w}. Clearly the PDF has the SDE $\Lambda_{\mathrm{w}}(x) \sim x^{\gamma_{\mathrm{w}}-1}$. The relationship between the universal scaling function $\Lambda_{\mathrm{w}}(x)$ for filling and the corresponding function $\Lambda_{\pi}^{\mathrm{SFL}}(x)$ for two-dimensional wetting will be central to our study.

5. Interfacial models of two-dimensional filling: II. Exact results and covariance

5.1. Transfer matrix results

We begin with the transfer matrix theory of filling in pure systems [5] based on the interfacial Hamiltonian

$$H_{\mathrm{w}}[l] = \int \mathrm{d}x \left\{ \frac{\Sigma}{2} \left(\frac{\mathrm{d}l}{\mathrm{d}x} \right)^2 + h(l - \alpha|x|) + W(l - \alpha|x|) \right\} \tag{103}$$

valid for open wedges. It is easiest to assume that the horizontal range is $[-X/2, X/2]$ with periodic boundary conditions at the end-points. Note that the model trivially recovers the interfacial Hamiltonian for planar wetting $H[l]$ (38) when $\alpha = 0$. Again we emphasize that the assumption of small α is not believed to be in any way important as regards the critical behaviour occurring near the filling transition and predictions based on the above interfacial model are supported by Ising model studies of filling at right-angle corners for different lattice types [11]. To obtain the partition function corresponding to the fluctuation sum over Boltzmann weights it is convenient to make the change of variable $\tilde{l} \equiv l - \alpha|x|$, in which case we can re-write the Hamiltonian as

$$H_{\mathrm{w}} = 2\Sigma\alpha\big(\tilde{l}_{\mathrm{e}} - \tilde{l}(0)\big) + H[\tilde{l}] \tag{104}$$

where $\tilde{l}_{\mathrm{e}} \equiv l(X/2)$ denotes the end-point interfacial height (relative to the wall) and $\tilde{l}(0) \equiv l(0)$ is the midpoint height above the bottom of the wedge. Thus the angle α enters the partition function only through a local exponential boost factor associated with the midpoint height (and end-points). The ensemble average $\langle l(0)\rangle$ defines the equilibrium midpoint height l_{w} and from (104) it is immediately apparent that

$$l_{\mathrm{w}} = -\frac{1}{2\Sigma}\frac{\partial f_{\mathrm{w}}}{\partial \alpha} \tag{105}$$

which is a precise version of (89). The same relation is also valid in the presence of random bond disorder and will prove useful later. The model can be analysed using continuum transfer matrix methods, which yield very general expressions for the wedge free energy and interfacial height PDF, valid for general choices of binding potential. In the thermodynamic limit $X \to \infty$ and in terms of the inner product defined in (45) the wedge free energy follows as

$$f_{\mathrm{w}}(\alpha, \theta, h) = -\ln\langle 0|\mathrm{e}^{2\Sigma\alpha l}|0\rangle. \tag{106}$$

The probability of finding the interface at height $\tilde{l}$ from the wall at position x along it is given by

$$P_{\mathrm{w}}(\tilde{l}, x) = \sum_n \frac{\langle n|\mathrm{e}^{2\Sigma\alpha l}|0\rangle \psi_n^*(\tilde{l})\psi_0(\tilde{l})\mathrm{e}^{(E_0-E_n)|x|}}{\langle 0|\mathrm{e}^{2\Sigma\alpha l}|0\rangle} \tag{107}$$

requiring knowledge of the full transfer matrix spectrum of the planar system. At the midpoint ($x = 0$) however, for which $\tilde{l} = l(0)$, symmetry considerations simplify the expression considerably and [5]

$$P_{\mathrm{w}}(\tilde{l}, 0) \equiv P_{\mathrm{w}}(l) = \frac{|\psi_0(l)|^2\mathrm{e}^{2\Sigma\alpha l}}{\langle 0|\mathrm{e}^{2\Sigma\alpha l}|0\rangle} \tag{108}$$

which only depends on the ground-state properties of the planar problem. This is indicative that the midpoint PDF will play a special role in the theory of wedge filling. Using these relations it is easy to establish that the filling transition is located at $\theta = \alpha$ (and $h = 0$) in precise accord with the thermodynamic prediction. Moreover the critical behaviour falls into two categories in agreement with the heuristic treatment of the previous section. For binding potentials with $p > 1$ the asymptotic criticality is MF-like with $\beta_{\rm w} = 1/p$ and $\nu_\perp = (1+p)/2p$ so that $l_{\rm w} \gg \xi_\perp$. In the FFL regime corresponding to $p > 1$ the behaviour in the asymptotic scaling regime is universal and the same as that found for systems with purely short-ranged forces using the boundary conditions (46). At $h = 0$ the scaling expressions pertinent to this critical regime are

$$l_{\rm w} = \frac{1}{2\Sigma(\theta-\alpha)} \tag{109}$$

$$P_{\rm w}(l;\theta-\alpha) = 2\Sigma(\theta-\alpha){\rm e}^{-2\Sigma(\theta-\alpha)l} \tag{110}$$

$$f_{\rm w} = \ln(\theta-\alpha) - \ln\theta \tag{111}$$

corresponding to critical exponents $\beta_{\rm w} = 1$ and $2 - \alpha_{\rm w} = 0(\ln)$.

In the presence of random bond disorder the generalization of the interfacial model (61) for filling transitions in open wedges is

$$H_{\rm w}[l] = \int {\rm d}x \left\{ \frac{\Sigma}{2}\left(\frac{{\rm d}l}{{\rm d}x}\right)^2 + h(l-\alpha|x|) + W(l-\alpha|x|) + V_r(x,l) \right\} \tag{112}$$

and for systems with purely short-ranged forces (and at coexistence $h = 0$) the model can be solved exactly by extending Kardar's replica trick theory described earlier [6]. The extension is possible because, similar to (104) the replicated Hamiltonian is the same as the corresponding wetting model apart from a sum over terms $2\Sigma\alpha(\tilde{l}_i(0) - \tilde{l}_{\rm e})$, which may be absorbed into the Bethe ansatz [6]. We omit the details and only quote the final results for the infinite wedge. The filling transition occurs at

$$\lambda = \kappa + \Sigma\alpha \tag{113}$$

which by virtue of (72) is equivalent to the condition $\theta = \alpha$. The mean midpoint height is given exactly by

$$l_{\rm w} = \frac{1}{2\kappa}\psi'\left(\frac{(\lambda - \Sigma\alpha)}{\kappa} - 1\right) \tag{114}$$

which recovers the pure result (109) in the limit $\kappa \to 0$. As $\theta \to \alpha$ at finite κ, the interfacial height diverges as

$$l_{\rm w} \sim \frac{\kappa}{2(\lambda - \Sigma\alpha - \kappa)^2} \tag{115}$$

equivalent to $l_{\rm w} \sim 1/(\theta-\alpha)^2$ and implying that $\beta_{\rm w} = 2$. The scaling form of the PDF describing the asymptotic divergence of the $l_{\rm w}$ is

$$P_{\rm w}(l;\theta,\alpha) = \frac{\Sigma(\theta-\alpha)}{\pi\sqrt{2l\kappa}}{\rm e}^{-l(\theta-\alpha)^2\Sigma^2/2\kappa}\int_0^\infty {\rm d}s\, \frac{\sqrt{s}{\rm e}^{-s/4}}{s + 2l(\theta-\alpha)^2\Sigma^2/\kappa}. \tag{116}$$

Finally the wedge free energy (at $h = 0$) is given exactly by

$$f_{\rm w}(\theta,\alpha) = \psi\left(\frac{\Sigma(\theta-\alpha)}{\kappa}\right) - \psi\left(\frac{\theta\Sigma}{\kappa}\right) \tag{117}$$

which exactly recovers the pure result (111) as $\kappa \to 0$. As $\theta \to \alpha$ the free energy shows the singular behaviour

$$f_{\rm w}^{\rm sing} \sim -\frac{\kappa}{\Sigma(\theta-\alpha)} \tag{118}$$

implying $\alpha_{\rm w} = 3$. For both pure and impure systems the wedge free energy diverges to $-\infty$ as $\theta \to \alpha$.

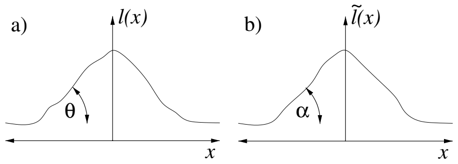

Figure 2. Interfacial configurations contributing to the one-point interfacial height PDF in two different geometries. (a) shows the triangular-like configuration an interface adopts when it is constrained to pass through some arbitrary point at height $l \gg l_\pi$ at bulk two-phase co-existence. (b) shows an interfacial configuration in a two-dimensional wedge geometry represented in terms of the relative height $\tilde{l}$ (see text). Near a filling transition $\theta \approx \alpha$ and the contributing profiles to the respective PDFs, $P_\pi(l)$ and $P_\mathrm{w}(l)$, are essentially the same.

5.2. Covariance laws for filling and wetting

The above results for two-dimensional fluctuation-dominated filling in pure and impure systems point to a remarkable connection with the scaling behaviour occurring for the SFL regime of critical wetting. This goes far beyond the identity of the exponents β_w and β_s suggested by the heuristic scaling theory. For systems with strictly short-ranged forces and at bulk coexistence ($h = 0$) we have established the following covariance relations:

$$l_\mathrm{w}(\theta, \alpha) = l_\pi(\theta - \alpha) \tag{119}$$

$$P_\mathrm{w}(l; \theta, \alpha) = P_\pi(l; \theta - \alpha) \tag{120}$$

$$f_\mathrm{w}(\theta, \alpha) = \tau(\theta) - \tau(\theta - \alpha). \tag{121}$$

The final relation between the wedge free energy and the point tension has not been reported before and is one of the central new results of our paper. These 'laws' are also valid in the asymptotic critical region, $\theta \to \alpha$, even in the presence of long-ranged forces provided the filling transition belongs to the FFL regime. We emphasize that the connection between filling and the critical wetting SFL regime is all the more remarkable because the FFL regime is broader. For example, recall that with purely thermal disorder the FFL corresponds to binding potentials with $p > 1$ whilst the critical wetting SFL regime corresponds to $p > 2$. Thus for model systems with $1 < p < 2$ the filling transition precisely mimics the properties of the SFL regime even though the wetting transition for the corresponding planar system belongs to the WFL regime. It is in this sense that the wedge geometry effectively turns off the influence of the long-ranged forces. We conjecture that the above covariance relations laws connecting filling and wetting are generally true in two dimensions provided the wandering exponent $1 \geqslant \zeta \geqslant 1/2$.

The fluctuation-induced covariance between filling and wetting has a simple geometric interpretation. In figure 2 are shown typical interfacial configurations contributing to the PDF for two different geometries. On the LHS is shown the typical triangular configuration an interface adopts at a planar wall when it is constrained to pass through a point at height l far in excess of the mean interfacial height l_π. On the RHS is the typical configuration for an interface in a two-dimensional wedge geometry plotted in terms of the relative height $\tilde{l} \equiv l(x) - \alpha|x|$. Close to the filling transition $\theta \approx \alpha$ and consequently the typical interfacial fluctuations contributing to the $P_f(l)$ and $P_\pi(l)$ in the different geometries are essentially the same. Similar remarks also apply in three dimensions for the cone geometry [9].

The covariance relations are extremely restrictive and contain a great deal of information about the allowed values of the critical exponents at two-dimensional filling and wetting. Indeed, it is worthwhile developing the consequences of these relations assuming only their validity together with the critical exponent relations derived earlier from standard scaling theory. Firstly, from the first relation (119), it necessarily follows that

$$\beta_{\mathrm{w}} = \hat{\beta}_{\mathrm{s}} = \frac{\zeta}{1-\zeta} \tag{122}$$

in agreement with the heuristic scaling theory. It is important to realize that this identification does *not* depend on the specific values of the critical exponents pertinent to the SFL regime since the divergence of $l_\pi(\theta)$ as $\theta \to 0$ is determined by the critical exponent $\hat{\beta}_{\mathrm{s}}$ (22) rather than by β_{s}. This is because the covariance relations are expressed in terms of the angles θ and α rather than the scaling fields t and t'. Using the derived exponent relations for filling we can now deduce the values of the other critical exponents in the FFL regime

$$2-\alpha_{\mathrm{w}} = \frac{1-2\zeta}{1-\zeta} \qquad \Delta_{\mathrm{w}} = \frac{1}{1-\zeta} \qquad \psi_{\mathrm{w}} = \zeta \tag{123}$$

which are all universal, determined only by ζ. The second covariance law for the PDFs contains even more information. In terms of the scaling functions this reads

$$\Lambda_{\mathrm{w}}(x) = \Lambda_\pi^{\mathrm{SFL}}(x) \equiv \Lambda(x) \tag{124}$$

which clearly indicates that the connection with the SFL regime is fundamental and not a merely fortuitous coincidence of critical exponent values. The identity of the scaling functions now has a truly remarkable consequence. To see this note that it necessarily follows that the SDE exponents γ_{w} and γ^{SFL} have the same value. Recalling the general critical exponent relations (26), (100) for these leads to the identification

$$1/\beta_{\mathrm{w}} = 2(1/\zeta - 1) - 1/\beta_{\mathrm{s}} \tag{125}$$

and using the above value for β_{w} we find

$$\beta_{\mathrm{s}} = \frac{\zeta}{1-\zeta} \tag{126}$$

which re-derives the random-walk predictions for the critical wetting SFL regime. Thus the covariance relations severely restrict the allowed values of the critical exponents for both two-dimensional filling and two-dimensional critical wetting.

Next we turn our attention to the free-energy covariance law. Taking the derivative of (121) w.r.t. α we find

$$l_{\mathrm{w}} = -\frac{\tau'(\theta-\alpha)}{2\Sigma} \tag{127}$$

and setting $\alpha = 0$ we arrive at a novel result relating the planar interfacial height to the point tension:

$$l_\pi(\theta) = -\frac{\tau'(\theta)}{2\Sigma} \tag{128}$$

valid for interfacial models with short-ranged forces (or in the asymptotic SFL critical regime). This relation has a number of consequences. First, equating the power-law critical singularities on either side yields

$$-\frac{2\beta_{\mathrm{s}}}{2-\alpha_{\mathrm{s}}} = \frac{2(2-\alpha_{\mathrm{l}})}{2-\alpha_{\mathrm{s}}} - 1 \tag{129}$$

which reduces to

$$\alpha_{\mathrm{l}} = \alpha_{\mathrm{s}} + \nu_{\|} \tag{130}$$

thus deriving the conjectured Indekeu–Robledo exponent relation. We emphasize that in this manipulation we have only used the general exponent relation (14) without having to introduce any results specific to $d = 2$. This is strongly suggestive that a generalization of (128), with possibly different numerical pre-factors, may well exist for SFL regime critical wetting in higher-dimensional systems. Secondly, beyond simple power-law singularities we can now see that the logarithmic divergence of the point tension for purely thermal systems found by ALU is, in fact, necessary in order that the interfacial height diverges as $l_\pi \sim \theta^{-1}$.

The values of all the other critical exponents for filling and wetting now follow from standard exponent relations. The connection between them can be summarized by

$$\beta_{\mathrm{w}} = \beta_{\mathrm{s}} \qquad \alpha_{\mathrm{w}} = \alpha_{\mathrm{l}} \qquad \Delta_{\mathrm{w}} = \nu_{\|} \tag{131}$$

where the LHS and RHS refer to the FFL and SFL regimes respectively.

Finally, for completeness, we remark that for pure systems it has been shown [6] that for the marginal case $p = 1, q = 2$ corresponding to the FFL/FMF boundary, the covariance laws for the interfacial height and PDF relate the behaviour at filling to the WFL/MF regime of wetting. The wedge free energy can be easily calculated for this case and is similar to (111) but has a numerical pre-factor $c = 2 + (1 + 8\Sigma b)^{1/2}$ in front of each logarithm. However we do not discuss the possible connection with the point tension because we are not confident that for such long-ranged forces τ is a well defined quantity. Whilst an expression for τ can be found for such systems using the PDF identification, and is in accord with the covariance law, we have not been able to extract τ using another, independent, method. We feel such a check is necessary since, as shown by ALU, even for short-ranged forces, the convolution definition of τ can lead to different results. Moreover for $p = 1$ it is not obvious that τ can be extracted using a generalization of the ALU correlation length identification. It may even be that the covariance relation between the wedge free energy and the point tension can be forwarded as a suitable definition of the point tension for interfacial models with this marginal interaction. This would certainly be consistent with the Indekeu–Robledo conjecture for the point tension singularity.

6. Scaling and covariance for the local compressibility

Our treatment so far has concentrated on critical singularities occurring at bulk two-phase coexistence $h = 0$. Given the precise connection between two-dimensional filling and wetting occurring at coexistence it is natural to enquire whether this extends to quantities defined for $h > 0$. Away from two-phase coexistence, however, any possible relation between two-dimensional filling and wetting is certainly subtler than that occurring for $h = 0$ because the pertinent gap exponents Δ_{w} and Δ are different. Thus the divergences of $l_{\mathrm{w}} \sim h^{-\psi_{\mathrm{w}}}$ and $l_\pi \sim h^{-\psi}$ along the respective filling and wetting critical isotherms are quite different and preclude a law of type (119). Similarly there can be no simple generalization of the free-energy relation (121) because the point tension is only defined for $h = 0$. This suggests that we first look for covariance relations between response functions for FFL filling and SFL critical wetting describing infinitesimal deviations from bulk coexistence. Such relations, should they exist, will also be notable because response functions are generally related to integrals over two-point functions, which would suggest that these too satisfy covariance relations.

Before we calculate the scaling expressions for PDF and local compressibility for two-dimensional filling we recall some pertinent results known for critical wetting.

6.1. SFL critical wetting

Differentiating the scaling ansatz for the profile $\rho(z)$ w.r.t. h immediately implies that in the scaling limit of the SFL regime, and up to an unimportant non-universal pre-factor D, the local compressibility $\chi_\pi \equiv \partial\rho(z)/\partial h$ evaluated at bulk coexistence ($h = 0$) has the form [28]

$$\chi_\pi(z;\theta) = D\theta^{-2\Delta/(2-\alpha_s)} X_\pi^{\mathrm{SFL}}(z/l_\pi(\theta)) \tag{132}$$

where $X_\pi(x)$ is a scaling function describing the universal position dependence. This is independent of the range of the forces and is specified by the dimension and type of disorder only. Again we emphasize this is valid in the asymptotic scaling limit $\theta \to 0$, $z \to \infty$ with z/l_π arbitrary. The SDE is controlled by the same exponent as the density profile so that

$$X_\pi^{\mathrm{SFL}}(x) \sim x^{\gamma^{\mathrm{SFL}}} \tag{133}$$

as $x \to 0$. By adopting the convention that the pre-factor is unity, the scale of X_π is fixed and we can regard the scaling function as universal. In effective Hamiltonian theory the behaviour of the compressibility is directly related to that of the PDF since from (28) we have

$$\chi_\pi(z) = (\rho_{\mathrm{v}} - \rho_{\mathrm{l}}) \int_0^z \mathrm{d}l\, \frac{\partial P_\pi(l)}{\partial h}. \tag{134}$$

The scaling form of the PDF, density profile and local compressibility emerges naturally from the interfacial model if we use the same boundary condition (46) but retain the hl term in the Hamiltonian. As shown by several authors, for $h > 0$ the ground-state wavefunction is an Airy function [39–41] implying

$$P_\pi(l;\theta,h) \propto \mathrm{Ai}^2\big(h^{1/3}l - \theta^2 h^{-2/3} W_\pi(h\theta^{-3})\big) \tag{135}$$

where, for the sake of clarity, we have dropped non-universal metric factors and written the field dependence in terms of $\theta \sim t'$. Taking into account the h dependence coming from the free-energy scaling function $W_\pi(x)$ and the normalization constant, it is straightforward to show that $\chi_\pi(z;\theta)$ scales according to the prediction (132) with a universal scaling function [28]

$$X_\pi^{\mathrm{SFL}}(x) = (x + \tfrac{1}{2}x^2)\mathrm{e}^{-x}. \tag{136}$$

Notice that the SDE behaviour of this function is in accord with the general requirement (133) although a different power-law determines the algebraic correction to the asymptotic exponential decay.

6.2. *FFL filling*

In zero field the midpoint local compressibility, $\chi_{\mathrm{w}}(z) \equiv \partial\rho_{\mathrm{w}}(z)/\partial h$, should also show scaling behaviour analogous to the behaviour occurring at SFL regime critical wetting. Following our treatment above it follows from the profile equation (98) that for $z \to \infty$, $l_{\mathrm{w}} \to \infty$ with fixed z/l_{w},

$$\chi_{\mathrm{w}}(z;\theta,\alpha) = \tilde{D}(\theta-\alpha)^{-\Delta_{\mathrm{w}}} X_{\mathrm{w}}(z/l_{\mathrm{w}}(\theta,\alpha)) \tag{137}$$

where $X_{\mathrm{w}}(x)$ is the appropriate scaling function, whose SDE is described by the critical exponent γ_{w}. Thus we expect

$$X_{\mathrm{w}}(x) \sim x^{\gamma_{\mathrm{w}}} \tag{138}$$

and by again adopting the convention that the critical amplitude is exactly unity we can fix the scale of the universal function $X_{\mathrm{w}}(x)$.

The behaviour of the midpoint PDF at filling can be easily calculated using the transfer matrix result (108) and after a little algebra we obtain

$$P_{\mathrm{w}}(l;\theta-\alpha,h) \propto \mathrm{e}^{-2\Sigma(\theta-\alpha)l - hl^2/\alpha} \tag{139}$$

which is considerably simpler then the planar result. Note that the h dependence of this scaling function has a simple geometrical meaning since the term l^2/α corresponds precisely to the area of the filled region of the two-dimensional wedge. From (139) it is easy to check our earlier prediction that, along the critical filling isotherm ($T = T_{\mathrm{fill}}$, $h \to 0$), the interfacial height diverges as $l_{\mathrm{w}} \sim h^{-\zeta}$. We find

$$l_{\mathrm{w}} \sim \left(\frac{\alpha}{\pi h}\right)^{1/2} \tag{140}$$

in perfect agreement with the expected behaviour for purely thermal disorder ($\zeta = 1/2$). It is also immediately seen from (139) that the roughness $\xi_{\perp} \sim l_{\mathrm{w}}$ along the critical isotherm. We mention in passing here that this behaviour contrasts with the singularities occurring at *complete* filling corresponding to $h \to 0$ for $T > T_{\mathrm{fill}}$. For this transition it is apparent from (139) that the critical behaviour is not fluctuation dominated and $l_{\mathrm{w}} \sim h^{-1}$ whilst $\xi_{\perp} \sim h^{-1/2}$. The divergence of l_{w} agrees with predictions based solely on thermodynamic and MF arguments, which remain valid because the fluctuation effects at complete filling are small even for the present two-dimensional system with short-ranged forces. Returning to the local compressibility we can readily calculate the desired expression for the zero-field local compressibility using the PDF (139). Taking care to account for the h dependence of the normalization factor we find that the local compressibility is precisely of the form (137) with $\Delta_{\mathrm{w}} = 2$ and a scaling function

$$X_{\mathrm{w}}(x) = (x + \tfrac{1}{2}x^2)\mathrm{e}^{-x} \tag{141}$$

which is identical to that derived for SFL regime critical wetting. Thus we write

$$X_{\mathrm{w}}(x) = X_{\pi}^{\mathrm{SFL}}(x) \equiv X(x). \tag{142}$$

In terms of the full angle dependence the scaling local compressibilities satisfy the simple covariance relationship

$$\frac{\chi_{\mathrm{w}}(z; \theta, \alpha)}{\chi_{\pi}(z; \theta - \alpha)} = \frac{\theta - \alpha}{\alpha} \tag{143}$$

valid in the asymptotic critical regime $\theta \to \alpha$. The identity of the local compressibility scaling functions for filling and SFL wetting is the main result of this section. Whilst we have only demonstrated this for pure systems we expect this is also valid for filling and wetting in other two-dimensional systems provided that $\zeta \geqslant 1/2$. Support for this conjecture comes from the derived values of the critical exponent relations. In particular in the limit $z/l_{\pi} \to 0$ and $z/l_{\mathrm{w}} \to 0$ the SDEs for the local compressibilities are identical and hence their ratio must be independent of z. Moreover the values of the exponents Δ_{w} and $2\Delta/(2 - \alpha_{\mathrm{s}})$ are always such that the ratio is proportional to $\theta - \alpha$ independent of ζ. It therefore seems highly likely that the covariance relation (143) is also valid for impure systems and can be checked in future studies.

7. Wedge covariance for pure systems revisited

Our discussion of the implications of the covariance relations in section 5 was simply based on comparison with the predictions of standard scaling theory for critical exponent relations and the SDEs. With a little more input concerning the properties of the interfacial Hamiltonian model we can also use the wedge-covariance relations to re-derive the results of the transfer matrix studies without explicit calculation. The following discussion is restricted to thermal disorder although a generalization to the impure systems may well be possible using the replica trick method.

In terms of the relative interfacial height $\tilde{l} - \alpha|x|$ we can write the wedge Hamiltonian as a perturbation from the planar model

$$H_{\mathrm{w}}[\tilde{l}] = H[\tilde{l}] + \delta H_{\mathrm{w}}[\tilde{l}] \tag{144}$$

where

$$\delta H_{\mathrm{w}}[\tilde{l}] = -2\Sigma\alpha \int \mathrm{d}x\, \delta(x)\tilde{l}(x) \tag{145}$$

and we have ignored $\tilde{l}$-independent terms and the boundary conditions concerning the endpoints $\tilde{l}_{\mathrm{e}}$, which do not matter in the thermodynamic limit. Because the planar interfacial Hamiltonian and the wedge perturbation are both local it immediately follows that, up to a trivial normalization constant, the midpoint height PDF for pure systems satisfies

$$P_{\mathrm{w}}(l) \propto P_{\pi}(l)\mathrm{e}^{2\Sigma\alpha l} \tag{146}$$

which is equivalent to (108). Wedge covariance of the PDF at bulk coexistence implies

$$P_{\pi}(l;\theta-\alpha) \propto P_{\pi}(l;\theta)\mathrm{e}^{2\Sigma\alpha l} \tag{147}$$

and setting $\alpha = \theta$ it follows that

$$P_{\pi}(l;\theta) \propto P_{\pi}(l;0)\mathrm{e}^{-2\Sigma\theta l} \tag{148}$$

where the position dependence of $P_{\pi}(l;0)$ is determined solely by the SDE. Using the known critical exponent relation for γ^{SFL} we conclude that within the SFL regime the PDF is necessarily of the form

$$P_{\pi}(l;\theta) \propto l^{2/\zeta-1/\beta_{\mathrm{s}}-3}\mathrm{e}^{-2\Sigma\theta l}. \tag{149}$$

From this it follows that $\hat{\beta}_{\mathrm{s}} = 1$ and since $\hat{\beta}_{\mathrm{s}} = \zeta/(1-\zeta)$ the only value of ζ consistent with the wedge covariance hypothesis in pure systems is

$$\zeta = \tfrac{1}{2} \tag{150}$$

implying that $\beta_{\mathrm{s}} = 1$. Similarly the universal scaling function for the PDF in the SFL must be simply

$$\Lambda(x) = \mathrm{e}^{-x}. \tag{151}$$

Now consider the PDF off coexistence and note that the exponential boost factor *does not* depend on the bulk field h. It follows that in the asymptotic critical regime, the scaling functions for filling and wetting satisfy the simple quotient relation

$$\frac{P_{\mathrm{w}}(l;\theta,\alpha,h)}{P_{\mathrm{w}}(l;\theta,\alpha,0)} \propto \frac{P_{\pi}(l;\alpha,h)}{P_{\pi}(l;\alpha,0)} \tag{152}$$

where the constant of proportionality is trivially determined from the normalization conditions on each PDF. Keeping the value of ζ arbitrary for the moment it follows that to first order in h the quotient has the expansion

$$\frac{P_{\mathrm{w}}(l;\theta,\alpha,h)}{P_{\mathrm{w}}(l;\theta,\alpha,0)} = 1 + \frac{K_{\zeta}h}{\alpha^2}(l^{1/\zeta} - \langle l^{1/\zeta}\rangle) + \cdots \tag{153}$$

where K_{ζ} is a pure number and $\langle l^{1/\zeta}\rangle$ denotes the appropriate moment of the interfacial height evaluated at $h = 0$. The various terms in this expansion arise for the following reasons: (1) the quotient must tend to unity as $h \to 0$; (2) the expansion must be linear in h because $P_{\pi}(l;\alpha,h)$ is a non-singular function of h for $\alpha > 0$; (3) the power-law dependence $l^{1/\zeta}$ is necessary since along the filling critical isotherm ($\alpha = \theta$, $h \to 0$) scaling demands that $l_{\mathrm{w}} \sim h^{-\zeta}$; (4) the dependence on α follows from conditions (2), (3) given the anticipated scaling form of PDF $P_{\pi}(l;\theta,h)$; (5) the additive term involving $\langle l^{1/\zeta}\rangle$ arises from the normalization condition on each PDF.

From (153) we immediately observe that the universal scaling functions $\Lambda(x)$ and $X(x)$ for FFL filling and SFL wetting must be related according to

$$X'(x) \propto \Lambda(x)(1 - c_{\zeta}x^{1/\zeta}) \tag{154}$$

where

$$c_\zeta = \frac{\left(\int_0^\infty s\,\Lambda(s)\,\mathrm{d}s\right)^{1/\zeta}}{\int_0^\infty s^{1/\zeta}\,\Lambda(s)\,\mathrm{d}s} \tag{155}$$

and the constant of proportionality in (154) is trivially fixed by the condition that $X(x) \sim x^{1/\zeta-1}$ for small x. At this point we can substitute the appropriate expressions $\Lambda(x) = \mathrm{e}^{-x}$ and $\zeta = 1/2$ for pure systems and integrate to find

$$X(x) = (x + \tfrac{1}{2}x^2)\mathrm{e}^{-x} \tag{156}$$

in agreement with the transfer matrix calculation. The differential equation (154) is also an effective method of calculating the covariant scaling function for the local compressibility at the FFL/FMF (or equivalently WFL/MF) borderline with $p = 1$, $q = 2$ for which the PDF function $\Lambda(x)$ has a non-trivial SDE [6]. Further work is required to see whether similar approaches can determine the allowed values of ζ, $\Lambda(x)$ and $X(x)$ for disordered systems without using the full transfer matrix formalism.

8. Discussion

In this paper we have investigated fluctuation effects occurring at two-dimensional filling and the fundamental connection with the SFL regime of critical wetting. Our study has revealed that in addition to the known covariance of the interfacial height and PDF [6, 9], the wedge free energy and midpoint local susceptibility are also related to the point tension and local susceptibility at wetting. These relations are extremely restrictive and determine the allowed values of the critical exponents at FFL filling *and* SFL wetting without further assumptions other than those of standard scaling theory. Moreover if wedge covariance is combined with knowledge of how the wedge Hamiltonian is perturbed from the planar interfacial model, then very specific predictions for the value of the wandering exponent, critical exponents and scaling functions can be obtained. Thus wedge covariance appears to play a similar role to the principle of conformal invariance for two-dimensional bulk critical phenomena in that it yields predictions over and above those of scaling and scale invariance. Wedge covariance also bring new insights into the nature of the SFL regime wetting transition itself. In particular we have shown that the covariance relation for the wedge free energy provides a means of deriving the conjectured Indekeu–Robledo relation for the critical singularity of the point tension and also explains its logarithmic divergence for pure systems. Other aspects of our work that have not been presented before include the derivation of an expression for the point tension for impure systems and the development of a scaling theory and derivation of critical exponent relations for two-dimensional filling transitions.

It is hoped that the present work motivates the further study of filling transitions in both two- and three-dimensional, pure and impure systems. Within the framework of the present, small-α interfacial model, future work could include discussion of two-point functions. These may well exhibit some covariance properties as suggested by the behaviour of the local compressibility. Nonlinear functional renormalization group analyses, both approximate and exact decimation [13] type, would also shed light on the likely expanded space of the SFL regime fixed point. Studies of fluctuation effects at filling using other models such as the full drumhead interfacial Hamiltonian or lattice Ising model, for which only limited results are known [11], would also be very welcome. It would also be interesting to see if the formal statistical mechanical theory of fluids at interfaces, with its powerful sum-rule and correlation function hierarchies [22, 42, 43], can be applied to the problem. Perturbative expansions of the many-body Hamiltonian analogous to (144) and (145) may prove revealing. Staying within the framework of effective Hamiltonian theory it would be highly informative if the nature of both three-dimensional wedge and cone filling were understood beyond the case of purely thermal disorder. It is likely that this would also shed more light on the nature of the SFL regime in higher dimensions, about which very little is currently known. Nevertheless the simple heuristic picture of how the filling of a two-dimensional wedge manages to precisely mimic the behaviour of the SFL regime does generalize rather naturally to the cone geometry, which similarly enforces the same qualitative type of conic interfacial configuration that determines large deviations in the one-point function at wetting. It is tempting to speculate that the Indekeu–Robledo critical exponent relation may also be intimately tied to a possible covariance for three-dimensional wedge free energy although much further work is required to quantify this.

Acknowledgments

AOP and AJW are very grateful to Dr Carlos Rascón for discussions and collaboration on related work. AJW and MJG thank the EPSRC for financial support.

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