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Wedge filling, cone filling and the strong-fluctuation regime

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Abstract

Interfacial fluctuation effects occurring at wedge- and cone-filling transitions are investigated and shown to exhibit very different characteristics. For both geometries we argue that the conditions for observing critical (continuous) filling are much less restrictive than for critical wetting, which is known to require the fine tuning of the Hamaker constants. Wedge filling is critical if the wetting binding potential does not exhibit a local maximum, whilst conic filling is critical if the line tension is negative. This latter scenario is particularly encouraging for future experimental studies.

Using mean-field and effective Hamiltonian approaches, which allow for breather-mode fluctuations which translate the interface up and down the sides of the confining geometry, we are able to completely classify the possible critical behaviours (for purely thermal disorder). For the three-dimensional wedge, the interfacial fluctuations are very strong and characterized by a universal roughness critical exponent $\nu_{\perp}^{W} = 1/4$ independent of the range of the forces. For the physical dimensions $d = 2$ and $d = 3$, we show that the effect of the cone geometry on the fluctuations at critical filling is to mimic the analogous interfacial behaviour occurring at critical wetting in the strong-fluctuation regime. In particular, for $d = 3$ and for quite arbitrary choices of the intermolecular potential, the filling height and roughness show the same critical properties as those predicted for three-dimensional critical wetting with short-ranged forces in the large-wetting-parameter ($\omega > 2$) regime.

1. Introduction

Following the seminal studies of Cahn [1] and Ebner and Saam [2], two fundamental questions concerning the nature of the wetting transition have drawn an enormous amount of attention [3,4]. Firstly, is the transition first order or continuous? In particular, how does the order depend on the range and balance of the competing intermolecular forces? Secondly, for continuous (critical) wetting transitions, what role do the interfacial fluctuations of the unbinding fluid interface play in determining the critical exponents characterizing the diverging length scales?

The answers to both these questions reveal a host of reasons why the laboratory observation of fluctuation effects at critical wetting is beset with difficulties. In brief, the well developed

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fluctuation theory of wetting concludes [3, 4] that three-dimensional critical wetting requires a fine tuning of the effective Hamaker constants appearing in the binding potential. This sensitivity means that critical wetting is a rather rare phenomenon of which only very few examples are known for fluid–fluid interfaces [5, 6]. Secondly, for systems with long-ranged forces, the critical exponents at critical wetting are mean-field-like (and depend on the range of the forces) and the interfacial roughness induced by fluctuations is very small. Even for short-ranged forces, where renormalization group (RG) theory based on effective interfacial models famously predicts dramatic fluctuation-induced effects [7], no appreciable deviations from simple mean-field-like behaviour have been observed in either Ising model simulation [8] or recent experimental studies [6]. At the very least, this indicates that the asymptotic critical regime for critical wetting is much smaller than initially expected [9]. The conclusion inevitably forced upon us appears to be that fluctuation effects at wetting transitions are of negligible practical importance.

The purpose of the present article is to compare and contrast these features of critical wetting transitions with the properties of continuous (critical) filling transitions occurring in both wedge- and cone-shaped geometries. The thermodynamics of the filling transition has been discussed independently by a number of authors [10–12] but only recently have the analogues of the above questions been addressed [13–17]. Here we present full details of a novel interfacial theory of wedge filling and also extend this approach to study fluctuation effects occurring at the filling transition of a fluid adsorbed in a cone-shaped geometry. These turn out to be completely different to those predicted to occur in the wedge. In particular we wish to draw attention to two striking features of conic filling which have not been reported before. First, the conditions for critical conic filling, even more than conditions for critical wedge filling, do not rely on any fine tuning of the binding potential structure and should be observable in cone geometries made from substrates that exhibit stronger first-order wetting. Secondly, we point out what appears to be an unexpected connection between the *geometry-induced* aspects of critical conic filling and the theory of the universal *strong-fluctuation* (SFL) regime of critical wetting [4, 18]. Specifically, from analysis of effective interfacial Hamiltonian models, we show that for the physically relevant dimensions $d = 2$ and $d = 3$, and also for almost all choices of the intermolecular interactions, the effect of the conic geometry on the asymptotic critical behaviour and the detailed scaling structure of the interfacial height probability distribution function (PDF) as one approaches a critical cone-filling transition is to mimic the way in which interfacial fluctuations determine the analogous exponents and the PDF for critical wetting transitions for planar wall–fluid (or fluid–fluid) interfaces belonging to the SFL scaling regime. This remarkable connection between conic filling and wetting has already been noted for $d = 2$ from the explicit results of exact transfer-matrix and replica trick studies of two-dimensional filling transitions (where, of course, the cone is analogous to a wedge) in both pure and impure bulk systems [14, 15]. Extending this theory, our analysis shows that the fluctuation properties of three-dimensional conic filling are quite distinct from those occurring at three-dimensional wedge filling [16] and are instead related to some of the most dramatic predictions of the theory of wetting for planar wall–fluid interfaces. Thus for $d = 3$ the divergence of the equilibrium-filling layer thickness and roughness at cone filling are universal and the same as the renormalization group predictions of Brezin, Halperin and Leibler [7] for critical wetting with short-ranged forces in the large-wetting-parameter ($\omega > 2$) regime.

Our article is arranged as follows. In the next section we briefly recall the well known fluctuation theory predictions for critical wetting, detailing the critical behaviour predicted to occur in the SFL regime for $d = 2$ and $d = 3$. In section 3 we present the main methods and results of the fluctuation theory of three-dimensional wedge filling emphasizing both the

conditions for critical filling and the predictions for fluctuation-dominated behaviour. A brief summary of these results has been given before [16]. We finish this section by turning to the special case of filling for $d = 2$. A breather-like soft mode which increases the lateral extent of the interface as it translates up and down the wedge is shown to be directly responsible for the scaling behaviour of the PDF. In section 4 we discuss three-dimensional cone filling, at the mean-field level and beyond, predicting universal geometry-dominated critical behaviour characterized by an appreciable interfacial roughness and critical exponents identical to those predicted for the planar wetting SFL regime. We argue that this equivalence of the PDFs at cone filling and SFL wetting is special to $d = 2$ and $d = 3$ only. We finish our article with a summary of our main results.

2. Fluctuation regimes at critical wetting

Consider the preferential adsorption of a thick liquid film at the interface between a planar wall and a bulk vapour phase at chemical potential μ and a subcritical temperature T. We suppose that at bulk two-phase coexistence, corresponding to chemical potential $\mu = \mu_{\rm sat}$, the wall–vapour interface is completely wetted by the liquid phase for temperatures $T > T_\pi$. Here we are interested in the values of the critical exponents describing the continuous divergence of the mean wetting film thickness $l_\pi \sim t'^{-\beta_s}$, roughness $\xi_\perp \sim t'^{-\nu_\perp}$ and transverse correlation length $\xi_\parallel \sim t'^{-\nu_\parallel}$ as $t' = (T_\pi - T)/T_\pi \to 0$. The subscript π is used to emphasize that these quantities are pertinent to planar wetting transitions. We denote the reduced temperature t' to avoid confusion with the filling reduced temperature introduced later. The standard theory of interfacial fluctuation effects at the wetting transition is based on analysis of the effective interfacial Hamiltonian [3, 4]

$$H[l] = \int \mathrm{d}\boldsymbol{x} \left\{ \frac{\Sigma}{2}(\nabla l)^2 + W(l) \right\} \tag{2.1}$$

where l is a collective coordinate describing the local height of the interface above the wall, Σ is the surface stiffness (tension) of the unbinding liquid–vapour interface and $W(l)$ is the usual binding potential which accounts for the direct influence of the molecular forces. Note that throughout this article we shall suppose that the factor β ($\equiv 1/k_B T$) is absorbed into all of the effective Hamiltonians, stiffnesses and potentials etc. Mean-field (MF) studies indicate that for critical wetting (with long-ranged forces) $W(l)$ is necessarily of the form

$$W(l) = -\frac{a}{l^p} + \frac{b}{l^q} + \cdots \qquad l > 0 \tag{2.2}$$

where $a \propto (T_\pi^{MF} - T)$ and $b > 0$ are effective Hamaker constants. Here the exponents p and q are specific to the particular ranges of the intermolecular forces. For $d = 3$ and for van der Waals forces the appropriate values are $p = 2$ and $q = 3$. For fixed dimension $d < 3$ the scaling theory of Lipowsky and Fisher [18] (which is supported by transfer-matrix and approximate non-linear renormalization group (RG) studies) predicts that the critical behaviour falls into three generic fluctuation classes labelled mean-field (MF), weak-fluctuation (WFL) and strong-fluctuation (SFL) scaling regimes. These regimes arise due to the interplay of the direct binding potential with the entropic repulsion originating from the interfacial wandering. We briefly recall the scaling argument here since the same ideas generalize to filling transitions in wedge geometries. First recall that for interfaces, the roughness $\xi_\perp$ and the transverse correlation length $\xi_\parallel$ are related via the wandering exponent $\xi_\perp \sim \xi_\parallel^{\zeta_\pi}$. We write ζ_π, keeping the subscript to avoid confusion with different wandering exponents that emerge for filling in wedges and cones. For thermal forces and $d < 3$ it is well known that

$$\zeta_\pi = \frac{3-d}{2} \tag{2.3}$$

with $\xi_\perp$ finite for $d > 3$ and $\xi_\perp \sim \sqrt{\ln \xi_\parallel}$ for the marginal case. Thus we are led rather naturally [18] to deduce that the bending energy term in (2.1) and also the entropic effect of interface collisions with the wall gives rise to a fluctuation contribution to the effective potential of the form $l^{-\tau}$ with $\tau = 2(d-1)/(3-d)$ for $d < 3$. The competition between these three terms gives rise to the three fluctuation regimes mentioned above. In the MF and WFL regimes the leading term in (2.2) is still dominant and the wetting transition temperature is unchanged by fluctuations. The critical exponents are non-universal and are given by [18]

$$\beta_s^{MF} = \frac{1}{q-p} \qquad \nu_\parallel^{MF} = \frac{q+2}{2(q-p)} \qquad \nu_\perp^{MF} = \zeta_\pi \nu_\parallel^{MF} \tag{2.4}$$

$$\beta_s^{WF} = \frac{1}{\tau-p} \qquad \nu_\parallel^{WF} = \frac{\tau+2}{2(\tau-p)} \qquad \nu_\perp^{WF} = \zeta_\pi \nu_\parallel^{WF}. \tag{2.5}$$

In the SFL regime, corresponding to $p > \tau$, and representing the critical behaviour in systems with short-ranged forces, the transition temperature is lowered by fluctuations and the critical exponents are universal. For $d = 2$ the critical exponents and the interfacial PDF, $P_\pi(l)$, are very well known (see for example [19, 20] and also references in [3, 4]) and are given by

$$\beta_s^{SF} = 1 \qquad \nu_\perp^{SF} = 1 \qquad \nu_\parallel^{SF} = 2 \qquad P_\pi(l) = \frac{1}{l_\pi} \mathrm{e}^{-l/l_\pi}. \tag{2.6}$$

Notice that in both the SFL and WFL regimes the interfacial fluctuations are very strong and $l_\pi \sim \xi_\perp$ for $d < 3$.

In three dimensions fluctuation effects are only predicted to occur for systems with short-ranged forces. For long-ranged forces the critical exponents are as shown in (2.4) with a near-negligible roughness, $\xi_\perp \approx \sqrt{\ln l_\pi}$. In our discussion of critical wetting with short-ranged forces we also ignore the added complication of the possible influence of coupled interfacial fluctuations [9], which only affect the size of the asymptotic critical regime. The simplest description of critical wetting is then based on analysis of the effective interfacial model (2.1) with a bare binding potential of the form [3, 4, 7, 9]

$$W(l) = -a\mathrm{e}^{-\kappa l} + b\mathrm{e}^{-2\kappa l} + \cdots \qquad l > 0 \tag{2.7}$$

together with the hard-wall restriction $W(l) = \infty$ for $l < 0$. Here κ denotes the inverse bulk correlation length of the adsorbed bulk phase whilst the constants a and b have the same temperature dependence as that outlined above for long-ranged forces. The mean-field predictions for short-ranged critical wetting are therefore $\beta_s = 0$ (ln) and $\nu_\parallel = 1$. The fluctuation theory of critical wetting with short-ranged forces was famously investigated by Brezin, Halperin and Leibler [7] using a linearized RG scheme and shows that the critical behaviour is strongly non-universal and falls into three regimes (labelled (I)–(III)) depending on the value of the dimensionless wetting parameter ω where

$$\omega = \frac{k_B T_\pi \kappa^2}{4\pi\Sigma}. \tag{2.8}$$

The three regimes correspond to the ranges $\omega < 1/2$, $1/2 < \omega < 2$ and $\omega > 2$ respectively. Usually attention focuses on the value of the transverse-correlation-length critical exponent which shows the strongest non-universal critical behaviour:

$$\begin{aligned} &\text{(I)} && \nu_\parallel = \frac{1}{1-\omega} \\ &\text{(II)} && \nu_\parallel = \frac{1}{(\sqrt{2}-\sqrt{\omega})^2} \\ &\text{(III)} && \nu_\parallel = \infty \end{aligned} \tag{2.9}$$

where the last case corresponds to an essential singularity. In all three regimes the roughness $\xi_\perp \sim \sqrt{l_\pi}$, so interfacial wandering has a much more pronounced influence on the equilibrium distribution of matter in the wetting film compared to systems with long-ranged forces. In regimes (I) and (II) the wetting temperature is unchanged from its mean-field value and the film thickness still grows logarithmically but with a different amplitude to in mean-field theory. The most dramatic effect of interfacial wandering is manifest in the regime (III) which bears all the hallmarks of the SFL regime. Here the wetting temperature is depressed by the fluctuations, and the critical exponents are given by

$$\text{(III)} \qquad \beta_s = 1 \qquad \nu_\perp = \frac{1}{2} \tag{2.10}$$

with an equilibrium PDF which is a simple Gaussian.

3. Fluctuation regimes at critical wedge filling

3.1. Three-dimensional wedge filling: phenomenology

Consider a three-dimensional wedge formed by the junction of two walls at angles $\pm\alpha$ to the horizontal with the height of the wall above the plane described by a height function $z_w(x, y) \equiv \tan\alpha|x|$. Thus the wedge has a 'V'-shaped cross-section in the x-direction with the wedge bottom oriented along the y-axis. Following our earlier discussion of wetting at planar walls we suppose that the wedge is in contact with a bulk vapour phase at saturation chemical potential $\mu = \mu_{\rm sat}$. General thermodynamic considerations [10–12] indicate that the wedge is completely filled by liquid for temperatures greater then the filling temperature T_F, which is specified by the elegant equality

$$\theta_\pi(T_F) = \alpha \tag{3.1}$$

where $\theta_\pi(T)$ denotes the temperature-dependent contact angle of the liquid drop at the planar wall–vapour interface. Thus, assuming the most common scenario where the contact angle decreases with temperature, the effect of the wedge geometry is to lower the temperature at which the liquid–vapour interface unbinds from the wedge bottom compared to the planar wall. The filling transition occurring as $t = (T_F - T)/T_F \to 0$ may be first order or critical corresponding to the discontinuous or continuous divergence of the equilibrium interfacial height $\langle l_0\rangle \equiv \langle l(x = 0, y)\rangle$ measured from the bottom of the wedge. Critical filling is also characterized [16] by the divergence of distinct correlation lengths describing fluctuations in the interfacial height along (ξ_y) and across (ξ_x) the wedge and also by the roughness $\xi_\perp$ of the unbinding interface. Note that the cross-wedge correlation length essentially measures the width of the flat, filled region of the wedge. The flatness of the filled region simply reflects the absence of any macroscopic curvature of the meniscus at two-phase coexistence. Recalling our earlier notation we define the wedge wetting critical exponents via

$$\langle l_0\rangle \sim t^{-\beta_s^W} \qquad \xi_\perp \sim t^{-\nu_\perp^W} \qquad \xi_x \sim t^{-\nu_x} \qquad \xi_y \sim t^{-\nu_y} \tag{3.2}$$

where we have adopted a suitable superscript, W (for wedge), for some of the exponents to avoid confusion with those pertinent to critical wetting and also for cone filling which we will consider later.

Wedge filling can also be studied using a simple modification of the effective interfacial Hamiltonian and for rather open wedges corresponding to small α (where $\tan\alpha \approx \alpha$) the appropriate model is [13–16]

$$H[l] = \int \mathrm{d}x \, \left\{ \frac{\Sigma}{2}(\nabla l)^2 + W(l - \alpha|x|) \right\} \tag{3.3}$$

where $l(x, y)$ denotes the height of the interface measured above the plane. As shown by Rejmer *et al* [13] this model can be justified from analysis of a more general drumhead model and with a binding potential interaction depending on the local normal distance of the interface to the wall rather than the simple vertical height used in (3.3). The simplifying approximations implicit in the above model do not affect any of the universal physics associated with the filling phase transition.

3.2. Mean-field theory

At MF level the equilibrium interfacial profile follows from the solution to the Euler–Lagrange equation found from the minimization of (3.3):

$$\Sigma \ddot{l} = W'(l - \alpha|x|) \tag{3.4}$$

which is solved subject to the boundary conditions $\dot{l}(0) \equiv \mathrm{d}l/\mathrm{d}x\big|_0 = 0$ and $l(x) \to l_\pi \pm \alpha x$ as $x \to \pm\infty$. This equation can be integrated once and leads to a simple condition for the mid-point height [13, 16]:

$$\frac{\Sigma\alpha^2}{2} = W(\langle l_0 \rangle) - W(l_\pi). \tag{3.5}$$

Note that in the limit $\langle l_0 \rangle \to \infty$, the RHS $\to \Sigma\theta_\pi^2/2$ which follows from Young's equation in the present small-angle limit. The above equation has an elegant graphical interpretation [13] from which one can determine the order of the filling phase transition occurring as $T \to T_F$ at fixed α or equivalently as $\alpha \to \theta_\pi$ at fixed temperature. Thus the MF condition for first-order/critical wedge filling is that, at the filling temperature T_F, the binding potential does/does not possess a local maximum separating the minimum at $l = l_\pi$ from the extremum at infinity. Thus wedges made from walls that exhibit critical wetting show critical filling, whilst wedges made from walls that exhibit first-order wetting show both first-order and critical filling, depending on whether the filling temperature is above or below the spinodal temperature T_s at which the first-order wetting binding potential develops a local maximum. Note that since the filling temperature can be lowered almost arbitrarily by increasing the wedge angle α, it follows that the wedge will typically show first-order filling if α is small and critical filling for larger values of α. The tricritical value of the wedge angle at which the order of the filling transition changes character is given by $\alpha^* = \theta_\pi(T_s)$, the precise value of which depends on how weak the first-order wetting transition is. Of course this argument presupposes that a spinodal temperature for the binding potential exists. This is certainly true for systems with short-ranged forces where it follows from the Landau theory of wetting. For example in the global phase diagrams of Nakanishi and Fisher [21] the locus of spinodal temperatures (for different surface fields) corresponds to the analytic extension of the critical wetting curve. The prediction that wedges made from walls exhibiting first-order wetting show critical filling can certainly be tested in Ising model simulation studies. For experimental systems, it may be that the mean-field condition for critical filling cannot be met because the spinodal temperature T_s is too low. However, as we shall see, fluctuation effects lead to a second mechanism for critical filling beyond the MF condition described above which may overcome this difficulty. Also, and perhaps of greater practical importance, we shall argue that the mechanism for critical filling in a cone is rather different to that for a wedge and is much more easily fulfilled.

To continue, from (3.5) it immediately follows that at a critical filling transition the MF value of the order parameter critical exponent is simply determined by the leading-order decay of $W(l)$. The exponent q plays no role and we find $\beta_s^W = 1/p$ which is totally different to the corresponding MF critical exponent $\beta_s \equiv 1/(q - p)$ for critical wetting. The MF values

of the other critical exponents follow from analysis of the height–height correlation function (with $\widetilde{y} \equiv y' - y$ and $\delta l \equiv l(x, y) - \langle l(x, y)\rangle$)

$$\mathcal{H}(x, x'; \widetilde{y}) \equiv \langle \delta l(x, y)\, \delta l(x', y')\rangle \tag{3.6}$$

and its Fourier transform

$$S(x, x'; Q) = \int \mathrm{d}\widetilde{y}\, \mathrm{e}^{\mathrm{i}Q\widetilde{y}} \mathcal{H}(x, x'; \widetilde{y}) \tag{3.7}$$

which exploits the translational invariance along the wedge. Notice that $S(x, x'; Q)$ is necessarily an even function of Q. At MF level, $S(x, x'; Q)$ follows from the solution to the Ornstein–Zernike equation

$$\int \mathrm{d}x''\, C(x, x''; Q)\mathcal{H}(x'', x'; Q) = \delta(x - x') \tag{3.8}$$

where the direct correlation function is defined by

$$C(x, x'; Q) \equiv \frac{\delta^2 \mathcal{H}[l]}{\delta l(x)\, \delta l(x')} \tag{3.9}$$

evaluated at the equilibrium height. Thus we arrive at the differential equation

$$(-\Sigma\, \partial_x^2 + \Sigma Q^2 + W''(l(x) - \alpha|x|))S(x, x'; Q) = \delta(x - x') \tag{3.10}$$

which must be solved subject to appropriate boundary conditions. These are simply that in the limit of large x, x', the correlation between two points on different sides of the filled region vanishes, whilst for those on the same side, we recover the standard planar wetting result.

To proceed it is best to consider the moment expansion

$$S(x, x'; Q) \equiv \sum_{n=0}^{\infty} Q^{2n} S_{2n}(x, x') \tag{3.11}$$

and first concentrate on the zeroth moment $S_0(x, x')$ which describes the position dependence of correlations in the fluctuations of the interfacial height across the wedge. Using standard techniques we find

$$S_0(x, x') = (|\dot{l}(x)| - \alpha)(|\dot{l}(x')| - \alpha) \left\{ \frac{1}{2\alpha W'(\langle l_0\rangle)} + \frac{\mathrm{Hv}(xx')}{\Sigma} \int_0^{\min(|x|,|x'|)} \frac{\mathrm{d}x}{(\dot{l}(x) - \alpha)^2} \right\} \tag{3.12}$$

where $\mathrm{Hv}(x)$ denotes the Heaviside step function ($\mathrm{Hv}(x) = 1, x > 0; \mathrm{Hv}(x) = 0, x < 0$). Thus the structure of correlations across the wedge reflects the properties of the equilibrium height profile $l(x)$ found from the solution to the Euler–Lagrange equation (3.4), which is particularly simple. In essence, the interface is flat such that $l(x) \approx \langle l_0\rangle$, for $x \lesssim \langle l_0\rangle/\alpha$, while for $x \gtrsim \langle l_0\rangle/\alpha$ the height decays exponentially quickly to its planar value l_π. Importantly, the length scale which controls the exponential decay is the wetting correlation length $\xi_\parallel$, which remains microscopic at the filling transition temperature. One consequence of this is that we can anticipate that the lateral width of the filled region of the wedge is trivially identified as $\xi_x \sim 2\langle l_0\rangle/\alpha$, so $\nu_x = \beta_s^W$. In this way we conclude that $S_0(x, x')$ is essentially position independent provided that $|x|, |x'| < \xi_x/2$, implying that the whole filled portion of the wedge fluctuates coherently. It also implies that there is negligible correlation between height fluctuations inside the filled region and those outside and similarly between positions on either side of the filled region. From (3.12) one can iteratively construct the position dependence of the higher moments using the integral equation

$$S_{2n+2}(x, x') = -\Sigma \int S_0(x, x'')S_{2n}(x'', x')\, \mathrm{d}x'' \tag{3.13}$$

which follows from the Ornstein–Zernike equation above. From this it follows that in the asymptotic critical (scaling) regime $S_{2n}(x, x')$ is position independent for $|x|, |x'| < \xi_x/2$ with

$$S_{2n+2}(x, x') = \frac{\alpha}{2W(\langle l_0\rangle)}\left(\frac{-\Sigma\langle l_0\rangle}{W'(\langle l_0\rangle)}\right)^n \tag{3.14}$$

and is negligible otherwise. This behaviour is consistent with the simple Lorentzian structure factor

$$S(x, x'; Q) = \frac{S_0(x, x')}{1 + \xi_y^2 Q^2} \qquad |x|, |x'| < \xi_x/2 \tag{3.15}$$

where $S_0(0, 0) \equiv \alpha/2W'(\langle l_0\rangle)$ and identifies the MF correlation length along the wedge ξ_y as

$$\xi_y = \left(\frac{\Sigma\langle l_0\rangle}{W'(\langle l_0\rangle)}\right)^{1/2}. \tag{3.16}$$

Substituting for $\langle l_0\rangle$ we find the desired MF critical exponent ν_y as $\nu_y = 1/p + 1/2$. The important observation here is that $\xi_y \gg \xi_x$, so the fluctuations are highly anisotropic and dominated by the modes along the wedge. Indeed as one approaches the bulk phase boundary, ξ_y becomes arbitrarily larger than ξ_x, implying that the fluctuations become pseudo-one-dimensional ones. The last length scale to calculate within the MF analysis is the mid-point roughness defined by $\xi_\perp^2 \equiv \langle[l(0, y) - \langle l_0\rangle]^2\rangle$ which can be identified from the relation

$$\xi_\perp^2 = \mathcal{H}(0, 0; 0) \tag{3.17}$$

where the RHS can be obtained from the Fourier inversion of $S(0, 0; Q)$. This leads to the roughness relation for the $d = 3$ wedge:

$$\xi_\perp \sim \left(\frac{\xi_y}{\Sigma\langle l_0\rangle}\right)^{1/2} \tag{3.18}$$

which is one of the central results of the MF analysis. Substituting for the divergence of ξ_y and l_0 we find that all dependence on the binding potential exponent p cancels, leading to a remarkable universal divergence

$$\xi_\perp \sim t^{-1/4} \tag{3.19}$$

valid for all ranges of intermolecular potential. In summary, the MF values of the length scale critical exponents at critical filling are

$$\beta_s^W = \frac{1}{p} \qquad \nu_y = \frac{1}{2} + \frac{1}{p} \qquad \nu_\perp^W = \frac{1}{4}. \tag{3.20}$$

Next we turn to the fluctuation theory of filling beyond MF approximation.

3.3. Fluctuation theory: breather modes and their excitations

The MF analysis presented above is only valid if the fluctuations are small in some sense. Since the divergence of $\xi_\perp$, even within MF theory, is algebraic we can simply use the 'contact condition' [18] that $\xi_\perp$ cannot be greater than $\langle l_0\rangle$ to determine the Ginzburg criterion for the breakdown of MF theory. Thus we can assert that the above critical exponents are valid provided that

$$\frac{\xi_\perp}{\langle l_0\rangle} \sim t^{-(1/4-1/p)} \ll 1 \tag{3.21}$$

which in the limit $t \to 0$ implies that p must be less then 4. For $p > 4$, fluctuation effects dominate and we can anticipate (analogously to the WFL and SFL regime behaviour of critical

wetting) that the roughness $\xi_\perp$ is comparable with the interfacial height $\langle l_0 \rangle$. Unfortunately it is very difficult to develop a full fluctuation theory of filling transitions based on the effective interfacial Hamiltonian (3.3) since, as is clear from the above remarks, the upper critical dimensions for wetting and filling are quite different. The situation is rather similar to that encountered in the theory of wetting where one would ideally like to develop a fluctuation theory based on analysis of, say, a semi-infinite Ising or Landau–Ginzburg–Wilson (LGW) model. Such a approach would afford a description of both bulk (and surface) critical behaviour and wetting. Since this has not proved possible, one instead focuses on effective models constructed to capture the essential physics of the phase transition in question. Of course, all Hamiltonians are effective Hamiltonians but some are more effective than others. The LGW model based on a local magnetization order parameter can (in principle) describe bulk and surface criticality in addition to wetting and filling. In turn, the effective interfacial Hamiltonian (3.3) based on a collective coordinate $l(x, y)$ is a theory of wetting and filling. The task here is to develop a simpler model than (3.3) which just affords a description of filling.

The theory of wedge filling which we propose is constructed from the full interfacial model under the assumption that the only fluctuations that determine the asymptotic critical behaviour arise from the pseudo-one-dimensional long-wavelength undulations in the local height of the filled region. We refer to fluctuations in the local height at fixed y as breather modes since they increase/decrease the local lateral extent of the filled region (and the volume of liquid beneath it). Thus we seek to derive a model based on a collective coordinate $l_0(y)$ which only describes these modes (see figure 1) and which is valid for sufficiently small wave-vectors $Q \ll 1/\xi_x$. Such a model can be easily constructed by generalizing the method introduced by Fisher and Jin [9, 22, 23] for the derivation of wetting interfacial models from the LGW Hamiltonian. Assuming that for a given constrained configuration of the mid-point height $l_0(y)$ all other fluctuations are small (relative to the soft mode), it follows that the desired filling Hamiltonian can be identified by

$$\exp(-H_W[l_0]) = \mathcal{T}r\{\exp(-H[l])\} \tag{3.22}$$

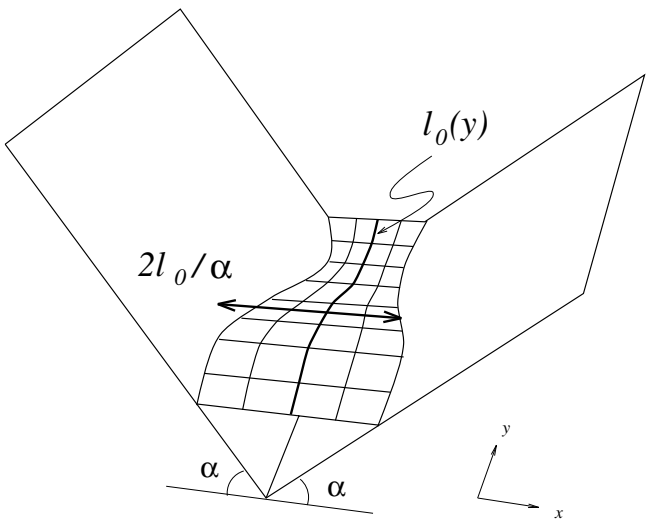

Figure 1. A schematic illustration of long-wavelength fluctuations of the interface occurring along the wedge. The diagram shows the relevant length scales motivating the derivation of the effective one-dimensional filling Hamiltonian.

where the $\mathcal{T}r$ denotes a partial trace with respect to the generalized crossing-criterion (GCC) constraint that $l(x = 0, y) = l_0(y)$. Since this trace is over non-critical fluctuations one can employ a saddle-point identification

$$H_W[l_0(y)] = H[l^\dagger(x, y; l_0(\cdot))] \tag{3.23}$$

where $l^\dagger(x, y; l_0(\cdot))$ denotes the profile that minimizes (3.3) subject to the GCC. As in the Fisher–Jin theory of wetting, the desired non-planar constrained configurations can be constructed perturbatively in terms of constrained profiles that are translationally invariant along the wedge (analogous to the planar constrained magnetization profiles) which we simply write as $l^\dagger(x; l_0)$ to avoid a proliferation of indices. These translationally invariant profiles satisfy the Euler–Lagrange equation (3.4) subject to the GCC $l^\dagger(x = 0; l_0) = l_0$. The resulting wedge-filling model has the form

$$H_W[l_0] = \int \mathrm{d}y \left\{ \frac{\Lambda(l_0)}{2} \left(\frac{\mathrm{d}l_0}{\mathrm{d}y} \right)^2 + V_W(l_0) \right\} \tag{3.24}$$

where $V_W(l_0)$ denotes the wedge binding potential and $\Lambda(l_0)$ is a position-dependent wedge line stiffness. Formally these quantities are determined by the relations

$$V_W(l_0) = \int_{-\infty}^{\infty} \mathrm{d}x \left\{ \frac{\Sigma}{2} \left(\frac{\mathrm{d}l^\dagger(x; l_0)}{\mathrm{d}x} \right)^2 + W(l^\dagger(x; l_0) - \alpha|x|) \right\} \tag{3.25}$$

(up to unimportant additive constants defined such that $V_W(l_\pi) = 0$) and

$$\Lambda(l_0) = \Sigma \int_{-\infty}^{\infty} \mathrm{d}x \left(\frac{\partial l^\dagger(x; l_0)}{\partial l_0} \right)^2. \tag{3.26}$$

The planar constrained profiles $l^\dagger(x; l_0)$ have the same simple near-flat structure as the equilibrium MF profile discussed earlier. This means that the evaluation of (3.25), (3.26) is particularly simple; for first-order and critical wedge filling we can make the approximation

$$H_W[l_0] = \int \mathrm{d}y \left\{ \frac{\Sigma l_0}{\alpha} \left(\frac{\mathrm{d}l_0}{\mathrm{d}y} \right)^2 + V_W(l_0) \right\}. \tag{3.27}$$

The qualitative and quantitative form of the filling potential depends on the order of the MF phase transition. For critical filling it has the expansion

$$V_W(l_0) = \frac{\Sigma(\theta_\pi^2 - \alpha^2) l_0}{\alpha} + a_F l_0^{1-p} + \cdots \tag{3.28}$$

and of course fluctuations are restricted to the region $l_0 > 0$ analogous to the hard-wall condition for wetting. It is important to note that the exponent p appearing in the second term above denotes the range of the forces for the analogous planar wall–fluid interface. Thus for non-retarded and retarded dispersion forces the appropriate values of p are 2 and 3 respectively. For systems with short-ranged forces this term is exponentially small, of order $\mathrm{e}^{-\kappa l_0}$. We also emphasize that the coefficient of the second term $a_F \equiv a/(p-1)\alpha$ is precisely that required so that upon minimization of the filling potential we recover the MF result for l_0. This is an important check on the self-consistency of our method. Finally, observe that the coefficient of the linear term is simply proportional to t, the relevant reduced temperature.

The critical filling potential shows a single minimum (located precisely at the MF value of l_0) which continuously moves out to infinity as $t \to 0$. The one-dimensional filling Hamiltonian can be studied using a number of different techniques including transfer-matrix

theory [16,24] and approximate RG methods[1]. However, there is no need to go to these lengths to extract the fluctuation regimes and the values of the critical exponents since they follow from a simple extension of the Lipowsky–Fisher scaling theory considered earlier. To see this we suppose that the influence of fluctuations at critical filling follows from analysis of an effective potential

$$V_{eff}(l_0) \equiv V_W(l_0) + V_{fl}(l_0) \tag{3.29}$$

which accounts for the entropic repulsion of the unbinding interface from the wedge bottom. Again the fluctuation term can be estimated from both the form of the bending energy contribution to (3.27) and also the number of collisions that the interface has with the wedge bottom. This we estimate to order l_0^{3-2/ζ_F} where ζ_F denotes the thermal wandering exponent for wedge filling (for $d = 3$) relating the roughness and the pertinent correlation length $\xi_\perp \sim \xi_y^{\zeta_F}$. The value $\zeta_F = 1/3$ follows from considering the invariance of the free part of the filling Hamiltonian under the scale transformation given by $y \mapsto y/b$ and $l_0 \mapsto b^{-\zeta_F} l_0$. Thus we arrive at an effective filling potential of the form

$$V_{eff}(l_0) \equiv V_W(l_0) + C l_0^{-3} \tag{3.30}$$

which has a single minimum at the equilibrium mid-point height. In this way we find two different fluctuation regimes for filling depending on whether the direct intermolecular potential or the entropic contribution determines the next-to-leading-order correction to the linear term in (3.28). The leading linear term is always relevant (in the RG sense) and reflects the influence of the wedge geometry on the statistical/thermodynamic properties of filling. This is rather similar to the theory of fluctuation effects at complete wetting transitions. In this way we predict that there exists a filling MF regime (FMF) for $p < 4$, with exponents given by (3.20), and a filling fluctuation-dominated regime (FFL) for $p > 4$, with

$$\beta_s^W = \frac{1}{4} \qquad \nu_y = \frac{3}{4} \qquad \nu_\perp^W = \frac{1}{4} \qquad \text{FFL}. \tag{3.31}$$

These predictions are fully confirmed by the explicit transfer-matrix analysis [16, 24]. For a final remark we turn to the effective one-dimensional Hamiltonian description of first-order filling. This is based on the model (3.27) but with a different potential $V_W(l_0)$ the form of which is shown in figure 2. In fact the structure of $V_W(l_0)$ for this case can be qualitatively deduced by noticing that the extrema of $V_W(l_0)$ must correspond to the possible solutions of the MF equation (3.5). For $\theta_\pi > \alpha$, $V_W(l_0)$ has only a single minimum which remains finite at $T = T_F$. However, for $\theta_\pi < \alpha$ a potential barrier appears separating the local minimum and the infinitely deep potential well at infinity. Note that exactly at the first-order filling transition temperature the minimum of $V_W(l_0)$ has a finite well depth relative to $V_W(\infty)$. This is quite unlike the behaviour of $W(l)$ at first-order wetting transitions. These remarks indicate that even if the mean-field condition for critical filling is not fulfilled, the influence of the one-dimensional breather-mode fluctuations may still drive the transition critical by causing the interface to tunnel away from the local minimum of the potential. Whether this happens or not depends on the range and depth of the minimum of $V_W(l_0)$ but will certainly be most important for systems with short-ranged forces (such as Ising models). Note that this tunnelling

[1] The linear RG theory of wetting (see for example [3]) can be applied to the wedge-filling Hamiltonian in the usual way by treating the potential term $W(l)$ perturbatively and expanding about the flow of the free contribution to $H_F[l_0]$ which is approximately invariant under rescaling with the filling wandering exponent $\zeta_F = 1/3$. In contrast to the case for wetting, the RG scheme is no longer exact at first order because of the mixing of slow and fast modes arising from the position dependence of the effective line stiffness. The linear term in the filling potential is always relevant and the approximate linear scheme should correctly describe the critical behaviour analogously to the RG theory of complete wetting. This approach recovers the predictions of the transfer-matrix method and scaling theory for the values of the critical exponents.

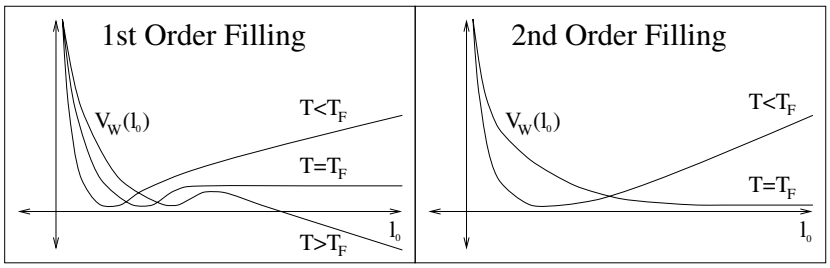

Figure 2. A schematic illustration of the wedge-filling potential on approaching a first-order and a continuous filling transition.

mechanism does not alter the filling transition phase boundary (3.1) which simply reflects the relevance of the linear term in $V_W(l_0)$. One may also note that this tunnelling must definitely occur out of coexistence for temperatures $T > T_F$ where it is responsible for the washing out of the pre-filling line. This fact is implicit in the discussion of first-order filling in Rejmer *et al* [13].

We mention only briefly here that it is trivial to investigate critical wedge filling from off-bulk coexistence using the effective model by allowing for a term of order $\delta\mu\, l^2$ in the filling potential, where $\delta\mu = \mu_{\rm sat} - \mu$ denotes the undersaturation. This clearly represents the contribution from the volume of undersaturated liquid in the filled region of the wedge. From this one can readily establish [16] that the filling thickness, roughness and correlation lengths all exhibit scaling with a gap exponent $\Delta = 5/4$ in the FFL regime. Thus the divergence of the mean interface height along the critical wedge isotherm ($T = T_F$, $\delta\mu \to 0$) within the fluctuation regime is given by $\langle l_0 \rangle \sim \delta\mu^{-1/5}$. This prediction may be easier to observe in future simulation studies than the $\langle l_0 \rangle \sim t^{-1/4}$ divergence pertinent to critical filling at bulk two-phase coexistence.

3.4. Wedge filling in two dimensions

It is a simple matter to extend the wedge-filling fluctuation theory to arbitrary dimensions d and in particular $d = 2$ where one can compare the predictions with the exact transfer-matrix solution of the full interfacial model (3.3). Consider a wedge in bulk d dimensions which is of 'V'-shaped cross-section in the x-direction but which is translationally invariant in the remaining $d-2$ (surface) dimensions. Denoting the position of the interface above the wedge bottom by $l(\vec{x}_\parallel)$ where $\vec{x}_\parallel$ denotes the $(d-2)$-dimensional vector parallel to the wedge orientation, the filling Hamiltonian trivially generalizes to

$$H_W[l_0] = \int \mathrm{d}\vec{x}_\parallel \left\{ \frac{\Sigma l_0}{\alpha} (\nabla l_0)^2 + V_F(l_0) \right\} \tag{3.32}$$

which clearly describes the $(d-2)$-dimensional thermal excitations of the breather interfacial mode. The scaling theory also generalizes in a natural way. First we calculate the d-dimensional wedge wandering exponent ζ_W by considering the invariance of the free part of (3.32) under scale transformations. This determines ζ_W as

$$\zeta_W = \frac{4-d}{3} \qquad d < 4 \tag{3.33}$$

relating the roughness and correlation length measured along the wedge (which we still denote as ξ_y) via $\xi_\perp \sim \xi_y^{\zeta_W}$ whereas for $d > 4$ there is no interfacial roughness induced by the breather

mode. For $d < 4$ the fluctuation contribution to the effective potential arising from the bending energy and entropy terms scales as

$$V_F(l_0) \sim l_0^{3(2-d)/(4-d)} \equiv l_0^{-\tau_W} \tag{3.34}$$

where τ_W is the wedge fluctuation exponent analogous to τ in the Lipowsky–Fisher theory of wetting.

This heuristic scaling theory predicts that for general dimension $d < 4$, the criticality at filling falls into a mean-field (FMF) or fluctuation-dominated (FFL) regime depending on whether p is less or greater than the marginal value $p^* = 2(d-1)/(4-d)$. The critical exponents are given by

$$\beta_s^W = \frac{1}{p} \qquad \nu_y = \frac{1}{p} + \frac{1}{2} \qquad \nu_\perp^W = \frac{4-d}{4} + \frac{(3-d)}{2p} \qquad \text{FMF} \tag{3.35}$$

$$\beta_s^W = \nu_\perp^W = \frac{(4-d)}{2(d-1)} \qquad \nu_y = \frac{3}{2(d-1)} \qquad \text{FFL} \tag{3.36}$$

and notice that it is only for $d = 3$ that the roughness exponent is universal, independent of the range of the forces. These predictions for critical singularities at wedge filling are, in general, very different to the predictions for critical wetting. However, for the special case of $d = 2$ there appears to be a connection between filling and critical wetting discussed below. For $d = 2$ the breather fluctuation theory predicts that the marginal intermolecular range is $p = 1$ and that the values of the FFL regime critical exponents are

$$\beta_s^W = \nu_\perp^W = 1 \qquad d = 2 \qquad \text{FFL} \tag{3.37}$$

with ν_y and ζ_W undefined. Note that these predictions are pertinent to all physical examples of intermolecular forces since they correspond to $p > 1$. The first thing to observe here is that the numerical values of the filling critical exponents β_s^W and $\nu_\perp^W$ in the $d = 2$ FFL regime are identical to the analogous critical wetting exponents in the ($d = 2$) SFL regime. As we shall now see, this coincidence extends to the full form of the PDF.

As well as predicting the critical exponents at filling, the fluctuation theory also predicts the precise scaling form of the mid-point PDF, $P_W(l_0)$. To see this, note that the case of wedge filling for $d = 2$ is special because the breather mode is only subject to zero-dimensional fluctuations since there is no direction along the wedge. As a result one can go beyond the above predictions for the values of the critical exponents and assert that in the asymptotic critical region, the mid-point PDF is given by

$$P_W(l_0) = N\mathrm{e}^{-V_F(l_0)} \tag{3.38}$$

where here (and below) N denotes a suitable normalization factor. Now from (3.28) we have $V_F(l_0) \sim \Sigma(\theta_\pi^2 - \alpha^2)l_0/\alpha \approx 2\Sigma(\theta_\pi - \alpha)l_0$, so in the critical regime the breather fluctuation theory leads to the scaling form of the PDF:

$$P_W(l_0) = N\mathrm{e}^{-2\Sigma(\theta_\pi - \alpha)l_0} \tag{3.39}$$

or equivalently

$$P_W(l_0) = \frac{1}{\langle l_0 \rangle}\mathrm{e}^{-l/\langle l_0 \rangle} \tag{3.40}$$

which is of course consistent with the values of the critical exponents quoted in (3.36). This prediction is remarkable for two reasons:

(I) The prediction is in exact agreement with the transfer-matrix result for the PDF based on the ($d = 2$) interfacial model (3.3). For quite arbitrary choices of binding potential the mid-point interface height distribution function is given by [14, 15]

$$P_W(l_0) = N\mathrm{e}^{2\Sigma\alpha l_0}|\Psi_0^{(\pi)}(l_0)|^2 \tag{3.41}$$

where $\Psi_0^{(\pi)}(l)$ is the ground-state eigenfunction appearing in the transfer-matrix spectrum for $d = 2$ wetting at a planar wall. This satisfies the well known Schrödinger equation [20]

$$-\frac{1}{2\Sigma}\frac{\mathrm{d}^2}{\mathrm{d}l^2}\Psi_0^{(\pi)}(l) + W(l)\Psi_0^{(\pi)}(l) = E_0\Psi_0^{(\pi)}(l) \tag{3.42}$$

where E_0 is the corresponding ground-state eigenvalue which is related to the contact angle by $E_0 = -\Sigma\theta_\pi^2/2$. From the properties of $\Psi_0^{(\pi)}(l)$ it follows that the filling transition is indeed characterized by the scaling regimes and corresponding critical singularities predicted by the general fluctuation theory. Moreover for $p > 1$, and far from the wall, the wave function decays as

$$\Psi_0^{(\pi)}(l) \sim \mathrm{e}^{-\Sigma\theta_\pi l} \tag{3.43}$$

so (3.39) and (3.41) are identical. The equivalence of the scaling form of the PDF with the breather-mode fluctuation theory and the full effective interfacial model completely supports our conjecture that it is the overall breather mode which translates the interface up and down the sides of the wedge, rather than the thermal wandering of the interface within the filled region, which determines the criticality at filling.

(II) The expression derived for the filling PDF in the FFL regime has an identical structure to the analogous interfacial height PDF, $P_\pi(l)$, for critical wetting in the SFL. Recall that this quantity is determined as $P_\pi(l) \sim |\Psi_0^{(\pi)}(l)|^2$ with the transfer-matrix approach, so in the SFL regime and the scaling limit we have the well known result, quoted earlier,

$$P_\pi(l) = \frac{1}{l_\pi}\mathrm{e}^{-l/l_\pi} \tag{3.44}$$

which is identical to the result for filling. In fact for $d = 2$ the connection between filling and critical wetting for purely thermal disorder extends to the marginal case $p = 1$ for filling where the structure of the PDF in the intermediate FMF/FFL region has the same form as the PDF for critical wetting at a WFL/MF borderline for which the specific heat exponent vanishes [15]. The PDF for this case is not simply a pure exponential function.

The equivalence of the film thickness (and roughness) critical exponents and PDFs for two-dimensional, fluctuation-dominated filling and wetting has also been established for the case of filling/wetting with random bond disorder described by the interfacial model [15]

$$H[l] = \int \mathrm{d}x \left\{ \frac{\Sigma}{2}\left(\frac{\mathrm{d}l}{\mathrm{d}x}\right)^2 + V_r(x, l(x)) + W(l - \alpha|x|) \right\} \tag{3.45}$$

with disorder averages satisfying

$$\overline{V_r}(x, l(x)) = 0 \tag{3.46}$$

and

$$\overline{V_r(x, l(x))V_r(x', l'(x))} = \Delta\delta(x - x')\,\delta(l(x) - l'(x')) \tag{3.47}$$

where Δ is a measure of the disorder. The study of filling transitions in this model allows us to test the possible connection between fluctuation-dominated two-dimensional filling and critical wetting in a system where the interfacial wandering exponent is different to that in the thermal case. It transpires that for systems with purely short-ranged forces the model (3.45) can be solved exactly using the transfer-matrix method [15] by extending Kardar's Bethe *ansatz* approach [25] used in his analysis of wetting. This again confirms the thermodynamic prediction for the location of the filling transition and identifies the universal filling critical exponents as

$$\beta_s^W = 2 \qquad \nu_\perp^W = 2 \tag{3.48}$$

which are identical to the analogous critical exponents β_s and $\nu_\perp$, determined by Kardar for critical wetting with random bonds with short-ranged forces corresponding to the SFL regime [4,25,26]. The expression for the scaling form of the mid-point interfacial height PDF $P_F(l_0)$ for $d = 2$ random bond filling is highly non-trivial, but again analysis shows that it is identical to the PDF for random bond wetting [15].

4. Conic filling

4.1. Phenomenology

Consider a non-planar wall–fluid interface in the shape of an infinite cone which makes an angle α to the horizontal. Thus, for open wedges (small α) the height of the wall above the plane is described by a height function $z_C(\vec{r}) = \alpha r$ with $\vec{r}$ the displacement vector along the horizontal plane with the origin at the cone apex. As before the wall is supposed to be in contact with a vapour phase at two-phase coexistence ($\mu = \mu_{\rm sat}$) with thermodynamics indicating that the cone is completely filled for $T > T_F$, where the conic filling temperature T_F satisfies the same condition $\theta_\pi(T_F) = \alpha$ as filling in the $d = 3$ wedge, equation (3.1). We allow for the possibility of first-order and critical cone filling corresponding to the discontinuous or continuous divergence of the mid-point filling height $\langle l_0 \rangle$ as $t \equiv (T_F - T)/T_F \to 0$. Also of interest is the roughness $\xi_\perp$ arising from the interfacial fluctuations of the unbinding liquid–vapour interface. The radius of the near-flat, liquid-filled region of the cone, which also characterizes height fluctuations in the central region, is trivially related to the height via $\xi_r \sim \langle l_0 \rangle / \alpha$. As with wedge filling, we anticipate that for radial positions $r \gtrsim \xi_r$ the interface displacement from the cone will be very close to the microscopic value l_π that it would have on a planar wall. Thus we define two length-scale critical exponents for critical cone filling by

$$\begin{aligned} \langle l_0 \rangle &\sim t^{-\beta_s^C} \\ \xi_\perp &\sim t^{-\nu_\perp^C} \end{aligned} \tag{4.1}$$

in an obvious notation. Here we seek to understand both the conditions under which critical cone filling can occur and the values of the critical exponents at the MF level and beyond. As we shall show, these are quite distinct from the situation for wedge filling.

Following our earlier treatment of wedge filling we anticipate that interfacial fluctuations manifest themselves in two different ways at conic filling. Firstly there is the usual wandering of the interface within the filled region determined by the value of the standard wandering exponent ζ_π which is of course marginal for $d = 3$ (concentrating on thermal fluctuations). Such fluctuations would occur even if the edges of the filled region were fixed to a given height, l_0 say, and would contribute terms of order $\sqrt{l_0}$ and $\sqrt{\ln l_0}$ to the interfacial roughness for $d = 2$ and $d = 3$ respectively. However, much more important than this is the breather mode that translates the entire flat region up and down the cone. We emphasize here that such fluctuations are of course possible within the present grand canonical ensemble where there is no volume constraint on the amount of liquid adsorbed. The fundamental distinction between three-dimensional wedge and cone filling arises because the breather mode is thermally excited by quasi-one-dimensional and zero-dimensional excitations respectively. In this respect three-dimensional conic filling is the higher-dimensional version of two-dimensional filling considered in the last section. Note that the effective dimensionality of the breather mode does not destroy the phase transition because the fluctuating field diverges as the filling temperature is approached.

4.2. Mean-field theory

Denoting the local interfacial height above the plane by $l(\vec{r})$, the natural starting point for the study of conic filling for open cones (small α) is the standard interfacial model

$$H[l] = \int \mathrm{d}\vec{r} \left\{ \frac{\Sigma}{2}(\nabla l)^2 + W(l - \alpha r) \right\} \tag{4.2}$$

where, again, $\vec{r}$ denotes the radial vector from the apex. To begin we chose binding potentials $W(l)$ of the type (2.2) corresponding to walls that exhibit critical wetting and set the exponent parameter $q = p + 1$. Numerical minimization of the model Hamiltonian for different ranges of the intermolecular potential shows that the filling transition is critical (for the present choice of critical wetting walls) and located precisely at $\theta_\pi = \alpha$. However, the numerics also indicates that the MF value of the critical exponent characterizing the divergence of $\langle l_0 \rangle$ appears to fall into two distinct regimes. For $p > 1$ the critical behaviour is universal and dominated by the geometry such that $\beta_s^C = 1$. On the other hand, if $p < 1$ the critical exponent is consistent with the identification $\beta_s^C = 1/p$, identical to that found within the MF theory of wedge filling. This intriguing MF critical behaviour follows from a simple variational theory of conic filling. Noting the simplicity of the equilibrium interfacial profiles obtained in our numerical minimization, we parametrize the possible height function by

$$l^\dagger(\vec{r}) = \begin{cases} l_0 & r < (l_0 - l_\pi)/\alpha \\ l_\pi + \alpha r & r > (l_0 - l_\pi)/\alpha \end{cases} \tag{4.3}$$

and determine the mid-point height dependence of the conic filling potential defined by

$$V_C(l_0) = H[l^\dagger] - H[l^\dagger]\Big|_{l^\dagger(0)=l_\pi}. \tag{4.4}$$

Note that this variational approximation becomes increasingly accurate as one approaches a critical filling transition, since the profile tends to a macroscopically flat meniscus. We can therefore anticipate that this approximation will recover the numerical results for the values of the critical exponents, although the correct values of the critical amplitudes will be sensitive to the tails of the profile. Minimization of the conic filling potential leads to the following integral equation for the mid-point height:

$$\frac{\Sigma(\alpha^2 - \theta_\pi^2)(l_0 - l_\pi)}{2} = \int_{l_\pi}^{l_0} W(l)\, \mathrm{d}l \tag{4.5}$$

which may be interpreted as a balance between surface and line tension contributions on the left and right sides respectively.

This equation has a simple graphical interpretation which precisely recovers the numerical results for the critical exponents in the $p > 1$ and $p < 1$ regimes quoted above. This variational approach also leads to a simple criterion for the order of the filling transition. It is easy to see that within this approximation the filling transition is continuous, provided that

$$\int_{l_\pi}^{\infty} W(l)\, \mathrm{d}l < 0$$

corresponding to an integral measure of the overall attractive/repulsive nature of the binding potential. As noted above, this expression is in essence a simple approximation to the line tension that does not include the necessary contribution from the tails of the profile. Thus beyond the variational approximation we expect that the correct condition for critical cone filling is that at the filling temperature, T_F, the line tension, σ, is negative. Similar remarks have been made recently by Kubalski and Napiórkowski [27] in the slightly different context

of droplet formation in conic geometries at constant liquid volume. Within mean-field theory the effective Hamiltonian expression for σ is (see [28] and references therein)

$$\sigma = \sqrt{2\Sigma}\int_{l_\pi}^{\infty}(\sqrt{\Delta W(l)} - \sqrt{\Delta W(\infty)})\,\mathrm{d}l \tag{4.6}$$

where $\Delta W(l) = W(l) - W(l_\pi)$. Thus the condition for critical cone filling is that at the filling temperature

$$\int_{l_\pi}^{\infty}(\sqrt{\Delta W(l)} - \sqrt{\Delta W(\infty)})\,\mathrm{d}l < 0. \tag{4.7}$$

This requirement is much less severe than that for both critical wetting and critical wedge filling and implies that even substrates which exhibit first-order wedge filling may still exhibit a continuous filling transition in a cone geometry. A comparison of the respective shapes of the binding potential needed for criticality for three-dimensional wetting, wedge filling and cone filling is shown in figure 3. Provided the condition for critical cone filling is met, the MF critical exponent falls into two regimes:

$$\beta_s^C = \begin{cases} \dfrac{1}{p} & \text{for } p < 1 \\ 1 & \text{for } p > 1. \end{cases} \tag{4.8}$$

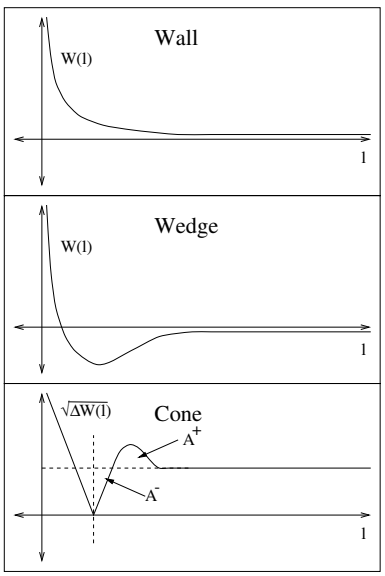

Figure 3. A schematic illustration of the qualitative form of the binding potential necessary for a continuous wetting/filling transition. For critical wetting at a planar wall (top) the potential decays monotonically exactly at T_π. For a wedge, the potential must show no local maximum at T_F. For a cone the line tension must be negative, equivalent to $A^+ < A^-$.

The universality of the critical behaviour in the geometry-dominated critical regime is reminiscent of the way in which fluctuation effects lead to universal critical behaviour at wetting transitions. This connection is explored further below.

4.3. Fluctuation theory: breather modes and the PDF

The effective zero dimensionality of the breather mode at conic filling suggests that we should analyse fluctuation effects in the same manner as we did for filling of a wedge/cone for $d = 2$. Recall that this simple approach gave the same precise scaling form of the mid-point interfacial height PDF (and hence the critical exponents) at filling as was found from the exact transfer-matrix theory. Accordingly we propose that the critical behaviour at conic filling is described by a PDF for the mid-point interfacial height of the form

$$P_C(l_0) = N\mathrm{e}^{-V_C(l_0)} \tag{4.9}$$

since the role of the cone potential for $d = 3$ is analogous to that of the wedge potential $V_W(l_0)$ for $d = 2$. It is a simple matter to show that $V_C(l_0)$ has the form

$$V_C(l_0) = \frac{\Sigma\pi(\theta_\pi^2 - \alpha^2)l_0^2}{2\alpha^2} - \frac{2\pi}{\alpha}|\sigma|l_0 + a_C l_0^{2-p} + \cdots \tag{4.10}$$

consistent with the MF values of the critical exponents discussed above. The first two terms in this expression represent the purely geometrical contributions arising form the area (surface tension) and circumference (line tension) of the filled region whilst the final term accounts for the direct influence of the specific intermolecular forces[2]. Here $a_c < 0$ and is determined by suitable integration of the planar binding potential. We have also assumed that the line tension σ is negative to facilitate critical filling as discussed above. For $p > 1$ the final term in (4.9) is irrelevant, geometry dominates and the PDF can be written as

$$P_C(l_0) = N\mathrm{e}^{-[1/(2\xi_\perp^2)](l_0 - \langle l_0 \rangle)^2} \tag{4.11}$$

and identifies the universal values of the critical exponents as

$$\beta_s^C = 1 \qquad \text{and} \qquad \nu_\perp^C = \frac{1}{2} \qquad \text{for } p > 1. \tag{4.12}$$

On the other hand if the second term in (4.10) is irrelevant and close to its most probable position, the PDF is Gaussian with critical exponents given by

$$\beta_s^C = \frac{1}{p} \qquad \text{and} \qquad \nu_\perp^C = \frac{1}{2} \qquad \text{for } p < 1. \tag{4.13}$$

Equations (4.10)–(4.13) are the main predictions of this section. Here we make two pertinent remarks:

(i) The MF value of the filling height critical exponent β_s^C is unchanged by fluctuations. However, the thermal fluctuations of the breather mode do lead to an appreciable interfacial roughness. The predictions (4.12) are appropriate for both experimental systems with long-ranged dispersion forces and simulation studies of Ising-like systems with short-ranged forces. For discrete-lattice-based Ising studies, it is probably more convenient to study adsorption in, for example, an inverted-pyramid-shaped geometry or at the corners of a three-dimensional cube. The critical exponents should be the same as for the cone in both of these cases although the critical amplitudes will be geometry sensitive.

(ii) The scaling form of the PDF and the values of the critical exponents in the universal geometry-dominated regime of cone filling are identical to the analogous critical singularities characteristic of the SFL regime of critical wetting short-ranged forces, i.e. regime (III) corresponding to $\omega > 2$ (defined in (2.9)). This is directly analogous to the observations made earlier for wedge/cone filling for $d = 2$.

[2] We are very grateful to J R Henderson for his comments on the necessary form of the line tension contribution to the conic filling potential.

The above predictions point to a remarkable coincidence between the universality of conic filling for $d = 2$ and $d = 3$ and the SFL regime of critical wetting in the same dimension which is encapsulated in the equivalence of the film thickness and roughness critical exponents as well as the interfacial height PDFs. Thus in the important geometry-dominated regimes of cone filling and for the physically relevant dimensions $d = 2$ and $d = 3$, one can identify

$$\beta_s^C = \beta_s^{SF} \qquad \nu_\perp^C = \nu_\perp^{SF} \qquad P_C(l_0) = P_\pi^{SF}(l_0). \tag{4.14}$$

The remarkable implication of these identifications is that knowledge of the adsorption and roughness critical exponents and also the scaling form the interfacial height probability distribution function does not necessarily give one enough information to determine the geometrical shape of the substrate.

4.4. Universal conic filling and the SFL regime

The above predictions beg the question, why does the influence of the cone geometry on the (universal) unbinding at filling mimic the fluctuations characteristic of critical wetting in the SFL? Usually, of course, if two different systems exhibit the same critical exponents one concludes, after identifying the appropriate order parameter, that they belong to the same universality class. We do not believe that this is the correct explanation because in this case there does not appear to be an analogue of the wetting correlation length critical exponent $\nu_\parallel$ for filling. By this we mean that in the cone, fluctuations across the filled region are characterized by a length scale ξ_r which is trivially related to $\langle l_0 \rangle$, in contrast to the case for wetting, where l_π and $\xi_\parallel$ are different. The implication of this is that the equivalence of the one-point PDFs does not extend to the two-point function which precludes use of any argument based solely on universality. In view of this we put forward a simple plausibility argument suggesting that the equivalence of the PDFs is not simply coincidence but *is* special to the physical dimensions $d = 2$ and $d = 3$. We emphasize that the specific results of our model calculations for the values of the critical exponents stand quite apart from this discussion.

Let us focus on the structure of the PDF for critical wetting at a planar wall for $d = 2$ and $d = 3$. The distribution function $P_\pi(l)$ is found by evaluating the (normalized) Boltzmann sum over all interfacial configurations that pass through the specified height l at an arbitrarily chosen position (which we take to be the origin $\vec{r} = 0$), equivalent to the identification $P_\pi(l) = N\mathrm{e}^{-F^*[l]}$ where $F^* = -\ln Z_1^*$ and Z_1^* is the partial partition function summing over this class of configurations. In turn, the constrained free-energy $F^*[l]$ is a functional of the constrained height profile corresponding to the (partial) average over all profiles that satisfy this constraint. For large $l \gg l_\pi$ the constrained profile determining the PDF naturally forms the shape of a triangle (for $d = 2$) and cone (for $d = 3$) characterized by the equilibrium contact angle θ_π. Thus the droplet shape of the constrained profile determining the asymptotics of $P_\pi(l)$ near critical wetting is essentially identical to the equilibrium height profile measured with respect to the local wall height near critical cone filling (since $\theta_\pi \sim \alpha$). This observation hints at a possible connection between the PDFs at wetting and cone filling. One may also reason that if there is any connection between the PDFs of filling and wetting, then it will only be valid when the direct effect of intermolecular interactions is unimportant, since the non-universal influence of these forces manifests itself in very different ways at the respective transitions. This is only true in the geometry-dominated regime of cone filling and the SFL regime of critical wetting.

On the other hand, it is easy to see that any connection between the two PDFs is not valid for all dimensions. The generalization of our simple fluctuation theory of cone filling presented above to arbitrary dimension d is immediate. Using the same variational approach

as described above, we arrive at a cone binding potential of the form (neglecting unimportant constants)

$$V_C(l) = tl^{d-1} - l^{d-2} + \cdots \tag{4.15}$$

representing the leading-order surface and (negative) line tension contributions. The influence of intermolecular forces is present through a term $\mathcal{O}(l^{d-1-p})$ which is higher order for $p > 1$ independently of the dimensionality. Using this cone potential to evaluate the PDF arising from the (zero-dimensional) thermal fluctuations of the breather mode leads to the following prediction for the universal, geometry-dominated cone-filling critical singularities in an arbitrary dimension in the range $2 \leqslant d < 4$:

$$\beta_s^C = 1 \qquad \text{and} \qquad \nu_\perp^C = \frac{4-d}{2} \tag{4.16}$$

which of course recovers our results for wedge/cone filling for $d = 2$ and cone filling for $d = 3$ as special cases. For $d > 4$ the roughness remains finite. Only for the physically important dimensions $d = 2, 3$ do the numerical values of these critical exponents coincide with the predictions for the SFL regime of critical wetting. Nevertheless we find it remarkable that for these special dimensions not only the values of the critical exponents but also the detailed forms of the PDFs are identical for filling and critical wetting. Finally we mention that the exponents quoted above allow us to identify the value of the wandering exponent for critical cone filling defined by $\xi_\perp \sim \xi_r^{\zeta_C}$. Noting that interfacial height is trivially related to the radial correlation length (lateral extent) of the filled region, we are led to the identification

$$\zeta_C = \frac{4-d}{2} \tag{4.17}$$

which shows the influence of the zero-dimensional breather mode on the distribution of matter. Obviously in two dimensions $\zeta_C = \zeta_W = 1$, since the cone and wedge geometries are identical.

5. Conclusions

In this article we have presented details of a general fluctuation theory of filling transitions at wedges and cones. The main results and conclusions of our study are summarized below:

(I) The dominant interfacial fluctuations at wedge and cone filling correspond to breather-like motion that translates the flat, filled region up and down the sides of the confining geometry.

(II) For three-dimensional wedge filling, the thermal excitations of the breather mode are described by a novel one-dimensional effective Hamiltonian which predicts a universal value of $1/4$ for the roughness critical exponent for all ranges of the intermolecular forces and also large-scale interfacial roughness and universal critical singularities for $p > 4$.

(III) For filling for $d = 2$, the simple picture of an effective zero-dimensional fluctuating breather mode correctly captures the critical exponents and precise scaling behaviour of the mid-point height PDF as found from the full transfer-matrix solution to the full interfacial model (of wetting and filling).

(IV) For two-dimensional filling with both thermal *and* random bond disorder, the scaling of the mid-point height PDF is identical to the corresponding results for SFL regime critical wetting in this dimensionality.

(V) Conic filling shows two different types of critical behaviour including a universal geometry-dominated regime for $p > 1$ pertinent to all physical types of intermolecular force. Applying the simple breather-like fluctuation picture to this phase transition yields a scaling form for the PDF and associated interfacial height and roughness critical exponents

identical to the SFL regime prediction for critical wetting in this dimensionality. We have argued that this equivalence of the PDFs is special to $d = 2$ and $d = 3$.

(VI) Even at MF level the conditions under which three-dimensional wedge and cone filling are continuous are different to the fine tuning required for critical wetting and are sensitive to the particular geometry. For critical wedge wetting one requires that the binding potential shape at $T = T_F$ shows no local maximum. On the other hand, cone filling is critical provided that the line tension is negative.

These conclusions, regarding both the conditions for criticality and the manifestations of interfacial fluctuations at wedge and cone filling, are in sharp contrast to the situation for critical wetting. Concentrating on the values of the thickness and roughness critical exponents as pertinent to realistic three-dimensional systems with non-retarded van der Waals forces ($p = 2$), we have

$$\beta_s = 1 \qquad \text{and} \qquad \nu_\perp = 0 \ (\ln) \qquad \text{for critical wetting} \tag{5.1}$$

$$\beta_s^W = \frac{1}{2} \qquad \text{and} \qquad \nu_\perp^W = \frac{1}{4} \qquad \text{for critical wedge filling} \tag{5.2}$$

$$\beta_s^C = 1 \qquad \text{and} \qquad \nu_\perp^C = \frac{1}{2} \qquad \text{for critical cone filling} \tag{5.3}$$

indicating that the geometry has a profound influence on the roughness of the interface. This reflects the special role of the breather mode at filling transitions. Consequently if critical wetting at a wall–fluid interface were ever seen experimentally, the observation of wedge and cone filling in this system would certainly provide a means of observing large-scale interfacial fluctuations. It should certainly be possible to test the predictions of universal and large-scale interfacial fluctuation-related behaviour in Ising model systems. We have also emphasized that the geometry dramatically alters the conditions for criticality and certainly relaxes the requirement of fine tuning the values of the Hamaker constants necessary for critical wetting. The condition for inducing continuous filling transitions is easiest to fulfil for the cone geometry and it is highly encouraging that the observation of critical filling in cones made from walls exhibiting first-order wetting is experimentally feasible. It may even be possible to further manipulate the conditions for criticality by considering filling in other geometries and by introducing chemical heterogeneity.

Throughout this article we have focused exclusively on the filling transition occurring as $T \to T_F$ at bulk two-phase coexistence. Also of interest is the influence of the geometry on complete wetting adsorption isotherms corresponding to the continuous divergence of the filling thickness for temperatures $T > T_F$ as $\mu \to \mu_{\rm sat}$ [13, 29, 30]. These transitions have also received much recent attention and show great sensitivity to the shape of the confining geometry [30]. For cones and wedges in all dimensions the divergence of the filling height is super-universal and given by

$$l_0 \sim \delta\mu^{-1} \tag{5.4}$$

where, as earlier, $\delta\mu$ denotes the undersaturation. However, unlike critical filling the breather mode does not change the nature of the roughness, so $\xi_\perp \sim \delta\mu^{-\zeta_\pi}$. Consequently at complete filling the substrate geometry radically alters the fluid adsorption but does not affect the character of interfacial fluctuations. The implication of this prediction for three-dimensional wedges is that the adsorption diverges as $\Gamma \sim \delta\mu^{-2}$ at complete filling in contrast to the familiar result $\Gamma \sim \delta\mu^{-1/3}$ for complete wetting at a planar wall with van der Waals forces [3]. This prediction has been confirmed unambiguously in recent experiments by Mistura and co-workers [31] for absorption of argon and krypton on a periodic array of wedges sculpted from an aluminium disc.

Finally it would be very interesting to explore the possible connection between conic filling and SFL critical wetting in two and three dimensions in more detail. Whilst for $d = 2$ the equivalence of the critical exponents and PDFs has been established exactly using transfer-matrix methods it would be extremely instructive to understand this from an RG perspective. This would perhaps throw light on a more detailed theory of three-dimensional cone filling based on the full interfacial model. Also our analysis of wedge and conic filling for $d = 3$ was limited to pure thermal disorder unlike our analysis for $d = 2$. Studies of three-dimensional wedge and cone filling in impure systems would be very illuminating. It may be that for impure systems, filling and SFL critical wetting only share common features for $d = 2$. If not, then any equivalence between the respective PDFs in three dimensions may prove to be a useful indirect method for evaluating their common critical exponents.

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