Critical Effects at 3D Wedge Wetting

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We show that continuous filling transitions are possible in 3D wedge geometries made from substrates exhibiting *first-order* wetting transitions, and develop a fluctuation theory yielding a complete classification of the critical behavior. Our fluctuation theory is based on the derivation of a Ginzburg criterion for filling and also on an exact transfer-matrix analysis of a novel effective Hamiltonian that we propose as a model for wedge fluctuation effects. The influence of interfacial fluctuations is very strong and, in particular, leads to a remarkable universal divergence of the interfacial roughness $\xi_\perp \sim (T_F - T)^{-1/4}$ on approaching the filling temperature T_F, valid for all possible types of intermolecular forces.

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There are two reasons why it is extremely difficult to observe interfacial fluctuation effects at continuous (critical) wetting transitions in the laboratory [1]. First, critical wetting is a rather rare phenomenon for which no examples are known for solid-liquid interfaces and only a limited number for fluid-fluid interfaces [2,3]. Second, the influence of interfacial fluctuations in three dimensions ($d = 3$) is believed to be rather small [1]. For example, for systems with long-ranged forces, the divergence of the wetting layer thickness ℓ on approaching the wetting temperature T_w is mean-field-like, $\ell \sim (T_w - T)^{-1}$, and the only predicted effect of fluctuations is to induce an extremely weak divergence of the width (roughness) $\xi_\perp$ of the unbinding interface: $\xi_\perp \sim \sqrt{-\ln(T_w - T)}$. Nonclassical critical exponents and an appreciable interfacial width are predicted only for systems with strictly short-ranged forces [4], but even here the size of the asymptotic critical regime is very small and beyond the reach of current experimental and simulation methods [3,5,6].

The purpose of the present Letter is to show that these problems do not arise for continuous (critical) filling or wedge-wetting transitions [7–9] occurring for fluid adsorption in three-dimensional wedges. First, we show, contrary to previous statements in the literature [8], that critical filling can occur in systems made from walls that exhibit first-order wetting transitions. Consequently, the observation of critical filling transitions is a realistic experimental prospect. Second, we argue that interfacial fluctuations have a strong influence on the character of the filling transition and, in particular, the interfacial roughness of the unbinding interface, which is shown to diverge with a universal critical exponent. The fluctuation theory we develop is based on the derivation of a Ginzburg criterion for the self-consistency of mean-field (MF) theory and also an exact transfer-matrix analysis of a novel interfacial Hamiltonian model for wedge wetting which we introduce to account for the highly anisotropic soft-mode fluctuations. This model leads to a complete classification of the critical behavior in $d = 3$ and predicts some remarkable fluctuation dominated phenomena which we believe may be tested in the laboratory.

To begin, we recall the basic phenomenology of wedge wetting and highlight the mechanism by which critical filling occurs in wedge geometries even for walls exhibiting first-order wetting transitions. Consider a wedge (in $d = 3$) formed by the junction of two walls at angles $\pm\alpha$ to the horizontal (see Fig. 1). Axes (x, y) are oriented across and along the wedge, respectively. We suppose the wedge is in contact with a bulk vapor phase at temperature T (less than the bulk critical value T_c) and chemical potential μ. Macroscopic arguments [7,8] dictate that at bulk coexistence, $\mu = \mu_{\rm sat}(T)$, the wedge is completely filled by liquid for all temperatures $T_c > T \geq T_F$ where T_F is the filling temperature satisfying $\Theta(T_F) = \alpha$. Here, $\Theta(T)$ is the temperature dependent contact angle of a liquid drop on a planar surface. Thus, filling occurs at a temperature lower than the wetting temperature T_w and may be viewed as an interfacial unbinding transition (of first or second order) in a system with broken translational invariance. We refer to any continuous filling transition occurring as $T \to T_F$, $\mu \to \mu_{\rm sat}(T_F)$ as critical filling. Also of interest is the complete filling transition which refers to the continuous divergence of the adsorption as $\mu \to \mu_{\rm sat}(T)$ for

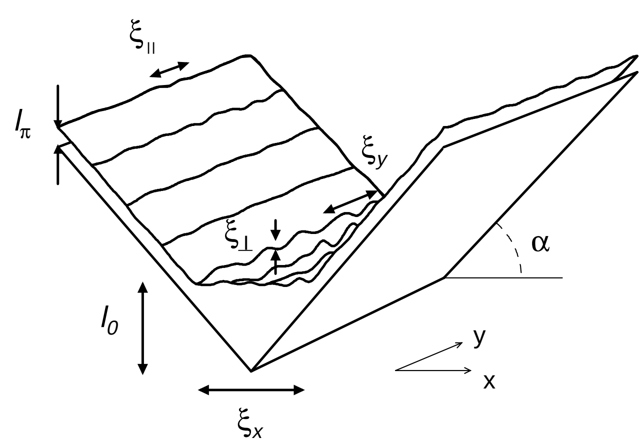

FIG. 1. Schematic illustration of an interface configuration in the wedge geometry showing the relevant diverging length scales at the filling transition. The planar adsorption ℓ_π and planar transverse correlation length $\xi_\parallel$ remain finite at the transition.

$T_c > T \geq T_F$ which is known to be characterized by geometry dependent critical exponents [10]. Here, we focus exclusively on critical filling and, in particular, the critical singularities occurring as $t \equiv (T_F - T)/T_F \to 0^+$ at bulk coexistence. The phase transition is associated with the divergence of four length scales (see Fig. 1) each characterized by a critical exponent: the midpoint ($x = 0$) height of the liquid-vapor interface $\ell_0 \sim t^{-\beta_0}$, the midpoint interfacial roughness $\xi_\perp \sim t^{-\nu_\perp}$, the lateral extension of the filled region $\xi_x \sim t^{-\nu_x}$, and the correlation length of the interfacial fluctuations along the wedge $\xi_y \sim t^{-\nu_y}$. So far, there has been no discussion of the values of these critical exponents for three-dimensional systems beyond a simple MF calculation for ℓ_0 [8]. On the other hand, transfer-matrix studies [9] in $d = 2$ indicate that fluctuation effects are very strong at wedge wetting and lead to universal critical exponents $\beta_0 = \nu_\perp = \nu_x = 1$. This is highly suggestive that fluctuation effects play an important role in $d = 3$, relevant to experimental studies.

Previous MF analysis [8] has shown that a suitable starting point for the study of wedge wetting in open wedges (small α) is the interfacial model

$$H[\ell] = \int \int dx\, dy \left[\frac{\Sigma}{2} (\nabla \ell)^2 + W(\ell - \alpha|x|) \right], \quad (1)$$

where $\ell(x, y)$ denotes the local height of the liquid-vapor interface relative to the horizontal, Σ is the liquid-vapor interfacial tension, and $W(\ell)$ is the binding potential modeling the wetting properties of the wall. At the MF level, this functional is simply minimized to yield an Euler-Lagrange equation for the y-independent equilibrium height profile $\ell(x)$, $\Sigma \ddot{\ell} = W'(\ell - \alpha|x|)$, where the dot and the prime denote differentiation with respect to x and ℓ, respectively. This differential equation is solved subject to the boundary conditions $\dot{\ell}(0) = 0$ and $\ell(x) - \alpha|x| \to \ell_\pi$ as $|x| \to \infty$. Here, ℓ_π denotes the MF planar wetting film thickness [i.e., $W'(\ell_\pi) = 0$] and remains microscopic at the filling transition. Integrating once the equation yields a simple equation for the midpoint height, $\Sigma \alpha^2/2 = W(\ell_0) - W(\ell_\pi)$, which can be solved graphically [8]. Note that at bulk coexistence Young's equation implies $W(\ell_\pi) = -\Sigma \Theta^2/2$ (within this small angle approximation) so that the present model immediately recovers the macroscopic result $\Theta(T_F) = \alpha$. Depending on the form of $W(\ell)$ (at T_F) the divergence of ℓ_0 as $T \to T_F^-$ is first order or continuous. The condition for critical filling is that between the global minimum of $W(\ell)$ at ℓ_π and the extremum at $\ell = \infty$ there is no potential barrier. Thus, walls exhibiting critical wetting necessarily form wedges exhibiting critical filling. However, for walls exhibiting first-order wetting, the filling transition is first order or critical depending on whether the transition temperature T_F is greater or less than the spinoidal temperature T_s ($<T_w$) at which the potential barrier in $W(\ell)$ appears. Since the macroscopic condition $\Theta(T_F) = \alpha$ implies that T_F can be trivially lowered by making the wedge angle more acute, it follows that walls exhibiting first-order wetting transitions will, in general, exhibit both types of filling transition (see Fig. 2). Note that the tricritical value of the wedge angle α^* separating the loci of first- and second-order filling transitions will itself be rather small for weakly first-order wetting so that the Hamiltonian (1) is still valid. The MF value of the height critical exponent β_0 for critical filling follows directly from the equation for ℓ_0 if we write the asymptotic decay of the binding potential as $W(\ell) \approx -A\ell^{-p}$ where A is a (positive) Hamaker constant and p depends on the range of the forces. For systems with short-ranged forces, this decay is exponentially small. A simple calculation then yields $\beta_0 = 1/p$ (quoted in Ref. [9] and implicit in Ref. [8]) so that, for dispersion forces (corresponding to $p = 2$), the MF prediction is $\beta_0 = 1/2$, while for short-ranged forces $\beta_0 = 0(\ln)$. The structure of the MF height profile $\ell(x)$ is particularly simple near critical filling [8] and has crucial consequences. In essence, the interface is flat [i.e., $\ell(x) \sim \ell_0$] for $|x| \lessapprox \ell_0/\alpha$, while for $|x| \gtrapprox \ell_0/\alpha$ the height decays exponentially quickly to its asymptotic planar value ℓ_π above the wall. Importantly, the length scale controlling this exponential decay is the wetting correlation length $\xi_\parallel \equiv \sqrt{\Sigma/W''(\ell_\pi)}$ which remains *microscopic* at the filling transition. One consequence of this is that the lateral width of the filled portion of the wedge is trivially identified as $\xi_x \sim 2\ell_0/\alpha$ so that $\nu_x = \beta_0$. More important consequences of the height structure are considered below.

We now turn to the main body of our analysis concerning the nature of fluctuation effects at critical filling and consider first fluctuations about the MF profile $\ell(x)$

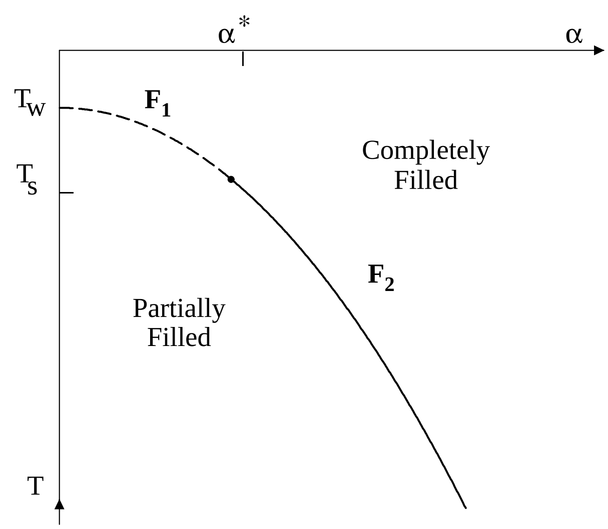

FIG. 2. Schematic surface phase diagram showing temperature vs the opening angle α for a system undergoing a first-order wetting transition at T_w in the planar case ($\alpha = 0$). The filling transition is only first order (**F**$_1$) if it takes place at a temperature above the spinoidal temperature T_s but becomes second order (**F**$_2$) if the filling temperature is less than T_s.

as measured by the height-height correlation function $H(x, x'; \tilde{y}) \equiv \langle \delta\ell(x, y)\delta\ell(x', y')\rangle$ where $\delta\ell(x, y) \equiv \ell(x, y) - \langle \ell(x, y)\rangle$ and $\tilde{y} \equiv y' - y$. To calculate the correlation function, we first exploit the translational invariance along the wedge and introduce the structure factor

$$S(x, x'; Q) = \int d\tilde{y}\, e^{iQ\tilde{y}} H(x, x'; \tilde{y}) . \qquad (2)$$

The assumption of MF theory is that fluctuation about $\ell(x)$ is small and hence a Gaussian expansion of $H[\ell]$ about the minimum suffices to determine the correlations. This leads to the differential (Ornstein-Zernike) equation

$$\{-\Sigma\partial_x^2 + \Sigma Q^2 + W''[\ell(x) - \alpha|x|]\} \times S(x, x'; Q) = \delta(x - x') , \qquad (3)$$

where we have adsorbed a factor of $k_B T$ into the definitions of Σ and $W(\ell)$. The structure of correlations across the wedge is manifest in the properties of the zeroth moment $S_0(x, x') \equiv S(x, x'; 0)$ which can be obtained analytically using standard methods. We find

$$S_0(x, x') = [|\dot{\ell}(x)| - \alpha][|\dot{\ell}(x')| - \alpha]\left\{\frac{1}{2\alpha W'(\ell_0)} + \frac{H(xx')}{\Sigma}\int_0^{\min(|x|,|x'|)} \frac{dx}{[\dot{\ell}(x) - \alpha]^2}\right\}, \qquad (4)$$

where $H(x)$ denotes the Heaviside step function [$H(x) = 1$ for $x \geq 0$, $H(x) = 0$ otherwise]. From the properties of the equilibrium profile $\ell(x)$, it follows that the length scale ξ_x also controls the extent of the correlations across the wedge. In fact, it can be seen that correlations across the wedge are very large and also (essentially) position independent, provided both particles lie within the filled region, implying that, at fixed y, the local height of the filled region fluctuates coherently. On the other hand, the correlations are totally negligible if one (or both) particles lie outside the filled region since their asymptotic decay is controlled by the microscopic length $\xi_\parallel$. These are important remarks central to the development of a general fluctuation theory of wedge wetting.

Turning next to correlations along the wedge, we note that a simple extension of the above analysis shows that the dominant singular contribution to the structure factor has a simple Lorentzian form,

$$S(x, x'; Q) \approx \frac{S_0(0,0)}{1 + Q^2\xi_y^2}; \qquad |x|, |x'| \lessapprox \xi_x/2 , \qquad (5)$$

with $S_0(0,0) = \alpha/2W'(\ell_0)$ which shows a very strong divergence as $T \to T_F^-$. The correlation length along the wedge is identified by $\xi_y \approx [\Sigma\ell_0/W'(\ell_0)]^{1/2}$. Substituting for the form of $W(\ell)$, and recalling the divergence of ℓ_0 at critical filling, leads to the desired MF result $\nu_y = 1/p + 1/2$ for the correlation length critical exponent as $T \to T_F$ at bulk coexistence. Note that $\xi_y \gg \xi_x$ so that the fluctuations are highly anisotropic and are totally dominated by modes parallel to the wedge direction. The final length scale that we calculate within the present MF/Gaussian analysis is the midpoint width $\xi_\perp$ defined by $\xi_\perp^2 \equiv \langle[\ell(0, y) - \ell_0]^2\rangle = H(0, 0; 0)$ which may be obtained from the Fourier inverse of $S(x, x'; Q)$. This leads to the intriguing relation

$$\xi_\perp \sim \sqrt{\frac{\xi_y}{\Sigma\ell_0}} , \qquad (6)$$

which is one of the central results of this paper. In this way, we are led to the remarkable prediction that the divergence of $\xi_\perp$ at critical filling is universal, independent of the range of the intermolecular forces, and of the form $\xi_\perp \sim t^{-1/4}$ which should be observable in experimental and computer simulation studies. We shall argue below that this result is not affected by fluctuation effects even when MF theory breaks down.

The first step in the development of a fluctuation theory for filling transitions is the derivation of a Ginzburg criterion. The MF analysis presented above should be valid if the fluctuations in the interfacial height are relatively small. Thus, we require $\xi_\perp/\ell_0 \ll 1$ or, equivalently, $t^{1/p - 1/4} \ll 1$, implying that MF theory, and the values of critical exponents quoted above are valid in three dimensions only for $p < 4$. For $p \geq 4$, fluctuation effects dominate, and we can anticipate that the roughness $\xi_\perp$ is comparable with the interfacial height ℓ_0. One way of approaching this problem is to formulate a renormalization group theory based on the effective Hamiltonian (1). This is an extremely difficult task and one which we believe is unnecessarily complicated. In view of the extreme anisotropy of fluctuations at filling transitions and their coherent nature across the wedge, we propose that the only fluctuations that are relevant for the asymptotic critical behavior are those arising from the thermal excitations of the midpoint height $\ell_0(y)$ along the wedge. More specifically, for a constrained nonplanar configuration for the midpoint distribution $\{\ell_0(y)\}$, we assume that all other fluctuations are small and, hence, following established methods [11], may be treated in saddle-point approximation. Thus, we are led to a simpler wedge Hamiltonian (of reduced dimensionality), $F[\ell_0(y)] = \min^\dagger H[\ell(x, y)]$ where the dagger denotes the constraint that $\ell(0, y) = \ell_0(y)\ \forall\ y$. In this way, we have derived the simpler one-dimensional model (of three-dimensional filling)

$$F[\ell_0] = \int dy\left[\frac{\Sigma\ell_0}{\alpha}\left(\frac{d\ell_0}{dy}\right)^2 + V_F(\ell_0)\right], \qquad (7)$$

where the coefficient of the gradient term is the local height dependent line tension describing the bending energy of long-wavelength fluctuations along the wedge and V_F is the effective wedge filling potential which has the general expansion

$$V_F(\ell) = \frac{\Sigma(\Theta^2 - \alpha^2)}{\alpha}\,\ell + \frac{A}{(p-1)\alpha}\,\ell^{1-p} + \dots . \tag{8}$$

Note that, in the critical regime, $[\Theta(T) - \alpha] \sim t$, so that minimization of (8) identically recovers the MF result for ℓ_0. For $p = 1$, the second term in (8) is logarithmic, while for short-ranged forces, it is exponentially small.

We propose that the effective Hamiltonian (7) contains all the essential physics associated with the asymptotic critical behavior at filling transitions. Two checks on this hypothesis are that, in MF and Gaussian approximation, the new model identically recovers the equation for the midpoint height and structure factor emerging from the more complicated model (1) in the same approximation. The great advantage of the new model is, of course, that due to its one-dimensional character it can be studied exactly using transfer-matrix techniques. The (normalized) eigenfunctions $\psi_n(\ell_0)$ and eigenvalues E_n of the spectrum are found by solving the differential equation (setting $k_B T = 1$ for convenience)

$$-\frac{\alpha\psi_n''(\ell_0)}{\Sigma\ell_0} + \frac{3\alpha\psi_n'(\ell_0)}{2\Sigma\ell_0^2} + V_F(\ell_0)\psi_n(\ell_0) = E_n\psi_n(\ell_0) \tag{9}$$

from which the quantities of interest can be calculated. In particular, the probability distribution for the midpoint height $\mathcal{P}(\ell_0) = |\psi_0(\ell_0)|^2$ and the wedge correlation length $\xi_y = 1/(E_1 - E_0)$. The solution of this eigenvalue problem for the wedge potential (8) gives a complete classification of the critical behavior at critical filling. The calculation confirms that MF theory is valid for $p < 4$ (predicting *independently* the same marginal value for p), while the criticality is fluctuation dominated for $p > 4$ and is characterized by universal critical exponents $\beta_0 = \nu_x = \nu_\perp = 1/4$ and $\nu_y = 3/4$. These exponents are pertinent to critical filling occurring in systems with short-ranged forces and may be tested in Ising model simulation studies similar to earlier work on critical wetting [5]. For experimental systems with dispersion forces ($p = 2$), our predictions are $\beta_0 = \nu_x = 1/2$, $\nu_\perp = 1/4$, and $\nu_y = 1$. We emphasize that these MF predictions are independent of our fluctuation model (7) since they follow from the full interfacial model (1).

To finish our Letter, we make three final remarks. The first concerns an important check of the general validity of our fluctuation theory. The fluctuation model (7) can be generalized to arbitrary bulk dimensions d corresponding to wedges which are translationally invariant in $d - 2$ directions. We have studied this model using functional renormalization group techniques and found two fluctuation regimes for general dimension $d < 4$. For $p < p_c \equiv 2(d-1)/(4-d)$, the critical exponent $\beta_0 = 1/p$, corresponding to MF behavior, while for $p > p_c$, the transition is fluctuation dominated and $\beta_0 = (4-d)/2(d-1)$. Importantly, for $d = 2$, these predictions correspond to the known values of the critical exponents for 2D wedge wetting found from exact transfer-matrix analysis [9] of the full interfacial model (1). Second, out of bulk two-phase coexistence $[\delta\mu \equiv \mu_{\mathrm{sat}}(T) - \mu > 0]$ and close to filling, the midpoint height, correlation lengths, and roughness show scaling behavior. For example, in the fluctuation-dominated regime, the solution of (9) shows that $\ell_0 = t^{-1/4}\Lambda(\delta\mu t^{-5/4})$ where $\Lambda(\zeta)$ is an appropriate scaling function. Thus, along the critical filling isotherm ($T = T_F$, $\delta\mu \to 0$), the height diverges as $\ell_0 \sim \delta\mu^{-1/5}$, which may be easier to observe in experimental and simulation studies. Third, the effective filling model that we have introduced can also be used to study complete filling occurring for $T > T_F$ as $\delta\mu \to 0$. However, the critical behavior here is found to be always MF like [10].

In summary, we have developed a fluctuation theory for critical effects at three-dimensional wedge wetting and given a complete classification of the possible critical behavior. We believe that these striking predictions are open to experimental verification, in wedge systems made from substrates exhibiting first-order wetting.

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