Critical Effects at 3D Wedge-Wetting

A. O. Parry, C. Rascón, A. J. Wood
Mathematics Department, Imperial College
180 Queen’s Gate, London SW7 2BZ, United Kingdom
(March 24, 2022)

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

PACS numbers: 68.45.Gd, 68.35.Rh, 68.45.-v

There are two reasons why it is extremely difficult to observe interfacial fluctuation effects at continuous (critical) wetting transitions in the laboratory. Firstly, 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 (1). Secondly, the influence of interfacial fluctuations in three dimensions ($d=3$) is believed to be rather small (2). For example, for systems with long-ranged forces, the divergence of the wetting layer thickness $\ell$ 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: $\xi_\perp \sim \sqrt{-\ln(T_w - T)}$. Non-classical critical exponents and an appreciable interfacial width are only predicted for systems with strictly short-ranged forces (3), but even here the size of the asymptotic critical regime is very small and beyond the reach of current experimental and simulation methods (3-3).

The purpose of the present article is to show that these problems do not arise for continuous (critical) filling or wedge-wetting transitions (3) occurring for fluid adsorption in three-dimensional wedges. First, we show, contrary to previous statements in the literature (3), 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 behaviour 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 vapour phase at temperature $T$ (less than the bulk critical value $T_c$) and chemical potential $\mu$. Macroscopic arguments (3) dictate that at bulk coexistence, $\mu = \mu_{\text{sat}}(T)$, 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 $T \rightarrow T_F$, $\mu \rightarrow \mu_{\text{sat}}(T_F)$ as critical filling. Also of interest is the complete filling transition which refers to the continuous divergence of the adsorption as $\mu \rightarrow \mu_{\text{sat}}(T)$ for $T_c > T \geq T_F$ which is known to be characterised by geometry dependent critical exponents (4). Here, we focus exclusively on critical filling and, in particular, the critical singularities occurring as $t \equiv (T_F - T)/T_F \rightarrow 0^+$ at bulk coexistence. The phase transition is associated with the divergence of four lengthscales (see Fig. 1) each characterised by a critical exponent: the mid-point $(x = 0)$ height of the liquid-vapour interface $\ell_0 \sim t^{-\beta_0}$, the mid-point 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 $\ell_0$ (5). On the other hand, transfer-matrix studies (3) in $d=2$ indicate that fluctuation effects are very strong at wedge-wetting and lead to universal critical exponents $\beta_0 = \nu_\perp = \nu_y = 1$. This is highly suggestive that fluctuation effects play an impor-
A planar transverse correlation length $\xi$ in the wedge geometry showing the relevant diverging length scales at the filling transition. The planar adsorption transition plays a crucial role in the wetting properties of the wall. At MF level, this functional is simply minimised to yield an exponential 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 yields $\beta_0 = 1/p$ (quoted in ref. 8) and implicit in reference 8 so that, for dispersion forces (corresponding to $p = 2$), the MF prediction is $\beta_0 = 1/2$ whilst for short-ranged forces $\beta_0 = 0(\ln)$. The structure of the MF height profile $\ell(x)$ is particularly simple near critical filling and has crucial consequences. In essence, the interface is flat (i.e., $\ell(x) \sim \ell_0$) for $|x| < \ell_0/\alpha$ whilst for $|x| > \ell_0/\alpha$, the height decays exponentially quickly to its asymptotic planar value $\ell_\pi$ 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 $\ell(x)$ as measured by the height-height correlation function $H(x, x'; y) \equiv \langle \delta \ell(x, y) \delta \ell(x', y') \rangle$ where $\delta \ell(x, y) \equiv \ell(x, y) - \langle \ell(x, y) \rangle$ and $y \equiv y' - y$. To calculate the correlation function, we first exploit the translational invariance along the wedge and introduce the structure factor

$$ S(x, x'; Q) = \int dy \, e^{iQy} H(x, x'; y). \tag{2} $$

The assumption of MF theory is that fluctuation about $\ell(x)$ are 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

$$ \left( -\Sigma \partial_x^2 + \Sigma Q^2 + W''(\ell(x) - \alpha|x|) \right) S(x, x'; Q) = \delta(x-x') \tag{3} $$

![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 transition plays a crucial role in the wetting properties of the wall. At MF level, this functional is simply minimised to yield an exponential 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 yields $\beta_0 = 1/p$ (quoted in ref. 8) and implicit in reference 8 so that, for dispersion forces (corresponding to $p = 2$), the MF prediction is $\beta_0 = 1/2$ whilst for short-ranged forces $\beta_0 = 0(\ln)$. The structure of the MF height profile $\ell(x)$ is particularly simple near critical filling and has crucial consequences. In essence, the interface is flat (i.e., $\ell(x) \sim \ell_0$) for $|x| < \ell_0/\alpha$ whilst for $|x| > \ell_0/\alpha$, the height decays exponentially quickly to its asymptotic planar value $\ell_\pi$ 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 $\ell(x)$ as measured by the height-height correlation function $H(x, x'; y) \equiv \langle \delta \ell(x, y) \delta \ell(x', y') \rangle$ where $\delta \ell(x, y) \equiv \ell(x, y) - \langle \ell(x, y) \rangle$ and $y \equiv y' - y$. To calculate the correlation function, we first exploit the translational invariance along the wedge and introduce the structure factor

$$ S(x, x'; Q) = \int dy \, e^{iQy} H(x, x'; y). \tag{2} $$

The assumption of MF theory is that fluctuation about $\ell(x)$ are 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

$$ \left( -\Sigma \partial_x^2 + \Sigma Q^2 + W''(\ell(x) - \alpha|x|) \right) S(x, x'; Q) = \delta(x-x') \tag{3} $$

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

$$S_0(x, x') = \left( |\ell(x)| - \alpha \right) \left( |\ell(x')| - \alpha \right) \times$$

$$\left\{ \frac{1}{2\alpha W'(\ell_0)} + \frac{H(x,x')}{\Sigma} \int_0^{\min(|x|,|x'|)} \frac{dx}{(\ell(x) - \alpha)^2} \right\}$$

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 $\xi_x$ 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 $\xi_y$. 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

$$S(x, x'; Q) \approx \frac{S_0(0, 0)}{1 + Q^2 \xi_y^2}, \quad |x|, |x'| \ll \xi_y/2,$$

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 $\xi_\perp \equiv (\Sigma \ell_0/W'(\ell_0))^{1/2}$. Substituting for the form of $W(\ell)$, and recalling the divergence of $\ell_0$ 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 lengthscale that we calculate within the present MF/Gaussian analysis is the mid-point 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

$$\xi_\perp \sim \sqrt{\frac{\xi_y}{\Sigma \ell_0}}$$

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.

![FIG. 2. Schematic surface phase diagram showing temperature vs. the opening angle $\alpha$ 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 $T_s$.](image)
notes 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)

\[
F[\ell_0] = \int dy \left[ \frac{\Sigma \ell_0}{\alpha} \left( \frac{df_0}{dy} \right)^2 + V_F(\ell_0) \right]
\]

(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

\[
V_F(\ell) = \frac{\Sigma(\Theta^2 - \alpha^2)}{\alpha} \ell + \frac{A}{(p-1)\alpha} \ell^{1-p} + \ldots.
\]

(8)

Note that, in the critical regime, \( (\Theta(T) - \alpha) \sim t \), so that minimisation of (7) identically recovers the MF result for \( \ell_0 \). For \( p = 1 \), the second term in (8) is logarithmic whilst for short-ranged forces, it is exponentially small.

We propose that the effective Hamiltonian (9) contains all the essential physics associated with the asymptotic critical behaviour at filling transitions. Two checks on this hypothesis are that, in MF and Gaussian approximation, the new model identically recovers the equation for the mid-point height and structure factor emerging from the more complicated model (8) 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)

\[
- \frac{\alpha \psi_n'(\ell_0)}{\Sigma \ell_0} + \frac{3 \alpha \psi_n''(\ell_0)}{2 \Sigma \ell_0^2} + V_F(\ell_0) \psi_n(\ell_0) = E_n \psi_n(\ell_0)
\]

(9)

from which the quantities of interest can be calculated. In particular, the probability distribution for the midpoint height \( P(\ell_0) = |\psi_0(\ell_0)|^2 \) 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 behaviour at critical filling. The calculation confirms that MF theory is valid for \( p < 4 \), whilst the criticality is fluctuation dominated for \( p > 4 \) and is characterised by universal critical exponents \( \beta_0 = \nu_y = \nu_\perp = 1/4 \) and \( \nu_y = 3/4 \). These exponents are pertinent to systems critical filling occurring in systems with short-ranged forces and may be tested in Ising model simulation studies similar earlier work on critical wetting (9). For experimental systems with dispersion forces \( (p = 2) \), our predictions are \( \beta_0 = \nu_\perp = 1/2, \nu_\perp = 1/4 \) and \( \nu_y = 1 \).

To finish our article, we make two final remarks. Firstly, out of bulk two-phase coexistence \( (\hat{\mu} \equiv \mu_{\text{sat}}(T) - \mu > 0) \) and close to filling, the mid-point height, correlation lengths and roughness show scaling behaviour. For example, in the fluctuation-dominated regime, the solution of (8) shows that \( \ell_0 = t^{-1/4} \Lambda(\hat{\mu} t^{-5/4}) \) where \( \Lambda(\zeta) \) is an appropriate scaling function. Thus, along the critical filling isotherm \( (T = T_F, \hat{\mu} \to 0) \), the height diverges as \( \ell_0 \sim \hat{\mu}^{-1/3} \), which may be easier to observe in experimental and simulation studies. Secondly, the effective filling model that we have introduced can also be used to study complete filling occurring for \( T > T_F \) as \( \hat{\mu} \to 0 \). The critical behaviour here is found to be MF-like \( (i.e., \xi_\perp \ll \ell_0) \) but also universal, independent of the range of the forces and is consistent with the hypothesis that the geometry of the wedge determines the critical behaviour for this transition (10). Fluctuation effects at this transition are rather less interesting than for critical filling.

In summary, we have developed a fluctuation theory for critical effects at three-dimensional wedge-wetting or filling transitions and given a complete classification of the possible critical behaviour. Fluctuations have been shown to have a much greater influence in the critical behaviour compared to that occurring for wetting transitions \( (d = 3) \) at planar surfaces and lead to a universal roughness exponent \( \nu_\perp = 1/4 \). We believe that these predictions are open to experimental verification, in wedge systems made form substrates exhibiting first-order wetting.

C.R. acknowledges economical support from the E.C. under contract ERBFMBICT983229. A.J.W. acknowledges economical support from the EPSRC.

[1] For a review, see, for example, S. Dietrich, in “Phase Transitions and Critical Phenomena”, (C. Domb and J.L. Lebowitz, eds.), Vol. 12, p. 1 (Academic Press, London, 1988).
[2] K. Ragil et al., Phys. Rev. Lett. 77, 1532 (1996).
[3] D. Ross, D. Bonn and J. Meunier, Nature 400, 737 (1999).
[4] E. Brézin, B.I. Halperin and S. Leibler, Phys. Rev. Lett. 50, 1387 (1983).
[5] K. Binder, D.P. Landau and D.M. Kroll, Phys. Rev. Lett. 56, 2272 (1986).
[6] A.O. Parry, J. Phys.: Condens. Matter, 8 10761 (1996), P.S. Swain and A.O. Parry, Europhys. Lett., 37 207 (1997).
[7] E.H. Hauge, Phys. Rev. A 46, 4994, (1992).
[8] K. Rejmer, S. Dietrich, M. Napiórkowski, Phys. Rev. E 60, (1999).
[9] A.O. Parry, C. Rascón and A.J. Wood, Phys. Rev. Lett. (to appear).
[10] C. Rascón and A.O. Parry, J. Chem. Phys. (to appear).
[11] M.E. Fisher, A.J. Jin and A.O. Parry, Ber. Bunsenges. Phys. Chem. 98, 357, (1994).