LETTER TO THE EDITOR

Critical wetting in power-law wedge geometries

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Abstract
We investigate critical wetting transitions for fluids adsorbed in wedge-like geometries where the substrate height varies as a power law, $z(x, y) \sim |x|^\gamma$, in one direction. As γ is increased from 0 to 1 the substrate shape is smoothly changed from a planar wall to a linear wedge. The continuous wetting and filling transitions pertinent to these limiting geometries are known to have distinct phase boundaries and critical singularities. We predict that the intermediate critical wetting behaviour occurring for $0 < \gamma < 1$ falls into one of *three* possible regimes depending on the values of γ, p and q. The unbinding behaviour is characterized by a high degree of non-universality, strongly anisotropic correlations and enhanced interfacial roughness. The shift in phase boundary and emergence of universal critical behaviour in the linear wedge limit are discussed in detail.

There is growing interest from theorists and experimentalists in fluid adsorption on micro-patterned and sculpted solid substrates [1–15]. Surface decoration and structure can substantially alter the character of fluid adsorption and lead to novel examples of interfacial phase transitions and enhanced fluctuation-related effects. There is also strong evidence that there are fundamental connections between geometry-induced and fluctuation-induced interfacial phenomena at wedge filling transitions [11] and also between wedge filling and unzipping transitions for double-stranded DNA [16].

The purpose of the present letter is to focus on interfacial adsorption in generalized 3D wedge-shaped geometries, which are translationally invariant in one direction (along the y-axis, say), but whose height above some reference plane varies as a power law $z(x, y) \sim |x|^\gamma$, for large distances in the x-direction. We refer to this particular class of surface geometry as the gamma wall, which may be viewed as an example of deterministic roughness [17–19]. Note that by increasing the exponent γ the wall morphology can be changed smoothly from a planar substrate ($\gamma = 0$) to a linear wedge ($\gamma = 1$) and eventually to a parallel-plate geometry ($\gamma = \infty$). The adsorption properties and interfacial fluctuation effects in

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each of these geometries, corresponding to wetting [20, 22], filling [9–11] and capillary condensation [21], respectively, are very different to each other and have attracted considerable theoretical and experimental interest. The central question that we ask here is: how do the wetting properties depend on the wall exponent γ? For substrates that are completely wetted by the fluid (corresponding to vanishing contact angle $\theta = 0$), recent work [12, 13] has shown that the adsorption isotherms for the gamma wall show a sensitive dependence on γ, which facilitate the crossover from continuous complete wetting ($\gamma = 0$) to first-order capillary condensation ($\gamma = \infty$) phenomena, through a sequence of novel interfacial behaviours, which emerge at intermediate values of γ. Here, we extend this study to the case where the (planar) substrate undergoes a continuous (critical) wetting transition at some temperature T_w and ask how the phase boundary and critical exponents characteristic of the interfacial unbinding depend on γ. As we shall show, this case is considerably more complex than the complete wetting scenario, due to the presence of large-scale interfacial fluctuation effects, which gives rise to strongly non-universal critical behaviour and distinct fluctuation regimes. Nevertheless, the critical properties characteristic of these regimes are precisely those that allow us to understand the changes in phase boundary and fluctuation-related properties that occur as the wall morphology is changed from a planar substrate ($\gamma = 0$) to a linear wedge ($\gamma = 1$).

Consider the interface between a non-planar substrate modelled as an inert spectator phase, whose height is described by a continuous function $z(x, y)$ in the shape of a generalized wedge (see figure 1), with the power-law behaviour described above. The substrate is in contact with a bulk vapour phase at temperature T and pressure p, which we will suppose is tuned to bulk two-phase coexistence $p = p_{sat}(T)$. The *planar* wall–fluid interface (corresponding to $\gamma = 0$) is taken to have a continuous wetting transition at temperature T_w, at which the contact angle $\theta(T)$ vanishes and the mean interfacial height l_π diverges. The mean-field critical singularities occurring at the wetting transition are found by minimizing the binding potential

$$W(l) = -\frac{t}{l^p} + \frac{b}{l^q}, \tag{1}$$

where $t \propto (T_w - T)/T_w$, $b > 0$ and the exponents p, $q > p$ depend on the ranges of the intermolecular forces. The critical exponents describing the divergence of the mean interfacial height $l_\pi \sim t^{-\beta_s}$, roughness $\xi_\perp \sim t^{-\nu_\perp}$ and parallel correlation length $\xi_\parallel \sim t^{-\nu_\parallel}$ are given by the well known expressions

$$\beta_s = \frac{1}{q - p}, \qquad \nu_\perp = 0(\sqrt{\log}), \qquad \nu_\parallel = \frac{(q + 2)}{2(q - p)} \tag{2}$$

and are not altered by thermal fluctuation [20, 21]. Note that the interfacial roughness $\xi_\perp$ is negligible compared to the wetting film thickness. Also, recall that the contact angle vanishes as $\theta \sim t^{(2-\alpha_s)/2}$, with $2 - \alpha_s = q/(q - p)$.

Elementary thermodynamic considerations, based on balancing bulk and surface tension contributions to the grand potential, show that the location of the surface phase boundary/wetting transition in the gamma-wall geometry depends qualitatively on the behaviour of $r = A_\gamma/A_\pi$, corresponding to the ratio of the total to planar (projected) area of the substrate. Thus, for $0 \leqslant \gamma < 1$ for which $r = 1$, the wetting phase boundary remains at $T = T_w$, whilst for $\gamma > 1$, for which $r = \infty$, the wedge is completely filled by liquid (gas) at all temperatures such that $\theta(T)$ is less (greater) than $\pi/2$. Thus, for $\gamma > 1$ the wetting transition at bulk coexistence is superseded by a first-order capillary condensation-like phenomena. This is closely related to the unbending phase transition occurring on corrugated surfaces [23]. Hereafter, we restrict our attention to the regime $\gamma \leqslant 1$ and focus on the fate of the planar wetting transition as γ is increased from 0 to 1.
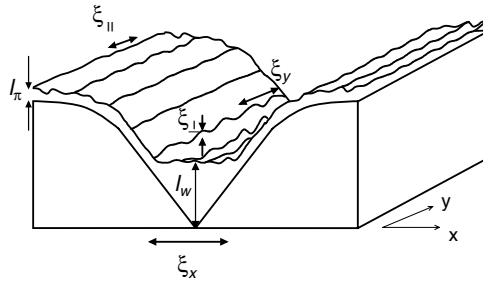
Figure 1. A schematic illustration of an interfacial configuration in a generalized wedge geometry. Diverging length scales are highlighted.

The critical behaviour occurring at the limit $\gamma = 1$, corresponding to the filling of a linear wedge, is known in some detail [9–11]. Writing the wall function $z(x, y) = \tan \alpha |x|$, with α the tilt angle, observe that the ratio $r = \sec \alpha > 1$. Accordingly, the phase boundary for the wedge wetting (filling) is shifted and again thermodynamic arguments dictate that it occurs at a lower filling temperature T_f, satisfying $\theta(T_f) = \alpha$ rather than $\theta(T) = 0$ [1]. For planar substrates that undergo critical wetting transitions, the linear wedge filling transition is also continuous, but is characterized by critical exponents distinct from those at critical wetting [10, 11]. Consider, for example, the divergence of the wedge mid-point interfacial height $l_w \sim t'^{-\beta_w}$, mid-point roughness $\xi_\perp \sim t'^{-\nu_\perp}$ and correlation length $\xi_y \sim t'^{-\nu_y}$, where the latter is measured along the wedge and $t' \propto (T_f - T)/T_f$. Calculations based on effective interfacial models show that the criticality falls into two regimes [10]. For $p < 4$ the critical exponents belong to a filling mean-field (FMF) regime with critical exponents $\beta_w = 1/p$, $\nu_\perp = 1/4$, $\nu_y = 1/2 + 1/p$, in which the roughness is much smaller than the film thickness, $\xi_\perp/l_w \ll 1$. For $p > 4$, on the other hand, there is a filling fluctuation (FFL) regime and the critical exponents take the universal values

$$\beta_w = \tfrac{1}{4}, \qquad \nu_\perp = \tfrac{1}{4}, \qquad \nu_y = \tfrac{3}{4}. \qquad (3)$$

In this regime, $\xi_\perp \sim l_w$ and the interfacial fluctuations are controlled by an effective wedge wandering exponent, so $l_w \sim \xi_\perp \sim \xi_y^\zeta$ with $\zeta = 1/3$. The universal value of $\nu_\perp$ implies that fluctuation effects, at the filling of a linear wedge, are always important and contrast sharply with those at the planar wetting transition.

With these preliminaries aside, we can now state precisely the two central questions addressed in this letter. First, we introduce critical exponents for the mid-point height, roughness and correlation length as $t \to 0$ by making the identifications

$$l_w \sim t^{-\beta(\gamma)}, \qquad \xi_\perp \sim t^{-\nu_\perp(\gamma)}, \qquad \xi_y \sim t^{-\nu_y(\gamma)}, \qquad (4)$$

where we have restricted ourselves to the (unknown) critical behaviour occurring in the range $0 < \gamma < 1$. Then, in evaluating the full dependence on γ, p and q of these critical exponents, we wish to understand two specific points:

(A) How does the critical behaviour reflect the discontinuous shift of the phase boundary from $\theta = 0$ to α as $\gamma \to 1^-$?

(B) How do the critical exponents change from their wetting to filling values? In particular, are any combinations of critical exponents continuous in this limit, allowing us to smoothly 'turn on' the fluctuation effects?

The starting point for our calculations is the interfacial Hamiltonian model

$$H[l] = \int \int dx\, dy \left[\frac{\Sigma}{2}(\nabla l)^2 + W(l - z(x, y)) \right], \tag{5}$$

where $l(x, y)$ is measured relative to the horizontal reference plane $z = 0$, Σ denotes the stiffness (surface tension) of the unbinding liquid–vapour interface and $W(l)$ is the binding potential (1). The model is only valid for substrate height functions $z(x, y)$ that have a shallow gradient $|\nabla z| \ll 1$ and thus suffices to determine the critical behaviour in the regime of interest, $0 \leqslant \gamma \leqslant 1$. The critical exponents are insensitive to the precise nature of the substrate shape near the $x = 0$ line and the power-law shape may be cut off at some appropriate short distance.

The results of our analytical and numerical studies show that the critical behaviour is strongly non-universal and depends sensitively on the values of γ, p and q. We concentrate on the interpretation of these results, making brief mention of our calculational details [24] at the end of our letter. Figure 2 shows how the critical behaviour falls into three possible categories labelled the planar mean-field (ΠMF), geometrical mean-field (GMF) and geometrical fluctuation (GFL) regimes, respectively. Within the ΠMF regime, $0 \leqslant \gamma < \gamma_1(q)$ with

$$\gamma_1(q) = \frac{2}{2 + q}, \tag{6}$$

the substrate shape does not alter the values of the wetting critical exponents and $\beta(\gamma)$, $\nu_\perp(\gamma)$ and $\nu_y(\gamma)$ are identical to β_s, $\nu_\perp$ and $\nu_\parallel$ shown in (2). For $\gamma > \gamma_1$, corresponding to the geometrical, GMF and GFL regimes, on the other hand, the wedge geometry alters the critical exponents from their planar values. In both these regimes the interfacial height diverges with a modified exponent

$$\beta(\gamma) = \frac{(2 - \alpha_s)}{2} \frac{\gamma}{(1 - \gamma)}. \tag{7}$$

Note that the critical exponent $\beta(\gamma) > \beta_s$, for $\gamma > \gamma_1$, so in the limit $t \to 0$ the mid-point height $l_w \gg l_\pi$. In figure 3 we show numerical results for the mid-point height for the case of non-retarded van der Waals forces ($p = 2$, $q = 3$) and $\gamma = 3/5$, for which we predict $\beta(3/5) = 9/4$. Notice that the initial divergence of the interfacial height is planar-like (with critical exponent $\beta_s = 1$), but crosses over to the asymptotic geometrical result as $t \to 0$. The boundary between the GMF and ΠMF regimes occurs when $\beta(\gamma_1) = \beta_s$, so there is a smooth crossover in the critical behaviour for the interfacial height at the ΠMF/GMF separatrix. The GMF and GFL regimes are distinguished from each other by the behaviour of the correlation length critical exponents $\nu_\perp(\gamma)$ and $\nu_y(\gamma)$. For $p < 4$ the GMF regime extends from γ_1 to the linear wedge limit $\gamma = 1^-$. For $p > 4$, on the other hand, the GMF regime terminates at $\gamma = \gamma_2$, where

$$\gamma_2(q, p) = \frac{2p}{q(p - 4) + 2p}. \tag{8}$$

Within the GMF regime, the roughness is still small compared to the film thickness, but is larger than in the ΠMF regime and $\nu_\perp^{GMF}(\gamma) > 0$. There is pronounced non-universality in this regime with

$$\nu_\perp^{GMF}(\gamma) = \frac{1}{4} + \frac{\beta(\gamma)}{4}\left[p - \frac{2(1 - \gamma)}{\gamma} \right] \tag{9}$$

and

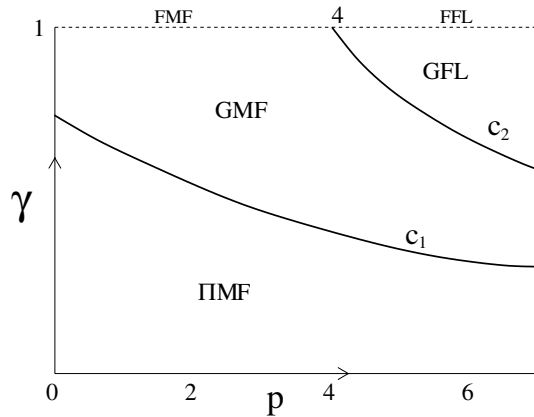$$\nu_y^{GMF}(\gamma) = \frac{1}{2} + \beta(\gamma)\left(1 + \frac{p}{2} \right). \tag{10}$$

Figure 2. Critical regimes for the gamma-wall wedge. The curves c_1 and c_2 represent the separatrixes $\gamma_1(q)$ and $\gamma_2(q, p)$, obtained for $q = p + n$, with n fixed.
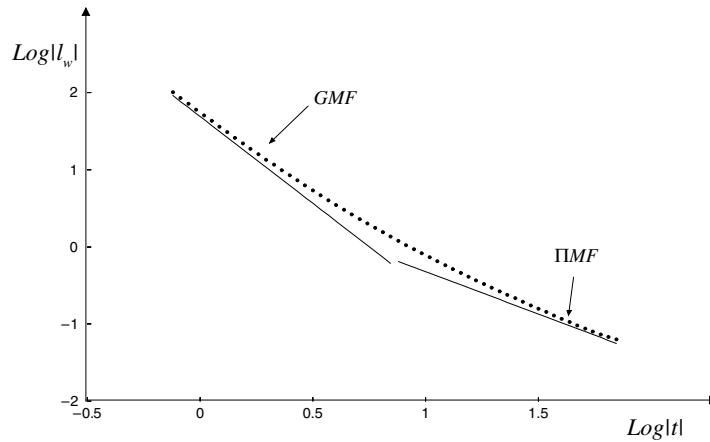

Figure 3. A log–log plot of the mid-point height ℓ_w versus t for $\gamma = 3/5$ and dispersion forces, showing crossover from planar-like (ΠMF) to GMF behaviour, with asymptotic criticality at $\beta(3/5) = 9/4$.

There is a smooth change from the ΠMF to the GMF regime for the fluctuation critical exponents, so, at the separatrix, $\nu_\perp^{\text{GMF}}(\gamma_1) = 0$. For $\gamma > \gamma_2$ (relevant for systems with $p > 4$ only), corresponding to the GFL regime, on the other hand, the wedge wetting transition in the gamma wall is fluctuation dominated and we can identify

$$\nu_\perp^{\text{GFL}} = \beta(\gamma), \qquad \nu_\perp^{\text{GFL}} = \zeta(\gamma)\nu_y^{\text{GFL}}, \tag{11}$$

where $\zeta(\gamma) = \gamma/(\gamma + 2)$ is the wedge wandering exponent for the gamma wall. Thus, in the GFL regime one has simple scaling relations between the diverging length scales, $l_w \sim \xi_\perp \sim \xi_y^{\zeta(\gamma)}$. For systems with purely short-ranged forces, the GFL regime spans the entire range $0 < \gamma < 1$ and $\beta(\gamma) = \nu_\parallel \gamma/(1 - \gamma)$.

Returning to the more general case, observe again that there is a smooth crossover between the behaviour of the fluctuation critical exponents at the separatrix between the GMF and GFL regimes with, for example, $\nu_\perp^{\text{GMF}}(\gamma_2) = \beta(\gamma_2)$. The geometrical regimes are also characterized by a strong degree of anisotropy, with the correlation length ξ_y much greater than the lateral

extent of the filled region $\xi_x \sim l_w^{1/\gamma}$. Interfacial fluctuations within the GMF and GFL regimes are pseudo-one-dimensional, in contrast with those in the ΠMF regime.

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

(I) The existence of three fluctuation regimes for critical wetting in the generalized wedge geometry contrasts with the case of complete wetting [12, 13], for which there are only two and no significant enhancement of fluctuation effects. Intriguingly, the numbers of regimes for critical and complete wetting in the gamma-wall wedge are the same as the numbers of regimes induced by thermal (or impurity-induced) fluctuation effects at planar critical and complete wetting transitions, respectively [21].

(II) In the geometry-affected regimes (GMF and GFL), the equilibrium profile $l_{eq}(x)$ has a particularly simple structure which can be seen to directly lead to the critical exponent identification (7). Near the centre of the wedge, the interface is flat and at nearly constant height $l_{eq}(x) \sim l_w$. At some distance $\xi_x \sim l_w^{1/\gamma}$, the interface strikes the wall and thereafter closely follows its shape. The interfacial height at the wedge mid-point is determined by the simple condition that the local angle of incidence between the interface and wall is equal to the contact angle. Observe that, as $\gamma \to 1^-$, the critical exponent for the interfacial height diverges. Including amplitude factors, we find that the mid-point height diverges as $l_w \sim (t_w/t)^{\beta(\gamma)}$, with t_w a non-universal constant. As $\gamma \to 1^-$ this implies that the height becomes macroscopic for all $t < t_w$, which represents a shift of the phase boundary from $t = 0$ to t_w. This is equivalent to the shift of the phase boundary from $\theta = 0$ to α for linear wedge filling and answers our first question (A).

(III) Some aspects of the interfacial fluctuations show a smooth change from wetting to filling-like behaviour, as γ is increased, and allow us to give a quantitative answer to question (B). This is most simply seen in the wedge wandering exponent $\zeta(\gamma) = \gamma/(\gamma + 2)$ pertinent to the GFL regime, which generalizes the linear wedge result $\zeta = 1/3$. Less obvious is the behaviour of the critical exponent ratio $\beta(\gamma)/\nu_\perp(\gamma)$, which also recovers the linear wedge result, such that

$$\lim_{\gamma \to 1^-} \frac{\beta(\gamma)}{\nu_\perp(\gamma)} = \frac{\beta_w}{\nu_\perp}, \tag{12}$$

where the RHS is equal to $4/p$ and 1 for $p < 4$ and $p > 4$, respectively.

For systems with non-retarded van der Waals forces (i.e. with binding potential exponents $p = 2$, $q = 3$) we make the following predictions. The planar result pertinent to the standard critical wetting transition $\beta_s = 1$, $\nu_\perp = 0$ and $\nu_\parallel = 5/2$ are unchanged within a ΠMF regime corresponding to $0 < \gamma < 2/5$. For $1 > \gamma > 2/5$ the transition belongs to the GMF and the critical exponents are geometry sensitive. For example, at $\gamma = 1/2$ we predict

$$\beta(1/2) = \tfrac{3}{2}, \qquad \nu_\perp(1/2) = \tfrac{1}{4}, \qquad \nu_y(1/2) = \tfrac{7}{2}. \tag{13}$$

The value of the roughness critical exponent $\nu_\perp(1/2) = 1/4$ is significant, since it is *independent* of the value of q and is therefore also valid for tricritical wetting. This degree of universality is similar to the true universality of $\nu_\perp$ predicted for linear wedge filling.

To finish, we make brief mention of the methods used in our calculations. In both the ΠMF and GMF regimes the roughness is much smaller than the interfacial height and mean-field methods are appropriate. Numerical results obtained by minimizing (5) are complemented by analytical approaches following approximate solutions to the Euler–Lagrange equation, based on standard variational methods. This is straightforward in the GMF regime, since the profile has a particularly simple structure. The results for the correlation length critical exponent ν_y and roughness exponent $\nu_\perp$ were first obtained by solving the Ornstein–Zernike

equation for the structure factor $S(Q)$, corresponding to the Fourier transform of the mid-point height–height correlation function $\langle l(y_1)l(y_2)\rangle$ with respect to wavevectors along the wedge. The critical behaviour in the GMF and GFL regimes can also be described using an effective one-dimensional model Hamiltonian $H_\gamma[l]$, which describes the energy cost of constrained interfacial configurations in terms of the mid-point height $l(y) = l(x = 0, y)$ only. The model can be derived from the underlying interfacial model (5) using standard methods, which have been previously applied to the linear wedge problem [10]. The dimensional reduction, explicit in this method, is justified by the extreme anisotropy of fluctuations in the GMF and GFL regimes as $t \to 0$.

The reduced dimensional effective interfacial Hamiltonian has the form

$$H_\gamma[l] = \int \mathrm{d}y \left[\sigma l^{1/\gamma} \left(\frac{\mathrm{d}y}{\mathrm{d}l} \right)^2 + V_\gamma(l) \right], \tag{14}$$

where σ is a non-universal constant (proportional to Σ) and $V_\gamma(l)$ is the wedge binding potential. Minimization of $V_\gamma(l)$ identically recovers the mean-field expression for l_w in the ΠMF and GMF regimes. For large l this has the expansion

$$V_\gamma(l) \propto l^{1/\gamma} [(\theta^2 - c_\gamma l^{2(1-\gamma)/\gamma}) + d_\gamma l^{-p}], \tag{15}$$

where c_γ and d_γ are non-universal constants. In the limit $\gamma \to 1^-$, we find $c_\gamma \to \alpha^2$ and $d_\gamma \to t/(p-1)$, so both $V_\gamma(l)$ and (14) smoothly recover the linear wedge model considered in [10]. From the one-dimensional model it is straightforward to derive all the critical exponents quoted earlier using standard methods.

In summary, we have investigated the geometry dependence of critical wetting exponents for fluids adsorbed in power-law wedges. Our results show that surface shape has both a stronger (and subtler) effect on critical wetting than complete wetting transitions, with criticality falling into three possible regimes which facilitate the crossover from planar wetting to linear wedge filling.

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