Universality for 2D Wedge Wetting

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We study 2D wedge wetting using a continuum interfacial Hamiltonian model which is solved by transfer-matrix methods. For arbitrary binding potentials, we are able to exactly calculate the wedge free energy and interface height distribution function and, thus, can completely classify all types of critical behavior. We show that critical filling is characterized by strongly universal fluctuation dominated critical exponents, while complete filling is determined by the geometry rather than fluctuation effects. Related phenomena for interface depinning from defect lines in the bulk are also considered.

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At present, experimental methods allow the shape of solid surfaces to be controlled at a nanoscopic level [1]. Fluids confined by such structured substrates can exhibit quite distinct adsorption characteristics compared to that occurring for planar systems [2]. This includes new types of interfacial phase transitions and critical phenomena which are not only of fundamental interest but may well play an important role in developing technologies such as super-repellent surfaces [3], self-assembly of three-dimensional structures [4], or microfluidics [5], among others [6]. An interesting example of these phenomena which has recently attracted new interest is the so-called *filling* or wedge wetting transition of a fluid adsorbed in a wedge [7,8], formed by the junction of two flat walls tilted at angles $\pm\alpha$ to the horizontal as shown in Fig. 1. Thermodynamic arguments predict that a wedge-gas interface is completely filled by a liquid phase (at bulk liquid-gas coexistence) for temperatures $T > T_\alpha$, where the filling temperature T_α is lower than the wetting temperature T_w of the planar ($\alpha = 0$) wall [9]. In fact, according to these macroscopic arguments, the location of the filling transition phase boundary is beautifully expressed in terms of the contact angle $\Theta_\pi(T)$ of the liquid drop on the planar substrate [9],

$$\Theta_\pi(T) = \alpha\,. \tag{1}$$

Thus, the liquid completely wets the wedge when the contact angle is smaller than the tilted angle α. Interestingly, this macroscopic result was predicted and confirmed experimentally [10] eight years before the seminal paper by Cahn on wetting in planar surfaces [11].

Recently, the macroscopic prediction (1) has been supported by mean-field analysis of a model system which also suggests that the qualitative order of the filling transition (first-order or continuous) follows that of the planar wetting transition [7]. Thus, for planar substrates exhibiting critical wetting transitions, the wedge offers two new examples of interfacial-like critical phenomena in which the interface height ℓ_0 (measured from the bottom of the wedge) diverges as the temperature and chemical potential are varied. Borrowing from the vocabulary used for wetting, we refer to the wedge filling transition occurring as $T \to T_\alpha^-$ (at bulk coexistence) as *critical filling*. In contrast, by *complete filling*, we refer to the divergence of ℓ_0 for temperatures $T > T_\alpha$ as the bulk chemical potential μ is increased towards saturation $\mu_{\rm sat}(T)$. However, apart from a few limited results available for the corner wetting transitions (corresponding to $\alpha = \pi/4$ and restricted to short range forces) [12], there has been no discussion in the literature of fluctuation effects, scaling regimes and universality classes for such filling transitions and how these compare with the rich phenomenology known for wetting [13]. With this aim in mind, we have studied an effective interfacial Hamiltonian model of filling in (bulk) dimension $d = 2$ and derived exact elegant results for various quantities of interest such as the excess wedge free energy and the probability distribution for the interface height. The formal analysis can be carried through for *arbitrary* choices of binding potential (i.e., all range of forces) allowing a complete classification of the critical behavior and the identification of universality classes. We will show that both critical and complete filling transitions are characterized by universal critical exponents independent of the intermolecular forces (unless they are unphysically long ranged). Interestingly, while the universality of the

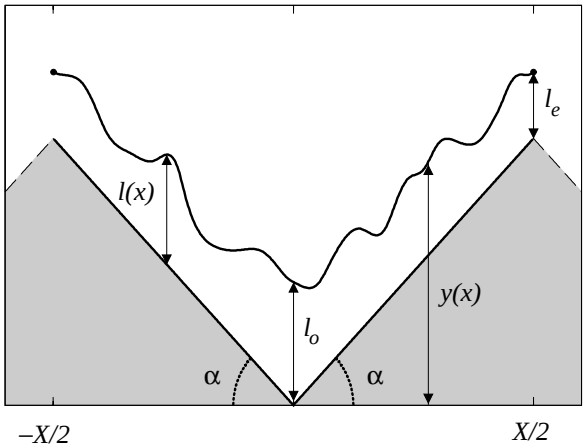

FIG. 1. Schematic illustration of an interface configuration $y(x)$ in the wedge geometry. The function $\ell(x)$ denotes the local distance to the wall. Other notation is defined in the text.

critical filling transition arises directly as a consequence of strong fluctuation effects, the universality encountered at complete filling has a geometrical and thermodynamic origin which is correctly captured by mean-field theory. In addition to this, we are able to verify the validity of the thermodynamic prediction (1) and also predict very similar phenomena occurring when interfaces are pinned in the bulk along a bent line of weakened bonds.

To begin, we introduce our model. We denote the local height of the liquid-gas interface relative to the horizontal by $y(x)$ and the height of the wall itself by $z(x) \equiv \alpha|x|$. The relative local height between the two is written $\ell(x) \equiv y(x) - z(x)$. The horizontal dimension of the wall/interface extends over the range $[-X/2, X/2]$ and periodic boundary conditions are applied at the ends; i.e., all configurations satisfy $y(X/2) = y(-X/2)$ (see Fig. 1). The interface interacts with the wall via a binding potential arising due to intermolecular wall-fluid and fluid-fluid forces and is also subject to thermal fluctuations governed by the stiffness Σ. We will concentrate on continuum wall-fluid systems and identify the stiffness Σ with the surface tension. We also set $k_B T = 1$ for convenience. For rather open edges, it is already known from earlier mean-field studies that the filling transitions are well described by the simple interfacial model

$$H[y] = \int_{-X/2}^{X/2} dx \left[\frac{\Sigma}{2} \left(\frac{dy}{dx} \right)^2 + W(y - z) \right], \quad (2)$$

which can be justified from analysis of a more general nonlinear model in the small angle α limit [7]. Before we outline our calculation and present our main results, we make some preliminary remarks which serve to establish our notation and also provide some points of comparison. These concern the *planar* limit $\alpha = 0$. For this case, it is well known that the partition function $Z_\pi(\ell_1, \ell_2; X)$ corresponding to the planar fluctuation sum with fixed boundary conditions $\ell(-X/2) = \ell_1$ and $\ell(X/2) = \ell_2$ is given by the spectral sum (or integral if scattering states are present) [14]

$$Z_\pi(\ell_1, \ell_2; X) = \sum_{n=0}^{\infty} \psi_n^*(\ell_1) \psi_n(\ell_2) e^{-E_n X}, \quad (3)$$

where the eigenfunctions and eigenvalues satisfy the Schrödinger equation

$$-\frac{1}{2\Sigma} \psi_n'' + W(\ell)\psi_n = E_n \psi_n . \quad (4)$$

Thus, in the thermodynamic limit $X \to \infty$, the excess free energy is given by E_0 which is in turn related to the contact angle [defined only for $T < T_w$ and $\mu = \mu_{\rm sat}(T)$] by $E_0 = -\Sigma \Theta_\pi^2/2$, valid for small angles Θ_π described by the interfacial model. Similarly, the normalized probability distribution for the interface height is $\mathcal{P}_\pi(\ell) \equiv |\psi_0(\ell)|^2$. For later purposes, it is also convenient to define the matrix elements

$$\langle m|f(\ell)|n\rangle \equiv \int d\ell\, \psi_m^*(\ell) f(\ell) \psi_n(\ell) . \quad (5)$$

These will appear in our solutions for the wedge free-energy and probability distribution function. The binding potentials that we consider are of the usual form [15]

$$W(\ell) = \bar{h}\ell + \frac{a}{\ell^p} + \frac{b}{\ell^q}; \qquad \ell > 0 , \quad (6)$$

with $\bar{h} \propto (\mu_{\rm sat} - \mu)$, a and b are effective Hamaker constants and $q > p > 0$ allow for general types of intermolecular potentials. Now, recall that for two-dimensional critical wetting transitions, the critical behavior generically belongs to one of three scaling regimes depending on the values of p and q. Specifically, for $q > p > 2$, $p < 2$ but $q > 2$ and, finally, $p < q < 2$, the behavior falls into the strong, weak, and mean-field fluctuation regimes with true universality only characteristic of the former [13]. For example, the mean interface height $\langle \ell \rangle_\pi \sim (T_w - T)^{-\beta_s}$ diverges with critical exponents $\beta_s = 1$, $\beta_s = 1/(2 - p)$, and $\beta_s = 1/(q - p)$ in the three regimes, respectively. For complete wetting, corresponding to $\bar{h} \to 0$ for $T > T_w$, there are only the weak and mean-field fluctuation regimes, and the interface height diverges as $\langle \ell \rangle_\pi \sim \bar{h}^{-1/3}$ and $\langle \ell \rangle_\pi \sim \bar{h}^{-1/(p+1)}$, respectively. These remarks will serve to illustrate how different the critical behavior at wedge filling is to standard planar wetting transitions.

We now turn our attention to the wedge geometry and outline the calculation of the partition function $Z^P_{\rm wedge}(X)$ for the present periodic system. The advantage of this choice of boundary conditions is that it allows us to extract the excess wedge free energy $F_{\rm wedge}(\alpha)$ rather easily from $F^P_{\rm wedge}(X) = -\ln Z^P_{\rm wedge}(X)$. To see this, note that in the thermodynamic limit $X \to \infty$, the periodic system reduces to two independent wedges because one must also consider the contribution from the (inverted) wedge at $x = \pm X/2$ characterized by an angle $-\alpha$. First, from $F^P_{\rm wedge}(X)$ we subtract the free energy $F^P_\pi(X)$ of a planar system (with periodic boundary conditions) extending on the same area, i.e., a flat wall tilted an angle α to the horizontal. This can be easily calculated with the same Hamiltonian, Eq. (2), but with $z(x) = \alpha x$ (for all x in the range $-X/2 < x < X/2$). This defines the excess periodic wedge free energy

$$\Delta F^P_{\rm wedge}(X) \equiv F^P_{\rm wedge}(X) - F^P_\pi(X) . \quad (7)$$

Thus, in the thermodynamic limit, we can write

$$\lim_{X\to\infty} \Delta F^P_{\rm wedge}(X) = F_{\rm wedge}(\alpha) - F_{\rm wedge}(-\alpha) , \quad (8)$$

illustrating the independent contributions from the wedge and inverted wedge. The partition function $Z^P_{\rm wedge}(X)$ is given by the fluctuation sum over all graphs $y(x)$ or, equivalently, over all relative positions $\ell(x) \equiv y(x) - z(x)$. Making this change of variable, we can rewrite the

energy, Eq. (2), of a configuration as

$$\tilde{H}[\ell] = \frac{\Sigma}{2}\,\alpha^2 X + 2\Sigma\alpha(\ell_0 - \ell_e) + \int_{-X/2}^{X/2} dx \left[\frac{\Sigma}{2}\left(\frac{d\ell}{dx}\right)^2 + W(\ell)\right],$$

where $\ell_0 \equiv y(0)$ and $\ell_e \equiv y(|X/2|) - z(|X/2|)$ are the midpoint and edge (relative) interface heights. Consequently,

$$Z^P_{\text{wedge}}(X) = e^{-\Sigma\alpha^2 X/2} \int\int d\ell_0\, d\ell_e\, Z_\pi\left(\ell_e, \ell_0; \frac{X}{2}\right) \times e^{2\Sigma\alpha(\ell_e-\ell_0)} Z_\pi\left(\ell_0, \ell_e; \frac{X}{2}\right).$$

Substituting the quantum mechanical result, Eq. (3), and taking the thermodynamic limit, we arrive at the general formula for the wedge free energy, valid for *all* binding potentials,

$$F_{\text{wedge}}(\alpha) = -\ln\langle 0|e^{2\Sigma\alpha\ell}|0\rangle, \tag{9}$$

where the inner product is defined in terms of the usual planar system eigen functions [see Eq. (5)]. Proceeding in this way, it is also possible to calculate the probability distribution $\mathcal{P}(\ell; x)$ for finding the interface at height ℓ from the wall at a distance x along it. We omit details and simply quote our final result obtained in the thermodynamic limit [16],

$$\mathcal{P}(\ell; x) = \sum_{n=0}^{\infty} \frac{\langle n|e^{2\Sigma\alpha\ell}|0\rangle \psi_n^*(\ell)\psi_0(\ell) e^{-(E_n - E_0)|x|}}{\langle 0|e^{2\Sigma\alpha\ell}|0\rangle}. \tag{10}$$

Note that, since the thermodynamic limit is taken first (at finite x), this result pertains to a single wedge system. There is no contribution due to the inverted wedge at $x = \pm X/2$. For the probability distribution of the inverted wedge, one simply reverses the sign of α and replaces $|x|$ by $|x - X/2|$. Note that when $\alpha = 0$, the wedge free energy vanishes and the probability distribution reduces to the standard planar result $\mathcal{P}_\pi(\ell)$. In addition, for $\alpha \neq 0$, only the $n = 0$ term survives in the limit $X \to \infty$ so that $\mathcal{P}(\ell; x) \to \mathcal{P}_\pi(\ell)$ infinitely far from the wedge bottom. The expression for the probability distribution simplifies considerably if we consider the local height probability at the midpoint $x = 0$. Writing $\mathcal{P}(\ell_0) \equiv \mathcal{P}(\ell; 0)$, we find

$$\mathcal{P}(\ell_0) = \frac{|\psi_0|^2 e^{2\Sigma\alpha\ell_0}}{\langle 0|e^{2\Sigma\alpha\ell}|0\rangle}, \tag{11}$$

which is one of the central results of our paper. We note that both Eqs. (9) and (10) are consistent since from the Hamiltonian definition the mean midpoint interface height satisfies $2\Sigma\langle\ell_0\rangle = -\partial F_{\text{wedge}}(\alpha)/\partial\alpha$. It is also possible to expand $\mathcal{P}(\ell; x)$ for small x and derive further explicit results which allow the calculation of the curvature of various local operators at $x = 0$. In the present paper, however, we simply concentrate on the properties of the wedge free energy $F_{\text{wedge}}(\alpha)$ and midpoint height distribution [16]. The essential observation to make here is that, relative to the planar distribution function $\mathcal{P}_\pi(\ell)$, the midpoint height probability $\mathcal{P}(\ell_0)$ has an exponential boost factor $e^{2\Sigma\alpha\ell}$ which decreases the pinning effect of the binding potential (provided $\alpha > 0$, of course). Because of this exponential term, the location (phase boundary) and character of the filling transition can immediately be traced to the asymptotics of the planar ground state wave function $\psi_0(\ell)$. If the decay of this function is too slow, the wedge distribution $\mathcal{P}(\ell_0)$ is no longer defined and the wedge is filled with liquid. Now, for bulk coexistence ($\bar{h} = 0$) and subwetting temperature ($T < T_w$), the asymptotic decay of $\psi_0(\ell)$ has the same functional form for all potentials of the form (4),

$$\psi_0(\ell) \sim e^{-\Sigma\Theta_\pi(T)\ell}; \qquad \bar{h} = 0, \quad T < T_w, \qquad \ell \to \infty, \tag{12}$$

where the specific p and q dependence only enters implicitly through the temperature dependence of the contact angle $\Theta_\pi(T) = \sqrt{2|E_0|/\Sigma}$. Thus, the location of the wedge filling transition within the present model exactly matches with the thermodynamic prediction, Eq. (1). Moreover, since $\Theta_\pi(T)$ is analytic away from T_w, we may identify $|\Theta_\pi(T) - \alpha| \propto T_\alpha - T$ and derive the universal critical singularities for critical filling

$$F_{\text{wedge}}(\alpha) \simeq \ln(T_\alpha - T), \qquad \langle\ell_0\rangle \sim (T_\alpha - T)^{-1}, \tag{13}$$

valid for *all* intermolecular forces (provided $p > 1$). Therefore, the universality of the critical wedge filling transition far exceeds that encountered at critical wetting, and is ubiquitous to all realistic solid-fluid interfaces. We also note that the transition is fluctuation dominated since the midpoint roughness $\xi_\perp \equiv \sqrt{\langle\ell_0^2\rangle - \langle\ell_0\rangle^2}$ also diverges with the same power law. The universality of the critical exponents for critical filling is one of the central predictions of our paper, and can be traced to the large scale interfacial fluctuation occurring at the bottom of the wedge. In contrast, mean-field calculations which ignore fluctuation effects predict highly nonuniversal critical behavior for critical filling. For example, minimization of the Hamiltonian, Eq. (2), leads to the prediction that the midpoint height diverges like $\langle\ell_0\rangle \sim (T_\alpha - T)^{-1/p}$ [16]. In $d = 2$, this prediction is valid only for systems with $p < 1$ which do not correspond to any known physical forces.

Next, we turn our attention to complete filling occurring for $\bar{h} \to 0$ and $T > T_\alpha$. For $\bar{h} \neq 0$, the asymptotic decay of $\psi_0(\ell)$ is faster than exponential due to the divergent linear term in $W(\ell)$. This dominates the midpoint probability function $\mathcal{P}(\ell_0)$ at large distances and ensures that the wedge is only partially filled when the system is out of bulk two-phase coexistence. The singularity arising in the evaluation of the wedge free energy and mean height $\langle\ell_0\rangle$ can be calculated using standard techniques.

For the mean height $\langle \ell_0 \rangle$, we find that the leading order behavior as $\bar{h} \to 0$ is

$$\langle \ell_0 \rangle = \begin{cases} \frac{\Sigma}{2} \frac{[\alpha^2 - \Theta_\pi^2(T)]}{\bar{h}}, & T_\alpha < T \leq T_w, \\ \frac{\Sigma \alpha^2}{2\bar{h}}, & T > T_w, \end{cases} \tag{14}$$

which is again independent of the intermolecular potential exponents p and q. In fact, these results are identical to those derived in the mean-field analysis of Rejmer *et al.* [7] equivalent to a simple minimization of the Hamiltonian (2). Thus, the universality of the complete filling exponents has a geometrical and thermodynamic origin rather than being a fluctuation related effect. We mention here that the prediction (14) for the case $T > T_w$ is consistent with earlier solid-on-solid model calculations of complete wetting at a corner [12]. In the light of these transfer-matrix and mean-field results, we conjecture that the critical singularities occurring at complete filling are of the form (14), independent of the dimensionality.

To conclude, we mention that very similar phenomena also occur for interface pinning in the bulk. Recall that an interface is always pinned along a straight line of weakened bonds, with depinning only occurring as the strength of the bonds approaches the bulk value [13]. However, this is not the case if the line of weakened bonds has a bend in it, as can be seen from the present transfer-matrix analysis. To model this system, we use the same function $z(x) = \alpha|x|$ to describe the local height of the line of weakened bonds but with a square-well potential of depth U and range $R/2$, chosen to mimic the local energy cost due to the bond weakness (restricting ourselves to systems with short-ranged forces). While in the planar system ($\alpha = 0$) the interface has equal probability of being found above and below the line, the bend at $x = 0$ breaks the symmetry and significantly enhances the probability of finding the interface above the line of weakened bonds. In fact, the interface unbinds and depins from the defect line at a nonzero value of the weakness parameter U_α satisfying $E_0(U_\alpha) = \Sigma\alpha^2/2$ where E_0 is the ground state energy of the square-well potential trivially found from solution of Eq. (4).

In summary, we have shown through exact transfer-matrix calculation that critical filling of liquid in a 2D wedge is characterized by strongly universal critical behavior. While critical filling is dominated by fluctuations, these do not affect complete filling which depends solely on the system geometry and whose critical behavior is correctly captured by mean-field theory. Similar behavior is expected for the 3D wedge. We also point out similar behavior occurring at defect lines in the bulk.

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