Crossover scaling of apparent first-order wetting in two-dimensional systems with short-ranged forces

Andrew O. Parry
Department of Mathematics, Imperial College London, London SW7 2B7, United Kingdom

Alexandr Malijevský
Department of Physical Chemistry, University of Chemical Technology Prague, Praha 6, 166 28, Czech Republic
and Institute of Chemical Process Fundamentals of the Czech Academy of Sciences, v.v.i., 165 02 Prague 6, Czech Republic

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Recent analyses of wetting in the semi-infinite two-dimensional Ising model, extended to include both a surface coupling enhancement and a surface field, have shown that the wetting transition may be effectively first-order and that surprisingly the surface susceptibility develops a divergence described by an anomalous exponent with value $\gamma_{11}^{\rm eff} = \frac{3}{2}$. We reproduce these results using an interfacial Hamiltonian model making a connection with previous studies of two-dimensional wetting, and we show that they follow from the simple crossover scaling of the singular contribution to the surface free-energy, which describes the change from apparent first-order to continuous (critical) wetting due to interfacial tunneling. The crossover scaling functions are calculated explicitly within both the strong-fluctuation and intermediate-fluctuation regimes, and they determine uniquely and more generally the value of $\gamma_{11}^{\rm eff}$, which is nonuniversal for the latter regime. The location and the rounding of a line of pseudo-prewetting transitions occurring above the wetting temperature and off bulk coexistence, together with the crossover scaling of the parallel correlation length, are also discussed in detail.

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I. INTRODUCTION

Abraham's exact solution of the semi-infinite planar Ising model showed a wetting transition that was continuous and strictly second-order, i.e., the surface specific-heat exponent takes the value $\alpha_s = 0$ [1]. Subsequent studies based on interfacial Hamiltonian models and also random-walk arguments gave strong support that this is the general result for two-dimensional (2D) wetting in systems with short-ranged forces, and it describes a universality class, referred to as the strong-fluctuation (SFL) regime [2–4]. In particular, renormalization-group analyses of interfacial models show that for systems with strictly short-ranged forces, the flow is described by only two nontrivial fixed points describing a bound phase (characterizing the SFL regime) and an unbound phase, respectively [5,6]. While first-order wetting transitions are possible in two dimensions, they require the presence of sufficiently long-ranged intermolecular forces [7–9]. However, very recently exact and numerical studies of the wetting transition in the Ising model, but now including an additional short-ranged field representing the enhancement of the surface coupling constant, have shown that the wetting transition is effectively first-order when the coupling constant is large [10]. This enhancement of the surface coupling, which acts in addition to a surface field, is similar to the well-known mechanism that drives wetting transitions first-order in mean-field treatments of Ising and lattice-gas models [11]. What is most surprising here is that it was observed that upon approaching the wetting temperature, the surface susceptibility and specific heat appear to diverge and are characterized by an anomalous exponent equal to $3/2$ before saturating to a very large finite value. In this paper, we place these results within the more general theory of 2D wetting based on interfacial Hamiltonians, and we show that they are consistent with a simple scaling theory for the crossover from apparent first-order to critical wetting within both the SFL and intermediate fluctuation scaling regimes—these are the regimes in which the interface has to tunnel through a potential barrier in order to unbind from the wall. We also discuss the location and rounding of a line of pseudo-prewetting transitions occurring above the wetting temperature, which serves to emphasize the effective first-order nature of the wetting transition.

II. SCALING AND FLUCTUATION REGIMES FOR 2D CRITICAL WETTING

Background: The fluctuation theory of wetting transitions, particularly those occurring in 2D systems, was successfully developed several decades ago; see, for example, the excellent and comprehensive review articles in Refs. [2–4]. Wetting transitions refer to the change from partial wetting (finite contact angle) to complete wetting (zero contact angle), which occurs at a wetting temperature T_w. Viewed in the grand-canonical ensemble, the wetting transition, occurring, say, at a wall-gas interface, is associated with the change from microscopic to macroscopic adsorption of liquid as $T \to T_w^-$ at bulk coexistence. The transition is therefore equivalent to the unbinding of the liquid-gas interface, whose thermal fluctuations are resisted by the surface tension σ. The transition may be first-order or continuous (often termed critical wetting), as identified from the vanishing of the singular contribution to the wall-gas surface tension $\sigma_{\rm sing} \equiv \sigma(\cos\theta - 1) \propto -(T_w - T)^{2-\alpha_s}$. Thus in standard Ehrenfest classification, the value $\alpha_s = 1$ corresponds to first-order wetting and is usually associated with the abrupt divergence of the equilibrium adsorption (proportional to the wetting film thickness $\langle \ell \rangle$) as $T \to T_w^-$. In three dimensions, the transition is also associated with a prewetting line of thin-thick

transitions extending above T_w and off coexistence, which terminates at a prewetting critical point. For critical wetting the exponent $\alpha_s < 1$, and we need to introduce additional critical exponents for the film thickness, $\langle \ell \rangle \propto (T_w - T)^{-\beta_s}$, and parallel correlation length, $\xi_\parallel \propto (T_w - T)^{-\nu_\parallel}$, which diverge continuously upon approaching the transition. In the near vicinity of the transition, the free-energy shows scaling $\sigma_{\rm sing} = t^{2-\alpha_s} W(ht^{-\Delta_s})$, where $t \propto (T_w - T)$ and h (measuring the bulk ordering field or deviation from liquid-gas coexistence) are the two relevant scaling fields for critical wetting. Here $W(x)$ is a scaling function, Δ_s is the surface gap exponent, and we have suppressed metric factors for the moment. As is well known, the scaling of the free energy is a powerful constraint on the critical singularities. For example, it follows that the exponents satisfy standard relations such as the Rushbrooke-like equality $2 - \alpha_s = 2\nu_\parallel - 2\beta_s$. With the additional assumption of hyperscaling, which in two dimensions implies $2 - \alpha_s = \nu_\parallel$, the gap exponent follows as $\Delta_s = 3\nu_\parallel/2$ leaving just one exponent undetermined. Random-walk arguments go further, and for short-ranged forces they determine uniquely the values of the critical singularities at critical wetting in terms of the interfacial wandering exponent for a free interface [2]. For pure systems with thermal disorder, this determines $\alpha_s = 0, \beta_s = 1$, and $\nu_\parallel = 2$ (and hence $\Delta_s = 3$) in keeping with Abraham's exact Ising model results. More recently, studies of fluid adsorption in other geometries, in particular wedge filling, have revealed a number of unexpected geometry-invariant properties of wetting [12] whose microscopic origins have been illuminated by very powerful field theoretic formulations of phase separation [13]. Finally, we note that scaling theories pertinent to first-order wetting transitions have also been developed and used in particular to analyze the critical singularities associated with the line tension [14,15]. We shall return to this later.

These remarks are completely supported by analyses of wetting based on interfacial Hamiltonians, which have been used extensively and very successfully to determine the specific values of the critical exponents and their more general dependence on the range of the intermolecular forces present [16]. In two dimensions, the energy cost of an interfacial configuration can be described by the mesoscopic continuum model

$$H[\ell] = \int dx \left[\frac{\Sigma}{2} \left(\frac{dl}{dx} \right)^2 + V(\ell) \right], \tag{1}$$

where $\ell(x)$ is a collective coordinate representing the local height of the liquid-gas interface above the wall. Here Σ is the stiffness coefficient, equivalent to the tension σ for isotropic fluid interfaces, while $V(\ell)$ is the binding potential, which models the direct interaction of the interface with the wall arising from intermolecular forces. The binding potential $V(\ell)$ can be thought of as describing the underlying bare or mean-field wetting transition that would occur if the stiffness were infinite and interfacial fluctuation effects are suppressed. To account for fluctuations, it is necessary to evaluate the partition function for the model (1). In two dimensions, the scaling properties of the interfacial roughness are insensitive to the choice of microscopic cutoff, which is reflected by a universal (not depending on microscopic details) relation between the roughness and the parallel correlation length. With an "infinite momentum" cutoff, the evaluation of the partition function Z is then particularly straightforward since it is equivalent to a path integral, and we can immediately write [17,18]

$$Z(\ell, \ell'; L) = \sum_n \psi_n^*(\ell) \psi_n(\ell') e^{-\beta E_n L}, \tag{2}$$

where $\beta = 1/k_B T$, L is the lateral extent of the systems, while ℓ, ℓ' are the end-point interfacial heights. Here ψ_n and E_n are the eigenfunctions and eigenvalues of the continuum transfer matrix, which takes the form of the Schrödinger-like equation [19]

$$-\frac{1}{2\beta^2 \Sigma} \psi_n''(\ell) + V(\ell)\psi_n(\ell) = E_n \psi_n(\ell). \tag{3}$$

In the thermodynamic limit ($L \to \infty$) of an infinitely long wall, the ground state identifies the singular contribution to the wall-gas surface tension $\sigma_{\rm sing} = E_0$, and the probability distribution for the interface position follows as $P(\ell) = |\psi_0(\ell)|^2$. Similarly, the parallel correlation length describing the decay of the height-height correlation function along the wall is determined within the transfer-matrix formulation as $\xi_\parallel = k_B T/(E_1 - E_0)$.

The analysis of 2D wetting transitions using this transfer-matrix approach has already been done in a great deal of detail by Kroll and Lipowsky [19]. Suppose the bare wetting transition is continuous as described by the binding potential $V(\ell) = a\ell^{-p} + b\ell^{-q} + h\ell$, where $q > p$ and the coefficient a is considered negative at low temperatures. Provided that $b > 0$, the condition $a = 0$ (and $h = 0$) represents the mean-field critical wetting phase boundary [20]. Solution of the Schrödinger equation shows that the critical wetting transition falls into several fluctuation regimes with the SFL regime, representative of short-ranged wetting holding for $p > 2$. For $p < 2$, we need only note that the transition still occurs at the mean-field phase boundary $a = 0$, although critical exponents are nonclassical if $q > 2$. However, in the SFL regime the wetting temperature is lowered below its mean-field value since the interface is able to tunnel away from the potential well in $V(\ell)$ even though $a < 0$. Calculation shows that the singular part to the free-energy exhibits the anticipated scaling behavior [2–4]

$$\sigma_{\rm sing} = t^2 W(h|t|^{-3}) \tag{4}$$

identifying the universal values of the critical exponents $\alpha_s = 0$ and $\Delta_s = 3$, as quoted above. Implicit here is the fact that the scaling function $W(x)$ is different below and above the wetting temperature, and we have replaced t with $|t|$ in the argument for convenience. The scaling of the free energy determines that the film thickness $\langle \ell \rangle \propto \frac{\partial \sigma_{\rm sing}}{\partial h}$ and correlation length $\xi_\parallel^2 \propto \frac{\partial^2 \sigma_{\rm sing}}{\partial h^2}$ must diverge as $\langle \ell \rangle \propto t^{-1}$ and $\xi_\parallel \propto t^{-2}$ as $T \to T_w^-$ at bulk coexistence. These also follow from direct calculation. Indeed, the interfacial model (1) goes further and recovers precisely the scaling properties of energy density and magnetization correlation functions known from the exact solution of the Ising model [21,22]. Above the wetting temperature that the scaling of $\sigma_{\rm sing}$ also identifies, the correct singular behavior $\sigma_{\rm sing} \propto h^{2-\alpha_s^{\rm co}}$, where $\alpha_s^{\rm co} = 4/3$ determines the singular contribution to the wall-gas surface tension at the *complete wetting* transition occurring

as $h \to 0$ [23,24]. Finally, we mention that the case of binding potentials that decay as an inverse square (i.e., $p = 2$), referred to as the intermediate-fluctuation (IFL) regime, is marginal and the critical behavior subdivides into three further categories [9].

In a related article, Zia, Lipowsky, and Kroll [7] also discussed what happens if the binding potential $V(\ell)$ has a form pertaining to a mean-field first-order wetting transition. Suppose that, at bulk coexistence, the potential has a long-ranged repulsive tail $V(\ell) = a\ell^{-p}$ (with $a > 0$), which competes with a short-ranged attraction close to the wall. They showed that if $p > 2$, the transition is continuous and belongs to the SFL regime universality class of short-ranged critical wetting. In this regime, fluctuation effects always cause the interface to tunnel through the potential barrier in $V(\ell)$ when T is sufficiently close to T_w. For $p < 2$, the transition is first-order ($\alpha_s = 1$) and the adsorption diverges discontinuously at the wetting temperature. The latter follows from (3) since at T_w there is a zero-energy bound-state wave function that determines that the probability distribution decays (ignoring unimportant constant factors) as $P(\ell) \propto \exp(-\ell^{1-\frac{p}{2}})$. Explicit results for $p = 1$ confirm this for a restricted solid-on-solid model [8]. The case $p = 2$ is marginal but displays first-order wetting with $\alpha_s = 1$ for $a > 3/8\beta^2\Sigma$ corresponding to subregime **C** of the IFL regime [9]. In this case, a zero-energy bound-state wave function also exists at T_w and determines that the probability distribution decays as $P(\ell) \propto \ell^{1-\sqrt{1+8\beta^2\Sigma a}}$. This algebraic decay means, rather unusually, that not all moments of the distribution exist at T_w [9]. Thus, for example, for $1/\beta^2\Sigma > a > 3/8\beta^2\Sigma$ the adsorption diverges continuously as $T \to T_w$ even though the transition is strictly first-order. For $3/8\beta^2\Sigma > a > -1/\beta^2\Sigma$, the wetting transition is continuous with nonuniversal exponents (subregime **B**); we shall return to this shortly. Note that the parallel correlation length for all 2D first-order wetting transitions also diverges continuously with a universal power law $\xi_\parallel \sim t^{-1}$ independent of p. This is equivalent to the statement of hyperscaling, which also holds in the SFL regime, since near T_w the next wave function above the ground state lies at the bottom of the scattering spectrum ($E_1 = 0$) and hence $\sigma_{\rm sing} = -k_B T/\xi_\parallel$. This scenario is subtly different from first-order wetting in three dimensions where $\xi_\parallel$, as defined through the decay of the height-height correlation function, remains finite as $T \to T_w^-$. However, a continuously diverging parallel correlation length, very similar to that occurring in two dimensions, can still be identified for 3D first-order wetting by considering the three-phase region near a liquid droplet or alternatively by approaching the wetting temperature T_w from above along the prewetting line [14,15].

III. APPARENT FIRST-ORDER BEHAVIOR IN THE SFL AND IFL REGIMES

One issue that has not been addressed concerns the size of the asymptotic critical region in either the SFL regime or subregime **B** of the IFL regime when the interface has to tunnel through the potential barrier in $V(\ell)$. Let us consider the SFL regime first. For systems with short-ranged forces and in zero bulk field, $h = 0$, this can be modeled by the very simple potential

$$V(\ell) = -U\Theta(R - \ell) + c\delta(\ell - R) \tag{5}$$

together with the usual hard-wall repulsion for $\ell < 0$. Here $\Theta(x)$ is the Heaviside step function. With $c \gg 1$ this potential models the competition between short-ranged attraction (of depth $U > 0$) and large but also short-ranged repulsion similar to that arising in the Ising model studies, where the surface enhancement term competes with a surface field. We emphasize that precisely the same crossover scaling described below emerges if we use a square-shoulder repulsion in place of the δ function. This choice of local binding potential is the simplest one that incorporates a short-ranged attraction and a repulsive potential barrier. It therefore has the same qualitative features as binding potentials describing first-order wetting constructed from more microscopic continuum models [20]. Here the coefficient c is regarded simply as an adjustable parameter in order to tune the size of the critical region, but, more generally, it will increase exponentially with the size and width of the potential barrier. Without loss of generality, we work in units where $R = 1$ and also set $2\beta^2\Sigma = 1$ for simplicity. Rather than vary the temperature, we equivalently decrease the depth of the attractive short-ranged contribution until the interface unbinds from the wall. Elementary solution of the Schrödinger equation for the potential (4) determines that the ground-state wave function behaves as $\psi_0(\ell) \propto \sin(\sqrt{U + E_0}\ell)$ for $\ell < R$ and $\psi_0(\ell) \propto e^{-\sqrt{|E_0|}\ell}$ for $\ell > R$. The δ-function contribution to the potential necessitates that $\psi_0'(R^-) - \psi_0'(R^+) = c\psi_0(R)$ and continuity of the wave function immediately gives

$$-\sqrt{-E_0} - \sqrt{U + E_0}\cot\sqrt{U + E_0} = c. \tag{6}$$

Therefore, the wetting transition occurs when $U = U_w$, where $-\sqrt{U_w}\cot\sqrt{U_w} = c$. For large $c \gg 1$, the latter condition simplifies to $U_w \approx c^2\pi^2/(1 + c)^2$. Writing $U \equiv U_w + t$, it follows that if t and c^{-1} are small, then the equation for the ground-state energy simplifies to

$$\sqrt{-E_0} \approx \frac{c^2}{2\pi^2}(E_0 + t), \tag{7}$$

and the solution of this quadratic equation determines that the singular part to the free-energy (recall that $\sigma_{\rm sing} = E_0$) behaves like

$$\sigma_{\rm sing} = -t_{\rm Gi}\left(1 - \sqrt{1 + \frac{t}{t_{\rm Gi}}}\right)^2. \tag{8}$$

Here we have introduced a thermal Ginzburg scaling field $t_{\rm Gi} = \pi^4/c^4$, which measures the size of the asymptotic critical regime [25]. For $t/t_{\rm Gi} \ll 1$, the free energy vanishes as $\sigma_{\rm sing} \approx -t^2/4t_{\rm Gi}$ consistent with the universal critical behavior characterizing the SFL regime ($\alpha_s = 0$). However, for $t/t_{\rm Gi} \gg 1$, which is outside the critical regime, the surface free energy vanishes as $\sigma_{\rm sing} \approx -t$ in accord with the expectations of a first-order phase transition. The expression (8) has a form consistent with phenomenological theories of crossover scaling $\sigma_{\rm sing} = -t\,A_{\rm cr}(t/t_{\rm Gi})$ with the scaling function behaving as $A_{\rm cr}(x) \to 1$ as $x \to \infty$ and $A_{\rm cr}(x) \sim x/4$ as $x \to 0$. Similar crossover scaling has been used for interfacial delocalization transitions in three dimensions [26]. Two derivatives of $\sigma_{\rm sing}$ with respect to t determine that the surface specific heat or

equivalently the surface susceptibility behaves as

$$\chi_{11} \propto \frac{1}{t_{\rm Gi}\left(1+\frac{t}{t_{\rm Gi}}\right)^{3/2}}, \tag{9}$$

which *outside* the critical regime, $\frac{t}{t_{\rm Gi}} \gg 1$, shows the same apparent power law $\chi_{11} \propto t^{-\gamma_{11}^{\rm eff}}$ with $\gamma_{11}^{\rm eff} = 3/2$ seen in the Ising model studies [10].

The present analysis can be generalized by considering tunneling through a potential barrier in the IFL regime. This can be modeled by simply adding a long-ranged term $a\ell^{-2}$ for $\ell > R$ to the potential $V(\ell)$ shown in (5). Recall that for $a > 3/4$ the wetting transition is first-order while for $3/4 > a > -1/4$ (and recall we have set $2\beta^2\Sigma = 1$) it is continuous. This subregime **B** is characterized by strongly nonuniversal critical exponents with, for example, $2-\alpha_s = 2/\sqrt{1+4a}$ from which all other exponents follow using hyperscaling, etc. [9]. Setting $a = 0$ recovers the results for the SFL regime described above. For completion, we note that for $a < -1/4$ the interface is bound to the wall with the condition $a = -1/4$ defining a line of wetting transition (subregime **A** of the IFL regime [9]). These wetting transitions, which display essential singularities, are no longer induced by variation of the short-ranged field U, and crossover scaling cannot be considered. Within subregime **B**, the presence of the δ-function repulsion at $\ell = R$ does not affect the asymptotic critical singularities, but once again it significantly reduces the size of the asymptotic regime. In this case, the wetting transition occurs when $-\sqrt{U_w}\cot\sqrt{U_w} = c - \frac{1}{2}(1-\sqrt{1+4a})$, and writing $U = U_w + t$, it is straightforward to show that for small t and small c^{-1} the ground-state energy E_0 satisfies an equation similar to (7) but with the left-hand side replaced with $-E_0$ raised to the power $(\sqrt{1+4a})/2$. In this way, we can see that the crossover from first-order behavior $\sigma_{\rm sing} \approx -t$ occurring for $t/t_{\rm Gi} \gg 1$ to the asymptotic criticality $\sigma_{\rm sing} = -t_{\rm Gi}(t/t_{\rm Gi})^{2-\alpha_s}$, with $\alpha_s < 1$, is described by the implicit equation (up to an unimportant multiplicative constant)

$$\left(-\frac{\sigma_{\rm sing}}{t_{\rm Gi}}\right)^{\frac{1}{2-\alpha_s}} = \frac{\sigma_{\rm sing}+t}{t_{\rm Gi}}, \tag{10}$$

which recovers trivially (8) when we set $\alpha_s = 0$. This now shows the role played by the exponent α_s in determining the crossover from apparent first order to critical wetting in two dimensions. In particular for *fixed* t, and in the limit $t_{\rm Gi} \to 0$, this has the expansion $\sigma_{\rm sing} = -t + O(t^{\frac{1}{2-\alpha_s}})$, where the coefficient of the singular correction term depends on $t_{\rm Gi}$. With $\alpha_s = 0$ this is the same expansion of the free energy, $\sigma_{\rm sing} = -t + O(\sqrt{t})$, found in the Ising model calculations in the strong surface coupling limit; see, in particular, Eqs. (15) and (17) of [10]. As noted by these authors, it is the presence of the nonanalytic correction to the pure first-order singularity, $\sigma_{\rm sing} = -t$, that determines the apparent divergence of the surface susceptibility and specific heat. It follows that, more generally, the value of the exponent $\gamma_{11}^{\rm eff}$ characterizing the apparent divergence of χ_{11} satisfies the exponent relation

$$\left(2-\gamma_{11}^{\rm eff}\right)(2-\alpha_s) = 1. \tag{11}$$

Thus in subregime **B** of the IFL regime, for $t/t_{\rm Gi} \gg 1$, the surface susceptibility would have a different apparent divergence $\chi_{11} \propto t^{-\gamma_{11}^{\rm eff}}$ with a nonuniversal exponent

$$\gamma_{11}^{\rm eff} = 2 - \sqrt{\frac{1}{4} + 2\beta^2 a\Sigma}, \tag{12}$$

and we have reinstated the dependence on the stiffness coefficient Σ for completion. This recovers the Ising model result on setting $a = 0$ corresponding to strictly short-ranged interactions. Note that as a is increased toward the boundary with subregime **C**, the value of $\gamma_{11}^{\rm eff}$ approaches unity. This means that exactly at the **B/C** regime border, the apparent divergence of χ_{11}, occurring for $t/t_{\rm Gi} \gg 1$, is almost indistinguishable from the asymptotic divergence $\chi_{11} \propto 1/t(\ln t)^2$ occurring as $t \to 0$ [9]. While the analysis described here applies only to systems with thermal interfacial wandering, the exponent relation (11) is strongly suggestive that the same anomalous 3/2 power-law divergence would be observed for apparent first-order wetting even in systems in which the interfacial unbinding is driven by quenched random-bond impurities since then the transition is also strictly second-order ($\alpha_s = 0$) [2,4,27].

Returning to the case of short-ranged forces pertinent to the SFL regime, we note that the expression (8) also determines the apparent and asymptotic divergences of the parallel correlation length. First note that the first excited state is bound to the wall ($E_1 < 0$) for $t > t_{\rm NT}$ but lies at the bottom of the scattering spectrum ($E_1 = 0$) for $t < t_{\rm NT}$. Here $t_{\rm NT}$ is the location of a nonthermodynamic singularity at which $\xi_\parallel$ has a discontinuity in its derivative with respect to t similar to that reported in [28]. For large $c \gg 1$, this occurs at $t_{\rm NT} \approx 3\pi^2$ far from the wetting transition and the crossover scaling region. This means that for $t < t_{\rm NT}$, the *same* hyperscaling or rather hyperuniversal relation $\xi_\parallel = k_B T/|\sigma_{\rm sing}|$ applies equally inside ($t/t_{\rm Gi} \ll 1$) and outside ($t/t_{\rm Gi} \gg 1$) the asymptotic critical regime. Thus implies that the correlation length shows a crossover between two different power laws: $\xi_\parallel \propto t^{-1}$ valid for $t/t_{\rm Gi} \gg 1$, characteristic of 2D first-order wetting, to $\xi_\parallel \propto t_{\rm Gi}t^{-2}$ for $t/t_{\rm Gi} \ll 1$ describing the asymptotic criticality of the SFL regime (2D second-order wetting).

IV. ROUNDED PREWETTING TRANSITIONS FOR $T > T_w$

Further insight into the crossover scaling behavior in the SFL regime can be seen off bulk coexistence by adding a term $h\ell$ or $h(\ell - R)$ to (5). In this case for small t, c^{-1}, and h, the ground-state energy is determined from the solution of

$$-h^{\frac{1}{3}}\frac{{\rm Ai}'\left(-E_0h^{\frac{2}{3}}\right)}{{\rm Ai}\left(-E_0h^{\frac{2}{3}}\right)} \approx \frac{c^2}{2\pi^2}(E_0+t), \tag{13}$$

which, for $t > 0$, recovers (7) when $h = 0^+$. Here ${\rm Ai}(x)$ is the Airy function, which determines the decay of the wave function for $\ell > R$ [23,24]. It follows that the singular part of the free energy scales as

$$\sigma_{\rm sing} = tW_{\rm cr}\left(\frac{h}{|t|^{\frac{3}{2}}}; t/t_{\rm Gi}\right), \tag{14}$$

which is the more general result involving a crossover scaling function of two variables and applies both above and below the

wetting temperature. In the asymptotic critical regime $t/t_{\rm Gi} \ll 1$, the scaling function $W_{\rm cr}(x;y) \to yW(xy^{-\frac{3}{2}})$ so that $\sigma_{\rm sing} = -\frac{t^2}{t_{\rm Gi}} W(ht_{\rm Gi}^{\frac{3}{2}}/|t|^3)$. This is precisely the same scaling shown in (4) but now including a dependence on $t_{\rm Gi}$ (which determines the size of the asymptotic critical regime) appearing via metric factors. It follows that upon approaching the wetting transition $T \to T_w^-$ at bulk coexistence, the adsorption ultimately diverges as $\langle \ell \rangle \propto \sqrt{t_{\rm Gi}} t^{-1}$, while for the parallel correlation length we recover the expression $\xi_\parallel \propto t_{\rm Gi} t^{-2}$ quoted above. These are the standard critical singularities for the SFL regime, but now they reveal the dependence of the critical amplitudes on $t_{\rm Gi}$. In particular, the amplitude for the divergence of the adsorption *vanishes* as $t_{\rm Gi} \to 0$, which is equivalent to the adsorption jumping from a microscopic to a macroscopic value. Note that the factors of $t_{\rm Gi}$ in $\sigma_{\rm sing}$, $\langle \ell \rangle$, and $\xi_\parallel$ are all consistent with the relation $\sigma_{\rm sing} \propto -\mathcal{A}\sigma \langle \ell \rangle^2/\xi_\parallel^2$, where, within the SFL regime, $\mathcal{A} = 8$ is a universal critical amplitude independent of $t_{\rm Gi}$. This is reminiscent of the "bending energy" contribution to the free-energy in the heuristic scaling theory wetting transitions [16], and it leads directly to the Rushbrooke equality $2 - \alpha_s = 2\nu_\parallel - 2\beta_s$ discussed earlier.

The crossover scaling of $\sigma_{\rm sing}$ shown in (14) depends on the scaling variable $h|t|^{-\frac{3}{2}}$, which is different from that appearing in (4) characteristic of the SFL regime. However, this power-law dependence is in complete agreement with the predictions of the phenomenological scaling theory of first-order wetting developed by Indekeu and Robledo [14,15]. Indeed, setting $\alpha_s = 1$ determines $\nu_\parallel = 1$ (from hyperscaling) and hence $\Delta_s = 3/2$ (from $\Delta_s = 3\nu_\parallel/2$), all of which are consistent with the behavior found for $\sigma_{\rm sing}$ and $\xi_\parallel$ for $t/t_{\rm Gi} \gg 1$. Note also that above the wetting temperature, and for $|t|/t_{\rm Gi} \gg 1$, we may approximate $\sigma_{\rm sing} \approx t\, W_{\rm cr}(h|t|^{-\frac{3}{2}}; -\infty)$. The value $3/2$ of the crossover (or equivalently the Indekeu-Robledo first-order) gap exponent now determines that in the limit $h \to 0$ we recover the correct complete wetting singularity $\sigma_{\rm sing} \propto h^{\frac{2}{3}}$, the amplitude of which must not depend on t. Thus the crossover scaling from (14) provides a consistent link between previous scaling theories of continuous and first-order wetting.

More explicitly, above the wetting transition and for $|t|/t_{\rm Gi} \gg 1$, which is away from the immediate vicinity of T_w, the approximate solution of (13) can be determined from a simple expansion of the Airy function around its first zero. In this way, it follows that the singular part to the free energy behaves as

$$\sigma_{\rm sing} \approx \frac{1}{2}\left(\lambda h^{\frac{2}{3}} + |t| - \sqrt{(\lambda h^{\frac{2}{3}} - |t|)^2 + 8ht_{\rm Gi}^{\frac{1}{2}}}\right), \qquad (15)$$

where here $\lambda \approx 2.338$ is the negative of the first zero of the Airy function. If we could set $t_{\rm Gi} = 0$, which corresponds of course to an artificial infinite potential barrier, then $\sigma_{\rm sing} = \min(|t|, \lambda h^{\frac{2}{3}})$. This determines a line of first-order phase transition extending away from bulk coexistence located at $|t| = \lambda h^{\frac{2}{3}}$. For small $t_{\rm Gi}$, these transitions are *rounded* on a scale set by $h^{\frac{1}{2}} t_{\rm Gi}^{\frac{1}{4}}$. Taking the derivative of $\sigma_{\rm sing}$ with respect to h determines that $\langle \ell \rangle \approx 0$ for $|t| < \lambda h^{\frac{2}{3}}$ while $\langle \ell \rangle \approx h^{-\frac{1}{3}}$ for $t > \lambda h^{\frac{2}{3}}$. The sharp increase in the film thickness, therefore, corresponds simply to a line of pseudo-prewetting transitions. This line meets the bulk coexistence axis tangentially, and the power-law dependence on h is in precise accord with the standard thermodynamic prediction for its location based on the Clapeyron equation [20]. Sitting at a given point along this line, the parallel correlation length scales as $\xi_\parallel = t^{-1}\tilde{\Lambda}(t/t_{\rm Gi})$, which follows from (14) and also direct calculation of the spectral gap $E_1 - E_0$. For $|t|/t_{\rm Gi} \gg 1$, this reduces to $\xi_\parallel = |t|^{-1}(|t|/t_{\rm Gi})^{\frac{1}{4}}$, which is very large if $t_{\rm Gi}$ is small. This length scale determines the rounding of the prewetting phase transition equivalent to the characteristic size of the domains of the thick and thin prewetting states, which are in pseudo-phase-coexistence. By moving along the prewetting line away from the wetting temperature, the length scale $\xi_\parallel$, and hence the size of the domains simply decreases, indicating that the thin-thick transition is eventually smoothed away by fluctuations, i.e., no prewetting critical point is encountered. On the other hand, moving toward the wetting transition while remaining along the pseudo-prewetting line, the parallel correlation length eventually crosses over to $\xi_\parallel \propto 1/|t|$. This is not indicative of any pseudo-thin-thick phase coexistence but rather the usual thermal wandering of the unbinding interface when T_w is approaching along the thermodynamic path $h \propto |t|^{\frac{3}{2}}$. The above remarks are all consistent with the general theory of the rounding of first-order phase transitions in pseudo-one-dimensional systems [29].

V. CONCLUSIONS

In this paper, we have shown that recent Ising's model studies that show apparent first-order wetting transitions are consistent with analysis of an interfacial Hamiltonian model, which also allows us to consider the properties of the transition in the presence of marginal long-ranged forces and occurring off bulk coexistence. Our study has revealed that the singular contribution to the surface free energy shows a simple crossover scaling due to the tunneling of the interface through a potential barrier, which generalizes the standard scaling theory of critical wetting linking it consistently with scaling predictions for first-order wetting. The form of the scaling function is explicitly calculated above and below the wetting transition and illustrates the rounding of a pseudo-first-order phase transition in this low-dimensional system. The crossover scaling occurring below T_w, which is determined within both the SFL and IFL regimes, allows us to trace the value $3/2$ of the anomalous exponent $\gamma_{11}^{\rm eff}$ highlighted in the Ising model studies directly to the strict second-order nature of the critical wetting transition, i.e., that $\alpha_s = 0$. It would be interesting to test the predicted nonuniversality of $\gamma_{11}^{\rm eff}$ in the IFL by adding a long-ranged external field to the Ising model, i.e., decaying as the inverse cube from the distance to the wall. Even for systems with short-ranged forces, our predictions for the location of a pseudo-prewetting line above the wetting temperature can also be tested in numerical studies of the Ising model with a strong surface coupling enhancement similar to that described in [10]. Finally, we mention that similar apparent first-order behavior and crossover scaling should also occur in two dimensions for the interfacial delocalization transition near defect lines in the bulk if these too are now modified to include enhanced couplings [4,30].

Scenarios involving apparent first-order interfacial unbinding or delocalization in three dimensions are more challenging. However, similar behavior may occur at wedge-filling transitions where fluctuation effects are enhanced compared to wetting, and interfacial tunneling through a potential barrier can occur [31,32].

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