Scaling-violation anomaly at critical wetting

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We present a theory of the three-dimensional critical wetting transition based on the surface-order-parameter interface Hamiltonian $H_2[l_1,l_2]$ recently used to study complete wetting. A renormalization group analysis highlights a scaling-violation anomaly whereby local structure factors at the wall and unbinding interface are characterized by mean-field and nonuniversal critical exponents, respectively. This reflects the combination of depinning, decoupling, and unbinding that are not properly distinguished in previous models. Comparisons with existing simulation studies are very encouraging. [S1063-651X(96)05206-3]

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The status of critical wetting theory has been controversial since Binder, Landau, and Kroll (BLK) [1] reported that data from extensive Monte Carlo simulations of wetting in an Ising model are very well fitted by mean-field (MF) theory [2], in sharp contrast to predictions of strong nonuniversality based on renormalization group analyses of a capillary-wave model [3]. Numerous authors have forwarded explanations for this anomaly, including early suggestions that the critical region is small [4] and later suggestions that the transition may be very weakly first order [5]. Disappointingly, these proposals do not make quantitative contact with the simulation results, which must be considered the goal of theory. Recently, however, some successes have been scored in this direction. In particular, it has been shown [6] that the adsorption data of BLK *above* the wetting temperature (and in zero bulk field) can be understood using capillary-wave ideas that take into account the finite-size (FS) geometry (which is of parallel-plate type with equal surface fields). Also, the results of more recent Ising model simulations [7] of a different FS system [8] (with competing surface fields) can be quantitatively explained using a surface-order-parameter interface Hamiltonian $H_2[l_1,l_2]$, which takes into account coupling between fluctuations near the wall and depinning interface [9,10]. These developments not only underline the subtlety of the problem at hand, but confirm that the theoretical expectation for the value of the all important wetting parameter ω (which is about unit [11]) *is* consistent with much of the available simulation data. While this is encouraging, the original observations of BLK concerning the MF scaling of the local susceptibility χ_1 (which is seen over several decades of the bulk field) seems all the more puzzling since this is certainly inconsistent with a value of ω of order unity, provided one accepts the predictions of scaling and capillary-wave theory.

In this paper we point out that observations of MF-like criticality and scaling in local observables at the wall can be fully reconciled with fluctuation-induced nonuniversal behavior near the unbinding fluid interface using the coupled Hamiltonian $H_2[l_1,l_2]$ mentioned above, which improves upon capillary-wave models of wetting. Specifically, we will show that a structure factor local to the fluctuating fluid interface exhibits the same dramatic nonuniversal criticality (at leading order) as the original Brézin-Halperin-Leibler (BHL) [3] predictions, but the analogous function at the wall only exhibits much weaker MF-like singularities. This surprising feature of the surface-order-parameter interface Hamiltonian corresponds to a violation of simple scaling theory, in contrast to the predictions of the standard capillary-wave model where scaling is obeyed [12]. This reflects the combined effects of unbinding, depinning, and decoupling of the collective coordinates, which are carefully modeled by the $H_2[l_1,l_2]$ Hamiltonian. We believe this goes a long way towards explaining the controversy surrounding critical wetting theory.

We begin by recalling some details of the critical wetting transition. At such a transition the adsorption of down-spins (phase β, say) at a wall-up-spin (phase α) interface with bulk field $H=0^+$ diverges continuously as $T\to T_W^-$ at fixed surface field H_1 or, equivalently, as the (negative) field H_1 is reduced to the critical value H_{1c}. The thickness l of the adsorbed film grows as $l\sim t^{-\beta_s}$, where t is the scaling temperature variable, and the transverse correlation length $\xi_\parallel \sim t^{-\nu_\parallel}$ as the capillary-wave fluctuations develop in the depinning down-spin–up-spin ($\alpha|\beta$) interface [13]. In nonzero bulk field the standard scaling ansatz [2] for the singular part of the free energy is $F_{\rm sing}=t^{2-\alpha_s}W(Ht^{-\Delta})$, where $\alpha_s=2-2\nu_\parallel+2\beta_s$ is the specific heat exponent and $\Delta=(d+1)\nu_\parallel/2$ is the gap exponent. At the MF level the exponents are $\alpha_s=0$, $\beta_s=0(\ln)$, $\nu_\parallel=1$, and $\Delta=2$. However, renormalization group (RG) predictions in $d=3$ based on a simple capillary-wave model yield

$$\nu_\parallel=\begin{cases}1/(1-\omega), & 0<\omega<\frac{1}{2}\\ (\sqrt{2}-\sqrt{\omega})^2, & \frac{1}{2}<\omega<2\\ \infty, & \omega>2\end{cases} \tag{1}$$

where $\omega=k_BT\kappa^2/4\pi\Sigma_{\alpha\beta}$ is the wetting parameter [11]. Here κ is the inverse bulk correlation length of the adsorbed β phase and $\Sigma_{\alpha\beta}$ is the stiffness coefficient of the unbinding interface. Explicit calculations [12] for the local susceptibility $\chi_1\equiv\partial m_1/\partial H$ (with m_1 the wall magnetization) show that scaling is obeyed (up to unimportant logarithmic factors) with gap exponent $\Delta=2\nu_\parallel(\omega)$. Hence along the critical isotherm ($t=0$, $H\to0^+$) capillary-wave theory predicts that χ_1 diverges as $\chi_1\sim H^{-1/2\nu_\parallel}$ at leading order. However, in marked contrast to this, the measurements of BLK unambiguously show that χ_1 grows with a critical exponent very

close to $-\frac{1}{2}$, which is consistent with a MF correlation critical exponent $\nu_\parallel \approx 1$ and not the predictions of BHL that imply $\nu_\parallel \sim 4$ for $\omega \sim 0.8$.

To understand this we employ the surface-order-parameter interface Hamiltonian $H_2[l_1,l_2]$ previously used to study coupling effects at the complete wetting transition (occurring for $T>T_W$ and $H\to 0^+$). The model is defined by the Hamiltonian [9]

$$H_2[l_1,l_2]=\int d\mathbf{y}[\tfrac{1}{2}\Sigma_{\mu\nu}(l_1,l_2)\boldsymbol{\nabla} l_\mu\cdot\boldsymbol{\nabla} l_\nu+U(l_1) + W_{(2)}(l_2-l_1)], \tag{2}$$

where the collective co-ordinate l_2 represents the position of the unbinding $\alpha|\beta$ interface, while l_1 models order-parameter fluctuations near the wall (characteristic of the ''noncritical'' wall-β interface), which are neglected in traditional capillary-wave theory. The binding potentials have distinct roles: $W_{(2)}$ has an expansion very similar to that appearing in standard capillary-wave models

$$W_{(2)}(l)=\overline{h}l-\tau e^{-\kappa l}+be^{-2\kappa l},\quad l>0, \tag{3}$$

where $\overline{h}\propto H$ and $b>0$, while the potential $U(l_1)$ simply binds l_1 to the wall. For zero bulk field $h=0$ we may write

$$U(l_1)=\frac{\tau^2 l_1^2}{2},\quad \overline{h}=0, \tag{4}$$

ignoring prefactors of order unity. This Gaussian approximation should suffice because (a) the fluctuations of l_1 are always much smaller than those of l_2, and (b) higher order terms in the expansion of $U(l_1)$ vanish quickly as $\tau\to 0$. The field τ vanishes at the MF wetting temperature $T_W^{\rm MF}$ and may be identified with the scaling field t if fluctuations do not alter the critical wetting temperature.

The stiffness matrix elements $\Sigma_{\mu\nu}(l_1,l_2)$ play an essential role in the theory. First we note that if the correct position dependence of $\Sigma_{22}(l_1,l_2)$ is taken into account, the model may exhibit a fluctuation induced first-order transition very similar to the simpler Fisher-Jin interfacial model [5], which does not account for the coupling of modes described by $H_2[l_1,l_2]$. However, the violation of scaling described here is a feature independent of the order of the transition. For simplicity we will initially ignore the position dependence of the $\Sigma_{\mu\nu}$ and specify the matrix elements by

$$\Sigma_{11}\sim\tau^2,\quad \Sigma_{12}=0,\quad \Sigma_{22}=\Sigma_{\alpha\beta},\quad \overline{h}=0 \tag{5}$$

which follows from the corresponding explicit expressions [9]. We shall return to the implication of the position-dependent stiffness matrix at the end of our paper. For the coupled model (2) with parameters defined as in (3)–(5) we find that the wetting transition is continuous and occurs at the MF wetting temperature $T_W^{\rm MF}$ for values of $\omega<2$ similar to the BHL analysis. However, the present theory highlights the subtlety of modeling the critical wetting transition. In addition to the familiar unbinding of the $l_2(\mathbf{y})$ coordinate as $\tau\to 0$, we note that the lower surface (a) *depins*, corresponding to the vanishing of the curvature of $U(l_1)$, and (b) *decouples* from $l_2(\mathbf{y})$ fluctuations because the cutoff for the $l_1(\mathbf{y})$ field satisfies $\Lambda_1\ll\sqrt{\beta\Sigma_{11}}$. Note that for the complete wetting transition, decoupling does not occur as $h\to 0$ (with $\tau<0$ fixed) because Σ_{11} does not vanish, and the effective value of the wetting parameter is renormalized [9]. This effect is negligible at the critical wetting transition and the wetting parameter (when it appears) takes the BHL form quoted after Eq. (1).

Connection with local observables at the wall and interface within the coupled theory is achieved through the calculation of the structure factor matrix elements

$$S_{\mu\nu}(Q)\equiv\int d\mathbf{y}\; e^{i\mathbf{Q}\cdot\mathbf{y}}\langle\delta l_\mu(\mathbf{0})\,\delta l_\nu(\mathbf{y})\rangle, \tag{6}$$

where $\delta l_\mu(\mathbf{y})\equiv l_\mu(\mathbf{y})-\langle l_\mu(\mathbf{y})\rangle$. At the MF level the three possible *order-parameter* correlation functions $\mathcal{G}(z_\mu,z_\nu;Q)$ (corresponding to the Fourier transforms of the pair correlation function) may be found using the exact identification [9]

$$\mathcal{G}(z_\mu,z_\nu;Q)=m'(z_\mu)m'(z_\nu)S_{\mu\nu}(Q), \tag{7}$$

with $z_\mu=\langle l_\mu\rangle$, and the prime denotes differentiation with respect to argument. The matrix elements may be calculated using the relation [14]

$$\mathbf{S}^{-1}(Q)=\begin{pmatrix}\partial_{11}^2 & \partial_{12}^2\\ \partial_{12}^2 & \partial_{22}^2\end{pmatrix}W(l_1,l_2)+\boldsymbol{\Sigma}Q^2, \tag{8}$$

where $\partial_{\mu\nu}^2\equiv\partial^2/\partial l_\mu\partial l_\nu$, $W(l_1,l_2)=U(l_1)+W_{(2)}(l_2-l_1)$ is the total binding potential, and $\boldsymbol{\Sigma}$ is the stiffness matrix. Here the second derivatives must be evaluated at the minimum of $W(l_1,l_2)$. For example, when both particles are at the wall ($z_1=z_2=0$) the model recovers the known non-Lorentzian form of the correlation function [15]

$$\mathcal{G}^{w\alpha}(0,0;Q)=\frac{1}{A+BQ^2-\Psi(Q\xi_\parallel)+O(Q^4)}, \tag{9}$$

which shows crossover to the noncritical ($w\beta$) interface function $\mathcal{G}^{w\beta}(0,0;Q)=[A+BQ^2+O(Q^4)]^{-1}$ as $\tau\to 0$. Here Ψ is the Lorentzian $\Psi(x)=C/(1+x^2)$ while A, B and C are finite when $\tau=0$ and may be considered constants. Note that the zeroth moment satisfies

$$\mathcal{G}_0^{w\alpha}(0,0)-\mathcal{G}_0^{w\beta}(0,0)=\frac{C}{A(A-C)}. \tag{10}$$

This result is consistent with an exact statistical mechanical sum rule that identifies the right-hand side as $\tau^{-\alpha_s}$ with $\alpha_s=0$ [16]. Quite generally the correlation functions are related to response functions. In particular, $\chi_{11}\equiv\partial m_1/\partial H_1=\mathcal{G}_0(0,0)$, while $\chi_1=\int dz\;\mathcal{G}_0(0,z)$.

Beyond the MF it is difficult to calculate $\mathcal{G}(z_\mu,z_\nu;Q)$ but it is straightforward to calculate the structure factors $S_{\mu\nu}(Q)$, which should shed light on the position dependence of critical singularities. First we note that at the MF level the structure factors obey the scaling expression

$$S_{\mu\nu}(Q,r,\xi_\parallel)=b^2S_{\mu\nu}(Qb,rb^2,\xi_\parallel/b), \tag{11}$$

where $r=U''(l_1)$ and b is an arbitrary spatial rescaling factor. This forms the basis of the RG analysis that allows calculation of the structure factors (and thermodynamic proper-

ties) beyond MF theory. This has been described in detail elsewhere [9] and incorporates an exact treatment of the Gaussian term (4) with a linear treatment of the relative potential $W_{(2)}(l_2-l_1)$. Note that a fully linear RG approximation cannot handle the decoupling of fluctuations, and it is essential to allow for nonlinear effects related to the fluctuations of the lower surface $l_1(\mathbf{y})$. The results of the calculation are described below. In zero bulk field the structure factor at the depinning interface diverges with a nonuniversal critical exponent

$$S_{22}(0)\sim\tau^{-2\nu_{\|}(\omega)},\quad \overline{h}=0, \tag{12}$$

which is the same as the BHL result for $\xi_{\|}^2$. In contrast, the wall structure factors $S_{11}(0)$ and $S_{12}(0)$ diverge much more slowly

$$S_{11}(0)=S_{12}(0)\sim\tau^{-2},\quad \overline{h}=0, \tag{13}$$

which would follow from a simple MF analysis. We have similarly calculated the singularities along the critical isotherm $t=0$, $h\to 0^+$ and find divergences consistent with *different* gap exponents at the wall and interface

$$\Delta_{22}=2\nu_{\|}(\omega),\quad \Delta_{11}=\Delta_{12}=2 \tag{14}$$

in an obvious notation. This clearly corresponds to a violation of simple scaling theory and implies that local observables at the wall may be characterized by MF singularities, in contrast to observables near the depinning interface that exhibit dramatic nonuniversal critical behavior familiar from the BHL theory. Importantly, these conclusions remain largely unaffected by the inclusion of position dependent stiffness coefficients. As mentioned earlier, allowing for these we find that the second-order wetting transition may become by a very weakly first-order one (provided the value of ω is not too big) along the same lines as the Fisher-Jin instability mechanism [5]. However, the structure factors $S_{11}(0)$ and $S_{12}(0)$ still exhibit MF-like criticality until τ is very close to the (renormalized) wetting temperature. Ironically the answer to the question originally posed by BLK, ''*Is MF theory valid?*'' is both yes *and* no and depends on where and what observations are made. The anomaly is reflected in thermodynamic properties that may show mixed behavior. For example, it is straightforward to calculate the singular part of the free energy $F_{\rm sing}$ in the model that ignores position dependence of the stiffness matrix elements. This is conveniently written as a correction term to the BHL result.

$$F_{\rm sing}(\tau,\overline{h})=F_{\rm sing}^{\rm BHL}(\tau,\overline{h})+h\Lambda(h\tau^{-\Delta_{11}}), \tag{15}$$

where $\Lambda(x)$ is a simple scaling function. Recall that the BHL term is consistent with hyperscaling $2-\alpha_s=2\nu_{\|}$ and is characterized by a gap exponent $\Delta=2\nu_{\|}$ as well as logarithmic terms. It is likely that most thermodynamic and response functions show such mixed behavior and that the simple separation of nonuniversal and MF-like singularities only occurs for the structure factors $S_{\mu\nu}(Q)$ when $Q=0$. Returning to the local susceptibility χ_1 it follows from (15) that the leading-order singularity is still of the BHL type. However, there exists a MF-like correction term that will be very difficult to eliminate in numerical studies unless T_W is known precisely.

In conclusion, we believe that it is now possible to have a theory of wetting based on the coupled Hamiltonian (2), at least qualitatively consistent with all the available data. Although a large value of $\nu_{\|}$ has not been seen directly, the zero-field adsorption data in the BLK simulations above T_W are consistent with strong fluctuation effects. Similarly, a value of $\omega\sim 0.8$ has already been extracted from reanalysis of more recent simulation data [10] based on the decoupling of fluctuations predicted by the surface-order-parameter interface Hamiltonian. The calculation described here explains how this observation can be married with measurements of a MF-like criticality for local observables at the wall. Although we have not been able to calculate the order-parameter correlation function at the wall, the structure factors $S_{\mu\nu}$ (which are an essential ingredient in the calculation of these and local susceptibilities) clearly show a scaling anomaly. At the very least, the calculation demonstrates that the original predictions of nonuniversal critical singularities are more sensitive to position than previously assumed. Obviously, future simulation studies should concentrate on measuring local susceptibilities near the unbinding interface if they want to directly observe the renormalized critical exponent $\nu_{\|}(\omega)$—although they should be mindful of the FS effects that hinder observation of semi-infinite behavior in the parallel plate geometry [6] of the BLK simulations.

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