RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 44, NUMBER 3 15 JULY 1991-I

Effective potentials, constraints, and critical wetting theory

Michael E. Fisher and Albert J. Jin
Institute for Physical Science and Technology, University of Maryland, College Park, Maryland 20742
(Received 4 March 1991)

Renormalization-group theory based on an effective wall-inteface potential $W(l;T,h)$, h being the external field, predicts *nonuniversality* for three-dimensional critical wetting with short-range forces; but Monte Carlo simulations disagree seriously. To illuminate this, general derivations of $W(l)$ are reported: perturbative analysis using a zero-crossing constraint on a mean-field profile to fix the interface location, l, reveals defects in previous results. However, leading renormalization-group predictions remain unchanged. A novel integral constraint for defining l is solved exactly and yields the same conclusion.

One of the most striking recent predictions of renormalization group theory[1-3] is the *nonuniversality* of the *critical wetting transition*[4] in a $(d=3)$-dimensional system with short-range forces. Specifically, all critical properties should depend strongly on the dimensionless parameter[1-4]

$$\omega = k_B T/4\pi\tilde{\Sigma}(T)\xi_\beta^2(T)\,, \tag{1}$$

where $\tilde{\Sigma}$ is the stiffness of the $\beta|\alpha$ interface which delocalizes from an inert wall at the transition when $T=T_{cW}$ while, ξ_β is the (finite) correlation length (normal to the wall) in the bulk phase, β, that forms the wetting layer, see Fig. 1.[4] As ω increases from 0 the exponent, $\nu_\parallel$, of the diverging *interfacial correlation length*, $\xi_\parallel$, varies as $1/(1-\omega)$ for $\omega < \frac{1}{2}$ (regime I); then as $1/[2-\sqrt{(8\omega)}+\omega]$, which diverges when $\omega \to 2-$ (regime II); thereafter $\nu_\parallel = \infty$ (regime III).[1,3,4]

Although experimental tests of this theory are not yet available, extensive Monte Carlo simulations of critical wetting in a simple-cubic Ising model with $\omega \simeq 1.0$ have been performed.[5,6] Surprisingly, however, nonuniversal behavior is *not* seen; indeed, the data are consistent merely with classical, mean field theory[7] which gives $\nu_\parallel = 1$ (as for $\omega = 0$)![5,6,8] Despite further studies,[8-11] this significant discrepancy remains unexplained.[4,11]

Here we examine carefully one crucial ingredient of the renormalization-group (RG) theory,[1-3] namely, the bare

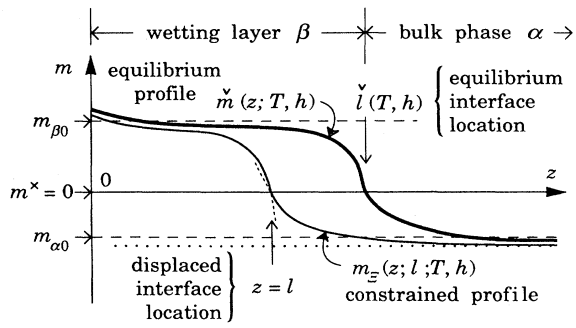

FIG. 1. Sketch of order-parameter profiles, $m(z)$, for critical wetting: note $\hat{l}(T,0) \to \infty$ when $T \to T_{cW}-$, the critical wetting temperature: see text for details.

effective wall-interface interaction $W(l)$, where $l(\mathbf{y})$ is the fluctuating, normal distance of the interface from the point $\mathbf{y}$ on the wall plane at $z=0$. We find[12] that the previously accepted conclusion,[1-3,13] namely

$$W(l;T,h) = \bar{h}l + w_1 e^{-\kappa_1 l} + w_2 e^{-\kappa_2 l} + \cdots \tag{2}$$

with $\kappa_n = n\kappa$ *and* $\kappa = 1/\xi_\beta$, is poorly founded[4(b)] and not, in general, accurate. Note that[4] $\bar{h} \sim -h\,(\to 0+)$ measures the deviation of the overall chemical potential or equivalent external field from coexistence of bulk α and β phases, while $w_1 \sim T - T_{cW}^0 \le 0$, where T_{cW}^0 is the mean-field critical wetting temperature; one supposes $w_2, \cdots > 0$.

Two points must be made:[4] (i) Whereas the *details* of $W(l)$, beyond the linear term and the residual rapid decay, would normally be *irrelevant* at criticality, $d=3$ is the *marginal dimensionality* for critical wetting[1(a),2] and the *precise* form of the first three terms in (2) is then essential to the critical behavior;[1-4] (ii) the RG theory[1-3] is based on an effective interface Hamiltonian, $\mathcal{H}_l[l(\mathbf{y})]$, rather than on a microscopic Hamiltonian, $\mathcal{H}[s(\mathbf{r})]$, with "spins" in d space at points $\mathbf{r}=(\mathbf{y},z)$: hence $W(l)$ is not given *a priori*. The introduction via suitable *constraints* of "collective coordinates," such as $l(\mathbf{y})$, and of corresponding potentials is not, of course, new in condensed matter physics; nevertheless we have found relatively little explicit and precise guidance in the literature.[14] Accordingly, we believe the concrete analysis presented here has interest beyond the particular problem of critical wetting.

To proceed systematically, one must first postulate an explicit microscopic criterion that specifies the collective coordinate, namely the location, $z=l(\mathbf{y})$, of the interface with respect to the wall at $z=0$. Then, the interface Hamiltonian may be defined (with $k_B=1$) via

$$\exp(-\mathcal{H}_l[l]/T) = \mathrm{Tr}_{l(\mathbf{y})}^{s(\mathbf{r})}\{\exp(-\mathcal{H}[s]/T)\}\,, \tag{3}$$

where Tr_l^s denotes a trace over the microscopic variables $s(\mathbf{r})$ *constrained* by a fixed interface conformation, $l(\mathbf{y})$.[14] Now fluid phases or lattice systems above the roughening transition[4] should be satisfactorily described at the order-parameter level with $s \Rightarrow m(\mathbf{r})$ and

$$\mathcal{H}[m(\mathbf{r})] = \int\{[\tfrac{1}{2}K\dot{m}^2 + \Phi(m)]dz + \Phi_1(m_1)\}d\mathbf{y} \tag{4}$$

where $\dot{m}=\nabla m(\mathbf{r})$, $m_1(\mathbf{y})=m(\mathbf{y},z=0)$, while for the wall coupling we may take[4,7,13] $\Phi_1=-h_1 m_1-\frac{1}{2}gm_1^2$, where h_1 is the surface field which induces wetting.

To progress further, we recall that the bulk phases, β and α, are *noncritical* at T_{cW} and hence argue[4] that a mean-field treatment of Tr_l^m should be adequate; of course, the "dangerous" critical modes arise from the capillary fluctuations of the interface to be treated via $\mathcal{H}_l[l]$. Thus we suppose $\Phi(m;T,h)=\Phi_0(m;T)-hm$ where $\Phi_0(m)$ has a double-well form with equal minima at $m=m_{\alpha 0}<0$ and $m=m_{\beta 0}>0$. For most applications α-β symmetry should *not* be imposed; likewise, nonzero values of h should be considered.[4]

Previous discussions,[1(a),2,13] although not fully explicit, more or less adopt the route outlined. At the next stage one concludes, neglecting l-independent terms,[4,12]

$$\mathcal{H}_l[l]=\int dy[\tfrac{1}{2}\tilde{\Sigma}(\nabla l)^2+W(l;T,h;h_1,g)]\,. \tag{5}$$

To determine $W(l)$ in leading approximation one need analyze only a flat interface, $\nabla l(\mathbf{y})\equiv 0$; then in (3) and (4) the task reduces to finding the *constrained interfacial profile*, $m_\Xi(z;l;T,h;h_1,g)$, see Fig. 1, by minimizing the mean-field free energy, $\mathcal{F}[m]\equiv\mathcal{H}[m(z)]$, whence $W(l)$ follows directly. Now when the constraint on l is relaxed there is a smooth optimal profile $\check{m}(z;T,h;h_1,g)$, see Fig. 1, which yields the mean-field theory[7] and gives a corresponding equilibrium interfacial displacement $\check{l}(T,h;h_1,g)$ $(\equiv\langle l\rangle_{\mathrm{mft}})$. Naturally one should require **A**: $m_\Xi(z;l=\check{l})=\check{m}(z)$ which ensures *consistency*, so that minimizing $W(l;T,h;h_1,g)$ on l reproduces the full mean-field behavior. It is clear, however that **A** is not a sufficient condition for determining $W(l)$.

Apparently with **A** in mind, previous workers have, explicitly or in essence,[1(a),2,12] adopted the *ansatz* $m_\Xi(z,l)\simeq\check{m}(z-\Delta l)$ with $\Delta l=l-\check{l}$. For $h=0$ this looks reasonable and, in standard m^4 theory, yields (2). However, the ansatz *violates* the mean-field boundary condition at the wall, namely, **B**: $K\dot{m}_1=d\Phi_1/dm_1$, which follows from (4); it also takes no account of distortions in the profile shape induced by the constraint. Furthermore, when $h\neq 0$ this method yields unacceptable terms in $W(l)$ like $e^{+\kappa l}$ and, in fact, one finds $W(l)\to\infty$ when $l\to l_c\simeq 2\check{l}$.[12] Another derivation[13(a)] of (2) uses an intermediate expression for $\check{m}$ in which $\check{l}$ appears; then $\check{l}$ is replaced by l and a version of **B** is neglected; however, for $l\neq\check{l}$ an unacceptable *discontinuity* in the approximate form for $m_\Xi(z;l)$ is implied.[12]

To do better one must first specify precisely the location, l, of a constrained interface. Given a putative profile, $m(z)$, it is natural to adopt (as is often done implicitly) a *crossing criterion*,[14] i.e., $m=m^\times$ at $z=l$ where, without loss of generality, one may take $m^\times=0$: see Fig. 1. The task is then simply to find the mean-field profile $m_\Xi(z;l)$ which satisfies the *constraint* **C**: $m_\Xi(z=l;l)=0$. This profile must solve the standard equation $K\partial_z^2 m=(\partial\Phi/\partial m)$, (i) for $z<l$, with the wall boundary condition **B**, above, imposed at $z=0$, and (ii) for $z>l$ with bulk boundary condition **D**: $\partial_z m\to 0$ as $z\to\infty$ and $m\to m_{\alpha\infty}(T,h)$. The profile $m_\Xi(z;l)$ will automatically obey **A** but necessarily has a *kink*, i.e., a discontinuity in slope, at $z=l$ whenever $l\neq\check{l}$: see Fig. 1.[15] The potential $W(l)$ then follows by evaluating (4).

Implementing this program for arbitrary $\Phi_0(m)$, or even for the standard rm^2+um^4 model, poses an unexpected challenge: we have resorted to a perturbative approach.[12] Note, first, that for $z\geq l$ one has[16] $m_\Xi(z;l)=\check{m}[z-(l-\check{l})]$ for *any* $\Phi(m)$. Consequently, the profile in this region does not contribute to the l dependence of $W(l)$. To handle $z\leq l$ with equal generality, we put $\varphi=m-m_{\beta\infty}$ and expand $\Phi(m)$ for $m\geq m^\times$ as

$$\Phi=\Phi_{\min}(T,h)+\tfrac{1}{2}\chi_\beta^{-1}\varphi^2+\varepsilon_3\varphi^3+\varepsilon_4\varphi^4+\cdots\,, \tag{6}$$

with $m_{\beta\infty}=m_{\beta 0}+\chi_\beta h+O(h^2)$, which is just the equilibrium value of m in the bulk β phase. Then to solve

$$\mathcal{L}\varphi\equiv K(\partial_z^2-\kappa^2)\varphi=3\varepsilon_3\varphi^2+4\varepsilon_4\varphi^4+\cdots\,, \tag{7}$$

for $z\leq l$, where $\kappa^2=\xi_\beta^{-2}=1/K\chi_\beta$, we treat $\varepsilon_3\propto\varepsilon$, $\varepsilon_4\propto\varepsilon^2,\cdots$ as small parameters.[17]

In zeroth order the profile solving (7) and satisfying **B** and **C** is simply

$$\varphi_\Xi=\varphi_0(z;l;T,h)\equiv Ae^{\kappa(z-l)}+Be^{-\kappa(z-l)}\,, \tag{8}$$

where $A(l;T,h;h_1,g)=m_{\beta\infty}(T,h)[1+O(e^{-\kappa l})]>0$, while

$$B(l;T,h;h_1,g)=\tau e^{-\kappa l}+O(m_{\beta\infty}e^{-2\kappa l})\,, \tag{9}$$

in which $\tau=[h_1+gm_{\beta\infty}(T,h)]/(K\kappa-g)$ turns out to be a crucial control parameter. Note that, in contrast to previous treatments, we allow for $h\neq 0$ at all stages; no anomalous or singular behavior arises.

Now, in computing iteratively the corrections to φ_Ξ, say, $\varphi_{i,i',\cdots}$ of order $\varepsilon_3^i\varepsilon_4^{i'}\cdots$, one necessarily encounters contributions like[12]

$$\mathcal{L}^{-1}(\varphi_0)^q=Cze^{\kappa z}+Dze^{-\kappa z}+\sum_{p=-q}^{q}E_p e^{p\kappa z}\,, \tag{10}$$

with p,q odd, where $E_p\propto B^{(q+p)/2}$ and $C,\,D\propto B^{(q\pm 1)/2}$. Evidently, not only do higher-order exponentials, $e^{\pm n\kappa z}$, arise but *resonances* with $e^{\pm\kappa z}$ terms on the right of (7) generate factors of z. On evaluating (4) in order to compute $W(l)$, one then meets integrals like $\int_0^l(\varphi_0)^p\times[\mathcal{L}^{-1}(\varphi_0^q)]^r dz$, etc., which lead to powers $e^{-\kappa n l}$ with $n>0$, but *also* to factors of l. Further iteration leads to successively higher powers of z and l. Indeed, indefinitely high powers of z, and thence l, appear and, at first sight, the process appears uncontrollable! However, careful analysis[12] shows that, in effect, each power of z and l carries a factor of at least $B\sim\tau e^{-\kappa l}$ or $e^{-\kappa l}$. As a consequence one discovers[12] that $W(l)$ is *not* of the form (2) *unless* $\Phi(m)$ is *precisely parabolic* for $m\geq m^\times$, i.e., $\varepsilon_3=\varepsilon_4=\cdots=0$; otherwise the coefficients w_j in (2) must be replaced by *polynomials* in l, namely,

$$W_1(l)=w_{10}(T,h)+w_{11}(T,h)\kappa l\,, \tag{11}$$

$$W_2(l)=w_{20}+w_{21}\kappa l+w_{22}(\kappa l)^2,\ \cdots\,, \tag{12}$$

of degree precisely j. In addition the linear term in (2) has the coefficient

$$\bar{h}=\Phi(m_{\beta\infty})-\Phi(m_{\alpha\infty})=(m_{\alpha 0}-m_{\beta 0})h+O(h^2)\,. \tag{13}$$

Of course, such changes in the behavior of $W(l)$ have consequences in the RG treatment. Accepting (11) and (12) with nonvanishing w_{11} and w_{22}, and following Ref. 3, one finds[12] that divergent corrections to the original critical behavior arise: e.g., for $\omega < \frac{1}{2}$ (regime I), the wetting layer thickness for $h=0$ then diverges as[18]

$$\kappa\langle l\rangle \approx (1+2\omega)(1-\omega)^{-1}\ln t^{-1} + \ln\ln t^{-1}, \qquad (14)$$

where $t=(T_{cW}-T)/T_{cW}$; the last term is new but surely hard to detect! A corresponding new term, $\ln\ln|h|^{-1}$ appears *at* $T=T_{cW}$ *and* in the *complete wetting*[4] behavior above T_{cW}.

However, this analysis neglects the τ-dependence noted in (9). When this is traced through one finds that the polynomial coefficients in (11) and (12) take the form

$$w_{jk}(T,h) \approx (a_{jk}+b_j\varepsilon\tau)\varepsilon^{2k}\tau^{|2k+2-j|^+} \qquad (15)$$

with $a_{jj}\equiv 0$, $|x|^+ = \max\{x,0\}$, and $k \le j$. This implies $w_{10}\sim\tau$, $w_{11}\sim\varepsilon^3\tau^4$, $w_{20}=O(1)$, $w_{21}\sim\varepsilon^2\tau$, $w_{22}\sim\varepsilon^5\tau^5, \cdots$.

Now recall that in (2) w_1 vanishes as criticality is approached like $t_0\equiv(T-T_{cW}^0)/T_{cW}^0$ (when $\omega\le 2$).[3] Evidently τ must (and does) also *vanish* like t_0. Hence the power-law corrections to w_{10} and w_{20} in (11) and (12) vanish rapidly as $t_0\to 0$. This has no relevance to the new complete wetting behavior but when the critical wetting calculations are reworked recognizing this, *only the correction factors* to the leading behavior are modified for $\omega<2$ (regimes I and II). [Thus the $\ln\ln t^{-1}$ term in (14) does not appear.] In regime III, when $\omega>2$, one finds that T_{cW} ($\neq T_{cW}^0$) and various amplitudes change but the leading divergent forms are again unaltered.[12] In summary, although the form (2) for $W(l)$ is generally incorrect when $l\to\infty$ at *fixed* T, h, and h_1, the deviations vanish sufficiently rapidly on approach to wetting criticality that the original RG predictions for the singular behavior[3] remain valid!

It is worth commenting that *multicritical* wetting[7] is determined in mean-field theory by $w_1=\cdots=w_k=0$ with $k=2$ for *tricriticality*. It follows from (15) that (2) remains valid for analyzing *tricriticality*; however, for the academic cases $k=3,4,\cdots$ one should note that W_4, $W_5\sim\tau^0 l$, W_6, $W_7\sim\tau^0 l^2$, etc., contrary to (2).

Although our conclusions are satisfying at one level, the discrepancy with Monte Carlo simulations stands unresolved. The crossing criterion used for l is appealing theoretically and its lack of dependence on the specific value of $m^\times$ suggests it is fairly robust. Nevertheless, it is not really satisfactory from a laboratory viewpoint. Accordingly, we have explored the alternative *integral criterion* embodied in

$$\bar{l}=\int_0^\infty dz\,[m(z)-m_{\alpha\infty}]^p/(m_{\beta\infty}-m_{\alpha\infty})^p, \qquad (16)$$

where $m_{\alpha\infty}(T,h)$ and $m_{\beta\infty}(T,h)$ are the bulk order-parameter values. When $p=1$ this definition relates $\bar{l}(\equiv l)$ to the *absorption*, which is a natural quantity to consider. However, while one can generally embody (16) as a constraint by using a Lagrange multiplier,[14] this approach fails when $p=1$ (basically because the constraint then perturbs the bulk phase α significantly even when $z\to\infty$).[12]

On the other hand, $p=2$ also provides a physically reasonable definition. Furthermore, if one adopts $\Phi_0=rm^2+um^4$, as usual,[7] it proves possible, although algebraically complex, to perform the analysis to determine $W(\bar{l})$ *explicitly*.[12] (This could also be done for $p=3$ and $p=4$.) The form (2) is now recaptured precisely with *no* factors of $\bar{l}$. Of course, the expressions for $w_1, w_2, \cdots$ differ from those found previously, although one still has $w_1\sim\tau$ and $w_2=O(1)$. The remaining changes result from the actual difference $l-\bar{l}$ which, as expected, can be shown[12] to be of order ξ_β ($=\xi_\alpha$). Once again, then, the potential $W(l)$ used in the RG theory[1-4] may be regarded as acceptable.

Our considerations thus strengthen the basis of the RG theory and so sharpen the disagreement between theory and simulation! Various suggested explanations have been published[4-8,10,11] but fewer remain viable. Most interesting might be relevant effects of lattice structure on critical wetting even when T exceeds $T_{\text{roughening}}$. Certainly, the lattice structure causes the difference between the stiffness $\tilde{\Sigma}$ and the tension Σ; but it is hard to understand its effects when both l and $\xi_\parallel$ become large. Perhaps, however, the simulations are as yet too small in size or still subject to technical difficulties. The issue warrants continued attention.[19]

We are grateful to Matthew P. A. Fisher, Daniel S. Fisher, Martin P. Gelfand, David Jasnow, and Reinhard Lipowsky for informative discussions and to the National Science Foundation for support (under Grant No. DMR 90-07811). K. Binder, E. Brézin, D. S. Fisher, B. I. Halperin, D. M. Kroll, D. P. Landau, R. Lipowsky, L. V. Mikheev, and R. K. P. Zia kindly commented on a draft version of the manuscript.

[1] E. Brézin, B. I. Halperin, and S. Leibler, (a) J. Phys. (Paris) **44**, 775 (1983); (b) Phys. Rev. Lett. **50**, 1387 (1983).

[2] R. Lipowsky, D. M. Kroll, and R. K. P. Zia, Phys. Rev. B **27**, 4499 (1983).

[3] D. S. Fisher and D. A. Huse, Phys. Rev. **32**, 247 (1985).

[4] For reviews see: (a) D. M. Kroll, J. Appl. Phys. **61**, 3595 (1987); (b) M. E. Fisher, in *Statistical Mechanics of Membranes and Surfaces*, edited by D. R. Nelson, T. Piran, and S. Weinberg (World Scientific, Singapore, 1989), p. 19, especially Sec. 1.6, Chap. 3.

[5] K. Binder, D. P. Landau, and D. M. Kroll, Phys. Rev. Lett. **56**, 2272 (1986); K. Binder and D. P. Landau, Phys. Rev. B **37**, 1745 (1988).

[6] K. Binder, D. P. Landau, and S. Wansleben, Phys. Rev. B **40**, 6971 (1989).

[7] H. Nakanishi and M. E. Fisher, Phys. Rev. Lett. **49**, 1565 (1982).

[8] G. Gompper, D. M. Kroll, and R. Lipowsky, Phys. Rev. B **42**,

961 (1990) simulated the solid-on-solid limit of the Ising model. They saw universal but nonclassical behavior corresponding to $\omega \simeq \frac{1}{4}$. However, this model has no bulk fluctuations and ξ_β is not well-defined. A comparison with the isotropic Ising model of Ref. 5 was interpreted in terms of a "length scale" which proves to be about twice as large as the isotropic bulk correlation length, ξ_β. In effect this requires ω *too small* by a factor of four.

[9]R. Lipowsky and M. E. Fisher, Phys. Rev. Lett. **57**, 2411 (1986); Phys. Rev. B **36**, 2126 (1987) studied the effects on the RG of nonlinear terms neglected in Ref. 3.

[10]T. J. Halpin-Healy and E. Brézin, Phys. Rev. Lett. **58**, 1220 (1987) suggested slow crossovers but gave no quantitative estimates.

[11]See, especially, G. Gompper and D. M. Kroll, Phys. Rev. B **37**, 3821 (1988), who beautifully verify the RG theory *on* the basis of (2), finding a wide critical region, but also suggest other possible sources of difficulty.

[12]See also A. J. Jin and M. E. Fisher (to be published). In (5) one actually finds that the stiffness $\tilde{\Sigma}(T)$ gains an increment, $\Delta\tilde{\Sigma}(l;T,h;h_1,g)$, which, however, decays as $le^{-\kappa l}$. Furthermore when this is included in the analysis of Ref. 3, it does not affect the leading critical singularities.

[13](a) R. Lipowsky, Z. Phys. B **55**, 345 (1984); (b) Habilitations-Schrift, Ludwig-Maximillians-Universität, München, 1987 (distributed by KFA Jülich as Jül-spez-438).

[14]See J. Rudnick and D. Jasnow, Phys. Rev. B **24**, 2760 (1981) and references therein, especially to Gervais and Sakita.

[15]Note that Fig. 5 in Ref. 14 is misleading since no kinks are shown in the profiles. A sharp kink can be avoided if a smeared localization or constraint function is used but the subsequent analysis is more complicated.

[16]Despite the resemblance to the ansatz criticized above, this is *exact* (for $z \geq l$, $m \leq m^\times$).

[17]Our approach is motivated by the double-parabola approximation introduced by Lipowsky, Ref. 13.

[18]As stated, this result supposes $w_{11}(\varepsilon_3,\varepsilon_4,\cdots) \neq 0$; however, w_{11} might vanish for certain values of $\varepsilon_3,\varepsilon_4,\cdots$.

[19]In work underway (M. E. Fisher and B. H. Wen) $\omega(T)$ is being reestimated for the $d=3$ Ising model; but first indications suggest previous work was sufficiently precise.