Critical Wetting in Three Dimensions

E. Brézin and B. I. Halperin
Physics Department, Harvard University,[a] *Cambridge, Massachusetts 02138, and Service de Physique Théorique, Centre d'Etudes Nucléaires de Saclay,*[b] *F-91190 Gif-sur-Yvette, France*

and

S. Leibler
Service de Physique Théorique, Centre d'Etudes Nucléaires de Sacaly, F-91190 Gif-sur-Yvette, France
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A critical wetting (or interface delocalization) transition occurs when the interface between two fluid phases becomes infinitesimally bound to an attracting wall. It is shown that the critical exponents at this transition depend continuously on the parameter $\omega \equiv k_B T_w/(4\pi\xi_b{}^2\sigma)$, where σ is the surface tension of the free interface, ξ_b is the bulk correlation length in the attracted fluid phase, and T_w is the transition temperature.

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In a previous article[1] we have shown that mean-field theory applied to the critical wetting transition holds above three dimensions but that fluctuation corrections ought to be important in the physically interesting case of $d=3$. The form of these corrections will be discussed in the present note. Let us recall that this transition occurs under suitable conditions in a binary fluid mixture below the consolute point T_c near a wall which adsorbs preferentially one of the components of the mixture[2] (we consider only the ideal case where the conditions far from the wall are precisely on the coexistence curve for the two fluids). This transition may be described as the delocalization of the interface between the two components of the mixture: At low temperatures the interface is localized in the vicinity of the wall (partial wetting), but at some finite temperature T_w below T_c the thickness of the wetting layer diverges. Within mean-field theory one finds that this transition may be first or second order according to the values of physical parameters such as the potential difference at the wall.[3]

Mean-field theory makes a number of detailed predictions for the phase transition in the second-order (critical wetting) case. The correlation length ξ which describes correlations parallel to the wall is predicted to diverge[1] as

$$\xi \simeq \xi_0 \tau^{-1}, \tag{1}$$

where $\tau \equiv (T_w - T)/T_c$, and ξ_0 is a constant. The distance z^* of the interface from the wall is predicted to diverge as

$$z^* \propto \ln(1/\tau) \tag{2}$$

while the singular part of the surface tension, which results from the binding of the interface to the wall, is predicted to obey

$$\delta\sigma \propto -\xi^{-2}. \tag{3}$$

We shall see below that when fluctuations are taken into account, the behavior at the critical wetting transition, for $d=3$, actually depends on the value of a dimensionless parameter

$$\omega \equiv k_B T/4\pi \xi_b{}^2 \sigma, \tag{4}$$

where ξ_b is the *bulk* correlation length of the fluid phase attracted to the wall and σ is the surface tension of the free interface. For $0<\omega<\frac{1}{2}$, we find instead of (1)

$$\xi = \xi_0 \tau^{-\nu}, \quad \nu = (1-\omega)^{-1}, \tag{5a}$$

while for $\frac{1}{2}<\omega<2$, we find

$$\xi = \xi_0 \tau^{-\nu}[\ln \tau^{-1}]^{-\tilde{\nu}}, \quad \nu = (\sqrt{2} - \sqrt{\omega})^{-2}, \quad \tilde{\nu} = [1+(\omega/8)^{1/2}]\nu \tag{5b}$$

and for $\omega > 2$,

$$\xi \propto \exp[c\tau^{-1}\ln(1/\tau)], \tag{5c}$$

where c is a constant.

Equations (2) and (3) describing the position of the interface, and relating $\delta\sigma$ to the correlation length ξ, remain valid in the presence of fluctuations. Note that (5a) and (5b) both give $\nu \to 2$ for $\omega \to \frac{1}{2}$ at the boundary of the first two regimes, while (5b) gives $\nu \to \infty$ for $\omega \to 2^-$. The smaller the value of the surface tension σ, the larger is the value of ω, and the more important are the fluctuation corrections to mean-field theory.

In all of our regimes, we find that the characteristic thickness δ of the interface diverges $\propto (z^*)^{1/2}$, as $T \to T_w$, and hence δ is small compared to z^*. Nevertheless, the rare fluctuations which bring a piece of the interface close to the wall are important for $\omega > \frac{1}{2}$, and it is these fluctuations which are responsible for the change in behavior described by (5b) and (5c).

Equation 5(a), for small values of ω, has recently been found independently by Lipowsky, Kroll, and Zia.[4] For large values of ω, these authors also report an exponential type of divergence, but for reasons we do not understand they do not find the logarithm in the exponential. (See also the earlier work by Kroll and Lipowsky.[5]) However, Lipowsky, Kroll, and Zia did not find the intermediate regime given by Eq. (5b) above, for $\frac{1}{2} < \omega < 2$.

In all of our discussions, the long-range interaction between the wall and the interface arising from van der Waals forces has been omitted. This is legitimate provided the bulk correlation length is very large, and we are thus limited to the regime in which T_w is very close to the consolute temperature T_c. For $T \to T_c$, however, the quantity ω, defined by (4), approaches a universal finite constant ω_c, according to the scaling and renormalization-group theories of the consolute point,[6] so that the systems of experimental interest will presumably have ω close to this value. A recent Monte Carlo simulation of the surface tension for the Ising model by Binder,[7] together with the determination of the correlation length by Tarko and Fisher,[8] leads to the estimate $\omega_c \approx 1.2$ (within a few percent). From experimental measurements of the surface tension and of the correlation length (above T_c)[9] and theoretical results[10] on ξ_0^+/ξ_0^- one obtains ω_c in the range 1.2 to 1.5, which puts us in the region where Eq. (5b) is valid with $\nu \gtrsim 10$. Because of "crossover effects" due to the van der Waals interaction and of the sensitivity of the exponent to the rather uncertain value of ω, it seems likely that a quantitative comparison between theory and experiment for the critical wetting transition will require a full analysis of the model with realistic potentials and cannot be restricted to the asymptotic critical behavior.[11]

Our calculations employ an interface displacement model in which one writes an effective Hamiltonian for the location $z(\vec{\rho})$ of the interface as the function of the coordinate $\vec{\rho} = (x, y)$ parallel to the wall (which we take to be the plane $z = 0$):

$$H/k_B T = \int d^2\rho \{ \tfrac{1}{2}(\nabla z)^2 + V(z) \}, \tag{6}$$

where V is a potential whose form will be specified, and we assume a short-wavelength cutoff on an appropriate microscopic scale. We have chosen units where the surface tension of the free interface obeys $\sigma/k_B T = 1$.

We begin by considering a model (model I) where V is given by

$$V_I(z) = -a e^{-\alpha z} + b e^{-2\alpha z}, \tag{7}$$

where α is the reciprocal of the bulk correlation length ξ_b so that the parameter ω of Eq. (4) is given in current units by

$$\omega = \alpha^2/4\pi. \tag{8}$$

Equation (7) has been derived in Ref. 1; the exhibited terms are the first two terms in a power-series expansion in $e^{-\alpha z}$, and it is valid to use this form provided that z is sufficiently *large and positive*. In Eq. (7) the parameter a vanishes linearly when T approaches T_w and b remains positive (its variation with T is negligible). This model leads to the mean-field results (1)–(3) if $\vec{\rho}$ has more than two dimensions, but for a two-dimensional interface we need to take into account the statistical fluctuations and follow as usual the renormalization-group approach. If we ignore the restriction $z > 0$ we can use a field-theoretic renormalization-group approach. In two dimensions all $U - V$ divergences correspond to internal lines starting and ending at the same point. For exponential interactions this leads to simple multiplicative renormalizations of a or b (Ref. 12) given by

$$a = a_R \exp(-\tfrac{1}{2}\alpha^2 \Delta_\Lambda), \tag{9a}$$

$$b = b_R \exp(-2\alpha^2 \Delta_\Lambda), \tag{9b}$$

in which Δ_Λ is the propagator at coinciding points, cut off at some wave number Λ, and μ is some arbitrary wave-number scale:

$$\Delta_\Lambda = \int \frac{d^2 q}{(2\pi)^2} (q^2 + \mu^2)^{-1} \theta(\Lambda^2 - q^2) = \frac{1}{2\pi} \ln\left(\frac{\Lambda}{\mu}\right) + O(\Lambda^{-2}). \tag{10}$$

The (bare) renormalization-group equations ($\Lambda \to \lambda\Lambda$ with fixed a_R and b_R) are thus given by

$$a(\lambda) = a\lambda^{-\omega}, \tag{11a}$$

$$b(\lambda) = b\lambda^{-4\omega}. \tag{11b}$$

At the scale $\lambda \sim 1/\xi$ all the short-distance fluctuations are integrated out and we can take the effective potential at that scale,

$$V_\xi(z) = -a\xi^\omega e^{-\alpha z} + b\xi^{4\omega} e^{-2\alpha z}, \tag{12}$$

and calculate the location z^* of the interface,

$$[\partial V_\xi/\partial z]_{z^*}=0, \qquad (13a)$$

and the correlation length as

$$\xi^{-2}=[\partial^2 V_\xi/\partial z^2]_{z^*}. \qquad (13b)$$

The solution to Eqs. (13) is

$$z^*=(4\pi\omega)^{-1/2}(1+2\omega)\ln\xi \qquad (14)$$

with ξ given by Eq. (5a) above.

The renormalization of model I is exact in the limit $T\to T_w$ provided that the important contributions come from z large and positive, where the potential $V(z)$ is small, and where terms beyond the first two exponentials are negligible. It is not sufficient that the mean value of the displacement z^* be large, however, because the thickness of the free interface also diverges in $d=3$. With this in mind the proper renormalization of $V(z)$ can be understood if we say that the bare mean-field potential is in effect convoluted with a Gaussian whose width δ represents the width of the interface:

$$V(z)\to\tilde{V}(z)=\int_0^\infty dz'\, V(z')(2\pi\delta^2)^{-1/2}\exp[-(z'-z)^2/2\delta^2]. \qquad (15)$$

The potential $V_{\rm I}(z)$ is the sum of two terms of the form $e^{-n\alpha z}$, with $n=1$ or 2. When these terms are substituted with Eq. (15) and the restriction $z'>0$ is taken into account, we find that the transformation is

$$e^{-n\alpha z}\to e^{-n\alpha z}\exp(n^2\alpha^2\delta^2/2)\int_{n\alpha\delta^2-z}^\infty \exp(-s^2/2\delta^2)ds/\delta(2\pi)^{1/2}. \qquad (16)$$

The integral in (16) will be a constant (unity) and the convolution will not modify the initial form of the potential if $[n\alpha\delta^2-z]/\delta$ is large and negative. If we take $z\approx z^*$, with z^* given by Eq. (14), and use $\delta^2\approx(1/2\pi)\ln\xi$ [which gives the thickness calculated in absence of $V_{\rm I}(z)$, taking into account fluctuations on the wavelength scale smaller than ξ], then the criterion for stability of model I for $\xi\to\infty$ is

$$n\alpha/2\pi-(1+2\omega)/(4\pi\omega)^{1/2}<0, \qquad (17)$$

for $n=1, 2$. These conditions are fulfilled for $\omega<\frac{1}{2}$.

For $\omega>\frac{1}{2}$ the stability criterion is violated for the repulsive term $be^{-2\alpha z}$ in the potential $V_{\rm I}$ of Eq. (7). Thus the dominant contribution to the repulsive part of the renormalized potential will actually come from relatively rare large excursions of the interface, corresponding to the values of $z'\approx 0$, in the integrand of Eq. (15). In this case, the exponential falloff of the repulsion at large distances has no physical importance, and we may replace the term $be^{-2\alpha z}$ by any convenient repulsion of sufficiently short range. In order to carry out the renormalization, it is most convenient to use a Gaussian repulsion, and we are thus led to our model II for the potential

$$V_{\rm II}(z)=-ae^{-\alpha z}+(c/\delta_0)\{\exp[-(z^2/2\delta_0^2)]\}. \qquad (18)$$

The renormalization-group equation (11a) for a is unchanged; the Gaussian interaction is treated in a similar way and we find that c is not renormalized but the thickness δ_0 increases as

$$\delta^2(\lambda)=\delta_0^2-(1/2\pi)\ln\lambda. \qquad (19)$$

We perform again a dilatation up to the scale $\lambda=1/\xi$ and solve Eqs. (13a) and (13b) with the potential $V_{\rm II}$. The results are now

$$z^*\approx(2/\pi)^{1/2}(\ln\xi-\tfrac{1}{8}\ln\ln\xi) \qquad (20)$$

with ξ given by Eq. (5b) above, provided that $\omega<2$.

We can now repeat the stability analysis of Eq. (16) above. Using the solution to model II, we find that $(\alpha\delta^2-z^*)\delta\to-\infty$ for $\omega<2$; thus the renormalization of the attractive exponential $-ae^{-\alpha z}$ indeed comes from large values of z' and the form of this term is unchanged. At the same time, we again find that $(n\alpha\delta^2-z^*)/\delta\to\infty$ for $n\geqslant 2$ if $\omega>\frac{1}{2}$. Thus it is consistent to ignore the exponential tail of the repulsion, and to replace it by a Gaussian.

For $\omega>2$, there is no stable renormalization of model II. We expect that the important contributions to the attraction as well as the repulsive terms will now come from short distances and therefore we may replace both terms by Gaussians; we use the form

$$V_{\rm III}(z)=-\frac{f}{\delta_0}\exp[-(z-\zeta)^2/2\delta_0^2]+\frac{g}{\delta_0}\exp[-(z+\zeta)^2/2\delta_0^2]. \qquad (21)$$

This model was earlier considered by Kroll and Lipowsky,[5] but our results differ somewhat from theirs. Under renormalization δ_0 increases according to Eq. (19), but ξ, f, and g remain unchanged. Solving again Eqs. (13), we now find

$$z^* \approx (2/\pi)^{1/2}(\ln\xi - \tfrac{3}{4}\ln\ln\xi) \qquad (22)$$

with ξ given by Eq. (5c). Again we may check that $[n\alpha\delta^2 - z^*]/\delta \to +\infty$, for $\omega > 2$, and $n \geq 1$. Thus we are justified in ignoring the exponential tails of the potential in this case, and the results of the two-Gaussian model should be correct.

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[(a)]Permanent address for B. I. Halperin.

[(b)]Permanent address for E. Brézin.

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[11]In general a van der Waals force $\propto 1/r^6$ will lead to a term $\propto 1/z^2$ in the effective potential $V(z)$ of Eq. (6). This term will become more important than the exponential terms when z^* becomes large and will generally lead to a small first-order character or to a suppression of the wetting transition, according to the sign of the coefficient.

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