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Order-Parameter Profile in Semi-Infinite Systems at Criticality

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A description of the decay into the bulk of surface perturbations in a system *at* its critical point is presented. The description, justified by detailed renormalization-group calculations, yields asymptotic order-parameter decay, $z^{-(d-2+\eta)/2}$, along with power-law behavior connected with surface exponents under suitable conditions. Comparison with the phenomenological theories of Widom and of Fisher and de Gennes is also made.

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Because of enhanced surface exchange interactions (or a surface magnetic field) a magnetic material can have ordering on its surface above the Curie temperature T_c. As long as $T > T_c$ the magnetization will decay exponentially to zero in the bulk. *At* the Curie temperature there is power-law decay to zero with increasing distance into the bulk material.[1]

A similar situation exists in the case of a binary fluid mixture in coexistence with its vapor. When the consolute point, at temperature T_s, is approached from below ($T \to T_s^-$), the meniscus separating the coexisting fluid phases disappears while the interface between the critically mixed fluid and its noncritical vapor remains intact. *At* the consolute point the composition of the mixture in the vapor phase relaxes exponentially with distance from the liquid-vapor interface to its bulk value; in the liquid the decay to the critical composition is, once again, a power law.

This latter system has been analyzed within a modified Cahn-Hilliard[2] (or mean-field) theory by Widom.[3] While an exponent for the power-law decay to bulk behavior in the critical liquid is obtained, Widom points out that mean-field theory, modified or not, must be applied with caution here. This is because the correlation length in the critical liquid is *infinite*, and in general, mean-field theory loses its validity as the correlation length becomes large.

The challenge that must be met in the construction of a proper theory of the decay of surface perturbations at the bulk critical point arises from two aspects of the problem. First, as already noted, the bulk correlation length is infinite. The absence of an obvious length scale complicates the incorporation of critical fluctuations into a description of the spatial variation of the order parameter.[4] Second, the surface perturbations cannot be treated via linear-response theory. Such an approach leads immediately to divergences. The problem is inherently nonlinear.

As it turns out we have been able to derive, in a relatively transparent and useful form, a valid theoretical description of the decay into the bulk

of surface perturbations in a system at its critical point. For simplicity we consider the case of a uniaxial magnetic system at criticality whose order parameter, $m(z)$, is *constrained* to take on a nonzero value, m_0, at its surface, $z=0$. We consider the behavior of $m(z)$ as a function of z, the distance into the bulk, and find that our form yields several interesting results. First, as $z \to \infty$, we have

$$m(z) \propto \begin{cases} z^{-(d-2+\eta)/2}, & 2<d<4 \\ (\ln z)^{1/2} z^{-1}, & d=4, \end{cases} \quad (1)$$

where d is the dimensionality of the system and η is the standard bulk exponent for the decay of critical correlations. Under suitable conditions we also find $m(z)$ exhibiting power-law behavior in z connected with the surface exponents recently discussed by Wilson[5] and Diehl and Dietrich.[6] Finally we are able to make contact with the phenomenological theory of Fisher and de Gennes[7] for the effect of wall perturbations in a system of finite width. Some of our asymptotic predictions coincide with theirs, but we see additional effects, and our picture is free of a pathology that afflicts the Fisher–de Gennes phenomenology.

The existence of a simple form yielding new as well as previously suggested results in a problem that combines critical fluctuations, nonlinearity, and nontrivial spatial inhomogeneity is, we believe, noteworthy. Furthermore, and of ultimate importance, this simple form can be justified within the framework of the renormalization-group approach to critical phenomena, as will be indicated shortly. A more detailed discussion of the picture presented here, including a technical description of the renormalization-group calculations, will be published elsewhere.

The uniaxial ferromagnet we consider has a scalar order parameter $s(\vec{x})$ and a reduced Hamiltonian

$$\mathcal{H} = -H/k_B T = -\int [\tfrac{1}{2}(\nabla s)^2 + \tfrac{1}{2} r s^2 + u s^4] d^3x. \quad (2)$$

The order parameter $s(\vec{x})$ corresponds to the local magnetization. In the case of the binary fluid it would correspond to the difference between the local and the critical composition. Standard renormalization-group arguments[8] lead typically to a free energy $\mathcal{F} \propto \ln\{\mathrm{Tr}_s[\exp(\mathcal{H})]\}$ that can be written in the form

$$\mathcal{F} = e^{-l^* d} \int [e^{2l^*} e^{(d-2+\eta)l^*} \tfrac{1}{2}(\nabla M)^2 + \tfrac{1}{2} t e^{\nu l^*} e^{(d-2+\eta)l^*} M^2 + u^* e^{2(d-2+\eta)l^*} M^4] d^3x + (F - S). \quad (3)$$

The term F in Eq. (3) denotes fluctuation corrections and S denotes subtractions. In a homogeneous system the quantity l^* is related to the correlation length, ξ, by $\xi = e^{l^*}$. (The microscopic length scale or lattice spacing has been set equal to unity.) In a momentum-space calculation e^{-l^*} is the lower cutoff for the wave numbers of the degrees of freedom that must be eliminated via renormalization-group recursion relations. The modified mean-field form on the right-hand side of Eq. (3) yields, with appropriate criteria for the choice of l^*, a scaling form for the free energy near criticality. The contribution $F - S$ also has this form.

The form (3) turns out to be adaptable to the problem of the decay of surface perturbations at criticality if one makes the *Ansatz* that l^* varies with position, or, in other words, if one accepts the notion of a *spatially varying correlation length.*

When the reduced temperature $t \propto T - T_c$ in Eq. (3) is zero, the standard criterion for l^* in a *homogeneous* system is[8]

$$12 u^* M^2 e^{(d-2+\eta)l^*} = 1. \quad (4)$$

Our adaptation of Eq. (3) allows a z dependence of l^* by use of Eq. (4) with M replaced by $m(z)$. The equation of state satisfied by $m(z)$ is obtained from Eq. (3) by differentiation with respect to $m(z)$, yielding

$$\delta\mathcal{F}/\delta m(z) = e^{-l^* d}[-e^{(d+\eta)l^*} d^2 m/dz^2 + 4u^* m^3(z) e^{2(d-2+\eta)l^*}] = 0. \quad (5)$$

Inserting our $l^*(z)$ obtained in terms of $m(z)$ via Eq. (4), we obtain for the equation of state

$$-d^2 m/dz^2 + f(u^*) m^{(d+2+\eta)/(d-2+\eta)} = 0. \quad (6)$$

the solution of which is

$$m(z) = [(d-2+\eta)(d+\eta)/4 f(u^*)]^{(d-2+\eta)/4} (z+z_0)^{-(d-2+\eta)/2}. \quad (7)$$

The asymptotic decay to zero of $m(z)$ is with the exponent noted in Eq. (1) above. Since $\xi \propto e^{l^*} \propto m(z)^{-2/(d-2+\eta)}$, we have $\xi \propto z + z_0$. The correlation length increases linearly with distance into the bulk.

The test of this *Ansatz* is the effect of fluctuations. They must behave as if there were a correlation length increasing linearly with z, and they must be consistent with the scaling hypotheses inherent in the form (3) for the free energy. Since this free energy is just the bulk free energy generalized to allow for a spatially varying correlation length, the criterion of consistency with scaling can be reduced to the requirement that the subtractions necessary to eliminate divergences of fluctuation corrections to mean-field theory be just those that eliminate divergences in the bulk, the infrared cutoff for fluctuations varying appropriately with distance from the surface. *If this were not so*, the recursion relations that absorb the effects of the subtractions would have to be altered, and there is no longer any guarantee that bulk critical exponents suffice in the description of the asymptotic decay of surface correlations.

The simplest way to proceed in the context of a field-theoretical approach to critical phenomena is via the interdimensional ϵ expansion where, in this case, $\epsilon = 4 - d$. To simplify the justification of our *Ansatz*, calculations here will be carried out in exactly four dimensions, where mean-field theory is asymptotically valid at the critical point. The generalization of our results to $4 - \epsilon$ dimensions is straightforward, but involves some technicalities, the complete elucidation of which is too involved for the present format.

Simple mean-field theory amounts to minimizing the Hamiltonian (2) with respect to the order parameter, $s(\vec{x})$. The functional extremum equation $\delta\bar{\mathcal{H}}/\delta s = 0$ with $r = 0$ yields $s_{\min} \equiv m_0(z)$ with

$$m_0(z) = [2u]^{-1/2}(z + z_0)^{-1}. \tag{8}$$

This is the limit of Eq. (7) when $d = 4$ and $\eta = 0$.[9] Writing $s(\vec{x}) = m_0(z) + \sigma(\vec{x})$ we have

$$\bar{\mathcal{H}} = -\int [\tfrac{1}{2}(dm_0/dz)^2 + u m_0^4]\, d^3x - \int [\tfrac{1}{2}(\nabla\sigma)^2 + 6u\sigma^2 m_0^2]\, d^3x + O(\sigma^3 m_0, \sigma^4), \tag{9}$$

where r, the unrenormalized reduced temperature, has been set equal to zero. The quadratic term in $\sigma(\vec{x})$ can be diagonalized if we express σ in terms of the eigenfunctions of

$$\mathfrak{L} = -\nabla^2 + 12u m_0^2 = -\nabla^2 + 6z^{-2}. \tag{10}$$

In Eq. (10) z_0 has been set equal to zero. The eigenfunctions of $\mathfrak{L}$ are

$$\psi_\lambda(\vec{x}) = e^{i\vec{q}\cdot\vec{\rho}} kz j_2(kz). \tag{11}$$

The eigenvalue, λ, is equal to $k^2 + q^2$. The vectors $\vec{q}$ and $\vec{\rho}$ are the $(d-1)$-dimensional wave vector and position vector in the plane of the surface. Given these eigenfunctions the four-dimensional propagator appearing in Feynman diagrams representing fluctuations is

$$G(\vec{x}, \vec{x}') = \frac{1}{16\pi^2 zz'}\left\{6 - 6\frac{(\Delta\rho)^2 + z^2 + z'^2}{2zz'} \ln\left(\frac{R_+^2}{R_-^2}\right) + 3\frac{(\Delta\rho)^2 + 4z^2z'^2}{2zz'}(R_-^{-2} + R_+^{-2})\right\}, \tag{12}$$

where $\Delta\vec{\rho} = |\vec{\rho} - \vec{\rho}'| \equiv \Delta\rho$ and $R_\pm^2 = (\Delta\rho)^2 + (z \pm z')^2$. In the bulk at criticality the bare propagator in four dimensions is, by contrast, given by

$$G_B(|\vec{x} - \vec{x}'|) \propto |\vec{x} - \vec{x}'|^{-2} = R_-^{-2}. \tag{13}$$

The infinite correlation length's effect shows up in the slow, power-law, decay of G_B for large $|\vec{x} - \vec{x}'|$. In Eq. (12) one sees a crossover from inverse-square behavior to a more rapid decay when $|\vec{x} - \vec{x}'| \sim \min(z, z')$. When the separation is large and well outside this crossover region, the decay of the propagator, while not exponential, is considerably more rapid than inverse square. From the crossover we infer an effective correlation length $\xi(z, z') \sim \min(z, z')$. This correlation length provides an infrared cutoff in Feynman integrals for the fluctuation corrections to thermodynamic functions, which in turn dictates an infrared cutoff for subtractions and momentum-shell recursion relations. We have verified to two-loop order that the subtractions required are the *same* as in the bulk. Thus no new recursion relations are required and fluctuation corrections ultimately take on the same scaling form as the modified mean-field theory in Eq. (3).

All this holds when $z_0 = 0$ in Eqs. (7) and (8), or when the order parameter has an infinite expectation value at the surface. When $m(0) = m_0$ is finite, an additional complication arises, but one which can be dealt with within an ϵ expansion. In fixing the order parameter at the surface we con-

strain the fluctuations, $\sigma(\vec{x})$, to be zero there. The eigenfunctions of the quadratic Hamiltonian, $-\nabla^2+6/(z+z_0)^2$, are made up of a linear combination of spherical Bessel and Hankel functions of order two. The correlation length goes as $z+z_0$ when z is large, but it goes as z when z is close to zero because the constraint on fluctuations produces an additional infrared cutoff for small z. The effective mean-field theory in Eq. (3) must be amended by the inclusion of the single-loop contribution to the fluctuations (which incorporates the additional infrared cutoff and generates a "mass"). With the single-loop term added the effective mean-field equation of state is

$$-e^{(d-\eta)l^*}(d^2m/dz^2)+4u^*m^3e^{2(d-2+\eta)l^*}-6K_4u^*me^{(d-2+\eta)l^*}=0. \quad (14)$$

If we take $l^*(z)$ to be given by Eq. (4) and insert an $m(z)\propto(z+z_0)^{-(d-2+\eta)/2}$ into Eq. (14), we find that the added term merely yields a small correction to the amplitude of $m(z)$ when u^* is small, without affecting the power law.[10] On the other hand, if we set $e^{l^*}=z$ the new term dominates and $m(z)$ satisfies

$$-d^2m/dz^2-6K_4u^*m(z)/z^2=0, \quad (15)$$

the solution of which is[11]

$$m(z)=Az^{p_+}+Bz^{p_-}, \quad (16)$$

with $p_\pm$ satisfying

$$p_\pm=\tfrac{1}{2}[1\pm(1-24K_4u^*)^{1/2}]\simeq 1\mp\epsilon/6. \quad (17)$$

In the above we have used the lowest-order result[8] $u^*=\epsilon/36K_4$. The exponents in Eq. (17) are the surface exponents to which we alluded earlier.[5,6]

The effective mean-field theory yielding *both* proper decay to bulk order *and* surface exponent behavior when it appears can be formed from the equation of state (14) with $l(z)=\ln[\xi(z)]$ given by

$$[6u^*m(z)^2e^{(d-2+\eta)l^*}+e^{2l^*}/z^2]=1. \quad (18)$$

Widom's[3] phenomenological equation of state yields a slightly different power-law decay than does our approach, and this can be traced to a failure to scale the gradient term in the free energy properly. The phenomenology of Fisher and de Gennes[7] yields a power-law decay into the bulk that is precisely the same as ours, but it does not allow for the possibility of surface exponents. Furthermore, if $m(z)$ goes through zero, as in the case of a thick slab with the order parameter constrained to take on equal and opposite values on the two faces, their correlation length, defined essentially through strict application of Eq. (4), goes to infinity and $m(z)$ is predicted to behave singularly when it passes through zero. Our approach allows us to retain a finite correlation length at that point, consistent with the kinds of fluctuations present when $m(z)\propto(z-z_1)$. No pathological singularities are seen to arise.

Details of the two-loop calculation will be presented elsewhere along with further discussion of "surface scaling" and additional considerations specific to the fluid case. The authors gratefully acknowledge support of the National Science Foundation through the Division of Materials Research.

[1]Bulk ordering in the presence of surface order has been termed the "extraordinary transition." See A. J. Bray and M. A. Moore, Phys. Rev. Lett. 38, 1046 (1977), and J. Phys. A 10, 1927 (1977); T. C. Lubensky and M. H. Rubin, Phys. Rev. B 12, 3885 (1975).

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[3]B. Widom, J. Chem. Phys. 67, 872 (1977), and in *Perspectives in Statistical Physics*, edited by H. J. Raveché (North-Holland, Amsterdam, 1981), Chap. 15.

[4]In standard interface calculations the inhomogeneity is confined to a distance on the order of the correlation length. Compare the present approach to J. Rudnick and D. Jasnow, Phys. Rev. B 17, 1351 (1978); T. Ohta and K. Kawasaki, Prog. Theor. Phys. 58, 467 (1977); D. Jasnow and J. Rudnick, Phys. Rev. Lett. 41, 698 (1978); D. Jasnow, T. Ohta, and J. Rudnick, Phys. Rev. B 20, 2774 (1979).

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[8]See, e.g., J. Rudnick and D. R. Nelson, Phys. Rev. B 13, 2208 (1976).

[9]For simplicity we neglect logarithmic corrections.

[10]Here one has a hint of the calculation of the asymptotic ($z\to\infty$) behavior for $\epsilon>0$ ($d<4$). The fluctuation corrections merely produce an ϵ expansion for the amplitude of the decay in Eq. (1).

[11]Equation (16) holds for $z\gtrsim 1$; recall that the lattice spacing has been set equal to unity. Whether or not a surface regime in which Eq. (16) applies will be observable depends on the magnitude of m_0. If m_0 is too large, the crossover to surface behavior occurs too near $z=0$ and Eq. (16) will not apply.