Pseudospinodal critical phenomena, renormalized instantons, and the one-loop equation of state

Yannis Drossinos
Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138

David Ronis*
Department of Chemistry, McGill University, 801 Sherbrooke Street West, Montreal, Quebec, Canada H3A 2K6
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A field-theoretic renormalization-group analysis of the Landau-Ginzburg ϕ^4 free energy inside the coexistence region is presented. Real and imaginary contributions to the free energy arising from spatially uniform and spherical-droplet functional saddle points are determined to first order in $\epsilon \equiv 4-d$ by solving a Jacobi equation in the Wentzel-Kramers-Brillouin approximation. An analytic, uniform approximation for the entire coexistence region is obtained, and the theory is renormalized explicitly. Inside the coexistence region, for $d<4$, two independent length scales arise: a correlation length that diverges along a mean-field pseudospinodal line and a new length (which we associate with the internal correlation volume of a single droplet) that diverges along an experimentally inaccessible line of ϕ^4 fixed points. The critical region, effective critical exponents, and pseudospinodals are discussed.

I. INTRODUCTION

Renormalization-group techniques[1,2] have been successfully applied to the determination of critical exponents and the equation of state for second-order phase transitions above the critical temperature, T_c. Below T_c, there exists a region of the phase diagram where the mean-field free energy develops two minima, a metastable and a stable one. Concomitant mean-field equations of state, e.g., the van der Waals equation of state, divide the coexistence region into metastable and unstable regions, separated by a well-defined spinodal curve along which thermodynamic quantities exhibit power-law singularities similar to those observed close to the critical point

The starting point of many investigations of the region inside the coexistence curve is provided by the droplet model, extensively studied by Fisher,[3] whereby droplet-like fluctuations of the stable phase in a background of the metastable phase are analyzed nonperturbatively. According to the classical droplet model and its variants,[3,4] the imbalance between the surface and volume terms in the free energy of formation of a droplet of the new phase results in an essential singularity of the free energy at $H=0$. Analytic continuation around the essential singularity, which is superimposed on a branch point, makes the contribution of the droplet-like fluctuations to the free energy imaginary.

Droplet-like fluctuations are assumed to play a key role in the decay of the metastable state via nucleation.[5] A field-theoretic description of nucleation close to coexistence was developed by Langer,[5] where the droplet was identified with the nonuniform solution of the Euler-Lagrange equation associated with a ϕ^4 free energy discussed by Cahn and Hilliard.[6] The field-theoretic droplet model reproduces the qualitative features of the classical droplet model, albeit with a slightly different prefactor to the dominant essential singularity.[5,7] Langer also showed[8] that the decay rate of the metastable state is proportional to the imaginary part of the free energy. Unger and Klein[9] extended Langer's analysis and considered nucleation close to the pseudospinodal. (One of the results of this work is a uniform expression for the imaginary part of the free energy for the whole coexistence region.) Both treatments, however, are mean-field calculations and, thus, nonapplicable to the critical region.

Houghton and Lubensky[10] studied nucleation near coexistence and close to a critical point by imposing a match condition[11] that forced fluctuation corrections to the instanton saddle point[7] to be finite. Their calculation, however, is not easy to extend to the region close to the pseudospinodal; the match condition they used does not exponentiate the logarithms that appear naturally in the renormalized expression for the real part of the free energy and is inappropriate for regions where the magnetization is small with respect to the temperature.

The interpretation of the imaginary part of the free energy as a nucleation rate suggests that the mean-field spinodal cannot be reached experimentally; measurements, however, deep inside coexistence may be extrapolated to define a pseudospinodal curve. Pseudospinodals have been observed in experiments[12] and in computer simulations.[4,13] An estimate of spinodal fluctuations based on the Ginzburg criterion[14] shows that the spinodal is "smeared" for $d<6$. Similarly, a study of a coarse-grained free energy[15] showed that the position of the pseudospinodal depends on the coarse-graining length. The absence of a sharp spinodal is reinforced by analytic calculations[16] that demonstrate a gradual transition in the kinetics from nucleation and growth to spinodal decomposition.

Since mean-field theory becomes more accurate as the interaction range tends to infinity, the existence of spinodals has been discussed in connection with the interparticle interaction range. Monte Carlo simulations[17]

and theoretical investigations[18] show that the mean-field spinodal can be approached arbitrarily closely by making the interaction range sufficiently large.

In this work we extend Langer's field-theoretic calculation to the whole coexistence region, and, by appropriately renormalizing the free energy, to the critical region; our final expression for the complex free energy incorporates both droplet-like and critical fluctuations. It should be stressed that our calculation is a static one, and thus, should be viewed as accurate only with regards to phenomena on a time scale shorter than the nucleation time.[19] In a later work,[20] a time-dependent version of the theory will be analyzed.

As is commonly done, we consider a model Landau-Ginzburg free energy for a system with a scalar, continuous order parameter ϕ in $d \equiv 4-\epsilon$ spatial dimensions:

$$\beta F \equiv \int d\mathbf{r} \left[\tfrac{1}{2}|\nabla\phi|^2 + \tfrac{1}{2}\tau\phi^2 + \frac{1}{4!}u\phi^4 - H\phi \right], \tag{1.1}$$

where H is an external field that couples to the order parameter and τ is the reduced temperature. The associated partition function is obtained by evaluating a functional integral over all possible field configurations, weighted by the Boltzmann probability distribution,

$$Z(H) \equiv \int D[\phi] e^{-\beta F}. \tag{1.2}$$

The appropriate thermodynamic potential becomes

$$\beta A \equiv -\ln[Z(H)]. \tag{1.3}$$

In the study of critical phenomena, the partition function is usually evaluated by the method of steepest descent, expanding about a local free energy minimum. For temperatures below T_c, the free energy develops two spatially uniform minima, a metastable and a stable one. The usual perturbative analysis of fluctuations, either via a Wilson-type or a field-theoretic renormalization-group transformation, considers only single-well fluctuations explicitly. Not surprisingly, the low-order expansions miss the essential singularity at coexistence, since the effect of the absolute minimum is included only perturbatively. In a sense, the perturbative expansions about a local minimum are similar in spirit to the calculation of Penrose and Lebowitz,[19] who analyzed metastable states by considering only a constrained class of uniform order parameter fluctuations.

Spatially nonuniform fluctuations are included in the evaluation of the partition function by considering another functional extremum of the free energy, which appears only inside the coexistence region. As was first pointed out by Langer,[5] the new saddle point, which has a spatially nonuniform order parameter, has one unstable direction. This nonuniform field configuration, which has been given numerous names in the literature (e.g., instanton, kink, soliton), is identified with the critical droplet that, at least close to coexistence, is responsible for nucleation. The instanton contribution to the free energy is purely imaginary.

In Sec. II we describe the nonuniform order-parameter profile and we consider fluctuation corrections to the two previously described saddle points. We show that the one-loop fluctuation contributions to the partition function may be evaluated by solving a Jacobi differential equation.[21,22] When the WKB approximate solutions are used, the resulting expression can be explicitly renormalized (here, by using the field-theoretic approach to the renormalization group and by subtracting divergences in minimal subtraction[1,2,23]). Note that while the calculation of the one-loop correction to the partition function via the solution of the Jacobi equation is not new, as far as we know, it is the first time that it has been applied to the general d-dimensional problem in polar spherical coordinates and where the renormalizability of the resulting expression has been explicitly demonstrated.

The perturbative expressions are made consistent with the renormalization-group equation by writing them in crossover form in Sec. III. We show that a consistent way to treat fluctuations inside the coexistence region requires that the scale parameter, which can be identified with a coherence length for nonlinear effects, be decoupled from the correlation length (i.e., $\chi^{1/2}$, where χ is the susceptibility). As a consequence, deep inside the coexistence region we find a new line along which the scale parameter diverges. This new curve, which we call the universal spinodal curve, is always inside the unstable region of the phase diagram ($\chi < 0$), and is a line of ϕ^4 fixed points (i.e., the corresponding exponents are nonclassical). The relative positions of the pseudospinodal and the universal spinodal curves determine the nature of the observed singularities far away from the coexistence curve. We show that the pseudospinodal is a mean-field line, although crossover from mean-field (at coexistence) to critical, to mean-field (at the pseudospinodal) behavior can be observed close to T_c (cf. Fig. 5). We evaluate the expression for the instanton contribution to the partition function, and find that the nucleation rate, which is proportional to the imaginary part of the free energy, decreases rapidly as the critical point is approached. Moreover, close to the critical point, the normalized imaginary part of the free energy, whose maximum occurs deep inside coexistence, becomes a universal function. Section IV summarizes our results and discusses possible extensions and limitations of our work. The appendices contain various technical details.

II. MEAN-FIELD INSTANTONS AND RENORMALIZED PERTURBATION THEORY

A. Single-instanton approximation and fluctuations about the instanton

The nonuniform order parameter corresponding to the saddle point configuration of the mean-field free energy will be written as

$$m(\mathbf{r}) = m_0 + \delta m(\mathbf{r}), \tag{2.1a}$$

where m_0 is the metastable solution of the mean-field equation of state and $\delta m(\mathbf{r})$ is the so-called instanton configuration. We shall consider only spherically symmetric droplets, for which the Euler-Lagrange equation becomes

$$\left.\frac{\delta\beta F}{\delta\phi(\mathbf{r})}\right|_{\phi(\mathbf{r})=m(\mathbf{r})} = -\partial_r^2\delta m - \frac{d-1}{r}\partial_r\delta m + x_0\delta m + \frac{u}{2}m_0\delta m^2 + \frac{u}{3!}\delta m^3 = 0, \tag{2.1b}$$

where

$$x_0 \equiv \tau + \frac{u}{2}m_0^2 \tag{2.1c}$$

is the inverse mean-field susceptibility.

For $d>2$ the boundary conditions are easily determined to be[6] (a) $\delta m(r)\to 0$ as $r\to\infty$, since the instanton describes a droplet of the stable phase in a background of the metastable phase; and (b)

$$\left.\frac{\partial\delta m}{\partial r}\right|_{r=0} = 0$$

so that the instanton remains finite at the origin. Unfortunately, except in $d=1$, a closed form solution to Eq. (2.1b) does not exist. Following Cahn and Hilliard[6] it will be solved variationally below [cf. Eq. (2.9)].

In the one-instanton approximation,[5] the partition function is given by the sum of the contributions from the two saddle points,

$$Z(H) \approx Z_0 + Z_1 = e^{-\beta F_0}\left[\det(\beta F_0^{(2)})\right]^{-1/2} + e^{-\beta F_1}\left[\det(\beta F_1^{(2)})\right]^{-1/2}, \tag{2.2a}$$

with

$$\beta F_i^{(2)} \equiv \left.\frac{\delta^2\beta F}{\delta\phi(\mathbf{r}_1)\delta\phi(\mathbf{r}_2)}\right|_{\phi=\phi_i(r)}, \tag{2.2b}$$

$i=0,1$. Henceforth, βF_0 and βF_1 denote the free energies at the metastable minimum, $\phi=m_0$, and at the instanton extremum, $\phi=m(r)$, respectively. The determinants arise from Gaussian integrations about the corresponding extrema and correspond to the usual loop expansion [Eq. (2.2a) is just the one-loop expression for the free energy[1]].

Perhaps the most common way to evaluate the determinants is by calculating the eigenvalues[1,2,5,7,9,21] of the operator defined in Eq. (2.2b); for the ϕ^4 model, this results in a Schrödinger-like equation of the form

$$\left[-\partial_r^2 - \frac{d-1}{r}\partial_r + \frac{l(l+d-2)}{r^2} + x_i\right]\psi_{n,l}^i = \lambda_{n,l}^{(i)}\psi_{n,l}^i, \tag{2.3a}$$

$i=0,1$, where

$$x_1 \equiv x(r) \equiv \tau + \frac{u}{2}[m_0+\delta m(r)]^2, \tag{2.3b}$$

and where x_0 was defined in Eq. (2.1c). In writing Eq. (2.3a), we have separated the equation in spherical coordinates and have used the fact that the rotational "energy" for angular momentum l is $l(l+d-2)/r^2$.[24] In terms of the eigenvalues the Gaussian determinant becomes

$$\det(\beta F_i^{(2)}) = \prod_{n,l}[\lambda_{n,l}^{(i)}]^{g_l}, \tag{2.4a}$$

where g_l is the degeneracy of the lth d-dimensional spherical harmonic;[24] i.e.,

$$g_l(d) \equiv \frac{2\left[l+\frac{d}{2}-1\right]\Gamma(l+d-2)}{\Gamma(d-1)\Gamma(l+1)}, \quad \text{for } l\geq 1. \tag{2.4b}$$

Note that the product over the eigenvalues includes both bound and continuum states.

Using these results, the one-instanton partition function becomes

$$Z(H) \approx Z_0\left[1+\frac{Z_1}{Z_0}\right] = e^{-\beta F_0}\prod_{n,l}[\lambda_{n,l}^{(0)}]^{-g_l/2}\left[1+\frac{Z_1}{Z_0}\right], \tag{2.5a}$$

where

$$\frac{Z_1}{Z_0} = e^{-\beta\Delta F_{\text{in}}^{(0)}}\prod_l^{\infty} A_l^{g_l}, \tag{2.5b}$$

with

$$A_l^2 \equiv \prod_n^{\infty}\frac{\lambda_{n,l}^{(0)}}{\lambda_{n,l}^{(1)}}, \tag{2.5c}$$

and

$$\beta\Delta F_{\text{in}}^{(0)} \equiv \beta F_1 - \beta F_0 = \int d\mathbf{r}\left[\tfrac{1}{2}|\nabla\delta m|^2 + \tfrac{1}{2}x_0\delta m^2 + \frac{u\delta m^3}{3!}(m_0+\delta m/4)\right]. \tag{2.5d}$$

The calculation of the eigenvalues from Eq. (2.3a) for a general order-parameter profile is a formidable task. The product over the eigenvalues, however, may be calculated in a simpler way because, as is discussed in Appendix A, the quantity A_l^2 is given by the ratio

$$A_l^2 = \frac{\Lambda_l^{(0)}(L)}{\Lambda_l^{(1)}(L)}, \tag{2.6}$$

where $\Lambda_l^{(i)}$ are solutions of the Jacobi differential equation[21,22] evaluated at L, the radius of a spherical box that encloses the system ($L\to\infty$). The Jacobi equation is

$$\left[\partial_r^2 + \frac{d-1}{r}\partial_r - \frac{l(l+d-2)}{r^2} - x_i\right]\Lambda_l^{(i)}(r) = 0, \tag{2.7a}$$

with boundary conditions

$$\lim_{r\to 0}\Lambda_l^{(i)}(r) = c_l r^l. \tag{2.7b}$$

The precise value of the parameter c_l is unimportant since it is independent of x_i (cf. Appendix A); hence, it is the same for the zero- and one-instanton problems and cancels out of A_l^2.

B. WKB approximation

Here, the Jacobi equation will be analyzed in the WKB approximation. This results in analytic expressions which can be used in renormalizing the theory. The singularity at the origin makes the naive WKB approximation break down at $r=0$ for $d>1$; however, the well-known Langer transformation[25] remedies this; i.e.,

$$r=e^z, \quad \text{and} \quad \Lambda_l^{(i)}(r)=e^{-z(d-2)/2}\Psi_l(z). \tag{2.8a}$$

Equation (2.7a) thus becomes

$$\frac{\partial^2\Psi_l}{\partial z^2}-Q(z)\Psi_l=0, \tag{2.8b}$$

where the "potential" is

$$Q(z)\equiv e^{2z}x_1(e^z)+\nu^2, \tag{2.8c}$$

with

$$\nu\equiv l+\frac{d}{2}-1. \tag{2.8d}$$

As a test of the WKB approximation we determined some of the eigenvalues, $\lambda_{n,l}^{(1)}$ [cf. Eq. (2.3a)] numerically, and compared them with the first- and second-order WKB approximations (also solving the required algebraic equations numerically). As Table I shows, close to coexistence first-order WKB does not give a negative eigenvalue for $l=0$ and the overall agreement is fairly poor. On the other hand, second-order WKB appears to be quite accurate. Similar features were observed in comparisons of fully numerical with first- and second-order WKB solutions to Eq. (2.8a), and it is the latter which is used below.

In determining the eigenvalues and in all the numerical work that follows the order-parameter profile was determined variationally. The solution of the Euler-Lagrange equation, Eq. (2.1b), has been extensively analyzed close to coexistence[5,7] (where the familiar tanh profile, characteristic of a one-dimensional interface, is obtained) and close to the pseudospinodal.[9] (Close to the pseudospinodal if the first derivative term is dropped the resulting equation has a closed-form solution,[6] although for $d\neq 1$ no obvious small parameter justifies this.) The trial function used combines the salient features of the solution in the two limits; in particular,

$$\delta m(r)=\delta m_0\left\{c_1\left[1-\tanh\left[\frac{r-R}{\xi}\right]\right]+c_2e^{-r/\xi}\right\}, \tag{2.9a}$$

TABLE I. Comparison of numerical and WKB eigenvalues for $\tau=-1$ and $u/u^*=0.9$.

l	n	1st order WKB	2nd order WKB	Numerical
		$\lambda_{n,l}^{(1)}$		
		$z\equiv\frac{\langle m\rangle-\langle m\rangle_{PS}}{\langle m\rangle_{coex}-\langle m\rangle_{PS}}=0.878$		
0	0	0.077 87	−0.020 84	−0.021 00
1	0	0.098 55	−0.000 11	−0.000 23
2	0	0.139 86	0.041 28	0.041 26
3	0	0.201 71	0.103 27	0.103 38
4	0	0.283 98	0.185 71	0.185 97
5	0	0.386 49	0.288 43	0.288 87
6	0	0.509 04	0.411 22	0.411 83
7	0	0.651 38	0.553 83	0.554 60
8	0	0.813 22	0.715 97	0.716 87
9	0	0.994 24	0.897 32	0.898 30
10	0	1.194 08	1.097 50	1.098 51
11	0	1.412 34	1.316 12	1.317 06
12	0	1.648 57	1.552 73	1.553 47
0	1	1.477 66	1.448 29	1.430 81
1	1	1.496 81	1.467 69	1.450 42
2	1	1.534 69	1.506 03	1.489 11
3	1	1.590 45	1.562 34	1.545 90
4	1	1.662 79	1.635 15	1.619 29
		$z=0.467$		
0	0	−0.228 79	−0.301 70	−0.322 27
1	0	0.064 25	0.003 37	−0.001 43
2	0	0.498 96	0.442 98	0.443 64
0	1	0.738 45	0.733 77	0.710 32
		$z=0.018$		
0	0	−0.057 12	−0.057 70	−0.062 48
1	0	−0.001 67	−0.004 29	−0.004 16

where δm_0 characterizes the order in the droplet, ξ the interfacial width, and R the radius of the instanton. The last exponential part was included to ensure that $\partial\delta m/\partial r$ vanish at $r=0$. The interfacial width and δm_0 were obtained numerically, and the constants c_i were determined by the conditions

$$\delta m(r=0)=\delta m_0 \quad \text{and} \quad \frac{\partial \delta m(r=0)}{\partial r}=0. \tag{2.9b}$$

It should be stressed that our qualitative results do not depend on the choice of the trial function. (More accurate numerical results will be obtained by using better trial functions for the order-parameter profile.) An obvious problem with our trial function is that it gives incorrect algebraic corrections to the dominant exponential decay as $r\to\infty$ (cf. Appendix B).

The potential $Q(z)$ either has no turning points, e.g., for large angular momentum, or two turning points, creating an attractive well that may support bound states. In the case of no turning points the second-order WKB solution[26] becomes

$$\Lambda_l^{(1)}(r)=c_l\nu^{1/2}r^l \times e^{\bar{S}_0[-\infty,\ln(r)]+S_1[\ln(r)]+S_2[-\infty,\ln(r)]}, \tag{2.10}$$

where the various exponential factors are defined in Appendix B. If there are two turning points, $z_A<z_B$, then connection formulas must be considered.[26] In the outer region, $z>z_B$, the solution thus becomes

$$\Lambda_l^{(1)}(r)=r^{1-d/2}B_l[\sin(\phi)e^{-S_0[z_B,\ln(r)]+S_1[\ln(r)]-S_2[z_B,\ln(r)]}+2\cos(\phi)e^{S_0[z_B,\ln(r)]+S_1[\ln(r)]+S_2[z_B,\ln(r)]}], \tag{2.11a}$$

where

$$\phi\equiv S_0[z_A,z_B]+\tilde{S}_2[z_A,z_B], \tag{2.11b}$$

and $\tilde{S}_2$ and the constant B_l are given in Eqs. (B4) and (B5), respectively.

The Jacobi equation for the metastable minimum is a modified Bessel equation,[27] whose solution is

$$\Lambda_l^{(0)}(r)=c_l\Gamma(\nu+1)2^\nu x_0^{-\nu/2}r^{1-d/2}I_\nu(x_0^{1/2}r), \tag{2.12}$$

where I_ν is the modified Bessel function of order ν. In our numerical work, in order to be consistent with the approximations used in Eqs. (2.10) and (2.11a), when the WKB expressions were used, we used the Debye asymptotic expansion for I_ν (which is equivalent to the WKB approximation). As before, only the second-order WKB was in good agreement with the exact solution.

Since the metastable minimum has uniform order parameter, the fluctuation correction to the free energy could have been analyzed in terms of a Fourier representation. For the sake of completeness, and as a check of the Jacobi equation method, in Appendix C we use the solution of the Jacobi equation to reproduce the standard ϕ^4 results. In particular, we show that, for any l, the product of eigenvalues of Eq. (2.3a) is given by Eq. (C5), which equals the solution of the Jacobi equation, Eq. (2.12), up to unimportant multiplicative factors which are independent of the thermodynamic variables (i.e., τ and x_0).

In our numerical work, for closely spaced turning points, i.e., when l is close to its maximum value for which the attractive potential supports bound states, the agreement of the second-order WKB approximation to the instanton Jacobi equation, Eq. (2.7a), was poor. For those values of l, rather than use the WKB approximation for closely spaced turning points the ratio A_l^2 was determined by numerically solving the differential equation

$$\left[\partial_r^2+\left[\frac{1-2\nu}{r}+2x_0^{1/2}\frac{I_{\nu-1}(x_0^{1/2}r)}{I_\nu(x_0^{1/2}r)}\right]\partial_r-x(r)+x_0\right]A_l^2(r)=0, \tag{2.13a}$$

with

$$A_l^2(r=0)=1 \quad \text{and} \quad \partial_r A_l^2(r=0)=0. \tag{2.13b}$$

As is the case in $d=1$,[21] the first term on the right-hand side of Eq. (2.11a) is exponentially small for $l\neq 1$ and L large; hence, only the second is needed for A_l^2. On the other hand, for $l=1$, $\phi=\pi/2$ (i.e., a Bohr-Sommerfeld quantization condition), and reflects the fact that in an infinite system, translational invariance guarantees the existence of a zero eigenvalue with eigenfunctions determined by the derivative of $\delta m(r)$ (cf. Refs. 5, 21, and 22) [cf. Eqs. (B6) and (B8)]. Furthermore, this leads to an exponential divergence in the ratio A_1^2 as $L\to\infty$. As is well known,[5,21,22] it is a spurious divergence, related to the way in which the eigenvalues corresponding to translation in a finite system (with small but nonzero eigenvalues) go to zero as $L\to\infty$. It may be eliminated by introducing collective coordinates,[22] $\delta m_{\text{trans}}(\mathbf{r})$, and integrating over them to obtain

$$\int \mathcal{D}[\delta m_{\text{trans}}(\mathbf{r})]=J_d\int d\mathbf{r}=VJ_d, \tag{2.14a}$$

where V is the system volume and the Jacobian, J_d, which is related to the norm of the translational eigenfunctions, is reexpressed, using the virial theorem,[22] as

$$J_d=\left[\beta\Delta F_{\text{in}}^{(0)}\right]^{d/2}. \tag{2.14b}$$

The importance of the overall factor of system volume will be discussed at the end of this section.

Following Schulman,[21] the remaining contribution to A_1^2 is obtained by dividing out the exponentially small eigenvalue and retaining the resulting well-behaved expression to give

$$VR_{\rm in}^{-d}J_d(\tilde{A}_1^2)^{d/2}, \tag{2.15a}$$

where

$$\tilde{A}_1^2 \equiv \lambda_{0,1}^{(1)} A_1^2 R_{\rm in}^2, \tag{2.15b}$$

and where $R_{\rm in}$ is a quantity with dimension of length which was introduced to make Eq. (2.15b) dimensionless. It will be identified with the instanton radius in the next section. In Appendix B an expression for A_1^2 in terms of the second derivative of the order-parameter profile is presented; cf. Eq. (B11).

For $l=0$ we found, in agreement with previous calculations,[5,7] that the ratio is negative, since $\cos(\phi)<0$. This is a consequence of the fact that each translational eigenvector has one angular node and therefore there must be a nodeless eigenfunction with lower energy; i.e., a state with negative eigenvalue. The corresponding Gaussian integration is performed by analytic continuation and it makes the instanton contribution to the free energy purely imaginary.

For the other values of l our numerical work shows that as $H\rightarrow 0$ the position of the attractive well goes to infinity, and therefore, the number of bound states for a given l diverges. The sum over the bound states generates logarithmic corrections to the instanton free energy, which have been discussed by Langer[5] and Günther *et al.*[7] We found, however, that by the time $l\sim 10$ they were corrections to an exponentially small quantity [$\sim\exp(-100)$], and thus unobservable (cf. Fig. 7). As the system is moved away from the coexistence line the number of bound states decreases rapidly (cf. Fig. 6); at the pseudospinodal, where the position of the attractive well is comparable to its interfacial width, only the negative eigenvalue and the translational states remain.

We rewrite the ratio A_l^2 in terms of $\Phi_l^{(i)}(L)$, the logarithms of $\Lambda_l^{(i)}(L)$, i.e.,

$$A_l^2=\frac{\Lambda_l^{(0)}(L)}{\Lambda_l^{(1)}(L)}\equiv e^{-[\Phi_l^{(1)}(L)-\Phi_l^{(0)}(L)]}. \tag{2.16}$$

As expected, the constant c_l and other unimportant constants drop out from the ratio. For closely spaced turning points A_l^2 was calculated by solving the differential equation Eq. (2.13a). Therefore, the single-instanton partition function becomes

$$\frac{Z_1}{Z_0}=\pm iR_{\rm in}^{-d}VJ_d e^{-\beta(\Delta F_{\rm in}^{(0)}+\Delta F_{\rm in}^{(2)})}, \tag{2.17a}$$

where the tree term, $\Delta F_{\rm in}^{(0)}$, is defined in Eq. (2.5d), and the one-loop term, $\Delta F_{\rm in}^{(2)}$, is expressed in terms of the solutions to the Jacobi equation

$$\beta\Delta F_{\rm in}^{(2)}\equiv\tfrac{1}{2}\sum_{l=0}^{\infty} g_l(d)(\Phi_l^{(1)}-\Phi_l^{(0)}). \tag{2.17b}$$

The factor of $\pm i$ is included because, as was mentioned earlier, A_0^2 is negative.

Up to now we have considered the single-instanton approximation to the partition function. In the so-called dilute gas approximation,[5,21,22] a summation over noninteracting, multi-instanton configurations exponentiates the single-instanton result to give

$$\beta A=-\ln[Z(H)]=-\ln(Z_0)-\frac{Z_1}{Z_0}. \tag{2.18}$$

It is important to note that the exponentiation ensures that the thermodynamic potential βA is extensive.

C. Renormalization

1. *Metastable minimum*

The first term in Eq. (2.18) is the usual expression for the thermodynamic potential; it is given by the standard perturbative analysis of the ϕ^4 free energy[1] (cf. Appendix C). Specifically, if the free energy is renormalized in minimal subtraction,[23] the following relations[2] of bare to renormalized quantities (denoted by subscripts "R") eliminate the ϵ^{-1} poles, with $\epsilon\equiv 4-d$,

$$u=\frac{(2\pi)^d}{S_d}u_R\left[1+\frac{3\tilde{u}_R}{2\epsilon}\right] \tag{2.19a}$$

and

$$\tau=\tau_R\left[1+\frac{\tilde{u}_R}{2\epsilon}\right], \tag{2.19b}$$

with

$$\tilde{u}_R\equiv\kappa^{-\epsilon}u_R, \tag{2.19c}$$

where κ is a quantity with dimension of inverse length that was introduced in the process of dimensional regularization. Since the coupling constant was redefined to absorb various angular factors (S_d is the area of a d-dimensional sphere), m and H are also rescaled by a factor of $S_d^{1/2}(2\pi)^{-d/2}$.

In terms of renormalized quantities the one-loop expression of the first term in Eq. (2.18) becomes[1,2]

$$\begin{aligned}-\frac{(2\pi)^d\ln(Z_0)}{S_d V}&=\tfrac{1}{2}\tau_R\langle m\rangle^2(1-\tfrac{1}{8}u_R)\\&\quad+\frac{1}{4!}u_R\langle m\rangle^4(1-\tfrac{3}{8}u_R)\\&\quad+\tfrac{1}{8}x_t^2\ln(x_t/\kappa^2),\end{aligned} \tag{2.20a}$$

where the renormalized one-loop minimum, $\langle m\rangle$, is

$$\langle m\rangle=m_0\left[1-\frac{u_R}{4}\ln(x_t/\kappa^2)\right]+O(\epsilon^2), \tag{2.20b}$$

and

$$x_t\equiv\tau_R+\frac{u_R}{2}\langle m\rangle^2. \tag{2.20c}$$

Note that the tree terms are $O(\epsilon^{-1})$.

2. *Instanton extremum*

Previous calculations of the instanton free energy considered[5,7,9] the sum over l up to l^*, a value beyond which no bound states could be supported by the attractive well; in particular, close to coexistence,[7] l^* was chosen to be proportional to H^{-1}. Note that this incorrectly assumes that the contribution from the continua of the zero- and the one-instanton configurations to the partition function cancel out. On the other hand, if the sum is extended to infinity, divergences appear which are reminiscent of the uv divergences that result in the usual perturbative treatment of the ϕ^4 free energy (the sum over l replaces the integration over wave vectors);[28] this is not surprising since letting $l \to \infty$ implies that a high wave-vector angular cutoff goes to infinity.

It is well known how to subtract these divergences.[2] As in the preceding section, we shall use the field-theoretic minimal subtraction approach to the renormalization-group,[23] after dimensionally regularizing all divergent quantities. Moreover, we shall renormalize the free energy in an ϵ expansion about $d=4$.

The free energy is made finite by renormalizing each extremum separately and taking the difference of the resulting expressions. As expected, in the thermodynamic limit, the same renormalization constants renormalize each contribution. Furthermore, in Appendix C, we carry out the renormalization procedure for the uniform order-parameter extremum by renormalizing the WKB solution to the Jacobi equation; we show that the standard ϕ^4 results are obtained in the thermodynamic limit when the sum over l is replaced by an integral. The same procedure renormalizes the instanton extremum.

The first step in the renormalization procedure is the subtraction of the additive temperature renormalization shift which eliminates the terms that diverge as l^{d-2}. Then, by adding and subtracting the term which becomes marginal at $d=4$, the one-loop corrections become

$$\beta\Delta F_{\rm in}^{(2)}=\beta\Delta F_{\rm WKB}^{(2)}+\beta\Delta F_{\rm sbt}^{(2)}, \tag{2.21a}$$

where, in the WKB approximation,

$$\beta\Delta F_{\rm WKB}^{(2)}\equiv\sum_{l=0}^{\infty}\frac{(l+1)^2}{2}\left[\Phi_l^{(1)}(\infty)-\Phi_l^{(0)}(\infty)-\int_0^{\infty}dr\left[\frac{r}{2(l+1)}[x(r)-x_0]-\frac{r^3}{8(l+1)^3}[x^2(r)-x_0^2]\right]\right]+O(\epsilon), \tag{2.21b}$$

and

$$\beta\Delta F_{\rm sbt}^{(2)}\equiv-\sum_{l=0}^{\infty}\frac{\Gamma(l+d-2)}{8\nu^2\Gamma(l+1)\Gamma(d-1)}\int_0^{\infty}dr\,r^3[x^2(r)-x_0^2]. \tag{2.21c}$$

The sum over l in Eq. (2.21b) is finite and is evaluated at $d=4$. In addition, the integration limits were extended to infinity since the integrands decay exponentially. Note that the second-order WKB terms [cf. Eqs. (B3) and (B4)] seem to introduce marginal divergences in the summand as $l\to\infty$. However, an integration by parts shows that the divergent terms vanish. The sum in $\beta\Delta F_{\rm sbt}^{(2)}$ is marginal and is evaluated in an ϵ expansion; this gives

$$\sum_{l=0}^{\infty}\frac{\Gamma(l+d-2)}{\left[l+\frac{d}{2}-1\right]^2\Gamma(l+1)}=\epsilon^{-1}(1+\gamma\epsilon)+O(\epsilon), \tag{2.22}$$

where $\gamma\equiv 0.577\,21\ldots$ is Euler's constant. It is worth noting that if the sum is replaced by an integral, the value of the marginal operator is $\epsilon^{-1}(1+\epsilon/2)$.

The ϵ^{-1} poles are eliminated by redefining τ and u (there is no wave-function renormalization in a one-loop calculation); as expected, the previously presented relations[2] of bare to renormalized quantities eliminate them. Substitution of Eqs. (2.19a) and (2.19b) in Eq. (2.5d), addition of the one-loop terms [cf. Eqs. (2.21) and (2.22)], and ϵ expansion of the integration measure gives

$$\beta\Delta F_{\rm in}^{(0)}+\beta\Delta F_{\rm in}^{(2)}=\frac{S_d^2}{(2\pi)^d}R_{\rm in}^{-\epsilon}\left[\int_0^{\infty}dr\,r^3\left[1-\epsilon\ln(r/R_{\rm in})\right]\left[\tfrac{1}{2}|\nabla\delta m|^2+\tfrac{1}{2}x_0\delta m^2+\frac{u_R\delta m^3}{3!}(m_0+\delta m/4)\right.\right.$$
$$\left.\left.-\tfrac{1}{4}[\gamma+\tfrac{1}{2}+\ln(\kappa r/2)][x^2(r)-x_0^2]\right]+4\beta\Delta F_{\rm WKB}^{(2)}\right]+O(\epsilon), \tag{2.23a}$$

where

$$x^2(r)-x_0^2=2u_R m_0 x_0\delta m+u_R(x_0+u_R m_0^2)\delta m^2+u_R^2\delta m^3(m_0+\delta m/4). \tag{2.23b}$$

In obtaining the last result we used the following expansion:

$$\frac{1}{\Gamma(d-1)}=\frac{2S_d^2}{(2\pi)^d}\left[1-\epsilon\ln(2)+\frac{\epsilon}{2}\right]+O(\epsilon^2). \tag{2.24}$$

Since the integration measure was expanded, we make the ansatz that $R_{\rm in}$, a yet unspecified measure of the instanton size, multiplies the $d=4$ free energy, cf. Eq. (2.23a), so that the expected instanton volume dependence is obtained nonperturbatively for all d. In the finite sum, Eq. (2.21b), renormalized quantities trivially replace bare ones because the difference is of higher order in ϵ and, for the same reason, they are multiplied by $R_{\rm in}^{-\epsilon}$. Henceforth, all quantities will be renormalized and we shall drop the "R" subscripts.

Close to the pseudospinodal, the instanton radius grows, ($R\sim x_0^{-1/2}$), and the $\ln(\kappa r)$ term in Eq. (2.23a) introduces logarithmic divergences;[29] since, as we show later, $\delta m(r)$ is proportional to x_0, the terms linear and quadratic in $\delta m(r)$ diverge logarithmically [cf. Eq. (2.23b)]. The divergences may be rewritten by adding and subtracting terms containing $\ln(x_0)$. Subsequently, by using the Euler-Lagrange equation, Eq. (2.1b), the term proportional to δm in Eq. (2.23b) can be expressed in terms of δm^2 and δm^3. With this, Eq. (2.23a) becomes

$$\begin{aligned}\beta\Delta F_{\rm in}^{(0)}+\beta\Delta F_{\rm in}^{(2)}=\frac{S_d^2}{(2\pi)^d}R_{\rm in}^{-\epsilon}\Bigg\{\int_0^\infty dr\, r^3[1-\epsilon\ln(r/R_{\rm in})]\Bigg[&\tfrac{1}{2}|\nabla\delta m|^2+\tfrac{1}{2}\left[x_t+\frac{u}{4}(x_t+u\langle m\rangle^2)\ln(x_t/\kappa^2)\right]\delta m^2\\&+\frac{u\delta m^3}{3!}\left[1+\frac{3u}{4}\ln(x_t/\kappa^2)\right](\langle m\rangle+\delta m/4)\\&-\tfrac{1}{4}[\gamma+\tfrac{1}{2}+\ln(rx_t^{1/2}/2)][x^2(r)-x_t^2]\Bigg]+4\beta\Delta F_{\rm WKB}^{(2)}\Bigg\},\end{aligned} \tag{2.25a}$$

where $\langle m\rangle$ and x_t were introduced earlier [cf. Eqs. (2.20b) and (2.20c)], and where $x(r)$ is henceforth defined using $\langle m\rangle$. Observe that the shift to the true one-loop minimum eliminates the divergence that arises from the term proportional to δm, and the other terms modify the tree free energy density.

The one-loop corrections to the free energy density

$$\beta\delta f=\tfrac{1}{2}|\nabla\delta m|^2+\tfrac{1}{2}\left[x_t+\frac{u}{4}(x_t+u\langle m\rangle^2)\ln(x_t/\kappa^2)\right]\delta m^2+\frac{u\delta m^3}{3!}[1+\tfrac{3}{4}u\ln(x_t/\kappa^2)](\langle m\rangle+\delta m/4) \tag{2.25b}$$

are the logarithmic corrections to the real parts of the corresponding N-point vertex functions, Γ_R^N, in the ordered phase; these diverge as $x_t\to 0$. They are eliminated, however, when the real part is made finite (see Sec. III). Furthermore, the coefficient of δm^2 is, up to the finite term $u^2\langle m\rangle^2/4$ [which may be added and subtracted from Eq. (2.25a) if desired], the perturbative expression of $\Gamma_R^{(2)}$ in the ordered phase.[30]

The instanton profile can be chosen to extremize the free energy functional with the free energy density given in Eq. (2.25b); any $O(1)$ modifications to the free energy density will result in order $\epsilon^{1/2}$ changes of the instanton [δm is $O(\epsilon^{-1/2})$]. However, since the instanton is an extremum, the corresponding corrections to the free energy will be $O(\epsilon)$ and thus of higher order in the ϵ expansion.

Hence, the instanton is now defined with respect to the real part of the one-loop free energy; in particular, the shift to $\langle m\rangle$ ensures that $m(r)$ decays to the one-loop value of the average order parameter and its defining equation uses the the one-loop inverse susceptibility.

One of the remaining logarithms in Eq. (2.23a) is eliminated by choosing $R_{\rm in}$ (cf. Ref. 31) to satisfy

$$\ln(\kappa R_{\rm in})\equiv\frac{\int_0^\infty dr\,\ln(\kappa r)r^3\beta\delta f}{\int_0^\infty dr\,r^3\beta\delta f}, \tag{2.26}$$

where $\beta\delta f$ is the instanton free energy density, Eq. (2.25b). Thus, the final expression for the renormalized instanton free energy is

$$\begin{aligned}\beta\Delta F_{\rm in}^{(0)}+\beta\Delta F_{\rm in}^{(2)}=\frac{S_d^2}{(2\pi)^d}R_{\rm in}^{-\epsilon}\Bigg\{4\beta\Delta F_{\rm WKB}^{(2)}+\int_0^\infty dr\,r^3\Bigg[&\tfrac{1}{2}|\nabla\delta m|^2+\tfrac{1}{2}\left[x_t+\frac{u}{4}(x_t+u\langle m\rangle^2)\ln(x_t/\kappa^2)\right]\delta m^2\\&+\frac{u\delta m^3}{3!}\left[1+\frac{3u}{4}\ln(x_t/\kappa^2)\right](\langle m\rangle+\delta m/4)\\&-\tfrac{1}{4}[\gamma+\tfrac{1}{2}+\ln(rx_t^{1/2}/2)][x^2(r)-x_t^2]\Bigg]\Bigg\}.\end{aligned} \tag{2.27}$$

Application of the virial theorem[7,22] on the free energy density, Eq. (2.25b), shows that the Jacobian, Eq. (2.14b), may be expressed as

$$\left[J_d\right]^{2/d} \equiv \frac{S_d^2}{(2\pi)^d} R_{\rm in}^{-\epsilon} \int_0^\infty dr\, r^3 \beta \delta f(r), \tag{2.28}$$

where δf is given in Eq. (2.25b). The corrections associated with Eq. (2.28), when exponentiated, are easily shown to be $O(\epsilon)$ and can thus be dropped.

Combining Eqs. (2.27) and (2.28) we obtain the final renormalized expression for the instanton partition function,

$$\frac{Z_1}{Z_0} = \pm i R_{\rm in}^{-d} V J_d e^{-\beta(\Delta F_{\rm in}^{(0)} + \Delta F_{\rm in}^{(2)})}. \tag{2.29}$$

Equation (2.29) can be used throughout the coexistence region and it smoothly extrapolates between the previously studied limits, $H \to 0$, coexistence, and $x_t \to 0$, pseudospinodal. However, since it was derived in an ϵ expansion it contains logarithmic divergences (which will be eliminated in the next section by considering renormalization-group flows). For the moment, only its mean-field limit will be compared with previously established results; the behavior in either limit is easily found by dimensional analysis based on the appropriate dominant length scale.

Close to coexistence the dominant length scale is the instanton radius, which, for $d \geq 2$, diverges as H^{-1}. It is easy to show that, as in the case of the classical droplet model, the tree free energy diverges as $H^{-(d-1)}$. Moreover, the prefactor of Eq. (2.29), i.e., logarithmic corrections to the free energy, diverges like $H^{-d(d-3)/2}$. The later exponent is in agreement with that of Günther *et al.*[7] for $2 < d < 5$, $d \neq 3$; for $d = 3$ the contribution of planar surface capillary modes become marginal,[5,7,32] introducing extra logarithmic corrections. Since the free energy, Eq. (2.27), was renormalized by ϵ expanding the degeneracy factors, $g_l(d)$, the special nature of $d = 3$ is not observed. Furthermore, numerically, it is only a logarithmic correction to an algebraically divergent quantity (which appears in an exponent.)

Close to the pseudospinodal, in mean field, the only relevant length scale is the mean-field correlation length, $x_0^{-1/2}$. (Note that in the mean-field limit x_0 equals x_t.) The rescaling of δm by

$$\delta m(r) \to \frac{2x_0}{u m_0} \delta m(x_0^{1/2} r) \tag{2.30}$$

shows that the only dimensionless parameter is $2x_0/3um_0^2$, which goes to zero at the pseudospinodal; hence, a trivial scaling form for the instanton profile is obtained. Using this it is easy to show that the tree free energy vanishes as $\sim x_0^{3-d/2}$. Since $R_{\rm in}$ is proportional to the mean-field correlation length the prefactor goes to zero as $x_0^{d(4-d/2)/2}$. Thus, close to the pseudospinodal the instanton contribution to the partition function goes to zero algebraically for $d < 6$ and exponentially for $d > 6$.

Spinodal nucleation, i.e., nucleation close to the pseudospinodal, far from the critical region has been studied by Unger and Klein.[9] Even though we find the same qualitative features, algebraic decay (exponential decay) for $d < 6$ ($d > 6$), our exponents for the prefactor differ; in their calculation of the Jacobian, Eq. (2.14b), the norm of the translational eigenvectors was determined by integrating a one-dimensional order-parameter profile in $d = 1$, whereas we used the virial theorem for a general dimension d.

It appears that $d = 6$ is a critical dimension for spinodal nucleation.[9] It has been suggested[33] that the pseudospinodal corresponds to a fixed point of a ϕ^3 free energy (this is essentially a consequence of dropping the quartic term of the free energy close to the pseudospinodal; however, the ϕ^3 theory is unbounded from below and it has an imaginary fixed-point coupling constant). Nevertheless, we have shown explicitly that, for a system with a critical point, no new renormalization constants are introduced by the ϕ^3 operator. In fact, it has been proven quite generally that the ϕ^3 composite operator does not introduce independent renormalization constants because it is related to lower-order operators by a Ward identity.[34]

III. EQUATION OF STATE INSIDE THE COEXISTENCE REGION

A. Renormalization-group equation and match conditions

As was mentioned earlier, the process of dimensional regularization introduces an arbitrary scale κ. The requirement that the bare theory be independent of that scale leads to the renormalization-group equation[1,2] for the renormalized, dimensionful, N-point vertex functions, $\Gamma_R^{(N)}$; in particular, the renormalization-group equation for H is

$$\left[\kappa\frac{\partial}{\partial\kappa} + \beta_u \frac{\partial}{\partial \tilde{u}_R} + \beta_\tau \frac{\partial}{\partial \tilde{\tau}_R} + \beta_m \frac{\partial}{\partial \tilde{m}_R} + \gamma_m\right] H(\tilde{u}_R, \tilde{\tau}_R, \tilde{m}_R, \kappa) = 0, \tag{3.1}$$

where the one-loop Wilson functions for the dimensionless variables, $\tilde{\tau} = \tau\kappa^{-2}$, $\tilde{m} = m\kappa^{-1+\epsilon/2}$, and $\tilde{u}$, are

$$\beta_u = \kappa \frac{\partial \tilde{u}_R}{\partial \kappa}\bigg|_B = -\tilde{u}_R(\epsilon - \tfrac{3}{2}\tilde{u}_R), \tag{3.2a}$$

$$\beta_\tau = \kappa \frac{\partial \tilde{\tau}_R}{\partial \kappa}\bigg|_B = -\tilde{\tau}_R(2 - \tfrac{1}{2}\tilde{u}_R), \tag{3.2b}$$

$$\beta_m = \kappa \frac{\partial \tilde{m}_R}{\partial \kappa}\bigg|_B = -\tilde{m}_R\left[1 - \frac{\epsilon}{2}\right], \tag{3.2c}$$

$$\gamma_m = -\tfrac{1}{2}\kappa \left. \frac{\partial \ln(Z_\phi)}{\partial \kappa} \right|_B = 0, \tag{3.2d}$$

and Z_ϕ is the wave-function renormalization constant, which is one to one-loop order. (Note that the derivatives with respect to κ are taken holding the bare parameters fixed.)

The renormalization-group equation is a quasi-linear partial differential equation and may be solved exactly.[35] Specifically, for the Wilson functions given in Eqs. (3.2a)–(3.2d), any function of

$$U(\kappa) \equiv \tilde{u}\kappa^\epsilon \left[1 + \frac{\tilde{u}}{u^*}(\kappa^\epsilon - 1) \right]^{-1}, \tag{3.3a}$$

$$T(\kappa) \equiv \tilde{\tau}\kappa^2 \left[1 + \frac{\tilde{u}}{u^*}(\kappa^\epsilon - 1) \right]^{-1/3}, \tag{3.3b}$$

and

$$M(\kappa) \equiv <\tilde{m}> \kappa^{1-\epsilon/2}, \tag{3.3c}$$

solves Eq. (3.1). Here, $<\tilde{m}>$ is the dimensionless average order parameter and $u^* \equiv 2\epsilon/3$ is the value of the coupling constant at the nontrivial fixed point. $U(\kappa)$, $T(\kappa)$, and $M(\kappa)$ are flowing coupling constant, temperature, and magnetization, respectively, and equal the corresponding renormalized, dimensionless variables at $\kappa = 1$.

Perturbative expressions for the vertex functions become consistent with the renormalization-group equation by rewriting them in terms of the flowing quantities [cf. Eqs. (3.3a)–(3.3c)], and ϵ expanding the differences. The resulting vertex functions are not only exact solutions of the renormalization-group equation, but they are also expressed in a form appropriate for the study of crossover effects.[2]

In addition to the transformation properties implied by the renormalization-group equation, quantities must transform correctly under changes in the length scale, e.g., $\kappa \to \kappa\rho$; namely, they must transform according to their canonical dimensions. Specifically, the general solution of Eq. (3.1) for an arbitrary length scale transformation is

$$H(u,\tau,\langle m \rangle,\kappa) = \rho^{d_H} \exp\left[\int_1^{\kappa\rho} \frac{dx}{x} \gamma_m(U(x)) \right] \times H[U(\kappa\rho), T(\kappa\rho), M(\kappa\rho)],$$

where d_H is the canonical dimension of H.

The equation of state inside the coexistence region was determined by differentiating the thermodynamic potential, Eq. (2.18), with respect to $\langle m \rangle$, thereby obtaining a complex expression for H. The real part is the standard one-loop, crossover form of the equation of state, whereas the imaginary part, which is discussed in Sec. III C, arises from the instanton contribution.

B. Real part of the equation of state

If the foregoing discussion is applied to the real part of the equation of state, we find that

$$H_{\text{real}} = \rho^{-3+\epsilon/2} M(\kappa\rho) \{ T(\kappa\rho) + \tfrac{1}{6} U(\kappa\rho) M^2(\kappa\rho) + \tfrac{1}{4} U(\kappa\rho) X_t(\kappa\rho) \ln[X_t(\kappa\rho)] \} + O(\epsilon^2), \tag{3.4a}$$

where

$$X_t(\kappa\rho) \equiv T(\kappa\rho) + \tfrac{1}{2} U(\kappa\rho) M^2(\kappa\rho), \tag{3.4b}$$

which is the standard result.[1] Of course, this result assumes the validity of the perturbative expressions, and in general, will break down near a critical point or line. On the other hand, since ρ is arbitrary, it can be adjusted such that only perturbative expressions in noncritical regions are needed—the connection to the critical region is established through dimensional analysis and the renormalization-group equation.

The connection between the scale parameter ρ and the thermodynamic variables is called the match condition.[1,2,11] The match condition is not completely arbitrary, but it is easy to show that *any* match condition written in terms of $U(\kappa\rho)$, $T(\kappa\rho)$, or $M(\kappa\rho)$ (i.e., without explicit κ dependence) will give functions that satisfy the renormalization-group equation exactly. Note, however, that if the match condition couples ρ to m, various perturbative results for the crossover forms of thermodynamic functions will satisfy the usual derivative thermodynamic relations (e.g., $\chi = \partial m / \partial H$) only perturbatively in ϵ.

Previously reported expressions for the real part of the equation of state in the critical region, although derived in different ways, may be written in terms of a match condition. The equation of state presented by Brézin *et al.*[36] implicitly assumes that ρ is eliminated via $M(\kappa\rho) = 1$. (Equivalently, m was chosen to be the independent variable that parametrizes the characteristics.) Another possible choice is $T(\kappa\rho) = 1$. Both choices do not exponentiate the logarithm in Eq. (3.4a) and they become meaningless when τ or $\langle m \rangle$ equals zero. Rudnick and Nelson[11] proposed a uniform approximation that exponentiates the logarithms by requiring that $X_t(\kappa\rho) = 1$. Their condition makes explicit the connection between the critical and the noncritical theories by evaluating the perturbative expression in a noncritical region, since their condition requires that the mean-field susceptibility (which is a measure of the strength of single-well fluctuations) be finite. It is noteworthy that the Nelson-Rudnick equation of state at the fixed point is exactly the same with the one derived from the linear parametric model,[37] with the normalizations chosen by Wallace,[38] and the same as the $n = 1$ equation of state proposed by Horner and Schäfer;[39] the equation of state derived by Lawrie[40] is similar to the latter for $n = 1$.

The simplicity of the Nelson-Rudnick condition is very appealing; unfortunately it cannot be used everywhere inside the coexistence curve because the corresponding equation of state sooner or later exhibits unphysical behavior. Since, for $d < 4$, $T(\kappa\rho)$ and $U(\kappa\rho)M^2(\kappa\rho)$ flow differently as $\rho \to \infty$ [cf. Eqs. (3.3)], there exists a finite value of the scale parameter, $\rho = \rho^*$, beyond which a real

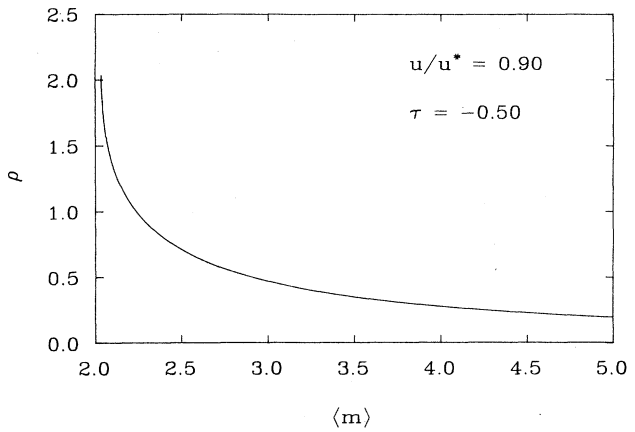

FIG. 1. Scale parameter determined by solving the Rudnick-Nelson match condition for $\tau=-0.50$ and $u/u^*=0.90$. The real solution to the match condition disappears at ρ^*, where $\partial\rho/\partial\langle m\rangle=\infty$.

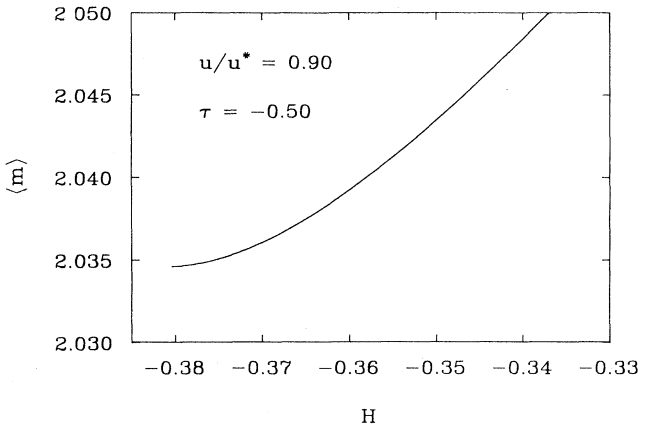

FIG. 2. Rudnick-Nelson one-loop equation of state for the scale parameter of Fig. 1; at ρ^* the susceptibility $\partial\langle m\rangle/\partial H$, vanishes.

nonperturbative solution of the match condition disappears. Moreover, the solution disappears in a completely unphysical way; it is easy to show that at ρ^* the *inverse* susceptibility diverges. Figure 1 depicts the scale parameter, determined by the Rudnick-Nelson match condition, as a function of m, and Fig. 2 the corresponding one-loop crossover form of the equation of state. Note that at ρ^* the susceptibility, $\partial m/\partial H$, vanishes, and $\partial\rho/\partial m=\infty$.

We propose a modification of the Nelson-Rudnick condition which exponentiates logarithmic singularities, to the appropriate order in the ϵ expansion, and which, for $T<T_c$, has a nonperturbative solution up to the point where ρ diverges. Our match condition modifies the temperature and the coupling constant terms in an ϵ-dependent way so that the two terms of the mean-field inverse susceptibility [cf. Eq. (3.4b)] diverge in the same way, and so that it reduces to the Nelson-Rudnick condition in an ϵ expansion. (A similar redefinition of τ and u was obtained by Lawrie.[40])

There exists a whole family of such match conditions; one possible choice is

$$T(\kappa\rho)\left[\frac{\alpha+U(\kappa\rho)T^2(\kappa\rho)}{\alpha+U(\kappa\rho)}\right]^{-[\beta(\kappa\rho)-1/2]/2}+\tfrac{1}{2}U(\kappa\rho)M^2(\kappa\rho)\left[\frac{\alpha+U(\kappa\rho)T^2(\kappa\rho)}{\alpha+U(\kappa\rho)}\right]^{-3[\beta(\kappa\rho)-1/2]/2}=1, \tag{3.5a}$$

where

$$\beta(\kappa\rho)\equiv\frac{1}{2}-\frac{U(\kappa\rho)}{4-U(\kappa\rho)} \tag{3.5b}$$

and $\beta(\kappa\rho)$ is a crossover form of the order-parameter critical exponent.[41] The match condition reduces to $T(\kappa\rho)=1$ for $\langle m\rangle=0$. The exponents in Eq. (3.5a) were determined by requiring that the overall factor of the scale parameter be ρ^2, two being the canonical dimension of the inverse susceptibility; the same exponents are obtained by naively exponentiating the logarithms in the one-loop perturbative expression for the inverse susceptibility. The arbitrary nonuniversal parameter α was introduced to ensure that Griffiths's analyticity[42] is satisfied. It is easy to show, however, that the equation of state is universal to the appropriate order in an ϵ expansion, $[\partial H/\partial\alpha=O(\epsilon^3)]$. Even when $\epsilon=1$ our numerical results suggest that the choice of α is not very important. Finally, the term containing the logarithm can be dropped to $O(\epsilon)$ in Eq. (3.4a). The resulting equation was used with numerical solutions to Eq. (3.5a) (with $\alpha=1$) and the result is shown in Figs. 3 and 4.

Figure 3 shows a typical phase diagram for a system described by a ϕ^4 free energy, and Fig. 4 presents a phase diagram for a free energy with an independent cubic interaction term.[43] We find that inside the coexistence region there exists a new curve, which we call the universal spinodal curve, along which ρ diverges (for a system without a cubic interaction term the universal spinodal curve is, by symmetry, the $H=0$ line). It is a line of ϕ^4 critical points that is always inside the unstable region ($\chi<0$).[44] For $d\geq 4$, and in the mean-field limit (e.g., $\kappa\to 0$), the pseudospinodal and the universal spinodal curves coincide. Since mean-field theory becomes exact for infinite-range interactions, our results for the infinite-range limit agree with previous works.[9,45]

The scale parameter ρ is finite along the pseudospinodal curve, except at T_c. It should be distinguished from the correlation length, defined as $\chi^{1/2}$, which diverges along the pseudospinodal. According to the interpretation of the renormalization-group transformation, ρ is a measure of the size of the correlation volume where fluc-

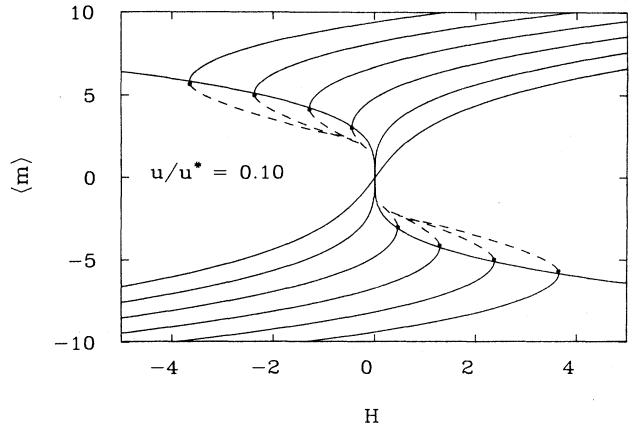

FIG. 3. One-loop crossover form of the equation of state derived from a free energy without an independent cubic interaction term, Eq. (3.4a). The scale parameter was determined by solving Eq. (3.5a). Isotherms are equally spaced between $\tau=-1.00$ and $\tau=0.25$ with $u/u^*=0.10$. The solid curve is the pseudospinodal curve (determined by numerically differentiating the equation of state), and the dashed curve is the unstable part of the equation of state. Small circles denote the points where the perturbative one-loop inverse susceptibility vanishes; even though it is not very noticeable in the curves, they do not lie on the numerically determined pseudospinodal. By symmetry, the coexistence and the universal spinodal curves are the $H=0$ line.

tuations are large and where nonlinear effects are important. Unlike those associated with the Cahn-Hilliard droplet, the fluctuation processes associated with ρ do not vanish at the pseudospinodal. If these are identified with some kind of droplet, then it will be finite in size at the pseudospinodal, although it is unlikely that such a droplet looks anything like the spherically symmetric solution of the Euler-Lagrange equations. As suggested by Klein in a slightly different context, such droplets are likely to be ramified[46] (here characteristic of fluctuations at the critical point).

The position of the universal spinodal curve in the phase diagram determines the nature of the observed singularities deep inside coexistence, because ρ controls the degree of deviation from mean-field results. The usual spinodal, along which the real part of susceptibility has an accidental, simple pole, lies in between the coexistence and the universal spinodal curves. The mean-field character of the pseudospinodal curve is demonstrated by considering the effective exponent δ, defined as

$$\chi^{-1}\sim(\langle m\rangle-\langle m\rangle_{\rm PS})^{\delta-1}\,, \tag{3.6a}$$

where $\langle m\rangle_{\rm PS}$ is the value of $\langle m\rangle$ at the pseudospinodal. Note that the value of m at the universal spinodal is

$$m_{\rm US}=\left[\frac{-2\tau}{u^*}\right]^{1/2}\left[\frac{u^*\tau^2}{1+u^*}\right]^{-\epsilon/[2(6-\epsilon)]}\,,\quad \text{for } \epsilon\geq 0. \tag{3.6b}$$

As Fig. 5 shows, the effective exponent $\delta-1$ exhibits three distinct regions: from the large m mean-field value ($\delta=3$), it crosses over to the critical value $[\delta=3+2\epsilon/(2-\epsilon)]$, and then, close to the pseudospinodal, to the small m mean-field value ($\delta=2$). As expected, when $u=u^*$ (the dashed curve in Fig. 5) (also $\tau\to 0$) or $\kappa\to 0$ (also $\tau\to-\infty$), only two regimes are observed. Thus, in agreement with the results of Unger and Klein,[9] the pseudospinodal away from T_c (or more generally, when the pseudospinodal and the universal spinodal are far apart) appears to be mean-field-like.

As a final note on the problem of thermodynamic inconsistency, Figs. 3 and 4 show that the slope of the equation of state at the universal spinodal, $\partial m/\partial H$, is zero; however, the perturbative expression for the susceptibility becomes infinite. Even though the two expressions differ by terms of $O(\epsilon^3)$, the difference becomes numerically large as $\rho\to\infty$.

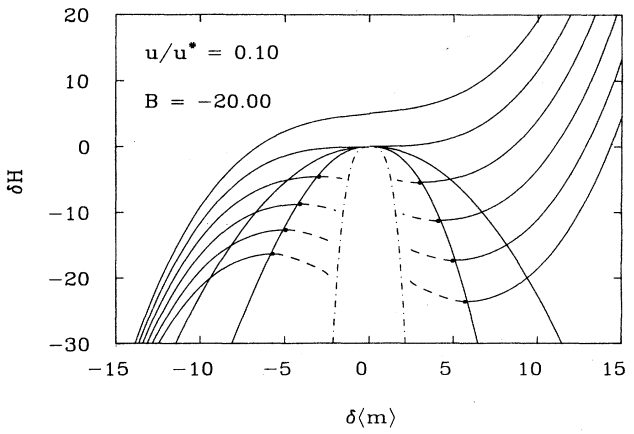

FIG. 4. One-loop crossover form of the equation of state derived from a free energy with an independent cubic interaction term, cf. Ref. 43. The coexistence (solid), pseudospinodal (solid), and universal spinodal (dot-dashed) curves are shown. Isotherms and u are as in Fig. 3. As described in Ref. 43 $\delta\langle m\rangle$ and δH are the order-parameter and conjugate external field, respectively.

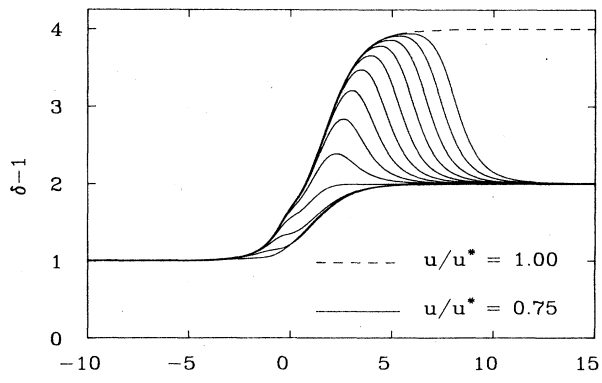

FIG. 5. Effective exponent $\delta-1$, given by $\delta-1\equiv\partial\ln(\chi^{-1})/\partial\ln(\langle m\rangle-\langle m\rangle_{\rm PS})$. The solid curves were obtained for $u/u^*=0.75$ and the dashed curve for $u/u^*=1.00$. The solid curves correspond to $\tau=-10^{-10}$, -10^{-9}, ..., -10, and -100, reading from top to bottom.

C. Imaginary part of the equation of state

The instanton contribution to the equation of the state is

$$H_{\rm in}=\pm i\ \frac{\partial}{\partial\langle m\rangle}[R_{\rm in}^{-d}(\beta\Delta F_{\rm in}^{(0)})^{d/2}e^{-\beta(\Delta F_{\rm in}^{(0)}+\Delta F_{\rm in}^{(2)})}], \tag{3.7}$$

where the instanton partition function, Eq. (2.29), is written in crossover form by expressing, in an ϵ expansion, the renormalized parameters in terms of the flowing quantities, and repeating the steps presented in Sec. II C. Note that the logarithms in the expression for the free energy density, Eq. (2.25b), provide the necessary $\ln(\kappa)$ terms to convert the order ϵ^{-1} terms (the tree free energy terms), into crossover form. The remaining terms are $O(1)$ and, thus, trivially convert into crossover form.

The quantities that appear in Eq. (3.7) are expressed in terms of the crossover form of the free energy density,

$$\beta\delta f(\kappa\rho,\tilde r)=\tfrac{1}{2}|\nabla_{\tilde r}\delta M|^2+\frac{1}{2}\left[X_t(\kappa\rho)+\frac{U(\kappa\rho)}{4}[X_t(\kappa\rho)+U(\kappa\rho)M^2]\ln(X_t(\kappa\rho))\right]\delta M^2$$
$$+\frac{U(\kappa\rho)\delta M}{3!}\left[1+\frac{3U(\kappa\rho)}{4}\ln(X_t(\kappa\rho))\right](M+\delta M/4), \tag{3.8a}$$

where $\tilde r=r/\rho$ is a dimensionless variable and δM is expressed in terms of the dimensionless variable, $\delta\tilde m=\delta m\kappa^{-1+\epsilon/2}$, by

$$\delta M=\delta\tilde m(\tilde r)(\kappa\rho)^{1-\epsilon/2}. \tag{3.8b}$$

Thus, in terms of the free energy density, we obtain

$$\beta\Delta F_{\rm in}^{(0)}=\frac{S_d^2}{(2\pi)^d}\left[\frac{\rho}{R_{\rm in}}\right]^{\epsilon}\int_0^{\infty}d\tilde r\,\tilde r^3\beta\delta f(\kappa\rho,\tilde r), \tag{3.8c}$$

and

$$\beta\Delta F_{\rm in}^{(2)}=\frac{S_d^2}{(2\pi)^d}\left[\frac{\rho}{R_{\rm in}}\right]^{\epsilon}\left[4\beta\Delta F_{\rm WKB}^{(2)}-\tfrac{1}{4}\int_0^{\infty}d\tilde r\,\tilde r^3[\gamma+\tfrac{1}{2}+\ln(\tilde r X_t(\kappa\rho)^{1/2}/2)][X^2(\kappa\rho,\tilde r)-X_t^2(\kappa\rho)]\right]. \tag{3.8d}$$

The expression for $\beta\Delta F_{\rm WKB}^{(2)}$ is trivially written in crossover form because it is a one-loop term. As before, the ratio $\ln(R_{\rm in}/\rho)$ is defined in Eq. (2.26) where the free energy density is replaced by its crossover form, Eq. (3.8a).

Houghton and Lubensky[10] analyzed the imaginary part of the free energy close to coexistence by imposing $M(\kappa\rho)=1$. As we mentioned in the Introduction, this match condition does not exponentiate the ϵ expanded logarithms and is inappropriate when the magnetization is comparable to the reduced temperature, whereas the match condition introduced earlier, Eq. (3.5a), is free of these difficulties. Furthermore, as in the case of the real part of the equation of state, it eliminates the explicit logarithms in the free energy density, Eq. (3.8a), thereby reducing the defining equation of the instanton to the same functional form as the original Euler-Lagrange equation, Eq. (2.1b), except that the solutions of the renormalization-group flow equations replace renormalized variables.

In our numerical work, whose results are presented in Figs. 6–9, the instanton was determined by extremizing the free energy functional with the free energy given in Eq. (3.8a). Even though the coefficient of the quadratic term is not the full one-loop perturbative expression for $\Gamma^{(2)}$ (it lacks the term $U^2M^2/4$), it is thermodynamically consistent with Eq. (3.4a). Namely, for a given τ, the instanton disappears at the value of $\langle m\rangle$ where the numerical derivative of H, after the match condition is imposed, vanishes. Moreover, numerically; the difference associated with this term is small.

The WKB expression in Eq. (3.8d) was evaluated using the crossover form (i.e., where $\tilde\tau$, $\langle\tilde m\rangle$, and $\tilde u$ were re-

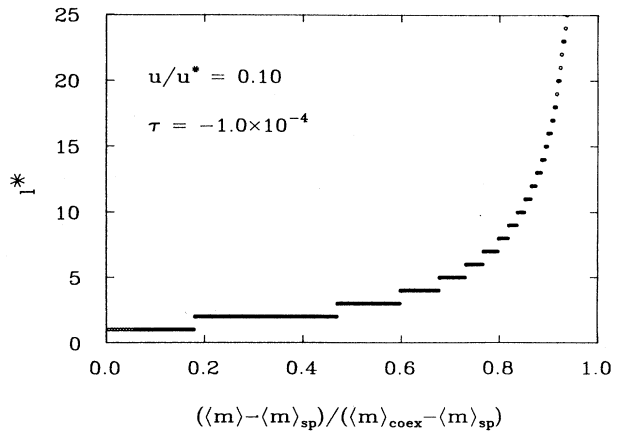

FIG. 6. Angular momentum, l^*, beyond which the attractive potential of the Jacobi equation, Eq. (2.8b), has no real turning turning points.

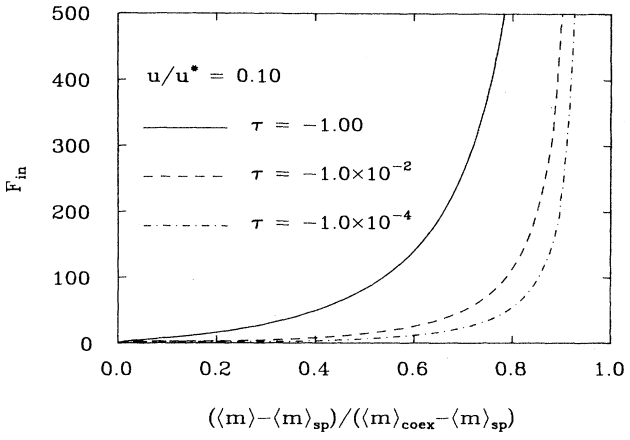

FIG. 7. One-loop crossover form of the droplet free energy, at $d=3$, for three different temperatures.

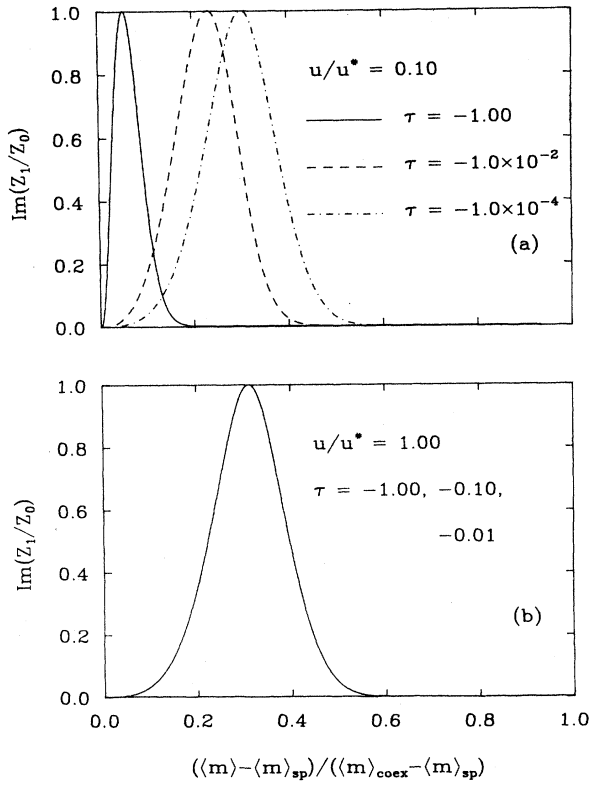

FIG. 8. One-loop crossover form of the imaginary part of the free energy (instanton contribution), at $d=3$. For each temperature the data were normalized to unity at their maximum value. As discussed in the text (cf. Table II), the maximum value, and hence nucleation rates, scale as $|\tau|^{\nu d}$. (a) $u/u^*=0.10$; (b) $u/u^*=1.00$. The lower graph, which is a superposition of three curves for different temperatures, shows that, when the scale parameter tends to infinity, the imaginary part of the free energy is a universal function.

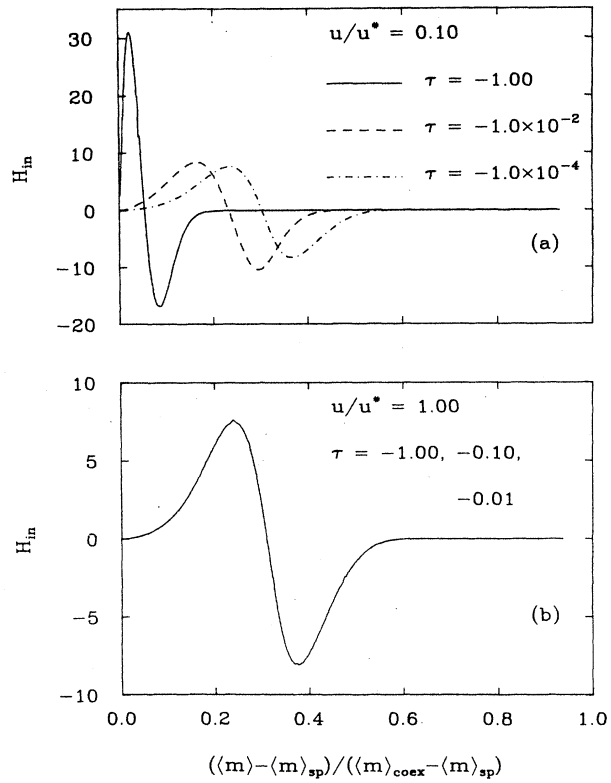

FIG. 9. Instanton contribution to the equation of state, determined by differentiating the free energy shown in Fig. 8. As in Fig. 8, for $u/u^*=1.00$, H_{in} is a universal function.

placed by T, M, and U, respectively) of the two-turning point, second-order WKB expression for $l=0,1$ [cf. Eqs. (2.11) and B(11)]. For $2\le l\le l^*+5$, where l^* is the maximum angular momentum beyond which the attractive potential of the instanton Jacobi equation Eq. (2.8b) has no turning points, slightly better results were obtained by numerically solving Eq. (2.13a) with x_0 replaced by X_l, etc. Note that the corresponding subtractions remain the same. The crossover, no-turning point, second-order WKB formulas, Eqs. (2.10), were used for the remaining contributions to the sum over l.

The maximum angular momentum value, l^*, is shown in Fig. 6. It is seen that l^* increases very rapidly close to coexistence. Moreover, even when $l^*\sim 10$ the droplet free energy, shown in Fig. 7, is so large that any logarithmic corrections to the free energy[5,7] are impossible to observe. The one-loop crossover form of the imaginary part of the free energy, at $d=3$ and for different temperatures and coupling constants, is presented in Fig. 8. In agreement with the mean-field result, the imaginary part of the free energy vanishes exponentially at coexistence and algebraically (exponentially) at the pseudospinodal for $d<6$ ($d>6$). Thus, at the pseudospinodal, where the system becomes macroscopically unstable [$\mathrm{Re}(\chi)=0$], the imaginary part of the free energy vanishes.

The curves in Fig. 8 are normalized to unity at their

TABLE II. Maximum value of the imaginary part of the free energy.

u/u^*	τ	$\max(iZ_1/Z_0)$
0.10	−1.00	1.148×10^{-5}
0.10	−0.01	3.033×10^{-7}
0.10	−0.0001	2.646×10^{-10}
1.00	−1.00	1.166×10^{-3}
1.00	−0.10	1.849×10^{-5}
1.00	−0.01	2.930×10^{-7}

maximum, and their maximum value is presented in Table II. As the critical point is approached the imaginary part of the free energy (and thus the nucleation rate of the metastable state) decreases rapidly. Moreover, as the scale parameter increases, or the coupling constant approaches u^*, the imaginary part of the free energy obeys scaling and tends to a universal function.

The maximum of the imaginary part of the free energy obeys a scaling law which is determined by noticing that the crossover from the spinodal region to the coexistence curve occurs when the free energy is of order unity. Hence, the dependence of the maximum on thermodynamic variables is determined only by the factor $R_{\rm in}^{-d}$, cf. Eq. (3.7), which behaves like $|\tau|^{\nu d}$ (here ν is the usual critical exponent that relates τ to the correlation length). This is the usual scaling law for the free energy density. The exponent extracted from the data of Table II is 1.8, in agreement with the prediction of the scaling law in the critical region for $d=3$ and $\nu=(2-\epsilon/3)^{-1}$. Figure 9 shows the imaginary part of the equation of state, obtained by differentiating the free energy shown in Fig. 8. As before, our results give a universal function for the imaginary part of the equation of state when $u=u^*$ or sufficiently close to T_c.

IV. DISCUSSION AND CONCLUSIONS

We have presented an equilibrium calculation of the one-loop, crossover form of the equation of state inside the coexistence region that incorporates fluctuations about both spatially uniform and nonuniform states. Single-phase fluctuations about a local free energy minimum were treated according to the standard ϕ^4 analysis. Droplet-like fluctuations of the new phase, which correspond to a spatially nonuniform, instanton free energy extremum were analyzed, and, in agreement with previous calculations,[5] their contribution to the free energy was purely imaginary. As Langer[8] has shown, the imaginary part of the free energy may be interpreted to be the nucleation rate of the metastable system and the instanton is the field-theoretic description of a nucleating droplet. We showed how the instanton contribution to the free energy is renormalized by evaluating the one-loop fluctuation corrections as a solution of a Jacobi differential equation, which was solved by second-order WKB, and by renormalizing the resulting expression. In agreement with the result of Brézin *et al.*[34] we found that the usual ϕ^4 renormalization constants sufficed to make the free energy finite. The resulting analytic expression extrapolates smoothly between the two previously studied limits; close to coexistence[5,7] the imaginary part vanishes exponentially whereas close to the pseudospinodal[9] it vanishes algebraically (exponentially for $d>6$). In the mean-field limit and close to the pseudospinodal our results are in qualitative agreement with the work of Unger and Klein,[9] but, as discussed in Sec. II, our exponents differ.

Perhaps, the main surprise of this work is that a consistent analysis of fluctuations inside the coexistence region requires that the scale parameter be decoupled from the correlation length (defined as $\chi^{1/2}$), thereby introducing two independent length scales. The scale parameter, which appears naturally in the field-theoretic approach to the renormalization group, is a measure of the coherence volume associated with nonlinear processes which typify the critical point. Its value was determined by introducing an ϵ-dependent modification of the Rudnick-Nelson[11] match condition.

The real part of the inverse susceptibility and the imaginary part of the free energy vanish at the pseudospinodal, along which the scale parameter remains finite (except at T_c). The scale parameter diverges along a line of ϕ^4 critical points, which we call the universal spinodal curve, that lies inside the unstable region of the phase diagram. Since the scale parameter determines how nonclassical critical exponents are, the position of the universal spinodal, which is experimentally inaccessible, governs the apparent singularities deep inside coexistence. In agreement with earlier work,[9] the pseudospinodal is a mean-field line, because the real part of the inverse susceptibility has an accidental pole.

We stress that the scale parameter is different from the thermal correlation length, which diverges at the spinodal. Here, the size of droplet-like fluctuations is linked to the thermal correlation length, and hence, the characteristic size of the droplets diverges at the spinodal (in much the same way as originally discussed by Cahn and Hilliard). Moreover, as has been found before,[9,17,18,46] their contribution to the extrapolated thermodynamic quantities vanishes at the spinodal; what remains are the critical-point fluctuations, which are not droplet- or cluster-like (at least not in any obvious manner), and which have a typical correlation length equal to the scale parameter.

Previous works[9,45] analyzed the existence of spinodals and the corresponding validity of mean-field theories in connection with the range of the interaction potential. In our analysis if the infinite-range limit is taken *before* fluctuations are considered, the essential singularity at coexistence disappears (in agreement with Langer's result[5]), and the universal spinodal coincides with the pseudospinodal. Thus, the usual mean-field results are obtained.

It has been argued[33] that the spinodal corresponds to a fixed point of a ϕ^3 free energy. However, we have shown that, for systems with a critical point, no new ϕ^3 renormalization constants appear to be necessary, and that the universal spinodal curve, which is determined by the ϕ^4 fixed point, governs the singularities. Furthermore, even though $d=6$ appears to be a critical dimension for nucleation close to the pseudospinodal[9,14] (since the rate at

which the imaginary part vanishes changes from algebraic to exponential), no new ir divergences were found for $4<d<6$. Thus, for $d>4$ critical fluctuations may be treated perturbatively.

It should be emphasized that the present calculation is based on a *static* treatment of fluctuations inside the coexistence region; thus, it must be considered as accurate only for timescales short in comparison with the nucleation time.[19] In particular, lines that lie inside the coexistence curve (the pseudospinodal and the universal spinodal curve), and appear sharp in a static analysis, are expected to become diffuse once the dynamics of the system is considered. In fact, preliminary results,[20] based on a nonequilibrium generalization of this static theory that incorporates the two length scales but not nucleation, suggest that the universal spinodal curve is smeared. Details will be presented in a future publication.

ACKNOWLEDGMENTS

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APPENDIX A: Derivation of the Jacobi equation

We generalize Schulman's derivation[21] of the Jacobi equation to a local, spherically symmetric potential in d dimensions. The one-loop correction to the mean-field free energy is given by the functional integral over the second-order variation of βF, Eqs. (2.2). By decomposing the fluctuations into d-dimensional spherical harmonics and using their orthonormality property we obtain

$$\int d\mathbf{r}_1 d\mathbf{r}_2 \beta F_i^{(2)} \delta\phi(\mathbf{r}_1)\delta\phi(\mathbf{r}_2) = \sum_l g_l(d) \int_0^L dr \left[r^{d-1} \left(\frac{\partial \delta\phi_l}{\partial r} \right)^2 + V_l(r) \delta\phi_l^2(r) \right], \quad \text{(A1a)}$$

where

$$V_l(r) \equiv r^{d-1} \left[\frac{l(l+d-2)}{r^2} + x_i(r) \right], \quad \text{(A1b)}$$

and the degeneracy $g_l(d)$ was defined in Eq. (2.4b). Since the l components of $\delta\phi$ decouple, it suffices to consider any one of them; moreover, we shall drop the subscript "l" to keep the notation simple.

We interpret the functional integral, Eq. (1.2), by the standard[21] discretization, whereby it is given as the $N\to\infty$ limit of an N-dimensional integral with $L=\Delta N$, keeping L fixed. For $d\neq 1$, the discretization of Eq. (A1a) poses some problems because it involves a derivative multiplying a function of r. It is well known that in such cases the discretization is not unique; we use the so-called Stratonovich choice[21] to obtain

$$\int_0^L dr \left[r^{d-1} \left(\frac{\partial \delta\phi}{\partial r} \right)^2 + V(r) \delta\phi^2(r) \right] = \sum_{j=1}^{N} \left[\tfrac{1}{2} \{ (\Delta j)^{d-1} + [\Delta(j+1)]^{d-1} \} \frac{1}{\Delta} (\delta\phi_{j+1} - \delta\phi_j)^2 + \Delta V_j \delta\phi_j^2 \right],$$
$$\equiv \frac{1}{\Delta} \delta\underline{\phi}^T \underline{A}(N) \delta\underline{\phi}, \quad \text{(A2)}$$

where $\delta\phi_j \equiv 0$ for $j\leq 0$ or $j\geq N+1$, and T denotes matrix transpose. The matrix elements of $\underline{A}(N)$ are

$$A_{i,j} \equiv \begin{cases} \tfrac{1}{2}\{[\Delta(j+1)]^{d-1} + 2(\Delta j)^{d-1} + [\Delta(j-1)]^{d-1}\} + \Delta^2 V_j, & \text{for } i=j, \\ \tfrac{1}{2}[(\Delta i)^{d-1} + (\Delta j)^{d-1}], & \text{for } i=j\pm 1, \\ 0 \quad \text{otherwise.} \end{cases} \quad \text{(A3)}$$

Thus, the fluctuation correction to the discretized functional integral becomes

$$\delta Z = \lim_{N\to\infty} (2\pi\Delta)^{-(N+1)/2} \int d\delta\phi_1 \ldots d\delta\phi_N \exp\left[-\frac{1}{2\Delta} \delta\underline{\phi}^T \underline{A}(n) \delta\underline{\phi} \right],$$
$$= \lim_{N\to\infty} \{ 2\pi\Delta \det[\underline{A}(n)] \}^{-1/2}. \quad \text{(A4)}$$

The matrix $\underline{A}(n)$ has a very simple form; its elements are all zero except those along the diagonal and the two adjacent lines. As a consequence, a recursion relation may be derived for $D_n \equiv \det[\underline{A}(n)]$;[21] namely,

$$D_n = A_{nn} D_{n-1} - A_{n,n-1}^2 D_{n-2}, \quad \text{(A5)}$$

with $D_{-1}\equiv 0$ and $D_0 \equiv 1$. Equation (A5) further simplifies if we write

$$D_n \equiv L_n \prod_{j=1}^{n} \psi_j, \quad \text{(A6a)}$$

with

$$\psi_j \equiv \tfrac{1}{2}\{(\Delta j)^{d-1}+[\Delta(j+1)]^{d-1}\}, \tag{A6b}$$

to obtain

$$-\frac{(\Delta n)^{d-1}}{2\Delta^2}(L_n-2L_{n-1}+L_{n-2})-\frac{[\Delta(n+1)]^{d-1}}{2\Delta^2}(L_n-L_{n-1})+\frac{[\Delta(n-1)]^{d-1}}{2\Delta^2}(L_{n-1}-L_{n-2})+V_nL_n=0. \tag{A7}$$

The last factor of Δ in the Gaussian determinant, Eq. (A4), is eliminated by defining

$$\Lambda(r)\equiv\Delta L_n \tag{A8a}$$

for $r\equiv\Delta n$. In the limit $\Delta\to 0$ the difference equation becomes a differential equation for $\Lambda(r)$,

$$-\frac{\partial^2\Lambda}{\partial^2 r}-\frac{d-1}{r}\frac{\partial\Lambda}{\partial r}+V(r)\Lambda(r)=0, \tag{A8b}$$

with boundary condition

$$\Lambda(0)=0. \tag{A8c}$$

For $d\neq 1$, the differential equation has a singularity at the origin that invalidates the usual derivation of the second boundary condition.[21] Here we obtain the second boundary condition by considering the original difference equation, Eq. (A7), for $\Delta\to 0$ with $n\Delta\sim o(1)$. In this limit, the term in $x_i(r)$ [cf. Eq. (A1a)] can be dropped. The solution to the resulting difference equation is independent of Δ and x_i, and is easily shown to behave as n^l for $n\gg 1$. This implies that

$$\Lambda\sim c_l r^l, \tag{A8d}$$

as $r\to 0$ with c_l independent of x; the constant c_l is unimportant because it cancels out from the ratio A_l^2.

Therefore, the Gaussian determinant in the functional integral,

$$\lim_{N\to\infty}[\Delta\det(\underline{A})],$$

equals the solution of the Jacobi equation, evaluated at the system size, L, up to unimportant multiplicative constants [cf. Eq. (A6a)].

APPENDIX B: SECOND-ORDER WKB

1. General expressions

The expressions used in Eqs. (2.11) are defined as follows[26]

$$S_0(t_A,t_B)=\int_{t_A}^{t_B}dz\,Q(z)^{1/2}, \tag{B1a}$$

$$\tilde{S}_0(t_A,t_B)=\int_{t_A}^{t_B}dz[Q(z)^{1/2}-\nu], \tag{B1b}$$

$$S_1(t_B)=-\tfrac{1}{4}\ln[Q(t_B)], \tag{B2}$$

$$S_2(t_A,t_B)=\frac{5Q'(t_B)}{48Q(t_B)^{3/2}}+\tilde{S}_2(t_A,t_B), \tag{B3}$$

with

$$\tilde{S}_2(t_A,t_B)=\tfrac{1}{48}\int_{t_A}^{t_B}dz\,Q''(z)Q(z)^{-3/2}, \tag{B4}$$

where primes denote derivatives. The expressions for the case with turning points are slightly more complicated because $\tilde{S}_2$ has a pole at the turning point; however, they are reproduced in many standard books on applied mathematics, see, e.g., Ref. 26 (whose notation we follow).

In terms of Eqs. (B1)–(B4), the constant B_l, cf. Eq. (2.11a), is

$$B_l=c_l\nu^{1/2}r_A^{\nu}e^{\tilde{S}_0[-\infty,\ln(r_A)]+\tilde{S}_2[-\infty,\ln(r_A)]}. \tag{B5}$$

2. Translational modes

The calculation of the almost zero translational eigenvalue $\lambda_{0,1}^{(1)}$ is an example of a boundary shape perturbation analysis for a system with Dirichlet boundary conditions.[47] The method is well known[5,21] and gives

$$\lambda_{0,1}^{(1)}=-\frac{L^{d-1}\phi_1(L)\phi_1'(L)}{\|\phi_1\|^2}, \tag{B6}$$

where

$$\|\phi_1\|^2\equiv\int_0^L dr\,r^{d-1}\phi_1^2, \tag{B7}$$

and

$$\phi_1\equiv\frac{\partial\delta m}{\partial r}. \tag{B8}$$

Moreover, the expression for the contribution of the translational modes to the Jacobian, cf. Eq. (2.15b), simplifies considerably because the Jacobi equation for the metastable minimum is exactly solvable, cf. Eq. (2.12), and ϕ_1 is an exact solution of the Jacobi equation for the instanton extremum, i.e.,

$$\Lambda_1^{(1)}(L)=\frac{c_1}{\phi_1'(0)}\phi_1(L). \tag{B9}$$

Thus,

$$\lambda_{0,1}A_1^2=\frac{L^{d-1}}{\|\phi_1\|^2}\phi_1(L)\phi_1'(0)2^{d/2}\Gamma\left[1+\frac{d}{2}\right]\times(x_0^{1/2}L)^{1-d/2}I_{d/2}(x_0^{1/2}L). \tag{B10}$$

Note that the explicit factors of L must cancel exactly in Eq. (B10). Since the order-parameter trial function, Eq. (2.9a), does not give the correct algebraic correction to the dominant exponential decay as $L\to\infty$, the second-order WKB solution to the $l=1$ Jacobi equation was used in Eq. (B10). This substitution gives

$$\lambda_{0,1}^{(1)}A_1^2=\frac{[\phi_1'(r=0)]^2}{\|\phi_1\|^2}x_0^{-d/2}d_{0,1}, \tag{B11a}$$

where the constant $d_{0,1}$, expressed in terms of the previously defined quantity B_1 [cf. Eq. (B5)], is

$$d_{0,1}=\frac{2^{d/2}}{(2\pi)^{1/2}}\Gamma\left[1+\frac{d}{2}\right]B_1 c_1^{-1}x_0^{d/4}\times\exp\left\{-S_0[t_B,\ln(L)]-S_2[t_B,\ln(L)]+x_0^{1/2}L\right\},\tag{B11b}$$

and t_B is the outer turning point. Note that B_l in Eq. (B11b) is evaluated at $\nu=d/2$.

APPENDIX C: ϕ^4 FREE ENERGY WITH UNIFORM ORDER PARAMETER IN POLAR SPHERICAL COORDINATES

1. Product of eigenvalues

The eigenvalue equation, Eq. (2.3a), for a system with uniform order parameter, expressed in polar spherical coordinates, becomes

$$\left[\partial_r^2+\frac{d-1}{r}\partial_r+\kappa_{\nu,n}^2-\frac{l(l+d-2)}{r^2}\right]\psi_{\nu,n}^0=0,\tag{C1}$$

where the eigenvalues are

$$\lambda_{\nu,n}^{(0)}=x_0+\kappa_{\nu,n}^2.\tag{C2}$$

x_0 and ν are defined in Eqs. (2.1c) and (2.8d), respectively.

The solution to Eq. (C1) is $r^{1-d/2}J_\nu(\kappa_{\nu,n}r)$, where $J_\alpha(x)$ is a Bessel function. Since $\psi_{\nu,n}^0$ vanishes at $r=L$,

$$\kappa_{\nu,n}=\frac{j_{\nu,n}}{L},\tag{C3}$$

where $j_{\nu,n}$ are zeroes of a Bessel function of order ν.[27] Thus, the product over the eigenvalues may be written, up to an unimportant multiplicative constant, as

$$\prod_{l,n}\lambda_{l,n}^{(0)}\propto\prod_{l=0}^{\infty}\prod_{n=1}^{\infty}\left[1+\frac{x_0L^2}{j_{\nu,n}^2}\right]^{g_l}.\tag{C4}$$

Use of the infinite product representation of a Bessel function[27] gives

$$\prod_{n=1}^{\infty}\left[1+\frac{x_0L^2}{j_{\nu,n}^2}\right]=\Gamma(\nu+1)(\tfrac{1}{2}x_0^{1/2}L)^{-\nu}I_\nu(x_0^{1/2}L).\tag{C5}$$

Finally, comparing Eq. (C5) with Eq. (2.12) shows that, for a given value of the angular momentum, the evaluation of the product of the eigenvalues and the exact solution of the Jacobi equation are equal up to unimportant multiplicative factors independent of the thermodynamic variables.

2. Renormalization

The one-loop fluctuation contribution to the tree free energy is

$$\ln[\det(\beta\Delta F_0^{(2)})]=\sum_{l,n}\ln(\lambda_{l,n}^{(0)}).\tag{C6}$$

We shall use Eq. (C5) for the product of the eigenvalues. Moreover, the uniform Debye asymptotic expansion[27] (whose first term is just the first-order WKB approximation to the Jacobi equation), will be used for the modified Bessel function. For $l\to\infty$ the sum becomes

$$\sum_{l,n}\ln(\lambda_{l,n}^{(0)})=\sum_{l=0}^{\Lambda}g_l(d)\left\{l\left[1+\frac{x_0L^2}{l^2}\right]^{1/2}-l\ln\left[1+\left[1+\frac{x_0L^2}{l^2}\right]^{1/2}\right]-\tfrac{1}{4}\ln\left[1+\frac{x_0L^2}{l^2}\right]\right\},\tag{C7}$$

where $g_l(d)$ is the degeneracy factor, Eq. (2.4b), and terms independent of the thermodynamic variables were dropped. An upper cutoff Λ was introduced to make the sum over l finite at $d=4$. For large values of l the sum may be replaced by an integral and the thermodynamic limit becomes transparent by the following rescaling of the integration variable,

$$l\to l(x_0^{1/2}L)^{-1},\tag{C8a}$$

which gives

$$\sum_{l,n}\ln(\lambda_{l,n}^{(0)})=x_0^{d/2}L^d\frac{2(d-1)}{\Gamma(d)}\int_0^{\Lambda}dl\,l^{d-1}\{(1+l^{-2})^{1/2}-\ln[1+(1+l^{-2})^{1/2}]\}+O(L^{d-1}).\tag{C8b}$$

In deriving Eq. (C8b) the following asymptotic expansion of the degeneracy factor was used:

$$g_l(d)\sim\frac{2(d-1)}{\Gamma(d)}l^{(d-2)},\quad\text{as}\quad l\to\infty.\tag{C9}$$

Note that the last term on the right-hand side of Eq. (C7) drops out in the thermodynamic limit. By subtracting the l^{d-2} divergences and ϵ expanding the marginal term at $d=4$, we rewrite Eq. (C8b) as

$$\sum_{l,n}\ln(\lambda_{l,n}^{(0)})=-x_0^{d/2}L^d\frac{\Gamma(\epsilon/2)2^\epsilon}{4d(d-2)\Gamma(3-\epsilon/2)}.\tag{C10}$$

In Cartesian coordinates, the usual perturbative expression for the fluctuation correction is

$$\sum_{l,n}\ln(\lambda_{l,n}^{(0)})=\frac{VS_d}{(2\pi)^d}\int_0^{\infty}dq\,q^{d-1}\left[\ln(q^2+x_0)-\ln(q^2)-\frac{x_0}{q^2}\right],\tag{C11a}$$

which, in an ϵ expansion, gives

$$\sum_{l,n}\ln(\lambda_{l,n}^{(0)})=-x_0^{d/2}V\frac{\Gamma(\epsilon/2)2^{\epsilon}}{4d(d-2)\pi^{d/2}}, \tag{C11b}$$

where V is the system volume and S_d is the surface area of a d-dimensional unit sphere. Since

$$V=\frac{S_d}{d}L^d, \tag{C12}$$

the two expressions, cf. Eq. (C10) and Eq. (C11b), are the same. Thus, for the case of a uniform order-parameter extremum, when the sum over l is replaced by an integral, the renormalized WKB solution of the Jacobi equation reproduces the standard ϕ^4 results.

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*To whom correspondence should be addressed.

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[28]For example, the leading order behavior of the terms in the sum is l^{d-2} as $l\rightarrow\infty$.

[29]The same logarithms seem to introduce divergences close to the coexistence curve. They are canceled, however, by the low-l part of the sum in the last term of Eq. (2.21b). In particular, if the sum is truncated at $l\sim x_0^{1/2}R$, it behaves as $\ln(x_0^{1/2})$ with $R\rightarrow\infty$, thereby canceling the logarithmic divergences.

[30]It can be shown that, close to coexistence, $(R/\xi\rightarrow\infty)$, if the sums over l are replaced by integrals, the coefficients of δm in the Taylor series expansion of Eq. (2.25a) become the perturbative expressions for the corresponding N-point vertex functions in the ordered phase (e.g., the term linear in δm vanishes and the coefficient of the quadratic term becomes the one-loop perturbative expression for the inverse susceptibility).

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