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Nucleation barriers, spinodals, and the Ginzburg criterion

K. Binder

Center for Polymer Studies and Department of Physics, Boston University, Boston, Massachusetts 02215
and Institut für Festkörperforschung, Kernforschungsanlage Jülich, Postfach 1913, D-5170 Jülich, West Germany*

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Nucleation theory is considered in d-dimensional systems which undergo a nearly mean-field-like transition, such as Ising magnets or mixtures with a large but finite range r of the interaction, or polymer mixtures with chain lengths $N_A = N_B = N \gg 1$. Near two-phase coexistence the nucleation free-energy barriers are $\Delta F^* \propto r^d(1-T/T_c)^{2-d/2}(\delta\psi/\psi_{\text{coex}})^{-(d-1)}$ and $\Delta F^* \propto N^{(d/2-1)}(1-T/T_c)^{2-d/2}(\delta\psi/\psi_{\text{coex}})^{-(d-1)}$, respectively, where ψ_{coex} is the order parameter, $\delta\psi$ the deviation of the order parameter in the metastable state from that at coexistence, and T_c the critical temperatures where the transition is second order. The crossover to nucleation near T_c where $\Delta F^*/k_B T_c = c(\delta\psi/\psi_{\text{coex}})^{-(d-1)}$, c for $d<4$ being a universal constant, is controlled by the same Ginzburg criterion as for the static critical properties, i.e., crossover occurs at $r^d(1-T/T_c)^{2-d/2} \approx 1$, $N^{(d/2-1)}(1-T/T_c)^{2-d} \approx 1$. In polymer mixtures, mean-field-like behavior occurs only for $d>2$. In the mean-field region, metastable states are well defined up to a narrow region near the spinodal curve ψ_{sp}; the width of this region is given by $[(\psi-\psi_{\text{sp}})/\psi_{\text{coex}}]^{(3-d/2)} \approx [r^d(1-T/T_c)^{2-d/2}]^{-1}$ or $[N^{(d/2-1)}(1-T/T_c)^{2-d/2}]^{-1}$, respectively. This rounding of the spinodal curve can again be understood by the Ginzburg criterion for the metastable state at ψ near ψ_{sp}. At the unstable side of the mean-field region, the linear theory of spinodal decomposition holds outside of correspondingly narrow regions close to the spinodal curve, too.

I. INTRODUCTION

This work is concerned with the theory of first-order phase transitions in the framework of continuum theories.[1-6] We consider models which are close to a mean-field limit, such as Ising magnets or binary mixtures with large but finite range r of interaction, or polymer mixtures with large but finite chain length N. These systems are described by a mean-field free-energy density $f(\phi)$, ϕ being the volume fraction of, e.g., species A in the mixture,

$$f(\phi)/T = \phi \ln\phi + (1-\phi)\ln(1-\phi) + 2\frac{T_c}{T}\phi(1-\phi) \ . \tag{1}$$

The conjugate thermodynamic variable is the chemical potential difference μ, $\mu/T = \partial f(\phi)/\partial\phi$; the corresponding problem of an Ising magnet with magnetization m in a magnetic field H then corresponds to this problem by using $\phi = (1-m)/2$, $\mu = 2H$, and considering the potential $g(\phi) = f(\phi) - \mu\phi$. The resulting Ginzburg-Landau-Wilson Hamiltonian which forms the basis of continuum nucleation theory then is, in d dimensions,

$$\frac{\Delta\mathscr{F}}{T} = \int d^dx \left[\frac{f[\phi(x)]}{T} + r^2[\vec{\nabla}\phi(\vec{x})]^2 \right] , \tag{2}$$

r being the range of interaction.

The analogous problem of a polymer mixture of two chains A,B with N_A, N_B subunits of size σ_A, σ_B each is described by the Flory-Huggins model[7]

$$\frac{f_{\text{polymer}}(\phi)}{T} = \frac{\phi}{N_A}\ln\phi + \frac{(1-\phi)}{N_B}\ln(1-\phi) + v\phi(1-\phi) \tag{3}$$

with $v>0$ being some effective interaction parameter. Unmixing occurs for $v > v_{\text{crit}}$, with $v_{\text{crit}} = 2/N$ for $N_A = N_B$. The resulting Ginzburg-Landau-Wilson Hamiltonian is

$$\frac{\Delta\mathscr{F}_{\text{polymer}}}{T} = \int d^dx \left[\frac{f_{\text{polymer}}(\phi)}{T} + r_p^2[\vec{\nabla}\phi(\vec{x})]^2 \right] \tag{4}$$

with[8]

$$36r_p^2 = \sigma_A^2/\phi + \sigma_B^2/(1-\phi) \ . \tag{5}$$

Note that the length r_p is of short range, as is the range of interactions in the polymer problem; the simplifying feature making the polymer problem (for $d>2$) mean-field-like is the largeness of the chainlength N (henceforth we consider $N_A = N_B = N$). Formally the ordinary binary mixture is obtained as a special case of Eq. (4) if we would put $N=1$, $r_p = r$.

Other systems for which mean-field theory is (at least nearly) valid include ferroelectrics and dipolar magnets for $d \le 3$, superconductors, and systems undergoing elastic phase transitions of various types[9]; these systems will not be explicitly considered here. In all these cases we do expect, however, that metastable states with at least very large (if not infinite) lifetimes do exist.[6,10-12] In the strict mean-field limit $r \to \infty$ the limit of metastability is the spinodal line, which behaves as a line of critical points[13-15] described by a "spinodal fixed point."[16] The equation of state which follows from (1) or (3) is shown in Fig. 1, which serves to clarify our notation.

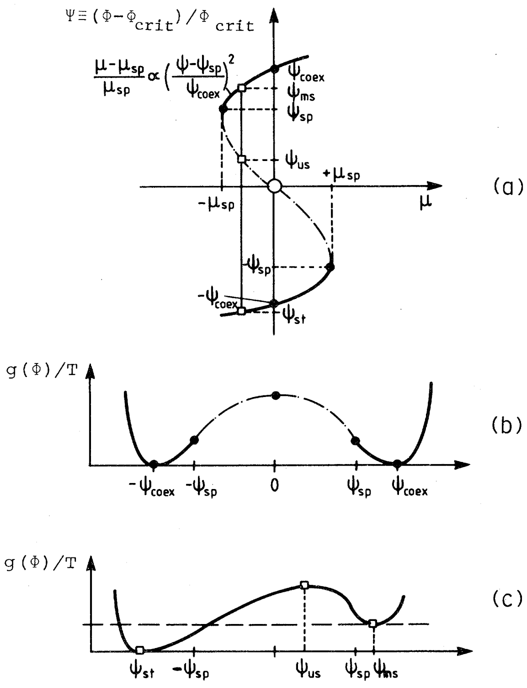

FIG. 1 (a) Order parameter $\psi=(\phi-\phi_{\text{crit}})/\phi_{\text{crit}}$ (note $\phi_{\text{crit}}=\frac{1}{2}$) plotted vs chemical potential difference μ ($\mu=0$ at coexistence for symmetric mixtures). Stable and metastable branch are shown as full curves, unstable branch dash-dotted. The values of the order parameter at the spinodals $\pm\mu_{\text{sp}}$ and associate chemical potentials $\pm\psi_{\text{sp}}$ are indicated. For a negative $\mu>-\mu_{\text{sp}}$ there occurs a stable state (ψ_{st}), an unstable state (ψ_{us}), and a metastable state (ψ_{ms}). (b) Thermodynamic potential $g(\phi)$ plotted vs ϕ for $\mu=0$, where two phases with $\psi=\pm\psi_{\text{coex}}$ can coexist in equilibrium. (c) Thermodynamic potential $g(\phi)$ for $-\mu_{\text{sp}}<\mu<0$.

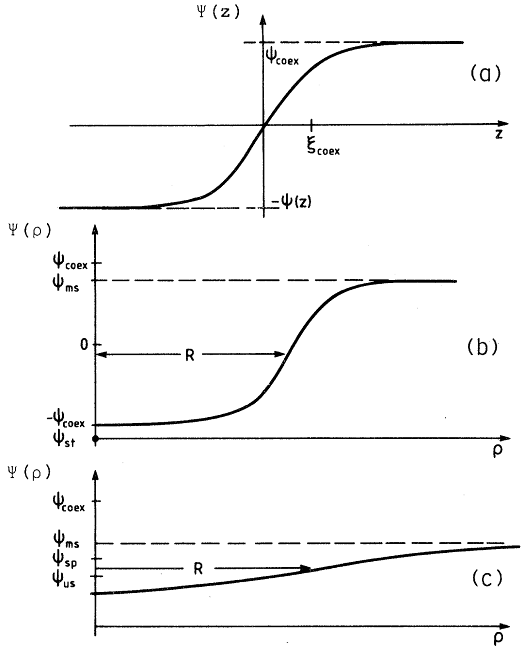

FIG. 2 (a) Order-parameter profile $\psi(z)$ across an interface between two coexisting bulk phases. The interface (hyper) plane is oriented perpendicular to the z direction. The (intrinsic) interface thickness is of the order of the correlation length at coexistence, ξ_{coex}. (b) Radial order-parameter profile for a marginally stable droplet of size $R\gg\xi_{\text{coex}}$ existing in a metastable state ψ_{ms} near ψ_{coex}. For $1-\psi_{\text{ms}}/\psi_{\text{coex}}\ll 1$ the profile reaches in the bulk of the droplet essentially an order parameter of $-\psi_{\text{coex}}$, and thus the profile essentially resembles that of (a). (c) Same as (b) for ψ_{ms} near ψ_{sp}. The order-parameter differences $\psi_{\text{sp}}-\psi_u$ and $\psi_u-\psi(\rho=0)$ are of the same order, see Cahn and Hilliard (1959) and Klein and Unger (1983) (Refs. 1 and 6).

II. CLASSICAL NUCLEATION THEORY NEAR THE COEXISTENCE CURVE: THE LONG-RANGE PROBLEM

It is assumed that the nucleation free-energy barrier is due to a spherical droplet of radius R. Denoting the volume and surface area of a d-dimensional unit sphere by V_d and S_d, the free-energy excess of a droplet is decomposed in a bulk and a surface term as

$$\Delta F(R)=-V_dR^d\mu\psi_{\text{coex}}+S_dR^{d-1}f_{\text{int}}\ . \tag{6}$$

The interface free energy per unit area f_{int} is taken to be that of a flat planar interface between coexisting phases [Fig. 2(a)]. This is legitimate for $|\mu|\ll|\mu_{\text{sp}}|$ [Fig. 2(b)] but not near the spinodal [Fig. 2(c)], as will be discussed below. The critical radius R^* where the droplet is marginally stable $\{\partial[\Delta F(R)]/\partial R\,|_{R^*}=0\}$ is then

$$R^*=\frac{(d-1)S_d}{dV_d}\frac{f_{\text{int}}}{\mu\psi_{\text{coex}}}=\frac{(d-1)S_d}{dV_d}\frac{f_{\text{int}}\chi_{\text{coex}}}{\psi_{\text{coex}}^2}\left[\frac{\delta\psi}{\psi_{\text{coex}}}\right]^{-1}, \tag{7}$$

where due to the smallness of μ one could eliminate μ in favor of $\delta\psi\equiv\psi_{\text{coex}}-\psi_{ms}=\chi_{\text{coex}}\delta\mu$, χ_{coex} being the susceptibility at coexistence curve. Then the nucleation barrier becomes

$$F^*\equiv\Delta F(R^*)=\left[\frac{S_d}{d}\right]^d\left[\frac{d-1}{V_d}\right]^{d-1}\frac{f_{\text{int}}^d\chi_{\text{coex}}^{d-1}}{\psi_{\text{coex}}^{2(d-1)}}\left[\frac{\delta\psi}{\psi_{\text{coex}}}\right]^{-(d-1)}. \tag{8}$$

We now focus attention to the vicinity of the critical point of the model defined by Eq. (2). For large but finite r this model has a mean-field-like critical region as long as for $d<4$ the condition is satisfied:

$$r^d(1-T/T_c)^{2-d/2}\gg 1\ , \tag{9}$$

as one can see most simply from the Ginzburg criterion (cf., e.g., Refs. 17–19 and Sec. V below). In this mean-field critical region the quantities f_{int}, χ_{coex}, ξ_{coex}, ψ_{coex} have the following behavior (see, e.g., Ref. 18):

$$\xi_{\text{coex}}\propto r(1-T/T_c)^{-1/2}\ ,\quad \chi_{\text{coex}}\propto(1-T/T_c)^{-1}\ ,\quad \psi_{\text{coex}}\propto(1-T/T_c)^{1/2}\ , \tag{10a}$$

and

$$f_{\text{int}} \propto f_{\text{bulk}} \xi_{\text{coex}} \propto T_c r (1-T/T_c)^{3/2} , \tag{10b}$$

where the proportionality sign stands for proportionality constants of order unity. Hence combining Eqs. (8) and (10) one finds

$$\frac{\Delta F^*}{T_c} \propto r^d \left[1 - \frac{T}{T_c} \right]^{2-d/2} \left[\frac{\delta\psi}{\psi_{\text{coex}}} \right]^{-(d-1)} . \tag{11}$$

The prefactor $r^d(1-T/T_c)^{2-d/2}$ has exactly the form that appears in the Ginzburg criterion, Eq. (9). Hence it is automatically ensured that in the mean-field critical region the nucleation barriers are always large, even if one moves away from the coexistence curve by making the small parameter $\delta\psi/\psi_{\text{coex}}$ larger. Although then the $\delta\psi$ dependence of Eq. (11) is no longer correct, the scale for the function $\Delta F^*/T_c$ is given by the factor $r^d(1-T/T_c)^{2-d/2}$ right up to the spinodal. Equation (11) is also consistent with the field-theoretic formulation of nucleation theory due to Günther *et al.*,[4] which in addition yields the leading (-logarithmic) correction to Eq. (11).

Equation (6), in fact, is more general than Eq. (2) and can also be applied in the non-mean-field region. This statement can be understood from the fact that for droplets which are very much larger than the correlation length ξ_{coex} a quasimacroscopic description in terms of bulk terms and surface corrections always must hold. It is also understandable from the point of view of a continuum theory, if one renormalizes the functional in Eq. (2) (see also Kaski *et al.*[20]) such that $f[\phi(\vec{x})]$ then yields the correct interfacial profile (cf. Refs. 21 and 22 for a discussion of this problem by renormalization-group expansions in $4-d$). On the level of Eq. (6), we just have to replace Eq. (10) by the non-mean-field critical behavior of these quantities,

$$\xi_{\text{coex}} = \xi_0 (1-T/T_c)^{-\nu} , \quad \chi_{\text{coex}} = \Gamma (1-T/T_c)^{-\gamma} ,$$
$$\psi_{\text{coex}} = B(1-T/T_c)^{\beta} , \tag{12a}$$

$$f_{\text{int}} = \hat{f} (1-T/T_c)^{(d-1)\nu} . \tag{12b}$$

Combining now Eqs. (8) and (12) one finds, instead of Eq. (11),

$$\frac{\Delta F^*}{T_c} = \left[\frac{S_d}{d} \right]^d \left[\frac{d-1}{V_d} \right]^{d-1} \frac{\hat{f}^d \Gamma^{d-1}}{B^{2(d-1)}} \left[\frac{\delta\psi}{\psi_{\text{coex}}} \right]^{-(d-1)} . \tag{13}$$

In this equation, the powers of $(1-T/T_c)$ cancel out because of the hyperscaling relation $d\nu = \gamma + 2\beta$. In addition, due to two-scale factor universality of Stauffer *et al.*,[23] the critical amplitude combination $\hat{f}^d \Gamma^{d-1}/B^{2(d-1)}$ is a universal constant, depending on dimensionality only[24]; for $d=2$ this constant is known exactly while for $d=3$ it is known approximately from experiments and numerical calculations.[25] In the mean-field critical region for $d<4$, neither hyperscaling nor universality holds, and thus the prefactor of the term $(\delta\psi/\psi_{\text{coex}})^{-(d-1)}$ in Eq. (11) depends both on the temperature distance from criticality, and the interaction range. At the boundary between mean-field and non-mean-field critical regions, given by Eq. (9) with the inequality sign taken as an equality, both Eqs. (11) and (13) give the same order of magnitude for arbitrary (small) $\delta\psi/\psi_{\text{coex}}$ and hence the crossover between the two expressions is ruled by the standard Ginzburg criterion.

III. CLASSICAL NUCLEATION THEORY NEAR THE COEXISTENCE CURVE: THE POLYMER MIXTURE

This problem has already been considered in Ref. 8 for $d=3$ but here it is generalized to arbitrary dimension. Equation (9) now has to be replaced by (see Sec. V below for a derivation and discussion of this result)

$$r_p^d N^{d/2-1} (1-v_{\text{crit}}/v)^{2-d/2} \gg 1 , \tag{14}$$

i.e., for $d>2$ and N large polymer mixtures have a mean-field critical region. Similarly, Eq. (10) is replaced by[8]

$$\xi_{\text{coex}} \propto r_p \sqrt{N} (1-v_{\text{crit}}/v)^{-1/2} ,$$
$$\chi_{\text{coex}} \propto N (1-v_{\text{crit}}/v)^{-1} , \quad \psi_{\text{coex}} \propto (1-v_{\text{crit}}/v)^{1/2} , \tag{15a}$$

and

$$f_{\text{bulk}} \propto T_c \frac{1}{N} \left[1 - \frac{v_{\text{crit}}}{v} \right]^2 ,$$
$$f_{\text{int}} \propto f_{\text{bulk}} \xi_{\text{coex}} \propto T_c r_p \frac{1}{\sqrt{N}} \left[1 - \frac{v_{\text{crit}}}{v} \right]^{3/2} . \tag{15b}$$

Using then Eqs. (8) and (15), one finds instead of Eq. (11)

$$\frac{\Delta F^*}{T_c} \propto r_p^d N^{d/2-1} \left[1 - \frac{v_{\text{crit}}}{v} \right]^{2-d/2} \left[\frac{\delta\psi}{\psi_{\text{coex}}} \right]^{-(d-1)} . \tag{16}$$

Just as for the ordinary mixtures, the crossover between the mean-field expression, Eq. (16), and the expression valid in the non-mean-field regime, which is also Eq. (13) in this case, is again ruled by the Ginzburg criterion. This is a rather trivial extension of the results of Sec. II, of course, since Eqs. (1) and (3) imply for $N_A = N_B = N$

$$N f_{\text{polymer}}(\phi)/T \equiv f(\phi)/T , \tag{17}$$

and hence

$$\frac{\Delta \mathcal{F}_{\text{polymer}}}{T} \equiv \frac{1}{N} \frac{\Delta \mathcal{F}}{T} \quad \text{with } r^2 \equiv r_p^2 N . \tag{18}$$

Thus the two problems can be simply scaled upon one another. Since the free energies in the polymer problem are a factor of N^{-1} smaller than in the corresponding ordinary mixture, one obtains a factor N^{-1} both in the Ginzburg criterion, Eq. (14), and the nucleation barrier.

IV. NUCLEATION THEORY NEAR THE SPINODAL

If $\delta\psi/\psi_{\text{coex}}$ is no longer very small, the function $(\delta\psi/\psi_{\text{coex}})^{-(d-1)}$ in Eqs. (11) and (16) has to be replaced by a more general function $h(\delta\psi/\psi_{\text{coex}})$, which can be found by looking for a marginally stable nonuniform but spherically symmetric solution $\phi(\rho)$ which leads to an extremum of Eqs. (2) or (4), respectively (see Cahn and Hilliard[1] and Klein and Unger[6]). While for general $\delta\psi/\psi_{\text{coex}}$ this requires numerical work, near ψ_{sp} one can show analytically that[6]

$$h\left[\frac{\delta\psi}{\psi_{\text{coex}}}\right] \propto \left[\frac{\psi-\psi_{\text{sp}}}{\psi_{\text{coex}}}\right]^{3-d/2}, \tag{19a}$$

and hence

$$\frac{\Delta F^*}{T_c} \propto r^d\left[1-\frac{T}{T_c}\right]^{2-d/2}\left[\frac{\psi-\psi_{\text{sp}}}{\psi_{\text{coex}}}\right]^{3-d/2} \tag{19b}$$

for the long-range problem, and

$$\frac{\Delta F^*}{T_c} \propto r_p^d N^{d/2-1}\left[1-\frac{T}{T_c}\right]^{2-d/2}\left[\frac{\psi_{\text{sp}}-\psi}{\psi_{\text{coex}}}\right]^{3-d/2} \tag{19c}$$

for the polymer problem. From Eqs. (19) one sees that one can come close to a spinodal line, if the system is nearly mean-field-like, as predicted,[11,12] and found in simulations by Heermann *et al.*[26]

The ultimate limit of metastability is reached when the nucleation barrier is no longer small, $\Delta F^*/T_c$ of order unity. There one then observes a smearing of the transition between nucleation and spinodal decomposition over a finite regime, rather than occurring at a well-defined sharp line. The width $\delta\psi_{\text{sp}}$ of this transition regime is immediately estimated from Eq. (19) as follows, for $d<6$:

$$\delta\psi_{\text{sp}}/\psi_{\text{coex}} \propto [r^d(1-T/T_c)^{2-d/2}]^{-2/(6-d)} \tag{20a}$$

for the case of ordinary mixtures or Ising magnets, and

$$\delta\psi_{\text{sp}}/\psi_{\text{coex}} \propto [r_p^d N^{d/2-1}(1-v_{\text{crit}}/v)^{2-d/2}]^{-2/(6-d)} \tag{20b}$$

for the polymer problem. Using the equation of state near ψ_{sp}, cf. Fig. 1(a),

$$\frac{\mu-\mu_{\text{sp}}}{\mu_{\text{sp}}} \propto \left[\frac{\psi-\psi_{\text{sp}}}{\psi_{\text{coex}}}\right]^2, \tag{21}$$

it is straightforward to express the width of the transition region in terms of $\delta\mu_{\text{sp}}/\mu_{\text{sp}}$ instead of $\delta\psi_{\text{sp}}/\psi_{\text{coex}}$ if desired. Again it is seen that the smearing of the spinodal is small in the mean-field critical regime, but it becomes large, of order unity, when one reaches the crossover region to the non-mean-field critical regime. In this nontrivial critical regime, the regime of "spinodal" nucleation, as studied by Klein and Unger,[6] and the gradual transition from nucleation to spinodal decomposition are no longer clearly distinguished. The situation is sketched in Figs. 3 and 4. In this paper we have focused attention on the two regimes which are easily accessible to analysis, the regime near coexistence (where classical nucleation theory is valid) and the regime of "spinodal nucleation." The regime between classical and spinodal nucleation (in between the two broken curves in Fig. 4) in the mean-field critical region is characterized by very high nucleation barriers and a treatment along the lines of Cahn and Hilliard[1] should be valid. In fact, we expect there is a smooth interpolation between classical and spinodal nucleation in this crossover regime [Fig. 3(a)]. The hard problems are the gradual transition between nucleation and spinodal decomposition, and the interpolation between this regime and classical nucleation in the non-mean-field critical region (Fig. 4, shaded area between the left broken line and the left dash-dotted line). It is this regime for which the speculation has been advanced [e.g., in Ref. 24, see also Ref. 27(a)] that a nonclassical droplet model might be a valid description (along the lines of the droplet model of Fisher[28]). For an initial study of this crossover regime see Ref. 27(b). In any case in this regime the nucleation barrier is described by a universal "scaling function" with nontrivial dependence on $\delta\psi/\psi$,[24,29,30] which remains to be calculated analytically. In the transition regime between nucleation and spinodal decomposition the metastable state is decaying so rapidly that a fully kinetic theory is required and the concept of a nucleation barrier loses its physical significance.

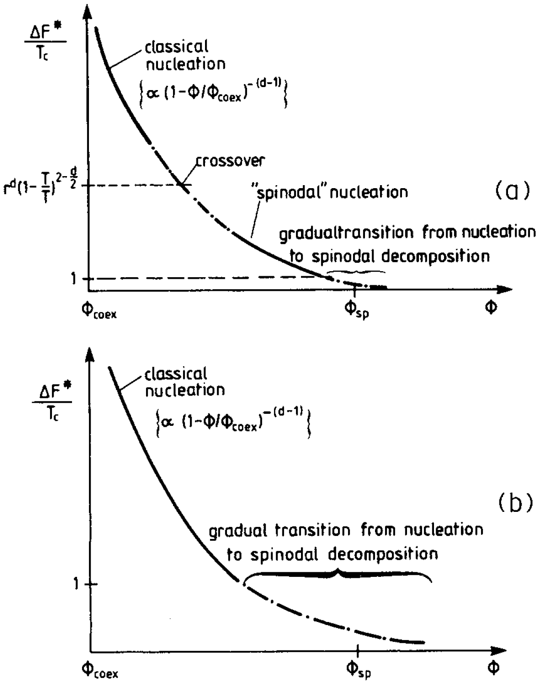

FIG. 3. Schematic plots of the free-energy barriers for the mean-field critical region, i.e., $r^d(1-T/T_c)^{2-d/2} \ll 1$, (a), and the non-mean-field critical region, i.e., $r^d(1-T/T_c)^{2-d/2} \gg 1$, $d<4$, (b). Note that due to large prefactors to the nucleation rate the constant of order unity, where the gradual transition from nucleation to spinodal decomposition occurs, is rather 10^1 than 10^0. The analogous plot for the polymer problem results replacing $r^d(1-T/T_c)^{2-d/2}$ by $r_p^d N^{d/2-1}(1-T/T_c)^{2-d/2}$.

V. GINZBURG CRITERIA

Why is the Ginzburg criterion[17] at all relevant for nucleation near a critical point? This question is answered recalling the derivation of the mean-field approximation for equilibrium properties near T_c from the more general expression for the free energy:

$$F=-T\ln \mathrm{Tr}\exp(-\mathscr{H}_{\mathrm{GLW}}/T)=-T\ln\int \mathscr{D}\phi \exp\left[-\int d^dx\{f[\phi(\vec{x})]+r^2[\vec{\nabla}\phi(\vec{x})]^2\}\right], \tag{22}$$

where the Ginzburg-Landau-Wilson (GLW) Hamiltonian was taken to be Eq. (2), and the trace operation then means the functional integral $\int\mathscr{D}\phi$. While Eq. (22) includes still all long-wavelength fluctuations, and hence the correct non-mean-field critical behavior, the mean-field approximation can be gotten from Eq. (22) assuming that the distribution

$$\exp\left[-\int d^dx\{f[\phi(\vec{x})]+r^2[\vec{\nabla}\phi(\vec{x})]^2\}\right]$$

is very sharply peaked around its maximum, which occurs for the minimum of $f[\phi(\vec{x})]$ with spatially homogeneous $\phi(\vec{x})$, so that we can replace this distribution by a δ function with $\phi=\phi_{\mathrm{min}}$. Below T_c this minimum, which really is a minimum in a high-dimensional configurational space representing the effect of fluctuations [Fig. 5(a)], corresponds to a nonzero order parameter ψ_{coex}. A necessary self-consistency condition is then to require that the mean square amplitude of fluctuations of the coarse-grained order parameters is smaller than the order-parameter square itself,

$$\langle[\delta\psi(\vec{x})]^2\rangle_T \ll \psi^2_{\mathrm{coex}}\ , \quad \text{“Ginzburg criterion .”} \tag{23}$$

Now the field-theoretic description of the nucleation barrier is quite similar to Eq. (22), with two distinctions: (1) We restrict the functional integral to states in the vicinity of the metastable state, and rather than the true partition function [which would be overwhelmingly dominated by the states near the stable minimum of $f(\phi)$] we thus obtain a restricted partition function. (2) We consider in addition a saddle point near the metastable minimum, which is due to a basically nonuniform state, consisting of a uniform metastable background and one “critical droplet.” Just as the stable and metastable minima, the saddle point occurs in a high-dimensional configurational space representing the effect of fluctuations [Fig. 5(b)]. The Cahn-Hilliard theory of nucleation then is again a sort of mean-field approximation, assuming that one single nonuniform spherically symmetric state which extremizes

$$\int d^dx\{f[\phi(\vec{x})]+r^2[\nabla\phi(\vec{x})]^2\}$$

dominates the functional integral. The nonuniform order-parameter profile resulting from this approximation is what has been shown schematically in Fig. 2. It is now clear that again *a necessary self-consistency condition must be to require that the mean-square amplitude of fluctuations of the coarse-grained order parameter along this radial profile must be smaller than the square of the order-parameter difference between $\rho=0$ and $\rho\to\infty$ as described by the profile itself,*

$$\langle[\delta\psi(\vec{x})]^2\rangle_T \ll [\psi(\rho\to\infty)-\psi(\rho=0)]^2\ . \tag{24}$$

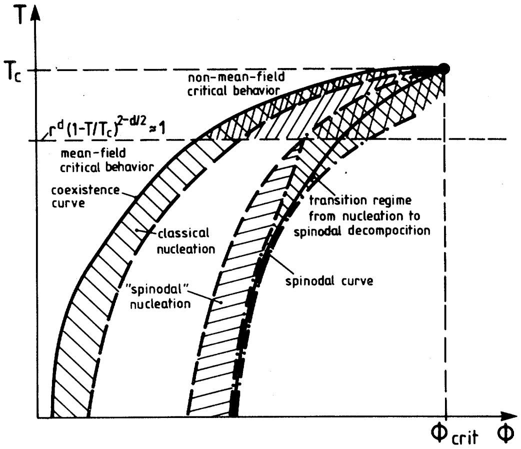

FIG. 4. Various regions in the temperature-composition plane near T_c. The regime inside the two dashed-dotted lines around the spinodal curve is the regime where a gradual transition from nucleation to spinodal composition occurs. The regime between coexistence curve and the left of the two broken lines is described by classical nucleation theory. In this regime, a further (smooth) crossover from mean-field-like critical behavior to non-mean-field behavior occurs. The regime between the right broken curve and the left dashed-dotted curve is the regime of “spinodal nucleation”: It exists only in the regime of mean-field critical behavior.

For classical nucleation near the coexistence curve this criterion is practically the same as the standard Ginzburg criterion, Eq. (23), since there $\psi(\rho\to\infty)-\psi(\rho=0)\approx 2\psi_{\mathrm{coex}}$ [Fig. 2(b)]. But for “spinodal nucleation” near the spinodal curve a different criterion will result, since there the difference $\psi(\rho\to\infty)-\psi(\rho=0)$ is of the same order as $\psi_{\mathrm{ms}}-\psi_{\mathrm{sp}}$ itself.

We evaluate the left-hand side of the inequalities (23) and (24) as usual, starting from the concept of an underlying microscopic lattice model with an order parameter ψ_i, i being the lattice index, which is coarse grained over cells of volume L^d centered at $\vec{x}$, the lattice spacing is set equal to unity,

$$\begin{aligned}\psi(\vec{x}) &\equiv \frac{1}{L^d}\sum_i \psi_i\ ,\\ \langle[\delta\psi(\vec{x})]^2\rangle_T &= \frac{1}{L^{2d}}\sum_{i,j}(\langle\psi_i\psi_j\rangle_T-\langle\psi\rangle_T^2)\\ &\approx \frac{1}{L^d}\int d^d\vec{x}[\langle\psi(0)\psi(\vec{x})\rangle_T-\langle\psi\rangle_T^2]\ ,\end{aligned} \tag{25}$$

where the integration is extended over a sphere of volume L^d. Taking now the Ornstein-Zernike form for the correlation function, as is appropriate for a mean-field theory,

$$\langle\psi(0)\psi(\vec{x})\rangle_T-\langle\psi\rangle_T^2 \propto r^{-2}x^{-(d-2)}\exp(-x/\xi)\ , \tag{26}$$

one finds

$$\begin{aligned}\langle[\delta\psi(\vec{x})]^2\rangle_T &\propto r^{-2}L^{-d}\int_0^L d\rho\,\rho^{d-1}\rho^{-(d-2)}\\ &\propto L^{2-d}r^{-2}=\xi^{(2-d)}r^{-2}\ ,\end{aligned} \tag{27}$$

where in the last step the maximum possible choice of a coarse-graining cell size, namely $L=\xi$, was taken. In us-

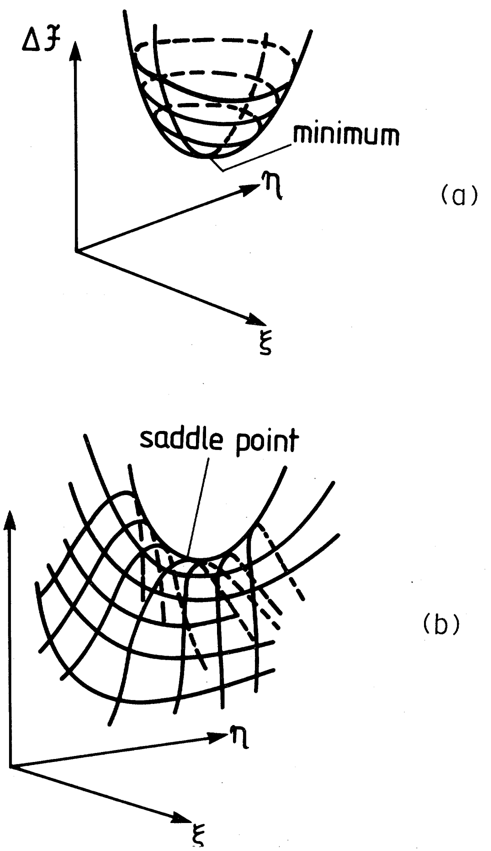

FIG. 5. Free-energy functional $\Delta\mathscr{F}$ schematically displayed as a function of two phase-space coordinates η,ξ. (a) shows a minimum (corresponding to a stable or metastable homogeneous phase), while (b) exhibits a saddle-point configuration, representing a metastable phase plus one droplet.

ing Eqs. (25)—(27) also for nucleation, we have considered essentially the effect of *"bulk fluctuations"* on the interface profile, which are independent of the coordinate ρ along the interfacial profile, of course. In addition to these bulk fluctuations of the local order parameter, there are also typical long-wavelength fluctuations associated with distortions of the local interface position away from its equilibrium position. These capillary waves, which for $d \leq 3$ lead to a complete delocalization of flat interfaces,[31,32] represent fluctuations of the droplet shape around its average (hyper-) spherical shape; although these fluctuations do have a pronounced effect on the droplet free energy [they lead to logarithmic corrections to the classical nucleation barrier, Eq. (11), see Langer[2] and Günther *et al.*[4]] they need not be considered here as their effect can be explicitly taken into account and does not alter our conclusions.

In equilibrium, or for nucleation near coexistence, Eqs. (23), (24), and (27) then yield

$$r^{-2}[r(1-T/T_c)^{-1/2}]^{2-d} \ll 1-T/T_c\ , \tag{28}$$

i.e., Eq. (9). In the case of the polymer problem, Eq. (26) is replaced by

$$\langle \psi(0)\psi(\vec{x})\rangle_T^2 - \langle \psi \rangle \propto r_p^2 x^{-(d-2)} \exp(-x/\xi)\ , \tag{29}$$

which correctly yields

$$\int d^d x [\langle \psi(0)\psi(x)\rangle_T - \langle \psi \rangle_T^2] \propto (\xi/r_p)^2$$
$$= N(1-v_{\text{crit}}/v)^1$$

if one uses

$$\xi \propto r_p \sqrt{N}(1-v_{\text{crit}}/v)^{-1/2}\ ,$$

cf. Eq. (15a). Then the mean-square fluctuation becomes

$$\langle [\delta\psi(\vec{x})]^2 \rangle_T = \xi^{2-d} r_p^{-2}\ , \tag{30}$$

and using Eqs. (15a) and (30) in Eqs. (23) and (24), one finds

$$r_p^{-2}[r_p\sqrt{N}(1-v_{\text{crit}}/v)^{-1/2}]^{2-d} \ll 1-T/T_c\ , \tag{31}$$

i.e., Eq. (14). At this point we comment on the fact that for $d=2$ the polymer problem even for arbitrarily large N is no longer meanfield like, reinterpreting the Ginzburg criterion following de Gennes[33,34]: Each polymer chain is spread out over a volume with linear dimensions of the polymer gyration radius, $R_g \propto r_p\sqrt{N}$. The concentration due to this particular polymer chain in one such volume region of size R_g^d is hence $c = N/R_g^d = r_p^{-d} N^{1-d/2}$. For $d>2$ and large N this concentration is very small, and thus in the same volume there must be monomers of a large number of other chains, once the overall concentration is of order r_p^{-d}, and hence a mean-field approximation is valid. For $d=2$, however, each chain can interact at most with a few other chains, since c is of the same order as the overall concentration, irrespective of N, and hence for $d \leq 2$ the mean-field approximation is then invalid.

Finally we proceed to apply Eq. (24) in the regime of spinodal nucleation, noting from Fig. 2(c) and Eqs. (24) and (27) that

$$r^{-2}\xi^{2-d} \ll (\psi-\psi_{\text{sp}})^2\ . \tag{32}$$

Recalling that ξ for $\psi \neq 0$ in mean-field theory is (cf., e.g., Ref. 13) in a normalization of ψ where the critical amplitude of ψ_{sp} is 1 as in the Ising model,

$$\xi \propto r\left[1-\frac{T_c}{T}(1-\psi^2)\right]^{-1/2}\ ,$$
$$\psi_{\text{sp}} = (1-T/T_c)^{1/2}\ , \tag{33}$$

we can rewrite ξ for ψ near ψ_{sp} as

$$\xi \propto r(1-T/T_c)^{-1/4}(\psi-\psi_{\text{sp}})^{-1/2}$$
$$= r(1-T/T_c)^{-1/2}(\psi/\psi_{\text{sp}}-1)^{-1/2}\ . \tag{34}$$

Then Eq. (32) becomes

$$1 \ll r^d(1-T/T_c)^{2-d/2}\,|\,\psi/\psi_{\text{sp}}-1\,|^{\,3-d/2}\ , \tag{35}$$

which is identical to the condition that the nucleation barrier $\Delta F^*/T$ is much larger than unity [cf. Eq. (19b)]. At this point it is interesting to note that for $d>6$ and $\psi \rightarrow \psi_{\text{sp}}$ the Ginzburg criterion is always satisfied. This self-consistency agrees with the result of Gunton and

Yalabik[16] that the "spinodal fixed point" of their renormalization-group analysis of a mean-field model was stable against finite range perturbations for $d > 6$, but unstable below. This point is discussed in more detail in Ref. 6. Of course, this self-consistency is only a necessary but not sufficient criterion for establishing the existence of a sharp spinodal line.[35]

In the polymer problem one has[8]

$$\xi \propto r_p \sqrt{N} \left[1 - \frac{v}{v_{\text{crit}}} (1-\psi^2) \right]^{-1/2}$$

and thus Eq. (34) is replaced by

$$\xi \propto r_p \sqrt{N} (1 - v_{\text{crit}}/v)^{-1/2} (\psi/\psi_{\text{sp}} - 1)^{-1/2} ,$$

and Eq. (32) is

$$r_p^{-2} \xi^{2-d} \ll (\psi - \psi_{\text{sp}})^2 . \tag{36}$$

Instead of Eq. (35) one finds

$$1 \ll r_p^d N^{d/2-1} (1 - v_{\text{crit}}/v)^{2-d/2} \, | \psi/\psi_{\text{sp}} - 1 |^{3-d/2} , \tag{37}$$

which is identical with the condition that the associated nucleation barrier, $\Delta F^*/T_c$ in Eq. (19c), is very large.

VI. Spinodal decomposition

It is natural to expect that the Ginzburg criteria derived in the previous section carry over to the other side of the spinodal curve, and rule there the validity of the Cahn-Hilliard[36] linear theory of spinodal decomposition. In fact, Eq. (32) still holds as a validity criterion, if we reinterpret ξ as characteristic wavelength $\lambda_m = 2\pi/k_m$ of the phase separation process, k_m being the wave vector where the growth is maximal.[36] Since

$$k_m \propto r^{-1} \left[\frac{1}{T} \left| \frac{\partial^2 f(\phi)}{\partial \phi^2} \right| \right]^{1/2}$$

$$\propto r^{-1} (1 - T/T_c)^{1/2} (\psi/\psi_{\text{sp}} - 1)^{1/2} , \tag{38}$$

a comparison of Eqs. (38) and (34) reveals that ξ, λ_m diverge in a completely analogous fashion as the spinodal curve is approached from either side. Hence, one immediately recovers Eq. (35) [or Eq. (37) for the polymer problem] as a condition, that there exists a regime of times $t < t_{\text{cr}}$, that the linear theory is valid. This means that the fluctuations present in the initial state at T_0 (or v_0, respectively) from which one quenches to the state at T (or v, in the polymer problem) $\langle [\delta\psi(\vec{x})]^2 \rangle_{T_0}$, are amplified by an exponential factor

$$\langle [\delta\psi(\vec{k},t)]^2 \rangle_T = \langle [\delta\psi(\vec{k})]^2 \rangle_{T_0} e^{t/\tau_{\vec{k}}} , \quad t < t_{\text{cr}} \tag{39}$$

where $\tau_{\vec{k}}^{-1}$ is the growth rate of fluctuations described by a wave factor $\vec{k}$. The crossover time t_{cr} at which the nonlinear effects become important is found as[37]

$$r^{-2} \xi^{2-d} e^{t_{\text{cr}}/\tau_{\vec{k}_m}} \approx (\psi - \psi_{\text{sp}})^2 , \tag{40a}$$

i.e.,

$$t_{\text{cr}}/\tau_{\vec{k}_m} \approx \ln[r(\psi - \psi_{\text{sp}})/\xi^{1-d/2}] . \tag{40b}$$

Thus the crossover time t_{cr} increases with the range of interaction only very weakly ($t_{\text{cr}} \propto \ln r$, or $t_{\text{cr}} \propto \ln N$, in the polymer problem[8]), and thus in all practical cases will hardly be much different from $\tau_{\vec{q}_m}$.

We hence conclude that for $t < t_{\text{cr}}$ very weak fluctuations characterized by a wavelength λ_m will grow, but λ_m does not change during this time, i.e., the fluctuations "compactify" [see also Ref. 6(b)], but do not coarsen, while for $t > t_{\text{cr}}$ one enters a basically nonlinear regime where the structure factor is peaked at $k_m(t)$ with $k_m(t \to \infty) \to 0$, i.e., the inhomogeneous structure coarsens. Indeed, a behavior rather similar to this has already been observed by Heermann and Klein,[38] but rather on the nucleation side of the spinodal line of a medium-range Ising model, where "ramified clusters" first "compactify" and only afterwards start to grow. These considerations are consistent with a rather smooth crossover between both decay mechanisms as one passes the spinodal line in these models.

Another justification for the application of Ginzburg criteria to spinodal decomposition is obtained by discussing the effects of nonlinear terms explicitly, which can be done approximately by the theory of Langer, Baron, and Miller[39] (see also Ref. 40). This theory leads to a closed set of nonlinear equations for the moments $\langle m^l \rangle$ of a coarse-grained scaled order parameter m and the scaled structure factor $S(\vec{q},\tau)$, $\vec{q}$ being a scaled wave vector and τ a scaled time.[39,40] For the case of a nonconserved order parameter, these equations are[40] (h being a scaled magnetic field)

$$\frac{\partial \langle m \rangle}{\partial \tau} = \langle m \rangle - \langle m^3 \rangle + h , \tag{41a}$$

$$\frac{\partial \langle m^2 \rangle}{\partial \tau} = 2 \left[\langle m^2 \rangle - \langle m^4 \rangle + h \langle m \rangle + \frac{1}{f_0} \left[1 \frac{d}{q_{\max}^d} \int_0^{q_{\max}} dq \, q^{d+1} S(\vec{q},\tau) \right] \right] , \tag{41b}$$

$$\frac{\partial \langle m^3 \rangle}{\partial \tau} = \ldots , \quad \frac{\partial S(\vec{q},\tau)}{\partial \tau} = -2\{ [q^2 + A(m)] S(\vec{q},\tau) - 1 \} , \tag{41c}$$

and the sum rule relating fluctuations and correlations similar as used in deriving the Ginzburg criterion (written for the equilibrium case)

$$\langle m^2 \rangle - \langle m \rangle^2 = \frac{1}{f_0} \frac{d}{q_{\max}^d} \int_0^{q_{\max}} dq \, q^{d-1} S_{\text{eq}}(q) . \tag{42}$$

The function $A(m)$ in Eq. (41c) is defined as

$$A(m) = \frac{1}{\langle (\Delta m)^2 \rangle} \left\langle \Delta m \frac{\partial \varphi}{\partial m} \right\rangle$$

$$= \frac{\langle m^4 \rangle - \langle m \rangle \langle m^3 \rangle}{\langle m^2 \rangle - \langle m \rangle^2} - 1 , \tag{43}$$

where a (scaled) free-energy density $\varphi(m) = -m^2/2 + m^4/4 - hm$ was assumed. The cutoff wave vector $q_{\max}$

is of order unity (if $q_{\max}=\alpha$ one has performed a coarse graining over a box of lengths ξ/α, and f_0 is the only nontrivial system-dependent parameter remaining in the scaled form of the theory).[39,40] If $f_0 \to \infty$, the higher-order parameters reduce to the lower-order ones [$\langle m^2 \rangle \approx \langle m \rangle^2$, cf. Eq. (42)], and then Eq. (41a) decouples from the rest of the hierarchy to become an equation $\partial\langle m \rangle/\partial\tau = \langle m \rangle - \langle m \rangle^3 + h$ which is exactly soluble.[12] In this limit one just recovers mean-field theory. This fact is also true for the conserved case.

Now the parameter f_0 can be expressed as[39,40]

$$f_0 = \text{const} \times \alpha^{-d}(1-T/T_c)^{-d\nu+(2\beta+\gamma)}\xi_0^d B^2/C \ , \tag{44}$$

where the constant is approximately[39] $3\pi^2$ while in a fully self-consistent theory[40] it can only be obtained numerically and is somewhat α dependent, but is always of order unity as well. Since the coarse-graining size should not exceed ξ, α should be unity (or larger), i.e., the maximum f_0 is obtained for $\alpha=1$ as chosen by Langer *et al.*[39] Using then the exponents for the non-mean-field critical region, due to the hyperscaling relation f_0 is temperature independent, and moreover the critical-amplitude combination $\xi_0^d B^2/C$ is a universal constant.[40] This universality of f_0, which is of order unity in the critical region, corresponds to the universality of the prefactor of the nucleation barrier in this region, Eq. (13). Since f_0 is not so large, nonlinear effects are predicted to be important immediately after the quench,[39] consistent with computer simulations and experiments.[41] Thus, in the non-mean-field regime neither "spinodal nucleation" nor "linear" spinodal decomposition occur. But the situation is again different with the mean-field exponents $\nu=\frac{1}{2}$, $\beta=\frac{1}{2}$, $\gamma=1$ [Eq. (10)], noting $\xi_0 \propto r$ in this regime, and hence

$$f_0 \propto r^d(1-T/T_c)^{d/2-2} \ , \quad r^d(1-T/T_c)^{d/2-2} \gg 1 \ . \tag{45}$$

Just as the factor $r^d(1-T/T_c)^{d/2-2}$ sets the scale for the nucleation free-energy barrier, Eq. (11), which is large in the mean-field critical regime, f_0 also sets the scale for the coarse-grained free-energy density in a correlation volume, as one can see from its definition, relating $f(\psi)$ and $\varphi(m)$ via[39,40]

$$f(\psi) \equiv f_0 \frac{k_B T}{(\xi/\alpha)^d}\varphi(m) \ . \tag{46}$$

It would be very interesting to study the crossover from initially linear spinodal decomposition in the mean-field regime to the fully nonlinear behavior in the non-mean-field critical regime approximately by numerically solving the Langer-Baron-Miller equations for a variety of values for f_0.

VII. CONCLUSIONS

In this paper, the validity of the mean-field theory of nucleation as formulated first by Cahn and Hilliard was investigated for systems with long but finite range of the forces and related problems (such as polymer mixtures). The width of the transition regime between nucleation and spinodal decomposition is estimated and interpreted in terms of a generalized Ginzburg criterion. Various crossovers between different types of nucleation are obtained, at least qualitatively (Figs. 3 and 4). The same arguments are found useful on the other side of the spinodal curve, too, where one can estimate the regime of times and temperatures where initially the linear theory of spinodal decomposition should hold.

Although our results are largely qualitative in character, they allow the interpretation of various observations found for such models in computer experiments. It is hoped that this paper will also stimulate experimental research to study nucleation and spinodal decomposition in systems whose critical behavior is mean-field-like or nearly so. It should also be a convenient starting point for more explicit and powerful analytical theories of the kinetics of first-order phase transitions in cases where f_0^{-1} can be treated as a small parameter.

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