Theory of spinodal decomposition in relaxational tricritical models

M. San Miguel,* J. D. Gunton, Gregory Dee, and Paramdeep S. Sahni
Physics Department, Temple University, Philadelphia, Pennsylvania 19122
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We present a theory for the late-stage spinodal decomposition for two relaxational tricritical models in which the order parameter is nonconserved and the subsidiary order parameter is either conserved or nonconserved. We find that for d-dimensional systems (for $d > 1$) the characteristic domain size grows in proportion to $t^{1/3}$ (Lifshitz-Slyozov) and $t^{1/2}$ (Cahn-Allen-Chan), respectively, where t is the time. A discussion is also given for the growth mechanism of a one-dimensional model. Our analysis in general involves linearizing the dynamical equations of motion around a stationary, but unstable state, which describes coexisting phases.

I. INTRODUCTION

A fundamental area in condensed matter physics is the subject of nonlinear phenomena in systems far from equilibrium. A number of fascinating instabilities[1,2] have been discovered in a variety of physically disparate systems which nevertheless have some qualitatively similar features. One example of such phenomena is the kinetics of first-order phase transitions, which include problems of metastability and instability, involving nucleation and spinodal decomposition processes, respectively. So far most of the theoretical and experimental studies in this area have dealt with systems below their critical points, with the order parameter either being conserved or nonconserved. Recently, however, some studies have been made of instabilities in tricritical systems. These include a linear stability analysis for the early-stage spinodal decomposition in ^{3}He-^{4}He mixtures,[3] a theory for nucleation in certain symmetric tricritical models such as a scalar metamagnet and a ^{3}He-^{4}He mixture,[4] and also a Monte Carlo study of spinodal decomposition in a two-dimensional metamagnet.[5] In addition, experimental studies have been made of spinodal decomposition[6–9] in an Fe-Al alloy, which is thought to have a tricritical point.

In this paper we extend this work by presenting a theory for the late-stage spinodal decomposition in simple relaxational models of a tricritical system involving two dynamical variables, the scalar order parameter ψ and a subsidiary order parameter c. Although our main interest is in the case in which ψ is nonconserved and c is conserved, such as describes a simple Ising-like model of a metamagnet or alloy, we also treat the simpler case in which both ψ and c are nonconserved. Since we do not consider a complex order parameter nor include hydrodynamics in our model, our work does not apply to ^{3}He-^{4}He mixtures. However, we expect that it would serve as a basis on which one could subsequently analyze such effects. Our theory is an extension of existing work on similar problems in critical phenomena. There exists essentially two late-stage theories in critical spinodal decomposition. The first is the Lifshitz-Slyozov prediction[10] that the characteristic domain size for a case in which the order parameter is conserved, such as a binary alloy, increases like $t^{1/3}$, where t is the time. In this case the surface tension also enters as a proportionality constant. The second case is a Cahn-Allen,[6] Chan[11] theory appropriate for a nonconserved order parameter, in which the characteristic growth rate is proportional to $t^{1/2}$ and is independent of surface tension. This result has also been derived in a more detailed perturbation theory by Kawasaki, Yalabik, and Gunton.[12] It should also be noted that earlier theories also predict a $t^{1/2}$ behavior, but these involve the surface tension.[13,14] In this paper we extend these calculations to the tricritical model, presenting two different derivations for the late-stage behavior for both the conserved and nonconserved cases. The first is based on a variational calculation originally due to Langer,[15] in which the key point to a late-stage theory involves linearizing the dynamical equations of motion around a stationary, but unstable, state which describes the coexistence of phases. The second involves a "solitary-wave" approach of Chan[11] (or equivalently of Cahn-Allen[6]). Although these two derivations appear at first sight to be quite different, we point out that in fact they are essentially equivalent descriptions. In both cases a fundamental quantity is the nucleating droplet appropriate for the tricritical model, which one might call a "tricritical soliton." It should also be noted that our theory of the late stage growth involves a calculation of a negative eigenvalue which characterizes the dynamical instability. This eigenvalue also enters as a dynamical prefactor for the nucleation rate of the tricritical model, so that the work presented here completes our earlier discussion[4] of nucleation in the scalar metamagnet.

The structure of our paper is as follows: In Sec. II we define our dynamical model and discuss its sta-

tionary state solutions. We also present a linear stability analysis for this model, in a slightly different form than originally presented by Hohenberg and Nelson[3] for ^{3}He-^{4}He mixtures. In Sec. III we discuss the Langer variational approach and apply it to two different examples of our model. One case is a one-dimensional array of our solitons, which is primarily of pedagogical interest for demonstrating various growth mechanisms. Another more interesting case is a d-dimensional array of isolated droplets. In the latter case we obtain the Lifshitz-Slyozov and Cahn-Allen-Chan results for the conserved and nonconserved tricritical models, respectively. In Sec. IV we present an alternative derivation based on Chan's approach and discuss the relation between the two derivations. Finally, we note that our late-stage theory for the tricritical model gives results quite analogous to the critical models already studied. In the Appendix we present a strict mean-field calculation of the nucleation rate for our model which may be of relevance to systems that can be well described by a mean-field theory and which possess a tricritical point, such as laser with saturable absorbers[16] and irradiated semiconductors.[17] Although this calculation does not involve any discussion of domain growth, it does involve an evaluation of a negative eigenvalue analogous to that calculated in the text.

II. STATIONARY CONFIGURATIONS AND EARLY TIME BEHAVIOR OF THE PHENOMENOLOGICAL MODELS

As a simple prototype of a tricritical system, we consider a Ginzburg-Landau model of a scalar metamagnet whose Hamiltonian[4] is

$$\mathcal{H}[\psi,c]=\int d\vec{x}\left[\frac{K^2}{2}(\nabla\psi)^2+\frac{l_0^2}{2}(\nabla c)^2+f(\psi,c)\right] , \tag{2.1}$$

$$f(\psi,c)=\frac{r}{2}\psi^2+u\psi^4+v\psi^6+\frac{\chi_n^{-1}c^2}{2}+\gamma c\psi^2-\Delta c , \tag{2.2}$$

where ψ is the sublattice magnetization, c the global magnetization, and Δ the applied magnetic field. We will describe the dynamics of this system by the nonlinear Langevin equations

$$\dot{\psi}=-\Gamma_\psi\frac{\delta\mathcal{H}}{\delta\psi}+\xi_\psi , \tag{2.3}$$

$$\dot{c}=-L_c\frac{\delta\mathcal{H}}{\delta c}+\xi_c , \tag{2.4}$$

where ξ_ψ and ξ_c are assumed as usual to be uncorrelated Gaussian white-noise random forces which satisfy the usual fluctuation-dissipation relations. We will consider two models, both having a nonconserved order parameter ψ. In model A, c is a nonconserved variable with

$$L_c=\Gamma_c , \tag{2.5}$$

whereas in model B, c is conserved with

$$L_c=-\Gamma_c\nabla^2 . \tag{2.6}$$

Model B is appropriate for the usual scalar metamagnets but model A is at least of some mathematical interest. It should also be noted that in the same way as theoretical studies of binary alloys have been useful in developing a theory of spinodal decomposition in binary fluids,[18] a theory for spinodal decomposition in the above models could be of some relevance for understanding tricritical systems for which hydrodynamic effects are important, as for example in ^{3}He-^{4}He mixtures. In this case ψ becomes a complex order parameter and c stands for the concentration of ^{3}He.

A. Stationary configurations

Since in the following sections of this paper we will study the late time behavior of models A and B by linearizing around certain stationary-state solutions of Eqs. (2.3) and (2.4), we briefly review the relevant stationary states obtained in Ref. 4. These states are the solutions of

$$\frac{\delta\mathcal{H}}{\delta\psi}=0 , \tag{2.7}$$

$$\frac{\delta\mathcal{H}}{\delta c}=0 . \tag{2.8}$$

The first set of solutions which will be of interest to us for the early stage analysis describe spatially homogeneous states (ψ_0, c_0) and will be considered in Sec. II B. The set of solutions which are relevant for the late time behavior describe an interface between the ordered and disordered phases. As in the case of critical phenomena, we can obtain the planar interface solution for the one-dimensional model. This solution can then be used to describe the d-dimensional situation in the case in which the droplet of one phase is considered sufficiently large that the interface is locally approximately planar, with ψ and c varying in the radial direction. To obtain this solution in the tricritical case,[4] one first develops a perturbation expansion in powers of the inverse correlation length. One then obtains an effective Hamiltonian $\hat{\mathcal{H}}[\psi]$ of the Riedel-Wegner form, with a characteristic triple-well shape below the tricritical point, where

$$\hat{\mathcal{H}}=\int d\vec{x}\left[\frac{K^2}{2}|\nabla\psi|^2+\frac{\tilde{r}}{2}\psi^2+\tilde{u}\psi^4+v\psi^6\right] , \tag{2.9}$$

where

$$\tilde{r}=r+2\Delta\gamma\chi_n , \quad \tilde{u}=u-\gamma^2\chi_n/2 , \tag{2.10}$$

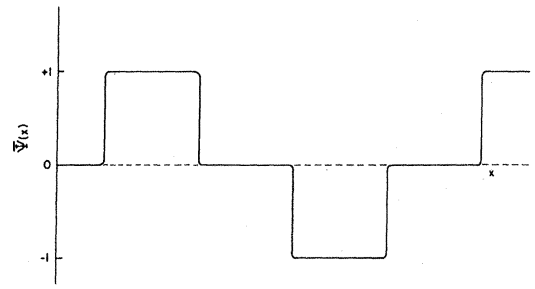

FIG. 1. A chain of tricritical solitons, $\bar{\psi}(x)$, is plotted as a function of position x.

and the condition for phase coexistence corresponds to a particular value of $\Delta=\Delta_0$ such that

$$\tilde{r}=\tilde{u}^2/2v \ . \tag{2.11}$$

In the remaining discussions we choose $\Delta=\Delta_0$. The stationary-state solutions are

$$\bar{\psi}^2(x)=\frac{\psi_s^2}{2}\left[1+\tanh\frac{x}{\xi}\right] ,$$

$$\bar{c}(x)=\chi_n[\Delta_0-\gamma\bar{\psi}^2(x)] \ , \tag{2.12}$$

where $\psi_s^2=-\tilde{u}/2v$ is the equilibrium value of ψ in the ordered region and the correlation length is given by $\xi=(\tilde{u}/2K^2v)^{-1/2}$. The profile given by Eq. (2.12) is the tricritical analog of the well-known hyperbolic tangent profile obtained in the mean-field theory of a critical interface. This latter profile has recently been termed the "van der Waals" soliton.[19] In the same sense one might call the solution given by Eq. (2.12) the tricritical soliton. One should also note that the $\bar{\psi}(x)$ obtained from Eq. (2.12) differs from the van der Waals soliton by having regions in which its values can be $-\psi_s$, zero and ψ_s, shown in Fig. 1. Finally, as we discuss in more detail in the next sections, it should be observed that although the solutions mentioned above are stationary states, they are in general unstable states except for $d=1$. Thus an infinitesimally small perturbation around a particular stationary state would grow, rather than decay, as the time increases. The main point of this paper is to examine the stability of the above states by using a linear stability analysis.

B. Early time behavior

The first case which we will consider is the early time behavior of model B after this system is quenched from a high temperature, disordered state to a state below the tricritical point. We will be concerned with the spinodal region in which the system is unstable, rather than the nucleation region considered in Ref. 4. The analysis presented here is of a Cahn-Hilliard[20] type, but modified as originally suggested by Hohenberg and Nelson[3] for ^{3}He-^{4}He mixtures to account for an initial transient process in which the order parameter rapidly develops. The subsequent analysis then allows us to identify the unstable modes for the scalar metamagnet. For the linear stability analysis we neglect the noise terms and linearize Eqs. (2.3) and (2.4) around the initial homogeneous equilibrium state above T_t, characterized by $\psi=\psi_0=0$ and $c=c_0$. The parameters of $\mathcal{H}$ correspond to the final state to which the system is quenched. Denoting $\delta\psi=\psi-\psi_0$ and $\delta c=c-c_0$, the linearized equations in Fourier space are

$$\frac{d}{dt}\begin{pmatrix}\delta\psi(\vec{k},t)\\ \delta c(\vec{k},t)\end{pmatrix}=-\begin{pmatrix}\Gamma_\psi & 0\\ 0 & L_c\end{pmatrix}\begin{pmatrix}(K^2k^2+f_{11}) & f_{12}\\ f_{12} & (l_0^2k^2+f_{22})\end{pmatrix}\times\begin{pmatrix}\delta\psi(\vec{k},t)\\ \delta c(\vec{k},t)\end{pmatrix}$$

$$\equiv -LM\begin{pmatrix}\delta\psi(\vec{k},t)\\ \delta c(\vec{k},t)\end{pmatrix} \ , \tag{2.13}$$

where here $L_c=\Gamma_c k^2$,

$$f_{11}=\left(\frac{\partial^2 f}{\partial\psi^2}\right)_{\psi_0,c_0}=r+12u\psi_0^2+30v\psi_0^4+2\gamma c_0 \ , \tag{2.14}$$

$$f_{12}=\left(\frac{\partial^2 f}{\partial\psi\partial c}\right)_{\psi_0,c_0}=2\gamma\psi_0 \ , \tag{2.15}$$

$$f_{22}=\left(\frac{\partial^2 f}{\partial c^2}\right)_{\psi_0,c_0}=\chi_n^{-1} \ . \tag{2.16}$$

The instability is in general characterized by a negative eigenvalue of the linear matrix LM, and the domain of instability is bounded by the points for which $\det LM=0$, where the negative eigenvalue becomes zero. In a mean-field approximation we can neglect the two gradient terms in $\mathcal{H}$ and the limit of instability is determined by

$$\Gamma_\psi\Gamma_c k^2(\det f)=0 \ . \tag{2.17}$$

That is,

$$0=2\gamma c_0+r+12u\psi_0^2+30v\psi_0^4-4\chi_n\gamma^2\psi_0^2 \ . \tag{2.18}$$

For the quench from an initial disordered state $\psi_0=0$, the system is unstable for $c_0<c_1$, where

$$c_1=-r/2\gamma \ . \tag{2.19}$$

In this situation Eqs. (2.13) are decoupled and we have a negative eigenvalue associated with an instability in ψ for $c_0<c_1$ and a positive eigenvalue for the c variable which is stable in this time domain. The fluctuation in c for $\psi_0=0$ would relax after a sufficient time to the equilibrium value $c_n=\chi_n\Delta_0$ of a disordered state. Thus this standard linear stability analysis for an initial, disordered state does not yield the expected instability in c which would lead to

phase separation. Rather, it simply shows that the initial behavior of the system after quench is one in which the nonconserved order parameter rapidly evolves, while the conserved, subsidiary order parameter c remains essentially constant. During this process ψ approaches a local equilibrium state specified by the final (quenched) temperature and magnetization c_0. This local equilibrium (constrained) value of ψ, $\psi=\psi_0'$, is obtained by setting $\dot{\psi}=0$ in Eq. (2.3) (and neglecting the noise term) which leads to the following relation:

$$c_0=(2\gamma)^{-1}(-r-4u\psi_0'^2-6v\psi_0'^4) \ . \tag{2.20}$$

Using this argument we then do a second linear stability analysis around (ψ_0',c_0) to obtain the physically significant, unstable modes in ψ and c. This yields Eqs. (2.13)–(2.18) but with ψ_0 replaced by ψ_0'. Equation (2.18) determines the domain of instability for the initial growth of ψ. The new Eq. (2.18) with ψ_0 replaced by ψ_0' determines the spinodal curve which defines the domain for the spinodal decomposition process; i.e.,

$$\tilde{u}\psi_0'^2+3v\psi_0'^4=0 \ . \tag{2.21}$$

The first solution $\psi_0'=0$ gives upon substitution in Eq. (2.20) as a spinodal value of c_0 the one obtained in Eq. (2.19). The second solution

$$\psi_0'^2=-\tilde{u}/3v \tag{2.22}$$

gives the spinodal value $c_0=c_\sigma$,

$$c_\sigma=-\frac{r}{2\gamma}+\frac{\tilde{u}}{3\gamma v}\left[u+\frac{\chi_n\gamma^2}{2}\right] \ . \tag{2.23}$$

These two spinodals are the ones derived in Ref. 3 and also obtained in Ref. 4 by a different argument. To determine the unstable modes (for a band of k) for a quench from a disordered state with $c_\sigma<c_0<c_1$, we calculate the negative eigenvalue of the matrix LM, which is given by

$$\begin{aligned}\omega_0=&[\Gamma_\psi(K^2k^2+f_{11})+\Gamma_c k^2(l_0^2k^2+f_{22})]/2\\&-\{[\Gamma_\psi(\kappa^2k^2+f_{11})-\Gamma_c k^2(l_0^2k^2+f_{22})]^2/4\\&+\Gamma_c\Gamma_\psi k^2 f_{12}^2\} \ .\end{aligned} \tag{2.24}$$

Since $\Gamma_c k^2/\Gamma_\psi \ll 1$ for the interesting long-wavelength fluctuations, we can expand Eq. (2.24) in powers of this parameter to obtain

$$\omega_0\simeq\Gamma_c k^2\bar{\chi}^{-1}+O\left[\left(\frac{\Gamma_c k^2}{\Gamma_\psi}\right)^2\right] \ , \tag{2.25}$$

where

$$\bar{\chi}^{-1}=l_0^2k^2+\chi_n^{-1}(\tilde{u}+3v\psi_0'^2)/(u+3v\psi_0'^2) \tag{2.26}$$

is the inverse of the constrained susceptibility defined in Ref. 3. It is worth noting that to this order ω_0 does not depend on Γ_ψ. The eigenvector $(\delta\psi,\delta c)$ associated with ω_0 identifies the direction of instability in the (ψ,c) space at point (ψ_0',c_0). To leading order in $\Gamma_c k^2/\Gamma_\psi$ this is

$$\frac{\delta\psi}{\delta c}=-\frac{\gamma}{4u\psi_0'+12v\psi_0'^3} \ , \tag{2.27}$$

which means that near the tricritical point where ψ_0' is small, the direction of initial instability is closer to the ψ axis than to the c axis.

So far our analysis of Eq. (2.18) has considered a quench from an initial, disordered state. For a quench from an ordered state, the linearized Eqs. (2.13) are no longer valid, since $\Gamma_\psi\delta\mathcal{F}/\delta\psi|_{\psi_0}$ is no longer zero. However, we can still argue that the existence of different time scales for the evolution of ψ and c implies that ψ will relax rapidly to the constrained value ψ_0'. Therefore although a different initial transient behavior exists, our analysis of the spinodal decomposition process remains essentially unchanged. This completes our discussion of the very early time behavior of model B. We have not considered the corresponding problem for model A, which would be more complicated to analyze due to the absence of a clear cut separation of time scales in ψ and c, which is the basis of the original Hohenberg-Nelson argument used above.

III. VARIATIONAL CALCULATIONS OF THE LATE-STAGE SPINODAL DECOMPOSITION

A. Basic equations

We now turn to the considerations of the late-stage time evolution, or coarsening of our models. In this section we will use a variational method of Langer[15,21] to obtain the characteristic late time domain growth for two simple but nontrivial examples. The first is a d-dimensional metamagnet (with $d>1$) in which we imagine a distribution of isolated tricritical droplets embedded in a background of the opposite phase. In the second example we consider a one-dimensional periodic array of droplets. In the d-dimensional model we find, making reasonable assumptions, that the late-stage coarsening is the same as for the binary alloy, namely, either a $t^{1/2}$ or a $t^{1/3}$ growth rate for models A and B, respectively. We first summarize the basic idea, which again involves linearizing Eqs. (2.3) and (2.4) but now around a quasiequilibrium, unstable steady-state solution $(\tilde{\psi},\tilde{c})$. The dynamical evolution of this configuration gives the asymptotic law of domain growth. Such a configuration for the three-dimensional case describes the interface between two phases and is considered to be a large isolated droplet of the emerging phase in a matrix of the other phase. On these grounds Langer[15] derived the Lifshitz-Slyozov

law for a binary alloy (conserved order parameter). This idea of considering small deviations from a planar equilibrium interface is also the basis of calculations of Cahn and Allen and of Chan for an order-disorder like transition. The $t^{1/2}$ law obtained by these authors is implicitly contained in Langer's original work, as is shown below. In the one dimensional system the unstable steady state $(\tilde{\psi},\tilde{c})$ models a periodic array of interfaces between ordered and disordered phases. The characteristic coarsening in this problem follows a logarithmic behavior in time.

The linearization of Eqs. (2.3) and (2.4) discussed above leads in general to the eigenvalue problem

$$L_{ij}M_{jk}\zeta_k=\omega\zeta_i \ , \tag{3.1}$$

where L is the matrix of kinetic coefficients in Eq. (2.13), M is the matrix defined in Eqs. (2.13)–(2.16) but with f_{ij} evaluated at $(\tilde{\psi},\tilde{c})$, and

$$\zeta_1=\psi-\tilde{\psi} \ , \tag{3.2}$$

$$\zeta_2=c-\tilde{c} \ . \tag{3.3}$$

The characteristic decay time τ for the system to evolve out of a stationary configuration can be shown to be given by[15]

$$\tau^{-1}=\sum_{\omega_n<0}|\omega_n| \ , \tag{3.4}$$

where the ω_n which are to be included in the sum are the negative eigenvalues of the stability problem described by Eq. (3.1). To calculate these negative eigenvalues (which characterize the unstable modes) we use a variational approach. First, we construct a set of states $\vec{\zeta}^{n*}$ conjugate to the set of eigenstates $\vec{\zeta}^{n}$, where $\vec{\zeta}^{n}$ is a column vector with components ζ_1^n and ζ_2^n, which satisfy

$$L\vec{\zeta}^{*}=\vec{\zeta} \ . \tag{3.5}$$

We have as an upper bound on the lowest eigenvalue ω of Eq. (3.1)

$$\omega_0\leq(\vec{\zeta},M\vec{\zeta})/(\vec{\zeta}^{*},\vec{\zeta}) \ , \tag{3.6}$$

where $\vec{\zeta}(\vec{r})$ and $\vec{\zeta}^{*}(\vec{r})$ are a trial function and its conjugate, respectively. Langer has argued on rather general grounds that a matrix such as M which describes the droplet instability should have a negative eigenvalue governing that instability. This negative eigenvalue can itself be shown to be related to the existence of an exact zero eigenvalue corresponding to a translational mode of the isolated droplet. In Ref. 4 we have explicitly calculated this negative eigenvalue λ_0 for this model. To obtain a negative ω_0 from Eq. (3.6) one therefore chooses as a trial function an eigenstate of M whose eigenvalue is negative. This is discussed in more detail in Secs. III B and III C for our model.

Finally, following Langer, one obtains an equation governing the coarsening of macroscopic droplets or zones by the following argument. We consider a periodic array of "spherical" zones in d dimensions, with $d>1$, some of which are growing and some shrinking with a characteristic lifetime τ. If there are N such zones per unit volume, then the rate of change of N is given by

$$N^{-1}\frac{dN}{dt}=-\tau^{-1} \ . \tag{3.7}$$

Since $N\sim R^{-d}$, where R is the characteristic size we have then

$$\frac{dR}{dt}\sim -R\tau^{-1} \ . \tag{3.8}$$

As an example of this approach we consider a system with a single, nonconserved order parameter. In this case from Eq. (3.1) we have $\tau^{-1}=\omega_0$ with $\omega_0=\Gamma\lambda_0$, where Γ is the kinetic coefficient and λ_0 is the single negative eigenvalue of M. Since[22] $\lambda_0\sim R^{-2}$ it then follows from Eq. (3.8) that

$$R\sim t^{1/2} \ , \tag{3.9}$$

where since λ_0 is independent of the surface tension, so is the proportionality constant in Eq. (3.9).

B. Metamagnet in d dimensions

In this case we consider the matrix M in Eq. (3.1) obtained by linearizing around the isolated droplet configuration $(\bar{\psi}(x),\bar{c}(x))$ given by Eq. (2.10). We have a single negative eigenvalue of LM, $\omega_0=\tau^{-1}$. This eigenvalue is, in addition to being the life time of the unstable configuration $(\bar{\psi}(\vec{x}),\bar{c}(\vec{x}))$, the "dynamical" prefactor which occurs in the expression for the nucleation rate.[22,23] Therefore our calculation of ω_0 as presented here completes our earlier analysis of the nucleation rate for the scalar metamagnet. To evaluate ω_0 for this example[24] we will use Eq. (3.6), taking as the trial function $\vec{\zeta}$ the eigenvector $\vec{v}^{0}$ associated with the negative eigenvalue λ_0 of M. The eigenvalue governing the droplet instability was calculated[4] from the effective Hamiltonian for ψ in d dimensions, $\mathcal{H}[\psi]$ given by Eq. (2.9), with the result

$$\lambda_0\sim -K^2(d-1)/R^2 \ . \tag{3.10}$$

To get a better understanding of the coupled equations which correspond to the linear stability analysis, we derive Eq. (3.10) and the associated eigenvector from the eigenvalue problem $M_{ij}v_j=\lambda v_j$ which for the radial part of v_i reads explicitly

$$\left[-K^2\frac{d^2}{dr^2}-K^2\frac{(d-1)}{r}\frac{d}{dr}+\frac{K^2l(l+d-2)}{r^2}+r+12u\bar{\psi}^2+30v\bar{\psi}^4+2\gamma\bar{c}\right]v_1+2\gamma\bar{\psi}v_2=\lambda v_1 \ , \tag{3.11}$$

$$2\gamma\bar{\psi}\nu_1+\left[-l_0^2\frac{d^2}{dr^2}-l_0^2\frac{(d-1)}{r}\frac{d}{dr}+l_0^2\frac{l(l+d-2)}{r^2}+\chi_n^{-1}\right]\nu_2=\lambda\nu_2 \ . \tag{3.12}$$

Comparison of these equations with the explicit form of Eqs. (2.7) and (2.8) for a spherical symmetrical configuration shows that $\lambda_1=0$ is an exact eigenvalue for $l=1$ with eigenfunction

$$\nu_1^1=\frac{d\bar{\psi}}{dr}, \quad \nu_2^1=\frac{d\bar{c}}{dr} \ . \tag{3.13}$$

This eigenvalue corresponds to the translational modes of the droplet and is contained in a band of eigenvalues defined by different values of l, where λ_0 corresponds to $l=0$. To calculate λ_0 we rewrite Eqs. (3.11) and (3.12) as

$$M_{ij}^l\nu_j=\lambda\nu_i \ , \tag{3.14}$$

$$M^l=M^{l-1}+\delta M^l \ , \tag{3.15}$$

where

$$\delta M^l=\begin{pmatrix}\dfrac{K^2(l-1)(l+d-1)}{r^2} & 0\\ 0 & \dfrac{l_0^2(l-1)(l+d-1)}{r^2}\end{pmatrix} . \tag{3.16}$$

The eigenvalues λ_l are obtained from a standard variational calculation as

$$\lambda_l\leq\frac{(\vec{\nu}^1,M^l\vec{\nu}^1)}{(\vec{\nu}^1,\vec{\nu}^1)}=\frac{(\vec{\nu}^1,\delta M^l\vec{\nu}^1)}{(\vec{\nu}^1,\vec{\nu}^1)} \ , \tag{3.17}$$

where we will assume that λ_l is equal to this bound. Since the eigenstates have to be localized around the interface position $r\sim R$, we can replace r^2 by R^2 in δM^l and in the volume integrals in Eq. (3.17). We then obtain a set of λ_l, with $\lambda_1=0$ and $\lambda_0<0$,

$$\lambda_0\simeq-\frac{(d-1)}{R^2}\frac{\int drR^{d-1}\left[K^2\left(\frac{d\bar{\psi}}{dr}\right)^2+l_0^2\left(\frac{d\bar{c}}{dr}\right)^2\right]}{\int drR^{d-1}\left[\left(\frac{d\bar{\psi}}{dr}\right)^2+\left(\frac{d\bar{c}}{dr}\right)^2\right]} \ . \tag{3.18}$$

In the spirit of the approximation scheme of Ref. 4 which leads to Eq. (2.10), we can safely neglect $\int dr\,(d\bar{c}/dr)^2$ with respect to $\int dr\,(d\bar{\psi}/dr)^2$ to obtain Eq. (3.10). The difference between λ_1 and λ_0 comes from the angular part of the Laplacian in Eqs. (3.11) and (3.12), and the radial part $\vec{\nu}^0$ of the eigenvalue associated with λ_0 is still given by Eq. (3.13).

We are now in position to deal with the dynamical problem. From the above discussion and Eqs. (3.5) and (3.6) we have

$$\omega_0\lesssim\frac{(\vec{\nu}^0,M^{l=0}\vec{\nu}^0)}{(\vec{\nu}^{0*},\nu^0)}=\frac{\lambda_0(\vec{\nu}^0,\vec{\nu}^0)}{(\vec{\nu}^{0*},\vec{\nu}^0)} \ . \tag{3.19}$$

1. Model A (nonconserved c)

From Eqs. (3.5) and (3.13) we have

$$\nu_1^{0*}(r)=\Gamma_{\psi}^{-1}\frac{d\bar{\psi}}{dr} \ ,$$

$$\nu_2^{0*}(r)=\Gamma_0^{-1}\frac{d\bar{c}}{dr} \ , \tag{3.20}$$

and from Eqs. (3.13), (3.18), (3.19), and (3.20)

$$\omega_0\simeq-\frac{d-1}{R^2}\frac{\int dr\left[K^2\left(\frac{d\bar{\psi}}{dr}\right)^2+l_0^2\left(\frac{d\bar{c}}{dr}\right)^2\right]}{\int dr\left[\Gamma_{\psi}^{-1}\left(\frac{d\bar{\psi}}{dr}\right)^2+\Gamma_c^{-1}\left(\frac{d\bar{c}}{dr}\right)^2\right]} \ . \tag{3.21}$$

For kinetic coefficients Γ_{ψ} and Γ_c of the same order of magnitude we can do the same approximation that leads from Eq. (3.18) to Eq. (3.10) and we obtain

$$\omega_0\simeq-K^2\Gamma_{\psi}(d-1)/R^2 \ . \tag{3.22}$$

This is the result for a model describing the relaxation of a nonconserved order parameter ψ already discussed in Sec. III A. To this order the coupling with c plays no important role. The same result [Eq. (3.22)] is of course obtained directly by using Eq. (3.10) instead of Eq. (3.18).

2. Model B (conserved c)

In this case

$$\nu_1^{0*}(r)=\Gamma_{\psi}^{-1}\frac{d\bar{\psi}}{dr} \ , \tag{3.23}$$

$$L_0\nu_2^{0*}(\vec{x})=-\Gamma_0\nabla^2\nu_2^{0*}(\vec{x})=\frac{1}{\sqrt{4\pi}}\frac{d\bar{c}}{dr} \ . \tag{3.24}$$

A solution of Eq. (3.24) in d dimensions can be easily worked out in an analogous way to the calculation in Ref. 15. We then have[25]

$$(\nu_2^{0*},\nu_2^0)\sim\Gamma_c^{-1}R^d\left[\int dr\frac{d\bar{c}}{dr}\right]^2=\Gamma_c^{-1}R^d(\Delta c)^2 \ , \tag{3.25}$$

where (Δc) is the difference of c values at both sides of the interface. We then have

$$\omega_0\simeq-\frac{d-1}{R^2}\frac{R^{d-1}\int dr\left[K^2\left(\frac{d\bar{\psi}}{dr}\right)^2+l_0^2\left(\frac{d\bar{c}}{dr}\right)^2\right]}{R^{d-1}\Gamma_{\psi}^{-1}\int dr\left(\frac{d\bar{\psi}}{dr}\right)^2+R^d\Gamma_c^{-1}(\Delta c)^2} \ . \tag{3.26}$$

Neglecting once again the $\int dr\,(d\bar{c}/dr)^2$ term and recalling that the interfacial tension σ to leading order[4]

$$\sigma \simeq K^2 \int dr \left[\frac{d\bar{\psi}}{dr}\right]^2 \tag{3.27}$$

we obtain

$$\omega_0 \simeq \frac{-(d-1)\sigma}{\Gamma_\psi^{-1}K^{-2}\sigma R^2 + \Gamma_c^{-1}R^3(\Delta c)^2} \ . \tag{3.28}$$

This is again the result one obtains using directly Eq. (3.10) instead of Eq. (3.18) in the above calculation. For normal values of Γ_ψ and Γ_c and in the limit in which we are working of large R we can neglect the first term in the denominator and, from Eq. (3.8) with $\omega_0 = \tau^{-1}$, we obtain the Lifshitz-Slyozov[10] law for a conserved one variable problem. This can be physically understood by considering that in the late stages the slow variable c takes over and the fast variable ψ is "slaved" as discussed in the stability analysis of Sec. II. It is interesting to see that this slaving is possible due to the coupling introduced by the coefficient γ. In the limit $\gamma = 0$ we have decoupled equations and the equation for c has no instability. This means that in this limit we should reobtain Cahn-Allen-Chan law for the nonconserved order parameter ψ. Indeed, if $\gamma = 0$ we have[4] $\Delta c = \gamma \chi_n \psi_s^2 = 0$ and we recover Eq. (3.21) from Eq. (3.27). In the above calculation it is also clear how σ cancels out for a nonconserved variable in agreement with the Cahn-Allen-Chan results.

C. Coarsening in a one-dimensional metamagnet

We wish to consider a one-dimensional version of model B as discussed already in Sec. III B. We will follow the procedures as set out in Sec. II A. To this end we first turn our attention to the numerator of expression (3.6). In Eq. (3.6), M is a matrix operator defined by Eqs. (2.13)–(2.16), and it is evaluated at the stationary-state values $\bar{\psi}$ and $\bar{c}$ given by Eq. (2.12). As we have already shown in Sec. III B the negative eigenvalue of M as calculated from the effective Hamiltonian $\hat{\mathcal{H}}[\psi]$ [Eq. (2.9)], and from the full Hamiltonian $\mathcal{H}[\psi,c]$ [Eq. (2.1)], are equal, to a good approximation. Therefore we will use a form of M derived from the effective Hamiltonian (2.9). This effective M can be constructed from the full coupled equations as follows. We first use the relation (2.12) to eliminate $\bar{c}$ in terms of $\bar{\psi}$. We then use the one-dimensional version of Eq. (3.12) to construct a relationship between the two eigenfunctions. We do this by neglecting the derivative term $(l_0^2\nabla_r^2)$ and using the value of $\lambda = 0$ associated with the eigenfunction which describes the translational symmetry. We then have an eigenvalue equation of the form

$$(-K^2\nabla_r^2 + \tilde{r} + 12\tilde{u}\bar{\psi}^2 + 30v\bar{\psi}^4)\nu_1 = \lambda_0\nu_1 \ . \tag{3.29}$$

We now rescale these equations using the following relations:

$$z = r/\xi \ , \quad m = \psi/\psi_s \ , \quad n = c/\gamma\chi_n\psi_s^2 \ , \tag{3.30}$$

where ψ_s is the equilibrium value of ψ. Using these rescaled quantities as well as Eq. (2.11) and the relations $\psi_s^2 = -\tilde{u}/2v$ and $\xi = (\tilde{u}^2/2v)^{-1/2}$ we get

$$\xi^{-2}[-\nabla_z^2 + 1 - 12m^2(z) + 15m^4(z)]\chi_1 = \lambda_0\chi_1 \ ,$$

where we have set the coefficient of the gradient and the lattice spacing equal to unity. χ_1 denotes the rescaled eigenfunction. Therefore the eigenvalue equation reduces to the following form:

$$[-\nabla_z^2 + 1 - 12m^2(z) + 15m^4(z)]\chi_1 = \epsilon\chi_1 \ , \tag{3.31}$$

where

$$\epsilon = \lambda_0\xi^2 \ . \tag{3.32}$$

We will call the operator in square brackets in Eq. (3.31) $\mathfrak{F}$. $\mathfrak{F}$ is of the form $-\nabla_z^2 + W(z)$ where $W(z)$ is a "potential." For a single interface we have that

$$m(z) = \frac{1}{\sqrt{2}}(1+\tanh z)^{1/2} \ . \tag{3.33}$$

We know that dm/dz is an eigenstate of $\mathfrak{F}$ with eigenvalue zero.

We now introduce a periodic array of N interfaces with a distance ρ between each interface. The operator which describes this array of interfaces will be of the form

$$\mathfrak{F} = -\nabla_z^2 + \tfrac{10}{4} + \tfrac{3}{2}\sum_j e^{i\pi j}\tanh(z-\rho j) - \tfrac{15}{4}\sum_j \operatorname{sech}^2(z-\rho j) \ . \tag{3.34}$$

This new "potential" is shown in Fig. 2. We now construct a set of mutually orthogonal trial functions χ_{iq} of the form

$$\chi_{iq} = \frac{1}{z\sqrt{2}}\frac{1}{\sqrt{N}}\sum_{j=0}^{N-1} e^{iq\rho j}\frac{\operatorname{sech}^2(z-\rho j)}{[1+\tanh(z-\rho j)]^{1/2}} \ . \tag{3.35}$$

If we insist on periodic-boundary conditions we have that

$$q = \frac{2\pi n}{N\rho}, \quad N\rho\xi = L \ , \tag{3.36}$$

where L is the physical length of the system and n is an integer. We should also note that q ranges in values from $-\pi/\rho$ to π/ρ. We then compute $(\chi_{1q}, \mathfrak{F}\chi_{1q})$ to first order in overlap integrals and get

$$(\chi_{1q}, \mathfrak{F}\chi_{1q}) \simeq -Ae^{-\rho}\cos q\rho \ , \tag{3.37}$$

where $A = 1.06$.

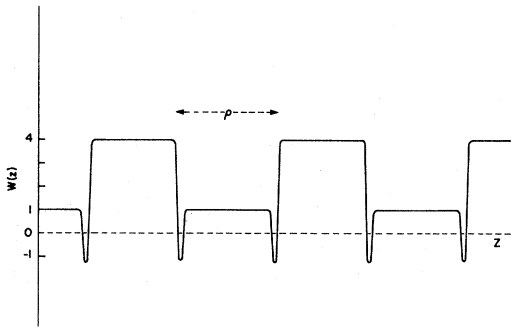

FIG. 2. $W(z)$ is the potential associated with N interfaces, where each interface is separated by a distance ρ. The variable z is the scaled unit of length; i.e., $z = x/\xi$.

We now turn our attention to the denominator of Eq. (3.6). There are, for this model, two terms to be considered. In the scaled notation these two terms are of the form $(\chi_{1q}^*, \chi_{1q}) + (\chi_{2q}^*, \chi_{2q})$, where χ_{1q}^* and χ_{2q}^* are related to χ_{1q} and χ_{2q} by the relation (3.5), namely,

$$\begin{pmatrix} \Gamma_\psi & 0 \\ 0 & -\xi^{-2}\Gamma_c \nabla_z^2 \end{pmatrix} \begin{pmatrix} \chi_{1q}^* \\ \chi_{2q}^* \end{pmatrix} = \begin{pmatrix} \chi_{1q} \\ \chi_{2q} \end{pmatrix} . \tag{3.38}$$

In the scaled form

$$\chi_{1q}^*(z) = \Gamma_\psi^{-1} \chi_{1q} \tag{3.39}$$

and

$$\nabla_z \chi_{2q}^*(z) = -\Gamma_c^{-1} \xi^2 \int \chi_{2q} dz . \tag{3.40}$$

We now use expression (3.40) to compute $\nabla_z \chi_{2q}^*$,

$$\nabla_z - \chi_{2q}^* = \frac{\xi^2}{\Gamma_c 2\sqrt{N}} \sum_{j=0}^{N-1} e^{iq\rho j}[1 + \tanh(z - \rho_j)] + C . \tag{3.41}$$

C can be determined from the periodicity condition, namely,

$$\int_{-\rho/2}^{N\rho - \rho/2} \chi_{2q} dz = 0 ,$$

where we have shifted the limits of integration. This gives $C = -B/\sqrt{N}\,(1 - e^{iq\rho})$ where $B = \xi^2/\Gamma_c$. Now

$$(\chi_{2q}^*, \chi_{2q}) = -\frac{\Gamma_c}{\xi^2} \int \chi_{2q}^* \nabla_z^2 \chi_{2q}^* dz = \frac{\Gamma_c}{\xi^2} \int |\nabla_z \chi_{2q}^*|^2 dz . \tag{3.42}$$

Then using Eq. (3.41) we find

$$(\chi_{2q}^*, \chi_{2q}) \simeq \frac{B\rho}{2(1 - \cos q\rho)} . \tag{3.43}$$

Also using Eqs. (3.35) and (3.39) we find that

$$(\chi_{1q}^*, \chi_{1q}) \simeq \frac{1}{4\Gamma_\psi} . \tag{3.44}$$

Therefore the denominator of expression (3.6) has the form

$$(\chi_{1q}^*, \chi_{1q}) + (\chi_{2q}^*, \chi_{2q}) = \frac{1}{4\Gamma_\psi} + \frac{\xi^2}{\Gamma_c} \frac{\rho}{2(1 - \cos q\rho)} . \tag{3.45}$$

Therefore combining Eq. (3.45) with Eq. (3.37) we have

$$\xi^2 \omega_{0q} \simeq -\frac{Ae^{-\rho} \cos q\rho}{\left(\frac{1}{4\Gamma_\psi} + \frac{\xi^2}{\Gamma_c} \frac{\rho}{2(1 - \cos q\rho)} \right)} . \tag{3.46}$$

If we neglect the first term in the denominator in the tricritical region, we have, using Eq. (3.32),

$$\omega_{0q} \simeq -\frac{2A\Gamma_c}{\xi^4 \rho} e^{-\rho} \cos q\rho (1 - \cos q\rho) . \tag{3.47}$$

This implies that the most unstable modes are those near values of q such that $q = \pm \pi/4\rho$. We will discuss the implications of such a result later. Proceeding on, we have from Eq. (3.4) that

$$\frac{1}{\tau} = \frac{DN}{\xi^4} \frac{e^{-\rho}}{\rho} , \tag{3.48}$$

where $D = 0.14\Gamma_c$. Therefore, following Langer, we interpret τ^{-1} as a rate at which the domains are dissolving or coalescing in a system of N interfaces; i.e.,

$$\frac{dN}{dt} \simeq -\tau^{-1} . \tag{3.49}$$

Using Eq. (3.36)

$$\frac{dl}{dt} = \frac{l^2}{L\tau} , \tag{3.50}$$

where l is defined as some average dimension of the coarsening domains. Then from Eqs. (3.49) and (3.50) we have that

$$\frac{dl}{dt} = \frac{C}{\xi^3} e^{-l/\xi} , \tag{3.51}$$

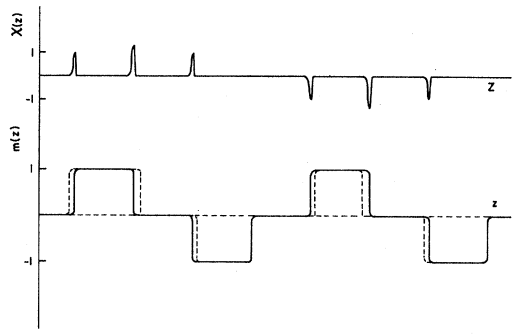

FIG. 3. We display $\chi(z)$ which is the eigenfunction (3.35) with $q = \pm \pi/4\lambda$. Also shown is the coarsening produced by this instability for a set of domains represented by the potential $W(z)$ shown in Fig. 2.

where $C = D$. Therefore we find that

$$l(t) = l_0 + \xi \ln\left[1 + c\frac{t}{\xi^4} e^{-l_0/\xi}\right] , \tag{3.52}$$

where l_0 is the initial "domain size." This is of the same form as originally obtained by Langer for a one-dimensional model of a conserved binary alloy.

Finally, it is of interest to consider the coarsening pattern one obtains by considering the unstable mode at $q = \pm \pi/4\rho$. The eigenfunction associated with this instability is shown in Fig. 3, together with the coarsening it would produce in a system.

IV. SHAPE-INVARIANT SOLUTION FOR LATE-STAGE GROWTH

In this section we reexamine the late-stage evolution of an isolated droplet (or set of droplets) discussed in Sec. III, as formulated in terms of a solution that preserves the profile of the interface during propagation. This approach was applied recently to obtain the late-stage growth of a system described by a time-dependent Ginzburg-Landau equation for a nonconserved order parameter.[11] As we will see, we obtain the same results for the late-stage growth of our tricritical models as obtained via the variational method.

The basic idea in this approach is to find a solitary wave solution which describes an invariant interface profile. This invariance is strictly true for the one-dimensional model and can be considered as asymptotically correct for the d-dimensional model. Following Chan we neglect any orientational dependence of ψ and c. We then write our nonlinear Langevin equations in matrix form, which in this approximation involves the radial part of the functions $\psi(\vec{x},t)$, $c(\vec{x},t)$, with $l = 0$:

$$-L^{-1}\frac{d}{dt}\begin{pmatrix}\psi(r,t)\\ c(r,t)\end{pmatrix} = \begin{pmatrix} -K^2\left(\frac{\partial^2}{\partial r^2} + \frac{(d-1)}{r}\frac{\partial}{\partial r}\right) + (r + 4u\psi^2 + 6v\psi^4) & 2\gamma\psi \\ \gamma\psi & -l_0^2\left(\frac{\partial^2}{\partial r^2} + \frac{(d-1)}{r}\frac{\partial}{\partial r}\right) + \chi_n^{-1} - \frac{\Delta}{c} \end{pmatrix}\begin{pmatrix}\psi(r,t)\\ c(r,t)\end{pmatrix} \tag{4.1}$$

$$= \begin{pmatrix} -K^2\frac{\partial^2}{\partial r^2} + r + 4u\psi^2 + 6v\psi^4 & 2\gamma\psi \\ \gamma\psi & -l_0^2\frac{\partial^2}{\partial r^2} + \chi_n^{-1} - \frac{\Delta}{c} \end{pmatrix}\begin{pmatrix}\psi(r,t)\\ c(r,t)\end{pmatrix} - \begin{pmatrix} K^2\frac{(d-1)}{r}\frac{\partial}{\partial r} & 0 \\ 0 & \frac{l_0^2(d-1)}{r}\frac{\partial}{\partial r} \end{pmatrix}\begin{pmatrix}\psi(r,t)\\ c(r,t)\end{pmatrix} . \tag{4.2}$$

Our stationary-state solution $(\bar{\psi},\bar{c})$ which describes a planar interface then satisfies the equation

$$0 = \begin{pmatrix} \left(-K^2\frac{\partial^2}{\partial r^2} + r + 4u\bar{\psi}^2 + 6v\bar{\psi}^4\right) & 2\gamma\bar{\psi} \\ \gamma\bar{\psi} & \left(l_0^2\frac{\partial^2}{\partial r^2} + \chi_n^{-1} - \frac{\Delta}{\bar{c}}\right) \end{pmatrix}\begin{pmatrix}\bar{\psi}\\ \bar{c}\end{pmatrix} , \tag{4.3}$$

which is the $d = 1$ form of Eqs. (2.7) and (2.8), whose approximate solution is Eq. (2.12). We now look for a particular solution of Eq. (4.2) of the form

$$\psi = \bar{\psi}(R(t) - r) , \tag{4.4}$$

$$c = \bar{c}(R(t) - r) , \tag{4.5}$$

where $R(t)$ denotes the time-dependent position of the center of the interface profile. The physical situation which we imagine here is the late-stage growth of an isolated droplet of one of our phases immersed in the background of the other phase. The instability discussed in Sec. III corresponds to the growth of the droplet and, as we will see, the negative eigenvalue obtained in that section is given here by $\dot{R}(t)/R(t)$. The point is that this instability develops in a way that is an approximate shape invariant solution of the equations. To obtain this solution we follow Chan and approximate the term $(d-1)/r$ which occurs in the Laplacian in Eqs. (4.1) and (4.2) by $(d-1)/R(t)$. Thus upon substitution of Eqs. (4.4) and (4.5) into Eq. (4.2) we obtain upon using Eq. (4.3)

$$-\frac{\dot{R}}{R}L^{-1}\begin{pmatrix}\frac{d\bar{\psi}}{dr}\\ \frac{d\bar{c}}{dr}\end{pmatrix} = [\delta M^{l=0}(r=R)]\begin{pmatrix}\frac{d\bar{\psi}}{dr}\\ \frac{d\bar{c}}{dr}\end{pmatrix} , \tag{4.6}$$

where $\delta M^{l=0}$ is defined in Eq. (3.16). Using our previous result

$$\nu_1^0 = \frac{d\bar{\psi}}{dr} , \quad \nu_2^0 = \frac{d\bar{c}}{dr} , \tag{4.7}$$

and the definition of $\vec{\nu}^*$ given in Eq. (3.5) we obtain

$$-\frac{\dot{R}}{R}\nu_i^{0*} = [\delta M^{l=0}(r=R)]_{ij}\nu_j^0 . \tag{4.8}$$

Taking the scalar product of Eq. (4.8) with ν_i yields

$$-\frac{\dot{R}}{R}=\frac{(\vec{v}^{0},\delta M^{l=0}\vec{v}^{0})}{(\vec{v}^{0*},\vec{v}^{0})} \quad . \tag{4.9}$$

The right-hand side of this equation is identified by Eq. (3.19) as the ω_0 calculated in Sec. III B. With this identification we recover from Eq. (4.9) the relation (3.8). Therefore the results of Sec. III on the asymptotic t dependence of R also follow from Eq. (4.9).

It is finally worth mentioning that the results of this section and also most of the ones in Sec. III are independent of the explicit form of the configuration $(\bar{\psi},\bar{c})$ given in Eq. (2.12).

We conclude by commenting on the relationship between the variational approach of Sec. III and the asymptotic solitary wave approach of this section. In the former case one first notes the existence of an exact translational symmetry to obtain an eigenvector with eigenvalue zero corresponding to "angular momentum" $l=1$. One then argues that this implies the existence of a negative eigenvalue λ_0 corresponding to $l=0$. The lifetime ω_0 is then calculated by a variational method using the $l=1$ eigenvector as a trial function (the radial part of the $l=0$ and $l=1$ eigenvectors are the same). In the solitary wave approach one starts with the $l=0$ equation and looks for a shape invariant solution which is the analog of the $l=1$ translational eigenvector. One then obtains an equation for $\dot{R}(t)/R(t)$ which is the same as Eq. (3.8) with $\tau^{-1}=\omega_0$. One can interpret both results for $\dot{R}(t)/R(t)$ as a generalization of the dynamical equation which governs the growth of a single critical droplet in the nucleation problem. In the coarsening problem, however, one has a distribution of droplets of varying sizes, with $\omega_0=\omega_0(R)$.

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APPENDIX

In this appendix we calculate the nucleation rate for a strict mean-field version of our model A in which ψ and c have constant values throughout the system. In this situation

$$\mathcal{H}[\psi,c]=Vf(\psi,c) \quad , \tag{A1}$$

where V is the volume of the system and Δ is now an arbitrary parameter. The probability density $P(\psi,c)$ obeys the Fokker Planck equation

$$\frac{\partial P(\psi,c)}{\partial t}=-\Gamma_{\psi}\frac{\partial}{\partial\psi}\left[V\frac{\partial f}{\partial\psi}-\frac{\partial}{\partial\psi}\right]P(\psi,c)$$
$$-\Gamma_{c}\frac{\partial}{\partial c}\left[V\frac{\partial f}{\partial c}-\frac{\partial}{\partial c}\right]P(\psi,c) \quad . \tag{A2}$$

The work of Kramers[26] as extended to include several variables yields for the nucleation rate[22,27,28]

$$I=\frac{|\kappa|}{2\pi}\left[\frac{\det M_0}{\det M}\right]^{1/2}e^{-\Delta\mathcal{H}} \quad , \tag{A3}$$

where $\Delta\mathcal{H}$ is the energy barrier

$$\Delta\mathcal{H}=V[f(\bar{\psi},\bar{c})-f(\psi_0,c_0)] \quad , \tag{A4}$$

(ψ_0,c_0) is the metastable minimum of f, and $(\bar{\psi},\bar{c})$ is the saddle point between (ψ_0,c_0) and the stable minimum. The matrix M is the matrix of second derivatives of f with respect to ψ and c, evaluated at $(\bar{\psi},\bar{c})$ and M_0 is the same matrix evaluated at the metastable point (ψ_0,c_0). The dynamical prefactor κ contains all of the kinetic information and is defined as ω_0 in Sec. III, the negative eigenvalue of LM, where L is again the matrix of the kinetic coefficients. For the case in which the variables are space dependent the energy barrier and the "statistical prefactor" $(\det M_0/\det M)^{1/2}$ have been evaluated in Ref. 4, while the dynamical prefactor κ has been evaluated in the main text of this paper. In the spirit of the approximations made in those calculations we shall evaluate $(\Delta\mathcal{H})$ to first order in $(\delta\Delta)=\Delta-\Delta_0$ where Δ_0 is given by Eq. (2.11); the prefactors in Eq. (A3) will be evaluated for $\Delta=\Delta_0$. The structure of the extrema of $f(\psi,c)$ was reviewed in Ref. 4. Local minima are located at the values

$$\psi_n=0 \quad , \tag{A5}$$

$$\psi_{+}^{2}=\frac{-4\tilde{u}+(16\tilde{u}^{2}-24v\tilde{r})^{1/2}}{12v} \quad , \tag{A6}$$

and local maxima at

$$\psi_{-}^{2}=\frac{-4\tilde{u}-(16\tilde{u}^{2}-24v\tilde{r})^{1/2}}{12v} \quad , \tag{A7}$$

where $\tilde{u}$ and $\tilde{r}$ have been defined in Eq. (2.10). The value of c at the extrema is related to ψ by

$$c=\chi_n(\Delta-\gamma\psi^{2}) \quad . \tag{A8}$$

For definitiveness we consider the case in which the metastable state is $\psi_0=\psi_n, c_0=\chi_n\Delta$. This corresponds to $\Delta>\Delta_0$ and ψ_{+}^{2} and the corresponding value of c are the absolute minima or stable states. Recalling that for $\Delta=\Delta_0$,

$$\tilde{r}=\tilde{r}_0\equiv\tilde{u}^{2}/2v \quad , \tag{A9}$$

we obtain to first order in $(\delta\Delta)$

$$\psi_{-}^{2}\simeq-\frac{\tilde{u}}{6v}-\frac{\gamma\chi_n\delta\Delta}{\tilde{u}} \tag{A10}$$

and so

$$\Delta\mathcal{H} = \mathcal{H}[\bar{\psi} = \psi_-, \bar{c} = \chi_n(\Delta - \gamma\psi_-^2)] - \mathcal{H}[\psi_0, c_0]$$
$$\simeq \left[-\frac{13}{72}\frac{\tilde{u}^3}{v^2} - \frac{1}{6}\frac{\gamma\chi_n\tilde{u}}{v}\delta\Delta \right] V \quad . \tag{A11}$$

We also have

$$M_0 = \begin{pmatrix} \tilde{u}^2/2v & 0 \\ 0 & \chi_n^{-1} \end{pmatrix} \tag{A12}$$

so that

$$\det M_0 = \chi_n^{-1}\tilde{u}^2/2v \tag{A13}$$

and

$$M = \begin{pmatrix} -\frac{2\tilde{u}}{3v}(\tilde{u} + \gamma^2\chi_n) & 2\gamma\left(\frac{-\tilde{u}}{6v}\right)^{1/2} \\ 2\gamma\left(\frac{-\tilde{u}}{6v}\right)^{1/2} & \chi_n^{-1} \end{pmatrix} \tag{A14}$$

so that

$$\det M = -\frac{2}{3}\frac{\tilde{u}^2}{v}\chi_n^{-1} \quad . \tag{A15}$$

The fact that $\det M < 0$ indicates the existence of one negative eigenvalue giving rise to the instability and a second positive one associated with the stable direction at the saddle point. From Eqs. (A13) and (A15) we have for the statistical prefactor

$$\left(\frac{\det M_0}{|\det M|}\right)^{1/2} = \tfrac{1}{2}\sqrt{3} \quad . \tag{A16}$$

Since L is positive definite, $(\det LM) < 0$ and we have again a positive and a negative eigenvalue of LM. The negative one is

$$\kappa = -\tfrac{1}{3}\Gamma_\psi\frac{\tilde{u}}{v}(\tilde{u} + \gamma^2\chi_n) + \frac{\Gamma_c\chi_n^{-1}}{2} - \left[\Gamma_\psi^2\frac{\tilde{u}^2}{9v^2}(\tilde{u} + \gamma^2\chi_n)^2 + \frac{\Gamma_c^2\chi_n^{-2}}{4} - \Gamma_\psi\Gamma_c\frac{\tilde{u}^2\chi_n^{-1}}{v} - \Gamma_c\Gamma_\psi\frac{\gamma^2\tilde{u}}{3v}\right]^{1/2} \quad . \tag{A17}$$

When $\Gamma_\psi = \Gamma_c = 1$, the dynamical problem becomes trivial since both variables relax on the same time scale and κ is identified with the negative eigenvalue of M. This negative eigenvalue is the curvature of $f(\psi,c)$ at the point $\bar{\psi}$, $\bar{c}$ in the direction of the "MPEP" (most probable escape path) connecting $(\bar{\psi},\bar{c})$ and (ψ_0,c_0). This particular case of coupled dynamical equations for two variables is the one considered in Ref. 29 where a more detailed description of the time evolution of a general $P(\psi,c)$ is given. The explicit expression for the nucleation rate follows from Eqs. (A3), (A11), (A16), and (A17):

$$I = \frac{\sqrt{3}}{4\pi}\left[\tfrac{1}{3}\Gamma_\psi\frac{\tilde{u}}{v}(\tilde{u} + \gamma^2\chi_n) + \frac{\Gamma_c\chi_n^{-1}}{2} - \left[\frac{\Gamma_\psi^2\tilde{u}^2}{9v^2}(\tilde{u} + \gamma^2\chi_n)^2 + \frac{\Gamma_c^2\chi_n^{-2}}{4} - \Gamma_\psi\Gamma_c\frac{\tilde{u}^2}{v}\chi_n^{-1} - \frac{\Gamma_\psi\Gamma_c}{3v}\gamma^2\tilde{u}\right]^{1/2}\right]$$
$$\times \exp\left[V\left(\frac{13}{72}\frac{\tilde{u}^3}{v^2} + \frac{1}{6}\frac{\gamma\chi_n\tilde{u}}{v}\delta\Delta\right)\right] \quad . \tag{A18}$$

Recalling that $\mathcal{H}$ includes an implicit factor of $\beta = 1/k_BT$, we see that the exponential term of Eq. (A18) has the same dependence on temperature and system size as the mean-field model of Griffiths, Weng, and Langer.[30] In the limit of $T \to 0$ or $V \to \infty$ the nucleation rate goes to zero and the metastable states have infinite lifetime (note that $\tilde{u} < 0$). In the calculation for the space-dependent variables the mean-field limit is taken[31] by letting the range of the interaction, given by the coefficient of $|\nabla\psi|^2$, go to infinity. One can then explicitly see that $\Delta\mathcal{H} \to \infty$, giving rise to infinitely long-lived metastable states.

*Permanent address: Departamento de Fisica Teorica, Universidad de Barcelona, Spain.

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