Simulation study of nucleation in a phase-field model with nonlocal interactions

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We examine the phenomenon of nucleation in a two-dimensional phase-field model in order to calculate quantities associated with a field-theoretic model and to determine the impact of spatially nonlocal interactions on both droplet morphology and nucleation rate. We use an approximate numerical technique, together with model *A* Langevin dynamics, in order to characterize the saddle surface that separates stable and metastable states in function space. We thus obtain the free energy of formation of a critical droplet as well as the statistical prefactor, which, except for a dynamical prefactor, determine the nucleation rate. The standard Ginzburg-Landau energy is employed and, in addition, we consider the role of a short-range, spatially nonlocal interaction on nucleation. [S1063-651X(98)04003-3]

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I. INTRODUCTION

A common feature of all metastable systems is that the decay of the metastable state is brought about by the nucleation and subsequent growth of some localized disturbance within the system [1]. One familiar example of this phenomenon is the transformation of water, supercooled below its thermodynamic freezing temperature, to ice by the formation of solid droplets of sufficient size within the liquid. Further, in some magnetic systems below the Curie temperature, it is found that a carefully prepared metastable state in which spins are mostly antialigned with an external field will transform into a more stable state by the formation of ''droplets'' of spins aligned with the field.

Given the importance of describing nucleation and growth processes in a variety of systems, there has been a great deal of work in this area. For example, a firm theoretical understanding of the decay of metastable states was established by Becker and Döring [2] who derived an expression for the nucleation rate by investigating the kinetics of cluster formation using a rate equation formalism. Modern theories of cluster dynamics are extensions and improvements of the Becker-Döring approach, which have established scaling theories of nucleation and led to some understanding of the link between nucleation and spinodal decomposition [3–5]. On the semimacroscopic scale, Langer [6] has developed a field theoretic approach to the description of nucleation based on nonlinear Langevin equations, which correspond to simple critical dynamics models. This approach has been used to study such problems as liquid-vapor transitions [7] and the nucleation of a crystalline solid from its melt [8]. These problems have also been studied by many authors, including those using density functional [9,10] and other approaches [11]. Indeed the literature in this field is too extensive to be reviewed in this work.

While a theoretical framework for describing both homogeneous and heterogeneous nucleation is in place, it is fair to say that there have been comparatively few definitive tests of the main predictions of these theories, particularly in systems with long-ranged interactions. There are many reasons for this, such as the practical experimental difficulties encountered in determining nucleation rates, the interpretation of these rates near critical points, the difficulty of measuring surface tensions, the breakdown of the independent droplet approximation due to interactions, etc. In the case of binary fluids, for example, a typical experimental determination of nucleation rates as a function of undercooling and supersaturation involves the identification of a cloud point at which a detectable number of droplets is formed. Such an identification is inherently ambiguous as it depends on the time scale of experimental observation. Further, in the vicinity of a critical point, it is necessary to take into account the effect of critical slowing down on droplet evolution [12]. In the case of nucleation in solids, while it is known that long-ranged elastic interactions can modify the driving force for nucleation, the associated modification of the nucleation rate is not well understood. In addition to experimental tests of nucleation theory, several workers have recently investigated nucleation theoretically in kinetic Ising ferromagnets with the aim of testing the aforementioned field-theoretic models [13].

With these limitations in mind, we examine here nucleation in a two-dimensional phase-field model in order to determine the impact of spatially nonlocal interactions on droplet morphology and nucleation rate. This will be accomplished by using computer simulation in conjunction with rate theory to constrain the system to be at a saddle point in function space. The utility of this approach becomes apparent when one considers the statistical uncertainties associated with observing spontaneous droplet nucleation in a dynamic simulation. Indeed, numerical calculations of nucleation rates in condensed systems must also account for the fact that nucleation is a rare event on the time scale of a simulation, particularly at small undercooling [14].

Now, from the geometric properties of the saddle surface we obtain all but the dynamical part of the nucleation rate, both with and without nonlocal interactions. It is of interest to determine how such interactions modify the saddle surface

and under what circumstances it is possible to renormalize the system in order to mimic the interaction-free picture. Specifically, we find that in the presence of a nonlocal interaction it is possible to describe the formation free energy and radius of a critical droplet in terms of standard field-theoretic expressions [6] for sufficiently large droplets as long as the range of the interaction is smaller than the approximate width of the droplet. Further, by determining the curvature of the saddle surface, we are able to predict how the nucleation rate will be altered by the nonlocal interaction. Given this information, we also determine the magnitude of the applied field required to maintain a metastable droplet. Finally, we consider the case of multiple droplets and assess the domain of validity of an independent droplet picture.

An essential part of our work is an approximate numerical technique that we use to facilitate the calculation of the properties of the saddle point. This calculation yields the free energy of formation of the critical droplet and the statistical prefactor, which, together, determine the nucleation rate to within a dynamical prefactor. It should be emphasized that our focus here is on the development of numerical techniques that are applied to a model of nucleation and growth in order to extract important nucleation parameters. This model is a practical extension of the simplified sharp-interface description of a critical nucleus and incorporates the spatial diffuseness of the interface.

This paper is organized as follows. In Sec. II the field-theoretic model of nucleation and our simulation methodology are summarized. In particular, an expression for the nucleation rate as a function of various model parameters is presented. Section III contains our basic results and interpretations for the standard Ginzburg-Landau (phase-field) model as well as for a short-range model of spatially nonlocal interactions. Section IV consists of a discussion and some conclusions.

II. NUCLEATION THEORY AND SIMULATION METHODOLOGY

Consider a simplified model of a two-phase system wherein a continuous, nonconserved order parameter field $\psi(\vec{r})$ distinguishes between these phases. This field embodies a coarse-grained description of the constituent phases in that it represents a local volume average of an important slow variable which characterizes the system. The dynamics of this model is given by the spatial and temporal evolution of this field as described by a prescribed equation of motion. Further, the system under consideration can be subjected to an external field (i.e., driving force), which biases the evolution and, in effect, determines the relative stability of the phases.

It is of interest here to examine nucleation in this system and, in particular, to determine the impact of spatially nonlocal interactions on critical droplet shape and the associated nucleation rate. While this will not be done in complete generality, it is possible to quantify the effects of a short-ranged interaction and to investigate numerically the importance of the range of the interaction in this problem. It is assumed that these nonlocal interactions are mediated by some Green function that connects the phase field at different points in space. For example, others have used appropriate long-

ranged elastic and electrostatic Green functions to discuss oxygen ordering in superconducting oxides [15] and transformation strains in ordered intermetallics [16].

It is assumed that $\psi(\vec{r})$ evolves according to the phenomenological Langevin equation appropriate for a nonconserved order parameter given by

$$\frac{\partial \psi(\vec{r},t)}{\partial t} = -\Gamma \frac{\delta F}{\delta \psi(\vec{r},t)} + \zeta(\vec{r},t), \qquad (1)$$

where Γ is a rate constant that sets the time scale for phase evolution, F is a free energy functional to be specified, and ζ is a noise term, which represents a heat bath. This equation is characteristic of model A, which is used extensively in critical dynamics studies [17]. Thus, a free energy functional is required, and we begin by employing

$$F[\psi] = \epsilon \int d^d r \left[\frac{1}{2} (\nabla \psi)^2 + V(\psi) - h\psi \right]$$
$$- \frac{\epsilon}{2} \int \int d\vec{r} \, d\vec{r}' \, G(\vec{r}-\vec{r}') \psi(\vec{r}) \psi(\vec{r}'), \qquad (2)$$

where the effective double-well potential is given by

$$V(\psi) = -\frac{\tau}{2} \psi^2 + \frac{g}{4} \psi^4, \qquad (3)$$

τ and g are parameters, ϵ is an energy coefficient (taken to be unity), h is an applied field and $G(\vec{r}-\vec{r}')$ is an interaction Green function to be specified later. The first term in Eq. (2) is the ''Ginzburg-Landau ψ^4'' free energy while the second term models a spatially nonlocal interaction mediated by $G(\vec{r}-\vec{r})$. Physically, h would correspond to an undercooling in the case of a supercooled liquid or to an external magnetic field in the case of a ferromagnet. With these assumptions the dynamical equation of motion for this system is

$$\frac{\partial \psi(\vec{r},t)}{\partial t} = \Gamma \Bigg(\nabla^2 \psi(\vec{r}) + h + \tau \psi(\vec{r}) - g \psi^3(\vec{r})$$
$$+ \int d\vec{r}' \, G(\vec{r}-\vec{r}') \psi(\vec{r}') \Bigg). \qquad (4)$$

A. Local interaction

Before considering a nonlocal interaction it is useful to first consider critical droplet formation in a spatially local model. It will be seen that the results for the local model will aid in the interpretation of the results for the nonlocal model over a spatially limited interaction range.

The local model [i.e., $G(\vec{r})=0$] supports a time-independent planar interface given appropriate far-field boundary conditions. So, if one seeks a function $\overline{\psi}(\vec{r})$ that extremalizes F subject to the conditions that $\psi(z \to \pm\infty) = \pm\sqrt{\tau/g}$ one finds that

$$\overline{\psi}(z) = \left(\frac{\tau}{g}\right)^{1/2} \tanh\left[\left(\frac{\tau}{2}\right)^{1/2} (z-Z)\right], \qquad (5)$$

where Z is the location of the front and it has been assumed that $h=0$. This interface is, in general, diffuse with a characteristic width $\sim \tau^{-1/2}$. Our focus in this work is on the

formation of droplets, and so we will consider only relatively large droplets for which small interfacial boundary elements are locally well described by planes. Consequently, in this limit, Eq. (5) holds approximately in the radial direction upon making the substitutions $z \to r$ and $Z \to R$.

Now, in order to discuss droplet formation it is helpful to calculate the formation free energy of a droplet and other quantities that characterize droplet shape. From a knowledge of these droplet properties Langer [6] has determined a nucleation rate. This was first accomplished by considering the difference in free energy between a system with and without a droplet defined by

$$\Delta F = F[\bar{\psi}] - F[\psi_{\text{ref}}], \tag{6}$$

where ψ_{ref} is the spatially uniform field of the reference state. Upon expanding this difference in powers of the field h, one finds to first order that

$$\Delta F \approx -2 \sqrt{\frac{\tau}{g}} \, h V_d + \sigma \Sigma_d, \tag{7}$$

where the surface tension σ is given by

$$\sigma = \frac{2\sqrt{2}\,\tau^{3/2}}{3g}, \tag{8}$$

and the d-dimensional volume and surface areas are given by

$$V_d = \frac{R^d 2\pi^{d/2}}{d\Gamma(d/2)}, \tag{9}$$

$$\Sigma_d = \frac{R^{d-1} 2\pi^{d/2}}{\Gamma(d/2)}, \tag{10}$$

respectively. From these results the radius R_c and formation free energy ΔF_c of a critical droplet can by found be minimizing ΔF with respect to R to obtain

$$R_c = \frac{\sqrt{2}\,\tau(d-1)}{3h\sqrt{g}}, \tag{11}$$

$$\Delta F_c = \frac{4\tau^{d+1/2}}{g^{d/2+1/2}h^{d-1}} \left(\frac{\sqrt{2\pi}}{3}\right)^d \frac{(d-1)^{d-1}}{d\Gamma(d/2)}. \tag{12}$$

One goal of the present study is to determine the nucleation rate I given τ, g, and the applied field h. As the formation of critical droplets is an activated process, this rate is determined by the attributes of the saddle surface that separates stable and metastables states. It turns out that

$$I = I_0 \exp\left[\frac{-\Delta F_c}{kT}\right], \tag{13}$$

where I_0 depends on the local geometry of the saddle surface and a kinetic prefactor. The relevant geometrical features of the saddle surface are measures of curvature and can be obtained by considering small excursions from the saddle point in function space. That is, one imagines the change in free energy associated with the fluctuation

$$u(\vec{r}) = \psi(\vec{r}) - \bar{\psi}(\vec{r}). \tag{14}$$

One then finds that

$$F[\psi] = F[\bar{\psi}] + \frac{1}{2} \int \int d\vec{r}\, d\vec{r}'\, u(\vec{r}) M(\vec{r},\vec{r}') u(\vec{r}') + \cdots, \tag{15}$$

where the operator M is

$$M(\vec{r},\vec{r}') \equiv \left(\frac{\delta^2 F}{\delta\psi(\vec{r})\,\delta\psi(\vec{r}')}\right)_{\bar{\psi}}. \tag{16}$$

Given the quadratic form above, it is clear that the eigenvalue spectrum of M will effectively characterize the saddle surface in the vicinity of the saddle point. Physically, one would expect that d of these eigenvalues are zero, corresponding to translations of the critical droplet. These modes arise from the broken translational symmetry in the problem and are not expected to affect the nucleation kinetics. In addition, the saddle point implies the existence of one negative eigenvalue, denoted here as λ_0. It can be expressed in terms of the model parameters by

$$\lambda_0 = -\frac{1}{R_c^2} = -\frac{9h^2 g}{2\tau^2(d-1)^2}. \tag{17}$$

All remaining positive eigenvalues, denoted by λ_i ($i > 0$), are frequencies associated with distortions of the critical droplet. Thus one can regard the prefactor $I_0 = I_0(\lambda_0, \lambda_i, T, \Gamma, V)$, where V is the volume of the system.

Langer [1,6] has determined I_0 explicitly for this model in the limit of a small applied field h. In particular he found that this prefactor can be expressed in terms of a product of a dynamical prefactor, κ, and a statistical factor, Ω_0, as

$$I_0 = \frac{|\kappa|}{2\pi} \Omega_0, \tag{18}$$

where

$$\Omega_0 = V \left(\frac{2\pi k_B T}{|\lambda_0|}\right)^{1/2} \left(\frac{\det(M_0/2\pi k_B T)}{\det(M'/2\pi k_B T)}\right)^{1/2}, \tag{19}$$

and where V is proportional to the system volume, M_0 is a generalization of Eq. (16) in which the derivative is to be evaluated in the reference state, and the prime indicates that only the positive eigenvalues were used to compute the determinant. The dynamical factor describes the initial rate of decay of the metastable state and can be related to the negative eigenvalue λ_0 if the system is maintained at fixed temperature and the nature of the coupling of the system to the required heat bath is known. For the system under consideration here, the rate constant Γ in the Langevin equation [Eq. (1)] sets the time scale for the evolution of a critical droplet.

It should be pointed out that the numerical determination of the spectra of M and M_0 can be quite computationally demanding in a discretized version of the system considered here as the dimensions of the matrix representations of these operators are often quite large. Thus, it is advantageous to consider projections of these matrices onto subspaces associated with a region near some real or fictitious interface. It is

expected that the eigenvalues of these submatrices will contain the most relevant information about the interface. The practical implementation of this procedure is discussed in Sec. III.

B. Nonlocal interactions

The impact of a spatially nonlocal interaction on nucleation will depend, in general, on the magnitude and range of the interaction. For simplicity here we consider the effect of a prototypical interaction of variable range. Our goal is to highlight the generic features of the interaction which alter nucleation kinetics rather than to model specific types of physical interactions.

For this purpose it is convenient here to adopt a Green function of the Yukawa form, which, in reciprocal space, is given by the Fourier transform [18]

$$G(k) = \frac{1}{k^2 + \gamma}, \tag{20}$$

where γ is (inversely) related to the range of the interaction. Now, the behavior of $G(k)$ near the center of the first Brillouin zone is given by the Maclaurin series expansion of the Green function

$$G(k) = \frac{1}{\gamma} - \frac{1}{\gamma^2} k^2 + \frac{1}{\gamma^3} k^4 + \cdots . \tag{21}$$

If the interaction range is relatively short or, equivalently, if γ is sufficiently large, it should be possible to use the approximation $G(k) \approx 1/\gamma - (1/\gamma^2)k^2$ as $\vec{k}$ can be restricted to the first Brillouin zone. Upon substituting the inverse Fourier transform of this approximate expression into Eq. (2) and using the convolution theorem one finds that the effect of the interaction when the free energy is extremalized is the approximate renormalization of the parameters τ, g, and h defined by

$$\bar{\tau} = \frac{\tau + 1/\gamma}{1 + 1/\gamma^2}, \tag{22}$$

$$\bar{g} = \frac{g}{1 + 1/\gamma^2}, \tag{23}$$

$$\bar{h} = \frac{h}{1 + 1/\gamma^2}. \tag{24}$$

Thus, in this limit, the equations describing the interface profile and the eigenvalues of M also describe the system with nonlocal interactions provided that τ, g, and h are replaced by their respective counterparts $\bar{\tau}$, $\bar{g}$, and $\bar{h}$. It then follows that the critical radius R_C, the eigenvalues of M, and the formation energy ΔF_C can be determined by replacing τ, g, and h by their corresponding renormalized values in Eq. (11) [19]. The range of validity of these approximations will be investigated in Sec. III.

C. Simulation methodology

In order to investigate the field-theoretic model, we have solved a spatially discretized version of the relevant Lange-vin equation [Eq. (1)] without noise. This was accomplished by defining the order-parameter field $\psi(\vec{r})$ on a 128×128 square lattice, with lattice parameter a, subjected to periodic boundary conditions. Given a prescribed initial condition, the field then evolved according to model A dynamics, reaching a stable or metastable state at long times. In addition, in some cases it was useful to construct the corresponding reciprocal lattice and perform some bookkeeping operations in this Fourier space, back transforming to real space as required. In particular, the formulation of the problem in reciprocal space is especially well suited to the study of nonlocal interactions mediated by a Green function. Finally, it is convenient to introduce the dimensionless time and mesh size variables $\bar{t} = \Gamma \epsilon t$ and $\delta = \Delta x/a$, respectively, and to indicate that the time step and mesh size used were 0.001 and 0.3 in these units.

The initial condition in our simulations corresponded to a nearly circular droplet, the square lattice frustrating circularity, of some stable phase ($\psi \approx +1$) embedded in a metastable ($\psi \approx -1$) background. Given the input parameters τ, g, and h such a droplet will grow (shrink) if it is larger (smaller) than some critical radius. As our goal was to investigate the properties of a critical droplet, we introduced a droplet of a given radius at zero temperature and varied the field h until this state was (meta)stable at late times. It was helpful here to allow the field to correctively adjust within our algorithm so as to more efficiently generate a critical droplet. In effect, we induce the system to be at a saddle point so that we may characterize the local geometry near this region of function space. (In this sense, the calculation here is reminiscent of the rate-theoretic numerical determination of diffusion coefficients in solids wherein a diffusing particle is constrained to be at or near a saddle surface separating lattice equilibrium states [20].) The droplet radius, defined as the average of the distances between interface points and droplet center, and formation energy were monitored over the course of the simulation, and this zero-temperature metastability requirement implied that these quantities were nearly constant over a time period of sufficient duration. In order to minimize the effects of the periodic boundary conditions, the radii selected were such that the associated droplet interface profiles did not overlap with the profiles of their image counterparts.

III. RESULTS

We studied the formation of a critical nucleus and the nucleation rate for a system in the presence of a nonlocal interaction. In this problem, our goal was to establish the domain of validity of the renormalized nucleation picture outlined in Sec. II B. As discussed above, it is of interest to determine how a spatial interaction with a finite range modifies the droplet formation energy and the modes associated with droplet formation. Such information will enhance our understanding of nucleation in the kinetics of phase formation in systems with competing interactions [21].

In the following we first discuss the simulations carried out to test the renormalization of the parameters and establish a range of validity. Next, we study in detail the properties of the critical nucleus by examining the radial profile for the order parameter and the behavior of the associated for-
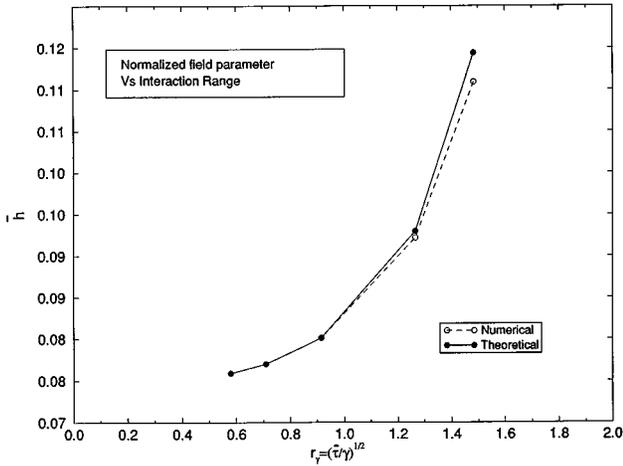
FIG. 1. The dependence of the renormalized field $\bar{h}$ on the scaled interaction range, $r_\gamma \equiv (\bar{\tau}/\gamma)^{1/2}$, as determined by a series of simulations and as predicted by Eq. (11). Note the deviation from the predicted behavior when the interface width is of the order of the interaction range.

FIG. 2. The critical droplet formation energy, normalized by the theoretical value ΔF_c, as a function of time (measured in iterations) for different interaction ranges. The interaction ranges are given by the scaled interaction parameter r_γ. It should be noted that for very short-range interactions this normalized formation energy is nearly unity at long times, as expected.

mation energy. Finally, we calculate the statistical prefactor Ω_0, which, along with the formation energy, effectively determines the nucleation rate. In all the above we make a comparison with Langer's theory of nucleation in the limit of a short interaction range.

A. Applied field, formation energy, and droplet profile

We first consider a system consisting of a stable droplet embedded in a metastable background with the parameter set $(\tau, g, R) = (5.0, 100.0, 10.56)$, where R is measured in units of the lattice parameter. The field parameter h, which is varied in our model to keep the droplet metastable over a long period of time, was measured for various interaction ranges, the range being governed by our choice of the parameter γ used in the Green function [Eq. (20)] [22]. This then permits us to examine the predictions of the renormalized nucleation picture. Figure 1 shows the dependence of the renormalized field $\bar{h}$ on the scaled interaction range, $r_\gamma \equiv (\bar{\tau}/\gamma)^{1/2}$, as determined from a series of simulations and as predicted by Eq. (11) upon replacing τ and g by their renormalized counterparts. It can be seen that the data deviates from the theoretical fit in the regime where the interaction range is of the order of the interface width ($\gamma \simeq \bar{\tau}$), as might be expected intuitively [23].

In the following discussion we consider metastable droplets with $(\tau, g) = (5.0, 100.0)$ and differing values of R. Consider next Fig. 2, a record of the dynamical evolution of the system containing a droplet with $R = 24.87$, which shows the normalized droplet formation energy $(F - F_{\text{ref}})/\Delta F_c$, where F_{ref} is the free energy of the spatially uniform reference state and ΔF_c is the (renormalized) theoretical formation energy, as a function of time (i.e., iterations). Several cases have been simulated corresponding to different interaction ranges as denoted by the scaled interaction range parameter r_γ. For short-range (large γ) interactions, it is evident from the figure that the normalized free energy decreases sharply at early times and is approximately unity at late times, as expected from the field-theoretic model of nucleation. The droplet ra-

dius R was also monitored during the simulation and found to be essentially constant over the course of the run with $R/R_c \approx 1$. The deviation in the formation energy from its predicted renormalized value is seen to increase upon increasing the interaction range, with significant differences occurring when $r_\gamma \approx 1.265$ (or $\gamma \approx 3$). This finding is consistent with the behavior of the renormalized field $\bar{h}$ for different interaction ranges (Fig. 1).
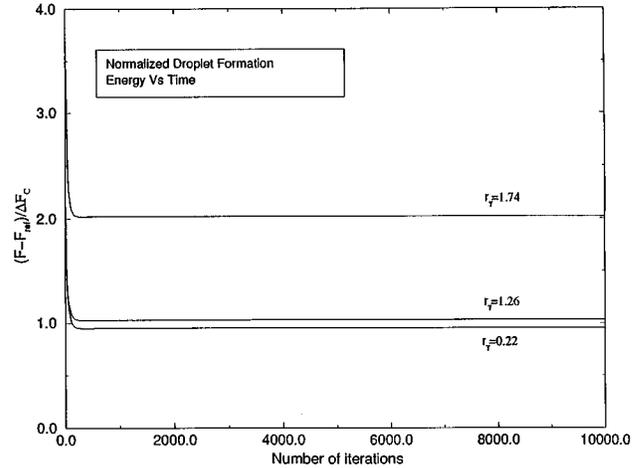
The time evolution of this system can be pictured by first recalling that, as noted above, the droplet model predicts a diffuse, as opposed to a sharp, interface profile. Thus, a droplet with an initially sharp interface must thicken over the course of a run, and this relaxation results in a reduction of the free energy and the concomitant creation of a transition region at the droplet interface of a given width. The approximate shape of the interface profile, at least for relatively large droplets, can be deduced by assuming that a given portion of the interface is, to some approximation, a planar front, and so the radial profile is essentially given by Eq. (5).

This characterization is validated in Fig. 3 in which the normalized interface profiles for the two systems with differing interactions ranges are plotted along with a hyperbolic tangent solution corresponding to a short-range interaction ($r_\gamma = 0.224$). The agreement between the actual and theoretical profiles is seen to be excellent. It should be recalled here that the width of the interface is $\sim \tau^{-1/2}$ and therefore, replacing τ by its renormalized value $\bar{\tau}$ leads to a change in width. Indeed, the profile in Fig. 3 with the more diffuse interface corresponds to a lower value of $\gamma (= 0.7)$

B. Nucleation rate—negative eigenvalue

Of particular interest in this study is the calculation of a nucleation rate I for a given driving force h. As discussed in the previous section, this calculation can be performed by determining the formation free energy (as in Fig. 2) and the eigenvalues of the matrix M. Of particular importance is the single negative eigenvalue λ_0 in that it characterizes the special geometrical features of the saddle surface. As a practical matter, however, the diagonalization of M here is quite com-
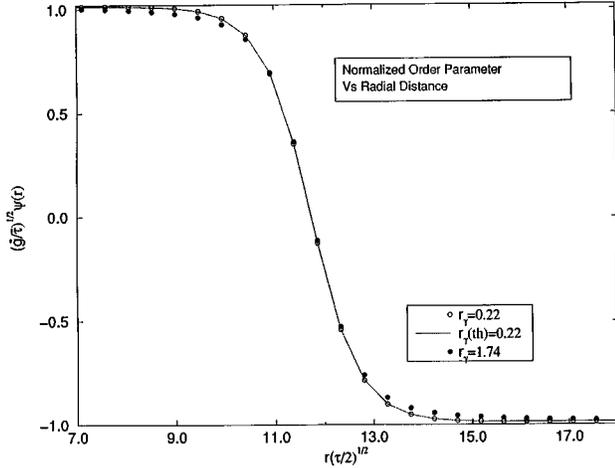
FIG. 3. The normalized order parameter vs the normalized distance, $r(\tau/2)$, for metastable critical droplets corresponding to different interaction ranges. For comparison with the short-range interaction profile, the theoretical tanh solution [Eq. (5)] is also shown and the agreement between these two profiles is seen to be excellent.

putationally intensive, given its size of $16\,384 \times 16\,384$, and so we consider a smaller submatrix corresponding to those lattice points in a narrow annular region around the interface. The width of this annulus must be greater than the interface width and is therefore determined by the parameter τ. The rationale for adopting this approximation is that the eigenvalues of interest are likely to be associated with the interface itself, and so a sufficiently wide annulus should capture the essential physics of the problem. The justification for this approximation was established *a posteriori* by examining the variation of the results with the size of the annular region. Further, an iterative search for λ_0 obviated the more time consuming full diagonalization of M.

The negative eigenvalues of M for various radii R_C in the limit $\gamma \to \infty$ obtained with this approach are shown in Fig. 4. As can be seen from the figure, the data fit the expected $1/R_C^2$
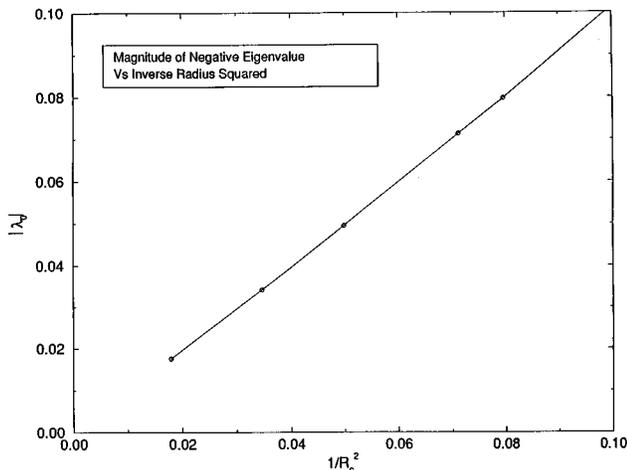
FIG. 4. The negative eigenvalues of the matrix M for a series of critical droplet radii R_c vs $1/R_c^2$. The linearity of this plot with corresponding unit slope is expected from the field-theoretic nucleation model [Eq. (17)].
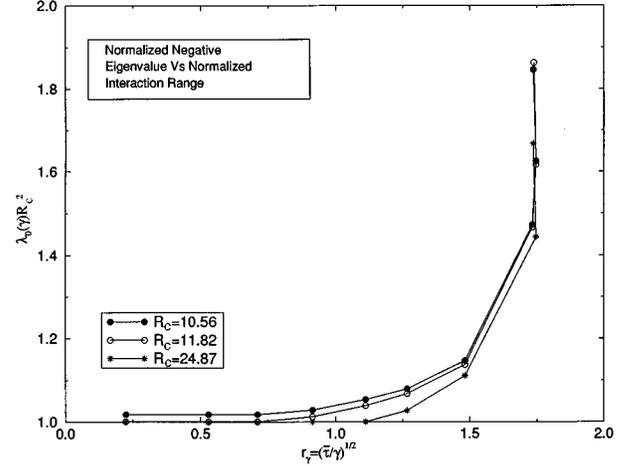
FIG. 5. The normalized negative eigenvalues of $R_C^2 \lambda_0(\gamma)$ vs normalized interaction range r_γ for several different critical droplet radii (in lattice units). Note that the normalized eigenvalues deviate from unity for an interaction range $1/\sqrt{\gamma}$, which is a substantial fraction of the interface width and that the renormalized nucleation picture works best for larger droplets, as expected.

functional form predicted by Eq. (17). One can repeat the procedure discussed above for systems containing the nonlocal interaction given in Eq. (20) and examine the dependence of $\lambda_0(\gamma)$ on the parameter γ. That is, one can introduce a critical droplet into a system with a given nonlocal interaction and obtain the negative eigenvalue in the spectrum of the corresponding operator M [Eq. (16)] by numerical iteration. The results of these calculations are illustrated in Fig. 5 where the normalized eigenvalue, $R_C^2 \lambda_0(\gamma)$ is plotted as a function of the reduced range r_γ for three different critical radii. Once again we find that the renormalized nucleation picture is valid for $r_\gamma = (\overline{\tau}/\gamma)^{1/2} \approx 1.0$ and therefore breaks down when the interaction range is of the order of the interface width. It is also clear from Fig. 5 that the deviation from the renormalized nucleation picture is dependent on droplet size, with larger deviations occurring for smaller droplets.

As a check of our numerical results, it was found that the value of λ_0 was quite insensitive to the width of the annular region for sufficiently large widths. This was true even for the longer range interactions considered here (e.g., $r_\gamma = 1.736$ or $\gamma \approx 0.7$).

Finally, an essential feature of Langer's theory is that the nucleating droplets are independent of each other. It is worth investigating the conditions under which the droplets interact, causing the theory to break down. To this end, we studied a system of two identical droplets of radius $R_c = 10.56$ at

TABLE I. The logarithms of $\det(M_0)$ and $\det(M')$ and the logarithm of Δ as a function of w (in units of the lattice parameter a) for a droplet of radius 10.56. Note the relative insensitivity of $\ln(\Delta)$ to w. The parameters τ and g employed here are 5.0 and 100.0, respectively

w	$\ln\det(M_0)$	$\ln\det(M')$	$\ln(\Delta)$
21	5312.45	5141.58	170.87
25	7586.07	7415.22	170.85
30	10911.49	10740.59	170.90

a fixed r distance apart, and varied the parameter γ so as to measure the droplet formation energy and the negative eigenvalue as a function of the interaction range r_γ. Both these quantities show a deviation from the corresponding independent droplet values when γ is sufficiently small [$\gamma\gamma \approx 2$ and the normalized distance of separation $r\sqrt{(\tau/2)} \approx 15.2$]. The negative eigenvalue was slightly more sensitive to variations in the interaction range, as might be expected.

C. Nucleation rate—positive eigenvalues

From Eq. (19) it is clear that the remaining positive eigenvalues are needed in order to calculate the prefactor I_0. For the moment we will focus only on the case of a spatially local interaction.

In this calculation we employed a circular calculation region with a sufficiently large radius, w. In particular, two such regions are employed, one in a spatially uniform reference system and an identical circular area in the corresponding system containing a critical droplet, and the ratio of products of positive eigenvalues [i.e., $\Delta = \det(M_0)/\det(M')$] is obtained. It is expected that the eigenvalues corresponding to modes not included will not contribute significantly to this quotient. This expectation was confirmed by calculating $\ln(\Delta)$ for various region radii, w, for a droplet of radius 10.56 with the results summarized in Table I. As can be seen from Table I $\ln(\Delta)$ is relatively insensitive to w for increasingly larger regions. It should be noted here that for this smaller droplet there are deviations in the relative formation energy $\Delta F/F_C = 0.93$ from the field-theoretic prediction.

In order to get a sense of the magnitude of these numbers consider $\ln\det(M_0)$. In this case the operator $M_0 = -\nabla^2 + 2\tau$, and so one can express $\ln\det(M_0)$ in terms of its spectrum by the approximate relation

$$\ln\det M_0 \approx \sum_{i=-w}^{w} \sum_{j=-(w^2-i^2)^{1/2}}^{(w^2-i^2)^{1/2}} \ln\left[2\tau + \frac{4}{\delta^2}\right.$$
$$\left. - \frac{2}{\delta^2}[\cos(i\pi/w) + \cos(j\pi/w)]\right], \quad (25)$$

where the Fourier transform of the lattice Laplacian operator has been employed. For $w = 21$ the double sum is 5237.6, within about 1% of the calculated value. A more accurate calculation would take into account the small impact of h on M and the nonperiodicity of the region of calculation. In any case, both $\ln[\det(M_0)]$ and $\ln[\det(M)]$ increase essentially linearly with the size of the calculation region, while $\ln(\Delta)$ involves the size of the diffuse interface region.

A more extensive investigation of the role of spatially nonlocal interactions in the present context would, of course, require the calculation of the full spectrum of M. Based on the results obtained here for the (most important) negative

eigenvalue, however, one would expect that these other nonnegative eigenvalues can also be renormalized over some interaction range.

IV. DISCUSSION AND CONCLUSIONS

The phenomenon of nucleation in a two-dimensional phase-field model with spatially nonlocal interactions has been studied by effectively characterizing the saddle surface that separates stable and metastable states in an abstract function space. This approach was necessitated by the fact that simulations of spontaneous nucleation are essentially impractical given the time scale of such a simulation. By considering an appropriate region that properly incorporates the diffuse interface that is characteristic of this system, we have obtained the free energy of formation of a critical droplet as well as the statistical prefactor, which are key ingredients of the nucleation rate. One perhaps surprising result of this work is that we have obtained self-consistent results for a range of droplet sizes given that the field-theoretic model assumes a ''large'' droplet. We have investigated the role of a spatially nonlocal interaction in determining the nucleation rate and have interpreted the results, over a restricted range of interaction parameter, in terms of a renormalized nucleation picture.

A complete description of the nucleation rate requires, in addition to the foregoing calculations, a determination of the dynamical prefactor κ in Eq. (18). κ depends on the coupling of our system with some external heat bath. Once this coupling is specified, κ is given in terms of the negative eigenvalue λ_0 [7] and the rate constant Γ, the latter setting the time scale for the evolution of the system. Thus, given our calculation here, it is possible to calculate the nucleation rate if the coupling to the heat bath is known.

Finally, it should be pointed out that the present discussion has focused on homogeneous nucleation in a system with an isotropic surface energy. In many realistic cases it is found that the presence of defects limits the supercooling of a system as these defects often become catalytic sites for the (heterogeneous) nucleation of a stable phase. Further, in the case of solid-solid nucleation, the surface energy associated with the boundary between a droplet and a metastable background can be anisotropic depending upon the crystal symmetries of the phases that are involved. Thus, the system described in this work is somewhat idealized, and it is our goal to extend it to more accurately describe nucleation in solids.

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[18] In two-dimensional real space $G(\vec{r}) = 2\pi K_0(\gamma|\vec{r}|)$, where K_0 is a modified Bessel function.

[19] For notational convenience the renormalized critical radius, eigenvalues and formation free energy will not be denoted with a bar.

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[22] As the effective parameters $\bar{\tau}$ and $\bar{g}$ change as γ changes, it is necessary to vary the field h if one wishes to work at fixed critical droplet size, R_C.

[23] Given the dimensions of the matrix representation of the operator M, it was necessary to employ an approximation in order to calculate the negative eigenvalues. While the Green function in Eq. (20) leads to many additional couplings in M, one still expects that this approximation is useful since the renormalized interface width $\sim \bar{\tau}^{-1/2}$ is relatively insensitive to γ for the interaction ranges considered here. This expectation was validated by noting that the values of $\lambda_0(\gamma)$ were quite insensitive to the width of the annular region for a sufficiently large width.