Formation of "filamentary" structures during nucleation

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A generalized Ginzburg–Landau equation describing the evolution of an order-parameter field is used to analyze the process of nucleation in first-order phase transitions. Even in a system with isotropic symmetry, the critical configuration of fluctuations in the order parameter is not spherical. It exhibits a tendency to form quasi-reduced-dimensionality folds of the density. Spherical nucleating regions arise predominantly near these density folds and form filamentary structures which reproduce the shape of these folds in a post-critical stage of the evolution.

Introduction. Key questions in research on first-order phase transitions are the onset and structure of a critical nucleation center, i.e., a large-scale fluctuation of the order parameter which initiates the transition of the entire distributed system from a metastable state to an absolutely stable state.[1–3]

In the phenomenological theory, the evolution of the order parameter in a non-equilibrium system is described by a generalized Ginzburg–Landau equation.[4–6] This is a nonlinear equation of the diffusion type, whose general form is

$$\psi_t = \gamma(\delta\mathcal{F}/\delta\psi), \tag{1}$$

where $\mathcal{F}$ is the Ginzburg–Landau functional of the system, γ is a positive kinetic coefficient, $\varphi(x, t)$ is the order-parameter field, and ψ_t is its time derivative.

Model (1) has recently been used[7] to study the kinetics of the nucleation and subsequent growth of domains of the new phase in 2D and 3D systems with Ginzburg–Landau functionals

$$\mathcal{F}[\psi] = \int d^a r\left[\frac{1}{2}(\bar{\nabla}\varphi)^2 + F(\varphi)\right] \tag{2}$$

of two types:

$$F(\varphi) = \frac{1}{2}\tau\varphi^2 - \frac{2}{3}a\varphi^3 + \tfrac{1}{4}b\varphi^4, \tag{3}$$

$$F(\varphi) = \frac{1}{2}\tau\varphi^2 - \frac{1}{2}a\varphi^4 + \tfrac{1}{6}b\varphi^6. \tag{4}$$

If all the constants in (3) and (4) are positive, and if $a^2 > \tau b$, then the function $F(\varphi)$ must have a metastable minimum at $\varphi = 0$, and it is favored from the energy standpoint if $\varphi = \varphi_0 \neq 0$:

$$\varphi_0=\frac{1}{2b}[a+(a^2-\tau b)^{1/2}], \quad \varphi_0^2=\frac{1}{b}[a+(a^2-\tau b)^{1/2}].$$

In this case this functional describes the behavior of the system between the binodal and the spinodal of the supercooling.

In Ref. 7 we focused on the structure and evolution of an isolated critical nucleation center of an energetically favored phase inside a metastable phase. In addition, we studied the kinetics of the formation of a stable phase from arbitrary mesoscopic irregularities in a fluctuating field through numerical simulation. We also demonstrated the special role played by stationary states, which are manifested as metastable attractors as the system moves toward an absolutely stable state.

At a certain temperature corresponding to a metastability of the disordered phase, the amplitudes of individual $\varphi(\mathbf{r})$excitations become large enough that these excitations qualify as critical nucleation centers. The most important result of Ref. 7 was the conclusion that the critical configuration of the order-parameter field is typically not spherical. The following two factors are responsible for this situation.

1. In general, local maxima of the randomly distributed density $\varphi(\mathbf{r})$ fall off in different ways along different directions $\mathbf{r}$, so among them there are always some whose decay rate along one (or two) directions is much smaller than along other directions (these are "folds"). These anisotropic density folds can be interpreted as quasi-reduced-dimensionality formations which evolve in accordance with a 1D or 2D version of Eq. (1).

2. The primary distinguishing feature in the evolution of density folds is that the density of the order parameter in a quasi-reduced-dimensionality nucleation center (which starts off much smaller than the equilibrium value) initially increases toward an equilibrium value φ_0. The nucleating region then expands, approaching a spherical shape, but it is now well above the critical size. This nucleation mechanism is triggered at an amplitude of the $\varphi(\mathbf{r})$ fluctuations which is below that required for initially spherical nucleation centers (for which an amplitude on the order of φ_0 is required). This mechanism should therefore be typical as the system goes from the paramagnetic phase into the metastability region.

Large-scale filamentary structure. The relaxation process described above becomes complicated because of a noise of fluctuations of the field $\varphi(\mathbf{r}; t)$ which cannot be eliminated at any temperature above absolute zero. The corresponding noise, $f(t, \mathbf{r})$, must be added to Eq. (1):

$$\varphi_t=-\gamma\frac{\delta\mathcal{F}}{\delta\varphi}+f(t,\mathbf{r}). \tag{5}$$

This noise automatically gives rise to nucleation centers, without the arbitrary specification of a distribution of these centers $\varphi(\mathbf{r}; 0)$. At the same time, this noise enhances considerably the simplified picture based on a study of the relaxation of a given configuration of the φ field.

A reduced-dimensionality excitation near the critical level relaxes very slowly [see Eq. (1)] and remains essentially constant over the time required for an isolated

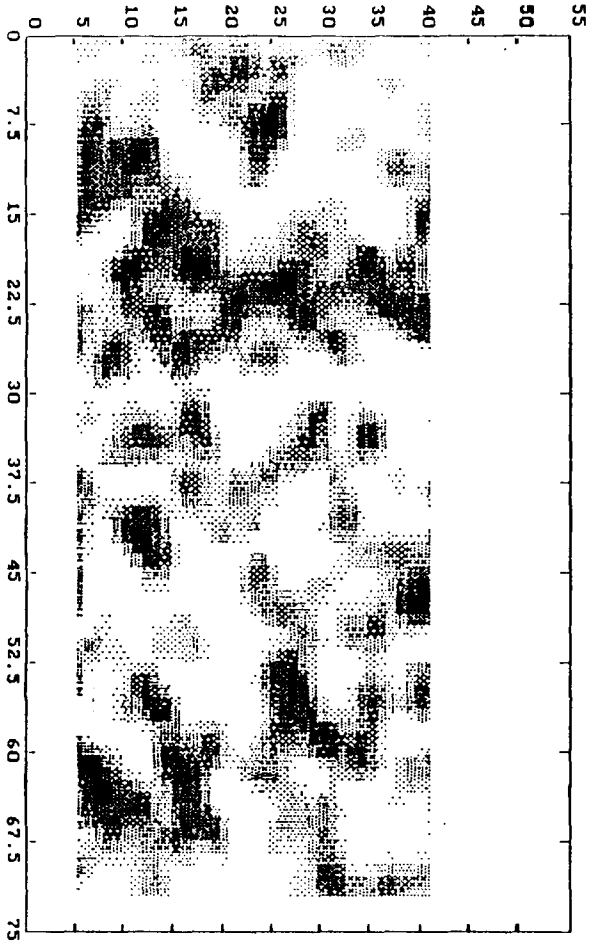

FIG. 1. Well-developed (extended) "filamentary" structure for model (3).

supercritical nucleation center to finally form. In turn, a large nucleating region of the new phase interacts with the field φ, "pinning" the surrounding region of elevated density (Fig. 1). On the other hand, the spatially extended fold in the φ field raises the probability for the appearance of new critical nucleation centers in its vicinity. This occurs in the direction in which the original spike is stretched out. A "filamentary" structure formed by numerous nucleating regions growing along the density fold arises on the map of the order-parameter density.

We have carried out a numerical simulation of the nucleation process on the basis of Eq. (5) for both forms of the local free-energy potential, (3) and (4), for various values of the parameters of the equation: the noise intensity and the relaxation constant. We also varied the structure of the interaction [the nonlocal gradient part of function (2)]. In all cases we observed a universal property of the fluctuating field φ: Long-lived filamentary structures form in an intermediate stage of the relaxation of the system to an equilibrium ordered state.

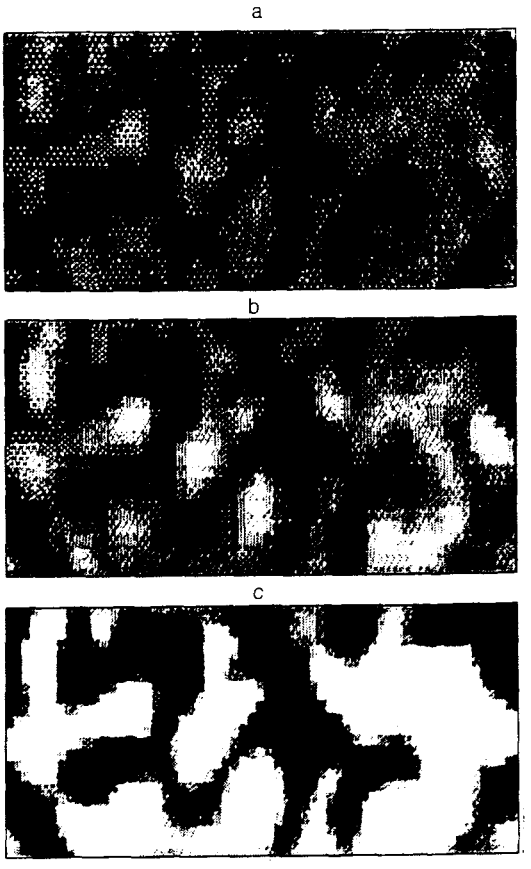

FIG. 2. Successive stages in the evolution of the field φ for model (4). a—Beginning of the formation of a "filamentary" structure; b—well-developed filamentary structure; c—beginning of the final stage of evolution.

Figure 1 shows a well-developed structure of this type, formed by a multitude of (spherical) domains of the new phase, for model (3), which contains the invariant φ^3 and which therefore allows a single sign for the equilibrium order of the field φ. The local order-parameter density is reflected by the level of gray, with the equilibrium value φ_0 corresponding to the maximum intensity.

A qualitatively similar structure is found in the case of even model (4), which allows equilibrium domains of both signs. In the kinetic stage of the evolution, the "walls" between the filaments with a fixed sign of the order parameter form from nucleating regions of the other sign. Figure 2 shows several typical stages in the development of such a structure. The maximum grey level corresponds to an order-parameter density of $+\varphi_0$. In the stage preceding Fig. 2a, the motion of the density spikes is random. Figure 2a shows a stage in which the pinning of density islands has already begun (on the order of 25% of the time after the appearance of the metastable state for which the given noise intensity is the critical level). Figure 2b shows a fragment of a well-developed filamentary structure. Finally, Fig. 2c demonstrates the onset of a agglomeration of nucleation centers into a domain structure ($\approx$75% of the time). The evolution from this point on is rather trivial, consisting of a gradual

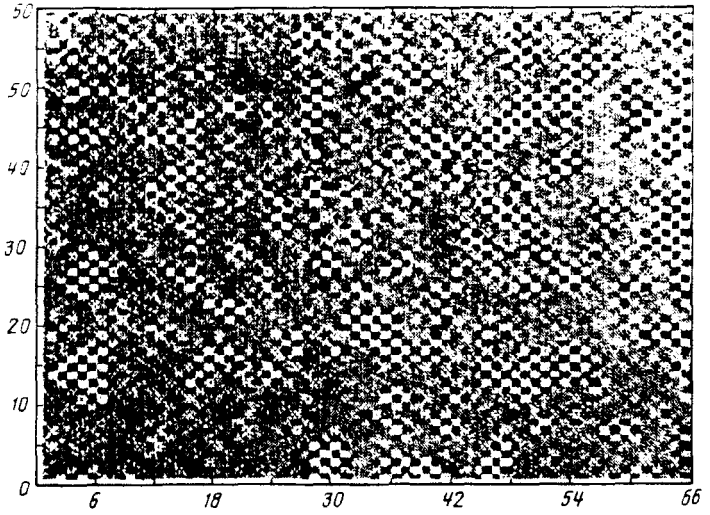

FIG. 3. "Filamentary" structure in the case of an "antiferromagnetic" interaction.

smoothing out of the boundaries and the disappearance of small inclusions of one phase in the other.

Figure 3 illustrates the stability of the process with respect to a change in the spatial dispersion of the interaction. An antiferromagnetic "checkerboard" phase corresponds to the ordered state in this case. The brightness reflects the amplitude of the antiferromagnetic order parameter, which is determined by the difference between the values of φ in the sublattices. In this case it is also difficult to trace the filamentary structure and individual nucleation centers.

Since the fluctuations of the field φ continue to occur after the appearance of nucleation centers of the new phase, the process described above is continually accompanied by the appearance of new density folds and the elongation of old ones. These folds attach to each other and form a percolation cluster, which gradually fills the entire space. In view of the random nature of the process, we would expect this cluster to be a fractal entity in intermediate stages of the evolution. However, the limited capabilities of our numerical simulation prevented us from definitively resolving this suggestion and from calculating the dimensionality of the fractal structure.

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