Automatic blocking of nucleation and the universality of kinetic phenomena in first-order phase transitions

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The kinetics of a first-order phase transformation are investigated using a unified mathematical approach based on the generalized Ginzburg–Landau model with a nonlocal thermodynamic potential. It is shown that since the formation of nuclei includes processes that prevent their appearance and growth in other regions in space, it should result in autostabilization of an intermediate mixed state. Various mechanisms for the formation of an effective long-range interaction in such systems are analyzed. The universality of the kinetic phenomena in first-order phase transitions, which is due to the self-consistent character of the blocking of the phase-separation process and is manifested by the establishment of universal relations between the effective parameters of the system, is pointed out for the first time. © *1995 American Institute of Physics.*

1. INTRODUCTION

It is well known that phase transformations in real physical systems are generally accompanied by the appearance of nonuniform long-range fields (elastic, dipole, etc.), which play a significant role in the kinetics of the phase transition. Consideration of the nonlocal interactions is crucial in the study of nucleation, which is a central question in the investigation of the kinetics of first-order phase transitions. The displacement of the temperature for the beginning of nucleation in solids by a finite amount from the phase-equilibrium temperature T_c, as well as the associated unavoidable thermodynamic hysteresis[1] and complete strictional blocking of the two-phase state,[2] which have been known for a long time, stimulated numerous investigations of the influence of long-range elastic fields on the nucleation process (see, for example, Refs. 3–8).

For the most part, the preceding theoretical studies started out with traditional models of a critical nucleus viewed as a quasihomogeneous spherical region of a new phase separated from the matrix by a negligibly thin boundary layer, with which a certain surface energy density σ is associated.[9,10] These models are valid in the early stages of evolution of the domains of the new phase. The evolution of arbitrary fluctuations of the order-parameter field and nucleation in a metastable medium were investigated in the context of a phenomenological theory in our recent papers,[11–13] and it was established that even in a system with isotropic symmetry, the critical configuration of the order-parameter fluctuations is not spherical and exhibits a tendency to form density folds, near which expanding spherical nuclei subsequently form in the post-critical stage of evolution of the system.

Numerical experiments and an analytic investigation of the kinetics of first-order phase transitions were performed on the basis of a generalized Ginzburg–Landau equation for the order-parameter field $\varphi(r,t)$ in physical systems described by the Ginzburg–Landau functional with the general structure

$$\int d\mathbf{r}'d\mathbf{r}[V(\mathbf{r}-\mathbf{r}')\varphi(\mathbf{r})\varphi(\mathbf{r}')+F(\varphi)],$$

where $V(\mathbf{r}-\mathbf{r}')$ characterizes the spatial dispersion of the interaction in the system and $F(\varphi(\mathbf{r}))$ is the local energy density, which has at least two minima as a function of φ, making it possible to describe the behavior of the system in the region of metastability.

The appearance of effective long-range nonuniform fields during first-order phase transitions causes the true physical picture of the kinetic processes to be richer than that described in the papers cited above. We shall demonstrate below that the long-range effects in the kinetics of a phase transformation can be included in a natural manner in a unified scheme for describing the evolution of a system toward equilibrium based on an evolution equation for an order parameter of the Ginzburg–Landau type, but with a "nonlocal energy density" $\tilde{F}(\varphi)$. The physical mechanism of nonlocality is generally based on the interaction of a field that is ordered during a first-order phase transition with other fields.

Besides the traditionally investigated long-range elastic and dipole fields, the temperature and concentration of a substance in a new phase (local concentration) can serve as the "interacting" component of the system. Strictly speaking, the "basic" kinetic equation for the field variable $\varphi(\mathbf{r},t)$ describing the ordering is supplemented by quasilinear parabolic equations for the components of the system that interact with the field of φ in this case.

The term containing the order parameter φ in the equation for the "interacting" component of the system acts as a nonlinear distributed source. Sometimes (as in the presence of striction effects, which manage to rapidly adjust to changes in the order parameter) a nonlocal source can be transferred directly into the evolution equation for the field variable $\varphi(\mathbf{r},t)$, which is then sufficient for describing the establishment of equilibrium in the system.

The equilibrium state of a system for assigned values of the external parameters can be either a homogeneous state corresponding to the minimum of the original local energy of

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the order-parameter field or a highly inhomogeneous state representing a superposition of the original metastable state and easily identifiable separate domains of a new phase. We discovered that regardless of their physical nature, systems which undergo a phase transformation with an effective nonlocal potential exhibit a universal type of behavior as they approach the (homogeneous or inhomogeneous) equilibrium state, which is akin to the universality of the critical phenomena accompanying second-order phase transitions. As before, the beginning of the nucleation process corresponds to the scenario described in Refs. 12 and 13.

In the following sections of this paper we thoroughly discuss the nature of the universality of the behavior of systems in the region of metastability on the basis of an analysis of the corresponding kinetic equations. The reduced system of kinetic equations which we constructed for the order parameter and the interacting component of the system makes it possible to investigate the overall scenario of the behavior of a system during a first-order phase transition observed in numerical experiments. Before proceeding to a detailed analysis of the mathematical models corresponding to specific realizations of long-range effects in the kinetics of first-order phase transitions, we show that an expansion of the free-energy density functional of an arbitrary system must contain several terms, whose roles may be significant or not, depending on the physical nature of the system under investigation. The appearance of nonlinear long-range interactions which prevent nucleation as a system passes from a metastable state to an equilibrium state is a manifestation of an effect just as common as the Le Châtelier principle in the linear thermodynamics of irreversible processes.

2. INITIAL MODEL AND MECHANISM FOR REALIZATION OF LONG-RANGE NONLINEAR INTERACTIONS IN THE KINETICS OF A FIRST-ORDER PHASE TRANSITION

The classical Ginzburg–Landau model used in nucleation theory is based on the use of a free-energy functional in the form

$$\mathcal{F}[\varphi]=\int d^dr[\tfrac{1}{2}(\nabla\varphi)^2+F(\varphi)], \tag{2.1}$$

where φ is the fluctuating order parameter, d is the dimensionality of the space, and, in addition, it is assumed (generally without special reservations) that the leading nonlinearities with respect to φ are contained only in the local energy density $F(\varphi)$, which, in the general case, is an arbitrary function of the order parameter and is invariant with respect to the symmetry group of the paraphase of the system under investigation. Bearing in mind the ensuing comparison with the results of the previous papers,[12,13] we shall restrict ourselves below to a scalar order parameter and, accordingly, to two types of expansions of the local part of the free energy:[1)]

a) $F(\varphi)=\frac{1}{2}\tau\varphi^2-\frac{2}{3}a\varphi^3+\frac{1}{4}b\varphi^4$, (2.2)

b) $F(\varphi)=\frac{1}{2}\tau\varphi^2-\frac{1}{2}a\varphi^4+\frac{1}{6}b\varphi^6$. (2.3)

The relaxation of the order-parameter field in the presence of the fluctuational noise $f(\mathbf{r},t)$, such that

$$\langle f(r,t)\rangle=0, \quad \langle f(r,t)f(\mathbf{r}',t')\rangle=\delta(\mathbf{r}-\mathbf{r}')\delta(t-t') \tag{2.4}$$

can be described satisfactorily by the equation

$$\varphi_t=-\gamma\frac{\partial\mathcal{F}}{\partial\varphi}+f(\mathbf{r},t), \tag{2.5}$$

where γ is a positive kinetic coefficient (henceforth $\gamma=1$), $\varphi(r,t)$ is the time-dependent order-parameter field, and φ_t is its derivative with respect to time. Since the well-known work of Landau and Khalatnikov,[15] various versions of this equation have been successfully utilized to investigate the appearance and growth of localized nonlinear excitations in systems near a phase-transition point, as well as the motion of the front of a first-order phase transition (see, for example, 16–20). The Ginzburg–Landau functional in the form (2.1) can be regarded as the first terms of a series expansion of the nonequilibrium thermodynamic potential $\mathcal{F}\{\varphi(\mathbf{r},t)\}$ in the small derivatives of the ordered field $\varphi(\mathbf{r})$. The same functional can be obtained with certain approximations on the basis of the microscopic Hamiltonian of the system.[21] In a somewhat more general case the functionals thus obtained with a very simple quadratic interaction of the density–density type have the form

$$\mathcal{F}[\varphi]=\tfrac{1}{2}\int d^dr\int d^dr'\,\varphi(\mathbf{r})V(\mathbf{r}-\mathbf{r}')\varphi(\mathbf{r}')+\int d^drF(\varphi). \tag{2.6}$$

We note that by the nature of the functional (2.6), the local part of the kernel $V(\mathbf{r}-\mathbf{r}')$ is already taken into account in the second, local term $\int d^drF(\varphi)$. This is equivalent to the substitution $V(\mathbf{r}-\mathbf{r}')\to V(\mathbf{r}-\mathbf{r}')-V(0)\delta(\mathbf{r}-\mathbf{r}')$. The corresponding kinetic equation for the order parameter is linear with respect to the nonlocal part:

$$\varphi_t=-\int d^dr'V(\mathbf{r}-\mathbf{r}')\varphi(\mathbf{r}')-dF(\varphi)/d\varphi+f(\mathbf{r},t). \tag{2.7}$$

The term $\int d^dr'V(\mathbf{r}-\mathbf{r}')\varphi(\mathbf{r}')$ in this equation describes the change in $\varphi(\mathbf{r})$ from one point in space to another.[2)] In the case of a simple (for example, monotonic) dependence of $V(\mathbf{r}-\mathbf{r}')$ on the distance, the first term in (2.6) can be expanded in powers of the gradients of φ to obtain the simple model (2.1) and a uniform distribution of the order parameter in the ordered phase. If the spatial dispersion of $V(\mathbf{r}-\mathbf{r}')$ is complex enough, such an expansion is impossible, and the ordered state contains some density waves of the field of φ. It can, however, be verified that in both cases the qualitative pictures of the nucleation process are practically identical and correspond completely to a scenario including the appearance of nuclei from low-dimensional density folds: the formation of "filamentary structures" and isotropization of separate domains of the new phase followed by their growth until they completely displace portions of the metastable phase [see our previous papers (Refs. 12 and 13)]. This means that a qualitative change in the process must be associated with the inherently nonlinear terms in Eq. (2.7). In fact, as was already noted, the blocking of the nucleation process expected in the general theory is a specific manifestation of the Le Châtelier principle. When applied to a first-

order phase transition, this should mean that the formation of a nucleus in some region of space includes a mechanism which slows or totally suppresses the appearance of nuclei at other sites. This highly nonlocal mechanism involves an effective interaction of order-parameter fluctuations at points in space that are relatively distant from one another. Just as nucleation is possible in model (2.5) owing to the nonlinear structure of the corresponding thermodynamic potential, the processes which suppress nucleation should be effective only when the amplitude of the local surges of the order-parameter field is sufficiently large, i.e., they should be described by highly nonlinear nonlocal functionals. We note that the partial blocking of the growth of nuclei observed in real experiments (see, for example, Ref. 22) would otherwise be impossible. In the general case, the functional $\mathscr{F}\{\varphi(\mathbf{r})\}$ contains all the nonlocal terms (especially when the fluctuational renormalization of the corresponding coefficients is taken into account[23]) and can be represented in the form

$$\mathscr{F}[\varphi]=\sum_{k=1}^{\infty}\int\prod_{i=1}^{k}d\mathbf{r}_i g_k\{\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_k\}\prod_{i=1}^{k}\varphi(\mathbf{r}_k), \quad (2.8)$$

from which any set of nonlocal terms can be isolated by formally setting particular coefficients g_k large. Which of them are significant in a theoretical investigation of the kinetics of a specific first-order phase transition is determined by the actual physical processes in the system undergoing the phase transformation.

As noted in the introduction, such processes include the reaction (striction) of a crystal lattice to a change in magnitude of the order parameter φ during a phase transition. In the very simple case of an isotropic medium and quadratic striction, the local seed functional of the free energy is modified in the following manner:

$$\mathscr{F}[\varphi,\mathbf{u}]=\int d^dr[\tfrac{1}{2}(\nabla\varphi)^2+F(\varphi)-g\varphi^2u_{ii}+\tfrac{1}{2}ku_{ii}^2$$
$$+\mu(u_{ik}-\tfrac{1}{3}\delta_{ik}u_{ll})^2]. \quad (2.9)$$

If the lattice vibrations manage to follow the variations of φ, we can utilize the condition $\delta\mathscr{F}[\varphi,u]/\delta u_{ik}=0$ to eliminate the variables u_{ik} and attain, after some standard transformations (see, for example, Ref. 24), an effective functional solely in terms of the field φ:

$$\mathscr{F}[\varphi]=\int d^dr\left[\tfrac{1}{2}(\nabla\varphi)^2+\tilde{F}(\varphi)+\frac{\kappa}{2V}\varphi^2(r)\int d^dr'\varphi^2(r')\right]. \quad (2.10)$$

Here $\tilde{F}(\varphi)$ is the renormalized local form of $F(\varphi)$ with the same structure as the original function $F(\varphi)$ (we shall henceforth omit the tilde), and the constant κ is defined by the expression

$$\kappa=\frac{q^2}{2V}[(k/2+2\mu/3)^{-1}-(k/2+2P/3)^{-1}]. \quad (2.11)$$

The constant P is determined by the external pressure or other constraints which prevent free expansion of the crystal (twins, defects, etc.) and, in turn, fixes the sign of κ. When $P>\mu$, $\kappa>0$; otherwise, $\kappa<0$. We note that the functional (2.10)–(2.11) was obtained in Ref. 25 in an investigation of continuous phase transitions in a compressible lattice (see also the corresponding references in Ref. 21).

The nonlocal construction $\int d^dr\varphi^2(\mathbf{r})\int d^dr'\varphi^2(\mathbf{r}')$ in the functional $\mathscr{F}[\varphi]$ generates a term with a long-range effect in the equation of motion for the field variable:

$$\partial\varphi/\partial t=\nabla\varphi-\partial F/\partial\varphi-\frac{\kappa}{2V}\varphi(\mathbf{r})\int d^dr'\varphi^2(\mathbf{r}'), \quad (2.12)$$

whose presence significantly accelerates or slows (or even totally stops) the ordering process, depending on the magnitude and sign of κ.

Let us discuss one more example of an interaction, which leads to a similar model. The local variation of the order parameter is accompanied by the evolution or absorption of heat (depending on whether the transition is to the low- or high-temperature phase). This results by means of heat conduction in heating (cooling) of the surrounding regions of space, which, of course, slows the transition process in all cases. This mechanism seems universal, and its effectiveness is determined only by the relationship between the rates of the nucleation and heat-conduction processes.

The local heating (cooling) of a system in a region where a nucleus appears can be taken into account by assuming that the quantity τ in expressions (2.2) and (2.3) is a function of position and time. The kinetic equation for the order parameter should be supplemented by an equation which describes the evolution of $\tau(\mathbf{r},t)$. The latter equation should be a heat-conduction equation with heat removal and with a source $\beta[\varphi]$, whose intensity is proportional to the rate of change of the free energy, i.e.,

$$\beta[\varphi]\propto\frac{d\mathscr{F}}{dt}=\frac{\delta\mathscr{F}[\varphi,\tau]}{\delta\varphi}\varphi_t.$$

As a result we have

$$\varphi_t=-\frac{\delta\mathscr{F}[\varphi,\tau]}{\delta\varphi}+f(\mathbf{r},t); \quad (2.13)$$

$$\tau_t=\alpha\Delta\tau-\xi(\tau,\tau_0)-\frac{\delta\mathscr{F}[\varphi,\tau]}{\delta\varphi}\varphi_t. \quad (2.14)$$

Here α is the thermal conductivity, $\xi(\tau,\tau_0)$ is the heat-transfer law, which relates the local temperature[3] τ to the temperature τ_0 of the heat bath [in the simplest model case it can be assumed that $\xi(\tau,\tau_0)=\sigma(\tau-\tau_0)$]. In a numerical investigation the system of equations (2.13)–(2.14) can be solved in parallel, which we actually did in our numerical experiments.

Before proceeding to a discussion of the results of the numerical experiments, we show that with some roughening of the model, the mechanism under consideration can be described in terms of a single field variable $\varphi(\mathbf{r},t)$, which evolves in accordance with an equation like (2.12). The physical arguments, which lead to a functional like (2.10) in this case, too, are fairly simple.

Each growing domain of the new phase creates a nonuniform temperature field $\tau(\mathbf{r},t)$ around itself. Owing to heat conduction, the temperature at other points in space deviates from τ_0, altering the conditions for the growth of other domains at those points. This signifies the appearance of an

effective long-range field accompanying the nucleation process in the system. Relating the variation of the temperature field to the order-parameter field $\varphi(r,t)$, we arrive at an energy functional $\mathscr{F}[\varphi]$ (Ref. 4) like (2.10). In fact, when the fluctuations of φ are "turned on" in a system with a temperature equal to the heat-bath temperature τ_0, after a unit of time the mean value of τ deviates from τ_0 by

$$\langle\tau\rangle-\tau_0=\frac{1}{V}\int d^dr\int_0^1 dt\,\tau_t$$

$$=\left(\frac{1}{1+\sigma}\right)\frac{1}{V}\int d^dr\int_0^1 d\varphi\,\frac{\delta\mathscr{F}[\varphi,\tau]}{\delta\varphi}. \qquad (2.15)$$

The mutual influence of the domains of the new phase $\varphi=\varphi_0\neq 0$ becomes significant when they become so large (and this is seen from the results of the numerical experiments) that the energy of the domain boundaries between the ordered and unordered phases can be neglected. In this case we have for the integrand in (2.15)

$$\int_0^{\varphi(\mathbf{r},t=1)} d\varphi\,\frac{\delta\mathscr{F}[\varphi,\tau]}{\delta\varphi}\approx\mathscr{F}(\varphi_0,\tau),$$

$$\langle\tau\rangle-\tau_0=\left(\frac{1}{1+\sigma}\right)\frac{1}{V}\int d^dr\mathscr{F}[\varphi_0,\tau]\sim\frac{1}{V}\int d^dr\varphi_0^2. \qquad (2.16)$$

Combining expressions (2.16) with (2.2) or (2.3), we arrive at a functional like (2.10), which was obtained to describe striction effects in the kinetics of a first-order phase transition. In some cases, this makes it possible, in principle, to disregard the specific mechanism for realizing the long-range effect accompanying the first-order phase transition and to formally analyze models with nonlocalities of the general form $\int\int d^dr d^dr'\varphi^2(\mathbf{r})Q(\mathbf{r}-\mathbf{r}')\varphi^2(\mathbf{r}')$.

3. RESULTS OF NUMERICAL EXPERIMENTS AND REDUCED KINETIC EQUATIONS

We numerically simulated the passage of a system from a metastable state to an equilibrium state using the integrodifferential equation (2.12) and the system of equations (2.13)–(2.14) for various values of the parameters appearing in these equations. The assignment of all the constants determining the functional (2.10) actually specifies the original degree of metastability (the difference between the energies of the original state and the lowest minimum of the energy functional) in the system under investigation, and the strength of the interaction of the order parameter with the long-range field of elastic strains. In the initial stage of nucleation, in which the mean $\int d^dr\varphi^2(\mathbf{r})/V$ is small, the correction to the local interaction is very small, and the process proceeds as predicted by the theory previously devised in Ref. 13, which totally disregards long-range effects. In particular, in the initial stages of the process the structure of the evolving field $\varphi(\mathbf{r},t)$ corresponds completely to that shown in the figures in Ref. 13 for the φ^6 and $\varphi^3+\varphi^4$ models. As the ordered regions grow, the contribution of the interaction $\int d^dr\varphi^2(\mathbf{r})/V$ also increases, causing the kinetic process to deviate significantly from that previously described. Here the subsequent scenario of the first-order phase transition, as well as the spatial structure of the state to which the system evolves, are determined to a considerable degree by the seed parameters of the nonlocal functional (2.10).

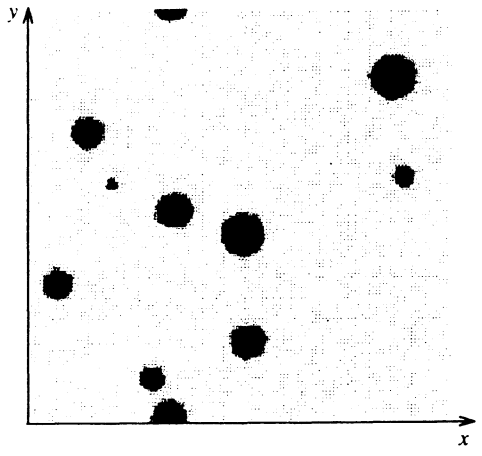

FIG. 1. Typical distribution of blocked nuclei of a new phase in the $\varphi^3+\varphi^4$ model. The amplitude of the order parameter is indicated by the intensity of the blackening (the intensity maximum corresponds to a nearly equilibrium φ in the ordered phase). A fragment of an ensemble of 200×300 cells calculated for $\tau=3.0$, $a=7.5$, and $b=3.4$ is shown. The fraction of the ordered phase on the effective binodal is 23%.

A typical distribution of blocked nuclei of the new phase in the $\varphi^3+\varphi^4$ model is shown in Fig. 1. The amplitude of the order parameter is indicated by the intensity of the blackening (the intensity maximum corresponds to a nearly equilibrium φ in the ordered phase). A qualitatively similar picture containing ordered domains of both signs is obtained for the φ^6 model. To avoid misunderstanding, it should be noted that the calculations performed on the two-dimensional ensemble correspond not to a two-dimensional system, as is sometimes assumed, but to a two-dimensional cross section of the three-dimensional distribution of the order parameter formed by a plane passing through a region of space in which one of the components of the gradient (nonlocal) terms can be neglected. This can also be said in regard to the "one-dimensional" distributions, which are actually calculated as cross sections of the complete space along the corresponding directions with two of the three relatively small gradients.

We also note that the pictures of the spatial distributions of $\varphi(\mathbf{r},t)$ obtained reproduce the isolated blocked nuclei, which are greatly separated from one another in space (by distances of the order of 30–100 lattice constants of the ensemble) so well that we even encountered some difficulties in graphically depicting the results for publication. For this reason, Fig. 1 shows a small fragment of the calculated ensemble consisting of 200×300 cells and containing a relatively rich cluster of nuclei of various scales. Note that during the numerical experiments we repeatedly observed the relatively rapid appearance of nuclei of various scales followed by the slow disappearance of the tiny nuclei and the establishment of a practically equilibrium structure with large domains of a single scale. However, even an ensemble of 200×300 cells is, unfortunately, insufficient for correctly

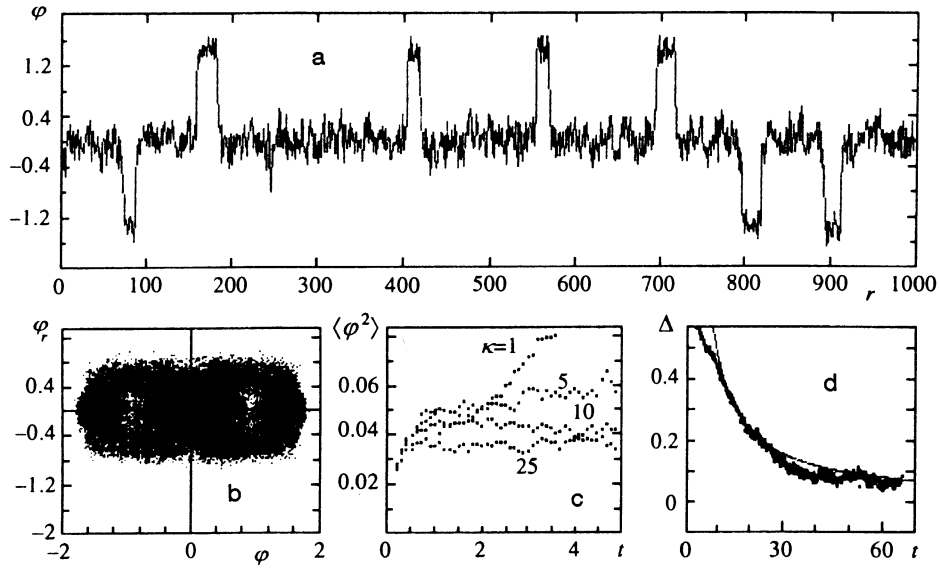

FIG. 2. a) One-dimensional slice of the distribution of $\varphi(r,t)$ for the φ^6 model with $\kappa=2$ at the time $t=70$ for $\tau=1$, $a=1.5$, and $b=1$. b) Phase portrait of the equation of motion. c) Time-dependent behavior of the fraction of the ordered phase taken with a weight φ^2. d) Variation of the deviation of the parameters of the system from the effective binodal with the time t.

calculating the correlation functions of the system for the purpose of elucidating the scale structure of the distribution, as well as for obtaining other statistics when the characteristic size of such domains equals 10–50 lattice constants and they number from 10 to 30 in the entire ensemble.

Several important laws governing the linear process can be understood on the basis of a numerical analysis of the "one-dimensional versions" of Eqs. (2.11), (2.12), and (2.13), respectively, which are very convenient for visualizing the results of the numerical experiments. As we have already noted in discussing Fig. 1, this is possible despite the fact that in its original formulation, the problem of a phase transition in a compressible lattice is essentially three-dimensional.

Figure 2a shows a one-dimensional slice of the distribution of $\varphi(r,t)$ for the φ^6 model (with $\kappa=2$ at time $t=70$). Isolated blocked nuclei with dimensions of the order of 10 (computational) lattice constants at distances of the order of 10^2 from one another are clearly seen. Figures 2b–2d, respectively, show the phase portrait of the equation of motion, the time-dependent behavior of the fraction of the ordered phase taken with a weight φ^2, where $\langle\varphi^2\rangle=\int dr\varphi^2/V$, and the decrease in the deviation of the system parameters with t from the effective binodal $\Delta=\tau_b-\tau-\kappa\int dr\varphi^2/V$, where $\tau_b\approx 1.6874$ is the calculated value of the phase-equilibrium temperature for the φ^6 model when $\tau=1$, $a=1.5$, and $b=1$.

It is not difficult to see the qualitative similarity between the phase portrait of the system and the portrait we previously obtained for a local system,[13] which reflects the aforementioned maintenance of the general appearance and growth of nuclei in the early stage of their evolution. The subsequent scenario of the evolution of the system depends strongly on the value of κ. When κ is small (see Fig. 2c), the fraction of the ordered phase increases without bound up to complete ordering of the system. If $\varkappa$ is sufficiently large ($\kappa \geqslant 2$), the system stabilizes at a certain concentration of the new phase, which is less than unity. The parameter Δ then vanishes.

Figures 3a and 3b depict the formation of an effective long-range interaction between domains of the new phase by means of a heat-conduction mechanism. For clarity, several profiles of the field $\varphi(\mathbf{r})$ and temperature $\tau(r)$ at different times are shown for several neighboring nuclei when the noise is turned off. When the noise is turned on, the nucleation process is qualitatively similar to that shown in Fig. 2. Figures 3c and 3d present plots of the time dependence of $\delta\tau=\int d^dr\tau(\mathbf{r})/V-\tau_0$ and $\langle\varphi^2\rangle=\int d^dr\varphi^2(\mathbf{r})/V$, as well as of the ratio between $\delta\tau$ and $\langle\varphi^2\rangle$, which tends to a constant asymptote as $t\to\infty$. The latter plots, which were obtained by simultaneously solving the equations for the order parameter and heat conduction, illustrate the possibility of reducing allowance for a heat-conduction mechanism to a model with an effective long-range field.

One shortcoming of the numerical solution, however, is that while permitting the study of all the details of a specific scenario, it does not make it possible to fully retain the behavior of the system as a whole as a function of the parameters of the original state. With this in mind, it would be useful to somehow reduce the original equations to a relatively simple quasi-mean-field model, which would make it possible to investigate the observed behavior as a whole.

First of all, we stress the fact already mentioned that the role of nonlocal interactions becomes significant when a domain of a new phase with clear-cut narrow boundaries and a value of the order parameter (within the nucleus) equal to the equilibrium value grows in one or more regions of space. In this case the value of $\int\varphi^2 d\mathbf{r}$ in expression (2.10) naturally increases, effectively altering the "temperature" at the remaining points in space (i.e., renormalizing the coefficient τ of the linear term in the local part of the equation of motion for the order parameter). Since the value of φ^2 in the ordered regions is essentially equal to its value at the free-energy minimum, $\int\varphi^2 d\mathbf{r}$ varies mainly due to the spatial expansion of the domains of the new phase. At the same time, the renormalization of the parameters of the equation results, in turn, in a smooth variation of the equilibrium value of φ^2, which, of course, must be consistent with the variation in

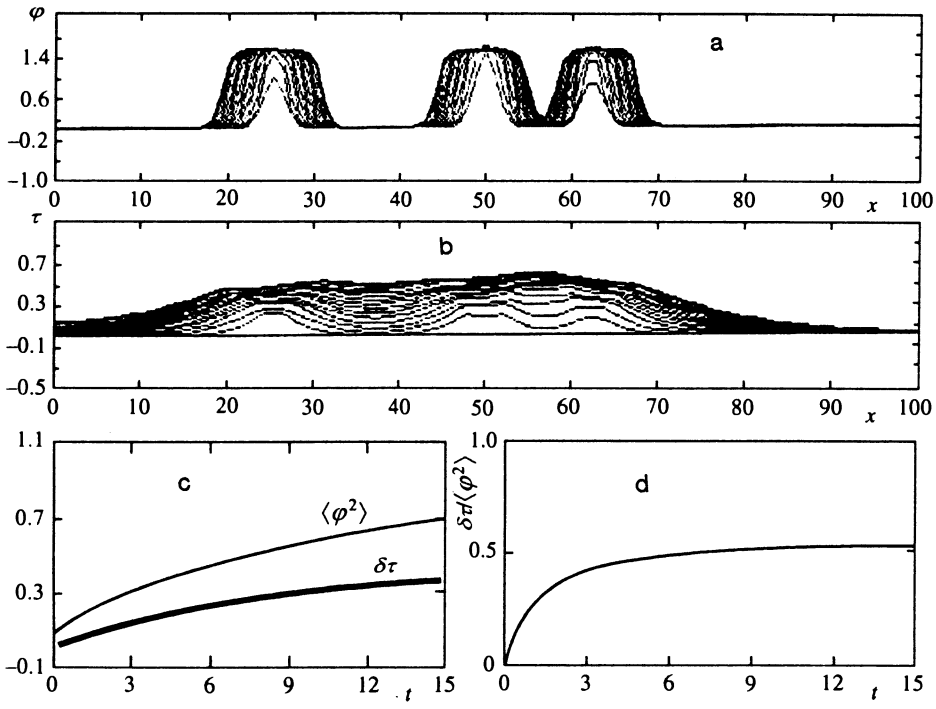

FIG. 3. a, b) Formation of an effective long-range interaction between domains of the new phase by a heat-conduction mechanism. For clarity, several profiles of the field $\varphi(r)$ (a) and of the temperature $\tau(r)$ (b) at various moments in time are shown for several neighboring nuclei when the noise is turned off. c) Plots of the time dependence of $\delta\tau=\int d^dr\,\tau(\mathbf{r})/V-\tau_0$ and $\langle\varphi^2\rangle=\int d^dr\,\varphi^2(\mathbf{r})/V$. d) Ratio between $\delta\tau$ and $\langle\varphi^2\rangle$, which tends to a constant asymptote as $t\to\infty$.

τ. The variations in φ and τ cease if the degree of metastability (the energy difference at the local minima) vanishes, and the value of φ coincides with its value at the renormalized energy minimum. All this provides the following procedure for reducing the integrodifferential equations. Instead of the infinite number of degrees of freedom of $\varphi(\mathbf{r})$, we retain only two integral characteristics: the value of $\varphi(\mathbf{r})\equiv\varphi$ within the ordered domains (which, as noted above, varies smoothly with time) and the effective fraction of the ordered phase, which is taken for convenience with the weight φ^2: $x=\int\varphi^2d^dr/V$. Then φ is described by the equation

$$\partial\varphi/\partial t=-\partial F/\partial\varphi-x\varphi, \tag{3.1}$$

while the corresponding equation for the variable x must be written down with consideration of the fact that the variation of $x=\int\varphi^2d^dr/V$ is related mainly to the spatial expansion of the domains of the new phase in the ordering process, whose rate (in the stages of evolution of the system in which the domains of the new phase have already formed) is proportional to the rate of motion of the domain boundary, which moves under essentially steady-state conditions.[12,27] The rate of such steady motion is determined by the degree of supercooling (superheating) of the system, and is equal to the density of the free energy $F(\varphi)$ at the point of the stable minimum $\varphi=\varphi_0$, in our case with accuracy to within a numerical factor. We recall that according to expressions (2.2) and (2.3), the energy density in a domain of a metastable phase with $\varphi=0$ is equal to zero.

Thus, the rate of change of $x=\int\varphi^2d^dr/V$ can be described by the equation $\gamma\partial x/\partial t=-F(\varphi)$, where, we recall, φ is understood to be the value of the order parameter within the ordered domains, which varies smoothly with time. Since we shall henceforth use the reduced model to describe the previously considered φ^6 and $\varphi^3+\varphi^4$ systems, in which x and τ are additive, it is convenient to introduce the quantity $(\tau+x)$ as a new variable, for which we shall henceforth retain the symbol τ (i.e., $\tau+x\to\tau$), and we shall call it the variable (effective) temperature. For the sake of definiteness, we fix the sign of the coefficient κ in front of the nonlocal term in the functional (2.10), or, more specifically, we assume that $\kappa>0$, which corresponds to the possibility of the blocking of nuclei. The reduced equations for the φ^6 model are

$$\begin{aligned}\frac{\partial\varphi}{\partial t}&=-\varphi(\tau-g\varphi^2+b\varphi^4),\\ \frac{\partial\tau}{\partial t}&=-\frac{\varphi^2}{2}\left(\tau-g\varphi^2+\frac{b\varphi^4}{3}\right).\end{aligned} \tag{3.2}$$

Even in such a simplified form, the analytic solution of these equations is nontrivial, as before, due to their nonlinear nature. Nevertheless, all the necessary qualitative information on the system of equations (3.2) can be extracted from an analysis of the topology of their phase portrait, which is uniquely specified in the present case by the position of the isoclines $\partial\varphi/\partial t=\partial\tau/\partial t=0$. Solving the corresponding algebraic equations with $\varphi\neq0$, we can easily obtain the single fixed point $\varphi_0=3g/2b$, $\tau_0=3g^2/4b$. A standard analysis of this point for stability gives the negative characteristics $\lambda_1=-2g\varphi_0^2$ and $\lambda_2=-\varphi_0^2/2$, so that this point is a stable node. In addition, the system (3.2) has a complete line $\varphi=0$ of stable fixed points. A similar picture is obtained for the $\varphi^3+\varphi^4$ model, which can be described by the reduced equations

$$\frac{\partial\varphi}{\partial t}=-\varphi(\tau-g\varphi+b\varphi^2), \tag{3.3}$$

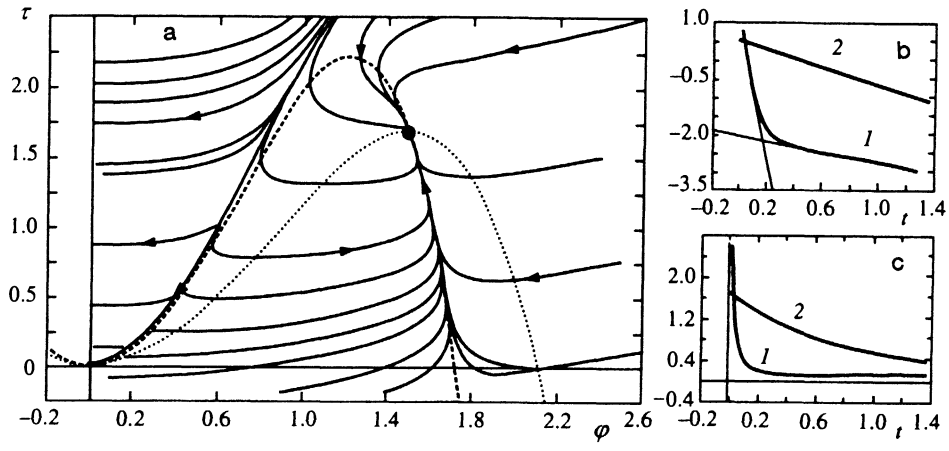

FIG. 4. a) Phase portrait of the system of equations (3.2). The isoclines of the verticals and horizontals are depicted by dashed and dotted lines, respectively. The separatrix and the path of the "large river," which are explained in the text, are seen directly. b) Distance from the image point to the large river (in practice, to the isocline of the verticals $\partial\tau/\partial t=0$ (curve *1*) and distance from the same point to the fixed point (curve *2*). The straight lines stress the behavioral crossover described in the text. c) Logarithms of both quantities, respectively.

$$\frac{\partial\tau}{\partial t}=\varphi^2\left(\frac{\tau}{2}-\frac{g\varphi}{3}+\frac{b\varphi^2}{4}\right)$$

and which also has a line of stable fixed points at $\varphi=0$ and, in addition, the stable fixed point $\varphi_0=2g/3b$, $\tau_0=2g^2/9b$.

Note that the stability of the fixed points is a general property of the reduced equations for an arbitrary structure of $F(\varphi)$. It can be seen that for any F, the system of linearized equations near a fixed point has the form

$$\partial\varphi/\partial t=-\varphi_0\tau-\varphi(F_{\varphi\varphi}(\varphi))|_{\varphi=\varphi_0},$$

$$\partial\tau/\partial t=-\varphi_0^2\tau/2, \qquad (3.4)$$

so that the desired characteristics $\lambda_1=-(F_{\varphi\varphi}(\varphi))|_{\varphi=\varphi_0}$ and $\lambda_2=-\varphi_0^2/2$ are automatically negative for a fixed qualitative structure of the free energy with two local minima at $\varphi=0$ and $\varphi=\varphi_0\neq 0$ (for which the corresponding second derivatives are negative: $(F_{\varphi\varphi}(\varphi))|_{\varphi=\varphi_0}<0$ and $-\varphi_0^2/2<0$).

The phase portrait of system (3.2) is shown in Fig. 4a. The separatrix separating the phase trajectories reaching the nontrivial fixed point φ_0 from the trajectories tending to the $\varphi=0$ line is clearly seen. These two classes of trajectories correspond to physically different behavioral scenarios of the system. If the structure of the seed function $F(\varphi)$ is such that the temperature τ for a given position of a nonzero minimum is excessively high (i.e., the initial point lies above the separatrix), all the trajectories tend to the $\varphi=0$ line, and ordering is impossible. If the initial values lie on the other side of the separatrix, the parameters of the system evolve quickly toward some universal relationship between them and then slowly approach a nontrivial fixed point (see Fig. 4c and its discussion in the next paragraph). The phenomenon just described of rapid evolution of the parameters toward a universal relationship is the essence of the so-called "large-river effect," which was recently discussed in reference to the theory of phase transitions from a somewhat different standpoint.[28] In the context of the present paper, the realization of this effect basically signifies the physical indistinguishability (universality) of the kinetics of a first-order phase transition for a large set of systems having fundamentally different initial properties. As far as we know, such universality has not previously been discussed in the literature in reference to first-order transitions.

The variation of the rate of motion of the image point after it gravitates toward the "large river" is clearly seen when its distance from the isocline of the verticals $\partial\tau/\partial t=0$ (i.e., $\tau/2-g\varphi/3+b\varphi^2/4=0$) is plotted as a function of time on a logarithmic scale (curve *1* in Fig. 4b). At small t it drops much faster than the distance τ from the corresponding value on the binodal (curve *2*). After the image point reaches the vicinity of the path of the large river, the distance from that point to the $\partial\tau/\partial t=0$ curve varies slowly thereafter, i.e., at the rate at which the system as a whole approaches the binodal, so that the slopes of curves *1* and *2* nearly coincide. The latter is clearly reflected in the crossover of the corresponding logarithmic slope (which is noted in the figure by the slanting straight lines).

The system spends most of its time in the vicinity of the large river, and in this sense its behavior (within the regions of attraction to the nontrivial point bounded by the separatrix) also depends little on how it reached the region of metastability. In addition, since in the limit $t=\infty$ its parameters tend to the point defined by the pair of conditions $F=\partial F/\partial\varphi=0$, it "closes itself up" at the binodal. As a result, equilibrium between the phases is established over a relatively broad region of the physical phase diagram, so that if the system is left alone, it remains in an inhomogeneous state, and in order to actually bring the system into a homogeneous ordered state, its parameters must be additionally altered, i.e., the binodal "line" has a finite width.

It is seen in the phase portrait that the trajectory defining the path of the large river lies between the isoclines and gravitates mainly toward the $\partial\tau/\partial t=F=0$ line, giving a good estimate for the desired relationship between the renormalized parameters, and being in good agreement with the physical picture described of smearing of the binodal, just where the condition $F(\varphi\equiv\varphi_+)=0$ holds. The separatrix is also located in the region between the isoclines (although, of course, in a different region of the phase space). This trajectory is unstable, but if seeds lie sufficiently close to it, the system also evolves very slowly. Thus, such a turning-point state is clearly observed in numerical experiments and should certainly be manifested in real experiments.

It should be recalled that the variable τ is the sum of the constant $\tau=(T-T_c)/T_c$, which is determined by the exter-

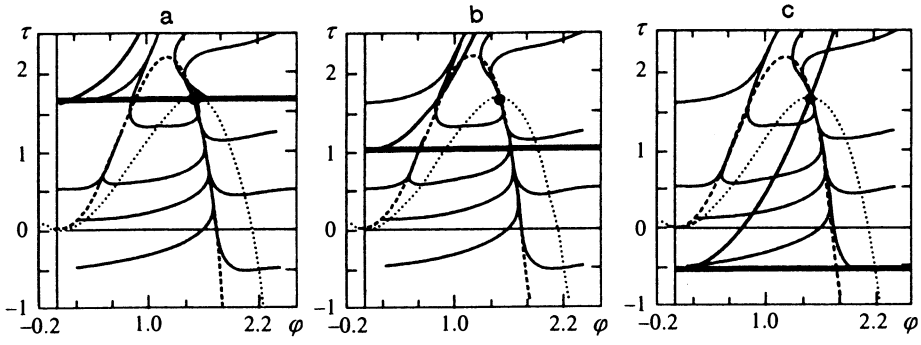

FIG. 5. Displacement of the boundaries (thick lines) of the possible location of the seed parameters as the temperature varies.

nal conditions, and the time-dependent "phase fraction" $x=\int\varphi^2 d\mathbf{r}/V$, which cannot exceed $\varphi^2\equiv\varphi_+^2$, where φ_+ is the position of the nonzero minimum of the energy $F(\varphi)$ renormalized by the interaction. This imposes certain constraints on the attainable values of $(\tau,\ \varphi)$ in the phase portrait (see Fig. 5). Physically, this means that if $\tau=(T-T_c)/T_c$ is so great (small) that even at 100% filling of the system by the new phase the renormalization of τ on account of x is insufficient to hold it on the binodal, the nuclei spread without bound, and the system unavoidably undergoes an ordinary first-order phase transition. Otherwise, the renormalized value of τ tends to the fixed value τ_0, and the system remains in an intermediate state with a fraction of the ordered phase specified by the difference $x=\int\varphi^2 d\mathbf{r}/V=\tau-\tau_0$. The other boundary of the region of observability of the effect described is the requirement that the fraction of the ordered phase be nonnegative: $x\geqslant 0$. Stated simply, the minimum possible value of τ coincides with the seed temperature and thus also assigns the condition of equality of the energies of the phases above which the appearance and growth of nuclei becomes possible at all. By varying the seed (i.e., the actual physical) temperature, we can shift the effective boundary for realization of the intermediate state, as illustrated by the frame formed by the thick lines in Figs. 5a–5c.

When Eqs. (3.2)–(3.3) were written down, to be specific we fixed the sign of the coefficient of x to correspond to the possibility of blocking of the nuclei. However, as discussed in the preceding section, the sign of this coefficient can be reversed. This is formally accomplished by reversing the sign in front of $\partial\tau/\partial t$ in Eqs. (3.2) and (3.3), which, as is easily verified, results in conversion of the stable node $\varphi_0=2g/3b$, $\tau_0=2g^2/9b$ into a saddle point. The entire phase portrait changes accordingly (see Fig. 6). In addition, it is seen from the pattern of flow lines that there is also some universalization of the behavior of the system here. When phase trajectories pass near the saddle point, the rate of evolution of the parameters of the system decreases with time (this can be verified directly by calculating the total flux $[(\partial\varphi/\partial t)^2+(\partial\tau/\partial t)^2]^{1/2}$), and then increases quickly as the system moves away from this point and the nucleus of the new phase rapidly grows. In this stage the parameters of the system are already universal to a considerable extent, so that its behavior is again essentially independent of the relationship between the seed constants. We note that we repeatedly observed just such development of the scenario in the numerical simulation of a phase transformation directly on the basis of the original equation (2.11) for a large number of sets of starting parameters and a suitable sign of κ.

In conclusion we mention one more interesting aspect of the problem. We previously recalled that the role of nonlocal contributions to the Ginzburg–Landau functional which are similar to those used in the present work was previously investigated in reference to the critical behavior of systems with a fluctuation region (see the review in Ref. 25). A system of renormalization-group equations was derived and analyzed, and it was shown that when the coefficient of x is positive, the phase trajectories reach a stable fixed point and that, otherwise, they leave the region of positive definiteness of the fourth-order form. The latter event is interpreted as instability of the continuous phase transition with respect to its breakdown into an abrupt process. These results are in

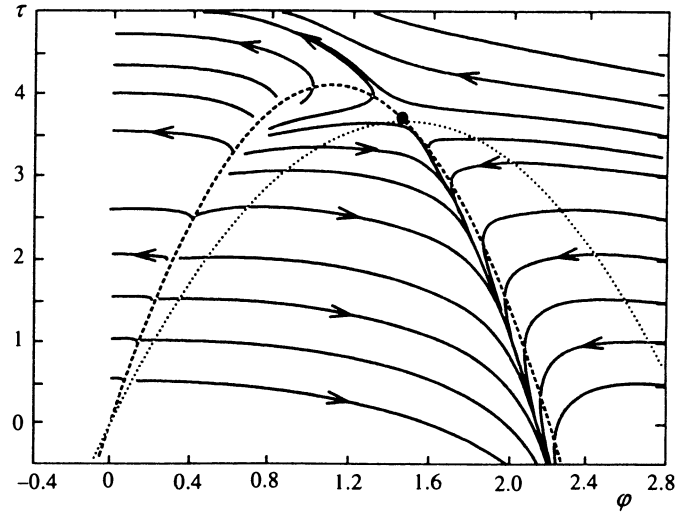

FIG. 6. Same as in Fig. 4 for the case of negative renormalization of the effective temperature $\varkappa/2V\int d^dr'\varphi^2(\mathbf{r}')$.

complete agreement with the results obtained in the present work.

The presence of fluctuations in the system (in numerical experiments they are simulated by a source of noise) smooths the original form of the free energy for a first-order transition in such a manner[29] that when the maximum of $F(\varphi_-)$ is low, it becomes qualitatively the same as in a second-order transition. This means that instead of a simple smooth transition from the results obtained in the present work to the results corresponding to the critical region, there should be real overlap between them for values of $F(\varphi_-)$ comparable to the characteristic scale of the fluctuations. In this context the agreement between both tendencies (universalization of the behavior of the system and breakdown of the transition to an abrupt process) when the nonlocal terms have the appropriate signs is very significant.

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[1)]These expansions have very broad applicability, since the problem for various systems near the critical point can be reduced to an investigation of standard catastrophes described by expansions (1.2) and (1.3) of Ref. 14. Ifall the constants here are positive and $a^2>\tau b$, $F(\varphi)$ must have a metastable minimum at $\varphi=0$ and must be energetically favorable when $\varphi=\varphi_0 \neq 0$: a) $\varphi_0=[\alpha+(a^2-\tau b)^{1/2}]/(2b)$, b) $\varphi_0^2 = [\alpha+(a^2-\tau b)^{1/2}]/b$. It is thus suitable for describing the behavior of a system between a binodal and a supercooling spinodal.

[2)]A formally different form of the kinetic equation, which "transfers" the nonlocality to the kinetic coefficient $\gamma: -\gamma(\mathbf{r}-\mathbf{r}')$ is frequently used in this case in the literature.

[3)]We note the difference between such a formulation of the problem and numerous investigations devoted to the thermal instability of a phase transformation front, which dealt with the evolution of heat and the removal of heat right at the phase transition front (see, for example, Ref. 26).

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