

Self-consistent theory of the transition of an unstable thermodynamic system from spinodal to heterophase kinetics

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The transition from a spinodal regime to a binodal regime is treated as an event in which a stochastic system loses its ergodic nature. The parameter Δ , a measure of the extent to which the system has lost its ergodic nature, determines the difference between the values of the isothermal and adiabatic susceptibilities. The width of the nonergodic region, ε_g , determines the size of region between the binodal and the spinodal on the phase diagram. The quantities Δ and ε_g are derived as functions of the intensity of the interatomic interaction, the anharmonicity, and the anisotropy on the basis of the Ginzburg–Landau model.

1. INTRODUCTION

The behavior of an unstable system which is undergoing a first-order phase transition is known to depend on the particular part of the phase diagram to which the system goes when it leaves the homogeneous disordered state. If it goes to a binodal region, the classical mechanism of nucleation and growth occurs:¹ First, there is a fluctuational nucleation of precipitates of the new phase, with a size R exceeding the critical size R_c . Then, as the limiting component is supplied to the precipitate by diffusion, the immediate vicinity of the precipitate becomes depleted of this limiting component. Finally, one observes a prolonged coalescence process, in the course of which small precipitates are swallowed by large ones, and the average precipitate size $\bar{R}(t)$ increases over time in accordance with $\bar{R} \propto t^{1/3}$ (Ref. 2). A point of fundamental importance is that in the binodal region the nucleating regions of the new phase form as a result of stabilization (by growing to a supercritical size $R > R_c$) of heterophase quasistatic fluctuations which constitute macroscopic regions of the new phase separated from the old phase by a sharp boundary. The order parameter in these regions initially takes on a value close to the equilibrium value. The system evolves only in terms of the size of the inclusions.³ In the spinodal region, in contrast, a homogeneous conversion occurs throughout the volume in an early stage. In the course of this homogeneous conversion, the order parameter reaches its equilibrium value. If a deficiency of the limiting component prevents the conversion from occurring over the entire volume, one should clearly observe a transition from a homogeneous regime to a heterophase regime in a late stage of the evolution. That transition is the subject of the present paper.

The spinodal and heterophase regimes have previously been described separately.^{1,2,4,5} Specifically, only the evolution of the amplitude $\eta(t)$ of the corresponding hydrodynamic mode (e.g., a concentration wave in a decaying solid solution) has been studied in the spinodal region, in a macroscopically homogeneous system.⁴ In the binodal region, in contrast, only the evolution of the characteristic size $R(t)$ of the heterogeneous system has been studied, at a fixed value of the order parameter η (Refs. 1 and 2). A complete description can be achieved by introducing a stochastic functional $\mathcal{P}\{\psi(\mathbf{r}, t)\}$, which determines the probability for the realization of a space-time distribution $\psi(\mathbf{r}, t)$ of an internal parameter representing the hydrodynamic mode.⁶

The approximation of Ref. 4 corresponds to the approximation

$$\mathcal{P}\{\psi(\mathbf{r}, t)\} = \delta\{\psi(\mathbf{r}, t) - \eta(t)\},$$

in which the order parameter $\eta(t) = \langle \psi(\mathbf{r}, t) \rangle$ reduces to the first moment of the stochastic field $\psi(\mathbf{r}, t)$. In the heterophase region, the functional $\mathcal{P}\{\psi(\mathbf{r}, t)\}$ is a step function, which takes on the value 1 in the region $\mathbf{r} - \mathbf{r}_i < R_i(t)$, corresponding to inclusion i , and the value 0 for other \mathbf{r} . The moment $\langle \psi(\mathbf{r}, t) \rangle = p$ reduces in this case to the volume fraction $p = (\bar{R}/\bar{L})^3$ of the precipitated phase, which is determined by the average inclusion size $\bar{R}(t)$ and by the average distance $\bar{L}(t)$ between inclusions.

Recent years have witnessed substantial progress in filling in the kinetic picture of the phase transition, covering the most important of these features in both the spinodal and binodal regions.^{7–12} For example, the wave representation $\psi_{\mathbf{k}}(t)$ of the coordinate dependence $\psi(\mathbf{r}, t)$ was used in Refs. 7–9 to analyze the late stages of the phase transition after a stage of spinodal decay. It was shown that the correlation function $C_{\mathbf{k}}(t) = \langle \psi_{\mathbf{k}}(t) | \psi_{\mathbf{k}}(0) \rangle$ has the form of the Ornstein–Zerne distribution at sufficiently large values of the wave vector \mathbf{k} , with a correlation length ξ . At small \mathbf{k} , on the other hand, one observes a scaling $C_{\mathbf{k}}(t) \propto f[\mathbf{k}L(t)]$ with a scale $L(t) \propto t^n$, where $n = 1/2, 1/3, 1/4$, which is much greater in magnitude than ξ . An analysis in Ref. 10 was carried out in \mathbf{r} space, but in addition to the binary function $C(\mathbf{r}, t)$ the third-order moment $g(t)$ was taken into consideration. This moment represents the asymmetry of the $\mathcal{P}\{\psi(\mathbf{r}, t)\}$ distribution. It was shown that the correlation radius $\xi(t)$ in the spinodal region decreases slightly as time elapses, while there is a significant increase in the asymmetry $g(t)$. As a result, the configurative point on the phase portrait reaches an attractive focus. It is perfectly clear that the next stage should be bifurcation, which takes the system out of the spinodal regime and puts it in the heterophase regime.

Such a bifurcation has not been described previously, but the model developed in Refs. 11 and 12 captures the features of the behavior of this system at both small distances $r \gtrsim \xi$ and large distances $r \gtrsim L(t)$. This is achieved, in contrast with Refs. 2–4 and 7–10, through an analysis of not only the moments of the stochastic functional of the type $C(\mathbf{r}, t)$ and $g(t)$ but also the form of the functional $\mathcal{P}\{\psi(\mathbf{r}, t)\}$ itself. The random field $\psi(\mathbf{r}, t)$ is broken up into a deterministic component $\eta(t)$ and a fluctuating component $\xi(t)$.

The former varies over distances $L(t)$, while the latter is correlated over distances $\sim \xi$. Introducing the conjugate parameter of η —the field m —we can find a self-consistent description of the kinetics of the transition in both the early stage, characterized by the quantity ξ , and the late stage, associated with the evolution of the characteristic size $L(t)$ (Refs. 11 and 12).

There is an obvious gap in this description. The description covers only the early and late limiting stages, not the transitional stage. It is the description of this transitional stage which is our goal in the present study. We start from a formal representation of the transition between these stages as a process in which the stochastic system loses its ergodic nature.¹³ Evidence in favor of using a representation of this sort comes primarily from the following obvious fact: In the early stages of the conversion, the field $\psi(\mathbf{r}, t)$ can take on arbitrary values at any spatial point \mathbf{r} , while in the late stages large values of $\psi(\mathbf{r}, t) \approx \eta(t)$ are reached only inside the inclusions (at $|\mathbf{r} - \mathbf{r}_i| < R_i$), and outside them we have $\psi(\mathbf{r}, t) \approx \xi(t) \ll \eta(t)$. The disruption of the supersymmetry which results from the loss of ergodic nature¹⁴ takes the following form in our case: Isolated excitations represented by occupation numbers $n(\mathbf{r}) = 0$ and 1 and collective excitations described by density waves of the atomic distribution $\psi_{\mathbf{k}}(t)$ lose their mutual equivalence in the late stages. In the homogeneous state in the early stages one can use either of these representations, which are linked by a lattice Fourier transformation, but when the macroscopic inhomogeneity arises in the late stages the system becomes represented by a modulated wave $\psi_{\mathbf{k}}(\mathbf{r}, t)$ (Ref. 15). The meaning here is that a hierarchical relationship is established among the collective excitations, with the result that they take on the properties of isolated excitations at large distances $\sim L$.

This loss of ergodic nature can be represented in a supersymmetric theory¹⁴ or by the coupled-mode method.¹⁶ Here we take the more graphic second approach, in which the loss of ergodic nature is represented by the appearance of a pole in the Laplace transform $C_{\mathbf{k}}(z)$ of the binary correlation function $C_{\mathbf{k}}(t)$ at zero complex frequency z . It thus becomes possible not only to reproduce the theoretical results of Refs. 11 and 12 but also to describe the features of the transitional regime.

2. BASIC RELATIONS

We start from the anisotropic model described by the Ginzburg–Landau Hamiltonian:

$$H = -\frac{A}{2} |\psi|^2 + \frac{B}{4} |\psi|^4 + \frac{\beta_{\alpha}}{2} |\nabla_{\alpha} \psi|^2, \quad (1)$$

where a repeated Cartesian index α means a summation; the coefficient A is zero on the spinodal line; and B and β_{α} are positive constants. In the linear approximation $A = \alpha \varepsilon$, where $\alpha > 0$ is a constant, the quantity $\varepsilon = T/T_s - 1$ determines the magnitude of the excursion of the system from the spinodal line. Ignoring the cubic anharmonicity corresponds to the symmetric dome of the spinodal.

Let us consider the technically simpler case of an unconserved order parameter¹¹ $\psi(\mathbf{r}, t)$. The stochastic equation of motion corresponding to Hamiltonian (1) takes the following form in this case:¹²

$$\dot{\psi} = [(A + \beta_{\alpha} \nabla_{\alpha}^2) - B |\psi|^2] \psi + \zeta(\mathbf{r}, t), \quad (2)$$

where the dot means differentiation with respect to the time, and this time is measured in a scale determined by the magnitude of the diffusion coefficient. The stochastic increment $\zeta(\mathbf{r}, t)$ represents white noise¹⁷

$$\langle \zeta(\mathbf{r}, t) \zeta(0, 0) \rangle = 2T \delta(\mathbf{r}) \delta(t), \quad (3)$$

whose intensity is determined by the temperature T .

To describe this system we formally write Eq. (2), for the spatial Fourier transform $\psi_{\mathbf{k}}(t)$ of the functional dependence $\psi(\mathbf{r}, t)$, in the form $\dot{\psi}_{\mathbf{k}}(t) = iL \psi_{\mathbf{k}}(t)$, which contains the Liouville operator L . The solution of this equation, $\psi_{\mathbf{k}}(t) = \exp(iLt) \psi_{\mathbf{k}}(0)$, makes it possible to write the relaxation function $C_{\mathbf{k}}(t) = \langle \psi_{\mathbf{k}}(t) | \psi_{\mathbf{k}}(0) \rangle$ and its Laplace transform $C_{\mathbf{k}}(z) = \langle \psi_{\mathbf{k}}(z) | \psi_{\mathbf{k}}(z) \rangle$ in the following way:¹⁸

$$C_{\mathbf{k}}(t) = -\langle \psi_{\mathbf{k}} | e^{-iLt} | \psi_{\mathbf{k}} \rangle, \quad C_{\mathbf{k}}(z) = -\langle \psi_{\mathbf{k}} | (z - L)^{-1} | \psi_{\mathbf{k}} \rangle, \quad (4)$$

where $\psi_{\mathbf{k}} \equiv \psi_{\mathbf{k}}(t=0)$. Introducing the projection operators

$$P = | \psi_{\mathbf{k}} \rangle \langle \psi_{\mathbf{k}} | \psi_{\mathbf{k}} \rangle^{-1} \langle \psi_{\mathbf{k}} | \equiv 1 - Q,$$

and using the operator identity

$$\frac{1}{A+B} = \frac{1}{A} - \frac{1}{A} B \frac{1}{A+B}$$

we find

$$C_{\mathbf{k}}(z) = -\chi_{0\mathbf{k}} [z + K_{\mathbf{k}}(z)]^{-1}, \quad \chi_{0\mathbf{k}} = \langle \psi_{\mathbf{k}} | \psi_{\mathbf{k}} \rangle. \quad (5)$$

The concentration correlation function $\psi_{\mathbf{k}}$ here represents the thermal dynamic susceptibility $\chi_{0\mathbf{k}}$. We are assuming that the field $\psi_{\mathbf{k}}$ and the corresponding flux $j_{\mathbf{k}} = i\omega_{0\mathbf{k}} \dot{\psi}_{\mathbf{k}}$ are not correlated with each other ($\omega_{0\mathbf{k}}$ is the frequency of the soft mode). The autocorrelation function of the fluxes is given by

$$K_{\mathbf{k}}(z) = -\langle j_{\mathbf{k}} | Q(z - L_Q)^{-1} Q | j_{\mathbf{k}} \rangle, \quad L_Q = QLQ. \quad (6)$$

Going through calculations for the flux $j_{\mathbf{k}}(t)$ of the type carried out for the original field $\psi_{\mathbf{k}}(t)$, we can put expression (6) in the form of the fraction (5):

$$K_{\mathbf{k}}(z) = -\omega_{0\mathbf{k}}^2 [z + M_{\mathbf{k}}(z)]^{-1}, \quad (7)$$

where the memory function $M_{\mathbf{k}}(z)$ represents the correlation function of the form (6) of the generalized forces $f_{\mathbf{k}}$. Expressing the force $f_{\mathbf{k}} \propto \dot{\psi}_{\mathbf{k}}$ in terms of the derivative of the flux, $j_{\mathbf{k}} \propto \psi_{\mathbf{k}}$, we can also put the memory function in the form of the fraction (5) or (7). Continuing this operation, we find a representation of the initial correlation function $C_{\mathbf{k}}(z)$ as an infinite chain fraction. This technique, developed by Mori,¹⁹ offers the convenience that the kernel of each fraction, (5) or (7), has a completely unambiguous physical meaning. For example, we easily see from the continuity equation $\dot{\psi} = -i\mathbf{k} \cdot \mathbf{j}_{\mathbf{k}}$ that the flux correlation function $D_{\mathbf{k}} = -ik^{-2} K_{\mathbf{k}}(z=i0)$ represents a diffusion coefficient, while $\varkappa_{\mathbf{k}}(z) = iz^{-1} D_{\mathbf{k}}$ represents the polarizability, which describes the correlation between the generalized polarization of the medium, $\mathbf{P}_{\mathbf{k}}(z) = iz^{-1} \mathbf{j}_{\mathbf{k}} = i(\mathbf{k}/k^2) \psi_{\mathbf{k}}(z)$, as a result of a stratification of the system. This circumstance allows a transparent interpretation of the physical meaning of the procedure of truncating an infinite chain by an expression of the form (5) or (7).

3. SELF-CONSISTENT REPRESENTATION OF THE NONERGODIC SITUATION

A stratification of the system leads to a loss of ergodic nature, with the result that the correlation function $C_{\mathbf{k}}(t)$ takes on a finite value $\Delta_{\mathbf{k}} \neq 0$ as $t \rightarrow \infty$. In the frequency domain, this event means the appearance of poles:¹⁶

$$\begin{aligned} \Delta_{\mathbf{k}} &= T \lim_{z \rightarrow i0} (-z C_{\mathbf{k}}(z)), \\ \delta_{\mathbf{k}}^2 &= \lim_{z \rightarrow i0} (-z M_{\mathbf{k}}(z)), \end{aligned} \quad (8)$$

where $\Delta_{\mathbf{k}}$ and $\delta_{\mathbf{k}}$ are macroscopic and microscopic parameters of the nonergodic nature, which are related by

$$\Delta_{\mathbf{k}} = T \chi_{0\mathbf{k}} \frac{\delta_{\mathbf{k}}^2}{\omega_{0\mathbf{k}}^2 + \delta_{\mathbf{k}}^2}, \quad (9)$$

which follows from (5), (7), and (8). The physical meaning of the parameters in (8) is as follows: The quantity $\Delta_{\mathbf{k}}$ specifies that difference between the final and mean values of the order parameter which is a consequence of the stratification of the system. The parameter $\delta_{\mathbf{k}}$ determines the width of the gap in the dispersion relation

$$\omega_{\mathbf{k}} = (\omega_{0\mathbf{k}}^2 + \delta_{\mathbf{k}}^2)^{1/2}.$$

The eigenfrequencies

$$\omega_{0\mathbf{k}} = \omega_0 (1 + \xi_{\alpha}^2 k_{\alpha}^2)^{1/2}, \quad \omega_{\mathbf{k}} = (\omega_{0\mathbf{k}}^2 + \delta_{\mathbf{k}}^2)^{1/2},$$

where $\omega_0^2 = \alpha \varepsilon$, $\xi_{\alpha}^2 = \beta_{\alpha} / \alpha \varepsilon$, determine the expressions

$$\Delta_{\mathbf{k}} = T (\chi_{0\mathbf{k}} - \chi_{\mathbf{k}}), \quad (10)$$

$$\chi_{0\mathbf{k}}^{-1} = \alpha \varepsilon + \beta_{\alpha} k_{\alpha}^2, \quad \chi_{\mathbf{k}}^{-1} = (\alpha \varepsilon + \delta_{\mathbf{k}}^2) + \beta_{\alpha} k_{\alpha}^2 \quad (11)$$

for the nonergodic parameter $\Delta_{\mathbf{k}}$, the isothermal susceptibility $\chi_{0\mathbf{k}} = \omega_{0\mathbf{k}}^{-2}$, and the adiabatic susceptibility $\chi_{\mathbf{k}} = \omega_{\mathbf{k}}^{-2}$.

To determine the parameters (8), we note that the generalized force is proportional to the quantity $B |\psi|^2 \psi$ according to the Langevin equation (2). The corresponding correlation function in the \mathbf{r}, t representation is then²⁰

$$M = B^2 \langle |\psi|^2 \psi | |\psi|^2 \psi \rangle. \quad (12)$$

Splitting the higher-order correlation function up into binary correlation functions in accordance with Wick's theorem, we find

$$\begin{aligned} \langle \psi^+(X) \psi(X) \psi^+(X) \psi^+(0) \psi(0) \psi(0) \rangle &\rightarrow \pm (6) n^2(X) n(-X), \\ n(X) &= \langle \psi^+(X) \psi(0) \rangle, \quad X = \mathbf{r}, t, \end{aligned} \quad (13)$$

where the coefficient specifies the number of such splittings possible. Using the expression for the relaxation function in terms of the correlation function,¹⁸

$$C(\mathbf{r}, t) = \langle \psi(\mathbf{r}, t) | \psi(0, 0) \rangle = \int_0^{1/\tau} n(\mathbf{r}, t - i\tau) d\tau, \quad (14)$$

in the spirit of the basic approximation of strongly coupled modes,¹⁶ we take the splitting of the memory function in terms of the original correlation function in the form²¹

$$M(\mathbf{r}, t) \approx 6B^2 \int_0^{1/\tau} n^3(\mathbf{r}, t - i\tau) d\tau, \quad (15)$$

The correlation function here is expressed in terms of the

Fourier transform $C(\mathbf{r}, \omega)$ of the relaxation function by means of the spectral representation¹⁸

$$n(\mathbf{r}, t) = T \int_{-\infty}^{\infty} d\omega e^{-i\omega t} \text{Im } C(\mathbf{r}, \omega), \quad (16)$$

on the axis of the real frequency ω .

As a result, the definition (8) leads to the self-consistency condition

$$M_{\mathbf{k}}(z) = M_{\mathbf{k}}^{(r)}(z) - \frac{1}{z} \frac{6B^2}{T} N^{-2} \sum_{\mathbf{k}_1, \mathbf{k}_2} \Delta_{\mathbf{k}_1} \Delta_{\mathbf{k}_2} \Delta_{\mathbf{k} - \mathbf{k}_1 - \mathbf{k}_2}, \quad (17)$$

where $M_{\mathbf{k}}^{(r)}(z)$ is the nonsingular part, and N is the total number of atoms. Combining (8), (9), and (17), we find the basic equation for determining the nonergodic parameters:²¹

$$\left(\frac{T \chi_{0\mathbf{k}}}{\Delta_{\mathbf{k}}} - 1 \right)^{-1} = \left(\frac{\delta_{\mathbf{k}}}{\omega_{0\mathbf{k}}} \right)^2 = \frac{6B^2 \chi_{0\mathbf{k}}}{T} N^{-2} \sum_{\mathbf{k}_1, \mathbf{k}_2} \Delta_{\mathbf{k}_1} \Delta_{\mathbf{k}_2} \Delta_{\mathbf{k} - \mathbf{k}_1 - \mathbf{k}_2}. \quad (18)$$

Let us analyze this equation. We first note that there is a trivial root $\Delta_{\mathbf{k}}^{(3)} = 0$ over the entire range of values of ε . Near the spinodal ($\varepsilon \ll 1$), the thermodynamic susceptibility $\chi_{0\mathbf{k}}$ increases without bound, and Eq. (18) is satisfied only under the condition $T \chi_{0\mathbf{k}} / \Delta_{\mathbf{k}} \gtrsim 1$. Near the spinodal we thus have a nonergodic region with $\Delta_{\mathbf{k}} \lesssim T \chi_{0\mathbf{k}}$, $\omega_{0\mathbf{k}} \ll \delta_{\mathbf{k}}$; according to (9) and (10), the isothermal susceptibility $\chi_{0\mathbf{k}}$ and the adiabatic susceptibility $\chi_{\mathbf{k}}$ are very different ($\chi_{0\mathbf{k}} \gg \chi_{\mathbf{k}}$). This region obviously corresponds to a two-phase binodal region. Far from the spinodal, the ergodic state corresponding to the trivial root $\Delta_{\mathbf{k}}^{(3)} = 0$ is the stablest. Here there is a homogeneous state. The point at which the ergodic nature is lost, $\varepsilon = \varepsilon_g$, thus determines the binodal line along our approach. In the region bounded by it, Eq. (18) has, in addition to $\Delta_{\mathbf{k}}^{(3)} = 0$, two other nonzero roots, $\Delta_{\mathbf{k}}^{(1)} \leq \Delta_{\mathbf{k}}^{(2)}$, which take on the same value $\Delta_{\mathbf{k}}^g$ at $\varepsilon = \varepsilon_g$. With distance from the binodal ($\varepsilon < \varepsilon_g$), the value of $\Delta_{\mathbf{k}}^{(1)} < \Delta_{\mathbf{k}}^g$ decreases, while $\Delta_{\mathbf{k}}^{(2)} > \Delta_{\mathbf{k}}^g$ increases. It can be shown¹⁶ that the root $\Delta_{\mathbf{k}}^{(2)}$ corresponds to a stable state.

To carry out a quantitative analysis of Eq. (18), we should take account of the circumstance that both of the functions $\chi_0(\mathbf{r})$ and $\Delta(\mathbf{r})$ vary over short distances $r \lesssim \xi$ in the coordinate representation, but the susceptibility does so near the coordinate origin $\mathbf{r} = 0$, while the nonergodic parameter does so at the surface of ordered domains. In the \mathbf{k} representation, this situation corresponds to a weak dispersion of the susceptibility $\chi_{0\mathbf{k}}$. Correspondingly, the nonergodic parameter $\Delta_{\mathbf{k}}$ takes on large values $\sim \Delta_s$ only at points \mathbf{k} spaced uniformly through the Brillouin zone with a period $\sim 2\pi/L$ determined by the characteristic size L of a domain. The nonergodic parameter

$$\Delta = N^{-1} \sum_{\mathbf{k}} \Delta_{\mathbf{k}} \quad (19)$$

is thus related to the maximum value of Δ_s on the surface of the domains by

$$\Delta = s \Delta_s, \quad s = 3\delta/L. \quad (20)$$

The parameter $s \ll 1$ here specifies the relative volume of the interface, of thickness $\delta = (\beta/\alpha)^{1/2} < \xi$. We can thus reduce the integral equation (18) to an algebraic equation:

$$\Delta = \frac{T}{N} \sum_k \{ \chi_{0k} - [\chi_{0k}^{-1} + (6B^2/Ts)\Delta^3]^{-1} \}. \quad (21)$$

We first ignore the dispersion and the anisotropy, assuming $\chi_{0k}^{-1} \approx \chi_0^{-1} = \alpha T_s (\varepsilon + \gamma)$, where $\gamma = \beta k_D^2 / \alpha T_s$ is an inhomogeneity parameter, and k_D is the Debye wave number. For the dimensionless nonergodic parameter $x = (B/\alpha T_s) s^{-1/2} \Delta$ we then find the simple equation

$$x \left\{ x^3 - b \frac{1+\varepsilon}{\gamma+\varepsilon} x^2 + \frac{b}{6} (1+\varepsilon) (\gamma+\varepsilon) \right\} = 0. \quad (22)$$

The solution of this equation is determined by the dimensionless temperature ε , the nonergodic parameter γ , and the nonlinearity parameter $b = (B/\alpha^2 T_s) s^{-1/2}$.

Analysis of the cubic equation (22) shows that the boundary value $x_g = (2/3)b(1+\varepsilon)/(\gamma+\varepsilon)$ is reached at

$$\varepsilon_g = \gamma \left(1 - c \frac{b}{\gamma} \right) \left\{ \left[1 + \left(2c \frac{b}{\gamma^2} - 1 \right) / \left(1 - c \frac{b}{\gamma} \right)^2 \right]^{1/2} - 1 \right\}, \quad (23)$$

where $c = 2^{1/2}/3$. A nonzero interval in which the ergodic nature is lost occurs at large values of the parameter b and small values of γ , in regions bounded by the condition

$$b > b_c, \quad b_c = \begin{cases} \gamma^2/2c, & 0 < \gamma < 2, \\ 2(\gamma-1)/c, & \gamma > 2. \end{cases} \quad (24)$$

The binodal regime is thus realized under conditions such that the nonlinearity is very influential in comparison with the inhomogeneity (Sec. 4).

According to (22), the dependence of the nonergodic parameter x on the distance ε from the spinodal line is as shown in Fig. 1. We see that an increase in the inhomogeneity parameter γ leads to a weakening of the nonergodic nature, while an increase in the nonlinearity b plays the opposite role. To demonstrate this behavior, we show in Fig. 2 the width ε_g of the nonergodic region and the maximum value x_0 of the nonergodic parameter on the spinodal line $\varepsilon = 0$ as functions of the parameters γ and b .

These results pertain to the isotropic case, in which all the inhomogeneity parameters β_α in expressions (11) for the susceptibilities χ_{0k}, χ_k are assumed to be identical. We turn now to the effect of a uniaxial anisotropy, determined by the value of the parameter $A = \beta_3/\beta_{1,2}$, where $\beta_1 = \beta_2 \neq \beta_3$. Replacing the summation over the Brillouin zone in (21) by an integration over a cylinder of radius k_D and height $2k_D$, in the standard way, we obtain the transcendental equation

$$x = \frac{2b}{\gamma A^2} [f(\delta) - f(\delta_1)],$$

$$f(\delta) = \frac{1}{2} \ln \left(1 + \frac{A^2}{1+\delta^2} \right) + (\delta^2 + A^2)^{1/2} \arctg (\delta^2 + A^2)^{-1/2} - \delta \arctg \delta^{-1}, \quad (25)$$

$$\delta^2 = \gamma^{-1} \varepsilon, \quad \delta_1^2 = \gamma^{-1} (\varepsilon + 6x^3/b).$$

A numerical analysis of this equation shows that the system behaves like the isotropic case of Eq. (22), but the nonergodic nature is manifested much more strongly than in the neglect of dispersion, as above. That this is true can be seen by comparing curves 1 and 2 in Fig. 3, the first of which was

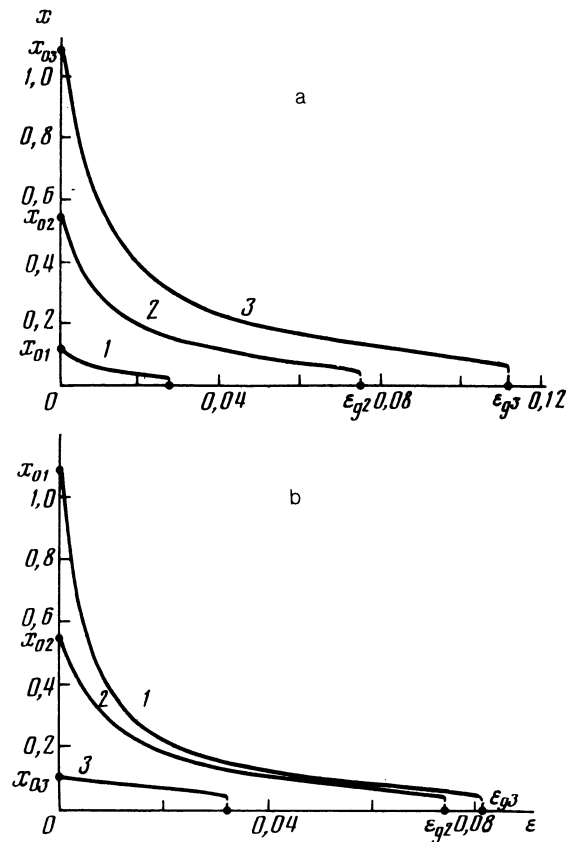


FIG. 1. The dimensionless nonergodic parameter versus the distance from the spinodal. a: For a constant value of the inhomogeneity parameter, $\gamma = 10^{-2}$, and several values of the nonlinearity parameter. 1— $b = 10^{-3}$; 2— $5 \cdot 10^{-3}$; 3— 10^{-2} . b: At a constant value of the nonlinearity parameter, $b = 5 \cdot 10^{-3}$, and at several values of the inhomogeneity parameter. 1— $\gamma = 5 \cdot 10^{-3}$; 2— 10^{-2} ; 3— $5 \cdot 10^{-2}$.

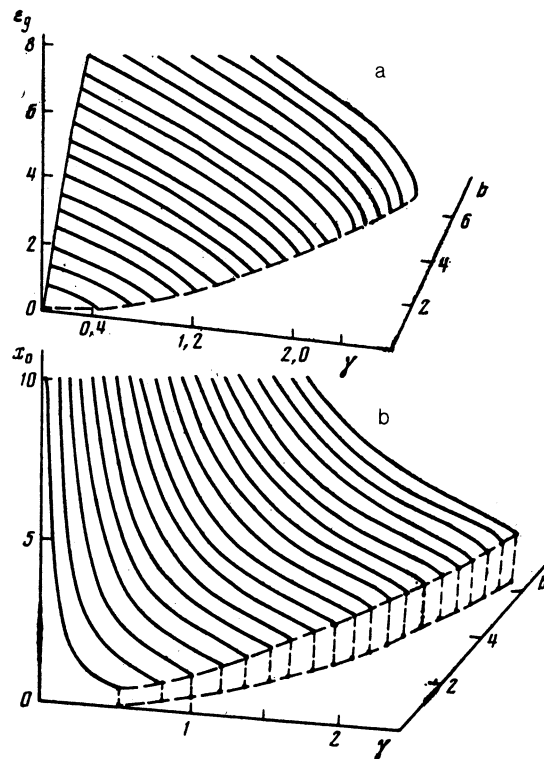


FIG. 2. Relative width of the binodal region, ε_g (a), and maximum value of the nonergodic parameter, x_0 (b), versus the inhomogeneity parameter γ and the nonlinearity parameter b .

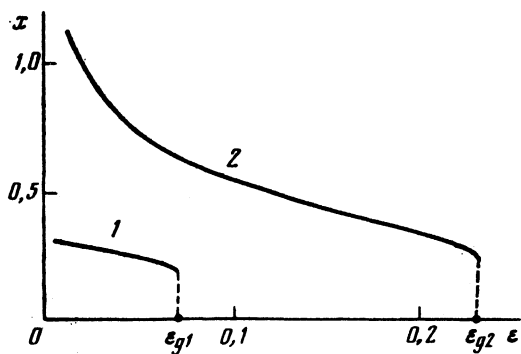


FIG. 3. The nonergodic parameter versus the distance from the spinodal for the isotropic nondispersive case (curve 1) and for the anisotropic case (curve 2; the anisotropy parameter is $A = 0.5$). For both cases, $\gamma = 0.3$ and $b = 0.1$.

found in the approximation $\chi_{ok}^{-1} = \alpha T_s (\varepsilon + \gamma)$, and the second under approximation (11).

It can also be seen from Fig. 4 that the growth of the anisotropy, reflected by a decrease in the parameter $A \leq 1$, leads to an intensification of the nonergodic nature. This intensification occurs in terms of both the value of the parameter x and the width of the temperature region, ε_g . There is also an expansion of the region of the parameters γ and b for which there is a nonergodic state. For example, the critical value γ_g of the inhomogeneity parameter, at which the ergodic nature is restored at once on the spinodal line ($\varepsilon = 0$), increases with increasing anisotropy according to Fig. 5.

4. DISCUSSION OF RESULTS

The basic assumption of the picture drawn here is that the transition from the spinodal regime to the binodal regime causes the stochastic system to lose its ergodic nature. As we know from the example of a spin glass,²² the characteristic feature of a nonergodic system of this sort stems from the degeneracy of the ground state with respect to a local gauge symmetry.²³ The result is a breakup of the phase space into "valleys" corresponding to isolated (or only slightly overlapping) subensembles.¹³ The energies of all these subensembles are approximately the same, and the transformations of the symmetry group send the system from one of these valleys into another.²²

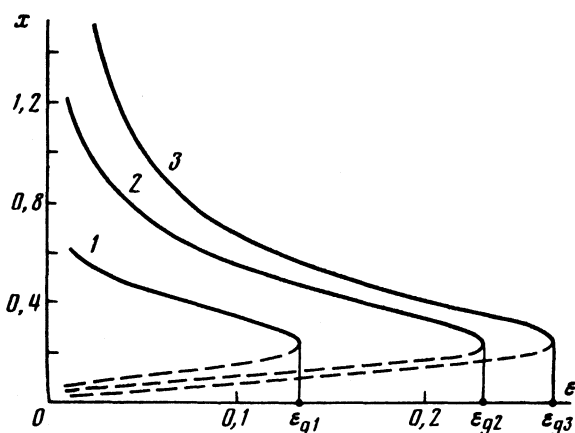


FIG. 4. The nonergodic parameter versus the distance from the spinodal for $\gamma = 0.3$, $b = 0.1$, and several values of the anisotropy parameter: 1— $A = 1$; 2—0.5; 3—0.1.

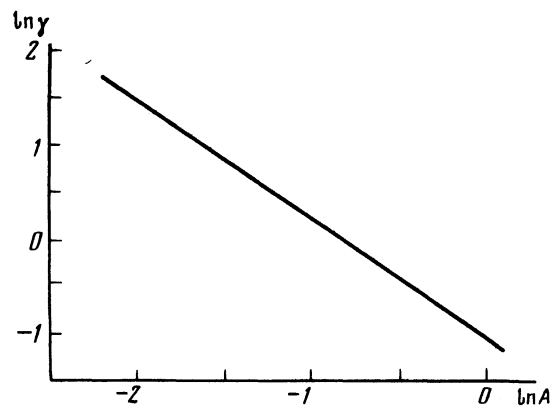


FIG. 5. Extreme inhomogeneity parameter at which a binodal region appears versus the anisotropy parameter ($b = 0.1$).

In spin glasses, the local gauge invariance stems from a frustration of constraints, which stems in turn from the random scatter of overlap integrals.²² Their role is played in our case by the gradient parameters β_α in (1). Since the quantity¹⁵ $\beta \sim \nu a^2$ is determined by the energy ν of the interatomic interaction (a is a lattice constant), it is not difficult to see that frustration of constraints also occurs at the interface. If, for example, we understand "ordering" to mean the appearance of a long-range order in an alloy of stoichiometric composition,¹⁵ then a normal constraint corresponds to the interaction of unlike atoms, and a frustrated constraint to the interaction of like atoms. It is this interaction which is realized at the boundary of an antiphase domain. In contrast with the spin glass, however, in which the values of the overlap integrals have a scatter at the outset, the scatter in the parameters of the interatomic interaction ν in the system under consideration here is a consequence of the formation of the domain walls themselves. The existence of these walls is in turn of a kinetic nature: The phase of the order parameter $\eta(\mathbf{r})$ is fixed in a random way at different points \mathbf{r} , and the growth of nucleating regions of ordered phase is accompanied by the formation of a "foam" of antiphase domains.²⁴

Along the self-consistent approach which we have been taking here, the macroscopic nonergodic parameter in (10) determines the adiabatic susceptibility $\chi_k = \chi_{ok} - \Delta_k/T$ in terms of a given isothermal susceptibility χ_{ok} . The absence of a nonergodic nature under the spinodal causes these two susceptibilities to become the same; when the spinodal is crossed, the adiabatic value decreases abruptly. In the course of further motion from the spinodal toward the binodal, the difference $\Delta\chi_k = \chi_{ok} - \chi_k$ decreases smoothly (Fig. 1) and then drops abruptly to zero on the binodal line. The maximum value of $\Delta\chi_k$ and the width ε_g (of the region between the binodal and the spinodal) decrease with increasing value of the parameter γ (which is determined by the strength ν of the interatomic coupling,¹⁵ and also with decreasing value of the anharmonicity constant b (Fig. 2)). The anisotropy of the interparticle interaction has a substantial effect. A strengthening of this interaction leads to a broadening of the region between the binodal and the spinodal and to an increase in the difference between the adiabatic and isothermal susceptibilities. Figure 5 shows the limiting value γ_g of the nonergodic parameter, at which the binodal splits off from the spinodal, as a function of the anisotropy A .

An important aspect of this heterogeneous system is the weakness of the departure from ergodicity. The reason for this situation is that while the number of frustrated constraints in ordinary spin-glass systems is on the order of the number of nodes, N (Ref. 22), in the case at hand this number is limited by the size of the surface of the domains and is thus smaller by a factor of $s^{-1} \gg 1$. As a result, the total number of valleys in this system is smaller by an equal factor, and since we have $s^{-1} \propto L \propto t^{1/2} \rightarrow \infty$ the nonergodic nature in (19) drops out of the picture as time elapses ($t \rightarrow \infty$), according to Eq. (20).

The presence of the geometric factor $s = 3\delta/L$ in the nonergodic parameter $\Delta \propto s^{1/2}$ and in the nonlinearity parameter $b \propto s^{-1/2}$ specifies the time dependence of the picture we have drawn here, which is determined by the growth of domains. On the one hand, there is a decrease in $\Delta \propto s^{1/2} \propto L^{-1/2} \propto t^{-1/4}$, because of this decrease in the number of valleys in the phase space. On the other hand, the increase in the nonlinearity parameter $b \propto s^{-1/2} \propto L^{1/2} \propto t^{1/4}$ with time means that condition (24) begins to hold only if there are sufficiently large domains. The nonergodic nature is thus manifested only beginning at a characteristic size

$$L_c = \left(\frac{3}{2}\right)^3 \frac{(\beta k_B)^4}{(BT_s)^2} \delta. \quad (26)$$

Since we usually have $L_c/\delta \sim 10 - 10^4$, the meaning of this result is that the thickness δ of the interface must not exceed $\delta_c \lesssim (BT_s)^{1/4} \alpha^{-1/2} a$. In other words, the existence of a nonergodic nature means that the domain size L must be much larger than the wall width δ and that there must be a strong nonlinearity of B against the background of the thermodynamic stimulus α to an ordering.

It can be seen from this discussion that the geometry of the problem has an important effect on the nonergodic conditions. We should point out in this connection that we have been discussing a very simple model of identical domains here. As in a spin glass,²² however, the nonergodic nature may lead to a hierarchical subordination in the ensemble of domains. This situation would imply that, because of the different sizes, the smallest domains are the first to combine as the heterogeneous system evolves; larger domains then combine; and so forth. A corresponding description can be found by a microscopic approach like that of Ref. 25 or on the basis of a phenomenological model.²⁶

The results found here show why the analytic description of the time evolution $C_k(t)$ and $L(t)$ (Refs. 11 and 12) is not the same as is found from the numerical results of Ref. 27. According to an analysis in Refs. 28 and 29, this discrepancy increases significantly after a long time, while it decreases with increasing noise. Along our approach, the measure of this discrepancy is the nonergodic parameter Δ . The magnitude of this parameter determines the difference between the dynamic susceptibility measured in the limit of an infinitely long experimental time and the thermodynamic value, given by a self-consistent theory²⁾ like that of Refs. 11 and 12. The decrease in the parameter $\Delta \propto \alpha$ with the temperature which we see in Figs. 1 and 3 means a decrease in this discrepancy with increasing noise intensity. On the other hand, the decrease in the maximum value of the nonergodic parameter x_0 , and in the width ε_g of the nonergodic region with increasing value of the inhomogeneity parameter $\gamma \propto \beta$

(Fig. 2) means a decrease in this discrepancy with increasing value of the gradient parameter β in (1). The latter increase leads to an increase in the wall with $\delta \propto \beta^{1/2}$. The meaning here is that if this discrepancy is strongly related to the nonergodicity, then the assumption²⁸ that the difference between the analytic and numerical results may decrease as the wall shrinks ($\delta \rightarrow 0$) is unjustified. This conclusion is also supported by the results of Ref. 29, where the use of a model with an infinitely thin wall did not improve the agreement (see Fig. 9 in Ref. 29). The discrepancy between the analytic results^{11,12} and the numerical data^{27,29} may of course also be affected by purely technical factors, such as the small step in the numerical simulation, the size of the modeled system, and so forth.^{28,29}

From a physical standpoint, the decrease in this discrepancy which results from an increase in the noise can be attributed to a restoration of the ergodicity of the system. The transition from the spinodal regime to the binodal regime, represented as a loss of ergodicity, signifies a breakup of the complete statistical ensemble into isolated subensembles.¹³ If the initial conditions of a deterministic system are fixed, it will evolve in the particular valley of phase space which is imposed in this manner. Since a thermodynamic representation of the system, which is used in the self-consistent-field approach,^{11,12} corresponds to an average over all states of the complete ensemble (and thus over all valleys), the behavior of a deterministic system in the absence of a noise, which is determined by the evolution of some subensemble, will deviate to the maximum extent from self-consistent evolution. In the absence of noise, the degree to which the results of the self-consistent theory disagree with experiment will thus be at a maximum. As the noise increases, the scatter in the initial conditions increases. Consequently, several ensembles—the exact number increasing with the noise intensity—will contribute to the description of the evolution of the system. There is, of course, a decrease in the difference between the thermodynamic behavior of the entire ensemble and the dynamic representation²⁶ of the system, which goes into several subensembles because of the scatter in the initial conditions.

From this point of view we also reach an understanding of the effect of the thickness of the interface on the evolution. According to Refs. 28 and 29, the self-consistent theory of Refs. 11 and 12 yields a scaling $C(r, t) \sim 1 - \text{const} L^{-2}$ for a smooth boundary, while for a sharp boundary it yields $C(0, t) \approx 1 - s = 1 - 3\delta/L$ (Ref. 29). This discrepancy is evidently due to the loss of ergodicity, since a smooth boundary is realized in the spinodal region, and a sharp one in the binodal region. Actually, this theory describes a transition from one behavioral regime to another, which occurs upon a change in external conditions. With regard to the self-consistent theory^{11,12} (see also Ref. 28), here the thermodynamic behavior of a system with smooth boundaries, corresponding to evolution throughout the phase space, is being described. As the boundary shrinks, this phase space breaks up into a set of valleys, and a deterministic system without a noise becomes trapped in one of these valleys. Consequently, as the thickness of the interface becomes smaller (and thus the measure of the deviation from ergodicity becomes larger), there should be an increase in the discrepancy between the self-consistent theory^{11,12} and the numerical simulation.^{27,29}

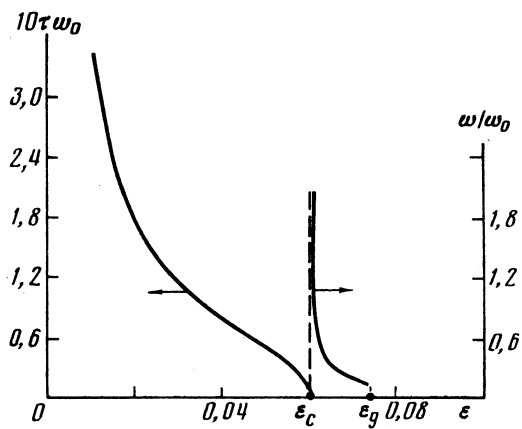


FIG. 6. Dispersion of the hydrodynamic mode responsible for the stratification of the system. Here $\tau = -i/\omega$ is the relaxation time in the dissipative regime.

We note in conclusion that the dispersion relation for the hydrodynamic mode responsible for the stratification of the system exhibits an extremely unusual behavior. While there is a gapless mode of restoration of the inhomogeneity under the spinodal,¹⁵ in the binodal region, for a given wave vector \mathbf{k} , there is a mode

$$\omega = \omega_0 [1 - x(\gamma + \varepsilon)/(1 + \varepsilon)]^{-1}, \quad (27)$$

which follows from (4) and (7) in accordance with the condition $C_{\mathbf{k}}(z) = \infty$. In the immediate vicinity of the spinodal, with $x \geq (1 + \varepsilon)/(\gamma + \varepsilon)$, $\varepsilon < \varepsilon_c$, this mode is dissipative. Further on (at $\varepsilon_c < \varepsilon < \varepsilon_g$), it is reactive, with a gap determined by the width $3\omega_0$. Figure 6 shows the behavior $\omega(\varepsilon)$.

We wish to thank the reviewer for comments regarding the presentation of these results and also for calling our attention to the importance of Ref. 28 to the interpretation of the results.

¹⁾ The case of the conserved parameter (such as the concentration of a decaying solid solution) leads to a more complex self-consistency equation.
²⁾ To avoid any misunderstanding, we should state that the procedure we

have used to impose self-consistency determines the nonergodic parameter Δ , while in Refs. 11 and 12 the procedure determined the order parameter η .

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