The theory of spatiotemporal evolution of nonequilibrium thermodynamic systems

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Contents

Abstract. A review of field theories of the new phase formation kinetics is presented based on the microscopic approach. The evolution of the system quenched across the first-order phase transition point is described in terms of the supersymmetric approach (which equally represents homogeneous and heterophase fluctuations). The dependences of the order parameter, susceptibilities, nonergodicity and memory parameters on the external conditions and the quenching rate are determined. The critical degree of nonequilibrium and the anharmonicity value for the transition from dissipative to reactive regimes (similar to the Belousov – Zhabotinsky reaction) are estimated.

1. Introduction

The main topic of this review is condensed systems subject to qualitative rearrangement (phase transitions in the broad sense) with changes in the external conditions. Strictly speaking, all such systems are nonequilibrium from the thermo-dynamic point of view. However, it is possible to distinguish systems for which the transformation can be described comprehensively in terms of the standard thermodynamic scheme, with a set of state parameters supplemented with the degree of freedom corresponding to the order parameter. It is such systems that are described

by Landau, whose pioneering works stimulated growing interest in systems undergoing phase transition.

Certainly, the original concept of phase transition has been substantially modified in the course of time. Specifically, it became clear that the order parameter determines the amplitude of the hydrodynamic mode, the dependence of which on coordinate and time describes the evolution of the system during transformation. Recent progress in the development of the synergetic concept has demonstrated that phase transition is the result of self-organisation involving not one but at least three hydrodynamic degrees of freedom, which correspond to the order parameter, its conjugate field, and the controlling parameter, respectively. The simplicity of Landau's picture is due to the fact that the field strength is proportional to the order parameter, whereas changes of the controlling parameter (normally reduced to temperature) are independent of the remaining degrees of freedom (but certainly not vice versa). This allows a sole degree of freedom, the order parameter, to be used to describe the quasistatic phase transition.

In systems very far from thermodynamic equilibrium, each of the above modes takes an independent value, and the process of self-organisation is the outcome of competition between the positive feedback between the order parameter and the controlling parameter, and the negative feedback between the order parameter and the conjugate field (the former relationship is the driving force of the transformation and the latter reflects the Le Chatelier principle). Such a trend towards autonomy of the hydrodynamic modes leads to markedly enriched scenarios of behaviour for a strongly nonequilibrium system. The result is that, in addition to relaxation to the equilibrium state, a reactive (auto-oscillatory) regime occurs, of which the most conspicuous manifestation is the Belousov – Zhabotinsky reaction.

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From the phenomenological point of view, the relaxation regime can occur if the relaxation time of the order parameter is much longer than the relaxation times of the remaining degrees of freedom. The auto-oscillation behaviour implies commensurability of characteristic times of changes in the order parameter and the controlling parameter. Given commensurability of relaxation times of all three degrees of freedom, the system may fall into the stochastic regime characterised by the strange attractor. A peculiar situation occurs if the relaxation time of the order parameter is much smaller than the other relaxation times. For example, the largest relaxation time in spin glasses is that of the conjugate field which hereby becomes the cold variable. For this reason, the quenching of such a system from the disordered state results in quenched disorder which is responsible for memory and causes the loss of ergodicity.

The objective of the present review is to examine a concept which allows the above systems to be investigated by the same approach. It will be shown below that the formal basis of this approach is the supersymmetric theory. With the use of this theory, it is possible, on the one hand, to provide a self-consistent description of single and collective excitations and, on the other hand, to associate the system's behaviour at the microscopic level (e.g. corresponding to spins and atoms) with that at the level of macroprocesses which reflect the spatiotemporal evolution of the phase formed during transformation. The review is organised in such a way as to introduce the flow concept of phase transition (Section 2) first in order to enable the reader to follow (without digression to other references) the development of the supersymmetric theory for both a thermodynamic system undergoing relaxation towards equilibrium (Section 3) and a strongly nonequilibrium system (Section 4).

Turning to a brief review of the subject in question, it is worth noting in the beginning that the most common mode of preparing a nonequilibrium system is the infinitely fast quench, from the phase diagram region corresponding to the homogeneous disordered phase, to the ordered region. Phase transition studies of such a system have been a focus of steady interest [9–24] since the papers of Cahn and Hilliard [1–4], Lifshitz [5], Cook [6], and Langer [7, 8] were published. The methodology of these studies differs in accordance with the categorisation of transformation mechanisms into spinodal and binodal. Studies of the spinodal mechanism make use of the wave representation of the order parameter field [9–11]. Athough this representation also involves late stages of the evolution when the macrostructure of the new phase has already formed, the binodal system is most naturally described in terms of an approach other than wave representation. Such an approach examines mature precipitates of the new phase, and the description may be reduced to the representation of the evolution of an ensemble of these precipitates [12–14].

Accordingly, two alternative methods can be used to describe a nonequilibrium thermodynamic system, that is a spinodal mechanism based on the pseudo-Bose representation of an ensemble of order parameter waves, and a binodal mechanism representing the system as a pseudo-Fermi ensemble of heterophase fluctuations. The real physical situation is certainly much more complicated. Indeed, it is quite clear that homogeneous and heterophase fluctuations are equally represented at the initial stage of evolution. Therefore, a consistent theory needs to be supersymmetric. Klein and Batrouni [17] were the first to suggest a formulation of this sort in application to a linearised model [1–4]. However, such a model is lacking in feedback and hence in self-consistency. Besides, Ref. [17] offers only arguments in favour of the supersymmetric field approach and discusses transformation properties of the corresponding action. As regards self-consistent studies based on the variation principle, they are hardly feasible in the framework of scheme [17] because it neglects nonlinearity.

Such a programme has been implemented, based on the standard field approach, in a series of works by Mazenko and coworkers [18–21] who noticed that the wave representation becomes invalid when interphase boundaries appear. These authors proposed, within the framework of this approach, to introduce an additional field l which actually stems from the coordinate representing the kink singularity $\eta = \tanh l$ for the dependence of the order parameter near the interface. This facilitated the development of a noncontradictory self-consistent scheme to describe a heterophase system even though the technique is not free from serious drawbacks. Indeed, fluctuations of the order parameter in each domain of the new phase appear to extend only over a piece of a given domain. Strictly speaking, a heterophase system is nonergodic even though the degree of nonergodicity is small because interatomic bonds are frustrated only at the interphase boundary. Nevertheless, the consistent field scheme becomes inapplicable, and this can probably account for the discrepancy between analytical results [18–21] and numerical experiments [22] (see also Refs [23, 24]).

Another consistent scheme representing these nonergodicity effects of a heterophase mixture has been developed in Ref. [24]. It is based upon the Mori correlation function technique in which the nonergodicity parameter is represented as a residue of the order parameter correlator at zero frequency. This approach allows the difference between static and dynamic susceptibility values to be described and the width of the binodal region to be found; also, it may be used to represent singularities of the hydrodynamic mode responsible for macrostructural evolution of the regular phase. However, this approach fails to provide information available with the Mazenko technique [18–21]. Obviously, it may be because the nonergodicity theory [24] serves as an alternative to the field approach [18].

It has already been mentioned that the cornerstone of the present review is the supersymmetric theory first suggested for the description of thermodynamic systems [25]. The theory is known to facilitate representation of memory effects and ergodicity breaking [26, 27] and is therefore a natural (and, in our opinion, the sole) candidate to be used as a tool for a comprehensive description of the evolution of nonequilibrium thermodynamic systems. In the context of this theory, the initial phase is characterised by latent symmetry (supersymmetry) of the stochastic system [26] which means that the difference between dynamic and quasistatic fluctuations is absent and ergodicity is not broken. Evidently, this behaviour corresponds to the stage which precedes nucleation of the new phase. The equivalence of fluctuations is lost at later stages when the system assumes the heterophase character with broken ergodicity. In other words, the stage of growth and coalescence of new phase precipitates is achieved.

The plan of the review is as follows: In Section 2, we investigate the formation of the new phase macrostructure based on microscopic data, that is the relationship between microlevels and macrolevels of phase transition. Two possible scenarios of such transformation, the continuous (spinodal) and the intermittent (binodal) mechanisms, are considered separately in Sections 2.1 and 2.2 respectively. In the former section, we develop a field theory as applied to the cases of conserved and nonconserved order parameters. Also, this section presents methods for the description of spatiotemporal correlation of the order parameter field as developed by Cahn, Cook, Langer, and Mazenko. It demonstrates that an appropriate correlator breaks down into fluctuation and condensate constituents. The former is characterised by the ordinary correlation length; the latter by the macroscopic length L which determines the characteristic size of the new phase domain. Time dependence $L(t)$ for cases of conserved and nonconserved order parameters as well as for the process of coalescence is deduced from naive considerations. The section provides a detailed description of the Mazenko field scheme which allows the above features to be consistently represented and demonstrates the important role of the sharp interface in this scheme.

Section 2.2 begins with the description of a scheme that allows representation of the critical nucleus of the phase as the soliton solution of the field equation. It is shown that the growth of the homogeneous fluctuation amplitude of the order parameter is accompanied by the slowdown of its movement as a whole, and a 'kink−antikink' pair representing the nucleus is formed in the binodal region. The second half of Section 2.2 provides a brief description of the behaviour of the ensemble of precipitates during the formation of the new phase in the process of decomposition of a solid solution. The stationary distribution function of precipitates in terms of their size is given along with characteristic times and sizes of the evolution of the dispersed system. The section compares two potential coalescence mechanisms: via atom diffusion from small precipitates to bigger ones, and caused by precipitate motion as a whole.

The central part of the present review, Section 3, is devoted to the construction of a supersymmetric scheme for the description of relaxation of a nonequilibrium thermodynamic system. Section 3.1 provides the initial relations to be used to formulate the supersymmetric representation of the problem of evolution of a nonequilibrium thermodynamic system. Its description is based on the Langevin equation, the generating functional of which can conveniently be written in terms of the standard field formulation as an integral over the auxiliary Bose field φ and a conjugate pair of the Grassmannian fields $\bar{\psi}, \psi$. These fields correspond to homogeneous and heterophase fluctuations of the order parameter η whose superposition with constituents $\bar{\psi}, \psi, \phi = \varphi + \dot{\eta}/2\Theta$, where Θ is generalised temperature, forms superfield Φ. This superfield appears to be organised in such a way that a fluctuation $\delta\eta \propto \bar{\psi}$ of the observed order parameter field results from either nucleation or suppression of a heterophase fluctuation $\delta\bar{\psi} \propto \dot{\eta}/2\Theta + \phi$, which is in turn caused by the nonzero ordering velocity $\dot{\eta}$ and field ϕ of homogeneous fluctuations created by the suppression of heterophase fluctuations $\delta\phi \propto -\psi$. Therefore, in contrast with Ref. [17], the superfield components we introduced possess explicit physical interpretations. From the formal point of view, the supersymmetric approach makes it

possible to formulate, in the standard way, the Lagrangian method for the examination of a nonequilibrium system. Specifically, its stochastic functional can be written as a functional integral of the quasi-Gibbs functional of probability of occurrence over initial and final distributions of the order parameter field. The effective thermodynamic potential $\Omega(\eta)$ in the exponent of this functional obeys the supersymmetric conditions $\Omega = 0$, $\delta\Omega/\delta\eta = 0$. In conclusion, Section 3.1 contains data illustrating the use of the Green function technique for the description of the initial and final stages of system evolution, the division into which results in supersymmetry breaking.

Section 3.2 examines the initial stage where there is no difference in the system's behaviour with respect to homogeneous and heterophase fluctuations, because of the absence of order. An method is proposed for construction of the supersymmetric diagram technique, which includes the following terms: the linear term determined by the external field which facilitates creation of one of the domain types; quadratic terms of which the first is of the usual harmonic form, the second is related to spatial heterogeneity, and the third to quenched disorder which increases with increasing quenching rate (apparent only at a later stage); and finally, nonlinear terms determined by the interaction between different superfield components and its anharmonic self-action (in a study of the relaxation time spectrum in Section 3.2, it is represented by a standard model Φ^4 whereas in Section 3.4, on the external field action, it is represented by a nonlinear pendulum). An expression for the pair correlator of a free superfield is calculated from which the supersymmetric structure of the full supercorrelator is found. It is demonstrated that the full supercorrelator in relaxing systems is expanded in three basic operators of the field superspace. Respective components of the supercorrelator represent retarded and advanced Green's functions related to the correlation between fields η and φ as well as a structure factor representing the autocorrelator of the ordering field η. The self-energy part exhibits a similar expansion. As a result, the supersymmetric Dyson equation reduces to three relations between its components, on the one hand, and components of the bare and exact supercorrelators, on the other hand. The system of these equations is closed in the framework of the diagram technique which allows components of the self-energy part to be expressed through the components of the supercorrelator. In this way, the relaxation time of the supersymmetric system has been determined.

The effects of nonlinearity responsible for supersymmetry breaking become more and more important as the fluctuations grow (see Section 3.3). In the energy representation, this is reflected in the appearance of infinitely high barriers which separate regions of superspace with the allowed field values $\bar{\psi}, \psi$ from regions with $\eta \neq 0$, $\varphi \neq 0$. The separation of regions with the allowed values of pseudo-Fermi and pseudo-Bose constituents of the superfield means that their time variations become coherent. For example, a change of a test-field φ will affect changes of the order parameter η at any infinitely remote time $t = \infty$. In other words, there is nonergodicity characterised by the parameter $\Delta = \langle \eta(\infty)\varphi(0) \rangle$, the value of which determines the difference between isothermal and adiabatic susceptibility. As regards coherent changes of the order parameter characterised by the Edwards−Anderson memory para-

meter $q = \langle \eta(\infty)\eta(0) \rangle$, coherence appears only after the separation of the pseudo-Bose components φ and η. This is attributable to the barriers that arise between regions of their allowed values under the quenched disorder conditions dependent on the finite value of quenching rate $\dot{T}$.

With regard to these nonergodicity and memory effects, equations for Green's functions and the structure factor have been rewritten in Section 3.3. Moreover, algebraic equations which define Δ, q, and susceptibility values in relation to $\dot{T}$ and external conditions have been derived from the self-consistency conditions at zero frequency. Specifically, parameters of interatomic interaction were used to obtain an expression for the critical quenching rate $|\dot{T}|_c$ which ensures complete fixation of the system in a disordered state (e.g. vitrification on quenching from a liquid). The memory parameter q was found to be independent of annealing conditions and to exhibit a power-like growth with increasing $|\dot{T}|$. At the same time, the nonergodicity parameter $\Delta \neq 0$ in the region near the spinodal point T_s, which shrinks with increasing quenching rate $|\dot{T}|$. Here, Δ grows for $T \to T_s$ and decreasing $|\dot{T}|$. The effective relaxation time of a nonequilibrium system decreases as the point of ergodicity breaking is approached and quenching rate $|\dot{T}|$ falls.

Section 3.4 examines effects of the external field H responsible for the orientation of ordered phase domains in a given direction (in systems like alloys with ordering, such a direction is given by the fixed phase of concentration waves [16]). It is demonstrated that in the supersymmetric representation this problem is equivalent to the solution of the stationary Schrödinger equation, the Hamiltonian of which is the square of the supercharge. In the context of the quasiclassical approximation, solution of the factorised equation yields the field dependence $j_0(H)$ for the average domain reorientation velocity: the dependence is linear at small H and falls to zero near the limit value of anisotropy field H_0; the temperature dependence $j_0(T)$ has a maximum in the intermediate region $T \sim H$ and falls to zero at the boundaries. A remarkable feature of the domain system in the external field is that the introduction of the field H breaks both the supersymmetry and the fluctuation–dissipation theorem which establishes proportionality between the correlator of fluctuations of the domain reorientation rate and generalised susceptibility $\partial j_0 / \partial H$. This accounts for instability in the domain system at values of H exceeding the characteristic anisotropy field H_0.

Section 3.4 winds up with a study of the coalescence process in which the existence of field H cannot be associated with any external factor but is rather caused by the Laplace pressure, which is caused by the interfacial curvature (the so-called diffusive interaction [12]). The stationary value of H can be determined from the condition of mutual compensation of the microscopic diffusive flow j and the macroscopic flow j_0 which describes rearrangement of the heterophase domain system. In terms of the linear approximation $j \propto H$, a stationary coalescence flow is shown to take nonvanishing values at the temperature separated from the spinodal by a region whose width decreases with increasing surface tension and in the course of time during which oversaturation with the limiting component is becoming smaller.

Section 3.5 presents interpretation of the results obtained from the supersymmetic theory. It is argued that the new structural level must be compared with the corresponding noise strength. Unlike the initial microscopic level, the macroscopic noise is counted from the spinodal point rather than the zero temperature, and its value in relative units is much lower because of the large spatio-temporal scale. Such patterns of noise distribution are responsible for the situation in which the macroscopic level is formed in the near-spinodal region. The width of this region decreases with growing quenching rate. This means that freezing of the system in the disordered ergodic state (in fact, vitrification on quenching from a liquid) is possible at quenching rates exceeding a critical value which lowers with increasing interatomic interaction and growing anharmonicity of the shape of the potential.

Section 3.5 is concluded with an examination of the spatiotemporal properties of the system's behaviour. First, the shape of Green's function for a two-level system is reduced, based on the formalism developed earlier in Section 3.3; this is followed by the determination of the relaxation time at the macrolevel. The relaxation time is shown to increase with distance from the nucleation point of a new level and also with growing quenching rate. The shape of the frequency–wave dependence of Green's function facilitates the representation of known asymptotics of time dependence $L(t)$ of the domain size for nonconserved and conserved order parameters and the coalescence process. Accordingly, the use of the fluctuation–dissipation theorem provides for the description of singularities of the structure factor at the macrolevel.

Sections 3.6 and 3.7 can be joined together in the sense that they both consider quasistatic phase transition. Section 3.6 examines homogeneous and heterophase fluctuations in combination. It demonstrates that, in terms of the super-symmetric approach, the problem is reduced to a self-consistent study of a mixture of noninteracting Fermi and Bose gases. Thermodynamic characteristics peculiar to either fluctuation type have been identified as well as correlation functions of the spatial distribution of the order parameter and interphase boundaries. It is shown that joint examination of the two kinds of fluctuations allows non-physical divergences in the short-wavelength limit to be eliminated and increases the jump of heat capacity at the point of transformation. The structure factor thus obtained has certain properties characteristic of both heterophase and homogeneous systems: in the long-wavelength limit, it reduces to Porod's law which reflects the existence of interfacial boundaries, whereas in the short-wavelength limit, it reduces to the Ornstein–Zernike dependence which describes the distribution of homogeneous fluctuations.

A distinctive feature of Section 3.7 is that the original Landau scheme is further developed to include the fluctu-ation component of the order parameter, besides the condensate one, and to take into account the presence of interfacial boundaries. In contrast to Sections 3.2–3.6 where these components were jointly examined using the correlation technique, Section 3.7 focuses on the investiga-tion into the spatiotemporal dependence of superfield components rather than its moments. Here, the application of the variation principle yields two pairs of linked equations for the Bose and Fermi components respec-tively. It turned out that in the case when condensate (η) and fluctuation (ϕ) constituents are used as the Bose components, one of the first pair of equations establishes the relation (i.e. expresses ϕ through η) whereas the other contains a second time derivative $\ddot{\eta}$. Symmetrisation of this

pair is achieved during transition from component ϕ to field $\varphi = \phi - \dot{\eta}/2T$, which represents the enveloping line of fluctuations of the generalised force. It is shown that in variables η, φ both equations assume the Landau–Khalatnikov form, with component φ contributing to the generalised force for component η; similar contribution for φ is made by the term $\psi\bar{\psi}\eta$ associated with interaction between Bose and Fermi constituents. As regards the second pair of equations (for the Fermi components ψ, $\bar{\psi}$), their primary form is that of mutually conjugate first-order differential equations. The standard combination of these relations leads to the continuity equation for quantity $\rho \propto \psi\bar{\psi}$ which represents the antiphase boundary density.

Analysis of these equations indicates that in the absence of external fields the boundaries are uniformly distributed in space, as expected, and their density remains unaltered in time. Equations for the Bose components can be reduced to the Landau theory only in the simplest case of a homogeneous stationary state. For the homogeneous non-equilibrium state, the time dependence $\eta(t)$ has the form of the Fermi step which represents spinodal ordering kinetics. In the inhomogeneous state $(\rho \neq 0)$, dependence $\eta(t)$ assumes the instanton form corresponding to the domain reorientation process in the ordered phase. The super-symmetric approach is unique in that it may be used not only to represent the kink describing the antiphase boundary but also to determine its thickness and the domain size in relation to boundary density. In other words, the super-symmetric approach includes the mechanism of spontaneous breakdown of translational invariance caused by condensation of the Fermi fields ψ, $\bar{\psi}$. To conclude Section 3.7, expressions for the phase nucleation energy and coefficient of surface tension are presented, as found with an approach analogous to supersymmetric quantum mechanics.

Section 4 is devoted to far-from-equilibrium thermo-dynamic systems. They are different from relaxing systems in that the equation of motion contains not only the first time derivative but also the second one. Accordingly, an arbitrary supercorrelator can be expanded on the basis of six [Eqn (4.6)] rather than three [Eqn (3.25)] operators. Examination in Section 4.1 indicates that such an enlarge-ment allows both the dissipative and the reactive regimes of the system's evolution to be taken into account even in the context of linear approximation. In the linear approx-imation, the spatiotemporal dependence has been found for the supercorrelator whose components give known hydrodynamic expressions for the structure factor and susceptibility (see Section 4.1). Explicit expressions for supersymmetric components of the self-energy part of the superfield propagator are obtained in the second order of the perturbation theory (Section 4.2). In the mean field approximation and in the second order of the perturbation theory, six equations are found which define the spatio-temporal dependence of correlators of different components of the order parameter (see Section 4.3). It is demonstrated that transition from dissipative to reactive behaviour occurs with a rise in the degree of the system's nonequilibrium. The critical degree of excitation of the system and the magnitude of anharmonicity necessary to ensure the reactive regime of behaviour is found in the first order in anharmonicity and in neglect of interatomic interaction.

Section 5, the conclusion, contains a brief review of results which can be obtained only by means of the supersymmetric approach.

2. Mechanisms of new phase formation and evolution

Let us assume that phase transformation is characterised by a complex order parameter,

$$\Psi = \eta \exp(\mathrm{i}\varphi) \,, \tag{2.1}$$

with modulus η and phase φ. Let us further confine ourselves to the examination of the simplest of all possible scenarios of phase transition in the course of which the system is rapidly brought from the disordered phase region $(\eta = 0)$ to the region of the phase diagram where the equilibrium value $\Psi_0 = \eta_0 \exp(\mathrm{i}\varphi_0)$ of parameter (2.1) differs from zero. The objective is to describe the process of spatiotemporal evolution of the system represented by dependence $\Psi(r, t)$ during transition from the nonequilib-rium disordered state to the equilibrium one [28].

It has been demonstrated [15] that two mechanisms of such evolution are feasible. If the system is transferred to the spinodal region of the phase diagram where ordered and disordered states are not separated by energetic barriers (curve 4 in Fig. 1), formation of the ordered phase occurs via a stage of enhanced dynamic (homogeneous) fluctu-ations of the order parameter (2.1). They represent the superposition of spatial waves $\psi_k(t)$ which grow smoothly in time with the amplitude $\eta_k(t) \equiv |\psi_k(t)|$ corresponding to the wavelength $\lambda = 2\pi/k$, where k is the wave vector (Fig. 2a). Quasistatic (heterophase) fluctuations exhibit quite different behaviour (Fig. 2b) in the binodal region of the phase diagram. Because of the energetic barrier between phase states $\eta = 0$ and $\eta = \eta_0$ (curve 3, Fig. 1), the order parameter amplitude remains practically unaltered while fluctuations are generated by a change in phase $\varphi(r, t)$ concomitant with the growth of the characteristic size $R(t)$.

No wonder, the above difference in the nature of fluctuations leads to fundamentally different scenarios of phase formation. The spinodal mechanism underlying the stabilisation of homogeneous fluctuations is described in Section 2.1 whereas the classical mechanism responsible for nucleation and further growth of a new phase through
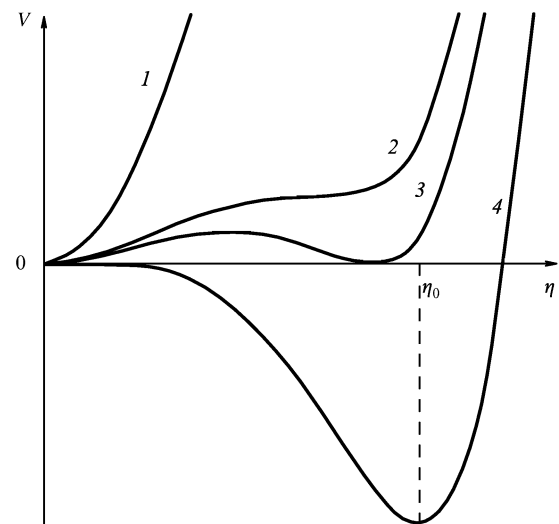

Figure 1. Dependence of synergetic potential on the order parameter at different degrees of excitation of the system.
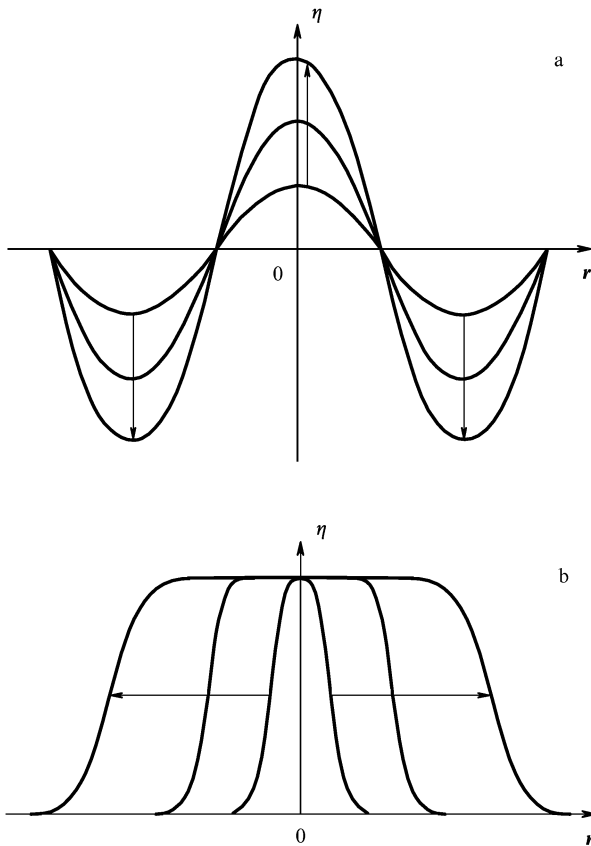
Figure 2. Dynamic (a) and quasistatic (b) fluctuations of the order parameter (arrows indicate direction of changes in the form of fluctuations as it grows) [15].

stabilisation of heterophase fluctuations is described in Section 2.2. Because the latter mechanism occurs in the binodal region of the diagram, it will henceforth be referred to as binodal, for short.

2.1 Spinodal mechanism

The problem to be examined can be reduced to the description of the relaxation of a nonequilibrium disordered phase towards the equilibrium ordered state. The relevant dissipation process is represented by the Langevin equation [29],

$$\dot{\Psi} = -\gamma \frac{\delta \Phi}{\delta \Psi} + \zeta \ , \qquad (2.2)$$

where the point denotes the time derivative, the first term on the right-hand side of the equation (first introduced by Landau and Khalatnikov [30]) describes the determinate contribution in a medium with kinetic coefficient γ, and the second term $\zeta = \zeta(r, t)$ is of stochastic (fluctuating) character. This means that on averaging over the statistic ensemble, the first moment $\langle \zeta(r, t) \rangle = 0$ while the second one may be nonzero. In the simplest case of so-called white noise, the spatiotemporal Fourier transform $\langle |\zeta_k(\omega)|^2 \rangle$ of the second moment does not depend on the wave vector k and frequency ω. In compliance with the fluctuation–dissipation theorem, in the classical limit for fluctuations $\delta \psi_k(\omega) = \psi_k(\omega) - \langle \psi_k(\omega) \rangle$ of the order parameter, $\langle |\delta \psi_k(\omega)|^2 \rangle = (2T/\omega) \operatorname{Im} \chi_k(\omega)$ where $\chi_k(\omega)$ is the susceptibility. In the case of the nonconserved quantity $\psi_k(\omega)$ in the limit k, $\omega \to 0$, expression $\omega^{-1} \operatorname{Im} \chi_k(\omega)$ takes the value

of $\gamma \tau^2$ where τ is the respective relaxation time [16]. As a result, the intensity of white noise fluctuations is defined by the equality

$$\langle \zeta(r, t) \zeta(0, 0) \rangle = 2T \gamma \delta(r) \delta(t) \ , \qquad (2.3)$$

which takes into account the relation $\zeta(r, t) = \tau^{-1} \delta \Psi(r, t)$, in conformity with the form of Eqn (2.2). The physical meaning of condition (2.2) is that fluctuations $\zeta(r, t)$ of the rate of order parameter changes are fully chaotic, that is they occur with zero values of both space and time correlation scales. In a memory-carrying medium, the colour noise regime is achieved, in which δ-functions on the right-hand side of Eqn (2.3) dissipate into peaks whose widths are determined by the said correlation scales.

The expression for the determinate force in Eqn (2.2) is given by the form of the dependence $\Phi[\Psi(r, t)]$ of the functional of the Landau thermodynamic potential on the spatiotemporal distribution of the order parameter. Let us use the standard Ginzburg–Landau expansion (model Ψ^4),

$$\Phi = \int \left(\frac{A}{2} |\Psi|^2 + \frac{B}{4} |\Psi|^4 + \frac{\beta}{2} |\nabla \Psi|^2 \right) dr \ , \qquad (2.4)$$

where the value of the thermodynamic potential is counted from the disordered phase, A, B, β are the expansion parameters defined by the place of the system on the phase diagram, and $\nabla = \partial/\partial r$. Substitution of Eqn (2.4) into Eqn (2.2) yields the time-dependent Ginzburg–Landau equation (in the dimensionless form):

$$\dot{\psi} = \psi(1 - |\psi|^2) + \nabla^2 \psi + \zeta \ , \qquad (2.5)$$

where quantities ψ, ζ, r, t are measured in units $\Psi_0 = (|A|/B)^{1/2}$, $\zeta_0 = \gamma |A| \Psi_0$, $\xi = (\beta/|A|)^{1/2}$, $\tau = (\gamma |A|)^{-1}$ respectively. If the dissipative term is taken into account in conjunction with the dynamic one which is due to the contribution of kinetic energy $\rho |\dot{\Psi}|^2/2$, the left-hand part of Eqn (2.5) will contain the term $(\xi/v\tau)^2 \ddot{\psi}$ where $v = (\beta/\rho)^{1/2}$ is the characteristic velocity and ρ is the effective density. This term is easy to eliminate by substituting the ordinary coordinate r by the running coordinate $r' = r - vt$ in which the velocity $v = vr/r$ determines the shift of dependence $\Psi(r, t)$ as a total. This means that the solution of Eqn (2.5) should looked for with regard to the possibility of its shifting with velocity v given by external conditions.

Eqns (2.2), (2.5) may be applied to nonconserved order parameter cases such as magnetisation, polarisation, long-range order in alloys, etc. The situation is altogether different in the conserved order parameter case, such as concentration in an alloy undergoing decomposition [16]. Here, the stochastic continuity equation:

$$\dot{\Psi} + \nabla j = \zeta \ , \qquad (2.6)$$

should be used instead of the Langevin equation (2.2), and j is expressed through the chemical potential $\mu = \delta \Phi/\delta \Psi$ by the Onsager relation

$$j = -M \nabla \mu \ , \qquad (2.7)$$

where $M > 0$ is the kinetic coefficient (motility). Hence, the initial equation of motion which takes the place of Eqn (2.2) assumes the following form:

$$\dot{\Psi} = \nabla \left(M \nabla \frac{\delta \Phi}{\delta \Psi} \right) + \zeta \ . \qquad (2.8)$$

Thus, the condition of conservation of the order parameter results in the appearance of two additional coordinate

derivatives in the definition of the determinate force and a change of its sign. If mobility M is independent of r, Eqn (2.8) can be presented in the form of

$$\dot{\Psi} = -\hat{\gamma}\frac{\delta\Phi}{\delta\Psi} + \zeta . \qquad (2.9)$$

This equation resembles Eqn (2.2) but contains the operator of the kinetic coefficient $\hat{\gamma} = -M\nabla^2$ which is reduced to the factor γ in the case of the nonconserved order parameter. In dimensionless quantities, the stochastic equation of motion can be written in the universal form:

$$\dot{\psi} = \hat{\Gamma}[(1 - |\psi|^2) + \nabla^2]\psi + \zeta , \quad \hat{\Gamma} = (-\nabla^2)^n , \qquad (2.10)$$

where $n = 0$ and 1 for nonconserved and conserved parameters respectively. At $n = 0$, expression (2.10) turns into (2.5), as expected. In the more complicated case of $n = 1$, all determinate terms on the right-hand side of this expression are preceded by operator $-\nabla^2$. The right-hand part of condition (2.3) undergoes a similar transformation, that is the kinetic coefficient γ for the conserved order parameter is substituted by the operator $\hat{\gamma} = -M\nabla^2$ where $M = D/T$ is the motility of atoms in a diffusive process characterised by coefficient D.

At the onset of decomposition, it is convenient to solve for Eqn (2.10) as the Fourier series

$$\psi(r, t) = \sum_k \psi_k(t)\exp(ik\cdot r) , \qquad (2.11)$$

which corresponds to the superposition of homogeneous fluctuations with amplitudes undergoing time-dependent changes according to the law

$$\psi_k(t) = \psi_k \exp[\alpha(k)t] \qquad (2.12)$$

with increment $\alpha(k)$. When decomposition is of short duration and fluctuations are so small that $|\psi_k(t)| \ll 1$, it is possible to linearise the equation of motion. This procedure makes fluctuations corresponding to different k independent while the increment takes the form of

$$\alpha(k) = k^{2n}(1 - k^2) , \quad n = 0; 1 . \qquad (2.13)$$

Therefore, in the long-wavelength limit restricted (in conventional units) by the reversed correlation length ξ^{-1}, the increment $\alpha(k) > 0$ and all fluctuations have smoothly growing amplitudes, in agreement with Eqn (2.12). Characteristically, the maximum growth rate for a nonconserved parameter ($n = 0$) is reached when decomposition occurs in the entire volume of the specimen ($k \to 0$) whereas the conservation condition $n = 1$ leads to the suppression of the longest-wavelength constituents [here, increment (2.13) amounts to the maximum value at $|k|^2 = 1/2$].

The linearised theory of Cahn and coworkers [1–4] appears to be irrelevant with regard to two aspects. First, it does not take into consideration the stochastic character of decomposition [term ζ in (2.10) is omitted]; second, it disregards interaction between fluctuations (nonlinearity). The first constraint was obviated by Cook [6] who noticed that, for correlator $C_k(t) = \langle|\psi_k(t)|^2\rangle$, the linearised Cahn's equation has the form of $\dot{C}_k(t) = 2\alpha(k)C_k(t)$. In this case, it is easy to guess from the comparison of the left-hand parts of this equation and the noise normalisation condition (2.3) that stochasticity can be taken into account by introducing the term $2T\Gamma(k)$ in which $\Gamma(k) = \gamma$ for the nonconserved and $\Gamma(k) = Mk^2$ for the conserved order parameters.

Therefore, the initial stage of spinodal decomposition is described by the equation

$$\dot{C}_k(t) = 2\alpha(k)C_k(t) + 2T\Gamma(k) , \qquad (2.14)$$

where inhomogeneity is accounted for by the presence of noise. The solution has the form of

$$C_k(t) = C_k(\infty) + [C_k(0) - C_k(\infty)]\exp[2\alpha(k)t] , \qquad (2.15)$$

where the final value is

$$C_k(\infty) = -\frac{T\Gamma(k)}{\alpha(k)} , \qquad (2.16)$$

and the quantity $C_k(0)$ is given by the initial conditions. A drawback of the Cook theory [6] is that substitution of increment (2.13) into Eqn (2.16) results in a formula of the Ornstein–Zernike type, $C_k(\infty) \propto (-1 + k^2)^{-1}$, with the opposite sign before the unit. Since this term corresponds to the lowest power $|\Psi|^2$ in Eqn (2.4), with a negative coefficient A, it is clear that the proper sign can be obtained with regard to nonlinear positive corrections of higher powers.

Such an attempt was first undertaken by Langer et al. [7, 8] who understood that a comprehensive description of the evolution of the system requires the examination of not only the equation of motion for the order parameter $\Psi(r, t)$ but also its stochastic nature as reflected in time-dependent changes of the distribution functional $P[\Psi(r, t)]$. Taking into account fluctuations in the mean field approximation [16] for expansion (2.4) results in the substitution of term 1 in Eqn (2.13) by $[1 - C(t)]$, where $C(t) \equiv C(r = 0, t)$. Therefore, introduction of nonlinearity means that the negative feedback is taken into consideration, which is responsible for a decreased growth rate of fluctuations. For all that, this does not change the sign of the lowest power in increment (2.13) which might cause correlator (2.16) to take the Ornstein–Zernike form, since $C(t) \le 1$ is invariably equal to or less than unity. It turned out [7, 8] that the above reversal of the sign can be accounted for only on the
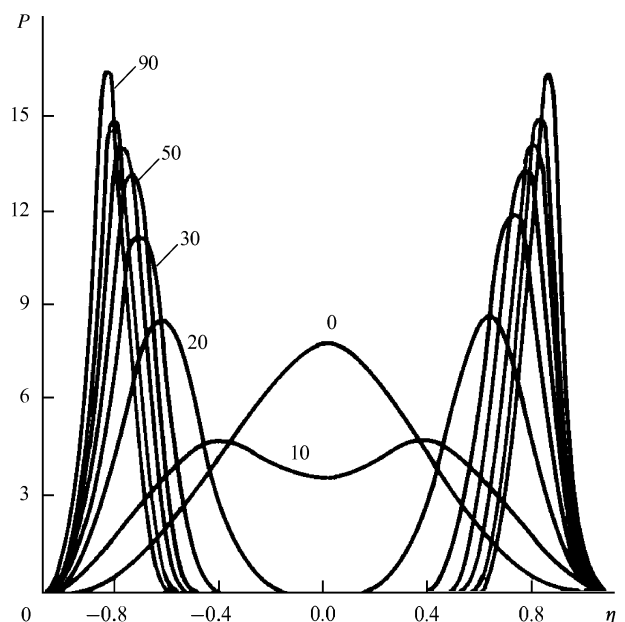

Figure 3. Changes in the order parameter distribution function with time (denoted by figures on the curves, in arbitrary units) [18].

assumption that the distribution $P[\Psi(r, t)]$ changes its form in the course of time as shown in Fig. 3. That is, at the outset of decomposition, the one-mode regime first occurs characterised by a central peak which is later transformed to two symmetric maxima centred on the finite values of the order parameter $\Psi \leqslant \Psi_0$, where Ψ_0 is the equilibrium value.

The physical sense of such transformation of the dependence $P[\Psi(r, t)]$ is in the subdivision of the decomposition process into two stages. At an earlier stage, the central peak whose width characterises the reversed correlation length ξ^{-1} occurs. In this case, the mean value of the order parameter $\eta \equiv \langle \Psi \rangle = 0$, and the only fluctuations $\phi(r, t)$ which are nonzero are those the intensity of which is characterised, in accordance with Eqn (2.3), by the correlator

$$\widetilde{C}_{k=0}(\omega = 0) \equiv \langle |\phi_{k=0}(\omega = 0)|^2 \rangle = 2T\chi\tau , \qquad (2.17)$$

where $\chi = |A|^{-1}$ is susceptibility, and $\tau = (\gamma|A|)^{-1}$ is relaxation time. The formation of two maxima centred on finite values $\pm\Psi(r, t)$ means the appearance at a later stage $(t \gg \tau)$ of nonzero averages, $\eta = \langle \Psi \rangle$. As a result, the entire field $\Psi(r, t)$ is separated into the condensate $[\eta(r, t)]$ and fluctuation $[\phi(r, t)]$ parts as follows:

$$\Psi(r, t) = \eta(r, t) + \phi(r, t) . \qquad (2.18)$$

Accordingly, correlator $C_k = \langle |\Psi_k|^2 \rangle$ has the form†

$$C_k = \eta_0^2 C_k^0 + \widetilde{C}_k ; \qquad C_k^0 = \eta_0^{-2}\langle |\eta_k|^2 \rangle , \qquad \widetilde{C}_k = \langle |\phi_k|^2 \rangle . \qquad (2.19)$$

The condensate constituent C_k^0 has a narrow peak near the point $k = 0$, with the width determined by the inverse domain size. In the r representation, $C^0(r, t) = \eta_0^{-2}\langle \eta(r, t)\eta(0, t) \rangle$ where the order parameter is given by the following equality [31]:

$$\eta(r, t) = \eta_0 \left[1 - \frac{3}{2}\langle \phi^2(r, t) \rangle \right] , \qquad \eta_0^2 = \frac{|A|}{B} . \qquad (2.20)$$

The fluctuation part of the correlator is written in the modified Ornstein–Zernike form

$$\widetilde{C}_k = \frac{2T\chi}{(\widetilde{\Sigma}_k - 1) + \xi^2 k^2} , \qquad (2.21)$$

where the self-energy part,

$$\widetilde{\Sigma}_k = 3 \frac{\eta^2 + \langle \phi^2 \rangle}{\eta_0^2} - 18 \frac{B}{T}\left(\frac{\eta}{\eta_0}\right)^2 \widetilde{\Pi}_k , \qquad (2.22)$$

is given by the polariser

$$\widetilde{\Pi}_k = \int \frac{dk'}{(2\pi)^d} \widetilde{C}_{k-k'}\widetilde{C}_{k'} , \qquad (2.23)$$

where d is the space dimensionality. It can be seen from Eqns (2.19)–(2.23) that in the course of time, the mean

†A characteristic feature of the nonequilibrium system being examined is broken homogeneity of time and space reflected in that the correlator

$$C(r_2, r_1; t_2, t_1) = \langle \psi(r_2, t_2)\psi(r_1, t_1) \rangle \qquad (2.24)$$

depends not only on the differences $r_2 - r_1$, $t_2 - t_1$ but also on the values of $r_1, r_2; t_1, t_2$ proper. However, below we shall need only equal-time correlators of the homogeneous system

$$C(r; t) = \langle \psi(r, t)\psi(0, t) \rangle . \qquad (2.25)$$

order parameter η increases while the fluctuation intensity $\widetilde{C}_k$ is damped. Indeed, the growth of $\eta(t)$ leads to a rise of the self-energy part in Eqn (2.22) which results, starting from time determined by condition $\widetilde{\Sigma}_k(t) = 1$, in the restoration of the correct shape of the Ornstein–Zernike dependence in Eqn (2.21) and is afterwards responsible for the decreased noise strength $\widetilde{C}_k(t)$. Also, it can be seen that the time moment t_0 separating early and late stages of decomposition is given by the condition

$$\widetilde{\Sigma}_k(t) = 1 . \qquad (2.26)$$

Because both signs $\pm\eta$ of the order parameter are equally probable, the total volume of the specimen is broken down at a later stage into domains of size $\sim L$ which greatly exceeds the correlation length ξ.

To summarise, the spatial distribution $\Psi(r)$ of the order parameter is characterised by two scales L, ξ, one of which defines the inhomogeneity of the average constituent $\eta(r)$, and the other that of the fluctuation component $\phi(r)$. At the late decomposition state $(t \gg t_0)$, these constituents become practically independent and their spatial correlation is characterised by a distribution of the Ornstein–Zernike type. However, if the dependence (2.21) for the short wavelength fluctuation component with a finite maximum holds, the maximum for the long-wavelength component must grow indefinitely at $t \to \infty$. In physical terms, it is the manifestation of discrete atomic structure at microscopic distances $\sim \xi$ which is the reason why the momentum conservation law is not satisfied and the Goldstone mode with Bogolyubov's singularity k^{-2} is not achieved. There is quite a different situation at macroscopic distances $\sim L$. Specifically, the presence of the Goldstone mode corresponds here to the absence of an energetic barrier which would interfere with the growth of the domain size $L(t) \to \infty$. However, since $\widetilde{\Sigma}_k(t) > 1$ at $t > t_0$, it follows from Eqn (2.21) that Bogolyubov's singularity for the constituent C_k^0 of correlator C_k can be achieved only if the corresponding self-energy part, Σ_k^0, is smaller than the fluctuation part, $\widetilde{\Sigma}_k$.

In order to establish the relationship between these two constituents, it should be borne in mind that linearisation (2.22) results in the relation $\widetilde{\Sigma}_k = 3C_k$. According to Eqn (2.16), the denominator in expression (2.23) is in fact the increment $\alpha(k)$ taken with the opposite sign, which accounts for the renormalisation of $\alpha(k = 0)$ being three times that reported in Refs [7, 8]. This is because in the former and the latter cases different constituents were determined: $\widetilde{\Sigma}_k$ and Σ_k^0 respectively. It is therefore suggested that fluctuation and condensate components are related through the equality

$$\widetilde{\Sigma}_k = 3\Sigma_k^0 , \qquad (2.27)$$

on which the study reported in Ref. [18] was focused.

Because of relation (2.27), amplification of fluctuations with time accounts, at $t = t_0$, for the equality (2.26) which is never satisfied for the condensate component $\Sigma_k^0(t)$, the growth of which at $t \to \infty$ is restricted by the condition $\Sigma_k^0(t) < 1$. Bearing this in mind, let us introduce the definition of characteristic lengths:

$$\widetilde{\xi} = \xi(\widetilde{\Sigma} - 1)^{-1/2} , \qquad (2.28a)$$

$$L = \xi(1 - \Sigma^0)^{-1/2} , \qquad (2.28b)$$

where $\widetilde{\Sigma}$ is the maximum value of the self-energy part $\widetilde{\Sigma}_k$ at high k, and Σ^0 is the same for Σ_k^0 at low k. Divergence of the renormalised correlation length $\widetilde{\xi}$ at $t = t_0$ means that definitions (2.28a), (2.28b) are applicable only at the stage of decomposition ($t \gg t_0$). Since $\Sigma^0(t) \to 1$, $\widetilde{\Sigma}(t) \to 3$ at $t \to \infty$, the domain size is $L(t) \to \infty$ while renormalisation of the correlation length reduces to factor $\widetilde{\xi}/\xi = 2^{-1/2}$ and is actually not essential.

To summarise, the above scheme gives correct limiting relations at later stages of decomposition: $\widetilde{\xi}(t) \approx 2^{-1/2}\xi$, $L(t) \to \infty$. In order to determine the shape of the dependence $L(t)$, the following qualitative considerations may prove sufficient. In the case of a nonconserved order parameter, the domain size changes at a rate of $\dot{L}(t)$ proportional to the Laplace pressure caused by the curvature of the domain surface $\sim L^{-1}$:

$$\frac{\dot{L}}{a} = \gamma \frac{a}{L}(\sigma a^2), \qquad \gamma \sim \frac{D}{Ta^2}. \tag{2.29}$$

Here, γ is the kinetic coefficient associated with the diffusion coefficient D through the Einstein–Smolukhovsky relation (a is interatomic distance, T is temperature) and σ is the coefficient of surface tension which determines the intensity of the Laplace force. Integration of Eqn (2.29) yields an asymptotic relation for the nonconserved order parameter:

$$L^2 = L_0^2 + D_b t, \qquad D_b \sim \frac{\sigma a^2}{T} D, \tag{2.30}$$

where L_0 is the initial domain size and D_b is the effective diffusion coefficient of the domain boundary.

The conserved order parameter case is more complicated. Here, two stages of decomposition should be distinguished. During the initial stage, limitations imposed by the conservation condition are not apparent for the entire specimen scale. At the coalescence stage, precipitates of size R are created ($R < L$), and their further growth proceeds via coalescence during which small precipitates are 'devoured' by bigger ones. It appears from the equation of motion (2.10) that the conservation condition adds two powers of the coordinate derivative in the expression for the generalised force. This suggests that an equation like Eqn (2.29) may also contain the factor L^{-2} for the domain size, on its right-hand side. The resultant dependence is $L^4 \propto t$. At the coalescence stage, precipitate surfaces are more important than domain boundaries. According to Ref. [12], the size of precipitates changes at a rate $\dot{R}$ which is proportional to the flow $j = D|\nabla\Psi| \approx D\eta_0(R)/R \approx DR_c/R^2$, where D is the coefficient of diffusion, $\eta_0(R) \approx R_c/R$ is the equilibrium order parameter value at the boundary of a precipitate with size R [12], $R_c = 2\sigma\Omega/\eta_0 T$ is the critical radius of the precipitate, Ω is the atomic volume, and η_0 is the equilibrium order parameter value in a heterophase precipitate system. Hence, equality

$$R^3 = R_0^3 + 3DR_c t \tag{2.31}$$

holds true at the coalescence stage, where R_0 is the initial precipitate radius. It is worthwhile to note that a decrease in the exponent of $L^p \propto t$ dependence from 4 to 3 is related to the fact that the rate $\dot{L}$ at the precoalescence stage is proportional to the divergence of flow j whereas during coalescence, the direct connection $\dot{L} \propto \dot{R} \propto j$ holds.

Thus, time dependence of the macroscopic scale of the system at late stages of spinodal decomposition is characterised by asymptotics,

$$L^p \propto t, \tag{2.32}$$

where the count is from the initial value of L_0^p. The exponent p runs through values 2, 3, 4 for the nonconserved order parameter, coalescence process, and the stage preceding it for the conserved parameter, respectively.

The above considerations concern only the qualitative aspect of the phenomenon being examined. They may be useful for the construction of a field theory [18, 19] which allows for an in-depth study of spinodal decomposition. It is represented by the initial correlator $C(r, t)$ of field $\Psi(r, t)$ and its constituents $C^0(r, t)$, $\widetilde{C}(r, t)$ which describe the condensate $[\eta(r, t)]$ and the fluctuation $[\phi(r, t)]$ components of the order parameter (2.18). However, quantity η, which takes values $\pm\eta_0$ at equilibrium, is of the Ising type and cannot be used as an alternating field in the functional integral which forms the basis for examining the field scheme. The primary cause for such a situation is broken ergodicity of the system caused by the formation of domains with different signs of the equilibrium order parameter $\pm\eta_0$. The resulting phase space of the system breaks down into two isolated regions, and it is impossible to carry out functional integration over the field $\eta(r, t)$ simultaneously for both of them. We describe below an approach intended to obviate these peculiarities [19].

This approach is based on the observation that ergodicity breaking is caused by the presence of clear-cut thin domain boundaries near which the spatial distribution of the order parameter along axis l perpendicular to the boundary can be approximated by the kink dependence $\eta(l) = \tanh(l/\widetilde{\xi})$, where the thickness $\widetilde{\xi} < \xi$ is infinitesimal. Therefore, a smooth change of the coordinate l in the limit $\widetilde{\xi} \to 0$ corresponds to the jump-like change of the order parameter during transition from one region of the phase to another. For this reason, Mazenko [19] proposed the introduction of an auxiliary field $l(r, t)$, instead of the Ising field $\eta(r, t)$, to which it is related through the following expression:

$$\eta = \tanh l = \int_0^\infty \frac{\sin(lz)}{\sinh(\pi z/2)} dz, \tag{2.33}$$

where the second equality gives the integral representation of function $\tanh l$. It is convenient to use because it permits easy averaging over field l; the distribution over this field is supposed to be the simplest of the nontrivial distributions, i.e. the Gaussian one. For example, for correlator $C^0(r, t) = \eta_0^{-2}\langle\eta(r, t)\eta(0, t)\rangle$ taken at coincident times t, the following expression can be obtained:

$$C^0(r, t) = \int_0^\infty \int_0^\infty dz_1 dz_2 \frac{\exp[-\Lambda(t)(z_1^2 + z_2^2)/2]}{\sinh(\pi z_1/2)\sinh(\pi z_2/2)}$$
$$\times \sin[\Lambda(r, t)z_1 z_2] \tag{2.34}$$

through correlator $\Lambda(r, t) = \langle l(r, t)l(0, t)\rangle$ of the auxiliary field. The character of this relation can be observed for one-point correlators $\Lambda(t) \equiv \Lambda(r = 0, t)$, $C^0(t) \equiv C^0(r = 0, t)$ at large times t, when the value of $\Lambda(t)$ is high and Eqn (2.34) yields

$$C^0(t) \approx 1 - \left[\frac{2}{\pi\Lambda(t)}\right]^{1/2}. \tag{2.35}$$

The presence of boundaries with thickness $\widetilde{\xi}$ at a distance L means that the equilibrium value $\pm\eta_0$ is achieved in the regions of size $\sim (L - \widetilde{\xi})$ contained in a domain of size $\sim L$. Therefore, a one-point condensate correlator in d-dimensional space has the value of $C^0(t) = \eta_0^{-2}\langle\eta^2(r, t)\rangle \sim [(L - \widetilde{\xi})/L]^d \approx 1 - d\widetilde{\xi}/L$ [19]. By substituting this value into Eqn (2.35), it is possible to find the limiting relation $\Lambda(t) \sim (L/d\widetilde{\xi})^2 \propto L^2(t)$. Thus, correlator $\Lambda(t)$ infinitely growing at $t \to \infty$ plays the role of an evolution parameter of the system (physical time).

Let us turn now to the derivation of equations for the main correlators in question, $C^0(r, t)$ and $\widetilde{C}(r, t)$. For the first of them, it follows from equation (2.10) that

$$\left\langle \eta(2)\left\{\frac{\partial\eta(1)}{\partial t_1} - \widehat{\Gamma}(1)\left[\eta(1) - \eta^3(1) + \nabla_1^2\eta(1)\right]\right\}\right\rangle = 0 . \quad (2.36)$$

Here, arguments $i = 1, 2$ define sets r_i, t_i, operator $\widehat{\Gamma} = (-\nabla^2)^n$, $n = 0$ and 1 for the nonconserved and conserved order parameters. Introduction of a higher power correlator,

$$K(1, 2) = \left\langle\left[\eta(1) - \eta^3(1)\right]\eta(2)\right\rangle , \quad (2.37)$$

yields the initial equation in the form

$$\left[\frac{\partial}{\partial t} - \widehat{\Gamma}(r)\nabla^2\right]C^0(r, t) - \widehat{\Gamma}(r)K(r, t) = 0 , \quad (2.38)$$

where $r = r_2 - r_1$, and coincident times $t_1 = t_2 \equiv t > t_0$ are adopted. Taking the l derivative of Eqn (2.33) twice, it is easy to obtain the relation

$$2K(r, t) = -\left.\frac{\partial C^0(r, t)}{\partial \Lambda(t)}\right|_{\Lambda(r, t)} , \quad (2.39)$$

where the condensate correlator is given by equality (2.34). The physical sense of this equality may be interpreted in the following way. If a monotonically increasing quantity $\Lambda(t) \sim L^2(t)$ is taken as a time parameter of evolution, then the highest-power correlator (2.37) determines a derivative of the condensate correlator $C^0(r, t)$ over the evolution parameter. Moreover, it is possible to introduce the derivative

$$B(r, t) = \left.\frac{\partial C^0(r, t)}{\partial \Lambda(r, t)}\right|_{\Lambda(t)} \quad (2.40)$$

with respect to the spatiotemporal dependence of the auxiliary correlator $\Lambda(r, t)$. As a result, relations (2.38)–(2.40) give equations for the auxiliary correlator:

$$B(r, t)\dot{\Lambda}(r, t) = 2K(r, t)\dot{\Lambda}(t) + \widehat{\Gamma}(r)\left[\nabla^2 C^0(r, t) + K(r, t)\right] . \quad (2.41)$$

Taken together, the relations (2.34), (2.39)–(2.41) constitute a closed system of integrodifferential equations which describe the evolution of the system. In the general case, these equations have only numerical solutions [19]. However, at later stages of decomposition, their analytical inspection is equally possible. Indeed, if the ratio $\Lambda(r, t)/\Lambda(t)$ is independent of time at $t \to \infty$, it is clear that the relationship between correlators C^0, Λ can be reduced to a simple dependence:

$$\Lambda(r, t) = \Lambda(t)\sin\left[\frac{\pi}{2} C^0(r, t)\right] . \quad (2.42)$$

Then, derivatives (2.39), (2.40) assume the forms

$$K(r, t) = \left[\pi\Lambda(t)\right]^{-1}\tan\left[\frac{\pi}{2} C^0(r, t)\right] ,$$

$$B(r, t) = \frac{2}{\pi\Lambda(t)}\left\{\cos\left[\frac{\pi}{2} C^0(r, t)\right]\right\}^{-1} . \quad (2.43)$$

Actually, the relations (2.42), (2.43) are the simplest approximation of the relationship between the condensate and auxiliary correlators at the late stage of decomposition. Their substitution into Eqn (2.38) allows the basic equation of the field theory to be found [19]:

$$\dot{C}^0(r, t) = \widehat{\Gamma}(r)\left\{\nabla^2 C^0(r, t) + L^{-2}\tan\left[\frac{\pi}{2} C^0(r, t)\right]\right\} , \quad (2.44)$$

where the characteristic scale

$$L \equiv (\pi\Lambda)^{1/2} = \sqrt{2}(1 - C^0)^{-1} \quad (2.45)$$

is introduced, in conformity with the limiting relation (2.35). In the case of the nonconserved order parameter where $\widehat{\Gamma}(r) = 1$, Eqn (2.44) is reminiscent of a diffusion equation in which, however, the domain growth does not result in the disappearance of the inhomogeneous term because of tangent divergence at $C^0(r, t) \to 1$.

In the search for a solution in the scaling form

$$C^0(r, t) = F[x(t)], \quad x(t) = \frac{r}{L(t)} , \quad (2.46)$$

let us substitute Eqn (2.46) into (2.44) to obtain

$$-\mu x\cdot\nabla_x F(x) = (-\nabla_x)^n\left\{\nabla_x^2 F(x) + \tan\left[\frac{\pi}{2} F(x)\right]\right\} , \quad (2.47)$$

where

$$\mu = L^{2n+1}\dot{L} . \quad (2.48)$$

The scaling solution (2.46) is acceptable only if the quantity μ in Eqn (2.48) is constant. Then, the definition (2.48) leads to dependence (2.32) where the quantity $p = 3$ corresponding to the coalescence process does not, however, appear for the reason which will be explained below.

At small distances ($r \ll L$), the condensate correlator has the form

$$C^0(r, t) \approx 1 - \alpha\frac{r}{L(t)}, \quad \alpha = \sqrt{\frac{2}{\pi(d - 1)}} , \quad (2.49)$$

where d is the dimensionality of the system. In the Fourier representation, relation (2.49) obeys Porod's law, $C_k^0(t) \propto (kL)^{-(d+1)}$ [32], dictated by the presence of antiphase boundaries. In fact, the association of the dependence (2.49) with the presence of the boundaries is easy to see [19] if the one-dimensional stepped distribution of the order parameter $\eta(r) = \eta_0\sin(r - r_0)$ is assumed, where r_0 is the boundary coordinate. In this case, averaging over its possible values yields the relation:

$$C^0(r) \equiv \frac{\eta_0^{-2}}{2L}\int_{-L}^{+L}\eta(r)\eta(0)\,dr_0 = 1 - \frac{|r|}{L} , \quad (2.50)$$

the form of which is in agreement with Eqn (2.49).

At macroscopic distances $r \gg L$, the form of the correlator $C^0(r, t) = F(x)$, $x = r/L(t) \gg 1$ is determined by the conservation law. In its absence ($n = 0$), Eqn (2.47) gives

$$F \propto x^{-(d-\pi/2\mu)}\exp\left(-\frac{\mu x^2}{2}\right) . \quad (2.51)$$

Hence the following expression holds true for the conserved order parameter $(n = 1)$:

$$F \propto x^{-2d/3} \exp\left(-\frac{3}{8}\,\mu^{1/3}x^{4/3}\right) \cos\left(\frac{3^{3/2}\mu^{1/3}}{8}\,x^{4/3} + \varphi_0\right),$$
(2.52)

where φ_0 is the initial phase. Characteristically, in the former case, there is a monotonous decrease in the correlation of $\pm\eta_0$ values in different domains whereas in the latter, there is oscillating regression.

Now, let us discuss the applicability of Eqn (2.44) to the description of coalescence [19]. It is necessary to remember that in transition from Eqn (2.10) for the full order parameter Ψ to Eqn (2.36) for its condensate constituent η, correlation with the fluctuation component ϕ was totally neglected. This is acceptable in the scaling regime when the precipitate radius R is proportional to the size L of the corresponding domain [it is exactly this situation that takes place at the decomposition stage prior to coalescence, when exponent p in the dependence (2.32) equals 4]. It is well known [33] that transition to coalescence is characterised by the establishment of the coherent regime in the diffuse flow (diffusive interaction). This means that components η, ϕ in the division of the order parameter (2.18) are no longer independent. This results in the appearance of the term $\Pi(r, t)$ in Eqn (2.44), which represents the effect of the stochastic diffusion process on ordering. The form of this term can be found by taking into consideration that the left-hand side of Eqn (2.44) undergoes the following transformation after substitution of the scaling dependence (2.46):

$$\dot{C}^0(r, t) = \dot{x}\nabla_x F(x) = -\frac{\dot{L}}{L}\,r\cdot\nabla C^0(r, t)\,.$$

Hence, it may be expected that the new term of the form

$$\Pi(r, t) = -z(t)r\cdot\nabla C^0(r, t)\,, \quad z(t) = z_0 L^{-p}(t)\,, \quad (2.53)$$

will make a comparable contribution at later stages of decomposition.

In order to find the value of exponent p, one has to turn to the equation for the fluctuation correlator $\widetilde{C}(r, t) = \langle\phi(r, t)\phi(0, t)\rangle$, the relation of which to the condensate constituent $C^0(r, t)$ is reflected in the presence of the term $-\Pi(r, t)$ with the reversed sign. There is one more discrepancy between the equation for $\widetilde{C}(r, t)$ and expression (2.44) which is attributable to the difference between fluctuation and condensate self-energy parts [see Eqn (2.27)]. It has been shown above that this makes the correlation length tend to the finite limit $\widetilde{\xi} = 2^{-1/2}\xi$ as the domain size L grows infinitely, in accordance with Eqns (2.28a), (2.28b). This means that instead of the Laplacian ∇^2 in Eqn (2.44), the equation for the diffusion component $\widetilde{C}(r, t)$ must include the difference $\nabla^2 - \widetilde{k}^2$, where $\widetilde{k} = 2\sqrt{2}\pi/\xi$ is the boundary value of the wave vector. As a result, equations replacing Eqn (2.44) in the description of coalescence can be written as [19]:

$$\left(\frac{\partial}{\partial t} + \nabla^4 + \frac{z_0}{L^p}\,r\cdot\nabla\right)C^0(r, t) = -\frac{\nabla^2}{L^2}\tan\left[\frac{\pi}{2}\,C^0(r, t)\right],\ (2.54)$$

$$\left[\frac{\partial}{\partial t} + \nabla^2(\nabla^2 - \widetilde{k}^2)\right]\widetilde{C}(r, t) = \frac{z_0}{L^p}\,r\cdot\nabla C^0(r, t)\,.$$
(2.55)

In the scaling regime, the condensate constituent has the form of Eqn (2.46), whereas for the fluctuation constituent

$$\widetilde{C}(r, t) = L^{-y}G(x)\,, \quad x = \frac{r}{L(t)}$$
(2.56)

is assumed where $G(x)$ is a certain function, and exponent y remains to be determined. It is obvious, on substituting Eqns (2.46), (2.56) into Eqn (2.55), that at $p > 2$ (conserved order parameter) the left-hand side is dominated by the term with factor $\widetilde{k}^2$ and the equation takes the form

$$-\widetilde{k}^2 L^{-2-y}\nabla_x^2 G(x) = z_0 L^{-p}x\cdot\nabla_x F(x)\,.$$
(2.57)

Hence, the relation

$$y = p - 2\,.$$
(2.58)

At the precoalescence stage, exponent $p = 4$, and $y = 2$ according to Eqn (2.58). The terms of Eqn (2.57) are of the order L^{-4}. At coalescence, $p = 3$, $y = 1$, and Eqn (2.57) acquires a lower order of smallness, L^{-3}. Thus, the establishment of the coherent diffusion regime leads to the crossover of exponent p in Eqn (2.32) from a larger to smaller value (from 4 to 3). This inference is supported by the results of a renormalisation group study [11].

It is worthwhile to note once again that the establishment of the coherent diffusion regime is due to the presence of precipitate boundaries the size R of which is not proportional to the domain size L (the theory in Ref. [12] also assumes $(R/L)^d \ll 1$). This is easy to see from the right-hand part of Eqn (2.54) for the condensate correlator. Indeed, in the absence of sharp precipitate boundaries, those values of coordinate $r \sim L$ are of special importance at which $1 - C^0(r, t) \sim (r/L)^2$, and the right-hand part of Eqn (2.54) has the order L^{-4}. As the boundaries appear, the correlator assumes the nonanalytic form (2.49) with a resulting decrease in the order of the nonlinear term in Eqn (2.54) to L^{-3}. It is this that necessitated substitution of Eqn (2.44) by (2.54).

2.2 Binodal decomposition

Let us first consider the transformation of heterophase fluctuations to the postcritical nucleus of the ordered phase in an uniform nonequilibrium system following its rapid transfer to the binodal region [34]. In this case, phase transition of the first order is achieved. Therefore, expression (2.4) for the thermodynamic potential of the system should be supplemented with the term $(C/6)|\Psi|^6$, in which coefficients A, C, β are assumed to be positive and coefficient B negative [16, 30]. In contrast to the spinodal decomposition case, it is convenient to take the quantity $\eta_0 = (3|B|/4C)^{1/2}$ as the scale of an order parameter change. Then, the thermodynamic potential measured in units of $\beta^{3/2}C^{-1/2}$ assumes the form

$$\Phi = \int\left[\varphi(\psi) + \frac{1}{2}\,|\nabla\psi|^2\right]\mathrm{d}^3r,$$
(2.59)

$$\varphi(\psi) = \frac{\Theta}{2}\,|\psi|^2 - \frac{1}{3}\,|\psi|^4 + \frac{1}{6}\,|\psi|^6,$$
(2.60)

where the parameter $\Theta = 16AC/(3B)^2$, determined by the external conditions, is introduced , and coordinate r is measured in the scale $\xi = (4/3)\sqrt{\beta C}|B|^{-1}$. By varying Eqn (2.59) over the distribution $\psi(r)$, equation

$$\nabla^2\psi = \left(\Theta - \frac{4}{3}\,|\psi|^2 + |\psi|^4\right)\psi$$
(2.61)

is obtained, with first integral

$$\frac{1}{2}|\nabla\psi|^2 = \varphi(\psi),\tag{2.62}$$

taking into account that the integration constant is zero because of the boundary conditions ($\nabla\psi = 0$, $\psi = 0$ at $r = \infty$). If the kinetic energy in expression (2.59) is represented by density $(1/2)|\dot\psi|^2$ where time is measured in units of $(4/3)\sqrt{\rho C}\,|B|^{-1}$ and ρ is the effective density, then the term $-\ddot\psi$ will appear on the left-hand side of Eqn (2.61). By introducing the coordinate $r' = r - vt$ with velocity v, it is easy to obtain the equation of motion in its previous form (2.61) albeit the right-hand side of integral (2.62) will contain the term $-(v^2/2)|\psi|^2$ where the velocity v is measured in units of $(\beta/\rho)^{1/2}$. Integration of the resultant expression yields the final form of the one-dimensional distribution of the order parameter for a heterophase fluctuation [34]:

$$|\psi(r)|^2 = \psi_m^2\Big\{1 + \big[1 - \psi_m^2(2 - \psi_m^2)^{-1}\big]\sinh^2(\zeta r')\Big\}^{-1},$$

$$\zeta^2 = \psi_m^2(2 - \psi_m^2), \quad r' = r - vt,\tag{2.63}$$

where the integration constant ψ_m gives the soliton amplitude (2.63). Its form (Fig. 4) is independent of velocity v and the parameter Θ which characterises external conditions and is given solely by the initial fluctuation amplitude ψ_m. Fig. 4 demonstrates that in the case of the first order phase transition, the order parameter fluctuation becomes heterophasic (i.e. well-defined boundaries appear) as soon as the amplitude attains the maximum value of $\psi_m = 1$.
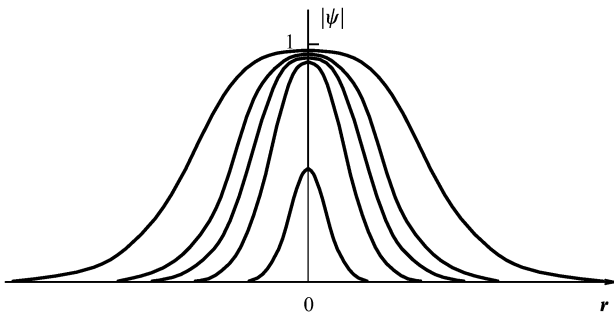

Figure 4. Changes in the soliton profile (2.63) with growing amplitude [34].

To elucidate the conditions facilitating this process, we substitute dependence (2.63) into the boundary condition

$$\varphi(\psi) - \frac{v^2}{2}|\psi|^2 = 0,\tag{2.64}$$

which follows from the generalisation of Eqn (2.62) for the case $v \neq 0$. In physical terms, it obeys the law of soliton energy conservation (for a soliton with velocity v). This leads to the relation

$$\psi_m^2 = 1 - \sqrt{3(v^2 - \Theta) + 1}\tag{2.65}$$

between the free parameters of the problem. Hence, it apears that the soliton's movement results in a decrease of its amplitude with increasing velocity v. Fig. 5 illustrates
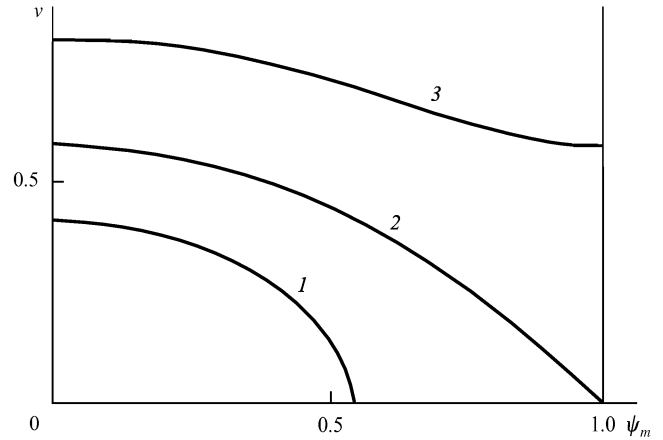

Figure 5. Dependence of soliton velocity on its amplitude (curve *1*: $\Theta < 1/3$, curve *2*: $\Theta = 1/3$, curve *3*: $\Theta > 1/3$) [34].
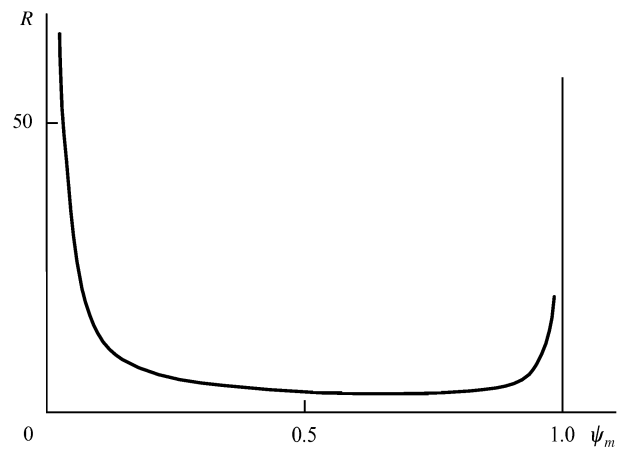

Figure 6. Dependence of soliton width R on the amplitude ψ_m [34].

this dependence for different values of parameter Θ. The value of $\Theta = 1/3$ may be regarded as the boundary one because only moving solitons occur at higher Θ whereas they are likely to stop with growing amplitude ψ_m in the opposite case of $\Theta < 1/3$. Physically, this means that condition $\Theta = 1/3$ defines the binodal line below which the classical mechanism of nucleation and growth is achieved, because only a soliton at rest can serve as the phase embryo.

Fig. 6 represents the dependence of the soliton characteristic width R on amplitude ψ_m as follows from Eqn (2.63). It is clear that the soliton disperses ($R \to \infty$) at both $\psi_m \to 0$ and $\psi_m \to 1$. The former case corresponds to the collapse of a heterophase fluctuation and the latter to soliton transition to the 'kink–antikink' pair. Evidently, this transition represents nucleus formation.

Taking into consideration the energy conservation law (2.62), it is easy to show that the total energy per soliton has the form

$$\sigma = 2\int_{-\infty}^{\infty}\varphi\big[\psi(r)\big]\,\mathrm{d}r\,.\tag{2.66}$$

Integration yields a dependence of the form shown in Fig. 7. Characteristically, the dependence $\sigma(\psi_m)$ in the

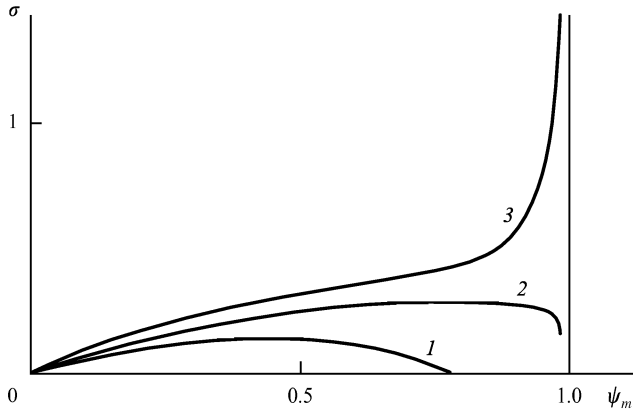**Figure 7.** Dependence of soliton energy on the amplitude (curve *1*: $\Theta < 1/3$, curve *2*: $\Theta = 1/3$, curve *3*: $\Theta > 1/3$) [34].

binodal region $(\Theta < 1/3)$ has a barrier which separates small amplitude values from maximally permissible ones. Above the binodal, the amplitude growth near $\psi_m = 1$ results in an unrestricted rise of the system's energy, as expected.

Nucleation of precipitates of the ordered phase at smoothly falling temperature is described below. The maximum soliton amplitude above the binodal is $\psi_m = 0$, and it follows from equality (2.65) that the velocity of the soliton reduces to the characteristic value of $v_m = \Theta^{1/2}$ (in the case of martensite transformation, v_m is the velocity of sound). Thus, solitons above the binodal represent waves of the ordering, i.e. dynamic fluctuations travelling with velocity $\Theta^{1/2}$. At a binodal point with $\Theta = 1/3$, heterophase fluctuations occur, the velocity v of which is significantly lower than v_m, the difference being the greater the higher the amplitude ψ_m. According to Eqn (2.65), this relation is described by the equality

$$\left(\frac{v}{v_m}\right)^2 = \left(1 - \frac{\Theta_c}{\Theta}\right) + \frac{1}{3}\left(1 - \psi_m^2\right)^2, \qquad (2.67)$$

where $v_m = \Theta^{1/2}$, $\Theta_c = 1/3$. Hence (see also Fig. 5), it appears that at $\psi_m \leqslant 1$, $\Theta \leqslant \Theta_c$, soliton velocity $v \ll v_m$. In other words, a heterophase fluctuation is created when the propagation of a dynamic ordering wave is arrested by the growth of its amplitude.

After having thus examined the nucleation patterns of a single embryo, let us now turn to the examination of the ensemble of nuclei during creation of the new phase. For definiteness, let us consider the decomposition of an oversaturated solid solution where the role of the order parameter is played by the deviation of the concentration from the average. It has already been mentioned that at the first stage, nuclei are formed in the course of fluctuation events. This process is characterised by stabilisation of all the precipitates of size R exceeding the critical R_{c0} value which is defined by oversaturation $\Delta_0 = \overline{C} - C_\infty$ through the equalities

$$R_{c0} = \frac{C_\infty}{\Delta_0} R_s, \qquad R_s = \frac{2\sigma\Omega}{T}, \qquad (2.68)$$

where σ is the coefficient of surface tension, Ω is the atomic volume, T is temperature in energy units, and $\overline{C}$, C_∞ are the average and equilibrium concentrations of the excess component near the plane interface $(R = \infty)$. The

equilibrium distribution of a precritical nucleus is given by the function [30]

$$f_0(R) = f_0(R_{c0}) \exp\left[\frac{4\pi\sigma}{T}(R - R_{c0})^2\right],$$

$$f_0(R_{c0}) \propto \exp\left(-\frac{4\pi\sigma R_{c0}^2}{3T}\right). \qquad (2.69)$$

The critical nuclei are formed by time

$$t_0 = \frac{R_{c0}^3}{DR_sC_\infty} \ln\frac{4\pi DR_sR_{c0}}{\Omega v_a}, \qquad (2.70)$$

where D is the diffusion coefficient and v_a is the characteristic velocity of atom migration. Under stationary conditions, the number of nuclei that reach the postcritical region for unit time in unit volume of the metastable phase is expressed by the equality [13]

$$j = \left(\frac{\sigma}{T}\right)^{1/2}\frac{D\Omega C_\infty}{2\pi R_{c0}^3}f_0(R_{c0}). \qquad (2.71)$$

In the case of considerable initial oversaturation $(\Delta_0 \gg C_\infty)$, further decomposition involves three stages [13]. During the first stage which covers the period from t_0 till time

$$t_1 \approx \frac{\Omega^2 v_a^2}{16\pi^2 D^3 R_s^2 \Delta_0} \exp\left(\frac{4\pi DR_sR_{c0}}{5\Omega v_a}\right), \qquad (2.72)$$

transition of nuclei to the postcritical region [its intensity is characterised by flow (2.71)] has no marked effect on oversaturation $[\Delta(t) \sim \Delta_0]$, and the critical radius R_c is not substantially changed with time:

$$\frac{R_{c0}}{R_c} = 1 - \left(\frac{t}{t_1}\right)^{5/2}. \qquad (2.73)$$

The distribution function $f(R,t)$ has the form shown in Fig. 8 and is in local equilibrium everywhere but in the narrow vicinity of a maximum size R_g which changes at a rate of [13]

$$\frac{dR_g}{dt} = D\Delta_0\frac{R_g - R_{c0}}{R_g^2}. \qquad (2.74)$$

As time $(t > t_1)$ grows further, the amount of the excessive component in precipitates becomes comparable with the amount in the matrix, and oversaturation falls rapidly
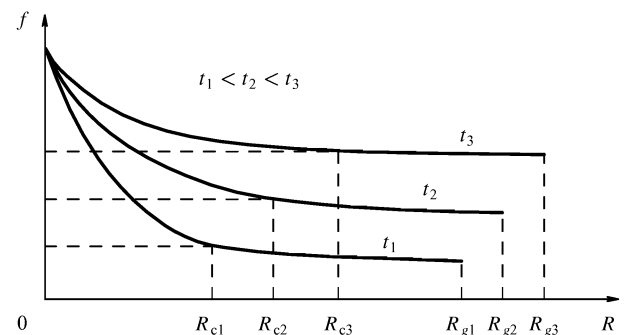

Figure 8. The form of the size distribution function of precipitates at the precoalescence stage $(R_c \ll R_g)$ [13].

while the critical radius R_c increases in agreement with the equality

$$R_c = R_{c0} \exp\left(\frac{At}{t_1}\right), \quad A \sim 1 , \qquad (2.75)$$

and approaches the slowly changing value of R_g. Most of the precipitates are of size $R > R_c$, and their number remains practically unaltered. However, starting from the time

$$t_2 = t_1 \ln \frac{64\pi^3 D^4 R_s^4 C_\infty t_1}{\Omega^3 v_a^3} , \qquad (2.76)$$

condition $R_c \ll R_g$ undergoes perturbation, and some precipitates pass from the postcritical region $(R > R_c)$ to the subcritical one $(R < R_c)$. Concurrently, the process of coalescence begins during which large precipitates 'devour' smaller ones. Here, $R_g = (3/2)R_c$ and the critical radius grows according to the law [12]:

$$R_c^3 = \frac{4}{9} D R_s C_\infty t . \qquad (2.77)$$

Precipitate distribution by size is described by a dome-shaped curve which shifts to larger sizes with time. A detailed description of coalescence can be found in Ref. [12]. Fig. 9 illustrates time dependence of the critical size of the nucleus at all stages of precipitate formation.
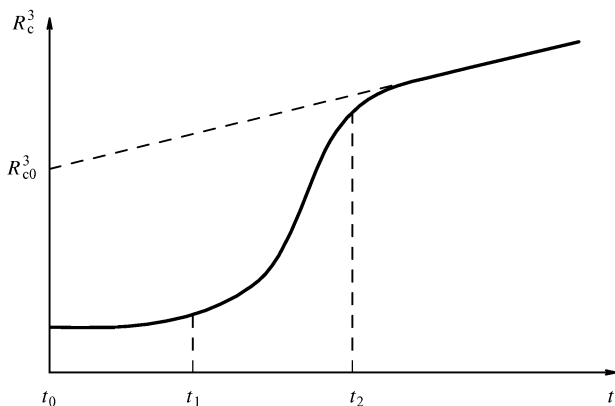

Figure 9. The form of time dependence of the critical volume (t_0 to t_1: the stage of a weak oversaturation change; t_1 to t_2: the stage of exhausted excess component; $t > t_2$: Lifshitz–Slyozov coalescence).

There are more mechanisms of coalescence besides the one described by Lifshitz and Slyozov where atoms of the component that is lacking are supposed to diffuse one by one from smaller to larger precipitates. A dispersed system may also coagulate because of the motion of individual precipitates in the matrix, which is possible if atoms withdraw from layers of the matrix lattice on one side of the inclusion to be incorporated into new layers on the other side. In fact, there are three mechanisms of precipitate diffusional motion. One is diffusive flows of vacancies in the matrix, another is associated with the transport of matrix atoms across precipitates, and the third mechanism is diffusion over the matrix/precipitate interface. In the two former cases, the diffusion coefficient of precipitates D_p has the order $D(\Omega/R^3)$ where D is the value for respective individual atoms and R is the precipitate size. In the case of surface diffusion with coefficient D_s, $D_p \sim D_s(\Omega^{4/3}/R^4)$. Thus, for characteristic size $R \sim 10 - 10^2$ Å, $D_p \lesssim 10^{-3}D$ for

the first and the second mechanisms and $D_p \lesssim 10^{-4}D_s$ when the third mechanism is operative.

The doubling time τ for the average precipitate volume is defined, to an order of magnitude, by the following expressions [16]. At the stage of precipitate growth from a solution $(t_1 < t < t_2)$, it is estimated as $\tau \sim t_1$ given by formula (2.72). When coalescence follows the Lifshitz–Slyozov kinetics [12],

$$\tau \sim \frac{T}{\Omega D\sigma} R^3 . \qquad (2.78)$$

In the case of diffusional motion in the matrix or a precipitate,

$$\tau_v \sim 0.1 \frac{R^5}{\Omega D p} , \qquad (2.79)$$

where p is the precipitate volume fraction. Finally, in the case of surface diffusive currents,

$$\tau_s \sim \frac{R^6}{\Omega^{4/3} D_s p} . \qquad (2.80)$$

Using values characteristic of metallic alloys: $R \sim 10 - 10^2$ Å, $\Omega \sim 10^{-23}$ cm^2, $p \sim 10^{-2}$, $T \sim 10^{-13}$ erg, $\sigma \sim 10$ erg cm^{-2}, one can obtain $\tau_v/\tau \sim 10 - 10^3$, $\tau_s/\tau \sim (10^3 - 10^6)D/D_s$. In other words, when the precipitate motion is limited by volume diffusion of vacancies, coagulation consistent with the Lifshitz–Slyozov kinetics is as a rule especially intensive whereas in the case of surface diffusion, coagulation caused by precipitate motion can prevail [for example, at low values of $R^3(D/D_s)$, i.e. at small sizes R and temperatures T].

3. Application of the supersymmetric approach to the description of relaxation of thermodynamic systems

The difference between the approaches described in Section 2 is obvious from the comparison of known models of homogeneous (dynamic) and heterophase (quasistatic) fluctuations. Fig. 2 shows that the former describe order parameter waves with changing amplitude whereas the latter describe nuclei of the new phase. It has already been mentioned that homogeneous and heterophase fluctuations provide good approximations to the spinodal and binodal ordering mechanisms respectively. It is crucial that homogeneous fluctuations as order parameter waves correspond to collective excitations of the thermodynamic system whereas nearly stepwise heterophase fluctuations correspond to single excitations. Because the actual distribution of the order parameter in the spinodal region is represented by superposition of homogeneous fluctuations, their ensemble may be regarded as the Bose ensemble. A heterophase fluctuation appears to obey the exclusion principle, that is it either occurs or does not at a given point (or rather in a physically small volume). In this sense, an ensemble of heterophase fluctuations is of the pseudo-Fermi type†.

†To avoid misunderstanding, it should be noted that the forthcoming discussion concerns the ensemble of classical objects (phase precipitates) as opposed to ordinary quantum systems like phonons or electron fluid. Therefore, the formal application of quantum statistics to such a system is nothing but a convenient tool previously used, for example, in the microscopic theory of atomic ordering in solid solutions [16].

These considerations outline the basis of the super-symmetric approach to the description of thermodynamic systems which follows.

3.1 Formulation of the problem

Let the process of phase transition be characterised by spatiotemporal dependence of the order parameter $\eta(r, t)$ which may be complex-valued. We shall confine ourselves to examining the simplest of all conceivable scenarios of phase transition during which the system is abruptly transferred from the disordered phase region ($\eta = 0$) to the phase diagram region where the equilibrium value of the order parameter (η_0) is not zero. Then, the evolution of the system is described by the Langevin equation having, in the context of the Ginzburg–Landau model, the form of Eqn (2.10) which can conveniently be presented as:

$$\dot{\eta}(r, t) = f(r, t) + \zeta(r, t) ;$$

$$f = \widehat{\Gamma}[\eta(1 - |\eta|^2) + \nabla^2\eta], \quad \widehat{\Gamma} = (-\nabla^2)^n . \tag{3.1}$$

Here, the term f is conditioned by the determinate force, ζ by fluctuations, and $n = 0$ and 1 for the nonconserved and conserved order parameters respectively. The quantity η in Eqns (3.1) and below is measured in units of the equilibrium value η_0 and the time differentiation, denoted by the point, is referred to the relaxation scale τ given by $\tau = \chi/\gamma$ for the nonconserved parameter (where χ is susceptibility, γ is kinetic coefficient) and by $\tau = \chi\eta_0^2 T/D\xi$ for the conserved parameter (where ξ is correlation length, T is temperature in energy units, D is diffusion coefficient) [16]. The fluctuation term $\zeta(r, t)$ is taken in the simplest form of white noise, the intensity of which is determined by the generalisation of equality (2.3):

$$\langle \zeta(r, t)\zeta(0, 0) \rangle = 2\Theta\widehat{\Gamma}\delta(r)\delta(t) . \tag{3.2}$$

In agreement with Eqn (3.1), quantities ζ, r, and t are measured in units of η_0/τ, ξ, and τ respectively, and the fluctuation intensity parameter $\Theta = (\chi/\eta_0^2\xi^3)T$ for the nonconserved parameter and $\Theta = (\tau/\eta_0^2\xi^2)D$ for the conserved one.

Let us use the method of the stochastic generating functional [25] in terms of the field formulation:

$$Z[u(r, t)] = \left\langle \int \exp\left[\int u(r, t)\eta(r, t)\,dr\,dt\right] \right.$$

$$\times \prod_{(r, t)} \delta[\dot{\eta}(r, t) - f(r, t) - \zeta(r, t)]$$

$$\times \text{Det}\left[\left(\frac{\partial}{\partial t}\right)_{t, t'}\delta(r - r') - \frac{\delta f(r, t)}{\delta\eta(r', t')}\delta(t - t')\right] D\eta(r, t) \right\rangle_{\zeta} , \tag{3.3}$$

where $u(r, t)$ is the arbitrary (test) field, $(\partial/\partial t)_{t, t'}$ is the operator of differentiation over time written in the functional-matrix form, and the determinant represents the Jacobian of transfer from the field $\zeta(r, t)$ to $\eta(r, t)$. Averaging over noise ζ is performed by means of Gaussian integration:

$$\langle\Phi\rangle_\zeta = \int \Phi \exp\left[-\frac{1}{4\Theta\widehat{\Gamma}}\int \zeta^2(r, t)\,dr\,dt\right] D\zeta(r, t) . \tag{3.4}$$

After introduction of the bosonic field $\varphi(r, t)$ and fermionic pair $\bar{\psi}(r, t)$, $\psi(r, t)$ representing Grassmannian variables with the property [35]:

$$\{\bar{\psi}, \psi\} = \{\psi, \psi\} = \{\bar{\psi}, \bar{\psi}\} = 0, \quad \psi^2 = \bar{\psi}^2 = 0 ;$$

$$\int d\psi = \int d\bar{\psi} = 0, \quad \int \psi\,d\psi = \int \bar{\psi}\,d\bar{\psi} = 1 , \tag{3.5}$$

with the use of identities

$$\delta(x) = \int_{-i\infty}^{i\infty} \exp(-\varphi x)\,D\varphi , \tag{3.6}$$

$$\text{Det}\,(A)_{r, r'} = \int \exp\left[-\int\int_{t, t'} \bar{\psi}(r, t)A(r, t; r', t')\right.$$

$$\left.\times \psi(r', t')\,dr\,dr'\,dt\,dt'\right] D\bar{\psi}(r, t)\,D\psi(r, t) , \tag{3.7}$$

for the case of potential forces $f(r) = -\delta V/\delta\eta(r)$, expression (3.3) takes the form of a functional integral of Euclidean field theory [26]

$$Z[u(r, t)] = \int \exp\left[\int u(r, t)\eta(r, t)\,dr\,dt\right]$$

$$\times \exp\left[-\frac{V(\eta_f) - V(\eta_i)}{2\Theta}\right] D\eta_f\,D\eta_i$$

$$\times \int_{\eta_i}^{\eta_f} \exp\left(-\Theta^{-1}\int \mathcal{L}\,dr\,dt\right) D\eta\,D\phi\,D\bar{\psi}\,D\psi \tag{3.8}$$

with the Lagrangian given by

$$\mathcal{L} = -\phi^2 - \phi\frac{\delta V}{\delta\eta(r)} + \frac{\dot{\eta}^2}{4} + \bar{\psi}(r)\left[\frac{\partial}{\partial t} + \frac{\delta^2 V}{\delta\eta(r)\delta\eta(r')}\right]\psi(r') . \tag{3.9}$$

In the derivation of Eqns (3.8), (3.9) and everywhere except Eqns (3.67)–(3.73) below, a new variable $\phi = \varphi + \dot{\eta}/2\Theta$ is introduced instead of φ, $\Theta\phi$ is substituted by ϕ, $\Theta^{1/2}\bar{\psi}$ by $\bar{\psi}$, and $\Theta^{1/2}\psi$ by ψ. In Eqn (3.8), η_i, η_f are the initial and final distributions of field $\eta(r)$ and $V[\eta(r)]$ is the synergetic potential of the nonequilibrium system. A remarkable feature of functional (3.8) is that, because of force potentiality, all irreversibility intrinsic in the dissipative system is contained in the Lagrangian-independent factor $\exp\{-[V(\eta_f) - V(\eta_i)]/2\Theta\}$ which also includes boundary values of the synergetic potential. Hence, it is possible to introduce the nonequilibrium analogue of the thermodynamic potential:

$$\Omega[\eta(r, t)] = \mathcal{F}[\eta(r, t)] - \mathcal{R}[\eta(r, t)] ;$$

$$\mathcal{F} = -\ln\int_{\eta_i}^{\eta_f} \exp\left(-\Theta^{-1}\int \mathcal{L}\,dr\,dt\right) D\eta\,D\phi\,D\bar{\psi}\,D\psi ,$$

$$2\Theta\mathcal{R} = V(\eta_i) - V(\eta_f) , \tag{3.10}$$

where $\mathcal{F}$ plays the role of free energy and $\mathcal{R}$ represents entropy production.

Expressions (3.8), (3.10) allow the variation principle of ergodicity breaking to be formulated [26]. Indeed, because the difference $V(\eta_i) - V(\eta_f)$ is too large for a strongly nonequilibrium system and the range of physically meaningful values $0 < \eta \leqslant 1$ is limited, an essential contribution to the integral over η_i is made only by a small region near

the minimum of functional $\Omega(\eta)$. On the other hand, to prevent divergence of the statistical sum

$$Z \equiv Z(0) = \int \exp\left\{-\Omega[\eta(r,\,t)]\right\} \mathrm{D}\eta_i\,\mathrm{D}\eta_f\,, \qquad (3.11)$$

it is necessary that condition $\Omega(\eta_0) = 0$ which reflects the presence of supersymmetry be satisfied at the point $\eta = \eta_0$ of the functional $\Omega(\eta)$ minimum. Therefore, the steady state is defined by the conditions:

$$\frac{\delta\Omega}{\delta\eta(r,\,t)} = 0 \qquad \text{or} \qquad \frac{\delta\mathcal{F}}{\delta\eta(r,\,t)} = \frac{f(r)}{2\Theta}\,,$$

$$\Omega[\eta(r,\,t)] = 0 \quad \text{or} \quad \mathcal{F}[\eta(r,\,t)] = \mathcal{R}[\eta(r,\,t)]\,, \quad (3.12)$$

where $f(r) = -\delta V/\delta\eta(r)$ is the force conjugate to the order parameter. When these conditions are met simultaneously, a nonequilibrium system is in the ergodic state near which dynamic and quasistationary fluctuations are indistinguishable. Evidently, such a situation is feasible only at small fluctuation amplitudes. As the amplitudes grow with the duration of annealing of a nonequilibrium system, condition $\Omega[\eta(r,\,t)] = 0$ is violated, which leads to the nonstationary nonergodic state with broken supersymmetry. Physically, this may be related to the fact that interface formation resulting from the appearance of heterophase fluctuations indicates the system's transition through the minimum barrier which separates the initial state $\eta_i(r,\,t) = 0$ from the final one $\eta_f(r,\,t) = \eta_0 \neq 0$. However, the homogeneous state itself η_0 is not reached and further evolution of the nonergodic domain system of the ordered phase will proceed as a diffusion of the configuration point across the form of the dependence $\Omega[\eta(r,\,t)]$. The presence of barriers on this dependence is associated with partitioning of the state space into isolated regions of metastable distributions $\eta(r,\,t)$ caused by ergodicity breaking.

Let us introduce a superfield for the quantitative analysis of the problem [25]:

$$\Phi = \eta + \bar{\chi}\psi + \bar{\psi}\chi + \bar{\chi}\chi\phi\,, \qquad (3.13)$$

with the Grassmannian coordinates $\bar{\chi}$, χ satisfying integration rules of the Eqn (3.5) type. It is easy to verify that the Lagrangian (3.9) in the supersymmetric representation takes the canonical form

$$\mathcal{L} = \int \left[\Phi\overline{D}D\Phi + V(\Phi)\right]\mathrm{d}\bar{\chi}\,\mathrm{d}\chi, \qquad (3.14)$$

where covariant superderivatives are introduced:

$$D = \frac{\partial}{\partial\bar{\chi}} + \frac{\chi}{2}\frac{\partial}{\partial t}\,, \qquad \overline{D} = \frac{\partial}{\partial\chi} + \frac{\bar{\chi}}{2}\frac{\partial}{\partial t}\,, \qquad (3.15)$$

which satisfy the commutation relations

$$\left(\overline{D}, D\right) = \frac{\partial}{\partial t}\,, \qquad \left(\overline{D}, D\right)^2 = \frac{\partial^2}{\partial t^2}\,. \qquad (3.16)$$

Operators (3.15) represent supersymmetry group generators with respect to combined shifts in time and the Grassmannian coordinate:

$$\exp(\bar{\varepsilon}D) : \quad \bar{\chi} \to \bar{\chi} + \bar{\varepsilon}\,, \qquad t \to t + \frac{\bar{\varepsilon}\chi}{2}\,;$$

$$\exp(\varepsilon\overline{D}) : \quad \chi \to \chi + \varepsilon\,, \qquad t \to t + \frac{\bar{\chi}\varepsilon}{2}\,. \qquad (3.17)$$

In this case, the constituents η, $\bar{\psi}$, ψ, ϕ of the superfield (3.13) undergo the following transformations:

$$\exp(\bar{\varepsilon}D) : \quad \delta\eta = \bar{\varepsilon}\psi\,, \quad \delta\psi = 0\,, \quad \delta\bar{\psi} = \bar{\varepsilon}\left(\frac{\dot{\eta}}{2} + \phi\right)\,, \quad \delta\phi = -\frac{\bar{\varepsilon}\dot{\psi}}{2}\,;$$

$$\exp(\varepsilon\overline{D}) : \quad \delta\eta = -\bar{\psi}\varepsilon\,, \quad \delta\bar{\psi} = 0\,, \quad \delta\psi = \left(\frac{\dot{\eta}}{2} - \phi\right)\varepsilon\,, \quad \delta\phi = -\frac{\dot{\bar{\psi}}\varepsilon}{2}\,. \qquad (3.18)$$

A peculiar feature of these transformations is that changes of the fields η, ϕ of the collective variables are expressed through the fields $\bar{\psi}$, ψ of the Grassmannian variables which appear to correspond to solitary formations in the form of heterophase fluctuations. Certainly, there is also the inverse relationship between variations in the Grassmannian and collective variables. The physical meaning of transformations (3.18) is that fluctuation $\delta\eta$ of the order parameter field arises (damps) because of the creation (collapse) of precursor precipitates of the ordered phase represented by the Grassmannian variables $\bar{\psi}$, ψ. Fluctuations of field ϕ are related to the phase nucleation (collapse) rate. In turn, fluctuations $\delta\bar{\psi}$, $\delta\psi$ representing creation and collapse of phase precipitates respectively are caused by the nonzero velocity of ordering $\dot{\eta}$ and the presence of fluctuation field ϕ. It is crucial that according to Eqns (3.15)–(3.18), the supersymmetric coordinates $\bar{\chi}$, χ of field (3.13) are associated with time changes. It is therefore appropriate to infer that the transition from the real field of the order parameter $\eta(r,\,t)$ to the superfield $\Phi(\bar{\chi},\chi;r,\,t)$ allows for consideration of the (weak) time dependence associated with the nonequilibrium character of the system.

It follows from the foregoing discussion that evolution of a nonequilibrium thermodynamic system includes two stages. At the initial stage, the system retains supersymmetry, and there is no difference between dynamic and quasistatic fluctuations. Supersymmetry is broken with the appearance of interphase boundaries when the system becomes nonergodic and enters the final stage. Evidently, the system is always supersymmetric in the linear regime. The initial stage in the binodal region is actually the incubation period of phase nucleation. In the spinodal region, the initial stage precedes formation of domain boundaries. The above phenomenological condition $\Omega = 0$ for supersymmetry breaking cannot be constructively used because the form of dependence $\Omega[\eta(r,\,t)]$ remains unknown. Therefore, the microscopic approach based on the correlation function technique should be employed if the system is to be described. When the generating functional (3.3), (3.8) is known, correlation functions are introduced in the following way:

$$S(r,\,t;\,r',\,t') \equiv \langle \eta^*(r,\,t)\eta(r',\,t')\rangle = \left.\frac{\delta^2 Z[u(r,\,t)]}{\delta u^*(r,\,t)\delta u(r',\,t')}\right|_{u=0}\,. \qquad (3.19)$$

This subject will be discussed at greater length in the next section. Here, suffice it to note that in the framework of Green's approach, the loss of supersymmetry is represented by expressions (2.18)–(2.27).

3.2 The initial stage

From the formal point of view, the description of the initial stage $(t < t_0)$ consists in characterisation of the time relaxation range of the dissipative system during transition

to the stationary supersymmetric state with the thermodynamic potential $\Omega = 0$. In order to develop the supersymmetric diagram technique, let us pick out from the Lagrangian relation (3.14) the following:

$$V(\Phi) = \frac{1}{2}(\nabla\Phi)^2 + \frac{1}{2}\,\Phi^2 - H\Phi + V_{\text{int}}(\Phi)\,, \qquad \nabla \equiv \frac{\partial}{\partial r}\,, \quad (3.20)$$

where dimensionless quantities are used (as above). In the absence of $V_{\text{int}}(\Phi)$, the supercorrelator†

$$\widehat{C}(z, z') = \langle\Phi(z)\Phi(z')\rangle\,, \qquad z \equiv (r, t, \chi) \quad (3.21)$$

is reduced to the bare correlator $\widehat{C}^{(0)}(z, z')$. Its form can be defined based on the least action principle corresponding to the Lagrangian (3.14). The resulting Euler equation for the free field has the form

$$\widehat{L}\Phi = 0\,, \qquad \widehat{L} \equiv (1 - \nabla^2) + (\overline{D}, D)\,. \quad (3.22)$$

Then, the bare correlator by definition obeys the equation

$$\widehat{L}(z)\widehat{C}^{(0)}(z, z') = \delta(z - z')\,, \quad (3.23)$$

where the supersymmetric δ-function is introduced

$$\delta(z) \equiv \delta(r, t; \chi) = -\overline{\chi}\chi\delta(r)\delta(t)\,. \quad (3.24)$$

To solve Eqn (3.23), all supermatrices may be represented as a combination of the three basic ones [27]:

$$E(\chi, \chi') = -(\overline{\chi} - \overline{\chi}')(\chi - \chi')\,,$$
$$P(\chi, \chi') = -(\overline{\chi} - \overline{\chi}')(\chi + \chi')\,, \qquad \Lambda(\chi, \chi') = 1\,. \quad (3.25)$$

Taking into consideration the products of arbitrary supermatrices:

$$A(\chi, \chi') = \int B(\chi, \chi'')C(\chi'', \chi')\,\mathrm{d}\overline{\chi}''\,\mathrm{d}\chi''\,, \quad (3.26)$$

it is easy to see that the basic operators $\widehat{E}$, $\widehat{P}$, $\widehat{\Lambda}$ corresponding to supermatrices (3.25) possess the properties:

$$\widehat{E}^2 = \widehat{E}\,, \qquad \widehat{P}^2 = \widehat{E}\,, \qquad \widehat{\Lambda}^2 = 0\,,$$
$$\widehat{E}\widehat{P} = \widehat{P}\,, \qquad \widehat{E}\widehat{\Lambda} = \widehat{\Lambda}\,, \qquad \widehat{\Lambda}\widehat{P} = -\widehat{P}\widehat{\Lambda} = \widehat{\Lambda} \quad (3.27)$$

and thus form a closed basis. Therefore, it is technically more convenient to take all supercorrelators in the operator rather than matrix representation and expand them on the basis of the unit supercorrelator $\widehat{E}$ taken alone, its square root $\widehat{P}$, and fermionic component $\widehat{\Lambda}$. For example, correlator (3.21) has the form

$$\widehat{C} = C_0\widehat{E} + C_1\widehat{P} + S\widehat{\Lambda}\,, \qquad C_\pm \equiv C_0 \pm C_1\,. \quad (3.28)$$

Using expressions (3.13), (3.21), it is easy to find that component $S(r, t)$ represents the structure factor $\langle\eta(r, t)\eta(0, 0)\rangle$ while the expression $C_-(r, t) = -\langle\eta(r_2, t_2)\varphi(r_1, t_1)\rangle$, $r = r_2 - r_1$, $t = t_2 - t_1$ [in which the switch-on moment of the test field $\varphi(r_1, t_1)$ precedes the appearance of the order parameter field $\eta(r_2, t_2)$ caused by this test field] leads after Laplace transformations to the retarded Green function.

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†To find this supercorrelator, it is taken into account that the super-average

$$\langle\Phi\rangle_s \equiv \int\langle\Phi\rangle\,\mathrm{d}\overline{\chi}\,\mathrm{d}\chi = \langle\phi\rangle = 0\,.$$

Hence, the fluctuation nature of the supercomponent ϕ corresponding to collective excitations is self-evident.

Turning back to the definition of the bare supercorrelator $\widehat{C}^{(0)}$, it is necessary to bear in mind that, following transition to the matrix representation of commutator $[\overline{D}, D]$ in (3.22) and the spatiotemporal Fourier transformation, the linear operator $\widehat{L} \equiv 1/\widehat{C}^{(0)}$ takes (after simple but cumbersome calculations) the form:

$$\widehat{L}_k(\omega) = \Theta^{-1}(\tau_k^{-1}\widehat{E} + i\omega\widehat{P} - 2\widehat{\Lambda})\,, \quad (3.29)$$

where $\tau_k = (1 + k^2)^{-1}$ is the dispersion time of relaxation measured in units of τ (thereafter, dependence on the wave vector k will be omitted for brevity, assuming $\tau_k = 1$). Then, solution of Eqn (2.23) yields expansion (3.28) in which components

$$C_\pm^{(0)}(\omega) = \frac{\Theta}{1 \pm i\omega}\,, \qquad S^{(0)}(\omega) = \frac{2\Theta}{1 + \omega^2} \quad (3.30)$$

correspond to the simplest case of Debye relaxation of the dissipative medium.

In order to obtain the full correlator (3.28), the model of field Φ^4 supertheory may be used. In the framework of this model, the action constituent

$$S_{\text{int}} = \int V_{\text{int}}(\Phi)\,\mathrm{d}r\,\mathrm{d}t\,\mathrm{d}\overline{\chi}\,\mathrm{d}\chi \quad (3.31)$$

defined by the interaction superpotential $V_{\text{int}}(\Phi)$ in Eqn (3.20) has the form:

$$S_{\text{int}} = \iint V_{\text{int}}(t, t'; \chi, \chi')\,\mathrm{d}t\,\mathrm{d}t'\,\mathrm{d}\overline{\chi}\,\mathrm{d}\chi\,\mathrm{d}\overline{\chi}'\,\mathrm{d}\chi'\,,$$

$$V_{\text{int}}(t, t'; \chi, \chi') = \frac{1}{2}\iint \Phi(r, t; \overline{\chi})\,\Phi(r, t'; \overline{\chi}')$$
$$\times v(r, r')\Phi(r', t; \chi)\,\Phi(r', t'; \chi')\,\mathrm{d}r\,\mathrm{d}r'\,, \quad (3.32)$$

where $v(r, r')$ is the two-particle potential. After separating explicitly the self-interaction term

$$v(r, r') = \frac{1}{2}\,v(r)\delta(r - r') - w(r - r')\,, \quad (3.33)$$

the following factorisation rule may be assumed in the mean superfield approximation:

$$V_{\text{int}}(t, t'; \chi, \chi') \rightarrow -U(t, \chi)\delta(t - t')(\overline{\chi} - \overline{\chi}')(\chi - \chi')$$
$$+ W(t, t'; \chi, \chi')\;;$$

$$U(t, \chi) = -\frac{1}{4}\int v(r)\,\Phi^4(r, t; \chi)\,\mathrm{d}r\,,$$

$$W(t, t'; \chi, \chi') = -\frac{w}{\Theta}\,C(t - t'; \chi, \chi')$$
$$\times \int \mathrm{d}r\,\Phi(r, t; \chi)\,\Phi(r, t'; \chi')\,,$$

$$w \equiv \int w(r - r')\,\mathrm{d}(r - r')\,, \qquad C(t; \chi, \chi') \equiv C_{k=0}(t; \chi, \chi')\,.$$

$$(3.34)$$

Then, the Dyson equation has the form

$$\widehat{C}^{-1} = \widehat{L} - \widehat{\Sigma} - \frac{2w}{\Theta^2}\,\widehat{C}\,, \quad (3.35)$$

where dependence on frequency ω is not shown explicitly.

Similar to Eqn (3.28), it is convenient to expand in the superbasis $\widehat{E}$, $\widehat{P}$, $\widehat{\Lambda}$ both the self-energy part,

$$\widehat{\Sigma} = \Sigma_0\widehat{E} + \Sigma_1\widehat{P} + \sigma\widehat{\Lambda}\,, \qquad \Sigma_\pm \equiv \Sigma_0 \pm \Sigma_1\,, \quad (3.36)$$

and the supermatrix $\widehat{D} \equiv \widehat{L} - \widehat{\Sigma}$,

$$\widehat{D} = D_0 \widehat{E} + D_1 \widehat{P} + D \widehat{\Lambda}, \qquad D_\pm \equiv D_0 \pm D_1 . \tag{3.37}$$

Then, the following relations for supercomponents of correlators $\widehat{C}$, $\widehat{D}$ can be obtained from Eqns (3.28), (3.30), (3.35)–(3.37) [27]:

$$C_\pm^{-1} - D_\pm + \frac{2w}{\Theta^2} C_\pm = 0 ; \qquad S = - \frac{DC_- C_+}{1 - (2w/\Theta^2) C_+ C_-} ,$$

$$C_0 = \frac{D_0 C_+ C_-}{1 + (2w/\Theta^2) C_+ C_-} , \qquad C_1 = - \frac{D_1 C_+ C_-}{1 - (2w/\Theta^2) C_+ C_-} ;$$

$$D \equiv -\frac{2}{\Theta} - \sigma, \qquad D_\pm \equiv \Theta^{-1}(1 \pm i\omega) - \Sigma_\pm . \tag{3.38}$$

Here, dimensionless quantities are used, and frequency and wave vector dependences are omitted.

The system (3.38) contains basic equations of the microscopic Φ^4 supertheory of dissipative systems. In the linear regime at $v = 0$, $w = 0$, these equations are reduced to formulas (3.30) of the Debye relaxation process. Taking into consideration that the characteristic combination $C_+(\omega) C_-(\omega)$ assumes a maximal real meaning at $\omega = 0$, it is clear from Eqn (3.38) that the point of stability loss in the system is given by the condition

$$\Theta_c^2 = 2wg^2, \qquad g \equiv \lim_{\omega \to 0} C_\pm(\omega) . \tag{3.39}$$

In order to determine the effective relaxation time,

$$\tau_0 = i\Theta \lim_{\omega \to 0} \frac{\partial C^{-1}(\omega)}{\partial \omega} , \tag{3.40}$$

in the nonlinear regime, it is necessary to close system (3.38), expressing the self-energy part through correlators $C_\pm$, S. According to Ref. [36], the contribution of the first and second order diagrams over $v/\Theta \ll 1$ yields [27] [cf Eqn (2.24)]:

$$\Sigma_\pm(t) = -\frac{3v}{\Theta} S(t = 0)\delta(t) + 2\left(\frac{3v}{\Theta}\right)^2 C_\pm(t) S^2(t) ,$$

$$\sigma(t) = \frac{2}{3}\left(\frac{3v}{\Theta}\right)^2 S^3(t) . \tag{3.41}$$

In the supersymmetric state, the fluctuation–dissipation theorem is fulfilled:

$$S(\omega) = \frac{2}{\omega} \operatorname{Im} C_-(\omega), \qquad \sigma(\omega) = \frac{2}{\omega} \operatorname{Im} \Sigma_-(\omega), \tag{3.42}$$

whence (with regard for spectral representation):

$$S(t \to 0) = C_-(\omega \to 0) = g ,$$

$$\sigma(t \to 0) = \Sigma_-(\omega \to 0) = -\frac{3v}{\Theta} g + \frac{2}{3}\left(\frac{3v}{\Theta}\right)^2 g^3 . \tag{3.43}$$

As a result, expression (3.40) for the effective relaxation time in the supersymmetric state takes the form of

$$\tau_0^{-1} = 2\left(\frac{3v}{\Theta}\right)^2 g^4 = \frac{9}{2}\left(\frac{v}{w}\right)^2 \left(\frac{\Theta_c}{\Theta}\right)^2 , \tag{3.44}$$

where the second equality ensues from the definition (3.39) for the quantity Θ_c. Notwithstanding the growth of $\tau_0(\Theta)$ with growing noise strength, there is no divergence of quantity τ_0 obtained at the point of stability loss Θ_c, as is the case with relaxation time $\tau(\Theta)$ of the soft mode. Thus, the system being examined has no infinitely high barriers

separating the supercomponents of field (3.13). It is this fact that accounts for the evolutionary transition (at $t = t_0$) from the homogeneous supersymmetric state to the heterophase nonergodic one.

3.3 The late stage

The late stage in the evolution of an unstable system characterised by the formation of the domain foam of the ordered phase has one more very important new feature, apart from the ergodicity breaking described in the preceding section. At this stage, the system acquires memory. Formally, this is associated with the division of the state space into isolated regions. As a result, the system's evolution even at large times exhibits marked history dependence (e.g. on quenching rate $\dot{T}$) which ensures that the configuration point primarily falls into a given region. From the physical point of view, memory effects are apparent in the explicit dependence of the evolution scenario of an unstable system on the mode of its preparation. For example, in the case of an infinitely rapid quench ($\dot{T} = -\infty$), the domains are so small that the limiting state of the metallic glass type is achieved [37]. At realistically available $\dot{T}$, the glass will instead have polycrystalline structure with domain size L which is the larger the lower $|\dot{T}|$. Finally, for quasistatic cooling ($\dot{T} \to 0$), ordering is primarily achieved in the volume of a single domain of size $L \to \infty$.

Thus, similar to glass, a nonequilibrium thermodynamic system requires for its description the introduction of the Edwards–Anderson parameter which is known to reflect the existence of memory effects [37, 38]. Following Ref. [27], it is easy to demonstrate that these effects arise from the randomness of the field $h(r, t)$ conjugate to the order parameter $\eta(r, t)$. If the average over the sample $\overline{h(r, t)} = 0$, and dispersion $[\overline{h^2(r, t)}]^{1/2} \equiv h \neq 0$, then action (3.32) acquires a quadratic 'striction' addition [27]:

$$S(h) = -\frac{h^2}{\Theta} \iint dt \, dt' \, d\bar{\chi} \, d\chi \, d\bar{\chi}' \, d\chi' \int dr \, \Phi(r, t; \chi) \, \Phi(r, t'; \chi') . \tag{3.45}$$

This results in the appearance of time-independent terms in correlators $S(t)$, $\sigma(t)$, and $D(t)$ that are contained in correlators (3.28), (3.36), and (3.37):

$$S(t) = q_0 + S_0(t), \qquad \sigma(t) = \xi + \sigma_0(t),$$

$$D(t) = -\frac{2}{\Theta} \delta(t) - \sigma_0(t) - \left(\frac{h}{\Theta}\right)^2 - \xi . \tag{3.46}$$

Here, functions $S_0(t)$, $\sigma_0(t)$ correspond to the absence of field ($h = 0$), and nonzero parameters q_0, ξ remain to be determined at $h \neq 0$.

It appears from the above that memory effects arise in the following way. As the quenching rate $|\dot{T}|$ grows, the system's disorder is frozen at microscopic scales which leads to the dispersion of field $h \propto |\dot{T}|^a$ where $a > 0$ is constant. This, in turn, results in the appearance of the nonzero parameter of vitrification $q_0 \propto h^b \propto |\dot{T}|^{ab}$, $b > 0$. Since $S(t \to \infty) \to q_0$, condition $q_0 \neq 0$ means that the system remembers its previous history even at infinite times.

In order to find parameter q_0, expressions (3.46) need to be substituted into the second equality of (3.38). If the time-independent contribution is explicitly separated, then

$$\left(1 - \frac{2w}{\Theta^2} g^2\right) q_0 = \left(\frac{h^2}{\Theta^2} + \xi\right) g^2 . \tag{3.47}$$

Equations for $C_\pm$, S can be obtained by substitution of S_0 and σ_0 for S and σ respectively in equalities (3.38). Moreover, $\Sigma_\pm$, σ_0 should be calculated taking into account q_0 which requires substitution of S from Eqn (3.46) into Eqn (3.41). The result is

$$\Sigma_-(\omega) = 2\left(\frac{3v}{\Theta}\right)^2 q_0^2 C_-(\omega) + \Sigma_-^{(0)}(\omega) ,$$

$$\sigma_0(\omega) = 2\left(\frac{3v}{\Theta}\right)^2 q_0^2 S_0(\omega) + \sigma^{(0)}(\omega) ;$$

$$\Sigma_-^{(0)}(t) = -\frac{3v}{\Theta}(g + q_0)\delta(t) + 2\left(\frac{3v}{\Theta}\right)^2$$
$$\times C_-(t)S_0(t)\big[2q_0 + S_0(t)\big] ,$$

$$\sigma^{(0)}(t) = 2\left(\frac{3v}{\Theta}\right)^2 S_0^2(t)\left[q_0 + \frac{1}{3}S_0(t)\right] ;$$

$$\xi = \frac{2}{3}\left(\frac{3v}{\Theta}\right)^2 q_0^3 . \tag{3.48}$$

In Eqn (3.48), terms linear in $C_-(\omega)$, $S_0(\omega)$ are separated because they have to be omitted in the Dyson equation (3.35). Following these substitutions, system (3.38) in the ω–representation reduces to

$$C_\pm^{-1} - D_\pm^{(0)} + 2\left[\frac{w}{\Theta^2} + \left(\frac{3v}{\Theta}\right)^2 q_0^2\right]C_\pm = 0 ;$$

$$\left\{1 + 2\left[\frac{w}{\Theta^2} + \left(\frac{3v}{\Theta}\right)^2 q_0^2\right]C_+C_-\right\}C_0 = D_0^{(0)}C_+C_- ,$$

$$\left\{1 - 2\left[\frac{w}{\Theta^2} + \left(\frac{3v}{\Theta}\right)^2 q_0^2\right]C_+C_-\right\}C_1 = -D_1^{(0)}C_+C_- ,$$

$$\left\{1 - 2\left[\frac{w}{\Theta^2} + \left(\frac{3v}{\Theta}\right)^2 q_0^2\right]C_+C_-\right\}S_0 = -D^{(0)}C_+C_- ;$$

$$D^{(0)} \equiv -\frac{2}{\Theta} - \sigma^{(0)} ,$$

$$D_\pm^{(0)} \equiv \Theta^{-1}(1 \pm i\omega) - \Sigma_\pm^{(0)} . \tag{3.49}$$

Similar to the early stage, expressions for $C_1(\omega)$, $S_0(\omega)$ have a pole which contains the memory parameter q_0, in contrast to Eqn (3.38). Substitution of expression (3.48) for ξ in Eqn (3.47) which defines the memory parameter yields

$$q_0 = 3^{-1/3}\left(\frac{h}{2v}\right)^{2/3} . \tag{3.50}$$

Thus, the quenched disorder $h \propto |\dot{T}|^a$ leads to the power-like growth of the memory parameter $q_0 \propto |\dot{T}|^{2a/3}$.

While switching on memory is reflected, according to Eqn (3.46), in the appearance of long–lived autocorrelations $S(t) = \langle\eta(t)\eta(0)\rangle$ of the order parameter, nonergodicity effects are apparent in the behaviour of the retarded Green function $C_-(t) = -\vartheta(t)\langle\eta(t)\varphi(0)\rangle$ which determines the response of the real field $\eta(r, t)$ to the test-field $\varphi(r, t)$ $[\vartheta(t) = 1$ at $t > 0$, $\vartheta(t) = 0$ at $t < 0]$. Similar to Eqn (3.46), nonzero terms appear in the limit $t \to \infty$:

$$C_-(t) = C_{-0}(t) + \Delta , \quad \Sigma_-(t) = \Sigma_{-0}(t) + \rho , \tag{3.51}$$

where $G_{-0}(t)$, $\Sigma_{-0}(t)$ are the ergodic constituents vanishing at $t \to \infty$ and Δ, ρ are the nonergodicity parameters to be determined. Since $\Delta S_0 \approx 0$, Eqns (3.48), (3.49) still hold after $C_\pm$ is substituted by $C_{\pm 0}$. Taking into account that in the limit $t \to \infty$ the full correlator $C_-(t) = \Theta\chi_0$ is reduced to isothermal susceptibility χ_0 and the ergodic constituent $C_{-0}(t \to \infty) = g$ to adiabatic susceptibility $\chi = g/\Theta$, it is possible to obtain from Eqn (3.51) the following [39]:

$$\frac{\Delta}{\Theta} = \chi_0 - \chi , \tag{3.52}$$

where isothermal susceptibility χ_0 is independent of temperature (unlike the initial thermodynamic susceptibility χ) but alters substantially with changes in $h \propto |\dot{T}|^a$.

In order to determine parameter Δ, let us substitute the elongated correlators (3.46), (3.51) into the self-consistency condition (3.41). In this case, relations (3.48) will be supplemented with

$$\rho = 2\left(\frac{3v}{\Theta}\right)^2 q_0^2 \Delta . \tag{3.53}$$

Separating constituents singular at $\omega = 0$ in the initial system of equations (3.38) for the correlator $S(\omega) = 2\pi q\delta(\omega) + S_0(\omega)$, with due regard for Eqns (3.47), (3.52), results in the following equations for quantities χ_0, q_0:

$$q_0\big[1 - 2(w + 6v^2 q_0^2)\chi_0^2\big] = h^2\chi_0^2 , \tag{3.54}$$

$$2\big[w + (3vq_0)^2\big]\chi_0^2 = 1 . \tag{3.55}$$

For the complete description of the system, it should be borne in mind that in addition to two susceptibilities: macroscopic $[\chi_0 = (g + \Delta)/\Theta]$ and microscopic $(\chi = g/\Theta)$, ergodicity breaking $(\Delta \neq 0)$ gives rise to the appearance of two memory parameters: the macroscopic Edwards–Anderson parameter q_0 and the microscopic parameter q. The following equations can be found for quantities g, q by analogy with Eqns (3.54), (3.55) but using the ergodic system (3.49) instead of the complete one (3.38):

$$q\left\{1 - 2\left[\frac{w}{\Theta^2} + \frac{2}{3}\left(\frac{3v}{\Theta}\right)^2 q^2\right]g^2\right\} = \left(\frac{h}{\Theta}\right)^2 g^2 ; \tag{3.56}$$

$$2\left[\frac{w}{\Theta^2} + \left(\frac{3v}{\Theta}\right)^2 q^2\right]g^2 = 1 . \tag{3.57}$$

To close the system of Eqns (3.54)–(3.57), it should be supplemented with equations

$$(\Theta^{-1} - \alpha_0) - 2\left[\frac{w}{\Theta^2} + \left(\frac{3v}{\Theta}\right)^2 q_0^2\right]\Delta - 2\frac{w}{\Theta^2}g = \frac{1}{g + \Delta} ,$$
$$\alpha_0 = \alpha(q_0) ; \tag{3.58a}$$

$$(\Theta^{-1} - \alpha)g - 2\frac{w}{\Theta^2}g^2 = 1 , \quad \alpha = \alpha(q) ; \tag{3.58b}$$

$$\alpha \equiv -\frac{3v}{\Theta}(q + g) + \frac{2}{3}\left(\frac{3v}{\Theta}\right)^2\big[(q + g)^3 - q^3\big] , \tag{3.58c}$$

which can be obtained given self-consistency of expressions (3.38), (3.48), (3.49) for Green's functions $C_{0\pm}(\omega)$ in the limit $\omega \to 0$. Actually, expressions (3.54), (3.56), (3.58a)–(3.58c) are the Sherrington–Kirkpatrick equations for a nonequilibrium system, as they are in spin glasses [38],

whereas equalities (3.55), (3.57) give the condition of ergodicity breaking of the Almeida–Tauless type. Letters a, b in the numbers of formulas denote macrolevels and microlevels respectively. Thus, expressions (3.55), (3.57) define the gapless mode of supersymmetry restoration at macrolevel and microlevel.

According to Eqns (3.50), (3.52), (3.54), (3.56), (3.57), the macrolevel parameters q_0, χ_0 and microlevel characteristics q, g are independent of temperature Θ and quenched disorder h respectively. Hence

$$q(\Theta, h) = q_g(\Theta), \quad g(\Theta, h) = g_g(\Theta), \qquad (3.59)$$

where q_g, g_g are values of quantities q, g on the line of ergodicity breaking $h_0(\Theta)$ defined by equality (3.58b) [values of q_g, g_g are given by the solutions of Eqns (3.56), (3.57)]. Assuming the dependence $h_0(\Theta)$ to be known, Eqns (3.54)–(3.57) may be used to obtain

$$q_0^3 = \frac{1}{3}\left(\frac{h}{2v}\right)^2, \quad \chi_0^{-2} = 2\left[w + (3vq_0)^2\right] ;$$

$$q^3 = q_g^3 = \frac{1}{3}\left(\frac{h_0}{2v}\right)^2, \quad g^{-2} = g_g^{-2} = 2\Theta^{-2}\left[w + (3vq_g)^2\right] . \qquad (3.60)$$

Analysis of the above relations indicates that the characteristic point Θ_c given by the condition $h_0(\Theta) = 0$ falls into the physical region of values only if the parameter $\zeta = 8w - 1 > 0$ is small. This parameter characterises the ratio of the interaction force to 'the force of one-particle repulsion' characterised by the inverse thermodynamic susceptibility χ^{-1}. For this reason, the condition $\zeta \ll 1$, reminiscent of the situation of displacement-type transitions [16], implies almost complete compensation of the above constituents. In this case, the smallness parameter is ζ rather than v even in the absence of smallness of the anharmonicity constant v. With this in mind, one has, near Θ_c,

$$\Theta_c = \frac{w^{1/2}}{3\sqrt{2v}}\zeta \approx \frac{\zeta}{12v}, \quad 0 < \zeta \equiv 8w - 1 \ll 1 ;$$

$$h_0 = \frac{v}{3\sqrt{2}}\left(\frac{\zeta|\varepsilon|}{v}\right)^{3/2}, \quad \varepsilon \equiv \frac{\Theta - \Theta_c}{\Theta_c} ;$$

$$q_0 = \left(\frac{h^2}{12v^2}\right)^{1/3}, \quad q = q_g = \left(\frac{h_0^2}{12v^2}\right)^{1/3} = \frac{\zeta|\varepsilon|}{6v} . \qquad (3.61)$$

Accordingly, the following expressions for susceptibilities and irreversible response near the line of ergodicity breaking $h_0(\Theta)$ are obtainable from Eqns (3.60), (3.52):

$$\chi_0 = \frac{1}{(2w)^{1/2}}\left[1 + \frac{(3vq_0)^2}{w}\right]^{-1/2} \approx 2\left[1 - \zeta^2|\varepsilon|^2\left(\frac{h}{h_0}\right)^{4/3}\right],$$

$$\chi = \frac{1}{(2w)^{1/2}}\left[1 + \frac{(3vq)^2}{w}\right]^{-1/2} \approx 2\left(1 - \zeta^2|\varepsilon|^2\right), \qquad (3.62)$$

$$\frac{\Delta}{\Theta} \approx \frac{(3vq_g)^2}{(2w)^{3/2}}\left[1 - \left(\frac{h}{h_0}\right)^{4/3}\right] \approx 2\zeta^2|\varepsilon|^2\left[1 - \left(\frac{h}{h_0}\right)^{4/3}\right] .$$

Characteristically, in the absence of quenching when $h \ll h_0$, weak temperature dependence of the nonergodicity

parameter $(\Delta/\Theta \propto |\varepsilon|^2)$ occurs whereas in the strong disorder case $(h \lesssim h_0)$ the following linear relation holds:

$$\Delta \approx 2^{7/3}3^{2/3}v^{1/3}\zeta(h_0^{2/3} - h^{2/3})|\varepsilon| \propto |\varepsilon(h)|, \qquad (3.63)$$

$$|\varepsilon(h)| \equiv \frac{\Theta}{\Theta_g(h)} - 1,$$

where $\Theta_g(h)$ is the line of ergodicity breaking defined by

$$\Theta_g = \Theta_c - 2^{-1/6}3^{-1/3}w^{1/2}\left(\frac{h}{v}\right)^{2/3}, \qquad (3.64)$$

which ensues from the expression $h_0(\Theta) = h$ and Eqn (3.61).

3.4 Effect of the field

It has been demonstrated in the last section that random values of the order parameter phase occur in different domains in the absence of the field H, which fixes it. This is responsible for the nonzero value of the memory parameter q which represents quenched dispersion of this phase over the entire volume. When field $H \neq 0$ is switched on, a flow $j_0 = \overline{\langle \eta(t) - \eta(0)\rangle}/t$ appears, caused by the domain growth with the phase given by field H and the increased domain numbers (the former cause is reflected in averaging over the microlevel statistical ensemble denoted by the angular brackets and the latter in averaging over the macroensemble of domains denoted by the bar). As a result, the specimen assumes the macroscopic value of the order parameter,

$$\overline{\langle \eta(t)\rangle} = \overline{\langle \eta(0)\rangle} + j_0(H)t, \qquad (3.65)$$

which grows smoothly with time. The most popular example of such situation is provided by reorientation of magnetic (electric) domains of a ferromagnetic (ferroelectric) in the external field. In this case, the role of the order parameter phase is reduced to spatial orientation of the domain magnetisation (polarisation) vector. In solid solutions undergoing decomposition (including metallic glasses), the role of field H is performed by the difference of chemical potentials of the alloy components which changes in accordance with the choice of concentration and temperature [16, 40]. A rise in the macroscopic value of the order parameter (3.65) is ensured by synchronisation of concentration wave phases. Such a situation is characteristic of crystalline states. In an amorphous alloy, the field H is reduced to the chemical potential of constituent components averaged over the composition while the growth of the order parameter value (3.65) is promoted by synchronisation of distribution waves of atomic density (averaged over the composition).

Because the process of domain reorientation is of stochastic nature, the action of field H is characterised not only by the flow $j_0 = \overline{\langle \dot{\eta}\rangle}$ but also by the dispersion

$$D_0 = \frac{\overline{\langle \{[\eta(t) - \eta(0)] - j_0t\}^2\rangle}}{2t}, \qquad (3.66)$$

which characterises the uncertainty of time evolution of the order parameter caused by diffusion at the macrolevel. Quantity D_0 indicates how readily domains can rearrange in the external field.

In order to determine field dependences $j_0(H)$, $D_0(H)$, it is appropriate to take advantage of the Hamiltonian formalism [26]. For this purpose, let us perform an integration over field ϕ in Eqn (3.8), introduce imaginary

time $\tau = it$, and return to the initial Grassmanian fields $\Theta^{-1/2}\bar{\psi}$, $\Theta^{-1/2}\psi$ [see below Eqn (3.9)]. As a result, the Lagrangian (3.9) takes the form of

$$\mathcal{L} = \frac{1}{4}\left\{\left[\frac{d\eta(r)}{d\tau}\right]^2 - \left[\frac{\delta V}{\delta\eta(r)}\right]^2\right\}$$
$$+ \Theta\bar{\psi}(r)\left[-i\frac{\partial}{\partial\tau} + \frac{\delta^2 V}{\delta\eta(r)\delta\eta(r')}\right]\psi(r') \ . \qquad (3.67)$$

Accordingly, for the momentum conjugate to the field $\eta(r)$, $p \equiv \partial\mathcal{L}/\partial(d\eta/d\tau) = (1/2)d\eta/d\tau$ and for the generalised momenta $\pi = \partial\mathcal{L}/\partial(d\psi/d\tau)$; $\bar{\pi} = \partial\mathcal{L}/\partial(d\bar{\psi}/d\tau)$ corresponding to the Grassmannian fields, $\pi = -i\Theta\bar{\psi}$, $\bar{\pi} = 0$. Then, the Hamiltonian $\mathcal{H} = p\,d\eta/d\tau + \pi\,d\psi/d\tau + \bar{\pi}\,d\bar{\psi}/d\tau - \mathcal{L}$ corresponding to Lagrangian (3.67) takes the form

$$\mathcal{H} = p^2(r) + \frac{1}{4}\left[\frac{\delta V}{\delta\eta(r)}\right]^2 - i\pi(r)\frac{\delta^2 V}{\delta\eta(r)\delta\eta(r')}\,\psi(r') \ . \qquad (3.68)$$

Let us now perform formal quantisation. It can be seen from Eqn (3.8) that in the framework of this procedure the role of the Planck constant is played by the noise power Θ. Introduction of the canonical operators

$$\widehat{p} = -i\Theta\frac{\partial}{\partial\eta}, \quad \widehat{\psi} = \frac{1}{2}(\widehat{a}^+ + \widehat{a}^-), \quad \widehat{\pi} = i\Theta(\widehat{a}^+ - \widehat{a}^-),$$
$$(3.69)$$

where $\widehat{a}^{\pm}$ are the Fermi creation and annihilation operators, brings the secondary quantised Hamiltonian to the form [26]

$$\widehat{\mathcal{H}} = -\Theta^2\frac{\delta^2}{\delta\eta^2(r)} + \frac{1}{4}\left[\frac{\delta V}{\delta\eta(r)}\right]^2 + \frac{\Theta}{2}\frac{\delta^2 V}{\delta\eta(r)\,\delta\eta(r')}(\widehat{a}_r^+, \widehat{a}_{r'}^-) \ . \qquad (3.70)$$

Here, the presence of the commutator reflects supersymmetry which prevents a shift of the energy reference level.

Following Ref. [41], it is easy to show that the condition of conservation of the fermion number $n = \int dr\,\langle\widehat{a}_r^+\widehat{a}_r^-\rangle$ leads to splitting the entire Schrödinger equation corresponding to the Hamiltonian (3.70) into a set of independent equations, each corresponding to a given n. Specifically, the minimal ($n = 0$) and maximal ($n = N$) numbers of heterophase fluctuations have corresponding Hamiltonians

$$\widehat{\mathcal{H}}_{\mp} = -\Theta^2\frac{\delta^2}{\delta\eta^2(r)} + \frac{1}{4}\left[\frac{\delta V}{\delta\eta(r)}\right]^2 \mp \frac{\Theta}{2}\frac{\delta^2 V}{\delta\eta^2(r)} \ , \qquad (3.71)$$

the wave functions of which satisfy the property $\widehat{a}^{\mp}|\Psi_{\mp}\rangle = 0$. The corresponding Schrödinger equations define the wave functional

$$\Psi_t[\eta(r)] \propto \exp\left\{\frac{V_t[\eta(r)]}{2\Theta}\right\}P_t[\eta(r)] \ , \qquad (3.72)$$

in which the functional $P_t[\eta(r)]$ of the ordering field distribution satisfies the Fokker–Planck and Kolmogorov equations. Evidently, this functional reduces to the subintegral expression in the statistic functional (3.11).

Hamilton's formalism is convenient in that the expression (3.70) may be represented as the square of the supercharges:

$$\widehat{Q} = \left[-\Theta\frac{\delta}{\delta\eta(r)} + \frac{1}{2}\frac{\delta V}{\delta\eta(r)}\right]\widehat{a}_r^- + \left[\Theta\frac{\delta}{\delta\eta(r)} + \frac{1}{2}\frac{\delta V}{\delta\eta(r)}\right]\widehat{a}_r^+ \ .$$
$$(3.73)$$

Accordingly, one has

$$\widehat{Q}\Psi = \Omega^{1/2}\Psi \ , \qquad (3.74)$$

instead of the Schrödinger equation. An immediate consequence is the existence of supersymmetry at $H = 0$. Then, energy $\Omega = 0$, and solution (3.72) of equation (3.74) gives the time-independent probability functional $P_t[\eta(r)]$. Obviously, it does not satisfy the stationary state defined by conditions (3.12) in which energy Ω plays the role of the thermodynamic potential of a nonequilibrium system.

Given the external field H, one has $\Omega(H) \neq 0$ while supersymmetry is broken and the wave functional (3.72) acquires an unnormalisable factor $\exp(j_0 t)$ determined by the macroflow $j_0(H)$. This requires solution of equation (3.74) with $\Omega \neq 0$. Such a problem has been examined in Ref. [26] in application to a nonlinear pendulum corresponding to the two-parametric potential

$$V[\eta(r)] = \int\{-H_0\cos\eta(r) - H[\eta(r) - \pi]\}\,dr, \qquad (3.75)$$

where constant H_0 defines the anisotropy field which precludes reorientation of domains. The quasiclassical solution [26] of Eqn 3.74 leads to the following expressions for the flow and the diffusion coefficient:

$$j_0 = \frac{4\pi\Theta}{I^2(H)}\sinh\frac{\pi H}{\Theta} \ ,$$

$$D_0 = D_0^{(0)} + \frac{\Theta}{2}j_0\frac{d\ln I(H)}{dH} \ , \qquad D_0^{(0)} = \Theta\frac{\partial j_0}{\partial H} \ . \qquad (3.76)$$

Here, the integral $I(H)$ has the form:

$$I(H) = \int_{\eta_1}^{\eta_1+2\pi}\exp\left[\frac{V(\eta)}{\Theta}\right]d\eta, \qquad \sin\eta_1 = \frac{H}{H_0} \ ,$$

where $V(\eta)$ is the subintegral function in Eqn (3.75). It is found by the steepest descent method that

$$I(H) \approx \left(\frac{2\pi\Theta}{H_0}\right)^{1/2}\left(1 - \frac{H^2}{H_0^2}\right)^{-1/4}$$
$$\times \exp\left\{\frac{H_0}{\Theta}\left[\left(1 - \frac{H^2}{H_0^2}\right)^{1/2} + \frac{H}{H_0}\sin^{-1}\frac{H}{H_0}\right]\right\} \ . \qquad (3.77)$$

Substitution of this expression into Eqn (3.76) leads to:

$$D_0 = j_0\left(\pi\coth\frac{\pi H}{\Theta} + \frac{1}{2}\sin^{-1}\frac{H}{H_0} + \frac{\Theta}{4}\frac{H}{H_0^2 - H^2}\right), \qquad (3.78)$$

which replaces the fluctuation–dissipation theorem in a nonequilibrium system.

According to the second equality (3.76), this theorem is satisfied only in a hypothetical case of $I(H) = \text{const} \equiv I$ in which the coefficient of microdiffusion is defined by the expression:

$$D_0^{(0)} = \left(\frac{I}{2\pi}\right)^{-2}\Theta\cosh\frac{\pi H}{\Theta} \ . \qquad (3.79)$$

Its characteristic feature is the finite value of the motility of the domain reorientation process at any real values of field $H < \infty$. In the limit $H \gg \Theta$, the value of $D_0^{(0)}$ is largely determined by the field. In the opposite case of $H \ll \Theta$, this value is proportional to temperature Θ. It is worthwhile to note that the field dependence $D_0^{(0)}(H)$ grows monotonically while temperature dependence $D_0^{(0)}(\Theta)$ decreases at $\Theta < \Theta^0$ and increases at $\Theta > \Theta^0$ where the boundary temperature $\Theta^0 = 2.619H$ is given by field
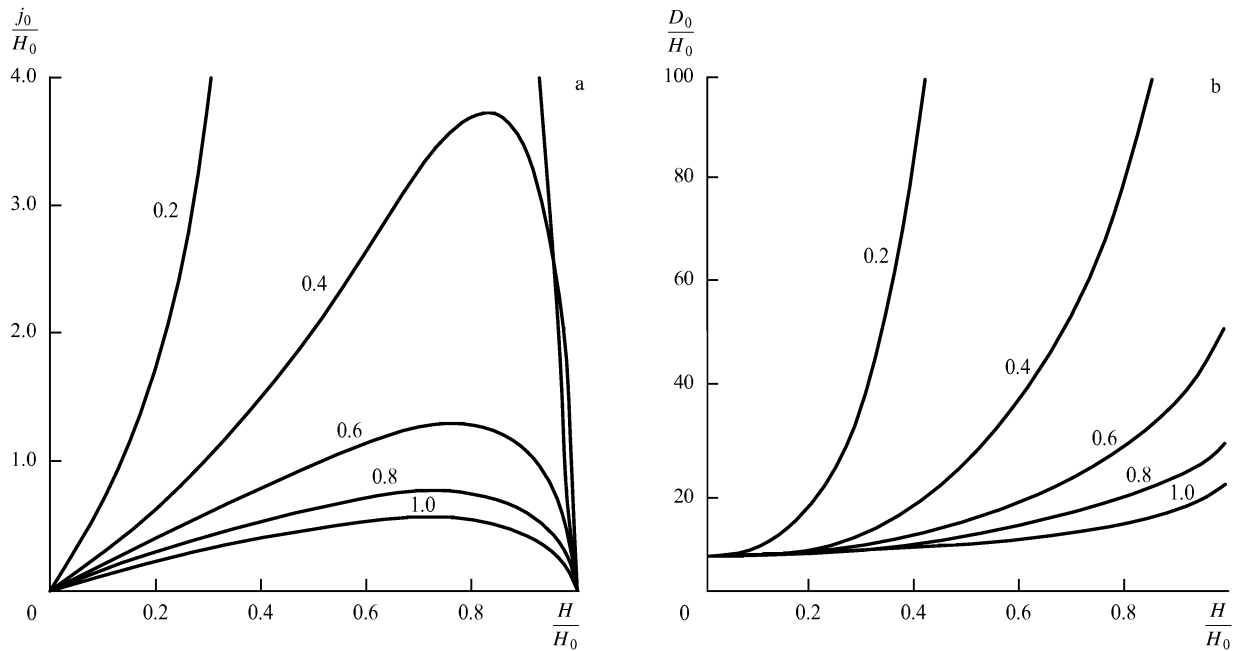
Figure 10. Field dependence of the rate (a) and motility (b) of ordered phase domain reorientation in the external field.

strength. The temperature–field dependence of the flow is of a similar character with the only exception that the flow $j_0 \propto H$ vanishes when $H \to 0$.

Actually, dependence (3.77) does not reduce to a constant, and expressions of the (3.79) type as well as the fluctuation–dissipation theorem become inapplicable. It can be seen from Eqns (3.76), (3.78) and Fig. 10 that supersymmetry breaking at $H \neq 0$ leads to additions which can be neglected only in the limit of an infinitely weak linear constituent of the potential (3.75) ($H \ll H_0$). With the growth of this potential to values of $H = H_0$, the macroflow j_0 vanishes while the coefficient of macrodiffusion D_0 grows infinitely. This means that the system of domains loses stability at $H = H_0$. This corresponds to their instantaneous reorientation with the field's growth to values of $H \geqslant H_0$ exceeding the intensity of the anisotropy field which fixes phase values in each domain.

It is clear that the above scheme is applicable not only in the presence of the external field H but also in the case of its spontaneous formation as a result of any collective effect in the behaviour of the domain ensemble. Specifically, such a situation may arise during diffusional interaction between different precipitates of the phase in the process of coalescence [12]. The primary cause of such interaction is known to be Laplace pressure, $2\sigma/R$, caused by the nonzero interfacial curvature $2/R$ (R is the radius of a spherical precipitate and σ is the coefficient of surface tension) [16]. On the one hand, this pressure is responsible for the microflow [12]:

$$j = \rho H \; ; \qquad \rho \equiv \left(\frac{R_{c0}}{R_c} \right)^3 ,$$

$$H \equiv \frac{R_c}{R} \left(1 - \frac{R_c}{R} \right) , \qquad R_c \equiv \frac{2\sigma \Omega C_\infty}{T\Delta} , \tag{3.80}$$

which determines the intensity of diffusion of less abundant component atoms towards a precipitate (here, the value of j is expressed in units of $R_c^2 D\Delta/R_{c0}^3$, D is the coefficient of

atomic diffusion, Δ is the oversaturation with the limiting component relative to the equilibrium value of concentration C_∞, Ω is the atomic volume, T is the temperature in energy units, R_c is the critical radius of the precipitate, and R_{c0} is its initial value). On the other hand, it appears from the above that the field H leads, at the precipitate structural level, to the macroscopic flow $j_0(H)$ given by the first equality in Eqn (3.76). Evidently, a two-level system is in the stationary state if flows j, j_0 are in equilibrium at different levels. The resulting self-consistency condition† $j(H) = j_0(H)$ for the field H and corresponding flows $j_0 = j = \rho H$ gives:

$$\rho H = \frac{4\pi\Theta}{I^2(H, \Theta)} \sinh \frac{\pi H}{\Theta} . \tag{3.81}$$

The forms of the dependences $H(\Theta)$, $j(\Theta)$ ensuing from this equation are shown for different values of the parameter ρ in Fig. 11. Their remarkable feature is the absence of diffusive interaction between H and the corresponding flow j in the immediate vicinity of point $\Theta = 0$. With the distance from this point at $\Theta = \Theta_d$, spontaneous field H and diffusive flow j emerge in a jump-like fashion, and their size exhibits weak growth in the physically meaningful temperature range $\Theta < 2H_0$. It can be seen from Figs 12a and 12b that the size of the spontaneous field H increases with decreasing parameter ρ whereas the corresponding diffusive flow j exhibits an initial growth followed by a drop at $\rho < 0.8$. The boundary temperature value Θ_d given by:

$$\frac{\Theta}{2H_0} \exp \left(\frac{2H_0}{\Theta} \right) = \frac{\pi}{\rho} \tag{3.82}$$

†Actually, this condition underlies the classical theory of coalescence [12]. However, this theory examines the dependence of flows j, j_0 on the precipitate radius R, for which reason equalities (3.80) are supplemented with definition $j_0 = \mathrm{d}R/\mathrm{d}t$, and the self-consistency condition $j(R) = j_0(R)$ leads to the equation of motion at the macrolevel.
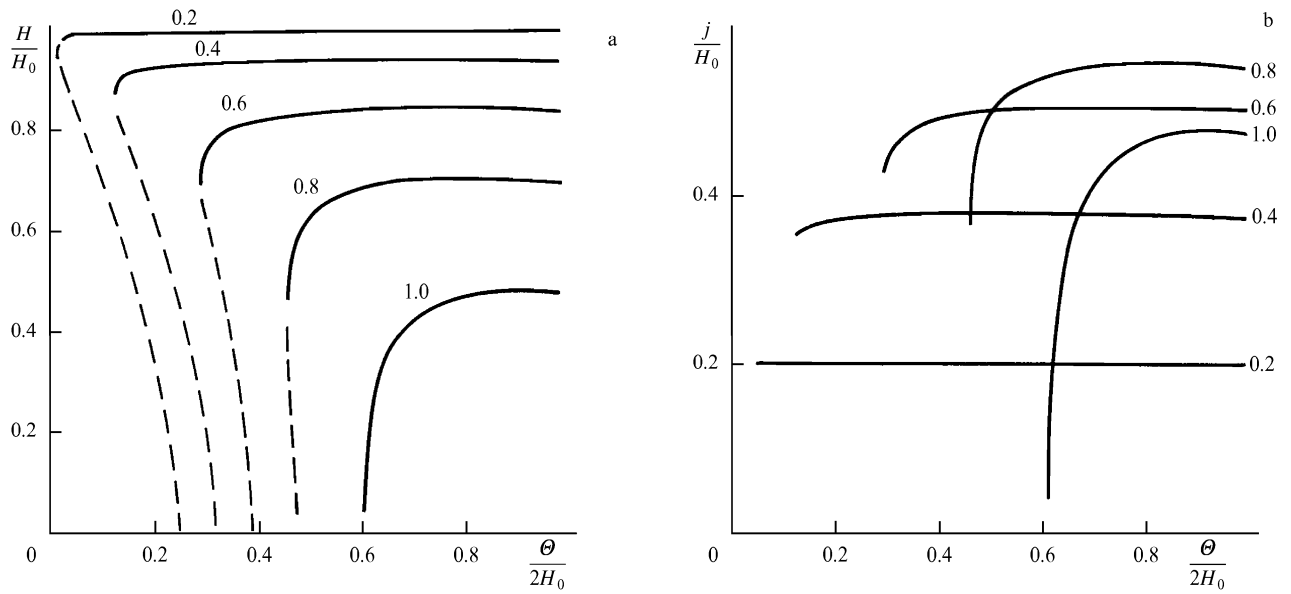
Figure 11. Temperature dependence of the diffusive interaction field of domains (a) and corresponding flow (b) during coalescence (figures at the curves denote values of parameter ρ).
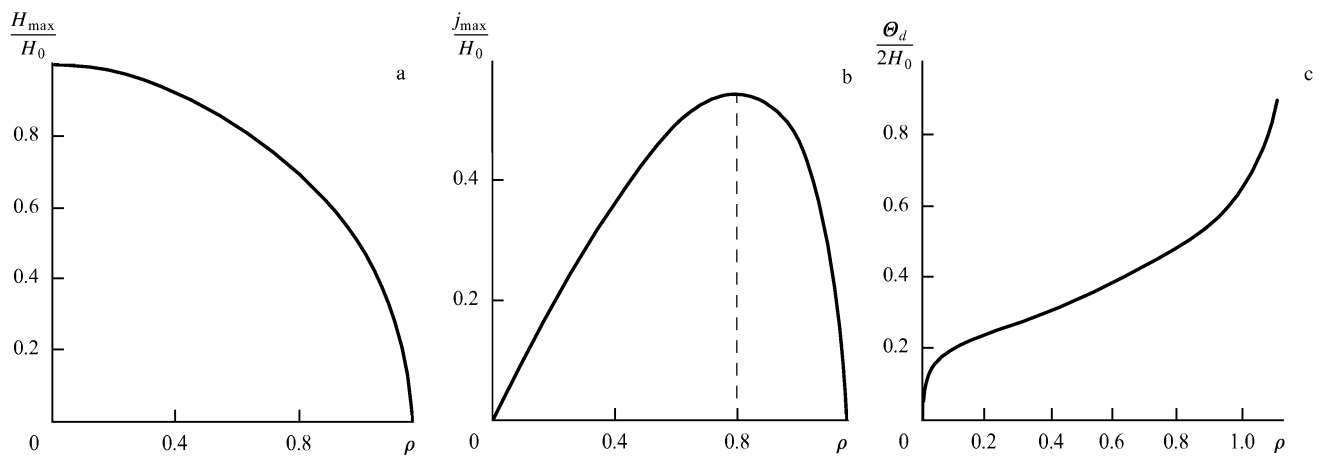

Figure 12. Dependence of the spontaneous field (a), spontaneous flow (b), and boundary temperature (c) characterising the establishment of the coherent regime of coalescence [parameter $\rho \propto (\Delta/\sigma)^3$] on the degree of oversaturation Δ and coefficient of surface tension σ.

falls in agreement with the dependence shown in Fig. 12c. Since the critical radius $R_c(t)$ grows monotonically with time, its initial value R_{c0} fulfils the condition $R_{c0} < R_c$, because of which parameter $\rho = (R_{c0}/R_c)^3$ is invariably less than unity and falls with time. A result is that the condition $\rho < \pi/e = 1.156$ for the availability of the solution of Eqn (3.82) is always satisfied. On the other hand, $\rho \propto (\Delta/\sigma)^3$, and Figs 11 and 12 show that the growth of surface tension σ and the decrease in oversaturation $\Delta(t)$ are responsible for the broader temperature range of coalescence and the greater strength of the spontaneous field H. Accordingly, the diffusive flow j grows in the beginning but decreases afterwards. Such behaviour must be apparent with the progress of time during which oversaturation $\Delta(t) \propto t^{-1/3}$ (and hence, parameter $\rho \propto t^{-1}$) decreases [12].

At first sight, the result indicating the absence of diffusional interaction (as well as coalescence) in the temperature range near the point $\Theta = 0$ (it will be shown

in Section 3.5 that it corresponds to the spinodal) appears quite unexpected. At any rate, the classical problem of coalescence [12] implies that this process occurs in the entire range of the phase diagram near the line of the first order phase transition corresponding to $C_\infty(T)$ in the notation of Eqn (2.68). However, it is clear from Eqn (3.81) that on the approach to point $\Theta = 0$, the size of the macroflow $j_0(H)$ on the right-hand side of the equality grows faster than the linear dependence $j = \rho H$ for the microflow. The result is that the nonzero value H of the diffusive field occurs only at $\Theta > \Theta_d$ where the boundary value of Θ_d is given by condition (3.82). Physically, it can be accounted for by the critical growth of heterophase fluctuations near the spinodal. Recently, Beysens and Jayalakshmi (Service de Physique de l'Etat Condensé, C E Saclay) have obtained experimental evidence in support of the above picture. It turned out that the classical coalescence law $R \propto t^{1/3}$ is apparent only far from the spinodal whereas in its vicinity $R \propto t$.

3.5 Analysis of the spatiotemporal behaviour of the relaxing system

The formalism presented in the previous section is in fact a scheme for the self-consistent description of two hierarchically subordinate structural levels of a system undergoing phase transition of the first order. The standard approach (see Ref. [16]) uses, at the microscopic level, a scheme which allows the equilibrium value η_0 of the order parameter and the corresponding susceptibility χ to be found. In the framework of our approach, characteristics of the microlevel are determined by the memory parameter $q = \eta_0^2$ and the adiabatic susceptibility χ, the values of which are given by Eqns (3.61), (3.62). The use of the supersymmetric approach representing both the hydrodynamic ordering mode and its spatiotemporal inhomogeneity allows the standard description [16] to be supplemented with characteristics of the macroscopic level representing evolution of a large-scale (domain or heterophase) structure of the ordered phase. Such characteristics include the memory parameter q_0 which determines, in accordance with Eqn (3.46), the degree of macrostructure freezing and the nonergodicity parameter Δ given by the first equality of Eqn (3.51) which is essentially the difference between isothermal (χ_0) and adiabatic (χ) susceptibilities [see Eqn (3.52)]. According to Eqn (3.61), the memory parameter q_0 is determined by the quenched disorder $h \propto |\dot{T}|^a$ caused by quenching at $\dot{T} \neq 0$ in the dispersion of microscopic values of the field conjugate to the order parameter. It is clear from Eqn (3.62) that the irreversible response value Δ is determined by both quenched disorder h and temperature ε. Because the memory parameter q_0 can also have nonzero values for the one-level system, it may be regarded as a less important characteristic compared with the nonergodicity parameter, whose value Δ becomes finite only with the appearance of several structural levels, which breaks supersymmetry with respect to homogeneous and heterophase fluctuations. In other words, the appearance of the nonzero nonergodicity parameter Δ suggests the formation of a new structural level which is hierarchically related to the initial microlevel.

The effect of the field responsible for domain orientation or its spontaneous switch-on in the process of coalescence results in rearrangement of the ordered phase macrostructure. The kinetics of this rearrangement are characterised by the macroflow j_0 found from Eqn (3.65) and the coefficient of macrodiffusion (3.66). The use of the nonlinear pendulum model in Section 3.4 indicates that field dependence of the macroflow $j_0(H)$ has a linear form at $H \ll H_0$, becomes saturated afterwards, and vanishes again as the field H approaches H_0 which characterises anisotropy (Fig. 10). The motility in domain reorientation at $H = 0$ has the finite value $D_0 = 2\pi H_0 \exp(-2H_0/\Theta)$ of the usual Arrhenius form and diverges as $(H_0 - H)^{-1/2}$ near the limit $H = H_0$. It has been noted in Section 3.4 that such a character of the field dependences $j_0(H)$ and $D_0(H)$ reflects instability of the domain system with respect to the orienting field H. As soon as the anisotropy field ($H \geqslant H_0$) is exceeded, the domains undergo sharp reorientation in the given direction H. Interestingly, supersymmetry breaking at finite values of H makes the fluctuation–dissipation theorem invalid [see Eqn (3.76)].

In the case of spontaneous switching of field H in coalescence [12], its self-consistent value is given by the condition (3.80) of compensation of microflow and macro-flow. It appears from Figs 11 and 12 and also from the dependence $\rho \propto \sigma^{-3} t^{-1}$ ensuing from Eqn (3.80) that the coalescence interval extends to the low temperature region with growing surface tension σ and time t. Concurrently, the maximum strength of the spontaneous field H smoothly increases till it reaches H_0 whereas the maximum flow first grows but then falls to zero.

Further progress in physical interpretation of the data obtained requires a detailed study of noise Θ distribution patterns between micro and macrolevels. For this purpose, it is necessary to bear in mind that in condition (3.2), the appearance of the macrolevel must be taken into account by introducing additional averaging over the macro-ensemble of domains. On the other hand, the macroscopic constituent $\zeta_0 = \langle \zeta \rangle$, devoid of stochasticity at the microlevel, needs to be separated from the whole stochastic current. This will lead to the division of the correlator $\overline{\langle \zeta(r, t) \zeta(0,0) \rangle}$ (where the angular brackets and the bar denote averaging over micro and macroensembles) into the microscopic $\{\langle [\zeta(r, t) - \zeta_0(r, t)][\zeta(0, 0) - \zeta_0(0, 0)] \rangle\}$ and macroscopic $[\overline{\zeta_0(r, t) \zeta_0(0, 0)}]$ constituents. Evidently, the noise strength of the former constituent is determined by Θ, as in Eqn (3.2). At the same time, the ordered phase characterised by the spinodal temperature Θ_s forms the basis of the macrostructure. Therefore, it is supposed that at the level corresponding to the latter constituent the strength of noise Θ_0 takes the form of[†]

$$\Theta_0 = \begin{cases} \Theta - \Theta_s & \text{at} \quad \Theta > \Theta_s, \\ 2(\Theta_s - \Theta) & \text{at} \quad \Theta < \Theta_s, \end{cases} \tag{3.83}$$

where the appearance of the factor 2 at $\Theta < \Theta_s$ reflects the usual '2-law'. Accordingly, condition (3.2) splits into:

$$\overline{\langle [\zeta(r, t) - \zeta_0(r, t)] [\zeta(0, 0) - \zeta_0(0, 0)] \rangle} = 2\Theta \widehat{\Gamma} \delta(r) \delta(t),$$

$$\overline{\zeta_0(r, t) \zeta_0(0, 0)} = 2\Theta_0 \delta(r) \delta(t); \quad \zeta_0(r, t) \equiv \langle \zeta(r, t) \rangle. \tag{3.84}$$

These expressions take into account that the conservation law cannot be fulfilled, which accounts for $\widehat{\Gamma}_0 = 1$. It should be noted that dimensionless noise intensities Θ, Θ_0 invariably ensure that $\Theta \gg \Theta_0$ even though real temperature values T and $T_0 = T - T_s$ may prove commensurable. Evidently, this is because of an increase in characteristic spatiotemporal scales and reflects damping fluctuations during transition from the microscopic level to the macroscopic one. For example, the role of such scales in the first equality of Eqn (3.84) is performed by correlation length ξ and relaxation time of the soft mode τ [see after Eqn (3.2)] whereas the second equality contains the characteristic domain size L (in the case of coalescence, it represents the initial value R_{c0} of the critical radius) and macroscopic time τ_0.

The above discussion has demonstrated that in formulas (3.61)–(3.64), (3.76)–(3.82) for quantities χ, q_0, Δ, j_0, D_0, by the strength of the noise one really means the effective temperature of the macrolevel, Eqn (3.83). For instance, expressions for characteristic points Θ_c, Θ_g and the nonergodicity parameter Δ take the form:

$$|\Theta_c - \Theta_s| = \frac{\zeta}{cv}, \qquad c = \begin{cases} 12, & \Theta > \Theta_s, \\ 24, & \Theta < \Theta_s; \end{cases}$$

[†] In terms of our approach, such an assumption reflects the hierarchical relationship between micro and macrolevels.

$$|\Theta_g - \Theta_c| = \frac{\zeta}{cv}\left(\frac{h}{h_c}\right)^{2/3}; \qquad h_c = \frac{\zeta^{3/2}}{(18v)^{1/2}};$$

$$\frac{\Delta}{\Theta_0} = 2\zeta^2|\varepsilon_0|^2\left[1 - \left(\frac{h}{h_0}\right)^{4/3}\right],$$

$$h_0 = h_c|\varepsilon_0|^{3/2}, \qquad \varepsilon_0 = \frac{\Theta - \Theta_c}{\Theta_c - \Theta_s}. \qquad (3.85)$$

In formulas (3.76)–(3.82) for kinetic characteristics, j_0, D_0 should be simply substituted by Θ_0. The temperature–field dependence $\Delta(\Theta_0, h)$ is illustrated by Fig. 13.
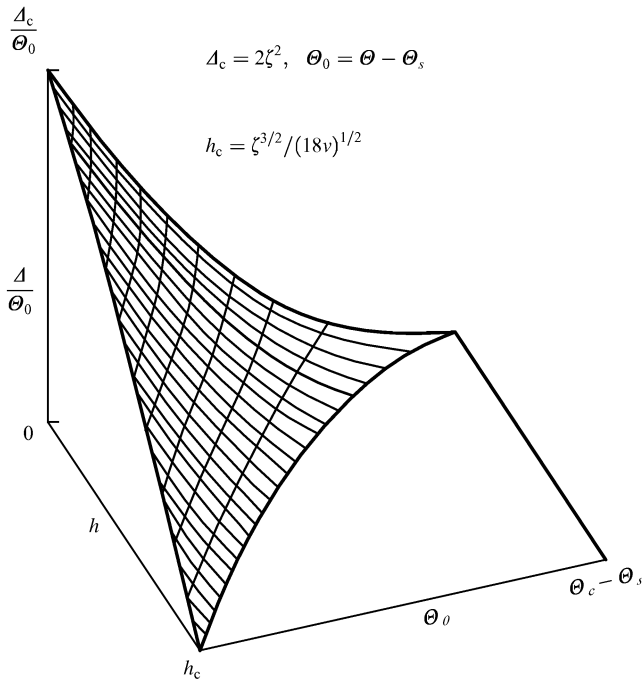

Figure 13. Dependence of the nonergodicity parameter Δ on temperature Θ_0 and quenched disorder h.

In the case of quasistatic cooling ($h = 0$), the system loses ergodicity in points $\Theta_c^{(\pm)}$ on both sides of the spinodal temperature Θ_s where Δ/Θ_0 attains its maximum value. This means that in accordance with the result of the theory of coupling modes [42], the presence of the macrolevel is most readily apparent near the spinodal temperature. This fact appears to reflect the critical amplification of hetero-phase fluctuations. As has been mentioned in Section 3.3, the dependence $\Delta(\varepsilon_0)$ for a quasistatic system is smooth. The $h \ll h_g$ situation has been analysed in Ref. [24], but the authors employed an alternative method of coupling modes in the context of which parameter ζ was not at all small. It turned out that the dependence $\Delta(\varepsilon_0)$ had a finite break at the binodal point $\Theta_c^{(\pm)}$.

If cooling is accomplished at a rate that ensures quenched disorder $h \sim h_0$, then, regardless of temperature, the system acquires macroscopic memory characterised by the Edwards–Anderson parameter $q_0 \propto h^{2/3}$. Moreover, the nonergodicity region becomes narrower, and its border Θ_g approaches the spinodal point Θ_s, in accordance with the second equality of (3.85). It can be seen from the respective ergodicity breaking diagram $h_0(\Theta_0)$ in Fig. 13 that by increasing quenching rate $|\dot{T}|$ at a

given temperature $\Theta_s < \Theta < \Theta_c$, it is possible to obtain such a disorder, $h > h_0$, at which the condition $\Delta = 0$ is fulfilled. This implies fixation of the unstable disordered state with respect to the formation of a new structural level (in the case of quenching from a liquid, such fixation corresponds to the formation of the amorphous state). The critical quenching velocity needed to maintain this process is given by the second equality of (3.85). Assuming that $\Theta_g = \Theta_c$, it is possible to find the critical disorder value

$$h_c = \frac{\zeta^{3/2}}{(18v)^{1/2}}, \qquad (3.86)$$

which ensures suppression of phase transition (formation of the amorphous state if quenching is accomplished from a liquid) over the entire temperature range.

It is clear that systems with large anharmonicity v and compensation of the interatomic interaction parameter w with respect to one-particle repulsion are most liable to amorphisation. By using the phenomenological relation $h = B|\dot{T}|^a$ where B, a are positive constants, one can obtain from Eqn (3.86) for the critical quenching rate:

$$|\dot{T}|_c = B^{1/a} \frac{\left(8w/A^2 - 1\right)^{3/2a}}{(18v)^{1/2a}}. \qquad (3.87)$$

where the transition to dimensional quantities is accomplished and the numerator contains the constant A which stands in front of the quadratic term in the Landau expansion. As a rule, the parameters of nonlinearity $v^{1/2}$, $w^{1/2}$ are always much smaller than the effective rigidity A of a spring which simulates the form of the atomic potential [16]. Therefore, to reduce $|\dot{T}|_c$, it is necessary to choose systems with a soft, highly anharmonic potential and strong interatomic interaction. It is this situation that occurs in systems of the 'metal–metalloid' type readily liable to amorphisation, where the marked difference between atomic radii of the constituent components is responsible for the growth of the anharmonicity parameter v and the existence of the strong covalent bond accounts for the high value of the interaction parameter w.

Let us now examine the spatiotemporal behaviour of a memory-carrying nonergodicity system. Definitions (3.40), (3.51) and limiting relations (3.43) indicate that the expression for advanced and retarded Green's functions has the following form up to the first nonvanishing powers of frequency:

$$C_{\pm}(\omega) = \Delta + g\Theta(\Theta \pm ig\tau_0\omega)^{-1}, \qquad \omega \ll 1. \qquad (3.88)$$

The use of Eqns (3.38)–(3.43), (3.46), (3.48), (3.49), (3.51), (3.53), (3.54), and (3.56) for effective relaxation time yields

$$\tau_0^{-1} = 2\left(\frac{3v}{\Theta}\right)^2 g^2\left(g^2 - q_0^2\right) \approx 2\zeta^2\left(1 - |\varepsilon|\right)^{-2}\left[1 - \left(\frac{h}{h_0}\right)^{4/3}\right],$$

$$\varepsilon = \frac{\Theta}{\Theta_s} - 1. \qquad (3.89)$$

A characteristic feature of this dependence is a decrease in relaxation time with increasing distance from the spinodal point Θ_s and falling rate of the quench. The presence of the nullifying square bracket corresponds to the divergence of quantity $\tau_0(h)$ in the limit of high quenching rates responsible for disorder $h \gtrsim h_0$. This suggests freezing of the disordered state as a result of the memory which

develops on quenching. In other words, an amorphisation-type process is achieved.

It has already been noted in the introduction that our approach allows not only a description of the effects of memory and nonergodicity which are characteristic attributes of a nonequilibrium thermodynamic system but also depiction of its spatiotemporal evolution. A crucial advantage of this supersymmetric approach is the possibility of describing both the nucleation stage and the later stage of precipitate growth. Unlike the classical approach [43, 44] which employs virtually unconnected models for the description of individual stages (see Chapters 4 and 5 in Ref. [43]), our method represents them as the initial and late stages of the same relaxation process in a nonequilibrium system. The method implies that division into nucleation and growth stages is a result of supersymmetry breaking which causes in the appearance of heterophase fluctuations in addition to homogeneous ones. The description of phase nucleation at the initial stage of the process requires a study of the eigenvalue spectrum of the supersymmetric Hamiltonian corresponding to the zero number of fermions (see Section 3.4). With supersymmetry breaking at the late stage, the pseudo-Fermi component appears, and only this constituent of the superfield needs to be examined for the description of the new phase growth. In terms of the traditional approach, the appearance of this component corresponds to the representation of a heterophase system by the stochastic ensemble of moving interfaces [45]. The complicated picture of the new phase growth as compared with the description of nucleation can be accounted for by the fact that the problem of nucleation may be reduced to finding eigenvalues whereas in the description of the growth stage, eigenfunctions (3.72) are also needed.

Setting aside the above general statement of the problem, it is worthy of note that the form of time dependence $L(t)$ for the domain size can be obtained from relation (3.88) which contains a characteristic combination $g\tau_0\omega$. Indeed, it follows from Eqn (3.29) that taking into account the spatial dispersion yields the standard Ornstein–Zernike dependence $\tau_k = \tau(1 + \xi^2 k^2)^{-1}$ (in dimensional units) for the relaxation time at the microlevel (inside the domain). According to Ref. [18], transition to the macrolevel representing the domains' behaviour results in the transformation of τ_k to the Bogolyubov singularity $\tau_{0k} = \tau_0(\xi k)^{-2}$, $\tau_0 = \chi_0 T/D_b L$ where χ_0 is the isothermal susceptibility and D_b is the coefficient of boundary diffusion. Taking into account the scaling relations $k \sim L^{-1}$, $\omega \sim t^{-1}$, this immediately gives $L^2 \propto t$ [5] for the nonconserved order parameter, from the condition $\Theta \sim g\tau_{0k}\omega$ of the commensurability of terms in the denominator of Eqn (3.88). It follows from Eqn (3.2) that in the presence of the conservation law in front of Θ, an additional factor $|k|^2$ appears. Accordingly, the relation $L^4 \propto t$ is valid at the precoalescence stage. At the onset of this stage, the coherent regime of diffusional interaction is established [12] which means the appearance of an effective field having the sense of a spontaneous atom flow j directed from smaller to larger precipitates. Unlike the usual diffusive flow ζ which is proportional to the chemical potential gradient and gives the strength of the white noise correlator $\langle|\zeta_k|^2\rangle = 2\Theta|k|^2$ proportional to the second power of the wave vector, the coherent flow† j_k is

†Its value is given by formula (3.80).

not associated with any gradient and is characterised by the correlator $\langle\zeta_k^* j_k\rangle \propto k$. Its addition to the usual term Θ in the denominator of Green's function (3.88) and comparison with term $g\tau_{0k}\omega$ allows the scaling dependence $L^3 \propto t$ intrinsic in the coalescence process to be found [12].

The above singularities of the Green function (3.88) allow the interpretation of large-scale correlations of the order parameter. In order to describe it, let us use the fluctuation–dissipation theorem $S = (2/\omega)\mathrm{Im}\,(C_- - \Delta)$ which has the following form after substitution of Eqn (3.88):

$$S_k(\omega) = \frac{2\Theta_k g^2 \tau_{0k}}{\Theta_k^2 + (g\tau_{0k}\omega)^2}\,. \qquad (3.90)$$

Hence [taking into consideration the aforementioned dependences τ_{0k}, Θ_k for the structure factor $S_k \equiv S_k(\omega = 0)$], asymptotic $S_k \sim k^{-p}$ where $p = 2, 4, 3$ for the cases of nonconserved and conserved order parameters and the coalescence process respectively. In the r-representation of d-dimensional space, such behaviour corresponds to the dependence of shape $S(r) \sim r^{p-d}$ which describes correlations at distances $r \ll L$. Applied to the case of the conserved order parameter $p = 4$, these asymptotics explain Porod's law [32] which describes the appearance of sharp interfaces [20]. For the nonconserved order parameter $p = 2$, there is the usual behaviour $S(r) \sim r^{-1}$ and in the case of coalescence $p = 3$, correlation of the order parameter undergoes slight variation with the distance.

It appears appropriate to draw a parallel between the presented analysis of correlation functions and the method of Mazenko and coworkers [19–21] based on the examination of equations of motion (2.54) and (2.55). Indeed, the latter method [19–21] indicates (see also Section 2.1) that in each of the above cases, the equations are dominated by terms of the order of L^{-p}. In the framework of our approach, this corresponds to preserving the largest term $\Theta_k \propto k^{p-2}$, $k \sim L^{-1}$ for the noise strength in expression (3.88) for Green's function. Naturally, both approaches yield identical results. However, Θ-containing conditions (3.84) of noise normalisation constitute a basic principle in thermodynamics of nonequilibrium systems. For this reason, the approach based on the analysis of their form appears to have an advantage over alternative methods.

3.6 Supersymmetric representation of order parameter fluctuations

The standard theory of phase transitions assumes that fluctuations of the order parameter are homogeneous. This allows for the representation of their field by the Fourier series where the major contribution is made by long-wavelength components. For this reason, determination of fluctuation corrections is reduced to calculation of the simplest Gaussian integrals (see Ref. [30]). However, this approach does not take into consideration the fact that a significant contribution may be the result not only of smooth changes of the order parameter field but also of soliton-like structures of the antiphase boundary type. In other words, the heterogeneous constituent should be taken into account along with homogeneous fluctuations [28].

This section is devoted to the solution of the problem first posed in Ref. [46]. Since the number of homogeneous fluctuations can grow indefinitely, and only one heterogeneous kink-type fluctuation can occur in a given point, we

represent them as the Bose and Fermi constituents of the same superfield [41].

In order to construct the theoretical scheme, let us write the Langevin equation [29] for the field of the nonconserved order parameter $\eta(r, t)$ in the following form [cf Eqns (2.2), (3.1)]:

$$\gamma^{-1}\dot{\eta} = -W(\eta) + \zeta, \qquad (3.91)$$

where the point denotes differentiation with respect to time, γ is the kinetic coefficient, and $-W(\eta)$ is the deterministic constituent of the force conjugate to the order parameter [its value reduces to the η-derivative of the thermodynamic (synergetic) potential $V(\eta)$: $W(\eta) = dV(\eta)/d\eta$]; the stochastic component of force $\zeta(r, t)$ is taken as white noise [cf Eqns (2.3), (3.2)]:

$$\langle \zeta(r, t)\zeta(0, 0) \rangle = 2 \frac{T}{\gamma} \delta(r)\delta(t), \qquad (3.92)$$

where T is the temperature in energy units and the angular brackets denote averaging over the Gauss distribution (see Section 3.4).

The correlator

$$S(r, t) = \langle \eta(r, t)\eta(0, t) \rangle \qquad (3.93)$$

plays the role of the observable quantity which is determined experimentally. Calculations described in Section 3.4 give the secondary quantised Hamiltonian [cf Eqn (3.70)]:

$$\widehat{\mathcal{H}} = -T \frac{\delta^2}{\delta\eta^2} + \frac{1}{4T} W^2(\eta) + \frac{1}{2} W'(\eta)\left(\widehat{a}^+, \widehat{a}^-\right), \quad (3.94)$$

where the prime denotes differentiation with respect to η and $\widehat{a}^{\pm}$ are Fermi creation–annihilation operators.

In the quadratic approximation, free energy has the form

$$V = \frac{1}{2\chi} \int \eta^2(r)\, dr + \frac{1}{2} \int w(r - r')\eta(r)\eta(r')\, dr\, dr', \quad (3.95)$$

where χ is susceptibility and the kernel $w(r - r')$ takes inhomogeneity into account. Transition to Fourier-transformants yields the full Hamiltonian of the system:

$$\widehat{H} \equiv \int \widehat{\mathcal{H}}(r)\, dr = \sum_k \widehat{\mathcal{H}}_k,$$

$$\widehat{\mathcal{H}}_k = -T \left| \frac{\delta}{\delta\eta_k} \right|^2 + \frac{\varepsilon_k^2}{4T} |\eta_k|^2 + \frac{1}{2} \varepsilon_k\left(\widehat{a}_k^+, \widehat{a}_k^-\right). \quad (3.96)$$

Here, k is the wave vector and $\varepsilon_k = \chi^{-1} + w_k$ is the bare spectrum taking into account the symmetry condition $w_k = w_{-k}$ in the last term.

Now, let us introduce bosonic operators of secondary quantisation $\widehat{b}^{\pm}$ in accordance with:

$$\widehat{b}^{\pm} = \left(\frac{\varepsilon_k}{4T}\right)^{1/2} \eta_k \mp \left(\frac{T}{\varepsilon_k}\right)^{1/2} \frac{\delta}{\delta\eta_k}. \quad (3.97)$$

Then, the Hamiltonian $\widehat{H}$ in Eqn (3.96) reduces to the sum of two constituents:

$$\widehat{H} = \widehat{H}_a + \widehat{H}_b,$$

$$\widehat{H}_a = \sum_k \varepsilon_k \left(\widehat{n}_k - \frac{1}{2}\right), \qquad \widehat{n}_k = \widehat{a}_k^+\widehat{a}_k^-,$$

$$\widehat{H}_b = \sum_k \varepsilon_k \left(\widehat{v}_k + \frac{1}{2}\right), \qquad \widehat{v}_k = \widehat{b}_k^+\widehat{b}_k^-. \quad (3.98)$$

Thus, the behaviour of the fluctuating system is represented by two equivalent terms $\widehat{H}_a$, $\widehat{H}_b$, the former of the Fermi type (operator $\widehat{n}_k$ takes only values of $n_k = 0, 1$) and the latter of the Bose type (operator $\widehat{v}_k$ has eigenvalues $v_k = 0, 1, 2, \ldots$). Apparently, the Fermi contribution corresponds to heterophase fluctuations of soliton-like nature reflected in the exclusion principle intrinsic to fermions. Accordingly, the bosonic term is related to ordinary homogeneous fluctuations, the number v_k of which in the continuum limit $k \to 0$ can be indefinitely large. The equivalence of heterogeneous and homogeneous fluctuations is reflected in the identical spectra ε_k of the two constituents [in the supersymmetric representation, this means symmetry conservation apparent in the equivalence of the Bose (η) and Fermi (ψ, $\bar{\psi}$) components]. Of primary importance is that zero energies $E_{a,b}^{(0)} = \mp(1/2)\sum_k \varepsilon_k$ of the Bose and Fermi components diverge if calculated separately but totally compensate each other when considered together. This finding indicates that the noncontradictory picture can be obtained only if the two kinds of fluctuations are subjected to combined analysis.

Let us evaluate the contribution of either type of fluctuations to the thermodynamic potential [30]:

$$\Omega_k = -T \ln \sum_{n_k} \left[\exp\left(\frac{\mu - \varepsilon_k}{T}\right) \right]^{n_k}, \qquad (3.99)$$

corresponding to a given k value (μ is the chemical potential defined by the conservation condition for the total number of fluctuations). The elementary summation over $n_k = 0, 1$ gives, for heterophase fluctuations,

$$\Omega_k^{(a)} = -T \ln \left[1 + \exp\left(\frac{\mu - \varepsilon_k}{T}\right) \right]. \qquad (3.100)$$

In the case of the Bose component, by n_k one should mean $v_k = 0, 1, 2, \ldots$ Then, summation of geometric progression gives

$$\Omega_k^{(b)} = T \ln \left[1 - \exp\left(\frac{\mu - \varepsilon_k}{T}\right) \right], \qquad (3.101)$$

where the same value of chemical potential μ is taken as for fermions, because of supersymmetry.

In the parabolic approximation, the dispersion law is written as

$$\varepsilon_k = \varepsilon_0 + \beta k^2, \qquad (3.102)$$

where $\varepsilon_0 = \alpha(T - T_c)$ is the soft mode 'frequency', T_c is the critical temperature, and α, β are positive constants. Moreover, the chemical potential for the nonconserved order parameter is $\mu = 0$ [30]. The result is that formulas (3.100) and (3.101) taken at $T = T_c$ and $k = 0$ give

$$\Omega_0^{(a)} = -T \ln 2, \qquad \Omega_0^{(b)} = -\infty. \qquad (3.103)$$

If the result obtained for the Bose contribution corresponds to the well-known critical rise in homogeneous fluctuations, then the first equality in Eqn (3.103) means the entropy jump $\Delta s = \ln 2$ per particle as a result of heterophase fluctuations.

The full thermodynamic potential of fluctuations $\Omega = \sum_k [\Omega_k^{(a)} + \Omega_k^{(b)}]$ has the form:

$$\Omega = TV \int_0^\infty \frac{k^2\, dk}{2\pi^2} \ln \tanh \frac{\varepsilon_k}{2T}, \qquad (3.104)$$

where the transition from summation over k to integration is accomplished, and V is the system volume. The resulting

formula is altogether different from the commonly used one (see for instance p. 524 in Ref. [30]) in that it contains the function tanh. The presence of this function appears to be of no consequence in the region of $\varepsilon_k \ll T$ which is largely responsible for the contribution to thermodynamic quantities, but at greater ε_k, $\ln \tanh(\varepsilon_k/2T) \approx 0$ so that there is no need to introduce the upper limit for the cut-off.

In the general case, the analytical determination of integral (3.104) is not feasible. However, given a fluctuation correction ΔC to thermal capacity, double differentiation with respect to temperature leads to the disappearance of the logarithm and the condition $\varepsilon_k \ll T$ allows for the approximation of hyperbolic functions by their arguments. The result is that the integral over k becomes analytical and the correction ΔC is expressed as

$$\Delta C = \frac{\alpha^{3/2} T_c^2 V}{2\pi^2 \beta^{3/2}} (T - T_c)^{-1/2} . \qquad (3.105)$$

Here, a large cofactor appears in the denominator, similar to the Levanyuk formula (see p. 525 in Ref. [30]). However, taking into consideration heterophase fluctuations leads to an $8/\pi \approx 2.55$-fold increase in the ΔC value.

Let us now consider the correlation function of fluctuations $S_k = \langle |\eta_k|^2 \rangle$. By determining η_k from Eqn (3.97) and omitting anomalous averages $\langle b_k^\pm b_{-k}^\pm \rangle$, it is easy to find, based on the Bose distribution $\langle \widehat{b_k^+ b_k^-} \rangle = [\exp(\varepsilon_k/T) - 1]^{-1}$, that

$$S_k = \frac{T}{\varepsilon_k} \cotanh \frac{\varepsilon_k}{2T} . \qquad (3.106)$$

By analogy with the fluctuation–dissipation theorem, the presence of the cotangent is apparent here when the fluctuation energy ε_k is smaller than the heat energy T. In the limit $\varepsilon_k \ll T$, one has $S_k = 2(T/\varepsilon_k)^2$ whence Porod's dependence can be obtained [provided Eqn (3.102) is taken into consideration at $T = T_c$]:

$$S_k = \frac{2T^2}{\beta^2 k^4} , \qquad (3.107)$$

which means an anomalous increase of fluctuations in the critical region. In the inverse limit $\varepsilon_k \gg T$, corresponding to the post-critical region, the Ornstein–Zernike distribution [30] is obtained:

$$S_k = \frac{T}{\alpha(T - T_c) + \beta k^2} . \qquad (3.108)$$

This method is equally suitable for the description of the spatial distribution of boundaries represented by the fermion correlator

$$\langle \Delta \widehat{n}(x) \Delta \widehat{n}(0) \rangle = \bar{n}\delta(x) + \bar{n}g(x), \quad \Delta \widehat{n}(x) = \widehat{n}(x) - \bar{n}(x) , \qquad (3.109)$$

where x is the coordinate perpendicular to the boundary, $\bar{n} = \langle \widehat{n} \rangle$ is the mean number of boundaries per unit length, and $g(x)$ the correlation function to be determined. By means of elementary calculations similar to those reported in paragraph 117 of Ref. [30], it is possible to obtain

$$g(x) = -\frac{1}{\bar{n}} \left| \int \frac{\exp(ikx)}{\exp[(\varepsilon_k - \mu)/T] + 1} \frac{dk}{2\pi} \right|^2 . \qquad (3.110)$$

Since it is assumed here that the mean density $\bar{n}$ of boundaries is preserved, the chemical potential $\mu \ne 0$, in contrast to formulas (3.103)–(3.108) that characterise

appearance and disappearance of fluctuations. Moreover, the weak effect of temperature on the boundary means that $\mu \gg T$, and the Fermi distribution can be approximated by the step function of size 1 in the range $[-k_F, k_F]$ where $k_F = \bar{n}/2\pi$ is the boundary value of the wave vector. Then, elementary computation of the integral in Eqn (3.110) yields

$$g(x) = -\frac{1}{\pi^2 \bar{n}} x^{-2} \sin^2(2\pi \bar{n} x) . \qquad (3.111)$$

Condition $g(x) < 0$ means effective repulsion of boundaries characterised by $g(0) = -4\bar{n}$.

3.7 The supersymmetric theory of phase transition

At first sight, the theory of phase transitions appears to be a well-established self-contained field of statistical physics. In reality, however, this is not true. To begin with, there is no universally accepted solution of the three-dimensional Ising problem, to say nothing about a number of nontrivial problems arising in the description of various situations. Nor is there a complete picture of phase transition, which would be indispensable if its most important features are to be characterised in greater detail using a common approach to the establishment of the relationship between the condensate and fluctuation constituents of the order parameter [20, 21], integrated representation of nucleation and growth stages [43, 44], description of macrostructural evolution of the ordered phase based on its microscopic structure [28], etc. We believe that the only candidate for the scheme of comprehensive representation of phase transition is the supersymmetric theory in which the role of bosonic components is played by condensate (η) and fluctuation (ϕ) constituents of the order parameter while fermionic components ψ, $\bar{\psi}$ characterise the behaviour of interphase boundaries. The construction of such a scheme is the objective of the present section [47].

The starting point of the supersymmetric representation of a statistical system is the Langevin equation which it is convenient to write as

$$\gamma^{-1}\dot{\eta} = -V' + \beta \nabla \eta + \zeta ;$$
$$V' = \frac{dV}{d\eta}, \quad V = \frac{A}{2}\eta^2 + \frac{B}{4}\eta^4 ;$$
$$\langle \zeta(r, t)\zeta(0, 0) \rangle = 2\frac{T}{\gamma} \delta(r)\delta(t) . \qquad (3.112)$$

Here, we have the simplest case of the one-component nonconserved order parameter η, the point denotes differentiation over time t, γ is the kinetic coefficient defining bare relaxation time, β is the inhomogeneity parameter, and $\zeta = \zeta(r, t)$ is the fluctuation field of the generalised force taken as white noise with the strength dependent on temperature T. The phase transition being considered is of the second order for which free energy $V(\eta)$ corresponds to the η^4-model of the field theory defined by parameters $A \propto T - T_c$; T_c is the critical temperature [30].

In the context of the field approach (see for instance Ref. [48]), it is convenient to pass from the stochastic equation (3.112) to the generating functional representing the Fourier transform averaged over noise $\zeta(r, t)$ in field $\eta(r, t)$ of the δ-function with the argument given by Eqn (3.112). Furthermore, according to the scheme proposed in Ref. [25] (see also Ref. [41]), it is convenient to get

rid of the δ-function by expanding it in a Fourier series in the ghost field φ, performing Gaussian averaging over noise ζ, and eliminating the Jacobian which takes into account transition from noise ζ to variable η, by introducing integration over the Grassmannian fields ψ, $\bar{\psi}$ from the respective exponential expression [see formulas (3.3)–(3.9)]. These components form the superfield [cf Eqn (3.13)]:

$$\Phi = \eta + T^{1/2}(\bar{\chi}\psi + \bar{\psi}\chi) + T\,\bar{\chi}\chi\phi\,,$$

$$\phi = \varphi + \frac{\dot{\eta}}{2T}\,, \tag{3.113}$$

where supercoordinates $\bar{\chi}$, χ (as well as supercomponents $\bar{\psi}$, ψ) satisfy the ordinary properties of Grassmanian variables (3.5). The supersymmetric Lagrangian of Eqn (3.112) obtained as a result of the above construction has the form:

$$\mathcal{L} = \gamma^{-1}\Phi\overline{D}D\Phi + \frac{\beta}{2}(\nabla\Phi)^2 + V(\Phi)\,, \tag{3.114}$$

where operators of superderivatives D, $\overline{D}$ are defined by equalities (3.15) and satisfy commutation relations (3.16). When these relations are taken into account, the equation of action extremum corresponding to the Lagrangian (3.114),

$$\left(\gamma^{-1}[\overline{D}, D] - \beta\nabla^2\right)\Phi + V'(\Phi) = 0\,,$$

$$V'(\Phi) \equiv \frac{dV(\Phi)}{d\Phi} = A\Phi + B\Phi^3 \tag{3.115}$$

leads to the system

$$(2T\gamma)^{-1}\ddot{\eta} + \left[-\beta\nabla^2 + V''(\eta)\right]\phi = -6B\psi\bar{\psi}\eta\,, \tag{3.116a}$$

$$\phi = -\frac{\gamma}{2T}\left[-\beta\nabla^2\eta + V'(\eta)\right]\,, \tag{3.116b}$$

$$\dot{\psi} + \gamma\left[-\beta\nabla^2 + V''(\eta)\right]\psi = 0\,, \tag{3.116c}$$

$$-\dot{\bar{\psi}} + \gamma\left[-\beta\nabla^2 + V''(\eta)\right]\bar{\psi} = 0\,, \tag{3.116d}$$

where

$$V''(\Phi) \equiv \frac{d^2 V}{d\Phi^2} = A + 3B\Phi^2\,. \tag{3.117}$$

The common feature of Eqns (3.116a)–(3.116d) is the nonlinear action of the condensate constituent η on all other components of the superfield (3.113). Characteristically, this relation for η, ψ, $\bar{\psi}$ is described by the second derivative $V''(\eta)$ of the Landau potential $V(\eta)$ whereas Eqn (3.116b) for the fluctuation constituent ϕ contains only the first derivative $V'(\eta)$. On the other hand, the Grassmannian components ψ, $\bar{\psi}$ influence only the condensate constituent η, but not the fluctuation one ϕ. Similarly, the fluctuation component ϕ affects only the condensate constituent η.

Equally notable is the mutual symmetry of Eqns (3.116c), (3.116d) for the Grassmannian fields $\psi(r, t)$, $\bar{\psi}(r, t)$: they can be derived one from the other by time inversion. Hence, an important conclusion: if dependence $\psi(t)$ describes real processes in a system undergoing transformation, then the conjugate field $\bar{\psi}(t)$ does the same for the time-reversed process. As regards equations for the condensate and fluctuation constituents η, ϕ, Eqn (3.116a) is of second order (with respect to time dependence) whereas Eqn (3.116b) reduces to the algebraic constraint equation. This reflects the asymmetry of the system with respect to the condensate and fluctuation

constituents of the superfield [it has already been mentioned that this asymmetry is also reflected in that the constraint equation (3.116b) contains the first derivative of the potential $V(\eta)$ while the remaining equations include the second derivative].

It is worthwhile to note that equations for the Bose components of the superfield can be made more symmetric if one passes from the fluctuation constituent ϕ to the ghost field φ using the second equality of (3.113). Indeed, equality (3.116b) will then take the form

$$\gamma^{-1}\dot{\eta} = -V'(\eta) + \beta\nabla^2\eta - 2\frac{T}{\gamma}\,\varphi\,. \tag{3.118}$$

Unlike the initial equation (3.112), Eqn (3.118) contains no stochastic terms. It appears from the comparison of Eqns (3.112) and (3.118) that the ghost field φ represents the enveloping line of fluctuations ζ of the generalised force. Differentiation of Eqn (3.118) with respect to time followed by substitution of the resulting expression for $\ddot{\eta}$ into Eqn (3.116a) yields

$$\gamma^{-1}\dot{\varphi} = -\left[-\beta\nabla^2 + V''(\eta)\right]\varphi + 6B\psi\bar{\psi}\eta\,. \tag{3.119}$$

The system (3.118), (3.119) in which the first derivative $V'(\eta)$ is included in the equation for the condensate constituent of the order parameter has a form similar to Eqns (3.116c), (3.116d). However, unlike the Grassmannian fields, this system is subject to the effect of additional forces. According to Eqn (3.118), the condensate constituent η changes at a rate influenced by the averaged fluctuation field φ, besides the self-consistent field, and the rate of changes in the averaged field depends [according to Eqn (3.119)] not only on interaction between φ and η but also on the external action $\psi\bar{\psi}\eta$.

As regards the solution of Eqns (3.116a)–(3.116d), it is obvious that the behaviour of the Grassmannian components is most simple to describe. In fact, multiplication of Eqn (3.116c) by $\bar{\psi}$ from the right and Eqn (3.116d) by ψ from the left followed by subtraction of the resultant expressions from each other leads to the continuity equation,

$$\dot{\rho} + \nabla j = 0\,;$$

$$\rho \equiv \gamma^{-1}\psi\bar{\psi}\,, \quad j \equiv \beta\left[\psi\nabla\bar{\psi} - (\nabla\psi)\bar{\psi}\right]\,. \tag{3.120}$$

Comparison with ordinary expressions of quantum mechanics (see for example paragraph 19 in Ref. [49]) indicates that coefficient β plays, in the context of the present approach, the role of the Planck constant† and the absence of the imaginary unit i in the definition of flow j formally indicates the imaginary character of time t. In a uniform case, $\nabla\psi = \nabla\bar{\psi} = 0$ and, according to Eqn (3.120), the quantity ρ is time-independent. Such a situation will be preserved in a nonuniform case provided the following condition is fulfilled:

$$\oint j\,dS = 0\,. \tag{3.121}$$

This condition implies that surface S does not embrace the topological singularities of fields $\psi(r)$, $\bar{\psi}(r)$ which appear to correspond to the sources of interphase boundaries. In this case, it is possible to transform to spatial Fourier images in Eqns (3.116c), (3.116d) ($-\nabla^2$ is substituted by the square of the wave vector $|k|^2$), and formal integration leads to the expression

$$\begin{bmatrix} \psi_k(t) \\ \bar{\psi}_k(t) \end{bmatrix} = \begin{pmatrix} \psi_{0k} \\ \bar{\psi}_{0k} \end{pmatrix} \exp\left\{ \mp\gamma \int_{t_0}^{t} [(A + \beta|k|^2) + 3B\eta_k^2(t')]\,dt' \right\},$$
$$(3.122)$$

where ψ_{0k}, $\bar{\psi}_{0k}$ are integration constants dependent on the choice of the initial time t_0. The resultant equality explicitly expresses the aforementioned fact that processes associated with time dependences $\psi_k(t)$, $\bar{\psi}_k(t)$ are related by time inversion. Substituting them into the definition (3.120) leads to $\rho_k(t) = \gamma^{-1}\psi_{0k}\bar{\psi}_{0k} \equiv \rho_k(0)$, suggesting invariability of boundary density on condition (3.121).

Before going on to solve equations for the Bose constituents η, ϕ (or η, φ), we shall show that the system (3.118), (3.119) gives rise to the equation for retarded Green's functions $G(r, t) = \langle \eta(r, t)\varphi(0, 0) \rangle$, where $t > 0$ and angular brackets denote averaging over fluctuations of the order parameter. Indeed, multiplying Eqn (3.118) by $\varphi(0, 0)$ and Eqn (3.119) (after the substitution $t \to -t$) by $\eta(0, 0)$ and invoking the property of spatiotemporal homogeneity, one can find in the mean field approximation (after summation of the results and averaging):

$$\left\{ \gamma^{-1}\frac{\partial}{\partial t} + [A + 3BS_0(r)] - \beta\nabla^2 \right\} G(r, t)$$
$$= -\frac{1}{2}\delta(r)\delta(t) + 3B[\gamma\rho(r) - G_0(t)]S(r, t) . \qquad (3.123)$$

Here, the autocorrelator of the condensate constituent $S(r, t) = \langle \eta(r, t)\eta(0, 0) \rangle$ is introduced, and $G_0(r) \equiv G(t = 0, r)$ and $S_0(r) \equiv S(t = 0, r)$ are the initial values. Characteristic features of this equation are renormalisation of the Landau parameter A as a result of nonlinearity (which obviously leads to a rise in transformation temperature) and the appearance of the nonlinear source associated with the existence of interphase boundaries and the self-action of the order parameter field. In order to determine the response function G from Eqn (3.123), it is necessary to know the behaviour of the autocorrelator S, the equation for which,

$$\left\{ \gamma^{-1}\frac{\partial}{\partial t} + [A + 3BS_0(r)] - \beta\nabla^2 \right\} S(r, t) = -2\frac{T}{\gamma}G(-t) ,$$
$$(3.124)$$

is derived in the same way as Eqn (3.123) after multiplication of equality (3.118) by $\eta(0, 0)$ and averaging. It is however appropriate to start from the analysis of the initial field equations (3.116a), (3.116b).

In the stationary homogeneous state, the spatiotemporal dependence disappears, which obviously means the impossibility of the occurrence of fluctuations. Therefore, it is necessary to assume $\ddot{\eta} = 0$, $\phi = 0$, $\dot{\psi} = \dot{\bar{\psi}} = 0$, $\nabla\Phi = 0$ in Eqns (3.116a)–(3.116d). This leads to the usual equilibrium conditions $\Phi = 0$ or $V'(\eta) = 0$. The former of these conditions corresponds to the initial nonequilibrium phase whereas the latter defines the equilibrium value of the order parameter $\eta_{00}^2 = -A/B$ in the ordered phase. Hence,

components of the superfield (3.113) in the stationary ordered state take values:

$$\eta_{00}^2 = -\frac{A}{B} , \qquad \psi_{00} = \bar{\psi}_{00} = 0 , \qquad \phi_{00} = 0 , \qquad \varphi = 0 . \quad (3.125)$$

Given the equivalence of all supercomponents in the disordered phase, this indicates that ordering results in spontaneous supersymmetry breaking which is apparent as the appearance of the condensate constituent $\eta_{00} \neq 0$. Creation of condensate η_{00} is accompanied by the appearance of the self-consistent field $h = \chi\eta_{00}$ where $\chi = |2A|^{-1}$ is susceptibility. This, in turn, accounts for the addition of $-h\eta$ to the Lagrangian (3.114). As a result, the mean stationary value of the fluctuation component ϕ in Eqns (3.116a)–(3.116d) is $\langle \phi \rangle = -\chi\eta_{00}/2T|A|$. Accordingly, the superaverage

$$\langle \Phi \rangle_s \equiv \int \langle \Phi \rangle \, d\bar{\chi}\,d\chi = -\langle \phi \rangle$$

becomes nonvanishing, which suggests supersymmetry breaking [41].

Let us consider the time course of ordering in a uniform system, proceeding from Eqns (3.116a), (3.116b) where $\psi\bar{\psi} = \gamma\rho$ is constant as follows from the analysis of relations (3.116c), (3.116d). Substitution of the fluctuation component ϕ from Eqn (3.116b) into Eqn (3.116a) yields the first integral:

$$\tau^2\dot{y}^2 = y^2\left(1 - y^2\right)^2 + \left(E - \frac{\rho}{\rho_c}y^2\right) ;$$

$$y \equiv \frac{\eta}{\eta_{00}} , \qquad \tau^{-1} \equiv \gamma|A| , \qquad \rho_c \equiv \frac{|A|\eta_{00}^2}{12T} , \qquad (3.126)$$

where E is the integration constant which plays the role of the starting point for the energy count. If it is assumed to be zero, it can be seen that the solution of Eqn (3.126) depends on the density of the Grassmannian field ρ. In the absence of the field ($\rho = 0$),

$$\eta^2 = \eta_{00}^2\left[1 + \exp\left(-\frac{t - t_0}{\tau}\right)\right]^{-1} , \qquad (3.127)$$

where t_0 is the integration constant. Evidently, this solution describes the spinodal ordering mechanism: in the initial state ($t \ll t_0$), one has $\eta_0 = 0$ whereas in the final state ($t \gg t_0$), the order parameter takes the equilibrium value η_{00}. The most significant change in dependence $\eta(t)$ occurs on the interval τ near the point $t = t_0$. This means that τ plays the role of relaxation time and t_0 denotes the moment when phase transition occurs. It follows from Eqn (3.127) that at $t \gg t_0$, the order parameter tends to the non-equilibrium value with relaxation time τ. In the opposite case of $t \ll t_0$, there is an exponential fall to zero with relaxation time $\tau/2$. This finding appears to reflect the well-known '2-law' since in the former case, the system undergoes ordering and in the latter case disordering.

When the Grassmanian field density ρ is positive, expression (3.127) gives

$$\eta^2 = \eta_{00}^2\left(1 - \frac{\rho}{\rho_c}\right)\left[1 + \left(\frac{\rho}{\rho_c}\right)^{1/2}\cosh\left(\frac{t - t_0}{\tau_{ef}}\right)\right]^{-1} ,$$

$$\tau_{ef} \equiv \frac{\tau}{2}\left(1 - \frac{\rho}{\rho_c}\right)^{1/2} . \qquad (3.128)$$

This dependence represents an instanton whose width τ_{ef} increases indefinitely and height $\eta(t_0)$ falls to zero with growing density $\rho \leqslant \rho_c$. Evidently, this process corresponds to mutual reorientation of ordered phase domains, the number of which is determined by ρ. From the viewpoint of energy, this means the system's transition from one well of potential $V(\eta)$ into another. The intensity of such transitions depends on the relationship between the height of the barrier $(\sim |A| \eta_{00}^2)$ separating the wells and temperature T. According to the last equality in (3.126), it is this relationship that determines the critical value of boundary density ρ_c. The physical sense of dependences (3.128) is that the stationary value of the order parameter in a domain decreases to zero at a rise of boundary density ρ to the critical value ρ_c while reorientation time τ_{ef} grows indefinitely. At $\rho \geqslant \rho_c$, the barrier between wells disappears, and the glass-type disordered state occurs.

Let us now examine the spatial patterns of stationary distribution of the ordered phase in the absence of fluctuations ($\phi = 0$). In this case, condition (3.116b) leads to a differential equation, the one-dimensional solution of which has the usual kink form:

$$\eta_0(x) = \pm \eta_{00} \tanh \frac{x - x_0}{\sqrt{2}\xi}, \qquad \xi^2 \equiv \beta |A|^{-1}. \qquad (3.129)$$

Evidently, this solution describes the flat antiphase boundary between domains which correspond to order parameter values $\pm \eta_{00}$. The correlation length ξ gives the thickness of the boundary and the integration constant x_0 its location.

In contrast to the canonical theory, our approach permits the establishment, in a self-consistent fashion, of the macroscopic scale $L \gg \xi$ corresponding to the domain size of the ordered phase. Taking into account fluctuations $\phi \neq 0$ and substituting their expression (3.116b) into the stationary equation (3.116a) with $\ddot{\eta} = 0$, it is possible to find for the spatial Fourier transform $y_q = \eta_k / \eta_{00}$ in relation to the dimensionless wave vector $\boldsymbol{q} = \xi \boldsymbol{k}$, that

$$y_q^2 = \frac{2}{3} \left\{ (1 - q^2) + \frac{1}{2} \left[(1 - q^2)^2 + \frac{3\rho}{\rho_c} \right]^{1/2} \right\}, \qquad (3.130)$$

where the sign in front of the square root is chosen in such a way as to ensure that the condition $y_q = 1$ is fulfilled at $\boldsymbol{q} = 0$, $\rho = 0$. The resultant dependence y_q^2 monotonically decreases from the value of $y_0^2 = (2/3)[1 + (1/2)(1 + 3\rho/\rho_c)^{1/2}]$, which corresponds to the long-wavelength limit $\boldsymbol{q} = 0$, to $y_q = 0$ at $q_0^2 = 1 + (\rho/\rho_c)^{1/2}$. Obviously, the latter value characterises the boundary thickness $d = \xi/q_0$, while the wave number q_1 at which the order parameter has equilibrium value $y_q^2 = 1$ gives the domain size $L = \xi/q_1$. If Eqn (3.130) is taken into account, the dependence of scales d, L on the density of boundaries $\rho \leqslant \rho_c$ has the form:

$$d = \xi \left[1 + \left(\frac{\rho}{\rho_c} \right)^{1/2} \right]^{-1/2}, \qquad L = \xi \left[\left(1 + \frac{\rho}{\rho_c} - 1 \right)^{1/2} \right]^{-1/2}. \qquad (3.131)$$

Thus, the boundary thickness $d(\rho)$ decreases in the range from ξ to $\widetilde{\xi} = 2^{-1/2}\xi \approx 0.707\xi$ and the domain size $L(\rho)$ from $L \approx \xi(2\rho_c/\rho)^{1/2}$ at $\rho \leqslant \rho_c$ and to $L_{\min} = (\sqrt{2} - 1)^{-1/2}\xi \approx 1.554\xi$ at $\rho = \rho_c$.

The state of a supersymmetric system given by the condensate constituent (3.129) and zero values

$$\phi_0 = 0, \qquad \psi_0 = 0, \qquad \bar{\psi}_0 = 0 \qquad (3.132)$$

of the remaining components of superfield Φ_0 is described above. The advantage of the supersymmetric approach is the possibility to reduce solution of the thermodynamic problem of considering fluctuations $\delta \Phi = \Phi - \Phi_0$ to the standard quantum–mechanical eigenvalue problem.

To begin with, let us expand the Lagrangian (3.114) up to quadratic terms in $\delta \Phi$. Then, in the equation of motion (3.115), $V'(\Phi)$ is substituted by $V''(\Phi)\delta\Phi$ and the equations for the components take the form

$$(2T\gamma)^{-1} \ddot{\eta} + (-\beta \nabla^2 + A + 3B\eta_0^2)\phi = 0, \qquad (3.133a)$$

$$\frac{2T}{\gamma} \phi + (-\beta \nabla^2 + A + 3B\eta_0^2)\eta = 0, \qquad (3.133b)$$

$$\gamma^{-1} \dot{\psi} + (-\beta \nabla^2 + A + 3B\eta_0^2)\psi = 0, \qquad (3.133c)$$

$$-\gamma^{-1} \dot{\bar{\psi}} + (-\beta \nabla^2 + A + 3B\eta_0^2)\bar{\psi} = 0. \qquad (3.133d)$$

Substitution of Eqn (3.133b) into Eqn (3.133a) leads to the second order equation, factorisation of which yields a pair of first order equations:

$$\pm \gamma^{-1} \dot{\eta} + (-\beta \nabla^2 + A + 3B\eta_0^2)\eta = 0. \qquad (3.134)$$

Their form is fully coincident with that of Eqns (3.133c), (3.133d) for Grassmannian fields. Therefore, in the system (3.116a)–(3.116d) corresponding to unbroken symmetry with totally different behaviour of the components, this difference is eliminated by supersymmetry breaking.

By substituting dependence (3.129) into Eqns (3.134), it is easy to shape them into the Schrödinger equation with imaginary time:

$$\mp (2\gamma)^{-1} \dot{\eta} = \widehat{H}_- \eta;$$

$$\widehat{H}_\pm = \frac{1}{2} \left(\widehat{p}^2 + W^2 \pm W' \right),$$

$$\widehat{p} = -i\beta^{1/2}\nabla, \quad W = (2B)^{1/2}\eta_0, \quad W' = \beta^{1/2}\frac{dW}{dx}. \quad (3.135)$$

The Hamiltonian $\widehat{H}_\pm$ has the form inherent in supersymmetric quantum mechanics with superpotential

$$W(x) = (2|A|)^{1/2} \tanh \frac{x - x_0}{\sqrt{2}\xi}. \qquad (3.136)$$

It is known [41] that a supersymmetric system has the energy level $E_0 = 0$ if the superpotential $W(x)$ has a different sign at the limit $x \to \pm\infty$. It is precisely such a case that is achieved by kink (3.136) which allows the conclusion that the system has the Goldstone mode of symmetry restoration, which corresponds to antiphase boundary motion (i.e. a change in coordinate x_0). Characteristically, even in the presence of a single 'kink–antikink' pair, the superpotential $W(x)$ has similar limits at $x \to \pm\infty$, and the motion of the boundaries may result in a change of the system energy associated with overcoming a barrier during collapse (nucleation) of the antiphase domain. The height of the barrier is defined by the first nonzero level,

$$E_1 = \frac{3}{2} |A|, \qquad (3.137)$$

of Hamiltonian $\widehat{H}_-$. Distributions of the condensate field constituent corresponding to levels E_0, E_1 have the form:

$$\eta_0'(x) = \pm \frac{\eta_{00}}{\sqrt{2}\xi} \cosh^{-2} \frac{x - x_0}{\sqrt{2}\xi} ,$$

$$\eta_1(x) \propto \sinh \frac{x - x_0}{\sqrt{2}\xi} \cosh^{-2} \frac{x - x_0}{\sqrt{2}\xi} . \qquad (3.138)$$

The first expression corresponds to space inhomogeneity caused by the presence of kink (3.129) and the second one to processes of domain reorientation. The energy of such reorientation has the form of Eqn (3.137), and characteristic energy of inhomogeneity [cf Eqn (2.66)]:

$$\sigma \equiv \beta \int \left[\eta_0'(x)\right]^2 \mathrm{d}x = \frac{4}{3\sqrt{2}} |A| \eta_{00}^2 \xi \qquad (3.139)$$

gives the coefficient of boundary surface tension.

4. Supersymmetry of strongly nonequilibrium thermodynamic systems

An important characteristic of open thermodynamic systems is the possibility of ordered structures being formed as noise (fluctuations) increases with movement from the equilibrium [29, 50]. In a uniform case, such structures are characterised by the amplitude corresponding to the hydrodynamic mode representing the order parameter, the value of which determines Bose condensate density. However, in the case of a well-developed (heterophase) spatial structure, it is also necessary to take into account the presence of sharp interphase (antiphase) boundaries [20, 21]. This means that an additional degree of freedom ψ needs to be introduced, besides the order parameter η, and its behaviour [although connected with field $\eta(r, t)$] must be regarded as self-consistent. Moreover, because the initial cause of rearrangement is enhanced fluctuations ϕ, a theory intended to represent a nonequilibrium thermodynamic system fully must also contain the fluctuation field $\phi(r, t)$.

The present section develops the supersymmetric scheme [51] which allows the aforesaid degrees of freedom to be represented in terms of the concept [25] as components of the superfield (3.13). It has been demonstrated in Section 3.1 that pseudo-Bose components η, ϕ represent the condensate and fluctuation constituents of the order parameter whereas the mutually conjugate Grassmannian components $\bar{\psi}$, ψ satisfying properties (3.5) represent behaviour of the boundaries. The validity of such a suggestion was confirmed in Sections 3.6 and 3.7 by the fact that in the simplest cases our supersymmetric scheme leads to the same results as the canonical theory of phase transitions. On the other hand, it gives the complete description of an arbitrary thermodynamic system which cannot be obtained using other approaches.

4.1 Linear approximation

It is clear from the foregoing discussion that the construction of the supersymmetric system is based on the Langevin equation (3.1) which establishes the relation between the rate of order parameter changes, the thermodynamic force, and the fluctuation field. Technically, it is not so convenient to work with the Langevin

equation itself as it is with the generating functional (3.8) corresponding to it, which has the form of a functional integral over superfield components η, ϕ, $\bar{\psi}$, ψ from the exponent of system action. Its Lagrangian takes the canonical form (3.14) in superfield representation (3.13).

In terms of the conventional variation procedure, the respective equation of free field motion has the form $\widehat{L}\Phi = 0$ where operator $\widehat{L}$ is represented in dimensional variables in the following way [cf Eqn (3.22)]:

$$\widehat{L} = \Theta^{-1}\left\{(1 - \xi^2\nabla^2) + \tau\left[\overline{D}, D\right]\right\} . \qquad (4.1)$$

Here, square brackets denote the commutator, Θ is the degree of the system's excitation (reducible to temperature in equilibrium systems), ξ is the correlation length taking into account microscopic inhomogeneity, $\nabla = \partial/\partial r$, τ is the bare relaxation time, and $\overline{D}$, D are covariant super-derivatives (supersymmetry group generators) with the form of Eqn (3.15) and satisfying properties (3.16). Hence, operators $\overline{D}$, D may be associated with the square root of the time derivative. In physical terms, this means that the scheme in question permits description not only of exponentially fast (Debye) relaxation but also of retarded processes reminiscent of glass structural relaxation [38].

Prior to the construction of the quantitative theory, it is worthwhile to note that operator (4.1) describes only dissipation processes corresponding to the initial Langevin equation. This is reflected in that the commutator $[\overline{D}, D]$ contains only the first power of the derivative $\partial/\partial t$. However, it is quite clear that, with growing degree of excitation Θ, the system can show reactive behaviour known to be associated with the second derivative $\partial^2/\partial t^2$ [16]. It appears from the second equality of Eqn (3.16) that this behaviour is taken into account by the addition of the term proportional to $[\overline{D}, D]^2$ in Eqn (4.1). As a result, the initial operator takes the form

$$\widehat{L} = \Theta^{-1}\left\{\left(1 - \xi^2\nabla^2\right) + \tau\left[\overline{D}, D\right] + \omega_0^{-2}\left[\overline{D}, D\right]^2\right\}, \qquad (4.2)$$

where ω_0 is the eigenfrequency of the system (soft mode frequency).

With the structure factor $S(r, t) = \langle\eta(r, t)\eta(0, 0)\rangle$ and generalised susceptibility $G(r, t) = \vartheta(t)\langle\eta(r, t)\varphi(0, 0)\rangle$ playing the role of observable quantities, it is further feasible to define the form of the equation of motion for the super-correlator,

$$\widehat{C}(r, t) = \left\langle \Phi(r, t)\Phi(0, 0) \right\rangle . \qquad (4.3)$$

It will be shown below that such a construction contains both experimentally measurable functions $S(r, t)$, $G(r, t)$ as the components. In the beginning, we shall confine ourselves to the examination of a free field corresponding to the operator (4.2) and afterwards examine the self-consistent Φ^4-theory. With this in mind, let us denote the free supercorrelator as $\widehat{C}^{(0)}$ and its components as $S^{(0)}$, $G^{(0)}$.

By definition,

$$\widehat{L}\widehat{C}^{(0)} = \widehat{\delta}, \qquad (4.4)$$

where the supersymmetric function δ is represented in the form of (3.24). Using equalities (3.15), (3.16), and (4.2) in

Eqn (4.4), we find, after Fourier transformation over the spatiotemporal components,

$$C_{\omega k}^{(0)}(\chi, \chi') = \frac{\Theta}{D_{\omega k}}\left[2\tau - i\tau\omega(\bar{\chi}'\chi - \bar{\chi}\chi')\right.$$

$$\left. - R_{\omega k}(\bar{\chi} - \bar{\chi}')(\chi - \chi') - \frac{\tau}{2}\omega^2\bar{\chi}\chi\bar{\chi}'\chi'\right] ; \quad (4.5)$$

$$D_{\omega k} \equiv R_{\omega k}^2 + \tau^2\omega^2, \quad R_{\omega k} \equiv \left(1 + \xi^2|k|^2\right) - \frac{\omega^2}{\omega_0^2}.$$

A characteristic feature of the supersymmetric structure of this expression is that all the terms can be separated into groups with 0, 2, and 4 supercoordinates. For this reason, it is convenient to expand the supercorrelator (4.3) in basic supermatrices:

$$B_\pm(\chi, \chi') = -\tau^{-1}\left(\bar{\chi}\chi \pm \bar{\chi}'\chi'\right),$$

$$T_\pm(\chi, \chi') = 1 \pm \tau^{-2}\bar{\chi}\chi\bar{\chi}'\chi',$$

$$F_\pm(\chi, \chi') = \tau^{-1}\left(\bar{\chi}'\chi \pm \bar{\chi}\chi'\right). \quad (4.6)$$

Then, expression (4.5) may be represented as

$$\widehat{C}_{\omega k}^{(0)} = \frac{\Theta\tau}{D_{\omega k}}\left\{R_{\omega k}\widehat{B}_+ + \left[1 - \left(\frac{\omega\tau}{2}\right)^2\right]\widehat{T} \right.$$

$$\left. + \left[1 + \left(\frac{\omega\tau}{2}\right)^2\right]\widehat{T}_- + R_{\omega k}\widehat{F}_+ - i\tau\omega\widehat{F}_-\right\}, \quad (4.7)$$

where superoperators $\widehat{B}_\pm$, $\widehat{T}_\pm$, $\widehat{F}_\pm$ have matrix elements defined by equalities (4.6). It should be emphasised that the bare correlator (4.7) does not possess 'projection' on component $\widehat{B}_-$.

Now, let us examine the properties of operators $\widehat{B}_\pm$, $\widehat{T}_\pm$, $\widehat{F}_\pm$. If we define the product of matrices (4.6) as:

$$A(\chi, \chi') = \tau^{-1}\int B(\chi, \chi'')C(\chi'', \chi')\,d\bar{\chi}''d\chi'', \quad (4.8)$$

it is easy to see that operators $\widehat{B}_\pm$, $\widehat{T}_\pm$, $\widehat{F}_\pm$ corresponding to them satisfy the multiplication rules shown in Table 1. If the superfield (3.13) is represented as the superspace vector $\Phi = (\eta\ \phi\ \bar{\psi}\ \psi)$, the action of basic operators is defined by the formulas:

$$\widehat{B}_+\Phi = \tau^{-1}(\eta\ \phi\ 0\ 0), \quad \widehat{B}_-\Phi = \tau^{-1}(-\eta\ \phi\ 0\ 0) ;$$

$$\widehat{T}_+\Phi = (-\phi\ -\tau^{-2}\eta\ 0\ 0), \quad \widehat{T}_-\Phi = (-\phi\ \tau^{-2}\eta\ 0\ 0) ;$$

$$\widehat{F}_+\Phi = \tau^{-1}(0\ 0\ \bar{\psi}\ \psi), \quad \widehat{F}_-\Phi = \tau^{-1}(0\ 0\ -\bar{\psi}\ \psi). \quad (4.9)$$

Hence, it is easy to see that the basic operators can be written in the form of matrices:

$$\widehat{B}_\pm = \tau^{-1}\begin{pmatrix} \pm1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}, \quad \widehat{T}_\pm = \begin{pmatrix} 0 & -1 & 0 & 0 \\ \mp\tau^{-2} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix},$$

$$\widehat{F}_\pm = \tau^{-1}\begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & \pm1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}. \quad (4.10)$$

Representation (4.7) is convenient because expansion of the supercorrelator in basic matrices (4.6) is possible not only for a free field but also in an arbitrary case. This is

Table 1. The multiplication rules of basic supermatrices.

	$\widehat{B}_+$	$\widehat{B}_-$	$\widehat{T}_+$	$\widehat{T}_-$	$\widehat{F}_+$	$\widehat{F}_-$
$\widehat{B}_+$	$\widehat{B}_+$	$\widehat{B}_-$	$\widehat{T}_+$	$\widehat{T}_-$	0	0
$\widehat{B}_-$	$\widehat{B}_-$	$\widehat{B}_+$	$-\widehat{T}_-$	$-\widehat{T}_+$	0	0
$\widehat{T}_+$	$\widehat{T}_+$	$\widehat{T}_-$	$\widehat{B}_+$	$\widehat{B}_-$	0	0
$\widehat{T}_-$	$\widehat{T}_-$	$\widehat{T}_+$	$-\widehat{B}_-$	$-\widehat{B}_+$	0	0
$\widehat{F}_+$	0	0	0	0	$\widehat{F}_+$	$\widehat{F}_-$
$\widehat{F}_-$	0	0	0	0	$\widehat{F}_-$	$\widehat{F}_+$

because operators $\widehat{B}_\pm$, $\widehat{T}_\pm$, $\widehat{F}_\pm$ form the complete basis: according to the multiplication rules (see Table 1), the product of any pair of operators is expressed through themselves. Characteristically, the squares of Bose operators $\widehat{B}_\pm$, $\widehat{T}_\pm$ reduce to a single Bose operator $\widehat{B}_+$ whereas the squares of Fermi operators $\widehat{F}_\pm$ give a single Fermi operator $\widehat{F}_+$. On the other hand, the Bose nature of operators $\widehat{B}_\pm$, $\widehat{T}_\pm$ and the Fermi nature of $\widehat{F}_\pm$ are reflected in the reducibility of products of operators of different groups to zero. Expansion into supercorrelators of the form of Eqn (4.7) appears to have first been used in Ref. [27]. However, the author examined the purely dissipative regime of spin glass behaviour which required the six-dimensional basis to be reduced to the three-dimensional one: $\widehat{E} = \widehat{B}_+ + \widehat{F}_+$, $\widehat{P} = \widehat{B}_- + \widehat{F}_-$, $\widehat{A} = (\widehat{T}_+ + \widehat{T}_-)/2$. Taking into consideration the reactive behaviour in our case leads to the splitting of three 'dissipative' operators $\widehat{E}$, $\widehat{P}$, $\widehat{A}$, into six independent ones, $\widehat{B}_\pm$, $\widehat{T}_\pm$, $\widehat{F}_\pm$ [51].

In order to find explicit expressions for experimentally measurable correlators, let us substitute the coordinate representation of superfield (3.13) into the definition (4.3). Then, taking into account Eqn (4.6),

$$\widehat{C}_{\omega k}^{(0)} = -\frac{\tau}{2}\left(\langle\eta_{\omega k}\phi_{-\omega\ -k}\rangle + \langle\phi_{\omega k}\eta_{-\omega\ -k}\rangle\right)\widehat{B}_+$$

$$+\frac{\tau}{2}\left(\langle\eta_{\omega k}\phi_{-\omega\ -k}\rangle - \langle\phi_{\omega k}\eta_{-\omega\ -k}\rangle\right)\widehat{B}_-$$

$$+\frac{1}{2}\left(\langle\eta_{\omega k}\eta_{-\omega\ -k}\rangle + \tau^2\langle\phi_{\omega k}\phi_{-\omega\ -k}\rangle\right)\widehat{T}_+$$

$$+\frac{1}{2}\left(\langle\eta_{\omega k}\eta_{-\omega\ -k}\rangle - \tau^2\langle\phi_{\omega k}\phi_{-\omega\ -k}\rangle\right)\widehat{T}_-$$

$$+\frac{\tau}{2}\left(\langle\psi_{\omega k}\bar{\psi}_{-\omega\ -k}\rangle - \langle\bar{\psi}_{\omega k}\psi_{-\omega\ -k}\rangle\right)\widehat{F}_+$$

$$-\frac{\tau}{2}\left(\langle\psi_{\omega k}\bar{\psi}_{-\omega\ -k}\rangle + \langle\bar{\psi}_{\omega k}\psi_{-\omega\ -k}\rangle\right)\widehat{F}_- \quad (4.11)$$

is found.

By comparing factors for identical basic operators in Eqn (4.7) and (4.11) for correlators

$$S_{\omega k} = \langle\eta_{\omega k}\eta_{-\omega\ -k}\rangle, \quad \widetilde{S}_{\omega k} = \tau^2\langle\phi_{\omega k}\phi_{-\omega\ -k}\rangle ;$$

$$\chi'_{\omega k} = \langle\eta_{\omega k}\phi_{-\omega\ -k}\rangle = \langle\phi_{\omega k}\eta_{-\omega\ -k}\rangle ;$$

$$G_{\omega k}^- = \langle\psi_{\omega k}\bar{\psi}_{-\omega\ -k}\rangle, \quad G_{\omega k}^+ = \langle\bar{\psi}_{\omega k}\psi_{-\omega\ -k}\rangle \quad (4.12)$$

one finds expressions

$$S_{\omega k}^{(0)} = 2\frac{\Theta\tau}{D_{\omega k}}, \qquad \widetilde{S}_{\omega k}^{(0)} = -\frac{1}{2}\frac{\Theta\tau}{D_{\omega k}}(\tau\omega)^2 \; ;$$

$$\chi_{\omega k}'^{(0)} = \frac{1}{2}\left(G_{\omega k}^{(0)+} - G_{\omega k}^{(0)-}\right), \qquad G_{\omega k}^{(0)\pm} = \mp\frac{\Theta}{R_{\omega k} \pm \mathrm{i}\tau\omega}, \quad (4.13)$$

where superscript $^{(0)}$ indicates that these expressions refer to the free field.

Comparison of formulas (4.13) with the results of the standard theory of phase transitions (see for instance Ref. [16]) shows that the former formula reduces to the usual expression for the structure factor in the Gauss approximation. At first sight, it seems quite unexpected that the fluctuation–dissipation theorem $S_{\omega k} = (2/\omega)\,\mathrm{Im}\,G_{\omega k}^-$ is fulfilled for autocorrelators of both the Bose $(S_{\omega k})$ and the Fermi $(G_{\omega k}^-)$ constituents of the superfield whereas in the standard case the place of the latter autocorrelator is taken by the function of response $\langle\eta_{\omega k}\varphi_{-\omega-k}\rangle$ of the order parameter η to the ghost field φ. It is easy to see that at least in terms of the approximation being used, the Fermi autocorrelator and the response function are identically coincident:

$$G_{\omega k}^- = \langle\eta_{\omega k}\varphi_{-\omega-k}\rangle \; . \tag{4.14}$$

In fact, with the relation $\varphi = \phi - \dot\eta/2$ between the ghost field φ and the fluctuation component of the superfield ϕ being taken into consideration, Eqn (4.14) immediately follows from equalities (4.12), (4.13).

The main finding in this section appears to be the equivalence of the autocorrelator of the Fermi component of the superfield and the function of response of the condensate constituent of the order parameter to the action of the fluctuation component (they both have Bose nature).

Finally, let us discuss the form (4.13) of the fluctuation correlator $\widetilde{S}_{\omega k}^{(0)}$. If the imaginary part of susceptibility $\chi_{\omega k}''^{(0)}$ is proportional, in the hydrodynamic limit $\omega, k \to 0$, only to the first power of frequency, then $\widetilde{S}_{\omega k}^{(0)} \propto \omega^2$ has the second degree of smallness. It is this fact that justifies the assumption of the absence of correlation between fluctuations in the hydrodynamic appoximation.

4.2 The supersymmetric diagram technique of the Φ^4 model
In designing the supersymmetric theory, it seems convenient to make use of the standard field-theory method of generating the functional [48] [cf Eqn (3.8)]:

$$Z\left[U(z)\right] = \int \exp\left[\int U(z)\Phi(z)\,\mathrm{d}z - \Theta^{-1}\left(S_0 + S'\right)\right]\mathrm{D}\Phi(z) \; . \tag{4.15}$$

Here, Φ is the superfield (3.13), $\mathrm{D}\Phi(z)$ stands for functional integration over its four components, z is the set of arguments consisting of coordinate r, time t, and super-coordinate χ, $U(z)$ is the auxiliary field, $S_0 = S_0[\Phi(z)]$ is the action functional of the free field, term

$$S' = \frac{v}{4}\int \Phi^4(z)\,\mathrm{d}z \tag{4.16}$$

represents the contribution associated with anharmonicity $v(r) = \mathrm{const} \equiv v$, and Θ in the degree of excitation reducible to temperature in an equilibrium system (see Sections 3.1 and 3.2). In the case of $U(z) = 0$, one has normalisation $Z = 1$ from Eqn (4.15) whereas double

variation over the auxiliary field $U(z)$ gives supercorrelator (4.3) [see Eqn (3.19)].

To pass to the construction of the perturbation theory, it is necessary to carry out formal expansion of expression (4.15) in powers of $(-S'/\Theta)$. This allows the supercorrelator (4.3) to be written in the form of the sum:

$$C(z,z') = \sum_{n=0}^{\infty}\frac{1}{n!}\left(\frac{-v}{4\Theta}\right)^n\left\langle\Phi(z)\left[\int\Phi^4(z_1)\,\mathrm{d}z_1\right]^n\Phi(z')\right\rangle_0, \tag{4.17}$$

where averaging

$$\langle\ldots\rangle_0 \equiv \int\ldots\exp\left\{-\Theta^{-1}S_0 + \int U\Phi\,\mathrm{d}z\right\}\mathrm{D}\Phi \tag{4.18}$$

is performed over the free field only. Because integral (4.18) has Gaussian character, $\langle\Phi(z)\rangle_0 = 0$ under unbroken supersymmetry conditions, and it is possible to use the Wick theorem:

$$\langle\Phi(z_1)\ldots\Phi(z_n)\rangle_0$$
$$= \begin{cases} 0, & \text{if } n \text{ odd}, \\ \sum\langle\Phi(z_{p_1})\Phi(z_{p_2})\rangle_0\ldots\langle\Phi(z_{p_{n-1}})\Phi(z_{p_n})\rangle_0, & \text{if } n \text{ even}, \end{cases}$$
$$\tag{4.19}$$

where summation is carried out over all possible pairings of cofactors. Similar to the ordinary case [36], the use of the Wick theorem (4.19) allows the supercorrelator (4.17) to be represented as an expansion in powers of free supercorrelators $C^{(0)}(z,z') = \langle\Phi(z)\Phi(z')\rangle_0$. The further problem is to determine coefficients of such expansion.

For this purpose, let us represent, as usual, the free supercorrelator $\widehat{C}^{(0)}$ as a thin bar, the full super-correlator $\widehat{C}$ as a thick bar, and anharmonicity $(-v/4\Theta)$ as a point. Similar to the universally accepted diagram technique [36], let us assume that integration is taken over internal variables $z_1, z_2, \ldots, z_n$ while external ones z, z' are fixed. Moreover, it is easy to show, as in the ordinary case, that disconnected diagrams lead to the factor $Z(0) = 1$ and may therefore be disregarded. The self-energy part $\widehat{\Sigma}$ included in the Dyson equation $\widehat{C}^{-1} = \widehat{C}^{(0)-1} - \widehat{\Sigma}$ has, in the two first orders of the perturbation theory, the form shown in Fig. 14, where it is taken into consideration that each point in expression $\widehat{C}^{(0)}\widehat{\Sigma}\widehat{C}^{(0)}$ must have four tails. It appears from the expressions explicitly written for the correlator in the first order,

$$C^{(1)}(z,z') = s_1\left(-\frac{v}{4\Theta}\right)\int\langle\Phi(z)\Phi^4(z_1)\Phi(z')\rangle_0\,\mathrm{d}z_1, \tag{4.20}$$

that the first cofactor $\Phi(z)$ can be paired with $\Phi^4(z_1)$ in four possible ways. Three other pairings remain for the last cofactor $\Phi(z')$. The resulting coefficient $s_1 = 4 \times 3/1! = 12$. Accordingly, in the second order, we have

$$C^{(2)}(z,z')$$
$$= s_2\left(-\frac{v}{4\Theta}\right)^2\iint\langle\Phi(z)\Phi^4(z_1)\Phi^4(z_2)\Phi(z')\rangle_0\,\mathrm{d}z_1\,\mathrm{d}z_2. \tag{4.21}$$
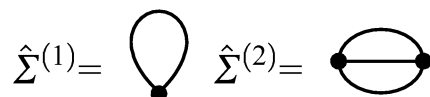

Figure 14. Contributions to the self-energy part.

It appears from the respective diagram in Fig. 14 that here cofactors $\Phi(z)$, $\Phi(z')$ can be paired with cofactors $\Phi^4(z_1)$, $\Phi^4(z_2)$ of different arguments only. Consequently, the number of pairings for the first argument equals 8 and for the second one is 4. Moreover, $3 \times 2 = 6$ additional pairings are possible in the remaining product $\Phi^3(z_1)\Phi^3(z_2)$. The result is $s_2 = (8 \times 4) \times (3 \times 2)/2! = 96$.

Thus, the use of the Wick theorem (4.19) and the Dyson equation gives the following expressions for contributions presented in Fig. 14:

$$\Sigma^{(1)}(z, z') = -3 \frac{v}{\Theta} C^{(0)}(z, z')\delta(z - z'),$$

$$\Sigma^{(2)}(z, z') = 6\left(\frac{v}{\Theta}\right)^2 \left[C^{(0)}(z, z')\right]^3 . \qquad (4.22)$$

Until now, the line of reasoning was not different from the standard one [36] since the supersymmetric structure of correlators was not disclosed and the formulas obtained, Eqns (4.22), are of the general form. In order to find explicit expressions for observable correlators, it is necessary to expand type (4.11) supercorrelators in basic matrices of the superspace $\widehat{B}_\pm$, $\widehat{T}_\pm$, $\widehat{F}_\pm$ [see Eqn (4.6)]. For the bare correlator $\widehat{C}^{(0)}$, it has the form of Eqn (4.7). The full correlator is represented by the expansion

$$\widehat{C} = g_0\widehat{B}_+ + g_1\widehat{B}_- + S_0\widehat{T}_+ + S_1\widehat{T}_- + G_0\widehat{F}_+ + G_1\widehat{F}_- , \qquad (4.23)$$

where indices of frequency ω and wave vector $\mathbf{k}$ are omitted for brevity. It follows from the analysis of form (4.11) of the bare correlator, that components $g_{0,1}$ have the sense of real and imaginary suceptibility constituents, $S_0 \pm S_1$ are the autocorrelators of condensate and fluctuation constituents of the order parameter, and $G_0 \pm G_1$ are the advanced and retarded Green's functions of the superfield Fermi constituent.

In order to define the explicit form of the self-energy part (4.22), it is necessary to substitute expansion (4.23) and take into consideration that the supersymmetric function δ has the form of (3.24) (it is convenient to return to the spatiotemporal representation to avoid convolutions over frequencies and wave vectors). Then, with regard for definitions (4.6), one has

$$\widehat{\Sigma}^{(1)} = -3 \frac{v}{\Theta}\left[(S_0 + S_1)\widehat{B}_+ + (g_0 - G_0)\widehat{T}_+ \right.$$
$$\left. -(g_0 - G_0)\widehat{T}_- + (S_0 + S_1)\widehat{F}_+\right]\delta(\mathbf{r})\delta(t) . \qquad (4.24)$$

It is worth noting that the Bose constituent $\widehat{B}_-$ is absent here as it is in the bare correlator (4.7). Moreover, the Fermi constituent $\widehat{F}_-$ is equally lacking. Both of them appear in the second order of the perturbation theory:

$$\widehat{\Sigma}^{(2)} = 6\left(\frac{v}{\Theta}\right)^2 \left\{3g_0(S_0 + S_1)^2\widehat{B}_+ + 3g_1(S_0 + S_1)^2\widehat{B}_- \right.$$

$$+\frac{1}{2}(S_0 + S_1)\left[(S_0 + S_1)^2 - 6(G_0^2 - G_1^2)\right.$$

$$\left. +3(S_0^2 - S_1^2) + 6(g_0^2 - g_1^2)\right]\widehat{T}_+$$

$$+\frac{1}{2}(S_0 + S_1)\left[(S_0 + S_1)^2 + 6(G_0^2 - G_1^2)\right.$$

$$\left. -3(S_0^2 - S_1^2) - 6(g_0^2 - g_1^2)\right]\widehat{T}_-$$

$$\left. +3G_0(S_0 + S_1)^2\widehat{F}_+ + 3G_1(S_0 + S_1)^2\widehat{F}_-\right\} . \qquad (4.25)$$

Following substitution into the supersymmetric Dyson equation (3.35), these formulas give the self-consistent description of an arbitrary thermodynamic system in terms of the Φ^4 model. In explicit form, Eqn (3.35) reduces to six equations appearing in front of basic matrices. These equations can be found by means of the (4.23)-type expansion for the supersymmetric self-energy part:

$$\widehat{\Sigma} = \sigma_0\widehat{B}_+ + \sigma_1\widehat{B}_- + E_0\widehat{T}_+ + E_1\widehat{T}_- + \Sigma_0\widehat{F}_+ + \Sigma_1\widehat{F}_- . \qquad (4.26)$$

Using equalities (4.24), (4.25), it is easy to find that the components of this expansion have the form:

$$\sigma_\pm(\mathbf{r}, t) = -3 \frac{v}{\Theta} S_+(t = 0)\delta(\mathbf{r})\delta(t) + 18 \frac{v^2}{\Theta^2} S_+^2(\mathbf{r}, t)g_\pm(\mathbf{r}, t);$$

$$\Sigma_\pm(\mathbf{r}, t) = -3 \frac{v}{\Theta} S_+(t = 0)\delta(\mathbf{r})\delta(t) + 18 \frac{v^2}{\Theta^2} S_+^2(\mathbf{r}, t)G_\pm(\mathbf{r}, t);$$

$$E_+(\mathbf{r}, t) = 6 \frac{v^2}{\Theta^2} S_+^3(\mathbf{r}, t) ;$$

$$E_-(\mathbf{r}, t) = -3 \frac{v}{\Theta}\left[g_0(\mathbf{r}, t) - G_0(\mathbf{r}, t)\right]\delta(\mathbf{r})\delta(t)$$

$$+18 \frac{v^2}{\Theta^2} S_+(\mathbf{r}, t)\left[3g_+(\mathbf{r}, t)g_-(\mathbf{r}, t) + S_+(\mathbf{r}, t)S_-(\mathbf{r}, t)\right.$$

$$\left. -3G_+(\mathbf{r}, t)G_-(\mathbf{r}, t)\right] . \qquad (4.27)$$

Here, quantities with indices $\pm$ and 0,1 are related through equalities of the type $\Sigma_{0,1} = (1/2)(\Sigma_+ \pm \Sigma_-)$. It should be emphasised that equalities (4.27) are written for the system exhibiting both dissipative and reactive behaviours. For the specific case of purely dissipative systems, they were first reported in Ref. [27].

4.3 The self-consistent Φ^4 theory

Let us use factorisation (3.34) to construct the self-consistent theory. In this case, the Dyson equation takes the form of Eqn (3.35) where term $\widehat{D} = \widehat{C}^{(0)-1} - \widehat{\Sigma}$ is represented as the following expansion [cf Eqns (3.37), (4.23)]:

$$\widehat{D} = d_0\widehat{B}_+ + d_1\widehat{B}_- + A_0\widehat{T}_+ + A_1\widehat{T}_- + D_0\widehat{F}_+ + D_1\widehat{F}_- . \qquad (4.28)$$

Here, coefficients $d_{0,1}$, $A_{0,1}$, $D_{0,1}$ are given in terms of the supersymmetric diagram technique (see Section 4.2) which differs from the traditional approach by several types of propagators and, consequently, coefficients in front of corresponding diagrams. The use of Eqn (4.7) yields

$$d_{0,1} = \frac{1}{2}(d_+ \pm d_-), \qquad A_{0,1} = \frac{1}{2}(A_+ \pm A_-),$$

$$D_{0,1} = \frac{1}{2}(D_+ \pm D_-) ;$$

$$d_\pm = \frac{1}{\Theta\tau}\left[\left(1 + \xi^2|\mathbf{k}|^2\right) - \left(\frac{\omega}{\omega_0}\right)^2\right] - \sigma_\pm ;$$

$$A_+ = -\frac{2}{\Theta\tau} - E_+, \qquad A_- = \frac{\omega^2\tau}{2\Theta} - E_- ;$$

$$D_\pm = \frac{1}{\Theta\tau}\left\{\left[\left(1 + \xi^2|\mathbf{k}|^2\right) - \left(\frac{\omega}{\omega_0}\right)^2\right] \mp i\omega\tau\right\} - \Sigma_\pm , \qquad (4.29)$$

where $\sigma_\pm$, $E_\pm$, $\Sigma_\pm$ are defined by equalities (4.27).

All previous formulas contain spatiotemporal dependence. In solving the supersymmetric Dyson equation, it is convenient to change to the respective Fourier components.

Then, substitution of expansions (4.23), (4.28) into Eqn (3.35) leads to the system

$$d_0 g_0 + d_1 g_1 + A_0 S_0 - A_1 S_1 - \frac{2w}{\Theta^2}(g_0^2 + g_1^2 + S_0^2 - S_1^2) = 1 \,,$$

$$d_0 g_1 + A_0 S_1 - A_1 S_0 + d_1 g_0 - \frac{4w}{\Theta^2} g_0 g_1 = 0 \,,$$

$$d_0 S_0 - d_1 S_1 + A_0 g_0 + A_1 g_1 - \frac{4w}{\Theta^2} g_0 S_0 = 0 \,,$$

$$d_0 S_1 - d_1 S_0 + A_0 g_1 + A_1 g_0 - \frac{4w}{\Theta^2} g_0 S_1 = 0 \,; \qquad (4.30a)$$

$$D_0 G_0 + D_1 G_1 - \frac{2w}{\Theta^2}(G_0^2 + G_1^2) = 1 \,,$$

$$D_0 G_1 + D_1 G_0 - \frac{4w}{\Theta^2} G_0 G_1 = 0 \,. \qquad (4.30b)$$

Interestingly, equations for the Bose ($g_{0,1}$, $S_{0,1}$) and Fermi ($G_{0,1}$) correlators are not linked. Apparently, the simplest is the extraction of Fermi components:

$$G_\pm^{-1} - D_\pm + \frac{2w}{\Theta^2} G_\pm = 0 \,;$$

$$G_0 = \frac{D_0 G_+ G_-}{1 + (2w/\Theta^2)G_+ G_-} \,, \quad G_1 = -\frac{D_1 G_+ G_-}{1 - (2w/\Theta^2)G_+ G_-} \,. \qquad (4.31)$$

Accordingly, for Bose components,

$$g_\pm^{-1} - d_\pm + \frac{2w}{\Theta^2} g_\pm$$

$$= \frac{A_+ A_-}{(4w/\Theta^2)g_0 - d_\mp}\left[1 - \frac{(2w/\Theta^2)g_\mp}{(4w/\Theta^2)g_0 - d_\pm}\right] \,;$$

$$g_0 = \frac{d_0 \mathcal{G}^2}{1 + (2w/\Theta^2)\mathcal{G}^2} \,, \quad g_1 = -\frac{d_1 \mathcal{G}^2}{1 - (2w/\Theta^2)\mathcal{G}^2} \,,$$

$$S_\pm = \frac{A_\pm g_\pm}{(4w/\Theta^2)g_0 - d_\mp} \,;$$

$$\mathcal{G}^2 \equiv g_+ g_-\left\{1 - \frac{A_+ A_-}{[(4w/\Theta^2)g_0 - d_+][(4w/\Theta^2)g_0 - d_-]}\right\} \,. \qquad (4.32)$$

In a general case, analysis of Eqns (4.31), (4.32) containing the complete description of the arbitrary thermodynamic system encounters great difficulty because the developed scheme takes into consideration both dissipative and reactive behaviours. In a weakly nonequilibrium system, e.g. in glasses, it is sufficient to take into account dissipation only. Formally, this means that $A_- = 0$, and the system of Eqns (4.31), (4.32) reduces to that investigated in Ref. [27] (see Sections 3.2 and 3.3). It turns out that strong nonequilibrium leads to ergodicity breaking characterised by the nonzero difference between adiabatic and isothermal susceptibilities and the appearance of memory, meaning that the structure factor $S_+(t)$ assumes nonzero values in the limit $t \to \infty$. It is evident from the last formula in Eqn (4.31) that the point of ergodicity breaking is defined by divergence of the Fermi correlator [cf Eqn (3.39)]:

$$\frac{2w}{\Theta^2} G_+ G_- = 1 \,. \qquad (4.33)$$

Characteristically, the self-consistent description of non-ergodicity and memory effects is possible only in the second order of the perturbation theory in anharmonicity v [27]. This can be accounted for by the fact that the self-energy part (4.24) defined in the first order of the perturbation theory does not contain components parallel to 'directions' $\widehat{B}_-$, $\widehat{F}_-$. On the other hand, behaviour of the dissipative system depends on the sum of basic operators $\widehat{T}_+$, $\widehat{T}_-$ rather than on either of them taken alone. Since coefficients in front of $\widehat{T}_+$, $\widehat{T}_-$ in Eqn (4.24) have opposite signs, their sum also vanishes. Therefore, the nonzero constituents oriented along 'directions' $\widehat{B}_-$, $\widehat{F}_-$, $\widehat{T}_+ + \widehat{T}_-$, which are responsible for memory and nonergodicity, appear only in the second order [see Eqn (4.25)].

Setting aside the comprehensive analysis of the strongly nonequilibrium nonergodic system with memory, let us examine a simpler case of the relationship between the reactive and dissipative constituents in the first order of the perturbation theory. Furthermore, let us neglect interatomic interaction ($w = 0$). Then, the system (4.32) takes the form:

$$g_\pm = \frac{d_\pm}{d_+ d_- - A_+ A_-} \,, \quad S_\pm = -\frac{A_\pm}{d_+ d_- - A_+ A_-} \,. \qquad (4.34)$$

With regard for Eqn (4.29), the divergence condition for the correlators obtained leads to the dispersion law

$$\omega = \mathrm{i}\frac{\omega_0^2 \tau}{\Theta} \pm \omega_0\left[\left(1 + 12\frac{v}{\Theta}S\right) - \left(\frac{\omega_0 \tau}{2\Theta}\right)^2\right]^{1/2} \,, \qquad (4.35)$$

where $S = S_+(t = 0)$ is the quadratic average of the order parameter. Given small degrees of nonequilibrium Θ, spectrum (4.35) has a purely dissipative character, and the system's behaviour does not differ from that reported in Ref. [27]. However, at degrees of excitation Θ exceeding the critical value

$$\Theta_{\mathrm{c}} = -6vS + \left[3vS + \left(\frac{\omega_0 \tau}{2}\right)^2\right]^{1/2} \,, \qquad (4.36)$$

frequency (4.35) acquires a real constituent which greatly exceeds the imaginary part when $\Theta \gg \Theta_{\mathrm{c}}$. This means that maximally excited systems can be in the stationary state where the hydrodynamic mode corresponding to the order parameter is in auto-oscillatory motion. The Belousov–Zhabotinsky reaction appears to be the most remarkable example of such behaviour [29]. According to Eqn (4.36), systems in which the stationary auto-oscillation state can occur must possess anharmonicity in excess of the critical value

$$v_{\mathrm{c}} = \frac{1}{24S}\left[1 + \sqrt{1 + (2\omega_0 \tau)^2}\right] \,. \qquad (4.37)$$

As expected, anharmonicity is less the higher the quadratic average of the order parameter S and the lower the soft mode frequency ω_0 and relaxation time τ. Such strict limitations account for the reason that systems with the behaviour of the Belousov–Zhabotinsky reaction type are relatively rare.

5. Conclusions

Analysis of the behaviour of the spatiotemporal structure in a nonequilibrium system indicates that the integrated picture of its evolution is available in terms of the self-consistent representation of condensate and fluctuation constituents of the order parameter and the density of interphase

boundaries as components of the unitary superfield. In this representation, Bose components correspond to the order parameter constituents while Fermi components correspond to the density of antiphase boundaries.

The supersymmetric approach allows phase nucleation and further precipitate growth to be described as the initial and the late stages respectively of the integrated relaxation process in the nonequilibrium system. Division into stages is regarded as supersymmetry breaking which suggests the appearance of heterophase fluctuations among homogeneous ones. This results in ergodicity breaking by the system.

The use of the supersymmetric approach makes it possible to represent the hydrodynamic mode of ordering and its spatial inhomogeneity, and also take into consideration retarded evolution of the structural relaxation type (along with the usual kinetic effects). This is achieved by taking into account the hierarchical relationship between microscopic and macroscopic structural levels of the system undergoing phase transition. Characteristics of the microscopic level are inherent in the standard ordering picture whereas those of the macrolevel represent the large-scale (domain or heterophase) structure of the ordered phase and its retarded evolution.

The supersymmetric theory allows for the self-consistent representation of the behaviour of homogeneous and heterophase fluctuations. This leads to the disappearance of nonphysical divergences in the expression for the thermodynamic potential while the heat capacity jump increases.

The joint examination of the reactive and dissipative behavioural regimes of a strongly nonequilibrium thermodynamic system implies broadening the basis of the superoperator space from three to six supermatrices in which the arbitrary supercorrelator is expanded. Coefficients of such an expansion give the structure factor and susceptibility of the condensate and fluctuation components of the order parameter as well as the distribution density of antiphase boundaries.

The first order of the supersymmetric perturbation theory suggests the possibility for a nonequilibrium thermodynamic system to exhibit reactive behaviour if the degree of excitation exceeds a critical value determined by the parameter of anharmonicity. Such conditions occur only in the systems where this parameter exceeds the threshold value inversely proportional to the average quadratic fluctuation of the order parameter.

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