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Kinetics of Polydomain Ordering at Second-Order Phase Transitions (by the Example of the $AuCu_3$ Alloy)

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Abstract Kinetics of polydomain spinodal ordering is studied in alloys of $AuCu_3$ type. We introduce four non-conserved long-range order parameters whose sum, however, *is* conserved and, using the statistical approach, follow the temporal evolution of their random spatial distribution after a rapid temperature quench. A system of nonlinear differential equations for correlators of second and third order is derived. Asymptotical analysis of this system allows to investigate the scaling regime, which develops on the late stages of evolution and to extract additional information concerning the rate of decrease of the specific volume of disordered regions and the rate of decrease of the average thickness of antiphase boundaries. Comparison of these results to experimental data is given. The quench below the spinodal and the onset of long-range order may be separated by the incubation time, whose origin is different from that in first-order phase transitions. Numerical integration of equations for correlators shows also, that it is possible to prepare a sample in such a way that its further evolution will go with formation of transient kinetically slowed polydomain structures different from the final $L1_2$ structure.

Keywords Connected long-range order parameters · Polydomain ordering · Statistical approach

1 Introduction

Order-disorder phase transitions in systems with the degenerate ground state go with formation of a polydomain structure. Domains in such a structure, being physically equivalent, differ either by crystallographic orientation or by inversion of atomic distribution over the equivalent sublattices.

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By now thermodynamically equilibrium states in systems described by one or several long-range order parameters have been determined and classified.

At the same time various kinetic characteristics of ordering, times of formation of a domain structure, temporal evolution of its length scales such as the size of antiphase domains (APD) and the thickness of transitive regions (antiphase boundaries, APB) are not fully explored. This is connected not so much with the accuracy and simplicity of the adopted kinetic equations as with the necessity of the statistical approach to the problem.

Let us bring an example. Consider a binary alloy, which is rapidly quenched from a high-temperature disordered phase, to a sufficiently low temperature where a long-range order is expected to develop. Immediately after the quench the alloy is characterized by the high-temperature random fluctuations of the order parameter(s). It is clear that the relevant statistical characteristics of these fluctuations will determine the kinetics (especially a polydomain one) of ordering. Mathematically this is explained by the fact that the quenched-in random fluctuations of the order parameters enter the initial conditions for kinetic equations. Thus the problem of polydomain ordering can be posed as finding the solution of deterministic equations subject to random initial conditions.

We shall demonstrate our statistical approach to the problem of polydomain ordering by the example of an alloy $AuCu_3$ crystallizing into an fcc lattice and described by four order parameters (according to the number of sublattices building fcc lattice). Various aspects of ordering kinetics in this alloy have been previously discussed in many works (see e.g. [1–4]). It was noticed in particular, that ordering can be initiated either via nucleation or by delocalized fluctuations as a second-order phase transition [2]. These two mechanisms have been observed both in experiments [3] and in computer simulation studies. X-ray scattering experiments permit to determine the pair correlator of the order parameter and to trace the crossover of the character of the corresponding random field from Gaussian to non-Gaussian.

Ordering in alloys with the number of sublattices bigger than two, proceeds in a complex way, involving formation of APDs of many types. Description of this process requires introducing several order parameters $\{p_i\}$; at equilibrium they assume certain values $\{p_{ie}\}$. Usually parameters p_i are physically equivalent; therefore their various transpositions represent physically equivalent ordered structures. This leads to existence of the corresponding number of types of APDs. Besides there can be nonequivalent ordered structures, not resulting from each other by a simple transposition of order parameters.

Phenomenological description of ordering kinetics in alloys includes deriving and solving kinetic equations for time- and space-dependent long-range order parameters $p_i(\mathbf{r}, t)$. Although the principal scheme for derivation of such equations is already developed (see [5, 6]), its practical realization is connected with substantial difficulties.

For this reason in the present paper we limit ourselves to fcc binary alloys of $AuCu_3$ type and the strictly stoichiometrical composition 25 at.% Au. We do not account for possible variations of concentration and focus only on the changes in degree of local order.

Kinetics of homogeneous single-domain ordering in $AuCu_3$ has been studied in [7]. It also can be viewed as description of ordering within a single domain entering the polydomain structure.

We are interested in formation and development of a polydomain structure, where possible types of ordering are $L1_2$ and $L1_0$, and the corresponding number of types of APDs may arise.

Structure and evolution of nonequilibrium inhomogeneous alloys are widely discussed and investigated, e.g. in [6, 8]. Some authors derive microscopic dynamical equations basing on the concept of chemical potentials, attributed to each lattice site, and solve them numerically [9]. In other studies ordering dynamics is computer simulated by Monte Carlo method [10].

Our phenomenological approach allows to obtain in a compact and clear form some general relations pertaining not only to ordering kinetics of the considered alloy, but also, as we hope, to kinetics of various phase transformations, going with formation of a polydomain structure. Most general issues of such kinetics were discussed by Lifshitz in [11].

In this paper we modify the previously proposed [12] statistical approach in order to give the phenomenological description (by the example of the $AuCu_3$ alloy) for phase transformation kinetics proceeding without nucleation, and characterized by several equivalent order parameters.

2 The Model and the Dynamic Equations

Let us consider a binary alloy of the AB_3 stoichiometry (25 at.% of the component A), which crystallizes into a fcc lattice and is a solid substitution solution. Vacancies are neglected. All sites of the fcc lattice are geometrically and energetically equivalent. Following Shockley [13] we shall divide the fcc lattice into four interpenetrating simple cubic sublattices, shifted with respect to each other by half of the face diagonal of the initial cube.

It is natural to characterize ordering of the alloy by distribution of the atoms A, and thus, automatically, of the atoms B, over the sites of the four specified sublattices. For example, in the state of complete order at $T = 0$, all atoms A are in the sites of one of the sublattices, whereas the atoms B occupy all sites of the other three. At high temperatures the alloy is disordered and the atoms A are distributed randomly and evenly over the four sublattices.

Therefore we shall use the occupation probabilities $p_A^i = p_i$ $(i = 1, \ldots, 4)$, being the probabilities to find an atom A in the site of each of the sublattices, as the long-range order parameters; and so it is already established in literature [14]. The four parameters so chosen are equivalent to each other due to equivalence of the four sublattices of an fcc lattice.

These parameters are not independent since their sum is, obviously, equal to concentration of the alloy multiplied by four

$$\sum_{i=1}^{4} p_i = 1. \tag{1}$$

We shall not consider in this paper concentration decomposition of the alloy, therefore (1) is valid at any point in the sample and for any instant of time.

It is necessary to say, that ordering in alloys is, generally speaking, accompanied by diffusion mass transfer of atoms [15, 16] over distances much exceeding interatomic one. Ordering itself is not a diffusion process. The ratio between the corresponding characteristic times (diffusion and non-diffusion) is of the order $(d/r_0)^2 \gg 1$, where d is the size of the domain, and r_0 is the quantity of the order of interatomic distance.

Hence for times not too late, aiming to reveal features inherent to ordering itself, it is possible to neglect the accompanying diffusion processes.

Relation (1) is fulfilled if to associate the parameters p_i with the lengths of the four perpendiculars dropped from an arbitrary point inside a regular tetrahedron (with the height equal to unity) onto its faces.

Hence there is a one-to-one correspondence between possible states of ordering of the alloy of $AuCu_3$-type and points lying inside the tetrahedron (Fig. 1) [17]. This allows to give an illustrative geometrical representation of an ordering process as a motion of one or several points along certain trajectory (trajectories) inside the tetrahedron.

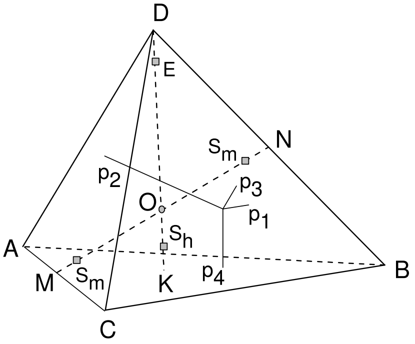


Fig. 1 Configurational space of the long-range order parameters of AuCu$_3$ alloy

Our investigation will be based on the expression for configurationally dependent part of thermodynamic potential of the alloy, written in the form of Ginzburg–Landau functional:

$$\Phi\{p_i, \nabla p_i; T\} = \int_V \left[\varphi(p_1, \dots, p_4) + \frac{r_0^2}{2}\sum_{i=1}^{4}(\nabla p_i)^2\right] n\,dV. \tag{2}$$

Here $\varphi(p_1, \dots, p_4; T)$ is the alloy free energy calculated for one lattice site, $n = 4N/V$, N is the number of sites in one sublattice, V is the volume of the sample, r_0 is the interaction radius.

Function φ corresponds to a homogeneous ordering. It has been obtained previously [17] using Gorsky–Bragg–Williams theory and the nearest-neighbor approximation. Within this approximation interaction is characterized by one parameter w called the mixing energy. Here is the expression for φ, in which all quantities with the dimension of energy are normalized to the mixing energy:

$$\varphi(p_1, \dots, p_4; \theta) \equiv \frac{F}{4Nw} = -\frac{1}{2}\sum_{i=1}^{4} p_i^2 + \frac{\theta}{4}\sum_{i=1}^{4}[p_i \ln p_i + (1 - p_i)\ln(1 - p_i)], \tag{3}$$

where $\theta = T/w$ is the temperature of the alloy normalized to w.

Further analysis of the ordering process will be carried out in the continuum approximation; the parameters p_i in (1), (2), (3) and henceforth will be regarded in general as functions of space coordinates and time, $p_i = p_i(\mathbf{r}, t)$. Constraint (1) is valid for any instant of time at any point of the sample due to the assumption of homogeneity of concentration.

The problem is posed as follows. At the instant of time, taken for initial, all p_i $(i = 1, \dots, 4)$ are set as function of coordinates:

$$p_i(\mathbf{r}, 0) = p_{i0}(\mathbf{r}); \tag{4}$$

the temperature is fixed. Then we follow the evolution of the fields of the order parameters $p_i(\mathbf{r}, t)$ at the fixed temperature.

To achieve our goal we must derive the system of kinetic equations for $p_i(\mathbf{r}, t)$. But first we should dwell on the problem of thermodynamic equilibrium of the alloy. This problem is solved in [6, 13, 18]. Let us discuss some results of these references, which will be necessary for further consideration, with the help of the geometrical representation of ordered states described above (Fig. 1) and the energy diagram of phase equilibria (Fig. 2).

At high temperatures $(\theta > \theta_c)$ there is only one state of thermodynamic equilibrium represented by the center of the tetrahedron (point O in Fig. 1, $p_{1e} = p_{2e} = p_{3e} = p_{4e} =$

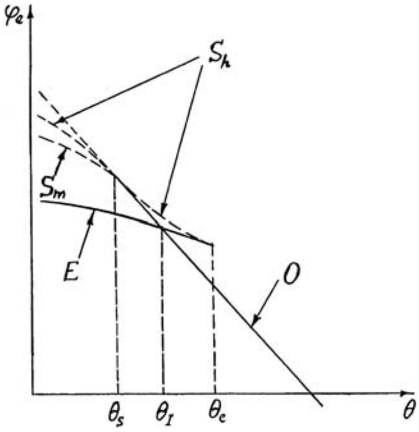


Fig. 2 Energy diagram of phase equilibria of AuCu$_3$ alloy

$1/4)$. This equilibrium is stable. It corresponds to the completely disordered state. In the temperature interval $\theta_s < \theta < \theta_c$ there are three equilibrium states. One of them, represented by the point S_h (and the equivalent points) on the tetrahedral height, corresponds to a saddle point of the free energy in the $\{p_i\}$-space (tetrahedral space). Hence, this equilibrium is unstable. In the energy diagram (Fig. 2) all states of unstable equilibrium are indicated by dashed lines.

The state represented by the point E (and by the three equivalent points located on tetrahedral heights near the vertexes) corresponds to a minimum of the free energy in the tetrahedral space. Hence, this equilibrium is stable. It corresponds to the ordered state when atoms of gold concentrate mainly in the sites of one of the sublattices. Obviously, there are four equivalent ordered variants of such type ($L1_2$). At the temperatures ranging from θ_s up to θ_c the disordered state remains stable, at the point O in the tetrahedral space the function φ has a minimum. In the interval $\theta_I < \theta < \theta_c$ the minimum of φ at the point O is deeper than the minimum at the point E; in the interval $\theta_s < \theta < \theta_I$ it is the opposite. Hence it is considered that above the point θ_I the alloy will finally prefer the disordered state, and below θ_I it will be ordered by the type $L1_2$.

In the low temperature region, $\theta < \theta_s$, there are four nonequivalent equilibrium states (points O, S_h, S_m on the tetrahedral medians and the point E), only one of them being stable (point E). The center of the tetrahedron will at low temperatures give a maximum to φ, whereas S_h and S_m will be its saddle points.

Points not coinciding with the extrema in the tetrahedral space and, hence, not falling on the lines in the phase diagram (Fig. 2), represent nonequilibrium states. On practice these states can be realized, for example, by a rapid cooling (quench) of the alloy from the high temperature region ($\theta > \theta_c$) to the temperatures below θ_c. Such quenching fixes initially the high-temperature disordered state, which is nonequilibrium at the quenching temperature. Then follows the evolution to the equilibrium state. Our task is to follow the ways, rates and possible intermediate stages of the disorder-order transition.

Let us introduce the nonequilibrium chemical potential of i-th sublattice ($i = 1, \dots, 4$), as a function of time and space coordinates

$$\mu_i(r,t) \equiv \frac{\delta\Phi}{\delta p_i} = \frac{\partial\varphi}{\partial p_i} - r_0^2 \Delta p_i, \tag{5}$$

Δ being the Laplacian, and the mean chemical potential of the alloy

$$\mu = \frac{1}{4}\sum_{k=1}^{4}\frac{\delta\Phi}{\delta p_k}. \tag{6}$$

The system of kinetic equations describing the alloy relaxation towards an equilibrium, is derived through non-trivial generalization of Allen-Cahn equation [19] (which in its turn is based on the Ginzburg-Landau approach). The original Allen-Cahn equation governs evolution of a single non-conserved order parameter. In our case there are four non-conserved order parameters such, however, that their sum *is* conserved. The necessary generalization is achieved by introducing the concept of partial chemical potentials of the four sublattices and the mean chemical potential of the alloy (5), (6). Thus we arrive to the following system:

$$\frac{\partial p_i}{\partial t} = -\gamma(\mu_i - \mu), \quad i = 1, \dots, 4. \tag{7}$$

Here μ_i is given by (5); γ is the kinetic coefficient proportional to the frequency of elementary interatomic exchanges.

The above symmetrical form of kinetic equations for several connected order parameters, which to our knowledge has not yet been proposed, reflects on one hand the physical symmetry of the problem (any transpositions of the four parameters p_i does not change the form of the system), and on the other hand permits to proceed in a simple and clear way to statistical description of alloy by means of a minimal number (two) of correlators.

System (7) can also be deduced from the postulate that the evolution of a nonequilibrium system follows a trajectory of the steepest descent of the free energy in the configurational tetrahedral space [20]. It is easy to see that (6) and (7) automatically hold the constraint (1).

Since we wish zero values of the order parameters to correspond to the disordered phase, let us introduce the new parameters η_i through the formulas

$$\eta_i = p_i - \frac{1}{4}, \quad i = 1, \dots, 4. \tag{8}$$

Constraint (1) will then become

$$\sum_{i=1}^{4}\eta_i(r, t) = 0. \tag{9}$$

Proceeding to the modified order parameters and introducing the dimensionless radius—vector $\mathbf{x}$ and time τ through the formulas

$$\mathbf{r} = r_0\mathbf{x}; \qquad \tau = \gamma t, \tag{10}$$

permit to rewrite the system (7) in a well-comprehensible form

$$\frac{\partial \eta_i(\mathbf{x}, t)}{\partial \tau} = \Delta\eta_i(\mathbf{x}, \tau) + \frac{1}{4}\sum_{k=1}^{4}\frac{\partial\varphi}{\partial\eta_k} - \frac{\partial\varphi}{\partial\eta_i}, \quad i = 1, \dots, 4. \tag{11}$$

Let us now, in a customary way, use the approximate expression for the free energy $\varphi(\eta_i)$, expanding it into a Taylor series in the powers of η_i and keeping terms up to the fourth power.

Using the explicit form (3) of the free energy, we obtain

$$\varphi(\eta_i, \theta) \approx \sum_{i=1}^{4} \left[-\frac{1}{2}\alpha(\theta)\eta_i^2 - \frac{a}{3}\eta_i^3 + \frac{b}{4}\eta_i^4 \right], \tag{12}$$

where

$$\alpha(\theta) = 1 - \frac{\theta}{\theta_s}, \quad a = \frac{4}{3}, \quad b = \frac{112}{27}, \tag{12$'$}$$

θ_s is the spinodal ordering temperature; in our model $\theta_s = \frac{3}{4}$.

Approximating function (3) with the expansion (12) is in fact strictly justified only for $\eta_i \ll 1$ and $|\theta - \theta_s| \ll 1$. However, polynomial (12) reproduces correctly the qualitative profile of the free energy in the whole range of variation of η_i.

The initial conditions for the kinetic equations (11) (where φ is substituted by (12)) are given by formula (4). Certainly they must fulfill the relation $\sum_{i=1}^{4} p_{i0}(\mathbf{x}) = 1$, i.e. $\sum_{i=1}^{4} \eta_{i0}(\mathbf{x}) = 0$ for all $\mathbf{x}$.

The prime physical interest in both experiment and theory is attracted to the case when the initial state is obtained by quenching the alloy from high temperatures down to the temperatures close to ordering spinodal θ_s.

As the alloy is quenched the high-temperature fluctuations of the order parameters are "frozen" in the sample. Therefore in different regions of the sample different initial conditions for further ordering are created. If the quenching temperature is close to θ_s ordering can be realized according to one of the four equivalent types. In other words, in different parts of the sample conditions are created for formation of APDs of four different but equivalent types. Ordering process will consist, essentially, in formation and development of a polydomain structure; in each domain will be realized one of the four possible ordered structures of the $L1_2$ type. Since domains of different types are physically equivalent and the initial conditions at quenching do not give preference to any of these types the volumes occupied by domains of each of the four types will be equal.

The "quenched-in" high-temperature fluctuations of the order parameters are random functions of coordinates, which play the role of initial conditions (4) at solving the system of kinetic equations (11). Mathematically the problem consists in solving the system of determined equations with random initial conditions. Hence, the solution at any moment will be a set of random functions of coordinates. Certainly, the physical interest is not in the random fields of the order parameters themselves, but instead in some of their averaged characteristics (moments and correlation functions). Since we deal with formation and evolution of a polydomain structure, we carry out averaging over the volume much bigger than this of one domain. We assume, that this averaging is equivalent to averaging over the ensemble of realizations generated by the initial conditions. As usual, we make assumption about the statistical homogeneity and isotropy of the problem. The described statistical approach to the problem of polydomain ordering has been previously suggested by us in [6, 12].

It can be pointed out right away that the average value of any of the four order parameters is equal to zero. Indeed, an arbitrary point of the alloy can belong by chance and with equal probability to any of the four types of domains, which grow in the sample. Therefore, it is quite natural, that the average value $\langle \eta_i(\mathbf{x}, t) \rangle = 0$. Let us give another proof of this statement based on averaging the equality (9):

$$\left\langle \sum_{i=1}^{4} \eta_i(\mathbf{x}, t) \right\rangle = \sum_{i=1}^{4} \langle \eta_i(\mathbf{x}, t) \rangle = 0.$$

Since, due to equivalence of the order parameters, all averages $\langle\eta_i\rangle$ are equal to each other, each of them is equal to zero as well. We recall that the initial conditions do not give preference to any of the four order parameters. Let us notice also, that it is the average squares of the order parameters, that play the principal role in analysis of the experimental data [8, 21].

The peculiarity of our problem is the average cube of any of the order parameters *not* being identically equal to zero. This can be readily verified by direct calculation for a developed polydomain structure with the account for the fact that domains of all four types occupy equal volumes.

Within the framework of the statistical approach the progress of multidomain ordering is indicated, essentially, by the increase of the average squares of the order parameters and evolution of their pair correlation functions.

In this situation we conclude, that the stochastic fields of the order parameters will be characterized fully enough by the correlation functions of the second and the third order. These functions will give a satisfactory description of structural evolution of an alloy of $AuCu_3$-type at the isothermal annealing.

3 The System of Equations for Correlation Functions

Within the framework of the statistical approach let us introduce the correlation functions of the second and the third order

$$K_{ik}(s,\tau)=\langle\eta_i(\mathbf{x}',\tau)\eta_k(\mathbf{x},\tau)\rangle;\qquad G_{ik}(s,\tau)=\langle\eta_i^2(\mathbf{x}',\tau)\eta_k(\mathbf{x},\tau)\rangle,\tag{13}$$

where $s=|\mathbf{x}'-\mathbf{x}|$, and angular brackets indicate averaging over the ensemble of realizations of the random order parameters. Here we assume the statistical homogeneity and isotropy of the studied system.

By virtue of equivalence of all four sublattices and by virtue of statistical homogeneity of the initial conditions, all diagonal correlation functions of the second order can be considered equal to each other and defined as:

$$K(s,\tau)=K_{ii}(s,\tau)=\langle\eta_i(\mathbf{x}')\eta_i(\mathbf{x})\rangle=\langle\eta_i'\eta_i\rangle,\quad i=1,\ldots,4.\tag{14}$$

The same statement applies as well to non-diagonal correlation functions, which we shall designate as

$$\tilde{K}(s,\tau)=K_{ik}(s,\tau)=\langle\eta_i(\mathbf{x}')\eta_k(\mathbf{x})\rangle\equiv\langle\eta_i'\eta_k\rangle\quad(i\neq k).\tag{15}$$

From equality (9) follows the relation between the diagonal and non-diagonal correlation functions of the second order:

$$K(s,\tau)+3\tilde{K}(s,\tau)=0.\tag{16}$$

All said above applies as well to correlators of the third order, therefore the relation holds:

$$G(s,\tau)+3\tilde{G}(s,\tau)=0.\tag{17}$$

Differentiating any correlation function of the second order (i.e. the first of expressions (13)) with time, and, accounting for the symmetry with respect to replacement $\mathbf{x}\leftrightarrow\mathbf{x}'$, we obtain the system of, generally speaking, sixteen kinetic equations of the kind

$$\frac{\partial K_{ik}}{\partial\tau}=2\left\langle\eta_i'\frac{\partial\eta_k}{\partial\tau}\right\rangle,\quad i,k=1,\ldots,4.\tag{18}$$

Using the dynamic equations (11) and (12) for free energy, let us transform the right-hand side of (18). It can be shown that because the diagonal correlation functions of the second order are equal to each other and the same is valid for the non-diagonal correlators, and by virtue of relation (16), all sixteen equations (18) are equivalent. We can therefore consider the kinetic equation only for the diagonal correlation function. It reads as follows:

$$\frac{\partial K(s,\tau)}{\partial \tau} = 2\left[\Delta K(s,\tau) + \alpha K(s,\tau) + aG(s,\tau) + b\left(\frac{1}{4}\sum_{k=1}^{4}\langle \eta_i' \eta_k^3\rangle - \langle \eta_i' \eta_i^3\rangle\right)\right], \quad (19)$$

where $G(s,\tau)$ is the diagonal correlation function of the third order defined by the second of (13). In order to uncouple the averages in the last two terms of (19) we assume, that the random field of the long-range order parameter $\eta_i(\mathbf{r},\tau)$ has a character close to Gaussian. Then we obtain the following representations of the averages:

$$\langle \eta_i' \eta_i^3\rangle = 3K_{ii}(0,\tau)K_{ii}(s,\tau) \equiv 3K(0,\tau)K(s,\tau), \quad (20)$$

$$\langle \eta_i' \eta_k^3\rangle = 3K_{kk}(0,\tau)K_{ik}(s,\tau) \equiv 3K(0,\tau)\tilde{K}(s,\tau) = -K(0,\tau)K(s,\tau). \quad (21)$$

Substituting (20) and (21) in (19) gives:

$$\frac{\partial K(s,\tau)}{\partial \tau} = 2[\Delta K(s,\tau) + (\alpha - 3bK(0,\tau))K(s,\tau) + aG(s,\tau)]. \quad (22)$$

Likewise, differentiating expression (13) for correlation function of the third order $G_{ik}(s,\tau)$ with time and taking into account the symmetry with respect to replacements $\mathbf{x} \leftrightarrow \mathbf{x}'$ and $i \leftrightarrow k$ give the kinetic equations for correlation functions of the third order

$$\frac{\partial G_{ik}}{\partial \tau} = 3\left\langle (\eta_i')^2 \frac{\partial \eta_k}{\partial \tau}\right\rangle, \quad i = 1,\ldots,4. \quad (23)$$

Using expressions (11), (12) and taking into account relation (17) it is easy to show, that the equations for diagonal and non-diagonal components of the correlation function G_{ik} are equivalent; therefore instead of sixteen equations (23) we have only one kinetic equation of the kind

$$\frac{\partial G}{\partial \tau} = 3\left[\Delta G + \alpha G + a\langle(\eta_i')^2\eta_i^2\rangle - b\langle(\eta_i')^2\eta_i^3\rangle - \frac{a}{4}\sum_{k=1}^{4}\langle(\eta_i')^2\eta_k^2\rangle + \frac{b}{4}\sum_{k=1}^{4}\langle(\eta_i')^2\eta_k^3\rangle\right]. \quad (24)$$

In order to close the system of equations for correlators of the second and the third order, we shall uncouple the averages in the last four terms of (24), basing on simple combinatory considerations. Let us notice that immediately after the quench as well as on early stages of evolution the field of order parameters is Gaussian due to the Gaussian character of the fixed high-temperature fluctuations (see e.g. [3, 22]). In case of a Gaussian field combinatory considerations, which we adopt to uncouple correlators, give the exact results (for even-order correlators, of course). It is quite natural to presume that the use of the same method for uncoupling correlators of both even and odd order will give acceptable results on all stages of evolution. Thus we have

$$\langle(\eta_i')^2\eta_i^2\rangle = K^2(0,\tau) + 2K^2(s,\tau); \quad (25)$$

$$\langle(\eta_i')^2\eta_k^2\rangle = K^2(0,\tau) + 2\tilde{K}^2(s,\tau) = K^2(0,\tau) + \frac{2}{9}K^2(s,\tau); \quad (26)$$

$$\langle(\eta_i')^2\eta_i^3\rangle = K(0,\tau)G(0,\tau) + 3K(0,\tau)G(s,\tau) + 6K(s,\tau)G(s,\tau); \tag{27}$$

$$\langle(\eta_i')^2\eta_k^3\rangle = K(0,\tau)G(0,\tau) + 3K(0,\tau)G(s,\tau) + 6\tilde{K}(s,\tau)\tilde{G}(s,\tau). \tag{28}$$

Then, in view of relation (17) and equalities (25)–(27), (24) takes on the form

$$\frac{\partial G}{\partial \tau} = 3\left[\Delta G(s,\tau) + [\alpha - 3bK(0,\tau)]G(s,\tau) + a^2K^2(s,\tau) - 4bK(s,\tau)G(s,\tau)\right]. \tag{29}$$

Finally, with the account for (22) and (29) we obtain the following system of equations for correlators of the second and the third order, which describes evolution of the alloy from a nonequilibrium state to a stable thermodynamic equilibrium:

$$\begin{cases} \frac{\partial K(s,\tau)}{\partial \tau} = 2[\Delta K(s,\tau) + (\alpha - 3bK(0,\tau))K(s,\tau) + aG(s,\tau)], \\ \frac{\partial G(s,\tau)}{\partial \tau} = 3[\Delta G(s,\tau) + [\alpha - 7bK(0,\tau)]G(s,\tau) + a^2K^2(s,\tau)]. \end{cases} \tag{30}$$

4 Asymptotic Analysis of the Ordering Process at Long Times

We adopt the scaling hypothesis, i.e. we assume that there exists a single characteristic length scale, which determines the statistical properties of the domain structure. If so, at any instant of time correlation function of the second order is characterized mainly by the correlation radius $r_c(\tau)$ and the dispersion $D(\tau) \equiv K(0,\tau)$. Hence in the limit $s \to 0$ the first of (30) can be presented as

$$\frac{dK(0,\tau)}{d\tau} \cong -\frac{2K(0,\tau)}{r_c^2(\tau)} + 2(\alpha - 3bK(0,\tau))K(0,\tau) + 2aG(0,\tau). \tag{31}$$

On the other hand, Fourier-transformation by coordinates of the first of (30) gives

$$\frac{dK(0,\tau)}{d\tau} = \left[-2q^2 + 2\alpha - 6bK(0,\tau) + 2a\frac{G(0,\tau)}{K(0,\tau)}\right]K(q,\tau). \tag{32}$$

The solution of the latter equation can be written as

$$K(q,\tau) = K(0,\tau)\exp(-2q^2\tau)\psi(\tau), \tag{33}$$

where

$$\psi(\tau) = \exp\left\{\int_0^\tau \left(2\alpha - 6bK(0,\tau) + 2a\frac{G(0,\tau)}{K(0,\tau)}\right)d\tau\right\}. \tag{34}$$

Using Fourier-transform of the correlation function, i.e. $K(\mathbf{q},\tau)$, gives the relation

$$\frac{1}{r_c^2(\tau)} = \frac{\int q^2K(\mathbf{q},\tau)d^3q}{\int K(\mathbf{q},\tau)d^3q}, \tag{35}$$

where $K(\mathbf{q},\tau)$ is defined by expressions (33) and (34). The initial correlation radius at the moment of quench $r_c(0)$ is found by the limiting transition $\tau \to 0$, i.e.

$$\frac{1}{r_c^2(0)} = \frac{\int q^2K(\mathbf{q},0)d^3q}{\int K(\mathbf{q},0)d^3q}. \tag{36}$$

From (35) and (33) it is easy to determine the asymptotic form of the correlation radius at long times ($\tau \to \infty$), which is $1/r_c^2(\tau) \sim 1/\tau$. More exact calculation yields the following interpolating formula:

$$r_c(\tau) \approx \sqrt{r_c^2(0) + \frac{4}{3}\tau}. \tag{37}$$

It is quite natural to associate the correlation radius with the average domain size. Formula (37) confirms the well-known conclusion (see e.g. [11, 22]) that the length scale of domain structure grows proportionally to the square root of time (Lifshitz-Cahn-Allen law). This result is deduced here from the independent and general considerations.

Computer simulation studies [23, 24] of ordering kinetics show that Lifshitz-Cahn-Allen law is in general fulfilled. Possible deviations can be due to anisotropy and the role of vacancies [23].

Interpolating formula (37) indicates the possibility of a crossover from the linear regime of domain growth at early times to the square-root law for late times. Such kinetics was experimentally observed by the X-ray intensity fluctuation spectroscopy [25] and time-resolved X-ray scattering [26].

By virtue of the scaling hypothesis the spatial dependences of correlators of the second and the third order coincide. Hence, on basis of (30), (31) and in consequence of interpolating formula (37), it turns out that at late times the moments $\langle \eta_i^2 \rangle$ and $\langle \eta_i^3 \rangle$ approach their equilibrium values according to the law

$$\langle \eta^2 \rangle_e - \langle \eta^2(\tau) \rangle \sim 1/\tau. \tag{38}$$

Within each particular domain the long-range order parameter achieves its equilibrium value $\langle \eta^2 \rangle_e$ exponentially fast [8]. Meanwhile the disorderliness in between the domains (i.e. in the antiphase boundaries) persists for a long while. The slow relaxation of the average square of order parameters (38) is resulted by slow decrease of the specific volume of disordered antiphase boundaries

$$\nu_{APB} \sim 1/\tau. \tag{39}$$

This is in fact a quantity accessible by conductivity experiments. Formula (39) is in agreement with the experimental data from [27], where ordering kinetics in the specific alloy Cu_3Au was investigated by measuring its time-resolved residual resistivity.

Additional information can be extracted from the law (39) on how the domain walls thickness varies in the process of ordering. Since the specific area of APBs has the dimension of the reciprocal length $S_{APB} \sim 1/r_c(\tau) \sim 1/\sqrt{\tau}$, their thickness decreases proportionally to inverse square root of time

$$\delta \sim 1/\sqrt{\tau}. \tag{40}$$

Of course, this result is relevant only if the annealing temperature is close to spinodal, i.e. $\alpha \equiv \frac{T_s - T}{T_s} \ll 1$. In this case at times $\sim \tau_0/\alpha (\tau_0 \approx 1/\gamma)$ form the long-wave fluctuations with the correlation length $\sim r_0/\sqrt{\alpha}$. This length is naturally corresponded to the extent of the transition regions between domains. At further evolution domains grow, starting from this correlation length, and the transition regions shrink starting from the same size down to r_0 proportionally to $1/\sqrt{\tau}$. Certainly, dependence (40) loses meaning when the thickness of domain walls becomes $\sim r_0$.

The main interest lies in the analysis of the system of equations (30) near the spinodal temperature θ_s when $|\alpha| \ll 1$ and the initial correlation radius is sufficiently small, so that

$r_c^2(0) \ll (1/\alpha) \ll L^2$, where L is the characteristic dimension of the crystallite (we recall, that time is being measured in the units of γ^{-1}, and the spatial dimensions—in the units of r_0—the radius of interatomic interaction). Then, asymptotically, at times $t \gg 1/\alpha$, in the limit $s \to 0$ and in view of representation (31) and interpolating formula (37), the system of equations (30) becomes

$$\begin{cases} \frac{1}{2}\frac{\partial K(0,\tau)}{\partial \tau} = [\alpha - 3bK(0,\tau)]K(s,\tau) + aG(s,\tau), \\ \frac{1}{3}\frac{\partial G(0,\tau)}{\partial \tau} = [\alpha - 7bK(0,\tau)]G(s,\tau) + a^2K^2(s,\tau), \end{cases} \tag{41}$$

with the initial conditions

$$K(0,0) = K_0, \qquad G(0,0) = G_0, \tag{42}$$

reflecting the initial dispersion of the long-range order parameter (K_0) and the initial asymmetry of the random field of the order parameter (G_0).

Analysis of the system of equations (41) with the initial conditions (42) permits to obtain information about the late stages of the ordering process. However even this simplified system cannot be solved analytically. We shall carry out its qualitative analysis basing on stability theory of Lyapunov. Introducing denotations $K(0,\tau) \equiv \langle \eta^2(\tau) \rangle = x(\tau)$ and $G(0,\tau) \equiv \langle \eta^3(\tau) \rangle = y(\tau)$, we shall rewrite system (41) as

$$\begin{cases} \frac{1}{2}\frac{dx}{d\tau} = (\alpha - 3bx)x + ay, \\ \frac{1}{3}\frac{dy}{d\tau} = (\alpha - 7bx)y + a^2x^2. \end{cases} \tag{43}$$

Let us find stationary points of system (43) in the limit $\tau \to \infty$. In this case lhs's of (43) tend to zero and the stationary points are defined by the following system of algebraic equations:

$$\begin{cases} (\alpha - 3bx)x + ay = 0, \\ (\alpha - 7bx)y + a^2x^2 = 0. \end{cases} \tag{44}$$

Solving it gives the following results. At $\alpha > 0$, i.e. at temperatures lower than θ_s, the system has three stationary points (see Fig. 3a). One of them, with coordinates $x = 0$, $y = 0$, is an unstable node and corresponds to the homogeneous disordered phase, which, as already mentioned, is unstable at these temperatures (see Fig. 2). The second point is a stable node and represents the ordered state on the line E in Fig. 2. The third point is a saddle. The latter represents in a generalized form the unstable equilibriums on the heights and medians of the tetrahedron (S_h and S_m).

Suppose we start from a certain point of "general position" in the phase diagram. The system will then evolve towards an ordered state.

At some specific initial conditions when the initial asymmetry $\langle \eta^3 \rangle_0$ is negative, the alloy "lingers" for a certain while near the saddle point, i.e. an intermediate, long-living structure is formed.

At $\alpha < 0$ the system also has three stationary points, but the node $x = 0$, $y = 0$ is stable this time, and the saddle point moves to the first quadrant (Fig. 3b). Thus there are two stable nodes, one of which corresponds to the ordered state, and the other to the disordered one. This is completely consistent with the diagram in Fig. 2. We see, that depending on the initial conditions, the system may come to one of the two stable equilibria. Instead of being

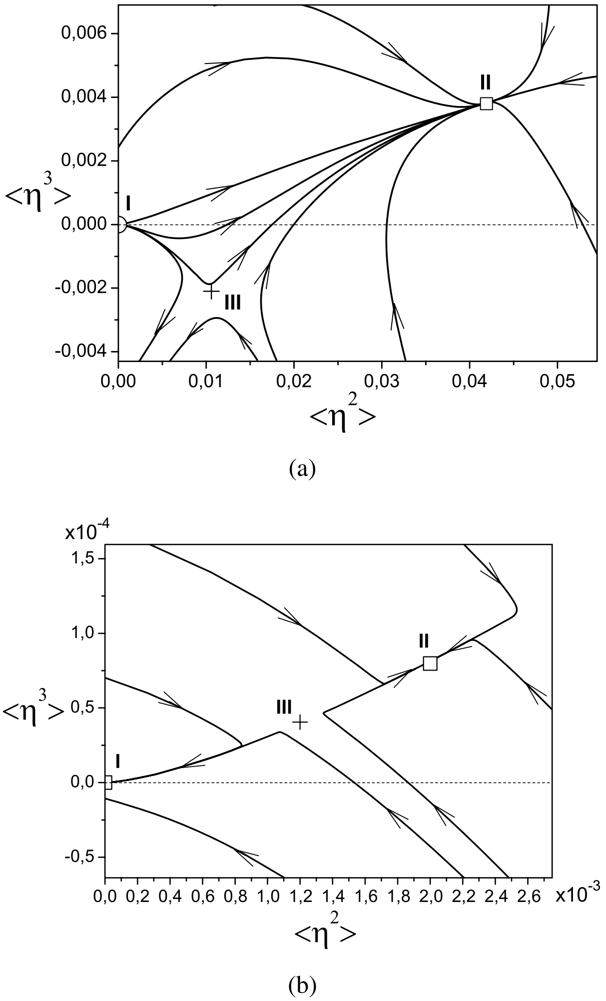


Fig. 3 (**a**) Phase-plane portrait of the ordering alloy for $\alpha = 0.4$. (**b**) Phase-plane portrait of the ordering alloy for $\alpha = -0.0294$

determined by the depth of the potential well, this choice will depend upon the proximity of the initial state to this or that equilibrium. Certainly, in the process of further evolution the alloy will finally arrive to the state corresponding to a deeper well, but this transition will proceed by nucleation and subsequent growth of nuclei, i.e. by an essentially different mechanism, than considered here.

Thus, depending on the technological prehistory, at $\theta > \theta_s$ evolution of the alloy may occur either in one stage as a second order-phase transition, or in two stages, so that a second-order transition will be followed by the first-order one. These phenomena were discussed separately in a number of studies (see e.g. [2]). Here we emphasize the possibility of their sequential occurrence, leading to either one- or two-stage scenario of evolution, determined by the thermal prehistory of the sample.

Apart from this the delay of the alloy in a state with intermediate long-living structure (point S_h of the tetrahedron) is possible.

At further rise in temperature the saddle point and the stable node, representing the ordered phase, merge and disappear according to the expressions

$$x_{1.2} = \frac{2a^2 + 15\alpha b}{63b^2}\left[1 \pm \sqrt{1 - \frac{189\alpha^2 b^2}{(2a^2+15\alpha b)^2}}\right], \qquad y_{1,2} = \frac{3b}{a}x_{1,2}^2. \tag{45}$$

In the diagram in Fig. 2 this situation corresponds to the point of ending of the lines E and S_h at the temperature θ_c. At temperatures exceeding θ_c there remains only one stationary point in the phase diagram—the stable node in the origin representing the disordered homogeneous phase.

5 Analysis of the Full Evolutionary Equations

Asymptotical analysis of the ordering process carried out in the previous section gives its full qualitative picture. In order to specify the details, in particular, of the initial and the intermediate stages of ordering it is necessary to solve the full system of equations (30) which, with the account for (31) and (37) can be written as

$$\begin{cases} \frac{1}{2}\frac{\partial K(0,\tau)}{\partial \tau} = [\alpha_{\mathit{eff}}(\tau) - 3bK(0,\tau)]K(0,\tau) + aG(0,\tau), \\ \frac{1}{3}\frac{\partial G(0,\tau)}{\partial \tau} = [\alpha_{\mathit{eff}}(\tau) - 7bK(0,\tau)]G(0,\tau) + a^2K^2(0,\tau), \end{cases} \tag{46}$$

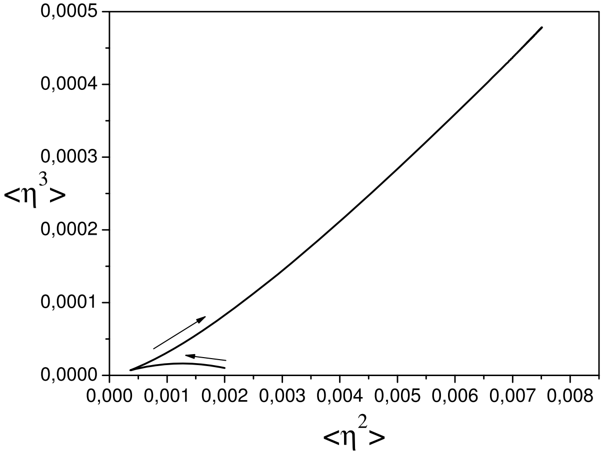
where

$$\alpha_{\mathit{eff}}(\tau) = \alpha - \left(\frac{4}{3}\tau + r_c^2(0)\right)^{-1}. \tag{47}$$

Note that one of the coefficients in system (46) depends explicitly on time. This does not change the results of the qualitative analysis of behavior of the system at long times; only the quantitative estimations of the relaxation time of the nonequilibrium alloy and of characteristic spatial scales may vary.

We have solved numerically the full system of equations (46) in order to follow all stages of evolution of the ordering system. The numerical analysis was carried out for different quenching temperatures θ and for various initial sizes of the ordered regions, which arose as a result of quenching (i.e. were varied the parameters α and $r_c(0)$). In addition, subject to variation were the initial dispersion and the asymmetry of the random field of the order parameters. It turned out, that for sufficiently small (positive) values of α (i.e. for temperatures $\theta \le \theta_s$) and values of $r_c(0) \ge 1$, owing to change of sign of $\alpha_{\mathit{eff}}(\tau)$ (see (47)), the ordering process has a nonmonotonic character: at first the dispersion of the order parameters $D(\tau) \equiv K(0,\tau) \equiv \langle \eta_i^2(\tau)\rangle$ decreases, i.e. occurs the disordering of small "quenched-in" fluctuations of the order parameters, and only then begins the formation and slow growth of ordered antiphase domains (Fig. 4). Theoretical results presented above can be used, in particular, for explaining the size effect on ordering. As reported in [28, 29] the disorder-order transition in FePt nanoparticles, epitaxially grown on a substrate, does not occur always at temperatures lower than the phase transition point, but only if the size of particles exceeds certain critical value ($d \ge r_*$) where r_* , depending on the substrate material, varies between 2–4 nanometers. In view of the above numerical results we may conclude, that the too small size of the particles $d < r_*$ limits the growth of the correlation radius (expression (47)). This results in suppression of the tendency of particles to exhibit long-range order (even at temperatures $\theta \le \theta_s$). In Fig. 4 this corresponds to the section of the phase trajectory going to the left (up to the turning point).

Fig. 4 Phase trajectories of the system for $\alpha = 0.01$, $r_c(0) = 5$, and the initial conditions: $x_0 = 0.002$; $y_0 = 0.00001$



Another meaning of the above result is that the incubation time, which precedes ordering under above-spinodal quenches (see [2]) may also exist if the quenching temperature falls below (but near) the spinodal. However, the reasons why the onset of long-range order is delayed are different in these two cases. In first-order phase transitions the incubation time is associated with formation of overcritical ordered nuclei. Unlike this, in case of second-order transition, discussed in the present paper, the disordered phase may persist for a certain while after the quench because of the small (of the order of interatomic distance) initial value of correlation radius. Ordering does not progress until the range of correlations reaches r_*.

Another interesting feature, which is explicitly observed at numerical integration of (46), is the possibility of formation of quasi-stationary intermediate polydomain structures corresponding to the Au_3Cu type of ordering of the $L1_2$ symmetry. However they are realized in a very narrow range of initial conditions and display themselves as intermediate horizontal sections (like "plateaus" or "steps") on evolutionary curves for $x(\tau) \equiv \langle \eta^2(\tau) \rangle$ and $y(\tau) \equiv \langle \eta^3(\tau) \rangle$ (Fig. 5). This corresponds to the kinetic slowdown of the representing point at the passing near the saddle point in the parametric diagram (Fig. 3a, b).

It follows from the numerical analysis, that for some specific initial conditions (x_0, y_0) such metastable intermediate structures may survive for a noticeably long time. The ordering alloy, prior to achieving a thermodynamically stable structure formed by domains of the ordered phase $AuCu_3$ (represented by the stable node III in Fig. 3), remains for an appreciable time in a kinetically slowed state corresponding to a structure, consisting of antiphase domains of Au_3Cu-type (saddle point II in Fig. 3). The living time of such intermediate structure is determined by the initial "frozen" fluctuations of the long-range order parameters.

Numerical integration of system (46) shows also, that for phase trajectories passing far from the saddle (point II in Fig. 3), ordering process occurs fast enough practically on all the extent of the trajectory, except for a close vicinity of the stable node III (Fig. 3), where is observed a slow (under the power law (38)) "ripening" of the polydomain structure due to domain coarsening and thinning of antiphase boundaries. This confirms the known results of numerical modeling of evolution of a polydomain structure in fcc alloys [8, 21].

It is worthwhile to dwell on the particular case when the alloy is quenched into a temperature interval $\theta_s < \theta < \theta_c$. The parameter α_{eff} will then remain negative in the whole course of ordering process. This situation is presented in the parametrical plots (Fig. 6) obtained from numerical integration of (46) for the fixed quenching temperature in the above-specified

Fig. 5 Evolutionary curves for $\langle\eta^2(\tau)\rangle$ and $\langle\eta^3(\tau)\rangle$ obtained from numerical integration of system (46) for $\alpha = 0.04$ and the initial conditions $x_0 = 0.0001$; $y_0 = -0.00000143$

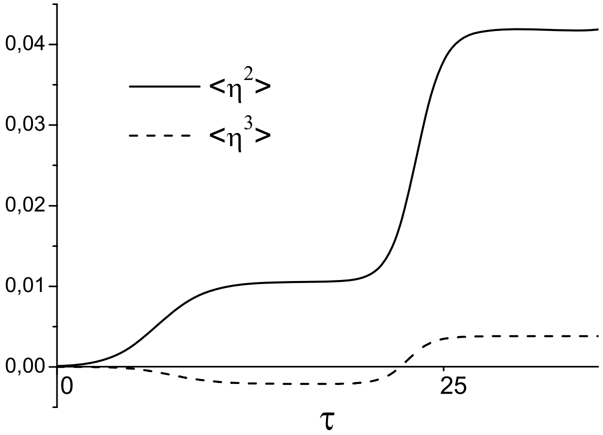
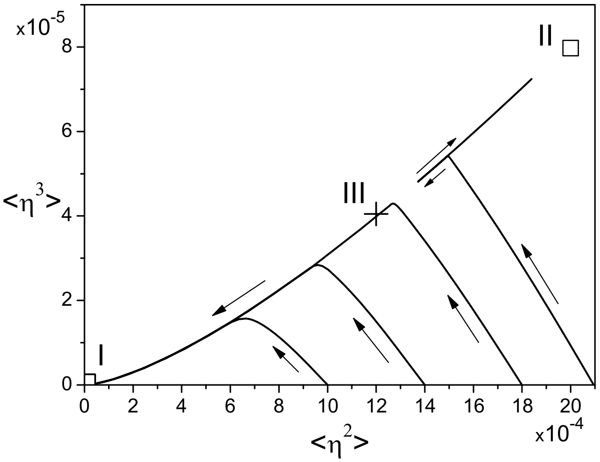


Fig. 6 Phase trajectories of the ordering alloy for $r_0 = 2000$ and $\alpha = -0.0294$; the initial conditions $\{x_0; y_0\} \to \{10^{-3},\ 1.4 \times 10^{-3},\ 1.8 \times 10^{-3},\ 2.1 \times 10^{-3}; 0\}$



interval and various initial conditions. In Fig. 6 it is seen, that phase trajectories, starting from the quenched fluctuations of sufficiently small amplitudes, are attracted to the stable node in the origin (point I), i.e. such ordered regions, "dissolve" and turn into a homogeneous disordered phase $A1$. On the contrary, if the initial values of the dispersion x_0 exceed some critical value, there will be a formation of the stable polydomain structure consisting of ordered domains of the type AuCu$_3$.

Thus, numerical calculation confirms once again the conclusion that at $\theta \geq \theta_s$ evolution of the alloy, depending on its thermal prehistory, can proceed either in one stage as a phase transition of the second order, with the direct formation of domains of the thermodynamically stable phase AuCu$_3$, or in two stages when first occurs the transition to the homogeneous disordered phase $A1$ not accompanied by nucleation, and then follows the first order phase transition to the stable AuCu$_3$ phase. However the latter (nucleation) stage of evolution remains beyond the framework of our consideration.

6 Conclusions

In the present paper we modify the previously proposed statistical approach for description of polydomain ordering kinetics in fcc alloys. Ordering is described through several order parameters and evolution of their random spatial distribution after the temperature quench. We obtain a closed system of differential equations for correlators of the second and the third order, and on its basis analyse numerically all stages of evolution for various quenching temperatures. The well-known square root law ($\sim\sqrt{\tau}$) for growth of the average size of domains is confirmed. In addition it is established, that at the stage of coarsening the thickness of antiphase boundaries decreases proportionally to the inverse square root of time ($\sim 1/\sqrt{\tau}$) and the specific volume of disordered regions decreases as the reciprocal time $1/\tau$. It is shown that for certain initial conditions at the intermediate stages of evolution may arise transitive long-living kinetically slowed superstructures. Apart from these details development of a polydomain structure consists essentially in formation and unlimited growth of ordered domains of $L1_2$ type. In an infinite sample during polydomain ordering the thermodynamic equilibrium is never achieved; there is only slowing-down of motion of antiphase boundaries.

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