

# Diffusive decomposition of solid solutions

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The present status of the theory of the late stage of diffusive decomposition of multicomponent solid solutions, owing to diffusive interaction of macrodefects, is reviewed. Methods for solving the systems of equations describing the decomposition process are analyzed. The evolution of the critical dimensions of precipitates and the transformation of an arbitrary distribution function into a universal function for different mechanisms of mass transfer are studied in detail. The conditions for coexistence of phases in the presence of decomposition of multicomponent systems are examined. The results of the theory are compared with experiment.

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## 1. INTRODUCTION

The widespread use of multicomponent dispersed systems in different areas of science and technology (ranging from the physics of semiconductors to photography, materials science, and chemical technology) has stimulated the intensive study of diffusion processes occurring in them. Since the free energy of a supersaturated solid solution which is in a metastable state and whose equilibrium diagram exhibits limited solubility of one or several components is greater than that of the equilibrium phases, diffusive decomposition—the formation and subsequent growth of regions of new phases in the form of different chemical compounds (or separate elements) of some of the dissolved components, giving rise to a transition of the system into an equilibrium heterophase state—occurs with time in such a solid solution.

Diffusive decomposition of multicomponent solid solutions is often crucial in many important processes and phenomena, such as creep of composite dispersion-hardened materials under conditions of high temperatures and irradiation, recrystallization of heterogeneous structures, dimensional and thermal instability of structural and fissioning materials, processes accompanying nucleation and crystal growth in multicomponent systems, sintering, hot pressing, etc. Decomposition can be extremely useful, and it forms, for example, the foundation of the technology for forming age-hardened alloys, but it can also present a very serious danger of degradation of materials owing to undesirable growth of different defects while the materials are in use, actually determining the lifetime of the material (swelling, degradation of semiconductors, etc.).

In practice macrodefects are often specially introduced into real structures in order to give them the required properties. Materials engineers now increasingly seek solutions to the problem of creating modern materials with the required complex of limiting properties in order to realize heterogeneous structures with finely dispersed precipitates of other phases. Thus the main idea of widely used dispersion-hardened materials consists of employing purposefully introduced inclusions of a second phase as stoppers for dislocations moving in the process of deformation. Precipitates of particles of a second phase play a decisive role in the formation of the required characteristics of high-strength steels, refractory alloys based on nickel, cobalt, and aluminum, and other different composite materials. Here the questions of the thermal stability of the structure of these materials and the absence of significant growth of the particles, which is a necessary condition for the preservation of the high mechanical and other characteristics at these temperatures, are of special significance.

Diffusive decomposition is the process that leads to the formation of heterogeneous structures in a solid with a definite volume distribution of macrodefects or to undesirable destruction of optimized structures. This is essentially what determines the enormous role of diffusive decomposition in the formation and evolution of different properties of solids (electrical, optical, mechanical, etc.). Without taking into account the distribution, interaction, and kinetics of such defects it is impossible to formulate a correct physical picture of the behavior of real materials under the conditions of external perturbations, and therefore it is impossible to plan, in a scientifically well-founded manner, the development of

materials with improved performance parameters and to optimize the performance characteristics of materials. Therefore the construction of a systematic kinetic theory, adequately describing the evolution of different types of defects, and extensive experimental investigation of this evolution comprise the foremost problem in many areas of solid state physics, materials science, and technology.

There exists in nature an infinite number of dispersed systems which are initially characterized by completely different size distributions of macrodefects. Therefore a complete theoretical description of the evolution of arbitrary dispersed systems appears to be an unsolvable problem, especially since in the overwhelming majority of the cases the initial distribution of macrodefects is, as a rule, unknown. It turned out, however, that under the conditions of diffusive decomposition any dispersed system, irrespective of its initial state, transforms asymptotically in time into a unique, in the corresponding variables, state, determined only by the mechanism of mass transfer operating in the system. This fundamental finding radically changes the situation and enables the prediction of the asymptotic states of dispersed systems at a late stage of diffusion decomposition.

New phases can form in the process of diffusive decomposition of supersaturated solid solutions by two fundamentally different mechanisms: spinodal decomposition or fluctuation nucleation and subsequent growth of discrete regions of new phases.<sup>1-5</sup> In spinodal decomposition the starting solution decomposes spontaneously into two solid solutions with identical structures and close lattice parameters; nucleation of a new phase is not necessary. Spinodal decomposition occurs in the entire volume of the solution with continuous reduction of the free energy of the system.

In decomposition by the second mechanism the formation of new phases, accompanied by a general reduction of the free energy, will not occur at the initial stages of the decomposition because of the energetically unfavorable effect of the appearance of an interface until viable precipitates with sizes exceeding some critical dimension appear.<sup>6</sup> For this reason the decomposition process in this case is at first of a fluctuation character and is determined by the fluctuation formation of supercritical precipitates. These ideas about the nucleation process are primarily associated with Volmer, Weber, Bekker, and Döring.<sup>7,8</sup> Making the assumption that the nuclei form not by means of a sudden large fluctuation, but rather as a result of a large number of small fluctuations and taking for the elementary processes which alter the sizes of the nuclei the attachment or evaporation of one atom, they were the first to formulate the kinetic problem for the case of stationary nucleation from supersaturated vapor and they obtained an expression for the flux of nuclei in size space. Ya. I. Frenkel<sup>9</sup> arrived at the important conclusion that precipitates of a new phase are also present in a stable system in the form of the so-called equilibrium heterophase fluctuations.

Further substantial progress was made in the fundamental work of Ya. B. Zel'dovich,<sup>10</sup> in which the general problem of the formation of precipitates of a new phase in a metastable system was studied. The kinetic equation obtained by Zel'dovich for the size distribution function of the precipitates of the new phase has the form of a Fokker-Planck equation with two coefficients, expressed in terms of

the probabilities of transitions associated with a change in the number of atoms (molecules) in the precipitate by one. The determination of these probabilities is the main problem in the description of the kinetics of decomposition of a metastable system. The existing relationship between the coefficients appearing in the kinetic equation, derived in Ref. 10 from the requirement on the distribution of equilibrium heterophase fluctuations, makes it possible to reduce the problem of describing the decomposition to finding one of the coefficients, for example, the rate of growth of the precipitates, if the distribution of the equilibrium heterophase fluctuations is known.<sup>11,12</sup> This approach is especially fruitful for small precipitates. The limitations in the case of large precipitates are linked primarily with the fact<sup>13,14</sup> that during the growth (dissolution) gradients of the concentrations of dissolved substances exist around the precipitates, while the distribution function of equilibrium heterophase fluctuations is determined on the basis of thermodynamics under the assumption that the solution around the precipitates is uniform.

References 7-10 form the foundation of the classical theory of nucleation. In this theory the description of the kinetics of the decomposition of a metastable phase is based on a kinetic equation of the Fokker-Planck type for the size distribution function of the precipitates of the new phase and the equations of material balance. The specific feature of this system is manifested in the structure of the transition probabilities, by means of which the coefficients in the kinetic equation are determined.

The process of diffusive decomposition of a metastable system, decomposing by the mechanism of nucleation of a new phase, can be divided into three stages. We shall consider a crystal which is supersaturated with point defects, which give rise to diffusion mass transfer (by atoms of the dissolved material accompanying the growth of precipitates of different phases from a supersaturated solid solution, by vacancies and interstitial atoms accompanying growth of pores and dislocation loops, by atoms of dissolved gas accompanying growth of gas-filled bubbles, etc.). The starting stage of the decomposition, when the supersaturation by point defects is quite high, is characterized by intensive formation of viable nuclei of macrodefects, whose size exceeds the critical size (in what follows, by macrodefects we shall mean precipitates of a second phase, pores, dislocation loops, and gas-filled cavities, at least one dimension of which is macroscopic). At this stage the amount of matter in the nuclei is small compared with the prescribed amount, and supersaturation is practically constant. The study of the kinetics of diffusive decomposition at this stage on the basis of classical ideas,<sup>7-10</sup> as already pointed out, borders on the microscopic theory and reduces to the calculation of the steady-state flux of nuclei of macrodefects in the size space. Although the system of equations itself is quite simple in this case, since the surface tension can be neglected, the solution at this stage depends substantially on the nucleation mechanisms. Definite progress has been achieved in the description of homogeneous nucleation and the transitional stage.<sup>15,16</sup> Heterogeneous nucleation, however, is decisively determined by the initial distribution of nucleation-initiating defects and cannot yet be given a complete theoretical description.

The transitional stage of decomposition begins when the amount of matter in the new phase is comparable to the starting amount, and the supersaturation begins to decrease. At this stage the number of precipitates is virtually constant, and the volume of the new phase increases primarily owing to the growth of precipitates.<sup>15,17</sup>

Finally, at the third and later stage of diffusive decomposition, when the nuclei attain quite large sizes and macroscopic concepts can be applied to them, while supersaturation becomes small, surface tension and the laws of conservation of point defects, forming a very unique kinetic growth of macrodefects, begin to play a determining role. This stage of decomposition was first discovered in 1900 by Ostwald.<sup>18</sup> It is characterized by the fact that the average size of macrodefects in dispersed systems at the later stage of decomposition increases as a result of diffusion mass transfer of matter from small particles to large particles (the large particles "consume" the small particles), which is encouraged by the decrease in the free energy of the system owing to the decrease in the area of the interface separating the phases. Fluctuation creation of new nuclei is, of course, practically excluded at this stage, since they must have macroscopic dimensions. Strong "diffusion" interaction arises between the macrodefects as a result of the fact that each macrodefect "feels" the self-consistent diffusion field of point defects, determined by the entire ensemble of macrodefects. This fact is linked in an obvious way with the laws of conservation of point defects in a solid solution and in macrodefects.

This phenomenon is called "ripening of the Ostwald type" or more often "coalescence," although the last term is essentially incorrect. Decomposition at this later stage, determined by the diffusive interaction of macrodefects, has been studied many times theoretically,<sup>19-22</sup> however solutions of an incomplete system of equations, leading to size distribution functions of macrodefects for which the law of conservation of point defects is not obeyed, were usually presented. The characteristic features of the kinetics of a dispersed system cannot be determined on the basis of such an incomplete description.

A systematic theory of the evolution of dispersed systems at the later stage of diffusive decomposition was first constructed in Refs. 23-25. It turned out that the transformation of any initial size distribution function of macrodefects into a unique universal distribution function, depending on the mass-transfer mechanism operating in the system, is determined by the law of conservation of point defects, which leads to substantially nonlinear kinetics. Thus the existence of a stable asymptotic state of dispersed systems, characterized by a universal distribution function, was first predicted and theoretically substantiated in Refs. 23-25. This leads to a unique kinetics of growth of the ensemble of macrodefects, whose average size  $\bar{R}$  varies with time at long times according to the " $t^{1/3}$  law," i.e.,  $\bar{R} \sim t^{1/3}$  (in the case when the mass transfer is controlled by volume diffusion of point defects), instead of the customary parabolic law, characteristic for diffusion processes.

It was later proved<sup>26-29</sup> that asymptotic states of dispersed systems also exist for other mechanisms of mass transfer (by means of grain-boundary diffusion, diffusion along the dislocation network, etc.). The theory of decomposition is generalized to multicomponent dispersed systems

in Refs. 30-35. It turned out that a universal (in appropriate variables) size distribution function of macrodefects, which is the same for precipitates of all phases which survive asymptotically in the process of competitive growth, also forms in such complicated systems at the later stage of decomposition.

Different aspects of the problem of diffusive decomposition of one-component and multicomponent supersaturated solid solutions were studied in a number of articles.<sup>36-71</sup>

We note that macrodefects can also grow by means of their diffusion as a whole in different force fields followed by coalescence on direct contact. These questions were analyzed in detail by Ya. E. Geguzin and M. A. Krivoglaz<sup>57</sup> and we shall not consider them here.

In this review we shall examine the present status of an important branch of physical kinetics—the theory of diffusive decomposition of multicomponent dispersed systems at the later stage, determined by diffusion interaction of macrodefects, when the possibility of fluctuation formation of viable nuclei of a new phase can be neglected, while supersaturation by point defects decreases.

## 2. THEORY OF DIFFUSIVE DECOMPOSITION OF ONE-COMPONENT SOLID SOLUTIONS

A systematic theory of diffusive decomposition of multicomponent dispersed systems must answer the following questions: which phases remain stable in the process of diffusive decomposition and what are the boundaries of the regions of coexistence of these phases? It must also describe the evolution of the characteristics of the precipitates of coexisting phases (the size distribution functions of macrodefects, the number and average size of macrodefects, etc.), and it must indicate the limits of applicability of the approximations adopted.

To understand better the basic characteristics of diffusive decomposition of multicomponent solid solutions at the late stage and the essential features of the method used to analyze the complex systems of nonlinear equations describing such decomposition, we shall first examine in detail the simplest case of diffusive decomposition of a one-component solid solution, namely, the late stage of the process, controlled by volume diffusion of the dissolved component.<sup>23-25</sup>

In what follows by macrodefects we shall mean precipitates of particles of a second phase, though all results can be transferred (with the appropriate changes) to other types of macrodefects.

### 2.1. Formulation of the problem

In formulating the problem we shall study large uniform systems in which there are no macroscopic diffusion fluxes, and for simplicity we shall assume that the precipitates are spherically shaped.

The equilibrium concentration  $c_R$  at the surface of precipitates of radius  $R$  is determined by the well-known Gibbs-Thompson relation

$$c_R = c_\infty + \frac{\alpha}{R}, \quad (2.1)$$

where  $c_\infty$  is the concentration of the saturated solid solution,  $\alpha = 2\sigma c_\infty v/kT$ ,  $\sigma$  is the interphase surface energy, and  $v$  is the volume per atom of the dissolved material.

Therefore the equilibrium concentration of the dissolved material is higher at the surface of small precipitates than at the surface of large precipitates, and a flux of the dissolved component from the small precipitates into the matrix and from matrix to the large precipitates thus appears. Neglecting the "interaction" between the precipitates in a polydispersed ensemble (which is valid because the ratio of the average size of the precipitates to the average distance  $\bar{l}$  between them is small,  $\bar{R} \ll \bar{l}$ ), we obtain for the diffusion flux of the dissolved material per unit surface area of the precipitates in the self-consistent diffusion field approximation

$$J_R = -D \left. \frac{\partial c}{\partial r} \right|_{r=R}.$$

The self-consistent field approximation can be used because of the smallness of  $\bar{R}/\bar{l} \sim Q_0^{1/3} \ll 1$ , where  $Q_0$  is the initial relative amount of matter in the precipitates. We note that even when  $Q_0^{1/3} \lesssim 1$  taking into account in an effective manner the distribution of precipitates does not qualitatively change the form of the diffusion flux.

The change in the volume of a precipitate is determined by the flow of dissolved atoms per unit time up to its surface:

$$\frac{d(4/3)\pi R^3}{dt} = -4\pi R^2 J_R = 4\pi R^2 D \left. \frac{\partial c}{\partial r} \right|_{r=R},$$

and therefore the change in the radius of the precipitate as a function of time is given by

$$\frac{dR}{dt} = D \left. \frac{\partial c}{\partial r} \right|_{r=R}.$$

To calculate  $\partial c/\partial r$  the corresponding diffusion problem must be solved:

$$\frac{dc}{dr} = D\Delta c, \quad c|_{r=R} = c_R, \quad c|_{R=\infty} = \bar{c}.$$

It is easy to see that if the initial saturation is small,  $\Delta_0 = c_0 - c_\infty \ll 1$ , in order to find  $J_R$  it is sufficient to solve the stationary diffusion problem. Indeed, the ratio of the characteristic time over which a stationary diffusion flux of the dissolved component is established at the surface of the precipitate  $\tau_{\text{dif}} \sim \bar{R}^2/D$  to the characteristic time over which the precipitate changes

$$\tau_{\text{char}} \sim \frac{\bar{R}}{D \partial c/\partial r} \sim \frac{\bar{R}^3}{D\Delta_0}$$

is

$$\frac{\tau_{\text{dif}}}{\tau_{\text{char}}} \sim \Delta_0 \ll 1.$$

Solving the steady-state diffusion equation ( $\partial c/\partial t = 0$ ), we obtain finally

$$\frac{dR}{dt} = \frac{D}{R} \left( \Delta - \frac{x}{R} \right). \quad (2.2)$$

It is obvious that this formula also holds in the case when the supersaturation is a function of the time, if the characteristic time over which the supersaturation varies is significantly longer than the time required for a steady-state flux to be established at the precipitate. We note that the boundary condition at the surface of the precipitate is predicated on the fact that local thermodynamic equilibrium is established at the surface of the precipitate. Once again, this is valid if the rates of growth of the precipitates are low or, in other words, the supersaturation is small  $\Delta_0 \ll 1$ .

As is evident from (2.2), for any value of the supersaturation  $\Delta$  there exists a critical radius  $R_c = \alpha/\Delta = 2\sigma v c_\infty/kT(c - c_\infty)$ , for which the precipitate is in equilibrium with the solid solution ( $dR/dt = 0$ ), and in addition when  $R > R_c$  the precipitate grows, while when  $R < R_c$  it dissolves. This obvious fact is the reason that the small precipitates are "consumed" by large precipitates. The supersaturation  $\Delta(t)$  itself, and together with it  $R_k(t)$  also, vary with time.

We shall now write the full system of equations describing the diffusive decomposition of a one-component system. The first equation is the equation of continuity in size space for the size distribution function of the precipitates of the precipitated phase  $f(R, t)$  at a given moment in time

$$\frac{\partial f}{\partial t} + \frac{\partial}{\partial R} \left( f \frac{dR}{dt} \right) = 0, \quad (2.3)$$

$$f|_{t=0} = f_0(R),$$

while  $dR/dt$  is determined by (2.2). The second equation is the equation of conservation of matter in the precipitated phase and in the solid solution

$$\Delta_0 + q_0 = Q_0 = \Delta + q, \quad (2.4)$$

where

$$q = \frac{1}{v_0} \cdot \frac{4\pi}{3} \int_0^\infty f(R, t) R^3 dR$$

is the number of atoms in the precipitated phase ( $v_0$  is the volume per atom in the precipitated phase), while  $Q_0$  is the total initial number of atoms of the material, including the initial number of atoms in the precipitates  $q_0$  per unit volume. The distribution function (2.3) is normalized to the number of particles per unit volume, so that

$$N = \int_0^\infty f dR$$

is the number of precipitates per unit volume.

Equations (2.3) and (2.4) form a complete system for finding the asymptotic solution under the given initial condition, when the fluctuation formation of nuclei of the phase can be neglected.

We note that only the hydrodynamic term is retained in Eq. (2.3). In reality, of course, this expression is approximate, and an equation of the Fokker-Planck type with the next terms in the expansion in the small parameter  $\alpha/\bar{R}$  in the flux  $dR/dt$  can be written down. One would think that these corrections could be very significant in the region where  $dR/dt$  is very small. Because the supersaturation decreases monotonically, however, this region is always moving, and precipitates with a given size reside in this region for only a very short time. Under these conditions the diffusion term does not play a significant role. This will become especially clear when we transform to relative variables.

## 2.2. Evolution of critical sizes

In what follows it is more convenient to employ relative variables  $(u, \tau)$ ,  $u = R/R_c = R\Delta/\alpha$ , and to replace supersaturation by  $x = \Delta_0/\Delta(t)$ . Equations (2.3) and (2.4) will assume the canonical form, if the "time" is replaced by the quantity  $\tau = \ln x^3$ , which for quite long times, when the supersaturation is small and is decreasing, gives a unique relationship with the standard time  $t$ . In these variables we obtain for  $du/d\tau$  from (2.2)

$$\frac{du^3}{d\tau} = \gamma(u-1) - u^3, \quad \gamma = \gamma(\tau) = \frac{3D}{\alpha^2} \left( \frac{d}{dt} \frac{1}{\Delta^3} \right)^{-1}; \quad (2.5)$$

where

$$3\Delta \frac{d}{dt} \frac{1}{\Delta} = \frac{d\tau}{dt}.$$

For the distribution function over relative sizes  $\varphi(u, \tau)$  we have  $\varphi(u, \tau) du = f(R, t) dR$ , and correspondingly the equation of continuity (2.3) assumes the form

$$\frac{\partial \varphi}{\partial \tau} + \frac{\partial}{\partial u} \left( \varphi \frac{du}{d\tau} \right) = 0, \quad \varphi|_{\tau=t=0} = \varphi_0(v), \quad (2.6)$$

where

$$v = u|_{\tau=0} = \frac{R\Delta_0}{\alpha},$$

while the equation of conservation of matter (2.4) assumes the form

$$1 = \frac{\Delta_0}{Q_0} e^{-\tau/3} + \kappa e^\tau \int_0^\infty \varphi(u, \tau) u^3 du, \quad (2.7)$$

where

$$\kappa = \frac{4\pi}{3} \frac{1}{Q_0} \frac{\alpha^3}{\Delta_0^3}.$$

Knowing the characteristic (2.5), as is well known, one can write the exact solution of (2.6) in the form  $\varphi(u, \tau) = \varphi_0(v) dv/du$  where  $v = v(u, \tau)$  is the characteristic (2.5). The law of conservation of matter assumes the form

$$1 - \frac{\Delta_0}{Q_0} e^{-\tau/3} = \kappa e^\tau \int_{v_0(\tau)}^\infty \varphi_0(v) u^3(v, \tau) dv, \quad (2.8)$$

where  $v_0(\tau)$  is the solution of the equation  $u(v_0, \tau) = 0$ , i.e.,  $v_0(\tau)$  is the lower limit of the initial sizes of the precipitates which have not dissolved by the time  $\tau$ . The introduction of the relative variables  $(u, \tau)$  is very important, since in these variables, starting at some instant of time, an ordered dissolution of precipitates always exists, while the distribution function at this time is determined by the asymptotic behavior of the initial distribution function. This enables the analysis of the complicated nonlinear system of equations describing diffusive decomposition. The equations (2.5)–(2.7) comprise a complete system for determining the asymptotic behavior of the critical sizes. The unknown function in these equations is  $\gamma(\tau)$ , and these equations can be used to determine  $\gamma$ , i.e., ultimately to determine  $\Delta(t)$  and therefore  $R_c(t)$  also.

There are three possibilities for the asymptotic behavior of  $\gamma(\tau)$  in the limit  $\tau \rightarrow \infty$ : 1)  $\gamma(\tau) \rightarrow \infty$ ; 2)  $\gamma(\tau) \rightarrow \text{const}$ ; 3)  $\gamma(\tau) \rightarrow 0$ . We shall start the analysis of these possibilities with the case  $\gamma \rightarrow \text{const}$ . Depending on the values of  $\gamma$  the graph of the rate  $du^3/d\tau = f(u)$  can touch the abscissa axis (at  $\gamma = \gamma_0 = 27/4$ ), pass below the axis (when  $\gamma < \gamma_0$ ), or have a section of positive values (for  $\gamma > \gamma_0$ ) (Fig. 1).

a) In the case  $\gamma \gg \gamma_0$  all points to the left of  $u_1$  move to the left and vanish on reaching the origin. All points to the right of  $u_1$  move toward the point  $u_2$  and asymptotically approach it from the left or right. Therefore the integral on the right side of (2.8) approaches in the limit  $\tau \rightarrow \infty$  the constant value

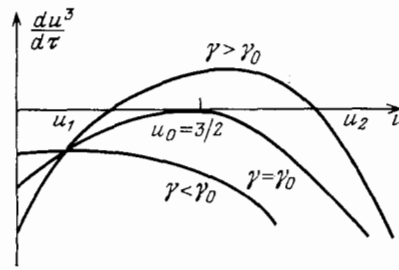


FIG. 1. Equation of motion  $du^3/d\tau = f(u)$  for different values of  $\gamma$ .

$$J_0 = u_2^3 \int_{u_1}^\infty f_0(v) dv,$$

while the total volume of matter in the precipitates on the right side increases as  $e^\tau$  ( $q = \kappa J_0 e^\tau \rightarrow \infty$ ), and Eq. (2.8) is not satisfied. The fact that the constant value  $\gamma > \gamma_0$  is reached only asymptotically does not change the assertions made above: it is only necessary to shift the point from which the time is measured and to refer the expression  $f_0(v)$  to the moment when  $\gamma(\tau)$  is already close to its asymptotic value.

b) In the case  $\gamma < \gamma_0$  all points move to the left, and the origin is reached within a finite time. By the time  $\tau$ , as follows from (2.5), all precipitates whose initial size is less than  $v_0(\tau)$ , determined from the equation

$$\int_0^{v_0(\tau)} \frac{3u^2 du}{u^3 - \gamma(u-1)} = \tau,$$

dissolve. For  $\tau \gg 1$  we have  $v_0(\tau) = e^{\tau/3}$ . Therefore the total volume of precipitates will be determined by the "tail" of the initial distribution:

$$q(\tau) = \kappa e^\tau \int_{e^{\tau/3}}^\infty f_0(v) u^3(v, \tau) dv \sim \kappa \int_{e^{\tau/3}}^\infty f_0(v) u^3 dv \rightarrow 0, \quad f_0(v) > \frac{1}{v^n}, \quad \text{for } v \rightarrow \infty, \quad n > 4.$$

In this case  $q(\tau)$  approaches zero, and Eq. (2.8) once again does not have a solution. The arguments presented for the cases  $\gamma > \gamma_0$  and  $\gamma < \gamma_0$  are even more valid for the cases  $\gamma \rightarrow \infty$  and  $\gamma \rightarrow 0$ , respectively. Therefore only the case  $\gamma(\tau) = \gamma_0 = 27/4$  need be studied. We note first that for the exact equality  $\gamma = \gamma_0$  all points to the right of the tangent point  $u_0 = 3/2$ , moving to the left, cannot intersect the tangent point  $u_0$ , called the "stopping point" and become "stuck" on it. Therefore, like in the case  $\gamma > \gamma_0$ , Eq. (2.8) cannot be satisfied ( $q(\tau) \sim e^\tau \rightarrow \infty$  as  $\tau \rightarrow \infty$ ). This means that the expression  $\gamma(\tau)$  must approach  $\gamma_0$  from below, i.e.,

$$\gamma = \gamma_0 (1 - \varepsilon^2(\tau)), \quad \varepsilon^2(\tau) \rightarrow 0, \quad \tau \rightarrow \infty.$$

At the same time, the points approaching  $u_0$  from the right "leak through" increasingly more slowly through the region of the stopping point  $u_0 = 3/2$ . The rate of leakage is determined by the value of  $\varepsilon(\tau)$ , which, like  $\gamma(\tau)$ , must be determined from Eq. (2.8) and the equation of motion (2.5). This form of the function  $\gamma(\tau)$  is necessary in order that the precipitates move in an ordered manner from right to left in relative sizes, which corresponds to  $du/d\tau < 0$  for all  $u$ . In the opposite case, "leakage" in the space of precipitate sizes on the right into the region on the left from the stopping point  $u_0 = 3/2$  will not occur, and since  $R_c(t) = \alpha/\Delta \rightarrow \infty$

for  $\tau \rightarrow \infty$ ,  $\Delta \rightarrow 0$ , the amount of material in the precipitates will increase without bound, which is impossible. The "leakage" must be such that there is enough time for a size distribution function satisfying the condition of balance of matter to form.

We note that for  $\gamma > \gamma_0 = \text{const}$  there formally exists an infinite number of special initial conditions under which  $du/d\tau$  vanishes at the point  $u = u_0$ . In addition, there exists an infinite number of solutions satisfying both the equation of continuity and the equation of balance of matter. If, however, fluctuations are taken into account, then this means that there is a definite probability for precipitates to appear to the right of  $u_0$ , which would immediately destroy the balance of matter. Therefore all such solutions (for  $\gamma > \gamma_0 = \text{const}$ ) are unstable and are physically meaningless.

It is shown in Ref. 23 that the amount of matter to the right of the stopping point  $u_0$  is negligibly small. If this matter is completely neglected, then this means that  $f$  must be set equal to zero together with  $\varepsilon^2(\tau)$ . We shall call this approximation the zeroth-order hydrodynamic approximation. Therefore in the zeroth-order approximation there does indeed exist a unique stable solution corresponding to  $\gamma = \gamma_0$ . Since in this approximation the rate  $du/d\tau$  must have a zero of second order, taking into account the fact that  $\varepsilon^2(\tau) = 0$ , the asymptotic values of  $u_0$  and  $\gamma_0$  and together with them the asymptotic values of the critical sizes and supersaturation can be immediately determined:

$$\left. \frac{\partial u}{\partial \tau} \right|_{u=u_0} = 0; \quad \left. \frac{\partial (du/d\tau)}{\partial u} \right|_{u=u_0} = 0, \quad (2.9)$$

whence we obtain the values  $u_0 = 3/2$  and  $\gamma_0 = 27/4$ , which we already know. Correspondingly, for the critical size we have from (2.5), taking into account the fact that  $R_c = \alpha/\Delta$ ,

$$R_c^3 = R_{k0}^3 + \frac{4}{9} D \alpha t, \quad \Delta = \left( \frac{4}{9} \frac{D}{\alpha^2} t \right)^{-1/3}, \quad (2.10)$$

where  $R_{c0}$  is the critical size of the system at the stage when the decomposition can be described by the asymptotic equations. It is easy to show that  $\bar{R} \sim R_c$  always holds, while for mass transfer by means of volume diffusion  $\bar{R} = R_c$ ,<sup>69,70</sup> and we arrive at the  $t^{1/3}$  law, determining the kinetics of the evolution of the ensemble of particles, i.e., at the later stage of diffusive decomposition the cube of the mean size of the particles is proportional to the time. Numerous experimental data show convincingly that this law is obeyed in the overwhelming majority of the cases of diffusive decomposition studied.<sup>71</sup> Some examples are presented in Sec. 4. Comparison with experiment shows<sup>71</sup> that the  $t^{1/3}$  law is quite powerful and even holds outside the limits of applicability of the theory (when  $\bar{R} \sim \bar{l}$ ).

The equations (2.10), obtained in the zeroth-order approximation, are asymptotically exact. A detailed analysis<sup>61</sup> yields corrections to the  $t^{1/3}$  law, which, naturally, depend on the parameters determining the asymptotic behavior of the initial distribution function  $f_0$ . The relative value of these corrections decreases rapidly as  $\tau$  increases, and the zeroth-order approximation (2.10) becomes all the more accurate with the passage of time.

The method developed in Ref. 61 makes it possible to construct an iterative process for finding corrections to  $R_c$  for arbitrary asymptotic behavior of the initial distribution functions and different mechanisms of mass transfer.

Thus the theory gives a complete description of the kinetics of evolution of the mean size of macrodefects in a dispersed system at the late stage of diffusive decomposition.

### 2.3. Asymptotic behavior of the distribution function

As already pointed out, in the zeroth-order approximation  $\gamma = \gamma_0$  and  $\varphi(u, \tau) = 0$ ,  $u > u_0 = 3/2$ . We denote

$$\frac{du}{d\tau} = -g(u) = \frac{1}{3u^2} \left( u - \frac{3}{2} \right) (u + 3),$$

and, obviously, the equation of continuity (2.6) has the asymptotic solution

$$\varphi = \begin{cases} \frac{1}{g(u)} \chi(\tau + \psi), & u \leq \frac{3}{2}, \\ 0, & u > \frac{3}{2}, \end{cases} \quad (2.11)$$

where

$$\psi = \int_0^u \frac{du}{g(u)} = \frac{4}{3} \ln(u+3) + \frac{5}{3} \ln\left(\frac{3}{2} - u\right) + \frac{1}{1-(2/3)u} - \ln \frac{3^3 e}{2^6 \tau^2},$$

while  $\chi$  is an arbitrary function, which must be determined from the condition of conservation of matter, which in this approximation (neglecting the term  $e^{-\tau/3} \ll 1$ ) has the form

$$\kappa e^\tau \int_0^{3/2} \chi(\tau + \psi) \frac{u^3}{g(u)} du = 1. \quad (2.12)$$

From here we obtain

$$\chi = A \exp[-(\tau + \psi)],$$

where

$$A = \left( \kappa \int_0^{3/2} e^{-\psi} \frac{u^3}{g(u)} du \right)^{-1} = \frac{3Q_0}{4\pi R_{c0}^3 \cdot 1.1} \approx 0.22 \frac{Q_0}{R_{c0}^3}.$$

Introducing the probability  $P(u)du$  that the size of the particle falls between  $u$  and  $u + du$  we obtain

$$P(u) = \begin{cases} \frac{3^4 e}{2^5 \tau^3} \frac{u^2 \exp\{-1/[1-(2/3)u]\}}{(u+3)^{7/2} [(3/2)-u]^{11/3}}, & u \leq u_0 = \frac{3}{2}, \\ 0, & u > u_0. \end{cases} \quad (2.13)$$

The number of precipitates per unit volume is given by

$$N(\tau) = \int_0^{3/2} \varphi(u, \tau) du = A e^{-\tau} = \left( \frac{3}{2} \right)^{2/3} A \frac{R_{k0}^3}{R_c^3}. \quad (2.14)$$

These formulas completely determine the asymptotic distribution of precipitates over sizes and in time. A graph of the probability density  $P(u)$ , determined by (2.13), is shown in Fig. 2a. Thus we have obtained one of the most important results of the theory—a universal size distribution function of precipitates, which is independent of the initial conditions, forms at the late stage of diffusive decomposition. In the size range  $R > (3/2)\bar{R}$  the distribution function equals zero in the zeroth-order approximation. This constant form of the function remains until the system arrives at equilibrium. In other words, during the decomposition process, with the passage of time and precisely at the late stage of decomposition, any dispersed system "forgets" its initial state and transforms into a state which is stable and asymptotically identical for all systems [in the relative variables  $(u, \tau)$ ], characterized by a universal distribution function

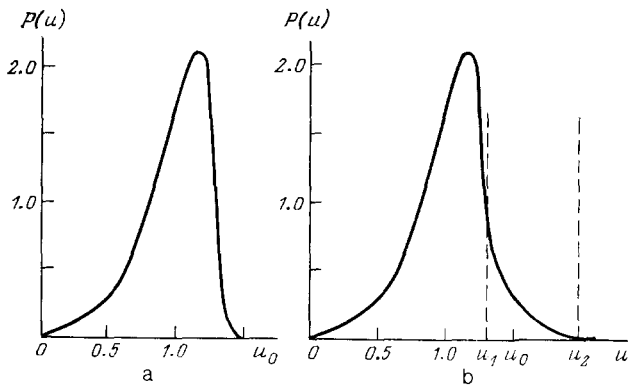


FIG. 2. Universal distribution function. a) Zeroth-order approximation (2.14). b) First order approximation.

which depends only on the mechanism of mass transfer operating in the system. In dimensional variables  $(R, t)$ , however, the distribution function varies continuously in time. It is therefore natural that this unique state could be observed experimentally (see the review of Ref. 71) only after it was first predicted theoretically in Ref. 23. Subsequently Wagner<sup>26</sup> obtained the results (2.10) and (2.13) by a simpler and clearer, but less rigorous method. The heuristic approach which he used is not closed, since the existence of an asymptotic solution in the form (2.11), where terms depending only on the time and only on the size can be separated, is assumed at the outset, and this is by no means obvious.

The results (2.10), (2.13), and (2.14) were obtained in the zeroth-order hydrodynamic approximation. In this approximation, however, the dynamics of the formation of the universal distribution function and its relationship with the initial distribution cannot be studied. It is also impossible to obtain the distribution function in the region of the stopping point  $u_0$  and beyond it, to calculate more accurately the asymptotic behavior from the time of saturation of the solution, and to determine the time  $\tau_0$  at which the asymptotic description of the diffusive decomposition as a function of time can be used with adequate accuracy. All these quantities are closely related with the structure of the initial distribution function.

A method which enables the derivation of an exact equation relating  $\varepsilon^2(\tau)$  with the structure of the initial distribution  $f_0$  and the determination of both  $\varepsilon^2(\tau)$  and the distribution function for all sizes, including also beyond the stopping point  $u_0$ , was developed in Ref. 61.

The behavior of  $\varepsilon^2(\tau)$ , as studied in detail in Ref. 61, is determined by the behavior of the initial distribution function for quite large sizes. In the limit  $\tau \rightarrow \infty$   $\varepsilon^2(\tau) \rightarrow 0$ , since as  $\tau$  increases under the conditions of ordered motion from right to left increasingly more distant regions of the initial distribution function, which is a decreasing function of its argument  $f_0(R) \leq 1/R^n$ , where  $n > 4$  as  $R \rightarrow \infty$ , form the distribution function at a given moment to the left of the stopping point, making the main contribution to the balance of matter. Indeed, since  $du/d\tau < 0$ , with the passage of time increasingly fewer particles remain to the left of the stopping point, and therefore they must "leak" more slowly through the transformation region near the stopping point so that there would be enough time for all excess matter to settle on

them. This means that the distribution function will "bunch up" in a self-consistent manner.

For asymptotic forms of  $f_0$  which decreases more rapidly than a power-law function, for example, an exponential asymptotic function

$$f_0(R) = \frac{A}{R^n} \exp\left(-\frac{R-R_0}{\tau_0}\right)^m \quad (m > 0, R \rightarrow \infty),$$

the transformation region rapidly becomes negligibly small and degenerates into the point  $u_0$ .

To determine more accurately the distribution function for all sizes (including beyond the stopping point for  $u > u_0$ ) it is necessary, generally speaking, to find the solution of the characteristic equation for an arbitrary function  $\varepsilon^2(\tau)$  and then the boundary conditions will lead to a functional equation for  $\varepsilon^2(\tau)$ . This program cannot be carried out analytically in general form. As shown in Ref. 61, the asymptotic behavior of physical initial distribution functions, decreasing with increasing size, is such that it is possible to develop an iterative procedure which permits reducing exactly or with adequate accuracy the problem to the solution of ordinary differential equations for  $\varepsilon^2(\tau)$  and finding the characteristic and together with it the distribution function for all sizes under quite general initial conditions. The distribution function calculated by the more accurate method (in the first hydrodynamic approximation) (see Fig. 2b) to the left of the transformation region for  $u \leq u_2$  is identical to the universal distribution obtained above (2.13) in the zeroth-order approximation. To the right of the transformation region, however, the distribution function depends substantially on the asymptotic behavior of the initial distribution function, which forms a "tail" decreasing with time beyond the stopping point  $u_0$ . The weaker the asymptotic behavior of the initial distribution function, the more matter there is in the "tail" of the distribution function and the later the times at which the late stage of the diffusion decomposition process appears.<sup>61</sup> The reason for the appearance of the "tail" lies in the fact that the system has not yet completely "forgotten" the initial distribution function, and this "memory" is manifested in the "tail" for  $u > u_0$ .

This result should be noted. Large precipitates beyond the stopping point  $u_0 = 3/2$  (for  $u \gtrsim 2$ ) are observed experimentally quite often on the histograms.<sup>71</sup> In the zeroth-order approximation, however, the theory predicts (2.13) that there are no precipitates with sizes  $R > (3/2)\bar{R}$ , on the basis of which some investigators even conclude that the theory is not valid.

We emphasize once again that there is no "tail" in the theoretical distribution function only in the zeroth-order approximation in the state in which the system will arrive asymptotically after some (for some systems possibly quite long) time. The methods developed in the theory<sup>61</sup> permit constructing not only with arbitrary accuracy the "tail" of the distribution function but also reconstructing, when necessary, the initial distribution  $f_0$  from the known "tail."

The accuracy with which the "tail" of the distribution function is determined for  $u > u_1$  is determined, as should be, only by the accuracy with which the characteristic is determined. Generally speaking, it makes no sense to improve specially the "hydrodynamic" approximation, since local fluctuations in the concentration at the precipitates will become more significant with the passage of time. This is at-

tributable primarily to the direct diffusion interaction ("collisions") of precipitates of the new phase, which can appear at distances less than their sizes. Taking this circumstance into account leads to the formation of an additional "tail" in the distribution function for  $u > u_0$ , which is determined primarily by the distribution function for  $u < u_0$ .

We note that the maximum of the distribution function does not coincide with the point at which the rate of growth is highest, but rather is shifted to the left. This is attributable to the fact that in any approximation the distribution function for  $u > u_0$  is a decreasing function. Therefore, having "leaked" through the region of the stopping point  $u_0$ , it has enough time to assume the maximum value only at some distance from  $u_0$ , which is also virtually independent of the initial conditions in the limit  $\tau \rightarrow \infty$ .

Thus far we have studied the decomposition of a supersaturated solid solution, when mass transfer between macrodefects occurs by means of volume diffusion. Many experiments have demonstrated (see, for example, Ref. 71) that depending on the external conditions and the structure of the material the predominant mechanism of mass transfer could be grain-boundary diffusion, diffusion over a dislocation network or along dislocations, or the kinetics can be controlled by the rate at which point defects cross the phase boundary, in other words, by the rate of formation of bonds on the growing surface of the macrodefect. It is therefore important to study the possibility of the existence of a stable asymptotic state in a dispersed system, if the process of growth of precipitates is controlled by some other mechanisms of mass transfer of point defects.

It is shown in Refs. 26, 27, 29, and 54 that the complete system of equations describing the late stage of diffusive decomposition controlled by different mechanisms of mass transfer in all cases remains the same as in the case of mass transfer via diffusion, and it is given by Eqs. (2.3) and (2.4). The difference lies only in the expression for the rate of growth, determined by the effective mechanisms of mass transfer, which in general form is given by the expression.

$$\frac{dR}{dt} = \frac{D_n a^{n-3}}{R^{n-3}} \left( \Delta - \frac{\alpha}{R} \right). \quad (2.15)$$

It turns out<sup>34,69,70</sup> that the method presented above for solving nonlinear systems of the type (2.3) and (2.4) is completely applicable to all problems of this type, whose velocity field can be represented in the form (2.15). Using this method it is possible to obtain the values of all parameters of decomposition ( $P_n(u)$ ,  $R_c$ ,  $u_0$ ,  $\gamma_0$ ) for specific mechanisms of mass transfer (for definite values of  $n$ ), which are given in Table I. Figure 3 shows the tabulated distribution functions for different mechanisms of mass transfer. Therefore even in the case when other mechanisms of mass transfer, differing from mass transfer by means of volume diffusion, operate, stable asymptotic states, characterized by universal distribution functions independent of the initial conditions and determined solely by the operative mechanisms of mass transfer, exist in a dispersed system. Such states, however, are intermediate states, since in the process of evolution the system finally transforms into the most stable asymptotic state, determined by mass transfer by means of volume diffusion.

In a real situation several of the mechanisms of mass transfer mentioned above can operate simultaneously. For example, transfer along grain boundaries, blocks, and dislo-

cation lines can occur together with volume diffusion. We note that all these mechanisms "operate" simultaneously for all precipitates of the new phase, since as a result of the diffusion interaction only the most rapidly growing precipitates survive at the late stage.

A method for solving the equations describing the diffusive decomposition under conditions of simultaneous operation of several mechanisms of mass transfer was developed in Ref. 56. The complete system of equations for determining the characteristics of diffusive decomposition under conditions of simultaneous operation of several mechanisms differs from the corresponding system (2.3) and (2.4) by the form of the velocity field (2.15), on whose right side the factor  $D_n a^{n-3}/R^{n-2}$  is replaced by a function  $A(R, t)$  containing terms determined by some separate mechanisms of mass transfer. They are all proportional to  $(a/R)^n$  ( $n = 2, 3, 4, \dots$ ). It is important that  $D(R) \rightarrow D_0$  as  $R \rightarrow \infty$ , and all fluxes are proportional to  $(\bar{c} - c_R)$ . Therefore in the general form  $dR/dt = f(\bar{c} - c_R, R, t)$ . Using the smallness of  $\bar{c} - c_R$  we can write

$$\frac{dR}{dt} \approx A(R, t) (\bar{c} - c_R). \quad (2.16)$$

The function  $A(R, t)$  is a quite complicated function. Its asymptotic behavior for very small precipitates is determined by the rate of formation of chemical bonds on the surface of the precipitate; in this case,  $A = \text{const}$ .<sup>56</sup> For larger precipitates  $A(R, t)$  is a sum of contributions from each of the operative mechanisms of mass transfer.

The most rapidly decreasing term is proportional to  $a/R$  and is determined by mass transfer with the help of volume diffusion, i.e., the final asymptotic form of the diffusive decomposition is determined by the mechanism of mass transfer by means of volume diffusion. Thus  $A(R, t)$  in this case has the form

$$A(R, t) = \frac{1}{R} \left( a_1 + \frac{b_1}{R} + \dots \right).$$

The constants,  $a_1, b_1, \dots$  are related with the angle-averaged components of the tensors of diffusion coefficients (determining the operative mechanisms of mass transfer), the surface tension tensor, and also the stress tensor for stresses accompanying the growth of precipitates of the new phase. Table I shows the values of  $a_1, b_1, \dots$  for the isotropic case for specific mechanisms.

Thus if several mechanisms of mass transfer can operate simultaneously in a dispersed system during diffusive decomposition, then in the course of evolution the system will continuously transform from one intermediate asymptotic state into another. At the same time, depending on the hierarchy of mass transfer mechanisms, the distribution function passes through a series of asymptotic forms (Table I) and finally ( $t \rightarrow \infty$ ) transforms into the form corresponding to the mechanism of volume diffusion. In the process of this transformation the position of the stopping point and together with it the kinetics of variation of the critical sizes of the precipitates change.

This method was used in Ref. 65 to analyze the histograms<sup>85</sup> under the assumption that the kinetics of growth of finely dispersed precipitates, studied in Ref. 85, is controlled by mass transfer by means of volume diffusion and chemical reaction on the precipitate-matrix boundary. The exact form of the theoretical distribution functions  $P(u, u_0)$  for different



TABLE I. Parameters of diffusive decomposition for different mechanisms of mass transfer.

| Controlling mechanism                 | $n$ | $u_0$           | $\gamma_0$                            | $\bar{u} = \frac{\bar{R}}{R_c}$ | $R_c = f(t)$   | $P_n(u)$   | References |
|---------------------------------------|-----|-----------------|---------------------------------------|---------------------------------|--|--|------------|
| Reaction on the interphase surface    | 2   | 2               | 4                                     | $\frac{8}{9}$                   | $R_c^2 = R_{c0}^2 + \frac{1}{2} \frac{2\sigma n_0 v^2 c_{\infty} k_p}{kT} t$     | $\begin{cases} \frac{24 e^3 u [-6/(2-u)]}{(2-u)^6}, & u \leq u_0 \\ 0, & u \geq u_0 \end{cases}$   | 26         |
| Volume diffusion                      | 3   | $\frac{3}{2}$   | $\frac{27}{4}$                        | 1,00                            | $R_c^3 = R_{c0}^3 + \frac{4}{9} \frac{2\sigma n_0 v^2 c_{\infty} D_0}{kT} t$     | $\begin{cases} \frac{3^4 e}{2^{5/3}} u^2 \exp \left[ -1 \left( 1 - \frac{2u}{3} \right) \right], & u \leq u_0 \\ 0, & u \geq u_0 \end{cases}$  | 23         |
| Grain-boundary diffusion              | 4   | $\frac{4}{3}$   | $\frac{256}{27}$                      | 1,03                            | $R_c^4 = R_{c0}^4 + \frac{27}{64} \frac{2\sigma n_0 v^2 c_{\infty} D_c}{kT} t$   | $\begin{cases} \left( \frac{3}{4} \right)^4 u^3 \exp \left( \frac{2}{4-3u} \right) \exp \left[ -\frac{1}{6\sqrt{2}} \operatorname{arctg}^{-1} \frac{u+(4/3)}{4/3\sqrt{2}} \right], & u \leq u_0, \\ 0, & u \geq n_0 \end{cases}$ | 27         |
| Diffusion along a dislocation network | 5   | $\frac{5}{4}$   | $\frac{3125}{256}$                    | 1,09                            | $R_c^5 = R_{c0}^5 + \frac{256}{625} \frac{2\sigma n_0 v^2 c_{\infty} D_D}{kT} t$ | The integral cannot be expressed in terms of elementary functions. It is calculated by numerical methods, as also in the case of general $n$ .   | 29         |
|                                       | $n$ | $\frac{n}{n-1}$ | $\frac{n^n}{(n-1)^{n-1}} = n u^{n-1}$ | $\int_0^{u_0} u P_n(u) du$      | $R_c^n = R_{c0}^n + \frac{n}{u_0} \frac{D_0 2\sigma n_0 v^2 c_{\infty}}{kT} t$   | $\begin{aligned} P_n(u) &= e^{-\psi_n(u)} \\ \psi_n(u) &= \int_0^u \frac{du}{g_n(u)} \\ g_n(u) &= -\frac{du}{d\tau} = \frac{1}{n u^{n-1}} [\gamma_0(u-1) - u^n] \end{aligned}$   | 69, 70     |

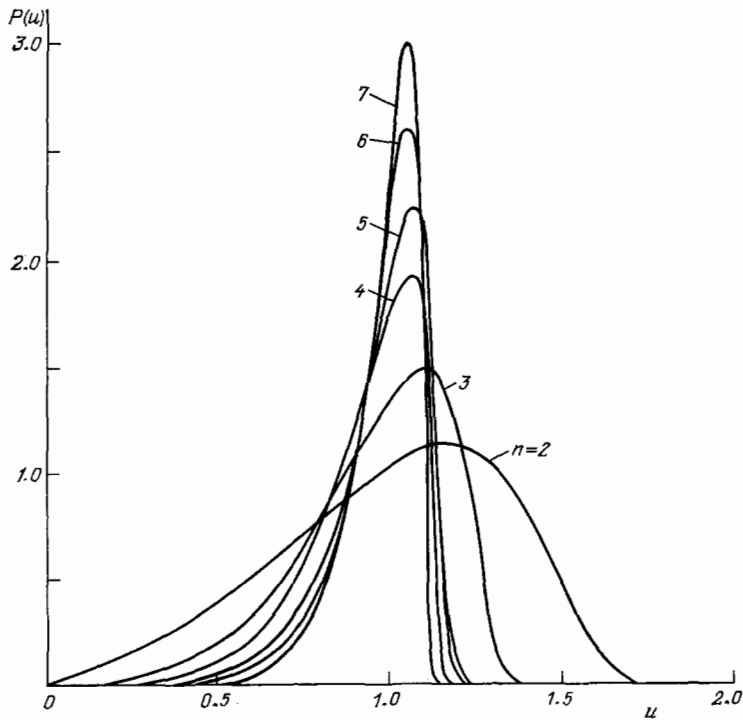


FIG. 3. Distribution functions corresponding to different mechanisms of mass transfer [for different values of  $n = 2-7$  (see Table 1)].

values of the parameters characterizing the contribution of different mechanisms of mass transfer was calculated on a computer. As can be seen from Fig. 4, for definite values of these parameters it is possible to obtain significantly better agreement between the theoretical function  $P(u, u_0)$  and the experimental data than for the case of one selected mechanism of mass transfer.

In the hydrodynamic approximation, as shown above, the "tail" of the distribution function vanishes asymptotically ( $\varphi(u, \tau) = 0, u > u_0$ ). Numerous experimental studies demonstrate<sup>71</sup> that while the  $t^{1/n}$  law is well satisfied the experimentally observed distributions in many cases are wider than those predicted by the theory, and in addition precipitates with relative sizes much greater than  $u_0$ , form-

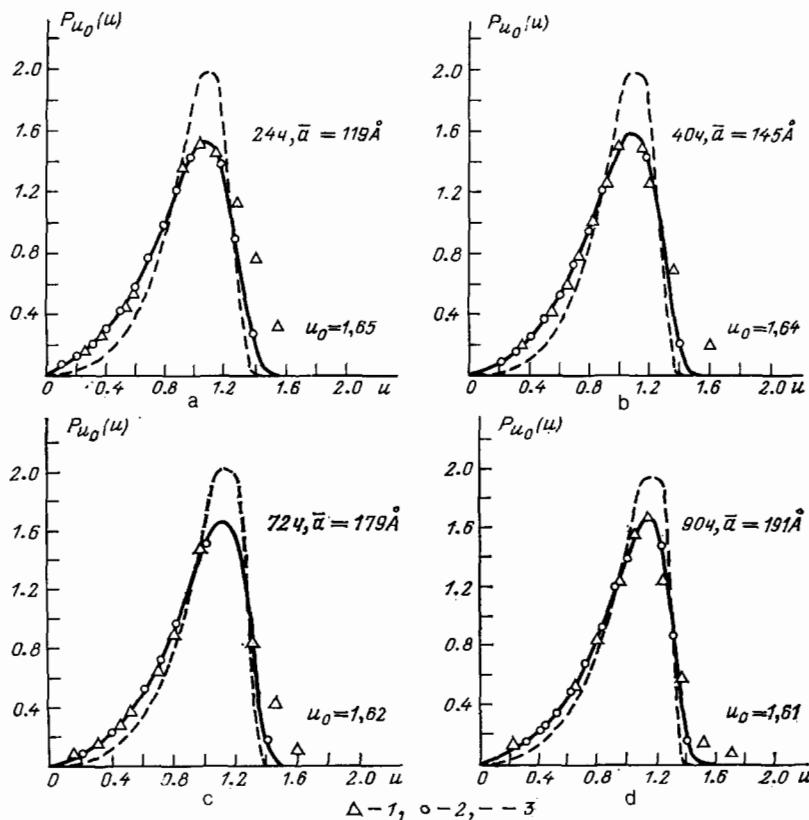


FIG. 4. Comparison of histograms with theoretical distribution functions. 1) experimental data<sup>85</sup> (Ni-6.35 Al, 625 °C); 2) theoretical distribution function for simultaneous action of two mass-transfer mechanisms; 3) universal function  $P(u)$  (2.13). For Figs. a-d  $t_a > t_b > t_c > t_d$ .

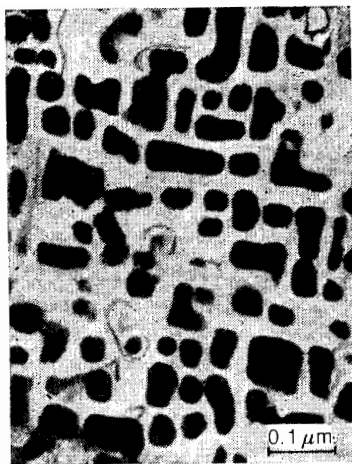


FIG. 5. Extraction replicas of NiAl precipitates in the alloys Ni-49 at. % Co-12 at. % Al.<sup>68</sup>

ing a quite extended "tail" beyond the stopping point, are often observed.<sup>65</sup> We have already discussed one reason for the appearance of a "tail," associated with the transformation of the initial distribution function into a universal function. We shall now study another possibility for the formation of a "tail" as a result of the significant volume fraction of the precipitates. The results obtained above are valid, strictly speaking, when the volume fraction of the precipitates approaches zero and the mean size of the precipitates is much smaller than the mean distance between them  $\bar{R} \ll \bar{l}$ . Equations (2.5) and (2.6) correspond, as already pointed out, to the "hydrodynamic" approximation in size space. The equation (2.5) expresses the velocity field  $du/d\tau = -g(u, \tau)$  at each instant of time as a function of the supersaturation  $\Delta(\tau)$ . Local fluctuations of the concentration near a growing or dissolving precipitate are thereby neglected, as a result of which the velocity in reality does not equal precisely its mean value  $-g(u, \tau)$ . This circumstance can be taken into account with the help of the mechanism of "collisions" between precipitates.<sup>24</sup> The main idea of this mechanism is that precipitates separated by distances of the order of their sizes coalesce; this is attributable to the spatial fluctuations of the distances between the precipitates at the initial stage of nucleation (we emphasize that the distances between the centers of the precipitates in this case remain fixed, and the precipitates do not move as a whole). The fact that this mechanism can occur in a real situation is clearly demonstrated in Fig. 5. From physical considerations as well as from the analysis performed in Sec. 2.2 it should be expected<sup>24</sup> that collisions should reduce the value of  $\gamma$  com-

pared with  $\gamma_0$ , since the precipitates transferred by collisions through the stopping point must have the possibility of leaking back. Using the method of successive approximations to solve Eqs. (2.5) and (2.6) it can be shown<sup>24</sup> that collisions alter somewhat the distribution function in the region of the stopping point and lead to the appearance of an exponentially decreasing infinitely extended "tail" of the order of  $Q_0$  beyond the stopping point.

Numerical methods for realizing on a computer the iterative procedure for calculating the collision integral<sup>24</sup> were employed in Ref. 68. The results obtained showed very clearly that when the volume fraction is taken into account with the help of "collisions" the rate of change of the mean size of the precipitates remains proportional to  $t^{1/3}$ , like in the zeroth-order approximation, but the rate constant increases as the volume fraction increases. When the volume fraction changes up to 60% the rate constant is approximately doubled. The effect of the volume fraction on the parameter  $\gamma$  (after 12 iterations) is also presented here.

Figure 6 shows the results of calculations of the distribution function  $P(u)$  and the collision integral  $J_{col}$  using the iteration procedure described above. As the number of iterations  $n$  is increased the distribution function shifts toward increasing values of  $u$ ; in addition, part of the matter is "transferred" by the "collisions" into the region beyond the stopping point  $u_0 = 3/2$ , which leads to the appearance of a "tail" in the distribution. As the number of iterations is increased the corrections to the "tail" become increasingly more accurate, though, naturally, they become increasingly smaller (Fig. 6) because of the good convergence of the iteration process.

The distribution function depends strongly on the volume fraction of precipitates  $Q_0$ , becoming increasingly wider and more symmetrical (since the largest changes occur in the vicinity of the stopping point). As  $Q_0$  increases the size of the "tail" of the distribution increases. The existence of precipitates with a large radius in the experimental histograms becomes easily explainable, since when "collisions" are taken into account there is in principle no upper limit to the sizes, though, undoubtedly, the probability for the appearance of large precipitates beyond the stopping point decreases rapidly as the sizes of the precipitates increase.

The effect of the volume fraction on the process of decomposition of solid solutions was studied in Refs. 43, 50, and 64, but in these studies attention was directed entirely toward a more accurate determination of the "hydrodynamic" rate of growth. The basic assumptions which are made in these studies in order to determine the effect of the remaining precipitates on the growth of a particular precipitate are quite arbitrary and are not self-consistent. In addition, it

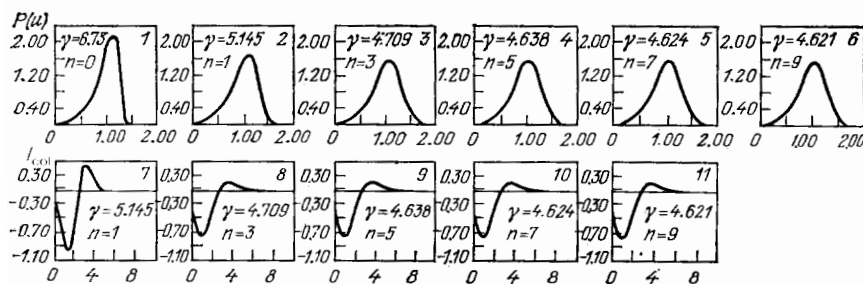


FIG. 6. Calculation of the distribution function  $P(u)$  (a) and the collision integral  $J_{col}$  (b) using an iteration procedure.<sup>24</sup> Volume fraction  $Q_0 = 0.2$ ;  $n$  is the number of iterations.<sup>68</sup>

should be noted that no matter how accurately the "hydrodynamic" rate of growth is determined, in this approximation it is impossible to obtain extended "tails" of the distribution function, since a stopping point always exists in this approximation. It is obvious that the volume fraction has a definite effect on the rate of growth of the precipitates, and it can introduce a significant quantitative change in the size distribution function without changing its qualitative character. This rate of growth can be determined in the most systematic and self-consistent manner by combining the "sphere of influence" approximation<sup>62</sup> and the "effective medium" approximation.<sup>50</sup>

In the above analysis a number of factors affecting the kinetics of diffusive decomposition—elastic stresses arising during the growth of the precipitates, anisotropy of precipitates and of the matrix, etc.—were ignored. It is shown in Ref. 24 that taking into account many of these factors reduces merely to renormalization of the coefficients of diffusion and supersaturation, but in the dimensionless variables this does not change either the form of the distribution function or the conclusions regarding its stability. The role of stresses, of course, can be substantially more complicated than described in Ref. 24 for spherically shaped precipitates, for example, if the solid solution and the precipitate are anisotropic. Precipitates shaped like needles, plates, ellipsoids, etc., are quite often observed experimentally. In this case the relative arrangement of the crystallographic axes and of the matrix affects the form of the growing precipitate. Since the arrangement of these axes is random, there is a distribution of precipitates not only over sizes but also over shape. In this case  $\varphi(\mu, \tau)$  also depends on the parameters characterizing the shape, while the equation of continuity (2.6) does not change. Integration over the shape parameters is added on the right side of Eq. (2.7). Equation (2.5) depends on these parameters, while the curves corresponding to it in the  $(du^3/d\tau, u)$  plane fill an entire band. If the precipitates are anisotropic, but grow in a similar manner, then, using the analysis performed in Sec. 2.2, it can be shown that the band asymptotically approaches the  $u$  axis from above. All precipitates with the exception of those whose shape corresponds to the top edge of the band have a finite negative velocity and vanish with time. Only precipitates with the most favorable form, for which all preceding results are valid, remain.

Diffusion growth in ionic crystals, glasses, and other nonmetallic systems exhibits a number of peculiarities compared with the decomposition in metallic matrices.<sup>59,71</sup> For ionic crystals the charge present on the diffusing particles and the appearance of electric fields in the material can have an important effect on the growth process. As shown in Ref. 44, this significantly deforms the distribution function and even leads to the appearance of "double-hump" distributions.

### 3. THEORY OF DIFFUSIVE DECOMPOSITION OF MULTICOMPONENT SOLUTIONS

We shall now consider the late stage of diffusive decomposition of multicomponent solid solutions. This case is the most common and the most practically interesting one, since the overwhelming majority of real materials are supersaturated multicomponent solid solutions, in which under certain conditions precipitates of different phases, determining the properties of these materials, form. The theory of the evolu-

tion of precipitates of these phases in the process of diffusive decomposition is constructed in Refs. 30–35. As will be evident from what follows the conditions of quasithermodynamic equilibrium distribute the matter of the components in a more advantageous manner over the phases and determine the regions of their coexistence, while the action of surface tension leads to a universal, in the zeroth order approximation (with respect to  $\alpha^s/\bar{R}^s \ll 1$ , where  $\bar{R}^s$  is the mean size of the precipitates of the  $s$ th phase while  $\alpha^s$  is proportional to the surface tension of the  $s$ th phase), size distribution of the precipitates of the coexisting phases.

At the earliest stage of diffusive decomposition the growth of the precipitates depends on the history of the material, and at quite long times a precipitate size distribution function which is independent of the initial distribution and which, because of the nonlinearity of the process, becomes universal in the zeroth-order approximation forms. The corrections depending on the initial conditions decrease as the decomposition process unfolds. The initial conditions also determine the time at which the system emerges into the asymptotic state. The emergence into the asymptotic state can be determined by comparing the theoretical and experimental distribution functions or by the saturation of any property of the material which is sensitive to the impurity concentration in the solid solution (dilatometry, lattice parameters, electrical resistance, etc.).

We shall study an  $N$ -component solid solution in which as a result of decomposition  $k$  different phases (of chemical compounds) consisting of components present in the solution can form. The possibility of coexistence of different phases in the matrix is determined by the ratio of the initial concentrations of the components, forming a phase, and the thermodynamic advantageousness of these phases. Among all chemical compounds which can exist in the given multicomponent system only those for which the solution is supersaturated can be stable. This condition is necessary, and for low concentrations of the components ( $c_i^0 \ll 1$ ) when the law of mass action is applicable to the chemical reactions which occur, it can be written in the form

$$\sum v_i^s \mu_i^s = \ln \frac{\prod_i (c_i^0)^{v_i^s}}{k_\infty^s} > 0, \quad (3.1)$$

where  $c_i^0$  is the initial concentration of the  $i$ th component in the solid solution,  $k_\infty^s$  is the equilibrium constant of the  $s$ th chemical reaction, and  $v_i^s$  and  $\mu_i^s$  are the stoichiometric coefficient and the chemical potential of the  $i$ th component of the  $s$ th phase. In this case, if the phases forming in the system do not contain common components, the condition (3.1) is also sufficient, i.e., the precipitates of different phases will grow independently. If, on the other hand, the phases contain common components, it turns out that although based on separate components for some phases the solution was at first supersaturated, in the process of decomposition the matter can be redistributed over the phases, and for these phases the solution will become unsaturated. For this reason the relation (3.1) in this case is only a necessary condition for selecting those phases whose precipitates can participate in further competitive growth occurring in the process of diffusive decomposition.

### 3.1. Basic system of equations and its solution

The full system of equations describing the process of diffusive decomposition in an  $N$ -component system, forming  $k$  phases with the stoichiometric composition, including pure components and compounds with the matrix material, consists of  $k$  equations of continuity (3.2),  $N$  laws of conservation of the matter of the components (3.3),  $\sum n^s - k$  stoichiometric relations for the diffusion fluxes  $J_{iR}^s$  and  $k$  laws of mass action (3.5):

$$\frac{\partial f^s}{\partial t} + \frac{\partial}{\partial R} (f^s v_R^s) = 0, \quad (3.2)$$

$$\frac{d\bar{c}_i}{dt} + \sum_{s_i} \frac{4\pi}{n_0} \int_0^\infty f^s R^2 J_{iR}^s dR = 0, \quad (3.3)$$

$$\frac{J_{iR}^s}{v_i^s} = \frac{J_{i'R}^s}{v_{i'}^s}, \quad (3.4)$$

$$\prod_{i=1}^h (c_{iR}^s)^{\nu_i^s} = k_R^s, \quad (3.5)$$

where  $f^s(R, t)$  is the distribution function of precipitates of the  $s$ th chemical compound (phase) in the matrix,  $\sum_{s_i}$  indicates summation over all phases containing the  $i$ th component,  $\bar{c}_i$  is the average concentration of the  $i$ th component in the solid solution at a given moment in time,  $c_{iR}^s$  is the equilibrium concentration of the  $i$ th component on the surface of the particles of the  $s$ th phase,  $n_0$  is the number of sites in the matrix per unit volume,  $k_R^s$  is the equilibrium constant of the  $s$ th chemical reaction on the surface of the precipitate of radius  $R$ , and  $n^s$  is the number of components in the  $s$ th phase. Since at the late stage of decomposition the supersaturation of the components  $\Delta_i$  is much less than unity, this makes it possible, as in the case of the one-component solutions, to use the expressions for the quasistationary fluxes of atoms of the  $i$ th kind toward the precipitates of the  $s$ th phase  $J_{iR}^s$  per unit surface area of precipitates with radius  $R$ , obtained in the self-consistent diffusion field approximation:

$$J_{iR}^s = \frac{D_i n_0}{R} (\bar{c}_i - c_{iR}^s),$$

where  $D_i$  is the coefficient of diffusion of the  $i$ th component in the matrix. In this case, the ratio of the characteristic time for establishing the diffusion flux of the most slowly diffusing component  $\tau_{\text{dif}} \sim \bar{R}_i / 6D_i$  to the characteristic time over which the size of the inclusions changes

$$\tau_{\text{char}} \sim \frac{\bar{R}_i}{D_i} \frac{dc}{dr} \sim \frac{\bar{R}_i^2}{D_i \Delta_i}$$

is  $\frac{\tau_{\text{dif}}}{\tau_{\text{char}}} \sim \Delta_i \ll 1$ . The smallness of the parameter  $\Delta_i$  also makes it possible to use the quasiequilibrium conditions on the surface of the precipitates. Since  $\Delta_i \rightarrow 0$ , at the late stage the laws of mass action can be employed, and the interaction of the components can be neglected.

Since the composition of the precipitates and therefore the ratio of the equilibrium concentrations also are independent of the radius for sufficiently large precipitates, the concentration of the components at the surface can be represented in the form  $c_{iR}^s = c_{i\infty}^s \exp \delta_R^s$ . Since  $(k_R^s)^{1/N^s} = (k_{\infty}^s)^{1/N^s} \exp(\alpha^s/R)$ , where  $\alpha^s = 2\sigma \bar{v}^s / kT$ ,

$$N^s = \sum_{i=1}^{n^s} \nu_i^s, \quad \bar{v}^s = \sum_{i=1}^{n^s} p_i^s \nu_i^s$$

is the average volume per atom of the compound,  $p_i^s = \nu_i^s / N^s$  are the reduced stoichiometric coefficients,  $\nu_i^s$  is the atomic volume of the  $i$ th component of the  $s$ th phase, and  $i = 1, 2, \dots, n^s$  is the number of components in the given phase, we obtain

$$\prod_{i=1}^{n^s} (c_{i\infty}^s)^{p_i^s} = (k_{\infty}^s)^{1/N^s}, \quad \delta_R^s = \frac{\alpha^s}{R}. \quad (3.6)$$

For the rate of growth of the precipitates of the  $s$ th phase, using the equations

$$\sum_{i=1}^{n^s} \frac{p_i^s J_{iR}^s}{D_i c_{i\infty}^s} = \frac{(D^s)^{-1} J_{iR}^s}{p_i^s} = \frac{n_0}{R} (\Delta^s - \gamma^s),$$

where

$$\Delta^s = \sum_{i=1}^{n^s} p_i^s \frac{\bar{c}_i - c_{i\infty}^s}{c_{i\infty}^s}, \quad \gamma^s = e^{\delta_R^s} - 1, \quad (D^s)^{-1} = \sum_{i=1}^{n^s} \frac{(p_i^s)^2}{D_i c_{i\infty}^s},$$

we obtain from (3.4)

$$v_r^s = \left( \frac{\partial r}{\partial t} \right)^s = \sum_{i=1}^{n^s} \nu_i^s J_{iR}^s = \frac{D^s \bar{v}^s n_0}{R} (\Delta^s - \gamma^s). \quad (3.7)$$

In the approximation which is well applicable for the overwhelming majority of precipitates, making the main contribution to the laws of conservation of matter, when the average size of the precipitates is already quite large,  $\bar{R}^s \gg \alpha^s$ , the rate of growth is given by the expression

$$\left( \frac{\partial R}{\partial t} \right)^s = \frac{D^s \bar{v}^s n_0}{R} (\Delta^s - \frac{\alpha^s}{R}). \quad (3.8)$$

Using (3.7) and integrating (3.3), taking into account (3.2), it is easy to transform the laws of conservation (3.3) into the form

$$\sum_{s_i} p_i^s = \sum_{s_i} \frac{p_i^s}{\bar{v}^s n_0} \frac{4\pi}{3} \int_0^\infty f^s R^3 dR = Q_i - \bar{c}_i, \quad (3.9)$$

where

$$Q_i = c_i^0 + \sum_{s_i} \frac{p_i^s}{\bar{v}^s n_0} \frac{4\pi}{3} \int_0^\infty f_0^s R^3 dR$$

is the total amount of matter of the  $i$ th component initially, and

$$J^s = \frac{4\pi}{3\bar{v}^s n_0} \int_0^\infty f^s R^3 dR$$

is the relative number of molecules of the  $s$ th phase in the precipitates per unit volume. The laws of conservation of matter written in the form (3.9) are a natural generalization of the law of conservation (2.4) for the one-component solution. Using  $\Delta^s$  and substituting  $\bar{c}_i$  from (3.9), we obtain

$$\Delta^s = \sum_{i=1}^{n^s} p_i^s \frac{Q_i - \sum_{s_i} p_i^s J^s - c_{i\infty}^s}{c_{i\infty}^s},$$

$$\Delta^s + \sum_{i=1}^{n^s} \frac{p_i^s}{c_{i\infty}^s} \sum_{s_i} p_i^s J^s = \sum_{s_i} \frac{p_i^s (Q_i - c_{i\infty}^s)}{c_{i\infty}^s}.$$

Introducing, as in the case of the one-component solutions, dimensionless variables and analyzing the conservation laws it can be shown<sup>33</sup> that in order for a solution to exist  $\Delta^s$  must approach zero as  $t^{-1/3}$ :

$$\Delta^s = \left( \frac{4}{9} \frac{D^s \bar{v}^s n_0 t}{(\alpha^s)^2} \right)^{-1/3}.$$

Since  $\Delta^s > 0$  and  $J^s > 0$ , the values of  $\bar{c}_i, c_{i\infty}^s$  and  $J^s$  are, generally speaking, functions of time, but for long times ( $t \rightarrow \infty$ ) they approach some constant limiting values, and in addition  $\Delta^s \rightarrow 0$ . This behavior is a consequence of the fact that the system approaches thermodynamic equilibrium. This implies that in the zeroth-order approximation (up to terms of order  $t^{-1/3}$ ) the system of equations (3.2)–(3.5) splits into  $s$  independent subsystems.

The situation noted above is an exceedingly important result of the theory, since the complicated system of nonlinear differential equations in the canonical variables can be written with asymptotic, with respect to time, accuracy as a collection of independent equations, determining the distribution functions and the parameters of decomposition of all precipitating phases.

The equations of continuity (3.2), together with the laws of variation of the sizes of the precipitates of the  $s$ th phase (3.8) and taking into account the fact that the volume of a precipitate of a given phase approaches constant values  $J^s \bar{v}^s n_0$ , determined by the laws of conservation of matter (3.9), constitute  $s$  complete, independent systems of equations, identical to the system obtained and studied in Refs. 23–25 for one-component solutions and which we examined in detail in Sec. 2. Therefore the method of solution described in Sec. 2 is completely applicable to each of the independent subsystems, which makes it possible to write out immediately the asymptotic solutions of this system for the  $s$ th phase, making the following substitutions in Eqs. (2.10) and (2.14)  $D \rightarrow D^s \bar{v}^s n_0$ ,  $Q_0 \rightarrow J^s \bar{v}^s n_0$ ,  $\alpha \rightarrow \alpha^s = 2\sigma^s \bar{v}^s / kT$ ,  $R_c^s = \alpha^s s / \Delta^s$ :

$$f^s(R, t) = \frac{\varphi(u^s, \tau^s)}{\bar{R}^s} = N^s(t) \frac{P^s(u^s)}{\bar{R}^s},$$

$$P^s(u^s) = \begin{cases} \frac{3^4 e (u^s)^2 \exp \left[ - \left( 1 - \frac{2}{3} u^s \right)^{-1} \right]}{2^{5/3} (u^s + 3)^{2/3} \left( \frac{3}{2} - u^s \right)^{11/3}}, & u^s = \frac{R}{\bar{R}^s} \leq \frac{3}{2}, \\ 0, & u^s \geq \frac{3}{2}, \end{cases} \quad (3.10)$$

$$N^s(t) = 0, 22 \frac{J^s \bar{v}^s n_0}{(\bar{R}^s)^3},$$

$$(\bar{R}^s)^3 = (R_c^s)^3 = \left( \frac{\alpha^s}{\Delta^s} \right)^3 = \frac{4}{9} D^s \bar{v}^s n_0 \alpha^s t + (R_c^s(0))^3.$$

This result is one of the basic results of the theory, which predicts the formation of a single, universal (in the appropriate relative variables  $u^s = R/\bar{R}^s$ ), asymptotic in time size distribution of the precipitates of arbitrary phases, precipitating in the process of diffusive decomposition of multicomponent solid solutions. Physically this is a result of the fact that the action of the interphase surface tension forms a universal, in appropriate variables, distribution function, which is identical for particles of all coexisting phases irrespective of their initial distributions. Thus, even in the most general case of a multicomponent dispersed system, there exists a unique, in appropriate variables, stable asymptotic state into

which the system transforms, completely “forgetting” the initial distribution.

The evolution of the average sizes of the precipitates of all phases also obeys a universal law—“the  $t^{1/3}$  law”—for decomposition controlled by volume diffusion of the components.

We note that although the form of the solution is universal, the solution itself depends on the system of  $(N + \sum_s n^s + k)$  limiting parameters  $\bar{c}_i, c_{i\infty}^s, J^s$ . To determine them it is necessary to use the limiting form of Eqs. (3.4), (3.6), and (3.9) as  $R \rightarrow \infty$ . As an additional system of equations (accurate up to terms of order  $t^{-1/3}$ ) it is necessary to use the condition of existence of the solution  $\Delta^s = 0$ , which at the later stage replaces the initial conditions on the distribution functions of the phases. Using (3.4), we obtain

$$\bar{c}_i - c_{i\infty}^s = \frac{p_i D^s}{D_i} \Delta^s. \quad (3.11)$$

From here it follows that asymptotically, when  $\Delta^s = 0$ ,

$$c_{i\infty}^{s_1} = c_{i\infty}^{s_2} = c_{i\infty}^{s_3} = \dots = c_{i\infty}^{s_n} = c_{i\infty} = \bar{c}_i. \quad (3.12)$$

This condition has a simple physical meaning: precipitates of only those chemical compounds for which the equilibrium concentrations of the common components are identical can exist. Therefore asymptotically the concentrations of the components on the surfaces of the precipitates are independent of the specific phase. The obtained asymptotic (in time) “kinetic” condition of coexistence of phases in the process of diffusive decomposition corresponds to the “thermodynamic” condition for coexistence of phases. Indeed, Eqs. (3.12) imply that the chemical potentials of the  $i$ th component are equal in the corresponding phases ( $\mu_i^s = \psi_i + kT \ln c_{i\infty}^s$ ). Introducing  $x_i = \bar{c}_i / Q_i$  and keeping in mind (3.11), we obtain from (3.6) and (3.9) a system of equations for determining the limiting parameters  $x_i$  and  $J^s$ :

$$\prod_i \left( x_i - \frac{p_i^s D^s \Delta^s}{D_i Q_i} \right)^{p_i^s} = \prod_i \left( 1 - \frac{1}{Q_i} \sum_{s_i} p_i^{s'} J^{s'} - \frac{p_i^s D^s \Delta^s}{D_i Q_i} \right)$$

$$= \frac{(k_\infty^s)^{1/N^s}}{\prod_i Q_i^{p_i^s}} = \tilde{k}_\infty^s.$$

These equations can be written with an accuracy up to terms of order  $(\Delta^s)^2$  in the form

$$\prod_i x_i^{p_i^s} = \prod_i \left( 1 - \frac{1}{Q_i} \sum_{s_i} p_i^{s'} J^{s'} \right)^{p_i^s} = \tilde{k}_\infty^s (1 - \Delta^s). \quad (3.13)$$

Solving the system (3.13), the values of the limiting parameters  $x_i$  and  $J^s$  can be obtained with an accuracy up to terms of order  $(\Delta^s)^2$ .

Physically it is clear that the collection of roots  $x_i$  and  $J^s$  of the system (3.13) must satisfy the inequalities  $0 \leq x_i \leq 1, J_i^s \geq 0$  ( $x_i > 1$  would indicate that the final amount of matter in the solution exceeds the given amount). It is easy to show that the collection of these roots is unique. Indeed, the left side of Eqs. (3.13) contains polynomials, which in the region of existence of the “physical” roots are monotonic functions, and they form in the space of the variables  $J^s$  in this region open hypersurfaces with a curvature

of the same sign, whose intersection determines the unique system of roots. If the concentration of some components exceeds their limit of solubility in the matrix, then the coexisting phases can be precipitates of pure components, while the corresponding rate constant of the chemical reaction equals the limiting solubility of these components  $\bar{c}_i$ , and in addition  $\nu_i = 1$ ,  $\nu_{i \neq i} = 0$ . Such a chemical reaction formally corresponds to the equation  $c_{i\infty} = c_i$ .

We note that all phases for which the solution is supersaturated must be included in (3.13). The solution of these equations asymptotically selects phases which asymptotically survive as a result of competitive growth during diffusive decomposition. If in (3.13) one of the roots  $J^s < 0$ , then we must set  $J^s = 0$ , and the corresponding law of mass action [i.e., the corresponding Equation (3.13)] need not be studied, since for this phase the solution becomes unsaturated in the process of decomposition. If, on the other hand, as a result of the solution it turns out that  $x_j > 1$ , then the solid solution is unsaturated for all chemical reactions in which the  $j$ th component occurs, and, as is evident from (3.13), all  $J^s$  must be set equal to zero and the corresponding laws of mass action need not be studied, while the system (3.13) must be solved anew with  $s_j$  fewer equations. If the system (3.13) decomposes into several subsystems, not containing common components, then for them the decomposition occurs independently.

It should be emphasized that the main results of the theory of diffusive decomposition of multicomponent solutions at the later stage regarding the formation of a universal distribution function and the fact that the full system of equations describing this process decomposes into  $s$  identical subsystems for determining the size distribution functions for each of the phases and  $s$  systems of algebraic equations for finding the limiting parameters, are independent of the mass-transfer mechanism and are determined solely by the conservation laws.

Only the form of the distribution function depends on the specific mechanism of atomic mass transfer, i.e., on the form of  $(dR/dt)^s$ . Brownian motion and coalescence of particles, the possibility of precipitation of the precipitate, and also the random appearance at small distances could alter somewhat the distribution function. These changes can be taken into account with the help of the "collision integral,"<sup>24</sup> which corresponds to the introduction of corrections to the volume fraction of the precipitates. Since the general system of equations decomposes into independent subsystems for each phase, all results regarding the effect of different factors (taking into account elastic stresses, anisotropy of the precipitates, fluctuations in the arrangement of the precipitates and their strong diffusion interaction) on the stability of the universal distribution function, obtained in the study of one-component solutions (see Sec. 2), are also valid for the case of multicomponent systems.

The system of equations (3.13) couples the external parameters, i.e., the parameters which are determined by the external conditions, with the internal, adjustable param-

eters. In the case under study the external parameters are  $Q_i$  and  $k_\infty^s$ , while the internal parameters are  $\bar{c}_i$  and  $J^s$ . In the general case the external conditions enable classification of the limiting parameters into external and internal. If, for example, the concentration of some component is maintained constant, then it becomes an external parameter, while the corresponding relative amount of the substance becomes an internal parameter, which must be determined from the system (3.13).

We note that if in the process of decomposition compounds with the matrix material are formed, then this is analogous to the precipitation of the pure component, and in this case we must set formally in the expressions obtained  $D_{\text{mat}} = \infty$  and the concentration of the matrix material must be regarded as given.

As an illustration we shall obtain in an explicit form some results for the simplest case of diffusive decomposition of precipitates with the stoichiometric composition of the type  $A_{\nu_1}^{(1)} A_{\nu_2}^{(2)}$ , dispersed in a matrix  $M$ .<sup>32,34</sup> This case often arises with the use of practically important materials, containing inclusions of the oxide, carbide, nitride, etc., type.

The system (3.13) in this case assumes the form

$$1 - x_i = \frac{p_i}{Q_i} J \quad (i = 1, 2), \quad p_i = \frac{\nu_i}{\nu_1 + \nu_2}, \quad (3.14)$$

$$x_1^{\nu_1} x_2^{\nu_2} = k_\infty^{1(\nu_1 + \nu_2)} (Q_1^{\nu_1} Q_2^{\nu_2})^{-1} = \tilde{k}_\infty. \quad (3.15)$$

We note that  $\tilde{k}_\infty < 1$  must always hold, since otherwise the solution would be unsaturated. The analytic solution of even such a simple system cannot be obtained in a general form. We shall find the solution for the physically most interesting limiting cases, often realized in practice. In a specific case the system (3.14) and (3.15) can be solved on a computer with the required accuracy.

1. We shall examine a weakly supersaturated solution ( $1 - x_i \ll 1$ ). Expanding the system (3.14) and (3.15) with respect to the small parameter  $(p_i/Q_i)J$ , we find

$$J = \frac{1 - \tilde{k}_\infty}{\frac{p_1^2}{Q_1} + \frac{p_2^2}{Q_2}}, \quad x_i = 1 - \frac{1 - \tilde{k}_\infty}{\frac{p_1^2}{Q_1} + \frac{p_2^2}{Q_2}}.$$

Taking into account the fact that  $c_{i\infty} \approx Q_i$  and using (3.10), we obtain

$$n(t) = \frac{0.22(1 - \tilde{k}_\infty)\nu n_0}{\left(\frac{p_1^2}{Q_1} + \frac{p_2^2}{Q_2}\right) \bar{R}^3}, \quad \bar{R}^3 = \frac{8}{9} \frac{\sigma \bar{v}^2 n_0}{kT \left(\frac{p_1^2}{D_1 Q_1} + \frac{p_2^2}{D_2 Q_2}\right)} t. \quad (3.16)$$

2. If the initial concentrations of the components correspond to the stoichiometric composition ( $Q_1/p_1 = Q_2/p_2$ ), solving (3.14) and (3.15), we obtain

$$n(t) = \frac{0.22\nu n_0 \left[ \frac{Q_2}{p_2} - \frac{1}{p_2} \left( \frac{p_2}{p_1} \right)^{p_1} k_\infty^{1/(\nu_1 + \nu_2)} \right]}{\bar{R}^3}, \quad (3.17)$$

$$\bar{R}^3 = \frac{8}{9} \frac{\sigma \bar{v}^2 n_0 t}{kT} \left[ p_2 \left( \frac{p_1}{D_1} + \frac{p_2}{D_2} \right) \right]^{-1} \left( \frac{p_2}{p_1} \right)^{p_1} k_\infty^{1/(\nu_1 + \nu_2)}.$$

3. When the initial concentrations of one of the components is much greater than that of a second one, for example,  $x_i \ll (Q_2/Q_1)(p_1/p_2) - 1$ , we have

$$n(t) = \frac{0.22\nu n_0 \frac{Q_1}{p_1}}{\bar{R}^3}, \quad \bar{R}^3 = \frac{8}{9} \frac{\sigma \bar{v}^2 n_0 t}{kT \left\{ \frac{p_1^2}{D_1 Q_1} \left[ \frac{\tilde{k}_\infty}{\left(1 - \frac{Q_1 p_2}{Q_2 p_1}\right)^{p_1}} \right]^{1/p_1} + \frac{p_2^2}{D_2 Q_2} \left(1 - \frac{Q_1 p_2}{Q_2 p_1}\right) \right\}}. \quad (3.18)$$

If the coefficient of mass transfer of one of the components is much higher than that of a second component, then, passing to the limit in (3.16)–(3.18) ( $D_1 \rightarrow \infty$ ), it is easy to obtain the results of Ref. 72. Thus an important feature of the diffusion process in multicomponent solid solutions, unlike one-component solutions, is the dependence (3.13) obtained for the parameters of decomposition on the ratios between the initial concentrations of the dissolved substances and rate constants of the chemical reactions at the boundaries of the precipitates. Physically this is determined by the fact that the concentrations of the components on the surface of the precipitates are rigidly coupled by the laws of mass action. In the case of multicomponent systems additional parameters  $Q_i$  appear, which are determined by the history of the material and make it possible to affect the rate of decomposition by means of optimal selection of the ratios of the relative quantities of the dissolved substances.

The results regarding the diffusive decomposition of one-component precipitates under conditions of simultaneous action of several mass-transfer mechanisms are extended in Ref. 65 to the case of binary precipitates of stoichiometric composition. The expressions obtained formally have the same form as in the case of the growth of one-component precipitates. However, an important difference is that the effective coefficients  $D_{\text{eff}}$  and  $(K_p)_{\text{eff}}$  appearing in the final formulas contain the concentrations  $c_{i\infty}$ , which are no longer given, but are determined self-consistently by the asymptotic form of the laws of conservation of matter and the law of mass action. In addition, it is important to emphasize that these coefficients depend on the external parameters  $Q_i$  and  $k_\infty^s$ . It is this dependence that permits, by varying the external parameters, to affect purposefully the characteristics of the diffusive decomposition in the transitional asymptotic region in order to improve the thermal and phase stability of the materials created.

We point out especially that the theory constructed also solves the inverse problem of determining the parameters of multicomponent systems in experiments on diffusive decomposition. This makes it possible to formulate a fundamentally new approach to the experimental measurement of important, but difficult to measure parameters of multicomponent systems—the rate constants of chemical reactions occurring in the solid  $k_\infty^s$ , the specific surface energies of the phases  $\sigma^s$ , and the partial coefficients of diffusion of the components of the precipitates  $D_i$ . To determine them the evolution in time of the experimental size distribution functions of the phases (histograms) must be compared with the theoretical function, depending on these parameters. In order to obtain agreement with the experimental size distribution function of the precipitates the constant parameters in the theoretical size distribution function must be determined with the required accuracy on a computer.<sup>73–75</sup>

It is also possible to determine the parameters  $k_\infty^s$ ,  $\sigma^s$  and  $D_i$  by measuring the rate constants of the decomposition. In the case of one-component solutions the quantities  $D$ ,  $\sigma$ , and  $c_\infty$  appear in the expression for the rate constant in the form of a linear combination, so that aside from data on the rate of decomposition independent experiments on the measurement of supersaturation must be carried out, as is done, for example, by Ardell.<sup>76</sup> In the decomposition of multicomponent solutions the rate constant, even in the simplest cases, is a nonlinear function of these parameters and the

relative amounts of the substances  $Q_i$ , and this makes it possible, by measuring the rate constant of decomposition for different values of  $Q_i$  and solving (3.13), to determine  $D_i$ ,  $\sigma^s$  and  $k_\infty^s$ . Thus in the case of a slightly supersaturated solution under conditions of decomposition  $A_{v_1}^{(1)} A_{v_2}^{(2)}$  [Eqs. (3.16)] the unknown parameters are  $D_1$ ,  $D_2$ ,  $\sigma$ , and  $k_\infty$  and, therefore, in principle four values of the rate constants of decomposition for different values of  $Q_1$  and  $Q_2$  (satisfying, of course, the condition of a slightly supersaturated solution) are sufficient to obtain from (3.16) a system of equations from which the unknown parameters can be determined numerically using a computer.

### 3.2. Regions of coexistence of phases

To determine the regions of coexistence of the phases it is necessary to find the boundaries of the regions of coexistence of all possible  $k$  phases in the space of the relative quantities of the substances  $Q_i$  in an  $N$ -component supersaturated solid solution. These boundaries are hypersurfaces with dimension  $(N - 1)$ . In the general case the equations for these surfaces are obtained after the  $J^s$  are found from (3.13) and equated to zero:

$$J^s(Q_1, Q_2, \dots, Q_N) = 0. \quad (3.19)$$

This hypersurface divides the  $N$ -dimensional space of  $Q_i$  into two regions. In the regions where  $J^s < 0$  (below the surface) the solid solution for the  $s$ th phase is unsaturated, and correspondingly this phase is not present. In the region  $J^s > 0$  (above the surface) the solid solution for the  $s$ th phase is supersaturated, and it precipitates in the form of deposits. The physical region of values corresponds to  $Q_i > 0$  and  $\sum_{i=1}^N Q_i < 1$ , which will be divided by the hypersurfaces of

all possible phases into cells in  $Q_i$  space. For values of  $Q_i$  lying in some cell, evidently only those phases coexist for which  $J^s(Q_1, Q_2, \dots, Q_N) > 0$ . Since the algebraic equations for determining  $J^s$  are nonlinear, and amongst their solutions it is necessary to select at each point of  $\{Q_i\}$  space those which satisfy the above-indicated physical conditions, the hypersurface  $J^s = 0$  in the general case will be piecewise continuous. If it is necessary to determine the hypersurface which separates the regions of coexistence and absence of phases containing the  $i$ th component,  $x_i = x_i(Q_1, \dots, Q_N)$  must be found from (3.13) and equated to unity, which corresponds to a saturated solution for the  $i$ th component.

As an example we shall present the solution of Eqs. (3.13) for a two-phase ( $s = 1, 2$ ) three-component ( $i = 1, 2, 3$ ) system in which the component  $i = 2$  appears in both phases. Following the procedure indicated above we obtain the equation for the surface in the three-dimensional space  $\{Q_1, Q_2, Q_3\}$  above which the phase I exists and below which the phase I is absent ( $J^I = 0$ ):

$$Q_2^I = \frac{k_1^{1/v_2}}{Q_3^{v_1/v_2}} + \frac{v_4}{v_3} Q_3 - \frac{v_4}{v_3} \frac{k_2^{1/v_3}}{k_2^{v_1/v_1 v_3}} Q_3^{v_1 v_4 / v_2 v_3}, \quad (3.20)$$

and the equation of the surface above which the phase II exists and below which the phase II is absent ( $J^{II} = 0$ ):

$$Q_2^{II} = \frac{k_2^{1/v_1}}{Q_3^{v_2/v_1}} + \frac{v_2}{v_1} Q_1 - \frac{v_2}{v_1} \frac{k_1^{1/v_1}}{k_2^{v_2/v_1 v_4}} Q_3^{v_2 v_3 / v_1 v_4}. \quad (3.21)$$



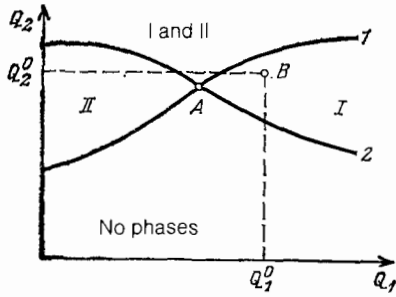


FIG. 7. Phase diagram of decomposition.

These surfaces intersect along the line  $Q_2^I = Q_2^{II}$ , which, as it is easy to see, is the same line on which the solution is saturated with respect to all components:  $\bar{k}_1 = \bar{k}_2 = 1$  or

$$\frac{k_1^{1/\nu_2}}{Q_1^{\nu_1/\nu_2}} = \frac{k_2^{1/\nu_1}}{Q_2^{\nu_2/\nu_1}} \quad (3.22)$$

The intersection of the surfaces (3.20) and (3.21) forms four regions. Both phases I and II exist above these surfaces. Both phases are absent below these surfaces—the solution is unsaturated. In the region which lies between the surfaces (3.20) and (3.21) [(3.20) is the lower one], only the phase I exists, and if (3.21) is the lower one only the phase II exists.

For convenience such a phase diagram of the decomposition is illustrated schematically in Fig. 7 in the projection on the plane  $Q_1 Q_2$  ( $Q_3 = \text{const}$ ). Here the lines 1 and 2 correspond to Eqs. (3.20) and (3.21), and the point A corresponds to Eq. (3.22). The position of the system for fixed external conditions is determined by the point B with the initial concentrations  $Q_1^0$  and  $Q_2^0$ .

A change in the phase relationships in the system under study or a transition of the system from one phase region into another could be associated either with a change in the position of the system in the space of the initial concentrations (Fig. 8a) or with a change in the boundaries of the regions of

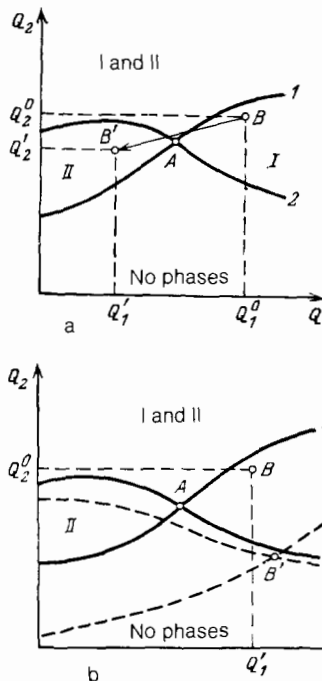


FIG. 8. Diagram of the changes in the phase relationships. a) Change in the initial conditions. b) Change in the position of the boundaries.

existence of the phases (Fig. 8b). Figure 8a shows how the system can be transferred from the state B (phase I) into the state B' (phase II) (I→II) by changing the initial concentrations ( $Q_1^0, Q_2^0 \rightarrow Q_1^1, Q_2^1$ ). By changing the initial conditions (the temperature, pressure, etc.), i.e., by changing  $k_\infty^s$  only [leaving unchanged the position of the point B (Fig. 8b)], it is possible to make a change in the boundaries of the regions of coexistence of the phases such that the system will transform into the other region (I→I and II).

We shall study also the solution which is slightly supersaturated with respect to all components ( $Q_i^{-1} \sum_{s_i} \nu_i^s J^s \ll 1$

and all  $k_\infty^s \approx 1$ ). In this case the system (3.13) can be linearized and solved in a concrete case. In other words, the hypersurfaces are determined in the space near their common line of intersection  $\bar{k}_\infty^s = \bar{k}_\infty^2 \dots \bar{k}_\infty^s = 1$ . For example, for the two-phase three-component system, setting, as done before, first  $J^I$  and then  $J^{II}$  equal to zero, we obtain the equations for the boundary surfaces of existence of the phases. We note that for  $J^s = 0$  the solution must be sought near  $k_\infty^s = 1$ , i.e.,  $Q_2^I = \frac{k_1^{1/\nu_2}}{Q_2^{\nu_1/\nu_2}} (1 + \epsilon)$ , while for  $J^{II} = 0$   $Q_2^{II}$

$$= \frac{k_2^{1/\nu_1}}{Q_3^{\nu_2/\nu_1}} (1 + \eta), \text{ where } \epsilon \ll 1, \eta \ll 1. \text{ As a result we obtain}$$

equations for the surfaces near the line  $\bar{k}_\infty^s = \bar{k}_\infty^s = 1$  which are identical to (3.20) and (3.21) in this region of  $Q_i$ . If the kinetic obstacles in the formation of any phase are sufficiently large, then in the real time scale it may not be realized, though it is asymptotically stable. In this case the transformation of the phase diagram with the passage of time must be taken into account. Solving the system (3.13), we obtain kinetic phase diagrams of decomposition which permit determining the stability of the phases taking into account their kinetic characteristics.

Thus for a solution which is slightly supersaturated with respect to all components

$$J^s = \frac{1 - \bar{k}_\infty^s}{\sum_i (p_i^s)^2 / Q_i} - \frac{D^s \sum_i (p_i^s)^2 / D_i Q_i}{\sum_i (p_i^s)^2 / Q_i} \Delta^s(t),$$

$$c_{i\infty}^s = Q_i - \frac{p_i^s (1 - \bar{k}_\infty^s)}{\sum_i (p_i^s)^2 / Q_i} - p_i^s \left[ \frac{1}{\sum_i (p_i^s)^2 / Q_i} + \frac{1}{D_i \sum_i (p_i^s)^2 / Q_i} \right] \Delta^s(t). \quad (3.23)$$

In this case the  $\bar{c}_i$  are determined from (3.11), while  $\Delta^s(t) = \text{const} \cdot t^{-1/3}$ . The expressions (3.23) determine the dynamics of the variation of the relative quantities in the precipitates  $J^s$  and the equilibrium concentrations  $c_{i\infty}^s$  in the asymptotic region. As is evident from (3.23), these quantities depend on time as  $t^{-1/3}$  and over sufficiently long times approach constant values.

It is obvious that the boundaries of the regions of existence of the phases are smeared owing to the nonuniform distribution of matter in the volume and fluctuations of the temperature and concentrations of the components. The regions of coexistence of the phases, as is evident from (3.20) and (3.21), depend on the relative quantities of the dissolved

substances  $Q_i$  and the rate constants of the chemical reactions  $k_\infty^s$ .

Thus in the process of diffusive decomposition of multi-component solid solutions surface tension forms a universal size distribution of the precipitates of the phases, while the conditions of quasithermodynamic equilibrium determine the phases which precipitate in an  $N$ -component solution. The types of phases can be altered by varying the ratios between the  $Q_i$  or the temperature, since  $k_\infty^s$  vary differently with the temperature.

The law of mass action in Eq. (3.5) can be easily replaced by the general equation of phase equilibrium at the boundaries of the precipitates. In this case

$$\frac{\prod_i (c_{iR}^s)^{\nu_i^s}}{k_R^s} = 1 \rightarrow F(c_{iR}^s) = 1.$$

As follows from the theory, this does not change the results regarding the decoupling of the system of Equations (3.2)–(3.5) into  $s$  independent subsystems, formation of the universal distribution function, and the law of evolution of critical sizes. Only the phase diagram of decomposition, i.e., the regions of coexistence of the phases and the amount of matter in the phases, determined by the algebraic system (3.13) and depending on the specific form of the equation for phase equilibrium  $F(c_{iR}^s) = 1$ , changes.

We note that all preceding results are valid if  $k < N$ , i.e., the number of coexisting phases does not exceed the number of components. If the external parameters  $p$  and  $T$  are taken into account, then the number of coexisting phases will be determined by Gibbs' rule  $k \leq N + 2$ .

To find all coexisting phases for  $k > N$  the system (3.13) must be divided into groups containing  $N$  phases. The total number of possible groups equals  $c_k^N$ . Then each of the  $c_k^N$  groups of equations must be solved, and only one of them will have roots (for fixed  $p$  and  $T$ ) corresponding to the physical conditions of coexistence of phases, discussed above ( $0 < J^s, 0 < x_i < 1$ ). The solution of this system selects those of the  $N$  phases which survive in the process of diffusive decomposition.

### 3.3. Formation of precipitates with nonstoichiometric composition

It has now been established reliably<sup>77–79</sup> that many compounds used as hardening precipitates are phases with variable composition, and the deviations from stoichiometry strongly affect many properties of real materials ( $\text{TiC}_{0.8\dots 1.2}$ ,  $\text{ZrO}_{1.75\dots 2.12}$ ,  $\text{TiV}_{2.0\dots 2.195} \times \text{H}_{6.0\dots 5.89}$ , and others).

Physically the nonstoichiometry of a compound (phase) is determined by components the number of whose positions can vary within some limits. The positions of stoichiometric components do not change, and their numbers in the crystal or molecule of the chemical compound and the ratios between them are constant. It is physically obvious that the values of the stoichiometric coefficients  $\nu_j$ , though they can vary within the region of homogeneity, under equilibrium conditions when minimizing the thermodynamic potential of the system are fixed asymptotically with the passage of time by the initial conditions—the ratio of the initial quantities and rate constants of the chemical reactions. This means that in this case precipitates with the stoichiometric composition also grow, but the corresponding coefficients  $\nu_j$

are additional internal factors (relative to the stoichiometric compounds) which must be determined. The nonstoichiometric compounds can be regarded in a certain sense as a solid solution with a limited solubility. As shown in Refs. 33, 34, 80, and 81, all equations and their solutions, determining the size distribution function, obtained above, can be employed in this case also. A significant difference is the appearance of additional equations for determining the quantities  $\nu_j$  in the system of algebraic equations relating the internal parameters on which the distributions depend  $c_\infty^s, p_e^s$  and  $J^s$  with the external parameters  $k_\infty^s$  and  $Q_e$ .

Thus, in the diffusive decomposition of precipitates with a nonstoichiometric composition, precipitates with a variable (not completely determined) composition or a composition determined by the limits of the region of nonstoichiometry, depending on the external conditions, can grow.

## 4. COMPARISON WITH EXPERIMENT

We shall now examine the questions which to some extent concern the experimental verification of the theory of diffusive decomposition. After the publication of Ref. 23, containing the basic assumptions of the theory in 1958, the number of studies concerning diffusive decomposition and kinetics of growth of particles in different materials increased markedly in the literature. An important class of materials for which the different aspects of the theory have been verified experimentally are steels and alloys of iron with precipitates of carbides, nitrides, and other phases,<sup>36–42,71</sup> age-hardened alloys of nickel, aluminum, etc.,<sup>37,41</sup> dispersion-hardened composite materials,<sup>82,83</sup> internally oxidized alloys,<sup>84</sup> glasses and ionic crystals,<sup>59,71</sup> etc. We will make no attempt to give an exhaustive review of the enormous number of experimental studies concerning diffusive decomposition, and we shall examine only those studies which, in our opinion, are most informative for comparing theory with experiment.

In a series of studies,<sup>37,85–87</sup> Ardell carried out careful studies with a representative statistical sample of the growth of  $\gamma'$  precipitates ( $\text{Ni}_3\text{X}$ , where X denotes Al, Ti, or Si) in nickel alloys, forming the basis for many refractory materials for high-temperature applications.

Figure 9 shows histograms of the  $\gamma'$  precipitates in the Ni–Al system.<sup>85</sup> For comparison the universal distribution function, corresponding to mass transfer by means of volume diffusion, as predicted by the theory, is also shown. It is evident that the agreement between the theory and experiment is good. In most cases the histograms have the form predicted by the theory: quite slow growth in the region of small sizes, the existence of a stopping point at  $3/2$ , and a sharp drop in the region of the stopping point. The data on the kinetics of growth of  $\gamma'$  precipitates<sup>86</sup> indicate convincingly that the  $t^{1/3}$  law, which is characteristic for mass transfer by means of volume diffusion (Fig. 10), is obeyed. The value of the experiments of Refs. 86 and 87 is increased by the fact that in these experiments the equilibrium concentration of the dissolved substance in the solid solution in nickel was measured independently with the help of magnetic measurements, which made it possible to study the kinetics of variations of supersaturation in the system studied. As the theory predicts, supersaturation decreases in proportion to

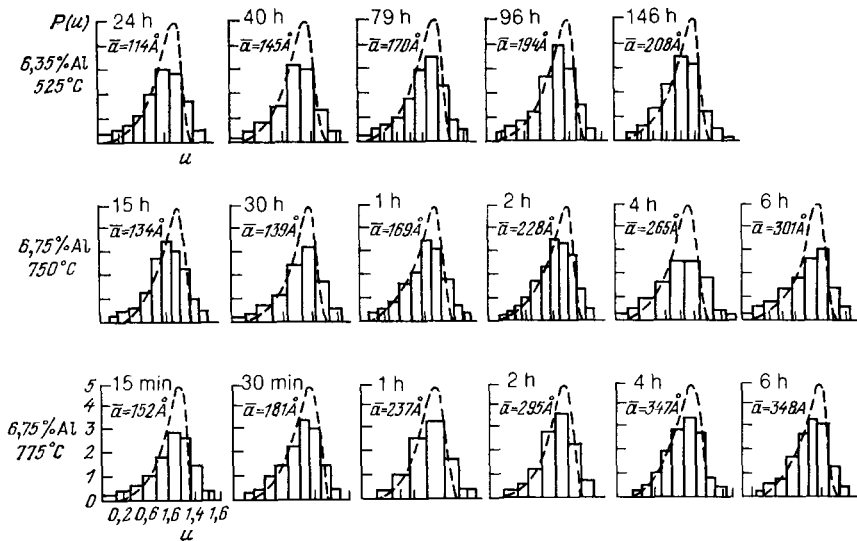


FIG. 9. Comparison of histograms with the distribution function  $P(u)$  (2.13).<sup>85</sup>  $\gamma'$  precipitates in the Ni-Al system.

$t^{-1/3}$ . Figure 11 shows a histogram of  $\text{Ni}_3\text{Al}$  precipitates in the alloy Ni—22 at. % Co—13 at. % Al.<sup>68</sup> The figure also shows the approximation of this histogram by the theoretical distribution function calculated on a computer by Davies *et al.*<sup>68</sup> using an iteration scheme. It is evident that the agreement between the theory and experiment is very good.

The evolution of the formation of the universal distribution function (2.13) from an arbitrary initial distribution is demonstrated clearly in Ref. 88 on the example of the growth of cementite  $\text{Fe}_3\text{C}$  precipitates in Fe—0.79 C alloys, spheroidized at 704 °C (Fig. 12). The histograms, which are quite smeared at the early stages of annealing, approach with the passage of time closer to the theoretical function (2.14), while the value of the stopping point approaches  $u_0 = 3/2$ .

The growth of precipitates in steels containing 0.25% vanadium was studied in detail in Ref. 89, where the kinetics of growth vanadium carbide, nitride, and carbonitride precipitates during annealing of the steel at a temperature of 790 °C was studied. At the starting stages of annealing the kinetics is described by the equation  $\bar{R}^2 \sim t$ , which corresponds, according to the theory, to control of the reaction on the interphase surface. At later stages of growth mass transfer along dislocations, giving rise to kinetics of growth  $\bar{R}^5 \sim t$

(see above), becomes important. Structural studies indeed reveal in this case a high density of dislocations, forming as a result of volume changes associated with the austenite-ferite transformation. For long annealing times the overwhelming majority of the precipitates are located on dislocations. Increasing the dislocation density by means of 5% cold deformation of steel increases the rate of growth of the precipitates  $V(\text{CN})$  by a factor of 30, while the  $t^{1/5}$  kinetics is observed at earlier annealing times, which confirms the validity of the assumption that growth is controlled by mass transfer along dislocations. It is interesting to note that the precipitates with the more complicated composition  $V(\text{CN})$  grow more slowly than VC, which also agrees qualitatively with the theory (Sec. 3).

It was shown in a study of the kinetics of growth of  $\text{ThO}_2$  particles in TD-nickel<sup>90</sup> with the use of a correlation analysis of the experimental data that the cubic growth law ( $t^{1/3}$  law) is obeyed with an exceedingly high confidence limits  $P = 0.995$ .

It is proved in Ref. 73, employing the methods of the mathematical theory for checking statistical hypotheses

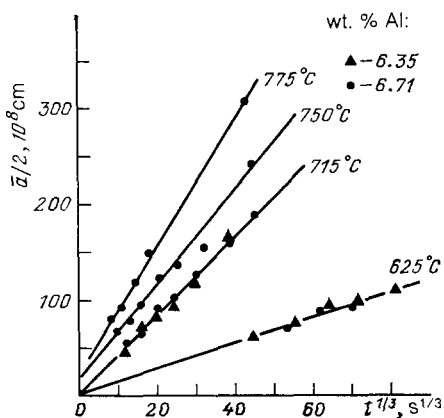


FIG. 10. Kinetics of growth of  $\gamma'$  precipitates in the Ni-Al system.<sup>86</sup>

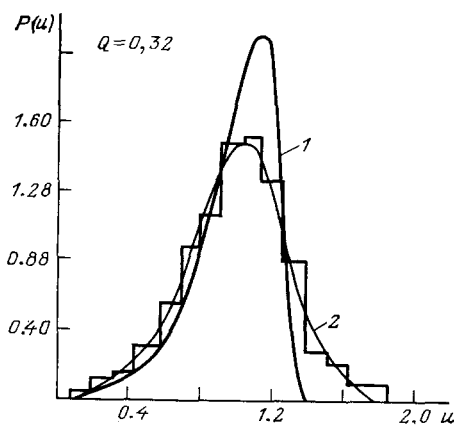


FIG. 11. Comparison of the distribution functions (1), calculated according to (2.13), and taking into account the collision integral  $J_{\text{col}}$  (2) with the histogram for  $\text{Ni}_3\text{Al}$  precipitates in the alloy (Ni—22 at. % Co—13 at. % Al).<sup>68</sup>

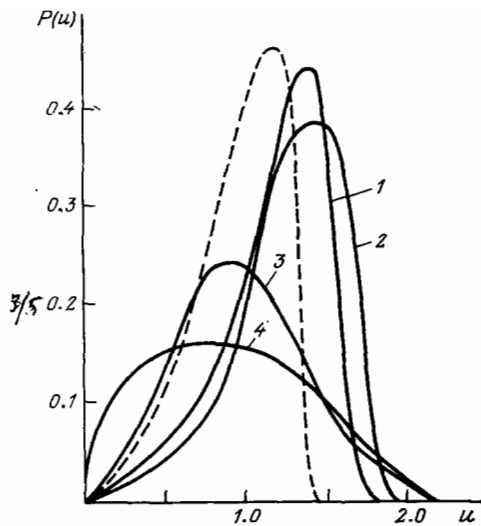


FIG. 12. Histograms of cementite particles for Fe-0.79 C steel, spheroidized at 704 °C. The numbers on the curves correspond to different annealing times with  $t_1 > t_2 > t_3 > t_4$ . For comparison the broken curve shows the universal function (2.13).

(Pearson's  $\chi^2$  test, Kolmogorov's criterion), that in a dispersed Mo-ZrO<sub>2</sub> system the size distribution function of the ZrO<sub>2</sub> particles is described asymptotically with the passage of time with a confidence limit of  $P = 0.95$  by the universal function (2.13), while a least-squares analysis of the points for the same mass transfer mechanism shows that the growth kinetics obeys with high accuracy the  $t^{1/3}$  law. To illustrate diffusive decomposition in nonmetallic systems we present the histograms of silver particles growing in KCl crystals at 700 °C<sup>91</sup> (Fig. 13). Good agreement between experiment and theory is observed when the histograms are compared with the theoretical function corresponding to mass transfer by means of diffusion along dislocation lines (see Table I). The possibility of growth of metallic precipitates in ionic crystals by means of migration of F centers along dislocation lines was confirmed by direct observations.<sup>92</sup>

Finally, we call attention to the results of numerical experiments, carried out by computer simulation methods, on the kinetics of segregation of phases in binary alloys, quenched from high temperatures. Analysis of the results of such experiments,<sup>67</sup> carried out based on the ideas about diffusive decomposition<sup>23-25</sup> presented in Sec. 2, shows that because of the difference in the solubilities of particles with different radii at the late stage, when the total number of particles begins to decrease, growth occurs mainly by means of "diffusive" interaction between large and small clusters ("consumption" of small particles by large particles). The distribution of large clusters at the late stage is described very well by the universal distribution (2.13) predicted by the theory, while the kinetics is described very well by the  $t^{1/3}$  law; in addition, there is not only qualitative agreement but also very good quantitative agreement with the theory.

## 5. CONCLUSIONS

The analysis in this review shows that quite a complete and systematic theory of the late stage of diffusive decomposition—a phenomenon which plays a determining role in the

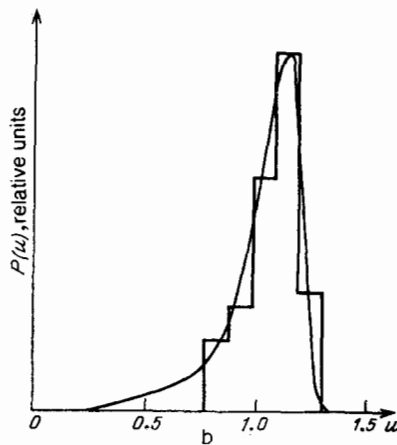
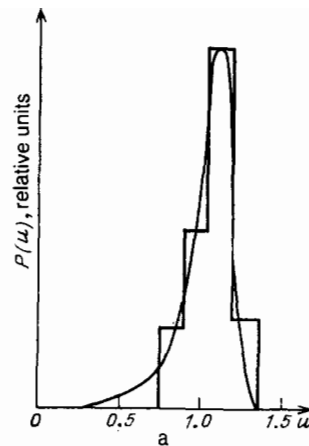


FIG. 13. Histograms of silver particles growing in a KCl crystal.<sup>91</sup> For comparison, the universal distribution function for mass transfer by means of grain-boundary diffusion (see Table I) is shown for different decomposition times: a) for  $2\bar{R} = 330 \text{ \AA}$ ; b) for  $2\bar{R} = 460 \text{ \AA}$ .

formation of modern materials with prescribed properties—has now been constructed.

The problem of diffusive decomposition of supersaturated multicomponent solid solutions has been formulated rigorously. A method for solving the fundamental systems of equations describing the decomposition process has been developed. The equations obtained and the proposed method for solving them enable the formulation and solution of many problems in the kinetics of diffusion processes in solids. This method is quite general and applicable for the mathematical description of a wide class of physical phenomena (recrystallization, swelling, sintering, degradation of the properties of semiconductors, etc.).

It was found that the nonlinear kinetics gives rise to very unique behavior of dispersed systems at the late stage of decomposition—any system asymptotically "forgets" its initial state with the passage of time and transforms into a unique (in the appropriate variables) stable asymptotic state, depending only on the mass-transfer mechanism operating in the system. Physically this is attributable to the fact that the interphase surface tension forms a universal (in the appropriate variables) size distribution function independent of the initial distributions, which is the same for precipitates of all existing phases. The conservation laws and the

laws of mass action in this case determine the phases which survive asymptotically in the process of competitive growth. The boundaries of the regions of coexistence of the precipitates of these phases of both stoichiometric and nonstoichiometric composition were determined, which makes it possible to construct decomposition phase diagrams. The evolution of the average size of macrodefects of a dispersed system at the late stage of decomposition, depending on the mass-transfer mechanism, is described by the law  $\bar{R} \sim t^{1/3}$ , and in addition the kinetics controlled by mass transfer by means of volume diffusion—the  $t^{1/3}$  law—is asymptotically stable.

Numerous experimental investigations on the most diverse materials have indicated convincingly that the theory of the late stage of diffusive decomposition agrees well with experiment both qualitatively and quantitatively. In the overwhelming majority of cases the kinetics of growth follows the theoretically predicted  $t^{1/3}$  law, when growth is controlled by volume diffusion of the components of the precipitates, while the distribution function has the universal form given by the expression (2.13). The experimentally observed broadening of the histograms, compared with the theoretical asymptotic distribution function, can be described correctly by the theory when the "collisions" and the transformation of the initial distribution function into the universal function are taken into account.

By studying the kinetics of the decomposition process it is possible to determine experimentally the important, but difficult to measure, physical characteristics of multicomponent systems—partial coefficients of diffusion of the components of the precipitates and the coefficients of specific interphase energy. The theory enables the development of a fundamentally new approach to the determination of the rate constants of chemical reactions which can occur in the solid. The acquisition of this unique information is of great scientific and applied value for optimization of the properties of real materials.

The theory constructed forms the scientific foundation for quantitative prediction of the evolution of complicated multicomponent systems and thereby their structurally sensitive properties, associated with the size distribution of macrodefects, in the process of diffusive decomposition. The stability criteria, formulated based on the theory, for dispersed systems<sup>41,42,82,83</sup> make it possible to develop practical recommendations, used in the development of new modern multicomponent materials with improved characteristics and high thermal dimensional and phase stability. As follows from the theory, minimal growth of precipitates requires low values of the specific interphase energy  $\sigma$ , solubility  $c_\infty$ , coefficients of diffusion  $D_i$ , etc. These criteria are indeed reflected in different refractory materials.

The exceedingly low values of  $\sigma \approx 0.2 \text{ J/m}^2$  in alloys of the nimonic type—nickel alloys hardened by  $\gamma'$  phase precipitates—suggest that these materials are highly stable at high temperatures. The validity of this idea has been adequately confirmed by successful application of these materials in gas turbines under conditions of high-temperature operation.<sup>42,93</sup> Based on this the highly heat resistant alloy Ford 406, for which very high creep resistance is characteristic,<sup>42,94</sup> has now been developed.

The principle of low solubility of the dispersed phase

was first realized in the production of tungsten (used in incandescent filaments) and TD-nickel hardened with thorium oxide.<sup>95</sup> A refractory alloy based on the Fe–Al system<sup>96</sup> and other refractory materials,<sup>42,97</sup> in which the dispersed phase has an extremely low solubility, were developed according to an analogous principle.

The introduction of active carbide-forming elements, which make it possible to form carbide precipitates with low solubility and low diffusion mobility, is a necessary condition in the technology of fabrication of high-quality steels.<sup>40,42</sup> The same principles are successfully used in the development of modern light alloys with high mechanical characteristics.<sup>41,82</sup>

There are still a number of questions in the problem of diffusive decomposition which must be resolved. The theory does not adequately address the interaction of macrodefects in the decomposition process. Experimental work,<sup>16</sup> in which it is shown that macrodefects alone can initiate growth of other defects, for example, in the precipitate-pore system, has appeared in recent years. Much can be expected from numerical experiments using computers regarding the problem of decomposition—beginning with simulation, construction of phase diagrams of the decomposition of multicomponent systems, and determination of the parameters of dispersed systems ( $D_i, k_\infty^s, \sigma^s$ ), and ending with the correct treatment of experimental data using statistical methods. One of the important problems of the theory on this level is the simulation of stepped heat treatment, which forms the foundation of the technology of many modern materials.

The role of elastic stresses in the process of diffusive decomposition can, in the general case, be more complicated. The effect of these stresses on the equilibrium form of the precipitates can be significant, especially in the presence of marked anisotropy (it is well known, for example, that cubic, plate-like, and needle-shaped precipitates in different systems can transform as a result of structural transformation during the decomposition process into spherical and diskotic precipitates with an orientation which differs from the initial orientation, etc.). This should significantly change the form of the diffusion fields and substantially affect the characteristics of decomposition. An exceedingly high stability of the microstructure of Fe–Al alloys with very finely dispersed, coherent, ordered deposits of  $\text{Fe}_3\text{Al}$ , even after prolonged annealing, in particular, the alloy Fe–15 at. % Al, in which the precipitates were less than  $100 \text{ \AA}$  in size and their density was of the order of  $10^{23} \text{ m}^{-3}$ , was discovered in Refs.98 and 99. A number of models based on taking into account stresses which appear have been proposed in order to explain such high stability. It should be acknowledged, however, that this interesting effect has not yet been satisfactorily explained theoretically.

The morphology, mechanisms, and kinetics of growth of precipitates, especially at the second, slow stage,<sup>100</sup> must be studied further both theoretically and experimentally. This is especially important because this effect is quite general; it is observed in other systems<sup>100</sup> and can be very useful for increasing the thermal stability of dispersion-hardened alloys in high-temperature applications. The theory addresses wholly inadequately the effect of different external actions (conditions of quenching, preliminary deformation, high

pressures, ultrasound, stepped heat treatment), which can significantly alter the kinetics of growth of the precipitates.<sup>101</sup>

A detailed explanation of the characteristic features of diffusive decomposition in ionic crystals and strongly disordered materials is also a problem to be addressed by the theory. Finally, a fundamental problem of the theory is to explain in a unified manner all stages and forms of diffusion decomposition. Most of these problems can be solved based on the ideas which have already been developed.

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