Kinetics of the spinodal decomposition of glasses

É. P. Fel'dman and L. I. Stefanovich

Donetsk Physicotechnical Institute, Academy of Sciences of the Ukrainian SSR

(Submitted 4 April 1990)
Zh. Eksp. Teor. Fiz. **98**, 1695–1704 (November 1990)

The spinodal decomposition of glasses accompanied by the formation of an intermediate decomposition structure is analyzed. A statistical approach is taken, and a nonlinear diffusion equation is used, to study all the stages of the spinodal kinetics. The analysis encompasses all possible relations among the mean composition, the size of the initial fluctuations, and the difference (at a fixed temperature) between the "upper" and "lower" spinodal concentrations. Near the critical point the spatial scale of the intermediate decomposition structure is determined by the relation between the contributions from nonlinear and "gradient" effects.

1. INTRODUCTION

During the rapid cooling of several metallic and inorganic melts, a solidified material (a glass) can be produced in a metastable or even labile state. In general, the material is unstable with respect to both fluctuations of the density (or of the free volume) and variations in composition (in two-component and multicomponent systems). To simplify the description we assume that the system is a two-component glass *AB* with a limited solubility of one component (*B*, say) in the solid state. In this case, the metastable region, bounded by curve *b*, the two-phase equilibrium curve, on the *T*-*c* diagram is accompanied by a region in which the system loses its stability even with respect to infinitesimal variations in the concentration $c(\mathbf{r})$. This second region is bounded by the spinodal curve *s* (Fig. 1).

If the system is rapidly shifted from the high-temperature region in which the homogeneous state is stable (point A_0 in Fig. 1) to the low-temperature region in which the homogeneous state is unstable (A_1 in Fig. 1), the medium, in a labile state, rapidly loses its spatial homogeneity. Undergoing a relaxation, it acquires a special grainy or cellular structure without any sharp phase boundaries. This sort of evolution of a continuous inhomogeneous structure (a spinodal decomposition) has been studied previously by several investigators (see, for example, Refs. 1–6).

Actually, a homogeneous initial state characterized by the (mean) concentration c_0 is never realized at low temperature. Random variations in composition (and density), fixed in space, essentially always form during the quenching of metallic melts (from the liquid state). This circumstance stems in part from technological factors: a spatial variation in the cooling conditions, turbulence of a flow, etc. Furthermore, even during a rapid quenching along the path from point A_0 to A_1 there is time for a partial concentration stratification to occur.

In a theoretical description of the kinetics of spinodal decomposition of glasses, one should therefore specify as parameters not only the temperature and the mean concentration c_0 but also the probabilistic characteristics of the initial concentration distribution, e.g., the initial correlation function. As we will see below, "frozen" initial fluctuations strongly influence the course of the entire concentration stratification of a glass in the spinodal region.

The evolution of frozen fluctuations was studied in Ref. 7 in the case in which the mean concentration of the melt is close to the spinodal concentration c_{s1}. In particular, the presence of a second spinodal concentration c_{s2} was ignored. It was therefore not possible to describe the late stages of the spinodal decomposition or to draw a complete picture of this phenomenon. In particular, it was not possible to explain the formation of intermediate decomposition structures. The analysis below is free of these limitations. We will work from Landau's concept[8] and the complete nonlinear Cahn equation[9] to find the basic characteristics of the concentration stratification of glasses in all stages of spinodal decomposition.

2. FORMULATION OF THE PROBLEM

Our starting point for writing a dynamic equation for the concentration $c(\mathbf{r}, t)$ is the standard expression for the diffusion flux density[10] in terms of the functional derivative of the free energy $F\{c(\mathbf{r}, t), T\}$ with respect to the concentration:

$$\mathbf{j}=-M\nabla\frac{\delta F}{\delta c(\mathbf{r})}. \tag{1}$$

Here *M* is a product of the concentration by volume and the mobility *u* of the atoms of species *B*.

The (infinite-dimensional) order parameter in this theory is the concentration $c(\mathbf{r}, t)$. A distinctive feature of this order parameter is that it satisfies a conservation law written as a continuity equation:

$$(\partial c/\partial t)+\operatorname{div}\mathbf{j}=0. \tag{2}$$

We wish to stress at the outset that Eq. (1), in contrast with exact relation (2), is valid only in the limit of a small gradient of the chemical potential. It cannot describe, for example, the fluctuational formation of nucleating regions and their subsequent growth. In other words, we can work from Eq. (1) to describe only spinodal decomposition; binodal decomposition lies outside the scope of this analysis.

As a completely acceptable form of the functional dependence of the free energy on the concentration we adopt the functional

$$F=\int[f_1(c)+\gamma(\nabla c)^2]\rho\,dV, \tag{3}$$

where ρ is the number of atoms per unit volume. At temperatures below the critical temperature T_c the free-energy density $f_1(c)$ can be written in the form proposed by Landau,[8] which is a form convenient for our purposes:

$$f_1(c)=\varepsilon_0[-(c_{s2}-c_{s1})^2(c-c_*)^2+{}^2/_3(c-c_*)^4], \tag{4}$$

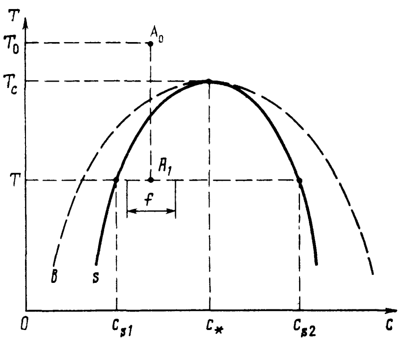

FIG. 1.

where $c_* \equiv (1/2)(c_{s1}+c_{s2})$, and c_{s1} and c_{s2} are defined as points at which the second derivative of the free-energy density with respect to the concentration vanishes, i.e.,

$$\left.\frac{\partial^2 f_1(c)}{\partial c^2}\right|_{c=c_{s1},c_{s2}}=0. \tag{5}$$

The spinodal curve s in Fig. 1 combines the plots of $c_{s1}(T)$ and $c_{s2}(T)$; its vertex (the critical point) has the coordinates c_* and T_c. The constant ε_0 agrees with T_c in order of magnitude. Expression (3) incorporates the interaction of regions with different concentrations (the nonlocal nature of the problem) through the introduction of a term proportional to $(\nabla c)^2$. The constant γ here satisfies $\gamma \sim \varepsilon_0 a^2$, where a is the atomic interaction range.

It is natural to assume that near the critical point we have $c_{s1,2}=c_* \mp \frac{1}{2}(1-T/T_c)^{1/2}$, and thus

$$c_{s2}-c_{s1}=(1-T/T_c)^{1/2}. \tag{6}$$

We introduce the deviation $v(\mathbf{r},t)$ of the concentration from its mean value c_0:

$$v(\mathbf{r},t)\equiv c(\mathbf{r},t)-c_0. \tag{7}$$

An equation for $v(\mathbf{r},t)$ is found by combining Eqs. (1) and (2) and using (3), (4), and (7). The resulting equation is extremely complicated and obscure. We will accordingly restrict the discussion to the simplest (and most important) case, that of small fluctuations:

$$v \ll c_0. \tag{8}$$

We also transform to a dimensionless time and to dimensionless spatial coordinates by making use of some scale values:

$$t_*=a^2/D_0 \quad (\text{where } D_0=u\varepsilon_0), \quad l_*=a\equiv(\gamma/\varepsilon_0)^{1/2}.$$

Without any loss of generality, in the case of an isotropic medium such as a glass, we can restrict the discussion to the one-dimensional case, in which the concentration depends on only the single coordinate x. As a result, we find the following equation within small terms of up to third order:

$$\frac{\partial v}{\partial t}=8c_0\left\{(c_0-c_{s1})(c_0-c_{s2})\frac{\partial^2 v}{\partial x^2}+(c_0-c_*)\frac{\partial^2 v^2}{\partial x^2}\right.$$
$$\left.+\frac{1}{3}\frac{\partial^2 v^3}{\partial x^2}-\frac{1}{4}\frac{\partial^4 v}{\partial x^4}\right\}. \tag{9}$$

We need to supplement this equation with an initial condition, which consists of the specification of the fluctuations at the time adopted as the initial time, e.g., at an instant when the temperature of the sample is fixed:

$$v(\mathbf{r},t)\,|_{t=0}=v_0(\mathbf{r}). \tag{10}$$

We will first carry out a preliminary qualitative analysis of Eq. (9).

If the system is, "on the average," outside the spinodal region, i.e., if $c_0<c_{s1}$ or $c_0>c_{s2}$ (Fig. 1), the coefficient in the first (and dominant) term on the right side of (9) is positive. Correspondingly, we are ignoring the other terms representing ordinary diffusion with a progressive smoothing of the fluctuations. If, on the other hand, the mean composition is inside the spinodal region, i.e., if $c_{s1}<c_0<c_{s2}$, the effective diffusion coefficient is negative, a rising diffusion occurs, and the fluctuations correspondingly grow (the concentration irregularities become larger). The length scale of the irregularities decreases as time elapses. In Cahn and Hilliard's linear theory,[1] the fluctuations are stabilized by the last term on the right side of (9), which stems from the gradient term in the free energy, (3).

It can be seen from Eq. (9) that it is important to incorporate the nonlinear terms (first) when c_0 is close to one of the spinodal concentrations (for definiteness, we will say c_{s1}) and (second) in the late stages of the decomposition, in which the relation $v \gtrsim (c_{s2}-c_{s1})$ holds. The term which is quadratic in v "pulls" the system into the spinodal region and gives rise to an asymmetry of the fluctuations, as was shown in Ref. 7. The cubic term, in contrast, stabilizes the fluctuations.

It is thus permissible to ignore the "gradient" term in the early stages of the decomposition. In the late stages, this term can be dealt with in a qualitative way by comparing it with the other terms in order of magnitude.

3. ANALYSIS OF THE EQUATIONS

We will thus study the truncated equation

$$\frac{\partial v}{\partial t}=8c_0\left[(c_0-c_{s1})(c_0-c_{s2})\frac{\partial^2 v}{\partial x^2}+(c_0-c_*)\frac{\partial^2 v^2}{\partial x^2}+\frac{1}{3}\frac{\partial^2 v^3}{\partial x^2}\right]. \tag{11}$$

Since the function $v_0(x)$ which appears in the initial condition is a random function, the solution $v(x,t)$ of Eq. (11) is also a random function of the coordinate x. The time enters this functional dependence parametrically. We are thus interested in finding correlation characteristics of the random function v. As was found in Ref. 7, the binary and ternary correlation functions are the ones of primary interest:

$$\langle v(x,t)v(x',t)\rangle\equiv K(x,x',t)=K(|x-x'|,t)\equiv K(s,t), \tag{12}$$

$$\langle v^2(x,t)v(x',t)\rangle\equiv G(x,x',t)=G(|x-x'|t)\equiv G(s,t). \tag{13}$$

The angle brackets here mean an average over an ensemble of realizations of the function $v(x,t)$. We recall that by definition we have $\langle v(x,t)\rangle=0$.

A system of coupled equations for the correlation functions of various orders is found from our basic equation, (11), by multiplying both sides by different powers of $v(x,t)$, beginning with the first, and then taking an average. The chain which results is uncoupled in the standard way, by writing the quaternary correlation functions as a sum of products of binary correlation functions:

$$\langle v^3(x,t)\,v(x',t)\rangle \to 3K(0,t)K(s,t), \tag{14}$$

$$\langle v^2(x,t)\,v^2(x',t)\rangle \to K^2(0,t)+2K^2(s,t). \tag{15}$$

The correlation functions of odd order (the third and fifth) play an important role here. We note in this connection that by working from the considerations in Refs. 6 and 7, primarily regarding the single-scale nature of the problem, we conclude that $G(s,t)$ can be replaced by $[G(0,t)/K(0,t]K(s,t)$ and that $\langle v^3(x,\ t)v^2(x',\ t)\rangle$ can be replaced by $K(0,t)G(0,\ t)+6G(0,t)K(s,t)$. It thus becomes possible to reduce the problem from an infinite chain of coupled equations for correlation functions of arbitrarily high order to the problem of analyzing a system of equations for the correlation function $K(s,t)$ and the quantity $G(0,\ t)\equiv\langle v^3(t)\rangle$, which is a measure of the asymmetry of the one-dimensional fluctuation distribution:

$$\frac{\partial K(s,t)}{\partial t} = 16c_0D_0\left[(c_0-c_{s1})(c_0-c_{s2})+(c_0-c_*)\frac{G(0,t)}{K(0,t)} + K(0,t)\right]K_{s^2}''(s,t), \tag{16}$$

$$\frac{dG(0,t)}{dt} = 24c_0D_0\left[(c_0-c_{s1})(c_0-c_{s2})\frac{G(0,t)}{K(0,t)} + 4(c_0-c_*)K(0,t) + 2G(0,t)\right]K_{s^2}''(0,t), \tag{17}$$

where

$$K_{s^2}''(s,t) \equiv \frac{\partial^2 K(s,t)}{\partial s^2}, \qquad K_{s^2}''(0,t) \equiv \left.\frac{\partial^2 K(s,t)}{\partial s^2}\right|_{s=0}.$$

It can be verified directly that Eq. (16) is satisfied by a Gaussian correlation function

$$K(s,t) = \frac{K_0R_0}{R(t)}\exp\left[-\frac{s^2}{2R^2(t)}\right] \tag{18}$$

under the condition that the correlation radius $R(t)$ satisfy the nonlinear equation

$$\frac{dR(t)}{dt} = 16c_0D_0\left[\frac{(c_0-c_{s1})(c_0-c_{s2})}{R(t)} + \frac{(c_0-c_*)G(0,t)}{K_0R_0} + \frac{K_0R_0}{R^2(t)}\right]. \tag{19}$$

Working from (17), and using (18), we can derive a second equation relating $G(0,t)$ and $R(t)$. Before we write the corresponding system of equations, we switch to the new dimensionless quantities

$$r(t)=R(t)/R_0, \quad \tau=t/t_0, \quad t_0=R_0^2/8c_0D_0K_0. \tag{20}$$

Parameters of the initial concentration distribution, specifically, the correlation radius R_0 of the frozen fluctuations and their initial dispersion K_0 (the square of the size of the fluctuations), appear in (18) and (20). We also introduce the parameters

$$\alpha \equiv \frac{(c_0-c_{s1})(c_0-c_{s2})}{K_0}, \qquad \beta \equiv \frac{c_0-c_*}{K_0^{1/2}} \tag{21}$$

and the normalized unknown function

$$g(\tau) \equiv G(0,\ \tau)/K_0^{3/2}. \tag{22}$$

The system of equations for $r(\tau)$ and $g(\tau)$ then takes the form

$$\frac{dr}{d\tau} = \frac{2\alpha}{r(\tau)} + \frac{2}{r^2(\tau)} + 2\beta g(\tau), \tag{23}$$

$$\frac{dg}{d\tau} = -\left[\frac{3\alpha}{r^2(\tau)} + \frac{6}{r^3(\tau)}\right]g(\tau) - \frac{12\beta}{r^4(\tau)}, \tag{24}$$

with the initial conditions

$$r(0)=1, \quad g(0)=g_0. \tag{25}$$

By solving system of equations (23) and (24) we can obtain basic generalized information about the concentration stratification, since this stratification determines the correlation radius, i.e., the length scale of the irregularities, the size of the fluctuations, $f(\tau) = [K_0/r(\tau)]^{1/2}$, and the asymmetry parameter $g(\tau)$. The latter makes it possible to evaluate the concentration in the precursors of the precipitates of the new phase and the volume of these precursors.

The parameter which primarily determines the evolution of the system is α. Its sign determines whether the system is, "on the average," inside or outside the spinodal region. The value of α is itself determined by the relation between the size of the initial fluctuations and the depth to which the system penetrates into the spinodal region ($\alpha<0$) or into the region of stability of a homogeneous state ($\alpha>0$). The parameter β primarily determines the asymmetry of the fluctuations. The temperature dependence of α and β stems from the temperature dependence $c_{s1}(T)$ and $c_{s2}(T)$.

4. DISCUSSION OF RESULTS

Equations (23) and (24), which constitute a system of first-order equations, fall in a category which is the subject of a voluminous literature (e.g., Ref. 11). Since the solution of our equations cannot generally be written in quadrature form, we will go through a semiquantitative analysis of the behavior $r(\tau)$ and $g(\tau)$ by making use of the well-known concept of the phase diagram of the system. For this purpose we first determine the singular points of our system of equations, by setting the right sides of (23) and (24) equal to zero. There are two singular points, with the coordinates

$$r_1 = \frac{4\beta^2-3\alpha+[(4\beta^2-3\alpha)^2-8\alpha^2]^{1/2}}{2\alpha^2}, \qquad g_1 = -\frac{\alpha r_1+1}{\beta r_1^2} \tag{26}$$

and

$$r_2 = \frac{4\beta^2-3\alpha-[(4\beta^2-3\alpha)^2-8\alpha^2]^{1/2}}{2\alpha^2}, \qquad g_2 = -\frac{\alpha r_2+1}{\beta r_2^2}. \tag{27}$$

These points are labeled 1 and 2 on the phase portraits (Fig. 2, a and b). A further analysis by the standard procedure shows that the first of these points is a saddle point, while the second is a stable node.

For the analysis below it is convenient to study the cases $\alpha<0$ and $\alpha>0$ separately. We also assume $g_0=0$, i.e., that the initial fluctuations have a symmetric distribution. For definiteness we assume $c_0<c_*$, i.e., $\beta<0$.

4.1. We assume $\alpha<0$, i.e., that the glass is in the spinodal region on the average (Fig. 2a).

As can be seen from Fig. 2, the separatrices are arranged in such a way that the phase trajectory corresponding to the initial condition which we have adopted terminates at the stable node (r_2, g_2). Consequently, a decomposition necessarily occurs; it terminates in the formation of an intermedi-

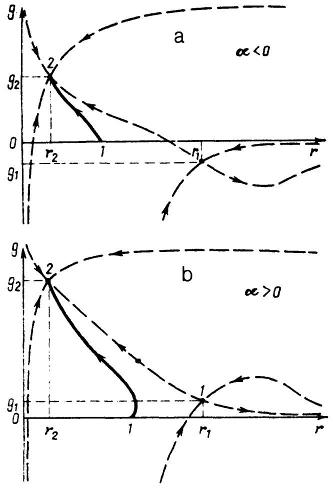

FIG. 2.

ate decomposition structure[12] characterized by a length scale r_2, a fluctuation size $(K_0/r_2)^{1/2}$, and an asymmetry parameter g_2.

In the important limiting case $|\alpha| \ll 1$, in which the mean concentration in the system is close to the spinodal concentration $(c_0 \approx c_{s1})$, we have $r_2 \approx (1/2)\beta^2$ and $g_2 \approx -4\beta^3$. Converting to dimensional quantities in accordance with (20), we find that the intermediate decomposition structure has a length scale

$$R_2 \approx \frac{2R_0K_0}{(c_{s2}-c_{s1})^2} = \frac{2R_0K_0T_c}{T_c-T} \tag{28}$$

and a fluctuation size

$$f_2 \approx \frac{c_{s2}-c_{s1}}{2^{1/2}} \approx \frac{(T_c-T)^{1/2}}{2^{1/2}T_c^{1/2}}. \tag{29}$$

The direction in which the process goes is determined by the relationship between the size of the frozen initial fluctuations, $f_0 \equiv K_0^{1/2}$, and the distance between the spinodal concentrations,

$$c_{s2}-c_{s1}=[(T_c-T)/T_c]^{1/2}$$

(Fig. 1). This distance depends on how close the temperature is to the critical point.

If the initial fluctuations are small, i.e., if $f_0 \gg |c_{s2} - c_{s1}|$, they will grow from an initial value f_0 to a final value $c_{s2} - c_{s1}$ as time elapses. The spatial scale of the fluctuations falls off from R_0 to a finite value R_2, given by (28). The asymmetry parameter simultaneously increases to $\langle v^3 \rangle \approx (c_{s2} - c_{s1})^3$.

If the initial fluctuations are instead extremely large, i.e., if $f_0 \gg |c_{s2} - c_{s1}|$, they will decrease to a size $|c_{s2} - c_{s1}|$, while the correlation radius will increase. Note, however, that the latter case could hardly be realized, since for initial fluctuations this large there would more probably be a binodal decomposition, i.e., a formation of nucleating regions of a new phase and their subsequent growth.

Our use of the term "intermediate decomposition structure" is justified by the circumstance that the actual spinodal decomposition has ended by the time at which point 2 is reached. The structure formed remains stable for a certain length of time.[7] A binodal decomposition then apparently occurs and terminates in a stratification of the system into stable phases. One might say that the intermediate decomposition structure is the initial structure or starting point for the phase transition by the mechanism of nucleation and growth.

It can be seen from (23) that we have $dr/d\tau = -2|\alpha| + 2$ at the initial time. Under the condition $|\alpha| > 1$, the correlation radius decreases monotonically. Under the opposite condition, $|\alpha| < 1$, there is first an increase in r, i.e., a smoothing of the irregularities, and then r decreases to r_2, while the fluctuations grow to f_2. The temporal characteristics of the spinodal decomposition and the role played by the gradient term in the energy are conveniently found in the particular case $\beta = 0$, in which the mean concentration is equal to the critical concentration $(c_0 = c_*)$. In this case, with $\alpha = -(c_{s2} - c_{s1})^2/4K_0$, Eq. (24) is satisfied by the trivial substitution $g(\tau) \equiv 0$, and Eq. (23) takes the form

$$\frac{dr}{d\tau} = -\frac{2|\alpha|}{r} + \frac{2}{r^2}. \tag{30}$$

Introducing $r_2 \equiv 1/|\alpha|$, we can write a solution of this equation which implicitly gives the functional dependence $r(\tau)$ as follows:

$$\frac{1}{2}(1+r+2r_2)(1-r) + r_2^2 \ln\frac{1-r_2}{r-r_2} = \frac{2\tau}{r}. \tag{31}$$

It follows from (31) that the correlation radius initially varies linearly with the time; it then approaches a limiting value r_2 exponentially. The time scale of the relaxation to the intermediate equilibrium is $\tau_s \sim r_2 = 1/|\alpha|$, or, in dimensional quantities,

$$t_s \sim \frac{R_0^2}{c_0D_0(c_{s2}-c_{s1})^2}. \tag{32}$$

The spinodal decomposition thus occurs over the customary diffusion time R_0^2/D_0, but in this case this time is renormalized by a factor

$$(c_{s2}-c_{s1})^{-2} \sim [(T_c-T)/T_c]^{-1},$$

which increases as the critical point is approached. In other words, the decomposition slows down strongly near the critical point.

The limitation on the growth of fluctuations during spinodal composition results from either nonlinear terms or the last term (the gradient term), according to (9). The corresponding criterion can be found by comparing the first and last terms on the right side of (9) or (equivalently) by comparing the value of r_2 with the Cahn length scale[1] for the fluctuations which are growing most rapidly, $\lambda_c \sim a(c_{s2} - c_{s1})^{-1}$. If

$$R_2 \equiv \frac{R_0}{|\alpha|} = \frac{R_0K_0}{(c_{s2}-c_{s1})^2} > \frac{a}{c_{s2}-c_{s1}}, \tag{33}$$

the growth of the fluctuations is limited by the nonlinear terms in (9), the size of the fluctuations at the end of the decomposition process is $c_{s2} - c_{s1}$, and the spatial scale of the irregularities is on the order of R_2, i.e., depends on the initial scale size.

If the inequality sign in (33) is reversed, the fluctuations are limited by the gradient terms. In accordance with

Ref. 1, we single out the length scale

$$\lambda_c \sim a\left[-\left(\frac{\partial^2 f}{\partial c^2}\right)\Big|_{c=c_0}\right]^{-1/2} \sim \frac{a}{c_{s2}-c_{s1}}. \quad (34)$$

The fluctuations, on the other hand, stabilize at a level

$$f_2 \sim \left[\frac{K_0 R_0 (c_{s2}-c_{s1})}{a}\right]^{1/2}, \quad (35)$$

which depends on the initial state of the glass.

These estimates remain qualitatively the same for essentially all c_0; the only exceptional cases are values of c_0 very close to c_{s1} (or c_{s2}). In the latter case, a special analysis will be required in order to distinguish the role played by the gradient term.

4.2. We assume $\alpha > 1$; i.e., the glass decomposes outside the spinodal region "on the average."

It can be seen from the phase portrait (Fig. 2b) that under the condition $\alpha \ll 1$ the phase trajectory corresponding to the "symmetric" initial condition $g_0 = 0$ terminates at a stable node. In other words, although the system is outside the spinodal region on the average, the decomposition occurs by the spinodal mechanism[7] because of the initial fluctuations. It terminates in the formation of an intermediate decomposition structure corresponding to point 2, i.e., to a stable node.

Before we take up the time dependence $r(\tau)$ we would like to point out that the temperature dependence of R_2 is quite different from that of λ_c, according to (6), (33), and (34). The two most important situations can be identified here on the basis of the distance between the temperature at which the spinodal decomposition is observed, T, and the critical temperature T_c: (a) $R_2 > \lambda_c$; (b) $R_2 < \lambda_c$. At temperatures very close to the critical temperature, relation (a) definitely holds; with distance from T_c, there is a transition to case (b).

We first consider the first situation ($R_2 > \lambda_c$). With $\beta \sim 1$ and $\alpha \ll 1$, the correlation radius $r \equiv R/R_0$ varies monotonically from unity to r_2 (curve 1 in Fig. 3). At sufficiently large values of α, the $r(\tau)$ dependence ceases to be monotonic. Specifically, $r(\tau)$ initially increases, as if it were approaching r_1, and then goes through a maximum and decreases, asymptotically approaching r_2 (curve 2 in Fig. 3). At a certain definite value $\alpha = \alpha_0 \sim 1$ the phase trajectory terminates at the point (r_1, g_1); i.e., $r(\tau)$ asymptotically approaches r_1 (curve 3 in Fig. 3). Finally, at $\alpha > \alpha_0$, a smoothing of the fluctuations occurs from the outset, with a subsequent transition to a uniform distribution of the components (curve 4).

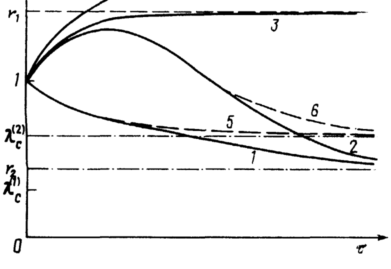

FIG. 3.

In the situation $R_2 < \lambda_c$, the evolution of the correlation radius $r(\tau)$ is generally like that in the case $R_2 > \lambda_c$, but now, under the condition $\alpha < \alpha_0$, the value of $r(\tau)$ asymptotically approaches $\lambda_c^{(2)}$ after a long time (curves 5 and 6 in Fig. 3). The meaning here is that under the condition $R_2 < \lambda_c$ the length scale of the intermediate decomposition structure is basically determined by the gradient terms in expression (3) for the free energy after a long time. In other words, the linear Cahn theory can be used in this case.

The system exhibits this behavior not only in the case $g_0 = 0$ but also in the case $g_0 \neq 0$. In the latter case, however, if there is a sufficiently large initial asymmetry of positive sign, the system has a tendency to undergo spinodal decomposition in accordance with the value of g_0. The situation changes radically only if, as c_0 varies (so α and β also vary), the two singular points on the phase diagram coalesce. In our model, this coalescence occurs under the condition

$$4\beta^2 = (3+\sqrt{8})\alpha. \quad (36)$$

If $\alpha > \alpha_{cr} = 4\beta^2/(3+\sqrt{8})$, there are no singular points on the phase diagram, so there is no spinodal decomposition. The evolution of the system in this case is a transition to a homogeneous state.

5. CONCLUSION

Spinodal decomposition is the time evolution of a system with a continuous inhomogeneous structure of a grainy or cellular type as the result of a thermodynamic instability.

The quantitative characteristics of such a structure and even the direction in which the evolution occurs are determined to a large extent by the "frozen" initial fluctuations of the composition (and of the density). Their role can be determined completely only if the possibility of large deviations of the mean concentration from the spinodal concentration is taken into account, with $c_0 - c_{s1} \sim c_{s2} - c_{s1}$. The corresponding theoretical description includes a nonlinear term av^3 in the basic equation, (9). Equivalently, this description incorporates the existence of a second spinodal concentration. It thus becomes possible to derive a new result, which is evidence of the existence of an intermediate decomposition structure; this result could not be derived in Ref. 7 specifically because there was no term av^3 in the main evolutionary equation.

In addition, the incorporation of this term makes it possible to draw completely definite quantitative conclusions about the final stage of the spinodal decomposition. Specifically, in the case of extremely small initial fluctuations, irregularities of the Cahn scale $\lambda_c \sim a(c_{s2} - c_{s1})^{-1}$; form in the final stage. The size of the fluctuations at the end of the decomposition satisfies $f_2 \ll c_{s2} - c_{s1}$ and [according to (35)] depends on the size of the initial fluctuations. In contrast with the length scale, the size of the fluctuations cannot in principle be derived without consideration of the initial state of the glass. For comparatively large initial fluctuations [the specific condition is given by (33)], irregularities with a size well above the Cahn scale emerge in the final stage, and the size of the fluctuations reaches its maximum, $\sim (c_{s2} - c_{s1})$. In this case the growth of the irregularities is limited by the nonlinear term av^3, while in the preceding case the limiting factor was the gradient term $\alpha\partial^4 v/\partial x^4$. Finally, for extremely large initial fluctuations, exceeding $c_{s2} - c_{s1}$, the spinodal decomposition goes in the opposite direction, toward a decrease in the size of the fluctuations, to $c_{s2} - c_{s1}$.

Analysis of the complete evolutionary equation reveals the temperature dependence of the decomposition time and that of the size of the irregularities near the critical point. It turns out that both of these quantities increase in proportion to $(T_c - T)^{-1}$.

It can be concluded from numerical estimates that the spinodal decomposition of typical metallic glasses causes an initial inhomogeneous structure with a mean inhomogeneity size $R_0 \sim 10^{-4}$ cm to transform into an intermediate, relatively stable decomposition structure with a far smaller inhomogeneity size, $R_2 \sim 10^{-6}$ cm. The time scale of the spinodal decomposition is determined primarily by the temperature (through the mobility and the proximity of the temperature to the critical point; for metallic glasses in the temperature interval 500–700 K, it varies over the range 10^4–10^7 s.

Since a discussion of spinodal decomposition pertains to inhomogeneities of mesoscopic scale (10^2–10^4 Å), the most convenient experimental method for studying this decomposition is small-angle x-ray scattering. The correlation function $K(s,t)$ is none other than the Fourier transform of the angular dependence of the scattering intensity. If the decomposition time is sufficiently long, this method would reveal the time dependence of both the size and composition of the inhomogeneities.

[1] J. W. Cahn and J. E. Hilliard, J. Chem. Phys. **28**, 258 (1958).
[2] M. Hillert, Acta Metall. **9**, 525 (1961).
[3] J. W. Cahn, Acta Metall. **9**, 795 (1961).
[4] J. W. Cahn, Acta Metall. **10**, 179 (1962).
[5] H. E. Cook, Acta Metall. **18**, 297 (1970).
[6] J. S. Langer, M. Baron, and H. D. Miller, Phys. Rev. A **11**, 1417 (1975).
[7] É. P. Fel'dman and L. I. Stefanovich, Zh. Eksp. Teor. Fiz. **96**, 1513 (1989) [Sov. Phys. JETP **69**, 858 (1989)].
[8] L. D. Landau, Zh. Eksp. Teor. Fiz. **7**, 19 (1937).
[9] J. W. Cahn, J. Chem. Phys. **42**, 93 (1965).
[10] J. S. Langer, Physica **73**, 61 (1974).
[11] A. A. Andronov, A. A. Bitt, and S. É. Khaĭkin, *Theory of Oscillations*, Nauka, Moscow, 1981, Chapter 5.
[12] A. Z. Patashinskiĭ and I. S. Yakub, Fiz. Tverd. Tela (Leningrad) **18**, 3630 (1976) [Sov. Phys. Solid State **18**, 2114 (1976)].

Translated by D. Parsons