Evolution of "frozen" concentration fluctuations during decomposition of glasses with near-spinodal compositions

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A two-component model is used in an investigation of the diffusion stage of the evolution of the large-scale structure of a glass (spinodal decomposition). A detailed analysis is made of a situation in which the average concentration c_0 is close to one of the spinodal concentrations. A generalized form of the Cahn–Hilliard diffusion equation is used to derive a system of equations relating second- and third-order correlation functions for concentrations at two different points. Analytic forms for the time dependence of the correlation radius and of the magnitude of the concentration fluctuations are obtained. It is shown that the presence of initial composition inhomogeneities reduces effectively the range of stability of a homogeneous state.

Spinodal decomposition is known to take place in those cases when the system can be transformed by some method to a region characterized by an absolute instability of a homogeneous state under the spinodal curve.[1] If this is done by fast cooling, then the cooling rate has to be very high in order to prevent phase stratification "on the way" to low temperatures where structural transformations are slowed down greatly because of the low mobility of atoms. It therefore follows that we can expect spinodal decomposition primarily in metallic and inorganic glasses which are formed in time intervals on the order of $\sim 10^{-9}$–10^{-3} s.

The published experimental data on metallic glasses[2] allow us to draw a definite conclusion that the homogeneous state of a glass can in practice be achieved directly after quenching. Normally a glass is inhomogeneous in composition, so that in the case of—for example—a two-component alloy AB the concentration $c(\mathbf{r})$ of the component B can be regarded as a random function of the coordinates. The spatial scale of the initial frozen fluctuations reaches hundreds and thousands of interatomic spacings and the magnitude of the fluctuations is usually small compared with the average concentration c_0. We shall not consider the origin of such fluctuations. Our task is to follow the evolution of these fluctuations with time at a fixed temperature T in the case where the point (c_0, T) is located near a spinodal curve. It should be stressed that we are speaking here of the vicinity of an arbitrary point on a spinodal curve and not necessarily a critical point of a solid solution. If we use $f(c, T)$ to denote the free energy of a glass per particle, the spinodal equation can be written in the form

$$(\partial^2 f/\partial c^2)_{c=c_s}=0. \tag{1}$$

We shall ignore the difference between the free energy and the thermodynamic potential and use c_s for the spinodal concentration. As a rule, at a fixed (and sufficiently low) temperature there are two concentrations that satisfy Eq. (1). We shall consider specifically that c_s which is the lower of these concentrations.

In writing down the equation describing the time evolution of the concentration $c(r)$ we begin from the analysis carried out by Cahn and Hilliard.[3] Following these authors, we ignore the mechanism responsible for the appearance of fluctuations and the subsequent growth of nuclei of the new phase, i.e., we consider only the generalized diffusion equation, when outside the spinodal region $[(\partial^2 f/\partial c^2)>0]$ the diffusion coefficient is positive, whereas within this region $[(\partial^2 f/\partial c^2)<0]$ it is negative (upward diffusion). For simplicity, we shall consider the one-dimensional problem when the concentration is a function of just one coordinate x.

It follows from Refs. 3 and 4 that the free energy of a sample with an inhomogeneous distribution of the composition is

$$F=\int [f(c(\mathbf{r}))+\gamma(\nabla c)^2]\rho(\mathbf{r})\,dv, \tag{2}$$

where ρ is the number of atoms per unit volume. The second term in the integrand allows for "surface" effects, i.e., for the interaction of regions with different compositions. These effects are important if the composition varies greatly over distances on the order of the interaction radius (amounting to one or two interatomic distances). Our aim is to concentrate on nonlinear effects and we shall ignore the gradient term in Eq. (2), bearing in mind that during the initial stage of decomposition the characteristic spatial scales of the fluctuations are large compared with the interatomic distances.

This gives the following form of the diffusion equation:

$$\frac{\partial c}{\partial t}=\frac{\partial}{\partial x}\left(D\frac{\partial c}{\partial x}\right), \tag{3}$$

where the diffusion coefficient

$$D=uc\,\partial^2 f/\partial c^2 \tag{4}$$

(u is the mobility) changes sign as the concentration c crosses the spinodal, i.e., at $c=c_s$.

If the average concentration c_0 is nearly spinodal, i.e.,

$$|c_0-c_s|/c_s\ll 1, \tag{5}$$

and fluctuations of $v(x,t)\equiv c(x,t)-c_0$ are small, so that

$$|v(x,t)|/c_s\ll 1, \tag{6}$$

it is natural to assume that in this region we have

$$\partial^2 f/\partial c^2\approx(\partial^3 f/\partial c^3)_{c=c_s}(c-c_s)\equiv\varepsilon(c-c_s). \tag{7}$$

We shall bear in mind that for our selection of c_s the third derivative obeys $(\partial^3 f/\partial c^3)_{c=c_s}\equiv\varepsilon<0$. Using the inequalities (5) and (6), we can rewrite Eq. (3) for the concentration fluctuations as follows:

$$\frac{\partial v}{\partial t}=\beta\Delta c_s\frac{\partial^2 v}{\partial x^2}-\frac{\beta}{2}\frac{\partial^2 v^2}{\partial x^2}, \tag{8}$$

where $\beta\equiv|\varepsilon|uc_s>0$, $\Delta c_s\equiv c_s-c_0$.

The initial condition for Eq. (8) is in the form of the initial distribution of the composition:

$$v(x,0)=v_0(x). \tag{9}$$

Since $v_0(x)$ is a random function of the coordinate, we are speaking here of the solution of a determinate equation with a random initial condition. It therefore follows that we have to describe the solutions of Eq. (8) in terms of probabilities.

The need to carry out a statistical analysis of spinodal decomposition of solid solutions was first pointed out by Langer *et al.*,[5] who also demonstrated a method that can be used here to analyze thermodynamic fluctuations. These fluctuations were allowed for by modifying the equation for the density $\rho\{v(x,t)\}$, so as to introduce the probability of the distribution of fluctuations of a random δ-correlated force proportional to temperature. Specific results were obtained in Ref. 5 by numerical solution of equations for the Fourier transform of a correlation function.

Our task is to follow the evolution of large-scale nonthermodynamic fluctuations, which appeared as a result of the technological history of a sample. Equation (8) can be used to write down a system of coupled equations for correlation functions of different orders. We assume that the system is statistically homogeneous, so that the pair correlation function

$$\langle v(x,t)v(x',t)\rangle\equiv K(x,x';t),$$

like the other correlation functions, depends only on the absolute value of the difference between the coordinates $s=|x'-x|$. By definition, the average value is

$$\langle v(x,t)\rangle=0. \tag{10}$$

The angular brackets represent averaging over the ensemble of realizations for a fixed time, in other words, time occurs in the main dynamic equation (8) and appears as a parameter of the equation for the correlation functions deduced from Eq. (8).

If we multiply Eq. (8) by $v(x',t)$ and average, we obtain

$$\left\langle\frac{\partial v(x,t)}{\partial t}v(x',t)\right\rangle$$
$$=\beta\Delta c_s\left\langle\frac{\partial^2 v(x,t)}{\partial x^2}v(x',t)\right\rangle-\frac{\beta}{2}\left\langle\frac{\partial^2 v^2(x,t)}{\partial x^2}v(x',t)\right\rangle. \tag{11}$$

In view of the symmetry properties of the correlation function the left-hand side of Eq. (11) represents, apart from a factor of 1/2, the time derivative of the second-order correlation function (which we simply call the correlator). It is known (see, for example, Ref. 6) that the derivatives on the right-hand side of the equal sign can be taken outside the averaging brackets. We introduce the following notation for the third-order correlation function:

$$G(x,x';t)=G(|x-x'|,t)\equiv G(s,t)=\langle v(x,t)v^2(x',t)\rangle. \tag{12}$$

Then, Eq. (11) can be rewritten in the form

$$\frac{\partial K(s,t)}{\partial t}=2\beta\Delta c_s\frac{\partial^2 K(s,t)}{\partial s^2}-\beta\frac{\partial^2 G(s,t)}{\partial s^2}. \tag{13}$$

We now multiply Eq. (8) by $v^2(x',t)$, then average:

$$\left\langle\frac{\partial v(x,t)}{\partial t}v^2(x',t)\right\rangle=\beta\Delta c_s\left\langle\frac{\partial^2 v(x,t)}{\partial x^2}v^2(x',t)\right\rangle$$
$$-\frac{\beta}{2}\left\langle\frac{\partial^2 v^2(x,t)}{\partial x^2}v^2(x',t)\right\rangle. \tag{14}$$

Multiplying Eq. (8) by increasing powers of $v(x',t)$, we obtain a system of coupled equations for different orders of correlation functions.

We shall employ the usual method for truncating a chain of equations by replacing the fourth-order correlation function in Eq. (14) with a sum of products of the pair correlators. However, this simplification does not suffice to solve the system (13)–(14). In spite of the obvious nonlinearity of the system, there is a further difficulty, which is establishment of a relationship between the left-hand side of Eq. (14) and the total time derivative of the third-order correlation function $G(s,t)$.

We now consider in greater detail the third-order correlation function. The fact that it differs from zero is an important feature of spinodal decomposition. The model of $G(s,t)$ for $s=0$, i.e., $\langle v^3(t)\rangle$, can be used as a measure of the asymmetry of the one-dimensional function describing the distribution of v. In turn, this asymmetry and its time dependence are quantitative characteristics of the decomposition process, because this process involves splitting a sample into regions with compositions which become increasingly different with time. Since this problem has only one time-dependent scale, which is the correlation radius, it is natural to assume that the dependence $G(s,t)$ on s repeats the dependence of the correlation function $K(s,t)$ on s. Consequently, by definition, we have

$$G(s,t)=\frac{G(0,t)}{K(0,t)}K(s,t). \tag{15}$$

Equation (15) is another consequence of the hypothesis of Langer *et al.*[5] about the nature of the two-dimensional function representing the distribution of a random quantity v:

$$p_2[v(x),v(x')]$$
$$=p_1[v(x)]p_1[v(x')]\left\{1+\frac{K(x,x')}{K^2(0)}v(x)v(x')\right\}. \tag{16}$$

In Eq. (16) the quantity $p_1[v(x)]$ represents a one-dimensional distribution function and we also have

$$K(0)=\lim_{s\to 0}K(s).$$

The hypothesis represented by Eq. (16) is very restrictive and is justified only at low values of v and high values of s, whereas the hypothesis represented by (15) is much less restrictive and is justified essentially whenever the physical problem is one-dimensional.

In the case described by Eq. (15) it is sufficient to determine the limiting form of the relationship (14) when $x\to x'$, i.e., $s\to 0$. In this limit the left-hand side of Eq. (14) represents, apart from a factor 1/3, the total derivative of $G(s,t)$.

Therefore, the system represented by Eqs. (13) and (14) transforms as follows:

$$\frac{\partial K(s,t)}{\partial t}=\left[2\beta\Delta c_s-\beta\frac{G(0,t)}{K(0,t)}\right]\frac{\partial^2 K(s,t)}{\partial s^2}, \qquad (17)$$

$$\left.\frac{\partial G(s,t)}{\partial t}\right|_{s\to 0}$$

$$=3\beta\Delta c_s\left.\frac{\partial^2 G(s,t)}{\partial s^2}\right|_{s\to 0}-\frac{3\beta}{2}\frac{\partial^2}{\partial s^2}[K^2(0,t)+2K^2(s,t)]|_{s\to 0}. \qquad (18)$$

The subsequent transformation (18) is elementary, but we must bear in mind that the derivative $(\partial K(s,t)/\partial s)_{s\to 0}$ vanishes. This follows[6] from the natural hypothesis that the random function $v(x,t)$ is differentiable with respect to x.

The final form of our system of equations is as follows:

$$\frac{\partial K(s,t)}{\partial t}=\left[2\beta\Delta c_s-\beta\frac{G(0,t)}{K(0,t)}\right]\frac{\partial^2 K(s,t)}{\partial s^2}, \qquad (19)$$

$$\frac{\partial G(0,t)}{\partial t}=3\beta\Delta c_s\frac{K''(0,t)}{K(0,t)}G(0,t)-6\beta K(0,t)K''(0,t), \qquad (20)$$

where

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

Equation (19) represents a diffusion equation with a time-dependent diffusion coefficient. We can check directly that the solution of this equation satisfying the necessary requirements is

$$K(s,t)=\frac{K(0)R_0}{R(t)}\exp\left(-\frac{s^2}{2R^2(t)}\right). \qquad (21)$$

Here, $R(t)$ is a time-dependent correlation radius and we have $R(0)=R_0$, whereas $K(0)$ determines the square of the initial fluctuation. Substituting Eq. (21) in Eq. (19), we get the ordinary differential equation

$$\frac{dR}{dt}=\frac{2\beta\Delta c_s}{R(t)}-\frac{\beta G(0,t)}{K(0)R_0}. \qquad (22)$$

Bearing in mind that

$$K(0,t)=K(0)R_0[R(t)]^{-1},\quad K''(0,t)=-K(0)R_0[R(t)]^{-3},$$

we can rewrite Eq. (20) in the form

$$\frac{dG(0,t)}{dt}=-3\beta\Delta c_s\frac{G(0,t)}{R^2(t)}+6\beta\frac{K^2(0)R_0^2}{R^4(t)}. \qquad (23)$$

The system of ordinary differential equations (22) and (23) subject to the initial conditions $R(t)|_{t=0}=R_0$ and $G(0,t)|_{t=0}=G_0$ can be used to obtain generalized information on the evolution of composition inhomogeneities, i.e., to find the correlation radius $R(t)$, the asymmetry of the distribution function $G(0,t)\equiv\langle v^3(t)\rangle$, and the mean-square fluctuation $f(t)=f(0)[R_0/R(t)]^{1/2}$.

We introduce the characteristic time and space scales:

$$t_*=R_0^2/\beta[K(0)]^{1/2},\quad R_*=R_0, \qquad (24)$$

and, using Eq. (24) we rewrite the time and space intervals in dimensionless form: $\tau\equiv t/t_*$, $r=R/R_0$. We also introduce the fundamental dimensionless parameter

$$\alpha\equiv\Delta c_s/[K(0)]^{1/2}\equiv(c_s-c_0)/[K(0)]^{1/2} \qquad (25)$$

and the dimensionless quantity

$$\gamma(\tau)=G(0,\tau)/[K(0)]^{3/2}.$$

If this notation is adopted, we find that Eqs. (22) and (23) yield the following second-order equation

$$\frac{d^2r}{d\tau^2}=-\frac{5\alpha}{r^2}\frac{dr}{d\tau}+\frac{6\alpha^2}{r^3}-\frac{6}{r^4} \qquad (26)$$

subject to the initial conditions

$$r(0)=1,\quad (dr/d\tau)_{\tau=0}=2\alpha-\gamma_0\quad(\gamma_0\equiv\gamma(0)), \qquad (27)$$

as well as an expression [which follows from Eq. (22)]

$$\gamma(\tau)=2\alpha/r(\tau)-dr/d\tau. \qquad (28)$$

A number of characteristics of the spinodal decomposition process can be illustrated clearly in terms of the exact solution in the case when $\alpha=0,\gamma_0=0$. This means that the average composition of a glass is exactly equal to the spinodal curve and the initial distribution is symmetric. In this case the time dependence of the correlation radius is

$$\tau=\frac{1}{2}\int_r^1\frac{x^{3/2}\,dx}{(1-x^3)^{1/2}}. \qquad (29)$$

If the time $\tau\ll 1$ is short, the correlation radius decreases in accordance with the law $r\approx 1-\tau^2$. There is a finite "collapse" time τ_c, i.e., the correlation scale vanishes in a finite time

$$\tau_c=\frac{1}{2}\int_0^1\frac{x^{3/2}\,dx}{(1-x^3)^{1/2}}, \qquad (30)$$

since the integral of Eq. (30) converges. The value of r vanishes in accordance with the power law:

$$r\approx 5^{2/5}(\tau_c-\tau)^{2/5}. \qquad (31)$$

Fluctuations of the concentration and asymmetry $\langle v^3(t)\rangle$ diverge proportionally to $(\tau_c-\tau)^{-1/5}$ and $(\tau_c-\tau)^{-3/5}$. We shall discuss the factors which limit the growth of fluctuations and asymmetry below; at this stage we consider Eq. (26) in detail.

Since Eq. (26) does not contain time explicitly, the order of the equation can be reduced by substituting $dr/d\tau=p(r)$:

$$\frac{dp}{dr}=-\frac{5\alpha}{r^2}+\frac{6}{pr^3}\left(\alpha^2-\frac{1}{r}\right),\quad p(1)=2\alpha-\gamma_0. \qquad (32)$$

Equation (32) cannot be solved in quadratures for arbitrary values of α and γ_0, but it can be analyzed to the extent necessary to obtain physical conclusions.

The only singularity of Eq. (32), with the coordinates $r_s=1/\alpha^2$, and $p=0$, is a saddle. Two singular integral curves intersect at this point and they divide the phase plane (r,p) into four sectors (Fig. 1). The cases $\alpha^2<1$ (a) and $\alpha^2>1$ (b) are best considered separately.

a) The integral curve is governed by the initial condition, i.e., by the value of $p(1)=(dr/d\tau)_{\tau=0}$. If this quantity is negative (curves 1 and 2), the correlation radius decreases monotonically and vanishes in a finite collapse time, which depends on α and γ_0. However, for

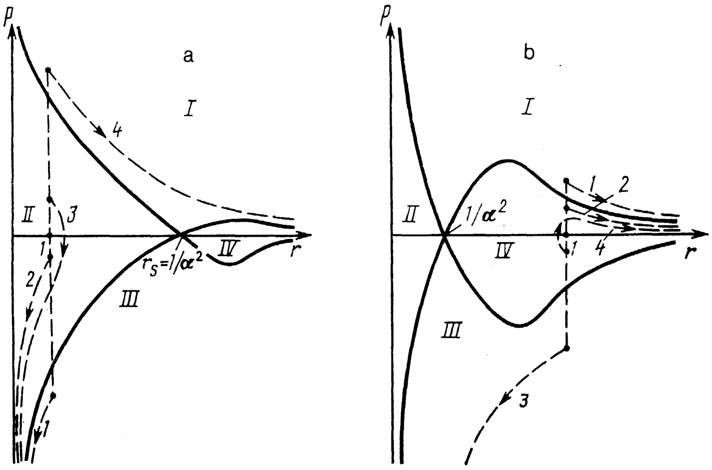

FIG. 1.

$p(1)\equiv 2\alpha-\gamma_0>0$, then we have to distinguish two subcases. In the case of relatively small values of $p(1)$ (curve 3) the correlation radius first increases, i.e., fluctuations decrease, and then r decreases to zero in a finite time. In all cases r tends to zero in accordance with the law

$$r\propto[\tau_c(\alpha,\ \gamma_0)-\tau]^{2/5},$$

whereas fluctuations and asymmetry of the distribution function diverge in accordance with the following laws:

$$f\propto[\tau_c(\alpha,\ \gamma_0)-\tau]^{-1/5},\quad \langle v^3(\tau)\rangle\propto[\tau_c(\alpha,\ \gamma_0)-\tau]^{-3/5}.$$

If $p(1)$ exceeds a certain critical value, the initial point on the phase path crosses from sector II to sector I and the nature of the path changes qualitatively. We now find that r does not tend to zero but to infinity, in other words, spinodal decomposition changes to equalization of the concentrations and the system becomes homogeneous (curve 4). It should be noted that the limit $r\to\infty$ corresponds to the conventional diffusion law $r\propto\tau^{1/2}$.

b) In this case when the absolute values of the negative $p(1)$ are large and r tends monotonically to zero (curve 3). When $2\alpha-\gamma_0\equiv p(1)$ is increased, the initial point on the path crosses from sector III to sector IV and the nature of the path changes qualitatively (curve 4): the initial correlation radius decreases, i.e., decomposition begins, but then it changes to homogenization ($r\to\infty$). In the case of positive values of $p(1)$ this equalization of the compositions is a monotonic process. In all cases we have $r\to\infty$ in accordance with the conventional diffusion law $r\propto\tau^{1/2}$.

More definite semiquantitative conclusions on the nature of spinodal decomposition and its change to homogenization can be obtained for the case $\gamma_0=0$, which is perhaps the most important one. If this condition is satisfied then we have also $\alpha<0$ and $c_0>c_s$, i.e., when the average composition is in the spinodal region, the correlation radius decreases with time to zero and fluctuations grow to infinity. During the initial stage, we have

$$r(\tau)\approx 1+2\alpha\tau. \tag{33}$$

The collapse stage is characterized by

$$r(\tau)\propto[\tau_c(\alpha)-\tau]^{2/5}. \tag{34}$$

If α is small, the decomposition time is governed (apart from the obvious dependence on the diffusion coefficient) by the initial fluctuations $\tau_c(\alpha)\sim 1$, i.e.,

$$t_c(\alpha)\propto R_0^2/\beta[K(0)]^{1/2}. \tag{35}$$

An increase in $|\alpha|$, i.e., a reduction in the initial fluctuations and a shift of the average composition to the spinodal region, reduces the decomposition time: $\tau_c(\alpha)\propto 1/|\alpha|$, i.e.,

$$t_c(\alpha)\propto R_0^2/\beta|c_s-c_0|. \tag{36}$$

We now consider the case $\alpha>0$ and $c_0<c_s$. In this case the system is "on the average" outside the spinodal stability region of the homogeneous state. Therefore, at first sight it might seem that the evolution of the system in this region involves equalization of the composition throughout the sample. In our case this would mean an increase in the correlation radius to infinity. In fact, we have an interval $\alpha<\alpha_{cr}$ within which the system is still experiencing spinodal decomposition.

The main feature of this situation becomes clear on inspection of Fig. 2. Although the average concentration is outside the spinodal region ($c_0<c_s$), there are some parts of the distribution (shown shaded) where the local composition is within the spinodal region.

If the number of such parts of the distribution is sufficiently large, they "pull" the whole system below the spinodal. We can also say that the fluctuations "smear out" the spinodal, transforming it from a curve into a region of relative width $\sim\alpha_{cr}$.

The positive value of α is manifested by an initial increase in the correlation radius and then the decomposition tendency takes over and we have $r\to 0$. If α is small and positive, the time taken for r to increase is of order α and as α is increased, the decomposition time rises linearly:

$$\tau_c(\alpha)\approx\tau_c(0)\,[1+a\alpha],$$

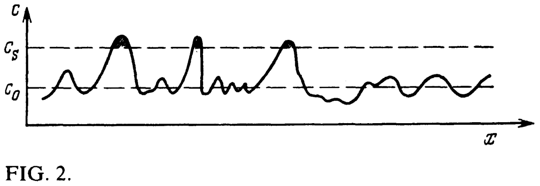

FIG. 2.

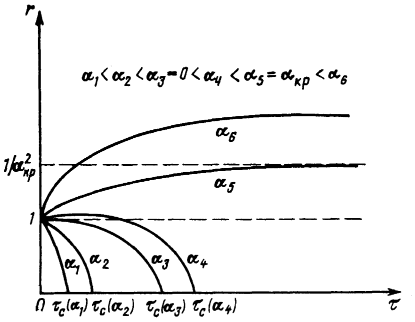

FIG. 3.

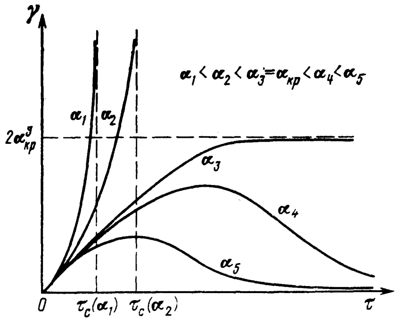

FIG. 4.

where $a \sim 1$. On further increase in α at the moment corresponding to when the singular integral curve intersects the initial point of the phase trajectory by the collapse time becomes $\tau_c(\alpha) \to \infty$. In region I of Fig. 1a we have $r(\tau) \to \infty$ for long times and the system assumes a homogeneous state by conventional diffusion. It follows from Fig. 1a that $\alpha_{cr} \lesssim 1$. The exact value of α_{cr} is found by a numerical solution of Eq. (32) and amounts to 0.82. A detailed analysis of the dependence $r(\tau)$ in the course of motion near a singular phase path leads us to the conclusion that in the limit $\alpha \to \alpha_{cr}$ the collapse time $\tau_c(\alpha)$ increases logarithmically to infinity:

$$\tau_c(\alpha)\,|_{\alpha\to\alpha_{cr}} \propto -\ln(\alpha_{cr}-\alpha). \tag{37}$$

In the derivation of Eq. (37) we made the following assumption: near a saddle singularity $(r_s, 0)$ the quantity $p = dr/d\tau$ depends almost linearly on $r_s - r$, so that the time of approach to the critical point is

$$\tau_{cr} \propto \int \frac{dr}{r_* - r},$$

where the integral diverges logarithmically.

Near $\alpha(T) = \alpha_{cr}$ the system exhibits critical behavior and the transition point itself, as well as the nature of the behavior, is governed by the frozen fluctuations. For $\alpha > \alpha_{cr}$, the correlation radius increases in accordance with the law

$$r \propto (\alpha\tau)^{1/2}, \tag{38}$$

i.e., the characteristic flattening time of the fluctuations is

$$t_*/\alpha \propto R_0^2/\beta|c_* - c_0|.$$

As expected, this time decreases as c_0 moves away from the spinodal in the direction of a stable homogeneous state. Figures 3 and 4 show $r(\tau)$ and $\gamma(\tau) \equiv \langle v^3(\tau)\rangle$ for different values of the parameter α. We are using here the results of the previous analysis and Eq. (28). The initial form of all the curves is universal: $\gamma(\tau) \approx 6\tau$. For $\alpha < \alpha_{cr}$, the quantity $\gamma(\tau)$ increases to infinity in a finite time $\tau_c(\alpha)$. For $\alpha > \alpha_{cr}$, then the rise of $\gamma(\tau)$ is replaced by a drop to zero. For $\alpha \gg 1$, the value of γ increases to $\sim 1/\alpha$ in a short time $\sim 1/\alpha$ and then falls to zero in accordance with the square root law: $\gamma(\tau) \propto (\alpha/\tau)^{1/2}$.

The asymmetry of the distribution $\langle v^3(t)\rangle$ generally describes the fact that the local deviations from the average composition of the glass in one direction are considerably greater than deviations in another direction. Naturally, because of the condition $\langle v(t)\rangle = 0$, the total volume of the regions with higher concentrations considerably exceeds that of the regions with the lower concentration. The process of such asymmetric stratification occurs for all values of α; however, it first slows down and then stops completely for large positive values of $\alpha > \alpha_{cr}$. Note that the initial asymmetry of the distribution of the composition ($\gamma_0 \neq 0$) enhances the tendency for spinodal decomposition.

Numerical estimates of typical decomposition times give $\sim 10^3$ s for ≈ 200 °C and of the order of several seconds at ≈ 500 °C. It means that at room and elevated temperatures it should be possible to investigate spinodal decomposition experimentally (for example, by the method of low-angle x-ray scattering).

The limitations of the adopted model impose the restriction that we cannot consider the time close to $\tau_c(\alpha)$. Allowance for the surface energy and the existence of a second spinodal point limits the correlation radius to a value of the order of the interaction radius. There is a corresponding limitation on the magnitude of the fluctuations and on the asymmetry of the distribution function. However, if the scale of the initial fluctuations is sufficiently large, the decomposition time is still governed by the same quantities as in our model.

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