Formation of a kinetically stable domain structure in the process of spinodal decomposition of binary polymer mixtures

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A nonlinear diffusion equation is used to study the process of spinodal decomposition of binary polymer mixtures. An analysis is made of the possibility of existence of kinetically stable spatially inhomogeneous steady-state solutions of the diffusion equation that correspond to partial equilibrium states. A numerical solution of the diffusion equation in combination with a study of the initial (linear) state of the process shows that of all the possible steady-state solutions only the structures with a spatial period of the order of the period corresponding to the maximum gain in the linear theory can be achieved kinetically. Possible paths of the subsequent evolution of the investigated metastable states are considered.

INTRODUCTION

The dynamics of phase separation of a system depends strongly on its viscosity. If the viscosity is low, phase separation begins in the metastable range by nucleation.[1] If the viscosity is sufficiently high for the temperature of the system to relax more rapidly than its composition, then a rapid change in temperature may make the system thermodynamically unstable. A spatially homogeneous state of a system is then destroyed by a process known as spinodal decomposition, the initial stage of which is described using a linearized diffusion equation.[2,3] It is natural to consider the whole phase separation process on the basis of a nonlinear diffusion equation. The analysis in the present study, based on a nonlinear equation, reveals a new intermediate stage of the process, which is typical of spinodal decomposition of polymer systems and is discussed below.

§1. DESCRIPTION OF THE PROCESS IN A LINEAR APPROXIMATION

Thermodynamic properties of a binary polymer mixture consisting of components A and B can be described using the Flory lattice model in terms of a free energy F which is defined (per lattice site) by the following expression[3]:

$$\frac{F}{k_BT}=\frac{F_0}{k_BT}+\frac{a^2(\nabla\varphi)^2}{36\varphi(1-\varphi)},$$
$$\frac{F_0}{k_BT}=\frac{\varphi\ln\varphi}{N_A}+\frac{(1-\varphi)\ln(1-\varphi)}{N_B}+\chi\varphi(1-\varphi). \tag{1}$$

Here, N_A and N_B are the degrees of polymerization of the components; χ is the interaction parameter; φ is the volume fraction of A; a is the average distance between neighboring monomers in a polymer molecule, assumed to be the same for A and B; k_B is the Boltzmann constant; T is the absolute temperature.

We shall assume that a certain initial distribution of the concentrations $\varphi(\mathbf{r}, 0)$ is established in space. We shall describe mathematically the evolution of this distribution by means of the equation

$$\frac{\partial\varphi}{\partial t}=\operatorname{div}\frac{\Lambda}{k_BT}\operatorname{grad}\frac{\delta F}{\delta\varphi}, \tag{2}$$

where Λ is a coefficient defined by the expression[4]

$$\Lambda=\frac{N_e\varphi(1-\varphi)a^2}{N_A(1-\varphi)\tau^A_{\text{micro}}+N_B\varphi\tau^B_{\text{micro}}},$$

here, τ^A_{micro} and τ^B_{micro} are the microscopic relaxation times; N_e is the average number of monomers between the links along the chain; $\mu=\delta F/\delta\varphi$ is the reduced chemical potential[3] which is described by the following expression after calculation of the variational derivative:

$$\frac{\mu}{k_BT}=\frac{1}{N_A}\ln\varphi-\frac{1}{N_B}\ln(1-\varphi)+\frac{1}{N_A}-\frac{1}{N_B}$$
$$+\chi(1-2\varphi)-\frac{a^2\nabla^2\varphi}{18\varphi(1-\varphi)}$$
$$-\frac{a^2(\nabla\varphi)^2}{36}\left(\frac{1}{(1-\varphi)^2}-\frac{1}{\varphi^2}\right). \tag{3}$$

We shall assume that the average concentration in the mixture is φ_0. If the function $\delta\varphi(\mathbf{r}, 0)=\varphi(\mathbf{r}, 0)-\varphi_0$ is represented by a Fourier expansion

$$\delta\varphi(\mathbf{r},0)=\sum_{\mathbf{k}}c(\mathbf{k})e^{i\mathbf{kr}}, \tag{4}$$

then linearization of Eqs. (2) and (3) relative to $\delta\varphi$ yields, subject to Eq. (4), the following expression for $\delta\varphi(\mathbf{r}, t)$ (Ref. 3):

$$\delta\varphi(\mathbf{r},t)=\sum_{\mathbf{k}}c(\mathbf{k})e^{-t/\tau(\mathbf{k})}e^{i\mathbf{kr}}, \tag{5}$$

where

$$\tau^{-1}(\mathbf{k})=$$
$$k^2\Lambda(\varphi_0)\left[\frac{1}{N_A\varphi_0}+\frac{1}{N_B(1-\varphi_0)}-2\chi+\frac{a^2k^2}{18\varphi_0(1-\varphi_0)}\right]. \tag{6}$$

Therefore, the function $\delta\varphi(\mathbf{r}, t)$ can be represented by a superposition of elementary concentration waves. It follows from Eq. (6) that if

$$1/N_A\varphi_0+1/N_B(1-\varphi_0)-2\chi>0$$

(when the system is above the thermodynamic stability boundary in the form of the spinodal), all the elementary concentration waves are damped out; if

$$1/N_A\varphi_0+1/N_B(1-\varphi_0)-2\chi<0$$

there is a critical wave number

$$k_c=\left[\frac{18}{a^2}\left(2\chi-\frac{1}{N_A\varphi_0}-\frac{1}{N_B(1-\varphi_0)}\right)\varphi_0(1-\varphi_0)\right]^{1/2} \qquad (7)$$

such that for $|\mathbf{k}|<k_c$ the corresponding elementary waves $\delta\varphi(\mathbf{k})$ grow exponentially with time. The wave number corresponding to the most rapidly growing modes is given by the expression[2] $k_m = k_c/\sqrt{2}$.

The actual nature of the process at times $t \gg \tau(k_c)$ can be established by a numerical investigation of the nonlinear equation (2).

§2. NUMERICAL MODELING OF THE SPINODAL DECOMPOSITION PROCESS

Equation (2) was solved in the interval $(0, L)$ subject to periodic boundary conditions. The initial condition was a sinusoidal perturbation

$$\varphi(x, 0)=\varphi_0+A\sin(2\pi mx/L),$$

where m is the number of periods which can be fitted in the interval $(0, L)$. In a study of this perturbation on a computer there is no need to assume that m is large. This can be deduced from the following considerations.

Let us assume that there is a unique solution of Eq. (2) in the region $D=(0,L)\times(0,t_*)$ with periodic boundary conditions and that $\varphi(x, 0)$ is a periodic function with a period L/m (m is an integer). Then, the solution in question is a solution of Eq. (2) in the region $D_1=(0,L/m)\times(0,t_*)$ with periodic boundary conditions and with the initial condition $\varphi(x, 0)$ which is extended periodically to D.

Hence, it follows that the period $\varphi(x, 0)$ is a multiple of the period $\varphi(x, t)$ in the problem under discussion. This can be applied directly to the multidimensional case. It is sufficient to take $m = 1$; the identity of the values of the solution at the ends and in the middle of the integral $(0, L)$ provides a good check of a solution of the difference problem (Fig. 1).

Adopting dimensionless variables $\xi = x/a$ and $\tau = t/\tau^A_{\text{micro}}$, and performing a discretization procedure, we obtain the corresponding difference approximation for Eq. (2) (see Appendix 1). The proposed difference scheme was realized in the form of a program.

Figure 1 shows the concentration profiles at different moments in time. The initial data used in the calculations were as follows: $N_e = 50$, $N_A = N_B = 1000$, $\chi = 0.0025$, $\varphi_0 = 0.5$, $A = 0.05$, $\tau^A_{\text{micro}} = \tau^B_{\text{micro}} = 10^{-11}$ sec, $\Delta\xi = (k_c a)^{-1} = 14.91$, $L = d = 10\Delta\xi$ (the spatial period d is in dimensionless coordinates).

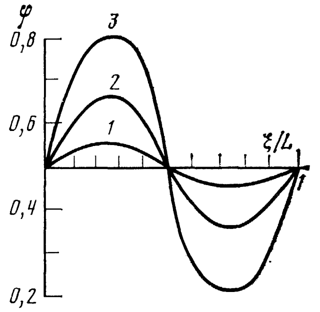

FIG. 1. concentration profiles calculated for different moments in time: 1) $\tau = 0$; 2) $\tau \doteq 1.5\times10^8$; 3) $\tau = 6\times10^8$.

The time taken to establish a steady-state distribution τ_{st} is 8×10^8. A comparison with the characteristic diffusion time $\tau_{\max} = N^3/N_e$, shows that in this case we have $\tau_{\text{st}}/\tau_{\max} = 30$.

A comparison of the establishment time with the time during which a single chain passes through one spatial period $\tau_d = \tau_{\max} d^2/R_0^2$ ($R_0 = N^{1/3}a$ is the diameter of a triangle) shows that τ_d and τ_{st} are quantities of the same order of magnitude.

These numerical experiments demonstrated that the spatial period of the steady-state distribution may be different from the period of the initial distribution if there is a change in the dimensions of the integration region L. For example, when the difference equations are solved with the sinusoidal half-period as the initial condition (see Appendix 1) for $L = 10(k_c a)^{-1}$, the steady-state period is L (Fig. 2a); at $L = 20(k_c a)^{-1}$ the solution period has a tendency to decrease (two humps in Fig. 2b), but subsequently the dip between the two humps filled up and finally the period of the steady-state structure became equal L. It is natural to expect that when L is increased then the periodic structures obtained, out of all the possible steady-state ones, is that with the maximum possible period (i.e., with the period equal to L); such a structure is preferred for thermodynamic reasons because of the minimum number of changes in the sign of the derivative $\delta\varphi/\delta x$ which occur in the interval $(0, L)$. However, if $L = 25(k_c a)^{-1}$, then the steady-state solution is one with the period $L/2$, whereas for $L = 30(k_c a)^{-1}$ the period of the solution is $L/3$ (Fig. 2c) and for $L = 40(k_c a)^{-1}$ the period is $L/4$.

We can thus see that a numerical investigation of the solutions of Eq. (2) has revealed two main facts: firstly, a steady-state distribution of the composition is not homogeneous and, secondly, the period of this distribution is relatively independent of the wavelength of the initial fluctuation.

§3. INVESTIGATION OF STEADY-STATE SOLUTIONS

We shall consider steady-state solutions of Eq. (2) in the case of a single spatial variable on an infinite straight line.

The diffusion flux

$$\frac{\Lambda}{k_BT}\nabla\frac{\delta F}{\delta\varphi}$$

vanishes and hence

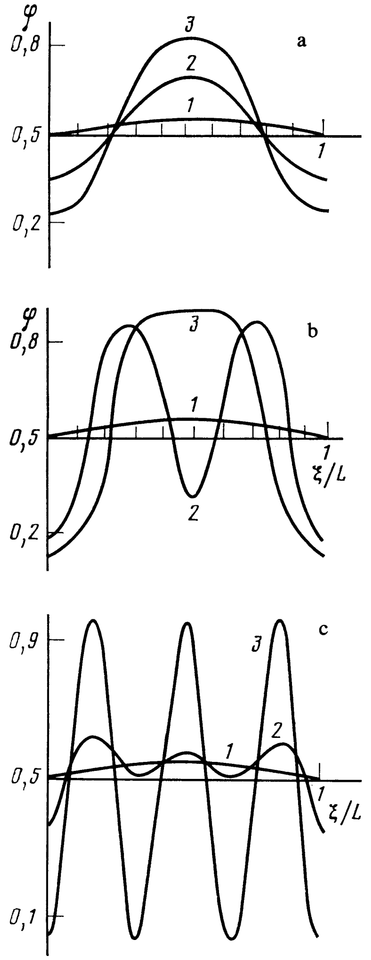

FIG. 2. Kinetics of concentration profiles calculated for various initial conditions: a) same as in Fig. 1, but with a different initial condition (curves 1, 2, and 3 correspond to $\tau=0$, $\tau=0.25\times10^9$, and $\tau=0.65\times10^9$); b) same as a but with a doubled size L of the integration region (curves 1, 2, and 3 correspond to $\tau=0$, $\tau=0.75\times10^9$, and $\tau=3\times10^9$); c) formation of a domain structure on successive increase in L (curves 1, 2, and 3 correspond to $\tau=0$, $\tau=0.4\times10^9$, and $\tau=2\times10^9$).

$$\frac{\partial}{\partial\xi}\left[\tilde{\mu}_0(\varphi)-2K(\varphi)\frac{\partial^2\varphi}{\partial\xi^2}-K_\varphi(\varphi)\left(\frac{\partial\varphi}{\partial\xi}\right)^2\right]=0,$$

where

$$\tilde{\mu}_0=\frac{1}{k_BT}\frac{\partial F_0}{\partial\varphi}=\frac{\ln\varphi}{N_A}-\frac{\ln(1-\varphi)}{N_B}+\frac{1}{N_A}-\frac{1}{N_B}+\chi(1-2\varphi),$$

$$K(\varphi)=\frac{1}{36\varphi(1-\varphi)},\quad K_\varphi=\frac{dK}{d\varphi}.$$

We then find that

$$\tilde{\mu}_0(\varphi)-2K(\varphi)\frac{\partial^2\varphi}{\partial\xi^2}-K_\varphi(\varphi)\left(\frac{\partial\varphi}{\partial\xi}\right)^2=C. \qquad (8)$$

The constant C is found by equating the average concentration to φ_0. This means that among the solutions of Eq. (8) there is one constant solution $\varphi=\varphi_0$. Hence, $C=\mu_0(\varphi_0)$. The integral of Eq. (8) is

$$\tilde{F}_0(\varphi)-\tilde{\mu}_0(\varphi_0)\varphi-K(\varphi)\gamma^2=h,$$

where $\tilde{F}_0=F_0/k_BT$, $\gamma=\partial\varphi/\partial\xi$. The behavior of the phase curves of Eq. (8) was determined qualitatively using the standard methods for investigating conservative systems.[5] Singularities of Eq. (8) are found from the conditions

$$\gamma=0,\quad(\tilde{\mu}_0(\varphi)-\tilde{\mu}_0(\varphi_0))\varphi(1-\varphi)=0.$$

The nature of the functions $\tilde{\mu}_0(\varphi)$ and $\tilde{F}_0(\varphi)$ depends on whether this system is above or below the critical point

$$\chi_{cr}={}^1/_2(1/N_A^{1/2}+1/N_B^{1/2})^2.$$

If the system is above the upper critical point, then for $\varphi_2(\chi)>\varphi_0>\varphi_1(\chi)$, the equation $\tilde{\mu}_0(\varphi)=\tilde{\mu}_0(\varphi_0)$ has three roots, whereas for $\varphi_0>\varphi_2(\chi)$ and $\varphi_0<\varphi_1(\chi)$, it has only one root. [The values $\varphi_1(\chi)$ and $\varphi_2(\chi)$ can easily be found graphically by parallel transfer of the tangents at the points of inflection $\tilde{F}_0$ until they become tangents to the required points.] The singularities $\varphi=0$, $\gamma=0$ and $\varphi=1$, $\gamma=0$ are unstable; the stability of singular points different from $\varphi=0$ and $\varphi=1$ is governed by the sign of the derivative $\delta^2\tilde{F}_0/\delta\varphi^2$ at these points, namely when $\partial^2\tilde{F}_0/\partial\varphi^2>0$ the singularity is stable, whereas for $\partial^2\tilde{F}_0/\partial\varphi^2>0$ it is unstable.

Region 1 of the phase plane (φ,γ) in Fig. 3a represents the range of existence of spatially periodic solutions and it is bounded by a separatrix passing through two unstable singularities. We can easily see that in the linear approximation the periodic paths close to the stable equilibrium position have the period $d_c=2\pi/k_c$, where k_c is given by Eq. (7). The period of the paths increases on approach to the boundary of region 1 (and this is why periodic structures with $d<d_c$ cannot exist) and becomes infinite on the boundary. Boundaries of regions 1, 2, and 3 and paths inside region 4 are kink-type solutions. The solutions corresponding to paths inside regions 2 and 3 are symmetric relative to the origin of the coordinate system and have an extremum at the origin, whereas they tend to zero (region 2) or to unity (region 3) at infinity.

We shall assume that $\varphi_0\in[\varphi_1(\chi),\varphi_2(\chi)]$ and that it approaches one of its ends. Then the stable singularity and one of the unstable ones approach and the singularity obtained for $\varphi_0=\varphi_i(\chi)$, where $i=1$ or 2, is a turning point of the first kind. When φ_0 emerges outside the interval (φ_1,φ_2), this singularity disappears and periodic solutions are no longer possible in the system under consideration (Fig. 3b). A phase picture of the system for $\chi<\chi_{cr}$ obtained for any value of φ_0

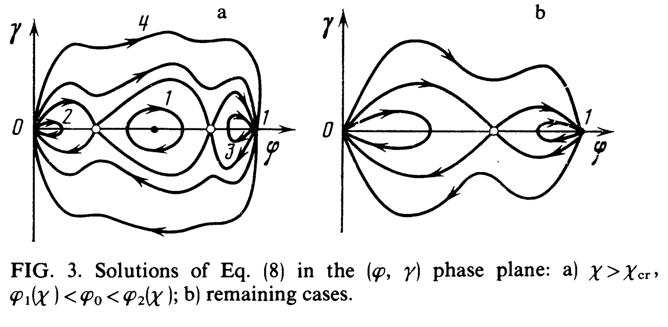

FIG. 3. Solutions of Eq. (8) in the (φ,γ) phase plane: a) $\chi>\chi_{cr}$, $\varphi_1(\chi)<\varphi_0<\varphi_2(\chi)$; b) remaining cases.

does not differ qualitatively from the picture of the system for $\chi > \chi_{\rm cr}$ in the case when $\varphi_0 < \varphi_1(\chi)$ or $\varphi_0 > \varphi_2(\chi)$.

The presence of singularities at $\varphi = 0$ and $\varphi = 1$ is associated with the nature of the function $K(\varphi) = 1/36\varphi(1-\varphi)$. The singularity of $K(\varphi)$ at $\varphi = 0$ and $\varphi = 1$ is due to the fact that the free energy of Eq. (1) cannot be expanded at low concentrations of the components. The correct expression should, as in Ref. 6, contain the nonlocal operator instead of the gradient term in Eq. (1) and then the steady-state solutions no longer have the singularities $\varphi = 0$, $\gamma = 0$ and $\varphi = 1$, $\gamma = 0$. In this case the phase curves in regions 2, 3, and 4 no longer begin or end at these points, i.e., the corresponding solutions are localized in finite spatial intervals. We are not interested in solutions over the whole straight lines; if $\chi > \chi_{\rm cr}$ and $\varphi_0 \in [\varphi_1(\chi), \varphi_2(\chi)]$ then the required solutions are periodic solutions in region 1, boundary of region 1, and spatially homogeneous solution (center of region 1); in the remaining cases only the spatially homogeneous (saddle point in Fig. 3b) solution remains.

It therefore follows that the very possibility of existence of nontrivial steady-state spatial distributions of the concentrations is due to the structure of the free energy functional which is close to the structure of the Ginzburg-Landau Hamiltonian[7] [the difference is in the appearance of asymmetry-contributing terms $\delta\varphi$ and $\delta\varphi^3$ in the expansion of Eq. (1) in terms of $\delta\varphi$].

The absolute minimum of the free energy F corresponds to the energy constant $h = 0$, whereas for periodic distributions corresponding to $h \neq 0$, there is only a local minimum of F. In other words, these periodic distributions correspond to partial equilibrium states. Therefore, a selection of a specific steady-state distribution is not determined by whether it is favorable from the thermodynamic point of view. The circumstance that the characteristic spatial scales of the structures found by numerical calculations are close to the length $d_m = 2\pi/k_m$ leads to the conclusion that the kinetics of the process has the dominant influence already in the linear stage.

§4. KINETICALLY ATTAINABLE PARTIAL EQUILIBRIUM STATES

It follows from the nature of the gain defined by Eq. (6) that the harmonics with $k_m^2 = k_c^2/2$ are amplified more than the others. During the early stages of spinodal decomposition we can use a linear theory and then the harmonics with $k^2 = k_m^2$ mask all the others. Therefore, selection of the period is governed by the kinetic and not by the thermodynamic preference at the beginning of the process, and restrictions on the exponential growth of fluctuations are imposed at later stages by "activation" of the nonlinear terms in Eq. (2).

We note now that in the case of a problem with periodic boundary conditions there may be a finite number of periods with $d_n = L/nd_c$. Among these there are always two periods competing in respect of the proximity to $d_m = 2\pi/k_m$. Clearly, they are equal to L/n and $L/(n+1)$ for a certain value of n; one of them is slightly larger and the other slightly smaller than d_m. If we now alter L, we find that for a discrete number of values of L_n, both L_n^{-2} and L_{n+1}^{-2} are quite close to d_m^{-2} and on passing through these values the kinetically preferred period changes from L/n to $L/(n+1)$. The condition from which L_n is found is

$$d_m^{-2} - (L_n/(n+1))^{-2} = (L_n/n)^{-2} - d_m^{-2}, \tag{9}$$

which gives

$$L_n = d_m(n^2+n+{}^1/_2)^{1/2}. \tag{10}$$

The values of the period before and after the abrupt change are

$$\begin{aligned} d(L_n-0) &= \frac{L_n}{n} = d_m\left(\frac{n^2+n+{}^1/_2}{n^2}\right)^{1/2}, \\ d(L_n+0) &= \frac{L_n}{n+1} = d_m\left(\frac{n^2+n+{}^1/_2}{(n+1)^2}\right)^{1/2}. \end{aligned} \tag{11}$$

The magnitude of the period discontinuity is

$$\begin{aligned} \Delta d_n = d(L_n+0) - d(L_n-0) &= -\frac{L_n}{n(n+1)} \\ &= -d_m\left(\frac{n^2+n+{}^1/_2}{n^2(n+1)^2}\right)^{1/2}. \end{aligned} \tag{12}$$

It follows that when the size of the one-dimensional region is altered, the steady-state period exhibits a finite number of bifurcations; the values of L_n and the parameters of the discontinuities are described by Eqs. (10)-(12). In the intervals from $L_n + 0$ to $L_{n+1} - 0$ the period clearly changes linearly (Fig. 4). It is clear from Fig. 4 that if $L < d_c$, there are no steady-state structures. The first bifurcation halves the period. The subsequent discontinuities become smaller and for large values of n the bifurcation occurs at $L_n \approx d_m(n+1/2)$ and the period tends to d_m {in fact, we can easily show that $L_n \in [d_m n, d_m(n+1)]$ and $L_n - d_m n \to 1/2$ as $n \to \infty$}.

The proposed description accounts qualitatively for the numerical results obtained above. [It should be pointed out that the value of L_n found from Eq. (10) and its estimates deduced from the results of numerical experiments are different. For example, L_1 is estimated (Fig. 2b) to be $20(k_c a)^{-1}$, whereas Eq. (10) gives $L_1 = d_c\sqrt{5} \approx 14(k_c a)^{-1}$. These discrepancies are explained by the fact that in the linear description of the period bifurcations we cannot allow for the spatial linkage between the growths of neighboring humps. The "precursors" of the first bifurcation of the period, governed by the two-hump nature of the concentration profile, appear already for $L = 15(k_c a)^{-1}$, but because of the nonlinearity of the initial equation the bifurcation itself occurs at higher

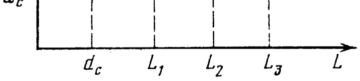

FIG. 4. Dependence of the period being established on the dimensions of the region.

values of L. Therefore, in reality the sequence of Eq. (10) corresponds to a series of values of L_n slightly greater than the values obtained in the linear approximation.]

It follows that competition between the thermodynamic preference and the kinetic attainability, discussed in Ref. 6 in connection with coil-spherulite transitions, is observed particularly clearly in the present case. In spite of the fact that the steady-state distribution that oscillates the minimum number of times corresponds—among the finite number of possible structures—to a minimum of the free energy functional (1), this distribution cannot be attained because it is not kinetically preferred since the difference between its period and d_m is large.

We might gain an impression that the thermodynamically most preferable state can never be achieved because the period d is finite. In reality this is not true because in the case of initial distributions close to those preferred for thermodynamic reasons the linear theory based on the expansion near the average value φ_0 can be immediately found to be inapplicable (the expansion is only valid for small deviations from φ_0, whereas at large values of L the thermodynamically preferred structures correspond to large deviations from φ_0). In this case the expansion should be carried out near a steady-state distribution which varies in space but is thermodynamically preferred. This problem is analogous to an investigation of the stability of steady-state distributions. The coefficients in front of the unknown function $\delta\varphi(x, t)$ in the linearized equation (2) become dependent on the steady-state solution and the problem of determination of the kinetically preferred period becomes much more difficult. We shall not consider it here, although it is quite clear that in the case of the initial distributions close to the thermodynamic minimum the concepts of the kinetic attainability and thermodynamic preference are identical.

The reasoning concerning the bifurcation of the period as a result of a change in the dimensions of the region under consideration can be applied to the case of k spatial variables. We shall be interested in the bifurcations of the components of the vector function $d = (d_1, \ldots, d_k)$, specified in a space of the dimensions of k-dimensional parallelepipeds, where a parallelepiped is described by a vector of dimensions $\mathbf{L} = (L_1, \ldots, L_k)$ and $L_i \geqslant 0$. The kinetic preference criterion remains the same. We can easily see that the bifurcations cannot occur simultaneously for several components of $\mathbf{d}$ (because in this case there is a suitable vector closer to a sphere of radius d_m).

The bifurcation surfaces for the component j are found from a condition similar to Eq. (9):

$$2\sum_{i=1}^{j-1}\left(\frac{L_i}{n_i}\right)^{-2}+2\sum_{i=j+1}^{k}\left(\frac{L_i}{n_i}\right)^{-2}+L_j^{-2}(2n_j^2+2n_j+1)=2d_m^{-2},$$
$$\frac{L_j}{n_j+1}\geqslant\frac{L_i}{n_i+1}. \tag{13}$$

The system of inequalities appears in Eq. (13) because when they are not satisfied, there is a more suitable vector $\mathbf{d}$ in the sense of the kinetic preference. The expression for L_j follows from Eq. (13):

$$L_j=\left\{\left[d_m^{-2}-\sum_{i=1}^{j-1}\left(\frac{L_i}{n_i}\right)^{-2}-\sum_{i=j+1}^{k}\left(\frac{L_i}{n_i}\right)^{-2}\right]\times\left(n_j^2+n_j+\frac{1}{2}\right)^{-1}\right\}^{-1/2}$$
$$L_j\geqslant L_i\frac{n_j+1}{n_i+1}. \tag{14}$$

Using Eq. (14), we obtain the parameters of the discontinuities from the formulas

$$d_j(L_j-0)=L_j/n_j,\quad d_j(L_j+0)=L_j/(n_j+1),$$
$$\Delta d_j=-L_j/n_j(n_j+1). \tag{15}$$

It is clear from Eqs. (14) and (15) that the bifurcation surfaces for each component j are labeled by k natural numbers and represent sections of k-dimensional pseudoellipsoids with semiaxes which are functions of n_i lying within the ranges where the inequalities of Eq. (13) are obeyed. Families of surfaces for different values of j intersect and at the points of intersection there may be an abrupt change in the value of each of the components d_j. Figure 5 shows the bifurcation lines for L_1 ($k = 2$ and $j = 1$). The lines for L_2 are obtained by relabeling of the axes. There are no steady-state solutions in the range $L_1^{-2} + L_2^{-2} > d_c^{-2}$.

We can see that the structure of the bifurcation surfaces is very complex, but we can expect that in the multidimensional case (or at least along one of the spatial dimensions) there is always a kinetically stable periodic structure with a scale close to d_c. Depending on the structure of the initial distribution $\varphi(\mathbf{r}, 0)$, it may belong to one of three types (in a three-dimensional space): spherical, layered, or cylindrical.

CONCLUSIONS

The fact that the above theory does not describe the coalescence stage, i.e., the transition to a complete thermo-

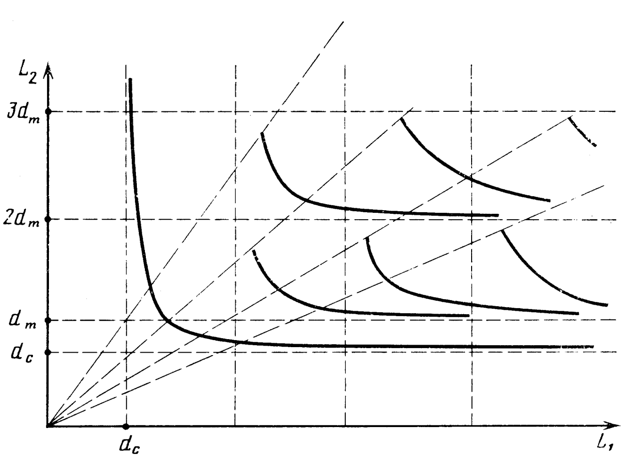

FIG. 5. Bifurcation lines for L_1.

dynamic equilibrium, is related to the approximate nature of Eq. (2). This equation ignores two fundamental factors.

Firstly, as shown in Appendix 2, the true relaxation equation is not local, in contrast to Eq. (2). The absence of an explicit dependence on the spatial coordinate imposes nonphysical restrictions on the cooperative behavior of a system and on the selection of a kinetically preferred steady-state structure, because the appearance of a characteristic size *d* of the initial distribution which is at first glance unrelated to the physics of the process of spinodal decomposition.[1] For example, if the initial distribution has *n* periods in the interval [0, *nd*], then the kinetically preferred period is given by the expression *dn/k*, where *k* is divisible by *n*; however, a slight change in the initial condition which makes it nonperiodic has the effect that *k* is no longer divisible by *n* (this is the general situation described in the preceding section). We can see that the dependence of the equation in respect of the spatial coordinate may result in a structural instability of the solution, i.e., it may alter greatly the period of the steady-state structure for a small change in the initial condition. The nonlocal nature of the correct equation should, however, suppress this structural instability. In fact, it follows from physical considerations that the processes of formation of macroscopic phases are related specifically with the cooperative behavior of a system on a larger scale; the cooperative behavior is a synonym for the nonlocal nature of the diffusion process.

Secondly, the correct equation contains a random external field which reflects the influence of small-scale fluctuations. After a long time it may result in the overcoming of a barrier separating the kinetically stable structures described above from those which are thermodynamically preferred. Further studies with allowance for both these factors are needed.

It follows that a qualitative picture of spinodal decomposition is as follows. During the first stage in a time $t \sim \tau_{\rm st}$ a kinetically stable structure is established and it depends on the initial distribution. We can apply here the local theory developed above. Then, after times $\tau_{\rm st} \ll t \ll \tau_n$ there is a slow change in this structure which results in the initial distribution being "forgotten" (this removes the structural instability of the system mentioned above).

The ratio $\tau_{\rm st}/\tau_n$ can be a small parameter in view of the smallness of the ratio R_0/d_m.

Coalescence may be expected after times much longer than τ_n because of the influence of real boundaries of the system or because of noise.

APPENDIX 1

The difference scheme can be written in the form

$$\varphi_{i,n+1}-\varphi_{i,n}=\frac{1}{2}\left(A_{i1,n}B_{i1,n}+A_{i,n}B_{i,n}\right)\left(\varphi_{i1,n}-\varphi_{i,n}\right)$$

$$\times\frac{\Delta\tau}{(\Delta\xi)^2}-\frac{1}{2}\left(A_{i1,n}+A_{i,n}\right)$$

$$\times\left(\varphi_{i2,n}-3\varphi_{i1,n}+3\varphi_{i,n}-\varphi_{i3,n}\right)\frac{\Delta\tau}{(\Delta\xi)^4}-\frac{1}{2}\left(D_{i1,n}A_{i1,n}+D_{i,n}A_{i,n}\right)$$

$$\times\left(\varphi_{i1,n}-\varphi_{i,n}\right)^3\frac{\Delta\tau}{(\Delta\xi)^4}+\frac{1}{2}\left(E_{i1,n}A_{i1,n}+E_{i,n}A_{i,n}\right)\left(\varphi_{i1,n}-\varphi_{i,n}\right)$$

$$\times\left(\varphi_{i2,n}-\varphi_{i1,n}-\varphi_{i,n}+\varphi_{i3,n}\right)\frac{\Delta\tau}{(\Delta\xi)^4}+\frac{1}{2}\left(A_{i,n}B_{i,n}+A_{i3,n}B_{i3,n}\right)$$

$$\times\left(\varphi_{i3,n}-\varphi_{i,n}\right)\frac{\Delta\tau}{(\Delta\xi)^2}+\frac{1}{2}\left(A_{i3,n}+A_{i,n}\right)$$

$$\times\left(\varphi_{i4,n}-3\varphi_{i3,n}+3\varphi_{i,n}-\varphi_{i1,n}\right)\frac{\Delta\tau}{(\Delta\xi)^4}$$

$$-\frac{1}{2}\left(D_{i3,n}A_{i3,n}+D_{i,n}A_{i,n}\right)\left(\varphi_{i3,n}-\varphi_{i,n}\right)^3\frac{\Delta\tau}{(\Delta\xi)^4}$$

$$+\frac{1}{2}\left(E_{i3,n}A_{i3,n}+E_{i,n}A_{i,n}\right)$$

$$\times\left(\varphi_{i3,n}-\varphi_{i,n}\right)\left(\varphi_{i4,n}-\varphi_{i3,n}-\varphi_{i,n}+\varphi_{i1,n}\right)\frac{\Delta\tau}{(\Delta\xi)^4},\qquad i=1,\ N_{nd}.$$

Here, $\Delta\xi$ and $\Delta\tau$ are the steps in space and time, N_{nd} is the number of nodes in a difference network,

$$D_{i,n}=\frac{\varphi_{i,n}+(1-\varphi_{i,n})^3}{\varphi^2_{i,n}(1-\varphi_{i,n})^2},\qquad E_{i,n}=\frac{(1-\varphi_{i,n})^2-\varphi^2_{i,n}}{\varphi_{i,n}(1-\varphi_{i,n})},$$

$$A_{i,n}=\frac{N_e}{18[N_A(1-\varphi_{i,n})+N_B\varphi_{i,n}\tau^B_{\rm micro}/\tau^A_{\rm micro}]}$$

$$B_{i,n}=18\left[\frac{\varphi_{i,n}}{N_B}+\frac{1-\varphi_{i,n}}{N_A}-2\chi\varphi_{i,n}(1-\varphi_{i,n})\right],$$

$$i1=i+1\ \text{for}\ 1\leqslant i<N_{nd},\quad i1=1\ \text{for}\ i=N_{nd},$$

$$i2=i+2\ \text{for}\ 1\leqslant i<N_{nd}-1,\quad i2=1\ \text{for}\ i=N_{nd}-1,$$

$$i2=2\ \text{for}\ i=N_{nd};$$

$$i3=i-1\ \text{for}\ 1<i\leqslant N_{nd},\quad i3=N_{nd}\ \text{for}\ i=1;$$

$$i4=i-2\ \text{for}\ 2<i\leqslant N_{nd},\quad i4=N_{nd}\ \text{for}\ i=2,$$

$$i4=N_{nd}-1\ \text{for}\ i=1.$$

The adopted two-layer difference scheme is explicit in time, and this imposes restrictions on $\Delta\tau$. In a numerical solution of the problem (2) it is more effective to apply implicit methods, for which the maximum possible time step can be considerably greater. A check of the stability of the calculations and of convergence to the solution of the initial equation is made by comparing the results obtained on reduction in the time and space steps. Moreover, in each time layer a check is made of the balance condition

$$\frac{\partial}{\partial t}\int_0^L\varphi(x,t)\,dx=0$$

and of the above condition of the space periodicity of $\varphi(x,t)$.

Numerical experiments show that for large periods of the initial perturbation the solution $\varphi(x,t)$ may lie beyond the limits of physical validity. This can be explained as follows: the surface energy which is responsible for the formation of structures is concentrated at relatively large values of *d* in small (compared with the spatial extent of the ground states) regions (this follows from an analysis of the periodic phase paths of the steady-state problem close to the boundary of region 1 in Fig. 3a; the corresponding concentration profiles are obtained from one another and the period d is increased by elongation along the spatial axis and then the ratios of the lengths of the regions corresponding to an abrupt change in φ in the surface layer to the length of the horizontal regions corresponding to the ground states tend to zero in the limit $d \to \infty$). The step in space in the difference scheme should be less than the size of these regions, i.e., it should be of the order of $(k_c a)^{-1}$. In the case of large d such a step is impossible to use because machine calculations would be too long. In the selection of the step considerably greater than the thickness of the surface layer we in fact exclude the gradient term from Eq. (2) and solve numerically the equation for outdiffusion which grows without limit beyond the spinodal for $t \to \infty$ (Ref. 8).

Figure 2a shows the concentration profiles at different times; the initial condition is half the period of a sinusoid. The initial data on the period are the same as in the preceding calculations, except that

$$\Delta\xi = {}^1/_2 (k_c a)^{-1}, \quad L = 10 (k_c a)^{-1}, \quad d = 20 (k_c a)^{-1}.$$

The time for the establishment of the steady state is $\tau_{\text{st}} = 0.65 \times 10^9$.

Calculations carried out assuming that $\Delta\xi = (k_c a)^{-1}$, $L = 20(k_c a)^{-1}$, $d = 40(k_c a)^{-1}$ give at $\tau = 3 \times 10^9$ a solution which is outside the physical validity range. However, when calculations are carried out using $\Delta\xi = 1/2(k_c a)^{-1}$, $L = 20(k_c a)^{-1}$, $d = 40(k_c a)^{-1}$ (corresponding to a doubling of the nodes in the same interval), a steady-state distribution is established in a time $\tau_{\text{st}} = 3 \times 10^9$ (Fig. 2b). It should be noted that the results shown in Fig. 4 were checked for different steps in time: the unlimited rise of $\varphi(x, t)$ is due to the fact that the surface layer cannot be "calculated satisfactorily" for the selected step. Therefore, in contrast to the usual situation encountered in difference solutions of evolution equations, such as the nonlinear heat conduction equation, when for any value of $\Delta\xi$ there is a stability threshold of the difference scheme $\Delta\tau$, in our case there is such a value of $\delta\xi_*$ that if $\Delta\xi \gtrsim \Delta\xi_*$, then the difference scheme may be unstable for any reduction in the time step.

APPENDIX 2

For the sake of simplicity, we shall consider a symmetric case of a mixture of A_N-mers and B_N-mers with equal average volume fractions $\bar{\varphi}_A = \bar{\varphi}_B = 1/2$. The relaxation equation for the density of monomers belonging to some specific chain S is meaningful because of the macroscopic nature of the chains, and in the linear theory[7] this equation can be written in the form

$$\partial\rho_S/\partial t = \nabla^2 \hat{\Lambda} [\hat{g}^{-1} \rho_S - \varepsilon],$$

where $\varepsilon(\mathbf{r}, t)$ is the molecular field acting on a point r at a moment t and affecting each chain link A (for links B this field has the opposite sign) and the kernels of the nonlocal operators of the kinetic Onsager coefficients $\hat{\Lambda}$ and of the correlation functions $\hat{g}$ can be calculated by methods of statistical theory.[9] The field ε consists of a regular contribution which is governed by the deviation of the local composition of the mixture from equilibrium and a random force which is a source of chain fluctuations: $\varepsilon(\mathbf{r}, t) = \varepsilon_p(\{\varphi(\mathbf{r}, t)\}) + \delta$. Both contributions to ε depend on the local composition and on its space and time derivatives, exactly as in the case of linear relaxation. (This is true if the characteristic scale of collective relaxation of the system is small compared with the corresponding scale of relaxation of individual macromolecules.) Therefore, they can be obtained by comparing the results of summation of both parts of the above equation over all macromolecules of the system with the linearized form of the de Gennes equation, which finally gives

$$\partial\psi(\mathbf{r}, t)/\partial t - \nabla^2 \hat{\Lambda}_S [\hat{g}_S^{-1} - (\chi/2)(1 - \psi^2)] \psi = \Delta_c,$$

where $\psi = \varphi_A - \varphi_B = 2\varphi_A - 1$, and Δ_c is a corresponding random force. [The approximation for the integral operators $\hat{\Lambda}_s$ and $\hat{g}_s$ with differential operators of the lowest nonzero order gives Eq. (2).] It should be pointed out that the physical idea of the above conclusion—that on a relatively small scale the relaxation is linear and the nonlinearity appears as a consequence of modulation of molecular fields on a large scale—clearly corresponds to the familiar Landau-Khalatnikov approximation.[1]

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1) In the case of real systems this scale is governed by the correlation radius representing the system before the onset of cooling. Therefore, the results obtained are strictly speaking applicable to the situation when before strong cooling the system is in equilibrium quite close to the spinodal.

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