# Nonlinear stage of spinodal decomposition in multilayered structures

A. S. Mel'nikov, I. M. Nefedov, A. A. Fraerman, and I. A. Shereshevskiĭ

*Institute of the Physics of Microstructures, Russian Academy of Sciences, 603600 Nizhniĭ Novgorod, Russia*

(Submitted 30 June 1995)
Zh. Éksp. Teor. Fiz. **109**, 683–688 (February 1996)

The nonlinear stage of spinodal decomposition in multilayered structures is investigated using the Cahn-Hillard equation. It is shown that in such a system diffusion-controlled relaxation involves a doubling of the period and that the precise scenario of this doubling depends sensitively on the total number of films in the structure. © *1996 American Institute of Physics.* [S1063-7761(96)02502-1]

The nonlinear stage of spinodal decomposition in multilayered structures is investigated in the present work. The interest in this problem is due primarily to the active investigation and diverse applications of multilayered structures consisting of ultrathin (~1 nm) metal films with limited solubility.[1] In solid solutions with limited solubility two phases differing with respect to the concentrations of the components coexist below the phase-separation temperature. Such a situation is realized, for example, in Fe/Cr, Co/Cu, and some other solid solutions. In a multilayered structure consisting of films with equilibrium concentrations, interdiffusion is suppressed, and an increase in its thermostability can be expected. However, it was shown in Ref. 2 that the one-dimensional periodic distribution of the concentration is unstable with respect to fluctuations of the film boundaries and that the growth rate of this instability increases with decreasing film thicknesses. Here we investigate the nonlinear stage of this process and show that in multilayered structures diffusion-controlled relaxation involves a doubling of the period and that the precise scenario of this doubling depends sensitively on the total number of films in the structure.

Let us consider a substitutional solid solution consisting of atoms of two kinds ($A$ and $B$), where the concentration of atoms of type $A$ is equal to $c$. The free energy of the decomposing solution has the form

$$F=\int\left[\frac{1}{2}\,\gamma(\nabla c)^2-\frac{1}{2}\,\alpha(c-c_0)^2+\frac{1}{4}\,\beta(c-c_0)^4\right]d\mathbf{r},\tag{1}$$

where $\alpha$, $\beta$, and $\gamma$ are positive coefficients, and $c_0$ is the mean concentration of the solution. For the equilibrium concentrations of the phases we have

$$c_e^{(1,2)}=c_0\pm\sqrt{\frac{\alpha}{\beta}}.\tag{2}$$

The diffusion-controlled relaxation equation

$$\frac{\delta c}{\delta t}-D\Delta\,\frac{F}{c}=0\tag{3}$$

in the dimensionless variables

$$c=(c-c_0)\sqrt{\frac{\beta}{\alpha}},\quad t=t\left(\frac{D\alpha^2}{4\gamma}\right),\quad r=r\sqrt{\frac{\alpha}{2\gamma}}$$

($D$ is a kinetic coefficient) takes the form of the Cahn-Hillard equation

$$\frac{\partial c}{\partial t}=-\Delta(\Delta c+2(c-c^3)),\tag{4}$$

and the equilibrium concentrations $c_e^{(1,2)}$ have the values ±1. Let us consider the evolution of the initial distribution corresponding to a multilayered structure of films with equilibrium concentrations:

$$c(z,t=0)=\sum_{n=1}^{N}(-1)^n\tanh(z-z_n(t=0)),\tag{5}$$

where $z_n$ is the coordinate of the $n$th boundary and $N$ is the total number of boundaries. We note that each of the terms in (5) is a solution of Eq. (4) when $\partial c/\partial t=0$. The first pair of boundary conditions for Eq. (4) imply the absence of diffusive fluxes on the boundaries:

$$j=\frac{\partial}{\partial z}\left(\frac{\partial^2 c}{\partial z^2}+2(c-c^3)\right)\Bigg|_{z=0,L}=0,\tag{6}$$

where $L$ is the total length of the structure. If surface segregation effects (see, for example, Ref. 3) are ignored, the second pair of boundary conditions has the form

$$\left.\frac{\partial c}{\partial z}\right|_{z=0,L}=0.\tag{7}$$

We have solved problem (4)–(7) analytically and numerically. The analytical solution is based on an assumption that the distortion of the shape of the boundaries as they move during the relaxation process is weak. We seek a solution of Eq. (4) in the form

$$c(z,t)=u(z,t)+\sum_{n=1}^{N}(-1)^n\tanh(z-z_n(t)).\tag{8}$$

Assuming that the rate of motion of the boundaries $V_n\partial z_n/\partial t$ and the correction $u(z,t)$ are small and that the process is steady-state ($\partial u/\partial t=0$), after integrating twice we obtain

$$\frac{\partial^2 u}{\partial z^2}-4u+6u\sum_{n=1}^{N}\cosh^{-2}(z-z_n(t))$$

$$=\sum_{n=1}^{N}(-1)^n V_n \ln\cosh(z-z_n(t))$$

$$+2\left\{\left[\sum_{n=1}^{N}(-1)^n\tanh(z-z_n(t))\right]^3\right.$$

$$\left.-\sum_{n=1}^{N}(-1)^n\tanh^3(z-z_n(t))\right\}+az+b, \qquad (9)$$

where $a$ and $b$ are integration constants.

We expand $u(z,t)$ in the eigenfunctions $\varphi_\lambda$ of the operator $\hat{H}$:

$$u=\sum_\lambda g_\lambda\varphi_\lambda,$$

$$g_\lambda=-\frac{1}{\lambda+4}\int_0^L f(z,t)\varphi_\lambda(z,t)dz,$$

$$\hat{H}=-\frac{\partial^2}{\partial z^2}-6\sum_{n=1}^{N}\cosh^{-2}(z-z_n).$$

Here $f(z)$ is the right-hand side of Eq. (9), and $\lambda$ denotes the eigenvalues of $\hat{H}$. The equation for the eigenfunctions $\varphi_\lambda$ has the form of the Schrödinger equation for a particle in a field of $N$ potential wells. Recalling the assumption that the correction $u(z,t)$ is small, we require that $f(z,t)$ be orthogonal to all the functions $\varphi_\lambda$ corresponding to $\lambda\simeq-4$. To within terms of order $\exp(-2(z_n-z_{n-1}))$, the eigenfunctions $\varphi_\lambda$ are $N$ linearly independent combinations of the functions $\cosh^{-2}(z-z_n)$, which are solutions of the Schrödinger equation for an isolated well centered at the point $z=z_n$ and $\lambda=-4$. As a result, we have the $N$ conditions

$$\int_0^L\frac{f(z)dz}{\cosh^2(z-z_n)}=0. \qquad (10)$$

The boundary conditions (6) take the form

$$a=\sum_{n=1}^{N}(-1)^n V_n=0, \qquad (11)$$

which corresponds to maintenance of the mean concentration as the phase boundaries move. Thus, we have a system of $N+1$ equations for determining the coordinates of the boundaries $z_n$ and the constant $b$:

$$\sum_{n=1}^{N}(-1)^n V_n\frac{z_m-z_n}{\tanh(z_m-z_n)}+(-1)^m 16[\exp(-2l_{m+1})$$

$$-\exp(-2l_m)]+b\approx 0, \quad m=2,3,\ldots,N-1,$$

$$\sum_{n=1}^{N}(-1)^n V_n\frac{z_1-z_n}{\tanh(z_1-z_n)}-16\exp(-2l_2)+b=0,$$

$$\sum_{n=1}^{N}(-1)^n V_n\frac{z_N-z_n}{\tanh(z_N-z_n)}-(-1)^N 16\exp(-2l_N)+b=0,$$

$$\sum_{n=1}^{N}(-1)^n V_n=0. \qquad (12)$$

Here $l_m=z^m-z_{m=1}$ is the thickness of the $m$th film. From the system of equations (12) it follows that the variations in the concentration distribution are due to the "interaction" of the boundaries and are small when the film thicknesses are small in comparison with the width of a phase boundary, which is of the order of unity in our variables. When this condition is satisfied, the assumptions made regarding the smallness of $V_n$ and $u(z,t)$ are justified. The derivative $\partial u/\partial t$ is $\sim V^2$, and, thus, the condition for a steady-state diffusion process is satisfied. In the derivation of Eqs. (12) we neglected terms of order $\exp(-2(l_m+l_{m+1}))$. Nevertheless, the motion of the $m$th boundary depends on the thicknesses of all the films in the multilayered structure, and this fact is formally expressed in the structure of the first term in Eqs. (12). This nonlocality is due to the interaction of the phase boundaries through the diffusion field of the solute atoms. We note that an interaction of this type is dominant in the case of two and three measurements and can be described in the Lifshits-Slezov model.[4]

We investigate the instability of an unrestricted multilayered structure with a period $2d$. For this purpose we seek a solution of Eqs. (12) in the form

$$z_n(t)=nd+\delta_n(t), \quad |\delta_n|\ll 1. \qquad (13)$$

Then for $\delta_n$ we obtain

$$\frac{d\delta_n}{dt}=-\frac{16\exp(-2d)}{d}(\delta_{n+2}-2\delta_n+\delta_{n-2}). \qquad (14)$$

It follows from (14) that the multilayered structure is absolutely unstable with respect to fluctuations of the thicknesses. The dependence of the fluctuation growth rate on the wave number $k$,

$$\lambda(k)=\frac{64\exp(-2d)}{d}\sin^2(kd), \quad 0\leqslant k\leqslant\frac{\pi}{d}, \qquad (15)$$

has a maximum at $k=\pi/2d$, which reflects a tendency to double the period. The expression (15) coincides with the growth rate obtained in Ref. 2.

Let us consider the case of four films having an initially identical thickness. From the symmetry of the problem it follows that

$$V_2=V_1+V_3=0. \qquad (16)$$

From the system of equations (12) we have $b=0$. Figure 1(a) displays the time dependence of the film boundaries. The thicknesses of the outermost films increase, while those of the central films decrease. The dependence of the dissolution time of the central films on the initial thickness $d$ has the form (Fig. 1b)

$$T=\frac{d-1}{16}\exp(2d). \qquad (17)$$

The crosses in Fig. 1b represent the results of the numerical solution of the problem (4)–(7) based on a splitting method.[5] Films of doubled thickness form after a time $T$.

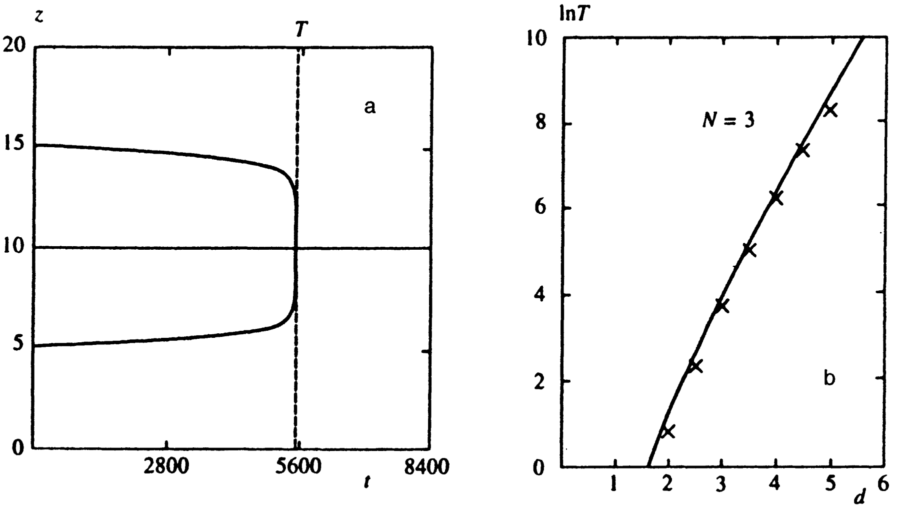

FIG. 1. a) Time dependence of the coordinates of the film boundaries ($N=3$, $d=5$); b) dependence of the logarithm of the dissolution time $T$ on the initial film thickness; solid line—calculation based on Eq. (17); ×—results of numerical simulation.

As the number of films is increased, the dynamics of the system becomes increasingly nontrivial. Figure 2a shows plots of the dependence of the coordinates of the boundaries in a multilayered structure of 16 films obtained as a result of a numerical solution of the problem. In this case the 3rd and 14th films dissolve first. The dependence of the dissolution time of these films on the initial thickness $d$ is presented in Fig. 2b. We observe (as in the case of four films) good agreement between the results of the analytical solution and the direct numerical simulation. The 8th and 9th films dissolve next. As a result, we have a structure with film thicknesses equal to $\sim 2d$.

Thus, the dynamics of diffusion-controlled relaxation in a multilayered structure resulting in doubling of the period has been investigated in this work. The actual agreement between the results of the numerical and analytical solutions of the problem confirms the correctness of the conception of phase boundaries moving without distortion for the case considered. The dependence of the precise scenario of the doubling on the total number of films in the structure is a consequence of the nonlocal interaction of the film boundaries. Although the rate of the process under consideration decreases exponentially with increasing layer thickness, this rate can be quite appreciable for ultrathin films. If it is assumed that the thickness of a phase boundary is $\sim a$ ($a$ is the interatomic distance) and that the period of the multilayered structure is $\sim 10a$, the diffusion rate decreases by about 30 fold. Nevertheless, owing to the large diffusion coefficient, this decrease can be insufficient for creating thermostable structures. On the other hand, this circumstance makes it possible to experimentally observe the effects considered in this communication.

We thank K. A. Gorshkov for some valuable comments and A. V. Shpiro for helping to perform the numerical calculations, as well as the participants in a seminar of the Department of Solid-State Physics of the P. N. Lebedev Physics Institute for discussing the results of this study. This work was carried out with financial support from the Russian Fund for Fundamental Research (grant No. 94-02-04380) and the International Science Foundation (grant No. R8R000). One of us (A.S.M.) acknowledges the financial support of the

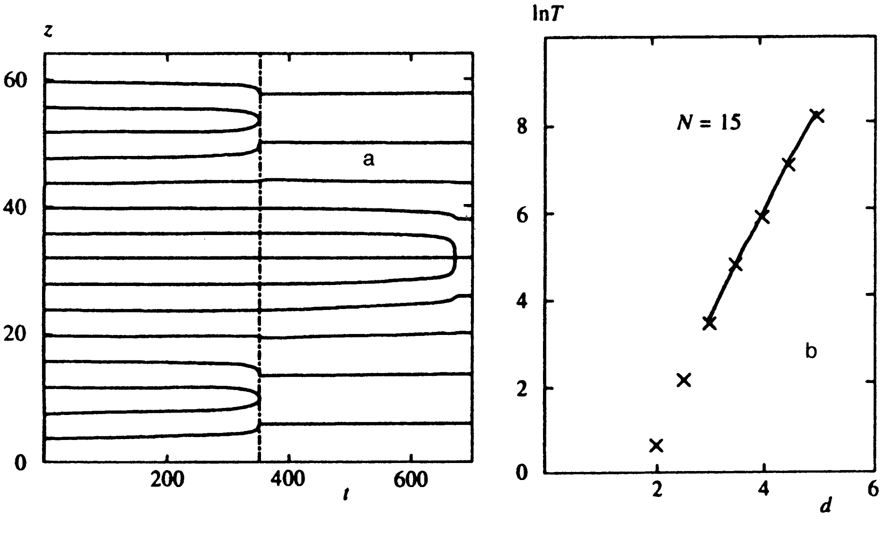

FIG. 2. a) Time dependence of the coordinates of the film boundaries ($N=15$, $d=4$); b) dependence of the logarithm of the dissolution time $T$ on the initial film thickness; solid line—solution of the system of equations (12); ×—results of numerical simulation.