

Research Letter

The Spatiotemporal Oscillations of Order Parameter for Isothermal Model of the Surface-Directed Spinodal Decomposition in Bounded Binary Mixtures

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The asymptotical behavior of order parameter in confined binary mixture is considered in one-dimensional geometry. The interaction between bulk and surface forces in the mixture is investigated. Its established conditions are when the bulk spinodal decomposition may be ignored and when the main role in the process of formation of the oscillating asymptotic periodic spatiotemporal structures plays the surface-directed spinodal decomposition which is modelled by nonlinear dynamical boundary conditions.

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1. Introduction

The problem of self-organization for order parameter in binary mixtures, which are confined with two flat walls, is important in physics of condense matter [1, 2]. At first, for the binary mixtures, this problem was considered by Binder, Puri, and Frisch. The existence of oscillating distributions of the order parameter (on a space variable for each fixed moment time) has been proved [2, 3]. Binder and Frisch considered also the Cahn-Hilliard (CH) equation for conserved-order parameter with nonlinear dynamical boundary conditions [1] and described a phase diagram for the problem. However, it is unknown what is being an attractor of the considered dynamical binary system, that is, what is being an asymptotic behavior of the solutions of such imposed boundary-value problem as a time $t \rightarrow \infty$.

The aim of the present paper is to establish how the attractor of trajectories for this problem is constructed. The achievements of the paper are as follows: (i) we show that the solutions tend to the limit functions as $t \rightarrow \infty$ with a finite set of discontinuities which are determined

by topological properties of the functions F_k , $k = 1, 2$ in the boundary conditions (in this case, we have the solutions of relaxation non-Fickian diffusion type); (ii) there are limit solutions with infinite (countable) and infinite (uncountable) number of discontinuities (in such case, we have the solutions of preturbulent type and turbulent type; accordingly, the set of points of discontinuities for the solutions of turbulent type is familiar to a Cantor-like set); (iii) there exist the solutions whose limit functions are discontinuities at all points. This solutions take up a particular place among the solutions and they lead to the appearance of the so-called “deterministic randomness,” namely, in order to characterize the long-time behavior of the solutions, it is necessary to proceed to a probabilistic description [4].

In such way, we consider the problem which was introduced in [1], but instead of the classical (CH) equation, we research the so-called modified Cahn-Hilliard (mCH) equation which is proposed by Galenko et al. [5, 6]. The modified equation is the model for diffusion and phase separation which takes into account hyperbolic relaxation of

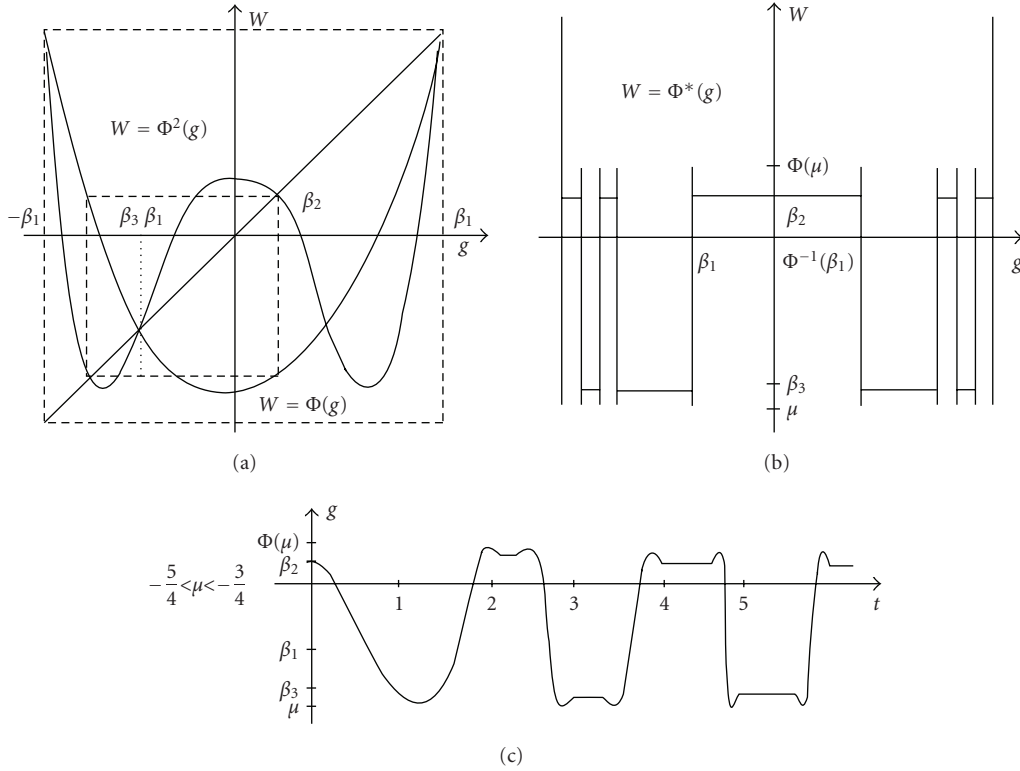


FIGURE 1: Asymptotically periodic distributions of the order parameter of the relaxation type. The map $\Phi : g \mapsto g^2 + \mu$. Here, β_1 and β_3 are stable ordered phases, and β_2 is unstable disordered phase. If the amplitude of initial bubbles is greater than β_2 , then there are the oscillations. If the amplitude of initial bubbles is less than β_2 , then asymptotic distributions of order parameter tend to the constant value β_1 [4].

the solute diffusion flux I . The flux can be determined by the formula (see [5, 6])

$$\begin{aligned} I(\cdot, t + \tau_D) &= I(\cdot, t) + \tau_D I_t(\cdot, t) + O(\tau_D) \\ &= -M(u)(\mathcal{F}'_u(u) - \epsilon_u^2 u_{xx})_x(\cdot, t), \end{aligned} \quad (1)$$

where $O(\tau_D) \rightarrow 0$ as $\tau_D \rightarrow 0$, u is the order parameter, τ_D is the delay time, M is the atomic mobility, \mathcal{F}'_u is the u -derivative of the free energy \mathcal{F} . We denote that $\epsilon_u^2 = 2F_0\zeta_b^2$, where F_0 is connection energy [6] which is normalized by $k_B T$. Here, k_B is the Boltzmann constant, and ζ_b is the bulk correlation length. A few advancements were made for strongly nonequilibrium phase separation. In 1986, Galenko and Lebedev [6] generalized the linearized (CH) equation to the case of existence of slowly relaxing variable. Their calculations show that the instability of the system is not standard diffusive type but rather it is controlled by the relaxation of a slow structural variable such as the diffusion flux determined by the formula (1).

In this paper, we consider the case only when the order parameter varies slowly in the bulk, and we determine the condition when this supposition is true. In this case, asymptotically stable equilibrium states of the system may be stabilized by nonlinear boundary conditions which are described by surface-directed spinodal decomposition (SDSD) in the binary system. As a result, the SDSD determines the limit distributions of order parameter which have

the form of traveling waves and its graphs are asymptotic periodic functions with finite, infinite (countable), or infinite (uncountable) number of discontinuities (Figure 1).

2. Formulation of the Problem

We consider binary mixtures with diffusion flux (1) and, additionally, we suppose that the equation $u_t + I_x = 0$ is true. Then, from (1), we obtain the (mCH) equation:

$$\tau_D u_{tt} + u_t = [M(u)(\mathcal{F}'_u(u) - \epsilon_u^2 u_{xx})_x]_x. \quad (2)$$

In [6], it is shown that (2) takes place for bulk spinodal decompositions with locally nonequilibrium diffusion. In what follows, we consider the boundary conditions in the common form [1]:

$$u_t \big|_{x=x_k} = F_k(h_k, g_k, \nu, u, u_x, u_{xx}, u_{xxx}) \big|_{x=x_k} \quad (3)$$

for the solutions of (2). Here, $x_1 = 0$, $x_2 = l$ and F_k are given functions, h_k describes surface attractive potentials (for magnetic liquid, it may be surface magnetic field [1]), and $g_k = J_s^{(k)}/J^{(k)}$, where $J^{(\cdot)}$ is modelled the bulk forces and $J_s^{(\cdot)}$ is modelled surface forces (in detail see [1, 2]). Next, ν is a constant (or a function) which is proportional to the bulk correlation length ζ_b . In [1], for example, it was considered (3) for $F_k = h_k + g_k(u) + \nu u_x - (\nu/4)^{2/3} u_{xx} - (\nu/4)^{1/3} u_{xxx}$. In the simplest case, if $F_1 = h_1 + g_1 u(0, t)$, then $u(0, t) =$

$u(0, 0) \exp(g_1 t) - h_1/g_1$. Thus, if $g_1 > 0$, then the surface order parameter increases in time, consequently, and the wall $x = 0$ is attractive. If $g_1 < 0$, the wall $x = 0$ is repulsive. In [2], it was considered (3) for $F_k = (\tau_v/\tau_s)(-u_x - h_k/\nu - (1/\nu)g_k(u))$, where τ_s and τ_v are the surface and bulk relaxation times accordingly. In typical cases $\tau_s \ll \tau_v$ [1].

Further, the self-organized structures (as in Figure 1) appear if and only if the Pfaffian form $F_2 du_1 - F_1 du_2 = 0$ is integrable, that is, it can be reduced to the form $dW(u_1, u_2) = 0$, where W is the known function, and $u_k = u(x_k, t)$. From the last equality, it follows that

$$u(l, t) = \Phi_\mu(u(0, t)), \quad \mu = \mu(h_k, g_k, \nu), \quad (4)$$

where Φ_μ is some function. So, if the Pfaffian form is integrable, then (3) may be reduced to (4). Next, we consider the initial conditions $u(x, 0) = u^{(0)}(x)$, $u_t(x, 0) = u^{(1)}(x)$. In common case, analytical solutions of this problem are unknown; but the boundary-value problem may be reduced to some simpler problem for spatial functions F_k and constant mobility M . The problem has unique solution such as in Figure 1. We confined ourselves to the polymer-polymer systems with the components A, B and the power of polymerization N_A, N_B , accordingly. The free energy (see [5]) is

$$\mathcal{F} = \frac{u_A}{N_A} \ln u_A + \frac{u_B}{N_B} \ln u_B + \kappa u_A u_B, \quad (5)$$

where $u_A + u_B = 1$, and κ is Flory-Huggins parameter. We denote $u_A = u$, $u_B = 1 - u$, and we consider, for simplicity, the case $N_A = N_B = N$. Then, we find from (5) by the linear approximation that

$$\mathcal{F}'_u = \left(\frac{4}{N} - 2\kappa \right) \left(u - \frac{1}{2} \right) \quad (6)$$

at a neighborhood of $u = 1/2$. Then, perturbations $u \mapsto u - 1/2$ of the equilibrium state $u = 1/2$ can be considered as the order parameter. As a result, due to (6), equation (2) can be rewritten in the form

$$u_{tt} + \lambda u_t = D_1 u_{xx} + D_2 u_x^2 - D_3 u_{xxxx} - D_4 u_x u_{xxx}, \quad (7)$$

where $t \mapsto t/\tau_v$, $x \mapsto x/l$, $\lambda = \tau_v/\tau_D$, and $D_1 = (M(1/2)\tau_v^2/\tau_D l^2)(4/N - 2\kappa)$, $D_2 = (M'_u(1/2)\tau_v^2/\tau_D l^2)(4/N - 2\kappa)$, $D_3 = M(1/2)\varepsilon_u^2 \tau_v^2/\tau_D l^4$, $D_4 = M'_u(1/2)\varepsilon_u^2 \tau_v^2/\tau_D l^4$. Here, l is the spatial length, $\tau_D = M\alpha_j$, α_j is the coefficient specifying non-Fickian diffusion (see [6]). So, τ_D is the relaxation time of the diffusion flux to its steady state. Further, we suppose that $D_2 \ll 1$ and $D_4 \ll 1$, in particular, it is possible when $M(u) \sim u(1 - u)$. Hence, we get from (7) that

$$u_{tt} + \lambda u_t = D_1 u_{xx} - D_3 u_{xxxx}. \quad (8)$$

Next, we consider the boundary conditions

$$\frac{\tau_s}{\tau_v} u_t(x_k, t) = h_k + 2g_k u(x_k, t) \quad (9)$$

for the solutions of (8), where h_k and g_k are some constant (in common case, they may be given functions). Moreover, we suppose that

$$u_x(0, t) = 0, \quad u_x(l, t) = 0. \quad (10)$$

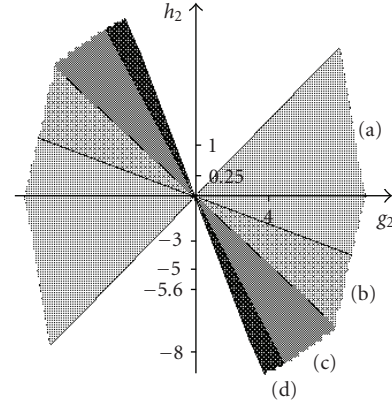


FIGURE 2: Phase diagram is obtained for the problem with nonlinear boundary conditions, which cause the surface-directed spinodal decomposition, by the theoretical method. Here (a) is the region of unique stable phase; (b) is the region of the spinodal decomposition; (c) is the region of the lamellar phase; (d) is the region of stochastic distributions of the order parameter.

3. Reduction to the Difference Equation with Continuous Time

Let

$$u(x, t) = f(\zeta) + g(\eta), \quad (11)$$

where $\nu = \sqrt{D_1}$, $\zeta = t + x/\nu$, $\eta = t - x/\nu$, and f, g are arbitrary functions. Substituting (11) into (8), we deduce

$$\frac{\beta}{\nu^4} f''''_{\zeta} + f'_{\zeta} = 0, \quad \frac{\beta}{\nu^4} g''''_{\eta} + g'_{\eta} = 0, \quad (12)$$

where $\beta = M(1/2)\varepsilon_u^2 \tau_v/l^4$. Integrating (12) along characteristics $dx/dt = \pm \nu$, we arrive at the differential-difference equation

$$\frac{\beta}{\nu^4} Y''''(t) + Y(t) = 0, \quad (13)$$

where $Y(t) = f(t+l/\nu) - g(t-l/\nu)$. Here, we used the relations $f(t) = g(t)$ and $f''''(t) = g''''(t)$ accurate within a constant. In one's turn, these relations follow from the first condition of (10). The general solution of (13) is

$$Y(t) = C_1 e^{-2\nu t} + C_2 e^{\nu t} \cos(\sqrt{3}\nu t) + C_3 e^{\nu t} \sin(\sqrt{3}\nu t), \quad (14)$$

where $\nu = (1/2)(\nu^4/\beta)^{1/3}$. It follows from the definition of $Y(t)$ and functional relation (4) that

$$f\left(t + \frac{l}{\nu}\right) = \Phi_\mu(f(t)) + Y(t), \quad (15)$$

where $f \mapsto 2f$. Henceforth, we consider the case $Y(t) \simeq \text{const}$, that is, $\nu t \ll 1$. Hence, we have two-parametric family of difference equations. The typical solutions of these equations are asymptotic periodic functions, such as in Figure 1. For example, let F_k be from (9). Then, from the above procedure, we find the first integral

$$c_0 (h_1 + 2g_1 u(0, t))^{g_2/g_1} = h_2 + 2g_2 u(l, t), \quad (16)$$

where c_0 is a constant. Let $h_1 = 0$, $g_2/g_1 = 2$. These values correspond to experimental values from [2]. From (16), we find

$$u(l, t) = \frac{c_0 g_2}{2} u^2(0, t) - \frac{h_2}{2g_2}. \quad (17)$$

For the sake of simplicity, we choose $c_0 g_2/2 = 1$. Thus, it follows from (17) that

$$f\left(t + \frac{l}{v}\right) + g\left(t - \frac{l}{v}\right) = (f(t) + g(t))^2 + \hat{\mu}, \quad (18)$$

where $\hat{\mu} = -h_2/2g_2$. Next, we deduce from (10), that is, $f(t) = g(t) + c_1$ and $f(t + l/v) = g(t - l/v) + c_2$, that

$$2f\left(t + \frac{l}{v}\right) + c_2 = (2f(t) + c_1)^2 + \hat{\mu}, \quad (19)$$

where $c_1 = f(0) - g(0)$, $c_2 = f(l/v) - g(-l/v)$, and $f(0)$, $f(l/v)$, $g(0)$ and $g(-l/v)$ depend on initial functions $u^{(0)}$ and $u^{(1)}$. Let $z(t) = 2f(t) + c_1$. Then, it follows from (19) that

$$z\left(t + \frac{l}{v}\right) = z^2(t) + \mu, \quad \mu = \hat{\mu} + c_1 - c_2. \quad (20)$$

4. Phase Diagram

The phase diagram for the solutions of (20) is shown on Figure 2. This diagram is similar to corresponding diagram which was obtained by numeric simulation in [1, 2], where it was considered similar boundary problem to (CH) equation [2].

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