Two-dimensional Model of Phase Separation of the Binary Polymer Blend in Spinodal and Binodal Regions

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SUMMARY: It had been shown in two-dimension case that the Chan-Hilliard-de-Gennes model describes the processes of phase separation both in spinodal and metastable regions. The nature of the structures birth different for different regions. It is rigid in metastable regions, while in spinodal regions it may be both rigid and smooth. Analytical expression for the boundaries separating the regions with rigid and smooth birth of the structures is obtained.

Introduction

Recently dynamics of thermally and chemically initiated phase separation of the binary polymer blend has been the subject of many experimental and theoretical studies. The processes in metastable and spinodal regions are usually described based on different initial equations. However, it was shown [1)], that non-linear Canh-Hillard-de-Gennes equation, which was earlier used only for polymeric blends in a spinodal region, is suitable also for the description of heterogeneous structures in a metastable region.

Numerical study of one-dimensional model in spinodal region has shown that linear stage of the process characterized by exponential growth of long-wave fluctuations of the concentration (the Cahn mode) is followed by consecutive formation of long-lived unstable structures. Respectively, the fluctuation concentration changes fast and abruptly upon transition from one structure to the other [2-4)].

It was found from numerical analysis of two-dimensional and three-dimensional models [5, 6)] that dynamical behavior of a polymer blend depends strongly on the initial distribution of concentration fluctuations. For their random distribution, a fluent evolution of the system, instead of abrupt transitions, is observed. It should be noted that rather small systems were

 CCC 1022-1360/00/$ 17.50+.50/0

considered, with few or none unstable structures. For these systems, as distinguished from one-dimensional case, the dynamic process could not be always followed up to thermodynamic equilibrium, because of time limitations. In this work we have first analyzed the dynamics for two-dimensional model in larger time ranges.

As far as heterogeneous structures (both thermodynamically stable and unstable) are important for the phase separation, conditions of their formation and lifetime should be clarified. For one-dimensional case, this was done in the work [1, 4)] based on bifurcation analysis of a non-linear diffusion equation and detecting of the leading eigenvalue for the operator linearized near stationary spatial structures. In a spinodal region, sub-regions were found which correspond to both a soft and rigid birth of spatial structures. In this work all results of [1, 4)] are summarized in application to a two model.

The statement of the problem

The dynamics of separation of polymers A and B binary blend upon one of the components (A) is described by the Chan-Hilliard-de-Gennes equation

$$\frac{\partial\varphi}{\partial t} = \mathrm{div}\left(\Lambda(\varphi)\nabla\frac{\delta F}{\delta\varphi}\right), \quad \text{where } \Lambda(\varphi) = \frac{N_e\varphi(1-\varphi)}{\tau_A N_A(1-\varphi)+\tau_B N_B\varphi}, \tag{1}$$

is the Onzager diffusion coefficient, $\delta F/\delta\varphi$ is a variation derivative of the free energy F for the Flory-de-Gennes model, with its local density determined by relations:

$$\frac{F}{k_B T} = \tilde{F} = \tilde{F}_0 + \tilde{F}_1$$
$$\tilde{F}_0 = \frac{F_0}{k_B T} = \frac{\varphi\ln\varphi}{N_A} + \frac{(1-\varphi)\ln(1-\varphi)}{N_B} + \chi\varphi(1-\varphi) \tag{2}$$

Equation (1) may be written as follows:

$$\frac{\partial\varphi}{\partial t} = \nabla(\Lambda\nabla\mu_0) - \nabla\left(\Lambda\nabla\left(2K\nabla^2\varphi + K\varphi(\nabla\varphi)^2\right)\right) \tag{3}$$

where $\mu_0 = \frac{\ln\varphi+1}{N_A} - \frac{\ln(1-\varphi)+1}{N_B} + \chi\cdot(1-2\varphi)$ is the system chemical potential.

Assume that boundary conditions for equation (1) are periodical on a rectangular cell with sides (L_1, L_2). As it follows from one-dimensional case, properties of stationary solutions as functions of L_1, L_2, χ, φ_0, N_A, N_B parameters and the way of their birth upon changing

of the above parameters provide some conclusions on the dynamics regularities. Therefore, for two-dimensional case we also first consider properties of stationary solutions of equation (1).

Stationary solutions

According to equation (1) and boundary conditions of periodicity, the integral over the cell $\iint\varphi(x,y)dxdy=\varphi_0$ keeps constant during the process. Therefore, we consider stationary solutions on a set of functions determined by this condition. Generally, many stationary solutions for equation (1) are available on this set. But if dimensions are small enough, there are no stationary solutions except uniform one $\varphi(x,y)\equiv\varphi_0$. However, if L_1, L_2, χ, φ_0, N_A, N_B parameters belong to the spinodal region, there are heterogeneous solutions for the cell dimensions L_1 and L_2 close to some critical values L_1^*, L_2^*. These critical values are associated with zero conditions of eigenvalue for the operator linearized on the homogeneous stationary solution. This is the necessary condition of branching. One or a few pairs of heterogeneous stationary solutions, depending on multiplicity of a zero eigenvalue, branch from the homogeneous solution. Branching can be supercritical or subcritical, similar to a one-dimension case [1]. The branching type, given other parameters, is determined by non-linear bifurcation analysis.

Bifurcation analysis

By substituting variables, we introduce the cell parameters L_1, L_2 into the equation (1). Let $\rho=1/L_1^2$, $\alpha=L_1^2/L^2$, $x'=x/L_1$, $y'=y/L_1$. Then linearized operator at the solution $\varphi=\varphi_0$ for problem (1) is:

$$L(z)=\Lambda\left(\mu_0'\rho\left(\frac{\partial^2 z}{\partial x^2}+\alpha\frac{\partial^2 z}{\partial y^2}\right)-2K\rho^2\left(\frac{\partial^4 z}{\partial x^4}+2\alpha\frac{\partial^4 z}{\partial x^2\partial y^2}+\alpha^2\frac{\partial^4 z}{\partial y^4}\right)\right) \qquad (4)$$

Eigenfunctions of operator (6) for periodical boundary conditions on cell $(0,L_1),(0,L_2)$ and corresponding eigenvalues are as follows (if $m\neq n$):

$$z = A^{+}\cos(2\pi nx + 2\pi my) + A^{-}\cos(2\pi nx - 2\pi my) + A_1^{+}\sin(2\pi nx + 2\pi my) + A_1^{-}\sin(2\pi nx - 2\pi my) + B^{+}\cos(2\pi mx + 2\pi ny) + B^{-}\cos(2\pi mx - 2\pi ny) + B_1^{+}\sin(2\pi mx + 2\pi ny) + B_1^{-}\sin(2\pi mx - 2\pi ny) \quad (5)$$

$$\lambda_{n,m} = -\Lambda(\varphi_0)\left(\frac{4\pi^2}{L_1^2}\right)\left(n^2 + \alpha m^2\right)\left(\mu_0'(\varphi_0) + 8\frac{\pi^2}{L_1^2}K(\varphi_0)\left(n^2 + \alpha m^2\right)\right) \quad (6)$$

It is obvious that if $\mu_0'(\varphi_0) > 0$ 0 all eigenvalues are below zero, and the homogeneous solution is stable. Critical values of parameters are determined by:

$$\mu_0' + 8K\pi^2\rho\left(n^2 + \alpha m^2\right) = 0 \quad (7)$$

If $\rho = 1/L_1^2$ is a bifurcation parameter, its critical values are as follows

$$\rho_{n,m}^{*} = -\frac{\mu_0'(\varphi_0)}{8\pi^2 K(\varphi_0)\left(n^2 + \alpha^2 m^2\right)} \quad (8)$$

Expansion of the stationary solution $\varphi(x, y)$ in powers of the parameter characterizing deviation of ρ from its critical value results in:

$$\varphi(x, y, \rho) = \varphi_0 + \varepsilon\varphi_1(x, y, \rho^*) + \varepsilon^2\varphi_2(x, y, \rho^*) + \varepsilon^3\varphi_3(x, y, \rho^*) + o\left(\varepsilon^3\right)$$
$$\rho = \rho^* + \varepsilon\rho_1 + \varepsilon^2\rho_2 + \varepsilon^3\rho_3 + o\left(\varepsilon^3\right) \quad (9)$$

Combination of these expressions with the stationary equation for φ, Taylor expansion of non-linear functions on φ in φ_0 vicinity, and setting the members with similar ε powers to be equal to zero yield recurrent relations for estimation of φ_i, ρ_i. The first order members over ε have φ_1 as eigenfunction of the linearized operator corresponding to zero eigenvalue.

$$L(\varphi_0, \rho^*)\varphi_1(x, y, \rho^*) = 0 \quad (10)$$

This equation does not fix coefficients of a linear combination in (6), the latter ones being undefined at this stage. The second order members determine the view for function $\varphi_2(x, y, \rho^*)$ and ρ_1. The equation is derived:

$$L(\varphi_0, \rho^*)\varphi_2(x, y, \rho^*) = \Phi(\varphi_1, \rho_1) \quad (11)$$

The right part of equation (11) is:

$$f_1(\varphi_0, \rho^*)\varphi_1^2 + \rho_1 f_2(\varphi_0, \rho^*)\varphi_1$$

hence, the necessary condition to have a solution of equation (11) (orthogonality of the right part with respect to φ_1) leads to value $\rho_1 = 0$. Provided this condition, φ_2 function from (11) is determined as a linear combination of cosines and sines of the arguments. The latter ones

are determined by φ_1^2 after replacing cosine and sine products by the corresponding functions of the arguments sum and difference. For $n=1$, $m=1$, φ_2 is:

$$\varphi_2(x,y,\rho^*)=c^+\cos(4\pi(x+y))+c^-\cos(4\pi(x-y))+s^+\sin(4\pi(x+y))+ s^-\sin(4\pi(x-y))+c_x\cos 4\pi x+c_y\cos 4\pi y+s_x\sin 4\pi x+s_y\sin 4\pi y \quad (12)$$

Combining (12) and (11) and setting the coefficients at linear independent functions equal to zero, we get the coefficients. The third order members yield the equation:

$$L(\varphi_0,\rho^*)\varphi_3(x,y,\rho^*)=\Phi_2(\varphi_2,\rho_2) \quad (13)$$

Suppose that the right part of this equation is orthogonal to the linearized operator eigenfunctions, corresponding to a zero eigenvalue. Then we get the equations for linear combination coefficients in (5) and for ρ_2 value. This is a nonlinear equation set. For $n=m=1$ it is:

$$\begin{aligned}&\rho_2\left(8\pi^2\Lambda(\varphi_0)(32\rho^*K(\varphi_0)+\mu_0)\right)A^+=A^+\left(p\widetilde{A}^+ +q\widetilde{A}^-\right)\\&\rho_2\left(8\pi^2\Lambda(\varphi_0)(32\rho^*K(\varphi_0)+\mu_0)\right)A^-=A^-\left(q\widetilde{A}^+ +p\widetilde{A}^-\right)\\&\widetilde{A}^+=\left(\left(A^+\right)^2+\left(A_1^+\right)^2\right),\quad \widetilde{A}^-=\left(\left(A^-\right)^2+\left(A_1^-\right)^2\right)\end{aligned} \quad (14)$$

If A^+ is replaced by A_1^+, and A^- by A_1^-, two more equations are obtained. Here, coefficients p, q are functions of coefficients from (1) and of their derivatives, including the third order ones. Two types of solutions are possible: either one of the coefficients is not zero, and others are zero, or the coefficients provide the equation: $A^{+2}+A_1^{+2}=A^{-2}+A_1^{-2}$. These amplitudes can always be considered as 1, because their changing corresponds to renormalization of ε, and does not change the solution. For the first case, one-dimensional structures appear because they are constant along straight line $x+y=\text{const}$ or $x-y=\text{const}$. Here, formula for ρ_2 coincides with the relevant formula for one-dimensional case provided that $N_A=N_B$:

$$\rho_2=\frac{9}{4}\frac{(\Psi-\Psi_1)(\Psi-\Psi_2)}{\mu_0'(\varphi_0)\pi^2N^2},\qquad \Psi_{1,2}=\frac{1-z\pm\sqrt{1/3+z(z-4/3)}}{z} \quad (15)$$

For the second case, expressions for ρ_2 are the same for all solutions, with an accuracy of renormalization depending on the amplitude value; assuming that $N_A=N_B$, the formula is:

$$\rho_2=\frac{9}{4}\frac{(40z-7)(\Psi-\Psi_1)(\Psi-\Psi_2)}{zN^2\pi^2\mu_0'(\varphi_0)} \quad (16)$$

Here:

$$z = \varphi_0(1-\varphi_0), \quad \Psi = N_A\chi, \quad \Psi_{1,2} = \frac{13z - 1 \pm 1/6\sqrt{321z^2 - 264z + 51}}{2z(7-40z)} \qquad (17)$$

Expanding (9), we get $\varepsilon = \sqrt{\dfrac{\rho - \rho^*}{\rho_2}} + o(\varepsilon)$. Then, if $\rho_2 > 0$, there exists a solution for $\rho > \rho^*$ and hence, for $L < L^*$. For this case, bifurcation over L is subcritical. A rigid birth of a pair of heterogeneous two-dimensional structures occurs at a certain $L = L^{**}$, as it is true for one-dimensional case. Here there is another possibility: a two-dimensional structure can appear from one-dimensional one by secondary bifurcation, because of a loss of stability with respect to two-dimensional perturbations. Figure 1 shows a probable bifurcation diagram. It corresponds to the points on the phase diagram (Fig. 2) in the region between a spinodal and curve $\Psi = \Psi_1$.

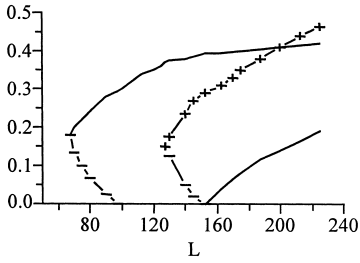

Fig. 1. Max $|\varphi - \varphi_0|$ with respect to size L.

Upon the dimension increase, the first bifurcation occurs, a rigid birth of a pair of one-dimensional structures in subcritical region at $L^{**} < L^* = L^*_{1,0} = 1/\sqrt{\rho^*_{1,0}}$. Then, at $L^*_{1,1} = 1/\sqrt{\rho^*_{1,1}}$ an unstable two-dimensional structure originates subcritically, with two positive eigenvalues. Its rigid birth is coupled with unstable structure having one positive eigenvalue. This structure exchanges its stability with a stable one-dimensional structure that appears earlier so that a two-dimensional structure becomes stable. A calculation of stability for one-dimensional structures with respect to two-dimensional perturbations [4] has revealed an unstability of one-dimensional structure.

Figure 2 shows the phase diagram where curve $\Psi = \Psi_s(\varphi)$ is a spinodal, and $\Psi = \Psi_1(\varphi)$ corresponds to the second radical in (15). In the area between these curves a rigid birth of one-dimensional structures occurs in a subcritical region over L. Curve $\Psi = \Psi_2(\varphi)$, where Ψ_2 is the second radical in (17), separates the region

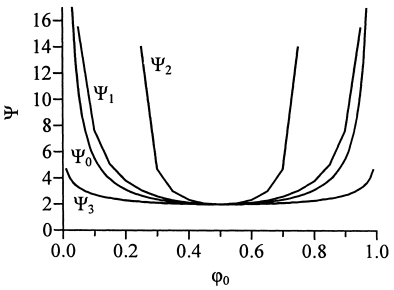

Fig. 2. Phase diagram (ψ, φ_0)

of a subcritical birth of a two-dimensional structure from the region of a supercritical one. In this region, the birth of one-dimensional structures, constant along straight lines $x + y = \text{const}$, $x - y = \text{const}$, occurs supercritically, and they are unstable. For $m = n \neq 1$, the regions of a subcritical birth are the same. For $m \neq n$, analytical expressions are rather complicated, and we do not present them.

Numerical modeling of two-dimensional structures

Numerical modeling of a two-dimensional problem is performed using a difference implicit scheme and the Newton method at each time step. Each linear problem is solved by the method of alternative directions, and linear boundary problem for each direction is solved by the cyclic sweep method, similarly to a one-dimensional case [4]. An alternative time step is chosen automatically from the given criteria of approximation accuracy and iteration convergence. Based on the plotted phase diagram, the parameters values favorable for two-dimensional or one-dimensional structures are predicted. Values $\chi = 0.003$, $N_A = N_B = 1000$, $\varphi_0 = 0.3$ and $\varphi_0 = 0.4$ correspond to subcritical bifurcation of two-dimensional structures, while for $\varphi_0 = 0.5$ all two-dimensional structures appear supercritically, and should be unstable. Therefore, one-dimensional structures are available. Figure 3a presents the calculation of the structure.

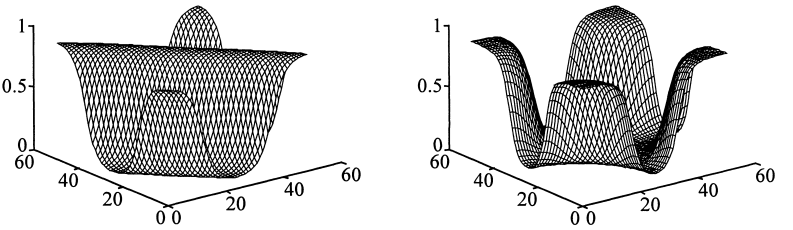

Fig. 3. Spatial distribution of volume fraction for component A.
a) $\varphi_0 = 0.4$, $L_1 = L_2 = 200$; b) $\varphi_0 = 0.5$, $L_1 = L_2 = 200$;

Numerical calculations for a two-dimensional case confirm the existence of structures in a binodal region in the frame of Cahn-Hillard-de-Gennes, similar to a one-dimensional region. A stepwise behavior of the free energy during equilibration, typical for numerical modeling in a one-dimensional case [2-4] and associated with a slow passing of the system in the vicinity of unstable stationary states, is also observed for a two-dimensional case. A number of the steps

is attributed to a number of unstable stationary states lying on the way to thermodynamic equilibrium. The steps width correlates with the inverse value of the leading positive eigenvalue of the operator linearized on this structure. These results are reduced in reference [4]. Such correlation is valid for a two-dimensional case as well. For numerical calculations for $\chi = 0.0025$, $\varphi_0 = 0.3$, $L_1 = L_2 = 300$, $\lambda = 5.97 \cdot 10^{-4}$, $\tau = 1/\lambda \approx 1600$, and the step width is about 1400. The larger is the system, the more is a number of steps.

Conclusion

For a large two-dimensional system, retardation scheme is realized, with a decisive role of long-lived structures, independent on initial conditions (either determinant or random). The lifetime for unstable structures is determined with a good accuracy by increments of solutions for diffusion equations linearized in the vicinity of these structures. Similar to one-dimensional case, a spinodal region is divided into sub-regions corresponding to a soft and rigid birth of spatial structures; the same description is possible for spinodal (upon rigid birth) and metastable regions.

Acknowledgments

This work was supported by the International Science and Technology Center (grant No. 96-358) and RFBR (grant No. 98-01-00559a)

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