Instabilities and Disorder of the Domain Patterns in Systems with Competing Interactions

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The dynamics of domains is studied in a two-dimensional model of the microphase separation of diblock copolymers in the vicinity of the transition. A criterion for the validity of the mean-field theory is derived. It is shown that at certain temperatures the ordered hexagonal pattern becomes unstable with respect to the two types of instabilities: the radially nonsymmetric distortions of the domains, and the repumping of the order parameter between the neighbors. Both these instabilities may lead to the transformation of the regular hexagonal pattern into a disordered pattern. [S0031-9007(97)02989-X]

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Formation of complex patterns consisting of domains with sharp walls is a beautiful example of self-organization in the systems both near and far from thermal equilibrium [1–6]. Recently, it became clear that long-range competing interactions are responsible for the formation of the domain patterns in the systems as diverse as ferroelectrics and ferrofluids, garnet ferromagnets, Langmuir monolayers, type-I superconductors in the intermediate state, diblock copolymers, and reaction-diffusion systems with long-range inhibition (see [6] and references therein). In such systems the formation of the uniform state favored by the local properties of the system is precluded by the long-range interaction which does not favor that uniform state. Thus, the system becomes separated into the domains of the alternating values of the "order parameter." As a result of this separation a lot of different equilibrium configurations, including highly symmetric ones, are possible.

In this Letter we will study the time-dependent model of a system with competing interactions in two dimensions. We will investigate the stability of the stationary states and show that they undergo instabilities which may change both the characteristic length scale and the morphology of the domain patterns. We will also show that the destabilization of the highly symmetric patterns typically leads to the formation of the disordered patterns.

The microphase separating diblock copolymer melts are a typical example of the systems with the long-range competing interactions. There the macroscopic phase separation of the mutually incompatible monomers is not allowed since the monomers are connected through the polymer chains. Ohta and Kawasaki obtained the free energy for this system in the case of the long polymer molecules [7],

$$F = \int d^d x \left(\frac{(\nabla\phi)^2}{2} + \frac{a\phi^2}{2} + \frac{b\phi^4}{4} + \frac{\alpha}{2} \int d^d x' [\phi(x) - \bar{\phi}] G(x - x') [\phi(x') - \bar{\phi}] \right), \tag{1}$$

where ϕ is the order parameter which is proportional to the difference of the monomer concentrations, a and b are the coefficients of the Landau-Ginzburg expansion, the last term in Eq. (1) is the long-range interaction characterized by the function G which reflects the connectivity of the chains, $\alpha \sim N^{-2}$ is the strength of this interaction, N is the number of monomers in a chain, and the constant $\bar{\phi}$ is determined by the block ratio. The function G satisfies

$$-\nabla^2 G(x - x') = \delta^{(d)}(x - x'). \tag{2}$$

The model given by Eqs. (1) and (2) in fact has a wider applicability and can be used to describe the stationary states in ceramic compounds with the long-range Coulombic interactions [8], ferroelectric semiconductors [9], high-temperature superconductors and degenerate magnetic semiconductors [10], reaction-diffusion systems with the long-range inhibitor [2,11], and reaction-controlled spinodal decomposition [12].

The formation of the domains in the system under consideration is due to the competition between the nonlocal interaction and the surface tension which is determined by the local terms in Eq. (1). For the equilibrium pattern the contributions of these two effects have to be comparable. According to Eq. (1), for the domain of size R we have

$$\sigma R^{d-1} \sim N^{-2} \phi^2 R^{d+2}, \tag{3}$$

where σ is the coefficient of the surface tension. Near the critical point $\sigma = \sigma_0 |t|^{\nu(d-1)}$, where $t = (T - T_c)/T_c$, T_c is the critical temperature and ν is the critical exponent of the Ising model [13]. Because of the long-range character of the nonlocal interaction, in estimating its contribution one can ignore the fluctuations of ϕ and put $\phi = \phi_0 |t|^\beta$ in Eq. (3), where β is the respective critical exponent of the Ising model. Then, according to Eq. (3), the characteristic size of the equilibrium domain near the critical point will be

$$R \sim N^{2/3} |t|^{[\nu(d-1) - 2\beta]/3}. \tag{4}$$

Substituting this expression into Eq. (3), we obtain that the free energy of a single domain $\Delta F \gg 1$ if

$$N \gg |t|^{[2\beta - \nu(d+2)]/2}. \tag{5}$$

If this condition is satisfied, we can use the mean-field approximation to describe the domain patterns in the vicinity of the phase transition.

In order to study the domain patterns in the mean-field limit let us introduce the new variables,

$$\phi' = \frac{\phi}{\phi_0|t|^\beta}, \qquad x' = \frac{x}{\xi},$$
$$\epsilon^2 = \frac{2\sqrt{2}\,\alpha\phi_0^2\xi_0^3}{3\sigma_0}|t|^{2\beta-\nu(d+2)}, \tag{6}$$

where $\xi = \xi_0|t|^{-\nu}$ is the correlation length, and write the free energy functional (up to a constant factor and dropping the primes),

$$F = \int d^dx\Big(\frac{(\nabla\phi)^2}{2} - \frac{\phi^2}{2} + \frac{\phi^4}{4} + \frac{\epsilon^2}{2}\int d^dx'[\phi(x) - \bar{\phi}]G(x - x')[\phi(x') - \bar{\phi}]\Big). \tag{7}$$

One should think of Eq. (7) as the mean-field representation of the domain interactions. When the condition of Eq. (5) is satisfied, we have $\epsilon \ll 1$, which implies the *strong segregation limit* [7]. Notice that in these units $R \sim \epsilon^{-2/3}$.

The evolution of the order parameter ϕ near the phase transition in the mean-field limit can be described by the time-dependent Landau-Ginzburg equation obtained from Eq. (7) [14]. This equation can be written as a pair of reaction-diffusion equations of the activator-inhibitor type in the limit of the fast inhibitor:

$$\frac{\partial\phi}{\partial t} = \nabla^2\phi + \phi - \phi^3 - \psi, \tag{8}$$
$$0 = \epsilon^{-2}\nabla^2\psi + \phi - \bar{\phi}, \tag{9}$$

where ϕ plays the role of the activator and ψ plays the role of the inhibitor [2], and the time scale has been absorbed into the definition of t. In the limit $\epsilon \to 0$ these equations are equivalent to the interfacial dynamics problem [11,15]. We would like to emphasize that in this limit Eqs. (8) and (9) are applicable to the systems with the conserved order parameter. Indeed, the equations of the interfacial dynamics mentioned above can be alternatively derived from the free energy given by Eq. (7) if one assumes the overdamped dynamics of the interface [11]. The latter is justified for the microphase separation in the diblock copolymer melts, where the hydrodynamic effects are important.

The domain patterns that form in this kind of systems have been recently studied in great detail in connection with the patterns forming in highly nonequilibrium systems [15–18]. Muratov and Osipov showed that in the case of Eqs. (8) and (9) only the patterns whose characteristic length scale (in these units) is of order $\epsilon^{-2/3}$ can be linearly stable [15–17]. Thus, if the condition in Eq. (5) is satisfied, on this length scale the mean-field approximation remains valid for the time-dependent theory as well.

When $|\bar{\phi}| < 1$ and $\epsilon \ll 1$, Eqs. (8) and (9) admit the solutions in the form of the stationary multidomain patterns, including the hexagonal patterns of circular domains of radius $\mathcal{R}_s$ and the period $\mathcal{L}_p$ in two dimensions [2,7,15–18]. It is clear that the period of these patterns (or, actually, the characteristic interdomain distance) must lie within $l \ll \mathcal{L}_p \lesssim L$, where $l \sim 1$ and $L \sim \epsilon^{-1}$ are the characteristic length scales of the variation of ϕ and ψ, respectively [2]. For $|\bar{\phi}|$ not very close to 1 the radius of the domains is comparable to $\mathcal{L}_p$. Since the characteristic size of the domains is of order $\epsilon^{-2/3}$, the period of the pattern must also be $\mathcal{L}_p \sim \epsilon^{-2/3} \ll L$, so the value of ϕ is close to $+1$ inside the domains and close to -1 outside.

Let us now study the stability of the hexagonal pattern. It is clear that the results obtained for this pattern should be qualitatively the same for an arbitrary multidomain pattern. In this case, according to Eq. (9), the relationship between the period and the radius of the domains is

$$\mathcal{R}_s = 3^{1/4}\mathcal{L}_p\Big(\frac{1 + \bar{\phi}}{4\pi}\Big)^{1/2}, \tag{10}$$

so the ratio $\mathcal{R}_s/\mathcal{L}_p$ can be conveniently used as a parameter instead of $\bar{\phi}$. According to the general asymptotic theory of instabilities of domain patterns in reaction-diffusion systems [16], the dangerous fluctuations of ϕ are localized in the domain walls and represent the small distortions of the domains. The damping decrement γ of such fluctuations is determined by the eigenvalues of a certain operator. Since the hexagonal pattern we are interested in is periodic, we can partially diagonalize this operator by considering the fluctuations modulated by the wave vector k which lies in the Brillouin zone, and obtain for the system under consideration [16]

$$\Big(-\gamma + \frac{m^2}{\mathcal{R}_s^2} + \lambda_0\Big)\delta_{mm'} = -3\sqrt{2}\,\epsilon^2\mathcal{R}_s R_{mm'}(k), \tag{11}$$

where m and m' are integers corresponding to the modes of the azimuthal distortions of the domains, λ_0 is a constant independent of m and k, $\delta_{mm'}$ is the Kronecker delta, and $R_{mm'}(k)$ is a certain matrix with the indices m and m'. It is possible to show (the details of the derivations will be given elsewhere) that the constant λ_0 is given by

$$\lambda_0 = -\frac{1}{\mathcal{R}_s^2} - \frac{3\epsilon^2\mathcal{R}_s}{\sqrt{2}}\Big(1 - \frac{2\pi\mathcal{R}_s^2}{\sqrt{3}\,\mathcal{L}_p^2}\Big). \tag{12}$$

Since the characteristic length scale of the pattern is much smaller than L, the Laplacian dominates in the equation for the Green's function involved in the calculation of $R_{mm'}(k)$ (see Ref. [16]), so this Green's function may be assumed to satisfy Eq. (2). With this fact in mind it is convenient to write the expression for $R_{mm'}(k)$ in the Fourier space,

$$R_{mm'}(k) = \frac{2\pi}{v}\sum_{k'}\frac{e^{i(m'-m)(\vartheta_{k+k'}+\pi/2)}}{|k + k'|^2} \times J_m(|k + k'|\mathcal{R}_s)J_{m'}(|k + k'|\mathcal{R}_s), \tag{13}$$

where k' runs over the reciprocal lattice, J_m are the Bessel functions, $\vartheta_{k+k'}$ is the angle between the vector $k + k'$ and the x axis, and $v = \sqrt{3}\,\mathcal{L}_p^2/2$ is the volume of

the elementary cell. Notice that for $\mathcal{R}_s \ll \mathcal{L}_p$ the off-diagonal elements of $R_{mm'}(k)$ become negligibly small, so for $|m| \geq 2$ we recover the instabilities of the localized domains—autosolitons [16]. As $\mathcal{R}_s$ gets bigger, the mixing between the vectors corresponding to the different values of m occurs. This mixing, however, is not very strong, so one can still label the eigenvectors of Eq. (11) with m.

As was shown qualitatively by Kerner and Osipov, for the most dangerous fluctuations the wave vector k will lie close to the edge of the Brillouin zone [2]. There are two basic types of fluctuations we need to consider: the fluctuations with $m = 0$ which lead to repumping of the order parameter between the neighboring domains [Fig. 1(a)] and the fluctuations with $m = 2$ which lead to the asymmetric distortions of the domains [Fig. 1(b)] [2]. The analysis of Eq. (11) shows that the most dangerous fluctuations with $m = 0$ have $k = \frac{1}{3}(b_1 - b_2)$, where b_1 and b_2 are the reciprocal lattice vectors which make a 120° angle, while the most dangerous fluctuations with $m = 2$ have $k = \frac{1}{2}(b_1 + b_2)$. The instability $\gamma < 0$ occurs with respect to repumping when $\mathcal{L}_p < \mathcal{L}_{p0}$ or with respect to the asymmetric distortion when $\mathcal{L}_p > \mathcal{L}_{p2}$, where $\mathcal{L}_{p0,2}$ depend on ϵ and $\mathcal{R}_s/\mathcal{L}_p$. The resulting stability diagram is presented in Fig. 2. Figure 2 also shows the period of the equilibrium hexagonal pattern obtained by Ohta and Kawasaki [7]. One can see that the equilibrium hexagonal pattern is stable for all values of $\mathcal{R}_s$ (except, possibly, for $\mathcal{R}_s/\mathcal{L}_p$ close to 0.5, where the assumption about the circular shape of the domains ceases to be valid). In two dimensions the equilibrium hexagonal pattern corresponds to the global minimum of the free energy if $\mathcal{R}_s/\mathcal{L}_p < 0.31$, whereas for $0.31 < \mathcal{R}_s/\mathcal{L}_p < 0.37$ (the second condition means that $\bar{\phi} < 0$, i.e., positive domains in the negative background) the global minimum corresponds to the lamellar pattern [7]. Figure 2, however, does not show the transition from the hexagonal to the lamellar pattern so, in fact, the equilibrium hexagonal pattern is always metastable.

Recall that the values of ϵ and $\bar{\phi}$ strongly depend on the temperature near the critical point. Suppose that the equilibrium hexagonal pattern formed as a result of the slow quench of the system below T_c. If now the temperature is abruptly raised, the domains may become unstable with respect to the asymmetric distortions. To study the kinetics of this process we solved Eqs. (8) and (9) numerically with the initial condition in the form of the hexagonal pattern plus small noise. This process is shown in Fig. 3(a). At the end of the simulation the system reaches an asymptotic state. One can see that the hexagonal pattern transforms into a highly disordered metastable pattern which consists of the domains of complex shapes. Notice that this effect was observed experimentally in different systems with competing interactions [19,20]. If the system temperature is quickly lowered, the pattern may destabilize with respect to repumping. The kinetics of this process is shown in Fig. 3(b). As the destabilization progresses, some of the domains start to "eat" their neighbors, which results in either an increase of the interdomain distance or in the fusion of some of the neighbors. A lot of the domains shrink and eventually disappear. All these processes create a lot of disorder. Eventually the distance between the domains becomes large enough so that the repumping is no longer realized, and the resulting pattern orders somewhat at late stages. However, the asymptotic pattern at the end of the simulation is still highly disordered. Notice that the repumping effect is observed in experiments and numerical simulations of systems with competing interactions [21,22].

In summary, we showed that the stationary multidomain patterns in the systems with long-range competing interactions may undergo instabilities affecting both the

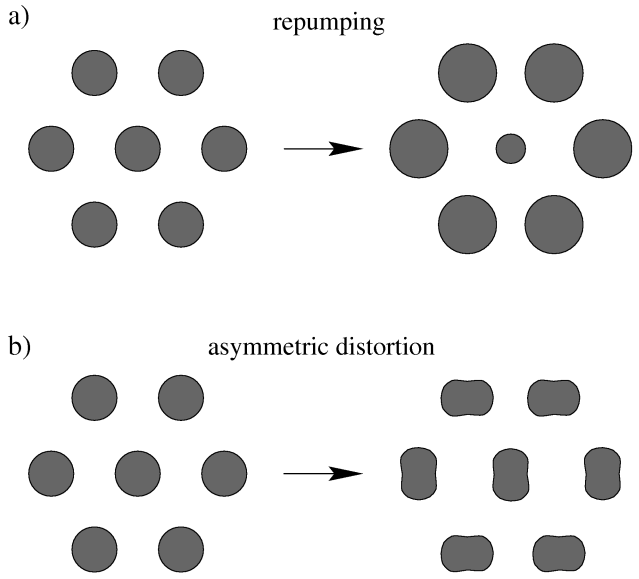

FIG. 1. Two major types of instabilities of the hexagonal pattern.

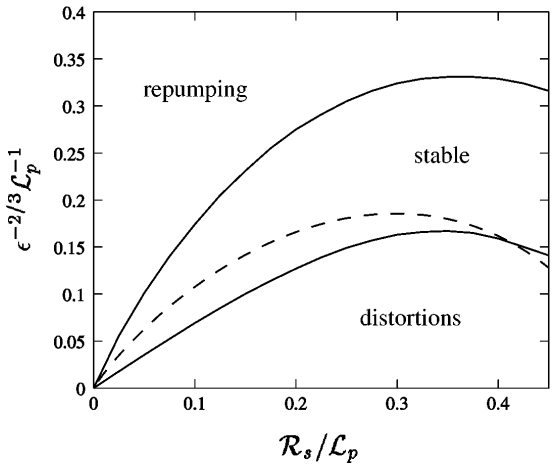

FIG. 2. Stability diagram for the hexagonal pattern. The dashed line corresponds to the equilibrium pattern.

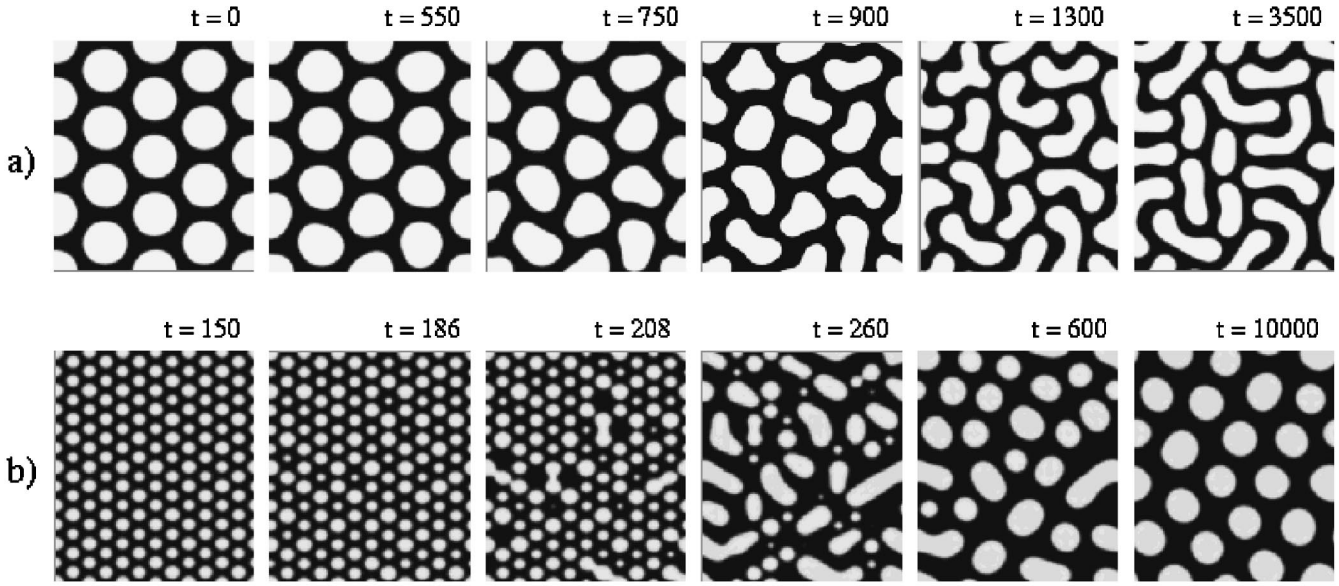

FIG. 3. (a) Destabilization of the hexagonal pattern with respect to the asymmetric distortions. Distributions of ϕ at different times for $\epsilon = 0.05$ and $\bar{\phi} = 0$. The system is 200×230. (b) Destabilization of the hexagonal pattern with respect to repumping. Distributions of ϕ at different times for $\epsilon = 0.025$ and $\bar{\phi} = -0.2$. The system is 200×230.

period and the shape of the domains which typically result in the formation of highly disordered metastable patterns.

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