

# Self-Propulsion of Cellular Structures in Chemically Reacting Mixtures

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## Abstract

A new model of phase-separating reactive binary mixtures is proposed. In this model both a phase separation and chemical reactions simultaneously take place and a traveling coherent structure can be formed through a Hopf bifurcation with finite wave number. Numerical simulations show that, depending on the parameters, either lamellar or hexagonal structures travel at constant speeds in two-dimensional systems.

## 1 Introduction

A great deal of effort has been made on the studies of pattern formation in nonlinear dissipative systems [1, 2]. Reaction-diffusion systems offer some important view points in elucidating the mechanism of pattern formation, since they have simple mathematical structures and show a rich variety of patterns [3, 4].

On the other hand, phase separation in condensed systems provides another mechanism of pattern formation. Domain morphology and kinetics of phase separation have been studied for many years both experimentally and theoretically [5]. In contrast to the case of reaction-diffusion systems, a typical pattern which appears in a phase separation process is transient and eventually disappears in a finite system, since the system relaxes into a trivial equilibrium state. However, it has been shown by theories [6, 7, 8] and experiments [9] that some chemical reactions can stabilize the steady-state morphology of phase-separating systems. These systems have periodic structures as stationary states.

Non-stationary patterns like traveling waves have mainly discussed so far within the framework of reaction-diffusion systems. Recently, however, Hildebrand et al. [10] (see also [11]) have found the traveling nanoscale structures

in surface chemical reactions. In their model both a chemical reaction and a first order phase transition (phase separation) simultaneously take place and the traveling structure appears through a Hopf bifurcation with finite wave number. This gives us a motivation to study the non-stationary pattern formation in phase-separating systems. It is worth a mention that traveling waves have experimentally observed in Langmuir monolayers [12], although, to our knowledge, there is no satisfactory theory for this phenomenon.

The aim of this paper is to propose a simple model of phase separation with a new type of chemical reactions which leads to the appearance of traveling structures and to present the result of numerical simulations of the model.

## 2 Model

Consider a binary mixture of molecules  $A$  and  $B$  which undergoes a phase separation. We assume that time evolution of the phase separation process is well described by the Cahn-Hilliard equation associated with the order parameter  $\psi \equiv \psi_A - \psi_B$ , where  $\psi_A$  and  $\psi_B$  are the local concentration of the molecules  $A$  and  $B$ , respectively and satisfy  $\psi_A + \psi_B = 1$ . When the chemical reaction of the type  $A \rightleftharpoons B$  takes place in the phase-separating system, the time evolution equation of the order parameter  $\psi(\mathbf{r}, t)$  at position  $\mathbf{r}$  and time  $t$  is given by [6]

$$\frac{\partial \psi}{\partial t} = \nabla^2 \frac{\delta F}{\delta \psi} - \alpha(\psi - \psi_0), \quad (1)$$

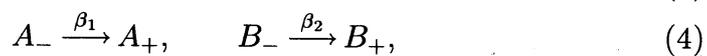
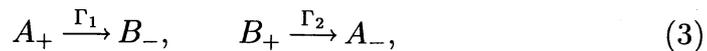
where  $\alpha$  and  $\psi_0$  are constants which depend on the reaction rates and  $F$  is the free energy functional of Ginzburg-Landau type:

$$F[\psi] = \int d\mathbf{r} \left[ \frac{c}{2} (\nabla \psi)^2 + w(\psi) \right], \quad (2)$$

where  $c$  is a positive constant and  $w(\psi)$  is a function of  $\psi$  with two degenerate minima. The last term in Eq. (1) arises due to the chemical reaction  $A \rightleftharpoons B$ . In the absence of this term Eq. (1) is the usual Cahn-Hilliard equation. Since the growth of fluctuations with large wavelength is suppressed in this system, the characteristic size of pattern formed can never reach macroscopic one. In a steady state a periodic structure such as lamellar (if  $\psi_0 = 0$ ) or hexagonal (if  $\psi \neq 0$ ) structures in a two-dimensional system can be formed. It should be noted that Eq. (1) has the same form as the equation which describes

phase separations in block-copolymer systems [13], the so called, microphase separation. The block-copolymer systems have periodic domain structures as equilibrium states [14].

Now we introduce our new model. Let us consider the following hypothetical system. The system is a phase-separating binary mixture of molecules  $A$  and  $B$ , which is similar to the system described above. Each molecule of  $A(B)$  has two internal states, say, active and inactive states which are denoted by  $A_+(B_+)$  and  $A_-(B_-)$ , respectively. Hence,  $A(B)$  component of the mixture consists of  $A_+(B_+)$  and  $A_-(B_-)$  subcomponents. Suppose the following reactions simultaneously take place,



where  $\Gamma_1$ ,  $\Gamma_2$ ,  $\beta_1$ , and  $\beta_2$  are the reaction rates. These reactions are externally controlled by, for example, irradiation with ultra-violet light. The rate equations for the concentrations of  $A$ ,  $B$ ,  $A_+$ , and  $B_+$  are given by

$$\dot{\psi}_A = -\Gamma_1\phi_A + \Gamma_2\phi_B \quad (5)$$

$$\dot{\psi}_B = \Gamma_1\phi_A - \Gamma_2\phi_B \quad (6)$$

$$\dot{\phi}_A = -\Gamma_1\phi_A + \beta_1(\psi_A - \phi_A) \quad (7)$$

$$\dot{\phi}_B = -\Gamma_2\phi_B + \beta_2(\psi_B - \phi_B) \quad (8)$$

where  $\psi_A$ ,  $\psi_B$ ,  $\phi_A$ , and  $\phi_B$  are the concentrations of  $A$ ,  $B$ ,  $A_+$ , and  $B_+$  molecules, respectively, and the dot above each symbol means the time derivative of its quantity. Here we have explicitly written only the reaction terms in these equations.

When the decay rate of  $A_+$  is equal to that of  $B_+$ , that is,  $\Gamma_1 + \beta_1 = \Gamma_2 + \beta_2$ , Eqs. (5)–(8) can be reduced, taking  $\psi_A + \psi_B = 1$  into account, to

$$\dot{\psi} = -2\Gamma_1\phi, \quad (9)$$

$$\dot{\phi} = -(\Gamma_1 + \beta_1)\phi + \frac{\Gamma_1\beta_1 + \Gamma_2\beta_2}{2\Gamma_1} \left( \psi + \frac{\Gamma_1\beta_1 - \Gamma_2\beta_2}{\Gamma_1\beta_1 + \Gamma_2\beta_2} \right), \quad (10)$$

where

$$\psi \equiv \psi_A - \psi_B, \quad (11)$$

$$\phi \equiv \phi_A - \frac{\Gamma_2}{\Gamma_1}\phi_B. \quad (12)$$

Hence the system can be described by these two variables in this case.

Based on the above consideration, we write down the model equations using appropriately scaled variables  $u(\mathbf{r}, t)$  and  $v(\mathbf{r}, t)$  which correspond to  $\psi$  and  $\phi$ , respectively:

$$\frac{\partial u}{\partial t} = \nabla^2[-D_u \nabla^2 u - \tau u + u^3] - \alpha v, \quad (13)$$

$$\frac{\partial v}{\partial t} = \lambda(u - I - \gamma v), \quad (14)$$

where  $D_u$  is the diffusion constant and  $\lambda$ ,  $\tau$ ,  $\alpha$ , and  $\gamma$  are positive constants and  $I$  is a constant which can be either positive or negative. Equations (13) and (14) have an equilibrium uniform solution:  $u = I$ ,  $v = 0$ . Since we are interested in a minimal model which produces a traveling structure in a phase-separating system, as a first step, we have ignored the diffusion term in Eq. (14), although some physical arguments are needed. Note that Eqs. (13) and (14) are reduced to Eq. (1) in the limit of  $\lambda \rightarrow \infty$ . On the other hand, when  $\lambda = 0$  and  $v = 0$ , they are equivalent to the Cahn-Hilliard equation. It should be also noted that the total amount of  $u$ , that is,  $\int d\mathbf{r} u$  is conserved in time if we choose an initial condition which satisfies  $\int d\mathbf{r}(u - I) = 0$  and  $\int d\mathbf{r} v = 0$ . The numerical simulations shown later will be carried out in this situation.

Before carrying out numerical simulations, we here analyze a linear stability of the system. Linearizing Eqs. (13) and (14) around the equilibrium solution  $u = I$ ,  $v = 0$ , and introducing the Fourier transform  $u_q = \int d\mathbf{r}(u - I) \exp(-i\mathbf{q} \cdot \mathbf{r})$ ,  $v_q = \int d\mathbf{r} v \exp(-i\mathbf{q} \cdot \mathbf{r})$ , with wave vector  $\mathbf{q}$ , we obtain

$$\frac{d}{dt} \mathbf{U}_q = L \mathbf{U}_q, \quad (15)$$

where  $\mathbf{U}_q \equiv {}^t(u_q, v_q)$ ,

$$L \equiv \begin{pmatrix} -q^2(D_u q^2 - \tilde{\tau}) & -\alpha \\ \lambda & -\lambda\gamma \end{pmatrix}, \quad (16)$$

$\tilde{\tau} \equiv \tau - 3I^2$  and  $q \equiv |\mathbf{q}|$ . Eigenvalues of the matrix  $L$  determine the stability of the equilibrium solution. If an instability occurs through a Hopf bifurcation at  $q = q_c > 0$ , we can expect that a standing or traveling structure whose

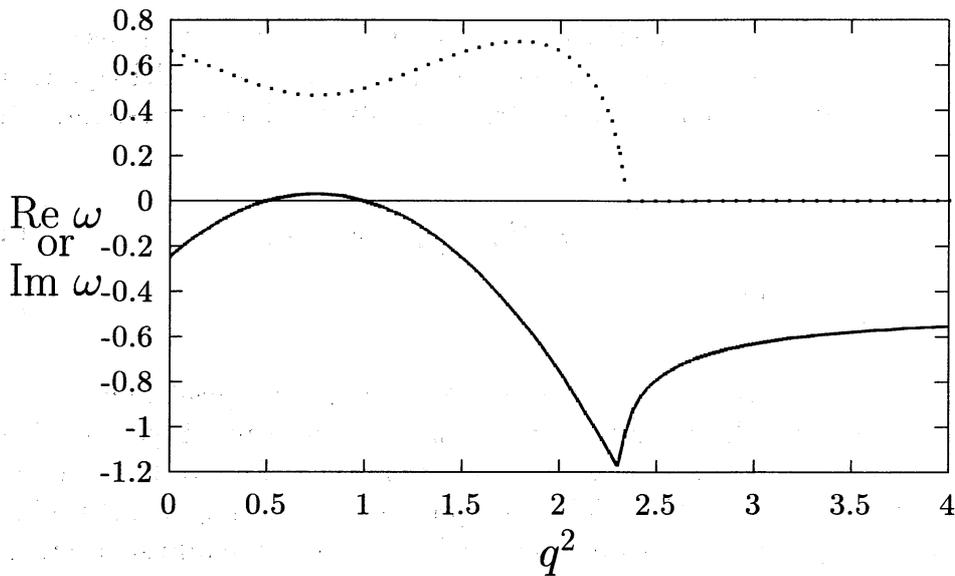


Figure 1: Dispersion relation for  $\lambda = 0.5$ ,  $\tilde{\tau} = 1.5$ , and  $D_u = \alpha = \gamma = 1$ .  $\text{Re } \omega(q)$  (solid line) and  $\text{Im } \omega(q)$  (dotted line) are plotted as functions of  $q^2$ .

length scale is characterized by  $q_c$  emerges. At this bifurcation point, one of the eigenvalues denoted by  $\omega(q)$  satisfies that  $\text{Re } \omega(q_c) = 0$  and  $\text{Re } \omega(q) < 0$  for all  $q$  except for  $q = q_c$  and  $\text{Im } \omega(q_c) > 0$ , where  $q_c$  is given by  $q_c^2 = \tilde{\tau}/(2D_u)$ . We plot  $\text{Re } \omega(q)$  (solid line) and  $\text{Im } \omega(q)$  (dotted line) as functions of  $q^2$  near the bifurcation point for  $\lambda = 0.5$ ,  $\tilde{\tau} = 1.5$ , and  $D_u = \alpha = \gamma = 1$  in Fig. 1. One can see that the unstable modes ( $\text{Re } \omega(q) > 0$ ) have their positive imaginary parts ( $\text{Im } \omega(q) > 0$ ). Note that the growth of long wavelength fluctuations is suppressed, since  $\text{Re } \omega(0)$  is always negative. In Fig. 2 we present the phase diagram in the parameter plane  $(\tilde{\tau}^2, \lambda)$ . The solid line in this figure displays the line determined by  $\text{Re } \omega(q_c) = 0$  and the dotted line displays the line determined by  $\text{Im } \omega(q_m) = 0$ , where  $q_m$  is the wave number which maximizes  $\text{Re } \omega(q)$ . For the parameters above the solid line the equilibrium solution is stable. In the closed region sectioned by these two lines, where  $\text{Re } \omega(q_m) > 0$  and  $\text{Im } \omega(q_m) > 0$ , standing or traveling waves can emerge.

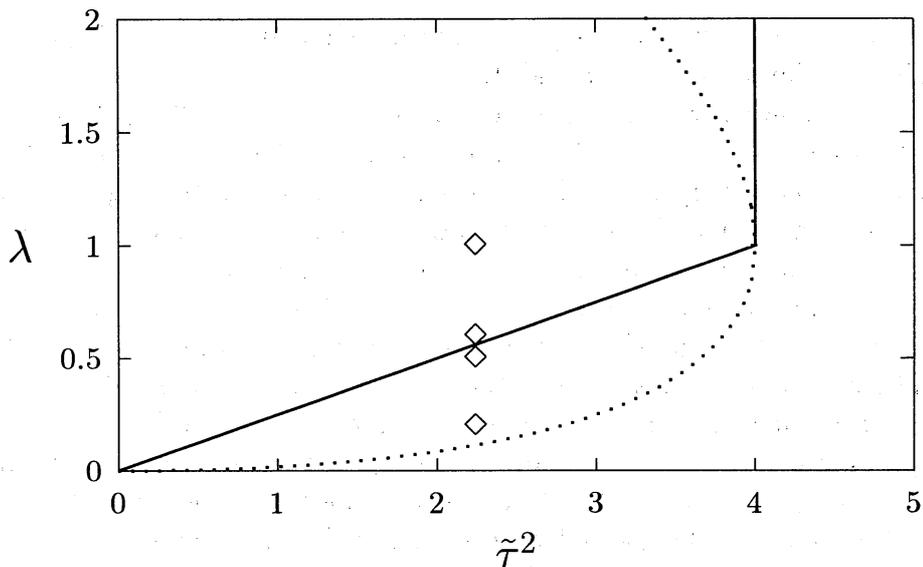


Figure 2: Phase diagram in  $(\tilde{\tau}^2, \lambda)$  plane obtained by the linear stability analysis of Eqs. (13) and (14) for  $D_u = \alpha = \gamma = 1$ . The solid line displays the line determined by  $\text{Re } \omega(q_c) = 0$  and the dotted line displays the line determined by  $\text{Im } \omega(q_m) = 0$ , where  $q_m$  is the wave number which maximizes  $\text{Re } \omega(q)$ . The symbols indicate the values of parameters used in the numerical simulations.

### 3 Numerical Simulation

We now numerically solve Eqs. (13) and (14) in two-dimensional systems for several pairs of parameters  $(\tilde{\tau}^2, \lambda)$  indicated by the symbols in Fig. 2 and the other parameters are fixed at  $D_u = \alpha = \gamma = 1$ . The computation has been carried out on the  $128 \times 128$  square lattice with the mesh size  $\Delta x = 0.5$  using the finite difference Euler scheme with a fixed time step  $\Delta t = 10^{-3}$  (we have also done the simulation with  $\Delta t = 10^{-4}$  and observed no qualitative difference in their results). We have used periodic boundary conditions and chosen as initial conditions the homogeneous states with small random perturbations which satisfy  $\int d\mathbf{r}(u - I) = \int d\mathbf{r}v = 0$ .

For the parameters above the solid line in Fig. 2 we have not observed any pattern, that is, the uniform solution is stable. Below this line, the system

is unstable and we have observed traveling lamellar and hexagonal patterns depending on the parameters  $I$  and  $\lambda$ .

Figure. 3 shows three snapshots of the system at  $t = 200$  (a), 500 (b), and 4000 (c) for  $I = 0$ ,  $\lambda = 0.5$ , and  $\tilde{\tau} = 1.5$ . The value of  $u$  is shown in gray scale, increasing from black to white. At the early stage irregular patterns with motions of distorted standing waves are formed [Fig. 3(a)]. After that, partially coherent lamellar structures which are traveling emerge [Fig. 3(b)]. The system eventually reaches the state in which the lamellar structure extended to the whole system is traveling at a constant speed [Fig. 3(c)]. These behaviors are similar to those reported by Hildebrand et al. [10] about surface chemical reaction systems. For the smaller value of  $\lambda = 0.2$  (other parameters are same as before) (Fig. 4), the amplitude of  $u$  becomes larger and the period when the standing-wave motion is observed becomes shorter [Fig. 4(a)]. The partially ordered lamellar structures with many defects are observed [Fig. 4(b)] and they are traveling in different directions each other even in the late stage [Fig. 4(c)].

Next we show the result for  $I = -0.6$ ,  $\lambda = 0.5$ , and  $\tilde{\tau} = 1.5$  in Fig. 5. At the early stage several droplet-like domains appear with distorted standing wave motions [Fig. 5(a)]. Later, these domains irregularly move accompanied with breakups and coalescences of domains [Fig. 5(b)] and finally form a regular hexagonal pattern traveling in one direction at a constant speed [Fig. 5(c)]. We also show the result for  $I = -0.6$ ,  $\lambda = 0.2$ , and  $\tilde{\tau} = 1.5$  in Fig. 6. In this case the standing wave motions are not observed at the early stage [Fig. 6(a)]. The domains are elongated and form partially coherent traveling structures [Fig. 6(b)] and a totally coherent stripe pattern which travels in one direction at a constant speed emerges at the final stage [Fig. 6(c)].

## 4 Conclusion

In conclusion, we have proposed a new model of phase-separating reactive binary mixtures which leads to emergence of the traveling structures. The traveling structures appear through Hopf bifurcations with finite wave numbers. We have demonstrated the numerical simulations which show the existence of the spontaneously traveling lamellar and hexagonal structures in two-dimensional systems.

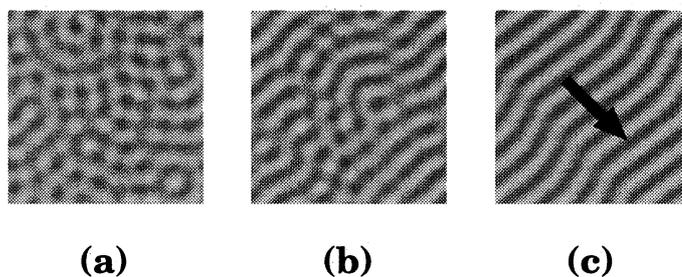


Figure 3: Three snapshots of the system at  $t = 200$  (a),  $500$  (b), and  $4000$  (c) for  $I = 0$ ,  $\lambda = 0.5$ , and  $\tilde{\tau} = 1.5$ . The value of  $u$  is shown in gray scale, increasing from black to white. The arrow in the figure (c) indicates the direction in which the lamellar pattern propagates.

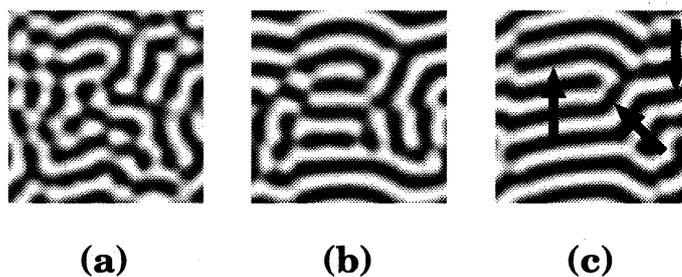


Figure 4: Three snapshots of the system at  $t = 100$  (a),  $500$  (b), and  $4000$  (c) for  $I = 0$ ,  $\lambda = 0.2$ , and  $\tilde{\tau} = 1.5$ . The value of  $u$  is shown in gray scale, increasing from black to white. The arrows in the figure (c) indicate the directions in which the partially ordered lamellar patterns propagate.

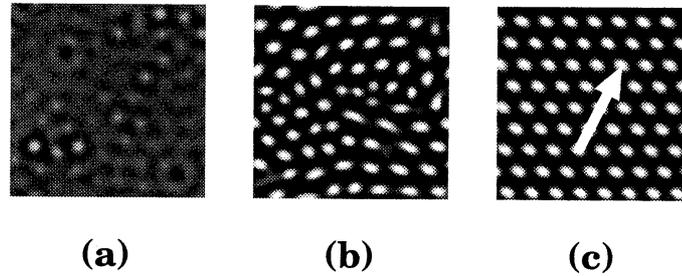


Figure 5: Three snapshots of the system at  $t = 100$  (a),  $200$  (b), and  $4000$  (c) for  $I = -0.6$ ,  $\lambda = 0.5$ , and  $\tilde{\tau} = 1.5$ . The value of  $u$  is shown in gray scale, increasing from black to white. The arrow in the figure (c) indicates the direction in which the hexagonal pattern propagates.

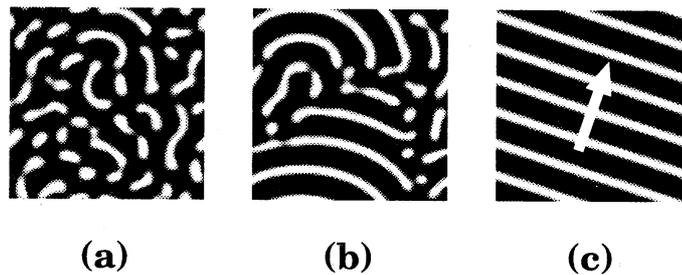


Figure 6: Three snapshots of the system at  $t = 100$  (a),  $500$  (b), and  $4000$  (c) for  $I = -0.6$ ,  $\lambda = 0.2$ , and  $\tilde{\tau} = 1.5$ . The value of  $u$  is shown in gray scale, increasing from black to white. The arrow in the figure (c) indicates the direction in which the stripe pattern propagates.

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