

Kinetic Pattern Formation with Intermolecular Interactions: A Modified Brusselator Model

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 Electronic Supplementary Information

Abstract In this work, we modify the traditional Brusselator model to incorporate the intermolecular interactions, based on which a systematic study is performed on the pattern formation mediated by chemical reaction and phase separation. It is found that if the chemical reaction dominates, the pattern formation will be inhibited by the phase separation while if the phase separation dominates, the chemical reaction will prevent, under certain conditions, the domain size from growing which results in dissipative patterns other than macroscopic phase separations.

Keywords Brusselator model; Regular solution; Phase separation

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INTRODUCTION

Two kinds of patterns are common in nature. One is generated thermodynamically and maintained as equilibrium states, such as the crystal structure, microphase separation of block copolymers,^[1] etc. Another arises kinetically, sustained far from equilibrium, having been, for instance, observed in hydrodynamic systems,^[2,3] reaction-diffusion systems,^[4,5] and most importantly in biological systems.^[6] The thermodynamic pattern is controlled by the principle of free energy minimization and has inspired diverse applications. The kinetic patterns, especially the patterns in the reaction-diffusion system, need specific kinetic analysis and have gained lots of interest for their connections to biological phenomena.^[7] Prigogine once designed a reaction-diffusion model, the Brusselator,^[8] and analyzed its pattern formation. Prigogine's work illustrates the great similarities between life and the kinetic patterns: both are non-linear, far from equilibrium and dependent on matter or energy import.^[9]

Despite its great success, the classical Brusselator model did not incorporate interactions or phase separations between chemicals, which have recently been realized to be important for various biological processes.^[10–12] In biological systems, phase separation and chemical reactions will influence each other. For example, cytoplasm in the cells is a “crowded” medium, where all kinds of interactions are inevitable and have been observed to induce substantial effect

on the rates of biochemical reactions.^[13] Phase separation driven by intermolecular reactions is also common for living systems. Numerous protein condensates essential to living process are assembled by liquid-liquid phase separations.^[14] However, theoretical studies of the coupling between chemical reactions and phase separations have been rarely reported and some of these studies are controversial. Glotzer *et al.*^[15] found that a simple binary chemical reaction coupled with intermolecular interactions (phase separation) would lead to Turing patterns. Unfortunately, this fascinating result was controversial.^[16,17] On the contrary, by a simple two-molecule model, Carati and Lefever^[18] showed that even for the reaction-diffusion system with intermolecular reactions, autocatalytic reaction was still needed to produce periodic patterns. Nevertheless, all of these studies have not systematically investigated the interplay between the chemical reaction and the phase separation. Their combining effects on the pattern formation are, thus, still not clear. Furthermore, to our best knowledge, the study on the Brusselator with intermolecular interactions has not been reported yet.

Therefore, in the current work, we will incorporate the intermolecular interactions into the classical Brusselator by following Carati *et al.*'s method^[18] and systematically study the interplay between the chemical reaction and the phase separation. In particular, their combining effects on the pattern formation will be addressed. This study is organized as follows. We will present, in the method section, the dynamical equations of the chemical reaction coupling with the phase separation as well as their stability analysis. In the results section, we first study the case of relatively weak interactions to see how intermolecular interactions influence the patterns

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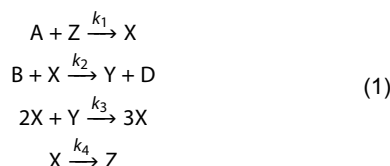
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formation dominated by the (autocatalytic) chemical reactions. Then we consider the case with relatively strong interactions and study how chemical reactions freeze the growing of the phase-separated domains to finally form the dissipative patterns. These results are obtained by the dynamical simulations aided by the stability analysis and will be summarized in a series of ternary state diagrams.

METHODS

Model Construction

The reaction model employed in this work is a modified Brusselator,



where six different chemical components are involved and, similar to the classical Brusselator,^[8] the concentrations of three components, A, B and D are assumed to be maintained constants. In particular, D will be removed once it is produced, so we do not need to consider D further. The third reaction in Eq. (1) is autocatalytic. Compared to the classic Brusselator,^[8] a new component Z has been introduced to meet the incompressibility constraint. This treatment enables us to perform the following dynamical simulations and it was first proposed by Decker and Lefever who used it to study the spatial constraint effect.^[19] The free energy of this system could be written as,

$$G(T, P)/k_B T = \int dr \rho [\phi_X \ln \phi_X + \phi_Y \ln \phi_Y + \phi_Z \ln \phi_Z + \chi \phi_X \phi_Y + \frac{b}{2} (|\nabla \phi_X|^2 + |\nabla \phi_Y|^2)] \quad (2)$$

where ϕ_X , ϕ_Y and ϕ_Z are the volume fractions of X, Y and Z, respectively, defined as $\phi_X = \rho_X/\rho$, $\phi_Y = \rho_Y/\rho$ and $\phi_Z = \rho_Z/\rho$ with $\rho = \rho_X + \rho_Y + \rho_Z$. For simplicity, this work only considers the interaction between the components X and Y with χ the Flory-Huggins parameter. Because the volume fractions of the left three components, A, B and D, are assumed to be constant, therefore, their contributions to the entropy part of the free energy are also constants and can be neglected.

The dynamical equations that govern the chemical reactions and phase separation read,

$$\begin{aligned} \frac{\partial \rho_X}{\partial t} &= k_1 a_A a_Z - k_2 a_B a_X + k_3 a_X^2 a_Y - k_4 a_X + D_X \nabla^2 a_X \\ &\quad - \nabla \phi_X (D_X \nabla a_X + D_Y \nabla a_Y + D_Z \nabla a_Z) \\ \frac{\partial \rho_Y}{\partial t} &= k_2 a_B a_X - k_3 a_X^2 a_Y + D_Y \nabla^2 a_Y \\ &\quad - \nabla \phi_Y (D_X \nabla a_X + D_Y \nabla a_Y + D_Z \nabla a_Z) \\ \frac{\partial \rho_Z}{\partial t} &= -k_1 a_A a_Z + k_4 a_X + D_Z \nabla^2 a_Z \\ &\quad - \nabla \phi_Z (D_X \nabla a_X + D_Y \nabla a_Y + D_Z \nabla a_Z) \end{aligned} \quad (3)$$

where D_X , D_Y and D_Z are diffusion coefficients of the corresponding components. As suggested by Lefever *et al.*,^[18,20] the concentrations in the reaction terms have been replaced

by activities, the exponential functions of chemical potentials $a = \exp[\mu/k_B T] = \exp[\delta G/k_B T \delta \phi]$, among which a_A and a_B are the activities of A and B, kept as constant, and a_X , a_Y and a_Z are activities of X, Y and Z expressed by exponents of chemical potential functions of ρ_X , ρ_Y and ρ_Z as follows,

$$\begin{aligned} a_X &= \rho_X \exp \left[\chi \phi_Y (1 - \phi_X) - \frac{b}{2} (|\nabla \phi_X|^2 + |\nabla \phi_Y|^2) - b \nabla^2 \phi_X \right] \\ a_Y &= \rho_Y \exp \left[\chi \phi_X (1 - \phi_Y) - \frac{b}{2} (|\nabla \phi_X|^2 + |\nabla \phi_Y|^2) - b \nabla^2 \phi_Y \right] \\ a_Z &= \rho_Z \exp \left[-\chi \phi_X \phi_Y - \frac{b}{2} (|\nabla \phi_Y|^2 + |\nabla \phi_X|^2) \right] \end{aligned} \quad (4)$$

The form of the diffusion terms in Eq. (3) is basically adopted from de Gennes' work^[21,22] where he tried to derive the dynamical equation for binary polymer blends. Note that the current form of the diffusion terms is important to maintain the incompressibility constraint; one can check that the three equations in Eq. (3) are added to zero and, therefore, there are only actually two degrees of freedom. One challenge that follows immediately is that the terms like $\nabla \phi \nabla a$ are difficult to numerically integrate. We use the discrete variational principle,^[23,24] which has been employed by us to simulate the dramatic deformation of vesicles,^[23] to design the numerical scheme for these terms (in the electronic supplementary information, ESI).

Stability Analysis

Because of the incompressibility constraint, only two equations in Eq. (3) are independent, so Eq. (3) can be simplified as follows:

$$\begin{aligned} \frac{1}{C} \frac{\partial \phi_X}{\partial t} &= A Z - B X + X^2 Y - X \\ &\quad + L [\beta \nabla^2 X - \nabla \phi_X (\beta \nabla X + \nabla Y + \theta \nabla Z)] \end{aligned} \quad (5)$$

$$\frac{1}{C} \frac{\partial \phi_Y}{\partial t} = B X - X^2 Y + L [\nabla^2 Y - \nabla \phi_Y (\beta \nabla X + \nabla Y + \theta \nabla Z)]$$

where most relevant quantities in Eq. (3) have been scaled to the dimensionless form:

$$\begin{aligned} L &= \frac{D_Y}{k_4} \quad \beta = \frac{D_X}{D_Y} \quad \theta = \frac{D_Z}{D_Y} \\ \tau &= k_4 t, \quad C = \left(\frac{k_4}{k_3} \right)^{\frac{1}{2}} \frac{1}{\rho} \\ A &= a_A \frac{k_1}{k_4}, \quad B = a_B \frac{k_2}{k_4} \\ X &= a_X \left(\frac{k_3}{k_4} \right)^{\frac{1}{2}}, \quad Y = a_Y \left(\frac{k_3}{k_4} \right)^{\frac{1}{2}}, \quad Z = a_Z \left(\frac{k_3}{k_4} \right)^{\frac{1}{2}} \end{aligned} \quad (6)$$

In the Brusselator model, activities of components A and B are normally controlled as constants, so the corresponding rescaled parts A and B are constants too. If we take A and B as the controlled parameters to carry out the stability analysis, we have to solve the following equations:

$$\begin{aligned} A &= \frac{X}{Z} = \frac{\phi_X}{1 - \phi_X - \phi_Y} \exp[\chi \phi_Y] \\ B &= XY = \frac{1}{C^2} \phi_X \phi_Y \exp[\chi (\phi_X + \phi_Y - 2\phi_X \phi_Y)] \end{aligned} \quad (7)$$

to find all possible homogeneous steady-state solutions for Eq. (5) under the constant A and B. Unfortunately, these two equations are transcendental and their analytical solutions are unavailable. The same set of A and B, always corresponds to several different homogeneous steady-state solutions and

finding all of them numerically is difficult. But we can overcome this difficulty by changing the controlled parameters from A and B to the steady-state solutions Φ_X and Φ_Y , instead. By plugging Eq. (7) into Eq. (5), we obtain the dynamical equations expressed, in terms of the new controlled parameters as:

$$\begin{aligned} \frac{1}{C} \frac{\partial \Phi_X}{\partial \tau} = & \frac{\Phi_X}{1 - \Phi_X - \Phi_Y} \exp[\chi \Phi_Y] Z + \chi^2 Y - \chi \\ & - \frac{1}{C^2} \Phi_X \Phi_Y \exp[\chi(\Phi_X + \Phi_Y - 2\Phi_X \Phi_Y)] X \\ & + L[\beta \nabla^2 X - \nabla \Phi_X(\beta \nabla X + \nabla Y + \theta \nabla Z)] \end{aligned} \quad (8)$$

$$\begin{aligned} \frac{1}{C} \frac{\partial \Phi_Y}{\partial \tau} = & \frac{1}{C^2} \Phi_X \Phi_Y \exp[\chi(\Phi_X + \Phi_Y - 2\Phi_X \Phi_Y)] X - \chi^2 Y \\ & + L[\nabla^2 Y - \nabla \Phi_Y(\beta \nabla X + \nabla Y + \theta \nabla Z)] \end{aligned}$$

The rescaled activities A and B can be recovered as $A = A(\Phi_X, \Phi_Y)$ and $B = B(\Phi_X, \Phi_Y)$ using Eq. (7). For the ideal solution case ($\chi = b = 0$), linear stability analysis of Eq. (8) gives the growth factor as a fourth-order polynomial of the wave number $\mathbf{k}$ for small $|\mathbf{k}|$,

$$\begin{aligned} \Gamma_0(\mathbf{k}) \approx & \frac{(\Phi_X)^2}{C^2} \left(\frac{\Phi_Y - \Phi_X}{1 - \Phi_X - \Phi_Y} - 1 \right) + L \frac{1 - [1 + \Phi_X(1 - \beta)] \Phi_Y}{1 - \Phi_X - \Phi_Y} |\mathbf{k}|^2 \\ & + \Phi_X L \frac{\Phi_Y - [\Phi_X + \Phi_Y - \beta(1 - \Phi_X - \Phi_Y)]}{C^2} |\mathbf{k}|^2 \\ & + L^2 [\Phi_X(\beta - 1) - \beta] |\mathbf{k}|^4 \end{aligned} \quad (9)$$

When χ and b are nonzero, the growth factor becomes more complicated and it can be expressed as:

$$\Gamma(\mathbf{k}) \sim \Gamma_0(\mathbf{k}) \exp[f(\Phi_X, \Phi_Y)] - b|\mathbf{k}|^6 - b^2|\mathbf{k}|^8 \quad (10)$$

where $f(\Phi_X, \Phi_Y)$ is an extremely complicated function related with the free energy density defined in Eq. (2).

For a given pair of controlled parameters Φ_X and Φ_Y (or equivalently $A(\Phi_X, \Phi_Y)$ and $B(\Phi_X, \Phi_Y)$), Eq. (8) has at least two homogeneous steady-state solutions, the trivial solution ($\phi_X=0, \phi_Y=1$) and the non-trivial solution ($\phi_X=\Phi_X, \phi_Y=\Phi_Y$). The trivial solution is always stable since its growth factor is, by Eq. (9) or Eq. (10), negative definite. For the non-trivial solution,

the above stability analysis and dynamical simulations reveal four possible endings of the state started from this solution: I) being stable *in situ*; II) evolving to the trivial solution ($\phi_X=0, \phi_Y=1$); III) evolving to stable states of the case (I); and IV) forming dissipative patterns. Obviously, only the state in (I) is stable. According to the above four possible endings, all possible (Φ_X, Φ_Y) could be divided into four types, which could be summarized in a ternary diagram, as four typical stability regions, in the parameter space (Φ_X, Φ_Y) with $\Phi_X > 0, \Phi_Y > 0$ and $0 < \Phi_X + \Phi_Y < 1$. Boundary of the region I can be identified by the linear stability analysis while numerical calculations or simulations are needed to draw the regions of II, III and IV.

The ternary diagram is completely determined by six model parameters, $C, L, \theta, \beta, \chi$ and b , while this work focuses on the influences of β, χ , and b . β is the relative diffusion coefficient of D_X versus D_Y , which characterizes the diffusion asymmetry and is normally used to control the pattern formation in the traditional Brusselator.^[8]

RESULTS AND DISCUSSION

Patterns Formed by Chemical Reactions

Patterns in small χ are mostly driven by chemical reactions. In this case, the phase separation, quantified by χ , will inhibit the pattern formation.

Fig. 1(a) shows the ternary stability diagram at $\chi=b=0.0$ and $\beta=0.05$, where the pattern region (region IV painted grey on the diagram) dominates. Patterns in the region IV (see the insets E and F in Fig. 1a for example) are actually the patterns of the classical Brusselator, generated and sustained by the non-linear autocatalytic reactions. Surrounding the pattern region IV are regions I, II and III. States in the region I are stable while states in the region III are unstable and will evolve to the region I as shown by the trajectory from G to H in Fig. 1(a). The trajectory G-H is given by the simulation. The region II is embedded in the region IV and the states in this region will be attracted to the trivial steady-state solution (0, 1) denoted by M (see the trajectory from P to M in Fig. 1b).

Just as shown in Figs. 1(a) and 1(b), increasing χ will shrinkage the pattern region IV, which implies that phase separa-

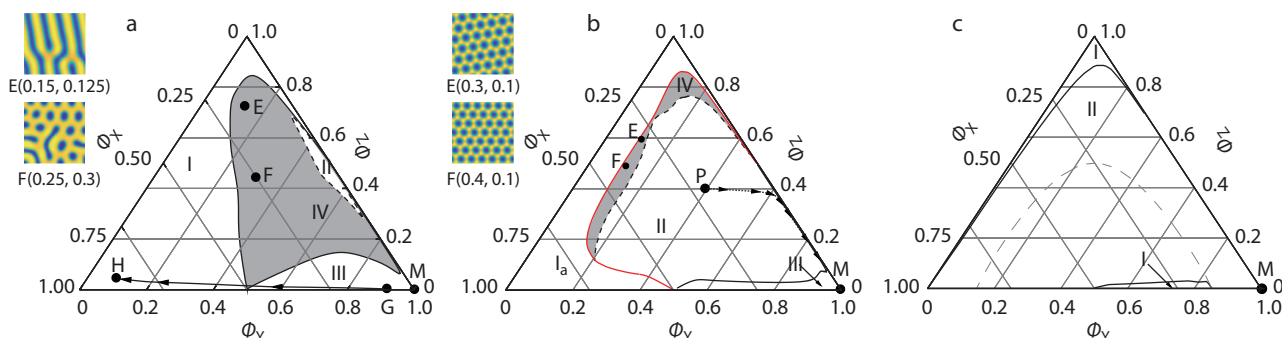


Fig. 1 Ternary stability diagrams of the modified Brusselators at $\chi=0.0$ and $b=0.0$ (a), $\chi=0.5$ and $b=0.25$ (b), and $\chi=4.0$ and $b=2.0$ (c). Other model parameters are $L=\theta=1.0$, $C=0.05$ and $\beta=0.05$. The diagrams are in the parameter space of (Φ_X, Φ_Y) or equivalently $(A(\Phi_X, \Phi_Y), B(\Phi_X, \Phi_Y))$ by Eq. (7). The diagram shows the stability of the state started from $(\phi_X = \Phi_X, \phi_Y = \Phi_Y)$. In Region I, all states are stable. In Region II, all states are not stable and will evolve to the trivial solution point M as shown in the trajectory P-M in (b); while states in Region III will evolve to the states in Region I as shown in the trajectory G-H in (a). In Region IV (gray), the homogeneous initial states will finally form dissipative patterns as shown in E and F in (a) and E and F in (b) (Yellow for X component). The dash-line phase boundaries in (a) and (b) are not very accurate due to the numerical reasons. The phase diagram of the mixture X, Y and Z without chemical reactions is shown using grey dash line in (c) as a reference diagram.

tion will inhibit the pattern formation driven by the autocatalytic reactions. Compared to the ideal-solution case of Fig. 1(a), periodic patterns are mostly formed at small ϕ_X and small ϕ_Y for the regular-solution case (Fig. 1b), where according to Eq. (4) intermolecular interactions have little influence in this region. It is expected that further increasing χ will further shrink the pattern region to the even smaller ϕ_X and ϕ_Y region and will, eventually, cause it to disappear (Fig. 1c). On the other hand, when $\chi > 2.0$ the intermolecular interaction will cause the mixture to separate at the relatively large ϕ_X and ϕ_Y , i.e. the phase region below the grey dash curve in Fig. 1(c); but this phase separation will be quickly suppressed by the chemical reactions for relatively small β and the system will become homogeneous again. Fig. 1(c) ($\chi = 4.0$) shows that these two effects will cause the pattern region to disappear, at least at our calculation accuracy.

Patterns Formed by Phase Separation

However, phase separation effect does not necessarily inhibit the pattern formation. If the catalyst X can diffuse much faster than Y ($\beta > 1$), then the catalyst X might not have time to fully ‘engage’ on the autocatalytic reactions and the phase separation will dominate and induce a new class of dissipative patterns. Fig. 2 shows the ternary stability diagram at $\chi = 4.0$, $b = 2.0$ and $\beta = 20.0$. Compared with the diagram without phase separation (for example, Fig. 1a), there are two I regions with one of them under the phase-separation line (the grey dash line in Fig. 2). All states in region III will evolve to the region I under the phase-separation line and a typical trajectory G-H is given in Fig. 2. Between the regions I and III, there is a thin layer of region

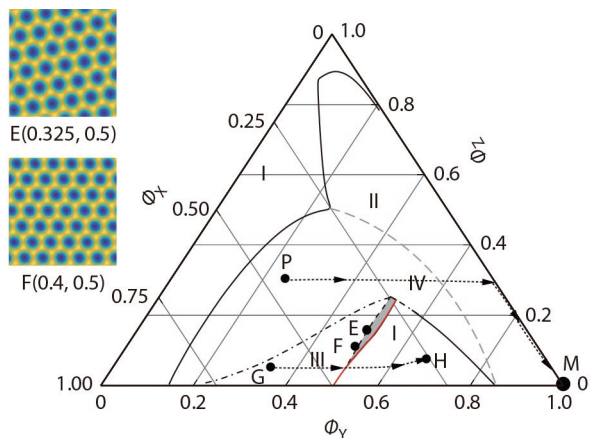


Fig. 2 Ternary stability diagram of the modified Brusselators at $\chi = 4.0$, $b = 2.0$, $\beta = 20.0$, $L = \theta = 1.0$ and $C = 0.05$. The diagram is in the parameter space of (ϕ_X, ϕ_Y) or equivalently $(A(\phi_X, \phi_Y), B(\phi_X, \phi_Y))$ by Eq. (7). The diagram shows the stability of the states started from $(\phi_X = \phi_X, \phi_Y = \phi_Y)$. There are two I Regions where all states are stable. In Region II, all states are not stable and will evolve to the trivial solution point M as shown in the trajectory P-M obtained by simulations; while states in Region III will evolve to the states in Region I as shown in the trajectory G-H. In Region IV (grey), the homogeneous initial states will finally form dissipative patterns as shown in E and F (yellow for X component). The dash-dot-line phase boundaries are not very accurate due to the numerical reasons. The phase diagram of the mixture X, Y and Z without chemical reactions is shown by using grey dash line as a reference diagram.

IV, where the new class of patterns are formed (see the two insets in Fig. 2). These could be referred to as the patterns induced by the phase separation. They are of the same kind as the patterns in the literature,^[18] in which Carati *et al.* have attributed them to the chemical freezing effect to the phase separation. However, they showed no specific example or theoretical analysis about this effect in their work.

In the current work, we present a linear analysis (Fig. 3) together with an example (Fig. 4) to investigate the chemical freezing effect. In this example, two simulations are performed; the first one serves as a reference simulation with no chemical reactions and it undergoes macroscopic phase separation (see upper snapshots in Fig. 4) while the second one has the same model parameter setting as the reference one but with the chemical reactions (see lower snapshots in Fig. 4). At the initial stage, there is not much difference between these two simulations, except that the chemical freezing pattern are more ‘regular’, for its growth factor curve is narrower (Fig. 3a). Then chemical reactions in the second simulation freeze the pattern in its early stage and modulate it into regular hexagonal patterns. Unfortunately, we find that it is difficult to give a theoretical explanation about this freez-

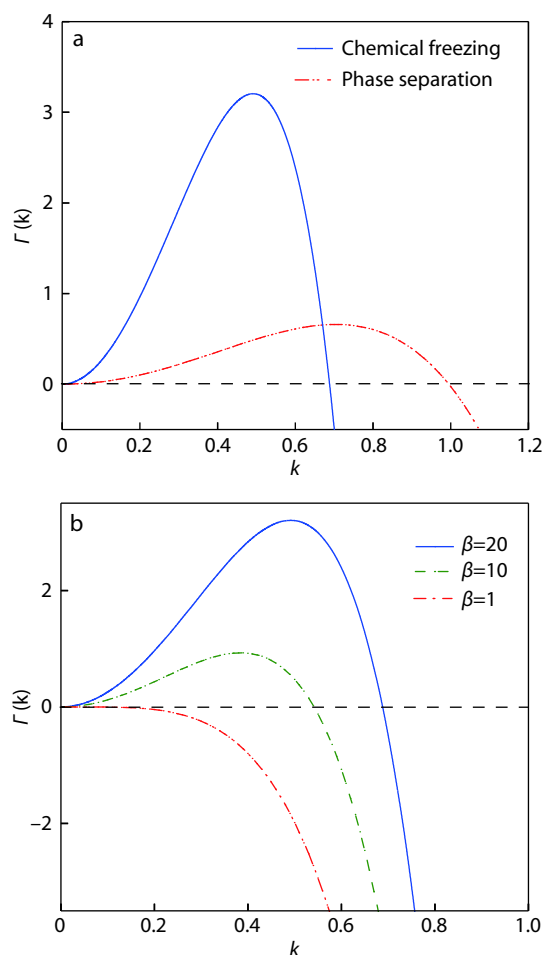


Fig. 3 Linear growth factors $\Gamma(k)$. (a) Growth factors for the pure phase separation and the phase separation with chemical reactions (Eq. 10) at $\phi_X = 0.49$ and $\phi_Y = 0.5$. (b) Growth factors for different β 's at $\phi_X = 0.49$, $\phi_Y = 0.5$, $\chi = 4.0$ and $b = 2.0$.

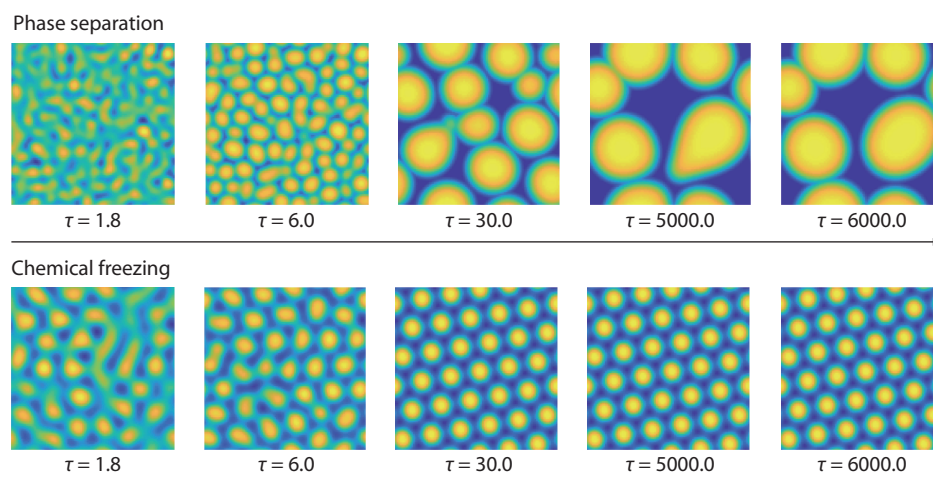


Fig. 4 Two simulations of the modified Brusselator model show the freezing effect of chemical reactions. The upper shows the snapshots at different scaled times of the reference simulation when the chemical reactions are turned off while the lower shows the simulation with chemical reactions. Both simulations share the same model parameters except for those related with the chemical reactions. Parameter setting: $\Phi_X=0.49$, $\Phi_Y=0.5$, $\chi=4.0$, $b=2.0$ and $\beta=20.0$. In these snapshots, blue is for X component and yellow is for Y component.

ing effect mostly because the linear stability analysis (LSA) is only valid at the very early stage of the dynamics; and the growth factor curves obtained by LSA in Fig. 3(a) have already shown that the chemical reactions will not completely suppress the large wave-length mode (small k near 0) at the very early stage of the dynamics.

Two more comments are in order: (a) Chemical freezing effect is largely influenced by the relative diffusive speed of the catalyst X measured by β . If the X diffuses slowly ($\beta < 1$), then it will have sufficient time to turn Y into X through autocatalytic reactions and no phase separation of X/Y is needed to lower the X-Y interaction energy. So as shown by the red curve in Fig. 3(b), almost all modes will be suppressed at the early stage. On the other hand, if X diffuses fast ($\beta > 1$), then X would choose to diffuse away from Y other than turn Y into X

through chemical reactions in order to reduce the X-Y interaction, which results in phase separations (green and blue curves in Fig. 3b). Because X can still turn Y into X through chemical reactions, there is a long-distance correlation between X and Y, implying a microphase separation, which can be seen in Fig. 4. (b) The whole dynamical picture in the region IV is complicated. In this study, we only discuss the simple patterns formed near their boundaries. The other more complicated patterns will be discussed in our future work.

Domain Size and Morphology of Patterns

We also investigate the dependence of the domain size of the pattern on the initial concentration of the catalyst, Φ_X , near the boundary of the region IV (the red boundary in Fig. 1b and Fig. 2). Near the boundary of the region IV, the local concentrations of components only deviate a little from the

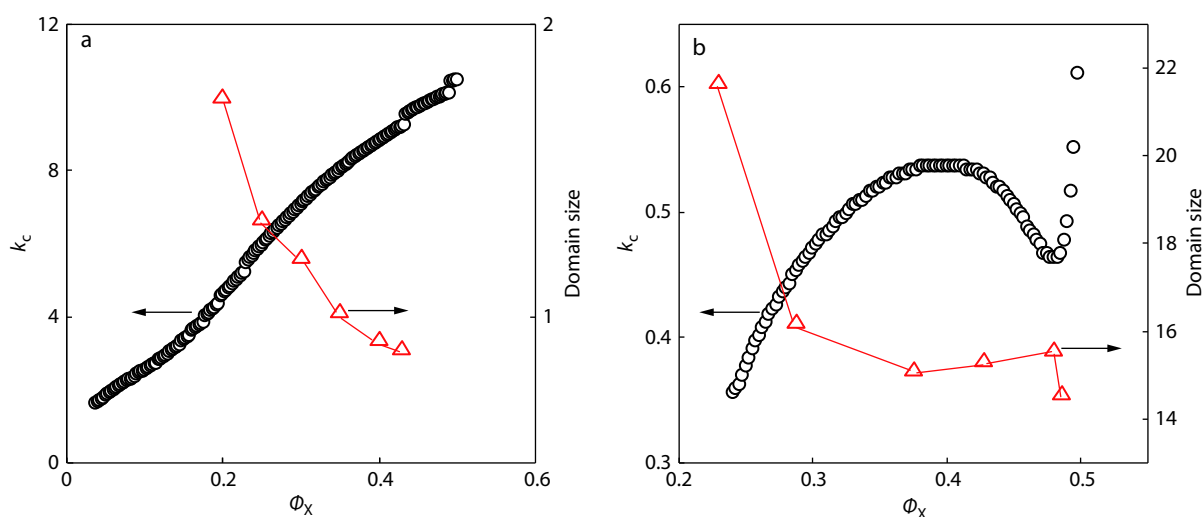


Fig. 5 Slow mode wave number k_c versus Φ_X (the black circles) and the domain size versus Φ_X (the red lines). The slow mode wave number is obtained by solving the equation $\partial f(\mathbf{k})/\partial \mathbf{k} = 0$ while the domain-size curves are obtained by directly measuring the domain size of the simulated patterns. (a) Shows the corresponding curves of the red line in Fig. 1(b), and (b) corresponds to the red line in Fig. 2.

initial concentrations, so the slow mode wave number k_c of the initial dynamics or its reciprocal, the wave length, can be used to estimate the domain size of the final patterns. Note that, the slow mode wave number can be obtained by solving the equation $\partial\Gamma(\mathbf{k})/\partial\mathbf{k} = 0$.

The results are shown in Figs. 5(a) and 5(b). For the chemical-reaction dominated case, which corresponds to IV in Fig. 1(b), the domain size of the pattern is a monotonically decreasing function of the initial concentration of the catalyst X. While for the phase-separation dominated case (IV in Fig. 2), the domain size as a function of Φ_X is not monotonic anymore, it will first decrease, then increase a little bit and decrease again.

During our simulations, we find one interesting, seemingly abnormal phenomenon about the influence of the interfacial energy on the size of the interface of the dissipative patterns.

For the phase-separation dominated case (Fig. 6), the interface of the domains becomes smaller for bigger interfacial energetic penalty (bigger b) and this is an expected phenomenon. Interestingly, for the chemical-reaction dominated case (Fig. 7), the tendency is reversed that increasing b will also increase the size of the interface. This abnormal phenomenon can be explained as follows. First, as we pointed out in the introduction section, patterns formed by the non-linear chemical reactions are not thermodynamic patterns and, instead, they are kinetic; therefore, minimum interfacial energy principle is not applicable in this case anymore. Second, bigger b might just happen to ‘work’ together with other model parameters to make interface bigger. However, the dependence of the size of interface on b is complicated and still not clear in theory, and we will try to resolve this puzzle in our future work.

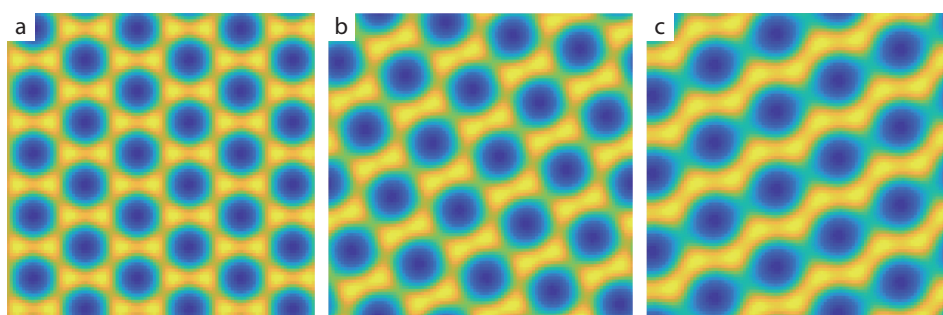


Fig. 6 Morphological transformation of dissipative patterns when the interfacial energy is increasing for the phase-separation dominated case. The snapshots show ϕ_X (yellow) profile at $\tau=6000$. (a) $\chi=4.0$ and $b=1.8$; (b) $\chi=4.0$ and $b=2.2$; (c) $\chi=4.0$ and $b=2.4$. Other parameters: $\Phi_X=0.275$, $\Phi_Y=0.5$, $\beta=20.0$, $L=\theta=1.0$ and $C=0.05$.

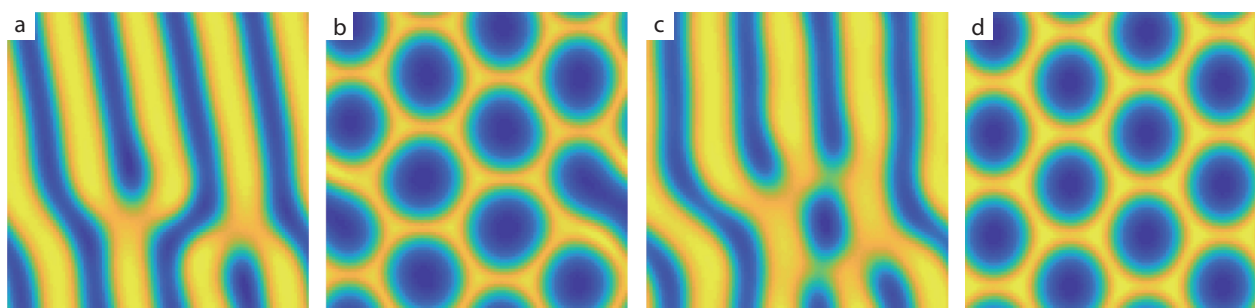


Fig. 7 Morphological transformation of dissipative patterns when interfacial energy is increasing for the chemical-reaction dominated case. The snapshots are taken at $\tau = 6000$ with yellow for X component. (a) $\chi=0.0$ and $b=0.0$; (b) $\chi=0.0$ and $b=0.05$; (c) $\chi=0.1$ and $b=0.0$; (d) $\chi=0.1$ and $b=0.05$. Other parameters: $\Phi_X=0.15$, $\Phi_Y=0.125$, $\beta=0.05$, $L=\theta=1.0$ and $C=0.05$. Note that these four snapshots give two sets of transformations for the ideal-solution case (from (a) to (b)) and for the regular-solution case (from (c) to (d)), respectively.

CONCLUSIONS

The traditional Brusselator model has been modified to include intermolecular interactions in this work. Based on the modified model, we systematically investigate the combining effects of the autocatalytic reactions and the phase separation on the pattern formation and obtain the following results. First, we find that when the chemical reaction dominates, the pattern formation will be inhibited by the phase separation and this finding has not been reported before. Second, similar to Carati and Lefever's work^[18] it is found that chemical reactions can freeze the domain growing originally initiated by

the phase separation and this freezing effect finally forms the dissipative pattern. Different from those thermodynamic patterns formed by block copolymers, we find an interesting phenomenon for these kinetic patterns that increasing the interfacial energy will also increase interface of the pattern for some cases.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/>

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