Solution landscapes of the diblock copolymer-homopolymer model under two-dimensional confinement

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We investigate the solution landscapes of the confined diblock copolymer and homopolymer in two-dimensional domain by using the extended Ohta–Kawasaki model. The projected saddle dynamics method is developed to compute the saddle points with mass conservation and construct the solution landscape by coupling with downward/upward search algorithms. A variety of novel stationary solutions are identified and classified in the solution landscape, including Flower class, Mosaic class, Core-shell class, and Tai-chi class. The relationships between different stable states are shown by either transition pathways connected by index-1 saddle points or dynamical pathways connected by a high-index saddle point. The solution landscapes also demonstrate the symmetry-breaking phenomena, in which more solutions with high symmetry are found when the domain size increases.

1 Introduction

The diblock copolymers are composed of two different blocks linked together through covalent bonding. A large number of copolymers interact with each other to produce a wide variety of microstructures, resulting from a compromise between phase segregation and polymer architecture.1, 2 The diblock copolymer materials have aroused great interest in both industrial and theoretical research. Moreover, an important commercialized application of copolymers is thermoplastic elastomers, which have been widely used as jelly candles, outer coverings for optical fiber cables, adhesives, bitumen modifiers, etc.3–5 Much scientific interest on the self-assembly of block copolymers is due to the pattern formation and the potential applications of the microstructures led by the confinement mechanism, which restricts degrees of freedom in space and breaks symmetry of the structure.6

Extensive experimental and theoretical studies have demonstrated that confinement can be used to control the self-assembly of diblock copolymers.7 The diblock copolymers under different confinements have been well studied, such as two-dimensional (2D) cylindrical confinement,8, 9 3D cylindrical confinement,10, 11 and 3D spherical or polyhedral confinement.12–14 Many novel morphologies have been discovered, for example, the onion-like and layered structures for symmetric copolymers under spherical confinement in experiments.15–17 These resulting morphologies are often distinctly different from those in the bulk phase18 and thus defined as the “frustrated phases”.19 Meanwhile, many mathematical models and numerical studies have been carried out to investigate the confinement of copolymers and their self-assembly, including Monte Carlo simulation,20 cell dynamics simulation,21 and the self-consistent field theory.22, 23

The first qualitative model for the block copolymers was proposed by Ohta and Kawasaki24 in the form of a generalized Landau free-energy functional with nonlocal term to describe the linkage between the different blocks in copolymers. This was carefully re-derived in a more mathematical formulation by Nishiura et al.25 and its singular limit was also discussed there. With this introduction to mathematical community, Choksi and many other people then started to work in this direction.26–29

The above Ohta-Kawasaki model was extended to a system composed of block copolymers and homopolymers with two phase variables to describe the macro-phase separation between the copolymers and homopolymers, as well as the micro-phase separation between the two components of the diblock copolymers.30, 31 Hereafter we call the extended Ohta–Kawasaki free-energy functional as the diblock copolymer-homopolymer (DCH) free-energy

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functional for simplicity. Multiple stable self-assembled phases can be found by the minimization of the DCH functional, such as layers, tennis balls, onions, and multipods under the nanococonfinements.[17,19,22] However, the relationships between different stable states and the landscape of possible stationary solutions of the DCH free-energy functional are still unclear.

The stationary solutions correspond to the solutions of the Euler-Lagrange equation of the DCH free-energy functional with the mass conservation. The Euler-Lagrange equation usually has multiple solutions, including both stable/metastable solutions, i.e., local minima, and unstable saddle points of the system. The properties of stationary solutions can be characterized by the Morse index of the solution. The Morse index of a stationary solution is equal to the number of negative eigenvalues of its Hessian matrix.[23] In particular, a local minimum or stable state can be regarded as an index-0 solution with no unstable directions. Compared to computing a stable state by gradient dynamics, the saddle point is much more difficult to find due to its unstable nature, while often plays critical roles in determining the properties of the model system. For instance, to find the transition pathways between two stable states, one needs to compute the transition state, which is an index-1 saddle point and the corresponding Hessian matrix has one and only one negative eigenvalue. It has attracted substantial attentions to find multiple stationary solutions of the nonlinear problems.[24] Considerable efforts have been made to develop various numerical algorithms, such as the minimax method,[25] the deflation technique,[26] the eigenvector-following method,[27] and the homotopy method.[28,29] In particular, Yin et al. proposed a novel saddle dynamics (SD) and implemented a high-index optimization-based shrinking dimer method to compute any-index saddle points.[30,31] By combining the SD with the downward and upward search algorithms, Yin et al. further constructed a solution landscape, which is a pathway map consisting of all stationary solutions and their connections, for the unconstrained systems.[32] This numerical approach has been successfully applied to the Landau-type free-energy functional, including the defect landscape of confined nematic liquid crystal on a square using a Landau-de Gennes model and the transition pathways between period crystals and quasicrystals by applying the Lifshitz–Petrich model.[33]

In this paper, we apply the DCH model to investigate the solution landscape of the diblock copolymers and homopolymers in 2D confinement. To deal with the mass-conservation constraint, we develop the projected saddle dynamics (PSD) method, which is a constrained version of the SD by using the projection operator. Then we systematically construct the solution landscapes with two critical parameters: one represents the preference intensity and the other corresponds to the domain size. A variety of novel stationary solutions are found in the solution landscapes, including Flower class, Mosaic class, Core-shell class, and Tai-chi class. Furthermore, the solution landscapes demonstrate the relationships between different stable states by either transition pathways connected by index-1 saddle points or dynamical pathways connected by a high-index saddle point. The solution landscapes also reveal the symmetry-breaking phenomena, in which more solutions with high symmetry are identified when the domain size increases.

The rest of the paper is organized as follows. The DCH model is briefly introduced in Section 2. The PSD method and the numerical algorithm of construction of a solution landscape are presented in Section 3. We numerically construct the solution landscapes with different preferences and domain sizes in Section 4. Final conclusions and discussions are presented in Section 5.

2 Diblock copolymer-homopolymer model

We consider the mixture of AB diblock copolymers and C homopolymers,[34] with two independent and conserved phase-field order parameters $\eta$ and $\phi$. $\eta$ represents the macro-phase separation with a phase boundary that can be understood as a confining surface, which arises naturally to separate the homopolymer phase from the copolymer phase. The copolymers are assumed to be immersed in an external-medium homopolymers or solvent, such as water. In the copolymer-rich domain, another variable $\phi$ describes the micro-phase separation between the block A and block B. When the above two systems interact with one another, the morphologies consist of the confinement surface and copolymer components within the surface, and then undergo a macro-phase and micro-phase separation described by $\eta$ and $\phi$, respectively.

The DCH free-energy functional can be written as a sum of short-range contribution and long-range contribution

$$F\{\eta;\phi\} = F_S\{\eta;\phi\} + F_L\{\eta;\phi\}. \tag{2.1}$$

The short-range contribution $F_S$ is given by

$$F_S\{\eta;\phi\} = \int_\Omega \left[ \frac{D_1}{2} |\nabla \eta|^2 + \frac{D_2}{2} |\nabla \phi|^2 + W(\eta, \phi) \right] \, dr, \tag{2.2}$$

where $\Omega$ is a Lipschitz-boundary domain in $\mathbb{R}^2$. $D_1, D_2$ are parameters controlling the size of the macro-phase and micro-phase separation interface, respectively. The potential is taken as the polynomial form,

$$W(\eta, \phi) = \frac{(\eta^2 - 1)^2}{4} + \frac{(\phi^2 - 1)^2}{4} + \frac{b_1}{2} \eta \phi - \frac{b_2}{2} \eta^2 \phi^2 - \frac{b_3}{2} \eta^2 \phi^2 + \frac{b_4}{2} \eta^4 \phi^2. \tag{2.3}$$

The first two terms in (2.3) exhibit double-well potential for $\eta$ and $\phi$, respectively, and the rest terms describe the coupling between the AB copolymers and the solvent C.[35,36] The coefficients $b_1$, $b_2$, $b_3$, and $b_4$ are positive constants, which are related to the molecular parameters and could be derived in principle by the generalized method.[37,38] These parameters are chosen so that $W(\eta, \phi)$ has a triple-well structure with three distinct minima corresponding to the phases of block A, block B and solvent C, respectively. Here, we set $b_1 = b_4 = 0$ and note that $b_1, b_2$ alter slightly the minimum points of $W(\eta, \phi)$ from the ideal values of $(\pm 1, \pm 1)$. When $b_1 = 0$, the free-energy functional is symmetrical corresponding to $\phi$, indicating that $\eta$ or the confining surface has equal preference for positive or negative $\phi$, such as the morphology of layer.[32,33] Conversely, the nonzero $b_1$ would cause symmetry breaking between micro-phase separated domains, i.e.,
the selective preference between block A ($\phi > 0$) and block B ($\phi < 0$).

The long-range contribution $F_L$ is given by

$$F_L(\eta; \phi) = \int_{\Omega} \frac{\alpha}{2} \left| (-\Delta)^{-\frac{1}{2}} (\phi - \bar{\phi}) \right|^2 d\mathbf{r},$$

where $\bar{\phi}$ represents the spatial average of $\phi$. In the original paper, Green functions are used to represent long-range interactions, which was replaced with a non-local operator, the fractional power of the Laplace operator for variational problems. The long-range contribution prevents the copolymers from forming a large macroscopic domain and brings about many fine structures, such as layers or onions. $\alpha$ is inversely proportional to the square of the total chain length of the copolymer and related to the bonding between block A and block B in the copolymers, hence is a measure of the connectivity between two blocks. When $\alpha = 0$, there is no linkage between A and B blocks, and the absence of the non-local term will induce the separation macroscopically. If $\alpha \neq 0$, we have microphases within the copolymer-rich domain and multiple morphologies arise.

Now we nondimensionalize the system with $\tilde{r} = r/\lambda$, then the rescaled free-energy functional is

$$\tilde{F}(\tilde{\eta}, \tilde{\phi}) = \int_{\Omega} \left( \frac{D_1}{2} |\nabla \tilde{\eta}|^2 + \frac{D_2}{2} |\nabla \tilde{\phi}|^2 + \lambda^2 \left( \frac{1}{4} (\tilde{\eta}^2 - 1)^2 + \frac{1}{4} (\tilde{\phi}^2 - 1)^2 \right) \right) d\mathbf{r},$$

where $\tilde{\Omega}$ is a unit square $[0, 1] \times [0, 1]$, and $\lambda$ is the length of the square domain. In what follows, we drop the tildes and all statements are in terms of the translated variables. Here both $\eta$ and $\phi$ are the conserved order parameters satisfying

$$\int_{\Omega} (\eta - \bar{\eta}) d\mathbf{r} = 0, \quad \int_{\Omega} (\phi - \bar{\phi}) d\mathbf{r} = 0.$$  

(2.6)

The stationary solutions of the DCH functional with mass conservation are the solutions of the Euler-Lagrange equations as follows,

$$\frac{\delta F(\eta; \phi)}{\delta \eta} = \xi_\eta = 0,$$

$$\frac{\delta F(\eta; \phi)}{\delta \phi} = \xi_\phi = 0.$$  

(2.7)

$\xi_\eta$ and $\xi_\phi$ are the Lagrangian multipliers to keep the mass conservation.

3 Numerical method

3.1 Projected saddle dynamics method

To find the multiple stationary solutions of the Euler-Lagrange equations (2.7) with the mass conservation (2.6), we need to develop an efficient numerical algorithm to compute the saddle points with mass conservation. The original SD method is designed for unconstrained gradient systems. Recently, Huang et al. proposed a constrained high-index saddle dynamics method to compute the constrained saddle points and construct the solution landscape with equality constraints by using Riemannian gradient and Hessian methods. In the DCH model, since the mass conservation is only a linear constraint, we propose a simple PSD method to compute index-$k$ saddle points ($k$-saddles) with the mass-conservation constraint. Here, the projection is defined as follows,

$$P(\xi) = \bar{\xi} - \int_{\Omega} \bar{\xi} d\mathbf{r}, \quad \bar{\xi} \in L^2(\Omega).$$

(3.1)

Both gradient and Hessian of $F(\eta; \phi)$ are updated by the projected forms. In addition, to eliminate the unphysical directions, we translate the order parameters $\eta$ and $\phi$ to $\bar{\eta} = \eta - \bar{\eta}$ and $\bar{\phi} = \phi - \bar{\phi}$ so that $\int_{\Omega} \bar{\eta} d\mathbf{r} = 0, \int_{\Omega} \bar{\phi} d\mathbf{r} = 0$. In the following, we also drop the hats and all statements are in terms of the translated variables.

The PSD for computing a mass-conserved $k$-saddle ($k$-PSD) is governed by the following dynamical equations

$$\dot{\eta} = -P \frac{\delta F(\eta; \phi)}{\delta \eta} + 2 \sum_{j=1}^k \left( P \frac{\delta F(\eta; \phi)}{\delta \eta} v_j + P \frac{\delta F(\eta; \phi)}{\delta \phi} w_j, v_j \right),$$

$$\dot{\phi} = -P \frac{\delta F(\eta; \phi)}{\delta \phi} + 2 \sum_{j=1}^k \left( P \frac{\delta F(\eta; \phi)}{\delta \eta} v_j + P \frac{\delta F(\eta; \phi)}{\delta \phi} w_j, w_j \right).$$

(3.2)

The equations (3.2) allow $[\eta; \phi]$ to move along an ascent direction on the subspace $\mathcal{Y} = \text{span}([v_1; w_1], \cdots, [v_k; w_k])$, and a descent direction on the subspace $\mathcal{Y}^\perp$, the orthogonal complement space of $\mathcal{Y}$. $[v_i; w_i] (i = 1 \cdots k)$ are the orthonormal and unit eigenvectors, i.e., $[v_i; w_i, [v_j; w_j]] = \delta_{ij} \rho$, corresponding to the smallest $k$ eigenvalues $\lambda_1, \cdots, \lambda_k$ of the Hessian $\nabla^2 F(\eta; \phi)$. They can be obtained via the constrained optimization problem and governed by the following equations

$$\begin{bmatrix} v_i \\ w_i \end{bmatrix} = \left( I - \sum_{j=1}^k \begin{bmatrix} v_j \\ w_j \end{bmatrix} \begin{bmatrix} v_j \\ w_j \end{bmatrix}^T \right) \begin{bmatrix} v_i \\ w_i \end{bmatrix} + 2 \sum_{j=1}^k \begin{bmatrix} v_j \\ w_j \end{bmatrix} \begin{bmatrix} v_i \\ w_i \end{bmatrix}^T,$$

$$\left( \begin{bmatrix} P \\ P \end{bmatrix} \right) \nabla^2 F(\eta; \phi) \begin{bmatrix} v_i \\ w_i \end{bmatrix}, \quad i = 1, \cdots, k.$$  

(3.3)

Here $I$ is the identity operator. The $k$-saddle $[\eta; \phi]$ and $k$ direction variables $[v_i; w_i]$ are coupled. We note that $v_1$ and $w_1$ are also needed to apply the projection $P$ to keep mass conservation, namely $\int_{\Omega} v_1 d\mathbf{r} = \int_{\Omega} w_1 d\mathbf{r} = 0$.

To avoid the direct calculation of Hessians, we approximate Hessian by using the central difference scheme for directional derivations on $k$ dimers centered at $[\eta; \phi]$. The $i$th dimer has a direction of $[v_i; w_i]$ with a small dimer length $2l$ and then $\nabla^2 F(\eta; \phi)$ is approximated by

$$\nabla^2 F(\eta; \phi) \begin{bmatrix} v_i \\ w_i \end{bmatrix} \approx \frac{\nabla F \left( \begin{bmatrix} \eta + l v_i \\ \phi + l w_i \end{bmatrix} \right) - \nabla F \left( \begin{bmatrix} \eta - l v_i \\ \phi - l w_i \end{bmatrix} \right)}{2l}.$$  

(3.4)

We choose periodic boundary conditions and apply the Fourier spectral method for the space discretization on $\Omega$. The numerical simulations are performed on a 2D $128 \times 128$ grid which was verified to give well-resolved numerical results. We use the explicit Euler scheme and Barzilai–Borwein gradient method to de-
termine the step sizes for time discretization of (3.2). Furthermore, we apply the locally optimal block preconditioned conjugate gradient (LOBPCG) method to compute the smallest k eigenvalues and the corresponding eigenvectors of the Hessian.

The initial condition is given as:

\[ \begin{bmatrix} \eta(0) \\ \phi(0) \end{bmatrix} = \begin{bmatrix} \eta^0 \\ \phi^0 \end{bmatrix}, \quad \begin{bmatrix} v_i(0) \\ w_i(0) \end{bmatrix} = \begin{bmatrix} v_i^0 \\ w_i^0 \end{bmatrix}, \quad i = 1, \ldots, k, \quad (3.5) \]

where \([\eta^0; \phi^0]\) are zero mean, and \([v_i^0; w_i^0], \ldots, [v_i^0; w_i^0]\) are the unit orthogonal vectors with zero mean.

3.2 Algorithm for the solution landscape

The solution landscape of the DCH model is constructed via two algorithms: downward search and upward search. The downward search algorithm enables us to efficiently search for all connected low-index saddles and minima from a high-index saddle, and the upward search algorithm aims to find the possible higher-index saddles. The details of two algorithms coupled with PSD method are as follows:

**Downward search algorithm:** Assuming we have an \(m\)-saddle \([\eta^*; \phi^*]\) and the \(m\) normalized vectors \([v_1^*; w_1^*], \ldots, [v_m^*; w_m^*]\) corresponding to the \(m\) negative eigenvalues of the Hessian matrix \(V^2 (\eta^*; \phi^*)\). Then we apply the \((m - 1)\)-PSD to search the \((m - 1)\)-saddles by choosing \([\eta^*; \phi^*] + \epsilon [v_m^*; w_m^*]\) as an initial state and \([v_1^*; w_1^*], \ldots, [v_{m-1}^*; w_{m-1}^*]\) as initial unstable directions. Once a new \((m - 1)\)-saddle is obtained, we continue to apply the \((m - 2)\)-PSD to search for the \((m - 2)\)-saddles.

By repeating the above procedure, we can establish a systematic search for all saddle points branched from this \(m\)-saddle as a parent and to construct a family tree that eventually connects to the local minima.

**Upward search algorithm:** If the parent state (the highest-index saddle point) is unavailable beforehand or multiple parent states exist, one can conduct the upward search to find the high-index saddle points starting from a local minimum or a low-index saddle point.

Starting from an \(m\)-saddle \([\eta^*; \phi^*]\), we apply the \((m + 1)\)-PSD to search for an \((m + 1)\)-saddle. The initial state is chosen as \([\eta^*; \phi^*] + \epsilon [v_{m+1}^*; w_{m+1}^*]\), and \([v_1^*; w_1^*], \ldots, [v_m^*; w_m^*]\) are taken as the initial ascent directions, in which \([v_{m+1}^*; w_{m+1}^*]\) is the eigenvector corresponding to the smallest positive eigenvalue of its Hessian matrix.

Each downward search represents the relaxation of a pseudodynamics, the so-called dynamical pathway, starting from a high-index saddle point to a local minimum. By combining the downward search and upward search, we are able to systematically find possible stationary solutions and uncover the connectivity of the solution landscape.

4 Results

Now we present the numerical results for the solution landscapes of the diblock copolymers and homopolymers under 2D confinement. To see the effect of the preference intensity \(b_1\) and the domain size \(\lambda\), we choose three cases: the equal preference, the selective preference, and the equal preference in a larger domain.

4.1 Solution landscape with equal preference

In the case of equal preference \((b_1 = 0, \lambda = 1)\), we plot three stable states (Layer 3Y, Layer 3B, and Layer 2) in Fig. 4.1. Some parameters are set as \(D_1 = D_2 = 0.0025, b_2 = 1, \alpha = 60, \eta = -0.5, \phi = 0\). Since the preference for block A (yellow) and block B (blue) are equal, Layer 3Y and Layer 3B are a pair of solutions only with block A and B switched, and the two blocks in Layer 2 have the same area and shape. From an energy point of view, Layer 2 is the stable phase with the lowest energy, while Layer 3Y and Layer 3B are the metastable phases.

![Fig. 4.1 Three stable states: Layer 3Y, Layer 3B and Layer 2 with equal preference](image)

The solution landscape with equal preference is shown in Fig. 4.2. The homogeneous phase \((\eta \equiv \eta, \phi \equiv \phi)\) is clearly a trivial solution, which is a 8-saddle. Using it as the parent state, we are able to find three distinct 5-saddles via the downward search, specifically, Flower 6 looks like a blooming flower with three yellow petals alternating with three blue petals, and Circle 2YS and Circle 2BS are a pair of solutions due to the equal preference of blue blocks and yellow blocks.

The periodic boundary condition implies that the Hessian at a non-homogeneous state has at least two zero eigenvalues in most cases, which explains why no 6-saddles or 7-saddles are found in Fig. 4.2. Down from these 5-saddles, a variety of complex morphologies in Triangle class and Flower class are obtained. In the Triangle class, the shapes of inner blocks are isosceles triangles with the apex angle less than 60 degrees (Triangle Y1 and Triangle B1), isosceles triangles with the apex angle greater than 60 degrees (Triangle Y2 and Triangle B2), and equilateral triangles (Triangle Y3 and Triangle B3). In Flower class, the asymmetric/symmetric flower solutions, Flower 4N1, Flower 4Y2, Flower 4B2, and Flower 4, have two yellow petals alternating with two blue petals. Flower 3Y has one yellow petal between two blue petals and Flower 3B has one blue petal between two yellow petals. The asymmetric Layer 3NY (Layer 3NB) is the transition state between the metastable solution Layer 3Y (Layer 3B) and the stable solution Layer 2 in Fig. 4.1.
Fig. 4.2 Solution landscape with equal preference. The height of a phase approximately corresponds to its energy. The \( \phi \) plot of each phase is shown in square domain with name on the top and index of corresponding saddle point at the bottom.

From the solution landscape, we can also extract the transition pathways between three stable states \( \text{Layer} \, 3Y \), \( \text{Layer} \, 3B \), and \( \text{Layer} \, 2 \) (Fig. 4.3). There are two transition pathways between \( \text{Layer} \, 3B \) and \( \text{Layer} \, 2 \): \( \text{Layer} \, 3B \rightarrow \text{Flower} \, 3B \rightarrow \text{Layer} \, 2 \) and \( \text{Layer} \, 3B \rightarrow \text{Layer} \, 3NB \rightarrow \text{Layer} \, 2 \) in Fig. 4.3(a). The latter one has the smaller energy barrier \( \Delta F \) (the energy difference between the transition state and the initial stable state), thus has higher possibility to take place. With the equal preference, it is easy to see the transition pathways between \( \text{Layer} \, 3Y \) and \( \text{Layer} \, 2 \) are analogous: \( \text{Layer} \, 3Y \rightarrow \text{Flower} \, 3Y \rightarrow \text{Layer} \, 2 \) (\( \Delta F = 4.1e - 3 \)) and \( \text{Layer} \, 3Y \rightarrow \text{Layer} \, 3NY \rightarrow \text{Layer} \, 2 \) (\( \Delta F = 3e - 4 \)). Fig. 4.3(b) shows the switching process between \( \text{Layer} \, 3B \) and \( \text{Layer} \, 3Y \), along which blue block and yellow block swap, connected by the transition state \( \text{Flower} \, 4 \) with two opposed blue petals and two opposed yellow petals. In the process from \( \text{Layer} \, 3B \) to \( \text{Flower} \, 4 \), the yellow block on both sides of the blue block push into the middle of blue block. The shape of blue block changes from an ellipse to an hourglass, and is further cut into two small petals. In the process from \( \text{Flower} \, 4 \) to \( \text{Layer} \, 3Y \), the two yellow petals connect together resulting in a yellow hourglass and relax to an ellipse between two small blue ellipses. From Fig. 4.2, \( \text{Layer} \, 3B \) and \( \text{Layer} \, 3Y \) can also be connected via \( \text{Layer} \, 2 \), that is, \( \text{Layer} \, 3B \rightarrow \text{Layer} \, 3NB \rightarrow \text{Layer} \, 2 \) (Fig. 4.3(a)) and \( \text{Layer} \, 2 \rightarrow \text{Layer} \, 3NY \rightarrow \text{Layer} \, 3Y \). In fact, this transition pathway has a lower energy barrier and is more probable than the one in Fig. 4.3(b).

4.2 Solution landscape with selective preference

We next study the solution landscape with selective preference (\( \delta_1 = 0.1, \lambda = 1 \)), namely the affinity of the blue block for homopolymers (solvent) is higher than that of the yellow one. This leads to the symmetry breaking of the morphologies in contrast to the one with equal preference. In Fig. 4.4, the homogeneous phase (8-saddle) is still the parent state, and the transition states between \( \text{Layer} \, 3Y \) and \( \text{Layer} \, 2Y \) are also \( \text{Layer} \, 3NY \) and \( \text{Flower} \, 3Y \). While due to the symmetry breaking, the structure of the solution landscape has changed dramatically. On one hand, we lose nearly half of the stationary solutions observed in Fig. 4.2. For instance, \( \text{Flower} \, 6 \) in Fig. 4.2 with alternative yellow and blue blocks merges into \( \text{Circle} \, 2YS \) with blue ring surrounding the yellow blocks at the center. Although \( \text{Flower} \, 6 \) disappears in the case of selective preference, \( \text{Flower} \, 4 \) still survives with larger blue petals and smaller yellow petals. Moreover, since the area of inner yellow blocks becomes smaller, \( \text{Flower} \, 4N1 \) in Fig. 4.2 merges into \( \text{Flower} \, 4Y2 \), and \( \text{Triangle} \, Y1 \) and \( \text{Triangle} \, Y2 \) in Fig. 4.2 merge into the regular triangle \( \text{Triangle} \, Y3 \). The \( \text{Layer} \, 3B \) solution loses stability and becomes an 1-saddle. On the other hand, new solutions appear. For example, the 5-saddle \( \text{Circle} \, 2YS \) connects to a new 4-saddle \( \text{Circle} \, 2YB \), and the 1-saddle \( \text{Flower} \, 3Y \) bifurcates into a new asymmetric 2-saddle \( \text{Flower} \, 3NY \).
4.3 Solution landscape with equal preference in a larger domain

We further investigate the solution landscape with equal preference in a larger domain ($b_1 = 0, \lambda = 1.4$). In Fig. 4.5, the homogeneous state becomes a 12-saddle and more stationary solutions emerge in the solution landscape, such as 9-saddle Pentagon $Y$ with the same symmetric property as a pentagon and 7-saddle Flower $8$ with four blue petals and four yellow petals. It is worth mentioning that we find novel stable solutions such as Dendritic $3B$, Layer 4 and Circle $2B$. The Dendritic $3B$ solution, which looks like a steering wheel, appears in the larger domain. This phase is bifurcated from Triangle $Y3$ and is a 2D analogy to the multipod phase in 3D. The layer numbers of the Layer-class solutions also increase to 3 (e.g. Layer $3B$) and 4 (e.g. Layer 4). The Circle $2B$ becomes a local minimum in the larger domain.

To illustrate the solution landscape more clearly, we classify the stationary solutions from 2-saddles to 6-saddles into four classes: Flower class, Mosaic class, Core-shell class, and Tai-chi class, according to the configuration and connections between them. Mosaic indicates the morphology has multiple alternative yellow and blue blocks. Core-shell represents the class of morphologies that one of the block polymers is surrounded by the other one completely or partially. It is similar to the Circle class, but loses the symmetry of the circle. Tai-chi indicates a class of morphologies that both the blue and yellow parts seem like the yin and yang fishes engaged with each other. If there exists one saddle point in Janos class, but loses the symmetry of the circle. Tai-chi indicates a class of morphologies that both the blue and yellow parts seem like the yin and yang fishes engaged with each other. If there exists one saddle point in the multipod phase in 3D. The layer numbers of the Layer-class solutions also increase to 3 (e.g. Layer $3B$) and 4 (e.g. Layer 4). The Circle $2B$ becomes a local minimum in the larger domain.

Flower class connecting to another saddle point in Mosaic class, we present this connection by an arrow from Flower to Mosaic in Fig. 4.5. Hence the connections between four classes are Flower $\leftrightarrow$ Mosaic $\leftrightarrow$ Core-shell $\leftrightarrow$ Tai-chi, but the connection from Core-shell class to Tai-chi class has not been found yet. These four classes play key role in connecting the high-index (index $>6$) saddle points to the transition states (1-saddles) and minima. For example, we observe the Flower class can be connected from the well defined 7-saddles Rhombus $Y$ and Flower $8$ and then connect to the lower-index saddle points Flower $4$, Dendritic $3N2$ and Layer $4N$. We can observe the Mosaic class can be connected from almost all 7-saddles and connect to almost all 1-saddles. Here, we treat each class as a whole and omit the detailed connections between the members of each class and the 1 (or 7)-saddles.

Fig. 4.6 shows four solution landscapes of Flower class, Mosaic class, Core-shell class, and Tai-chi class. In each class, different solutions have subtle differences. The Flower class, including a typical state Flower $6$ and many axisymmetric structures, was shown in Fig. 4.6(a). The Mosaic class with the richest solutions is shown in Fig. 4.6(b). For instance, 2-saddle Mosaic $6$ is the typical mosaic, which looks like a floor tile with three yellow blocks alternating with three blue blocks in the elliptic confinement. The Core-shell class can connect to the circle phase Circle $2B$ (minimum), shown in Fig. 4.6(c). The typical core-shell is 3-saddle Core-shell $2B3$. At last, we also observe the beautiful Tai-chi class
in Fig. 4.6(d). The typical tai-chi phase is 5-saddle Tai-chi 2 with long tails and finally connects to a 2-saddle tai-chi with short tails.

From the solution landscape in Fig. 4.5, there exist multiple transition pathways between the stable states (Dendritic 3B, Layer 3B, Layer 4 and Circle 2B). For example, there are two transition pathways between Dendritic 3B and Layer 3B: Dendritic 3B → Dendritic 3N1 → Layer 3B and Dendritic 3B → Dendritic 3N3 → Layer 3B. However, not all pairs of stable states can be connected by a single transition state. For example, Circle 2B cannot be directly connected to Dendritic 3B or Layer 4. Thus, the transition pathways between them need multiple transition states. More specifically, the transition pathway between Circle 2B and Dendritic 3B can be Circle 2B → Core-shell 2BB → Lay 3B → Dendritic 3N3 → Dendritic 3B. Fig. 4.7 shows the 3-saddle Core-shell 2BB is the stationary solution in the intersection of the smallest closures of all four stable states. The dynamical pathways from Core-shell 2BB can be constructed to connect every stable state passing through one 2-saddle and one 1-saddle. Our numerical results highlight the differences between transition pathways mediated by multiple transition states (1-saddles) and dynamical pathways mediated by single high-index saddle point.

4.4 Symmetry breaking

Finally, we investigate the symmetry-breaking phenomena shown in the solution landscapes with different preference intensity and domain size. In view of the previous results, symmetric (reflectional and rotational) properties are quite useful to classify the morphologies for the equal preference as in Figs. 4.2 and 4.5. The solutions in $D^k$ coincide by itself when rotating by angles $\frac{2\pi j}{k}$, $j = 1, \ldots k - 1$, or reflecting about the symmetry axes. For instance, the highest-index homogeneous phase has $D^\infty$ symmetry (any rotation and reflection is allowed).

In Fig. 4.8, one can observe the symmetry-breaking process from circular-shape states that has $D^\infty$ to the lower symmetric solutions with some $D^k$($2 \leq k < \infty$) symmetry, e.g. (a) Circle 2YS ($D^\infty$) ⇒ Flower 6 and Triangle Y3 ($D^3$); (b) Circle 2YS and Circle 2YB ($D^\infty$) ⇒ Flower 4 and Layer 3Y ($D^2$); (c) Circle 3Y ($D^\infty$) ⇒ Pentagon Y ($D^5$) ⇒ Flower 8 ($D^8$) ⇒ Flower 6, Core-shell 2Y3, and Dendritic 3Y ($D^3$) ⇒ Square Y, Rhombus Y, Flower 4, Core-shell 2Y2, and Layer 3Y ($D^2$).

Fig. 4.8 also shows the effect of the preference intensity and the domain size on the symmetric property. In the case of equal preference, there are 8 symmetric solutions in Fig. 4.8(a). While, as $b_1$ is changed from 0 to 0.1, the selective preference breaks the symmetry and the number of symmetric solutions is reduced to 6 in Fig. 4.8(b). As stated before, Flower 6 and Triangle B3 disappeared. For the case of equal preference in a larger domain (Fig. 4.8(c)), the number of symmetric solutions increases to 21. This is because the larger domain can accommodate more copolymer molecules and multiple finer structures, e.g., the novel phases Pentagon Y, Flower 8, Square Y and Rhombus Y.

We also note that the highest symmetry $D^k$ increases from $D^1$ to $D^5$ when the domain size $\lambda$ is changed from 1 to 1.4, except of $D^\infty$. Thus, we expect that, for the stationary solutions of polygonal
shapes (except of the homogeneous and circle phases), the upper bound of \( k \) in symmetry group \( D^k \) will continuously increase with the increase of the domain size in the case of equal preference.

![Diagram showing comparison of symmetric properties of solutions in solution landscapes]

Fig. 4.8 The comparison of symmetric properties of the solutions in the solution landscapes with (a) equal preference in Fig. 4.2, (b) selective preference in Fig. 4.4 and (c) equal preference in a larger domain in Fig. 4.5. The notation “×2” means there exists a pair of phases, e.g., Circle 2YS and its counterpart Circle 2BS.

5 Conclusions and Discussions

In this work, we studied the solution landscapes of diblock copolymers and homopolymers in a 2D confinement with the DCH model. The PSD method is developed to efficiently compute the high-index saddle points with mass conservation and construct the solution landscape of the DCH free-energy functional by coupling with downward/upward search algorithms.

We systematically constructed the solution landscapes by varying the preference intensity and the domain size. In the case of equal preference, branching from the homogeneous phase, the solution landscape was obtained, including the Circle solution, Flower-type solutions, Triangles-type solutions and Layer-type solutions. Furthermore, the solution landscape reveals the informative transition pathways between stable/metastable phases. While, with selective preference, the solution landscape loses nearly half of the stationary solutions compared with the one of the equal preference. We can observe the symmetry-breaking phenomenon and the surface has more preference for the blue blocks, which starts to surround the yellow blocks, with the increase of the preference intensity \( b_i \). These results are consistent to the work by E. Avalos et al. and the solution landscape provides good guideline for experiments. In the case of equal preference in a larger domain, the solution landscape shows more novel and interesting stationary solutions. In particular, we can classify the solutions as Flower class, Mosaic class, Core-shell class, and Tai-chi class. The relationships between different stable/metastable states are shown by the dynamical pathways connected by a single high-index saddle point (Core-shell 2BS). We further demonstrate that the symmetry-breaking phenomena largely exist in the solution landscapes from high-index saddle points to local minima. The number of stationary solutions with symmetry \( D^k \) and the upper bound of \( k \) increase as the domain size increases.

The numerical results of solution landscapes of the DCH model propose several follow-up questions. First, the extension of the solution landscape from 2D to 3D is a fertile ground. The richer and more complex solutions are expected in the solution landscape in the 3D confinement, such as the multipod solution and twisted solution. On the other hand, the viewpoint of symmetry becomes more important in 3D case and more studies will be proceeded in the subsequent work. The framework of solution landscape is believed to be a promising approach to find new exotic morphologies with the tight control of the initial conditions (saddle point and associated unstable directions), which overcomes the difficulty of tuning initial guesses to search stationary solutions needed in most numerical methods. To deal with the mass-conservation constraint, the PSD method is developed using the typical \( L^2 \) inner product. We note that the study of SD can also be extended to incorporate the use of different inner products for defining the dynamic systems. One way is to apply the Cahn-Hilliard dynamics using the \( H^{-1} \) inner product to avoid imposing the additional conservation constraint. It is interesting to develop the high-index saddle dynamics using the \( H^{-1} \) inner product to compute any-index saddle points with mass-conservation constraint in the future work.

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