Nucleation of Ordered Phases in Block Copolymers

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Nucleation of various ordered phases in block copolymers is studied by examining the free-energy
landscape within the self-consistent field theory. The minimum energy path (MEP) connecting two
ordered phases is computed using a recently developed string method. The shape, size, and free-energy
barrier of critical nuclei are obtained from the MEP, providing information about the emergence of a
stable ordered phase from a metastable phase. In particular, structural evolution of embryonic gyroid
nucleus is predicted to follow two possible MEPs, revealing an interesting transition pathway with an
intermediate perforated layered structure.

Block copolymers are macromolecules composed of two or more chemically distinct subchains. The competition between the block repulsion and chain connectivity leads to the self-assembly of a rich array of ordered phases [1]. For simple block copolymers such as linear *AB* diblock and *ABC* triblock copolymers, a good understanding of their phase behavior has been obtained due to intensive experimental and theoretical research in the past years [2,3]. It has been well established that *AB* diblock copolymers exhibit a number of ordered phases, including lamellae (L), hexagonally packed cylinders (C), spheres on a body-centered-cubic lattice (S), and the bicontinuous networked gyroids (G). The rich physics contained in block copolymers makes them a paradigm for the study of the formation of, and phase transitions between, different ordered phases [2].

When an ordered phase becomes unstable, the initial transition pathway depends on its thermodynamic stability. When the ordered phase is thermodynamically unstable, phase transition proceeds via spinodal decomposition. For block copolymer phases undergoing spinodal decomposition, theoretical studies have been carried to understand the most probable kinetic pathways by examining the most unstable modes of the ordered phases [4–7]. When the ordered phase is metastable, phase transition proceeds via nucleation and growth [8]. For block copolymer phases undergoing nucleation, their kinetic pathways have been examined by Wickham *et al.* [9] within the content of classical nucleation theory, in which the anisotropic interfacial free energy is calculated first, the shape of the critical nucleus is then obtained using the well-known Wulff construction. On the other hand, finding accurate critical nucleus presents a challenging task due to the anisotropic nature of the problem and the existence of a number of length scales. These length scales are the interfacial width between microdomains, the period of the microdomains,

the width of the droplet interface, and the critical droplet size.

In the context of large deviation theory, it can be shown that the most probable transition path between two stable phases is a minimum energy path (MEP) associated with the free energy (F) of the system [10]. The MEP is a curve or a string, ψ, in the configuration space connecting the two local minima (the two stable phases) of F and satisfies, $(\nabla F)^{\perp}(\psi) = 0$, where $(\cdot)^{\perp}$ denotes the component of $(\cdot)$ normal to the string ψ [11]. Recently, E *et al.* [11] have proposed a string method to compute the MEPs for bistable systems by evolving a set of strings in the configuration space. The string method has been successfully applied to the study of membrane adhesion [12] and capillary condensation [13]. Very recently, we have shown that, with appropriate initialization procedure and methods to enforce physical constraints, the string method can be used to obtain MEP connecting two ordered phases undergoing a first-order phase transition [14]. In this Letter, we apply the string method to the self-consistent field theory (SCFT) of block copolymers. We will examine the nucleation of a variety of ordered phases, and make predictions for the structure, size, shape, and free energy barrier of the critical nuclei of the different phases.

The string method starts with a free-energy functional of the system, $F[\phi(\vec{r})]$, where $\phi(\vec{r})$ is an order parameter differentiating the different phases of the system. $F[\phi(\vec{r})]$ has at least two minima, $\phi_m(\vec{r})$ and $\phi_s(\vec{r})$, corresponding to the metastable and stable phases, respectively. Nucleation in this theoretical framework corresponds to a transition (a rare event), driven by stochastic forces such as thermal fluctuations, from the metastable state to the stable state. The most probable transition pathway follows the MEP $[\psi(\alpha, \vec{r})]$ connecting these two phases, which is parameterized by a variable α ($\alpha \in [0, 1]$) such that $\psi(\alpha = 0, \vec{r}) = \phi_m(\vec{r})$ and $\psi(\alpha = 1, \vec{r}) = \phi_s(\vec{r})$. The critical nu-

cleus is the saddle point of the free-energy surface, corresponding to the free-energy maximum along the MEP. Starting with an initial string in the phase space connecting the two states, the string on the energy surfaces, $\psi_t(\alpha, \vec{r})$, is relaxed according to the evolution equation, $\dot{\psi} = -(\nabla F)(\psi) + l\vec{\tau}$, where τ is the unit tangent vector of ψ and the scalar field l is a Lagrange multiplier determined by the parameterization of the string. The MEP corresponds to the steady state of this evolution equation, $\psi(\alpha, \vec{r}) = \psi_{t=+\infty}(\alpha, \vec{r})$.

Our model system consists of n AB diblock copolymer chains contained in a volume V. Each chain is characterized by a degree of polymerization N and an A-volume fraction f. The SCFT free energy of the system can be written as a functional of the conjugate fields $w_\pm(\vec{r})$ [15]

$$H[w_-, w_+] = \int d\vec{r} \left[\frac{1}{\chi N} w_-^2 - w_+ \right] - V \ln Q[w_-, w_+],$$

where χ is the Flory-Huggins parameter and Q is the single-chain partition function in the w fields. The single-chain partition function is related to the w fields via the propagators, $Q = \frac{1}{V} \int d\vec{r} q(\vec{r}, 1)$. The propagators $q(\vec{r}, s)$ and $q^+(\vec{r}, s)$ satisfy the modified-diffusive equations, $\frac{\partial q(\vec{r}, s)}{\partial s} = \nabla_r^2 q(\vec{r}, s) - w(\vec{r}, s) q(\vec{r}, s)$ and $\frac{\partial q^+(\vec{r}, s)}{\partial s} = -\nabla_r^2 q^+(\vec{r}, s) + w(\vec{r}, s) q^+(\vec{r}, s)$, with the initial conditions $q(\vec{r}, 0) = 1$ and $q^+(\vec{r}, 1) = 1$. Here, the "time"-dependent field is defined by $w(\vec{r}, s) = w_A(\vec{r}) = w_+(\vec{r}) - w_-(\vec{r})$ for $s \in [0, f]$ and $w(\vec{r}, s) = w_B(\vec{r}) = w_+(\vec{r}) + w_-(\vec{r})$ for $s \in [f, 1]$. With the definition of the propagators, the functional derivatives of the free energy are specified by

$$\frac{\delta H}{\delta w_-(\vec{r})} = \frac{2}{\chi N} w_-(\vec{r}) + [-\phi_A(\vec{r}) + \phi_B(\vec{r})],$$
$$\frac{\delta H}{\delta w_+(\vec{r})} = -1 + \phi_A(\vec{r}) + \phi_B(\vec{r}),$$

(1)

where the density fields ϕ_α are given by $\phi_A(\vec{r}) = \frac{1}{Q} \times \int_0^f ds q(\vec{r}, s) q^+(\vec{r}, s)$, $\phi_B(\vec{r}) = \frac{1}{Q} \int_f^1 ds q(\vec{r}, s) q^+(\vec{r}, s)$. The extrema of the free energy functional corresponding to the solutions of $\frac{\delta H}{\delta w_\pm} = 0$. Requiring $\frac{\delta H}{\delta w_+} = 0$ leads to the incompressibility condition $\phi_A + \phi_B = 1$ and a relationship w_+ (w_-) which can be calculated numerically. With the incompressibility condition, the free energy functional becomes $F[w_-] = H[w_-, w_+(w_-)]$. The equilibrium phase behavior of a diblock copolymer melt is obtained by finding the minima of the free energy functional or solutions of the Euler-Lagrange equation $\frac{\delta H}{\delta w_\pm} = 0$. This is a highly nontrivial problem, but by now, we have a wealth of information regarding the equilibrium phase diagram [3,15] including the linear stability [5,6] of the different phases. On the other hand, nucleation of an ordered phase from a metastable phase in block copolymers has received less attention, with the exception of the work of Wickham et al. [9] and the work of Matsen for the epitaxial transitions of C ↔ S and C ↔ G [16]. In the current work, we examine the nucleation process systematically using the

string method applied to the free energy functional $F[w_-(\vec{r})]$ [17].

In what follows, we will focus on the nucleation of cylinders from lamellae (L → C) and gyroids (G → C), as well as the nucleation of gyroids from cylinders (C → G) and lamellae (L → G), leaving the other possible transitions to a future publication. Given any point $\psi(\alpha, \vec{r}) = \phi(\vec{r})$ along the string—corresponding to a state of the physical system along the transition pathway—the nuclear structure of the system is examined by defining a pointwise phase-density function $\Phi(\vec{r})$ [14]

$$\Phi_s(\vec{r}) \equiv \frac{|\phi - \phi_m|(\vec{r})}{|\phi - \phi_m|(\vec{r}) + |\phi - \phi_s|(\vec{r})},$$

$$|\phi_1 - \phi_2|(\vec{r}) \equiv \int w(\vec{r}' - \vec{r})[\phi_1(\vec{r}') - \phi_2(\vec{r}')]^2 d\vec{r}',$$

(2)

where weight function $w(\vec{r})$ is the *mollifier*, $[w(\vec{r}) = Ce^{R^2/(|\vec{r}|^2 - R^2)}, (R > 0)]$ [18]. The boundary between different ordered phases can be specified by, e.g., $\Phi_s = 0.5$.

The nucleation of cylinders from a metastable lamellar phase is examined at a fixed $f = 0.45$ and varying χN in the range between the mean-field spinodal point of the lamellae and the L-C coexistence point [5,6]. The initial cylinders were oriented parallel to the lamellar plane, in agreement with previous studies [9]. The periods of the L (D_l) and C (D_c) phases are related epitaxially, $D_l = \sqrt{3} D_c / 2$. For all the χN values examined, the critical nucleus is found to be lenslike. The volume of the critical nucleus increases as χN is increased. The generic shape of a critical nucleus can be described by an ellipsoid with three normal axes a, b and c, which are given in Table I in unit of D_c. The typical value of the nucleation barrier if about $10^{-1} nk_B T$, while the typical size of the critical nucleus is about $(10–20)D_c^3$, containing 10–20 cylinders. The nucleation barrier and critical nucleus size increase slightly as χN is increased. These results are consistent with the earlier classical nucleation theory calculations of Wickham et al. [9]. Furthermore, the structure of the L-C interface is obtained from the critical nucleus solution (not shown). One important observation is that the thickness of the L-C interface is comparable to the size of the nuclei. Therefore, the classical nucleation theory is, in general, not applicable to the current problem.

We now turn to the more interesting and previously unexplored nucleation processes involving the bicontinuous gyroid phase. We examine the G → C transition at $f = 0.425$, $\chi N = 11.20$, and the C → G transition at $f = 0.425$, $\chi N = 12.90$. In both cases, the free-energy per chain, $H[\psi(\alpha)] = F/nk_B T$, along the final string (MEP) reaches one maximum at the critical nucleus state. The G (C) → C (G) critical nucleus has a volume of $25.753(27.845)D_c^3$, and the nucleation barrier is obtained as $0.6278(6.3829)nk_B T$, respectively. The shape of the critical nucleus in both cases is a distorted sphere with fcc-packed bulges (Fig. 1). Similar results of the C ↔ G transitions have been found at other values of f and χN.

TABLE I. Size and shape of the ellipsoidlike L → C critical nucleus characterized by three major axes a, b, and c in unit of D_c. The nucleation barrier is in unit of nk_BT, and volume of critical nucleus D_c^3.

χN	a	b	c	b/a	c/a	Barrier	Volume
11.185	1.7392	2.1974	0.6069	1.263	0.349	0.34800	11.227
11.190	1.8913	2.2967	0.7704	1.214	0.407	0.37515	13.512
11.195	2.0517	2.3726	0.7178	1.156	0.350	0.40620	15.914
11.200	1.9849	2.5018	0.9016	1.260	0.454	0.43616	17.695

The availability of the MEP provides information about the formation pathway of the critical nucleus. In the case of G → C transition, the formation of the cylinders proceeds via the fracture of the gyroids, as shown in the top panel of Fig. 2. The fracture and reconnection propagate throughout the material as the nucleus grows. The bottom panels of Fig. 2 shows that the emergence of the gyroids from the cylinders proceeds through the distortion, disconnection, and reconnection of the cylinders. An intermediate fivefold junction is observed just before the formation of a cylindrical unit cell. These morphological structures involving gyroid-cylinder transitions are consistent with the SCFT analysis by Matsen [16], as well as results from dynamic SCFT simulations by Honda and Kawakatsu [19] and experiments by Park et al. [20].

In the cases presented above, only one transition state corresponding to the critical nucleus is observed. A more interesting behavior is observed in the lamellae-to-gyroids (L → G) transition at $f = 0.405$, $\chi N = 13.05$. In this case, two MEPs have been obtained. The first one correspond to the usual MEP with one maximum, whereas the second MEP exhibits two maxima and one intermediate minimum (Fig. 3). The morphologies of the nuclei corresponding to these extremal points are shown in Fig. 3. Along the first MEP, there is one critical nucleus, corresponding to a gyroidal droplet. On the other hand, the transition along the second MEP possesses two critical nuclei, corresponding to hexagonally modulated layers (HML) at the first maximum and a gyroidal structure at the second maximum. The intermediate minimum can be classified as a structure corresponding to the hexagonally perforated layers (HPL) with perforations stacked in an $ABCABC\ldots$ sequence. The L → HPL and HPL → G critical nuclei have a relatively smaller volume of $19.140D_c^3$ and $14.744D_c^3$, respectively,

while their shapes are distorted spheres (not shown). The HPL phase has been observed in many experiments [21] although theoretical studies have shown that the HPL is a metastable phase for diblock copolymers [3]. Because the L → HPL path has a smaller free-energy barrier as compared with the L → G path along the first MEP, we expect that the gyroids will most probably take the second path to a HPL structure. This prediction provides an explanation of the prevalence of the HPL in gyroid-forming block copolymers observed in experiments [22].

In summary, the nucleation of ordered diblock copolymer phases is investigated by examining the minimum energy path (MEP), which is computed using the string method applied to the self-consistent field theory of polymers. The structure, shape, and size of critical nuclei of the different ordered block copolymer phases are obtained from the saddle point on the MEP. The interior structure of the critical nucleus is found to be significantly different from the corresponding bulk phase; thus, in general, the classical nucleation theory is not applicable to the phase transition of ordered phases in block copolymers. The morphological structures along the MEP provide information about the emergence of a stable phase from its embryos. In particular, it is predicted that the emergence of a gyroidal nucleus from lamellae can be a two-step process, starting from a nucleus with hexagonally modulated layers to an intermediate hexagonally perforated layers, then
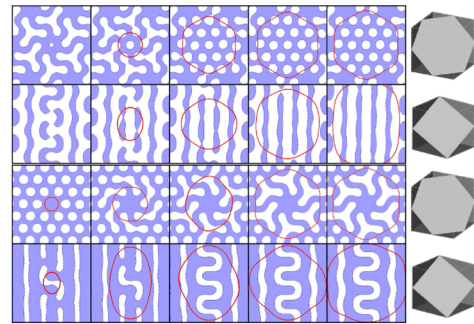
FIG. 2 (color online). Emergence of C (G) from the G (C) phase on the G ↔ C nucleation pathway at $f = 0.425$, $\chi N = 11.20$ (top), and $\chi N = 12.90$ (bottom). The plots from left to right correspond to the points with $\alpha = 1/33$, $3/33$, $5/33$, $7/33$, $9/33$ on the string. For each set of plots, the upper panel is in the [110]-[$\bar{1}\,\bar{1}\,2$] plane, whereas the lower panel is in the [110]-[111] plane. The dark area is B rich (the dark-light boundary is $\phi_A = 0.425$ isosurface). The lines are the nucleus boundary defined by $\Phi(\vec{r}) = 0.5$ isosurface. The critical nuclei are at $\alpha = 5/33$.
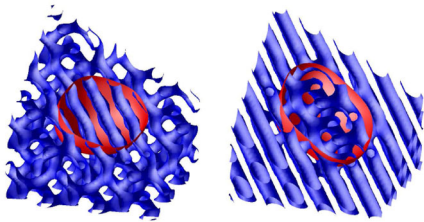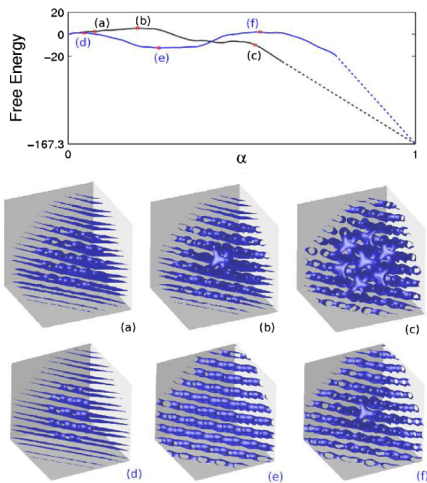

FIG. 1 (color online). G ↔ C critical nucleus at $f = 0.425$, $\chi N = 11.20$ (left) and 12.90 (right). The AB interface is $\phi_A = 0.5$ isosurface. The nucleus boundary is represented by the $\Phi(\vec{r}) = 0.5$ isosurface.

FIG. 3 (color online). (Upper) Free energy along the two MEPs for the L $\rightarrow$ G transition at $f = 0.405$, $\chi N = 13.05$. The string parameter $\alpha \in [0, 1]$ is an energy-weighted string arclength. The later part of both curves are omitted, indicated by the dotted line. The crosses on the first curve, (a), (b), and (c), are three states along the MEP, where (b) is the L $\rightarrow$ G saddle point. The crosses on the second curve, (d), (e), and (f), denote the L $\rightarrow$ HPL saddle point, the intermediate HPL phase, and the HPL $\rightarrow$ G saddle point, respectively. (Lower) The corresponding morphologies of the states (a)–(c) and (d)–(f).

from the perforated layers to gyroids with networked cylinders. The results from the current study are consistent with available experimental and theoretical results. In addition, the current study provides an explanation of the propensity of the HPL structures in gyroid-forming block copolymers. Many of the predictions on the nuclear structures can be tested in future experiments and simulations. A combination of the nucleation theory and stability analysis provides a comprehensive picture of the initial phase transition pathways of ordered block copolymer phases. Furthermore, it should be emphasized that the knowledge of initial phase transition pathways and the methodology from the current study are applicable to any physical systems undergoing phase transitions involving ordered phases.

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[17] The computation domain is a box with a mesh of 64^3 or 128^3 grid points. The strings are descretized into 64 points. The energy curve in Fig. 3 is noisy due to the finite number of point along the string. Furthermore, the string is parametrized using an energy-valued monitor function, which distributes the representative points more densely around the saddle point.

[18] The radius R of the mollifier is chosen such that the phase density is a smooth function, and at the same time, it reflect the local difference between the new and old phases. The location of the interface between the old and new phases depends on the choice of the mollifier and the level set. The results presented in the paper are obtained by choosing $R = 1.5D_c$.

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