Discovering Ordered Phases of Block Copolymers: New Results from a Generic Fourier-Space Approach

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A generic Fourier-space approach to solve the self-consistent field theory of block copolymers is developed. This approach is based on the fact that, for any computational box with periodic boundary conditions, all spatially varying functions are spanned by the Fourier series determined by the size and shape of the box. The method reproduces all known diblock copolymer phases. The application of this method to a model ''frustrated'' triblock copolymer leads to a phase diagram with a number of new phases. Furthermore, the capability of the method to reproduce experimentally observed structures is demonstrated using the knitting pattern of triblock copolymers.

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In recent years, block copolymers have become a paradigm for the study of self-assembly of soft matter. In particular, the rich and fascinating ordered phases of block copolymer melts and solutions have received tremendous attention both experimentally and theoretically [1,2]. Theoretical studies have focused on the development of frameworks which are capable of relating molecular architecture and composition to equilibrium ordered phases. It has been well established that the self-consistent field theory (SCFT) provides a particularly successful framework for the study of the phase behavior of block copolymers [3,4]. A comprehensive treaty on SCFT is given in a recent monograph by Fredrickson [5].

From a mathematical point of view, finding the solutions of the SCFT presents a complex and challenging problem. One successful approach is to solve the SCFT equations using numerical techniques. The first exact numerical solutions of three-dimensional ordered diblock copolymer phases were obtained using a spectral method proposed by Matsen and Schick in 1994 [6]. In its most general form, the spectral method provides a complete description of the SCFT equations, which allows high precision calculations of free energies and phase diagrams. For practical reasons, most previous calculations assumed that the symmetry of the ordered phases is known *a priori* [7]. Recently, SCFT calculation using the spectrum method reveals a new continuous phase with space group *Fddd* (the O^{70} phase) in diblock copolymers [8] and was indeed observed later in a poly(styrene-*b*-isoprene) melt [9]. Parallel to the spectrum methods, real-space numerical methods to solve the SCFT equations have been developed [5]. Noticeable efforts along this direction include the work of Drolet and Fredrickson [10] and Bohbot-Raviv and Wang [11]. Drolet and Fredrickson proposed a combinatorial screening method, which involves a direct implementation of SCFT in real space in an adaptive arbitrary cell. Later, a split-step method for solving the diffusion equation was introduced by Rasmussen and Kalosakas which improves the efficiency of the calculations [12].

In this Letter, we propose a generic spectral approach for the discovery of complex ordered structures of block copolymers. Our approach is based on the observation that, in any computational box with periodic boundary conditions, all spatially varying functions are periodic functions whose period is dictated by the computational box. Therefore, these functions can be expanded as Fourier series, and SCFT equations can be cast in terms of the expansion coefficients. The solutions of the SCFT equations can then be obtained using any of the available numerical techniques [5]. The essence of this new approach is to use the full power of the spectral method, in which the symmetry of the ordered phases is not presumed. Furthermore, our Fourier-space method has the advantage of identifying new complex structures, especially continuous structures, more easily and definitively. In what follows, we choose linear multiblock copolymers to demonstrate our method, although the approach is very general and can be easily extended to any molecular architecture.

We consider n linear multiblock copolymers, modeled as flexible Gaussian chains with a degree of polymerization N, in a volume V. Within the SCFT, the many-chain problem is reduced to that of an independent chain subject to mean fields due to the presence of the other chains [4,5]. The fundamental quantity is the polymer segment probability distribution function $q(\mathbf{r}, s)$, representing the probability of finding segment s at position $\mathbf{r}$. This distribution function satisfies a modified diffusion equation $\partial q(\mathbf{r}, s)/\partial s = (b^2/6)\nabla^2 q(\mathbf{r}, s) - \omega(\mathbf{r}, s) q(\mathbf{r}, s)$, with the initial condition $q(\mathbf{r}, 0) = 1$. Here b is a statistical segment length of the polymer (assumed to be the same for all blocks), and

$\omega(\mathbf{r}, s)$ is the mean field which is defined as $\omega_\alpha(\mathbf{r})$ when the s is on the α block. The partition function of a single chain subject to the mean field $\omega(\mathbf{r}, s)$ can be written as $Q = \int d\mathbf{r} q(\mathbf{r}, N)$. The free energy per chain of the system is given by

$$\frac{F}{nk_BT} = -\ln\left(\frac{Q}{V}\right) + \frac{1}{V}\int d\mathbf{r}\left[\frac{1}{2}\sum_{\alpha,\beta}\chi_{\alpha\beta}\psi_\alpha(\mathbf{r})\psi_\beta(\mathbf{r}) - \sum_\alpha \omega_\alpha(\mathbf{r})\psi_\alpha(\mathbf{r}) + \xi(\mathbf{r})\left(1 - \sum_\alpha \psi_\alpha(\mathbf{r})\right)\right], \quad (1)$$

where $\chi_{\alpha\beta}$ are the Flory-Huggins parameters between species α and β, $\psi_\alpha(\mathbf{r})$ is the concentration distribution of the component α, and $\xi(\mathbf{r})$ is a pressure field that ensures the local incompressibility. Minimizing the free energy (i.e., taking the mean-field approximation) leads to the SCFT equations [4,5], which can be solved by either real- or reciprocal-space methods.

In the spectral method, all spatially varying functions are expanded in terms of a set of basis functions [4,6]. In most previous studies, the basis functions are generated using the symmetry of some presumed ordered phases. In the current approach, a generic set of basis functions is generated by the computation box; thus, a spatially varying function is expanded in the form $g(\mathbf{r}) = \sum_{\mathbf{G}} g(\mathbf{G}) e^{-i\mathbf{G}\cdot\mathbf{r}}$, where the wave vectors $\mathbf{G}$ are determined by the size and shape of the box. In the case of a cubic box with length D, the wave vectors are $\mathbf{G}_i = (2\pi/D)(h_i, k_i, l_i)$, where $h_i, k_i, l_i = 0, \pm 1, \pm 2, \ldots$. With this generic set of basis functions, in principle the symmetry of the ordered phases will emerge from the solutions. In what follows, we restrict to centrosymmetric phases for simplicity, and the expansion takes the form

$$g(\mathbf{r}) = \sum_{h,k,l} g_{hkl}\sqrt{2}\cos\left[-2\pi\left(h\frac{x}{D} + k\frac{y}{D} + l\frac{z}{D}\right)\right] = \sum_i g_i\sqrt{2}\cos[-\mathbf{G}_i\cdot\mathbf{r}]. \quad (2)$$

The basis functions $f_i(\mathbf{r}) = \sqrt{2}\cos(-\mathbf{G}_i\cdot\mathbf{r})$ can be indexed by $i = 1, 2, 3, \ldots$ such that each set of (h, k, l) corresponds to one i. These basis functions are orthonormal eigenfunctions of the Laplace operator satisfying $\nabla^2 f_i(\mathbf{r}) = -\lambda_i D^{-2} f_i(\mathbf{r})$ and $V^{-1}\int d\mathbf{r} f_i(\mathbf{r}) f_j(\mathbf{r}) = \delta_{ij}$. The eigenvalues $\lambda_i = 4\pi^2(h_i^2 + l_i^2 + k_i^2)$ form an ascending series, beginning with $\lambda_1 = 0$ and $f_1(\mathbf{r}) = 1$. With these definitions, the SCFT equations can be cast in terms of the expansion coefficients. A number of numerical methods are available to solve the SCFT equations [5]. In what follows, we use a simple numerical procedure similar to that of Matsen and Schick [6,13]. For a multiblock copolymer with fixed chain length N, compositions f_α, and Flory-Huggins parameters $\chi_{\alpha\beta}$, the SCFT equations can be solved to obtain a set of solutions corresponding to the minima of the free energy functional. The amplitudes $\psi_{\alpha,i}$ are then used to reconstruct the concentration distribution of the component α. The space group of the structure can be determined by the wave vectors $\mathbf{G}_i = (2\pi/D)(h_i, k_i, l_i)$ that correspond to nonzero coefficients $\psi_{\alpha,i}$. These reciprocal vectors can be mapped to those corresponding to the Bragg reflections of the morphology. A comparison of these wave vectors with the crystallography table, for example, Ref. [14], can be used to identify the space group and lattice parameters.

To test the validity of our new approach, we first applied it to AB diblock copolymers. Up to 294 basis functions were used, and the concentration and (self-consistent) field accuracy was calculated to 10^{-6} (for $\chi N < 25$ and $0.1 < f \le 0.5$). A large number of ordered structures emerge from the solutions. In addition to the well-known four equilibrium stable phases (bcc spheres, hexagonal cylinders, gyroids, and lamellae), the solutions include a number of additional structures: an ordered network phase with space group symmetry $Fddd$ (the O^{70} phase), a $P6_3mmc$ or $R\bar{3}m$ perforated lamellae, an $Pn3m$ double diamond, and a $P4mm$ phase (which is a network of fourfold connected struts of a minority component forming a tetragonal lattice T^{99}). We have confirmed that the generic spectrum method leads to equilibrated lamella, cylinder, gyroid, O^{70}, and sphere phases at the compositions and χ_{AB} values consistent with the Matsen-Schick [6] and Tyler-Morse [8] phase diagrams.

In order to demonstrate the predictive power of the new approach, we applied it to linear ABC triblock copolymers. However, exploring their high-dimensional phase space thoroughly is a formidable task [15–17]. Instead, we focus on the so-called frustrated systems [17], in which the interaction between the two end blocks is the smallest among the three interactions, i.e., $\chi_{AC} \ll \chi_{AB} \approx \chi_{BC}$. Such systems include poly(styrene-*b*-butadiene-*b*-methyl methacrylate) (PS-PB-PMMA) [18], poly(styrene-*b*-isoprene-*b*-methyl methacrylate) [19], and poly(styrene-*b*-butadiene-*b*-ε-caprolactone) [20]. To simplify the calculation, we considered an idealized model with $\chi_{AB} = \chi_{BC}$ and equal statistical Kuhn lengths $b_A = b_B = b_C$. For the set of interaction parameters $\chi_{AB}N = \chi_{BC}N = 35$ and $\chi_{AC}N = 15$, a large number of ordered phases emerge from our calculations (Fig. 1). These structures can be classified into several groups: (i) equilibrium diblock copolymer phases, which are a lamellar (L), gyroid (G), cylinder (C), sphere (S), or disordered phase (D); (ii) core-shell analogs of the G, C, and S phases found in diblock copolymers, in which the middle-block domain forms a shell around the network of one of the end blocks and the other block forms the matrix; (iii) alternating versions of the L, G, C, and S phases, in which the end blocks organize in alternating sublattices and the middle block forms the matrix; (iv) possible combination of the L, G, C, and S phases, including lamellae with cylinders at the interfaces [$L + C$(I)], lamel-

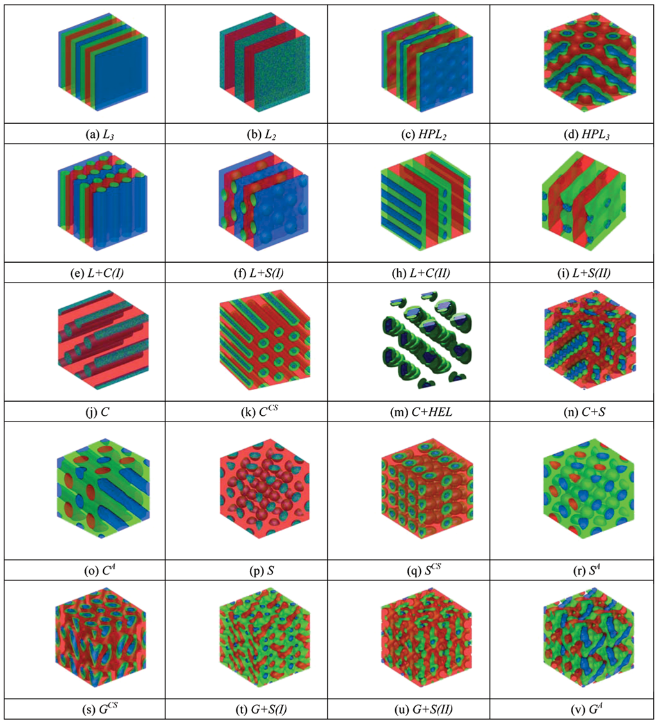
(a) L_3 (b) L_2 (c) HPL_2 (d) HPL_3
(e) $L+C(I)$ (f) $L+S(I)$ (h) $L+C(II)$ (i) $L+S(II)$
(j) C (k) C^{CS} (m) $C+HEL$ (n) $C+S$
(o) C^A (p) S (q) S^{CS} (r) S^A
(s) G^{CS} (t) $G+S(I)$ (u) $G+S(II)$ (v) G^A

FIG. 1 (color). Ordered phases obtained using the generic spectrum approach for model linear *ABC* triblock copolymers with $\chi_{AB}N = \chi_{BC}N = 35$ and $\chi_{AC}N = 15$. Blue, green, and red represent domains rich in *A*, *B*, and *C* blocks, respectively.

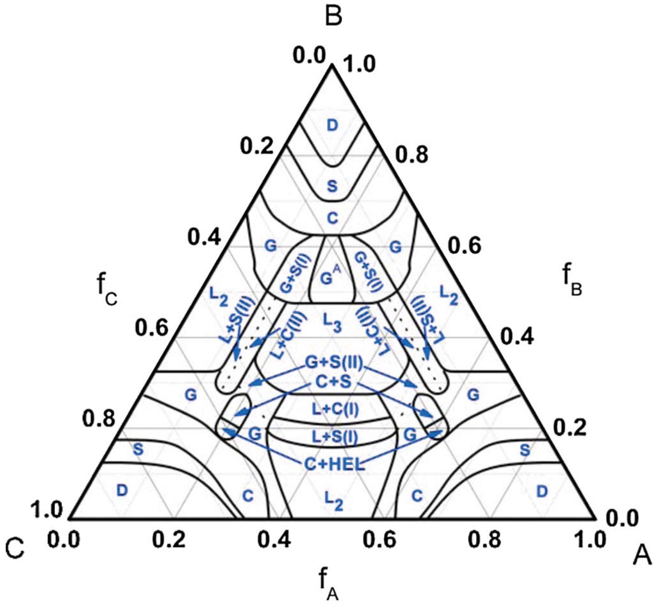

FIG. 2 (color). Phase diagram of a model linear *ABC* triblock copolymer with $\chi_{AB}N = \chi_{BC}N = 35$ and $\chi_{AC}N = 15$. Dotted lines are phase boundaries that are not determined exactly.

lae with cylinders inside a domain $[L + C(\mathrm{II})]$, lamellae with spheres at the interfaces $[L + S(\mathrm{I})]$, lamellae with spheres inside a domain $[L + S(\mathrm{II})]$, gyroid with spheres at the interfaces $[G + S(\mathrm{I})]$, and gyroid with spheres inside a domain $[G + S(\mathrm{II})]$; (v) other decorated phases, such as helical rings on cylinders (C + HEL); (vi) metastable phases such as hexagonally perforated lamellae (HPL).

Figure 2 shows the calculated phase diagrams for the triblock copolymer with $\chi_{AB}N = \chi_{BC}N = 35$ and $\chi_{AC}N = 15$. The increment of the volume fractions f_A, f_B, and f_C in the phase diagram is 0.025. The phase diagram is symmetric about the line $f_A = f_C$, due to the use of the symmetric interaction parameters $\chi_{AB} = \chi_{BC}$. A notable feature is that large area of lamellar (L) region exists in the center and near the middle of each binary edge of the phase triangle, which is separated into subregions by decorated phases such as $L + S(\mathrm{II})$ near the *AB* or *BC* edge and $L + C(\mathrm{I})$ and $L + S(\mathrm{I})$ near the *AC* edge. In the subregion at the center of the phase triangle, *A*, *B*, and *C* form well segregated layers—“three-color” structure (L_3)—while a “two-color” structure (L_2) in which only two layers can be observed along each of the edges. The region of the G phase near the B corner, which includes the alternating G phase (G^A) near the isopleth $f_A = f_C$ and the core-shell version (G^{CS}) near the *AB* or *BC* edge, is separated by the $G + S$ phase, in which the sphere is formed by one of the end block. Near the *A* or *C* corner, a C + HEL phase is surrounded by the G phase, in which one of the end block forms the cylinder and the middle block forms the helix that winds the cylinder. The C and S phases form continuous arcs across the three corners of the triangle. In the *A*-rich corner, both phases consist of a *C* core coated by a *B* shell immersed in an *A* matrix, while in the *C*-rich corner the order is reversed (with *A* core/*B* shell/*C* matrix). In the *B*-rich corner, alternating C and S phases form near the isopleth $f_A = f_C$, while near the *AB* and *BC* edges core-shell versions of the C and S phases are

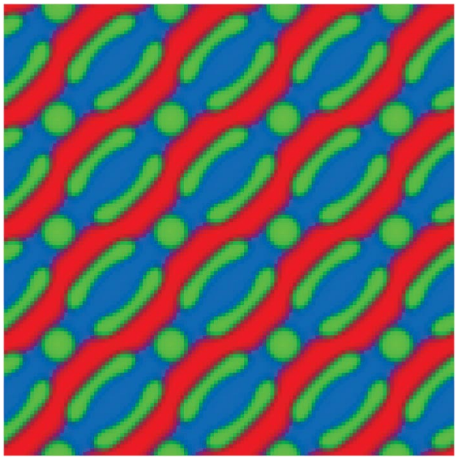

FIG. 3 (color). Knitting pattern obtained for the linear *ABC* triblock copolymer with $\chi_{AB}N = 27$, $\chi_{BC}N = 59$, $\chi_{AC}N = 11.5$, $f_A = 0.36$, $f_B = 0.31$, and $f_C = 0.33$. The statistical segment lengths are $b_A = 0.61$ nm, $b_B = 0.68$ nm, and $b_C = 0.65$ nm. Blue, green, and red represent domains rich in *A*, *B*, and *C* blocks, respectively.

stable. The phase triangle qualitatively agrees with the phase behavior observed for PS-PB-PMMA triblocks reported by Abetz and Goldacker [21]. Moreover, the calculated phase sequence $L_3 \rightarrow L + C(\mathrm{I}) \rightarrow L + S(\mathrm{I}) \rightarrow L_2$ near the isopleth $f_A = f_C$ with decreasing f_B follows the experiment exactly.

As another application of the current approach, we studied a model system for polystyrene-*b*-poly(ethylene-co-butylene)-*b*-poly(methyl methacrylate) (SEBM) triblock copolymers [22], which exhibits a fascinating two-dimension "knitting pattern" (KP) morphology. The KP phase was observed in a $S_{35}EB_{27}M_{38}$ sample with a number averaged molecular weight 1.22×10^5 and volume fractions $f_{\mathrm{PS}} = 0.36$, $f_{\mathrm{PEB}} = 0.31$, and $f_{\mathrm{PMMA}} = 0.33$. The statistical segment lengths are $b_A = 0.61$ nm, $b_B = 0.68$ nm, and $b_C = 0.65$ nm (PS, PEB, and PMMA are referred to as A, B, and C, respectively), with a reference monomer volume of 0.145 nm^3 [23]. Consistent with the Hildebrandt approximation, we take $\chi_{AB}N = 27$, $\chi_{BC}N = 59$, and $\chi_{AC}N = 11.5$ [18]. The calculation is carried out in 2D using 160 basis functions. It is observed that the KP structure is sensitive to the block copolymer parameters. For the chosen parameters, an equilibrium KP morphology (Fig. 3) is predicted.

In summary, we have developed a generic approach for the discovery of complex ordered phases of block copolymers. The approach is based on a generic Fourier-space method. The essential idea is to expand all of the spatial varying functions into a generic set of basis functions. The symmetry of the equilibrium phases emerges from the solutions. The space group of the ordered phases can be identified by mapping to scattering vectors. Application of the generic approach to diblock copolymers reproduces all known diblock phases. A model frustrated *ABC* triblock copolymer is chosen to further demonstrate its predictive power. A phase diagram of the model *ABC* triblock copolymer is constructed. A number of new phases are predicted for the triblock copolymers. Finally, the method is applied to a realistic model of a SEBM triblock copolymer, in which the fascinating KP phase was predicted to occur at the parameters that mostly match the experiment conditions. We believe that the generic spectral approach is a powerful method to predict new ordered phases for complex block copolymers. These ordered structures can be used as input for the more accurate and efficient real-space [5] or reciprocal-space [6] methods.

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