Commun. Comput. Phys.
doi: 10.4208/cicp.150811.111012a

Vol. **14**, No. 2, pp. 443-460
August 2013

Discovery of New Metastable Patterns in Diblock Copolymers

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Received 15 August 2011; Accepted (in revised version) 11 October 2012

Available online 4 January 2013

Abstract. The ordered patterns formed by microphase-separated block copolymer systems demonstrate periodic symmetry, and all periodic structures belong to one of 230 space groups. Based on this fact, a strategy of estimating the initial values of self-consistent field theory to discover ordered patterns of block copolymers is developed. In particular, the initial period of the computational box is estimated by the Landau-Brazovskii model as well. By planting the strategy into the whole-space discrete method, several new metastable patterns are discovered in diblock copolymers.

AMS subject classifications: 65M70, 76A15

Key words: Metastable patterns, diblock copolymers, self-consistent field theory (SCFT), space group theory, initial values.

1 Introduction

In the last decade, ordered patterns formed by block copolymers have attracted great attention. Block copolymers are composed of different chemical block chains. The self-assembly behavior of block copolymers is driven by various interactions among the different blocks, the volume fraction of blocks, and the topological constraint of the chain architecture. Ordered equilibrium patterns are a result of the delicate balance among these complex competing factors. Potential applications of these ordered patterns include lithographic templates for nanoparticle synthesis, photonic crystals and high density magnetic storage media [1]. Therefore, how to search for the ordered patterns becomes

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especially important for the development of nanotechnology using block copolymers. It also presents a complex and challenging problem for studying the phase behavior of the block copolymers [2].

In AB diblock copolymers, a number of ordered patterns have been discovered, such as lamellae (LAM), hexagonally packed cylinders (HPC), hexagonally perforated lamellae (HPL), spheres in body-centered-cubic (BCC) lattice, spheres in face-centered-cubic (FCC) lattice, bicontinuous double gyroid (DG), bicontinuous double diamond (DD) and *Fddd* patterns [3, 4]. Among these rich ordered patterns, the metastable patterns play an important role. They often become the dominant state for the entire system and are observed over a range of time and size scales in phase transitions [5–7]. For example, metastable phase HPL is observed as an intermediate phase in LAM$\rightarrow$DG transition [8]. Another important fact is that the metastable patterns in diblock copolymers may be stable in other polymeric systems. For example, the pattern A-15 in AB diblock copolymers is metastable, however, it is a stable pattern in AB_n graft diblock copolymers [9]. DD, HPL are the stable patterns in the blends of AB diblock copolymer and A homopolymer, and also metastable ones in AB diblock copolymer melt [10]. Therefore, it is important to develop an efficient strategy to capture as many ordered patterns as possible, including stable and metastable ones.

Theoretically, the SCFT provides a successful framework for studying the equilibrium phase behavior of block copolymers. By searching for the solutions of the self-consistent field equations, one can find the equilibrium ordered patterns of block copolymers. However, SCFT is a set of highly nonlinear equations with multi-solutions. The equations have a strong nonlocality that emerges from the connection of propagators and density, mean external fields. The solutions are also dependent on the interacting parameters and compositions. Finding all solutions of SCFT analytically is beyond today's technology. A successful alternative is to solve the self-consistent field equations numerically.

Generally, there are three main parts required to study nonlinear equations with multi-solutions: the initial values, the discrete schemes and the nonlinear iterative methods. Two kinds of numerical versions are developed to discretize the self-consistent field equations. The first type is the projective-space discrete method which discretizes equations in a special subspace based on specific problems. According to the specific pattern and its symmetric group in microphase-separated block copolymers, the self-consistent field equations can be expanded in terms of a set of symmetric basis functions [11]. This method is a powerful tool to analyze the phase behavior of the known phases. However, it is generally granted that this method is unable to discover new patterns. The second type is the whole-space discrete method whose approximated space is the whole space. This method can be carried out both in real space [12] and in Fourier-space [13]. It has also been demonstrated that the whole-space discrete methods are able to capture new patterns [12, 13]. In recent years, an efficient pseudospectral method has been introduced to solve the modified diffusion equations in SCFT [14,15] for the whole-space discrete methods. It fully takes advantage of the best performance of real space and Fourier-space and reduces the computational complexity to $\mathcal{O}(N\log N)$, with the number of spectral modes