

Hard-Surface Effect and Mixed Lamellae in Symmetric Diblock Copolymer Thin Films

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INTRODUCTION

Block copolymers have great potential for applications in nanotechnology, due to their microphase separation into spatially periodic structures on the length scale of 10–100 nm, direct control of the self-assembled morphology, and the uniformity of these nanostructures. Nano-confinement of block copolymers can be used to produce novel morphologies that cannot be obtained in the bulk and to control the morphology through the confining surfaces. The influence of confinement on the microphase separation and morphology of block copolymers is also of fundamental interest in polymer science.

The simplest and most understood case of confined block copolymers is that of symmetric diblock copolymers confined between two flat, hard, parallel and homogeneous surfaces. Such systems have been extensively studied by experiments, Monte Carlo simulations and various theories over the past decade. The surfaces have several effects on the thin-film morphology: First, a surface generally exhibits an energetic preference for one of the two blocks, due to the difference in surface-block interactions. This results in lamellae oriented parallel to the surfaces. Second, the two surfaces have a confining effect. When the surface separation D is incommensurate with the bulk lamellar period L_0 (i.e., when D/L_0 is not an integer in the case of two surfaces preferring the same type of segments, or not half an odd integer in the case of two surfaces preferring different types of segments), such frustration forces the copolymers to change their lamellar period to be different from L_0 , or even to adopt a different (perpendicular) lamellar orientation to restore L_0 when the frustration is large.

The third effect, referred to as the "hard-surface effect"¹, is that a neutral and hard surface induces the formation of perpendicular lamellae. This effect has been less studied in the literature. While it has been mainly attributed to the surface-induced compatibilization between A and B segments (i.e., the A-B repulsion is effectively reduced near the surfaces due to either the polymer segmental density decrease from that in the interior of the film²⁻⁴ or the "missing-neighbor" effect³), the nematic ordering of copolymer segments near a hard surface is also responsible for this^{5,6}. Monte Carlo simulations have also revealed that chain ends enrich near hard surfaces and that copolymer chains close to the surfaces orient parallel to them.^{1,7}

By tuning the surface-block interactions and the thickness of the confined film, one can therefore obtain parallel lamellae, perpendicular lamellae, and even mixed lamellae of parallel orientation near one surface and perpendicular orientation near the other^{1,8-15}. While the mixed lamellae have been observed in experiments and Monte Carlo simulations, Tang⁴ and Fasolka et al.¹⁴, both using lattice self-consistent field (SCF) calculations in 2D, reached contradictory conclusions regarding whether the mixed lamellae are a stable phase or not. While Matsen concluded from his continuum SCF calculations in 2D that the mixed lamellae of symmetric diblock copolymers are unstable, this was based on a questionable assumption that mixed lamellae, if they were to occur, would be most stable between either identical or antisymmetric surfaces².

In this work, we use real-space SCF calculations to study in detail the hard-surface effect and the stability of mixed lamellae, and map out the phase diagrams of symmetric diblock copolymer thin films using 3D calculations.

METHODS

Self-Consistent Field Calculations. We perform 3D continuum SCF calculations in real space, without *a priori* knowledge about the possible morphologies, and construct the phase diagram through free-energy comparison. Following the work of Matsen², we introduce a

surface field for each surface to represent its preference for the two blocks, and impose an overall polymer segmental density profile $\phi_C(x)$, where x denotes the direction perpendicular to the surfaces, to mimic the polymer density decrease near the surfaces due to the chain entropy loss (hard-surface effect). At a given surface separation and preference, we adjust the calculation cell sizes in the directions parallel to the surfaces to minimize the system free energy, and identify the most stable morphology by comparing the free energies of all the morphologies obtained from different initial guesses.

RESULTS

Using different functional forms of the overall polymer segmental density profile $\phi_C(x)$, we studied in detail the hard-surface effect and found that, in addition to the surface-induced compatibilization between A and B segments, the change in chain conformations near a hard surface from those in the interior of the film also plays an equally important role that favors the perpendicular lamellae over the parallel lamellae. Furthermore, the functional form of $\phi_C(x)$ strongly affects the accuracy of numerical SCF calculations for confined systems.

For symmetric diblock copolymer thin films confined between two homogeneous surfaces, we have found three different mixed lamellae as stable phases. The formation of these structures is closely related to the undulations of A-B interfaces in perpendicular lamellae caused by the surface preference. We have further analyzed the structure and phase transitions of various morphologies in detail, and compared our calculations results with available experiments and Monte Carlo simulations.

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