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The nature of phase transitions of symmetric diblock copolymer melts under confinement

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Abstract

The effects of confinement, both the structure frustration and the surface field, on phase transitions of symmetric diblock copolymer melts are investigated within several theoretical methods on the mean-field level. Confinements are applied by restricting polymer chains in the finite spaces of slabs. The surface can be neutral or preferential depending on the strength of the surface field. Within the one-dimensional self-consistent mean-field theory, for the neutral surface case, an oscillative behavior is observed for the size dependence of the order–disorder transition (ODT) point $(\chi N)_t$ due to the structure frustration. The spinodal $(\chi N)_s$ for this corresponding confined system is also calculated using the Gaussian fluctuation theory and the Landau–Brazovskii theory, and $(\chi N)_s$ coincides exactly with $(\chi N)_t$. On the other hand, the surface effect plays the role to decrease $(\chi N)_t$ due to the surface-induced spatial oscillation for the preferential surface case. In all confined systems considered, the ODT for symmetric diblock copolymer melts is a continuous second-order phase transition in the present mean-field calculation.

Keywords: Diblock copolymer; Phase transition; Confinement

1. Introduction

Diblock copolymers can undergo a microphase separation transition (MST) to form a variety of ordered structures in nanoscale. The bulk phase behavior has been extensively studied, both experimentally and theoretically. Up to present, a phase diagram has been constructed successfully for diblock copolymer melts [1–7].

Leibler [6] first developed a mean-field theory to investigate phase transitions in diblock copolymer melts. Basically, this method is a Landau expansion of the free energy around the high-temperature homogeneous phase, resorting to the random phase approximation (RPA). Thus, this theory is restricted to the weak segregation regime. Within this mean-field theory, the MST, or the order–disorder transition (ODT), coincides with the spinodal for symmetric diblock copolymers of $f = 0.5$ and the transition is second order, while the MST is first order for the asymmetric case of $f \neq 0.5$. Here, f is the volume fraction of A monomer of the diblock chains. Fredrickson and Helfand [7] treated the composition fluctuations in diblock copolymer melts by extending Brazovskii theory to diblock copolymers. In their treatment, Leibler's Landau-type free energy functional was reduced to a form considered by Brazovskii, and then the self-consistent Hartree approximation was performed for the fluctuations. In this theory of fluctuation, the MST turns out to be weakly first-order for the symmetric diblock copolymers.

In recent years, confined systems have been of great theoretical and experimental interests [8–49]. Confinements play a significant role when the size of the system becomes comparable to the typical length characterizing the structure of the system, and the bulk phase diagram will be modified generally.

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The thin film of block copolymers has been intensively explored in the past decade [8–24]. Most of the theoretical investigations focused on the lamella-forming symmetric diblock copolymer melts confined between two parallel hard walls, which are called as slabs in this paper. Turner [8] developed a strong segregation theory, which considers symmetric (the same block is in contact with both surfaces) and antisymmetric (each block is in contact with one of the surfaces) lamellar morphologies oriented parallel to the confining surfaces, to study the equilibrium behavior of the diblock copolymer lamellar phase confined in the slabs. They predicted that, depending on the interfacial energy of confining surfaces and the film thickness, the free energy of the symmetric and antisymmetric lamellar morphologies can attain local minima when the film thickness conforms to an integer or half-odd-integer multiple of the natural bulk period of the lamellar structure. Walton et al. [9] extended this theory by including the possibility of the perpendicularly oriented lamellar structure, in which the natural bulk lamellar period can be realized. Further generalization of this theory was done by Turner et al. [10], where the mixed morphologies (different combinations of parallel and perpendicular lamellar pattern) of the film were shown to be unstable, while pure parallel and perpendicular morphologies can be formed for both small and large distances between the walls depending on the surface tension. Binder and Kikuchi [11,12] carried out Monte Carlo simulations to study the phase behaviors of thin film, where the surface field is repulsive to one of the blocks. Sommer et al. [13] predicted that lamellae orient perpendicular to the perfectly neutral walls. Based on the self-consistent field calculations, Tang [14] and Fasolka et al. [15] constructed the phase diagram of the film, whose thickness is equal to or below the bulk natural lamellar period.

On the other hand, the surface-induced ordering for diblock copolymer systems has also been extensively investigated. Fredrickson [35] used a mean-field theory in the weak segregation regime to study the surface ordering phenomena for symmetric diblock copolymers in contact with a surface having preferential interaction with one of the two blocks. Just above the bulk ODT, the order parameter, which is the deviation of the A monomer concentration from its average value f, behaves a decaying oscillation characterized by a correlation length ξ, which diverges as the ODT is approached. Below the ODT, the system is characterized by a spatially modulated pattern. Further investigations [36] by including higher order, nonlinear corrections to the mean-field theory resulted in a non-divergent ξ. Kielhorn and Muthukumar [37] investigated the effect of a patterned surface on the phase separation kinetics of a thin polymer film using the Cahn–Hilliard–Cook model and the pattern-induced spinodal waves perpendicular to the surface is observed. Freed et al. [38–40] employed an analytical density-functional self-consistent field theory to study the density profiles of homopolymer blends, homopolymer melts, homopolymer solutions and diblock copolymer melts near the patterned surfaces. Tan et al. [41] investigated the surface-induced structure in the body-centered-cubic phase of diblock copolymers employing the Landau–Brazovskii theory. Tsori and Andelman [42–46] have extensively explored the ordering mechanism for confined diblock copolymers based on a coarse-grained Ginzburg–Landau free energy functional and various surface-induced patterns were observed in their model.

In general, confinements introduce two factors into the systems, i.e., the structure frustration and the surface effect. The structure frustration comes from the commensurability between the size of the confinement and the natural period of the bulk ordered structure, while the surface effect is due to the interaction between the surfaces and the polymers. The interplay between them determines the phase behavior. On the other hand, it is worthwhile to distinguish these two effects for a better understanding and this can be realized by establishing neutral surfaces. Experimentally, a general method for neutralizing the surface has been successfully demonstrated [18]. Also, neutral surfaces can be obtained conveniently in theoretical model. Most recently [49], within the Gaussian fluctuation theory [50–53] and the Landau–Brazovskii theory [53–55], we studied the spinodal behavior of the homogeneous diblock copolymer melts confined in neutral slabs, cylindrical pores and spherical pores, corresponding to the one-, two- and three-dimensional confinements, respectively. The effects of structure frustration are well represented.

In the present work, first we study theoretically the phase transitions in confined symmetric ($f = 0.5$) diblock copolymer melts within the reciprocal self-consistent mean-field theory (SCMFT). We assume that the ordered structure is the parallel lamella (the diblock copolymer chains are perpendicular to the surfaces). Thus, we only need to do the calculation of the SCMFT in one dimension along the direction of confinement. Although the assumption on the ordered structure orientation along the confinement may not be realistic in some neutral confined systems since the polymer chains can relax the confinement effects by arranging themselves along the free dimensions in the confined system [49], the frustration effects can be focused and understood intensively in our one-dimensional calculation along the confined direction. And our conclusions on the frustration effect will be generally true for the three-dimensional confined systems, in which there is no free dimension and the confinement must play its role to modify the phase behaviors. Hereafter, we will use MST and ODT alternatively for convenience of the presentation. By choosing the strength of the surface field, we investigate the confined systems with neutral surfaces and preferential surfaces, respectively.

In the bulk symmetric diblock copolymer melts, the MST coincides exactly with the spinodal in the mean-field theory. To check this for the confined case, we carry out the spinodal calculation for the homogeneous diblock melts confined by neutral surfaces with the parallel lamella using the Gaussian fluctuation theory and the Landau–Brazovskii theory.

Formally, the SCMFT, the Gaussian fluctuation theory and the Landau–Brazovskii theory can be derived from a general self-consistent field theory by a systematic expansion method [50–53]. Compared to the previous works, the phase transitions in the confined diblock copolymer melts are understood intensively by the combination of these different theoretical