Available online at www.sciencedirect.com
ScienceDirect
Polymer 48 (2007) 4278–4287
polymer
www.elsevier.com/locate/polymer

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

Bing Miao [a], Dadong Yan [a,*], Robert A. Wickham [b], An-Chang Shi [c]

[a] Beijing National Laboratory for Molecular Sciences (BNLMS), State Key Laboratory of Polymer Physics and Chemistry, Joint Laboratory of Polymer Science and Materials, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China
[b] Department of Physics, St. Francis Xavier University, Antigonish, Nova Scotia B2G 2W5, Canada
[c] Department of Physics and Astronomy, McMaster University, Hamilton, Ontario L8S 4M1, Canada

Received 16 February 2007; received in revised form 4 May 2007; accepted 18 May 2007
Available online 25 May 2007

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.

---

* Corresponding author. Tel.: +86 10 82617358; fax: +86 10 62559373.
E-mail address: yandd@iccas.ac.cn (D. Yan).

0032-3861/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2007.05.045

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 methods on the mean-field level. Especially, the SCMFT calculation can give the clear picture of the evolution of the structures in the confined space and determine the ODT exactly, while the Gaussian fluctuation theory and the Landau–Brazovskii theory determine the spinodal of the confined melts. Thus, the nature of the transitions can be understood clearly by putting the information from all the theories together.

This paper is organized as follows. In Section 2 the SCMFT both in the real space and reciprocal space is applied to the present system. In Section 3 the main results and discussions are given. In Section 4 the conclusions and possible future work are presented.

2. Self-consistent mean-field theory

We consider an incompressible melt of AB diblock copolymers confined in a finite volume V. The degree of polymerization of the diblock copolymer chains is N. The composition of α monomer is f_α, where $f_\alpha = f$ and $1-f$ for $\alpha = \mathrm{A}$ and B, respectively. The monomer statistical Kuhn length is b. We take $b_\mathrm{A} = b_\mathrm{B} = b$ for simplicity. In the following, we will use the convention in which all lengths are scaled by the Gaussian radius of gyration, $R_\mathrm{g} = b\sqrt{N/6}$, and the chain arc length is scaled by N. Within the mean-field approximation to the many-chain Edwards theory, the free energy density functional can be written as

$$\beta F = -\ln Q_\mathrm{c} + \frac{1}{V}\int \mathrm{d}\mathbf{r}\{\chi N\phi_\mathrm{A}(\mathbf{r})\phi_\mathrm{B}(\mathbf{r}) - \omega_\mathrm{A}(\mathbf{r})\phi_\mathrm{A}(\mathbf{r}) - \omega_\mathrm{B}(\mathbf{r})\phi_\mathrm{B}(\mathbf{r}) - V(\mathbf{r})[\phi_\mathrm{A}(\mathbf{r}) - \phi_\mathrm{B}(\mathbf{r})] - \eta(\mathbf{r})[1-\phi_\mathrm{A}(\mathbf{r}) - \phi_\mathrm{B}(\mathbf{r})]\}, \quad (1)$$

where $\beta = 1/k_\mathrm{B}T$ with the Boltzmann's constant k_B and the temperature T; χ is the Flory–Huggins parameter; ϕ_A and ϕ_B are the monomer densities; ω_A and ω_B are the self-consistent mean fields conjugate to the monomer densities; Q_c is the single-chain partition function in the presence of the self-consistent mean fields ω_A and ω_B; η is the Lagrange multiplier to ensure the incompressibility condition; $V(\mathbf{r})$ is the surface field which introduces the contribution from surface interaction to the free energy by coupling to the monomer densities.

Minimization of the free energy density F with respect to ϕ_A, ϕ_B, ω_A, ω_B and η leads to a set of mean-field equations

$$\omega_\mathrm{A}(\mathbf{r}) = \chi N\phi_\mathrm{B}(\mathbf{r}) - V(\mathbf{r}) + \eta(\mathbf{r}), \quad (2)$$

$$\omega_\mathrm{B}(\mathbf{r}) = \chi N\phi_\mathrm{A}(\mathbf{r}) + V(\mathbf{r}) + \eta(\mathbf{r}), \quad (3)$$

$$\phi_\mathrm{A}(\mathbf{r}) = \frac{1}{Q_\mathrm{c}}\int_0^f \mathrm{d}s\, q(\mathbf{r},s)q^\dagger(\mathbf{r},s), \quad (4)$$

$$\phi_\mathrm{B}(\mathbf{r}) = \frac{1}{Q_\mathrm{c}}\int_f^1 \mathrm{d}s\, q(\mathbf{r},s)q^\dagger(\mathbf{r},s), \quad (5)$$

$$\phi_\mathrm{B}(\mathbf{r}) + \phi_\mathrm{B}(\mathbf{r}) = 1 \quad (6)$$

with

$$Q_\mathrm{c} = \frac{1}{V}\int \mathrm{d}\mathbf{r}\, q(\mathbf{r},s)q^\dagger(\mathbf{r},s). \quad (7)$$

The key quantity in this calculation is the end-integrated propagators $q(\mathbf{r}, s)$ and $q^\dagger(\mathbf{r}, s)$, which are proportional to the probability of finding the monomer s at the spatial position $\mathbf{r}$. They satisfy the modified diffusion equations

$$\frac{\partial q(\mathbf{r},s)}{\partial s} = \nabla^2 q(\mathbf{r},s) - \omega(\mathbf{r},s)q(\mathbf{r},s), \quad (8)$$

$$-\frac{\partial q^\dagger(\mathbf{r},s)}{\partial s} = \nabla^2 q^\dagger(\mathbf{r},s) - \omega(\mathbf{r},s)q^\dagger(\mathbf{r},s), \quad (9)$$

where $\omega(\mathbf{r}, s) = \omega_\mathrm{A}(\mathbf{r})$ for $0 \le s \le f$ and $\omega(\mathbf{r}, s) = \omega_\mathrm{B}(\mathbf{r})$ for $f < s \le 1$. The initial conditions are $q(\mathbf{r}, 0) = 1$ and $q^\dagger(\mathbf{r}, 1) = 1$.

This set of equations in real space is complete and can be solved numerically by iteration. In the present study, we focus on the lamella-forming symmetric diblock copolymers. Thus, we assume that the ordered structure is the parallel lamella with the chains perpendicular to the surface. This assumption leads to the one-dimensional calculation along the direction of confinement. The surface can be neutral or preferential to the diblock chains depending on the strength of the surface field $V(\mathbf{r})$. To deal with the symmetric diblocks, it should be noted that the MST coincides exactly with the spinodal for the bulk system in the mean-field theory.

We formulate the SCMFT in the reciprocal space in terms of the appropriate basis functions for the geometric spaces considered. The basis set $\{f_n(\mathbf{r})\}$ is chosen to be the eigenfunctions of the Laplace operator ∇^2, or,

$$\nabla^2 f_n(\mathbf{r}) = -\lambda_n f_n(\mathbf{r}) \quad (10)$$

with λ_n as the corresponding eigenvalues. As Fredrickson has argued for the investigation of confined systems [55], we take the Neumann boundary conditions in this research, in which the gradients of the eigenfunctions are zero at the boundaries, or $\nabla f_n(\mathbf{r})|_\mathrm{boundary} = 0$.

For the confinement of slabs, the direction perpendicular to the two parallel surfaces is chosen as x axis, while the other two directions are homogeneous and can be neglected in the present one-dimensional calculation. Thus,

$$f_n(\mathbf{r}) = \begin{cases} 1 & n = 0 \\ \sqrt{2}\cos(k_n x) & n = 1,2,3\ldots \end{cases} \quad (11)$$

with the corresponding eigenvalues

$$\lambda_n = k_n^2. \quad (12)$$

Here, $k_n = n\pi/D$ is determined from the boundary condition, or, $\sin(k_n 0) = \sin(k_n D) = 0$, where D is the separation of the slabs.

Since the set of $\{f_n(\mathbf{r})\}$ is complete

$$\sum_n f_n(\mathbf{r}) f_n^*(\mathbf{r}') = \delta(\mathbf{r}-\mathbf{r}') \tag{13}$$

and orthogonal

$$\frac{1}{V}\int \mathrm{d}\mathbf{r}\, f_n^*(\mathbf{r}) f_m(\mathbf{r}) = \delta_{n,m}, \tag{14}$$

we can expand all the spatially dependent quantities in terms of $f_n(\mathbf{r})$,

$$\phi_\mathrm{A}(\mathbf{r}) = \sum_n \phi_{\mathrm{A},n} f_n(\mathbf{r}), \tag{15}$$

$$\phi_\mathrm{B}(\mathbf{r}) = \sum_n \phi_{\mathrm{B},n} f_n(\mathbf{r}), \tag{16}$$

$$q(\mathbf{r},s) = \sum_n q_n(s) f_n(\mathbf{r}), \tag{17}$$

$$q^\dagger(\mathbf{r},s) = \sum_n q_n^\dagger(s) f_n(\mathbf{r}), \tag{18}$$

$$\omega(\mathbf{r},s) = \sum_n \omega_n(s) f_n(\mathbf{r}), \tag{19}$$

$$V(\mathbf{r}) = \sum_n V_n f_n(\mathbf{r}), \tag{20}$$

$$\eta(\mathbf{r}) = \sum_n \eta_n f_n(\mathbf{r}). \tag{21}$$

In principle, the number of basis functions for the expansion should be infinity. However, we can take a finite number of $f_n(\mathbf{r})$ in actual calculations, if the convergence of the result is realized.

In terms of these basis functions, the modified diffusion equations of Eqs. (8) and (9) have the following form

$$\frac{\mathrm{d}q_n(s)}{\mathrm{d}s} = -\sum_l H_{nl}(s) q_l(s), \tag{22}$$

$$\frac{\mathrm{d}q_n^\dagger(s)}{\mathrm{d}s} = \sum_l H_{nl}(s) q_l^\dagger(s), \tag{23}$$

where

$$H_{nl}(s) = \lambda_n \delta_{nl} + \sum_m \Gamma_{nml}\omega_m(s) \tag{24}$$

with

$$\Gamma_{nml} = \frac{1}{V}\int \mathrm{d}\mathbf{r}\, f_n(\mathbf{r}) f_m(\mathbf{r}) f_l(\mathbf{r}). \tag{25}$$

This matrix equation can be solved in terms of the eigenvalues and eigenfunctions of the matrix $H_{nl}(s)$ to obtain the end-integrated propagators $q_n(s)$ and $q_n^\dagger(s)$. A detailed exposition of this process is given in Appendix.

The mean-field equations in the reciprocal space can be expressed as

$$\omega_{\mathrm{A},n} = \chi N \phi_{\mathrm{B},n} - V_n + \eta_n, \tag{26}$$

$$\omega_{\mathrm{B},n} = \chi N \phi_{\mathrm{A},n} + V_n + \eta_n, \tag{27}$$

$$\phi_{\mathrm{A},n} = \frac{1}{Q_\mathrm{c}} \sum_{ml} \Gamma_{nml} \int_0^f \mathrm{d}s\, q_m(s) q_l^\dagger(s), \tag{28}$$

$$\phi_{\mathrm{B},n} = \frac{1}{Q_\mathrm{c}} \sum_{ml} \Gamma_{nml} \int_f^1 \mathrm{d}s\, q_m(s) q_l^\dagger(s), \tag{29}$$

$$\phi_{\mathrm{A},n} + \phi_{\mathrm{B},n} = \delta_{n,1} \tag{30}$$

with

$$Q_\mathrm{c} = \sum_n q_n(s) q_n^\dagger(s). \tag{31}$$

Notice that in Eq. (31) the sum is actually independent of s. We solve this set of equations numerically by standard iteration. In the present reciprocal SCMFT calculation, all the structures satisfying the symmetry of the basis functions' set are scanned. As a result, the structure with the lowest free energy is picked out spontaneously at a given condition, and the density distribution and the corresponding free energy of the chosen structure are obtained.

3. Results and conclusions

Within the reciprocal SCMFT, we explore the confinement effects, both the structure frustration and the surface effect, on the phase behavior in the confined lamella-forming symmetric diblock copolymer melts. The surfaces can be neutral or preferential in the model depending on the strength of the surface field $V(\mathbf{r})$, which is taken to have the following form in the one-dimensional calculation,

$$V(x) = -V_0\left[\mathrm{e}^{-x^2/\zeta^2} + \mathrm{e}^{-(x-D)^2/\zeta^2}\right], \tag{32}$$

where V_0 (scaled by $k_\mathrm{B}T$) and ζ are the strength and the correlation length of $V(\mathbf{r})$, respectively. For simplicity without loosing physics, we fix ζ to investigate the effect of V_0.

In order to investigate the nature of phase transitions in the confined system, we define an order-parameter-like quantity ψ_ϵ, which is a measure of the amplitude of the density distribution deviation from homogeneous, given by

$$\psi_\epsilon = \frac{1}{2\epsilon}\int_{D/2-\epsilon}^{D/2+\epsilon} \mathrm{d}x[\phi_\mathrm{A}(x) - f]^2, \tag{33}$$

where ϵ is a small quantity taken to be R_g in the calculation. From the definition, ψ_ϵ is zero for the homogeneous (disordered) phase and begins to take a nonzero value when the

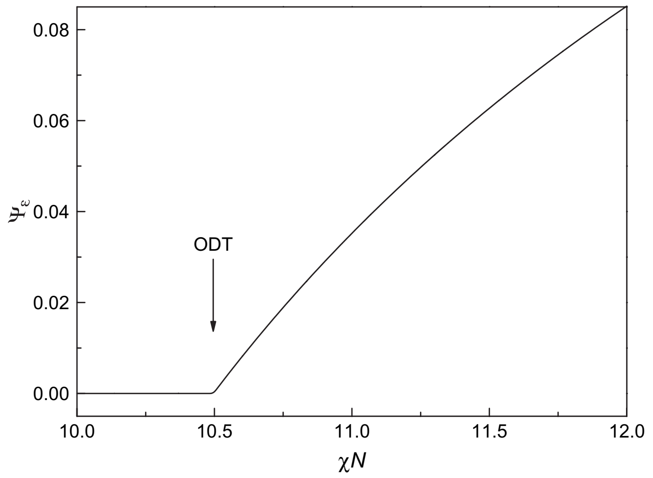

Fig. 1. The evolution of the order parameter ψ_ϵ with χN for the symmetric diblock copolymers confined between two slabs of $D = 3.2R_g$ with neutral surfaces.

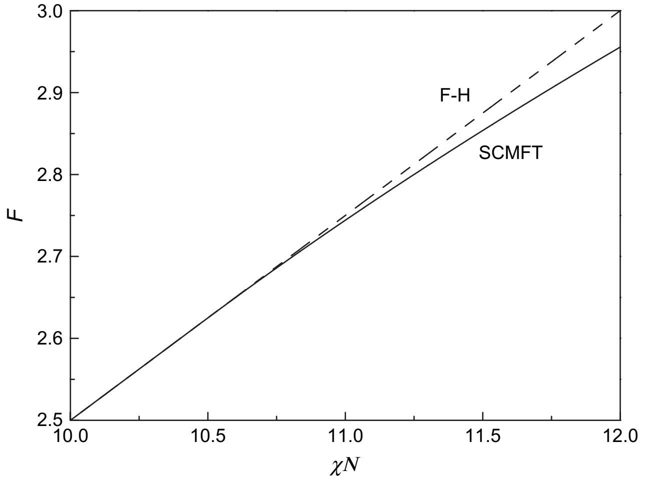

Fig. 3. The free energy curves as a function of χN for the symmetric diblock copolymers confined between two slabs of $D = 3.2R_g$ with neutral surfaces. The solid line is from the SCMFT for different ordered structures, which corresponds to different χNs. The dashed line is from the Flory–Huggins theory for the homogeneous structure.

system becomes ordered. Although ψ_ϵ is not a well-defined parameter, it is an appropriate parameter in practice for the investigation of ODT. For convenience of the presentation, we will call ψ_ϵ as the order parameter.

3.1. Neutral surfaces

By setting the strength of the surface field V_0 to be zero, the neutral surface is realized in the model. This allows us to investigate the effect of the structure frustration separately.

Firstly, we study the symmetric diblock copolymer melts confined between two parallel slabs with smaller separation of $D = 3.2R_g$. In Fig. 1, we illustrate the evolution of the order parameter ψ_ϵ with χN (or the temperature). The order parameter ψ_ϵ goes continuously to zero when χN decreases (or the temperature increases) to the critical value of 10.5. It is the signature of a second-order phase transition. The corresponding evolution of the structure, or the density distribution, with χN is shown in Fig. 2, in which the lamellar pattern changes continuously to homogeneous when χN decreases to the critical value of 10.5. The continuous nature of the ODT is further verified in Fig. 3 by the free energy shown in solid line, corresponding to the evolution of structure in Fig. 2. With the decrease of χN, the free energy of the most stable structures from the SCMFT calculation is plotted together with the Flory–Huggins free energy, $F = \beta^{-1} f(1-f)\chi N$, corresponding to the disordered structure. When χN decreases to the critical value of 10.5, the free energy of the lamellar structure continuously transits to the free energy of the disordered structure.

Secondly, we study the system with larger separations of slabs by SCMFT. In Fig. 4, we illustrate the order parameter evolution for the symmetric diblocks confined in slabs with $D = 7.5R_g$. A new jump at $\chi N = 10.85$ appears besides the continuous ODT, which is the signature of a first-order

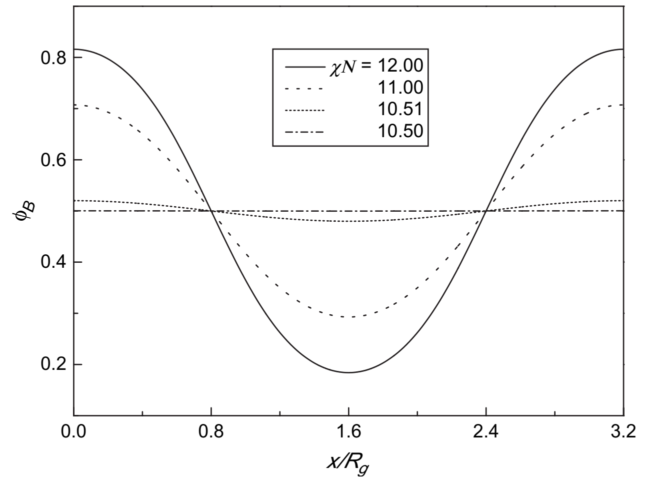

Fig. 2. The evolution of the spatial density distribution ϕ_B with χN for the symmetric diblock copolymers confined between two slabs of $D = 3.2R_g$ with neutral surfaces.

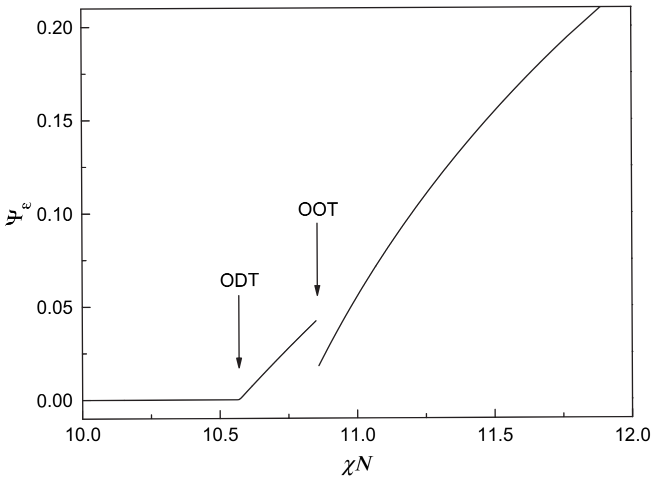

Fig. 4. The order parameter curve as a function of χN for the symmetric diblock copolymers confined between two slabs of $D = 7.5R_g$ with neutral surfaces. The jump of the order parameter happens at $\chi N = 10.85$.

order–order transition (OOT). In order to understand this transition clearly, we plot the corresponding transition picture of density pattern in Fig. 5. It is evident that the jump of ψ_ϵ corresponds to a first-order OOT. For this OOT, with the increase of the temperature, the morphology in the finite space evolves from the symmetric lamella to the antisymmetric one, accompanying an increase of a layer. This is consistent with the physical intuition that the polymer chains are not so stretched at higher temperature due to the entropy effect and one more layer can be accommodated.

In experiments, the size of the confinement is an important control parameter. We illustrate the size dependence of the ODT point, $(\chi N)_\mathrm{t}$ in Fig. 6. For a small enough separation D, since no fluctuations can happen, $(\chi N)_\mathrm{t}$ goes to infinity. As D increases, $(\chi N)_\mathrm{t}$ first falls down to a minimum at a given D, then oscillates and eventually approaches the bulk value of $(\chi N)_\mathrm{t}^0 = 10.5$. Furthermore, the value of each minimum is exactly $(\chi N)_\mathrm{t}^0$. The observation that $(\chi N)_\mathrm{t}$ recovers $(\chi N)_\mathrm{t}^0$ for the large D is consistent with the physical intuition, of which the confinement is in fact removed from the system when the size of confinement is large enough.

The ODT coincides exactly with the spinodal point of the bulk symmetric diblock copolymer melts. To check this in the confined case, we calculate the spinodal point using the Gaussian fluctuation theory, which was described thoroughly in Ref. [49]. In Fig. 6, the size dependence of the spinodal point is also shown as $(\chi N)_\mathrm{s}$. It turns out that the spinodal coincides with the ODT exactly. This is also an indication of the fact that the ODT is a continuous transition in this confined system.

Also, we plot the size dependence of $(\chi N)_\mathrm{s}$ from the Landau–Brazovskii theory. It fits other two lines well with slight deviations due to the fact that the Landau–Brazovskii theory is only an approximation to the Gaussian fluctuation theory by an expansion around the critical wave vector q_0, whose results are only correct when k_n is near q_0.

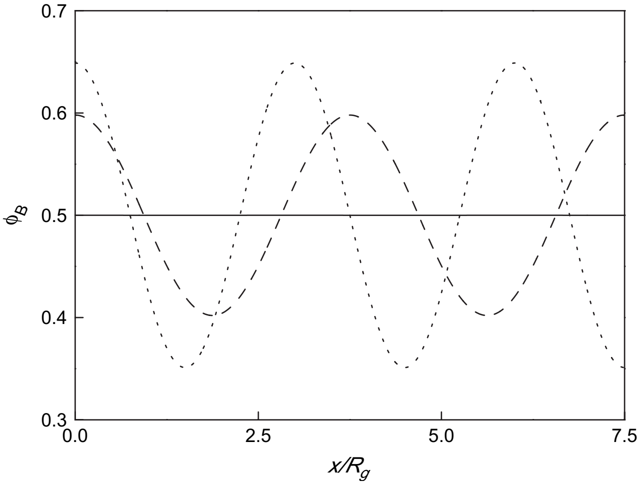

Fig. 5. The structure curve for the typical OOT transition for the symmetric diblock copolymers confined between two slabs of $D = 7.5R_\mathrm{g}$ with neutral surfaces. The structure of the dashed line transits into the structure of the dotted line as χN decreases past 10.85. The solid line characterizes the disordered structure.

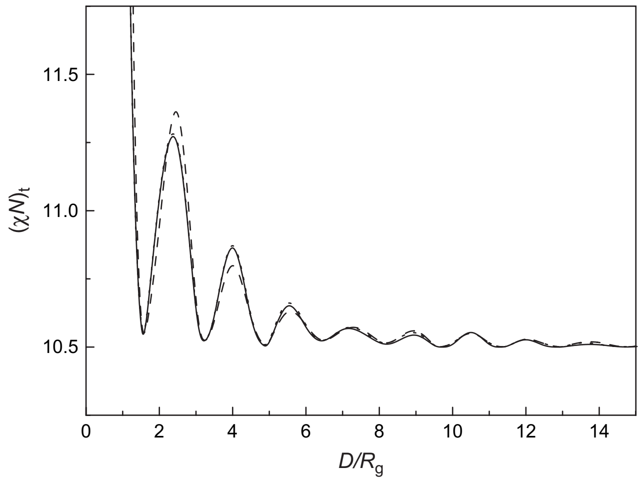

Fig. 6. The size dependences of $(\chi N)_\mathrm{t}$ and $(\chi N)_\mathrm{s}$ for the symmetric diblock copolymer melts confined between two slabs with neutral surfaces. The results from the SCMFT and the Gaussian fluctuation theory are represented as solid line and dotted line, respectively, which are almost overlapped. The dashed line is from the Landau–Brazovskii theory.

In Fig. 6, the parts near minima agree well for these three different methods. It can be easily understood as follows. Within the Landau–Brazovskii theory [49], $(\chi N)_\mathrm{s} = (\chi N)_\mathrm{s}^0 + \xi_0^2/\ 8q_0^2[(k_n^2 - q_0^2)^2]_\mathrm{min}$. D^*, at which the minima $(\chi N)_\mathrm{s} = 10.5$ occur, can be exactly determined by $k_{n^*} = n^*\pi/D^* = q_0$, leading to $D^* = n^*\pi/q_0 = (n^*/2)L_0$. Here, $n^* = 1, 2, 3\ldots$, and the natural period $L_0 = 2\pi/q_0$. This analysis indicates that the spinodal point is kept unchanged from the bulk value when D^* is an integer or half-odd-integer multiple of the natural period L_0 for the confined homogeneous melts. Furthermore, the morphology formed here can be observed from the SCMFT calculation. If D^* is an integer multiple of L_0 ($n^* =$ even integer), the symmetric parallel lamella is formed; If D^* is a half-odd-integer multiple of L_0 ($n^* =$ odd integer), the antisymmetric parallel lamella is formed. At most cases $D \neq D^*$, the symmetric or antisymmetric lamella is stretched or compressed, and the corresponding $(\chi N)_\mathrm{s}$ from the Gaussian fluctuation or the Landau–Brazovskii theory increases from 10.5. This increase of $(\chi N)_\mathrm{s}$ has been understood well due to the incommensurability between k_{n^*} and q_0. On the other hand, since $(\chi N)_\mathrm{s} = (\chi N)_\mathrm{t}$ in the present case, we can understand this increase by analyzing $(\chi N)_\mathrm{t}$. Within the SCMFT, the morphology after the ODT is calculated. For most D the stretched or compressed lamellae lead to energy penalty, which effectively increases $(\chi N)_\mathrm{t}$ at the ODT. Only the D^* at which no extra energy penalty happens leads to $(\chi N)_\mathrm{t} = 10.5$.

It is helpful to understand the structure frustration by analyzing the different fluctuation modes in the confined melts. As mentioned in Ref. [49], the fluctuation modes can be classified in terms of the basis $f_n(\mathbf{r})$, with the corresponding fluctuation energy cost $(C^\mathrm{RPA})_n^{-1}$. By simple calculation, the energy cost $(C^\mathrm{RPA})_0^{-1}$ mode is infinity. This is due to the incompressibility of the system. In Fig. 7, we illustrate the size dependence of $2e_n$, which is proportional to the fluctuation energy cost, for the modes of $n = 1$–4. Here, e_n is the

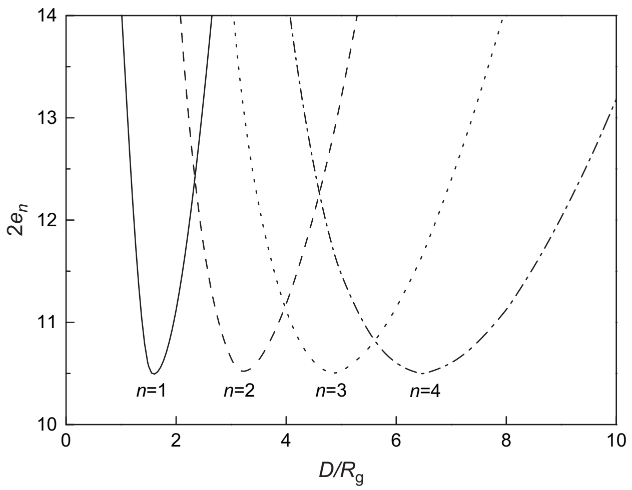

Fig. 7. The size dependence of the eigenvalue of $\tilde{C}^{-1}$, or e_n, for the symmetric diblock copolymer melts confined between two slabs with neutral surfaces. The eigenvalue e_n is proportional to the fluctuation energy cost of the mode n. The solid, dashed, dotted and dash-dotted lines correspond to the modes of $n = 1-4$, respectively.

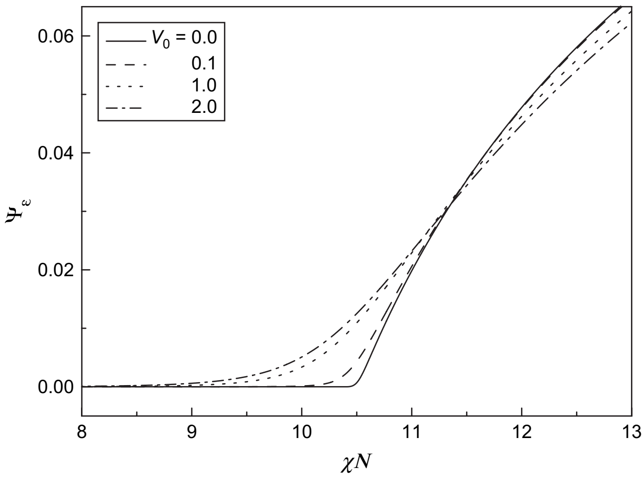

Fig. 8. The order parameter curves as a function of χN for the symmetric diblock copolymer melts confined between two slabs of $D = 10R_g$ with preferential surfaces of different surface strengths of V_0. The solid, dashed, dotted and dash-dotted lines correspond to the cases of $V_0 = 0$, 0.1, 1 and 2, respectively.

eigenvalue of $\tilde{C}^{-1}$. For a given size D, the spinodal is determined by the mode n^* with the lowest energy cost, or $(\chi N)_s = 2e_{n^*}$. It is evident that n^* is dependent on D and $n^* = 1-4$, in order with the increase of D. This is exactly the representation of the structure frustration effect. Depending on the compatibility between the characteristic length of the fluctuation mode and the natural period, the most unstable fluctuation mode n^* jumps from one to another.

It should be noted that all the results bear a restriction to the one-dimensional calculation on the assumption of forming parallel lamella after the MST. In fact, this assumption is not always realistic and other structures, like the perpendicular lamella, can be formed in some cases. On the other hand, the frustration effect can be focused on and understood clearly by combining the above three different theoretical frameworks in the present model. The frustration effect of confinement from the present calculation will be generally true for the confined systems in which there is no free dimension for fluctuation.

3.2. Preferential surfaces

In most experiments, the surfaces have a preferential affinity to one of the components of the diblock copolymers. By setting the strength of the surface field $V_0 > 0$, the surfaces prefer to contact with one kind of the monomers, let us say B monomer in the present study.

As V_0 is an important control parameter in experiments, we investigate the effect of V_0 within the SCMFT. In Fig. 8, the effect of V_0 on the ODT is illustrated by the order parameter plot for $D = 10R_g$ and $V_0 = 0$, 0.1, 1 and 2. For $V_0 = 0$, an exact ODT can be defined from the order parameter curve, which has been investigated in last section. With the increase of V_0, the transition becomes weaker. Actually, for a large V_0, we cannot define an exact ODT in the finite space. This is due to the fact that the strong preferential surface can induce an oscillating pattern over the whole finite space even when the temperature is high, and the disordered phase cannot be defined effectively. In order to circumvent this problem, we take a weak surface field and a relatively large space. At the same time, by the definition of the order parameter ψ_ϵ, we always look into the chosen range of $\epsilon(=R_g)$ to investigate the ODT. Based on this consideration, we choose $V_0 = 0.1$ and a relatively large size.

In Fig. 9, we illustrate the order parameter evolution with χN for $D = 3L_0 = 9.6R_g$ and $V_0 = 0.1$. The corresponding density pattern evolution is plotted in Fig. 10. Two transitions happen during the evolution. At large χN (low temperature), the lamellar structure L_2 is stable for the system. With the

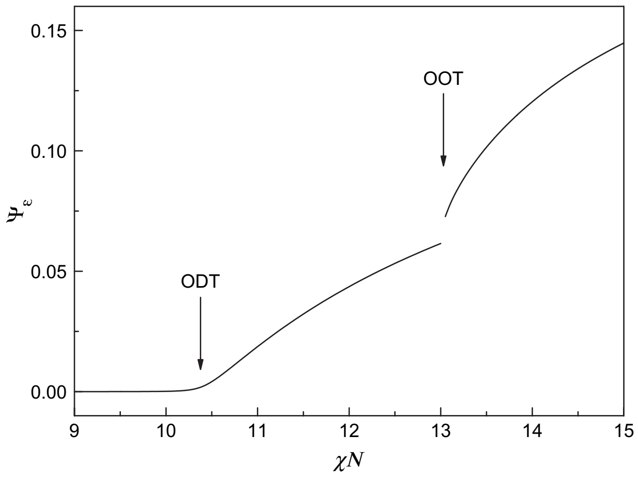

Fig. 9. The evolution of the order parameter ψ_ϵ with χN for the symmetric diblock copolymer melts confined between two slabs of $D = 3L_0 = 9.6R_g$ and $V_0 = 0.1$. The jump of the order parameter happens at $\chi N = 13.0$.

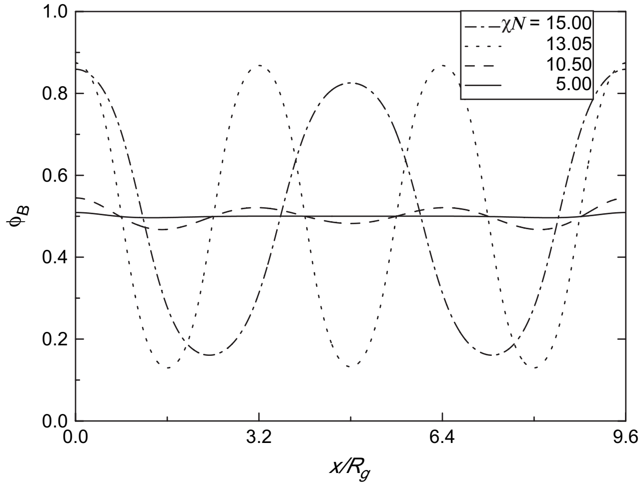

Fig. 10. The evolution of the spatial density distribution ϕ_B with χN for the symmetric diblock copolymers confined between two slabs of $D = 3L_0 = 9.6R_g$ and $V_0 = 0.1$.

decreasing of χN (high temperature), the order parameter ψ_ϵ behaves a jump, corresponding to a first-order OOT from L_2 to L_3. For the different morphologies mentioned above, we follow the notation in Ref. [28]. Further increasing the temperature, a continuous ODT from L_3 to the disordered phase occurs at $(\chi N)_t$.

In Fig. 11, we show the size dependence of $(\chi N)_t$ for $V_0 = 0.1$. It indicates that $(\chi N)_t$ is effectively decreased by the surface effect. Due to the connectivity of the two blocks, the preferential surfaces can induce an oscillating pattern for the diblock melts near the surfaces, which will help the disordered homogeneous phase far from the surfaces to be ordered. With the increase of D, $(\chi N)_t$ increases and approaches to $(\chi N)_t^0$, finally recovering to $(\chi N)_t^0 = 10.5$ for D larger than $15L_0$. This is consistent with the physical intuition, of which the confinement is in fact removed when its size is large enough.

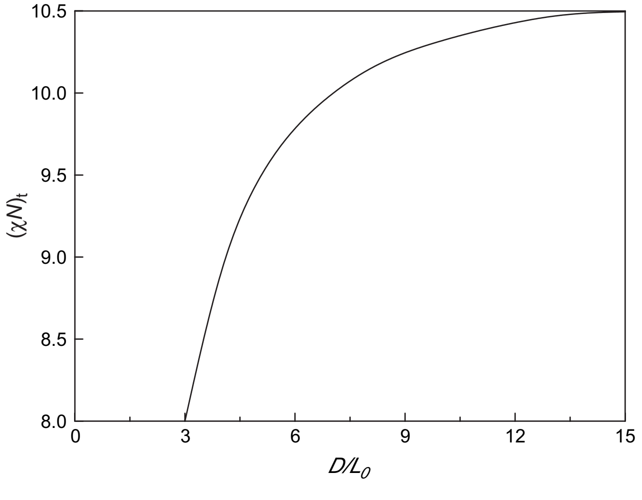

Fig. 11. The size dependence of $(\chi N)_t$ for the symmetric diblock copolymer melts confined between two slabs of $V_0 = 0.1$.

4. Conclusions

The phase transitions of confined symmetric diblock copolymer melts are investigated by adopting several theoretical methods on the mean-field level. Compared to the previous works, the combination of these different theoretical methods can give a more comprehensive and detailed picture of phase transitions, and the nature of phase transitions is understood more clearly.

Within the reciprocal SCMFT, we investigate the effects of confinement, both the structure frustration and the surface effect, on the phase transitions of confined symmetric diblock copolymer melts. By assuming the lamellae formed orient parallel to the surface, we only carried out the SCMFT in one-dimension along the direction of the confinement. The surface can be neutral or preferential in the model depending on the strength of surface field.

The neutral surfaces are realized by taking V_0 as zero. In this case, the MST, or the ODT, is a continuous second-order phase transition for the confined symmetric diblock copolymer melts by analyzing the evolution of the order parameter and the free energy with the temperature. The first-order OOT is also observed in the present model. Furthermore, we employ the Gaussian fluctuation theory and the Landau–Brazovskii theory to calculate the spinodal point. The size dependences of $(\chi N)_t$ from the SCMFT, of $(\chi N)_s$ from both the Gaussian fluctuation theory and the Landau–Brazovskii theory are plotted together. They agree well with each other. Thus, $(\chi N)_t$ coincides with $(\chi N)_s$ for the confined symmetric diblock copolymer melts, which indicates that the MST is a continuous second-order transition furthermore. An oscillative behavior for the size dependence of $(\chi N)_t$ and $(\chi N)_s$ is observed, which can be understood well as structure frustration. Especially, the analysis of the most unstable fluctuation mode in the confined melts makes the structure frustration effect more transparent.

If the surface field is large enough and preferential to one component of diblock copolymer, an exact ODT cannot be defined for a finite system. To circumvent this, the SCMFT calculation is carried out in a relatively large space with a weak surface field. The first-order OOT occurs at low temperature, while the ODT is still continuous. The surface effect plays its role to decrease $(\chi N)_t$ effectively. This is due to the fact that the preferential interaction can help the diblock copolymer chains to be ordered.

The observation that the ODT is continuous second-order transition bears a restriction to the mean-field nature of the present calculation, which is valid when the degree of polymerization N is large enough. Physically, due to the connectivity of the two blocks, diblock copolymers cannot behave a true continuous transition with a critical point. The transitions for diblock copolymers belong to the Brazovskii universality class, which are characterized by having large field fluctuations in the vicinity of a shell of nonzero wave vectors and exhibit a fluctuation-induced first-order transition. In particular, for the symmetric bulk diblock melts, the fluctuation effects change the second-order nature in Leibler's mean-field theory to first-order. Thus, it is expected that the inclusion of fluctuations will modify the second-order nature in the present mean-field calculation to first-order for the confined symmetric diblock system.

In the present model, the structure frustration and the surface effect for confined systems become more transparent and can be understood quite well. On the other hand, all the results are limited to the one-dimensional calculation with the assumption that the lamella formed is parallel to the surface. In the future work, we will relax this constraint and carry out calculations in more realistic three-dimension.

Acknowledgements

We would like to acknowledge the helpful discussions with Dr. Hongge Tan, Dr. Shuang Yang. This work is supported by the National Natural Science Foundation of China (NSFC) 20340420327, 20474074, 20490220, 20575085, and the 973 Project 2004CB720606. A.-C.S. and R.A.W. acknowledge the support from Natural Science and Engineering Research Council (NSERC) of Canada. R.A.W. also acknowledges Institute of Chemistry, Chinese Academy of Sciences for hosting during the period when a portion of this work was done.

Appendix

In this, we give a detailed exposition to solve the modified diffusion equation in reciprocal space.

The modified diffusion equations have the form

$$\frac{\mathrm{d}q_n(s)}{\mathrm{d}s} = -\sum_l H_{nl}(s) q_l(s), \tag{A1}$$

$$\frac{\mathrm{d}q_n^\dagger(s)}{\mathrm{d}s} = \sum_l H_{nl}(s) q_l^\dagger(s), \tag{A2}$$

where

$$H_{nl}(s) = \lambda_n \delta_{nl} + \sum_m \Gamma_{nml} \omega_m(s). \tag{A3}$$

with

$$\Gamma_{nml} = \frac{1}{V} \int \mathrm{d}\mathbf{r} f_n(\mathbf{r}) f_m(\mathbf{r}) f_l(\mathbf{r}) \tag{A4}$$

The solution of this equation can be found in terms of the eigenfunctions and eigenvalues of the matrix $H_{nm}(s)$. For $s < f$,

$$\sum_m H_{nm}(s) \Psi_{\mathrm{A},m}^{(u)} = \epsilon_{\mathrm{A}}^{(u)} \Psi_{\mathrm{A},n}^{(u)}. \tag{A5}$$

For $s > f$,

$$\sum_m H_{nm}(s) \Psi_{\mathrm{B},m}^{(u)} = \epsilon_B^{(u)} \Psi_{\mathrm{B},n}^{(u)}. \tag{A6}$$

For $s < f$, we do the expansion

$$q_n(s) = \sum_u q^{(u)}(s) \Psi_{\mathrm{A},n}^{(u)}, \tag{A7}$$

where $q^{(u)}(s)$ satisfies

$$\frac{\mathrm{d}q^{(u)}(s)}{\mathrm{d}s} = -\epsilon_{\mathrm{A}}^{(u)} q^{(u)}(s) \tag{A8}$$

with the solution

$$q^{(u)}(s) = e^{-\epsilon_{\mathrm{A}}^{(u)} s} q^{(u)}(0). \tag{A9}$$

Here, $q^{(u)}(0)$ is determined from the initial condition $q(\mathbf{r}, 0) = 1$ in the following way

$$q^{(u)}(0) = \sum_n \Psi_{\mathrm{A},n}^{(u)} q_n(0) \tag{A10}$$

with

$$q_n(0) = \frac{1}{V} \int \mathrm{d}\mathbf{r} f_n(\mathbf{r}) q(\mathbf{r}, 0) = \frac{1}{V} \int \mathrm{d}\mathbf{r} f_n(\mathbf{r}) = \delta_{n,0}. \tag{A11}$$

Then

$$q^{(u)}(0) = \sum_n \Psi_{\mathrm{A},n}^{(u)} q_n(0) = \Psi_{\mathrm{A},0}^{(u)}. \tag{A12}$$

Thus, for $s < f$, we have

$$q_n(s) = \sum_u \mathrm{e}^{-\epsilon_{\mathrm{A}}^{(u)} s} \Psi_{\mathrm{A},0}^{(u)} \Psi_{\mathrm{A},n}^{(u)}. \tag{A13}$$

For $s \geq f$, the appropriate expansion is

$$q_n(s) = \sum_u q^{(u)}(s) \Psi_{\mathrm{B},n}^{(u)}, \tag{A14}$$

and an analogous development gives

$$q^{(u)}(s) = \mathrm{e}^{-\epsilon_{\mathrm{B}}^{(u)} (s-f)} q^{(u)}(f), \tag{A15}$$

where

$$q^{(u)}(f) = \sum_n \Psi_{\mathrm{B},n}^{(u)} q_n(f) \tag{A16}$$

with

$$q_n(f) = \sum_u \mathrm{e}^{-\epsilon_{\mathrm{A}}^{(u)} f} \Psi_{\mathrm{A},0}^{(u)} \Psi_{\mathrm{A},n}^{(u)}. \tag{A17}$$

Then

$$q^{(u)}(f) = \sum_{u_1} \mathrm{e}^{-\epsilon_{\mathrm{A}}^{(u_1)} f} L_{\mathrm{AB}}^{(u_1,u)} \Psi_{\mathrm{A},0}^{(u_1)}. \tag{A18}$$

Here, we define

$$L_{\mathrm{AB}}^{(u_1,u_2)} = \sum_n \Psi_{\mathrm{A},n}^{(u_1)} \Psi_{\mathrm{B},n}^{(u_2)}. \tag{A19}$$

Thus, for $s \geq f$, we have

$$q_n(s) = \sum_{u_1} \sum_{u_2} \mathrm{e}^{-\epsilon_{\mathrm{A}}^{(u_1)} f} \mathrm{e}^{-\epsilon_{\mathrm{B}}^{(u_2)} (s-f)} L_{\mathrm{AB}}^{(u_1,u_2)} \Psi_{\mathrm{A},0}^{(u_1)} \Psi_{\mathrm{B},n}^{(u_2)}. \tag{A20}$$

The propagator $q_n^{\dagger}(s)$ can be obtained by the analogous treatment for $q_n(s)$. The only difference is to start with $s > f$ and take the initial condition $q^{\dagger}(\mathbf{r}, 1) = 1$. Here we will give the result directly. For $s > f$,

$$q_n^{\dagger}(s) = \sum_{u} \mathrm{e}^{-\epsilon_{\mathrm{B}}^{(u)} (1-s)} \Psi_{\mathrm{B},0}^{(u)} \Psi_{\mathrm{B},n}^{(u)}. \tag{A21}$$

For $s \leq f$,

$$q_n^{\dagger}(s) = \sum_{u_1} \sum_{u_2} \mathrm{e}^{-\epsilon_{\mathrm{A}}^{(u_1)} (f-s)} \mathrm{e}^{-\epsilon_{\mathrm{B}}^{(u_2)} (1-f)} L_{\mathrm{AB}}^{(u_1,u_2)} \Psi_{\mathrm{A},n}^{(u_1)} \Psi_{\mathrm{B},0}^{(u_2)}. \tag{A22}$$

Here, the modified diffusion equations of the end-integrated propagators, $q_n(s)$ and $q_n^{\dagger}(s)$, have been solved by expressing them in terms of the eigenvalues and eigenfunctions of $H_{nl}(s)$.

References

[1] Bates FS, Fredrickson GH. Phys Today 1999;52:32.
[2] Hamley IW. The physics of block copolymers. Oxford: Oxford University Press; 1998.
[3] Matsen MW. J Phys Condens Matter 2002;14:R21.
[4] Matsen MW, Schick M. Phys Rev Lett 1994;72:2660.
[5] Ohta T, Kawasaki K. Macromolecules 1986;19:2621.
[6] Leibler L. Macromolecules 1980;13:1602.
[7] Fredrickson GH, Helfand E. J Chem Phys 1987;87:697.
[8] Turner MS. Phys Rev Lett 1992;69:1788.
[9] Walton DG, Kellogg GJ, Mayes AM, Lambooy P, Russell TP. Macromolecules 1994;27:6225.
[10] Turner MS, Johner A, Joanny JF. J Phys I (Paris) 1995;5:917.
[11] Kikuchi M, Binder K. J Chem Phys 1994;101:3367.
[12] Binder K. Adv Polym Sci 1999;138:1.
[13] Sommer JU, Hoffmann A, Blumen A. J Chem Phys 1999;111:3728.
[14] Tang WH. Macromolecules 2000;33:1370.
[15] Fasolka MJ, Banerjee P, Mayes AM, Pickett G, Balazs AC. Macromolecules 2000;33:5702.
[16] Potemkin II. Macromolecules 2004;37:3505.
[17] Knoll A, Horvat A, Lyakhova KS, Krausch G, Sevink GJA, Zvelindovsky AV, et al. Phys Rev Lett 2002;89:035501.
[18] Kellogg GJ, Walton DG, Mayes AM, Lambooy P, Russell TP, Gallagher PD, et al. Phys Rev Lett 1996;76:2503.
[19] Matsen MW. J Chem Phys 1997;106:7781.
[20] Morkved TL, Jaeger HM. Europhys Lett 1997;40:643.
[21] Pickett GT, Balazs AC. Macromolecules 1997;30:3097.
[22] Geisinger T, Müller M, Binder K. J Chem Phys 1999;111:5241.
[23] Huinink HP, Brokken-Zijp JCM, Van Dijk MA, Sevink GJA. J Chem Phys 2000;112:2452.
[24] Yin Y, Sun P, Chen T, Li B, Jin Q, Ding D, et al. ChemPhysChem 2004;5:540.
[25] He XH, Song M, Liang HJ, Pan CY. J Chem Phys 2001;114:10510.
[26] Sevink GJA, Zvelindovsky AV, Fraaije JGEM, Huinink HP. J Chem Phys 2001;115:8226.
[27] Xiang H, Shin K, Kim T, Moon SI, McCarthy TJ, Russell TP. Macromolecules 2004;37:5660.
[28] Li W, Wickham RA, Garbary RA. Macromolecules 2006;39:806.
[29] Yu B, Sun P, Chen T, Jin Q, Ding D, Li B, et al. Phys Rev Lett 2006;69:138306.
[30] Tasinkevych M, Ciach A. J Chem Phys 2001;115:8705.
[31] Babin V, Ciach A, Tasinkevych M. J Chem Phys 2001;114:9585.
[32] Babin V, Ciach A. J Chem Phys 2001;115:2786.
[33] Ciach A, Babin V, Tasinkevych M. Colloids Surf A 2002;208:51.
[34] Ciach A. Prog Colloid Polym Sci 2004;129:40.
[35] Fredrickson GH. Macromolecules 1987;20:2535.
[36] Tang H, Freed KF. J Chem Phys 1992;97:4496.
[37] Kielhorn L, Muthukumar M. J Chem Phys 1999;111:2259.
[38] Seok C, Freed KF, Szleifer I. J Chem Phys 2000;112:6443.
[39] Seok C, Freed KF, Szleifer I. J Chem Phys 2000;112:6452.
[40] Seok C, Freed KF, Szleifer I. J Chem Phys 2004;120:7174.
[41] Tan HG, Yan DD, Shi AC. Macromolecules 2004;37:9646.
[42] Tsori Y, Andelman D. Europhys Lett 2001;53:722.
[43] Tsori Y, Andelman D. Eur Phys J E 2001;5:605.
[44] Tsori Y, Andelman D. J Chem Phys 2001;115:1970.
[45] Tsori Y, Andelman D. Macromolecules 2001;34:2719.
[46] Tsori Y, Andelman D. Interface Sci 2003;11:259.
[47] Yang YZ, Qiu F, Zhang HD, Yang YL. Polymer 2006;47:2205.
[48] Huang Y, Liu XB, Zhang HL, Zhu DS, Sun YJ, Yan SK, et al. Polymer 2006;47:1217.
[49] Miao B, Yan DD, Han CC, Shi AC. J Chem Phys 2006;124:144902.
[50] Shi AC, Noolandi J, Desai RC. Macromolecules 1996;29:6487.
[51] Laradji M, Shi AC, Noolandi J, Desai RC. Macromolecules 1997;30:3242.
[52] Laradji M, Shi AC, Desai RC, Noolandi J. Phys Rev Lett 1997;78:2577.
[53] Shi AC. J Phys Condens Matter 1999;11:10183.
[54] Brazovskii SA. Sov Phys JETP 1975;41:85.
[55] Kats EI, Lebedev VV, Muratov AR. Phys Rep 1993;228:1.