

## A Self-consistent Field Study on the Adsorption of Symmetrical Triblock Copolymers between Two Parallel Planes<sup>\*</sup>

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**Abstract** Using the continuum self-consistent field theory (SCFT), the adsorption of flexible symmetrical triblock polymers onto the surfaces of two identical parallel planes immersed in a neutral solution was studied. The effects of various parameters, such as the interface adhesive energy, the polymer composition and the bulk polymer concentration, on the conformations and total adsorption amount of polymers were explored. It was found that the dependence of the amount of bridges on the interface adhesion and that of the amount of tails on the length of adhesive blocks were both non-monotonous. The amounts of the four chain conformations scaled nearly linearly to the copolymer bulk concentration. The non-equivalence of the dependence of the adsorbed structure behaviors on the interface affinity and the length of sticky blocks was revealed as well.

**Keywords:** SCFT; Symmetrical triblock adsorption; Conformation.

### INTRODUCTION

Polymer adsorption is a common phenomenon<sup>[1]</sup>, which is essential in many industrial and biological processes, such as adhesion, trilogy, and fluid and mechanical property modifications. The adsorbed polymers may present various microscopic conformations<sup>[2]</sup> near the interfaces, such as loop, tail and bridge, depending on the interaction with objectives confining them.

When polymers adsorb onto surfaces, the adsorbed polymer layers can provide either repulsion or attraction between two surfaces<sup>[3, 4]</sup>. When a linear chain has only one adhesive end, it usually gives rise to a repulsion between two surfaces due to the steric hindrance, for example, polymer brushes in good solvents. When the polymer chains have two or more adsorptive functional groups, there may be several possibilities: the chains can form either loops or tails which give a repulsive contribution to the interaction between two surfaces, or bridges which give an attraction.

Polymer adsorption at interfaces has been widely studied theoretically. Pioneering studies by de Gennes<sup>[5, 6]</sup>, Fler<sup>[7–9]</sup>, and Scheutjens<sup>[10–12]</sup> have demonstrated two different scenarios of adsorption. One is called reversible equilibrium adsorption, in which the polymer layer maintains a strict thermodynamic equilibrium with the bulk solution by equaling their chemical potentials, always presenting an attractive interaction. The other one, named as irreversible restricted adsorption, corresponding to the case that the amount of adsorbed polymers is constant when the surfaces confined them are brought together, can suggest either attractive or repulsive interaction, depending on whether the polymer adsorption is saturated. Using an approach derived by Johner and Joanny<sup>[13]</sup>,

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Bjorling<sup>[14, 15]</sup> *et al.* have investigated an end-absorbing model both in symmetric and asymmetric cases. They found a simple scaling relationship for the height of loop. The attraction induced by bridge in the symmetric case is much weaker than that in the asymmetric case. Witten<sup>[16, 17]</sup> and co-workers found that the number of bridges is proportional to the mean-square end-to-end distance of the polymer. They also argued that the attraction is due to the penetration of telechelic polymers into the opposite adsorbed layer when the two objectives are compressed. Russell<sup>[18, 19]</sup> found an attractive interaction for telechelic chains between two flat plates analytically and numerically predicted an  $O(k_B T)$  attraction yielded between two curved surfaces, occurring at a separation less than the height of a single grafted layer. Misra and Mattice<sup>[20–23]</sup> have performed Monte Carlo (MC) simulations to study the adsorption of telechelic polymers between two solid parallel flat plates. They carefully calculated the population of various chain conformations, and found that the fraction of bridge can be expressed as a function of the dimensionless penetration depth. Experimentally, Qiu<sup>[24]</sup> and Cosgrove<sup>[25]</sup> investigated the weak adsorption of homopolymers between two planar or curved surfaces and they found that with compressing the two surfaces the system presenting repulsion shows no interpenetration between adsorbed layers.

The results mentioned above mainly focus on the interaction between two surfaces with the adsorption of neutral homopolymers in bad solvents or end-functional telechelic polymers. More recently, people have paid close attention to the studies of the adsorption of triblock copolymers. Wijmans<sup>[26]</sup> found that the polymer adsorption behaviors explicitly depend on both the adsorption energy and the length of adsorbing block, not their products. Peng and Hu<sup>[27, 28]</sup> used Monte Carlo to model the bridge effect of asymmetrical triblock copolymers for which the two adsorbed surfaces or blocks are not identical, where it was found that the bridge fraction can be expressed as a function of the relative distance between two surfaces for the symmetrical case. Using a symmetry index, the bridge fractions of both the symmetrical case and asymmetrical one can be related by an algebraic relation. Experimentally, Dai<sup>[29, 30]</sup> reported direct force measurements on the interactions of end-adsorbed PS-PEO diblock and PEO-PS-PEO triblock copolymers onto bare mica surfaces in toluene. They found that the force profiles evolve from attraction to repulsion after successive compression-decompression cycles.

Comparing with homopolymers or diblock copolymers, the adsorption of triblock copolymers seems not well documented. There are only a few MC works, which mainly focused on the case of athermal solvents, keeping the number of polymer chains between two surfaces unchanged, while the interaction in the system was not addressed. This might be due to the tremendous cost of calculation or a lack of effective and convenient algorithm to evaluate the free energy of the system by the simulation method. The SCFT<sup>[31]</sup>, which is a kind of statistical field method, has the advantage of less calculation and more exact formalism, and it is easy to figure out the conformations of adsorbed polymers. Thus, in the present paper, we seek a more quantitative description of the conformation population of triblock copolymers confined between two parallel planes by using a continuous SCFT.

This paper is organized as follows. In section 2, we outline the formalism of SCFT for a polymer solution in the grand canonical ensemble, and then describe the method used to calculate the properties of structure in the system. In sections 3, we present the results of the conformations, including their dependence on the various system parameters, such as the distance between the two parallel plate surfaces, the interaction energy between the monomers and the surfaces, the chain composite ratio and the bulk concentration of the macromolecules. In the final section, we conclude with a summary of our results.

## SCFT FORMALISM

In this section, we detail the model and the SCFT framework used to study the equilibrium conformations of the system. In our theory, we consider a system with volume  $V$ , confined between two parallel planes. There are  $n_C$  ABA triblock copolymers with total length  $N_C$  immersed in neutral solvents S of number  $n_S$ . For simplicity, we only consider the most symmetrical structure that both A blocks of each side have the same monomer number  $N_A$ . The length of B block is  $N_B$ . A translational invariance along lateral direction is assumed, so the system under study becomes one dimensional in the  $x$  axis whose length is  $L$ , thus reducing the computational cost.

The first step of field study is to figure out the partition function of a thermodynamical system, yielding the free energy written in term of functional form. However, it is usually forbidden to calculate the physical property analytically in this form, the most common approach in polymer community is to execute mean-field approximation. This is fulfilled by a minimization of the free energy functional<sup>[31, 32]</sup>, which, in dimensionless form, is given by

$$\begin{aligned} \frac{F}{\rho_0 k_B T} = & \int dx \{ \chi_{AB} \phi_A(x) \phi_B(x) + \chi_{AS} \phi_A(x) \phi_S(x) + \chi_{BS} \phi_B(x) \phi_S(x) \} - \int dx \{ \phi_A(x) \omega_A(x) \\ & + \phi_B(x) \omega_B(x) + \phi_S(x) \omega_S(x) \} - e^{\Delta\mu_C} L Q_C - e^{\Delta\mu_S} L Q_S + \int dx \phi_A(x) U_A(x) \end{aligned} \quad (1)$$

where  $\phi_i$  and  $\omega_i$  are the dimensionless volume fractions and their conjugated auxiliary fields of species  $i$ , with  $i = A, B$  and  $S$ . For sake of brevity, through the paper, all the equations have been nondimensionalized.  $U(x)$  is the short-range attraction between A blocks and the two surfaces with magnitude  $U_0$  and range  $2b$ .  $\chi_{jk}$  ( $j, k = A, B, S$  and  $j \neq k$ ) denote the Flory-Huggins interaction parameters between monomers of different blocks and that with solvent molecules,  $Q_C$  and  $Q_S$  denote the partition functions for a single triblock polymer chain and the solvent molecules, respectively.  $Q_S = \frac{1}{L} \int_0^L e^{-\alpha_S(x)} dx$  and  $Q_C = \frac{1}{L} \int_0^L q_A^c(x, N_A) dx$ , where the properties of  $q_A^c(x, N_A)$  will be discussed subsequently,  $\Delta\mu_C$  and  $\Delta\mu_S$  are the chemical potentials of the macromolecules and the solvents in the bulk buffer.  $k_B T$  is the thermal energy, chosen as reduced unit of energy. It's reasonable to assume that the sizes of the monomers of the polymers  $\rho_0 = b^{-3}$  and that of solvent molecules are equal, with  $b$  the Kuhn length of the triblock copolymers, which is chosen as the reduced unit of length.

Taking the saddle approximation,  $\partial F / \partial \omega_i(x) = 0$ ,  $\partial F / \partial \phi_i(x) = 0$ , we can obtain the self-consistent field equations:

$$\phi_A(x) = 2e^{\Delta\mu_C} \int_0^{N_A} q_A^c(x, t) q_A(x, N_A - t) dt \quad (2)$$

$$\phi_B(x) = e^{\Delta\mu_C} \int_0^{N_B} q_B(x, t) q_B^c(x, N_B - t) dt \quad (3)$$

$$\phi_S(x) = e^{\Delta\mu_S} e^{-\alpha_S(x)} \quad (4)$$

$$\omega_A(x) = \chi_{AB} \phi_B(x) + \chi_{AS} \phi_S(x) + U(x) + \eta(x) \quad (5)$$

$$\omega_B(x) = \chi_{AB} \phi_A(x) + \chi_{BS} \phi_S(x) + \eta(x) \quad (6)$$

$$\omega_S(x) = \chi_{AS} \phi_A(x) + \chi_{BS} \phi_B(x) + \eta(x) \quad (7)$$

$$\phi_A(x) + \phi_B(x) + \phi_S(x) = 1 \quad (8)$$

In the equations mentioned above,  $q_j(x, t)$  with  $j = A$  and  $B$  are the propagators, denoting the statistical weight of a subchain located at  $x$  in  $t$  steps, and  $q_j^c(x, t)$  are their complementary propagators. They all satisfy the following modified diffusion equations, respectively, applied by the Dirichlet boundary conditions for the two adsorbed surfaces. However, because of the different chemical classes, they experience different fields, if  $j = A$ ,  $\omega_j = \omega_A$ , otherwise  $\omega_j = \omega_B$ :

$$\frac{\partial q_j(x, t)}{\partial t} = \frac{1}{6} \nabla^2 q_j(x, t) - \omega_j(x) q_j(x, t) \quad (9)$$

$$\frac{\partial q_j^c(x, t)}{\partial t} = \frac{1}{6} \nabla^2 q_j^c(x, t) - \omega_j(x) q_j^c(x, t) \quad (10)$$

As mentioned previously, for a specific polymer adsorption condition, the polymers can be further classified into being either adsorbed onto the surfaces or free in solution. The unique advantage of continuous SCFT is that different conformations such as free, tail, loop and bridge can easily be calculated statistically by defining proper propagators. The detailed steps are outlined as follows<sup>[33, 34]</sup>. Because of the affinity of the surfaces with monomer A of triblock copolymers and the special boundary condition, there are only two peaks named  $P_1$  and  $P_2$  which located near the surfaces for the volume fraction of the A block  $\phi_A(x)$ , respectively, and there must be one point along the volume profile of  $\phi_A(x)$  called  $P$  whose value is the lowest between  $P_1$  and  $P_2$ . Because of symmetry assumed above, we can always obtain the relation  $\phi_A(P_1) = \phi_A(P_2)$ . The final goal by defining these specific points is to find the points  $C_1$  and  $C_2$ , that  $\phi_A(C_1) = \phi_A(C_2) = \phi_A(P) + \frac{1}{5}(\phi_A(P_1) - \phi_A(P))$ .

To calculate the structure of the adsorbed polymer chains, the region between points  $C_1$  and  $C_2$  is defined as the adsorbed layer. The regimes between the left surface and point  $C_1$  and the right surface and point  $C_2$  are denoted as the left boundary layer and the right boundary layer, respectively. To examine the different conformations of polymer chains appearing in the system, we should define the following propagators.  $q_F(x, t)$  is the propagator corresponding to free chains in the adsorbed layer with none of their segments falling into the two boundary layers.  $q_L(x, t)$  denotes the propagator of polymer chains with none of their composite falling into the right boundary layer, and we can define  $q_R(x, t)$  have the corresponding meaning in the same way.  $q_L^a(x, t) = q_L(x, t) - q_F(x, t)$  and  $q_R^a(x, t) = q_R(x, t) - q_F(x, t)$  denote the propagators of polymer chains with any of their segments falling into the left boundary layer and the right boundary layer, respectively. All the propagators defined above satisfy the same modified diffusion equations as  $q_j(x, t)$  and  $q_j^c(x, t)$  do used in calculating the volume fractions of triblock copolymer, but with different boundary conditions and auxiliary chemical fields, depending on their species. Take the  $q_F(x, t)$  for example, it is demonstrated as follows:

$$\frac{\partial q_F(x, t)}{\partial t} = \frac{1}{6} \nabla^2 q_F(x, t) - \omega_j(x) q_F(x, t)$$

with

$$\omega_j(x) = \begin{cases} \omega_A(x), & \text{if } 0 \leq t \leq N_A \\ \omega_B(x), & \text{if } N_A < t < N_A + N_B \\ \omega_A(x), & \text{if } N_A + N_B \leq t \leq 2N_A + N_B \end{cases} \quad (11)$$

$q_F(x, t)$  vanishes on the surfaces of the two boundary layers. However,  $q_L(x, t)$  vanishes on the surface of the left plane and the boundary layer of the right plane, and  $q_R(x, t)$  vanishes on the surface of the right plane and the boundary layer of the left plane.

Using the propagators of the adsorbed chains and free chains, the volume fractions contributed from the different chain conformations can be obtained:

$$\phi^F(x) = e^{\Delta\mu_C} \int_0^{N_C} q_F(x, t) q_F(x, N_C - t) dt \quad (12)$$

$$\phi_L^L(x) = e^{\Delta\mu_C} \int_0^{N_C} q_L^a(x, t) q_L^a(x, N_C - t) dt \quad (13)$$

$$\phi_L^R(x) = e^{\Delta\mu_C} \int_0^{N_C} q_R^a(x, t) q_R^a(x, N_C - t) dt \quad (14)$$

$$\phi_L^T(x) = e^{\Delta\mu_C} \int_0^{N_C} q_L^a(x, t) q_F(x, N_C - t) dt \quad (15)$$

$$\phi_R^T(x) = e^{\Delta\mu_C} \int_0^{N_C} q_R^a(x, t) q_F(x, N_C - t) dt \quad (16)$$

$$\phi^B(x) = \phi_A(x) + \phi_B(x) - \phi^F(x) - \phi^L(x) - \phi^T(x) \quad (17)$$

where  $N_C = 2N_A + N_B$  is the total number of monomers per chain,  $\phi^F(x)$  denotes the density profile of the free chains,  $\phi_L^L(x)$  and  $\phi_L^T(x)$  are the loop and tail volume densities near the left plane, respectively.  $\phi_R^L(x)$  and  $\phi_R^T(x)$  are the loop and tail volume densities near the right plane, respectively,  $\phi^B(x)$  is the volume fraction of bridge conformation.

Other way to quantify the various chain conformations is to define the amount for each conformation, we can introduce the parameter  $\Sigma^B = \int_0^L \phi^B(x) dx$ , which is the total amount of triblock copolymers distributed as bridge conformation. Analogously, we can define the similar quantities for other conformations, which are denoted as  $\Sigma^F$ ,  $\Sigma^L$  and  $\Sigma^T$ , respectively.

In this numerical work, the modified diffusion equations are solved by Crank-Nelson method. All the quadratures are obtained by trapezoid method, and a simple iteration method is used to solve the nonlinear set of equations. The self-consistency of the solutions is considered as to be obtained if the largest error value of iterations is smaller than a prescribed convergence parameter (e.g.  $10^{-6}$ ).

## RESULTS AND DISCUSSION

In this section, we present the numerical results for the dependence of various conformations between two identical parallel plates on different factors, such as the separation between the two parallel planes, the adhesive energy of the surfaces, the component of triblock copolymers and the bulk concentration of copolymer. The total length of the triblock copolymers is set as  $N_C = 2N_A + N_B = 100$ . In order to prevent the complex from phase separation, the Flory-Huggins interaction parameters are chosen as  $\chi_{AB} = 0$ ,  $\chi_{AS} = 0$  and  $\chi_{BS} = 0$ . In another words, the only difference between the two blocks is their affinities with the surfaces.

### *Dependence of the Chain Conformations on the Separation between the Two Parallel Planes*

Firstly, we investigate the effect of distance between two planes. The monomer number of A block is fixed as  $N_A = 10$ , and the adsorption energy of both planes is chosen as  $U_0 = -0.5$  with range of  $2b$ .

Figures 1(a), 1(b) and 1(c) show the polymer volume fractions of bridge, loop, and tail, respectively. These intuitive results show that, the space between the two planes should be separated into two regions: the region near the surfaces and the region far away from the surfaces. When we compress the two surfaces, the loop fraction  $\phi^L(x)$  and the tail fraction  $\phi^T(x)$  decrease in the former region. While, in the latter region,  $\phi^L(x)$  increases, and  $\phi^T(x)$  first increases and then decreases. The bridge fraction  $\phi^B(x)$  always increases rapidly in space. These results are consistent with the findings of Misra<sup>[20–23]</sup> *et al.* and Peng<sup>[27, 28]</sup> *et al.* Furthermore, we found that the volume fraction of the free conformation  $\phi^F(x)$  decreases in space (Fig. 1d). Differently from MC simulations which keep the number of polymers in the system constant, the number of triblock copolymers in our study is not fixed, hence, when two planes carrying adsorbed polymer layers are brought together, the polymers are completely free to adjust their conformations. The polymers may leave the gap between two planes to maintain the chemical equilibrium with bulk solution or transform from free, loop or tail to bridge (and vice versa) to lower the total free energy of the system. Therefore, according to the classification of de Gennes<sup>[5, 6]</sup> and Fleer<sup>[7, 8, 10, 11]</sup>, what we are investigating is a completely reversible equilibrium situation.

The polymer structural characteristics in an adsorption system are mainly determined by the interplay between two competing factors<sup>[35, 36]</sup>: (a) the reduction in entropy arising from the confinement of polymers between the surfaces and (b) the energy gained due to the adsorption of polymers. When the volume of polymer solution is reduced, the former factor leads to depletion of polymer into buffer while the latter one prefers to hold thicker adsorption layers. In the following subsections, we will continue to consider the results highlighting the influences of surface adsorption energy, the component of copolymers and bulk polymer concentration upon the conformation characteristics of polymers, *i.e.* the distribution of polymers among free, loop, tail and bridge.

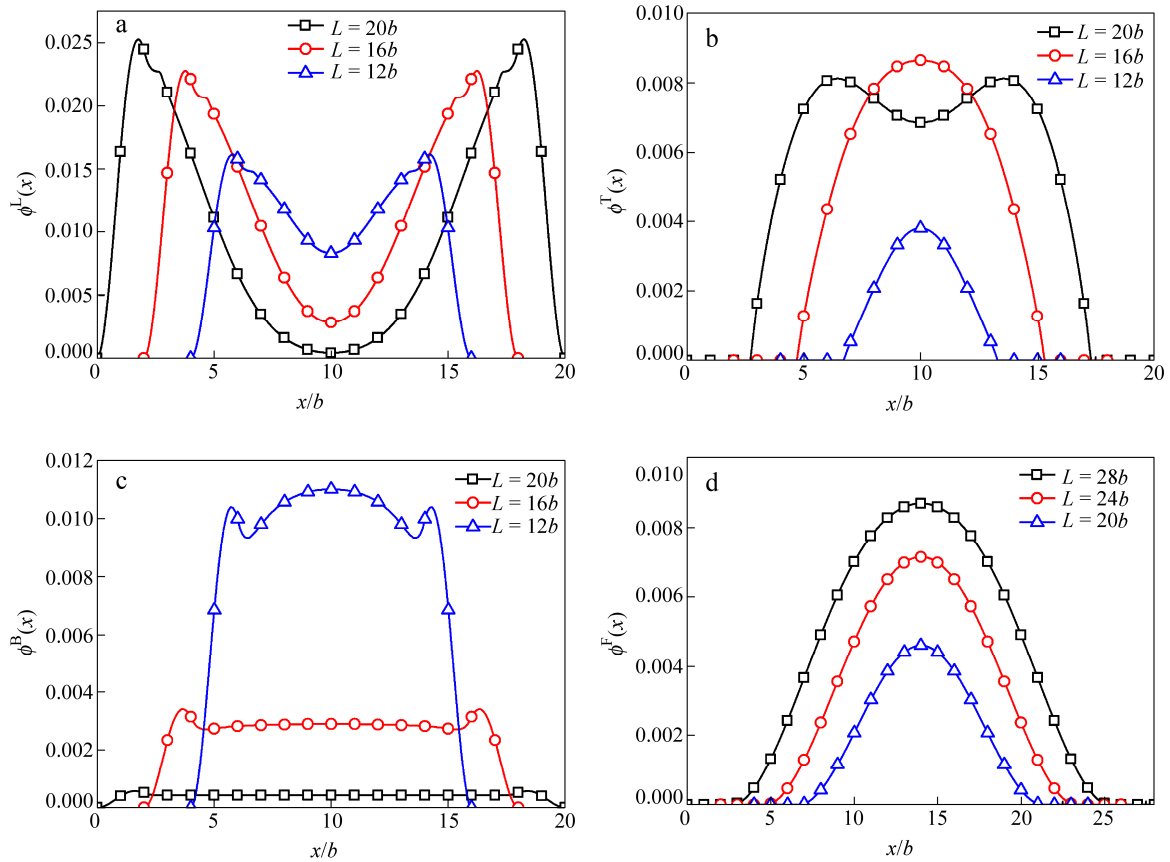


**Fig. 1** The density profiles of (a) loop, (b) tail, (c) bridge and (d) free as function of the separation between the two parallel planes for  $N_A = 10$ ,  $U_0 = -0.5$  and  $\phi_C^0 = 0.01$

### Dependence of the Chain Conformations on the Adsorption Energy

Because of the existence of the adhesive interfaces, the behavior of triblock copolymer can be greatly different from other systems, such as depletion flocculation and homopolymer brushes. In this subsection, the bulk concentration is still fixed as  $\phi_C^0 = 0.01$  and the length of A block is chosen as  $N_A = 10$ .

Figure 2(a) depicts the amounts of free, loop, tail and bridge, respectively. As well known, polymer solution is an entropy sensitive system, the amount of free chains decreases linearly when the two planes are brought together. Differently, it clearly shows that the amounts of loop and tail decrease only at rather small separations between the two parallel planes, just before they finally disappear. That is because at larger distances, polymers adsorbed onto different planes cannot feel each other, only when they begin to overlap, they transform into bridge conformation with small amount of free chains. It also suggests that the amount of tail always exhausts more quickly than that of loop. At a separation  $L$  less than  $20b$ , the conformations for triblock copolymers become dominated by bridge. As can be seen, the amount of bridge starts to reduce as well at  $L = 8b$  after passing a maximum. That is because in so small dimension, the available volume for each polymer is so limited that the strong steric interaction and entropy deriving force dominate over the attraction between the chains and the two planes, more polymers are squeezed out into buffer solution even two ends of polymer chains are attached onto the opposite planes.

It is expected that the locations (separations between planes) where the free chains disappear, the loop and tail start to decrease and finally vanish, and the bridge begins to emerge, are mainly governed by the affinity of interfaces with the adsorbed blocks. This argument is immediately proven in Figs. 2(b), 2(c) and 2(d).

Furthermore, the general trend is that the stronger the interface adhesion, the larger the amounts of adsorption favored conformations, such as loop and bridge.

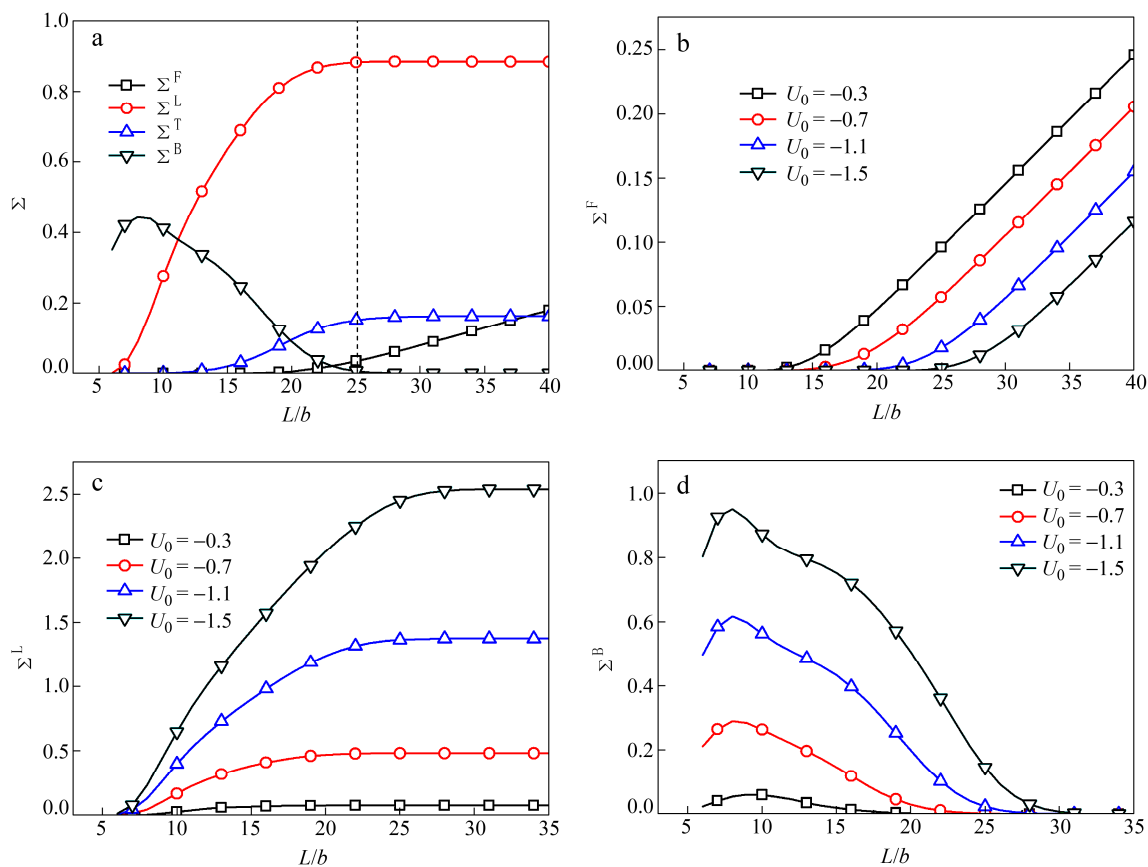


**Fig. 2** (a) The amounts of all four conformations as function of the separation between the two parallel planes for  $N_A = 10$ ,  $U_0 = -0.5$  and  $\phi_c^0 = 0.01$ ; The amounts of (b) free, (c) loop, (d) bridge as function of the separation between the two parallel planes for four different surface affinities  $U_0 = -0.3$ ,  $U_0 = -0.7$ ,  $U_0 = -1.1$  and  $U_0 = -1.5$  with other parameters set as those in 2(a)

For tail, although some of the above characteristics are still hold true, its detailed variations are more complex, as can be seen in Fig. 3(a) and 3(b). At  $L = 35b$  in our parameter conditions, the amount of tail increases with interface adhesion because of the weak entropy effect. However, at medium  $L = 25b$  and small  $L = 15b$  separations, the entropy confinement becomes more important, it first increases then transforms into loop and bridge to acquire more adsorption energy as well as to minimize the total free energy of system.

#### Dependence of the Chain Conformations on Chain Component

Significant difference in adsorption behaviors between triblock copolymers and homopolymers can be expected, because the adsorption behaviors of polymers highly depend on their component. We fix the interface affinity  $U_0 = -0.9$  and the bulk concentration of copolymer  $\phi_c^0 = 0.01$ .

In Fig. 4(a), we present the variation of the amount of bridge for four different lengths of A blocks. It can be noted that the effect of the separation on general trend of the variation of bridge is the same as those discussed in previous subsections. However, the dependence of amount of bridge on the length of adhesive block shows more complex behavior, as can be seen in Fig. 4(b). It first increases with the length of A block then decreases after passing a maximum. This interesting phenomenon can be explained as follows. When A block is short, the sticky energy obtained by each chain upon adsorption is weak, thus the copolymers are more likely to take

conformations other than bridge. When A block is longer, the minus enthalpy energy becomes stronger, thus more chains prefer to present as bridge conformation. However, when A block is even longer, the adhesion free energy obtained by the two long end blocks dominates over the entropic effect, thus the chains prefer to adsorb on the same surface to form loops, therefore, the amount of bridge reduces again. The results in this and previous subsections illustrate that the conformations of triblock copolymer adsorbed onto planes are determined by both the interface energy and the chain component. When the total adsorption energy obtained by every chain is weak, most chains are more likely to be free, therefore the amounts of tail, loop and bridge are very small, and at the same time, the location where the transformation among adsorbed structures takes place is in shorter distance. However, when both factors are strong, the general trends will change inversely.

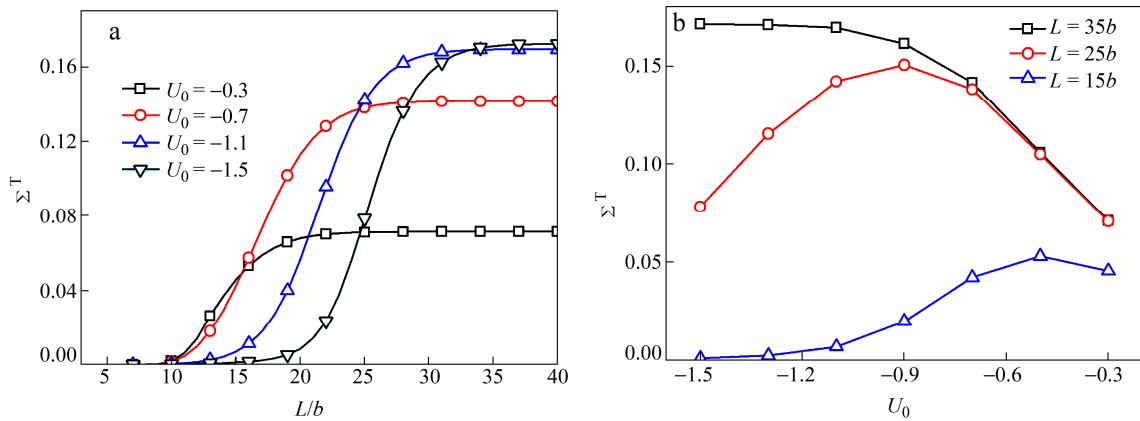


**Fig. 3** (a) The amount of tail as function of the separation between the two parallel planes for four different surface affinities  $U_0 = -0.3$ ,  $U_0 = -0.7$ ,  $U_0 = -1.1$  and  $U_0 = -1.5$  with other parameters set as  $N_A = 10$  and  $\phi_c^0 = 0.01$ ; (b) The amount of tail as function of the surface affinities at three different separations between the two parallel planes  $L = 15b$ ,  $L = 25b$  and  $L = 35b$  with other parameters set as those in 3(a)

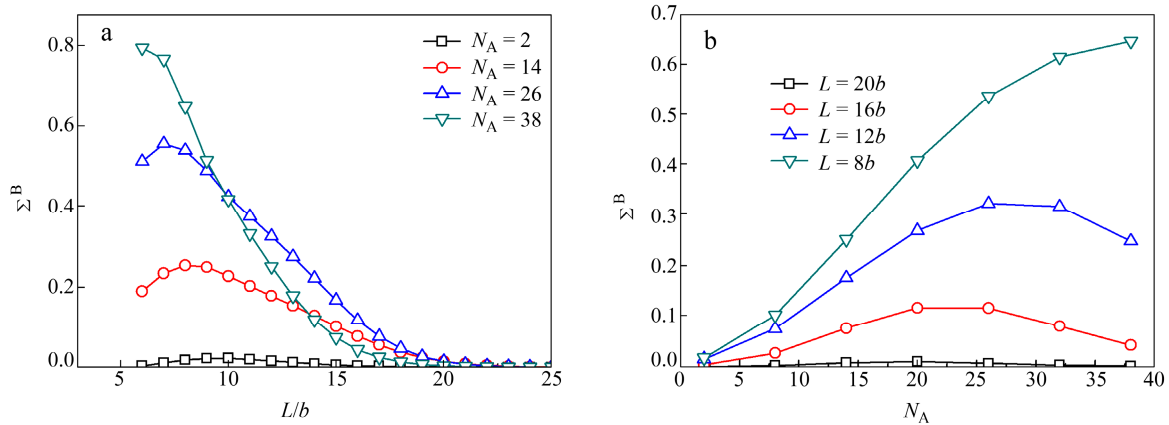


**Fig. 4** (a) The amount of bridge as function of the separation between the two parallel planes for four different length of adhesive block A  $N_A = 2$ ,  $N_A = 14$  and  $N_A = 26$ , other parameters are set as  $U_0 = -0.9$  and  $\phi_c^0 = 0.01$ ; (b) The amount of bridge as function of lengths of adhesive block A at four different separations between the two parallel planes  $L = 8b$ ,  $L = 12b$ ,  $L = 16b$  and  $L = 20b$  with other parameters set as those in 4(a)

#### Dependence of the Chain Conformations on the Bulk Concentration

In this subsection, we examine the influence of the bulk concentration on the chain conformations. On one hand, it can further complete our insights of the adsorption behaviors of triblock copolymers, on the other hand, it will provides more robust evidences to demonstrate the statements made previously.

In Figs. 5(a), 5(b), 5(c) and 5(d), we have found that the dependence of each conformation on the separation between the two surfaces is similar. It shows that with increasing the bulk copolymer concentration, the amounts of all the conformations increase and the trends become more rapid. Because at low concentrations, the correlation between different chains is weak, and in higher concentrations, the intermolecular interaction becomes stronger, the locations where exchange of conformations happens are at larger separations.

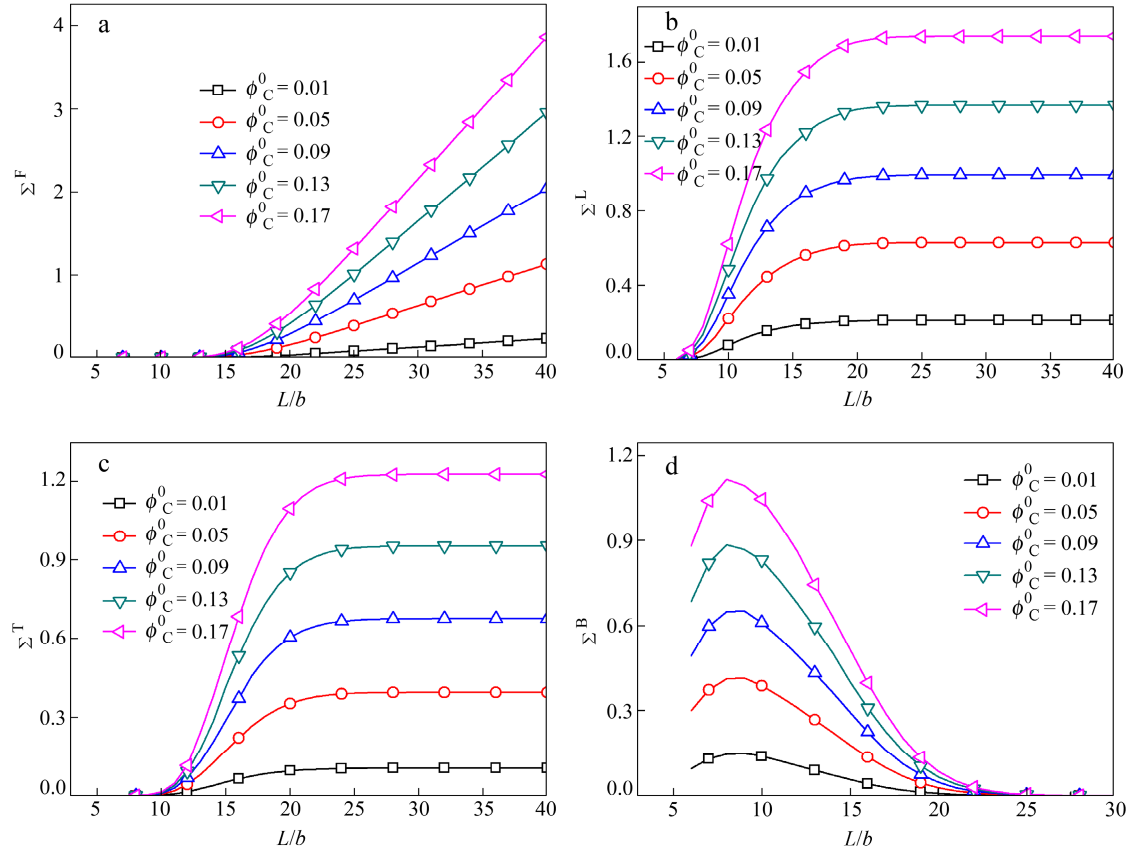


**Fig. 5** The amount of (a) free, (b) loop, (c) tail and (d) bridge as function of the separation between the two parallel planes for five different copolymer bulk concentrations  $\phi_C^0 = 0.01$ ,  $\phi_C^0 = 0.03$ ,  $\phi_C^0 = 0.05$ ,  $\phi_C^0 = 0.07$  and  $\phi_C^0 = 0.09$  (other parameters are set as  $N_A = 10$  and  $U_0 = -0.9$ .)

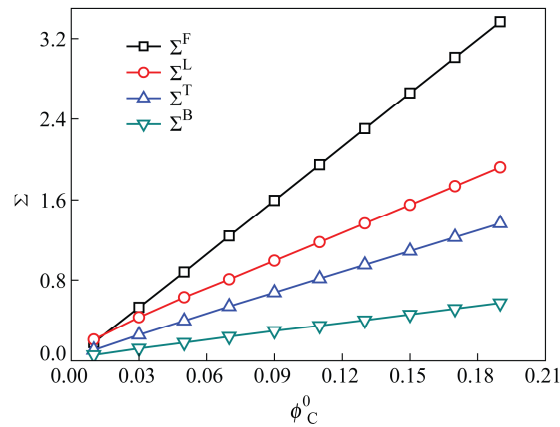


**Fig. 6** The amounts of all four conformations as function of the copolymer bulk concentrations for  $N_A = 10$  and  $U_0 = -0.9$

Furthermore, Fig. 6 shows the dependence of the amount of bridge at  $L = 15b$  and the amounts of other conformations at  $L = 35b$  on bulk concentration. It is found that, with the increase in the copolymer bulk concentration, the amounts of all conformations increase almost linearly with different slopes, respectively.

## SUMMARY

In this work, the continuum SCFT for flexible polymers is applied to study the adsorption of triblock copolymers between two parallel planes. An effective numerical method is generalized to consider the various conformations for the copolymers.

We mainly investigate the dependence of conformations, such as free, loop, tail and bridge, on the separation between the two planes, the surface affinity for the adhesive blocks, the chain component and the copolymer bulk concentration. It is found that with decreasing separation, the amounts of free, loop and tail all decrease and that of bridge increases. However, the locations, where the amount of free disappeared, the amounts of loop and tail began to decrease and finally vanish, and the amount of bridge began to increase, were greatly parameter dependent. Specifically, the stronger the surface attraction potential, the larger the distance where the transformation of conformations happens. Further, the amount of tail presents a non-monotonous dependence on the surface attraction, and the amount of bridge showed a non-monotonous dependence on the length of the adhesive blocks as well. At last, it was found that with increasing the bulk concentration of polymers, the amounts of all the four conformations increased nearly linearly.

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