

Structure and Interaction of Adsorbing Symmetrical Triblock Polyampholyte Solution between Two Planes*

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Abstract In this paper, the continuum self-consistent field theory (SCFT) is applied to study the structure and the interaction of the adsorption of symmetrical ABA polyampholytes (PAs) between two neutral planes. It is found that the amounts of all the conformations decrease with the increase of the charge fraction of polymer chain, and increase with the increase of the bulk salt concentration and become saturated at high bulk salt concentration. The effective interaction between the two planes presented a long-range repulsion. Splitting it into various components and relating with the dependence of the variations of the conformations on environment parameters, we try to find the origin of the total long-range interaction between the two planes.

Keywords: Polyampholyte adsorption; Conformations; Interaction; SCFT.

INTRODUCTION

Polyelectrolyte (PE)^[1–3] is a kind of ubiquitous charged polymers in industry and biology systems, which can be found in a lot of applications. For example, in bulk solutions, they can modify the rheology properties of colloid systems, such as additives to control their stability^[4–6]. Senior application is to prepare useful core-shell structure by assembly of PEs in drug delivery^[7–10]. At surface or interface, they can be used as regulators to tune their wetting or lubrication properties^[11–14].

In this paper, we mainly focus on the adsorption of triblock polyampholytes (PAs) confined between two neutral planes. PA^[15–17] is a kind of PE carrying ions with opposite valences. Polymer adsorption, in neutral^[18–20] or charged systems^[21–23], is an important problem in polymer science and has attracted a lot of attentions. Scientists mainly concern two issues: the structure of adsorbing polymers and the interaction between surfaces. If only one end of polymer in semi-dilute solution can adsorb onto surface, the inter-chain repulsion makes them to form a brush-like conformation. When both ends of polymer, such as telechelic polymer or multiblock copolymer bearing different affinities with the surfaces, can adsorb, the resulting structure can present considerable amount of loop, except that of tail. When two adsorbed layers are brought together, the density at the middle of two surfaces increases and the resulting steric repulsion can stabilize the colloid system. However, if bridge conformation can arise, the total free energy can be further reduced by more stretched chain which

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fetches the colloids together, a long-range effective interaction can cause coagulation of colloid system. The above analysis is just a simple classification, in real environment all the conformations couple and the final interaction is extraordinarily complicated^[24–26].

Experimentally, the structure and interaction of polymer-mediated interfaces can be investigated by surface force apparatus^[27], atomic force microscopy^[28] and thin film pressure balance, *etc.* For example, using surface force measurement, Klein^[11–13, 29] studied the interactions of a series of bare, neutral and charged polymer-mediated surfaces. Huck^[30] synthesized and characterized triblock PA brush consisting of cationic, neutral and anionic segments. Theoretically, using lattice self-consistent field theory, Scheutjens and Fleer^[31, 32] investigated the microscopic conformations and interaction in systems of neutral homopolymers, diblock and triblock copolymers. Matsen^[33, 34] detailedly compared the degree of coincidence between the results, concerning the structure and interaction in strong polyelectrolyte-mediated planar brushes, of analytical strong-stretching theory and numerical self-consistent field theory (SCFT). Tong^[35] examined the microscopic conformations of two charged squares immersing in solution of strong polyelectrolytes bearing opposite valence. Qu^[36] generalized continuum SCFT to study responsive behaviors of diblock PA brushes. Using random phase approximation, Dobrynin *et al.*^[37] investigated the interaction between two charged surfaces immersed in solution of PAs with random positive and negative charged fractions. Broukhno *et al.*^[38] investigated the force between two planar charged surfaces adsorbed by triblock PAs by Monte Carlo method, they mainly concerned the effects of bulk concentration and the length of PAs.

In this paper, we devote to explore the structure and interaction of triblock PAs confined between two neutral planes, and we expect to provide more insights of charged polymer adsorption in colloid science. Comparing with simulation methods and experiment results, continuum SCFT bears advantages in the both issues in polymer adsorption. It can both easily statistically calculate the various conformations and needs less cost of calculation in elevating the interaction with efficient algorithm. Thus, we try to reach our goal by the following steps, using continuum SCFT. We first calculate the distribution of all the conformations, then obtain the total effective free energy and its various components. The information of variation of the microscopic structure and more detailed free energy parts is expected to help us to find the essential principle determining the stability of the system.

The rest of this article is organized as follows: In the second section, we describe the theoretical framework and numerical algorithm used to obtain the statistical characteristics of adsorbed polymers and the equations for the interaction between the two planes. In the third section, we first calculate the structure of adsorbed layer and then discuss the variation of interaction by correlating that of conformations. Finally, we conclude with a summary of our results.

Model and Theoretical Formalism

In this section, we describe the model and the theoretical framework for triblock PAs adsorbed onto two parallel planes. The system is schematically presented in Fig. 1. In the space between two planes with separation L along the x axis, there are n_p ABA triblock copolymer molecules with length N_C and n_s molecules of neutral solvent S. The Kuhn length of monomers of the polymer is b , which is chosen as reduced length of system, and we assume the size of monomer and that of solvent molecule are the same. For simplicity, the lengths of the two positive A blocks are the same, which are chosen as N_A , and the length of negative B block is N_B . Thus we can acquire the relation $N_C = 2N_A + N_B$. The two planes can reversibly adsorb the A block by potential $U(x)$ with magnitude U_0 and interaction range $2b$. The system also contains n_+ cations and n_- anions, and it is reasonable to neglect their sizes.

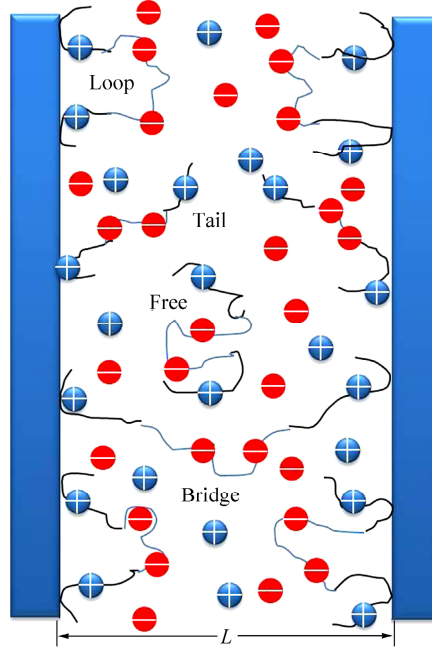


Fig. 1 Schematic illustration of the adsorption of symmetrical triblock polyampholytes onto two parallel planes. The adsorbing A block by short-range potential is positive and the middle non-adsorbing B block is negative. They form four various microscopic conformations, *i.e.* free chains, loop, tail and bridge.

In a grand-ensemble system, the free energy Hamiltonian^[39, 40] is given as follows,

$$\begin{aligned} \frac{F}{\rho_0 k_B T} = & \int dx [\chi_{AB} \phi_A(x) \phi_B(x) + \chi_{AS} \phi_A(x) \phi_S(x) + \chi_{BS} \phi_B(x) \phi_S(x)] - \int dx [\phi_A(x) \omega_A(x) + \\ & \phi_B(x) \omega_B(x) + \phi_S(x) \omega_S(x)] - Le^{\Delta\mu_C} Q_C - Le^{\Delta\mu_S} Q_S - Le^{\Delta\mu_+} Q_+ - Le^{\Delta\mu_-} Q_- \\ & + \int dx \phi_A(x) U(x) - \int dx \frac{1}{8\pi\rho_0 l_B} |\nabla\Psi(x)|^2 + \int dx \eta(x) [\phi_A(x) + \phi_B(x) + \phi_S(x) - 1] \end{aligned} \quad (1)$$

In above equation, $\phi_i(x)$ is the dimensionless volume density of species i , with $\omega_i(x)$ the corresponding auxiliary field in SCFT. l_B is the Bjerrum length and $\rho_0 = b^{-3}$. χ_{ij} are the Flory-Huggins parameters between segments i and j . $\psi(x)$ is the electrostatic potential and $\eta(x)$ is the field to ensure incompressibility condition. $\Delta\mu_C$, $\Delta\mu_S$ and $\Delta\mu_{\pm}$ are the chemical potential of triblock copolymers, solvent molecules and mobile ions, respectively, with Q_C , Q_S and $Q_{\pm}$ their corresponding partition functions, respectively. The specific form of partition functions are given as follows,

$$Q_S = \frac{1}{L} \int dx e^{-\alpha_S(x)} \quad (2)$$

$$Q_{\pm} = \frac{1}{L} \int dx e^{\mp\psi(x)} \quad (3)$$

$$Q_C = \frac{1}{L} \int dx q_{A1}^a(x, N_A) \quad (4)$$

Taking mean field approximation $\partial F/\partial\phi_i(x)$, $\partial F/\partial\omega_i(x)$, $\partial F/\partial\psi(x)$ and $\partial F/\partial\eta(x)$, we can obtain the self-consistent field set of equations

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

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

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

$$\phi_A(x) = e^{\Delta\mu_C} \int_0^{N_A} dt q_{A1}(x, t) q_{A1}^a(x, N_A - t) + e^{\Delta\mu_C} \int_0^{N_A} dt q_{A2}(x, t) q_{A2}^a(x, N_A - t) \quad (8)$$

$$\phi_B(x) = e^{\Delta\mu_C} \int_0^{N_B} dt q_B(x, t) q_B^a(x, N_A - t) \quad (9)$$

$$\phi_S(x) = e^{\Delta\mu_C} e^{-\omega_S(x)} \quad (10)$$

$$\phi_{\pm}(x) = e^{\Delta\mu_{\pm}} e^{\mp\psi(x)} \quad (11)$$

$$-\frac{1}{4\pi l_B} \nabla^2 \psi(x) = p\phi_A(x) - p\phi_B(x) + \phi_+(x) - \phi_-(x) \quad (12)$$

$$\phi_A(x) + \phi_B(x) + \phi_S(x) = 1 \quad (13)$$

In above equations, $q_i(x, t)$ with $i = A1, B$ and $A2$ are the propagators of block i in SCFT, with $q_i^a(x, t)$ their complementary propagators, which all satisfy the following modified diffusion equations:

$$\frac{\partial q_i(x, t)}{\partial t} = \frac{1}{6} \nabla^2 q_i(x, t) - \omega_i^{\text{eff}}(x) q_i(x, t) \quad (14)$$

$$\frac{\partial q_i^a(x, t)}{\partial t} = \frac{1}{6} \nabla^2 q_i^a(x, t) - \omega_i^{\text{eff}}(x) q_i^a(x, t) \quad (15)$$

where if $i = A1, A2$, $\omega_i^{\text{eff}}(x) = \omega_A(x) + p_A\psi(x)$, otherwise $\omega_i^{\text{eff}}(x) = \omega_B(x) - p_B\psi(x)$. Here p_A and p_B are the charge fraction of block A and B. They all have the Dirichlet boundary condition for both surfaces and the initial conditions as

$$q_{A1}(x, 0) = 1, q_B(x, 0) = q_{A1}(x, N_A), q_{A2}(x, 0) = q_B(x, N_B) \quad (16)$$

and

$$q_{A2}^a(x, 0) = 1, q_B^a(x, 0) = q_{A2}^a(x, N_A), q_{A1}^a(x, 0) = q_B^a(x, N_B) \quad (17)$$

We solve the set of equations by Broyden^[41] method and the modified diffusion equation by classical Crank-Nicolson method.

As mentioned in the introduction, using the numerical results of SCFT, by defining proper propagators, we can easily obtain quantities of various microscopic conformations:

$$\phi^F(x) = e^{\Delta\mu_C} \int_0^{N_C} dt q_F(x, t) q_F(x, N_C - t) \quad (18)$$

$$\phi^L(x) = e^{\Delta\mu_C} \int_0^{N_C} dt q_L^a(x, t) q_L^a(x, N_C - t) + e^{\Delta\mu_C} \int_0^{N_C} dt q_R^a(x, t) q_R^a(x, N_C - t) \quad (19)$$

$$\phi^T(x) = e^{\Delta\mu_C} \int_0^{N_C} dt q_F(x, t) q_L^a(x, N_C - t) + e^{\Delta\mu_C} \int_0^{N_C} dt q_F(x, t) q_R^a(x, N_C - t) \quad (20)$$

$$\phi^B(x) = \phi_A(x) + \phi_B(x) - \phi^F(x) - \phi^L(x) - \phi^T(x) \quad (21)$$

These equations are the density profiles of free chains, loop, tail and bridge, respectively, with

$$\Sigma^F = \int_0^L dx \phi^F(x)$$

$$\Sigma^L = \int_0^L dx \phi^L(x)$$

$$\Sigma^T = \int_0^L dx \phi^T(x)$$

and

$$\Sigma^B = \int_0^L dx \phi^B(x)$$

as their corresponding amounts, respectively. The detailed derivation^[35, 42, 43] obtaining above equations is given in Appendix I.

We can also easily obtain the interaction between the two planes, which is given as follow

$$\Delta U(L) = \Delta F_p(L) + \Delta F_s(L) + \Delta F_u(L) + \Delta F_e(L) + \Delta F_{DL}(L) \quad (22)$$

In order to find the origin of the total effective interaction between the two planes, we split them into various parts, $\Delta F_p(L)$, $\Delta F_s(L)$, $\Delta F_u(L)$, $\Delta F_e(L)$ and $\Delta F_{DL}(L)$, are the contributions from polymer chains, solvent molecules, the surface adhesion, electrostatic field and the mobiles ions, respectively. Their specific forms are given in Appendix II.

RESULTS AND DISCUSSION

In this section, we present the numerical results of SCFT. We mainly concern about the effects of the charge fraction of polymer chain, the bulk salt concentration and the component of polymer chain. Two issues we devoted to investigate are the structure of adsorbing polymers and the effective free energy interaction between the two neutral adsorbed surfaces. Our path is to find out the dependences of structure on the various parameters mentioned above and then investigate the variation of interaction by correlating the information of structure obtained previously.

For simplicity, we only consider the symmetrical case that the lengths of the two adsorbing A blocks of each end are the same and the adhesive potential between monomer A and the two surfaces are the same as well. In order to avoid the study of the complex microphase separation that may appear, we set all the Flory-Huggins interaction parameters $\chi_{ij} = 0$ with $i, j = A, B$ and S , $i \neq j$. So the monomer A and monomer B are different by their charge valences and affinities with the surfaces confined them. The charge fraction of block A and that of block B are chosen as $p_A = p_B = p$. The bulk concentration of triblock copolymers in all the calculations is set as $\phi_C^0 = 0.1$ and the attraction between the monomer A and the two surfaces is $U_0 = -0.5$. The total length of each triblock chain is $N_C = 2N_A + N_B = 100$. The monomer size is equal to $b = 0.5$ nm and the Bjerrum length $l_B = 0.7$ nm.

Density Profiles of Components of System

In this subsection, we present the densities of various components and conformations of polymers, these figures will first give us an intuitive insight and can considerably help us to explain the variation of structure and effective interaction between the two planes.

Figure 2 presents the density profiles of the two components of polymers, the mobile cations and anions, respectively. Because of the adsorption of surfaces, block A prefers to accumulate themselves near the surfaces with block B locating itself tightly due to the connectivity between the two blocks and the electrostatic attraction. Near the surfaces, because of the electrostatic interactions with polymers, the mobile anions and cations have the corresponding distributions and their net result is an electrostatic double-layer near the two surfaces.

Figure 3 presents the density profiles of various conformations, such as free chains, loop, tail and bridge, respectively. According to the dependences of the conformations on the separation between the two planes, the system should be split into two regimes: the regime near surfaces and that far away from surfaces. It clearly shows that, with the decrease of the separation between the two planes, the different conformations have

different behaviors. The density of free chains decreases and that of bridge increases in these two regimes. The density of loop decreases in the former regime and increases in the latter regime. Finally, the density of tail presents more complex variation: it always decreases in the first regime, but first increases due to the overlap of the two adsorbing layers of polymers and then decreases due to strong depletion effect.

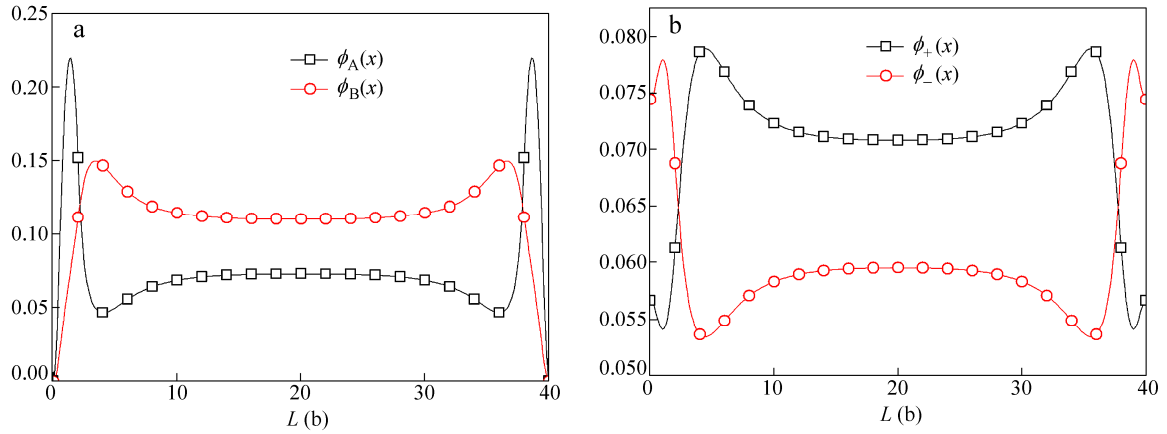


Fig. 2 The density profiles of (a) the components of polymers and (b) these of mobile cations and anions (The parameters are chosen as $N_A = 20$, $p = 0.3$, $c_S = 0.05$ mol/L).

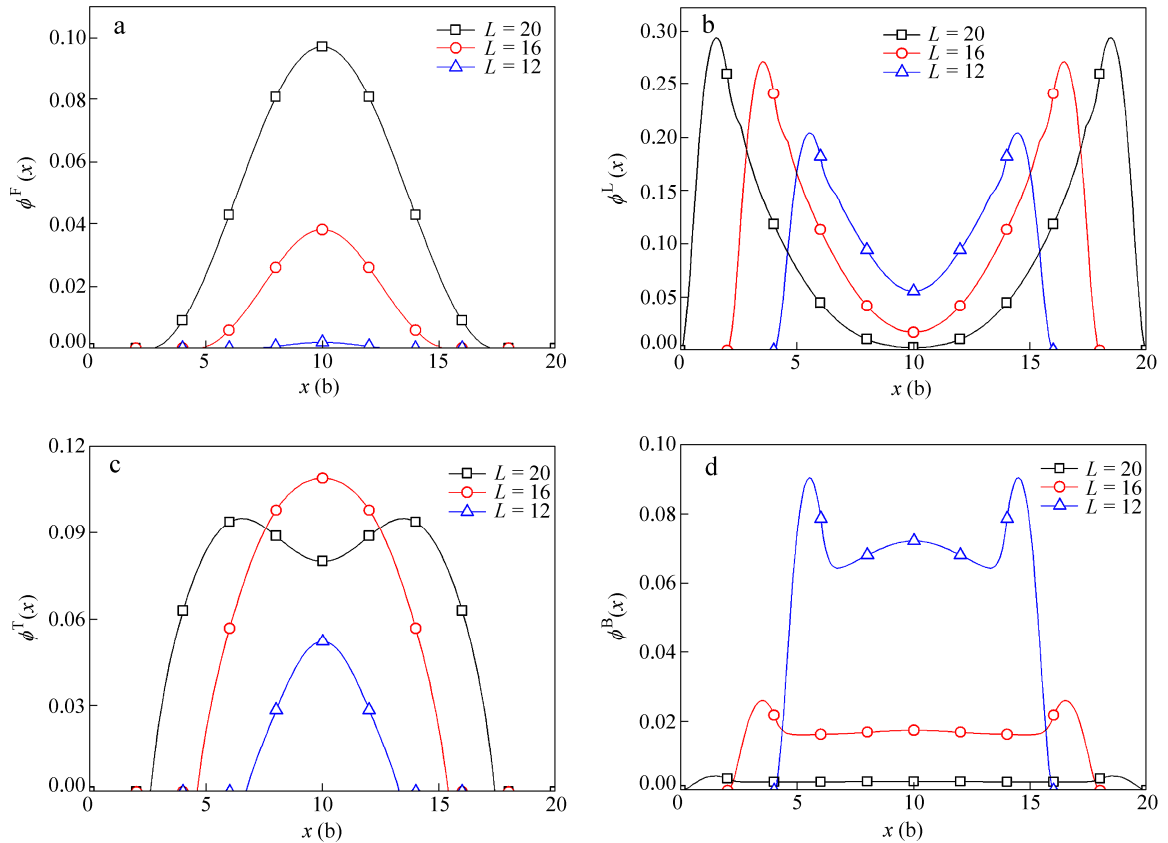


Fig. 3 The density profiles of the microscopic conformations of (a) free chain, (b) loop, (c) tail, and (d) bridge between the two adsorbed planes (The parameters are chosen as these in Fig. 2.)

There are three mechanisms determining the structure and the effective interaction between surfaces: (a) the surfaces prefer to hold the sticky blocks nearby, (b) the entropy effect makes copolymer chain present a more open configuration and (c) the backbone of charged polymer becomes stiffer at higher charge fraction and lower bulk salt concentration. Their specific behavior will be revealed when we consider the effect of the charge fraction of polymer chain p , the bulk salt concentration c_s and the length of adsorbing block N_A .

Effect of Charge Fraction of Polymer

In this subsection, we mainly concern the effect of the charge fraction of polymer. Increasing the charge fraction of PA will cause the follow phenomena: (i) increasing the stiffness of the backbone of polymer chain, (ii) increasing the electrostatic attraction between two blocks with opposite signs of charges, (iii) increasing the amounts of mobile ions in solution. These behaviors compete with each other and the total system locates itself at the equilibrium in which the free energy is the minimum of phase space.

Figure 4(a) depicts the dependence of the amounts of the chains with conformations of the free chain, loop, tail and bridge on the separation between the two planes, respectively. It is found that with decreasing the separation between the two planes, the amount of free chains decreases linearly due to the entropy effect, the amounts of loop and tail decrease at closer separations between the two parallel planes when the adsorbing layers belong to the opposite planes begin to overlap, and they finally disappear. It also suggests that the amount of tail always exhausts more quickly than that of loop. The amount of bridge first increases and become dominated over that of other conformations, and then decreases after it passes a maximum. This phenomenon can be

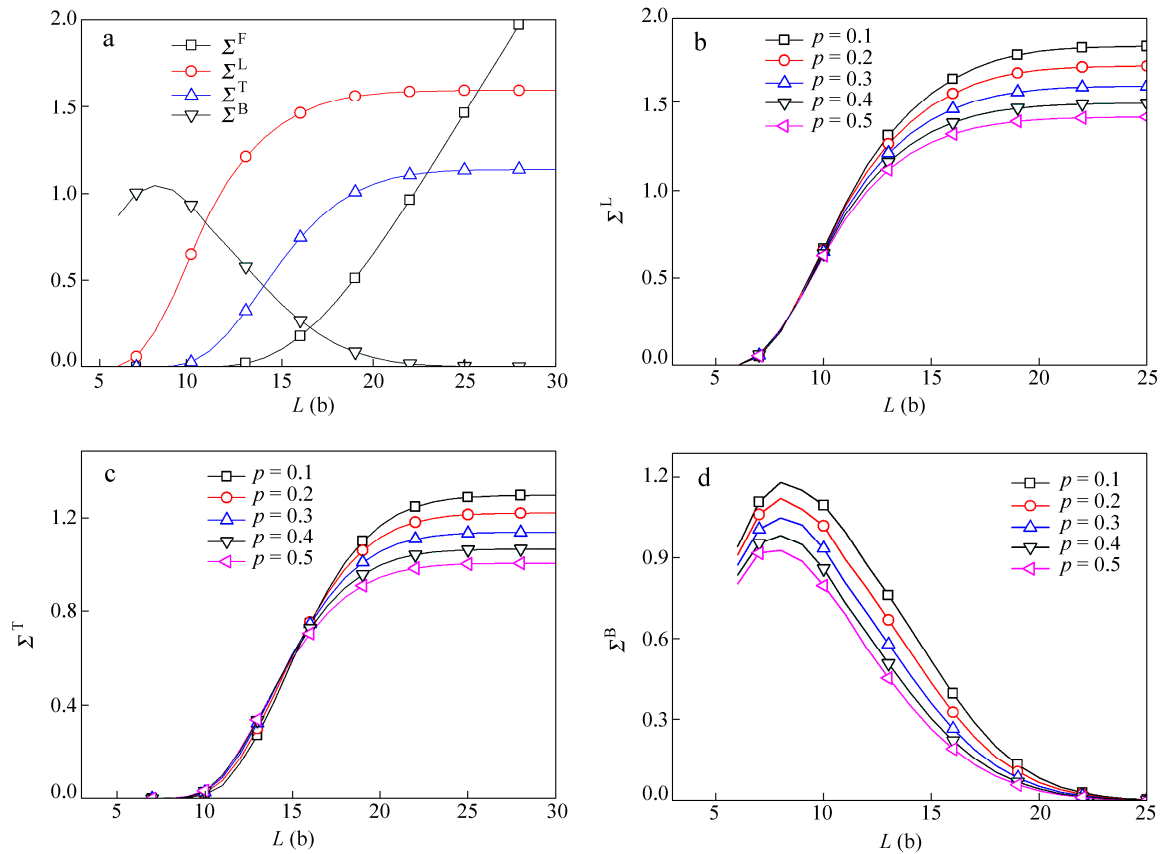


Fig. 4 (a) The amounts of the microscopic conformations with $p = 0.3$; The dependences of amounts of (b) loop, (c) tail and (d) bridge conformations on the separations for different charge fractions of polymer (Other parameters are chosen as $c_s = 0.05$ mol/L and $N_A = 10$.)

explained as follows: to reduce the free energy of system, at larger separation between the two planes, the system can transform loop and tail conformations to bridge conformation because its formation can acquire more minus adhesion and makes polymer chains exhibit more open configurations with larger entropy. However, this trend cannot always continue until the confinement effect of the space between the two planes at narrow space become so strong that it dominates over the adhesion between the sticky A blocks and surfaces, thus decreases its amount by squeeze the adsorbing polymer chains into the bulk solution.

It can be seen in Figs. 4(b)–4(d) with the increase of the charge fraction of polymers, the PA chain presents larger dimension because of stronger electrostatic repulsion between the negative B blocks. By this reason, it is more difficult for the surface to adsorb polymer and all the conformations decrease their amounts, since the A block is relatively short ($N_A = 10$) and has less attraction to B block.

Let us investigate the dependence of the interaction between the two adsorbed planes on the charge fraction of polymer chains p . As one can see in Fig. 5(a), there is a long-range repulsion between the two planes, and it increases its magnitude when we increase the charge fraction. The origin of the long-range repulsion can be further studied when we spilt the total interaction into various components. According to our calculations, the double layer interaction of mobile ions ΔF_{DL} , the conformation of polymer chains ΔF_P and the surface adhesion ΔF_U are the three main contributions.

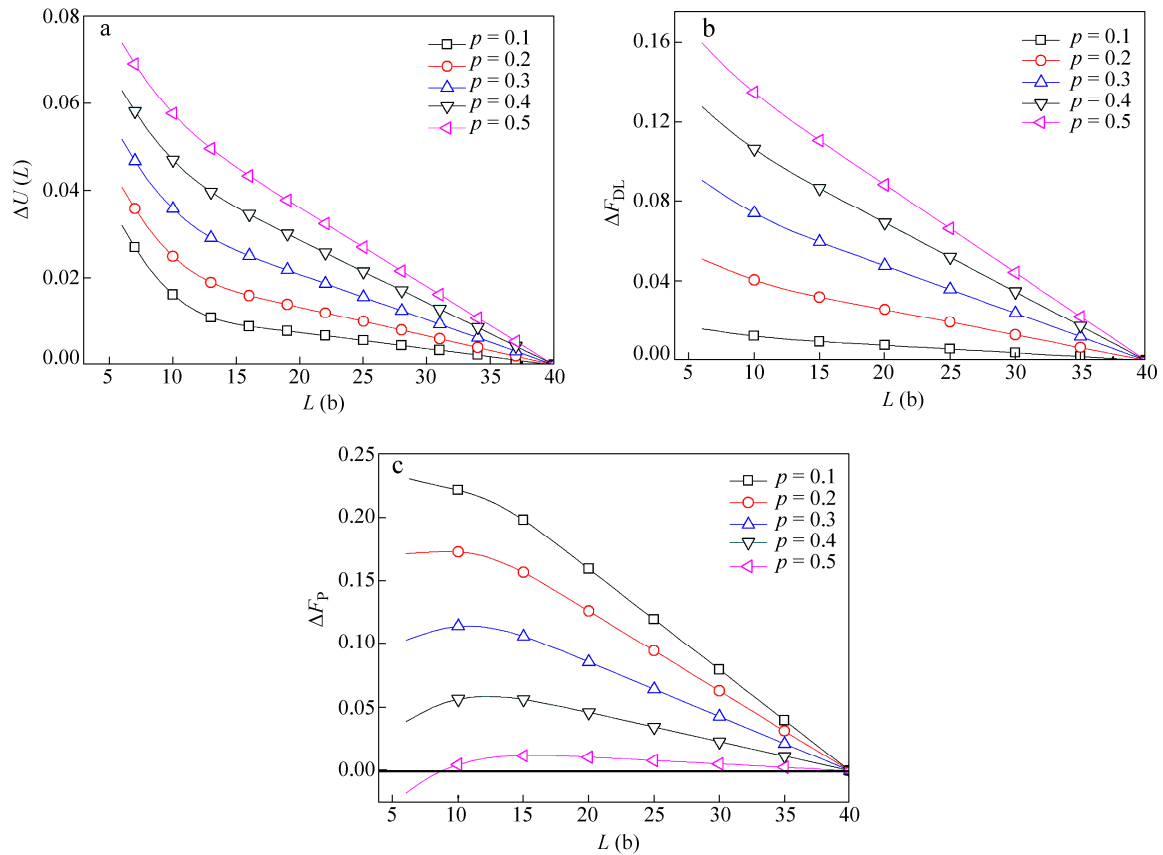


Fig. 5 (a) The total effective interaction between the two adsorbed planes for different charge fractions of polymer chain, (b) the contribution from double-layer forming by the mobile ions, and (c) the contribution to the total interaction from polymer chains for different charge fractions (Other parameters are chosen as $c_S = 0.05$ mol/L and $N_A = 10$.)

When we increase p , ΔF_U , which only depends on the structure near the two surfaces, is nearly unchanged. ΔF_{DL} increases its magnitude. Simultaneously, the backbones of polymer chains become stiffer, thus, it is more difficult for them to be adsorbed onto the surfaces and more amount of polymers is squeezed into the bulk solution, and ΔF_P decreases its magnitude. As can be seen in Fig. 5, differently from its neutral counterpart, because the interchain electrostatic attraction, ΔF_P is long-range as ΔF_{DL} does. More qualitatively, ΔF_{DL} dominates over ΔF_P at high charge fraction and becomes the main source of the total interaction between the two planes.

Effect of Bulk Salt Concentration

In this subsection, we mainly consider the dependence of conformations and the interaction between the two planes on the bulk salt concentration. Adding salt into the charged polymer solution will increase the concentrations of mobile cations and anions, and affect the translational entropy. According to the Debye theory^[44], adding salt also enhances the electrostatic screening, and reduces the stiffness of the backbone of polymer chains.

From the calculation, we find that increasing the salt bulk concentration the amounts of all the various conformations and thus the amount of adsorbed polymers increase. Typical examples are the variations of the amounts of loop and bridge, which are shown in Fig. 6. Their dependences on the bulk salt concentration become saturated at high salt concentration (see the inserts in Fig. 6). This is because when electrostatic screening of system is enhanced, the interchain and intrachain electrostatic interactions become weaker and the surfaces can adsorb more polymer chains with less stiffer backbone.

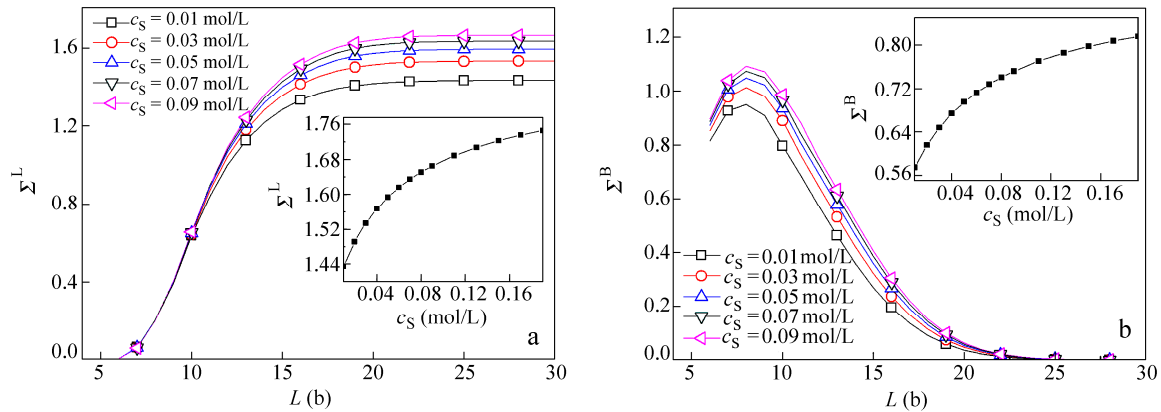


Fig. 6 The dependence of (a) the amount of loop conformation and (b) that of bridge conformation on the separation between the two planes for different bulk salt concentrations

The insert figures are the dependence of the amount of loop at $L = 25$ and that of bridge at $L = 12$ on the bulk salt concentration, respectively. Other parameters are chosen as $p = 0.3$ and $N_A = 10$.

Figure 7(a) displays the dependence of the interaction on the distance between the two planes for different bulk salt concentrations. It can be seen that increasing the bulk salt concentration weakens the long-range interaction between the two planes, and the interaction will become saturated at high concentrations. Simultaneously, the stronger electrostatic screening resulting from the applied salt decreases ΔF_{DL} until it becomes saturated at high bulk salt concentration. However, due to the softer backbone of polymer chain resulting from the higher bulk salt concentration, it becomes easy for the polymers to be adsorbed onto the planes, and the resulting steric interaction between the opposite adsorbed layers increases the magnitude of ΔF_P . As expected, it becomes saturated as ΔF_{DL} does for the same reason and dominates over ΔF_{DL} at high bulk salt concentration. It should be noted that the decrease of ΔF_P by further compressing the two planes is a kind of depletion interaction.

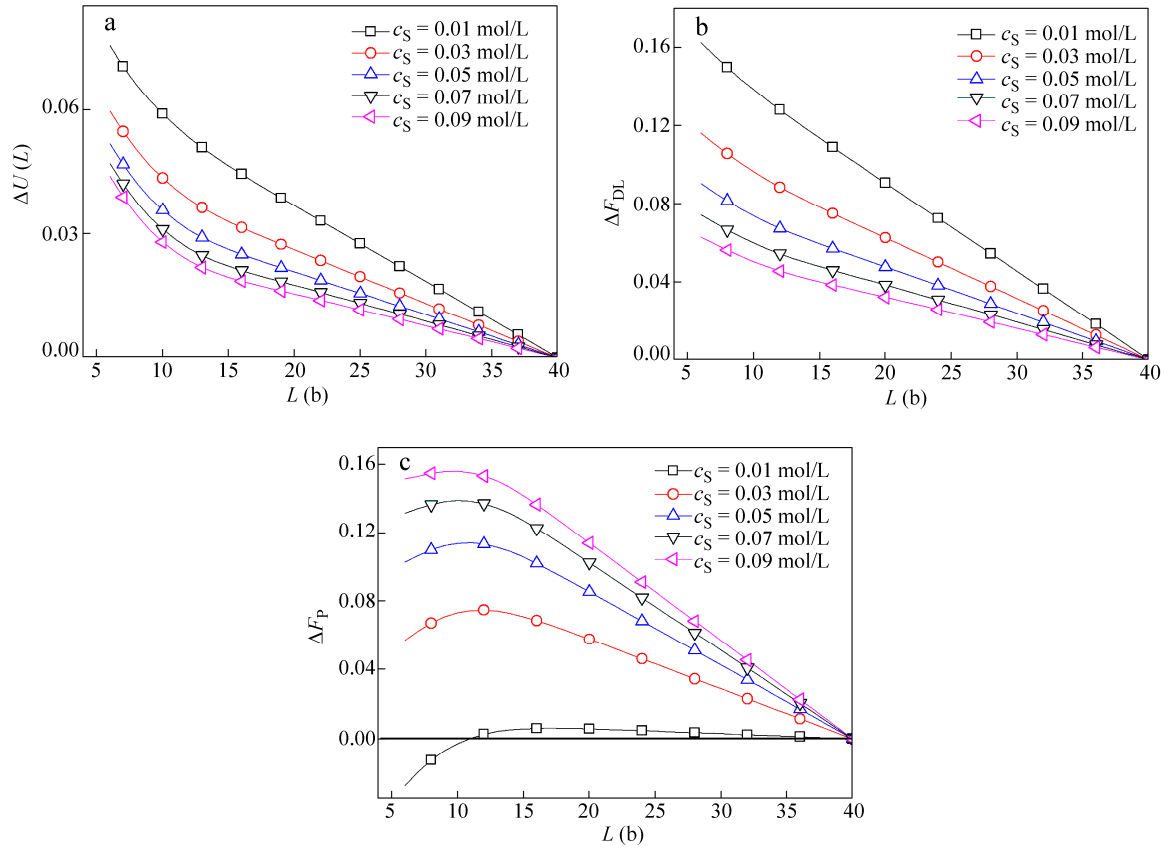


Fig. 7 (a) The total effective interaction between the two adsorbed planes for different bulk salt concentrations, (b) the contribution to the total interaction from double-layer forming by the mobile ions, and (c) that from polymer chains for different charge fraction (Other parameters are chosen as $p = 0.3$ and $N_A = 10$.)

Effect of the Length of Adsorbing Block A

Above calculations mainly concern the factors affecting the long-range electrostatic interaction. For triblock PAs, the adsorption behavior can also be tuned by the component of polymer chains. Thus in this subsection, we consider the dependences of the conformations and interaction between the two planes on the length of the adsorbing A blocks. Increasing the length of A block increases the acquired adsorbed energy for each chain, and the attraction between two blocks with opposite charge valences can be considerably changed as well.

The calculations show that the dependences of the conformations on the separation between the two planes are the same as those in previous sections when we increase the length of the adhesive blocks. However, the dependence of the amount of bridge conformation presents an interesting phenomenon: it first increases and then decreases, as can be seen in Fig. 8. This phenomenon can be explained as follows: when the adsorbing block is short, the affinity between the adsorbing block and surfaces is weak and the entropy effect becomes dominant, so more chains prefer to exhibit as bridge conformation and this increases its amount. However, when the length of the adsorbing A blocks increases, the acquired adhesion makes the chain prefer to adsorb onto the same plane to form loop conformation, thus the amount of bridge decreases.

The interaction between the two planes presents a non-monotonous characteristic when we increase the length of the adsorbing A blocks, as can be seen in Fig. 9. It first decreases and then increases its magnitude.

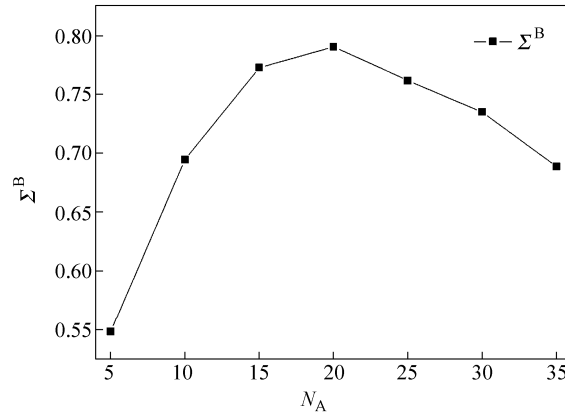


Fig. 8 The dependence of the amount of bridge conformation on the length of the adsorbing blocks (Other parameters are chosen as $p = 0.3$ and $c_S = 0.05$ mol/L.)

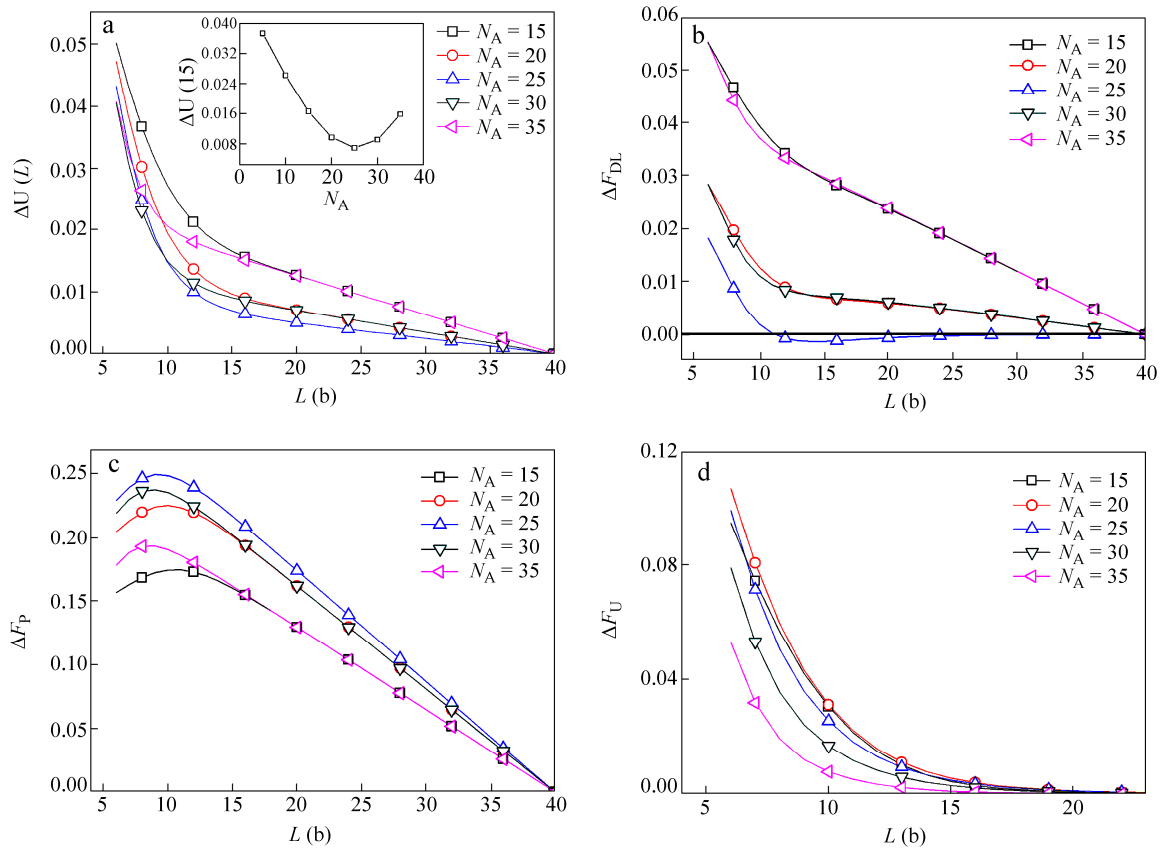


Fig. 9 (a) The total effective interaction between the two adsorbed planes for different lengths of the adsorbing blocks, (b) the contribution to the total interaction from double-layer forming by the mobile ions, (c) the contribution to the total interaction from polymer chains, and (d) the contribution to the total interaction from the adhesion of surfaces for different lengths of the adsorbing blocks (Other parameters are chosen as $p = 0.3$ and $c_S = 0.05$ mol/L.)

Interesting finding is that, in our calculations, the case $N_A = 25$ presents the lowest repulsion between the two planes, the repulsion at $N_A = 15$ and $N_A = 35$, and $N_A = 20$ and $N_A = 30$ nearly converge because of the symmetry of the system. In this case, the surface adhesion ΔF_U decreases its magnitude. Other two main

contributions, ΔF_{DL} and ΔF_P , present the same dependence on the length of the adsorbing A blocks as that of the total interaction between the two planes. It should be noted that (where), when $N_A < 25$, the contribution from cations in ΔF_{DL} is repulsive and the contribution from anions is attractive, when $N_A > 25$, the reverse behavior happens and when $N_A = 25$, the two term become the same order, this is the reason why the net ΔF_{DL} becomes trivial.

SUMMARY AND CONCLUSIONS

In this paper, the continuum SCFT is applied to study the structure and the interaction between two planes adsorbed by symmetrical triblock PAs with short-range neutral potential. We mainly concern the effects of the charge fraction of polymer chain, the bulk salt concentration and the length of attractive blocks.

By defining proper propagators, we investigate the dependences of various conformations on the parameters mentioned above. It is found that the amounts of free chain, loop and tail are reduced, and that of bridge increases when we compress the two planes, the locations where the conformations translate highly depend on the environment parameters. The amounts of all the conformations decrease with the increase of charge fraction of polymer, and increase with the increase of the bulk salt concentrations and became saturated at high c_s . With increasing the length of the adhesive block, the amount of bridge first increases and then decreases.

The second issue we studied is the interaction between the two parallel planes. The total system consists of the polymer solution except electrolytes and a double-layer forming by mobiles ions, and the contribution to the interaction from the double-layer cannot be ignored. Because of the existence of the long-range electrostatic interaction, although bridge conformation can arise, the resulting interaction between the two planes always presents a long-range repulsion. However, as one can see, the formation of bridge can considerably tune it. Further insight into the origin of the total long-range interaction between the two planes can be found when we split it into various components. It was found that the total repulsion mainly came from three parts: the contribution from the surface adhesion, the contribution from the polymer chains and that of double-layer forming by the mobile ions. The contribution from the polymers became dominant at high charge fraction of polymer chains because of their increasing stiff of backbone. The contribution from the double-layer became dominant at low bulk salt concentration due to less electrostatic screening.

Lastly, in this paper we mainly consider the adsorption of symmetrical triblock PAs by short-range neutral potential between two parallel planes. In future work, we will study the adsorption of PAs between two cylindrical or spherical objects, as well as the effects nonsymmetrical characteristics of system and polydispersity of polymers. The adsorption of triblock PAs by electrostatic potential will also be pursued.

APPENDIX I

In order to study the various microscopic conformations in the triblock copolymer adsorption system, after obtaining the solution to the set of self-consistent field equations, according to the density profile of block A, the space between the two planes can be separated into different regimes: because of symmetry of system, there must be two maximums along the density profile of block A, which are named M_1 and M_2 with $\phi_A(M_1) = \phi_A(M_2)$ respectively. There is also a point P whose value is the lowest between M_1 and M_2 . Our goal is to find two points

B_1 and B_2 , which satisfy the relation $\phi_A(B_1) = \phi_A(B_2) = \phi_A(B_P) + \frac{1}{6}[\phi_A(M_1) - \phi_A(B_P)]$ and they locate between

B_1 and B_2 respectively. The regime between point B_1 and B_2 is named the adsorption layer and the rest regimes are the left boundary layer and right boundary layer, respectively. We can define proper propagators to obtain the microscopic conformations. $q_F(x, t)$ is the propagator of free chains in adsorption layer condition and it obeys Dirichlet boundary. $q_L(x, t)/q_R(x, t)$ is propagator evolved in the left/right boundary layer and the adsorption layer, it vanishes at the left adsorbed surface and the right/left surface of the adsorption layer. They all satisfy the modified diffusion equation in different effective field depending on their chemical species, taking the propagator of free chain $q_F(x, t)$ as an example,

$$\frac{\partial q_F(x,t)}{\partial t} = \frac{1}{6} \nabla^2 q_F(x,t) - \omega^{\text{eff}}(x) q_F(x,t) \quad (\text{A1})$$

with

$$\omega^{\text{eff}}(x) = \begin{cases} \omega_A(x) + p_A \psi(x), & 0 \leq t \leq N_A \\ \omega_B(x) - p_B \psi(x), & N_A < t < N_A + N_B \\ \omega_A(x) + p_A \psi(x), & N_A + N_B \leq t \leq N_C \end{cases} \quad (\text{A2})$$

After further defining the propagators

$$q_L^a(x,t) = q_L(x,t) - q_F(x,t)$$

and

$$q_R^a(x,t) = q_R(x,t) - q_F(x,t)$$

we can obtain their density profiles which are given as follows,

$$\phi^F(x) = e^{\Delta\mu_C} \int_0^{N_C} dt q_F(x,t) q_F(x, N_C - t) \quad (\text{A3})$$

$$\phi^L(x) = e^{\Delta\mu_C} \int_0^{N_C} dt q_L^a(x,t) q_L^a(x, N_C - t) + e^{\Delta\mu_C} \int_0^{N_C} dt q_R^a(x,t) q_R^a(x, N_C - t) \quad (\text{A4})$$

$$\phi^T(x) = e^{\Delta\mu_C} \int_0^{N_C} dt q_F(x,t) q_L^a(x, N_C - t) + e^{\Delta\mu_C} \int_0^{N_C} dt q_F(x,t) q_R^a(x, N_C - t) \quad (\text{A5})$$

$$\phi^B(x) = \phi_A(x) + \phi_B(x) - \phi^F(x) - \phi^L(x) - \phi^T(x) \quad (\text{A6})$$

and it is straightforward to define their corresponding amounts.

APPENDIX II

Using the form of the free energy Hamiltonian, the extra interaction of adsorption system with respect to the bulk solution which by setting the separation between the two planes enough large can be easily obtain

$$\Delta F(L) = F(L) - F(\infty) \quad (\text{B1})$$

and the effective interaction between the two planes is

$$\begin{aligned} \Delta U(L) &= \Delta F(L) - \Delta F(\infty) \\ &= \Delta F_p(L) + \Delta F_s(L) + \Delta F_u(L) + \Delta F_e(L) + \Delta F_{DL}(L) \end{aligned} \quad (\text{B2})$$

with the specific expression of its various components are given as follows,

$$\Delta F_p(L) = \int_0^L dx [\phi_A(x) \omega_A(x) + \phi_B(x) \omega_B(x) - \phi_A^0 \omega_A^0 - \phi_B^0 \omega_B^0] + L e^{\Delta\mu_C} [Q_C - Q_C^0] \quad (\text{B3})$$

$$\Delta F_s(L) = \int_0^L dx [\phi_s(x) \omega_s(x) - \phi_s^0 \omega_s^0] + L e^{\Delta\mu_s} [Q_s - Q_s^0] \quad (\text{B4})$$

$$\Delta F_u(L) = \int_0^L dx U(x) \phi_A(x) \quad (\text{B5})$$

$$\Delta F_e(L) = \frac{1}{8\pi} \int_0^L dx |\nabla \psi(x)|^2 \quad (\text{B6})$$

$$\Delta F_{DL}(L) = L e^{\Delta\mu_+} [Q_+ - Q_+^0] + L e^{\Delta\mu_-} [Q_- - Q_-^0] \quad (\text{B7})$$

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