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# Adsorption of triblock copolymers confined between two plates: An analytical approach

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#### ABSTRACT

We present an approximate analytical approach to the adsorption problem of ABA triblock copolymers confined between two parallel plates in a  $\theta$  solvent and give the expression of the propagator q(x, t) as a piece-wise function by solving the modified diffusion equation. In this way, the role of separation between the two plates, adsorption energy and block lengths on segment concentration profile, chain conformations, and interaction potential is then investigated, which agrees well with the numerical results. It is demonstrated that there are parallels between lengthening adsorbing A blocks and increasing surface affinity: strong adsorption and long adsorbing blocks favor the formation of loops and bridges, whereas more tails and free chains exist in the case of weak adsorption and short A blocks at large separations. For moderate and strong adsorptions, the bridging fraction begins to plummet at a separation larger than the end-to-end distance of non-adsorbing B block  $R_{\rm B}$  and becomes negligible at above  $2R_{\rm B}$  owing to the entropy effect. The depth of the potential well in the interaction potential profile depends on the adsorption energy and A block length, while the location of the potential minimum corresponds to the onset of the sharp decrease in bridges.

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#### I. INTRODUCTION

Adsorption of polymers on surface/interface provides an efficient way to modify the interface properties or colloidal suspension behavior.<sup>1</sup> It serves as a model system for both experimental and theoretical studies in polymer physics and plays an important role in industrial and biological applications.<sup>2–8</sup> Compared with the case of homopolymers, the interactions between two colloidal surfaces coated with block copolymers can be modulated more easily and regulated with more diversity and have thus attracted widespread attention for several decades. For a diblock copolymer with one block adsorbed on the surface and the other dangling in a good solvent, there turns out to be only steric repulsion between the adsorbed layers of the two surfaces brought close together, which is conducive to the stability of colloidal suspensions.<sup>9,10</sup> Triblock copolymers with two adsorbing end blocks and one non-adsorbing middle block, however, can lead to not only repulsion but also attraction between two surfaces, acting as stabilizers or flocculants. The former occurs

when both ends are adsorbed on the same surface to form loops or when one end is dangling in the solution to form tails, while the latter occurs when the two adsorbing blocks are adsorbed on different surfaces to form bridges (Fig. 1). The proportion of these conformations plays a key role in determining the nature of interactions between the interfaces.

The adsorption behavior of triblock copolymers has been widely investigated experimentally. Dai and Toprakcioglu<sup>11</sup> first reported the interactions of end-adsorbed triblock copolymer layers against a bare mica surface in toluene using surface force apparatus. They found the appearance of an attractive force between the two mica sheets and attributed it to polymer "bridges" conformation. Recently, Deguchi *et al.*<sup>12</sup> have measured the interaction force between two hydrophilic silica chips in poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (PEO–PPO–PEO) triblock copolymer solutions by atomic force microscopy. They found that the length of the PEO block has significant influence on the formation of bridges, thus consid05 July 2024 09:06:13



FIG. 1. A schematic diagram of possible conformations of ABA triblock copolymers confined between two parallel plates.

erably affecting the attractive force. In addition, it is frequently reported that the loop conformation of triblock copolymers exhibits strong steric repulsion and enhanced anti-fouling and lubrication properties compared to those of the corresponding diblock brush copolymers.<sup>13-15</sup>

On the theoretical aspect, Evers et al.<sup>16-18</sup> proposed a selfconsistent field theory (SCFT) for the adsorption of block copolymers as an extension of the Scheutjens-Fleer lattice theory<sup>19</sup> for homopolymers. They considered two cases: one is full equilibrium in which the chemical potential of each species between the surfaces remains equal to that in bulk solution, and the other is restricted equilibrium in which the amount of polymer chains between the surfaces is fixed. For ABA triblock copolymers, the length effect of adsorbing A block on the interaction curve is investigated in their work, and they revealed an optimal A block length. With this method employed, Wijmans et al.<sup>20</sup> have shown that lengthening adsorbing A block does not always have exactly the same effect as increasing adsorption energy, while the total available adsorption energy (the product of the A block length and their segmental adsorption energy) is held constant. They also found that the attractive interaction becomes weak when two adsorbing end blocks of ABA triblock copolymers have different lengths. Recently, using a continuum SCFT method, Mei and Qiu<sup>21</sup> have found that the amounts of the four chain conformations are scaled almost linearly to the bulk concentration. Monte Carlo simulations have also been implemented to handle the properties of ABA triblock copolymers confined between two parallel plates. By using this method, Nguyen-Misra et al.22 indicated that both the fraction of A segments adsorbed and the number of bound A segments per adsorbed A block increase as either adsorption energy or A block length increases. Peng et al.<sup>23</sup> have also revealed that the largest bridging fraction can be achieved only when symmetrical chains are confined between two same surfaces.

Physically, the end-adsorbing triblock copolymers bear a resemblance to a special polymer brush with "stickers" at the free ends of the grafted chains to some extent. For this reason, Milner and Witten<sup>24</sup> modeled the strongly adsorbing telechelic polymers

by cutting a chain into two grafted half-chains with equal lengths and thus introducing the theory of grafted polymer brushes.<sup>25</sup> The results showed that the interaction has an attractive minimum near the brush-contact separation 2h and the strength of this attraction is of order  $kT(R/h)^2$  per adsorbed chain, where R is the free radius of a chain and h is the height of an isolated brush. Johner and Joanny<sup>26,2</sup> presented a model system, in which a brush grafted on one plate with a given grafting density is in contact with another parallel plate adsorbing the free-end points, based on a SCFT for grafted chains independently elaborated by Milner et al.<sup>25</sup> and Zhulina et al.<sup>28</sup> Only bridges and dangling chains are considered in the system. They found that both a shear force and a pulling force applied to the adsorbing plate can reduce the fraction of bridges and eventually lead to rupture, whereas a compressional force favors bridging. Afterward, Björling<sup>29</sup> extended the above-mentioned model to the system where the free ends of a grafted chain are obliged to form either a loop on the same grafting surface or a bridge to the other surface. He analytically examined the attractive interaction mediated by end-adsorbing polymers and found that when chain ends are adsorbed onto a single surface, the approaching of another bare surface results in a strong bridging attraction. However, if both slit surfaces are symmetrically covered with adsorbed polymers, this attraction will be much weaker.

Although the above-mentioned studies contribute to an indepth understanding about the adsorption of ABA triblock copolymers, these methods are complex and involve a large number of calculations. Due to the feature of complex topological structure, it is not easy to derive some analytical results in contrast to homopolymer adsorption, which has undergone extensive investigation by researchers, such as de Gennes,30 Chervanyov,31,32 and Semenov et al.33 Therefore, there is a need to present analytical treatments that can give a quantitative description of conformation statistics and interaction potential profiles, which is also helpful to capture the mechanism of bridge-induced attraction in a simple way. In the present paper, we construct a theoretical model for the adsorption of triblock copolymers confined between two plates in a  $\theta$  solvent and analytically obtain the propagator q(x, t) as a piece-wise function by solving the modified diffusion equations. Finally, we give the analytical results of segment concentration distribution, chain conformations, and interaction potential between the two plates, which agrees well with the numerical calculations. The outline of this paper is as follows: in Sec. II, we detail the theoretical model and solve the modified diffusion equation, and the expressions for the system properties. In Sec. III, the dependence of segment concentration distribution, chain conformations, and interaction potential on the separation between the two plates, adsorption energy, and block lengths is investigated in detail. The main conclusions are summarized in Sec. IV.

#### **II. THEORETICAL APPROACH**

#### A. Solution of the modified diffusion equation

We consider a polymer solution with volume V confined between two parallel impenetrable plates (Fig. 1), whose separation is denoted by L. For infinite large plates, there is a homogeneous polymer concentration distribution parallel to the plates, so the system is reduced to a one-dimensional model and all quantities are solely a function of the variable x (perpendicular to the surface, as shown in Fig. 1). By using the symmetry, we set the location of the middle plane between the two plates as the origin of the x axis so that the two plates are located at x = -L/2 and x = L/2, respectively. There are  $N_c$  ABA triblock copolymer chains in our system, each consisting of  $N = 2N_A + N_B$  segments, where  $N_A$  denotes the length of the A block at either end of a chain and  $N_{\rm B}$  denotes the length of the non-adsorbing middle B block. For simplicity, we have assumed symmetrical triblock chains where two end A blocks have the same length. The following analytical treatment can be easily extended to asymmetrical or multiblock chains: A and B segments are considered to have equal Kuhn length, denoted by b. Near the surface of either plate exists an adsorption potential for A segments, and this potential could be modeled as a square potential well with a width of  $\delta$  and strength of  $-U_0$ . That is to say, there is an attractive interaction when the distance between an A segment and any plate is shorter than  $\delta$ , and the adsorption energy gained per A segment adsorbed will be  $U_0$ . Hence, the width of the region that has no adsorption potential is  $d = L - 2\delta$ . At the same time, in no case will there be interactions between B segments and the plates.

In this paper, we use thermal energy kT as the reduced unit of energy and Kuhn length b as the reduced unit of length. In terms of the above-mentioned assumptions, the symmetrical ABA triblock copolymers are ideal chains and are treated as continuous Gaussian chains without an excluded volume effect. The only difference between A and B block is the external potential felt by different blocks. The key quantity is the propagator q(x, t), which is the statistical weight of a random walk chain that starts anywhere and ends at position x in t steps. It satisfies the modified diffusion equation in the one-dimensional form

$$\frac{\partial q(x,t)}{\partial t} = \frac{1}{6} \frac{\partial^2 q(x,t)}{\partial x^2} - U(x,t)q(x,t), \tag{1}$$

with the initial and boundary conditions

$$\lim_{t \to 0^+} q(x,t) = 1, \tag{2}$$

$$q\left(-\frac{L}{2},t\right) = q\left(\frac{L}{2},t\right) = 0.$$
 (3)

Compared with the homopolymer adsorption case [the external potential U(x) is a univariate function], the external potential of an ABA chain also depends on the contour variable *t* along the chain in the equation above. The equation resembles the time-dependent Schrödinger equation of wavefunction q(x, t), where the segment index *t* is an analog of time. A plot of the external field U(x, t) in the *x*-*t* plane is shown in Fig. 2. However, this diffusion equation cannot be solved analytically as a whole unless U(x, t) can be transformed into a function independent of *t*. For this reason, we have to express q(x, t) as a piece-wise function,

$$q(x,t) = \begin{cases} q^{(1)}(x,t), & t \in (0,N_{\rm A}], \\ q^{(2)}(x,t), & t \in (N_{\rm A},N_{\rm A}+N_{\rm B}], \\ q^{(3)}(x,t), & t \in (N_{\rm A}+N_{\rm B},N]. \end{cases}$$
(4)

Each piece  $q^{(j)}(x, t)$  (*j* = 1, 2, 3) satisfies the following equation:

$$\frac{\partial q^{(j)}(x,t)}{\partial t} = \frac{1}{6} \frac{\partial^2 q^{(j)}(x,t)}{\partial x^2} - U^{(j)}(x) q^{(j)}(x,t).$$
(5)

**FIG. 2.** A two-dimensional representation of the external field U(x, t), whose values are indicated in the corresponding domains.

The potential  $U^{(j)}(x)$  corresponding to a different piece of  $q^{(j)}(x, t)$  is given by

$$U^{(1)}(x) = U^{(3)}(x) = \begin{cases} -U_0, & x \in \left(-\frac{L}{2}, -\frac{d}{2}\right] \cup \left[\frac{d}{2}, \frac{L}{2}\right), \\ 0, & x \in \left(-\frac{d}{2}, \frac{d}{2}\right), \\ +\infty, & \text{otherwise,} \end{cases}$$
(6)

$$U^{(2)}(x) = \begin{cases} 0, & x \in \left(-\frac{L}{2}, \frac{L}{2}\right), \\ +\infty, & \text{otherwise.} \end{cases}$$
(7)

Now, the potential is only a function of x, which makes it possible to separate variables x and t in Eq. (5), and thus,  $q^{(j)}(x,t)$  can be written in the form of an eigenfunction expansion,

$$q^{(j)}(x,t) = \sum_{i} C_{i} q_{i}^{(j)}(x) e^{-E_{i}^{(j)}t},$$
(8)

where  $C_i$  are the combination coefficients determined by the initial condition. The eigenfunctions  $q_i^{(j)}(x)$  and eigenvalues  $E_i^{(j)}$  satisfy the "stationary Schrödinger equation,"

$$\left(-\frac{1}{6}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + U^{(j)}(x)\right)q_i^{(j)}(x) = E_i^{(j)}q_i^{(j)}(x). \tag{9}$$

By solving this equation, we may obtain  $q^{(j)}(x, t)$  expressed as a sum of series in terms of Eq. (8). The cutoff approximation is then applied to execute the sum in q(x, t) with finite terms.

We handle moderate adsorption strength with typical potential  $(-U_0 = -1.0 \text{ to} - 3.0)$  in this paper, which corresponds to the common case met in experiments. For the first piece  $q^{(1)}(x,t)$  with

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 $t = 0 \sim N_{\rm A}$ , we can solve for the eigenfunctions by substituting  $U^{(1)}(x)$  in Eq. (6) into Eq. (9). The result is as follows:

$$q_{i}^{(1)}(x) = \begin{cases} C_{i}' \sin m_{i}\left(x + \frac{L}{2}\right), & x \in \left[-\frac{L}{2}, -\frac{d}{2}\right], \\ C_{i}' \sin (m_{i}\delta) \frac{f_{i}(k_{i}x)}{f_{i}(k_{i}d/2)}, & x \in \left(-\frac{d}{2}, \frac{d}{2}\right), \\ -C_{i}' \sin m_{i}\left(x - \frac{L}{2}\right), & x \in \left[\frac{d}{2}, \frac{L}{2}\right], \end{cases}$$
(10)

where  $C'_i$  are the normalization coefficients of  $q_i^{(1)}(x)$ , satisfying

$$1 = \int \left(q_i^{(1)}(x)\right)^2 \mathrm{d}x.$$
 (11)

In Eq. (10), we have defined

$$f_i(x) = \begin{cases} \cosh(x), & i = 0, \\ \cos(x), & i = 1, 2, \dots, \end{cases}$$
(12)

and

$$m_i = \sqrt{6(U_0 + E_i^{(1)})},\tag{13}$$

$$k_i = \sqrt{6 |E_i^{(1)}|}.$$
 (14)

Note that  $m_i$  and  $k_i$  are related to the corresponding eigenvalues  $E_i^{(1)}$ . Combined with the continuity conditions at x = -d/2 (or x = d/2 equivalently), one obtains the following equations the eigenvalues must satisfy:

$$m_0 \cot(m_0 \delta) = -k_0 \tanh \frac{k_0 d}{2}, \qquad (15)$$

$$m_i \cot(m_i \delta) = k_i \tan \frac{k_i d}{2}, \quad i = 1, 2, 3 \dots$$
 (16)

In our study, we always fix  $\delta = 1$ . We have assumed that there is exactly one bounded state, that is to say, there is only one solution to Eq. (15). This assumption is valid when  $0.5 < U_0 < 3.7$  and  $\delta = 1$ . Thus,  $i = 1, 2, 3, \ldots$  represent the unbounded states. However, more bounded states will appear if  $U_0 > 3.7$ , which is not considered in this paper. The reason is that for the case of a strong enough adsorption ( $U_0 > 2.0$ ), almost all chains are adsorbed on the plates and the properties of the system gradually become unchanged, as we will see in the next section. The analytical solutions of these two transcendental equations is not accessible so we make approximations by means of series expansion and give the following approximate results for the eigenvalues  $E_0^{(1)}$  and  $E_1^{(1)}$ :

$$E_0^{(1)} = -U_0 + \frac{\left(\frac{3\pi}{4} - 1 + \sqrt{2 - \frac{\left(\frac{9\pi^2}{16} - \frac{3\pi}{2} - 1\right)}{3U_0}}\right)^2}{6\left(1 + \frac{1}{3U_0}\right)^2},$$
 (17)

$$E_1^{(1)} = \frac{-s + \sqrt{s^2 + 20}}{d^2}, \quad s = \frac{30 \tan \sqrt{6U_0}}{d\sqrt{6U_0}} + 5.$$
(18)

The above-mentioned approximations are confirmed to be highly accurate at moderate adsorption strength with  $1.0 < U_0 < 3.0$  via further testing, but note that they could become less accurate and even invalid under an extremely small or large adsorption energy. Therefore,  $q^{(1)}(x, t)$  can be written as

$$q^{(1)}(x,t) = C_0^{(1)} q_0^{(1)}(x) e^{-E_0^{(1)}t} + C_1^{(1)} q_1^{(1)}(x) e^{-E_1^{(1)}t} + r(x,t), \quad (19)$$

where the last term in the right side of Eq. (19) is

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$$r(x,t) = \sum_{i=2} C_i^{(1)} q_i^{(1)}(x) e^{-E_i^{(1)}t}$$
(20)

and  $C_i^{(1)}$  are the combination coefficients,

$$C_i^{(1)} = \int q_i^{(1)}(x) \mathrm{d}x. \tag{21}$$

The ground state corresponding to the first term in Eq. (19) is a bounded state that is mainly contributed by loop and bridge conformations. Under some assumptions, such as the case of strong adsorption and long chains, it is enough to only keep the ground state, which is called the ground state dominance approximation.<sup>30</sup> However, it shows poor performance in the description of nonadsorbed conformations on account of the assumptions that may not always hold. For moderate adsorption potential and separation between the two plates, our analysis shows that taking the first two terms into consideration is sufficient. The ground state basically represents the adsorbed state of polymer chains, while tails and free chains are reasonably described by the first excited state. The analytical solution obtained by two-state dominance approximation (the ground state and first excited state) is in very good agreement with the accurately numerical solution, except for the case of extremely weak adsorption at large separation.

The second piece of the propagator,  $q^{(2)}(x,t)$  with  $N_A < t < N_A + N_B$ , is exactly one-dimensional infinite potential well problem in quantum mechanics. The result is

$$q^{(2)}(x,t) = \sum_{n=0} C_n^{(2)} \sqrt{\frac{2}{L}} \cos \frac{(2n+1)\pi x}{L} e^{-E_n^{(2)}t}, \qquad (22)$$

where

$$E_n^{(2)} = \frac{(2n+1)^2 \pi^2}{6L^2}.$$
 (23)

In fact, retaining the initial two terms is sufficiently accurate for our analysis in most cases. The combination coefficients  $C_n^{(2)}$  in Eq. (22) can be determined from the initial condition  $q^{(2)}(x, N_A) = q^{(1)}(x, N_A)$ ,

$$C_n^{(2)} = \frac{\int q^{(1)}(x, N_{\rm A}) \sqrt{\frac{2}{L}} \cos \frac{(2n+1)\pi}{L} x \mathrm{d}x}{\mathrm{e}^{-E_n^{(2)} N_{\rm A}}}.$$
 (24)

Finally, similar to Eq. (19), the third piece is given by

$$q^{(3)}(x,t) \approx C_0^{(3)} q_0^{(1)}(x) e^{-E_0^{(1)}t} + C_1^{(3)} q_1^{(1)}(x) e^{-E_1^{(1)}t}, \quad (25)$$

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where  $C_i^{(3)}$  need to be determined from the condition  $q^{(3)}(x, N_A + N_B) = q^{(2)}(x, N_A + N_B)$ ,

$$C_i^{(3)} = \frac{\int q^{(2)}(x, N_{\rm A} + N_{\rm B}) q_i^{(1)}(x) \mathrm{d}x}{\mathrm{e}^{-E_i^{(1)}(N_{\rm A} + N_{\rm B})}}.$$
 (26)

#### **B.** Calculation of system properties

We have obtained the approximate analytical expression for the propagator q(x, t), a piece-wise function in the form of Eq. (4). With this quantity, all statistic information can be derived. The density for a symmetrical triblock chain of length N with its *t*th segment fixed at position x is proportional to q(x, t)q(x, N - t). Multiplying it by a normalizing factor, one finds the density of the *t*th segment at position x as

$$\rho(x,t) = \frac{N_c}{Z}q(x,t)q(x,N-t), \qquad (27)$$

where Z is the partition function of a single triblock copolymer chain in the system. Obviously, Z should be independent of t in light of its physical implication, and it is given by

$$Z = S \int q(x,t)q(x,N-t)dx = S \int q(x,N)dx, \qquad (28)$$

where S = V/L is the cross-sectional area of the system. Integrating  $\rho(x, t)$  with respect to *t* results in the concentration distribution of A or B segments,

$$\phi_{\rm A}(x) = 2 \frac{N_{\rm c}}{Z} \int_0^{N_{\rm A}} q(x,t) q(x,N-t) {\rm d}t, \qquad (29)$$

$$\phi_{\rm B}(x) = \frac{N_{\rm c}}{Z} \int_{N_{\rm A}}^{N_{\rm A}+N_{\rm B}} q(x,t)q(x,N-t){\rm d}t. \tag{30}$$

Furthermore, the canonical free energy of the system reads

$$F = -N_{\rm c} \ln Z + \ln N_{\rm c}!.$$
 (31)

Next, we turn to the conformation statistics of the triblock copolymers. For the joint segment connecting A and B blocks together, that is, the  $N_A$ -th segment and the symmetrical  $(N_A + N_B)$ th segment, the density distribution is the probability of finding that segment, given by

$$\rho(x, N_{\rm A}) = \frac{N_{\rm c}}{Z} q(x, N_{\rm A}) q(x, N_{\rm A} + N_{\rm B}). \tag{32}$$

This expression is the same for  $\rho(x, N_A + N_B)$ . Let  $R_{g,A}$  be the radius of gyration of one A block. In order to describe the conformations of adsorbed polymer chains, the region from the left (right) plate to the location with vertical distance less than  $\delta + R_{g,A}$  is defined as the left (right) adsorbed boundary layer, and the rest of the region in the system is defined as the middle layer. If a joint segment of a polymer chain is located in the boundary layer, the corresponding end block close to this joint segment will be regarded as adsorbed on the plate. Then, we label the joint segments  $t = N_A$  and  $t = N_A + N_B$  as I and II, respectively. They are, in fact, indistinguishable for symmetrical triblock copolymers. Integrating the (unnormalized) density of the joint segment I over different regions, we then obtain

$$P(I_{left}) = \frac{1}{P_{tot}} \int_{-L/2}^{-d/2+R_{g,A}} \rho(x, N_A) dx,$$
 (33)

$$P(I_{\rm mid}) = \frac{1}{P_{\rm tot}} \int_{-d/2+R_{\rm g,A}}^{d/2-R_{\rm g,A}} \rho(x, N_{\rm A}) dx,$$
(34)

$$P(I_{\text{right}}) = \frac{1}{P_{\text{tot}}} \int_{d/2 - R_{\text{gA}}}^{L/2} \rho(x, N_{\text{A}}) dx, \qquad (35)$$

where  $P(I_{left})$ ,  $P(I_{mid})$ , and  $P(I_{right})$  are the probabilities of the joint segment I situated in the left boundary layer, middle layer, and right boundary layer, respectively, and

$$P_{\rm tot} = \int_{-L/2}^{L/2} \rho(x, N_{\rm A}) dx$$
 (36)

is a normalizing factor. Next, we need to determine the probability density distribution of the joint segment II. If the joint segment I is constrained inside the left boundary layer, the corresponding propagator will become<sup>34</sup>

$$\tilde{q}(x, N_{\rm A}) = \begin{cases} q(x, N_{\rm A}), & x \in \left(-\frac{L}{2}, -\frac{d}{2} + R_{\rm g,A}\right), \\ 0, & \text{otherwise.} \end{cases}$$
(37)

Taking Eq. (37) as the initial condition and solving the modified diffusion equation Eq. (5) for j = 2 as before, we can obtain the solution  $\tilde{q}(x, t), t \in (N_A, N_A + N_B]$ . It is the statistical weight of a chain that starts anywhere and ends at position x after t steps as long as joint I stays inside the left boundary layer,

$$\tilde{q}(x,t) = \sum_{n=1,\text{odd}} \tilde{C}_n \sqrt{\frac{2}{L}} \cos \frac{n\pi x}{L} e^{-E_n^{(2)}t} + \sum_{n=2,\text{even}} \tilde{C}_n \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} e^{-E_n^{(2)}t}, t \in (N_A, N_A + N_B], \quad (38)$$

where  $\tilde{C}_n$  can be determined by the initial condition in Eq. (37). Thus, the density distribution (unnormalized conditional probability) of joint segment II can be expressed as

$$\tilde{\rho}(x, N_{\rm A}+N_{\rm B}) = \frac{N_{\rm c}}{Z} \tilde{q}(x, N_{\rm A}+N_{\rm B})q(x, N_{\rm A}). \tag{39}$$

Similarly, integrating  $\tilde{\rho}(x, N_{\rm A} + N_{\rm B})$  over different regions gives the conditional probabilities of the joint segment II confined inside the left boundary layer, the middle layer, and the right boundary layer, given that joint segment I stays in the left boundary layer,

$$P(\mathrm{II}_{\mathrm{left}} \mid \mathrm{I}_{\mathrm{left}}) = \frac{1}{\tilde{P}_{\mathrm{tot}}} \int_{-L/2}^{-d/2 + R_{\mathrm{gA}}} \tilde{\rho}(x, N_{\mathrm{A}} + N_{\mathrm{B}}) \mathrm{d}x, \qquad (40)$$

$$P(\mathrm{II}_{\mathrm{mid}} \mid \mathrm{I}_{\mathrm{left}}) = \frac{1}{\tilde{P}_{\mathrm{tot}}} \int_{-d/2 + R_{\mathrm{g},\mathrm{A}}}^{d/2 - R_{\mathrm{g},\mathrm{A}}} \tilde{\rho}(x, N_{\mathrm{A}} + N_{\mathrm{B}}) \mathrm{d}x, \qquad (41)$$

$$P(II_{right} | I_{left}) = \frac{1}{\tilde{P}_{tot}} \int_{d/2-R_{gA}}^{L/2} \tilde{\rho}(x, N_{A} + N_{B}) dx, \qquad (42)$$

$$\tilde{P}_{\text{tot}} = \int_{-L/2}^{L/2} \tilde{\rho}(x, N_{\text{A}} + N_{\text{B}}) \mathrm{d}x.$$
(43)

On the other hand, if joint segment I is confined in the middle layer, the corresponding propagator is given by

$$\tilde{\tilde{q}}(x, N_{\rm A}) = \begin{cases} q(x, N_{\rm A}), & x \in \left(-\frac{d}{2} + R_g, \frac{d}{2} - R_g\right), \\ 0, & \text{otherwise.} \end{cases}$$
(44)

In the same way, we can arrive at the density distribution of joint segment II, given that joint segment I stays in the middle layer  $\tilde{\rho}(x, N_{\rm A} + N_{\rm B})$ , as well as the corresponding conditional probabilities, such as  $P(\text{II}_{\rm left} \mid \text{I}_{\rm mid})$  and  $P(\text{II}_{\rm mid} \mid \text{I}_{\rm mid})$ .

Taking the symmetry of the left and right boundary regions into consideration, one may finally derive the proportion of different conformations of polymer chains, including loops, bridges, tails, and free chains,

$$P(\text{loop}) = 2P(I_{\text{left}})P(II_{\text{left}} \mid I_{\text{left}}), \qquad (45)$$

$$P(\text{bridge}) = 2P(I_{\text{left}})P(II_{\text{right}} \mid I_{\text{left}}), \qquad (46)$$

$$P(\text{free}) = P(I_{\text{mid}})P(II_{\text{mid}} | I_{\text{mid}}), \qquad (47)$$

$$P(\text{tail}) = 2P(I_{\text{left}})P(II_{\text{mid}} \mid I_{\text{left}}) + 2P(I_{\text{mid}})P(II_{\text{left}} \mid I_{\text{mid}}).$$
(48)

Furthermore, the validity of these approximations we made above for the analytical treatment is verified by our numerical calculations, in which the modified diffusion equation is evaluated by using the Crank–Nicolson implicit difference method.

#### **III. RESULTS AND DISCUSSION**

In the following, we will present the results for segment concentration distributions, chain conformations, and interaction potential between two parallel plates based on the above-mentioned analytical expressions and discuss how the controlling parameters influence these properties.

#### A. Segment concentration distribution

The cross-sectional area of the system *S* is set as  $50 \times 50$ . We assume that there are ten triblock copolymer chains of length N = 100 confined in the system and the length of A blocks  $N_A$  is 10, which corresponds to a situation of dilute solution. Figure 3 shows the spatial distributions of A and B segment concentrations at different adsorption energies  $U_0$  using Eqs. (29) and (30), where the separation between the two plates is fixed as L = 12. It can be found that the concentration of A segments displays two symmetrical sharp peaks near the surfaces on both sides because of the attraction between A blocks and the plates. Due to the chain connectivity, B segments tend to concentrate on the position a little far from the plate on the corresponding side. Instead, there appears to be a local concentration minimum of B segments in the middle of the two plates.



**FIG. 3.** The effect of adsorption energy  $U_0$  on the segment concentration distribution of A (solid) and B (dashed) segments, with  $N_c = 10$ , N = 100,  $N_A = 10$ , L = 12,  $\delta = 1$ , and S = 2500.

x

When the adsorption energy becomes as low as the thermal energy (weak adsorption), i.e.,  $U_0 = 1.0$ , a local maximum of A segment concentration will appear in the middle of the two plates because some chains become free. Meanwhile, because polymers are depleted by the impenetrable plates, these free dangling chains tend to concentrate in the middle of the two plates. At the same time, the two concentration maxima of B segments become less distinct and gradually merge. As the adsorption gets stronger, the two symmetrical sharp peaks of A segment concentration shift gradually toward the plate surfaces and more A segments are adsorbed on the surfaces. At the same time, the local maximum in the middle will gradually disappear. For the case of considerably strong adsorption ( $U_0 > 2.0$ ), the concentration distribution of A segments is almost independent of  $U_0$ , implying a nearly complete adsorption of A segments on the surfaces. On the other hand, the concentration profile of B segments undergoes relatively small changes when  $U_0 \ge 1.5$  because of the absence of attraction between B segments and surfaces.

#### B. Chain conformations

In this part, we discuss the probability distributions of different chain conformations in terms of Eqs. (45)-(48) derived in Sec. II. The influence of different factors, including the separation between the two plates, adsorption energy, and block lengths, on the conformations of confined triblock copolymer chains is analyzed in the tail conformation.

Figure 4 shows the probabilities of loop, bridge, free, and tail conformations as functions of the separation L between the two plates at different adsorption energies. When the two plates are very close to each other, triblock chains stay in a compressed and entropically unfavorable state. The great majority of end A blocks of polymers are thus adsorbed on the surface to lower the interaction energy so as to form loops or bridges. The proportion of loop and bridge conformations is fairly equal since the chance is equal for one A block to be adsorbed on each surface, given that the other A block of the chain has been adsorbed on one surface. Generally, with an increase in L, the proportion of bridge conformation drops gradually



**FIG. 4.** Probabilities of (a) loop, (b) bridge, (c) free, and (d) tail conformations, as functions of separation between the two plates, for N = 100,  $N_A = 10$ , and  $\delta = 1$  and for various values of  $U_0$  ranging from 1.0 to 3.0.

before the bridges disappear [Fig. 4(b)]. At large separations, loop or tail and free conformations, will dominate. Their relative proportion depends on the strength of adsorption. In the following, we will discuss the effect of the adsorption energy.

We can roughly divide the adsorption into strong adsorption and weak adsorption on the basis of how the conformations change with *L*. When  $U_0$  increases to about 1.5 or larger, we may call it strong adsorption regime. In this case, the polymer chains almost adopt only the loop/bridge conformations and the free conformation is negligible. At a very short separation *L*, both loop and bridge conformations decrease slightly with the increase in *L*, as a few of them are converted into tails and free chains to get more conformational entropy. On increasing the separation between the two plates further, the bridging chain will be gradually stretched, giving rise to the desorption of one adsorbed end block. A small fraction of the dangling A blocks forms tails. However, most dangling A blocks tend to be adsorbed on the same plate as another block from the same chain at equilibrium, forming the loop conformation. Thus, loops dominate at large separations in strong adsorption regime. The case of small adsorption energy (such as  $U_0 \approx 1.0$ ) belongs to the weak adsorption. As the free energy reduced by adsorption is insufficient to compensate the entropy loss, the adsorbing A blocks are inclined to be desorbed and stay inside the middle space when the plate separation increases. With the increase in *L*, the proportion of loops decreases monotonically. The bridges decrease even faster, while the proportion of free chains increases significantly. On the other hand, tail conformation first increases and then decreases with increasing *L* because the translational entropy of the whole chain promotes the tendency of chains to detach from the adsorbed state at large separations.

Next, we investigate how the chain conformations are affected by the length of adsorbing A blocks, which is an important controlling factor in experiments. For doing so, we vary the length  $N_A$  from 3 to 10, while keeping  $U_0$  fixed at 2.0 and  $N_B$  at 80. The results are shown in Fig. 5. Similar to the case of weak adsorption regime, the polymer chains are liable to be desorbed when A blocks are short. Basically, lengthening adsorbing A blocks plays an analogous but not an equivalent role in increasing the adsorp-



FIG. 5. Probabilities of (a) loop, (b) bridge, (c) free, and (d) tail conformations, as functions of separation between two plates, for  $U_0 = 2.0$ ,  $N_B = 80$ ,  $\delta = 1$ , and various values of  $N_A$ .



**FIG. 6.** Probabilities of (a) loop and (b) bridge conformations as functions of separation between two plates, for  $U_0 = 2.0$ ,  $N_A = 10$ ,  $\delta = 1$ , and various values of  $N_B$ . The abscissas of the diamond symbols on the curves correspond to the separations where the interaction potential curves in Fig. 9 reach their own minima. The inset shows the probability of the bridge conformation as a function of  $L/R_B$ .

tion energy. The longer the A blocks are, the more loops and bridges will form and the less tails and free chains there will be. For short A blocks with  $N_A = 3$ , increasing the separation between the two plates leads to a quick decrease in loop and bridge conformations, accompanied by the obvious raising of free conformation. However, when  $N_A \ge 4$ , the loop fraction displays non-monotonic variation with the separation. It increases significantly with the increase in *L* at medium separation [Fig. 5(a)], followed by a slight decrease at small separation. The proportion of various conformations remains unchanged at very large separations. It is noted that the bridge conformation has an interesting feature, i.e., the separation where bridges almost disappear is nearly independent of  $N_A$ .

The length of the middle non-adsorbing B blocks has an important influence on the conformations. Figure 6 shows the effect of separation between the two plates on the probabilities of loop and bridge conformations for a variety of lengths of B blocks in strong adsorption regime. Longer B blocks allow bridges to survive at larger separation between the two plates by changing bridge-loop conversion. For the bridge conformation, we rescale L by the end-to-end distance of B blocks  $R_{\rm B}$ , as illustrated in the inset of Fig. 6(b). Here,  $R_{\rm B} = N_{\rm B}^{1/2}$ . These curves for different  $N_{\rm B}$  values can overlap well. When the two plates are separated further, the entropy loss caused by stretching B blocks of bridges should be responsible for the significant decrease in the bridging fraction for  $L > R_{\rm B}$ . Denote  $L_0$  as the separation at which distance the probability of bridges falls to 0.01, and then, the bridge conformation will be negligible once the separation is beyond  $L_0$ . Interestingly, we find that  $L_0$  is proportional to approximately  $2R_{\rm B}$ . It is also worth noting that the effect of  $N_{\rm B}$  on the loop conformation is mainly attributed to the change in bridging fraction. Our further analysis shows that the length of non-adsorbing B blocks has a tiny effect on the proportion of tails and free chains.



**FIG. 7.** Interaction potential curves as a function of separation between two plates for various adsorption energies via analytical (solid curves for  $U_0 = 1.0, 1.1, 1.2, 1.5$ , and dotted for  $U_0 = 2.0$ ) and numerical ("×" symbols) methods, for  $N_c = 10$ ,  $\delta = 1$ ,  $N_A = 10$ ,  $N_B = 80$ , and S = 2500.

#### C. Interaction potential

The interaction potential curves of the system will be investigated in this part by using Eq. (31). The interaction potential is defined as  $W = F(L) - F(\infty)$ , where F(L) is the free energy of the system at distance L from one plate to another.  $F(\infty)$ denotes the free energy for  $L \rightarrow \infty$  and it is replaced by F(L = 100), obtained from strictly numerical solutions in the following study. Figures 7–9 show the effect of the adsorption energy, length of adsorbing A block, and length of the non-adsorbing B block on the interaction potential of the system containing ten polymer chains, respectively. For comparison, both analytical and numerical methods are employed. We found that the analytical results are in good agreement with the numerical ones.



**FIG. 8.** Interaction potential curves as a function of separation between the two plates for various adsorbing A block lengths via analytical (solid curves for  $N_A = 3, 4, 5, 10$ , and dotted for  $N_A = 20$ ) and numerical ("×" symbols) methods, for  $N_c = 10$ ,  $\delta = 1$ ,  $U_0 = 2.0$ ,  $N_B = 80$ , and S = 2500.



**FIG. 9.** Interaction potential curves as a function of separation between the two plates for various non-adsorbing B block lengths via analytical (solid curves) and numerical ("×" symbols) methods, for  $N_c = 10$ ,  $\delta = 1$ ,  $U_0 = 2.0$ ,  $N_A = 10$ , and S = 2500. The inset shows the location of the potential minimum  $L_m$  as a function of the end-to-end distance of B block  $R_B$ . The dashed line is a diagonal line.

As shown in Fig. 7, the system has a high repulsive potential at small separation between the two plates due to strong compression of the confined polymers. The interaction potential decreases with an increase in the adsorption energy and then holds unchanged in the strong adsorption regime with  $U_0 \ge 1.5$ . It is noted that our system contains a constant number of polymer chains at any separation, which corresponds to the case of constrained adsorption between two large colloidal particles, usually happening in experiments. Therefore, the interaction potential does not equal to zero at large separation (such as L = 25) since it always decreases gradually with the separation. When the adsorption potential is weak, the interaction potential curve should always decrease monotonically. As shown in the previous section, tails and free chains will be the dominant conformations as L is not too small so that the bridging attraction is too weak to offset the entropy-induced repulsion, and meanwhile, the translational entropy of the free chains will always increase with an increase in the system volume. Once the adsorption energy reaches the critical value of  $U_0 = 1.1$ , the dominant conformations become loops and bridges at medium distances. In this case, a minimum of the interaction energy appears at  $L \approx 10$ , indicating an attractive interaction arising from the dominance of bridging interaction over the repulsive force. This potential well shifts slightly to smaller L and becomes deeper as the adsorption energy increases before  $U_0$  enters strong adsorption regime. Our analytical calculation (solid curves) is in good agreement with a strict numerical solution at a moderate adsorption energy.

The interaction potential curves of varying A block lengths (Fig. 8) resemble those of the changing adsorption energy in trend. The potential well appears only as  $N \ge 4$ , and it becomes deeper with lengthening A blocks and eventually holds unchanged when  $N_A$  reaches about 10. Meanwhile, the interaction potential minimum is located at L = 10 irrespective of the  $N_A$  values. The results also show that the accuracy of our analytical treatment is very high.

Figure 9 shows the effect of B block length on the interaction potential curves with parameters of  $U_0 = 2.0$  and  $N_A = 10$ . In all cases, the analytical prediction is pretty accurate. At short separation, the repulsive potential decreases rapidly with the decrease in B block length because short chains lose less conformational entropy when compressed. The location of the potential well  $L_m$  moves toward larger L values as B blocks get longer, and this separation is proportional to the size of B blocks ( $L_m \approx R_B$ , see the inset). Instead, the depth of the potential well does not depend on  $N_B$ . By careful determination to the location  $L_m$  of the minima, we found that at these separations, the bridge conformation proportions are almost the same [the diamonds shown in Fig. 6(b)], and it corresponds to the onset of the sharp decrease in bridges. Based on the above-mentioned argument, the minima of the interaction potential should depend on the content of bridges, and the system will lose the bridge conformation quickly once the separation between the two plates is larger than  $L_m$ .

#### **IV. CONCLUSION**

In summary, we present an analytical approach to treating the adsorption problem of ABA triblock copolymers confined between two parallel plates in a  $\theta$  solvent. We solve the modified diffusion equation by using series expansion and provide the expression of the propagator q(x,t) as a piece-wise function. Proper truncation is applied to the series expression of each piece of q(x,t), producing accurate enough results compared with numerical computations. Based on the analytical expressions, the system properties, including segment concentration distribution, chain conformations, and interaction potential between the two plates are then derived. We investigate the effect of the separation between the two plates, adsorption potential, and the length of A and B blocks on these system properties and find good agreement between the analytical and numerical results.

Lengthening adsorbing A blocks exhibits a similar influence as increasing the surface affinity. The strong adsorption and long adsorbing blocks favor the formation of loops and bridges, whereas more tails and free chains appear in the case of weak adsorption and short A blocks. On the other hand, when the adsorption energy per segment adsorbed is relatively small, the proportion of the adsorbed states exhibits less enhancement by lengthening A blocks compared to strengthening the adsorption potential. The reason is that the adsorption of longer A blocks is a mixed blessing: They benefit more from the adsorption energy but suffer more from entropy loss, which leads to a non-equivalent increase in the total adsorption energy gained.

Long A blocks and strong adsorption potential are in favor of forming adsorbed conformations, including bridges. However, it is just longer B blocks that allow bridges to survive at larger separations between the two plates. The bridging fraction is mainly a function of  $L/R_{\rm B}$ . For not large separation between the two plates  $L < R_{\rm B}$ , with increasing separation a fraction of A segments tends to be desorbed from surfaces to gain entropy rather than adsorption energy, giving rise to a gradual decrease in the bridging fraction. For  $L > R_{\rm B}$ , the entropy loss caused by stretching is responsible for the significant decrease in the bridging fraction. The attractive interaction potential between the two plates may appear to be attributed to the formation of large amount of bridges. The depth of the potential well depends on the adsorption energy and A block length, while the location of the potential minimum  $L_{\rm m}$  is approximately equal to  $R_{\rm B}$ .

Under certain conditions, such as near the  $\theta$  temperature or in semidilute solutions,<sup>35</sup> the excluded volume effect could be neglected, which satisfies the assumption of the Gaussian chain model. In the above-mentioned analytical treatment, we assume  $\chi_{AB}$  = 0. However, the different short range interaction between A and B segments may induce non-zero  $\chi_{AB}$  parameter, which will play an additional role in the conformation of copolymers. The repulsive interaction between A and B segments is expected to result in more bridges and tails and thus may strengthen the attractive force between the two plates, whereas the attractive interaction between A and B segments may favor the formation of loop conformation and will weaken the attractive force between two plates. This analytical model, despite its ignorance of other interactions between colloidal particles, provides important physical insights into the adsorption of triblock copolymers on surfaces and serves as a simple and quantitative reference for the practical system.

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#### AUTHOR DECLARATIONS

#### Conflict of Interest

The authors have no conflicts to disclose.

#### Author Contributions

**Ji-Yu Chen**: Conceptualization (supporting); Data curation (equal); Formal analysis (lead); Investigation (lead); Methodology (equal); Software (equal); Visualization (lead); Writing – original draft (lead). **Lu-Wei Zhong**: Data curation (equal); Investigation (supporting); Resources (equal); Software (supporting); Writing – original draft (supporting). **Er-Qiang Chen**: Conceptualization (supporting); Funding acquisition (equal); Project administration (equal); Supervision (supporting); Validation (equal); Writing – review & editing (equal). **Shuang Yang**: Conceptualization (lead); Formal analysis (equal); Funding acquisition (lead); Methodology (lead); Project administration (equal); Resources (equal); Supervision (lead); Validation (equal); Writing – review & editing (equal).

#### DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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