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Simulation Study on Translocation of Confined Chain Through Interacting Nanopore

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The translocation of a confined polymer chain through an interacting nanopore has been studied using two-dimensional bond fluctuation model with Monte Carlo dynamics. For different pore-polymer interaction, the average escaping time $\langle\tau_{\mathrm{esc}}\rangle$ of the polymer chain through the nanopore, increases roughly linearly with the chain length and the nanopore length, respectively. However, the large repulsive and attractive pore-polymer interaction adds the difficulty of the monomers of the chain entering and leaving the nanopore, respectively, leading to the nonmonotonical dependence of $\langle\tau_{\mathrm{esc}}\rangle$ on the pore-polymer interaction. The detailed translocation dynamics of the chain through the interacting nanopore is investigated too.

Key words: Monte Carlo simulation, Polymer translocation, Pore-polymer interaction, Escaping time

I. INTRODUCTION

The translocation of biopolymers through nanometerscale pores is one of the most crucial processes in biology, such as DNA and RNA translocations across nuclear pores, protein transport through membrane channels, and virus injection [1–3]. Moreover, translocation processes might eventually prove useful in various technological applications, such as rapid DNA sequencing [4, 5], gene therapy, controlled drug delivery, *etc.* [6]. In addition to its biological relevance, the translocation dynamics is also a challenging topic in polymer physics. Accordingly, the polymer translocation has attracted a considerable number of experimental [7–10], theoretical [11–15], and numerical researchers [16–19].

When the size of chain molecule is larger than that of the cross section of nanopore, the polymer chain suffers a free energy barrier due to the loss of a great number of available configurations [11, 12], so that most polymer translocation phenomena require a driving force, such as ratchet mechanisms [20, 21], electric fields [4, 14, 22–24], chemical potential gradients [19, 25], and selective adsorption on one side of the membrane [26]. However, various groups have revealed that a polymer chain can escape spontaneously from a confined space to the other larger space through a nanopore [12, 27–30]. In our previous work [29, 30], the translocation of a single self-avoiding walking (SAW) chain, confined in a finite size

square through a non-interacting nanopore, has been studied using Monte Carlo simulation method. The results indicate that the whole translocation process consists of two stages. In the first trapping stage, the chain experiences a period of time, τ_{trap}, to overcome the free energy barrier. In the second escaping stage, the chain successfully escapes through the nanopore instead of totally pulling back to the donor square, and the consumed time is designated as escaping time τ_{esc}. So, the total translocation time $\tau=\tau_{\mathrm{trap}}+\tau_{\mathrm{esc}}$. However, τ is found to depend non-monotonically on the polymer chain length N, which is attributed to the excluded volume effect.

On the other hand, Muthukumar has presented that the interaction between the polymer and pore can affect the translocation process of the chain significantly [12]. Previously, the influence of the pore-polymer interaction on the trapping stage of the translocation of a single self-avoiding walking SAW polymer chain in a confined square to another lager square has been studied. The free energy barrier for the chain to overcome during the trapping stage is found to vary linearly with the polymer-pore interaction, resulting in the exponential dependence of the average trapping time, $\langle\tau_{\mathrm{trap}}\rangle$, on the polymer-pore interaction [31]. In this work, the effects of the pore-polymer interaction on the escaping stage of the translocation of the chain is examined using two-dimensional bond fluctuation model (BFM) with Monte Carlo dynamics. The dependence of $\langle\tau_{\mathrm{esc}}\rangle$ on the polymer chain length, nanopore length, and pore-polymer interaction is investigated. Further study on the detailed translocation dynamics of the chain is pre-

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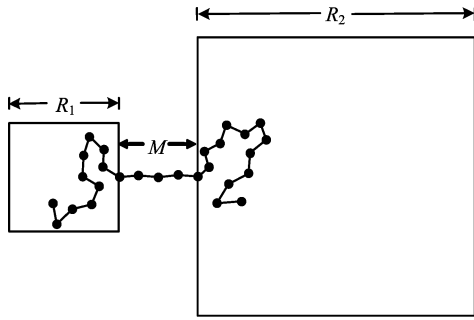*Author to whom correspondence should be addressed. E-mail: yjxie@ustc.edu.cn

FIG. 1 Schematic representation of a N-monomer polymer chain in the process of the translocation through a nanopore of length M from the confinement. The nanopore is so narrow that the "hairpin" translocation is forbidden.

sented to investigate the effect mechanism of the pore-polymer interaction on the translocation of the chain.

II. MODEL AND SIMULATION METHOD

The two-dimensional BFM combined with single-segment Monte Carlo moves was used in our simulation, since the excluded volume effect plays an important role on the static and dynamical properties of confined polymer chain in the lower dimension [32]. Two square lattice spaces with different sizes R_1=30 and R_2=800 are connected by a nanopore of length M. The nanopore is narrow enough so as to ensure that the polymer chain was stretched out in the nanopore (Fig.1).

A chain that consists of N monomers is initially placed in the donor square (of size R_1) with one end of which was positioned at the pore entrance. The interaction between monomers and that between monomer and surface are supposed to be self-avoiding. The chain is then allowed to reach an equilibrium conformation using the standard Monte Carlo method, but with the constraint that the first monomer, placed at the pore entrance, is fixed. This constraint makes the chain kept in the donor space during the relaxation.

Once the chain is in the equilibrium conformation, the first monomer at the pore entrance is released from its constraint and the simulation of the polymer chain moving through the pore begins. When monomers are inside the pore, the average interaction energy per monomer is taken as E. The reduced interaction $\varepsilon=E/k_BT$ is used in the work with the Boltzmann constant k_B and the temperature T. The trial move will be accepted with a probability $p=\min(1, e^{-\Delta E})$ if the self-avoidance is satisfied. Here ΔE is the energy change for each trial move. The time unit is one Monte Carlo step (MCS) during which N trail movements are attempted. In this woork, we put aside the question of how the chain first enters the nanopore, instead focusing, on the dynamics once one end has been inserted. So, the first monomer is not allowed to go back to the donor space

during the translocation.

The typical motion of the polymer chain viewed in our simulation is as follows. Once the first monomer at the entrance of the pore is loosed, the chain continues to perform its conformational changes inside the donor square. After a certain time, the front end of the chain spills into the nanopore and quickly arrives at the receipt square. However, this step does not necessarily lead to a successful translocation in spite of the fact that the monomer density is higher in the donor. The free energy barrier arising from the losing of chain conformation will pull the chain back into the nanopore. The chain will undergo back and forth motion if the numbers of monomer entering the receipt square is smaller than a critical number. In the end, when enough monomers above the critical numbers are pushed inside the recipient square by a sequence of random events, the chain will transport into the receipt square and a successful translocation occurs. The elapsed time for the final successful escape is named escaping time τ_{esc}. In this work, all data are averaged over at least 10^3 independent runs. And, the standard statistical error is less than 5%.

III. SIMULATION RESULTS AND DISCUSSION

As presented above, Fig.2(a) presents the average escaping time, $\langle \tau_{esc} \rangle$, against the polymer chain N for different pore-polymer interaction ε. Here the pore length is fixed at M=6. It can be seen that, for different ε, $\langle \tau_{esc} \rangle$ increases linearly with N. As noted by de-Gennes, the free energy per chain confined inside a square of size R_1 is

$$F \approx \frac{k_B T N}{R_1^{1/\nu}} \qquad (1)$$

where ν is the exponent defining the N dependence of the radius of gyration R_g ($R_g \approx N^\nu$) of the chain in the absence of any confinement [34]. So, the free energy of the chain increases with N, leading to a faster translocation. To address this issue, we calculate the average escaping velocity which issimply described that the length of the nanopore plus the polymer length is divided by the escaping time,

$$\bar{v} = \frac{L_{chain} + M}{\langle \tau_{esc} \rangle}$$
$$\simeq \frac{(N-1)l_{av} + M}{\langle \tau_{esc} \rangle} \qquad (2)$$

where l_{av} is the average bond length for our simulation [32]. It can be seen that, with the increase of N, the translocation of the chain becomes faster (Fig.2(b)). Whereas, the distance for the escape of the chain increases with N. The consequence of these two factors is that $\langle \tau_{esc} \rangle$ increases linearly with N (Fig.2(a)).

On the other hand, from Fig.2(a) it can be seen that for strong attractive pores as well as repulsive pores
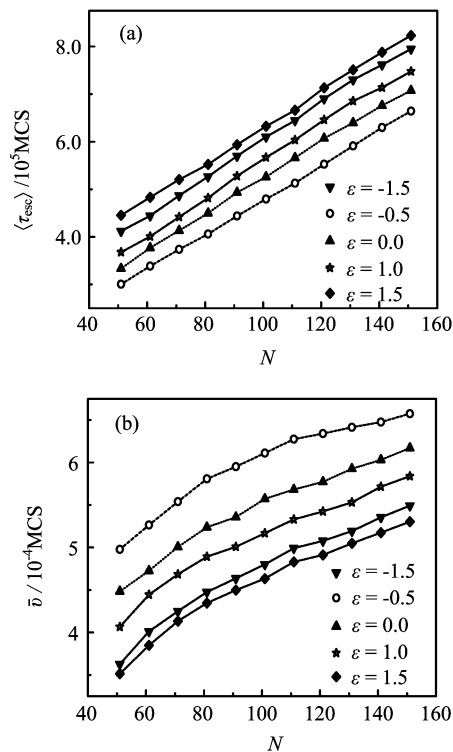
FIG. 2 N dependence of (a) the average escaping time $\langle \tau_{esc} \rangle$ and (b) the average escaping velocity $\bar{v}$ on the length of the nanopore M=6 for different interaction ε.
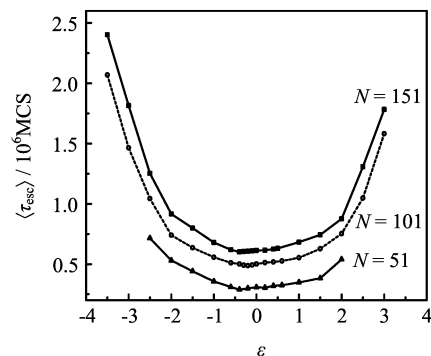

FIG. 3 The dependence of the average escaping time $\langle \tau_{esc} \rangle$ on the interaction ε for systems with different chain length N. The nanopore length M=6.
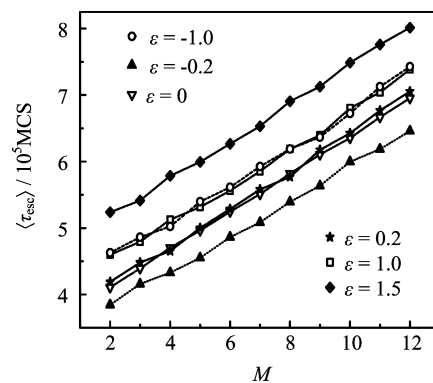

FIG. 4 The average escaping time $\langle \tau_{esc} \rangle$ plotted against the length of nanopore M for different interaction ε. The chain length N=101.

($|\varepsilon| \gg 0$) the average escaping time $\langle \tau_{esc} \rangle$ is larger than that of weak or non-interacting pores. To clarify the effect of ε on $\langle \tau_{esc} \rangle$, we present the dependence of $\langle \tau_{esc} \rangle$ on the interaction ε (Fig.3). As can be seen, for strong attractive or repulsive pores ($|\varepsilon|$ is large), $\langle \tau_{esc} \rangle$ increases rapidly with increasing $|\varepsilon|$. This means that the translocation of chain is very sensitive to the pore-polymer interaction ε if $|\varepsilon|$ is large. For the translocation of multiple chains from a concentrated region through an interacting nanopore, the average escaping time decreased monotonically with increasing the interaction ε [33], which is quite different from the translocation of a single chain illustrated in Fig.3. This difference may be attributed to the inter-chain interaction of multiple chains. On the other hand, for a single chain translocation through a nanopore, the increase of the escaping time of the chain with increasing interaction ε when $\varepsilon > 0$ can be seen, though it is not obvious. Unfortunately, in such an occasion, the single polymer chain simulated by Luo is very difficult to enter the pore [33], the simulation result for strong repulsive interaction cannot be obtained accordingly. It should be noted that, for each N, a weak attractive pore-polymer interaction is helpful for the translocation though this effect is not remarkable. The possible explanation will be presented below.

We now turn out to investigate how the escaping time $\langle \tau_{esc} \rangle$ varies with the M. For the same N, with the increase of M, the free energy of the chain keeps constant, and the distance for the chain translocation becomes longer, leading to the increase of $\langle \tau_{esc} \rangle$. The simulation results validate our above analysis that $\langle \tau_{esc} \rangle$ increases roughly linearly with increasing M (Fig.4).

To understand the effect of the interaction on the translocation of the chain, we investigate the detailed translocation dynamics of the chain. The number of the monomers having passed the entrance of the nanopore n_1 during the translocation, for three different interactions ε=-2.0, 0, and 2.0, is recorded (Fig.5).

Obviously, the trapping stage of the chain for systems with different pore-polymer interactions can be distinguished from each other. For strong attractive interactions, *e.g.* ε=-2.0, the chain almost starts the escaping process immediately just experiencing the trapping stage for a very little time (Fig.5(a)). For a non-interacting pore, ε=0, or a weak attractive as well as repulsive pore (not shown), the chain experiences a few trial events before a successful escaping process and, the trapping time is longer (Fig.5(b)). However, for strong repulsive interactions, *e.g.* ε=2.0, the chain undergoes many trial escaping events before the final successful translocation, and the trapping time becomes much longer (Fig.5(c)). During the second stage, the
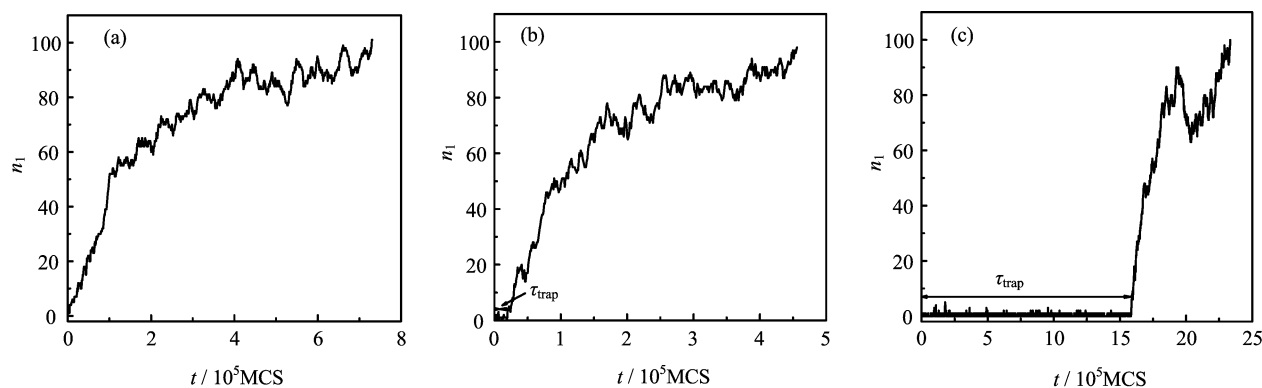
FIG. 5 The variation of the monomer number having passed the entrance of the nanopore, n_1, with the simulation time t for different pore-polymer interaction ε. $M=6$. It should be noted that for different ε the time scale is also different. (a) $\varepsilon=-2.0$, (b) $\varepsilon=0$, and (c) $\varepsilon=2.0$.

systems with different interactions show similar behaviors, and the only difference is $\tau_{\rm esc}$. $\tau_{\rm esc}$ increases with increasing $|\varepsilon|$. For strong repulsive-interacting pores, the monomers of the chain are difficult to enter the pore, leading to the increase of the escaping time of the chain. For strong attractive-interacting pores, the monomers are easy to enter the nanopore, whereas it is very difficult for them to leave the nanopore and enter the receipt space, resulting in the increase of the escaping time accordingly. However, a weak attractive interaction depresses the free energy barrier of the monomers entering the nanopore with increasing little difficulty for them to leave the nanopore. Therefore, the translocation becomes faster (Fig.3).

IV. CONCLUSION

We have investigated the translocation of a single polymer chain confined in a finite size square through an interacting nanopore to a lager size square using two-dimensional bond fluctuation model (BFM) with Monte Carlo simulation. We examined the influence of the pore-polymer interaction, chain length, and pore length on the escaping stage of the translocation of the chain through an interacting pore. For different pore-polymer interaction ε, the average escaping time of the chain, $\langle\tau_{\rm esc}\rangle$, increases roughly linearly with the chain length N as well as the length of nanopore M. However, with the increase of ε, $\langle\tau_{\rm esc}\rangle$ first decreases then increases rapidly again, indicating that the translocation of the chain is very sensitive to the interaction. The detailed translocation dynamics of the chain through the interacting nanopore is also investigated. The simulation results indicate that the large repulsive pore-polymer interaction adds the difficulty of the monomers of the chain entering the nanopore. However, the chain will spend a considerable amount of time to leave a strong attractive nanpore. That is why the escaping time of the chain changes nonmonotonically with the pore-polymer interaction.

Due to the larger size of the receipt square than the contour length of the chain, it can be regarded as an infinite space. However, if the size is comparable with the radius of the chain, the receipt square will affect the translocation process. On the other hand, different size of the donor will influence this process since the free energy of the confined chain is related to it. Our further work will focus on the influence of the size of the donor as well as the receipt square on the translocation of a single polymer chain.

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