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Effect of Interaction upon Translocation of Confined Polymer Chain Through Nanopore

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The effect of the interaction between nanopore and chain monomer on the translocation of a single polymer chain confined in a finite size square through an interacting nanopore to a large space has been studied by two-dimensional bond fluctuation model with Monte Carlo simulation. Results indicate that the free energy barrier before the successful translocation of the chain depends linearly on the chain length as well as the nanopore length for different pore-polymer interaction, and the attractive interaction reduces the free energy barrier, leading to the reduction of the average trapping time.

Key words: Monte Carlo simulation, Polymer translocation, Interaction, Free energy barrier

I. INTRODUCTION

The translocation of biopolymers through a nanopore plays an important role in many biological phenomena. Examples include translocation of protein across a cellular membrane or endoplasmic reticulum [1, 2], injection of RNA and RNA from a virus to bacteria after their synthesis [3], gene swapping between the guest and the host bacteria through pili, *etc*. Understanding this process will enable us to deepen our comprehension of many fundamental problems in cell biology, and may eventually provide various useful applications in biotechnologies and industrial processes, *e.g.*, in DNA sequencing [4, 5], in oil recovery and separation, and in gene therapy [6, 7], *etc*. Accordingly, the polymer translocation dynamics has attracted a lot of attention from experiments [5−9], analytical theories [10−14], and computer simulations [15−24].

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 [10, 11], so that most polymer translocation phenomena require a driving force, such as ratchet [25, 26], electric fields [9, 21, 27, 28], chemical potential gradients [29, 30] and selective adsorption on one side of the membrane [31]. Muthukumar studied the translocation of a single Gaussian chain from one sphere to another larger sphere through a narrow pore theoretically [32]. Results indicated that the interaction between the polymer and pore significantly modifies the entropic barrier landscape of translocation. As the pore

length increased, the translocation process underwent a transition from entropic barrier mechanism to a mechanism dominated by the pore-polymer interaction ε [32]. This shift in mechanism leads to nonmonotonic dependence of the translocation time τ on the pore length [11]. A Gaussian chain, however, can be used only to describe polymer translocation in a θ solution, which is difficult to make in experiments. The excluded volume effect significantly affects the conformational entropy of confined polymers and their dynamic behaviors. The authors utilized the self consistent field theory to calculate the translocation time by taking the excluded volume effect into design consideration [32]. As expected, their results differ from those predicated for the Gaussian chain. The self consistent field theory, however, can handle only small excluded volume parameter and is not suitable for calculating the translation time when the excluded volume parameters become large. In our previous work [19, 33], the translocation of a single self-avoiding walk (SAW) chain, confined in a finite size square, through a non-interacting nanopore has been studied by Monte Carlo simulation method. We found that the entropy barrier height decreases linearly with the polymer chain length N and increases with the pore length. However, the translocation time depends nonmonotonically on the polymer length. The excluded volume effect causes this nontrivial dependence.

In the present work we extend our previous work [19, 33] by considering the effect of the pore-polymer interaction on the translocation of a single SAW chain from a confined square to another lager square. The dependence of the free energy barrier and the translocation time on the interaction is investigated. We find that the attractive pore-polymer interaction reduces the free energy barrier of the chain when entering the nanopore,

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which leads to the decrease of the trapping time before the successful translocation of the chain. However, strong attractive and repulsive interactions make monomers difficult to leave and enter the nanopore respectively, resulting in the nonmonotonical dependence of the translocation time on the pore-polymer interaction. Further study on the detailed translocation dynamics of the chain is presented to investigate how the pore-polymer interaction affects the translocation of the chain.

II. MODEL AND SIMULATION METHOD

The two-dimensional bond fluctuation model (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 [34]. Two square lattice spaces with different sizes R_1=30 and R_2=800 are connected by a nanopore 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 of length N is initially placed in the donor square (of size R_1) with one end 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 moves through the pore begins. When monomers are inside the pore, the average interaction energy per monomer is taken as E. The reduced interaction $\varepsilon=E/(k_{\mathrm{B}}T)$ is used in the work with k_{B} (Boltzmann constant) and T (temperature). The trial move will be accepted with a probability $p=\min(1, \mathrm{e}^{-\Delta E})$ 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 work, we put aside the question of how the chain first enters the nanopore, focusing, instead 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
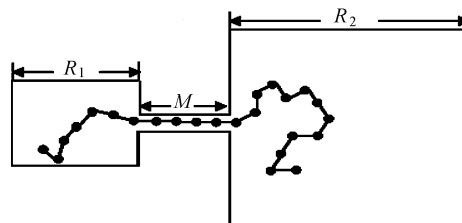

FIG. 1 Schematic representation of a N-monomer polymer chain in the process of the translocation through a nanopore of length M from the confinement. The nanopore is so narrow that the "hairpin" translocation is forbidden.

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 are smaller than a critical number. The time for the chain consumed in this period to overcome the free energy barrier is the trapping time τ_{trap}. 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 spontaneously transport into the receipt square and a successful translocation occurs. The elapsed time for the final successful escape is named translocating time τ_{trans}. Namely, during the translocating time τ_{trans} the chain successfully worms through the pore without totally pulled back. In this work, we just present the effect of interaction on the detailed translocation dynamics of chain through the relationship between the average trapping time $\langle\tau_{\mathrm{trap}}\rangle$ and N and M for different pore-polymer interaction ε, and all data of $\langle\tau_{\mathrm{trap}}\rangle$ are averaged over at least 10^3 independent runs. And, the standard statistical error is less than 5%. Therefore, we do not include the error bars in these figures, similar to what Luo has done [22].

III. SIMULATION RESULTS AND DISCUSSION

The dependence of $\langle\tau_{\mathrm{trap}}\rangle$ on N is presented in Fig.2 for different interaction ε. It can be seen that, for each value of ε, $\lg\langle\tau_{\mathrm{trap}}\rangle$ decreases linearly with the increases of N,

$$\lg \langle\tau_{\mathrm{trap}}\rangle \propto -N \qquad (1)$$

And, the slopes of the lines for different ε are all the same.

In order to understand these observations, one notes that with N increases, the confinement depresses the conformational entropy of the chain, and hence increases the free energy of the chain in the donor. It takes shorter time for the chain to go over the free energy barrier. Based on Arrhenius equation the reaction
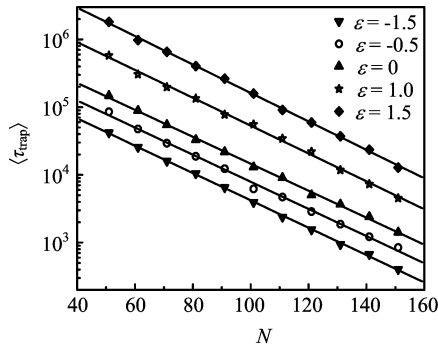
FIG. 2 The dependence of the average trapping time $\langle\tau_{\mathrm{trap}}\rangle$ on the chain length N for different pore-polymer interaction ε. The length of nanopore M=6.
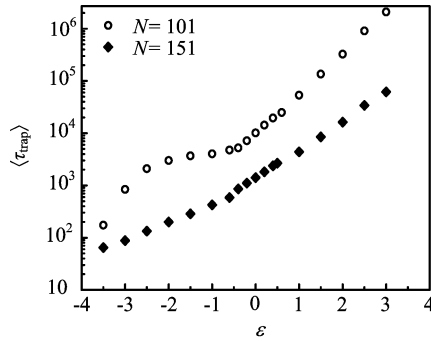

FIG. 3 The dependence of the average trapping time $\langle\tau_{\mathrm{trap}}\rangle$ on the interaction ε. The length of nanopore M=6.

rate k $\left(\sim\tau_{\mathrm{trap}}{}^{-1}\right)$ for the present situation is given by

$$k \propto \exp\left(-\frac{\Delta F}{k_{\mathrm{B}}T}\right) \qquad (2)$$

Where ΔF is the free energy barrier. Combining with Eq.(1), we have

$$\Delta F \propto -N \qquad (3)$$

That is to say, the free energy barrier for the chain trapping depends linearly on N. In this situation, since the length of M keeps constant, the interaction ε alters the same free energy barrier for different N, namely, ε just influences the intercept and, the slopes of the lines for systems with different ε are therefore the same.

From Fig.2 it can be seen that, for the same N, $\langle\tau_{\mathrm{trap}}\rangle$ decreases with the increase of pore-polymer ε. To clarify this effect, the simulations were performed for a range of the interaction $-3.5\leq\varepsilon\leq3.0$ with N=101 and 151. It can be seen that, for $\varepsilon>-0.4$, there is linear relationship between $\lg\langle\tau_{\mathrm{trap}}\rangle$ and ε (Fig.3). It is easily understood since increasing ε will increase the free energy barrier. According to Arrhenius equation, $\langle\tau_{\mathrm{trap}}\rangle$ exponentially increases with ε.

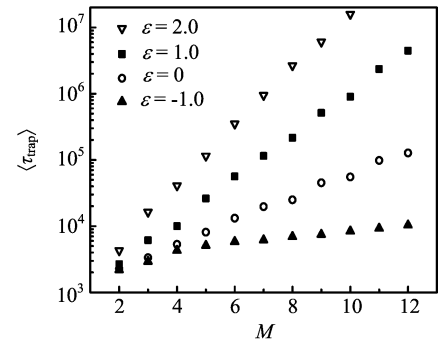For the interacting nanopore, with the pore length increasing, the free energy barrier for the chain trapping

FIG. 4 The average trapping time $\langle\tau_{\mathrm{trap}}\rangle$ as a function of the length of nanopore M for different interaction ε. The chain length N=101.

alters, leading to $\langle\tau_{\mathrm{trap}}\rangle$ changes accordingly. Figure 4 displays the dependence of $\langle\tau_{\mathrm{trap}}\rangle$ on the length of the nanopore M for different ε. The logarithm of $\langle\tau_{\mathrm{trap}}\rangle$, increases linearly with M,

$$\lg\langle\tau_{\mathrm{trap}}\rangle \propto M \qquad (4)$$

Combining with Eq.(2), we yields

$$\Delta F \propto M \qquad (5)$$

Namely, the free energy barrier of ΔF is proportional to M, which is similar to the dependence of ΔF on N (Eq.(3)). However, different from Fig.3, the slope of the line becomes large with increasing ε. It is easy to be understood. Since the free energy barrier is related to M, the change of ε will influence the front factor of the right-hand side of Eq.(5), leading to the alteration of the line slope accordingly.

IV. CONCLUSION

In conclusion, we investigated the translocation of a single polymer chain confined in a finite size square through an interacting nanopore to a lager size square by using two-dimensional BFM with Monte Carlo simulation. We find that the logarithm of the average trapping time of the chain, $\lg\langle\tau_{\mathrm{trap}}\rangle$, depends linearly on the chain length N as well as the length of nanopore M for different pore-polymer interaction ε. The slope of the line for the former keeps constant, however, that for the latter varies with increasing ε. Based on the Arrhenius equation, the free energy barrier that the chain overcomes before translocation depends linearly on N as well as M.

V. ACKNOWLEDGMENT

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