

Effect of Solvent Viscosity on the Driven Translocation of Charged Polymers through Nanopores

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Abstract The effect of viscosity of non-translocated (*cis*) side, η_{cis} , on the driven translocation of charged polymers through nanopores is investigated using Langevin dynamics simulation. Results show that the translocation of polymer chains can be regulated by changing η_{cis} . As η_{cis} decreases, the translocation time τ decreases, and the exponent δ in the scaling relation with driving force f , $\tau \sim f^{-\delta}$, increases whereas α in the scaling relation with chain length N , $\tau \sim N^\alpha$, decreases. Simultaneously, the conformation of the polymer chain at the *cis* side gravitates towards an equilibrium state. The results imply a relationship between the translocation and the conformation of polymer chains. To verify this hypothesis, we change the conformation of polymer by artificially relaxing the translocating polymer *via* adding an additional relaxation time in the simulation. A sufficient large additional relaxation time for the translocating polymer chain at the *cis* side only or at both *cis* and *trans* sides results in exponents α and δ both close to 1, in contrast to $\alpha=1.36$ and $\delta=0.8$ for the translocation without the additional relaxation. The additional relaxation for the polymer chain at the *cis* side accelerates the translocation and plays a more important role than that for polymer chain at the *trans* side.

Keywords Polymer; Nanopore; Translocation; Langevin dynamics simulation

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INTRODUCTION

The translocation of polymer chains through a nanopore has become one of the most active research topics for over two decades.^[1–8] Polymer translocation is essential for many biological processes, such as virus injection and protein transport through membrane channels.^[9] The translocation dynamics of polymer chains through nanopores has motivated a lot of experiments and simulations to understand its physical mechanism. Meanwhile, a great progress has been achieved in the aspects of the application of nanopore-based DNA sequencing technology.^[10–16]

Earlier experiments showed that the translocation time τ was roughly in linear proportional to the polymer length N , *i.e.*, $\tau \sim N$, while inversely proportional to the voltage bias V as $\tau \sim V^{-1}$.^[1,17,18] However, nonlinear dependence of τ on V was also observed when V was low.^[3,19] On the other hand, theoretical works based on the Fokker-Planck formalism suggested a scaling relation $\tau \sim N^\alpha f^{-\delta}$ to describe the dependence of τ on N and driving force f inside pores.^[20] Here, the driving force f is in linear proportional to voltage bias V in experiments. Theoretical methods are generally based on the assumption that the polymer translocation can be regarded as a

quasi-equilibrium process. An obvious reason is that the translocation of polymer is quite slow. Sung and Park proposed that $\tau \sim N^2/D \sim N^3$ for unbiased translocations at $Nf \ll 1$ and $\tau \sim N/D \sim N^2$ for driven translocations at $Nf \gg 1$ by assuming that the chain diffusivity D is inversely proportional to chain length N (Rouse dynamics).^[21] Muthukumar however assumed that the local diffusivity of the monomer across the pore is a constant and suggested $\alpha=2$ for the unbiased translocation (small Nf) and $\alpha=1$ and $\delta=1$ for the driving case with large Nf .^[22] By sufficiently slowing down the translocation of polymer to reach the quasi-equilibrium assumption, Polson *et al.* found $\alpha=2$ for the translocation of a polymer through an extremely narrow pore with strong friction using Monte Carlo simulations.^[23]

However, it was pointed out that the polymer chains during the translocation are in an out-of-equilibrium state, *i.e.*, quasi-equilibrium assumption is not satisfied even for the unbiased case.^[24] One obvious reason is that the unbiased translocation time $\tau \sim N^2$ is faster than the relaxation time $\tau_r \sim N^{1+2\nu}$ of polymer chain in solution (Rouse dynamics). Then, exponent $\alpha = 1 + 2\nu$ for the unbiased translocation and $\alpha = 1 + \nu$ for the driven case were proposed.^[24,25] Here, ν denotes the Flory exponent of polymer chains. $\nu=0.588$ for three-dimensional (3D) polymers with excluded-volume effect.^[24] To explain the basic physics for the out-of-equilibrium process of the driven translocation, Sakaue came up with the tension propagation (TP) theory.^[26] The tensile force propagating

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along the chain backbone at the *cis* side is set up by the driving force acting on the monomer inside the pore. Therefore, the conformation of the translocating polymer chain deviates from the equilibrium one. Sarabadani *et al.* further developed iso-flux tension propagation (IFTP) theory to take the total effective friction into account, including the pore friction and the tension front at the *cis* side,^[27] and $\alpha = 1 + \nu$ was proposed for the driven translocation of a long flexible polymer.^[7,28] However, these theories neglect the influence of translocated monomers at the *trans* side for flexible polymers. The chain at the *trans* side is also in the out-of-equilibrium state and the *trans* side friction also plays a role on the translocation.^[8,29] Most of simulations found the value of α was between 1 and $1 + \nu$.^[30–33] For example, Luo *et al.* found $\alpha = 1 + \nu = 1.588$ for self-avoiding polymer under slow translocation in low driving force or high friction and $\alpha = 1.37$ under fast translocation.^[31] And a theoretical work based on the tension imbalance also predicted $\alpha = (1 + 2\nu)/(1 + \nu) \approx 1.37$ for the driven translocation of linear flexible polymers.^[34] Some experiments on DNA driven translocations also showed α between 1 and $1 + \nu$.^[4,35]

On the other hand, simulations usually found $\delta < 1$ for the driven translocations.^[31] The reason for $\delta < 1$ was also attributed to the out-of-equilibrium conformation of polymer chains during the translocation.^[36] The out-of-equilibrium effect causes an extra drag force that results in a small effective driving force.^[29]

It is therefore very important and interesting to understand the effect of out-of-equilibrium conformation of polymer chains on the translocation dynamics.^[37] It was found that the translocation time was dependent on the polymer conformation during the translocation and it could be decreased when the translocation takes place under the quasi-equilibrium condition.^[37] To compare the influence of polymer conformation on the translocation, we have tried to vary the solvent viscosity of the *cis* side, η_{cis} . In this work, the effect of η_{cis} on the driven translocation of a flexible charged polymer chain is studied using Langevin dynamics (LD) simulations. We find that the translocation time τ and the translocation exponents α and δ are dependent on η_{cis} . As η_{cis} decreases, the polymer conformation at the *cis* side gravitates towards the equilibrium one and both α and δ tends to 1. To explain this simulation result, we then study the effect of polymer conformation on the translocation dynamics by introducing an artificial relaxation process. That is, we add an additional relaxation time t_{add} for monomers at the *cis* side and/or *trans* side when the number of translocated monomers changes. Thus, the polymer conformation is artificially relaxed during the translocation. Results show that the scaling exponents α and δ for the translocation time τ (not including t_{add}) can be changed by the additional relaxation. The translocation time τ decreases when the polymer chain at the *cis* side or at both sides is relaxed additionally. And a sufficient large additional relaxation time for the polymer chain at both *cis* and *trans* sides results in exponents close to $\alpha = 1$ and $\delta = 1$.

SIMULATION MODEL AND SIMULATION METHODS

Our simulations are performed in 3D space. The polymer chain

is modeled as a coarse-grained (CG) bead-spring chain composed of identical polymer monomers with the diameter σ and mass m . To mimic the translocation process of DNA molecules, we adopt a charged polymer (polyelectrolyte) chain with the charge $q = -e$ for each monomer. A polymer chain of length N is consisted of N monomers. An impenetrable wall parallel to the *yz* plane divides the whole space into a *cis* side on the left and a *trans* side on the right. Periodic boundary conditions (PBCs) are adopted in the *y* and *z* directions. The system sizes at both sides are large enough to hold the whole polymer chain freely, usually at least 10 times as large as the radius of gyration of polymer chain. The typical system size adopted in the simulation is $200\sigma \times 80\sigma \times 80\sigma$ for polymers of length $N = 96$. A nanopore located at the middle of the wall is the only way for the polymer chain translocating from the *cis* side to the *trans* side.

The bond potential of two bonded monomers in the polymer chain is given by the finitely extensible nonlinear elastic (FENE) potential:

$$U(b) = \begin{cases} -\frac{k_F}{2}(b_{\max} - b_{\text{eq}})^2 \ln \left[1 - \left(\frac{b - b_{\text{eq}}}{b_{\max} - b_{\text{eq}}} \right)^2 \right], & b_{\min} < b < b_{\max} \\ \infty, & \text{otherwise} \end{cases} \quad (1)$$

where k_F is the spring constant, b represents the bond length, $b_{\max}$ is the maximum bond length, and b_{eq} is the equilibrium bond length. Any two non-bonded monomers interact with each other *via* a truncated and shifted Lenard-Jones (LJ) potential:

$$U(r) = \begin{cases} 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] - 4\epsilon \left[\left(\frac{\sigma}{r_{\text{cut}}} \right)^{12} - \left(\frac{\sigma}{r_{\text{cut}}} \right)^6 \right], & r < r_{\text{cut}} \\ 0, & r \geq r_{\text{cut}} \end{cases} \quad (2)$$

where ϵ is the potential depth and r_{cut} is the cutoff distance. When the distance r between two monomers is larger than r_{cut} , the LJ potential is shifted to 0. The screened Coulomb potential between two non-bonded monomers with charge q is defined as:

$$U_{\text{Coul}}(r) = \frac{q^2}{4\pi\epsilon_w r} \exp(-\kappa r) \quad (3)$$

where ϵ_w is the dielectric constant of the solution and κ is the inverse screened length. Other types of electrostatic interactions are not included in the present work.^[38]

The wall of thickness σ is consisted of one layer of wall beads. Here wall beads of size σ are arranged in a square lattice with length σ . The nanopore of size $s \times s$ is at the middle of the wall. The interaction energy between polymer monomers and wall beads is expressed as a repulsive Weeks-Chandler-Andersen (WCA) potential:^[39]

$$U_{\text{WCA}}(r) = \begin{cases} 4\epsilon_{\text{PW}} \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 + \frac{1}{4} \right], & r < 2^{1/6}\sigma \\ 0, & r \geq 2^{1/6}\sigma \end{cases} \quad (4)$$

where ϵ_{PW} is the WCA interaction strength.

A polymer chain of length N is indexed from 1 to N . The evolution of the position vector $\mathbf{r}_i$ of the i^{th} monomer is determined by the Langevin equation:

$$m \frac{d^2 \mathbf{r}_i}{dt^2} = -\nabla U - \eta \frac{d\mathbf{r}_i}{dt} + \mathbf{F}_i + \mathbf{f}, \quad (5)$$

where m is the mass of the monomer, η is the friction coefficient, and U is the potential energy. $\mathbf{F}_r$ is the random force which has zero mean $\langle \mathbf{F}_r \rangle = 0$ and obeys the fluctuation-dissipation theorem $\langle \mathbf{F}_r^2 \rangle = 6\eta k_B T$ with k_B the Boltzmann constant and T the absolute temperature. For simplification, only the monomer inside the nanopore experiences a driving force $\mathbf{f} = q\mathbf{E}$ with $\mathbf{E}$ the electrical field. In the LD simulation, solvent is regarded as a background which maintains the temperature of the simulation system. We use the modified velocity-Verlet algorithm to update monomers' position and velocity according to the Langevin equation.

We would like to point out that hydrodynamic interaction (HI) effect of the solvent is not considered in the present LD simulation, although the HI effect can affect the structures and dynamics of the polymers as well as the translocation of polymer.^[40] The translocation time, after considering the HI effect, is slightly reduced but the values of scaling exponents that represent translocation dynamics are roughly not influenced.^[41] However, the HI effect on polymer transition is not obvious for short chains.^[42]

We use thermal energy $k_B T$, monomer diameter σ , and monomer mass m as the units of energy, length, and mass, respectively. The unit of time is $\tau_{\text{LJ}} = (m\sigma^2/k_B T)^{1/2}$. Simulation parameters in the present work are: the equilibrium bond length $b_{\text{eq}}=0.8$, the maximum bond length $b_{\text{max}}=1.3$, the spring constant of FENE potential $k_F=200$, the LJ potential depth $\epsilon=1$, the WCA interaction strength $\epsilon_{\text{PW}}=1$, the dielectric constant of the solution $\epsilon_w=78.5\epsilon_0$, and the inverse screened length $\kappa=0.5$. Here ϵ_0 is the dielectric constants of vacuum. The typical time step for LD simulation is $\Delta t=0.005$. To map our CG polymer model to single stranded DNA (ssDNA) molecule, the length unit is about $\sigma=1.6$ nm.^[43,44] The viscosity coefficients are set as η_{cis} and η_{trans} for the *cis* and *trans* sides, respectively, to mimic different solvent properties at both sides. The cutoff distance in the simulation is set as $r_{\text{cut}}=2.5$ for the intra-polymer LJ interaction as well as for the screened Coulomb potential. The screened length $\kappa^{-1}=2\sigma=3.2$ nm corresponds to salt concentration of about 0.01 mol/L.^[45,46] In simulation, the ionic effect at such a small salt concentration is weak, thus the electrostatic interactions are strong enough to compensate the pairing potential inside the DNA.^[44] We find that the polymer chain is coil-like at these parameters.^[47,48] And the nanopore in the present simulation is a square of $2\sigma \times 2\sigma$ in the cross section.

The initial configurations of polymer chains are generated at the *cis* side with one end of the polymer is fixed near the nanopore. Then, we relax the one-end fixed polymer chain for a sufficiently long time until it reaches an equilibrium state. The equilibrium time is longer than the relaxation time calculated from the end-to-end vector autocorrelation function

$$\rho(t) = \frac{\langle \mathbf{R}(t) \cdot \mathbf{R}(0) \rangle}{\langle R^2 \rangle}. \text{ When the equilibrated initial configuration is obtained, we begin the translocation process by releasing the fixed end monomer. Because of random thermal forces, monomers may return back to the } cis \text{ side even if they have entered the } trans \text{ side.}$$

To study the effect of solvent viscosity of the *cis* side on the translocation, we change η_{cis} while keep $\eta_{\text{trans}}=1$ as a con-

stant. As the dynamics of polymer chains is faster at small viscosity, changing the viscosity will change the translocation time of polymer chains.^[49] Since the polymer chain is in an out-of-equilibrium state during the driving translocation, the change of η_{cis} may affect the polymer conformation. At low η_{cis} , the polymer chain at the *cis* side will be closer to the equilibrium state.

To artificially relax the polymer chain, we adopt an additional relaxation time t_{add} during the translocation process. Our method is similar to that adopted by Kwon and Sung.^[37] If the number of translocated monomers at the *trans* side changes, i.e., +1 or -1, we pause the translocation process and add a relaxation process. We add the relaxation process for the part of polymer at the *cis* and/or *trans* side. Depending on the additional relaxation process, we classify four relaxation modes: (1) normal mode (Mode 00) without addition relaxation; (2) *cis* side relaxation mode (Mode 10) where the non-translocated part in the *cis* side is relaxed with time t_{add} but monomers inside the pore and of the translocated part are fixed as shown in Fig. 1(a); (3) *trans* side relaxation mode (Mode 01) where only the translocated part at the *trans* side is relaxed with time t_{add} as shown in Fig. 1(b); (4) double relaxation mode (Mode 11) where both parts at the *cis* side and *trans* side are relaxed with time t_{add} while the monomers inside the nanopore are fixed. After the relaxation process is completed, the translocation process will continue until the next additional relaxation process begins.

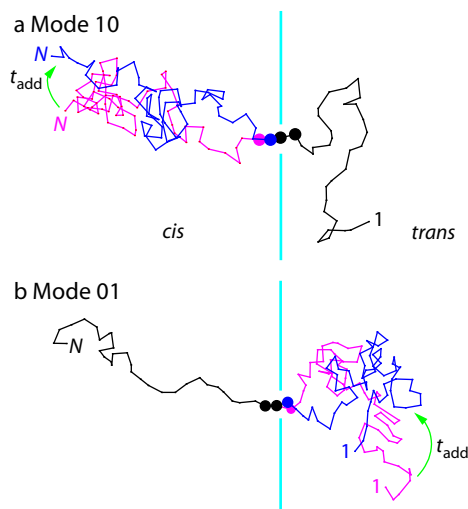


Fig. 1 A sketch of polymer chain translocation modes: *cis* side relaxation Mode 10 (a) and *trans* side relaxation Mode 01 (b). The black lines represent the fixed polymer conformation at the *trans* side (a) and at the *cis* side (b). The magenta line and the blue line represent the polymer conformation before and after the relaxation process, respectively.

The translocation time τ is defined as the duration time for the whole polymer chain passes through the nanopore. In the simulation, τ is the time interval between the entering of one of the end monomers into the pore and the arriving of all monomers at the *trans* side. For the additional relaxation case, the value of τ does not include the time for the additional relaxation process. Here, the translocation time τ is aver-

aged over 1000 independent simulation runs.

RESULTS AND DISCUSSION

Effect of Solvent Viscosity

The translocation time τ of polymer chain through nanopore is dependent on η_{cis} of the *cis* side. The viscosity of the *trans* side, η_{trans} , is set as 1. The dependence of τ on η_{cis} is presented in Fig. 2(a) for the polymer of length $N=96$. For both driving forces $f=2.6$ and 6.4, we find that τ increases with increasing η_{cis} . Results show that low η_{cis} will accelerate the translocation of polymer chain. The decrease of τ with decreasing η_{cis} can be attributed to the drop of viscosity force for the translocation. The magnitude of the viscosity force at the *cis* side can be expressed approximately as $\eta_{cis}v \sim \eta_{cis}L/\tau$ with $L = (N-1)b$ as the contour length of polymer chain which can be roughly regarded as a constant. Fig. 2(b) presents the variation of η_{cis}/τ with η_{cis} for the polymer of length $N=96$ at the driving force $f=2.6$ and 6.4. We find that the viscosity force represented by η_{cis}/τ at the *cis* side increases with increasing η_{cis} .

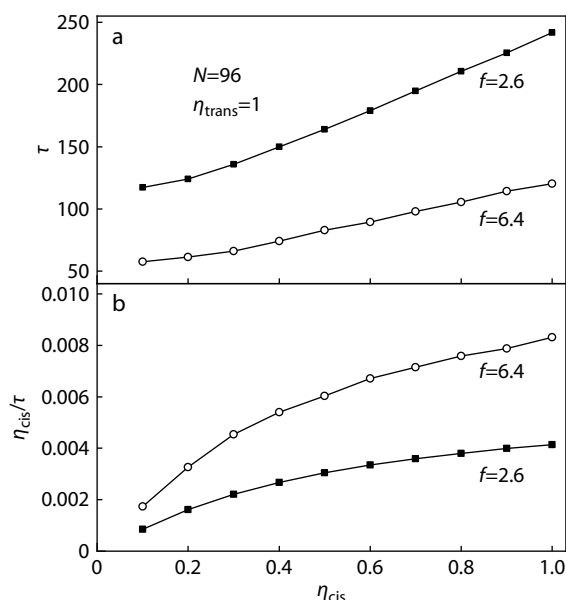


Fig. 2 The translocation time τ (a) and value η_{cis}/τ (b) versus the solvent viscosity η_{cis} of the *cis* side for polymer of length $N=96$ at the driving force $f=2.6$ and 6.4.

To understand the influence of η_{cis} on the translocation behaviors of polymer chains, we have simulated the scaling behaviors of the translocation time τ on the driving force f and on the polymer length N at different η_{cis} . Fig. 3 presents the variations of τ versus f and N for different η_{cis} whereas η_{trans} is fixed as 1. It is interesting to see that both the exponent δ in the scaling relation $\tau \sim f^{-\delta}$ and the exponent α in the scaling relation $\tau \sim N^\alpha$ are dependent on η_{cis} . At low η_{cis} , the exponent δ increases in the low f region whereas the exponent α decreases. Both the exponents δ and α tend to 1 at low η_{cis} . Theoretical study, based on the quasi-equilibrium assumption of polymer translocation, suggested $\alpha=1$ and $\delta=1$ for the driven translocation.^[22] Therefore our simulation results imply that the polymer chains are close to equilibrium state at low η_{cis} . In

other words, one can speed up the equilibrium process of polymer chains by lowering η_{cis} . Since the polymer chain is always in the out-of-equilibrium state at sufficient large f , the behavior of translocation dynamics in the large f region is therefore not discussed in the present work.

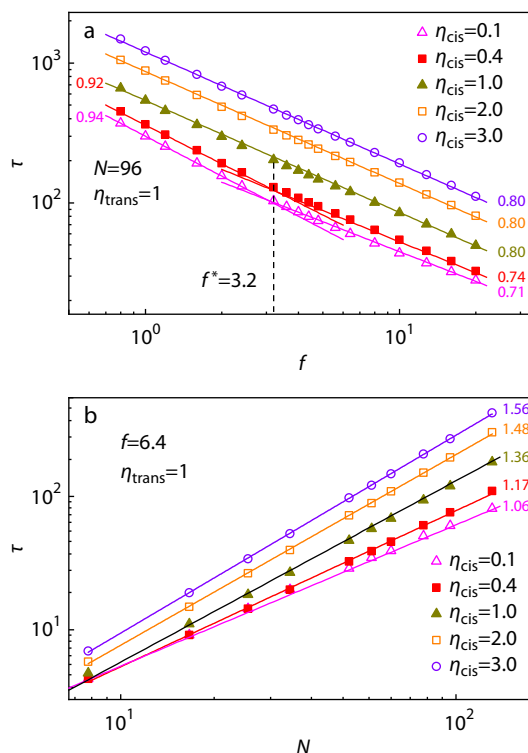


Fig. 3 Log-log plot of the translocation time τ versus the driving force f (a) and chain length N (b) at different viscosity coefficient η_{cis} at the *cis* side. The numbers near straight lines show the slope of β (a) and α (b).

To check whether the polymer chain is close to the equilibrium state at low η_{cis} , we investigated the chain conformation of the translocating polymer chain at different η_{cis} . The mean square end-to-end distances, $\langle R^2 \rangle_{cis}$ and $\langle R^2 \rangle_{trans}$, for chain blocks at the *cis* and *trans* sides during the translocation are calculated. Since the non-translocated block at the *cis* side and the translocated one at the *trans* side are analogous to an end-grafted chain, the mean square end-to-end distances of the corresponding fully equilibrated end-grafted chain denoted as $\langle R^2 \rangle_0$ is also simulated. The value of $\langle R^2 \rangle_0$ is independent of the viscosity of solvent, but $\langle R^2 \rangle_{cis}$ and $\langle R^2 \rangle_{trans}$ are dependent on the viscosity of solvent. The simulation results for the variation of $\langle R^2 \rangle$ with block length N_{block} are presented in Fig. 4 for polymer chain at different viscosities (η_{cis}) and at different driving forces (f). Here, N_{block} denotes the number of polymer monomers (chain length) at the *cis* side or at the *trans* side. For example, $N_{block}=96$ of polymer monomers at *cis* side means the whole polymer is at the *cis* side, while $N_{block}=96$ at the *trans* side means the whole polymer is at the *trans* side.

Fig. 4(a) shows that $\langle R^2 \rangle_{cis}$ of polymer at the *cis* side is larger than $\langle R^2 \rangle_0$ whereas $\langle R^2 \rangle_{trans}$ of polymer at the *trans* side is smaller than $\langle R^2 \rangle_0$, which clearly indicates that the poly-

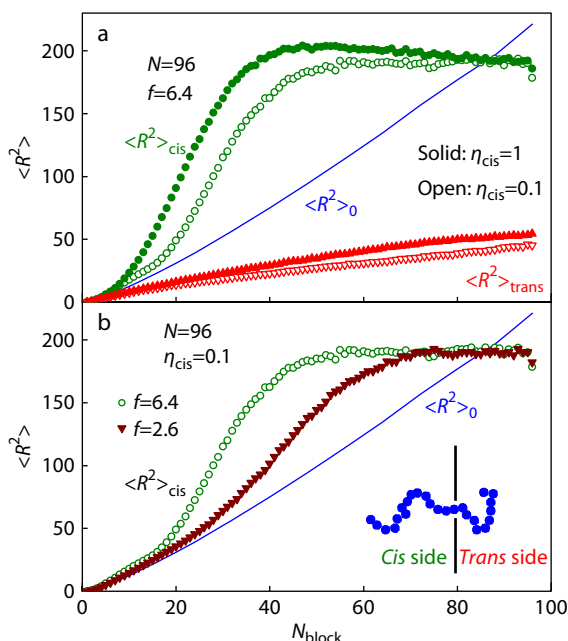


Fig. 4 (a) The mean-square end-to-end distance $\langle R^2 \rangle$ versus block length N_{block} for both blocks at the *cis* and *trans* sides during the translocation of polymer with $\eta_{\text{cis}}=0.1$ and 1. Polymer length $N=96$ and driving force $f=6.4$. (b) $\langle R^2 \rangle$ versus N_{block} for the chain block at the *cis* side for two driving forces $f=2.6$ and 6.4. Polymer length $N=96$ and $\eta_{\text{cis}}=0.1$. The blue curves represent $\langle R^2 \rangle_0$ of the fully equilibrated end-grafted chain.

mer chain is in an out-of-equilibrium state during the driven translocation. And the non-translocated block at the *cis* side is in a stretched state while the translocated block is in a compressed state. The only exception is the situation at the very beginning of the translocation (large N_{block} for the *cis* side) where $\langle R^2 \rangle_{\text{cis}}$ is smaller than $\langle R^2 \rangle_0$. In simulations, $\langle R^2 \rangle_{\text{cis}}$ and $\langle R^2 \rangle_{\text{trans}}$ are averaged over all possible chain conformations during the translocation. We could like to point out that the number of chain conformations is different for different block lengths due to the random forward and backward motion during the translocation.^[48] The decrease of $\langle R^2 \rangle_{\text{cis}}$ at the very beginning of the translocation is due to the frequent forward and backward motion. Because of the out-of-equilibrium effect during the translocation, the size of backward conformation is thus decreased at the very beginning of the translocation. Thus $\langle R^2 \rangle_{\text{cis}}$ at large N_{block} is smaller than $\langle R^2 \rangle_0$.

We also find, from Fig. 4(a), that the conformation of polymer chain at the *cis* side is closer to the equilibrium state for small η_{cis} because the dynamics of polymer chain becomes fast at small viscosity. At the same time, the conformation of polymer chain at the *cis* side is closer to the equilibrium state at small driving force because the translocation time increases with decreasing f . At low driving force and small η_{cis} , such as $f=2.6$ and $\eta_{\text{cis}}=0.1$ shown in Fig. 4(b), the conformation of polymer chain at the *cis* side is quite close to an equilibrium state.

Addition Relaxation

Based on the simulation results of the above section, it is interesting to know that the effect of equilibrium on the transloca-

tion of polymers. To equilibrate the polymer chain during the translocation, we introduce arbitrarily an additional relaxation process for the polymer chain. During the additional relaxation process, the polymer chain at the non-translocated (*cis*) and/or at the translocated (*trans*) sides is relaxed for a time t_{add} . However, the translocation time τ in this work does not include the time for the additional relaxation process.

Fig. 5(a) presents the dependence of τ on t_{add} for the double-side relaxation case (Mode 11) under driving forces $f=2.6$ and 6.4. Here, polymer length is set as $N=96$. We find that τ decreases with the increasing t_{add} , indicating that the additional relaxation of whole polymer accelerates the translocation. The decrease of τ is consistent with the previous simulation results for polymer translocation in good and poor solvents.^[37] However, τ saturates quickly, and we find $t_{\text{add}}=5$ is roughly long enough for the polymer ($N=96$) reaching saturation value. For $t_{\text{add}}=5$, in fact we find the total added time during the translocation is longer than the relaxation time of the polymer in dilute solution (not shown). Meanwhile, the mean-square end-to-end distance becomes closer to the equilibrium value when the additional relaxation is provided.^[37] Fig. 5(b) shows the variation of $\langle R^2 \rangle_{\text{cis}}$ and $\langle R^2 \rangle_{\text{trans}}$ with t_{add} for the block length $N_{\text{block}}=48$ (half of polymer length $N=96$) at $f=6.4$. We find that both $\langle R^2 \rangle_{\text{cis}}$ and $\langle R^2 \rangle_{\text{trans}}$ gradually tend to reach $\langle R^2 \rangle_0$ with the increasing t_{add} . The results shown in Fig. 5(b) clearly confirm the relationship between the translo-

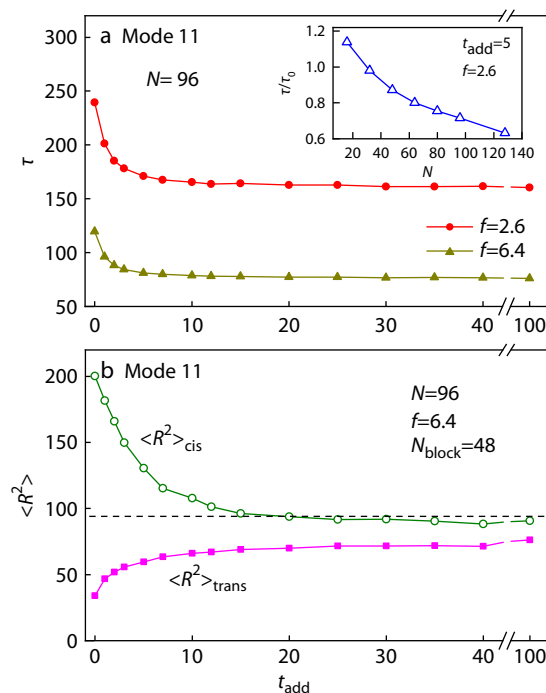


Fig. 5 (a) Plots of the translocation time τ versus the additional relaxation time t_{add} for polymer length $N=96$ at driving forces $f=2.6$ and 6.4 for Mode 11. The inset shows the variation of the reduced translocation time τ/τ_0 with the chain length N under driving force $f=2.6$; (b) Plots of the mean square end-to-end distances $\langle R^2 \rangle_{\text{cis}}$ and $\langle R^2 \rangle_{\text{trans}}$ versus t_{add} for polymer length $N=96$ at driving force $f=6.4$ for Mode 11. The block lengths at both sides are the same, that is, $N_{\text{block}}=48$. The horizontal dashed line shows $\langle R^2 \rangle_0 \approx 94.3$ for the corresponding equilibrated end-grafted chain.

cation time and polymer conformation, in agreement with the results observed in the above section. Since τ saturates at about $t_{\text{add}}=5$, we simply regard $t_{\text{add}}=5$ as long enough for the polymer chain to reach equilibrium state.

It is known that the out-of-equilibrium polymer produces an extra drag force that retards the translocation.^[29] There is a tension force propagates along the backbone of the chain for the driven translocation.^[26] The non-translocated monomers have large directional velocity that results a large friction force. However, the conformation of polymer chain is closer to equilibrium state at larger t_{add} . Then the tension force as well as the velocity of polymer is decreased, and the polymer experiences a smaller drag force. Therefore, the translocation time decreases with t_{add} .

We have also simulated other polymer lengths. The inset of Fig. 5(a) shows the relationship between the reduced translocation time τ/τ_0 and N . Here τ_0 is the translocation time of the normal translocation case without additional relaxation (Mode 00). The ratio τ/τ_0 is less than 1 for long polymers with $N>30$, meaning that the additional relaxation can reduce the translocation time. Moreover, we find that τ/τ_0 decreases with increasing N , that is, the effect of the additional relaxation becomes stronger for longer chain, so we select the polymer of relatively long length ($N=96$) in our simulations. The result of $\tau/\tau_0>1$ for very short chains ($N<30$) is due to the fact that the translocation time τ of Mode 11 maybe increased (only at small t_{add} and the phenomenon is more significant for short chains).

We have calculated the dependence of τ on the driving force f for different relaxation modes for the polymer of length $N=96$. The results are presented in Fig. 6 for $t_{\text{add}}=5$. For Mode 00, we find a single exponent $\delta=0.8$ in the scaling relation $\tau \sim f^{-\delta}$, which is in agreement with the previous simulation results for driven translocations.^[29,31] However, for other three modes, we find τ decreases rapidly in the small f region and it tends to decrease slowly in the large f region.

The separation force for the two regions is about $f_c=3.5$. The exponent δ values for $f<f_c$ at Modes 10, 01, and 11 are

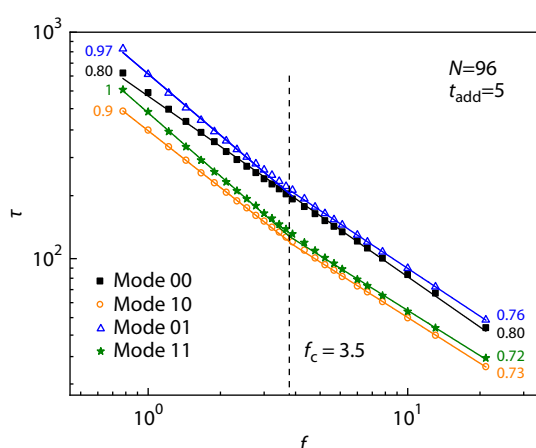


Fig. 6 Log-log plots of the translocation time τ versus the driving force f for polymer length $N=96$ at different relaxation modes 00, 10, 01, and 11 with $t_{\text{add}}=5$. The numbers near lines indicate the slopes below and above f_c . The vertical dashed line at $f_c=3.5$ is a guide to the eye.

higher than 0.8, while δ for $f>f_c$ is smaller than 0.8. For $t_{\text{add}}=5$ which is supposed large enough for equilibrating polymer conformation as shown in Fig. 5(a), we find $\delta=1$ for Mode 11 and $\delta=0.97$ for Mode 01 in the small f region ($f<f_c$). The polymer at Mode 11 can be considered as in quasi-equilibrium state during the translocation process and thus the exponent $\delta=1$ for $f<f_c$ at Mode 11 is consistent with theoretical prediction under quasi-equilibrium assumption.^[22] Whereas for large force $f>f_c$, the small value of δ indicates that the polymer chain is in an out-of-equilibrium state. The possible reason is that the local polymer conformation near the pore cannot be equilibrated due to the large driving force since the local conformation near pore is deformed significantly. It is well known that the polymer is far from equilibrium state under large driving force.^[29] Nevertheless, the finite additional relaxation time can be always neglected at extremely large force. Therefore, both the translocation time and the value of δ will be the same as those of the normal case (Mode 00) at extremely large force.^[31]

The scaling relation $\tau \sim f^{-\delta}$ at different t_{add} s is studied for the polymer chain at Mode 11. Fig. 7 presents the dependence of τ on f for the polymer of length $N=96$ with different values of t_{add} . Note that the $t_{\text{add}}=0$ case corresponds to Mode 00 with a single scaling exponent $\delta=0.8$. We also find two scaling exponents of δ for $f<f_c=3.5$ and $f>f_c$ when addition relaxation is introduced. For $f<f_c=3.5$, we find δ increases with t_{add} very quickly and it tends to the value of 1 even at $t_{\text{add}}=2$. We also notice that the value of f_c is roughly independent of t_{add} from our simulations up to $t_{\text{add}}=100$. The variation of the exponent δ below and above f_c with t_{add} for the polymer of length $N=96$ is presented in the inset of Fig. 7. The exponent δ increases from 0.8 to about 1 very quickly for $f<f_c$ and decreases to about 0.72 for $f>f_c$. Thus, it seems that the polymer dynamics reaches the equilibrium limit when t_{add} reaches 2 for $f<f_c$.

For the Mode 11 case, two parts of the polymer chain at both sides are relaxed simultaneously. In order to know which part plays a more important role on the transition of polymer, we have compared the results of three relaxation modes

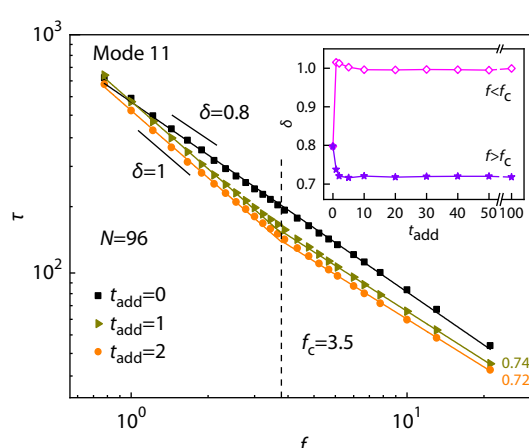


Fig. 7 Log-log plot of the translocation time τ versus the driving force f for polymer with $N=96$ under different $t_{\text{add}}=0, 1$, and 2. The vertical dashed line at $f_c=3.5$ is a guide to the eye. The inset shows the variation of the exponent δ below and above f_c with t_{add} for the polymer of length $N=96$.

(Modes 01, 10, and 11). Fig. 8 presents the results of τ with t_{add} of polymer length $N=96$ for these three relaxation modes. The translocation time of Mode 00, τ_0 , is also indicated. The number of translocation steps, n , is presented in the inset of Fig. 8. Value of n_0 is the corresponding value of Mode 00. Different behaviors are observed for Mode 10 and Mode 01.

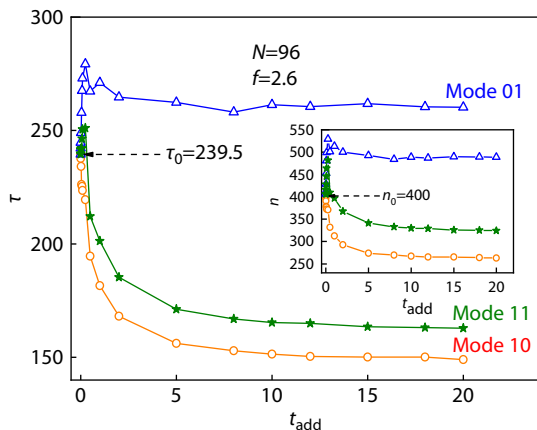


Fig. 8 Plots of the translocation time τ versus t_{add} for the polymer of length $N=96$ under the driving force $f=2.6$ at three Modes 01, 10 and 11. The translocation time is $\tau_0=239.5$ at Mode 00. The inset presents the number of translocation steps, n , with $n_0=400$.

It can be observed that τ of Mode 01 is larger than τ_0 , which means the effect of the additional relaxation at the *trans* side slows down the polymer translocating. And the increase in τ of Mode 01 is very sharply, but it saturates fast. The behavior of n is similar. The value of n of Mode 01 is larger than n_0 , which means that it is easy to draw the translocated monomers back to the *cis* side after the additional relaxation. Thus, the translocation time is increased for Mode 01. Whereas τ of Mode 10 decreases gradually and tends to saturate after $t_{\text{add}}=5$, which means that the equilibration of the non-translocated monomers accelerates the translocation of polymer. At the same time, the value of n is also smaller than n_0 .

Because of the contradictory effect of the two relaxation modes (Modes 01 and 10) on the translocation time, we observe that τ of Mode 11 is larger than τ_0 for very small t_{add} and it is smaller than τ_0 for large t_{add} . That is, the effect of the translocated monomers dominates at small t_{add} while the effect of the non-translocated monomers dominates at large t_{add} . For the same reason, τ of Mode 11 locates between those of Mode 01 and Mode 10. Nevertheless, the increase in τ of Mode 11 at small t_{add} is quite limited, we mostly observe a decrease in τ for Mode 11 as we discussed previously in this work. And we find τ of Mode 11 is closer to that of Mode 10, implying that the equilibration of the *cis* side is more important.

We also studied the dependence of the translocation time τ on the chain length N . Fig. 9 presents the results for modes 00, 10, 01, and 11. The additional relaxation time is $t_{\text{add}}=5$ and the driving force is set as $f=2.6$. For Mode 00, the exponent α in the scaling relation $\tau \sim N^\alpha$ is about 1.36, which is in agreement with a lot of simulation results and theory works for linear flexible polymer chains.^[34,48] The exponent α of Mode 01 is close to that of Mode 00, indicating again that the equilib-

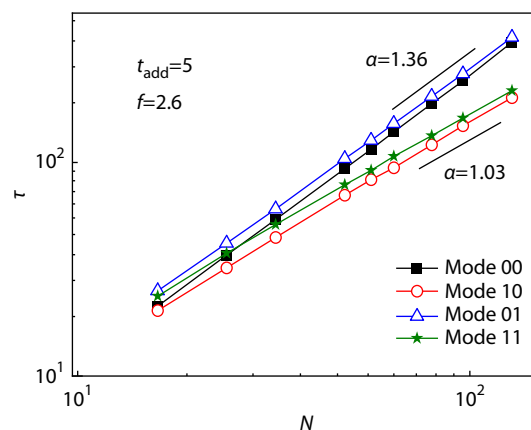


Fig. 9 Log-log plots of the translocation time τ versus the chain length N for four different relaxation modes. The additional relaxation time is $t_{\text{add}}=5$ and the driving force is $f=2.6$. Two straight lines show the slope of $\alpha=1.36$ and $\alpha=1.03$, respectively.

ration of *trans* side is not important. However, the exponent α values of Mode 10 and Mode 11 decreased significantly. We find $\alpha \approx 1.03$ for Mode 11, close to value of 1 proposed for driven translocation based on the assumption of quasi-equilibrium for polymer conformation. Our results clearly confirm the exponent α of driven translocation will close to 1 if the polymer chain is fully equilibrated during the translocation or the chain can be always in equilibrium state. This is in agreement with simulation results by reducing the translocation speed of polymer.^[23] Moreover, the exponent α of Mode 10 is close to that of Mode 11, implying again that the equilibration of the *cis* side is more important than that of the *trans* side.

CONCLUSIONS

In summary, we have simulated the effect of the viscosity of the *cis* side, η_{cis} , on the driven translocation of polymer using Langevin dynamics simulation. The translocation of polymer chains can be regulated by changing η_{cis} . The translocation time decreases with decreasing η_{cis} , and the exponent δ in the scaling relation $\tau \sim f^{-\delta}$ increases whereas the exponent α in the scaling relation $\tau \sim N^\alpha$ decreases with decreasing η_{cis} . Results show that the conformation of polymer chain at the *cis* side is quite close to an equilibrium state at low η_{cis} , indicating that translocation is closely related to the polymer conformation during the translocation.

Then, we artificially relax the polymer chain at the *cis* side and/or *trans* side to study the effect of equilibration of polymer chains on the translocation time. During the translocation, the conformation of polymer is relaxed additionally by introducing an additional relaxation time for the polymer chain at *cis* and/or *trans* sides. Results show that the additional relaxation for the non-translocated part at the *cis* side speeds up the translocation while that for the translocated part at the *trans* side slows down the translocation process. However, the relaxation for the non-translocated part dominates the translocation and thus the translocation time of both sides' relaxation is close to that of only *cis* side's relaxation. A sufficient large addition relaxation time for chains at both *cis* and *trans* sides results in exponents $\alpha=1$ and $\delta=1$, in contrast

to $\alpha=1.36$ and $\delta=0.8$ for the translocation without the additional relaxation.

NOTES

The authors declare no competing financial interest.

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