Conformation-dependent translocation of a star polymer through a nanochannel

Zhu Liu,¹ Jiannan Liu,¹ Mengying Xiao,¹ Rong Wang,^{1,a)}
and Yeng-Long Chen^{2,a)}

¹Key Laboratory of High Performance Polymer Materials and Technology of
Ministry of Education, Department of Polymer Science and Engineering,
State Key Laboratory of Coordination Chemistry, School of Chemistry
and Chemical Engineering, Nanjing National Laboratory of Microstructures,
Nanjing University, Nanjing 210093, China

²Institute of Physics, Academia Sinica, Taipei 11529, Taiwan

(Received 23 April 2014; accepted 11 August 2014; published online 10 September 2014)

The translocation process of star polymers through a nanochannel is investigated by dissipative particle dynamics simulations. The translocation process is strongly influenced by the star arm arrangement as the polymer enters the channel, and a scaling relation between the translocation time τ and the total number of beads N_{tot} is obtained. Qualitative agreements are found with predictions of the nucleation and growth model for linear block co-polymer translocation. In the intermediate stage where the center of the star polymer is at the channel entrance, the translocation time is found to have power law-dependence on the number of arms outside the channel and very weakly dependent on the number of arms in the channel. Increasing the total number of star arms also increases the star translocation time.

© 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4893637>]

I. INTRODUCTION

Selective molecular transport through a narrow channel or a biomimetic membrane nanopore is an important biological transport process,¹ including the transportation of DNA and RNA through nuclear pore complexes, protein transport across membrane channels, and injection of viruses into the host cell nucleus. The translocation process has potential applications in filtration and diagnostic devices^{2–4} such as rapid DNA sequencing, gene therapy, and controlled drug delivery. The physics of macromolecule translocation has been examined intensively by experimental^{5–16} and theoretical^{17–55} studies over the past decade. Most of the prior studies have focused on linear polymer chains translocation through nanopores and narrow channels. In comparison, fewer studies have attempted to elucidate the translocation mechanism of polymers with complex branched or star topology, for which molecular conformation and changes to the molecular conformation could strongly affect the translocation process. Polymer topology plays an important role in their physical properties, particularly under strong confinement.^{56–66} One example is the human astrovirus,^{67,68} which is a cause of diarrhea and has a distinctive star-like appearance. The relation between its topology and its biological functions has been of significant interest.

A star polymer is a special branched polymer network composed of more than two flexible arms branching from a central core. With possible applications for nano-scale self-assembly, the physical properties of star polymers has attracted considerable attention both theoretically^{69–79} and experimentally.^{80–84} Compared with linear polymers, the translocation process of star polymers through a nanochannel is far more complex due to the change in polymer conformation during translocation. Recent experiments by Ge *et al.*⁸³ on the ultra-filtration of star polymers of

^{a)}Authors to whom correspondence should be addressed. Electronic addresses: wangrong@nju.edu.cn and yenglong@phys.sinica.edu.tw

different star arm numbers and lengths revealed that the critical flow rate ($q_{c,star}$) strongly depends on the total number of arms and the number of forward arms in the nanochannel during translocation. Past theoretical analysis by Brochard-Wyart and de Gennes^{76,79} on how a star polymer crawls through a nanopore under an elongational flow field predicted that the translocation time of a star polymer depends not only on the total number of arms f but also on the number of forward arms f_{front} that initially enter the nanopore. More recently, Debnath and Sebastian⁷⁵ investigated star polymer transition dynamics in a double-well potential, mimicking the free energy change as the star polymer freely translocates a nanochannel. Freed *et al.*^{85–87} further improved the calculation of the confinement energy of linear and three-armed star polymers and included the effects of flow field. Muthukumar *et al.*^{20,22–24,27} compared the translocation of a linear polymer through a pore with the nucleation and growth process, which successfully captures the qualitative dependences of the translocation time with the chain length and pore size. The theory considered three stages in translocation process: (1) a very slow process for the first monomer to enter the channel; (2) the nucleation of a stable nucleus within the channel; and (3) the eventual exit of the chain. Due to the long-time nature of the stage (1), a Fokker-Planck equation analysis has been employed to examine the translocation dynamics for the nucleation and the exit stages.

Prior theoretical analysis of linear polymer translocation using the Fokker-Planck equation may be extended to examine star polymers. We consider flow-driven polymer translocation through a small channel. The effect of flow is considered as the chain chemical potential difference between the *cis* and *trans* sides of the channel, as shown in Fig. 1. The driving force due to the chemical potential gradient or flow velocity in the x -direction can be written as

$$\frac{\partial \mu}{\partial x} = -F_x. \quad (1)$$

Since flow is much faster in the narrow channel, we can ignore the flow elsewhere and write the chemical potential as

$$\mu = \begin{cases} -\alpha a, & x < a \\ -\alpha x, & a < x < b, \\ -\alpha b, & x > b \end{cases} \quad (2)$$

$a < x < b$ spans the channel length $L = b - a$, and $\alpha > 0$ is a constant coefficient related to F_x .

FIG. 1. Schematic representation of the simulation model. Only the xz -plane is shown.

For a chain much longer than the channel, the free energy profile of a linear chain is

$$E(m) = m\Delta\mu, \quad (3)$$

where $\Delta\mu = -\alpha(b - a)$ captures the flow-driven translocation potential and m is the number of beads reaching the *trans* side.

For star polymers, Eq. (3) is modified to include the dependence on the number of forward arms (f_{front}) that initially enter the channel and the number of backward arms in the *cis* side (f_{back}). Therefore, the total arm number f of the stars is equal to $f_{\text{front}} + f_{\text{back}}$. The arms are assumed to be parallel to each other as they translocate through the channel. Once one segment reaches the *trans* side, f_{front} or f_{back} beads exit to the *trans*-side simultaneously. Thus, the free energy can be written as

$$E(m) = \begin{cases} mf_{\text{front}}\Delta\mu, & 0 \leq m \leq N_s \\ (m - N_s)f_{\text{back}}\Delta\mu + N_sf_{\text{front}}\Delta\mu, & N_s \leq m \leq 2N_s \end{cases}, \quad (4)$$

where N_s is the length of one arm of star polymer. Since the channel is short with respect to the chain, the nucleation time is much shorter than the growth time. So, we consider the growth time as the translocation time. The average translocation time is measured by the mean first passage time of the corresponding Fokker-Planck equation.²⁰ For a linear polymer, the equation can be written as

$$\frac{\partial W_m(t)}{\partial t} = \frac{\partial}{\partial m} \left(\frac{k_0}{k_B T} \frac{\partial E(m)}{\partial m} W_m(t) + k_0 \frac{\partial W_m(t)}{\partial m} \right), \quad (5)$$

where $W_m(t)$ is the probability that the equivalent linear polymer has m segments in the *trans* side at time t . k_0 is a system-dependent rate constant. It can be shown that the translocation time τ for a linear polymer is given by

$$\begin{aligned} \tau &= \frac{1}{k_0} \int_0^{N-1} dx \int_0^x dy \exp\left(\frac{E(x) - E(y)}{k_B T}\right) \\ &= \frac{N}{k_0 |\Delta\mu|} \left\{ 1 - \frac{k_B T}{N|\Delta\mu|} \left[1 - \exp\left(-\frac{N|\Delta\mu|}{k_B T}\right) \right] \right\}. \end{aligned} \quad (6)$$

In the limits of strong and weak flow, we have²⁰

$$\tau \approx \begin{cases} \frac{k_B T}{k_0 |\Delta\mu|} N, & \frac{N|\Delta\mu|}{k_B T} \gg 1 \\ \frac{N^2}{2k_0}, & \frac{N|\Delta\mu|}{k_B T} \rightarrow 0 \end{cases}. \quad (7)$$

Equation (7) gives $\tau \sim N$ under strong flow. For weak flow, chain diffusion dominates the translocation process and $\tau \sim N^2$.

For star polymers, effective potential contributions from the arms in and out of the nano-channel need to be considered separately, in the same manner as the translocation of a linear di-block copolymer with a “forward block” and a “backward block.” The translocation time is given by

$$\begin{aligned}
\tau = & \frac{N_s}{k_0 f_{\text{front}} |\Delta\mu|} \left\{ 1 - \frac{k_B T}{f_{\text{front}} N_s |\Delta\mu|} \left[1 - \exp\left(-\frac{f_{\text{front}} N_s |\Delta\mu|}{k_B T}\right) \right] \right\} \\
& + \frac{N_s}{k_0 f_{\text{back}} |\Delta\mu|} \left\{ 1 - \frac{k_B T}{f_{\text{back}} N_s |\Delta\mu|} \left[1 - \exp\left(-\frac{f_{\text{back}} N_s |\Delta\mu|}{k_B T}\right) \right] \right\} \\
& \times \left\{ 1 - \frac{f_{\text{back}}}{f_{\text{front}}} \left[1 - \exp\left(-\frac{f_{\text{front}} N_s |\Delta\mu|}{k_B T}\right) \right] \right\}. \quad (8)
\end{aligned}$$

In the asymptotic limits, we have

$$\tau \approx \begin{cases} \left(\frac{1}{f_{\text{front}}} + \frac{1}{f_{\text{back}}} \right) \frac{k_B T}{k_0 |\Delta\mu|} N_s, & \frac{N_s |\Delta\mu|}{k_B T} \gg 1 \\ \frac{(2N_s)^2}{2k_0}, & \frac{N_s |\Delta\mu|}{k_B T} \rightarrow 0 \end{cases}. \quad (9)$$

The qualitative dependences are similar to the linear polymer translocation process at first glance.²³ In the weak flow region, the process is diffusion dominated with a scaling exponent $\nu=2$; in the strong flow region, it is flow driven with a scaling exponent $\nu=1$; in the intermediate region, the dynamics depends on the cooperation and competition between these two processes. Although the F-P analysis provides the scaling law between the translocation time and the total number of beads, it does not show qualitative difference between the linear and star polymer topology without accounting for the topology effect on the polymer configuration energy in the channel. In Eq. (8), the translocation time is represented by two terms contributed from the forward and the backward arms separately. The backward term has an extra coefficient, which comes from the chemical potential difference between the forward and backward arms. The theoretical model does not account for intra-polymer interaction of real polymers, which strongly affects the translocation process particularly for translocation across pores of size comparable to the polymer width. Other influences such as the effect hydrodynamic flow on star polymer conformation during translocation also need to be fully included.

In this work, we employed the dissipative particle dynamics method (DPD) to investigate how star polymer translocation depends on the star arm length, arm number, and the intermediate conformations at the nanochannel entrance. Detailed comparisons of the translocation time dependence on the number of star arms and arm length are made between the DPD simulation^{88,89} and the theoretical predictions of Muthukumar *et al.*,^{20,22–24,27} applied to star polymers. The rest of this paper is organized as follows. In Sec. II, details of the simulation method and coarse-grained star polymer are presented. In Sec. III, the analysis of the simulations results of star polymer translocation time is presented. Section IV concludes our study.

II. DISSIPATIVE PARTICLE DYNAMICS

The DPD simulation method was proposed by Hoogerbrugge and Koelman⁹⁰ in 1992 and successfully applied by Groot and Warren⁹¹ in 1997. As a coarse-grained molecular dynamics scheme, DPD is an effective technique in simulating mesoscale hydrodynamics. Each DPD particle is regarded as a collection of molecules, whose time evolution is governed by Newton's equation of motion⁹¹

$$m \frac{d\vec{v}_i}{dt} = \vec{f}_i. \quad (10)$$

There are three types of forces between DPD particles, conservative force ($\vec{F}_{ij}^C$), dissipative force ($\vec{F}_{ij}^D$), and random force ($\vec{F}_{ij}^R$). Force summation over all particles has been shown to capture interactions. The total DPD force on particle i is given by

$$\begin{aligned}
\vec{f}_i^{\text{DPD}} &= \sum_{j \neq i} \left(\vec{F}_{ij}^{\text{C}} + \vec{F}_{ij}^{\text{D}} + \vec{F}_{ij}^{\text{R}} \right) \\
&= \begin{cases} \sum_{j \neq i} \left[a_{ij} \left(1 - \frac{r_{ij}}{r_{\text{C}}} \right) \vec{e}_{ij} - \gamma \omega^2(r_{ij}) (\vec{e}_{ij} \cdot \vec{v}_{ij}) \vec{e}_{ij} + \sigma \omega(r_{ij}) \frac{\theta_{ij}}{\sqrt{\Delta t}} \vec{e}_{ij} \right], & r_{ij} < r_{\text{C}} \\ 0, & r_{ij} \geq r_{\text{C}}. \end{cases} \quad (11)
\end{aligned}$$

where a_{ij} is the repulsive interaction parameter between particles i and j , $\vec{r}_{ij} = \vec{r}_i - \vec{r}_j$, $r_{ij} = |\vec{r}_{ij}|$, $\vec{e}_{ij} = \vec{r}_{ij}/r_{ij}$. The friction coefficient γ governs the overall magnitude of the dissipative force, and σ is the noise amplitude that governs the intensity of the random forces. k_{B} is the Boltzmann's constant, T is the equilibrium temperature. The friction coefficient γ and noise σ are related by⁹¹

$$\sigma^2 = 2\gamma k_{\text{B}}T. \quad (12)$$

The weight function $\omega(r_{ij})$ provides the range of interaction for the DPD particles and renders the model local in the sense that the particles interact only with their neighbors. The following relation is satisfied:⁹¹

$$\omega(r_{ij}) = \begin{cases} 1 - \frac{r_{ij}}{r_{\text{C}}}, & r_{ij} < r_{\text{C}} \\ 0, & r_{ij} \geq r_{\text{C}} \end{cases} \quad (13)$$

and θ_{ij} is a random variable with normal distribution, Δt is the time-step. We take r_{C} as the characteristic length scale and $k_{\text{B}}T$ as the characteristic energy scale in our simulations, which are both set at 1. The remaining simulation parameters are $\sigma = 3$, $\gamma = 4.5$, and $\Delta t = 0.02$.

Neighboring beads in the polymer molecule are connected by the finite extension nonlinear elastic (FENE) potential, given by⁹²

$$V_{\text{FENE}}(r_{ij}) = \begin{cases} -0.5kR_0^2 \ln \left[1 - \left(\frac{r_{ij}}{R_0} \right)^2 \right], & r_{ij} < R_0 \\ \infty, & r_{ij} \geq R_0. \end{cases} \quad (14)$$

The FENE spring constant $k = 30$ and maximum extension $R_0 = 1.5r_{\text{C}}$ keep the average spring length smaller than the bead diameter and to make bond crossings energetically unfavorable.⁹²

For polymer segments in the nanochannel, the loss of available configurations due to spatial constriction leads to an effective entropic barrier. Therefore, an external driving force is required to overcome the entropic barrier and speed up the translocation. In our model, an external force F_x is applied in the direction parallel to the nanochannel axis (x) on each solvent bead in order to apply the flow field. The external force F_x is defined in the unit of $k_{\text{B}}T/r_{\text{C}}$. In our simulations, if the external force $F_x < 1.0$, the translocation time is too long and the translocation probability is too small; if the external force $F_x \gg 1.0$, the return (failed translocation attempts) times will increase, which is consistent with Yang's observation.⁴⁰ In order to obtain effective statistical average for translocation probability and translocation time, we take the fluid force to be $F_x = 1.0$. The flow rate dependence is included in the supplementary material Figure S1,⁹³ with a scaling law $\tau \sim F_x^{-0.82 \pm 0.01}$.

A modified version of the velocity-Verlet algorithm was used to integrate the equations of motion⁹¹

$$\begin{aligned}
r_i(t + \Delta t) &= r_i(t) + v_i(t)\Delta t + 0.5f_i(t)\Delta t^2, \\
\tilde{v}_i(t + \Delta t) &= v_i(t) + \lambda f_i(t)\Delta t, \\
f_i(t + \Delta t) &= f_i[r_i(t + \Delta t), \tilde{v}_i(t + \Delta t)], \\
v_i(t + \Delta t) &= v_i(t) + 0.5\Delta t[f_i(t) + f_i(t + \Delta t)].
\end{aligned} \quad (15)$$

For simplicity, the masses of the particles are set at 1, so that the force acting on a particle equals its acceleration.⁹¹ $\lambda = 0.65$ is a parameter chosen to improve the stability of the velocity Verlet algorithm.

The simulation box is rectangular with dimensions $50 \times 20 \times 20$ (DPD unit). The periodic boundary condition is applied in the flow direction. The nanochannel is modeled as a cylindrical channel with length $L = 6$ and diameter $D = 4$. A bounce-back reflection of polymer/fluid beads when these particles penetrate into the wall region is performed to enforce wall impenetrability. For more details on the implementation of the wall boundary, we referred to Refs. 94–96.

Simulations for freely jointed star polymers under a constant hydrodynamic flow field were carried out in the simulation box containing a total number of 53026 DPD particles at a number density of 3. The star polymers have f arms with N_s beads (N_s depends on particular cases) per arm, yielding a total number of beads $N_{\text{tot}} = N_s f + 1$. Based on previous computational studies,⁹¹ the repulsive parameter between the polymer and solvent particles is chosen to be $a_{ii} = 25k_B T$.

Initially, the first bead of the chain is placed just inside the entrance of the nanochannel ($x = 22.1$, $y = 10.0$, and $z = 10.0$), and the rest of the star polymer is generated randomly on the *cis* side. The first 1000 time steps are used to relax the initial configuration of the polymer chain, with the first bead fixed in position and without adding external forces on each solvent particle. Then an external force is applied to each fluid particle but not on the polymer particles to generate flow, and the solvent beads around the polymer chain push the polymer across the nanochannel. Three steps can be clearly identified during the translocation process. First, the polymer is pulled into the nanochannel by the flowing solvent particles. Second, the polymer chain segments approaching the channel continuously deform to enter the channel under flow. Third, the polymer travels through the nanochannel and completes translocation.

The translocation time τ is defined as the time interval between the beginning of the translocation, which is the moment the temporarily fixed end of polymer is pulled into the channel by the driving force, and the last bead exiting the nanochannel. τ is in the unit of $\sqrt{m_b r_C^2 / k_B T}$ with $m_b = 1$ being the mass of a polymer bead. It should be noted that not all simulation runs results in successful translocations. We have carried out a set of runs with different initially relaxed chain configurations and taken into account only the average translocation time over all successful runs until at least 200 successful translocation events are recorded (Tables 1–8 in the supplementary material⁹³). The number of the translocation samples that are collected is sufficiently large to obtain reliable numerical results (Figures S2 and S3 and Tables 1–8 in the supplementary material⁹³).

In order to verify the reliability of the simulation method and model, the translocations of a linear polymer is first examined with a set of simulation runs. The translocation time τ is found to follow the scaling relationship $\tau \sim N^{1.34 \pm 0.05}$ (Figure S4 in the supplementary material⁹³). This is in quantitative agreement with previous experimental results observed for short DNA molecules (in the range 150–3500 base pairs) translocation through the solid-state nanopore,^{5,6} as well as with other theoretical and simulation results.^{31–35,37,38,49}

III. RESULTS AND DISCUSSION

A. Translocation dependence on total number of beads/arm length

The dependence of translocation time on the arm length is first investigated for three-armed star polymer ($f = 3$) before extending to more general cases. As shown in Fig. 2, the translocation time appears to be weakly dependent on the arm length for short polymers. For longer armed stars with $N_{\text{tot}} > 31$, τ appears to follow a best fit power-law dependence with $\tau \sim N^{1.09 \pm 0.04}$, with regression coefficient = 0.997. Within statistical error, the observed power-law exponent agrees with the theoretical prediction of 1 in Eq. (9).

The transition from weak to power-law dependence may be understood by considering the radius of gyration for the star polymer. For the star polymer with three arms, the effective chain length in the flow direction is $N_{\text{eff}} = \frac{2}{3} N_{\text{tot}}$, where N_{eff} is the effective chain length. For $N_{\text{tot}} = 31$, the chain coil size is approximately $2\langle R_g \rangle^{0.5} = (\frac{2}{3} \frac{N_{\text{tot}}}{6})^{0.5} = 3.72$, which is very close to the channel diameter $d = 4$. Thus, the star polymer with short arms only needs to change its

FIG. 2. Translocation time τ as a function of total number of polymer beads N_{tot} for $f=3$, $N_s=5, 7, 10, 15, 20, 25, 30$, and 35 .

conformation slightly to pass through the narrow channel and the translocation time does not strongly depend on N_{tot} .

Compared to linear polymers of the same total number of beads (Figure S4 in the supplementary material⁹³), the dependence is weaker for star polymers. An obvious reason is that the multi-armed conformation shortens the polymer extension. In addition, the linear polymer passes through the narrow nanochannel in single-file extended conformation during translocation, while the scenario for entry of the star polymer is more complex. Two possible conformations, i.e., one-arm-forward and two-arm-forward translocation events are observed. Flow is faster near the nanochannel entrance and inside the nanochannel, and the net driving force exerted on the star polymer chain is stronger for more beads subject to the stronger flow field. These two reasons will tend to decrease the translocation time of star polymer.

How does the star polymer conformation affect the translocation process? A microscopic picture can be constructed by examining the translocation time and the probability ratio of two different conformations of star polymers during the translocation process for $f=3$ stars, as shown in Fig. 3.

FIG. 3. Snapshots of the translocation events of a star polymer ($N_{\text{tot}}=76$) transporting across the nanochannel in one-arm-forward conformation (left) and two-arm-forward conformation (right).

The distribution of these two conformations, denoted as P_1^{trans} and P_2^{trans} , indicate the successful translocation ratios of the one-arm-forward and two-arm-forward translocation events to all successful translocation attempts, respectively. A successful translocation event is referred to the chain fully transporting through the nanochannel. If the first bead retracts from the nanochannel, the event is not considered successful before the first particle reenters the channel. As shown in Fig. 4, P_1^{trans} is the dominant conformation in the overall successful translocation event. P_1^{trans} increases with the increase of the total number of beads N_{tot} , while P_2^{trans} decreases with N_{tot} . The decrease of P_2^{trans} with increasing N_{tot} is due to the decreasing likelihood for finding the ends of two arms simultaneously entering the channel in an equilibrated state.

The average translocation times τ_1 and τ_2 for star polymer in one-arm-forward and two-arm-forward translocation paths are found for $N_{\text{tot}} > 31$ and shown in Fig. 5. For $N_{\text{tot}} < 31$, the chain size is smaller than the channel. It can be observed that the translocation time and the scaling exponent in one-arm-forward translocation conformation are both larger than for the two-arm-forward translocation conformation, which may be explained by considering three-armed star polymer conformation as a combination of the single-file and hairpin model during translocation, as shown in Fig. 3. In the one-arm-forward conformation, the backward two arms form a hairpin loop; in the two-arm-forward conformation, the forward two arms form a hairpin loop. The location of the hairpin loop during translocation leads to a chemical potential difference along the star polymer. This leads to faster translocation for the two-arm-forward conformation and is consistent with predictions of linear and hairpin translocation in prior studies.²⁷ The larger scaling exponent for the one-arm-forward path may be related to the relatively smaller driving force compared with that for the multi-arm-forward path.

B. Translocation dependence on arm number

The above results and analysis found that the translocation time strongly depends on the chain conformation, f_{front} and f_{back} ($=f - f_{\text{front}}$), during the translocation. The effects of f_{front} and f_{back} have also been observed in previous studies,^{76,83} in which f_{front} and f_{back} are related to the critical flow rate for successful translocation. We further investigate the role of chain conformation on translocation by considering separately the entrance process of the “front” and “back” parts of the star polymer into the nanochannel. The relationship between τ , the time interval

FIG. 4. Histogram of P_1^{trans} and P_2^{trans} as a function of total number of beads N_{tot} for translocation events with one-arm-forward conformation (black) and two-arm-forward conformation (red). The spheres show the overall translocation probability.

FIG. 5. Translocation time τ_1 and τ_2 as a function of the total number of beads N_{tot} for the three-arm star in one-arm-forward (triangles) and two-arm-forward (squares) translocation conformations, respectively.

between the entrance of the central bead into the channel and exit of last bead from the channel, and f_{front} and f_{back} is examined by further varying the star polymers conformation with increased number of arms.

The simulations are performed with the initial position of the central bead of the star fixed at the channel entrance. The forward arms are generated in the channel in parallel alignment and the backward arms are randomly generated in the *cis* side. The configurations are allowed to relax. After equilibration, flow is introduced and the star polymer is driven through the channel. The translocation processes of $f=5$ and 8 stars, with identical arm length $N_s = 10$ and varying number of initial forward arms in the channel, are systematically investigated to find the conformational effects on their translocation time.

τ is found to decrease with increasing number of forward arms, as shown in Figs. 6(a) and 6(b). The dependence can be characterized with a power-law fit, which found the best-fit slopes are -0.30 ± 0.05 and -0.35 ± 0.02 for $f = 5$ and $f = 8$, respectively. The qualitative trend with the decrease of f_{front} corresponds to a reduction of the overall hydrodynamic force on the polymer, as there are fewer beads in the nanochannel where the flow is fastest. At the same time, more arms in the *cis* side increases the entropic barrier required to deform the backward

FIG. 6. Translocation time τ as a function of the ratio of forward arms f_{front} and total arms f , f_{front}/f , for (a) $f=5$, $f_{\text{front}} = 1, 2, 3, 4$ and (b) $f=8$, $f_{\text{front}} = 2, 3, 4, 5, 6$ with identical arm length $N_s = 10$.

arms for the star polymer arms entering the nanochannel.⁸³ Thus, the translocation time is shorter with more forward arms initially in the channel. These results explicitly demonstrate the significant roles of the star conformation, with f_{front} and f_{back} strongly affecting the translocation time. However, one caveat is that the probability of multiple arms entering the channel in the forward conformation is lower as the f_{front} increases, as found in Fig. 4. The average translocation time, which is an ensemble average over all possible initial conformations, will have smaller contribution from the events with larger f_{front} .

The importance of the star conformation during translocation is further investigated by separating the role of the forward and backward arms during translocation. The effect of the initial number of forward arms on star polymer translocation is considered by varying f_{front} with fixed number of f_{back} . Since the probability of multiple arms entering a nanochannel depends strongly on the channel to arm size ratio and also on the arm configurations as the polymer enters the channel. For a star polymer with multiple arms, if a simulation is initiated with all the star arms located on the *cis* side, it is difficult to generate the desired forward arm number in the channel. In order to investigate the role of chain conformation on translocation, we initialized the simulation by placing the desired number of forward arms in the channel.

As shown in Fig. 7, τ is higher for $f_{\text{back}} = 4$ than for $f_{\text{back}} = 2$, due to the larger entropic barrier required for the star arms in the *cis* side to enter the nanochannel, as expected. It is found that τ decreases as f_{front} increases from 1 to 3, as previously observed for the $f = 5$ and 8 star polymers. However, for $f_{\text{front}} > 3$, τ remains nearly constant. This may be understood from the balance of the pulling force due to f_{front} arms and the entropic barrier that both the front and back arms need to overcome to enter the nanochannel. As f_{front} increases, segmental density inside the nanochannel $\rho = f_{\text{front}}/(r_c D^2)$ increases, leading to increased energetic cost for chain segments to remain in the channel. At high densities in the nanochannel, the energetic cost increases with the number of beads ($\Delta E_{\text{config}} \sim f_{\text{front}} N_s$), which increases the flux to push the front arms out of the entrance to counter the hydrodynamic force due to increased flow (also increasing with $N_s f_{\text{front}}$). For $f_{\text{front}} < 3$, the hydrodynamic force on the forward arm can overcome the loss of chain configurational entropy to pull the star polymer in the channel. For $f_{\text{front}} > 3$, loss of chain configurational free energy in the nanochannel counter-balances the increase hydrodynamic force, leading to the weak dependence of τ on f_{front} . This effect has strong dependence on the chain conformational change during translocation, and it would not

FIG. 7. Translocation time τ as a function of f_{front} with $N_s = 10$ for $f_{\text{back}} = 2$ (squares) and 4 (spheres).

FIG. 8. Translocation time τ as a function of backward arm number f_{back} with identical arm length $N_s = 10$ for $f_{\text{front}} = 1$ (squares), 2 (spheres), and 3 (triangles).

be predicted by the theoretical analysis with the implicit assumptions neglecting chain conformation changes.

The importance of the backward arm conformations on star translocation is further investigated by varying the number of backward arms with fixed number of forward arms in the nanochannel. The simulations are performed by initiating $f_{\text{front}} = 1, 2$, and 3 arms in the nanochannel, and equilibrate the $f_{\text{back}} = 2, 3, 4, 5, 6$, and 7 backward arms on the *cis* side. Each arm of the star polymer has an identical arm length $N_s = 10$.

As found previously, τ decreases as f_{front} increases from 1 to 3, as shown in Fig. 8. It is observed that τ increases as f_{back} increases. A power law fit finds the exponent is approximately 0.3 for the three values of f_{front} examined, although the fitting regime is limited. This observation is in stark contrast to Eq. (9), which finds $\tau \sim 1/f$. The difference is due to the assumption that all arms enter and exit the channel together, which ignores the severe conformation change of the star arms as they enter the channel. In addition, the backward arms cannot enter the channel simultaneously due to the severe spatial constraint, leading to a strong dependence on f_{back} . For large mismatches between the star polymer and the nanochannel sizes, the backward arms must undergoes a conformational elongation in the flow direction in order to enter the nanochannel.

IV. CONCLUSIONS

In this paper, we report the dynamics of star polymer translocation through a nanochannel under a flow field by DPD simulations, focusing on the dependence of the translocation time on the star polymer arm number, arm length, and intermediate conformations. The simulation results find for three-armed stars, $\tau \sim N_{\text{tot}}^{1.09 \pm 0.04}$, which agrees with theoretical predictions of Fokker-Planck equation. In this regime, the chain conformation change during translocation does not strongly affect the star translocation due to the significantly lower probability of translocation with multiple arms entering the nanochannel simultaneously. For the three-armed star, two intermediate conformations are observed and the translocation time of two-arm-forward conformation is significantly faster than the one-arm-forward conformation.

We further investigate the conformation dependence of star polymer by examining the process in two stages by varying the number of forward arms and the number of backward arms

when the star center is at the channel entrance. The translocation time τ is weakly dependent on the number of forward arms f_{front} for $f_{\text{front}} > 3$ due to increased intra-polymer repulsion in the nanochannel. τ is also found to increase strongly as the number of backward arms increase due to severe spatial constraint on the number of arms that can enter the channel at the same time. Our findings elucidate how the conformation change of a star polymer during translocation affects the translocation time. These results provide a fundamental advancement in understanding the structural conformation effects on star polymers.

We reach the results above based on the assumption that the polymer chain is long enough with respect to the length of the nanochannel. Furthermore, since we put the first particle in nanochannel, the law of entering the channel from entirely free states is also remained to study. The dynamics of a star polymer confined in a nanoscale channel needs more deep study in order to solve many complicated problems in both theoretical and biochemical research.

ACKNOWLEDGMENTS

We thank Professor Kaifu Luo and Professor Robert Wickham for giving us a lot of valuable suggestions. Z.L., J.N.L., M.Y.X., and R.W. gratefully acknowledge financial support from National Natural Science Foundation of China (Nos. 21474051, 20874046, 21074053, and 51133002), National Basic Research Program of China (No. 2010CB923303), Program for Changjiang Scholars and Innovative Research Team in University (PCSIRT) and National Science Fund for Talent Training in Basic Science (No. J1103310). The numerical calculations in this paper have been done on the IBM Blade cluster system in the High Performance Computing Center (HPCC) of Nanjing University.

- ¹M. Muthukumar, *Annu. Rev. Biophys. Biomol. Struct.* **36**, 435–450 (2007).
- ²A. Meller, *J. Phys. Condens. Matter* **15**, R581–R607 (2003).
- ³D. Branton, D. W. Deamer, A. Marziali, H. Bayley, S. A. Benner, T. Butler *et al.*, *Nat. Biotechnol.* **26**, 1146–1153 (2008).
- ⁴Z. Siwy and S. Howorka, *Handbook of Single-Molecule Biophysics*, edited by P. Hinterdorfer and A. van Oijen (Springer, 2009), pp. 293–339.
- ⁵M. Wanunu, J. Sutin, B. McNally, A. Chow, and A. Meller, *Biophys. J.* **95**, 4716–4725 (2008).
- ⁶A. J. Storm, *Nano Lett.* **5**, 1193–1197 (2005).
- ⁷A. Spiering, S. Getfert, A. Sischka, P. Reimann, and D. Anselmetti, *Nano Lett.* **11**, 2978–2982 (2011).
- ⁸J. Mathe, A. Aksimentiev, D. R. Nelson, K. Schulten, and A. Meller, *Proc. Natl. Acad. Sci. U.S.A.* **102**, 12377–12382 (2005).
- ⁹J. J. Kasianowicz, E. Brandin, D. Branton, and D. W. Deamer, *Proc. Natl. Acad. Sci. U.S.A.* **93**, 13770–13773 (1996).
- ¹⁰J. B. Heng, A. Aksimentiev, C. Ho, P. Marks, Y. V. Grinkova, S. Silgar, K. Schulten, and G. Timp, *Nano Lett.* **5**, 1883 (2005).
- ¹¹H. Ge and C. Wu, *Macromolecules* **43**, 8711–8713 (2010).
- ¹²D. Fologea, *Nano Lett.* **5**, 1905–1909 (2005).
- ¹³Q. J. Chen, J. Liu, A. E. P. Schibel, H. S. White, and C. Wu, *Macromolecules* **43**, 10594–10599 (2010).
- ¹⁴L. Chen and A. T. Conlisk, *Biomol. Microdevices* **13**, 403–414 (2011).
- ¹⁵J. W. Yeh, A. Taoni, Y. L. Chen, and C. F. Chou, *Nano Lett.* **12**, 1597–1602 (2012).
- ¹⁶M. Cabodi, S. W. P. Turner, and H. G. Craighead, *Anal. Chem.* **74**, 5169 (2002).
- ¹⁷S. Matysiak, A. Montesi, M. Pasquali, A. Kolomeisky, and C. Clementi, *Phys. Rev. Lett.* **96**, 118103 (2006).
- ¹⁸J. Cohen, A. Chaudhuri, and R. Golestanian, *Phys. Rev. Lett.* **107**, 238102 (2011).
- ¹⁹J. Chuang, Y. Kantor, and M. Kardar, *Phys. Rev. E* **65**, 011802 (2001).
- ²⁰C. T. A. Wong and M. Muthukumar, *J. Chem. Phys.* **128**, 154903 (2008).
- ²¹W. C. Yu and K. F. Luo, *J. Am. Chem. Soc.* **133**, 13565–13570 (2011).
- ²²M. Muthukumar, *Phys. Rev. Lett.* **86**, 3188–3191 (2001).
- ²³M. Muthukumar, *J. Chem. Phys.* **111**, 10371 (1999).
- ²⁴C. Y. Kong and M. Muthukumar, *J. Chem. Phys.* **120**, 3460–3466 (2004).
- ²⁵I. Huopaniemi, K. F. Luo, T. Ala-Nissila, and S.-C. Ying, *Phys. Rev. E* **75**, 061912 (2007).
- ²⁶I. Huopaniemi, K. Luo, T. Ala-Nissila, and S. C. Ying, *J. Chem. Phys.* **125**, 124901 (2006).
- ²⁷C. Forrey and M. Muthukumar, *J. Chem. Phys.* **127**, 015102 (2007).
- ²⁸K. F. Luo and R. Metzler, *J. Chem. Phys.* **134**, 135102 (2011).
- ²⁹K. F. Luo, T. Ala-Nissila, S.-C. Ying, and A. Bhattacharya, *Phys. Rev. E* **78**, 061911 (2008).
- ³⁰K. F. Luo, T. Ala-Nissila, S.-C. Ying, and A. Bhattacharya, *Phys. Rev. Lett.* **99**, 148102 (2007).
- ³¹K. F. Luo, T. Ala-Nissila, S. C. Ying, and R. Metzler, *Europhys. Lett.* **88**, 68006 (2009).
- ³²K. Luo, R. Metzler, T. Ala-Nissila, and S.-C. Ying, *Phys. Rev. E* **80**, 021907 (2009).
- ³³K. Luo and R. Metzler, *J. Chem. Phys.* **133**, 075101 (2010).
- ³⁴H. Vocks, D. Panja, G. T. Barkema, and R. C. Ball, *J. Phys. Condens. Matter* **20**, 095224 (2008).
- ³⁵V. V. Lehtola, R. P. Linna, and K. Kaski, *Phys. Rev. E* **78**, 061803 (2008).
- ³⁶H. M. Ding, W. D. Tian, and Y. Q. Ma, *ACS Nano* **6**, 1230–1238 (2012).

- ³⁷A. Cacciuto and E. Luijten, *Phys. Rev. Lett.* **96**, 238104 (2006).
- ³⁸A. Bhattacharya, W. H. Morrison, K. Luo, T. Ala-Nissila, S. C. Ying, A. Milchev, and K. Binder, *Eur. Phys. J. E* **29**, 423–429 (2009).
- ³⁹K. Yang and Y.-Q. Ma, *Nat. Nanotechnol.* **5**, 579–583 (2010).
- ⁴⁰S. Yang and A. V. Neimark, *J. Chem. Phys.* **136**, 214901 (2012).
- ⁴¹S. Kraszewski, M. Tarek, and C. Ramseyer, *ACS Nano* **5**, 8571–8578 (2011).
- ⁴²Y. D. He, H. J. Qian, Z. Y. Lu, and Z. S. Li, *Polymer* **48**, 3601–3606 (2007).
- ⁴³J. Y. Guo, X. J. Li, Y. Liu, and H. J. Liang, *J. Chem. Phys.* **134**, 134906 (2011).
- ⁴⁴M. Tagliazucchi, O. Peleg, M. Kroeger, Y. Rabin, and I. Szleifer, *Proc. Natl. Acad. Sci. U.S.A.* **110**, 3363–3368 (2013).
- ⁴⁵O. Peleg, M. Tagliazucchi, M. Kroeger, Y. Rabin, and I. Szleifer, *ACS Nano* **5**, 4737–4747 (2011).
- ⁴⁶A. Nikoubashman and C. N. Likos, *J. Chem. Phys.* **133**, 074901 (2010).
- ⁴⁷Y. H. He, M. Tsutsui, R. H. Scheicher, F. Bai, M. Taniguchi, and T. Kawai, *ACS Nano* **7**, 538–546 (2013).
- ⁴⁸Y. H. He, M. Tsutsui, C. Fan, M. Taniguchi, and T. Kawai, *ACS Nano* **5**, 5509–5518 (2011).
- ⁴⁹K. Luo, S. T. T. Ollila, I. Huopaniemi, T. Ala-Nissila, P. Pomorski, M. Karttunen, S.-C. Ying, and A. Bhattacharya, *Phys. Rev. E* **78**, 050901 (2008).
- ⁵⁰K. Zhang and K. Luo, *Soft Matter* **9**, 2069–2075 (2013).
- ⁵¹H. Yong, Y. Wang, S. Yuan, B. Xu, and K. Luo, *Soft Matter* **8**, 2769–2774 (2012).
- ⁵²H. W. de Haan and G. W. Slater, *Phys. Rev. E* **87**, 042604 (2013).
- ⁵³M. G. Gauthier and G. W. Slater, *Phys. Rev. E* **79**, 021802 (2009).
- ⁵⁴M. G. Gauthier and G. W. Slater, *J. Chem. Phys.* **128**, 175103 (2008).
- ⁵⁵S. Guillouzie and G. W. Slater, *Phys. Lett. A* **359**, 261–264 (2006).
- ⁵⁶G. Zifferer, *Macromol. Theory Simul.* **8**, 433–462 (1999).
- ⁵⁷A. Sikorski, *Macromolecules* **35**, 7132–7137 (2002).
- ⁵⁸L. A. Molina and J. J. Freire, *Macromolecules* **32**, 499–505 (1999).
- ⁵⁹E. M. Harth, S. Hecht, B. Helms, E. E. Malmstrom, J. M. J. Fréchet, and C. J. Hawker, *J. Am. Chem. Soc.* **124**, 3926–3938 (2002).
- ⁶⁰P. K. Lin, C. C. Hsieh, Y. L. Chen, and C. F. Chou, *Macromolecules* **45**, 2920–2927 (2012).
- ⁶¹J. Z. Y. Chen and D. E. Sullivan, *Macromolecules* **39**, 7769 (2006).
- ⁶²J. Z. Y. Chen, D. E. Sullivan, and X. Yuan, *Europhys. Lett.* **72**, 89–95 (2005).
- ⁶³Y.-L. Chen, *Biomicrofluidics* **7**, 054119 (2013).
- ⁶⁴Y.-L. Chen, P. K. Lin, and C. F. Chou, *Macromolecules* **43**, 10204 (2010).
- ⁶⁵Y.-L. Chen, Y.-H. Lin, J.-F. Chang, and P.-K. Lin, *Macromolecules* **47**, 1199–1205 (2014).
- ⁶⁶T. Cui, J. D. Ding, and J. Z. Y. Chen, *Phys. Rev. E* **78**, 061802 (2008).
- ⁶⁷K. A. Dryden, M. Tihova, N. Nowotny, S. M. Matsui, E. Mendez, and M. Yeager, *J. Mol. Biol.* **422**, 650–658 (2012).
- ⁶⁸J. Dong, L. Dong, E. Mendez, and Y. Tao, *Proc. Natl. Acad. Sci. U.S.A.* **108**, 12681–12686 (2011).
- ⁶⁹Y. Wang, A. Masur, Y. Zhu, and J. Ziebarth, *J. Chromatogr. A* **1217**, 6102–6109 (2010).
- ⁷⁰M. Ripoll, R. G. Winkler, and G. Gompper, *Eur. Phys. J. E* **23**, 349–354 (2007).
- ⁷¹M. Ripoll, R. G. Winkler, and G. Gompper, *Phys. Rev. Lett.* **96**, 188302 (2006).
- ⁷²M. M. Nardai and G. Zifferer, *J. Chem. Phys.* **131**, 124903 (2009).
- ⁷³S. Masatsugu, N. Nakagawa, and K. Ohno, *Macromolecules* **42**, 3170–3178 (2009).
- ⁷⁴Z. Li, Y. Li, Y. Wang, Z. Sun, and L. An, *Macromolecules* **43**, 5896–5903 (2010).
- ⁷⁵A. Debnath and K. L. Sebastian, *Phys. Rev. E* **76**, 051803 (2007).
- ⁷⁶P. G. de Gennes, *Adv. Polym. Sci.* **138**, 91–105 (1999).
- ⁷⁷P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, NY, 1979).
- ⁷⁸M. Daoud and J. P. Cotton, *J. Phys. (France)* **43**, 531–538 (1982).
- ⁷⁹F. Brochard-Wyart and P. G. de Gennes, *C. R. Acad. Sci., Paris* **323**, 473–479 (1996).
- ⁸⁰W.-B. Zhang, J. He, K. Yue, C. Liu, P. Ni, R. P. Quirk, and S. Z. D. Cheng, *Macromolecules* **45**, 8571–8579 (2012).
- ⁸¹D. M. Meunier, P. B. Smith, and S. A. Baker, *Macromolecules* **38**, 5313–5320 (2005).
- ⁸²H.-J. Lee, K. Lee, and N. Choi, *J. Polym. Sci., Part A: Polym. Chem.* **43**, 870–878 (2005).
- ⁸³H. Ge, S. Pispas, and C. Wu, *Polym. Chem.* **2**, 1071–1076 (2011).
- ⁸⁴J. M. J. Fréchet, *J. Polym. Sci., Part A: Polym. Chem.* **41**, 3713–3725 (2003).
- ⁸⁵K. F. Freed and C. Wu, *J. Chem. Phys.* **135**, 144902 (2011).
- ⁸⁶K. F. Freed and C. Wu, *Macromolecules* **44**, 9863–9866 (2011).
- ⁸⁷K. F. Freed, J. Dudowicz, E. B. Stukalin, and J. F. Douglas, *J. Chem. Phys.* **133**, 094901 (2010).
- ⁸⁸P. B. Warren, *Curr. Opin. Colloid Interface Sci.* **3**, 620–624 (1998).
- ⁸⁹P. Espanol and P. Warren, *Europhys. Lett.* **30**, 191–196 (1995).
- ⁹⁰P. J. Hoogerbrugge and J. Koelman, *Europhys. Lett.* **19**, 155–160 (1992).
- ⁹¹R. D. Groot and P. B. Warren, *J. Chem. Phys.* **107**, 4423 (1997).
- ⁹²M. Kroger and S. Hess, *Phys. Rev. Lett.* **85**, 1128–1131 (2000).
- ⁹³See supplementary material at <http://dx.doi.org/10.1063/1.4893637> for translocation time as a function of driving force, probability distribution of translocation time for 3-armed polymers, translocation time as a function of linear chain length, translocation time as a function of successful times, and successful and failed translocation events in the study.
- ⁹⁴M. Revenga, I. Zuniga, and P. Espanol, *Comput. Phys. Commun.* **121**, 309–311 (1999).
- ⁹⁵I. V. Pivkin and G. E. Karniadakis, *Phys. Rev. Lett.* **96**, 206001 (2006).
- ⁹⁶I. V. Pivkin and G. E. Karniadakis, *J. Comput. Phys.* **207**, 114–128 (2005).