

# Effect of Interchain Interactions on the Translocation of Polymer Chains Through Small Holes

Chao Wang,<sup>1</sup> Meng-Bo Luo<sup>1,2</sup>

<sup>1</sup>Department of Physics, Zhejiang University, Hangzhou 310027, People's Republic of China

<sup>2</sup>Laboratory of Solid State Microstructures, Nanjing University, Nanjing 210008, People's Republic of China

Received 12 April 2006; accepted 20 August 2006

DOI 10.1002/app.25381

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** The translocation of polymer chains through a small hole was simulated with the dynamic Monte Carlo method. The dependence of the relaxation time ( $\tau_1$ ) and escaping time ( $\tau_2$ ) on the chain concentration ( $C$ ) was studied. The interchain interaction played an important role in the translocation process. Different behaviors were discovered at low and high  $C$  regions.  $\tau_1$  presented a power law

behavior with  $C$  at low and high  $C$  values with exponents of  $-1$  and  $-3$ , respectively.  $\tau_2$  was roughly independent of  $C$  at low  $C$  values but decreased with power law exponent  $-1.3$  at high  $C$  values. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 1200–1205, 2007

**Key words:** chain; diffusion; Monte Carlo simulation

## INTRODUCTION

The translocation of polymer chains through small holes is a fundamental event in various biological processes, such as in the transport of proteins through channels in biological membranes,<sup>1–3</sup> the translocation of RNA molecules through pores in cell nuclear membranes, the transfer of DNA molecules from virus to host cell, and the transfer of genes between bacteria.<sup>4</sup> It also relates to the migration of DNAs through microfabricated channels and devices,<sup>5</sup> gene therapy, drug delivery, gel electrophoresis,<sup>6,7</sup> and size exclusion chromatography.<sup>8</sup> It has attracted great attention in experiments,<sup>9–14</sup> analytical theories,<sup>15–20</sup> and computer simulations.<sup>21–25</sup> In the experimental study of biological macromolecules through biological membranes,<sup>9–11</sup> the size of the nanopore through which macromolecules translocate is much larger than the microscopic bond length of the chain backbone, so it is reasonable to adopt a coarse-grained approximation to simulate the translocation processes of polymer chains.<sup>21–25</sup>

Single-chain systems that contain only one polymer have been well studied with several driving mechanisms, such as the ratchet mechanism,<sup>18</sup> electric field,<sup>9–11</sup> chemical potential difference,<sup>15,16,19,20</sup> and

selective absorption on one side of the membrane.<sup>23,26</sup> However, a lot of natural systems, such as drug release from a capsule<sup>27–29</sup> and gel electrophoresis,<sup>5,30</sup> are comprised of a number of chains. In such kinds of multichain systems, the interchain interaction plays an important role in the polymer translocation processes, and the translocation processes are much more complicated than that of single-chain systems. In this study, we tried to examine the effect of chain concentration ( $C$ ) on the translocation of polymer chains through a small hole. The dependence of the relaxation time ( $\tau_1$ ) and escaping time ( $\tau_2$ ) on  $C$  was studied, and different behaviors were found at low and high  $C$  regions.

## MODEL AND SIMULATION METHOD

Our simulation system was embedded in a simple cubic lattice. The simulated box was a cuboid with spacing  $L_x$ ,  $L_y$ , and  $L_z$  in the  $x$ ,  $y$ , and  $z$  directions, respectively. Periodic boundary conditions were considered in the  $x$  and  $y$  directions, whereas in the  $z$  direction, there were two infinitely large flat walls located at  $z = 0$  and  $L_z + 1$ , respectively. Polymers were confined between in these two impenetrable walls. A small hole was located at the center of the upper wall at  $z = L_z + 1$ , through which polymer chains could escape from the box. Above the upper wall, there was a large space without any chain.

A polymer chain of length  $n$  was comprised of  $n$  self-avoiding identical segments, and every segment occupied one lattice site. Bond length between two sequential segments was equal to the lattice constant, which was set as the unit of length. The interaction

Correspondence to: M.-B. Luo (luomengbo@zju.edu.cn).

Contract grant sponsor: Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry.

Contract grant sponsor: Natural Science Foundation of Zhejiang Provincial; contract grant number: Y405406.

between segments and that between the segment and surface were supposed to be self-avoiding; that is, segments could not share the same lattice site and contact the flat surfaces.

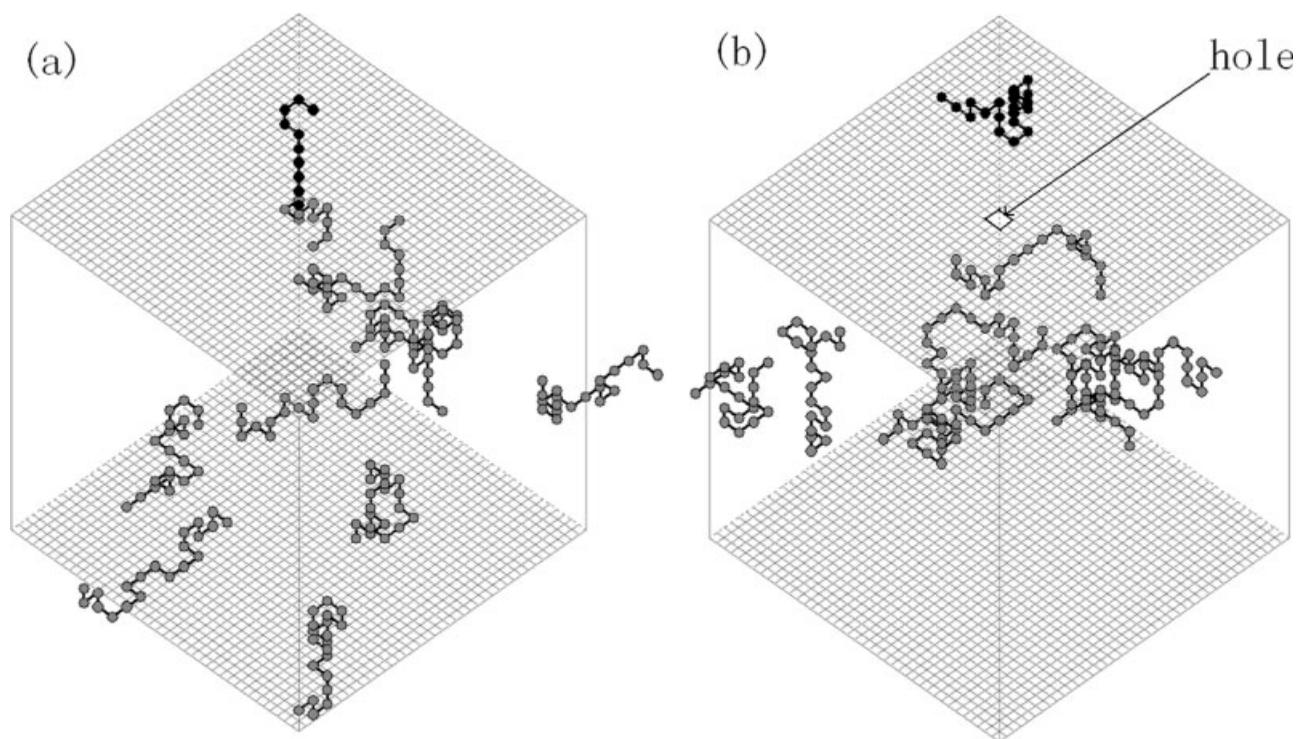
The dynamics of the polymer chains consisted of local and global Brownian movements. Simulation details can be found in ref. 25. The local movement contained three elementary motions of segments: the end rotation,  $90^\circ$  crankshaft rotation, and kink jump motion. Although for the global movement slithering snakelike reptation was considered for two end segments, every attempted reptation led the whole chain to move one lattice forward or backward. For every end segment, the probability of choosing reptation was arbitrarily set to 0.5. The time unit was 1 Monte Carlo step, during which  $Nn$  trial movements were attempted, where  $N$  and  $Nn$  represent the number of polymer chains and the total number of segments, respectively. The trial move was accepted only if the self-avoidance was satisfied. With the local and global movements, polymer chains changed their configurations and spatial locations.

At the beginning of the simulation, we closed the hole and put  $N$  identical chains of length  $n$  into the simulation box. After a sufficient time of Brownian movement, the system arrived at an equilibrium state. Then, we opened the hole on the upper surface and

investigated the translocation of chains through this hole. The moment we opened the hole was set as the starting time ( $t = 0$ ). Assuming there was an infinitely large space above the upper surface, we removed the chain if all of its segments were out of the box.

A certain time later, one of the chain's two end segments arrived at the hole, and the front several segments of the chain wormed out of the box by random back-and-forth motion. However, this step did not necessarily lead to a successful escape; all the segments outside the box might be pulled back by entropic force. After several such attempts, however, a successful escape eventually occurred. In Figure 1, we show two snapshots of chain configurations at different times: a chain escaping through the hole and its eventual escape from the box. We considered the smallest hole in this study, that is, a hole that comprised only one lattice site. The smallest hole could prevent multichain escape and thus made the problem relatively simple.

In this study, the whole event of chain escape from the box was separated into two stages with different timescales:<sup>22</sup> (1) a relaxation stage with timescale  $\tau_1$ , where one end segment eventually arrived at the hole and resulted in a successful chain escape, and (2) an escaping stage with timescale  $\tau_2$ , where one chain completely escaped from the box after the last arrival



**Figure 1** Snapshots of our system: (a) a chain escaping through the hole and (b) a whole chain that escaped from the box. The gray and dark circles represent segments inside and outside of the box, respectively. The two surfaces with small squares represent the walls. The hole with size of one lattice site is at the middle of the upper wall. The parameters were as follows: box size =  $20 \times 20 \times 20$ ,  $n = 20$ , and  $N = 10$ .

of the successfully escaping chain's front end at the hole. Figure 2 shows the variation of segment number outside the box during the escaping process. Here, one can see that there were several temporary tries before the final successful escape. We mainly investigated the dependence of  $\tau_1$  and  $\tau_2$  on the initial  $C$  of polymer before the dislocation of the chain.  $C$  is defined as the initial fraction of polymer segments:

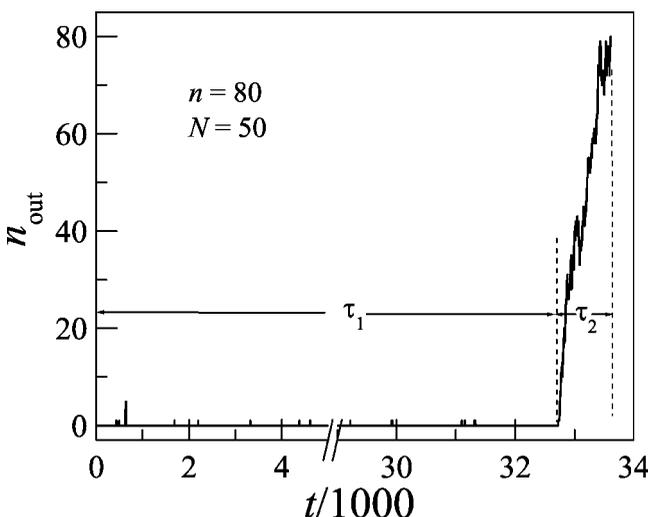
$$C = \frac{Nn}{V}. \quad (1)$$

where  $V (L_x \times L_y \times L_z)$  is the total number of lattice sites of the simulation box and  $N$  is the polymer number before the translocation. With this definition,  $C$  was a constant during the translocation of one polymer chain.

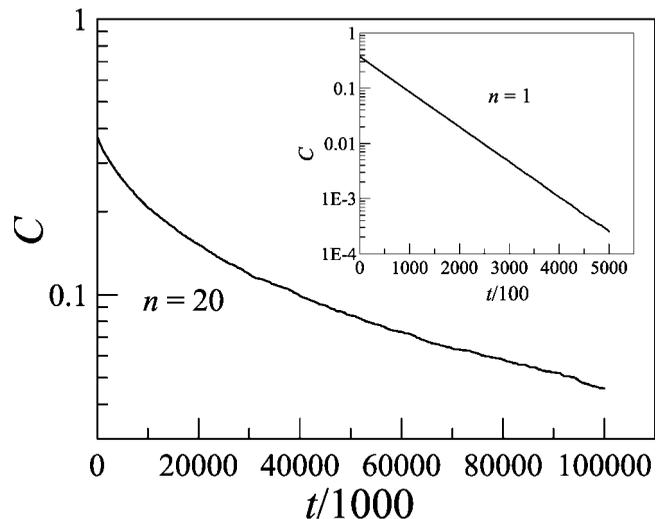
### SIMULATION RESULTS AND DISCUSSIONS

Figure 3 presents the time dependence of  $C$  inside the simulation box. Here, the polymer length  $n = 20$ , and the box was  $20 \times 20 \times 20$ . The initial  $N$  was 150; that is, the initial  $C$  was 0.375. In the semilogarithmic plot of  $C$  versus time  $t$ , the decrease in  $C$  was nonlinear. For comparison, we also measured the translocation of hard spheres (or particles) in the same condition. The result is shown in the insert of Figure 3. Here, a hard sphere was equivalent to a polymer chain with  $n = 1$  in our system. For the hard-sphere system, the permeation was very fast, and the dependence of  $C$  in the logarithmic scale was linear with time. Therefore, we concluded that chain structure played an important role in the translocation.

For the hard-sphere system, diffusion induced by the difference in  $C$  could be phenomenologically



**Figure 2** Variation of segment number out of the box ( $n_{\text{out}}$ ) with time  $t$ . Box size =  $20 \times 20 \times 20$ ,  $n = 80$ , and  $N = 50$ .



**Figure 3** Semilogarithmic plot of  $C$  of the polymer segments versus time  $t$  for chains of  $n = 20$  translocation through a hole from a box of size of  $20 \times 20 \times 20$ . The initial  $C$  was 0.375. The insert shows the semilogarithmic plot of  $C$  versus  $t$  for hard-sphere particles, which was equivalent to a chain of  $n = 1$ .

described by the Fick's law. Net flux  $[j(z,t)]$  was set up as

$$j(z,t) = -Ds \frac{dC}{dz} \quad (2)$$

where  $D$  is the diffusion constant,  $s$  is the area of the hole, and  $dC/dz$  is the spatial gradient of concentration. In our model, assuming  $C$  inside the box was uniform and  $C = 0$  outside the box, we then calculated the decrease rate of hard spheres in the box as<sup>25</sup>

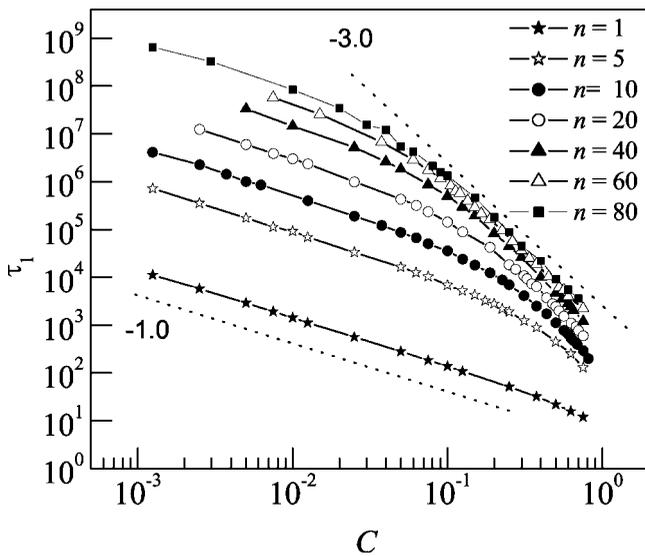
$$\frac{dN}{dt} = -CDs \quad (3)$$

where  $N$  is the total number of hard spheres. Then, for the hard-sphere system, we have

$$\frac{dC}{C} \propto -dt \quad (4)$$

because  $C \propto N$ . Thus,  $C$  decayed exponentially with time  $t$ , as presented in the insert of Figure 3. However, polymer chain systems do not obey such a simple behavior. The reason is that both interchain interactions and entropic barrier depend on concentration of the polymer.<sup>22,25</sup> The interchain interaction pushed the polymer out of the box, while the entropic barrier drug the permeation of the polymer.

For hard spheres,  $\tau_1$  could be expressed as  $\tau_1 \propto C^{-1}$  when we set the time interval  $dt$  as  $\tau_1$  and the bead decrement  $dN$  as  $-1$  in eq. (3). Our simulation result gave a simple power law ( $\tau_1 \propto C^{-1}$ ) for the hard-sphere system. Here, we measured  $\tau_1$  from the simula-



**Figure 4** Log-log plot of  $\tau_1$  versus  $C$  for systems with  $n$ 's = 1, 5, 10, 20, 40, 60, and 80. The dotted line at the bottom and the dashed line at the top have slopes of  $-1.0$  and  $-3.0$ , respectively. The smallest two  $C$ 's for  $n = 80$  were obtained from the simulations in boxes of size  $40 \times 40 \times 40$  and  $30 \times 30 \times 30$ , whereas all other  $C$ 's were simulated in a box of size  $20 \times 20 \times 20$ .

tion, as shown in Figure 2, instead of calculating it from the time dependence of  $C$ .<sup>25</sup> Then, we investigated the dependence of  $\tau_1$  on  $C$  for the polymer chain translocation.

Figure 4 presents the dependence of  $\tau_1$  on  $C$ . For the multichain system, the power law  $\tau_1 \propto C^{-1}$  was only satisfied at very low  $C$ 's. Although simulations were carried out in a box of size  $20 \times 20 \times 20$ , the size effect was negligible. We did not find an obvious size effect even for the longest  $n$  (80) because the results obtained from the box sizes  $40 \times 40 \times 40$ ,  $30 \times 30 \times 30$ , and  $20 \times 20 \times 20$  were roughly on the line with a slope of about  $-1$ . The whole  $C$  range could be divided into three regimes with two crossover points,  $C_1^*$  and  $C_2^*$ : (1) a low- $C$  regime where  $C < C_1^*$  and  $\tau_1$  showed a power law behavior with  $C$  described by  $\tau_1 \propto C^{-1}$ , (2) a high- $C$  regime where  $C > C_2^*$  and  $\tau_1$  could be roughly expressed as  $\tau_1 \propto C^{-3}$ , and (3) an intermediary  $C$  regime where  $C_1^* < C < C_2^*$  and where the decrease in  $\tau_1$  sped up gradually with increasing  $C$ . A clear description for the relationship between  $\tau_1$  and  $C$  can be expressed as

$$\tau_1 \propto \begin{cases} C^{-1}, & C < C_1^* \\ C^{-3}, & C > C_2^* \end{cases} \quad (5)$$

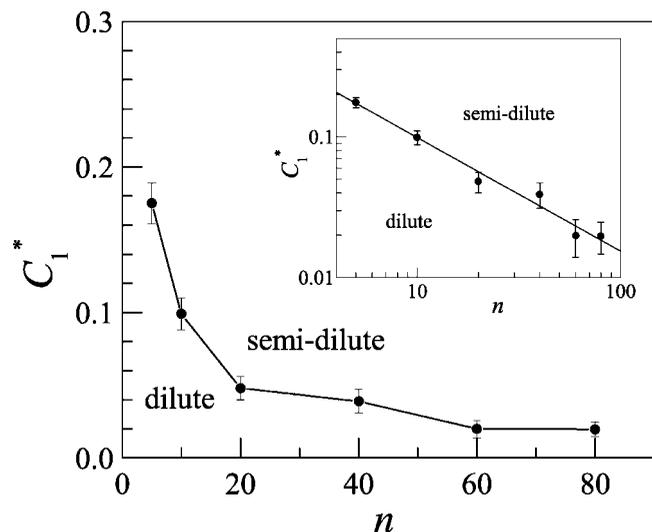
Below  $C_1^*$ , the translocation behavior of the polymer chains was the same as that of hard spheres. Therefore, we could not distinguish hard sphere and polymer chain from the dependence of  $\tau_1$  on  $C$ . In other

words, the chain structure did not play role at low  $C$ 's. That means that chains were independent of each other and that the system could be regarded as polymer chains in a dilute solution. Above  $C_1^*$ , chains began to intersect each other, and the chain structure played a role in the translocation process; then, the system at  $C > C_1^*$  could be regarded as a semidilute solution. Therefore, the value  $C_1^*$  separated the dilute and semidilute solutions. The dependence of the value  $C_1^*$  on  $n$  is presented in Figure 5. We found that  $C_1^*$  can be roughly expressed as

$$C_1^* \propto n^{-0.81} \quad (6)$$

The exponent  $-0.81$  was very close to theoretical value  $-0.80$  for self-avoiding walking chains in solution.<sup>31,32</sup> However, it was unclear what happened near  $C_2^*$ . At such a high  $C$  ( $C_2^*$ ), the polymers should have been highly entangled and should have interacted strongly with each other.

We also studied the dependence of  $\tau_2$  on  $C$ . Figure 6 gives the dependence of  $\tau_2/n$  on  $C$  for the multichain systems with  $n$  values of 10, 20, 40, 60, and 80. At low  $C$ , the value  $\tau_2/n$  was roughly independent of  $C$ . Particularly, the free  $\tau_2$  of the single-chain system was almost equal to that of the multichain system at low  $C$ . Therefore, we named it the *free escaping regime*, where  $\tau_2$  was roughly a constant and was independent of  $C$ . The size effect on  $\tau_2$  was also negligible. For  $n = 20$ ,  $\tau_2$ 's obtained from different system sizes were almost independent of system size at low and high  $C$ 's. We also did not find a size effect, even for the longest  $n$  (80) that we considered in this study. The constant  $\tau_2$  region was a little wider than the free relaxation region characterized by  $C_1^*$ . The interchain interactions among the polymers were negligible at



**Figure 5** Plot of transitional  $C_1^*$  of  $\tau_1$  versus  $n$ . The curve separates the dilute and semidilute solutions. The insert presents the log-log plot of  $C_1^*$  versus  $n$ .

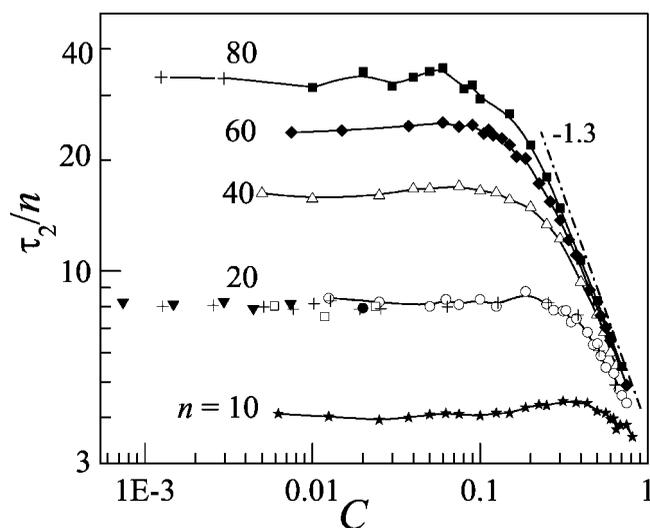
small  $C$  ( $< C_1^*$ ), so each chain behaved like one single chain in the system. At  $C$  values just above  $C_1^*$ , however, the interaction was still very weak, and the driving force was much smaller than the entropic barrier that blocked the chain; therefore, the change in  $\tau_2$  might have been too small to be observed.

At high  $C$ 's, however, the interchain interactions played an important role in the chain translocation process.  $\tau_2$  decreased with  $C$  and could be described by a power law relation at high  $C$ 's:

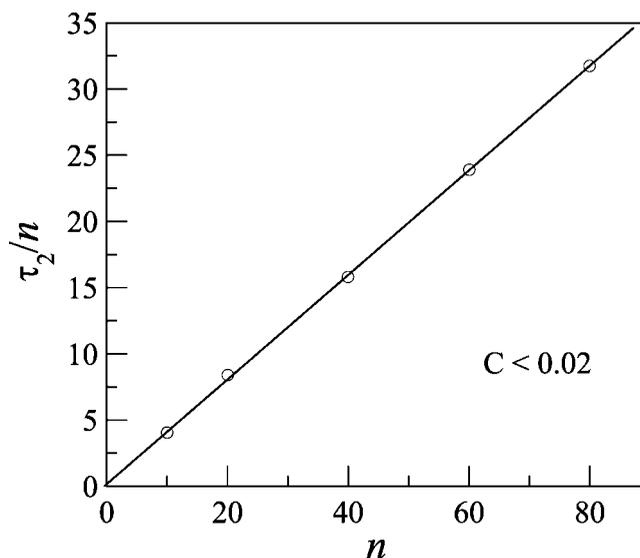
$$\tau_2 \propto nC^{-1.3} \quad (7)$$

This regime was named the *driving escaping regime*. The driving escaping regime appeared at lower  $C$  values for longer chains. In this regime, the single-segment ( $\tau_2/n$ ) was independent of  $n$ . That means that the flow rate of the segment was independent of  $n$  at high  $C$ 's. However, in the free escaping regime,  $\tau_2/n$  increased with  $n$ . Figure 7 presents the dependence of  $\tau_2/n$  on  $n$  at  $C < 0.02$ .  $\tau_2$  could be expressed as  $\tau_2 \propto n^2$  in the free escaping regime, in agreement with theoretical prediction with Fokker–Planck formalism by the assumption of a constant rate to translocate one segment through the small hole.<sup>16</sup>

We know that at low  $C$ 's, the polymer chains inside the box were far away from each other, and the effective chain–chain interaction was negligible. So when one chain was escaping, it mainly suffered from the entropic force resulting from the variation of the chain's configurations with position. Generally, the



**Figure 6** Plot of the average  $\tau_2/n$  versus  $C$  for systems with  $n$ 's = 10, 20, 40, 60, and 80. The dashed line has a slope of  $-1.3$ . Simulations were carried out in a box of size  $20 \times 20 \times 20$ , except the following. The (+) smallest two  $C$ 's for  $n = 80$  were obtained from the simulations in boxes of size  $40 \times 40 \times 40$  and  $30 \times 30 \times 30$ . For  $n = 20$ , several box sizes were used: (●)  $10 \times 10 \times 10$ , (□)  $15 \times 15 \times 15$ , (○)  $20 \times 20 \times 20$ , (+)  $25 \times 25 \times 25$ , and (▼)  $30 \times 30 \times 30$ .



**Figure 7** Dependence of the average  $\tau_2/n$  on  $n$  at low  $C$  ( $< 0.02$ ). The  $\tau_2/n$  shown here were averaged over low  $C$  ( $< 0.02$ ) in Figure 6.

entropic force imposed on a long chain is larger than that on a short chain, which results in a large  $\tau_2$  for the long chain to translocate one segment forward, as described in Figure 6. However, at high  $C$ 's, the interchain interaction builds up, and it drives the chain out of the system. As we know, the size of a random SAW chain can be characterized by the mean square radius of gyration of  $\langle R_G^2 \rangle \propto n^{2\nu}$  with exponent  $\nu \approx 0.6$  in random coil states. Therefore, the interchain interaction of long chains will be stronger than that of short chains at the same  $C$ ; that is, the interaction will be built at a lower  $C$  for a longer chain. This was in agreement with our findings that the driving escaping regime appeared at lower  $C$  values for longer chains.

## CONCLUSIONS

We investigated the translocation of polymer chains through a small hole with a dynamic Monte Carlo method. The whole event of the translocation was composed of a relaxation stage with a timescale  $\tau_1$  and an escaping stage with a timescale  $\tau_2$ . Both  $\tau_1$  and  $\tau_2$  were dependent on  $C$ . At low  $C$ 's,  $\tau_1$  showed a power law behavior with  $C$  ( $\tau_1 \propto C^{-1}$ ), like that found for the hard-sphere systems. This indicated that the interchain interaction was negligible, and therefore, the crossover point  $C_1^*$ , which separated the dilute and semidilute solutions, was defined. Although at high  $C$  regions ( $C > C_2^*$ ), where the interchain interaction was very strong,  $\tau_1$  decreased quickly with increasing  $C$  as  $\tau_1 \propto C^{-3}$ . We identified two stages in the escape process: a free escaping regime at low  $C$ 's, where  $\tau_2$  was a constant independent of  $C$ , and a driving escaping regime at high  $C$ 's where  $\tau_2$  could be expressed as  $\tau_2 \propto$

$nC^{-1.3}$ . We concluded that the interchain interaction played an important role in the chain translocation process.

## References

1. Simon, S. M.; Blobel, G. *Cell* 1991, 65, 371.
2. Akeson, M.; Branton, D.; Kasianowicz, J. J.; Brandin, E.; Deamer, D. W. *Biophys J* 1999, 77, 3227.
3. Helenius, J.; Ng, D. T. W.; Marolda, C. L.; Walter, P.; Valvano, M. A.; Aebi, M. *Nature* 2002, 415, 447.
4. Alberts, B.; Bray, D. *Molecular Biology of the Cell*; Garland: New York, 1994.
5. Han, J.; Craighead, H. G. *Science* 2000, 288, 1026.
6. Chang, D. C. *Guide to Electroporation and Electrofusion*; Academic: New York, 1992.
7. Zimm, B. H.; Levene, S. D. *Q Rev Biophys* 1992, 25, 171.
8. Yan, W. W.; Kirkland, J. J.; Bly, D. D. *Modern Size-Exclusion Liquid Chromatography*; Wiley: New York, 1979.
9. Han, J.; Turner, S. W.; Craighead, H. G. *Phys Rev Lett* 1999, 83, 1688.
10. Henrickson, S. E.; Misakian, M.; Robertson, B.; Kasianowicz, J. *J. Phys Rev Lett* 2000, 85, 3057.
11. Meller, A.; Nivon, L.; Branton, D. *Phys Rev Lett* 2001, 86, 3435.
12. Kwan, K. S.; Subramaniam, C. N. P.; Ward, T. C. *Polymer* 2003, 44, 3061.
13. Kwan, K. S.; Subramaniam, C. N. P.; Ward, T. C. *Polymer* 2003, 44, 3071.
14. Mattozzi, A.; Neway, B.; Hedenqvist, M. S.; Gedde, U. W. *Polymer* 2005, 46, 929.
15. Sung, W.; Park, P. J. *Phys Rev Lett* 1996, 77, 783.
16. Muthukumar, M. *J Chem Phys* 1999, 111, 10371.
17. Lubensky, D. K.; Nelson, D. R. *Biophys J* 1999, 77, 1824.
18. Slater, G. W.; Guo, H. L.; Nixon, G. I. *Phys Rev Lett* 1997, 78, 1170.
19. Dimarzio, E. A.; Mandell, A. L. *J Chem Phys* 1997, 107, 5510.
20. Tian, P.; Smith, G. D. *J Chem Phys* 2003, 119, 11475.
21. Chern, S. S.; Cárdenas, A. E.; Coalson, R. D. *J Chem Phys* 2001, 115, 7772.
22. Muthukumar, M. *Phys Rev Lett* 2001, 86, 3188.
23. Milchev, A.; Binder, K.; Bhattacharya, A. *J Chem Phys* 2004, 121, 6042.
24. Lansac, Y.; Maiti, P. K.; Glaser, M. A. *Polymer* 2004, 45, 3099.
25. Luo, M. B. *Polymer* 2005, 46, 5730.
26. Park, P. J.; Sung, W. *J Chem Phys* 1998, 108, 3031.
27. Kost, J.; Langer, R. *Adv Drug Delivery Rev* 1991, 6, 19.
28. Santini, J. T., Jr.; Cima, M. J.; Langer, R. *Nature* 1999, 397, 335.
29. Grayson, A. C. R.; Choi, I. S.; Tyler, B. M.; Wang, P. P.; Brem, H.; Cima, M. J.; Langer, R. *Nat Mater* 2003, 2, 787.
30. Viovy, J. L. *Rev Mod Phys* 2000, 72, 813.
31. de Gennes, P. G. *Scaling Concepts in Polymer Physics*; Cornell University: New York, 1979.
32. Doi, M. *Introduction to Polymer Physics*; Oxford: New York, 1995.