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Dynamic Monte Carlo study on the permeation of polymer chains through small holes

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Abstract

The permeation of polymer chains through a small hole is simulated using dynamic Monte Carlo method. The dependence of the permeation velocity v on concentration C of polymer chain, chain length n and hole size s is investigated. The velocity v increases non-linearly with C, differing from linear dependence of hard sphere system, indicating that inter-chain interaction plays an important role in the permeation process. At the same concentration, the velocity decreases with the chain length n via a relation $v=a+bn^{-\phi}$, where the exponent ϕ increases linearly with C. Such a behavior is different from a single chain system. The possible physical reason is addressed. The velocity is proportional to hole size when the chain size is smaller than the hole size, but it decreases obviously if the chain size is much larger than the hole size.

Keywords: Permeation; Polymer chain; Diffusion

1. Introduction

The dynamics of polymer chains worming through a narrow hole is a fundamental topic in various biological processes, such as the translocation of proteins across biological membranes and that of RNAs across a nuclear membrane after their synthesis. It also relates to the transport mechanisms of drug delivery, gel electrophoresis, and exclusion chromatography. Therefore, the topic has received considerable attention from both experimental and theoretical perspectives [1–15]. Theoretically, translocation time τ of a polymer chain worming through a small hole as well as its scaling behaviors on chain length n can be derived by applying Fokker–Planck diffusion equation [2,7,11]. For the case of a single chain driven through a hole on a planar membrane by chemical potential difference $\Delta\mu$ per segment, Sung and Park [2] revealed that the scaling behavior changes from $\tau\sim n^3$ to $\tau\sim n^2$ at characteristic chain length $n_c=k_BT/\Delta\mu$ by assuming the diffusion coefficient $D\sim n^{-1}$ to be a constant in the course of translocation. Muthukumar [7] found different scalings, $\tau\sim n_2/k_0$ for small $n\Delta\mu/k_BT$ and $\tau\sim n(k_BT/k_0\Delta\mu)$ for large $n\Delta\mu/k_BT$, using a chain length independent parameter k_0. Here k_0 is defined as the rate constant to translocate one monomer through the hole, which is similar to the diffusion coefficient D to some extent. The driving force can also be set up by free energy difference F_d between in and out of a confinement since, polymer in the confinement is in an entropy unfavorable state. Park and Sung [4] had investigated the translocation of polymer chain from a sphere and found that $\tau\sim n^2$ for $R<R_G$ and $\tau\sim n^3$ for $R\gg R_G$, here R and R_G are the radius of confinement and the radius of gyration of polymer, respectively. While for a SAW chain, Muthukumar's simulation revealed that the escaping time τ is proportional to $n(n/\rho)^{5/9}$, where ρ is the monomer density prior to escape [8]. Baumgärtner and Skolnick [1] simulated the translocation of polymer directly through lipid bilayer, driven by a concentration imbalance inside and outside of the lipid bilayer as a higher concentration exists at high-curvature regions. Polymer chain driven through nano-scale holes by external force had also been simulated [9,14].

All these investigations attempted to describe the behavior of a single polymer chain translocating through a hole. However, many natural systems, like drug releasing from a capsule [16–18] and gel electrophoresis [19,20],

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contain multi-chains. In such multi-chain systems, inter-chain interactions will play important role in chain diffusion since, they attribute the free energy difference. Thus a multi-chain system is more complicated than a single chain one. This work tries to find out rules of multi-chain translocating through a small hole. We study the permeation of linear polymer chains through a hole from a box in which chains are confined. The dependences of the permeation velocity on the concentration of the polymer chains, the chain length and the hole size are studied.

2. Model and simulation method

Our simulation system is embedded in the simple cubic (SC) lattice. A polymer chain of length n is comprised of n self-avoiding identical segments on the lattice. One segment occupies one lattice site. Bond length between two sequence segments equals the lattice constant, which is used as length unit. The simulated box is a cuboid with spacings L_x, L_y and L_z in x, y and z directions, respectively. Periodic boundary conditions (PBC) are considered in the x and y directions, while in z direction there are two infinitely large flat surfaces locating at $z=0$ and L_z+1, respectively. The surfaces are impenetrable except a small hole of size $s=s_x\times s_y$ located in the center of the upper surface at $z=L_z+1$ through which polymers can permeate. Above the upper surface, there is an infinite space. Fig. 1 shows the scheme of our systems. The interactions between segments of chains and between chain and surface are self-avoiding, i.e. segments cannot share the same lattice site and contact the flat surfaces.

At the beginning of simulation, we close the hole and put initial N_0 identical chains of chain length n in the simulated box with volume $V=L_x\times L_y\times L_z$. We let the chains undergo a long enough time of Brownian movement to establish an equilibrium state. Then we open the hole on the upper surface and investigate the permeation of chain through the hole. The moment we open the hole is set as time $t=0$. As we have assumed there is an infinitely large space above the upper surface, we remove the chain if all of its segments are above the hole. Therefore, the chain number N in the simulation box decreases with time.

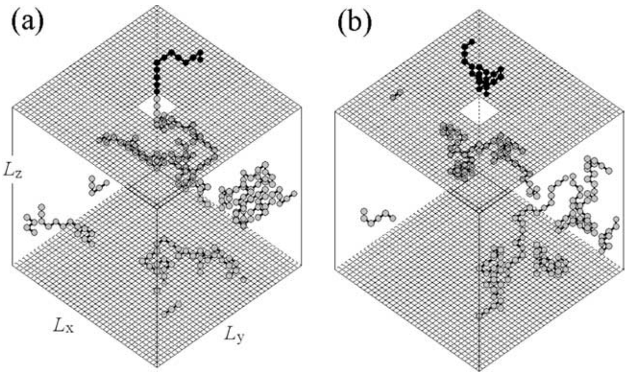

Fig. 1. Snapshots of our simulation system. The basic simulated box size is $L_x\times L_y\times L_z$. A big square in the upper surface is a small hole through which chain escapes from the box. The grey and dark circles represent segments inside and outside of the box, respectively. (a) A chain is permeating through the hole, and (b) a whole chain escapes from the box.

The Brownian movement of polymer chain involves local and global movements. The local movement contains three elementary motions of segments: the end-segment, normal-segment and 90° crankshaft motions, as described in Ref. [21]. With the local movement, one, two or three segments adjust their spatial locations. While the global movement, reputation in this work, leads the whole chain worming one lattice constant ahead. The reputation is only tried for two end segments. The probability for end segment choosing reputation is arbitrarily set to be 0.5. The time unit is one Monte Carlo step (MCS) during which Nn trial moves are attempted. The trial move will be accepted only if self-avoidance is obeyed. Polymer chains continue undergoing random movements and their configuration as well as spatial location changes with time. After a period of time, one segment of a polymer chain begins to permeate through the hole. Though the segments outside of the box can be pulled back into the box again because of random continuous forth and back motion, more and more segments permeate outward with time and eventually a whole chain escapes from the box through the hole. In Fig. 1, we show two snapshots of chain escaping at different times.

We investigate the rule of the permeation velocity of chain, $v=\mathrm{d}(Nn)/\mathrm{d}t$, i.e. its dependence on chain length n, concentration $C=Nn/V$ inside the box, hole size s et al. Normally, diffusion caused by spatial gradient of the concentration can be phenomenologically described by Fick's law, that is, a net flux $j(z,t)$ of particles is proportional to the concentration gradient $\mathrm{d}C/\mathrm{d}z$,

$$j(z,t)=-Ds\frac{\mathrm{d}C}{\mathrm{d}z} \tag{1}$$

Here, D is the diffusion constant and s is the area of hole. In our model, the concentration C inside the box is assumed uniform and $C=0$ outside the box, we then obtain the variation of segment number Nn at time t, or the permeation velocity

$$v=-\frac{\mathrm{d}(Nn)}{\mathrm{d}t}=\frac{NnDs}{Vd}=CDs \tag{2}$$

where $d=1$ is the thickness of the hole. The permeation velocity v describes the decrease rate of segment number, i.e. in unit time v segments (equals to v/n chains) permeate through the hole.

Eq. (1) was obtained by simply considering the random Brownian movement of particles with a concentration gradient. However, the present problem is much more complicated for the following two reasons: (1) a chain itself has conformational entropy difference between inside and outside of the box and (2) a chain changes its configuration during permeation process thus a resistance force against the permeation is imposed by the small hole. Therefore, a complicated diffusion rule deviating from hard particle system is expected. In this paper, we have monitored the time evolution of the polymer chain number N in the box. A chain length and concentration dependent permeation velocity v is found and the dynamics of permeation of chain are investigated. The results shown below are averaged over at least 10^4 independent runs.

3. Simulation results and discussion

At first, we have simulated the permeation of simple hard sphere particles through holes. Each particle occupies one lattice site, which can be treated as $n=1$ in the chain model. The permeation velocity v can be determined from the time evolution of the particle number N. Linear dependence relations $v \propto C$ and $v \propto s$ are found, implying that the diffusion constant D is a constant which is independent of concentration and hole size.

While for polymer chains, we observe a non-linear dependence of the velocity v on the concentration C. Fig. 2 gives the typical time evolution of the chain number N within the box. Here the polymer chain length n is 20, the box size is $20\times20\times20$, the initial chain number N_0 is 150, and the hole size is 3×3. We have checked the size effect by comparing results gotten from $10\times10\times10$ to $40\times40\times40$ for the largest chain length $n=100$. We did not find obvious size effect for box size $20\times20\times20$, thus all simulations are performed in a box of size $20\times20\times20$ in this work that saves much simulation time. The dependence of the permeation velocity on the concentration is given in the insert of Fig. 2. The permeation velocity v increases nonlinearly with the concentration C. Such a behavior quite differs from the linear dependence relation $v \propto C$ of simple sphere particles. The physical reason may be that the size of polymer chain is bigger than a simple summarization of segments n, for instance, the size of a random SAW chain can be characterized by the radius of gyration of $\langle S^2\rangle^{3/2} \sim n^{3\nu}$ with $\nu \approx 0.6$ in random coil states. Therefore, the repulsive inter-chain interaction increases nonlinearly with concentration. If we assume $v=CDs$ (Eq. (2)) holds in the permeation process, we find that the diffusion coefficient D increases with concentration C. Therefore, we conclude that the diffusion coefficient in the non-equilibrium case is different from that in equilibrium state, where self-diffusion constant D decreases with the increase of concentration [22, 23]. Since, the repulsive inter-chain force imposed on the escaping chain is dependent on the concentration, so it is reasonable to observe a concentration dependent diffusion coefficient. And the concentration gradient is very large in the permeation process, thus a simple Fick's law might be insufficient to describe it.

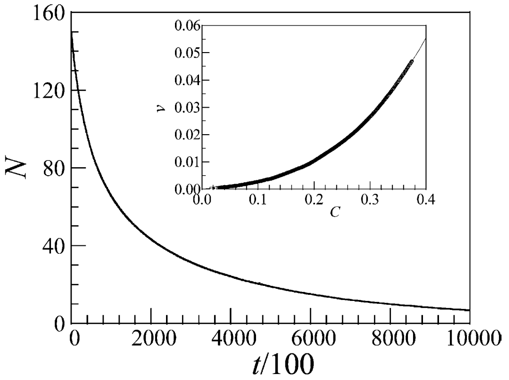

Fig. 2. Plot of the chain number N versus the time t for chains of length $n=20$ permeating through a 3×3 hole from a box of size $20\times20\times20$. The insert shows the dependence of the permeation velocity v on the concentration C.

From the permeation velocity v, we can determine the total escaping time τ one chain needed to escape from the box. The total escaping time τ can be expressed approximated as $\tau=n/v$ by setting the time interval dt as τ and the segment decrease d(Nn) as $-n$ in Eq. (2). Fig. 3 presents the total escaping time τ as a function of concentration C. The total escaping time τ decreases with C and it can be roughly expressed as a power law, $\tau \sim C^{-\alpha}$. We find three concentration regimes with different exponent α within our simulated concentration range: (1) a low concentration regime with exponent $\alpha=1$; (2) a mediate concentration regime with $\alpha=2$; and (3) a high concentration regime with $\alpha=3$.

The total escaping time τ is a summation of (1) relaxation time τ_1 for chain relax around the hole and finally one end of chain finding the hole and (2) escaping time τ_2 for the whole chain passing through the hole. Both the relaxation time τ_1 and the escaping time τ_2 depend on concentration C, chain length n and hole size s. Without multi-chain escaping, i.e. no two or more chains escaping at the same time, chains diffuse through the hole one by one independently and the velocity v can be simply expressed as $v=n/(\tau_1+\tau_2)$. The probability of one chain locating near the hole as well as the free energy difference F_d increases with the concentration, thus both τ_1 and τ_2 decrease with the increase of C. As an

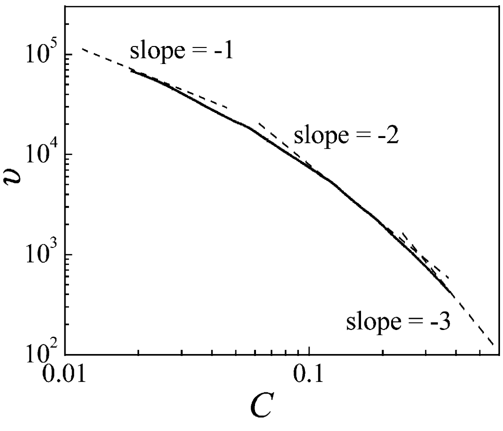

Fig. 3. Plot of the total escaping time τ versus the concentration C for chains of length $n=20$ permeating through a 3×3 hole from a box of size $20\times20\times20$. Dashed lines are of slopes -1, -2 and -3, respectively.

example, we have calculated these two time scales for chain of length $n=20$ escaping through 1×1 hole. We find that τ_1 decreases from 312,000 at concentration $C=0.00625$ to 2250 at $C=0.5$, and τ_2 also decreases from 169 at concentration $C=0.00625$ to 123 at $C=0.5$. A more complicated ingredient is the chain length n. A simple reason is that the chain length n itself is also included in the equation $v=n/(\tau_1+\tau_2)$. Besides, there are two contrary effects on time τ_1 and τ_2. The equilibrium diffusion coefficient in solution decreases with n [24], that will increase the relaxation time τ_1 with the increase of chain length n. We find τ_1/n slightly increases from 910 of $n=20$ to 1140 of $n=100$ for chains diffusing through 1×1 hole at $C=0.25$. Also, the escaping time τ_2 increases with n as that in single chain translocation process [2,7,8,11]. But there is one possibility that decreases the escaping time τ_2 for long chains. For that the size of polymer chain is bigger than a simple summarization of segment n and increases non-linearly with n, therefore, the inter-chain interaction (or the free energy difference) increases with n that will promote the escape of chain out of the hole, i.e. decreases the escaping time τ_2. However, our simulation reveals that the escaping time τ_2/n always increases with n: it increases from 7.9 of $n=20$ to 19.5 of $n=100$ for chains diffusing through 1×1 hole at $C=0.25$. Finally, with a bigger hole, chain becomes easier to find the hole that decreases τ_1 and chain also becomes easier to escape with a small escaping time τ_2 since, a larger hole imposes a weaker resistance. Also there exists multi-chain escaping when the hole size bigger than 1×1, that also decreases τ_1 obviously.

Now we explore the dependence of the permeation velocity on the chain length. Fig. 4 gives the dependence of the permeation velocity v on the polymer chain length n. The velocity decreases with the chain length, which can be described by a scaling law

$$v = a + bn^{-\phi} \tag{3}$$

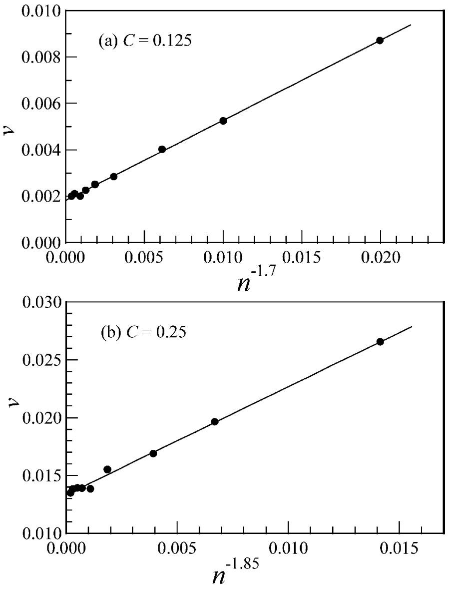

Fig. 4. Dependence of the permeation velocity v on the chain length n for two concentrations: (a) $C=0.125$ and (b) $C=0.25$. Chains permeate through the hole of size 3×3 from $20\times20\times20$ simulation box. Simulated chain lengths are $n=10$, 15, 20, 30, 40, 50, 60, 80 and 100.

The exponent ϕ and coefficients a and b are determined by the least square fitting. The exponent ϕ and coefficient b are found to be linearly dependent on the concentration as shown in Fig. 5. However, the coefficient a increases nonlinearly with C. For large chain length n, as $n^{-\phi}$ approaches zero, we have the velocity $v=a$. At low concentration, the value a tends to be zero, indicating it is very difficult for a long chain to permeate through a small hole like single chain model [7]. However, the velocity increases gradually with concentration, implying that inter-chain interaction takes effect even at very low concentrations.

Then we obtain a chain length dependent relation of the total escaping time τ of chain from the definition $\tau=n/v=n/(a+bn^{-\phi})$. The asymptote values of τ can be expressed as

$$\tau \propto \begin{cases} n^{1+\phi}, & a \ll bn^{-\phi} \\ n, & a \gg bn^{-\phi} \end{cases} \tag{4}$$

At low concentrations, the parameter a is close to zero so that $a \ll bn^{-\phi}$ is satisfied, then we expect the total escaping time $\tau \propto n^{1+\phi}$. Since, the parameter a increases faster than

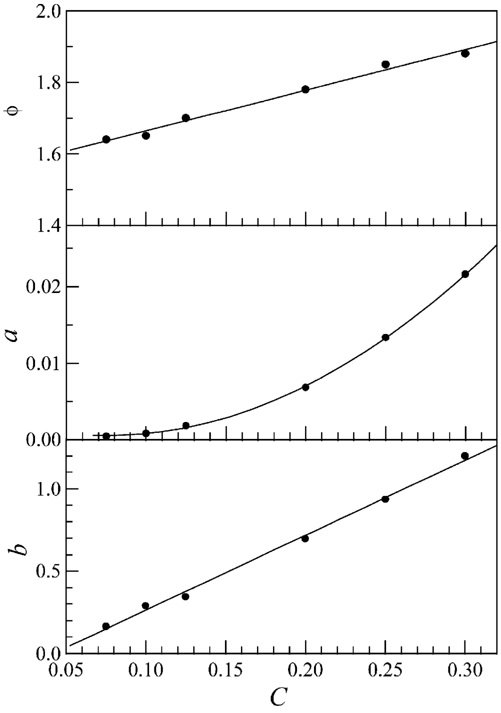

Fig. 5. Plot of the scaling exponent ϕ, and coefficients a and b versus concentration C. Simulation parameters are: box size $20\times20\times20$, hole size $s=3\times3$, and concentration $C=0.25$. Straight lines in the top and the bottom panels are linear fittings and smooth curve in the middle panel is binomial fitting.

the parameter b (Fig. 5), then at high concentrations $a \gg bn^{-\phi}$ will be satisfied, then we expect the total escaping time $\tau \propto n$. The results show that the inter-chain interaction plays a very important role in the chain permeation. It changes the scaling exponent from 1 at high concentration to $1+\phi$ at low concentration.

Finally, the effect of the hole size on the permeation of polymer chains has also been studied. The permeation velocity increases with the hole size since, the barrier F_b decreases with the increase of the hole size. The dependence of the permeation velocity v on the hole size s is presented in Fig. 6 for a short chain $n=20$ and a long chain $n=100$. The velocity v is roughly proportional to the hole size for the short chain. But for the longer chain, a non-linear character appears at small s. We know that the size of chain is of chain length dependence. For the SAW chain in dilute solution, the square radius of gyration $\langle S^2 \rangle \approx 6$ and 45 for $n=20$ and 100, respectively. When the size of chain is much bigger than the hole size, the resistance force imposed by the small hole increases dramatically and v decreases. Fig. 6 implies that the velocity difference between two chain lengths, $\Delta v = v(n_1) - v(n_2)$ with $n_1 < n_2$, increases with the hole size, indicating that we should use large hole in order to accelerate the separation of chains according to the length.

The exponent ϕ and coefficients a and b are determined by the least square fitting of Eq. (3). Fig. 7 gives the dependence of these parameters on the hole size s at concentration $C=0.25$. The exponent ϕ shows a suddenly increase from $s=1\times1$ to $s=2\times2$, and then decrease steadily with increasing hole size. There is no multi-chain escaping for the hole of size 1×1, but there exist multi-chain escaping for large hole 2×2. To describe the multi-chain escaping phenomenon, we have calculated the probability of two chains escaping from the hole simultaneously, i.e. the ratio of two-chain escaping process in all escaping processes. For instance, the two-chain escaping probability is about 0.025 for $n=20$ through a 2×2 hole. The probability decreases with chain length and becomes about 0.016 for chain $n=100$. Therefore, the increase of permeation velocity v for short chain is bigger than long chain that causes a sudden increase of the exponent ϕ. With the increase of the hole size, however, the difference of the two-chain escaping probabilities between two chain lengths dies away, thus the exponent ϕ decreases with increasing the hole size. But we find that both coefficients a and b increase monotonously with the hole size s. Since, b increases with the hole size s, then the velocity difference between two chain lengths Δv increases with the hole size.

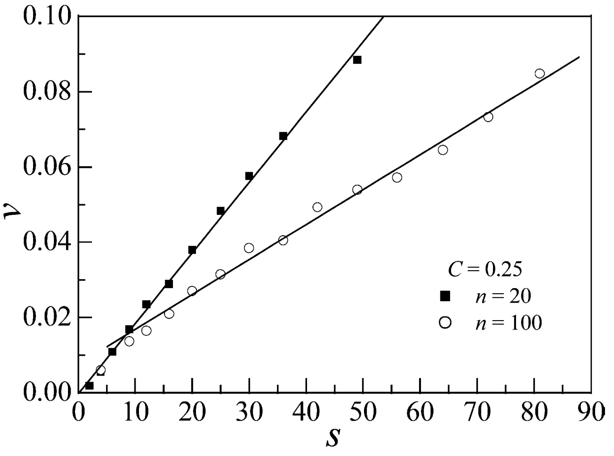

Fig. 6. Plot of the permeation velocity v versus the hole size s for chain lengths $n=20$ and 100 at concentration $C=0.25$. Simulation box is $20\times20\times20$. Straight lines are guides for eyes.

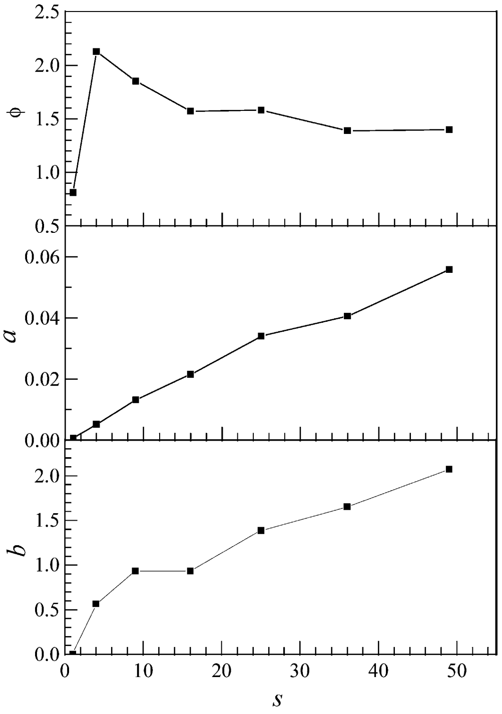

Fig. 7. Plot of the scaling exponent ϕ, and coefficients a and b versus the hole size s. Simulation parameters are: box size $20\times20\times20$, and concentration $C=0.25$.

4. Conclusions

We have studied the permeation of the polymer chains through small holes by using dynamic Monte Carlo method. The results show that the inter-chain interaction is very important in the chain permeation process, as we find that the permeation velocity nonlinearly depends on the concentration of the polymer chains. The velocity decreases with the chain length n, which can be expressed as $v=a+bn^{-\phi}$. The exponent ϕ increases with concentration C, indicating that velocity difference $\Delta v = v(n_1) - v(n_2)$ becomes more obvious at high C. The velocity is proportional to the hole size if the chain size is smaller than the hole size, but it decreases obviously if the chain size is much larger than the hole size. We also find the velocity difference Δv increases with the hole size. Behaviors different from a single chain system are also observed and discussed.

Acknowledgements

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