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Dynamic Monte Carlo study on the probability distribution functions of tail-like polymer chain*

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Abstract: The configurational properties of tail-like polymer chains with one end attached to a flat surface are studied by using dynamic Monte Carlo technique. We find that the probability distribution of the free end in *z* direction $P(R_z)$ and the density profile $\rho(z)$ can be scaled approximately by a factor β to be a length independent function for both random walking (RW) and self-avoiding walking (SAW) tail-like chains, where the factor β is related to the mean square end-to-end distance $<R^2>$. The scaled $P(R_z)$ of the SAW chain roughly overlaps that of the RW chain, but the scaled $\rho(z)$ of the SAW chain locates at smaller βz than that of the RW chain.

Key words: Probability distribution, Monte Carlo simulation, Tail-like polymer chain
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INTRODUCTION

Polymer chains with one end attached to a surface by means of physical or chemical interaction have become one of the important polymer science subject, which are useful for many applications, such as polymer compatibilizers, copolymer microphases, colloid stabilization, polymeric surfactants (Milner, 1991). Grafting polymers can improve the power efficiency of electrorheological fluids, enhance photoluminescence of nano materials, and increase dispersion stability. On this topic, a simple but interesting case is that one single polymer chain attached to a flat surface with one of its two end beads (Gottstein *et al.*, 1997; Luo *et al.*, 2001; Sikorski, 2002; Huang and Han, 2004). For this case, some configurations diminish owing to the restriction of the surface, giving rise to a number of interesting properties and also significantly affecting the macroscopic properties of the whole system (Tanaka, 1977; Metzger *et al.*, 2002). The chain is in an entropic unfavored state near the surface, so it stretches out to maintain large entropy and thus leaves a small bead density near the surface (Milner, 1991). One of the authors investigated the excluded volume effect of chain bead on the conformational properties of the tail-like chain and found that the excluded volume has nearly the same effect on mean square end-to-end distance $<R^2>$ and mean square radius of gyration $<R_G^2>$ (Luo and Huang, 2003).

In this paper, dynamic Monte Carlo (MC) simulations are carried out for linear self-avoiding walking (SAW) free chain, SAW tail-like chain, and random walking (RW) tail-like chains on the simple cubic (SC) lattice. The repulsive effect of the flat surface on the size and probability distribution functions of SAW tail-like chain are investigated.

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TAIL-LIKE CHAIN MODEL AND CALCULATION METHOD

Simulations are performed on the simple cubic (SC) lattice. The flat surface is assumed infinitely large and impenetrable to polymer chain and lies at z=0, direction z being perpendicular to the flat surface. The lattice layers numbered z=1, 2, …. A SAW polymer chain, comprised of n+1 beads (n bonds) consecutively linked with bond length l=1 in the SC lattice unit, is generated randomly with MC method at the beginning of simulation. The first bead is set on the flat surface and immobile forever, while the other beads cannot contact the flat surface. So we put the first bead at (0, 0, 0), the second at (0, 0, 1), with the others chosen randomly (one site from all possible sites).

After creating a chain, we let the polymer chain undergo a series of Brownian motion resulted from random collisions between chain beads and solvent molecules. The dynamical lattice model of a linear polymer chain was described in detail previously (Gurler *et al*., 1983). In the dynamic model, a bead is chosen randomly and one of the three elementary motions: the end-bead, normal-bead and 90° crank-shaft motions, is attempted. The trial move will be accepted if the following conditions are satisfied simultaneously: (1) self-avoidance is obeyed (for SAW chain), (2) the new site locates at z>0. Each trial move is called one bead cycle. In dynamic MC simulation, the natural time unit is one MC step (MCS) during which all chain beads attempt to move once. In the tail-like chain model, as a matter of fact, the first two beads are immobile, therefore one MCS contains $n-1$ bead cycles. But for the free chain, one MCS contains n+1 bead cycles since all n+1 beads are movable. In this work, the tail-like chain is relaxed for about 10 times as long as the relaxation time τ of the free chain before the results are recorded (Huang *et al*., 2001). For example, $\tau\approx$87000 for free SAW chain of length n=400, then the SAW tail-like chain will take 870000 MCS for relaxation. To minimize the statistical error, 50000 independent runs are performed in the present calculation.

RESULTS AND DISCUSSION

In this paper, the configurational properties of the tail-like polymer chain are calculated using the dynamic MC method. The chain lengths used in this work ranged from 10 to 400. For comparison, the configurational properties of the free polymer chain are also calculated. We sample the independent configurations at each regular time τ for the free chain (at 10τ for the tail-like chains).

Fig.1 shows the effect of flat non-interacting surface on the size of the linear SAW tail-like chain. The effect is characterized by two parameters: (1) $\alpha_R=\langle R^2\rangle_T/\langle R^2\rangle_F$, the ratio of mean square end-to-end distance of tail-like chain to that of free chain; and (2) $\alpha_G=\langle R_G^2\rangle_T/\langle R_G^2\rangle_F$, the ratio of mean square radius of gyration of tail-like chain to that of free chain. Here the subscripts 'T' and 'F' refer to the tail-like chain and the free chain, respectively. We find that both parameters are almost independent of chain length for long chains. The asymptotic values are $\alpha_R\approx1.32$ and $\alpha_G\approx1.07$. The value α_R is consistent with theoretical result for RW chain (Tanaka, 1977) and random flight (RF) chain (Luo *et al*., 2001), indicating that the surface has almost the same effect on $\langle R^2\rangle$ of the long chains, regardless of the excluded volume. However, the value $\alpha_G\approx1.07$ is slightly bigger than $\alpha_G\approx1.03$ of the RW chain (Tanaka, 1977) and the non-reversal random walking chain (Huang *et al*., 2000), indicating that the repulsive effect of the surface on the radius of gyration of the SAW chain is stronger than that on the radius of gyration of the RW chain. Since $\alpha_R>\alpha_G$, we then conclude that $\langle R_G^2\rangle$ is less sensitively

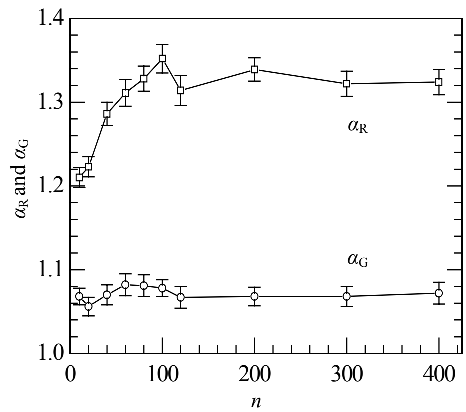

Fig.1 The effect of surface on the size of SAW chain. $\alpha_R=\langle R^2\rangle_T/\langle R^2\rangle_F$, the ratio of mean square end-to-end distance of tail-like chain to that of free chain; $\alpha_G=\langle R_G^2\rangle_T/\langle R_G^2\rangle_F$, the ratio of mean square radius of gyration of tail-like chain to that of free chain

influenced by the surface than $<R^2>$.

To have better understanding of the repulsive effect of the surface, we also investigated the probability distribution of the free end bead in z direction $P(R_z)$ and the density profile $\rho(z)$ of the tail-like chains. Here, R_z is the z component of end-to-end vector $\boldsymbol{R}$, i.e. the vertical distance of the free end bead from the surface. $P(R_z)$ is the probability of finding the free end bead at layer z in the lattice model. Theoretically, for long chains without excluded volume, such as RF chain, Gaussian chain and RW chain, etc., $P(R_z)$ can be roughly expressed as

$$P(R_z)=2\beta^2 z\exp(-\beta^2 z^2) \quad (1)$$

where $\beta^2=3/(2nb^2)$. Here b is mean bond length of chain and b=1 for the RW chain on the SC lattice. The probability distributions for both RW and SAW chains are shown in Fig.2a. The excluded volume effect of SAW chain is obvious as the end bead of the SAW chain locates farther from the surface than the RW chain. A minimum near the surface reflects the repulsive effect of the surface. For the RW chain, the probability distribution $P(R_z)$ can be scaled by β as

$$P'(R_z)\equiv P(R_z)/\beta=2\beta z\exp(-\beta^2 z^2) \quad (2)$$

if the distance z is scaled to be βz. Then we find the scaled probability $P'(R_z)$ is almost independent of chain length. We plot $P'(R_z)$ in Fig.2b for two RW chains with length n=100 and 300. Within the statistical error, they can be regarded as equivalent. Since $<R^2>=4n/3$ for the RW tail-like chain (Luo *et al.*, 2001), we can rewrite β as $\beta=\sqrt{2/<R^2>}$ or $\beta^2=2/<R^2>$. It is interesting to see that the probability distribution $P(R_z)$ of the SAW tail-like chain can also be scaled by $\beta=\sqrt{2/<R^2>}$ with $<R^2>$ of the SAW tail-like chain. We find that $P'(R_z)$ of the SAW chain roughly overlaps that of the RW chain as shown in Fig.2b. So we conclude that the probability distribution of the free end bead $P(R_z)$ can be expressed by Eq.(1) with $\beta^2=2/<R^2>$ for both RW and SAW tail-like chains. We thus also suggest that Eq.(1) may be also suitable for describing the probability distribution $P(R_z)$ for other lattice chain models as well as non-lattice chain models.

From Eq.(2), it is easy to obtain the peak of scaled probability distribution $P'(R_z)$ by differentiating $P'(R_z)$ with respect to z. The peak locates at

$$\beta z_0=\sqrt{2}/2, \quad (3)$$

i.e. we have

$$z_0=1/2\sqrt{<R^2>}. \quad (4)$$

Then, from Eq.(1), we get the peak value

$$P(z_0)=\frac{2}{\sqrt{<R^2>}}\exp(-1/2)=1.213<R^2>^{-1/2}. \quad (5)$$

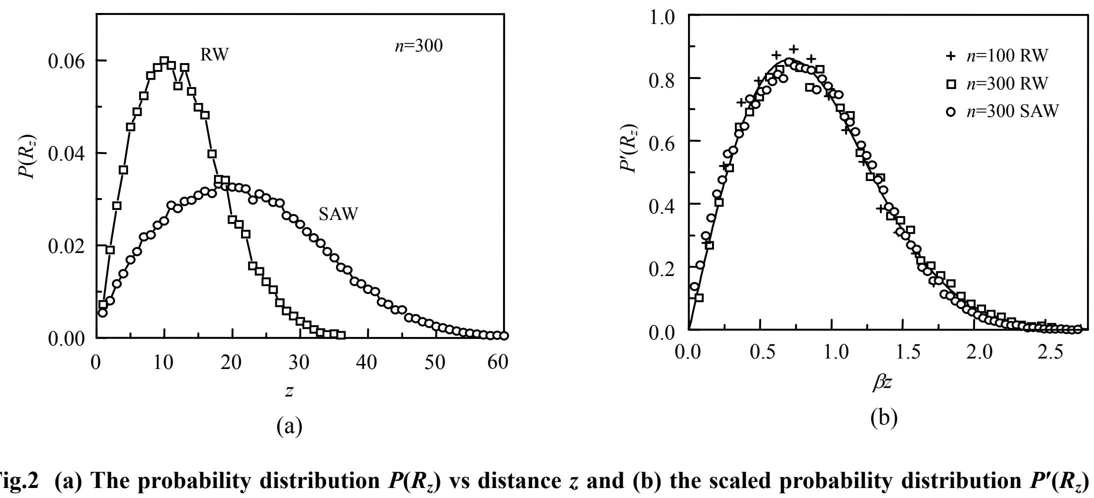

Fig.2 (a) The probability distribution $P(R_z)$ vs distance z and (b) the scaled probability distribution $P'(R_z)$ vs scaled distance βz for tail-like RW and SAW chains. Solid line in panel (b) is the theoretical prediction of Eq.(2). The factor $\beta=\sqrt{2/<R^2>}$

For example, our MC result of $<R^2>$ is about 400 for the RW chain and 1306 for the SAW chain, respectively. Then we get the peak position z_0=10 and 18 from Eq.(4), and we get the peak value $P(z_0)$=0.061 and 0.034 from Eq.(5) for the RW chain and the SAW chain, respectively. These values are listed in Table 1, and are consistent with those shown in Fig.2a. The scaled peak location βz_0 and peak value $P'(z_0)$ are listed in Table 2 for both chain models. They are almost independent of chain model and chain length, as Fig.2b shows.

Fig.3a gives the density profile $\rho(z)$ for both RW and SAW tail-like chains of length n=300. The density $\rho(z)$ is the chain's bead density, i.e. the probability of finding a chain's bead at layer z above the surface. $\rho(z)$ is a summation of $P(R_z)$ with chain length from 1 to n, so

$$\rho(z) \propto \frac{\sum_{j=1}^{n} P_j(z)\Omega(j)}{\sum_{j=1}^{n}\Omega(j)} \tag{6}$$

where $P_j(z)=P(R_z)$ of chain with length j, and $\Omega(j)$ is the total configuration number of the chain with length j. The theoretical function of $\rho(z)$ is unknown even for the RW chain. However, we could expect the expression $\rho(z)$ is similar to $P(R_z)$ since $\rho(z)$ is a summation of a set of $P(R_z)$ of different chain lengths. It is clearly seen that the profile $\rho(z)$ is similar to $P(R_z)$. However, since $\rho(z)$ is a summation of $P(R_z)$ from 1 to the largest chain length n, we then find the peak of $\rho(z)$ will be closer to y axis than $P(R_z)$. The peak location z_1 of $\rho(z)$ and the peak value $\rho(z_1)$ of chain length n=300 are listed in Table 1 for both RW and SAW chains. One can see that value z_1 is smaller than z_0.

We find $\rho(z)$ can also be scaled by $\beta=\sqrt{2/<R^2>}$ to be roughly a chain length independent function $\rho'(z)=\rho(z)/\beta$ versus βz as shown in Fig.3b. Here we take the RW chain as an example. But we find the scaled density profile $\rho'(z)$ of the SAW chain does not overlap that of the RW chain: the scaled density profile $\rho'(z)$ shifts left comparing with that of the RW chain. The scaled peak location βz_1 of the SAW chain is smaller than that of the RW chain, but the scaled peak value $\rho'(z)$ of the SAW chain is roughly equal to that of the RW chain (Table 2).

Table 1 Results of the mean-square end-to-end distance $<R^2>$, peak location z_0 and peak value $P(z_0)$, and peak location z_1 and peak value $\rho(z_1)$ for the RW and SAW tail-like chains with length n=300

	$<R^2>$	z_0	$P(z_0)$	z_1	$\rho(z_1)$
RW	400	10	0.061	7	0.081
SAW	1306	18	0.034	11	0.044

Table 2 Scaled values of peak location βz_0 and peak value $P'(z_0)$, and peak location βz_1 and peak value $\rho'(z_1)$ for the RW and SAW tail-like chains with length n=300

	βz_0	$P'(z_0)$	βz_1	$\rho'(z_1)$
RW	0.707	0.858	0.495	1.15
SAW	0.707	0.858	0.428	1.13

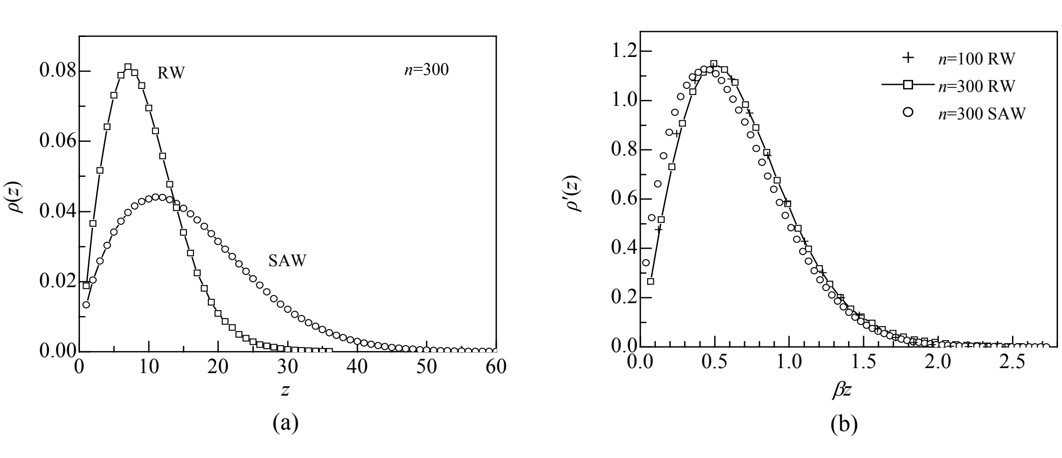

Fig.3 (a) The density profile $\rho(z)$ vs distance z and (b) the scaled density profile $\rho'(z)$ vs scaled distance βz for tail-like RW and SAW chain. The factor $\beta=\sqrt{2/<R^2>}$

CONCLUSION

In summary, dynamic Monte Carlo simulations of the tail-like SAW polymer chains have been performed on the simple cubic lattice. The repulsive effect of the surface to polymer chain is studied. We find the mean-square end-to-end distance $<R^2>$ and the mean-square radius of gyration $<R_G^2>$ of the tail-like chain are bigger than that of the free chain. The asymptotic values of ratios are $\alpha_R \approx 1.32$ and $\alpha_G \approx 1.07$ for the SAW chain model. The results suggest that the $<R_G^2>$ is less sensitively influenced by the surface than $<R^2>$. The repulsive effect of the surface is clearly presented by the probability distribution of end bead in z direction $P(R_z)$ and the density profile $\rho(z)$ of the tail-like chain. We find $P(R_z)$ and $\rho(z)$ can be scaled by $\beta=\sqrt{2/<R^2>}$: a function independent of chain length. The scaled $P(R_z)$ of the SAW chain roughly overlaps that of the RW chain. But the scaled $\rho(z)$ of the SAW chain shifts to smaller βz compared with that of the RW chain.

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