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Dynamic Monte Carlo simulation of linear SAW polymer chain near a flat surface*

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Abstract: Investigation of the conformational properties of a SAW polymer chain near an impenetrable, non-interacting flat surface showed that the chain at first contracted and orientated itself to slightly parallel when it pulled close to the surface and at last elongated and reoriented itself to slightly perpendicular to the surface at very small distance from the surface. Simulation showed that most of the disappeared configurations were of large size at moderate distance from the surface while they were of small size at very small distance from the surface; and that the mean-square end-to-end distance $<R^2>$ was much more prone to be influenced by the surface than the mean-square radius of gyration $<S^2>$. The orientational correlation between the direction of the longest principal axis of the moment of inertia and end-to-end vector was also discussed.

Key words: Polymer, Conformation, Probability distribution, Monte Carlo simulation
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INTRODUCTION

The conformational property of polymer chains subject to a geometrical constraint is one of the most interesting topics in polymer science (Milner, 1991; Malfreyt and Tildesley, 2000; Vacatello, 2001). The geometrical constraint can be a solid surface, a liquid/liquid interface, a vacuum/liquid interface, etc. So the topic has many applications in technology such as adsorption onto interface, stabilization of colloids and partition equilibrium in gel permeation chromatography. It is therefore of great importance to have good understanding of how the geometric constraint perturbs the chain's configuration.

Flexible polymer chain in solution can assume a large number of configurations due to many internal degrees of freedom. When it is located near a non-absorbing and impenetrable barrier, it is an unfavorable entropy situation in that a part of the configurations disappear. The chain thereby experiences an effective repulsion from the barrier (Casassa, 1984; 1995). Tanaka (1977) derived theoretically the mean square end-to-end distance $<R^2>$ and the mean square radius of gyration $<S^2>$ of the random-flight chain near an impermeable, non-interacting flat surface. Recently, investigation of the influence of the excluded volume on the conformational property of linear tail-like chain (chain with one end fixed onto the surface) (Luo and Huang, 2003) revealed that the excluded volume had nearly the same effect on $<R^2>$ as on $<S^2>$.

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In the present work, self-avoiding walking (SAW) polymer chains near an impenetrable, non-interacting flat surface were simulated by means of dynamic Monte Carlo simulation on the simple cubic lattice. The chain was assumed to sit in the upper half space with one end fixed at z_0, with the flat surface located at z=0. The dependence of $<R^2>$, $<S^2>$ and orientation of SAW polymer chain on z_0 were studied.

SIMULATION MODEL

Simulations were performed on the simple cubic lattice. The lattice spacing was set as length unit. A SAW polymer chain, comprised of n+1 identical segments (number from 0 to n) consecutively linked with bond length l=1, was first generated with static Monte Carlo method. The first segment was arbitrarily set at (0, 0, z_0) and immovable forever, while other segments could choose one site from all possible sites. Except for the first segment in the z_0=0 case, all the segments could not contact the flat surface; that is, the chain located in the z>0 half space.

After creating a chain, a segment was chosen randomly and one of the three elementary motions, the end-segment, normal-segment and 90° crankshaft motions, was tried. The method was discussed in detail by Gurler *et al*.(1983). This trial move will be accepted if the following two conditions are satisfied: (1) self-avoidance is obeyed, (2) the new site locates at z>0. Each trial move is called a segment cycle, n+1 segment cycles consist of one Monte Carlo step (MCS). Then the chain was relaxed for about 10 times as long as the relaxation time τ of the free SAW chain before the results were recorded. The value τ was calculated as $\tau=0.25n^{2.13}$. For each run, dynamic Monte Carlo simulation lasted for 1000τ and thus 100 independent configuration samples were recorded. In the present calculation, 1000 independent runs were performed. Therefore, all quantities in this work are thus averaged over a total of 1000×100 independent configuration samples.

Basic formulas

The square end-to-end distance R^2 was calculated from the end-to-end vector

$$\boldsymbol{R}=\boldsymbol{r}_n-\boldsymbol{r}_0, \tag{1}$$

with $\boldsymbol{r}_0$ and $\boldsymbol{r}_n$ being the vector of the first segment and the last segment, respectively.

To determine the square radius of gyration S^2, we constructed the radius of gyration tensor $\boldsymbol{S}$

$$\boldsymbol{S}=\frac{1}{n+1}\sum_{k=0}^{n}\boldsymbol{s}_k\cdot\boldsymbol{s}_k^{\mathrm{T}}=\begin{pmatrix}S_{xx} & S_{xy} & S_{xz}\\ S_{xy} & S_{yy} & S_{yz}\\ S_{xz} & S_{yz} & S_{zz}\end{pmatrix} \tag{2}$$

Here, $\boldsymbol{s}_k$ is the position vector of segment k in a frame of reference with its origin at the center of mass. The square radius of gyration S^2 can be calculated as

$$\boldsymbol{S}^2=S_{xx}+S_{yy}+S_{zz} \tag{3}$$

$\boldsymbol{S}$ is a symmetric matrix and can be diagonalized with three eigenvalues L_1^2, L_2^2 and L_3^2 ($L_1\le L_2\le L_3$) and three corresponding eigenvectors $\boldsymbol{q}_1$, $\boldsymbol{q}_2$ and $\boldsymbol{q}_3$. The eigenvector $\boldsymbol{q}_3$ is a unit vector that represents the direction of the longest principal axis L_3. The angle φ ($0\le\varphi\le 90°$) between the direction of the longest principal axis L_3 and that of $\boldsymbol{R}$ is calculated by

$$\varphi=\cos^{-1}\left(\frac{|\boldsymbol{q}_3\cdot\boldsymbol{R}|}{\boldsymbol{R}}\right) \tag{4}$$

RESULTS AND DISCUSSION

The mean-square end-to-end vector $<R^2>$, the mean-square radius of gyration $<S^2>$, and mean $<\varphi>$ were calculated for a series of z_0 ranging from zero to a large value. The probability distributions $P(S)$ at some special z_0s were also investigated. In

this paper, the polymer chain lengths considered were 20, 40, up to 100. However, no significant difference in the dependence of the conformational properties on z_0 was found for these chain lengths, so here we only give the results of n=100. For this case, the largest z_0 we simulated was 40. Though it was less than the chain length n=100, we found that all conformational properties had already converged; and that the chain behaved as a free chain. In this paper, the free chain referred to the chain at z_0=40.

Chain size

Fig.1 shows the dependence of the mean-square radius of gyration $<S^2>$ on the distance z_0 of the first segment of the chain. When z_0=0, i.e. the first segment was adsorbed onto the flat surface, we found that $<S^2>\approx 46.1$, or about 1.04 times as large as that of the free chain. Then $<S^2>$ decreased rapidly with z_0, and at the value z_0=11, $<S^2>$ reached its minimum 42.6, or only about 0.96 times as large as that of the free chain. With further increasing of z_0, $<S^2>$ rose up and at last reached the limit value 44.2 of the free chain. Such a variation of size $<S^2>$ against z_0 is in agreement with Tanaka's analytical results of random-flight chains (Tanaka, 1977). The critical value of z_0 at which $<S^2>$ reaches minimum is named as z_c hereafter for convenience. Like the situation in the random-flight chain model (Tanaka, 1977), the value of z_c also increases with chain length for the SAW chain model. For example, we found that z_c was about 8 for chain length n=50.

The behavior of $<S^2>$ can be explained from the probability distribution $P(S)$. $P(S)$ is calculated as $P(S) = \dfrac{N(S)}{N\cdot\Delta S}$, where $N(S)$ is the number of simulated configurations whose radius of gyration S is within (S–½ΔS, S+½ΔS) and N is total simulated configuration number. We chose ΔS=0.2 in this work, which was small enough to obtain smooth $P(S)$ curves. For a free flexible polymer chain, its size (R^2 or S^2) has a definite distribution, like the probability distribution $P(S)$ shown in Fig.2 for large z_0 = 40. When it is placed near a surface, some configurations disappeared. At small z_0, we found that the distribution $P(S)$ shifted to large S (see Fig.2 for z_0=0 case), indicating that most of the disappeared configurations were flexible configurations of small size. The reason was that the chain segments were usually arranged around the first segment for small size configurations, so small size configuration was more prone to be repelled by the surface than large size configuration at small z_0. With increasing z_0, the number of repelled configurations decreased and some small size configurations began to appear, resulting in the decrease of $<S^2>$. Around z_c, the relatively flexible ones were no longer repelled by the surface because of their small dimensions. On the contrary, the downward extended ones which were of large size were still repelled by the surface, thus one finds a minimum of $<S^2>$. Fig.2 shows that the distribution $P(S)$ shifts to small size S for $z_0 = z_c$ case, or the probability of small S increases. With further incr-

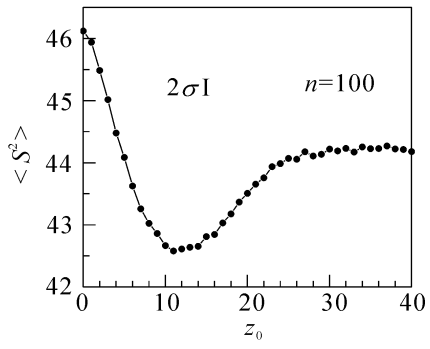

Fig.1 Plot of the mean-square radius of gyration $<S^2>$ vs the normal-to-surface distance z_0 of the first segment. The error bar 2σ is roughly independent of z_0

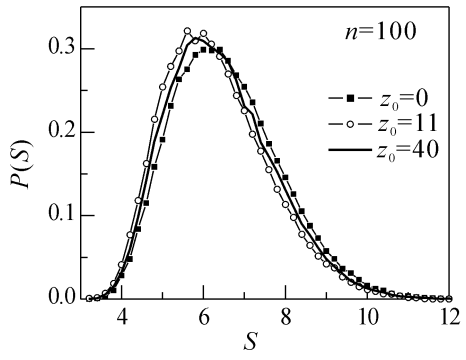

Fig.2 Probability distributions $P(S)$ at z_0 = 0, 11 and 40

ease of z_0, the number of these repelled larger size configurations decreases, so $<S^2>$ increases again.

The dependence of mean-square end-to-end distance $<R^2>$ on z_0 was also calculated. Instead of showing $<R^2>$-z_0 plot we give the $<R^2>/<S^2>$-z_0 curve here, see Fig.3.

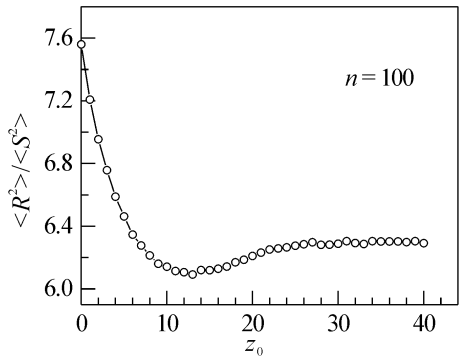

Fig.3 The dependence of ratio $<R^2>/<S^2>$ on z_0 for chain near flat surface. The height of the error bar is nearly equal to that of the symbol

We found $<R^2>/<S^2>$ was not a constant for the entire z_0, indicating that the effect of the flat surface on $<R^2>$ was different from that on $<S^2>$. At small z_0, especially at z_0=0, the value $<R^2>/<S^2>$ was much bigger than that of the chain at z_0=40, suggesting that the increase in $<R^2>$ was much larger than that in $<S^2>$, i.e. the excluded effect on $<R^2>$ caused by the surface was much stronger. However, near z_c=11, the result showed that the decrease in $<R^2>$ was more obvious than that in $<S^2>$. In short, $<R^2>$ was more prone to be affected by the surface.

In conclusion, we found that the polymer chain was significantly elongated for small z_0, but contracted for moderate z_0 due to the effect of the surface.

Chain orientation

Besides the variation of chain size and shape, we also found that the orientation of the chain varied with z_0. We also calculated the angle θ ($0 \le \theta \le 90°$) between the direction of the longest principal axis of the chain's inertia moment and that of the z axis,

$$\theta = \cos^{-1}\left|\boldsymbol{q}_3 \cdot \boldsymbol{e}_z\right| \tag{5}$$

Here $\boldsymbol{e}_z$ is the unit vector of the direction z. The dependence of the mean angle $<\theta>$ on the normal-to-surface distance z_0 is shown in Fig.4. At large z_0, the chain is free, so the direction $\boldsymbol{q}_3$ is uniformly-distributed in space; which leads to the theoretical probability distribution $P(\theta)=\sin\theta$ and the mean value $<\theta>=57.3°$. With the decrease of z_0, $<\theta>$ increases at first and reaches its maximum at z_0 =10 which is close to z_c, indicating the chain orientates itself to slightly parallel to the surface. Below z_c, however, $<\theta>$ drops rapidly, which means the chain reorients itself to slightly perpendicular to the surface. At z_0=0, $<\theta>$ reaches its minimum.

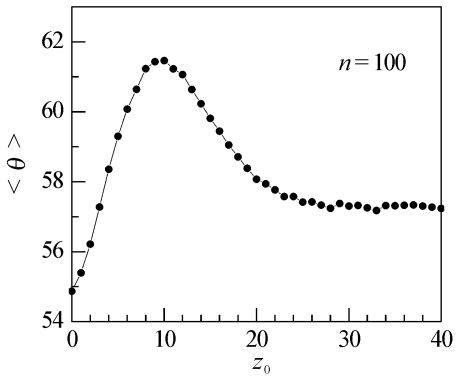

Fig.4 Dependence of the mean angle $<\theta>$ on the normal-to-surface distance z_0

Comparing the variation of $<R^2>$ and $<S^2>$, we can depict the following picture when the chain is moved to the flat surface from large z_0: At first, the chain contracts and at the same time orients itself to slightly parallel to the surface; when it is very close to the surface, the chain becomes elongated and reorients itself to slightly perpendicular to the surface. Such a behavior of the chain orientation is quite different from that of chain in polymer melt. It was found that the chains near the surface were flattened parallel to the surface and formed nearly two-dimensional structure (Madden, 1987; Kumar *et al.*, 1988). Therefore, the interactions between chains play an important role in polymer melts.

Orientational correlation between q_3 and R

The correlation between the direction of poly-

mer configuration $\boldsymbol{q}_3$ and that of the end-to-end vector $\boldsymbol{R}$ was studied in this section. The orientational correlation between $\boldsymbol{q}_3$ and $\boldsymbol{R}$ is described by the mean angle $<\varphi>$ (Eq.(4)) (Bruns, 1992). As the mean-square distance between two segments i and j of a chain is roughly given by $R_{ij}^2 \propto |j-i|^{2\nu}$, the root-mean-square end-to-end distance is on average the longest distance between any two segments. Here ν is the scaling exponent, and $\nu \approx 0.6$ for the SAW chain. This suggests a certain correlation between the direction of end-to-end vector and that of the longest principal axis. If no correlation exists, the mean value $<\varphi>$ should be 57.3° (Luo *et al.*, 2001). A small value of $<\varphi>$ indicates such a correlation.

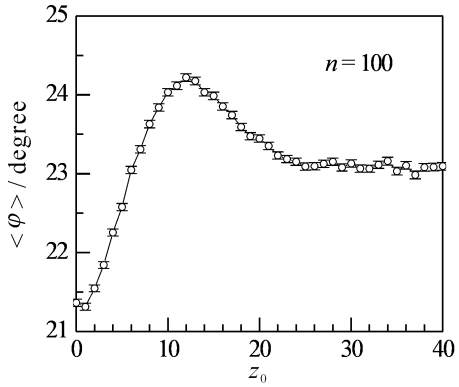

Fig.5 Dependence of the mean angle $<\varphi>$ on the normal-to-surface distance z_0

Fig.5 shows that the mean angle $<\varphi>$ of free chain is about 23°, which is much smaller than 57.3°, suggesting the correlation between $\boldsymbol{R}$ and the longest principal axis of the moment of inertia L_3. When $z_0 = 0$, $<\varphi>$ is about 21.5°, even smaller than that of free one, indicating that such a correlation is enhanced when the chain is very close to the surface.

We have known that most of the disappeared configurations were of large size at moderate z_0, whereas they were of small size at very small z_0. Thus according to the results presented in Fig.5, one could expect that configurations of large size on average have small angle φ, and vice versa. In order to reveal the relation between size and angle φ, we also calculated $<R^2>_\varphi$ and $<S^2>_\varphi$ for the configurations with angle φ ranging in $(\varphi-\Delta\varphi, \varphi+\Delta\varphi)$. The dependence of $<R^2>_\varphi$ and $<S^2>_\varphi$ on the angle φ for free chain is shown in Fig.6. One can see that both $<R^2>_\varphi$ and $<S^2>_\varphi$ decrease gradually with φ, indicating that the configurations of large size really have small angle φ on average. Therefore the variation of $<\varphi>$ shown in Fig.5 is consistent with our conclusion that most of the disappeared configurations were of large size at moderate z_0, whereas they were of small size at very small z_0.

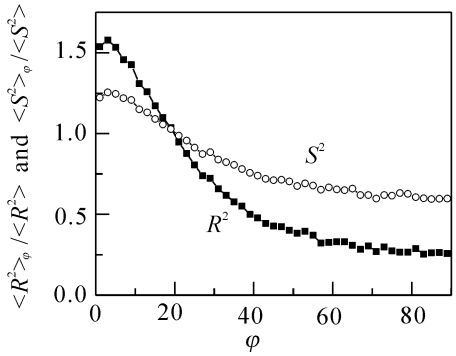

Fig.6 The plot of $<R^2>_\varphi/<R^2>$ and $<S^2>_\varphi/<S^2>$ vs angle φ for free chain of length n = 100. $<R^2>_\varphi$ and $<S^2>_\varphi$ are only averaged over the configurations with angle φ locating in the range $(\varphi-\Delta\varphi, \varphi+\Delta\varphi)$. $<R^2>$ and $<S^2>$ are averaged over whole configurations. $\Delta\varphi = 1°$ is used in calculation

CONCLUSIONS

We studied the conformational properties of a SAW polymer chain near a flat surface with dynamic Monte Carlo method. We found that the size and its probability distribution depended on the distance z_0 of the first segment of the chain. Compared with free chain, the confined chain is significantly elongated at small z_0 and is contracted at moderate z_0. Value $<S^2>$ is maximum at z_0=0, then it decreases and reaches the minimum at moderate z_0; later on it increases with increasing z_0 and at last reaches the value of the free chain. Simulation results suggested that the mean-square end-to-end distance $<R^2>$ was much more prone to be influenced by the surface than the mean-square radius of gyration $<S^2>$. The surface also affects the orien-

tation of the chain. Behaving in a different way as size and asphericity, the mean angle $<\theta>$ reaches its maximum at moderate z_0, indicating that the chain orientates itself slightly parallel to the surface at moderate z_0 and slightly perpendicular to the surface at very small z_0. From the behavior of angle $<\varphi>$, we conclude that the correlation between the direction of end-to-end vector $\boldsymbol{R}$ and that of the longest principal axis L_3 is enhanced when the chain is close to the surface. Simulation results showed that most of the disappeared configurations were of large size at moderate z_0 while they were of small size at very small z_0.

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