

DYNAMIC MONTE CARLO STUDY ON THE CORRELATION BETWEEN SHAPE AND SIZE OF LINEAR POLYMER CHAINS*

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Abstract The correlation between shape and size of linear chains on the simple cubic lattice is investigated using a dynamic Monte Carlo technique. A positive correlation between the asphericity parameter A and the square of the end-to-end distance R^2 , as well as that between A and the square of the radius of gyration S^2 , is found for both RW and SAW chains, indicating that a chain conformation of small size is usually more spherical than one of large size. The result can explain why the shape of the SAW chain deviate much more from a sphere than that of the RW chain, and can also explain the similar dependence of size and shape on chain stiffness and on the distance of the first bead of a chain from an infinitely large flat surface.

Keywords Correlation, Dynamic Monte Carlo, Polymer chain

INTRODUCTION

Flexible polymer chains can assume a large number of conformations due to many internal degrees of freedom. Kuhn was the first to recognize that the instantaneous spatial conformations of polymer chains in dilute solutions were highly anisotropic, though isotropy was acquired over a long time through orientational averaging or over a great number of conformations^[1]. The study of the shape of polymer chains has been of interest to chemists as well as physicists^[2–12], since the anisotropy of polymers has important physical consequences and is critical in the interpretation of viscous flows and other hydrodynamic phenomena of dilute solutions of macromolecules^[13].

Many definitions have been developed for describing the shape of polymer chains^[11], and all relate to the components of the squared radius of gyration: L_1^2 , L_2^2 and L_3^2 ($L_1 \leq L_2 \leq L_3$). As early as 1971, Šolc and Stockmayer^[2, 3] introduced $\langle L_1^2 \rangle : \langle L_2^2 \rangle : \langle L_3^2 \rangle$ to measure the shape of flexible polymer chains. They estimated the ratios to be 1:2.7:11.7 based on a random walk (RW) of 100 bonds on a simple cubic (SC) lattice using the Monte Carlo (MC) technique. Yoon and Flory^[4] obtained almost the same results for unperturbed long polyethylene (PE) chains with the second-order interaction approximation. The alternative definition is $\langle sf_1^* \rangle : \langle sf_2^* \rangle : \langle sf_3^* \rangle$, where $\langle sf_i^* \rangle = \langle L_i^2 / S^2 \rangle$ are the reduced components. Zifferer^[11] investigated both definitions for three types of chain on tetrahedral lattice: theta, nonreversal random walk (NRRW) and self-avoiding walk (SAW) chains. The shape of polymer chains can also be investigated using the mean asphericity parameter $\langle A \rangle$ defined as^[5]

$$\langle A \rangle = \left\langle \frac{\sum_{i>j}^3 (L_i^2 - L_j^2)^2}{2(\sum_{i=1}^3 L_i^2)^2} \right\rangle \quad (1)$$

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in three dimensions. This parameter ranges from zero for spherically symmetric chain conformations to one for rod-shaped ones. For a linear RW chain, $\langle A \rangle \approx 0.396$ in the infinite chain limit^[5].

Many MC simulations showed that a relationship might exist between the chain's shape and its size. Bruns^[7] found that the asphericity of linear SAW chains on a SC lattice is greater than that of RW chains. He estimated the limiting values of $\langle L_1^2 \rangle : \langle L_2^2 \rangle : \langle L_3^2 \rangle$ to be about 1:2.98:14.0 for the SAW chains. Similar results were obtained from MC simulations for linear off-lattice polymer chains: the ratios $\langle L_1^2 \rangle : \langle L_2^2 \rangle : \langle L_3^2 \rangle \approx 1:2.71:12.1$ for RW chains while they are about 1:2.92:13.9 for chains in a good solvent^[8]. In our previous paper, MC simulations on PE chains with different short-range interactions showed that, for the same finite chain length, the values $\langle L_1^2 \rangle : \langle L_2^2 \rangle : \langle L_3^2 \rangle$ increase with increasing polymer size^[9]. All of these facts indicate that a correlation between the shape and the size may exist for linear polymer chains. Indeed, Zifferer^[11] studied this correlation for tetrahedral lattice chains in athermal and theta systems, and found that a chain of large size (measured by the squared end-to-end distance R^2 or the squared radius of gyration S^2) has a much large possibility to have a big asphericity parameter A , *vice versa*. We introduced the correlation function to characterize the correlation between the shape and the size, and really found a positive correlation between the asphericity parameter A and the size for linear RW chain on the three-choice tetrahedral lattice^[14].

In this work, the correlation between the asphericity parameter A and the size is investigated using Dynamic Monte Carlo simulation for both linear RW and SAW chains on a SC lattice. After a description of the chain model and calculation method, we will report our numerical results. We find that there exists a positive correlation between A and the size (R^2 and S^2) for both chains. The relationship is then confirmed by investigating the dependence of A and S^2 on chain stiffness and that on the distance of the first bead of chain from an infinitely large flat surface.

CHAIN MODEL AND CALCULATION METHOD

A polymer chain, comprised of $n + 1$ beads (n bonds) consecutively linked with bond length $l = 1$ in the simple cubic lattice unit, is first generated by the Monte Carlo method. Afterwards, a bead is chosen randomly and one of the three elementary motions, the end-bead, normal-bead and 90° crankshaft motions, is attempted. This motion method was discussed earlier in detail by Gurler *et al.*^[15]. Each trial move is called a bead cycle, and $n + 1$ bead cycles consist of one Monte Carlo step (MCS). To avoid the correlation between two conformations, we measure the chain's size and asphericity parameter at regular time interval τ , here τ is the relaxation time of the chain. For each run, we discard the first 10τ to ensure reaching equilibrium, then record the quantities of the subsequent 1000τ for averaging. The relaxation time τ is calculated from $\tau \approx 0.22n^{1.88}$ MCS for the RW chain and $\tau \approx 0.25n^{2.13}$ MCS for the SAW one^[15]. For instance, $\tau \approx 87000$ MCS for the SAW chain of length $n = 400$. The averaged results are then also averaged over 100 independent runs, that is, in the present calculation each datum is averaged over 1000×100 independent chain conformations.

The radius of gyration tensor S is calculated as

$$S = \frac{1}{n+1} \sum_{i=0}^n s_i s_i^T = \begin{pmatrix} S_{xx} & S_{xy} & S_{xz} \\ S_{xy} & S_{yy} & S_{yz} \\ S_{xz} & S_{yz} & S_{zz} \end{pmatrix} \quad (2)$$

Here $S_i = \text{col}(x_i, y_i, z_i)$ is the position of bead i in a frame of reference with its origin at the center of mass. The tensor S can be diagonalized to form a diagonal matrix with three eigenvalues L_1^2 , L_2^2 and L_3^2 . The correlation between the asphericity parameter A and the squared end-to-end distance R^2 (or the squared radius of gyration S^2) can be characterized by the correlation coefficient C_{A,R^2} (or C_{A,S^2}). Generally, given N pairs of observations on two variables u and v , the correlation coefficient $C_{u,v}$ is defined as

$$C_{u,v} = \frac{\frac{1}{N} \sum_{i=1}^N (u_i - \langle u \rangle)(v_i - \langle v \rangle)}{\sigma(u)\sigma(v)} \quad (3)$$

Here $\sigma(u)$ and $\sigma(v)$ are the standard errors of variables u and v , respectively, and $\langle u \rangle$ and $\langle v \rangle$ are the mean values. The standard error $\sigma(u)$ is defined as

$$\sigma(u) = \sqrt{\frac{1}{N} \sum_{i=1}^N (u_i - \langle u \rangle)^2} \quad (4)$$

for large N .

RESULTS AND DISCUSSION

The correlation coefficients C_{A,R^2} and C_{A,S^2} are calculated for both RW and SAW chains on the SC lattice. Monte Carlo simulations are carried out for chain length from 10 to 500.

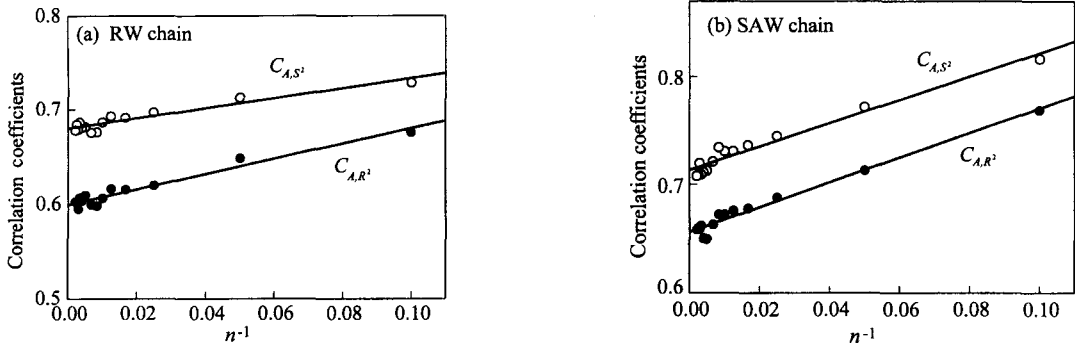


Fig. 1 Correlation coefficients C_{A,R^2} and C_{A,S^2} for the RW (a) and SAW (b) chains plotted as a function of inverse chain length n^{-1} . Circle: MC results. Solid line: linear fit of the MC results

Figure 1 shows the dependence of C_{A,R^2} and C_{A,S^2} on the chain length n . Note that both C_{A,R^2} and C_{A,S^2} are greater than zero for all chain lengths, indicating a positive correlation between the asphericity parameter A and the size (R^2 and S^2) for both chains. Therefore, it is reasonable to expect that the shape of a chain conformation of small size is often more spherical than that of one of large size. Actually, we find that the value $\langle A \rangle$ of the SAW chain is bigger than that of the RW one at any chain length, in agreement with expectation. For example, at $n = 500$, we find $\langle R^2 \rangle = 1910 \pm 35$, $\langle S^2 \rangle = 305 \pm 7$ and $\langle A \rangle = 0.433 \pm 0.007$ for the SAW chain, while for the RW chain, they are 510 ± 8 , 83.5 ± 1.7 and 0.397 ± 0.005 , respectively. In addition, this expectation is also consistent with the results of Bruns^[7] and Forni *et al.*^[8]. Our MC simulation results are also consistent with Zifferer's recent findings for chains on a tetrahedral lattice^[11].

We find that both C_{A,R^2} and C_{A,S^2} decrease with increasing chain length n , revealing that the correlation between A and size weakens when the chain length goes up. Values C_{A,R^2} and C_{A,S^2} can be expressed approximately as

$$\begin{aligned} C_{A,R^2} &\approx 0.599 + 0.806n^{-1} \\ C_{A,S^2} &\approx 0.680 + 0.536n^{-1} \end{aligned} \quad (5.1)$$

for the RW chain and

$$\begin{aligned} C_{A,R^2} &\approx 0.656 + 1.14n^{-1} \\ C_{A,S^2} &\approx 0.713 + 1.09n^{-1} \end{aligned} \quad (5.2)$$

for the SAW chain, respectively. Comparing the results of the RW chain with that on a three-choice tetrahedral lattice^[14], $C_{A,R^2} \approx 0.596 + 2.20n^{-1}$ and $C_{A,S^2} \approx 0.677 + 1.98n^{-1}$, one can conclude that, for the RW chain, the limits of C_{A,R^2} and C_{A,S^2} are nearly independent of lattice type. However, whether they are still of lattice type independence for the SAW chain deserves further investigation.

Moreover, one can find that the correlation coefficient C_{A,S^2} is always bigger than C_{A,R^2} for the same chain length n (Fig. 1), indicating that the correlation between A and S^2 is stronger than that between A and R^2 . The asphericity parameter A , as well as the squared radius of gyration S^2 , is related to the location of all beads of the chain, whereas the squared end-to-end distance R^2 is simply related to two beads (the ends), so it is reasonable to assume that C_{A,S^2} is bigger than C_{A,R^2} . Concerning whether C_{A,S^2} and C_{A,R^2} are of similar chain length dependence and the relation $C_{A,S^2} > C_{A,R^2}$ holds for any chain length, we investigate the correlation between A and S^2 below.

To have a good understanding of the correlation, we have studied the probability distribution of the asphericity parameter A , $P(A)$. We investigate the distributions $P(A)$ for four size ranges where $S^2/\langle S^2 \rangle$ falls into $(0, 0.5)$, $(0.5, 1.0)$, $(1.0, 1.5)$ and $(1.5, \infty)$ as well as for the whole size range, i.e., $S^2/\langle S^2 \rangle \in (0, \infty)$. Figure 2 presents the results for both the RW and the SAW chains of length $n = 400$. It clearly shows that the conformation of large size usually has a large asphericity parameter A , confirming the conclusion of the existence of positive correlation between asphericity parameter and size. For the $P(A)$ of the whole size range, we find that the peak of $P(A)$ shifts to large A and becomes wider after introducing the excluded volume of chain segment, which is consistent with the result that the mean asphericity $\langle A \rangle$ of the SAW chain is bigger than that of the RW chain.

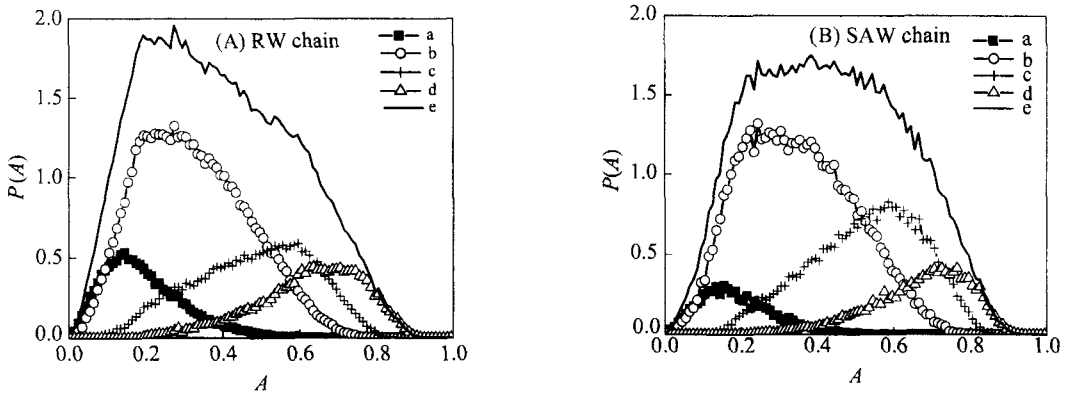


Fig. 2 The probability distribution of the asphericity parameter, $P(A)$, for five different size ranges: (a) $S^2/\langle S^2 \rangle \in (0, 0.5)$, (b) $S^2/\langle S^2 \rangle \in (0.5, 1.0)$, (c) $S^2/\langle S^2 \rangle \in (1.0, 1.5)$, (d) $S^2/\langle S^2 \rangle \in (1.5, \infty)$ and (e) $S^2/\langle S^2 \rangle \in (0, \infty)$

The chain length $n = 400$; (A) RW chain; (B) SAW chain

We have also divided the total 100000 chain conformations samples into four parts according to their squared radius of gyration S^2 and asphericity parameter A : (1) $S^2 < \langle S^2 \rangle$ and $A < \langle A \rangle$, (2) $S^2 > \langle S^2 \rangle$ and $A > \langle A \rangle$, (3) $S^2 < \langle S^2 \rangle$ and $A > \langle A \rangle$, and (4) $S^2 > \langle S^2 \rangle$ and $A < \langle A \rangle$. We define the contributions to the correlation coefficient C_{A,S^2} of each part as

$$C_{A,S^2}^k = \frac{\frac{1}{N} \sum_i^{(k)} (A_i - \langle A \rangle)(S_i^2 - \langle S^2 \rangle)}{\sigma(A)\sigma(S^2)} \quad (6)$$

here the summation is over the samples in part k ($k = 1, 2, 3, 4$), while the standard errors $\sigma(A)$ and $\sigma(S^2)$, the mean values $\langle A \rangle$ and $\langle S^2 \rangle$ are of the total samples. Comparing with the definition of C_{A,S^2} (Eq. 3), we can get

$C_{A,S^2} = C_{A,S^2}^1 + C_{A,S^2}^2 + C_{A,S^2}^3 + C_{A,S^2}^4$ with the contributions $C_{A,S^2}^1 > 0$, $C_{A,S^2}^2 > 0$, $C_{A,S^2}^3 < 0$ and $C_{A,S^2}^4 < 0$.

Table 1 lists the statistical probabilities of these four parts and their contributions to the correlation coefficient C_{A,S^2} for both the RW and the SAW chains of length $n = 400$. It is clear that, for both types of chain, the probabilities, as well as the contributions to C_{A,S^2} , of the first two parts ($k = 1$ and 2) are much larger than those of the last two parts ($k = 3$ and 4). That is, among all chain conformations, the probability of finding a conformation with $S^2 < \langle S^2 \rangle$ and $A < \langle A \rangle$ or with $S^2 > \langle S^2 \rangle$ and $A > \langle A \rangle$ is much larger, revealing the existence of the positive correlation between A and S^2 .

Table 1. The probabilities P^k and the contributions to the correlation coefficient C_{A,S^2}^k of four parts:

(1) $S^2 < \langle S^2 \rangle$ and $A < \langle A \rangle$, (2) $S^2 > \langle S^2 \rangle$ and $A > \langle A \rangle$, (3) $S^2 < \langle S^2 \rangle$ and $A > \langle A \rangle$,
and (4) $S^2 > \langle S^2 \rangle$ and $A < \langle A \rangle$ for chain length $n = 400$ *

Part	RW chain		SAW chain	
	P^k	C_{A,S^2}^k	P^k	C_{A,S^2}^k
1	0.4510	0.2820	0.4261	0.3229
2	0.3068	0.4493	0.3351	0.4354
3	0.1625	-0.0307	0.1537	-0.0282
4	0.0797	-0.0166	0.0851	-0.0181
total	1.0000	0.6840	1.0000	0.7120

* For the RW chain, $\langle S^2 \rangle = 66.6$ and $\langle A \rangle = 0.395$, while for the SAW chain, $\langle S^2 \rangle = 230.8$ and $\langle A \rangle = 0.435$

The superscript k ($k = 1, 2, 3, 4$) denotes the mentioned four different parts. The last row is for the total samples.

An equivalent means of testing the correlation between the asphericity parameter A and the chain size is through examination of the dependence of the shape and the size on the chain stiffness. In this way, we define a two-bond configuration with two successive perpendicular bonds having energy ε higher than that with two parallel bonds. Again, we take the SAW chain as an example. The motion of chain conformations is more complex for this chain model. In dynamic MC simulations, besides the self-avoiding condition, the change of conformations is also determined using the standard Metropolis algorithm: accept if $e^{-\Delta E/k_B T} > r$, where r is a random number uniformly distributed on the interval $(0, 1)$ and ΔE the energy shift due to the change of chain conformations. In each run, we slowly increase the energy ε (in $k_B T$ unit) from 0 to 4 in steps of 0.1. The results of $\langle S^2 \rangle$ and $\langle A \rangle$ for chain length $n = 100$ are shown in Fig. 3 as a function of the energy ε . One can see that both $\langle S^2 \rangle$ and $\langle A \rangle$ increase with increasing ε , in agreement with the conclusion that there exists a correlation between asphericity parameter A and chain size. We argue that a similar relationship will also hold for the SAW chain model with nearest neighbor interaction^[16].

The behavior of a polymer chain, confined to a restricted spatial region, is of importance for many practical problems^[17, 18]. The mean size ($\langle R^2 \rangle$ and $\langle S^2 \rangle$) of a random-flight chain near an impermeable, infinitely large planar surface was studied earlier by Tanaka^[19]. Assuming that the noninteracting surface lies at $z = 0$ of an orthogonal coordinate system (X, Y, Z), Tanaka demonstrated that both $\langle R^2 \rangle$ and $\langle S^2 \rangle$ depend on z_0 , the distance of the first bead of chain from the surface. But how the shape depends on z_0 is still not investigated. From the fact that the mean asphericity parameter $\langle A \rangle$ is correlated with size $\langle S^2 \rangle$, one could expect that $\langle A \rangle$

behaves the same as $\langle S^2 \rangle$ does. To validate this expectation, we have investigated the dependence of $\langle S^2 \rangle$ and $\langle A \rangle$ on z_0 for the RW chain on the SC lattice, and taken the chain length $n = 400$ as an example. The results are shown in Fig. 4. It is clear that $\langle S^2 \rangle$ and $\langle A \rangle$ have almost the same behavior, indicating that the concept of correlation is also valid for the geometrically constrained chain.

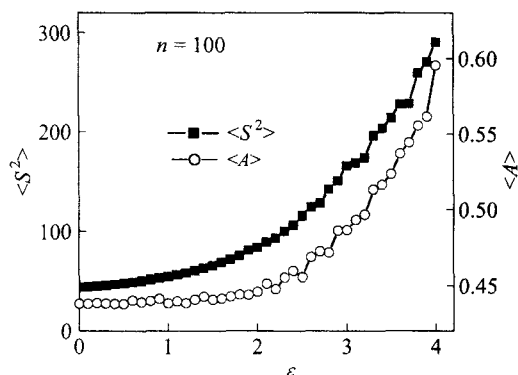


Fig. 3 MC results of the mean-square radius of gyration $\langle S^2 \rangle$ (left-hand scale) and the mean asphericity parameter $\langle A \rangle$ (right-hand scale) plotted versus the energy ε (in $k_B T$ units) for the SAW chain of length $n = 100$

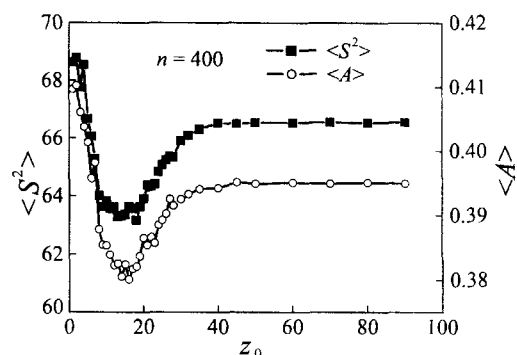


Fig. 4 MC results of the mean-square radius of gyration $\langle S^2 \rangle$ (left-hand scale) and the mean asphericity parameter $\langle A \rangle$ (right-hand scale) plotted versus the distance z_0 of the bead of chain from a flat surface for the RW chain of length $n = 400$

In conclusion, the correlation between shape and size has been studied using the dynamic MC technique for linear RW and SAW chains on the simple cubic lattice. We have proved the existence of a positive correlation between the asphericity parameter A and chain size.

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