

SHAPE OF POLYMER CHAINS ON A TETRAHEDRAL LATTICE*

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Abstract The shape of unperturbed polymer chains was studied using the Monte Carlo technique on a tetrahedral lattice. The asphericity A , the ratios $\langle L_2^2 \rangle / \langle L_1^2 \rangle$ and $\langle L_3^2 \rangle / \langle L_1^2 \rangle$ were calculated for different values of polymer chain length n , conformational energy ε ($\varepsilon \geq 0$) and temperature T . The asphericity A decreases with the increase of chain length and tends to reach its limiting value rapidly with the decrease of γ ($\gamma = \varepsilon / k_B T$). For large n , A is about 0.525 ± 0.005 , the ratios $\langle L_2^2 \rangle / \langle L_1^2 \rangle$ and $\langle L_3^2 \rangle / \langle L_1^2 \rangle$ are about 2.7 and 12.0, respectively, and are almost independent of γ , but for short chains, they depend on γ .

Key words Shape, Polymer chain, Monte Carlo technique

INTRODUCTION

Flexible polymer chains can assume a large number of conformations due to many internal degrees of freedom^[1, 2]. In 1934, Kuhn^[3] pointed out that the instantaneous shape of a polymer chain was not spherical, though the average shape was spherical after averaging over many conformations and orientations. The shape of polymer chains is of importance for many phenomena, and has witnessed great progress^[4-11].

Šolc and Stockmayer^[4, 5] were the first to use $\langle L_1^2 \rangle : \langle L_2^2 \rangle : \langle L_3^2 \rangle$ to measure the shape of flexible polymer chains, where L_1^2 , L_2^2 , and L_3^2 ($L_1 \leq L_2 \leq L_3$) are the eigenvalues of the radius of gyration tensor and $\langle \rangle$ denotes the statistical average over a large number of conformations. They estimated this value to be 1:2.7:11.7 based on the random walk of 50 bonds and 100 bonds on a simple cubic lattice using a Monte Carlo (MC) technique. Yoon and Flory^[6] estimated the ratio to be about 1:2.7:12.0 for unperturbed long polyethylene (PE) chains with second-order interaction approximation. Bruns and Carl^[7] studied the shapes of linear and star-like polymer chains on a cubic lattice at θ temperature, and they found very little difference between the θ temperature chain model and the RW chain model.

The asymmetry of a chain, which is measured as the asphericity A , is another important parameter for evaluating the shape of polymer chains. The asphericity A of a polymer chain is defined as

$$A = \frac{\langle (L_1^2 - L_2^2)^2 + (L_2^2 - L_3^2)^2 + (L_3^2 - L_1^2)^2 \rangle}{2 \langle (L_1^2 + L_2^2 + L_3^2)^2 \rangle} \quad (1)$$

in three dimensions^[8]. For an infinitely long random walk chain, the asphericity is $10/19$ (≈ 0.526) in three dimensions.

The dependence of asphericity A on conformational energy and temperature for a chain model related with temperature may be interesting since it is well known that the size of polymer chains obviously relies on temperature. In this paper, the shape of unperturbed polymer chains in dilute solutions was investigated using the

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MC technique. The polymer chains were generated based on the threefold rotational isomeric state (RIS) approximation model on a tetrahedral lattice. We found that the shape of short polymer chains is affected by conformational energy and temperature.

CHAIN MODEL AND CALCULATION METHOD

A polymer chain of length n consisting of n bonds of identical bond length and $n + 1$ beads of unit mass, each bead locating on a tetrahedral lattice, is simulated by the MC technique. Each bond has three states: t , g^+ and g^- , corresponding to the bond rotational angle $\phi = 0^\circ$, 120° and 240° , respectively. We only consider first-order interaction of the polymer chain and the *gauche* states (g^+ and g^-) have an energy difference ε ($\varepsilon > 0$) with respect to the *trans* state, i.e., $\varepsilon = E_g - E_t$. We choose $E_{g^+} = E_{g^-} = E_g = \varepsilon$ and $E_t = 0$ as the potential reference.

The chain is constructed by adding beads step-by-step on a rectangular coordinate. The determination of the state of a bond depends on its two predecessors in the chain, and the first and the second bonds of the chain are fixed originally. For this reason and the isotropy of space, the coordinates of the first three beads are fixed arbitrarily as (0,0,0), (1,1,1) and (0,2,2), respectively. The position of the fourth one and so on can be chosen from three positions, which correspond to three states (t , g^+ , g^-). The probabilities of choosing these states are:

$$p_t = \frac{\exp(-E_t/k_B T)}{\exp(-E_t/k_B T) + 2\exp(-E_g/k_B T)} = \frac{1}{1 + 2\exp(-\varepsilon/k_B T)} \quad (2)$$

$$p_{g^+} = p_{g^-} = \frac{\exp(-E_g/k_B T)}{\exp(-E_t/k_B T) + 2\exp(-E_g/k_B T)} = \frac{\exp(-\varepsilon/k_B T)}{1 + 2\exp(-\varepsilon/k_B T)}$$

where k_B is the Boltzmann constant and T is the absolute temperature. After a number e , between 0 and 1, has been generated randomly by computer, a state can be chosen based on e . If $e \leq p_t$, state t is chosen for the fourth bead; if $p_t < e \leq (p_t + p_{g^+})$, state g^+ is chosen; otherwise, state g^- is chosen. The operation is repeated for the fifth one, and so on.

One can see that from our chain model, there are two tunable parameters: first-order conformational energy ε and temperature T . Succinctly, we introduce a dimensionless parameter $\gamma = \varepsilon/k_B T$. Then the conformational properties of the polymer chain are only characterized by the chain length n and the parameter γ . Especially, in the case of $\gamma = 0$, meaning an infinitely high temperature or $\varepsilon = 0$, the chain model returns to a random walk model on the tetrahedral lattice. The flexibility of the chain drops when γ rises.

After a chain is successfully constructed, the radius of gyration tensor S can be calculated from^[9]:

$$S = \frac{1}{n+1} \sum_{i=0}^n s_i s_i^T = \begin{pmatrix} S_{xx} & S_{xy} & S_{xz} \\ S_{xy} & S_{yy} & S_{yz} \\ S_{xz} & S_{yz} & S_{zz} \end{pmatrix} \quad (3)$$

here $s_i = \text{col}(x_i, y_i, z_i)$ is the position vector of bead i in a frame of reference with its origin at the center of mass. The tensor S is a symmetric matrix and can be sectioned diagonally to form a diagonal matrix L with three eigenvalues L_1^2 , L_2^2 and L_3^2 .

The asphericity A , the mean values $\langle L_1^2 \rangle$, $\langle L_2^2 \rangle$ and $\langle L_3^2 \rangle$ are calculated after a large number of chain samples have been generated. Ten thousand chain samples are constructed for each chain length n and parameter γ in this work.

RESULTS AND DISCUSSION

Figure 1 shows the dependence of the asphericity A on the chain length n for $\gamma = 0, 1, 2, 3$ and 4. The asphericity A decreases with the chain length for all values of γ , though it is not very profound for the case of $\gamma = 0$,

indicating that the spherical symmetry of the polymer chain increases with the chain length. Moreover, the values of asphericity A tend to reach their limiting values when chain lengths go up. Approximately, the values of the asphericity A for chain length $n = 1000$ can be taken as the limiting value when $\gamma \leq 2$. They are listed in Table 1. We find the deviation among them is very small. Though the asphericity A does not reach its limiting value when $n = 1000$ for $\gamma \geq 3$, one can see that the slope of the plot for A versus $1/n$ is very large. Therefore, it is reasonable to predict that the values of A will reach the same limit for different γ . From Fig. 1 and Table 1, we predict the limiting value of A is 0.525 ± 0.005 , very close to the theoretical value $0.526^{[8]}$. This also indicates that the shape of an infinitely long unperturbed chain is independent of the conformational energy ε or temperature T . But conformational energy ε and temperature T affect the shape of short chains.

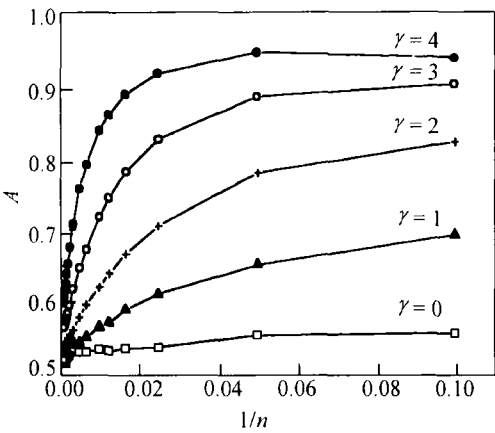


Fig. 1 Dependence of asphericity A on chain length n for different values of parameter γ

Both chain length n and parameter γ affect the spherical symmetry of a polymer chain. For a short chain, it is well known that there exists a short chain effect which makes the chain stiffer, and the short chain effect diminishes with increasing chain length. Therefore, the asphericity A of chains decreases with increasing chain length, while the chain stiffness increases with γ . With the increase of γ , the t state in chain conformation becomes more preferential than g states, so the asphericity A also decreases with decreasing γ . Therefore increasing the chain length n or decreasing parameter γ will make the asphericity A smaller.

Table 1. Monte Carlo results of the asphericity A , the ratios $\langle L_2^2 \rangle / \langle L_1^2 \rangle$ and $\langle L_3^2 \rangle / \langle L_1^2 \rangle$ of polymer chain of length $n = 1000$ for different γ values

γ	0	0.125	0.25	0.5	1.0	2.0
A	0.520	0.526	0.525	0.530	0.530	0.539
$\langle L_2^2 \rangle / \langle L_1^2 \rangle$	2.71	2.72	2.75	2.69	2.76	2.84
$\langle L_3^2 \rangle / \langle L_1^2 \rangle$	11.9	12.1	12.2	12.0	12.4	13.0

In this work, we also investigate the ratio $\langle L_1^2 \rangle : \langle L_2^2 \rangle : \langle L_3^2 \rangle$ of the polymer chain. Figure 2 shows the dependence of the ratios $\langle L_2^2 \rangle / \langle L_1^2 \rangle$ and $\langle L_3^2 \rangle / \langle L_1^2 \rangle$ on the chain length for $\gamma = 0, 1, 2$. The variation of these ratios is very similar to that of A . Because these ratios are very large for $\gamma = 3$ and $\gamma = 4$, these two plots are not shown in Fig. 2. Fortunately, the profile of these two curves is also very similar to that of $\gamma = 0, 1, 2$, and they have similar tendency when n tends toward infinitely large values. One can find that at the same chain length, these ratios increase with γ , while at the same γ , they decrease with increasing chain length. For the infinitely long chain, the ratio $\langle L_1^2 \rangle : \langle L_2^2 \rangle : \langle L_3^2 \rangle$ approaches the same value for different γ , which is about 1:2.7:12.0. This indicates that the shape of an infinitely long unperturbed chain is independent of the conformational energy ε or temperature T .

For sufficiently large n , though the size, e.g. the mean-square end-to-end distance $\langle R^2 \rangle$ or the mean-square

radius of gyration $\langle S^2 \rangle$ is dependent on parameter $\gamma^{[12]}$, the shape of polymer chains is nearly independent of parameter γ , manifesting that there exists the character of self-similarity for the shape of long polymer chains. Therefore, the shape of long chains possesses universality and is independent of the change of environment, e.g. the change of temperature T .

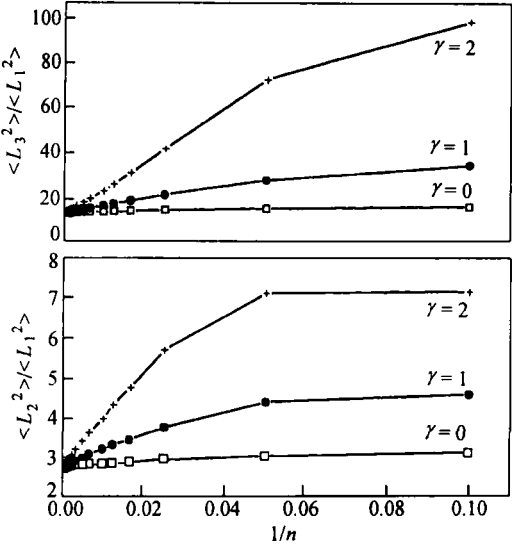


Fig. 2 Dependence of the ratios $\langle L_2^2 \rangle / \langle L_1^2 \rangle$ and $\langle L_3^2 \rangle / \langle L_1^2 \rangle$ on the chain length n for different values of parameter γ

However, for short- and medium-length chains, their shape and size change with the change of environment. At low temperature, $A \approx 1.0$, the shape of the chain is nearly rodlike; with increasing temperature T , A decreases, that is, the spherical symmetry of the chain increases. At very high temperature, the chain is ellipsoidal with $A \approx 0.525$.

At very small γ , especially at $\gamma = 0$, one can see that the shape is almost independent of the chain length n . So the self-similarity of the shape also exists. With the increase of chain length n , the size ($\langle R^2 \rangle$ or $\langle S^2 \rangle$) increases, but the shape almost remains the same. Thus, one cannot determine the chain length by measuring its shape at small γ .

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