Eur. Polym. J. Vol. 23, No. 12, pp.997-999, 1987
Printed in Great Britain

0014-3057/87 $3.00+0.00
Pergamon Journals Ltd

MONTE CARLO SIMULATION FOR THE CONFORMATION OF A POLYMER CHAIN CONFINED IN A SPHERE **

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** Project supported by the Science Fund of the Chinese Academy of Science

(Received 23 September 1986)

ABSTRACT

This paper uses Monte Carlo simulation on a diamond lattice model to calculate the dimension of a polymer chain confined in a sphere while considering the hindrances of bond angle and potential barrier. The results agree with those of Wu Dacheng and Qian Renyuan et al. Further, an empirical formula relating to $\bar{h}^2/h_o^2$ is obtained. This formula can also be derived according to equiprobability hypothesis.

INTRODUCTION

As early as 1954, Wall et al. studied the conformation of a polymer chain in dilute solution by the Monte Carlo method (1). Later, Casassa calculated the dimensions and the entropy of a random flight chain confined to one dimension (2). Recently, Wu Dacheng and Qian Renyuan et al. gave the variation of the dimensions of a random flight chain with different confinements in combination with the cubic lattice model (3,4). While considering the hindrances of bond angle and potential barrier of a polyethylene chain, we calculated $\bar{h}^2$ for a polymer chain confined in a sphere and h_o^2 of the non-confined polymer chain in combination with the diamond lattice model with the Monte Carlo simulation. Then the relationship between $\bar{h}^2/h_o^2$ and the diameter of the sphere was discussed. Further, the model adopted in this paper is comparable to the regular tetrahedral geometric configuration of the C-C chain and better self-avoidance over short range.

CALCULATION METHOD

In a growing polymer chain, the formation of the next bond can occur in three ways (FIGURE 1) viz. trans ($\phi = 120^\circ$), right-gauche ($\phi = 120^\circ$) and left-gauche ($\phi = 240^\circ$). The rotational potential curve of the C-C chain is shown in FIGURE 2.

For the chain in the equilibrium state, the probabilities of the three conformations are

$$P_t = \frac{1}{1 + 2\exp(-\varepsilon/kT)} \quad (1), \qquad P_g = P_{g'} = \frac{\exp(-\varepsilon/kT)}{1 + 2\exp(-\varepsilon/kT)} \quad (2)$$

where P_t, P_g and $P_{g'}$ are the probabilities of trans and the two gauches respectively, k is the Boltzmann constant and ε is the energy difference between the g(or g') and t conformations. In this paper T = 300 K and ε = 0.026 ev.

During simulation, the mean square of the end-to-end distance $\bar{h}_o^2$ of the non-confined macromolecular chain spaced on the diamond lattice was first calculated, then $\bar{h}^2$ for the chain confined in spheres with various diameters. The bond distance of the macromolecular chain is l = 1.54 Å and the diameters, D, of the spheres are given by $D/2R_o$ = 0.5, 1.0, 1.5, 2.0, 2.5 etc. where $R_o^2 = h_o^2/6$ is the radius of gyration of the non-confined chain.

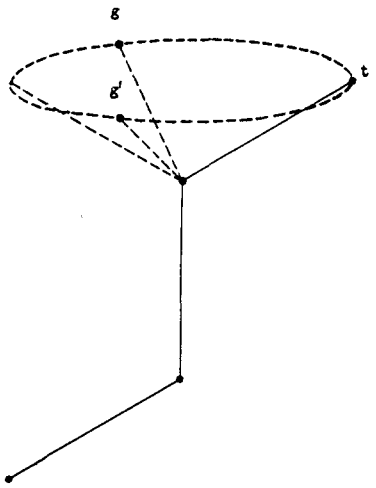

FIGURE 1. Three linking ways of the C–C chain. t - trans; g,g' - gauche.

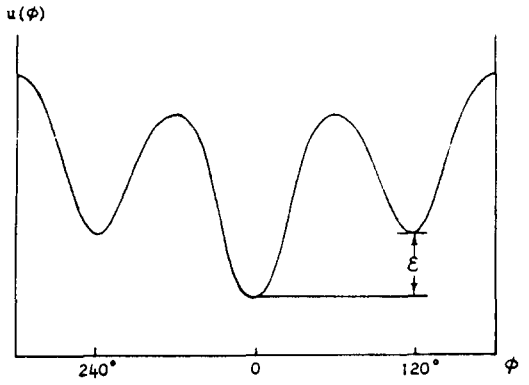

FIGURE 2. Rotational potential curve of the C–C chain.

RESULTS AND DISCUSSION

For a non-confined chain $\bar{h}_o^2 = 4509\ (A)^2$ and $R_o = 27.42$ A; the simulation results for the confined chain are listed in TABLE 1.

TABLE 1. Comparison of the simulation results for the confined chain with with the calculated results from the empirical formula.

Quantity	Results				
$D/2R_o$	0.5	1.0	1.5	2.0	2.5
$\bar{h}^2/\bar{h}_o^2$	0.0242	0.0929	0.231	0.411	0.608
$Y = 0.1(D/2R_o)^2$	0.025	0.100	0.225	0.400	0.625

From the calculated results, when $D/2R_o$ is not too large, it can be seen that there is an approximate relation between $\bar{h}^2/\bar{h}_o^2$ and $D/2R_o$

$$\bar{h}^2/\bar{h}_o^2 \approx 0.1\ (D/2R_o)^2 \qquad (3)$$

If the sphere is not too large, it is assumed that the probabilities of the distribution of the ends of polymer chains at the lattice points are approximately equal. When the number of samples is large enough, it is reasonable to replace the lattice points with continuous coordinates. Then

$$\bar{h}^2 = \frac{3}{4\pi(D/2)^3} \int_0^{D/2} r^2\, 4\pi r^2\, dr = \frac{3(D/2)^2}{5} \qquad (4)$$

$$\because \bar{h}_o^2 = 6R_o^2 \qquad \therefore \bar{h}^2/\bar{h}_o^2 = 0.1\ (D/2R_o)^2$$

From this discussion, it is concluded that

(i) our calculated results with the diamond lattice model are consistent with those of Wu Dacheng et al. who used a cubic lattice model. As $D/2R_o$ decreases, $\bar{h}^2/\bar{h}_o^2$ declines gradually and eventually tends to zero;

(ii) when the diameter D of the confined sphere is not too large, the probabilities of distribution at the lattice points of the ends of polymer chains are assumed to be equal so

$$\bar{h}^2 = \frac{3}{4\pi (D/2)^3} \int_0^{D/2} r^2 \, 4\pi r^2 dr$$

Further, we have an empirical relationship between $\bar{h}^2/\bar{h}_o^2$ and $D/2R_o$

$$\bar{h}^2/\bar{h}_o^2 = 0.1 \, (D/2R)^2$$

This relationship is in good agreement with the results calculated by Monte Carlo simulation.

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