

Studies of Distribution Function $P(S)$ of Polymer Chains[†]

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ABSTRACT: The distribution function $P(S)$ of the radius of gyration can not be calculated exactly. In this paper, we calculate the distribution function $P(S)$ of the unperturbed linear polymer chains by using Monte Carlo simulation on the simple cubic lattice. Our function $P(S)$ doesn't agree with the Flory–Fisk function $P(S)$, and comparisons with some theoretical predictions are made.

KEY WORDS Radius of Gyration / Probability Density Function / Monte Carlo Simulation /

Configurational properties of polymer molecules play important roles in the interpretation of many aspects of polymer behavior. Many properties of polymer molecules rely heavily on some knowledge of the average and the distribution of molecular dimensions of the polymer chain. Basic parameters that have most often been used to describe the dimensions of the polymer chain are the end-to-end vector \mathbf{R} and the radius of gyration S . Important in various theories of polymer behavior are the probability density function $P(S)$ and $P(\mathbf{R})$, and the mean square radius gyration $\langle S^2 \rangle$ and the mean square end-to-end distance $\langle R^2 \rangle$ of polymer chains. The mean square $\langle S^2 \rangle$ and $\langle R^2 \rangle$ can be calculated by

$$\langle S^2 \rangle = \int_0^\infty S^2 \cdot P(S) dS \Big/ \int_0^\infty P(S) dS \quad (1)$$

$$\langle R^2 \rangle = \int_0^\infty 4\pi R^4 \cdot P(\mathbf{R}) d\mathbf{R} \Big/ \int_0^\infty 4\pi R^2 \cdot P(\mathbf{R}) d\mathbf{R} \quad (2)$$

In general, the even moments of the S distribution and the \mathbf{R} distribution are formally defined by

$$\langle S^{2p} \rangle = \int_0^\infty S^{2p} \cdot P(S) dS \Big/ \int_0^\infty P(S) dS \quad (3)$$

$$\langle R^{2p} \rangle = \int_0^\infty 4\pi R^{2(p+1)} \cdot P(\mathbf{R}) d\mathbf{R} \Big/ \int_0^\infty 4\pi R^2 P(\mathbf{R}) d\mathbf{R} \quad (4)$$

and using the probability density function $P(S)$ and $P(\mathbf{R})$, we can calculate the polymer expansion factors, α_S and α_R . Thus, the probability density function $P(S)$ and $P(\mathbf{R})$ are more important in the study of polymer conformations. Studies of the function $P(\mathbf{R})$ have long history,^{1–5} and the function $P(\mathbf{R})$ of polymethylene chain with a short number of bonds ($N=10$) can be given accurately,⁶ but the function $P(S)$ has not yet been completely determined even for a freely jointed chain.

The distribution function $P(S)$ of the radius of gyration was first investigated by Fixman⁷ and Forsman and Hughes.⁸ The function $P(S)$ is obtained by using the Wang–Uhlenbeck method and the result is⁹

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$$P(S) = \frac{1}{2^{1/2} \langle S^2 \rangle_0^{1/2} \pi \cdot t^3} \sum_{k=0}^{\infty} \frac{((2k+1)!(4k+3)^{3.5} / (2^k k!)^2) ((1 - 5/(8t_k)) K_{1/4}(t_k) + (1 - 3/(8t_k)) K_{3/4}(t_k)) \exp(-t_k)}{(5)}$$

where K_s are the modified Bessel functions of the second kind and t_k is defined by

$$t_k = (4k+3)^2 / 8t, \quad (6)$$

where

$$t = S^2 / \langle S^2 \rangle_0. \quad (7)$$

If we use asymptotic expansions of $K_{1/4}$ and $K_{3/4}$, we have expansion of $P(S)$ valid for small t ,

$$P(S) = 18(6/(\pi \langle S^2 \rangle_0))^{1/2} t^{-2.5} (1 - (19/36)t + (105/1296)t^2 - \dots) \exp(-9/(4t)) \quad (\text{for small } t) \quad (8)$$

$P(S)$ valid for large t was obtained by Fujita and Norisuye¹⁰

$$P(S) = (2^{1/2} \pi^{5/2} / \langle S^2 \rangle_0^{1/2}) t (1 + 9/(4\pi^2 t) + (8\pi^2 + 15)/(32\pi^4 t^2) + \dots) \exp(-\pi^2 t/4) \quad (\text{for large } t). \quad (9)$$

Finally, Flory and Fisk¹¹ used the empirical relationship given by eq 10 to represent the probability function $P(S)$ of the radius of gyration

$$P(S) = (\text{const}) S^6 \exp(-3.5S^2 / \langle S^2 \rangle_0). \quad (10)$$

All these equations are only fitted approximately for the freely jointed chain. In this paper, we investigate the function $P(S)$ of the unperturbed linear polymer chain by using Monte Carlo simulation on the simple cubic, and the method is called the 'computer experiment.'

CALCULATION METHOD

If C_N is the number of samples and $f_N(S)\Delta S$

is the number of walks whose radius gyrations lie between S and $S + \Delta S$, we have

$$\int_S^{S+\Delta S} P(S) dS = C_N^{-1} f_N(S) \Delta S \quad (11)$$

If C_N is large enough and ΔS small enough, the left of eq 11 may be written

$$\int_S^{S+\Delta S} P(S) dS = P(S + \Delta S/2) \Delta S \quad (12)$$

thus,

$$P(S + \Delta S/2) = C_N^{-1} f_N(S) \quad (13)$$

ΔS is equal to $0.05 \langle S^2 \rangle^{1/2}$ in our calculation. In this paper, linear polymers without excluded volume were generated using the simple cubic lattice model, and $b = 1$ (bond length).

RESULTS AND DISCUSSION

Monte Carlo simulation is carried out for chains of length from 50 to 400 bonds and we use 100000 samples. We calculated the function $P(S)$ using Monte Carlo simulation and according to eq 3, 9, and 10. The results are shown in Figures 1 and 2.

Through studying Figures 1 and 2, our

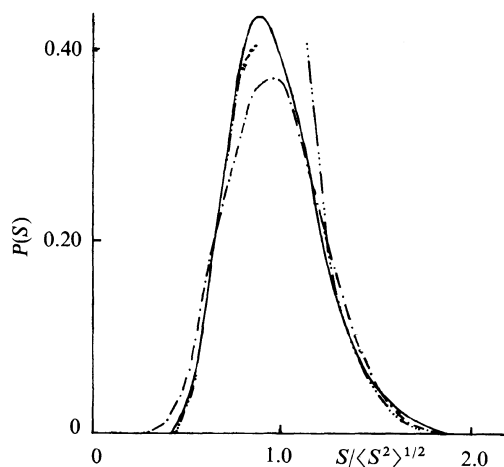


Figure 1. Probability density function $P(S)$ for a chain of 100 bonds ($\langle S^2 \rangle = 16.8$). (—), Monte Carlo; (---), Flory and Fisk; (-·-·-), eq 8; (·····), Fujita and Norisuye.

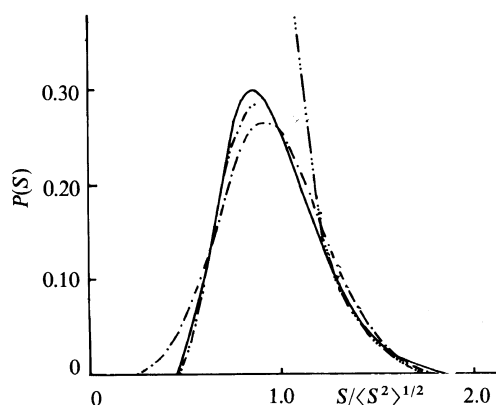


Figure 2. Probability density function $P(S)$ for a chain of 200 bonds ($\langle S^2 \rangle = 33.3$). (—), Monte Carlo; (---), Flory and Fisk; (-·-·-), Fujita and Norisuye; (- - -), eq 8.

function was found not to agree with the Flory–Fisk function $P(S)$. The Flory–Fisk function $P(S)$ is greater than our function $P(S)$ for $S < 0.65\langle S^2 \rangle^{1/2}$ and $1.05\langle S^2 \rangle^{1/2} < S < 1.65\langle S^2 \rangle^{1/2}$, and less than our function for $0.65\langle S^2 \rangle^{1/2} < S < 1.05\langle S^2 \rangle^{1/2}$ and $S < 1.65\langle S^2 \rangle^{1/2}$. The maximum of the Flory–Fisk function is less than that of our function. The function $P(S)$ according to eq 8 agrees well with our function for small S , and the Fujita–Norisuye function $P(S)$ also agrees well with our function for S , $1.30\langle S^2 \rangle^{1/2} < S < 1.60\langle S^2 \rangle^{1/2}$, but the deviation is large for large S , $S > 1.65\langle S^2 \rangle^{1/2}$.

To analyze the function in more detail, we calculate the ratio $\langle S^{2p} \rangle / \langle S^2 \rangle_0^p$ ($\langle S^2 \rangle_0 = Nb^2/6$) according to eq 3 and the Flory–Fisk function, and by Monte Carlo simulation. The results are given in Table I. In Table I, the ratio $\langle S^{2p} \rangle / \langle S^2 \rangle_0^p$ is equal to the Flory–Fisk results for $p = 1, 2, 3$, and the deviation is less than 0.80%, but greater than the Flory–Fisk results, and the deviation is greater 7.0% for $p = 4$ and 12.0% for $p = 5$. This agrees with our function. In the next paper, we will investigate the function $P(S)$ of polymethylene chain using

Table I. Values of $\langle S^{2p} \rangle / \langle S^2 \rangle_0^p$ under different conditions

Monte Carlo					
N	$\langle S^2 \rangle / \langle S^2 \rangle_0$	$\langle S^4 \rangle / \langle S^2 \rangle_0^2$	$\langle S^6 \rangle / \langle S^2 \rangle_0^3$	$\langle S^8 \rangle / \langle S^2 \rangle_0^4$	$\langle S^{10} \rangle / \langle S^2 \rangle_0^5$
30	0.9960	1.2523	1.9123	3.5072	7.5432
60	1.0030	1.2627	2.0152	3.8456	8.7676
90	1.0080	1.2602	1.9705	3.7440	8.4010
120	1.0050	1.2792	2.0460	3.9220	9.2035
150	1.0061	1.2796	2.0463	4.0216	9.4449
180	1.0020	1.2830	2.0477	3.9934	9.2865
210	1.0006	1.2794	2.0359	3.9716	9.1991
240	1.0028	1.2773	2.0319	3.9747	8.6637
270	1.0029	1.2758	2.0311	3.9508	8.6747
300	1.0052	1.2756	2.0340	3.9745	8.8802
350	1.0078	1.2780	2.0366	3.9761	8.9054
average (150~350)		1.2780	2.0366	3.9761	9.0099
Flory and Fisk		1.2857	2.0204	3.7522	8.0404

Monte Carlo simulation and the rotational-isomeric state (RIS) model.

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