

NOTES

**Distribution Density Function  $P(S)$  of Self-Avoiding Walk Chains**

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Configurational properties of polymer chains play a vital role in the interpretation of many aspects of polymer behavior. Theories of viscosity of concentrated and dilute polymer solution,<sup>2</sup> solution thermodynamics and determination of molecular weights of polymers in solution,<sup>1</sup> viscosity of polymer melts,<sup>2,3</sup> and rubber elasticity<sup>1</sup> rely heavily on some knowledge of the average and/or the distribution of molecular dimensions of the polymer chain. Important in various theories of polymer behavior are the probability density distribution functions  $P(S)$  and  $P(R)$  and the mean squares  $\langle S^2 \rangle$  and  $\langle R^2 \rangle$ . The mean squares  $\langle S^2 \rangle$  and  $\langle R^2 \rangle$  can be obtained from the probability density functions  $P(S)$  and  $P(R)$ , thus, the functions  $P(S)$  and  $P(R)$  are more important. The studies of probability function  $P(R)$  have long history, and many results have been obtained.<sup>4-10</sup> The distribution function  $P(S)$  of linear polymer chains was investigated approximately by Fixman and Forsman and Hughes,<sup>11,12</sup> and we also study the functions  $P(S)$  of the unperturbed linear polymer chains and the unperturbed uniform star polymer chains using Monte Carlo method.<sup>13,14</sup> In this paper, we study the function  $P(S)$  of polymer chains with excluded volume.

CALCULATION METHOD

The algorithm used in this Monte Carlo study is an inversely-restricted sampling routine developed by Rosenbluth and Rosenbluth.<sup>15</sup> Here the weighting function  $w_n$  is necessary since some configurations are generated more often than others, and a weighting function must be introduced so that all configurations are counted equally. If  $W$  is the weight of  $C_n$  samples of polymer chains and  $C_n$  is the number of samples, thus,

$$W = \sum_{i=1}^{C_n} w_n(i) \tag{1}$$

If  $P(S)$  is the probability density distribution function, and  $f_n(S)\Delta S$  is the probability of walks whose radius of gyrations lie between  $S$  and  $S + \Delta S$ , we have

$$\int_S^{S+\Delta S} P(S)dS = W^{-1}f_n(S)\Delta S \tag{2}$$

If  $C_n$  is large enough,  $\Delta S$  small enough, and  $P(S)$  decreases or increases monotonously, the left of eq 2 may be written

$$\int_S^{S+\Delta S} P(S)dS = P(S + \Delta S/2)\Delta S \tag{3}$$

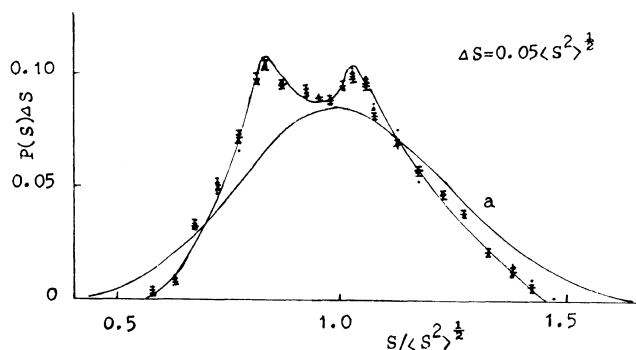
Thus,

$$P(S + \Delta S/2) = W^{-1}f_n(S) \tag{4}$$

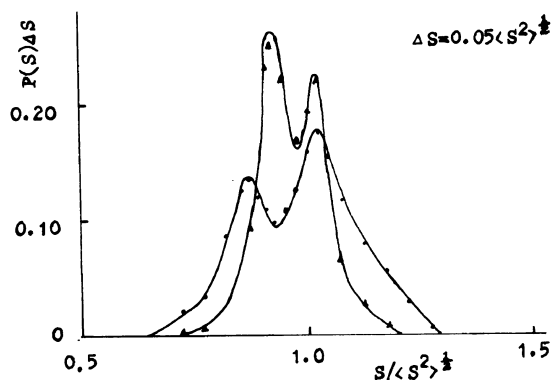
$\Delta S$  is equal to  $0.05\langle S^2 \rangle^{1/2}$  in our calculation. In the region of inflection point, in order to decrease the deviation, we use  $\Delta S$  more small. Since the number of configurations is very large for long polymer chains with excluded volume, in this paper, we only study the probability functions  $P(S)$  of short linear chains and short uniform star chains. Here the simple cubic lattice model is adopted.

RESULTS

Simulations are carried out for linear polymer chains of  $n=11, 51,$  and  $101$  beads, and uniform star chains of  $f=3,$  and  $5$  with  $n=31$  beads per branches. We use from 100000 samples to 100000 samples. We calculate the probability density distribution function  $P(S)$  using eq 4, and the results are given in Figures 1 and 2. The modified Rosenbluth-Rosenbluth method<sup>16</sup> (i.e., the Scanning method) were developed by Meirovitch and Lim to investigate the configurational properties of polymer chains. We find that the difference between two method for short polymer chains is insignificant. For example, the maximum deviation of the function  $P(S)$  for linear polymer chain of  $n=101$  beads is only 8.0%. In Figure 1, we calculate the probability function  $P(S)\Delta S$  of linear polymer chains with excluded volume (self-avoiding linear chains) with different chain length  $n=$



**Figure 1.** Probability  $P(S)\Delta S$  vs.  $S/\langle S^2 \rangle^{1/2}$  for linear polymer chains with excluded volume. (•)  $n=11, \langle S^2 \rangle=2.64$ ; (▲)  $n=51, \langle S^2 \rangle=18.4$ ; (+)  $n=101, \langle S^2 \rangle=41.5$ . (⊥) standard deviations for  $n=101$  chain.



**Figure 2.** Probability  $P(S)\Delta S$  vs.  $S/\langle S^2 \rangle^{1/2}$  for uniform star chains with excluded volume. ( $\circ$ )  $f=3$ ,  $n=31$ ,  $\langle S^2 \rangle=27.8$ ; ( $\blacktriangle$ )  $f=5$ ,  $n=31$ ,  $\langle S^2 \rangle=34.5$ .

11, 51, and 101 beads, and find the probability function  $P(S)\Delta S$  is nearly independent of chain length  $n$ , and the results are almost similar for different chain length. In Figure 1, we also calculate the standard deviations of  $P(S)$  for polymer chain of  $n=101$  beads. However, the probability function  $P(S)\Delta S$  of self-avoiding linear chains are different from the unperturbed linear polymer chains. In the case of the unperturbed linear chains, for example, line a is  $P(S)\Delta S = C(S^8 \exp(-4.5S^2/\langle S^2 \rangle))$ ,<sup>14</sup>  $P(S)$  has only one extremum.  $P(S)$  of self-avoiding chains have two extrema, one is near  $S=0.82\langle S^2 \rangle^{1/2}$  and another near  $S=1.02\langle S^2 \rangle^{1/2}$ . In Figure 2, we also calculate the probability function  $P(S)$  of self-avoiding uniform star chain

with chain length  $n=31$  beads, and find the functions  $P(S)$  of star chains are similar to self-avoiding linear chains, and  $P(S)$  also have two extrema. With increasing the number of branches  $f$ , the region of radius of gyration decrease, and maximum of  $P(S)$  increases. This means radius of gyration is more concentrated with large  $f$ . However, the functions  $P(S)$  of self-avoiding linear chains and self-avoiding uniform star chains can not expressed in the simple equation.

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