MODELING AND SIMULATION OF STAR POLYMERS IN TWO DIMENSIONS

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Abstract

Designing and studying computer models of polymeric materials enhances student learning of the properties of these molecules. We have developed a simulation of ideal linear and star polymers on a two-dimensional square lattice by employing random numbers to decide upon the direction of polymer growth. Each configuration so generated forms an independent sample for statistical averaging. The mean-square radius of gyration, $\langle S^2 \rangle$, and its error have been computed for linear polymers and for star polymers with three to six arms. The data follows the expected scaling laws. The g ratio, $\langle S^2 \rangle_{star} / \langle S^2 \rangle_{linear}$, is in excellent agreement with the theoretical predictions of Zimm and Stockmeyer, who showed that $g = (3f - 2) / f^2$, where f is the number of branches in the star polymer. This project is suitable for junior/senior majors in engineering, mathematics or science.

Introduction

Understanding the nature of polymeric materials is important for students in a variety of specialties. Computer modeling[1][2] has greatly enhanced our understanding of these materials. The key to comprehending their behavior is to understand how molecular constitutients give rise to observable macroscopic properties[3]. At a very high level of abstraction all the atoms making up the monomer building blocks are grouped into a spherical "bead" and then the polymer is treated as a set of such linked beads. These beads can be connected in many different ways. In a linear chain, for example, the beads are linked so that each is connected to only two others, except of course for the end beads. In a star polymer there is a core bead which is connected to a number of linear branches. Hence, if m is the number of beads in one linear branch of a star polymer containing f branches, the total number of beads in the star polymer, N, is given by

$$N = fm + 1. \quad (1)$$

Real polymers display "excluded" volume effects because units cannot pass through each other. Ideal polymer systems, however, allow for this possibility and the units can even overlap during their movement. Ideal polymer systems are important because they represent the first approximation to real polymers. Moreover, many properties of ideal polymers can be calculated exactly by studying random walks. The computer algorithms needed for simulating ideal polymers are much simpler than those needed to study real polymers [4].

Although every polymer can assume a different spatial configuration in time, its over all shape can be characterized by its mean-square radius of gyration, $\langle S^2 \rangle$. It is well-known that for very long ideal polymers, $\langle S^2 \rangle$ follows a scaling law [5]

$$\langle S^2 \rangle = A (N - 1)^B \quad (2)$$

in which the coefficient, A, is determined by the details of the polymer model but the exponent, B, is a universal quantity equal to 1.00 for all ideal polymers. By calculating the mean-square radius of gyration of a linear chain and a star polymer separately, we can determine a useful parameter for comparing the shapes of two different kinds of polymers. This parameter is called the g ratio and it is defined as the ratio of the radii of gyration:

$$g = \langle S^2 \rangle_{star} / \langle S^2 \rangle_{linear} \quad (3)$$

Zimm and Stockmeyer [6] showed for ideal polymers that

$$g = (3f - 2) / f^2 \qquad (4)$$

The goal of this project was to test the validity of this theoretical g ratio using computer simulated models of linear and star polymers. The computer programming and analysis were further simplified by employing a two-dimensional system.

Method

In these simulations the polymers are described in a two - dimensional, X -Y coordinate system. The location of the geometric center of each bead in the polymer is defined by two, one-dimensional arrays, X and Y. The initial bead is always assigned the coordinate of the origin (0, 0). The distance between two connected units is assumed to be a constant of magnitude one. The polymers are "grown" on the two-dimensional square lattice by using a random number, RN between 0 and 1, to select one of the four possible directions of "growth": right, left, up or down. Hence, if the up choice is made after the i -1 - th bead has already been placed, the coordinate of the new i-th bead becomes

$$X[i] = X[i - 1] \qquad (5a)$$

and

$$Y[i] = Y[i - 1] + 1 \qquad (5b)$$

This process is continued until a total of N coordinate locations have been generated.

A star polymer is created by first growing one branch, with m beads, from the central core by the procedure already described for the linear chain. The growth of the second branch begins again from the central core bead until the m additional beads are placed. Then the next branch is begun and the process is continued until all f branches have been completed.

The computer program which performs the simulation of the linear and star polymer was written in C and compiled and executed in a Linux environment on a Dell PC using the open source gcc compiler.

In summation, the total number of times that the random walk growth process is executed is, N for a linear chain, and fm for a star polymer. These procedures generate one configuration. Each random walk growth process has been repeated Nc times so that Nc independent polymer configurations are created for data collection. The current simulations used Nc = 300,000.

The square radius of gyration, S^2, for both the linear chain and the star polymer for the same total number of beads, N, has been computed for each generated configuration k from the equation

$$S^2(k) = 1 / (2N^2) \sum_{i,j}^{N} [(X_i(k) - X_j(k))^2 + (Y_i(k) - Y_j(k))^2] \qquad (6)$$

where $X_i(k)$ and $Y_i(k)$ are the X and Y coordinates of the i-th bead in the k-th configuration and $X_j(k)$ and $Y_j(k)$ are the corresponding coordinates of the j-th bead. The set of $S^2(k)$ values were then further averaged over the total number of configurations generated to determine the mean-square radius of gyration, $\langle S^2 \rangle$ and its standard deviation from the mean, $\sigma_{\langle S^2 \rangle}$ employing the equations [7]

$$\langle S^2 \rangle = (1/Nc) \sum_{k=1}^{Nc} S^2(k) \qquad (7a)$$

$$\sigma_{\langle S^2 \rangle} = [(\langle S^4 \rangle - \langle S^2 \rangle^2) / (Nc-1)]^{1/2} \qquad (b)$$

Results

Table I presents the simulation results for all the systems studied. The number in parenthesis denotes one standard deviation in the last displayed digit. Note that a star polymer with two branches (f = 2) is equivalent to a linear chain. It is clear from the radius of gyration data that polymers with a given number of units N become more compact as the number of branches increases.

Table I Simulation Data for $\langle S^2 \rangle$

N	f =2	f =3	f =4	f =5	f =6
61	10.17(1)	8.02(1)	6.54(1)	5.52(1)	4.79(1)
121	20.14(2)	15.78(1)	12.78(1)	10.72(1)	9.24(1)
181	30.17(4)	23.56(2)	19.02(2)	15.91(1)	13.69(1)
241	40.13(5)	31.36(3)	25.29(2)	21.13(1)	18.13(1)
301	50.25(6)	39.21(4)	31.56(2)	26.33(2)	22.59(1)

Weighted nonlinear least-squares fits [7] to the $\langle S^2 \rangle$ data in Table I gave the parameters reported in Table II. The number in parenthesis denotes one standard deviation in the last displayed digit. The agreement of these empirical exponents with the expected ideal value of 1.00 is reasonable. Star polymers with a fixed total number of units will have shorter branches as the number of branches increases, and thus will not be as effective in probing the large polymer limit.

Table II Power Law Fit Parameters for $\langle S^2 \rangle = A\,(N-1)^{B}$

f	A	B
2	0.175(1)	0.992(1)
3	0.141(1)	0.986(1)
4	0.119(1)	0.978(1)
5	0.103(1)	0.971(1)
6	0.092(1)	0.963(1)

The $\langle S^2 \rangle$ simulation data are plotted along with the power law fit equations in Figure 1.

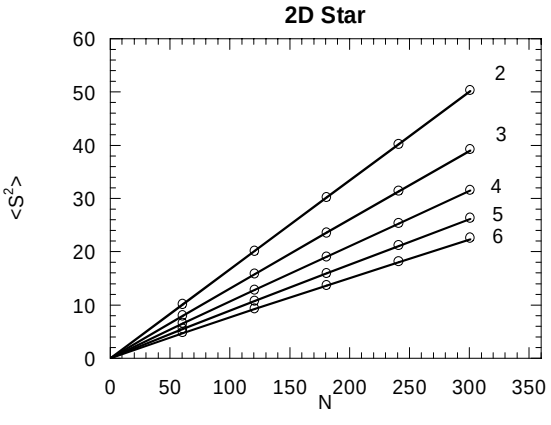

Figure 1: The variation of $\langle S^2 \rangle$ with N for two dimensional star polymers. The lines are the fit equations and the circles are the simulation values for f = 2, 3, 4, 5, and 6.

One notes the excellent fit for each f value over the entire range of N.

The g ratios have been calculated from the radius of gyration data in Table I and the error in this quantity has been computed from the standard equation [7] relating the error in a ratio $\sigma_{A/B}$ to the error in the numerator σ_A and the error in the denominator σ_B

$$\sigma_{A/B} = (A/B)\,[\,(\sigma_A/A)^2 + (\sigma_B/B)^2\,]^{1/2} \quad (8)$$

The simulation g ratios are listed in Table III. The number in parenthesis denotes one standard deviation in the last displayed digit.

Table III Simulation g ratios

N	f = 3	f = 4	f = 5	f = 6
61	0.788(1)	0.643(1)	0.543(1)	0.471(1)
121	0.784(1)	0.634(1)	0.532(1)	0.459(1)
181	0.781(1)	0.631(1)	0.527(1)	0.454(1)
241	0.781(1)	0.630(1)	0.527(1)	0.452(1)
301	0.780(1)	0.628(1)	0.524(1)	0.450(1)

These computer results are for finite N whereas the Zimm-Stockmeyer equation is for infinite N. To determine the value of g as N approaches infinity, one plots g vs. 1/N so that when $N \rightarrow \infty$, $1/N \rightarrow 0$. The g value for infinite N can thus be found by determining the intercept of this graph after fitting a weighted least-squares linear line in 1/N to each set of data in the tables. The extrapolated g ratios are displayed in Figure 2 and compared to the Zimm-Stockmeyer predictions in Table IV.

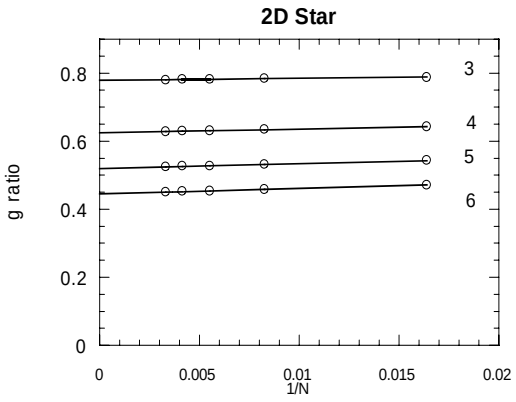

Figure 2: The g ratio for two dimensional stars. The lines are the fit equations and the circles are the simulation values for f = 3, 4, 5, and 6.

Table IV Comparison of extrapolated computer g ratios to the theoretical infinite bead values

f	Computer	Theory[1]
3	0.779 (1)	0.778
4	0.625 (1)	0.625
5	0.520 (1)	0.520
6	0.445 (1)	0.444

1 See reference 6

One notes that there is excellent agreement, within the statistical errors, with the theoretical predictions.

Conclusion

A random walk model has been employed for simulating linear and star polymers on a two-dimensional lattice. The mean-square radius of gyration and its error have been determined for a range of N. It is found that the data obey the expected power law with a power nearly equal to 1.0. The g ratio, which is one measure of the shape differences between star and linear polymers, has an extrapolated value, for all the systems studied, which is in excellent agreement with the Zimm-Stockmeyer theoretical predictions [6]. These types of simulations provide projects in which students can get experience in developing models, programming in some high level language, performing statistical analysis and employing graphing software; a skill set which will be very useful in their future careers.

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Biorgraphical Information

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