MODELING AND SIMULATION OF TWO DIMENSIONAL STAR POLYMERS WITH THE PIVOT ALGORITHM

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Abstract

We have developed a simulation of ideal linear and star polymers in two dimensions in which the polymers are moved by the Pivot algorithm. Multiple runs are performed to enhance the statistical quality of the data generated. Properties such as the mean-square radius of gyration, the g ratio and the asphericity have been computed and compared to the theoretical predictions for linear and star polymers with three to six arms. There is excellent agreement for all properties studied. The graphical capabilities of the Maple software package have been employed to examine individual configurations and to make computer movies of the dynamical motion. This type of project is suitable for junior/senior majors in engineering, mathematics or science.

Introduction

In a previous article in this journal Varriale and Bishop[1] have described a "coarse-grained" model of polymeric materials which could serve as an entrée to the methods of computer modeling for engineering, mathematics and science students. In that article all the atoms making up the detailed monomer building blocks of a polymer were grouped into circular "beads". Individual beads were linked together to form the polymer. These beads were joined together by starting with a central core bead and growing f linear "arms" outward on a two dimensional square lattice. A linear chain was generated by growing two arms from the central bead. 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

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

This two dimensional model was further simplified by allowing the bead units to pass through each other and even to overlap. This ideal model serves as a first approximation of real polymers. Also many properties of such simplified polymer models can be calculated exactly from the theory of random walks [2] [3]. In the current work we have simulated polymers in two-dimensional continuous space; i.e. not confined to a lattice. Many of the theoretical ideas apply to both of our models.

Although every polymer can assume a different spatial configuration at any time, an overall shape can be characterized by the 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 [3].

$$\langle S^2 \rangle = C (N - 1)^P \qquad (2)$$

in which the coefficient, C, is determined by the details of the polymer model but the exponent, P, is a universal quantity equal to 1.00 for all ideal polymers. A useful parameter for comparing the shapes of linear and star polymers is called the g ratio and it is defined as the ratio of the radii of gyration:

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

Zimm and Stockmeyer[4] showed for ideal polymers that

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

Even more details about the shapes of polymers can be determined from the matrix representation of the tensor of components of the radius of gyration. The trace of this tensor, the sum of the diagonal elements, is equal to $\langle S^2 \rangle$ and the eigenvalues, λ_1 and λ_2 , are the

components of $<S^2>$ along the principal orthogonal axes. Rudnick and Gaspari[5] have defined the asphericity, A, of polymers in two dimensions as

$$A = <(\lambda_1 - \lambda_2)^2> / <(\lambda_1 + \lambda_2)^2> \quad (5)$$

and the average asphericity, <A>, as

$$<A> = <(\lambda_1 - \lambda_2)^2 / (\lambda_1 + \lambda_2)^2> \quad (6)$$

Note that in these equations A involves a ratio of averages whereas <A> involves an average of a ratio. The shape of a two dimensional polymer can vary from an extended rod shape in which λ_2 is essentially 0 so that A and <A> have a value of one, to a disk for which $\lambda_1 = \lambda_2$ and both A and <A> are zero. In between these extremes a polymer configuration can be imagined as enclosed inside an ellipse with semi-major axis equal to λ_1 and semi-minor axis equal to λ_2. This is shown in Figure 1 where an ellipse has been drawn enclosing a 21 bead four arm star polymer. The graphics capabilities of Maple[6] have been employed in making this figure.

The goal of this project was to compare $<S^2>$, the g ratio, A and <A> values calculated from computer simulation to theoretical predictions for linear and star polymers.

Method

In the simulations, 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 started in a fixed configuration in which the arms are placed about the center bead so that they lie at equal angles from each other; e.g. when f = 3 the arms are set at 120º apart. The beads are moved in continuous space by the Pivot algorithm [7]. First, a random number is used to select one of the beads as a "pivot" with coordinates (Xp,Yp). A second random number is then employed to determine the rotation angle, θ, such that θ falls between 0º and 360º. This angle is used to move all the higher

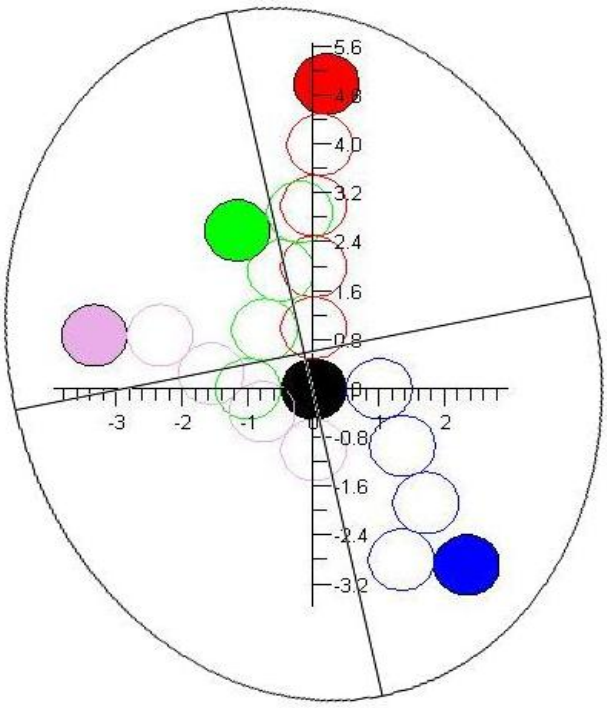

Figure 1: A four arm star polymer enclosed in an ellipse whose semi-major axis is λ_1 and whose semi-minor axis is λ_2. The end and center beads are shaded so that their motion can be more easily followed.

indexed beads on that arm about the pivot bead to new locations. If the center bead is selected as the pivot, another random number is employed to choose which entire arm is to be rotated about the center bead. The new locations are given [8] by

$$X' = Xp + (X - Xp)\cos\theta - (Y - Yp)\sin\theta \quad (7a)$$

$$Y' = Yp + (X - Xp)\sin\theta + (Y - Yp)\cos\theta \quad (7b)$$

In Eqs. 7a and b, X',Y' are the new coordinates whereas X,Y are the original coordinates before the pivot move. This procedure is illustrated in Figure 2 for a linear chain.

This procedure generates one configuration. The process is continued for NTOTAL moves (typically NTOTAL = 5 X 10^6). However, the initial state is not representative of the final equilibrium state and therefore, NonEq moves (typically 1 X 10^6) need to be discarded before the averaging process begins. However, even in equilibrium, the states are not statistically independent. Hence, data is collected at a spacing of 500 moves. The resulting random snapshots of polymer configurations are used for data analysis. In addition, sixteen different seeds were employed with the random number generator in order to obtain additional independent configurations and thus to enhance the statistical quality of the data. Figure 3 illustrates that for a 61 unit linear chain the initial S^2 value has relaxed after about 200 pivot moves such that it fluctuates about a mean value. This type of figure is often called a time series.

The computer program which performs the simulation was written in C and compiled and executed in a Linux environment on a Dell PC using the open source gcc compiler. Further understanding of the system's behavior was achieved by employing the animate feature of Maple [6] to visualize the changing polymer configurations as the simulation progressed.

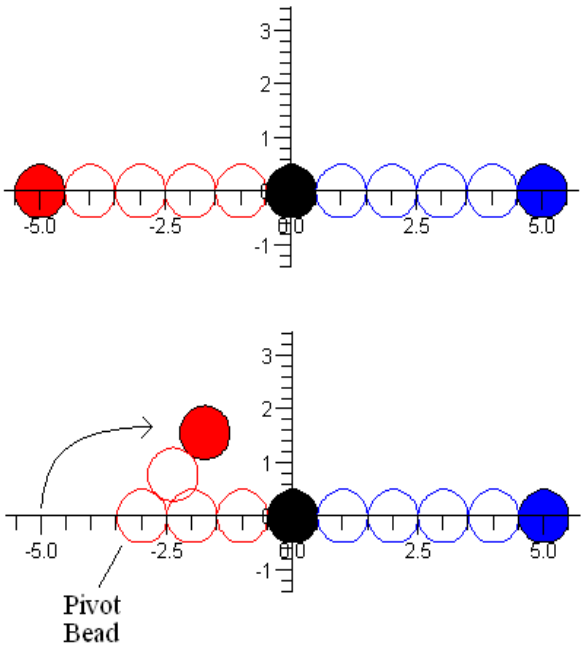

Figure 2: Top: the initial linear chain configuration. Bottom: the results of a pivot move.

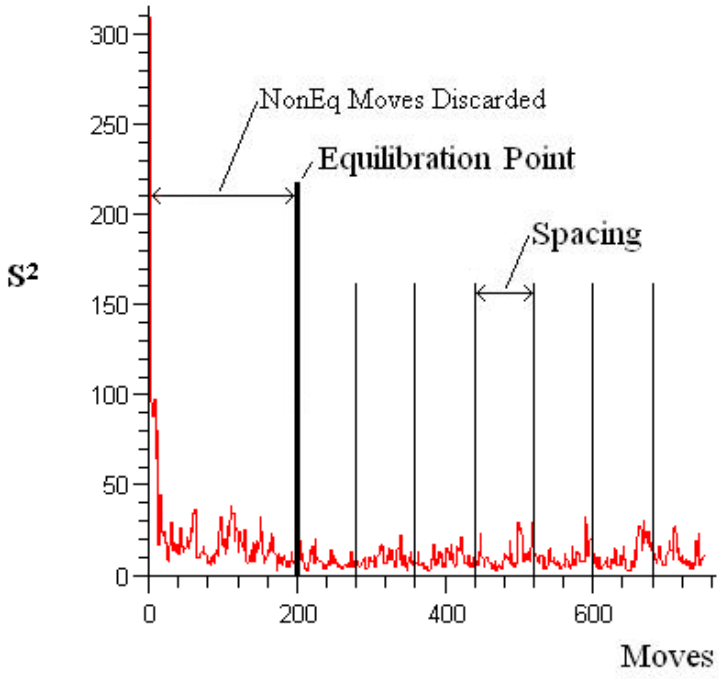

Figure 3: The time series for S^2. The discarded non-equilibrium region and the move spacing used to sample data are illustrated.

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

$$S^2(k) = 1/(2N^2) \sum_{i,j}^{N} [\ (X_i(k) - X_j(k))^2 + (Y_i(k) - Y_j(k))^2\ ] \quad (8)$$

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.

$\leftrightarrow$

The radius of gyration tensor, T, for the k-th configuration has the following matrix components

$$T_{11} = (1/N) \sum_{j=1}^{N} (X_j - XCM)^2 \quad (9a)$$

$$T_{12} = T_{21} = (1/N) \sum_{j=1}^{N} (X_j - XCM)\ (Y_j - YCM) \quad (9b)$$

$$T_{22} = (1/N) \sum_{j=1}^{N} (Y_j - YCM)^2 \quad (9c)$$

where XCM and YCM are the components of the center of mass:

$$XCM = (1/N) \sum_{j=1}^{N} X_j \quad \text{and} \quad YCM = (1/N) \sum_{j=1}^{N} Y_j \quad (10)$$

It is simple to analytically find the eigenvalues of the matrix representation of this 2 X 2 tensor in terms of the above sums.

The set of property values, $Q = S^2$ and the components of A, were then further averaged over the total number of samples, Ns, generated to determine the mean value <Q> and the

standard deviation from the mean, $\sigma_{<Q>}$ employing the equations [9]

$$<Q> = (1/Ns) \sum_{k=1}^{Ns} Q(k) \qquad (11a)$$

$$\sigma_{<Q>} = [(<Q^2> - <Q>^2) / (Ns-1)]^{1/2} \qquad (11b)$$

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 $<S^2>$.

N	f =2	f =3	f =4	f =5	f =6
61	10.14(2)	7.99(1)	6.52(1)	5.52(1)	4.79(1)
121	20.15(2)	15.80(2)	12.78(1)	10.73(1)	9.25(1)
181	30.13(6)	23.52(2)	19.01(2)	15.91(1)	13.65(1)
241	40.18(7)	31.42(4)	25.28(4)	21.13(3)	18.14(2)
301	50.21(9)	39.16(4)	31.61(3)	26.35(2)	22.59(2)

Weighted nonlinear least-squares fits [9] to the $<S^2>$ 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 and even better than was found for the polymer growth model [1]. The Pivot algorithm is better at sampling the possible configurations than the growth algorithm. Also star polymers with a fixed total number of units will have shorter branches as the number of branches increases. Hence, the exponent fits less well with the ideal value of 1.00 as f increases.

Table II Power Law Fit Parameters for $<S^2> = C (N - 1)^P$.

f	C	P
2	0.173(1)	0.994(1)
3	0.140(1)	0.988(1)
4	0.116(1)	0.983(1)
5	0.101(1)	0.976(1)
6	0.090(1)	0.969(1)

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 [9] 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,

$$\sigma_{A/B} = (A /B) [(\sigma_A/ A)^2 + (\sigma_B / B)^2]^{1/2} \qquad (12)$$

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(2)	0.643(2)	0.544(1)	0.472(1)
121	0.784(1)	0.634(1)	0.533(1)	0.459(1)
181	0.781(2)	0.631(1)	0.528(1)	0.453(1)
241	0.782(2)	0.629(1)	0.526(1)	0.451(1)
301	0.780(2)	0.630(1)	0.525(1)	0.450(1)

These computer results are for finite N whereas the Zimm-Stockmeyer equation, Eq. 4, 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 compared to the Zimm-Stockmeyer predictions in Table IV. One finds excellent agreement between the computer simulation data and the theoretical predictions.

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

f	Extrapolated	Eq. 4
3	0.779 (2)	0.778
4	0.626 (1)	0.625
5	0.520 (1)	0.520
6	0.444 (1)	0.444

The simulation results for A and <A> are contained in Tables V and VI, respectively. This data reveals that the asphericity of star polymers decreases as the number of arms increases; e.g. the polymers become more disk like in their shape. As was the case for the g ratio we have extrapolated a linear fit in 1/N to predict values for a simulation with an infinite number of beads. These extrapolations are compared to the theoretical predictions [10] in Table VII.

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

Conclusion

The Pivot algorithm has been used to simulate linear and star polymers in two dimensions. The mean-square radius of gyration and its error have been determined for a wide range of N. It is found that the data obey the expected power law with a power nearly equal to 1.00. The g

Table V The ratio of the averages, A.

N	f = 2	f = 3	f = 4	f = 5	f = 6
61	0.565(3)	0.395(2)	0.301(1)	0.242(1)	0.201(1)
121	0.568(4)	0.399(2)	0.305(1)	0.246(1)	0.206(1)
181	0.570(4)	0.401(1)	0.309(2)	0.248(1)	0.207(1)
241	0.570(4)	0.404(2)	0.308(2)	0.250(1)	0.209(1)
301	0.571(5)	0.404(2)	0.309(1)	0.250(1)	0.209(1)

Table VI The average of the ratio, <A>.

N	f = 2	f = 3	f = 4	f = 5	f = 6
61	0.391(1)	0.315(1)	0.257(1)	0.216(1)	0.184(1)
121	0.394(1)	0.318(1)	0.261(1)	0.218(1)	0.187(1)
181	0.395(1)	0.319(1)	0.262(1)	0.220(1)	0.188(1)
241	0.395(1)	0.320(1)	0.262(1)	0.220(1)	0.190(1)
301	0.395(1)	0.320(1)	0.262(1)	0.220(1)	0.189(1)

Table VII Comparison of extrapolated computer A and <A> values to the theoretical infinite bead values.

f	A Extrapolated	A Theory*	<A> Extrapolated	<A> Theory*
2	0.572(3)	0.571	0.396(1)	0.396
3	0.405(1)	0.404	0.321(1)	0.321
4	0.311(1)	0.311	0.264(1)	0.264
5	0.252(1)	0.252	0.221(1)	0.222
6	0.211(1)	0.212	0.191(1)	0.191

* See reference 10

ratio has an extrapolated value, for all the systems studied, which is in excellent agreement with the Zimm-Stockmeyer theoretical predictions [4]. In addition, the asphericity is also in excellent agreement with Wei's analytical results [10]. These types of simulations provide interesting projects in which students can get experience in computational science. This will be very useful in their future careers.

Acknowledgements

We wish to thank the Manhattan College Computer Center for generous grants of computer time. We also wish to thank Professor Paula A. Whitlock for helpful comments on the manuscript.

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