

MODELING AND SIMULATION OF IDEAL LINEAR AND RING POLYMERS WITH BROWNIAN DYNAMICS

Brian T. Merriman and Marvin Bishop
 Department of Mathematics/Computer Science
 Manhattan College

Abstract

We have developed a simulation of ideal linear and ring polymers in which the polymers are moved by Brownian dynamics. Properties such as the mean-square radius of gyration, the g-ratio, the asphericity and the form factor have been computed and compared to theoretical predictions. There is good agreement for all properties studied. The graphical capabilities of the Maple software package have been employed to examine individual configurations. This type of project is suitable for junior/senior majors in engineering, mathematics or science.

Introduction

In a set of previous articles in this journal we have described [1-5] a "coarse grained" model of polymeric materials. All the atoms making up the detailed monomer building blocks of a polymer were grouped into spherical "beads" and the individual beads were then linked together to form the polymer of interest. This model could be further simplified by allowing the bead units to pass through each other and even to overlap. Such an ideal model serves as a first approximation of real polymers. In this article we explore the differences between ideal linear and ring polymers by computing a variety of their properties. This investigation formed the basis of an independent studies project.

Although every polymer can assume a different spatial configuration at any time, an overall size can be characterized by the mean-square radius of gyration, $\langle S^2 \rangle$. Here, $\langle \rangle$ denotes an average over the polymer configurations. It is well-known that for very large polymers, $\langle S^2 \rangle$ follows the scaling laws [6]

$$\begin{aligned} \langle S^2 \rangle_{\text{linear}} &= C_1(N-1)^P \quad \text{and} \\ \langle S^2 \rangle_{\text{ring}} &= C_2N^P \end{aligned} \quad (1)$$

where N is the number of beads. The coefficients C_1 and C_2 are 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 sizes of linear and ring polymers is called the g-ratio and it is defined as the ratio of the radii of gyration:

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

Zimm and Stockmeyer [7] showed that for the ideal polymers studied here $g = 1/2$.

Details about the shapes of polymers can be determined from the matrix representation of the tensor of components of the radius of gyration. Its eigenvalues, λ_1 , λ_2 and λ_3 , are the components of $\langle S^2 \rangle$ along the principal orthogonal axes. The trace of this tensor, $\lambda_1 + \lambda_2 + \lambda_3$, is equal to $\langle S^2 \rangle$. By convention, the λ values are ordered by magnitude such that $\lambda_1 \geq \lambda_2 \geq \lambda_3$ and then averaged. Rudnick and Gaspari [8] have defined the asphericity, A , of polymers in three dimensions as

$$A = \frac{\sum_{i>j}^3 (\lambda_i - \lambda_j)^2}{2 \left(\sum_{i=1}^3 \lambda_i \right)^2} \quad (3)$$

and the average asphericity, $\langle A \rangle$, as

$$\langle A \rangle = \frac{\sum_{i>j}^3 (\lambda_i - \lambda_j)^2}{2 \left(\sum_{i=1}^3 \lambda_i \right)^2} \quad (4)$$

Note that in these equations A involves a ratio of averages whereas $\langle A \rangle$ involves an average of a ratio. The shape of a polymer can vary from an extended rod in which λ_2 and λ_3 are essentially zero so that A and $\langle A \rangle$ have a value of one, to a sphere for which $\lambda_1 = \lambda_2 = \lambda_3$ and both A and $\langle A \rangle$ are zero. In between these extremes a polymer configuration can be imagined as enclosed inside an ellipsoid with semi-major axis equal to λ_1 and semi-minor axes equal to λ_2 and λ_3 .

Another important structural property of polymers is the scattering factor, $S(K)$. This function provides information about the spatial monomer distribution of polymer materials. It is defined [9] as the Fourier transform of the density-density auto-correlation function and is given by

$$S(k) = (1/N^2) \sum_{m,n}^N \langle \exp[i\mathbf{k} \cdot (\mathbf{R}_n - \mathbf{R}_m)] \rangle \quad (5)$$

where \mathbf{k} is the momentum transfer of the scattering experiment and \mathbf{R}_n and \mathbf{R}_m are the positions of the n -th and m -th monomers.

In an ideal polymer model the configurations obey random statistics and have a Gaussian distribution. Then the scattering factor for a linear polymer is given by the Debye [9] function

$$S(k)_{\text{linear}} = 2 [X - 1 - \exp(-X)] / X^2 \quad (6)$$

where $X = k^2 \langle S^2 \rangle_{\text{linear}}$.

The corresponding function for rings has been obtained by Casassa [10]

$$S(k)_{\text{ring}} = (1/W) \exp(-W^2) \int_0^W \exp[-t^2] dt \quad (7)$$

where $W = X^{1/2}/2$ and $X = k^2 \langle S^2 \rangle_{\text{ring}}$.

The goal of this project was to determine and then compare $\langle S^2 \rangle$, the g -ratio, A , $\langle A \rangle$ and $S(k)$ values calculated from computer simulation to theoretical predictions for linear and ring polymers.

Method

In the simulations, the location of the geometric center of each bead in the polymer is defined by their X , Y , and Z coordinates. The first bead is always assigned the coordinates of the origin $(0, 0, 0)$. The distance between two connected units is maintained to be nearly 1.0 by a harmonic spring force. This force differentiates a linear polymer from a ring since rings have an additional connection between the first and the last units. In addition to these harmonic inter-bead forces, Brownian dynamics [11] simulations also model solvent effects by including random and frictional forces.

The polymers are started in the XY plane in different configurations depending upon the total number of beads, N . When N is a multiple of three the initial configuration is a triangle whereas when N is a multiple of four, it is a square. The beads are moved in time by using a small time step for integrating the resultant equations of motion. The Verlet [11] integration algorithm is employed. The initial state is not representative of the final equilibrium state and therefore, the first 50,000 integration steps are discarded before the averaging process begins. Since data at adjacent time intervals will be highly correlated, the data are collected at a spacing of 25,000 time steps. The resulting random snapshots of polymer configurations are used for subsequent data analysis. Typically, we generate 1,000 such equilibrated samples.

The computer program which performs the simulation was written in C and compiled and executed in a Linux environment on a Dell laptop using the open source gcc compiler. Further understanding of the system's behavior was achieved by employing the graphic features

of Maple to visualize the changing polymer configurations as the simulation progressed.

The radius of gyration tensor, T_{ab} , for the p -th configuration has the following matrix components

$$T_{ab}(p) = (1/N) \sum_{i=1}^N [R_i(p) - R_{CM}(p)]_a [R_i(p) - R_{CM}(p)]_b \quad (8)$$

where a and b indicate two directions in a Cartesian frame, $R_i(p)$ is the position of the i -th bead and $R_{CM}(p)$ is the center of mass defined as

$$R_{CM}(p) = (1/N) \sum_{i=1}^N R_i(p) \quad (9)$$

The eigenvalues of the matrix representation of this 3 X 3 radius of gyration tensor were determined by solving the resultant cubic equation.

The set of any property values for each polymer configuration were then further averaged over the total number of samples generated to determine the mean value and the standard deviation from the mean employing the usual equations [12]

Results

Table I presents the simulation results for all the systems studied. The number in parenthesis denotes one standard deviation in the last

displayed digits. The 95% confidence interval is about twice these reported error bars. It is clear from the data that for a given number of units N , ring polymers, as expected, are much more compact than linear chains.

Weighted nonlinear least-squares fits [12] to the $\langle S^2 \rangle$ data in Table I gave exponent values of 0.97 ± 0.01 and 0.99 ± 0.01 for the linear and ring polymers, respectively. These empirical exponents are in reasonable agreement with the ideal value of 1.00.

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 [12] relating the error in a ratio to the error in the numerator and the error in the denominator. The simulation g -ratios are listed in Table II. The number in parenthesis denotes one standard deviation in the last displayed digits.

These simulation results are for finite N whereas the theoretical equations are for infinite N . To determine the value of g as N approaches infinity, we plot 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 -ratio is found to be 0.522 ± 0.010 compared to the theoretical prediction of 0.500. The computer result is slightly outside the 95% confidence interval.

Table I The Simulation Data.

		Linear			Ring	
N	$\langle S^2 \rangle$	A	$\langle A \rangle$	$\langle S^2 \rangle$	A	$\langle A \rangle$
64	10.64(17)	0.505(30)	0.382(6)	5.51(6)	0.290(13)	0.242(4)
128	21.71(34)	0.505(30)	0.387(6)	11.10(13)	0.286(13)	0.244(4)
195	32.47(51)	0.509(31)	0.384(6)	16.94(19)	0.295(13)	0.249(4)
284	45.84(74)	0.507(34)	0.374(6)	24.01(28)	0.297(15)	0.244(4)

Table II Simulation g-ratios.

N	g-ratio
64	0.518(11)
128	0.511(10)
195	0.522(10)
284	0.524(10)

The simulation results for A and $\langle A \rangle$ in Table I show, as expected, that the asphericity of ring polymers is substantively lower than the linear chains; e.g. the rings are much more sphere-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 give $A = 0.508 \pm 0.032$ and $\langle A \rangle = 0.379 \pm 0.006$ for linear chains and $A = 0.296 \pm 0.014$ and $\langle A \rangle = 0.248 \pm 0.004$ for rings. The known values for linear chains are 0.526 [13] and 0.394 [13]. The corresponding values for rings are 0.294 [13] and 0.246 [13]. Both linear and ring results are in reasonable agreement with the theoretical values. That the ring values are in better agreement with the predictions reflects the fact that the rings have, because of the connectivity constraint, reached their asymptotic large N value earlier than the linear polymers.

The form factor has also been computed by averaging over the angles between \mathbf{k} and

$\mathbf{R}_n - \mathbf{R}_m$ in Eq. 5 to give [11]

$$S(k) = \frac{1}{N^2} \sum_{m,n} \langle \frac{\sin(k(R_n - R_m))}{k(R_n - R_m)} \rangle \quad (10)$$

The results are presented in Figure 1. The reciprocal of the form factor is plotted to emphasize differences at higher k values (smaller distances). Note that Eqs. 6 and 7 give the relationship between x and k . The Brownian dynamics results for both ideal linear and ring polymers are in fine agreement with the equations which have been derived for infinite N . At low x values (large distances) there is essentially no difference in the form factors of the two polymers. However, at large x (small distance) the detailed polymer structure has a significant effect.

Conclusion

Brownian dynamics has been used to generate linear and ring polymer configurations. The mean-square radius of gyration has been determined for different values of N . It is found that the data obey the expected power law with a power nearly equal to 1.00. The g -ratio has an extrapolated value which is in reasonable agreement with the Zimm-Stockmayer

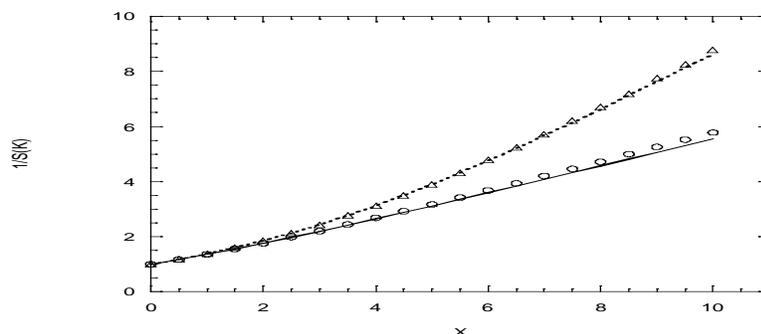


Figure 1: The reciprocal of the form factor, $S(K)$, vs X . The solid and dotted lines are the theoretical Debye and Casassa predictions for linear and ring polymers, respectively, whereas the circles and triangles are the corresponding simulation results when $N = 284$.

theoretical prediction [7]. In addition, the asphericity and the form factors are also in good agreement with the theoretical results. 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.

Appendix: The Manhattan College Undergraduate Research Program

Manhattan College has a long tradition of involving undergraduates in research and was one of the original members of the Oberlin 50. This is a group of undergraduate institutions whose students have produced many Ph.D.s in engineering and science. At Manhattan College, students can elect to take an independent study course for 3 credits during the academic year. In addition, the College provides grant support to the students for 10 weeks of work during the summer. I have personally recruited the students from my junior level course in Systems Programming. Previously published articles in this journal by Manhattan College student co-authors are a very effective recruitment tool. The students have also presented their results at a variety of undergraduate research conferences including the Hudson River Undergraduate Mathematics Conference and the Spuyten Duyvil Undergraduate Mathematics Conference.

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Biographical Information

Brian T. Merriman was an undergraduate student in the computer science program at Manhattan College. He completed a B.S. in computer science at Manhattan College in 2011.

Marvin Bishop is a Professor in the Department of Mathematics and Computer Science at Manhattan College. He received his PhD from Columbia University, his M.S. from New York University and his B.S. from City College of New York. His research interests include simulation and modeling and parallel processing.