

MONTE CARLO STUDIES OF IDEAL THREE DIMENSIONAL LINEAR POLYMERS

Gregory Zajac and Marvin Bishop
Departments of Computer Science and Mathematics
Manhattan College

Abstract

Computer modeling is an important skill for engineering and science students to acquire. Monte Carlo simulations of ideal three dimensional polymers provide an opportunity for students to develop their computer skills while deepening their knowledge of the behavior of such materials.

Introduction

In a previous publication in this journal, Varriale II and Bishop [1] used a Monte Carlo growth method to simulate two dimensional ideal linear and star polymers. They computed polymer properties such as the mean-square radius of gyration, $\langle S^2 \rangle$, and the mean asphericity, $\langle A \rangle$, of both linear and star polymers and found excellent agreement with theoretical values. Perrelli and Bishop [2] extended this simulation method to investigate ideal two dimensional H-comb polymers and found similar good agreement with theoretical predictions. In this work, the Monte Carlo growth method is used to examine ideal linear polymers in three dimensions. A wide variety of properties are computed and compared to theoretical predictions.

Method

The program has been written using a procedural approach. Three dimensional polymers are constructed on an integer coordinate system. Given the numbers N and M, the simulation is performed by creating M independent samples each containing N units (beads). Samples are constructed by starting the first bead at the origin (0, 0, 0). Subsequent beads are placed by randomly selecting one of six possible directions: North, South, East,

West, Up, or Down. Each bead is placed one unit apart from the previously placed bead. In this study of ideal polymers, a location that has already been used by another bead is allowed to be chosen so that beads can overlap. After each polymer is completely constructed, a number of properties are computed for that configuration.

One important property of polymers is their shape, which can be determined from the matrix representation of the radius of gyration tensor,

\leftrightarrow
T. This is a 3 by 3 symmetric tensor with nine components but only six are unique. It can be written as

$$T^{ab}(k) = (1/N) \sum_{i=1}^N [Q_i^a(k) - Q^a CM_i(k)] * [Q_i^b(k) - Q^b CM_i(k)] ; a, b = X, Y, or Z \quad (1)$$

Here, $Q_i(k)$ represents the X, Y, or Z components of the location of the i-th bead in the k-th sample and $QCM_i(k)$ represents the corresponding center of mass:

$$QCM_i(k) = (1/N) \sum_{i=1}^N Q_i(k) . \quad (2)$$

\leftrightarrow
The eigenvalues of T, λ_1 , λ_2 , and λ_3 , are the components of the radius of gyration along the principal orthogonal axes [3]. They are determined for a given sample by using the Cardano-Vieta solution to the cubic characteristic equation. The λ values of each configuration can be ordered by magnitude. One can envision [4] the polymer as enclosed in an

ellipsoidal envelope with semi-major axis λ_1 and semi-minor axes λ_2 and λ_3 . Rudnick and Gaspari [3] defined the asphericity of the k-th sample of a configuration, $A(k)$, in three dimensions as

$$A(k) = [(\lambda_1 - \lambda_2)^2 + (\lambda_1 - \lambda_3)^2 + (\lambda_2 - \lambda_3)^2] / [2(\lambda_1 + \lambda_2 + \lambda_3)^2] \quad (3)$$

The asphericity ranges from a value of 0 when $\lambda_1 = \lambda_2 = \lambda_3$ and the polymer has the shape of a perfect sphere, to 1 when $\lambda_2 = \lambda_3 = 0$ and the polymer has the shape of a straight rod.

The overall size of a polymer is characterized by its radius of gyration and, in the special case of a linear chain, by its end-to-end distance. The squared radius of gyration of the k-th sample, $S^2(k)$, is equal to the sum of the diagonal elements of the radius of gyration tensor,

$$S^2(k) = \lambda_1 + \lambda_2 + \lambda_3 \quad , \quad (4)$$

and the squared end-to-end distance of the k-th sample of linear chains, $R^2(k)$, is

$$R^2(k) = (X_N - X_1)^2 + (Y_N - Y_1)^2 + (Z_N - Z_1)^2 \quad . \quad (5)$$

Here N and 1 refer to the last and first bead, respectively.

It is well-known [5] that for large polymers, both $\langle R^2 \rangle$ and $\langle S^2 \rangle$ follow scaling laws:

$$\langle R^2 \rangle = C_1 (N - 1)^{2\nu} \quad , \quad (6a)$$

and

$$\langle S^2 \rangle = C_2 (N - 1)^{2\nu} \quad . \quad (6b)$$

The coefficients, C_1 and C_2 , are model dependent amplitudes but the exponent, 2ν , is universal and equal to 1.0 for ideal polymers. It is also well-known [5] that $\langle S^2 \rangle / \langle R^2 \rangle = 1/6$ for long ideal linear chains.

Results

The simulation has been developed using the Visual Studio C++ compiler on a PC. All the runs for $N = 100, 150, 200, 250$ and 300 in Tables IA and IB employed 10,000 samples. The program averages the data over all the samples. Since the polymer generation process provides independent samples, the mean and standard deviation of the mean of general properties can be computed from the usual simple equations [6], but more care is needed in computing the errors of the ratios. In these tables the number in parenthesis denotes one standard deviation in the last displayed digit; for example, $\langle \lambda_1 \rangle = 12.86(8)$ means that $\langle \lambda_1 \rangle = 12.86 \pm 0.08$.

Table IA: General Properties.

Property	100	150	200	250	300
$\langle \lambda_1 \rangle$	12.86(8)	19.12(12)	25.71(16)	31.84(20)	38.45(24)
$\langle \lambda_2 \rangle$	2.88(1)	4.32(2)	5.74(3)	7.19(4)	8.61(4)
$\langle \lambda_3 \rangle$	1.07(1)	1.60(1)	2.14(1)	2.66(1)	3.20(1)
$\langle S^2 \rangle$	16.81(9)	25.03(13)	33.60(17)	41.69(21)	50.26(26)
$\langle R^2 \rangle$	99.75(81)	149.19(122)	200.79(162)	250.98(204)	302.45(250)
$\langle A \rangle$	0.395(2)	0.394(2)	0.395(2)	0.393(2)	0.395(2)

Table IB: Ratio Properties.

Property	100	150	200	250	300
$\langle \lambda_1 \rangle / \langle S^2 \rangle$	0.765(1)	0.764(1)	0.765(1)	0.764(1)	0.765(1)
$\langle \lambda_2 \rangle / \langle S^2 \rangle$	0.171(1)	0.172(1)	0.171(1)	0.173(1)	0.171(1)
$\langle \lambda_3 \rangle / \langle S^2 \rangle$	0.064(1)	0.064(1)	0.064(1)	0.064(1)	0.064(1)
$\langle S^2 \rangle / \langle R^2 \rangle$	0.169(1)	0.168(1)	0.167(1)	0.166(1)	0.166(1)
$\langle R^2 \rangle / \langle R^2 \rangle^2$	1.175(2)	1.180(3)	1.177(2)	1.180(3)	1.181(3)
$\langle R^4 \rangle / \langle R^2 \rangle^2$	1.657(12)	1.667(12)	1.653(11)	1.662(11)	1.682(12)
$\langle R^6 \rangle / \langle R^3 \rangle^2$	2.555(51)	2.550(42)	2.505(38)	2.530(41)	2.616(41)
$\langle R^6 \rangle / \langle R^2 \rangle^3$	3.838(95)	3.853(81)	3.761(74)	3.818(79)	3.977(82)
$\langle R^8 \rangle / \langle R^4 \rangle^2$	4.184(327)	4.064(265)	3.938(239)	4.010(256)	4.235(265)
$\langle R^8 \rangle / \langle R^2 \rangle^4$	11.494(700)	11.291(512)	10.762(433)	11.082(490)	11.988(484)

The $\langle S^2 \rangle$ and $\langle R^2 \rangle$ data in Table IA were fit by a weighted nonlinear least-squares program [6] to determine the exponent in the scaling laws, Eqs.6a and 6b. It was found that 2ν had the value of 0.99 ± 0.01 for $\langle S^2 \rangle$ and 1.00 ± 0.01 for $\langle R^2 \rangle$. These results are consistent with the theoretical value of 1.00.

The computer results in the Tables are for finite N whereas the theoretical results are for infinite N. Another scaling law for any property Pr is

$$Pr = Pr_\infty (1 - K / N^\Delta) \quad (7)$$

Here Pr_∞ is the value of Pr for infinite N, K is a constant, and Δ is the finite scaling exponent. In the ideal polymer regime Δ has a value of 1.0. The Pr_∞ value can thus be found by fitting a weighted least-squares line [6] in $1/N$ to each set of data in the Tables.

The error in ratio calculations involving the division of separately averaged quantities which might be correlated has been determined by employing the equation derived by Bishop and Clarke [7]. They related the error in a ratio to the separate errors in the numerator and in the denominator. If the ratio is given as $Z = \langle X \rangle / \langle Y \rangle^P$, where P is any power, the

standard deviation of the mean of Z, $\sigma_{\langle Z \rangle}$, is determined by the standard deviations of the mean of $\langle X \rangle$ and the mean of $\langle Y \rangle$, $\sigma_{\langle X \rangle}$ and $\sigma_{\langle Y \rangle}$, respectively.

$$\sigma_{\langle Z \rangle} = Z [(\sigma_{\langle X \rangle} / \langle X \rangle)^2 + P^2 (\sigma_{\langle Y \rangle} / \langle Y \rangle)^2 - 2P \text{covar}(\langle X \rangle, \langle Y \rangle) / (\langle X \rangle \langle Y \rangle)]^{1/2} \quad (8)$$

Here, $\text{covar}(\langle X \rangle, \langle Y \rangle)$ is the covariance of $\langle X \rangle$ and $\langle Y \rangle$. It is defined by

$$\text{covar}(\langle X \rangle, \langle Y \rangle) = (\langle XY \rangle - \langle X \rangle \langle Y \rangle) / (M - 1) \quad (9)$$

The various ratio values and their errors were determined from Eqs. 8 and 9. Note that the ratios involve the quotient of averaged quantities rather than the average of the quotient. The results appear in Table IB. Then the best linear fit was extrapolated in $1/N$ to 0 (e.g. $N \rightarrow \infty$). The final extrapolated values are presented in Table II along with known results. Most of the simulation values reported in Table II are well within two standard deviations of the mean or in the 95% confidence interval. The error bars for the end-to-end distance moments grow larger as the exponent of the moment increases because of the large numerical values present in the quotient.

Table II: Comparison of Simulation and Literature Results.

Property	Extrapolated	Literature
$\langle \lambda_1 \rangle / \langle S^2 \rangle$	0.764(1)	0.7646(5)[a]
$\langle \lambda_2 \rangle / \langle S^2 \rangle$	0.172(1)	0.1721(1)[a]
$\langle \lambda_3 \rangle / \langle S^2 \rangle$	0.064(1)	0.06333(5)[a]
$\langle A \rangle$	0.394(2)	0.394[b]
$\langle S^2 \rangle / \langle R^2 \rangle$	0.164(1)	0.167[c]
$\langle R^2 \rangle / \langle R \rangle^2$	1.182(3)	1.178[d]
$\langle R^4 \rangle / \langle R^2 \rangle^2$	1.675(14)	1.667[d]
$\langle R^6 \rangle / \langle R^3 \rangle^2$	2.568(52)	2.577[d]
$\langle R^6 \rangle / \langle R^2 \rangle^3$	3.892(100)	3.889[d]
$\langle R^8 \rangle / \langle R^4 \rangle^2$	4.034(330)	4.200[d]
$\langle R^8 \rangle / \langle R^2 \rangle^4$	11.409(644)	11.667[d]

[a] reference 8 [b] reference 9 [c] reference 5 [d] reference 7

Solc [10] also simulated ideal linear polymers in three dimensions. He found that $\langle \lambda_1 \rangle$, $\langle \lambda_2 \rangle$ and $\langle \lambda_3 \rangle$ were in the ratio of 11.8:2.69:1.00. Our ratio of 11.9:2.69:1.00 is in fine agreement with his results.

Conclusion

We have investigated three dimensional ideal linear polymers using a Monte Carlo growth method. Many different properties have been computed. There is fine agreement with theoretical results and other simulations. Modeling projects such as the one described here provide a clear demonstration of some aspects of polymers and thus strongly enhance student understanding and intuition.

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 PhDs in engineering and science. At Manhattan College,

students can elect to take an independent study course for three credits during the academic year. In addition, the College provides grant support to the students for ten 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

Gregory Zajac is currently a student in mathematics with a minor in computer science at Manhattan College.

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