MONTE CARLO STUDIES OF IDEAL TWO DIMENSIONAL LINEAR POLYMERS

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Abstract

Monte Carlo computer simulation is a useful tool for exploring the properties of ideal two dimensional linear polymers. Monte Carlo simulations provide an opportunity for students to develop their computer skills while deepening their knowledge of the behavior of polymers. The current simulations are in excellent agreement with theoretical predictions.

Introduction

In a previous publication in this journal, Zajac and Bishop [1] employed a Monte Carlo growth method to simulate three dimensional ideal linear polymers. They computed many different polymer properties such as the mean-square radius of gyration, $<S^2>$ and the mean asphericity, $<A>$, and found excellent agreement with theoretical values. In this work, their Monte Carlo growth method is used to examine ideal linear polymers in two dimensions. A wide variety of properties are computed and compared to theoretical predictions.

Method

Two 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). Two kinds of lattices were studied: a square lattice and a triangular lattice. In both lattices polymer samples are constructed by starting the first bead at the origin (0, 0). In the case of the square lattice subsequent beads are placed by randomly selecting one of four possible directions: North, South, East, or West, whereas in the case of the triangular lattice one of the following six possible directions is chosen: Northeast, East, Southeast, Southwest, West and Northwest. 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 calculated 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, $\overleftrightarrow{T}$. This is a 2 by 2 symmetric tensor with four components but only three are unique. It can be written as

$$T^{ab}(k) = (1/N) \sum_{i=1}^{N}(Q^a_i(k) - Q^aCM_i(k)) *$$

$$(Q^b_i(k) - Q^bCM_i(k)) ; \quad a, b = X \text{ or } Y \quad (1)$$

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

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

The eigenvalues of $\overleftrightarrow{T}$, λ_1 and λ_2, are the components of the radius of gyration along the principal orthogonal axes [2]. They are determined for a given polymer sample by using the standard solution to the quadratic characteristic equation. The λ values of each configuration can be ordered by magnitude. One

can envision [3] the polymer as enclosed in an elliptical envelope with semi-major axis λ_1 and semi-minor axis λ_2. Rudnick and Gaspari [2] defined the asphericity of the k-th sample of a configuration, A(k), in two dimensions as

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

The asphericity ranges from a value of 0 when $\lambda_1 = \lambda_2$ and the polymer has the shape of a perfect circle, to 1 when $\lambda_2 = 0$ 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,

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

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

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

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

It is well-known [4] that for large polymers, both $<R^2>$ and $<S^2>$ follow scaling laws:

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

and

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

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 [4] that $<S^2> / <R^2> = 1/6$ for infinitely long ideal linear chains. These universal quantities are independent of dimension for ideal chains.

Results

The simulations have been programmed using the gcc C compiler on a Linux machine. All the runs for N = 1001, 1501, 2001 and 2501 employed M = 160,000 polymer samples. The program averages the data over all the samples. Since the polymer growth generation process provides independent samples, the mean and standard deviation of the mean of general properties can be computed from the usual simple equations [5] but more care is needed in computing the errors of the ratios. In all the tables the number in parenthesis denotes one standard deviation in the last displayed digit; for example, $<\lambda_1> = 138.96(26)$ means that $<\lambda_1> = 138.96 \pm 0.26$.

The $<S^2>$ and $<R^2>$ data in Tables IA and IIA were fit by a weighted nonlinear least-squares program [5] to determine the exponent in the scaling laws, Eqs.6a and 6b. It was found that 2ν had the value of 1.00 ± 0.01 for $<S^2>$ and 1.01 ± 0.01 for $<R^2>$ on a square lattice and 1.00 ± 0.01 for $<S^2>$ and 1.00 ± 0.01 for $<R^2>$ on a triangular lattice. These results are in excellent agreement 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 P is

$$P = P_\infty (1 - K / N^\Delta) . \quad (7)$$

Here P_∞ is the value of P 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 P_∞ value can thus be found by fitting a weighted least-squares line [5] 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 equations derived by Bishop and

Clarke [6]. They related the error in a ratio, to the separate errors in the numerator and in the denominator. See Zajac and Bishop [1] for the detailed equations.

The ratio results appear in Tables IB and IIB. Then the best linear fit was extrapolated in 1/N to 0 (e.g. N → ∞). The final extrapolated values are presented in Table III along with known theoretical results. All of the simulation values reported in Table III 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 IA: General Properties as a function of N: Square Lattice.

Property	1001	1501	2001	2501
$\langle\lambda_1\rangle$	138.96(26)	207.69(38)	278.05(51)	347.45(63)
$\langle\lambda_2\rangle$	27.75(4)	41.70(6)	55.670(8)	69.50(10)
$\langle S^2\rangle$	166.71(27)	249.39(40)	333.72(53)	416.95(66)
$\langle R^2\rangle$	997.33(251)	1491.43(374)	2001.24(501)	2502.84(626)
$\langle A\rangle$	0.397(1)	0.396(1)	0.397(1)	0.397(1)

Table IB: Ratio Properties as a function of N: Square Lattice.

Property	1001	1501	2001	2501
$\langle\lambda_1\rangle/\langle S^2\rangle$	0.834(1)	0.833(1)	0.833(1)	0.833(1)
$\langle\lambda_2\rangle/\langle S^2\rangle$	0.166(1)	0.167(1)	0.167(1)	0.167(1)
$\langle S^2\rangle/\langle R^2\rangle$	0.167(1)	0.167(1)	0.167(1)	0.167(1)
$\langle R^2\rangle/\langle R\rangle^2$	1.275(1)	1.274(1)	1.273(1)	1.273(1)
$\langle R^4\rangle/\langle R^2\rangle^2$	2.010(5)	2.006(5)	2.003(5)	2.002(5)
$\langle R^6\rangle/\langle R^3\rangle^2$	3.429(21)	3.411(21)	3.419(25)	3.419(25)
$\langle R^6\rangle/\langle R^2\rangle^3$	6.083(48)	6.043(47)	6.047(53)	6.043(54)
$\langle R^8\rangle/\langle R^4\rangle^2$	6.087(139)	6.026(138)	6.132(173)	6.138(181)
$\langle R^8\rangle/\langle R^2\rangle^4$	24.588(419)	24.243(422)	24.604(581)	24.606(619)

Table IIA: General Properties as a function of N: Triangular Lattice.

Property	1001	1501	2001	2501
$\langle\lambda_1\rangle$	138.94(25)	208.27(38)	278.55(51)	348.69(64)
$\langle\lambda_2\rangle$	27.87(4)	41.86(6)	55.74(8)	69.76(10)
$\langle S^2\rangle$	166.81(26)	250.13(40)	334.29(53)	418.45(66)
$\langle R^2\rangle$	1001.12(251)	1497.19(376)	2005.49(501)	2506.91(630)
$\langle A\rangle$	0.396(1)	0.396(1)	0.397(1)	0.397(1)

Table IIB: Ratio Properties as a function of N: Triangular Lattice.

Property	1001	1501	2001	2501
$\langle\lambda_1\rangle/\langle S^2\rangle$	0.833(1)	0.833(1)	0.833(1)	0.833(1)
$\langle\lambda_2\rangle/\langle S^2\rangle$	0.167(1)	0.167(1)	0.167(1)	0.167(1)
$\langle S^2\rangle/\langle R^2\rangle$	0.167(1)	0.167(1)	0.167(1)	0.167(1)
$\langle R^2\rangle/\langle R\rangle^2$	1.272(1)	1.274(1)	1.274(1)	1.275(1)
$\langle R^4\rangle/\langle R^2\rangle^2$	2.003(5)	2.008(5)	1.999(5)	2.012(5)
$\langle R^6\rangle/\langle R^3\rangle^2$	3.423(21)	3.437(24)	3.391(24)	3.443(21)
$\langle R^6\rangle/\langle R^2\rangle^3$	6.051(47)	6.092(53)	5.992(52)	6.111(48)
$\langle R^8\rangle/\langle R^4\rangle^2$	6.095(139)	6.179(163)	6.037(162)	6.139(140)
$\langle R^8\rangle/\langle R^2\rangle^4$	24.452(418)	24.922(532)	24.124(533)	24.850(422)

Table III: Comparison of Simulation and Literature Results.

Property	Square Lattice Extrapolated	Triangular Lattice Extrapolated	Literature
$\langle\lambda_1\rangle/\langle S^2\rangle$	0.832(2)	0.833(2)	0.832938[a]
$\langle\lambda_2\rangle/\langle S^2\rangle$	0.168(2)	0.167(2)	0.167062[a]
$\langle A\rangle$	0.397(2)	0.398(2)	0.3964[b]
$\langle S^2\rangle/\langle R^2\rangle$	0.167(2)	0.167(2)	0.1667[c]
$\langle R^2\rangle/\langle R\rangle^2$	1.272(2)	1.277(2)	1.273[d]
$\langle R^4\rangle/\langle R^2\rangle^2$	2.004(8)	2.010(8)	2.000[d]
$\langle R^6\rangle/\langle R^3\rangle^2$	3.416(48)	3.429(32)	3.395[d]
$\langle R^6\rangle/\langle R^2\rangle^3$	6.010(78)	6.084(73)	6.000[d]
$\langle R^8\rangle/\langle R^4\rangle^2$	6.138(245)	6.124(216)	6.000[d]
$\langle R^8\rangle/\langle R^2\rangle^4$	24.433(798)	24.820(661)	24.000[d]

[a] reference 7 [b] reference 8 [c] reference 4 [d] reference 6.

Conclusion

We have investigated two dimensional ideal linear polymers using a Monte Carlo growth method on both a square and a triangular lattice. Many different properties have been computed. There is excellent agreement with theoretical results. 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.

Acknowledgements

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Biographical Information

Adam J. Barillas and Tylor Borgeson are currently students majoring 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 and parallel processing.