MONTE CARLO STUDIES OF LINEAR SELF-AVOIDING WALK POLYMERS

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Abstract

Self-avoiding walks are a more realistic model of polymers than random walks. This paper explores the properties of such walks by employing Monte Carlo computer simulations. The ability to construct such models and to develop a computer simulation are important skills for engineering and science students to acquire.

Introduction

In a previous publication in this journal, Zajac and Bishop [1] used a Monte Carlo (MC) growth method to simulate three dimensional ideal linear N "bead" polymers. They computed a variety of properties such as the mean-square radius of gyration, $\langle S^2 \rangle$, its components along the principal orthogonal axes [2], λ_1, λ_2, and λ_3, the mean-square end-to-end distance, $\langle R^2 \rangle$, and the mean asphericity, $\langle A \rangle$. They found excellent agreement with theoretical values. In this work, their MC growth method on a simple cubic lattice is extended to examine self-avoiding walk linear polymers. A wide variety of properties are computed and compared to theoretical predictions.

Method

The self-avoiding walk growth algorithm utilizes portions of the ideal linear polymer growth algorithm described in Zajac and Bishop [1], with major modifications to account for the self-avoidance condition. The first polymer bead is placed at the origin (0, 0, 0) of a simple cubic lattice. The second bead is randomly placed in any of the six possible lattice site locations.

Then a new random number is used to select the possible location where the third bead could be placed. However, before allowing that bead to be put at the new location, a test is made to ensure that another bead is not already occupying that lattice site. This procedure grows a non-intersecting chain and is continued until N beads have been successfully placed. Each bead is placed one unit apart from the previously placed bead. If at any time in the process the chain intersects itself, it is erased and a new chain is started. After each polymer is completely constructed, a number of properties are calculated for that configuration, as was done in Zajac and Bishop [1]. The process is continued until M independent samples have been created.

It becomes increasingly difficult to grow chains using this direct static sampling Monte Carlo method [3]. Indeed, the probability of obtaining a chain with N beads decreases exponentially:

$$\text{Prob} = C\, e^{-\lambda N}. \qquad (1)$$

Here, C is the normalization coefficient and λ is the attrition constant. This has a theoretical value [3] of 0.248 for a simple cubic lattice. Figure 1 illustrates how the number of accepted chains decreases as a function of N. Fitting the four MC data points gives $C = 2.1799 \times 10^7$ and $\lambda = 0.24174$, which is in excellent agreement with the theoretical prediction.

Figure 2 presents a typical configuration of a 35-bead chain. The points mark the lattice sites and the lines mark the lattice edges.

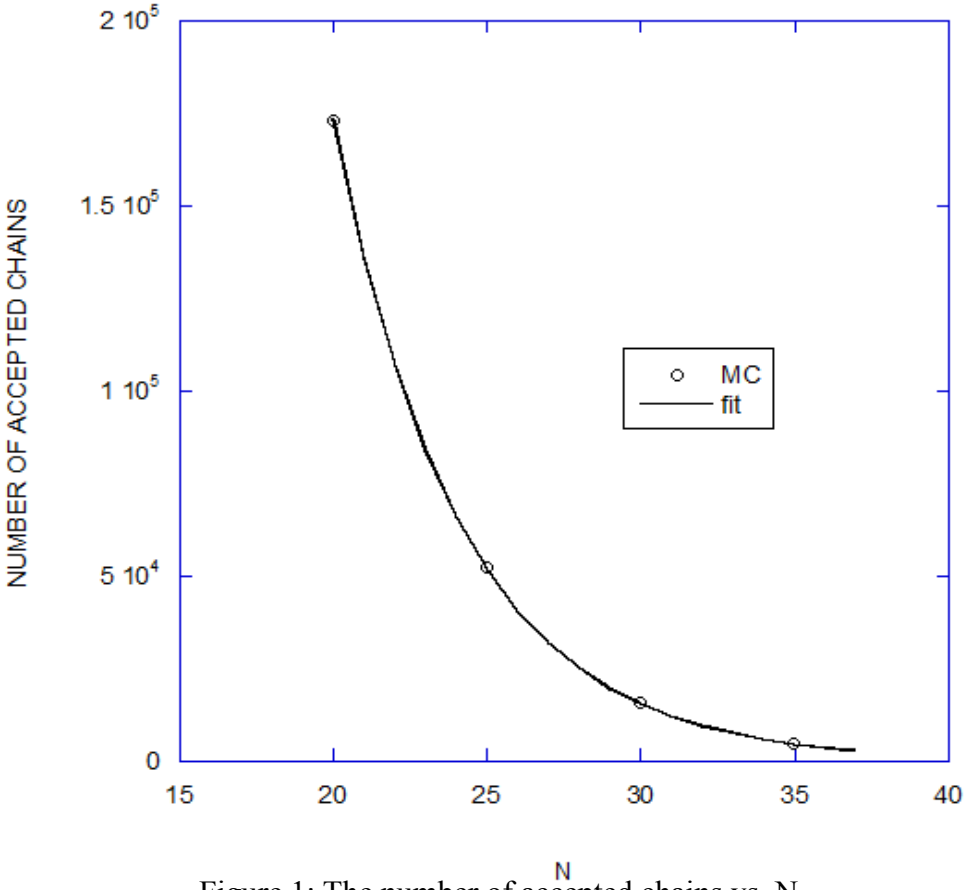

Figure 1: The number of accepted chains vs. N.
The circles indicate the MC results and the solid line the exponential fit.

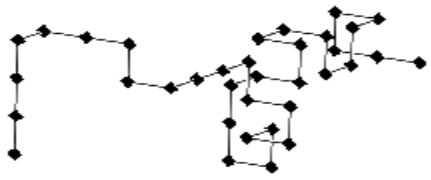

Figure 2: A 35-bead chain.

Accurate values of the ratios of powers of the end-to-end distances were not obtained for the self-avoiding walk polymers because of both the smaller number of samples generated, M, as N was increased and the limit on the value of N which can be examined with a MC growth algorithm. Since the self-avoiding walk polymers are more stretched out than the random walk ones, the magnitudes of the powers of the end-to-end distance are very large and the ratios are influenced by rounding and other similar numerical errors.

Results

The simulations were performed using the Linux C++ compiler. All the data for the runs when N = 20, 25, 30, and 35 are in Tables IA and IB. Since the polymer generation process provides M independent samples, the mean and standard deviation of the mean of general properties can be computed from the usual simple equations [4], but more care is needed in computing the errors of ratios [1]. In these tables the number in parenthesis denotes one standard deviation in the last displayed digit; for example $\langle\lambda_1\rangle$ = 4.56(1) means that $\langle\lambda_1\rangle = 4.56 \pm 0.01$.

The $\langle S^2\rangle$ and $\langle R^2\rangle$ data in Table IA were fit by a weighted nonlinear least-squares program [4] to determine the exponent in their scaling laws [5]. It was found that 2ν had the value of 1.18 ± 0.01 for $\langle S^2\rangle$ and 1.19 ± 0.01 for $\langle R^2\rangle$. These results are consistent with the theoretical value [6] of 1.176 and are larger than the known exponent [5] for random walk polymers, 1.00. The self-avoidance condition causes the chains to be expanded and therefore the exponent is expected to be larger. The computer results displayed in the tables are for finite N whereas the theoretical values are for infinite N. The data have been extrapolated in $1/N^{\Delta}$ to 0 (e.g. $N \rightarrow \infty$) via the method reported in Zajac and Bishop [1], but now the correction to scaling exponent, Δ , has a value of 0.47 [7] instead of the random walk value of 1.00. The final extrapolated values are presented in Table II along with known results. All of the simulation results reported in Table II are within two standard deviations of the mean, or in the 95% confidence interval, compared to literature values.

Table IA: General Properties.

Property	20	25	30	35
M	172880	51961	15413	4612
$\langle\lambda_1\rangle$	4.56(1)	6.01(1)	7.48(3)	9.07(7)
$\langle\lambda_2\rangle$	0.939(1)	1.24(1)	1.56(1)	1.88(1)
$\langle\lambda_3\rangle$	0.309(1)	0.409(1)	0.513(2)	0.627(4)
$\langle S^2\rangle$	5.81(1)	7.66(1)	9.55(3)	11.57(7)
$\langle R^2\rangle$	36.42(6)	48.26(14)	60.16(32)	72.87(71)
$\langle A\rangle$	0.446(1)	0.445(1)	0.441(2)	0.441(3)

Table IB: Ratio Properties.

Property	20	25	30	35
$\langle\lambda_1\rangle/\langle S^2\rangle$	0.785(1)	0.785(1)	0.783(1)	0.783(2)
$\langle\lambda_2\rangle/\langle S^2\rangle$	0.162(1)	0.161(1)	0.163(1)	0.162(1)
$\langle\lambda_3\rangle/\langle S^2\rangle$	0.053(1)	0.053(1)	0.054(1)	0.054(1)
$\langle S^2\rangle/\langle R^2\rangle$	0.160(1)	0.159(1)	0.159(1)	0.159(1)

Table II: Comparison of Extrapolated Simulations and Literature Results.

Property	Extrapolated	Literature
$\langle\lambda_1\rangle/\langle S^2\rangle$	0.775(6)	0.785[a]
$\langle\lambda_2\rangle/\langle S^2\rangle$	0.164(5)	0.162[a]
$\langle\lambda_3\rangle/\langle S^2\rangle$	0.058(5)	0.053[a]
$\langle A\rangle$	0.425(9)	0.429(2)[b]
$\langle S^2\rangle/\langle R^2\rangle$	0.156(5)	0.1603(8)[c]

(a) reference 8 (b) reference 9 (c) reference 10.

The results for shape factors, $\langle\lambda_1\rangle/\langle S^2\rangle$, $\langle\lambda_2\rangle/\langle S^2\rangle$, and $\langle\lambda_3\rangle/\langle S^2\rangle$, 0.775(6), 0.164(5), and 0.058(5), respectively are different than those for random walk polymers [1], 0.764(1), 0.172(1), and 0.064(1). This indicates that the self-avoiding chains are less spherical than random chains. In observing the shape factors in Table II, it is apparent that $\langle\lambda_1\rangle/\langle S^2\rangle$ has a larger value than the $\langle\lambda_1\rangle/\langle S^2\rangle$ value for a random chain [1]. Thus, the self-avoiding chain extends out further in one direction than a regular random chain. A self-avoiding chain has a more prolate (cigar-like) shape than a regular random chain. This occurs because a self-avoiding chain is unable to fold in on itself. It is important to note that a perfectly spherical chain would have shape factor values of 1/3, 1/3, and 1/3.

Conclusion

We have investigated three dimensional self-avoiding linear polymers on a lattice 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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References

1. G. Zajac and M. Bishop, "Monte Carlo Studies of Ideal Three Dimensional Linear Polymers", Comp. Educ. J., 5(4), 107 (2014).

2. J. Rudnick and G. Gaspari, "The Asphericity of Random Walks", J. Phys. A, 19, L191 (1986).

3. A.D. Sokal, in *Monte Carlo and Molecular Dynamics Simulations in Polymer Science*, ed. K. Binder, (Oxford University Press, New York, 1995).

4. P.R. Bevington, *Data Reduction and Error Analysis for the Physical Sciences*, (McGraw-Hill, New York, 1969).

5. P.G. de Gennes, *Scaling Concepts in Polymer Physics*, (Cornell University Press, Ithaca, 1979).

6. J.C. Le Guillou and J. Zinn-Justin, "Critical Exponents for the n-Vector Model in Three Dimensions from Field Theory", Phys. Rev. Lett., 39, 95 (1977).

7. J.C. Le Guillou and J. Zinn-Justin, "Critical Exponents from Field Theory", Phys. Rev. B, 21, 3976 (1980).

8. J. Mazur, C. Guttman and F. McCrackin, "Monte Carlo Studies of Self-Interacting Polymer Chains with Excluded Volume. II. Shape of a Chain", Macromolecules, 6, 872 (1973).

9. M. Bishop, J.H.R. Clarke, A. Rey and J.J. Freire, "The Shape of Linear and Star Polymers with and without Excluded Volume", J. Chem. Phys., 94, 4009 (1991).

10. N. Madras and A.D. Sokal, "The pivot algorithm: A highly efficient Monte Carlo method for the self-avoiding walk", J. Stat. Phys., 50, 109 (1988).

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