

MONTE CARLO SIMULATIONS OF IDEAL TWO DIMENSIONAL H-COMBS

Matthew J. Perrelli 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 two 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 linear and star polymers. They computed polymer properties such as the mean-square radius of gyration, $\langle S^2 \rangle$, the g-ratio and the mean asphericity, $\langle A \rangle$, of both linear and star polymers and found excellent agreement with theoretical values. In this paper their methods are extended to investigate H-combs. These are the simplest polymers containing two junctions.

Their structure has a central branch connecting the two junctions, each of which has two other branches connected to it. Thus, there are a total of five branches; one internal and four external (see Figure 1). Two dimensional H-comb polymers were also studied by Gorry and Bishop [2] employing a different Monte Carlo technique: the Pivot algorithm.

In Figure 1, E and F mark the two junctions and C, D, G, and H the branch ends of the H-comb; A and B mark the ends of the linear chain.

Method

The simulations investigated linear and H-comb polymers with the same total number of units. The programs have been written using a semi-object oriented approach. All the logic for individual polymer samples has been separated from the output and display logic. However, a

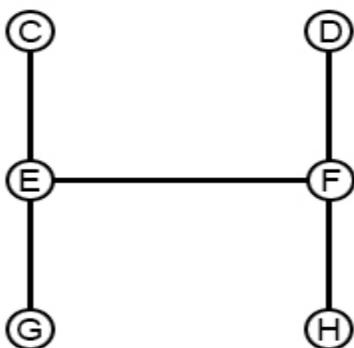


Figure 1A: H-comb polymer.



Figure 1B: Linear Polyme.

complete separation of all attributes would not be beneficial in the simulation process since the overhead of constructing and traversing all those objects would considerably lengthen the simulation times. Therefore, a single sample class holding all of the information for a given configuration of each polymer has been written.

Two dimensional polymers are constructed on an integer coordinate system and the different types of polymers follow the same basic rules. 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). Subsequent beads are placed by randomly selecting one of four possible directions: North, South, East or West. 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, or after all N beads have been added, a number of properties are calculated for that configuration.

To expand this project in order to investigate H-comb polymers, a number of changes had to be made to the sample logic. Since this type of polymer is no longer linear, growth has to occur on separate branches of the configuration. Branches are selected in a particular order and grown evenly. A coordinate data type has been implemented to keep track of the heads, or most recently added bead of each of the branches, so that they could be grown independently. An H-comb is constructed by first growing a three branch star polymer, i.e. a polymer with three random branches attached to a common junction. Then two more branches are added to one of the star branch ends.

The main routine uses all the calculated information to collect averages across many samples. Since the polymer generation process provides independent samples, the mean and standard deviation of the mean can be computed

from simple equations [3]. All the data items are saved on external files.

One important property of H-comb polymers is their shape which can be determined from the matrix representation of the radius of gyration

↔

tensor, T. This 2 by 2 tensor is given by

$$T_{11}(k) = \frac{1}{N} \sum_{i=1}^N (X_i(k) - X_{CM_i}(k))^2 \quad (1a)$$

$$T_{12}(k) = T_{21}(k) = \frac{1}{N} \sum_{i=1}^N (X_i(k) - X_{CM_i}(k)) (Y_i(k) - Y_{CM_i}(k)) \quad (1b)$$

$$T_{22}(k) = \frac{1}{N} \sum_{i=1}^N (Y_i(k) - Y_{CM_i}(k))^2 \quad (1c)$$

Here, $X_i(k)$ and $Y_i(k)$ are the x and y components of the location of the i-th bead in the k-th sample and $X_{CM_i}(k)$ and $Y_{CM_i}(k)$ are the x and y components of the center of mass:

$$X_{CM_i}(k) = \frac{1}{N} \sum_{i=1}^N X_i(k) \quad (2a)$$

$$Y_{CM_i}(k) = \frac{1}{N} \sum_{i=1}^N Y_i(k) \quad (2b)$$

↔

The eigenvalues of T, λ_1 and λ_2 , are the components of the radius of gyration along the principal orthogonal axes [4]. The λ values of each configuration can be ordered by magnitude. One can envision [5] the polymer as enclosed in an elliptical envelope with semi-

major axis λ_1 and semi-minor axis λ_2 . Rudnick and Gaspari [4] defined the asphericity of the k -th sample of a configuration 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 trace, 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 [6] that for large polymers, both $\langle R^2 \rangle$ and $\langle S^2 \rangle$ follow scaling laws.

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

and

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

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 [6] that $C_2 / C_1 = 1/6$ for long ideal linear chains.

A useful parameter for comparing the compactness of linear and branched polymers is the g -ratio which is defined as the ratio of the radii of gyration:

$$g = \langle S^2 \rangle_{\text{branched}} / \langle S^2 \rangle_{\text{linear}} \quad (7)$$

Casassa and Berry [7] obtained a general equation for the g -ratio of uniform, ideal comb polymers with f three-functional junctions regularly spaced along the backbone:

$$g = r - r^2 (1 - r) / (f + 1) + 2 r (1 - r)^2 / f + (3f - 2) (1 - r)^3 / f^2 \quad (8)$$

Here, r is the ratio of the number of units in the comb backbone to the total number of units in the polymer. In the case of H-combs (see Figure 1), $r = 3/5$ and $f = 2$, so $g = 0.712$.

Results

The simulation has been developed by using the Visual Studio C++ compiler on a PC. First, the dependence of average properties on the number of samples was investigated by examining polymers containing $N = 100$ beads. Runs generated 100, 1000, and 10000 samples. The data are contained in Table I. Note that there are no data for $\langle R^2 \rangle$ in the case of H-combs since there is no overall end-to-end distance

In Table I the number in parenthesis denotes one standard deviation in the last displayed digit so that for example, $\langle \lambda_1 \rangle = 13.28(98)$ means that $\langle \lambda_1 \rangle = 13.28 \pm 0.98$. As expected, the error decreases as the square root of the number of samples since the error in a property value decreases by a factor of about ten when using 10000 samples compared to the error value when using 100 samples. Also since there is only a slight difference in the property values

between 1000 and 10000 samples, 10000 samples should be sufficient for accuracies of about 1%.

Then, fixing the number of samples at 10000, the variation of the property values with the number of beads was studied. These results are contained in Tables IIA and IIB.

Table I: Effect of the Number of Samples, M, for Linear and H-comb Polymers.

Linear				H-comb		
Property	100	1000	10000	100	1000	10000
$\langle \lambda_1 \rangle$	13.28(98)	14.03(32)	14.06(10)	8.28(46)	9.56(18)	9.44(6)
$\langle \lambda_2 \rangle$	2.89(16)	2.80(5)	2.81(2)	2.55(14)	2.63(4)	2.64(1)
$\langle S^2 \rangle$	16.17(105)	16.83(33)	16.86(11)	10.83(52)	12.18(20)	12.08(6)
$\langle A \rangle$	0.375(22)	0.401(8)	0.396(2)	0.286(21)	0.308(7)	0.305(2)
$\langle R^2 \rangle$	97.04(859)	98.98(299)	100.48(101)			

Table IIA: Effect of the Number of Beads, N, for linear chains.

Property	100	200	400	800
$\langle \lambda_1 \rangle$	14.06(10)	27.72(20)	55.84(43)	112.08(89)
$\langle \lambda_2 \rangle$	2.81(2)	5.66(3)	11.34(6)	22.62(14)
$\langle R^2 \rangle$	100.48(101)	200.28(203)	411.17(438)	813.12(813)
$\langle S^2 \rangle$	16.86(11)	33.38(21)	67.18(45)	134.70(93)
$\langle A \rangle$	0.396(2)	0.386(2)	0.386(2)	0.390(2)

Table IIB: Effect of the Number of Beads, N, for H-combs.

Property	100	200	400	800
$\langle \lambda_1 \rangle$	9.44(6)	18.71(11)	36.99(23)	74.73(47)
$\langle \lambda_2 \rangle$	2.64(1)	5.15(3)	10.19(5)	20.61(10)
$\langle S^2 \rangle$	12.08(6)	23.87(12)	47.18(25)	95.34(50)
$\langle A \rangle$	0.305(2)	0.310(2)	0.311(2)	0.308(2)

It is clear from the radius of gyration data in the Tables that H-combs are more compact than linear chains with the same number of beads and that the shape of the H-combs is more symmetrical than the linear chains. The $\langle S^2 \rangle$ and $\langle R^2 \rangle$ data in the Tables were fit by a weighted nonlinear least-squares program [3] to determine the exponent in the scaling laws, Eqs.6a and 6b. It was found that 2ν in the linear

chain case was 1.00 ± 0.01 for $\langle S^2 \rangle$ and 1.00 ± 0.01 for $\langle R^2 \rangle$ and that $2\nu = 0.99 \pm 0.01$ for $\langle S^2 \rangle$ in H-combs. These values are all consistent with the theoretical value of 1.00.

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

$$P = P_{\infty}(1 - K / N^{\Delta}) \quad (9)$$

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 [3] in $1/N$ to each set of data in the Tables.

The error in ratio calculations, such as the g -ratio, which involves the division of separately averaged quantities, has been determined from the standard equation [3] relating the error in a ratio to the errors in the numerator and in the denominator. First, the various ratio values and their errors were determined. Then the best linear fit was extrapolated in $1/N$ to 0 (e.g. $N \rightarrow \infty$). The final extrapolated property values are presented in Table III along with known exact results. Most of the simulation values reported in Table III are well within two standard deviations of the mean or in the 95% confidence interval. Even in the worst case, the average asphericity for linear chains has about a 2% - 3% difference from the exact value.

Gorry and Bishop [2] also simulated ideal linear and H-comb polymers in two dimensions. Their work was not restricted to a fixed lattice. In their model the initial polymer configuration

was constructed by linking together tangent circular beads with a diameter of one. A random number was used to select one of the beads as a pivot and another random number was employed to generate a random angle between 0° and 360° . All the beads further along the branch of the pivot bead were rotated by this angle. In this model successive samples are not independent and it was necessary to both discard the beginning phase of the simulation and to collect data at sufficiently large intervals. Gorry and Bishop found for H-combs that the extrapolated g -ratio and asphericity had values of 0.713 ± 0.002 and 0.310 ± 0.001 , respectively. These results are in fine agreement with both the exact and the simulation values reported in Table III.

Conclusion

We have investigated two dimensional ideal linear and H-comb polymers using a Monte Carlo growth method. The radius of gyration, g -ratio, and asphericity have been computed. There is fine agreement with both exact results and other simulations. The data reveal that H-combs are more symmetrical than linear chains. 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.

Table III: Comparison of Results for Linear and H-comb Polymers.

Property	Linear		H-comb	
	Extrapolated	Exact	Extrapolated	Exact
$\langle \lambda_1 \rangle / \langle S^2 \rangle$	0.830(7)	0.833[a]	0.785(5)	0.784[d]
$\langle A \rangle$	0.385(2)	0.396[b]	0.311(2)	0.309[d]
g -ratio			0.704(5)	0.712[e]
C2/C1	0.164(2)	0.167[c]		

[a] reference 8 [b] reference 9 [c] reference 6 [d] reference 10 [e] reference 7

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

We wish to thank the Manhattan College Computer Center for providing time on their machines. We also wish to thank Professor Paula Whitlock for many useful conversations about Monte Carlo calculations.

References

1. R. Varriale II and M. Bishop, "Modeling and Simulation of Star Polymers in Two Dimensions", *Comp. Educ. J.*, XVII (3), 44 (2007).
2. D. Gorry and M. Bishop, "Modeling and Simulation of Two Dimensional H-Comb Polymers with the Pivot Algorithm", *Comp. Educ. J.*, XVIII (3), 95 (2008).
3. P. R. Bevington, *Data Reduction and Error Analysis for the Physical Sciences*, (McGraw-Hill, New York, 1969).

4. J. Rudnick and G. Gaspari, "The Asphericity of Random Walks", *J. Phys. A*, 19, L191 (1986).
5. A.M. Dunn and M. Bishop, "Modeling and Simulation of Two Dimensional Star Polymers with the Pivot Algorithm", *Comp. Educ. J.*, XVIII (1), 64 (2008).
6. P.G. de Gennes, *Scaling Concepts in Polymer Physics*, (Cornell University Press, Ithaca, 1979).
7. E.F. Casassa and G.C. Berry, "Angular distribution of Intensity of Rayleigh Scattering from Comblike Branched Molecules", *J. Poly. Sci., A-2*, 4, 881 (1966).
8. G. Wei, "Exact Shapes of Random Walks in Two Dimensions", *Physica A*, 222, 152 (1995).
9. G. Wei, "New Approaches to the Shapes of Arbitrary Random Walks", *Physica A*, 222, 155 (1995).
10. C. von Ferber, M. Bishop, T. Fozaglia and C. Reid, manuscript in preparation (2014).

Biographical Information

Matthew J. Perrelli is currently a student in the computer science program 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.