COMPUTER SIMULATION STUDY OF THE SHAPES OF THREE DIMENSIONAL STAR POLYMERS

Andrew M. Dunn, J. Yates Monteith and Marvin Bishop
Department of Mathematics/Computer Science
Manhattan College
Manhattan College Parkway
Riverdale, New York 10471

Abstract

Ideal and excluded volume tangent hard sphere linear and star polymers with three to six arms have been simulated in three dimensions by employing the Pivot algorithm. Properties such as the mean-square radius of gyration, the g ratio and the asphericity have been computed and compared to theoretical predictions and other computer simulations which used a variety of polymer models. Fine agreement is obtained for all the properties studied for ideal polymers and our simulations are consistent with the findings of other simulations of excluded volume polymers. The present theories are not sufficiently accurate in the case of excluded volume. These three dimensional simulations help students to develop insight into the molecular properties of polymeric materials.

Introduction

The ability to abstract and model the complex world of nature is a very valuable skill which should be taught to all engineering, mathematics and science students. One application area of simulation which requires students to combine knowledge from a variety of important fields is the modeling of polymeric materials. A student will need to connect information from chemistry, computer programming, statistics, algorithm development and graphics in order to construct and analyze polymer models. Such models have been examined in an independent studies simulation and modeling project at Manhattan College.

In a number of previous publications in this journal we have introduced some simple models of star polymers. The properties of these polymers have been explored with a large number of different experimental and theoretical methods [1]. Star polymers are of interest because they represent the simplest case of branching and yet have many applications [2]. One important property of such molecules is their shape [3]. Varriale and Bishop [4] studied the shapes of non-excluded volume (NEV) ideal star polymers by employing a growth algorithm and Dunn and Bishop [5] used the Pivot algorithm [6] to dynamically move parts of the NEV star polymer in their computer simulations. Both of these investigations were limited by being in two dimensions and by not allowing for the polymer units to interact. Real polymers exist in three dimensions and display excluded volume (EV) effects because units cannot pass through each other. NEV polymer systems allow this possibility and the units can even overlap. By introducing more realistic models, students are exposed to how complex features of the real world can be handled.

In this article we extend the simulations of Dunn and Bishop [5] to three dimensions and then modify their model to examine EV systems. In a star polymer there is a central bead which is connected to a number of linear branches. If m is the number of spherical beads in one linear branch of a star polymer containing f branches, the total number of beads in the star polymer, N, is given by

$$N = f\,m + 1 \qquad (1)$$

As in the earlier work a polymer's overall shape can be characterized by the mean-square radius of gyration, $\langle S^2 \rangle$, where $\langle\rangle$ denotes an average over the polymer configurations. It is well-known [7] that $\langle S^2 \rangle$ follows a scaling law

$$< S^2 > \approx (N - 1)^P \qquad (2)$$

in which the exponent, P, is a universal quantity. For NEV polymers, P = 1.00 in all dimensions whereas P is approximately 1.20 for EV polymers in three dimensions. The same P value is expected for both linear and star polymers.

The shapes of two different kinds of polymers can be compared by calculating separately the mean-square radius of gyration of a linear chain and a star polymer with the same number of units. The ratio of these quantities is called the g ratio.

$$g = <S^2>_{star} / <S^2>_{linear} \qquad (3)$$

Zimm and Stockmeyer [8] showed that NEV star polymers in any dimension have

$$g = (3 f - 2) / f^2 \qquad (4)$$

and Miyake and Freed [9] calculated g theoretically for EV systems.

The shapes of polymers can be examined in more detail by calculating the matrix representation of the tensor of components of the radius of gyration. The trace of this tensor, the sum of the diagonal elements $\lambda_1 + \lambda_2 + \lambda_3$, is equal to $<S^2>$ and the eigenvalues, λ_1, λ_2 and λ_3, are the components of the radius of gyration along the principal orthogonal axes [10]. Rudnick and Gaspari [11] defined the asphericity, A, of a polymer as

$$A = \frac{< \sum_{i>j}^{3} (\lambda_i - \lambda_j)^2 >}{< 2 \left(\sum_{i=1}^{3} \lambda_i \right)^2 >} \qquad (5a)$$

and the average asphericity, <A>, as

$$<A> = \frac{< \sum_{i>j}^{3} (\lambda_i - \lambda_j)^2 >}{2 < \left(\sum_{i=1}^{3} \lambda_i \right)^2 >} \qquad (5b)$$

Note that in these equations A involves a ratio of averages whereas <A> involves an average of a ratio.

The shape of a three dimensional polymer can vary from a fully extended rod in which λ_2 and λ_3 are essentially 0 so that A and <A> have a value of one, to a sphere for which $\lambda_1 = \lambda_2 = \lambda_3$. Then both A and <A> 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. Jagodzinski [12] obtained theoretical predictions of A and <A> for both NEV and EV polymers.

The goal of this project is to compute $<S^2>$, the g ratio, A and <A> calculated from Pivot computer simulations for linear and star polymers in three dimensions. Our results are then compared to both theoretical predictions and other simulation models.

Method

In the simulations the center of the first bead is always assigned the coordinates of the origin. The distance between two connected units is assumed to be a constant of magnitude one; i.e. adjacent beads are tangent. The polymers are started in a fixed configuration in which the arms are placed about the center bead so that they lie at equal angles from each other; e.g. when f = 3 the arms are set at 120º apart. Also the polymers are started in the X-Y plane. The beads are moved in continuous space by the Pivot algorithm [6]. First, a random number is used to select one of the beads as a "pivot" with coordinates (Xp,Yp,Zp). If it is an arm bead then all the higher indexed beads on that arm are rotated about the pivot bead according to three randomly chosen Euler angles: α, β, and γ. There are a number of different conventions in use concerning the Euler angles. Here, we first rotate the coordinate system (X,Y,Z) by an angle α about the z axis, then perform a second rotation by an angle β about the new y axis and

finally rotate by an angle γ about the new z axis. The matrix describing the total transformation is the matrix product of the three matrices describing one-single axis rotation [13]:

R = Rz(γ) Ry(β) Rz(α). The transformation equations for the coordinates (X',Y',Z') of the rotated beads are given by

$$X' = Xp + (X - Xp)(\cos\alpha \cos\beta \cos\gamma - \sin\alpha \sin\gamma) - (Y - Yp)(\cos\alpha \cos\beta \sin\gamma + \sin\alpha \cos\gamma) + (Z - Zp)\cos\alpha \sin\beta \quad (5a)$$

$$Y' = Yp + (X - Xp)(\sin\alpha \cos\beta \cos\gamma + \cos\alpha \sin\gamma) - (Y - Yp)(\sin\alpha \cos\beta \sin\gamma - \cos\alpha \cos\gamma) + (Z - Zp)\sin\alpha \sin\beta \quad (5b)$$

$$Z' = Zp - (X - Xp)\sin\beta \cos\gamma + (Y - Yp)\sin\beta \sin\gamma + (Z - Zp)\cos\beta \quad (5c)$$

This new trial configuration is accepted or rejected depending upon whether or not any beads overlap each other. If the center bead is selected as the pivot, another random number is employed to choose which entire arm is to be rotated about the center bead.

This process is continued for 5 X 10^6 moves but the first 1 X 10^6 moves are discarded before averaging begins. These discarded moves represent the equilibration of the initial arbitrary configuration. Data are collected at a spacing of 500 moves. The resulting random instantaneous snapshots of polymer configurations are used for analysis. In the NEV case all configurations are accepted but in the EV case only non overlapping moves are allowed. The fraction of EV accepted moves ranged from 0.13-0.18, depending upon N and f. To enhance the statistical quality of the data, sixteen different seeds were employed to generate sixteen independent trajectories. Production runs were performed on the eight processor Manhattan College parallel computer. We have employed the Maple software to visually track the changing configurations. A typical configuration for a four arm N = 41 EV star is presented in figure 1 using the Maple plottools library.

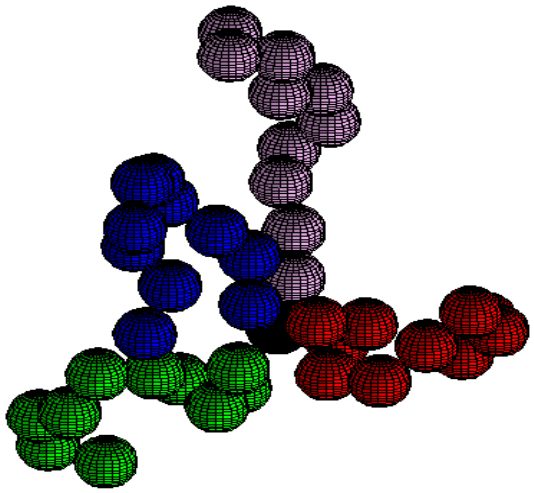

Figure 1: A four arm 41 bead EV star.

The square radius of gyration, S^2, for both the linear chain and the star polymer for the same total number of beads, N, were computed for each saved configuration as in the earlier work of Varriale and Bishop [4] and Dunn and Bishop[5]. This set of S^2 values were then further averaged over the total number of independent configurations saved to determine the mean-square radius of gyration, $\langle S^2 \rangle$, and its standard deviation from the mean, $\sigma_{\langle S^2 \rangle}$, employing the usual equations [14]. The eigenvalues of the matrix representation of the 3 X 3 radius of gyration tensor were determined by solving the resultant cubic equation. Individual A and <A> values were also averaged over the total number of independent samples generated to find their mean and error values.

Results

Table I presents the $\langle S^2 \rangle$ simulation results for all the systems studied. The number in parenthesis denotes one standard deviation in the last displayed digit. It is clear that the EV systems are quite expanded compared to the NEV polymers.

Table I Radius of Gyration Simulation Data

NEV

N	f = 2	f = 3	f = 4	f = 5	f = 6
61	10.17(1)	8.02(1)	6.54(1)	5.52(1)	4.79(1)
121	20.14(2)	15.78(1)	12.78(1)	10.72(1)	9.24(1)
181	30.17(4)	23.56(2)	19.02(2)	15.91(1)	13.69(1)
241	40.13(5)	31.36(3)	25.29(2)	21.13(1)	18.13(1)
301	50.25(6)	39.21(4)	31.56(2)	26.33(2)	22.59(1)

EV

N	f = 2	f = 3	f = 4	f = 5	f = 6
61	30.57(4)	22.87(2)	17.91(1)	14.64(1)	12.36(1)
121	71.58(7)	53.91(3)	42.37(4)	34.72(1)	29.34(1)
181	117.19(11)	88.66(7)	69.81(5)	57.28(4)	48.46(3)
241	166.24(19)	126.02(11)	99.30(5)	81.64(5)	69.09(3)
301	217.44(30)	164.92(18)	130.43(10)	107.25(5)	90.93(5)

Weighted nonlinear least-squares fits [14] to the $\langle S^2 \rangle$ data in Table I vs. the number of bonds, N - 1, gave the exponents reported in Table II. The number in parenthesis denotes one standard deviation in the last displayed digit The agreement of these empirical exponents with the expected NEV and EV values of 1.00 and 1.20, respectively, is good. Much longer chains would be needed to obtain higher accuracy.

Table II Power Law Fit for P.

f	NEV	EV
2	0.992(1)	1.22(1)
3	0.986(1)	1.23(1)
4	0.978(1)	1.23(1)
5	0.971(1)	1.24(1)
6	0.963(1)	1.24(1)

Table III Simulation g ratios

NEV

N	f = 3	f = 4	f = 5	f = 6
61	0.790 (1)	0.644 (1)	0.543 (1)	0.472(1)
121	0.784 (2)	0.635 (1)	0.533 (1)	0.459(1)
181	0.781 (1)	0.631 (1)	0.528 (1)	0.453(1)
241	0.779 (1)	0.630 (1)	0.525 (1)	0.451(1)
301	0.778 (2)	0.628 (1)	0.525 (1)	0.449(1)

EV

N	f = 3	f = 4	f = 5	f = 6
61	0.748 (1)	0.586 (1)	0.479 (1)	0.404(1)
121	0.753 (2)	0.592 (1)	0.485 (1)	0.410(1)
181	0.757 (1)	0.596 (1)	0.489 (1)	0.414(1)
241	0.758 (1)	0.597 (1)	0.491 (1)	0.416(1)
301	0.759 (2)	0.600 (1)	0.493 (1)	0.418(1)

The g ratios have been calculated from the radius of gyration data in Table I and the error has been computed from the standard equation [14] relating the error in a ratio A/B to the error in the numerator A and the error in the denominator B. The simulation g ratios are listed in Table III.

These computer results are for finite N whereas the theoretical findings are for infinite N. To determine the value of g as N approaches infinity, one plots g against 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. Table IV compares our NEV extrapolated values of g to the theoretical predictions [8] and our EV g values to the simulation results of other researchers [15, 16, 17] and the theoretical predictions [9]. In the NEV case there is excellent agreement with the theoretical predictions. In the EV case our simulation values for g are in good agreement with other simulations but the theoretical predictions are quite different. The disagreement with the computer simulations gets worse as the number of arms increases. This result is not unexpected since the theory is a first order one and does not properly account for the interactions as more and more arms cluster around the central core bead.

The simulation results for A and <A> are contained in Tables V and VI, respectively.

Table IV Comparison of g ratios to theoretical and other computer simulation results

NEV

f	Extrapolated	Theory [8]
3	0.776 (1)	0.778
4	0.624 (1)	0.625
5	0.520 (1)	0.520
6	0.444 (1)	0.444

EV

f	Extrapolated	Computer [15]	Computer [16]	Computer [17]	Theory [9]
3	0.761 (1)	0.76 (1)	0.766	0.768	0.798
4	0.601 (1)	0.60 (1)	0.611	0.613	0.667
5	0.495 (1)	0.51 (1)	0.508		0.580
6	0.419 (1)	0.43 (1)	0.439	0.435	0.519

Table V The ratio of the averages, A.

NEV

N	f = 2	f = 3	f = 4	f = 5	f = 6
61	0.522 (3)	0.355 (1)	0.267 (1)	0.212 (1)	0.176 (1)
121	0.523 (3)	0.357 (1)	0.270 (1)	0.216 (1)	0.179 (1)
181	0.525 (3)	0.359 (1)	0.270 (1)	0.217 (1)	0.180 (1)
241	0.527 (2)	0.360 (2)	0.272 (1)	0.218 (1)	0.181 (1)
301	0.526 (3)	0.360 (1)	0.271 (1)	0.218 (1)	0.182 (1)

EV

N	f = 2	f = 3	f = 4	f = 5	f= 6
61	0.565 (3)	0.329 (1)	0.216 (1)	0.151 (1)	0.111 (1)
121	0.558 (2)	0.334 (1)	0.226 (1)	0.163 (1)	0.124 (1)
181	0.556 (2)	0.337 (1)	0.229 (1)	0.169 (1)	0.129 (1)
241	0.554 (3)	0.338 (1)	0.232 (1)	0.172 (1)	0.133 (1)
301	0.553 (3)	0.340 (1)	0.234 (1)	0.174 (1)	0.135 (1)

Table VI The average of the ratio, <A>.

NEV

N	f = 2	f = 3	f = 4	f = 5	f = 6
61	0.391 (1)	0.301 (1)	0.239 (1)	0.196 (1)	0.166 (1)
121	0.392 (1)	0.303 (1)	0.241 (1)	0.198 (1)	0.168 (1)
181	0.393 (1)	0.303 (1)	0.240 (1)	0.199 (1)	0.168 (1)
241	0.395 (1)	0.303 (1)	0.242 (1)	0.200 (1)	0.169 (1)
301	0.394 (1)	0.304 (1)	0.241 (1)	0.199 (1)	0.169 (1)

EV

N	f = 2	f = 3	f = 4	f = 5	f = 6
61	0.459 (1)	0.304 (1)	0.207 (1)	0.147 (1)	0.109 (1)
121	0.450 (1)	0.305 (1)	0.215 (1)	0.158 (1)	0.121 (1)
181	0.445 (1)	0.306 (1)	0.218 (1)	0.163 (1)	0.126 (1)
241	0.443 (1)	0.307 (1)	0.220 (1)	0.165 (1)	0.129 (1)
301	0.441 (1)	0.308 (1)	0.221 (1)	0.167 (1)	0.131 (1)

These data reveal that the asphericity of star polymers decreases as the number of arms increases; e.g. the polymers become more sphere-like. A linear fit in 1/N allows one to predict values for a simulation with an infinite number of beads. These extrapolated values are compared to the theoretical predictions [18] for NEV polymers in Table VII and to the simulation results of other researchers [19, 20, 21] and the theoretical predictions [12] for EV polymers. In the NEV case there is excellent agreement with the theory. The EV computer simulations, which used very different polymer models, agree with each other to better than 3% but the theory values are significantly different. This is not surprising since the theoretical calculation is only to first order.

Table VII Comparison of extrapolated computer A and <A> values to theoretical and other computer simulation results.

NEV A and <A>

f	A Extrapolated	Theory [18]	<A> Extrapolated	Theory [12]
2	0.528 (2)	0.526	0.395 (1)	0.394
3	0.361 (1)	0.361	0.304 (1)	0.304
4	0.273 (1)	0.273	0.242 (1)	0.243
5	0.220 (1)	0.220	0.201 (1)	0.201
6	0.183 (1)	0.183	0.170 (1)	0.171

EV A

f	Extrapolated	Computer [19]	Computer [20]	Computer [21]
2	0.551 (2)	0.543 (2)	0.547	0.549 (1)
3	0.342 (1)	0.345 (3)	0.344	0.349 (3)
4	0.237 (1)	0.243 (1)	0.244	
5	0.179 (1)	0.185 (1)		
6	0.140 (1)	0.146 (1)	0.148	0.145 (2)

EV <A>

f	Extrapolated	Computer [19]	Computer[20]	Computer[21]	Theory[12]
2	0.437 (1)	0.429 (2)	0.433	0.430 (1)	0.416
3	0.308 (1)	0.306 (1)	0.307	0.313 (1)	0.273
4	0.224 (1)	0.227 (1)	0.227		0.193
5	0.171 (1)	0.177 (1)			0.144
6	0.136 (1)	0.140 (1)	0.143	0.140 (1)	0.112

Conclusions

The Pivot algorithm has been used to simulate ideal and excluded volume linear and star polymers in three dimensions. The mean-square radius of gyration and its error have been determined for a wide range of N. It is found that the data obey the expected power law with a power nearly equal to 1.00 for NEV and 1.20 for EV polymers, respectively. The g ratio has an extrapolated value, for all the NEV systems studied, which is in excellent agreement with the Zimm-Stockmeyer theoretical predictions [8]. The present computer simulations agree very well with the studies of other workers, who used a variety of simulation models---some on lattices and others employing continuous potentials. That the results of all of these different investigations agree so well provides additional strong evidence for the universal properties of large star polymers.

These three dimensional simulations help students to develop insight into molecular motions and properties. This ability will be very useful in further studies in engineering and science.

Acknowledgements

We wish to thank the Manhattan College Computer Center for generous grants of computer time. A. M. Dunn and J. Y. Monteith thank Manhattan College for a summer research grant. We also wish to thank Professor Paula A. Whitlock for helpful comments on the manuscript.

References

1. Douglas, J.F., Roovers, J. and Freed, K.F., Macromolecules, 23, 4168 (1990).

2. Likos, C.N., Phys. Rep., 348, 267 (2001).

3. Rudnick, J. and Gaspari, G., Science, 237, 384 (1987).

4. Varriale, R. and Bishop, M., Comp. Educ. J., XVII, 44 (2007).

5. Dunn, A.M.and Bishop, M., Comp. Educ. J., XVIII, 64 (2008)..

6. Madras, N. and Sokal, A.D., J. Stat. Phys., 50, 109 (1988).

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

8. Zimm, B.H. and Stockmayer, W.H., J. Chem. Phys., 17, 1301 (1949).

9. Miyake, M. and Freed, K.F., Macromolecules, 16, 1228 (1983).

10. Solc, K. and Stockmeyer, W.H., J. Chem. Phys., 54, 2756 (1971).

11. Rudnick, J. and Gaspari, G., J. Phys.A, 19, L191 (1986).

12. Jagodzinski, O., J. Phys.A, 27, 1471 (1994).

13. Hearn, D. and Baker, M.P., "*Computer Graphics*", Prentice-Hall, London, 1986.

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

15. Whittington, S.G., Lipson, J.E.G., Wilkinson, M.K. and Gaunt, D.S., Macromolecules, 19, 1241 (1986).

16. Batoulis, B J. and Kremer, K., Macromoecules, 22, 4277 (1989).

17. Zifferer, G., Macromol.Theory Simul, 8, 433 (1999).

18. Wei, G., Macromolecules, 30, 2130 (1997).

19. Bishop, M., Clarke, J.H.R., Rey, A., and Freire, J.J., J. Chem. Phys., 94, 4009 (1991).

20. Zifferer, G., J. Chem. Phys., 110, 4668 (1999).

21. Timoshenko, E.G., Kuznetsov, Y.A. and Connolly, R., J. Chem. Phys., 116, 3905 (2002).

Biographical Information

Andrew M. Dunn and J. Yates Monteith completed B.S. degrees in computer science at Manhattan College in 2008. Andrew M. Dunn is currently a graduate student in computer science at the University of New Hampshire and J.Yates Monteith is now a graduate student in computer science at Clemson University.

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.