COMPUTER MODELING OF H-COMB POLYMERS

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Abstract

We have developed simulations of tangent, hard sphere H-comb polymers in both the ideal and excluded volume regimes. The polymer configurations are changed by the Pivot algorithm and then the mean-square radius of gyration and g-ratio are calculated. These computer results are compared to a variety of simulations of other polymer models, theoretical predictions and experimental results. It is found that the extrapolated g-ratio values are in good agreement with other simulation work, theory and experiments and that the results in the excluded volume regime are nearly the same as for the ideal regime. This type of project provides an interesting area of study in a modeling and simulation course.

Introduction

Engineering, mathematics and science students need to develop the ability to make ideal models which can be programmed for a computer. Modeling of polymeric materials provides an important arena in which chemistry, computer programming, statistics, algorithms, and graphics come together. Such models have been examined in an independent study simulation and modeling course given at Manhattan College.

In two previous articles in this journal, Gorry and Bishop [1] and Dunn, Monteith and Bishop [2] have investigated a variety of polymer models. Gorry and Bishop studied two dimensional H-comb polymers and Dunn, Monteith and Bishop examined three dimensional star polymers. In these models all the atoms making up the monomeric polymer building blocks are grouped into circular or spherical "beads", respectively. Polymers were constructed by linking individual beads appropriately. In this paper we examine some structural properties of three dimensional H-combs. These polymers have a central branch connecting two junctions together. Each of these junctions also has two other branches attached to them. Thus, H-comb polymers contain one internal branch and four external branches. If m is the number of monomers in a branch there are a total of N = 5m + 1 units in a uniform H-comb. Figure 1 illustrates an H-comb with m = 3. The graphics capabilities of the Maple software package have been employed to draw this figure.

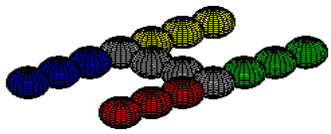

Figure 1: An H-comb with 16 beads.

An overall polymer size can be measured by the mean-square radius of gyration, $\langle S^2 \rangle$. Here $\langle\rangle$ denotes an average over the polymer configurations. It is well-known that for large polymers, $\langle S^2 \rangle$ follows the scaling law [3]

$$\langle S^2 \rangle = C\,(N - 1)^{2\nu} \qquad (1)$$

in which the coefficient, C, is a model dependent amplitude but the exponent, 2ν, is universal for a given spatial dimension, d, and universality class; 2ν has the value of about 1.20 in three dimensions for excluded volume (EV) chains and the value of 1.0 in all

dimensions for random walk, nonexcluded volume (NEV) chains. NEV polymer models allow polymer beads to overlap but this is prohibited with EV models. The same exponent values are expected for both large linear and branched polymers.

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

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

An equation for the g-ratio of general uniform NEV comb polymers with a regular spacing of branch points has been obtained by a number of researchers. Here we will employ the functional form derived by Casassa and Berry [4]:

$$g = \lambda - \lambda^2(1 - \lambda) / (f + 1) + 2\lambda (1 - \lambda)^2 / f + (3f - 2)(1 - \lambda)^3 / f^2 \qquad (3)$$

in which λ is the ratio of the number of units in the backbone to the total number of units. The g-ratio value of an H-comb polymer is obtained when $f = 2$ and $\lambda = 3/5$.

The goal of this article is to compute $\langle S^2 \rangle$ and the g-ratio from accurate Monte Carlo computer simulations for three dimensional NEV and EV H-comb polymers. Our results are compared to theoretical predictions, other simulation models and experiments.

Pivot Monte Carlo

Tangent hard sphere polymer models have been simulated using a Monte Carlo Pivot [5] algorithm. Our polymer models are essential the same as those previously employed by Gorry and Bishop [1] for H-combs and Dunn, Monteith, and Bishop [2] for star polymers. The distance between two connected units is assumed to be a constant of magnitude one; e.g. adjacent beads are tangent.

In the H-comb polymer, the center of the first junction bead is assigned as the origin of the XYZ coordinate system. The polymer is initially started with each of its five arms either horizontally or vertically directed from the junction beads. The first three arms extend vertically in the positive direction, vertically in the negative direction, and horizontally in the positive direction from the first junction bead, respectively. The third arm connects the two junctions. The last two arms extend vertically in the positive and negative direction from the second junction bead.

The polymers are started in the X-Y plane. The beads are moved in continuous space by the Pivot algorithm [5]. First, a random number is used to select one of the beads as a "pivot". If the first junction bead is chosen as the pivot, then one of the first three arms is randomly selected to be moved. Likewise, if the second junction bead is selected, then either the third, fourth, or fifth arm will be moved. In the case in which the third arm is chosen, depending upon which junction was selected, either the first and second arms, or the fourth and fifth arms are also moved as a unit with the third arm.

Once a set of beads has been selected to be moved, we generate three randomly chosen Euler angles: α, β and γ. Then all selected beads are moved in accordance with the rotation equations given in Dunn, Monteith, and Bishop [2]. If the pivot selected is an arm bead, then all the higher indexed beads on that arm are rotated about the pivot bead. In the EV case the new trial configuration is accepted or rejected depending upon whether or not any beads overlap each other; no such testing is performed in the NEV case. In a linear chain the beads are linked so that each is connected to two others, except of course for the end beads. Then the movement rules change the configuration of only one part of the chain.

These bead movement procedures generate one configuration. The process is continued for 5×10^6 moves but the first 1×10^6 moves are discarded before the averaging process begins. These discarded moves represent the

equilibration of the initial arbitrary configuration. Data is collected at a spacing of 500 pivot moves and the resulting random snapshots of polymer configurations are used for data analysis. In the NEV case the acceptance ratio is one; i.e. all configurations are accepted. In the EV case the acceptance ratio ranged from 10-36%, depending upon the polymer architecture and N. In order to obtain additional independent configurations and thus enhance the statistical quality of the data, sixteen parallel runs employing different random number seeds were performed.

If X^{α}_{j} denotes the α component of the three dimensional position vector of the j-th bead, then the center of mass coordinates, X^{α}_{CM} of a given configuration are given by

$$X^{\alpha}_{CM} = (1/N) \sum_{j=1}^{N} X^{\alpha}_{j} \quad \text{for } \alpha = 1,2,3 \qquad (4)$$

and the square radius of gyration of this configuration is then calculated as

$$\langle S^2 \rangle = (1/N) \sum_{\alpha=1}^{3} \sum_{j=1}^{N} (X^{\alpha}_{j} - X^{\alpha}_{CM})^2 \qquad (5)$$

Each saved configuration is employed in the calculation. The set of property values were then further averaged over the total number of saved samples to determine the values of the mean and the standard deviation from the mean, employing the usual equations [6].

Results

Linear and H-comb polymers in the NEV and EV regimes have been simulated. We have repeated the recent Pivot MC star polymer simulations of Dunn, Monteith and Bishop [2] for linear chains (two arm stars) with increased accuracy by studying polymers with as many as 931 beads in comparison to their maximum number of 301 beads.

Table I presents the radius of gyration simulation results for all the systems investigated. The number in parenthesis denotes one standard deviation in the last displayed digits. It is clear from the radius of gyration data that polymers with a given number of units N become more compact as the number of branches increases. As expected, NEV polymers are much more compact than their EV counterpart because excluded volume effects cause the polymer units to avoid each other and thus expand the polymer.

Table I Simulation Data for $\langle S^2 \rangle$.

NEV

N	linear	H-comb
241	40.19(6)	28.75(3)
301	50.15(8)	35.83(3)
541	90.03(16)	64.26(11)
751	125.17(21)	89.07(13)
931	155.32(17)	110.67(15)

EV

N	linear	H-comb
241	166.45(16)	116.18(8)
301	217.60(27)	152.28(14)
541	440.91(65)	310.49(23)
751	653.50(82)	459.97(50)
931	844.62(90)	595.33(58)

Weighted nonlinear least-squares fits [6] to Eq. 1 using the $\langle S^2 \rangle$ data in Table I gave the values reported in Table II for the exponent, 2ν. The number in parenthesis denotes one standard deviation in the last displayed digit. As expected, our simulation data exponents agree well with the predicted values [3] of 1.0 (NEV) and approximately 1.20 (EV).

Table II The Scaling Exponent, 2ν, for $\langle S^2 \rangle$.

N	NEV	EV
linear	0.998(1)	1.200(1)
H-comb	0.995(1)	1.207(1)

The g-ratios have been calculated from the radius of gyration data in Table I and the error in these quantities have been computed from the standard equation relating the error in a ratio to the error in the numerator and the error in the denominator. The simulation g-ratios are listed in Table III. The number in parenthesis denotes one standard deviation in the last displayed digit.

Table III Simulation g-ratios for H-combs.

N	NEV	EV
241	0.715(1)	0.698(1)
301	0.714(1)	0.700(1)
541	0.714(2)	0.704(1)
751	0.712(2)	0.704(1)
931	0.713(1)	0.705(1)

However, these computer results are for finite N whereas the theories are for infinite N. The scaling law is given by

$$g = g_\infty (1 - K / N^{\Delta}) \qquad (6)$$

where g_∞ is the value of the g-ratio for infinite N, K is a constant and Δ is the finite scaling exponent. In the NEV regime Δ has a value of 1.0 and it is believed that for three dimensional EV polymers [7] it has the value of 0.47. To determine the value of g as N approaches infinity, one plots g vs. $1/N^{\Delta}$ 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 $1/N^{\Delta}$ to each set of data in the tables. We find that for NEV and EV H-combs the extrapolated g-ratio values are 0.712 ±0.001 and 0.713 ±0.002, respectively. The NEV value compares excellently with the theoretical prediction of Eq. 3 (0.712). The g-ratio of EV H-combs has been calculated with simulation methods by Lipson et al [8] for different lattices (fcc 0.71±0.02, bcc 0.72±0.02, sc 0.71±0.02, and tetrahedral 0.70±0.03), by Bishop and Saltiel [9] (0.71±0.03) and by Shida, Ohno and Kawazoe [10] (0.72). Roovers and Toporowski [11] and Rahnman et al [12] have also reported g-ratio values from their experiments with polystyrenes (0.69±0.02) and with polybutadienes (0.72±0.02), respectively. Renormalization group theory [13] predicts a g-value of 0.720.

Conclusions

The Monte Carlo Pivot algorithm has been used to simulate continuum, tangent hard sphere linear and H-comb polymers in the ideal and excluded volume regime. The radius of gyration and the g-ratio and their respective error bars have been determined for a wide range of N. The values obtained by researchers using very different computer models agree very well, providing additional strong evidence for universal properties of polymers. It is found that the extrapolated g-ratio computer values are in fine agreement with other simulation work and theory in the NEV regime. The experiments and the renormalization group g-ratio values are also in good agreement with the simulation studies in the EV regime. There is only a slight difference between the NEV and EV results, indicating that H-comb polymers behave essentially as ideal systems. These types of simulations provide interesting application examples for a simulation and modeling course.

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