MODELING AND SIMULATION OF TWO DIMENSIONAL H-COMB POLYMERS WITH THE PIVOT ALGORITHM

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Abstract

We have developed a simulation of ideal H-comb polymers in two dimensions in which the polymers are moved by the Pivot algorithm. The mean-square radius of gyration, the g ratio, and the asphericity have been computed and compared to theoretical predictions. Excellent agreement is obtained. The H-comb properties are compared to those of single junction 3-arm and 5-arm stars. It is found that the effect of two junctions in the polymeric structure dominates the influence of the number of arms. This kind of project is suitable for students in a modeling and simulation course.

Introducation

In two previous articles in this journal, Varriale and Bishop [1] and Dunn and Bishop [2] have developed ideal models of star polymers. In these models, the monomer building blocks are represented by circular "beads". Polymers were constructed by linking individual beads. Two different algorithms were employed for studying these molecules. In the first simulation [1] the polymer was "grown" from a central bead on a two dimensional square lattice. If m represents the number of beads in each linear branch of a polymer containing f branches, the total number of monomer beads in a star polymer, N, can be calculated using

$$N = fm + 1 \qquad (1)$$

In the second study [2] the star polymers were initialized in an arbitrary configuration and the arms were moved via the Pivot algorithm [3]. In both models, a number of different polymer properties were computed by averaging over randomly generated configuration snapshots. The mean-square radius of gyration, $\langle S^2 \rangle$, the g ratio and the asphericity were studied and it was found that the Pivot simulation model was more efficient and accurate than the growth model.

An interesting question is how the number of junctions in the polymer will influence these properties. H-combs are the simplest two junction polymers. These molecules have a central arm connecting the two junctions, each of which has two other arms attached to it. Hence, f = 5 in equation 1.

Method

Construction of the H-comb required modifications of Dunn and Bishop's [2] procedure for star polymers. The center of the first junction bead is assigned as the origin of the X-Y coordinate system. The distance between the centers of two connected beads is assumed to be a constant of magnitude one. The polymers are initially configured with each of the 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. Figure 1 illustrates an initial H-comb when N = 11. The graphical capabilities of the Maple Software package [4] have been used to draw the H-comb from the X,Y coordinate data.

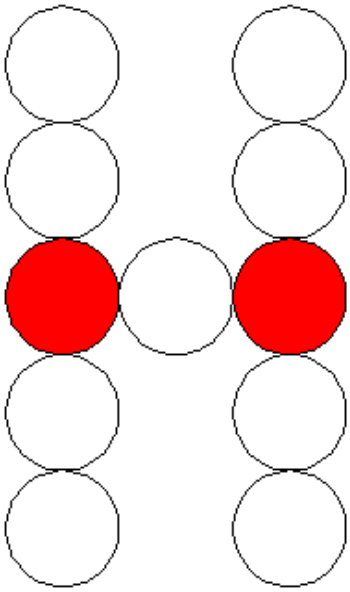

Figure 1: A H-Comb Polymer with junctions shaded; N = 11.

The beads are moved in continuous space by the Pivot algorithm [3]. A random number is used to select one of the beads as a "pivot" with coordinates (Xp, Yp). 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, then 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, another random number is employed to generate a random angle, θ, between 0º and 360º. All selected beads are moved in accordance with the standard two dimensional rotation equations [5]. In Eqs. 2a and b, X' and Y' are the new coordinates whereas X and Y are the original coordinates before the pivot move.

$$X' = Xp + (X - Xp)\cos\theta - (Y - Yp)\sin\theta \quad (2a)$$

$$Y' = Yp + (X - Xp)\sin\theta + (Y - Yp)\cos\theta \quad (2b)$$

The radius of gyration, the g ratio, and the asphericity have been computed according to the equations given in Dunn and Bishop [2]. The H-comb simulation results have the same level of statistical accuracy as the star simulations because the same total number of samples has been used in the averaging.

Results

Table I presents the present H-comb $\langle S^2 \rangle$ simulation results alongside Dunn and Bishop's findings for linear, 3-arm and 5-arm stars. The number in parenthesis denotes one standard deviation in the last displayed digit. Note that a star polymer with two branches is equivalent to a linear chain. 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 and that the 3-arm stars are more similar in their $\langle S^2 \rangle$ values to H-combs than 5-arm stars. Thus, the number of junctions has a greater influence than the number of arms on the properties of these kinds of molecules. This result is not surprising because one can visualize the structure of an H-comb molecule as composed of two 3-arm stars with a common arm.

Table I Simulation Data for $<S^2>$

N	Linear	3-arm star	5-arm star	H-comb
61	10.14(2)	7.99(1)	5.52(1)	7.43(1)
121	20.15(2)	15.80(2)	10.73(1)	14.59(2)
181	30.13(6)	23.52(2)	15.91(1)	21.69(4)
241	40.18(7)	31.42(4)	21.13(3)	28.85(5)
301	50.21(9)	39.16(4)	26.35(2)	35.97(8)

It is well known [6] that long polymers follow the scaling law

$$<S^2> = C (N - 1)^P \quad (3)$$

where C is model dependent and P is universal and equal to 1.00 for all ideal polymers. Linear, star, and H-comb polymers are expected to have the same value of P. Weighted nonlinear least-squares fits [7] to the H-comb $<S^2>$ data in Table I gave P = 0.98 ± 0.01, which is in very good agreement with the expected 1.00.

The g ratios have been calculated from the H-comb and linear polymer radius of gyration data in Table I and the error in this quantity has been computed from the standard equation [7] relating the error in a ratio $\sigma_{A/B}$ to the error in the numerator σ_A and the error in the denominator σ_B, The resulting simulation g ratios are listed in Table II. The number in parenthesis denotes one standard deviation in the last displayed digit.

Table II Simulation g ratios.

N	3-arm star	5-arm star	H-comb
61	0.788(2)	0.544(1)	0.733(2)
121	0.784(1)	0.533(1)	0.724(1)
181	0.781(2)	0.528(1)	0.720(2)
241	0.782(2)	0.526(1)	0.718(2)
301	0.780(2)	0.525(1)	0.716(2)

One notices that the g ratios for the 3-arm star are much closer to the H-comb results than the values for a 5-arm star. However, these computed results are for finite N whereas the theoretical prediction is for infinite N. To determine the value of g as N approaches infinity, one plots g vs. 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 the data in the table. The extrapolated H-comb g ratio is 0.713 ± 0.002, which is in excellent agreement with the theoretical value [8] of 0.712.

The simulation results for the asphericity are contained in Tables III and IV, respectively. A and <A> are defined in Dunn and Bishop[2] in terms of the ellipse which encloses the molecule. These data reveal that the asphericity of star polymers decreases as the number of arms increases; e.g. the polymers become more disk-like in their shape. However, increasing the number of junctions causes the structure to be less circular. As was the case for the g ratio we have extrapolated a linear fit in 1/N to predict values for a simulation with an infinite number of beads. This extrapolation gave A = 0.426 ± 0.003 and <A> = 0.310 ± 0.001 for H-combs, whereas Dunn and Bishop found that A = 0.405 ± 0.001 and <A> = 0.321 ± 0.001 for 3-arm stars, and A = 0.252 ± 0.001 and <A> = 0.221 ± 0.001 for 5-arm stars. These values again indicate that H-combs are more similar to 3-arm than 5-arm stars.

Table III The ratio of the averages, A.

N	3-arm star	5-arm star	H-comb
61	0.395(2)	0.242(1)	0.395(2)
121	0.399(2)	0.246(1)	0.410(3)
181	0.401(1)	0.248(1)	0.415(3)
241	0.404(2)	0.250(1)	0.419(3)
301	0.404(2)	0.250(1)	0.420(4)

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

N	3-arm star	5-arm star	H-comb
61	0.315(1)	0.216(1)	0.296(1)
121	0.318(1)	0.218(1)	0.302(1)
181	0.319(1)	0.220(1)	0.304(1)
241	0.320(1)	0.220(1)	0.307(1)
301	0.320(1)	0.220(1)	0.307(1)

Conclusion

The Pivot algorithm has been used to simulate H-comb polymers in two 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. The g ratio has an extrapolated value which is in excellent agreement with the theoretical prediction [8] of 0.712. In addition, the mean square radius of gyration, the g ratio, and the asphericity all indicate that H-comb polymers are much more similar to 3-arm than 5-arm stars. These types of simulations provide interesting projects in which students obtain experience in model development, programming, statistics and graphics. Such tools will be very useful in their future careers.

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