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The shapes of simple three and four junction comb polymers

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A scheme originally proposed by G. Wei [Physica A **222**, 152 (1995); Physica A **222**, 155 (1995)] is redesigned to produce numerical shape parameters of arbitrary tree-branched polymers based on the Kirchhoff matrix eigenvalue spectrum. This method and two different Monte Carlo techniques (pivot and growth) are employed to investigate the asphericity of three and four junction comb polymers in both the ideal and excluded volume regimes. It is found that the extrapolated g-ratio and asphericity values obtained by all of these methods are in excellent agreement with each other and the available theory in the ideal regime and that polymers with a complete set of interior branches display a more sphere-like shape. © *2015 AIP Publishing LLC.* [http://dx.doi.org/10.1063/1.4905101]

I. INTRODUCTION

It is well known[1–3] that the presence of branching alters the behavior of polymeric materials. Star polymers have one central junction connecting the various branches. H-combs are the simplest polymers containing two junctions. These molecules have a central branch connecting the two junctions, each of which has two other branches attached to it. Hence, there are a total of five branches: one internal and four external. The simplest three junction polymers are the TTT and HH-comb molecules. TTT polymers have seven branches (see Figure 1). Two are internal (e.g., connect junctions) and five are external whereas in HH-combs there are eight branches: two internal and six external. The simple four junction comb polymers examined herein have either nine or eleven branches (see Figure 1); now three of the branches are internal and either six or eight are external. If m is the number of monomers in a branch and b is the number of branches, there are a total of $N = b*m+1$ units in these uniform combs.

An overall polymer size can be measured by the mean-square radius of gyration, $\langle S^2\rangle$, where $\langle\ \rangle$ denotes an average over the polymer configurations. If $\langle S^2\rangle_b$ and $\langle S^2\rangle_l$ are the mean-square radii of gyration of a branched and linear structure with an identical number of monomers, then the g-ratio is defined as

$$g = \frac{\langle S^2\rangle_b}{\langle S^2\rangle_l}. \tag{1}$$

Casassa and Berry[4] obtained a general equation for the g-ratio of uniform, ideal non-excluded volume (NEV) comb polymers with f three-functional junctions regularly spaced along the backbone,

$$g = 1 - r - \frac{r^2(1-r)}{(f+1)} + \frac{2r(1-r)^2}{f} + \frac{(3f-2)(1-r)^3}{f^2}. \tag{2}$$

Here, r is the ratio of the number of units in the comb backbone to the total number of units in the polymer. In case of five branch combs, $r = 3/5$ and $f = 2$, so $g = 89/125 = (0.7120)$. In the seven branch case, $r = 4/7$, $f = 3$, and $g = 229/343 = (0.6676)$ whereas for nine branches, $r = 5/9$, $f = 4$, and $g = 155/243 = (0.6379)$. The g-ratios of NEV eight and eleven branch polymers were determined by von Ferber *et al.*[5] from the form factor. These values are $37/64 = (0.5781)$ and $683/1331 = (0.5131)$ for eight and eleven branches, respectively.

Note that a more general formula allowing for the two outer junctions to have functionality f_1 while the inner junctions display a functionality f_2 has been derived in Ref. 5 from the scattering functions.

Details about the shapes of polymers can be determined from the radius of gyration tensor. Its eigenvalues ordered by magnitude are $e_1 \le e_2 \le e_3$. These are the principal moments of gyration along the principal orthogonal axes.[6] The average trace of this tensor, $e_1+e_2+e_3$, is equal to $\langle S^2\rangle$. The eigenvalues of each simulated configuration are ordered by magnitude as above giving triplets $e_1 \le e_2 \le e_3$. Rudnick and Gaspari[7,8] have defined the asphericity, A, of polymers in three dimensions as

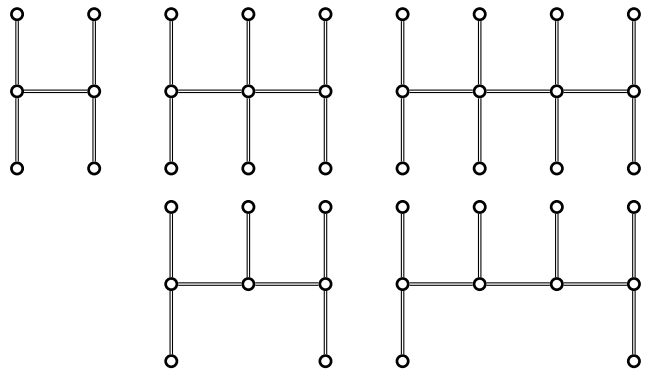

FIG. 1. Sketch of comb polymers discussed in this work. Top row: 5, 8, and 11 branch combs; bottom row: 7 and 9 branch combs.

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$$A = \frac{\langle \sum_{i>j}^{3} (e_i - e_j)^2 \rangle}{\langle 2\left(\sum_{i=1}^{3} e_i\right)^2 \rangle}, \tag{3}$$

where the averages $\langle \ldots \rangle$ are over all triplets as produced by the simulation. The average asphericity, $\langle A \rangle$, in turn is determined as

$$\langle A \rangle = \langle \frac{\sum_{i>j}^{3} (e_i - e_j)^2}{2\left(\sum_{i=1}^{3} e_i\right)^2} \rangle. \tag{4}$$

Again, the averages are over all triplets of eigenvalues determined from the simulated configuration. Note that in these equations, A involves a ratio of averages whereas $\langle A \rangle$ involves an average of a ratio.

The shape of a three dimensional linear polymer can vary from a fully extended rod in which e_2 and e_3 essentially vanish so that A and $\langle A \rangle$ have unit value, to a sphere for which $e_1 = e_2 = e_3$. In the latter case, both A and $\langle A \rangle$ are zero. More complex polymer structures such as those studied here can obtain a fully extended rod shape only in the NEV regime where the units can overlap each other. Nevertheless, even in the excluded volume (EV) regime, a nearly extended rod shape is possible if the external branches line up parallel to the backbone. In between the extremes of a rod and a sphere, a polymer configuration can be imagined as approximately enclosed inside an ellipsoid with semi-major axis equal to e_1 and semi-minor axes equal to e_2 and e_3.

In this article, we compute the g-ratio, A, and $\langle A \rangle$ from both theoretical equations and accurate Monte Carlo (MC) computer simulations for NEV and EV multi-branch comb molecules.

II. METHODS

A. Theory

Various universal ratios for Gaussian (NEV) tree-branched macromolecules may be computed by a method originally developed by Wei,[9,10] in the following referred to as "Wei's method." This approach is exact in two dimensions and gives a very good approximation in three dimensions. In general, Wei's method can be applied to any structure for which the Kirchhoff matrix and its corresponding eigenvalues are known. Here, this method is employed to predict universal shape ratios of branched combs.

A specific feature of the present implementation of the approach is that the universal ratios are determined by extrapolating to infinite size branches. For completeness, we give a short comprehensive account of Wei's method. Let $\lambda_1, \ldots, \lambda_{N-1}$ be the N - 1 non-zero eigenvalues of the $N \times N$ Kirchhoff matrix, K, of a Gaussian structure with N beads. Define the diagonal matrix

$$\Lambda_N(y) = \begin{pmatrix} \lambda_1 + y & & 0 \\ & \ddots & \\ 0 & & \lambda_{N-1} + y \end{pmatrix}. \tag{5}$$

Then a reduced variant of the characteristic polynomial of K can be written as

$$P_N(x) = \mathrm{Det}[\Lambda_N(-x)] = \prod_{j=1}^{N-1} (\lambda_j - x). \tag{6}$$

Here, Det[·] denotes the determinant of the corresponding matrix excluding the zero eigenvalue $\lambda_N = 0$. The $N-1$ zeros of the polynomial P_N are the non-zero eigenvalues of K. The essential functions needed for the calculation of the shape parameters can now be defined. Using the notation $y = x/N$, we write these as

$$D_N(x) = \mathrm{Det}[\Lambda_N^{-1}(0)]\mathrm{Det}[\Lambda_N(y^2)] = P_N^{-1}(0) P_{N-1}(-y^2) \tag{7}$$

$$= [\prod_{j=1}^{N-1} \lambda_j^{-1}] \prod_{j=1}^{N-1} (\lambda_j + y^2) \tag{8}$$

and

$$S_{1,N}(x) = \frac{1}{N^2} \mathrm{Tr}[\Lambda_N^{-1}(y^2)] = \frac{1}{N^2} \sum_{j=1}^{N-1} (\lambda_j + y^2)^{-1}. \tag{9}$$

Following Wei,[9,10] the functions $S_{k,N}$ for $k = 2,3,\ldots$ correspond to traces of higher powers of Λ_N^{-1},

$$S_{2,N}(x) = \frac{1}{N^4} \sum_{j=1}^{N-1} (\lambda_j + y^2)^{-2}, \tag{10}$$

$$S_{3,N}(x) = \frac{1}{N^6} \sum_{j=1}^{N-1} (\lambda_j + y^2)^{-3}. \tag{11}$$

The asphericity, A, in two or three dimensions, $d = 2,3$, can now be obtained using[9,10]

$$\langle A_d \rangle = \frac{d(d+2)}{2} \int_0^\infty x^3 D_N^{-d/2}(x) S_{2,N}(x) \mathrm{d}x \tag{12}$$

$$= \frac{d(d+2)}{2} \int_0^\infty \mathrm{d}y \sum_{j=1}^{N-1} \frac{y^3}{(\lambda_j + y^2)^2} \left[\prod_{k=1}^{N-1} \frac{\lambda_k}{\lambda_k + y^2} \right]^{d/2}. \tag{13}$$

Independent of the dimension, the g-ratio of the radius of gyration of the branched structure with respect to that of a linear chain with the same number of beads is given by

$$g = S_{1,N}(0) / S_{1,N}^{\mathrm{chain}}(0) = \sum_{j=1}^{N-1} \lambda_j^{-1} / \sum_{k=1}^{N-1} \hat{\lambda}_k^{-1}. \tag{14}$$

Here, the $\hat{\lambda}_k$ are the non-zero eigenvalues of the Kirchhoff matrix of a linear chain with N beads.

B. Numerical evaluation applying Wei's method

For certain specific comb-like structures, Wei[9,10] has derived analytical results for the shape parameters. Here, however, we seek to determine shape parameters for standard comb structures. For this purpose, we pursue another approach by extrapolating results for combs composed from finite discrete chains of beads. As an example, let us explain how we determine the shape parameters for the 7-branch comb—see the 7-branch structure in Fig. 1. Here, we initially set up the Kirchoff

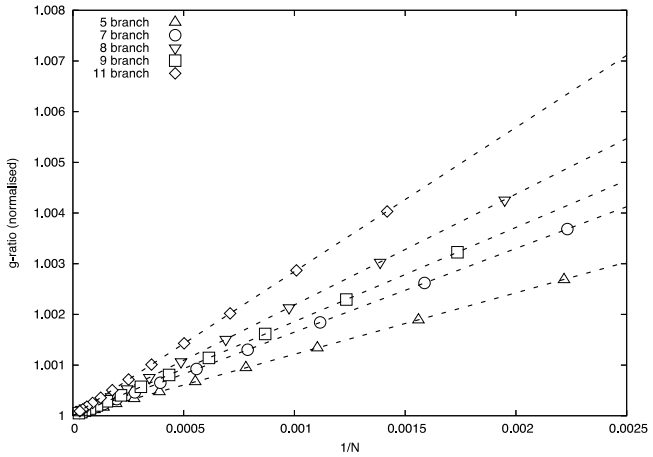

FIG. 2. Extrapolation for the three dimensional g-ratios of the comb polymers discussed. Note that in order to show all the extrapolated results in a single graph, the target g-ratio is normalized to 1 for all five combs.

matrix, K, for this structure with 64 beads per branch. Avoiding double counting, this results in a structure with $N = 449$ beads corresponding to $1/N \approx 0.0022$. We then calculate the shape parameters for this initial structure. The corresponding values for the g-ratio and the asphericity of the 7-branch comb are marked by rightmost disk-shaped markers in Figs. 2 and 3. We continue by increasing the number of beads per chain by factors of $\sqrt{2}$, up to a structure with 4096 beads per chain and thus a total of $N = 28\,673$ beads corresponding to $1/N \approx 3.49 \times 10^{-5}$.

Wei's method as detailed in Sec. II A is then applied to determine the shape parameters of the given structures as a function of the total number of beads N. The extrapolated value for the given shape parameter is determined in the limit of $1/N \to 0$. As displayed in Figs. 2 and 3, the results scale perfectly with $1/N$ as seen from the straight line extrapolations. Thus, extrapolated results may be extracted from these series. This procedure is illustrated in Fig. 2 for the g-ratio and in Fig. 3 for the asphericity. The final results concerning the combs discussed in this paper are given in Table I for the g-ratio and in Table II for the average asphericity $\langle A \rangle$. Estimated

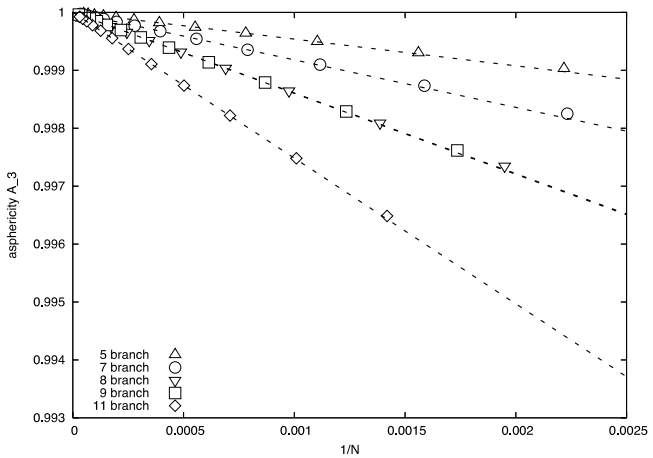

FIG. 3. Extrapolation for the three dimensional asphericities of the comb polymers discussed. Note that in order to show all the extrapolated results in a single graph, the target asphericity is normalized to 1 for all five combs.

TABLE I. Comparison of extrapolated pivot MC, growth MC, and Wei's method g-ratios to the theoretical infinite bead values reported in the literature for NEV combs.

	Pivot MC	*Growth MC*	*Wei*	*Theory*
5 branch	0.712(1)[a]	0.711(5)	0.7120(0)	0.7120[b]
7 branch	0.666(1)[c]	0.668(5)	0.6676(1)	0.6676[b]
8 branch	0.578(1)[c]	0.574(4)	0.5781(0)	0.5781[c]
9 branch	0.638(2)[c]		0.6378(6)	0.6379[b]
11 branch	0.512(2)[c]		0.5131(1)	0.5131[c]

[a]See Reference 13.
[b]See Reference 4.
[c]See Reference 5.

errors given for Wei's method in Tables I and II are based on the statistical error taken from the extrapolation.

C. Monte Carlo

In the first MC method employed here, tangent hard sphere polymer models have been simulated using a Monte Carlo pivot[11] algorithm. These polymer models are essentially the same as those previously used by Zweier and Bishop[12,13] for H-combs. We have simulated systems with N ranging from 211 to 1431. The details of the simulations are contained in Kosmas, Reid, and Bishop.[14]

In our second MC method, chain growth on a simple cubic lattice has been employed to examine five, seven, and eight branched NEV combs. Details of this approach are contained in Zajac and Bishop.[15] Here, N ranged from 100 to 480 since the starting beads of each branch were overlapped at the junctions.

If $X_j^{(\alpha)}$ denotes the α component of the three dimensional position vector of the j-th bead, then the center of mass

TABLE II. Comparison of extrapolated pivot MC, growth MC, and Wei method for A and $\langle A \rangle$.

	NEV			
	A *Pivot MC*	$\langle A \rangle$ *Pivot MC*	$\langle A \rangle$ *Growth MC*	$\langle A \rangle$ *Wei*
5 branch	0.379(1)[a]	0.296(1)[a]	0.297(2)	0.29747(4)
7 branch	0.385(2)	0.294(1)	0.296(2)	0.29455(7)
8 branch	0.332(1)	0.261(1)	0.260(1)	0.26087(5)
9 branch	0.394(4)	0.295(2)		0.29579(4)
11 branch	0.327(3)	0.253(2)		0.25323(4)
	EV			
	A *Pivot MC*			$\langle A \rangle$ *Pivot MC*
5 branch	0.385(2)[a]			0.318(2)[a]
7 branch	0.393(3)			0.321(2)
8 branch	0.334(2)			0.280(2)
9 branch	0.411(8)			0.333(4)
11 branch	0.350(4)			0.288(4)

[a]See Reference 12.

TABLE III. The ratio of the averages, A, for three junction combs.

7 branch			8 branch		
N	NEV	EV	N	NEV	EV
211	0.380(2)	0.400(1)	241	0.328(2)	0.341(1)
351	0.383(2)	0.400(1)	401	0.331(2)	0.339(1)
561	0.384(2)	0.397(2)	561	0.330(2)	0.339(1)
631	0.383(2)	0.397(1)	721	0.332(1)	0.338(1)
701	0.383(2)	0.397(2)	881	0.330(1)	0.338(1)

TABLE V. The average of the ratio, $\langle A \rangle$, for three junction combs.

7 branch			8 branch		
N	NEV	EV	N	NEV	EV
211	0.292(1)	0.333(1)	241	0.258(1)	0.290(1)
351	0.293(1)	0.332(1)	401	0.260(1)	0.287(1)
561	0.294(1)	0.329(1)	561	0.259(1)	0.287(1)
631	0.292(1)	0.328(1)	721	0.260(1)	0.286(1)
701	0.293(1)	0.328(1)	881	0.260(1)	0.285(1)

coordinates, $X_{CM}^{(\alpha)}$, of a given configuration are

$$X_{CM}^{(\alpha)} = \frac{1}{N}\sum_{j=1}^{N} X_j^{(\alpha)}, \text{ for } \alpha = 1,2,3 \tag{15}$$

and the matrix components of the gyration tensor, Q, may be written in the form

$$Q_{\alpha\beta} = \frac{1}{N}\sum_{j=1}^{N}(X_j^{(\alpha)} - X_{CM}^{(\alpha)})(X_j^{(\beta)} - X_{CM}^{(\beta)}). \tag{16}$$

The square radius of gyration of this configuration is then calculated as

$$S^2 = Q_{11} + Q_{22} + Q_{33}. \tag{17}$$

The set of values was 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.

III. RESULTS

The pivot MC g-ratios have been previously calculated[5] from the radius of gyration data, and the errors 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. However, these computer results are for finite N whereas the theories are for infinite N. Infinite N g-ratio values have been obtained by fitting a scaling law as explained in Zweier and Bishop.[12] These extrapolated g-ratios for NEV systems are compared to other findings in Table I. The extrapolated data of Zajac and Bishop[15] are less accurate than the pivot MC simulation results. Nonetheless, the growth algorithm data agree with the other findings well within two standard deviations of the mean, or the 95% confidence limit. In all the results reported in the tables, the number in parenthesis denotes one standard deviation in the last displayed digits.

Both Wei's method and the MC simulations are in excellent agreement with each other and the theoretical predictions. The g-ratios of the eight and eleven branch combs, which have a complete set of interior branches, have a relatively lower value than those found for the five, seven, and nine branch combs.

The pivot MC simulation results for the asphericities A and $\langle A \rangle$ are contained in Tables III–VI, respectively. The error in the A calculation, which involves the division of separately averaged quantities, was determined similarly as the data in Table I. One would not expect A and $\langle A \rangle$ to be the same since the numerator and denominator in Eqs. (3) and (4) are highly correlated. The data display only a weak dependence on N. The EV values of A and $\langle A \rangle$ are larger than their respective NEV values because of the repulsions in the EV polymers.

As was the case for the g-ratio, the data have been extrapolated to predict values for an infinite polymer. Table II lists these extrapolated values. The value found for $\langle A \rangle$ of NEV H-comb polymers is in excellent agreement with the theoretical prediction of Wei;[16] 0.297. As expected, the results indicate that the polymers become more sphere-like in their shape as the structure changes to higher branching and a complete set of interior branches. There are currently no theoretical predictions for the asphericity of these branched combs in the EV regime. We plan to obtain these predictions for EV branched comb polymers by building on our previous work on EV star polymers.[17]

IV. CONCLUSIONS

Wei's method and the Monte Carlo pivot and growth algorithms have been used to investigate branched comb

TABLE IV. The ratio of the averages, A, for four junction combs.

9 branch			11 branch		
N	NEV	EV	N	NEV	EV
775	0.392(2)	0.413(2)	771	0.329(2)	0.349(1)
847	0.393(2)	0.413(2)	881	0.329(2)	0.349(2)
901	0.393(1)	0.413(2)	991	0.329(2)	0.349(1)
991	0.393(3)	0.413(2)	1101	0.329(2)	0.350(2)
1171	0.393(3)	0.413(1)	1211	0.330(2)	0.350(1)
1261	0.393(2)	0.413(2)	1321	0.329(2)	0.349(1)
1351	0.393(2)	0.412(2)	1431	0.328(1)	0.349(1)

TABLE VI. The average of the ratio, $\langle A \rangle$, for four junction combs.

9 branch			11 branch		
N	NEV	EV	N	NEV	EV
775	0.295(1)	0.337(1)	771	0.252(1)	0.291(1)
847	0.295(1)	0.337(1)	881	0.252(1)	0.291(1)
901	0.295(1)	0.337(1)	991	0.252(1)	0.291(1)
991	0.294(1)	0.337(1)	1101	0.253(1)	0.292(1)
1171	0.295(1)	0.336(1)	1211	0.253(1)	0.291(1)
1261	0.295(1)	0.337(1)	1321	0.252(1)	0.290(1)
1351	0.295(1)	0.336(1)	1431	0.252(1)	0.290(1)

polymers in the ideal and excluded volume regime. The g-ratio, the asphericities, and their respective error bars have been determined for a wide range of N. It is found that the extrapolated g-ratio and asphericity values of all the techniques are in excellent agreement with each other and the available theory in the NEV regime but that more theoretical work is needed in order to determine these quantities in the EV regime.

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[1]C. N. Likos, Phys. Rep. **348**, 267 (2001).
[2]J. F. Douglas, J. Roovers, and K. F. Freed, Macromolecules **23**, 4168 (1990).
[3]J. J. Freire, Adv. Polym. Sci. **143**, 35 (1999).
[4]E. F. Casassa and G. C. Berry, J. Polym. Sci., Part A-2 **4**, 881 (1966).
[5]C. von Ferber, M. Bishop, T. Forzaglia, and C. Reid, Macromolecules **46**, 2468 (2013).
[6]K. Solc and H. Stockmeyer, J. Chem. Phys. **54**, 2756 (1971).
[7]J. Rudnick and G. Gaspari, Science **237**, 384 (1987) and references therein.
[8]J. Rudnick and G. Gaspari, J. Phys. A: Math. Gen. **19**, L191 (1986).
[9]G. Wei, Physica A **222**, 152 (1995).
[10]G. Wei, Physica A **222**, 155 (1995).
[11]N. Madras and A. D. Sokal, J. Stat. Phys. **50**, 109 (1988).
[12]S. Zweier and M. Bishop, J. Chem. Phys. **131**, 116101 (2009).
[13]S. Zweier and M. Bishop, Comput. Educ. J. **XVIIII**(4), 99 (2009).
[14]M. Kosmas, C. Reid, and M. Bishop, J. Phys. A: Math. Theor. **43**, 185002 (2010).
[15]G. Zajac and M. Bishop, "Monte Carlo Studies of Ideal Multi-Branched Polymers," Comput. Educ. J. (in press).
[16]G. Wei, *International Microsymposium in Memory of Professor Dr. Xi-De Feng's 80th Birthday and 60 Years of Teaching,* (Beijing, China, 1995), p. 116.
[17]C. von Ferber, J. Y. Monteith, and M. Bishop, Macromolecules **42**, 3627 (2009).