Shapes of Two-Dimensional Excluded Volume Continuum Star Polymers

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ABSTRACT: The shapes of excluded volume, two-dimensional star polymers are explored with the renormalization group and Monte Carlo computer simulation of a tangent hard disk model. The mean-square radius of gyration, the *g*-ratio, and the asphericity of linear and star polymers are examined. The standard ϵ expansion for the *g*-ratio is modified to use the known value of the radius of gyration expansion exponent rather than only the first-order expansion value. Good agreement is obtained with the current Monte Carlo Pivot algorithm results and previous simulations of other polymer models. Our approach also improves the predictions of the *g*-ratio in three dimensions, significantly enhancing the accuracy of the renormalization group for calculating shape properties.

1. Introduction

Star polymers are of continuing interest experimentally for their many applications[1,2] and theoretically as they constitute the simplest, yet nontrivial, case of branching in polymers.[3] Therefore, properties of star polymers have been investigated with a number of different experimental and theoretical methods.[4,5] Here, we focus on the important shape properties of these molecules.[6]

The shapes of three-dimensional star polymers have been extensively explored by a variety of simulation and theoretical approaches. A sampling of the many papers includes the work of Whittington, Lipson, Wilkinson, and Gaunt[7] who used a Monte Carlo growth algorithm on a simple cubic lattice, Batoulis and Kremer[8] who used a dimerization technique on a fcc lattice, Zifferer[9] who employed a tetrahedral lattice and the Pivot[10] algorithm, Bishop, Clarke, Rey, and Freire[11] who also used the Pivot[10] algorithm but for a continuum coarse-grained model in combination with the Lennard-Jones interaction potential and a Gaussian bond distribution, Timoshenko, Kuznetsov, and Connolly[12] who used the Metropolis method with an off-lattice system, and Dunn, Monteith, and Bishop[13] who used the Pivot algorithm with tangent hard sphere polymers. All of these studies were in excellent agreement with the theoretical predictions of Zimm and Stockmayer[14] and Wei[15] for the properties of non-excluded volume (NEV), ideal star polymers. The excluded volume (EV) simulations agreed with each other to better than 3% but differed by a larger percentage from the renormalization group (RG) theory values of Miyake and Freed,[16] Allessandrini and Carignano,[17] and Jagodzinski.[18]

The shapes of two-dimensional star polymers have been much less explored. NEV star polymers in two dimensions have recently been investigated by Varriale and Bishop[19] and Dunn and Bishop[20] using two different Monte Carlo computer simulation methods. Varriale and Bishop[19] employed a square lattice and a growth algorithm. This algorithm is very efficient for studying NEV systems since there is no problem with overlapping units. Dunn and Bishop[20] applied the Pivot algorithm to study a continuous coarse grained model of tangent hard disks. Both of these simulation studies agreed excellently with the theoretical predictions which have the same values in all dimensions for ideal polymers. We are aware of only a few previous computer simulation investigations of the shape of two-dimensional EV linear and star polymers. Whittington, Lipson, Wilkinson, and Gaunt[7] performed exact enumeration studies for nonintersecting walks on a square lattice; Bishop, Clarke, Rey, and Freire[21] and Bishop, Clarke, and Freire[22] used the Pivot algorithm with Lennard-Jones interactions accounting for EV effects. Their model also employed a Gaussian bond distribution instead of fixed bond lengths.

In this article we provide both new RG theoretical predictions as well as high-precision Monte Carlo simulation data to examine the shapes of two-dimensional tangent hard disk linear and star polymers. Our model is essentially the same as the one employed previously by Dunn and Bishop[20] to study ideal two-dimensional polymers. In this model all the atoms making up the monomeric polymer segments are grouped into a circular "bead". In a linear chain the beads are linked so that each is connected to two others, except of course for the end beads. In the tangent disk model, the distance of the centers of two linked disks equals the sum of their radii. In a star polymer there is a central bead which is connected to a number of linear branches. Hence, if m is the number of beads in one linear branch of a star polymer containing f branches, the total number of beads in the star polymer, N, is

$$N = fm + 1 \tag{1}$$

Dunn and Bishop[20] examined NEV polymer systems in which the model allowed units to pass through each other and even to overlap. We have modified their polymer model by not allowing any overlaps. We employ the Pivot[10] algorithm to generate configurations in our EV simulations.

Although every polymer can assume a different spatial configuration in time, an overall size can be characterized 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 EV polymers $\langle S^2 \rangle$ follows the scaling law[23]

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

in which the coefficient, C, is determined by the details of the polymer model but the exponent, 2ν, is a universal quantity exactly equal[24] to 3/2 for linear EV polymers in two dimensions. This exponent is expected to be the same for large EV star polymers.

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A useful parameter for comparing the compactness of star polymers to linear chains is called the g-ratio, which is defined as the ratio of the mean-square radius of gyration of a star polymer, $\langle S^2(f)\rangle$, to that of a linear polymer, $\langle S^2(1)\rangle$, with the same overall number of beads:

$$g = \frac{\langle S^2(f)\rangle}{\langle S^2(1)\rangle} \tag{3}$$

First-order ϵ-expansions for this quantity have been obtained by Miyake and Freed[16] and Allessandrini and Carignano:[17]

$$g = \frac{3f-2}{f^2}\left[1 - \frac{\epsilon}{8}\left\{\frac{13(f-1)(f-2)}{2(3f-2)} - \frac{4(f-1)(3f-5)}{3f-2}\ln 2 + \ln f\right\}\right] \tag{4}$$

where $\epsilon = 4 - d$ and d is the spatial dimension. Their results are derived from a first-order calculation of the mean-square radius of an f-arm star polymer:

$$\frac{\langle S^2(f)\rangle}{N^{2\nu}} = \frac{\alpha_l(3f-2)}{6}\frac{}{f^2}f^{1-2\nu}\left[1 - \frac{\epsilon}{8}\left\{\frac{13}{12} + \frac{(f-1)(f-2)}{3f-2}\frac{13}{2} - \frac{4(f-1)(3f-5)}{3f-2}\ln 2\right\}\right] \tag{5}$$

Here, ν is the radius of gyration exponent and α_l is a nonuniversal factor depending on the length scale l. The ratio $g_0(f) = (3f-2)/f^2$ is the g-ratio for NEV stars ($\epsilon = 0$) which is independent of dimension. This quantity was first determined by Zimm and Stockmeyer.[14]

Details about the shapes of polymers can be determined from the radius of gyration tensor. Its eigenvalues, λ_1 and λ_2, are the components of $\langle S^2\rangle$ along the principal orthogonal axes.[25] The trace of this tensor, $\lambda_1 + \lambda_2$, is equal to $\langle S^2\rangle$. By convention, the λ values of each configuration are ordered by magnitude such that $\lambda_1 \geq \lambda_2$ and then averaged. Rudnick and Gaspari[26] have defined the asphericity, A, of polymers in two dimensions as

$$A = \frac{\langle(\lambda_1 - \lambda_2)^2\rangle}{\langle(\lambda_1 + \lambda_2)^2\rangle} \tag{6}$$

and the average asphericity, $\langle A\rangle$, as

$$\langle A\rangle = \left\langle\frac{(\lambda_1 - \lambda_2)^2}{(\lambda_1 + \lambda_2)^2}\right\rangle \tag{7}$$

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 two-dimensional polymer can vary from a fully extended rod, in which λ_2 is essentially 0 so that A and $\langle A\rangle$ have a value of one, to a disk for which $\lambda_1 = \lambda_2$. Then both A and $\langle A\rangle$ are zero. In between these extremes a polymer configuration can be imagined as enclosed inside an ellipse with semimajor axis equal to λ_1 and semiminor axis equal to λ_2.

The goal of this paper is to obtain $\langle S^2\rangle$, the g-ratio, A, and $\langle A\rangle$ calculated from both RG theory and Pivot Monte Carlo computer simulations. Our results are also compared to other theoretical predictions and simulation models for linear and star polymers in two dimensions.

2. Renormalization Group

For the analytical treatment we apply a general d-dimensional formalism. Let X_j denote the d-dimensional position vector of the jth bead and $X_j^{(\alpha)}$ its α-component with $\alpha = 1,..., d$ and $j = 1,..., N$. Then the gyration tensor Q is given as

$$Q_{\alpha\beta} = \frac{1}{2N^2}\sum_{i,j=1}^{N}(X_i^{(\alpha)} - X_j^{(\alpha)})(X_i^{(\beta)} - X_j^{(\beta)}) \tag{8}$$

The d-dimensional asphericity A_d may then be cast in the following general form:[27]

$$A_d = \frac{d}{d-1}\frac{\mathrm{tr}\,\hat{Q}^2}{(\mathrm{tr}\,Q)^2} \quad \text{with } \hat{Q} = Q - \mathbf{1}\frac{\mathrm{tr}\,Q}{d} \tag{9}$$

while the trace of the gyration tensor is the square radius of gyration

$$S_d^{\,2} = \mathrm{tr}\,Q \tag{10}$$

When averaging over configurations of a given polymer molecule, its architecture is conveniently described by the Kirchhoff matrix or discrete Laplacian Δ_{ij} defined as

$$\text{for } i \neq j\text{:}\quad \Delta_{ij} = \begin{cases} -1 & \text{if } i,j \text{ are linked} \\ 0 & \text{otherwise} \end{cases} \qquad \Delta_{ii} = -\sum_{j\neq i}\Delta_{ij} \qquad i,j = 1...N \tag{11}$$

The average of the asphericity A_d over polymer configurations is then calculated as

$$\langle A_d\rangle = \int\prod_{\alpha,j}\mathrm{d}X_j^{(\alpha)}\,A_d(X)\mathrm{e}^{-h_u(X)} \tag{12}$$

This average is taken with respect to the Hamiltonian h_u which in the general case incorporates the excluded volume interaction parametrized[18] by u:

$$h_u(X) = \sum_{i\neq j}\frac{-\Delta_{ij}}{2l^2}(X_i - X_j)^2 + ul^d\delta^d(X_i - X_j) \tag{13}$$

Here, the short-range excluded volume interaction is represented by the d-dimensional delta function δ^d and its strength by the dimensionless parameter u. The variable l defines the length scale. Let us first discuss the case of no excluded volume interaction (NEV), i.e., $u = 0$. Then the squared length scale l^2 determines the mean-square distance between adjacent beads. Furthermore, as has been shown by Eichinger[28] and Wei,[29] in this case the shape

Table 1. Estimates of the Mean Asphericity $\langle A_d\rangle$ and the g-Ratio from RG Calculations in Two ($d = 2$) and Three ($d = 3$) Dimensions[a]

	$d=2$			$d=2$			$d=3$		
f	$\langle A_2(f)\rangle_0$	$b(f)$	$\langle A_2\rangle_\epsilon$	$g_0(f)$	$g_{\epsilon=2}(f)$	$g_{d=2}(f)$	$g_{\epsilon=1}(f)$	$g_{d=3}(f)$	MC
1	0.3964	0.139	0.4425	1.000	1.000	1.000	1.000	1.000	
2	0.3964	0.139	0.4425	1.000	1.000	0.875	1.000	0.974	
3	0.3210	−0.308	0.2608	0.778	0.819	0.651	0.798	0.763	0.76(1)[b]
4	0.2636	−0.690	0.1737	0.625	0.709	0.518	0.667	0.626	0.60(1)[b]
5	0.2221	−1.050	0.1242	0.520	0.640	0.434	0.580	0.535	0.51(1)[b]
6	0.1914	−1.417	0.092 77	0.444	0.594	0.377	0.519	0.471	0.43(1)[b]
8	0.1494	−2.028	0.059 26	0.344	0.539	0.303	0.441	0.388	0.338[c]
10	0.1223	−2.735	0.040 09	0.280	0.508	0.257	0.394	0.337	0.277[c]
12	0.1035	−3.382	0.029 27	0.236	0.490	0.227	0.363	0.302	0.235[c]

[a] Quantities with an ϵ subscript are obtained from the standard ϵ expansion whereas those with a d subscript are from our new approximation. Quantities with a 0 subscript are for NEV conditions. The numbers in the MC column are Monte Carlo computer simulation results. [b] Reference 7. [c] Reference 9.

parameters of the polymer are entirely determined by the characteristic polynomial of the Kirchhoff matrix

$$P_N(\lambda) = \det(\Delta - \lambda \mathbf{1}) \tag{14}$$

or, in the infinite chain limit $N \to \infty$, by a corresponding limiting function $P_N(\lambda) \to P(\lambda)$. For a molecule of a given architecture the latter limit is taken in such a way that the relative sizes of all chains of the molecule are preserved. For the calculation of the mean asphericity a particular simplification has been proposed by Diehl and Eisenriegler[30] and worked out for star polymers by Jagodzinski.[18] The mean asphericity for the regular f-branched NEV star polymer in the latter formulation is given by the following integral:[18]

$$\langle A_d(f)\rangle_0 = \frac{d(d+2)}{8}\int_0^\infty \mathrm{d}x \frac{(\cosh x)^{d(1-f)/2}}{x(\cosh 4x - 1)}\left(\frac{x}{\sinh x}\right)^{d/2}[2 + 4fx^2 - 2(f-2)x \sinh 2x - 4(f-2)x^2 \cosh 2x + fx \sinh 4x - 2\cosh 4x] \tag{15}$$

Numerical values of this integral for $d = 2$ are tabulated in Table 1 for selected values $1 \le f \le 12$. These numbers coincide with those given by Wei[29] ($f = 10$ is not considered there).

To treat the excluded volume (EV) interaction, an RG study of eq 12 has been performed for regular f-branched star polymers in the infinite chain limit. In terms of an expansion in ϵ the resulting first-order correction to eq 15 can be written as[18]

$$\langle A_d(f)\rangle_\epsilon = \left(1 + \frac{3\epsilon}{8}b(f) + ...\right)\langle A_d(f)\rangle_0 \tag{16}$$

where the values of $b(f)$ as calculated by numerical integration are given in Table 1. As can be seen from these values one has $b(f) < 0$ for $f \ge 3$, and the absolute value grows rapidly with f. A naive application of eq 16 would thus result in negative estimated values for $f \ge 6$ in contradiction to the exact lower limit $\langle A_d\rangle \ge 0$. We therefore follow Jagodzinski[18] in using the systematic ϵ-expansion of the reciprocal value of the correction factor corresponding to a (0,1) Pade approximant which ensures well-defined $f \to \infty$ asymptotics:

$$\langle A_d(f)\rangle_\epsilon = \frac{1}{1 - \frac{3\epsilon}{8}b(f) + ...}\langle A_d(f)\rangle_0 \tag{17}$$

Numerical values for the asphericity of two-dimensional ($\epsilon = 2$) regular polymer stars according to this approximant are listed in Table 1 as $\langle A_2\rangle_\epsilon$. Compared with the extrapolated results of the Monte Carlo simulation given in the next section the agreement is quite remarkable.

Both Miyake and Freed[16] and Allessandrini and Carignano[17] systematically expanded the g-ratio to $O(\epsilon)$ using the first-order result for the radius of gyration exponent $\nu = 1/2 + \epsilon/16$. The resulting g-ratios for $d = 2$ are listed in Table 1 as $g_{\epsilon=2}(f)$. The space dimension d enters the g_ϵ ratio exclusively through the ϵ-expansion of the EV interaction. However, the process of expanding the radius of gyration exponent to first-order results in a loss of a lot of information since a high-order resummation yields[31] $\nu = 0.588$ when $d = 3$. Moreover, when $d = 2$ the exact result,[24] $\nu = 3/4$, significantly deviates from the first-order value $\nu_\epsilon = 0.625$.

To employ this higher-order resummation and the exact information about ν, we therefore propose to calculate the g-ratio by inserting into eq 5 the known value for ν and only then performing the ratio in eq 3. However, there is a penalty in applying this procedure. In a strict ϵ expansion the ln 2 term in eq 4 is compensated by a ln f term for $f = 2$, ensuring equality of the $f = 1$, 2 results, but this condition is now lost. Table 1 reports the results of our procedure as g_d for $d = 2$, and for completeness we also include our findings for $d = 3$. Compared with the strict ϵ expansion our two-dimensional RG results show significantly improved agreement with our extrapolated simulation findings. In particular, for $d = 2$ this approach is in accordance with the observation of simulations that $g_0 \ge g_{EV}$, a rule violated by the g_ϵ approach. Furthermore, our three-dimensional RG scheme, $g_{d=3}$, is in much better agreement with computer simulations[7,9] than the Miyake and Freed[16] and Allessandrini and Carignano[17] approach using $g_{\epsilon=1}(f)$. It proves to be compatible with the above inequality for $f = 3$ and consistently gives values that are lower and thus closer to the simulation result. We conclude that this method represents a significant advance in accuracy compared to the standard ϵ expansion.

3. Pivot Monte Carlo

The simulation procedure is very similar to that employed by Dunn and Bishop.[20] The star polymer is modeled by $N = fm + 1$ beads, all represented by disks of identical radius. The center bead is always assigned the coordinates of the origin. The m beads of each of the f arms form a chain connected to the center bead by one of its ends. The distance between the centers of two connected units is assumed to be a constant of magnitude one; e.g., adjacent beads are tangent. The polymers are started in a 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 120° apart. The beads are moved in continuous space by the Pivot algorithm.[10] First, a random number is used to select one of the beads as a "pivot" with coordinates (X_p,Y_p). A second random number is then employed to determine the rotation angle, θ, such that θ falls between 0° and 360°. This angle is used to move all the higher indexed beads on that arm about the pivot bead to new locations. 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. The new locations are given by

$$X' = X_p + (X - X_p)\cos\theta - (Y - Y_p)\sin\theta \tag{18}$$

$$Y' = Y_p + (X - X_p)\sin\theta + (Y - Y_p)\cos\theta \tag{19}$$

In eqs 18 and 19, X' and Y' are the new coordinates whereas X and Y are the original coordinates before the pivot move. In the EV case this new trial configuration is accepted or rejected depending upon whether or not any beads overlap each other.

This procedure generates one configuration. The process is continued for 5×10^6 moves. However, the initial state is not representative of the equilibrium situation, and 1×10^6 moves are discarded before the averaging process begins. Data are 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 7 to 11%, depending upon N and f. In order to obtain additional independent configurations and thus enhance the statistical quality of the data, 16 parallel runs were performed using different seeds for random number generation.

Defining the center-of-mass coordinates of a given configuration as

$$X_{CM}^{(\alpha)} = \frac{1}{N}\sum_{j=1}^{N} X_j^{(\alpha)}, \quad \text{for } \alpha = 1, 2 \tag{20}$$

the matrix components of the gyration tensor eq 8 may be equivalently rewritten in the form

$$Q_{\alpha\beta} = \frac{1}{N}\sum_{j=1}^{N}(X_j^{(\alpha)} - X_{CM}^{(\alpha)})(X_j^{(\beta)} - X_{CM}^{(\beta)}) \tag{21}$$

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

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

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.[32]

Table 2 presents the radius of gyration simulation results for all the systems studied. The number in parentheses denotes one standard deviation in the last displayed digits. Note that a star polymer with two branches ($f = 2$) is equivalent to a linear chain. It is intuitively clear and also confirmed by the data that polymers with a fixed overall number of units N become more compact as the number of branches increases. Compared to the NEV case, this effect is weakened by the EV interaction between the branches of the star polymer, which leads to a stretching of the chains.

Weighted nonlinear least-squares fits[32] to eq 2 using the $\langle S^2 \rangle$ data in Table 2 gave values for the exponent, 2ν, equal to 1.501(1), 1.505(1), 1.505(1), 1.509(1), and 1.502(1), for $f = 2$, 3, 4, 5, and 6, respectively. The number in parentheses denotes one standard deviation in the last displayed digit. The agreement of these simulation data exponents with the expected EV value[24] of 3/2 is excellent. The scaling exponent of EV systems is larger than that found for ideal polymers, 1, since the excluded volume effects cause the polymer units to avoid each other and thus expand the polymer.

The g-ratios have been calculated from the radius of gyration data in Table 2, and the error in these ratios have been computed from the combination of the error in the numerator and the error in the denominator.[32] The simulation g-ratios are listed in Table 3. The number in parentheses denotes one standard deviation in the last displayed digit.

These computer results are for finite N whereas the theories are for infinite N. It is believed that the finite scaling exponent, Δ, for two-dimensional polymers lies between 0.8 and 1.5. To determine the value of g as N approaches infinity, one plots g vs $1/N^{\Delta}$ so that when $N \rightarrow \infty$, $1/N^{\Delta} \rightarrow 0$. 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 have done the fit using Δ values of 0.8, 1.0, and 1.5, and the results are within one standard deviation of each other. Hence, only the Δ value of 1.0 is reported in the tables. The extrapolated g-ratios can be compared to other simulation results in Table 4 and to the RG predictions in Table 1. One finds excellent agreement among the different computer simulation data even though the Whittington, Lipson, Wilkinson, and Gaunt[7] study was performed on a square lattice with exact enumeration and the work by Bishop, Clarke, and Friere[22] studied continuum polymers using the Pivot algorithm and a Lennard-Jones potential to mimic excluded volume effects. They also employed a Gaussian distribution of bond lengths instead of the fixed bond lengths employed in other simulation models. While the original RG theoretical predictions[16,17] are not in good agreement with the simulation findings, we see that using the known result for the exact two-dimensional exponent successfully improves the estimator of the g-ratio. This approach also improves the three-dimensional predictions. However, the theory is still only first order in ε, and it would be interesting to compare a second-order theory of the g-ratio to the simulation data. Cardy[33] has predicted some exact amplitude ratios for two-dimensional polymer chains. However no such results are known for the g-ratio of star polymers.

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

N	$f = 2$	$f = 3$	$f = 4$	$f = 5$	$f = 6$
61	65.88(7)	45.20(4)	33.50(1)	26.23(2)	21.74(1)
121	186.76(17)	128.13(7)	94.97(6)	74.40(4)	61.25(4)
181	343.49(18)	235.98(13)	174.86(13)	137.11(9)	112.80(8)
241	528.16(56)	363.98(27)	269.86(19)	211.92(18)	174.55(15)
301	738.53(46)	508.87(28)	377.96(32)	297.32(24)	244.87(28)

Table 3. Simulation g Ratios

N	$f = 3$	$f = 4$	$f = 5$	$f = 6$
61	0.686(1)	0.509(1)	0.398(1)	0.330(1)
121	0.686(1)	0.509(1)	0.398(1)	0.328(1)
181	0.687(1)	0.509(1)	0.399(1)	0.328(1)
241	0.689(1)	0.511(1)	0.401(1)	0.330(1)
301	0.689(1)	0.512(1)	0.403(1)	0.332(1)

Table 4. Comparison of Extrapolated Computer g Ratios to Simulation Results for Other EV Polymer Models

f	extrapolated	simulation[a]	simulation[b]
3	0.689(1)	0.68(1)	0.69(1)
4	0.511(1)	0.51(1)	0.51(1)
5	0.402(1)	0.40	0.40(1)
6	0.330(1)	0.33	0.34(1)

[a] Reference 7. [b] Reference 22.

Table 5. Ratio of the Averages, A

N	$f = 2$	$f = 3$	$f = 4$	$f = 5$	$f = 6$
61	0.635(2)	0.258(1)	0.138(1)	0.083(1)	0.054(1)
121	0.633(2)	0.268(1)	0.149(1)	0.095(1)	0.064(1)
181	0.630(1)	0.272(1)	0.154(1)	0.099(1)	0.069(1)
241	0.629(2)	0.273(1)	0.156(1)	0.102(1)	0.071(1)
301	0.629(1)	0.274(1)	0.158(1)	0.103(1)	0.073(1)

Table 6. Average of the Ratio, $\langle A \rangle$

N	$f = 2$	$f = 3$	$f = 4$	$f = 5$	$f = 6$
61	0.515(1)	0.248(1)	0.135(1)	0.082(1)	0.053(1)
121	0.510(1)	0.256(1)	0.146(1)	0.093(1)	0.064(1)
181	0.507(1)	0.258(1)	0.150(1)	0.098(1)	0.068(1)
241	0.506(1)	0.259(1)	0.152(1)	0.100(1)	0.070(1)
301	0.506(1)	0.259(1)	0.154(1)	0.102(1)	0.072(1)

Table 7. Comparison of Extrapolated Computer A and $\langle A \rangle$ Values to Another Simulation Model

	A		$\langle A \rangle$	
f	extrapolated	simulation[a]	extrapolated	simulation[a]
2	0.627(1)	0.627(2)	0.503(1)	0.503(4)
3	0.278(1)	0.279(3)	0.263(1)	0.263(3)
4	0.162(1)	0.163(3)	0.158(1)	0.157(3)
5	0.108(1)	0.105(2)	0.107(1)	0.103(2)
6	0.077(1)	0.075(1)	0.076(1)	0.075(1)

[a] Reference 21.

The simulation results for A and $\langle A \rangle$ are contained in Tables 5 and 6, respectively. The error in the A calculation, which involves the division of separately averaged quantities, has been determined as for Table 3. The data indicate that the asphericity of star polymers decreases as the number of arms increases; e.g., the polymers become more disklike in their shape. As was the case for the g-ratio, a linear fit in $1/N^{\Delta}$ has been extrapolated to predict values for an infinite number of beads. Most results with Δ values of 0.8, 1.0, and 1.5 were within 1 standard deviation, and the largest differences still fell within 2 standard deviations. The tables report the findings with $\Delta = 1.0$.

Table 7 compares our extrapolated values of A and $\langle A \rangle$ to a different simulation model, and Table 1 contains the RG predictions. There is excellent agreement, within the error bars, between the present simulations and the previous computer studies of Bishop, Clarke, Rey, and Freire.[21] Rudnick and Gaspari[26] derived an equation for NEV linear chains ($f = 2$) which predicts that $A = 4/7$ in all dimensions, and Aronovitz and Nelson[27] used RG methods to find that the correction for EV linear chains in two dimensions is 0.016. Hence, in two dimensions EV linear chains are predicted to have $A = 0.587$.

4. Conclusions

Both RG methods and the MC Pivot algorithm for a tangent hard disk model have been used to study excluded volume continuum linear and star polymers in two dimensions. The radius of gyration, the *g*-ratio, and the asphericities have been determined for a wide range of *N*. It is found that our extrapolated computer values are in excellent agreement with other simulation work. That the values of all the different computer investigations agree so well provides additional strong evidence for the universal properties of star polymers. The RG theories have been improved upon by employing more accurate values of the radius of gyration expansion exponent in the ϵ expansions. Our procedure represents a significant enhancement of the RG predictive power for shape properties.

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References and Notes

(1) Likos, C. N. *Phys. Rep.* **2001**, *348*, 267.
(2) Star Polymers. von Ferber, C., Holovatch, Yu., Eds. *Condens. Matter Phys.* **2002**, *5*.
(3) Schäfer, L.; von Ferber, C.; Lehr, U.; Duplantier, B. *Nucl. Phys. B* **1992**, *374*, 473.
(4) Douglas, J. F.; Roovers, J.; Freed, K. F. *Macromolecules* **1990**, *23*, 4168.
(5) Freire, J. J. *Adv. Polym. Sci.* **1999**, *143*, 35.
(6) Rudnick, J.; Gaspari, G. *Science* **1987**, *237*, 384.
(7) Whittington, S. G.; Lipson, J. E. G.; Wilkinson, M. K.; Gaunt, D. S. *Macromolecules* **1986**, *19*, 1241.
(8) Batoulis, J.; Kremer, K. *Macromoecules* **1989**, *22*, 4277.
(9) Zifferer, G. *Macromol. Theory Simul* **1999**, *8*, 433.
(10) Madras, N.; Sokal, A. D. *J. Stat. Phys.* **1988**, *50*, 109.
(11) Bishop, M.; Clarke, J. H. R.; Rey, A.; Freire, J. J. *J. Chem. Phys.* **1991**, *94*, 4009.
(12) Timoshenko, E. G.; Kuznetsov, Y. A.; Connolly, R. *J. Chem. Phys.* **2002**, *116*, 3905.
(13) Dunn, A. M.; Moneith, J. Y.; Bishop, M. *Comp. Educ. J.* **2008**, *XVIII*, 74.
(14) Zimm, B. H.; Stockmayer, W. H. *J. Chem. Phys.* **1949**, *17*, 1301.
(15) Wei, G. *Macromolecules* **1997**, *30*, 2130.
(16) Miyake, A.; Freed, K. F. *Macromolecules* **1983**, *16*, 1228.
(17) Allessandrini, J. L.; Carignano, M. A. *Macromolecules.* **1992**, *25*, 1157.
(18) Jagodzinski, O. *J. Phys. A* **1994**, *27*, 1471.
(19) Varriale, R.; Bishop, M. *Comp. Educ. J.* **2007**, *XVII*, 44.
(20) Dunn, A. M.; Bishop, M. *Comp. Edu. J.* **2008**, *XVIII*, 64.
(21) Bishop, M.; Clarke, J. H. R.; Rey, A.; Freire, J. J. *J. Chem. Phys.* **1991**, *95*, 608.
(22) Bishop, M.; Clarke, J. H. R.; Freire, J. J. *J. Chem. Phys.* **1993**, *98*, 3452.
(23) de Gennes, P. G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(24) Nienhuis, B. *Phys. Rev. Lett.* **1982**, *49*, 1062.
(25) Solc, K.; Stockmeyer, H. *J. Chem. Phys.* **1971**, *54*, 2756.
(26) Rudnick, J.; Gaspari, G. *J. Phys. A* **1986**, *19*, L191.
(27) Aronovitz, J. A.; Nelson, D. R. *J. Phys. (Paris)* **1986**, *47*, 1445.
(28) Eichinger, B. E. *Macromolecules* **1980**, *13*, 1.
(29) Wei, G. *Macromolecules* **1997**, *30*, 2125.
(30) Diehl, H. W.; Eisenriegler, E. *J. Phys. A* **1989**, *22*, L87.
(31) Le Guillou, J. C.; Zinn-Justin, J. *Phys. Rev. B* **1980**, *21*, 3976.
(32) Bevington, P. R. *Data Reduction and Error Analysis for the Physical Sciences*; McGraw-Hill: New York, 1969.
(33) Cardy, J.; Mussardo, G. *Nucl. Phys. B* **1993**, *410*, 451.

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