Lattice Models of Branched Polymers: Combs and Brushes

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ABSTRACT: This paper is concerned with the statistics and dimensions of simple branched molecules having two branch points. Exact enumeration and Monte Carlo results are presented for uniform combs and brushes on a variety of lattices in three dimensions. In particular, the interference between the branches as reflected by the number of conformations and by the dimensions of the branches is examined. The mean square radius of gyration and the associated ratio g are calculated, and the insensitivity of g to solvent effects is discussed.

I. Introduction

A problem of continuing interest is the prediction of the effects of branching on the properties of polymers in solution. To this end there have been numerous studies, both theoretical and experimental, on uniform star-branched molecules. These are structure in which f branches, each having the same number of monomers, n, emanate from a single branch point. Well-characterized stars of varying functionality have been synthesized,[1] and properties such as the radius of gyration (in solvents of differing quality), second virial coefficient, intrinsic viscosity, and diffusion coefficient[2-4] have been measured experimentally.

The theoretical description of simple branched structures was initiated by Zimm and Stockmayer,[5] and while this work did not incorporate excluded volume effects, some of the predictions have proved to be very robust. Two recent theoretical treatments of regular stars are capable of incorporating the effects of varying solvent quality: the scaling theory of Daoud and Cotton[6] and the chain conformation space renormalization group approach of Miyake and Freed.[7] Bridging the experimental and theoretical work have been a number of Monte Carlo studies,[8-11] some of which focus on the "ideal" or random walk case. While these two terms are used interchangeably to describe a linear chain having Gaussian statistics, experimentally referred to as Θ-conditions, their application to the branched case is less well-defined. In several of these papers polymer configurations are weighted through the use of a nearest-neighbor interaction energy in order to probe the effects of excluded volume on the dimensional properties of stars. In previous work,[12-14] we have focused on the region of fully developed excluded volume, using both Monte Carlo and exact enumeration techniques, and have compared our results with theoretical predictions and experimental estimates of various properties. The statistics of these systems can be characterized (in the asymptotic limit $N \to \infty$) by the expression

$$c_n(f) \sim N^{\gamma(f)-1}\mu^N \tag{1}$$

in which $c_n(f)$ is the number of configurations of uniform stars having a total of $N = (nf + 1)$ monomers. It has been shown[13] that the growth constant μ is independent of f and is identical with that for a self-avoiding walk (SAW). The critical exponent, $\gamma(f)$, decreases as f increases; this is a reflection of the growing interference between branches as f gets larger and is in agreement with the trend predicted by the Miyake and Freed treatment.[7] More experimentally accessible is the ratio $g(f)$ of the mean square radius of gyration, $\langle S_N^2(f)\rangle$, of the branched molecule to that of the linear one ($f = 1$) having the same degree of polymerization. Again, in the asymptotic limit, it is assumed that

$$\langle S_N^2(f)\rangle = A(f)N^{2\nu(f)}[1 + DN^{-\Delta} + ...] \tag{2}$$

Often only the dominant term is considered, but a correction of the above form, with $\Delta = 0.47$, is predicted by renormalization group treatments.[15] In both theoretical treatments[6,7] $\nu(f)$ is thought to be independent of f and equal to ν, the exponent associated with a self-avoiding walk; the simulation results support this. Thus $g(f)$ is obtained through the amplitude ratio $A(f)/A(1)$, where $A(1)$ is the limiting amplitude for a self-avoiding walk. Estimates of $g(f)$ for $f = 3$-6 were found to be in good agreement with both experimental results and theoretical predictions.[14] In the latter category, the Zimm-Stockmayer[5] and experimental values are impressively close over the range of f, while the renormalization group predictions[7] are slightly higher, a trend which becomes more marked with increasing f. Interestingly, it would appear that $g(f)$ is insensitive to solvent quality, a point which will be discussed in more detail later in this work. Finally, the star systems have also been characterized through the f dependence of the end-to-end branch length.[12,14]

The recent interest in uniform stars has probably been fueled by the developement of reliable synthetic routes whereby well-characterized structures can be produced. A logical extension of these studies involves a straightforward change in topology, i.e., an increase in the number of branch points, preferably in a controlled fashion. In this paper we consider such structures with the branch points arranged regularly along the backbone of the molecule. We refer to structures in which every branch point has functionality *three* as combs and to those having at least one branch point of functionality greater than three as *brushes*. While a few experimental studies have appeared on comb molecules, most have been concerned with the synthetically more straightforward case of the branches randomly distributed along the chain.[16] There have been some simulation studies on these systems, most notably one by McCrackin and Mazur[17] in which excluded volume effects were incorporated. Theoretical predictions on randomly branched combs are limited to the case for which Gaussian statistics apply.[5,18] The connection between experimental data and such a calculation is still unclear.

This paper is primarily concerned with the particular example of a uniform comb with two branch points (an H-comb), for which there exist both some experimental data and several theoretical predictions on the ratio g, one of which addresses the good-solvent regime. Roovers and Toporowski[19] were able to synthesize polystyrene molecules having two branch points of functionality three, regularly spaced along the backbone chain, and to measure the ra-

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dius of gyration and intrinsic viscosity in two solvents considered to be good and Θ-solvents for linear polystyrene.

The theoretical description of uniform combs is less advanced than that of stars. For the case in which the subchains of a uniform comb are assumed to follow random walk statistics[5,18,20]

$$g = \lambda - \frac{1}{p+1}\lambda^2(1-\lambda) + \frac{2\lambda}{p}(1-\lambda)^2 + \frac{3p-2}{p^2}(1-\lambda)^3 \quad (3)$$

where p is the number of branches and λ is the fraction of polymer in the backbone. These quantities would be 2 and $^3/_5$, respectively, for a uniform H-comb, leading to $g = 0.712$. In a more recent treatment Douglas and Freed[21] combined two-parameter theory and renormalization group methods in order to treat excluded volume effects on a number of polymer properties, including g for uniform comb polymers. Although they expect their treatment, called renormalized two-parameter (RTP) theory, to apply over the whole range of excluded volume interaction, the paper focuses on the good-solvent region for which they give a value of $g = 0.720$. The results listed above will be discussed in more detail in section III.

In this work, we present exact enumeration and Monte Carlo results for uniform and slightly nonuniform H-combs and for some brushes on a variety of lattices in three dimensions. In section II, we examine the statistics of these systems, estimating γ and making comparisons with $\gamma(3)$ and $\gamma(5)$ for uniform stars. In section III, we discuss the mean square radius of gyration and the associated ratio g and compare our results to those available in the literature. Section IV is concerned with the dimensions of the internal bridging segment relative to that of the external branches. Here it is interesting to note the effects of varying the branch length and the functionality of one of the branch points on the dimensions of the bridge. Finally, our results are discussed in section V.

II. Statistics

In this section we report some results on the n dependence of the number of embeddings of uniform combs and brushes with n edges in each branch. We shall consider first the case of 2-combs (i.e., those with the topology H). In this case there are five branches and the total number of monomers is given by $N = 5n + 1$. It is expected that $c_n(\mathrm{H})$ is described by a relationship having the same functional form as eq 1, and it has been proved[22] that the growth constant μ is the growth constant of self-avoiding walks.

We have estimated $c_n(\mathrm{H})$ for several lattices in three dimensions, using an inversely restricted Monte Carlo method,[23] with a sample size typically of the order of 50 000. We have also calculated $c_n(\mathrm{H})$ exactly for small n, and the Monte Carlo results are in excellent agreement with these data. We have estimated the exponent $\gamma(\mathrm{H})$ by extrapolating $\ln (c_n/\mu^N)/\ln N$ against $1/\ln N$, and we show some typical results in Figure 1. Our final estimate is $\gamma[\mathrm{H}] = 0.91 \pm 0.02$.

This should be compared with our estimate in two dimensions[22] of $\gamma[\mathrm{H}] = 0.79 \pm 0.02$. The extent to which this value is lower than the corresponding value for a self-avoiding walk (about $^4/_3$ in two dimensions and about $^7/_6$ in three dimensions) reflects the interference between the branches of the comb. It is clear that this interference is much greater in two dimensions than in three dimensions, as one would expect. (In four and higher dimensions the value of this exponent would be expected to be unity, the Bethe lattice value, for any fixed topology.) The value

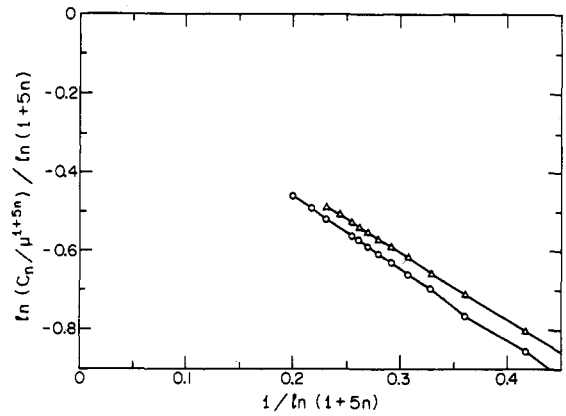

Figure 1. Extrapolation of $\ln (c_n/\mu^{1+5n})/\ln (1 + 5n)$ against $1/\ln (1 + 5n)$ to estimate $\gamma(\mathrm{H}) - 1$ for the simple cubic (○) and face-centered cubic (△) lattices.

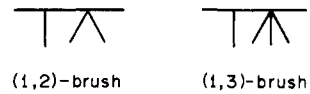

Figure 2. (1,2)-brush and a (1,3)-brush.

of $\gamma(\mathrm{H})$ is lower than that of a 3-star[14] (1.05 ± 0.03), indicating more interference in the case of combs. However, it is higher than that of a 4-star (0.88 ± 0.03) and, a fortiori, than that of a 5-star (0.55 ± 0.05), indicating that the five branches interfere less in the case of a comb.

This effect of interferences can also be seen when we compare the value of the exponent γ with the corresponding value for brushes. In Figure 2 we show examples of (1,2)- and (1,3)-brushes. We have estimated the value of $\gamma(1,2)$ and $\gamma(1,3)$, and the estimates are

$$\gamma(1,2) = 0.68 \pm 0.03$$

and

$$\gamma(1,3) = 0.4 \pm 0.1$$

The value of the exponent decreases as the functionality of the branch point increases, reflecting the interference between the branches. The magnitude of the decrease is similar to that found when the functionality of the branch point of a star is increased.

III. Radius of Gyration

As mentioned in the introduction, the radius of gyration of a uniform star having f branches is described (in the limit $N \to \infty$) by eq 2. A similar expression is expected to be valid for comb and brush molecules, with ν also being equal to the exponent characterizing a self-avoiding walk. Evidence for this is shown in Figure 3 in which $\ln \langle S_N^2 \rangle$ is plotted against $\ln N$ for the cases of SAW, H-combs, 3-stars, and 5-stars on the simple cubic lattice. Both Monte Carlo (sample sizes 70 000–100 000) and exact enumeration data have been included, and it is clear that the dimensions of the molecules are governed by the same exponent. Thus, it is the limiting amplitude which characterizes the variation of $\langle S_N^2 \rangle$ with topology for these simple branched structures, and it is the ratio of amplitudes which can be compared with experimental data. In order to estimate these amplitudes the results are plotted as shown in Figure 4. Here we compare the data for a uniform H-comb with that for a 5-star on the simple cubic lattice.[14] The 5-star is more compact than the comb, which is, in turn, more compact than the linear chain. Presumably the difference arises because the crowding of monomers around the single $f = 5$ branch point of the star is more effective in reducing the size of the molecule than

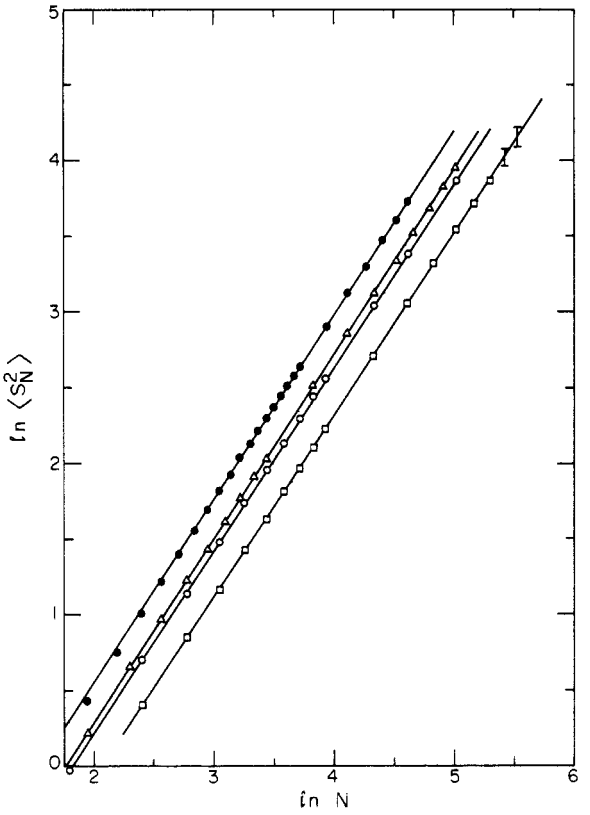

Figure 3. log–log plot of the mean square radius of gyration against the degree of polymerization for self-avoiding walks (●), 3-stars (△), H-combs (○), and 5-stars (□), on the simple cubic lattice.

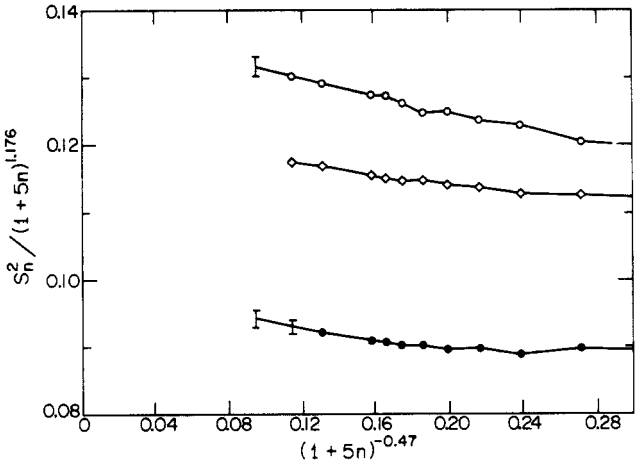

Figure 4. Scaled mean square radius of gyration $\langle S_N^2\rangle/(1 + 5n)^{1.176}$ against $1/(1 + 5n)^{0.47}$ for H-combs on the simple cubic (○) and bcc (◇) lattices. The results for 5-stars on the simple cubic lattice (●) are given for comparison.

the packing restrictions imposed by the presence of two $f = 3$ branch points. Thus, it seems that for these classes of structures g will always be less than unity, a conclusion supported by experimental results and by theoretical estimates.

Figure 4 also illustrates the data for H-combs on the body-centered cubic [bcc] lattice. The numbers have been normalized so that the step length is unity, and the amplitudes estimated from these plots are given in Table I.

Finally, we consider the effects of varying the fraction of mass in the external arms relative to the bridging arm. Now the topology is fixed, but the relative branch lengths change. On the tetrahedral lattice only, structures were

Table I
Estimates of the Amplitudes for the Mean Square Radius of Gyration of an H-Comb

	A[H]	A[1], self-avoiding walk	g
face-centerd cubic	0.116 ± 0.001	0.164 ± 0.002	0.71 ± 0.02
body-centered cubic	0.123 ± 0.002	0.172 ± 0.002	0.72 ± 0.02
simple cubic	0.138 ± 0.002	0.195 ± 0.002	0.71 ± 0.02
tetrahedral[a]	0.186 ± 0.001		0.77 ± 0.03
	0.168 ± 0.001	0.24 ± 0.01	0.70 ± 0.03
	0.156 ± 0.001		0.65 ± 0.03

[a] The three values for the tetrahedral lattice correspond to the internal branch having twice as many monomers as, the same number of monomers as, and half as many monomer as the external branch, respectively.

Table II
Estimates of the Ratio g for H-Combs

	experimental		random	renormalized
this work	good solvent	θ-solvent	walk	two parameter
0.71 ± 0.01	0.69 ± 0.02	0.69	0.712	0.72

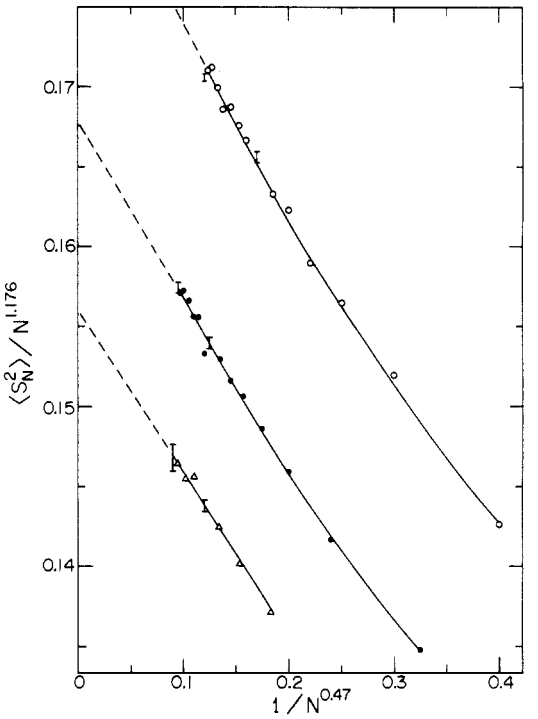

Figure 5. As Figure 4 but for H-combs on the tetrahedral lattice with external branches twice as long (△), equal to (●), and half as long as (○) the internal branch.

grown having branch:bridge ratios of 0.5, 1.0, and 2.0. The results for the radius of gyration are given in Figure 5. The relative amplitudes indicate that, for a given degree of polymerization, the presence of short stubby chains will be more influential in swelling the molecule than will longer arms.

Table I summarizes the values of g obtained for the different lattices, and in Table II the average of these is compared with the experimental results of Roovers and Toporowski[19] and with a number of theoretical predictions. The values are all very close, the most notable difference being that the theoretical estimates are, for the most part, slightly higher than the experimental ones. As in the case of uniform stars, the extent to which excluded volume effects are incorporated is not very strongly reflected in the ratio g. This point is addressed in greater detail in the Discussion.

Table III
Estimates of the Amplitude for the Mean Square Lengths of the Internal [B_i] and External [B_e] Branches of an H-Comb

	B_i[H]	B_e[H]	B_i[H]/B_e[H]
face-centered cubic	1.39 ± 0.02	1.14 ± 0.01	1.22 ± 0.03
body-centered cubic	1.48 ± 0.02	1.21 ± 0.02	1.22 ± 0.03
simple cubic	1.65 ± 0.02	1.35 ± 0.02	1.22 ± 0.03
tetrahedral[a]	2.05 ± 0.02		
	2.18 ± 0.02	1.80 ± 0.02	1.21 ± 0.03
	2.34 ± 0.02		

[a] For the tetrahedral lattice the three values correspond to the same conditions as in Table I.

IV. Internal and External Branch Lengths

If there were no excluded volume effect, then the mean square end-to-end length of the internal branch (joining the two branch points) would be the same as the mean square end-to-end length of an external branch (joining a branch point to a vertex of degree one). Excluded volume effects should expand the internal branch more than the external branches. To investigate this, we have estimated for large n, and calculated exactly for small n, the values of these mean square lengths, $\langle R_n^2(\text{ext})\rangle$ and $\langle R_n^2(\text{int})\rangle$, and used these data to estimate the corresponding amplitudes B_e and B_i by assuming, in analogy with self-avoiding walks,[15] the form

$$\langle R_n^2(\text{ext})\rangle = B_e n^{2\nu}(1 + D_e n^{-\Delta} + \ldots) \qquad (4)$$

with a similar expression for the dimensions of the internal branch.

Estimates of the amplitudes B_e and B_i are given in Table III for various lattices, together with the amplitude ratios B_i/B_e. It appears that these amplitude ratios are lattice-independent quantities, depending only on the dimension. There is clear evidence of increased expansion of the internal branch, this effect being greater in two dimensions than in three. We also note that the amplitudes for the external branches are very similar to the corresponding amplitudes for 3-stars (e.g., $B(3) = 1.35 \pm 0.01$ for the simple cubic lattice). We have also investigated the effects of varying the relative mass contained in the backbone by generating combs (on the tetrahedral lattice) in which the ratio of the number of monomers in the external branch to the number of monomers in the internal branch is 0.5, 1.0, and 2.0. As can be seen in Figure 6, the effect of increasing the monomer density is to swell the internal branch.

The same effect occurs in the case of brushes. In Figure 7 we show the dimensions of the internal branch of combs, (1,2)-brushes, and (1,3)-brushes on the simple cubic lattice, with the corresponding results for 3-stars included for comparison. The expansion of the internal branch increases as the functionality of the branch point in the brush increases. In the case of brushes there are two different kinds of "external" branches. The ones incident on a branch point of functionality three have dimensions similar to the arms of a 3-star, while the other external branches have dimensions similar to those of a four-star or 5-star for (1,2)- and (1,3)-brushes, respectively.

V. Discussion

In this paper we have extended our exact enumeration and Monte Carlo studies to include uniform branched polymers having two branch points, in particular combs and (1,2)- and (1,3)-brushes. In our previous work on simple branched polymers[14] we studied the effects of increasing the functionality of the single branch point on the statistical and dimensional properties of uniform stars.

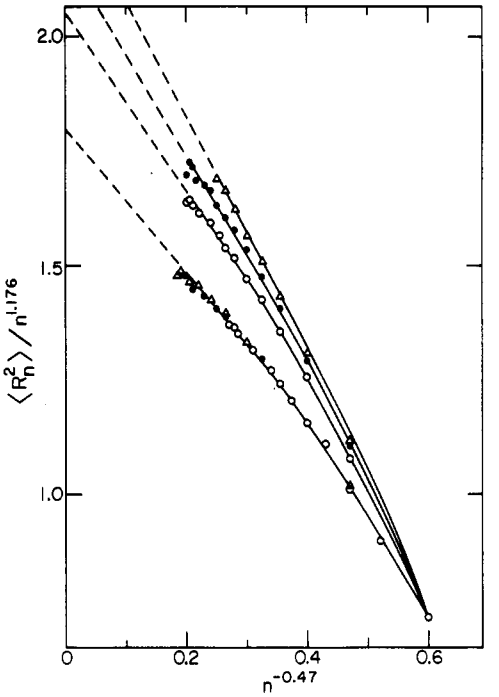

Figure 6. Scaled dimensions of the internal branches of H-combs on the tetrahedral lattice with external branch twice as long as (△), equal to (●), and half as long as (○) the internal branch. Results for the external branch fall on the single bottom curve.

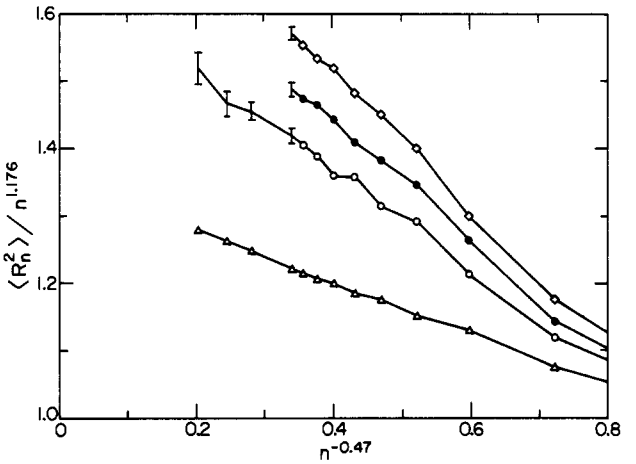

Figure 7. Scaled dimensions of the internal branch for 1,3-brushes (◇), 1,2-brushes [●], and H-combs (○) on the simple cubic lattice. Results for the branch length of a 3-star (△) are given for comparison.

Some features of the systems considered here are quite new; in particular, we now have different kinds of branches within one structure. For combs the results in section IV clearly show the expansion of the internal segment relative to the external branches, the latter having an average mean square end-to-end distance similar to that of the branches in 3-stars. In the case of stars the presence of one branch point was seen to expand a branch relative to a self-avoiding walk; therefore, it is logical that the dimensions of the bridging segment in a comb or a brush would reflect the influence of two branch points. Varying the ratio of monomers in the internal/external branches also resulted in a swelling of the internal segment, as clearly indicated in Figure 6, due to the influence of increased monomer density. Both of these effects were present in the case of (1,2)- and (1,3)-brushes that incorporated additional branches at one branch point; increased crowding at this position and the presence of the monomers in the new

branches not only yielded a larger value for $\langle R_n^2(\text{int})\rangle$ but also removed the indistinguishability of the two sets of external branches, the ones around $f = 4$ and 5 being expanded relative to those at $f = 3$. Note that neither the existing theoretical work nor the experimental work on combs is able to differentiate between the contributions of internal and external branches to the dimensions of the molecule. In this case simulation studies not only bridge experiment and theory but also lead to results that had not been accessible through other techniques.

As in the case of stars, comparison of our value for g with experimental results and theoretical estimates indicates that this ratio is relatively insensitive to solvent quality. There has been some comment on this in the literature: in a paper on the effects of local segment concentration on the solution behavior of stars and combs, Candau et al.[24] discussed the change in the expansion factor, α^2, in going from a linear to a branched molecule, where for a given structure

$$\alpha^2 = \langle S^2\rangle / \langle S^2\rangle_0 \tag{5}$$

$\langle S^2\rangle_0$ denoting the case of unperturbed, or Gaussian, statistics. Of course

$$\alpha_b^2/\alpha_l^2 = g/g_\theta \tag{6}$$

The authors noted that literature values of α^2 were similar for branched and linear polymers and suggested that this could be due to an inappropriate definition of the Θ-dimensions. The latter is associated both with the temperature at which $\alpha^2 = 1$ and with the temperature at which the second virial coefficient vanishes. For linear chains these two are expected to be coincident and hence *that* temperature is *defined* as the Θ-temperature. For the branched case the two criteria are not fulfilled at the same temperature; the authors proposed that, instead of measuring $\langle S^2\rangle$ for the branched molecule at the Θ-condition for the linear molecule and identifying this as $\langle S^2\rangle_0$, α^2 be redefined as the ratio of $\langle S^2\rangle$ (measured experimentally or calculated) to a theoretical estimate under conditions of no excluded volume. Their recomputed α^2 values are significantly higher for branched than for linear structures, leading to $g > g_\theta$; this approach has not been adopted by other authors. Roovers and Toporowski[19] note similar observations concerning g for both H- and star-polystyrene molecules, and Douglas and Freed[21] find, using RTP theory to calculate g/g_θ, that for stars and combs this ratio falls between 1.00 and 1.10, reflecting only very small changes in expansion with solvent quality. McCrackin and Mazur,[17] in their simulation studies of randomly branched combs, define g_θ for conditions that produce the critical exponent $2\nu = 1$, the value associated with Gaussian statistics in the linear case, and then find that g/g_θ is always less than unity. They ascribe the analytical predictions of a ratio greater than one as arising from inadequate treatment of the branched polymer under Θ-conditions, commenting that by treating the good-solvent effect through a perturbation expansion about the random walk state, a swelling upon increase in branching is built-in to the description, automatically leading to $g/g_\theta > 1$.

The problem, if it can be called such, is one of definition. For the linear case it has proved useful to develop theoretical models that incorporate Gaussian statistics because there is a relationship between a set of experimental conditions and this description and well-defined criteria for linking the two. The same cannot be said for branched molecules; there is no obvious way of choosing a set of experimental conditions that correspond to a similar kind of theoretical description. Hence g/g_θ does not seem to be a very useful ratio in that it is difficult to draw conclusions about the structure or strength of interactions by comparing g with g_θ.

This is not to say that excluded volume interactions are unimportant in determining the conformation of a branched polymer in solution. Indeed, the behavior of quantities such as the mean square radius of gyration depends crucially upon the quality of the solvent.

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