Statistical and Metric Properties of Long-Chain Combs

J. E. G. Lipson

Department of Chemistry, Dartmouth College, Hanover, New Hampshire 03755

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ABSTRACT: Computer simulation results on statistical and metric properties of long-chain combs are presented. The branches in the comb contain a fixed number of segments and are regularly placed along the backbone such that their number increases linearly with the total number of segments. Three cases have been studied, representing three ratios for the number of segments per branch relative to the number between branch points. Comparison of g ($= \langle S^2\rangle_{comb}/\langle S^2\rangle_{SAW}$, where $\langle S^2\rangle$ represents the mean-square radius of gyration, and SAW stands for self-avoiding walk) with g_{bb} ($= \langle S^2\rangle_{bb,comb}/\langle S^2\rangle_{SAW}$), the analogue of g for the backbone, shows that the combs are both expanded and contracted relative to the dimensions of a SAW. Analysis of the statistical data provides evidence that the growth constants for these kinds of combs are different from that of a SAW on the same lattice; this is in contrast to the case of structures having only one or two branch points.

1. Introduction

There has been an increasing amount of interest over the past few years in branched polymer molecules having simple topologies. Examples of these include stars (in which there is a single branchpoint), starburst molecules (which branch in a fashion reminiscent of a Cayley tree), combs (which have branchpoints of 3° placed at regular or random intervals along a backbone chain), and brushes. There are two slightly different topologies both described as a brush: in one case the structure is similar to that of a comb, but the branchpoints are 3° and higher; in the other case the branches are grafted onto a surface, instead of a line. In the category of combs much of the latest work[1-3] has been for the case in which there are only two branchpoints with the segments evenly distributed among the branches; these are called regular H-combs.

The topology of interest in this work is pictured in Figure 1; the number of branches increases linearly with the number of segments in the molecule, while the branch lengths are fixed. Therefore in the asymptotic limit of infinite degree of polymerization the fraction of material in the branches remains finite. Long-chain combs form one class of liquid crystal polymers; although these are usually studied in nematic solvents, or in the melt, some work has been done in dilute solution for the purpose of molecular weight determination.[4] Other kinds of comb-shaped polymers have also been synthesized recently,[5,6] although there is (as yet) a dearth of data on solution properties. This lattice simulation study will focus on dilute-solution properties; three values have been chosen for the ratio of the number of segments per branch (m) to the number along the backbone between branchpoints (n): 3/10 (type I), 6/6 (type II), and 9/4 (type III).

The quantities of interest in this study involve both the statistical and metric properties of long-chain combs. The dimensions of a *linear* chain are typically characterized through both the mean-square end-to-end length, $\langle R^2\rangle$, and the mean-square radius of gyration, $\langle S^2\rangle$. Many studies have appeared on linear chains, and a large body of evidence indicates the following relationship holds between $\langle S^2\rangle$ and N, the number of segments in the chain:[7]

$$\langle S^2\rangle = AN^{2\nu}[1 + (BN^{-1}) + (CN^{\Delta})] \qquad (1)$$

A, B, and C are amplitudes, and ν and Δ are critical exponents. An analogous functional form can be written for the N-dependence of $\langle R^2\rangle$. Thus, in considering the N-dependence of $\langle S^2\rangle$, the leading order term is of the order $N^{2\nu}$; the other terms are sometimes referred to as "corrections to scaling", and their importance depends on the system being studied. For the case in which there is no excluded volume, the chains can be described using Gaussian statistics;[8] B and C are equal to zero, and ν is identically 0.5. Experimentally, this situation corresponds to a choice of solvent and temperature, giving what is known as "Θ conditions" for the polymer solution being studied. For the case in which lattice sites can be occupied only once (the fully-developed limit of excluded volume) the linear chains are self-avoiding walks (SAWs); this would correspond to a polymer in a good solvent. Here, the best estimate[7] for ν is 0.588 and for Δ is −0.47, although work in this area is still ongoing. Previous lattice Monte Carlo studies on regular stars[9] (all branches have the same number of segments) and H-combs[1] have shown that the functional form given by eq 1 also applies to these systems, with the value of the leading critical exponent, ν, being the same as that for SAWs. In addition, it appears that when the number of branches per branchpoint is small (say, less than 10), the correction-to-scaling terms are relatively unimportant; i.e., the amplitudes B and C are small.[10]

Figure 1. Topology of a long-chain comb. See the text for ratios of m/n used in the study.

For the long-chain combs being studied here the only end-to-end length of interest is $\langle R^2\rangle_{bb}$, that of the backbone. With respect to the radius of gyration, both $\langle S^2\rangle$ and $\langle S^2\rangle_{bb}$ can be calculated and, in principle, are accessible experimentally. In fact, noone has yet done the labeling studies which would lead to results on $\langle S^2\rangle_{bb}$. Of course, Monte Carlo calculations for both $\langle S^2\rangle$ and $\langle R^2\rangle$ will be lattice-dependent. However, much evidence has accumulated to support the notation that ratios such as

$$g = \langle S^2\rangle/\langle S^2\rangle_{SAW} \qquad (2)$$

are lattice-independent, where the quantity in the numerator is for the structure of interest and that in the denominator is for the SAW having the same number of segments. Regular stars and SAWs are well described by the leading order scaling term in eq 1; therefore, in the asymptotic limit g for regular stars can be calculated through the amplitude ratio A(star)/A(SAW). As the

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lattice-independence implies, local structural detail is believed to be unimportant in this limit; therefore, g obtained experimentally for a regular five-branched polystyrene star in a good solvent would be the same as that for a five-branched polyethylene star in a good solvent, as long as both series of measurements were done for high-molecular-weight samples.

In a previous paper[11] some of the metric properties of the systems described in Figure 1 were investigated. Of particular interest were $\langle S^2 \rangle$ and the ratios g and h; h is the ratio of the friction coefficients for the branched and linear structures having the same number of segments. Evidence was provided showing that eq 1 is still a suitable functional form with which to describe $\langle S^2 \rangle$ (and $\langle R^2 \rangle$), and it was concluded that, with respect to their metric properties, self-avoiding long-chain combs of the sort discussed here have the same critical exponents as SAWs. However, it appears that corrections to scaling play a more important role in describing the N-dependence of $\langle S^2 \rangle$ (for example) for combs than for SAWs, regular stars, or H-combs. In addition, a comparison of the Monte Carlo results for g and h with those obtained analytically using a Gaussian model[12-15] showed significant differences. This was in contrast to the results of similar comparisons for stars[9] and H-combs[1] which indicated that the ratio g is relatively insensitive to the effects of excluded volume. On the basis of the simulation results, it was argued that the Gaussian model is less successful at describing systems with a significant (i.e., not fixed) number of branchpoints than when used for those with one or two branchpoints. It also appeared[11] that the dimensions of the comb were not very sensitive as to whether the branches were arranged regularly or randomly since the simulation results, which were for regular placement of the branches, agreed well with some experimental results[16,17] for random placement.

In this work both the metric properties of the comb's backbone (as a function of the ratio m/n), and the statistical properties of these systems are of interest. For linear chains the N-dependence of the number of lattice configurations, c_N, can be expressed in the asymptotic limit by[18]

$$c_N \sim N^{\gamma-1}\mu^N \quad (3)$$

where μ is the growth constant (which is lattice-dependent), and γ is a critical exponent (which depends on the dimension but not on the particular lattice used). For regular stars and H-combs it has been proven[19] that the growth constant is identically that for a SAW. This means that it has been straightforward to analyze statistical data on these systems so as to extract an estimate of the exponent γ, allowing an investigation of how this exponent depends on the number of branches in a star, for example. However, when the number of branches increases with the total number of segments, the growth constant associated with the whole class of such structures is different from the SAW value.[20] The long-chain combs described here make up only a vanishingly small subset of the structures possible when the number of branchpoints increases linearly with the total number of segments. However, it is still true that both the exponent and the growth constant must be determined from analysis of the Monte Carlo data.

The results described in this work were obtained using an inversely-restricted Monte Carlo algorithm, often referred to as the Rosenbluth and Rosenbluth algorithm.[21] Three different combs were studied, as indicated in Figure 1, modeled on the tetrahedral lattice. N ranged between about 20 to about 210 segments; one chain at a time was generated, and only one segment was allowed on any lattice site. Therefore, the simulation was intended to model a dilute solution ($c < c^*$) of long-chain comb polymers in a good solvent. Each new value of N used represented a sufficient increase in the number of segments so as to add another branch. For each N a completely new set of configurations was generated, thus avoiding correlations between data for successive values of N. The number of configurations generated in each case depended on N and on the system being studied. For values of N less than about 100, roughly 100 000–200 000 configurations were typically generated, while for N greater than 100, about 300 000–400 000 configurations were produced. These were generated in batches of 10 000–20 000 so that standard deviations about the mean could be calculated for each quantity of interest; these ranged from 2–5%. The confidence limits given in the tables reflect uncertainty in the graphical fits.

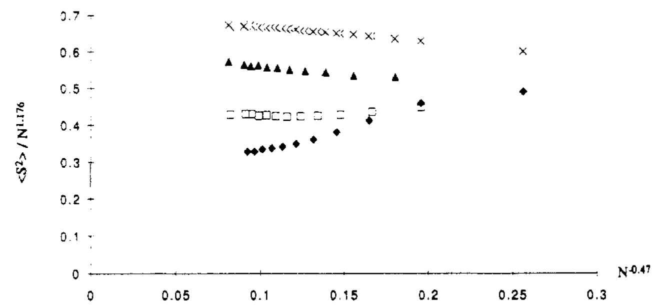

Figure 2. $\langle S^2 \rangle / N^{1.176}$ plotted against $N^{-0.47}$: (×) SAW; (▲) type I comb; (□) type II comb; (◆) type III comb.

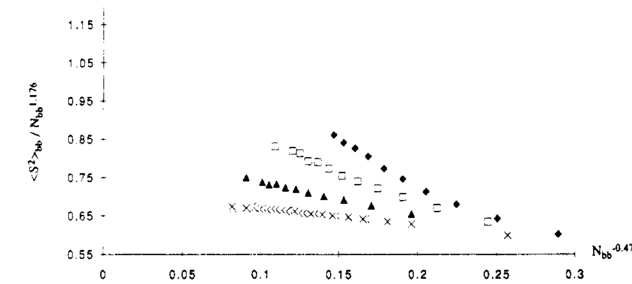

Figure 3. $\langle S^2 \rangle_{bb} / N_{bb}^{1.176}$ plotted against $N_{bb}^{-0.47}$. Symbols as described in the caption to Figure 2.

The following paper is divided into three sections. In section 2 the metric properties are discussed, in section 3 the statistical properties are discussed, and section 4 contains both a summary and the conclusions to be drawn from this work.

2. Metric Properties

There is a fundamental difference in the effect of repeated branching on the overall dimensions and on the backbone dimensions; this is evident in a comparison of Figures 2 and 3. Figure 2 shows $\langle S^2 \rangle / N^{1.176}$ plotted against $N^{-0.47}$ for all three kinds of combs and for SAWs. Taking eq 1 to hold for all these systems, the intercept in each case is the amplitude, A. In previous work amplitude estimates were obtained by fitting the data to eq 1 in its entirety using the method of differential corrections;[22] results for the ratio g are given in Table I. As is clear from Figure 2, the effect of incorporating branches is to reduce the dimension of the comb relative to that of a SAW having the same number of segments. The presence of longer, more closely-spaced branches (type III) results in a greater degree of contraction than that from having shorter, more widely-spaced branches (type I). This can be contrasted with the results of Figure 3, which shows $\langle S^2 \rangle_{bb} / N_{bb}^{1.176}$

Table I
Values of g and g_{bb} for Combs and SAWs on the Tetrahedral Lattice

	SAW	type I	type II	type III
g	1.0	0.43 ± 0.02	0.66 ± 0.02	0.88 ± 0.04
g_{bb}	1.0	1.2 ± 0.1	1.4 ± 0.2	1.6 ± 0.2

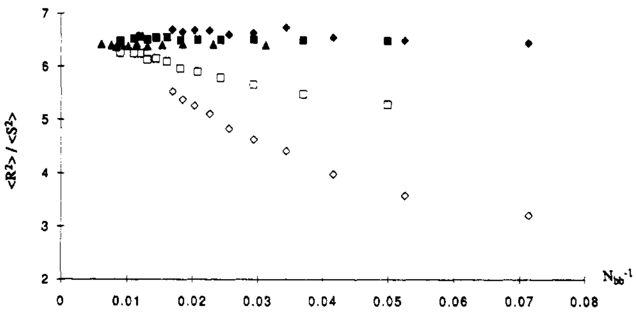

Figure 4. $\langle R^2\rangle/\langle S^2\rangle_{bb}$ (filled symbols) and $\langle R^2\rangle/\langle S^2\rangle$ (open symbols) plotted against N_{bb}^{-1}. Symbols as described in the caption to Figure 2.

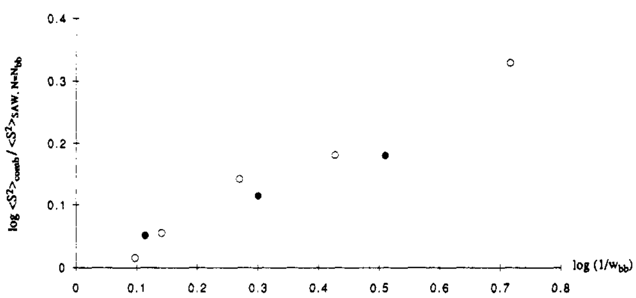

Figure 5. $\log\left(\langle S^2\rangle_{comb}/\langle S^2\rangle_{SAW,N=N_{bb}}\right)$ plotted against $\log(1/w_{bb})$. Filled circles represent simulation results; open circles represent the experimental results of ref 25.

plotted against $N_{bb}^{-0.47}$ for all three combs; the SAW data are included again, for comparison. The backbone in each case is expanded relative to a SAW having the same number of segments. The effect is most pronounced in the type III combs and least pronounced in the type I combs. These data have also been fitted using the method of differential corrections, and the results for g_{bb} are given in Table I. As noted above, this quantity is also accessible experimentally, although labeling studies would be required. Given the preceding comments, it is not surprising to find that g-values are less than unity, while g_{bb}-values are greater than unity. The results listed in Table I show that g_{bb} is between 2 and 3 times greater than g in each case. This implies that there is sufficient difference between these two ratios for each type of comb so as to make them distinguishable through experimental measurements.

Recall that for a linear chain obeying Gaussian statistics the ratio $\langle R^2\rangle/\langle S^2\rangle$ is exactly equal to 6.0. When excluded-volume effects are incorporated, the value increases and different predictions have been made, ranging between about 6.25[23] and about 6.37.[24] Figure 4 shows $\langle R^2\rangle_{bb}/\langle S^2\rangle_{bb}$ plotted against N_{bb}^{-1} for the three types of combs along with the analogous results using $\langle S^2\rangle$ instead of $\langle S^2\rangle_{bb}$. These results indicate that there is a relatively narrow band within which the ratio $\langle R^2\rangle/\langle S^2\rangle$ appears to be headed in the asymptotic limit, roughly between 6.4 and 6.8. Clearly when this ratio is formed using $\langle S^2\rangle_{bb}$, the data converge at much lower N, even though N (total) achieved a maximum value of about 210, while N_{bb} only reached between 59 (type III) and 164 (type I) segments.

Finally, Figure 5 provides a limited comparison with some experimental data on combs.[25] The log–log plot shows $\langle S^2\rangle_{comb}/\langle S^2\rangle_{SAW,N=N_{bb}}$ plotted against $(1/w_{bb})$, where w_{bb} is the weight fraction material in the backbone.

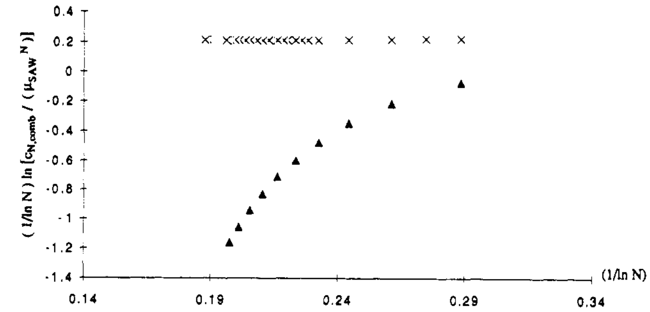

Figure 6. $(1/\ln N)\ln[c_{N,comb}/(\mu_{SAW}^{N})]$ plotted against $1/\ln N$. Symbols as described in the caption to Figure 2.

The experimental results were obtained by using $\langle S^2\rangle$ for the backbone *before* the branches were attached and combining this with $\langle S^2\rangle_{comb}$ results. In order to compare with this, the Monte Carlo results were obtained by interpolating the SAW data to find $\langle S^2\rangle_{SAW,N=N_{bb}}$ and combining this with $\langle S^2\rangle_{comb}$ results to form the required ratio. No error estimates are available for the experimental data, while for the Monte Carlo data the error bars would be approximately the size of the symbols. The agreement between the two sets of results is good; of course a more interesting comparison would be with experimental results in which $\langle S^2\rangle$ had been determined for the backbone with the branches attached, through labeling studies.

3. Statistical Properties

It is reasonable to suppose that, in the asymptotic limit, the functional form for the N-dependence of the number of configurations of long-chain combs will be that of eq 3. Whittington has recently proven the existence of the growth constant, μ_{comb}, for regular combs.[26] Using the form of eq 3, but dividing both sides by μ_{SAW}^N, yields

$$c_{N,comb}/(\mu_{SAW}^{N}) \sim N^{\gamma_{comb}-1}\,(\mu_{comb}/\mu_{SAW})^{N} \qquad (4)$$

Taking the logarithm of both sides and dividing by $\ln N$ gives

$$(1/\ln N)\ln[c_{N,comb}/(\mu_{SAW}^{N})] \sim (\gamma_{comb}-1) + N\ln(\mu_{comb}/\mu_{SAW})/\ln N \qquad (5)$$

For regular stars it has been proven that $\mu_{star} = \mu_{SAW}$.[19] For that case a plot of $(1/\ln N)\ln[c_{N,star}/(\mu_{SAW}^{N})]$ against $1/\ln N$ yields a straight line whose intercept gives the critical exponent. Undertaking the same kind of analysis with the data on combs is not as fruitful, as Figure 6 shows. Comparing the SAW results with those for the type III combs, the N-dependence of the slope implies that $\mu_{comb} \neq \mu_{SAW}$. Hence, both the growth constant and the critical exponent for combs must be treated as unknowns and extracted from the simulation data. This can be accomplished by plotting $(1/N)\ln[c_{N,comb}/(\mu_{SAW}^{N})]$ against $(\ln N)/N$, as shown in Figure 7. The slope of the straight line yields an estimate of the critical exponent and the intercept an estimate of the growth constant; a plot of the SAW data yields an intercept of zero, as expected. The results are summarized in Table II.

What can be concluded from these results? In order to be able to analyze these data it is necessary to assume that corrections to the scaling equation are unimportant; this is a standard assumption. Consider first the critical exponent: For the SAW results analyzed here the exponent obtained is 1.21, compared to the best renormalization group estimate of 1.1615.[27] For the combs, the estimates for the exponent differ noticably from the SAW value, although they are much closer to the value for a SAW

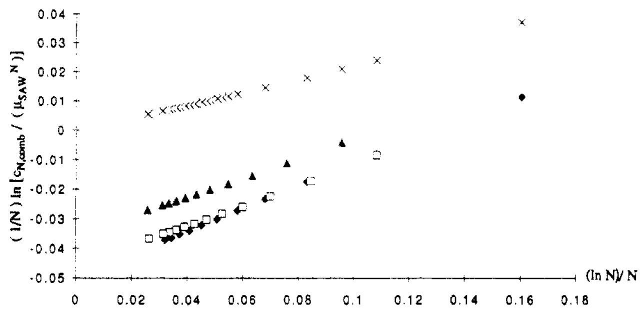

Figure 7. $(1/N)\ln[c_{N,\text{comb}}/(\mu_{\text{SAW}}{}^N)]$ plotted against $(\ln N)/N$. Symbols as described in the caption to Figure 2.

Table II
Growth Constant and Critical Exponent (γ) for Combs and SAWs on the Tetrahedral Lattice

	SAW	type I	type II	type III
$\mu_{\text{comb}}/\mu_{\text{SAW}}$	1.00 ± 0.01	0.96 ± 0.01	0.96 ± 0.01	0.96 ± 0.01
γ	1.21 ± 0.01	1.32 ± 0.03	1.34 ± 0.03	1.38 ± 0.03

than to that, say, for an unrestricted tree,[28] where the exponent (analogous to $\gamma - 1$) in three dimensions is -1.55.[29]

It is possible to investigate the effects on the critical exponent of going from a SAW to a regular comb analytically, if one works on a Bethe lattice. Although a Bethe lattice cannot allow the effects of excluded volume to be incorporated, it may be instructive to determine what features are necessary in order to find an change in the exponent. Consider, first, a SAW of N segments on a Bethe lattice having a lattice coordination number of z_B. The number of configurations is easily written as

$$c_{N,\text{SAW}}(\text{B}) = z_B(z_B - 1)^{N-1} \approx N^0(z_B - 1)^N \quad (6)$$

Therefore, $\gamma_{\text{SAW}}(\text{B}) = 1$ and $\mu_{\text{SAW}}(\text{B}) = (z_B - 1)$. Next, consider a comb having t teeth, therefore, $2t + 1$ sections in total, amongst which the N segments can be distributed. For the case of a strictly regular comb there is only one way to distribute the N segments, but that constraint shall not be applied just yet. If all possible distributions are allowed, such that each section has at least one segment, the total number of configurations is given by

$$c_N(\text{B},t) = \sum_{m_1}\sum_{m_2}\cdots\sum_{m_{2t}}(1/\sigma)z_B(z_B - 2)^t(z_B - 1)^{N-t-1} \quad (7)$$

The sums represent the number of ways of distributing the segments among the $2t$ sections (since with N segments in total, the number in the $(2t + 1)$st section would then be determined) and are subject to the constraint that each section has at least one segment and that

$$\sum_{j=1}^{2t+1} m_j = N \quad (8)$$

σ is a symmetry factor which has a value of 1 if the structure has no center of symmetry and a value of 2 if it does. If the restriction of having the same number of segments per section is now applied, then all of the sums in eq 7 are just replaced by a factor of 1. In addition, if $t = \alpha N$ ($\alpha < 1$), then eq 7 becomes

$$c_{N,\text{comb}}(\text{B},t) = (1/\sigma)z_B(z_B - 2)^{\alpha N}(z_B - 1)^{N(1-\alpha)-1} \quad (9)$$

Just as for the case of the SAW on the Bethe lattice, it seems that $\gamma = 1$ (i.e., there is a factor of N^0). It is easy to see what is required in order to find a nonzero exponent for N: some relaxation of the requirement that the segments all be distributed equally amongst the sections. Therefore, some degree of randomness must be incorporated in order to see a change in the exponent. Of course, this argument does not prove that such a change is needed on the tetrahedral lattice, for example, in order for the critical exponent to change. However, it does hint that the constraints imposed by having such a regular structure may be too severe to effect a change in the universality class.

For all three types of combs the growth constant is close to the SAW value; however, it will be argued here the difference is real. Consider the case of a regular comb having t teeth, n segments between branchpoints along the backbone, and m segments per branch, placed on a lattice having coordination number z. Whittington has proven that the growth constant for such a structure exists and is finite;[26] simple combinatoric arguments allow the calculation of a weak upper bound on the number of configurations for the system described above. In particular, consider the number of ways of placing segments in the $(t + 1)$ sections of backbone (with n segments per section) and then segments in the t teeth (with m segments per tooth) at regular intervals along the backbone. If the only restriction upon placement of a segment is that it not overlap with the previously-placed segment, the result is $[z(z - 1)^{(n-1)}(z - 1)^{t(n+m-1)}(z - 2)^t]$ for the number of configurations ($c_N(\text{est})$), which is certainly greater than the number of completely self-avoiding configurations possible. An estimate of the growth constant, $\mu_{\text{comb}}(\text{est}) > \mu_{\text{comb}}(\text{real})$, is obtained as

$$\ln \mu_{\text{comb}}(\text{est}) = \lim_{N\to\infty} (1/N) \ln (c_N(\text{est})) = \lim_{t\to\infty} [1/(n + m)] \ln [(z - 2)(z - 1)^{n+m-1}] \quad (10)$$

Since n and m are fixed, this limit corresponds to $t \to \infty$. Consider the case in which $n = m = 1$, and $z = 4$. Then $\mu_{\text{comb}}(\text{est}) = 2.45$; this is roughly 85% of the value of the growth constant for a SAW on the tetrahedral lattice, which is 2.876. Unfortunately, for higher values of n and m the bound is too weak to be useful.[30]

In very recent work Nemirovsky et al.[31] have examined the configurations and statistics of a single chain using their lattice cluster theory and conclude that the growth constant for the single chain is less than that of a SAW on the same lattice. Their Figure 10 shows the entropy per monomer for a regular comb against the branching density, for a series of concentrations. The entropy per monomer in the asymptotic limit is identically the growth constant, μ, and in the terminology of the present paper the branching density is $1/(n + m + 1)$ for each type of comb. The results of this Monte Carlo study correspond to what Nemirovsky et al. consider to be the infinite dilution limit, described by their eq 14. These equations are applicable to the hypercubic lattice; hence, their numbers cannot be directly compared with those given here. However, it is interesting to look at how their prediction for the ratio of $\mu_{\text{comb}}/\mu_{\text{SAW}}$ compares with the Monte Carlo results since, as noted above, ratios of lattice-dependent quantities are expected to be lattice-independent. Using their eq 14 for all three types of combs studied here, this ratio is, to two significant figures, equal to 0.98. Just as the Monte Carlo results of the present study show, this is close to, but strictly less than, unity.

4. Summary and Conclusion

In this work some of the statistical and metric properties of long-chain combs having branches of a fixed number of segments, evenly spaced along the backbone, have been investigated. It has been shown that, while the overall dimensions of the comb are reduced relative to a SAW having the same number of segments, the backbone is expanded. This difference is reflected in g-values which are less than unity and g_{bb}-values which are greater than unity. With respect to the statistical properties, it is proposed that the growth constant for long-chain combs is different than that for SAWs. Results for the critical exponent are less conclusive; it is possible that some degree of randomness, either in the branch lengths or branch placement, would be needed in order for the critical exponent to change definitively from the SAW value.

The results of this study, combined with those from the earlier work,[11] show both similarities and differences between long-chain combs and SAWs. The presence of many branchpoints on the backbone leads to the interesting case of having a system which is, in a sense, both expanded and contracted relative to SAW. In addition, it is evident that the inadequacy of the Gaussian model in dealing with the effects of a branchpoint is magnified by the presence of so many branchpoints. Hence, that approach to estimating ratios of metric quantities is less useful for long-chain combs than it proved to be for stars and H-combs. Further experimental work on long-chain combs should bear out both of these observations. Unfortunately, there is no experimental technique available to investigate the statistical properties of these systems. One conjecture should be testable using simulation studies: that some degree of randomness in the comb may lead to a significant change in the value of the critical exponent γ.

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