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LETTER TO THE EDITOR

Lattice models of branched polymers: uniform combs in two dimensions

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Abstract. We establish rigorously the relationship between the growth constant of uniform trees with two branch points and that of self-avoiding walks. For combs, we estimate the corresponding exponent and study the mean-square lengths of the internal and external branches.

Recently there has been considerable interest in uniform star polymers. These are structures having f branches with equal numbers (n) of bonds meeting at a common vertex and having a total of $N = nf + 1$ monomers. Simulation studies (Lipson *et al* 1985, Wilkinson *et al* 1986, Whittington *et al* 1986) have been very useful in testing the predictions of scaling (Daoud and Cotton 1982) and renormalisation group (RG) treatments (Miyake and Freed 1983) of these systems, but have raised questions about the accuracy of the RG treatment for high values of f. The simulation results (Mazur and McCrackin 1977, Zimm 1984a, b, Freire *et al* 1986, Whittington *et al* 1986) are in close agreement with experimental measurements (Huber *et al* 1984) of $g(f)$, the ratio of the mean-square radius of gyration of an f star to that of a linear polymer with the same number of monomers. They confirm that $g(f)$ is relatively insensitive to the effects of excluded volume. However, excluded volume effects are clearly important in determining the detailed structure of the polymer as well as the critical exponents.

The effects of excluded volume on the properties of uniform branched polymers with more than one branch point have received little attention (Berry and Orofino 1964, Roovers and Toporowski 1981, Douglas and Freed 1984) and we report here the first simulation study of such systems. In this letter, we focus on uniform combs with two vertices of degree three (H combs) in two dimensions. We prove rigorously that the growth constant of such structures is equal to μ^5, where μ is the growth constant of self-avoiding walks, and present exact enumeration and Monte Carlo results for the number of H combs and for the mean-square end-to-end lengths of the internal and external branches. The internal branch is that which joins the two branch points; in the absence of excluded volume effects there would be no difference in the dimensions of the two kinds of branches.

First we derive some rigorous results on the growth constant of H combs and some related structures, namely brushes with two branch points, one of which is of degree d_1 and the other of degree d_2, i.e. a $(d_1 - 2, d_2 - 2)$ brush. We shall consider a hypercubic lattice in d dimensions, so that the lattice coordination number is $2d$, and write the coordinates of a lattice point as $(x_1, x_2, \ldots, x_d)$ where the x_k are integers. Suppose

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that the number of (weak) embeddings per lattice site of such a brush with n edges in each branch is $b_n(d_1-2,\ d_2-2)$. We shall show that

$$\lim_{n\to\infty} n^{-1}\log b_n(d_1-2,\ d_2-2)=(d_1+d_2-1)\log\mu \qquad (1)$$

where μ is the growth constant for self-avoiding walks.

To derive an upper bound on b_n we consider each uniform star with d_1 branches and n edges in each branch. Translate the star so that its vertex of degree d_1 is at the origin. Now for each branch in turn, translate each star in turn with (d_2-1) branches so that the end point of the chosen branch of the d_1 star coincides with the branch point (of degree d_2-1) of the (d_2-1) star. The set of graphs obtained by this construction includes all $(d_1-2,\ d_2-2)$ brushes so that

$$b_n(d_1-2,\ d_2-2)\leqslant d_1 s_n(d_1)s_n(d_2-1)$$

where $s_n(f)$ is the number of weak embeddings of an f star. Hence

$$\limsup_{n\to\infty} n^{-1}\log b_n(d_1-2,\ d_2-2)\leqslant d_1\log\mu+(d_2-1)\log\mu \qquad (2)$$

where we have used the fact that the growth constant of uniform f stars is μ^f (Wilkinson *et al* 1986).

Let the number of self-avoiding walks with n edges be c_n. Consider the subset $(C^{\ddagger}(n))$ of these walks in which the two vertices of unit degree have respectively the *minimum* and *maximum* x_d coordinates of all vertices in the walk. Let the number of n-edge walks in this subset be $c_n^{\ddagger}$. It has been shown by Hammersely and Welsh (1962) that

$$\lim_{n\to\infty} n^{-1}\log c_n^{\ddagger}=\lim_{n\to\infty} n^{-1}\log c_n\equiv\log\mu.$$

In turn, translate each member of $C^{\ddagger}(n)$ so that the vertex of unit degree with minimum x_d coordinate is at the origin. Suppose that the other unit degree vertex is then at $(x_1^0, x_2^0, \ldots, x_d^0)$. We now construct $2d-1$ *wedges* as follows:

$$W_{2k-1}:\quad \{(x_1, x_2, \ldots, x_d)|x_k\leqslant 0,\ x_k<x_l\leqslant 0\ \forall l\neq k\}$$

$$W_{2k}:\quad \{(x_1, x_2, \ldots, x_d)|x_k\geqslant 0,\ -x_k<x_l\leqslant 0\ \forall l\neq k\}$$

where k runs from 1 to $(d-1)$. In addition

$$W_{2d-1}:\quad \{(x_1, x_2, \ldots, x_d)|x_d\leqslant 0,\ |x_l|\leqslant|x_d|\ \forall l\neq d\}.$$

These $2d-1$ wedges all contain the origin but are otherwise disjoint. In addition, none of them contains any point with positive x_d coordinate.

We now construct a set (S) of stars with d_1 branches by concatenating d_1-1 self-avoiding walks of n edges each confined to a wedge $W_1, W_2, \ldots, W_{d_1-1}$ and a walk from $C^{\ddagger}(n)$. These graphs are stars (since none of the arms can overlap) and these stars can be constructed in

$$c_n^{\ddagger}\prod_{k=1}^{d_1-1} c_n(W_k)$$

ways, where $c_n(W)$ is the number of self-avoiding n-step walks confined to the wedge W. Only vertices in the walk from $C^{\ddagger}(n)$ have positive x_d coordinate and a single vertex (of degree 1) has maximum x_d coordinate. This vertex has coordinates $(x_1^0, x_2^0, \ldots, x_d^0)$. We now construct wedges $V_1, V_2, \ldots, V_{2d-1}$ which

(i) all contain $(x_1^0, x_2^0, \ldots, x_d^0)$,

(ii) are otherwise mutually disjoint and

(iii) have $x_d \geqslant x_d^0$

in a similar way to the construction of $W_1, W_2, \ldots$. We concatenate each member of S with self-avoiding walks in each of the wedges $V_1, V_2, \ldots, V_{d_2-1}$ to form brushes with functionalities d_1 and d_2. This can be done in

$$c_n^{\ddagger} \prod_{k=1}^{d_1-1} c_n(W_k) \prod_{l=1}^{d_2-1} c_n(V_l)$$

ways and this quantity is a lower bound to $b_n\ (d_1-2, d_2-2)$. Hence

$$\liminf_{n\to\infty} n^{-1} \log b_n(d_1-2, d_2-2) \geqslant [(d_1-1)+(d_2-1)+1] \log \mu \tag{3}$$

where we have made use of a result of Hammersley and Whittington (1985) that self-avoiding walks in diverging wedges have growth constant μ. Equation (1) then follows from (2) and (3).

The proof of the upper bound using concatenation of two stars has the advantage that it yields the exponent inequality

$$\gamma(d_1-2, d_2-2) \leqslant \gamma(d_1) + \gamma(d_2-1) - 1.$$

Although this is weak for small d_1, d_2 it may prove useful for larger functionalities.

We assume the usual asymptotic form for the number, $c_n(H)$, of H combs having n edges in each branch:

$$c_n(H) \sim n^{\gamma(H)-1} \lambda(H)^n$$

where $\lambda(H) = \mu^5$. The exact values of $c_n(H)$ for small n are given in table 1 for the honeycomb, square and triangular lattices. Some of these data, together with some preliminary Monte Carlo data obtained by an inversely restricted sampling technique (Rosenbluth and Rosenbluth 1955), are presented in figure 1 where we plot $\ln[c_n(H)/\lambda^n]/\ln N$ against $1/\ln N$, where $N = 5n+1$. This is asymptotically linear, as expected, and has an intercept equal to $\gamma(H)-1$.

Our overall estimate

$$\gamma(H) = 0.79 \pm 0.02$$

is in excellent agreement with the recent result $\gamma = \frac{25}{32} = 0.781\,25$ due to Duplantier (1986). This is significantly lower than our corresponding estimate $\gamma(3) \simeq 1.07$ (Wilkinson *et al* 1986) for 3-stars and, *a fortiori*, than for self-avoiding walks. Thus increasing

Table 1. Exact enumeration data for H combs in two dimensions.

n	Honeycomb	Square	Triangular
1	$1\frac{1}{2}$	18	207
2	36	1 924	195 762
3	822	202 544	222 954 753
4	14 970	26 925 290	
5	279 603		
6	7027 476		

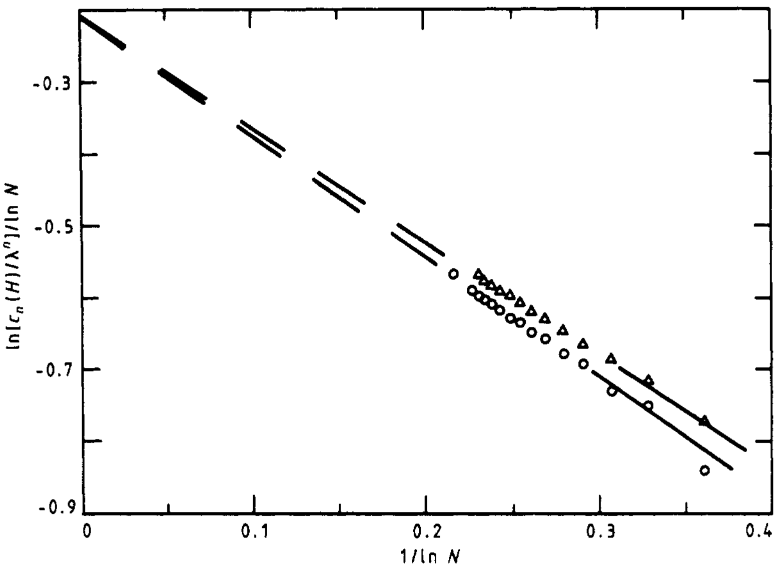

Figure 1. Exact enumeration and Monte Carlo estimates of $\gamma(H)$ for the square (○) and triangular (△) lattices. The largest error bars are about equal to the size of the symbols.

the number of vertices of degree three decreases the value of the exponent γ, reflecting the increasing interference between the branches. A 5-star has the same number of branches as an H comb and has a lower value of $\gamma(5) \simeq -0.29$ (Wilkinson *et al* 1986), reflecting the increased interference around the higher functionality branch point.

Another property which is expected to reflect the effects of excluded volume is the mean-square length of a branch of the comb. All of the external branches are equivalent and are expected to be less expanded than the internal branch. The asymptotic behaviour should be

$$\langle R_n^2(H)\rangle_x \sim B_x n^{2\nu}$$

where x can be i or e, denoting the internal or external branch. Our data are consistent with the exponent ν being identical in the two cases and equal to the self-avoiding walk value, $\nu = \frac{3}{4}$ (Nienhuis 1982). In table 2 we give the exact values of $\langle R_n^2(H)\rangle_\mathrm{i}$ and $\langle R_n^2(H)\rangle_\mathrm{e}$ for the square and honeycomb lattices for small n. The relative expansion

Table 2. Exact values of $\langle R_n^2(H)\rangle_\mathrm{i}$, $\langle R_n^2(H)\rangle_\mathrm{e}$ and their ratio for the square and honeycomb lattices.

	Square lattice			Honeycomb lattice		
n	$\langle R_n^2\rangle_\mathrm{i}$	$\langle R_n^2\rangle_\mathrm{e}$	$\langle R_n^2\rangle_\mathrm{i}/\langle R_n^2\rangle_\mathrm{e}$	$\langle R_n^2\rangle_\mathrm{i}$	$\langle R_n^2\rangle_\mathrm{e}$	$\langle R_n^2\rangle_\mathrm{i}/\langle R_n^2\rangle_\mathrm{e}$
1	1	1	1	1	1	1
2	3.151 77	2.783 78	1.132 19	3	3	1
3	5.940 91	5.256 54	1.130 19	6.463 51	5.620 44	1.150 00
4	9.489 40	7.848 19	1.209 12	10.154 31	9.027 66	1.124 80
5				14.875 79	13.121 76	1.133 67
6				20.044 30	16.592 25	1.208 05

of the internal branch is clearly reflected and the sequences of ratios $\langle R_n^2(H)\rangle_i/\langle R_n^2(H)\rangle_e$, although difficult to extrapolate, appear to be converging to a common limit. In fact, we expect this amplitude ratio to be a universal quantity. Our estimate for the value of this ratio is obtained from Monte Carlo data for the square lattice. In figure 2 we plot $\langle R_n^2(H)\rangle_x/n^{1.5}$ against $1/n$ for $x = \mathrm{i}$ and e. We estimate that the values of the amplitudes are

$$B_i = 1.31 \pm 0.02$$

and

$$B_e = 0.96 \pm 0.01.$$

This latter value is identical, within the error bars, to the value for 3-stars, $B(3) = 0.966 \pm 0.001$ (Whittington *et al* 1986). The amplitude ratio is $B_i/B_e = 1.36 \pm 0.04$, considerably greater than unity.

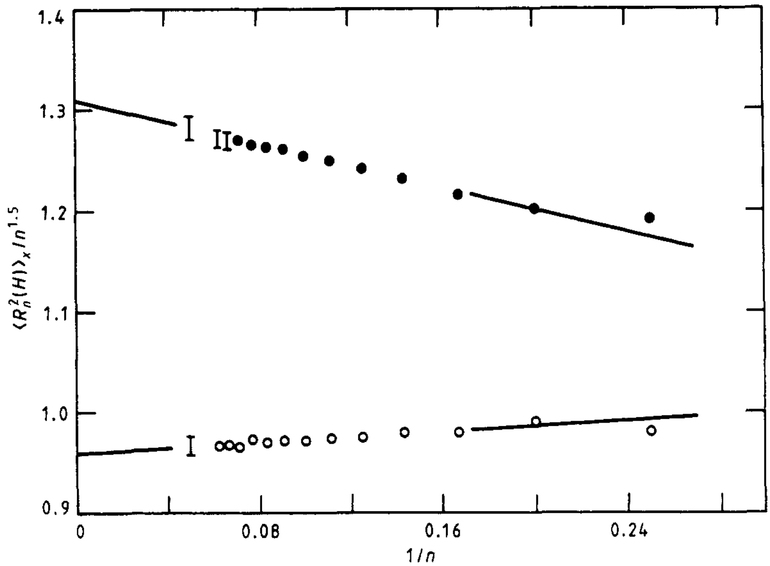

Figure 2. Monte Carlo estimates of the mean-square length of the internal (●) and an external (○) branch of an H comb on the square lattice scaled by $n^{1.5}$ plotted against $1/n$ where n is the branch length.

In summary, we have rigorously established the relationship between the growth constant of H combs and that of self-avoiding walks; we have given the first numerical estimate of the exponent $\gamma(H)$ in two dimensions and have discussed how the arrangement of branches in a uniform branched polymer affects the corresponding exponent; we have shown that the internal branch is expanded relative to the external branch of a comb, that the amplitude characterising the growth of the dimension of the external branch is similar to that of a 3-star and we have estimated the ratio of the amplitudes for internal and external branches. We conjecture that this amplitude ratio is a universal quantity depending only on dimension and that the amplitude for the external branch is identical to that for a branch of a 3-star.

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