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Lattice models of branched polymers: statistics of uniform stars

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Abstract. We investigate the statistical properties of uniform star polymers with f branches, modelled on lattices in two and three dimensions. We show that the growth constant exists and is equal to μ^f, where μ is the self-avoiding walk limit. The f dependence of the corresponding critical exponent $\gamma(f)$ is studied using exact enumeration and Monte Carlo techniques and the results are compared with the predictions of Miyake and Freed, obtained using chain conformation space renormalisation group methods.

1. Introduction

Over the last few years, there has been considerable interest in excluded-volume effects in branched polymer molecules. This was initiated by the field-theoretic approach of Lubensky and Isaacson (1979) but a good deal of work has also been carried out on the lattice version of this model (see Gaunt *et al* (1984) for a general discussion). The particular case of uniform star-branched polymers has been considered in some detail, since such molecules can now be synthesised having a variety of numbers (f) of branches and with various numbers (n) of monomers per branch (see for instance Roovers *et al* 1983).

A certain amount of theoretical work on uniform stars has also appeared (Daoud and Cotton 1982, Miyake and Freed 1983, 1984, Birshtein and Zhulina 1984, Vlahos and Kosmas 1984). Mazur and McCrackin (1977) studied these systems using Monte Carlo methods, as did Kolinski and Sikorski (1982), but their data were not analysed in a way which allows easy comparison with the recent theories mentioned above.

Suppose that the number of uniform stars with n monomers in each of the f branches is $s_n(f)$; then one expects that asymptotically ($n \to \infty$)

$$s_n(f) \sim n^{\gamma(f)-1} \lambda(f)^n. \tag{1.1}$$

Using a chain conformation space renormalisation group method, Miyake and Freed (1983) predict that

$$\gamma(f) = 1 + \tfrac{1}{8}\varepsilon[1 - \tfrac{1}{2}(f-1)(f-2)] + O(\varepsilon^2), \tag{1.2}$$

where $\varepsilon = 4 - d$ and d is the spatial dimension.

In a preliminary publication (Lipson *et al* 1985), we have studied a lattice version of this problem using exact enumeration and Monte Carlo techniques and have estimated $\gamma(3)$ and $\gamma(4)$ for several lattices in two and three dimensions. In this work, we extend these data to $f=5$ and 6, report improved statistics for the Monte Carlo calculations and perform a more detailed analysis. In addition, we show rigorously that the growth constant $\lambda(f)$ (see (1.1) above) exists and is identically equal to μ^f, where μ is the self-avoiding walk limit.

2. The growth constant of uniform stars

In this section, we shall prove the existence of the growth constant for uniform stars and relate it to that for self-avoiding walks. We consider the hypercubic lattice with the lattice vertices at the integer points in a d-dimensional Euclidean space, and with the branch point of the star at the origin. The maximum number of branches in the star is equal to $2d$, the coordination number of a d-dimensional hypercubic lattice.

Let $s_n(f)$ be the number of uniform stars with f branches, having n edges in each branch, weakly embeddable in the lattice. Similarly, let $t_n(f)$ be the number of stars with a *total* of n edges in f (not necessarily equal) branches and let c_n be the number of self-avoiding walks with n edges. Lipson and Whittington (1983) have shown that

$$\lim_{n\to\infty} n^{-1}\log t_n(f) = \lim_{n\to\infty} n^{-1}\log c_n \equiv \log\mu. \tag{2.1}$$

Since uniform stars are a subset of these stars,

$$s_n(f) \leqslant t_{nf}(f) \tag{2.2}$$

so that

$$\lim_{n\to\infty}\sup n^{-1}\log s_n(f) \leqslant \log\mu^f. \tag{2.3}$$

We now define a region of the lattice which we call a 'wedge'. Let $(x_1, x_2, \ldots, x_d)$ be the coordinates of a lattice point. For $0 \leqslant \varepsilon \leqslant 1$, the wedge $W_k(\varepsilon)$ is the set of lattice points which satisfy the conditions

$$-(1-\varepsilon)x_k \leqslant x_p \leqslant (1-\varepsilon)x_k \qquad \forall p \neq k \tag{2.4}$$

and

$$x_k \geqslant 0. \tag{2.5}$$

k is an integer which runs from 1 to d. Similarly, W_{-k} is the set of points which satisfy analogous conditions to (2.4) and (2.5) but with the inequalities reversed. That is, there is a wedge directed along each positive and along each negative coordinate axis. If $c_n(W)$ is the number of self-avoiding walks with n edges, starting at the origin and confined to lie in a wedge W, Hammersley and Whittington (1985) have shown that

$$\lim_{n\to\infty} n^{-1}\log c_n(W) = \log\mu \tag{2.6}$$

for any ε strictly less than unity. If we choose ε strictly greater than zero, these wedges are disjoint except that they all share the same origin. If we consider the graphs obtained by taking the union of n-edge self-avoiding walks confined to f separate wedges, we see that there are $c_n(W)^f$ such graphs and that these graphs are a subset of the uniform stars with f branches and n edges in each branch. This observation, together with (2.6) and (2.3), establishes that

$$\lim_{n\to\infty} n^{-1} \log s_n(f) = \log \mu^f. \tag{2.7}$$

Hence, the growth constant is given by

$$\lambda(f) = \mu^f. \tag{2.8}$$

Finally, we note that constructions such as those described above can be used to derive upper and lower bounds on $\gamma(f)$. We have explored this approach but found the resulting bounds to be weak.

3. Estimates of $\gamma(f)$

In this section we report exact enumeration and Monte Carlo data on uniform stars, with $f \leq 6$, weakly embeddable in various lattices in two and three dimensions. We use these data to estimate the critical exponent $\gamma(f)$ and compare our results with the predictions of Miyake and Freed (1984).

We have generated exact enumeration data for uniform stars on the square (SQ), triangular (T), diamond (D), simple cubic (SC), body-centred cubic (BCC) and face-centred cubic (FCC) lattices. The results are tabulated in the appendix, tables A1-3. Since the growth constant $\lambda(f)$ is given in terms of the self-avoiding walk limit μ by (2.8), we have used the best unbiased numerical estimates of μ (Watts 1975) and performed a biased ratio analysis to estimate $\gamma(f)$; that is, we extrapolate the sequence (see Gaunt and Guttmann 1974)

$$\gamma_n(f) = 1 + n\{[s_n(f)/\mu^f s_{n-1}(f)] - 1\}. \tag{3.1}$$

In figure 1 we show the n dependence of $\gamma_n(f)$ for $f = 3, 4, 5$ and 6 on the triangular lattice. It is clear that $\gamma(f)$ decreases as f increases and that the values of the exponent are close to the $O(\varepsilon)$ predictions of Miyake and Freed (indicated by arrows in the figure). This strengthens the conclusions drawn from figure 1 in Lipson *et al* (1985).

The universality of this exponent with respect to different lattices is illustrated in figure 2 where we show the n dependence of $\gamma_n(3)$ for the square and triangular lattices. For each lattice the limit of the sequence is consistent with the $O(\varepsilon)$ prediction of Miyake and Freed.

We expect that the exponent is sufficiently robust that its value is not affected if the branch lengths differ by one or two monomers. We call such stars *quasi-uniform stars*. This is confirmed by the results shown in figure 2 for quasi-uniform stars on the square lattice having $(n, n, n+1)$, $(n, n+1, n+1)$ and $(n-1, n, n+1)$ monomers in the respective branches. (The exact enumeration data are given in the appendix, table A4.) Indeed the data for such stars are remarkably well converged and show only a small odd-even oscillation compared with uniform stars. In general, odd-even oscillations arise for lattices in which only even-edged polygons can be embedded. The reduced odd-even alternation may reflect the smaller contribution of polygon terms to the generating function in the cases where the sum of the number of edges of two branches is odd. This reduced odd-even oscillation allows us to make a reasonably precise estimate of $\gamma(3)$. Taking account of the results for quasi-uniform stars, as

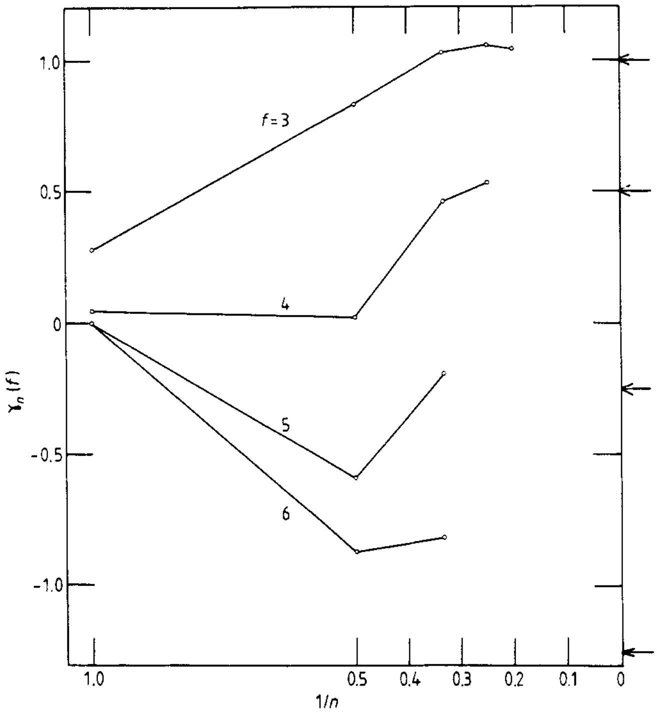

Figure 1. Ratio estimates of $\gamma_n(f)$ for the traingular lattice.

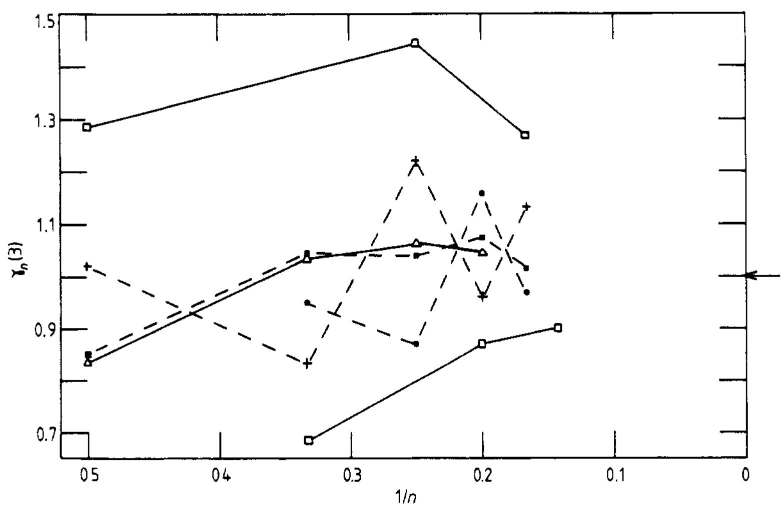

Figure 2. Ratio estimates of $\gamma_n(3)$ for uniform and quasi-uniform stars in two dimensions. △, (n, n, n) triangular; □, (n, n, n) square; +, $(n, n, n+1)$ square; ■, $(n, n+1, n+1)$ square; ●, $(n-1, n, n+1)$ square.

well as for uniform stars on the square and triangular lattices, we estimate that

$$\gamma(3) = 1.05 \pm 0.05. \tag{3.2}$$

We have generated samples of uniform stars on the simple cubic lattice with up to six branches and with up to 50 edges in each branch, using an inversely restricted Monte Carlo method (Rosenbluth and Rosenbluth 1955). Sample sizes were typically about 500 000. We have used these results to estimate the total number of stars, $s_n(f)$. It follows from (1.1) and (2.8) that we can estimate $\gamma(f)-1$ from the intercept of a plot of $\log(s_n(f)/\mu^{nf})/\log(nf)$ against $1/\log(nf)$. The results for three dimensions are shown in figure 3, where we make use of the unbiased estimate of $\mu = 4.6838$ (Watts

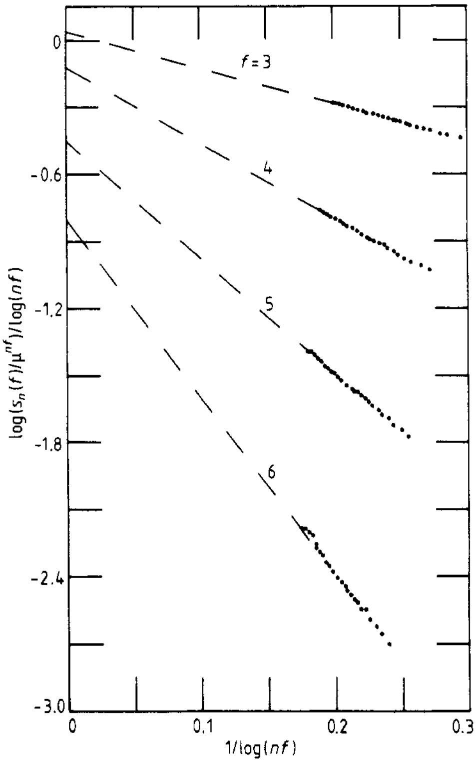

Figure 3. Monte Carlo estimates of $\gamma_n(f)$ for the simple cubic lattice.

Table 1. Comparison of estimates for $\gamma(f)$ from Monte Carlo data and from an $O(\varepsilon)$ renormalisation group treatment.

	$d=2$		$d=3$	
f	Miyake and Freed (1983)	Present estimate	Miyake and Freed (1983)	Present estimate
3	1	1.07 ± 0.02	1	1.05 ± 0.03
4	0.5	0.52 ± 0.04	0.75	0.88 ± 0.03
5	−0.25	-0.29 ± 0.04	0.375	0.55 ± 0.05
6	−1.25	-1.33 ± 0.05	−0.125	0.20 ± 0.05

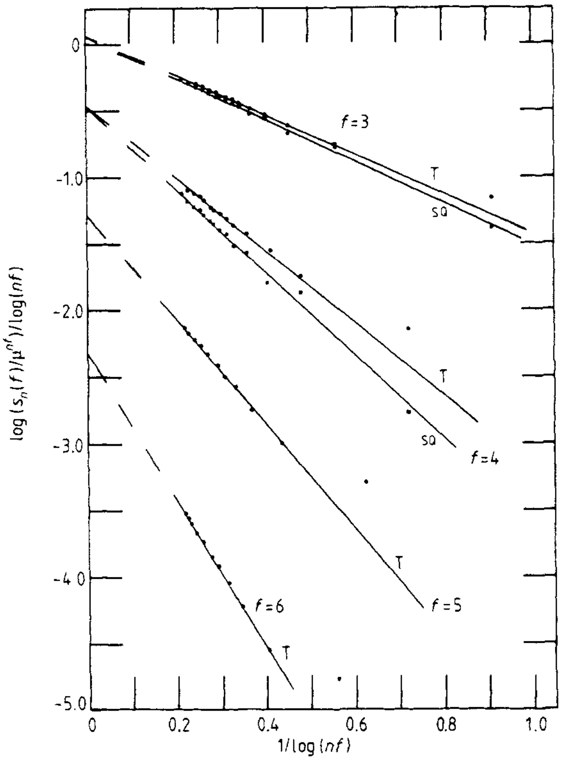

Figure 4. Monte Carlo estimates of $\gamma_n(f)$ for the square (SQ) and triangular (T) lattices.

1975) for the simple cubic lattice. Our estimates of $\gamma(f)$ in three dimensions are given in table 1.

We have carried out similar calculations for the square and triangular lattices but the sampling method is now much less efficient, because of the serious problem of trapping. Consequently, we have restricted our calculations to values of $n \leqslant 30$. Our estimates of $\gamma(f)$, based upon data for the square and triangular lattices and plotted in figure 4, are also presented in table 1. The agreement between the series analysis and Monte Carlo estimates in two dimensions for $f = 3$ is very satisfactory.

4. Discussion

The obvious qualitative feature of the results in table 1 is the decrease in $\gamma(f)$ as f increases. This reflects the interference between the different branches, which becomes more marked as f increases and which is felt more strongly in two dimensions than in three. Indeed, on a Bethe lattice, for which there is no interference between branches, $\gamma(f) = 1$ for all f. Our results suggest that the Miyake and Freed treatment overestimates the interference effects in three dimensions. The resulting underestimation of the exponent (in three dimensions), which is small for $f = 3$, becomes progressively more serious as f increases. It is not clear to what extent this disagreement will be reduced by extending their treatment to $O(\varepsilon^2)$. Indeed, as Miyake and Freed themselves point out, their use of a point potential becomes a serious limitation at high f values, where packing considerations near the branch point become important. This view is consistent with the scaling theory of Daoud and Cotton (1982) which incorporates an extended close-packed region close to the branch point.

In two dimensions, one might expect that these limitations would be even more serious but, in fact, the agreement between the $O(\varepsilon)$ and the Monte Carlo estimates is surprisingly good. It may be that truncating the ε expansion at $O(\varepsilon)$ in two dimensions is the optimum approximation in view of the fact that the expansion is asymptotic. In this connection, a determination of the $O(\varepsilon^2)$ terms would be useful.

Finally, we wish to comment on the connection between these results and a conjecture presented in a previous paper (Gaunt *et al* 1984). There we argued that the universality class for lattice trees with specified topologies depends on the number, b, of branches, through the critical exponent $(\gamma+b-1)$. Uniform (and quasi-uniform) stars form a subset of all lattice trees. Clearly, the number of highly irregular stars is far greater than the numbers of uniform and quasi-uniform stars, and it is this former subset which dominates and leads to the exponent $(\gamma+b-1)$.

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Appendix

Exact enumeration data for uniform and quasi-uniform stars with f branches.

Table A1. $f=3$.

n	SQ	T	D	SC	BCC	FCC
1	4	20	4	20	56	220
2	84	1 312	108	2 260	17 240	226 780
3	1 380	94 956	2 700	227 172	4 657 016	231 118 428
4	28 164	6 903 764	64 348	24 159 620	1 340 720 088	
5	504 084	498 757 752	1 489 236			
6	9 675 548		36 814 788			
7	175 236 508		877 342 204			

Table A2. $f=4$.

n	SQ	T	D	SC
1	1	15	1	15
2	47	2 280	81	7 605
3	1 297	555 939	5 601	3 019 767
4	70 257	145 989 303	350 613	
5	2 809 521		20 663 877	
6	136 065 237		1 482 001 791	

Table A3. $f = 5$ and 6.

	$f=5$		$f=6$	
n	T	SC	T	SC
1	6	6	1	1
2	1 524	13 050	322	8 867
3	1 133 598	18 555 414	651 167	

Table A4. $f = 3$ for the SQ lattice.

n	$(n, n, n+1)$	$(n, n+1, n+1)$	$(n-1, n, n+1)$
1	36	100	
2	668	1 700	520
3	11 588	31 692	9 392
4	224 620	587 796	166 952
5	4 093 036	10 961 516	3 163 280
6	76 845 956	201 836 388	57 805 704

References

Birshtein T M and Zhulina E B 1984 *Polymer* **25** 1453

Daoud M and Cotton J P 1982 *J. Physique* **43** 531

Gaunt D S and Guttmann A J 1974 *Phase Transitions and Critical Phenomena* vol 3, ed C Domb and M S Green (New York: Academic) p 181

Gaunt D S, Lipson J E G, Martin J L, Sykes M F, Torrie G M, Whittington S G and Wilkinson M K 1984 *J. Phys. A: Math. Gen.* **17** 211

Hammersley J M and Whittington S G 1985 *J. Phys. A: Math. Gen.* **18** 101

Kolinski A and Sikorski A 1982 *J. Polymer Sci. Polymer Chem.* **20** 3147

Lipson J E G and Whittington S G 1983 *J. Phys. A: Math. Gen.* **16** 3119

Lipson J E G, Whittington S G, Wilkinson M K, Martin J L and Gaunt D S 1985 *J. Phys. A: Math. Gen.* **18** L469

Lubensky T C and Isaacson J 1979 *Phys. Rev.* A **20** 2130

Mazur J and McCrackin F 1977 *Macromol.* **10** 326

Miyake A and Freed K F 1983 *Macromol.* **16** 1228

—— 1984 *Macromol.* **17** 678

Roovers J, Hadjichristidis N and Fetters L J 1983 *Macromol.* **16** 214

Rosenbluth M N and Rosenbluth A W 1955 *J. Chem. Phys.* **23** 356

Vlahos M G and Kosmas M K 1984 *Polymer* **25** 1607

Watts M G 1975 *J. Phys. A: Math. Gen.* **8** 61