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LETTER TO THE EDITOR

A lattice model of uniform star polymers

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Abstract. We present Monte Carlo and exact enumeration results for three- and four-arm stars on a variety of lattices. We estimate the exponents for the number of stars and the mean square end-to-end length of a branch, and compare these results with scaling and renormalisation group predictions.

Recently there has been increased interest in studying the configurational and dynamic properties of star-branched polymers (Huber *et al* 1984, von Meerwall 1984). This has been stimulated in part by the development of synthetic routes whereby well characterised stars of varying functionality can be produced (Roovers *et al* 1983). Early theoretical studies considered the unperturbed chain, but the θ point of these molecules has yet to be well defined experimentally. In modelling the stars with excluded volume two kinds of treatments have emerged. Daoud and Cotton (1982) (see also Birshtein and Zhulina 1984) have developed a scaling theory incorporating three concentration regimes: a close-packed core, surrounded by a region in which concentration effects screen out excluded volume and, finally, in the long-chain limit, a region where excluded-volume effects dominate. Miyake and Freed (1983) have produced a more rigorous treatment using chain conformation renormalisation group techniques (see also Vlahos and Kosmas 1984). Their picture differs from that of Daoud and Cotton, and they are able to make predictions concerning both metrical and statistical properties.

Both treatments predict that the exponent characterising the large-n behaviour of the mean square radius of gyration, $\langle S_N^2(f)\rangle$, for a uniform f-arm star with $N = nf$ monomers is independent of f, and is equal to the corresponding exponent for the linear chain (2ν). In addition Miyake and Freed (1983) obtain the following form for the mean square end-to-end length, $\langle R_n^2(f)\rangle$, of a branch having n monomers

$$\langle R_n^2(f)\rangle \sim A(f) n^{2\nu(f)} \tag{1}$$

where $A(f)$ is an increasing function of f and $\nu(f) = \nu$, independent of f.

Miyake and Freed also predict that the critical exponent characterising the number of configurations of a uniform f-arm star decreases with increasing f as

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

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

In this letter we present Monte Carlo and exact enumeration results for uniform stars weakly embeddable in a variety of lattices, and compare our data with the above predictions. Although some Monte Carlo work has already appeared on related systems (Mazur and McCrackin 1977, Kolinski and Sikorski 1982) it was not analysed to test these results.

We have enumerated exactly the numbers of stars having three and four branches on the triangular, square, simple cubic, tetrahedral, body-centred cubic and face-centred cubic lattices, for small n. Assuming that the number of stars with a total of N edges is given asymptotically by

$$s_N(f) \sim B(f) N^{\gamma(f)-1} \mu^N \tag{3}$$

we estimate $\gamma(f)$ from the ratios $r_n = s_{fn}/s_{f(n-1)}$ by extrapolating the sequence (see Gaunt and Guttmann 1974)

$$\gamma_n(f) = 1 + n[(r_n/\mu^f) - 1]. \tag{4}$$

The growth constant μ can be proved to be identical to that for a self-avoiding walk. A proof of this assertion will appear in a subsequent publication.

Results for the triangular and square lattices are shown in figure 1, together with $\frac{1}{2}(\gamma_n + \gamma_{n-1})$ for the square lattice, to reduce the effect of odd-even oscillations. In these calculations we have made use of unbiased estimates of μ due to Watts (1975). The $O(\varepsilon)$ estimates of Miyake and Freed, for $f = 3$ and 4, are shown by arrows. There is strong evidence that the sequences $\{\gamma_n\}$ for $f = 3$ and 4 converge to different limits, and that these limits are close to the $O(\varepsilon)$ predictions of Miyake and Freed.

Analogous results for $f = 3$ in three dimensions are presented in figure 2. Again, the sequences seem to be converging (despite rather erratic behaviour for the tetrahedral lattice) to a limit close to that ($\gamma(3) = 1$) predicted by Miyake and Freed.

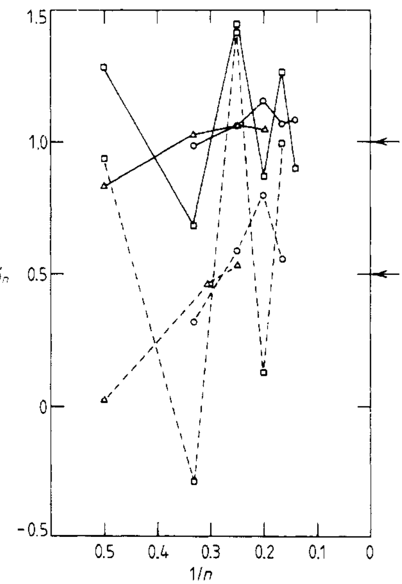

Figure 1. Ratio estimates of $\gamma(f)$ for the square (□ and ○) and triangular (△) lattices. The full (broken) lines are for $f = 3(4)$, respectively. The arrows indicate the $O(\varepsilon)$ estimates of Miyake and Freed (1983).

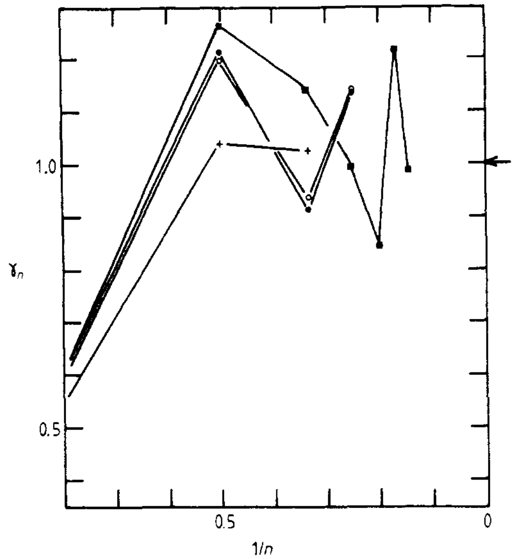

Figure 2. Ratio estimates of $\gamma(3)$ for the tetrahedral (■), simple cubic (○), body-centred cubic (●) and face-centred cubic (+) lattices. The arrow indicates the $O(\varepsilon)$ estimate of Miyake and Freed (1983).

In addition, we have generated samples of configurations of uniform stars, with three and four arms, on the tetrahedral and simple cubic lattices using an inversely restricted Monte Carlo procedure (Rosenbluth and Rosenbluth 1955). The number of edges in *each* arm ranges from 50 to 80, and we have used sample sizes of between 300 000 and 500 000.

Defining $W_N(f) = s_N(f)/\mu^N$, it follows from (3) that

$$\ln W_N/\ln N = (\gamma-1) + \ln B(f)/\ln N + o((\ln N)^{-1}) \tag{5}$$

and figure 3 shows the Monte Carlo data for four-arm stars on the tetrahedral and simple cubic lattices. Both sets of data approach the same intercept, corresponding to $\gamma(4) = 0.9^{+0.1}_{-0.2}$. Similar results (not shown) for three-arm stars indicate that $\gamma(3) = 1.1 \pm 0.05$. These error bars reflect both the statistical uncertainty and the uncertainty due to possible errors in μ. These values should be compared with the predictions of Miyake and Freed and of Vlahos and Kosmas of $\gamma(3) = 1$ and $\gamma(4) = 0.75$. The qualitative result, that $\gamma(f)$ decreases with increasing f, is confirmed by our Monte Carlo and exact enumeration data. The numerical discrepancies could be due to uncertainties in our treatment arising from (i) additional uncertainties in estimates of μ or (ii) insufficiently long arms, or could arise from neglect of terms of order ε^2 and higher in the renormalisation group treatments.

We have calculated $\langle R_n^2(f)\rangle$ exactly for small n and estimated this quantity for small and larger values of n using Monte Carlo methods. The agreement for small n is excellent, the discrepancy never being larger than 0.1%. We have assumed that (1) describes the behaviour of $\langle R_n^2(f)\rangle$ and have estimated $\nu(f)$ from appropriate log-log plots. In three dimensions, it is clear that $\nu(3)$ and $\nu(4)$ are both close to 0.6. If we *assume* that $\nu(f) = 0.6$ and estimate $A(f)$ (see figure 4) we find that $A(4)$ is larger than $A(3)$, although both are lattice dependent. We estimate that $A(4)/A(3) = 1.05 \pm 0.01$

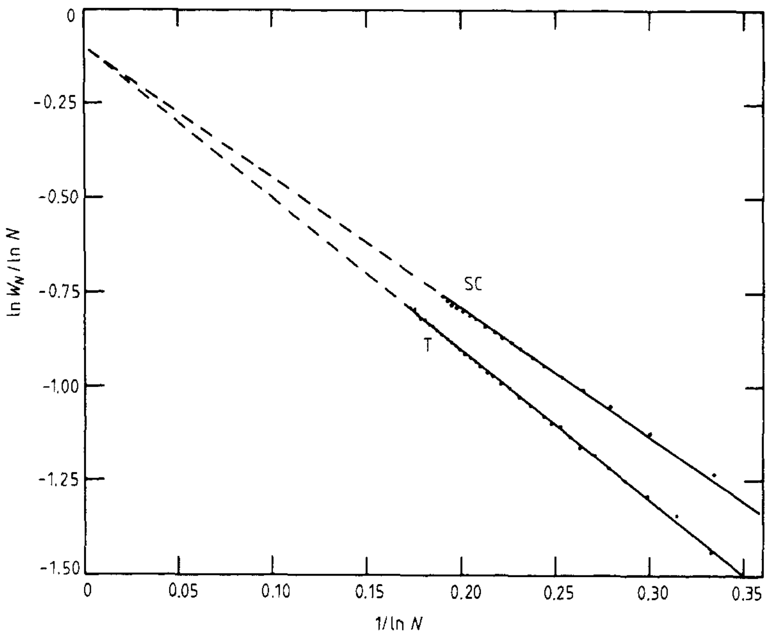

Figure 3. Monte Carlo estimates of $\gamma(4)$ for the tetrahedral (T) and simple cubic (SC) lattices.

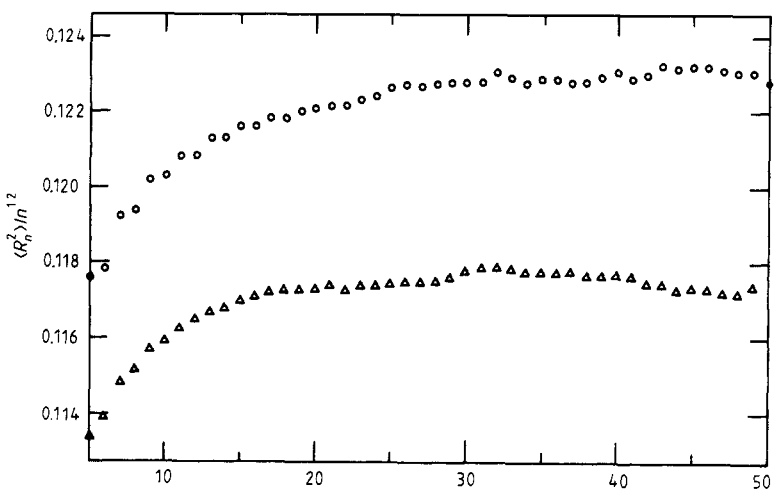

Figure 4. Monte Carlo estimates of $A(f)$ for $f=3$ ($\triangle$) and $f=4$ ($\bigcirc$) for the simple cubic lattice.

for the simple cubic lattice, and 1.04 ± 0.02 for the tetrahedral lattice. These results are consistent with the ratio $A(4)/A(3)$ being ***universal*** (i.e. lattice independent), and compare well with Miyake and Freed's prediction (to first order in ε) that $A(4)/A(3) = 1.056$ in three dimensions.

In summary, our results suggest (i) that the configurational exponent for f-branched stars decreases as f increases, and (ii) that the mean square length of a branch increases with f. This is in complete qualitative agreement with the results of Miyake and Freed. There are, however, some discrepancies between our numerical estimates and their $O(\varepsilon)$ result for the exponent $\gamma(f)$. We plan to investigate this further, and to extend our calculations to include the mean-square radius of gyration. This is of particular interest in that it should allow us to differentiate between the scaling and renormalisation group theories.

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