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The growth constant of uniform star polymers in a slab geometry

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Abstract. We consider uniform star-branched polymer molecules, modelled by the corresponding graph weakly embedded in a simple cubic lattice, confined to a parallel-sided slab. In three (and higher) dimensions we show that the limiting entropy per bond is independent of the number of branches in the star and is equal to the connective constant of a self-avoiding walk on that subset of the lattice. In two dimensions, however, the limiting entropy per bond of a three-branch star is shown, for a particular case, to be strictly less than that for a self-avoiding walk and we present numerical evidence that this is a general result in two dimensions.

1. Introduction

The statistics and dimensions of uniform star polymers have attracted a good deal of attention recently, partly because such molecules can now be synthesised in a controlled way (Roovers *et al* 1983). These molecules can be modelled as connected graphs, weakly embeddable in a lattice, having one vertex of degree f on which are incident f branches each containing n vertices. In particular, the statistics of such systems have been studied by Miyake and Freed (1983), Wilkinson *et al* (1986) and Duplantier (1986).

The work on uniform stars has been restricted to stars on a lattice with no additional geometrical constraints. On the other hand, self-avoiding walks have been studied with a variety of such constraints (see, e.g., Hammersley and Whittington 1985 and references therein). We shall be concerned here with the particular case of walks or stars on a d-dimensional lattice confined between two parallel $(d-1)$-dimensional hyperplanes. In the case of self-avoiding walks, the effect of this constraint has been well studied by scaling arguments (Daoud and de Gennes 1977), exact enumeration (Middlemiss and Whittington 1976, Guttmann and Whittington 1978), Monte Carlo methods (Wall *et al* 1978), transfer matrix methods (Klein 1980) and by self-consistent field approaches (see, e.g., Levine *et al* 1978). In addition, some rigorous results have been obtained for this problem (Wall *et al* 1977, Wall and Klein 1979, Whittington 1983, Hammersley and Whittington 1985).

The aim of this work is to investigate the effect on the limiting entropy per bond of an f-branch uniform star of confining the star between two parallel planes a distance L apart. In particular, we consider the f dependence of this quantity and show that the behaviour in two dimensions is quite different from the behaviour in three and higher dimensions.

2. Three and higher dimensions

In this section we examine the behaviour of uniform star polymers confined to a parallel-sided slab in three dimensions. The extension to $d \geq 3$ dimensions, where the system is confined by two parallel $(d-1)$-dimensional hyperplanes, is straightforward.

Consider a simple cubic lattice, whose vertices are the integer points in R^3 with coordinates (x, y, z). Consider now a slab which consists of the subset of the these vertices such that

$$0 \leq z \leq L. \tag{2.1}$$

If $c_n(L, z)$ is the number of n-step self-avoiding walks starting at $(0, 0, z)$ confined to this slab, and $c_n(L) = \Sigma_z c_n(L, z)$, then it has been shown that the connective constant $\kappa(L)$ defined by

$$\kappa(L) = \lim_{n\to\infty} n^{-1} \log c_n(L) \tag{2.2}$$

exists (Whittington 1983).

If the walk is confined to a wedge $W(\alpha, L)$ within this slab, such that

$$0 \leq x \qquad 0 \leq y \leq \alpha x \qquad 0 \leq z \leq L \tag{2.3}$$

for some particular positive value of α, then if we define $c_n(\alpha, L)$ as the number of n-step self-avoiding walks starting at the origin and satisfying (2.3) it is straightforward to prove, by an extension of an argument due to Hammersley and Whittington (1985), that

$$\lim_{n\to\infty} n^{-1} \log c_n(\alpha, L) = \kappa(L) \tag{2.4}$$

for all $\alpha > 0$. This result is also true if the walk begins at $(0, 0, z)$ for any z such that $0 \leq z \leq L$.

Suppose that $s_n(f, L)$ is the number of uniform stars with f arms, having n edges in each arm, confined in the slab defined by (2.1) and having the vertex of degree f at $(0, 0, z)$ with z satisfying $1 \leq z \leq L-1$. (For the moment we restrict ourselves to $L > 1$.) Clearly these stars are included in the set of graphs obtained by joining f self-avoiding walks in the slab, at their common origin, so that

$$s_n(f, L) \leq c_n(L)^f. \tag{2.5}$$

To obtain a lower bound on $s_n(f, L)$ we proceed as follows. We first construct six disjoint wedges:

$$\begin{aligned}
&W_1: && x \geq 1,\ 1 \leq y \leq x,\ 0 \leq z \leq L \\
&W_2: && y \geq 2,\ 1 \leq x \leq y-1,\ 0 \leq z \leq L \\
&W_3: && x \leq -1,\ -1 \geq y \geq x,\ 0 \leq z \leq L \\
&W_4: && y \leq -2,\ -1 \geq x \geq y+1,\ 0 \leq z \leq L \\
&W_5: && x \leq -1,\ y \geq 1,\ 0 \leq z \leq L \\
&W_6: && x \geq 1,\ y \leq -1,\ 0 \leq z \leq L.
\end{aligned} \tag{2.6}$$

If we define u_1, u_2, u_3 as unit steps along the positive x, y and z directions, and $\bar{u}_1$, $\bar{u}_2$, $\bar{u}_3$ as the corresponding steps in the negative directions, then we can join the vertex $(0, 0, z)$, $0<z<L$, to a vertex in each of these wedges by one of the following 'links':

$$
\begin{aligned}
l_1 &= u_3 u_2 u_1 \bar{u}_3 \\
l_2 &= u_2^2 u_1 \\
l_3 &= \bar{u}_3 \bar{u}_2 \bar{u}_1 u_3 \\
l_4 &= \bar{u}_2^2 \bar{u}_1 \\
l_5 &= \bar{u}_1 u_2 \\
l_6 &= u_1 \bar{u}_2 .
\end{aligned}
\tag{2.7}
$$

We now construct a subset of the f-arm stars by constructing the graphs obtained as the union of (i) the vertex $(0, 0, z)$, (ii) the 'links' $l_1, \ldots, l_f$ and (iii) f walks of $n-k_1, n-k_2, \ldots, n-k_f$ steps confined to the wedges $W_1, \ldots, W_f$ respectively, where k_i is the number of edges in the link l_i. Since the wedges W_1, $W_2, \ldots$, are disjoint the resulting graphs are uniform stars with f arms, having n edges in each arm. Hence

$$s_n(f, L) \geqslant \prod_{i=1}^{f} c_{n-k_i}(\alpha_i, L) \tag{2.8}$$

where each $\alpha_i > 0$. Taking logarithms, dividing by fn and letting n go to infinity in (2.5) and (2.8) we have

$$\lim_{n\to\infty} (nf)^{-1} s_n(f, L) = \kappa(L). \tag{2.9}$$

This 'limiting entropy per bond' is independent of f and is equal to the corresponding quantity for self-avoiding walks confined to the same slab. This argument extends easily to $d>3$ but not, as we shall see in § 3, to $d=2$.

If we consider only $f \leqslant 5$, the above argument can be extended to $L \geqslant 1$ and, if $f \leqslant 4$, to $L \geqslant 0$.

3. The two-dimensional case

For a self-avoiding walk on the square lattice confined to a 'slab' so that $0 \leqslant y \leqslant L$, the value of the connective constant is known exactly for $L=1$ and 2 (Wall *et al* 1977) and accurate numerical estimates (Klein 1980) are available up to $L=6$. In particular, $\kappa(1) = \log[\frac{1}{2}(1+\sqrt{5})] = 0.481\,21\ldots$. (Note that, in the literature, there are different usages of the term 'connective constant' and of the symbol κ.)

To establish that the arguments of § 2 do not apply to $d=2$, we examine the case $f=3$, $L=1$. A typical configuration for $n=4$ is shown in figure 1(a). Two arms of the star are essentially rigid while the third arm behaves as a self-avoiding walk with constraints. In fact,

$$s_n(3, 1) = 4c_n^+(1) \tag{3.1}$$

where $c_n^+(1)$ is the number of n-step self-avoiding walks confined to $0 \leqslant y \leqslant 1$ with the added restriction that the 'right-most' vertex is of unit degree. An unfolding argument (Hammersley and Welsh 1962) readily establishes that

$$\lim_{n\to\infty} n^{-1} \log c_n^+(1) = \lim_{n\to\infty} n^{-1} \log c_n(1) = \kappa(1) \tag{3.2}$$

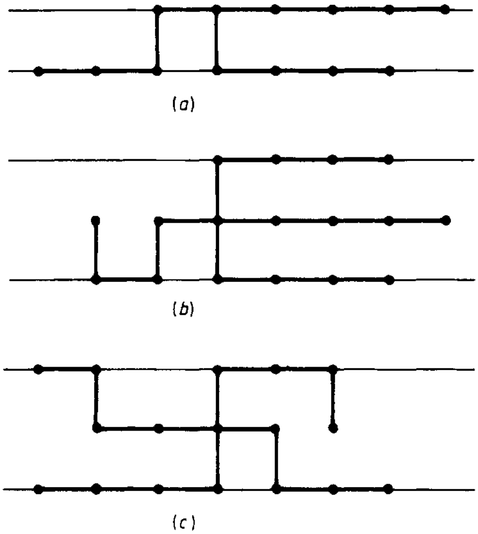

Figure 1. Configurations of (a) a three-arm star with $L=1$ and (b) and (c) a four-arm star with $L=2$.

so that, from (3.1) and (3.2), we have

$$\lim_{n\to\infty}(3n)^{-1}\log s_n(3, 1)=\tfrac{1}{3}\kappa(1)\equiv\kappa(3, 1)$$

and the limiting entropy per bond is less than for a correspondingly confined self-avoiding walk.

To investigate whether this is a general phenomenon for $d=2$, we have enumerated three-arm and four-arm stars for $L\leqslant 5$. The results are given in tables 1 and 2. The estimates of $\kappa(f, L)$ given in table 3 were obtained from a standard ratio analysis of these data.

Of course, it is easy to derive bounds on $\kappa(f, L)$ in terms of $\kappa(1, L)\equiv\kappa(L)$. The upper bound $\kappa(f, L)\leqslant\kappa(1, L)$ follows immediately from a consideration of f self-avoiding n-step walks confined to $0\leqslant y\leqslant L$ and incident on a common vertex of degree

Table 1. Exact values of $s_n(3, L)$ for the square lattice.

n/L	2	3	4	5
2	56	134	218	302
3	244	1 024	2 252	3 618
4	1 352	8 756	25 932	50 606
5	5 644	58 840	229 844	551 528
6	27 916	444 648	2 204 964	6 258 592
7	110 336	2 890 492	18 774 128	63 293 672
8	514 696	20 449 996	170 951 360	675 942 548
9	2 056 456	129 640 568	1 434 555 408	
10	9 026 316	867 253 220	12 497 069 624	
11	35 934 772	5424 148 496		
12	151 499 524			
13	604 131 112			

Table 2. Exact values of $s_n(4, L)$ for the square lattice.

n/L	2	3	4	5
2	14	52	99	146
3	28	336	1 260	2 508
4	120	3 824	26 338	76 212
5	326	25 136	289 926	1 272 336
6	1 764	258 100	4 324 590	25 339 868
7	6 430	1 889 572	47 871 664	379 453 424
8	36 776	18 841 216	679 686 348	6888 523 084
9	161 922	152 269 216		
10	835 838	1432 867 852		
11	3 685 184			
12	17 634 384			
13	79 036 106			
14	365 380 978			

Table 3. Estimates of $\kappa(f, L)$ for the square lattice.

L/f	1, 2	3	4
1	0.4812	0.1604	—
2	0.6492	0.44 ± 0.01	0.36 ± 0.01
3	0.7359	0.57 ± 0.01	0.55 ± 0.01
4	0.7880	0.68 ± 0.01	—
∞	0.9702	0.9702	0.9702

f. The lower bound

$$\kappa(4, L) \geq \tfrac{1}{2}[\kappa(1, \tfrac{1}{2}L - 1) + \kappa(1, \tfrac{1}{2}L)] \qquad L \text{ even}$$

with a similar result for L odd, is easily derived by considering the four arms of the star to be confined to the 'tubes'

$$T_1: \qquad 0 < x, \tfrac{1}{2}L \leq y \leq L$$

$$T_2: \qquad 0 \geq x, 1 + \tfrac{1}{2}L \leq y \leq L$$

$$T_3: \qquad 0 \leq x, 0 \leq y \leq \tfrac{1}{2}L - 1$$

$$T_4: \qquad 0 > x, 0 \leq y \leq \tfrac{1}{2}L$$

with appropriate edges added to join the arms at $(0, \tfrac{1}{2}L)$. The result that

$$\lim_{n\to\infty} \lim_{L\to\infty} (4n)^{-1} \log s_n(4, L) = \lim_{L\to\infty} \lim_{n\to\infty} (4n)^{-1} \log s_n(4, L)$$

then follows easily, using arguments due to Hammersley and Whittington (1985).

These bounds are rather weak and are therefore not useful numerically. However, in special cases it is possible to do somewhat better. We shall consider the special case of $f = 4$, $L = 2$. The vertex of degree 4 must have a y coordinate equal to unity and we take it to be at $(0, 1)$. The four vertices connected to it must be at $(1, 1)$, $(-1, 1)$, $(0, 2)$ and $(0, 0)$ and the arrangement of the four arms of the star must be either as shown in figure 1(b) or figure 1(c). For the arrangement corresponding to figure 1(b), the configurations of three of the arms are fixed and the fourth arm has $c_n^+(1,2)$ configurations. This implies the lower bound:

$$\lim_{n\to\infty}(4n)^{-1}\log s_n(4,2)\geq\tfrac{1}{4}\kappa(2).$$

We now consider the set of configurations which correspond to figure 1(c). To do this we first consider the number $p_n(L)$ of (undirected, unrooted) polygons confined to $0\leq y\leq L$. The behaviour of this quantity as n goes to infinity has been discussed by Klein (1980). In particular, Klein has evaluated the corresponding connective constant $\kappa_0(L)$ for small L and has shown that it is not equal to $\kappa(L)$.

We shall confine ourselves to the case $L=2$. We translate each polygon so that the minimum x coordinate of any vertex is unity. Each polygon includes the vertex $(1,1)$ and at least one of $(1,2)$ and $(1,0)$. Let $q_n(2)$ be the number of such polygons which contain $(1,0)$ and call this set $Q^+(n,2)$. Clearly $q_n(2)\geq\frac{1}{2}p_n(2)$. If we now consider polygons translated so that their maximum x coordinate is -1, and consider the subset, $Q^-(n,2)$, which contains the vertex $(-1,2)$, as well as $(-1,1)$, we see by symmetry that the number of these is also $q_n(2)$. We now concatenate each polygon from the set $Q^+(2n,2)$ with each polygon from the set $Q^-(2n,2)$, adding the vertices $(0,0)$, $(0,1)$ and $(0,2)$, together with the edges $(0,0)-(0,1)$, $(0,0)-(1,0)$, $(0,1)-(1,1)$, $(0,1)-(0,2)$, $(0,1)-(-1,1)$ and $(0,2)-(-1,2)$, and deleting the edges $(-1,1)-(-1,2)$ and $(1,1)-(1,0)$, forming a figure eight with the vertex of degree 4 at the point $(0,1)$, and confined between $y=0$ and $y=2$. If we now remove one vertex and the two incident edges from each of the circuits of this figure eight to leave a 4-star with n edges in each arm, we have the lower bound

$$\lim_{n\to\infty}(4n)^{-1}\log s_n(4,2)\geq\lim_{n\to\infty}(4n)^{-1}\log[(\tfrac{1}{2}p_{2n}(2))^2]$$

so that

$$\kappa(4,2)\geq\kappa_0(2)=\log(1.414)=0.3464\ldots$$

where we have taken the numerical value from Klein (1980). The value of this lower bound is extremely close to our numerical estimate from series analysis and may be the best possible.

4. Discussion

The primary result of this paper is the proof that the limiting entropy per bond of an f-arm star confined between two parallel planes in three (or higher) dimensions is the same as for a self-avoiding walk. We have also shown, by a counterexample, that this is is not the case in two dimensions. For the two-dimensional case we have used exact enumeration and series analysis techniques to estimate the limiting entropy for various cases and have used these results to argue that this difference between the two- and higher-dimensional cases is a general phenomenon.

The interesting question is to what extent this phenomenon can be related to other cases of objects in confined geometries? The obvious example is the observation of Klein that the connective constant of a polygon between two parallel lines, in two dimensions, is lower than that for a corresponding self-avoiding walk. In each case the underlying effect is that one part of the object 'shades' a region of the space so that it is inaccessible to another part of the object. This shading is an essentially two-dimensional feature.

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