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LETTER TO THE EDITOR

Self-avoiding walks in a slab of finite thickness: a model of steric stabilisation

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Abstract. The technique of exact enumeration coupled with series analysis has been used to study the behaviour of the properties of long self-avoiding walks on a square lattice slab as the thickness (D) of the slab is varied. Scaling arguments due to Daoud and de Gennes predict the variation of mean-square end-to-end distance and of free energy with D. Our results are consistent with these scaling predictions for the mean-square end-to-end distance, but suggest that the free-energy crossover exponent is closer to unity than the value ($\frac{4}{3}$) predicted by scaling.

The behaviour of a macromolecule confined between two planes is of interest as a model of the phenomenon of steric stabilisation of dispersions (Napper 1977, Gerber and Moore 1977). Random walk models of this situation have been studied for several years (e.g. Hesselink 1969, 1971, Richmond and Lal 1974, Chan *et al* 1976) and more recently the important excluded volume effect has been incorporated by a study of self-avoiding walks between two planes (Daoud and de Gennes 1977, Middlemiss *et al* 1977, Wall *et al* 1977a,b).

A scaling theory has been developed by Daoud and de Gennes (1977) who consider a single n-step self-avoiding walk between two planes a distance D apart. The crossover from three-dimensional behaviour at large D to two-dimensional behaviour at small D is assumed to take place when the characteristic walk length becomes comparable to D. The characteristic walk length is given by An^{ν}, where ν is very close to $\frac{3}{5}$ for the three-dimensional model, is close to $\frac{3}{4}$ for the two-dimensional model, and is exactly 1 for the one-dimensional model. They then proposed the scaling *ansatz*

$$\langle R_n^2 \rangle \sim Bn^{6/5}(n^{3/5}/D)^{\theta} \tag{1}$$

when $n^{3/5} > D$, so that by requiring $\langle R_n^2 \rangle \sim An^{3/2}$ in this case, they obtained $\theta = \frac{1}{2}$. A repetition of their argument for the two-dimensional case, that of a self-avoiding walk between two lines, leads to the result

$$\langle R_n^2 \rangle \sim Cn^2 D^{-2/3} \tag{2}$$

when $D < n^{3/4}$, that is, $\theta = \frac{2}{3}$.

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A similar scaling argument is also given for the change in free energy, $\Delta A(D)$, which takes place on bringing up one of the planes from infinity to D. The result is

$$\Delta A(D) \sim hD^{-1/\nu} \tag{3}$$

where the values of ν are given above.

In this Letter we confine our attention to the two-dimensional version of this problem, corresponding to a self-avoiding walk between two parallel lines of the square lattice (whose vertices are the integer points in $E^{(2)}$). The walk can therefore visit lattice points with any x coordinate but with y coordinate restricted to the range $y \in [0, D-1]$, that is, with D available 'lattice-lines'. Wall *et al* (1977a) have shown rigorously that in two dimensions

$$\lim_{n\to\infty} n^{-2}\langle R_n^2(D)\rangle \equiv f(D) \tag{4}$$

exists for all finite D, and have explicitly evaluated $f(2)$ and given the leading asymptotic term in $f(3)$. Note that $f(1)$ corresponds to the trivial case of a one-dimensional self-avoiding walk. Further, Wall *et al* (1977b) have calculated the number of self-avoiding walks of n steps $c_n(D)$, and hence the 'effective coordination number' $\mu(D)$ for $D=2$ and 3, where $\ln \mu(D) = \lim_{n\to\infty} \ln c_n(D)/n$.

However, in order to test the scaling predictions, one needs to know $f(D)$ and $\mu(D)$ for a wider range of values of D. We have therefore enumerated self-avoiding walks on the square lattice, with origin at (0, 0), subject to the above restrictions. Exact values of $\langle R_n^2(D)\rangle$ for $D \leqslant 6$ and $n \leqslant 20$ and exact values of the number of n-step self-avoiding walks $c_n(D)$ for $D=2$ (all n), $D=3$ ($n \leqslant 22$), $D=4$ ($n \leqslant 22$), $D=5, 6$ ($n \leqslant 20$), $D=7$ ($n \leqslant 18$) have been obtained by enumeration. These enumerations will be published subsequently.

Using standard methods of series analysis (see e.g. Gaunt and Guttmann 1974), principally ratio techniques with extrapolations using Neville tables, we have obtained estimates of $f(D)$ for $D \leqslant 6$ and $\mu(D)$ for $D \leqslant 7$. Our estimates for $D=2$ and 3 agree almost exactly with the results of Wall *et al* (1977b), thereby giving us considerable confidence in the extrapolation techniques.

From these estimates of $f(D)$ and $\mu(D)$, and writing $f(D) \sim gD^{-\theta}$, we can estimate θ from the sequence $\{\theta_D\}$ whose elements are given by

$$\theta_D = \frac{\ln(f(D)/f(D-1))}{\ln[(D-1)/D]}. \tag{5}$$

Our estimates of $f(D)$ and the corresponding sequence $\{\theta_D\}$ are shown in table 1.

Table 1. Estimates of the exponent θ defined by $f(D) \sim gD^{-\theta}$. For $D \leqslant 3$ the results are exact.

D	$f(D) = \lim_{n\to\infty} \langle R_n^2(D)\rangle/n^2$	$\theta_D = \frac{\ln(f(D)/f(D-1))}{\ln[(D-1)/D]}$
1	1·0	
2	0·5236	0·933
3	0·3899	0·745
4	0·315	0·741
5	0·272	0·659
6	0·24	0·686

Although the sequence $\{\theta_D\}$ is rather erratic, the results are consistent with a value of θ between 0·6 and 0·7, and are therefore entirely consistent with the scaling prediction of $\theta = \frac{2}{3}$.

To estimate the D dependence of the free energy, we note that we can write (Middlemiss *et al* 1977)

$$\frac{\Delta A(D)}{nkT} = \ln \mu(\infty) - \ln \mu(D) \sim hD^{-\phi} \tag{6}$$

where, as above, ϕ can be estimated from the sequence $\{\phi_D\}$ whose elements are given *mutatis mutandis* by (5). Our estimates of $\mu(D)$, and hence $\Delta A(D)/nkT$ and ϕ_D are given in table 2. For $\mu(\infty)$ we have used the value (Sykes *et al* 1972) of 2·6385. From these results it appears that ϕ is very close to unity, and it is difficult to reconcile these results with the scaling prediction $\phi = 1/\nu = \frac{4}{3}$. Notice that the (exact) random walk result is $\phi = 2$, so that the effect of the excluded volume is to introduce a very strong stabilising influence.

Table 2. Estimates of the exponent ϕ defined by $\Delta A(D)/nkT \sim hD^{-\phi}$. For $D \leq 3$ the result are exact. $\mu(\infty) = 2{\cdot}6385$.

D	$\mu(D)$	$b_D = \ln \mu(\infty) - \ln \mu(D)$	$\phi_D = \dfrac{\ln(b_D/b_{D-1})}{\ln[(D-1)/D]}$
1	1·0000	0·97025	
2	1·61804	0·48903	0·988
3	1·9146	0·32074	1·040
4	2·074	0·2408	0·997
5	2·180	0·1909	1·04
6	2·25	0·159	0·99
7	2·30	0·137	0·96

Although the series are quite short, and the calculation involves a double extrapolation, it would be surprising if the results for the free energy were less reliable than those derived from the mean-square-length series. Indeed, the method of exact enumeration is likely to be more successful in estimating the radius of convergence of a series (that is, the free energy calculation) than the amplitude of a singularity (which is the parameter calculated in the mean-square-length calculation).

The only predictions for self-avoiding walks between barriers other than the scaling arguments of Daoud and de Gennes are contained in Domb (1973). Although he distinguishes between different boundary conditions, for the 'free-surface' case (which is the one considered both here and by Daoud and de Gennes) Domb's predictions agree with those of Daoud and de Gennes in three dimensions. However, in two dimensions Domb's arguments for the finite size effect do not apply, and so these predictions cannot be considered complete for the case considered here. However, in finite magnetic systems the analogue of free energy scaling is the approach of the critical temperature to its bulk value as D increases. Again there are differences depending on the boundary conditions chosen, but there are disagreements even for the free-surface case. Fisher (1971) and Bray and Moore (1978, private communication) suggest that

$$T_c(\infty) - T_c(D) \sim AD^{-\lambda}$$

with $\lambda = 1/\nu$, where ν is the usual bulk correlation length exponent as T approaches T_c from above. Earlier series work on the Ising model by Allan (1970) indicated that $\lambda = 1$ for the three-dimensional problem—though as Domb points out, the shortness of the series used may have been responsible for this conclusion. Possibly the most significant result however is the exact calculation of Fisher and Barber (1972) for the spherical model. For dimensionality $d \geqslant 3$ (since the spherical model does not have a phase transition for $d = 2$) and for 'free-surface' boundary conditions, they found $\lambda = 1$, in disagreement with scaling predictions for $d > 3$. However, even the applicability of this result is not clear, since the spherical model in a restricted geometry does not in general correspond to the $n = \infty$ limit of the n-vector model (Knops 1973), and so the appropriateness of using the bulk exponent ν in the scaling argument is open to doubt in this case.

We believe that the situation is still unclear, and hope that this Letter will provoke further examination of these important questions.

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